

Chemicals obtained from petroleum source is called petrochemical.

e.g - polythene

LPG → mixture of
propane - butane
 $C_3 - C_4$

→ Synthesis gas:

Almost all petrochemicals are obtained from these 3 major raw material:

1. Carbon monoxide/Hydrogen (synthesis gas or syn gas)

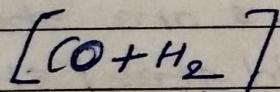
from reforming reaction of natural gas (NG, CH_4)

2. Olefins from pyrolysis of ethane, propane-butane (LPG) or distillation

3. Aromatics from catalytic reforming of gasoline

• Manufacturing of syn gas:

Production of synthesis gas from methane or other hydrocarbons



Raw material for synthesis gas:

1. Natural gas
2. Petroleum liquids
3. Biomass
4. Coal

• Synthesis gas is obtained by either steam reforming or partial oxidatⁿ process.
(of methanol)

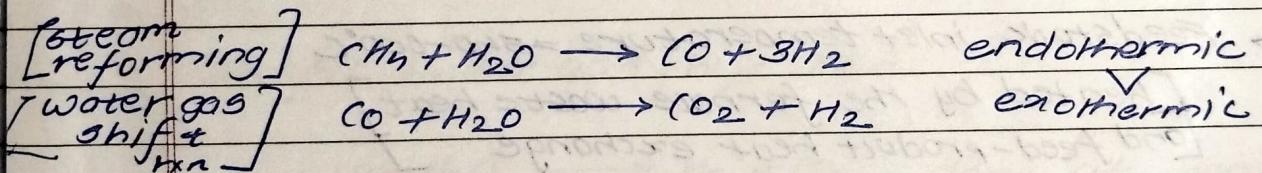
→ Composition of syn gas from steam reforming
(95% conversion of CH_4)

<u>Components</u>	% volume
CO	15.5
CO_2	8.1
H_2	75.7
N_2	0.2
CH_4	0.5
H_2S	0

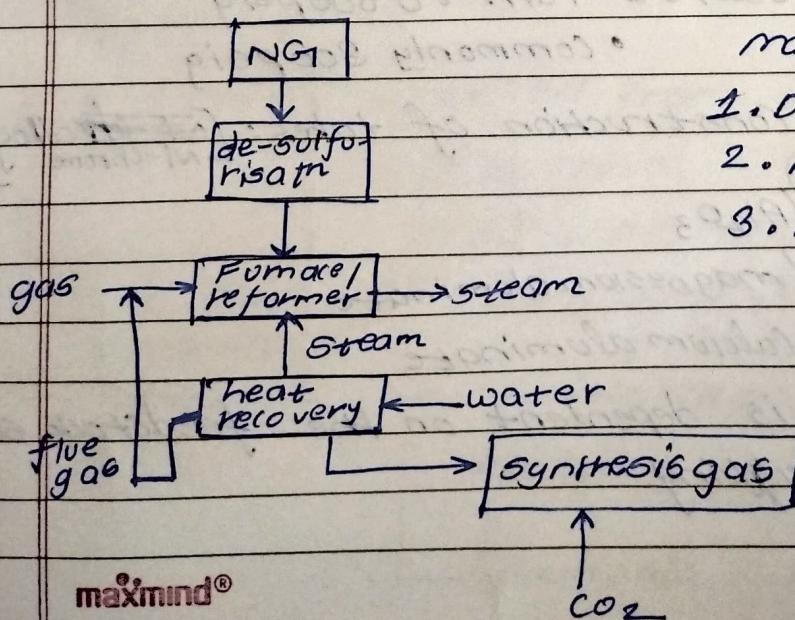
note: $\frac{\text{H}_2}{\text{CO} + \text{CO}_2}$ ratio is important to determine quality of end product

? Refinery off gasses:

→ Primary rxn for methane steam reforming:



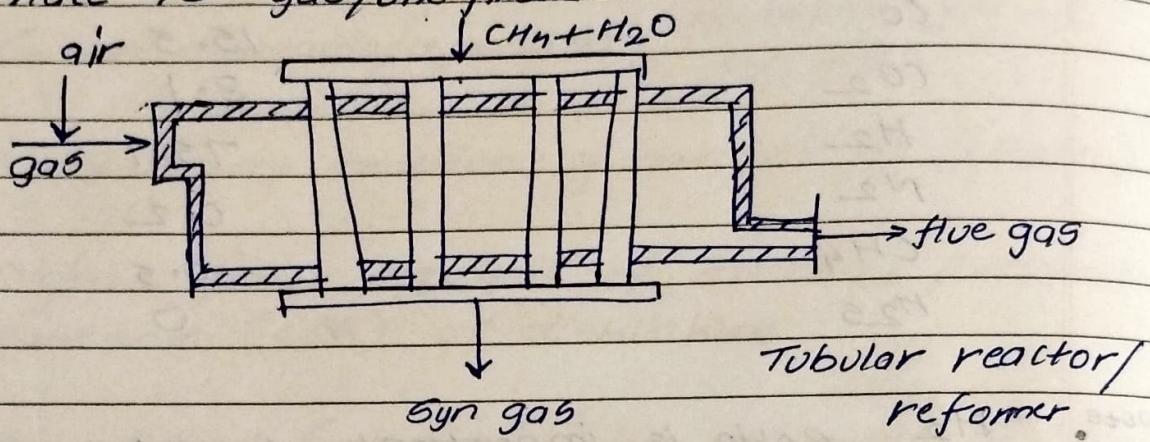
→ Flowsheet of steam reforming:



- main components of plant:
1. Desulfurisation
 2. Reforming
 3. Heat recovery

- Reformer \rightarrow furnace with tube banks 1
- Heat required for endothermic reaction \leftarrow Radiation heat from furnace

- Furnace is gas/oil fired



Major Furnace types:

1. Kellogg (down-fired)
2. Foster-Wheeler (terraced, side-fired)
3. Babcock (side fired)
4. Chemico (up fired)

→ Feedstock inlet temperature = 540–600°C
 [heated by the furnace waste heat]
 [and feed-product heat exchange]

Reformer outlet temp. $< 900^\circ\text{C}$

Reforming pressure = 1 atm to 600 psig

• Commonly 300 psig

Material of construction of tubes: [~~nickel alloy~~] Ni-chrome

Catalyst: $\text{Ni}/\text{Al}_2\text{O}_3$
 (6-10%)

Ni/magnesium aluminate

Ni/calcium aluminate

Catalyst life is dependent on the feedstock sulfur content and coking.

Disadvantages:

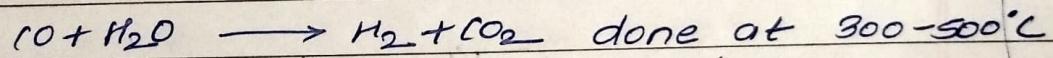
- Need for heat resistant tubes
- Inefficient use of reactor as the catalyst occupies a small space.

→ $H_2/CO \Rightarrow 1-3$ for petrochemical production.

- Required ratio in the syn gas for production of chemicals:-

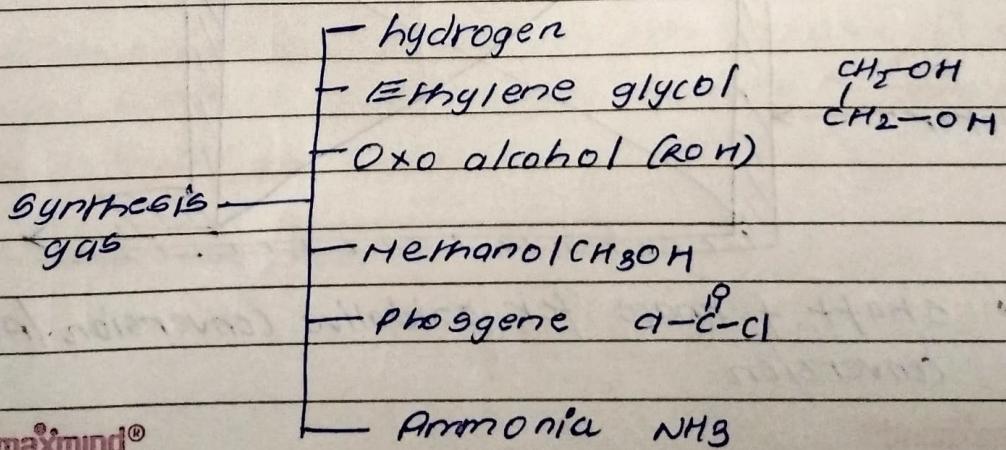
1. Generally requires H_2/CO ratio b/w 1-3
2. Reformer effluent exhibits H_2/CO ratio 5-10
3. CO_2 addition to the reformer feed dilutes the syn gas/ producer gas.
4. CO_2 addn to reformer feed → done for low pressure operation.
5. CO_2 addn to product gas → done for high pressure operation.

Catalytic water gas shift rxn



catalyst - Iron-chromium
at low S environment

→ chemicals produced from syn gas:

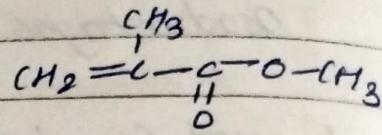


Methanol

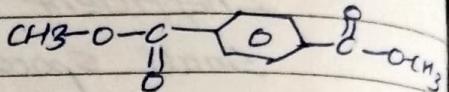
→ Formaldehyde
Methyl chloride

→ Methyl amines

→ Methyl methacrylate



→ Dimethyl terephthalate



→ Acetic acid CH_3COOH

Ammonia (NH_3)

→ Urea

→ Nitric acid

→ Hydrazine

→ Methyl amine

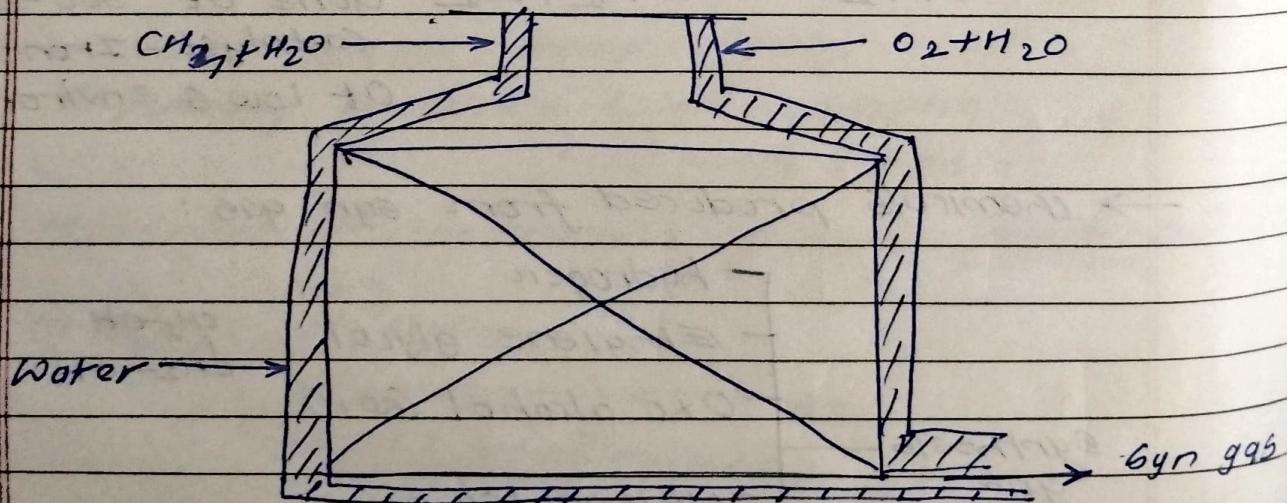
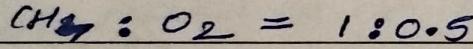
→ Acrylonitrile

→ Hexamethylene tetramine

→ Overall reactn is endothermic:

Supply O_2 to combust methane and generate energy.

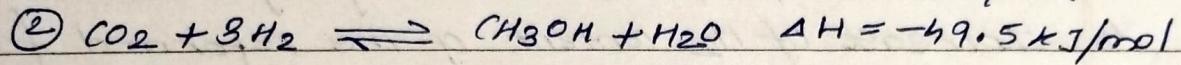
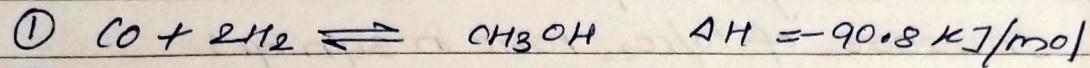
In this case steam supply is less as compared to steam supply in no combustion of methane.



- Shaft furnace for oxidative conversion / Autothermal conversion

- Does not require any external heating.

→ Methanol synthesis:-



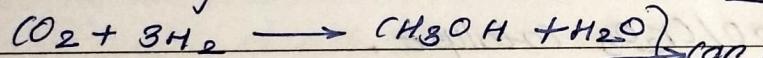
① & ② are exothermic and occur simultaneously in reactor.

• Carbon efficiency (%)

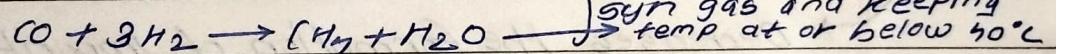
$$100 \times \left(\frac{\text{no. of moles of methanol produced}}{\text{no. of moles of CO+CO}_2 \text{ in synthesis gas}} \right)$$

• Side rxn:

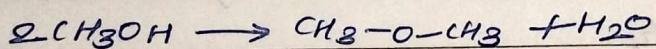
1. Reactn of residual CO_2 with H_2



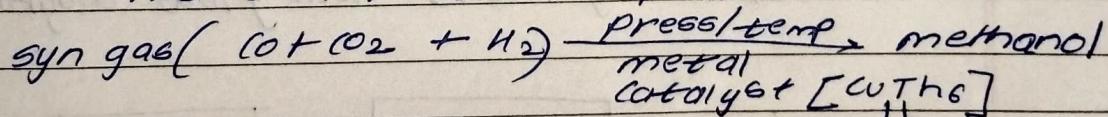
2. Methanation



3. Formation of methyl ether



→ Modern methanol production plant:



High pressure plant \rightarrow 250-300 atm Temp \rightarrow 300-400°C
 Low pressure plant \rightarrow 50-100 atm Temp \rightarrow 240-270°C

\rightarrow catalyst $[\text{ZnO}/\text{Cr}_2\text{O}_3]$

Also for low pressure \rightarrow catalyst $[\text{Cu/ZnO}/\text{Al}_2\text{O}_3]$

very sensitive to
impurities in syn gas
Eg: halogenated
compounds

Hence, it is required to purify syn gas before methanol production rxn.

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→ Production of methanol is favoured by :-

1. Evaluation of pressure → slow react
2. Reductⁿ of temperature
3. Increase of CO/CO₂ ratio in syn gas
4. Increase of H₂ content of the reformed feed at least for pressure above 6×10^6 Pa absolute

→ 2. → # Lower the reaction rate, slow approach to thermodynamic equilibrium → to overcome this situation, catalyst along with catalyst activators are used.

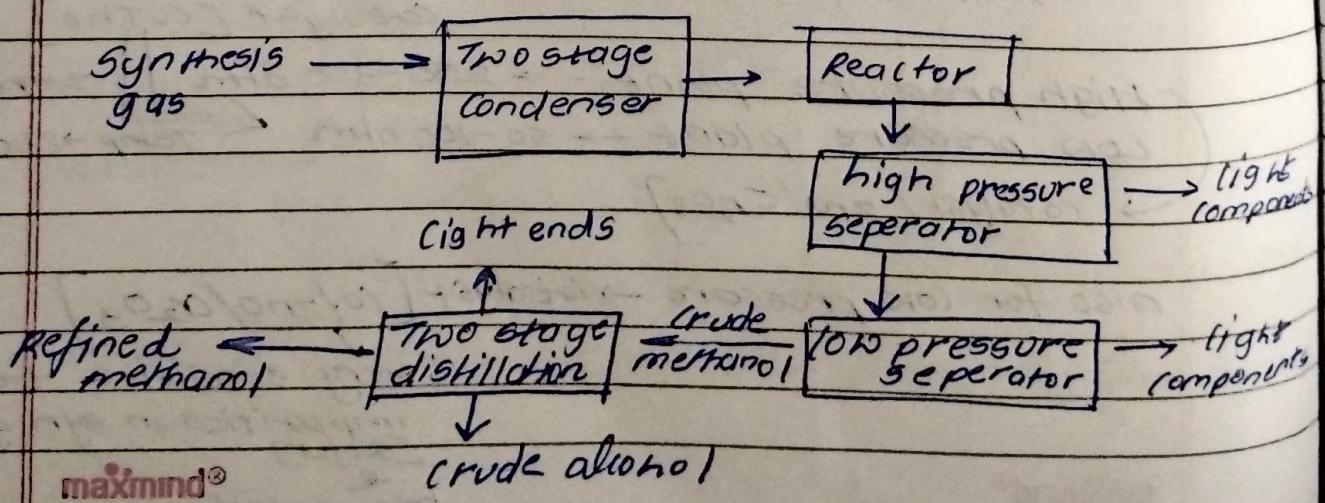
• New catalyst : Metallic Cu + Th

that ThCu₆ is the best one

(ThCu₆) is 10 time more active than a commercial Cu/ZnO/Ch₃O₃ catalyst.

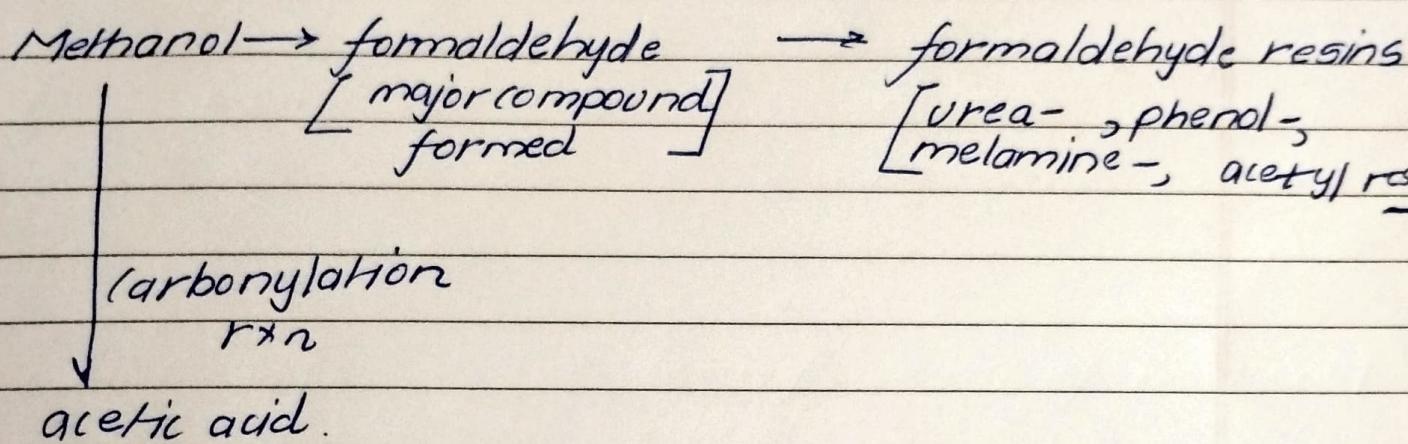
→ Decreases the formation of impurities (by-products), such as CH₄. It has good stability upto 475 h.

→ Methanol synthesis block flow diagram :



→ Uses of methanol:

1. Mostly used for production of chemicals:



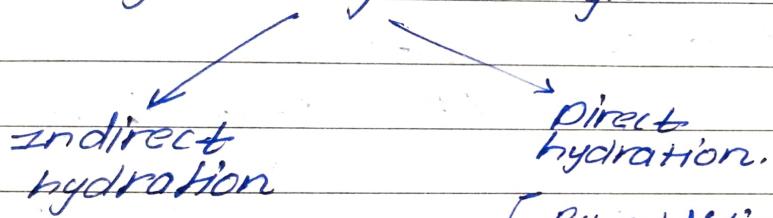
2. Pure methanol as fuel (as octane enhancer)

→ Fuel additive such as methyl tertary butyl ether (MTBE) production from methanol, but production of MTBE is limited by the availability of isobutylene.

of isobutylene.

Ethanol: 1. fuel extender
2. Octane enhancer

- Process for manufacturing of ethanol (b.p. $\approx 78^\circ\text{C}$)
 1. Fermentation
 2. Synthesis from ethylene



[By addition of water]

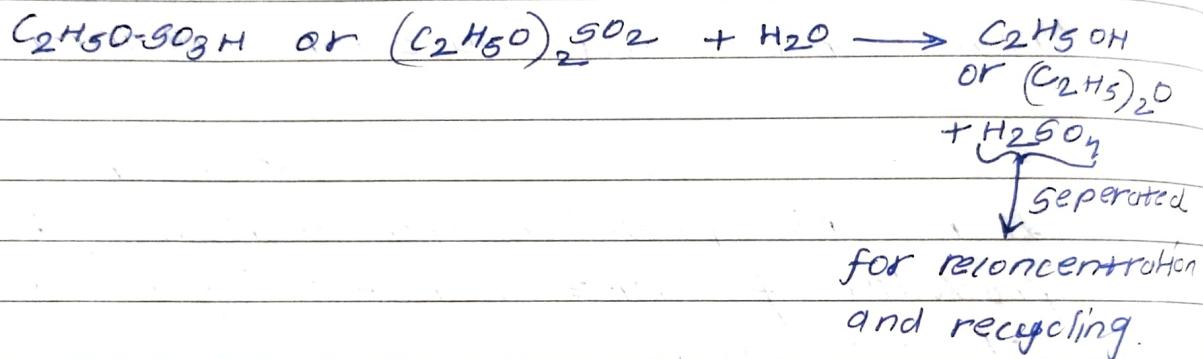
[Action of sulphuric acid, followed by hydrolysis of esters formed]

- Indirect hydration of ethylene :-
(esterification/ hydrolysis)

- Formation of ethyl acid sulfate or diethyl sulfate by the reaction between ethylene and sulfuric acid.

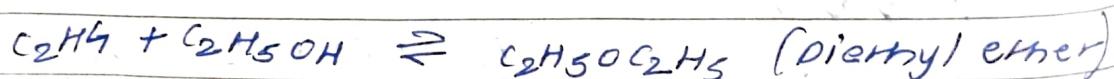
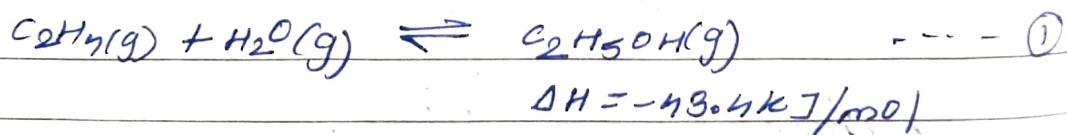


- Hydrolysis of sulfuric esters :



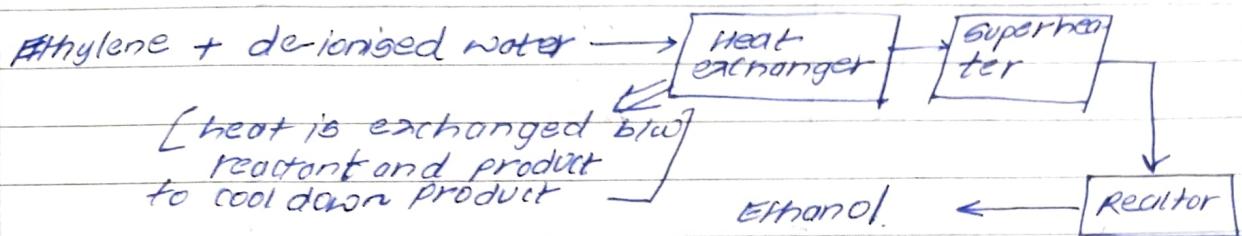
- Direct hydration of ethylene :

Addition of water directly to ethylene, this is a gaseous phase catalytic rxn



- A. (1) is exothermic then it should be favoured at low temperature but at low temperature rxn (2) is favoured.

B. Rxn (1) is favoured at higher pressure, but at higher pressure ethylene polymerises to give butene and higher polymers, which produces higher alcohols after hydrolysis.



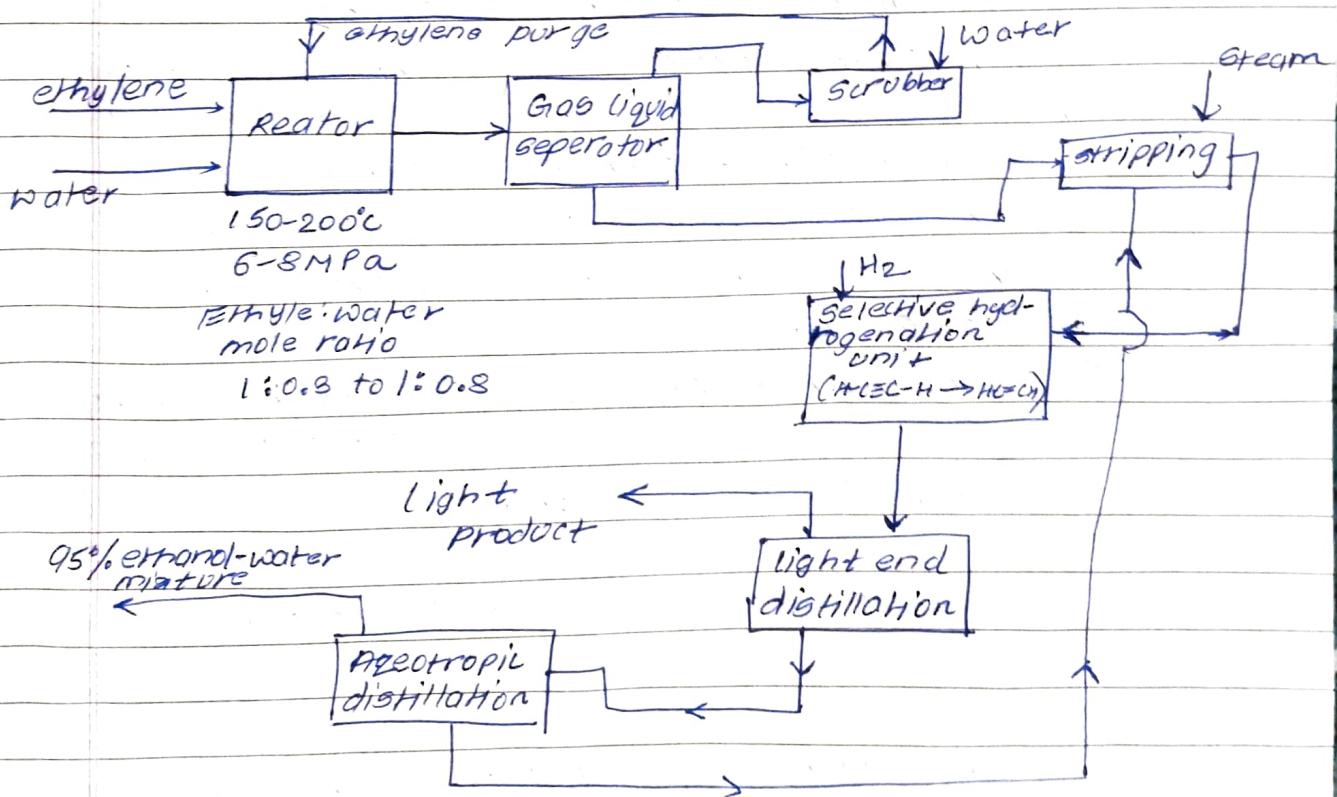
Reaction conditions:

temp = 150-200°C

Pressure = 6-8 MPa

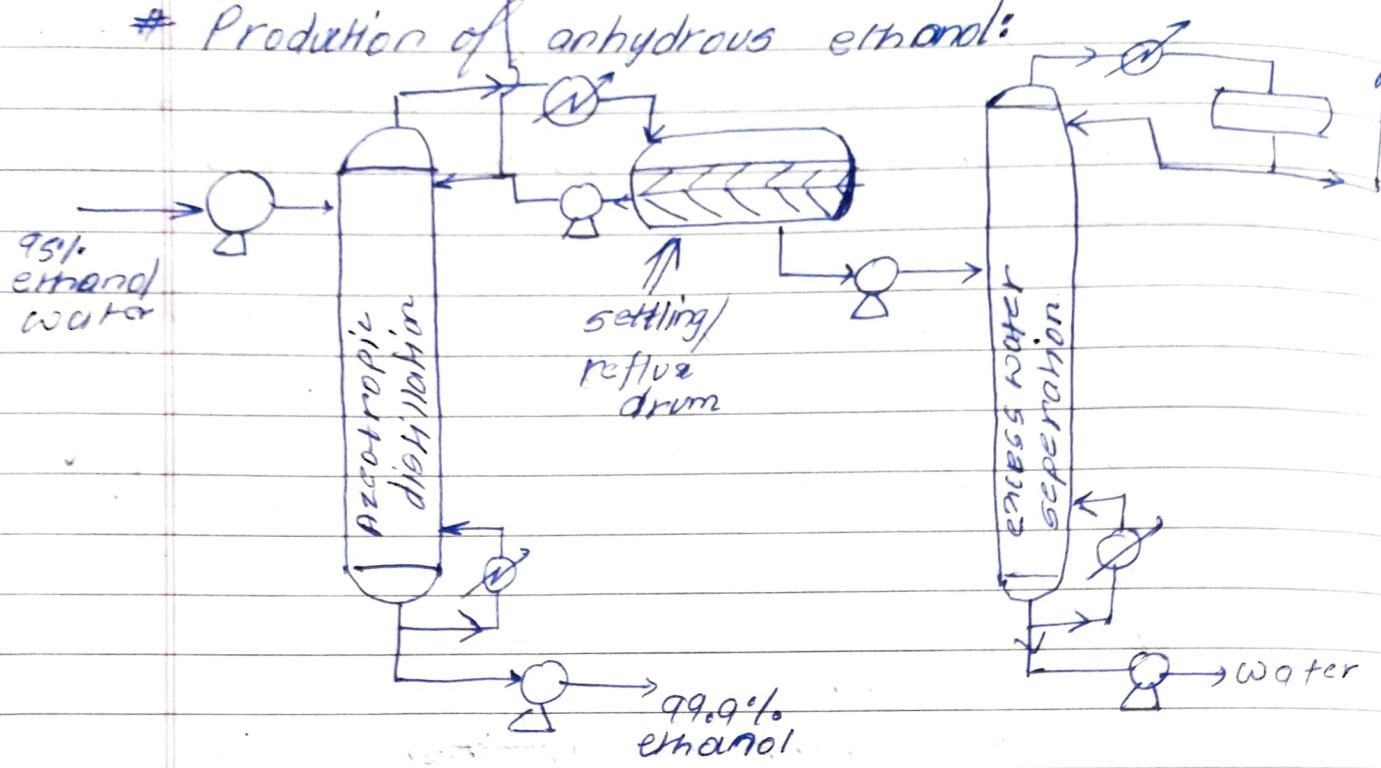
Catalyst → phosphoric acid deposited on silica.

→ Alkali e.g. NaOH is added into to product stream to neutralise the phosphoric acid carried away from catalyst into the product stream.



Ethanol manufacture from ethylene by direct maximind® hydration process [Shell process]

Production of anhydrous ethanol:



- In azeotropic distillation benzene is used as a solvent
- Distillation occurs at atmospheric pressure
- a) First column (55-65 trays) → produces anhydrous alcohol at the bottom and a ternary azeotrope at top.
[water + ethanol + benzene]

wt % composition of ternary azeotrope →

water 7.4%, ethanol is 18.5%, and benzene 74.1%

Top product after cooling and condensing and settling gives two layers:

1. benzene rich top layer (also contains ethanol & water in lesser fractn)

used as reflux to the column.

2. water rich bottom layer is sent to the second column.

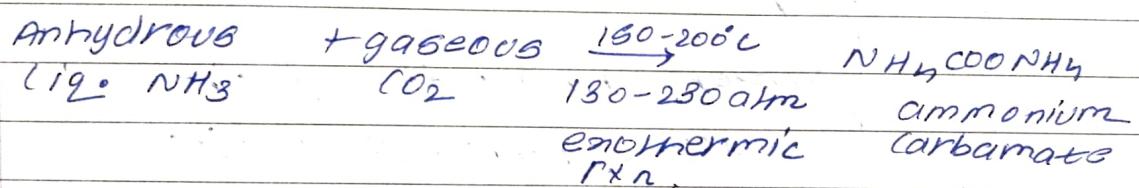
- b) Second column: Top product of second column is the azeotropic mixture of ternary compounds, sent to the 1st column as reflux

Use of ethanol:

- As a fuel additive, but also depends on energy demand
- As a solvent and ~~so~~ chemical availability.

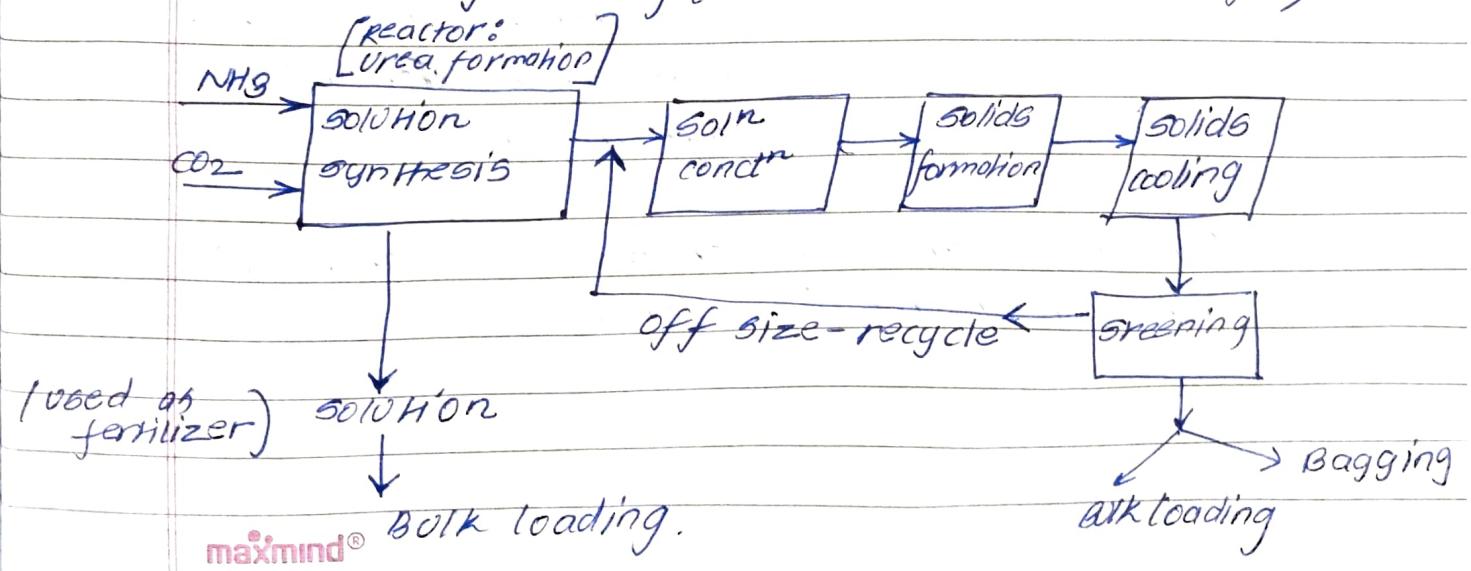
Urea ($\text{CO}(\text{NH}_2)_2$) [Also called as amide of carbamic acid or diamide of carbonic acid]
 Carbonic acid $\Rightarrow \text{CO}(\text{OH})_2$ { Carbamic acid $\Rightarrow \text{NH}_2\text{COOH}$

→ Urea production:- Anhydrous liquid NH_3 + gaseous CO_2



↓
dehydration and decomposition
 $\text{CO}(\text{NH}_2)_2$
 [Urea]

⇒ Urea manufacturing (7 unit operation stages)



→ urea solids is prepared from melt
urea melt → urea solid [operations] ↗ Prilling ①
 ↗ granulating ②

both ① & ② gives solids.

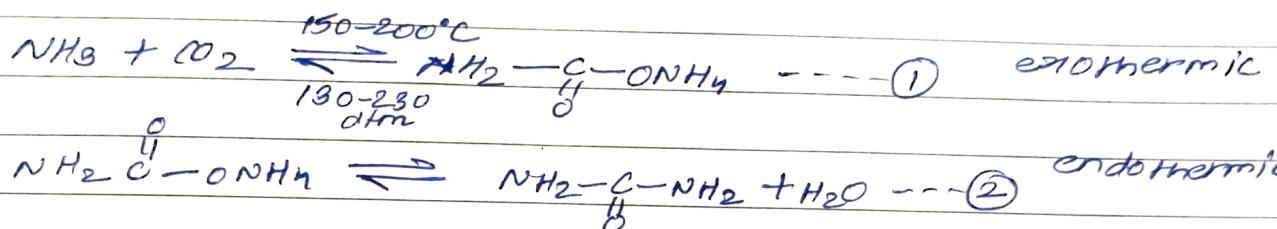
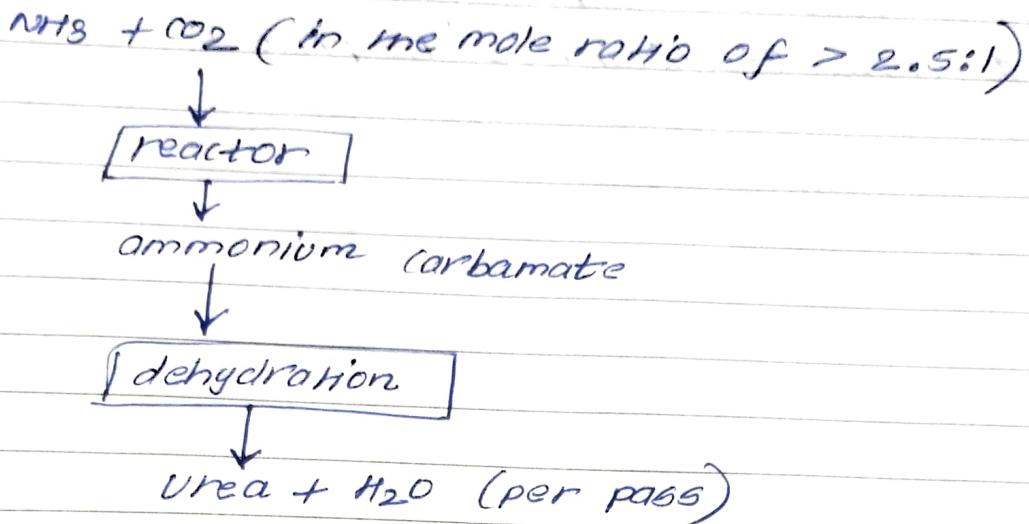
- ① gives smaller particles of urea.
- ② gives larger particles of urea.

- Urea prills are used for manual spreading.
- Urea granules are used for machine spreading.
- Prilling - molten urea is fed from the top of a prilling tower
 - ↓ counter current flow of air
 - cooled, solidified spherical urea solids.
- Types of prilling ⇒ 1. Fluidised
2. non-fluidised.
- Granulation types ⇒ 1. Drum granulation
2. Pan granulation.

Drum granulation → solids are built up in layers on seed granules in a rotating drum granulator/cooler
[4 ft in diameter]

Pan granulation → similar to drum granulation only
the equipment is different.

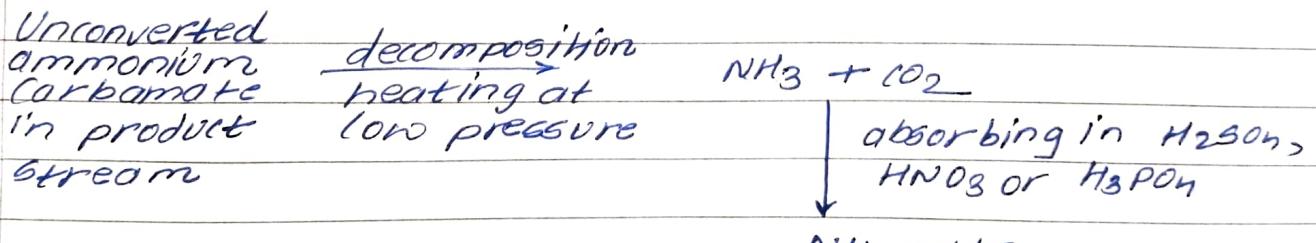
- One pass process:



→ equilibrium depends on temp. & pressure.

Pressure in ① should be greater than ②

Problem in one pass! Difficulty in separating ~~the~~ ammonium carbamate from ~~Urea + H₂O~~ and cannot be recycled.



Most popular urea production process:

→ Solution recycling process:

$\text{NH}_3 + \text{CO}_2$ (recovered from reactor after several stages of decomposition) is absorbed in water and the whole soln is recycled to reactor again as **maxmind®** ammonical aqueous solution of ammonium carbamate.



Urea production technology:

1. Urea stamicarbon BV process