

Petrochemical Technology

PRODUCTION OF OLEFINS

(Olefins by Steam Cracking)

Importance of Ethylene and Propylene in the Chemical Industry

Lower olefins: Ethylene and Propylene

- The largest volume petrochemicals produced
- Annual global production of ethylene in 2022 was about 226 million tons with a continuous annual increase of over 10%; Global propylene production in 2022 was about 150 MMT
India (2022-23) : $C_2 = \approx 7.3$ MT, $C_3 = \approx 5.9$ MT
- Ethylene and propylene have no end use; they are building blocks for a large variety of chemicals and petrochemical products
- Polymers are the dominating end-users

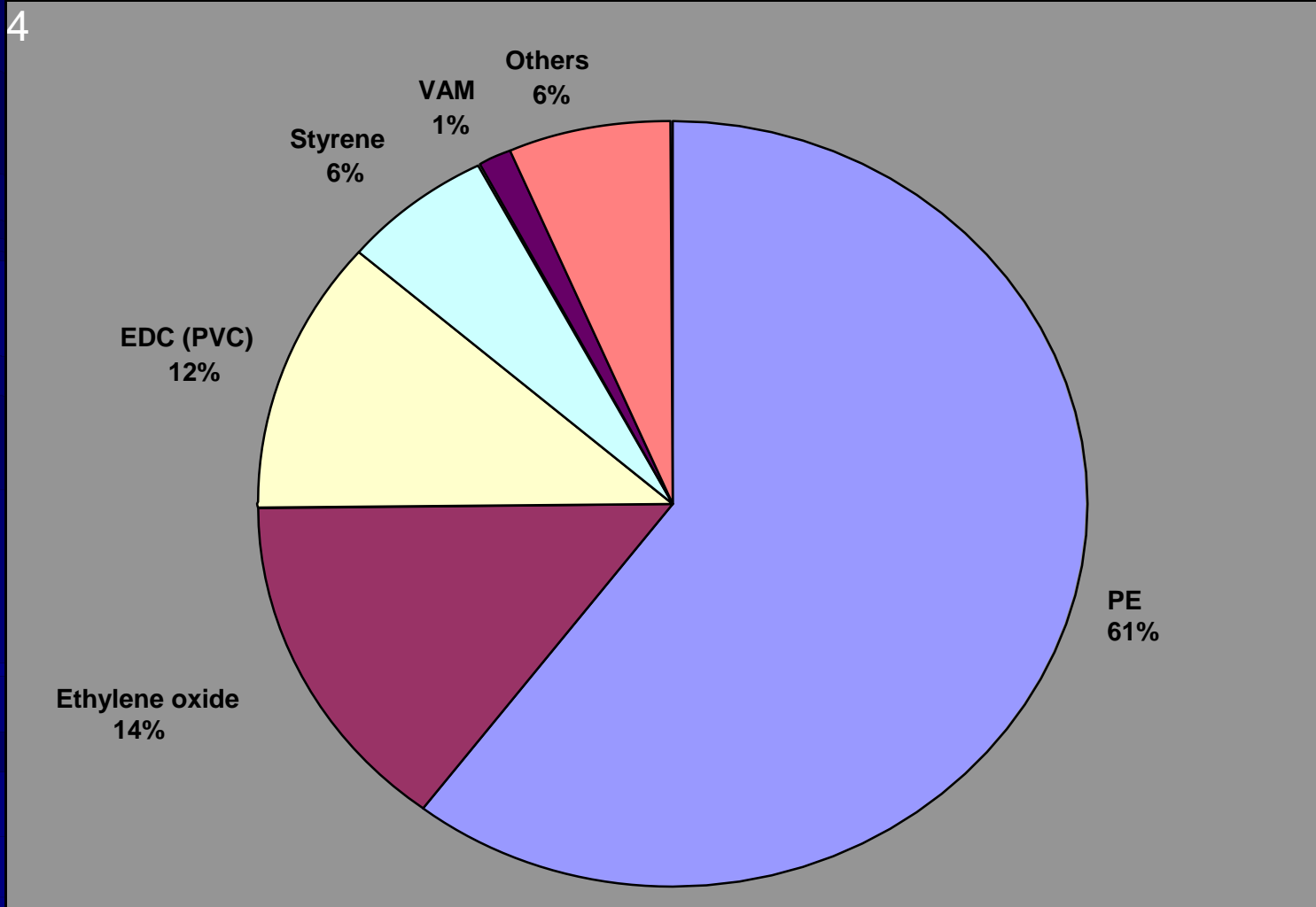
India's ethylene net availability ('000 tonnes)					
Particulars	2020-21	2021-22	2022-23	2023-24*	2024-25*
Capacity	7477	7477	7853	8677	8677
Production	7158	7311	7312	7595	7761
Imports	50	59	56	31	60
Exports	134	118	35	70	120
Net availability	7074	7253	7333	7557	7701

Sources: Chemicals & Petrochemicals Manufacturers Association of India, and Polymerupdate Research;
*Estimates

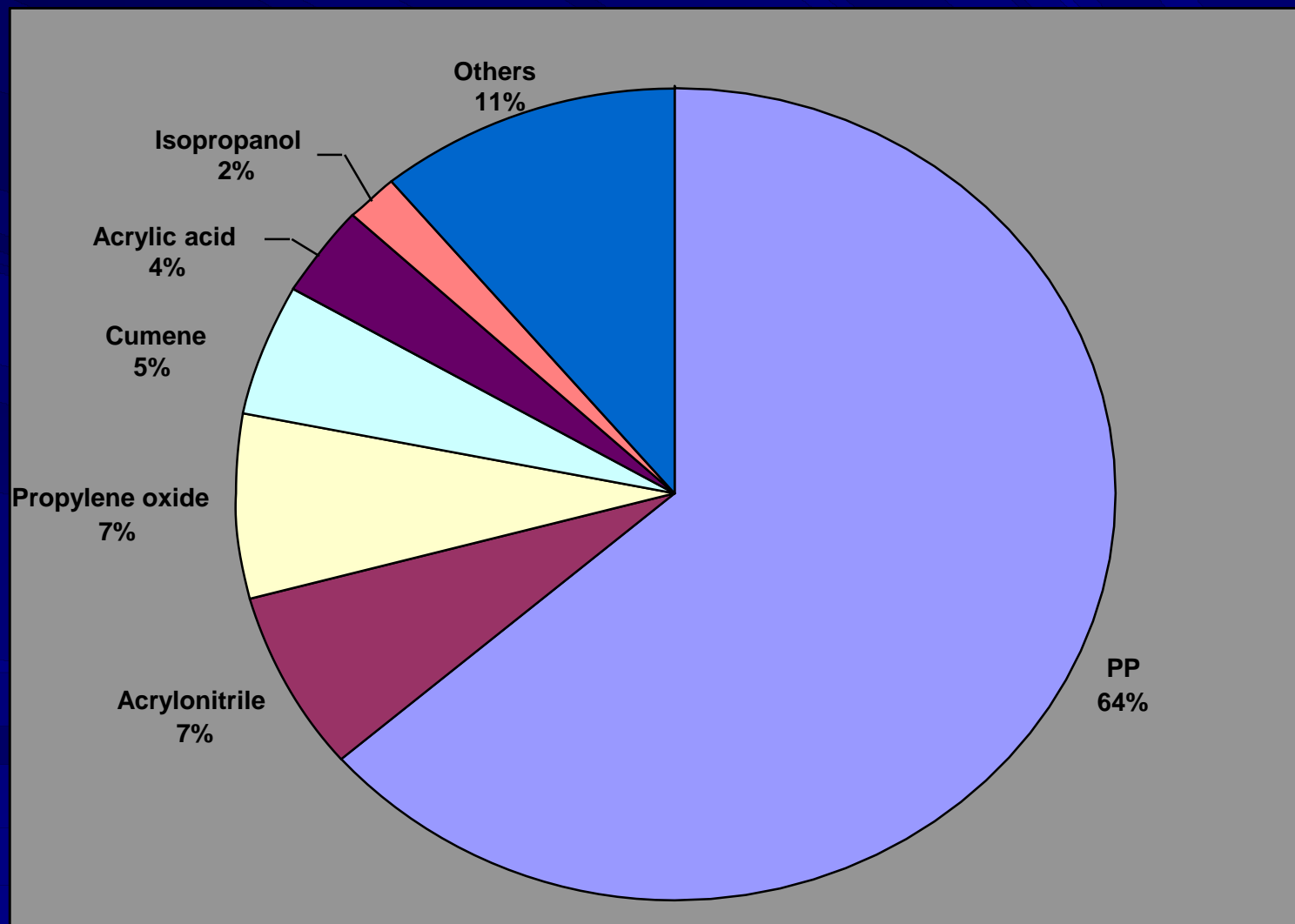
India's propylene net availability ('000 tonnes)					
Particulars	2020-21	2021-22	2022-23	2023-24*	2024-25*
Capacity	6614	6614	7071	7602	7602
Production	5621	5835	5908	5735	5923
Imports	10	27	15	0	0
Exports	15	0	0	0	0
Net availability	5615	5862	5923	5735	5923

Sources: Chemicals & Petrochemicals Manufacturers Association of India, and Polymerupdate Research;
*Estimates

Building block for petrochemicals – ethylene consumption



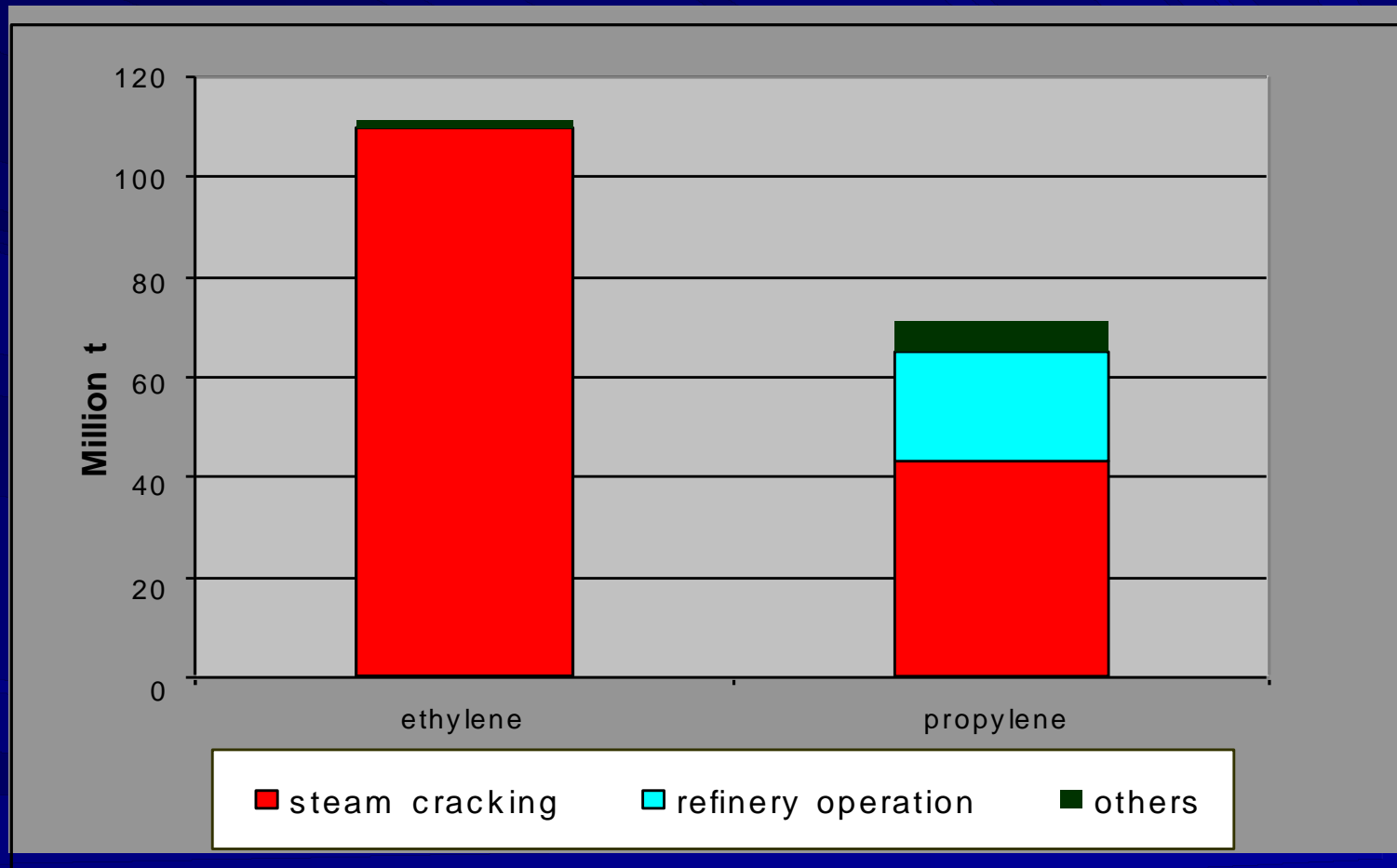
Building block for petrochemicals – propylene consumption



Ethylene milestones

- 1913: Standard Oil's scientist patented thermal cracking process
- 1930s: Ethylene was first separated from coke oven gas and the first commercial plant for the production of ethylene was built by Linde at that time
- 1941: Jersey Standard (ExxonMobil's predecessor) developed the world's first steam cracker at Baton Rouge
- 1950s: Ethylene emerged as a large-volume intermediate, replacing acetylene as prime material for synthesis
- Today ethylene is primarily produced by thermal cracking of hydrocarbons in the presence of steam. Plant capacities are up to 1-1.5 million t/y ethylene.
- Other processes are also available or under development

Olefin production by processes



Industrial Installations of the methanol-to-olefins technology (pilot/demonstration-scale or commercial-scale, post-2000)

No.	MTO technology	Licensor/operator	Scale	Catalyst	Process conditions (T, P, WHSV)	Catalyst performance (C, S, Y)
1	UOP/hydro advanced MTO (with olefin cracking)	UOP (Feluy, Belgium)	0.2 MM MTPA	SAPO-34 (attrition-resistant formulation)	400–550 °C, 1–4 atm	~100%, 80%+ C-selectivity to C ₂ , C ₃ , olefins
2	D-MTO (Dalian Institute of Chemical Physics)	Shenhua China Energy (Mongolia, China)	0.6 TPA	SAPO-34	400–550 °C, 4–5 atm	N/A
3	S-MTO (Sinopec MTO)	Sinopec	0.2 MM TPA	SAPO-34	400–550 °C, 1–5 atm	N/A
4	MTP (Lurgi)	Shenhua Group with Ningxia Provincial Govt. (Ningxia, China)	0.5 MM TPA	SAPO-34	N/A	N/A
5	MTP (Lurgi)	Datang Int'l Power with China Datang (Mongolia, China)	0.5 MM TPA	SAPO-34	N/A	N/A
6	Honeywell UOP	Jiangsu Sailboat Petrochemical company (Jiangsu Province, China)	0.8 MM TPA	SAPO-34	400–550 °C, 1–5 atm	~100%, ~85% to C ₂ + C ₃
7	Honeywell UOP	Wison China Energy (Nangxin Province, China)	0.3 MM TPA	SAPO-34	400–550 °C, 1–5 atm	~100%, 85% to C ₂ + C ₃

Present and future processes to ethylene and propylene production

Steam cracking	Dominating technology
Refinery processes	Minor importance for ethylene Important for propylene only
MTO Methanol to Ethylene and Propylene	UOP/Hydro MTP process commercialized
MTP Methanol selectively to Propylene	Commercialization phase
Green Ethylene <ul style="list-style-type: none">- Biomass via Fermentation to Ethanol and Dehydration of Ethanol- Biomass > Syngas > Fischer Tropsch	Commercialization phase First large scale production by Braskem in Sep 2010 (200 ktpa of bioethylene)

The chemical industry of the 50's in India was based entirely on ethanol.

ICI manufactured low-density polyethylene at Rishra in West Bengal using ethylene produced from ethanol.

Synthetics and Chemicals Ltd. produced Styrene Butadiene Rubber using ethanol at Bareilly in Uttar Pradesh.

Polychem Ltd. manufactured polystyrene from ethylene based on ethanol at Vishakhapatnam in Andhra Pradesh.

Chemicals and Plastics Ltd. manufactured Polyvinyl Chloride at Metturdam in Tamil Nadu, which too was based on ethanol.

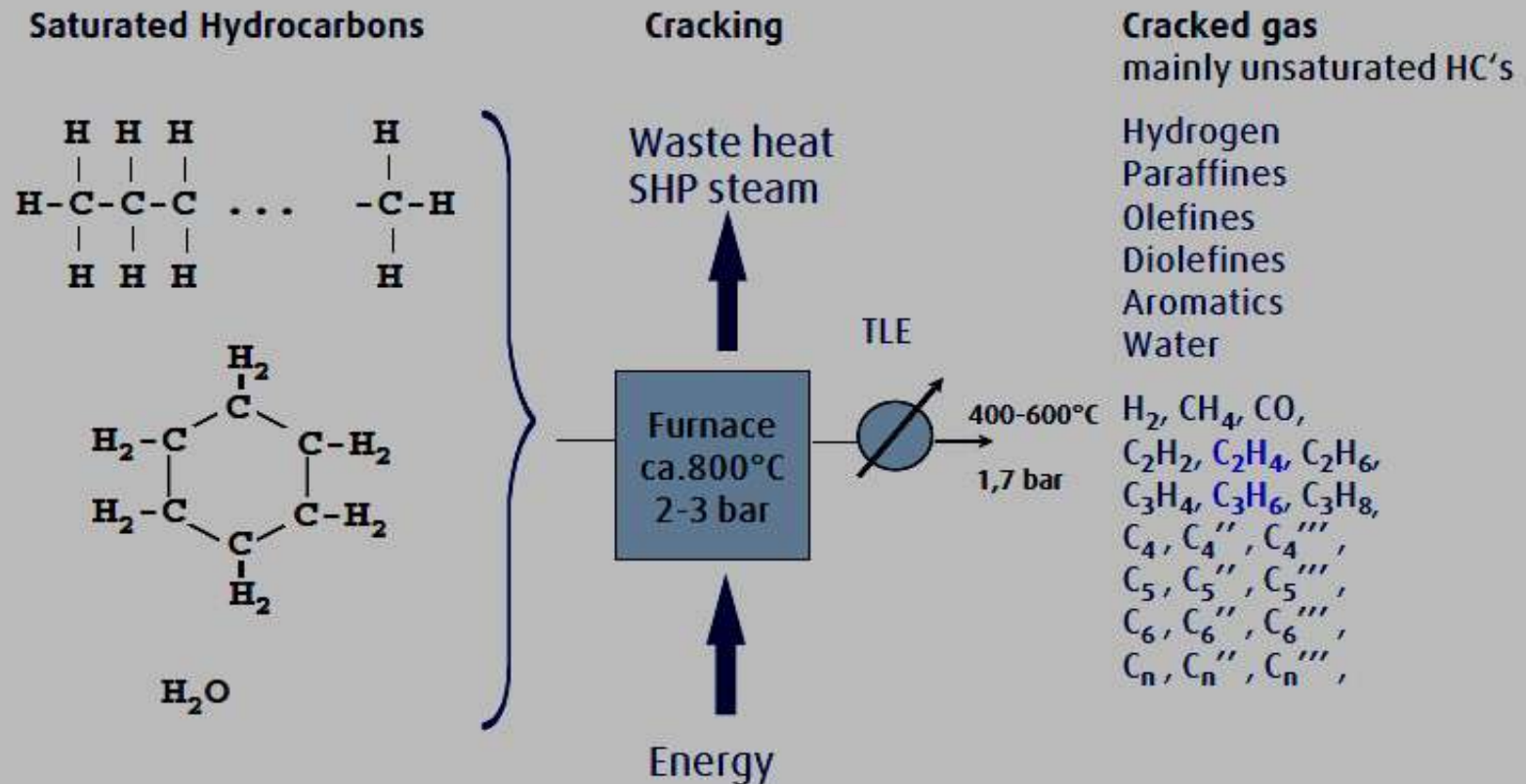
Olefinic Complexes in India

Naphtha Crackers	Ethylene Capacity (MTs)
Reliance Industries Ltd., Vadodara, Gujarat	1,75,000
Reliance Industries Ltd, Hazira, Gujarat	8,87,000
Haldia Petrochemicals Ltd, Haldia, West Bengal	7,00,000
Indian Oil Corporation Ltd., Panipat, Haryana	8,00,000
Sub- Total	25,62,000
Natural Gas Crackers	
Reliance Industries Ltd., Nagothane, Maharashtra	4,21,400
Gas Authority of India Limited, Pata, UP	8,50,000
Reliance Industries Ltd, Dahej, Gujarat	4,00,000
Sub- Total	16,71,400
Dual Feed Crackers	
Brahmaputra Cracker and Polymer Limited (BCPL)	2,13,100
ONGC Petro additions Ltd. (OPaL)*	11,00,000
Sub- Total	13,13,100
Off Gas Cracker	
Reliance Gas industry, Jamnagar	15,00,000
Sub- Total	15,00,000
Total	70,46,500

Characteristics of Steam Cracking

- Steam cracking is a pyrolysis process
- A hydrocarbon mixture is heated in metal tubes inside a furnace in the presence of steam to a temperature at which the hydrocarbon molecules thermally decompose
- For ethane the primary reaction is dehydrogenation:
$$\text{C}_2\text{H}_6 \rightarrow \text{H}_2\text{C}=\text{CH}_2 + \text{H}_2$$
- Other free radical reactions also occur
 - Cracking and dehydrogenation of longer molecules resulting in hydrogen, methane, ethylene, propylene, butadiene and heavier
 - Continued dehydrogenation to form acetylene, aromatics and coke
- These reactions require a residence time of less than one second and are endothermic

Principle of the cracking process



Key words for cracking

■ Yield

Product/Feed

■ Cracking severity

Depth of cracking

–Propylene/Ethylene ratio
(used for liquid feed)

e.g., P/E=0.45 T~ 850 °C; P/E=0.60 T~810 °C

–Conversion
(used for gas feeds)

Conversion rate of feed component
e.g., 60-70 % for ethane

■ Dilution steam ratio

Steam/HC feed

e.g., 0.5 kg/kg for naphtha

■ Residence time

Residence time of one molecule in the
cracking coil

e.g., 0.1 – 0.5 sec

■ Run time

Time between two decokings

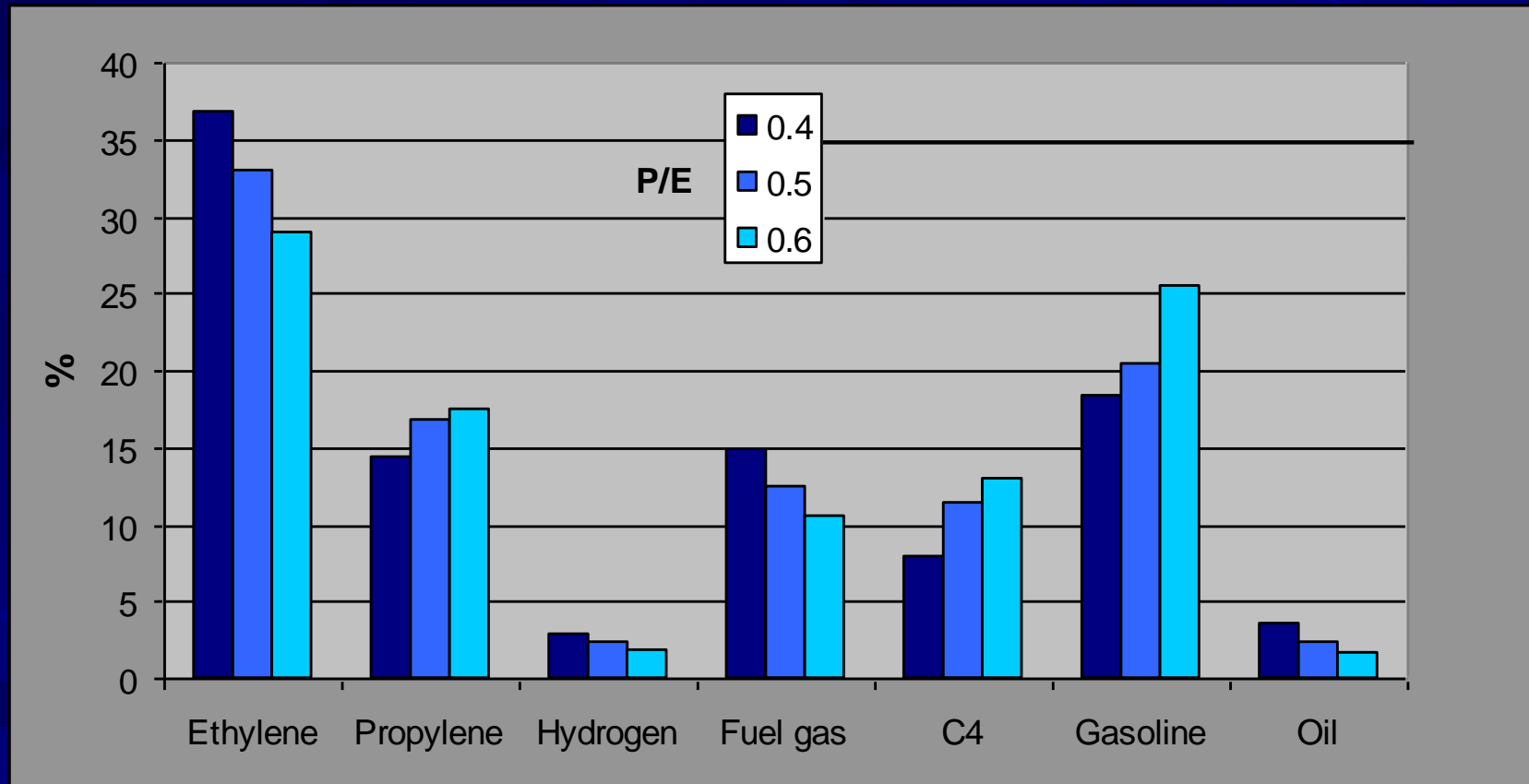
e.g., 50 – 80 days

Cracking Conditions

- **Residence time** **0.1 – 0.5 sec**
 - Short residence time favours primary reactions where olefins are formed
 - Long residence time favours secondary reactions where olefins are destroyed
- **Pressure** **2 – 3 bar**
 - High pressure favours secondary reactions
 - Low pressure favours primary reactions
- **Dilution steam** **0.3 – 0.8 kg/kg**
 - Reduces partial pressure of HC
 - Suppresses secondary reactions
 - Prevents excessive coke formation
 - Heavier feedstock needs more steam
- **Temperature** **800 – 850 °C**
 - High temperature promotes the formation of lower olefins, low temperatures favour oligomerization
 - Fast temperature rise favours ethylene and propylene
 - The heavier the feed the lower the temperature – coke formation!

Severity vs. product yield

Yields for naphtha feed



Raw Materials and Products

Wide range of feedstocks

■ Gaseous feeds

- Ethane
- Propane
- n-butane/i-butane

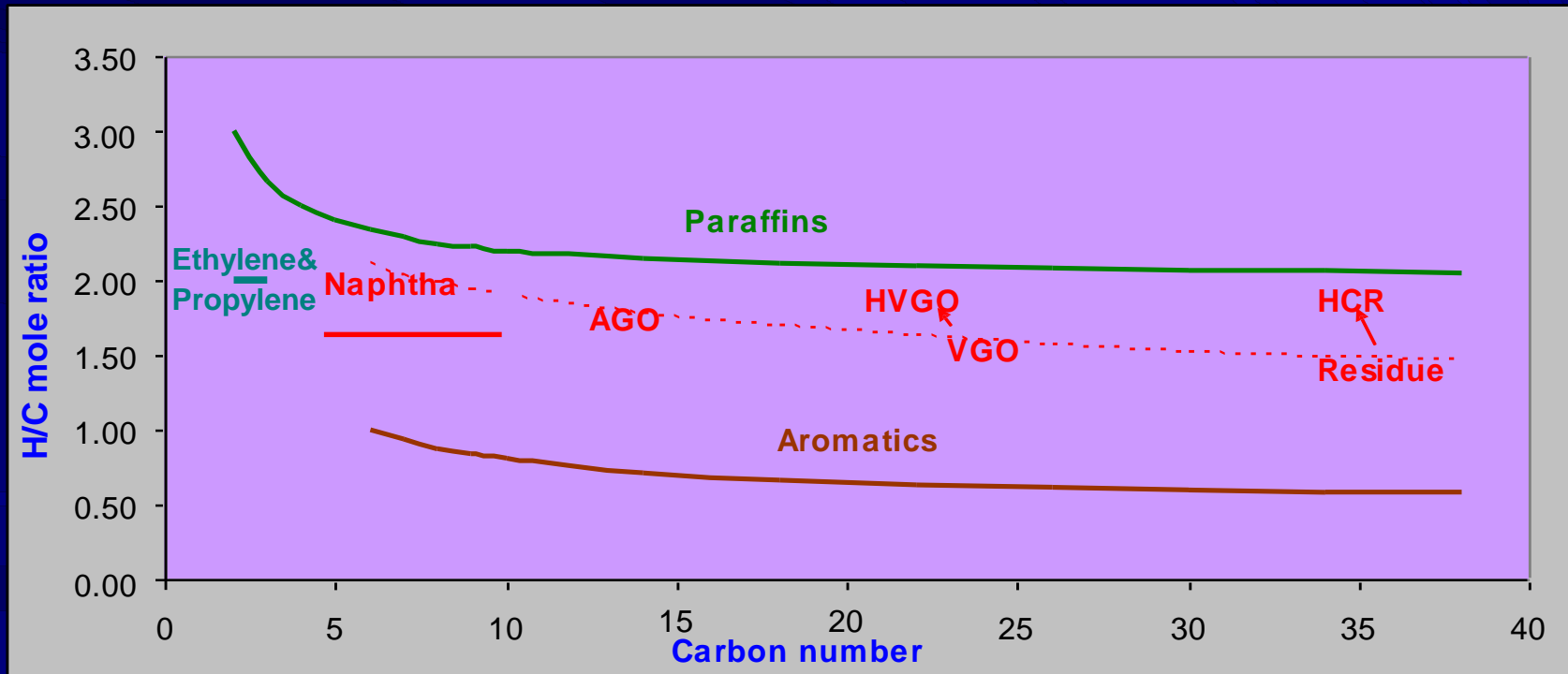
■ Liquid feeds

- Condensates from natural gas
- Naphtha
- Atmospheric gas oil (AGO)
- Hydrocracker residue (HCR)
- hydrogenated vacuum gas oil (HVGO)

Liquid feeds

Main components

- Paraffins
- Naphthenes
- Olefins and aromatics (associated components in heavy feedstocks)



Cracker yields for various feed stocks

Feedstock	Ethylene	Propylene	Butadiene	BTX	Others
Ethane (20.2% H)	84	1.4	1.4	0.4	12.8
Propane	44	15.6	3.4	2.8	34.2
n-Butane	44.4	17.3	4.0	3.4	30.9
Lt. Naphtha	40.3	15.8	4.9	4.8	34.2
Full Range Naphtha (11.8% H)	31.7	13.0	4.7	13.7	36.9
Reformer Raffinate	32.9	15.5	5.3	11.0	35.03
Lt. Gas Oil	28.3	13.5	4.8	10.9	42.5
Hy. Gas Oil	25.0	12.4	4.8	11.2	46.6
Crude Residue	21.0	7.0	2.0	11.0	59.0

Cracked Gas Composition Vs. Feedstock

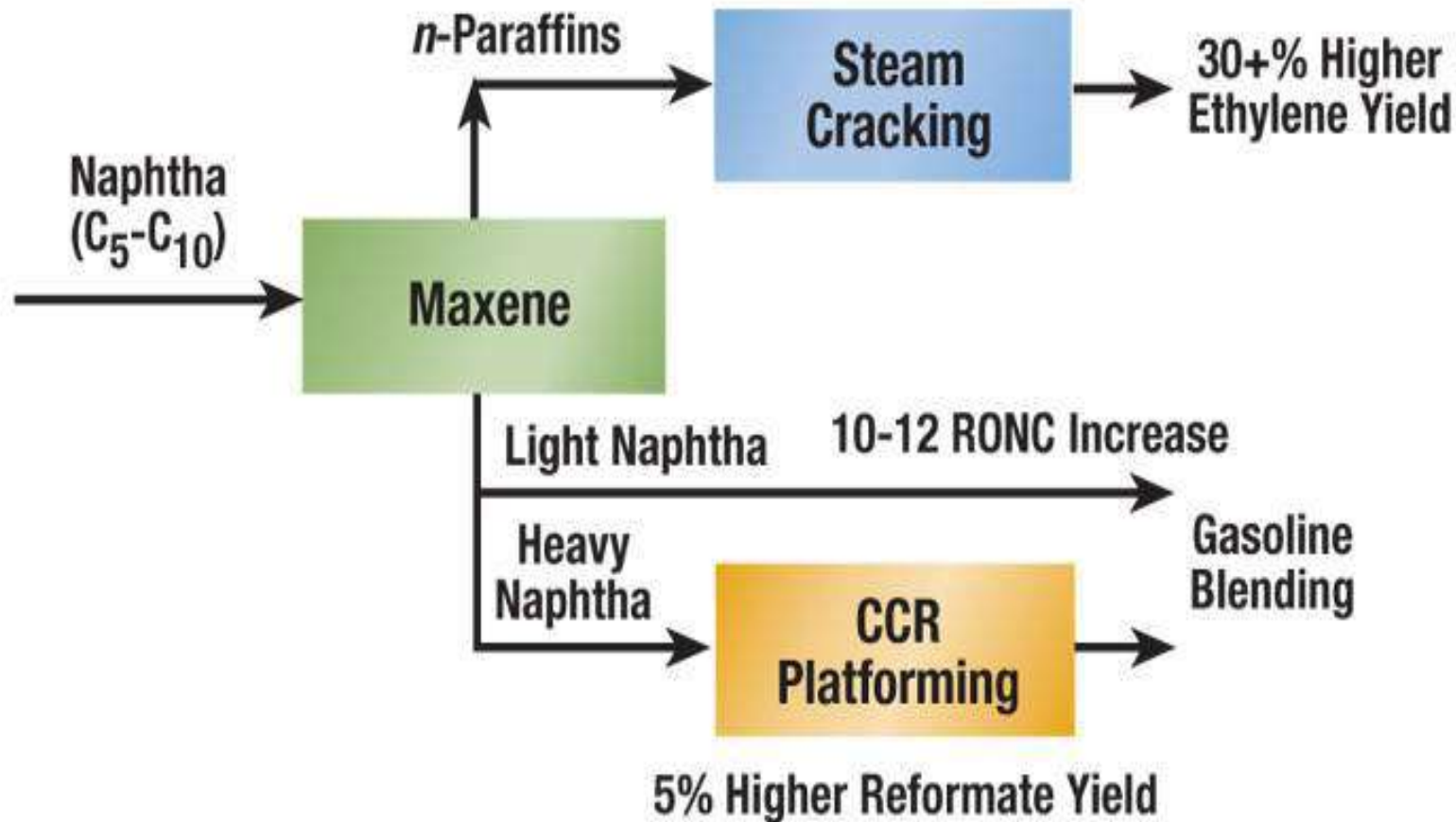
Wt%

	Ethane	Propane	n-C ₄ /i-C ₄	Naphtha	AGO
H₂+CO	4.06	1.70	1.23	1.03	0.71
CH₄	3.67	23.37	21.75	15.35	10.69
C₂H₂	0.50	0.67	0.50	0.69	0.34
C₂H₄	52.45	39.65	31.74	31.02	24.85
C₂H₆	34.76	4.57	3.67	3.42	2.75
C₃H₆+C₃H₄	1.15	13.28	19.85	16.21	14.28
C₃H₈	0.12	7.42	0.69	0.38	0.31
C₄	2.24	4.03	12.90	9.54	9.61
Pyrolysis Gasoline	0.87	4.27	6.41	19.33	20.6
Pyrolysis Fuel Oil	0.16	1.11	1.26	3.01	15.78

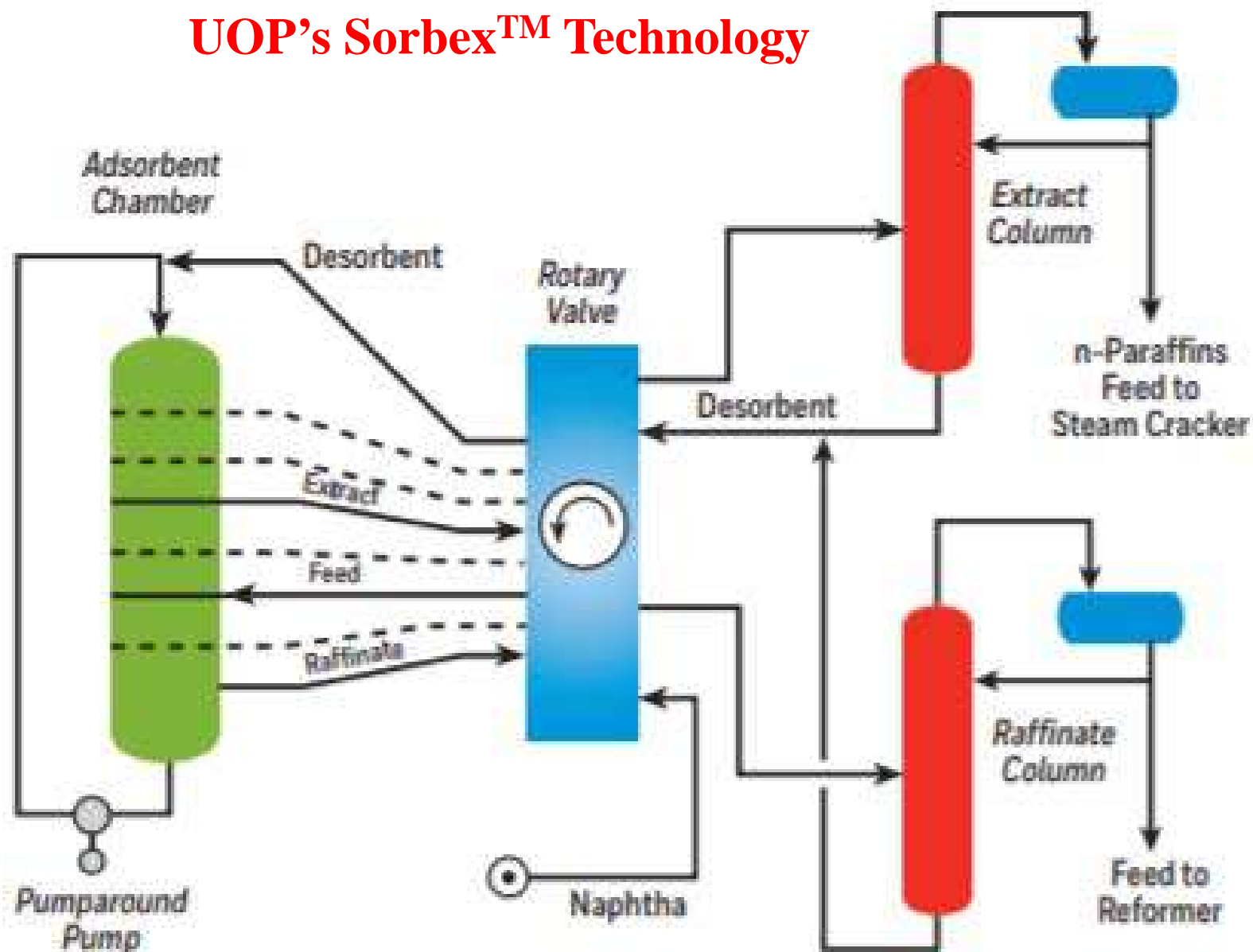
Considerations for feedstocks

- Paraffins are the best raw materials
- Lower carbon number gives higher ethylene yield
- Cracking severity influences product yield
- Now-a-days, Steam crackers are being integrated into refineries. Therefore,
 - both gaseous and liquid feeds are used,
 - profitability is a very complex issue and evaluated together with refinery operation

UOP's MaxEne Process for Increased Ethylene Yield



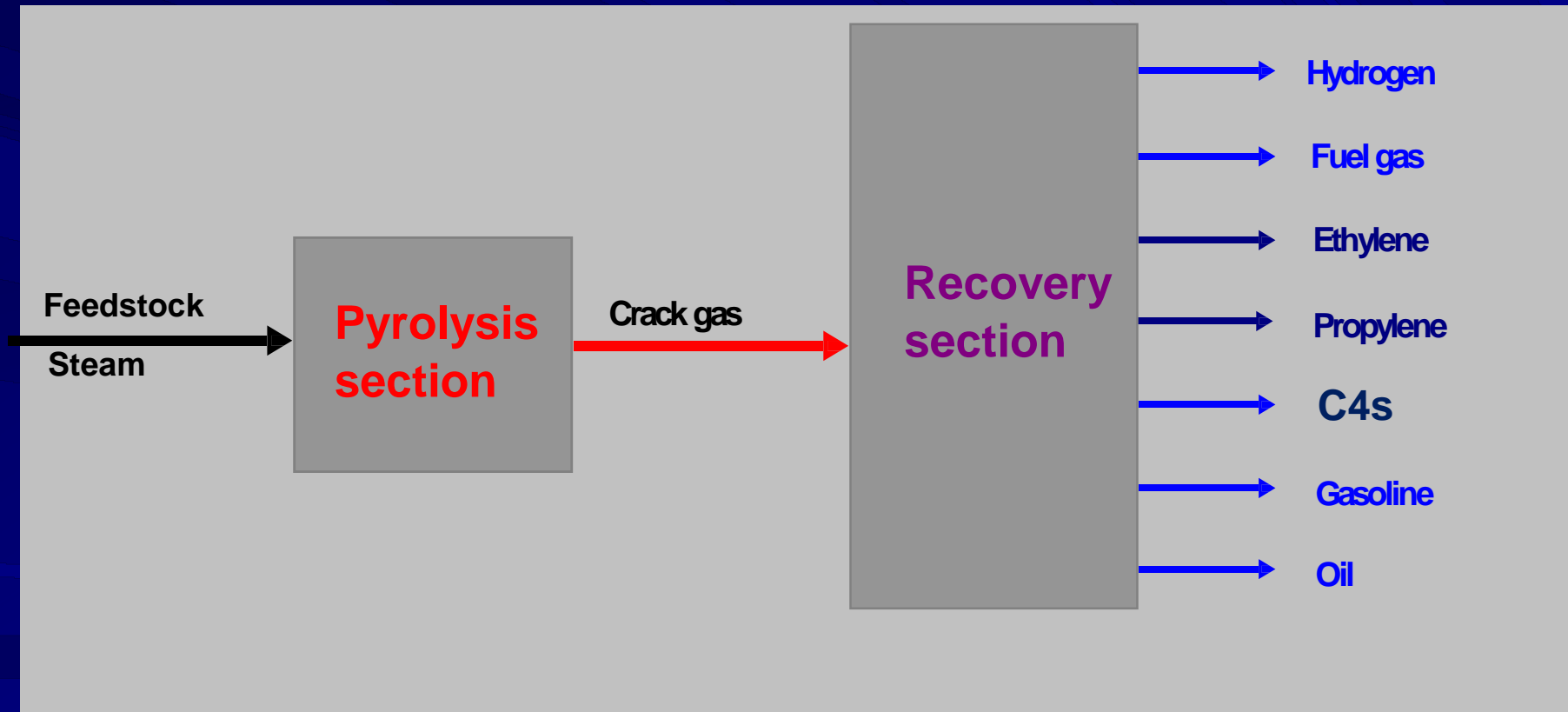
UOP's Sorbex™ Technology



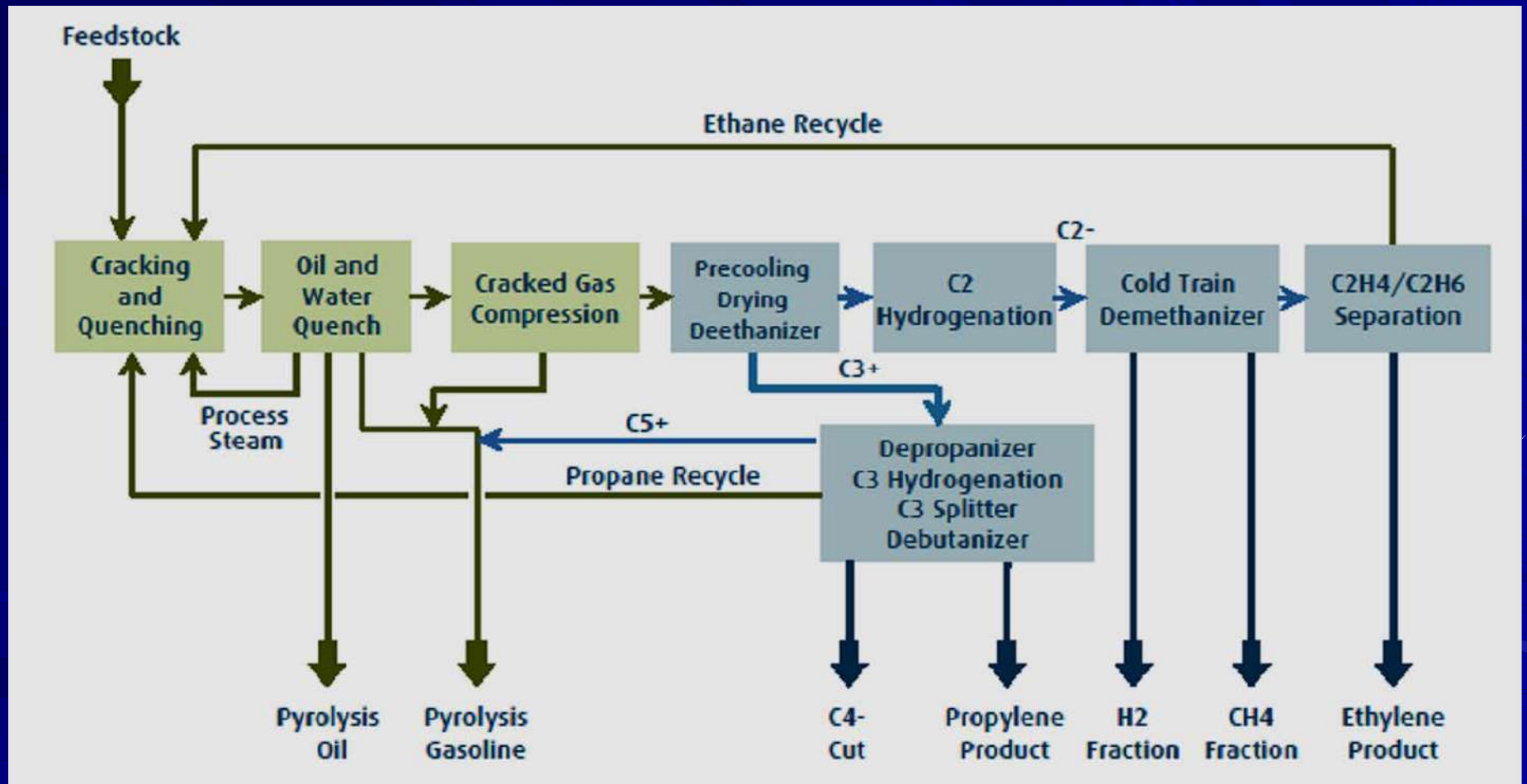
The n-paraffin purity in the MaxEne extract is typically 93% with a recovery of 87% of n-paraffins from the incoming feed.

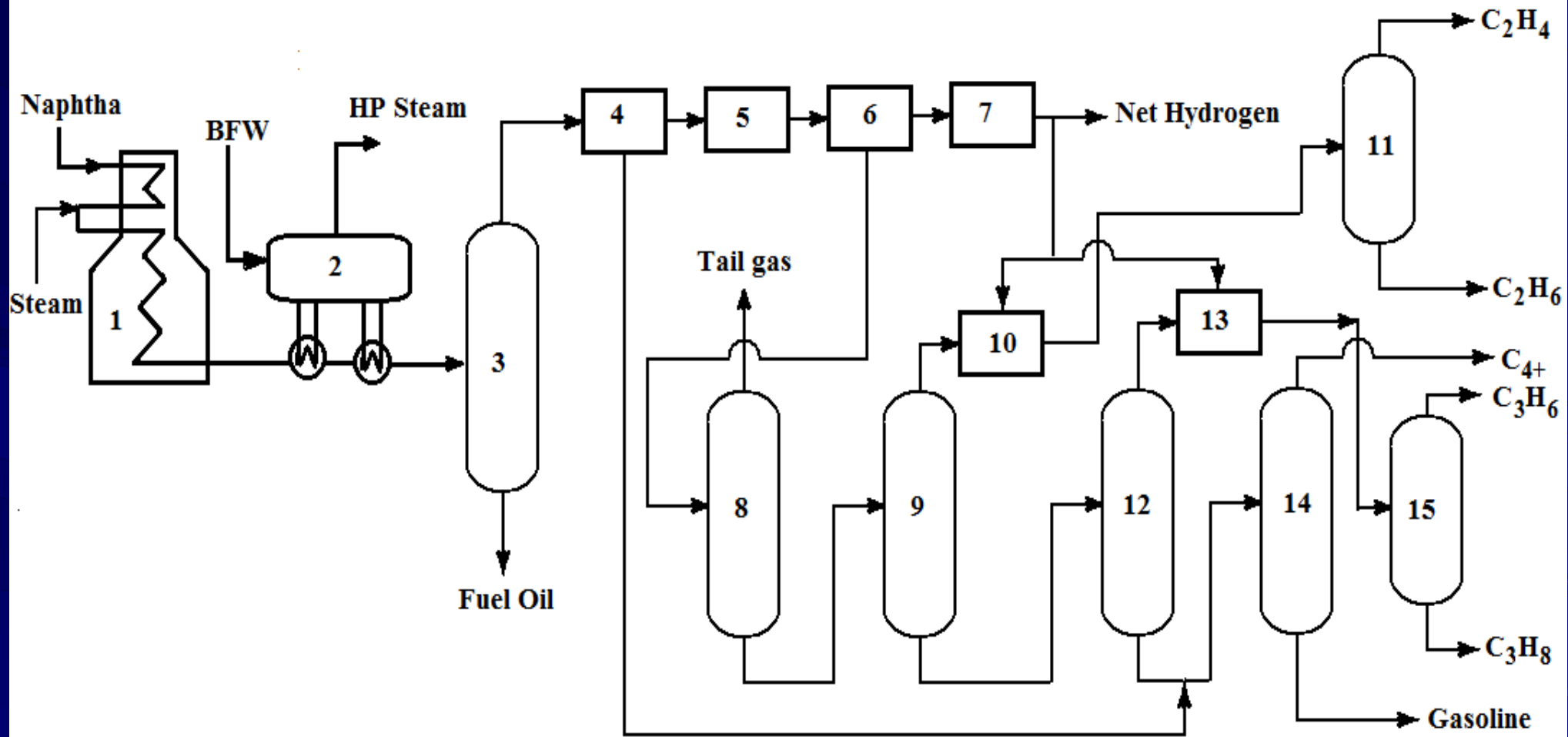
MaxEne Process Flow

Main and byproducts



Olefins production block diagram





Olefins Production by Naphtha Cracking

1: Pyrolysis Furnace; 2: Steam Generating Facility; 3: Product Fractionator; 4: Compressor & Cooler Section; 5: Acid Gas Removal & Drying Unit; 6: Demethanizer Feed Preparation; 7: Hydrogen Purification System; 8: Demethanizer; 9: Deethanizer; 10: Hydrogenation Unit; 11: C2-Splitter; 12: Depropanizer; 13: Hydrogenation Unit; 14: Debutanizer; 15: C3-Splitter

Process design considerations

Ethylene process is one of most complex systems in petrochemical industry. The following challenges have to be faced:

- Safety first
- High energy efficiency and minimum environmental emissions
- Low production costs and low investment costs
- High plant reliability
- Simple operation
- Good maintainability
- Minimum losses

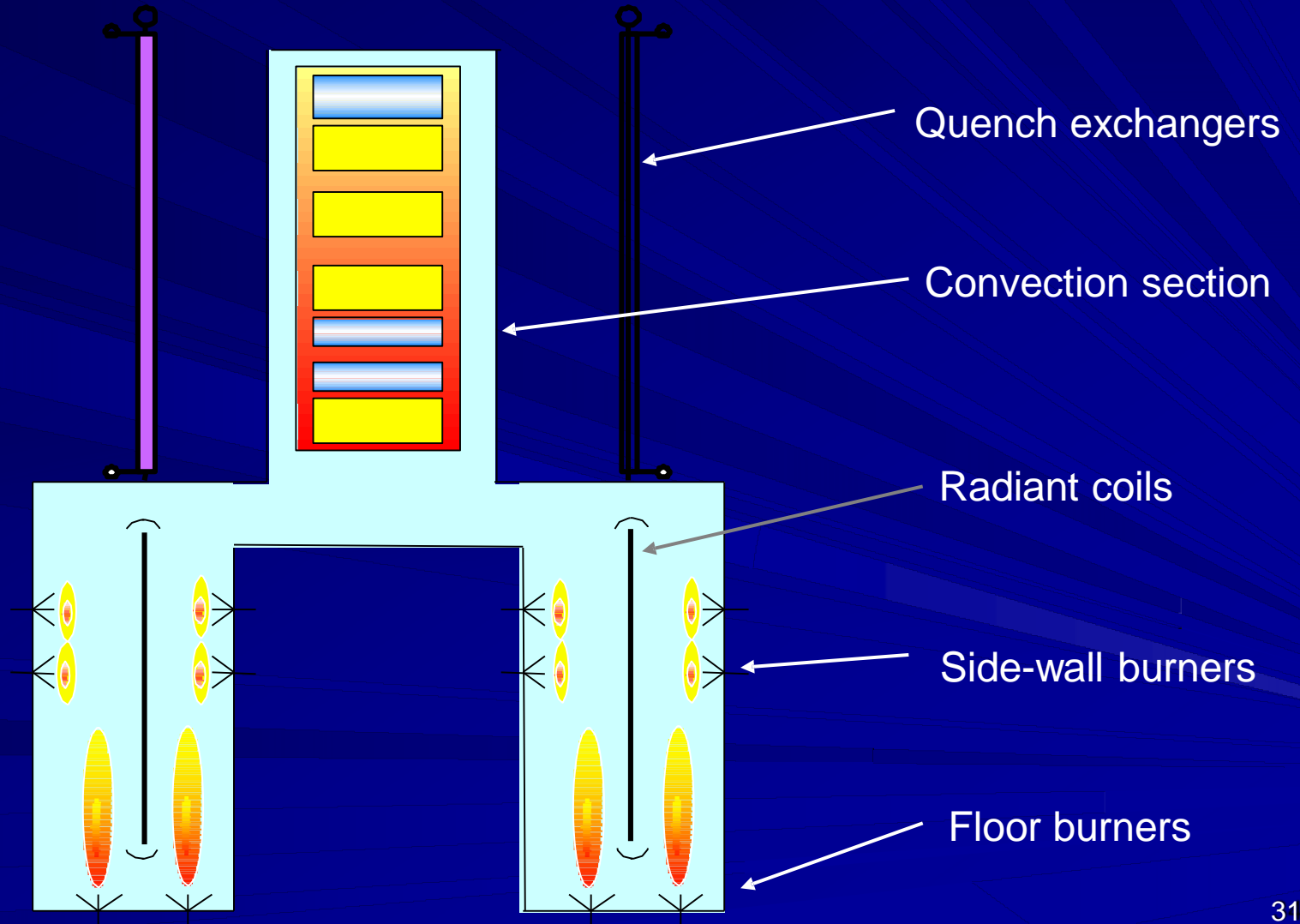
Tasks of a cracking furnace

- Production of ethylene and propylene by endothermic cracking reaction
- Preheating of feed and dilution steam by utilization of waste heat
- Cooling of the cracked gas to freeze chemical reactions
- Production of superheated HP steam by utilization of waste heat

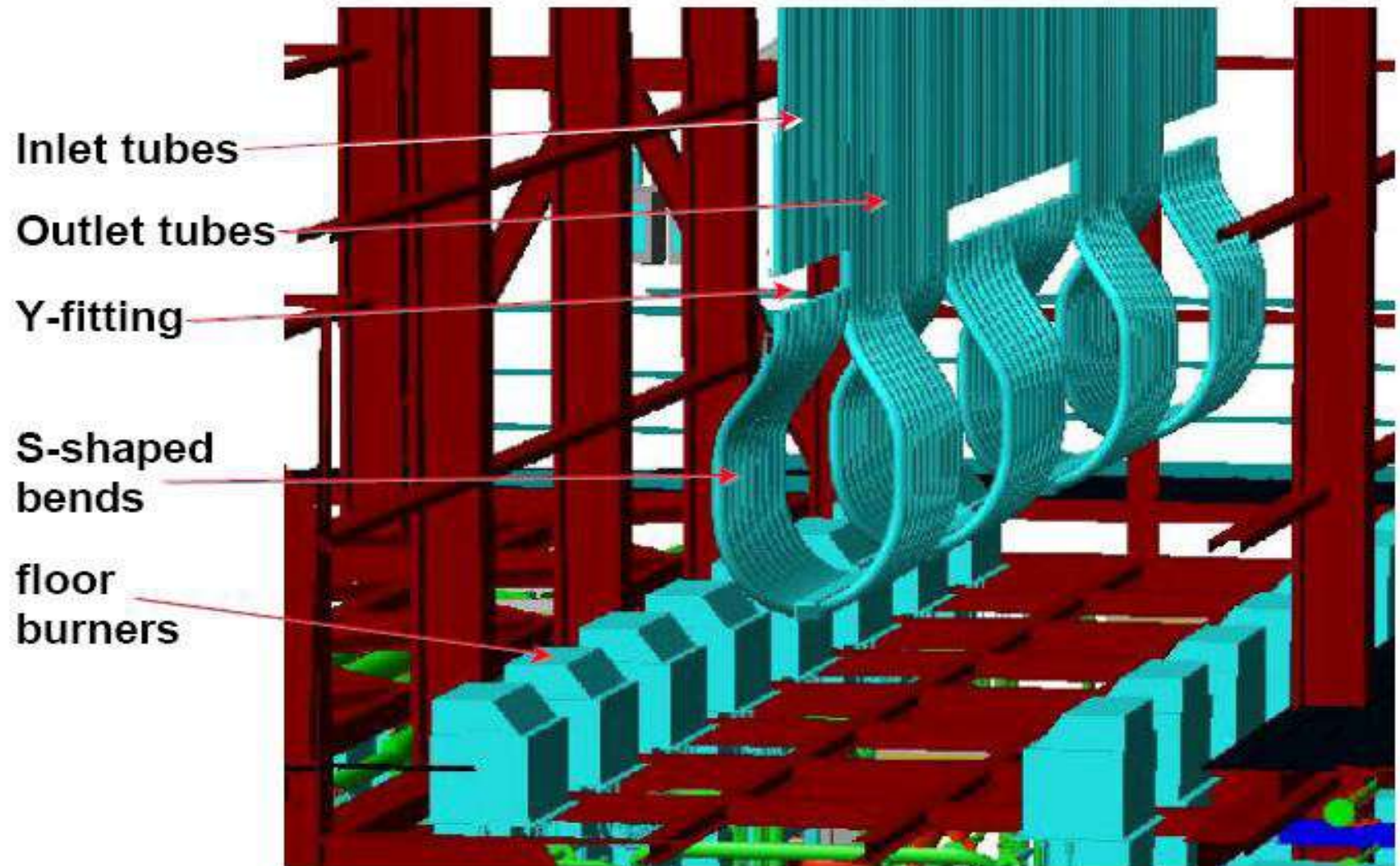
Cracking furnaces

- Radiant section: thermal cracking reactions (800 – 850 °C)
- Convection section: heat recovery from hot flue gas
 - Feed preheating
 - Boiler feed water preheating
 - Process steam superheating
 - Freezing cracking reactions in order to avoid product losses by secondary reactions (400 - 600 °C)

Cracking furnace



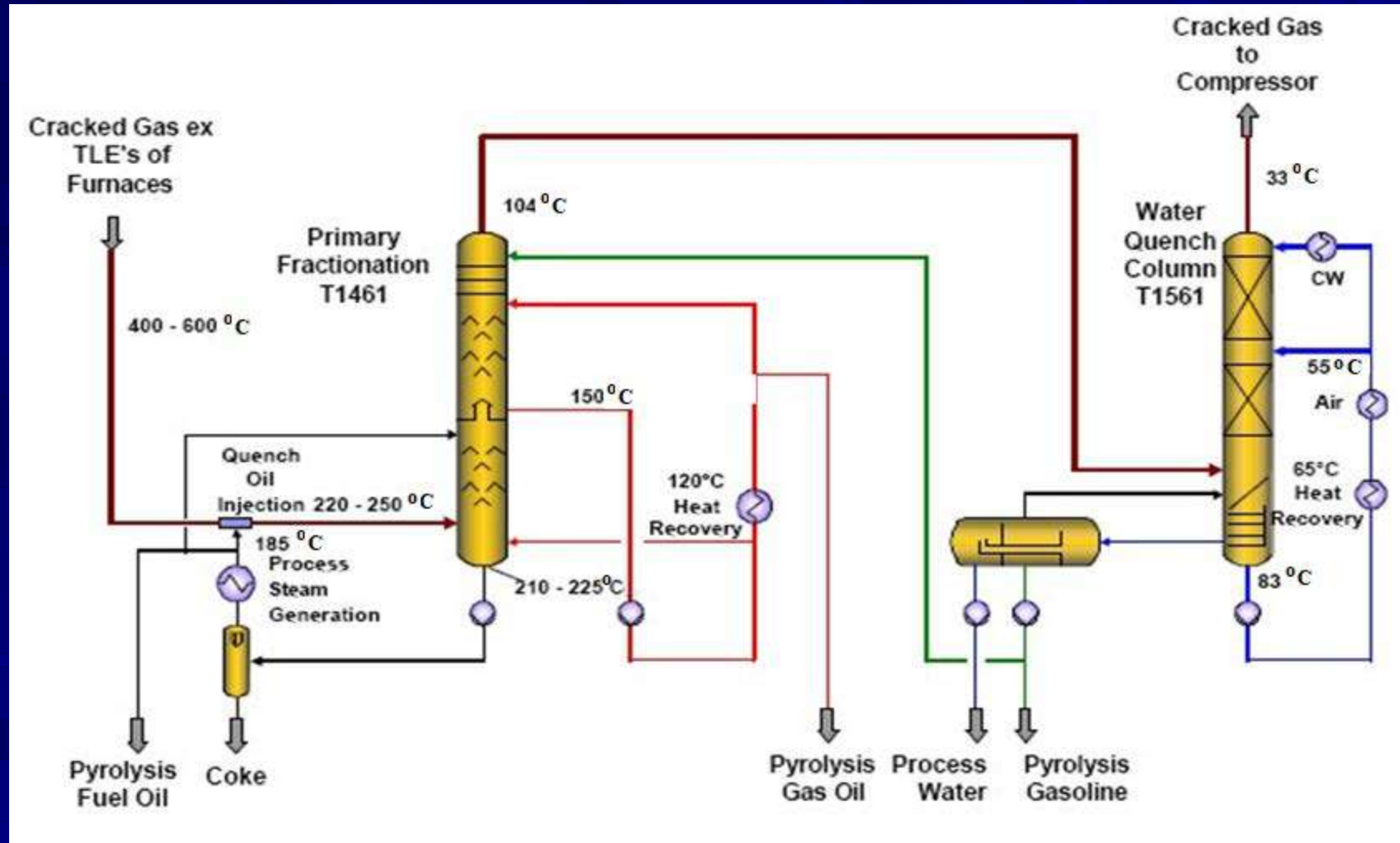
Tube arrangement in the radiant zone



Oil and water quench

- Further **cracked gas cooling** by direct oil injection downstream the quench coolers (220 - 250 °C)
- **Oil Fractionation (primary fractionation) and Quench Oil Cycles**
 - Two quench oil cycles (Pyrolysis Fuel Oil and Pyrolysis Gas Oil) are used as heat carrier to cool the cracked gas (~100 °C) and to shift the recovered heat to consumers
 - Both quench oil cycles are formed by condensing the heavy ends of the cracked gas
 - Process steam generation by hot quench oil
- **Water Scrubbing (Water quench column)**
 - Cracked gas is cooled by water circulation to ambient (~30 °C) temperature to condense heavy gasoline and process (dilution) steam
 - Circulating water is withdrawn from the bottom of the column and pumped to several consumers for low temperature heat recovery

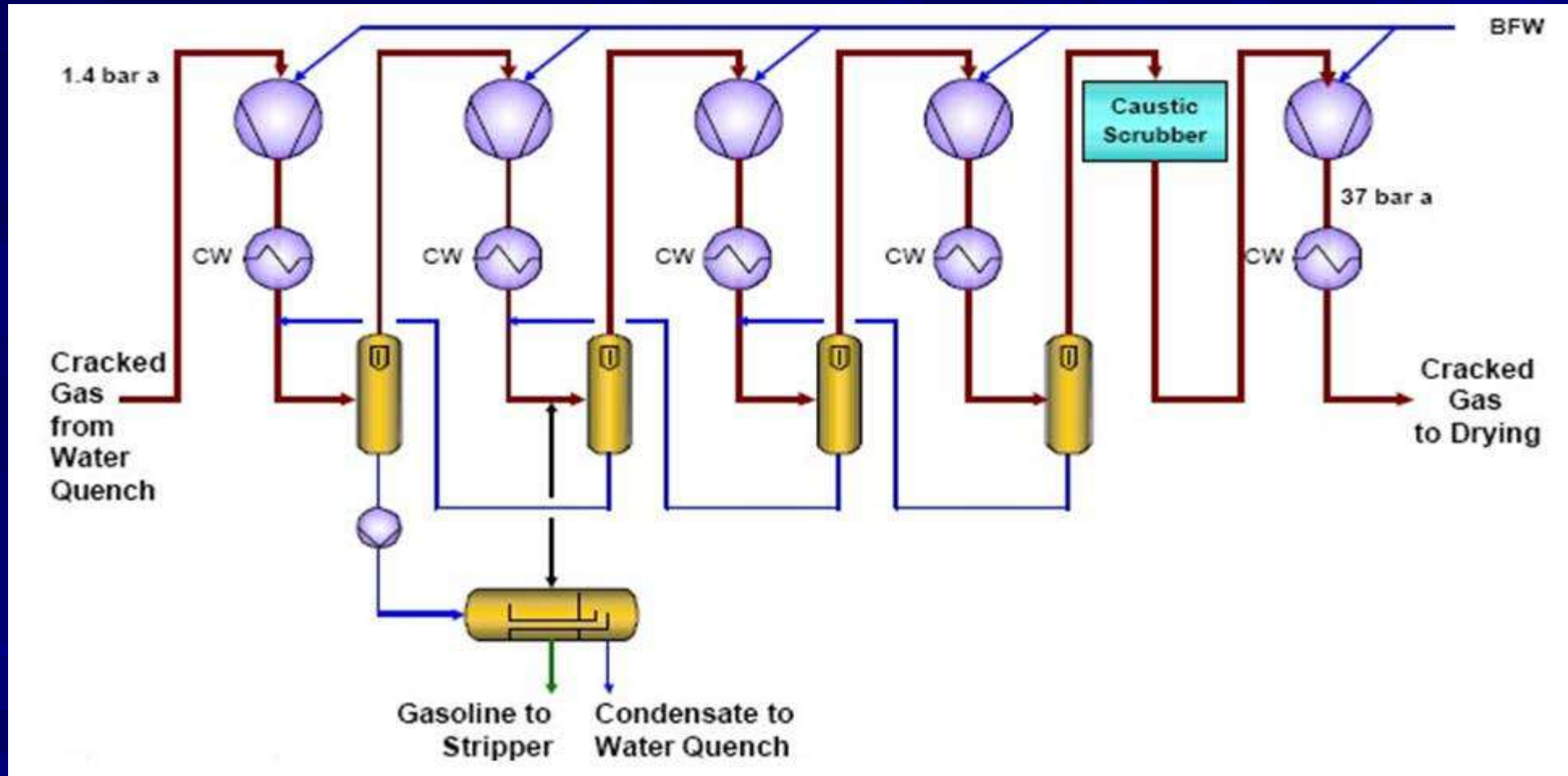
Hot section: Oil fractionating and water quench column



Cracked gas compression

- **Cracked gas is compressed** with a 5-stage centrifugal compressor
 - Suction pressure: 0.5 bar (g)
 - Discharge pressure: 32-36 bar (g)
- The **compressor** is driven by an extraction/condensation **steam turbine**.
- Process water and gasoline are condensed in the interstage **coolers** and knocked out in the interstage **separators**. Gasoline is directed to hydrogenation and separation.
- **Caustic Scrubbing:** removal of the acid components CO_2 and H_2S in a 3-stage caustic scrubber

Cracked gas compressor Section



Cold section 1

■ **Precooling, drying, deethanizer**

- Cracked gas cooling to drying temperature
- Cracked gas **drying** to eliminate water content
- Cooling to -40 °C (cooling with propylene refrigerant and cold streams from the low temperature section)
- Separation of C_2 - and C_3 + fraction (deethanizer)

■ **C_3 + processing**

- C_3/C_4 + separation (depropanizer)
- C_3 hydrogenation: conversion of methyl-acetylene and propadiene to propylene and propane
- C_3H_6/C_3H_8 separation: **propylene** product, propane recycle
- C_4/C_5 separation

Cold section 2

■ C₂ hydrogenation

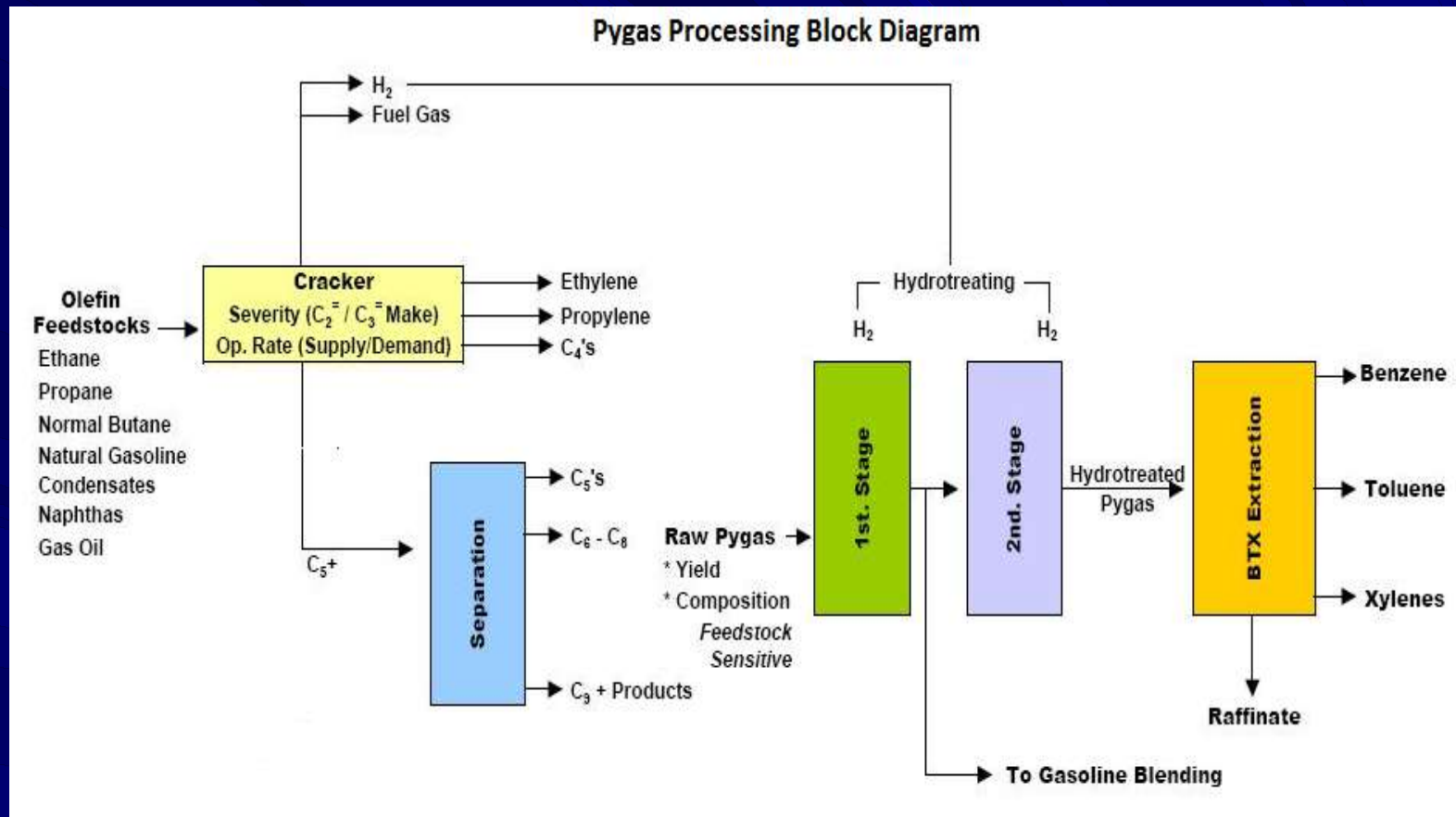
- Acetylene is selectively hydrogenated to ethylene
- Max. 1 ppm acetylene downstream the catalytic reactor

■ Low temperature section (cold train)

- C₂- fraction is cooled with ethylene refrigerant and expanded cold streams (-145 °C)
- Separation of C₂ from C₁ and hydrogen from methane: ethylene, ethane, and almost all methane is condensed, the remaining gas consists of a hydrogen-rich fraction

■ C₂ splitter

- To separate **ethylene** (top product) and ethane (recycled to feed)



Typical Naphtha Cracker Pygas (C₅ – 200 °C) Composition

Component	Paraffins + Naphthenes	Olefins	Diolefins	Benzene	Toluene	Xylenes	Styrene	C ₉ + Aromatics	Total Aromatics
Composition (wt%)	11.8	5.5	18.0	28.0	14.0	7.2	3.0	12.5	64.7