



IIT ROORKEE



NPTEL ONLINE
CERTIFICATION COURSE

WASTE TO ENERGY CONVERSION

SYNGAS UTILIZATION 2

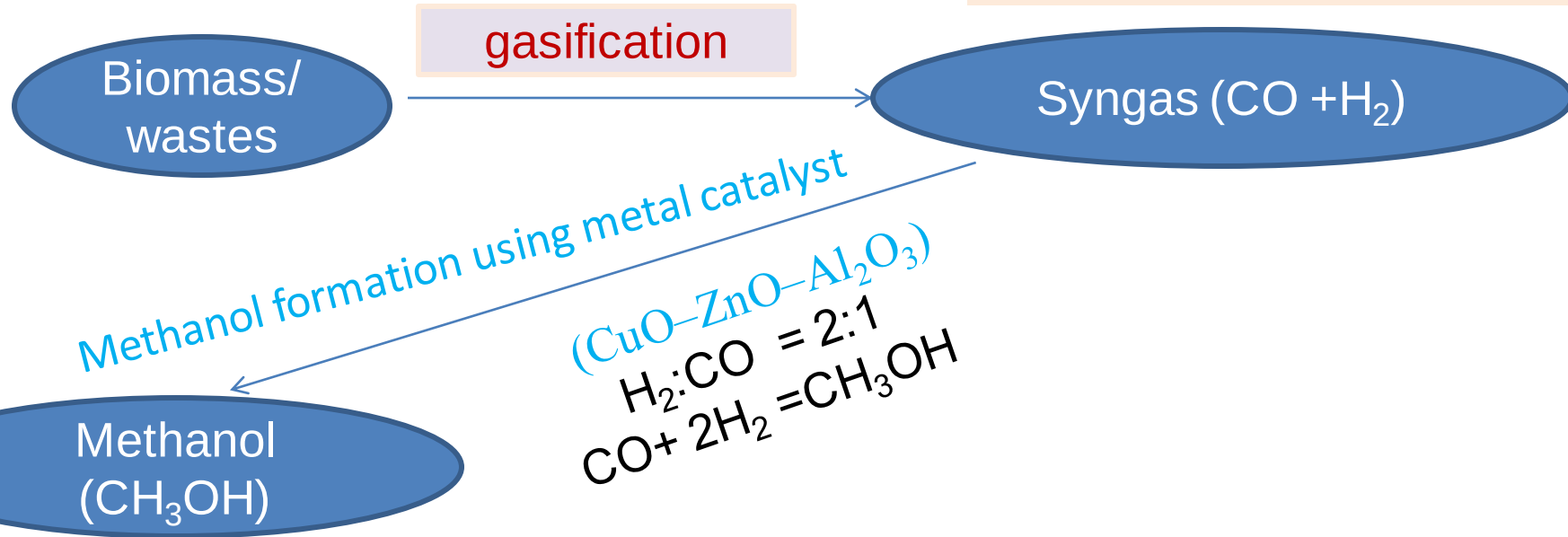
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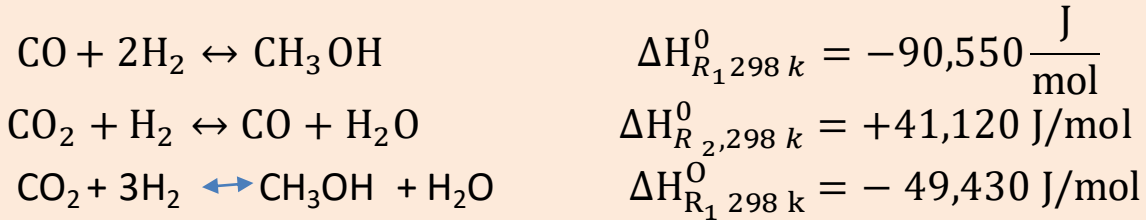
- Syngas utilization options
- Syngas cooling and conditioning
 - Acid gas removal
 - Shift reactions
- Some important utilization
 - F.T synthesis
 - Methanol
 - DME
 - Higher alcohol
 - SNG
 - Hydrogen





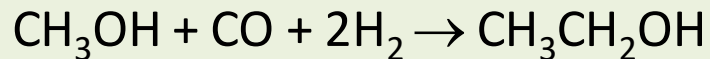
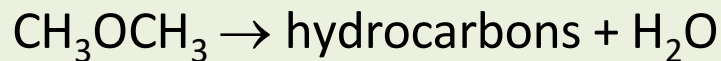
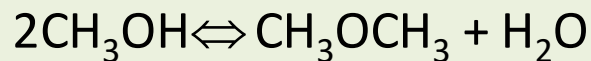
- Two important processes for methanol production from syngas (a mixture of CO, CO₂ and H₂) are patented by ICI and Lurgi.
- The ICI process was first commercialized in 1970 and currently accounts for more than 70% of undergoing projects.

- Methanol synthesis from carbon oxides and hydrogen is usually achieved over copper and zinc oxides catalysts ($\text{CuO-ZnO-Al}_2\text{O}_3$) according to the following main reactions:



- Methanol synthesis is exothermic reaction and favoured at high pressure and low temperature. Syngas feed is characterized by R-value $[(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)]$, the desirable R-value is around 2. Due to equilibrium constraint, per pass CO conversion is limited to around 25 percent.
- The process operates at 220 to 250 °C and 5 to 8 MPa pressure and uses a series of catalytic adiabatic reactor beds

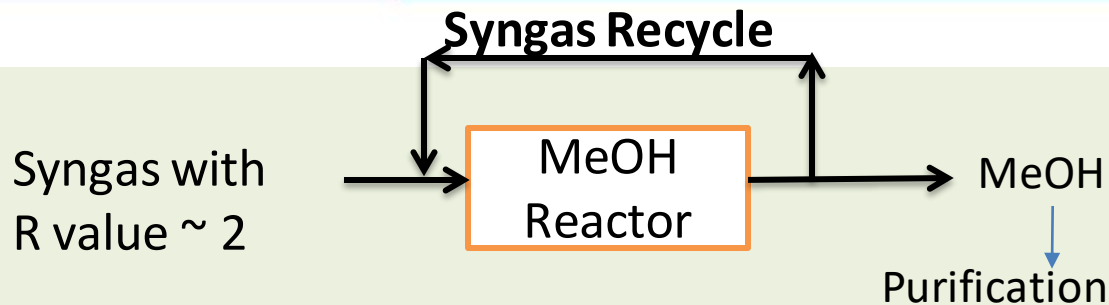
Other reactions



Other catalysts

Other catalyst are Cr/ZnO, Zr-K and Zr-Mn-K (Cr/ZnO requires high pressure (240-300 bar) and temperature (350-400 °C))

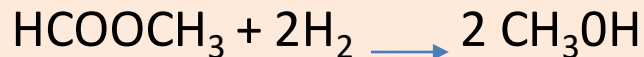
Use: Synthesis of many chemicals like dimethyl ether (DME), ethylene, propylene, polyolefin, oxo-chemicals, methyl acetate, acetic anhydride, acetic acid, acetate ester, keten, diketens & derivative, VAM, PVA etc.



Low temperature low pressure MeOH synthesis (Homogeneous phase reaction)

Two processes have been proposed for this method:

- Brookhaven National Laboratory (BNL) method
 - It employs a homogeneous Ni catalyst and alkoxide in an organic solvent (triethylene glycol dimethyl ether, i.e., triglyme)
- Methyl formate (MF) formation method
 - Employs a mixture of copper-based oxide and alkoxide as a catalyst in organic solvent triglyme

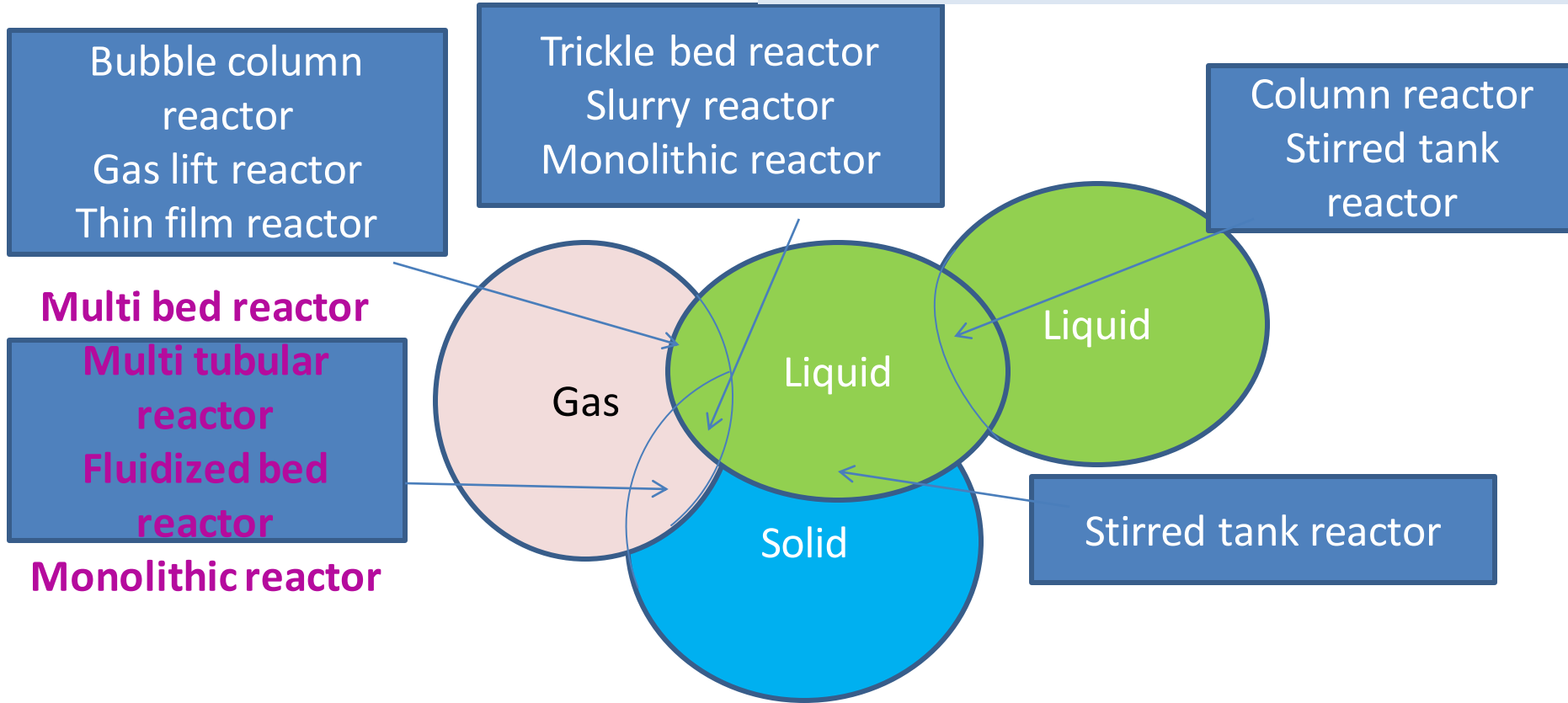


Both processes are operated at around 100 °C, where high equilibrium conversion of carbon monoxide to methanol is expected. Pressure is around 20-25 bar.



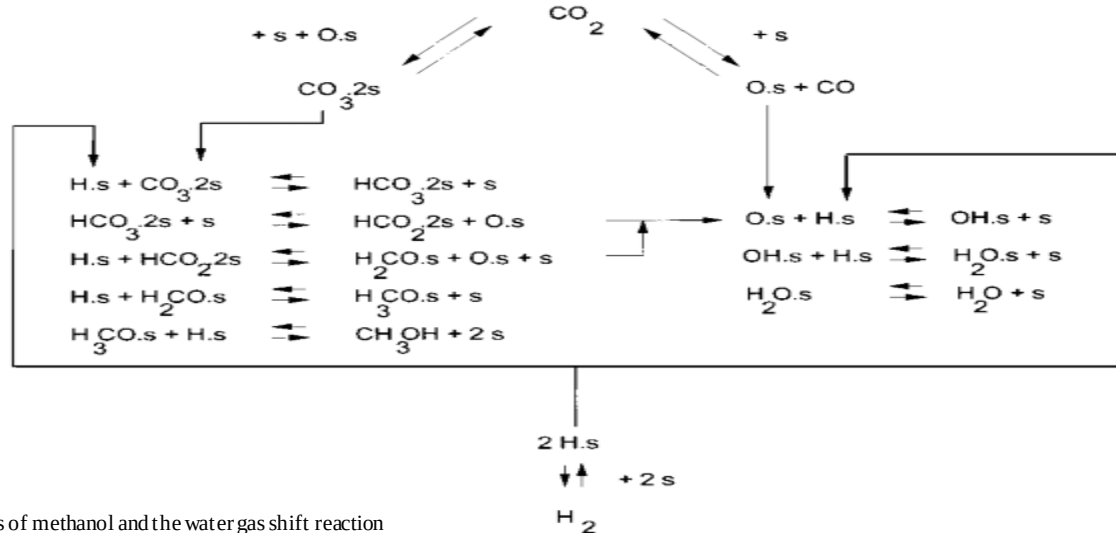
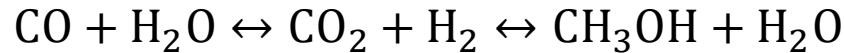
Methanol synthesis

Reactor selection for methanol synthesis

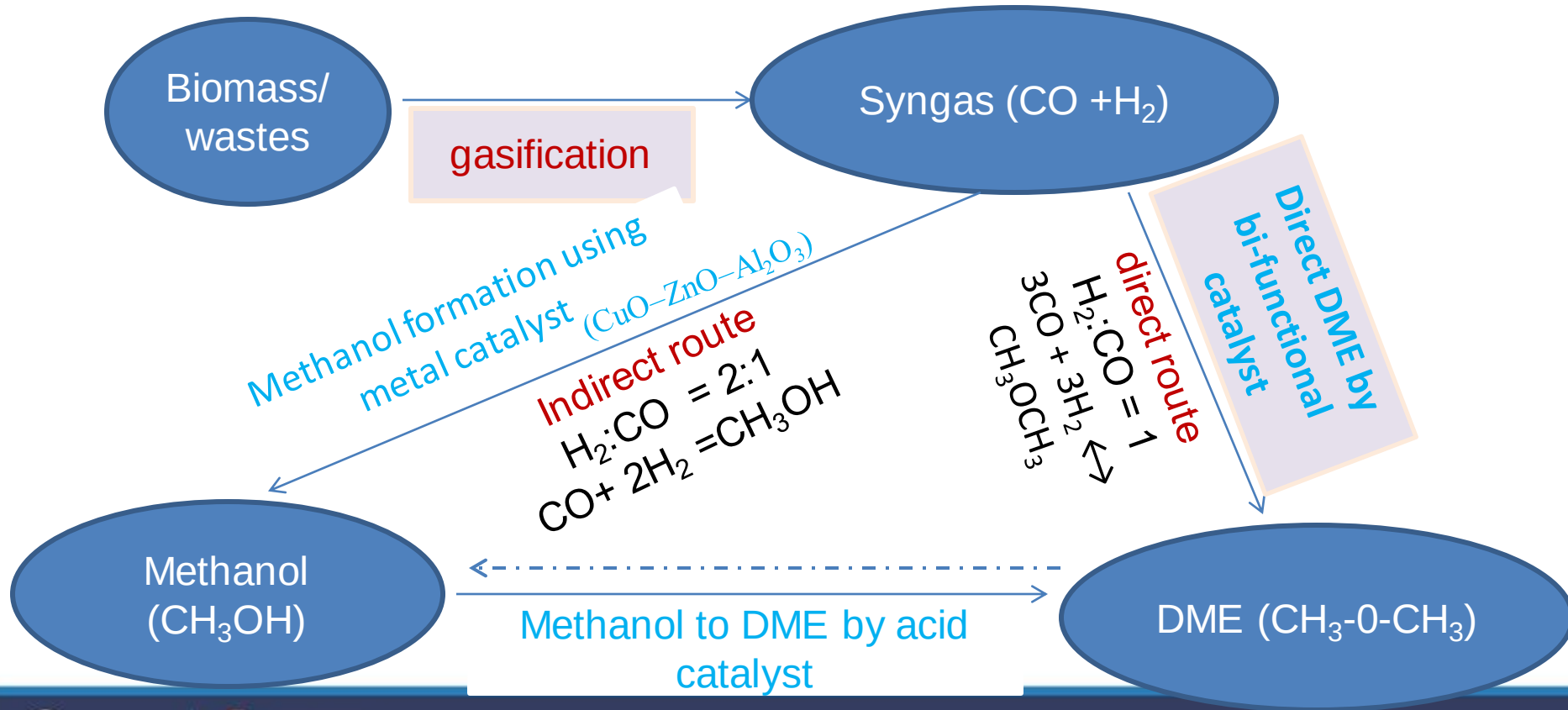


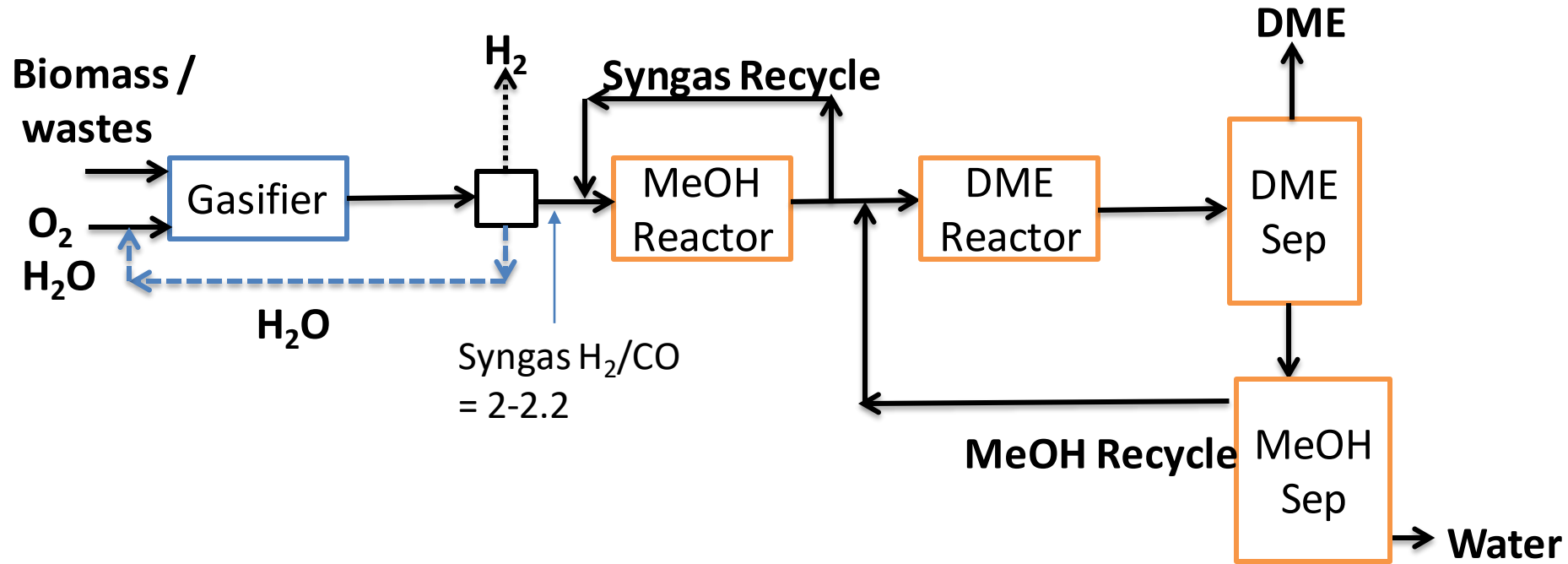
- Generally, a multi-tubular packed bed reactor with recycle stream is employed in methanol synthesis.
- In the typical plant operation, the catalyst lifetime is about 2 years. However, the catalyst is highly sensitive to sulphur poisoning. Therefore, sulphur level in feed gas needs to be reduced to less than 0.5 ppm.
- Catalyst deactivation also occurs due to thermal sintering of catalyst. Above 300 °C , CuO starts to crystalize which reduces the activity of catalyst.
- Plant economy is the function of operating temperature, pressure and recycle ratio.
- CO₂ is considered as carbon source for methanol rather than CO. CO is interconverted to CO₂ through water gas shift reaction. Also, 5-8% of CO₂ in syngas feed is required to initiate the methanol synthesis reaction.
- Temperature of reactor is controlled by controlling steam pressure through shell side.

- Froment proposed a redox type mechanism along with water shift reaction. Both reactions proceed on the copper phase of the catalyst. The role of ZnO is limited to structural promotion, at least under the typical industrial conditions.



Reaction scheme for the synthesis of methanol and the water gas shift reaction





Reactions and catalysts

using dehydration catalyst like alumina along with the Cu/Zn /Al based catalysts

Properties

DME has low auto-ignition temperature, very high cetane number, high oxygen content, very low particulate emissions.

Use

DME is suitable as source of hydrogen for Fuel Cells. It can also be used as additive to bio-fuels (methanol) to improve their ignition characteristics. LPG substitute, diesel engine.

Technology licensors

Chevron, Haldor Topsoe, TOTAL, NKK, Itochu, Mitsubishi and others are offering their technology for new DME plants



Commercial plants

- China's current annual output of DME is 120,000 tons.
- It plans to produce 20 million tonnes of DME based on coal feedstock by 2020. Already on the roll is a 200,000 tonnes coal to DME plant at Shanghai being developed by XinAo group.
- Other countries which are taking strides in setting up DME plants are Japan, Iran, Russia and Qatar.

Issues with syngas utilization from biomass and wastes through liquid fuel production

- Competitiveness in fuel market.
- FT fuels/ Methanol/ DME can be competitive either by increasing the plant capacity or reducing heat loss by heat integration in the process.
- Conventional GTL technology utilized by Shell and Sasol is only economic for plants producing 30,000 barrels per day or more.
- Biomass and waste gasifiers are of low capacity . Hence for its application through this route , compact reactors with heat integration are necessary.
- Development of micro reactors and other compact reactor with heat integrations increases the possibility of this fuel production routes from stranded resources including syngas generated from biomass and wastes.



- Recently, smaller scale GTL plants are designed to be economic at 1,500 b/d to 15,000 b/d by Velocys. Reactor is microchannel reactor
- Velocys' first commercial plant is now under construction in Oklahoma City, OK. The plant is a joint venture between Velocys, Waste Management Inc, NRG Energy, and Ventech Engineers, and will use renewable landfill gas as a feedstock. Commercial operations expected in 2016.
- Another plant in the planning stages is in Ashtabula, Ohio near Lake Erie using natural gas from the Marcellus Shale. Initial production will be 2,800 b/d with expansion potential up to 10,000 b/d as well as high-value solvents, lubricants and waxes.

<http://breakingenergy.com/2014/11/03/small-scale-gtl-could-be-the-next-big-thing/>

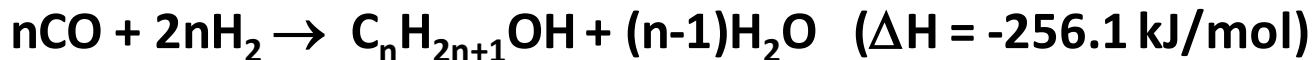


- Oberon fuel has developed small scale MeOH plant, which can utilize syngas produced from natural gas as well as bio gas containing upto 50 % of CO₂.
- Typical capacity of the plant using syngas derived from NG as well as biogas is 10000 gallons/day DME Or 11,300 gallons/day methanol
- Foot print of the plant is 40000 square feet.
- Feedstock requirement is 12,40,000 standard cubic feet NG /day Or 15,40,000 standard cubic feet biogas (72% CH₄ / 28% CO₂) per day

<http://www.oberonfuels.com/products/production-units/>

Higher Alcohols synthesis

Reactions



Catalyst

Molybdenum sulfide with promoters, Cu/ Co/Cr (IFP), rhodium and other group VIII metals along with methanol synthesis catalysts like Cu/ ZnO.

Use

As a fuel



Higher Alcohols synthesis

Commercial plants

The production of higher alcohols from syngas is still in bench scale research stage and there is no such commercial plant in the world.

Recently, Bio Engineering Resources, Inc. (BRI) has produced ethanol from syngas through biological route.

Biomass has been used as feedstocks. A sulfur tolerant strain has been used to produce ethanol (3 %)

The process is effective at 38-40 °C with CO rich syngas.

SNG production

Reactions : Substitute natural gas (SNG) can be produced by “methanation,” which uses hydrogen and a nickel oxide catalyst to convert the syngas into SNG and water as per the following equations:



Catalysts : The commercially used catalyst for methanation is supported Ni on alumina. Raney Ni and Rh on alumina can also be used alternatively. The activity of some methanation catalysts are shown below:

$\text{Ru} > \text{Ir} > \text{Rh} > \text{Ni} > \text{Co} > \text{Os} > \text{Pt} > \text{Fe} > \text{Mo} > \text{Pd}.$

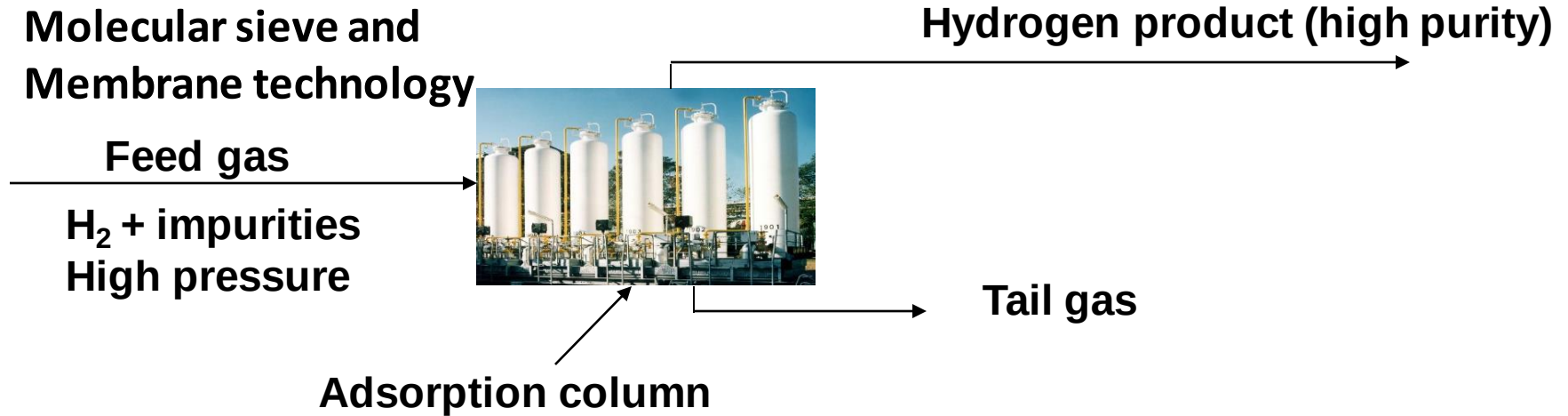
Use ; Gaseous fuel



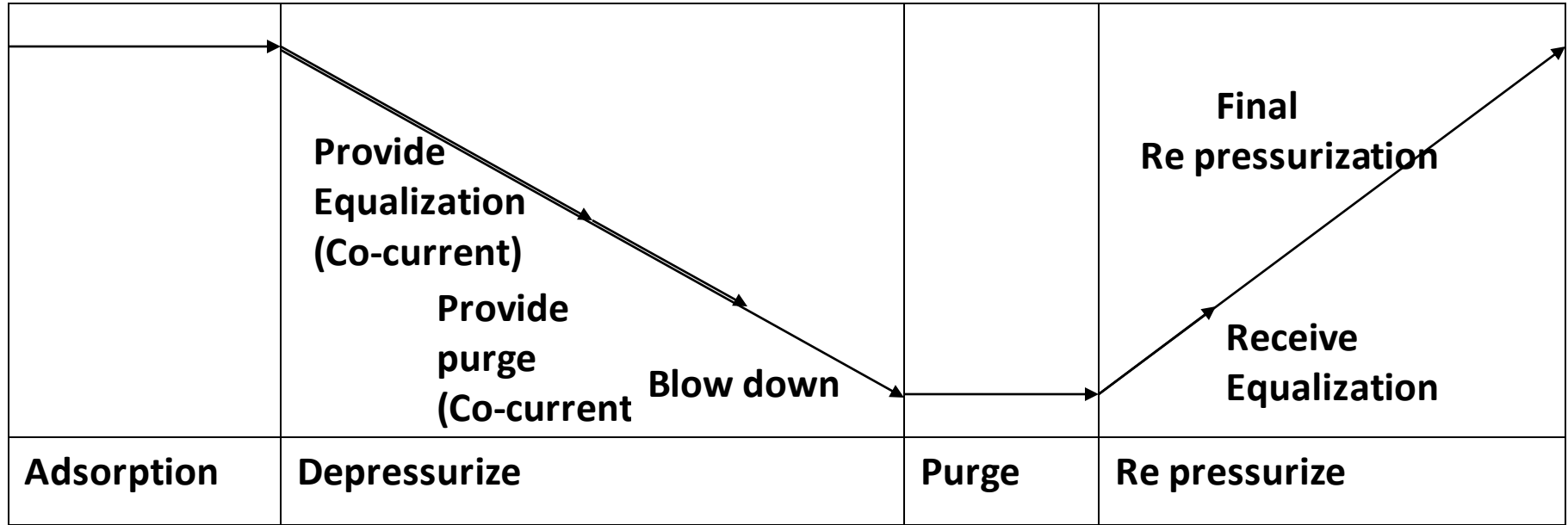
Hydrogen production

- Pressure swing adsorption (PSA)
- Molecular sieve and
- Membrane technology

Pressure swing adsorption for hydrogen separation



Adsorbent	Impurity adsorbed	Adsorbents for PSA and removal of impurities
Silica gel	Ethane, propane, butane and heavier hydrocarbons	
Activated carbon	Methane, carbon dioxide	
Molecular sieve 5A	Methane, carbon monoxide, nitrogen	
Activated alumina	Water	



→ **Pressure changes at various internal steps of PSA** ←

Thanks...

