Master of Science in *Energy Engineering*
Renewables for Environmental Sustainability

http://beep.metid.polimi.it/

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School of Industrial and Information Engineering
Academic Year 2017-18

Lecture notes for:
Bioenergy and Waste-to-Energy Technologies

Prof. Federico Viganò – Department of Energy
With the contributions of ing. M. Fantini, ing. E. Martelli, prof. S. Consonni

Lecture outline

- *The biorefinery concept*
- *Syngas cleaning*
  - *Tar removal*
- *Syngas applications*
  - *FT (Fisher-Tropsch) process*
  - *DME (DiMethyl Ether) process*
- *Examples of integrated bio-refineries*
  - *Production of FT*
  - *Production of DME*
  - *Production of MixOH*

The biorefinery concept

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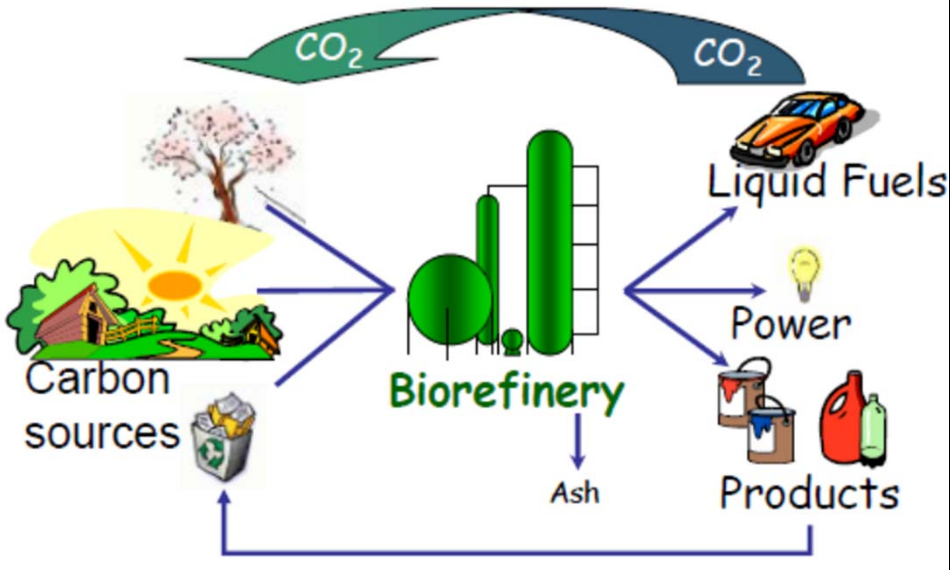

The biorefinery concept

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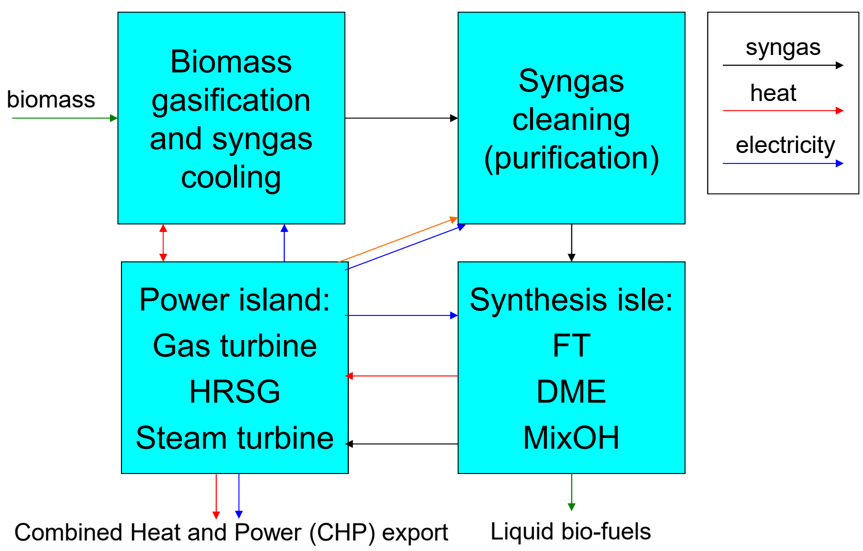

The biorefinery concept

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Potential → Exploiting the synergies among different processes:

- Residual fuels (unconverted syngas, char, tar) can be used to produce heat and power both for internal use and for export.
- Waste process heat can be efficiently recovered for heat & power production.
- Processes can use efficiently produced heat (steam).
- No need to push chemical conversion processes if the unconverted feedstock is efficiently valorized as heat and / or power.

Drawback → Very complex system, entailing a number of technologies:

- TC process island to convert biomass into easier intermediate (e.g. syngas).
- Purification island to remove all unwanted and / or pollutant species.
- Synthesis island to synthetize final products (fuels, chemicals).
- Power island to recover waste heat a fuel as useful heat and power.

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Syngas cleaning

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Bio-syngas, as well as Coal-syngas, contains a set of compounds which may cause pollution, damage internal combustion engines (both gas turbines and reciprocating engines), as well as poison the catalyst materials used in synthesis reactors.

The main contaminants are:

1. TAR (heavy hydrocarbons)
2. ALKALI SALTS / METALS ($CaCO_3$, KCN, Na_2S..)
3. COS and H_2S
4. DUST (fly ashes + unconverted carbon particles entrained by the gas)
5. NH_3 (ammonia)
6. HCl (hydrochloric acid) and Cl (Chloride)

While boilers can accept these contaminants without major issues, gas engines, gas turbines and chemical reactors can accept only very limited amounts of these contaminants.

Syngas cleaning

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mg/Nm³	TAR	DUST	ALKALI	NH_3	CHLORIDE	COS+H2S
Gas engines	< 50	< 50	< 1	< 50	< 10	< 100
Gas turbines	< 5	< 30	< 0.25	0*	0**	< 250 ppm**
Chemicals and syn-fuels production	< 5	0	0	0	0	0

* NH_3 and HCN would generate fuel bound NO_x

** Cl (HCl) and Sulphur species (H_2S + COS) will cause rapid corrosion of hot section parts.

Particles are removed by means of FILTERS and SCRUBBERS: at temperature below 600°C.

Alkali condense and solidify into small particles which can be captured by means of dust filters/scrubbers.

NH_3 must be removed not only to preserve the downstream equipment but also to limit NO_X production since part of NH_3 is converted into NO_x during combustion. NH_3 can be destroyed/converted into N_2 and H_2 over Ni and Fe based catalysts. Ni and Fe based catalysts are usually adopted for tar reduction. As an alternative, NH_3 can be removed by means of water scrubbing.

Syngas cleaning

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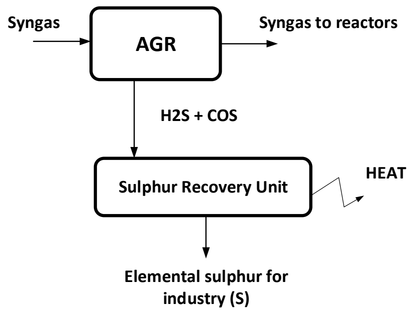
H_2S and COS are not problematic in power applications since their content in biomass syngas is limited and their presence is not a concern for gas engines, boilers and gas turbines (H_2S and COS react with O_2 and generates SO_2).

Since the S content in most biomass is very low (< 0,1%$_{wt}$), the syngas content is < 100 ppm and then the associated SO_2 emissions meet the current environmental limitations. H_2S and COS represent an issue in biomass to chemicals plants because most of the available catalysts are poisoned by these species. As a consequence, H_2S and COS must be removed by means of dedicated (expensive) processes, usually referred to as "ACID GAS REMOVAL PROCESSES" (AGR).



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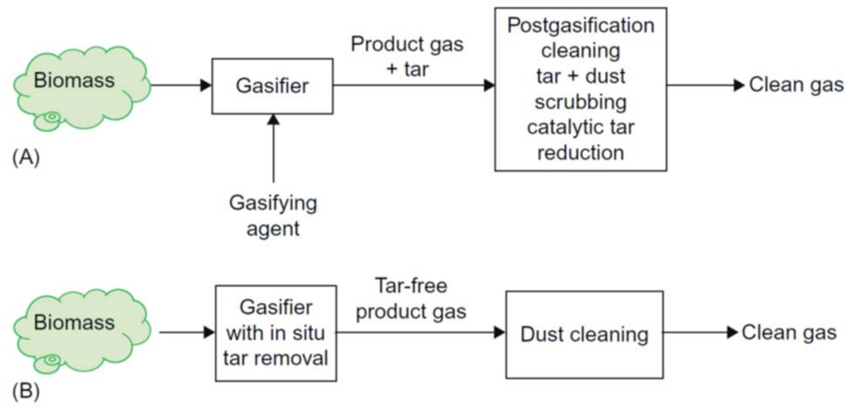
Primary (in situ) and Secondary (post) reduction



Tar removal (secondary reduction)

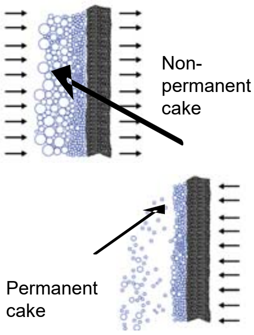
Fluidized bed and fixed bed gasifiers have the disadvantages of generating significant amount of tar which may cause clogging/plugging of the downstream equipment (as well as deactivation of catalysts).

Tar can be removed from the syngas stream by means of two approaches:

1. Physical removal devices (cyclones, barrier filters, wet scrubbers, wet electrostatic precipitators): they capture and remove also alkali salts which may be contained in the syngas. Below 600 °C alkali salts become solid particles (< 5 μm) which can be captured by filters and wet scrubbers or ESP.
2. Cracking systems: thermal or catalytic cracking.

Physical removal

Barrier filters: candle filters (ceramic or metallic) are porous solids which do not allow the passage of the finest solid particles. These particles form a layer, called FILTER CAKE which stops tar molecules. Un-condensable gases (CO, CO_2, H_2 etc.) can pass through the filter cake because of their smaller size. Fabric filters are based on the same operating principle of candle filters but can operate at lower temperatures (250 °C).

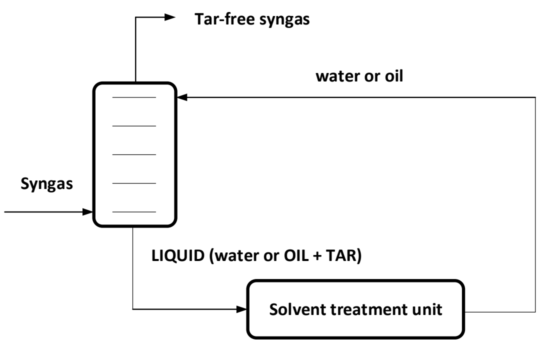


Wet electrostatic precipitators: An ESP is a particulate control device that uses electrostatic forces to move particles entrained within an exhaust stream onto collection surfaces. The entrained particles are electrostatically charged when they pass through a corona, a region where gaseous ions flow. Electrodes in the center of the flow path are maintained at high voltage and generate the electrical field that forces the particles to the collector walls.

Physical removal

Wet scrubbers: have a very high removal efficiency (ε_{TAR} ~ 90%), however they need a system to separate tars from the solvent (either water or oil).

Tar is absorbed by water because most of the molecules are polar. Scrubbers remove also NH_3, alkali, chlorides and dust.



Cracking systems

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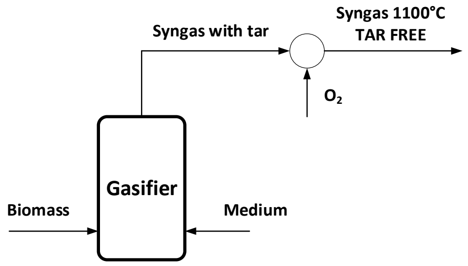
Thermal cracking consists in increasing the syngas temperature up to 1100 °C by introducing extra oxygen into the syngas downstream of the gasifier. This method is effective and cheap but it decreases the CGE.



Tar molecules are broken into smaller molecules: CO, H_2, CH_4 and H_2O. However, due to the post-combustion taking place at the injection of O_2 into the syngas, part of the fuel species (CH_4, CO, H_2) are oxidized and then the syngas LHV is decreased. As a result, the CGE of the overall gasification unit (with tar cracking system) is penalized.

Cracking systems

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Catalytic cracking consists in passing the tar rich syngas through a catalytic bed which favors the achievement of the full chemical equilibrium (it pushes the syngas composition toward chemical equilibrium, where no tar is present).

Depending on the syngas composition, the catalyst promotes the following two reactions:

$$C_nH_m + nH_2O \rightarrow (n + \frac{m}{2})H_2 + nCO \_\_\_\_\_\_ STEAM\_REFORMING\_OF\_HYDROCARBONS$$

$$C_nH_m + nCO_2 \rightarrow \frac{m}{2}H_2 + 2nCO \_\_\_\_\_\_\_\_ DRY\_REFORMING$$

These catalysts are the same adopted in the oil industry to process hydrocarbons and are commercially available. They operate at temperatures of 800 – 900 °C. Issues are due to the deactivation and attrition of the catalyst. Bio-syngas is rich of entrained solid particles and metal/alkali compounds which damage the catalyst surface reducing progressively its effectiveness.

Catalytic tar crackers convert also NH_3 into N_2 and H_2.

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Syngas applications

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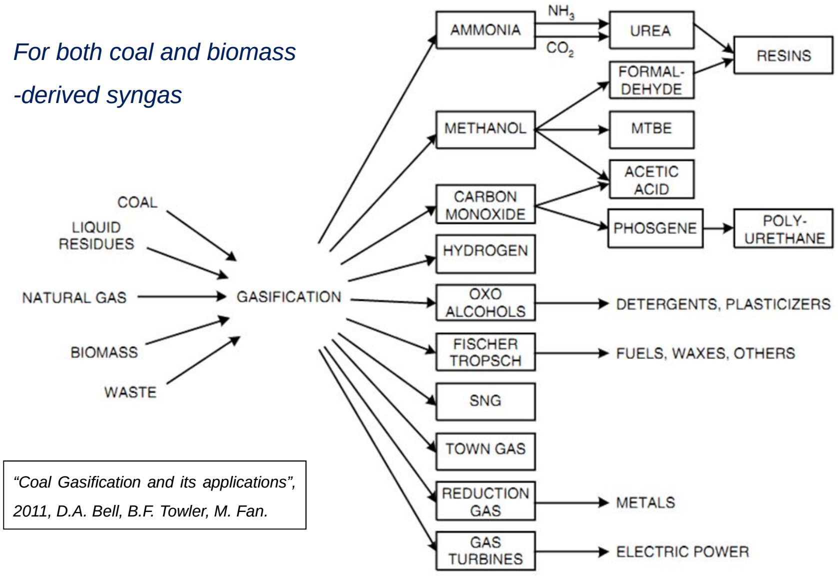
For both coal and biomass -derived syngas



"Coal Gasification and its applications", 2011, D.A. Bell, B.F. Towler, M. Fan.

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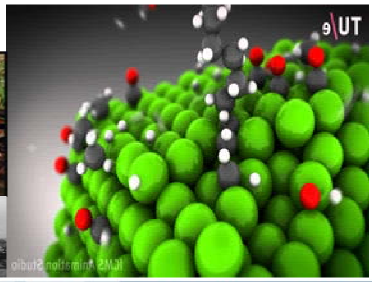
Fischer Tropsch (FT) process

History:

- Sabatien & Senderens (1902) produced a mixture of hydrocarbons
  - Not favorable at the time
  - No single product formed
  - Priority given to methanol and ammonia
- Fischer and Tropsch
  - Used base catalyst like alkalized iron and produced “synthol”
  - Temperature of about 400-450 °C @ 150 atm
  - Higher hydrogen to CO ratio produced better product
  - Tested this fluid like substance in 1922 NSU motorbike
  - Seated 2 people and outperformed the reference fuel

https://www.youtube.com/watch?v=44OU4JxEK4k



Fischer Tropsch (FT) process

Encouraging performance led to World War II fuel supply → First plant built in Germany in 1934, by 1938, 660,000 tons per-annum produced.

http://wiredspace.wits.ac.za/jspui/bitstream/10539/11587/4/Chapter%202%20-%20Literature%20review%20-%20FTS.pdf

Year	Company or companies	Technology	Production level (bpd)	Country
1955	Sasol	Sasol I	500	South Africa
1980	Sasol	Sasol II	11 000 (later 20 000)	South Africa
1982	Sasol	Sasol III	11 000 (later 20 000)	South Africa
1992	PetroSA	Sasol's slurry phase technology	20 000	South Africa
1993	Shell	Shell middle distillate synthesis (SMDS) fixed-bed technology	15 000	Malaysia
2005	Sasol and Qatar Petroleum, in alliance with Chevron	Sasol's slurry phase technology	34 000	Qatar
2007	Chevron Nigeria (Sasol/Chevron alliance) and Nigeria National Petroleum Company	Sasol's slurry phase technology	34 000	Nigeria
2009	Shell and Qatar Petroleum	Shell middle distillate synthesis (SMDS) fixed-bed technology	140 000	Qatar
2011	Exxon Mobile and Qatar Petroleum	Advanced gas conversion for the 21st century (AGC-21) technology	154 000	Qatar

Reaction step / mechanism

- Associative adsorption of CO and splitting of C/O bond
- Dissociative adsorption of 2 H_2
- Transfer of 2 H to the oxygen to give H_2O
- Desorption of H_2O
- Transfer of 2 H to the carbon to give CH_2

Alkane (paraffins) formation

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

- Favored by high H_2/CO ratio.
- Strong hydrogenating catalyst is needed.

Alkene (olefins) formation

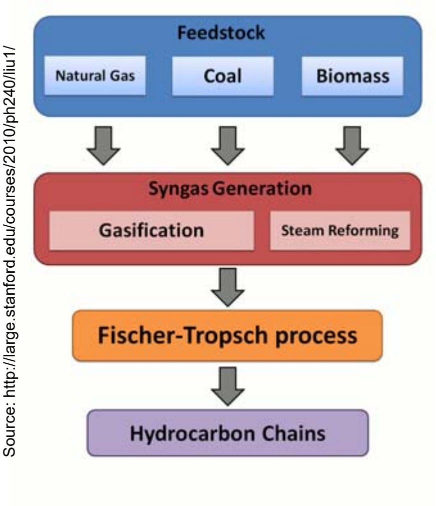
$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$$

- Favored by low H_2/CO ratio.
- Less strong hydrogenating catalyst is needed.

***Water gas shift** reaction helps adjusting H_2/CO ratio.*

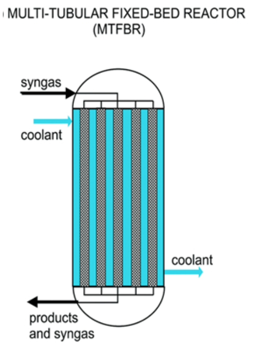
Useful products

Source: http://large.stanford.edu/courses/2010/ph240/liu1/

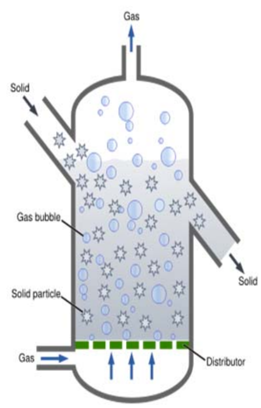


- Gas-to-liquids (GTL)
- Biomass-to-liquids (BTL)
- Coal to liquid (CTL)
- Can be used to produce
  - Diesel Fuel
    Jet Fuel
    Kerosene
  - Waxes
    Lubricants
  - Naphtha
    Gasoline
    Detergents

Technology / Reactors

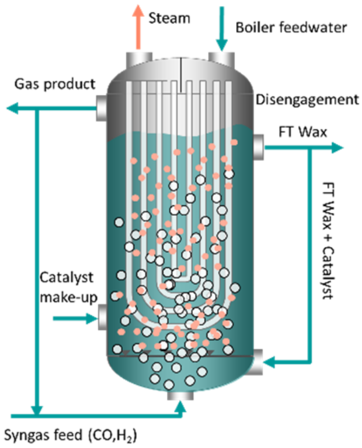


Fixed Bed Reactors
- Originally used
- Challenges associated with removal of heat



Source: http://www.altenergymag.com/emagazine/2014/02/india-sustainable-communities-proposal/2216
http://pubs.rsc.org/en/content/articlelanding/2015/cy/c4cy01547a#!divAbstract

Fluidized Bed Reactors
- Better temperature control
- High yields for Gasoline and light products



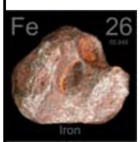
Slurry Reactors

- Small catalyst particles suspended in a liquid with low vapor pressure
- Low Temperature
- Flexible design
- High yield for waxes

Source: http://www.altenergymag.com/emagazine/2014/02/india-sustainable-communities-proposal/2216

Based on Transition Metals:

- Iron (Fe)



  - Low Cost
  - Higher Water Gas Shift activity
  - Suitable for lower syngas (H_2/CO)
- Cobalt (Co)

  - More Active
  - Less Water Gas Shift activity
  - Higher Cost
- Nickel (Ni)

  - Promotes Methane formation
  - Generally not desired
- Ruthenium (Ru)

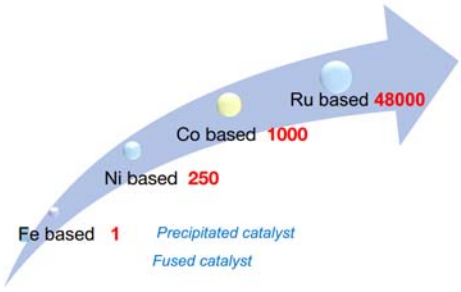
  - High molecular weight Hydrocarbons
  - High Cost
  - Not generally used

Source:http://periodictable.com/Elements/027/

Promoters / Cost

- Fe-based catalysts
  - promoted with Alkali metals
  - to obtain high basicity, and to stabilize catalyst
  - higher alkali level higher the shift to longer chains
  - addition of copper: enhances reducibility
- Co Based Catalysts
  - promoted with small amounts of noble metals
  - reduces temperature/pressure
  - yields less olefins and oxygenated products

Possible catalyst cost basis



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DME – DiMethyl Ether & Methanol

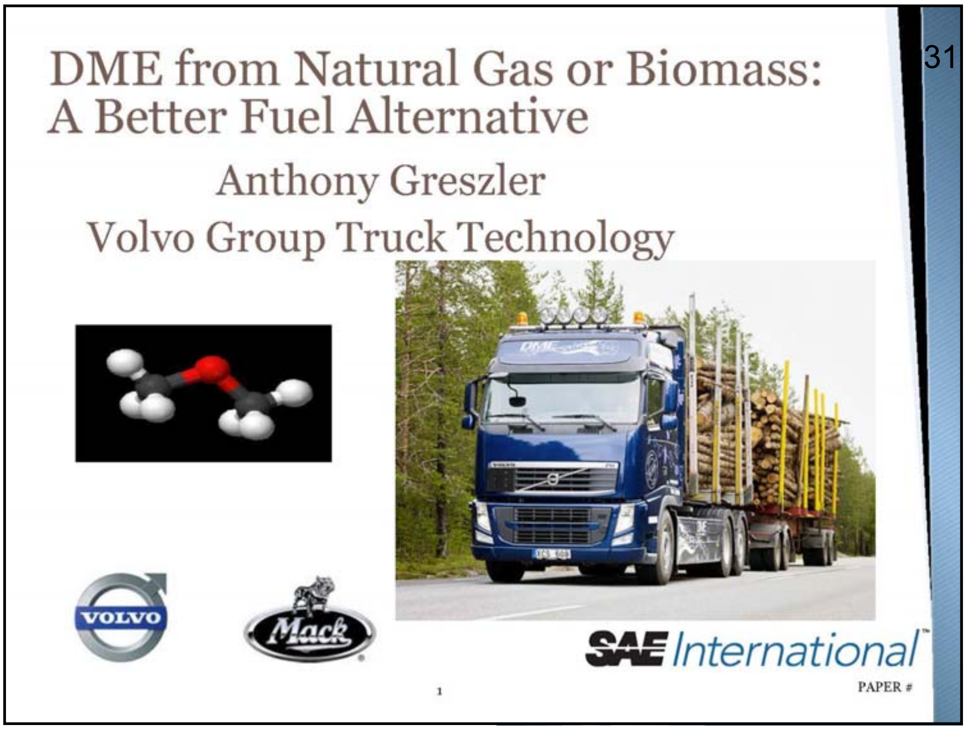
- DME – DiMethyl Ether – CH_3OCH_3
  - Substitute of LPG
  - Fuel for gas turbines
  - Fuel for Diesel engines
  - Properties:

MM, kg/kmol	46.07	Explosion limit, % in air	3.4~17
Boiling point, °C	-24.9	Ignition temperature, °C	235
Melting point, °C	-138.5	Vaporization heat, kJ/kg	410 (-20°C)
Vapor pressure, MPa	0.51（20 °C)	LHV, MJ/kg	28.4
Critical temperature, °C	127 °C	Flash point, °C	-41
Critical pressure, MPa	5.37	Liquid density kg/m^3	668 (20 °C)

- Methanol CH_3OH
  - Substitute of gasoline

DME – DiMethyl Ether & Methanol

	DME	Diesel	Propane	Butane	Methanol
Formula	CH_3OCH_3	$CH_{1.83}$	C_3H_8	C_4H_{10}	CH_3OH
MM, kg/kmol	46.07	190~220	44.11	58.13	32.01
Boiling point, °C	-24.9	180~360	-42	-0.5	65
Vapour pressure, bar	5.1		8.4	2.1	0.32
Liquid density, kg/m^3	668	840	501	610	790
Liquid viscosity x 10^4, Pa*s	0.15	5.35~6.28	0.10	0.18	0.768
LHV, MJ/kg	28.43	42.5	46.36	45.74	19.5
Cetane number	55~60	40~55	Octane number →		112
Vaporization heat, kJ/kg	410	250	370	358	1110
C, % by mass	52.2	86.7	81.8	82.8	37.5
O, % by mass	34.8	0	0.0	0.0	50.0
H, % by mass	13.0	13.3	18.2	17.2	12.5
g of CO_2 per MJ of LHV	67.3	74.2	64.7	66.4	70.5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DME from Natural Gas or Biomass:
A Better Fuel Alternative
Anthony Greszler
Volvo Group Truck Technology
VOLVO
Mack
SAE International
PAPER #
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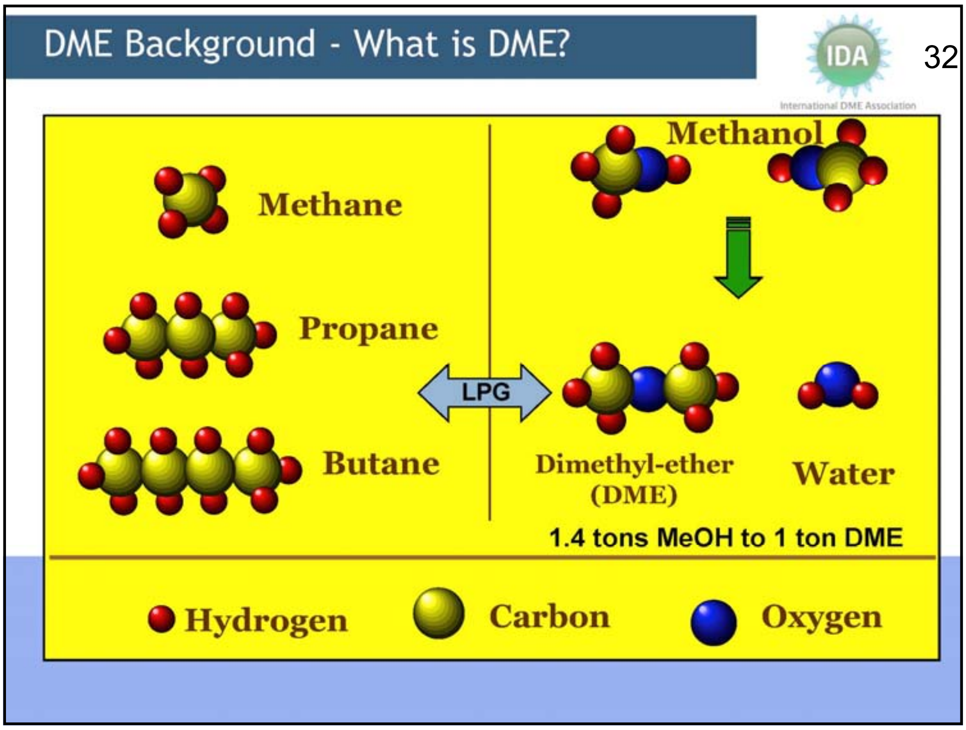
DME Background - What is DME?
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IDA
International DME Association
Methane
Propane
Butane
LPG
Methanol
Dimethyl-ether
(DME)
Water
1.4 tons MeOH to 1 ton DME
Hydrogen
Carbon
Oxygen

DME - WHY?

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- **Excellent diesel cycle fuel (high cetane)**
- **Easy to store and transport (liquefies at low pressure & no venting)**
- **Clean (near zero soot) combustion (no DPF)**
- **Cost Effective**
- **High well-to-wheel efficiency**
- **Low Global Warming Potential**
  - GWP = 1.2 @ 20 yr; .3 @100 yr
- **Synthesis from variety bio based feedstocks**
  - High biomass to fuel conversion efficiency
- **Synthesis from natural gas**
- **Power density for long-haul**
- **Non toxic**

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Demonstration Project- 10 Trucks, 1M km

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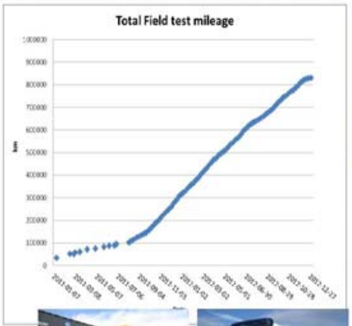

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Fuel distribution

- Available technology modified for DME
- Safety regulations based on LPG
- Low cost, ~200 k€ per filling station
- Easy to achieve

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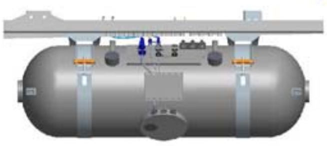
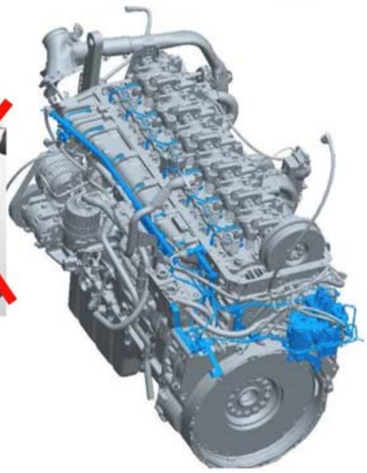
DME Vehicle technology





- Diesel base engine unchanged
- Diesel cycle efficiency preserved
- New fuel system
- No soot → no DPF
- NOx control possible via SCR or heavy EGR
- Modified engine control software
- DME compatible materials where needed

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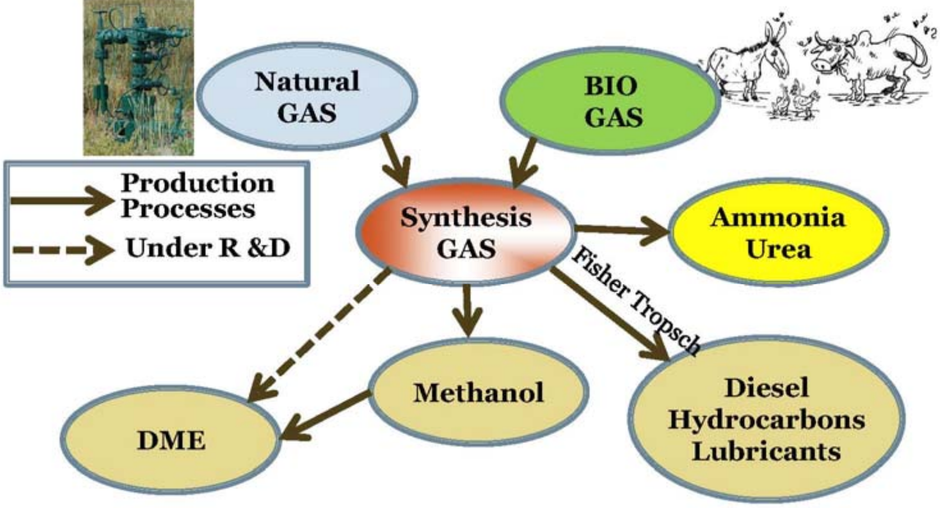
Natural/Bio Gas Thermo-Chemical Conversion 37



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Why Convert NG to DME? 38

Vehicle
- Low cost fuel tanks
- No DPF
- Longer driving range
- Potentially lower cost than diesel vehicle at high volume

Distribution Infrastructure
- No high pressure gas or cryogenic liquid
- Low cost, stable, long-term storage (no boil-off)
- Low cost fueling stations (like LPG)
- Transportation via low-cost tankers
- Potential for smaller, affordable production plants near feedstock and/or users

Total Operating Coast
- Diesel cycle fuel efficiency (potentially better than diesel)
- Fuel cost potential less than diesel (NG or biogas feedstock)

Environment
- No smoke
- Low Global Warming Potential <u>and</u> No boil-off
- Petroleum use reduction

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Actions Needed to Move Forward 39

Engine Development
- Combustion optimization
- Emission development and certification
- Component refinement and cost
- Reliability and durability demonstration

Fuel Infrastructure
- Fuel certification
- Infrastructure build out starting with dedicated and regional fleets
- Process refinement: efficiency & cost

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DME Summary 40

- Excellent environmental properties
- Energy efficient
- Cost efficient
- Global potential for diesel replacement (gasification of biomass or NG)
- Technology demonstrated
- Energy carrier for the future

The time is right and the opportunity is here!

Thank you!

VOLVO Mack SAE International

6th Asian DME Conference, Seoul, Korea (September 17-18, 2009)

DME Production Process

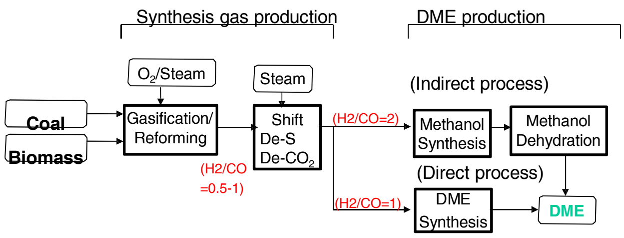
from Coal & Biomass

Yotaro Ohno

JFE Techno-Research Corporation

DME production from Coal & Biomass

- Coal resource is relatively abundant, but limited for growing future use.
- Biomass resources is abundant and renewable, and carbon neutral, but, dispersed and bulky, inadequate for long distance transportation.
- Efficient conversion into DME is important to secure resource and control CO_2 emission.



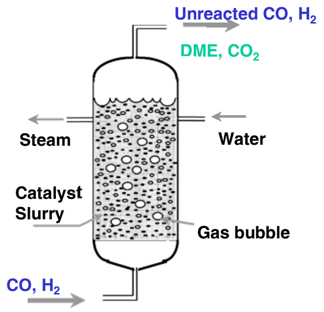
Characteristics of JFE DME Synthesis Process

• DME (CH_3OCH_3) is synthesized from H_2/CO=1.0 synthesis gas.

This reaction is highly exothermic, rather than Methanol synthesis, reaction temperature control is important to avoid catalyst degradation.

•Slurry Phase Reactor, in which Temperature is homogeneous. Reactor temperature can be controlled to the optimum point by steam pressure.

•JFE's proprietary catalyst system is adequate to slurry phase reaction.



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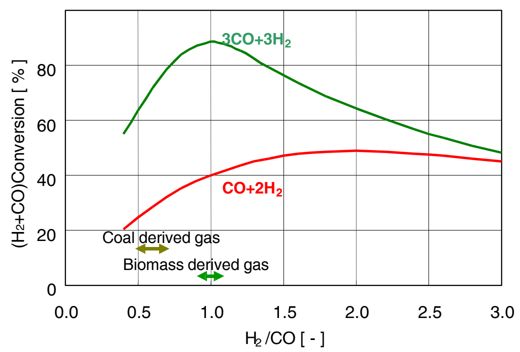
Equilibrium Conversion (260ºC, 5MPa)

• DME synthesis is, having the maximum conversion at H_2/CO=1.0, advantageous to synthesis gas from Coal (H_2/CO=0.5-0.7) or Biomass



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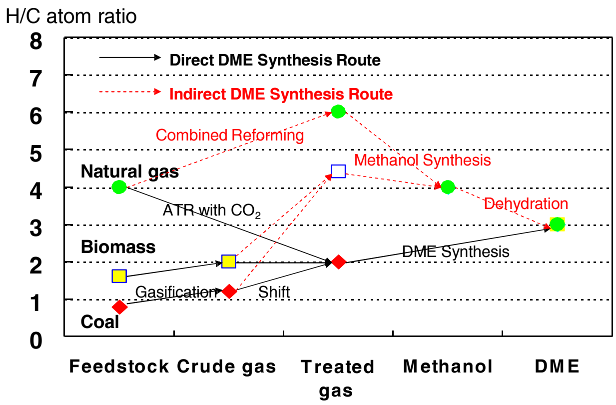
H/C Change on Process Route from Feedstock to DME

•On Direct DME synthesis route, H/C change is smaller and Process efficiency is higher, especially starting from Coal and Biomass.



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Coal Quality for Gasification

• Coal is classified by VM content : 65-7% (H/C: 1.2-0.5)

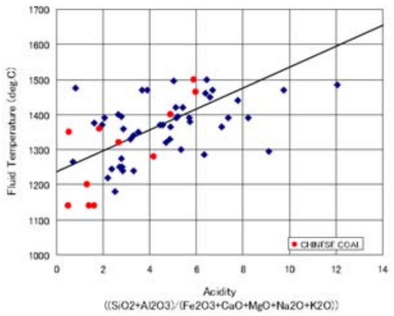
Lignite, Sub-bituminous, Bituminous and Anthracite

Proximate analysis (air-dried%) : VM,FC, Ash, Moisture

Ultimate analysis (dry%) : C, H, N, O, S, Others

•Heating value HHV(MJ/kg) estimated using Ultimate analysis
HHV =0.339C+1.433(H-O/8)+0.094S
HHV decreases with higher content of Ash, Moisture

• Fluid temperature of Ash Tf (ºC) correlated with Acidity of Ash
Tf can be changed by Adding flux materials; Lime stone (CaO), Iron Oxide (Fe_2O_3), or by Mixing with low Tf coal.



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Coal Gasification Process

- Gasification Temperature should be sufficiently high to minimize residual CH_4 and tar and for stable slag discharge.

  Entrain bed (Pulverized coal) is suitable, rather than Fixed bed or Fluidized bed (Lump coal).
- Coal feed type to pressurized gasifier

  Dry feed is better than Slurry feed for higher gasification efficiency.
- Inert gas(CH_4,N_2) content in synthesis gas should be minimum for higher efficiency in down stream synthesis.

  O_2 concentration should be as high as possible.

  Dry CO_2 is used as carrier gas in place of N_2.
- Large scale coal gasifier such as 2000 ton/day is already available, equivalent to 1,000 ton/day of DME production.

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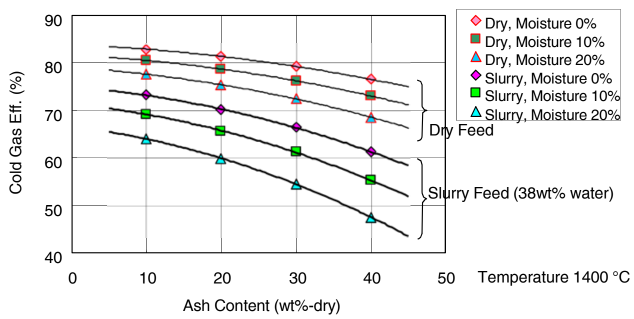
Cold Gas Efficiency (CGE) of gasification

- High ash content, high moisture give lower CGE.
- Dry feed gives higher CGE by 10–20 % than Slurry feed for the same ash content and moisture.



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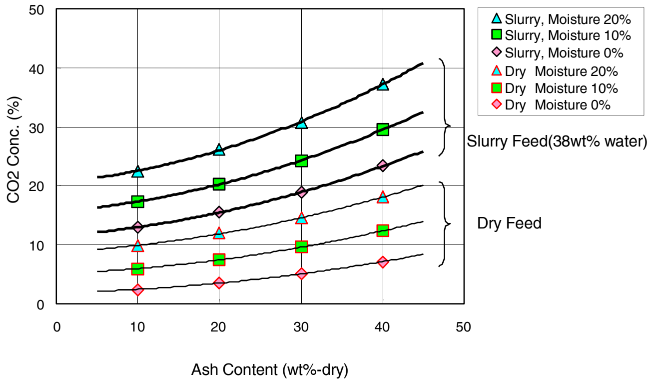
CO_2 Concentration in raw syngas

- Higher CO_2 concentration in synthesis gas results in more CO_2 removal and less efficient process.



Synthesis Gas Preparation

- Removal of catalyst poisoning impurities

H_2S,COS,NH_3,HCN,etc

Required level is thesame for Methanol synthesis and DME synthesis.

- Adjustment of H_2/CO to stoichiometric ratio

H_2/CO=2 for Methanol synthesis, H_2/CO=1 for DME synthesis

by Shift reaction

Heating value of synthesis gas decreases with Shift reaction

as it is exothermic. Steam is required as reactant for shift reaction.

- Removal of CO_2

CO_2 is removed by solvent absorption.

A part of H_2 and CO is absorbed by solvent and lost with CO_2.

Steam is required to regenerate absorbent of CO_2.

Effect of CO_2 on Methanol and DME synthesis

Methanol synthesis in the fixed bed reactor

•For Methanol synthesis, $R=(H_2-CO_2)/(CO+CO_2)=2$ should be satisfied.

In coal derived gas, no excess H_2. CO_2 consumes H_2 and gives water, methanol production decreases and distillation load increases.

• CO_2 content at reactor inlet must be as low as possible.

DME synthesis in the slurry phase reactor

•Slurry is saturated with CO_2 generated by DME synthesis reaction and CO_2 in synthesis gas has little effect on DME synthesis.

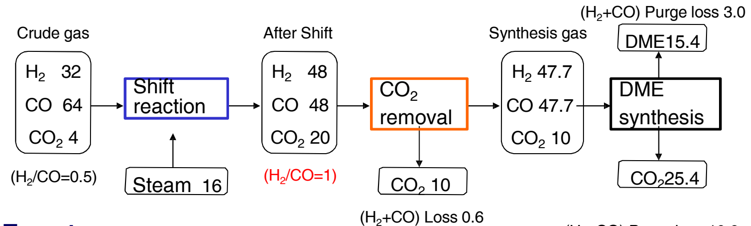
•Partial CO_2 removal is sufficient and Energy consumption for CO_2 removal is smaller.

• Residual CO_2 goes out of reactor with by-produced CO_2.

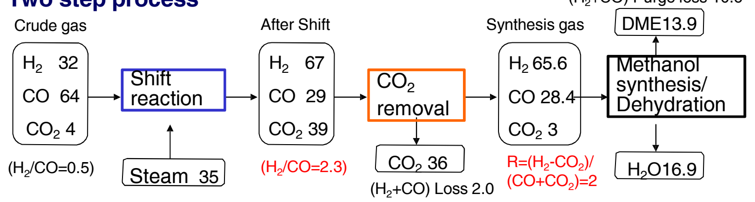
Comparison of Material balance of DME production

JFE process (Unit: kmol)

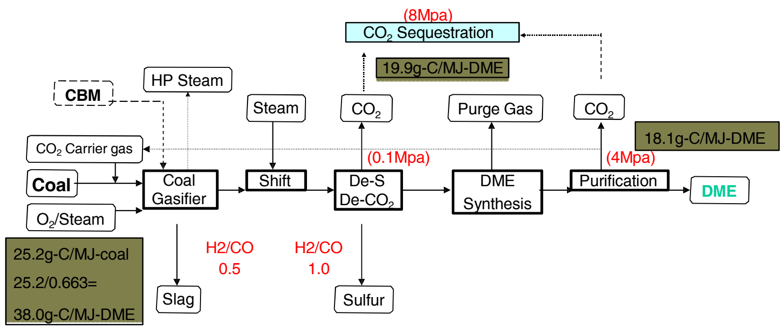
DME production is 10% more than Two step process.



Two step process



Total System of DME Production from Coal



: CO2 Emission , Cold gas efficiency from Coal to DME : 66.3%

Coal consumption: 1.5 dry-t/t-DME, Oxygen consumption: 1.2 t/t-DME

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Total Cold Gas Efficiency of DME Production

- Total Cold gas efficiency of Dry feed/JFE process is 20% higher than Conventional process(Slurry feed/Two step).

Gasification/Synthesis	Dry feed/ JFE process	Dry feed/ Two step	Slurry feed/ Two step
Cold gas efficiency of gasification	83.3%	83.3%	76.9%
Cold gas efficiency from coal to synthesis gas	81.2%	78.3%	73.2%
Cold gas efficiency from synthesis gas to DME	81.7%	74.9% (78X0.96)*	74.9% (78X0.96)*
Total cold gas efficiency	66.3%	58.6%	54.8%
CO2 emission at plant site (g-C/MJ-DME)	19.9	24.9	27.9

* Assumption of Cold gas efficiency for Methanol synthesis: 78% and for Dehydration: 96%

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Characteristics of Biomass as Feedstock

•Terrestrial biomass actually used are of so many kinds, but non-edible aspect is very important.

Wood chip, Bark, Saw dust, Switch grass, Bermuda grass, Agricultural residues such as Rice husk, Bagasse, Cotton stalks, Corn stalks, Coconut shell

•Size and shape is various. Pulverizing biomass is not so easy as coal, biomass is generally used as sized lump. Biomass feeding technology should be adapted to specific feedstock.

• Chemical composition(dry%) is almost same:

C 45-50%, H 5-6%, O 44%, H/C(atom ratio)=1.6

Ash content is small 1%(wood)-10%(grass).

Moisture content is high 20-70%.

• Heating value HHV(MJ/dry-kg)=0.457C(dry%)-2.70

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Biomass Gasification Process-1

•Most of the gasification is conducted by Partial combustion with oxygen/air. With higher O_2 content, N_2 content in produced gas is lower.

Fixed bed (down-draft or up-draft), Circulating fluidized bed,

Fluidized bed with fluidizing media, Entrained bed

•The other type of gasification is Steam reforming in fluidized bed with indirect heating by circulating solid media or external heater.

•As sticking of fed materials and slagging of ash often happen at high temperature, Gasification temperature is relatively low at around 850 ºC and produced gas contains CH_4 and Tar.

•For stable operation of down-stream process, Tar should be removed, or reformed together with CH_4 by secondary reforming into H_2 and CO.

•Biomass contains more oxygen than Coal, CO_2 content in synthesis gas is higher.

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Biomass Gasification Process-2

•Sulfur content of biomass is very low, but crude gas from biomass contains around 10ppm of H_2S+COS, which is tolerable as fuel gas, but should be removed as synthesis gas to avoid catalyst degradation in down stream process.

• Ash is discharged as dry ash by mechanical device.

•So many types of Biomass gasifiers have been developed for fuel gas of power generation, but few for synthesis gas.

Reliable gasifier is the key for synthetic fuel production from biomass.

•Biomass gasification scale is small because of high cost of long distance transportation: Maximum scale could be of several 100 ton/day.

•With coal/biomass mixture feed, coal may compensate instability of biomass supply and increase thermal efficiency because plant scale can be bigger with it. Reactivity of coal is important.

Example of Biomass Gasifier 1
IISc Fixed Bed Gasifier (Down-draft)

•40 units of IISc' Gasifier are used mainly in India for power generation fuel gas, Maximum scale around 1200kWe (30 ton/day).

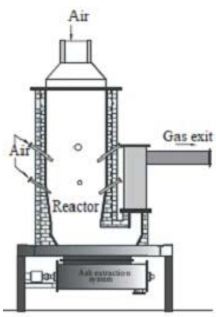
Gas composition(dry%) with Air blowing: H_2 20%,CO 20%, CH_4 4%, CO_2 8%,N_2 48%

For synthesis gas production, N2 content should be reduced.

•AIST, Japan has conducted pilot test of similar type of gasifier. (0.1 ton/day)

With O_2 in blow increasing from 21 to 31.5%, N_2 in syngas decreases from 47 to 32% and Carbon conversion rises from 92 to 96%.

With syngas, bench scale tests were conducted for DME synthesis and FT synthesis. (www.aist.go.jp)



Ref: Technology of Biomass Gasification(IISc)

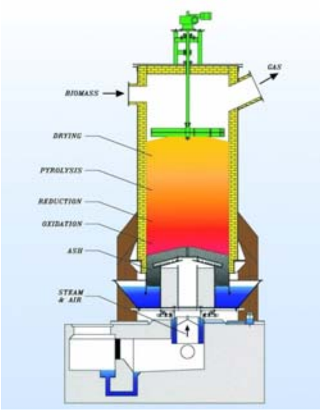
Example of Biomass Gasifier 2
Volund Fixed Bed Gasifier (Up-draft)

•Development had started in 1989 and a commercial plant of 41ton/day has been built in 1996 in Harboore in Denmark. Gas cleaning system has been improved until 2003.

Typical gas composition with Air/steam blowing: H_2 19.0, CO 22.8, CH_4 5.3, CO_2 11.9, N_2 40.7%.

Gas is used for gas engine power generation or boiler fuel. Power generation efficiency attains to 29%.

•JFE(Exclusive licensee in Asia) has constructed three commercial plant (60-100ton/day) in Japan.



Ref: www.volund.dk

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Example of Biomass Gasifier 3
VVBGC Pressurized Circulating fluidized bed

(VVBGC: Växjö Värnamo Biomass Gasification Center)

•Air blowing test conducted as IGCC system successfully for 8500 hours in 1994-2000 in Värnamo, Sweden.

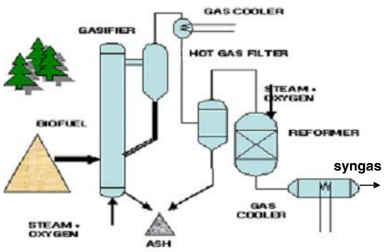
100ton-Ds/day,pressure:20 bar

•CHRISGAS Project (2005-)

(Clean Hydrogen Rich Gas)

Revamp of plant and hot test were completed in 2007.

Modification to Oxygen blowing with Secondary reforming of tar methane will start in 2009.



Ref: www.vvbgc.se

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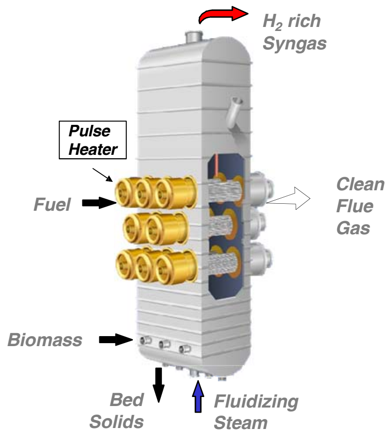
Example of Biomass Gasifier 4

TRI Steam Reformer with External Pulse Heater

- •Commercialized for Black liquor(115 ton/day) in Canada
- •Proprietary indirectly-heated steam reforming process at medium temperature and low pressure
- •Black liquor is gasified with high temperature steam in deep fluidized bed.
- Chemicals in black liquor become small particles, which are bed solids, and discharged at bottom.
- •Application to Solid (Wood chip, Rice hull, Saw dust,etc.) under Pilot test

Black liquor composition (%):

C 36.8, H 3.7, N 0.1, S 3.1, O 10.6, Ash (Na, K, Cl,etc.) 45.8



By courtesy of TRI (www.tri-inc.net)

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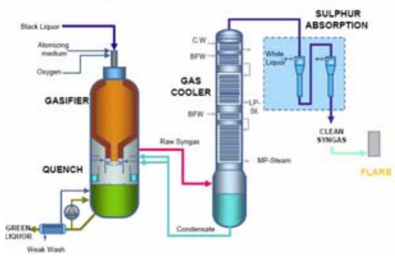
Example of Biomass Gasifier 5

Chemrec Black liquor entrained bed gasifier

•Similar to GE coal/heavy residue gasifier. Black liquor is gasified at high temperature with oxygen and produce synthesis gas without tar.

•Chemicals in black liquor is solved in quench water and recovered as green liquor.

- •Pilot plant(20ton-Ds/day) has been now operated successfully for 9,900 hours in Sweden since 2005.
- •DME pilot plant(4-5ton/day) is under construction and will start in2010.
- •DME will be supplied to Volvo truck test.



Ref: www.chemrec.se

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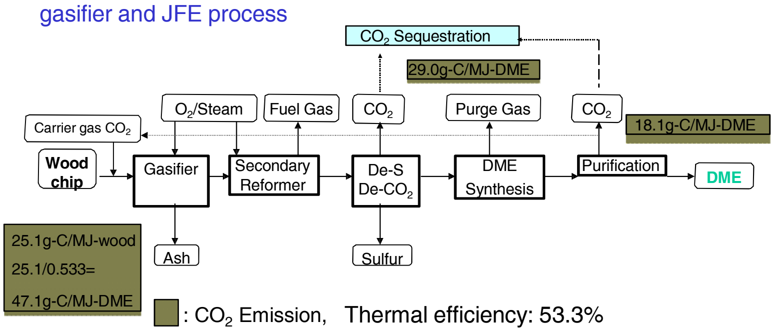
DME production from Biomass (Wood chip)

•DME production system of Oxygen blowing Pressurized CFB gasifier and JFE process



: CO_2 Emission, Thermal efficiency: 53.3%

•Unit consumption: Wood chip 3.0t-Ds/t-DME, Oxygen 1.5 t/t-DME

•Purge gas and a part of synthesis gas are used as fuel gas in DME production system.

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Synthesis gas composition and Cold gas efficiency

•Raw gas contains CH_4 and tar, which is reformed with O_2 and steam in Secondary reformer. H_2S and a part of CO_2 are removed.

Conc.(%)	Raw gas	Reformed gas	Synthesis gas
H_2	10-15	23.2	47.0
CO	10-15	22.8	46.0
CO_2	20-25	19.5	6.5
N_2		0.20	0.4
CH_4	10-12	0.05	0.1
Tar	2-5	0	0
H_2O	40	34.25	0
H_2S		10ppm	<0.1ppm

•Cold efficiency: 73% from Wood chip to Clean synthesis gas, 59.1% for Total system, Thermal efficiency including fuel gas: 53.3%

•Wood chip composition(dry-wt%): C 50.0, H 6.0, O 42.0,N 0.3, S 0.025, Ash 1.7, LHV 18.9MJ/dry-kg, Moisture(after dryer) 15.0%

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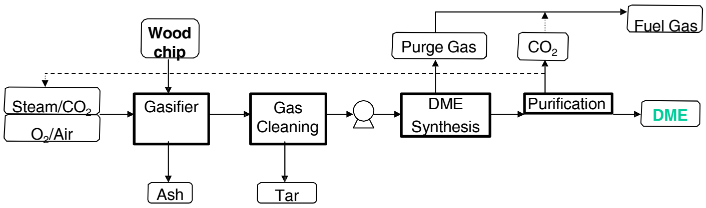
DME production with O_2 enriched air

•Small scale DME production system of Down-draft Fixed bed gasifier with O_2 enriched air and JFE process



•Steam/CO_2 is added to keep gas temperature in front of blowing nozzle.

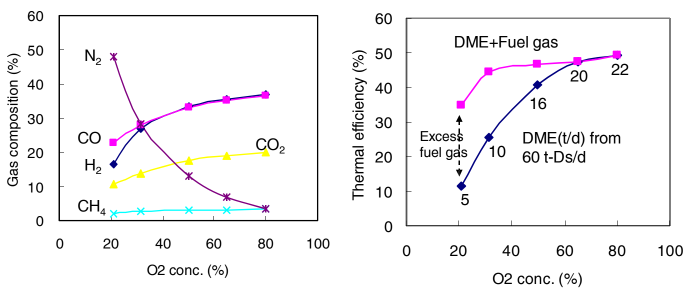
•Gasifier is operated at ambient pressure, after gas cleaning, synthesis gas is compressed to synthesis pressure.

• All utilities in this system are supplied by fuel gas and recovery heat.

Oxygen enrichment and DME production

•N_2 content in synthesis gas goes down with O_2 content in Air+O_2. H_2/CO is controlled with recycled CO_2.

•Over O_2= 50%, Thermal efficiency of DME production exceeds 40% and DME production gets closer to a full oxygen operation level.



Conclusions

- Coal preparations such as Coal washing, Drying, Control of Ash fluid temperature is recommended to improve Gasification efficiency.
- With Dry feed, Cold gas efficiency of gasification is better than with slurry feed.
- O_2 of high purity and Dry CO_2 as carrier gas should be used to minimize inert content in synthesis gas.
- Total Cold gas efficiency of Dry feed/JFE process is 20% higher than Conventional process (Slurry feed/Two step).
- Biomass gasification process for synthesis gas should be developed more intensively to realize Feasible Biomass to DME and Secondary reforming is important to reduce tar and methane.
- For small scale DME production from biomass, oxygen enrichment blowing could be practical for less equipment cost and relatively high DME production capacity.

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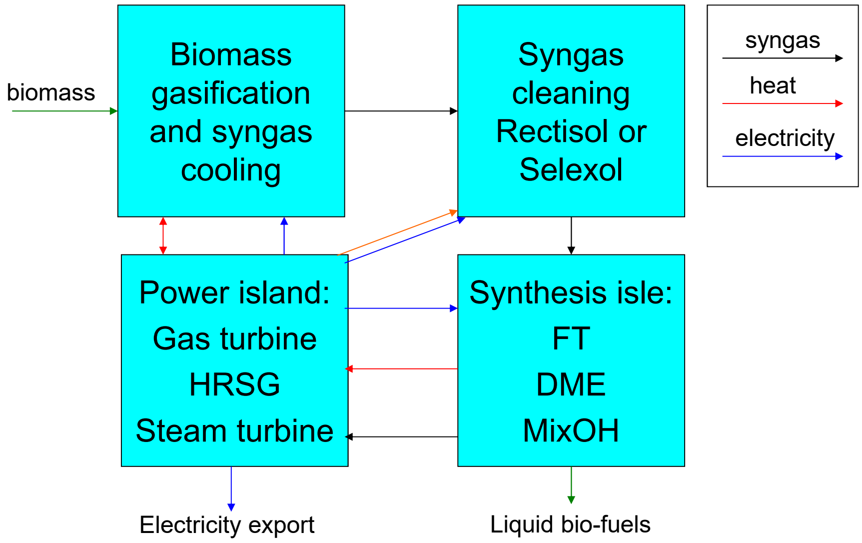
Lecture outline

- *The biorefinery concept*
- *Syngas cleaning*
  - *Tar removal*
- *Syngas applications*
  - *FT (Fisher-Tropsch) process*
  - *DME (DiMethyl Ether) process*
- *Examples of integrated bio-refineries*
  - *Production of FT*
  - *Production of DME*
  - *Production of MixOH*

Examples of integrated bio-refineries



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  - *Production of MixOH*

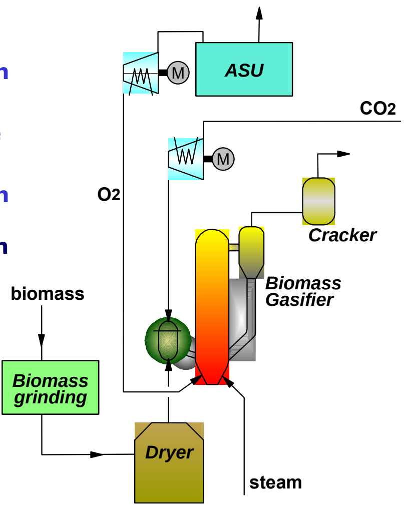
Production of FT → gasifier

Selection of gasification process:
- Fuel = biomass
- Large-scale plant
- High "Cold Gas Efficiency"
- Stringent constraints on syngas dilution

Selection of feeding system:
- Flexibility with respect to biomass type
- Gasification pressure > 30 bar
- Stringent constraints on syngas dilution

A circulating fluidized-bed gasifier has been selected:

- Operating temperature: 950 °C
- Pressure: 37 bar
- Steam flowrate: 25% of dried biomass
- O_2 flowrate: ~38% of dried biomass
- Feeding system: CO_2 lock-hoppers



Production of FT → Technologies adopted

- **Pre-treatment unit:**
  - Drying from 50 wt% to 20 wt% moisture
  - Milling to 5 mm, with 15 kWe/MW_{LHV} consumption
- **Gasifier**
- **Catalytic (Ni) cracking of tar:**
  - Complete conversion of tar
  - Complete conversion of NH_3 ($2\ NH_3 \rightarrow 2\ N_2 + 3\ H_2$)
  - 1 wt% of CH_4 in treated syngas
- **Full quench cooling**
- **Rectisol for syngas purification**
- **Gas turbine (GE6FA) to valorise unconverted syngas**
- **3-level heat recovery steam cycle with water cooled condenser**

Production of FT → Syngas cooling

Syngas must be cooled down to ambient temperature for the Rectisol purification.

Syngas cooling takes place in two steps:

1) Water quench (950°C → 210°C) + possible scrubber

- Removal of entrained particulate
- Removal of water-soluble compounds (HCN, chlorides and alkali)
- Removal of possible condensed tar

2) Thermal recovery (210°C → 35°C, with Fe catalyst; 410°C → 35°C with Co catalyst)

- Superheating of LP steam
- Evaporation of LP steam
- Preheating of LP feedwater
- Evaporation of HP steam
- Preheating of IP and HP steam
- Evaporation of IP steam

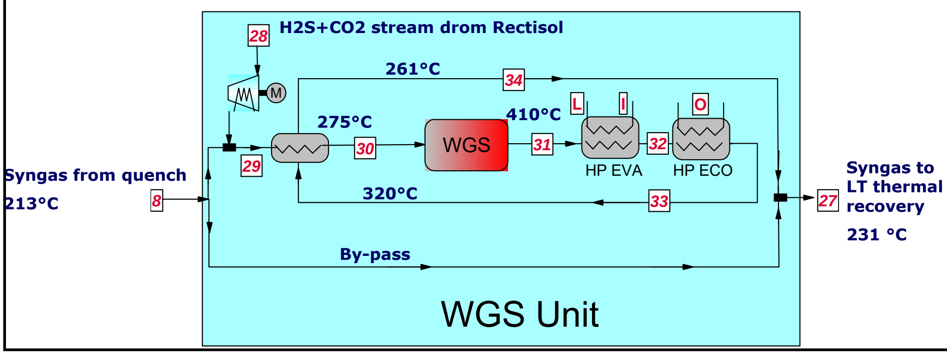
Production of FT → WGS (with Co catalyst)

H_2/CO ratio in syngas from biomass gasification is circa one. FT Co-based catalyst requires H_2/CO ratio equal to 2. A WGS (Water-Gas-Shift) unit is required to change syngas composition.

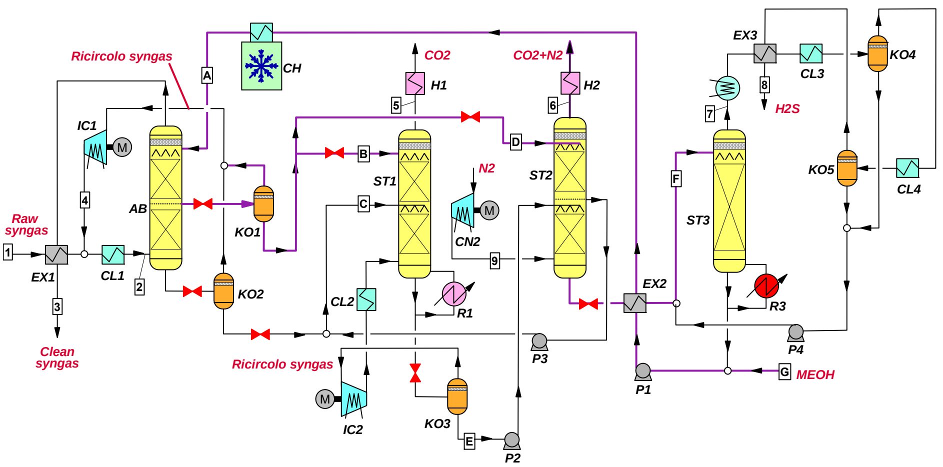
Specs for acidic CoMoS catalyst:

- Range of operating temperature = 250°C – 500°C
- Concentration of H_2S ≥ 300 ppm

Since biomass syngas contains about 100 ppm of H_2S, an H_2S-rich stream is recirculated from the Rectisol unit to upstream of WGS reactor.



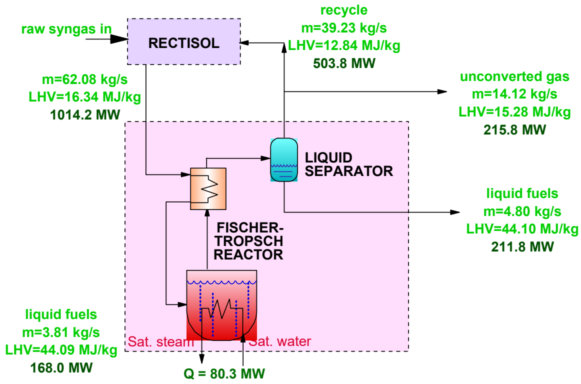
Production of FT → Rectisol unit



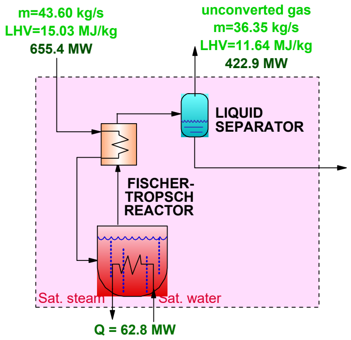
Sulphur removal: down to 0.1 ppmv for the Fe catalyst, and down to 4 ppbwt for the Co catalyst

Production of FT → Fe catalyst synthesis island

Case with recirculation

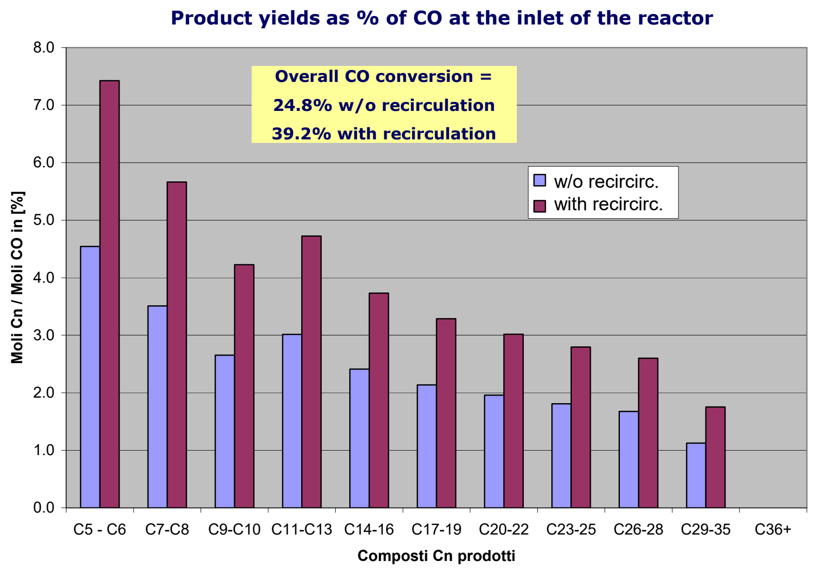


Case w/o recirculation (i.e. once-through)

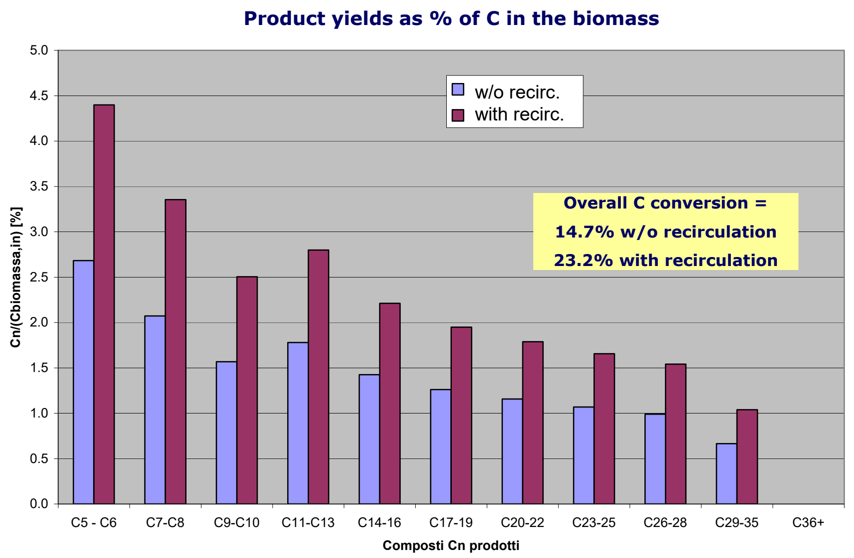


As in the case of Co catalyst, heat is made available at 230°C (→ production of steam at 28 bar).

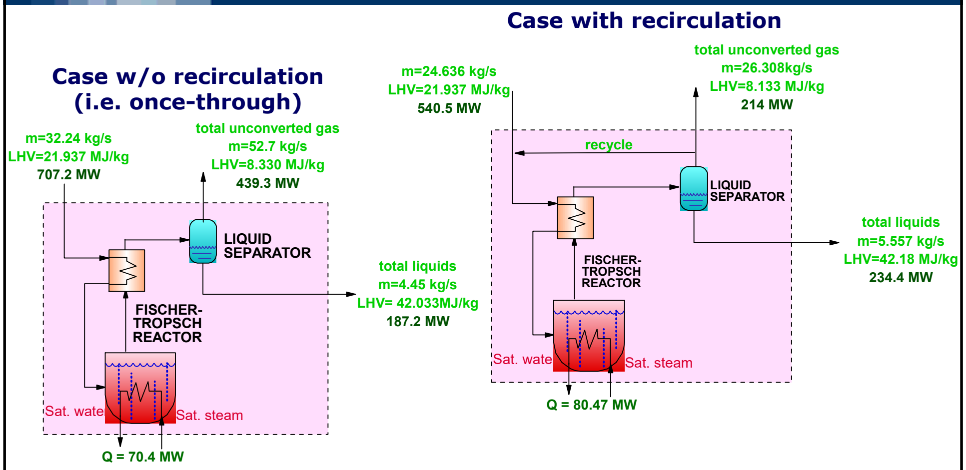
Production of FT → Fe catalyst yields



Production of FT → Fe catalyst yields



Production of FT → Co catalyst synthesis island

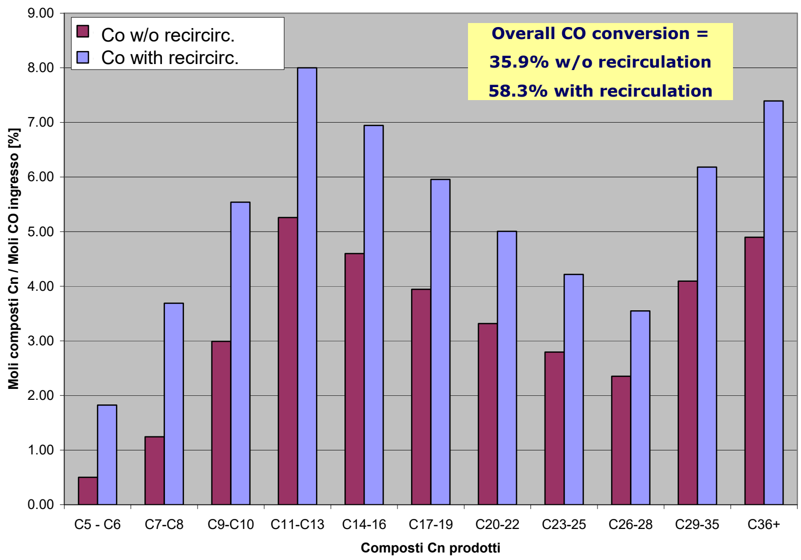


As in the case of Fe catalyst, heat is made available at 230°C (→ production of steam at 28 bar).

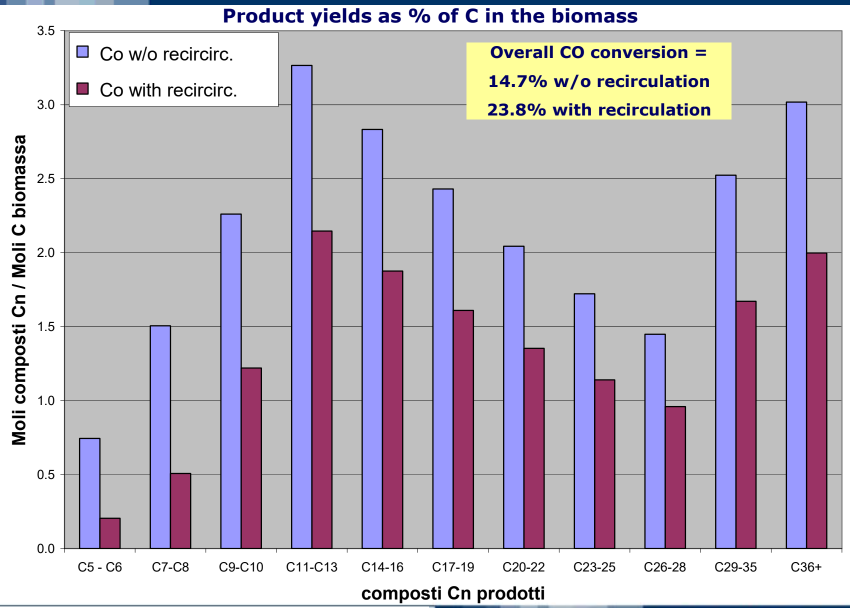
Unconverted gases and vapours are compressed to 20.5 bar, diluted with CO_2 (form the Rectisol unit), saturated and used as gas turbine fuel.

Production of FT → Co catalyst yields

Product yields as % of CO at the inlet of the reactor



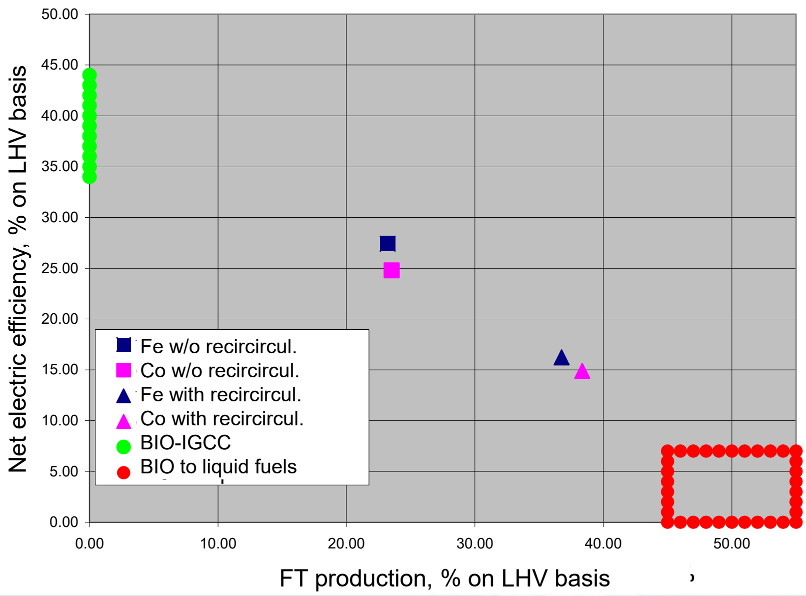
Production of FT → Co catalyst yields



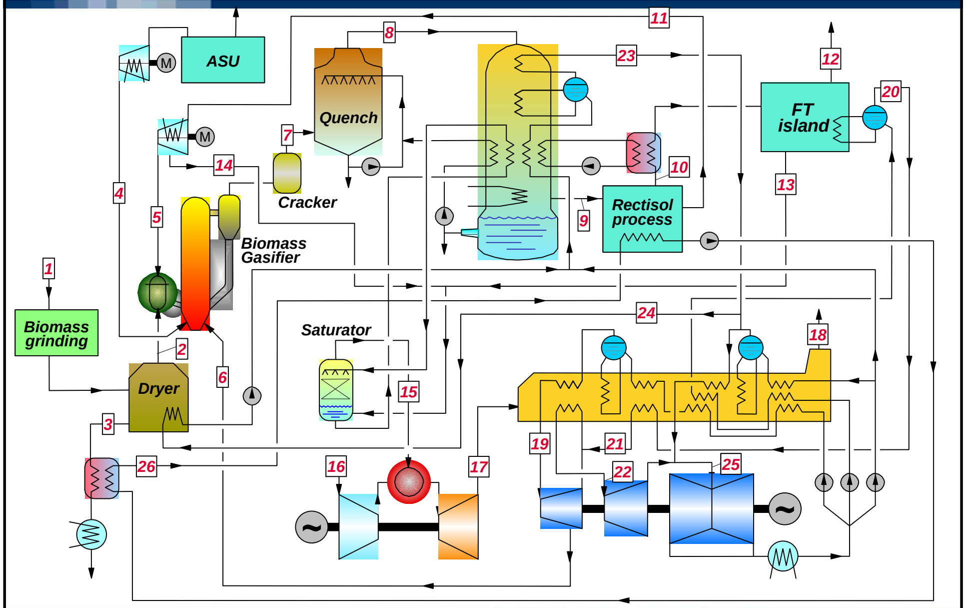
Production of FT → Summary of considered cases

	Fe catalyst	Co catalyst
W/o recirc.	2 GTs GE6FA Biomass: 89.30 kg/s Th. input: 724 MW (PCI) Production FT: 2372 bbl/day 168 MW Net electric power: 199 MW	2 GTs GE6FA Biomass: 98.17 kg/s Th. input: 796 MW (PCI) Production FT: 2644 bbl/day 187 MW Net electric power: 197 MW
With recirc.	1 GT GE6FA Biomass: 71.10 kg/s Th. input: 577 MW (PCI) Production FT: 2992 bbl/day 212 MW Net electric power: 94 MW	1 GT GE6FA Biomass: 75.35 kg/s Th. input: 611 MW (PCI) Production FT: 3310 bbl/day 234 MW Net electric power: 91 MW

Production of FT → Summary of considered cases



Production of FT → Fe catalyst w/o recirculation



Production of FT → Co catalyst w/o recirculation

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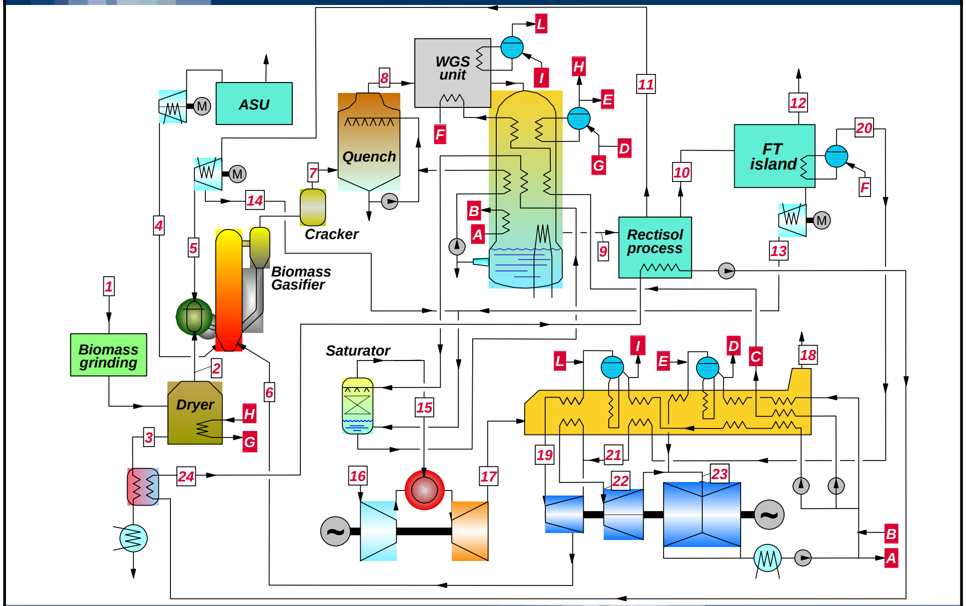

F. Viganò

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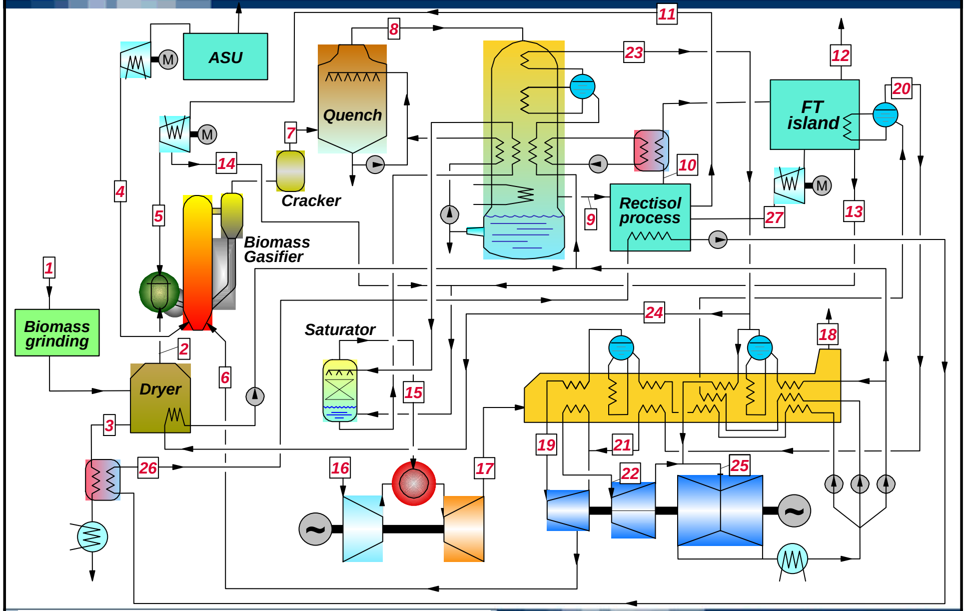
Production of FT → Fe catalyst with recirculation

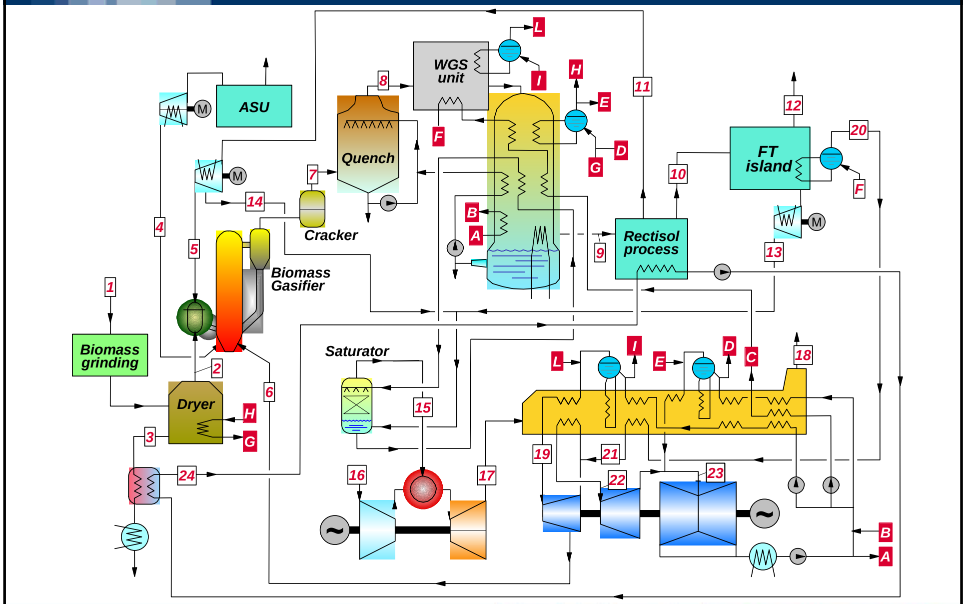
86



F. Viganò

POLITECNICO DI MILANO

Production of FT → Co catalyst with recirculation



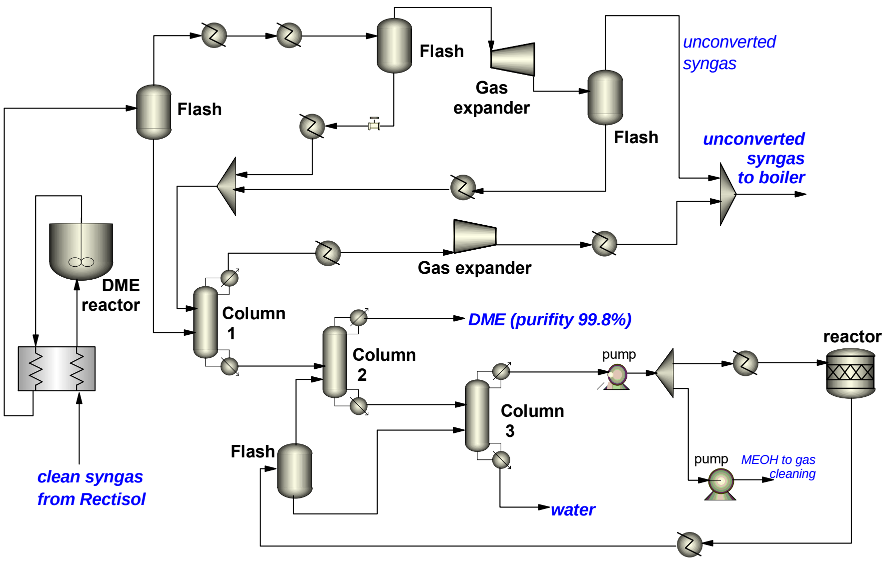
Lecture outline

- The biorefinery concept
- Syngas cleaning
  - Tar removal
- Syngas applications
  - FT (Fisher-Tropsch) process
  - DME (DiMethyl Ether) process
- Examples of integrated bio-refineries
  - Production of FT
  - Production of DME
  - Production of MixOH

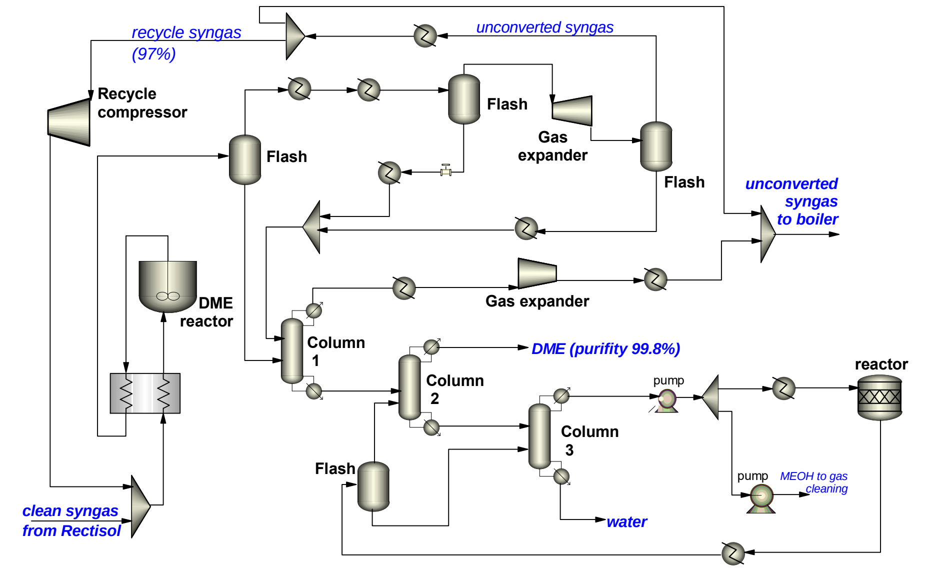
Production of DME

DME synthesis reactor	
Type	Gas-liquid-solid slurry, $CuO/ZnO/Al_2O_3$ + γ-Al_2O_3 catalyst
Operating conditions	260 °C, 62.5 bar
Saturated steam produced	38 bar
DME separation	
Gas-liquid separation	60.6 bar, 40 °C
DME purity	99.80%
Methanol dehydration reactor	
Operating conditions	Inlet T, p: 250 °C, 15 bar; Adiabatic, conversion efficiency of 80%

Production of DME → synthesis island w/o rec.



Production of DME → synthesis island with rec.



Lecture outline

- *The biorefinery concept*
- *Syngas cleaning*
  - *Tar removal*
- *Syngas applications*
  - *FT (Fisher-Tropsch) process*
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  - *Production of DME*
  - *Production of MixOH*

Production of MixOH

93

$CO + 2H_2 \leftrightarrow CH_3OH$ ΔH^0_{298} = - 94,084 kJ/mol

$CH_3OH + H_2 \rightarrow CH_4 + H_2O$ ΔH^0_{298} = -115,394 kJ/mol

$CH_3OH + CO + 2H_2 \rightarrow C_2H_5OH + H_2O$ ΔH^0_{298} = -165,294 kJ/mol

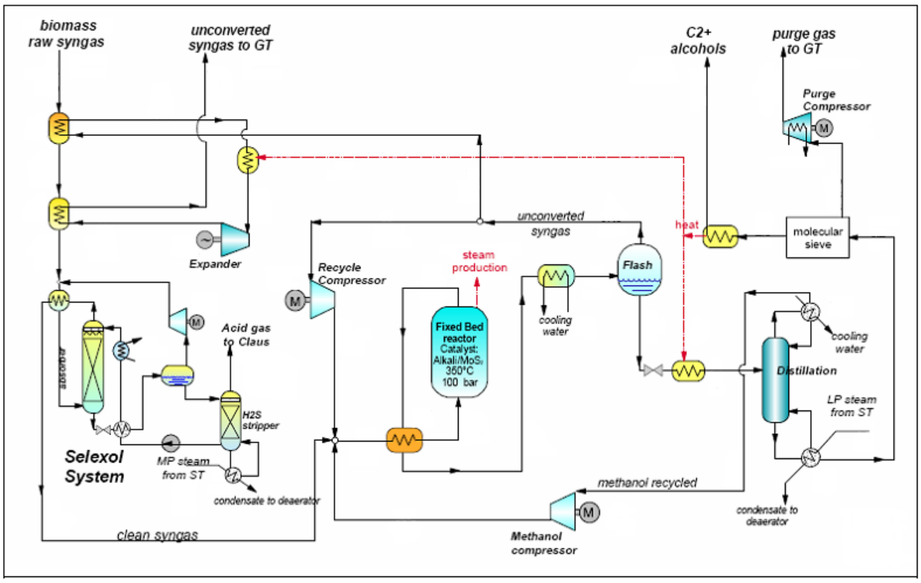
$C_2H_5OH + CO + 2H_2 \rightarrow C_3H_7OH + H_2O$ ΔH^0_{298} = -151,534 kJ/mol

$CO + H_2O \leftrightarrow H_2 + CO_2$ ΔH^0_{298} = - 41,270 kJ/mol

- Ru-based homogenous catalyst
- It is a modified methanol synthesis catalyst (alkali-doped ZnO/chromia or Cu-based)
- Fischer-Tropsch like catalysts (supported Co and Fe)
- **MoS_2 -based catalysts with alkali promoters**
  - Sulphur tolerant
  - Shift active
  - Selective toward linear alcohols

Production of MixOH → Synthesis island

94



Production of MixOH → Reactor specs

Clean syngas parameters	H_2S molar fraction ~50 ppm
Unconverted syngas recycle ratio	90%
Methanol recycle ratio	100%
Reactor	Type: fixed bed Reaction temperature ~350 °C Pressure ~100 bar GHSV ~3000 liters/h/kg of catalyst
Molecular sieve	20% ethanol and 97% water are removed to purge gas