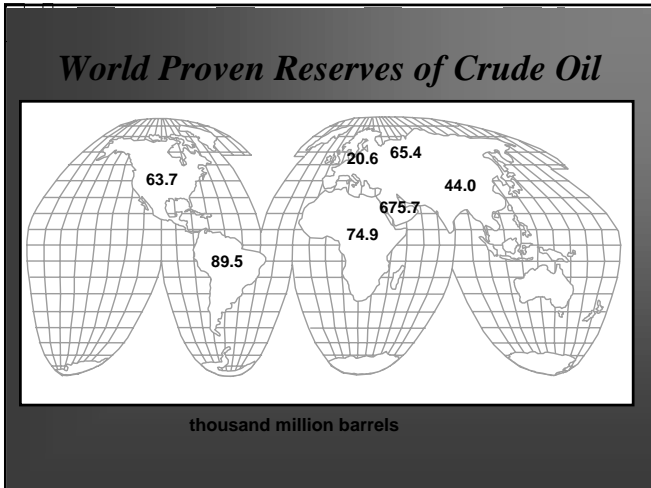
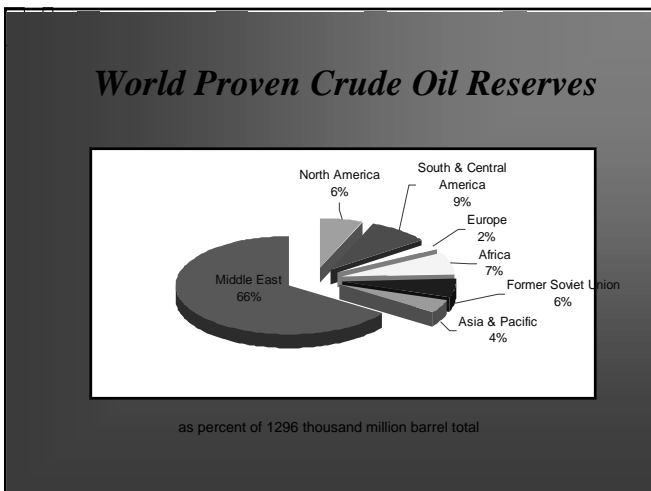


CHAPTER 3

CRUDE OIL PROCESSING AND PRODUCTION OF HYDROCARBONS

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Petroleum Composition

- Petroleum is a complex mixture of hydrocarbons
- Mostly saturated or aromatic (~10%)
- Small amounts of S (up to 10%), O (up to 5%), N (up to 1%), can have trace amounts of V, Fe, Al, Ca, Cu, Ni, Na, U
- Molecules range greatly in size and are separated into fractions based on boiling point

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4

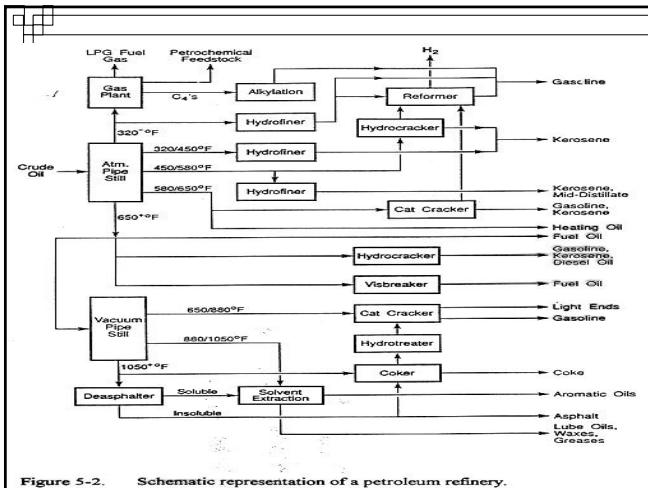


Figure 5-2. Schematic representation of a petroleum refinery.

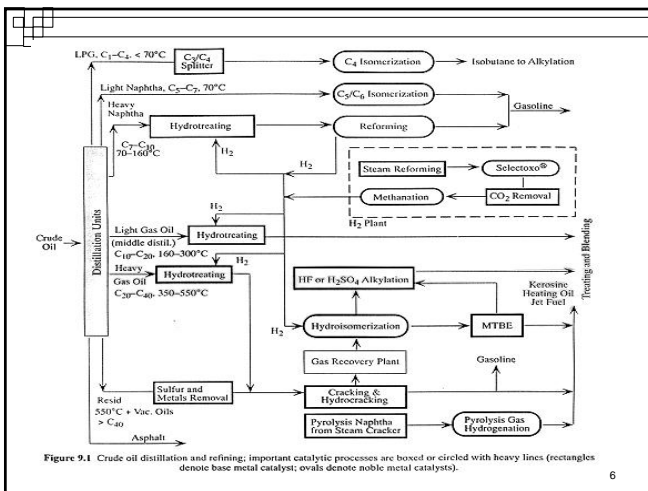
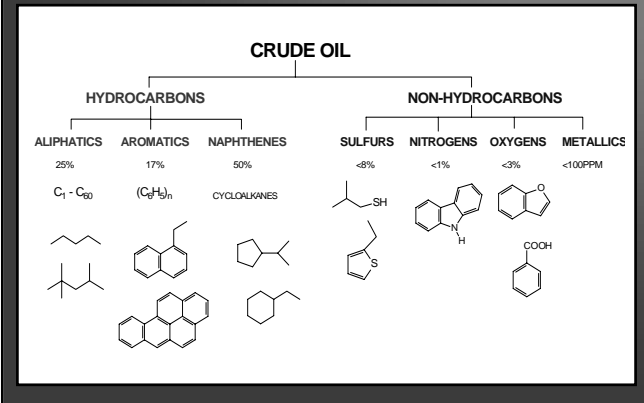


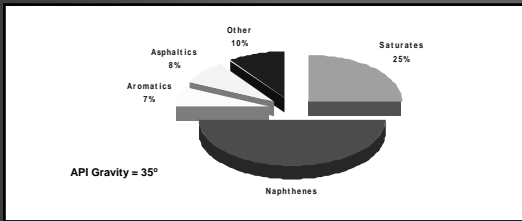
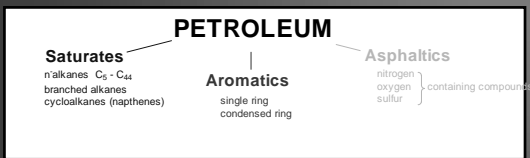
Figure 9.1 Crude oil distillation and refining; important catalytic processes are boxed or circled with heavy lines (rectangles denote base metal catalysts; ovals denote noble metal catalysts).

6

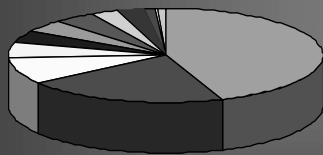
Composition of Crude Oil



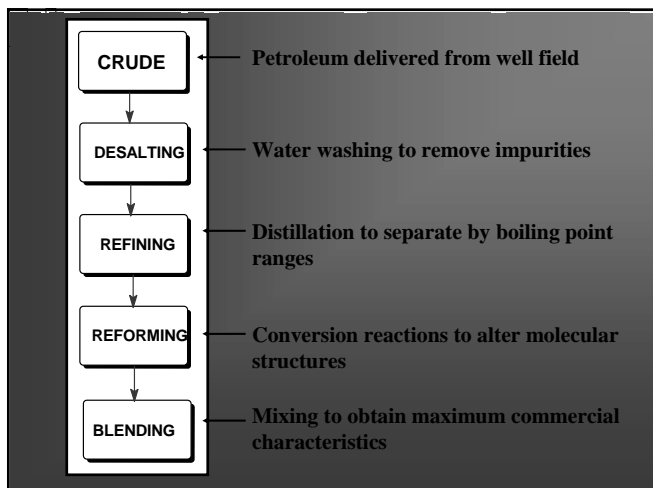
Crude Oil Classification



The Uses of Crude Oil



- | | |
|--------------------------|----------------------|
| Gasoline | Distillate Fuel Oil |
| Kerosene Jet Fuel | Residual Fuel Oil |
| Liquefied Refinery Gases | Still Gas |
| Coke | Asphalt and Road Oil |
| PETROCHEMICAL FEEDSTOCKS | Lubricants |
| Kerosene | Other |



Hydrocarbons

- Simplest organic compounds
 - Contain only carbon and hydrogen
 - Alkanes
 - Methane, propane, butane used as fuels
 - Single covalent bond between carbon atoms
 - Regular changes in physical properties as size of molecules change
 - Natural gas and petroleum mainly alkanes
 - Crude oil has carbon compounds with > 5 carbon atoms
 - Methane can also be produced by volcanoes, bacteria, and as a derivative of coal.

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Petroleum Products

- Separating different alkanes from petroleum...
 - Difficult, due to similar properties
 - Fractional distillation is used
 - Crude oil heated, and vapors are removed and condensed at progressively higher temperatures
 - Gasoline – low concentration in crude oil
 - Cracking: process of breaking larger hydrocarbons into smaller ones using a catalyst
 - Polymerization = small molecules joined together using heat, pressure and catalysts

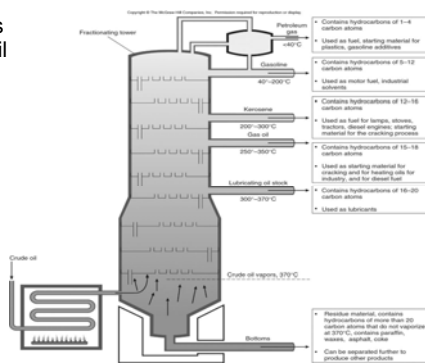
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Octane Rating of Gasoline

- Measure of tendency to prevent “knocking” (pre-detonation)
 - Higher octane = fewer “knocks”
 - Heptanes (straight-chain) = 0
 - Isooctane (branched-chain) = 100
 - Octane boosters
 - Tetraethyl lead
 - MTBE
 - Methanol and reformulated gasoline

Hydrocarbon Distillation

- Distillation towers separate crude oil into fractions according to the boiling points of each fraction.

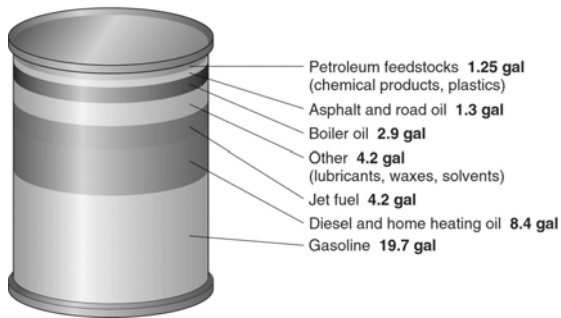


Spills and Leaks

- Types of spills and leaks
 - Accidental spills and leaks
 - Exxon Valdez – Most significant spill
 - Seepage from underground storage tanks
 - Deliberate spills and dumping
 - Ships illegally purging sumps and bilges
 - Natural seeps and leakage
 - Leakage of oil and gas along natural fractures (Santa Barbara beach example)
- Effects
 - Short-term: birds, fish, and other marine/land animals
 - Long-term: some spills have had a long-term positive impact!

Refining Crude Oil – End Products

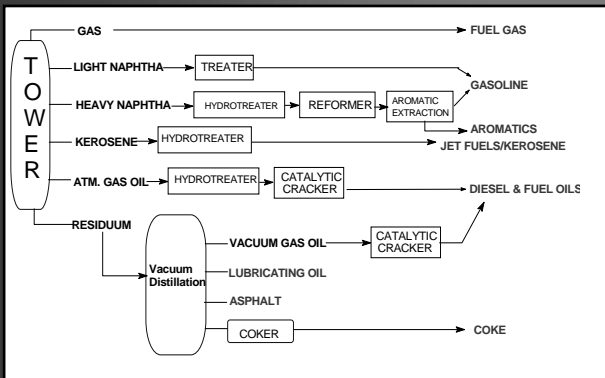
Barrel of Crude Oil



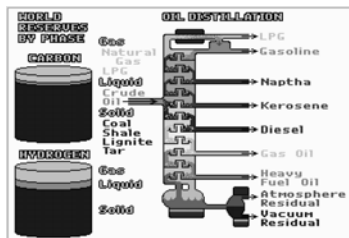
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16

Petroleum Refining



The Refining Process



- Distilling column separates crude into fractions based on b.p.
- A column can separate ~25,000 barrels/day

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18

Crude Oil Refining

Distillate Fraction	Boiling Point (°C)	Carbon Atoms per Molecule
Gases	below 30	1-4
Gasoline	30-210	5-12
Naphtha	100-200	8-12
Kerosene & Jet Fuel	150-250	11-13
Diesel & Fuel Oil	160-400	13-17
Atmospheric Gas Oil	220-345	
Heavy Fuel Oil	315-540	20-45
Atmospheric Residue	over 450	over 30
Vacuum Residue	over 615	over 60

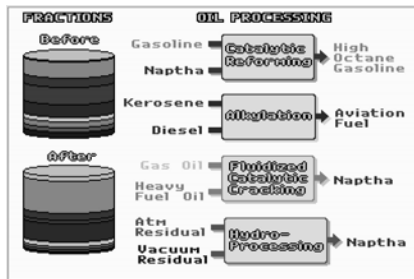
Distillation Fractions

- The demand for different fractions varies with the time of year.
- Gasoline is consumed in large amounts during summer.
- Fuel oil is consumed for heating in winter
- Demands also vary with regional climates
- Refineries are able to alter the ratios of the fractions produced to meet demand & maximize profit

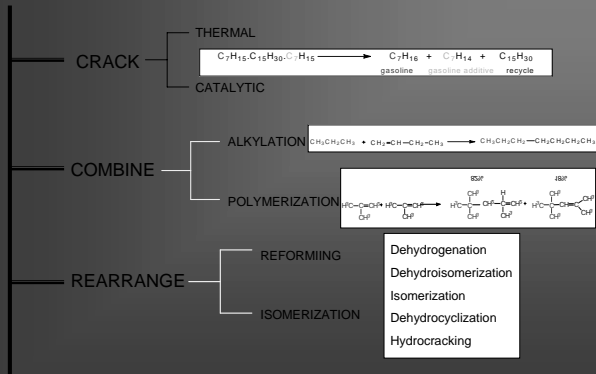
Oil Processing

The distilled fractions can be altered in chemical reactors to produce increased amounts of high demand fuels.

Chemical Alteration Processes

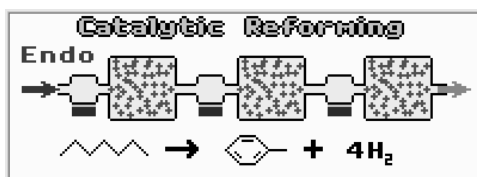


Conversion Reactions



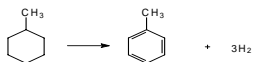
Catalytic Reforming

- Produces high octane gasoline
- feedstocks are heated to 500°C & passed through a series of reactors containing Pt/Al₂O₃ catalyst
- Products are aromatic hydrocarbons

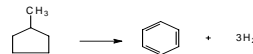


Catalytic Reforming – Conversion Reactions

Dehydrogenation of cycloalkanes to aromatics



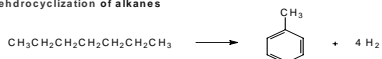
Dehydroisomerization of cyclopentanes to aromatics



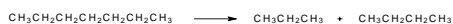
Isomerization of alkanes



Dehydrocyclization of alkanes



Hydrocracking of alkanes



Catalytic Reforming- Reformer Feeds

- The feed to a catalytic reformer is normally a heavy naphtha fraction produced from atmospheric distillation units.
- Naphtha from other sources such as those produced from cracking and delayed coking may also be used.
- Before using naphtha as feed for a catalytic reforming unit, it must be hydrotreated to saturate the olefins and to hydrodesulfurize and hydrodenitrogenate sulfur and nitrogen compounds.

Catalytic Reforming- Reformer Feeds

- Olefinic compounds are undesirable because they are precursors for coke, which deactivates the catalyst. Sulfur and nitrogen compounds poison the reforming catalyst.
- The reducing atmosphere in catalytic reforming promotes forming of hydrogen sulfide and ammonia.
- Ammonia reduces the acid sites of the catalyst, while platinum becomes sulfided with H₂S.
- Feeds with a high naphthene content are easier to aromatize than feeds with a high ratio of paraffins

Catalytic Reforming - 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.

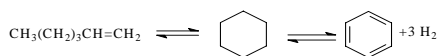
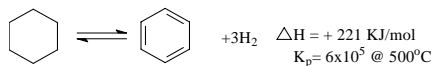
Catalytic Reforming- Reforming Catalysts

- 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.
- A ratio of 0.5 or less for Pt/Re in the new generation catalysts versus 1.0 for the older ones can tolerate much higher coke levels. Reforming units can perform similarly with higher coke levels (20-25% versus 15-20%).
- These catalysts can tolerate higher sulfur naphtha feeds (>1 ppm). Higher profitability may be realized by increasing the cycle length.

Catalytic Reforming- Reforming Reactions

Aromatization

- The dehydrogenation of naphthenes and the dehydrocyclization of paraffins.

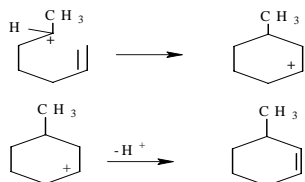


$$\Delta H = +266 \text{ KJ/mol}$$
$$P_p = 7.8 \times 10^4 \text{ @ } 500^\circ\text{C}$$

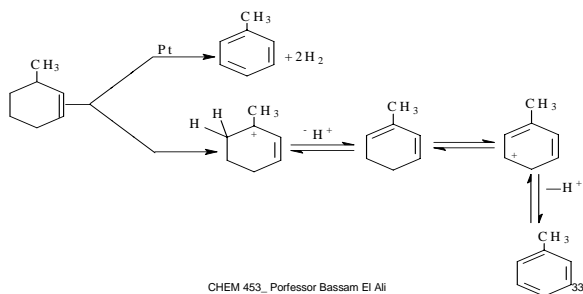
Selectivity to benzene from reforming n-hexane over a platinum catalyst

LHSV	Temp., °F	% Conversion	Selectivity to Benzene	Selectivity to Isohexane
2	885	80.2	16.6	58
2	932	86.8	24.1	36.9
2	977	90.4	27.4	23.4

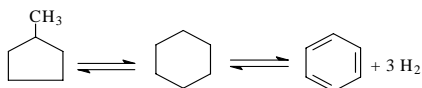
- The cyclization of paraffins over the platinum catalyst, the formed olefin species reacts with the acid catalyst forming a carbocation.
- Carbocation formation may occur by abstraction of a hydride ion from any position along the hydrocarbon chain.
- However, if the carbocation intermediate has the right configuration, cyclization occurs. For example, cyclization of 1-heptene over the alumina catalyst can occur by the following successive steps:



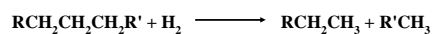
- The formed methylcyclohexane carbocation eliminates a proton, yielding 3-methylcyclohexene. 3-Methylcyclohexene can either dehydrogenate over the platinum surface or form a new carbocation by losing H- over the acid catalyst surface.
- This step is fast, because an allylic carbonium ion is formed. Losing a proton on a Lewis base site produces methyl cyclohexadiene.



- Isomerization of alkylcyclopentanes may also occur on the platinum catalyst surface or on the silica/alumina.
- For example, methylcyclopentane isomerizes to cyclohexane. The formed cyclohexane can dehydrogenate to benzene.



- Hydrocracking is a hydrogen-consuming reaction that leads to higher gas production and lower liquid yield.
- This reaction is favored at high temperatures and high hydrogen partial pressure. Bond breaking can occur at any position along the hydrocarbon chain.



- 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 is a cracking reaction of an aromatic side chain in presence of hydrogen.
- Like hydrocracking, the reaction consumes hydrogen and is favored at a higher hydrogen partial pressure.
- This reaction is particularly important for increasing benzene yield when methylbenzenes and ethylbenzene are dealkylated.
- Although the overall reaction is slightly exothermic, the cracking step is favored at higher temperatures.
- Hydrodealkylation may be represented by the reaction of toluene and hydrogen.



Catalytic Reforming - Reforming Process

- Catalytic reformers are normally designed to have a series of catalyst beds (typically three 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. Isomerization and hydrocracking reactions are slow.
- They have low equilibrium constants and may not reach equilibrium before exiting the reactor.

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Catalytic Reforming - Reforming Process

- 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.

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Catalytic Reforming - Reforming Process

- 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. Liquid hourly space velocity (LHSV) is an important operation parameter expressed as **the volume of hydrocarbon feed per hour per unit volume of the catalyst**. Operating at lower LHSV gives the feed more contact with the catalyst.

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Catalytic Reforming - Reforming Process

- Regeneration of the catalyst may be continuous for certain processes that are designed to permit the removal and replacement of the catalyst during operation.
- 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).

Catalytic Reforming - Reforming Process

- Products from catalytic reformers (the reformate) is a mixture of aromatics, paraffins and cycloparaffins ranging from C6-C8.
- 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.

Catalytic Reforming - Reforming Process

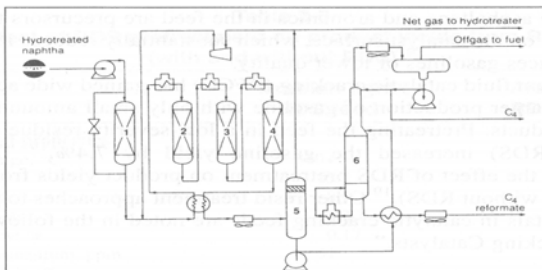


Figure 3-5. Flow diagram of a Chevron Rheinforming unit: (1) sulfur sorber, (2-4) reactors, (5) separator, (6) stabilizer

Catalytic Cracking

- Catalytic cracking (Cat-cracking) - 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 (isomerization and dehydrocyclization reactions).
- Products from catalytic cracking - lower olefin content in the liquid products (more saturated hydrocarbons than in thermally cracked products).

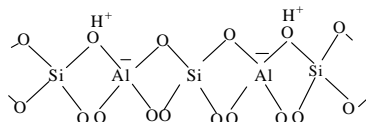
- The feeds to catalytic cracking units - gas oils to crude residues.
- Heavier feeds contain higher concentrations of basic and polar molecules as well as asphaltenes.
- Basic nitrogen compounds, which are readily adsorbed on the catalyst acid sites and lead to instantaneous albeit temporary deactivation.

- Polycyclic aromatics and asphaltenes contribute strongly to coke formation.
- Excessive asphaltene and aromatics in the feed are precursors to carbon formation on the catalyst surface, which substantially reduces its activity and produces gasoline of lower quality.
- Residuum fluid catalytic cracking (RFCC) - a larger production of gasoline with only small amounts of low value products.

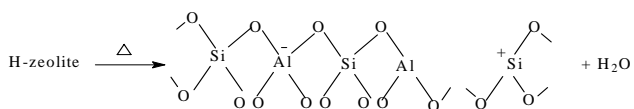
Cracking Catalysts

- Acid-treated clays - first catalysts used in catalytic cracking processes- replaced by synthetic amorphous silica-alumina (more active and stable).
- Incorporating zeolites (crystalline alumina-silica) with the silica/alumina catalyst improves selectivity towards aromatics.
- Both Lewis and Brønsted acid sites promote carbonium ion formation.
- Zeolites - holes in the crystal lattice, which are formed by the silica-alumina tetrahedra. 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.


- Four oxygen anions in the tetrahedron are balanced by the +4 oxidation state of the silicon cation.
 - Four oxygen anions connecting the aluminum cation are not balanced.
 - -1 net charge should be balanced. Metal cations such as Na^+ , Mg^{2+} , or protons (H^+) balance the charge of the alumina tetrahedra.
 - Brønsted acid sites in HY zeolites mainly originate from protons that neutralize the alumina tetrahedra.



- When HY-zeolite (X- and Y zeolites are cracking catalysts) is heated to temperatures in the range of 400-500°C, Lewis acid sites are formed.




A Lewis acid site




- **Zeolites** as cracking catalysts are characterized by higher activity and better selectivity toward **middle distillates** than **amorphous silica-alumina** catalysts (a greater acid sites density and a higher adsorption power for the reactants on the catalyst surface).
- Higher selectivity of zeolites
 - smaller pores, which allow diffusion of only smaller molecules through their pores.
 - higher rate of hydrogen transfer reactions.
 - Silica-alumina matrix has the ability to crack larger molecules.

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- Aluminum distribution in zeolites is also important to the catalytic activity.
 - A non balance in charge between the silicon atoms in the zeolite framework creates active sites, which determine the predominant reactivity and selectivity of FCC catalyst.
 - Selectivity and octane performance are correlated with unit cell size, which in turn can be correlated with the number of aluminum atoms in the zeolite framework.

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- Deactivation of zeolite catalysts - coke formation and to poisoning by heavy metals.
 - 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, and contamination by metals such as vanadium and sodium.

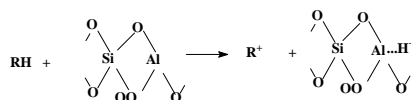
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- Pretreating the feedstocks with hydrogen is not always effective in reducing heavy metals, and it is expensive.
- Other means : modifying the composition and the microporous structure of the catalyst or adding metals like Sb, Bi or Sn, or Sb-Sn combination.
- Antimony organics have been shown to reduce by 50% gas formation due to metal contaminants, especially nickel.

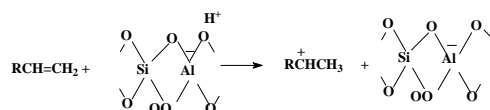
Cracking Reactions

- Difference between thermal and catalytic cracking : carbocation intermediate, compared to the free radical intermediate.
- 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.

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

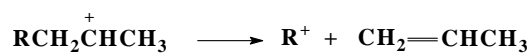


3. Reaction of a carbonium ion formed from step 1 or 2 with another hydrocarbon by abstraction of a hydride ion

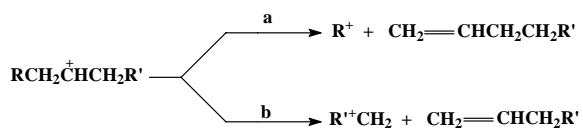


- Abstraction of a hydride ion from a tertiary carbon is easier than from a secondary, which is easier than from a primary position.
- The formed carbocation can rearrange through a methide-hydride shift similar to what has been explained in catalytic reforming.
- This isomerization reaction is responsible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

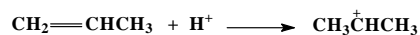
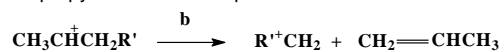
- The most important cracking reaction, however, is the carbon-carbon beta bond scission.



- The carbon-carbon beta scission may occur on either side of the carbocation, with the smallest fragment usually containing at least three carbon atoms.

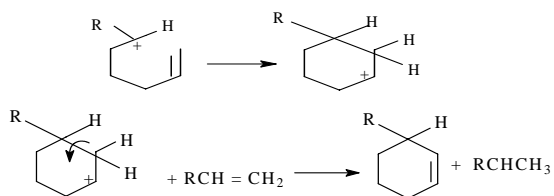
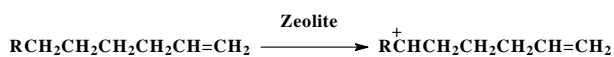


- If R = H in the above example, then according to the beta scission rule (an empirical rule) only route b becomes possible, and propylene would be a product.

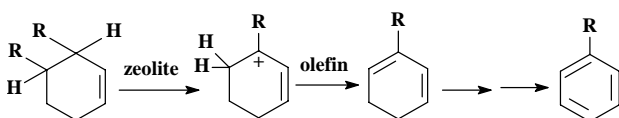


- The propene may be protonated to an isopropyl carbocation.
- An isopropyl carbocation cannot experience a beta fission.
- It may either abstract a hydride ion from another hydrocarbon, yielding propane, or revert back to propene by eliminating a proton. This could explain the relatively higher yield of propene from catalytic cracking units than from thermal cracking units

- Aromatization of paraffins can occur through a dehydro-cyclization reaction. Olefinic compounds formed by the beta scission can form a carbocation intermediate with the configuration conducive to cyclization.



- The next step is the **abstraction of a hydride ion** by a Lewis acid site from the zeolite surface to form the more stable **allylic** carbocation. This is again followed by a proton elimination to form a cyclohexadiene intermediate. The same sequence is followed until the ring is completely aromatized.






Cracking Process

- Most catalytic cracking reactors are either fluid bed or moving bed.
- The more common is fluidized bed process (FCC). The catalyst is an extremely porous powder with an average particle size of 60 microns.
- Catalyst size is important, because it acts as a liquid with the reacting hydrocarbon mixture.
- In the process, the preheated feed enters the reactor section with hot regenerated catalyst through one or more risers where cracking occurs.
- A riser is a fluidized bed where a concurrent upward flow of the reactant gases and the catalyst particles occurs.



Cracking Process

- 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.

- 
- Fluid catalytic cracking produces unsaturates, especially in the light hydrocarbon range C3-C5, which are used as petrochemical feedstocks and for alkylate production.
 - In addition to hydrocarbon gases, FCC units produce gasoline with high octane numbers (due to the high aromatic content, branched paraffins and olefins), gas oils, and tar.

■ The ratio of these products depends greatly on the different process variables.

■ Higher conversions increase gas and gasoline yields. Higher conversion also increases coke formation. Process variables that increase conversion are higher temperatures, longer residence times, and higher catalyst/oil ratio.

CHEM 453_ Professor Bassam El Ali 64

Deep Catalytic Cracking

■ Deep catalytic cracking (DCC) is a catalytic cracking process which selectively cracks a wide variety of feedstocks into light olefins.

■ The reactor and the regenerator systems are similar to FCC.

■ However, innovation in the catalyst development, severity, and process variable selection enables DCC to produce more olefins than FCC.

■ In this mode of operation, propylene plus ethylene yields could reach over 25%. In addition, a high yield of amylenes (C5 olefins) is possible.

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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.

■ Products from hydrocracking processes lack olefinic hydrocarbons.

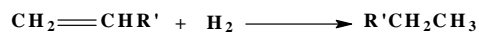
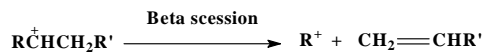
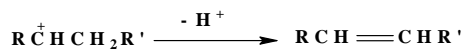
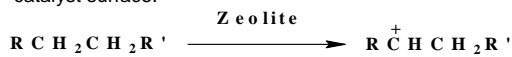
■ The product slate ranges from light hydrocarbon gases to gasolines to residues. Depending on the operation variables, the process could be adapted for maximizing gasoline, jet fuel, or diesel production.

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Hydrocracking Catalysts and Reactions

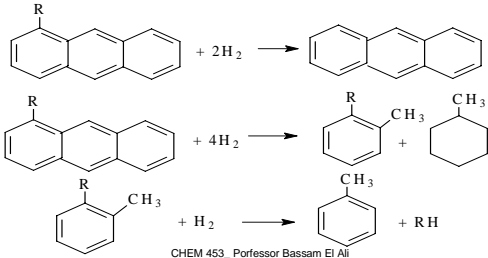
- The dual-function catalysts used in hydrocracking provide high surface area cracking sites and hydrogenation-dehydrogenation sites.
- Amorphous silica-alumina, zeolites, or a mixture of them promote carbonium ion formation.
- Catalysts with strong acidic activity promote isomerization, leading to a high iso/normal ratios.
- The hydrogenation-dehydrogenation activity, on the other hand, is provided by catalysts such as **cobalt, molybdenum, tungsten, vanadium, palladium, or rare earth elements.**

- As with catalytic cracking, the main reactions occur by carbonium ion and beta scission, yielding two fragments that could be hydrogenated on the catalyst surface.
- The first-step is the formation of a carbocation over the catalyst surface:

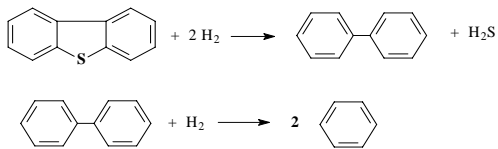


- Most products from hydrocracking are saturated. For this reason, gasoline from hydrocracking units have lower octane ratings than those produced by catalytic cracking units.
- They have a lower aromatic content due to high hydrogenation activity.
- Products from hydrocracking units are suitable for jet fuel use.
- Hydrocracking 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.
- Dealkylation, fragmentation, and hydrogenation of substituted polynuclear aromatics may also occur. The following is a representative example of hydrocracking of a substituted anthracene.



- The reactions proceed at different rates depending on the process variables.
- Hydrodesulfurization of complex sulfur compounds such as dibenzothiophene also occurs under these conditions.
- The desulfurized product may crack to give two benzene molecules:

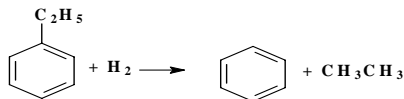
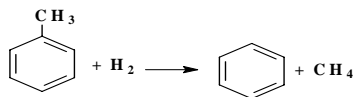


Hydrocracking Process

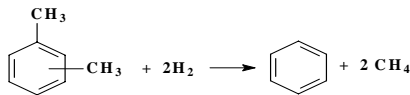
- Most commercial hydrocracking operations use a single stage for maximum middle-distillate optimization or a two-stage operation.
- In the single stage process two operation modes are possible, a once-through mode and a total conversion of the fractionator bottoms through recycling.
- In the once-through operation low sulfur fuels are produced and the fractionator bottoms are not recycled.
- In the total conversion mode the fractionator bottoms are recycled to the inlet of the reactor to obtain more middle distillates.
- In the 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.

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 reformat, 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. For example, toluene dealkylates to methane and benzene, while ethylbenzene produces ethane and benzene. In each case one mole of H_2 is consumed:



- Dealkylation of polysubstituted benzene increases hydrogen consumption and gas production (methane). Unconverted toluene and xylenes are recycled.



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. The process is relatively simple: choosing the desulfurization process depends largely on the feed type, the level of impurities present, and the extent of treatment needed to suit the market requirement.

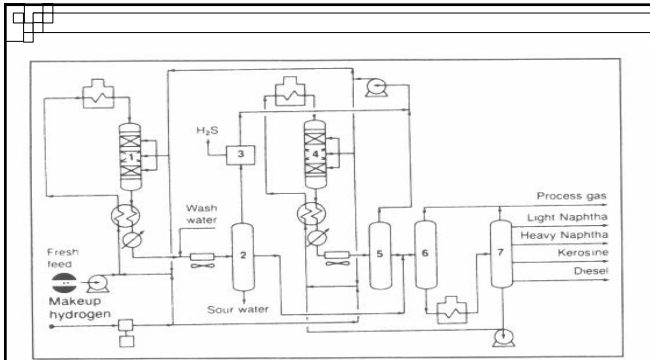


Figure 3-8. Flow diagram of a Chevron hydrocracking unit: (1, 4) reactors, (2, 5) HP separators, (3) recycle scrubber (optional), (6) LP separator, (7) fractionator.

Products from hydrodesulfurization of feeds with different sulfur levels

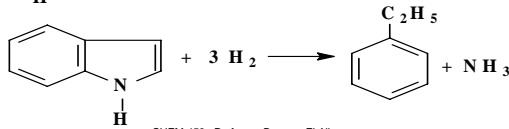
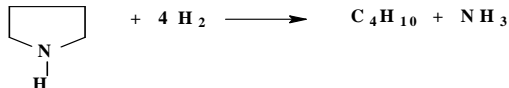
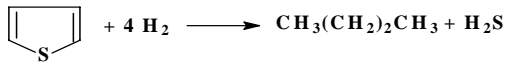
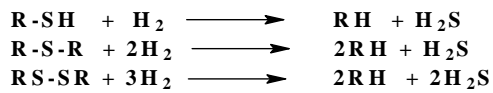
Process	VGO*	VRDS**	VGO+ VRDS	RDS***
Feed sulfur, wt %	2.3	4.1	2.9	2.9
Product sulfur, wt %	0.1	1.28	0.5	0.5
Product yields				
C1-C4 wt %	0.59	0.56	0.58	0.58
H ₂ S, NH ₃ , wt %	2.44	3.00	2.55	2.55
C ₅ +, wt %	97.51	97.34	97.46	97.67
C ₅ +, LV %	100.6	102.0	101.0	101.5
Hydrogen consumption				
scf/bbl	330	720	450	550
scf/lb sulfur	47	71	56	69

* Vacuum gas oil hydrotreater
 ** Vacuum residuum hydrotreater
 *** Atmospheric residuum desulfurization hydrotreating

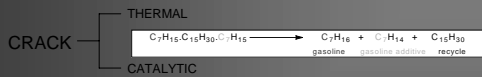
- In this process, the feed is mixed with hydrogen, heated to the proper temperature, and introduced to the reactor containing the catalyst.
- The conditions are usually adjusted to minimize hydrocracking.
- Typical reactor temperatures range from 260 to 425°C. Hydrogen partial pressure and space velocity are important process variables.
- Increasing the temperature and hydrogen partial pressure increases the hydrogenation and hydrodesulfurization reactions.
- Lower space velocities are used with feeds rich in polyaromatics.

Hydrotreatment Catalysts and Reactions

- Catalysts used in hydrotreatment (hydrodesulfurization, HDS) processes should be sulfur-resistant. The cobalt-molybdenum system supported on alumina was found to be an effective catalyst.
- The catalyst should be reduced and sulfided during the initial stages of operation before use. Other catalyst systems used in HDS are NiO/MoO₃ and NiO/WO₃.
- Because mass transfer has a significant influence on the reaction rates, catalyst performance is significantly affected by the particle size and pore diameter.
- Reactions occurring in hydrotreatment units are mainly hydrodesulfurization and hydrodenitrogenation of sulfur and nitrogen compounds.
- In the first case H₂S is produced along with the hydrocarbon. In the latter case, ammonia is released.



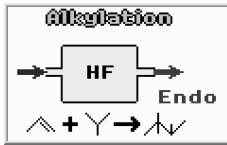
Conversion Reactions



- REARRANGE
- REFORMING
 - ISOMERIZATION
- Dehydrogenation
Dehydroisomerization
Isomerization
Dehydrocyclization
Hydrocracking

Alkylation Process

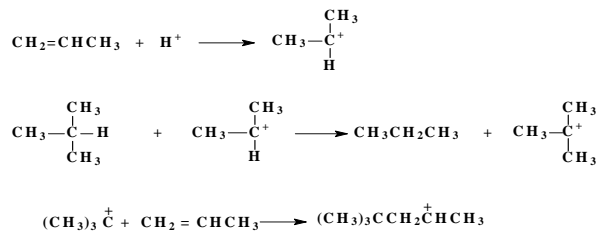
- Acid catalyzed reaction between isobutene and various light olefins, and the product is known as the alkylate.
- Produces high octane gasoline
- Requires an acid catalyst (usually H_2SO_4 or HF)
- Products have high degree of branching
- Octane rating:
aromatic > branched chain > straight chain



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82

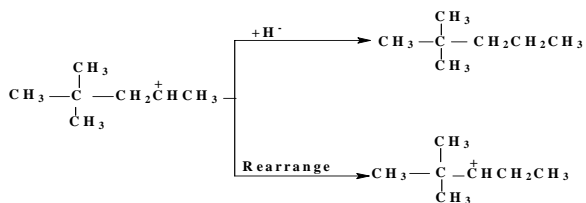
- For example, when propene is used with isobutene, a mixture of C5 isomers is produced.



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83

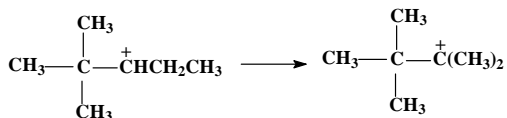
- The formed carbocation from the last step may abstract a hydride ion from an isobutene molecule and produce 2,2-dimethylpentane, or it may rearrange to another carbocation through a hydride shift.



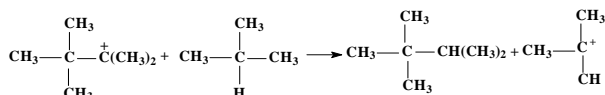
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84

- The new carbocation can rearrange again through a methide/hydride shift.



- The rearranged carbocation finally reacts with isobutene to form 2,2,3-trimethylbutane.
- The final product contains approximately 60-80% 2,2-dimethylpentane and varying amounts of 2,2,3-trimethylbutane and 2-methylhexane.



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85

- The presence of impurities such as butadiene affects the product yield and properties. Butadiene tends to polymerize and form acid-soluble oils, which increases acid makeup requirements. For every pound of butadiene in the feed, ten pounds of additional make-up acid will be required.
- Other olefins that are commercially alkylated are isobutene and 1- and 2-butenes. Alkylation of isobutene produces mainly 2,2,4-trimethylpentane (isooctane).

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86

Ranges of operating conditions for H₂SO₄ and HF alkylation

Process catalysts	H ₂ SO ₄	HF
Temperature, °C	2-16	16-52
Isobutane/olefin feed	3-12	3-12
Olefin space velocity, vo/hr./vo	0.1-0.6	-
Olefin contact time, min	20-30	8-20
Catalysts acidity, wt %	88-95	80-95
Acid in emulsion, vol %	40-60	25-80

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87

Isomerization Process

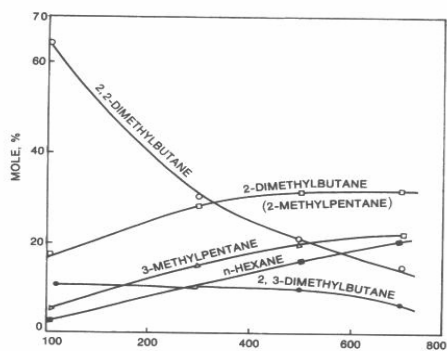
- Isomerization is a small-volume but important refinery process.
- Like alkylation, it is acid catalyzed and intended to produce highly-branched hydrocarbon mixtures.
- The low octane C5/C6 fraction obtained from natural gasoline or from a light naphtha fraction may be isomerized to a high octane product.
- Dual-function catalysts activated by either inorganic or organic chlorides are the preferred isomerization catalysts.

- A typical catalyst is platinum with a zeolite base.
- These catalysts promote 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.
- An olefin formed on the catalyst surface could be protonated to form the carbocation.
- The carbocation isomerizes by a 1,2-hydride/methide shift.

Oligomerization of Olefins (Dimerization)

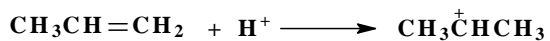
- This process produces polymer gasoline with a high octane.
- Dimerization was first used (1935) to dimerize isobutylene to diisobutylene, constituted of 2,4,4-trimethyl-1-pentene (80%) and 2,4,4-trimethyl-2-pentene (20%). Both phosphoric and sulfuric acid were used as catalysts.
- At present, the feedstock is either a propylene-propane mixture or propylene-butane mixture where propane and butane are diluents.

- 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.



Vapor phase equilibrium for hexanes.

- The polymerization reaction starts by protonating the olefin and forming a carbocation. For example, protonating propene gives isopropyl carbocation. The proton is provided by the ionization of phosphoric acid.



■ The next step is the reaction of the carbocation with the olefin (propene or butene).

$$\text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\overset{+}{\text{C}}\text{HCH}_3 \longrightarrow \text{CH}_3\overset{\text{CH}_3}{\underset{|}{\text{C}}}\text{HCH}_2\overset{+}{\text{C}}\text{HCH}_3$$

$$\begin{array}{l}
 \text{CH}_3 \\
 | \\
 \text{CH}_3\text{-CH-CH}_2\overset{+}{\text{C}}\text{HCH}_3 \\
 \left\{ \begin{array}{l}
 \xrightarrow{\text{CH}_3\text{CH}=\text{CH}_2} \text{CH}_3\overset{\text{CH}_3}{\underset{|}{\text{C}}}\text{H}-\text{CH}=\text{CHCH}_3 \\
 \text{Dimer} \\
 \\
 \xrightarrow{\text{CH}_3\text{CH}=\text{CH}_2} \text{CH}_3\overset{\text{CH}_3}{\underset{|}{\text{C}}}\text{H}-\text{CH}_2\overset{\text{CH}_3}{\underset{|}{\text{C}}}\text{HCH}=\text{CH}-\text{CH}_3 \\
 \text{Trimer}
 \end{array} \right.
 \end{array}$$

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■ The newly-formed carbocation either eliminates a proton and forms a dimer or attacks another propene molecule and eliminates a proton, giving the trimer.

■ Further propagation of the trimer produces a C9 carbonation which may further react with another propene molecule and eventually produce propylene tetramer.

■ The product is a mixture of dimers, trimers, tetramers, and pentamers having an average RON (Research Octane Number) = 95.

$$\begin{array}{l}
 \text{CH}_3 \\
 | \\
 \text{CH}_3\text{-CH-CH}_2\overset{+}{\text{C}}\text{HCH}_3 \\
 \left\{ \begin{array}{l}
 \xrightarrow{\text{CH}_3\text{CH}=\text{CH}_2} \text{CH}_3\overset{\text{CH}_3}{\underset{|}{\text{C}}}\text{H}-\text{CH}=\text{CHCH}_3 \\
 \text{Dimer} \\
 \\
 \xrightarrow{\text{CH}_3\text{CH}=\text{CH}_2} \text{CH}_3\overset{\text{CH}_3}{\underset{|}{\text{C}}}\text{H}-\text{CH}_2\overset{\text{CH}_3}{\underset{|}{\text{C}}}\text{HCH}=\text{CH}-\text{CH}_3 \\
 \text{Trimer}
 \end{array} \right.
 \end{array}$$

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Fluidized Catalytic Cracking

- Breaks large molecules into smaller ones
- Requires a large amount of heat input
- Reaction quickly fouls the catalyst ($\text{SiO}_2/\text{Al}_2\text{O}_3$) with a coke covering on the catalytic surface
- Coke burned off exothermically in a regenerator
- Regeneration provides heat for cracking process

Fluidized Catalytic Cracking

$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ $\text{C}_{16}\text{H}_{34} \rightarrow 2 \text{C}_8\text{H}_{17}$

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Hydroprocessing

- Two steps: hydrotreating & hydrocracking
- Hydrotreating (hydrogenation)- increases saturation without breaking molecule
- Hydrocracking- breaks molecule into smaller molecules in the presence of a metal catalyst.
- Hydrocracking requires more heat and pressure than hydrotreating



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97

PRODUCTION OF OLEFINS

- The most important olefins and diolefins: ethylene, propylene, butylenes, and butadiene.
- Butadiene is normally coproduced with C2-C4 olefins from different cracking processes.
- Separation of these olefins from catalytic and thermal cracking gas streams could be achieved using physical and chemical separation methods.

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98

PRODUCTION OF OLEFINS

- The petrochemical demand for olefins is much greater than the amounts these operations produce.
- Most olefins and butadienes are produced by steam cracking hydrocarbons.
- Butadiene can be alternatively produced by other synthetic routes discussed with the synthesis of isoprene, the second major diolefin for rubber production.

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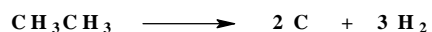
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STEAM CRACKING OF HYDROCARBONS (Production of Olefins)

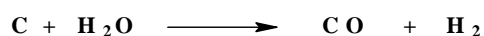
- The main route for producing light olefins, especially ethylene, is the steam cracking of hydrocarbons.
- The feedstocks for steam cracking units range from light paraffinic hydrocarbon gases to various petroleum fractions and residues.
- The simplest paraffin (alkane) and the most widely used feedstock for producing ethylene is ethane.
- ethane is obtained from natural gas liquids. Cracking ethane can be visualized as a free radical dehydrogenation reaction, where hydrogen is a coproduct.



- 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.
- Superheated steam also reduces carbon deposits that are formed by the pyrolysis of hydrocarbons at high temperatures.
- For example, pyrolysis of ethane produces carbon and hydrogen:



- Ethylene can also pyrolyze in the same way.
- The presence of steam as a diluent reduces the hydrocarbons' chances of being in contact with the reactor tube-wall.
- Deposits reduce heat transfer through the reactor tubes.
- Steam reduces this effect by reacting with the carbon deposits (steam reforming reaction).



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:

$$\text{CH}_2=\text{CH}_2 + \dot{\text{C}}\text{H}_3 \longrightarrow \text{CH}_3\text{CH}_2\dot{\text{C}}\text{H}_2 \longrightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{H}\cdot$$

$$\text{CH}_2=\text{CH}_2 + \text{CH}_3\dot{\text{C}}\text{H}_2 \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{H}_2 \longrightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{H}\cdot$$

Higher hydrocarbons found in steam cracking products are probably formed through similar reactions.

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- In the furnace and in the transfer line exchanger, coking is a significant problem.
- Catalytic coking occurs on clean metal surfaces when nickel and other transition metals used in radiant tube alloys catalyze dehydrogenation and formation of coke.
- Coke formation reduces product yields, increases energy consumption, and shortens coil service life.

CHEM 453_Pofessor Bassam El Ali 104

- Coking is related to feedstock, temperature, and steam dilution.
- When coke reaches an allowable limit as indicated by a high pressure drop, it should be removed.
- Coke could be reduced by adding antifoulants, which passivate the catalytic coking mechanism.

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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.

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Steam Cracking Process

- After the cracked gas is treated to remove acid gases, hydrogen and methane are separated from the pyrolysis products in the demethanizer.
- 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.

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Process Variables

- **Temperature**
 - Steam cracking reactions are highly endothermic. Increasing temperature favors the formation of olefins, high molecular weight olefins, and aromatics.
 - Optimum temperatures are usually selected to maximize olefin production and minimize formation of carbon deposits.
 - Reactor temperature is also a function of the feedstock used. Higher molecular weight hydrocarbons generally crack at lower temperatures than lower molecular weight compounds.
 - For example, 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.

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■ **Residence Time**

- In steam cracking processes, olefins are formed as primary products.
- Aromatics and higher hydrocarbon compounds result from secondary reactions of the formed olefins.
- Short residence times are required for high olefin yield.
- When ethane and light hydrocarbon gases are used as feeds, shorter residence times are used to maximize olefin production and minimize BTX and liquid yields.

■ **Residence Time**

- Residence times of 0.5-1.2 sec are typical.
- Cracking liquid feedstocks for the dual purpose of producing olefins plus BTX aromatics requires relatively longer residence times than for ethane.
- However, residence time is a compromise between the reaction temperature and other variables..
- Millisecond furnace, which operates between 0.03-0.1 sec with an outlet temperature range of 870-925°C

■ **Steam/Hydrocarbon Ratio**

- A higher steam/hydrocarbon ratio favors olefin formation.
- Steam reduces the partial pressure of the hydrocarbon mixture and increases the yield of olefins.
- Heavier hydrocarbon feeds require more steam than gaseous feeds to additionally reduce coke deposition in the furnace tubes.
- Liquid feeds such as gas oils and petroleum residues: Steam to hydrocarbon weight ratios range between 0.2-1 for ethane and approximately 1-1.2 for liquid feeds.

■ **Feedstocks**

- Feeds: light hydrocarbon gases to petroleum residues.
- Long chain hydrocarbons crack more easily than shorter chain compounds and require lower cracking temperatures.
- For example, it was found that the temperature and residence time that gave 60% conversion for ethane yielded 90% conversion for propane.
- The rates of cracking hydrocarbons differ according to structure.
- Paraffinic hydrocarbons are easier to crack than cycloparaffins, and aromatics tend to pass through unaffected.
- Isoparaffins such as isobutene and isopentane give high yields of propylene.

The following are typical operating conditions for an ethane cracking unit and the products obtained:

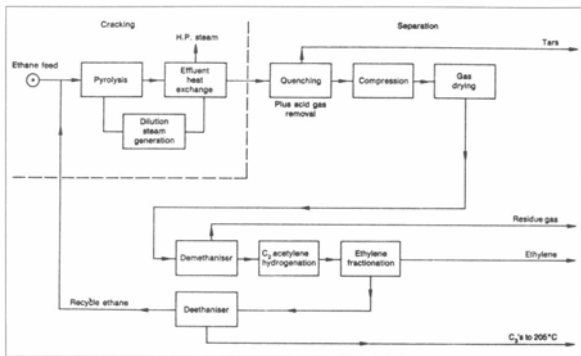
Conditions:

- Temperature, °C 750-850
- Pressure, Kg/cm² 1-1.2
- Steam/HC 0.5

Yield wt %

- Hydrogen + methane 12.9
- Ethylene 80.9
- Propylene 1.8
- Butadiene 1.9
- Other* 2.5

* Other: Propane 0.3, butanes 0.4, butenes 0.4, C₅+ 1.4



Cracking Liquid Feeds

- Liquid feedstocks for olefin production are light naphtha, full range naphtha, reformer raffinate, atmospheric gas oil, vacuum gas oil, rest. dues, and crude oils.
- The ratio of olefins produced from steam cracking of these feeds depends mainly on the feed type.
- For example, steam cracking light naphtha produces about twice the amount of ethylene obtained from steam cracking vacuum gas oil under nearly similar conditions.

CHEM 453_ Professor Bassam El Ali 115

Cracking Liquid Feeds

- Liquid feeds are usually cracked with lower residence times and higher.
- maximum olefin yields are obtained at lower hydrocarbon partial pressures, pressure drops, and residence times. These variables may be adjusted to obtain higher BTX at the expense of higher olefin yield.

CHEM 453_ Professor Bassam El Ali 116

Cracking Liquid Feeds

- One advantage of using liquid feeds over gas feedstocks for olefin production is the wider spectrum of coproducts. For example, steam cracking naphtha produces, in addition to olefins and diolefins, pyrolysis gasoline rich in BTX.
- The following conditions are typical for naphtha cracking:
 - Temperature °C: 800
 - Pressure atm.: Atmospheric
 - Steam/HC Kg/Kg: 0.6-0.8
 - Residence time sec: 0.35

CHEM 453_ Professor Bassam El Ali 117

Cracking Liquid Feeds

- Steam cracking raffinate from aromatic extraction units is similar to naphtha cracking.
- However, because raffinates have more isoparaffins, relatively less ethylene and more propylene is produced.

Ultimate yields from steam cracking various feedstocks

Yield, wt %	Feedstock					
	Ethane	Propane	Butane	Naphtha	Gas oil	Saudi NGL
H ₂ + CH ₄	13	28	24	26	18	23
Ethylene	80	45	37	30	25	50
Propylene	2.4	15	18	13	14	12
Butadiene	1.4	2	2	4.5	5	2.5
Mixed butenes	1.6	1	6.4	8	6	3.5
C5+	1.6	9	12.6	18.5	32	9

Products from steam cracking naphtha at high severities

Products	Cracking severity	
	Low	High
Methane	10.3	15
Ethylene	25.8	31.3
Propylene	16.0	12.1
Butadiene	4.5	4.2
Butenes	7.9	2.8
BTX	10	13
C5+	17	9
Fuel oil	3	6
Other***	5.5	6.6

Feed:

Sp. gr 60/60oF	0.713
Boiling range °C	32-170
Aromatics	7

**Weight percent

***Ethane (3.3 and 3.4%), acetylene, methylacetylene, propane, hydrogen.

- Processes used to crack **gas oils** are similar to those for naphtha.
- Gas oil throughput is about 20-25% higher than that for naphtha.
- The ethylene cracking capacity for AGO is about 15% lower than for naphtha.
- There must be a careful balance between furnace residence time, hydrocarbon partial pressure, and other factors to avoid problems inherent in cracking gas oils.

Product composition from cracking atmospheric gas oil and vacuum gas oil

Products*	AGO		VGO	
	Severity Low	Severity High	Low	High
Methane	8.0	13.7	6.6	9.4
Ethylene	19.5	26.0	19.4	23.0
Ethane 3.3	3.0	2.8	3.0	
Propylene	14.0	9.0	13.9	13.7
Butadiene	4.5	4.2	5.0	6.3
Butenes 6.4	2.0	7.0	4.9	
BTX 10.7	12.6			
C5-205°C**	10.0	8.0	18.9	16.9
Fuel oil 21.8	19.0	25.0	21.0	
Other** 1.8	2.5	1.4	1.8	

*Weight %.
 **Other than BTX.
 ***Acetylene, methylacetylene, propane, hydrogen.

PRODUCTION OF DIOLEFINS

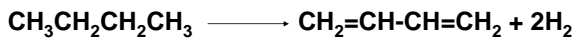
- Diolefins are hydrocarbon compounds that have two double bonds.
- Conjugated diolefins have two double bonds separated by one single bond. Due to conjugation, these compounds are more stable than monoolefins and diolefins with isolated double bonds.
- Conjugated diolefins also have different reactivities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

■ Butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$)

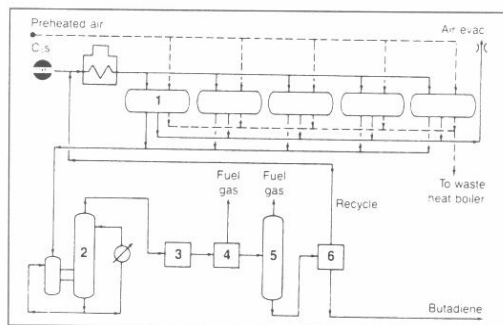
- Butadiene is the raw material for the most widely used synthetic rubber, a copolymer of butadiene and styrene (SBR). In addition to its utility in the synthetic rubber and plastic industries (over 90% of butadiene produced), many chemicals could also be synthesized from butadiene.

■ Production of 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 could also be produced by the catalytic dehydrogenation of butanes or a butane/butene mixture.

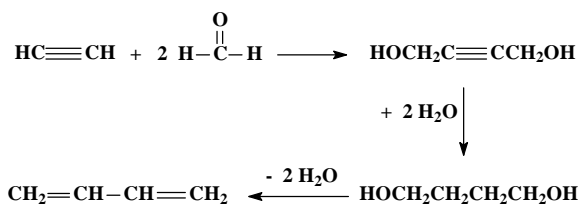


- The first step involves dehydrogenation of the butanes to a mixture of butenes which are then separated, recycled, and converted to butadiene.
- The Lummus fixed-bed dehydrogenation of C4 mixture to butadiene.
- The process may also be used for the dehydrogenation of mixed amylenes to isoprene.
- In 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.

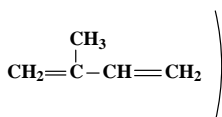


Flow diagram of the Lummus process for producing butadiene:(1) reactor, (2) quenching, (3) compressor, (4) cryogenic recovery, (5) stabilizer, (6) extraction.

- 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 diol is hydrogenated to 1,4-butanediol. Dehydration of 1,4-butanediol yields butadiene.



Isoprene

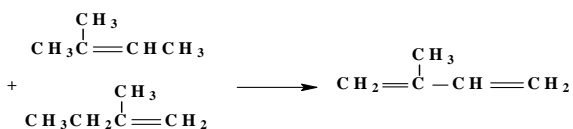


- Isoprene (2-methyl 1,3-butadiene) is the second most important conjugated diolefin after butadiene.
- Most isoprene production is used for the manufacture of cis-polyisoprene, which has a similar structure to natural rubber.
- It is also used as a copolymer in butyl rubber formulations.

Production of isoprene

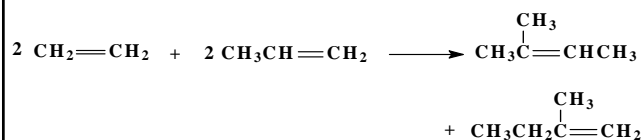
Dehydrogenation of Tertiary Amylenes (Shell Process)

- 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%.

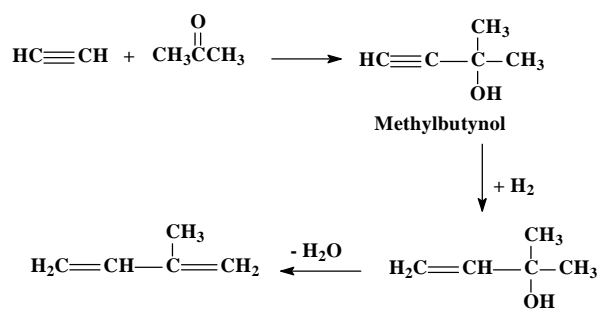


Production of isoprene

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

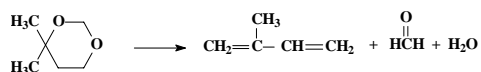
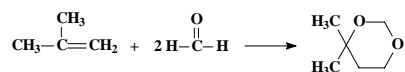


Isoprene from Acetylene and Acetone



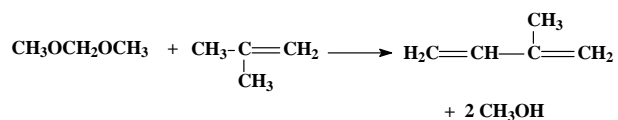
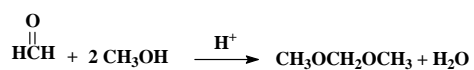
Isoprene from Isobutylene and formaldehyde (IFP Process)

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



Isoprene 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.
- The second step is the vapor phase reaction of methylal with isobutene to produce isoprene.



Isoprene 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.

