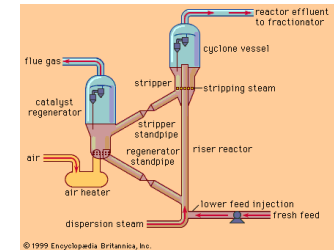


Conversion Processes

- Upgrade lower-value materials such as heavy residues to more valuable products such as naphtha and LPG.
- Improve the characteristics of a fuel. For example, a lower octane naphtha fraction is reformed to a higher octane reformat product.
- Reduce harmful impurities in petroleum fractions and residues to control pollution and to avoid poisoning certain processing catalysts.
- Conversion processes are either thermal or catalytic.



Thermal Conversion Processes

- 3 techniques: coking, viscosity breaking, and steam cracking.
- Steam cracking is of special importance as a major process designed specifically for producing light olefins.



Coking Processes

- Thermal cracking process for heavy residues with high **asphaltene** and **metal** contents.
- These residues cannot be fed to catalytic cracking units because their impurities deactivate and poison the catalysts.
- Products include hydrocarbon gases, cracked naphtha, middle distillates, and coke.
- The gas and liquid products characterized by a high percentage of unsaturation.
- Hydrotreatment is usually required to saturate olefinic compounds and to desulphurise products from coking units.



Thermal Cracking Reactions

- The first step in cracking is the thermal decomposition of hydrocarbon molecules to two free radical fragments.
- Occurs by homolytic carbon-carbon bond scission at any position along the hydrocarbon chain.
- $\text{RCH}_2\text{CH}_2\text{CH}_2\text{R}' \rightarrow \text{RCH}_2\dot{\text{C}}\text{H}_2 + \text{R}'\dot{\text{C}}\text{H}_2$
- The radicals may further crack, yielding an olefin and a new free radical.

Thermal Cracking Reactions

- Cracking usually occurs at a bond beta to the carbon carrying the unpaired electron.
- $\text{RCH}_2\dot{\text{C}}\text{H}_2 \rightarrow \dot{\text{R}} + \text{CH}_2=\text{CH}_2$
- Further β bond scission of the new free radical R^\cdot can continue to produce ethylene until the radical is terminated.

Thermal Cracking Reactions

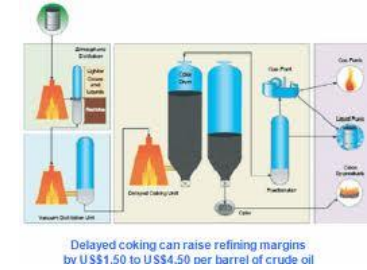
- Free radicals may also react with a hydrocarbon molecule from the feed by abstracting a hydrogen atom.
- Reaction here
- Abstraction of a hydrogen atom can occur at any position along the chain.

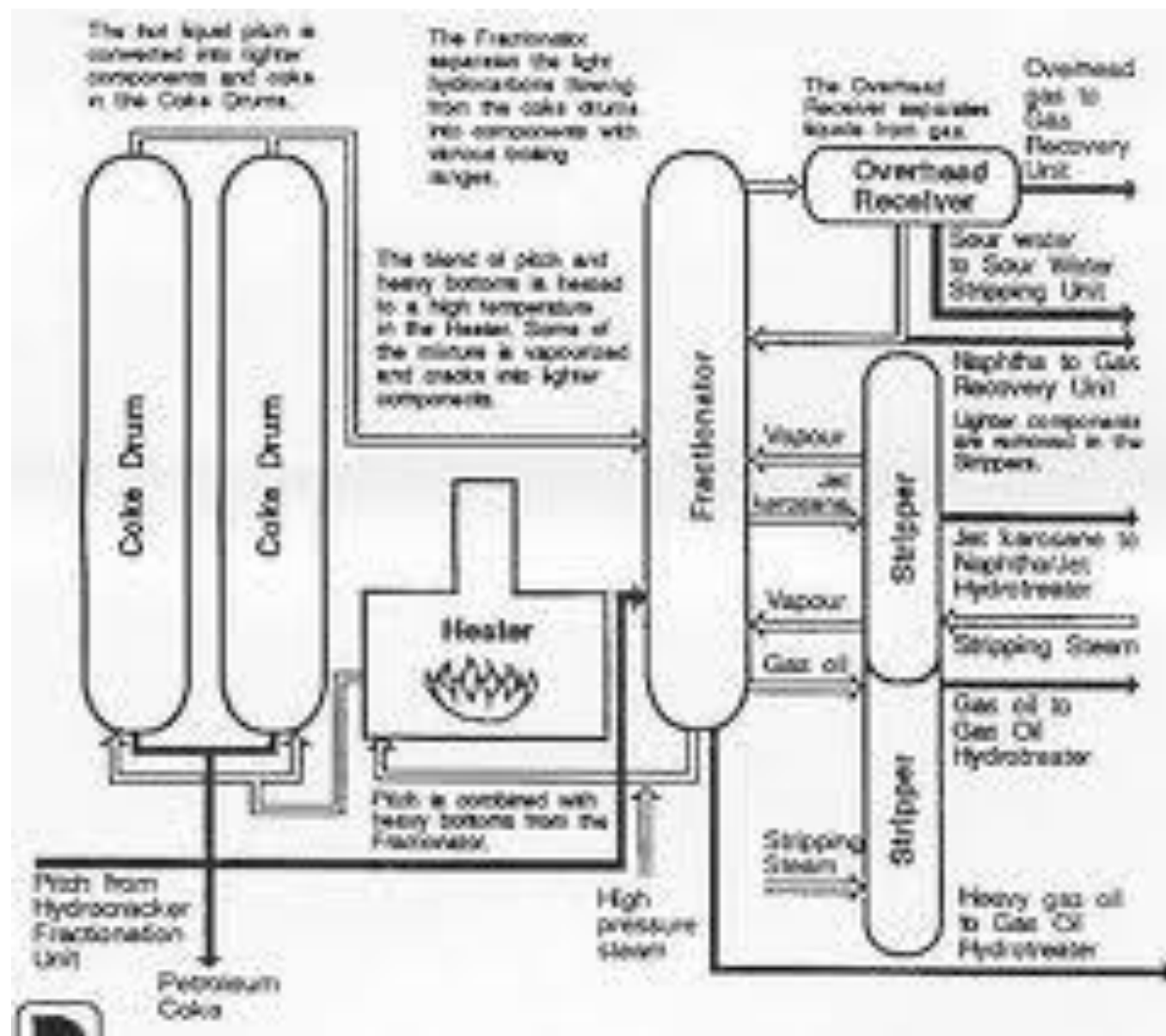
Thermal Cracking Reactions

- Rate of hydrogen abstraction is faster from a tertiary position than from a secondary, which is faster than from a primary position.
- The secondary free radical can crack according to the beta scission rule, and a terminal olefin is produced.
- Reactions here

Coking

- Two processes delayed coking and fluid coking.
- In delayed coking, the reactor system consists of a short contact-time heater coupled to a large drum in which the preheated feed “soaks” on a batch basis. Coke gradually forms in the drum.
- A delayed coking unit has at least a pair of drums.
- When the coke reaches a predetermined level in one drum, flow is diverted to the other so that the process is continuous.
- Vapors from the top of the drum are directed to the fractionator where they are separated into gases, naphtha, kerosine, and gas oil.





Delayed Coking

- Operating conditions for delayed coking are 25–30 psi at 480–500°C
- Improved liquid yields could be obtained by operating at lower pressures.



**Feeds and products from a delayed coker unit
(using different feeds)⁵**

Operating conditions:

Heater outlet temperature, °F	900–950
Coke drum pressure, psig	15–90
Recycle ratio, vol/vol feed, %	10–100

Yields:

Feedstock	Middle East vac. residue	Vacuum residue of hydrotreated bottoms	Coal tar pitch
Gravity, °API	7.4	1.3	–11.0
Sulfur, wt %	4.2	2.3	0.5
Conradson carbon, wt %	20.0	27.6	—
Products, wt %			
Gas + LPG	7.9	9.0	3.9
Naphtha	12.6	11.1	—
Gas oil	50.8	44.0	31.0
Coke	28.7	35.9	65.1

Delayed Coking

- Primary factor that determines the quality of coke is the feed quality
- Factors that govern the reactions are the coke drum size, the heating rate, the soak time, the pressure, and the final reaction temperature.

Delayed coking

- Coke produced from delayed coking is described as delayed sponge, shot, or needle coke depending on its physical structure.
- Shot coke is the most common when running the unit under severe conditions with sour crude residues.
- Needle coke is produced from selected aromatic feedstocks.
- Sponge coke is more porous and has a high surface area.

Fluid Coking

- In the fluid coking process, part of the coke produced is used to provide the process heat.
- Cracking reactions occur inside the heater and the fluidized-bed reactor.
- The fluid coke is partially formed in the heater. Hot coke slurry from the heater is recycled to the fluid reactor to provide the heat required for the cracking reactions.
- Fluid coke is formed by spraying the hot feed on the already-formed coke particles.



Reactor temperature is about 520°C, and the conversion of feed into coke is immediate, with complete disorientation of the crystallites of product coke.



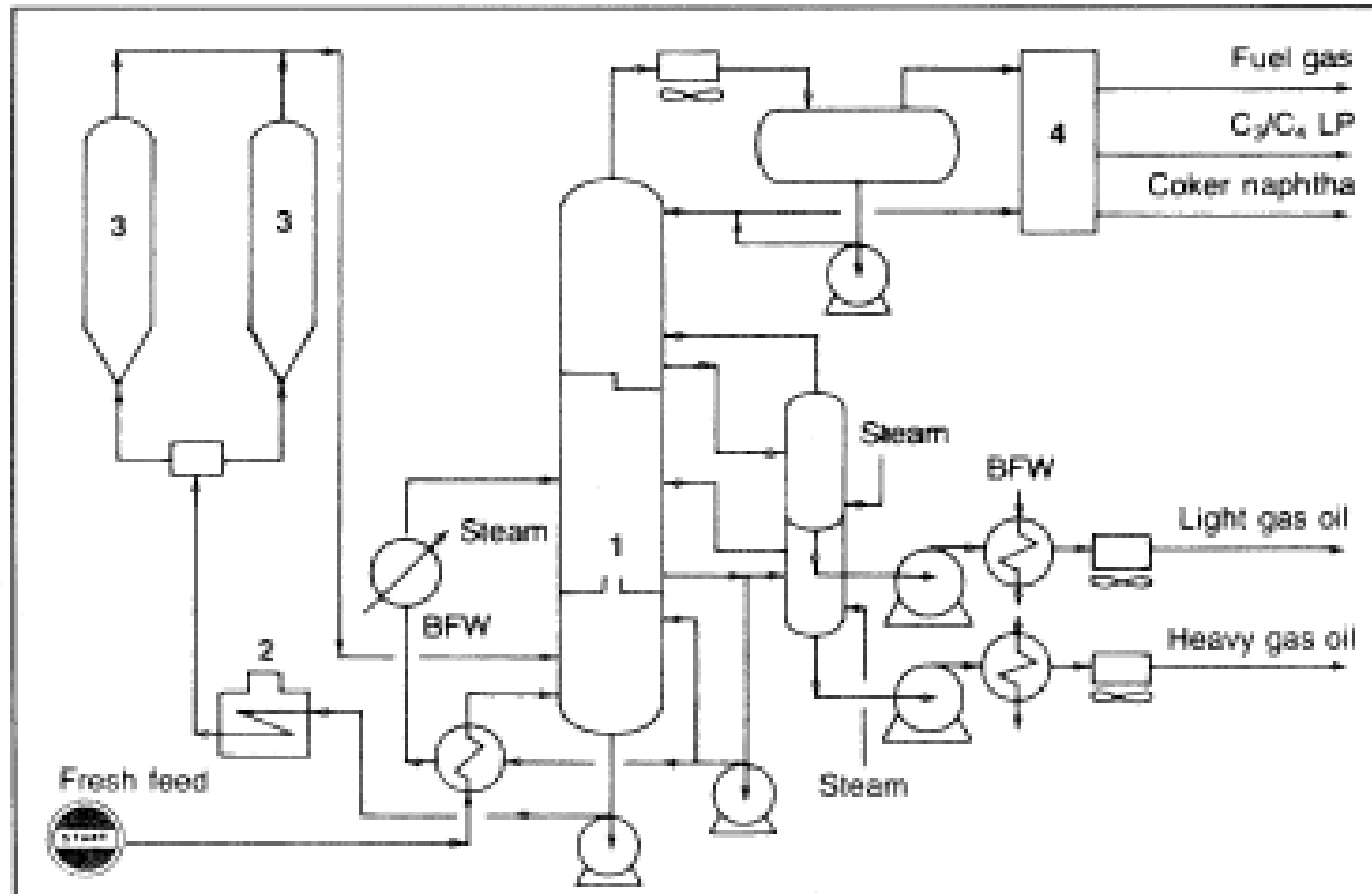


Figure 3-3. Flow diagram of a delayed coking unit.⁵ (1) coker fractionator, (2) coker heater, (3) coke drum, (4) vapor recovery column.

Fluid coking

- The process concentrates metals, but does not reduce the sulfur content of the coke.
- In addition to high sulphur content, the coke has low volatility, poor crystalline structure, and low grindability index.
- The intergration of fluid coking with gasification is known as flexicoking

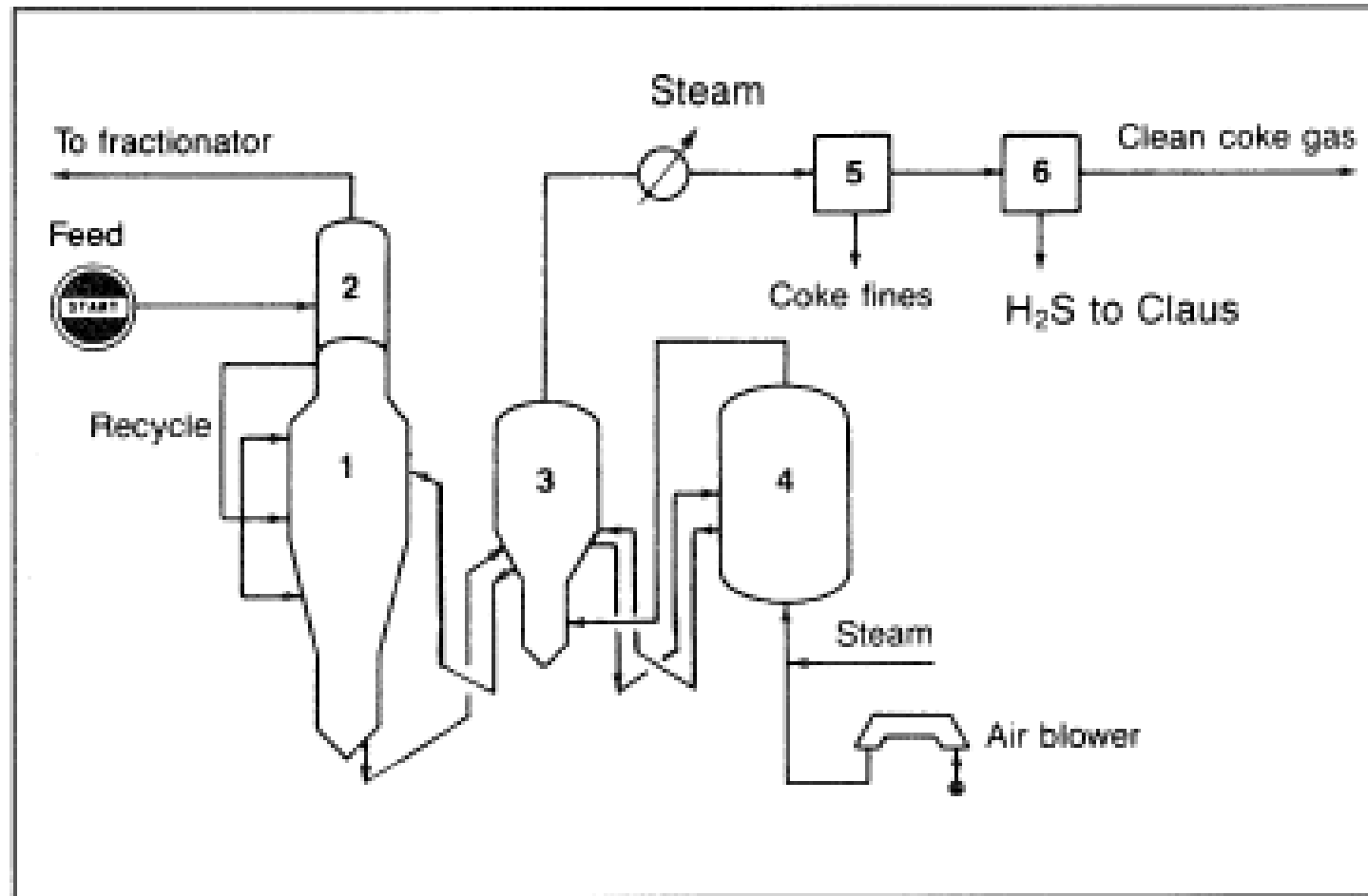


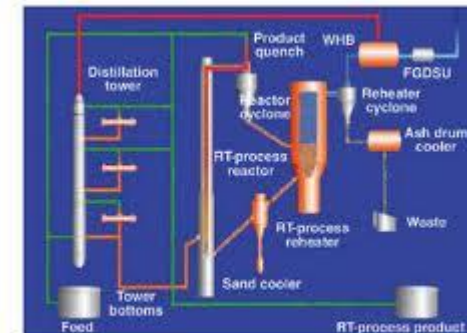
Figure 3-4. Flow diagram of an Exxon flexicoking unit:⁵ (1) reactor, (2) scrubber, (3) heater, (4) gasifier, (5) coke fines removal, (6) H₂S removal.

Viscosity Breaking

- Viscosity breaking aims to thermally crack long-chain feed molecules to shorter ones.
- The process operates at approximately 450°C using short residence times.
- The viscosity and the pour point of the product are reduced.

Catalytic Conversion Processes

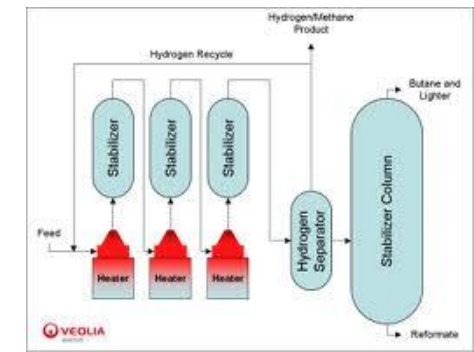
- Naphtha catalytic reforming
 - Catalytic cracking
 - Hydrocracking
 - Hydrodealkylation
 - Isomerization
 - Alkylation
 - Polymerization
-
- In these processes, one or more catalyst are used.



Naphtha Catalytic Reforming

Catalytic Reforming

- To improve the octane number of a naphtha feedstock by changing its chemical composition.
- In general, aromatics have higher octane ratings than paraffins and cycloparaffins.
- Reforming is the key process for obtaining benzene, toluene, and xylenes (BTX).
- Similar to aromatics, branched paraffins have high octane ratings.



Reforming

- The feed to a catalytic reformer is normally a heavy naphtha fraction produced from atmospheric distillation units.
- Olefinic compounds are not desirable because they are precursors for coke which deactivates the catalyst
- Sulphur and nitrogen also poison the catalyst and must be removed from the feed by hydrodesulphurisation and hydrodenitrogenisation

Reforming

- Feeds with a high naphthene content are easier to aromatize than feeds with a high ratio of paraffins
- Feeds with higher end points ($\approx 200^{\circ}\text{C}$) are favorable because some of the long-chain molecules are hydrocracked to molecules in the gasoline range.
- These molecules can isomerize and dehydrocyclize to branched paraffins and to aromatics, respectively.

Naphtha Catalytic Reforming

- Aromatization
- Isomerization
- Hydrocracking
- Hydrodealkylation



Aromatization

- **Two reactions:**
 - dehydrogenation of naphthenes
 - dehydrocyclization of paraffins.
- Dehydrogenation of naphthenes
- Reaction here

Aromatization

- Reaction here
- This reaction is fast; and reversible, highly endothermic, and the equilibrium constant is quite large (6×10^5 @ 500°C).
- The yield of aromatics is favored at higher temperatures and lower pressures.

Aromatization

- Dehydrocyclization of paraffins
- Reaction here
- $K_p = 7.8 \times 10^4$ @ 500°C
- The relative rate of this reaction is much lower than the dehydrogenation of cyclohexanes.

Isomerization

- The skeletal rearrangement of paraffins and cycloparaffins in a catalytic reactor
- The octane number of the reformat product increases.
- Isomerization reactions occur on the platinum catalyst surface or on the acid catalyst sites.
- Reactions here

Hydrocracking

- Reaction here
- Reaction is favoured at high temp and high hydrogen partial pressure.
- Higher gas production and low liquid yield
- Bond breaking can occur at any position along the hydrocarbon chain.
- Some hydrocracking occurs under conditions of aromatization.

Hydrocracking

- long-chain molecules produce C6, C7, and C8 hydrocarbons
- For more aromatics yield, the end point of the feed may be raised to include higher molecular weight hydrocarbons in favor of hydrocracking and dehydrocyclization.
- However, excessive hydrocracking is not desirable because it lowers liquid yields.

Hydrodealkylation

- Hydrodealkylation is a cracking reaction of an aromatic side chain in presence of hydrogen.
- Reaction here
- The reaction consumes hydrogen and is favored at a higher hydrogen partial pressure.
- It is particularly important for increasing benzene yield when methylbenzenes and ethylbenzene are dealkylated.

Hydrodealkylation

- Overall reaction is slightly exothermic, the cracking step is favored at higher temperatures.
- As in hydrocracking, this reaction increases the gas yield and changes the relative equilibrium distribution of the aromatics in favor of benzene.

Reforming Processes



- Catalytic reformers have typically a series of three catalyst beds
- The first bed usually contains less catalyst than the other beds.
- This arrangement is important because the dehydrogenation of naphthenes to aromatics can reach equilibrium faster than the other reforming reactions.
- Dehydrocyclization is a slower reaction and may only reach equilibrium at the exit of the third reactor.

Reforming Processes

- Isomerization and hydrocracking reactions are slow.
- They have low equilibrium constants and may not reach equilibrium before exiting the reactor.
- The second and third reactors contain more catalyst than the first one to enhance the slow reactions and allow more time in favor of a higher yield of aromatics and branched paraffins.
- Because the dehydrogenation of naphthenes and the dehydrocyclization of paraffins are highly endothermic, the reactor outlet temperature is lower than the inlet temperature.



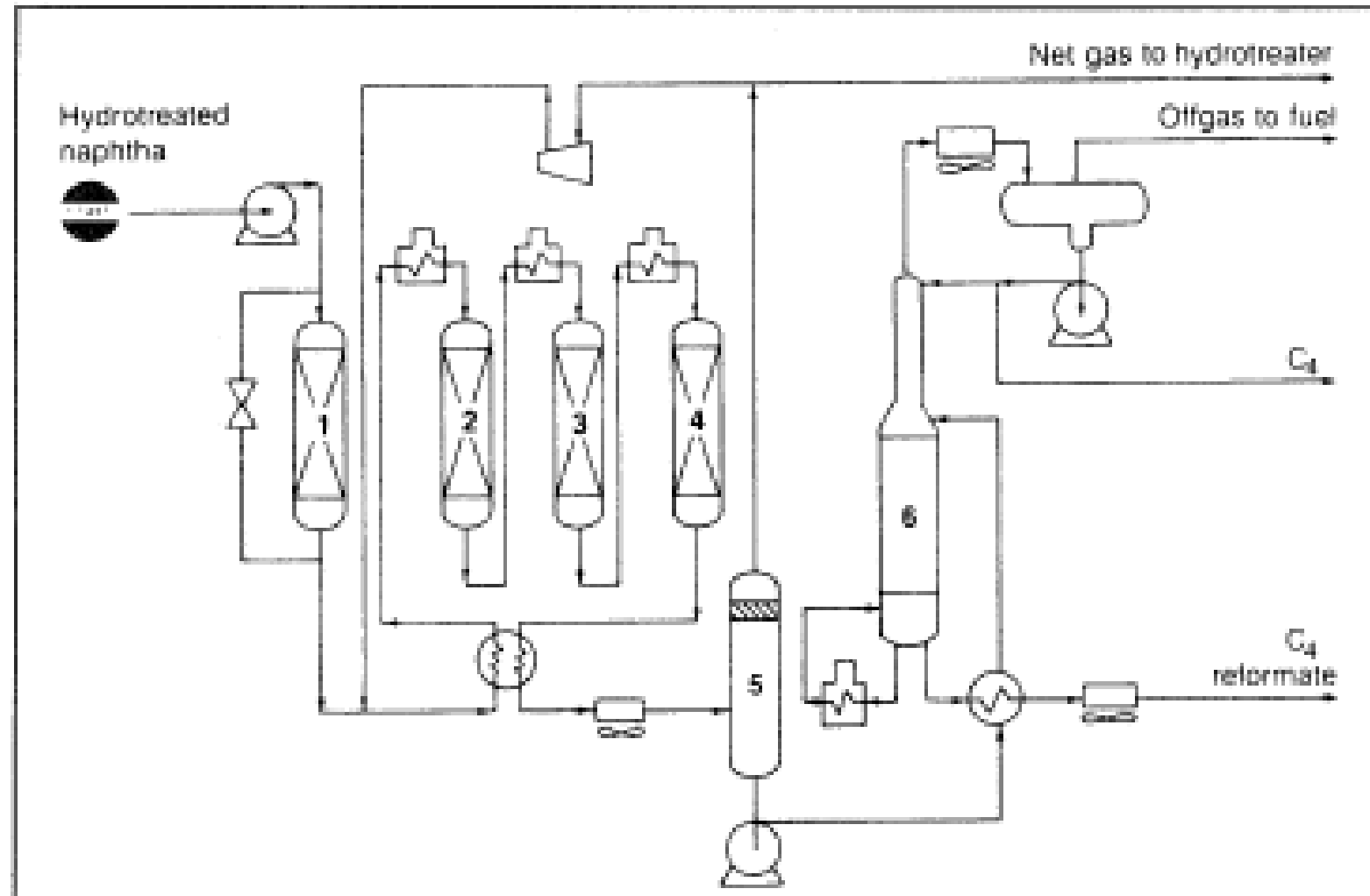


Figure 3-5. Flow diagram of a Chevron Rheiniforming unit:¹⁵ (1) sulfur sorber, (2–4) reactors, (5) separator, (6) stabilizer.

Reforming Processes



- The effluent from the first and second reactors are reheated to compensate for the heat loss.
- Normally, catalytic reformers operate at approximately 500–525°C and 100–300 psig, and a liquid hourly space velocity range of 2–4 hr⁻¹.
- Operating at lower LHSV gives the feed more contact with the catalyst.
- Regeneration of the catalyst may be continuous for certain processes that are designed to permit the removal and replacement of the catalyst during operation.

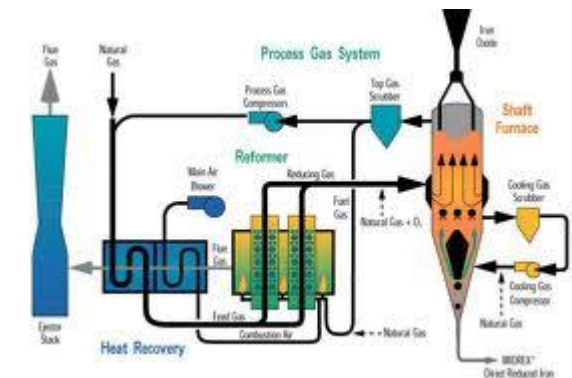
Reforming Processes

- In certain other processes, an additional reactor is used (Swing reactor).
- When the activity of the catalyst is decreased in one of the reactors on stream, it is replaced with the stand-by (Swing) reactor.
- In many processes, regeneration occurs by shutting down the unit and regenerating the catalyst (Semi-regenerative).
- Products from catalytic reformers (the reformate) is a mixture of aromatics, paraffins and cycloparaffins ranging from C6-C8.



Reforming Processes

- The mixture has a high octane rating due to presence of a high percentage of aromatics and branched paraffins.
- Extraction of the mixture with a suitable solvent produces an aromatic-rich extract, which is further fractionated to separate the BTX components.



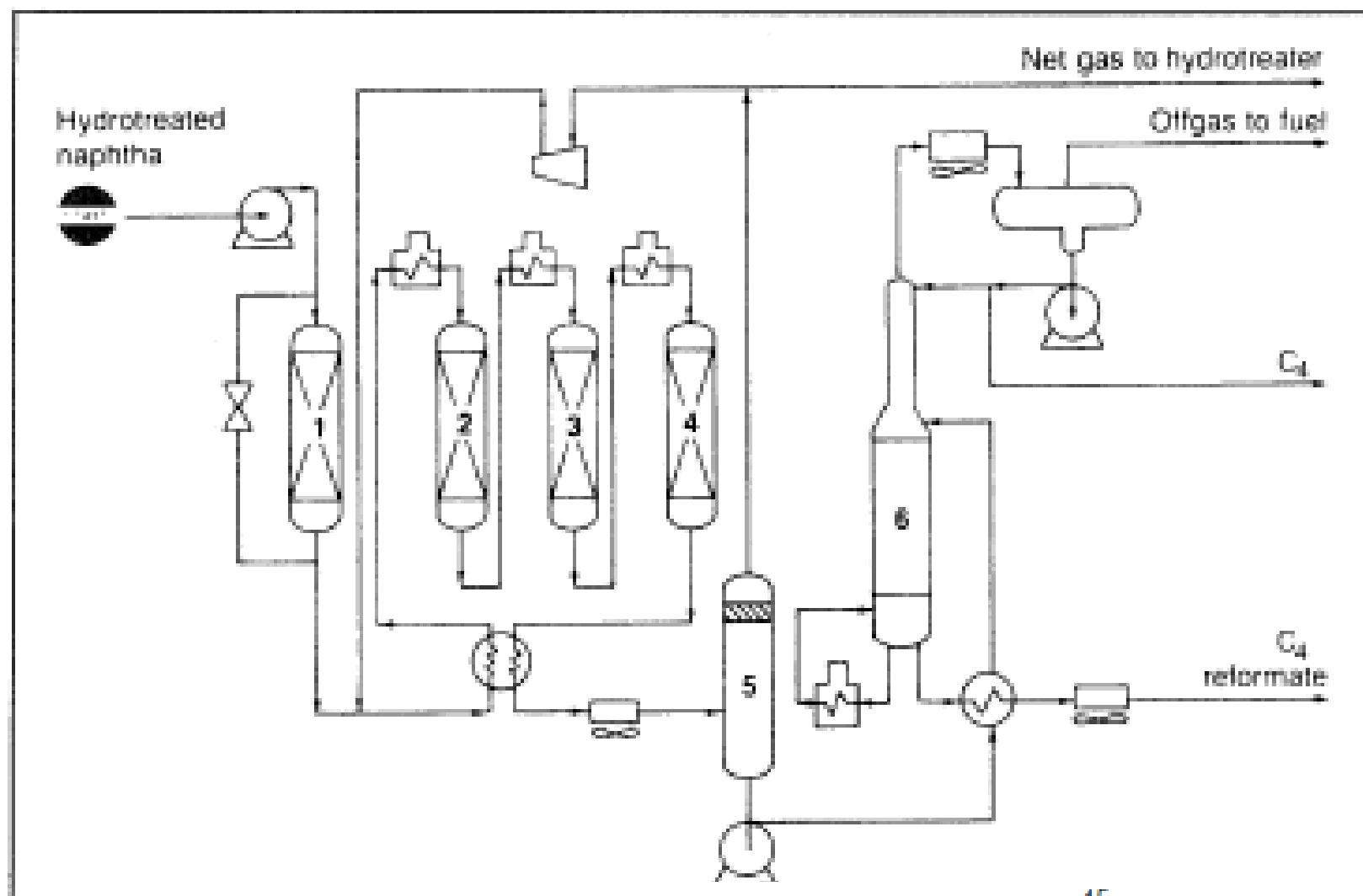


Figure 3-5. Flow diagram of a Chevron Rheiniforming unit:¹⁵ (1) sulfur sorber, (2–4) reactors, (5) separator, (6) stabilizer.

Reforming Catalysts

- The catalysts generally used in catalytic reforming are dual functional to provide two types of catalytic sites, hydrogenation-dehydrogenation sites and acid sites.
- The former sites are provided by platinum, which is the best known hydrogenation-dehydrogenation catalyst and the latter (acid sites) promote carbonium ion formation and are provided by an alumina carrier.
- The two types of sites are necessary for aromatization and isomerization reactions.



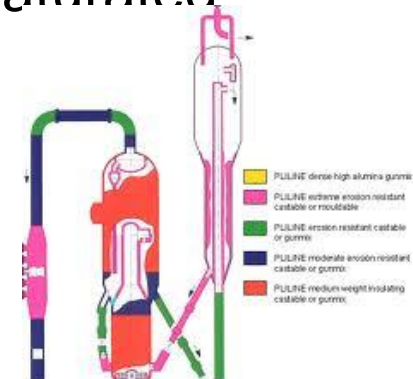
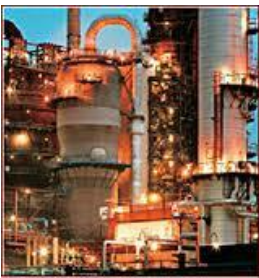
Reforming Catalysts

- Bimetallic catalysts such as Pt/Re were found to have better stability, increased catalyst activity, and selectivity.
- Trimetallic catalysts of noble metal alloys are also used for the same purpose.
- The increased stability of these catalysts allowed operation at lower pressures.

Catalytic Cracking

Catalytic cracking

- The principal aim is to crack lower-value stocks and produce higher-value light and middle distillates.
- The process also produces light hydrocarbon gases, which are important feedstocks for petrochemicals.
- Catalytic cracking produces more gasoline of higher octane than thermal cracking.
- Products from catalytic cracking units are more saturated (stable) than those from thermal cracking units

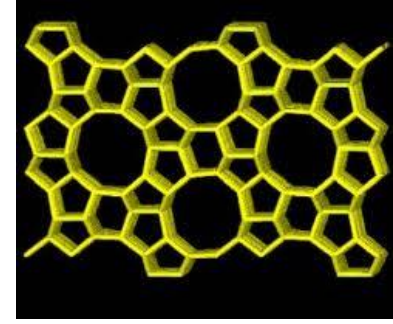


Catalytic cracking

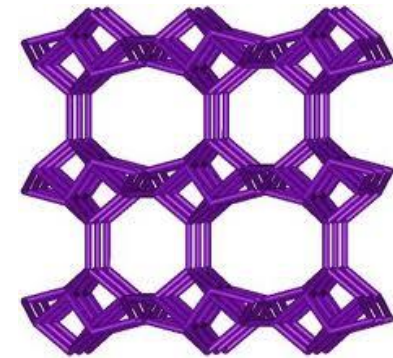
- The feeds to catalytic cracking units vary from gas oils to crude residues.
- Heavier feeds contain higher concentrations of basic and polar molecules as well as asphaltenes which deactivates the catalyst.
- Polycyclic aromatics and asphaltenes contribute strongly to coke formation and produce gasolines of lower quality.
- The most common type of catalytic cracker is the Residium Fluid Catalytic Ccracker (RFCC).



Cracking catalysts



- Earlier catalysts were acid-treated clays
- Present catalysts consist of zeolites incorporated into synthetic amorphous silica-alumina which is more stable.
- These catalysts have both Lewis and Bronsted acid sites that promote carbonium ion formation.
- An important structural feature of zeolites is the presence of holes in the crystal lattice, which are formed by the silica-alumina tetrahedra.



Cracking catalysts

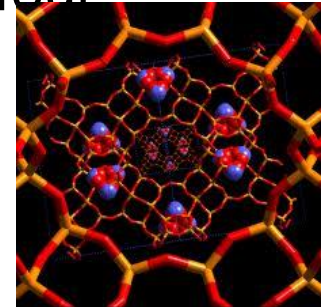
- Each tetrahedron is made of four oxygen anions with either an aluminum or a silicon cation in the center.
- Each oxygen anion with a -2 oxidation state is shared between either two silicon two aluminum, or an aluminum and a silicon cation.
- The four oxygen anions in the tetrahedron are balanced by the $+4$ oxidation state of the silicon cation, while the four oxygen anions connecting the aluminum cation are not balanced.
-

Cracking catalysts

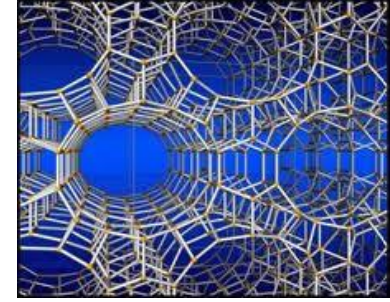
- Insert structure of zeolites/catalyst

Cracking catalysts

- In general, there are two types of catalyst deactivation that occur in a FCC system, reversible and irreversible.
- Reversible deactivation occurs due to coke deposition.
- This is reversed by burning coke in the regenerator.
- Irreversible deactivation results as a combination of four separate but interrelated mechanisms:
 - zeolite dealumination,
 - zeolite decomposition,
 - matrix surface collapse,
 - Contamination by metals such as vanadium and sodium.



Cracking Reactions



- Catalytic cracking occurs through via carbocation intermediate, compared to the free radical intermediate in thermal cracking.
- Carbocations are longer lived and accordingly more selective than free radicals.
- Acid catalysts such as amorphous silica-alumina and crystalline zeolites promote the formation of carbocations.



Cracking reactions

- 1. Abstraction of a hydride ion by a Lewis acid site from a hydrocarbon
- 2. Reaction between a Bronsted acid site (H^+) and an olefin
- 3. Reaction of a carbonium ion formed from step 1 or 2 with another hydrocarbon by abstraction of a hydride ion
- Insert reactions

Cracking catalysts

- Abstraction of a hydride ion from a tertiary carbon is easier than from a secondary, which is easier than from a primary position.
- The formed carbocation can rearrange through a methide-hydride shift
- This isomerization reaction is responsible for a high ratio of branched isomers in the products.

Cracking reactions

- The most important cracking reaction, however, is the carbon-carbon beta bond scission.
- A bond at a position beta to the positively-charged
- carbon breaks heterolytically, yielding an olefin and another carbocation.
- **Insert reaction**
- The new carbocation may experience another beta scission, rearrange to a more stable carbonium ion, or react with a hydrocarbon molecule in the mixture and produce a paraffin.

Cracking reactions

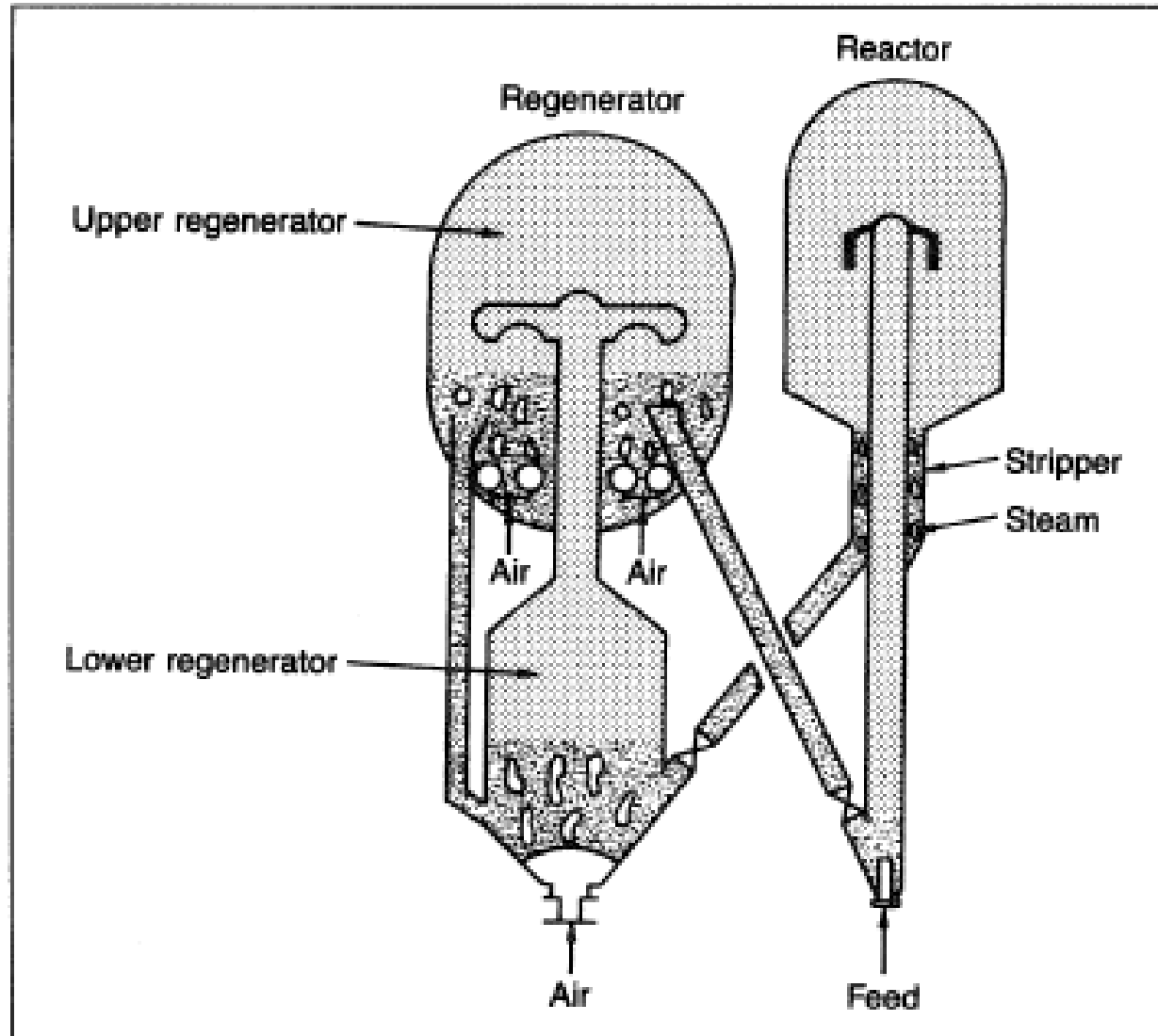
- Insert Reactions and explain final formation

Cracking reactions

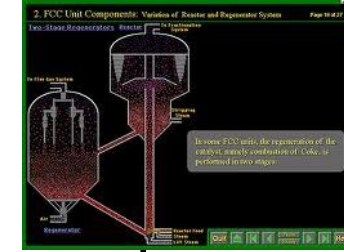
- During the cracking process, fragmentation of complex polynuclear cyclic compounds may occur, leading to formation of simple cycloparaffins.
- These compounds can be a source of C6, C7, and C8 aromatics through isomerization and hydrogen transfer reactions.

The Cracking Process

- Most catalytic cracking reactors are either fluid bed or moving bed.
- In the more common fluidized bed process (FCC), the catalyst is an extremely porous powder with an average particle size of 60 microns.
- In the process, the preheated feed enters the reactor section with hot regenerated catalyst through one or more risers where cracking occurs.

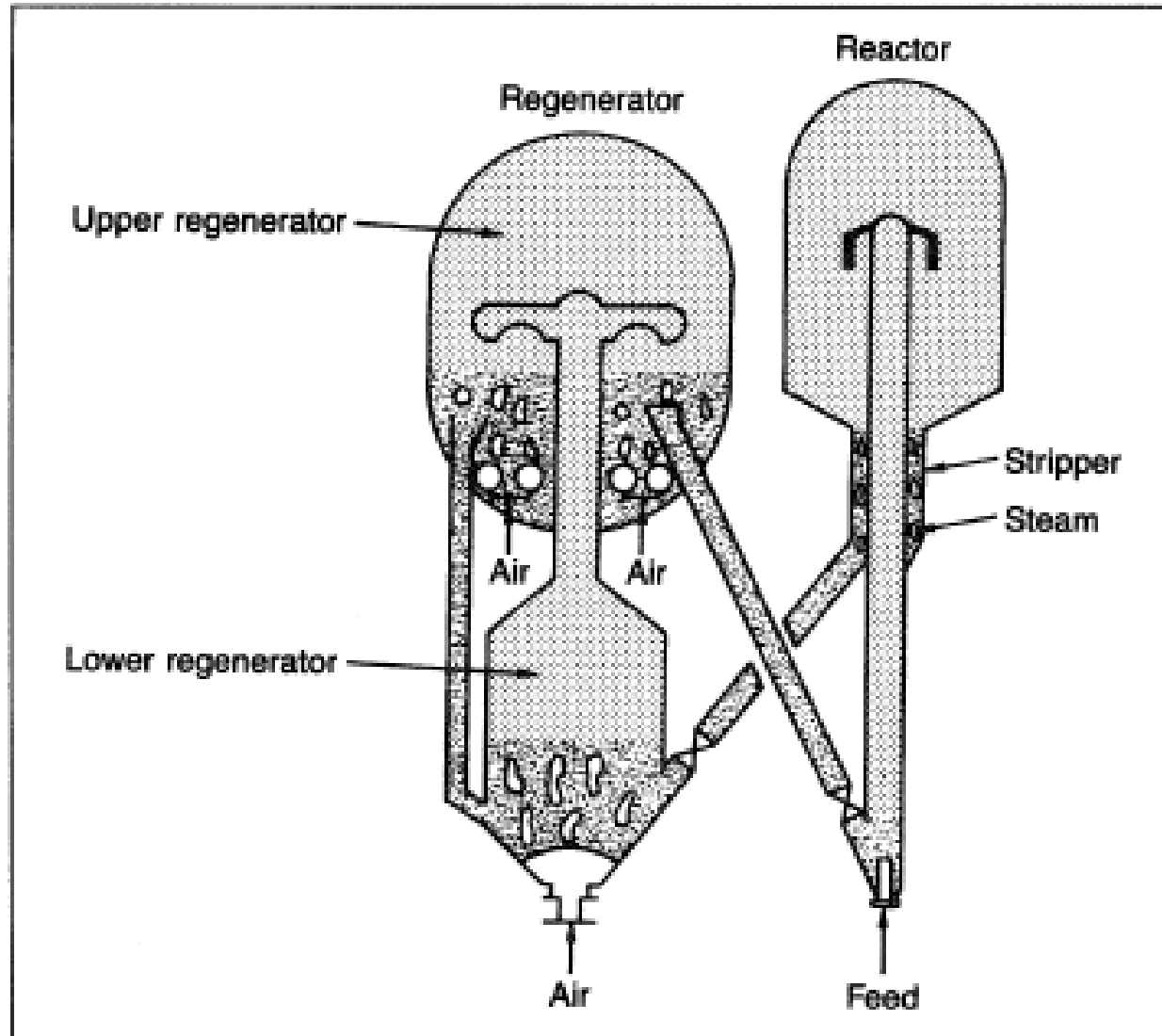


Cracking process



- A riser is a fluidized bed where a concurrent upward flow of the reactant gases and the catalyst particles occurs.
- The reactor temperature is usually held at about 450–520°C, and the pressure is approximately 10–20 psig.
- Gases leave the reactor through cyclones to remove the powdered catalyst, and pass to a fractionator for separation of the product streams.
- Catalyst regeneration occurs by combusting carbon deposits to carbon dioxide and the regenerated catalyst is then returned to the bottom of the riser.





Cracking process

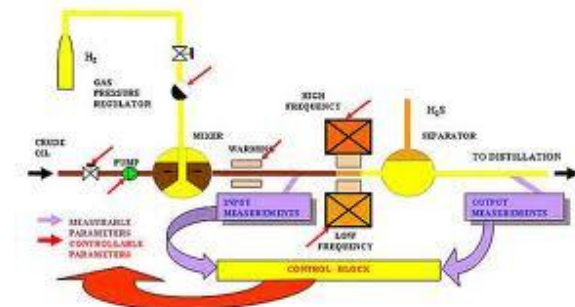
- Products from FCC
 - C3–C5 hydrocarbon unsaturates used as petrochemical feedstocks and for alkylate production.
 - Gasolines with high octane numbers, gas oil and tar
- The ratio of these products depends greatly on the different process variables.
- In general, higher conversions increase gas and gasoline yields.
- Higher conversion also increases coke formation.

Cracking process

- In the moving bed processes, the preheated feed meets the hot catalyst, which is in the form of beads that descend by gravity to the regeneration zone.
- As in fluidized bed cracking, conversion of aromatics is low, and a mixture of saturated and unsaturated light hydrocarbon gases is produced.
- The gasoline product is also rich in aromatics and branched paraffins

Hydrocracking Process

- Hydrocracking is essentially catalytic cracking in the presence of hydrogen.
- It is one of the most versatile petroleum refining schemes adapted to process low value stocks.
- Generally, the feedstocks are not suitable for catalytic cracking because of their high metal, sulfur, nitrogen, and asphaltene contents.
- The process can also use feeds with high aromatic content.



Hydrocracking

- The products from hydrocracking range from light hydrocarbon gases to gasolines to residues.
- Products from hydrocracking processes lack olefinic hydrocarbons.



Hydrocracker Plant



Hydrocracking Catalysts and Reactions

- The main hydro-cracking reaction could be illustrated by the first-step formation of a carbocation over the catalyst surface:
- The catalysts must provide high surface area cracking sites and hydrogenation-dehydrogenation sites.
- Amorphous silica-alumina, zeolites, or a mixture of them promote carbonium ion formation.
- The hydrogenation-dehydrogenation activity, on the other hand, is provided by catalysts such as cobalt, molybdenum, tungsten, vanadium, palladium, or rare earth elements.

Hydrocracking reactions and catalysts

- Insert Reaction Sequence here
- This reaction sequence could be represented as follows:

Hydrocracking reactions and catalysts

- Most products from hydrocracking are saturated.
- For this reason, gasolines from hydrocracking units have lower octane ratings than those produced by catalytic cracking units; they have a lower aromatic content due to high hydrogenation activity.
- Products from hydrocracking units are suitable for jet fuel use.



Hydrocracking reactions and catalysts

- Hydrocracking also produces light hydrocarbon gases (LPG) suitable as petrochemical feedstocks.
- Other reactions that occur during hydrocracking are the fragmentation followed by hydrogenation (hydrogenolysis) of the complex asphaltenes and heterocyclic compounds normally present in the feeds.
- Dealkylation, fragmentation, and hydrogenation of substituted polynuclear aromatics may also occur.



Hydrocracking reactions and catalysts

- The following is a representative example of hydrocracking of a substituted anthracene.
- Reaction here

Hydrocracking reactions and catalysts

- Most commercial hydrocracking operations use a single stage reactor.
- In the single stage process two operation modes are possible, a once-through mode and a total conversion of the fractionator bottoms through recycling.
- In the once-through operation low sulfur fuels are produced and the fractionator bottoms are not recycled.

Hydrocracking Processes

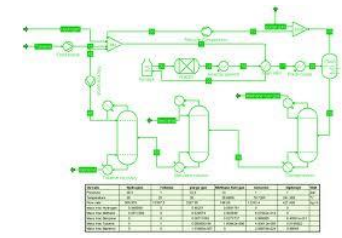
- In the total conversion mode the fractionator bottoms are recycled to the inlet of the reactor to obtain more middle distillates.
- In a two-stage operation, the feed is hydrodesulfurized in the first reactor with partial hydrocracking.
- Reactor effluent goes to a high-pressure separator to separate the hydrogen-rich gas, which is recycled and mixed with the fresh feed.

Hydrocracking Processes

- The liquid portion from the separator is fractionated, and the bottoms of the fractionator are sent to the second stage reactor.
- Hydrocracking reaction conditions vary widely, depending on the feed and the required products.
- Temperature and pressure range from 400 to 480°C and 35 to 170 atmospheres.
- Space velocities in the range of 0.5 to 2.0 hr⁻¹ are applied.

Hydroalkylation Processes

Hydrodealkylation Process



- This process is designed to hydrodealkylate methylbenzenes, ethylbenzene and C₉ + aromatics to benzene.
- The petrochemical demand for benzene is greater than for toluene and xylenes.
- After separating benzene from the reformate, the higher aromatics are charged to a hydrodealkylation unit.
- The reaction is a hydrocracking one, where the alkyl side chain breaks and is simultaneously hydrogenated.

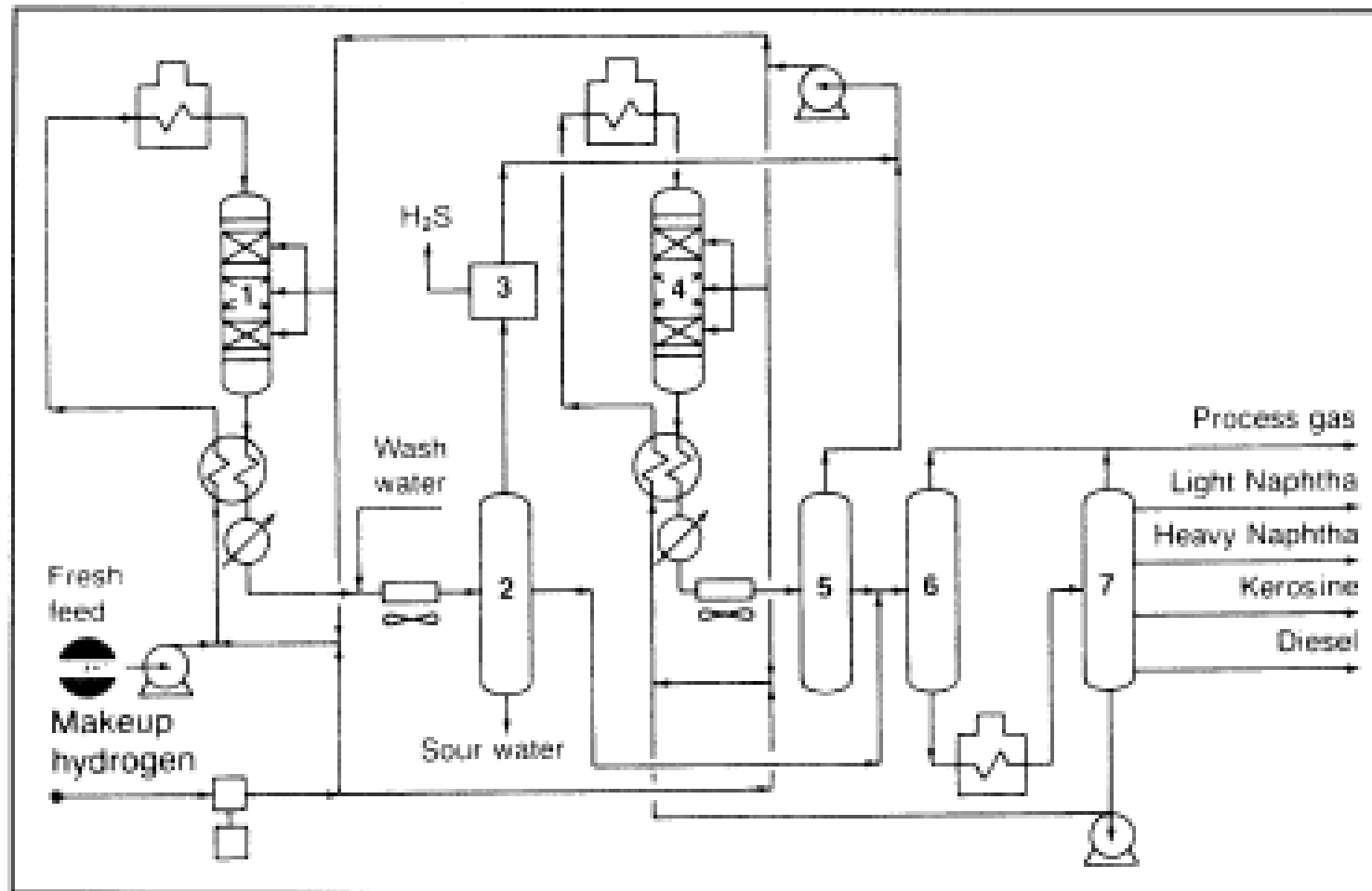


Figure 3-8. Flow diagram of a Chevron hydrocracking unit:29 (1,4) reactors, (2,5) HP separators, (3) recycle scrubber (optional), (6) LP separator, (7) fractionator.

Hydrodealkylation Process

Insert Reactions

Hydrotreatment Processes

- Hydrotreating is a hydrogen-consuming process primarily used to reduce or remove impurities such as sulfur, nitrogen, and some trace metals from the feeds.
- It also stabilizes the feed by saturating olefinic compounds.
- Feeds to hydrotreatment units vary widely; they could be any petroleum fraction, from naphtha to crude residues.



Hydrotreatment Processes

- In this process, the feed is mixed with hydrogen, heated to the proper temperature, and introduced to the reactor containing the catalyst.
- Typical reactor temperatures range from 260 to 425°C.
- Increasing the temperature and hydrogen partial pressure increases the hydrogenation and hydrodesulfurization reactions.
- The conditions are usually adjusted to minimize hydrocracking.

Hydrotreatment Processes

- Lower space velocities are used with feeds rich in polyaromatics.
- Total pressure varies widely—from 100 to 3,000 psi—depending on the type of feed, level of impurities, and the extent of hydrotreatment required.



Hydrotreatment Catalysts and Reactions

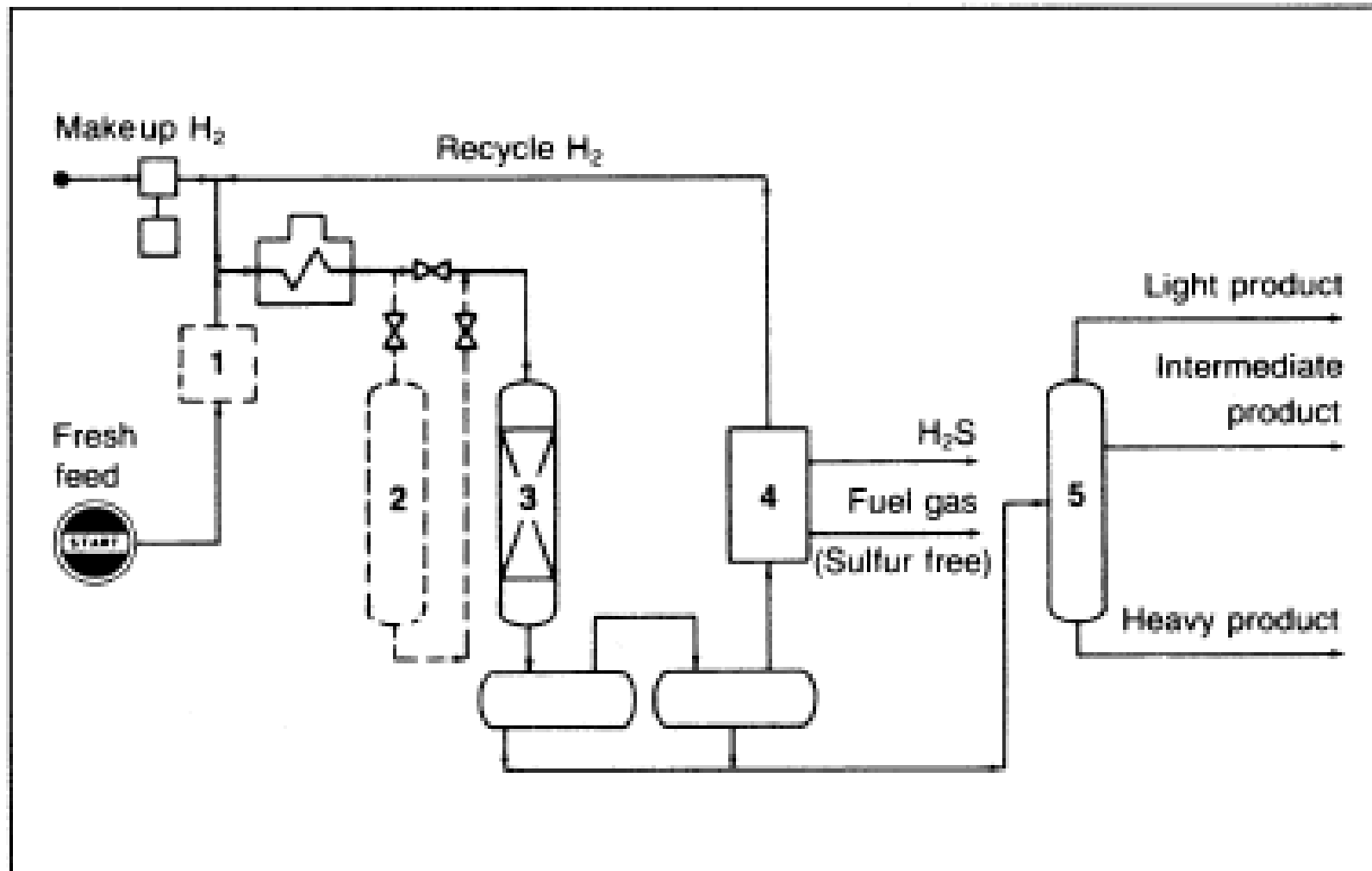
- The cobalt-molybdenum system supported on alumina is found to be an effective catalyst.
- Other catalyst systems used in HDS are NiO/MoO₃ and NiO/WO₃.

Hydrotreatment Catalysts and Reactions

- Reactions occurring in hydrotreatment units are mainly hydrodesulfurization and hydrodenitrogenation of sulfur and nitrogen compounds.
- Insert reactions here
- In the first case H_2S is produced along with the hydrocarbon. In the latter case, ammonia is released

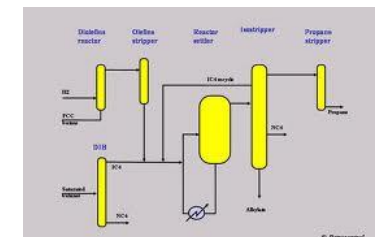
Hydrotreatment Catalysts and Reactions

- Reaction conditions are 300–400°C and 35–70 atm. For light distillates; 340–425°C and 55–170 atm. for heavy petroleum residua.
- Liquid hourly space velocities (LHSV) in the range of 2–10 hr⁻¹ are used for light products, while it is 0.2–10 hr⁻¹ for heavy residues.



Alkylation Process

- Alkylation produces larger hydrocarbon molecules in the gasoline range from smaller molecules.
- The products are branched hydrocarbons having high octane ratings
- Alkylates are the best of all possible motor fuels, having
- both excellent stability and a high octane number.
- Either concentrated sulfuric acid or anhydrous hydrofluoric acid is used as a catalyst for the alkylation reaction.



Alkylation

Insert all reactions here

Alkylation

- Alkylation generally applied to the acid catalyzed reaction between isobutane and various light olefins, and the product is known as the alkylate.
- Other olefins that are commercially alkylated are isobutene and 1- and 2-butenes.
- Alkylation of isobutene produces mainly 2,2,4-trimethylpentane (isooctane).

Alkylation

- Both sulfuric acid and hydrofluoric acid catalyzed alkylations are low temperature processes.
- One drawback of using H_2SO_4 and HF in alkylation is the hazards associated with it.

Isomerization Process

- It is an acid catalyzed and intended to produce highly-branched hydrocarbon mixtures.
- The low octane C₅/C₆ fraction obtained from natural gasoline or from a light naphtha fraction may be isomerized to a high octane product.
- A typical catalyst is platinum with a zeolite base.

Isomerization processes

- These catalysts serve the dual purpose of promoting carbonium ion formation and hydrogenation-dehydrogenation reactions.
- The reaction may start by forming a carbocation via abstraction of a hydride ion by a catalyst acid site.
- Alternatively, an olefin formed on the catalyst surface could be protonated to form the carbocation.
- Insert Reactions here

Oligomerization of Olefins (Dimerization)

- This process produces polymer gasoline with a high octane number.
- Both phosphoric and sulfuric acid were used as catalysts.
- At present, the feedstock is either a propylene-propane mixture or propylene-butane mixture where propane and butane are diluents.

Polymerization processes

- The product is an olefin having a high octane number.
- When propylene is used, a trimer or a tetramer is formed.
- The polymerization reaction is highly exothermic, so the temperature has to be controlled.
- The presence of propane and butane in the mixture acts as a heat sink to absorb part of the reaction heat.
- Typical reaction conditions are 170–250°C and 25–100 atm.

Polymerization processes

Insert Reactions here

Olefins and their production

- The most important olefins and diolefins used to manufacture petrochemicals are ethylene, propylene, butylenes, and butadiene.
- A small fraction of olefins is obtained from catalytic and thermal cracking gas streams.
- However, the petrochemical demand for olefins is much greater than the amounts these operations produce.
- Most olefins and butadienes are produced by steam cracking hydrocarbons.



steam cracking of hydrocarbons

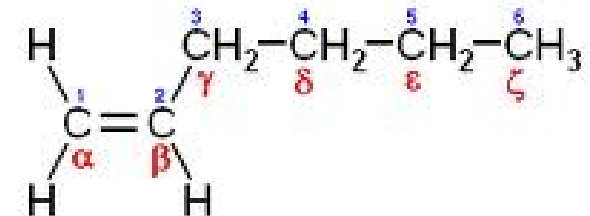
- The feedstocks for steam cracking units range from light paraffinic hydrocarbon gases to various petroleum fractions and residues.
- The cracking reactions are principally bond breaking, and a substantial amount of energy is needed to drive the reaction toward olefin production.
- The simplest paraffin (alkane) and the most widely used feedstock for producing ethylene is ethane.

Olefins

- Cracking ethane can be visualized as a free radical dehydrogenation reaction, where hydrogen is a coproduct:
- Insert reaction
- The reaction is highly endothermic, so it is favored at higher temperatures and lower pressures.
- Superheated steam is used to reduce the partial pressure of the reacting hydrocarbons

Olefins

- Superheated steam also reduces carbon deposits that are formed by the pyrolysis of hydrocarbons at high temperatures.
- Additionally, the presence of steam as a diluent reduces the hydrocarbons' chances of being in contact with the reactor tube-wall



Olefins

- Many side reactions occur when ethane is cracked.
- A probable sequence of reactions between ethylene and a formed methyl or an ethyl free radical could be represented:
- Reactions here

Olefins

- Propene and 1-butene, respectively, are produced in this free radical reaction.
- Higher hydrocarbons found in steam cracking products are probably formed through similar reactions.
- When liquid hydrocarbons such as a naphtha fraction or a gas oil are used to produce olefins, many other reactions occur.
- The main reaction, the cracking reaction, occurs by a free radical and beta scission of the C-C bonds.

Olefins

- This could be represented as:
- Reactions here

Olefin Production

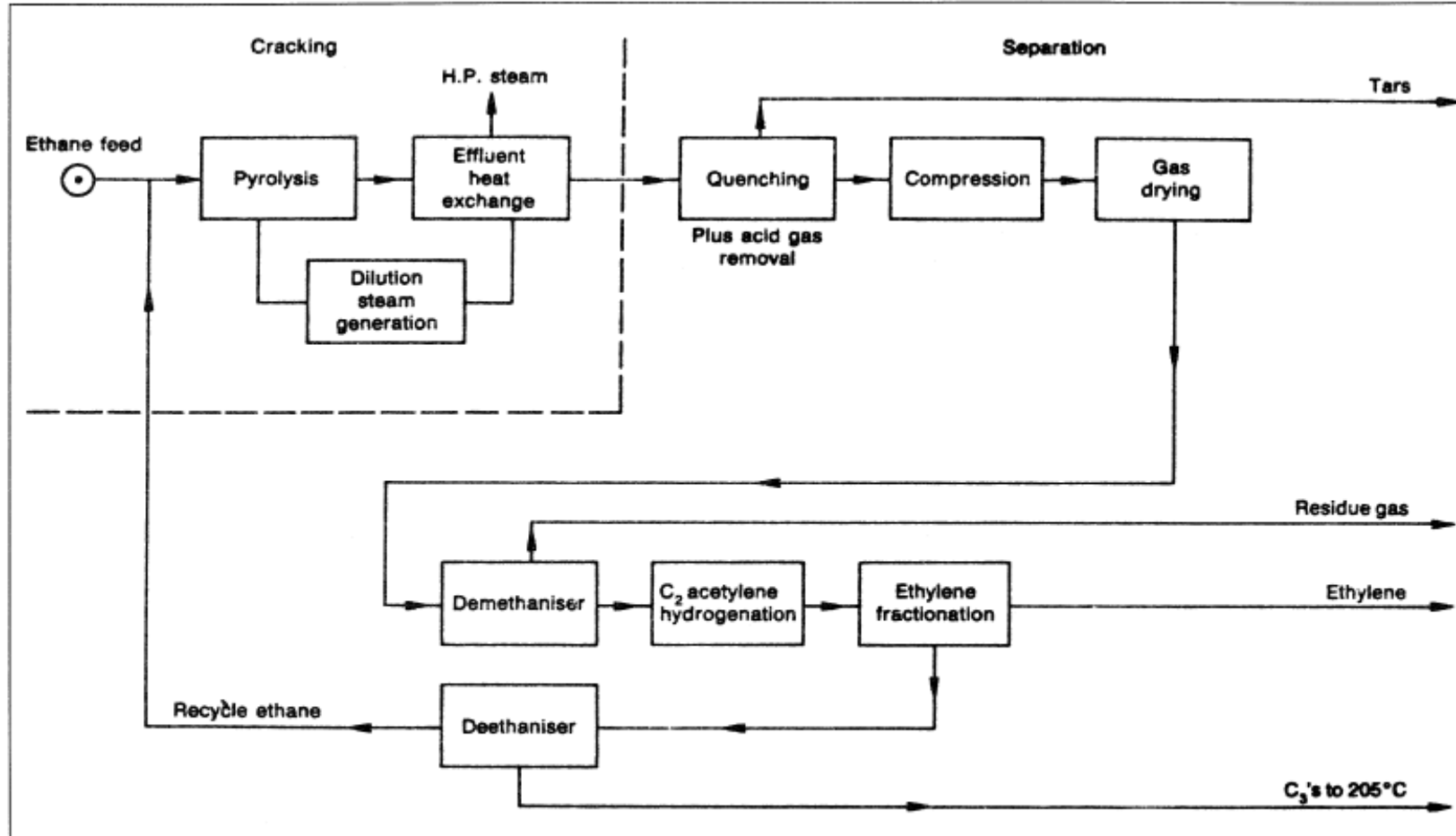


Figure 3-12. Block diagram for producing ethylene from ethane.

Steam Cracking Process

- A typical ethane cracker has several identical pyrolysis furnaces in which fresh ethane feed and recycled ethane are cracked with steam as a diluent.
- The outlet temperature is usually in the 800°C range.
- The furnace effluent is quenched in a heat exchanger and further cooled by direct contact in a water quench tower where steam is condensed and recycled to the pyrolysis furnace.
- After the cracked gas is treated to remove acid gases, hydrogen and methane are separated from the pyrolysis products in the demethanizer.

Steam Cracking Process

- The effluent is then treated to remove acetylene, and ethylene is separated from ethane and heavier in the ethylene fractionator.
- The bottom fraction is separated in the deethanizer into ethane and C₃₊ fraction.
- Ethane is then recycled to the pyrolysis furnace.

Process Variables

- Optimum temperatures are selected to maximize olefin production and minimize formation of carbon deposits.
- A typical furnace outlet temperature for cracking ethane is approximately 800°C, while the temperature for cracking naphtha or gas oil is about 675–700°C.
- Short residence times are required for high olefin yield.
- Residence times of 0.5–1.2 sec are typical.
- A higher steam/hydrocarbon ratio favors olefin formation.
- Steam reduces the partial pressure of the hydrocarbon mixture and increases the yield of olefins.

Steam/Hydrocarbon ratio

- Steam to hydrocarbon weight ratios range between 0.2–1 for ethane and approximately 1–1.2 for liquid feeds.
- Long chain hydrocarbons crack more easily than shorter chain compounds and require lower cracking temperatures.
- For example, the temperature and residence time that gave 60% conversion for ethane yielded 90% conversion for propane.

Feed Stock Composition

- Paraffinic hydrocarbons are easier to crack than cycloparaffins, and aromatics tend to pass through unaffected.
- Isoparaffins such as isobutane and isopentane give high yields of propylene.
- This is expected, because cracking at a tertiary carbon is easier:

Production of Diolefins

- Diolefins are hydrocarbon compounds that have two double bonds.
- [Reactions here](#)
- Conjugated diolefins have two double bonds separated by one single bond.
- Due to conjugation, these compounds are more stable than monoolefins and diolefins with isolated double bonds.
- Conjugated diolefins also have different reactivities than monoolefins.
- The most important industrial diolefinic hydrocarbons are butadiene and isoprene.

Butadiene (CH₂ = CH-CH = CH₂)

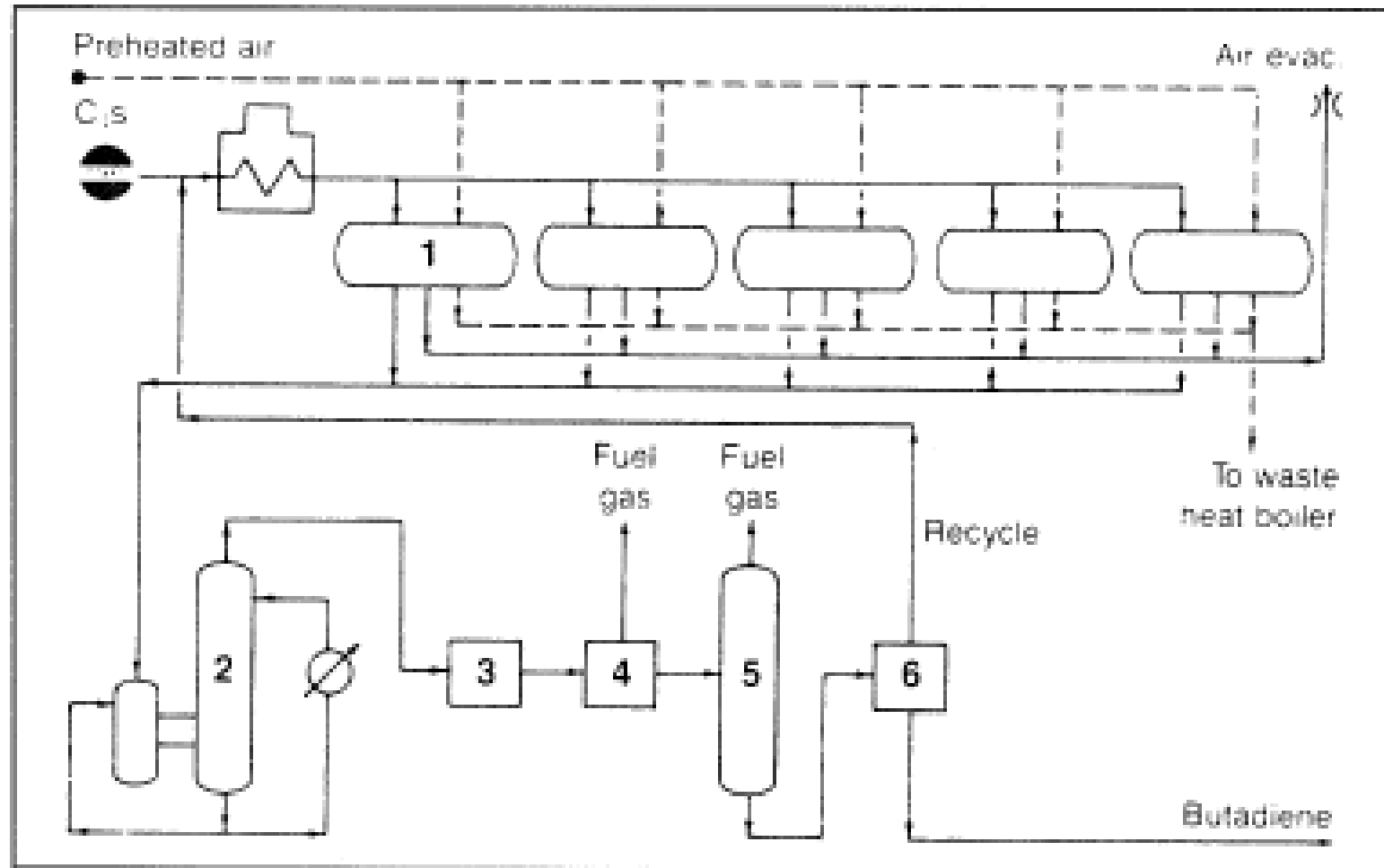
- Butadiene is the raw material for the most widely used synthetic rubber, a copolymer of butadiene and styrene (SBR).
- In addition to its utility in the synthetic rubber and plastic industries many chemicals could also be synthesized from butadiene.
- Butadiene is obtained as a by-product from ethylene production.
- It is then separated from the C₄ fraction by extractive distillation using furfural.

Butadiene

- Butadiene could also be produced by the catalytic dehydrogenation of butanes or a butane/butene mixture.
- Reactions here
- The first step involves dehydrogenation of the butanes to a mixture of butenes which are then separated, recycled, and converted to butadiene.
- The process may also be used for the dehydrogenation of mixed amylenes to isoprene.

Butadiene

- In the process, the hot reactor effluent is quenched, compressed, and cooled.
- The product mixture is extracted: unreacted butanes are separated and recycled, and butadiene is recovered



Butadiene

- The Phillips process uses an oxidative-dehydrogenation catalyst in the presence of air and steam.
- The C₄ mixture is passed over the catalyst bed at 900 to 1100°C.
- Hydrogen released from dehydrogenation reacts with oxygen, thus removing it from the equilibrium mixture and shifting the reaction toward the formation of more butadiene.

Butadiene

- In some parts of the world, as in Russia, fermented alcohol can serve as a cheap source for butadiene.
- The reaction occurs in the vapor phase under normal or reduced pressures over a zinc oxide/alumina or magnesia catalyst promoted with chromium or cobalt.
- Acetaldehyde has been suggested as an intermediate: two moles of acetaldehyde condense and form crotonaldehyde, which reacts with ethyl alcohol to give butadiene and acetaldehyde.

Butadiene

- Butadiene could also be obtained by the reaction of acetylene and formaldehyde in the vapor phase over a copper acetylide catalyst.
- The produced 1,4-butyne-1,3-diol is hydrogenated to 1,4-butanediol.
- Dehydration of 1,4-butanediol yields butadiene.

Isoprene

- Isoprene (2-methyl 1,3-butadiene) is the second most important conjugated diolefin after butadiene.
- Most isoprene production is used for the manufacture of cis-polyisoprene, which has a similar structure to natural rubber.
- It is also used as a copolymer in butyl rubber formulations.

Isoprene Production

- There are several different routes for producing isoprene.
- The choice of one process over the other depends on the availability of the raw materials and the economics of the selected process.
- While most isoprene produced today comes from the dehydrogenation of C₅ olefin fractions from cracking processes, several schemes are used for its manufacture via synthetic routes.

Dehydrogenation of Tertiary Amylenes (Shell Process)

- t-Amylenes (2-methyl-1-butene and 2-methyl-2-butene) are produced in small amounts with olefins from steam cracking units.
- The amylenes are extracted from a C₅ fraction with aqueous sulfuric acid.
- Dehydrogenation of t-amylenes over a dehydrogenation catalyst produces isoprene.
- The overall conversion and recovery of t-amylenes is approximately 70%.

Dehydrogenation of Tertiary Amylenes (Shell Process)

- The C₅ olefin mixture can also be produced by the reaction of ethylene and propene using an acid catalyst.
- The C₅ olefin mixture is then dehydrogenated to isoprene.

From Acetylene and Acetone

- A three-step process based on the reaction of acetylene and acetone in liquid ammonia in the presence of an alkali metal hydroxide.
- Reaction here
- The product, methylbutynol, is then hydrogenated
- to methylbutenol followed by dehydration at 250–300°C over an acidic heterogeneous catalyst.
- Reaction here

From Isobutylene and Formaldehyde (IFP Process)

- The reaction between isobutylene and formaldehyde produces a cyclic ether (dimethyl dioxane).
- [Reaction here](#)
- Pyrolysis of dioxane gives isoprene and formaldehyde.
- The formaldehyde is recovered and recycled to the reactor.
- [Reactions here](#)

From Isobutylene and Methylal (Sun Oil Process)

- In this process, methylal (dimethoxymethane) is used instead of formaldehyde.
- The advantage of using methylal over formaldehyde is its lower reactivity toward 1-butene than formaldehyde, thus allowing mixed feedstocks to be used.
- Also, unlike formaldehyde, methylal does not decompose to CO and H₂.
- The first step in this process is to produce methylal by the reaction of methanol and formaldehyde using an acid catalyst.
- **Reaction here**

Isoprene production

- The second step is the vapor phase reaction of methylal with isobutene to produce isoprene.
- 2-Butene in the C₄ mixture also reacts with methylal but at a slower rate to give isoprene. 1-Butene reacts slowly to give 1,3-pentadiene.
- [Reactions here](#)

From Propylene (Goodyear Process)

- Another approach for producing isoprene is the dimerization of propylene to 2-methyl-1-pentene.
- The reaction occurs at 200°C and about 200 atmospheres in the presence of a tripropyl aluminum catalyst combined with nickel or platinum.
- The next step is the isomerization of 2-methyl-1-pentene to 2-methyl-2-pentene using an acid catalyst.
- 2-Methyl-2-pentene is finally pyrolyzed to isoprene.