

# ***Design and Operations of Natural Gas Handling Facilities***

Course prepared for the training department of  
**National Iranian Gas Company**

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شرکت ملی گاز ایران

مدیریت پژوهش و فناوری

**امور تدوین استانداردها**

## **World Natural Gas Occurrence and Production**

### **- International Gas Statistics**

- Natural gas is a major world energy source.
- World natural gas reserves are estimated at 5893 TCF.
- About 72 percent of the world's natural gas reserves are found in the Middle East and the former Soviet Union.

## Natural Gas Origin

- Biogenic methane
- Thermogenic methane
- Metamorphism
- Abiogenic methane

Biogenic methane results from the decomposition of organic matter by methanogens, which are methane-producing micro-organisms and which pervade the near surface of the Earth's crust in regions devoid of oxygen, where temperatures do not exceed 97 degrees Celsius (207 degrees Fahrenheit). Methanogens also live inside the intestines of most animals (people included) and in the cud of ruminants such as cows and sheep, where they aid in the digestion of vegetable matter. Because the methane generated in the subsurface is less dense than the rocks in which it is produced, it diffuses slowly upward through tiny, interconnected pore spaces and fractures, and it can eventually reach the Earth's surface and dissipate into the atmosphere. In places, however, the diffusion of methane is impeded by impermeable rock layers and gas can become trapped in structures. If enough gas accumulates under these impermeable layers, the structures can be drilled and gas can be extracted for use as an energy source.

Thermogenic methane is formed in a manner similar to oil. As organic particles deposited in mud and other sediment become deeply buried and compressed, higher temperatures cause carbon bonds in organic compounds to break down and form oil with minor amounts of gas. At increased temperatures (caused by increased burial depth), methane becomes the dominant product until it eventually replaces oil altogether. The simultaneous formation of both oil and gas in the early stage of the thermal decomposition process is the principal reason for the association of oil and gas in accumulations present in the upper 2 to 3 km of the Earth's crust. In deep parts of basins and possibly even in subduction zones methane may be the only hydrocarbon formed.

At greater burial depths, metamorphism may drive off all hydrogen atoms from organic compounds and leave a residue of carbon, often in the form of graphite. Under certain conditions in the deep crust, graphite may react with water; this reaction results in the recombining of carbon and hydrogen into methane. Recent studies on quartzvein systems indicate the presence of large fluxes of deep crustal gases and fluids; the volume of methane transported can be as large as 50 to 500 trillion cubic feet for a single giant vein system.

Abiogenic methane is formed by another process that involves non-organic carbon- and hydrogen-rich gases, which exist deep within the Earth. They form as either primordial gases that seep from our planet's interior or as gases liberated from crustal rocks during metamorphism. As these gases migrate upward and interact with crustal minerals, they react to form the elements and compounds present in the atmosphere (nitrogen, oxygen, carbon dioxide, argon and water). In volcanic regions today, there is a continual outgassing of carbon dioxide and water, which originated deep in the Earth. If these same gases were to migrate through rocks at high pressures, and in the absence of oxygen, methane would be the dominant stable compound. Perhaps methane is forming in this matter deep beneath the Earth's large continental regions where high pressure and low oxygen conditions prevail.

## **History of Natural Gas**

- Dates back to thousands years ago
- Persians and Indians used it for religious practices
- Chinese used it to desalt sea water
- British Commercialized natural gas

Centuries ago, man noticed that lightning ignited natural gas seeping from the ground and creating a "burning spring." The most famous legend about natural gas originated on Mount Parnassus in Greece approximately 1,000 B.C. A goat herdsman discovered a burning spring on the mountain. A temple was built on that spot and the priestess, Oracle of Delphi, spoke of prophecies inspired by the burning spring.

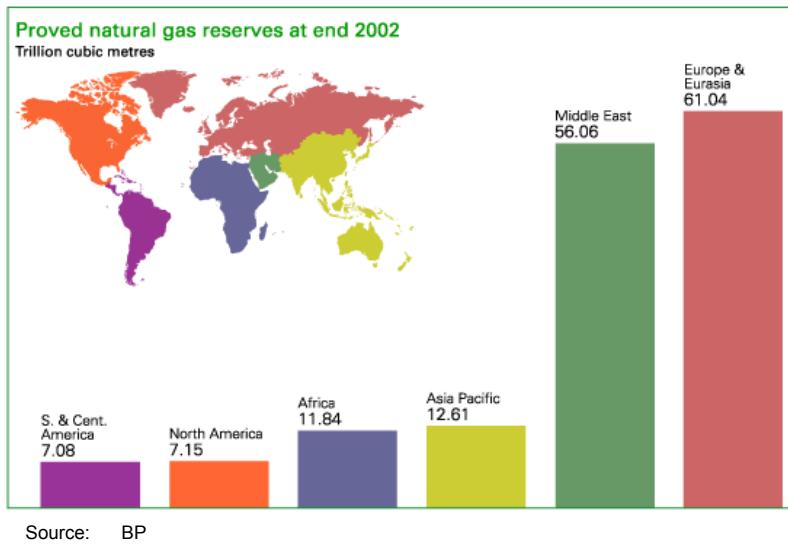
Burning springs of natural gas were prominent in religious practices of ancient Persia and India, where temples were constructed around these "eternal flames." The Greeks, Persians, and Indians did not recognize the energy value or potential usefulness of natural gas. Ancient Chinese realized that natural gas could work for them. About 500 B.C., they used natural gas to make portable water by piping it from shallow wells through bamboo poles to evaporate salt from sea water.

Britain commercialized the natural gas industry around 1785. This was gas manufactured from coal, not from naturally occurring natural gas. A Scotsman, William Murdoch, improved upon a method of manufacturing natural gas and used it to light his home. Shortly afterwards, the first natural gas company illuminated London streets with gaslights.

Manufactured natural gas arrived in the United States in 1816, when the city of Baltimore, Maryland installed gaslights. Baltimore's gas was also manufactured from coal. This gas had a much lower energy content and more impurities than today's natural gas.

Other sources of natural gas were discovered, which were superior in performance and price. Early explorers noticed natural gas seeping up from the ground in the eastern United States and along the California coast. As early as 1626, French missionaries had recorded that Indians ignited gases in the shallows of Lake Erie and in streams flowing into the lake. The American natural gas industry began in this area, known as New York.

In Canada, Amoco drilled the first well in the general region (1957), in northeastern British Columbia, at Beaver River B-63K, which was completed as a gas well. Amoco also made the first Northwest Territory discovery –and the largest in the region – in 1966 at Pointed Mountain. By the late sixties Panarctic Petroleum, a consortium of industry and government, was formed to further Canadian based exploration efforts in the Arctic. In 1969 Panarctic made a significant gas discovery at Drake Point on Melville Island. Canada is the world's third natural gas producer after Russia and the United States



Total proven natural gas reserves is estimated to be around 156 TCM. With current production rate (~2.5 TCM) the world average ratio of Reserves to Production (R/P) is estimated to be approximately 61 years.

## World Natural Gas Reserves (2002)

### Natural gas

#### Proved reserves

	At end 1982 Trillion cubic metres	At end 1992 Trillion cubic metres	At end 2001 Trillion cubic metres	At end 2002 Trillion cubic metres	Share of total	R/P ratio
USA	5.78	4.73	5.02	5.19	183.5	3.3%
Canada	2.75	2.71	1.69	1.70	60.1	1.1%
Mexico	2.15	2.01	0.84	0.25	8.8	0.2%
<b>Total North America</b>	<b>10.67</b>	<b>9.45</b>	<b>7.55</b>	<b>7.15</b>	<b>252.4</b>	<b>4.6%</b>
Argentina	0.71	0.64	0.78	0.76	27.0	0.5%
Bolivia	0.16	0.12	0.68	0.68	24.0	0.4%
Brazil	0.07	0.12	0.22	0.23	8.1	0.1%
Colombia	0.13	0.20	0.12	0.13	4.5	0.1%
Peru	0.03	0.20	0.25	0.25	8.7	0.2%
Trinidad & Tobago	0.31	0.25	0.66	0.66	23.5	0.4%
Venezuela	1.53	3.58	4.18	4.19	148.0	2.7%
Other S. & Cent. America	0.19	0.22	0.28	0.18	6.4	0.1%
<b>Total S. &amp; Cent. America</b>	<b>3.14</b>	<b>5.34</b>	<b>7.16</b>	<b>7.08</b>	<b>250.2</b>	<b>4.5%</b>
Azerbaijan	n/a	n/a	0.85	0.85	30.0	0.5%
Denmark	0.07	0.11	0.08	0.08	3.0	0.1%
Germany	0.18	0.34	0.34	0.32	11.3	0.2%
Italy	0.12	0.37	0.23	0.23	8.0	0.1%
Kazakhstan	n/a	1.85	1.84	1.84	65.0	1.2%
Netherlands	1.47	1.95	1.77	1.76	62.0	1.1%
Norway	1.64	2.00	1.25	2.19	77.3	1.4%
Poland	n/a	0.16	0.14	0.17	5.8	0.1%
Romania	n/a	0.21	0.10	0.10	3.6	0.1%
Russian Federation	n/a	47.40	47.57	47.57	1680.0	30.5%
Turkmenistan	n/a	2.74	2.86	2.01	71.0	1.3%
Ukraine	n/a	1.08	1.12	1.12	39.6	0.7%
United Kingdom	0.72	0.54	0.73	0.70	24.6	0.4%
Uzbekistan	n/a	1.84	1.87	1.87	66.2	1.2%
Other Europe & Eurasia	35.76	0.44	0.24	0.24	8.4	0.2%
<b>Total Europe &amp; Eurasia</b>	<b>39.96</b>	<b>61.02</b>	<b>61.00</b>	<b>61.04</b>	<b>2155.8</b>	<b>39.2%</b>

Source: BP

\*Over 100 years.

†Less than 0.05.

‡Less than 0.05%.

#1982 excludes Central European members.

n/a not available.

# World Natural Gas Reserves (2002)

## Natural gas

### Proved reserves

	At end 1982 Trillion cubic metres	At end 1992 Trillion cubic metres	At end 2001 Trillion cubic metres	At end 2002 Trillion cubic metres feet	Share of total	R/P ratio
Bahrain	0.22	0.16	0.09	0.09	3.3	0.1%
Iran	13.67	19.80	23.00	23.00	812.3	14.9%
Iraq	0.82	3.10	3.11	3.11	109.8	2.0%
Kuwait	0.97	1.50	1.49	1.49	52.7	1.0%
Oman	0.08	0.48	0.83	0.83	29.3	0.5%
Qatar	1.76	6.43	14.40	14.40	508.5	9.2%
Saudi Arabia	3.43	5.18	6.22	6.36	224.7	4.1%
Syria	0.04	0.20	0.24	0.24	8.5	0.2%
United Arab Emirates	0.81	5.79	6.01	6.01	212.1	3.9%
Yemen	—	0.39	0.48	0.48	16.9	0.3%
Other Middle East	†	0.01	0.05	0.05	1.6	•
<b>Total Middle East</b>	<b>21.78</b>	<b>43.05</b>	<b>55.91</b>	<b>56.06</b>	<b>1979.7</b>	<b>36.0%</b>
Algeria	3.15	3.62	4.52	4.52	159.7	2.9%
Egypt	0.20	0.44	1.56	1.66	58.5	1.1%
Libya	0.61	1.31	1.31	1.31	46.4	0.8%
Nigeria	0.92	3.40	3.51	3.51	124.0	2.3%
Other Africa	0.48	1.06	0.84	0.84	29.5	0.5%
<b>Total Africa</b>	<b>5.26</b>	<b>9.82</b>	<b>11.74</b>	<b>11.84</b>	<b>418.1</b>	<b>7.6%</b>
Australia	0.50	0.52	2.55	2.55	90.0	1.6%
Bangladesh	0.20	0.72	0.30	0.30	10.6	0.2%
Brunei	0.19	0.40	0.39	0.39	13.8	0.3%
China	0.84	1.40	1.37	1.51	53.3	1.0%
India	0.41	0.73	0.65	0.76	26.9	0.5%
Indonesia	0.84	1.82	2.62	2.62	92.5	1.7%
Malaysia	0.96	1.92	2.12	2.12	75.0	1.4%
Pakistan	0.52	0.88	0.71	0.75	26.4	0.5%
Papua New Guinea	—	0.40	0.35	0.35	12.2	0.2%
Thailand	0.31	0.24	0.36	0.38	13.3	0.2%
Vietnam	—	0.01	0.19	0.19	6.8	0.1%
Other Asia Pacific	0.20	0.61	0.66	0.69	24.5	0.4%
<b>Total Asia Pacific</b>	<b>4.99</b>	<b>9.66</b>	<b>12.27</b>	<b>12.61</b>	<b>445.3</b>	<b>8.1%</b>
<b>TOTAL WORLD</b>	<b>85.90</b>	<b>138.34</b>	<b>155.64</b>	<b>155.76</b>	<b>5501.5</b>	<b>100.0%</b>
						<b>60.7</b>

Source: BP

\*Over 100 years.  
†Less than 0.05%.  
•Less than 0.05%.  
#1982 excludes Central European members.  
n/a not available.

## World Natural Gas Production (2002)

### Natural gas

#### Production\*

	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	Change 2002 over 2001	2002 share of total
Billion cubic metres													
USA	514.5	520.4	541.8	534.3	541.7	543.1	549.2	541.6	551.4	557.7	547.7	-1.8%	21.7%
Canada	127.8	139.0	149.1	158.7	163.6	165.8	171.3	177.4	183.2	186.8	183.5	-1.8%	7.3%
Mexico	26.2	25.4	25.9	26.6	28.0	31.7	34.3	37.2	35.8	35.3	34.8	-1.4%	1.4%
<b>Total North America</b>	<b>668.5</b>	<b>694.8</b>	<b>716.8</b>	<b>719.6</b>	<b>723.3</b>	<b>740.6</b>	<b>754.8</b>	<b>756.2</b>	<b>770.4</b>	<b>779.8</b>	<b>766.0</b>	<b>-1.8%</b>	<b>30.3%</b>
Argentina	20.1	21.5	22.3	25.0	28.9	27.4	29.6	34.6	37.4	37.1	36.1	-2.9%	1.4%
Bolivia	3.0	3.0	3.3	3.2	3.2	2.9	3.0	2.5	3.5	5.1	5.4	5.6%	0.2%
Brazil	4.0	4.5	4.5	4.8	5.5	6.0	6.3	6.7	7.2	7.6	9.1	20.4%	0.4%
Colombia	4.0	4.2	4.2	4.4	4.7	5.9	6.3	5.2	5.9	6.1	6.2	1.0%	0.2%
Trinidad & Tobago	6.0	5.9	6.2	6.1	7.1	7.4	8.6	11.7	14.1	14.7	16.8	13.6%	0.7%
Venezuela	21.6	23.3	24.7	27.5	29.7	30.8	32.3	27.4	27.9	29.1	27.3	-6.0%	1.1%
Other S. & Cent. America	2.2	2.1	2.2	2.2	2.3	2.4	2.5	2.1	2.1	2.3	2.1	-5.8%	0.1%
<b>Total S. &amp; Cent. America</b>	<b>60.9</b>	<b>64.5</b>	<b>67.4</b>	<b>73.2</b>	<b>81.4</b>	<b>82.8</b>	<b>88.6</b>	<b>90.2</b>	<b>98.1</b>	<b>102.0</b>	<b>103.0</b>	<b>1.0%</b>	<b>4.1%</b>
Azerbaijan	7.4	6.3	6.0	6.2	5.9	5.6	5.2	5.6	5.3	5.2	4.8	-7.3%	0.2%
Denmark	4.1	4.5	4.9	5.3	6.4	7.9	7.6	7.8	8.1	8.4	8.4	0.2%	0.3%
Germany	14.9	14.9	15.6	16.1	17.4	17.1	16.7	17.8	16.9	17.4	17.4	-0.3%	0.7%
Italy	18.2	19.5	20.6	20.4	20.0	19.3	19.0	17.5	16.2	15.2	15.1	-1.2%	0.6%
Kazakhstan	7.6	6.2	4.2	5.5	6.1	7.6	7.4	9.3	10.8	10.8	12.3	13.2%	0.5%
Netherlands	69.1	70.0	66.4	67.0	75.8	67.1	63.6	59.3	57.3	61.9	59.9	-3.2%	2.4%
Norway	25.8	24.8	26.8	27.8	37.4	43.0	44.2	48.5	49.7	53.9	65.4	21.4%	2.6%
Poland	2.8	3.6	3.4	3.5	3.6	3.6	3.6	3.4	3.7	3.9	4.0	2.0%	0.2%
Romania	21.8	20.6	18.7	18.0	17.2	15.0	14.0	14.0	13.8	13.6	10.8	-20.7%	0.4%
Russian Federation	597.4	576.5	566.4	555.4	561.1	532.6	551.3	551.0	545.0	542.4	554.9	2.3%	22.0%
Turkmenistan	56.1	60.9	33.3	30.1	32.8	16.1	12.4	21.3	43.8	47.9	49.9	4.3%	2.0%
Ukraine	19.6	17.9	17.0	17.0	17.2	17.4	16.8	16.9	16.7	17.1	17.2	0.8%	0.7%
United Kingdom	51.5	60.5	64.6	70.8	84.2	85.9	90.2	99.1	108.3	105.8	103.1	-2.6%	4.1%
Uzbekistan	39.9	42.0	44.0	45.3	45.7	47.8	51.1	51.9	52.6	53.5	53.8	0.5%	2.1%
Other Europe & Eurasia	15.8	16.2	15.6	15.6	14.0	13.3	12.3	11.4	11.3	11.2	11.1	-0.4%	0.4%
<b>Total Europe &amp; Eurasia</b>	<b>952.0</b>	<b>944.4</b>	<b>907.5</b>	<b>904.0</b>	<b>944.8</b>	<b>899.3</b>	<b>915.4</b>	<b>934.8</b>	<b>959.5</b>	<b>968.2</b>	<b>988.1</b>	<b>2.0%</b>	<b>39.1%</b>

Source: BP

# World Natural Gas Production (2002)

## Natural gas

### Production\*

Billion cubic metres	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	Change 2002 over 2001	2002 share of total
Bahrain	6.5	6.9	7.1	7.2	7.4	8.0	8.4	8.7	8.8	9.1	9.2	1.1%	0.4%
Iran	25.0	27.1	31.8	35.3	39.0	47.0	50.0	56.4	60.2	63.3	64.5	1.9%	2.6%
Kuwait	2.6	5.4	6.0	9.3	9.3	9.3	9.5	9.6	9.6	9.5	8.7	-8.3%	0.3%
Oman	2.9	2.8	2.9	4.1	4.4	5.0	5.2	5.5	8.4	14.0	14.8	5.7%	0.6%
Qatar	12.6	13.5	13.5	13.7	17.4	19.6	22.1	24.9	27.9	29.3	5.0%	1.2%	
Saudi Arabia	38.3	40.0	42.8	42.9	44.4	45.3	46.8	46.2	49.8	53.7	56.4	5.0%	2.2%
Syria	1.6	1.4	1.5	1.9	2.5	3.8	4.3	4.5	4.2	4.3	4.1	-5.9%	0.2%
United Arab Emirates	22.2	23.0	25.8	31.3	33.8	36.3	37.1	38.5	38.4	45.0	46.0	2.2%	1.8%
Other Middle East	2.4	2.8	3.4	3.4	3.5	3.3	3.2	3.4	3.4	3.0	2.6	-15.2%	0.1%
<b>Total Middle East</b>	<b>114.1</b>	<b>122.9</b>	<b>134.8</b>	<b>148.9</b>	<b>158.0</b>	<b>175.4</b>	<b>184.1</b>	<b>193.9</b>	<b>207.7</b>	<b>229.8</b>	<b>235.6</b>	<b>2.5%</b>	<b>9.3%</b>
Algeria	55.3	56.1	51.6	58.7	62.3	71.8	76.6	86.0	84.4	78.2	80.4	2.7%	3.2%
Egypt	8.4	10.0	10.6	11.0	11.5	11.6	12.2	14.7	18.3	21.5	22.7	5.5%	0.9%
Libya	6.1	5.8	5.8	5.8	5.8	6.0	5.8	4.7	5.4	5.6	5.7	1.0%	0.2%
Nigeria	4.3	4.9	4.4	4.8	5.4	5.1	5.1	6.0	12.5	18.4	17.7	-3.6%	0.7%
Other Africa	1.1	2.7	2.9	3.0	3.8	4.9	5.0	5.4	5.9	6.6	6.7	1.9%	0.3%
<b>Total Africa</b>	<b>75.2</b>	<b>79.5</b>	<b>75.3</b>	<b>83.3</b>	<b>88.8</b>	<b>99.4</b>	<b>104.7</b>	<b>116.8</b>	<b>126.5</b>	<b>130.3</b>	<b>132.2</b>	<b>2.2%</b>	<b>5.3%</b>
Australia	23.5	24.5	28.1	29.3	30.1	29.9	31.1	31.6	32.8	33.6	34.5	2.7%	1.4%
Bangladesh	5.7	6.1	6.6	7.4	7.6	7.6	7.8	8.3	10.0	10.7	11.2	4.3%	0.4%
Brunei	9.8	10.3	10.4	11.8	11.7	11.7	10.8	11.2	11.3	11.4	11.5	0.5%	0.5%
China	15.1	16.2	16.6	17.6	19.9	22.2	22.3	24.3	27.2	30.3	32.6	7.7%	1.3%
India	15.3	15.9	16.6	19.6	20.7	23.0	24.7	25.9	26.9	27.3	28.4	4.0%	1.1%
Indonesia	54.2	55.9	62.5	63.4	67.5	67.2	64.3	71.0	68.5	66.3	70.6	6.4%	2.8%
Malaysia	22.8	24.9	26.1	28.9	33.6	38.6	38.5	40.8	45.3	47.3	50.3	6.3%	2.0%
New Zealand	4.7	4.9	4.4	4.1	4.9	5.1	4.5	5.2	5.5	5.8	6.3	9.5%	0.3%
Pakistan	11.5	12.2	13.2	14.6	15.4	15.6	16.0	17.3	18.9	19.9	20.9	5.1%	0.8%
Thailand	7.5	8.4	9.5	10.4	12.2	15.2	16.3	17.7	18.6	18.0	18.9	4.9%	0.7%
Other Asia Pacific	4.4	4.6	5.0	5.1	5.4	5.7	6.1	6.4	8.5	12.6	16.5	31.2%	0.7%
<b>Total Asia Pacific</b>	<b>174.5</b>	<b>183.9</b>	<b>199.1</b>	<b>212.2</b>	<b>229.0</b>	<b>241.8</b>	<b>242.4</b>	<b>259.7</b>	<b>273.5</b>	<b>283.2</b>	<b>301.7</b>	<b>6.5%</b>	<b>11.9%</b>
<b>TOTAL WORLD</b>	<b>2045.2</b>	<b>2080.0</b>	<b>2100.9</b>	<b>2141.2</b>	<b>2235.3</b>	<b>2239.3</b>	<b>2290.0</b>	<b>2351.6</b>	<b>2435.7</b>	<b>2493.3</b>	<b>2527.6</b>	<b>1.4%</b>	<b>100.0%</b>

Source: BP

## World Natural Gas Consumption (2002)

### Consumption

	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	Change 2002 over 2001	2002 share of total
Billion cubic metres													
USA	583.4	597.9	611.6	638.0	649.6	653.3	642.2	644.3	673.6	642.4	667.5	3.9%	26.3%
Canada	71.7	76.8	78.8	80.2	85.3	83.8	84.9	83.0	83.0	82.8	80.7	-2.6%	3.2%
Mexico	28.9	26.5	27.0	28.1	28.6	32.3	35.4	37.4	38.5	39.0	42.1	8.0%	1.7%
<b>Total North America</b>	<b>684.0</b>	<b>701.2</b>	<b>717.4</b>	<b>746.3</b>	<b>763.5</b>	<b>769.4</b>	<b>762.5</b>	<b>764.7</b>	<b>795.1</b>	<b>764.2</b>	<b>790.3</b>	<b>3.4%</b>	<b>31.2%</b>
Argentina	22.3	23.6	24.3	27.0	28.8	28.5	30.5	32.4	33.2	31.2	30.3	-3.0%	1.2%
Brazil	4.0	4.5	4.5	4.8	5.5	6.0	6.3	7.1	9.3	11.7	13.7	16.7%	0.5%
Chile	1.7	1.6	1.7	1.7	1.7	2.8	3.3	4.1	6.2	6.0	6.5	3.2%	0.3%
Colombia	4.0	4.2	4.2	4.4	4.7	5.9	6.2	5.2	5.9	6.1	6.1	1.2%	0.2%
Ecuador	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	*
Peru	0.4	0.4	0.4	0.4	0.4	0.2	0.4	0.4	0.3	0.4	0.4	19.5%	*
Venezuela	21.6	23.3	24.7	27.5	29.7	30.8	32.3	27.4	27.9	29.1	27.3	-6.0%	1.1%
Other S. & Cent. America	6.8	6.8	7.3	7.3	8.2	8.8	10.2	11.5	12.1	12.9	13.5	4.7%	0.5%
<b>Total S. &amp; Cent. America</b>	<b>60.9</b>	<b>64.5</b>	<b>67.2</b>	<b>73.1</b>	<b>78.9</b>	<b>83.1</b>	<b>89.3</b>	<b>88.7</b>	<b>94.0</b>	<b>97.9</b>	<b>98.0</b>	<b>0.2%</b>	<b>3.9%</b>
Austria	6.0	6.4	6.5	6.8	7.3	7.7	7.6	7.7	7.3	7.8	8.1	4.4%	0.3%
Azerbaijan	11.8	8.7	8.1	8.0	5.9	5.6	5.2	5.6	5.4	7.8	7.9	1.7%	0.3%
Belarus	16.8	15.5	12.3	13.0	12.5	15.0	15.0	15.2	16.2	16.1	16.1	2.5%	0.7%
Belgium & Luxembourg	10.0	11.0	10.6	11.8	11.3	12.5	13.8	14.0	14.9	14.9	14.8	1.3%	0.8%
Bulgaria	4.3	4.1	4.1	5.0	5.2	4.1	3.5	3.0	3.3	3.0	2.9	-3.4%	0.1%
Czech Republic	5.8	5.9	6.3	7.3	8.4	8.5	8.5	8.6	8.3	8.9	8.9	-0.5%	0.4%
Denmark	2.4	2.8	3.0	3.5	4.1	4.4	4.8	5.0	4.9	5.1	5.1	-0.1%	0.2%
Finland	2.7	2.8	3.1	3.2	3.3	3.2	3.7	3.7	3.7	4.1	4.1	0.1%	0.2%
France	31.4	32.3	30.9	32.9	36.1	34.6	37.0	37.7	39.7	41.9	42.8	2.2%	1.7%
Germany	63.0	66.4	67.9	74.4	83.6	79.2	79.7	80.2	79.5	82.9	82.6	-0.4%	3.3%
Greece	0.1	0.1	†	†	0.2	0.2	0.8	1.4	1.9	1.9	2.0	4.4%	0.1%
Hungary	8.2	9.0	9.4	10.2	11.4	10.8	10.9	11.0	10.7	11.9	11.9	0.4%	0.5%
Iceland	—	—	—	—	—	—	—	—	—	—	—	—	—
Republic of Ireland	2.1	2.4	2.4	2.6	3.0	3.1	3.1	3.3	3.8	4.0	4.1	2.7%	0.2%
Italy	45.7	46.8	45.3	49.9	51.5	53.2	57.2	62.2	64.9	63.7	63.6	-0.1%	2.5%
Kazakhstan	13.5	13.0	10.3	10.8	9.0	7.1	7.3	7.9	9.7	10.1	9.7	-3.7%	0.4%
Lithuania	3.0	1.7	2.0	2.3	2.5	2.6	2.3	2.4	2.7	2.8	2.9	1.1%	0.1%
Netherlands	36.7	37.9	36.9	37.8	41.7	39.1	38.7	37.9	39.2	39.1	39.3	0.6%	1.6%
Norway	2.6	2.7	2.9	2.9	3.2	3.7	3.8	3.6	4.0	3.8	3.9	5.0%	0.2%
Poland	8.7	9.0	9.2	9.9	10.6	10.5	10.6	10.3	11.1	11.5	11.2	-2.6%	0.4%
Portugal	—	—	—	—	—	—	—	—	—	—	—	—	—
Romania	25.4	25.2	24.2	24.0	24.2	26.0	18.1	17.1	17.2	16.7	17.4	4.7%	0.7%
Russian Federation	417.3	416.0	390.9	338.8	379.9	350.4	387.7	363.6	377.2	377.7	389.4	4.2%	0.3%
Slovakia	5.5	5.2	5.0	5.7	6.2	6.3	6.4	6.4	6.5	6.9	7.6	10.2%	0.3%
Spain	6.5	6.5	7.2	8.3	9.3	12.3	13.1	15.0	16.9	18.2	20.8	14.4%	0.8%
Sweden	0.7	0.8	0.8	0.8	0.9	0.8	0.9	0.8	0.7	0.7	0.8	7.7%	*
Switzerland	2.1	2.2	2.2	2.4	2.6	2.5	2.6	2.7	2.7	2.8	2.8	-0.4%	0.1%
Turkey	4.5	5.0	6.5	6.8	9.0	9.4	9.9	12.0	14.1	16.0	17.4	8.4%	0.7%
Turkmenistan	9.3	9.3	10.2	8.0	10.0	10.1	10.3	11.3	12.6	12.9	13.2	2.9%	0.5%
Ukraine	103.5	92.9	81.3	76.2	82.5	74.3	68.8	73.0	73.1	70.9	69.8	-1.6%	2.8%
United Kingdom	56.4	60.7	66.6	71.5	84.1	87.0	93.1	96.5	96.3	94.7	97.4	-1.8%	3.7%
Uzbekistan	37.3	40.7	41.3	42.4	43.3	45.4	47.0	49.3	47.1	51.1	52.4	2.6%	2.1%
Other Europe & Eurasia	21.7	16.2	13.3	13.3	13.8	14.8	14.7	13.0	13.2	14.5	13.3	-7.9%	0.5%
<b>Total Europe &amp; Eurasia</b>	<b>965.0</b>	<b>982.8</b>	<b>921.7</b>	<b>927.8</b>	<b>976.7</b>	<b>936.8</b>	<b>953.3</b>	<b>981.7</b>	<b>1011.6</b>	<b>1023.1</b>	<b>1043.8</b>	<b>2.1%</b>	<b>41.2%</b>

# World Natural Gas Consumption (2002)

## Consumption

Billion cubic metres	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	Change 2002 over 2001	2002 share of total
Iran	25.0	26.6	31.8	35.2	38.9	47.1	51.8	59.8	63.0	65.0	67.9	+4.5%	2.7%
Kuwait	2.6	5.4	6.0	9.3	9.3	9.3	9.5	8.6	9.6	9.5	8.7	-8.3%	0.3%
Qatar	12.6	13.5	13.5	13.5	13.7	14.5	14.8	14.0	10.8	11.4	10.7	-5.7%	0.4%
Saudi Arabia	38.3	40.0	42.8	42.9	44.4	45.3	46.8	46.2	49.8	53.7	56.4	+5.0%	2.2%
United Arab Emirates	18.8	19.6	21.7	24.8	27.2	29.0	30.4	31.4	31.4	38.1	39.3	+3.2%	1.5%
Other Middle East	13.3	13.9	14.9	16.1	17.3	19.6	20.5	21.5	22.1	23.0	22.7	-1.5%	0.9%
<b>Total Middle East</b>	<b>110.6</b>	<b>119.0</b>	<b>130.7</b>	<b>141.8</b>	<b>150.8</b>	<b>164.8</b>	<b>173.8</b>	<b>181.5</b>	<b>186.7</b>	<b>200.7</b>	<b>205.7</b>	<b>+2.5%</b>	<b>8.1%</b>
Algeria	20.7	18.6	19.6	21.0	21.6	20.2	20.9	21.3	21.8	25.9	26.3	+1.6%	1.0%
Egypt	8.4	9.7	10.4	11.0	11.3	11.6	12.0	14.3	18.3	21.5	22.7	+5.5%	0.9%
South Africa	—	—	—	—	—	—	—	—	—	—	—	—	—
Other Africa	11.2	11.6	11.9	12.8	14.3	14.4	14.9	15.4	17.0	17.9	18.4	+3.0%	0.7%
<b>Total Africa</b>	<b>40.3</b>	<b>39.9</b>	<b>41.9</b>	<b>44.8</b>	<b>47.2</b>	<b>46.2</b>	<b>47.8</b>	<b>51.0</b>	<b>57.1</b>	<b>65.3</b>	<b>67.4</b>	<b>+3.3%</b>	<b>2.7%</b>
Australia	16.9	17.4	19.4	20.1	20.4	20.3	21.3	21.5	22.6	23.8	24.0	+0.8%	0.9%
Bangladesh	5.7	6.1	6.6	7.4	7.6	7.6	7.8	8.3	10.0	10.7	11.2	+4.3%	0.4%
China	15.1	16.2	16.6	17.7	17.7	19.3	19.3	21.4	24.5	27.8	30.1	+8.0%	1.2%
China Hong Kong SAR	—	—	—	†	1.7	2.6	2.5	2.7	2.5	2.5	2.4	-5.0%	0.1%
India	15.3	15.9	16.6	19.6	20.7	23.0	24.7	25.9	26.9	27.2	28.2	+3.8%	1.1%
Indonesia	22.6	23.9	27.3	30.1	31.4	31.9	27.8	31.8	32.3	33.4	34.7	+4.0%	1.4%
Japan	56.0	56.3	60.3	61.2	66.1	65.1	69.5	74.6	76.2	79.0	77.4	-2.0%	3.1%
Malaysia	11.7	13.0	13.6	13.7	17.8	16.7	17.4	16.1	24.3	25.8	27.0	+4.9%	1.1%
New Zealand	4.9	4.7	4.4	4.2	4.7	5.1	4.5	5.2	5.5	5.7	5.5	-3.5%	0.2%
Pakistan	11.5	12.2	13.3	14.6	15.4	15.6	16.0	17.3	18.9	19.9	20.9	+5.1%	0.8%
Philippines	—	—	—	†	†	†	†	†	†	†	0.1	+100.0%	0.1%
Singapore	1.1	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.3	1.8	+38.6%	0.1%
South Korea	5.1	6.4	8.5	10.2	13.5	16.4	15.4	18.7	21.0	23.1	26.2	+13.4%	1.0%
Taiwan	3.2	3.1	4.0	4.3	4.5	5.1	6.4	6.2	6.9	7.4	8.5	+14.7%	0.3%
Thailand	7.5	8.4	9.5	10.0	11.8	14.6	15.9	17.4	20.5	22.5	25.9	+14.9%	1.0%
Other Asia Pacific	2.7	3.1	3.3	3.4	3.7	4.2	4.5	4.8	4.9	4.9	4.7	-5.2%	0.2%
<b>Total Asia Pacific</b>	<b>179.3</b>	<b>188.2</b>	<b>204.9</b>	<b>218.0</b>	<b>238.5</b>	<b>249.0</b>	<b>254.5</b>	<b>273.4</b>	<b>298.5</b>	<b>315.1</b>	<b>330.3</b>	<b>+4.8%</b>	<b>13.0%</b>
<b>TOTAL WORLD</b>	<b>2040.1</b>	<b>2075.6</b>	<b>2083.8</b>	<b>2151.8</b>	<b>2255.6</b>	<b>2248.3</b>	<b>2287.2</b>	<b>2341.0</b>	<b>2443.0</b>	<b>2466.3</b>	<b>2535.5</b>	<b>+2.8%</b>	<b>100.0%</b>
of which:													
European Union 15	263.7	280.4	280.9	302.5	336.0	334.9	349.1	365.5	376.6	382.8	385.6	+0.8%	15.2%
OECD	1068.0	1105.4	1132.4	1189.7	1255.6	1262.9	1275.0	1304.8	1354.4	1340.4	1372.7	+2.4%	54.1%
Former Soviet Union	628.2	609.0	567.0	547.0	553.9	519.1	529.4	536.2	551.9	553.1	568.7	+2.8%	22.4%
Other EMEs	343.9	361.1	384.3	415.1	446.1	466.3	482.4	500.1	536.9	572.6	594.0	+3.7%	23.4%

\*Less than 0.05%.

†Less than 0.05%.

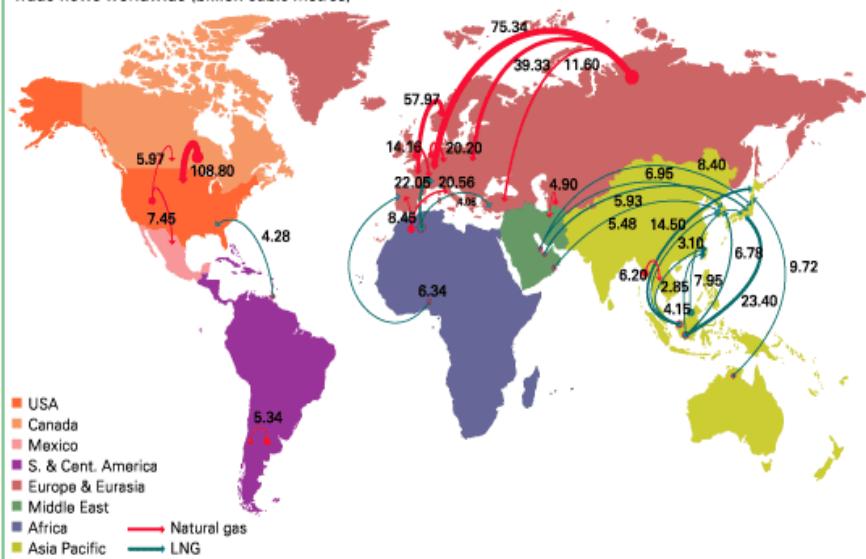
Notes: The difference between these world consumption figures and the world production statistics on page 22 is due to variations in stocks at storage facilities and liquefaction plants, together with unavoidable disparities in the definition, measurement or conversion of gas supply and demand data.

As far as possible, the data above represents standard cubic metres (measured at 15°C and 1013 mbar), as it is derived directly from tonnes of oil equivalent using an average conversion factor; it does not necessarily equate with gas volumes expressed in specific national terms.

Natural gas consumption data expressed in billion cubic feet per day is available at [www.bp.com/centres/energy](http://www.bp.com/centres/energy).

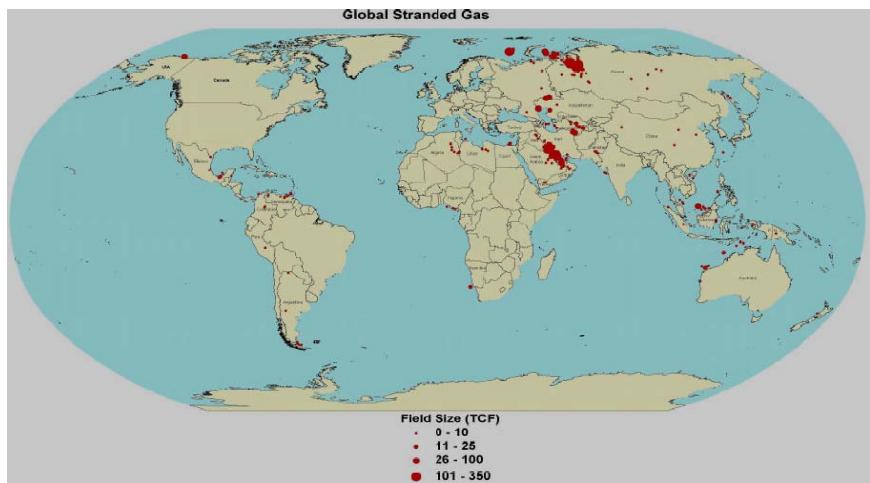
### Major trade movements for natural gas

Trade flows worldwide (billion cubic metres)



Source : BP

## Global Stranded Gas Reserves



## Iran Natural Main Gas Reserves



Iran South Gas Reserves

## North American Natural Gas Reserves (2001)

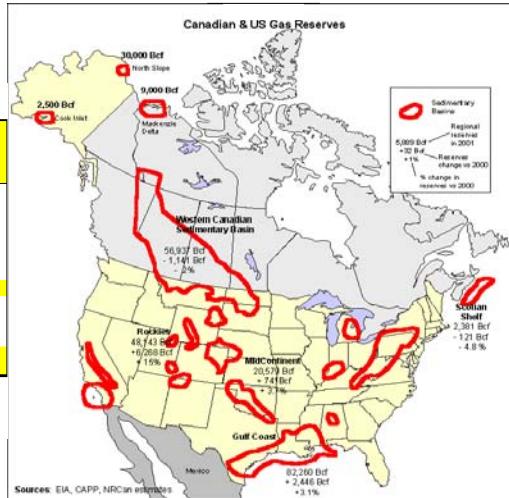
Tab  
North American Reserves

	Jan. 1, 2001 (Bcf)	Jan. 1, 2000 (Bcf)	Jan. 1, 1999 (Bcf)	% Change 00vs99	% Change 01vs00	Bcf Change 2001Vs 2000
Gulf Onshore <sup>1</sup>	56,088	54,963	51,993	4.6%	3.2%	1,725
Gulf Offshore	26,172	25,451	26,422	-3.7%	2.8%	721
Total Gulf	82,260	79,814	78,415	3.6%	3.1%	2,446
US Midcontinent	20,579	19,838	21,375	-7.2%	3.7%	741
US Rockies	48,143	41,875	38,900	7.6%	15.0%	6,268
Other US	26,445	25,879	25,345	2.1%	2.2%	566
<b>Total US Reserves</b>	<b>177,427</b>	<b>167,406</b>	<b>164,041</b>	<b>2.1%</b>	<b>6.0%</b>	<b>10,021</b>
Western Canada	56,937	58,078	59,089	-1.7%	-2.0%	-1,141
Scotian Shelf	2,381	2,502	2,502	0.0%	-4.8%	-121
Other Canada <sup>2</sup>	415	429	436	-1.5%	-3.3%	-14
<b>Total Canada</b>	<b>59,733</b>	<b>61,010</b>	<b>62,027</b>	<b>-1.6%</b>	<b>-2.1%</b>	<b>-1,277</b>
<b>TOTAL N.A. Reserves</b>	<b>237,160</b>	<b>228,416</b>	<b>226,068</b>	<b>1.0%</b>	<b>3.8%</b>	<b>8,744</b>

Sources: EIA US Crude Oil, Natural Gas, and Natural Gas Liquids Reserves 2000 Annual Report (US data), and Canadian Association of Petroleum Producers (Canadian data).

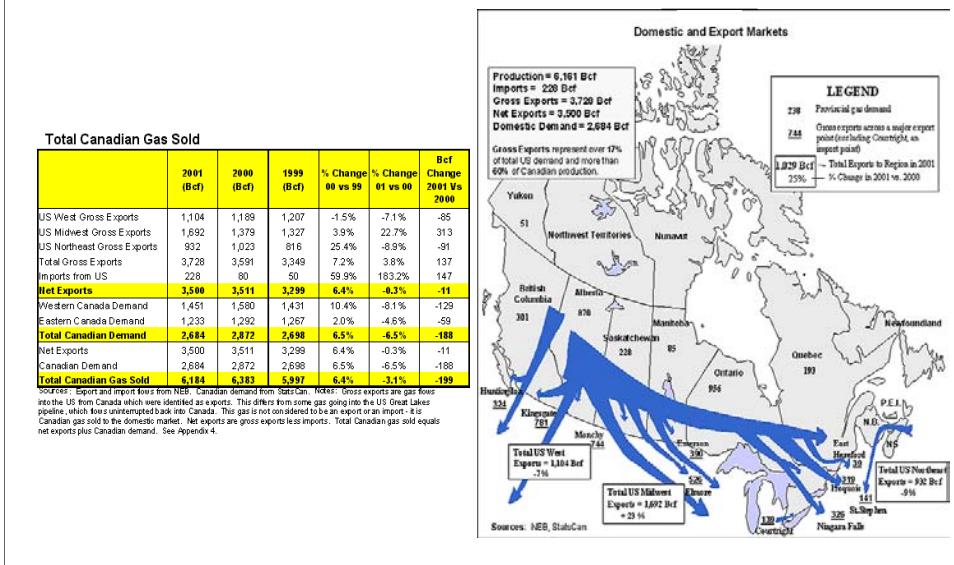
1. Gulf Onshore includes all reserves in Texas, Louisiana, Mississippi, and Alabama onshore, plus the state offshore reserves of these states.

2. Many Ontario.



The major North American natural gas fields are shown in this slide. As can be seen the Western Canadian Sedimentary Basin (WCSB) is the largest basin comprising many different fields and natural gas reserves. The estimated “gas in place” values are also shown on the map as well as the accompanying table.

## Canadian natural gas production/demand by region (2001)

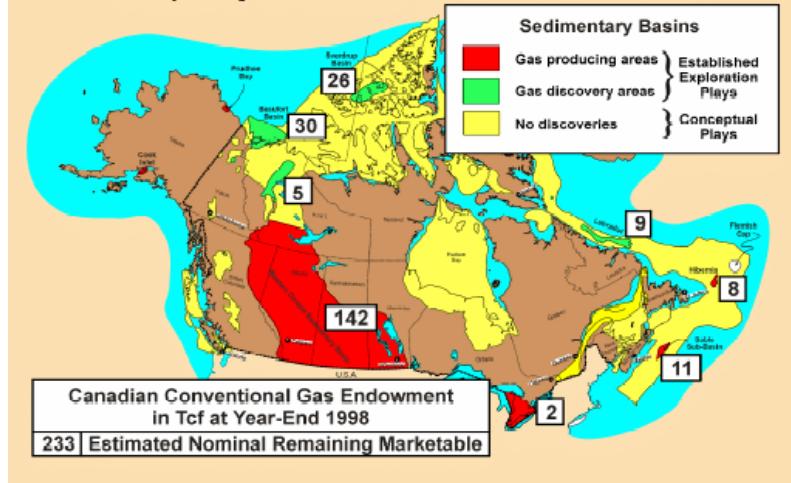


Canadian annual production capacity is currently about 7 TCF (~ 20 BCF/D); more than 85% of which is produced in Alberta.

## Canadian Natural Gas

### NATURAL GAS POTENTIAL IN CANADA - 2001

A Report by the Canadian Gas Potential Committee



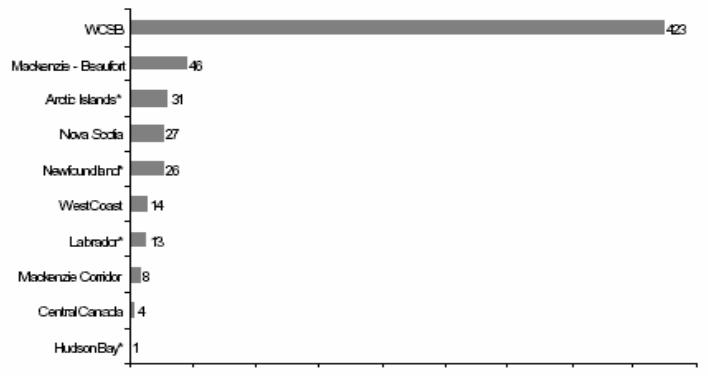
The Western Canada Sedimentary Basin (WCSB) holds the great bulk (over 71%) of Canada's endowment.

## Canadian Natural Gas (2001)



Canadian Gas Potential Committee

Endowment: Gas in Place (tcf)



\* Unlikely source of supply

Newfoundland and Labrador's share is about 40 TCF although there is a great potential for more natural gas in the future. Newfoundland and Labrador does not produce any gas at the moment but there are plans to exploit the gas resources using new transportation techniques.

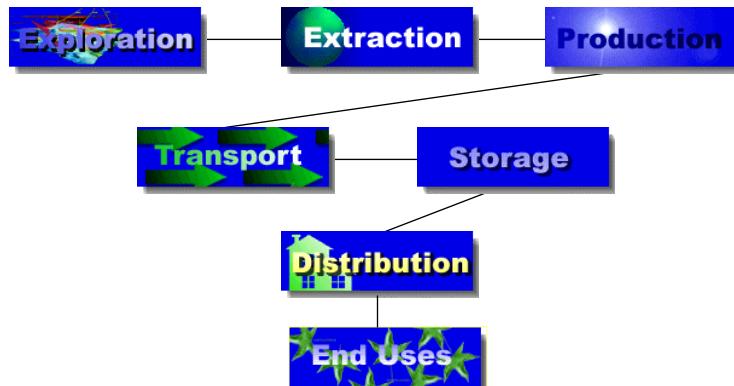
The conclusions reached by the Canada Gas Potential Committee (CGPC) in their 2001 Report are:

- The Western Canadian Sedimentary Basin will be the primary source of future Canadian gas supply.
- Near frontier regions (Nova Scotia and the Mackenzie Delta and Corridor) will supplement WCSB supply.
- Remote frontier regions are technologically and economically inaccessible as a gas supply source.
- Non-conventional resources hold promise, but will require further research.
- New gas supplies will require high levels of exploration, development and other capital expenditures.

## **NIGC – Near Future Natural Gas Processing Infrastructure**

- 345 million cubic meters production per day by 2004
- Upgrading Valie Asr plant for Parse Phase 1, 2 and 3 (75-100 MMCMD), 2003
- A 2<sup>nd</sup> Valie Asr for the South Pars Phases 4 and 5 (50 MMCMD), 2005
- Bid Boland-II for Pazanan, Gachsaran and Bibi Hakimeh fields, Ethane recovery and EOR projects in South (56 MMCMD), 2005
- Parsian plants -phase 1 in 2005 and 2/section 1 in 2002 & section 2 in 2007(55, 22 and 20 MMCMD)
- Ilam for Tangeh Bijar reservoir (6.8 MMCMD), 2004
- Gesho in 2005 (14 MMCMD)
- Masjed Soleiman in 2003 (1 MMCMD)
- In addition to several other phases of South Pars

## Natural Gas Value Chain



"Gas well gas" comes from wells that are drilled strictly for the purpose of extracting hydrocarbons and are not associated with production of petroleum. Typically E&P companies will obtain the rights to explore a prospect by purchasing leases outright from land owners (private or government). The process is more involved for leases in offshore areas, and lease purchases are conducted through a sealed bid process. The preliminary work is done and a capital commitment is made to drill the well, a mobile drilling platform is secured in position and the drilling work is begun. As you become more familiar with the producing community, pay attention to how much of a producer's capital budget is dedicated to exploratory drilling. This will give you insight into the producer's long- and short-term goals. With the technological advances that have been made in the past few years, geologists now have a superior set of tools to aid their search for natural gas reservoirs. Once the target zone is reached, the drilling stops, and the fractionation process begins. **Fractionation** involves injecting materials down the well bore and expelling them into the surrounding rock to begin the flow of gas up the well shaft to the surface. Since the gas in rock formations is under intense pressure, gas will flow at a very high rate (up to 1500 psi), when it is released to the surface. This rate is far too high for efficient handling, so the driller will place a choke on the well opening to regulate the flow of gas from the well. Well data is often described in terms such as, "the well flowed at 10/m<sup>3</sup>/day through a 13/64<sup>th</sup>s choke." This means a particular well is flowing 10 million cubic feet per day through an opening in the well shaft that is 13/64 inches in diameter. By the way, that's a pretty respectable well, especially if the reservoir is reasonably large, such as three billion cubic feet (BCF).

At this point the driller will cap the well, remove all the equipment and the production group will take over. The production group will perform tests to determine the quality of the gas, and the company can then make the decision to begin production or keep the well capped until perceived economic conditions improve. **Gathering** can be defined as the wide portfolio of services that is required to move gas from the wellhead and to condition it for sale and transport on a downstream pipeline. These activities include:

Compression services

Gas processing

Liquids extraction

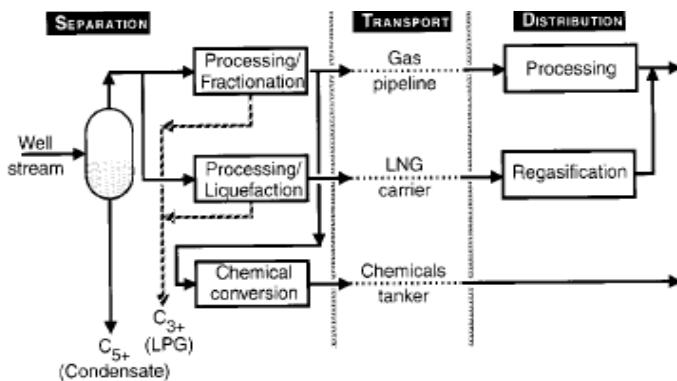
**Gas processing** is another service that the gatherer will provide for a fee to production that is upstream (behind) the gatherer's facilities. Processing is used to

Remove water vapor from gas (**dehydration**).

Remove CO<sub>2</sub> and/or H<sub>2</sub>S from gas through amine separation.

Liquids extraction is typically performed at the same location as processing. Extraction entails separating most of the liquefiable hydrocarbons from the methane. The liquids are then sold and transported to a liquids pipeline for (presumably) a profit. The residue gas (lean gas) is then recompressed and made available to the pipeline that will take it from the plant and deliver it to market.

# Natural Gas Processing



Natural gas hydrocarbon as produced from a reservoir is a complex mixture of hundreds of different compounds of hydrogen and carbon , all with different densities, vapour pressures, and other physical characteristics. A typical well stream is a high velocity, turbulent, constantly expanding mixture of gases and hydrocarbon liquids, intimately mixed with water vapour, free water, solids, and other contaminants. As it flows from the hot, high pressure reservoir, the well stream undergoes continuous pressure and temperature reduction. Gases evolve from liquids, water vapour condenses, and some of the well stream changes in character from liquid to bubbles, mist, and free gas. The high velocity gas is carrying liquid droplets, and the liquid is carrying gas bubbles.

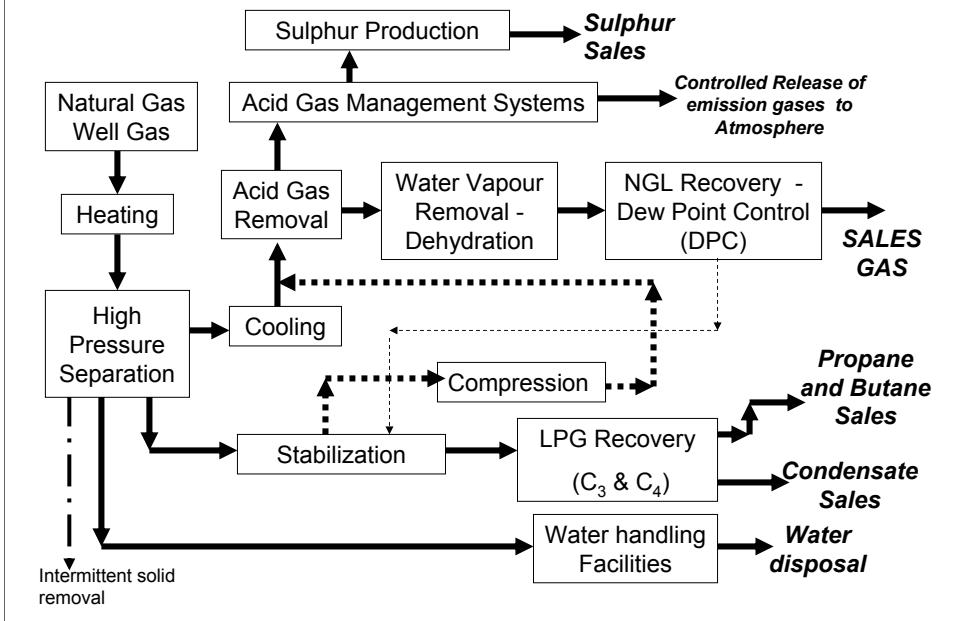
Field processing is required to remove undesirable components and to separate the well stream into salable gas and hydrocarbon liquids (Propane, butane, stabilized condensate or  $C_5^+$ ). Field processing of natural gas actually consists of following basic processes:

- Separation of gas from free liquids such as crude oil, hydrocarbon condensate, water and entrained solids
- Processing the gas to remove condensate and recoverable hydrocarbon vapours
- Processing the gas to remove condensable water vapour, which under certain conditions might cause hydrate formation
- Processing the gas to remove other undesirable components, such as hydrogen sulfide and carbon dioxide

Some of theses processes are accomplished in the field, but in some cases, the gas goes to a plant facility for further treatment.

In order to have the gas prepared for any purposes the gas has to undergo above mentioned processes. Gas then may be transferred in pipelines with pipe line quality specifications; it may be cooled down to very low temperatures and be liquefied as transported to end use location in the LNG form; or may be chemically converted to synthetic fuels and other chemicals. We will discuss all the above processes in this course.

## Gas Processing Facility Block Diagram



Extensive processing of the gas produced at the well is sometimes required. In every case, the specific processing needed is determined by the flow rate, composition, temperature, and pressure of the produced gas and by the components/impurities that must be removed to meet *delivery specifications*. Processing may vary from simple separation plus dehydration all the way to compression, Natural Gas Liquids (NGL) recovery, and dehydration or dew point control (DPC). The hydrocarbon portion of natural gas may be suitable as a SALES GAS as produced. On the other hand, if the condensate is high, these liquids must be recovered and either stored or transported. Field location, sales specifications, environmental requirements, and economics determine the extent to which non-hydrocarbon contaminants are removed and the ultimate destination of various streams to sales, flare, or disposal. The above block diagram is a comprehensive scheme of various unit operations, or modules, carried out in field and plant processing of natural gas. All the various modules shown may not necessarily present in every system. Further, the modules used in a given application may not be arranged in the sequence shown, although in general the sequence is typical. The choice of modules to be used and the sequencing of these modules is determined during the design phase of field or plant development. As shown in the figure, liquid water, and solids should be separated from the gas stream as early as practical. Then the individual streams can be treated with less difficulty. The first unit operation is the physical separation of the distinct phases, which are gas and possibly liquid hydrocarbon, liquid water, and or solids. The gas should be always kept above the hydrate formation temperature therefore line heating is required especially in cold environments. The gas may be cooled down and sent to next step in which the gas is treated for the removal of acid gas components (CO<sub>2</sub> and H<sub>2</sub>S) which are corrosive and may be toxic. Hydrogen sulfide removal should be complete. While the extent of carbon dioxide removal depends on the intended use of the gas. Environmental regulations usually limit venting or flaring hydrogen sulfide to atmosphere, so conversion to elemental sulphur is necessary. Dehydration is necessary to prevent formation of hydrate, an ice like substance which may plug processing equipment or pipe lines at high pressures. In some cases the potential NGL (higher hydrocarbons, e.g., ethane, propane and higher) are sufficiently valuable to justify their recovery. The higher hydrocarbons may also condense during transportation and create high pressure friction loss and problems for pipeline and compression systems. If the well pressure is low gas may be required to be compressed to allow pipeline transport (normally within the pressure range of 700-1200 psi). Environmental considerations should be always taken into account for the release of any by-products including gaseous components (such as carbon dioxide, and sulfur compounds), as well as liquid and solid co-products (e.g., water, elemental sulfur, pipe line scale and corrosion products, etc.). In addition to main processing modules described above, ancillary equipment is also required. The general arrangement of production equipment for "safe, pollution-free, and efficient production of oil and gas" is discussed in **American Petroleum Institute (API) Recommended Practice (RP) 2G**. This RP deals specifically with Offshore structures, but many of the guidelines are pertinent for land facilities. Examples of ancillary equipment are: **test separators** for periodic determination of the production rate of individual wells-such testing is often a legal requirement; **heat exchange equipment** (line heaters, refrigeration, compression inter-cooling, acid gas removal, dehydration, etc.); **automatic safety systems** (overpressure control, liquid overflow, excessive temperature, flares and safety relief systems) based on **API RP 14C, 520, and 521**; as well as **electrical power generation; instrument air supply; sewage disposal; fire fighting, sanitary and drinking water supply**.

## **FLUID PROPERTIES**

### **Characterization of Natural Gas and Its Products**

<u>SPECTRUM OF PRODUCED HYDROCARBONS</u>  FLUID TYPE	TYPICAL GOR		STOCK-TANK LIQUID	
	BSTO/BRF	SCF/BSTO	°API	COLOR
Associated gas from: •Low Shrinkage crude (Low GOR) –Ordinary crude •High Shrinkage Oil (high GOR) – volatile oil	>0.5	<2,000	<45	Very dark – black oil
	<0.5	2,000-3,300	>40	Colored – dark brown
Retrograde gas – gas condensate	>0.35	3,300-50,000	50-60	Water white
Wet gas	-	>50,000	>50	colorless
Dry gas	-	-	-	colorless

Preparing natural gas for transportation and sale involves two process goals:

1. Separation of natural gas from free liquids (condensate, crude or brine) and entrained solids (sand)
2. Removal of impurities and any condensate formed to meet sales/re-injection specifications while observing all environmental regulations

Sales specifications can be described in terms of the composition and properties of the produced hydrocarbons -gas, crude and condensate.

The desired components of the crude oil and natural gas are hydrocarbons – organic compounds formed from carbon and hydrogen atoms. These components range from the simplest hydrocarbon – methane ( $\text{CH}_4$ ) all the way up to paraffin hydrocarbons with 35 or more carbon atoms, poly nuclear aromatics with 20 or more carbon atoms. Natural gas is primarily consists of methane ( $\text{C}_1$ ) while crude oil is principally liquid hydrocarbons with more complex molecular structure having four or more carbon atoms. Although crude oil is regarded as a liquid and natural gas as a gas, in the reservoir, crude oil almost always contains dissolved gaseous components including methane and other light hydrocarbons that are released as the pressure on the oil is reduced. As the gas is evolved from the crude-oil the liquid volume decreases, known also as **Shrinkage**. The gas produced is called **Associated**, or **separator**, or **casinghead gas**. Shrinkage is expressed in terms of barrels of **Stock-Tank Oil (BSTO)** per **Barrel of Reservoir Fluid (BRF)**. The table in this slide list some fluid characteristics of five common types wellstream reservoir hydrocarbons. Similarly, hydrocarbon gases from a natural gas reservoir may contain small amounts of heavier hydrocarbons that are separated as a liquid called **Condensate**. Natural gas containing condensate is called **wet gas**. Conversely if no condensate forms when the gas is produced or the heavier content of the gas is removed using gas processing techniques to a reduced dew point temperature, the gas is called **dry gas**. When crude oil is separated from its associated gas during production, the total gas evolved while reducing the oil to atmospheric pressure divided by the volume of the remaining crude is called **gas-to-oil ratio** or **GOR**. GOR is expressed as the total standard cubic feet of gas evolved per 60°F barrel of stock-tank or atmospheric-pressure oil (SCF/BSTO). Standard conditions in English Engineering (Imperial) units are 60° F and 1 atmosphere or 14.7 psi (pounds per squared inch). The total GOR depends on the number of separation stages used in crude processing sequence as well as the operating pressure of each stage. For wet natural gas, the liquid content is given in barrels of condensate per million standard cubic feet of gas (BBL/MMSCF) or in US gallons of condensate per thousands cubic feet (GPM).

## Fluid Properties – Natural Gas Constituents

Class	Components	Formula	Abbreviation	Typical composition (volume %)
Hydrocarbons	Methane	CH <sub>4</sub>	C <sub>1</sub>	59.0-92.0
	Ethane	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub>	3.0-10.0
	Propane	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub>	1.0-15.0
	i-Butane	iC <sub>4</sub> H <sub>10</sub>	iC <sub>4</sub>	0.3-2.5
	n-Butane	nC <sub>4</sub> H <sub>10</sub>	nC <sub>4</sub>	0.3-7.5
	i-Pentane	iC <sub>5</sub> H <sub>12</sub>	iC <sub>5</sub>	0.1-2.0
	n-Pentane	nC <sub>5</sub> H <sub>12</sub>	nC <sub>5</sub>	0.1-2.0
Inert Gases	Hexanes and heavier	-	C <sub>6</sub> <sup>+</sup>	1.0-3.0
	Nitrogen	N <sub>2</sub>	N <sub>2</sub>	0.2-5.0
	Helium	He		0.01-0.1
	Argon	Ar		a few ppm
	Hydrogen	H <sub>2</sub>		a few ppm
	Oxygen	O <sub>2</sub>		a few ppm
Acid gases	Hydrogen sulfide	H <sub>2</sub> S		0.01-10.0
	Carbon Dioxide	CO <sub>2</sub>		0.2-10.0
Sulphur compounds	Mercaptans	R-SH		10-1000ppm
	Sulfides	R-S-R		1.0-10.0ppm
	Disulfides	R-S-S-R		1.0-10.0ppm
Water vapour/Liquid slugs	Free water or brine	H <sub>2</sub> O		variable
	Corrosion inhibitors	-		variable
	Methanol and glycol	CH <sub>3</sub> OH(MeOH), EG, etc.		variable
Solids	Millscale or rust	-		variable
	Reservoir fines and iron sulfide	FeS		variable

Natural gas may contain the substances shown in the table shown on this slide. The primary constituents are paraffin hydrocarbons which are alkanes ( $C_nH_{2n+2}$ , n=1 to 5). The amount of hydrocarbons heavier than hexane is usually very small. The C<sub>6</sub><sup>+</sup> fraction of natural gas may contain aromatics such as **benzene**, **toluene**, **ethylbenzene** and **xylanes (BTEX)** which are important hydrocarbons from environmental points of view. The allowable amount of these hydrocarbon released from natural gas facilities is increasingly lowered by environmental agencies. As said before, the main constituent of natural gas is methane used as a primary fuel, although it is being used as a feedstock to many petrochemical and gas conversion facilities. A portion of the heavier hydrocarbons can be recovered profitably in gas processing facilities as one or more liquid products. These liquefiable components (**condensate**) may be recovered as a single liquid stream which is transported to a separate plant for fractionation into salable products. Common **Natural Gas Liquid (NGL)** products are: **Ethane** - a petrochemical feedstock; **Propane** and **Liquefied Petroleum Gas (LPG**, a mix of propane and butanes) - industrial or domestic fuels and petrochemical feed stocks; **n-Butane** - gasoline additive for vapour pressure control; **i-Butane** - feed stock for refinery processes; **natural gasoline (Stabilized Condensate** - mixture of C<sub>5</sub><sup>+</sup> hydrocarbons) – refinery and petrochemical feedstock. Natural gas itself after removal of impurities and heavier hydrocarbons can be liquefied as **Liquefied Natural Gas (LNG)** to allow transport by ocean going vessels.

Non-hydrocarbon gas or inert gases include nitrogen, helium, argon, hydrogen, and oxygen. The most prevalent inert gas is nitrogen. In most natural gases the nitrogen content is below 2 to 3 mole or volume percent, however natural gases containing 30 mole percent or even higher quantities of nitrogen have been found in various location around the world. Nitrogen lowers the heating value of natural gas. Since the gas is usually sold on the basis of its energy content with a fixed minimum heating value, the nitrogen content is limited to fairly low amounts in commercially salable gas. The other important inert gas is helium. Helium has no harmful effect other than lowering the heating content but since its amount in natural gas is of the order of few hundredths of a percent it is not treated as a contaminant. Recovered helium however is very valuable and royalty payments are requested when a reservoir contains economically recoverable helium. The concentration of other inert gases are extremely small in natural gas and they have only detected by very accurate mass spectrographic techniques. Hydrogen sulfide and carbon dioxide (also known as **acid gases**) are found in many natural gases and may occur in very high percentages. Hydrogen sulfide is very toxic and corrosive while carbon dioxide is corrosive. A natural gas with no carbon hydrogen sulfide is called **sweet gas**. Conversely a **sour gas** contains hydrogen sulfide. Removal of hydrogen sulfide to very low content (4 ppmv or 0.25 grains/100SCF, pipeline specifications) is required before the gas is let to pipelines. Other sulfur compounds are present in small quantities. Free water or brine is undoubtedly present in many gas reservoirs and should be knocked out using gas-liquid separators. At high pressure and low temperatures water and natural gas form a solid **hydrate** capable of plugging flow lines. Water vapour is considered a contaminant that must be removed. Solids may be present from various sources such as pipe scale and rust or fines from the reservoir. Methanol and EG are injected top prevent hydrate formation therefore exist in natural gas streams as a contaminant. Mercury and Arsenic have also been found in various natural gas streams.

## Fluid Properties – Natural Gas physical properties

- PVT behavior and equations of state
- Molecular weight
- Density and specific gravity
- Critical pressures and temperatures
- Gas compressibility factor
- Viscosity
- Specific heat (heat capacity)
- Heating value (Wobbe number)
- Thermal conductivity

In designing gas production, processing, transport, and handling systems a complete knowledge of gas properties is crucial. It is important to know and predict the amount, composition, and density of any phases present in any process situation. **Figure 23-2** of the **Gas Processors Suppliers Association (GPSA)** data book summarizes the important physical properties (constants) for pure hydrocarbons and non-hydrocarbon constituents in natural gas mixtures. Before discussing the physical constants it is important to understand how a gas behaves under various temperature and pressure conditions.

## Fluid Properties – Equations of State

- Behavior of ideal gas
- Behavior of a real (non-ideal) gas
- Compressibility factor approach
- Important equations of state
  - ✓ Van der Waals
  - ✓ Benedict-Webb-Rubin (BWR)
  - ✓ Soave-Redlich-Kwong (SRK)
  - ✓ Peng-Robinson (PR)
  - ✓ Virial

All fluids follow physical laws that define their state under physical conditions. These laws are mathematically represented by **equations of state (EOS)** which essentially correlate pressure, temperature, and volume values. Many different empirical equations of state have been developed over the years, ideal gas equation of state being the simplest one used. An ideal gas is defined as a gas in which the molecules occupy negligible volumes and there is no interaction between the molecules, collisions between them are purely elastic – implying no energy loss on collision. At low pressures (<400 psi) most gases exhibit an almost ideal behavior. The ideal gas can be stated as follows:  $PV=nRT$ , where  $P$  and  $T$  are absolute pressure and temperature,  $n$  is the number of moles, and  $V$  is the volume occupied by the gas.  $R$ , the constant of proportionality in this equation is called **universal gas constant**. The value of  $R$  can be easily determined from the fact that 1 lbmole (pound mole) of any gas occupies 378.6 ft<sup>3</sup> at **standard conditions** (14.73 psia and 60°F or 520° R). Similarly in **CGS** system of units 1 gmole of any gas occupies 22,400 cubic centimeters (cc or milliliters) in **normal conditions** (1 atmosphere and 0° C).

$$R = PV/nRT = (14.73 \times 378.6)/(1 \times 520) = 10.732 \text{ (psia)(ft}^3\text{)/(lbmole)(}^\circ\text{R)}$$

In **SI** units where the  $P$  is in kPa,  $T$  is in K and  $V$  in m<sup>3</sup>, the value of  $R$  to use is 8.314 kPa-m<sup>3</sup>/kgmole.K or kJ/kgmole.K

In general, gases do not exhibit ideal behavior. The reason is that none of the assumption made above actually exist in reality. Molecules for even spars systems occupy a finite volume; intermolecular forces such as electrostatic or Coulomb and attraction and repulsion forces exist even for a perfectly non-polar gas such as argon; and molecular collisions are never perfectly elastic. To correct for non-ideality, the simplest equation of state uses a correction factor known as **compressibility factor, Z**:  $PV=nZRT$ .  $Z$ , therefore, can be considered as the ratio of the volume of gas occupied by real gas to its volume under the same  $T$  and  $P$  if it is ideal. This is the most widely used real gas equation of state.  $Z$  is a function of temperature and pressure and usually can be estimated using **Figures 23-3, 23-4, 23-5, 23-7, 23-8, and 23-9 of the GPSA data book**. **Van der Waals** equation is probably the most basic EOS and, although seldom used today, it serves as a conceptual basis for understanding and developing other equations. Most other cubic EOS's (SRK, PR, etc) were derived as a correction to this equation. SRK is the most widely used EOS in commercial process simulators and gives sufficient accuracy for natural gas applications. PR is the Canadian counterpart of SRK and produces results almost as accurate as those of SRK. (see **Page 25-7** of 11<sup>th</sup> edition of GPSA for a list of important equations of state).

**Van der Waals:** 
$$P = \frac{RT}{V - B} - \frac{A}{V^2}$$

**SRK :** 
$$P = \frac{RT}{V - B} - \frac{A}{T^{0.5}V(V + B)}$$
 **A and B are constants**

## Fluid Properties – Molecular Weight – Mole concept

- Weight of a mole of any substance
- Different units in Imperial, SI and CGS systems
- Moles = Weight of a gas component divided by its molecular weight
- Average molecular weight =

$$MW = \sum [y_N \cdot (MW)_N]$$

Average molecular weight for a mixture of natural gas is calculated using the following formula:

$$MW = \sum [y_N \cdot (MW)_N]$$

$y_N$  = mole fraction of component  $N$  = moles of component  $N$  in gas phase divided by total moles in gas phase.

**Moles = Weight of a gas component divided by its molecular weight**

For instance moles for 32 lbs of methane is  $32/16=2 \text{ lbmole}$ . Molecular weight of individual compounds can be found in **Figure 23-2** of GPSA data book. Since molecular weight is the weight of one mole of a compound it can have various weight units depending on the unit system used. Number of moles is also represented in different forms depending on the unit systems used; therefore for instance we may have  $2.2 \text{ lbmoles}$  of methane which equal to  $1 \text{ kgmole}$  of methane in SI system of units. Therefore, the number of moles is not the number of molecules rather an indication of weight of the compounds in molar basis. One *grmole* of each compound of course contain  $6.23 \times 10^{23}$  molecules, therefore one *lbmole* contains  $6.23 \times 10^{23}/453.5$  molecules of the same compound.

## Fluid Properties – Density and Specific Gravity

- Density = mass of a unit volume (lb/ft<sup>3</sup> or kg/m<sup>3</sup>)
- $S = MW/29$  (for gases)

$$\rho_g = 0.093 \frac{(MW)P}{TZ} \quad \text{or} \quad \rho_g = 2.7 \frac{SP}{TZ}$$

- $S.G.$  = density of liquids/density of pure water @ 60°F
- $^{\circ}\text{API} = 141.5/S.G. - 131.5$  (for liquid hydrocarbons such as crude oil)

Density ( $\rho$ ) = mass of unit volume (lb/ft<sup>3</sup> or kg/m<sup>3</sup>)

$S.G.$  = density of liquids/density of pure water @ 60°F

$^{\circ}\text{API} = 141.5/S.G. - 131.5$

Specific gravity of petroleum fractions may be estimated using the chart of **Figs. 23 -12 and 23-14** of the *GPSA* data book.

Specific gravity of gases = density of the gas/density of air at standard conditions of temperature and pressure (i.e., 14.7 psi and 60°F);

for gases:  $S = MW/29$

where  $MW$  = molecular weight of gas

$S$  = specific gravity (for air=1)

Density of the gas is given as:

$$\rho_g = 2.7 \frac{SP}{TZ}$$

or,

$$\rho_g = 0.093 \frac{(MW)P}{TZ}$$

where

$\rho_g$  = density of gas, lb/ft<sup>3</sup>

$S$  = specific gravity of gas (air=1)

$P$  = absolute pressure, psia (gauge pressure = atmospheric pressure; at sea level 14.7 psi)

$T$  = absolute temperature, °R (temperature in °F + 460)

$Z$  = gas compressibility factors (will be discussed shortly, see also charts given in **Figures 23-7 to 23-9** from *GPSA* data book)

$MW$  = gas average molecular weight

## Fluid Properties – Critical Pressure and Temperature

- Critical temperature= the maximum temperature at which the component can exist as a liquid
- Critical pressure= vapour pressure of a substance at its critical temperature
- Beyond critical temperature and pressure there is not distinction between a liquid and a gas phase

$$P_{PC} = \sum y_N P_{CN} \quad \text{and} \quad T_{PC} = \sum y_N T_{CN}$$

$P_{CN}$  and  $T_{CN}$  from Figure 23-2 GPSA

$$P_{PC} = 709.604 - 58.718 S$$

Thomas et al. equation

$$T_{PC} = 170.491 + 307.344 S$$

For pure components, critical pressure and temperature data can be found from **Figure 23-2** of the GPSA data book. For mixture, **Kay's** mixing rule can be used to find the effective critical properties:

$$P_{PC} = \sum y_N P_{CN} \quad \text{and} \quad T_{PC} = \sum y_N T_{CN}$$

Where  $P_{PC}$  and  $T_{PC}$  are the **pseudocritical** pressure and temperature, respectively, for the mixture and  $y_N$  is the mole fraction of component  $N$  in the gas mixture. These are called *pseudo* because they are used a correlation basis rather than as a very precise representation of mixture critical properties.

In absence of better data the **Thomas et al.** equation may be used to obtain the **pseudocritical** properties from the gas specific gravity as follows:

$$P_{PC} = 709.604 - 58.718 S$$

$$T_{PC} = 170.491 + 307.344 S$$

Where  $S$  is the specific gravity of gas. This equation is only accurate within the limits of up to 3% H<sub>2</sub>S, 5% N<sub>2</sub>, or a total impurity (non-hydrocarbon) content of 7% beyond which errors in critical pressure exceeds 6%. It should be noted that the gas gravity method is not very accurate. If the analysis of the gas is available, it must be used in accordance with the **Kay's** mixing rule.

## Fluid Properties – Gas Compressibility Factor

- Standing-Katz compressibility charts (Figures 23-3, 23-4, and 23-5 GPSA)
- Brown-Katz-Oberfell-Alden charts (Figures 23-7, 23-8, and 23-9 GPSA)
- Acid gas content consideration by Wichert-Aziz correction factors

$$T'_{PC} = T_{PC} - \varepsilon \quad \text{and} \quad P'_{PC} = \frac{P_{PC} T'_{PC}}{T_{PC} + B\varepsilon(1-B)}$$

$\varepsilon$  from Figure 23-10 GPSA

- Compressibility from equations of state

Several different correlations are available for this important parameter. The basic correlations use the corresponding states concept. According to the **Van der Waals' law of corresponding states**, the physical characteristics of a substance are a function of its relative proximity to the critical point. This means that the deviation from ideal behavior of gases is the same if they are located at the same state relative to their critical state. Therefore the relevant temperature and pressure values that express the departure of a real gas from ideal behavior are the reduced pressure,  $P_r$ , and reduced temperature,  $T_r$ :

$$Z = f(P_r, T_r)$$

Where  $P_r = P/P_c$  and  $T_r = T/T_c$ . For gas mixtures, the reduced parameters are denoted as **pseudoreduced temperature**  $T_{Pr}$  ( $=T/T_{PC}$ ), and **pseudoreduced pressure**,  $P_{Pr}$  ( $=P/P_{PC}$ ).

There are several ways to calculate compressibility factor:

1- **Standing-Katz** charts: **Figures 23-3, 23-4, and 23-5** of GPSA data book are used to estimate the compressibility using the reduced temperature and pressure values. These charts are generally reliable for sweet natural gases with minor amounts of non-hydrocarbons such as  $N_2$ .

2- **Brown-Katz-Oberfell-Alden** charts: **Figures 23-7, 23-8, and 23-9** of GPSA data book are used to predict the compressibility for low molecular weight natural gases. These figures cover a wide range of molecular weights (15.95 to 26.10), temperatures (-100° to 1000° F), and pressures (up to 5,000 psia). For gases whose molecular weights lie in between the molecular weights shown in Figs. 23-7 through 23-9, linear interpolation should be used to compute the compressibility. In general compressibilities for gases with less than 5% noncondensable components, such as nitrogen, carbon dioxide, and hydrogen sulfide, are predicted with less than 2% error. When molecular weight is above 20 and compressibility is below 0.6, errors as large as 10% may occur. Natural gases which contain  $H_2S$  and  $CO_2$  exhibit different compressibility factor behavior than do sweet gases. The **Wichert and Aziz** equation should be used to correct for the acid gas content. **Figure 23-10** of the GPSA data book is used to find the correction factor and then correct the *pseudocritical* pressure and temperatures determined by **Kay's rule** as follows:

$$T'_{PC} = T_{PC} - \varepsilon \quad \text{and} \quad P'_{PC} = \frac{P_{PC} T'_{PC}}{T_{PC} + B\varepsilon(1-B)}$$

where  $\varepsilon$  is the correction factor and  $B$  is the mole fraction of  $H_2S$ . These values of critical pressure and temperature are used to find the corrected Z factor for acid gas containing gases. Equations of state may also be used to calculate Z factor by replacing  $Z=PV/RT$  in EOS, a cubic equation is obtained which should be solved for Z values. Numerical techniques are used to solve these cubic equations.

## Fluid Properties – Gas Viscosity

- Carr et al. correlation (Fig. 23-32 and 23-33 GPSA)
- Viscosity of gas mixture from single component data:

$$\mu_{1g} = \frac{\sum_{N=1}^n \mu_{1gN} y_N M W_N^{0.5}}{\sum_{N=1}^n y_N M W_N^{0.5}}$$

- Lee et al. for natural gas:

$$\mu_g = K \exp(X \rho_g^y) \text{ where, } K = \frac{10^{-4}(9.4 + 0.02MW)T^{1.5}}{209 + 19MW + T}$$

$$X = 3.5 + 986/T + 0.01MW \text{ and } y = 2.4 - 0.2X$$

- GPSA charts – Fig.s 23-30 through 23-38
- Dean and Stiel method

$$\xi = 5.4402 \frac{T_{PC}^{1/6}}{(\sum y_N M W_N)^{1/2} P_{PC}^{2/3}}; \text{ for } T_{Pr} > 1.5, \xi \mu_g = 166.8(10^{-5})[0.1338 T_{Pr} - 0.0932]^{5/9},$$

$$\text{and for } T_{Pr} \leq 1.5, \xi \mu_g = 34.0(10^{-5}) T_{Pr}^{8/9}$$

The viscosity of a fluid, a measure of its resistance to flow, is defined as the ratio of the shear force per unit area to local velocity gradient. The viscosity as defined above is shown by the Greek letter  $\mu$  and called **dynamic viscosity**. In addition, the ratio of the dynamic viscosity of a fluid to its density, known as **kinematic viscosity** ( $\nu = \mu / \rho$ ) is also used in many flow problems. Viscosity is usually measured in centipoise, with 1 cp equal 0.01 g/(cm.sec) in CGS system of units, or  $2.01 \times 10^{-5}$  lbsec/ft<sup>2</sup> or  $1.0 \times 10^{-3}$  N.s/m<sup>2</sup> or 0.001 Pa.s. The most accurate method to determine viscosity is obviously to measure it for a given fluid under the desired conditions. This, however, is not generally possible, given the various complex mixtures of hydrocarbon and non-hydrocarbon compounds present in oil and gas industries. Some common methods of predicting gas viscosity are given below:

1. **Carr et al.** correlation for natural gas: This method only needs gas gravity or average molecular weight to calculate viscosity. The correlations were presented in graphical forms as given in **Figures 23-32 and 23-33** of the GPSA data book. *Figure 23-32* is used first to calculate the viscosity at one atmosphere pressure and any given temperature. Corrections for non-hydrocarbons such as CO<sub>2</sub>, H<sub>2</sub>S, and nitrogen are provided. Then *Figure 23-33* can be used to correct for pressure based on the corresponding state principle.
2. Viscosity from single-component data: If the analysis of gas is known, it is possible to calculate the viscosity of the gas mixture from the component viscosities. First viscosity is determined at one atmosphere (or any low pressure) and the given temperature using the **Herning and Zippere** mixing rule as:

$$\mu_{1g} = \frac{\sum_{N=1}^n \mu_{1gN} y_N M W_N^{0.5}}{\sum_{N=1}^n y_N M W_N^{0.5}}$$

where,  $y_N$  = mole fraction of component N in the gas mixture; and  $\mu_{1gN}$  = pure component viscosity at 1 atmosphere pressure and the desired temperature. The pressure correction is made using the Carr et al.'s charts. Viscosity of some natural gas constituents can be found from **Figure 3-16** of Ref. 5 (**Kumar's Gas Production Engineering**).

3. **Lee et al.** Correlation for natural gas: Lee et al. provide an analytical expression which can be used for programming purposes. where,  $T$  is °R,  $\rho_g$  is in g/cm<sup>3</sup>, and  $\mu_g$  is in cp. This equation however it does not correct for impurities such as CO<sub>2</sub>, H<sub>2</sub>S, and N<sub>2</sub>.

$$\mu_g = K \exp(X \rho_g^y) \text{ where, } K = \frac{10^{-4}(9.4 + 0.02MW)T^{1.5}}{209 + 19MW + T}$$

$$X = 3.5 + 986/T + 0.01MW \text{ and } y = 2.4 - 0.2X$$

4. **Dean and Stiel** method:

$$\xi = 5.4402 \frac{T_{PC}^{1/6}}{(\sum y_N M W_N)^{1/2} P_{PC}^{2/3}}; \text{ for } T_{Pr} > 1.5, \xi \mu_g = 166.8(10^{-5})[0.1338 T_{Pr} - 0.0932]^{5/9},$$

$$\text{and for } T_{Pr} \leq 1.5, \xi \mu_g = 34.0(10^{-5}) T_{Pr}^{8/9}$$

## Fluid Properties – Specific Heat

- **Definition:** amount of heat required to raise the temperature of a unit mass of a substance through unity
- $C_p$  and  $C_v$  and their relationships (Maxwell's equation)
 
$$C_p - C_v = -T \frac{(\partial P / \partial T)_v^2}{(\partial P / \partial v)_T} \quad \text{for ideal gases} \quad C_p - C_v = R$$
- $C_p$  determination
  - Hankinson's gravity  $C_p^o = A + B \cdot T + C \cdot S + D \cdot S^2 + E(T \cdot S) + F \cdot T^2$
  - Kay's mixing rule  $C_p^o = \sum_{N=1}^n y_N C_{pN}^o$
- $C_p$  of natural gas mixture, pressure corrections (Kumar's Book – Table 3-3, Figures 3-17 and 3-19)

**Specific heat** or **heat capacity** is a basic thermodynamic quantity and is defined as the amount of heat required to raise the temperature of a unit mass of a substance through unity. It is an intensive property of a substance and can be measured at constant pressure ( $C_p$ ) and constant volume ( $C_v$ ). They can be expressed in thermodynamic terms as:

$$C_p = (\partial h / \partial T)_p \quad \text{and} \quad C_v = (\partial u / \partial T)_v$$

Where ***h*** is the molal enthalpy (**Btu/lbmole**), ***u*** is the molal internal energy (**Btu/lbmole**). Using Maxwell's relationship it can be shown:

$$C_p - C_v = -T \frac{(\partial P / \partial T)_v^2}{(\partial P / \partial v)_T} \quad \text{for ideal gases} \quad C_p - C_v = R$$

For non ideal gases the equations of states may be used to find the relationship between the two.

The low pressure isobaric ( $C_p^o$ ), can be determined primarily by two methods:

**Hankinson et al.'s** gas gravity technique: the value for  $C_p^o$  is calculated in **Btu/lbmole.<sup>°F</sup>** from the gas specific gravity **S** at any temperature **T (°F)**:

$$C_p^o = A + B \cdot T + C \cdot S + D \cdot S^2 + E(T \cdot S) + F \cdot T^2$$

Where fro a temperature range of 0 to 200°F:

$$A = 4.6435, \quad B = -0.0079997, \quad C = 5.8425, \quad D = 1.1533, \quad E = 0.020603, \quad \text{and} \quad F = 9.849 \times 10^{-6}$$

And for a temperature range of 0 to 600°F:

$$A = 3.7771, \quad B = -0.001105, \quad C = 7.5281, \quad D = 0.65621, \quad E = 0.014609, \quad \text{and} \quad F = 0.0$$

The effective mixture specific heat or heat capacity at low pressure can also be calculated using **Kay's** rule:

$$C_p^o = \sum_{N=1}^n y_N C_{pN}^o$$

Where the heat capacity for some common constituents of natural gas can be obtained from **Table 3-3** of Ref. 5 (**Kumar's Gas Production Engineering**) or **Figure 13-6** of the 11<sup>th</sup> edition of the GPSA databook. The isobaric specific heat ( $C_p$ ), at the pressure of interest can subsequently be determined by correcting  $C_p^o$  for pressure using **Figure 3-19** of the above referenced book (**Kumar**).

$C_v$  is usually determined indirectly. First  $C_p$  is calculated using any of the previous methods. Then **Figure 3-17** of **Kumar's** book is used to determine  $C_p - C_v$  and finally  $C_v$  is calculated. As indicated before the relationship between  $C_p$  and  $C_v$  can be calculated using **Maxwell's** relationship and the appropriate equation of state

## Fluid Properties – Heating Value/Wobbe Index

- Definitions:
  - Gross Heating Value (GHV) or Higher Heating Value (HHV): Total energy transferred as heat in an ideal combustion reaction at a standard temperature and pressure in which all water formed appears as liquid
  - Net Heating Value (NHV) or Lower Heating Value (LHV): Total energy transferred as heat in an ideal combustion reaction at a standard temperature and pressure in which all water formed appears as vapour
- Heating value determination:  $H_v = \sum y_N H_{vN}$
- Wobbe Index:  $W_o = HHV/S^{1/2}$

The heating value is defined as the total energy transferred as heat in an ideal combustion reaction at a standard temperature and pressure. If water formed as a combustion product appears as liquid the heating value is called **Gross Heating Value (GHV)** or **Higher Heating Value (HHV)**; however if the water appears in vapour form the heating value is called **Net Heating Value (NHV)** or **Lower Heating Value (LHV)**. The values from HHV and LHV are obtained from **Fig. 23-2** of the GPSA data book. The heating value can be calculated per unit volume of an ideal gas, or per unit volume of a real gas as follows:  $H_v = \sum y_N H_{vN}$ , where  $H_{vN}$  is the heating value of individual components of natural gas and  $y_N$  is the mole fraction of component  $N$  in the natural gas mixture. To calculate the ideal heating value produced or used from a given period of time,  $H_v$  must be multiplied by the ideal gas volumetric flow rate of gas for the period. For real gases the heating value is divided by compressibility factor when a real gas flow rate is employed. Therefore  $H/Z$  is heating value per unit volume of real gas.

The gas heating quality is commonly expressed by the **Wobbe** index  $W_o$ , which is defined in the following equation  $W_o = HHV/S^{1/2}$ ; with the higher heating value  $HHV$  and  $S$  the gas specific gravity. For natural gases the **Wobbe** index ranges between 960 and 1540  $Btu/\text{ft}^3$  (10 and 16  $kWh/m^3$ ). The **Wobbe** index is the ratio of the heat of combustion of a gas to its specific gravity. For light hydrocarbon gases the **Wobbe** index is almost a linear function of the gas' specific gravity. The **Wobbe** index, having the units of energy per unit volume, is a comparative measure of thermal energy flow through a given size nozzle. If the **Wobbe** index remains constant, a change in the gas composition will not lead to a noticeable change in the air-fuel ratio and combustion rate. But this change in composition will change the volumetric energy content and knock resistance of the mixture. The **Wobbe** Index is the best indicator of the similarity between a specific natural gas and propane-air mixture. The **Wobbe** Index is a number indicating the interchange ability of fuel gases. It relates fuel gas heating characteristics in a manner that is useful for blending fuel gases, or to obtain a constant heat flow from a gas of varying composition. The **Wobbe** Index does not relate to such technical factors as flame temperature, heat transfer coefficients or temperature gradients.

## Fluid Properties – Thermal conductivity

- Significance of thermal conductivity – Heat transfer calculations and heat exchanger (line heater, shell and tube, air cooler, etc.) design
- Determination of thermal conductivity – gas and liquid (GPSA Fig.s 23-40 through 23-45)
- Lenoir et al. pressure corrections
- Gas mixture thermal conductivity

$$k_m = \frac{\sum(y_N k_N \cdot \sqrt[3]{MW_N})}{\sum(y_N \cdot \sqrt[3]{MW_N})}$$

Thermal conductivity for natural gas mixtures at elevated pressure can be calculated from an atmospheric value and a pressure correction. **Figures 23-40** through **23-43** of the GPSA data book present low pressure thermal conductivity data of gases developed from published data. The pressure correction of Lenoir et al. shown in **Fig. 23-41** of the above data book is applied to these low pressure data. The thermal conductivity of liquid paraffin hydrocarbons is plotted in **Fig. 23-44** and the thermal conductivity of liquid petroleum fractions in **Fig. 23-45** of the same data book. To determine the thermal conductivity of a gaseous mixture of defined components, the thermal conductivity of each component at the given temperature is read from charts provided and the thermal conductivity of the mixture is determined by the **cube root rule**. This rule is applicable to mixtures of simple gases; it does not apply to CO<sub>2</sub> mixtures because the thermal conductivity goes through maximum:

$$k_m = \frac{\sum(y_N k_N \cdot \sqrt[3]{MW_N})}{\sum(y_N \cdot \sqrt[3]{MW_N})}$$

Where  $k_m$  is the thermal conductivity of the mixture and  $k_N$  and  $y_N$  are the thermal conductivity and mole fraction of component  $N$  in the gas mixture, respectively.

## Phase Behavior - Fundamentals

- Single component fluid
- Two component fluid
- Multi-component fluid
- Phase diagrams (envelopes)
  - Pressure-Temperature-Volume (*PVT*)
  - Pressure-Temperature (*PT*)
  - Pressure composition
  - Composition-composition
- Phase rule

The properties exhibited by any substance depend upon its phase, namely, whether it is in the solid, liquid, or gaseous phase. Substances can be classified into two types – pure or single component, and multicomponent. Phase behavior relationships can be determined from laboratory pressure-volume-temperature (*PVT*) studies, or using theoretical/ empirical methods such as the equations of state. These relationships are frequently shown graphically as **phase diagrams** to enhance qualitative understanding of the phase behavior of compounds. For design purposes, however, precise quantitative phase behavior data are crucial. Some fundamental concepts will be discussed in the next few slides.

A phase diagram for a single component has three axis: *P*, *T*, and *V*. Usually, *P-T* diagrams only are used for a single component system. For multi-component systems, the mixture composition becomes an additional variable. Generally, three types of phase diagrams are used for mixtures: (a) Pressure vs. temperature or *P-T* diagrams, holding the composition fixed; (b) pressure composition diagrams, keeping pressure and temperature fixed; (c) composition-composition diagram, keeping pressure and temperature fixed.

Gibb's phase rule for degrees of freedom of a system is written as:

$$N = C - P + 2$$

Where *N* = number of degrees of freedom of the system

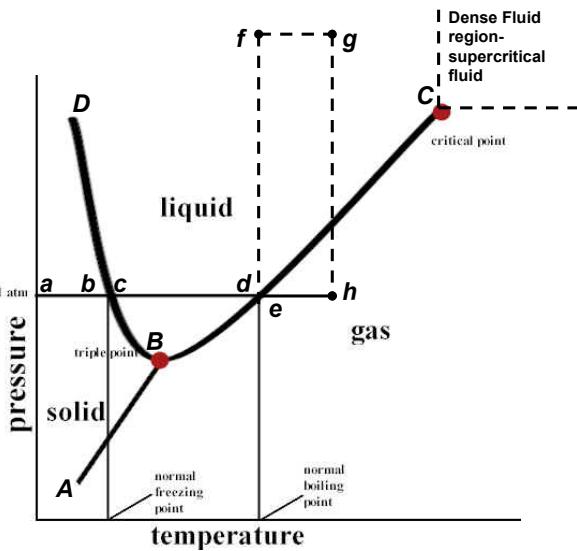
*C* = number of distinct chemical components (or compounds) in the system

*P* = number of phases in the system

The number of degrees of freedom is the number of variables that must be defined to fix physical state of the system. Usually, pressure, temperature, and composition serve as the variable. For instance, consider a mixture with *C* components, if only two phases exist (e.g., vapour and liquid), therefore *P*=2 and the degrees of freedom will be *N*=*C*-2+2=*C*, therefore in order to specify this system we can have a number of variables (unknowns) equal to the number of components in that system; in this system if the pressure and temperature is known the composition of the system or the concentration of all *C* components can be considered unknown and *C* equations may be written from equilibrium relations to calculate *C* variables.

## Phase Behavior – Single Component Systems

- Phase Equilibrium
  - gas-liquid
  - gas-solid
  - Liquid-solid
- Triple point
- Critical point



The diagram shown on this slide presents a typical  $P$ - $T$  phase diagram for a single-component system. The equilibrium lines **AB**, **BC**, and **BD** indicate the combinations of pressure and temperature at which the adjacent phases shown on the diagram exist in equilibrium. Line **AB** represents the equilibrium between solid and vapour. A solid above this line will sublime directly to vapour phase without ever going to liquid phase, on reduction of pressure to below line **AB**. An example of this is *dry ice*. Line **BD** indicates the solid liquid equilibrium. Line **BC** is equilibrium between liquid and vapour phases. At the **triple point** all three phases are in equilibrium. From the **phase rule**, it can be seen that for a single-component system with three phases, the degrees of freedom is  $N = C-P+2=1-3+2=0$ . Therefore, the triple point is a unique point that defines the whole system. The equilibrium lines, however, represent only two phases in equilibrium and the degree of freedom  $N=1$ , therefore, specifying temperature or pressure fixes other variables for the system. In the single phase regions,  $N=2$ , and both pressure and temperature must be known to determine the location (or state) of the system in the phase diagram. The Liquid-vapour (gas) line begins at the triple point, **B**, and ends at the critical point **C**. At the critical point, liquid and gaseous phases become indistinguishable and their *intensive* properties (properties independent of the amount of fluid; for example density, viscosity) become identical. The temperature and pressure corresponding to critical point are termed **critical temperature**,  $T_C$  and **critical pressure**,  $P_C$  respectively, and are a uniquely defined numerical value for every pure substance. More formal definitions are:

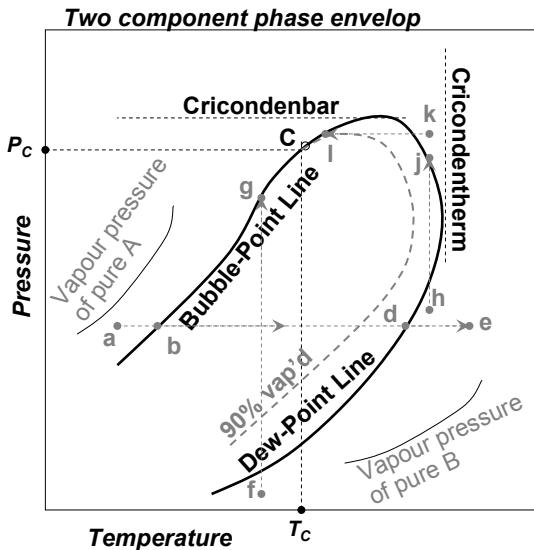
**Critical temperature:** The temperature above which a substance cannot be liquefied by the application of pressure alone

**Critical pressure:** The pressure at which gas exists in equilibrium with liquid phase at the critical temperature. Also defined as the saturation pressure corresponding to the critical temperature.

Consider an isobaric (constant pressure) process represented by the line **abcdeh**. From **a** to **b** the system is completely solid, and the energy requirements for achieving the increase in temperature are simply proportional to the specific heat of solid phase. From **b** to **c**, pressure and temperature remain constant, but an energy equal to the latent heat of fusion is required to convert the solid to liquid. The energy supplied is converted to internal energy. The temperature increase from **c** to **d** requires energy proportional to the specific heat of the liquid phase. At **d** the liquid is a saturated liquid – any further addition of energy will cause vapourization at constant pressure and temperature. Energy equal to the latent heat of vapourization is required to accomplish the phase change. At **e**, the vapour is termed saturated. At higher temperatures, for example at **h**, it is called superheated. If one proceeds from **d** by a compression process at constant temperature to **f**, liquid will at some point begin to disappear into seemingly gaseous phase. Above the critical point at **f**, the system is in a *fourth* phase that exhibits properties different from gas. The properties of this fluid are in between those of liquid and gas, though not correlatable to either. For example, it is denser than a regular gas, and is more compressible than a regular liquid. For conditions far removed from the two phase region, particularly at pressure and temperature conditions above the critical point, it is impossible to define the state of the system, and is best referred to as being in the *fluid state*. Sometimes the fluid at above critical conditions are called *gas* rather than *vapour*, the distinction being that the vapour is condensable but the gas is not.

## Phase Behavior: Two-Component Systems

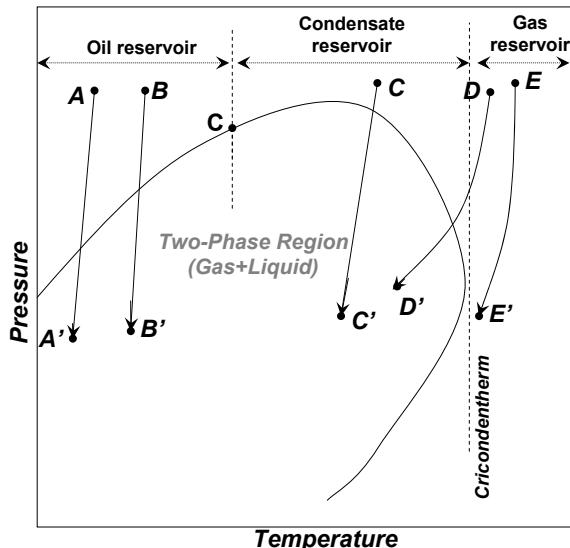
- Concept of phase envelope
- Equilibrium lines
  - Bubble point
  - Dew point
- Critical point
- Cricondentherm
- Cricodenbar
- Retrograde phase change



Addition of a second pure component complicates the  $P$ - $T$  diagram. The figure on this slide shows that the one component, vapour pressure line becomes an **envelop**. For the two phase mixture with two components the phase rule yields  $N=2$ . Therefore both  $P$  and  $T$  must be specified to define the state of the system; the two phase locus (region) is an area not a line. The location of the phase envelop depends on the vapour pressure curves of the pure components and the composition of the mixture. In this diagram the more volatile (lower boiling point) component, A, has its vapour pressure line on the left (lower  $T$  and higher  $P$ ). The higher boiling component, B, is represented by the vapour pressure curve on the right. It should be noted that the critical point of the mixture at C, is much higher than the critical points of the individual components. In a two component system the boiling and condensation will not occur at constant temperature and pressure. Therefore instead of boiling point or condensation point, we have **bubble-point** and **dew-point** lines. The **bubble-point** line is the locus at which vapourization begins. The **dew-point** line is the locus at which condensation begins. The bubble-point and dew-point lines meet each other at **critical point, C**. Any particular  $P$ - $T$  diagram corresponds to a fixed composition for the overall mixture. In addition to bubble-point and dew-point lines, the diagram also shows a constant percent-vapourization line for 90% vapourized. This line converges to the critical point as do all constant percentage vapourization lines. Assume we have a liquid, with known composition represented by the shown phase envelope, at point **a**. The liquid is obviously **subcooled** because the temperature is below the saturation point (bubble point, **b**). If we heat the liquid at constant pressure, the mixture reaches point **b** and it starts boiling (vapourization starts). As vapourization continues at constant pressure, the temperature rises, as opposed to pure compound boiling in which the temperature remains constant. Therefore there is boiling range rather than a boiling point. When the last drop of liquid vapourizes, the dew-point curve is reached at point **d**. If heating continues the saturated vapour at point **d** is further warmed up and we will have a superheated vapour at point **e**. If we start with a superheated vapour at point **f**, with a temperature below the critical temperature, and increase the pressure at constant temperature (isothermal) in an isothermal compression, the dew point is first reached. Then progressive condensation occurs until the mixture is all liquid at the bubble point, **g**. This behavior is regarded as **normal condensation**. Assume we start with a superheated vapour at point **h**, this time at a temperature above critical point ( $T_c$ ). Another new behavior arises. If we compress isothermally, we reach the dew point and condensation results, as expected. Further increase in pressure at first results more condensation, but a point is reached at which condensation begins to decrease in amount. With continued pressure increase, the dew point is again reached at point **j**. This phenomenon is known as **retrograde vaporization**. If we start from point **j**, a reverse process will happen and we will have a **retrograde condensation** process. Line **kI** depicts a second type of retrograde vapourization. In this case a decrease in temperature at a constant pressure (above critical pressure) from point **k** at first yields liquid formation, but at some point the liquid begins to evaporate and the dew point is once again reached at point **I**. This is a bit confusing because we expect a mixture to get more liquid like as it is chilled. Nevertheless, it is a fluid remaining above the liquid phase at dew point **I**; this fluid may be termed **dense phase**. The highest pressure at which liquid and vapour can coexist can be greater than critical pressure. This pressure is referred to as **cricodenbar**. Similarly the highest temperature at which the two phases may coexist is called **cricondentherm**.

## Phase Behavior: Multi-Component Systems

- Full wellstream
- Source of phase diagrams
- Quantitative phase behavior
- Phase behavior in separators

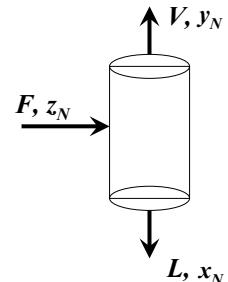


The basic phase behavior for a multi-component system is the same as for binary mixtures. All of the aforementioned phase regions, important phase lines (e.g., critical point, bubble-point and dew point lines), and phase transition phenomena are the same as the two-component systems. This is because, according to the phase rule, composition for all but one component, or  $C-1$  variables, must be specified to define the mixture. Only two degrees of freedom remain – exactly the same as for a binary mixture. The  $P-T$  diagram for a multi-component mixture of given composition has a shape very similar to that of a binary mixture. Phase envelopes for most naturally occurring hydrocarbon mixtures are very broad because the components have a wide boiling range. Phase diagrams of typical full well streams are shown in this slide. The diagram shown in this slide represents the general shape of the phase diagram for a *reservoir fluid*. The type of reservoir and fluid produced from it depend upon the location of the reservoir temperature and pressure relative to the phase diagram. Line **AA'** shows the situation for a low GOR crude with little dissolved gas. Point **A** represents the reservoir temperature and pressure. As the oil flows out of the reservoir, into the wellbore, and up to the producing string to the wellhead, both the temperature and pressure decrease. The temperature decreases for two reasons. First the temperature of the surrounding rock decreases toward the surface, second vapourization may take place due to reduction of pressure and the energy required to evaporate the lower boiling components is provided by the flowing fluid itself. The pressure, similarly, drops for two reasons. As fluid travels up the string, the hydrostatic head is decreased and thus the pressure. In addition, there is frictional pressure drop in tubing. The net effect of temperature/pressure reduction is to bring the fluid below its bubble point and into the **two phase region**. A few crude oils do not reach the bubble-point curve and evolve no associated gas; such oil is called to as **dead oils**. The curve **BB'** corresponds to the situation of a high GOR crude oil. More gas is evolved than for curve **AA'**. If the fluid  $T$  and  $P$  lie in the region to the left of the (lower temperature) of the critical point, the produced fluid is termed a **crude oil**. Line **CC'** shows the behavior of a retrograde condensate fluid as it is produced, something between a natural gas and a crude oil. In this case the relative amount of both gas and liquid may be very high (see table concerning the characteristic of reservoir fluids). If the reservoir temperature lies between the critical temperature and the *cricondentherm*, the reservoir is usually termed **condensate reservoir** and the produced fluid is called **retrograde condensate**. If the pressure in the condensate reservoir falls below the dew point condensation will occur in the reservoir and some valuable hydrocarbons may remain in the reservoir. High pressure gas injection usually is needed to maintain the pressure. Curve **DD'** depicts the situation for a **wet natural gas**. The reservoir conditions are in the gas or dense fluid region to the right of *cricondentherm*. Curve **EE'** represents the reservoir and producing condition for a **dry natural gas**.

Phase envelopes are measured in *PVT* laboratories or predicted from equilibrium calculations. Experimental methods are very time consuming and expensive. Computer calculations are the method of choice in developing phase envelopes and produce rather satisfactory results for design purposes. In most natural gas, or generally petroleum, production operations, it is important to know the phase present, their relative quantities and rather accurate composition of constituents in each phase as a function of temperature and pressure, in order to design the system. It is desirable to control these phases by controlling the operating conditions. Therefore it is important to understand the concept of equilibrium and the calculation techniques.

## Phase Behavior: Vapour-Liquid Equilibria

- Thermodynamic criteria for equilibrium-equality of fugacities:  $f_{N,v} = f_{N,l}$
- Equilibrium ratio ( $K$  values):  $K = y_N/x_N$
- Equilibrium calculations
  - Equilibrium flash:  $V_N = \frac{K_N F_N}{1/(V/L) + K_N}$
  - Bubble point:  $\sum z_N \cdot K_N = 1.0$  guarantees vapour is present  
 $\sum z_N \cdot K_N > 1.0$  guarantees liquid is present
  - Dew point:  $\sum x_N = \sum z_N / K_N = 1.0$   
 $\sum z_N / K_N > 1.0$  guarantees liquid is present



A gas-liquid flash separator

Phase equilibrium is reached when there is no net transfer of material from one phase to another. Such transfer involves a decrease in the total free energy of the system. Thus, when the equilibrium is attained, the total free energy, also called Gibbs free energy, will be at its minimum value. It can be mathematically shown that according to thermodynamic principles the fugacity of individual components in the liquid and gas phases should be equal or:

$$f_{N,v} = f_{N,l}$$

The amount of hydrocarbon fluid that exists in the gaseous phase or the liquid phase at any point in the process is determined by flash calculations. At a given pressure and temperature each component of the hydrocarbon mixture will be in equilibrium.  $K$  values relate the compositions in gas and liquid phases:

$$K_N = \frac{V_N/V}{L_N/L}$$

Where,

$K_N$  = Constant for component  $N$  at a given temperature and pressure (given in Charts in [pages 25-11 to 25-24](#) or of the GPSA data book, SI 11<sup>th</sup> edition)

$V_N$  = moles of component  $N$  in the vapour phase

$V$  = total moles in the vapour phase

$L_N$  = moles of component  $N$  in the liquid phase

$L$  = total moles in the liquid phase

Moles of components in the liquid and gas phase may be calculated from the following equations which are derived by mass balance on a gas liquid separator:

$$V_N = \frac{K_N F_N}{1/(V/L) + K_N} \quad \text{and} \quad L_N = \frac{F_N}{K_N(V/L) + 1}$$

where  $F_N$  = Total moles of component  $N$  in the fluid (e.g., feed to a separator)

Mass balance also results in the following equation for a separator:  $L = \frac{F}{1 + (V/L)}$

For **bubble point calculations**, the question is at what temperature will a liquid feed with a known composition ( $z_N$ ), begin to vaporize at the given pressure  $P$ ? Calculations are based on the concept that the first tiny bubble of vapour formed is in equilibrium with the feed at essentially unchanged composition,  $z_N$ . The composition of the vapour bubble is, by previous definition,  $y = Kz$ , for each component. The sum of mole fractions of any mixture must be identically one:  $\sum y_N = \sum z_N \cdot K_N = 1.0$ . Thus, our task is to find  $T$  such that when the  $K$ s are obtained for that  $T$  and the given  $P$ , the sum of  $z_N \cdot K_N$ s is indeed equal to one within an acceptable tolerance. The procedure involves trial and error calculations. The same procedure is followed for dew point calculations. In here, we consider that when the first tiny drop of liquid is condensed, the feed composition remains unchanged. Therefore the trial and error calculations are to determine the temperature at which the condensation starts so that:  $\sum x_N = \sum z_N / K_N = 1.0$

## Phase Behavior: Water Hydrocarbon Systems

- Water and hydrocarbons are insoluble in liquid phase
- Problems with water saturated gas
  - Excessive pressure drop
  - Plugging due to ice and hydrate formation
  - Severe corrosion in acid and sour gas lines
- Water content of natural gas
  - **McKetta and Wehe** charts: Fig. 20-3, GPSA
  - **Robinson et al.** correlation for sour gases: Fig.s 20-10 and 20-11, GPSA
  - **Campbell charts:**  $W = y_{hc} W_{hc} + y_{CO_2} W_{CO_2} + y_{H_2S} W_{H_2S}$  and Fig.s 20-8 and 20-9, GPSA)
  - **Equation of state methods:** SRK, PR and commercial process simulators (e.g. HYSYS, ASPEN, PROSIM, PROII, AMSIM, AQUASIM, SSI, DESIGNII, PROCESS, etc.)

Although in the liquid phase, water and hydrocarbons are virtually insoluble, it is important to focus on the behavior of gas-water systems in the gas phase. The reason is that natural gases as produced at the wellhead are nearly always saturated with water. When water-saturated natural gas flows in a pipeline the following problems can occur: (1) Liquid water can collect in pipelines and therefore increase pressure drop and/or cause slug flow; (2) Free water also can freeze into ice and/or form solid hydrates and so reduce the gas flow or even plug the line capacity; and (3) Acid gases –  $H_2S$  and  $CO_2$  – dissolve in free water and can cause severe corrosion. Therefore water is a *universal impurity or contaminant* in natural gas systems. Design of oilfield gathering lines and natural gas dehydration and hydrate inhibition facilities requires two key phase-behavior predictions: (1) The water content of saturated natural gases and (2) The hydrate formation temperature and pressures.

The best way to determine the water content of natural gas is to use experimental techniques. The use of **Bureau of Mines Dew-Point tester (ASTM D 1142-63)** and the standard ASTM procedure is regarded an acceptable technique in oil and gas industries. Other electronic measurement devices are available and can be used. It is not always possible to use experimental equipment and calculation procedures are needed to best estimate the water content in natural gas for design purposes. **Figure 20-3** of the GPSA data book (**McKetta** correlation) can be used to determine the saturated water vapour content of sweet, lean, natural gases. Similar charts were prepared by others which result in rather accurate predictions (about 5% average error) for gases containing up to 10%  $CO_2$  and/or  $H_2S$  at pressure below 500 psia. This simple method becomes increasingly inaccurate with increasing pressure, temperature, and acid gas content. For acid gas-containing gases, the two most common correlations are as follows:

1. **Robinson et al.** charts: Robinson et al. convert the carbon dioxide concentration into an equivalent  $H_2S$  concentration by multiplying the actual  $CO_2$  composition by 0.75. Then they present charts of water content (bbl/MMscf) as ordinate and temperature ( $^{\circ}F$ ) as abscissa for several pressures and five natural gas mixtures (see **Figures 20-10** and **20-11** of the GPSA data book). Pressure interpolation should be logarithmic. The Robinson et al. charts are based on computer calculations using SRK equation of state and are less empirical than the Campbell method.

2. **Campbell** Charts: The Campbell method, uses the following empirical combination rule:

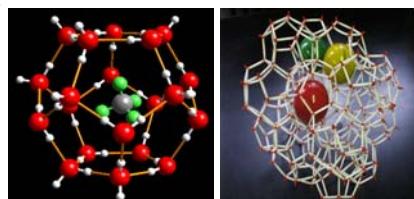
$$W = y_{hc} W_{hc} + y_{CO_2} W_{CO_2} + y_{H_2S} W_{H_2S}$$

Where  $W$  = water content of sour gas (lb water/MMscf);  $W_{hc}$  = water content of sweet gas (lb water/MMscf) (can use McKetta chart),  $y_{hc}$  = mole fraction of all components except acid gases;  $W_{CO_2}$  = effective water content of  $CO_2$  in lb water/MMscf from **Figure 20-9** GPSA data book),  $W_{H_2S}$  = effective water content of  $H_2S$  in lb water/MMscf from **Figure 20-8** GPSA data book);  $y_{CO_2}$  and  $y_{H_2S}$  = mole fraction of  $CO_2$  and  $H_2S$  respectively.

3. **Equation-of-state method:** the previous hand calculation methods are suitable for quick calculation when simulation software is not available. rigorous three-phase (gas-water rich liquid-hydrocarbon rich liquid) computer-based flash calculation can predict the distribution of all the components in all three phases. the SRK and PR have been used for such rigorous calculations and most commercial process simulators such as **ASPEN**, **HYSYS**, **PROSIM**, etc. are capable of performing such calculations in the matter of milliseconds with high speed computers available nowadays.

## Phase Behavior: Water Hydrocarbon Systems–Natural Gas Hydrates

- Gas hydrate - pipeline trouble maker or ?
- Prediction of hydrate formation conditions
  - **Katz** Gas gravity
  - **Wilson-Carson-Katz** equilibrium-constant method
  - **Baillie and Wichert** method
  - **Equation of state** methods
- Comparison of techniques to predict hydrate formation conditions



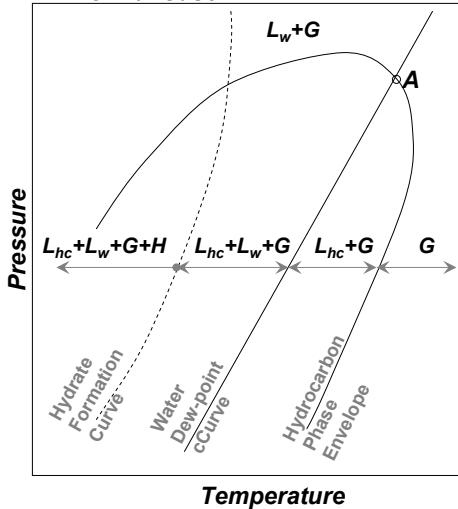
Natural gas molecules smaller than n-butane can react with liquid water or free water to form crystalline, snow-like solid solutions called **hydrates**. Hydrates have specific gravities ranging from 0.96 to 0.98 and therefore float on water and sink in hydrocarbons. They are 90 wt.% water: the other 10% is composed of one or more of the following compounds: methane, ethane, propane, iso- and normal-butane, nitrogen, CO<sub>2</sub>, and H<sub>2</sub>S. The water molecules link to each other and form cage-like structures, called **cathrates**, that are stabilized by the natural gas guest molecules. Smaller natural-gas molecules (C1, C2, H<sub>2</sub>S, and CO<sub>2</sub>) form more stable, body centered cubic structures, known also as **structure I**, while small quantities of larger molecules (C3, iC4) usually produce less stable diamond lattices (**structure II**). Hydrate formation causes many operating problems, such as partial or complete blocking of gas-gathering flow lines, fouling and plugging of heat exchangers, erosion of turbo-expanders, etc. Hydrates have been, however, found a good carrier of natural gas. Technologies are currently being developed to use hydrates as a means to transport natural gas in solid form (*Solid Natural Gas* or *SNG* as compared with *LNG* and *CNG* means of transportation). Very massive natural gas reserves in the world is in the form of hydrate underneath of ocean floors. Natural gas reserves in the form of hydrates are millions of times larger than the existing conventional natural gas reserves. Amount of gas in hydrate its hydrate form in only one of US offshore gas reservoirs can supply the natural gas demand of the US for about 200 years. Therefore, studying gas hydrates behavior have gone far beyond the problems it creates for gas transmission pipelines. The temperature and pressure at which hydrates form may be estimated by a number of different methods summarized as follows:

1. **Katz's gas gravity** method: In this approach the hydrate formation temperature is simply estimated from just one graph (**Figure 20-15** of the GPSA data book) using the gas specific gravity or molecular weight. The method is more suitable for low specific gravity natural gases ( $S = 0.7$  or smaller).
2. **Wilson-Carson-Katz** equilibrium-Constant method: In the **equilibrium-constant** or **K-value** method, hydrate formation conditions are computed in a manner directly analogous to the standard vapour-liquid dew-point calculations. Vapour-hydrate K-values were developed by Wilson-Carson and Katz for the following hydrate forming gases: methane, ethane, propane, hydrogen sulfide (H<sub>2</sub>S), and carbon dioxide (CO<sub>2</sub>). Later others found the K values for other hydrate forming compounds such as iso-butane, normal-butane, etc. **Figures 20-19 through 20-25** of the GPSA data book are used to find the values for several gas components at different temperature and pressure conditions. The method is as follows: (1) estimate a hydrate formation temperature; (2) look up  $K_{V,S}$  values from **Figures 20-19 through 20-25** of the GPSA data book; (3) compute  $\sum z_N / K_{V,S,N}$ ; and (4) repeat steps (1) to (3) until  $\sum z_N / K_{V,S,N} = 1.0$ .
3. **Baillie-Wichert** method: The method is based on the use of graph (**Figure 20-27** of the GPSA data book) which is developed using a large number of hydrate formation conditions generated using HYSYS process simulator. The chart can be used for sweet natural gases as well as sour gases.
4. **Equation-of-state** method: These methods are based on the fundamental equation of phase equilibrium and thermodynamic principles. Most commercial process simulators can perform hydrate formation prediction very efficiently and the hand calculations method stated above are only useful when such computer software are not available. SRK, PR and other advanced equations of state are used for these calculations.

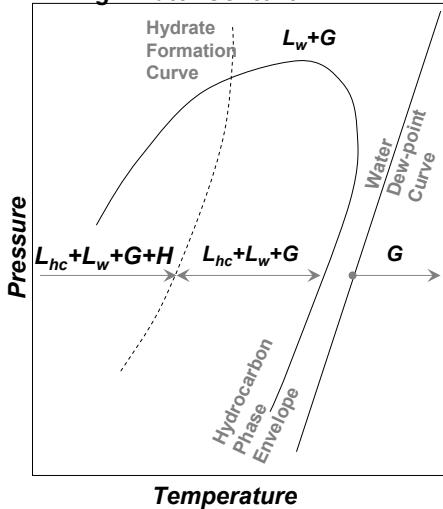
A brief comparison for the different techniques is as follows: The gas gravity method should be considered a first order estimate. The equilibrium-constant method represents a considerable improvement over the gas-gravity method. The equation-of-state (or computer calculation) methods are superior both in accuracy and ease of extrapolation.

## Water Hydrocarbon Systems: Overall Phase Behavior of Natural Gas- Hydrates Systems

**A. Normal Case**



**B. High Water Content**



The overall phase behavior for a water-hydrocarbon system may be summarized using the phase envelopes shown on this slide. The water dew-point (vapour pressure/boiling point) and hydrate curves are superimposed on the water free phase envelopes. This techniques only approximates the true phase behavior, because the presence of water changes the hydrocarbon phase diagram, and vice versa. However rigorous three phase calculations indicate that the hydrocarbon dew-point line and water dew-point line are not affected significantly. **Diagram A** represents the usual behavior of a water-hydrocarbon mixture. There are five regions in which the various phases may occur, as shown. To the right of the dew-point curves, only the gas phase (G) is present. At pressures greater than that at point **A**, water-rich liquid condenses first ( $L_w + G$ ) when the gas is cooled at constant pressure. The water dew-point is said to control. At pressures below than that of point **A**, hydrocarbon-rich liquid condenses first ( $L_{hc} + G$ ) when the gas is cooled. The hydrocarbon dew-point controls in this region. Further cooling yields also water-rich liquid when the water dew-point curve is reached ( $L_{hc} + L_w + G$ ). Additional cooling ultimately produces hydrate formation conditions ( $L_{hc} + L_w + G + H$ ). **Diagram B** shows the phase diagram for a mixture containing a relatively large amount of water in the gas. In this case, the water dew-point line controls at all pressures in the gas phase region next to the water dew-point curve. The  $L_{hc} + G$  zone is not present.

The main purpose of phase diagrams shown on this slide is to indicate the basic behavior of water-natural gas mixtures. If amounts and composition of phases are desired, three phase equilibrium calculations must be done using commercial process simulators or in-house computer programs.

For design purposes the amount and heavy hydrocarbon content of natural gas should be tuned such that the water dew point and hydrate formation curves are shifted to the left of the phase envelope. In that case the water condensation and hydrate formation would only happen at very low temperatures. The role of the design engineer is to make sure that the conditions for the formation of water, liquid hydrocarbons, and hydrates are unfavorable when the gas gets prepared to be delivered to the pipe line.

## Phase Behavior: Carbon Dioxide Frost Point

- Significance of CO<sub>2</sub> freezing- design of turbo-expansion facilities and cryogenic NGL recovery systems
- CO<sub>2</sub>-methane equilibrium (Liquid-solid-vapour systems) (see Ref.1, also Fig.s 25-5 and 25-6 of GPSA data book)
- Natural gas-CO<sub>2</sub> systems (see Ref. 1)
- Predicting CO<sub>2</sub> formation conditions (GPSA charts vs. process simulators)

Solid carbon dioxide can form when natural gases containing significant amounts of carbon dioxide are cooled below -70° F (triple point of pure CO<sub>2</sub>). Solid carbon dioxide can plug and /or damage cryogenic NGL recovery equipment, especially the expander and the demethanizer. Therefore, prevention of solid carbon dioxide formation is of great interest to the designers of deep-cut (high NGL/ethane) recovery projects. Obviously, determination of the temperature and pressure conditions at which solid CO<sub>2</sub> **frost point**, is important. Because natural gas is predominantly methane, the CO<sub>2</sub>-CH<sub>4</sub> binary should be considered first. Without going too much to the details of rather complicated three-phase (vapour-liquid-solid) equilibrium of the carbon dioxide-methane or natural gas mixtures (see Ref.1, also **Fig.s 25-5 and 25-6** of GPSA data book for further details), in any NGL recovery project, the question well be “*how far can we cool a natural gas with certain amount of carbon dioxide before CO<sub>2</sub> starts freezing?*” **Fig. 13-64** of the GPSA data book will provide a quick estimate for the possibility of formation of solid CO<sub>2</sub>. If operating conditions are in the methane liquid region as shown by the insert graph, the dashed solid-liquid phase equilibrium line is used. For other conditions the solid isobars define the approximate CO<sub>2</sub> vapor concentration limits. For example, consider a pressure of 300 psia. At -170° F, the insert graph (top right on **Fig. 13-64**) shows the operating conditions to be in the liquid phase region. The dashed solid liquid phase equilibrium line indicates that 2.1 mol percent CO<sub>2</sub> in the liquid phase would be likely to form solids. However, at the same pressure and -150° F, conditions are in the vapor phase, and 1.28 mole percent CO<sub>2</sub> in the vapor could lead to solids formation. This chart represents an approximation of CO<sub>2</sub> solid formation. Detailed calculations should be carried out if **Fig. 13-64** indicates operation in a marginal range. In summary to use the GPSA chart, knowing the pressure and temperature and using the insert graph, first determine whether a liquid or vapour phase condition exists. If the system is in liquid phase the dotted line determines the allowable CO<sub>2</sub> content otherwise the Solid-vapour phase equilibrium isobars are used to determine the allowable CO<sub>2</sub> or the frost point temperature and pressure conditions. Based on the Gibbs phase rule since we have three phases and two components (since cryogenic processing is not used for rich/heavy HC containing gas streams, natural gas is considered to be mainly methane - single component), the number of variables (degree of freedom) is  $N = C-P+2=2-3+2=1$ . Therefore only one variable is needed to specify the system. In using **Fig. 13-64**, if the pressure and temperature are given, the only remaining variable will be CO<sub>2</sub> composition. If the pressure and CO<sub>2</sub> composition are given, the chart may be used to determine the only remaining variable which is the CO<sub>2</sub> frost temperature. Using thermodynamic principles governing the SLV phase equilibrium of carbon dioxide-natural gas systems, commercial process simulators, such as HYSYS, can easily predict the CO<sub>2</sub> frost conditions for a natural gas with known composition.

## Natural Gas Properties/Phase Behavior and Scope of Natural Gas Field Processing

- Process objectives
  - Transportable gas
  - Salable gas
  - Maximized condensate (NGL) production
- Gas type and source
  - Gas-well gas
  - Associated gas
  - Gas condensate
- Location and size of the field
  - Remoteness
  - Climate
  - size

In concluding the discussions on physical properties and phase behavior of natural gases, it is important to know why these topics should be covered and how the material could be related to the design and planning of natural gas facilities. The important factors in selecting the scope of processing generally include the ***process objectives, the type or source of the gas, and the location and size of the field***. In the new few slides we discuss the significance of gas physical properties and phase behavior of natural gas systems on the accurate design of natural gas processing facilities. Without a sound knowledge of the basic concepts, the design practice will not give rise to any meaningful results.

## Scope of Natural Gas Field Processing: Process objectives

- Transportable gas
  - Hydrate formation
  - Corrosion
  - Excessive pressure drop (two-phase flow)
  - Compression requirement (dense phase flow)
- Salable gas
  - Sales quality-pipe line spec. (see Fig. 2-4, GPSA)
  - Heating value-inert gas and condensate recovery
- Maximized condensate (NGL) production
  - Maximizing crude production
  - Retrograde condensate gas processing
  - Inherent value of NGL

Processing of a gas stream may have one of the three basic objectives shown on this slide:

**Transportable gas:** Production of a transportable gas stream implies minimal processing in the field and transport through a pipeline to a final processing plant. Three main constituents or concern are: water, hydrogen sulfide ( $H_2S$ ), and condensate. In order to economically design the pipeline diameter the gas should be transported in high pressure (high density) conditions. Since the pipeline is exposed to the ambient temperature, relatively low temperatures may be encountered. Water must be removed to a level that will prevent hydrate formation in the pipeline. Therefore it is important to treat the gas such that the hydrate formation curve on the phase envelope is shifted to the lower temperature regions of the envelope. If the *lowest expected temperature (LET)* is higher than the hydrate point in the gas, then water removal may not be absolutely necessary. Corrosion due to water formation may be controlled by corrosion inhibitors. Hydrogen sulfide corrosion may also be dealt with if internal pipe coating materials are used for short distances. If the hydrocarbon dew-point is less than the *LET*, then no processing is required for condensate removal either. If the *cricondenbar* of the gas is higher than the *LET*, pipeline pressure may fall into the retrograde zone and condensation will occur. If condensate is not removed, the pipeline path passes into the retrograde zone and two phases are produced. Two phase flow requires a larger pipe diameter than single-phase flow. A slug catching facility should also be designed to handle the condensate. If it is decided to remove the condensate, the gas should be cooled down followed by a phase separation process. The phase diagram of a liquids-depleted natural gas is different in the sense it is more compact with narrower two-phase region. Therefore the transport pass has little chance to hit the dew-point curve and thus no condensation will occur. If it is decided to compress the gas and transport the dense-phase, the gas should be maintained at a pressure higher than the *cricondenbar* throughout the pipeline, which of course prevents the formation of two phases at any point. In any given case a sound understanding of the phase behavior is required before any cost-benefit analysis can be made to select the preferable design.

**Salable gas:** production of *sales-quality* gas requires all processing required to meet **pipeline specifications** (see **Fig. 2-4** of the *GPSA* data book).  $H_2S$  and  $CO_2$  must be removed, if present in sufficient amount. Dehydration is also required, generally after the compression because free water is condensed in the compressor after-cooler. Recovery of condensate depends on the heating value requirement of the sales gas, and hydrocarbon dew point specifications. If the condensate content is low it is not necessary to remove it. If the gas contains nitrogen, it may be necessary to retain the heavier hydrocarbons in order to meet the heating value specifications. Techniques to recover NGL will be discussed in the proceeding sections. From the standpoint of phase diagram, the task is to move the state of the system to the left of the dew-point line of the gas. In other words, cool the gas below its dew-point temperature. Then the resulting condensate may be recovered.

**Maximum liquid production:** The three situations shown on this slide motivate maximum condensate recovery. Condensate is often more valuable if recovered from associated gas and injected into crude oil to enhance its quality (*API* degree). Processing of retrograde condensate gas is performed to recover the gas and inject the gas to the reservoir to maintain the formation pressure and reduce the possibility of hydrocarbon retrograde condensation due to lowered pressure conditions. *NGL* recovery enhances the profit in many gas exploitation projects as it is as valuable as the best quality crude oils. Once again a knowledge of phase behavior and gas properties is crucial in accurate design of any retrograde condensate of NGL recovery project.

## Scope of Natural Gas Field Processing: Type and Source of Natural Gas

1. Gas-well gas
  - Wet or dry
  - Lean or rich
  - Sour or sweet
2. Associated gas
  - Enhanced oil recovery (EOR)
  - Enhancement crude production
3. Gas condensate
  - Pressure maintenance
  - Gas cycling operations

As discussed before, there are three basic types of natural gas as shown in this slide. Gas type influences its processing primarily in relation to the amount of liquefiable hydrocarbon contained. Gas-well gas, whether **wet** (accompanied by a liquid phase) or **dry** (no liquid phase can be separated from the gas at wellhead conditions), is composed mainly of methane. The condensate content is not particularly high and may not have to be reduced to produce a salable gas. The only motivation for condensate recovery would be if the liquefiable components were more valuable as liquid products than as sales-gas components. If the heavy hydrocarbon content of the gas ( $C_3^+$ ) is high (more than %2.5-3.0) it is called a **rich gas**. NGL recovery from these natural gases is usually profitable. Otherwise the gas is termed **lean gas**. The gas may also contain noticeable quantities (>100 ppm) of acid gases ( $CO_2$  and  $H_2S$ ), therefore it is called **sour gas**, there are some natural gases, particularly in offshore location with not much acid gases; these gases are termed **sweet**. Obviously a sweet dry natural gas is ready to be injected to pipelines and no processing is required. In most cases however the gas should be treated for removal of water vapour before recompression for the reason explained before.

**Associated gas** or the gas which is separated when crude is processed for storage in atmospheric stock tanks, is very rich in liquefiable components and typically must undergo condensate recovery to meet hydrocarbon dew-point or maximum heating value requirement.

The so-called **gas-condensate reservoirs** contain reservoir fluid having a high percentage of dissolved heavier hydrocarbons. As the pressure in the formation falls, the fluid may reach its dew point in the retrograde region. Then liquid hydrocarbon termed **condensate** forms as the pressure continues to decline. Because of its small volume, the condensate is not produced but remains in the reservoir. An important aspect of the phase behavior of natural gas in the design of natural gas processing facility and the management of retrograde condensate reservoirs, is that if the pressure in the condensate reservoir falls below the dew-point line during production, condensation will take place in the reservoir itself. Valuable heavier liquid hydrocarbons will likely remain in the reservoir and not be produced. Pressure maintenance by gas re-injection is sometimes practiced in such a reservoir. The reservoir fluid produced from a gas-condensate formation also undergoes a decrease in pressure and temperature as it flows up the well string. Condensate is formed and recovered by phase separation at the wellhead. If the residue gas from the wellhead separator is compressed and recycled back into the formation, reservoir pressure will be maintained near the original reservoir pressure and in the dense-phase region; the condensate will be retained in the gas supercritical dense phase and can be produced, thus conserving this material. **Gas cycling** in condensate reservoirs has been practiced for many years and continues to be. Wellhead separator gas is still rich in liquefiable components; condensate is recovered from it in modern plants. In other words, after the condensate is removed from the produced gas in the wellhead separator, further processing of the gas is used to recover additional condensate from the rich separator gas; these techniques will be discussed in the subsequent lectures in this course. Alternative methods of maintaining pressure in gas-condensate reservoirs are partial gas recycling, nitrogen injection, and water-flooding. These aspects of oil and gas industries are beyond the scope of this course.

## **Scope of Natural Gas Field Processing: Field Location, Size, and Operation**

- Remoteness
  - Offshore *vs.* onshore (land) reservoirs
  - Platform design
  - Floating gas processing (a new concept)
- Climate
  - Design consideration for harsh environment
  - Cold *vs.* warm
  - Dry *vs.* humid
- Size
  - Reservoir capacity
  - Production rate: small *vs.* large
- Gas handling facilities operations

The geographical location of the gas or oil field is an important factor in choosing the processing scheme. There are at least two aspects of location that are important: *remoteness* and *climate*. In addition, there is the important factor of *size*.

**Remoteness:** remoteness refers to the distance from population or consumption centers and therefore to ease of transport of personnel and material to and from the production facility, as well as ease of maintenance, availability of support personnel, etc. Offshore platforms are examples of remote locale. Even these locations are not strictly comparable because of the factor of the sea *vs.* dry land. Platform facilities must be placed on decks that are extremely limited with respect to size and allowable weight; only those operations absolutely needed are performed. Currently, most offshore production is sweet, thus reducing the required processing; however more and more gas is showing traces of H<sub>2</sub>S as sea water is used for water-flooding. Special orientation or process equipment should be selected for offshore facilities to comply with the space available on an offshore facility. A dry-land facility, however, has essentially unlimited area available and can support operations not practical or desirable offshore, such as treating or processing involving fire hazards. From the stand point of phase behavior most offshore reservoirs are high pressure reservoirs; therefore require high pressure gas and water injection design considerations. Natural gas reservoirs usually contain rather larger quantities of water and therefore hydrates formation is a major problem. Most large natural gas hydrates reservoirs are located in offshore areas and pose significant problems in efficient recovery of gas from these huge hydrocarbon resources.

**Climate:** the hostility of the environment is important. Temperature obviously affects the tendency for hydrate formation. A tropical location such as offshore Malaysia or Indonesia or Middle Eastern desert locations may pose little problem. The opposite extreme is North slope Alaska, Canadian prairies, or North Sea production sites, where process equipment may have to be housed.

**Size:** magnitude of production rate is also very important. Small flow rates justify only simple operations; large rates can sustain sizable and complex processing facilities. Large reservoirs in remote areas may be worth studying while small offshore reserves in harsh environment require special technologies to justify their exploitation. The amount of valuable and recoverable hydrocarbons is an important factor in choosing a particular reservoir for development studies. Phase behavior thermodynamics plays a major rule in determining the amount of recoverable hydrocarbon and production rate of any hydrocarbon reservoir.

**Gas Handling Facilities Operations.** Major processes and equipment will be discussed in this course. Principle optimum operating conditions, design criteria and operational problems as well as trouble shooting procedures will be presented with the purpose of having the gas processing facility work at their optimum operating conditions. Millions of dollars may be wasted because of high chemical losses, excessive fluids recirculation rates, improperly operating pumps, needless energy consumption, frequent plant shutdowns, and excessive equipment replacement. It is very important to know at what conditions the individual pieces of process equipment should work.

## **GAS AND LIQUID SEPARATION**

- **Purpose, principles and terminology**

- Separation equipment- common components
- Types of separators
- Separation principles
- Separator design
- Factors affecting separation
- Operational Problems

**Purpose:** Phase separation of the production stream is usually performed as soon as it is conveniently possible because: (1) it is technically easier to process the gas, crude oil, and produced water phases separately; (2) the produced water is often corrosive. Therefore, removing the water often allows less costly materials of construction to be used downstream and reduces corrosion damages; (3) Less energy is required to move the separated single phases – phase separation permits the back pressure to be lowered and this, in turn, increases well production.

**Principles of Separation:** Three principles used to achieve physical separation of gas and liquids or solids are momentum, gravity settling, and coalescing. Any separator may employ one or more of these principles, but the fluid phases must be "immiscible" and have different densities for separation to occur.

**Terminology:** Separating vessels are referred to by many names such as: **Separator, trap or knockout drum** (KO drum), **flash chamber**, **scrubber**, and **filter**. This terminology is applied regardless of shape, and often, is not clear. However, the following definitions given in the GPSA data book and Ref. 7, are generally accepted:

**Separator:** This name is usually applied to field vessels used to separate gas, oil, and water coming directly from an oil or natural gas well, or a group of wells (i.e., "**production separator**"). A separator is primarily used to separate, using only physical principles (no chemical or electromechanical principles are involved), a combined liquid-gas stream into phases that are relatively free of each other. Two phase separator achieve only vapour-liquid separation, while three phase separator also remove free water from natural gas liquids or crude oil.

**Filter Separators:** A filter separator usually has two compartments. The first compartment contains filter-coalescing elements. As the gas flows through the elements, the liquid particles coalesce into larger droplets and when the droplets reach sufficient size, the gas flow causes them to flow out of the filter elements into the center core. The particles are then carried into the second compartment of the vessel (containing a vane-type or knitted wire mesh mist extractor) where the larger droplets are removed. A lower barrel or boot may be used for surge or storage of the removed liquid. These separators are designed to remove small quantities of mist, oil fogs, rust and scales, and dust from gases. Typical applications are upstream of compressors, dehydration and gas processing facilities, and town border stations.

**Flash Tank:** A vessel used to separate the gas evolved from liquid flashed from a higher pressure to a lower pressure.

**Line Drip:** Typically used in pipelines with very high gas to-liquid ratios to remove only free liquid from a gas stream, and not necessarily all the liquid. Line drips provide a place for free liquids to separate and accumulate.

**Liquid-Liquid Separators:** Two immiscible liquid phases can be separated using the same principles as for gas and liquid separators. Liquid-liquid separators are fundamentally the same as gas-liquid separators except that they must be designed for much lower velocities. Because the difference in density between two liquids is less than between gas and liquid, separation is more difficult.

**Scrubber or Knockout:** A vessel designed to handle streams with high gas-to-liquid ratios. The liquid is generally entrained as mist in the gas or is free-flowing along the pipe wall. These vessels usually have a small liquid collection section. The terms are often used interchangeably.

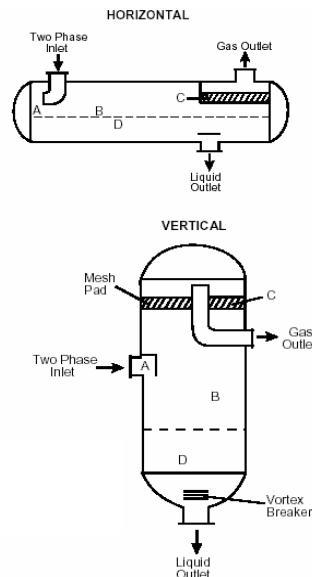
**Separator:** A vessel used to separate a mixed-phase stream into gas and liquid phases that are "relatively" free of each other. Other terms used are scrubbers, knockouts, lined rips, and decanters.

**Slug Catcher:** A particular separator design able to absorb sustained in-flow of large liquid volumes at irregular intervals. Usually found on gas gathering systems or other two phase pipeline systems. A slug catcher may be a single large vessel or a manifolded system of pipes.

**Three Phase Separator:** A vessel used to separate gas and two immiscible liquids of different densities (e.g. gas, water, and oil).

## Gas and Liquid Separation: Separation Equipment- Major Parts

- A - Primary Separation
- B - Gravity Settling
- C - Coalescing
- D - Liquid Collecting



To perform its separation function efficiently, a well designed separator must: control and dissipate the energy of the well stream as it enters the separator, and provide low enough gas and liquid velocities for proper gravity segregation and vapour-liquid equilibrium; remove the bulk of the liquid from the gas in the primary separation section; have a large settling section of sufficient volume to refine the primary separation by removing any entrained liquid from the gas; minimize turbulence in the gas section to ensure proper settling; have a mist extractor (or eliminator) near the gas outlet to capture and coalesce the smaller liquid particles that cannot be removed by gravity; control the accumulation of froth and foam in the vessel; prevent re-entrainment of the separated gas and liquid; have proper control devices for controlling back pressure and liquid level; and provide reliable equipment for ensuring safe and efficient operations including pressure gages, thermometers, liquid level indicating instruments, safety relief valves and gas and liquid discharge (dump) valves. Regardless of shape, separation vessels usually contain four major sections, plus the necessary controls. These sections are shown for horizontal and vertical vessels in the figure shown in this slide. The primary separation section, **A**, is used to separate the main portion of free liquid in the inlet stream. It contains the inlet nozzle which may be tangential, or a diverter baffle to take advantage of the inertial effects of centrifugal force or an abrupt change of direction to separate the major portion of the liquid from the gas stream. The secondary or gravity section, **B**, is designed to utilize the force of gravity to enhance separation of entrained droplets. It consists of a portion of the vessel through which the gas moves at a relatively low velocity with little turbulence. In some designs, straightening vanes are used to reduce turbulence. The vanes also act as droplet collectors, and reduce the, and reduce the distance a droplet must fall to be removed from the gas stream. The coalescing section, **C**, utilizes a coalescer or mist extractor which can consist of a series of vanes, a knitted wire mesh pad, or cyclonic passages. This section removes the very small droplets of liquid from the gas by impingement on a surface where they coalesce. A typical liquid carryover from the mist extractor is less than 0.013 ml per m<sup>3</sup>.The sump or liquid collection section, **D**, acts as receiver for all liquid removed from the gas in the primary, secondary, and coalescing sections. Depending on requirements, the liquid section should have a certain amount of surge volume, for degassing or slug catching, over a minimum liquid level necessary for controls to function properly. Degassing may require a horizontal separator with a shallow liquid level while emulsion separation may also require higher temperature, higher liquid level, and/or the addition of a surfactant.

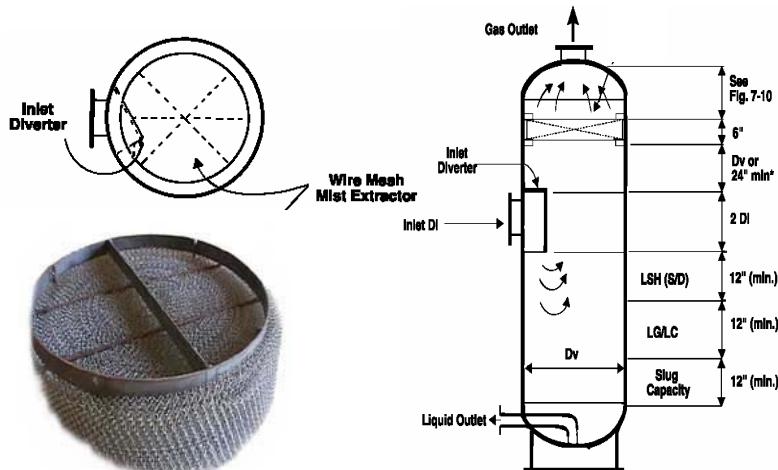
# Gas and Liquid Separation - Types of Separators

- Gravity (vertical vs. horizontal)
- Centrifugal
- Filter coalescing
- Impingement
- Comparison of separators – advantages vs. disadvantages

As shown in the previous slide, an inlet baffle or diverter directs the inlet stream against the separator walls. Giving the inlet fluids this centrifugal motion achieves the primary separation by reducing the momentum and spreading the inlet liquid into a thin film over a large part of the internal shell area. In all gravity separators, the resulting large surface area helps the vapour-liquid separation and the separated liquid falls by gravity into the liquid collection section while the gas rises. Large liquid drops can fall out of the rising gas; however, the smaller drops are removed by the mist extractor. Separators may be categorized into three basic types: **vertical**, **horizontal** and **spherical**. The **vertical** and **horizontal** types which are more widely used, will be discussed here. The spherical separators are rarely used in natural gas processing and therefore will not be discussed. Horizontal and vertical separators without mist extractors are used to remove particles with sizes above 100 *microns*. Adding mist extractors at the gas outlet increases the particle removal efficiency to a considerable level. Installing filter elements in the primary separation section of **horizontal separators** will also increase the efficiency of solid and liquid particles removal significantly. Particle removals up to 100% can be expected for particles larger than 2 *microns*. Impingement plays an important factor in separating small particles. Vane and blade-type impingement elements are widely used in most gravity separators to enhance the liquid/solid separation efficiency. By changing sudden gas flow direction, the impingement elements knock the very small particles out of the stream and help to reduce the particles momentum to a level that efficient separation is more probable. Centrifugal separators or cyclonic separators are increasingly gaining importance especially for offshore facilities where the floor space is at a premium. The fluid is tangentially entered into the separators which have a round cross-sectional. The centrifugal acceleration created induced by the inherent kinetic energy of the fluid, is used to separate the particles. The small cyclonic elements may be installed inside the separator as well. Therefore the inlet may not necessarily have a tangential geometry with respect to the cross section area of the separator.

**Horizontal separators** are smaller and less expensive than the vertical separators for a given gas capacity. In the gravity section of a horizontal vessel, the liquid droplets are more easily settled out of the gas continuous phase, however since the interface surface area is larger the liquids may be re-entrained back to the gas outlet. The surge control is more difficult in horizontal separators; therefore horizontal separators are not suitable if occasional large slugs of liquids are expected. The selection of a suitable separator is a very subjective issue and designers have their own preferences in selecting one against the other. As general guidelines the following, the relative merits and common applications of vertical and horizontal separators may be summarized as follows: **Vertical separators** are used when sand, paraffin, or wax are produced, the plot space is limited (e.g., on an offshore or floating facility), rather smaller flow rates, and the GOR may be either very high or very low (less than 2,000 or greater than 50,000 scf/bbl). Vertical separators are more versatile than horizontal, the liquid level control is not so critical and have full diameter for gas flow at top and liquid flow at bottom. They are however more expensive than horizontal and require larger diameters for a given gas capacity, more difficult to skid mount and ship due to height limitation when transported, and more difficult to reach and service top-mounted instruments and safety devices. **Horizontal separators** are used for large volumes of gas and/or liquids, high to medium GORs, foaming crudes, three phase separations. They are cheaper than vertical separators, require smaller diameter for a same gas rate, lend themselves to skid mounting and shipping (more suitable for offshore construction), and have larger surge volume capacity. The horizontal separators however have some draw backs including that only part of the shell is available for passage of gas, occupy more plan space unless “stack-mounted”, liquid level control is critical and more difficult to clean produced sand, mud, wax, paraffin, etc. **Double-Barrel** separators are expensive and should be used when there is a large capacity under surging conditions, a better separation of solution gas is required and when a horizontal separator should be used but we need more stable liquid level control (such as what usually occurs in floating systems or FPSOs).

## Gas and Liquid Separation: Separation Equipment- vertical separator

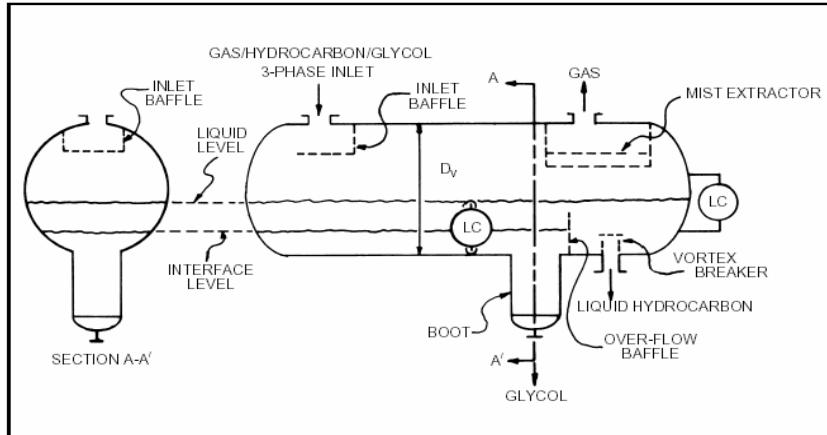


Source: Natco

**Vertical separators** without mist extractors will remove only liquid drops larger than 100 *microns*. This poor level of separation may be satisfactory for slug catchers and surge vessels. Baffle or other internals are often used to minimize agitation in the liquid collection section. The well stream or any other liquid or solid containing gas stream enters a vertical separator through an inlet diverter that causes an efficient primary separation by three simultaneous actions on the stream: gravity settling, centrifugation, and impingement of the inlet fluids against the separator shell in a thin film. The gas from the primary separation section flows upward, while the liquid falls downward into the liquid collecting section. In some designs, the smaller liquid particles are removed in the centrifugal baffles or impingement elements located near the top. A mist extractor at the gas outlet removes any entrained liquid droplets from the gas in the *micron* size range. The liquid particles coalesce and accumulate with in the fiber mesh of the mist extractor, until they become large enough to fall into the liquid collecting section. As mentioned before vertical separators are more suitable for low gas flow rates or when the plan area is limited. They have the advantage of having a high capacity for liquid surge control. A false cone bottom can be easily fitted to handle sand and solid accumulation problems. However they are more expensive to fabricate and more expensive to transport to locations as discussed before.

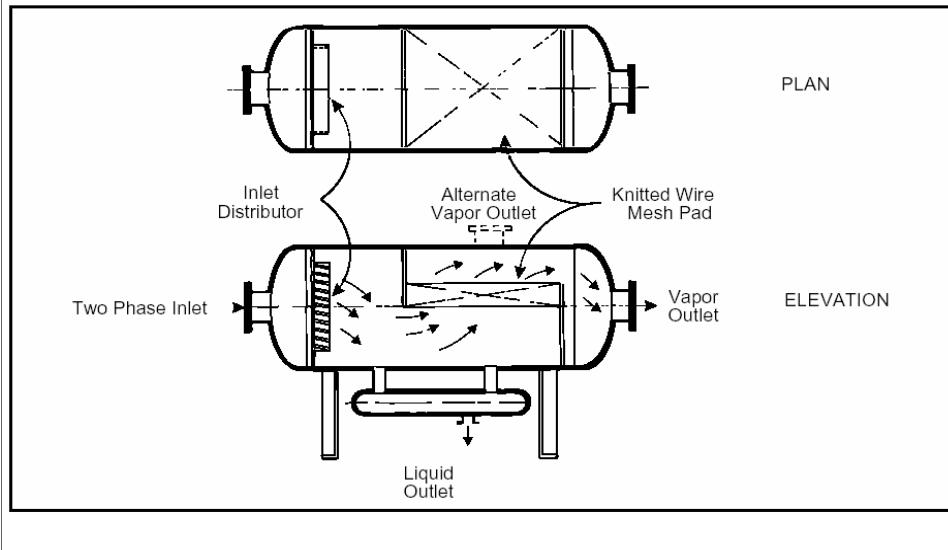
## Gas and Liquid Separation: Separation Equipment- Horizontal separators

Example Horizontal Three-Phase Separator with Wire Mesh Mist Extractor



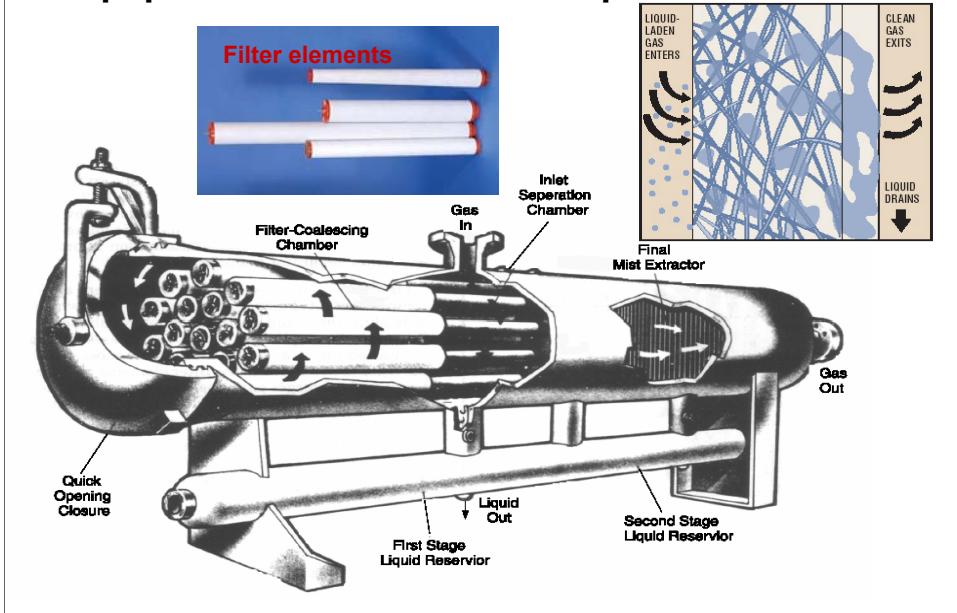
In **horizontal separators**, the kinetic energy of the inlet stream is dissipated by one of several types deflection baffles shown in the next slides. Baffles and/or other internals are used to reduce turbulence in the liquid collecting section, thus facilitating the rise and escape of entrained gas bubbles. Flow distributors such as weirs, plates, or vortex re-entrainment into the liquids as they are withdrawn. These separators may be of a single-tube or double-tube design (see next slide). Impingement elements can also be used to enhance the separation efficiency as discussed in vertical separators. A mist extractor is usually used near the gas outlet. Horizontal separators have a much greater gas-liquid interface area, permitting higher gas velocities. They can however handle high gas velocities economically and efficiently. They are cheaper to fabricate and ship than vertical separators. Horizontal separators are almost always used for medium to high GOR wells, for foaming well streams and for liquid-liquid separation (or three phase separation). They are however much harder to clean if the stream contains solids and sand. Liquid level control may become critical if frequent slugging is probable.

## Gas and Liquid Separation: Separation Equipment, Two-Barrel (Double-Tube) horizontal separator



In **two-barrel** or **double-tube** horizontal separators, the secondary settling and liquid collecting sections are housed separately as shown in this slide. The upper tube acts as the separator section, while the lower tube merely functions as a liquid collection (accumulation) section. Therefore a two-barrel separator is similar to a horizontal separator in which the whole upper tube cross section area is exposed to gas flow and the liquid capacity is enhanced by providing a separate section in the lower tube. As the liquid generated in the upper section it is immediately drained to the lower section through the liquid drains provided along the length of the separator. These separators are more suitable for floating facilities where the sloshing of liquid is frequent. The slide shows typical installation of wire-mesh or other impingement-type mist extraction devices within a horizontal vessel. The liquid is withdrawn from the lower barrel.

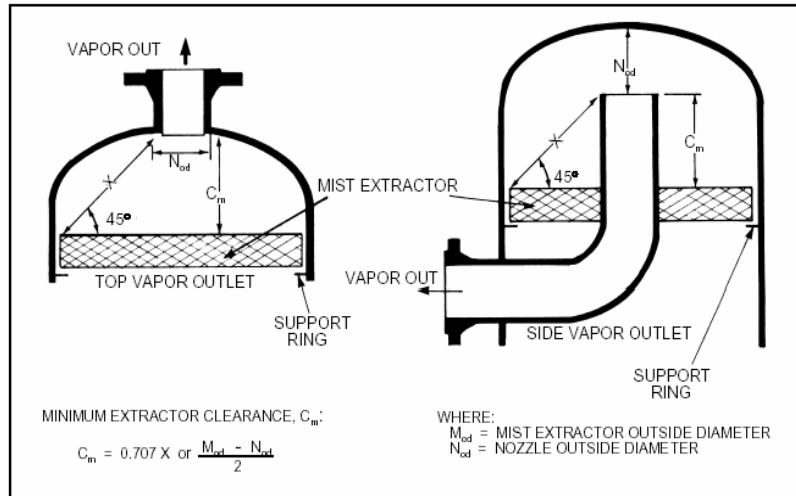
## Gas and Liquid Separation: Separation Equipment- horizontal filter separator



In **filter coalescing separators**, feed gas containing liquid mist, oil fog, dust, rust, or pipeline scale enters a large chamber upstream of the filter elements. This ensures that the gas surrounds the coalescing elements, thus using all the provided surface area. As the feed gas flows through the filter, solids remain outside of the filter. Liquid fog and mist droplets are retained by the filter fibers until they coalesce into larger drops, which are then forced through the filter element by the feed gas. These large droplets separate readily from the feed gas either by gravity or by mist extractors. Such filter coalescers can remove 100% of all particles larger than 2 *micrometers* (*microns* or  $\mu\text{m}$ ) and 99% of those 0.5 *microns* in size. Design is proprietary, and it is base on the vendors filter elements. The slide shows a typical inlet filter coalescer separator, the filter elements and mechanism by which the small particles are separated by the filter element fibers. A lower barrel is provided for efficient separation of liquids.

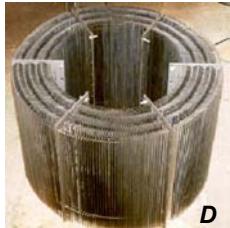
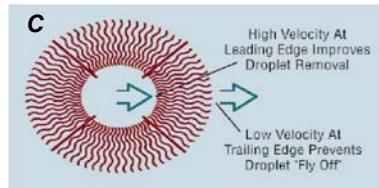
## Gas and Liquid Separation: Separation Equipment- mist eliminator arrangement

Example Minimum Clearance — Mesh Type Mist Eliminators



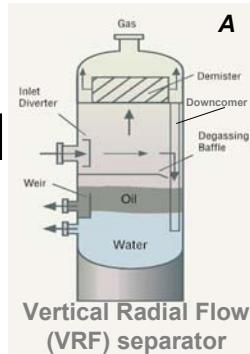
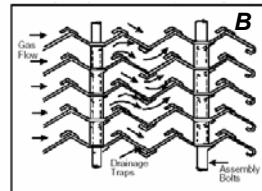
Well designed and operated mist extractors (eliminators) can be very effective at removing liquid mist from gas streams. In the final analysis, liquid removal is accomplished by gravity; that is, by the large density difference between the heavy ( $40-60 \text{ lb/ft}^3$  or  $500-770 \text{ kg/m}^3$ ) liquid and the light ( $< 4 \text{ lb/ft}^3$  or  $50 \text{ kg/m}^3$ ) gas. Wire-mesh or fibrous mist extractors are widely used, however their use is limited to clean inlet streams where plugging by solid is unlikely. Wire-mesh mist extractors are made by knitting wire typically 0.002-0.020 in. diameter and are available in carbon or stainless steel, monel, nickel, aluminum, or plastic. A common type is made from 0.011 in. wire and has a void fraction of 98%, a bulk density of  $12 \text{ lb/ft}^3$ , and a surface area of  $110 \text{ ft}^2/\text{ft}^3$  ( $360 \text{ m}^2/\text{m}^3$ ). In the past wire-mesh designs consisted of a random distribution of wire; however, a structured order of wire-mesh arrangements now available. A 4-to 6-inch thick pad is often used at pressure drops of 0.1-1.0 in. water. Droplets as small as 5 microns and liquid entrainment lower than  $0.1 \text{ gal/MMscf}$  can be achieved. Wire mesh pads capture liquid drops by three mechanisms: inertial impaction, direct interception, and Brownian capture (random movements of very small particles). Dirty liquids such as crude oil plug, wire mesh mist extractors very easily. The figure demonstrates a typical wire mesh installation in a vertical vessel.

## Gas and Liquid Separation: Separation Equipment- Vane (radial/axial) mist extractor arrangement



Natco™ radial vanes

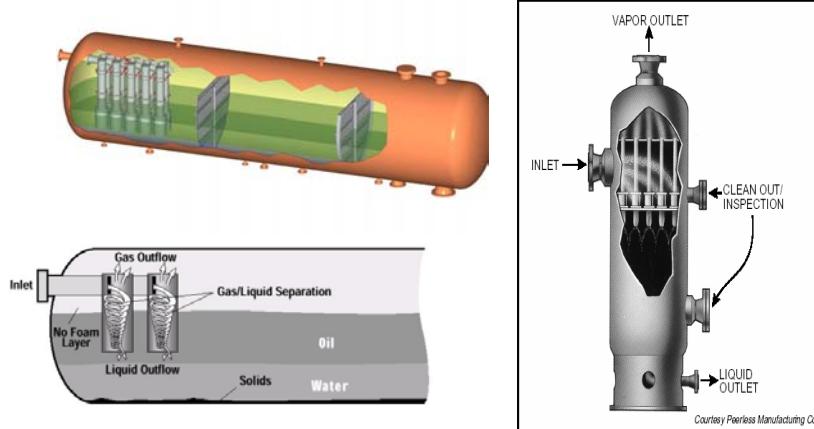
$$J = \rho_g \cdot V_t^2 = 20 \text{ lb/(ft.sec}^2)$$



Vane and blade type impingement devices are different from wire-mesh in that they do not drain the separated liquid back through the rising gas stream. Rather, the liquid can be routed into a downcomer, which carries the fluid directly to the liquid collection part. A vertical separator with a typical vane mist extractor is shown on this slide (see Figure A). The vanes remove fluid from the gas stream by directing the flow through a tortuous path. A cross section of a typical vane is shown in Figure B on this slide. The liquid droplets being much heavier than the gas , are subjected to inertial forces which throw them against the walls of the vane. This fluid is then drained by gravity from the vane elements into a downcomer. Vane type separators are generally considered to achieve the same separation performance as wire mesh, with the added advantage that they do not readily plugged and can often be housed in smaller vessels. Vane type separators designs are proprietary and are not essentially designed with standard equations., Manufacturers of vane type separators should be consulted for detailed design of their specific equipment. Figure D shows a radial flow vane mist extractor designed by Natco. The radial flow of gas through the vanes is illustrated in Figure C. A gas momentum equation recommended by the GPSA data book can be used to calculate the approximate face area of a vane type mist extractor similar to that illustrated on this slide:  $J = \rho_g \cdot V_t^2 = 20 \text{ lb/(ft.sec}^2)$ , where gas velocity,  $V_t$ , is the real gas velocity through the extractor cross section and  $\rho_g$  is the gas density at the operating conditions of the separator. The plates out which the vanes are manufactures are usually spaced 0.5-3 i. apart, can be made of carbon or stainless steel, PVC or polypropylene. Excellent removal (>90%) of drops larger than 10 microns is often claimed and entrainment losses of 0.1 gal/MMscf are often guaranteed. Typical pressure drops vary from 2 or 3 to 6 to 8 in. of water. Although they do not plug with solids or paraffin and wax, cleaning provisions should be made (e.g., suitably located manholes for steam lances).

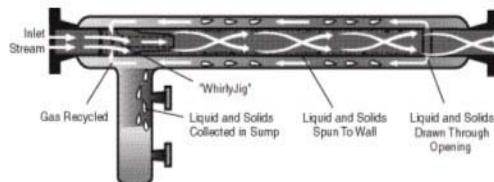
## Gas and Liquid Separation: Separation Equipment- Centrifugal separator

Example Vertical Separator with Centrifugal Elements



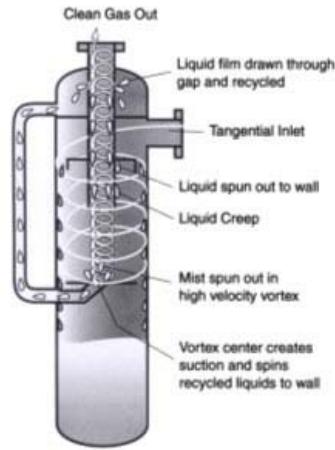
Gas-liquid cyclonic separation technologies are increasingly gaining a rather great importance in the oil and gas industries especially for offshore applications where the footprint area is important. Gravity separators are relatively large and expensive. The trend in offshore process industries is to improve separation efficiency with more compact designs. Recently, much emphasis has been put on developing separation systems based on the use of centrifugal forces to enhance gas-liquid/solid separation. This slide shows some typical separators in which cyclonic separation has been used to remove liquid from gas streams. The slides on the left show horizontal separators in which internally installed cyclones increase the efficiency of horizontal separators in handling large slug incidents. The figure on the right shows a vertical separator in which cyclones have enhanced the capacity of a vertical separator to remove liquid and solid particles from large gas flow rates. Design of cyclonic separators are proprietary and manufacturers should be consulted when the need is felt to use the equipment for certain application. However there are a number of good technical papers in the literature dealing with design aspect of these very efficient pieces of separation equipment. Some typical applications are: test separators; production separators; sub-sea or sub-surface separation; upstream of conventional separators to increase the overall efficiency of the separation process, increasing the efficiency of an existing horizontal or vertical separator in handling larger gas or liquid flow rates or enhancing separation efficiencies. Cyclone separators as mentioned before are much smaller compared to conventional separators however they are very sensitive to flow rate changes. Therefore they are more suitable for applications where the flow fluctuations are not very prominent.

## Gas and Liquid Separation: Separation Equipment- Swirl/cyclonic separators



Porta-Test Whirlyscrub I™

Source: Natco



WhirlyScrub V

This slide shows further examples of using centrifugal acceleration in separating gas and liquids. Natco is a major manufacturer of cyclonic and conventional separators in North America. Other major manufacturers are *Burges-Manning, BHR Group* in Britain, many others in Europe and North America.

## Gas and Liquid Separation –Separation principles

$$F_D = C_D A \rho \left[ \frac{V_t^2}{2g} \right] \quad \text{Drag force}$$

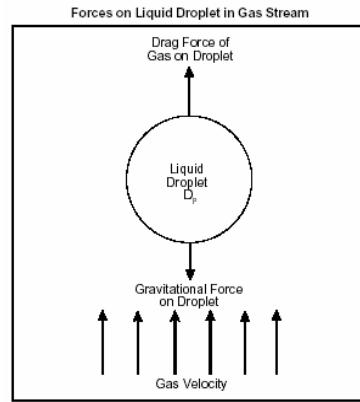
$$V_t = \frac{1.78 \times 10^{-6} (\Delta S.G.) d_m^2}{\mu} \quad \text{Stock's terminal velocity for:}$$

$Re < 1.0$

*Re for actual natural gas and crude operations are much larger than 1.0, therefore the following equations should be iteratively used to calculate the terminal velocity and drag coefficient:*

$$V_t = 0.0119 \left[ \left( \frac{\rho_l - \rho_g}{\rho_g} \right) \frac{d_m}{C_D} \right]^{1/2}$$

$$C_D = \frac{24}{Re} + \frac{3}{Re^{1/2}} + 0.34$$



Liquid droplets will settle out of a gas phase if the gravitational force acting on the droplet is greater than the drag force of the gas flowing around the droplet (see Fig. shown on this slide). These forces can be described mathematically using the terminal or free settling velocity:

### Gravity Settling Theory

Equating the buoyancy and drag force results a general equation from which terminal velocity of settling liquid particles may be calculated; Drag force is defined as:

$$F_D = C_D A \rho \left[ \frac{V_t^2}{2g} \right]$$

where,  $F_D$  = drag force,  $\text{lb}$ ;  $C_D$  = drag coefficient;  $A$  = Cross sectional area of droplets,  $\text{ft}^2$ ;  $\rho$  = density of continuous phase (gas),  $\text{lb/ft}^3$ ;  $V_t$  = droplet terminal velocity,  $\text{ft/s}$ ;  $g$  = gravity acceleration =  $32.2 \text{ ft/s}^2$ . For laminar flow  $C_D = 24/Re$ ;  $Re$  the Reynolds number =  $\rho V_t D / \mu$ . For very low  $Re$  ( $< 1.0$ ), the terminal velocity may be calculated from the following equation:

$$V_t = \frac{1.78 \times 10^{-6} (\Delta S.G.) d_m^2}{\mu}$$

This is called “**Stock’s Terminal Velocity**” where,  $\Delta S.G.$  = difference in specific gravities relative to water; usually  $S.G.$  of gases are much smaller than that of liquids and therefore,  $\Delta S.G. \approx S.G.$  (specific gravity of the liquid phase);  $d_m$  = droplet diameter in **microns** or micrometers ( $10^{-6} \text{ m}$ );  $\mu$  = viscosity of gas in **cp** (centipoises)

For natural gas and crude production facilities the above equation has limited applications as the Reynolds numbers are much higher than what is assumed for the above equation.  $C_D$  is therefore should be calculated from the following equation:

$$C_D = \frac{24}{Re} + \frac{3}{Re^{1/2}} + 0.34$$

and the terminal velocity is calculated from:

$$V_t = 0.0119 \left[ \left( \frac{\rho_l - \rho_g}{\rho_g} \right) \frac{d_m}{C_D} \right]^{1/2}$$

Where,  $\rho_l$  and  $\rho_g$  = liquid and gas densities in  $\text{lb/ft}^3$ ;  $d_m$  = particle diameter, **micron**

## Gas and Liquid Separation –Separation principles: Terminal Velocity/Residence Time calculations

- Terminal velocity iterative calculations:

1. Start calculating  $C_D$  using:  $V_t = 0.0204 \left[ \left( \frac{\rho_l - \rho_g}{\rho_g} \right) d_m \right]^{1/2}$
2. Calculate  $Re$  as:  $Re = 0.0049 \frac{\rho_g d_m V_t}{\mu}$
3. Calculate new values for  $C_D$ :  $C_D = \frac{24}{Re} + \frac{3}{Re^{1/2}} + 0.34$
4. Calculate new values for  $C_D$ :  $V_t = 0.0119 \left[ \left( \frac{\rho_l - \rho_g}{\rho_g} \right) \frac{d_m}{C_D} \right]^{1/2}$
5. Go to step 2 and iterate until  $C_{D,new} - C_{D,old} \leq 0.001$

- Residence time definition: Effective vessel volume/flow rate or:

$$t = V/Q$$

$C_D$  may be calculated by an iterative solutions as follows:

Start with a  $C_D$  value of 0.34 which results in calculating the terminal velocity from the following equation:

$$V_t = 0.0204 \left[ \left( \frac{\rho_l - \rho_g}{\rho_g} \right) d_m \right]^{1/2}$$

Calculate  $Re$  as:

$$Re = 0.0049 \frac{\rho_g d_m V_t}{\mu}$$

Calculate new values for  $C_D$  from equation:

$$C_D = \frac{24}{Re} + \frac{3}{Re^{1/2}} + 0.34$$

Recalculate  $V_t$  from equation Recalculate  $V_t$  from equation :

$$V_t = 0.0119 \left[ \left( \frac{\rho_l - \rho_g}{\rho_g} \right) \frac{d_m}{C_D} \right]^{1/2}$$

Go to step 2 and iterate until the new and old values of  $C_D$  are within a reasonable error margin (e.g.  $C_{D,new} - C_{D,old} \leq 0.001$ )

Industry field experience in natural gas and crude oil treatment operations shows that the design should be such that drop sizes larger than 100 microns can be removed; demister should be able to handle liquid droplets between 10-100 microns.

### Retention time

Retention time is the time liquid needs to spend in the liquid collection section of the separator and is calculated from the following general equation:

$$t = V/Q$$

Where,  $V$  = volume of liquid collection section in  $\text{ft}^3$ ,  $Q$  = volumetric flow rate of liquid in  $\text{ft}^3/\text{s}$  or  $\text{bpd}$  (barrels per day). For normal services times between 0.5 to 3 minutes are used but if foaming is a major concern times up to 4 times of above values may be used.

Re-entrainment of liquid droplets due to high gas velocity may occur if the length to diameter is larger than 4 to 5.  $L/D$  ratios of < 4-5 for a half full liquid vessel is usually considered.

## **Gas and Liquid Separation – Separator Design**

- Gas capacity
- Liquid capacity
- Gas Capacity Calculations: Souders-Brown's Technique
- Vessel design considerations
- Separator design using manufacturers separator performance charts
- Computer based techniques - Computational Fluid Dynamics (CFD), etc.

To efficiently design gas-liquid separators, appropriate considerations should be taken to provide sufficient gas and liquid capacity for the two phases to be separated. Several techniques are available to calculate the gas and liquid capacities for separators. The most widely used techniques will be presented here. A short cut technique was presented by **Souders and Brown** which will be discussed here. There are some design considerations other than the calculating the required gas and liquid capacities such as the right geometry of the separating vessels and the required data and specification of the gas and liquids when they are withdrawn from the separating vessels.

Other techniques to size a gas-liquid separator will also be discussed; these include the use of manufacturers charts and advanced computational techniques.

## Gas and Liquid Separation – Sizing Equations

- **Horizontal separator**

– Gas Capacity:  $dL_{eff} = 420 \left[ \frac{TZQ_g}{P} \right] \left[ \left( \frac{\rho_g}{\rho_l - \rho_g} \right) C_D \right]^{1/2}$

Or:  $dL_{eff} = 42K \left[ \frac{TZQ_g}{P} \right]$ , where,  $K = \left[ \left( \frac{\rho_g}{\rho_l - \rho_g} \right) C_D \right]^{1/2}$  from Fig. 4.10 Ref.8

– Liquid Capacity:  $d^2 L_{eff} = \frac{t_r Q_l}{0.7}$

– Seam to seam length:  $L_{ss} = L_{eff} + d/12$  for gas capacity and  $L_{ss} = 4/3 L_{eff}$  for liquid capacity

- **Vertical Separators**

– Gas capacity:  $d^2 = 5,040 \left[ \frac{TZQ_g}{P} \right] \left[ \left( \frac{\rho_g}{\rho_l - \rho_g} \right) C_D \right]^{1/2}$

– Or:  $d^2 = 420K \left[ \frac{TZQ_g}{P} \right]$ , where  $K$  is defined as above and found from Fig. 4.10 Ref. 8

– Liquid capacity:

$$d^2 h = \frac{t_r Q_l}{0.12}$$

– Seam-to-seam length:  $L_{ss} = \frac{h+76}{12}; \dots \text{or} \dots L_{ss} = \frac{h+d+40}{12}$

### Sizing Horizontal Separators:

1. To determine the length and diameter for 100 **micron** liquid droplets separation, the following equation may be used:

$$dL_{eff} = 420 \left[ \frac{TZQ_g}{P} \right] \left[ \left( \frac{\rho_g}{\rho_l - \rho_g} \right) C_D \right]^{1/2}$$

Where,  $d$  = vessel diameter, **in**;  $L_{eff}$  = Effective length of the vessel, **ft**;  $Q_g$  = gas flow rate, **MMSCFD**;  $P$  = Operating pressure, **psia**;  $T$  = Operating temperature, **°R**;  $Z$  = Gas Compressibility (dimensionless);  $C_D$  = Drag Coefficient (dimensionless);  $d_m$  = liquid droplet diameter to be separated, **micron**;  $\rho_g$  and  $\rho_l$  = gas and liquid densities, **Ib/ft<sup>3</sup>**

For  $dm = 100$  **microns**, the above equation may be further simplified to the following:

$$dL_{eff} = 42 \left[ \frac{TZQ_g}{P} \right] K \quad \text{where, } K = \left[ \left( \frac{\rho_g}{\rho_l - \rho_g} \right) C_D \right]^{1/2}$$

where  $K$  values may be estimated from special charts for gas and crude services (see **Fig. 4.10** of Ref. 8, Arnold-Stewart).

2. The liquid capacity is calculated from the following equation:

$$d^2 L_{eff} = \frac{t_r Q_l}{0.7}$$

Where,  $L_{eff}$  = Effective length in **ft**;  $t_r$  = desired retention time for liquid, **min.**;  $Q_l$  = Liquid flow rate, **bpd**;  $d$  = vessel diameter, **in.**

3. Seam-to-Seam length is calculated from the following equations:

$$L_{ss} = L_{eff} + d/12 \text{ for gas capacity and } L_{ss} = 4/3 L_{eff} \text{ for liquid capacity}$$

### Sizing Vertical Separators:

Gas capacity is calculated from the following equation:  $d^2 = 5,040 \left[ \frac{TZQ_g}{P} \right] \left[ \left( \frac{\rho_g}{\rho_l - \rho_g} \right) C_D \right]^{1/2}$

for  $dm = 100$  microns we may simplify the equation as follows:

$$d^2 = 420 \left[ \frac{TZQ_g}{P} \right] K, \text{ where } Ks \text{ are estimated from charts of } \text{Fig 4.10} \text{ of Ref. 8 and other parameters are as before.}$$

Liquid capacity is calculated from:  $d^2 h = \frac{t_r Q_l}{0.12}$ , where,  $h$  = height of liquid volume, **in**; and  $t_r$  = desired retention time for liquid, **min.**

Seam-to-seam length is calculated from one of the following equations:  $L_{ss} = \frac{h+76}{12}; \dots \text{or} \dots L_{ss} = \frac{h+d+40}{12}$

## Gas and Liquid Separation: Sizing Equations-Souders-Brown Technique

*Terminal Velocity Equation*

$$V_t = 0.0119 \left[ \left( \frac{\rho_l - \rho_g}{\rho_g} \right) \frac{d_m}{C_D} \right]^{1/2}$$

$$V_t = K_{SB} \sqrt{\frac{\rho_l - \rho_g}{\rho_g}}$$

*Souders-Brown Equation*

**API Spec. 12 J (1989) Recommendations for  $K_{SB}$  values**

Separator type	Height, H or Length, L (ft)	API Recom'd. $K_{SB}$ (ft/sec.)	Most commonly used $K_{SB}$ Value (ft/sec.)
Vertical	5	0.12-0.24	0.12 without and 0.2 with mist extractor
	10	0.18-0.35	0.18 without and 0.3 with mist extractor
Horizontal	10	0.40-0.50	0.38 with mist extractor
	Other lengths	0.4-0.5(L/10) <sup>0.565</sup>	-

## Gas Capacity Calculations - Souders-Brown's Technique

The following equation is used to calculate the terminal velocity for liquid or solid particles falling within a gravity separator.

$$V_t = 0.0119 \left[ \left( \frac{\rho_l - \rho_g}{\rho_g} \right) \frac{d_m}{C_D} \right]^{1/2}$$

*Souders and Brown* used this equation to derive the form of their classic equation for maximum allowable gas velocity but collected the constants on the left part of the above equation into one coefficient,  $K_{SB}$ . The *Souders and Brown* equation relates the vessel diameter to the rising velocity of the vapour to handle the gas capacity as follows:

$$V_t = K_{SB} \sqrt{\frac{\rho_l - \rho_g}{\rho_g}}$$

Where:

$V_t$  = Terminal velocity which should be equivalent to the actual gas velocity in a separator

$K_{SB}$  = a constant (see **Figure 7-9** in the **GPSA** data book) or the table shown on this slide.

## Gas and Liquid Separation: Vessel design considerations

- Liquid residence time: 2-4 min
- Liquid-gas interface (minimum diameter/height): 6 ft. vertical height; 26 in. horizontal diameter
- Gas specification: 0.1 gal/MMscf
- Liquid re-entrainment: API Spec. 12J
- Pipe connections:
- Fabrication cost
- Optimum length to diameter (L/D) or aspect ratio

API Spec. 12J (1989)	
Oil gravity °API	API recom'dn Liquid retention time (min)
Above 35	1
20 30	1 to 2
10 20	2 to 4

Sizing separators is not an exact science. Of course the best method to use reliable field data. In the absence of these data one must resort to experience. Some of the basic factors that must be considered in designing separators are:

**Liquid residence time:** sufficient residence time must be provided for the liquid to fall out of the gas phase and for gas bubbles to escape from the liquid phase. If problems such as foaming, wax deposition, slug flows, and so forth are not encountered, then the API Spec. 12J (1989) Recommendations for liquid retention time shown on this slide may be used when field or pilot data are not available. From field experience the following liquid retention times are also suggested: Oil-gas separation, 1 min (or API table), High pressure oil-water-gas separation, 2 to 5 min.; Low pressure oil-water-gas separation 5 to 10 min. at > 100°F, 10-15 min at 90°F, 15-20 min. at 80°F, 20-25 min. at 70°F, 25-30 min. at 60°F.

**Liquid-gas interface:** For a *vertical separator*, the liquid-gas interface (at which the feed enters) should be at least 2 ft. from the bottom and 4 ft from the top of the vessel. This implies a minimum *vertical* separator height of 6 ft. For *horizontal separators*, the feed enters just above the gas-liquid interface that may sometimes be off centered to adjust for a greater gas (or liquid) capacity needed. The gas-liquid interface, however, must be kept at least 10 in. from the bottom and 16 in. from the top of the vessel. This implies a minimum *horizontal* separator diameter of 26 in. In practice, novel design techniques violate these rules of thumb by providing additional features. Therefore, standard vertical separators less than 6 ft. and standard horizontal separators of diameter less than 26 in. are available and have been used successfully.

**Gas specification:** A common specification for the effluent gas from a well-designed and properly operated separator is 0.1 gallon of liquid per MMscf of gas.

**Liquid re-entrainment:** High gas velocity at the gas-liquid interface may cause momentum transfer from the gas to the liquid, creation of waves and ripples in the liquid, and eventually separation of broken-away droplets from the liquid phase. There are some maximum recommended gas-velocity criteria based on the liquid-phase Reynolds number and interfacial viscosity values. However these criteria require surface tension data between the liquid and gas phases. Vendors recommend a maximum  $K_{SB}$  above which re-entrainment can occur. The general rule of thumb is to limit the aspect ratio to a maximum of 4 to 5 for half full horizontal separators. Standard sizes are listed in **API Spec. 12J** (1989) as follows:

Diameters (in.): OD 12.75 (horizontal only), 16, 20, 24,

OD or ID: 30, 36, 42, 48, 54, 60, etc.

Lengths (seam-to-seam, ft.): 5, 7.5, 10, 12.5, 15, 17.5, etc.

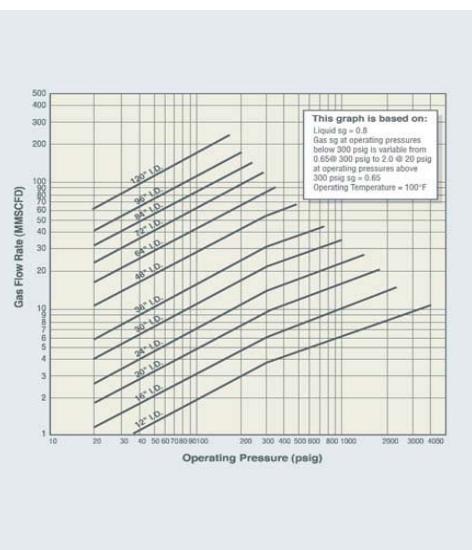
**Pipe connections:** The feed pipe may be sized using the standard empirical erosion velocity limit (API RP 14E, 1991):

$V_e = c / \sqrt{\rho_{mix}}$  where,  $V_e$  is fluid velocity, **ft/sec.**;  $c$  constant 125 for non-continuous service and 100 for continuous service, newer editions of **API** suggest that values of  $c$  from 150 to 200 may be used for continuous, non-corrosive or corrosion-controlled services if no solids are present.  $\rho_{mix}$  is gas/liquid density at operating  $T$  and  $P$ , **lb/ft³**. single-phase exit nozzles and pipes may be sized using allowable pressure drops or rule of thumb velocities (See **API RP 14E** or **Figure 4.10 Ref. 8**).

**Fabrication costs:** vessel fabrication costs may be calculated by  $C_T = f C_c \rho_s (\pi L D^2 + 2 C_a C_h D^3)$ , where  $C_T$  is the total cost in US\$,  $f$  is vessel thickness/vessel diameter,  $C_c$  cost factor per unit mass to manufacture a vessel shell (~ 1-2 \$/lb for carbon steel);  $\rho_s$  is density of steel (480 **lb/ft³** for carbon steel);  $C_a$  is surface area of vessel head/(vessel diameter)<sup>2</sup>=1.09 for 2:1 elliptical heads;  $C_h$ =cost per unit mass to manufacture a vessel head compared to that of vessel shell, usually 1.5 to 3.0. Note that the vessel weight may be estimated by deleting  $C_c$  and  $C_h$  from this equation, neglecting the small difference between shell and head thicknesses (see **Ref. 7**).

The **length to diameter** or **aspect** or **slenderness** ratio (**L/D**): For a horizontal or vertical separator should be kept between 3 and 8, due to consideration of fabrication costs, etc. Most common separators are designed for aspect ratios of 3 to 4. For horizontal vessels the cost equation given in **Ref. 7** may be differentiated to yield the **optimum L/D**. When the gas capacity is controlling:  $(L/D)_{opt} = 1 + 2.846 \{(1-h_D)C_a C_h\}^{0.5}$ , where  $h_D$  is the ratio of *liquid height in the vessel/vessel diameter*. When liquid capacity is controlling:  $(L/D)_{opt} = 5.95 (C_a C_h h_D)^{0.5}$ .

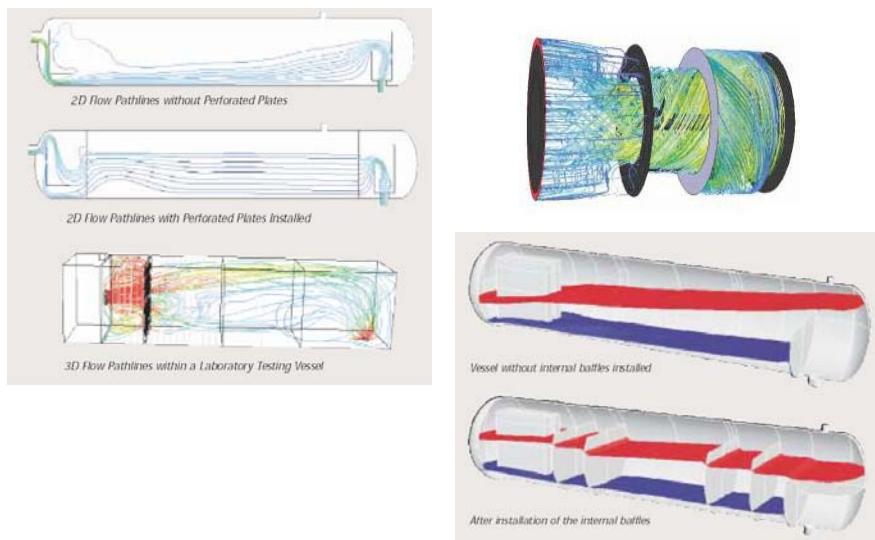
## Gas and Liquid Separation: Separator Design-manufacturers charts



Source: Natco

The *Souders-Brown* relationship provides only an approximate approach. A better design can usually be made using actual manufacturers' field test data that account for the dependence of gas capacity on the separator height (for vertical) or length (for horizontal). Filed experience show this dependence that is not accounted for by the *Souders-Brown* equation. The table shown on right side of this slide shows a typical NATCO gas capacity chart. The figure on the left is another illustration for various separator types as a function of their size and operating pressure. The actual liquid settling volume for standard separators can be determined from their specification given in tables such as the one shown on this slide. Usually the charts are given for some specific conditions the corrections factors are also provided to correct for the actual pressure, temperature, gas/liquid flow rates, and specific gravities.

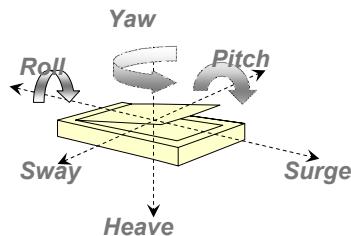
## Gas and Liquid Separation: Separator Design-CFD modelling



Computational fluid dynamics (*CFD*) can provide a two-or three dimensional modelling of the fluid flow inside a separator. *CFD* solves the non-linear *Navier Stokes* equations using finite element or finite difference mathematical techniques. This approach replaces the differential equations with simplified algebraic equations, and the resolution of the grids or networks can be made sufficiently fine to yield accurate flow profiles. An accurate and converged solution may require a modern high speed computer workstation to perform the required extremely large number of calculations. *CFD* represents the volume available for flow using many cells. Open space is represented by live or open cells, wall cells simulate solid boundary surfaces; and porous cells simulate vanes, fibrous filters, packing ,etc. *CFD* have been used extensively. The figures shown on this slide illustrate the type of gas and liquid patterns and velocity distribution resulted from a *CFD* analysis for horizontal separator, flow through perforated baffles, cyclonic internals, etc. Using this computer techniques the cost for developing new designs will significantly be reduced; very few experiments are required and the fabrication costs for models and prototypes will be cut to a large extent.

## Gas and Liquid Separation: Factors Affecting Separators Performance

- Operating and design pressure and temperature
- Fluid composition and properties (density, Z-factor, etc.)
- Fluid (gas and liquid) flow rates
- Degree of separation
- Two vs. three phase
- Gas vs. oil - sand and solids?
- Surging/slugging tendencies
- Foaming and Corrosive tendencies
- Offshore floating vs. land base static facilities



Motion	Linear motion			Angular motion		
	Surge	Sway	Heave	Roll	Pitch	Yaw
Single point anchored tanker	☒		☒	☒	☒	☒
Semi-submersibles			☒	☒	☒	☒
Tension-leg platforms	☒	☒				
Guyed tower platforms	☒	☒				
Articulated tower	☒	☒				

As it is true for all vapour-liquid equilibrium processes, gas liquid separation is affected by the separator operating pressure and temperature, and composition of the fluid feed to the separator. From the general phase diagrams for naturally occurring hydrocarbon mixtures, such as those discussed before, it is clear that as the pressure increases, or the temperature decreases, there will be greater liquid recovery, up to a point referred to as optimum. Vapour-liquid equilibrium flash calculations will yield the optimum pressure and temperature quite easily. From a practical stand point, however, it may not be possible to operate at this optimum point because of the costs involved, operational problems, or enhanced storage system vapour losses. Generally, with increasing pressure the gas capacity of the separator increases. The reasons are the effect pressure has on gas and liquid densities, actual flowing volume, and the allowable velocity through the separator. With increasing temperature, the separator capacity usually decreases, due to the effect of temperature on the flowing volume and gas and liquid densities. The fluid properties such as density, Z factor are all functions of composition and operating temperature and pressure of the separator. Actual gas and liquid volumetric flow rates directly affect the design of the separators as they influence the residence time and the allowable velocities in the vessel. The degree of separation is also an important factor;; it determines the type of internals, geometry and size of gas separation zone. It is critically important to estimate the amount of free water which may be separated in the vessel; the free water affects the type of separators and the control feature of the separation process. It is also important to realize what fluid service the separator is designed for. Is a crude (Low GOR) or a natural gas (High GOR) process; is it a rich gas with lots of water vapour or it is a dry gas with little possibility for condensate accumulation. It is also important to know if slugging is a major factor. The type, size and control systems for high slug separators can influence the final design and selection of the right separator and its internals. Foaming is also considered to be a determining factor as it determines the liquid residence time and the type of internals that should be selected. Presence of solid as discussed before can certainly influence the type of separators. Corrosion and presence of acid gases affects the type of material of construction and corrosion allowances when the separator is mechanically designed. As exploration and production heads into deeper waters, **floating production facilities (FPF)** become increasingly more economical than fixed platforms. FPF respond to wave motion, and production separators are one of the process units that are most sensitive to motion. Figure on the top right of the slide shows the various linear and angular velocities of a floating system. Pitch and roll are the two most important factors affecting the performance of process units containing liquids. Pitch is the most harmful as it causes both spirit level and resonant waves. Heave causes resonant waves and causes control problems. Separators should be positioned carefully on FPF; the separator should be installed as close to the center of gravity of the FPF to minimize the effect of heave motion and the separator axis should preferably aligned along the axis of least pitch. Well designed, internal baffles or wave breakers can dampen undesirable wave motion that would otherwise cause liquid level control problems, reduce separation, and disrupt float or displacer sensors. Improper design can make the problem worse. Double barrel designs seem to reduce the harmful effects of floating systems as the liquid tube is completely separated from the droplet separation zone. In some new designs three horizontal vessels are stacked vertically and connected by three risers. Many other design features are available and produced by major manufacturers.

## Gas and Liquid Separation: Operations

- Potential Problems
  - Foaming
  - Fouling –
    - Solid/sand deposition
    - Hydrate, paraffin, wax
  - Corrosion
  - Liquid carryover and gas blowby
  - Flow variations
- Maintenance
- Troubleshooting

Specialized design procedures are warranted for foaming crudes, CO<sub>2</sub> rich stream, solids removal or sand production, waxes, paraffins, hydrates, and floating offshore and sub-sea separators. Potential surges in flow must also be addressed.

### ***Operation problems:***

•Foaming: foam is often a big problem in crude oil degassing and depressurizing separators; essentially foam can occupy one-half of the separator volume. Foam is of less significance in natural gas treating services. Foam is formed as the oil pressure is reduced in the reservoir, well bore, tubing string or flow lines.

•Fouling: Paraffins are large molecular weight hydrocarbons which tend to solidify at low temperatures within the internals especially at demister mesh pads or vanes. Therefore provisions should be made at man-holes and inlet and outlet nozzles for steam or solvent clean outs. The temperature of separators should be kept above cloud point which is the temperature at which paraffins or waxy material start to solidify. Hydrates are crystalline compounds which may plug lines and inlet and gas exit nozzles and control valves and instruments in gas lines. Temperature and amount of water should be carefully watched when the separator is designed.

•Sand: Sand creates major problems especially erosion corrosion in nozzles where the fluid velocity may be high. It also tends to accumulate at low fluid speed and dead zones. Use of sand jets and multiple drain lines is one way to reduce the risk of solid deposition. When the possibility of sand deposition is high, designers should avoid lots of corners and dead volume spaces.

•Corrosion: Acid gas containing stream, especially when wet, cause sever problems. Therefore, either the contaminants should be removed or proper material of construction should be selected. Stainless steel cladding in wet parts or high alloy steel should be considered for sour services.

•Liquid Carry Over: Caused by clogged liquid outlet, foam and high flow rates above design rates. Sources of problem should be identified and eliminated.

•Gas Blow-By: Bubbles may remain in the liquid and leave the separator from the liquid outlet; caused from low liquid level, vortexing and liquid level control failure.

**Maintenance:** maintenance should include the following: Daily, e.g., checking liquid levels, pressure and temperatures, replacing broken gages; periodically, e.g., lubricating valves, cleaning gage columns, checking dump valves, level controllers, and back pressure controls; Yearly, e.g., checking pressure relief valves, sometimes regulatory organization require monthly checks for offshore facilities

## Gas and Liquid Separation: Operations-Troubleshooting

1. Low liquid level
2. High liquid level
3. Low pressure in separator
4. High pressure in separator
5. All the oil going out gas line
6. Mist going out gas line
7. Free gas going out oil valve
8. Gas going out water valve on three-phase
9. Too much gas going to tank with the oil
10. Condensate and water not separating in 3-phase
11. Diaphragm operated dump valve not working

- |   |  |
|---|--|
| <ol style="list-style-type: none"><li>1. Low liquid level<ul style="list-style-type: none"><li>• Fluid dump valve opening too wide or trim cut out</li><li>• Drain valve open or leaking</li><li>• No fluid entering</li></ul></li><li>2. High liquid level<ul style="list-style-type: none"><li>• Fluid control dump valve closed or plugged</li><li>• Block valve around dump valve closed</li><li>• Inlet valve to next vessel closed</li><li>• Separator overload</li></ul></li><li>3. Low pressure in separator<ul style="list-style-type: none"><li>• Back pressure control valve is not working</li><li>• Leaking safety relief valve</li><li>• Inlet valve closed</li></ul></li><li>4. High pressure in separator<ul style="list-style-type: none"><li>• Back pressure control valve is not working</li><li>• Valves downstream of separator closed</li></ul></li><li>5. All the oil going out gas line<ul style="list-style-type: none"><li>• Dump valve not open</li><li>• Block valve closed on piping to tank</li><li>• Separator or piping plugged</li></ul></li><li>6. Mist going out gas line<ul style="list-style-type: none"><li>• Vessel too small (overloaded separator)</li><li>• Plug mist extractor</li><li>• Improper liquid level</li><li>• Foaming problem</li></ul></li></ol> | <ol style="list-style-type: none"><li>7. Free gas going out oil valve<ul style="list-style-type: none"><li>• Too low level in separator</li><li>• Dump valve not seating</li><li>• No vortex breaker or breaker plugged or damaged</li></ul></li><li>8. Gas going out water valve on three-phase<ul style="list-style-type: none"><li>• Same as free gas going out oil valve</li></ul></li><li>9. Too much gas going to tank with the oil<ul style="list-style-type: none"><li>• Retention time too low (vessel overloaded)</li><li>• Foaming oil</li><li>• Too much pressure drop from separator to tank</li><li>• Condensates to tank too cold</li></ul></li><li>10. Condensate and water not separating in 3-phase<ul style="list-style-type: none"><li>• Paraffin problem causing water not to be free</li><li>• Adjusting weir out of adjustment</li><li>• Not enough retention time (overloaded vessel)</li><li>• Leak in adjustable weir</li></ul></li><li>11. Diaphragm operated dump valve not working<ul style="list-style-type: none"><li>• Pilot failure<ul style="list-style-type: none"><li>▫ Supply gas failure</li><li>▫ Orifice stopped up</li><li>▫ Out of adjustment</li></ul></li><li>• Broken valve stem</li><li>• Plugged tubing</li><li>• Ruptured diaphragm</li><li>• Stopped up vent in upper case</li><li>• Leak in line from pilot to valve</li></ul></li></ol> |
|---|--|

## **NATURAL GAS SWEETENING** **(Acid Gas Removal)**

- Purpose and Introduction
- Process classification
  - Batch vs. continuous
  - Solvent vs. solid based
- Batch Processes
  - Solid vs. liquid/slurry based
- Continuous Processes
  - Alkanol-Amine based solvents
  - Mixed solvents (enhanced/activated/formulated)
  - Physical solvents
  - Direct conversion – Liquid phase oxidation of H<sub>2</sub>S
  - Adsorption on solids
  - Membranes
- Process Selection Guidelines
- Design Procedures and Guidelines
- Operations – Problems and Troubleshooting

With increasing demand for natural gas, natural gas containing significant amount of acid gases -hydrogen sulfide and carbon dioxide – are being tapped for utilization after purification. By far the most stringent specification for selling natural gas are those related sulfurous gases. In most places in the world, H<sub>2</sub>S, is nearly always limited to 0.25 grains/100 scf (4 ppmv) and the specification may be as low as 1 ppmv in some countries. The maximum total sulfur content including mercaptans (RSH), carbonyl sulfide (COS), disulfides (RSSR), etc., is usually to 10 to 20 grains/100 scf. However, some transcontinental pipelines now also require as low as 0.25 grains/100 scf of organic sulfur compounds. Carbon dioxide, CO<sub>2</sub>, is usually included with nitrogen as an inert gases. The inert gas specifications is within the range of 2 to 3%, therefore, there are occasions where **sweetening - removal of acid gas components from sour gas streams** - requires only H<sub>2</sub>S removal. When CO<sub>2</sub> concentration exceeds the specifications and/or cryogenic processing follows, removal to as low as 100 ppmv may be needed. There are more than 30 to 40 natural gas sweetening processes. There are many ways to classify the gas sweetening processes. One would be to calssify them as batch vs. continuous. The other would be to categorize them based on the sort of reactant which removes the impurities, which can be either solid or liquid. These processes may be classified as follows:

1. Batch Processes; in theses processes the reactants which remove the impurities from gas streams are discarded after they were completely loaded with impurities. The use of these processes is limited to removing very small amounts of sulfur, i.e., low gas flow rate and/or small concentrations of hydrogen sulfide. Various technologies developed by several companies use reactants, which may be both liquid and solid
2. Aqueous amine (alkanolamine) and chemical solutions. These solution undergo reversible reactions with acid gases and can be regenerated (usually by applying heat) in a cyclic process to remove rather large amounts of sulfur, and CO<sub>2</sub> when needed. Several types of amine solutions may be used depending on the sour gas specifications. Potassium carbonate, alone or mixed with amine solutions with other activators, has been used for removal of carbon dioxide from gas streams in petrochemical and crude oil refining industries for many years.
3. Mixed solutions: These solutions are usually a mix of amine solutions with other physical solvents and water, which can also absorb organic sulfur compounds and capable of high acid gas loadings.
4. Physical solvents: Unlike amine solutions these solvents remove the impurities without any chemical reaction involved between the solvent and acid gases. They can be regenerated without heat and simultaneously dry the gas. They are used for bulk removal of large amount of CO<sub>2</sub> from high pressure natural gas.
5. Direct conversion or liquid phase oxidation of hydrogen sulfide: These solutions practically remove only hydrogen sulfide and convert (neutralize) it to elemental sulfur in the liquid phase at low temperatures. The solutions are usually regenerated by contacting them with air.
6. Adsorption: The media for acid gas removal is a very porous (large surface area) solid materials, known as molecular sieves. The solids can be regenerated by applying heat or change of pressure in a cyclic process. The use is limited to low acid gas concentrations, and the gas can be simultaneously dried.
7. Membranes: Membrane technology is a rather new technique to remove impurities from gas streams; it has been limited to removal of water from air streams and separation of nitrogen from air. However, its use is expanding to other applications such as acid gas removal and natural gas dehydration. The technology is more suitable for CO<sub>2</sub> removal, although Air Products claims that their technology can be used for H<sub>2</sub>S removal as well.

Amine and batch processes are used for over 90% of all onshore wellhead applications. Amine processes are preferred fro larger acid gas containing sour gases. The choice between a batch or amine process is related to sulfur and acid gas content of acid gas. We will discuss the various aspects of acid gas removal processes including process selection criteria, design procedures, as well as operations of gas sweetening plants.

## Acid Gas Removal: Batch Processes

- Batch Processes specifics and applications
- Process description
  - Solid based
    - Iron sponge
    - SULFATREAT®, H<sub>2</sub>S Scavenger, Natco
    - SulfaTreat®, SulfaTreat Co., M-I LLC
    - Molecular sieves: MOLSIV®, MOLSIV COSMIN 105 A in POLYBED™ PSA SYSTEMS from UOP sieves, Union Carbide Corp.; SILIPORITE® Molecular sieves from TOTAL
  - Liquid and slurry Iron oxide slurry
    - Caustic soda
    - Formaldehyde-methanol-water mix (Inhibit®, Scavinox®, Di-Cem®)
    - Zinc based slurries (Chemsweet®, Natco)
    - Nitrite solutions (Sulfa-Check®, Exxon)
- Design guidelines
- Operations and trouble shooting

These processes are based upon physical or chemical absorption (to liquid media) or adsorption (solid media) of acid gases. Although not as widely used as liquid based continuous processes, they offer advantages such as simplicity, high selectivity (only H<sub>2</sub>S is generally removed), and process efficiency almost undependable of pressure. These processes are best applied to gases with moderate concentrations of H<sub>2</sub>S, and where CO<sub>2</sub> could be retained in the gas. A fixed bed of solid particles or liquid filled column are generally used to remove acid gases. . Typically, in batch processes the gas stream must flow through a vessel filled with solid granules, liquid/slurry that remove the acid gases and hold them in the vessel. When the solid bed or the liquid is saturated with the impurities, the vessel must be removed from service and the solid and/or liquids replaced. Many chemicals can absorb acid gases. The trick is to find an inexpensive, non-hazardous material that has a high capacity for H<sub>2</sub>S and produces an environmentally acceptable waste. Currently marketed processes are shown on this slide.

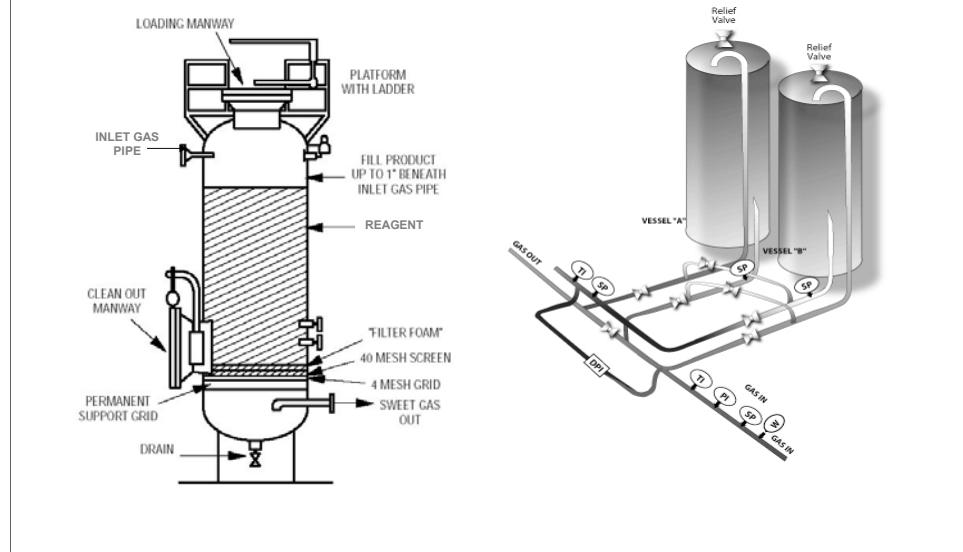
**Iron sponge** is the oldest process although it is increasingly being replaced by more efficient processes. Because the bed consists of solid particles, the superficial gas velocity is higher and the tower diameter is smaller than for liquid or slurry processes. The chemical cost is low, however a major drawback is the labor needed to empty the tower and dispose of the pyrophoric spent sponge. Iron sponge consists of wood chips or shavings impregnated with hydrated ferric oxide and sodium carbonate. The technology is being replaced by more efficient **SulfaTreat®** process which is also an iron based process uses a porous form of iron oxide and therefore has much larger capacity per unit volume of the bed.

**Sulfatreat** beds are much smaller for the same gas capacity when compared to iron sponge beds. Iron is a very strong oxidizing element and oxidizes sulfur compounds and neutralize them either to other forms of less harmful sulfur compounds or to the elemental sulfur itself.

**Molecular sieves** which are very porous materials - they can be found in nature or made synthetically our of minerals – can be used to remove acid gases. Due to the basic nature of theses compounds , acid gases are adsorbed on the very large surface area available within the pore volumes of these compounds. Molecular sieves may be regenerated, therefore, gas sweetening with molecular sieves may be considered as semi batch processes.

There are batch liquid based processes to remove sulfur compounds from natural gas streams. These were developed as an alternative to iron sponge. Solutions such as **Inhibit**, **Scavinox**, and **Dichem** are mixtures of formaldehyde, methanol and water. They react with H<sub>2</sub>S to form cyclic carbon-sulfur compounds known as form thionals. Formaldehyde is a carcinogenic compounds therefore the use of these processes has been restricted in many places of the world. Slurries of iron oxide have been used to selectively absorb H<sub>2</sub>S, however due to problems including premature H<sub>2</sub>S break through and foaming were discontinued. Natco's **Chemsweet®** is a zinc oxide-based process. Zinc oxide is also a very strong chemical agent which react with sulfur compounds. The **Chemsweet®** white powder which is a mixture of zinc oxide, zinc acetate and a dispersant is mixed one part in five part of water. The presence of CO<sub>2</sub> is not important as the pH is low enough to prevent significance absorption of CO<sub>2</sub>. **Sulfa-Check®** is Exxon's contribution. It is an aqueous solution of sodium nitrite buffered to stabilize the pH above 8. The reaction of nitrite solution with H<sub>2</sub>S forms elemental sulfur, ammonia, and caustic soda. There are other side reactions and therefore the disposal of the spent solution which is slurry of fine sulfur particles in a solution of sodium and ammonium salt is a main problem. **Caustic soda** is the standard base and reacts effectively with acid gases. Again the products of the reactions and disposal of the spent solutions is always a headache that gas processors have to put up with. Caustic wash is recommended to remove very small amount of RSH (mercaptans) and other organic sulfur compounds) from gas streams. The NaSH product cannot be dumped indiscriminately, and injection to deep wells is no longer condoned. The best is to sell it to a nearby paper company for bleaching wood pulp.

## Acid Gas Removal: Batch Processes - Design



The figures shown on this slide show typical contact tower for batch processes. The vessel is cylindrical with elliptical heads. It is equipped with inlet and outlet gas nozzles, the loading and clean out manways. For liquid service mist eliminator and a gas distributor are needed. The sour gas enters from the top (in a solid-based process) or from the bottom (in liquid-based processes) and passes through the reagent (solid or liquid/slurry). In liquid/slurry services, the rise of gas bubbles through the liquid provides the agitation required to keep the slurry mixed and solid particles in a suspension form. The sweetened gas leaves the vessel from the opposite end. Vessel height must be sufficient to maintain an adequate disengaging space, i.e., the distance between the top of slurry and the mist eliminator. Vessel diameter is a function of the actual gas flow rate at operational conditions. A minimum superficial gas velocity (i.e., actual gas volumetric flow rate divided by the cross section area of the vessel) is needed to provide the agitation that keeps the slurry mixed or the allowable pressure drop in solid beds. Too high a superficial velocity results in excessive expansion of the slurry or frictional pressure drop in solid beds. Vessel height is dictated by the bed life desired between charges. Normal bed life is 30 to 90 days.

**Design:** Operation at a typical superficial velocity of 2 to maximum 10 ft/min results in a favorable working conditions. For iron sponge beds, a velocity of 10 ft/min results in a low loading (0.25 lb S/ lb sponge). When gas bubbles flow through a liquid or slurry, they quickly reach a constant terminal velocity of about 48 ft/min. The volume of the liquid expands by the volume of gas in the liquid. The expansion factor,  $f$ , is the ratio of dynamic volume –or liquid depth in a vessel of constant diameter – to the static volume or depth. The expansion factor should not be less than 1.03 to provide mixing of the solution or above 1.20 where liquid entrainment occurs. The following design parameters are introduced:

1. Gas flow rate,  $Q$ , MMscfd
2. Operating pressure,  $P$ , psig
3. Operating temperature,  $T$ , °F
4. H<sub>2</sub>S inlet concentration, (ppmv), if the H<sub>2</sub>S concentration is in grains H<sub>2</sub>S /100scf, multiply by 15.9 to get ppmv)
5. Compressibility factor,  $Z$  – use **Figures 23-3 to 23-5** of the GPSA data book
6. Expansion factor,  $f$  (use 1.1 to 1.2)

When the bubbles rise at 48 ft/min,  $f$  is related to the superficial velocity  $V_s$  in ft/min as follows:

$$V_s = 48(f-1)/f$$

## Acid Gas Removal: Batch Processes – Design Procedure

1. Calculate the gas actual flow rate,  $Q_a$ , at  $T$  and  $P$
2. Calculate the internal cross-sectional area,  $A$ , and the internal vessel diameter,  $ID$
3. Calculate daily chemical requirement
4. Select a static bed height,  $L$
5. Bed life
6. Charge requirements
7. Check with supplier
8. Check the contact time
9. Check the heat effects

1. Calculate the gas actual flow rate,  $Q_a$ , at  $T$  and  $P$ : 
$$Q_a = \frac{19.63Q(T + 460)Z}{(P + 14.7)}$$

2. Calculate the internal cross-sectional area,  $A$ , and the internal vessel diameter,  $ID$ :  $ID = [A/0.7854]^{0.5} \text{ ft}$ , consider a vessel  $ID$  that provides at least this internal diameter after considering the wall thickness.

3. Calculate daily chemical requirement

- Iron sponge IS=0.013  $Q(\text{ppmv H}_2\text{S})$
- Chemsweet CS=0.248  $Q(\text{ppmv H}_2\text{S})$
- Sulfa-Check SC= 0.0474  $Q(\text{ppmv H}_2\text{S})$
- Caustic soda: depends on the  $\text{CO}_2$  content
- NaSH: NS=0.109  $Q(\text{ppmv H}_2\text{S})$  gal 20% NaOH/day

Process	Superficial velocity ft/min	Cross sectional area, ft <sup>2</sup>
Iron sponge	10.0	$0.1Q_a$
Chemsweet	6.5	$0.16Q_a$
Sulfa-Check	8.0	$0.11Q_a$
Caustic soda	8.0	$0.13Q_a$

4. Select a static bed height,  $L$ : typically 10 to 20 ft. The volume,  $RV$ , of reactant is:  $RV=0.7854 (ID)^2(L) \text{ ft}^3$ . Note the bubbling gas into a liquid increases the volume (and the height in the tower) by the volume of the gas bubbles in the liquid at any given time. This increase in bath height – up to 20% - must be considered in selecting the shell length of the tower.
5. Bed life,  $BL$ , is: for Iron Sponge  $BL=RV/IS$  days; for Chemsweet  $BL=11.7 RV/CS$  days; for Sulfa-Check  $BL = 7.5 RV/SC$  days
6. Charge requirements: for Iron Sponge  $RV$  bushels; for Chemsweet 11.7  $RV$  lb of solids and 7.0  $RV$  gal water; for Sulfa-Check 7.5  $RV$  gallons. These correspond to a minimum vessel diameters, reactant volume, and bed lives. To increase the bed life, the tower diameter and height can be increased. However reducing the superficial gas velocity below 2 ft/min causes channelling in iron sponge towers. For slurries, operational velocities below 1 ft/min are not recommended because of poor mixing.
7. Check with supplier: Usually supplier provide the information required for design purposes. In most case for batch process they provide the sizing information for the required service. It is recommended to have contact with them and check their sizing information with the above recommended calculations.. For iron sponge beds, make sure the mass velocity is less than  $(\rho_g)^{0.5}$  lb/min ft<sup>2</sup>. This occurs only with liquid hydrocarbons and density over 30 lb/ft<sup>3</sup>.
8. Check the contact time by determining the space velocity acfh/ft<sup>3</sup> of bed. This should be less than 180 acfh/ft<sup>3</sup> for low  $\text{H}_2\text{S}$  contents and 90 acfh/ft<sup>3</sup> for over 50 grains/100scf gas.
9. Check the heat effects: the sulphur deposition or absorption should be less than 15 grains/min ft<sup>2</sup> of bed area

## Acid Gas Removal: Batch Processes – Operations

Operations	Trouble shooting
<ul style="list-style-type: none"><li>• General<ul style="list-style-type: none"><li>– Check the design parameters</li><li>– Condensatation and hydrate</li><li>– Damaged reagent</li><li>– Pressurization</li><li>– Daily operations</li></ul></li><li>• Solid beds<ul style="list-style-type: none"><li>– Bed support</li><li>– Particle entrainment</li><li>– Excessive pressure drop</li><li>– Before loading inspections</li><li>– After loading inspections</li></ul></li><li>• Liquid/Slurry baths<ul style="list-style-type: none"><li>– Water supply</li><li>– pH</li><li>– Foam tests</li><li>– Water make-up</li><li>– Liquid carry over</li></ul></li></ul>	<ul style="list-style-type: none"><li>• Solid bed<ul style="list-style-type: none"><li>-Channeling (low gas velocity)</li><li>-Hydrate formation/condensation</li><li>-Check water pH (&gt;8.0, add soda if needed)</li><li>-Pressure drop (check for damaged solids)</li><li>-Liquid formation (poor upstream separation)</li></ul></li><li>• Liquid/Slurry beds<ul style="list-style-type: none"><li>-Sour gas velocity (&lt;10 ft/min, check liquid carry over)</li><li>-Inlet gas T (between 50-98 °F, hydrate/drying)</li><li>-Bath level (anti-foam?, add water if too low)</li><li>-Outlet H<sub>2</sub>S conc. (rising rapidly? Check with supplier or add more reagent, zinc oxide/buffer)</li><li>-Slurry/liquid pH, should be within the range</li><li>-Hydrocarbon condensation (causes foaming)</li><li>-Settling solid particles (low or interrupted flow rate)</li><li>-RSH and RSSR and COS in inlet gas (&lt;25%)</li><li>-Distributor plate (check and clean the plugged holes)</li></ul></li></ul>

The keys to trouble free operations are proper installation of the tower and preparation of the reactant. It is important to make sure that superficial velocity of the sour gas is within the design range. For solid-based beds too low a velocity results in poor gas distribution, gas channeling and loss of adsorption efficiency. The high r low velocity effects were already discussed for slurry and liquid-based baths. During cold days, condensation and hydrate formation should be anticipated. A high pressure drop across a solid bed may help the cooling for these phenomena to occur. An inlet separator help to prevent solid reagent damage due to water or liquid hydrocarbon entrance into the bed. The damaged solids may cause increased pressure drop across the bed (as much as 200 psi within a single day). For liquid/slurry system the damage may be even more disastrous: increased bath volume, formation of water/hydrocarbon emulsions, foaming and finally liquid carry over. When the vessel is pressurized it is important to note that , too rapid a pressurization from the top, compacts the solid particles and strains the bed support. Too rapid pressurization from the bottom, either lifts the solid and settles them unevenly or bump liquids into the mist eliminator. Start the gas slowly and increase the pressure gradually. It is important to do daily inspection (unless it is impractical) and check the gas flow rate, inlet and outlet H<sub>2</sub>S and other sulfur compounds concentrations, the liquid height, bath pH and water collected in the bottom of the solid beds. Larger installation may require continuous H<sub>2</sub>S monitors.

Other major operational issues for solid beds and slurries are listed on this slide. For solid beds: a strainer should be provide to remove entrained particles; differential pressure should be checked in case a shut down or by pass is needed due to very high pressure drop incidents; solid reagents' conditions should be checked before they are charge to make sure they have the appearance indicated in the specification sheets. When the beds are loaded., care should be taken not to damage the particles by dropping a large quantity at once. For slurry/liquid baths: it is important to check the water supply, drinking water or steam condensate are satisfactory; avoid using produced water or pond water which may induce foaming. The bath pH should be controlled regularly to make sure the pH is within the spec. provided by the supplier. Standard foam test should be performed regularly to make sure if any antifoam is required before foaming becomes out of control. It is important that the inlet gas is saturated with water. A downstream separator with a sight glass will help to warn if there is any liquid carry over.

The troubleshooting guidelines are shown on this slide. The major problems are premature H<sub>2</sub>S breakthrough; rapid buildup of the pressure drop across the solid bed, and foaming with liquid carry over in liquid/slurry systems. The usual cause of these problems is the condition of the inlet gas. If the gas is too close to or at its HC dew point, any cooling condenses hydrocarbons, and if it is unsaturated with respect to water, it dries the charge. It is important to keep the gas a few degrees above its HC dew point (or the bed temperature above the HC dew point of the gas) and nearly saturated with water

## Acid Gas Removal: Continuous Processes

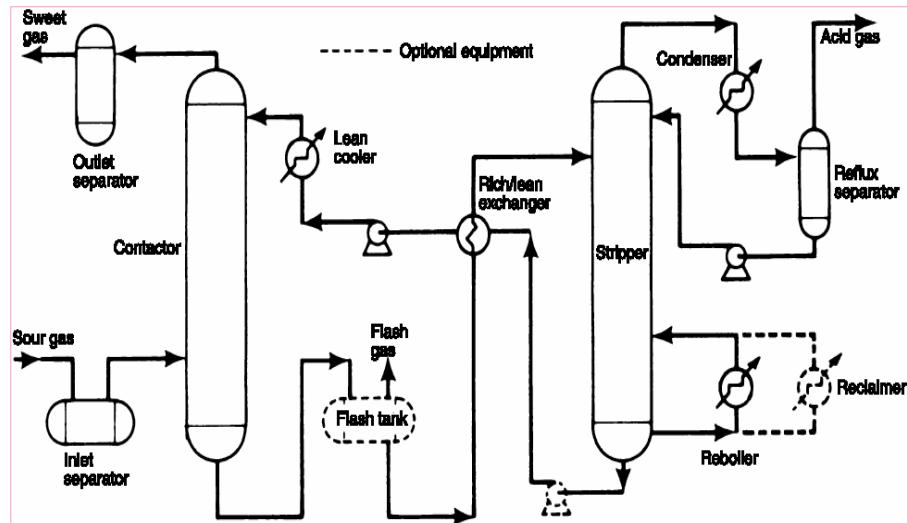
- Why continuous?
- Process choices
  - Chemical solvents
    - Amine and mixed solvents
      - MEA, DEA, TEA, MDEA, Shell ADIP® DIPA, Flour Econamine ® DGA
      - Hot potassium carbonate: Catacarb® (Eickmeyer), Benfield® (UOP)
      - Formulated/special solutions: UOP Ucarsoi®, BASF activated MDEA
    - Physical solvents: Norton Co. Selexol®, Flour Flexorb®, Shell Sulfinol® D&M, Linde Rectisol®, Lurgi Purisol®, IFP IFPEXOL®
    - Direct Conversion of H<sub>2</sub>S: GTP-Merichem LO-CAT®, Shell Sulferox®, BG Stretford®, Linde Sulfinol®
    - Membrane Technologies: Dow Cynara™, UOP SEPAREX™, Air Products PRISM® membrane, Liqui-Cel® Membrane

Batch processes despite their aforementioned advantages are limited to some particular applications. Uninterrupted operation of these processes requires two or more towers, so that at least one is on stream when another is being recharge. For large gas flow rates and when the concentration of acid gases are high the construction and operating costs of batch processes are not justifiable. Continuous processes in which uninterrupted operations with single equipment are normally used to remove impurities from natural gas streams.

The continuous processes may be classified as shown on this slide. They are mostly based on the use of a solvent which can be regenerated and reused in acyclic process. Therefore the solvent inventory of the plant is never completely disposed off unless it is severely contaminated with impurities. A continuous flow of the solvent in the gas absorption systems continuously removes the impurities from the gas stream. The gas leaves the absorption system incessantly, and the solvent is routed to a regeneration system in which it is stripped off the acid gases and return to the absorption section. Most gas sweetening processes use aqueous solutions of alkanolamines. The alkanolamines of industrial significance are listed on this slide. They are the alcohol derivatives of ammonia. The alkalinity of ammonia is reduced as more hydrogen atoms are replaced by alcohol (ethanol) molecules. Therefore MEA (monethanolamine) is a stronger base and reacts faster with acid gases. A physical solvent may be added to enhance the performance of the amine in special situations. Potassium carbonate is another basic reagent which can react with acid gases. The hot carbonate processes developed by UOP and Unocal are mainly used in petrochemical and refining industries to remove CO<sub>2</sub> from gas streams. Formulated amines which are hybrids of amine and physical solvents together with corrosion inhibitors and activators to enhance the ability of the solvents for better removal of carbon dioxide and/or mercaptans and sulfur compounds, or simultaneous removal of acid gases and water have been introduced. In physical solvent-processes the solvent physically absorb the acid gases as opposed to chemical solutions in which reversible chemical reactions take place between the acid gas and the chemical reagents. Physical solvents dissolve the hydrocarbon constituents of natural gas (especially the larger molecular weight compounds), therefore it is important to note that if these components are wanted in the sales gas or not and in what quantities. The most widely used processes are listed in this slide. In direct conversion processes hydrogen sulfide (H<sub>2</sub>S) is simultaneously removed and chemically converted to sulfur. The solutions are regenerated by air. There for the alternative term of Liquid Phase Oxidation is also used for these processes.

As explained before, acid gases may be continuously removed from gas stream using the permeation phenomenon. Several technology suppliers offer these technology. Unlike liquid based systems, membranes remove impurities without any chemical or physical dissolution of acid gases. The system is simple and almost maintenance free. Membranes may also be used as gas-liquid contact equipment to contact the aforementioned chemical agents with the gas. New technologies are being developed, especially for offshore and floating facilities, in which the size of equipment is significantly reduced. The membrane base gas-liquid contactors are not sensitive to sea motion and therefore are more recommended for offshore operations

### Typical Amine (physico-chemical) Process Flow Diagram



The flow diagram shown on this slide illustrates the arrangement of the equipment needed for **amine process**. The process flow diagram for formulated amines are almost the same. There are two basic parts: the high pressure process gas contactor and scrubbers, the size of which depends on the sour gas flow rate and pressure, and the low pressure regeneration system that is sized primarily according to the amine circulation rate. The sour gas enters the system through an inlet separator to remove any water or hydrocarbon liquids. Then the gas enters the bottom of the amine absorber and flows counter current to the amine solution. The absorber can be either trayed or packed tower. Conventional packing is used for smaller towers (<20") and trays or structured packing for larger towers. An outlet separator may be included to recover entrained amines from the sweet gas. The amine solution leaves the bottom of the absorber carrying with it the acid gases. This solution containing the CO<sub>2</sub> and H<sub>2</sub>S is referred to as the **rich amine**. From the absorber the rich amine is flashed to a flash tank to remove almost all the dissolved hydrocarbon gases and entrained hydrocarbon liquids (condensates). A small percentage of the acid gases will also flash to the vapour phase in this vessel. From the flash tank, the rich amine proceeds to the rich/lean amine exchanger. This exchanger recovers some of the sensible heat from the lean amine stream to decrease the heat duty of the amine reboiler. The heated rich amine then enters the amine stripping tower where heat from the reboiler breaks the bonds between the amines and acid gases. The acid gases are removed overhead and lean amine is removed from the bottom of the stripper. The hot **lean amine** (amine with very little no acid gas content) solution proceeds to the rich/lean exchanger and then additional coolers to lower its temperature to no less than 10°F above the inlet gas temperature. This prevents hydrocarbons from condensing in the amine solution when the amine contacts the sour gas. The cooled lean amine is then pumped up to the absorber pressure and enters the top of the absorber. As the amine solution flows down the absorber it absorbs the acid gases. The rich amine is then removed at the bottom of the tower and the cycle is repeated. Of the amine introduced before, diethanolamine (DEA) is the most common. Methyl-diethanolamine (MDEA) is a very important amine. It is important because it needs less energy to be regenerated and it is selective towards H<sub>2</sub>S removal. Most modern formulated amines are MDEA based. **Figure 21-5** of the GPSA data book summarizes the physical properties of the common gas treating solvents.

## Acid Gas Removal: Amine processes - Amine Used

- *Alcohol derivatives of ammonia:* NH<sub>3</sub>
- *Monoethanolamine (MEA):* HOC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>
- *Diethanolamine (DEA):* (HOC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NH
- *Diglycolamine (DGA):* H(OC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NH<sub>2</sub>
- *Methyldiethanolamine (MDEA):* (HOC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NCH<sub>3</sub>
- *Triethanolamine (TEA):* (HOC<sub>2</sub>H<sub>4</sub>)<sub>3</sub>N
- *Diisopropanolamine (DIPA):* (HOC<sub>3</sub>H<sub>6</sub>)<sub>2</sub>NH

**Monoethanolamine** — Gas sweetening with monoethanolamine (*MEA*) is used where there are low contactor pressures and/or stringent acid gas specifications. MEA removes both H<sub>2</sub>S and CO<sub>2</sub> from gas streams. H<sub>2</sub>S concentrations well below 0.25 grains/100scf (5.7 mg/m<sup>3</sup>) can be achieved. CO<sub>2</sub> concentrations as low as 100 ppmv can be obtained at low to moderate pressures. COS and CS<sub>2</sub> are removed by MEA, but the reactions are irreversible unless a reclaimer is used. Even with a reclaimer, complete reversal of the reactions may not be achieved. The result is solution loss and build-up of degradation products in the system. Total acid gas pick up is traditionally limited to 0.3-0.35 moles of **acid gas/mole** of MEA and solution concentration is usually limited to 10-20 mass%. Inhibitors can be used to allow much higher solution strengths and acid gas loadings. Because MEA has the highest vapor pressure of the amines used for gas treating, solution losses through vaporization from the contactor and stripper can be high. This problem can be minimized by using a water wash.

**Diethanolamine** — This process employs an aqueous solution of diethanolamine (*DEA*). *DEA* will not treat to pipeline quality gas specifications at as low a pressure as will *MEA*. Although **mole/mole** loadings as high as 0.8-0.9 have been reported, most conventional *DEA* plants operate at significantly lower loadings because of corrosion. The process flow scheme for conventional *DEA* plants resembles the *MEA* process. The advantages and disadvantages of *DEA* as compared to *MEA* are: The **mole/mole** loadings typically used with *DEA* (0.35-0.8 mole/mole) are much higher than those normally used (0.3-0.4) for *MEA*. Because *DEA* does not form a significant amount of non re-generable degradation products, a reclaimer is not required. Also, *DEA* cannot be reclaimed at reboiler temperature as *MEA* can. *DEA* is a secondary amine and is chemically weaker than *MEA*, and less heat is required to strip the amine solution. *DEA* forms a re-generable compound with COS and CS<sub>2</sub> and can be used for the partial removal of COS and CS<sub>2</sub> without significant solution losses.

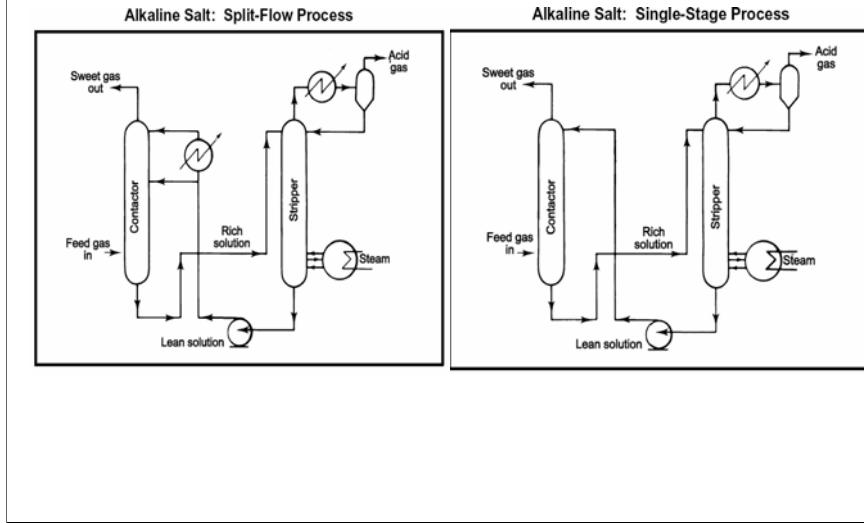
**Diglycolamine** — This process uses Diglycolamine® brand [2-(2-aminoethoxy)] ethanol in an aqueous solution. *DGA* is a primary amine capable of removing not only H<sub>2</sub>S and CO<sub>2</sub>, but also COS and mercaptans from gas and liquid streams. Because of this, *DGA* has been used in both natural and refinery gas applications. *DGA* has been used to treat natural gas to 0.25 grains/100scf (5.7 mg/m<sup>3</sup>) at pressures as low as 125 psig (860 kPa, ga). *DGA* has a greater affinity for the absorption of aromatics, olefins, and heavy hydrocarbons than the *MEA* and *DEA* systems. Therefore, adequate carbon filtration should be included in the design of a *DGA* treating unit. The process flow for the *DGA* treating process is similar to that of the *MEA* treating process. The three major differences are: Higher acid gas pick-up per volume of amine can be obtained by using 50-70% solution strength rather than 15-20% for *MEA* (more moles of amine per volume of solution). The required treating circulation rate is lower. This is a direct function of higher amine concentration. Reduced reboiler steam consumption. Typical concentrations of *DGA* range from 50% to 70% *DGA* by weight. *DGA* has an advantage for plants operating in cold climates where freezing of the solution could occur. The freezing point for 50% *DGA* solution is -30 °F (-34°C). Because of the high amine degradation rate *DGA* systems require reclaiming to remove the degradation products. *DGA* reacts with both CO<sub>2</sub> and COS to form non-regenarable products.

**Methyldiethanolamine** — Methyldiethanolamine (*MDEA*) is a tertiary amine which can be used to selectively remove H<sub>2</sub>S to pipeline specifications at moderate to high pressure. If increased concentration of CO<sub>2</sub> in the residue gas does cause a problem with contract specifications or downstream processing, further treatment will be required. The H<sub>2</sub>S/CO<sub>2</sub> ratio in the acid gas can be 10-15 times as great as the H<sub>2</sub>S/CO<sub>2</sub> ratio in the sour gas. Some of the benefits of selective removal of H<sub>2</sub>S include: Reduced solution flow rates resulting from a reduction in the amount of acid gas removed; Smaller amine regeneration unit; Higher H<sub>2</sub>S concentrations in the acid gas resulting in reduced problems in sulfur recovery. CO<sub>2</sub> hydrolyzes much slower than H<sub>2</sub>S. This makes possible significant selectivity of tertiary amines for H<sub>2</sub>S. This fact is used by several companies who provide process designs using *MDEA* for selective removal of H<sub>2</sub>S from gases containing both H<sub>2</sub>S and CO<sub>2</sub>. Because the reaction between CO<sub>2</sub> and tertiary amines forms the acid-base adduct, tertiary amines are ideally suited for bulk removal of CO<sub>2</sub> from natural gas streams. The bulk removal of CO<sub>2</sub> requires only a modest heat input for regeneration. The combination results in economic bulk removal of CO<sub>2</sub> from high CO<sub>2</sub> content gas streams.

**Triethanolamine** — Triethanolamine (*TEA*) is a tertiary amine and has exhibited selectivity for H<sub>2</sub>S over CO<sub>2</sub> at low pressures. *TEA* was the first amine commercially used for gas sweetening. It was replaced by *MEA* and *DEA* because of its inability to remove H<sub>2</sub>S and CO<sub>2</sub> to low outlet specifications. *TEA* has potential for the bulk removal of CO<sub>2</sub> from gasstreams. It has been used in many ammonia plants for CO<sub>2</sub> removal.

**Diisopropanolamine** — Diisopropanolamine (*DIPA*) is a secondary amine which exhibits, though not as great as tertiary amines, selectivity for H<sub>2</sub>S. This selectivity is attributed to the steric hindrance of the chemical.

## Acid Gas Removal: Hot Potassium Processes



The basic process was developed by the U.S. Bureau of Mines and employs an aqueous solution of potassium carbonate ( $K_2CO_3$ ). The contactor and stripper both operate at temperatures in the range of 230–240°F (110–116°C). The process is not suitable for gas streams containing only  $H_2S$ . If  $H_2S$  is to be removed to pipeline specification or there are low  $CO_2$  outlet specifications, special designs or a two-stage system may have to be used. Potassium carbonate processes are somewhat effective in removing carbonyl sulfide and carbon disulfide.

There are three basic process flow variations for the potassium carbonate process. The flow scheme required depends on the outlet specification of the natural gas. These are:

### Single Stage Process

The single stage process is shown in the figure on the right side of the above slide. Potassium carbonate is pumped to the top of a packed or trayed contactor where it contacts the gas stream. The rich solution flows to the stripper where the acid gases are stripped with steam. The lean solution is then pumped back to the contactor to complete the cycle.

### Split Flow Process

In this process scheme (see left on the above slide), the lean solution stream is split. Hot solution is fed to the middle of the contactor for bulk removal. The remainder is cooled to improve equilibrium and is fed to the top of the contactor for trim acid gas removal.

### Two Stage Process

In this process scheme (not shown here) the contactor is like that of the split flow process. In addition, the stripper is in two sections. A major portion of the solution is removed at the mid point of the stripper and pumped to the lower section of the contactor. The remainder is further stripped with steam and then cooled prior to entering the top of the contactor. Numerous improvements have been made to the potassium carbonate process resulting in significant reduction in capital and operating costs. At the same time, lower acid gas concentration in the treated gas can now be achieved. The most popular of the carbonate processes are:

### Benfield® Process

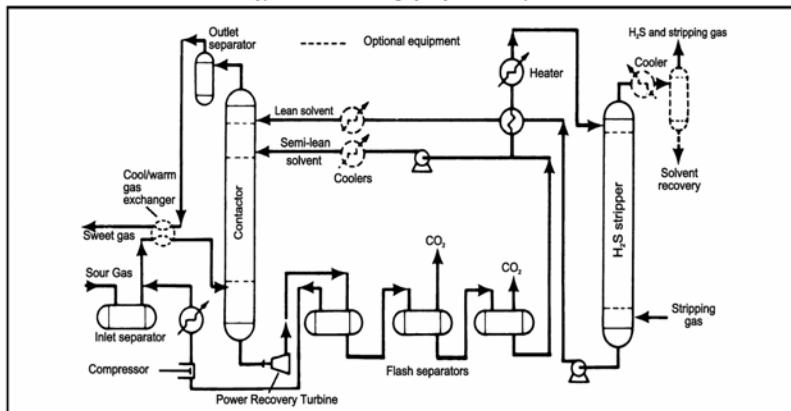
The Benfield® Process is licensed by UOP. Several activators are used to enhance the performance of the potassium carbonate solution.

### Catacarb® Process

The Catacarb® Process is licensed by Eickmeyer and Associates. Activators, corrosion inhibitors, potassium salts, and water are contained in the solution. This process is mostly used in the ammonia industry.

# Acid Gas Removal: Physical Solvent Processes

Typical Gas Sweetening by Physical Absorption



These processes are based on physical absorption and operate with a flow scheme as shown on this slide. In general, a physical solvent process should be considered when: the partial pressure of the acid gas in the feed is greater than 50 psii (345 kPa); the heavy hydrocarbon concentration in the feed gas is low; bulk removal of the acid gas is desired; and selective removal of H<sub>2</sub>S is desired. These processes are economically attractive because little or no energy is required for regeneration. The solvents are regenerated by: multi-stage flashing to low pressures; regeneration at low temperatures with an inert stripping gas; and heating and stripping of solution with steam/solvent vapors. In general, physical solvents are capable of removing COS, CS<sub>2</sub>, and mercaptans. In certain instances, physical absorption processes are capable of simultaneously dehydrating and treating the gas although additional equipment and higher energy requirements may be needed to dry the solvent. The processes operate at ambient or sub ambient temperature to enhance the solubility of the acid gases. The solvents are relatively non-corrosive so carbon steel can be used. Chemical losses are low due to low solvent vapor pressure. Physical solvents will absorb heavy hydrocarbons from the gas stream resulting in high hydrocarbon content in the acid gas stream as well as possibly significant hydrocarbon losses. Some of the physical absorption processes are summarized below.

## Selexol®

This process uses a polyethylene glycol derivative as a solvent. The solvent is selective for RSH, CS<sub>2</sub>, H<sub>2</sub>S, and other sulfur compounds. The process can be used to selectively or simultaneously remove sulfur compounds, carbon dioxide, water, as well as paraffinic, olefinic, aromatic and chlorinated hydrocarbons from a gas or air stream. Because water and heavy hydrocarbons are highly soluble in Selexol®, the treated gas from a Selexol® unit normally meets both water and hydrocarbon dew point specifications. The vendor states that the solvent is very stable, no degradation products are formed or disposed of, and no solvent reclaiming is required. Depending on the applications, the operating pressure could be as low as ambient though higher pressure is preferred. Operating temperature varies from 0°F (-18°C) to ambient. Selexol® is a **Union Carbide Corporation** technology.

## Fluor Solvent

This process patented by the **Fluor Corporation**, is based on the use of anhydrous propylene carbonate. The temperature of the lean solution to the absorber is usually well below ambient, and some method of refrigerating the solvent is usually necessary.

## Rectisol Process

This process uses methanol as a solvent, and was developed by the German **Lurgi Company** and **Linde A. G.** Because of the vapor pressure of *methanol*, the process is normally applied at temperatures of -30 to -100°F (-35°C to -73°C) for the *Rectisol* solution. It has been applied for the purification of natural gas for LNG production. The process is best suited where there are limited quantities of ethane and heavier components and has been used more in Europe than the U.S and Canada.

## Ifpexol

*Ifpexol* also uses refrigerated methanol for the complete treatment (dehydration, NGL recovery and sweetening) of natural gas. The *Ifpexol* process is based on two independent steps : **Ifpex-1** : methanol is used as hydrate inhibitor in a cold process for NGL extraction. The mixture of methanol and water recovered at the low temperature separator is regenerated by simple stripping with a fraction of the feed gas and pure water is produced. **Ifpex-2** : refrigerated methanol/water mixture is used as a solvent for the extraction of acid gases (CO<sub>2</sub>/H<sub>2</sub>S). Being a physical solvent process, *Ifpex-2* fits best for bulk acid gas removal and also allows the removal of the organic sulphur species. A key feature of *Ifpex-2* is that acid gases are obtained dry and under some pressure which brings important savings for acid gas reinjection. *Ifpexol* was developed by the **Institut Français du Pétrole (IFP)**.

## Purisol

This process was developed by **Lurgi** and is licensed by the **Ralph M. Parsons Company**. The solvent used in this process is N-methyl-2-pyrrolidone (*NMP*), a high boiling point liquid. Like *Selexol*, *Purisol* exhibits a selectivity for H<sub>2</sub>S. *Purisol* has not been used much in the U.S and Canada.

## Catasol

This process is licensed by **Eickmeyer** and Associates. *Catasol* solvents are reported to have selectivity for H<sub>2</sub>S/CO<sub>2</sub>, CO<sub>2</sub>/propane, and COS/CO<sub>2</sub>.

## Acid Gas Removal: Formulated Solutions (Special/hybrid or mixed Solvents)

- Formulated Solutions
  - Dow **GAS/SPEC™**
  - UOP **UcarsoI™** series
  - Huntsman **EXTREAT™**
  - BASF **activated MDEA® or aMDEA®**
- Sterically hindered amines, Exxon FLEXSORB®
- Hybrid (mixed solutions)
  - Shell Sulfinol® M & D
  - UOP Hi-Pure®

**Formulated Solvents** — Formulated Solvents is the name given to a new family of amine-based solvents. Their popularity is primarily due to equipment size reduction and energy savings over most of the other amines. All the advantages of *MDEA* are valid for the *Formulated Solvents*, usually to a greater degree. Some formulations are capable of slipping larger portions of inlet CO<sub>2</sub> (than *MDEA*) to the outlet gas and at the same time removing H<sub>2</sub>S to less than 4 ppmv. For example, under ideal conditions of low absorber pressure and high CO<sub>2</sub>/H<sub>2</sub>S ratios, such as *Claus* (sulphur recovery units) tail gas clean-up units, certain solvent formulations can slip upwards to 90 percent of the incoming CO<sub>2</sub> to the incinerator. While at the other extreme, certain formulations remove CO<sub>2</sub> to a level suitable for cryogenic plant feed. Formulations are also available for CO<sub>2</sub> removal in ammonia plants. Finally, there are solvent formulations which produce H<sub>2</sub>S to 4 ppmv pipeline specifications while reducing high inlet CO<sub>2</sub> concentrations to 2% for delivery to a pipeline. This case is sometimes referred to as bulk CO<sub>2</sub> removal. This need for a wide performance spectrum has led *Formulated Solvent* suppliers to develop a large stable of different *MDEA-based* solvent formulations. Most Formulated Solvents are enhancements to *MDEA* discussed above. Thus, they are referred to as *MDEA-based* solvents or formulations. Benefits claimed by suppliers are: *For New Plants*: reduced corrosion; reduced circulation rate; lower energy requirements; smaller equipment due to reduced circulation rates. *For Existing Plants*: increase in capacity, i.e., gas through-put or higher inlet acid gas composition; reduced corrosion; lower energy requirements and reduced circulation rates

Formulated Solvents are proprietary to the specific supplier offering the product. Companies offering these solvents are **Dow Chemical Company** (offering *Formulated Solvents* under the name **GAS/SPEC™**, **Huntsman Corporation** (marketing Formulated gas treating solvents under the **EXTREAT™** name), **Union Carbide Corporation** (marketing the **UCARSOL™** family of Formulated Solvents), and German BASF (marketing the **activated MDEA® or aMDEA®** formulated) solvents.

These companies offer their Formulated Solvents on an "as is" sale basis. This means there is no technology (process) license fee involved to use the solvent; therefore, no process warranty is included. Some suppliers do offer free services such as process/performance simulation, on-site technical service, solvent analysis, etc. Check with the current suppliers for their present warranty and service policy as these items are subject to change.

**Sterically Hindered Amines** — Other amines have been used to treat sour gas. One specialty amine has been constructed by a process defined as steric hindrance (hindered amines are amines containing a bulky substitute group to the nitrogen atom in the ammonia molecule to lower the stability of carbamate ion – a transient combination of CO<sub>2</sub> and the amine). The actual structure of the amine has been formed to accommodate a specific process requirement. This type of amine and the associated technology is different than Formulated Solvents, which create the desired formulations by blending different components with a standard amine such as *MDEA*. An example of this technology is FLEXSORB® solvents, marketed by **Exxon Research and Engineering Company**.

### Sulfinol® Process

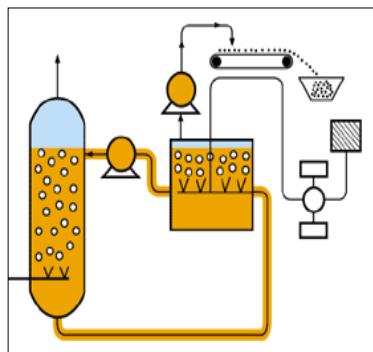
The **Sulfinol®** Process, licensed by **Shell E&P Technology** Company, is used to remove H<sub>2</sub>S, CO<sub>2</sub>, COS, CS<sub>2</sub>, mercaptans and polysulfides from natural and synthetic gases. *Sulfinol* is a mixture of *Sulfolane* (a physical solvent), water and either *DIPA* or *MDEA* (both chemical solvents). It is this dual capacity as both a physical and a chemical solvent that gives *Sulfinol* its advantages. *Sulfinol* with *DIPA* (**Sulfinol-D**) is used when complete removal of H<sub>2</sub>S, CO<sub>2</sub>, and COS is desired. *Sulfinol* with *MDEA* (**Sulfinol-M**) is used for the selective removal of H<sub>2</sub>S in the presence of CO<sub>2</sub>, with partial removal of COS. Both *Sulfinols* can reduce the total sulfur content of treated gas down to low ppm levels. The advantages of *Sulfinol* are: low energy requirements; low foaming and non-corrosive nature; high acid gas loadings; some removal of trace sulfur compounds. The disadvantages of *Sulfinol* are; higher heavy hydrocarbon co-absorption; reclaimer sometimes required when removing CO<sub>2</sub>.

### Hi-Pure® Process

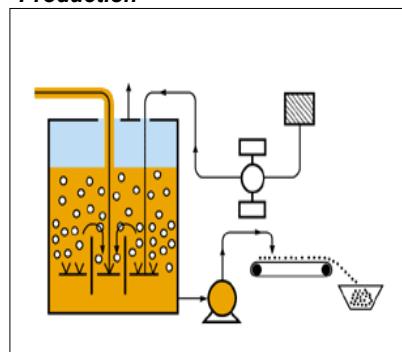
The *Hi-Pure* process is a combination conventional *Bentfield* potassium carbonate process and alkanolamine process. The gas stream is first contacted with potassium carbonate followed by contacting with an amine. The process can achieve outlet CO<sub>2</sub> concentrations as low as 30 ppmv and H<sub>2</sub>S concentrations of 1 ppmv.

## Acid Gas Removal: Direct Conversion-Liquid Phase Oxidation of H<sub>2</sub>S (Liquid-Redox Processes)

A. Sour Gas Treatment



B. Acid Gas Treatment/Sulfur Production



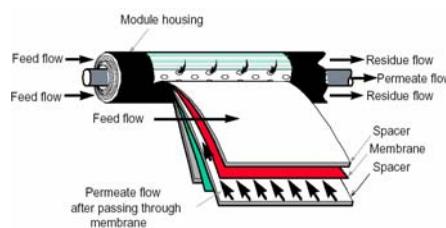
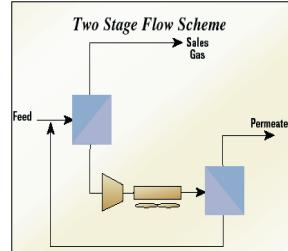
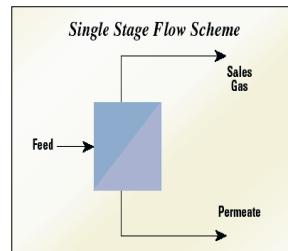
Iron chelate processes belong to a process group referred to as **liquid redox sulfur recovery**. Processes in this group absorb H<sub>2</sub>S from gas streams and produce elemental sulfur by reacting oxygen with the H<sub>2</sub>S to form elemental sulfur and water. Liquid redox sulfur recovery processes all share the following major operations: sour gas cleaning by absorption of H<sub>2</sub>S into a circulating alkaline solution; conversion of the formed HS<sup>-</sup> to elemental sulfur via the action of an auxiliary redox reagent (iron and vanadium are two most important reagents); separation and recovery of solid sulfur; regeneration of the spent auxiliary reagent via reaction with oxygen dissolved in the solution.

The addition of an auxiliary redox reagent (ARR) increases the rate of reaction and directs the oxidation to elemental sulfur. Because they share major process operations and are based on similar process chemistries, the process flow sheets and equipment requirements for liquid redox systems are rather similar. The processes which are members of the iron-based subgroup of redox processes are **LO-CAT®** (now marketed by **Gas Technology Products LLC**), IFP **Sulfint®** and Shell **SulFerox®** all work based on chelated iron liquid redox processes.

Vanadium based processes are very similar to iron-chelate processes. Vanadium is a heavy metal and the processes involve environmental and health issues. The two most widely used processes are British Gas **Stretford®**, and German **Linde Sulfolin®**.

The liquid redox processes are more suitable for low sulfur production applications (<10-12 ton/day sulfur). They are very efficient in reducing the sulfur emissions of gas processing facilities to environmentally acceptable levels. They are also very suitable when the sulfur concentration varies with time or the low sulfur concentration where the Claus sulfur recovery process is not capable of handling.

# Acid Gas Removal: Membrane – Gas Permeation Processes



## MEMBRANE SEPARATION PROCESS

Gas permeation is the transport of gas molecules through a thin polymeric film from a region of high pressure to one of low pressure. Gas permeation is based on the principle that different gases permeate through polymeric films at different rates due to differences in diffusivity and solubility. Separation efficiency is affected by the gas composition, pressure differential, pressure ratio, separation factor, and temperature. Pressure drop through the membrane is high, so the gas which permeates is available only at lower pressure. For the natural gas not permeating the membrane, the pressure drop will be similar to that through any other process unit. membrane systems are used primarily for bulk CO<sub>2</sub> removal from natural gas streams. The systems are modular, skid mounted units containing either spiral wound or hollow fiber membrane elements. The elements are housed in pressure tubes in various configurations depending on system requirements. The advantages of membrane systems over conventional processes are site specific, but may include: lower capital and energy costs; reduced space requirements, faster delivery time and lower installation costs due to smaller, lighter modular design; lower operating costs and limited manpower requirements due to simplified operation and maintenance; increased adaptability to changing feed flow and composition; elimination of dehydration equipment; faster, easier start-up and shutdown. Membranes however suffer, in some cases, from poor separation efficiency due to close permeation rates for various constituents of natural gas. For instance methane and some heavier hydrocarbon constituents of natural gas have very close permeation rates with those of acid gases and water for common polymeric membranes, therefore a significant amount of methane and heavier hydrocarbons may be lost when this technology is used for acid gas and water removal from natural gas streams.

## APPLICATIONS

membrane systems are typically used in the following applications and markets:

**Natural Gas Upgrading** –membrane systems remove carbon dioxide and water vapor to pipeline specifications and lower the H<sub>2</sub>S level. Systems can be installed either onshore or offshore, at the wellhead or at gathered facilities

**Enhanced Oil Recovery (EOR) Operations** – membrane systems are used to recover carbon dioxide from EOR floods for recycle injection. Systems can be used as a base load system, designed as part of the recovery plant, or as a de-bottlenecking unit upstream of the existing recovery plant. **OPERATING**

### Range

Commercial applications have demonstrated the versatility of membrane systems. Typical feed conditions range between 400 and 1400 psig with CO<sub>2</sub> levels from 3 to ~70%. Commercial systems have been designed and operated at feed flow rates ranging from 5 MSCFD to over 250 MMSCF.

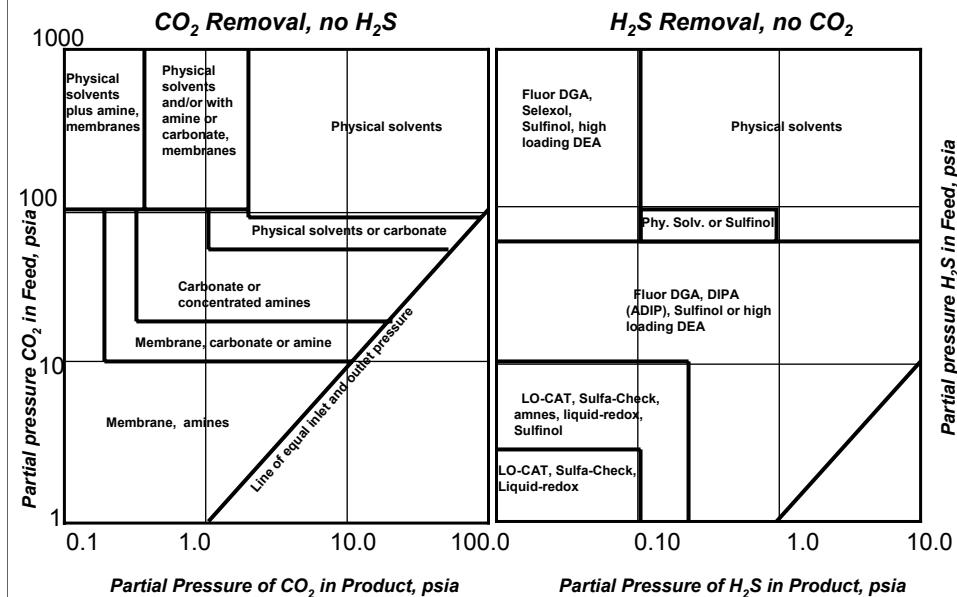
Technology suppliers usually offer complete membrane system design including comprehensive feed pretreatment schemes to extend membrane life. Major players in membrane technology are: *Dow Cynara™, UOP SEPAREX™, Air Products PRISM® membrane, Liqui-Cel® Membranes*

## Acid Gas Removal: Process Selection

1. The types and concentrations of impurities in the gas, and the degree of removal desired
2. Concentration of non-H<sub>2</sub>S Sulfur compounds (COS, RSH, RSSR, CS<sub>2</sub>, COS, polysulfide, etc.)
3. Selectivity of acid gas removal required, if any.
4. Temperature and pressure at which the sour gas is available, and at which the sweet gas is to be delivered
5. Volume of gas to be treated
6. CO<sub>2</sub>/H<sub>2</sub>S ratio in the gas
7. The presence and amount of heavy hydrocarbons and aromatics in the gas
8. Economics of the process

There are many variables in gas treating, which makes the precise definition of the area of application of a given process very difficult. Among several factors, the factor shown on this slide the most significant that need be considered. The concentration of acid gas components are important to consider. Some processes effectively remove large amounts of acid gases, but not to low enough levels (e.g., physical solvents). Other remove to ultra-low values, but cannot handle large amounts of acid components in the incoming gas economically (e.g., liquid-redox). The presence of non-H<sub>2</sub>S sulfur compounds (e.g., mercaptans) may eliminate some of the sweetening processes (for instance MDEA alone cannot remove mercaptans effectively). Selectivity of a process implies the degree of removal of one acid gas component relative to another. Some processes remove both H<sub>2</sub>S and CO<sub>2</sub> (most alkanolamines), while others are designed to selectively remove only H<sub>2</sub>S (MDEA and DIPA blends). Generally, it is important to consider the selectivity of a process fro H<sub>2</sub>S versus CO<sub>2</sub> to ensure desired extent of removal of theses components. For this reason, CO<sub>2</sub> to H<sub>2</sub>S ratio in the gas is also an important parameter. Operating conditions affect the performance of several sweetening processes. Also, different processes discharge the sweetened gas stream at different pressure and temperature levels relative to the conditions of the incoming gas (i.e., pressure drop is a definite result of any gas processing process, however some process have inherently larger pressure drops such as solid bed adsorption processes). Thus, the inlet and outlet conditions desired are significant variables to consider. It may be economic in some cases to alter inflow conditions to suit process, and out flow conditions to meet pipeline requirements. Usually for physical solvent processes, a high pressure inlet gas with high concentration of acid gases are required, therefore if we are dealing with a natural gas stream containing a large concentration of CO<sub>2</sub> and a low pressure, the gas should be pressurized to a level suitable for the selected process. Some processes are economical for large gas volumes (e.g., most amine and formulated amine processes), while others lose their economic advantages when large volumes of gas are to be treated (e.g., membrane, liquid-redox and batch processes). Gas composition should also be considered, since some processes are adversely affected by the presence of heavier fractions, while others may strip the gas of some of its hydrocarbon constituents (Shell *sulfinol*, and most physical solvent processes). The desirability of recovering sulphur as elemental sulphur reduces the choices considerably. Processes with sulfur recovery have become very important in recent years, and will further become so in the future due to environmental problems caused by sulphur emissions. Sulphur is a by-product, generally in demand in some part of the world by fertilizer and chemicals industry. Therefore sulfur recovery may be attractive from an economical point of view, although in some places there is no demand and it is prefered to inject the sulfur compounds to depleted hydrocarbon reserves.

## Acid Gas Removal: Process Selection Charts

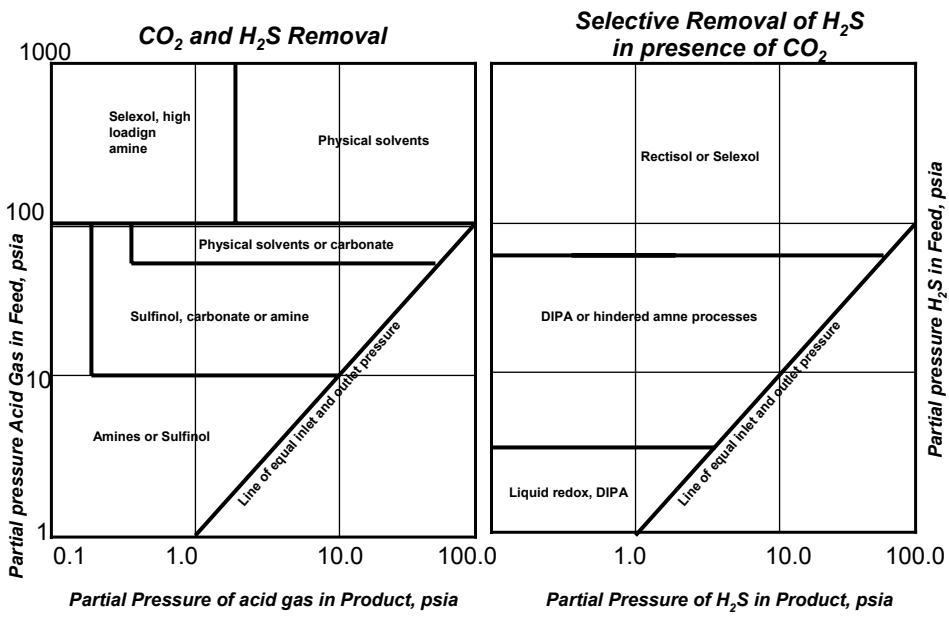


Decisions in selecting a gas treating process can many times be simplified by gas composition and operating conditions. High partial pressures , usually above 50 psi (345 kPa) of acid gases enhance the probability of using a physical solvent. The presence of significant quantities of heavy hydrocarbons in the feed discourages using physical solvents. Low partial pressures of acid gases and low outlet specifications generally require the use of amines for adequate treating. Process selection is not easy and a number of variables must be weighed prior to making a process selection. The graphs shown on this and the next slide can be used as screening tools to make an initial selection of potential process choices. Graphs should be used only for an initial guide to select a number of good candidates and should never replace good engineering judgment. A comprehensive feasibility study and cost-benefit analysis will determine which process is more economical. To select the process, determine flow rate, temperature, pressure, concentration of the acid gases in the inlet gas, and allowed concentration of acid gases in the outlet stream. With this information, calculate the partial pressure of acid gases as follows:

$P_i = y_i P_t$ , where,  $P_i$  is partial pressure of component  $i$ , **psia**,  $P_t$  system pressure, **psia**, and  $y_i$  is the mole fraction of component  $i$ . Next, determine if one of the four following situation is required and use the appropriate guide:

- Removal of H<sub>2</sub>S with no CO<sub>2</sub> present
- Removal of H<sub>2</sub>S and CO<sub>2</sub>
- Removal of CO<sub>2</sub> with no H<sub>2</sub>S present
- Selective removal of H<sub>2</sub>S with CO<sub>2</sub> present

## Acid Gas Removal: Process Selection Charts



## Acid Gas Removal: Amine Plant Design

- Process simulation using **ASPEN/HYSYS, TSWEET, etc.**

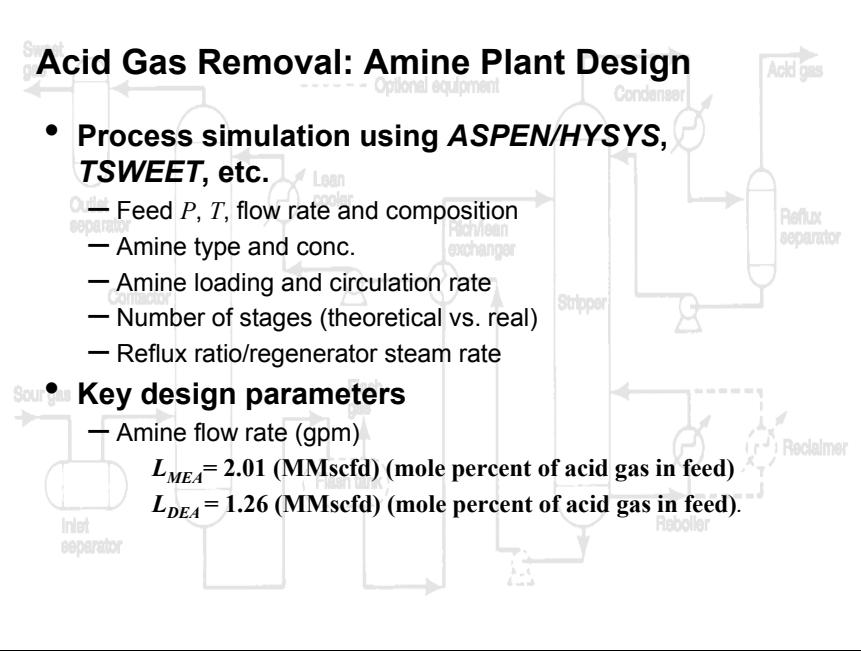
- Feed P, T, flow rate and composition
- Amine type and conc.
- Amine loading and circulation rate
- Number of stages (theoretical vs. real)
- Reflux ratio/regenerator steam rate

- Key design parameters

- Amine flow rate (gpm)

$$L_{MEA} = 2.01 \text{ (MMscfd)} \text{ (mole percent of acid gas in feed)}$$

$$L_{DEA} = 1.26 \text{ (MMscfd)} \text{ (mole percent of acid gas in feed).}$$



The type of equipment and design procedure for *MEA* and *DEA* systems are similar. Process simulators such as *Hypotech HYSYS*, **ASPEN** and BR&E **TSWEET** are extensively used to simulate and analyze amine processes. Very reliable simulation can be obtained using these simulators and the material and energy balance information can be used to design the processes. The simulators are equipped with tower and separator design and heat exchanger hydraulic and thermal design modules or can be linked to exchanger design packages such *Hypotech HTFS* or *Heat Transfer Consultants (HTC) STX* to design heat exchangers (shell and tubes and air coolers).

Typically, these programs require considerable input. For example:

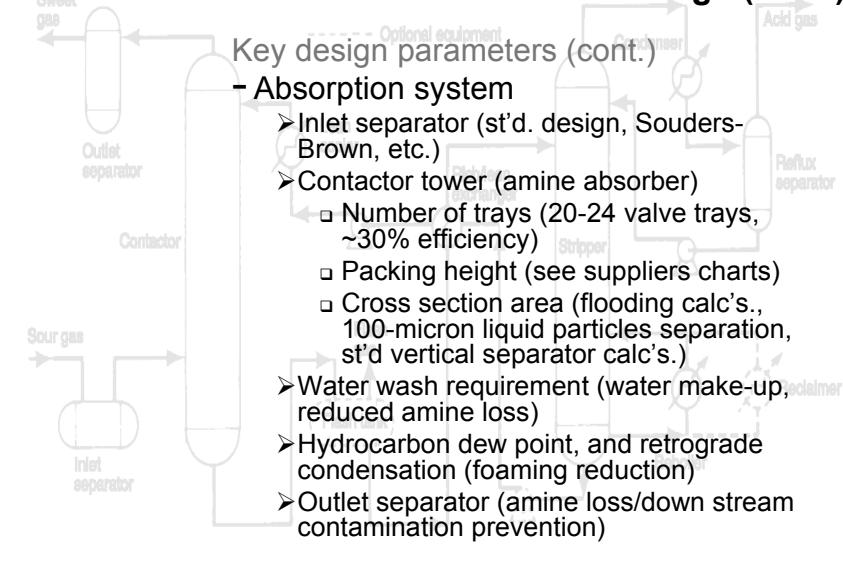
1. The type and concentration of the amine solution
2. The lean amine loading or amine circulation rate
3. The residence time of the amine solution in contactor or the percent approach to equilibrium or the efficiency of trays (sometimes based on acid gas components)
4. The number of theoretical stages in the contactor and regenerator
5. The reflux ratio
6. Or steam required per gallon of circulation

Often some of the input data must be calculated, e.g., acid gas loadings. These programs allow the user to: compare amine solutions – type and concentration – quickly; optimize the number of stages in the contactor and regenerator; obtain the heat duties and size equipment; get the physical properties of the amine solutions; re-rate an existing plant from a different amine solution.

For special formulations such as Shell *Sulfinol*, UOP *Ucarsol* and BASF activated *MDEA*, the licensee should be contacted. These companies usually provide the detail design information and perform simulation free of charge for evaluation purposes.

The important design parameters in amine systems are shown on this and the following slides. One of the most important parameters which determines the size and therefore the final cost of the gas sweetening plant is the amine or solvent circulation rate. Amine plants are sometimes referred to by the amine flow rate (e.g., a 2,500 *gpm* plant). The amine flow rate is generally a good indication of the size of process equipment. The circulation rate for amine systems can be determined from the acid gas flow rates by selecting a solution concentration and an acid gas loading. The following simple formulas can be used to determine the amine flow rates:  $L_{MEA} = 2.01 \text{ (MMscfd)} \text{ (mole percent of acid gas in feed)}$ ; and  $L_{DEA} = 1.26 \text{ (MMscfd)} \text{ (mole percent of acid gas in feed)}$ , where  $L_{MEA}$  and  $L_{DEA}$  are in gallons per minute or *gpm*. For design purposes, the following solution strengths and loading are recommended to provide an effective system without excessive corrosion: for *MEA*, amine weight fraction is about 20% and acid gas loading is 0.33 mole acid gas/mole *MEA*; for *DEA* the amine strength is 35 wt.% and acid gas loading is 0.5 mole acid gas/mole *DEA*. In the modern plant designs, especially when the concentration of  $\text{CO}_2$  which should be removed is very high (>5-6%), lower acid gas loadings are considered for *DEA* (~0.35-max. 0.4). For the above recommended concentration the densities at 60°F for the *MEA* and *DEA* are: 20% *MEA* = 8.41 *lb/gal* (1,046 *kg/m³*), and 35% *DEA* = 8.71 *lb/gal* (1,083 *kg/m³*). For high loaded *DEA* system (especially when  $\text{H}_2\text{S}$  concentrations are high, acid gas loadings up to 0.7 have been chosen for design purposes. This high acid gas loadings are not recommended for modern gas sweetening plant design practices. The above simple flow rate calculation equations are obtained by straight forward mass balance around the absorption tower.

## Acid Gas Removal: Amine Plant Design (cont.)



### Key design parameters (cont.)

#### - Absorption system

- Inlet separator (st'd. design, Souders-Brown, etc.)
- Contactor tower (amine absorber)
  - Number of trays (20-24 valve trays, ~30% efficiency)
  - Packing height (see suppliers charts)
  - Cross section area (flooding calc's., 100-micron liquid particles separation, st'd vertical separator calc's.)
- Water wash requirement (water make-up, reduced amine loss)
- Hydrocarbon dew point, and retrograde condensation (foaming reduction)
- Outlet separator (amine loss/down stream contamination prevention)

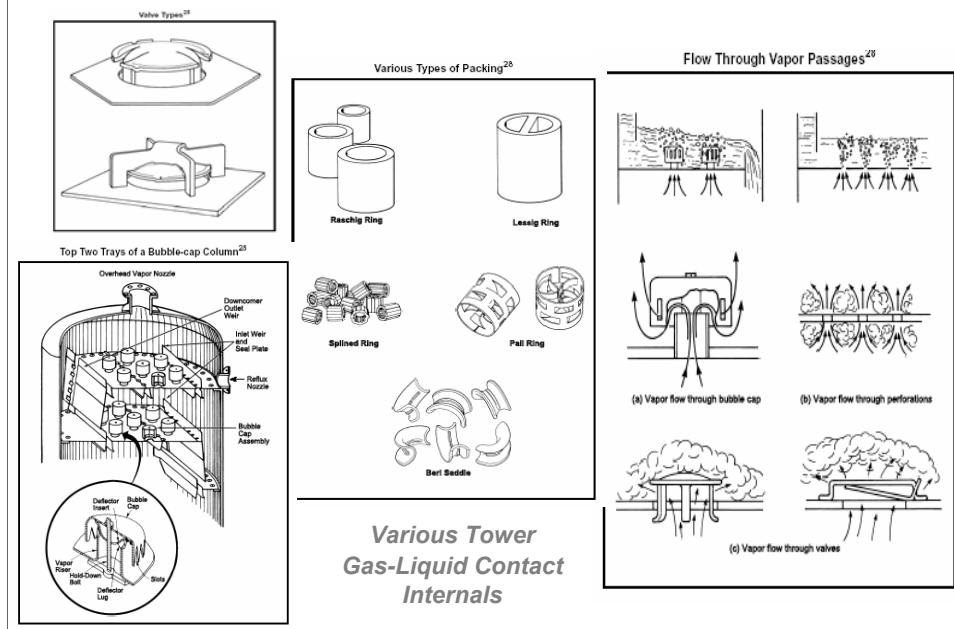
The high pressure process gas system consists of an inlet separator, contact tower, and outlet separator. The inlet separator (scrubber), removes slugs and drops of condensed hydrocarbon, produced water, corrosion inhibitors, and well treating chemicals from the inlet sour gas stream. It should be located as close as possible to the amine contactor. It can be complemented, but not replaced, by any integral scrubber in the contactor tower. Removal of contaminants from the inlet gas may be enhanced by washing the gas with water. This is an additional processing step and is needed only when the sour gas contains drops or particles too small to be effectively removed by conventional filter separators. Entrained liquids, most commonly slugs of produced water (often saline), must be removed because they quickly contaminate the amine solution and cause problems such as foaming, equipment fouling, high corrosion rates, solvent loss, and sour effluent gas. Entrained liquids are the most frequent contamination source for all sweetening processes.

Amine absorbers use counter-current flow through a trayed or packed tower to provide intimate mixing between the amine solution and the sour gas. Typically, small diameter towers use stainless steel packing, while larger towers use stainless steel trays. For normal acid gas concentrations (>2-3 % total acid gas), number of standard trays are between 20 to 24 (equivalent to approximately 7 to 8 theoretical stages). Variation in solution concentration or acid gas content or loading may require further investigation to determine the number of trays. Valve-type trays are the most common and efficient contacting internals. In a trayed tower the amine falls from one tray to the one below. It flows across the tray and over a weir before flowing into the next downcomer. The gas bubbles up through the liquid and creates a froth that must be separated from the gas before it reaches the underside of the next tray. For preliminary design a minimum diameter capable of separating 150-200 micron droplets (for gas capacity for a vertical separator, using the equation explained in *gas-liquid separation equipment* part of this course) can be assumed. The gas velocity should be reduced by 25 to 35% from the above calculations, to avoid jet flooding and by 15 to 20% to allow for foaming. The size of packed towers must be obtained from manufacturers' published literature. Structured packing, (e.g., supplied by **Koch-Glitch**) present very efficient gas-liquid contact and produce very little pressure drop compared to tray towers and conventional packing. The standard design requires the inclusion of a mist pad above the top tray. The typical tray spacing is 18 to 24 inches and the distance between the top tray and the mist pad is 3 to 4 feet. Some contactors have a water wash consisting of two to five trays above the lean amine feed tray. This eliminates amine carry over and conveniently add make-up water. Most of *MEA* units at low pressures should have wash water trays as the vapour pressure of *MEA* is such that the water wash may be useful in reducing *MEA* losses in the overhead sweet gas. *DEA* systems normally do not need this as the vapour pressure of *DEA* is rather lower. The best way to monitor the performance of the contactor and detect foaming is with a differential pressure (*DP*) cell connected to the gas inlet and outlet. Accordingly connections for a *DP* cell should be provided.

Hydrocarbon dew-point in the contactor at both the inlet and outlet conditions should be checked. It is important to note that the dew-point increases as the acid gases are removed, and hydrocarbon condensation is one of the most common causes for excessive foaming. Retrograde condensation should also be checked as hydrocarbon condensation can result from a temperature rise or a pressure drop in the contactor. Note that due to heat of reaction between the acid gases and amine the solution gradually is warmed up as it flows down the contactor. The gas pressure drops due to friction as it flows up the amine absorber (contactor).

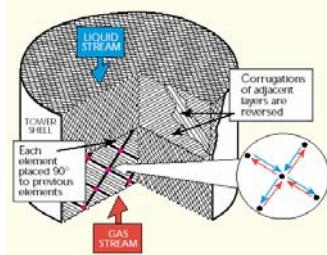
The outlet gas separator removes any liquid carry over from the sweet gas and prevents contamination of downstream equipment. It also signals excessive foaming in the contactor.

## Acid Gas Removal: Amine Plant Design (cont.)



Various gas-liquid contact devices are shown on this slides.

## Acid Gas Removal: Amine Plant Design (cont.)



Source: Koch-Glitch

A typical (generally includes all types of internals in one column; not representing a working tower) gas-liquid contact device is illustrated on this slide. Structured packing materials are also shown.

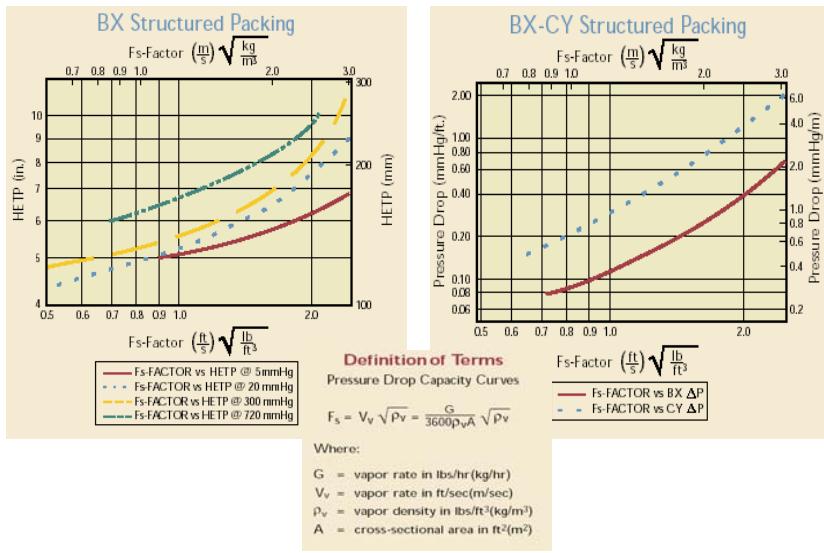
## Acid Gas Removal: Amine Plant Design (cont.)



*Source: Koch-Glitch*

A closer look at the tower internals may be taken here. High performance structured and packing as well as valve trays and other tower internals are shown on this slide.

## Acid Gas Removal: Amine Plant Design (cont.)



### Definition of Terms

Pressure Drop Capacity Curves

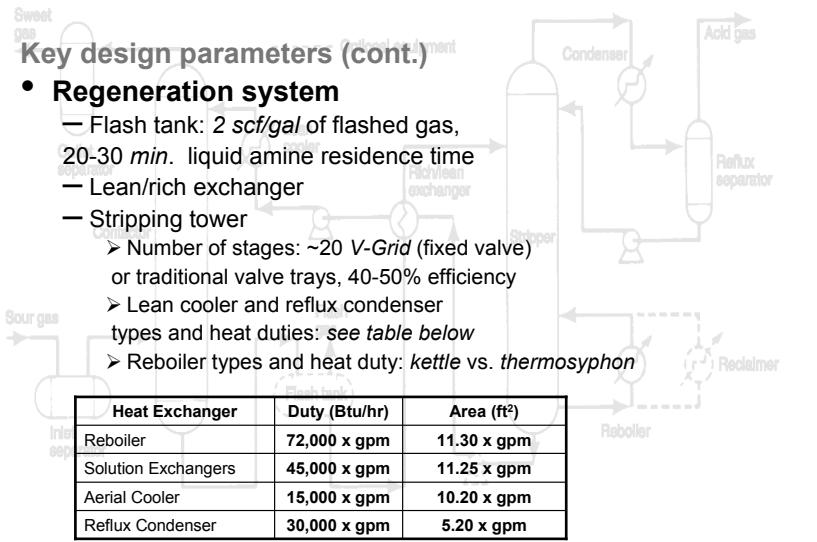
$$F_s = V_v \sqrt{\rho_v} = \frac{G}{3600\rho_v A} \sqrt{\rho_v}$$

Where:

- G = vapor rate in lbs/hr(kg/hr)  
V<sub>v</sub> = vapor rate in ft/sec(m/sec)  
ρ<sub>v</sub> = vapor density in lbs/ft<sup>3</sup>(kg/m<sup>3</sup>)  
A = cross-sectional area in ft<sup>2</sup>(m<sup>2</sup>)

Typical performance charts for structured packing are shown on this slide. Typically a height between 10 to 15 inches can act as one theoretical tray as compared with 3 x (18-24")=54-72 inches in trayed towers (it should be noted that typical tray spacing is between 18-24" and three trays act as one theoretical tray). The pressure drops are much lower in structured packing due to a more streamlined flow of gas and liquid.

## Acid Gas Removal: Amine Plant Design (cont.)



The regeneration system consists of a **flash tank**, **rich/lean amine heat exchanger**, **stripping tower** and its auxiliaries, **filters**, and **aerial coolers**. There are also reflux, booster and circulation pumps. Primary amines require reclaimer as well.

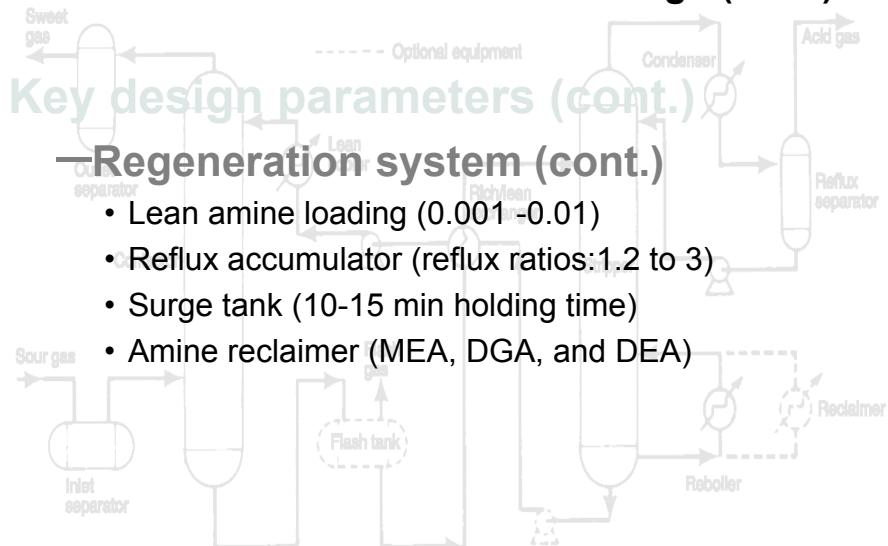
The amine solution absorbs hydrocarbons (HC) as well as acid gases in the contact tower. These flash out when the pressure is reduced. The flash tank provides the residence time for this degassing of the rich amine solution. HC absorption depends on the inlet gas composition and pressure. For lean sour gas the rule of thumb is **2 scf/gal**. Recommended residence times are **20-30 minutes** fro two-phase vessels. When the flash gas is used for fuel it is needed that the gas be treated with lean amine in an integrated small column attached to the flash separator. HC contamination often promotes foaming and equipment fouling. Down stream facilities such as sulfur plants will be troubled if HCs are stripped off the amine solution in the stripping tower. Flash tank reduces the heat duty of the stripper reboiler. Standard gas-liquid separator design procedure should be followed to design the flash tank.

The **lean/rich heat exchanger** preheats the rich amine solution and reduces the duty of the reboiler. It also cools the lean amine and reduces the duty of the aerial lean amine cooler.. Both shell and tube and plate and frame heat exchangers are used . The rich amine usually passed through the tube side with a low inlet velocity – 2 to 4 ft/sec. – to reduce corrosion. This low velocity sometimes cause fouling in the tube side of the exchanger when solid particulates are present. Typically the temperature change for both streams is 70 to 100°F and the **pressure drops 2 to 5 psi**. Using two or more exchangers in series is common practice to accommodate a temperature cross; for example the exit rich amine stream is hotter than the exit lean amine stream. Again standard heat exchanger design procedures are followed. Software packages such as **HTFS** and **HTC-STX** are very effective in designing new exchangers and rating the existing ones. The **reflux condenser** and **lean amine cooler** are **air-cooled, forced draft fin-fan heat exchangers** with automatic louvers for temperature control. A 10% safety factor should be considered for heat duty. For small facilities (<200 gpm) the two exchangers may be combined on one structure with a common fan. Air circulation is advisable when the ambient temperature is expected below 10°F. Sometimes a trim cooler, using water, is needed for the lean amine systems. The summer ambient air temperature is a very critical factor when the air-coolers are designed and affects the size and cost of manufacturing of these important process devices. A design summer air temperature of 110°F is chosen for most North American and European designs while an air temperature of 130-135°F is not unusual for the Middle Eastern gas sweetening plants.

T typical **regenerator** or **stripping tower** (sometimes it is called **still** as well) is comprised of a trayed or packed tower operating at **10-20 psig**. The same sizing procedure as explained for the contactor can be used. A standard design consists of 20 (Nutter V-grid or valve) trays spaced 24 inches apart working in . This is equivalent to 7 to 10 theoretical plates when the tray efficiency is 40 to 50%. The trays are designed for liquid and jet flood rates of 65 to 75% with a foam factor a 0.75. Small **amine reboilers** are direct fired heaters that use natural gas. The fire tube surface is based on a heat flux of 6,500 to 8,500 Btu/hr. ft<sup>2</sup> to keep the tube wall temperature below 300°. Larger reboilers use a stream or hot oil bundle. There is usually more corrosion with thermosyphon than kettle type designs. Forced circulated, oil medium heated, vertical (non-kettled) reboilers are recommended for heat sensitive amines including both MEA and DEA as the heat exchanger tube wall temperature can be maintained well below degradation temperatures. Sending the amine in the tube side also provides the condition to use tube insert inside the tubes to further reduce the risk of amine thermal degradation in amine reboilers. A number of good references are available for design of amine reboilers (see for instance this recent article **Optimize reboiler design** by Chen Edward Foster Wheeler USA), *Hydrocarbon Processing*, v 80, n 7, July, 2001, p 61-67 and **Effectively design and simulate thermosyphon reboiler systems**, part 1 and 2 by Martin G.R. et al. *Hydrocarbon Processing*, v 74, n 7, Jul, 1995, p 67.

The reboiler duty is: (1) the heat to bring the acid amine solution to the boiling point, (2) the heat to break the chemical bonds between the amine and acid gases, (3) the heat to vaporize the reflux, and ((5) the heat losses from the reboiler and still. A safety factor of 15 to 20% is needed for start up. The heat duties and transfer areas of the regeneration equipment can be estimated from the amine circulation rate as shown in the table on this slide.

## Acid Gas Removal: Amine Plant Design (cont.)



### Regeneration system (cont.)

- Lean amine loading (0.001-0.01)
- Reflux accumulator (reflux ratios: 1.2 to 3)
- Surge tank (10-15 min holding time)
- Amine reclaimer (MEA, DGA, and DEA)

Lean amine loading is a major factor in determining the reboiler duty and the performance of the amine contactor. Too much of acid gas in the lean amine results in off-spec acid gas (particularly H<sub>2</sub>S) in the product (sweetened gas). It is very important to carefully monitor the acid gas loading by occasional analyses. The lean loading may be adjusted by fine adjustment of steam flow rate (heat duty) to the rebiler. Measurement of lean amine loadings is not as accurate as it is for that of rich amine (due to lower concentrations), however, using chromatography or other analytical techniques, it can be measured even on-line. Lean loadings within the range 0.001-0.01 mole acid gas/ mole of amine are recommended for typical operations.

The condensate formed in the reflux air-cooler (typically 130-145°F) is routed to an accumulator. The **reflux accumulator** separates the reflux or condensed water from the water-saturated acid gases. The water is returned to the still and the acid gases are sent to sulfur recovery or flared. Flaring is not a very acceptable practice these days and is being replaced by incineration or other sulfur treatment options. A mist pad is usually included. A means of measuring the reflux rate is most helpful and recommended. The **reflux rate** ( moles of water returned to the still mole of acid gases leaving the reflux condenser) varies from 3.0 for primary amines and low CO<sub>2</sub>/H<sub>2</sub>S ratio (< 0.01-0.1 mole ratio) to 1.2 for tertiary amine and high CO<sub>2</sub>/H<sub>2</sub>S ratios (>0.3-3).

A **surge tank** holding about 10-15 minutes of flow is needed in most amine circulation loops. This is usually an extension of the firetube-type reboiler for smaller units (<20-100 gpm) and a separate vessel for large systems (>300 gpm). The vessel provides some surge capacity and a means to charge the amine when the system is shut down or during the start-up operations.

**Reclaimer.** It was believed that only primary amines required additional regeneration to remove several impurities accumulated in them during the long term operation of the gas sweetening plants. *MEA* and *DGA* plants are designed with a semi-continuous distillation kettle attached to the stripper reboiler. It has been shown that *DEA* and other amines including *MDEA*, also undergo degradation reactions and require regular reclaiming or purification exercises. Heat distills the amine and water under stripper pressure conditions, leaving the contaminants in the reclaimer. A slip stream of 1 to 3% of the lean amine flow rate is feed continuously to the reclaimer. Alkaline solutions such as sodium hydroxide or carbonate are injected to reverse the non-reversible amine salts with stronger acid gases (e.g., formic and acetic acids) and sulfur compounds, especially COS and CS<sub>2</sub>, present in the gas. Other contaminants are amine degradation products, iron sulfide, and high boiling hydrocarbons. These are removed as a sludge at the end of each cycle. Reclaiming helps to have fewer operational problems as most of the operational problems in amine plants stem from contaminated solutions.

## Acid Gas Removal: Amine Plant Design (cont.)

### Key design parameters (cont.)

#### —Filters

- Mechanical (for particulates)
- Carbon (for dissolved hydrocarbons, surfactants, well treating chemicals, compressor lube oil - **NOT RECOMMENDED FOR AMINE DEGRADATION PRODUCTS!**)
- Split flow requirements (10-25% of circ. rate)

#### —Pumps

- Amine charge
- Amine booster
- Reflux
- Aerial cooler

Pump	Horsepower
Amine Charge/Circulation	$\text{gpm} \times \text{psig} \times 0.00065$
Booster	$\text{gpm} \times 0.06$
Reflux	$\text{gpm} \times 0.06$
Lean cooler	$\text{gpm} \times 0.36$

**Filters.** Both mechanical filters for particulates and activated carbon filters for heavy hydrocarbons are needed. Installing filters in both rich and lean amine lines is the preferred but most costly approach. For H<sub>2</sub>S services, installing filters in rich amine line is more troublesome. Cleaning and replacement of filter cartridge requires careful purge and release of H<sub>2</sub>S containing rich amine, therefore most filters in sulfur services are installed on the lean amine line. A mechanical filter in the rich amine line just after the flash tank prevents fouling of heat transfer surfaces and plugging in the rich/lean heat exchanger and amine stripper internals. Including a carbon filter reduces the tendency to foam by adsorbing hydrocarbons that would otherwise be removed in the amine regenerator (stripper). For small units, the mechanical filter should be full flow and remove 95% OF 10 microns or larger particles. For large units with high circulation rates (>300-500 gpm range), a slip stream is more practical.

Carbon filter is often installed in the lean line before the lean amine cooler to improve the quality of the amine feed stream. Activated carbons were wrongly believed to remove amine degradation products. There are compelling scientific evidence that carbon filters are not able to remove amine degradation products very efficiently. Activated carbon is very effective in removing dissolved higher HCs, surfactants, well treating chemicals, compressor lube oils, and all organically natured chemicals from amine streams. For design purposes carbon filter vessels stream containing granular carbon in the range of 4-30 mesh, a flow rate of 2-10 gpm/ft<sup>2</sup> of bed area, and a retention time of 5 to 10 minutes are recommended. The carbon particles mesh size should be preferably about 5-10. The carbon filter is usually sized for 10-25 percent of the circulation rate. Several different carbon materials are used for amine systems supplied by major suppliers such as **Norit** in Europe, **Calgon** in United States, **Takeda** in Japan and many others all over the world especially in China.

**Pumps.** The **amine booster** and **reflux pumps** are centrifugal, preferably in-line or horizontal, with **TEFC** (*Totally Enclosed Fan Cooled*) motors. One hundred percent stand by capacity is recommended. Selection of the circulation pump depends on the contactor pressure and the amine circulation rate. A 50% or 100% standby capacity is normally considered for these pumps. For high pressure low capacity services, reciprocating pumps are used for charge amine pumps, however, centrifugal pumps are widely used for low pressure (~100 psig) and multistage horizontal centrifugal pumps for high pressure (>700 psig) or high circulation rates (> 300 gpm). In sizing and rating pumps a low positive suction pressure (**NPSH**) of 3-10 psig is used. Motor sizes can be estimated from the amine circulation rate as shown in the table on this slide.

## Acid Gas Removal: Amine Plant Design (cont.)

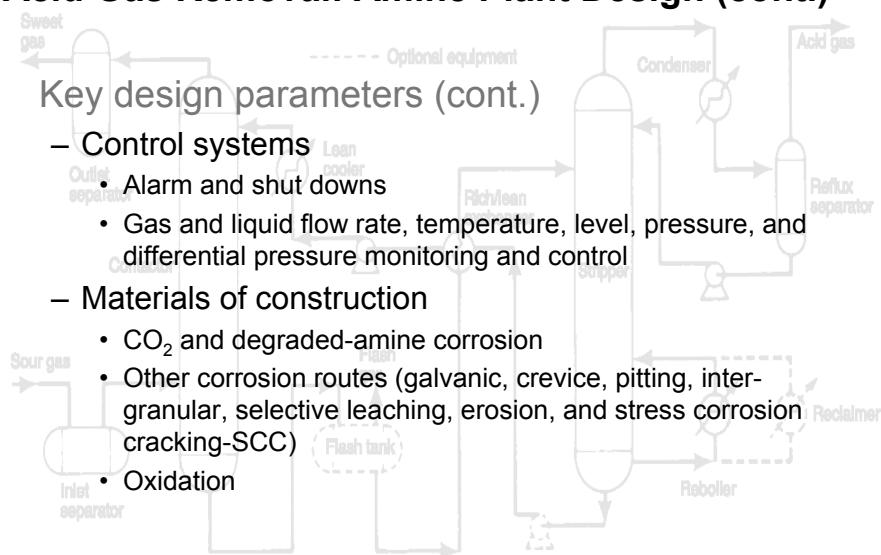
### Key design parameters (cont.)

#### – Control systems

- Alarm and shut downs
- Gas and liquid flow rate, temperature, level, pressure, and differential pressure monitoring and control

#### – Materials of construction

- CO<sub>2</sub> and degraded-amine corrosion
- Other corrosion routes (galvanic, crevice, pitting, intergranular, selective leaching, erosion, and stress corrosion cracking-SCC)
- Oxidation



The alarm and shutdown panel can be electronic or pneumatic. In either case a process or safety malfunction shuts the unit down, sounds the alarm horn , and indicates the condition responsible. As a minimum, the following should trigger a **plant shutdown**:

Emergency manual shutdown

Treated gas	Off spec.
Inlet separator	High level
Lean amine cooler	High temperature
Reflux condenser	High temperature
Surge tank	Low level
Amine reboiler	High pressure, High temperature, Flame failure
Cooler fans	High vibration

Amine treating is a proven technology and no special considerations should be taken into account for amine plant process control systems and conventional gas and liquid flow rate, temperature, level, pressure and differential pressure and monitoring and control system can be used. **Control Systems**

Amine plants manufacturers have extensive experience with Distributed Control Systems (DCS) and Programmable Logic Controller (PLC) and can design, supply and configure the control system to suit each client's control and operating philosophy. The DCS and PLC systems may include major control system suppliers such as **Foxboro** I/A, **Fisher-Rosemount**, **Moore**, **Allen-Bradley**, **Modicon**, etc. Human Machine Interface (HMI) systems are also included which may have Wonderware In Touch for PLC systems. The graphical operator interfaces that are supplied with the control systems by these manufacturers allow operators to view and control the process unit(s). All control systems supplied usually have the following capabilities: Control and Alarm Setpoint Adjustments; PID Control Loop Adjustments; Analog Input (4-20 mA); Analog Outputs (4-20 mA); Digital Input (24 VDC); Digital Output (24 VDC); RTD / Thermocouple Input . HMI systems and DCS have the following additional capabilities: Multiply security levels; process data trending; process reports; alarm generation and reports.

**Construction Materials.** A large number of literature reviews exists concerning the types of corrosion that occur in amine plants (see for instance: **Understanding corrosion in alkanolamine gas treating plants**; DuPart, M.S. (*Dow Chemical USA*); Bacon, T.R.; Edwards, D.J., Source: *Hydrocarbon Processing*, v 72, n 4, Apr, 1993, p 75-80; and **Reduce corrosion in amine gas absorption columns**, Mogul, M.G (*Belzona Inc*), Source: *Hydrocarbon Processing*, v 78, n 10, Oct, 1999, 7 pp. Typical corrosion types can be summarized as: **general, galvanic, crevice, pitting, intergranular, selective leaching, erosion, and stress corrosion cracking (SCC)**. SCC is very important because gas stream containing H<sub>2</sub>S cause metals to "sulfide stress crack". Carbon steel (CS) becomes susceptible when the H<sub>2</sub>S partial pressure exceeds **0.05 psia** at system pressures **above 65 psia**. Corrosion problems are more sever in MEA systems due to the inherent more corrosive nature of MEA. In considering the susceptibility of steel to SCC the key property is **hardness**. National Association of Corrosion Engineers (N.A.C.E.) publication **MR-01-75** is the leading guideine for specifying the appropriate metal hardness. The two most important procedures used are **Brinell Hardness** to determine the hardness as **BHN** and **Rockwell** C/B number (**RC**). There are standard ASTM or NACE techniques to measure the hardness based on these procedures.

In addition to H<sub>2</sub>S corrosion, the following factors must be considered: **CO<sub>2</sub> Corrosion**, especially when the rich amine temperature exceeds 150°F. **Amine degradation products** especially ethylene-diamine and oxazolidone compounds are very corrosive, they will form in high CO<sub>2</sub> loading conditions. Limiting CO<sub>2</sub> loading (<0.25-0.30) and corrosion inhibitors for high loadings are recommended.; **Electrolytic (galvanic) corrosion** due to presence of unlike metals in aqueous environment; Oxidation corrosion due to free oxygen in the make up water and feed gas stream; inert gas blanketing in amine storage and surge tanks and de-aerated (boiler feed) water are recommended. **Oxygen** also causes a different form of amine degradation whose products form heat stable salts which contribute to enhanced corrosion in amine plants.

## Acid Gas Removal: Amine Plant Design (cont.)

- Key design parameters (cont.)

- Material of construction (cont.)
  - ✓ Stress relieve all pressure vessels and HXs, piping in sour gas and rich amine service
  - ✓ Corrosion allowance: 0.0625" ASME vessels and 0.05" for pipes (CS only)
  - ✓ CS (*RC-22 or 241 BHN*) for shell heads and externals
  - ✓ CS for baffles, lugs and clips and other internals
  - ✓ SS 300 or 400 series for demister, and tower internals (valves, caps, bolts, etc.)
  - ✓ CS (<150°F) SS 300 series (> 150°F) for tube and tube sheets of HXs
  - ✓ CS for fire tubes
  - ✓ CS for case and SS (300/400) for fluid ends and internals of HP pumps (>200 psig)
  - ✓ Ductile iron case and SS (300/400) for fluid ends and internals for LP pumps (<200 psig)
  - ✓ Ductile iron impellers for centrifugal pumps, SS 300 impellers for rich amine and temperatures > 150°F
  - ✓ CS for general valves and tubing; SS 300 for T > 150°F; SS for feed lines to stripper, stripper overhead, condenser tubes and upper stripper trays
  - ✓ Low velocity line sizing (**<2-5 ft/sec**)
  - ✓ Avoid slip-on flanges and cavities in manufacturing
  - ✓ DP for amine flow and SS 316 and 316L for most transducers and control instruments and valves

For most application the guidelines shown on this slide, for material selection will provide adequate life and good corrosion resistance.

Amine systems are extremely corrosive due to acid gas concentrations and relatively high temperatures. It is critically important that all carbon steel (CS) exposed to the amine be stress relieved after the completion of welding on the particular piece including all pressure vessels, heat exchangers if shell and tube, reboilers, coolers, headers and piping in sour gas or rich amine service. A system fabricated from stress-relieved carbon steel for DEA solutions, as recommendation this slide, will not suffer excessive corrosion. For MEA systems, corrosion-resistant metals (stainless steel 304) should be used in some particular areas indicated on this slide.

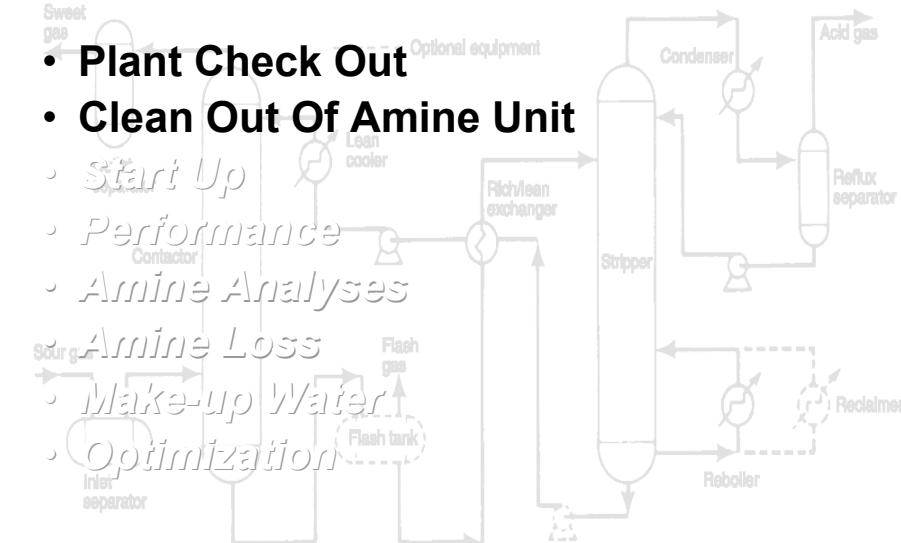
**Corrosion prone areas** in an amine systems are presented here and it is recommended to use SS 304, even for DEA systems, in the following areas: **absorber and stripper trays or packing; lean/rich exchanger and reflux condenser tubes; any part of the reboiler tube bundle exposed to vapour phase, reclaimer tubes; pressure reduction valves and pipes leading to flash tank; pipe from the rich/lean exchanger to the stripper inlet.** SS cladding is sometimes provided in the lower part of amine contactor and flash tank, especially if the system is designed for high rich amine acid gas loadings. Corrosion allowances indicated are strongly recommended; no corrosion allowance is required for stainless steel parts. Carbon steel with an "as welded condition" maximum hardness RC-22 is recommended for shells, head, and all externals. Steels of fine grain manufacture are least susceptible to corrosion and should be specified for all pressure containing parts. For internals the material should be compatible with the shell and head material. For wetted part tower internals subject to high velocities, low carbon stainless steel series 300 (e.g., 304L) or 400 series (e.g., AL410S). For heat exchanger and fire-tubes, and pump parts the guidelines shown should be followed. For ordinary (sweet gas and utility lines) valves and piping, carbon steel should be used. It is highly recommended to avoid using ductile or cast iron valves because of lack of impact resistance and tensile strength. When only CO<sub>2</sub> is removed, 300 series SS (e.g., 304) for services above 150°F should be used. SS should be used as discussed before for the feed line to stripper, stripper overhead, reflux condenser tubes, and stripper trays, specially the upper ones. All amine lines should be sized for low fluid velocity, e.g., 2 to 5 ft/sec. It is recommended to avoid using slip-on flanges, or other fabrication techniques that provide cavities which collect the corrosive amine solutions. Seal welds should be used to fill in all gaps, e.g., tray support rings. Differential Pressure (DP) cell with SS 316 nozzle or venturi restriction elements are preferred due to lower solid deposition and crevice/pitting corrosion incidents.

# Acid Gas Removal: Amine Gas Sweetening Plants - Operations

- Plant Check Out
- Clean Out Of Amine Unit

- Start Up
- Performance
- Amine Analyses

- Amine Loss
- Make-up Water
- Optimization

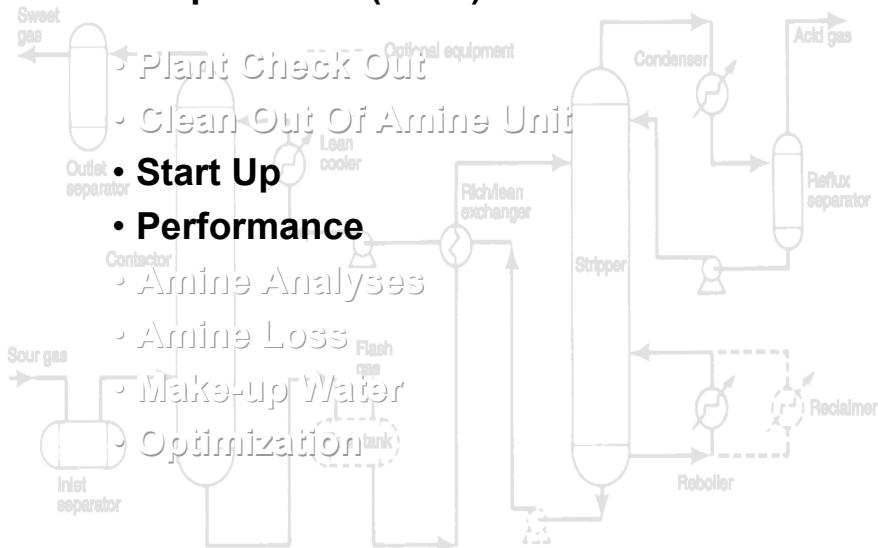


Amine plants are far more difficult to operate compared to batch and membrane based units. Accordingly it is important to follow the assembly, start up, and operation procedures. A thorough understanding of the system, function and operation of all equipment should be attained by the operators. For this reason, it is recommended that each operator make a *completeness check* of the plant and mark off on the *Mechanical Flowsheets /P&IDs*. Each system should be checked for the following:

**Plant Completeness Check.** (1) before assembly, all received materials should be checked and order placed for damaged items; (2) after the assembly, make sure that the piping begins and terminates at the proper locations, valves are properly located and operable, drains and vents are installed and either valved or plugged, strainers, blinds and spectacle blinds are installed properly, flanges are rated properly, bolted correctly and have gaskets, control valves and relief valves are installed as tagged, Check that valves have been installed properly. Some valves allow flow in only one direction; (3) to prepare the plant for clean ups, blinds should be installed on the inlet gas line to prevent accidental or premature pressurization of the system; (4) Process and Instrument Diagrams (*P&IDs*) are used to assure that all vessels, valves, instruments, etc. are tagged; interconnecting pipes, tubing, and wiring are clean and correctly installed; and all leads to control panel are functioning; (5) all mechanical equipment should be checked for lubrication, alignment, rotation, etc. Pumps should be packed and filter elements put into filters; ensure that there is sufficient oil present in the engines, compressors, force feed lubrication systems, lubricators and pumps. ensure that sufficient coolant is present in the engine/compressor cooling systems. (6) Pressure, flow, temperature and level instruments should be checked for calibration; (7) Check relief valve settings; ensure that floats or displacers have been installed for all level controls and switches; (8) Vessels, pipes, and pressure containers should be pressure tested using water or clean gas and leaks be repaired; (9) alarms, shutdown systems and safety devices should be checked and understood and assurance be made that settings conform to process design; carefully review the operating instructions for all pieces of equipment and carry out the recommended pre-startup checks (10) location and use of breathing apparatus, fire extinguishers, hose carts, first aid kits, etc. should be reviewed; location of emergency shutdown facilities and their use should be reviewed. Now, blinds can be removed and fuel gas, instrument air, and power supply be established.

**Cleaning of Equipment and Piping.** When the plant was hydrostatically tested by the construction personnel, it should also have been flushed and blown out. Cleaning removes protective oils, valve grease, mill scale, rust, and other contaminants which foul amine solution. The wash-out procedure is very similar to actual start-up and operation. New units should be washed using a soda ash (5 wt.%) or caustic solution (1%) with de-ionized rinse. Used units may need an acid wash to remove rust and sulfide scale (circulation of 9% sulfamic acid plus 1% citric acid plus 6% degreaser in hot water). The cleaning procedure is as follows: (1) the unit is charged with 5% sodium carbonate (soda ash) (or 0.2% caustic soda) solution. Heat up the reboiler to 200°F. (2 Check plunger pumps may leak slowly for lubrication; piston pumps should not leak.); (3) start the reflux condenser fan, increase heating to establish a reflux; (4) Pressurize contactor tower slowly. By pass all filters. Start amine cooler fan and booster and charge pumps (5) vent trapped air from valves at high points; (6) Establish an operating level in the contactor; (7) circulate for six hours; periodically open vessel bottom and piping drains and flush for one minute. Add soda ash as required. (8) shutoff the reboiler, fans and pumps when systems has cooled to 180°F. (9) drain system; use blanket gas to keep air out.; (10) refill the system with de-ionized water; (11) repeat the wash-out procedure; circulate for about eight hours, flushing low points every two hours and observe the cleanliness; (12) if clean, drain sufficient water to add enough amine to obtain the desired solution strength. If water is too dirty, flush completely and fill with proper strength of amine solution; (13) circulate for two hours to mix thoroughly; (14) open the block valves on filters and close by-pass valves. The plant is now ready for start up.

## Acid Gas Removal: Amine Gas Sweetening Plants - Operations (cont.)



### • Start Up

### • Performance

### • Amine Analyses

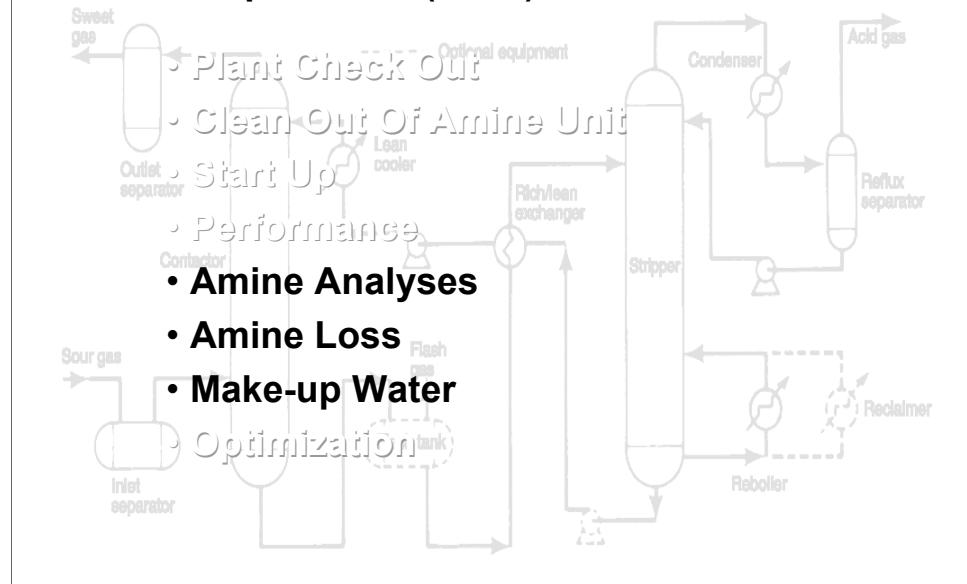
### • Amine Loss

### • Make-up Water Optimization

**Plant start up.** Before any of the equipment is placed in operation, ensure that the steps described in previous slide, **Plant Check Out** and **Clean Out of Amine Unit**, have been carried out. Following the checkout of plant control and shutdown logic, plant electrical system, instrument air system, purging and leak check of all equipment components and piping systems, and charging of all chemicals and lubricants, the Plant Facilities are now ready to commence startup. Start up procedures are usually provided by the designers and manufacturers of the process equipment. A brief start up procedure may be presented as follows: (1) block valves on process gas flows should be initially closed; (2) Turn on power to electrical panels; make sure all alarms and shutdown signals are operational; (3) start reboiler, fans, reflux pumps, booster and charge (circulation) pumps as described previously in wash out cycles; (4) open the inlet gas valve slowly to pressurize the contactor; keep the flow rate about half of the design flow rate and leave the sales gas line valve closed; (5) check amine solution concentration; (6) circulate until the still overhead temperature at the condenser inlet reaches the minimum operating temperature (usually 190-200°F); (7) open the sales gas valve and increase the gas flow rate to the desired operating rate. Operation may have been manual so far. If every thing is under control and all the parameters are within the range specified by design and operating manuals, switch to the fully automatic mode. None of the safety shut downs should activate. Amine units are usually part of a larger plants which may include gas dehydration and dew-point control, sales gas recompression, refrigeration systems, safety and flare systems, utility supply facilities, etc.. Therefore the start-up and commissioning of the amine unit should be synchronized with other processes and units within the entire gas processing plant.

**Normal Operation/Performance Routine Checks. Daily duties and routine checks** including: prepare a daily check list; some of the checks would be as follows: record all pressure and temperature readings and compare to expected operational conditions as well as readings for previous daily reports; check inlet filter/separator, amine contactor, and regenerator ΔP readings. As well, observe lean/rich exchanger pressure drops on both sides of the plate/frame or shell and tube exchanger; look for sudden increases in differential pressure; check all fluid levels: inlet filter separator bottom section, amine contactor, sweet gas scrubber, flash tank, reboiler surge section; check and record temperatures and pressures in all equipment; record ambient temperature; check the steam rate, amine reboiler temperature, and pressure; check amine reflux condenser temperatures, lean amine cooler temperatures; check amine concentration; check carbon and mechanical filter ΔP readings; check additives (e.g., antifoam) injection pump discharge pressure, pulsation, observe for vibration, and check lubrication of gearbox and packing; check booster and reflux pump discharge pressures; check operation of lean amine cooler/condenser air-coolers' louvers; check H<sub>2</sub>S analyzer, check acid level, tape supply; check and record amine flow; add make-up water as required; add amine with the appropriate strength as required. **Weekly Checks** including: check operations of amine reboiler controls and shutdowns and adjust accordingly; check all recorders and calibrate if required; check all underground drain tank levels. check amine concentration; acid gas in feed and sales gas should be checked daily during the first two weeks and thereafter weekly checks should be performed; perform amine foam test as required.

## Acid Gas Removal: Amine Gas Sweetening Plants - Operations (cont.)



Typical **operating ranges** are as follows: (1) rich amine upstream of stripper:  $P = 40-80 \text{ psig}$ ,  $T = 100-180^\circ\text{F}$ ; (2) amine exchanger, rich side:  $T_{in}=100-180^\circ\text{F}$ ,  $T_{out}=190-220^\circ\text{F}$ , lean side  $T_{in}=240-250^\circ\text{F}$ ,  $T_{out}=1170-190^\circ\text{F}$ ; (3) amine cooler:  $T_{in}=170-190^\circ\text{F}$ ,  $T_{out}=100-130^\circ\text{F}$ ; (4) reflux condenser:  $T_{in}=190-225^\circ\text{F}$ ,  $T_{out}=100-130^\circ\text{F}$ ; (5) reflux pump:  $P_s=4-6 \text{ psig}$ ,  $P_d=30-40 \text{ psig}$ ; (6) booster pump:  $P_s=4-6 \text{ psig}$ ,  $P_d=50-65 \text{ psig}$ ; (7) amine charge pump:  $P_s=5-40 \text{ psig}$ ,  $P_d=50 \text{ psig}$  over contactor operating pressure.

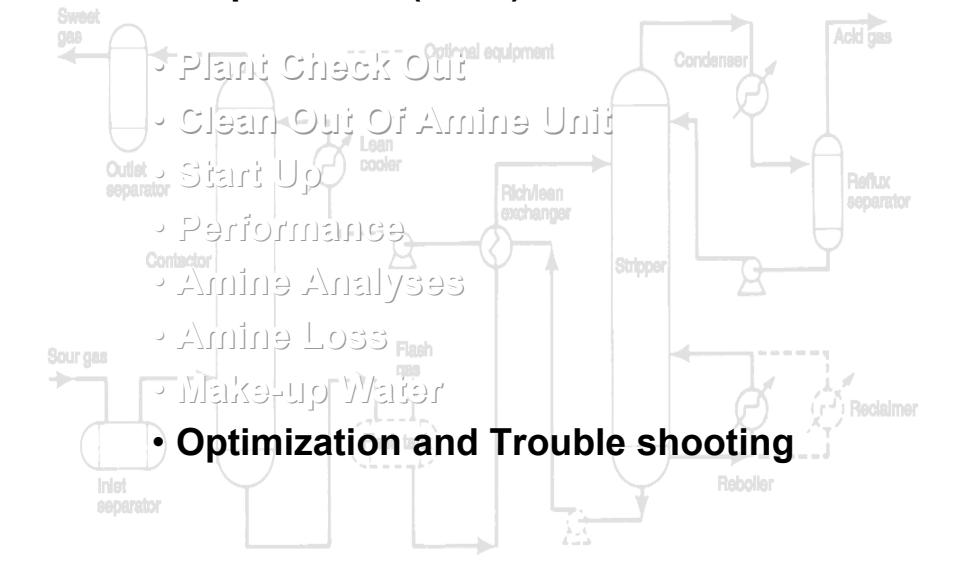
**Amine Analysis.** The colour of the regenerated solution can be most informative: **light brown**: good condition and well regenerated; **green**: very fine FeS particles (<1micron) larger FeS particles are **black** and will settle; **blue, green**: copper or nickel, copper oxide reacts with MEA to form a light blue complex (very unlikely in DEA plants); orange and dark red: iron compounds complexed with amine; red, brown: either oxidation or thermal degradation. Primary amine may smell like ammonia; secondary amine smell like a wet ash-tray.

The following analysis may be used to determine the condition of the amine. For procedures and interpretation consult the **Dow Gas Conditioning Fact Book (1962)**. **Alkalinity titration** for amine concentration; **gas chromatography** (GC) for free amine and degradation products, acid gas content; **total and primary nitrogen**; acid gas loading; **Karl Fischer** for water content; **Elemental analysis** by **atomic absorption** (AA) or iron, chlorine, aluminum, copper, sodium, etc.; **foam test** for extent and strength of foam.

**Amine Loss.** There are two types of day-to-day losses: those that are an integral part of the process and those due to leaks, spills, and mishandling. Sometimes the mishandling is much larger than the process losses. There are also upsets (e.g., foaming in the contactor) and contamination (e.g. inlet separator dumps produced water into the contactor). Process losses include the following: (1) sweet gas from the contactor: MEA is volatile enough to result 0.45 lb/MMscf of process gas; **DEA, DGA, DIPA and MDEA** are much less volatile and the losses are 0.02 to 0.03 lb/MMscf (2) Entrainment from the contactor: this averages 0.5 to 3.0 lb/MMscf. Entrainment losses can be reduced by operating at 70% of the flooding velocity and installing a demister in the top of the tower. Water wash trays above the top tray are the most effective solution. (3) gas from the flash tank and liquids from a three phase tank: these losses are very small (4) reflux overhead gas: these are very small because the vapour and liquid do not contain much amine. **Reclaiming**: this loss depends on how often the primary or secondary amines are reclaimed. Usually between 5-15% of the total amine inventory in the plant is lost in every reclaiming exercise. **Amine consumption** for a well designed and operated with few upsets averages **2 lb/MMscf** for **DEA, DIPA, and MDEA**. Losses for **MEA** are about **3 lb/MMscf** because of the volatility and reclaiming. **DGA** losses are intermediate.

**Makeup Water.** This replaces operating losses from the contactor – the sweet gas is hotter and therefore more humid than the sour gas – and the off gas from the reflux condenser. Periodic additions suffice for small units. Continuous addition is recommended for larger units especially when acid gas rate is high. The makeup water may be combined with the reflux to the stripper or fed to wash trays in the top of contactor tower. Makeup water may contain contaminants that accumulate in the unit and so cause foaming, corrosion, plugging, and fouling. Makeup water should meet the following specifications: 20 ppm chloride, 100 ppm TDS (*total dissolved solids*), 50 ppm total hardness, 10 ppm sodium/potassium and 10 ppm iron.

## Acid Gas Removal: Amine Gas Sweetening Plants - Operations (cont.)



A very good article published by Abry and DuPart (Dow Gas/Spec Technology group) gives guidelines for optimizing an amine plant based on historical plant data and how to cut costs, use less amine and reduce corrosion see **Amine Plants Troubleshooting and Optimization**; Abry R.G.F. and DuPart, R.S.; Source: *Hydrocarbon Processing*, v 74, n 4, Apr, 1995, p 41-50). Authors report how the process information is designed to circumvent upsets and to facilitate control. The authors also show how this plant data can be used to optimize the facility if operated away from design conditions. The optimization presented in this reference considered a decrease in inlet gas flow rate with the same concentration of acid gas components. Most operating companies usually exceed design inlet gas flow rates with higher concentration of acid gas components, therefore their analyses are somewhat unrealistic and perhaps overly optimistic. Note that the larger the unit, the greater is the need for optimization. The weekly amine analysis is most informative as most amine problems are triggered by contaminated solutions. Amine concentration should be closely watched – too high (>35% for *DEA*, 30 % for *MEA* and 50% for *MDEA* and *DGA*) increases the corrosion rate, and too low (<25% for *MEA* and *DEA* and <35-40% for *MDEA* and *DGA*) increases the circulation rate and wastes fuel. Acid gas loading is also very important – rich stream too high (>0.35 for most amines) increases the corrosion rate, and too low indicates (<0.2) inefficient use of amine and too high a circulation rate. Lean stream too high indicates (>0.1) poor regeneration and too high a circulation rate, and too low (<0.001) means unnecessary regeneration and fuel usage. pH should also be checked – too low add soda ash. Makeup water quality should be checked regularly, as it is a major source of contaminant introduction to amine solutions. The reflux ratio is usually not measured. However, it should be checked and monitored carefully. The optimum values depend on the amine system. Keeping the regenerator overhead temperature below 225°F and the reflux condenser effluent near 130°F is recommended. Check also the temperature approach of the lean/rich amine heat exchanger. Departure from design and/or startup condition denotes fouling. Once again, amine solution quality is very important as most amine plants work fairly well hardly with any problems with clean solutions. Amine degradation products (both *DEA* and *MEA*) play a major role in amine plants problems. They increase viscosity of the solution and therefore affect the power requirement to transport the liquid, most of them are corrosive and hence are a precursor to particle formation and fouling. Amine degradation reduces amine concentration (strength) and therefore causes a rise in amine circulation rate. The reduction of amine strength by formation of degradation products is not detectable by simple alkali titration techniques or nitrogen content tests as amine degradation products are amine themselves. Accurate gas chromatography is the only way by which these compounds may be identified and measured. Amine solutions should have identification chart in which weekly amine regular test results are carefully recorded and examined. Continuous increase in amine degradation products, heat stable salts, dangerous ions (e.g., Na, Cl, etc.), and foaming behavior are symptoms of an ill solution. Sources of contaminants should be identified and the problem should be treated accordingly. Sometimes, there is no solution to the problems and the solvent should be changed or reclaimed completely. Large gas sweetening plants are recommended to reclaim their solutions regularly (e.g., once in one or two year continuous operation). Some plants may need more frequent reclamation depending on the nature of the gas entering to the plant and choices of equipment and other operational parameters including rich amine acid gas loading, lean/rich amine exchanger effluent temperatures, and reboiler performance.

## Acid Gas Removal: Amine Gas Sweetening Plants - Operations (cont.)

### • Troubleshooting

- Gas is not sweet
- Amine solution not regenerated
- Dirty, degraded amine
- Excessive corrosion
- Foaming of amine solution

- Sulfur is present in amine loop
- Too much solid accumulation
- Amine changes color continuously

*(Note: Labels in the diagram are: Sour gas, Inlet separator, Flash tank, Stripper, Reboiler, Recalmer, Rich lean exchanger, Condenser, Reflux separator, Acid gas, and Optional equipment.)*

#### 1. Gas is not sweet

- Amine solution conc. is too low
- Amine flow rate is too low
- Insufficient amine regeneration; increase steam rate
- Reflux rate and temp. are too low; increase steam rate
- Too high stripper pressure
- Foaming in contactor and liquid carry over to outlet separator

#### 2. Amine solution not regenerated

- Reboiler temp., pressure and reflux ratio not are at design
- Leaks in amine lean/rich HX
- Foaming in stripper
- Too high stripper pressure
- broken trays and packing (due to severe corrosion)

#### 3. Dirty, degraded amine

- Gas contain oxygen
- Faulty inert blanketing in amine surge and storage tanks
- Contaminated makeup water (free oxygen); sparge amine with sweet gas to strip oxygen. Oxygen can enter when the fed gas contains vapour recovered from stock tanks, and can oxidize H<sub>2</sub>S to elemental sulfur.
- Too high rich amine acid gas loading (especially CO<sub>2</sub>)
- Inadequate circulation in reboiler (thermosyphon, due to reboiler inlet/outlet plugging)

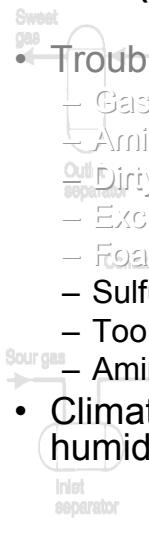
#### 4. Excessive corrosion

- Amine concentration is too high
- Amine is highly degraded; replace or reclaim
- Makeup water is contaminated (check chlorine and oxygen content)
- Insufficient amine regeneration
- Insufficient amine filtration; increase filter rate or change filter elements
- Oxygen is present; eliminate
- Fluid velocities are too high
- Temperature to stripper too high

#### 5. Foaming of amine solution

- Dirty amine (too much solids)
- Degraded amine
- Liquid HC in gas or amine
- Inlet gas temperature too low (HC cond.)
- Lean amine temp. too low (>10°F above inlet gas)
- Wrong or off spec. chemicals (amine, antifoam, etc.)
- Surfactants and corrosion inhibitors
- Very fine particles in gas and amine
- Inadequate cleaning before startup
- Too much or too little antifoam
- Contaminated makeup water
- Add antifoam always downstream of carbon filters
- Cotton-sizing chemicals or small carbon particles being washed off a newly installed cloths and/or carbon filter
- Incoming gas contains salt or produced water and very fine particles

## Acid Gas Removal: Amine Gas Sweetening Plants (cont.) - Operations Case Studies



### Troubleshooting

- Gas is not sweet
- Amine solution not regenerated
- Dirty, degraded amine
- Excessive corrosion
- Foaming of amine solution
- Sulfur is present in amine loop
- Too much solid accumulation
- Amine changes color continuously

### • Climate adjustment (winterization, heat and humidity consideration)

6. Sulfur is present in amine loop (Khangiran - Hashemi Nejad gas plant, Iran)
  - Polysulfide and fine sulfur in the gas (better inlet filtration, amine reclamation, and sulfur wash at wellhead with sulfur solvents)
  - Dissolve oxygen in amine
7. Too much solid accumulation (Kangan- Valieasr gas plant, Iran)
  - Corrosion rate is high - corrosion product accumulation: reduce rich amine loading, degradation products high; reclaim solution
  - Inlet gas contains very fine particles; better inlet filter cartridge (<0.1 micron, inlet gas water wash)
8. Amine changes color continuously (Bandar Imam - new amine unit, Iran)
  - Troubled thermosyphon reboiler
  - Severe corrosion, plugged stripper line to reboiler
  - Plugged reboiler inlet /outlet lines
  - High acid gas loading (>0.7)
  - Insufficient stripping (broken trays; carbon steel trays were used)
  - Reclamation is required

Amine units should also be adjusted for different climates. For cold climates they are **winterized** which includes: (1) extra insulation for already insulated equipment and insulation of equipment not normally insulated (e.g., contactor tower); (2) air-recirculation louvers on air-coolers; (3) Heat tracing of the amine piping and stagnant ports, e.g., level gauges, external float gages, switches and controllers. Heat may be electric, steam, hot oil, etc.; (4) frost protection in foundation design to prevent movement; and (5) some manufacturers prefer to erect a building around the equipment, then only uncovered equipment needs special protection. This of course would be very difficult for very large plants.

In very hot areas (Southern US or the Middle East, the air coolers in the very hot and humid summer days are the major problem makers. High design air temperatures and higher design factors are usually used for these heat exchangers. Humidity creates major corrosion problems on the exterior of process equipment. High quality coatings are needed for most process equipment. Cooling and lubricating systems on prime movers and electrical motors need extra attention during hot summer days. Therefore the designer should always keep an eye on the climate when the design phase is completed.

\* There are a number of very good technical papers at **Brian Research and Engineering (BR&E)** web site (<http://www.bre.com/technicalpapers/technicalpaper-home.asp>) concerning the design and simulation of gas conditioning processes.

## **NATURAL GAS DEHYDRATION**

- Introduction- purpose of gas dehydration
- Pipeline specification
- Hydrate prevention
- Methods of dehydration
  - Absorption dehydration using glycol
  - Solid bed adsorption
  - Expansion refrigeration (*LTX* units)
- Design techniques
- Operations of dehydration facilities

Water vapour is the most common undesirable impurity found in natural gas. By virtue of its source, natural gas is almost always associated with water, usually in the range of *400 to 500 lb water vapour/MMscf* gas. The primary reason for removal of water from gas is the problem of gas hydrate formation. As discussed before, in the hydrate formation in natural gas systems, ice-like hydrates can plug flow lines and natural gas processing equipment and lead to sever operational problems. Other reasons for removing water are: (1) liquid water promotes corrosion, particularly in presence of acid gas such as H<sub>2</sub>S and CO<sub>2</sub>; (2) slugging flow may result if liquid water condenses in the flowlines that can result in very high pressure drops; (3) water freezes in cryogenic and refrigeration systems used for LNG recovery; and (4) water vapour reduces the heating value of the gas. For these reasons, ***pipeline specification*** for natural gas restrict the water content to a value not greater than ***6-8 lb/MMscf***. In some areas water content may be limited to as low as ***2-4 lb/MMscf*** (e.g., in Canada). Because most gas sweetening processes involve the use of an aqueous solution, dehydration is often done after gas sweetening. Nevertheless, partial dehydration, or hydrate inhibition, are commonly necessary at the wellsite itself. Various aspect of gas dehydration and hydrate prevention techniques will be discussed in the next few sessions. The major dehydration processes are shown on this slide and will be discussed further in details. Design techniques for each techniques will be presented and operational problems and troubleshooting techniques discussed.

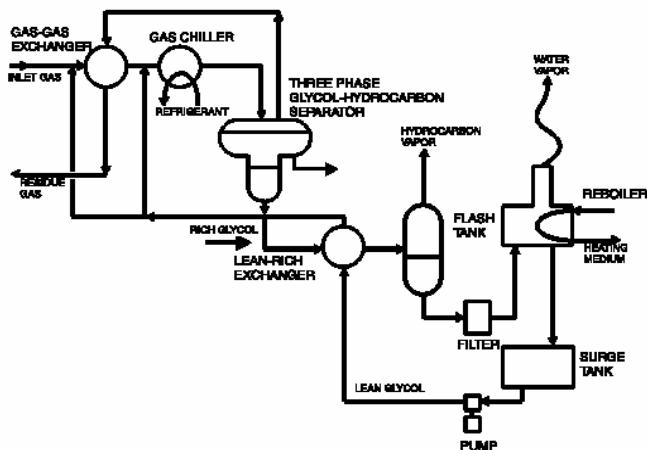
## Natural Gas Dehydration- Hydrate Prevention

- Line heating and Low Temperature Exchange Units (LTX)
- Inhibition by additives
  - Types and selection of additives
  - Inhibitor requirements
  - Prediction of inhibitor requirements
  - Injection techniques
  - Operations and troubleshooting

The permanent solution for hydrate problems is dehydration of the gas to a sufficiently low dew point. Commonly used dehydration methods will be discussed later. At the wellhead two techniques are applicable: (1) heating the gas stream so that it becomes under-saturated, and maintaining flowlines and equipment at temperatures above hydrate point; (2) in case where liquid water is present and liquid lines and the flowlines and equipment cannot be maintained above hydrate temperature, inhibiting hydrate formation by injecting additives that depress both hydrate and freezing temperature. Note that in practice, hydrates are a problem only when allowed to accumulate and grow to a size that restricts or stops flow. Otherwise, they are of no consequence. Flow line heating is used upstream of chokes and in short gathering lines because: initial investment is modest, heaters operate with a minimum of attention, and fuel is readily available, often at low costs. One other method of assuring that hydrates do not form is to assure that the amount of water vapour in the gas is always less than the amount required to fully saturate the gas at the flowing conditions. Low temperature exchange (LTX) units use the high flowing temperature of the well stream to melt the hydrates after they are formed. Since they operate at low temperatures, they also stabilize the condensate and recover more of the intermediate hydrocarbon components than would be recovered in a straight multistage flash separation process. LTX units will be discussed in a bit more details later in dehydration processes part of this course.

For long flowlines (over 1 or 2 miles) the gas approaches ambient temperature and chemical injection may be used. Many chemicals depress the temperature at which hydrates and/or ice form. They can be categorized into two classes, namely **thermodynamic inhibitors** which alter the chemical potential of the hydrate phase such that the hydrate formation point is displaced to a lower temperature/or a higher pressure and **kinetic inhibitors** – polymeric chemicals- which when added to a production stream, will not change the hydrate formation temperature but will delay the growth of hydrate crystals. Examples of kinetic inhibitors are N-vinylpyrrolidone (5 ring), sacharides (6 ring), and N-vinylcaprolactam (7 ring) polymeric chemicals. Some kinetic inhibitors are anti-agglomerators (e.g., ammonium alkyl aromatic sulphonate or alkyl glycoside surfactants) which when added to gas stream with a continuous oil phase, will minimize hydrate crystals from agglomerating or growing in size. The continuous oil phase provides a medium to transport the very fine hydrate crystals through the piping systems while crystal growth is delayed. The use of kinetic inhibitors and/or anti-agglomerators in actual field is a rather new and evolving technology. At the current time to get an optimum mixture for a specific application, it is necessary to set up a controlled bench test using the actual fluid and perform field tests. The most common thermodynamic inhibitors which are widely used are an alcohol – usually **methanol** - or one of **glycols**, e.g., **ethylene glycol (EG)** or **diethylene glycol (DEG)**. All may be recovered and re-circulated, but economics of methanol recovery will not be favorable in most cases. Methanol is a preferred choice in many instances, because it disperses well in the gas stream, is readily available in bulk, is the least expensive, and consequently, does not require recovery. Methanol however, can cause contamination problems in downstream gas dehydration plants (i.e., methanol is co-absorbed with water to glycol and increases heat load to glycol regenerator, increases corrosion in glycol units and reduce capacity of solid desiccants). Methanol injection is very useful in cases where low gas volumes prohibit dehydration processing. It is preferable in cases where hydrate problems are relatively mild, infrequent, or periodic, inhibitor injection is only a temporary phase in the field development program, or inhibition is done in conjunction with primary dehydration system. Methanol is soluble in liquid hydrocarbons, about 0.5% by weight. If there is condensate in stream, additional methanol is required because some of the methanol will dissolve in the condensate. Also, some of the methanol vaporizes and goes into the gas state. Ethylene glycol is the most common recoverable inhibitor. It is less soluble in hydrocarbons and has less vaporization loss than methanol. Methanol may be used at any temperature (at higher temperature methanol loss, of course, will be considerable), but **DEG** is usually not chosen below 15°F because of its high viscosity and difficulty of separation from liquid hydrocarbons. Above 20°F **DEG** might be preferred over **EG** due to lower vaporization losses. While ethylene glycol exhibits higher depression of the hydrate formation temperature than **DEG** on a per weight basis, methanol is superior to both **EG** and **DEG** on a per weight basis.

# Natural Gas Dehydration- Hydrate Prevention



*Typical Glycol injection system*

To be effective, the inhibitor must be present at the very point where the wet gas is cooled to its hydrate temperature. For example, in refrigeration plants glycol inhibitors are typically sprayed on the tube-sheet faces of the gas exchangers so that it can flow with the gas through the tubes. As water condenses, the inhibitor is present to mix with the water and prevent hydrates. Injection must be in a manner to allow good distribution to every tube or plate pass in chillers and heat exchangers operating below the gas hydrate temperature. The inhibitor and condensed water mixture is separated from the gas stream along with a separate liquid hydrocarbon stream. At this point, the water dew-point of the gas stream is essentially equal to the separation temperature. Glycol-water solutions and liquid hydrocarbons can emulsify when agitated or when expanded from a high pressure to a lower pressure, e.g., JT expansion valve. Careful separator design will allow nearly complete recovery of the diluted glycol for regeneration and re-injection. The figure shown on this slide is a flow diagram for a typical EG injection system in a refrigeration plant. The regenerator in a glycol injection system should be operated to produce a regenerated glycol solution that will have a freezing point below the minimum temperature encountered in the system. This is typically 75-80 mass%.

## Natural Gas Dehydration- Hydrate Prevention

- Inhibition by additives
  - Types and selection of additives
  - Process consideration
  - Injection techniques
  - Prediction of inhibitor requirements
  - Operations and troubleshooting

As mentioned before, to be effective, glycols must be sprayed into the wet gas as very small droplets. If intimate mixing of the fine liquid glycol spray and the natural gas is not achieved, then glycol injection may not prevent hydrate formation. With methanol the injection is not as critical because all or a considerable fraction of methanol evaporates into the gas stream, thus providing protection. The relative costs of methanol injection, glycol injection, and flow line heating can be summarized as follows. Methanol injection has a *low investment cost* but a *high operating cost* due to the chemical consumption. Injection of *EG* and *DEG* requires a higher initial cost but a relatively low operating cost. Line heaters are characterized by intermediate investment cost; the operating cost depends on the value of the fuel consumed. Line heaters obviously are more competitive for shorter pipelines. One rule of thumb is that **glycol units are used when the required methanol injection rate exceeds 30 gal/hr.** While glycol can prevent hydrates, it will not attack or dissolve hydrates already present. On the other hand, methanol can dissolve existing hydrates to some degree. A pipeline plugged with hydrates can be unplugged by reducing the pipeline pressure. Be sure to reduce the pressure on both sides of the plug. **Reducing the pressure on only one side of hydrate plug in a pipeline is EXTREMELY DANGEROUS..** The hydrate plug can break loose, then the pipeline pressure drives the ice-hard hydrate plug towards the lowered pressure side at very high velocity. When the hydrate hits a bend or restriction it can break the pipe and even expose a buried pipeline. Such accidents have resulted in loss of lives and extensive equipment damage.

**Injection techniques.** In the early days, gravity-type injection systems were used. A gravity injection system consists of a capacity tank, a sight glass, and a valve manifold to maintain equal pressure across the chemical and to regulate its entry into the flowing line. This resulted in a generally sporadic injection and poor inhibitor dispersion, leading to freeze-offs (hydrate formation) during operations. Newer systems have been introduced that feed the additive at a uniform rate into the gas stream, such as the pneumatically powered chemical injection pumps. Continuous injection is also desirable from the standpoint of field personnel who can then operate on a regular basis. Further, precise chemical requirements can be predicted and bulk purchases made at possibly lower rates. The injection pumps are usually of the positive-displacement types, so that they pump a constant amount of chemical into the gas stream, regardless of the pressure of the gas against which they must inject chemicals. Since positive displacement pumps do not sense any buildup of discharge pressure, a rupture disk is put at the discharge end of the pump. The pump injects chemical downward into running end of a vertically installed tee of a size about one *inch*. The tee functions as a sort of mixing valve. Metering devices are installed to permit chemical injection at a proportional-to-flow rate, eliminating frequent manual adjustment. As a precautionary measure in field operations, all valves and accumulator systems where free water may accumulate are pre-charged with methanol to prevent hydrate formation. Full cone spray nozzles are recommended when glycol is injected upstream or over the tube sheet of heat exchangers. The spray should cover the whole surface of the tube sheet otherwise tubes closer to the shell may be plugged with hydrate. Just ahead of each spray nozzle a 5-micron filter element minimizes clogged nozzles.

## Natural Gas Dehydration- Hydrate Prevention: Inhibitor Requirements

- Inhibition by additives

– Types of additives:  $W = \frac{(d)(MW)(100)}{(d)(MW) + K_H}$

– Process:  $(d)(MW) + K_H$

– Injection techniques

inhibitor	EG	DEG	Methanol
$K_H$	4000	4000	2335
MW	62	106	32

- Prediction of inhibitor requirements

- Hammerschmidt's equation

- Computer simulation

- Operations and troubleshooting

Prediction of inhibitor requirements. The minimum amount of inhibitor required may be calculated using two approaches: **Hammerschmidt correlation** and **computer simulation**.

Hammerschmidt's equation estimates the minimum inhibitor concentration in the exit liquid stream that is required to prevent hydrate formation using the following equation:

$$W = \frac{(d)(MW)(100)}{(d)(MW) + K_H}$$

Where  $W$  is the weight percent pure inhibitor in liquid water phase;  $d$  = desired depression of hydrate formation temperature, °F;  $MW$  = molecular weight of inhibitor; and  $K_H$  = **Hammerschmidt** constant for inhibitor given in the table shown on the slide. This equation has been successfully used from glycol injection systems as low as -40 to -50 °F that require 0.4 mole fraction of EG (70 wt.%). This equation should not be used beyond 20-25% for methanol and 60-70% for glycols. For concentrated methanol solutions and temperature as low as -160 °F the following equation should be used:  $d = -129.6 \ln(1-x_{MeOH})$ , where,  $x_{MeOH}$  is **mole fraction** of methanol in aqueous phase. When glycol injection is performed below 20 °F, the freezing points of EG and DEG must be considered. Crystallization from EG and DEG is given in **Figure 20-44** of the GPSA data book. It is common practice to keep glycol concentration between 60-70 weight percent.

The Hammerschmidt's equation can be rearranged to calculate the lowering of the gas hydrate freezing point for a given weight percent inhibitor in the aqueous phase:

$$d = \frac{WK_H}{(100)(MW) - W(MW)}$$

A material balance may be used together with the Hammerschmidt's equation to calculate the pure inhibitor using the following equation:

$$W_G = I \left( \frac{(d)(MW) + K_H}{(d)(MW)} \right) - \frac{100}{W_{in}}$$

Where,  $W_G$  is water removed from gas stream (**Ib/MMscf**),  $I$  pure inhibitor required (**Ib/MMscf**), and  $W_{in}$  is concentration of inhibitor in outlet inhibitor stream.

**Computer simulations.** Equations of state methods of predicting hydrate formation without inhibitor was discussed before. The same simulation packages can be used to predict hydrate formation when inhibitors (EG, DEG, methanol) are present. A recent good article by Nasrifar et. al (**Predict Gas Hydrate-Forming Temperatures** by Nasrifar K., Moshfeghian M., Johannes A.H., and Maddox, R.N., Source: *Hydrocarbon Processing*, v 78, n 4, Apr, 1999, p 7780) gives the basics of mathematical models used in these programs.

## Natural Gas Dehydration- Hydrate Prevention: Operations and Troubleshooting

- **Operations**
  - Vapour losses
  - Corrosion
  - Glycol losses
  - Glycol-water-oil separation
- **Troubleshooting**
  - Preventing freeze-offs
  - Improving Glycol-Condensate Separation

### • Operational Problems

**Vapour losses.** Glycols have very low vapour pressures and accordingly vapour-phase losses should be very small. Vapourization losses are very low below 100°F and may be estimated as 0.23 lb/MMscf. Methanol on the other hand, is quite volatile and vapour-phases losses must be included. **Figure 20-51** of the GPSA data book are used fro methanol vapourization losses.

**Corrosion.** A full-flow filter comparable to that in a dehydration process is needed to remove solids particles that promote corrosion and degradation. The pH of glycol solutions does not appear to affect emulsion-breaking time. However, some corrosion inhibitors do have a pronounced effect upon emulsion stability. Almost all degradation products are acidic. Corrosion is minimized by adding inhibitors to hold the solution pH near 7.2. Common inhibitors and the concentrations at which they are used are: MEA (1-2 wt.%), Nacap® (0.3 wt.%), Boraz® (0.3 wt.%) and K<sub>2</sub>HPO<sub>4</sub>.

**Glycol losses.** Glycols are lost in three ways: (1) solution in liquid hydrocarbons; (2) vapourization and entrainment in the exit gas; (3) Decomposition in and carry over from regenerator. Glycol solubility in hydrocarbon liquids increases with (1) molecular weight, i.e., DEG is more soluble than EG; (2) temperature; and (3) weight percent of glycol in water. Glycol solubility also depends on the type of hydrocarbon liquid present. Glycols are more soluble in aromatics and naphthenes than in paraffinic HCs. At 60°F and 50-70 wt.% glycol, solubilities are 10-50 ppm for EG and 20-100 ppm for DEG. These losses are approximately **0.3 to 3.0 gallons of glycol/1000 bbl of condensate**. Solubility will be lower at lower temperatures. **Carry over losses** from separator and regenerator vary widely with equipment design and operation but usually are less than **0.2 gal/MMscf**. Total losses of **1 gal/100 bbl condensate** are not uncommon. Vapour losses were discussed above.

**Glycol-water-oil separation.** All vessels for separating glycol-water-oil mixtures (below 30-40°F) should be designed for a residence time of about 30 minutes for maximum efficiency. This residence time is found by dividing the vessel volume by the volumetric flow rate of the inlet mixture. Above 30-40 °F, a residence time of 20 minutes may be adequate if foaming or emulsions are no problems. If possible, it is recommended that separation be carried out at 80-100°F, which lowers the viscosity and promotes settling.

### • Troubleshooting

**Prevention of freeze-ups.** Check the following: (1) check the upstream FWKO for complete water, salt and solid separation; (2) check gas-glycol contact (is the atomizing nozzle eroded or plugged?); glycol should be sprayed in a very fine mist to form glycol film on all surface; (3) check glycol flow rate;; make sure pump works properly; (4) check glycol conc., use hydrometers; check also for the presence of salt and other contaminants

**Improving Glycol-Condensate Separation.** As discussed in vapour-liquid and liquid-liquid separators section of this course, the potential troubles should be first identified. If condensate samples taken downstream of the separator appear cloudy, then the glycol-condensate separation is incomplete. Possible causes are: (1) excessive gas velocities in the separator (too small a separator); (2) inadequate liquid retention time (overloaded separator); (3) foaming and/or emulsion foaming; (4) plugging of the glycol dump valve; and (5) improper operation of the liquid level controller.

**Defoamers** and/or **emulsion-breaking** chemicals can be added to temporarily control foam or emulsion formation. Permanent resolution requires that the sources of the foam and/or emulsion be determined and eliminated. It should be noted that the glycol-condensate separation is much easier at higher temperatures (60-70 °F) and lower pressures. Internal heaters can be devised within problematic separators.

## Natural Gas Dehydration- Glycol Absorption

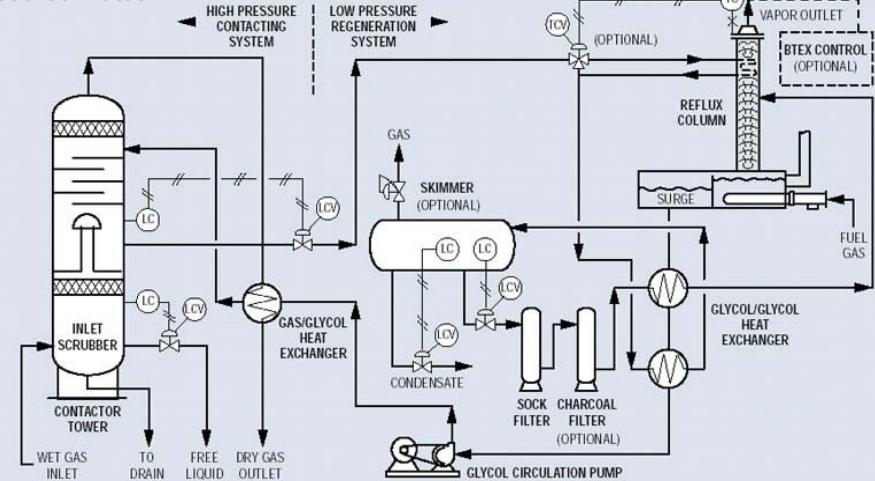
- Advantages over other methods of dehydration:
  - Solid desiccant
  - Expansion refrigeration (LTS or LTX units)
- Choice of glycol (EG and DEG vs. TEG)
- Process description and elements
- Design methods
- Process operations

As explained before, natural gas may be dehydrated to pipeline specifications by several processes, including liquid desiccants (glycols), solid desiccants (alumina, silica gel, molecular sieves), and expansion refrigeration. In the liquid state, water molecules are highly associate because hydrogen of bonding. The hydroxyl groups in glycals form similar associations with water molecules. This explains why **glycols** are such good absorbers of water. **Solid desiccants** are characterized by an internal porous structure that contains very large surface area (e.g., 200-800 m<sup>2</sup>/g). These desiccants exhibit a high affinity fro water and their water capacities ranges from 5 to 15% on a weight basis and can dry natural gas to less than 0.1 ppm water or a dew-point of -150°F. Expansion refrigeration processes are known also as **low temperature separation (LTS)** units. These process are also known as **low temperature exchange (LTX)** units. They employ the **Joule-Thompson (JT)** effect to both dry the gas and recover natural gas liquids. These units, therefore, may be called **JT units** as well. The JT expansion requires a large pressure drop to obtain all of cooling needed to dehydrate the gas. Therefore, expansion refrigeration, with or without hydrate inhibition, is normally used when the prime objective is hydrocarbon recovery. Usually the choice of dehydration method is between glycol and solid desiccants. Glycol dehydration possesses the following advantages over solid desiccants: (1) lower installed costs; it has been reported that solid desiccant plants cost 50% more at 10 MMscfd and 33% more at 50 MMscfd (see Ref. 9); (2) lower pressure drop – 5 to 10 psi vs. 10-50 psi for dry desiccant units; (3) Glycol systems are continuous more suitable for high flow rates; (4) recharging reagents is much easier and does not require interruption; (5) less regeneration heat requirement per pound of water removed; (6) more flexible in the presence of some contaminants that foul solid desiccants; and (7) glycol units can dehydrate natural gas to very low water content (0.5 lb/MMscf). They have, however, the following disadvantages: (1) water dew point below -25°F requires special design and is difficult; (2) is susceptible to contamination; (3) corrosive when contaminated. Advantages of solid desiccants are: (1) dew-points down to -150°F is readily achievable; (2) less affected by small changes of gas pressure, temperature, or flow rate; (3) less corrosive and have no foaming problems; (4) no moving part and motion sensitive equipment, which makes them more suitable for floating facilities. However the solid desiccants suffer from the following disadvantages: (1) higher capital cost and pressure drop; (2) can be poisoned by heavy HC and H<sub>2</sub>S, CO<sub>2</sub>,sulfur compounds, etc.; (3) mechanical breaking of desiccant solid particles; (4) high space and weight requirement; (5) high heat regeneration requirements and utility costs. The above comparison shows why glycol dehydration is by far the most commonly used process.

Choice of glycol. Four commercially important glycals are: **ethylene glycol (EG)**, **diethylene glycol (DEG)**, **triethylene glycol (TEG)**, and **tetraethylene glycol (TREG)**. TEG has gained almost universal acceptance as the most cost effective choice because: (1) TEG is more easily regenerated to a concentration of 98.00-99.95% in an atmospheric stripper because of its high boiling point and decomposition temperature. This permits higher dew-point depression of natural gas in the range of 80-150°F; (2) TEG has an initial theoretical decomposition temperature of 404 °F, while that of **DEG** is only 328°F; (3)vapourization losses are lower than **EG** and **DEG**; (4) is not too viscous above 70°F as **TREG** is. For more than 50 years sweet and sour natural gases have been dehydrated using **TEG**. Dew-point depressions range fro 40-150°F, while inlet gas pressures and temperatures vary from 75 to 2,500 psig and from 55 to 160°F, respectively.

## Natural Gas Dehydration- Glycol Absorption

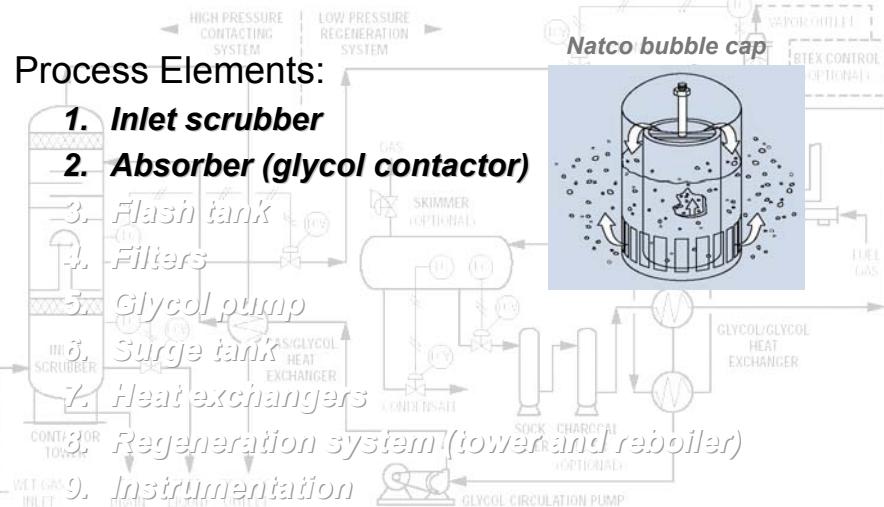
Source: Natco



**A typical glycol absorption process**

**Process Description.** As shown in the process flow diagram on this slide, wet natural gas first flows through an inlet separator or scrubber to remove all liquid and solid impurities. Then the gas flows into and upward through the absorber or contactor where it is contacted countercurrently and dried by glycol. Finally, the dried gas passes through a gas/glycol heat exchanger, and then into the sales line. **Reconcentrated** or **lean** glycol enters the top of the contactor where it flows downward from tray to tray and absorbs water from the rising gas. The wet or **rich** glycol leaves the contactor and flows through a coil in the accumulator where it is preheated by hot lean glycol. In some more efficient process (as shown in the *Natco* process on this slide), rich glycol is also preheated on top of the regeneration tower by hot water vapour. The coil at top of the stripper provides a water reflux at the top of the stripper. This temperature control insures that the water leaving the still does not carry over excess glycol. Heat exchange between the cool, rich glycol and hot lean glycol is improved by using two or more shell and tube heat exchangers in series. The increased heat recovery reduces fuel consumption in the reboiler and protects the glycol circulation pump from being overheated; it also allows the flash tank and filter to operate at approximately 150°F. After glycol-glycol heat exchange, the rich solution is flashed to remove dissolved hydrocarbons. The latter can be used as fuel and/or a stripping gas. The glycol is filtered before being heated in the regenerator column. This prevents impurities such as solids and heavy hydrocarbons from plugging the packed column and fouling the reboiler fire tube. The solution then enters the stripping or regeneration column and flows down the packed section into the reboiler. Steam generated in the reboiler strips water from the liquid glycol as it rises up the packed bed. The water vapour and desorbed natural gas are vented from the top of the stripper. The hot reconcentrated glycol flows out of the reboiler into accumulator where it is cooled by heat exchange with **rich** glycol. Finally the **lean** glycol flows through the glycol/gas exchanger and is pumped back into the top of contactor. The pump is protected by filtering the lean glycol as it leaves the accumulator. At the high pressure of the contactor tower, **TEG** absorbs hydrocarbons most of which are stripped off in the flash tank. Aromatic hydrocarbons have rather better solubility in **TEG** and are not completely flashed off in the flash tank. The water vapour leaving the stripper column from the top contains some aromatic compounds which are known to be carcinogenic. The release of these aromatic compounds, namely **benzene**, **toluene**, **ethylbenzene** and **xylanes** (ortho, meta and para) known also as **BTEX**, which have rather close boiling points to that of water, has been restricted by regulating (environmental) organization. Therefore most of the modern glycol regeneration stills are equipped with **BTEX** removal systems. The **BTEX** removal systems may work base on effective incineration or condensation of stripper overhead and separation of **BTEX** in liquid phase. Minor quantities of **BTEX** may still be present in liquid water, therefore water disposal should be according to water disposal regulations.

## Natural Gas Dehydration- Glycol Absorption



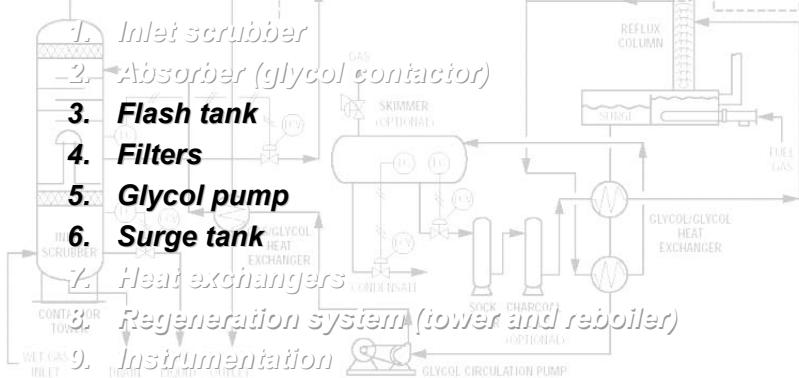
### Process Elements

**Inlet scrubber.** About half of all gas dehydration problems are caused by inadequate scrubbing of the inlet gas. Five of more common contaminant that impair the performance of the TEG units are: (1) entrained or free waters which increase the glycol circulation, reboiler heat duty, and fuel costs and overloads the unit. Glycol may carry over from contactor and/or regenerator in overloaded units; (2) oils and hydrocarbons-dissolved aromatic or asphaltic hydrocarbons reduce the drying capacity of the glycol and water, cause foaming. Undissolved oils can plug the absorber trays and can coke on the heat transfer surfaces in the reboiler and increase the viscosity of TEG; (3) salts within the entrained brine dissolve in glycol and make it corrosive to steel, even stainless, and can deposit on the fire tubes in the reboiler, causing hot spots and fire tube burnout; (4) down-hole additives such as corrosion inhibitors, acidizing and fracturing fluids cause foaming, corrosion, and hot spots if they deposit on the fire tubes; (5) solids (such as sand and corrosion products, e.g., rust or FeS) promote foaming, erode valves and pumps, and eventually plug trays and packing. Complete scrubbing of the incoming wet gas is absolutely essential for satisfactory performance. Many large units place a scrubber or separator upstream of the contactor, and possibly a filter coalescer. The scrubber should be sized to handle 125% of the maximum gas flow rate and have a high-liquid-level shut down.

**Glycol contactor.** The glycol contactor is very similar to amine contactor. As shown on the previous slide, the contactor consists of an integral scrubber at the bottom, a mass transfer or drying section in the middle , and a glycol cooler and mist extractor at the top. The integral scrubber complements the inlet scrubber and should not be used as a substitute. The tower usually contains between 4 to 12 bubble cap or valve trays. Although valve trays are more efficient (33 vs. 25% fro bubble caps), bubble caps are usually used. Bubble caps do not weep at low gas rates and do not drain the trays. They are also suitable for viscous fluids. Because glycols tend to foam, the trays should be spaced at least 18" and preferably 24-30 in apart. The contactor should be exactly vertical, otherwise, the unequal liquid level on the trays seriously impairs the gas/liquid contact . **TEG circulation** rates vary from **1.5 to 4 gal TEG per lb water removal**. Smaller units with 4 to 6 trays were often operated at 3 gal/lb water. In larger units of eight or more trays, the TEG circulation rate is reduced to 2 gal/lb water with simultaneous reduction in reboiler duty. Due to BTEX's environmental issue most modern design tend to use lower glycol rate and larger number of contactor trays for efficient water removal as well as lower BTEX emission problems. Good glycol-gas contact becomes difficult on the trays with less than 2 gal/lb water. A woven wire mesh mist eliminator reduces liquid glycol losses to less than **1 lb/MMscf**. A minimum of **1.5 times the tray spacing** should be allowed for **disengaging height** above the last top tray.

## Natural Gas Dehydration- Glycol Absorption

### Process Elements:



**Flash Tank.** While TEG absorbs approximately 1 scf of natural gas per gal at 1000 psig and 100°F, heavier hydrocarbons (HCs) in the natural gas, including aromatic compounds are much more soluble. A two-phase separator with a 5-10 min liquid retention time prevents excess gaseous HCs from entering the regeneration system, where they will be flashed off the glycol solution and increase glycol losses and possibly break the ceramic packing. A three phase separator with a 20-30 min liquid retention time is preferred when the gas gravity is high and glycol absorbs significant quantities of heavier HCs. The gas condensate-glycol separation is best performed at 100-150°F and at 50-75 psig. These conditions permit the flash gas to be used for fuel or stripping gas without compression. The pressure condition should provide sufficient driving force for the liquid to pass through all down stream equipment, e.g., HXs and filters, etc. When oil removal is required, the rich glycol can be preheated before flashing which reduces the viscosity and enhances the separation. The higher temperature, however, increases the heavy HC solubility. Horizontal separators are more efficient; however if the space is limited vertical ones may be designed to do the job as well.

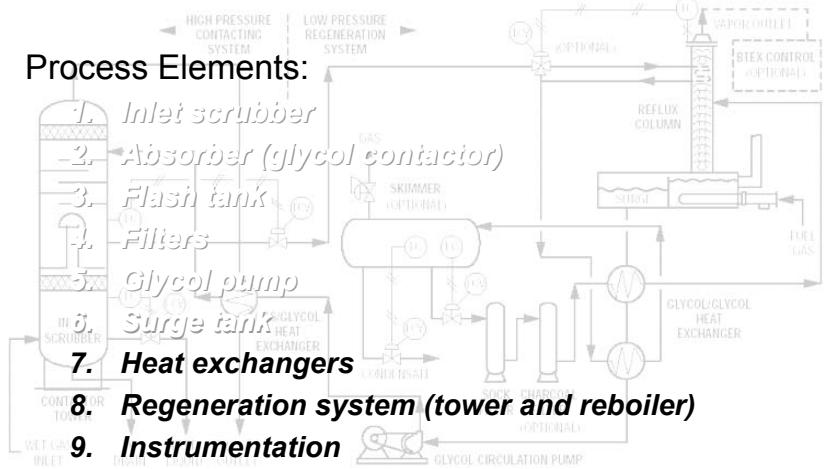
**Filters.** The solid content in the glycol should be kept below 0.01 weight percent (100ppmv) to prevent pump wear, plugging of HXs, foaming, fouling of contactor trays and regenerator packing, crevice or cell corrosion, and hot spot on the fire tubes. **Cloth** or **Sock filters** are designed to remove 5-micron and larger particles. Placing the filters after the glycol-glycol exchanger exploits the lower glycol viscosity and therefore lower pressure drop. The filters are designed for an initial pressure drop of 3-6 psi and should be changed when the pressure drop reaches 15-25 psi. Filters should be regularly checked for paraffin plugging. Activated carbon filters are also used to remove dissolved hydrocarbons, surfactants, well treating chemicals, compressor lube oils, etc. from glycol. Coal based carbons have better strength and will not create dusting problems. A more preferred allowable flow rate to carbon filters is 1-2 gpm/ft<sup>2</sup> of carbon bed area, however, an alternative design recommends carbon filter vessels operating on full glycol stream containing granular carbon in the range of 4-30 mesh, a flow rate of 2-10 gpm/ft<sup>2</sup> of bed area, and a retention time of 5 to 10 minutes.

**Glycol pump.** Three types of pump are available: (1) high-pressure-gas operated (e.g., **Texsteam**); (2) high-pressure-liquid operated (e.g., **Kimray**); (3) electric-motor driven. Two glycol pumps each capable of providing 100% circulation are usually used. For large units an electric-motor driven, horizontally mounted, multiple cylinder displacement pump with a high-pressure-liquid stand-by pump is preferred. For smaller units and in remote areas, a high pressure-liquid or gas-driven glycol pump is often used. High-pressure rich glycol is taken from the bottom of the chimney tray of the contactor and used to supply part of the power for this double-acting pump. High pressure gas from the contactor supplies the remainder of the power. This additional gas consumption increases with increasing contactor pressure. Typical rates are 1.7 scf/gal TEG at 300 psig and 5 to 6 scf/gal TEG at 1000 psig.

**Surge Tank.** The **surge tank** must be large enough to handle a complete drain-down of TEG from the absorber-tower trays. During normal operation, the **surge tank** should be half full. A gas blanket is recommended to prevent air (oxygen) contamination.

## Natural Gas Dehydration- Glycol Absorption

### Process Elements:



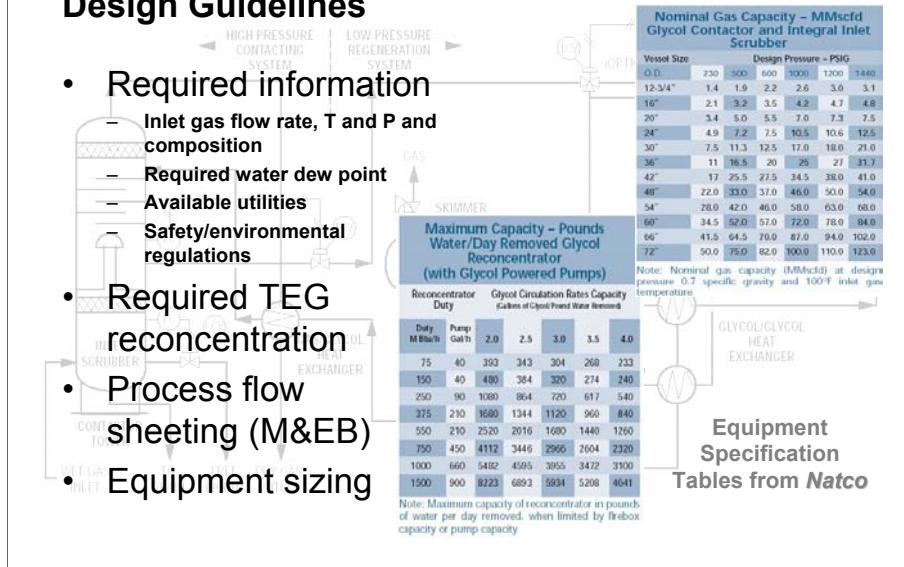
**Heat Exchangers (HXs).** The heat exchanger extracts heat from the hot, lean glycol returning to the contactor and delivers it to rich glycol flowing to the regenerator, thus saving energy. If changes to gas flow rate is expected, it is best to have an additional firing rate or increased flow of heat transfer fluid should be available for the reboiler. The HXs should be designed to accomplish the following: (1) supply lean glycol to contactor 5-15°F warmer than the dried gas leaving the absorber. In smaller units, the glycol is cooled in a coil located in the contactor just below the demister. In larger units a separate external gas-glycol exchanger or an air cooler is used. Failure to cool the glycol reduces the drying efficiency of glycol contactor; (2) maintain the top of stripper tower at 210°F (at sea level), a bit lower than the dew point of pure water. The cold rich glycol may be used as coolant for the reflux coil; (3) control the preheat of rich glycol entering the stripping tower (and thus the maximum heat recovery from the lean glycol leaving the regenerator). Too high a temperature flushes water vapour and produces two-phase flow. An approach of 60-90°F at the hot end is most desirable in the lean/rich glycol heat exchanger. This heat exchanger has a large temperature cross; that is the temperature of the exit lean glycol is much lower than that of the exit rich glycol. This type of flow requires true counter-current flow. Double pipe (finned-tube inside) or plate and frame exchangers are usually used. Two or more exchangers in series are often used in large units to control the temperature at which the rich glycol enters the flash tank and filters.

**Regeneration system.** Re-concentration occurs both in the vertical stripping column and the reboiler. In smaller units, the column is frequently mounted on top of the reboiler. **Stripping column** contains a stripping section usually filled with 4 to 8 ft of ceramic packing (1- to 1.5-in Intalox saddle or Pall rings). Trays are sometimes used in very large units. The water in the rich glycol leaves the still as steam. The cooling coil in the top of the tower condenses some of the exit steam to provide reflux for the column. This arrangement controls condensation and reduces glycol losses. The air cooled, finned condensers used in many older units provided excessive ambient cooling in cold weather and in adequate cooling in hot weather. The **reboiler** provides the heat necessary to boil the water out of the glycol solution. **Direct-fired heaters** are often used, but they constitute an open flame hazard. In some locations, such as offshore platforms, indirect heating with oil or steam is required by fire code and prudent practice. Use of exhaust gases from gas turbines and engines as the heating medium (when available) achieves substantial energy savings. TEG does not undergo significant thermal degradation if the bulk glycol temperature in the reboiler is kept below 400°F and maximum fire tube skin temperature should not exceed 430°F. Accordingly, the U-shaped fire tube should be sized so that the average heat flux is 6000-8000 Btu/hr.ft<sup>2</sup>. Heat flux is not uniform throughout the fire tube but is highest near the flame in the bottom tube. Installation of *turbulators* (e.g., Smick Turbulator) in the return leg of U-shaped fire-tube improves the heat flux distribution, lowers the stack-gas temperature, reduces the stack-gas temperature, reduces fuel consumption by at least 8%, extends fire-tube life, and minimizes glycol degradation.

**Instrumentation.** API Recommendation Practice **API RP 14C** and **14E** provide very useful guidelines for engineering design of glycol systems including requirements for instrumentation and control systems of dehydration units. All government and fire/safety regulations issued by insurance companies and company specifications should be carefully considered. The obvious recommendation is to keep the instrumentation as simple as above-mentioned specification and regulations will allow.

# Natural Gas Dehydration- Glycol Absorption: Design Guidelines

- Required information
  - Inlet gas flow rate, T and P and composition
  - Required water dew point
  - Available utilities
  - Safety/environmental regulations
- Required TEG re-concentration
- Process flow sheeting (M&EB)
- Equipment sizing

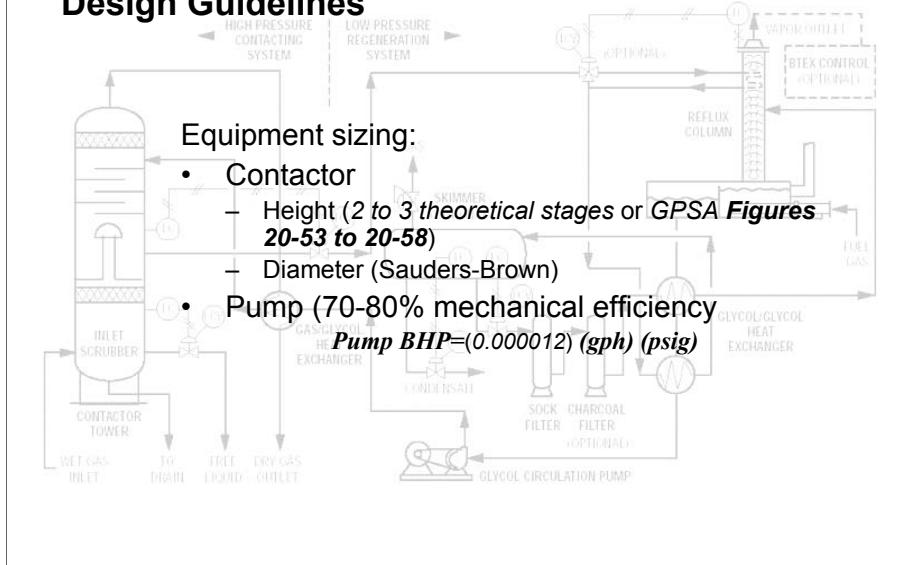


Standard units can be sized readily from manufacturers published graphs and tables, e.g., Natco. (see tables on this slide). Several rules of thumb can be used for preliminary sizing, while computer programs and process simulation software permit more rigorous designs. No matter which design approach is selected, the following sequence is recommended: (1) obtain design information- the primary variables usually required include gas flow rate (MMscfd), gas gravity, gas inlet temperature and composition including acid gases, operating pressure (psia), maximum working pressure in contactor (psia), and outlet water content required (lb/MMscf). Availability of utilities and safety/environmental regulations for discharging stripper overhead is very important; (2) Select an appropriate combination of lean glycol concentration and circulation rate, and contactor trays; (3) size the equipment.

Glycol to water **circulation rate** is generally within the range of **2 to 5 gallons TEG per lb water** removed. Due to environmental concern over **BTEX** emissions designers tend to select lower range of circulation rate and increase the number of trays to achieve the required gas water-content specification. This also helps to have lower energy consumed per unit weight of water removed. Concentration of the **lean TEG** from the regenerator ranges from 99.0% to 99.9%; most designs use **99.5%** lean glycol concentration. The dehydrated natural gas leaving the contactor cannot contain less water than that which would be in equilibrium with the entering lean reconcentrated glycol. Equilibrium is never completely achieved, although depending on **TEG** flow rate and number of trays it can be very closely approached. In practice, the water dew-point of the dried gas leaving contactor is 5-10°F higher than the equilibrium dew-point. *This fact and the rule of thumb that the dew-point depression is 60°F for the first four trays, plus 7°F for each additional trays, are good first estimates.* **Figure 20-54** of the GPSA data book shows the equilibrium water dew point at different temperatures for gases in contact with various concentrations of glycol. At 100 °F contact temperature there is an equilibrium water dew-point of about 30 °F for 98% glycol and 10 °F for 99% glycol.

The glycol to water circulation rate depends on the lean glycol concentration, and the number (and efficiency) of trays in the contactor. Lean TEG concentration is determined by what the regenerator can deliver (which is primarily a function of the amount of stripping gas supplied to the regenerator, and the permissible lower limit of glycol viscosity the plant and equipment can handle. Frequently, dehydration requirements are expressed in terms of dew-point depression. This can be calculated easily as the difference between the inlet and outlet gas dew-point temperatures. Sometimes, the inlet gas temperature is known, and outlet gas water content is specified. In either case, the inlet and outlet gases are assumed to be saturated, and their water content, or dew point temperature, is determined using any of the available correlations. The higher the concentration of the lean glycol the greater the dew-point depression for a given glycol circulation rate and number of trays. The relationship between circulation rate and number of equilibrium stages employs the absorption calculation techniques set out in *Chemical Engineering* standard text books (see Unit Operation by McCabe et al.). This calculation has been illustrated by **Figures 20-53 to 20-58** of the GPSA data book. These figures show that increasing the lean glycol concentration have a much greater effect on percent water removal (dew-point depression) than increasing the circulation rate. To obtain a 85% water removal, a circulation rate of 3.45 gal TEG/lb water at 99.9% lean glycol concentration, 4.0 gal TEG/lb water at 99.5%, or in excess of 5 gal TEG/lb water at 99% is required when the number of theoretical trays is only one (see **Figure 20-55**). When the number of theoretical trays is increased to two a 4 gal TEG/lb water flow rate can remove more than 93% of the water when a 99.5% lean glycol TEG is charged to the contactor (see **Figure 20-56**); for three theoretical trays more than 97.3 % of the water will be removed if a 99.5% TEG is circulated back to the glycol contactor (see **Figure 20-59**).

## Natural Gas Dehydration- Glycol Absorption: Design Guidelines



Glycol system sizing involves specifying the correct contactor diameter and number of trays, which establishes its overall height; selecting a glycol circulation rate and lean glycol concentration; and calculating the reboiler heat duty. As discussed before, the number of trays, glycol concentration and circulation rate are all interrelated.

**Contactor.** Random and structured packing can be used in place of the traditional, bubble cap-trayed towers (see **amine sweetening design procedures** discussed before). Packing can result in a 25% shorter contactor tower and the resulting reduction in tower size and weight which is very welcome on offshore platforms. Sizing contactors involves specifying: (1) the type and number of trays; (2) the *TEG* circulation rate; and (3) the column diameter. The GPSA charts (**Figures 20-53 to 20-58**) may be used for preliminary sizing. The number of trays are selected so that the required water removal (dew-point depression) is obtained. As mentioned before this has to be done considering the effect of glycol flow rate and lean glycol concentration. Process simulator may be used for a rigorous process analysis. The commercial software (e.g., *BR&E Tsweet*, *Hypotech HYSYS*, etc.) can generate a complete mass and energy balance analysis including producing temperature and composition profiles for trays and tower hydraulics calculations. There are some charts presented by others which present the dependence of circulation rate, number of trays as a function of dew-point depression at 600 psi pressure and for two temperatures of 80 and 100 °F (see charts presented by *Olbrich* in Ref. 1). With all variables constant, the rule of thumb is that, dew-point depressions increases 0.9 °F (about 1% change in water removal) for every 100 psi increase in contactor pressure. Dew-point depression vary very little with temperature, and linear interpolation is recommended between 80 °F and 100 °F. GPSA charts are produced for typical contactor pressure and temperature conditions and are good enough for preliminary sizing and could be used without any consideration for pressure and temperature. The diameter of the contactor can be conservatively estimated either from manufacturers charts (e.g., *Natco* charts) or from the *Saunders-Brown* correlation using the following equation:  $V_{max} = C_{SB} J (\rho_L - \rho_g)^{1/2} / \rho_g^{1/2}$ , where,  $V_{max}$  is maximum gas superficial velocity,  $C_{SB}$  = *Saunders-Brown* coefficient are shown in the following table, and  $\rho_L$  and  $\rho_g$  are density of gas and liquid.

**Pump.** A reciprocating pump is sized using manufacturers catalogues or by standard mechanical energy balance and an assumed pump efficiency of 70-80%. the *BS&B Co.* recommends the following quick estimates based on 80% efficiency and 90% motor efficiency:

$$\text{Pump BHP} = (0.000012) \text{ (gph)} (\text{psig})$$

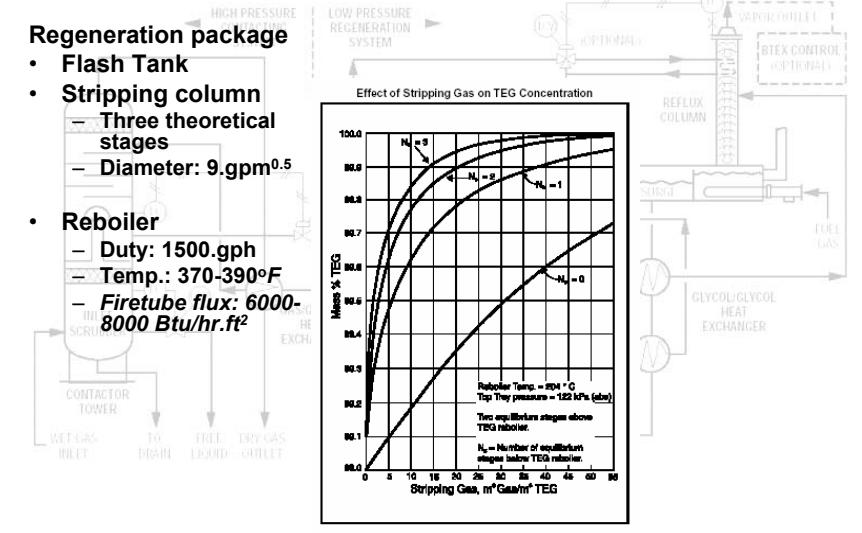
$$\text{Electrical kW} = (0.000011) \text{ (gph)} (\text{psig})$$

Where, *gph* is *TEG* flow rate in gallons per hour

	$K_{SB}$ ft/sec (m/s)	$C_{SB}$ ft/hr (m/h)
<b>Bubble Cap Trays</b> 20" (50 cm) spacing	0.14(0.043)	504 (154)
24" (60 cm) spacing	0.16(0.049)	576 (176)
30" (75 cm) spacing	0.17(0.052)	612 (187)
<b>Packing</b>	Structured	0.3-0.4 (0.091-0.122)*
Random 1" (2.5 cm) Pall rings	0.13-0.18(0.04-0.055)	468-648 (143-198)
2" (5.0 cm) Pall rings	0.19-0.26(0.058-0.079)	684-936 (208-285)

\* Depending on packing density and vendor

# Natural Gas Dehydration- Glycol Absorption: Design Guidelines



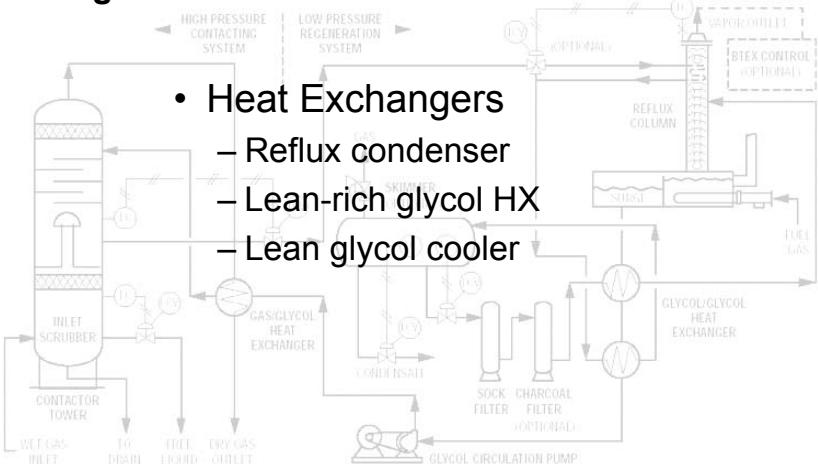
**Flash Tank.** The wet rich glycol is flashed at 50-100 psia and 100-150°F. Recommended liquid retention times are 5-10 minutes for two-phase (gas-glycol) and 20-30 minutes for three phase (gas-liquid HC-glycol) separation. Other guidelines are: (1) vertical separator **height (ft)** =  $3.4 + 0.4 \text{ gpm}$ , where **gpm** is gallons per minute of glycol, and **minimum height** of 4 ft and **maximum height** of 10 ft and **minimum diameter** of 1.5 ft.; (2) horizontal separators: **length/diameter ratio** = 3, **minimum length** of 3 ft and **minimum diameter** of 2 ft.

**Stripping Column.** Process simulators usually consider the stripping column as three theoretical trays: one for the reboiler, one for the packed stripping column and one for the reflux condenser. The diameter of the stripping column is based on the required vapour and liquid loads at the base of the column. Manufacturers' charts or standard sizes based on reboiler heat duty may also be used to determine the column diameter. Alternatively the following approximate equation can be used: **diameter (in.)** =  $9(\text{glycol circulation, gpm})^{0.5}$ . Conservative design and field tests data dictate that the packed section should be at least 4 ft high, and that this height be increased to 8 ft for a MMBtu/hr unit. These are recommendation for small units and where ceramic saddles are used. In case structured packing is used, suppliers (e.g., Koch-Glitch) should be consulted for the height and diameter consideration.

Stripping gas is normally used only when increased lean glycol concentration above 98.5 to 98.9 is desired, which can be reached with normal reboiler temperature and back pressure on the column. If the glycol circulation rate must be increased above design on an existing unit and the reboiler cannot reach the desired temperature, it is often possible to use stripping gas to achieve the desired lean glycol concentration. **Figure 20-64** of the GPSA data book shows the effect of stripping gas on lean glycol concentration (see also the slide).

**Reboiler.** Reboiler duty may be estimated by the following equation:  $Q_R \text{ in Btu/lb water} = 900 + 966 (\text{gal TEG/lb water})$  this estimate does not include stripping gas and makes no allowance for combustion efficiency. Alternatively the following simple equation may be used to estimate reboiler duty:  $Q \text{ in Btu/hr} = 1500 \text{gph}$ , where **gph** is the flow rate of glycol in gallons per hour. Use the following guidelines to size the reboiler: (1) design duty is calculated requirement duty plus 5% of the condenser and glycol exchange duties; (2) vapour disengagement area is based on 14,000 Btu/hr.ft<sup>2</sup> heat flux across the vapour liquid interface; (3) reboiler shell L/D ratio is 5; (4) Minimum diameter *D* is 1.5ft, minimum length *L* = 3.5 ft. Standard units are available for small sizes. Reboiler temperature should be kept below TEG decomposition temperature (400°F); a temperature range of 370-390°F is usually used. This effectively limits the lean glycol temperature to between 98.5 and 98.9%. When higher lean glycol concentrations are required, stripping gas can be used or reboiler should be run under vacuum. Pressure above atmospheric in the reboiler can significantly reduce lean glycol concentration and dehydration efficiency. The column should be adequately vented and the packing replaced periodically to prevent excess back pressure on the reboiler. At pressure below atmospheric pressure (vacuum) the boiling point of the rich glycol/water mixture decreases, and a greater lean glycol concentration is possible at the same reboiler temperature. Reboilers are rarely operated at a vacuum in field gas installation, because the added complexity and the fact that any air leaks will result in glycol degradation. In addition it is always less expensive to use stripping gas. If a lean concentration of 99.5% is required, consider using a reboiler pressure of 500 mmHg(10 psia) as well as using stripping gas. As mentioned before a heat flux of between 6,000 to 8,000 Btu/hr.ft<sup>2</sup> is used to size the fire tube.

## Natural Gas Dehydration- Glycol Absorption: Design Guidelines



**Heat Exchangers.** Typically three following heat exchangers are used. These units may be designed using conventional design procedures. Typical guidelines are as follows:

**Reflux condenser.** design duty is calculated as design requirement plus 5% for fouling and flow variations

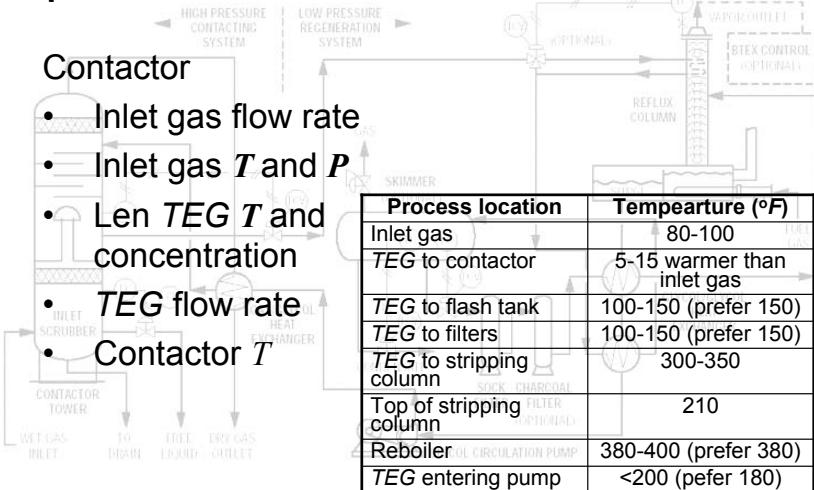
**Lean-rich glycol HX.** (1) design duty is calculated as design requirement plus 5% for fouling and flow variation; (2) the entering temperatures of lean and rich glycol streams are known; a hot end (lean glycol in-rich glycol out) temperature approach of 60 °F maximizes the preheat of the rich glycol; (3) two or more heat exchangers should be placed in series to avoid any temperature cross. In smaller units, the exchanger may be replaced by a surge tank and heat transfer coil. The shell volume is based on a 30-min retention time, and  $L/D = 1.5 \text{ ft}$ ,  $L = 3.5 \text{ ft}$ .

**Lean glycol cooler.** the lean glycol outlet temperature should be 5 to 10 °F warmer than the inlet gas temperature to contactor. Therefore, the lean glycol is cooled from 180-200 °F to 110-120 °F. This may be accomplished in (1) a double pipe exchanger for smaller units (<25 MMscfd), and (2) an aerial, fin-fan exchanger or water-cooled, shell and tube exchanger for larger units. Again the design heat duty must provide for a 5 to 10% allowance for fouling and flow variations.

## Natural Gas Dehydration- Glycol Absorption: Operations

### Contactor

- Inlet gas flow rate
- Inlet gas  $T$  and  $P$
- Lean TEG  $T$  and concentration
- TEG flow rate
- Contactor  $T$



A correctly designed and properly operated TEG unit will dehydrate natural gas with only minor difficulty. The table shown on this slide summarizes the important operating temperatures. The potential ease of operation often leads to the glycol unit being virtually ignored. Millions of dollars may be wasted because of high glycol losses, excessive TEG recirculation rates, improperly operating pumps, needless energy consumption, frequent plant shutdowns, and excessive equipment replacement. It is very important to know at what conditions the individual pieces of process equipment should work. Let's start with the contactor tower.

**Contactor tower.** The operating efficiency of the glycol-gas contactor depends on the inlet gas flow rate, temperature, and pressure as well as on the lean glycol concentration. The effect of these variables are now discussed.

**Inlet gas flow rate.** Obviously the load (lb water to be removed/hr) varies directly with the feed gas flow rate. Increases in gas flow rate, especially for trayed towers can create very detrimental effect on the performance of the tower. Structured packing is not susceptible to blowing fluid from the trays because the fluid flows as wetted film on the packing surface. Most towers are conservatively designed to handle flowrates 5 to 10% , and sometimes up to 20% above capacity. The lower flow limits is determined by the aforementioned over-design and the approximate 5 to 1 turn down ratio of the bubble caps.

**Inlet gas  $T$  and  $P$ .** The inlet gas may be assumed to enter the contactor saturated with water vapour; therefore, its water content and quantity of water to be picked up by the glycol depend on the inlet gas  $T$  and  $P$ . Using McKetta charts (**Figure 20-3 GPSA**) shows that at 1000 psia, the water content increases from 33 to 62 to 102 lb/MMscf as the temperature increases from 80 to 100 to 120°F. The pressure effect, while very significant, is not as sever: at 100°F the water content is 62, 72, and 87 lb/MMscf at 1000, 800, and 600 psia, respectively. An increase in gas inlet temperature or reduction of its pressure increases the load on the unit. Sudden change of pressure may also affect the glycol flow rate and damage the tower internals.

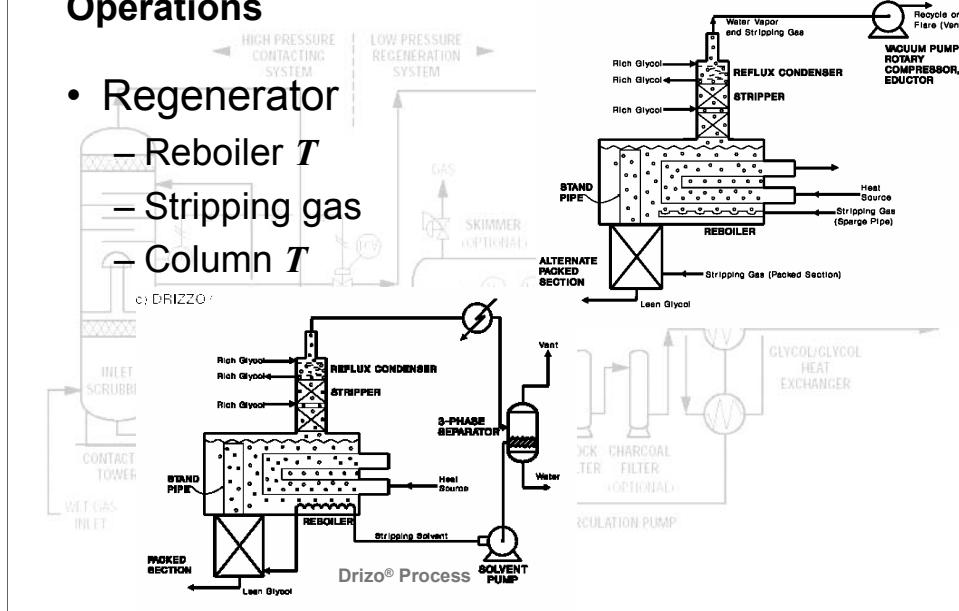
**Entering TEG temperature and concentration.** As we discussed before the drying ability of glycol depends on the amount of water in it. Drying ability of TEG increases dramatically with concentration (See GPSA charts, **Figures 20-55 to 20-59**). The equilibrium water dew point decreases with decreasing temperature (see GPSA **Figure 20-54**), but cooling the glycol increases the viscosity and its tendency to foam.

**Glycol circulation rate.** The water pick up by glycol increases with increasing inlet-glycol concentration, decreased glycol temperature, higher flow rate and the number of contactor trays. A glycol flow rate of 3 gal/lb water was commonly used in the past, however, recent energy conservation and environmental concerns (BTEX) have lowered the circulation to **2 gal/lb** water.

**Dehydration temperature.** While TEG can dehydrate natural gas at operating temperatures from 50 to 130 °F. The preferred temperature range is 80-100 °F. Below 70 °F the glycol is too viscous. This reduces tray efficiency, promotes foaming, and increases glycol losses. Below 50 °F the drop in dehydration efficiency is very pronounced. Above 10 °F the inlet gas contains too much water, and the drying ability of glycol is reduced. The inlet glycol temperature should be 5-15 °F above the gas temperature to reduce the chance of HC condensation which promotes foaming. If the glycol enters more than 15 °F above the effluent gas temperature, TEG vapourization losses and sales gas dew point are increased unnecessarily.

# Natural Gas Dehydration- Glycol Absorption: Operations

- Regenerator
  - Reboiler  $T$
  - Stripping gas
  - Column  $T$



While the degree of glycol reconcentration depends mainly on the reboiler temperature, additional reconcentration is readily obtainable by use of stripping gas. Glycol losses from the top of the stripping column can be minimized by temperature control.

**Reboiler temperature.** The concentration of water in the lean glycol leaving the reboiler varies with the reboiler temperature and pressure. Reboiler temperature was discussed in the design section.

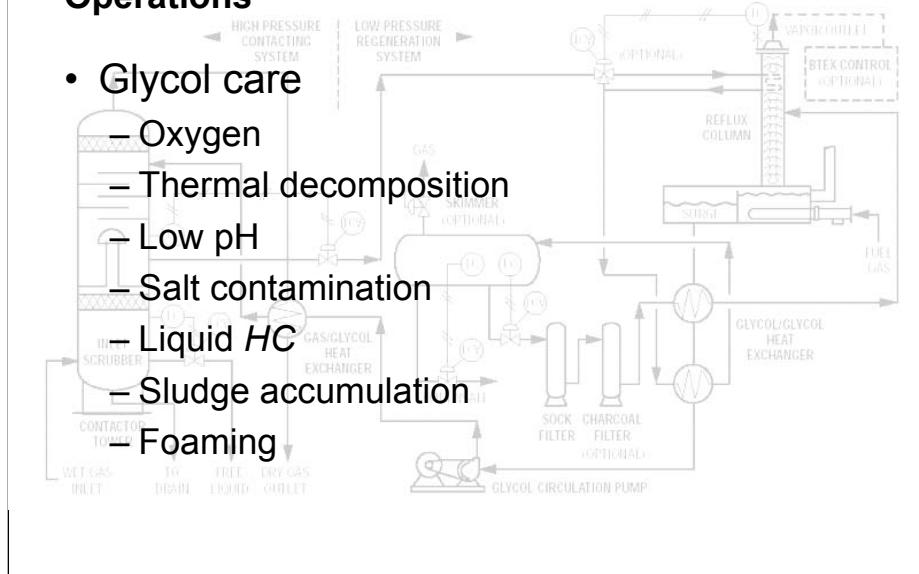
**Stripping gas.** As mentioned before if concentrations above 98.9% is required, stripping gas should be sparged directly into the reboiler as shown on this slide. Glycol concentration up to 99.6 or more can readily be achieved. Alternative more complicated concentration methods are (1) reducing the reboiler pressure with and ejector or vacuum pump; (2) Employing azeotropic distillation with iso-octane (**Drizo®** process); 99.99% pure TEG may be obtained by this process. Stripping gas effect was discussed in design procedure part.

Stripping column temperature. The temperature at the top of stripping column should be kept around 210°F, by varying the flow of rich glycol to a reflux generating, cooling coil located at top of the stripping column. If the temperature drops much below 200°F, water vapour condensation becomes excessive, which may flood the column, overfill the reboiler, increase column pressure, and blow liquids out the top vent. Glycol losses may increase if the temperature goes beyond 220°F as discussed before.

## Natural Gas Dehydration- Glycol Absorption: Operations

- Glycol care

- Oxygen
- Thermal decomposition
- Low pH
- Salt contamination
- Liquid HC
- Sludge accumulation
- Foaming



Similar to amine sweetening systems glycol is the main reagent for water removal from natural gas. Its care is of crucial significance in sound operation of the whole glycol dehydration unit. The key to avoiding many operating and corrosion problems is to keep the glycol clean. The major contamination problems have been identified as follows:

**Oxygen in system.** Sources of oxygen include storage tanks without inert gas blankets, leaking pumps, and -rarely- the inlet gas. A gas blanket consisting of a very small flow of fuel gas into the top of liquid storage tanks will keep air from entering vessel. Oxygen gradually reacts with glycol and degrades the solution. These degradation products are corrosive.

**Thermal degradation.** Glycols like amines degrade at high temperatures. Overheating can be avoided by keeping the reboiler temperature below 400°F, using heat fluxes less than 8,000 Btu/hr.ft<sup>2</sup>, and by checking the fire tube regularly for hot spots caused by deposits of tar and or salts. The hot spots are best observed in nights; if the flame is shut off, they continue to glow bright red.

**Low pH.** Solution in a glycol unit that is not downstream of an amine unit become acidic and corrosive, especially when the gas contains acid gases ( $H_2S$  and  $CO_2$ ). The optimum glycol pH is 7.0 to 8.5; a pH above 9.0 promotes foaming and emulsion formation. Corrosive acids formed by glycol decomposition or oxidation and dissolved acid gases can be neutralized by bases such as borax, triethanolamine (TEA), NACAP. These bases should be added slowly an in small amounts, e.g., 1 lb of amine/400 gallons of glycol, because excess base can precipitate while the glycol is being neutralized. The glycol pH should be checked weekly. Using pH meters or pH test papers.

**Salt contamination.** Salt deposits on the reboiler fire deposit cause hot spots and fire tube failures. The glycol should be drained and the unit cleaned when the salt level exceeds 2500 ppmw. Special equipment, such as a separate glycol reclaimer or ion exchange resin bed, is required for removing salt from TEG. Produced water should be prevented from entering the contactor by use of upstream filter separators.

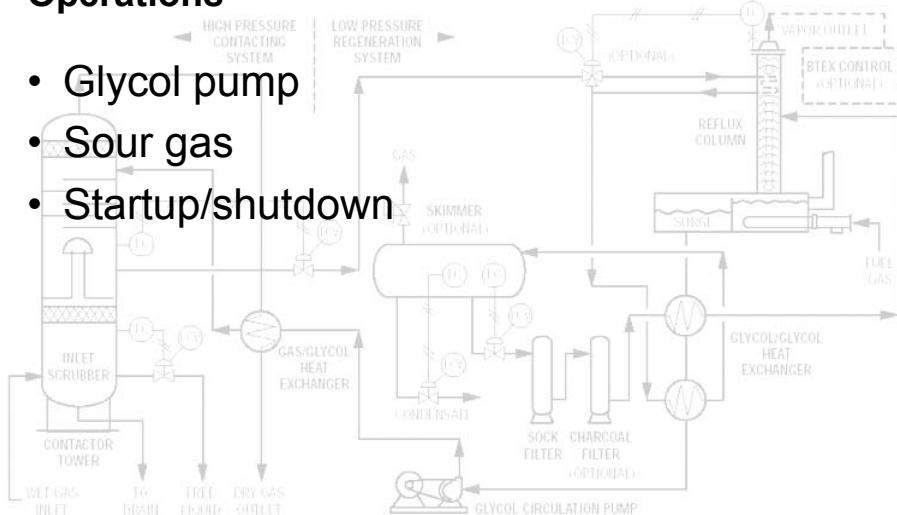
**Liquid hydrocarbons.** Liquid hydrocarbons are either entrained with inlet gas, are condensed by the lean glycol, entering contactor, colder than the sales gas, or simply absorbed from the gas by glycol. Hydrocarbon contamination should be minimized by scrubbing the inlet gas, keeping the lean glycol 10°F warmer than the sales gas, adequately sizing the three phase separator, and using carbon filtration. Liquid hydrocarbons if permitted to enter the stripper, flow down the column and flash rapidly in the reboiler and can blow liquid out of the stripper. In very cold climates, heat losses through the contactor walls can lead to HC condensation. Insulating and/or housing the contactor may be justified.

**Sludge accumulation.** Dust, sand, pipeline scale, reservoir fines, and corrosion products such as iron sulfide and rust are picked up by the glycol if not removed by the inlet separator or integral scrubber. These solids, together with tarry hydrocarbons (asphaltene), eventually settle out and form an abrasive, sticky, black gum which can erode the glycol pump and other equipment, plug the contactor trays and packing in the stripper, and deposit on the fire tubes. Proper filtration of both the rich and lean glycol streams should keep the **solids concentration below 0.01 weight percent**.

**Foaming.** Foaming may be mechanical or chemical. **Mechanical foaming** is caused by excessive-high gas flow rates in the contactor. Contaminants such as solid particles, salts, corrosion inhibitors, and liquid hydrocarbons cause **chemical foaming**. Foaming is best detected by monitoring pressure drop across the contactor. Erratic readings followed by a sudden increase of 2 to 5 psi are symptom of foaming. As mentioned in amine sweetening contaminants are the major cause of foaming. Sources of contaminants should be identified and the problem is treated accordingly. Glycol foaming and amine foaming have very similar symptoms and sources (see amine troubleshooting for further details). Glycol reclamation is recommended when foaming cannot be controlled by conventional techniques such as careful monitoring, elimination of contaminants and their sources, use of three phase flash sepoarator and maintannce of pH between 7 and 8, and injection of reasonable amount of antifoam agents.

## Natural Gas Dehydration- Glycol Absorption: Operations

- Glycol pump
- Sour gas
- Startup/shutdown



**Glycol pump.** Proper pump care is essential; when the pump fails there is no circulation and no dehydration. Pumps are heart of any process system and without a healthy heart the process is always in trouble and may finally die out (shut-down). A stand by pump should always be included, and small replacement parts should be available. The manufacturers' instruction should be followed when installing new packing. Packing is dry when new and will probably absorb glycol and expand. If installed too tightly, the packing will not receive enough lubrication from glycol and may burn and score the plungers. In glycol powered pumps, the high-pressure, rich glycol can leak through the internal seal rings and dilute the low-pressure, reconcentrated glycol. This internal leakages leading to contamination may be detected by sampling the lean glycol as it enters and leaves the pump.

**Sour gas.** TEG is being used successfully to dry both natural gases containing  $H_2S$  and  $CO_2$  and pure  $CO_2$  streams. The presence of  $H_2S$  and/or  $CO_2$  requires: (1) The water content of the incoming sour natural gas stream must be carefully determined because sour gases have an increased capacity for water (see *phase behavior of hydrocarbon-water systems* discussed before); (2) both  $H_2S$  and  $CO_2$  are more soluble than methane in glycol and the absorbed acid gases should be removed from glycol. The glycol-gas flash separator suffices when acid gas concentrations are not too high. Better stripping of the acid gas from the sour glycol may be required to control reboiler corrosion and/or environmental pollution; (3) the pH of the TEG solution must be monitored closely. Frequent addition of bases and buffers (e.g., amines and Nacap) may be required.

**Startup and Shutdown.** Following **startup procedure** is recommended for glycol units: (1) purge system with inert gas or natural gas; (2) pressure contactor slowly; (3) start pump and establish glycol circulation through the contactor and regenerator; (4) establish fire in the reboiler and bring bath temperature up slowly; (5) establish gas flow through contactor slowly, taking care not to blow the glycol off the trays; (6) adjust controls for desired operating conditions. In cold climates the TEG solution must be heated to 100 °F before starting circulation – glycol at 0 °F cannot be pumped. A cold startup can be expected by bypassing the glycol-glycol heat exchanger until the glycol warms up.

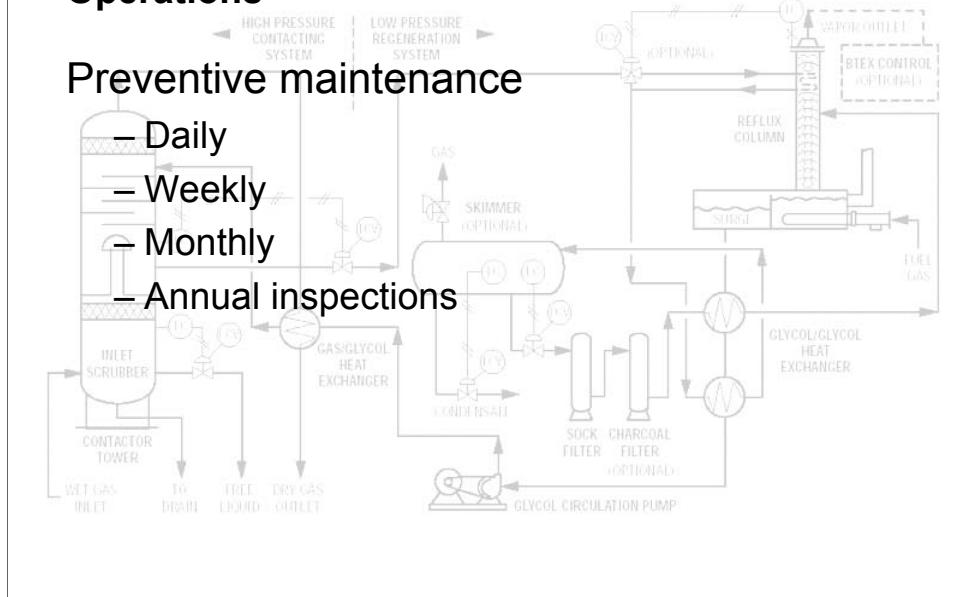
The following recommended **shutdown procedure** helps to avoid localized overheating and subsequent decomposition of glycol: (1) shut off the gas and close inlet and outlet valves to the contactor; (2) shut off heat to the reboiler and close burner manifold valves; (3) circulate glycol until reboiler temperature drops to 175 °F. Gradual increase of reflux ratio by letting more rich glycol going to the reflux coil helps to cool the reboiler more quickly; (4) stop glycol pump and close appropriate valves; (5) bleed off pressure in the contactor slowly. During extended downtimes, perform the following maintenance: (1) flush absorber and regenerator with water and drain; (2) clean pumps; (3) remove packing from the pumps and coat plungers with rust inhibitors.

Preventive maintenance.

# Natural Gas Dehydration- Glycol Absorption: Operations

## Preventive maintenance

- Daily
- Weekly
- Monthly
- Annual inspections



Preventive maintenance reduces costs. The goal is to repair equipment only when needed; early diagnosis of troubles is the best approach. Such diagnosis require thorough online inspections and servicing, and diligent record keeping.

**Daily inspections** should include: (1) check controllers for proper operation; (2) replace broken thermometers and pressure gages; (3) measure and record: sales gas flowrate an dew-point, contactor temperature and pressure, glycol circulation rate (pump stroke/min), glycol temperature at top of contactor, glycol temperature entering pump, reboiler bath temperature, stripper top temperature. In addition if required: (1) add glycol to surge tank; note time and amount added; (2) replace filters when pressure differential reaches 10 psi for soft cartridges and 25 psi for rigid cartridges; (3) replace strainers when plugged; (4) repair leaks

**Weekly inspection** include sampling glycol from the storage tank or the filter drains upstream of the glycol pump and check for the following: (1) fine black particles which settle when shaken –this FeS or  $Fe_3O_4$  precipitates indicates ongoing corrosion and potential failure of the filter; (2) smell the sample carefully (if acid gases are present special care should be taken); a sweet, aromatic odor like burnt sugar or overripe banana suggest thermal degradation; (3) check the flow characteristics of the sample. A black, thick, viscous solution indicates that heavy HCs are being absorbed from the gas; (4) check for an oily layer floating on the glycol which also indicates that heavy, nonvolatile HCs are being condensed. Such evidence of glycol contamination should be confirmed by a complete glycol analysis.

**Monthly inspection.** Every month or sooner if contamination is suspected, the glycol should be sampled and analyzed for hydrocarbons, water, solids, iron, chlorides, specific gravity, pH, and if deemed appropriate, glycol components analysis. The following conclusion may arise from such a glycol analysis: low pH due to glycol decomposition and corrosion; hydrocarbon presence due to faulty carbon filters and problem in flash tank; low specific gravity and water presence due to problems in regenerator; high solid due to corrosion, glycol decomposition, filter failure, carry over from inlet separator and corrosion; high iron due to corrosion; high chloride due to brine carry over from separator, scrubber. Monthly inspection also include sampling both the lean and rich glycol streams and comparing with optimum values. A check on surge tank and glycol makeup is worthwhile also. Reclaimed glycol should be checked thoroughly before re-use. Virgin glycol is recommended for makeup (99% TEG with less than 1% EG, DEG, and TREG and buffered with pH 7-8). Contaminated glycol should be checked fro foaming and a suitable defoamer found. The defoamer should be added until the source of contamination has been identified and removed.

The ideal time for cleaning is when the unit is shutdown fro repairs. A good cleaning job can improve plant operation greatly, however a poor job can severely contaminate the glycol for a long time. The best approach is to sample the contaminants and see what dissolves the deposits. Recommended solutions are: hot water for salts, acid wash followed by neutralization with caustic or sodium carbonate and rinse with hot water for rust and FeS, hydrocarbon solvent or acetone for tarry deposits. Temperature of 140-150°F and high circulation rates improve the cleaning process.

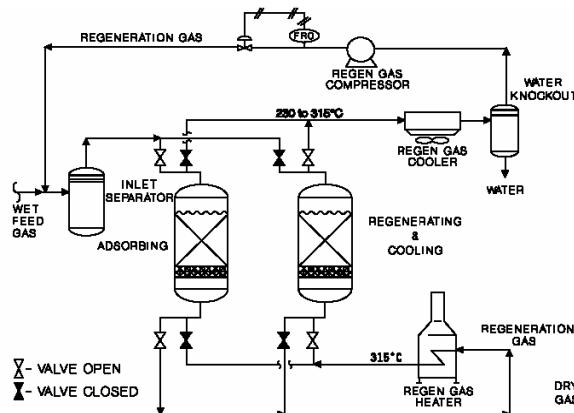
Hot spots and subsequent burnout of reboiler fire tubes are caused by improper firing and/or deposits on the outside of the tubes. Adjust burner controls monthly and clean the reboiler thoroughly **once a year**.

# Natural Gas Dehydration- Glycol Absorption: Troubleshooting

- |  |   |
|--|---|
| <ul style="list-style-type: none"> <li>• High exit gas dew-point</li> <li>• High glycol loss (should be &lt; 0.1 gal/MMscf)           <ul style="list-style-type: none"> <li>– Loss from contactor</li> <li>– Loss from stripping column</li> <li>– Loss from separator</li> <li>– Leaks and spills</li> </ul> </li> <li>• Glycol contamination</li> <li>• Poor glycol regeneration</li> </ul> | <ul style="list-style-type: none"> <li>• Low glycol circulation</li> <li>• High pressure drop across contactor</li> <li>• High stripping column temperature</li> <li>• High reboiler pressure</li> <li>• Firtube fouling/ hotspots/ burnout</li> <li>• Low reboiler temperature</li> <li>• Flash separator failure</li> </ul> |
|--|---|

- |  |   |
|--|---|
| <ol style="list-style-type: none"> <li>1. High exit gas dew-point           <ul style="list-style-type: none"> <li>• Change in gas rater, T and P</li> <li>• Low glycol rate (&lt;1.5gal/lb water)</li> <li>• Poor regeneration</li> <li>• (off design operating condition</li> <li>• Faulty inlet separator</li> </ul> </li> <li>2. High glycol loss (should be ~ 0.1 gal/MMscf)           <ul style="list-style-type: none"> <li>• Loss from contactor               <ul style="list-style-type: none"> <li>✓ Inlet separator passing liquids</li> <li>✓ Foaming in contactor</li> <li>✓ Mist eliminator plugged or too close to top tray</li> <li>✓ Lean glycol too hot</li> <li>✓ Plugged contactor trays</li> <li>✓ Excessive gas velocity in contactor</li> <li>✓ Tray spacing not enough</li> </ul> </li> <li>• Loss from stripping column               <ul style="list-style-type: none"> <li>✓ Too much stripping gas</li> <li>✓ Flash tank passing condensate</li> <li>✓ Broken, dirty, plugged tower packing</li> <li>✓ Insufficient reflux or too high T at stripper overhead</li> </ul> </li> <li>• Loss from separator (dumped glycol with HC)</li> <li>• Leaks and spills (check piping, fitting, valves and gaskets, pumps, etc.)</li> </ul> </li> <li>3. Glycol contamination           <ul style="list-style-type: none"> <li>• Oil carry over (e.g., compressor lube, etc.), brine, corrosion inhibitors, well treating chemicals,, sand, corrosion scale, from inlet separator</li> <li>• Oxygen leak and low pH control</li> <li>• Glycol overheating in reboiler, hot spots</li> <li>• Improper filtration, plugged filters, filter bypassing</li> <li>• Improper cleaning of glycol unit</li> </ul> </li> <li>4. Poor glycol regeneration           <ol style="list-style-type: none"> <li>1. Low reboiler T and/or stripping gas</li> <li>2. Leak in lean/rich glycol HX or glycol pump</li> <li>3. Overloaded or fouled reboiler, low (Btu) fuel</li> <li>4. Dirty or broken packing or foaming in tower</li> <li>5. High pressure or flooding in tower</li> </ol> </li> </ol> | <ol style="list-style-type: none"> <li>5. Low glycol circulation           <ul style="list-style-type: none"> <li>• Check for plugged strainers, lines, filters</li> <li>• Vapour lock in lines and pump</li> <li>• Low level in accumulator</li> <li>• Excessive packing gland leakage</li> <li>• Contactor pressure too high</li> </ul> </li> <li>6. High pressure drop across contactor           <ul style="list-style-type: none"> <li>• Off-design operation</li> <li>• Excessive gas rate</li> <li>• Plugged trays and/or demister, glycol foaming</li> </ul> </li> <li>7. High stripping column temperature           <ul style="list-style-type: none"> <li>• Low reflux or leaking reflux coil</li> <li>• Flooded column or foaming</li> <li>• Light HC carryover in rich glycol</li> </ul> </li> <li>8. High reboiler pressure           <ul style="list-style-type: none"> <li>• Broken or plugged (dirt and tar) packing</li> <li>• Restricted vent line</li> <li>• Excessive boilup rate or excessive reflux</li> <li>• Lug of light HC enters stripper</li> </ul> </li> <li>9. Firtube fouling/ hotspots/ burnout           <ul style="list-style-type: none"> <li>• Salt, solids, dust and scale on fire tube</li> <li>• Coke , tar deposition due to overheating</li> <li>• Glycol level drops exposing firtubes – low level shutdown</li> </ul> </li> <li>10. Low reboiler temperature           <ul style="list-style-type: none"> <li>• Small fire tube, or reboiler</li> <li>• Controller set-point too low (&lt;375°F)</li> <li>• Inaccurate thermometer</li> <li>• Water carry over from inlet separator</li> </ul> </li> <li>11. Flash separator failure           <ul style="list-style-type: none"> <li>• Check level control and dump valves</li> <li>• Excessive circulation</li> </ul> </li> </ol> |
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## Natural Gas Dehydration- Solid desiccants



**Example Solid Desiccant Dehydrator Twin Tower System (Source: GPSA)**

### SOLID DESICCANT DEHYDRATION

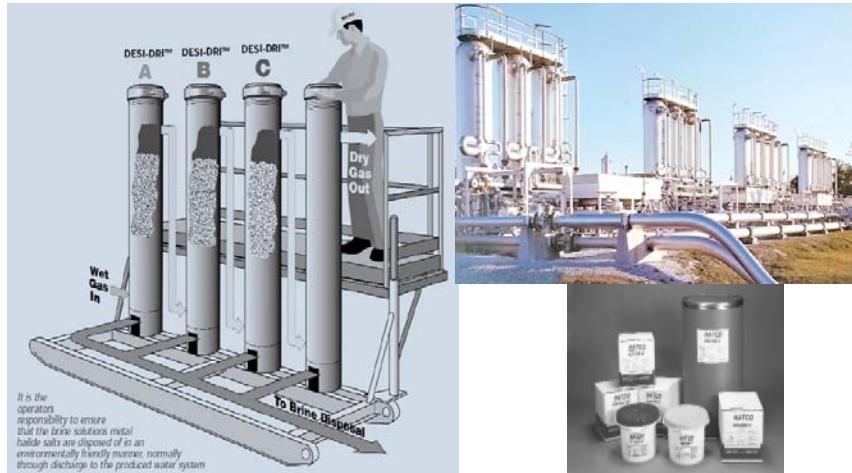
There are several solid desiccants which possess the physical characteristic to adsorb water from natural gas. These desiccants generally are used in dehydration systems consisting of two or more towers and associated regeneration equipment. See figure shown on this slide for a simple two-tower system. One tower is on stream adsorbing water from the gas while the other tower is being regenerated and cooled. Hot gas is used to drive off the adsorbed water from the desiccant, after which the tower is cooled with an unheated gas stream. The towers are switched before the on-stream tower becomes water saturated. Solid desiccant units generally cost more to buy and operate than glycol units. Therefore, their use is typically limited to applications such as high H<sub>2</sub>S content gases, very low water dew-point requirements, simultaneous control of water and hydrocarbon dew-points, and special cases such as oxygen containing gases, etc. In processes where cryogenic temperatures are encountered, solid desiccant dehydration usually is preferred over conventional methanol injection to prevent hydrate and ice formation. Solid desiccants are often used for the drying and sweetening of NGL liquids. Desiccants in common commercial use fall into one of three categories:

1. *Gels* – alumina or silica gels manufactured and conditioned to have an affinity for water.
2. *Alumina* – a manufactured or natural occurring form of aluminum oxide that is activated by heating.
3. *Molecular Sieves* – manufactured or naturally occurring aluminosilicates exhibiting a degree of selectivity based on crystalline structure in their adsorption of natural gas constituents.

**Silica Gel** is a generic name for a gel manufactured from sulfuric acid and sodium silicate. It is essentially pure silicon dioxide, SiO<sub>2</sub>. It is used for gas and liquid dehydration and hydrocarbon (i-C<sub>5</sub><sup>+</sup>) recovery from natural gas. When used for hydrocarbon removal, the units are often called **HRUs (Hydrocarbon Recovery Units)** or **SCUs (Short Cycle Units)**. When used for dehydration, *silica gel* will give outlet dew-points of approximately -76°F (-60°C). **Alumina** is a hydrated form of alumina oxide (Al<sub>2</sub>O<sub>3</sub>). It is used for gas and liquid dehydration and will give outlet dew-points in the range of -94°F (-70°C). Less heat is required to regenerate alumina than for molecular sieve, and the regeneration temperature is lower. However, molecular sieves give lower outlet water dew-points. **Molecular sieves** are a class of aluminosilicates and possess the highest water capacity, will produce the lowest water dew-points, and can be used to simultaneously sweeten and dry gases and liquids. Their equilibrium water capacity is much less dependent on adsorption temperature and relative humidity. They also are usually more expensive. Molecular sieve dehydrators are commonly used ahead of *NGL* recovery plants designed to recover ethane. These plants typically operate at very cold temperatures and require very dry feed gas to prevent formation of hydrates. Dehydration to a -148°F (-100°C) dew-point is possible with molecular sieves. Water dew-points less than -148°F (-100°C) can be accomplished with special design and strict operating parameters. The table presents the important properties of commercial solid desiccants.

Desiccant	Shape	Bulk Density kg/m <sup>3</sup>	Particle Size	Heat Capacity kJ/(kg • K)	Approx. Minimum Moisture Content of Effluent Gas (mg/kg)
Alumina Gel Alcoa H-151	Spherical	830	6 mm	0.840	5-10
Activated Alumina Alcoa F-1	Granular	830	6-2 mm		0.1
Silica Gel Sorbead®-R	Spherical	785	5-2 mm	1.050	5-10
Silica Gel Sorbead®-H	Spherical	720	7-2 mm	1.050	5-10
Mole Sieve Davison-4A	Spherical	670-720	5-2 mm or 2-1 mm	1.000	0.1
Mole Sieve Linde-4A	Extruded Cylinder	640-705	3 or 1.5 mm	1.000	0.1

## Natural Gas Dehydration- Solid desiccants



**Natco's solid desiccant beds**

The continuous process requires two (or more) vessels with one on-line removing water while the other is being regenerated. Generally a bed is designed to be on-line in adsorption for 8 to 24 hours. When the bed is taken off-line, the water is removed by heating the sieve to 450-600°F (230-320°C), depending on the desiccant used and the performance specification. The regeneration gas used to heat the bed is usually a slipstream of dry process gas. The regeneration gas is returned to the process after it has been cooled and the free water removed. Any heat source can be used including waste heat from engines and turbines. This is an important design consideration since heat is often a major operating cost.

Gas flow during adsorption is typically downflow. This allows higher gas velocities (thus smaller diameter towers) since bed fluidization is avoided. Regeneration gas flow is up flow during the heating cycle. In that way, any residual water left on the desiccant will be at the top of the bed and will not affect the effluent dew-point when adsorption is resumed. In addition, upflow heating helps to strip any contaminants from the top of the bed extending desiccant life. Regeneration gas flow during the cooling cycle may be upflow if the gas is completely free of water. This saves two switching valves per tower which can significantly reduce capital costs. If the cooling gas contains water, cooling flow should be downflow to avoid preloading of the desiccant at the bottom of the bed with water.

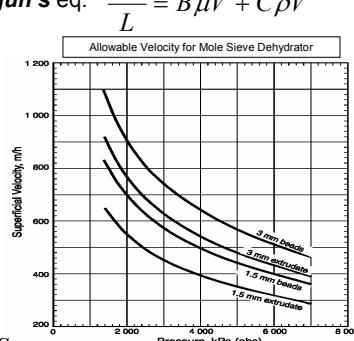
## Natural Gas Dehydration- Solid desiccants: Design

- Allowable gas superficial velocity
- Pressure drop - vessel diameter: **Ergun's eq.**

Particle type	B	C
1/8" bead	0.056	0.0000889
1/8" extrudate	0.0722	0.000124
1/16" bead	0.152	0.000136
1/16" extrudate	0.238	0.000210

- Cycle time (6-8 hours)
- Bed length: Saturation Zone ( $L_s$ ) and Mass Transfer Zone heights ( $L_{MTZ}$ )

$$S_s = \frac{W_r}{0.13(C_{ss})(C_T)} \quad \text{and} \quad L_s = \frac{4S_s}{\pi D^2(\text{bulk density})}$$



### Design

The allowable superficial velocity through the bed is the first parameter that must be estimated. The pressure drop through the bed is related to the superficial velocity by a modified **Ergun** equation:

$$\frac{\Delta P}{L} = B\mu V + C\rho V^2$$

Where,  $\Delta P$  is pressure drop in psi,  $L$  is bed height in ft.,  $B$  and  $C$  are constant for particles shape and size as given on the slide,  $\mu$  is gas viscosity in cp,  $\rho$  is gas density in lb/ft<sup>3</sup>, and  $V$  is superficial gas velocity in ft/min. **Fig. 20-69** of GPSA data book shown on this slide was derived from the **Ergun's** equation assuming a gas composition and setting  $\Delta P/L$  equal to 0.33 psi/ft (7.50 kPa/m). The design pressure drop through the bed should be about 5 psi (35 kPa). A design pressure drop higher than 8 psi (55 kPa) is not recommended as the desiccant is fragile and can be crushed by the total bed weight and pressure drop forces. Remember to check the pressure drop after the bed height has been determined. Once the allowable superficial velocity is estimated, calculate the bed diameter using the following equation:  $D=(4q/\pi V)^{0.5}$ , where  $D$  is diameter in ft.,  $q$  volumetric gas flow rate in actual conditions in ft<sup>3</sup>/min.

The next step is to choose a cycle time and calculate the mass of desiccant required. **Eight to twelve hour cycles** are common. Cycles of greater than 12 hours may be justified especially if the feed gas is not water saturated. Long cycles mean less regenerations and longer sieve life, but larger beds and additional capital investment.

During the adsorption cycle, the bed can be thought of as operating with three zones. The top zone is called the **saturation** or **equilibrium zone**. The desiccant in this zone is in equilibrium with the wet inlet gas. The middle or **mass transfer zone (MTZ)** is where the water content of the gas is reduced from saturation to < 1 ppmv. The bottom zone is unused desiccant and is often called the **active zone**. If the bed operates too long in adsorption, the mass transfer zone begins to move out the bottom of the bed causing a "breakthrough". At breakthrough, the water content of the outlet gas begins to increase and will eventually reach feed gas water content when the **MTZ** is completely displaced. Both water capacity and the rate at which solid desiccants adsorb water decline as the material ages. The object of the design is to install enough desiccant such that after three to five years, the mass transfer zone will be at the bottom of the bed at the end of the adsorption cycle. In the saturation zone, molecular sieve is expected to hold approximately 13 lb (kg) of water per 100 lb (kg) of sieve. New sieve will have an equilibrium capacity near 20%; 13% represents the approximate capacity of a 3-5 year old sieve. This capacity needs to be adjusted when the gas is not water saturated or the temperature is above 75°F (24°C). See **Fig. 20-70** and **20-71** of GPSA data book to find the correction factors for molecular sieve. To determine the mass of desiccant required in the saturation zone, calculate the amount of water to be removed during the cycle and divide by the effective capacity.

$$S_s = \frac{W_r}{0.13(C_{ss})(C_T)} \quad \text{and} \quad L_s = \frac{4S_s}{\pi D^2(\text{bulk density})} \quad \text{Eq. 20-11 (GPSA)}$$

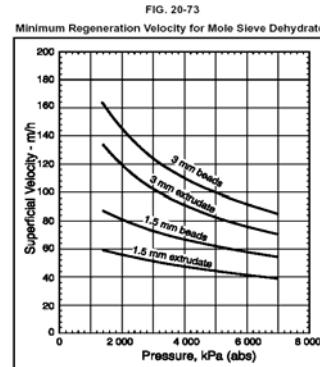
Where  $S_s$  is amount of molecular sieve in saturation zone,  $L_s$  length of packed bed in saturation zone,  $W_r$  is water removed per cycle in lb,  $C_{ss}$  and  $C_T$  are correction factors from **Fig's. 20-70 and 20-71**, Molecular sieve bulk density is 42-45 lb/ft<sup>3</sup> (670-720 kg/m<sup>3</sup>) for spherical particles and 40-44 lb/ft<sup>3</sup> (640-700 kg/m<sup>3</sup>) for extruded cylinders. Even though the **MTZ** will contain some water (approximately 50% of the equilibrium capacity), the saturation zone is estimated assuming it will contain all the water to be removed.

## Natural Gas Dehydration- Solid desiccants: Design (cont.)

- Length of mass transfer zone

$$L_{MTZ} = (V/35)^{0.3} (Z)$$

- Bed regeneration
  - Heat duty
  - Regeneration gas rate
- General comments on using



The length of the mass transfer zone can be estimated as follows:  $L_{MTZ} = (V/35)^{0.3} (Z)$ , Where:  $Z = 1.70$  for 1/8" (3 mm) sieve and 0.85 for 1/16" (1.5 mm) sieve. The total bed height is the summation of the saturation zone and the mass transfer zone heights. Approximately **six feet free space above and below the bed is needed** to insure proper gas distribution. A second method uses Eq. 20-11, but replaces the saturation capacity of 13% with an "effective desiccant capacity" which includes the *MTZ* effect, temperature, and relative humidity corrections. When using this method, an effective capacity of 8-10% is typically assumed. This method is adequate for most planning and feasibility calculations.

### Regeneration Calculations

The first step is to calculate the total heat required to desorb the water and heat the desiccant and vessel. A 10% heat loss is assumed:

$$Q_w = (1800 \text{ Btu/lb}) (\text{lbs of water on bed})$$

$Q_w$  = desorption of water heat duty (**Btu**)

$$Q_{si} = (\text{lb of sieve})(0.24 \text{ Btu/lb.}^{\circ}\text{F})(T_{rg} - T_p)$$

$Q_{si}$  = duty to heat mole sieve to regeneration temp. (**Btu**)

$$Q_{st} = (\text{lb of steel})(0.12 \text{ Btu/lb.}^{\circ}\text{F})(T_{rg} - T_p)$$

$Q_{st}$  = duty to heat vessel and piping to regeneration temp. (**Btu**)

$$Q_{hl} = (\text{heat loss}) = (Q_w + Q_{si} + Q_{st})(0.1)$$

$Q_{hl}$  = regeneration heat loss (**Btu**)

$$Q_{tr} = 2.5 (Q_w + Q_{si} + Q_{st} + Q_{hl})$$

$Q_{tr}$  = Total regeneration heat duty (**Btu**)

For determination of the regeneration gas rate, calculate the total regeneration load; the **2.5 factor** corrects for the change in temperature difference (**out - in**) across the bed with time during the regeneration cycle. The heating time is usually 50% to 60% of the total regeneration time which must include a cooling period. For **8 hour adsorption cycles**, the regeneration normally consists of 4 1/2 hours of heating, 3 hours of cooling and 1/2 hour for standby and switching. For longer cycles the heating time can be lengthened as long as a minimum pressure drop of 0.01 psi/ft (230 Pa/m) is maintained. The mass flow rate of regeneration gas is calculated using the following equation:

$$m_{rg} = Q_{tr}/(C_p)(600^{\circ}\text{F}-T_i)(\text{heating time}), \text{ where } m_{rg} \text{ is in lb/hr, } C_p \text{ is gas heat capacity in Btu/lb.}^{\circ}\text{F and } T_i \text{ is bed initial temperature.}$$

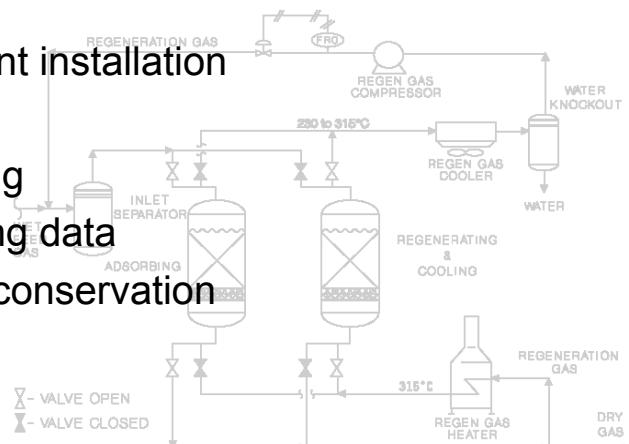
**Fig. 20-73** of GPSA data book shown on this slide can be used to estimate the required minimum velocity to meet 0.01 psi/ft (230 Pa/m).

### General Comments

The regeneration cycle frequently includes depressuring/repressuring to match the regeneration gas pressure and/or to maximize the regeneration gas volume to meet the velocity criterion. Some applications, termed pressure swing adsorption, regenerate the bed only with depressurization and sweeping the bed with gas just above atmospheric pressure. Moisture analyzers for very low water contents require care to prevent damage to the probes. When inserted into the beds, sample probes and temperature probes must be installed to reach the center of the gas phase. Solid desiccant towers are insulated externally or possibly internally. Internal refractory requires careful installation and curing, usually before the desiccant is installed. It saves energy but the greatest benefit is it can dramatically reduce the required heating and cooling times. This is often an important benefit for systems where regeneration times are limited. The primary disadvantage is the potential for wet gas bypassing the desiccant through cracks and defects in the insulation during the adsorption cycle. Bottom bed support typically includes three to five layers of inert ceramic balls in graduated sizes (smallest on top). On top of the bed, a hold-down screen is provided, again covered with a layer of ceramic balls. In some cases, a layer of less expensive desiccant can be installed on the top of the bed to catch contaminants such as free water, glycol, hydrocarbons, mines, etc. This may extend the bed life. Good inlet separation of entrained contaminants is absolutely essential for long desiccant life. Since solid desiccants can produce dust, 1  $\mu\text{m}$  filters are frequently installed at the outlet of the dehydration unit to protect downstream equipment. Operating performance should be monitored periodically to adjust adsorption cycle length so that adequate dehydration is obtained. Performance tests are scheduled on a routine basis, ranging from monthly during early operations to six months or longer. The size of the unit and frequency of regeneration cycles also affect the timing of performance tests.

## Natural Gas Dehydration- Solid desiccants: Operations

- Desiccant installation
- Startup
- Switching
- Operating data
- Energy conservation



**Desiccant installation.** Desiccant should be loaded carefully and uniformly into the vessel using a cloth or plastic sock that reaches from the top loading nozzle to the bed supports at the bottom. The desiccant normally settles 5 to 7% during the first few weeks of operation. If desired, the vessel then can be topped with additional desiccant, and then the top screen and support balls can be installed

**Startup.** Good dry-out is essential. Hydrostatic testing makes dry-out, especially if internal insulation is used. First purge and drain all vessels, dead-ended piping, low spots, heat exchanger shells, etc. Methanol can be helpful.

**Switching.** If low pressure regeneration gas is used, *never re-pressure faster than 50 psi/min*. Notice that re-pressure and depressurization valves shown in the figure shown previously are positioned so as not to lift the bed.

**Operating data.** Adequate daily records are essential for troubleshooting. It is recommended to take the following data: (1) feed gas flow rate, pressure, and temperature at least daily; (2) complete feed gas analysis once a month; (3) Outlet gas humidity continuously if unit feeds cryogenic plant and at least once a shift if meeting pipeline spec.; (4) temperature profiles of the gas entering and leaving the regeneration tower for both heating and cooling; (5) the towers should be equipped with pressure drop taps so that the pressure drop across the desiccant bed can be monitored as required.

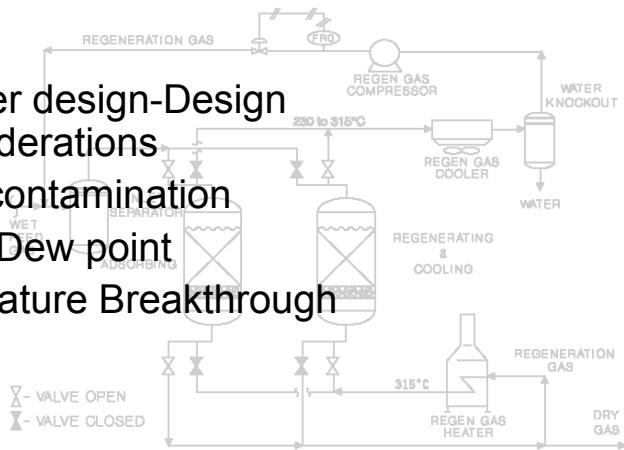
**Energy conservation.** A quick estimate of the regeneration heat duty requirements is that about *6,500 Btu is needed for every lb of water removed*. It is suggested to observe the following guidelines to conserve energy in solid bed desiccant units:

- (1) Use waste heat such as hot exhaust from gas turbines that drive the pressure boosting compressors. Safety considerations and operating problems can be involved;
- (2) The most popular cycle time is eight hours, but larger beds with 10-12 hour cycles are optimum;
- (3) Internal insulation of the solid bed can save 20-30% of the required energy. A two- to three-year payback time is possible;
- (4) Use a compressor to recycle the regeneration gas. This requires less energy than dropping the entire feed gas stream pressure across control valve in order to drive a slip stream through the regeneration loop (i.e., place recycle booster compressor upstream of the heater).
- (5) Desiccant capacity does decrease with use, and design is based on the relatively constant one-year to four-year old value. Therefore, when the desiccant is new, the dehydration cycle can and should be lengthened. Installing a sample probe near the bottom of the bed permits operation at the maximum cycle time.

Computer monitoring and control can contribute in saving energy in dehydration units. Thermocouples mounted along the tower wall are used to optimize both the drying and regeneration cycles. Maximum desiccant loading during drying and minimum regeneration heat can be realized

## Natural Gas Dehydration- Solid desiccants: Troubleshooting

- Proper design-Design considerations
- Bed contamination
- High Dew point
- Premature Breakthrough



Most solid desiccant units are reliable and require relatively little operating attention. However, poor design, operation, and maintenance can cause unnecessary expenses such as frequent desiccant change-outs, excessive plant shut downs, and equipment replacements. The proper design and other issue discussed below can make a solid bed system run more smoothly and without major operating problems.

**Design considerations.** Following design checklist is recommended for avoiding operating problems. Therefore if you are in the design team or checking a design make sure the following guidelines are taken into account: **(1)** can the unit handle the worst (largest) inlet water loading? **(2)** if dehydration and regeneration occur at different pressures, how will the desiccant beds be protected from excessive pressure swing? **(3)** will the selected switching valves prevent leakage of wet regeneration gas into dry gas? **(4)** Are the dehydration and regeneration gas flow rates designed for proper flow distribution? **(5)** Is the regeneration gas heater adequately sized for the maximum load? **(6)** How will any hydrocarbon liquids condensed in the regenerator cooler be handled? **(7)** Can the water in the regenerator gas cooler freeze? **(8)** Does the design include suitable temperature and water content monitors, recorders, and shutdown devices? **(9)** will chemical reactions between methane, hydrogen sulfide, carbon dioxide, mercaptans, and oxygen occur at the high regeneration gas temperature? **(10)** Has all equipment been inspected to verify compliance with design specifications? **(11)** Have all internals refractories been cured properly? **(12)** Has the desiccant been loaded according to vendor's recommendations

**Bed contamination.** The most frequent cause is incomplete removal of contaminants in the inlet gas separator. Another possibility is lubricating oil from compressors used to boost the regeneration gas pressure. Also, if the regeneration gas leaving the separator is mixed with the feed gas to dehydrator, then a separator malfunction can dump liquid hydrocarbons and water onto the desiccant.

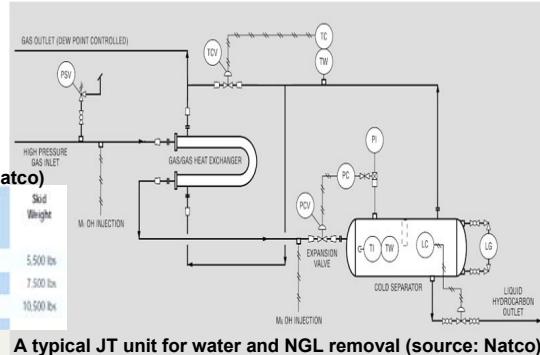
**High dew-point.** High dew-point is one of the two common problems that can occur and cause operating problems. Possible causes are: **(1)** "wet" inlet gas bypasses the dehydrator through cracks in the internal insulation. Cracks in a liner or in sprayed-on insulation can be detected by "hot spots" and peeling paint on the outer shell. Other symptoms are fast water breakthrough and an unusually rapid rise in the effluent gas temperature during regeneration. **(2)** Leaking valves also permit wet gas to bypass the dehydrators. Even a slight leak of hot gas usually produces detectable temperature rise in what should be the cold side of the valve. Ultrasonic leak detection transducers are also useful. **(3)** Incomplete desiccant regeneration; **(4)** Excessive water content in the wet feed gas due to increased flow rate (MMscfd), higher temperatures, and lower pressure.

**Premature Breakthrough.** Satisfactory dew-points are observed at the beginning but not for the entire duration of drying cycle. Desiccant capacity should decrease with use but should stabilize at 55-77% of the initial capacity. However, premature symptoms of "old age" are caused by unrecognized increase in inlet water loading, increase in heavy hydrocarbon ( $C_4^+$ ) in feed gas, methanol vapour in feed, desiccant contamination or incomplete regeneration.

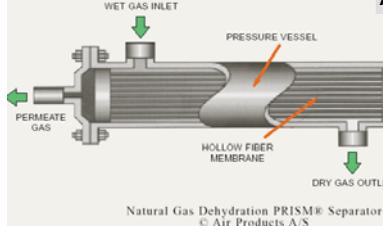
# Natural Gas Dehydration- Refrigeration and Membrane

Manufacturer selection guide (source: Natco)

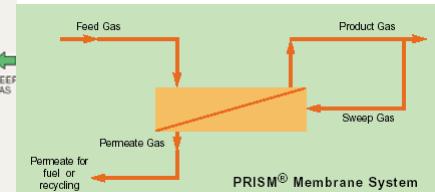
Standard Size	Heat Exchanger Duty Btu/H	Cold Separator Size	Gas Capacity MMstd/d	Skid Dimensions	Skid Weight
Level T-2	108,000	20' OD x 7'-6" S/S	2	40'W x 21'-6" L	5,500 lbs
Level T-5	270,000	20' OD x 7'-6" S/S	5	40'W x 22'-4" L	7,500 lbs
Level T-10	538,000	24' OD x 7'-6" S/S	10	40'W x 26'-0" L	10,500 lbs



A typical JT unit for water and NGL removal (source: Natco)



Natural Gas Dehydration PRISM® Separator  
© Air Products A/S



Membrane systems (Source: Air Products)

## Dehydration by Refrigeration

The dehydration of natural gas can also be achieved by refrigeration and/or cryogenic processing down to  $-148^{\circ}\text{F}$  ( $-100^{\circ}\text{C}$ ) in the presence of methanol hydrate and freeze protection. The condensed water and methanol streams decanted in the cold process can be regenerated by conventional distillation or by a patented process called **IFPEX-1®**. In the latter process illustrated in schematic form in previous slides a slip stream of water saturated feed gas strips essentially all the methanol in the cold decanted methanol water stream originating in the cold process at feed gas conditions to recirculate the methanol to the cold process. The water stream leaving the stripper contains generally less than 100 ppm wt of methanol. No heat is required for the process and no atmospheric venting takes place. **LTX** units and **JT** refrigeration units may be used to simultaneously dehydrate and recover NGL from natural gas streams. The slide shown on this slide illustrates a simple **JT** unit. Liquid recovery units will be discussed in more details in the next section of this course.

## Dehydration by Membrane Permeation

Membranes can be used to separate gas stream components in natural gas such as water,  $\text{CO}_2$  and hydrocarbons according to their **permeabilities**. Each gas component entering the separator has a characteristic permeation rate that is a function of its ability to dissolve in and diffuse through the membrane. The driving force for separation of a gas component in a mixture is the difference between its partial pressure across the membrane. As pressurized feed gas flows into the metal shell of the separator, the fast gas component, such as water and  $\text{CO}_2$ , permeate through the membrane. This permeate is collected at a reduced pressure, while the non-permeate stream, i.e., the dry natural gas, leaves the separator at a slightly lower pressure than the feed. The amount of methane and other natural gas components in the permeate stream is dependent on pressure drop and the surface area of the membranes. However, 5–10% of the feed stream is a realistic figure. Dehydration by membrane permeation is therefore normally only considered for plants that can make use of low pressure natural gas fuel. Typical applications offered by main technology suppliers (e.g. Air Products) offshore/onshore:

Low capacity: Retrofit installations

De-bottlenecking

Drying fuel gas

Medium/high cap.: Drying associated gas

Drying lift gas

Alternative to glycol/methanol injection

Current status of Membrane Technology is: industry proven in multiple applications;  $\text{H}_2$  and  $\text{CO}_2$  recovery since 1978; Experience in  $\text{N}_2$  generation since 1983; Air dehydration since 1987; Natural gas dehydration since 1992

**Typical performance:** Wet feed gas pressure: 750 to 1000 psig (50-70 barg); Water content: 500-2000 ppmv; Temperature:  $50^{\circ}\text{F}$  ( $10^{\circ}\text{C}$ ) above saturation; Feed gas quality: Free of solids and droplets  $>3\mu\text{m}$ ; 99.98% removal of droplets  $<3\mu\text{m}$ ; Dry product gas pressure: 720-970 psig (48-68 barg); Water content: 20-100 ppmv; Permeate flow rate: 3-5% of feed flow; Permeate gas pressure: 7-60 psi (0.5-4 barg)

## Natural Gas Dehydration- Process Selection

- Dehydration methods advantages and disadvantages
  - TEG (glycol dehydration)
  - Solid desiccants
  - Low temperature
  - Membranes
- Selection recommendations

Every application certainly merits individual consideration. Nevertheless each dehydration method has its own advantages and disadvantages that define where it is especially attractive. Accordingly, the key advantages and disadvantages of various dehydration methods are now listed. Then the usual areas of application of each method are outlined.

**TEG (glycol dehydration).** Advantages and disadvantages of glycol systems were discussed before (see glycol dehydration section of the course)

**Solid beds.** Advantages and disadvantages of solid desiccant systems were also discussed before. (see glycol dehydration section of the course)

**Low temperature Separation (LTS).** **Advantages** are: (1) when adequate well head pressure is available, *LTS* separation can meet pipeline specifications fro water and HC dew-points; (2) power consumption is minimal, and so operating costs are low; (3) corrosion is minimal, especially when hydrate inhibitors are not used. **Disadvantages** are: (1) LTS processes are unattractive when adequate wellhead pressure is not available; (2) adding hydrate inhibitors and using external refrigeration increases both capital cost and operating expenses.

Selection recommendation. *TEG* is by far the most popular choice and is probbaly the best choice unless one of the following recommendations is pertinent:

**Solid desiccants.** Solid desiccants are usually preferred for: (1) natural gas dehydration to pipeline spec's. (4-7 lb water/MMscf or water dew-points of 10-30°F) where *TEG* is not suitable – for example, aboard floating production platforms where wave action disturbs glycol flow on the contactor trays; or when the gas is sour; (2) dehydration of high pressure (supercritical) carbon dioxide because of excessive carbon dioxide solubility in glycol; (3)dehydration of natural gas fro cryogenic (<-30°F) processes e.g., ethane recovery or LNG plants. (4) simultaneous removal of water and hydrocarbons to meet both water and hydrocarbon dew-point specifications (5) recovery of liquid hydrocarbons from lean (0.5 gpm C<sub>3</sub><sup>+</sup> or less) natural gas (often with refrigeration). A diligent cost-benefit study should be done when solid desiccant units are selected over refrigeration systems for simultaneous removal of water and HC at very high natural gas capacities (>300 MMscfd). Usually propane refrigeration systems are used for large capacity liquid and water removal plants.

**Low Temperature Separation (LTS) processes.** These processes are attractive for: sweet gas with a wellhead pressure considerably greater than pipeline pressure. The refrigeration cycle- assisted *LTS* units are attractive when the C<sub>3</sub><sup>+</sup> content of natural gas exceed 2-2.5% for large capacity natural gas water and liquid removal or dew-point control units. Most of the large facilities (>300 MMscfd) which treat sour wet natural gas use *LTS* units rather than solid bed and glycol dehydration units.

**Membrane.** Membrane have been more attractive for low gas flow rates (<150 MMscfd). They are very reliable and almost maintenance free. The major draw back of membrane systems, for gas dehydration, is the wasted gas through membrane sheets as methane and water have close permeation rates for most commercial polymer membranes and methane passes through membrane together with removed water.

## NATURAL GAS LIQUID RECOVERY

- Why NGL recovery?
- NGL components and specifications
- Introduction to low temperature processes
- Processing objectives
  - Transportable gas
  - Sales gas
  - Maximum NGL recovery
- Value of NGL
- Liquid Recovery Processes

Recovery of natural gas liquids (*NGL*) from natural gas is quite common in natural gas processing, and can be, at times assume great economic importance. Huge quantities of solution gas produced from crude oil used to be flared routinely. Phasing out this wasteful practice has required greatly increased *NGL* recovery. It may be needed to further process the separated liquids and fractionate them into various liquefied petroleum gas (*LPG*) components of ethane, propane, isobutane and normal butane. *LPG* products are defined by their vapour pressures and must meet some certain criteria (see **Figure 2.1** of the *GPSA* data book.) The un-fractioned natural gas liquids product (*NGL* or mostly  $C_5^+$  *HCs*) is defined by the properties in to **Figure 2.2** of the *GPSA* data book. The *NGL* cannot contain heavy end hydrocarbons that can boil at more than 375°F. In most instances gas processing plants are installed because it is more economical to extract and sell the liquid products even though this lowers the heating value of gas. Another objective of gas processing and liquid recovery is to lower the *Btu* content of the gas to meet the maximum allowable heating limit set by a gas sales contract. If the gas is too rich in heavier *HCS*, the gas will not work properly in burners that are designed for lower heating values. A common maximum limit is about 1,000 *Btu/scf*. **Figure 2-5** of *GPSA* data book depicts the specifications for liquefied petroleum gases this table is derived from *ISO 9162-1989*.

**Processing objective.** As stated before the three main alternatives of liquid-recovery processing are: to produce transportable gas, to meet sales gas specifications., or to maximize liquid recovery. These objectives very discussed before (see **Page 42**).

**Value of NGL components.** The value of the increased volume of liquids sales may be significantly higher than the loss in gas sales revenue because of a decreased in heating value of the gas. In deciding whether it is economical to remove liquids from natural gas stream, it is necessary to evaluate the decrease in gas value after extraction of the liquid. The break even values for various valuable *HCS* (ethane, propane, butanes, etc.) in natural gas can be determined knowing their net heating values and liquid densities. For the four major components these values are:

<b>Gas component</b>	<b>LHV (Btu/scf)</b>	<b>scf/gallon</b>	<b>Equivalent Value\$/gallon (\$3.00/MMBtu gas price)</b>
Ethane	1618	37.5	0.1820
Propane	2316	36.4	0.2529 = $(\$3/MMBtu)(2316Btu/scf)(36.4\text{scf/gallon})$
Butane	3010	31.8	0.2872
Pentane	3708	27.7	0.3081

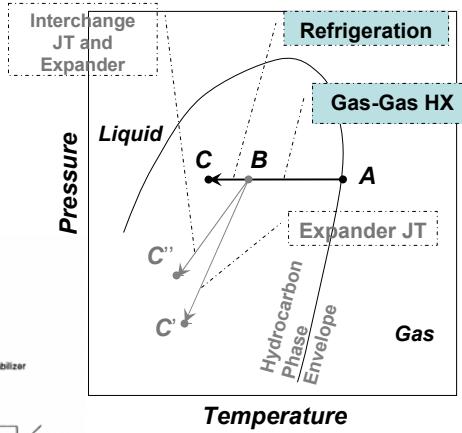
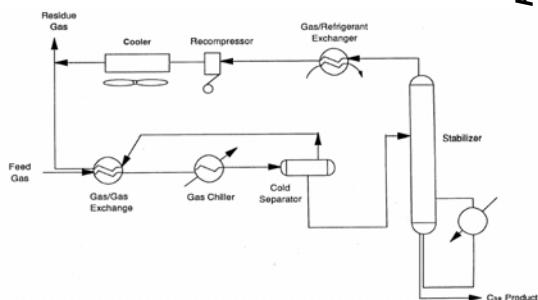
These are the bare *minimum* values below which the molecules will be more valuable as gas. The difference between the actual sales price of the liquid and the break-even price of the liquid in the above table provides the income to payout the capital cost, fuel cost, and other operating and maintenance costs necessary to make the recovery of the gas economically attractive. Obviously as the price of gas increases (per *MMBtu*), the attractiveness of getting the valuable *HCS* diminishes. Propane and other *NGL* components can be added to crude oil to improve its quality (*API* gravity). A similar approach may be taken to calculate if it is worth to extract liquids. For instance for propane the minimum bare value is \$0.2529/gal which converts to \$10.63/bbl. The crude would have to be worth more than \$10.63 a barrel to make the liquid recovery and crude blending economical.

Ethane is another very important natural gas constituent. It is sometimes more valuable as *NGL* and other times worth more as sales gas; therefore *NGL* recovery units should be versatile –capable of either producing or rejecting ethane liquid product.

Major *NGL* recovery techniques and process will be discussed in this section with emphasis on refrigeration and cryogenic processes.

# Natural Gas Liquid Recovery- Processes

- **Refrigeration**
- **JT-Valve expansion (LTS)**
- **JT-Turbine Expansion**
- **Oil absorption**
- **Solid bed adsorption**



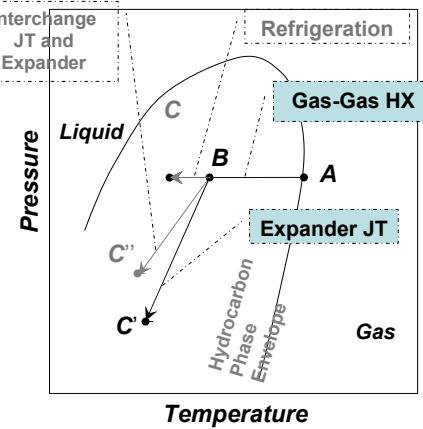
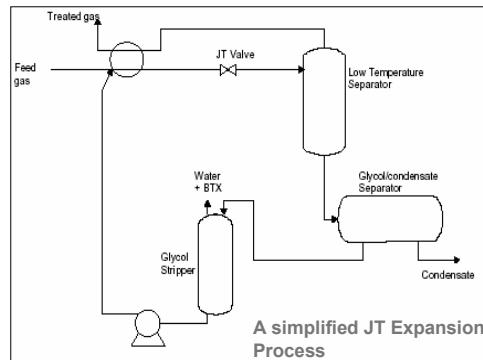
The figure in this slide shows a phase diagram for a typical natural gas, either a gas-well gas or associated gas. Obviously any cooling will induce condensation and yield NGL. Considering similar conditions, the higher the pressure, the more condensation can be expected. Therefore cooling, using refrigeration processes (temperatures above -30 to -35°F) or cryogenic cooling (<-35°F) are very effective techniques to remove liquid components from natural gas streams. In cooling processes (e.g., refrigeration or cryogenic), the most widely techniques are either external refrigeration using refrigeration cycles (e.g., propane refrigeration cycle) or expansion cooling using Joule-Thompson thermodynamic effect employing **valve** or **turbine expansion** techniques. In these cooling technique no external component is used and liquid recovery is performed through heat transfer processes. Another NGL recovery technique is the use of so called **mass transfer agents (MGA)**. The two most important MGA processes are the use of liquid absorption solvents or solid adsorption materials.

**Refrigeration.** Refrigeration in the figure shown on this slide is the simplest and most direct process for NGL recovery. External or mechanical refrigeration is supplied by a vapour-compression cycle that typically uses propane as the refrigerant or working fluid. Mechanical refrigeration will be described later. As can be seen on this slide, the **gas-to-gas (gas-gas)** heat exchanger recovers additional refrigeration by passing the gas leaving the cold separator countercurrent to the warm inlet gas. The temperature of the cold gas stream leaving this exchanger "approaches" that of the warm inlet gas. Economically this approach can be as close as 5°F or slightly less, however in most design cases the approach is taken around 8 to 10°F to avoid any temperature cross or very large heat exchangers. The chiller is typically a shell and tube, kettle type unit. The process gas flows inside the tubes and gives its energy to the liquid refrigerant surrounding the tubes. The refrigerant (often C<sub>3</sub>) boils off and leaves the chiller vapour space essentially as a saturated vapour. The refrigeration process is shown as line ABC in the phase envelop on this slide. From A to B indicates gas to gas exchange; from B to C, chilling. Gas-gas exchange is very common in NGL recovery processes. The condensed liquid is then fed to a stabilizer (or fractionation column) to meet typical specifications such as vapour pressure or composition (%C<sub>2</sub> if recovering C<sub>3</sub>). **Ethylene glycol (EG)** is often injected at the inlet of the gas-gas exchanger and/or chiller to prevent **hydrate formation**, or **freeze-up**, in these exchangers. **Freeze-up** will partially block exchanger tubes, thus increasing pressure drop and decreasing heat exchange. The weak glycol solution, containing condensed water, is separated in the cold separator, regenerated and recycled. Glycol injection was described in detail before (see *Hydrate Prevention* section of the course).

## Natural Gas Liquid Recovery- Processes: Joule-Thompson (JT) Valve Expansion

$$\mu = \left( \frac{\partial T}{\partial P} \right)_H$$

$$\mu = \frac{1}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_p - V \right]$$



The definition of a **Joule-Thompson (JT)** process is a *change in pressure at constant enthalpy*; the Joule-Thomson coefficient is the derivative of temperature with respect to pressure with enthalpy held constant (remember, you always have to say what you are holding constant with these thermodynamic derivatives). So, what happens when you expand a fluid at constant enthalpy? As the pressure is lowered, the fluid expands, and this changes the interactions between the molecules (because on average they are farther apart). An expansion will often raise the internal energy by lessening the attractive intermolecular forces. The net effect of this change may be for the enthalpy to go up. Since the enthalpy is kept constant (no energy is given or taken from the gas), the actual conditions for *Joule-Thomson* expansion are constant enthalpy, so in order for the enthalpy to go back down to its original value the temperature must go down. The total energy (measured by the enthalpy) stays the same, but the temperature has to go down to compensate for the increase in enthalpy due to expansion. This may be explained in thermodynamic terms but it is not necessary to know exactly what happens to molecule to recover the liquids from gas streams. The important matter is that if a gas is expanded under adiabatic condition (zero exchange of energy with environment – complete insulation), the temperature drops and these decrease of temperature can be accurately calculated using thermodynamic relations and equations of states. *JT* coefficient is the variation of temperature with pressure at constant enthalpy and is defined as follows:

$$\mu = \left( \frac{\partial T}{\partial P} \right)_H$$

Using the fact that  $dH=0$ , we can obtain the following expression for the Joule-Thomson coefficient:

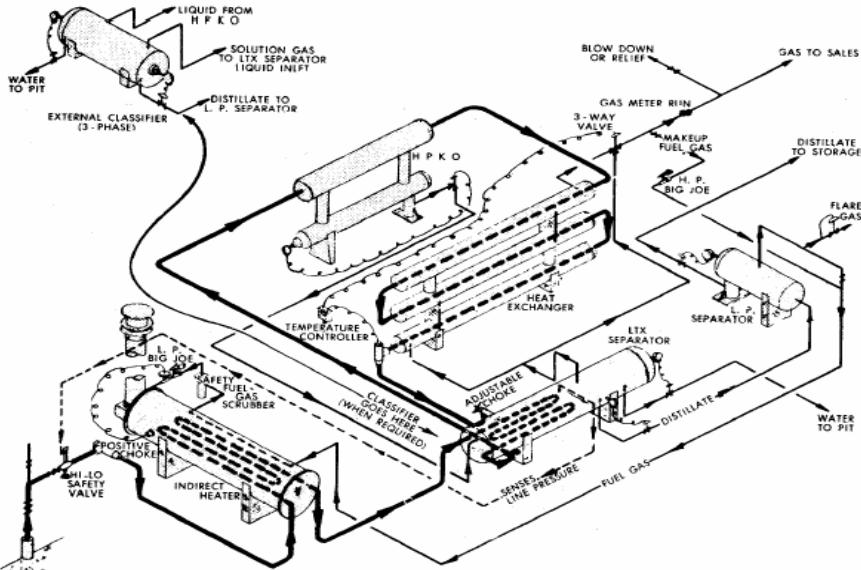
$$dH = \left( \frac{\partial H}{\partial T} \right)_p dT + \left( \frac{\partial H}{\partial p} \right)_T dp = 0.$$

$$\mu = \frac{1}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_p - V \right]$$

This equation can be obtained for different equations of state (equations relating *PVT* behavior of gas) and the temperature variation can be determined with satisfactory accuracy for design purposes. For idea gases *JT* coefficient is always zero. So an idea gas does not undergo any temperature change due to adiabatic expansion. However real gases especially at high pressure do experience temperature drop upon *JT* expansion process.

A simple flow diagram of the JT expansion liquid recovery process is shown on this slide. The inlet gas passes through the gas-gas exchanger, then to an *expansion* or *choke* valve. The expansion is essentially a constant enthalpy process. Non-ideal behavior of the inlet gas causes the temperature to fall with the pressure reduction, as shown by line **ABC** on the phase envelope. The temperature change depends primarily on the pressure drop. The JT process is a **self-refrigeration** process, as opposed to *external refrigeration*. Generally sales gas must be recompressed if the pressure is lowered below the pipeline pressure. Thus *JT* expansion is more favorable when wellhead gas is produced at very high pressure and can be expanded to sales-line pressure.

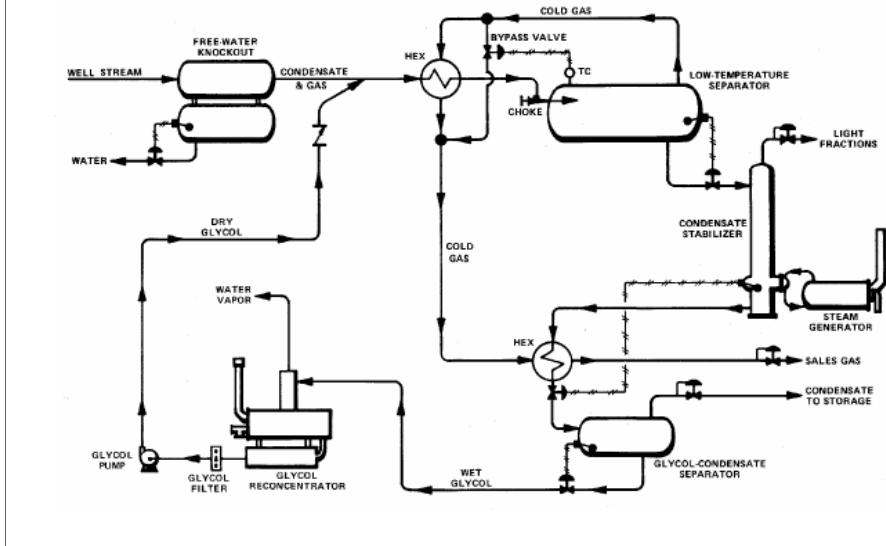
## Natural Gas Liquid Recovery- Processes: LTS Units



### Low Temperature Separation

Two methods can be used to reduce the hydrocarbon dew point. If sufficient pressure is available, the removal can be accomplished by expansion refrigeration in an *LTS* (Low Temperature Separation) unit. The expansion refrigeration system uses the Joule-Thomson effect to reduce the gas temperature upon expansion. This temperature reduction results in not only hydrocarbon liquid condensation but also water condensation. The water is generally removed as hydrates in this process, melted and removed. Thus, the process can actually accomplish dew point control of both water and hydrocarbons in a single unit. The figure on this slide shows one example of an *LTS* system. The high pressure gas may first go through a heater. This heater is often not needed, depending on the gas conditions. The gas then enters the heat exchanger coil in the bottom of the separator where the gas is cooled by exchange with the condensed liquid and hydrates. Any water or condensate produced at this point is removed in the high pressure separator (*H PKO*). The gas from the separator is then heat exchanged with the outlet product gas for further cooling. The temperature must be controlled at this point to prevent hydrate formation in the exchanger. The gas from this point passes through the pressure reducing valve where the Joule-Thomson expansion occurs. The hydrocarbon liquid and hydrates produced from this expansion fall to the bottom of the low temperature separator. The hydrates are melted and both the water and condensate are removed by level control. The gas leaving the separator has a hydrocarbon dew point equal to the temperature and pressure of the separator. The hydrocarbon and water dew points achievable with this process are limited by the pressure differential available as well as the composition of the feed gas. The *LTS* system can only be used where sufficient pressure is available to perform the desired processing and separation. It is an attractive process step if sufficient liquid removal can be achieved at the available operating conditions.

## Natural Gas Liquid Recovery- Processes: LTS Units

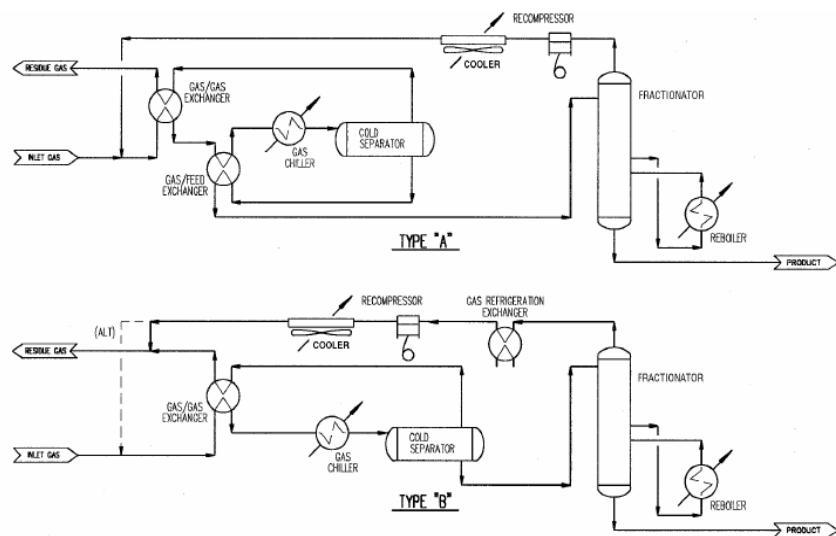


A further modification to this process is to add glycol injection to the high pressure gas to allow the achievement of lower water dew points when available pressure is limited. The figure on this slide shows an *LTS* system with glycol injection. The use of the glycol eliminates the need to heat the *LTS* liquid phase and helps to ensure that no hydrate formation will block the process equipment upstream of the *LTS* separator.

### Refrigeration

Often excess pressure is not available to operate an *LTS* system. An alternative to the expansion refrigeration system is to utilize a mechanical refrigeration system to remove heavy hydrocarbon components and reduce the gas dew point. The schematic for a refrigeration dew point control unit was shown before. This process flow is essentially the same as that used for straight refrigeration *NGL* recovery. The gas pressure is generally maintained through the process allowing for equipment pressure drops. The gas is heat exchanged and then cooled by the refrigeration chiller to a specified temperature. Liquid is separated in the cold separator. The temperature of the separator is set to provide the desired dew point margin for sales gas operations. This temperature specification must take into account the gas which is recombined from the liquid stabilization step as well as potential variations in the feed gas pressure. Provision must be made in this process for hydrate prevention. This can be accomplished by either dehydration upstream of the unit or by integrating the dehydration with the refrigeration unit. Use of glycol injection is usually the most cost effective means of controlling water dew points. The only drawback is that the refrigeration must be in operation to accomplish the dehydration. If it is desired to operate the dehydration at times independent of the refrigeration, then separate units are used.

## Natural Gas Liquid Recovery- Processes: Refrigeration



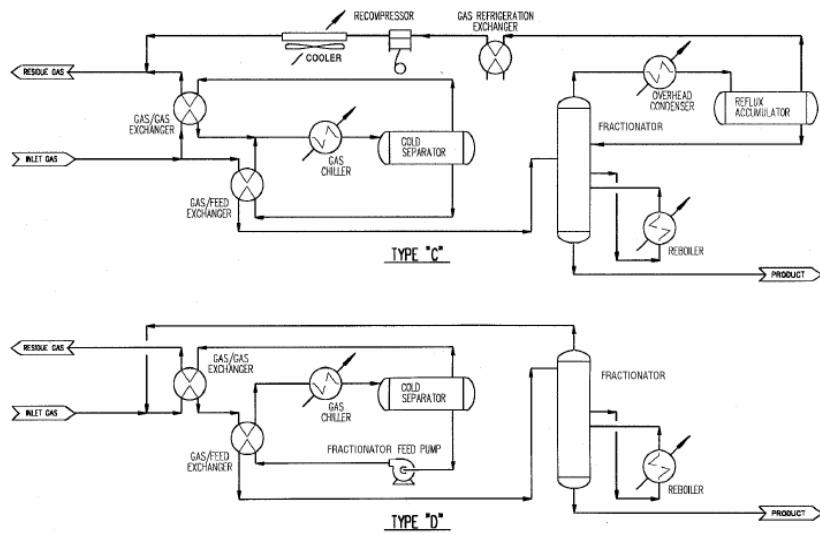
### STRAIGHT REFRIGERATION

The straight refrigeration process is quite flexible in its application to NGL recovery. As outlined in the previous section, the process can simply be used for dew point control when modest liquid recovery is needed or desired. Alternatively, the process can be used for high propane recovery and, in the case of rich gases, for reasonable quantities of ethane recovery. The recovery level is a strong function of the feed gas pressure, gas composition and temperature level in the refrigeration chiller. *Figure 16-7* of the GPSA data book shows curves for estimating the recovery achievable as a function of temperature and gas richness for a given processing pressure (Liquid content in this figure is propane plus). Generally speaking, higher recovery efficiencies can be achieved with richer feed gas. The straight refrigeration process is typically used with a glycol injection system. This configuration is limited in the temperature of operation by the viscosity of the glycol at the lower temperatures. Also, refrigeration is typically provided by propane refrigeration which is limited to  $-44^{\circ}\text{F}$  ( $-42^{\circ}\text{C}$ ) refrigerant at atmospheric pressure and thus a processing temperature of about  $-40^{\circ}\text{F}$  ( $\text{C}$ ). In order to go lower in processing temperature, upstream dehydration and alternative refrigeration systems must be considered. *Figure 16-8* of the GPSA data book illustrates the ethane recovery efficiency which can be expected. As with propane recovery, for a given temperature level, higher extraction efficiency can be achieved with richer gas. However, ethane recovery of over 30% can be achieved from a gas as lean as  $0.4 \text{ ft}^3 (\text{m}^3)/1000 \text{ ft}^3 (\text{m}^3)$  gas ( $\text{C}_3^+$ ).

### Process Alternatives

There are many variations in the straight refrigeration process. Four of the most common variations will be discussed here. In the first scheme (**Type A**) the gas is cooled against the residue gas and the cold separator liquid before being chilled with refrigeration. This scheme uses a top-feed fractionator with the overhead being recompressed and recycled to the inlet. The use of the liquid/feed gas exchanger helps reduce the chiller load. In this case, the residue gas from the cold separator has a dew point of the cold separator operating conditions. The second scheme (**Type B**) also uses a top-feed fractionator, but the cold separator liquid is fed directly to the fractionator. This fractionator operates with a lower overhead temperature which justifies exchange with the refrigeration system. The overhead after being warmed is recompressed and blended with the residue gas from the cold separator. In this configuration the fractionator overhead usually raises the residue gas dew point somewhat. The cold separator temperature must be set to ensure that the desired dew point specification of the combined stream is achieved.

## Natural Gas Liquid Recovery- Processes: Refrigeration



The third process (**Type C**) uses a refluxed fractionator. This type design usually has the highest liquid recovery efficiency, but has a higher cost due to the overhead system added. The fourth (**Type D**) variation can be used where the cold separator liquid can be pumped and the stabilizer run at an elevated pressure. This eliminates the need for a recompressor. Any one or a combination of the following conditions:

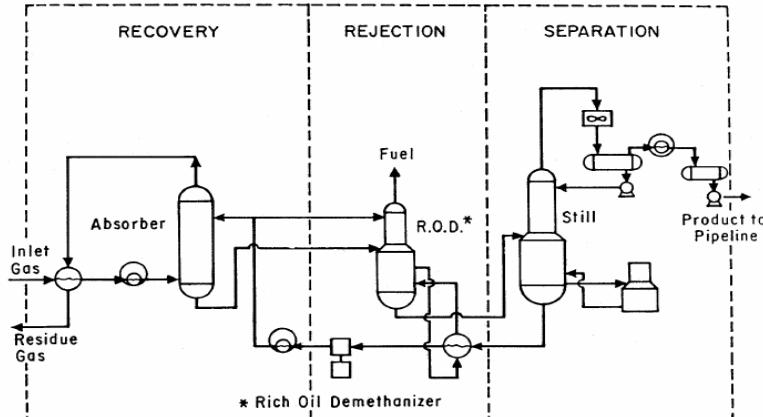
- Higher separator pressure
- Richer gas
- Recovery limited to propane-plus

will lead to higher recycle/recompression rates. This results in more refrigeration horsepower, more recompressor horsepower, more fractionator heat, and larger equipment. These conditions favor the second and third schemes. Any one or a combination of the following conditions:

- Lower separator pressure [around 600 psig (4100 kPa,g)]
- Leaner gas (below 0.4 ft<sup>3</sup> (m<sup>3</sup>)/1000 ft<sup>3</sup> (m<sup>3</sup>) gas C<sub>3</sub><sup>+</sup>)
- Recovery includes ethane

will lead to lower recycle/recompression rates. These conditions favor the first scheme, or the fourth scheme if the separator pressure is not higher than 400-450 psig (2750-3100 kPa,g). Separator pressure below 400 psig (2750 kPa,g), especially with lean gas, will result in poor product recovery. Regardless of the exact configuration employed, the capacity of the specific refrigeration system varies directly with refrigerant condensing temperature and evaporating temperature. Condensing temperature is set by the condensing medium available at the plant site, and the process chiller temperature is set by the refrigerant evaporating temperature. Refrigerant power requirements vary with condensing and evaporating temperatures. Lower condenser temperature and higher evaporating temperature require lower power per unit of refrigeration required.

## Natural Gas Liquid Recovery- Processes: Oil absorption



Flow Diagram of a Refrigerated Lean Oil Absorption Process

### LEAN OIL ABSORPTION

Absorption is the physical process where a vapor molecule of a lighter hydrocarbon component will go into solution with a heavier hydrocarbon liquid (nonane, decane and heavier) and be separated from the gas stream. The process can be operated at ambient temperatures if only the heavier NGL products are desired. A refrigerated system enhances the recovery of lighter hydrocarbon products such as ethane and propane. The absorbing fluid (lean oil) is usually a mixture of paraffinic compounds having a molecular mass between 100 and 200. Lean oil absorption processes have the advantage that the absorber can operate at essentially feed gas pressure with minimal loss of pressure in the gas stream which exits the process. Plants, whether ambient or refrigerated, are constructed of carbon steel. This type process was used from the early part of the 20<sup>th</sup> century and plants are still in use today. However, most lean oil plants have been shut down or replaced with more modern straight refrigeration or turboexpander process plants. The lean oil process requires large processing equipment with excessive energy requirements. Lean oil absorption units are still used in many refinery operations.

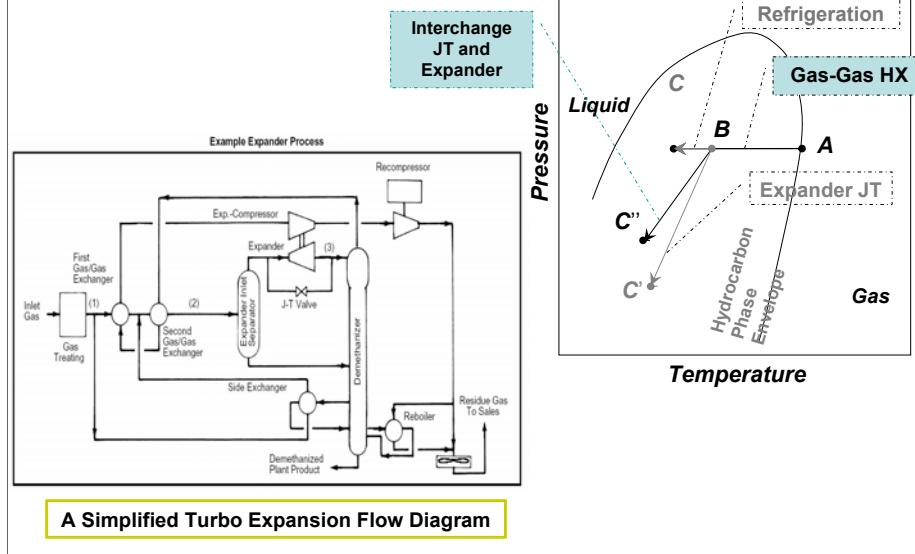
### Process Considerations

The desired composition of the lean oil is determined by the absorber pressure and temperature. The optimum molecular mass lean oil is the lowest weight oil which can be retained in the absorber with acceptable equilibrium losses to the residue gas. Lean oil absorption plants operating without refrigeration will require a higher molecular mass oil, usually in the 150-200 molecular mass range. Refrigerated lean oil absorption systems can operate with an absorbing medium as low as 100 molecular mass with proper design. Since the absorption is on a molar basis, it is desired to contact the gas stream with the maximum number of moles of lean oil to maximize the recovery of products from the gas. However, the circulation rate is units of volume, e.g. cubic meters per hour. Therefore, a plant designed to circulate a heavier molecular weight oil can circulate more moles of oil with the same equipment if the molecular weight is lowered. Many absorption oil recovery plants designed to originally operate at ambient temperatures have been modified to include a refrigeration system that allows both the lean oil and the gas to be chilled before entering the absorber. The reduced temperature increases the absorption and allows circulation of less oil of lower molecular mass because the vaporization rate into the residue gas is reduced. Oil is also lost with the NGL product. Oil losses with the product can be minimized by improving fractionation in the lean oil still. Many refrigerated lean oil absorption plants can recover enough heavy ends from the gas stream to offset oil losses from the absorber, thereby making its own absorption oil. If the gas stream contains compounds that cause the absorption oil molecular mass to exceed design, a lean oil stripper can be used on a side stream of circulating lean oil to remove the heavy components. It is important to maintain the molecular mass of the absorption oil at the design value because the circulating equipment, heat exchangers, and distillation process are designed to utilize a particular molecular mass fluid.

### Refrigerated Lean Oil

The figure on this slide shows a typical refrigerated lean oil absorption process. The actual equipment configuration changes with different gas feeds and product recoveries. Raw gas enters the plant inlet separator upstream of the main process where inlet liquids are separated. The gas then enters a series of heat exchangers where cold process gas and the refrigerant reduce the feed gas temperature. This reduction in temperature results in condensation of the heavier hydrocarbons in the inlet gas. The gas is then fed to the bottom of the absorber where it flows upward countercurrent to the lean oil which is introduced at the top of the column. The lean oil has also been chilled to aid in NGL absorption. This column has trays or packing which increase the contact of the gas and lean oil. The lean oil physically absorbs the heavier hydrocarbons from the gas. The lighter components stay in the gas and leave the top of the absorber. The oil and absorbed hydrocarbons leave the bottom of the absorber as "rich oil." The rich oil flows to the Rich Oil Demethanizer (ROD) where heat is applied to the rich oil stream to drive out the lighter hydrocarbons which were absorbed. Some of the cold lean oil is also fed to the top of the ROD to prevent loss of desirable NGLs from the rich oil. The rich oil from the ROD is then fed to a fractionation tower or "still." The still is operated at a low pressure and the NGLs are released from the rich oil by the combination of pressure reduction and heat addition in the still. The operation of the still is critical to the overall plant operation as this is not only the point where the desired product is produced, but the lean oil quality from the bottom of the column is important in the absorption of NGLs in the absorber. The refrigeration required for the oil and gas chilling and the heat inputs to the ROD and still are the key parameters which must be controlled to operate a lean oil plant efficiently.

## Natural Gas Liquid Recovery- Processes: JT Turbine Expansion

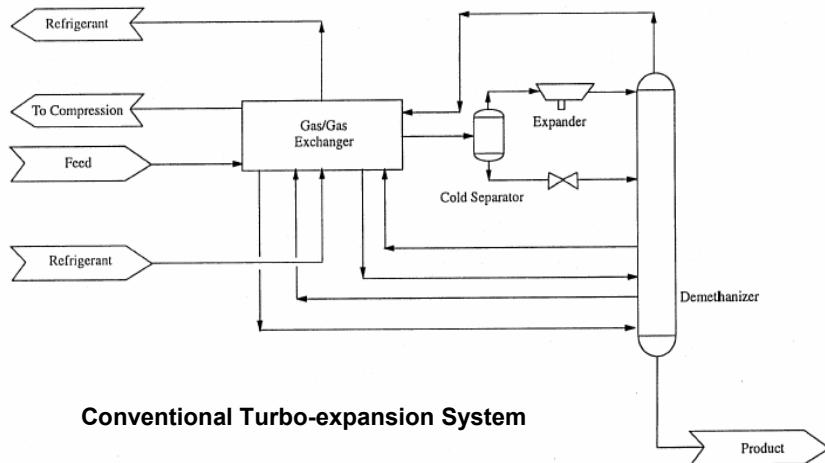


Mechanical refrigeration systems are intended for applications where moderate to high propane recoveries are desired, mostly **dew-point control (DPC)** applications. In order to achieve higher propane recoveries and ethane recovery, cryogenic temperatures are required. Generally, the natural gas processing industry considers cryogenic processing to be processes which operate below  $-50^{\circ}\text{F}$  ( $-45^{\circ}\text{C}$ ). Depending on gas composition and pressure, normally temperatures within the range of  $-80$  to  $-150^{\circ}\text{F}$  are required. In order to achieve these temperatures, a combination of pressure expansion and chilling is used. There are three general methods which can be used to achieve the conditions necessary to attain high ethane recovery levels, namely , **1. J-T Expansion; 2. Turboexpander; and 3. Mechanical refrigeration**. Each of these processes has been used successfully, with the *turboexpander* being the predominant process of choice for ethane recovery facilities. The NGL recovery ( $\text{C}_3^+$ ) recovery in these processes depends on the choice of process and operating conditions

### TURBOEXPANDER PROCESSING

In the so called cryogenic or expander plant, the chiller or *JT* valve is replaced by an expansion turbine. As the entering gas expands it supplies work to the turbine shaft, thus reducing the gas enthalpy. This decreases in enthalpy causes a much larger temperature drop than found in the simple *JT* valve expansion. The expansion process is indicated as line **ABC"** in the phase envelope. The turboexpander process dominates ethane recovery facility design. The process as originally conceived utilized a top feed, non refluxed demethanizer working typically at  $100$  to  $450\text{ psia}$ . During the expansion, condensate is formed but turbine is designed to withstand this condensation. Typically between  $6$  to  $8\%$  of the feed gas is condensed in the cold separator which is usually at  $-30$  to  $-60^{\circ}\text{F}$ . The expander lowers the pressure from the inlet gas value (e.g.,  $600$  to  $900\text{ psia}$ ), to the demethanizer pressure. Typical inlet gas temperatures to demethanizer are  $-130$  to  $-150^{\circ}\text{F}$ , sufficiently low that a great deal of the ethane is liquefied. Expander plants typically condense  $8$  to  $12\%$  of the feed gas. The demethanizer tower stabilizes the raw liquid product by reducing the methane content to a suitably low level. The molar ratio of methane to ethane in the bottom product is typically  $0.02$  to  $0.03$ . The bottom temperature is often below ambient, so that the feed gas may be used as the heat transfer medium for the reboiler. This provides additional refrigeration to the feed and yields higher ethane recovery, typically  $80\%$ . Additional refrigeration also can be obtained by using the feed gas for side-reboiling heat in the demethanizer. As higher and higher recovery levels have been desired, alternative designs have been developed. The focus of these designs is to produce reflux for the demethanizer to attain lower overhead temperatures and higher ethane recovery. The turboexpander process has been applied to a wide range of process conditions and, in addition to ethane recovery projects, is often used as a process for high propane recovery. The process can be designed to switch from ethane recovery to ethane rejection operation with minimal operating changes.

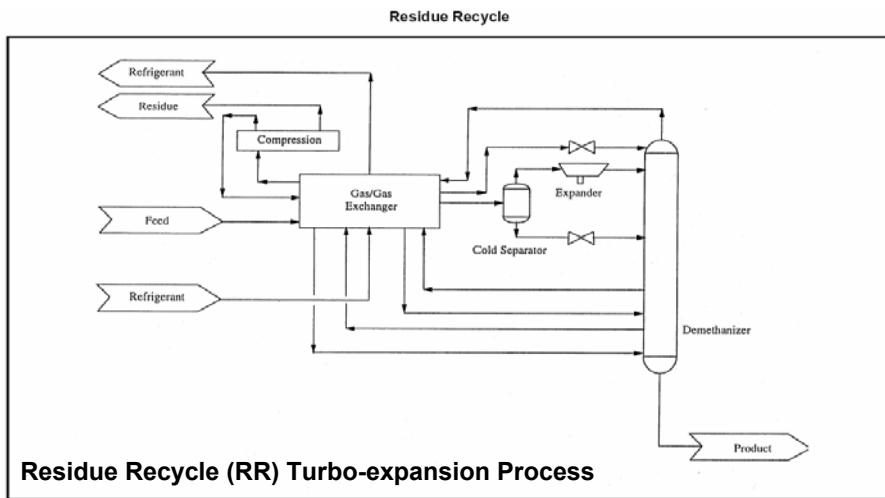
## Natural Gas Liquid Recovery- Processes: JT Turbine Expansion



### Conventional Process

The original turboexpander process is shown on this slide. Dry feed gas is first cooled against the residue gas and used for side heating of the demethanizer. Additionally, with richer gas feeds, mechanical refrigeration is often needed to supplement the gas chilling. The chilled gas is sent to the cold separator where the condensed liquid is separated, flashed and fed to the middle part of the demethanizer. The vapor flows through the turboexpander and feeds the top of the column. A J-T valve is installed in parallel with the expander. This valve can be used to handle excess gas flow beyond the design of the expander or can be used for the full flow if the expander is out of service. In this configuration the **ethane recovery** is limited to about 80% or less. Also, the cold separator is operated at a low temperature to maximize recovery. Often the high pressure and low temperature conditions are near the critical point of the gas making the operation unstable. Another problem with this design is the presence of CO<sub>2</sub>, which can solidify at operating temperatures found in this process. The critical design points are the expander outlet and the top few stages of the demethanizer. The CO<sub>2</sub> freezing problem and the methods of solid CO<sub>2</sub> formation prediction were discussed before. One alternative to the conventional design is the use of two expanders where the expansion occurs in two steps. While this design can help with approach to critical in the cold separator, it does little for solid formation conditions in the demethanizer column. This design has been used in a few plants but other modifications have been developed which relieve both the critical conditions and CO<sub>2</sub> freezing problems.

# Natural Gas Liquid Recovery- Processes: JT Turbine Expansion

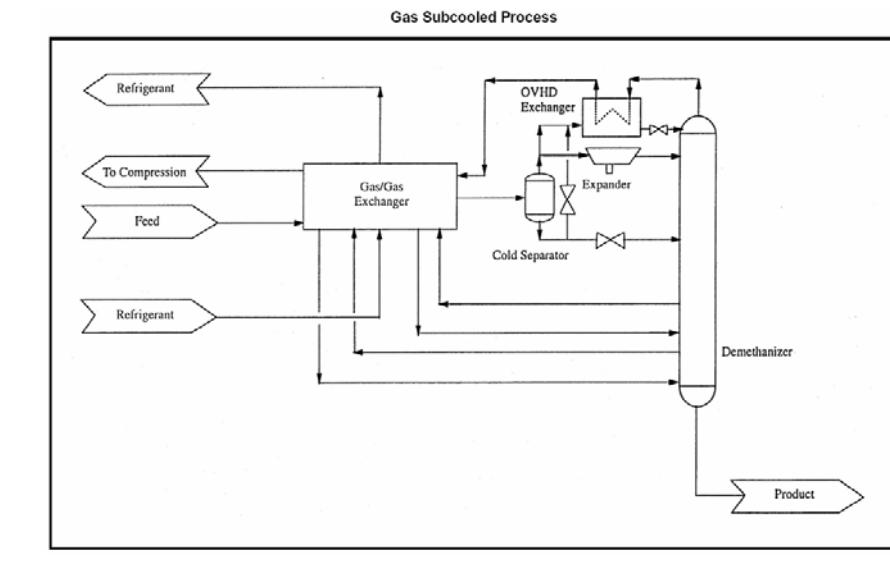


## Residue Recycle

To increase the ethane recovery beyond the 80% achievable with the *conventional* design, a source of reflux must be developed for the demethanizer. One of the methods is to recycle a portion of the residue gas, after recompression, back to the top of the column. The process flow is similar to the conventional design except that a portion of the residue is brought back through the inlet heat exchange. At this point the stream is totally condensed and is at the residue gas pipeline pressure. The stream is then flashed to the top of the demethanizer to provide reflux. The expander outlet stream is sent a few trays down in the tower rather than to the top of the column. The reflux provides more refrigeration to the system and allows very high ethane recovery to be realized. The recovery level is a function of the quantity of recycle in the design.

The **residue recycle (RR)** system has been used successfully in numerous facilities. It is CO<sub>2</sub> tolerant and the recovery can be adjusted by the quantity of recycle used. The RR process can be used for very high ethane recoveries limited only by the quantity of horsepower provided.

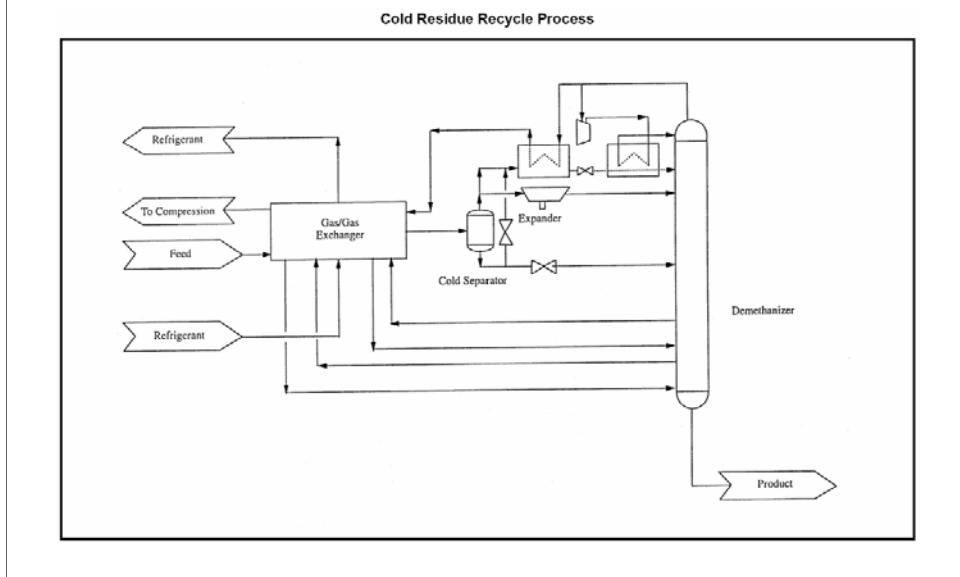
## Natural Gas Liquid Recovery- Processes: JT Turbine Expansion



### GSP Design

The **Gas Subcooled Process (GSP)** was developed to overcome the problems encountered with the conventional expander process. This process, shown in the figure on this slide, alters the conventional process in several ways. A portion of the gas from the cold separator is sent to a heat exchanger where it is totally condensed with the overhead stream. This stream is then flashed to top of the demethanizer providing reflux to the demethanizer. As with the *RR* process, the expander feed is sent to the tower several stages below the top of the column. Because of this modification, the cold separator operates at much warmer conditions well away from the system critical (therefore more tolerable to  $\text{CO}_2$  freeze-off). Additionally, the residue recompression is less than with the conventional expander process. The horsepower is typically lower than the *RR* process at recovery levels below 92%. The GSP design has several modifications. One is to take a portion of the liquid from the cold separator along with the gas to the overhead exchanger. Generally, this can help to further reduce the horsepower required for recompression. Also, the process can be designed to just use a portion of the cold separator liquid for reflux. This modification is typically used for gases richer than  $0.4 \text{ ft}^3(\text{m}^3)/1000\text{ft}^3(\text{m}^3)$  gas. The GSP design is very  $\text{CO}_2$  tolerant; many designs require no up front  $\text{CO}_2$  removal to achieve high recovery.  $\text{CO}_2$  levels are very composition and operating pressure dependent, but levels up to 2% can usually be tolerated with the GSP design. A new process scheme has been developed to combine the GSP and RR processes into an integrated process scheme. This concept is based on applying the best features of each process to the integrated design. This combination can result in higher ethane recovery efficiency than can be achieved with GSP.

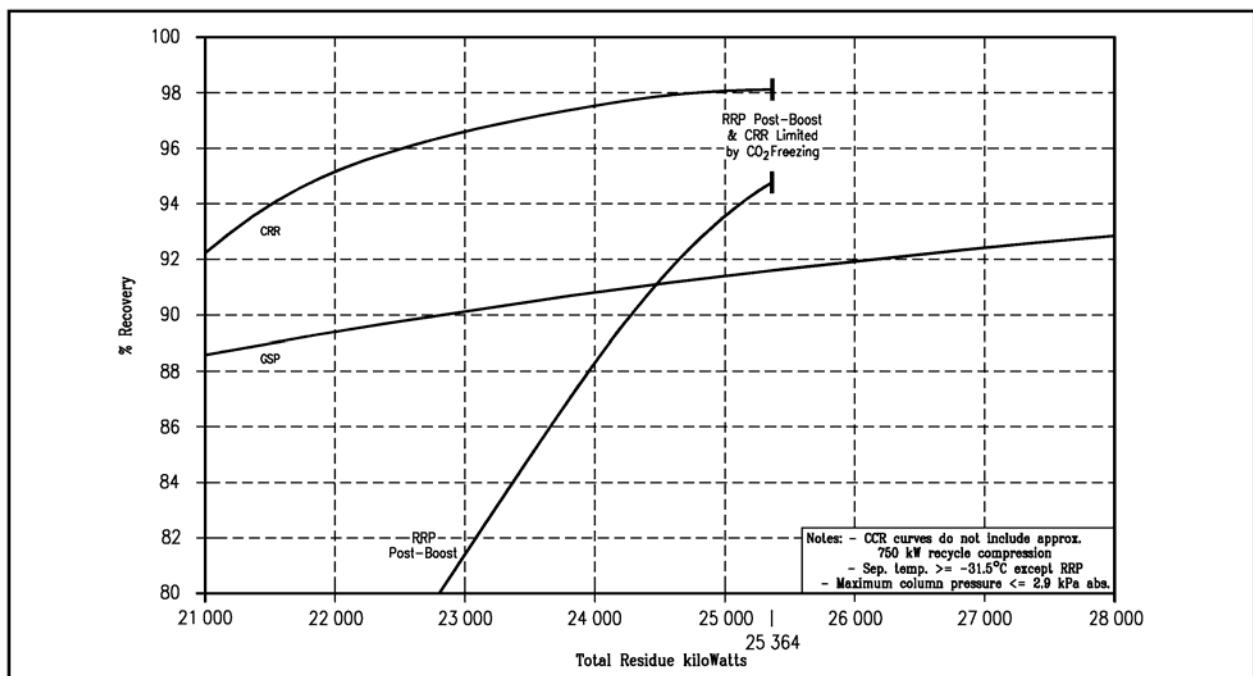
# Natural Gas Liquid Recovery- Processes: JT Turbine Expansion



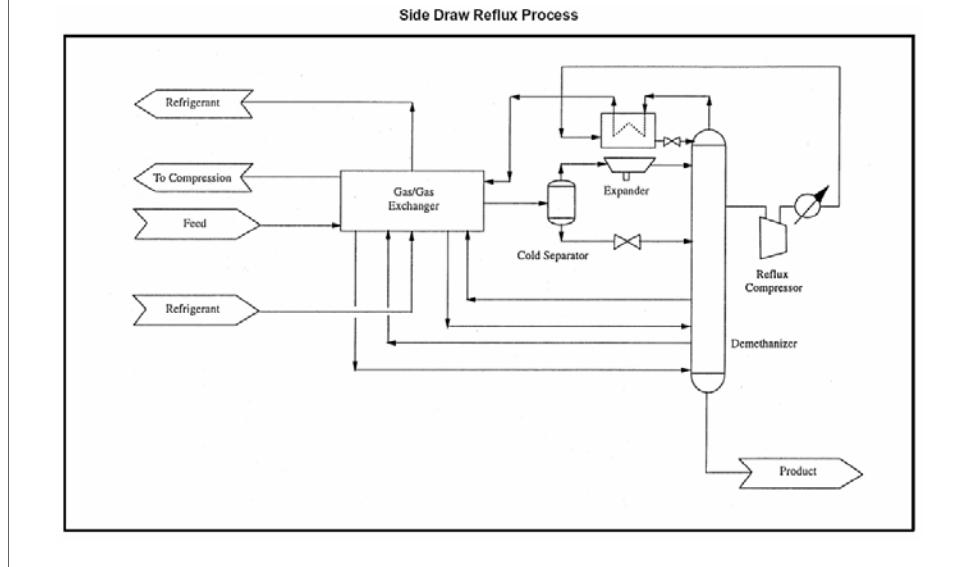
## **Cold Residue Recycle Process (CRR)**

The **Cold Residue Recycle (CRR)** process is a modification of the **GSP** process to achieve higher ethane recovery levels. The process flow in the figure shown on this slide is similar to the **GSP** except that a compressor and condenser have been added to the overhead system to take a portion of the residue gas and provide additional reflux for the demethanizer. This process is attractive for extremely high ethane recovery. **Recovery levels above 98%** are achievable with this process. This process is also excellent for extremely high propane recovery while rejecting essentially all the ethane. A comparison of the **RR**, **GSP** and **CRR** processes for one particular case is shown in the figure below. This comparison is typical for these processes. The **RR** design is the least efficient up to about 91%. Above this point the **RR** design can achieve higher ethane recovery than the **GSP** design. As can be seen, the **RR** process is quite sensitive to available power. The **GSP** design has a rather flat recovery curve and is a good choice for recoveries around 90+. The **CRR** process has the highest recovery for the available residue recompressor power, but consideration must be given to the cost of the additional overhead system equipment and recycle compressor.

**Example % Ethane Recovery vs. Residue Power**



## Natural Gas Liquid Recovery- Processes: JT Turbine Expansion



### Side Draw Reflux (SDR) Process

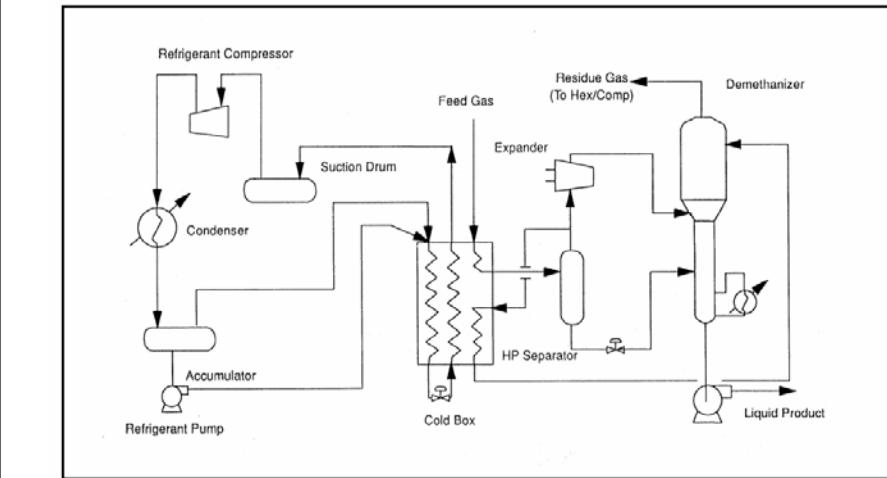
The **Side Draw Reflux (SDR)** process is another modification of the **GSP**. In this design, a stream is taken off the demethanizer, boosted in pressure and condensed to provide reflux. This design is interesting in cases where the residue gas stream will contain inert s such as H<sub>2</sub> which make the subcooling of the cold separator overhead infeasible. The stream taken from the side of the demethanizer is free of the inert components and condenses easily. As with the **CRR** process, the extra equipment associated with this reflux system must be justified on additional liquid recovery.

In expander plants, the low temperatures make material selection very important. Carbon steel is suitable down to -20 °F but become brittle at lower temperatures. Charpy impact tested carbon steel (A516 Gr. 50 or 60) can be used as low as -50 °F. Between -50 to -150 °F, 3.5% Ni steel is used (A203 Gr. B, D and E plates and equivalent material for valves, pipes and fittings), and stainless steel for below -150 °F. The extremely low temperatures also require a very low water content in the inlet gas to prevent hydrate formation and water freeze-offs throughout the cryogenic process. Solid desiccants processes especially with molecular sieves are the most favorable options. If the feed gas contains more than about 0.5-1.0 mole percent carbon dioxide, solid CO<sub>2</sub> may form in the expander outlet gas or in the demethanizer near the top. This may dictate CO<sub>2</sub> removal from feed gas when heating-value specification would not dictate such.

Approximately 98% of the energy lost in the expander is recovered in a brake compressor that partially recompresses the residue gas. Additional recompression is required to restore the gas to sales line pressure.

## Natural Gas Liquid Recovery- Processes: Mixed Refrigerant

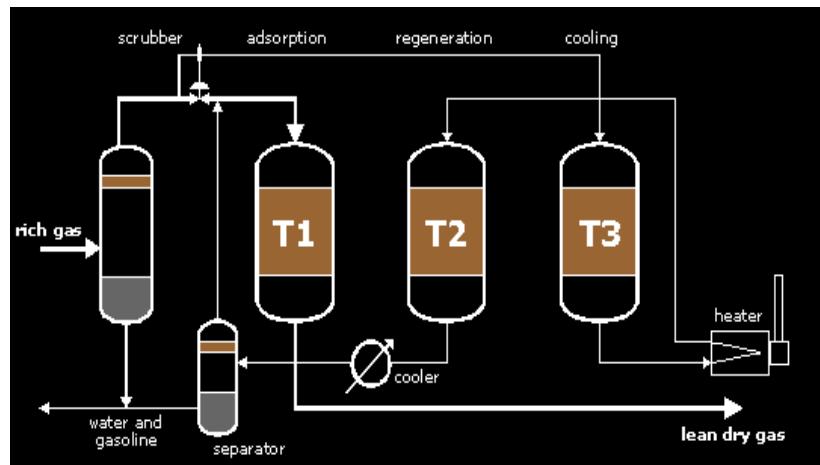
Mixed Refrigerant NGL Recovery Process



### MIXED REFRIGERANT PROCESS

The use of a mixed refrigerant process is an interesting alternative to the turboexpander process. Such processes have been used widely in *LNG* processing and to a lesser extent in *NGL* recovery. One of the characteristics of the process is that low temperatures can be achieved with significantly reduced inlet gas pressure. The chilling can be achieved totally with mechanical refrigeration or with a mixture of refrigeration and expansion. If inlet compression is contemplated for a turboexpander plant, then mixed refrigerant processing can be an economic alternative. The figure on this slide shows one type of mixed refrigerant process. In this case the feed gas is chilled to cold separator temperature where the liquid is sent to the demethanizer as in an expander process. The overhead vapor is split and the majority sent through an expander to the upper part of the demethanizer. A portion of the gas is cooled further in the main heat exchanger and sent to the top of the demethanizer as reflux. Alternatively, the turboexpander can be eliminated and the total stream cooled in the main exchanger and fed to the demethanizer. The residue gas would be exchanged with the feed in the main heat exchanger. The refrigeration is provided by a single mixed refrigerant system designed to provide the necessary low temperature conditions. The refrigerant would typically be a methane, ethane, propane mixture with some heavier components as dictated by the design conditions. A critical aspect of the design is to maintain the desired refrigerant composition during plant operation.

## Natural Gas Liquid Recovery- Processes: Solid Bed Adsorption



**Solid Bed Adsorption Dew Point Control Units**

**Solid desiccants**, such as silica gel or molecular sieves, and activated carbon can be used as a mass transfer agent (MTA) process for condensate recovery. The process is continuous with respect to the gas but cyclical with respect to solid because the latter must be regenerated when it becomes saturated with condensate. Regeneration is accomplished by passing heated recycle or bypass gas through the bed. The condensate is recovered from the regeneration gas by cooling, condensation, and phase separation. A typical cycle time for the process is two to three hours. For this reason the process is sometimes referred to as quick cycle adsorption. The units are also called hydrocarbon recovery units (HRU). Discussions on solid bed adsorption were presented in natural gas dehydration section of this course and will not be repeated here again. Solid adsorption processes are very energy intensive because of the regeneration process. The adsorption beds are very heavy and expensive. This process option is not often used, especially for large facilities ( $>250\text{-}300 \text{ MMscfd}$ ) but may be considered for small facilities in remote areas.

## Natural Gas Liquid Recovery- Process Selection

- NGL content of the gas
  - Low: expander process
  - High: external refrigeration
- Inlet gas pressure
  - High: LTS
  - Low: Turbine expansion or refrigeration
- Gas flow rate
  - Low: simple valve JT unit, solid adsorption or membranes
  - Large: more complex plants
- Location (offshore, onshore, or remote areas)

Quick realizations regarding selection of a condensate recovery process are difficult. In some cases, an economic comparison between viable alternatives will be required, however, a few guidelines can be offered:

If the **NGL content of the feed gas is low**, the **expander** process will probably be the method of choice. For gases very **rich in NGL**, **simple refrigeration** is probably the best choice, while oil absorption or expansion are usually not satisfactory.

If the **inlet gas pressure is very high**, **low temperature separation (LTS)** may be attractive; this process has been used in recent years, both on and offshore. It is important that the reservoir pressure remain high for the intended life of the plant. **Low inlet gas pressure** favors an **expander** plant or **straight refrigeration** (if the gas is very rich).

**Very low gas rates** may justify only a very **simple** process, such as an automatically-operated **JT unit**. **Large flow rates** justify a **more complex** plant with more complex controls and more operating personnel.

Especially if few in number, **remote wells** may dictate **simple operation** and processing, such as **LTS**. A **large number of wells** may justify a **central processing facility** with more **complex processing**. **Offshore locations** usually demand **simple** processing due to expensive platform area and low weight requirements.

In summary, unique factors influence the process choice for each application. More and more expander plants are being used due to their simplicity and low operating cost. Such plants also can be adapted to ethane rejection, making them more versatile and responsive to product prices.

## Natural Gas Liquid Recovery - Process Design

- Process flowsheeting/simulation
  - EOSs (SRK, PR, etc.)
  - Software packages (BR&E PROSIM®, Hyprotech HYSYS®, Aspen®, Chemshire Design II®, SSI PROCESS® and PRO/II® etc.)
- Equipment selection
  - HXs
  - Towers
  - Turboexpanders
  - Pumping and storage

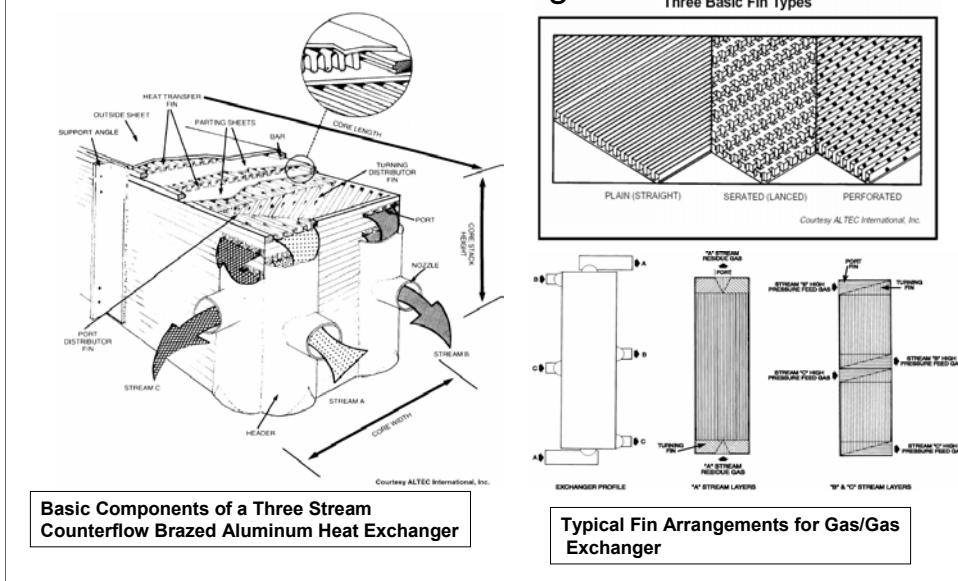
The design of gas processing plants requires many repetitive calculations. In the past, design calculations were done entirely by hand, so that charts and tables of thermodynamic and other properties were very necessary tools. Beginning about 1960, many calculations were programmed for mainframe digital computers, which greatly improved the ability of designers to do their work efficiently and accurately. Many problems could be solved that previously could not be done at all by hand. The introduction of handheld calculators around 70's increased hand computing power a great deal, particularly after programmable calculators were introduced. Microcomputers have totally changed design; almost all the required calculations can now be done at the desk using stand alone personal computers. Developments in equation-of-state calculations and in available commercial process simulator packages motivate these changes and are summarized here.

**Equations of State.** Significant breakthroughs have been made in predicting *PVT* relations and other thermodynamic properties using equations of state (*EOS*). **Soave-Redlich-Kwong (SRK)** is the most widely used *EOS* in which by the use of **Pitzer's eccentric factor** and special mixing rules, prediction of mixture enthalpies and entropies and vapour-liquid equilibrium *K*-values are readily and accurately possible. **Peng-Robinson (PR)** is another widely used *EOS* by which predictions for mixtures containing acid gases such as  $H_2S$  and  $CO_2$  are also allowed. Ideal gas heat capacities are used to establish ideal-gas enthalpies and entropies. The *EOS* are used to evaluate enthalpy and entropies for both real gases and liquids, as well as vapour-liquid equilibrium *K*-values. In turn *K*-values are used to establish the number and composition of phases present by standard flash calculations. These *EOS*-prediction calculations are sufficiently complex that they would never be applied without digital computers. Other important *EOS* are **Grayson-Streed** version of **Chao-Seader** used for refinery simulation, especially when hydrogen is present. Good for moderate temperatures and pressures; it is the fastest of all. *SRK* and *PR* are used more for light hydrocarbons and natural gas processing to high *P* and low *Ts* (up to 2,000 psia and -170°F). *PR* was first in predicting hydrate formation and  $CO_2$  frost. *SRK* is now modified to handle sour gases, hydrate and  $CO_2$  frost prediction as well, and *SOUR SRK* option can now be found in most of commercial process simulators. Both *SRK* and *PR* results in very accurate predictions of equilibrium and thermodynamic properties for natural gas processing design purposes. They are however not very accurate in predicting liquid densities, especially if the accurate composition for  $C_7^+$  are not available. **Benedict-Web-Rubin-Starling (BWRs)** is more superior than *SRK* and *PR* but components are limited. It gives rather more accurate liquid densities.

**Software Packages.** Commercial process simulators utilizing *EOS* to predict volumetric, thermodynamic, and phase equilibrium properties incorporate the methods into flow-sheet simulation programs. The major packages widely used today are listed on this slide. The modern packages all produced very good design flow-sheets. They require input data and a good process knowledge and engineering sense to produce accurate mass and energy balance results. As mentioned for the amine plant simulation, these commercial simulators are capable of doing hydraulic calculations for tower design (for various tray and packing types) and can be linked to heat exchanger design software such as **Hyprotech HTFS** or **Heat Transfer Consultants HTC-LTX** for detailed heat exchanger design.

Equipment selection. The principle process elements in any liquid recovery process are listed on the slide. Heat exchangers are the most widely equipment piece as the heat transfer is the major process in getting liquids out of the gas. Towers and pumps are also extensively used in these processes. Turboexpanders are the main process elements in any cryogenic or ethane recovery process. Their selection and sound performance is of crucial significance in the proper performance of deep-cut recovery units. They will be discussed in a bit more details in the next few slides.

## Natural Gas Liquid Recovery – Equipment Selection: Heat Exchangers



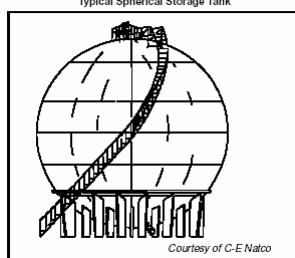
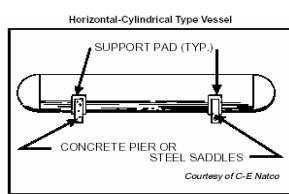
The important heat exchangers used in NGL recovery processes are traditional shell and tube heat exchanger designed according to TEMA guidelines and double pipe/hair pin exchangers for small facilities, and more modern type of exchangers especially plate and frame and plate-fin or aluminum-brazed heat exchangers. A lot of references are available for the design and operations of traditional heat exchangers. Plate and frame exchangers are becoming increasingly popular due to lower pressure drop and more compact designs. Selection of material is very important in the proper design and operation of heat exchangers.

An important type of heat exchangers used in expander plants is the plate-fin exchanger. These especial-purpose exchangers are made of brazed-aluminum, which can operate satisfactorily at very low temperatures. These exchangers are compact and efficient. Their chief drawback is the need to prevent solids from entering them. The narrow channels become clogged easily and the exchanger then performs poorly. Temperature shocks must be avoided also. Of course, shell and tube heat exchangers can be and are also used. A brazed aluminum heat exchanger is composed of alternating layers of corrugated fins and flat separator sheets called parting sheets. A stack of fins and parting sheets comprise the heat exchanger, sometimes referred to as the "core." The heat exchanger is normally specified by its outside dimensions in the following order: Width (W) x Stack Height (H) x Length (L). The number of layers, type of fins, stacking arrangement, and stream circuiting will vary depending on the application requirements. The basic aluminum components of the heat exchanger are shown on this slide for a typical three

stream counterflow exchanger. **Nozzles:** Nozzles are the pipe sections used to connect the heat exchanger headers to the piping. **Headers** — Headers are the half cylinders which provide for the distribution of fluid from the nozzle to or from the ports of each appropriate layer within the heat exchanger. **Ports:** Ports are the opening in either the side bar or the end bar, located under the headers, through which the fluids enter or leave the individual layers. **Distributor Fins:** Distributor fins distribute the fluid between the port and the heat transfer fins. **Heat Transfer Fins:** The heat transfer fin provides extended heat transfer surface. All fins, both heat transfer and distributor, provide connecting structure between the parting sheets, which is necessary for the structural and pressure holding integrity of the heat exchanger. Typical heat transfer fin thicknesses range from 0.006" to 0.025" (0.15 to 0.58 mm). **Parting Sheets:** The parting (separator) sheets contain the fluids within the individual layers in the exchanger and also serve as primary heat transfer surface. Typical parting sheet thicknesses range from 0.80 to 2.0 mm. **Outside Sheets:** Outside (cap) sheets serve as the outside parting sheets. They are typically 6 mm thick and serve as an outer protective surface of the exchanger. **Bars:** The side and end bars enclose the individual layers and form the protective perimeter of the exchanger. Solid extruded bars from 12 to 25 mm wide are typically used. **Support Angles:** Support angles are typically 90 degree extruded aluminum angles welded to the bar face of the exchanger for the purpose of supporting or securing the exchanger in its installed position. Other support configurations are available. **Battery:** A multiple exchanger assembly, sometimes referred to as a "battery," consists of two or more exchangers piped or manifolded together into a single assembly, with the individual exchangers arranged either in a parallel, series, or combination parallel-series arrangement. **Cold Box:** Individual exchangers and batteries are often installed in a "cold box." A cold box consists of a welded, airtight carbon steel casing, rectangular or cylindrical in shape, which supports and houses the heat exchangers, piping, other related cryogenic equipment, and insulation material.

Further details related to design and installation of these heat exchangers are given in Ref. 2 (GPSA data book)

## Natural Gas Liquid Recovery – Equipment Selection: Towers, Pumps, and Storage

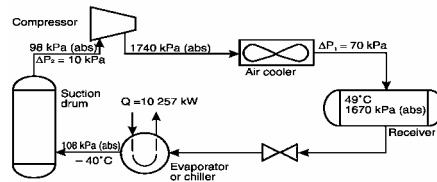


The demethanizer is the only unique tower in most *NGL* and ethane recovery plants. Most of stabilizer and demethanizer and deethanizer towers have between 8 to 12 theoretical trays. This translates into between 20-36 actual trays depending on the type of trays and their efficiencies. Stainless steel (SS 304) is used as the construction material for demethanizer towers as the temperature may easily go below 150°F and under these sever low temperatures only series 300 stainless steel have the right properties. The demethanizer towers usually have two distinct diameters as the liquid and gas flow rates varies from the bottom to the top of the tower. Due to high cost of material and fabrication, normally the top 5 to 10 trays have higher diameters due to the fact that the liquid and vapour flow rates are higher. Centrifugal pumps are generally used for liquid products. Care must be taken that *NGL* product pumps be installed with adequate suction head to avoid cavitation problems. Products are their bubble points in the surge or storage tanks; therefore any significant pressure drop in the flow lines below the bubble point pressure will cause vapourization and pump cavitation. Liquid hydrocarbon storage is discussed in Section 6 of the *GPSA* data book (**Ref. 2**). Horizontal cylindrical, either insulated or bare, are generally used. Insulated tanks are preferred for more volatile products, such as a demethanizer or deethanizer raw product liquid. Spherical tanks may be used for large storage of *LPG* or other volatile liquids where large atmospheric cylindrical tanks are used for stabilized *NGL* products. Proper pressure control and venting and vapour recovery systems should be considered for large atmospheric tanks.

# Natural Gas Liquid Recovery – Refrigeration Cycle

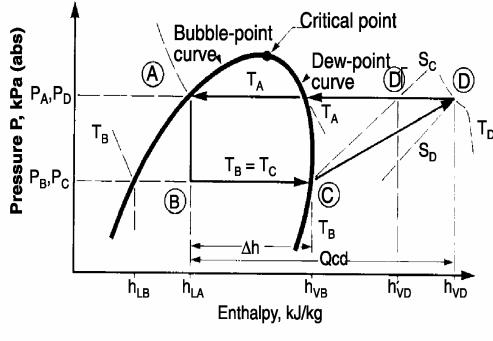
## Simple Cycle

- Process flow diagram



- Vapour compression P-H diagram

1. Expansion
2. Evaporation
3. Compression
4. Condensation



## Refrigeration Cycle

The refrigeration effect can be achieved by using one of these cycles: (a) Vapor compression-expansion; (b) Absorption; (c) Steam jet (water-vapor compression)

By utilizing the Pressure-Enthalpy (**P-H**) diagram, the refrigeration cycle can be broken down into four distinct steps: (1) **Expansion**; (2) **Evaporation**; (3) **Compression**; (4) **Condensation**. The vapor-compression refrigeration cycle can be represented by the process flow and P-H diagram shown on this slide.

**Expansion Step** — The starting point in a refrigeration cycle is the availability of liquid refrigerant. Point **A** represents a bubble point liquid at its saturation pressure,  $P_A$ , and enthalpy,  $h_{LA}$ . In the expansion step, the pressure and temperature are reduced by flashing the liquid through a control valve to pressure  $P_B$ . The lower pressure,  $P_B$ , is determined by the desired refrigerant temperature,  $T_B$  (point **B**). At point **B** the enthalpy of the saturated liquid is  $h_{LB}$ , while the corresponding saturated vapor enthalpy is  $h_{VB}$ . Since the expansion step (**A** – **B**) occurs across an expansion valve and no energy has been exchanged, the process is considered to be isenthalpic. Thus the total stream enthalpy at the outlet of the valve is the same as the inlet,  $h_{LA}$ . Since point **B** is inside the envelope, vapor and liquid coexist. In order to determine the amount of vapor formed in the expansion process, let  $X$  be the fraction of liquid at pressure  $P_B$  with an enthalpy  $h_{LB}$ . The fraction of vapor formed during the expansion process with an enthalpy  $h_{VB}$  is  $(1-X)$ . Equations for the heat balance and the fraction of liquid formed are:

$$(X) h_{LB} + (1 - X) h_{VB} = h_{LA} \quad (\text{Eq. 1}) \quad \text{and} \quad X = \frac{h_{VB} - h_{LA}}{h_{VB} - h_{LB}} \quad (\text{Eq. 2}) \quad \text{and} \quad 1 - X = \frac{h_{LA} - h_{LB}}{h_{VB} - h_{LB}} \quad (\text{Eq. 3})$$

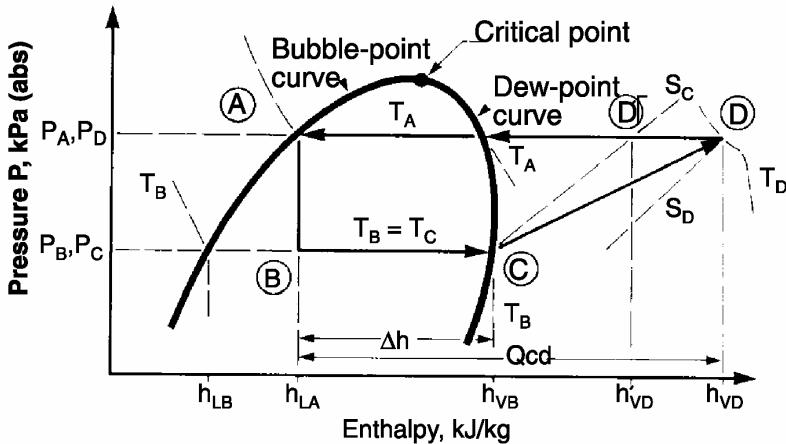
**Evaporation Step** — The vapor formed in the expansion process (**A-B**) does not provide any refrigeration to the process. Heat is absorbed from the process by the evaporation of the liquid portion of the refrigerant. As shown in the figure, this is a constant temperature, constant pressure step (**B-C**). The enthalpy of the vapor at point **C** is  $h_{VB}$ . Physically, the evaporation takes place in a heat exchanger referred to as an evaporator or a chiller. The process refrigeration is provided by the cold liquid,  $X$ , and its refrigerant effect can be defined as  $X(h_{VB} - h_{LB})$  and substituting from **Eq. 2**, the **effect** becomes:

$$\text{Effect} = h_{VB} - h_{LA} \quad (\text{Eq. 4})$$

The **refrigeration duty** (or refrigeration **capacity**) refers to the total amount of heat absorbed in the chiller by the process, generally expressed as **kW**. The refrigerant flow rate is given by:

$$m = \frac{Q_{ref}}{h_{VB} - h_{LA}} \quad (\text{Eq. 5})$$

## Natural Gas Liquid Recovery – Refrigeration Cycle



**Pressure Enthalpy Diagram**

**Compression Step** — The refrigerant vapors leave the chiller at the saturation pressure  $P_C$ . The corresponding temperature equals  $T_C$  at an enthalpy of  $h_{VB}$ . The entropy at this point is  $S_C$ . These vapors are compressed **isentropically** to pressure  $P_A$  along line **C – D'**.

The **isentropic (ideal) work**,  $W_i$  for compressing the refrigerant from  $P_B$  to  $P_A$  is given by:

$$W_i = m (h'_{VD} - h_{VB}) \quad (\text{Eq. 6})$$

The quantity  $h'_{VD}$  is determined from refrigerant properties at  $P_A$  and an entropy of  $S_C$ . Since the refrigerant is not an ideal fluid and since the compressors for such services do not operate ideally, isentropic efficiency,  $\eta_i$ , has been defined to compensate for the inefficiencies of the compression process. The actual work of compression,  $W$ , can be calculated from:

$$W = \frac{W_i}{\eta_i} = \frac{m(h'_{VD} - h_{VB})}{\eta_i} = m(h_{VD} - h_{VB}) \quad (\text{Eq. 7})$$

The enthalpy at discharge is given by:

$$h_{VD} = \frac{(h'_{VD} - h_{VB})}{\eta_i} + h_{VB} \quad (\text{Eq. 7a})$$

The work of compression can also be expressed as:

$$BP = W/3600 \quad (\text{Eq. 7b}),$$

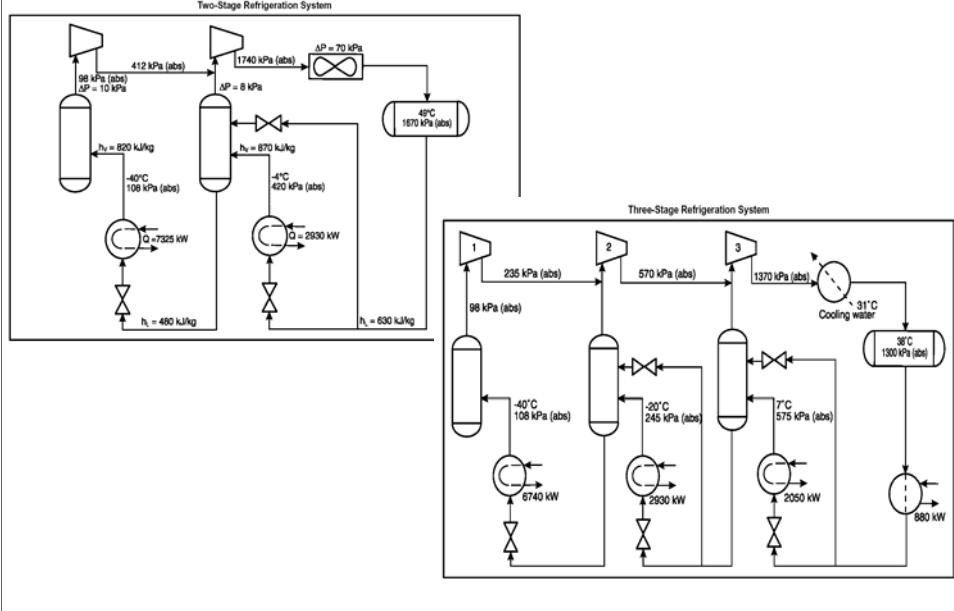
where **3600 kJ/h = 1 kW**.

**Condensation Step** — The superheated refrigerant leaving the compressor at  $P_A$  and  $T_D$  (Point **D**) is cooled at nearly constant pressure to the dew point temperature,  $T_A$ , and refrigerant vapors begin to condense at constant temperature. During the desuperheating and condensation process, all heat and work added to the refrigerant during the evaporation and compression processes must be removed so that the cycle can be completed by reaching Point **A** (the starting point) on the **P-H** diagram, as shown in the figure. By adding the refrigeration duty to the heat of compression, we calculate the condensing duty,  $Q_{cd}$ , from:

$$Q_{cd} = m [(h_{VB} - h_{LA}) + (h_{VD} - h_{VB})] = m (h_{VD} - h_{LA}) \quad (\text{Eq. 8})$$

The condensing pressure of the refrigerant is a function of the cooling medium available — air, cooling water, or another refrigerant. The cooling medium is the heat sink for the refrigeration cycle. Because the compressor discharge vapor is superheated, the refrigerant condensing curve is not a straight line. It is a combination of desuperheating and constant temperature condensing. This fact must be considered for proper design of the condenser.

## Natural Gas Liquid Recovery – Refrigeration Cycle: Single, vs Multistage Systems



**System Pressure Drop** — Some typical values for pressure drops that must be considered are: condenser pressure drop: 3 to 7 psi (20 to 50 kPa); line hydraulic losses Evaporator to Compressor\*: 0.1 to 1.5 psi (0.7 to 10 kPa); compressor to condenser: 1.0 to 2.0 psi (0.7 to 14 kPa); condenser to receiver: 0.5 to 1.0 psi (3.5 to 7 kPa)

\* This is an important consideration in refrigeration services with low suction pressure to compressor.

### Refrigeration Stages

Refrigeration systems utilizing one, two, three, or four stages of compression have been successfully operated in various services. The number of levels of refrigeration generally depends upon the number of compression stages required, interstage heat loads, economics, and the type of compression.

**One-Stage System** — A typical one-stage refrigeration system was shown in the figure on previous slide, where the data were for **pure propane** refrigerant.

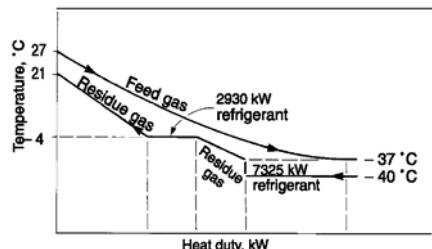
**Two-Stage System** — Savings in the 20% range can often be achieved with a two-stage refrigeration system and interstage flash **economizer**. Additional savings can be realized by removing process heat at the interstage level rather than at the low stage level. A typical two-stage system with an intermediate load is shown in the figure on this slide with data for pure propane.

**Three-Stage System** — Additional power savings can be achieved by using a three-stage compression system. As with a two-stage system, flash economization and/or an intermediate heat load can be used. The savings, while not as dramatic as the two stage versus one-stage, can still be significant enough to justify the additional equipment. A typical three stage propane system is shown on this slide.

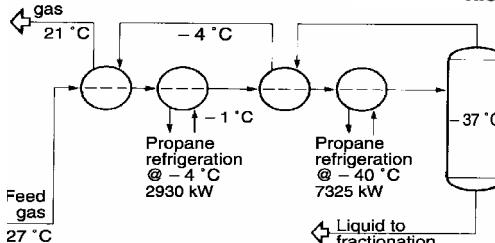
# Natural Gas Liquid Recovery – Refrigeration Cycle: Single, vs Multistage Systems

Effect of Staging on a Propane Refrigeration System

	Stages, n		
	1	2	3
Refrigeration Duty, kW	293	293	293
Refrigeration Temperature, °C	-40	-40	-40
Refrigerant Condensing Temperature, °C	38	38	38
Compression Requirements, kW	218	176	167
Reduction in BP, %	Base	19.2	23.3
Condenser Duty, kW	511	469	462
Change in condenser duty, %	Base	-8.2	-9.6



Residue gas



Two-Stage Cooling

Two-Level Chilling System

**System Configuration** — Energy consumption is frequently reduced as the number of stages is increased. For a propane refrigeration system, the table shown on this slide illustrates the effect of interstages without using refrigeration at intermediate levels. However, the installation cost of such refrigeration systems increases as the number of stages increases. The optimum overall cost will be a function of the specific system and has to be determined for a set of economic criteria. The compression power for refrigeration can be reduced further by shifting refrigerant load from cooler levels to warmer levels. The figure on this slide shows a refrigeration system using two levels of chilling. The gas is initially chilled to  $-1^{\circ}\text{C}$  ( $30^{\circ}\text{F}$ ) with  $-4^{\circ}\text{C}$  ( $25^{\circ}\text{F}$ ) propane and then to  $-37^{\circ}\text{C}$  ( $-35^{\circ}\text{F}$ ) with  $-40^{\circ}\text{C}$  ( $-40^{\circ}\text{F}$ ) propane. The selection of the  $-4^{\circ}\text{C}$  ( $25^{\circ}\text{F}$ ) level results from equal compression ratios for each stage. The interstage pressure and corresponding refrigerant temperature may be fixed by either equipment or process conditions. Equal compression ratios per stage are chosen whenever possible to minimize horsepower.

## Condensing Temperature

Condensing temperature has a significant effect on the compression power and condensing duty requirements. It has been shown that the effect of the condensing temperature on refrigeration requirements for one, two, and three stage systems can be very significant. Results for a one-stage propylene refrigeration system are summarized in the table shown here. The table illustrates that the colder the condensing temperature, the lower the power requirements for a given refrigeration duty. Traditionally, the heat sinks for most refrigeration systems have been either cooling water or ambient air. If cooling water or evaporative condensing is utilized, a  $80$  to  $100^{\circ}\text{F}$  ( $27$  to  $38^{\circ}\text{C}$ ) temperature can be achieved. The following table also indicates, to a certain extent, the effect on operations between summer and winter conditions as well as between day and night operations.

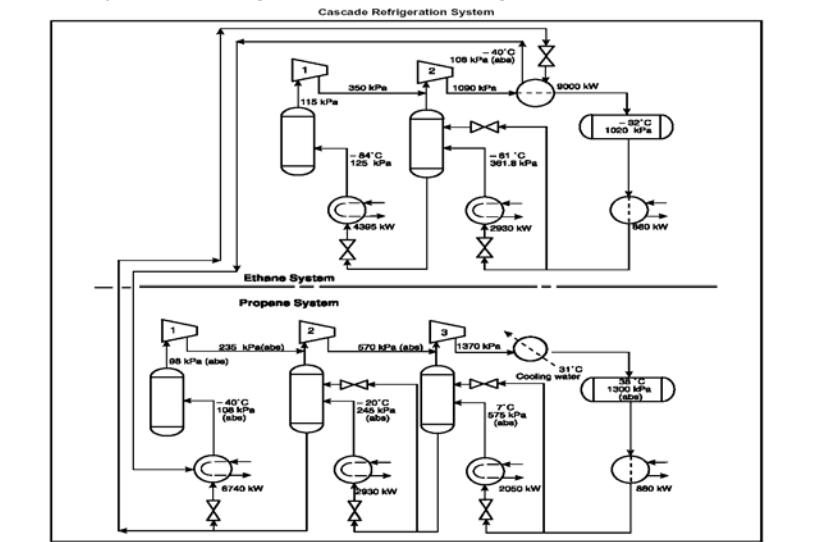
Effect of Condensing Temperature

Condensing Temperature, °C	16	27	38	49	60
Refrigeration Duty, kW	293	293	293	293	293
Refrigeration Temperature, °C	-46	-46	-46	-46	-46
Compression Requirement, kW	157	199	248	320	413
Change in BP, %	-36.6	-19.8	Base	28.8	66.4
Condenser Duty, kW	451	492	539	613	709
Change in Condenser Duty, %	-16.3	-8.7	Base	13.6	31.5

## Refrigerant Subcooling

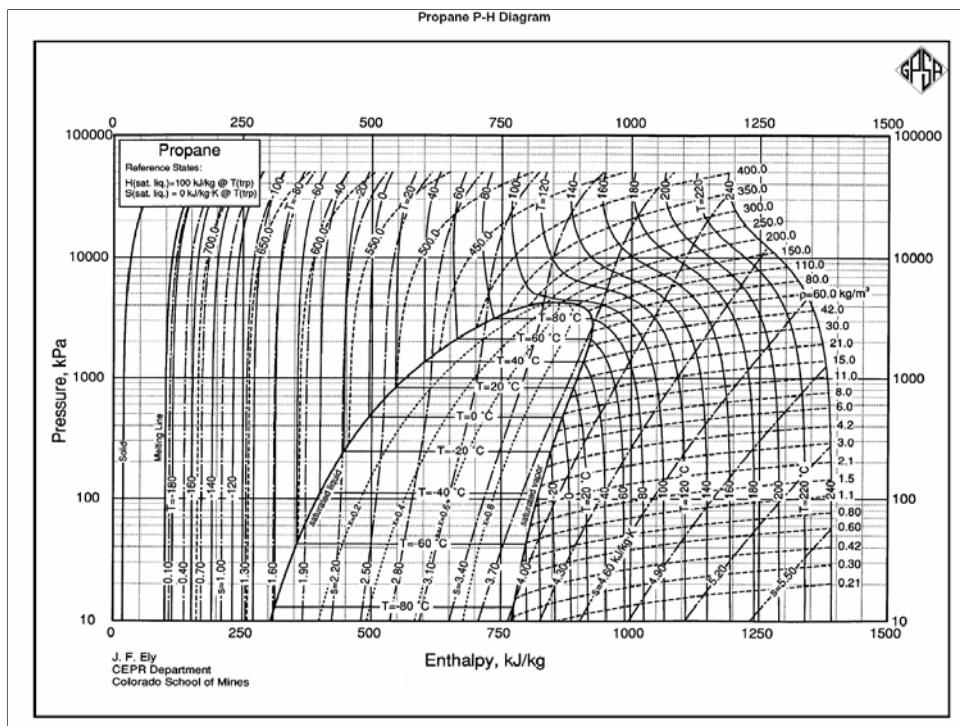
Subcooling liquid refrigerants is common in refrigeration systems. Subcooling the refrigerant reduces the energy requirements. It is carried out when an auxiliary source of cooling is readily available, and the source stream needs to be heated. Subcooling can be accomplished by simply installing a heat exchanger on the appropriate refrigerant and process streams. Usually the cold liquid from the LTS (low temperature flash separator) downstream of the chiller is used to subcool refrigerant.

# Natural Gas Liquid Recovery – Refrigeration Cycle: Refrigerant Cascading



## Refrigerant Cascading

In the cascading of refrigerants, warmer refrigerants condense cooler ones. Based on the low temperature requirements of a process, a refrigerant that is capable of providing the desired cold temperature is selected. For example, the lowest attainable temperature from ethane refrigerant is  $-120^{\circ}\text{F}$  ( $-85^{\circ}\text{C}$ ) (for a positive compressor suction pressure), whereas the lowest temperature level for propane is  $-40^{\circ}\text{F}$  ( $-40^{\circ}\text{C}$ ) (for a similar positive pressure). In a refrigeration cycle, energy is transferred from lower to higher temperature levels economically by using water or ambient air as the ultimate heat sink. If ethane is used as a refrigerant, the warmest temperature level to condense ethane is its critical temperature of about  $90^{\circ}\text{F}$  ( $32^{\circ}\text{C}$ ). This temperature requires unusually high compression ratios — making an ethane compressor for such service complicated and uneconomical. Also in order to condense ethane at  $90^{\circ}\text{F}$  ( $32^{\circ}\text{C}$ ), a heat sink at  $84^{\circ}\text{F}$  ( $29^{\circ}\text{C}$ ) or lower is necessary. This condensing temperature is a difficult cooling water requirement in many locations. Thus a refrigerant such as propane is cascaded with ethane to transfer the energy from the ethane system to cooling water or air. An example of a cascaded system is shown on this slide, where an ethane system cascades into a propane system. The condenser duty for the ethane system is  $30.71 \text{ MMBtu/hr}$  ( $9000 \text{ kW}$ ). This duty becomes a refrigeration load for the propane system along with its  $23 \text{ MMBtu/hr}$  ( $6740 \text{ kW}$ ) refrigeration at  $-40^{\circ}\text{C(F)}$ . Therefore, the propane refrigeration system has to be designed to provide a total of  $53.71 \text{ MMBtu/hr}$  ( $15740 \text{ kW}$ ) at  $-40^{\circ}\text{C(F)}$  in addition to  $10 \text{ MMBtu/hr}$  ( $2930 \text{ kW}$ ) at  $-4^{\circ}\text{F}$  ( $-20^{\circ}\text{C}$ ) and  $7 \text{ MMBtu/hr}$  ( $2050 \text{ kW}$ ) at  $45^{\circ}\text{F}$  ( $7^{\circ}\text{C}$ ).



## Refrigerant Properties

**P-H** diagrams are used for hand calculations of refrigeration cycles. The **P-H** diagram for Propane is shown on this slide. Similar diagrams can be found in **Section 24** of the GPSA data book (**Ref. 2**).

Physical properties of pure component refrigerants in common use are given in **Fig. 14-13** of the GPSA data book. The vapor pressure curves for ethane, ethylene, propane, propylene, and Refrigerant 22 (R-22) are available in **Figure 23.28** and **23-29** of the GPSA data book. Vapor pressure data for other refrigerants can be obtained from refrigerant manufacturers. Enthalpy data are necessary in designing any refrigeration system. Pressure-enthalpy diagrams for pure ethane, ethylene, propane, propylene, and R-22 are available in **Section 24** of the GPSA data book. Enthalpy data for other refrigerants can be obtained from refrigerant manufacturers.

## Power and Condenser Duty Estimation

Since many gas processing plants require mechanical refrigeration, generalized charts were developed to aid in a modular approach for designing refrigeration systems.

Because of the complexity of generalizing refrigeration systems, the charts have been developed for four of the most common refrigerants: ethylene, propylene, propane, and Refrigerant 22.

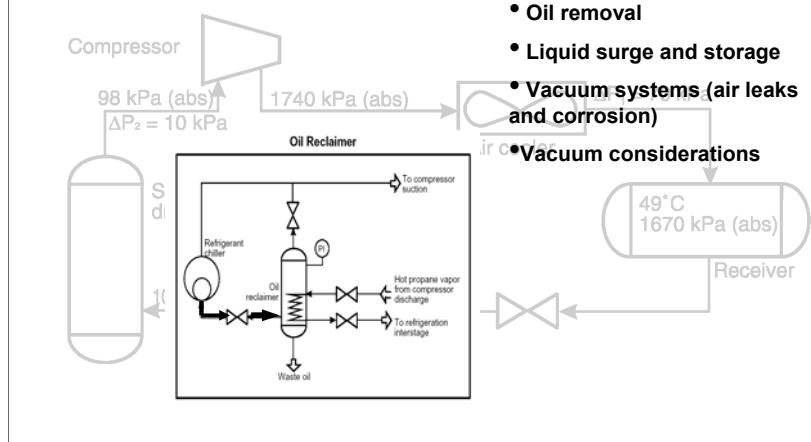
In order to apply these curves to most of the commercially available compressors, a **polytropic efficiency** of 0.77 was assumed. The **polytropic efficiency** was converted into an **isentropic efficiency** to include the effects of compression ratio and specific heat ratio ( $k = Cp/Cv$ ) for a given refrigerant. For well balanced and efficient operation of the compressor, an equal compression ratio between stages was employed. The refrigeration level is defined as the temperature of the dew point vapor leaving the evaporator. The pressures at the compressor suction and side load inlet nozzles were adjusted by 1.5 psi (10 kPa) to allow for pressure drop. These charts also include a 5 psi (35 kPa) pressure drop across the refrigerant condenser for ethylene, and a 10 psi (70 kPa) drop for propane, propylene, and Refrigerant 22. Before developing any system, one must define refrigerant temperature and condensing temperature of the refrigerant based on the medium used for condensing. To achieve maximum energy conservation and minimum energy cost, it is necessary to match the process conditions and refrigeration compressor design to obtain the best efficiency. After defining the lowest refrigerant level and the condensing temperature, the pressure at the evaporator and condenser can be established from the vapor-pressure curve for a specific refrigerant. All examples and data in this section are based upon pure component properties. In practice, pure hydrocarbon refrigerants are not always available. Impurities may cause significant deviations in design and performance.

**One-Stage Systems** — **Figs. 14-14** through **14-17** of the GPSA data book, provide data for estimating gas power and condenser duty requirements for one-stage refrigeration systems using ethylene, propane, propylene, and R-22 refrigerants.

**Two-Stage Systems** — The data for estimating gas power and refrigerant condenser duty requirements for two stage refrigeration systems utilizing ethylene, propane, propylene, and R-22 are shown in **Figs. 14-18** through **14-21** of the GPSA data book.

**Three-Stage Systems** — The data for estimating gas power and condenser duty requirements for three-stage refrigeration systems utilizing ethylene, propane, propylene, and R-22 are presented in **Figs. 14-22** through **14-25**.

# Natural Gas Liquid Recovery – Design and Operating considerations



## Design and Operating Considerations

The following are some of the important parameters that should be considered while designing any refrigeration system to provide a safe, reliable, and economical operation.

**Oil Removal.** Oil removal requirements from evaporators are related to the type of the refrigerant, lubricant, evaporator, and compressor used in the refrigeration cycle. The figure shown on this slide, illustrates the application of an oil reclaimer in a propane refrigerant cycle. In order to remove oil from the refrigerant, a slip stream of refrigerant from the bottom of the chiller is drained into the reclaimer where hot propane refrigerant from the compressor discharge is used to evaporate the refrigerant into the compressor suction. The oil is removed from the bottom of the reclaimer. Similar arrangements can be utilized for other hydrocarbon and ammonia refrigerants. Operation may be designed for either manual or automatic. Where halocarbon refrigerants and/or synthetic lubricants are employed, it is imperative that the oil reclaimer system be approved by the compressor manufacturer.

**Liquid Surge and Storage.** All refrigeration systems should have a liquid surge and storage vessel, commonly called a receiver. A surge vessel is required on all systems where the operating charge in the evaporator(s) and the condenser(s) varies due to variable load conditions. In addition to accommodating a varying refrigerant charge, the receiver drains the condenser(s) of liquid so that the effective condensing surface is not reduced by liquid backing up. The refrigerant charge in a receiver may vary over a wide range, from a minimum at full load to a maximum at no load. Systems with inadequate surge vessels often cause problems as they lose the liquid seal due to load variations that always occur. Surge vessels or receivers are relatively inexpensive and when sizing them, consideration should be given to: (1) a volume equal to 100% of the system inventory at 80% full level, and (2) the availability and quantity of refrigerant makeup.

**Vacuum Systems.** Refrigeration systems can operate with a suction pressure below atmospheric pressure. These vacuum systems require special considerations: Where hydrocarbons are used with reciprocating compressors (which employ rod "packing"), **air can enter the compressor** and possibly form a hazardous mixture. Extreme care should be taken where such systems are used. These systems must have a manual or automatic purge system. Double acting packing should be employed. Where halocarbons such as R-11, R-114, R-113, and other low pressure, high volume refrigerants are employed with centrifugal compressors, the deep vacuums may "draw" air and moisture through flanges, seals, etc. This **water-oxygen combination in the presence of halocarbons forms acid** and causes "crevice corrosion" of the tubes along with some other problems. A positive purge system must be employed and frequent monitoring of the moisture content in the refrigerant is suggested. High pressure halocarbons R-12, R-22, and others are employed in vacuum systems with reciprocating, centrifugal, and screw compressors. These systems will suffer from the same corrosion problems as defined above, but to a lesser extent. However, since they are generally used at lower temperatures, water in the system can freeze the control valve and in the evaporator. Refrigerant dryers are required in these systems. A good purge system is also required. Ammonia has been employed with reciprocating, centrifugal, and screw compressors in vacuum service for many years. Since water will not freeze in the presence of ammonia and the aqua-ammonia formed is only slightly corrosive, this type system has few problems during operation. A good purge system is recommended.

## Considerations for Vacuum

### Refrigeration Systems:

1. Eliminate all flanges where possible;
2. Weld all piping;
3. Use weld in-line valves;
4. Use steel "refrigeration type" stop valves with "back seating" feature and seal caps instead of hand wheels. All suction line valves should be angle valves to reduce pressure drop.
5. Install and maintain a good dryer on halocarbon and hydrocarbon systems.
6. Install a purge unit to keep the system free of air and non-condensables.
7. All control valves should have bellows-type seals instead of packing if the internal pressure is below atmospheric.
8. An oxygen analyzer is required to detect the presence of air.

# Natural Gas Liquid Recovery – Design and Operating considerations

- Material of construction

- ✓ no copper in presence of ammonia and sulfur compounds

- ✓ Steel is preferred (CS down to -20°F)

- ✓ Aluminum alloy and SS for very low  $T_s$

- ✓ ANSI B31.3 and B31.5 design codes

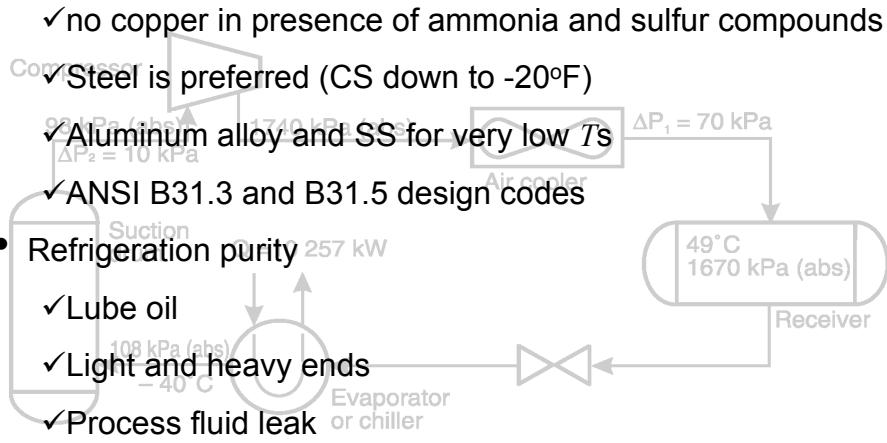
- Refrigeration purity

- ✓ Lube oil

- ✓ Light and heavy ends

- ✓ Process fluid leak

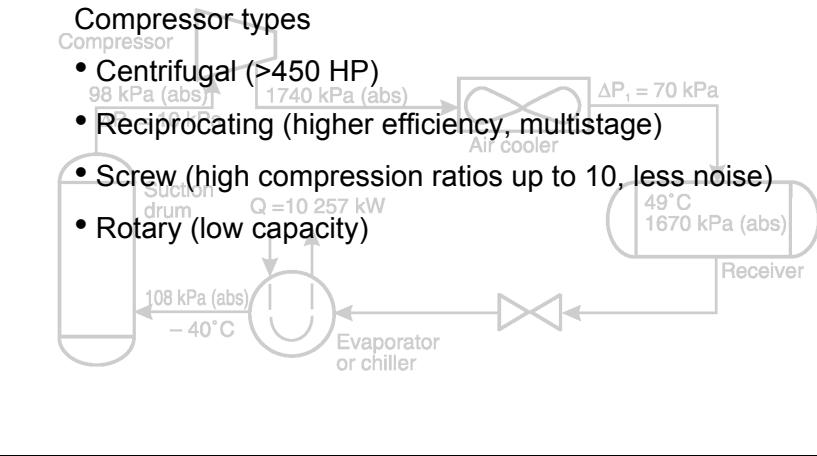
- ✓ Air leak and humidity (use drier or methanol wash/purge)



**Materials of Construction** — Materials of construction for refrigeration systems relate specifically to the type of refrigerant used. Some of the basic guidelines are: (1) **No copper or copper-based alloys** can be used with **ammonia** refrigeration systems. (2) Where  **$\text{SO}_2$ ,  $\text{H}_2\text{S}$ , or similar corrosive chemicals** are in the process side or are present in the atmosphere, **copper or copper-based alloys are unsuitable** (3) Generally, copper and copper alloys can be employed with hydrocarbon and halocarbon refrigerants; however, for most systems **steel piping and components are recommended**. (4) Due to the ambient temperature vapor pressure of most refrigerants, the refrigeration system is normally designed for 250 psig (1725 kPa) or greater. The low temperature components of the system will operate at temperatures and coincident pressures far below the design pressures. Generally speaking, carbon steel can be used to -20°F (-29°C). The ASME pressure vessel code section 8 addresses the issue of material selection and impact testing for systems operating below -20°F (-29°C). Certain provisions in that code may allow carbon steel use for components which operate at pressures less than 25% of design pressure. In many applications, **Charpy** impact testing will be required. The **ANSI B31.3** pipe code is generally used for most refrigeration systems in gas processing plants. This code has some provisions for use of materials to -49°F (-45°C) which are normally limited to -20°F (-29°C) and should be consulted for application in this area. There also exists an **ANSI B31.5 "Refrigeration Piping Code"** which has been used in some applications. (5) Various alloys and aluminum are normally used for low temperature operations and may be economically advantageous at temperatures above -20°F (-29°C).

**Refrigerant Purity** — Refrigerant contaminants can consist of several components: (1) Lubricating oil tends to accumulate in the chiller. Lube oil contamination is reduced by controlling the amount of compressor cylinder lubrication, using synthetic lubricants, providing a good compressor discharge vapor separator to eliminate free oil, and providing a good reclaimer to remove oil accumulation. (2) Lighter constituents in the refrigerant charge, such as ethane for a propane system, tend to accumulate in the refrigerant receiver, causing higher condensing pressure. Light component contamination is controlled by the type of refrigerant which is purchased. It can be further reduced by purging the receiver vapors. If the process plant inlet pressure is sufficiently low, the accumulator can be purged into the plant inlet for recovery of the hydrocarbons. (3) Butane and heavier constituents in a propane refrigeration system tend to accumulate in the chiller. Heavy component contamination is normally not a severe problem, and it is best controlled by draining from the bottom of the lowest temperature chiller. (4) Process fluid constituents may leak into the refrigerant in the chiller. (5) Air can be introduced through the compressor packing if cylinder pressures are below atmospheric. (6) Moisture, if present, will form ice and plug up the system either at the control valves or in the chiller. Moisture normally enters the system with the purchased refrigerant charge; it can be the source of considerable operating problems until it is removed. Some refrigeration systems employ a continuous drier, some only a moisture indicator. The problem can usually be eliminated by injecting methanol in the system and draining it from the chiller. Moisture must also be removed prior to the start-up of a new system, normally by evacuating the system, purging the system with nitrogen or dry gas, injecting methanol, or a combination of these.

## Natural Gas Liquid Recovery – Refrigeration Compressors



### Types of Compressors

There is a variety of compressors to choose from for refrigeration services. The most common are centrifugal, reciprocating, and screw compressors. The type of refrigerant used also influences the compressor choice. Small, up to 200 *HP* (150 *kW*), halocarbon-type refrigeration systems normally use reciprocating compressors which have the crankcase vented to the compressor suction. This type compressor can also be used for propane, but the problem of propane solubility in the oil at higher temperatures requires special lubricating oil and a crankcase heater. Refrigeration load also influences the compressor selection. Centrifugal compressors are not normally economical below about 540 *HP* (400 *kW*) with motor drivers, or about 800 *HP* (600 *kW*) with turbine drives. Above 1,000 *HP* (750 *kW*), and particularly where the load is close to an even multiple of this number, the use of centrifugal compressors becomes more economical. For lower powers, reciprocating, screw, and rotary compressors are commonly used.

**Centrifugal Compressors** — At the normal process temperatures encountered in gas processing, a three or four wheel centrifugal compressor is normally required for refrigeration service. This offers the opportunity of utilizing multiple interstage flash economizers and permits multiple chiller temperature levels for further reductions in power. Centrifugal compressor capacity is controlled by speed variation or suction or discharge pressure throttling. Discharge throttling can cause surge. It is also possible to recirculate refrigerant discharge vapors to the compressor suction during operation at lower loading in order to avoid surge problems. Such recirculation results in wasted power and is one of the primary drawbacks to utilizing centrifugal units. For more details on Centrifugal Compressors, refer to Section 13 of the GPSA data book (*Ref. 2*).

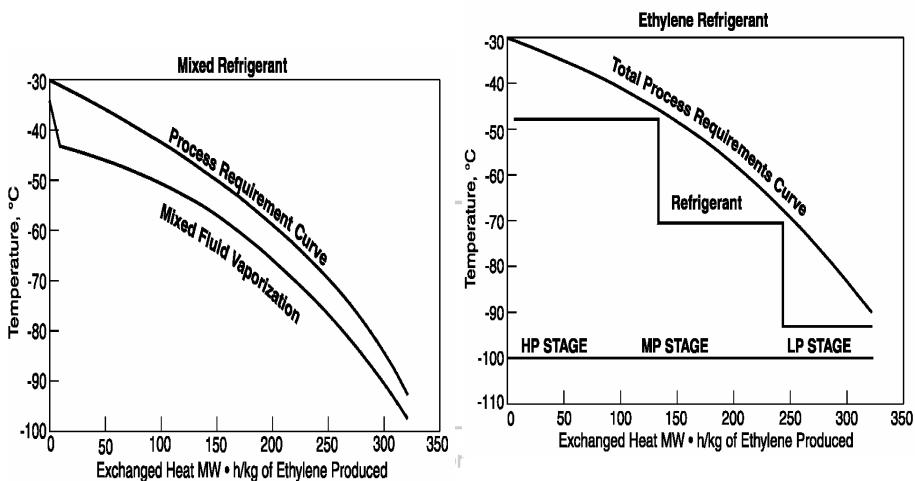
**Seal Gas and Lube Oil System.** Centrifugal compressors are sealed at the shaft by *labyrinth* seals. To protect against possible entry of oil into the refrigerant, an outward leakage of gas is permitted out of each *labyrinth* seal. However, to prevent a loss of valuable refrigerant, there is a provision at the middle of the compressor end *labyrinth* seal to inject a stream of less valuable gas (referred to as *seal gas*). The *seal gas* is supplied at a pressure higher than the pressure behind the compressor wheel at a rate slightly higher than that leaking out through the seals. It is the *seal gas* that leaks out, thus retaining the more valuable refrigerant. The *seal gas* leaks by the seals and combines with the lube oil leaving the unit and enters the lube oil surge tank. A *seal gas filter* is usually provided at the inlet to the refrigerant compressor. The filter element should be changed out at regular intervals. The *seal gas* flow for a given pressure on the *seal gas* is set by factory clearances designed into each *labyrinth* seal.

**Reciprocating Compressors** — Process temperatures generally dictate two stage compression in a reciprocating machine. This affords the opportunity for one interstage economizer, and also one additional level of chilling. In a conventional refrigeration system, the first stage cylinder is normally quite large as a result of the low suction pressure. The economizer also reduces first stage volume, cylinder diameter, and consequently rod load. Capacity adjustment is accomplished by speed variation, variable clearance on the cylinders, valve lifters, and recirculation of refrigerant vapor to the suction. As with centrifugal compressors, recirculation does result in wasted power. It is also possible to throttle the refrigerant suction pressure between the chiller and compressor in order to reduce cylinder capacity. However, suction pressure control can result in wasted power and the possibility of below atmospheric suction pressure, which should be avoided. For more details on Reciprocating Compressors, refer to Section 13 of the *Ref 2*.

**Screw Compressors** — Screw compressors have been used in refrigeration systems for many years. They can be employed with all refrigerants. The limitation for suction pressure is about 3 *psi* (21 *kPa*) with standard discharge pressures at 350 *psi* (2400 *kPa*). Discharge pressures of over 725 *psi* (5000 *kPa*) are also available. Screw compressors are gaining popularity in the gas processing industry. Screws can operate over a wide range of suction and discharge pressures without system modifications. **There are essentially no compression ratio limitations with ratios up to 10 being used.** They operate more efficiently in the 2 to 7 ratio and are comparable in efficiency to reciprocating compressors within this range. Automatic capacity control can provide capacity adjustments from 100% down to 10% with comparable reduction in power requirements. Screw compressors normally operate at 3600 *rpm* direct coupled to motor drives. However, they can operate over a range of speeds from 1500 to 4500 *rpm*. Engine drives, gas turbines, and expanders can also be used as drivers.

**Rotary Compressors** — There is a limited application for large rotary compressors. This is the low-temperature field in which the rotary serves the purpose of a high volume low stage or booster compressor. These booster compressors are applied at saturated suction conditions ranging from -124°F to -6°F (-87°C to -21°C) with R-12, R-22, ammonia, and propane refrigerants. Available units range in power from 10 to 600 *HP* (7 to 450 *kW*) and in displacement from 60 to 3600 *ft³/min* (*cfm*) or 2 to 102 *m³/min* in a single unit.

## Natural Gas Liquid Recovery – Mixed refrigerant



### Mixed Refrigerants

Cryogenic processes which remove heat below ambient temperature generally use pure compounds as refrigerants in a closed mechanical refrigeration system. However, when it is not necessary to remove the heat at a practically constant temperature, it may be advantageous to use a mixture of refrigerants. In a proper composition, a mixed refrigerant can minimize temperature differences between the process stream and the refrigerant during heat exchange. This match provides an efficient chilling system. The most common conventional refrigerants, R-22 and propane, exhibit atmospheric boiling temperatures of -41 and -44°F (-41°C and -42°C), respectively. Lower temperatures can be obtained utilizing propylene, ethane, and ethylene, which have atmospheric boiling temperatures of -54, -128, and -155°F (-48°C, -89°C, and -104°C), respectively. However, these refrigerants require the use of a cascade system because condensation at ambient temperatures is not feasible. One alternative is the use of a mixed refrigerant; for example, ethane-propane. The ethane lowers the evaporation temperature while still permitting condensation at ambient temperatures, albeit at considerably higher pressures. The figures shown on this slide, compare the shape of process chilling curves for an ethylene refrigerant cycle with a mixed refrigerant cycle. The shape of the refrigerant vaporization curve is a function of the composition of the mixed refrigerant. In these figures the composition of the mixed refrigerant is methane 8 mol %, ethylene 37 mol %, and propane 55 mol %. Some of the design parameters to be considered while evaluating the application of a mixed refrigerant cycle include:

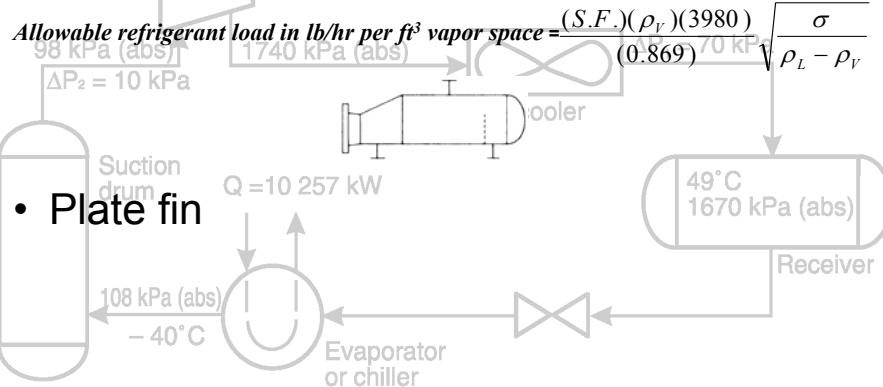
- Compressor suction pressure.
- Shape of vaporization curve.
- Compressor discharge pressure and compression ratio.
- Type of controls.
- Type of compressor.

Mixed refrigerants present the problem of component segregation with the lighter components concentrating in the receiver, and the heavier components concentrating in the chiller unless the refrigerant is totally vaporized. Because of the high condensing pressure, mixed refrigerants significantly increase the power per ton of refrigeration.

## Natural Gas Liquid Recovery – Refrigeration Chillers

- Kettle type

Compressor



### Chillers

**Kettle Type Chiller** — The most common type of chiller employed in the gas processing industry is the kettle type. The refrigerant is expanded into the shell of the kettle where a level is maintained to completely submerge the process tube bundle. A level control maintains the proper amount of refrigerant in the kettle. When using a kettle type chiller, care should be taken to provide adequate vapor disengaging space above the operating level of liquid refrigerant. This type chiller improperly designed and operated is probably the largest single cause of compressor failure due to liquid carryover. **Figs. 14-28 and 14-29** of the GPSA data book, taken from **TEMA** tentative standards, represent design data for sizing vapor disengaging space for kettle type chiller in refrigeration services. The following equation allows determination of allowable refrigerant load:

$$\text{Allowable refrigerant load in lb/hr per ft}^3 \text{ vapor space} = \frac{(S.F.)(\rho_v)(3980)}{(0.869) \sqrt{\frac{\sigma}{\rho_L - \rho_v}}}$$

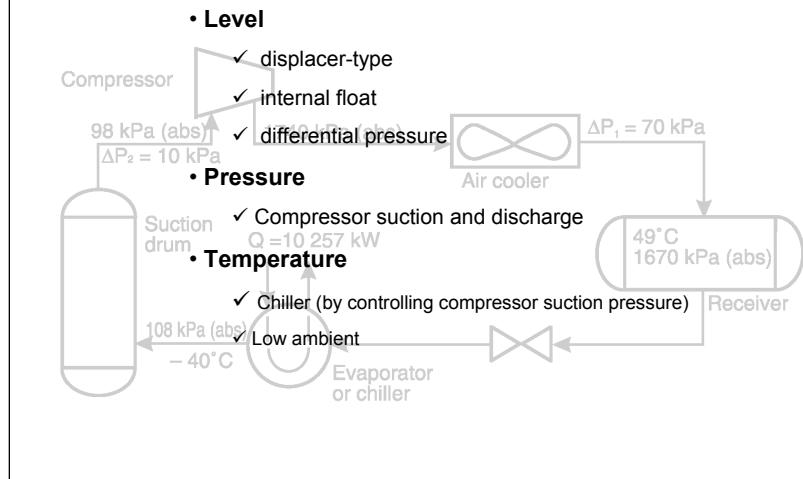
Where, S.F. is safety factor =  $\frac{1}{2}$  and

$\rho_v$  and  $\rho_L$  are vapour and liquid densities in  $\text{lb/ft}^3$

**Plate-Fin Chillers** — Modern cryogenic plants frequently employ plate-fin exchangers for gas cooling and chilling. When the design calls for a hot gas-gas exchanger, a gas chiller, and a cold gas-gas exchanger in sequence, then it may be convenient to put these services in single plate-fin exchanger. Also, plate-fin exchangers offer significant savings for low temperature application where stainless steel is needed for shell and tube units. Significant pressure drop savings can be realized by using single or multiple units for chilling services.

For other types of heat exchangers, refer to **Sections 9 and 10 of Ref. 2**.

# Natural Gas Liquid Recovery – Refrigeration Control System



**Level Controls** — External cage (**displacer-type**) level controls are the most commonly used in refrigeration services and are probably the most reliable and easy to maintain instruments. However, because the float chamber is external to the refrigeration system, it is imperative that the float chamber and connecting lines to the chiller be adequately sized and well insulated. Vaporization of refrigerant (due to heat leak) in the float chamber can result in difficulty in maintaining proper level. **Internal float level** controls eliminate this problem, but present some problems in instrument maintenance. A **differential pressure** device is also frequently used for chiller level control; it affords good control when properly installed. The **high pressure side connection from the liquid phase should be large, well insulated**, and installed in such away that lubricating oil cannot accumulate and cause erroneous readings. The **low pressure side connection to the vapour phase should be un-insulated and possibly even liquid sealed or heated** to prevent liquid accumulation. The same problem exists in level indication. External gauge glasses should have large connecting lines to the chillers and good insulation. Bull's-eye sight glasses are much better for direct indication of chiller level and normally do not present any maintenance problem other than cleaning the glass. Frost plugs are sometimes used and give an approximate level indication while requiring no maintenance.

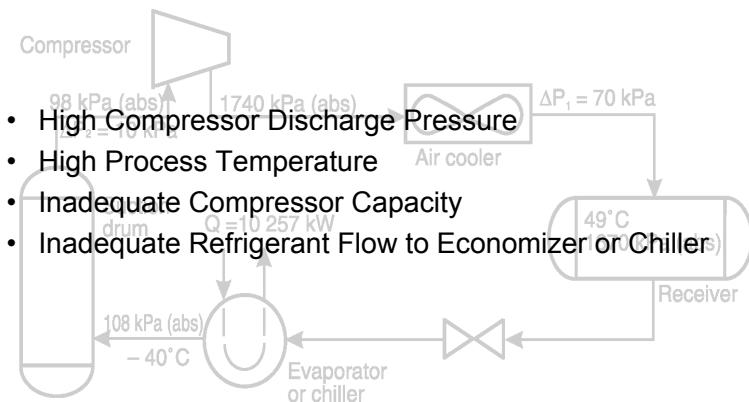
**Pressure Controls** — Refrigerant compressor high suction pressure control may be desirable when there are multiple refrigerant compressors in the system. Without high suction pressure control, loss of one refrigerant compressor can result in overloading of the other compressors and loss of all units in an unattended operation. However, suction pressure control can also result in power waste if the compressor suction is throttled unnecessarily. The refrigerant compressor hot gas bypass is used to prevent compressor suction pressure from getting too low. If the process load decreases, the hot gas bypass will open to maintain a satisfactory compressor suction pressure in an unattended plant. If hot gas bypass remains open, the compressor capacity should be adjusted to reduce bypassing in order to conserve energy. Screw compressors need no such arrangements as they can be automatically unloaded to satisfy the suction pressure settings.

**Evaporator Temperature** — The evaporator (or chiller) temperature is normally controlled by controlling the refrigerant pressure on the chiller. This may be accomplished by using back pressure valves, refrigerant compressor speed, or hot gas bypass around the compressor.

**Low Ambient Controls** — All refrigeration systems should have low ambient controls where ambient temperature is below  $39^\circ\text{F}$  ( $4^\circ\text{C}$ ). These controls, which maintain a preset pressure differential between the condenser and the evaporator pressures, are necessary for continuous operation and for start-up at low ambients. There are several approaches to these controls:

1. For air coolers used as condensers, louvers, air recirculation systems, and fan cycling are employed.
2. For both shell and tube condensers and air coolers, condensing pressure can be controlled by installing a pressure regulating valve actuated by condensing pressure set at a minimum predetermined pressure in the line between the condenser and the liquid receiver. In addition, a small pressure regulator set at a predetermined pressure is installed in a line between the discharge line and the liquid receiver. This regulator will direct enough hot gas to the receiver to keep the pressure high enough to operate the evaporator liquid control valve.
3. Where a shell and tube condenser is used, a water flow control valve operated by condenser pressure can be utilized. This type control may cause sediment and scaling in the condenser.
4. Where evaporative condensers are used, several methods can be employed to control condensing pressure depending upon the ambient temperature and type of installation.
  - The condenser can be selected to operate as an aircooler at temperatures below  $32^\circ\text{F}$  ( $0^\circ\text{C}$ ) (water system shut down and drained) while employing a fan cycling controller.
  - A system as described above in item 2 can be employed.
  - Where the system is indoors with the condenser outdoors, an indoor water sump can be employed with a fan cycling controller.

## Natural Gas Liquid Recovery – Refrigeration Operations and trouble shooting



### **High Compressor Discharge Pressure.**

Check accumulator temperature. If the accumulator temperature is high, check:

1. Condenser operation for fouling.
2. High air or water temperature.
3. Low fan speed or pitch.
4. Low water circulation.

If condensing temperature is normal, check for:

1. Non-condensables in refrigerant.
2. Restriction in system which is creating pressure drop.

### **High Process Temperature**

Check refrigerant temperature from chiller.

If refrigerant temperature is high and approach temperature on chiller is normal, check:

1. Chiller pressure.
2. Refrigerant composition for heavy ends contamination.
3. Refrigerant circulation or kettle level (possible inadequate flow resulting in superheating of refrigerant).
4. Process overload of refrigerant system.

If refrigerant temperature is normal, and approach to process temperature is high, check:

1. Fouling on refrigerant side (lube oil or moisture).
2. Fouling on process side (wax or hydrates).
3. Process overload of chiller capacity.

### **Inadequate compressor capacity**

Check:

1. Process overload of refrigerant system.
2. Premature opening of hot gas bypass.
3. Compressor valve failure.
4. Compressor suction pressure restriction.
5. Low compressor speed.

### **Inadequate Refrigerant Flow to Economizer or Chiller**

Check:

1. Low accumulator level.
2. Expansion valve capacity.
3. Chiller or economizer level control malfunction.
4. Restriction in refrigerant flow (hydrates or ice).

## NATURAL GAS TRANSPORTATION

- World demands low carbon fuels (environmental concerns)  
Wood → Coal → Oil → Gas → H<sub>2</sub> → Other alternatives
- Electricity-generation technologies trends:  
Conventional gas and coal fired power plants (30%) → natural gas combined cycle (60%) → Fossil fuel cells (predominantly natural gas)
- Transportation challenges
  - Pipeline
  - LNG (Liquefied Natural Gas)
  - CNG (Compressed Natural Gas)
  - NGH or Natural Gas Hydrate
  - ANG (Adsorbed Natural Gas)
  - Gas Chemical Conversion (GTL, etc.)

Natural gas is more abundant around the world than was estimated just ten years ago. The world energy sources has evolved during the last two hundred years from a reliance on more carbon intensive fuels to less carbon content fuels; from wood with a carbon intensity of about 1.25 (i.e., carbon to hydrogen atoms ratio) to natural gas (methane) with a carbon intensity of 0.65. The trend for global energy consumption is moving towards no-carbon content fuels such as hydrogen. Electricity generation technologies are improved so that the efficiencies become higher (the 60 % promised combined cycle efficiencies) and the emissions become lower (with the fuel cell technologies and zero emission promises) and we see the natural gas relation with this improvements.

As the demand for natural gas increases for the above reasons, the demand for technologies and modern techniques to transport the gas from remote areas to consumption centers increases. United States, Europe, Japan, China and India are the major energy markets in the world. Almost 2/3 of the known conventional gas reserves are located in the Russian confederation and the Middle East region where the long distance between the gas resources and its final consumption markets is the major obstacle in efficient exploitation of the gas.

There are of course transportation challenges which should be fulfilled especially for remote and offshore reserves. There are four basic options to utilize offshore and remote gas production and transport it to markets or to another location for further processing or utilization: **1)** Gas gathering and transmission to shore, in a gaseous phase, by pipeline; **2)** Volume reduction through either liquefaction or compression (**LNG**, **CNG**) followed by marine vessel Transportation; **3)** Conversion to other products, by changing the "methane" molecule (methanol, synthetic crude), followed by marine vessel transportation to markets; **4)** Conversion to other energy form such as electric power and transmission by a subsea cable to shore.

The current established technologies for long distance transportation of natural gas are pipeline and **LNG**; pipeline would normally be considered first. However, based on most locations, the distances to shore accompanied with relatively small gas volumes may be cost prohibitive if a new system has to be considered. In absence of an existing gas gathering and transmission system the other utilization options would then economically make more sense. Volume reduction options as an alternative to pipeline then have to be considered next, followed by true conversion alternatives where the "methane" molecule is chemically converted into an other product such as ammonia, methanol or synthetic hydrocarbon liquid. It should, however, be noted that these technologies have not seen to date any offshore applications.

While pipelines are more economical for distances below 2000-3000 km., there are of course emerging technologies such as **marine CNG**, **hydrate** and **absorbed natural gas (ANG)** with their own advantages and constraints each of which requires a separate discussion. Another choice to transport gas to consumption markets is to convert (chemically) it to liquid products including middle distillates, methanol, **DME**, etc. These technologies are called **gas-to-liquids** or **GTL**. Although **GTL** is used more for conversion of gas to middle distillates such as naphtha, kerosene, diesel and gasoline, it is alternatively used for other gas conversion technologies such as *methanol* and *dimethyl ether (DME)* production.

There are other routes to exploit natural gas by converting the gas to electricity and exporting the gas through wire and using the gas to make steel; these are options which have been used for many years in many parts of the world. Of course natural gas has been the main choice to enhance the production capacity of crude reserves for years now and for many years to come.

An overview of the above mentioned technologies with emphasis on **LNG**, **CNG** and **GTL** will be presented here.

## Natural Gas Transportation – LNG technologies

- Why to liquefy?
- World LNG market and production
- Production options
  - Large scale commercial production
  - Small peak shaving facilities
- Existing technologies
  - Cascade Refrigeration
  - Mixed refrigerant/*Precooled and dual mixed refrigerant*
  - Expander cycle
- Major technology players
  - ConocoPhilips (*cascade*),
  - Shell (*dual mixed refrigerant or DMR*)
  - Linde/Statoil (*hybrid cascade MRC*),
  - APCI® (*pre-cooled mixed refrigerant, MCR™*),
  - Technip TEALARC®, *Hybrid cascade-mixed refrigerant*
  - Black & Veatch Prico® *simple MRC*
  - IFP LIQUEFIN™ (*dual mixed refrigerant*)

### LIQUEFIED NATURAL GAS PRODUCTION

The principal reason for liquefying natural gas is the 600-fold reduction in the volume which occurs with the vapor-to liquid phase change. This volume reduction is important in the transportation and storage of the gas. In the liquid state, the gas can be transported in discrete quantities, can be economically stored in tanks for use as required, and can be transported long distances not feasible with gas pipelines. Currently Major producers and exporters of LNG in the world are Nigeria, Oman, Qatar, Malaysia, Libya, Trinidad, Brunei, Australia. There are major projects either under construction or feasibility studies in Iran and Egypt which will affect the market of LNG in very near future. The existing world annual LNG demand was about 150 billion cubic meter (2002 BP statistics) and Japan, Korea, France and Spain as the major importers of LNG. Japan consumes almost 50% of the world LNG production alone, Korea 16%, and France and Spain almost 8% each. China, India and the United States are predicted to join the league of major importers of LNG in the next few years. US gas consumption in 2002 was about 1,800 million cubic meter per day (23 TCF/year or 26% of world gas production). Imported LNG constituted only 1% of US gas consumption. US share of world LNG import is currently only 4%, however due to the sever natural gas crunch in the United States, it is predicted that this country becomes one of the major LNG importers of the world within the next 10-15 years needing about **35-40 billion standard cubic meter** of gas in LNG from per year (approximately 20-25% of world LNG market). Based on the current predictions, the prices of gas will remain above \$4/MMBtu. This will significantly affect the world LNG trade and make most LNG projects profitable in the long run. Due to environmental issues related to use of coal for power generation, China's growth in consumption of natural gas for power generation will be significant. This will be true for India as well. The next slide shows LNG market in 2002. (see also natural gas consumption and production numbers in Pages 8 to 12 of the course notes).

The major technology players are listed on this slide.

## World LNG trade (2002)

### Natural gas

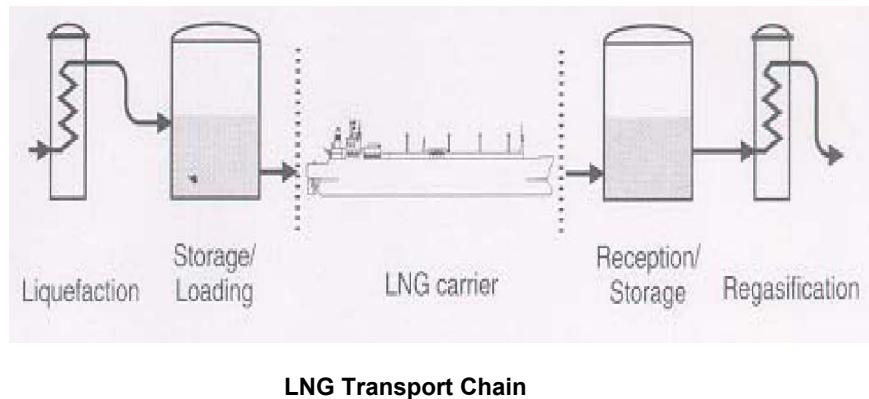
#### Trade movements 2002 – LNG\*

Billion cubic metres

To	USA	Trinidad & Tobago	From										Total imports		
			Oman	Qatar	UAE	Algeria	Libya	Nigeria	Australia	Brunei	Indonesia	Japan	Malaysia		
<b>North America</b>															
USA	-	4.28	0.09	0.99	-	0.75	-	0.23	-	0.07	-	-	0.07	-	6.48
<b>S. &amp; C. America</b>															
Puerto Rico	-	0.58	-	0.05	-	-	-	-	-	-	-	-	-	-	0.63
<b>Europe</b>															
Belgium	-	-	-	-	0.10	3.20	-	-	-	-	-	-	-	-	3.30
France	-	-	0.54	-	-	10.20	-	0.80	-	-	-	-	-	-	11.54
Greece	-	-	-	-	-	0.50	-	-	-	-	-	-	-	-	0.50
Italy	-	-	-	-	-	2.20	-	3.50	-	-	-	-	-	-	5.70
Portugal	-	-	-	-	-	-	-	0.43	-	-	-	-	-	-	0.43
Spain	-	0.46	0.76	2.20	0.50	5.95	0.63	1.61	0.07	0.08	-	-	-	-	12.26
Turkey	-	-	-	-	-	4.08	-	1.27	-	-	-	-	-	-	5.35
<b>Asia Pacific</b>															
Japan	1.70	-	1.09	8.40	5.93	-	-	-	9.72	7.95	23.40	-	14.50	0.05	72.74
South Korea	-	-	5.48	6.95	0.32	-	-	-	0.24	1.04	6.78	0.15	3.10	-	24.06
Taiwan	-	-	-	-	-	-	-	-	-	-	4.15	-	2.85	-	7.00
<b>TOTAL EXPORTS</b>	<b>1.70</b>	<b>5.32</b>	<b>7.96</b>	<b>18.59</b>	<b>6.85</b>	<b>26.88</b>	<b>0.63</b>	<b>7.84</b>	<b>10.03</b>	<b>9.14</b>	<b>34.33</b>	<b>0.15</b>	<b>20.52</b>	<b>0.05</b>	<b>149.99</b>

Source: BP

## Natural Gas Transportation – LNG technologies



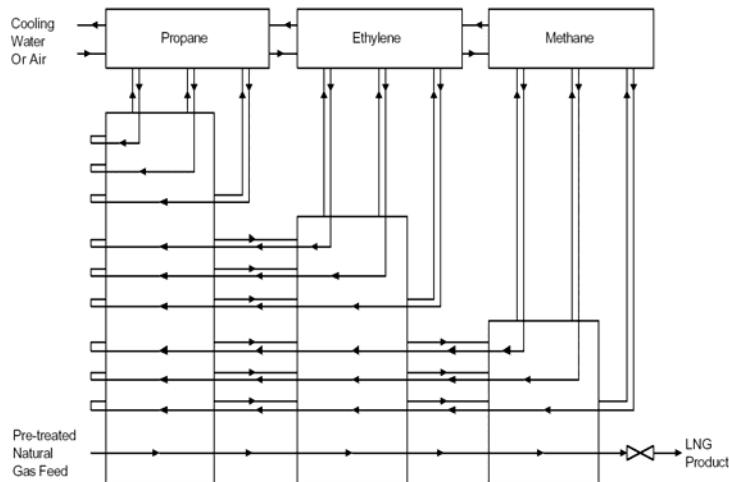
Because methane is the primary component of natural gas, the production of **Liquefied Natural Gas (LNG)** involves the chilling of the entire natural gas feed stream to cryogenic temperatures sufficient to totally condense the gas stream. Liquefaction is carried at a pressure determined by economic factors. The temperature at which natural gas is stored in liquid form is close to methane normal boiling point - 259°F (-161.5°C). Common to all *LNG* liquefaction processes is the need to pretreat the gas to remove components, such as CO<sub>2</sub> and water, which will solidify in the liquefaction step. The liquefaction unit also has to remove hydrocarbon components, such as benzene and cyclohexane, which can solidify. After liquefaction the gas is stored in appropriate storage tanks and loaded into LNG ships which can carry the gas to very long distances. The liquid should be then transferred to storage facilities at destination sites, vaporized, and pumped to pipelines therefore, regasification facilities are required before the gas could be delivered to the pipeline.

Two types of *LNG* facilities have been developed: **1) large base load** units for continuous *LNG* production to export markets, and **2) small peak shaving** plants for gas distribution systems. The *large scale based load* units are typically designed with emphasis on process efficiency. In addition to the process units involved in the liquefaction step, *base load LNG* plants tend to be large complex facilities which involve product storage, loading and complete stand-alone utility systems. *Peak shaving* facilities differ from base load units in several aspects. *Peak shaving* plants are much smaller, operate only a portion of the year, and are often located near the point of use for the gas. The design emphasis is thus on capital cost minimization rather than thermodynamic efficiency. In order to produce the low temperature necessary for liquefaction, mechanical refrigeration systems are utilized. Three types of **liquefaction** processes can be used to accomplish this refrigeration:

1. **Cascade Refrigeration** Process
2. **Mixed Refrigerant** Process
3. **Precooled Mixed Refrigerant** Process

Each of these processes has been used for liquefaction facilities with the *PreCooled* process being the predominant technology in base load units. The *Cascade* and *Mixed Refrigerant* processes have both been used in a wide range of process sizes in both base load and peak shaving units with the *Mixed Refrigerant* process being the dominant technology in *peak shaving* units.

## Natural Gas Transportation – LNG Processes



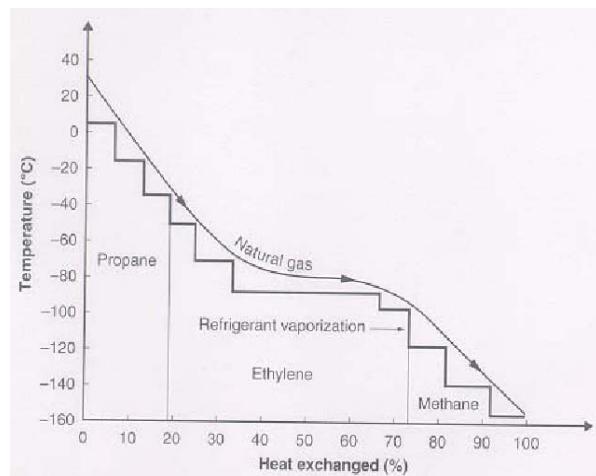
Schematic of Cascade Process (simplified)

### Cascade Refrigeration

The first LNG liquefaction units utilized the cascade refrigeration process. These facilities use the classical cascade cycle where three refrigeration systems are employed: propane, ethylene and methane. Two or three levels of evaporating pressures are used for each of the refrigerants with multistage compressors. Thus the refrigerants are supplied at eight or nine discrete temperature levels. Using these refrigeration levels, heat is removed from the gas at successively lower temperatures. The low level heat removed by the methane cycle is transferred to the ethylene cycle, and the heat removed in the ethylene cycle is transferred to the propane cycle. Final rejection of the heat from the propane system is accomplished with either water or air cooling. Early facilities used a closed methane refrigeration loop. More modern designs use an open methane loop where the methane used for refrigerant is combined with the feed gas and forms part of the LNG product. The efficiency and cost of the process is dependent on the number of refrigeration levels provided in each refrigeration system. The refrigeration heat exchange units traditionally were based on shell and tube exchangers or aluminum plate fin exchangers. Newer designs incorporate plate fin exchangers in a vessel known as “core-in-kettle” designs. A critical design element in these systems is the temperature approach which can be reached in the heat exchangers.

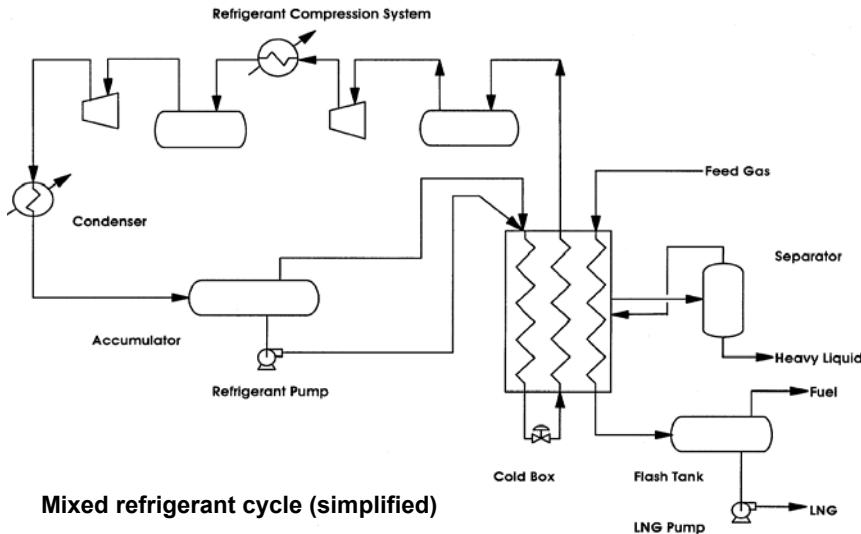
Natural gas is cooled, condensed and sub-cooled in heat exchange with propane, ethylene (or ethane), and finally methane in three discrete stages, as shown on this slide. Each refrigerant circuit normally has three or four refrigerant expansion and compression stages. After compression, propane is condensed with cooling water or air, ethylene is condensed with evaporating propane, and methane is condensed with evaporating ethylene. The cascade cycle requires less power than any other liquefaction cycle, mainly because the refrigerant flow is lower than in other cycles. It is also flexible in operation as each refrigerant circuit can be controlled separately. The mean temperature differences between the composite curves are wide relative to those of the mixed refrigerant cycle so the cascade cycle requires less heat exchanger surface area. The main disadvantage of the cascade cycle is the relatively high capital cost due to each refrigeration circuit having its own compressor (with associated suction drums and interstage coolers) and refrigerant storage. A large plot area is required. The large number of equipment items also means maintenance and spares costs tend to be comparatively high. Whilst the cascade cycle is efficient and has low surface area, the complex machinery configuration is an important penalty. Economies of scale dictate that the cascade cycle is suited to very large train capacities where the low heat exchanger area and low power requirement offset the cost of having multiple machines. The cascade cycle can then be competitive against the **Air Products and Chemicals Inc. (APCI) Pre-Cooled Mixed Refrigerant** the dominant cycle in base-load plants for thirty years. The **Phillips Optimized Cascade** process was used for the 3.2 million tons per annum *Atlantic LNG* project at Point Fortin, Trinidad, which started up in Summer 1999, and has been used again for the second and third trains. The success of this project is due to a number of factors but it has rightly initiated industry-wide reappraisal of the use of cascade refrigeration technology.

## Natural Gas Transportation – LNG Processes



**Natural Gas Liquefaction Profile of Temperature as a Function of Heat Removed**

## Natural Gas Transportation – LNG Processes (cont.)

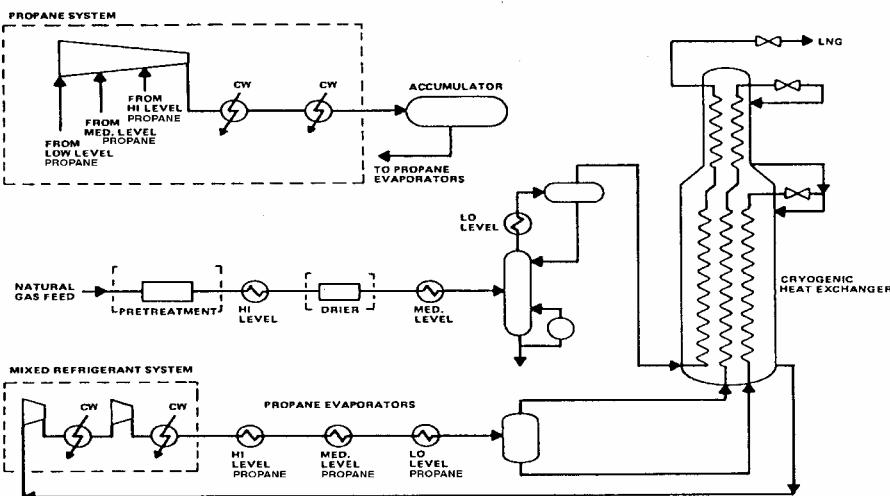


### Mixed Refrigerant Processes

After initial developments of cascade LNG plants, the mixed refrigerant cycle was developed to simplify the refrigeration system. The **mixed refrigerant cycle (MRC)** system uses a single mixed refrigerant composed of nitrogen, methane, ethane, propane, butane and pentane. Various forms of MRC have been used in base-load plants and in smaller-scale plants. The machinery configuration is simple and the power requirement is usually not much higher than for a cascade cycle. The refrigerant composition is specified so that it evaporates over a temperature range similar to that of the natural gas being liquefied and provides close matching of composite cooling and warming curves. The closeness of the match of these two curves is a direct measure of the efficiency of the process. The small temperature driving forces give increased thermodynamic efficiency, reduced power consumption and hence smaller machinery. Even so, a typical MRC usually has a lower efficiency than a cascade cycle because refrigerant flow is high and the associated thermodynamic losses lead to inefficiency. Furthermore, the MRC is normally susceptible to changes in feed conditions, which may necessitate large design margins to be used or reduced performance to be accepted. Compared to the cascade cycle the MRC has a simple process configuration and less equipment as there is only one compressor and fewer vessels for refrigerant separation. The process (see the slide) has two major components: the refrigeration system and the main exchanger cold box. The cold box is a series of aluminum plate fin exchangers which provide very close temperature approaches between the respective process streams. The low pressure refrigerant is compressed and condensed against air or water in a closed system. The **PRICO®** cycle is the simplest form of mixed refrigerant cycle. Mixed refrigerant is compressed and passes through the main exchanger where it is condensed. It is then expanded across a Joule-Thomson valve and evaporated as it returns counter-currently through the exchanger back to the compressor. The refrigerant is not totally condensed before being sent to the cold box. The high pressure vapor and liquid refrigerant streams are combined and condensed in the main exchanger. The condensed stream is flashed across a J-T valve and this low pressure refrigerant provides the refrigeration for both the feed gas and the high pressure refrigerant. Removal of pentane and heavier hydrocarbons from the feed gas is accomplished by bringing the partially condensed gas out of the cold box and separating the liquid at an intermediate temperature. The liquid removed is then further processed to produce a specification C<sub>5</sub><sup>+</sup> product. Light products from this separation are returned to the liquefaction system.

On larger MRC plants it is cost-effective to pre-cool the feed gas by a separate propane refrigeration system. This chills the natural gas prior to liquefaction and the cost of the propane compressor can be justified based on the overall power saving. The **APCI®** propane pre-cooled MRC has been used on virtually all base-load plants in the last twenty years and has been optimized to give similar or lower power consumption than a cascade design. **Dual mixed refrigerant** cycles have also been utilized, in which a separate mixed refrigerant is used to pre-cool the natural gas feed, the primary mixed refrigerant or both. These can offer similar power consumption to the propane pre-cooled cycle, have less equipment and potentially enable larger train sizes. Developments in MRC technology for small and mid-scale LNG plants are very important. These improve the efficiency of the natural gas chilling step by using mixed refrigerant, as with the dual mixed refrigerant concept, but with only one main refrigerant circuit. Power consumption is similar to the propane pre-cooled or dual refrigerant cycles but only a single compressor is needed. As machinery cost is a major component of overall project cost for a small or mid-scale facility, reducing the number of cycle compressors from two to one reduces capital cost significantly.

## Natural Gas Transportation – LNG Processes (cont.)



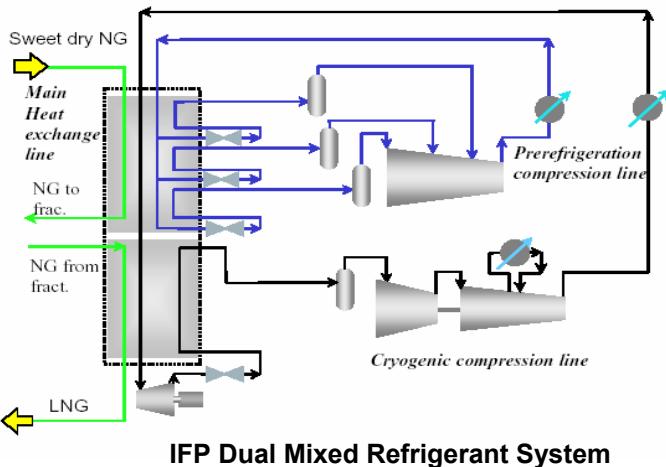
**Precooled Mixed Refrigerant Process**

### Precooled Mixed Refrigerant Process

The propane precooled mixed refrigerant process (shown on this slide) was developed from a combination of the cascade and mixed refrigerant processes. In this process, the initial cooling of the feed gas is accomplished by using a multistage propane refrigeration system. The gas is cooled with this system to around  $-40^{\circ}\text{C}(F)$  at which point the gas is processed in a scrub column to remove the heavy hydrocarbons. The gas is then condensed in a two step mixed refrigerant process. The chilling of the gas is accomplished in a single, large, spiral-wound heat exchanger. This exchanger allows extremely close temperature approaches between the refrigerant and the gas to be achieved. The mixed refrigerant in this process is a lighter mixture composed of nitrogen, methane, ethane and propane with a molecular mass around 25. The mixed refrigerant after recompression is partially cooled with air or water and then further cooled in the propane refrigeration system. The partially condensed refrigerant from the propane chilling is separated and the high pressure vapor and liquid streams sent separately to the main exchanger. The liquid is flashed and provides the initial chilling of the gas. The high pressure vapor is condensed in the main exchanger and provides the low level, final liquefaction of the gas. As in the other processes, the *LNG* leaves the exchanger subcooled and is flashed for fuel recovery and pumped to storage.

Air Products' *MCR™* process is based on a propane precooled, mixed-refrigerant cycle with the company's spool-wound *MCR* main cryogenic heat exchanger. The process is claimed to be a synergistic hybrid of the cascade *LNG* process and the all mixed refrigerant process. The propane precooling step is the same for the cascade and the *MCR* and is more efficient than mixed refrigerant over the precooling temperature range of 104 to  $-22^{\circ}\text{F}$  ( $40$  to  $-30^{\circ}\text{C}$ ). However, over the liquefaction and subcooling temperature range of  $-22$  to  $-256^{\circ}\text{F}$  ( $-30^{\circ}\text{C}$  to  $-160^{\circ}\text{C}$ ), heavy and light mixed refrigerant stages, together, are more efficient than pure component ethylene and methane multiple pressure cascades. A single *MCR* main cryogenic heat exchanger replaces the multiple ethylene and methane cold boxes required by the cascade process for a world scale plant.

## Natural Gas Transportation – LNG Processes (cont.)

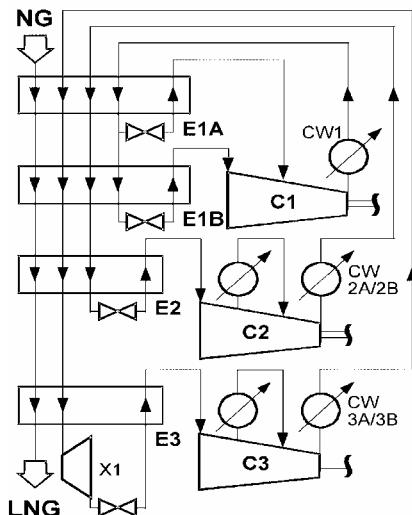


Both Shell and IFP developed LNG production processes based on dual mixed refrigeration or DMR. The IFP process is shown on this slide. The *IFP Liquefin™* process is a dual mixed refrigerant cycle process, incorporating new patented features. The basic principle of this process can be described by referring to the simplified flow scheme in the figure shown on this slide. The pre-refrigeration of the gas is achieved by using a mixed refrigerant instead of propane. In this process, the pre-refrigeration cycle is operated at a much lower temperature than in a conventional dual-cycle process: the temperature is decreased down to a range of -60°F to -110°F (-50°C to -80°C). At these temperatures, the cryogenic mixed refrigerant can be completely condensed, no phase separation is necessary and moreover the quantity of cryogenic refrigerant is substantially reduced: the weight ratio between the cryogenic mixed refrigerant and *LNG* can be lower than unity. The overall necessary power is decreased, as the quantity of cryogenic mixed refrigerant is lower, and as a good part of the energy necessary to condense it is shifted from the cryogenic cycle to the pre-refrigeration cycle. Moreover, this shifting of energy allows to get a better repartition of the exchange loads: the same number of cores in parallel can be used all along between the ambient and the cryogenic temperature, allowing a very compact design for the heat exchange line. In the *Liquefin™* process, both mixed refrigerants are used in the same way as pure components. The mixed refrigerant is condensed and vaporized at different pressure levels in each section, without any phase separation or fractionation. This helps also to get a very simple, compact exchange line. A very significant advantage of this new scheme is the possibility to adjust the power balance between the two cycles making it possible to use the full power provided by two identical gas turbines. *IFP* claims that *Liquefin™* has all the positive features of the cascade process with a much better efficiency and a smaller number of rotating equipment:

- **No integrated cascade:** As the mixed refrigerant of the second cycle is fully condensed, the two mixed refrigerants can be used in a similar way to the pure refrigerants used in the cascade process.
- **A balanced power:** the process is easily adjustable to get the same power for each cycle, thus allowing to use two identical gas turbines. It avoids the difficulty, encountered with the *C<sub>3</sub>/MR* cycle, of having to transmit power somehow from the pre-cooling to the cryogenic cycle.
- **Compact heat-exchange line:** the *Liquefin™* process has also been designed to make the best use of plate-fin heat-exchangers. A single heat exchange line is used to cool gas from ambient temperature down to cryogenic temperatures. The process has been conceived to make the exchange line simple and compact.

*Shell* claims that their *dual mixed refrigerant (DMR)* process is a combination of plant simplification and enhanced safety and that the technology also has the advantage of operating on more flexible specifications regarding feedgas and refrigerant. For offshore facilities, *DMR* is self-contained, meaning it generates its own refrigerants on the ***floating LNG (FLNG)*** facility. *DMR* does not require the initial fill and replenishment of costly propane produced onshore and then transported to the *FLNG* facility. Eliminating the use of propane and butane storage and export in *Shell's FLNG* design also enhances safety.

## Natural Gas Transportation – LNG Processes (cont.)

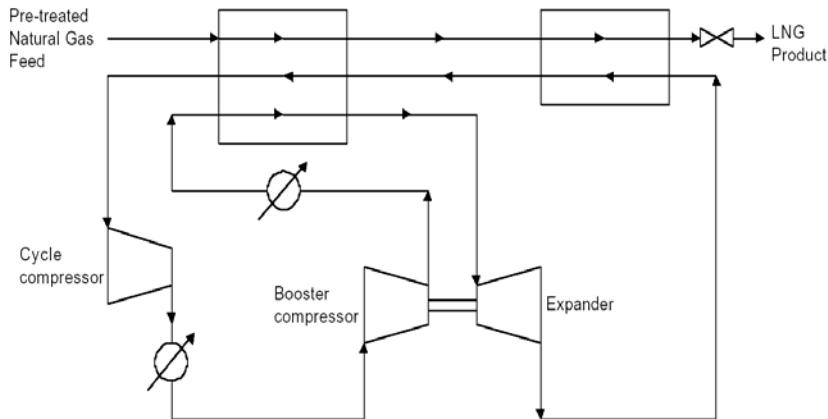


**Hybrid Mixed Fluid-Cascade Process Liquefaction Technology**  
Statoil - Linde Proprietary MFCP

### Mixed Fluid Cascade Process

The figure on this slide shows a sketch of the **Linde** patented **MFCP™**, consisting of three mixed refrigerant cycles arranged in cascade. The pre-cooling cycle with a mixture of ethane and propane is compressed in compressor C1, liquefied in sea water cooler CW1 and sub-cooled in plate fin heat exchanger E1A. One part is throttled to an intermediate pressure and used as refrigerant in E1A. The other part is further sub-cooled in plate fin heat exchanger Compared to other *LNG* baseload processes the *MFCP* offers, as a main advantage, that both spiral wound heat exchangers for natural gas liquefaction and sub-cooling are of similar size. This split of the liquefaction and subcooling cycle capacity into two results in smaller suction volumes for the recycle compressors C2 and C3 and also smaller diameters of the heat exchangers E2 and E3. Therefore, these spiral wound heat exchangers are well within the limits of **Linde's** manufacturing capabilities and are not the limiting factor for the size of the liquefaction train.

## Natural Gas Transportation – LNG Processes (cont.)



Turbine Expansion Cycle Process

In its simplest form, compression and work-expansion of gas as shown here on this slide, provide refrigeration in a closed cycle. Work-expansion reduces the cycle fluid temperature to a sufficiently low temperature to produce *LNG*. The work generated is recovered through a booster-compressor brake, which supplements the cycle compressor and reduces overall power consumption.

The cold, low pressure gas stream from the expander is returned through various stages of heat exchange where its refrigeration is given up to the incoming natural gas and incoming cycle gas. The warmed cycle gas is then re-compressed by the main cycle compressor and booster-compressor. The **refrigerant cycle gas can be either nitrogen or methane** so feed gas can be used directly. Nitrogen permits sub-cooling of the natural gas to temperatures low enough to eliminate flashing on letdown of the *LNG*. Expander cycles have a number of advantages over both cascade and mixed refrigerant cycles. They enable rapid, simple start-up and shutdown which is important if frequent shutdowns are anticipated, such as on peak-shave plants. As the refrigerant is always gaseous and the heat exchangers operate with relatively wide temperature differences, changes in feed gas composition are easily tolerated with minimal requirement for change of the refrigerant circuit. The cycle fluid is maintained in the gaseous phase so avoiding any concerns of distributing vapour and liquid phases uniformly into the heat exchanger. Two-phase distributors can thus be avoided and this, along with the small heat exchangers, results in a relatively small cold box. Many of these issues are important in consideration of *LNG* production offshore. The single major disadvantage of the expander cycle is its relatively high power consumption, compared with the cascade and mixed refrigerant cycles. For small plants, the simplicity of the cycle and the small number of equipment items can make up for the high power consumption but the expander cycle struggles to be competitive for larger onshore facilities. The basic single expander cycle can be modified to increase efficiency. For example, power consumption can be reduced by approximately 20% by natural gas pre-cooling with a conventional vapour compression cycle, typically using propane. This introduces extra complexity but is cost-effective if the additional equipment cost is offset by the reduction in size and cost of the nitrogen cycle machinery.

An alternative to propane pre-cooling is to employ two expanders, operating over different temperature levels. This has been conventional practice in the liquefaction of nitrogen and oxygen for over twenty years. Two expanders allow closer matching of the composite curves than with a single expander, giving reduced temperature driving forces and higher thermodynamic efficiency. Power consumption is similar to a pre-cooled single expander cycle but without the need of a separate refrigeration system. This concept minimizes the inventory of hazardous hydrocarbon. From a site safety and overall plot plan perspective this can be very important.

## Natural Gas Transportation – LNG Processes: Process comparison

**Table 1. Comparison of Liquefaction Cycle Efficiencies**

CYCLE	APPROXIMATE POWER CONSUMPTION RELATIVE TO CASCADE CYCLE
Cascade cycle	1.00
Single stage mixed refrigerant cycle	1.25
Mixed refrigerant cycle with propane pre-cooling	1.15
Multi-stage mixed refrigerant cycle	1.05
Single expander cycle	2.00
Single expander cycle with propane pre-cooling	1.70
Double expander cycle	1.70

Approximate specific power for each cycle relative to a cascade is shown in **Table 1**. Comparing the cascade cycle with the more efficient mixed refrigerant cycles, the difference in power consumption is small. Depending on the extent of process optimization work it may even be negligible. The complexity of the cascade cycle, and the large number of equipment items, ensures that it can only be competitive for very high capacities. The specific energy requirement for *LNG* production depends on feed conditions, ambient conditions and on compressor efficiency (which depends on the type and size). **Specific powers** of around **0.2 HP/lb** (0.33 kWh/kg) of *LNG* are typical for a cascade cycle. The power consumption of alternative cycles and process options can be compared using **Table 1** to permit initial economic evaluation and cycle selection before process design is performed.

## Natural Gas Transportation – LNG Processes: Process comparison (cont.)

**Table 2. Liquefaction Cycle Evaluation**

CRITERIA	CASCADE	MRC	EXPANDER
Efficiency	High	Moderate/High	Low
Complexity	High	Moderate	Low
Heat exchanger type	Plate-fin	Plate-fin or wound coil	Plate-fin
Heat exchanger area	Low	High	Low
Flexibility	High	Moderate	High

**Table 3. Evaluation of Multi-Stage MRC Performance**

NUMBER OF STAGES	POWER REQUIRED RELATIVE TO ONE STAGE
1	1
2	0.93
3	0.90
4	0.88
5	0.87

A broad comparison of each cycle is summarized in **Table 2** to assist in cycle selection. Because of the differing attributes of the various cycles, more than one type of cycle can be applicable for a given *LNG* capacity. Expander plants are favored on the smallest *LNG* facilities with single compressor *MRC* plants being economical on larger peak shave plants. For base-load plants, propane pre-cooled *MRC* or dual cycle designs are favored due to their high efficiency. Cascade plants are appropriate for the largest base-load capacities.

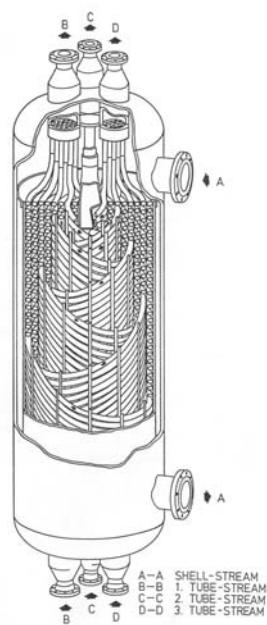
Table 3 shows effect of multistaging in performance of *LNG* plants. As the number of compression refrigeration stages increases the thermodynamic performance increases but the plant complexity also increases. A trade off should exist which will only be known after an accurate cost-benefit study. Usually three stage is the maximum number of stages which have been used in most large scale commercial *LNG* plants.

## Natural Gas Transportation – LNG Processes: LNG heat exchanger

### The coil-wound heat exchanger

- **Produces by:**
  - Air Products and Chemicals Inc. in USA
  - Linde in Germany
- **The heat exchangers are made in aluminum.**
- **Dimensions of a the main LNG coil-wound heat exchanger is as follows:**

• Height	10-50 m
• Diameter	3-5 m
• Core tube diameter	1 m
• Tube length	70-100 m
• Tube diameter	10-15 mm



Spiral wound heat exchangers are one of the most widely used and the most efficient heat exchangers for natural gas liquefaction processes. *Air Products* and *Linde* are the two most well known manufacturers of this type of heat exchangers. Some typical dimension data are provided in this figure.

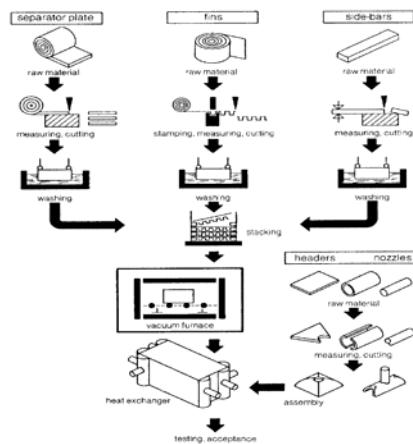
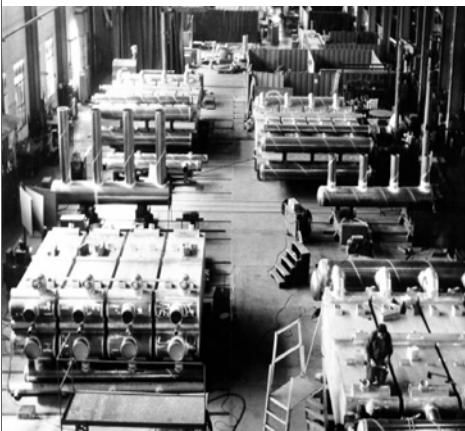
## Natural Gas Transportation – LNG Processes: LNG heat exchangers



**Spiral Wound Heat Exchanger Under Construction,**  
**Source: Linde**

This slide shows a spiral wound heat exchanger under construction at *Linde* workshops. 10-15 mm tubes are used to enhance the heat transfer surface area.

## Natural Gas Transportation – LNG Processes: LNG heat exchangers



**Plate Fin Exchangers Under Manufacturing Process**

Manufacturing process of plate fin heat exchangers are shown on this slide. The aluminum brazed exchangers are also widely used in *LNG* processes.

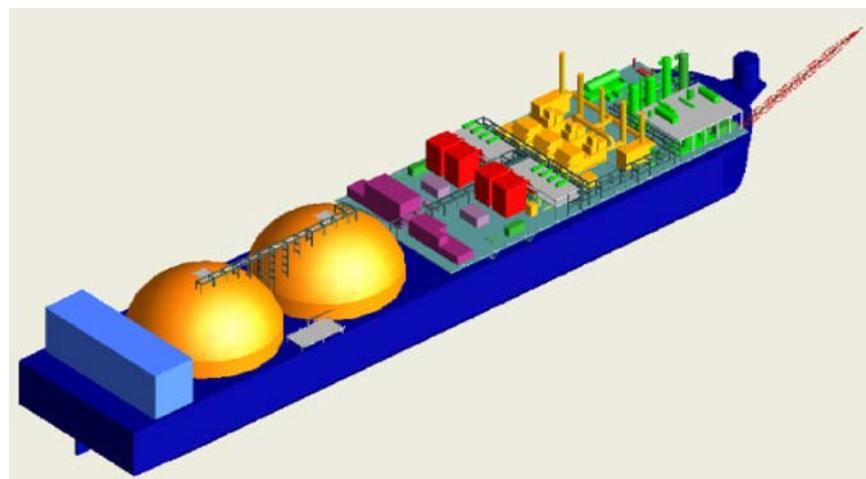
## Natural Gas Transportation – LNG Processes: LNG heat exchangers



Spiral Wound Heat Exchangers During Fabrication Process And Within The Cold Box  
Together With Plate Fin Exchangers (Mossel Bay Plant In South Africa)

The pictures show how *Linde* demonstrated and proved the correctness of the thermodynamic, hydraulic and geometrical design as well as the mechanical integrity of their ***Spiral Wound Heat Exchangers (SWHE)*** concept; a spiral wound heat exchanger with three individual tube bundles in one unit was designed and fabricated by *Linde*. It was installed in parallel to plate fin heat exchangers within the existing *Linde LNG* plant at the Mossgas (GTL plant) Refinery in Mossel Bay, South Africa. The performance tests, in which the liquefier was operated in stable conditions from around 20 up to 110 % of the name plate capacity, was claimed confirmed the predicted process scenarios. In addition robustness tests have been carried out, in which the coldest tube bundle of the liquefier was exposed to rapid temperature changes with gradients exceeding 18 °F/min (10 °C/min) or warming up by 104 to 122°F (40 to 50 °C) in less than 20 minutes as to simulate plant failures. As the Mossel Bay LNG plant is mainly used for peak-shaving and back up purposes, controlled frequent shut-downs are quite common. Since the start up of the SWHE in September 1998 the exchanger was exposed to about 30 controlled shutdowns. *Linde* claims the SWHE so far has given satisfaction with respect to mechanical integrity as well as smooth performance. The figures on this slide also show the installation of the complete SWHE in a prefabricated *Cold Box*. Air products have also similar claims about their SWHE concepts.

## Natural Gas Transportation – LNG Processes: Offshore/Floating Facilities



Model of a Nominal 2.0 Million Tons per Annum Floating LNG Facility  
that uses a Double Nitrogen Expander Cycle

For natural gas utilization from small or remote fields, or to avoid associated gas flaring from oil production, offshore liquefaction can be appropriate if the cost of piping gas to shore is prohibitive. Floating LNG facilities may be quickly moved between fields and produce gas sooner than would otherwise be possible. Many concepts for floating LNG facilities have been developed along lines similar to **Floating Production, Storage and Offloading (FPSO)** facilities, which are now commonplace for oil production. For liquefaction offshore, the criteria for technology selection differ from those for onshore liquefaction and this leads to an interesting conclusion as to the best choice of technology. The most important criteria offshore is to minimize the space required to give a safe plant, due to the effect on overall vessel size and overall cost. Offshore plants must also be insensitive to vessel motion, simple to operate and flexible to changes in feed gas rate or composition. They may be required to shutdown quickly in bad weather and should offer rapid start-up after such shutdowns or when moving between fields. In contrast to onshore liquefaction where energy efficiency has a large effect on overall cost, **energy efficiency is of secondary importance offshore**. The **expander cycle** gives a compact facility with the liquefaction plant, utilities and storage all in close proximity, minimizing ship size and therefore cost. The space requirements for the cascade and MRC cycle are greater in comparison because of the need for hydrocarbon refrigerant storage tanks. The expander cycle is inherently safe because storage of hydrocarbon refrigerant is not required; either nitrogen or methane is used as cycle fluid. A comparison is given in **Table 4** on the next slide, of the available liquefaction cycles versus key criteria for offshore facilities. In addition to being compact and inherently safe, the expander cycle refrigerant is always in the gaseous phase, the cold box is relatively short and no fractionation columns are required, so limiting the effect of vessel motion. In fact, the expander cycle is better than the *cascade* and *MRC* cycles against virtually all evaluated criteria. The first reported work on offshore liquefaction of natural gas concluded twenty years ago that the most appropriate technology was a nitrogen expander cycle with pre-cooling by mechanical refrigeration and liquefaction in aluminum plate-fin heat exchangers. Similar technology had been used extensively on LNG peak-shaving applications at plant capacities of up to 100 tons per day.

A similar concept was proposed recently by *BHP/Linde* for offshore LNG production from the *Bayu-Undan* field in the *Timor Sea* and has been recommended recently, for smaller plant capacities, by the European Union funded Project *Azure*. Recent design and engineering studies, including formal safety assessments, carried out for LNG capacities up to 3 million tons per annum, have demonstrated the suitability of the double nitrogen expander cycle. A model of such a facility is shown on this slide. Major technical issues including LNG storage, LNG transfer have been evaluated using well-proven concepts. It can be concluded that expander technology, extensively proven onshore, is highly appropriate for LNG production in offshore developments.

## Natural Gas Transportation – LNG Processes: Offshore/Floating Facilities (cont.)

**Table 4. Liquefaction Cycle Evaluation against Criteria for Use Offshore**

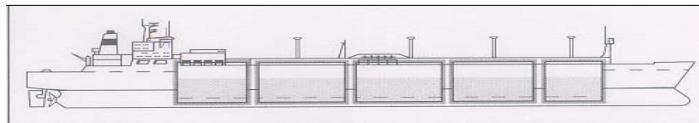
CRITERIA	CASCADE	MRC	EXPANDER
Uses proven technology	Yes	Yes	Yes
Overall space requirement	High*	Moderate*	Low
Refrigerant storage hazard	Yes	Yes	No
Sensitivity to vessel motion	Moderate	Moderate	Low
Simplicity of operation	Moderate	Moderate	High
Ease of start-up / shutdown	Moderate	Low	High
Flexibility to feed gas changes	High	Moderate	High
Efficiency	High	High	Low
Total Capital Cost	High	Moderate	Low

\* Due to requirement for hydrocarbon refrigerant storage

On this slide, different *LNG* processes have been compared for offshore applications. It has been concluded that expander technology is one of the most promising while other technology providers (e.g., Shell) also claim that their technologies are as competitive.

## Natural Gas Transportation – LNG Processes.

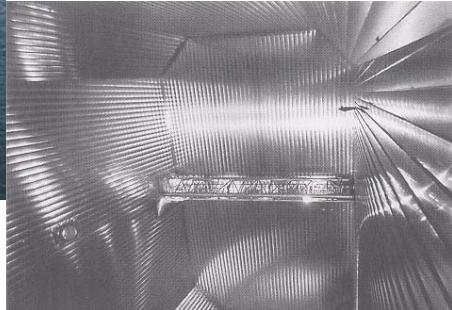
### LNG Carriers



**LNG Carrier with Gas Transport Membranes**



**LNG Tanks Interior**



Very special ship design is required for *LNG* carriers. The hull designed is usually a double-hull system with two layers of heat barrier and insulation. Gas evaporation is used to keep the system at the low required temperature and the evaporated gas is used for ship utility or as fuel for ship engine.

## Natural Gas Transportation – LNG Carriers

**LNG Carrier With Spherical Self Supporting Tanks**



An *LNG* carrier with spherical self supporting tanks is shown on this picture.

## Natural Gas Transportation – LNG Storage

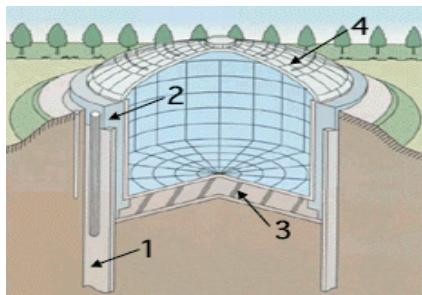
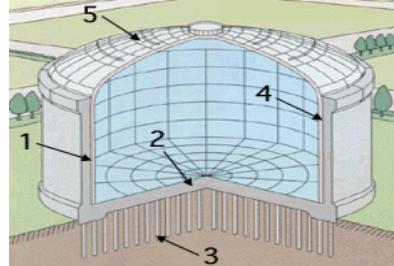


Figure 1. Underground LNG storage Tank



Figure 2. Aboveground LNG storage Tank



There are basically two types of *LNG* (liquid natural gas) storage tanks: above ground, and underground. To construct supply storage tanks that are both safe and reliable, main manufacturers designs them using cutting-edge analyses and design technology.

### Underground storage tanks

These are composed of continuous diaphragm walls, side walls and basemat slabs, and each tank has different requirements of performances. Major manufacturers have developed computer programs that can integrate all of these components into the design to make the design process much easier and faster.

In addition, when the ground freezes due to the low temperature of the *LNG*, frost heaving pressure and thermal stress act on the tanks. Main components of under-ground *LNG* storage tanks are shown on this slide (See *Figure 1*) as follows:

1. Continuous diaphragm wall
2. Side wall
3. Basemat slab
4. Roof

### Above-ground storage tanks

Recently, *LNG* storage tanks using prestressed concrete in exterior tank liner (PCLNG tanks) have come into mainstream use due to, among other things, their effective use of storage sites. *LNG* storage tank manufacturers have developed systems that calculate the optimum amount of prestress to be used in the design. Dynamic analysis systems that consider the interaction among ground, piles and tanks during an earthquake, and apply it to the design process have also been developed. Main components of above-ground *LNG* storage tanks are shown on this slide (See *Figure 2*) as follows:

1. Exterior tank liner (prestressed concrete wall)
2. Basemat slab
3. Steel pile
4. Interior tank liner
5. Exterior tank roof

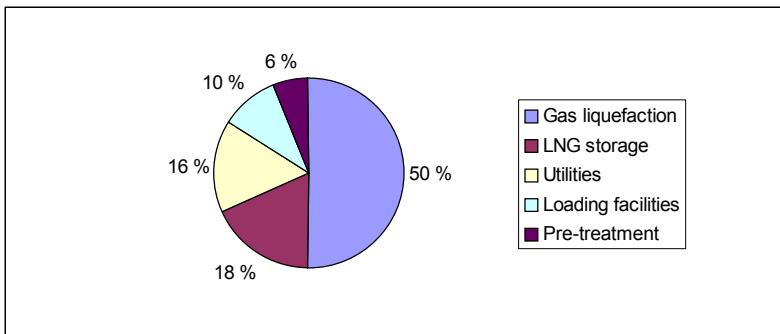
## Natural Gas Transportation – Base Load Plants

### Current LNG projects

LNG Plant / Current Project	Selected Technology	Largest train [MTPA]	Planned start-up
RASGAS Expansion, train 3 and 4, Qatar	APCI C <sub>3</sub> /MR	4.7	2004-5
Nigeria Expansion train 3	APCI C <sub>3</sub> /MR	3.0	2002
Atlantic LNG Expansion train 2 and 3, Trinidad	Phillips Cascade	3.3	2003
MLNG Tiga Expansion train 7 and 8, Malaysia	APCI C <sub>3</sub> /MR	3.6	2003
Northwest Shelf Expansion, train 4 Australia	APCI C <sub>3</sub> /MR	4.2	2004
Egypt SEGAS LNG	APCI C <sub>3</sub> /MR	5.0	2004
Nigeria Plus, train 4 and 5	APCI C <sub>3</sub> /MR	3.1	2005
Snøhvit, Hammerfest, Norway	Statoil/Linde MFCP	4.3	2006

The table on this slide shows some of the major ongoing LNG projects in the world and the relevant technologies used. Air Products and Chemicals Inc. APCI's *MCR™* technology has been one of the most widely used and efficient technologies.

## Natural Gas Transportation – LNG Plants Economics



**Breakdown of Liquefaction Plant Capital Costs**

(Finn et al. 1999)

The slide shows the effect of variables on the economics of LNG facilities. Gas liquefaction equipment and installation cost is the major element followed by LNG storage facilities. A 4 million ton per year facility will cost somewhere around \$ 1-1.5 billion.

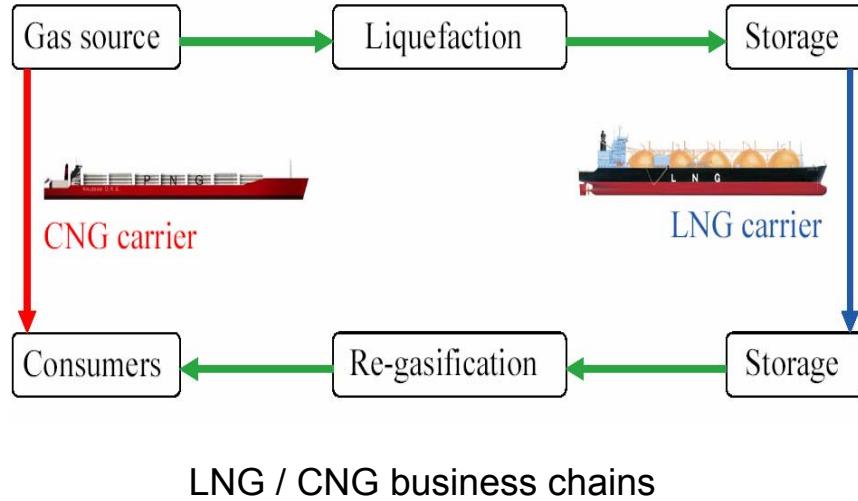
## Natural Gas Transportation – Marine CNG

- Marine transportation of compressed natural gas
  - Potential markets for CNG concepts
  - Trends in CNG technology
  - CNG carrier projects and designs
- Main Technology Players
  - Williams (Cran & Stenning)- **Coselle™** (Canada)
  - EnerSea LLC, **VOTRANS™** (USA)
  - TransCanada, **GTM** (Canada)
  - TransOcean, **Cassettes** (Canada)
  - Knutsen, **PAS™** (Norway)

LNG Carriers are currently the only commercial means of shipping natural gas by sea. While LNG Carriers are efficient at shipping large volumes of gas over long distances, the expense of the liquefaction plant and associated facilities make LNG too expensive for many markets. In numerous instances worldwide, gas reserves are located near potential markets, but the high cost of LNG liquefaction and transportation prevents its exploitation, especially when the gas reserves or market demand is small. The gas therefore remains **stranded** – not economical to be transported to demand centers. The invention of the **Coselle** pressure vessel by **Cran & Stenning** of Calgary, Alberta, Canada and the development of the **Coselle** Compressed Natural Gas (CNG) Carrier was a promising step to improve the economics of shipping natural gas over short sea routes, and from modest reserves. This invention also ignited renewed interest in CNG marine transportation and a few other concepts entered the scene: **Enerseas' VOTRANS** and **TransCanada's GTM**. The general promise from all these CNG concepts is to economically exploit modest reserves in moderate daily volumes over shorter transportation distances, thus unlocking reserves which would remain stranded where either pipeline or LNG are considered. An overview of current CNG technologies will be presented here which compares these to pipeline and LNG and provides general insight regarding the commercialization of this concept.

A number of joint industry projects have been conducted by the suppliers of various CNG technologies an *EPC* and *engineering* firms (e.g. *Fluor*) to confirm the technical and economic feasibility of the CNG concepts. At present, *Fluor* is conducting studies for various clients worldwide and actively seeking project applications for several CNG technologies. It is believed that a CNG concept is generally more cost effective than the LNG and pipeline alternatives when initial gas volumes are modest;  $5.4 \times 10^6$  to  $13.4 \times 10^6 \text{ Nm}^3/\text{d}$  (200 to 500 MMscfd), and distances are between 800 and 3,200 kilometers (500 and 2,000 miles). The scalability of the CNG system and the opportunity to reuse its major assets (the ships) makes the concept even more attractive.

## Natural Gas Transportation – Marine CNG



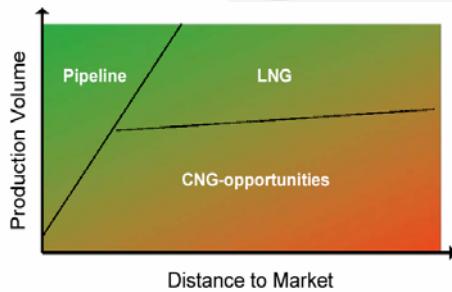
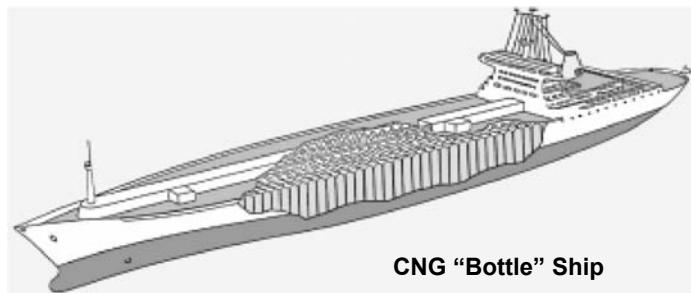
### Marine CNG Concepts Overview

Over the past 40 years there have been several attempts to develop a commercially viable CNG Carrier. In the late 1960's a CNG ship using vertical pressure bottles for CNG storage was tested in New Jersey Harbour. However, this and subsequent attempts failed to produce a commercial CNG Carrier, primarily because of the prohibitively high cost of the pressure containers. The discovery and development by Cran & Stenning of a new type of pressure containment vessel, called a **Coselle**, was the first attempt to improve the economics of the marine CNG systems. promises to improve the economics of CNG marine transport. This fact generated renewed interest in this gas transportation option and other concepts and CNG Marine Transportation proponents entered the scene. Williams has recently acquired the rights (August 2001) to commercialize the **Coselle** technology and is in the process of finalizing the technology for code classification purposes, with a full-scale prototype to be built this summer (small scale models have been completed and are undergoing testing). Potential projects are under evaluation, with the first anticipated to be in operation and delivering gas by early 2005.

Most recently, **EnerSea Transport** of Houston with the **Volume Optimized Transport and Storage (VOTRANS®)** and **TransCanada Pipelines** of Calgary with the **Gas Transportation Module (GTM)** are also in the process of commercializing their CNG technologies as alternatives to **Coselle**. A number of other players have joined the group of marine CNG technology suppliers. The **Knutsen PNG** and **Trans Ocean cassette** technologies are two on the other CNG systems. The major and ongoing focus of all proponents is on increasing the gas to container weight ratio either through improved materials (non-metallic components, higher yield steel) or through increasing the weight per volume of gas ratio by finding an optimum pressure/temperature relationship.

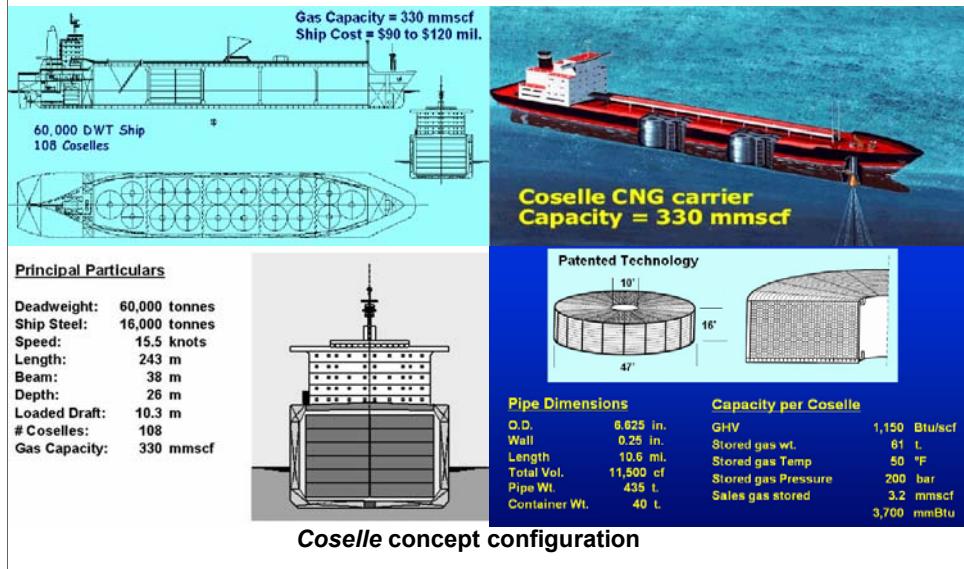
As it is shown on this slide the main advantage of the CNG systems is the elimination of the very costly liquefaction and re-vapourization (re-gasification) as well as storage loading and unloading elements of the **LNG** facilities.

## Natural Gas Transportation – Marine CNG



This slide shows, qualitatively, how the different gas transportation technologies compete. As mentioned before pipeline is the first to consider, while depending on volume of production or the size of the reservoir other two options namely *LNG* and *CNG* may be considered.

## Natural Gas Transportation – Marine CNG

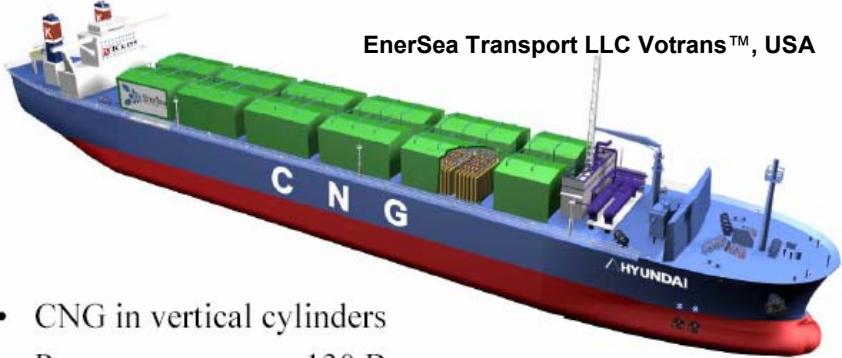


The central idea behind the **Coselle** is to create a large but compact CNG storage system, using pipe. A typical **Coselle** is shown in the figure on this slide. It consists of several miles of small diameter (6" gas pipe line grade) pipe coiled into a carousel (hence the word "Coselle"). A large portion of a typical CNG Carrier's capital cost is the gas containment system and associated safety and gas control systems. Therefore, the safety and cost of the gas containment system is critical to the economics of CNG marine transport. It is claimed that **Coselles** cost a fraction of conventional pressure bottles (or bullets) and yet maintain at least an equivalent level of safety. For example, a **Coselle CNG Carrier** of 330 MMcf capacity would cost about \$110 million whereas an equivalent CNG "bottle-ship" would cost at least \$300 million.

In a typical **Coselle CNG Carrier** the ship is designed as a double-hulled 60,000-dwt bulk carrier concept in order to develop the ship requirements and cost. In this design, **Coselles** are carried in stacks of 6 high within the ship's hold. In total there are 18 stacks of **Coselles** (108 **Coselles** per ship). Each **Coselle** holds 3.2 MMcf of sales gas so the ship's capacity is around 345 MMcf. Figures on this slide show a general arrangement of the ship with its principal particulars. For safety, the holds are inerted with nitrogen in order to eliminate the danger of fire below deck. All valves and fittings are installed above deck to facilitate servicing.

A major obstacle for sound commercialization of **coselle** technology is the cost of fabrication of complex **coselle** spaghetti! The difficulty in inspection of this complex structure and the cost involved should be added to the weak points of this technology.

## Natural Gas Transportation – Marine CNG



- CNG in vertical cylinders
- Pressure: 130 Bar
- Temperature: -29°C

- 700 mmscf CNG
- Lean Gas at -20°F & 1,750 psi
- Specific Gravity 0.61
- Vertical Orientation of Tanks
- 42-inch Diameter Pipe by 36 m Tall
- 2400 Pipe Tanks Required
- 100 Pipe Tank Modules – 24 pipes
- Ship Speed 18 knots

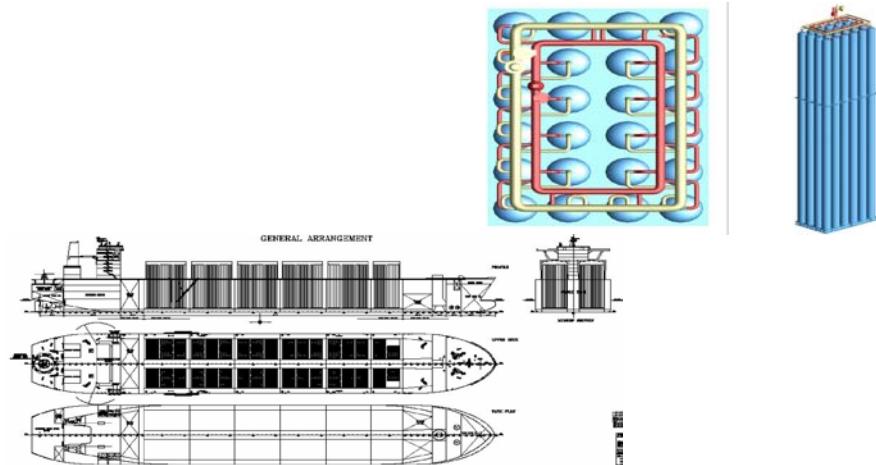
### Volume Optimized Transport and Storage (VOTRANS)

An alternative approach to *Coselle* is **VOTRANS™** by *Enersea Transport LLC* of Houston. This system has been defined as total gas transport system (not just another gas container concept). Here, a volume optimized gas delivery process includes dedicated transport ships carrying long, large diameter pipes in an insulated cold storage cargo package. Loading and unloading is similar to other CNG concepts, but apparently at much lower pressures. According to the proponents, ship design options have been developed for custom designed ships with horizontal or vertical tanks for storage from 300 to 2,000 MMscf per ship. Horizontal tanks are preferred for larger capacities. It is believed that these large capacity ships present the opportunity for CNG to be transported from higher rate production centers and over much greater distances than commonly considered economically advantageous. Options including a conversion of existing single-hull tankers to CNG transport service for capacities from 300 to 1,2000 MMscf were also considered and are available. The conversion options have received considerable interest due to their potential for further reducing costs and schedule. It is believed that the first VOTRANS could be in operation by 2005, providing that a suitable project is found.

Further, according to the proponents, regulatory bodies and ship classification agencies have confirmed that viable paths to approval exist for either VOTRANS option. The authorities are generally in favour of the concept with regard to the straightforward approach to construction by avoiding use of exotic materials and complicated fabrication techniques. To date, *EnerSea* has conducted extensive Hazard Identification workshops with teams from two leading class societies which have confirmed that *EnerSea's* CNG shipping concepts should present no greater hazards than existing gas ship.

*Enersea* explains their the key to their technology as using the right thermodynamic conditions to store the gas optimally. In their last presentation at OTC they explain that natural gas is a complex fluid that exhibits non-ideal gas properties when compressed above 70 bar (1000psi). The non-ideal characteristics can be accommodated by adjusting the "Ideal Gas Law" through the introduction of what is commonly called the "Z-factor". The gas industry has generated much documentation and many calculation models to estimate/predict the Z-factor effects in gas compression engineering. *EnerSea's* *Volume-Optimized TRANsport and Storage (VOTRANS™)* technology has recognized the relationship between the weight of containment systems and the Z-factor effect in gas storage design. By chilling gas to a suitably low temperature (usually well below 0°C), it is possible to compress great quantities of gas into long tubular containers such that the ratio of the weight of the gas stored to the weight of the container is optimized. The cost of compression and the cost of the containers (and, therefore, the ships) can be greatly reduced by storing cold gas at relatively moderate pressures. These savings are somewhat offset by costs for refrigeration and insulation, but operational considerations and the sensitivity of cost effective ship design to the weight of CNG containers clearly reveals the value of lighter containers.

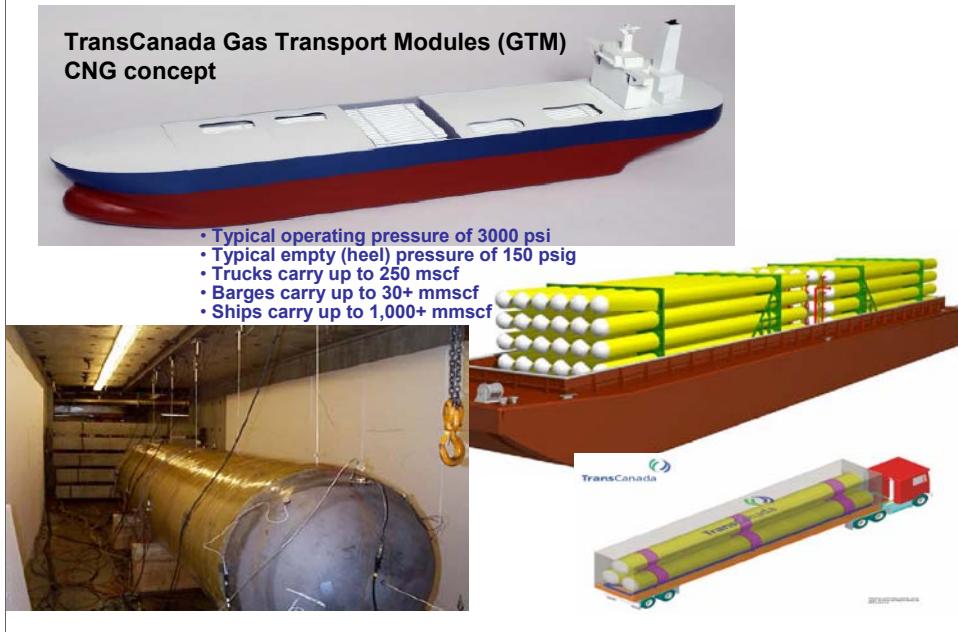
## Natural Gas Transportation – Marine CNG



EnerSea Votran<sup>®</sup> - Vertical Containment System

It is claimed that the VOTRANS™ principles work well and generally apply to tubular containers of any material. However, due to the relative cost and proven reliability of steel pipe containers, the first generations of CNG ships will carry large diameter, high strength steel pipe tanks. Steel pipe tank modules are claimed to be incorporated in their current ship design. The pictures on this slide show the configuration of EnerSea's VOTRANS™ system.

## Natural Gas Transportation – Marine CNG



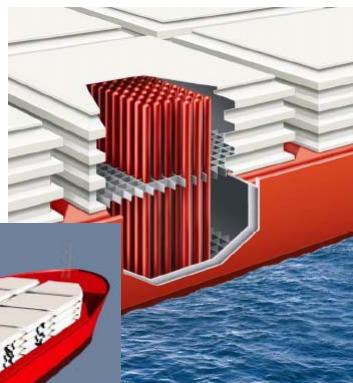
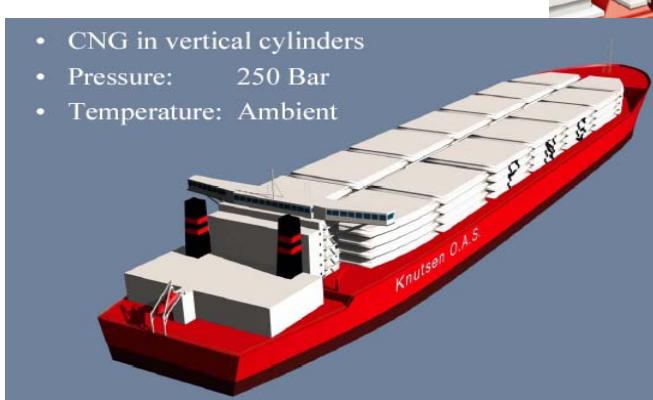
### Gas Transportation Module (GTM)

Similarly to VOTRANS, TransCanada are using straight long large diameter (48") pipes. The gas is stored and transported basically at ambient temperature and at pressure similar to the *Coselle* concept, i.e. about 3,000 psig. However, TransCanada took a different approach to the container material. The individual container design (48 inch diameter and 80 feet long) is based on their *Composite Reinforced Line Pipe (CRLP)* concept. This is a proven pipeline technology and several pipeline sections using this material are in operation and subject to testing in Alberta, Canada. The steel pipe has an outer coating of fiberglass and resin. While the outer coating contributes to the actual wall thickness for pressure containment, the reduction in weight is significant. The proponents concentrate initially to develop smaller vessels/barges (about 100 MMscf) and believe that the first project employing the *GTM* on barges will see a river application and be in operation in the not too distant future. Evaluations and conceptual engineering are ongoing for larger ships similar in size to the other *CNG* marine transportation concepts. A typical *GTM* barge is illustrated on this slide.

## Natural Gas Transportation – Marine CNG

**Knutsen OAS PNG® system, Norway**

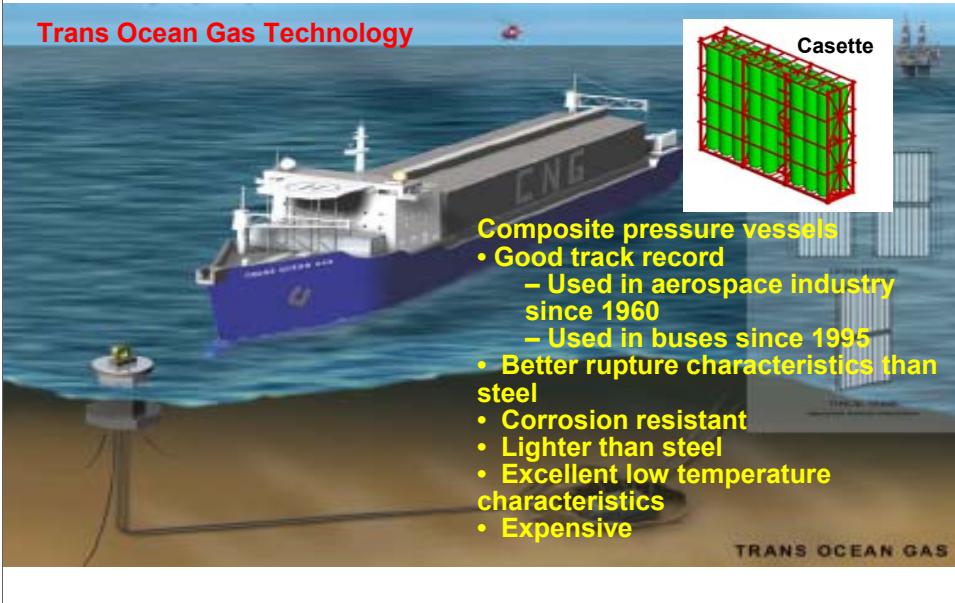
- CNG in vertical cylinders
- Pressure: 250 Bar
- Temperature: Ambient



The Norwegian **Knutsen** has been working on their own concept for a while and they seem to be ready to launch their first demonstration ship shortly. Their concept is based on high pressure (250 bar) storage at ambient temperature. The company has its roots back to 1896, when the founder of the **Knutsen** company bought his first vessel. The company grew steadily and in the 1930s the company was the third largest shipping group in Norway. In the first years the company was a typical North Sea trader and also engaged in fishing activities, but soon the company expanded into tanker and liner trades. It built up a liner trade between Europe and South America, and later liner trades in the Orient.

In the early 1970s the company invested in the tanker business, and when the tanker crisis came in the end of the 70s, the company ran into financial problems. In 1984 the **Knutsen** family left the company and the shipping activities were re-organized with new owners. The technical details of **Knutsen's** system have not been disclosed and it is not clear how it is different from other aforementioned technologies. Pictures on this slide show the artistic view of the pressurized natural gas (PNG) of **Knutsen**. Over the last summer (2003), **Knutsen's** manufacturing partner Europipe, of Germany, concluded tests of a prototype vertical pipe cylinder fabricated using standard materials, built to the specifications laid down in the DNV regulations. **Knutsen** and *Den Norske Veritas* (DNV) seem to be pioneering in setting the first regulation s for CNG carrier ships. **Knutsen's** management claims that PNG could be more economic than LNG over distances of 2,500-3,000 nautical miles, where their PNG operation would not require investments in storage and liquefaction facilities upstream, and storage and re-gasification facilities downstream. It is also claimed that a 3 cu m, fitted with 1,000 containment cylinders, would bring access to more remote coastal markets than was feasible for LNG. Their system seem to have the highest specific weight performance as not precaution is taken to reduce the specific weight. Ordinary steel pipes are used and it is claimed that the very weight of the containment system could come to be an advantage, because it means that no ballast water is required!

## Natural Gas Transportation – Marine CNG



### Composite pressure vessels

- Good track record
  - Used in aerospace industry since 1960
  - Used in buses since 1995
- Better rupture characteristics than steel
- Corrosion resistant
- Lighter than steel
- Excellent low temperature characteristics
- Expensive

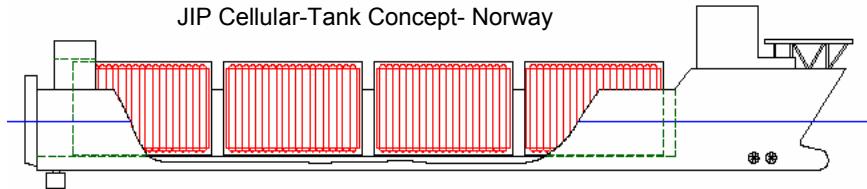
**Trans Ocean Gas** describes their technology as follows:

The compressed natural gas (CNG) transportation method developed by Trans Ocean Gas Inc, is a simple application of existing technology. Using composite pressure vessels similar to those used in the natural gas vehicle industry, *Trans Ocean Gas* can safely transport large quantities of natural gas in a ship. The safety & reliability of composite pressure vessels has been proven through numerous critical applications in the aerospace, national defense, and natural gas vehicle industries. Utilizing composite pressure vessels for ship-based CNG transportation is therefore the optimal global solution. The composite pressure vessels to be used for the *Trans Ocean Gas* method are actually fibred reinforced plastic (*FRP*) pressure vessels. Using *FRP* pressure vessels will overcome all the deficiencies of steel-based gas containment systems proposed by others. Most notably, *FRP* pressure vessels have nonviolent rupture characteristics. If ever punctured by a foreign object, the structural integrity of an *FRP* pressure vessel will remain in tact. The weight of an *FRP* cylinder is 1/6<sup>th</sup> to 1/3<sup>rd</sup> that of a comparable steel cylinder. The actual weight is dependent on the proportion of carbon or glass fiber used to manufacture the pressure vessel. It is the lightweight nature of *FRP* pressure vessels that make them the most practical for CNG transportation. *FRP* bottles have an internal liner made of high-density polyethylene and are therefore corrosion resistant. The liner provides a non-permeable gas barrier that transfers all pressure to the filament fibers that are wound around the liner. The liner is also used in the manufacturing process as the mandrel to wind on the load-carrying filament fibers. As the fibers are wound on, they are drawn through an epoxy resin bath. When cured, the filament fibers are held in place by the epoxy matrix.

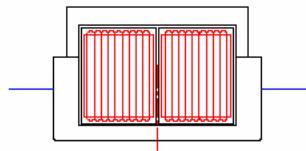
*FRP* pressure vessels are corrosion resistant. Since the system can store hydrocarbon liquids containing CO<sub>2</sub> and water, costly processing of raw natural gas is not required before loading. Such contaminants are common components of raw natural gas and most often highly corrosive. Because *FRP* pressure vessels are corrosion resistant, the useful life of the gas containment system is assured. Fiber reinforced pressure vessels first gained respect through critical applications in the national defense & aerospace industries. Reliability has been proven through extensive applications in the natural gas vehicle industry, with several thousand *FRP* pressure vessels installed on the rooftops of public busses fueled by natural gas. The lightweight nature of *FRP* pressure vessels will allow *Trans Ocean Gas* to use high-speed and voluminous container ship hull forms as CNG carriers. Containership capacity is measured in total equivalent units or *TEU*'s, where a unit is the standard 20 foot modal container with a gross weight of 20 metric tons. To install *FRP* pressure vessels in a CNG carrier, *Trans Ocean Gas* has designed a modular steel frame or **cassette**. Each cassette will support 18 pressure vessels, held vertically in 3 groups of six. As indicated previously, a conventional upper and lower manifold tie the pressure vessels together *within a cassette*. Thus, each 40ft x 40ft x 10ft wide cassette becomes a single natural gas storage unit. Each cassette will store approximately 1.7 MMscf of natural gas, and occupy about 10 *TEU*'s of space. When fully loaded, a standard cassette will weigh about 200 metric tons.

The main drawback of *FRP* system is the high cost of manufacturing. For the same gas capacity and pressure, *FRP* tanks are about 100% more expensive than steel pipes (based on a recent study of the *Gas Technology Institute (GTI)*, Illinois, USA. The glass wound steel pipes of *TransCanada* are about 30% more expensive.

## Natural Gas Transportation – Marine CNG



- CNG in large cellular tanks
- Pressure: 200 bar
- Temperature: Ambient



This is a similar concept to *Knutsen* vertical pipe system known as **JIP cellular concept**. The operating temperature and pressure of this technology is the same as other high pressure systems.

## Natural Gas Transportation – Marine CNG

### 1. Trends in CNG technology

- Lower transport temperatures to attain higher densities
- Higher strength and lighter weight materials
  - High strength steel pipes (X80)
  - Wrapped steel pipes with nylon or carbon fibers
  - Composite pressure vessels

### 2. CNG Technology comparison

- Low investment cost
- Low threshold gas volume
- CNG ships can be built competitively in many places
- CNG is energy efficient:  $\frac{1}{2}$  that of an LNG process
- Offshore Loading/unloading is possible
- Lower security risk compared to LNG (lower gas volumes will be released in case of accidents)

The principal gas transportation options are *LNG* and pipelines with *CNG* as a niche opportunity application. There are some characteristic differences between the three concepts, which are worth mentioning at this point. The characteristic difference between a *CNG* project and a *LNG* project is that the onshore facilities required for *CNG* are comparatively simple and inexpensive. The characteristic difference between a *CNG* project and a pipeline project is that the pipeline is fixed, and may have to transit several political jurisdictions, whereas *CNG* Carriers transit directly between the host countries and can be easily re-deployed in response to changing market demands. These considerations result in several important project advantages for marine *CNG* systems:

- 80% of the investment is in ships, which are movable assets. This fact lowers the investment risk, facilitates easier financing terms and in some situations even enjoys favourable offshore taxation.
- The threshold volume that is required for a marine *CNG* project is relatively small and can easily grow in steps with demand. Marine *CNG* can begin at modest volumes with few ships and match growing demand by increasing compression and adding ships. One of the major economic hurdles for *LNG* and pipelines is that large threshold volumes are generally required.
- *CNG* ships are basically standard bulk carriers and could be built in most reasonably sized shipyards so prices will be competitive.
- *CNG* is energy efficient. The energy consumed in a *CNG* project is about:
  - $\frac{1}{2}$  that of a *LNG* project,
  - $\frac{1}{4}$  that of a *methanol* project, and
  - $\frac{1}{8}$  that of a *GTL* project.
- Loading and unloading from offshore terminals is possible and so harbours can be avoided in situations where the harbour is crowded, or costly, or where the authorities would prefer the ship to moor away from populated areas. Also loading associated gas directly from offshore facilities is possible. Associated gas, in many instances is either flared (e.g., Nigeria) or re-injected (Canada's East Coast). Where nearby markets exist, ship-based *CNG* could provide an economic means of delivering this unutilized gas to consumers.
- There may be a perception, particularly in the current political climate, that there are possible increased security risks for transportation of *LNG* in large "visible" ships.

## Natural Gas Transportation – Marine CNG



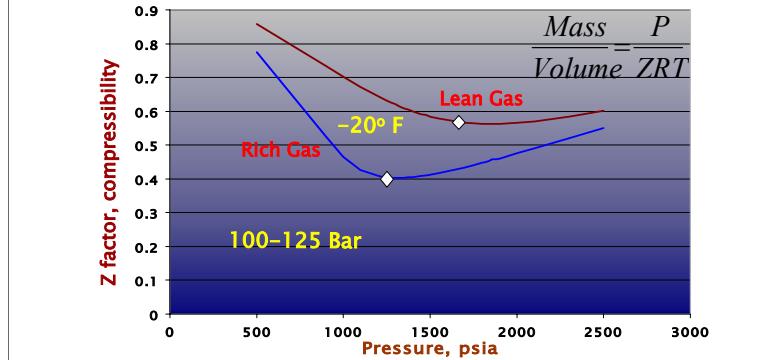
**Burst and Fatigue Tests of CNG Tanks (after 4,000 and 40,000 loading/unloading cycles, respectively)**

Getting the certification required to commercialize the CNG technologies, requires exhaustive test and regulatory approval programs. This technology is being certified gradually by regulatory organization all over the world (e.g. ABS, NDV, etc.). The pictures show burst and fatigue test of a typical high pressure steel tank. It is very important that the CNG carriers are equipped with inspection (*NDT*) systems such as on-line Ultrasonic and Acoustic Emission (*AET*) fault and failure detection techniques. Regular inspection of the CNG systems are costly and it is important that the CNG ships are equipped with as much on-line inspection and monitoring systems as it is economically possible to reduce the number of inspections required.

## Natural Gas Transportation – Marine CNG

### Specific weight calculations for pressure vessels:

- Assumptions**
- ANSI B31.8
  - SW= Weight of stored gas/weight of storage tank



$$\text{ANSI B31.8 pipe thickness: } t = \frac{PD}{2FETS} = \frac{PD}{k_1}$$

$$\text{Standard gas volume} = \frac{\pi}{4} (D - 2t)^2 L \left( \frac{P \alpha}{ZT} \right)$$

$$\text{Tank weight} = \frac{\pi}{4} [D^2 - (D - 2t)^2] L \rho_s$$

$$\text{Specific weight} = \frac{\text{Tank weight}}{\text{Standard gas volume}} = \frac{2t}{D - 2t} \left[ \frac{\rho_s ZT}{P \alpha} \right]$$

Substituting  $t$  in the specific weight equation we will have:

$$\text{specific weight} = \left[ \frac{2 \frac{PD}{k_1}}{D - 2 \frac{PD}{k_1}} \right] \left[ \frac{\rho_s ZT}{P \alpha} \right] = \frac{2 \rho_s ZT}{\alpha (k_1 - 2P)}$$

$\alpha$  is temperature-pressure correction factor and  $k_1$  is the constant product of F (design location factor=0.72 for sparsely populated areas, E=longitudinal joint factor=1.0 for 42" welded pipe, T=temperature derating factor =1.0 for -20°F to 250°F). These two constants may be calculated as follows"

$$\alpha = \frac{520^\circ R}{14.7 \text{ psia}} = 35.4^\circ R / \text{psia}$$

$$k_1 = 2FETS = 2(0.72)(1)(1)(80,000 \text{ psi}) = 115,200 \text{ psi}$$

**Specific weight** for the two following conditions can be calculated:

At  $T = -20^\circ F = 440^\circ R$  and  $P = 1750 \text{ psia}$ , specific weight= 0.06

At  $T = 77^\circ F = 537^\circ R$  and  $P = 3600 \text{ psia}$ , specific weight= 0.11

This means ships with lower pressure and temperature are 50% lighter and therefore more economical.

## Natural Gas Transportation – Marine CNG: Case study

### **Relative Capital Cost**

Case (MMscfd)	200	400	600
LNG (Base at 200 MMSCFD)	1.00	1.37	1.63
Pipeline	1.32	1.57	1.90
CNG (ships chartered)	0.07	0.11	0.15

### **Relative Annual Operating Cost**

Case (MMscfd)	200	400	600
LNG (Base at 200 MMSCFD)	1.00	1.58	2.11
Pipeline	0.34	0.42	0.52
CNG	1.20	1.91	2.58

### **Relative Transport Tariffs**

Case (MMscfd)	200	400	600
LNG (Base at 200 MMSCFD)	1.00	0.72	0.60
Pipeline	0.98	0.58	0.47
CNG	0.48	0.39	0.35

As one of the in-house studies conducted by *Fluor* related to CNG marine transportation, the CNG Coselle concept was used as a benchmark to evaluate the CNG potential for export of Newfoundland gas in comparison to LNG and pipeline. For this case study, it is assumed that gas produced in the Jeanne d'Arc Basin offshore Newfoundland will be gathered and transported via a subsea pipeline to shore. A gas plant located at Come-by-Chance, Newfoundland will process and condition the gas to a pipeline specification. The export gas will then be shipped using the Coselle CNG vessels to the Boston area. In summary, the case study basis is as follows: **(a)** Shipping Distance: 925 miles **(b)** Shipping Volumes: 200 to 600 MMscfd **(c)** Coselle Storage Pressure: 3,000 psig; **(d)** Coselle Heel Pressure: 150 psig; **(e)** Gas Loading: Continuous Gas Offloading: Continuous

It is further assumed that the export gas will be available at the gas plant gate at a pressure of 1,000 psig and dehydrated. The gas then has to be compressed to pressure 3,000 psig, after-cooled, refrigerated and loaded onto the Coselle CNG ship via a near-shore loading terminal. A *Submerged Anchor Loading (SAL)* is envisaged for the loading and offloading duties. The terminals are connected to shore through subsea flowlines and to the ship through high-pressure flexible hoses. The number of CNG ships and the ship size were suited for each of the three selected capacity points, i.e., 200, 400 and 600 MMscfd. The ships will travel at 15.5 knots. For the given transportation distance and the range of capacities the number of ships and cycle times are as follows:

<b>Transportation Volumes (MMscfd) 200</b>	<b>400</b>	<b>600</b>
Ship Size (MMscf)	310	403
Number of Ships	5	7
<u>Cycle Times (days):</u>		
Loading	1.55	1.01
Offloading	1.55	1.01
One-way Voyage	2.16	2.16
Mooring and Overlap	0.25	0.25
Total Cycle Time	7.67	6.59
		5.92

At the receiving end in Boston, a near-shore *SAL* terminal with high and low pressure flowlines to shore are envisaged. Onshore facilities will consist of inlet separators/scrubbers and a scavenging compressor to evacuate the Coselles to a pressure of 150 psig. It is assumed that the gas will be offloaded into a 1,000 psig

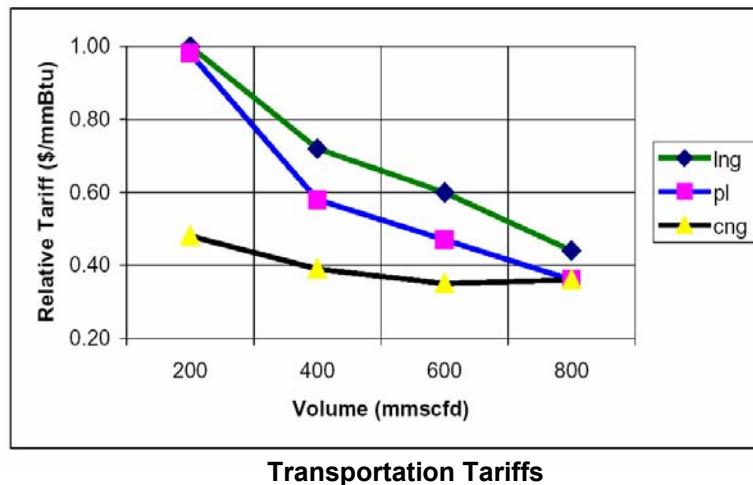
pipeline system. After the offloading operation and disconnect, the CNG Coselle vessel will start a return voyage to Newfoundland.

For the LNG alternative a liquefaction plant, adjacent to the gas plant is assumed. LNG will be exported to the Boston area using chartered standard LNG tankers. At the receiving end in Boston, LNG storage and re-gasification facilities are envisaged.

The pipeline alternative consists of a subsea pipeline from Newfoundland to Nova Scotia with a landfall in Goldboro and a parallel terrestrial pipeline to the M&NE system to Boston. For both alternatives, three capacity points (200, 400 and 600 MMscfd) and design scenarios were considered, similarly to the CNG case.

For the evaluation purpose all three options are ultimately compared on capital and operating cost and transportation tariffs. The capital and operating cost for the LNG and pipeline cases were developed using publicly available data as well as *Fluor's* in-house data developed for similar projects. The CNG Coselle costs were obtained from data published by *Cran & Stenning*. *Fluor's* cost data were used for some gas processing components associated with the CNG Coselle system. The reported costs are relative in nature and reflect 2000 U.S. dollars. It is, however, believed that these relations will remain basically the same in current market situation. The results of the study are shown on this slide.

## Natural Gas Transportation – Marine CNG



Using the capital and operating costs, the transportation tariffs were then calculated. The tariffs are normally expressed in \$ per million Btu and are here again reported as relative numbers only. For the *CNG* and *LNG* options, the gas carriers were assumed to be chartered and the charter costs are included as operating costs. The *CNG* ships were assumed to be chartered under similar conditions to the current *LNG* carriers. The charter term is twenty years and the ships are assumed to be 100% financed at 8% for twenty years with an 11% *IRR* for the operator. For the remaining facilities, including pipelines, 70% debt at 10% interest with 12-year repayment and 18% return on equity were assumed. The resulting transportation tariffs for the three systems are then as follows:

It can be seen from the above, that the *CNG Coseille* compares favourably with *LNG* and pipelines for the given transportation distance and the target range of capacities.

Figure 8 provides an illustration how the three concepts relate economically to each other over a broader range of capacities past 600 MMSCFD.

It appears that the pipeline concept will match the *CNG* tariffs at transportation volumes of about 800 MMscfd. Beyond this capacity, a pipeline becomes the economic choice. For the *LNG* concept to match the pipeline or *CNG* economics either larger volumes or longer distances, probably 1,500 to 2,000 miles, have to be considered.

## Natural Gas Conversion/Utilization Technologies

- Gas to Liquids (GTL)/Fischer-Tropsch (FT) technologies
- Direct Conversion/Ethylene, Acetylene, higher HC, ...
- Methanol to Olefins (MTO), Propylene (MTP) and DME
- Methanol to Gasoline (MTG)
- Gas to Electricity (GTE)
- Gas to Steel (GTS)
- Enhanced Oil Recovery (EOR)

There are many options to utilize natural gas as seen in this slide. Of course one of the most widely noticed options these days is the conversion of natural gas to middle distillates or the so called **Gas to Liquids** or **GTL** using the **Fischer Tropsch (FT)** technology. Methane may also be directly converted to ethylene, acetylene through partial oxidation routes. The idea of getting methane directly converted to more valuable products such as ethylene, or **Oxidative Coupling of Methane (OCM)**, has made many scientists and research groups work very hard on the technology. The number of papers on the research topic has declined lately due to the fact that the process is not thought to be economically viable as compared with conventional routes such as naphtha cracking.

Natural gas of course as explained before may be converted to methanol and methanol is the precursor for the production of olefins such as propylene and *di-methyl ether (DME)*. Mobil has developed a technology to convert methanol to gasoline, however there has been no other projects in this area.

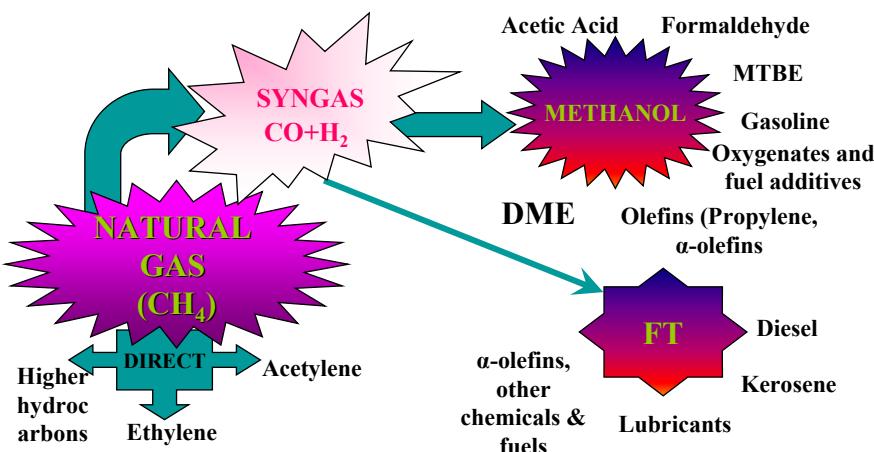
There are other routes to exploit natural gas by converting the gas to electricity and exporting the gas through wire and using the gas to make steel; these are options which have been used for many years in many parts of the world. Of course natural gas has been the main choice to enhance the production capacity of crude reserves for years now and for many years to come.

Gas to liquids, or **GTL**, is a catalytic process that chemically converts natural gas (methane) into liquid hydrocarbons - diesel, naphtha, and waxes. The goal of **GTL** is to convert isolated natural gas reserves into products that are easy to transport and sell in the marketplace.

The **GTL** process chemically converts natural gas (methane) molecules into other compounds. Once converted, these liquids are stable and will remain in the liquid state. LNG, on the other hand, is only a change of state - that is gaseous methane is cryogenically chilled and changed into liquid methane at - 260°F. It is still methane and will return to the gaseous phase if allowed to warm up to ambient conditions. GTL and LNG are similar in that the goal of both processes is to convert isolated natural gas reserves into something that can be efficiently transported to market. They are also similar in that both processes are very capital intensive, and must be done on a large scale to be economical. Although **GTL** and **LNG** are often discussed as competitors, they really are not. Both are viable processes to monetize isolated gas, but they serve different end markets. In some site-specific areas of the world, they may compete for the same feedstock gas, but generally there is so much isolated, or stranded, gas in the world, that there will be more than enough to go around. **GTL** and **LNG** will both be thriving and growing businesses in the future.

Much of the talk today about **GTL** competing with **LNG** is mainly about **GTL** being seen as a gas-monetization alternative to **LNG**. **LNG** has been around for many years. And, although it has been limited by market demand, it is the industry standard. The **GTL** process has also been around for many years, but is just now becoming economically viable.

## Gas Conversion Alternatives



This slide summarizes the route for natural gas conversion alternatives. As explained before natural gas may be converted to synthesis gas or a mixture of carbon monoxide and hydrogen through known technologies (e.g. steam reforming, partial oxidation or POX, autothermal reforming or a combination of these technologies, etc.). There are technologies under development right now which could extensively change the economy of all conversion alternatives through synthesis gas routes, namely the use of oxygen selective or ion transfer membranes (ITM) and plasma technologies. By using these technologies the air separation units (ASUs) will be eliminated from the gas conversion projects and that reduces the cost of these projects by a large extent. The carbon dioxide emissions will also be reduced which is another positive bonus from an environmental point of view. Syngas may be converted to methanol using proven and available technologies and methanol in turn, as explained before, may be converted to an array of many chemicals, fuels and fuel additives. Synthesis gas may also be converted to fuels and so called GTL products through the Fischer Tropsch route. **Each 1 MMscf of gas can be converted to approximately 100-120 barrels of middle distillate products.** As discussed before natural gas may also be directly converted to ethylene and other higher hydrocarbons by partial oxidation routes or plasma technologies.

## **Natural Gas as a Feedstock for Chemicals**

- Methanol as a main intermediate to produce oxygenates
  - ✓ MTBE
  - ✓ DME,
  - ✓ Acetic Acid,
  - ✓ Formaldehyde, etc.
- Ammonia and Urea as fertilizers
- Acetylene
- Ethylene

Natural gas is recognized as a major feed to many chemicals and petrochemicals production facilities. The inherent lower sulfur content of pipelined natural gas and its lower cost make it the feedstock of choice for many petrochemical projects. It may be converted to methanol which is the main intermediate for many oxygenates and fuel additive compounds. It is also the main feed to most ammonia, urea, acetylene projects and of course there is a potential to convert methane to ethylene.

## Gas-to-Liquids Technology: Process

- Shell (Deutch)- POX-Fixed bed cobalt-Shell upgrading
- Exxon-Mobil (USA) – POX-Slurry iron
- Sasol-Chevron (South Africa)- Topsoe combined autothermal syngas , Slurry iron GTL, Chevron upgrading
- Statoil-NIOC/RIPPI-PetroSA (Norway, Iran, SouthAfrica), Lurgi combined autothermal and slurry cobalt, IFP upgrading
- Syntroleum (USA), air partial oxidation, slurry iron
- Conoco- Gas Solution Technology

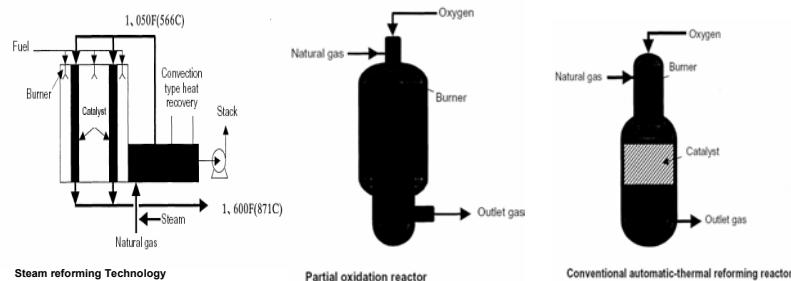
The main *GTL* technology players are listed here on this slide. The amount of investment on this rather old technology is tremendous. The environmental issues related to the use of clean (low sulfur content) fuels have triggered a new era in developing new technologies. *GTL* technology is a rather complex system comprising mainly of three basic processes: 1- synthesis gas production 2- FT synthesis and 3- Upgrading (hydrogenation and hydrocracking and subsequent refining) of synthetic crude. Various companies have their own preferred technology to undertake above processes. They may use a combination of different techniques to produce clean fuels. *Shell* is one of the pioneers of the *GTL* technology having almost every single process from its own. The *Shell* partial oxidation technology used for gasification processes is used to convert natural gas to synthesis gas. *Shell* uses fixed bed tubular reactor and cobalt catalyst fro FT synthesis and being a historical refiner has its own technology to upgrade the synthetic fuel produced. *Sasol* has a long history of producing middle distillates and all sorts of petrochemicals from gasification of coal. They have developed various FT reactor and catalysts and are for many years have been the sole commercially producer of chemicals and fuels based on FT technologies. They have adapted their technology to produce theses products originating from natural gas. They have technology agreement with Danish *Haldor Topsoe* to use their autothermal reforming technology exclusively for their integrated syngas-FT process and they have similar agreement with *Chevron* to use heir technology to complete the *GTL* process.

*NIOC* started to work with *Statoil* and the South African oil company (*PetroSa*) to develop and commercialize the *Statoil* *FT* technology which was at the stage of bench scale reactors. With joint investment this technology is advancing to its completion stages.

Other companies such as *Conocoa* and *Syntroleum* each have taken similar steps to commercialize their technology. *Shell* and *PetroSa* are the two existing major producer of *GTL* products from natural gas producing 12,000 and 35,000 bbl/d respectively. There are several feasibility studies underway all around the world two of which were just completed last year in Iran.

*Qatar* has struck two contracts with *Sasol-Chevron*, *Conoco* and *Shell* to produce hundreds of thousands of *GTL* products starting 2005.

# Synthetic Gas Production Technology



Conventional Synthesis Gas Production Processes

## Steam reforming method

Of the processes currently finding commercial applications, the most fruitful has been steam reforming of natural gas. In the reaction, a multi-tubular reactor is filled with catalyst and heat is added from the exterior. This process is extremely productive, but it poses a number of problems: energy consumption is extensive, for instance; the  $H_2/CO$  ratio of the synthetic gas obtained is large, ranging from 3 to 5, and construction costs are high (see figures on this slide).

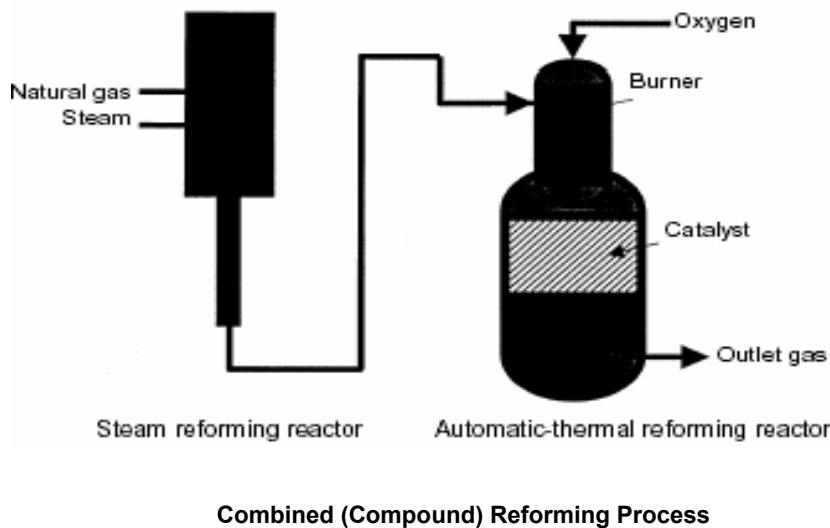
## Partial oxidation method

The next production process is the partial oxidation method. In comparison to the steam reforming method, the reactor is simple. Another distinguishing characteristic of the partial oxidation method is that energy consumption is low because the reaction is exothermic. Still there are drawbacks. Outlet temperature is high at 2700°F (1500°C); the costs of the reaction materials are rising, and soot can easily emerge.

## Automatic-thermal reforming method

In the automatic-thermal reforming method, the reactions of both partial oxidation and steam reforming are instigated in one reforming reactor. The advantage of this method is that synthetic gas of higher pressure can be obtained than by the steam reforming method. Among the drawbacks, on the other hand, is the fact that large volumes of  $CO_2$  are produced and the top of the combustion compartment reaches high temperatures close to 3600°F (2000°C).

## Synthetic Gas Production Technology

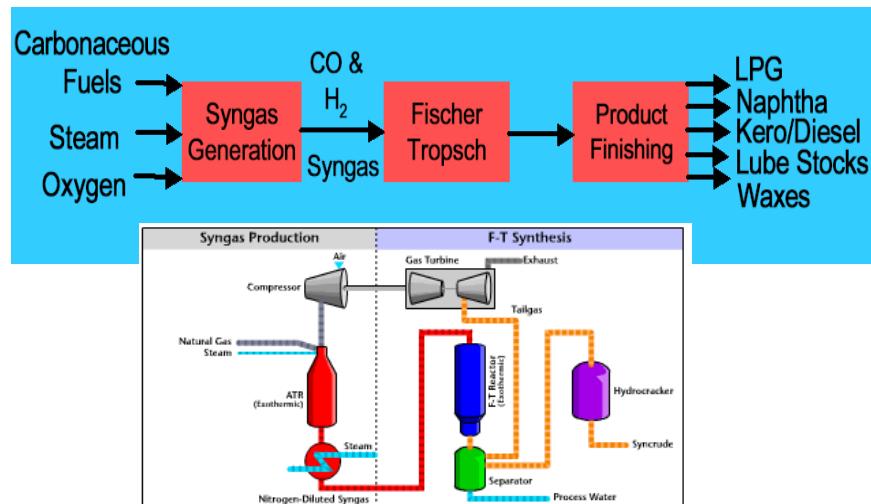


### Compound reforming method

The compound reforming method combines the steam-reforming reactor with the automatic-thermal reactor. A major feature of this method is that the early-stage steam reforming reaction and the late stage automatic-thermal reforming reaction take place in separate devices. The advantage, as a result, is that low-pressure gas at the outlet of steam reforming reaction can be transformed into high-pressure gas by means of automatic-thermal reforming. In addition, costs are reduced because a compressor is not required. The disadvantages, on the other hand, are that there are two reactors and construction costs are high.

A recent survey (*Petroleum Energy Survey*, report 7, 1999) indicates that the orientation of improvements in processing is toward conversion from steam reforming to oxidation processes such as partial oxidation and automatic-thermal reforming. Accordingly, the catalytic partial oxidation method, the subject of this survey, is seen as an extension of this trend in improvements.

## Gas-to-Liquids Technology: Process



In Gas to Liquids transport processes the natural gas is converted into a liquid via syngas ( $\text{CO} + \text{H}_2$ ) using a *Fischer Tropsch* (FT) or an oxygenate method. The produced liquid can then be a fuel, usually a clean burning motor fuel (syncrude) or methanol, ammonia or some precursor for plastics manufacture, e.g. dimethylether (DME). This can be used for transportation, LPG substitute or power generation fuel or as a chemical feedstock. The liquid is shipped in a suitable tanker. Methanol is a gas to-liquids option that has been in commission since the mid 1940s. Trinidad is a major world contributor, with some 5 plants and 3 to come producing around 8,500 tonnes of methanol per day and using 290 MMscfd of natural gas. While this route was originally an inefficient conversion process that used much gas to produce only a small amount of methanol, optimized technology has improved the efficiency to 30-35 MMBTU per tonne methanol (from over 50) and there is now a larger output per unit of capital invested. Methanol can be used in internal combustion engines as a fuel, but the market for methanol as a fuel is limited, although the development of fuel cells for motor vehicles may change this. Methanol is best used as a basic chemical feedstock for the manufacture of plastics. Other GtL processes are being developed to produce clean fuels, e.g. syncrude, diesel, or many other products including lubricants and waxes, from gas but require complex (expensive) chemical plant with novel catalyst technology, and are currently only in their pilot stage. The State of Qatar has great ambitions to produce GtL products from its shared natural gas reserves with Iran and may be the first country to produce clean fuels commercially this way.

## Markets for GTL Products

- Current middle distillate market: 26 MMBPD increasing to 34 by 2015
- Diesel demand: 12.5-13 MMBBLD (2000) increasing to 16-17 by 2010
- Huge market for GTL products
- Japan and Europe as the main demand regions
- 20% blend with conventional diesel
- Advantages of GTL over LNG

It is beyond the scope of this course to deal with the market and economics of different alternatives for natural gas utilization, however, because of the importance of the *GTL* projects, an overview of the market for *GTL* products and its economics will be presented here. Facts and figures show a large market for middle distillate products; a 35 *MMBPD* demand will be around 34 *MMBPD* within the next 15 years. The demand for diesel is about 12-13 million barrel per day now and will easily expand to about 18-20 million barrels within the next 10 years. There is a huge market for the *GTL* products. The portion of a sizable *GTL* plant's (e.g., 60-70 thousands *barrel per day*) product to the middle distillate market is about 0.1-0.2 %. Diffusing in the market for other gas conversion alternatives such as *LNG* with much smaller markets is comparatively more difficult. The target markets for *GTL* products are Japan and European countries where the strict environmental regulations pushes the sulfur content in the diesel fuel to its limits. It is now highly believed that without *GTL* diesel the sulfur standards may not be fulfilled. At the present time a 20% blend with conventional diesel produced by petroleum refineries is considered as a good mix to materialize those sulfur content standards. As the availability of the *GTL* diesel is increasing, it is predicted that even more stringent diesel requirements will be introduced which will further expand the market and demand for *GTL* products. As it can be seen there is no worry regarding the market place of *GTL* products in future. The market for *GTL* products, especially middle distillates (diesel and naphtha), is huge relative to the potential supply from *GTL* plants. The demand for middle distillates is about 35 million barrels per day (35 *MMBPD*) and growing at approximately 4% per year. A large-scale *GTL* plant will only produce 50,000 to 100,000 *BPD*. This is only about 0.2% of the total demand and only 5% of the demand growth. The *GTL* products are of premium quality and will be highly desirable in the marketplace.

- Diesel: The diesel has no sulfur, has a high cetane rating (70+), and has low density. All of these characteristics make it a premium fit with the future diesel specifications.
- Naphtha: The naphtha has no sulfur and is made up of straight-chain molecules that are ideal for petrochemical crackers.
- Waxes: The heavy paraffins, or waxes, also have no sulfur and make ideal base stock for premium lubricants and other specialty products.

As mentioned before, the market for *GTL* products is huge. Assuming a similar 500 *MMCFD* gas inlet to a *GTL* plant and an *LNG* plant, the *GTL* products produced would be only 0.2% of the world demand for middle distillates whereas the *LNG* produced would be about 4% of the worlds *LNG* demand. The market for *GTL* should easily absorb the products without impacting the price. The additional 4% of *LNG* would certainly be high enough to impair the price. Another way to compare the two products is that for the same market impact of one *LNG* plant, you could build approximately 20 *GTL* plants (Source: *ConocoPhilips* web page).

Another advantage of *GTL* products over *LNG* is that the middle distillates are easy to transport and store. Unlike *LNG* that requires cryogenically refrigerated tankers and storage tanks, *GTL* products are low vapor pressure liquids that can be shipped, stored, and distributed easily, safely, and at low cost using conventional equipment.

## Economics of GTL Projects

- Capex reduction trends from US\$ 50,000/BBLD in 1987 to around 22,000 now
- \$19 vs \$24/BBL production costs compared with grass-root refinery designs
- Break down of factors affecting GTL economy:
  - Capex: 52%
  - Opex: 24%
  - Gas price: 22%
  - Others: ~2%

But let's see how the the projects may look like from the economics point of views. There have been lots of improvements in the economics of the *GTL* projects as the capital investment index (*CAPEX*) numbers are down to around US\$ 20,000/*BBLD* from 50,000 in 1987 when Shell built its first commercial *GTL* plant in Malaysia or numbers pertaining similar plants with different technologies in South Africa. We think there are still room for lots of further improvements and optimizations. Even with existing numbers, the calculations show that a barrel of diesel (with 2005 standards) using the *GTL* projects, costs US\$19 as compared to a grass route designed refinery with a cost per barrel of about US\$ 24.

Break down of factors affecting the *GTL* projects are as shown in this slide. As can be seen *CAPEX* has the highest effect on the economics of the *GTL* projects. Unlike what was believed to be a major cost factor in the *GTL* projects, gas price has the lowest effect among the major factors affecting the economics. Therefore, the challenge as mentioned earlier, will be to bring the *CAPEX* to the levels which make these projects economically viable. One way is through technology improvements such as the development of new catalysts, membrane technology, advancement in air separation technologies and heat and process integration. An alternative approach will be engineering optimizations through finding synergies with compatible technologies due to be constructed in the vicinity of the *GTL* plant. This of course should be considered on a case-by-case basis and depends on location of the project and the existing industrial infrastructure in the area.

The factors affecting a *GTL* project are similar to those for *LNG* projects. The most important factor is the availability of large, low-cost gas reserves that need a market. A list of other important factors follows:

- Large gas reserves are required: 4 - 5 *TCF* minimum are required to provide a 500 - 600 *MMscfd* supply for 25+ years.
- Expansion opportunities are desired: Beyond the minimum reserves, ideally 10 - 20 *TCF* should be available to allow future expansion opportunities (similar to *LNG*).
- Low gas price is necessary: Just like *LNG*, *GTL* projects are very capital intensive and require low-cost feedstock gas that is isolated from high-priced gas markets.
- Rich gas is better: The higher the *BTU* content of the feedstock gas, the better. Again, like *LNG*, natural gas liquids can provide additional revenue to support the capital-intensive project.
- Integration opportunities are helpful: If a *GTL* project can be integrated with other industrial facilities and share common infrastructure, the project will be enhanced.