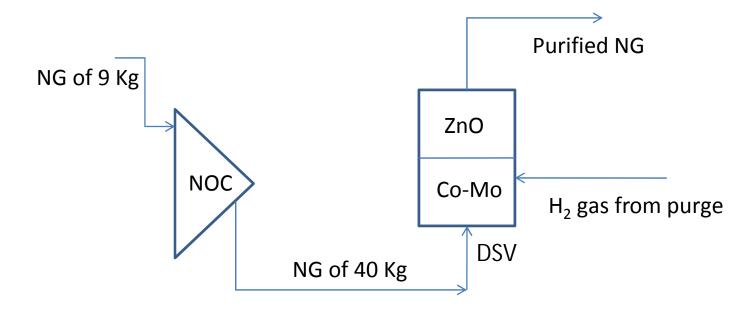
Synthesis Gas Production

Via Steam Reforming

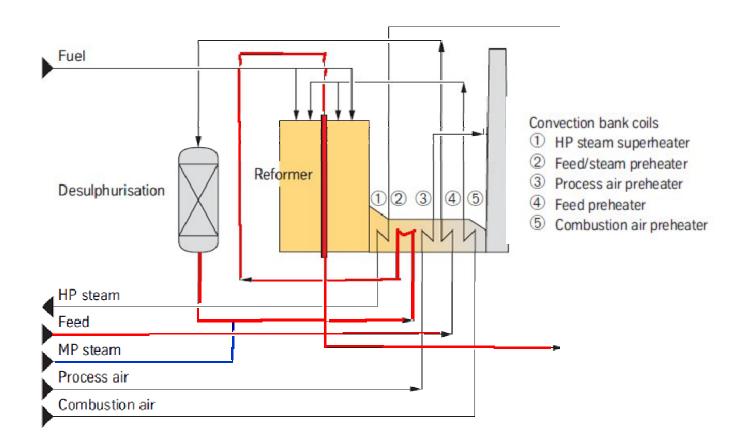
PNG Purification Section

- Desulphurization vessel
- Reactions



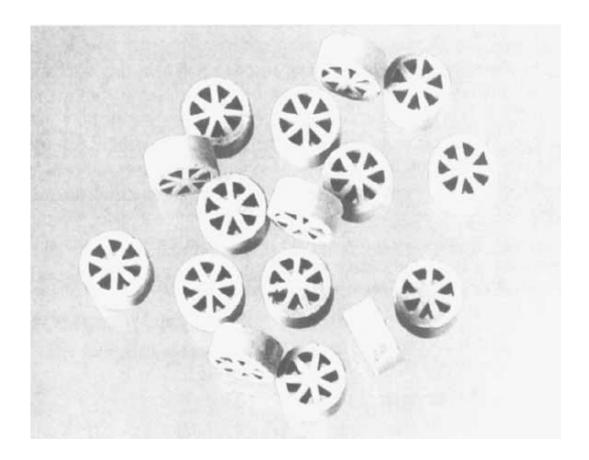
Primary Reforming

Two section – furnace and convection zone



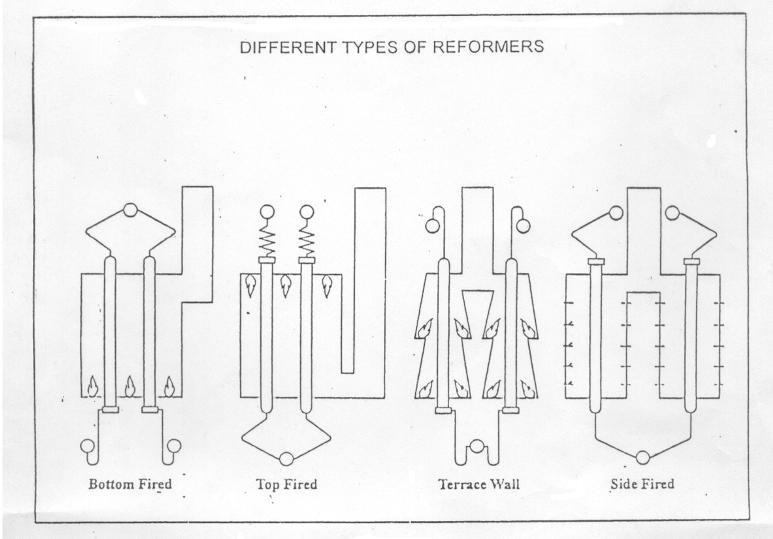
Primary Reformer

- Reactions
- Catalyst
- Classification of PRF according to disposition of burner
- Most important design Variables are life-time of reformer tubes (high Cr alloy), catalyst activity, service life, heat transfer and pressure drop.
- Material deterioration occurs due to the alternating thermal and mechanical stress, external and internal oxidation and carburization.



"Wagon Wheel" primary reforming catalyst (UCI)

Furnace Design and Layout



Top fired reformer

- Firing occurs at one level. No of burner per tube is less than side fired.
- Radiation efficiency is higher than other design
- Burner is located in close to the coldest point
- Less structural steel is needed
- But heat input is adjustable only a limited degree

Side Fired Reformer

- Provide very uniform heat distribution and can be adjusted by control for the individual burner
- The larger number of burners makes fuel and preheated combustion air distribution more complicated and more expensive.
- Radiation efficiency is lower than top fired
- Lower residence time of flue gas can favor Nox formation

Bottom Fired Reformer

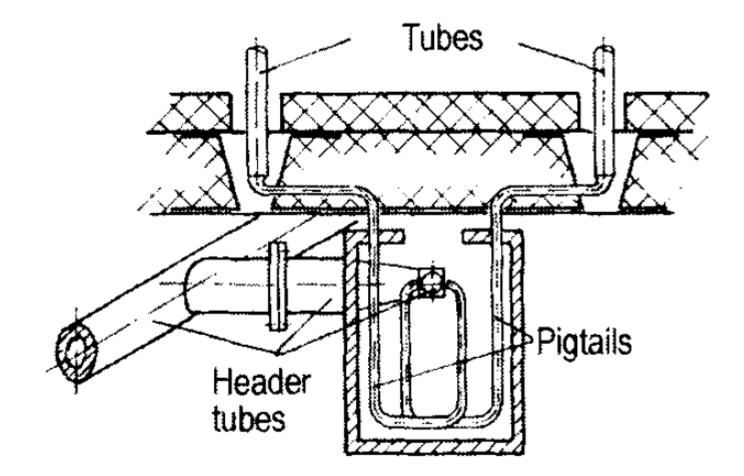
- Is not very common in modern plant
- Constant heat flux along the length and highest temperature at the outlet

Terraced Wall Type Reformer

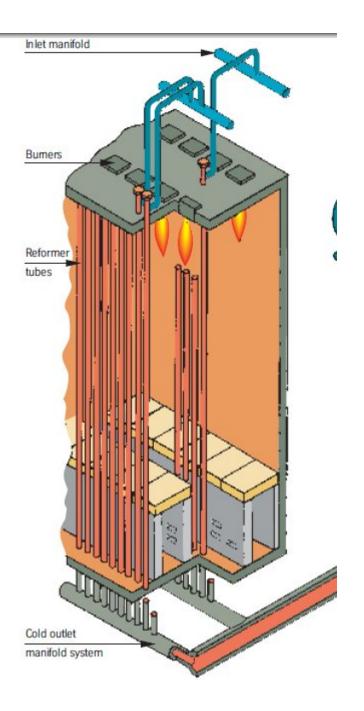
- Developed by Foster Wheeler company and is intermediate between the side fired and bottom fired
- Heat flux of any location can be controlled because of the position of the burner

Selection of Reformer

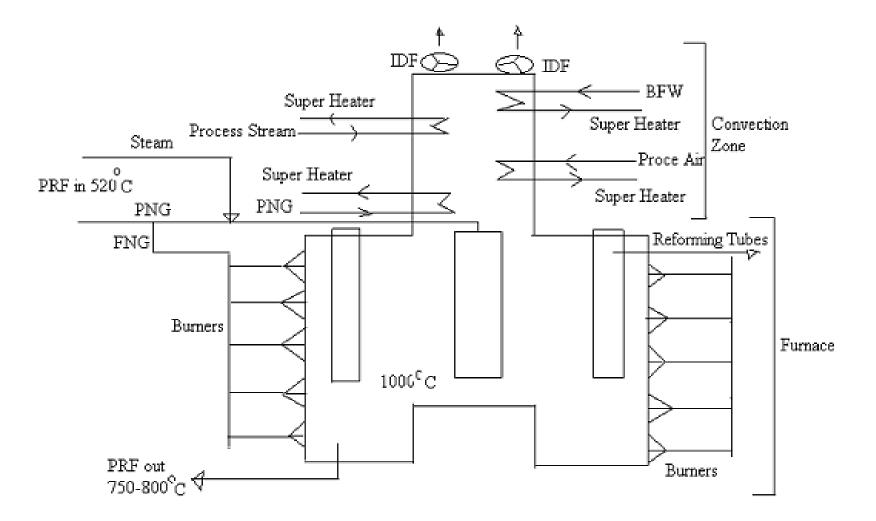
- Firing type
- Mechanical Design
 - * Axial load of catalyst and tubes must be well balanced by spring hangers or pigtails
 - * Proper design is necessary to avoid thermal bending of the tube during expansion



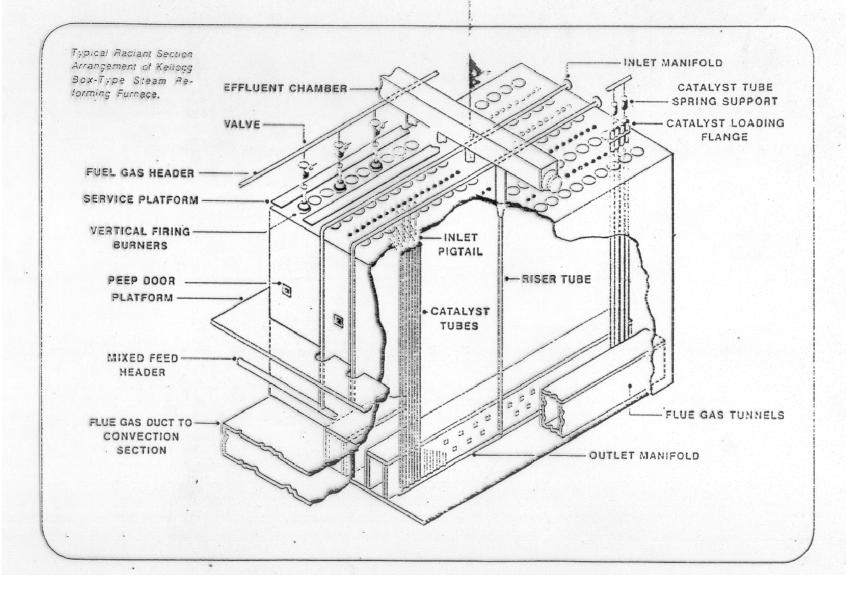
Uhde's Primary Reformer



KAFCO's Primary Reformer

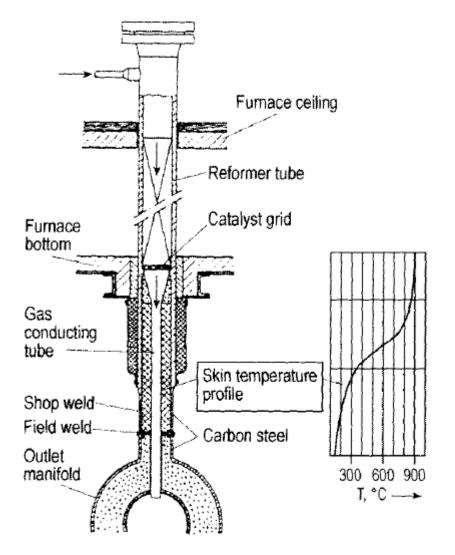


Cross Sectional View of a Primary Reformer

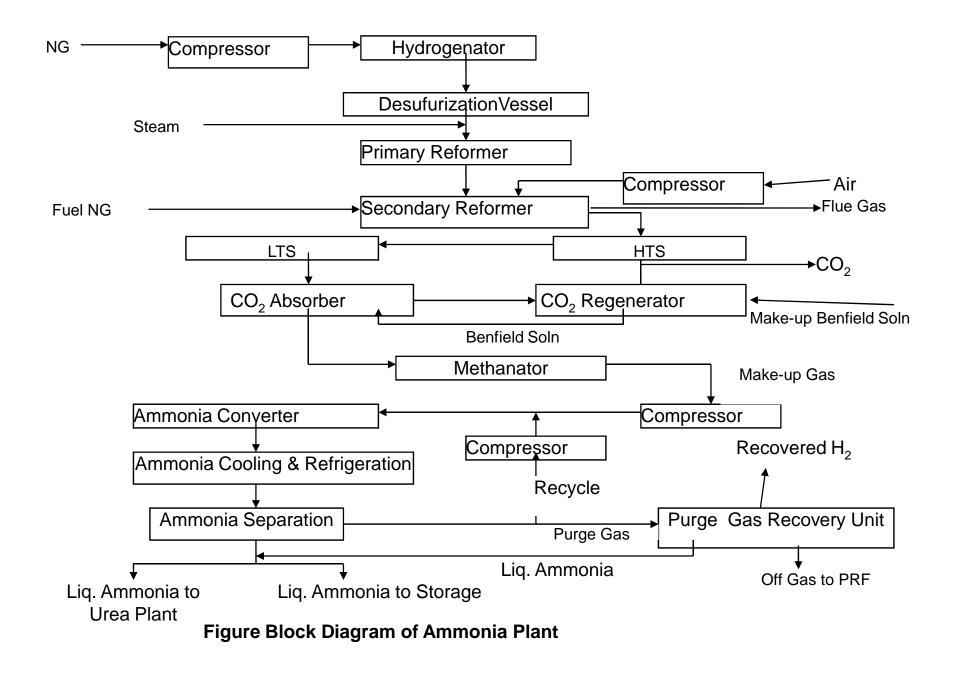


Tube Skin Temperature

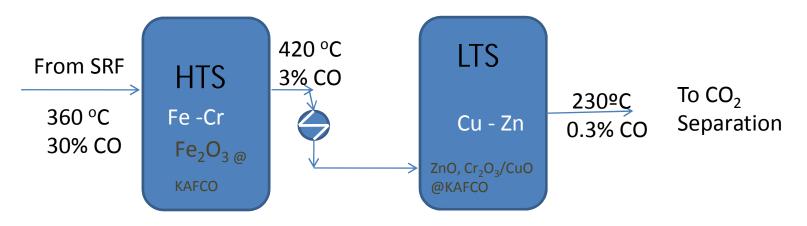
- Used to detect possible defects in lining
- Higher skin temperature cause uncontrolled stresses of the line
- Low silica refractory material is required to avoid plugging of the downstream equipment



High Temperature Shift Converter (HTS) and Low Temperature Shift Converter (LTS)



- CO retains in the CO₂ separation process which is poisonous for NH₃ synthesis catalyst.
- Thus for all synthesis gas producing process from NG, naptha, heavy oil or coal by steam reforming or partial oxidation requires shift reaction with the exception of coke oven gas.
- Reaction: CO + $H_2O \rightarrow H_2 + CO_2$ (Exothermic) PRF SRF
- High T Reac on rate ↑, Low T– equilibrium is more favorable, that is why two shift converter is used.



CO Conversion – Final Purification

Methanation

- Main objective of final purification is to remove residual CO and CO₂. Three different methods have been developed:
- Copper Liquor Scrubbing:
 - Early plants. Use Scrubbing solution contains cupric and cuprous ammoniacal salts of acids such as formic, acetic or carbonic plus an excess of ammonia. These salts forms complexes with the CO and hold it loosely.
 - Reactions:

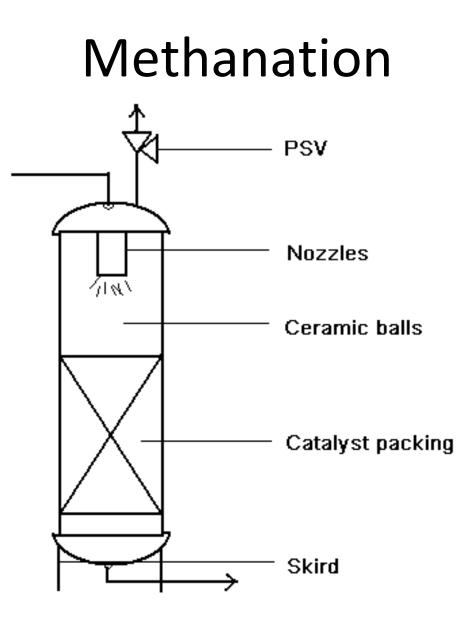
 $Cu(NH_3)_2A + CO + NH_4OH \leftrightarrow Cu(NH_3)_3A.CO + H_2O$

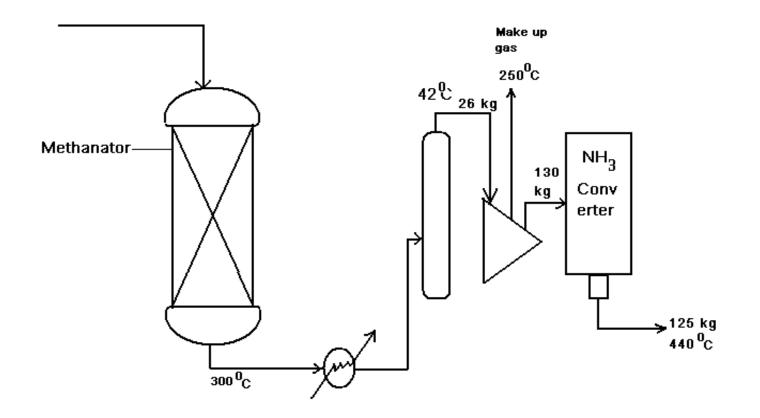
 $2NH_4OH + CO_2 \leftrightarrow (NH_4)_2CO_3 + H_2O$

- More expansive than methanation.
- High operating cost and difficult to control.
- Methanation: Simple, low cost, relatively trouble free

Cryogenic Scrubbing

- Most complete purification than any other methods
- Not only C'oxides removes but also reduce CH₄ and Ar content to low level.
- No purging is required
- Used mainly in conjunction with partial oxidation for synthesis gas production
- In steam reforming process, its use is limited due to high cost of air separation plant.





CO₂ Absoption

- To avoid catalyst poisoning and the produced CO₂ in this section is also a raw-material of urea manufacturing.
- Choice of Solvent:
 - Pressure: Must be of raw syngas
 - Concentration: Required CO₂ concentration of treated syngas. Raw syngas conc depends on feedstock.
 - Poisons: O2, CO, CO2 HCN in raw syngas can irreversibly react with the solvent. Such poisoning may require expensive pretreatments if solvent loss is not tolerated.
 - Utilities: Availability of LP steam for regeneration of solvent and driving the pumps.

CO₂ removal processes

- Water scrubbing, monoethanolamine (MEA) and absorption with hot potassium carbonate are widely used.
- □ WATER SCRUBBING:
 - Simple,
 - Inexpensive

- H₂ dissolves with CO₂
- H_2 loss is significant

□ MEA ABSOPRTION:

- Slightly above ambient temperature
- Pressure up to 600 psig
- Regeneration involves both pressure release and reboiling
- Heat duties are some-what higher than water scrubbing
- Corrosion protection requires above 230°F (Inhibitor)
 Reactions: 2 HOCH₂CH₂NH₂ + H₂O + CO₂ = (HOCH₂CH₂NH₃)₂CO₃ (HOCH₂CH₂NH₃)₂CO₃ + H₂O + CO₂ = 2 HOCH₂CH₂NH₂ + 2HCO₃

☐ HOT POTASSIUM CARBONATE

- High capacity for CO2
- Regenera on involves pressure release (Temp \uparrow)

 Activated by additives e.g., glycol, sucrose, dextrose, levulose, EG, methyl alcohol formaldehyde and lactose to increase the rate of CO₂ absorption.

- The identity of additives are proprietary under the name of BENFIELD, GIMMARCO-VETROCOKE, CATACARB, CARSOL and so on.

Reaction: $K_2CO_3 + CO_2 + H_2O = 2KHCO_3$

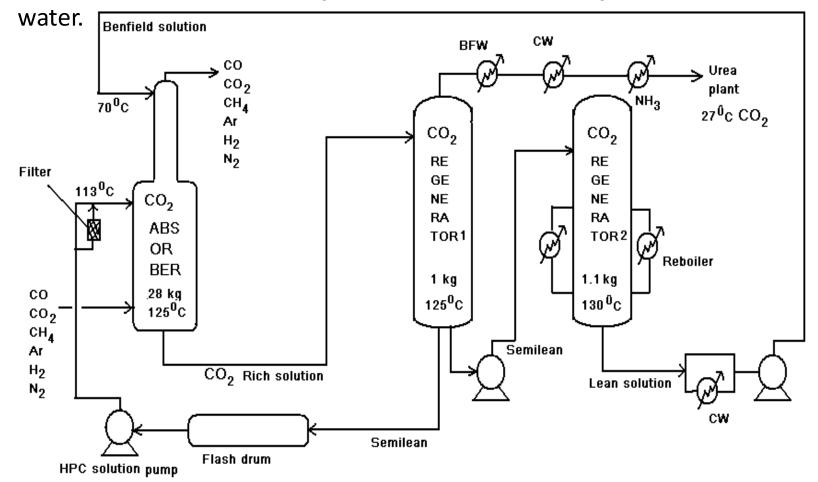
Name of Process	Temperature	Pressure
Benfield (Hot Potassium Carbonate with additives)	240 °F	400 psig
Giammarco-Vetrocoke (Hot potassium carbonate activated by As ₂ O ₃ , glycine and various ethanol amines)	50-100°C	75 atm and higher
Catacarb (Hot pottassium carbonate activated by amine- borate)	Temperature depends on purity	300-400 psig
Dual-Solvent Process (MEA-TEA)	60-90 oC	25-27 atm
Rectisol Process (organic solvents mostly methanol)	< 0°C	_

Design of CO₂ Removal Processes

- Absorption tower design of CO₂ removal is similar to general absorption tower design. Difference with the general absorption tower design is in size and the types of internals used to improve vapor-liquid contact.
- Regeneration tower design:
 - ➢ REDUCTION
 - Simplest, Desorption by releasing pressure
 - Dissolved CO2 is loaded under pressure is released in several stage
 - If inert waste N2 from air-separation unit is available, then this can be used indefinitely to strip the solvent most indefinitely.
 - Otherwise hot regeneration is required.
 - ➢ REGENERATION BY HEATING
 - Additional heat exchange surface requires for cooling the solvent before admission to the absorber if the absorber is to operate at low pressure.

Benfield Process

Benfield solution: 29% K₂CO₃, 2.9% DEA and 0.9% V₂O₅ with remaining



Catacarb single stage low heat design

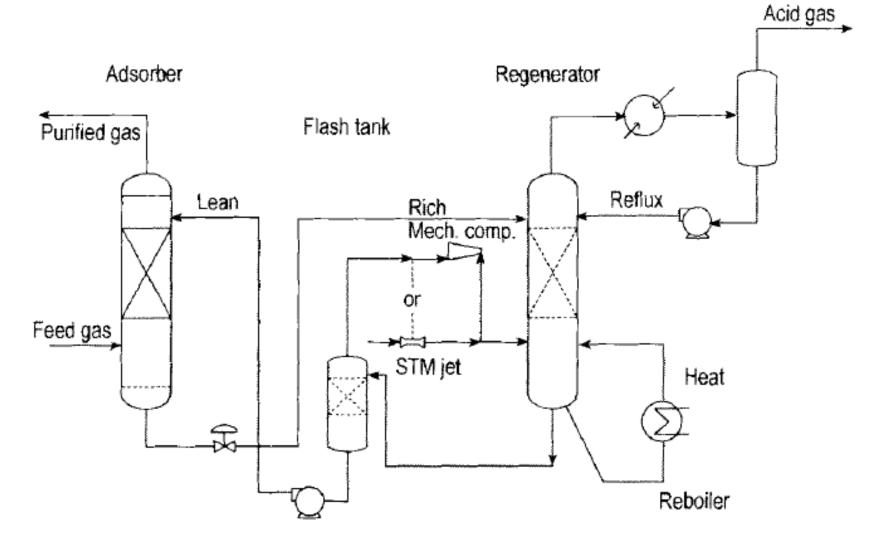
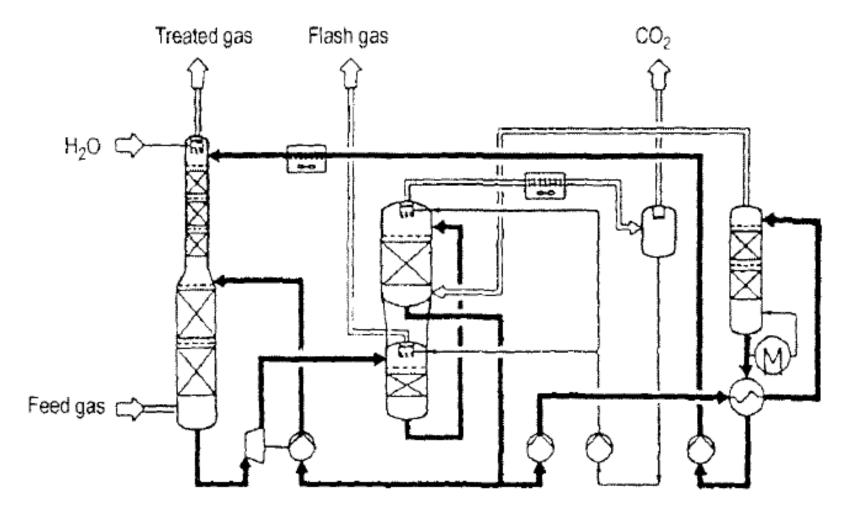


Figure 68. Catacarb single stage low heat design.

BASF aMDEA process



Selexol UOP process

