Conversion Processes

1. THERMAL PROCESSES

2. CATALYTIC PROCESSES

CATALYTIC PROCESSES

A. Fluid Catalytic Cracking (FCC)

B. Hydrotreating

C. Hydrocracking

D. Catalytic Reforming

E. Alkylation

A. Catalytic Cracking

- Main incentive for catalytic cracking is the need to increase gasoline production.

- Feedstocks are typically vacuum gas oil.

- Besides C-C cleavage many other reactions occur:
  - isomerization
  - protonation and deprotonation
  - alkylation
  - polymerization
  - cyclization and condensation

- The catalytic cracking process is very flexible, and operating parameters can be adjusted to meet changing product demand.

- *Catalytic cracking breaks complex hydrocarbons into simpler molecules* in order to increase the quality and decrease the amount of residuals.
- This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock into lighter fractions such as kerosene, gasoline, liquified petroleum gas (LPG), heating oil, and petrochemical feedstock.
- Catalytic cracking is similar to thermal cracking except:
1. catalysts facilitate the conversion of the heavier molecules into lighter products.
2. Use of a catalyst acts under much less severe operating conditions than in thermal cracking.
- Typical temperatures are from 850°-950° F at much lower pressures of 10-20 psi.

- Cracking is catalyzed by solid acids which promote the rupture of C-C bonds. The crucial intermediates are *carbocations* (+ve charged HC ions) formed by the action of the acid sites on the catalyst.

- The catalysts used in refinery cracking units are:
  ✓ Zeolite
  ✓ aluminum hydrosilicate
  ✓ treated bentonite clay
  ✓ fuller's earth
  ✓ Bauxite
  ✓ silica-alumina

- catalysts form:
  ✓ powders
  ✓ beads
  ✓ Pellets
  ✓ shaped materials called extrudites

- There are three basic functions in the catalytic cracking process:

1. **Reaction:** Feedstock reacts with catalyst and cracks into different hydrocarbons

2. **Regeneration:** Catalyst is reactivated by burning off coke

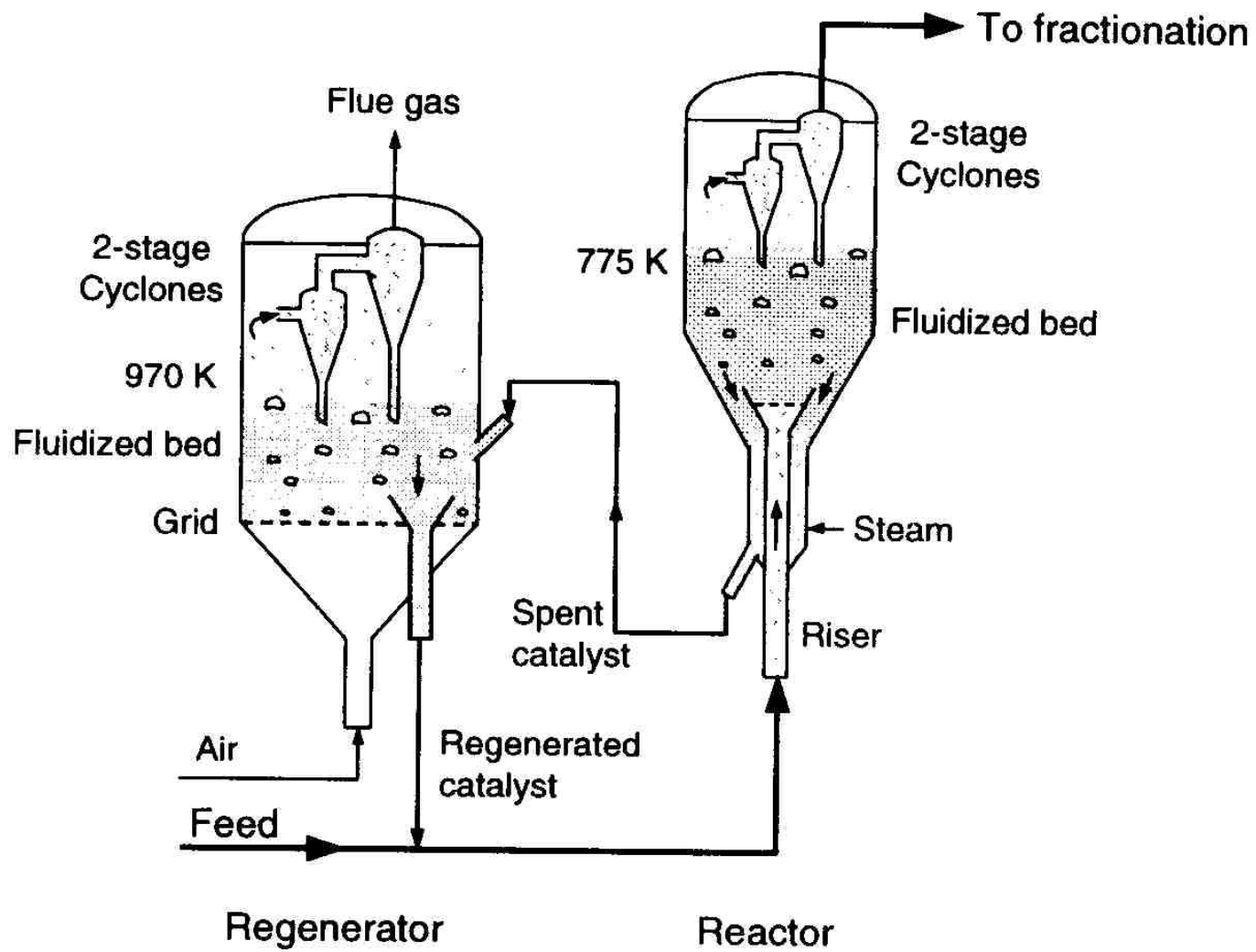3. **Fractionation:** Cracked hydrocarbon stream is separated into various products.

- The three types of catalytic cracking processes are

1. fluid catalytic cracking (FCC)
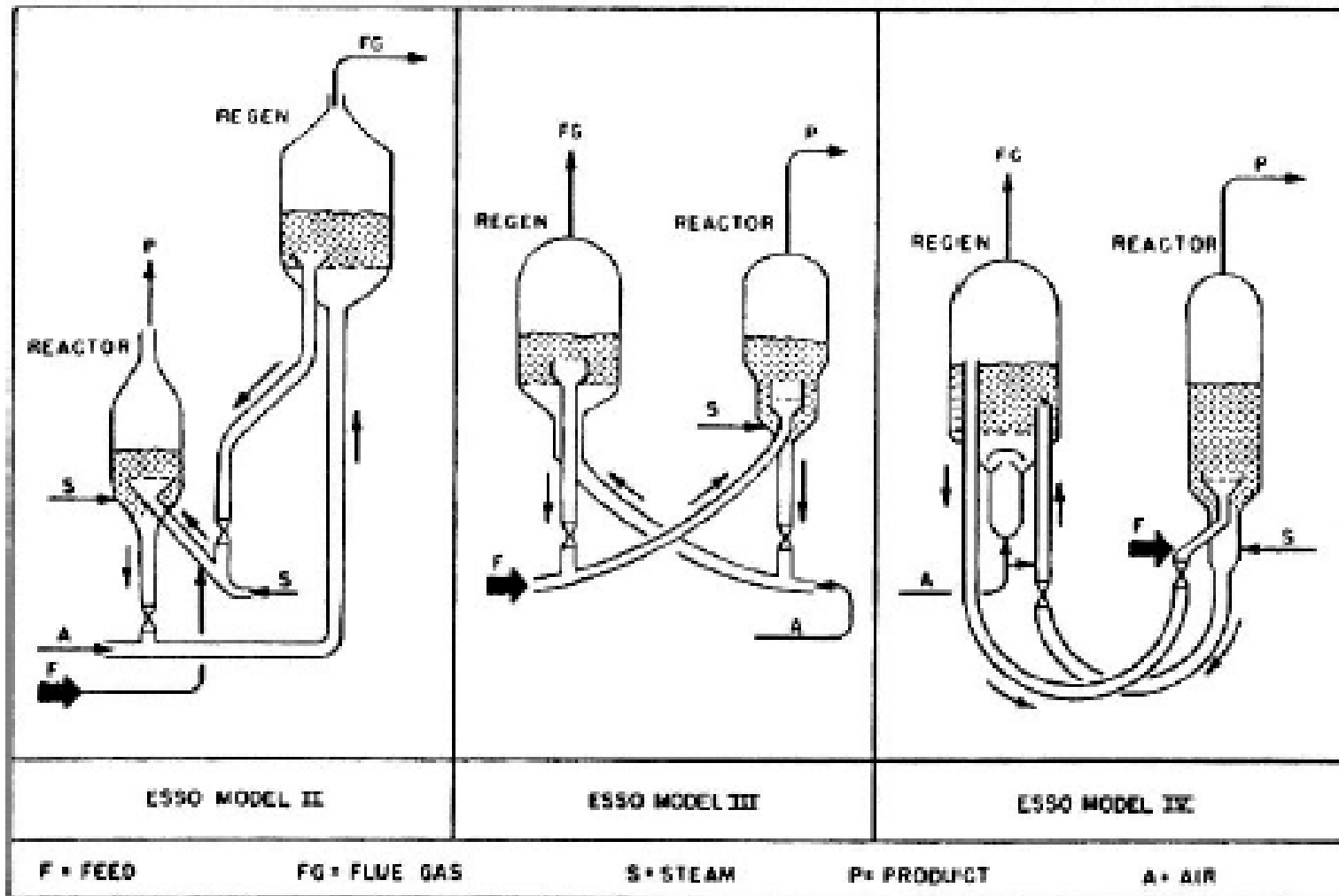2. moving-bed catalytic cracking
3. Thermofor catalytic cracking

A-1) Fluid Catalytic Cracking

- Oil is cracked in the presence of a finely divided catalyst, which is maintained in an aerated or fluidized state by the oil vapours.

- The fluid cracker consists of a catalyst section and a fractionating section that operate together as an integrated processing unit.

- The catalyst section contains the reactor and regenerator, which, with the standpipe and riser, form the catalyst circulation unit.

- The fluid catalyst is continuously circulated between the reactor and the regenerator using air, oil vapors, and steam as the conveying media.

- Preheated feed is mixed with hot, regenerated catalyst in the riser and combined with a recycle stream, vapourized, and raised to reactor temperature (485-540°C) by the hot catalyst.

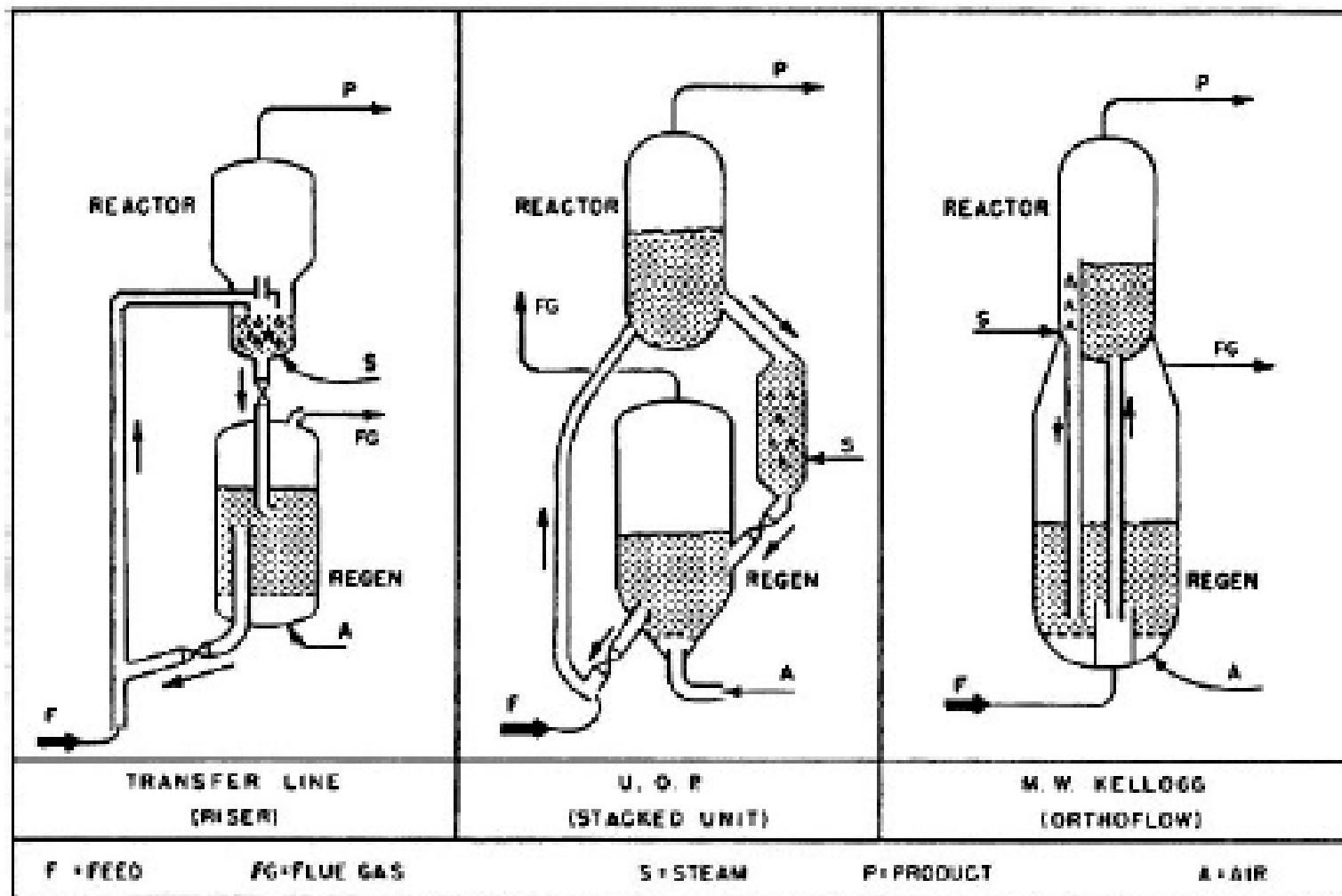- As the mixture travels up the riser, the charge is cracked at 0.7-2 bar.

- Spent catalyst is regenerated to get rid of coke that collects on the catalyst during the process.
- Spent catalyst flows through the catalyst stripper to the regenerator, where most of the coke deposits burn off at the bottom where preheated air and spent catalyst are mixed.
- Fresh catalyst is added and worn-out catalyst removed to optimize the cracking process.
- Fluid catalytic cracking or "cat cracking," is the basic gasoline-making process.
- Using intense heat (~1,000 F), low pressure and a powdered catalyst, the cat cracker can convert most relatively heavy fraction molecules.
- The FCC cracker consists of a catalyst section and a fractionating section that operate together as an integrated processing unit.
- The catalyst section contains the reactor and regenerator, which, with the standpipe and riser, forms the catalyst circulation unit.
- The fluid catalyst is continuously circulated between the reactor and the regenerator using air, oil vapors, and steam as the conveying media.

- A typical FCC process involves mixing a preheated hydrocarbon charge with hot, regenerated catalyst as it enters the riser leading to the reactor.
- The charge is combined with a recycle stream within the riser, vaporized, and raised to reactor temperature (900°-1,000° F) by the hot catalyst. As the mixture travels up the riser, the charge is cracked at 10-30 psi.
- In the more modern FCC units, all cracking takes place in the **riser.**
- This cracking continues until the oil vapors are separated from the catalyst in the reactor cyclones.
- The resultant product stream (cracked product) is then charged to a
- fractionating column where it is separated into fractions, and some of the heavy oil is recycled to the riser.
- Spent catalyst is regenerated to get rid of coke that collects on the catalyst during the process.
- Spent catalyst flows through the catalyst stripper to the regenerator, where most of the coke deposits burn off at the bottom where preheated air and spent catalyst are mixed.
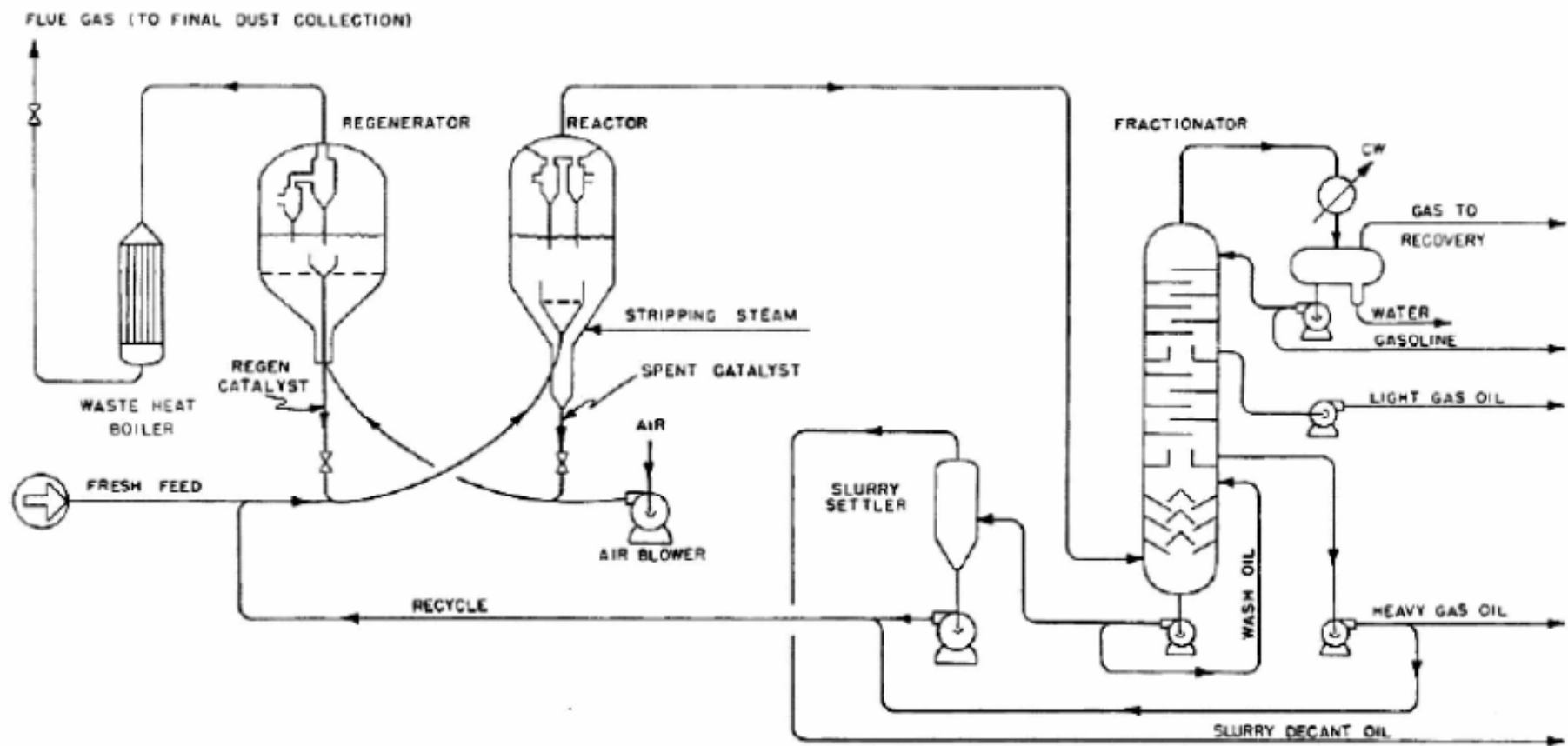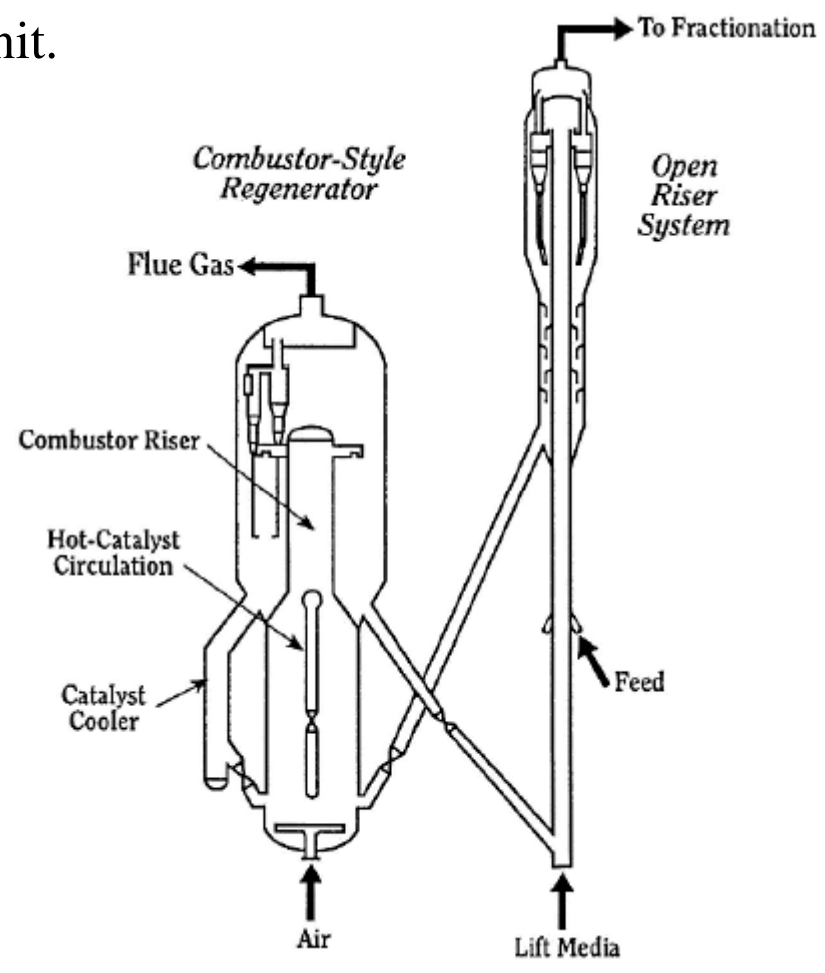- Fresh catalyst is addedand worn-out catalyst removed to optimize the cracking process.

To fractionation

Flue gas

2-stage Cyclones

970 K

Fluidized bed

Grid

Air

Feed

Regenerated catalyst

Regenerator

Spent catalyst

2-stage Cyclones

775 K

Fluidized bed

Steam

Riser

Reactor

10

REGEN REACTOR

FG = FLUE GAS

ESSO MODEL II   ESSO MODEL III   ESSO MODEL IV

F = FEED   FG = FLUE GAS   S = STEAM   P = PRODUCT   A = AIR

Older fluid catalytic-cracking (FCC) unit configurations.

Older fluid catalytic-cracking (FCC) unit configurations.   12

FLUE GAS (TO FINAL DUST COLLECTION)

REGENERATOR

REACTOR

FRACTIONATOR

CW

GAS TO RECOVERY

STRIPPING STEAM

WATER

GASOLINE

WASTE HEAT BOILER

REGEN CATALYST

SPENT CATALYST

LIGHT GAS OIL

AIR

FRESH FEED

AIR BLOWER

SLURRY SETTLER

WASH OIL

RECYCLE

HEAVY GAS OIL

SLURRY DECANT OIL

13

UOP FCC style unit.

To Fractionation

Combustor-Style
Regenerator

Open
Riser
System

Flue Gas

Combustor Riser

Hot-Catalyst
Circulation

Catalyst
Cooler

Feed

Air

Lift Media
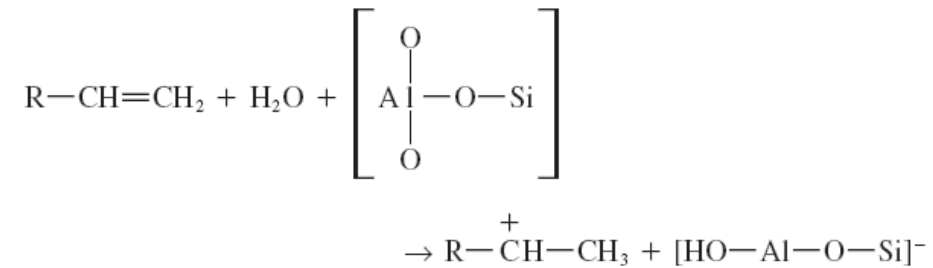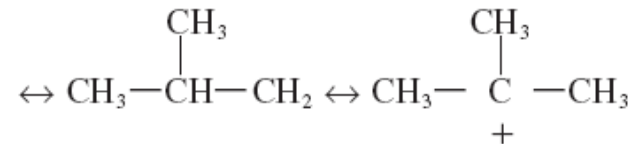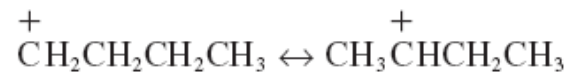
CRACKING REACTIONS

- primary reactionsPrimary reactions are designed as those involving the initial carbon–carbon bond scission and the immediate neutralization of the carbonium

✓ Paraffin → paraffin + olefin

✓ Alkyl naphthene → naphthene + olefin

✓ Alkyl aromatic → aromatic + olefin

- secondary reactions

1. carbonium ions are formed initially by a small amount of thermal cracking of n-paraffins to form olefins.

2. These olefins add a proton from the catalyst to form large carbonium ions which to form small carbonium ions and olefins.

3. The small carbonium ions propagate the chain reaction by transferring a hydrogen ion from a n-paraffin to form a small paraffin molecule

- *Step 1*: Mild thermal cracking initiation reaction.
- $nC_8H_{18} \rightarrow CH_4 + RECHCCH_2$
- *Step 2*: Proton shift.

$$R-CH{=}CH_2 + H_2O + \begin{bmatrix} & O & \\ & \| & \\ Al & -O-Si \\ & | & \\ & O & \end{bmatrix}$$

$$\rightarrow R-\overset{+}{C}H-CH_3 + [HO-Al-O-Si]^-$$

- *Step 3*: Beta scission.

$$R-\overset{+}{C}H-CH_3 \rightarrow CH_3CH_2{=}CH_2 + \overset{+}{C}H_2CH_2CH_2CH_3$$

- *Step 4*: Rearrangement toward more stable structure. The order of carbonium ion stability is tertiary> secondary> primary.

$$\overset{+}{C}H_2CH_2CH_2CH_3 \leftrightarrow CH_3\overset{+}{C}HCH_2CH_3$$

$$\leftrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2 \leftrightarrow CH_3-\underset{+}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

- *Step 5*: Hydrogen ion transfer.

$$CH_3-\underset{+}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 + C_8H_{18} \rightarrow i\text{-}C_4H_{10} + CH_3\overset{+}{C}HCH_2R$$

Thus another large carbonium ion is formed and the chain is ready to repeat itself.

CRACKING OF PARAFFINS

- The catalytic cracking of paraffins is characterized by

1. high production of C3 and C4 hydrocarbons in the cracked gases

2. reaction rates and products determined by size and structure of paraffins

3. isomerization to branched structures

4. aromatic hydrocarbons formation resulting from secondary reactions involving olefins.

OLEFIN CRACKING

- The catalytic cracking rates of olefinic hydrocarbons are much higher than those of the corresponding paraffins.

- The main reactions are :

1. Carbon–carbon bond scissions

2. Isomerization

3. Polymerization

4. Saturation, aromatization, and carbon formation

- Olefin isomerization followed by saturation and aromatization are responsible for the high octane number and lead susceptibility of catalytically cracked gasolines.

- The higher velocity of hydrogen transfer reactions for branched olefins results in ratios of iso- to normal paraffins higher than the equilibrium ratios of the parent olefins.

- naphthenes act as hydrogen donors in transfer reactions with olefins to yield isoparaffins and aromatics.

CRACKING OF NAPHTHENIC HYDROCARBONS

- dehydrogenation to aromatics

- There is also carbon–carbon bond scission in both the ring and attached side chains but at temperatures below 1000°F (540°C) the dehydrogenation reaction is considerably greater.

- Dehydrogenation is very extensive for C9 and larger naphthenes and a high-octane gasoline results.

- The non-ring liquid products and cracked gases resulting from naphthenic hydrocarbon cracking are more saturated than those resulting from cracking paraffins.

AROMATIC HYDROCARBON CRACKING

- Aromatic hydrocarbons with alkyl groups containing less than three carbon atoms are not very reactive.

- The predominant reaction for aromatics with long alkyl chains is the clean **splitting off of side chains** without breaking the ring.

CRACKING CATALYSTS

- Commercial cracking catalysts can be divided into three classes:

(1) acid-treated natural aluminosilicates

(2) amorphous synthetic silica-alumina combinations

(3) crystalline synthetic silica-alumina catalysts called zeolites or molecular sieves.

- Most catalysts used in commercial units today are either class 3 or mixtures of classes 2 and 3 catalysts.

- The advantages of the zeolite catalysts
1. Higher activity
2. Higher gasoline yields at a given conversion
3. Production of gasolines containing a larger percentage of paraffinic and aromatic hydrocarbons
4. Lower coke yield (and therefore usually a larger throughput at a given conversion level)
- 5. Increased isobutane production
- 6. Ability to go to higher conversions per pass without overcracking

The high activity of zeolitic cracking catalyst permits short residence time cracking and has resulted in most cracking units being adapted to riser cracking operations

Comparison of Amorphous and Zeolite Catalysts

	Amorphous	Zeolite
Coke, wt%	4	4
Conversion, vol%	55	65
C_5+ gasoline, vol%	38	51
C_3- gas, wt%	7	6
C_4's, vol%	17	16

- The catalytic effects of zeolitic catalysts can be achieved with only 10 to 25% of the circulating catalyst as zeolites and the remainder amorphous silica-alumina cracking catalyst.

- Amorphous catalysts have higher attrition resistance and are less costly than zeolitic catalysts.

- thus obtain the benefits of the higher activity and gasoline selectivity of the zeolites and the lower costs and make-up rates of the amorphous catalysts.

Poisons of cracking catalysts

- basic nitrogen compounds, iron, nickel, vanadium, and copper

❖ The nitrogen reacts with the acid centers on the catalyst and lowers the catalyst activity.

❖ The metals deposit and accumulate on the catalyst and cause a reduction in throughput by increasing coke formation and decreasing the amount of coke burn-off per unit of air by catalyzing coke combustion to CO2 rather than to CO.

❖ nickel has about four times as great an effect on catalyst activity and selectivity as vanadium

❖ deposition of nickel and vanadium reduces catalyst activity by occupying active catalytic sites, promote the formation of gas and coke and reduce the gasoline yield at a given conversion level.

A-2) Moving Bed Catalytic Cracking

- The moving-bed catalytic cracking process is similar to the FCC process.

- The catalyst is in the form of pellets that are moved continuously to the top of the unit by conveyor or pneumatic lift tubes to a storage hopper, then flow downward by gravity through the reactor, and finally to a regenerator.

- The regenerator and hopper are isolated from the reactor by steam seals.

- The cracked product is separated into recycle gas, oil, clarified oil, distillate, naphtha, and wet gas. 25

A-3)Thermofor Catalytic Cracking

- the preheated feedstock flows by gravity through the catalytic reactor bed.

- The vapors are separated from the catalyst and sent to a fractionating tower.

- The spent catalyst is regenerated, cooled, and recycled.

- The flue gas from regeneration is sent to a carbon monoxide boiler for heat recovery.

PROCESS VARIABLES

- the major operating variables
1. charge stock
2. the cracking temperature
3. catalyst/oil ratio
4. space velocity
5. catalyst type and activity,
6. recycle ratio.
- For a better understanding of the process, several terms
- should be defined.

- ❖ *Activity*: *Ability to crack a gas oil to lower boiling fractions.*

- ❖ *Catalyst/oil ratio* *(C/O) : lb catalyst/lb feed.*

- ❖ *Conversion :*

- ❖ *100 (volume of feed _ volume of cycle stock)/volume of* feed.

- ❖ *Cycle stock*: *Portion of catalytic-cracker effluent not converted to*

- ❖ naphtha and lighter products [generally the material boiling above 430°F (220°C)]

- ❖ *Efficiency : (% gasoline / %conversion) x 100.*

- ❖ *Recycle ratio : Volume recycle / volume fresh feed.*

- ❖ *Selectivity: The ratio of the yield of desirable products to the yield of* undesirable products (coke and gas).

❖ ***Space velocity****: Space velocity may be defined on either a volume* (LHSV) or a weight (WHSV) basis.

 In a fluidized-bed reactor, the LHSV has little meaning because it is difficult to establish the volume of the bed.

The weight of the catalyst in the reactor can be easily determined or calculated from the residence time and C/O ratio.

❖ ***LHSV :***

Liquid hour space velocity in volume feed/(volume catalyst) (hr).

❖ ***WHSV :***

❖ *(Weight hour space velocity in lb feed)/(lb catalyst) (hr).*

❖ ***Severity factor*** *= (C/O) / WHSV*

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- Within the limits of normal operations, increasing

1- Reaction temperature

2- Catalyst/oil ratio

3- Catalyst activity

4- Contact time

5. Decrease in space velocity

- results in an increase in conversion

- It should be noted that an increase in conversion does not necessarily mean an increase in gasoline yield, as an increase in temperature above a certain level can increase conversion, coke and gas yields, and octane number of the gasoline but decrease gasoline yield.

Comparison between thermal and catalytic cracking

Catalytic cracking differences with Thermal Cracking

1. uses a catalyst
2. lower temperature
3. lower pressure
4. more flexible
5. different reaction mechanisms (ionic vs. free radical)
6. High thermal efficiency
7. Good integration of cracking and regeneration
8. High yields of gasoline and other distillates
9. Low gas yields
10. High product selectivity
11. Low n-alkane yields
12. High octane number
13. Chain-branching and high yield of C4 olefins
14. High yields of aromatics.

B- Catalytic hydrotreating

- *Catalytic hydrotreating is a hydrogenation process used to remove about* 90% of contaminants such **as nitrogen, sulfur, oxygen, and metals** from liquid petroleum fractions.

- hydrotreating is done prior to processes such as catalytic reforming so that the catalyst is not contaminated by untreated feedstock and catalytic cracking so reduce sulfur and improve product yields, and to upgrade middle-distillate petroleum fractions into finished kerosene, diesel fuel, and heating fuel oils.

- hydrotreating converts olefins and aromatics to saturated compounds.

Hydrotreating
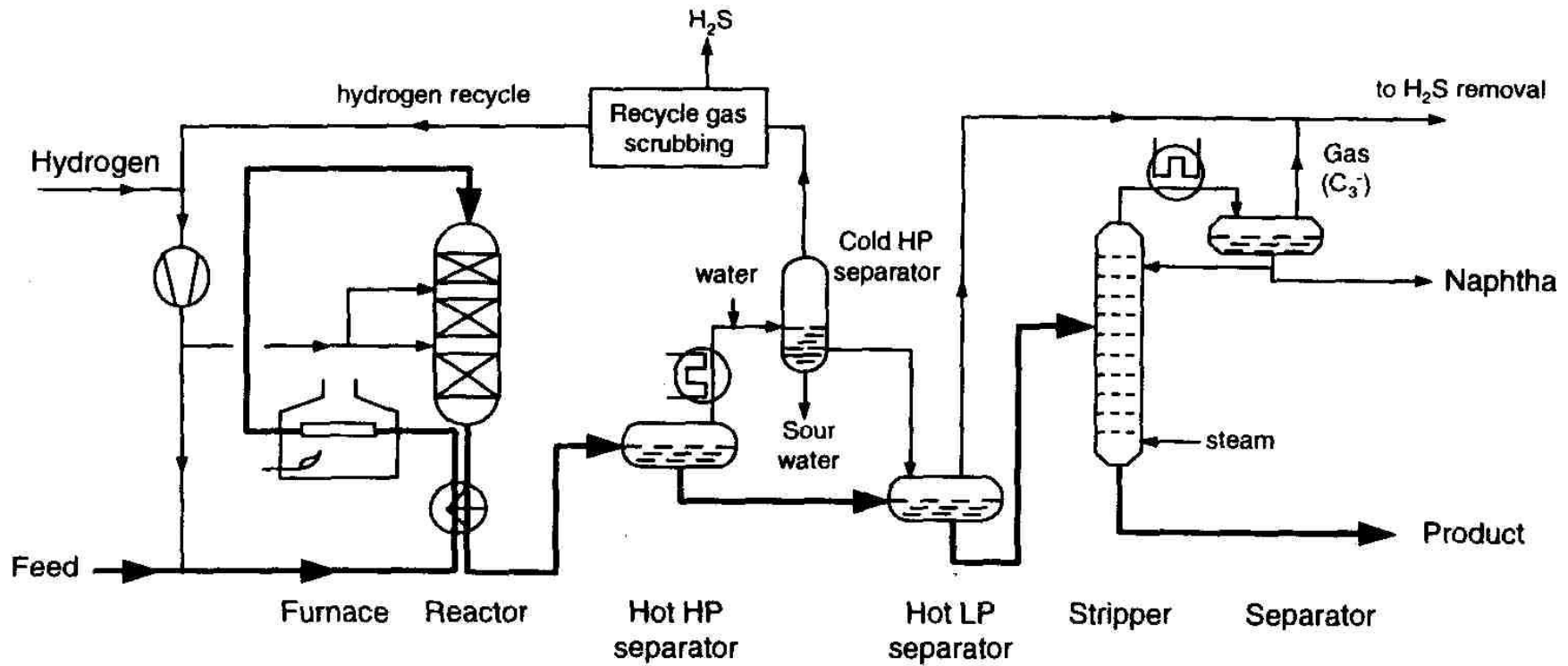
Hydrotreating: trickle-bed reactor
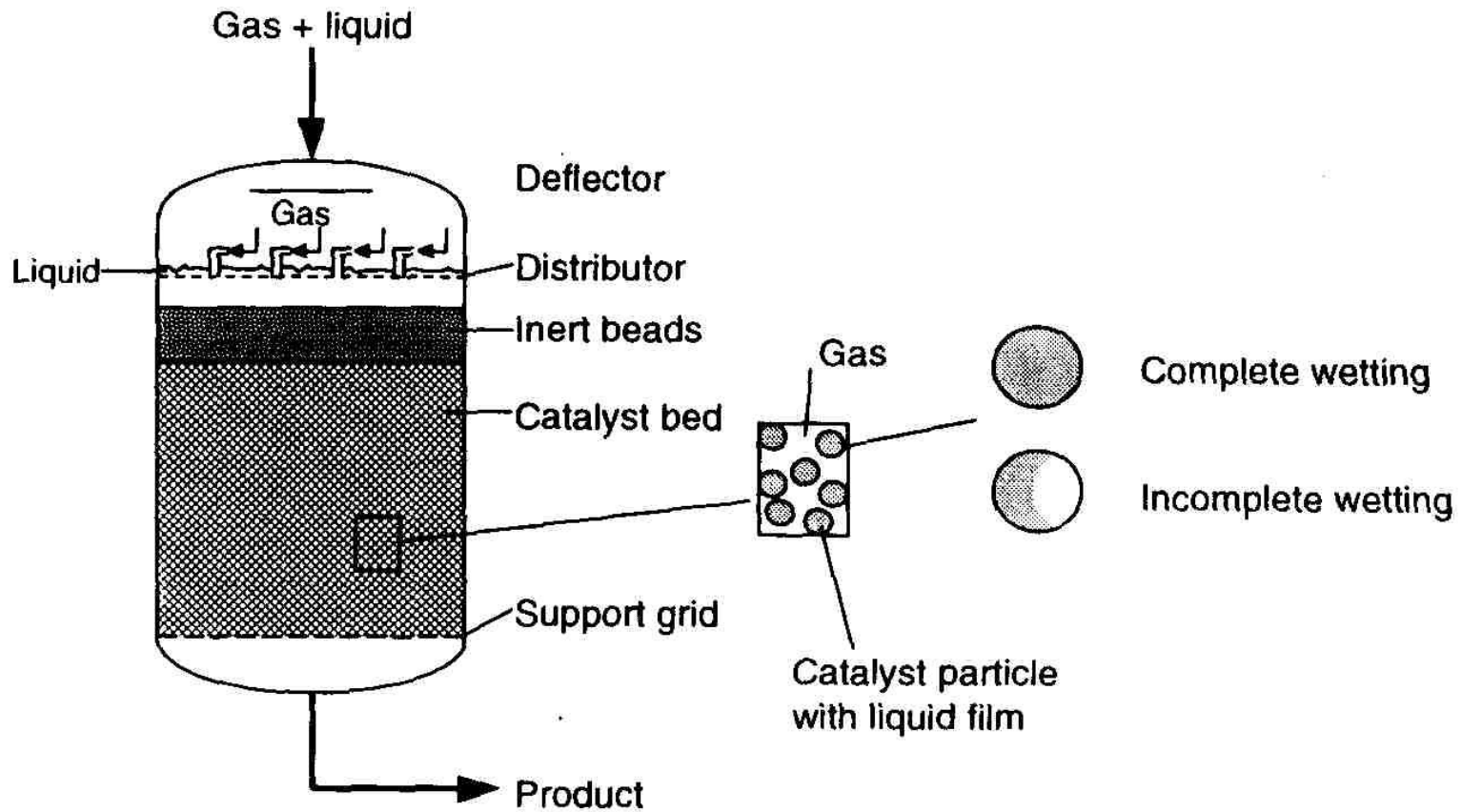
Catalytic Hydrodesulfurization Process

- Hydrotreating for sulfur removal is called hydrodesulfurization.

- In a typical catalytic hydrodesulfurization unit, the feedstock is deaerated and mixed with hydrogen, preheated in a fired heater (600°-800° F) and then charged under pressure (up to 1,000 psi) through a fixed-bed catalytic reactor.

- In the reactor, the sulfur and nitrogen compounds in the feedstock are converted into hydrogen sulfide (H_2S) and ammonia (NH_3).

- The reaction products leave the reactor and after cooling to a low temperature enter a liquid/gas separator.

- The hydrogen-rich gas from the high-pressure separation is recycled to combine with the feedstock, and the low-pressure gas stream rich in H_2S is sent to a gas treating unit where H_2S is removed.

- The clean gas is then suitable as fuel for the refinery furnaces.

- The liquid stream is the product from hydrotreating and is normally sent to a stripping column for removal of H_2S and other undesirable components.

- In cases where steam is used for stripping, the product is sent to a vacuum drier for removal of water. Hydrodesulfurized products are blended or used as catalytic reforming feedstock.

Catalytic Hydrodesulfurization
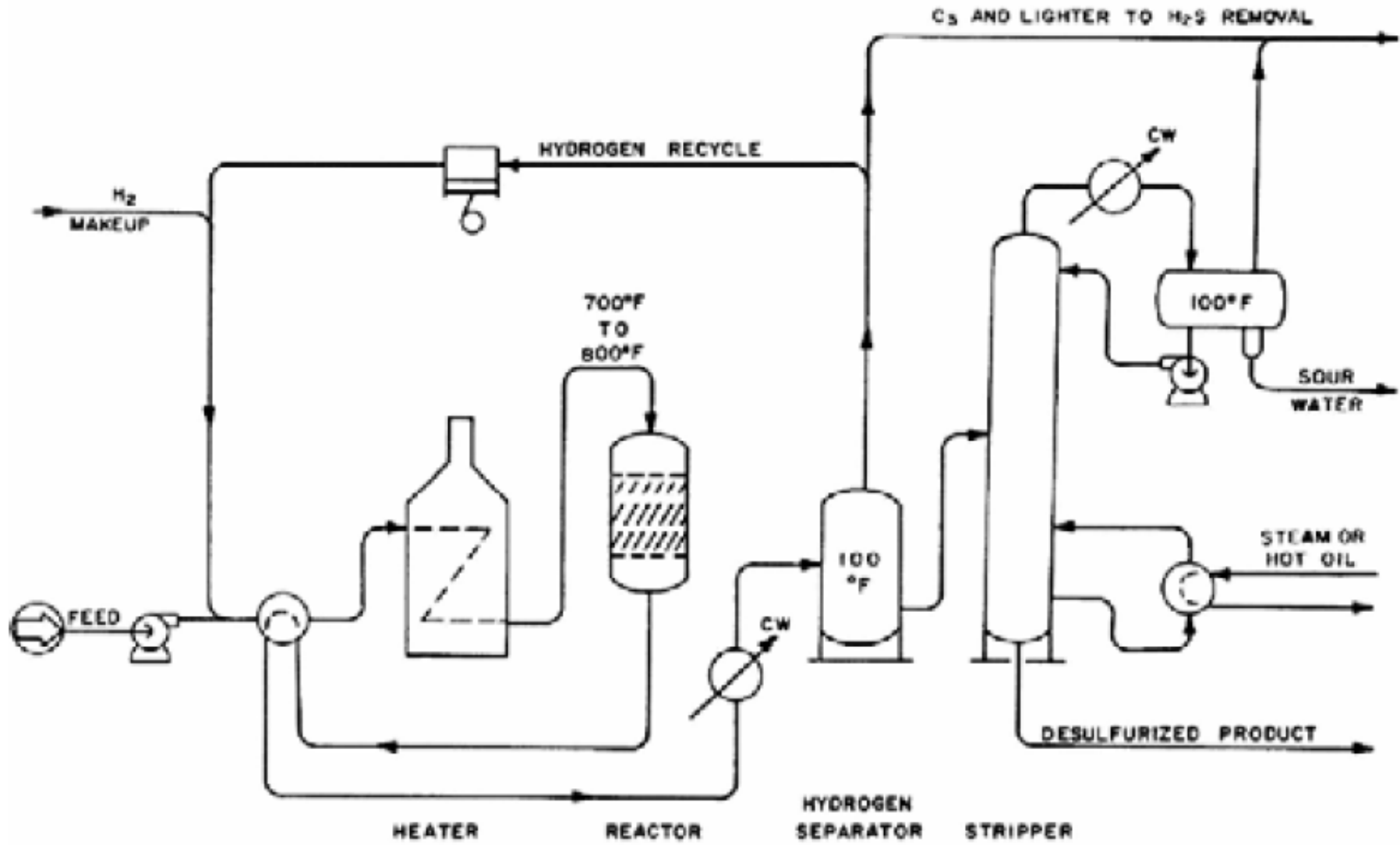
C. Hydrocracking

- *Hydrocracking is a two-stage process combining catalytic cracking and* hydrogenation, wherein heavier feedstocks are cracked in the presence of hydrogen to produce more desirable products.

- The process employs high pressure, high temperature, a catalyst, and hydrogen.

- The hydrocracking process largely depends on the nature of the feedstock and the relative rates of the two competing reactions, hydrogenation and cracking.

- Heavy aromatic feedstock is converted into lighter products under a wide range of very high pressures (1,000-2,000 psi) and fairly high temperatures (750°-1,500° F), in the presence of hydrogen and

- special catalysts.

- Hydrocracking produces relatively large amounts of isobutane for alkylation feedstock. Hydrocracking also performs isomerization for pour-point control and smoke-point control, both of which are important in high-quality jet fuel.

Hydro cracking feed stocks

- Hydrocracking is used for feed stocks that are difficult to process by either catalytic cracking or reforming, since these feed stocks are

1. high polycyclic aromatic content

2. high concentrations of the two principal catalyst poisons, sulfur and nitrogen compounds.

Important role of hydrogen

1. When the feedstock has a high paraffinic content, the primary function of hydrogen is to prevent the formation of polycyclic aromatic compounds.

2. to reduce tar formation and prevent buildup of coke on the catalyst.

3. Hydrogenation also serves to convert sulfur and nitrogen compounds present in the feedstock to hydrogen sulfide and ammonia.

Hydrocracking Process

- Preheated feedstock is mixed with recycled hydrogen and sent to the first-stage reactor, where catalysts convert sulfur and nitrogen compounds to H_2S and NH_3. Limited hydrocracking also occurs.

- After the hydrocarbon leaves the first stage, it is cooled and liquefied and run through a separator. The hydrogen is recycled to the feedstock.

- The liquid is charged to a fractionator.

- The fractionator bottoms are again mixed with a hydrogen stream and charged to the second stage. Since this material has already been subjected to some hydrogenation, cracking, and reforming in the first stage, the operations of the second stage are more severe (higher temperatures and pressures). Again, the second stage product is separated from the hydrogen and charged to the fractionator.

- Depending on the products desired (gasoline components, jet fuel, and gas oil), the fractionator is run to cut out some portion of the first stage reactor outturn.

- Kerosene-range material can be taken as a separate side-draw product or included in the fractionator bottoms with the gas oil.

- The fractionator bottoms are again mixed with a hydrogen stream and charged to the second stage.

- Since this material has already been subjected to some hydrogenation, cracking, and reforming in the first stage, the operations of the second stage are more severe (higher temperatures and pressures).

- Like the outturn of the first stage, the second stage product is separated from the hydrogen and charged to the fractionator.

Difference between FCC and HYDCRC

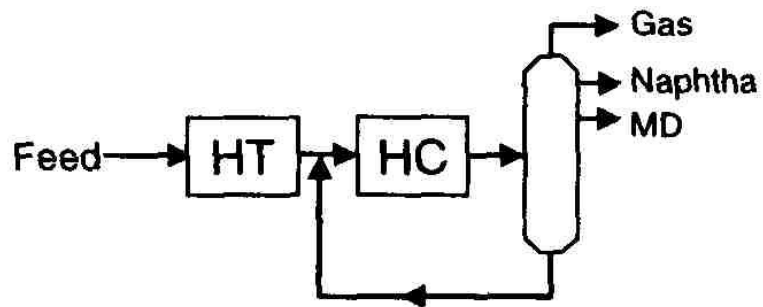| FCC	HYDCRC
Carbon rejection	Hydrogen addition
Endothermic	Exothermic
Acid catalyst	Metal catalyst on acid support
More gas	less gas
More coke	less coke but a costly process

Hydrocracking process configuration
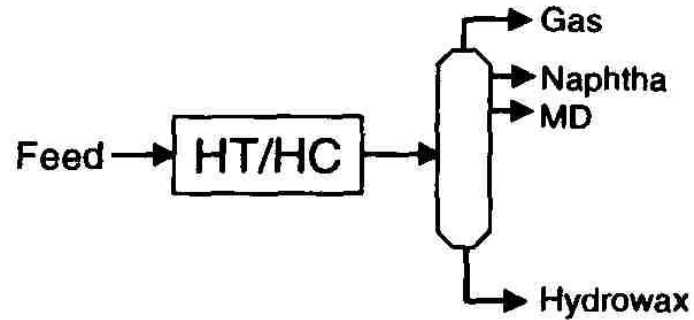
Single stage / once through
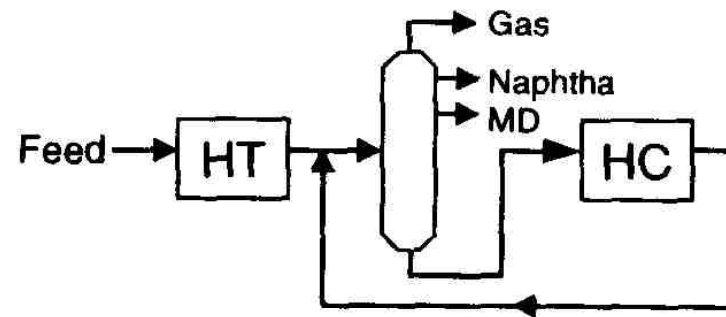
Two stage

Series flow

Hydrocracking flow scheme

Fresh hydrogen

Hydrogen recycle

Purge

to acid gas and NH$_3$ removal

Quench H$_2$

Quench H$_2$

C$_1$ – C$_4$

Naphtha

Middle distillates

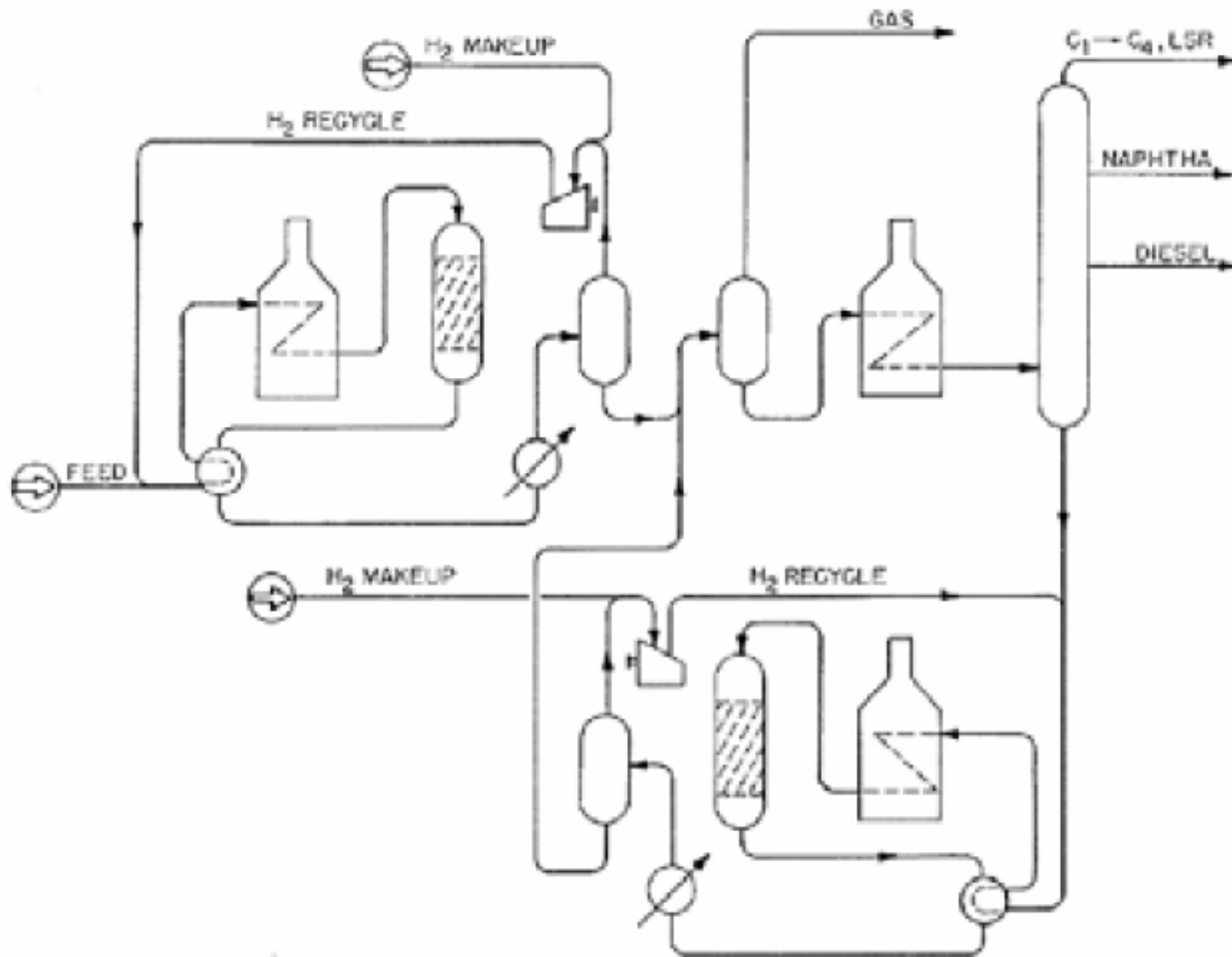Feed

Furnace   Reactor   Furnace   Reactor   High/Low pressure separators   Fractionator
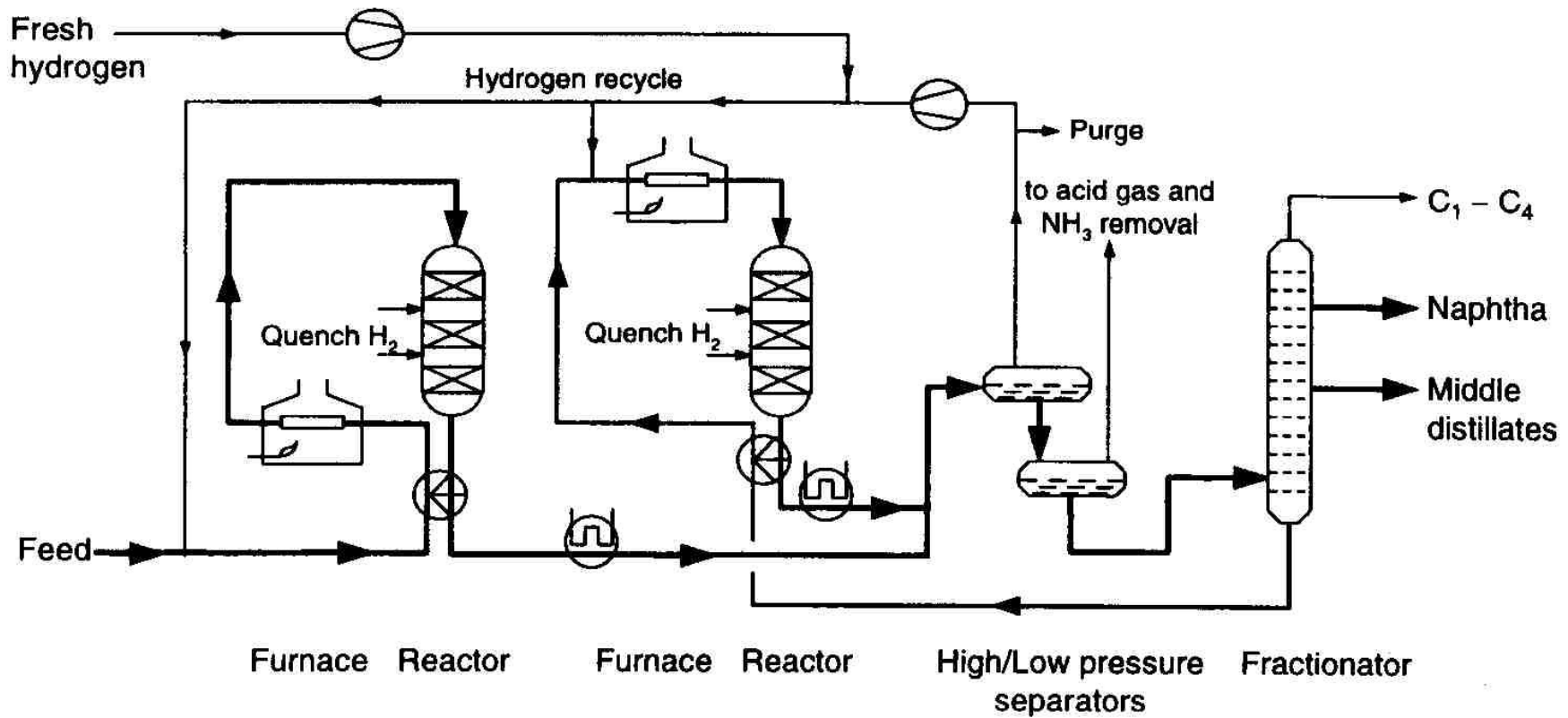
Two-Stage Hydrocracking

D. Catalytic Reforming

- Catalytic reforming is an important process used to convert low-octane naphthas into high-octane gasoline blending components called reformates.

- Reforming represents the total effect of numerous reactions such as cracking, polymerization, dehydrogenation, and isomerization taking place simultaneously.

- Hydrogen, a significant by-product, is separated from the reformate for recycling and use in other processes.

- Depending on the properties of the naphtha feedstock (as measured by the paraffin, olefin, naphthene, and aromatic content) and catalysts used, reformates can be produced with very high concentrations of benzene, toluene, xylene, (BTX) and other aromatics useful in gasoline blending and petrochemical processing.

Feedstocks of catalytic reformers

- The typical feed stocks to catalytic reformers are
1. Heavy straight-run (HSR) gasolines
2. Naphthas 82–190°C
3. heavy hydrocracker naphthas
- These are composed of the four major hydrocarbon groups: paraffins, olefins, naphthenes, and aromatics (PONA).
- Typical feed stocks and reformer products have the following PONA analyses (vol %):

Component	Feed	Product
Paraffins	30–70	30–50
Olefins	0–2	0–2
Naphthenes	20–60	0–3
Aromatics	7–20	45–60

- The paraffins and naphthenes undergo two types of reactions in being converted to higher octane components: cyclization and isomerization.
- The ease and probability of either of these occurring increases with the number of carbon atoms in the molecules and it is for this reason that only the HSR gasoline is used for reformer feed.
- The LSR gasoline C5 -82°C is largely composed of lower-molecular-weight paraffins that tend to crack to butane and lighter fractions and it is not economical to process this stream in a catalytic reformer.
- Hydrocarbons boiling above 204°C are easily hydrocracked and cause an excessive carbon laydown on the catalyst.

Feedstock and Product

Feedstock: Heavy Naphtha
Paraffins   45-55 %
Olefins   0-2 %
Naphthenes   30-40 %
Aromatics   5-10 %
Product: High Octane Gasoline:
Paraffins   30-50 %
Olefins   0 %
Naphthenes 5 –10 %
Aromatics   45-60 %

REACTIONS

- As in any series of complex chemical reactions, reactions occur which produce undesirable products in addition to those desired.

- Reaction conditions have to be chosen that favor the desired reactions and inhibit the undesired ones. Desirable reactions in a catalytic reformer all lead to the formation of aromatics and isoparaffins as follows:

1. Paraffins are isomerized and to some extent converted to naphthenes. The naphthenes are subsequently converted to aromatics.

2. Olefins are saturated to form paraffins which then react as in.

3. Naphthenes are converted to aromatics.

4. Aromatics are left essentially unchanged.

- Reactions leading to the formation of undesirable products include:

1. Dealkylation of side chains on naphthenes and aromatics to form butane and lighter paraffins

2. Cracking of paraffins and naphthenes to form butane and lighter paraffins

- As the catalyst ages, it is necessary to change the process operating conditions to maintain the reaction severity and to suppress undesired reactions

Reaction	Example	ΔH^{o}_{298} (kJ/mol)

Isomerization   C—C—C—C—C—C—C ⟶ C—C—C—C—C—C with C branch   −4

Cyclization   C—C—C—C—C—C—C ⟶ (cyclohexane)—C + H₂   +33

Aromatization   (cyclohexane)—C ⟶ (benzene)—C + 3 H₂   +205

Combination   (cyclopentane)—C—C ⟶ (cyclohexane)—C ⟶ (benzene)—C + 3 H₂   +177

Scheme 3.4   Reactions occurring during catalytic reforming.

There are four major reactions that take place during reforming. They are:

(1)   Dehydrogenation of naphthenes to aromatics
(2)   Dehydrocyclization of paraffins to aromatics
(3)   Isomerization
(4)   Hydrocracking
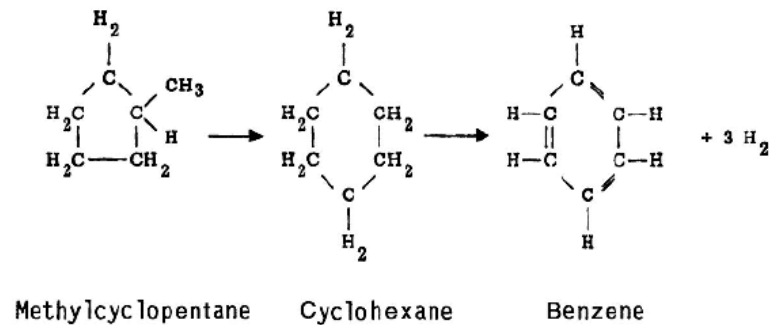
Dehydrogenation Reactions

- The dehydrogenation reactions are highly **endothermic and cause a decrease in temperature** as the reaction progresses.

- the dehydrogenation reactions have the highest reaction rates of the reforming reactions which <u>necessitates the use of the inter-heaters between catalyst beds</u> to keep the mixture at sufficiently high temperatures for the reactions to proceed at practical rates.

- Aromatics have a higher liquid density than paraffins or naphthenes with the same number of carbon atoms, so 1 volume of paraffins produces only 0.77 volumes of aromatics, and 1 volume of naphthenes about 0.87 volume.

- Conversion to aromatics increases the gasoline end point because the boiling points of aromatics are higher than the boiling points of paraffins and naphthenes with the corresponding number of carbons.
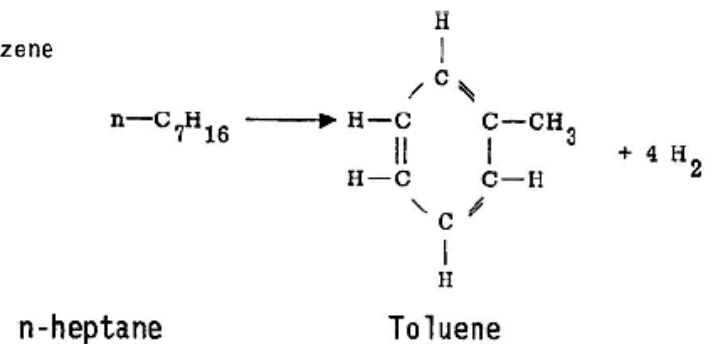
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Dehydrogenation reactions

1. Dehydrogenation of alkylcyclohexanes
 to aromatics (faster than others):

Methylcyclohexane   Toluene
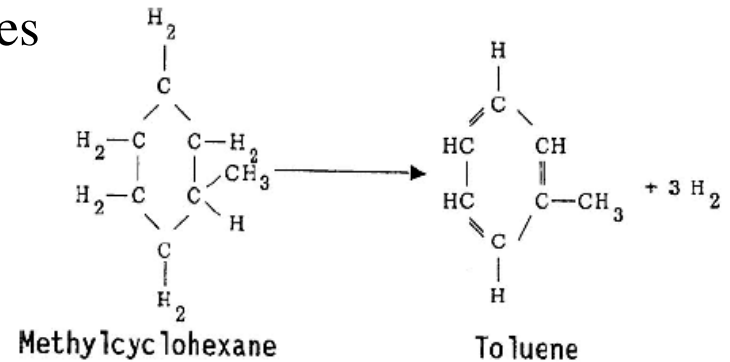
2. Dehydroisomerization of alkylcyclopentanes to aromatics:

Methylcyclopentane   Cyclohexane   Benzene

3. Dehydrocyclization of paraffins
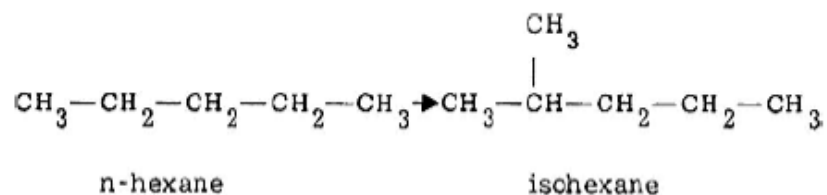to aromatics:

n-heptane   Toluene

Dehydrogenation reactions

- The yield of aromatics is increased by:

1. High temperature (increases reaction rate but adversely affects chemical equilibrium)

2. Low pressure (shifts chemical equilibrium ''to the right'')

3. Low space velocity (promotes approach to equilibrium)

4. Low hydrogen-to-hydrocarbon mole ratios (shifts chemical equilibrium ''to the right,'' however, a sufficient hydrogen partial pressuremust be maintained to avoid excessive coke formation)
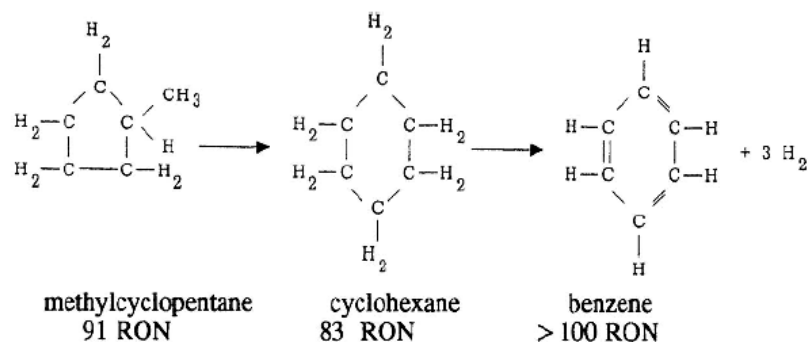
Isomerization Reactions

❖ Isomerization of paraffins and cyclopentanes usually results in a lower octane product than does conversion to aromatics.

❖ These are fairly rapid reactions with small heat effects.

1. Isomerization of normal paraffins to isoparaffins:

$$CH_3-CH_2-CH_2-CH_2-CH_3 \rightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_3$$

n-hexane   ischexane

2. Isomerization of alkylcyclopen⬚   ⬚
     conversion to benzene:

methylcyclopentane   cyclohexane   benzene
91 RON   83 RON   > 100 RON

Isomerization Reactions

✓ Isomerization yield is increased by:

1. High temperature (which increases reaction rate)

2. Low space velocity

3. Low pressure

✓ There is no isomerization effect due to the hydrogen-to-hydrocarbon mole ratios, but high hydrogen-to-hydrocarbon ratios reduce the hydrocarbon partial pressure and thus favor the formation of isomers.

Hydrocracking Reactions

- The hydrocracking reactions are **exothermic** and result in the production of lighter liquid and gas products.

- They are relatively slow reactions and therefore most of the hydrocracking occurs in the last section of the reactor.

- The major hydrocracking reactions involve the cracking and saturation of paraffins.

- The concentration of paraffins in the charge stock determines the extent of the hydrocracking reaction

$$C_{10}H_{22} + H_2 \rightarrow \text{Decane} + \text{Isohexane} + \text{n-butane}$$
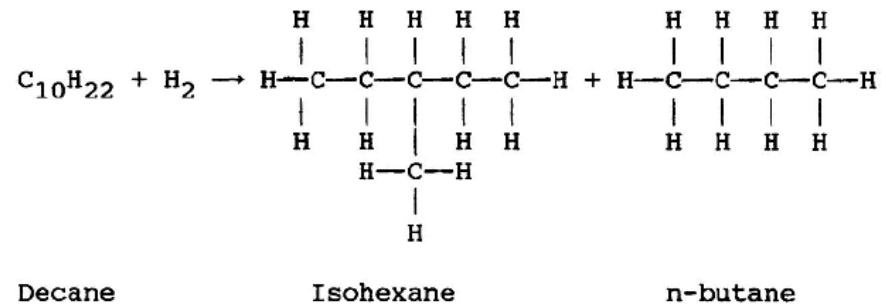
- Hydrocracking yields are increased by:

1. High temperature

2. High pressure

3. Low space velocity

- In order to obtain high product quality and yields, it is necessary to carefully control the hydrocracking and aromatization reactions. Reactor temperatures are carefully monitored to observe the extent of each of these reactions.

Catalysts

- Most processes use platinum as the active catalyst.

- Sometimes platinum is combined with a second catalyst (bimetallic catalyst) such as rhenium or another noble metal.

- There are many different commercial catalytic reforming processes including platforming, powerforming, ultraforming, and Thermofor catalytic reforming.

FEED PREPARATION

- The active material in most catalytic reforming catalysts is platinum.

- Certain metals, hydrogen sulfide, ammonia, and organic nitrogen and sulfur compounds will deactivate the catalyst.

- Feed pretreating, in the form of hydrotreating, is usually employed to remove these materials.

- The hydrotreater employs a cobalt–molybdenum catalyst to convert organic sulfur and nitrogen compounds to hydrogen sulfide and ammonia, which then are removed from the system with the unreacted hydrogen.

- The metals in the feed are retained by the hydrotreater catalyst.

- Hydrogen needed for the hydrotreater is obtained from the catalytic reformer.

- If the boiling range of the charge stock must be changed, the feed is redistilled before being charged to the catalytic reformer.

Classification of process

- Reforming processes are classified as
a) Continuous
b) Cyclic
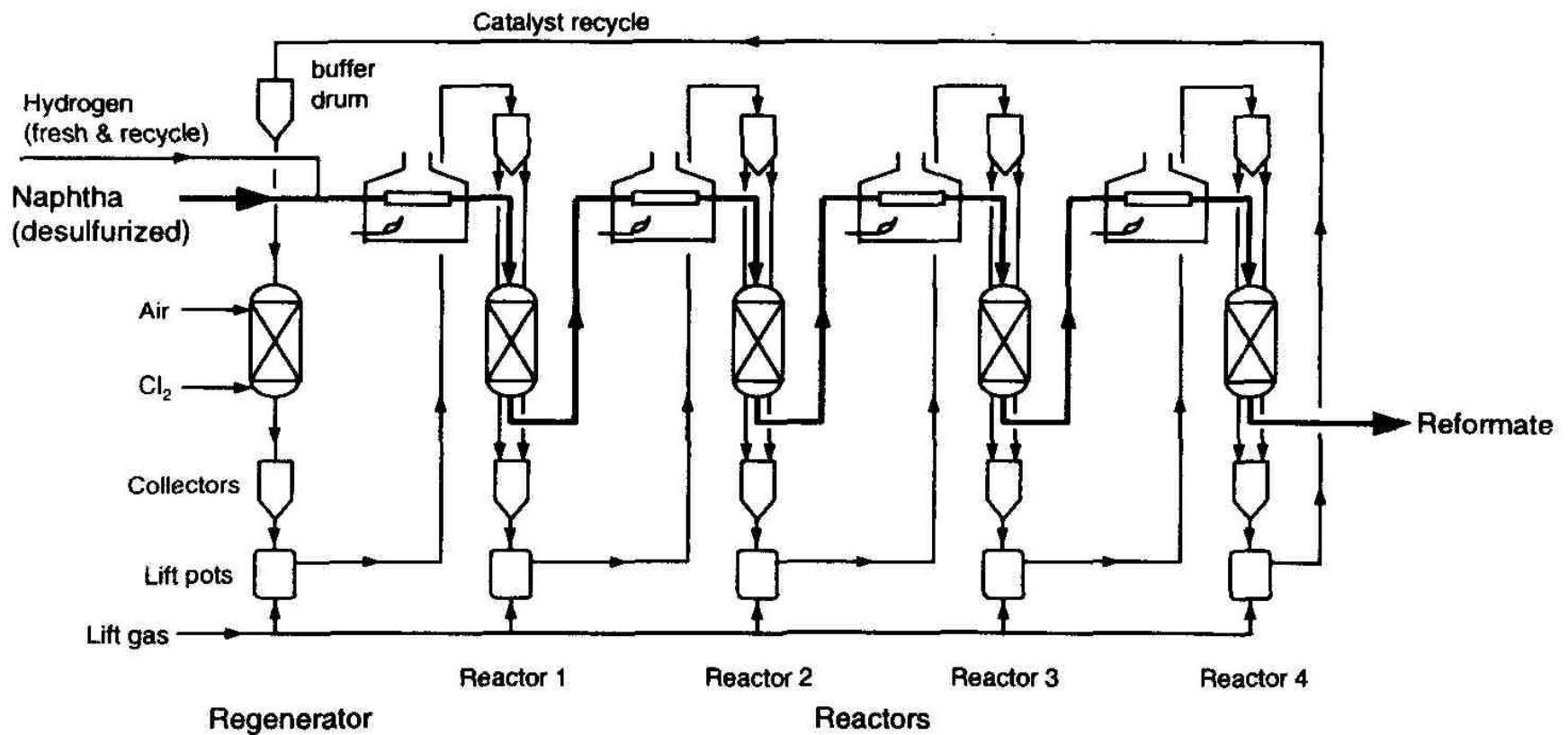c) Semi-regenerative depending upon the frequency of catalyst regeneration.

a) *Continuous process*

- *The equipment for the continuous process is* designed to permit the removal and replacement of catalyst during normal operation.

1. The catalyst can be regenerated continuously

2. Catalyst maintained at a high activity.

3. The higher capital costs

4. possible lower operating costs due to lower hydrogen recycle rates and pressures need to keep coke laydown at an acceptable level.

Continuous catalyst regeneration (CCR Platforming) catalytic

Legend:
R = Reactor
H = Heater
CFE = Combined Feed Exchanger
SEP = Separator
REG = Regeneration Section
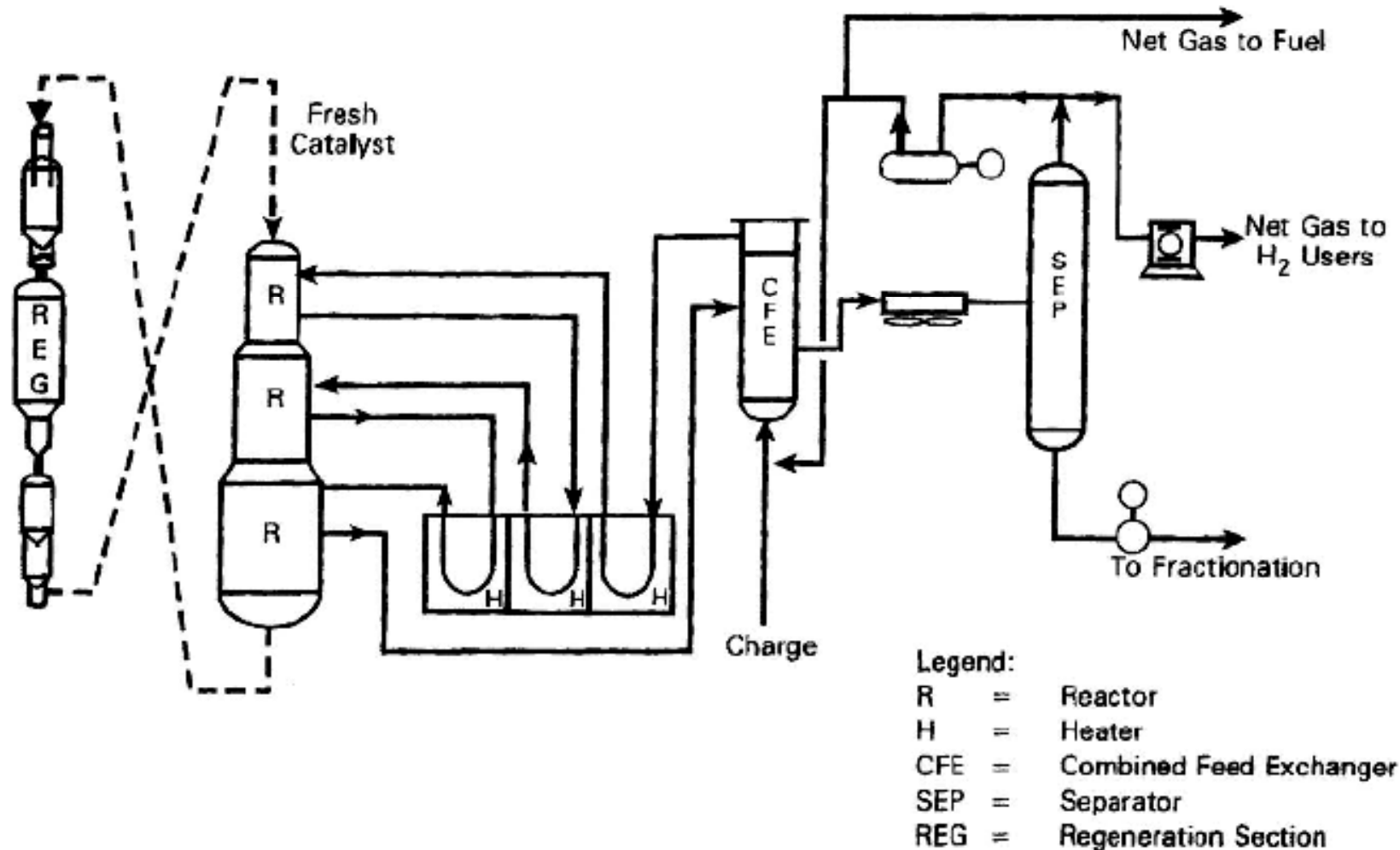
# Continuous regenerative reforming

b) *Semi-regenerative Process*

- the advantage: minimum capital costs.

- Regeneration requires the unit to be taken off-stream.

- Depending upon severity of operation, regeneration is required at intervals of 3 to 24 months.

- High hydrogen recycle rates and operating pressures are utilized to minimize coke laydown and consequent loss of catalyst activity.

- The reforming semiregenerative reforming process is typical of fixed-bed reactor reforming operations and will be described here.

- pretreated feed and recycle hydrogen are heated to 498–524°C before entering the first reactor. In the first reactor, the major reaction is the dehydrogenation of naphthenes to aromatics and, as this is strongly endothermic, a large drop in temperature occurs. To maintain the reaction rate, the gases are reheated before being passed over the catalyst in the second reactor. As the charge proceeds through the reactors, the reaction rates decrease and the reactors become larger, and the reheat needed becomes less. Usually three or four reactors are sufficient to provide the desired degree of reaction and heaters are needed before each reactor to bring the mixture up to reaction temperature. In practice, either separate heaters can be used or one heater can contain several separate coils.

- The reaction mixture from the last reactor is cooled and the liquid products condensed. The hydrogen-rich gases are separated from the liquid phase in a drum separator, and the liquid from the separator is sent to a fractionator to be debutanized.

- The hydrogen-rich gas stream is split into a hydrogen recycle stream and a net hydrogen by-product which is used in hydrotreating or hydrocracking operations or as fuel.

- The reformer operating pressure and the hydrogen/feed ratio are compromises among obtaining maximum yields, long operating times between regeneration, and stable operation. It is usually necessary to operate at pressures from 345–2415 kPa and at hydrogen charge ratios of 3–8 mol H2/mol feed . Liquid hourly space velocities in the area of 1 to 3 are in general use.

- The original reforming process is classified as a semi-regenerative type because catalyst regeneration is infrequent and runs of 6 to 24 months between regeneration are common. In the cyclic processes, regeneration is typically performed on a 24- or 48-hour cycle, and a spare reactor is provided so that regeneration can be accomplished while the unit is still on-stream. Because of these extra facilities, the cyclic processes are more expensive but offer the advantages of low pressure operation and higher yields of reformate at the same severity. 64

Catalytic reforming, semi-regenerative
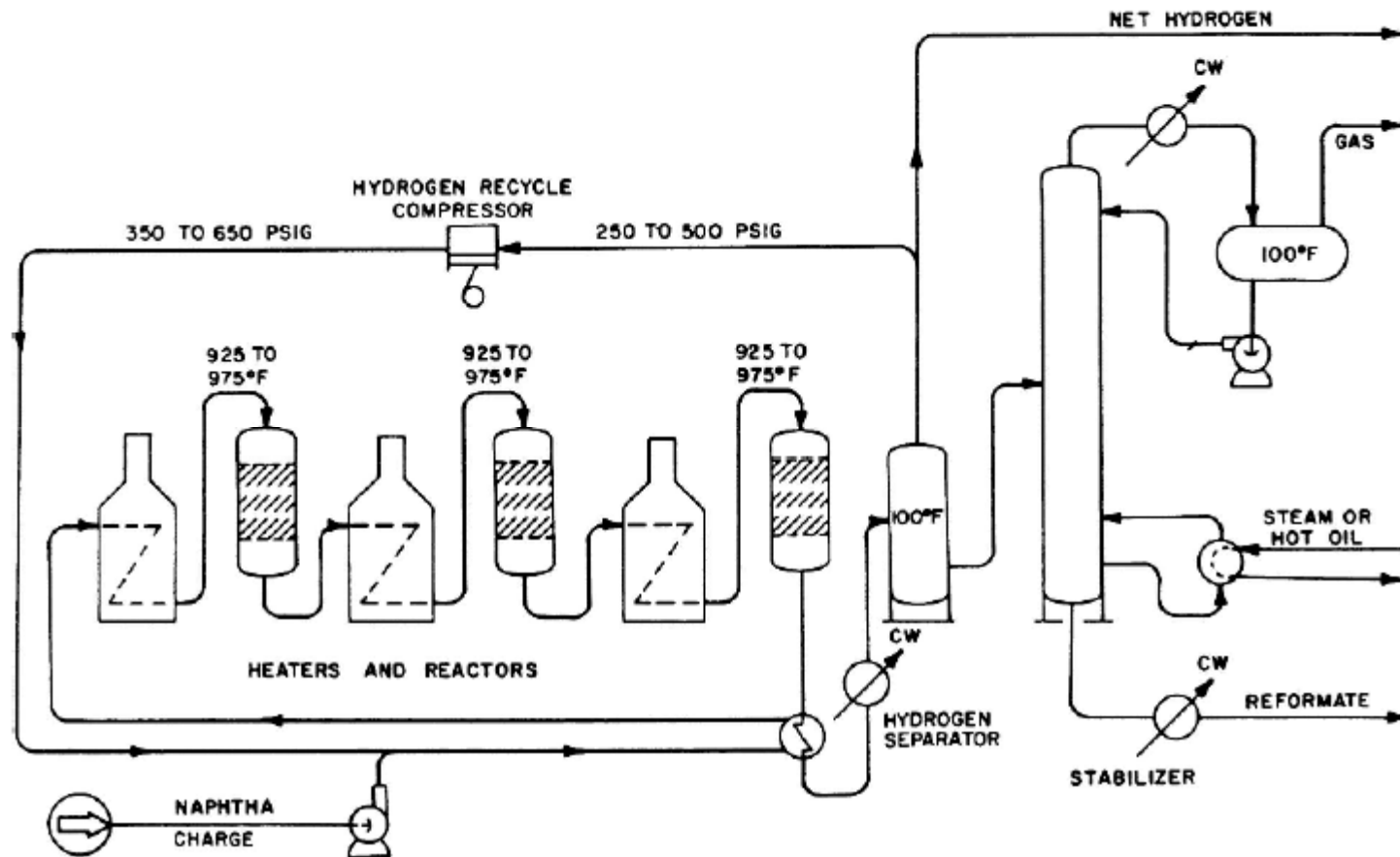
Semi-regenerative catalytic reforming
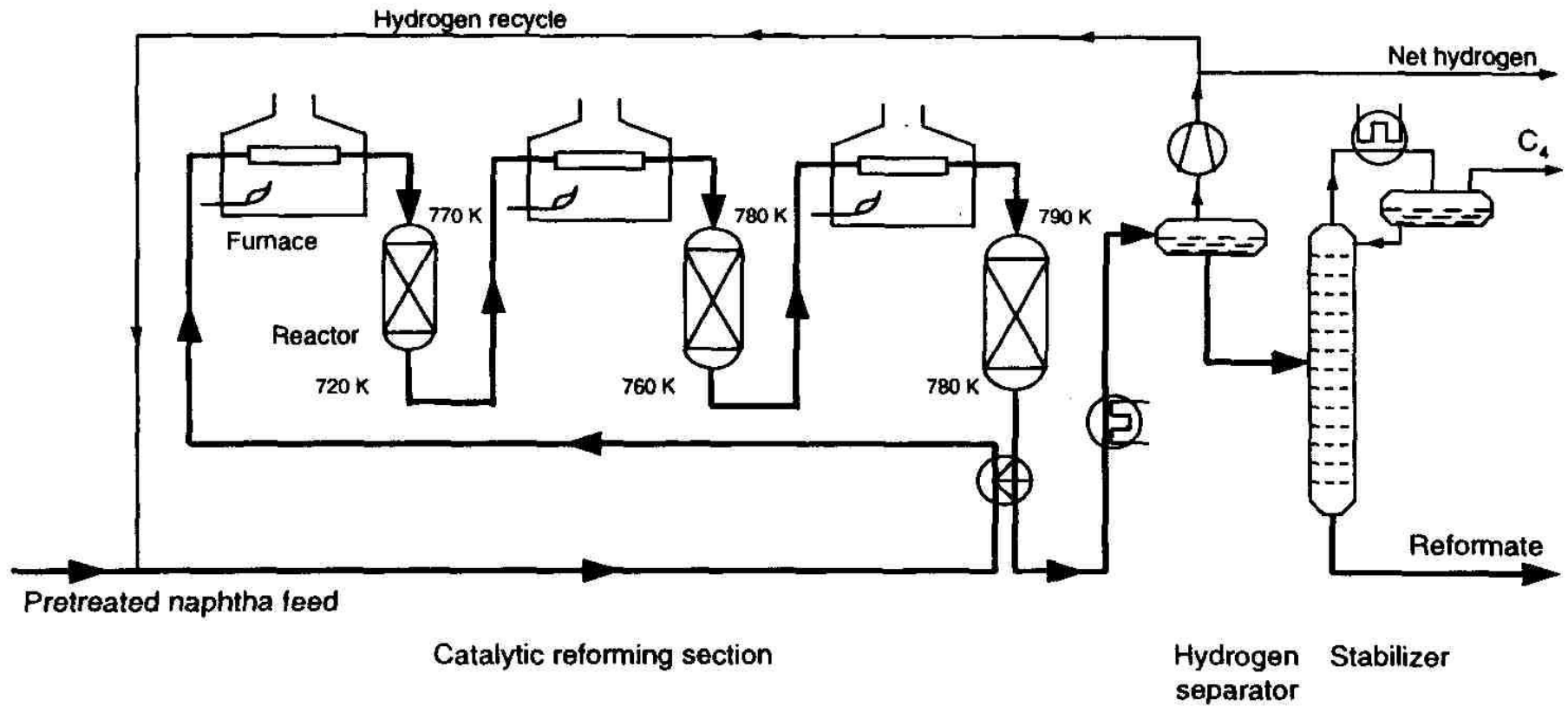
c) *Cyclic process*

- *Is* characterized by having a swing reactor in addition to those on-stream in which the catalyst can be regenerated without shutting the unit down.

- When the activity of the catalyst in one of the on-stream reactors drops below the desired level, this reactor is isolated from the system and replaced by the swing reactor.

- The catalyst in the replaced reactor is then regenerated by admitting hot air into the reactor to burn the carbon off the catalyst.

- After regeneration it is used to replace the next reactor needing regeneration.

- In the cyclic processes, regeneration is typically performed on a 24- or 48-hour cycle, and a spare reactor is provided so that regeneration can be accomplished while the unit is still on-stream.

- Because of these extra facilities, the cyclic processes are more expensive

Catalytic reforming scheme
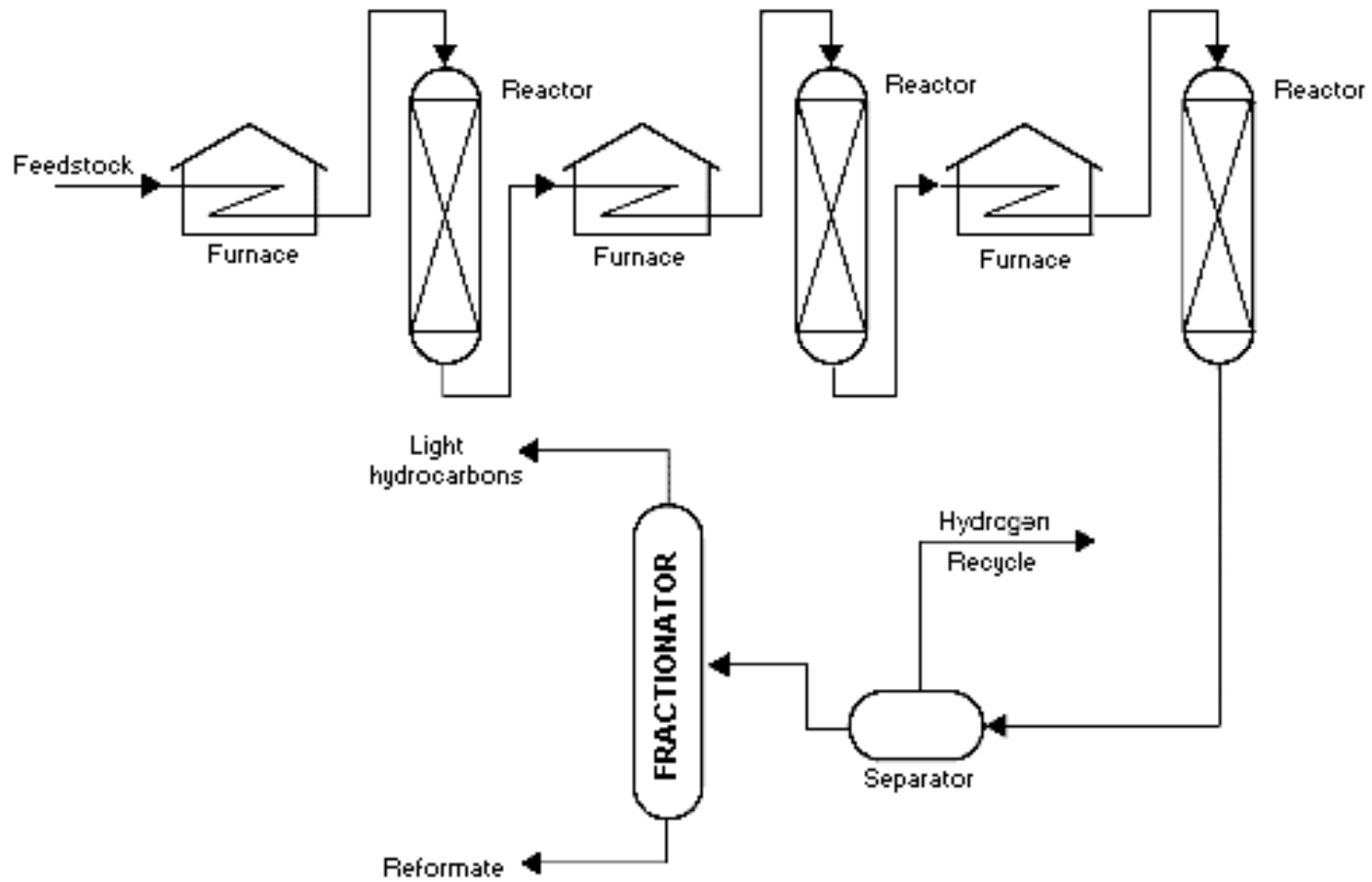
Process Description

- The pretreated feed and recycle hydrogen are heated to 925 to 975°F (498–524°C) before entering the first reactor.

- In the first reactor, the major reaction is the dehydrogenation of naphthenes to aromatics and, as this is strongly endothermic, a large drop in temperature occurs.

- To maintain the reaction rate, the gases are reheated before being passed over the catalyst in the second reactor.

- As the charge proceeds through the reactors, the reaction rates decrease and the reactors become larger, and the reheat needed becomes less.

- Usually three or four reactors are sufficient to provide the desired degree of reaction and heaters are needed before each reactor to bring the mixture up to reaction temperature.

- A typical gas composition leaving each of the reactors in a four reactor system, with a HSR naphtha feed of 180–380°F; severity, 99 RON; and pressure, 163 psi (1124 kPa) is as follows:

	Feed	1	2	3
P	60	59	50	29
N	29	8	6	5
A	11	33	45	87
Total	100	100	96	87

Note: Reactor outlet, mol/100 mol feed.

- The reaction mixture from the last reactor is cooled and the liquid products condensed.

- The hydrogen-rich gases are separated from the liquid phase in a drum separator, and the liquid from the separator is sent to a fractionator to be debutanized.

- The hydrogen-rich gas stream is split into a hydrogen recycle stream and a net hydrogen by-product which is used in hydrotreating or hydrocracking operations or as fuel.

- The reformer operating pressure and the hydrogen/feed ratio are compromises among obtaining maximum yields, long operating times between regeneration, and stable operation.

- It is usually necessary to operate at pressures from 50 to 350 psig (345–2415 kPa) and at hydrogen charge ratios of 3–8 mol H2/mol feed (2800–7600 scp/bbl).

- Liquid hourly space velocities in the area of 1 to 3 are in general use.

Catalytic Reforming, Semi-regenerative Process

# Catalytic reforming reactors
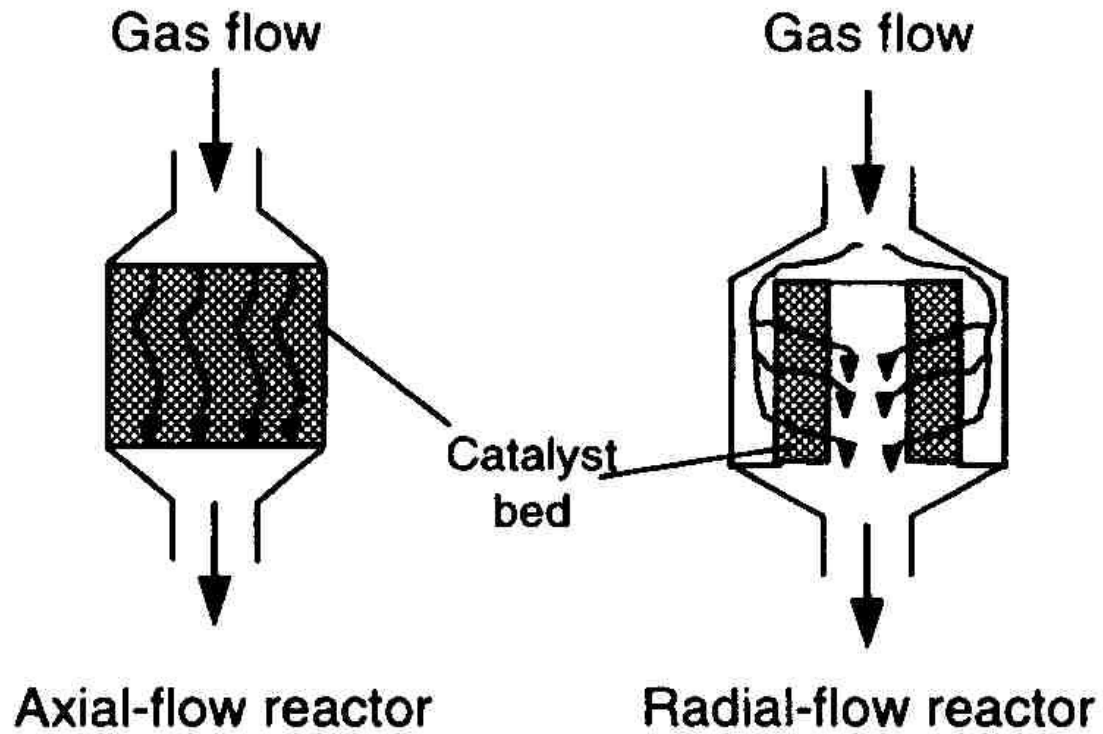
E. Alkylation

- Alkylation combines low-molecular-weight olefins (primarily a mixture of propylene and butylene) with **isobutene** in the presence of a catalyst, either **sulfuric acid or hydrofluoric acid**.

- The product is called alkylate and is composed of a mixture of high-octane, branched-chain paraffinic hydrocarbons.

- Alkylate is a premium blending stock because it has exceptional antiknock properties and is clean burning. The octane number of the alkylate depends mainly upon the kind of olefins used and

Sulphuric acid alkylation process

- In cascade type sulfuric acid (H_2SO_4) alkylation units, the feedstock (propylene, butylene, amylene, and fresh isobutane) enters the reactor and contacts the concentrated sulfuric acid catalyst (in concentrations of 85% to 95% for good operation and to minimize corrosion).

- The reactor is divided into zones, with olefins fed through distributors to each zone, and the sulfuric acid and isobutanes flowing over baffles from zone to zone.

- The reactor effluent is **separated into hydrocarbon and acid phases** in a settler, and the acid is returned to the reactor. The hydrocarbon phase is hot-water washed with caustic for pH control before being successively depropanized, deisobutanized, and debutanized. The alkylate obtained from the deisobutanizer can then go directly to motor-fuel blending or be rerun to produce aviation-grade blending stock. The **isobutane is recycled** to the feed.

Sulphuric acid alkylation process
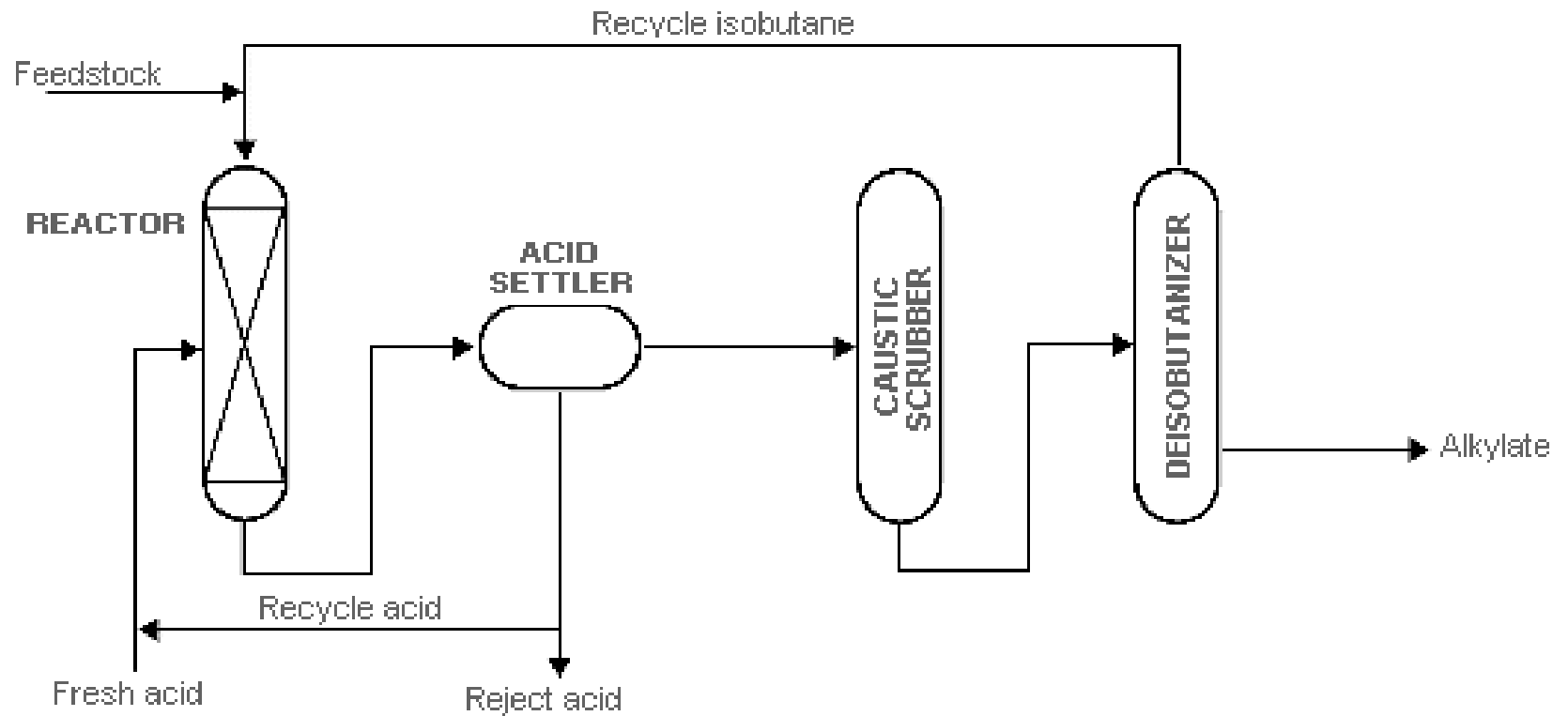
Sulphuric acid alkylation process
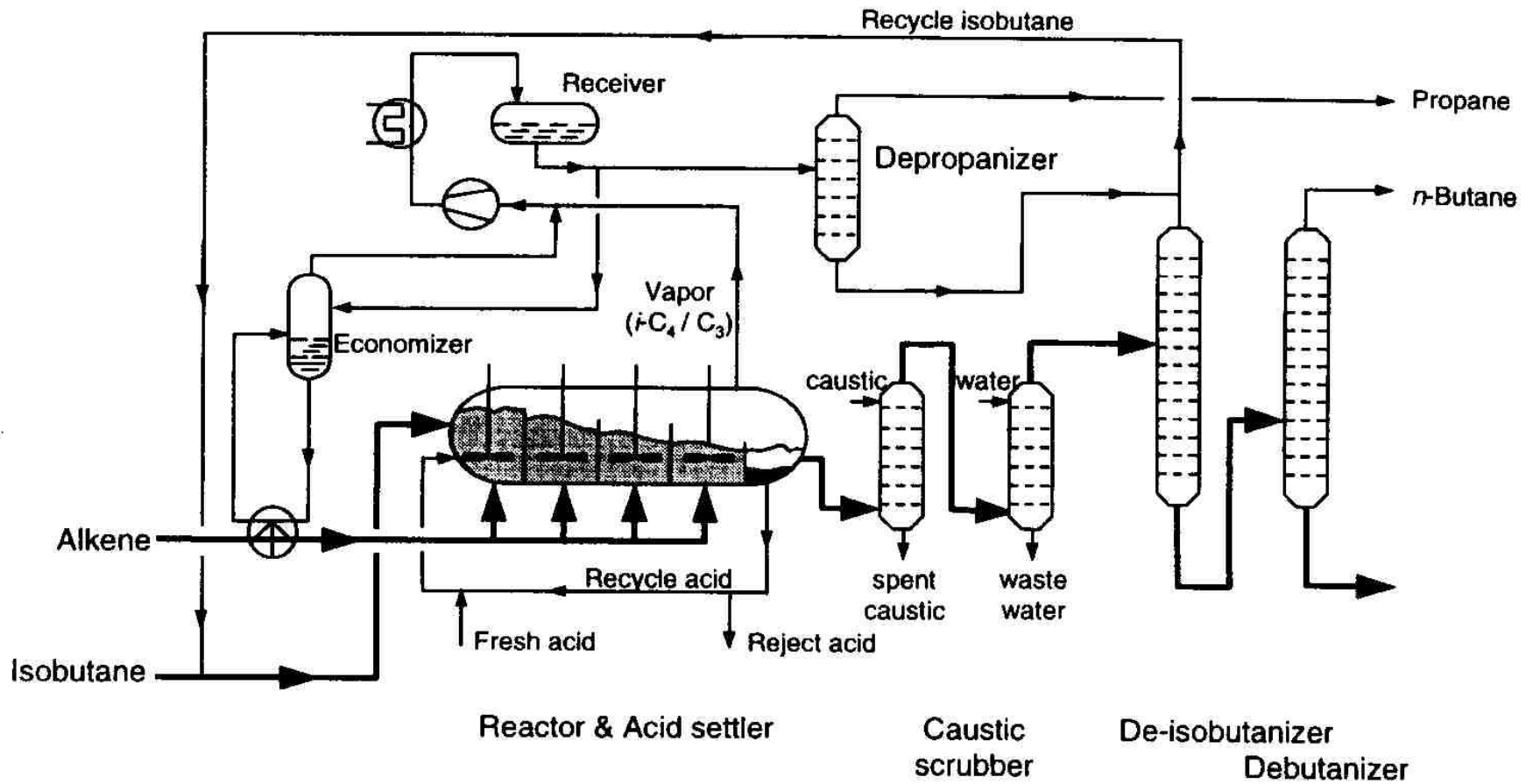
Alkylation with H_2SO_4 in Stratco contactor with autorefrigeration