

UPGRADING PROCESSES

Catalytic Cracking

Catalytic cracking is the most important and widely used refinery process for converting heavy oils into more valuable gasoline and **lighter** products, with 10.6 MMBPD (over 1 million tons/day) of oil processed in the world. Originally cracking was accomplished thermally but the catalytic process has almost completely replaced thermal cracking **because more gasoline having a higher octane and less heavy fuel oils and light gases are produced.**

Fluid catalytic cracking (FCC) technology is a technology with more than 60 years of commercial operating experience. The process is used to convert higher-molecular-weight hydrocarbons to lighter, more valuable products through contact with a powdered catalyst at appropriate conditions.

Historically, the primary purpose of the FCC process has been to produce gasoline, distillate, and C3/C4 olefins from low-value excess refinery gas oils and heavier refinery streams. FCC is often the heart of a modern refinery because of its adaptability to changing feedstocks and product demands and because of high margins that exist between the FCC feedstocks and converted FCC products.

As oil refining has evolved over the last 60 years, the FCC process has evolved with it, meeting the challenges of cracking heavier, more contaminated feedstocks, increasing operating flexibility, accommodating environmental legislation, and maximizing reliability. The FCC unit continuously circulates a fluidized zeolite catalyst that allows rapid

cracking reactions to occur in the vapor phase. The cracking reactions are carried out in an up-flowing vertical reactor-riser in which a liquid oil stream contacts hot powdered catalyst.

The oil vaporizes and cracks to lighter products as it moves up the riser and carries the catalyst along with it. The reactions are rapid, requiring only a few seconds of contact time. Simultaneously with the desired reactions, coke, a material having a low ratio of hydrogen to carbon, deposits on the catalyst and renders it less catalytically active. Catalyst and product vapors separate in a disengaging vessel with the catalyst continuing first through a stripping stage and second through a regeneration stage where coke is combusted to rejuvenate the catalyst and provide heat for operation of the process.

The regenerated catalyst then passes to the bottom of the reactor-riser, where the cycle starts again. Hydrocarbon product vapors flow downstream for separation into individual products.

- 1- The light gases produced by catalytic cracking contain more olefins than those produced by thermal cracking.
- 2- The cracking process produces carbon (coke) which remains on the catalyst particle and rapidly lowers its activity. To maintain the catalyst activity at a useful level, it is necessary to regenerate the catalyst by burning off this coke with air. As a result, the catalyst is continuously moved from reactor to regenerator and back to reactor.**

3- The cracking reaction is **endothermic** and the regeneration reaction **exothermic**. Some units are designed to use the regeneration heat to supply that needed for the reaction and to heat the feed up to reaction temperature. These are known as “**heat balance**” units.

4- Average riser reactor temperatures are in the range 900 to 1000 °F (480–540 °C), with oil feed temperatures from 500 to 800 °F (260–425 °C) and regenerator exit temperatures for catalyst from 1200 to 1500 °F (650–815 °C).

The catalytic-cracking processes in use today can all be classified as either **MOVING-BED or FLUIDIZED-BED** units. There are several modifications under each of the classes depending upon the designer or builder, but within a class the basic operation is very similar.

1) Moving Bed:

In which **the catalyst was allowed to fall slowly by gravity** through the reactor and a regenerator vessels and was returned mechanically to the top.

2) Fluidized Bed:

Is based on the fluidization properties of fine powders, which enabled **the catalyst to be transported continuously between the reactor and regenerator**.

The fluidized system has been more widely used than the moving bed and now represents about 80 % of all cracking plants.

Catalysts:

both systems use basically similar catalysts but produced in a different form, in the shape of **BEDS** for moving bed and **FINE POWDER** for fluidized bed.

- 1- Acid treated clays ground to a powder
- 2- Synthetic silica- alumina catalysts of higher activity (amorphous)
- 3- Crystalline synthetic silica – alumina catalyst called **ZEALOTS** or **MOLECULAR SIEVES**.

The advantages of zealots over the natural and synthesis amorphous catalyst are:

- 1) Higher activity.
- 2) Higher gasoline yields at a given conversion.
- 3) Production of gasoline containing a larger % of paraffinic and aromatic HC.
- 4) Lower coke yield.
- 5) Increased iso-butane production.
- 6) Ability to go for higher conversion per pass without over cracking.

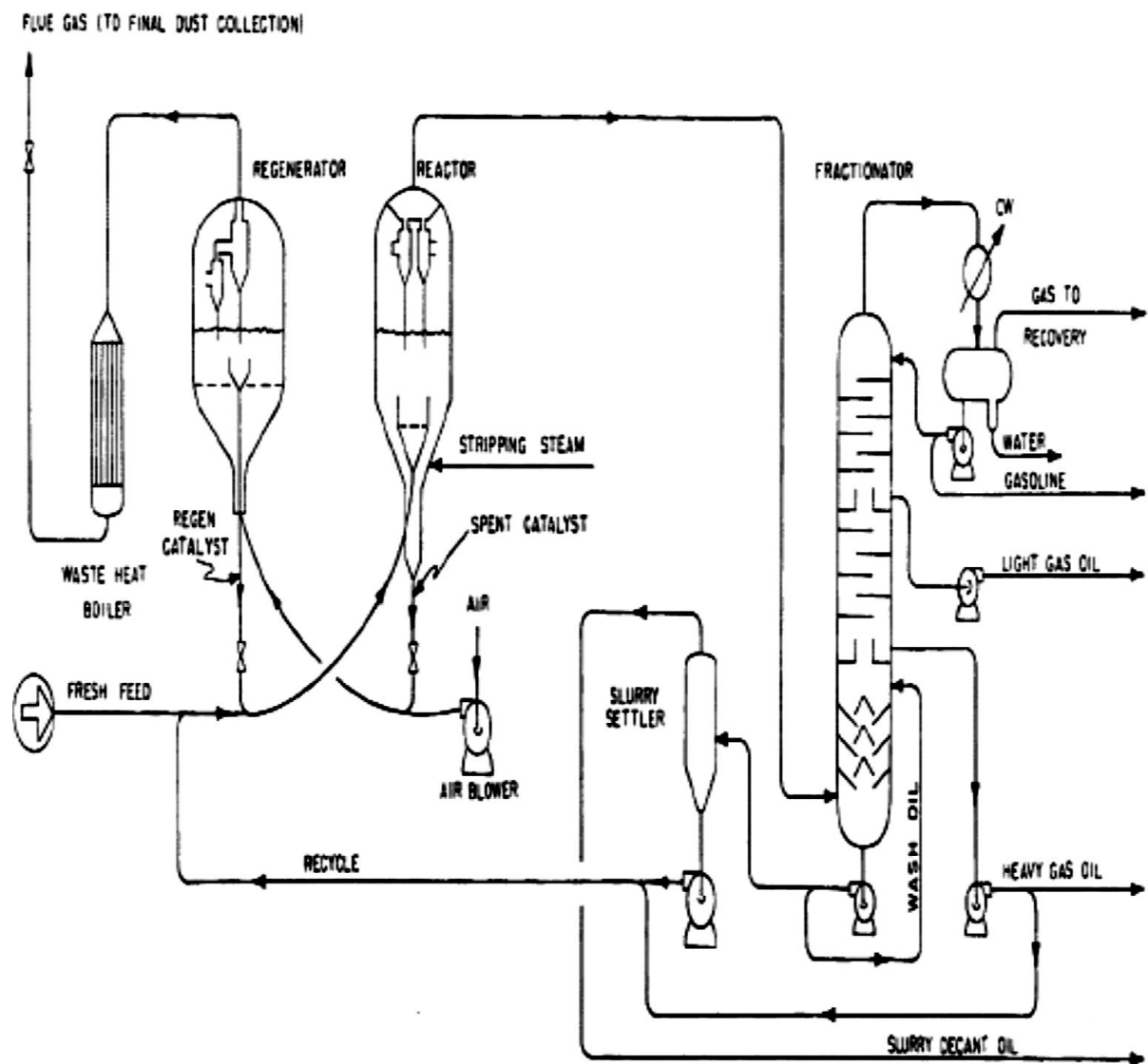
THE PROCESS FLOWS of BOTH TYPES of PROCESSES are SIMILAR:

- 1- **THE HOT OIL FEED** is contacted with the catalyst in either the feed riser line or the reactor.
- 2- **AS THE CRACKING REACTION PROGRESSES**, the catalyst is progressively deactivated by the formation of coke on the surface of the catalyst.

- 3- **THE CATALYST and HYDROCARBON VAPORS** are separated mechanically, and oil remaining on the catalyst is removed by **STEAM STRIPPING** before the catalyst enters the regenerator.
- 4- **THE OIL VAPORS** are taken overhead to a **FRACTIONATION TOWER** for separation into streams having the desired boiling ranges.
- 5- **THE SPENT CATALYST** flows into the regenerator and is reactivated by burning off the coke deposits with air. Regenerator temperatures are carefully controlled to prevent catalyst deactivation by overheating and to provide the desired amount of carbon burn-off.
- 6- **THE FLUE GAS AND CATALYST** are separated by cyclone separators and electrostatic precipitators. The catalyst in some units is steam-stripped as it leaves the regenerator to remove adsorbed oxygen before the catalyst is contacted with the oil feed.

In addition to the nature of the charge stock, the major operating variables effecting the conversion and product distribution are:

- 1- the cracking temperature, 2- catalyst/oil ratio, 3-space velocity,
- 4- catalyst type and activity, and 5- recycle ratio.



Catalytic Cracking Unit

UPGRADING PROCESSES

CATALYTIC HYDROCRACKING

Hydrotreating and hydrocracking are among the oldest catalytic processes used in petroleum refining. They were originally employed in Germany in 1927 for converting lignite to gasoline and later used to convert petroleum residues to distillable fractions. The first commercial hydrotreating installation in the United States was at Standard Oil Company of Louisiana in Baton Rouge in the 1930s. Following World War II, growth in the use of hydrocracking was slow. The availability of Middle Eastern crude oils reduced the incentive to convert coal to liquid fuels, and new catalytic cracking processes proved more economical for converting heavy crude fractions to gasoline. In the 1950s, hydrodesulfurization and mild hydrogenation processes experienced a tremendous growth, mostly because large quantities of by-product hydrogen were made available from the catalytic reforming of low-octane naphthas to produce high-octane gasoline.

The first modern hydrocracking operation was placed on-stream in 1959 by Standard Oil Company of California. The unit was small, producing only 1000 barrels per streamday (BPSD). As hydrocracking units were installed to complement existing fluid catalytic cracking (FCC) units, refiners quickly recognized that the hydrocracking process had the flexibility to produce varying ratios of gasoline and middle distillate. Thus, the stage was set for rapid growth in U.S. hydrocracking capacity from about 3000 BPSD in 1961 to about 120,000 BPSD in just 5 years. Outside the United States, early applications involved production of liquefied petroleum gas (LPG) by hydrocracking naphtha feedstocks. The

excellent quality of distillate fuels produced when hydrocracking gas oils and other heavy feedstocks led to the choice of the hydrocracking process as a major conversion step in locations where diesel and jet fuels were in demand. Interest in high-quality distillate fuels produced by hydrocracking has increased dramatically worldwide.

The interest in the use of hydrocracking has been caused by several factors, including:

- (1) the demand for petroleum products has shifted to high ratios of **gasoline and jet fuel** compared with the usages of diesel fuel and home heating oils,
- (2) **by-product hydrogen** at low cost and in large amounts has become available from catalytic reforming operations, and

Some of the advantages of HYDROCRACKING are:

- 1. Better balance of gasoline and distillate production.
- 2. Greater gasoline yield.
- 3. Improved gasoline pool octane quality and sensitivity.
- 4. Production of relatively high amounts of isobutane in the butane fraction.
- 5. **Upgrade (IMPROVE) (Feed) heavy cracking stocks, aromatics, cycle oils, and coker oils to (Produce) gasoline, jet fuels, and light fuel oils.**

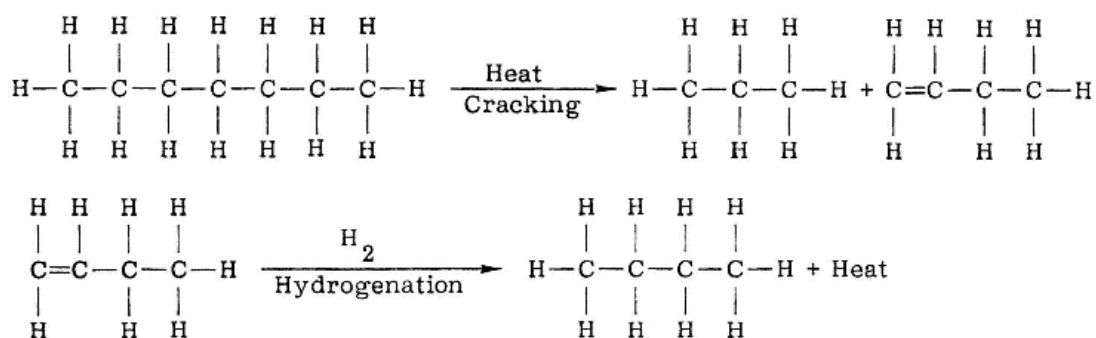
In a modern refinery catalytic cracking and hydrocracking work as a team. **The catalytic cracker** takes the more easily cracked paraffinic atmospheric and vacuum gas oils as charge stocks, **while the hydrocracker** uses more aromatic cycle oils and coker distillates as

feed. The cycle oils that result from cracking operations with zeolite catalysts tend to be highly aromatic and therefore make satisfactory feedstocks for hydrocracking. Vacuum and coker gas oils are also used as hydrocracker feed.

Hydrocracking Reactions:

The mechanism of hydrocracking is that of CATALYTIC CRACKING with HYDROGENATION superimposed.

Catalytic cracking is the scission (separation) (detachment) of a carbon–carbon single bond, and hydrogenation is the addition of hydrogen to a carbon–carbon double bond. An example of the scission of a carbon–carbon single bond followed by hydrogenation is the following:



This shows that cracking and hydrogenation are complementary, for cracking provides olefins for hydrogenation, while hydrogenation in turn provides heat for cracking.

The cracking reaction is **ENDOTHERMIC** and the hydrogenation reaction is **EXOTHERMIC**. The overall reaction provides an excess of heat because the amount of heat released by the exothermic hydrogenation reactions is much greater than the amount of heat consumed by the endothermic cracking reactions. This excess heat causes the reactor temperature to increase and accelerate the reaction rate.

This is controlled by injecting cold hydrogen as quench into the reactors to absorb the excess heat of reaction.

Almost all hydrocracking catalysts use silica-alumina as the cracking base but the rare-earth metals vary according to the manufacturer. Those in most common use are platinum, palladium, tungsten, and nickel.

THE HYDROCRACKING PROCESS:

With the exception (exclusion) of the H-Oil and LC-Fining processes, **all hydrocracking and hydroprocessing processes in use today are fixed-bed catalytic processes with liquid downflow.**

The hydrocracking process may require either one or two stages, depending upon the process and the feed stocks used. The process flows of most of the fixed-bed processes are similar and the GOFining process will be described as a typical fixed-bed hydrocracking process.

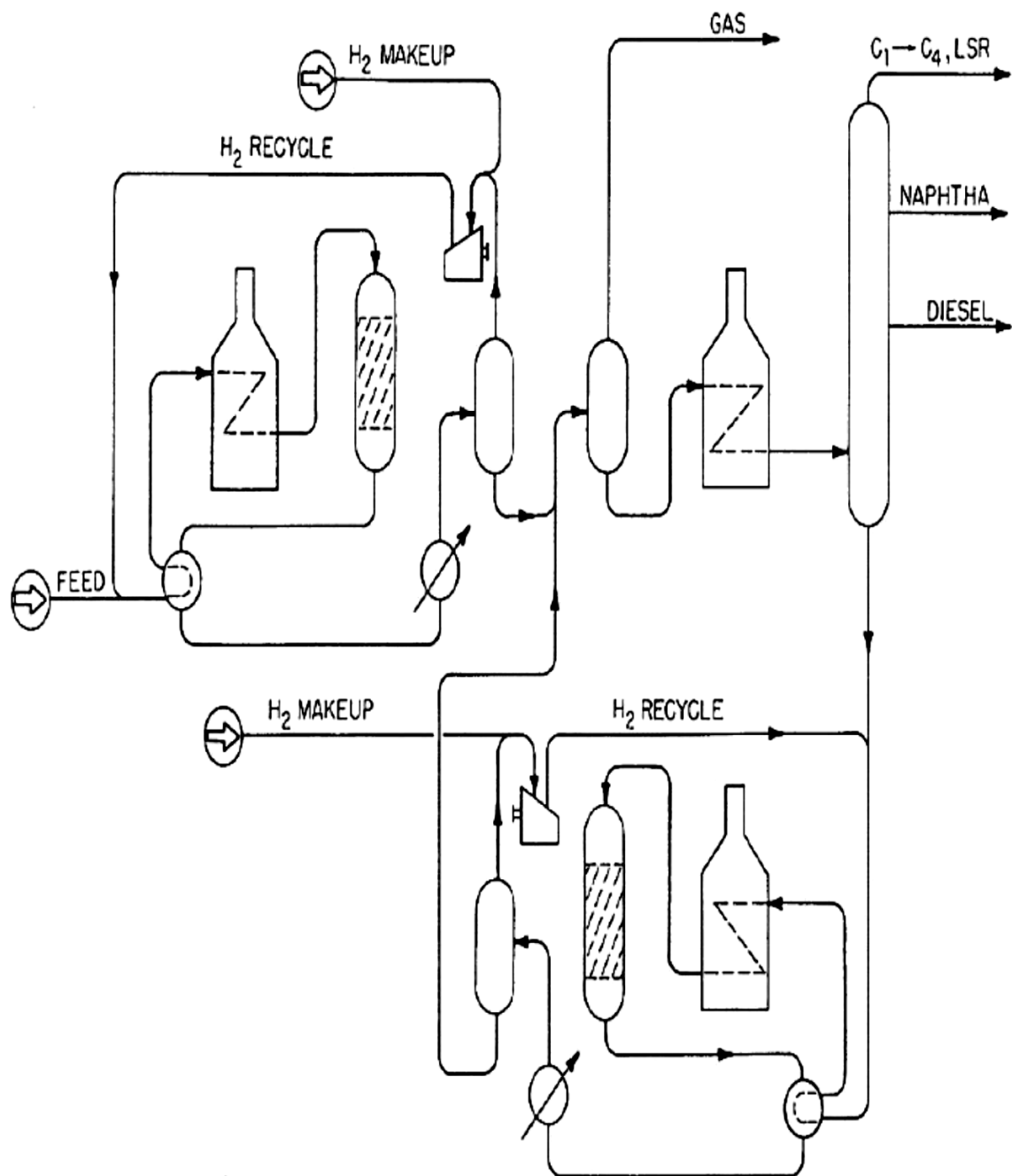
The GOFining process is a fixed-bed regenerative process employing a molecular-sieve catalyst impregnated with a metal. The process employs either **SINGLE-STAGE** or **TWO-STAGE** hydrocracking **WITH TYPICAL OPERATING CONDITIONS** ranging from 660 to 785°F and from 1000 to 2000 psig (350–420°C and 6900–13,800 kPa).

The temperature and pressure vary with the age of the catalyst, the product desired, and the properties of the feedstock.

The decision to use a single- or two-stage system depends upon the size of the unit and the product desired. **If only one stage is used**, the process

flow is the same as that of the first stage of the two-stage plant except the fractionation tower bottoms is recycled to the reactor feed.

- 1- **THE FRESH FEED** is mixed with makeup hydrogen and recycle gas (high in hydrogen content) and passed through a heater to the first reactor.
- 2- The hydrocracking reactor(s) is operated at a sufficiently high temperature to convert 40 to 50 vol% of the reactor effluent to material boiling below 400°F (205°C).
- 3- The reactor effluent goes through heat exchangers to a high-pressure separator where the hydrogen-rich gases are separated and recycled to the first stage for mixing both makeup hydrogen and fresh feed.
- 4- The liquid product from the separator is sent to a fractionator where the **C4 and lighter gases** are taken off overhead, and the **light and heavy naphtha, jet fuel, and diesel fuel boiling range streams** are removed as liquid sidestreams.
- 5- The unit can be operated to produce all gasoline and lighter products or to maximize jet fuel or diesel fuel products.
- 6- The bottoms stream from the fractionator is mixed with recycle hydrogen from the second stage and sent through a furnace to the second-stage reactor.
- 7- The second-stage product is combined with the first-stage product prior to fractionation.



Two stage Hydrocracker.

UPGRADING PROCESSES

CATALYTIC **REFORMING** & ISOMERIZATION

In **catalytic reforming**, the change in the boiling point of the stock passed through the unit is relatively small as **the hydrocarbon molecular structures are rearranged to form higher-octane aromatics with only a minor amount of cracking.** Thus catalytic reforming primarily increases the octane of motor gasoline rather than increasing its yield; in fact, there is a decrease in yield because of hydrocracking reactions which take place in the reforming operation.

The typical feedstocks to catalytic reformers are **heavy straight-run (HSR) gasolines and naphthas** [180–375 °F (82–190 °C)] and **heavy hydrocracker naphthas**. These are composed of the four major hydrocarbon groups: **paraffins, olefins, naphthenes, and aromatics (PONA)**. Typical feedstocks and reformer products have the following **PONA analyses (vol %)**:

Component	Feed	Product
Paraffins (P)	30–70	30–50
Olefins (O)	0–2	0–2
Naphthenes (N)	20–60	0–3
Aromatics (A)	7–20	45–60

The paraffins and naphthenes undergo two types of reactions in being converted to higher octane components: **CYCLIZATION & ISOMERIZATION.**

Hydrocarbons boiling above 400 °F (204 °C) are easily hydrocracked and cause an excessive carbon laydown on the catalyst. As in any series of complex chemical reactions, reactions occur which produce undesirable products in addition to those desired. Reaction conditions have to be chosen that favor the desired reactions and inhibit the undesired ones.

There are FOUR MAJOR REACTIONS that take place during reforming.

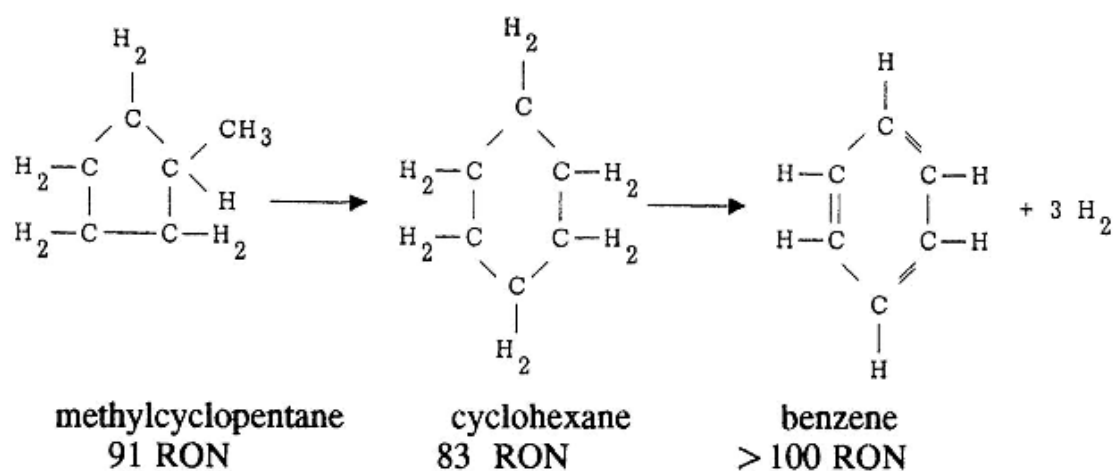
- (1) **dehydrogenation** of naphthenes to aromatics,
- (2) **dehydrocyclization** of paraffins to aromatics,
- (3) **isomerization**, and
- (4) **hydrocracking**.

- 1) The **DEHYDROGENATION** of cyclohexane derivatives is a much faster reaction than either the **DEHYDROISOMERIZATION** of alkylcyclopentanes or the **DEHYDROCYCLIZATION** of paraffins, however, all three reactions take place simultaneously and are necessary to obtain the aromatic concentration needed in the reformat product **TO GIVE THE OCTANE IMPROVEMENT NEEDED.**

2) Isomerization Reactions

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

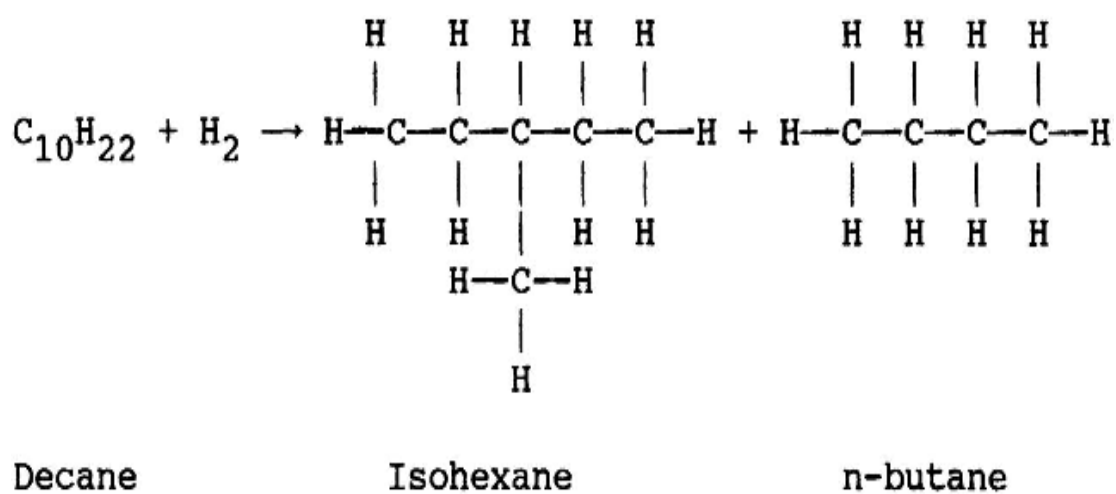
- 1. **Isomerization of normal paraffins to isoparaffins:**
- 2. **Isomerization of alkylcyclopentanes to cyclohexanes, plus subsequent conversion to benzene:**



3) Hydrocracking Reactions

The hydrocracking reactions are exothermic and result in the production of lighter liquid and gas products. They are relatively slow reactions and therefore most of the hydrocracking occurs in the last section of the reactor.

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



All of the REFORMING CATALYST in general use today contains platinum supported on an alumina base. In most cases rhenium is combined with platinum to form a more stable catalyst which permits operation at lower pressures

CATALYTIC REFORMING PROCESS

Reforming processes are classified as **CONTINUOUS, CYCLIC, or SEMIREGENERATIVE** depending upon the frequency of catalyst regeneration.

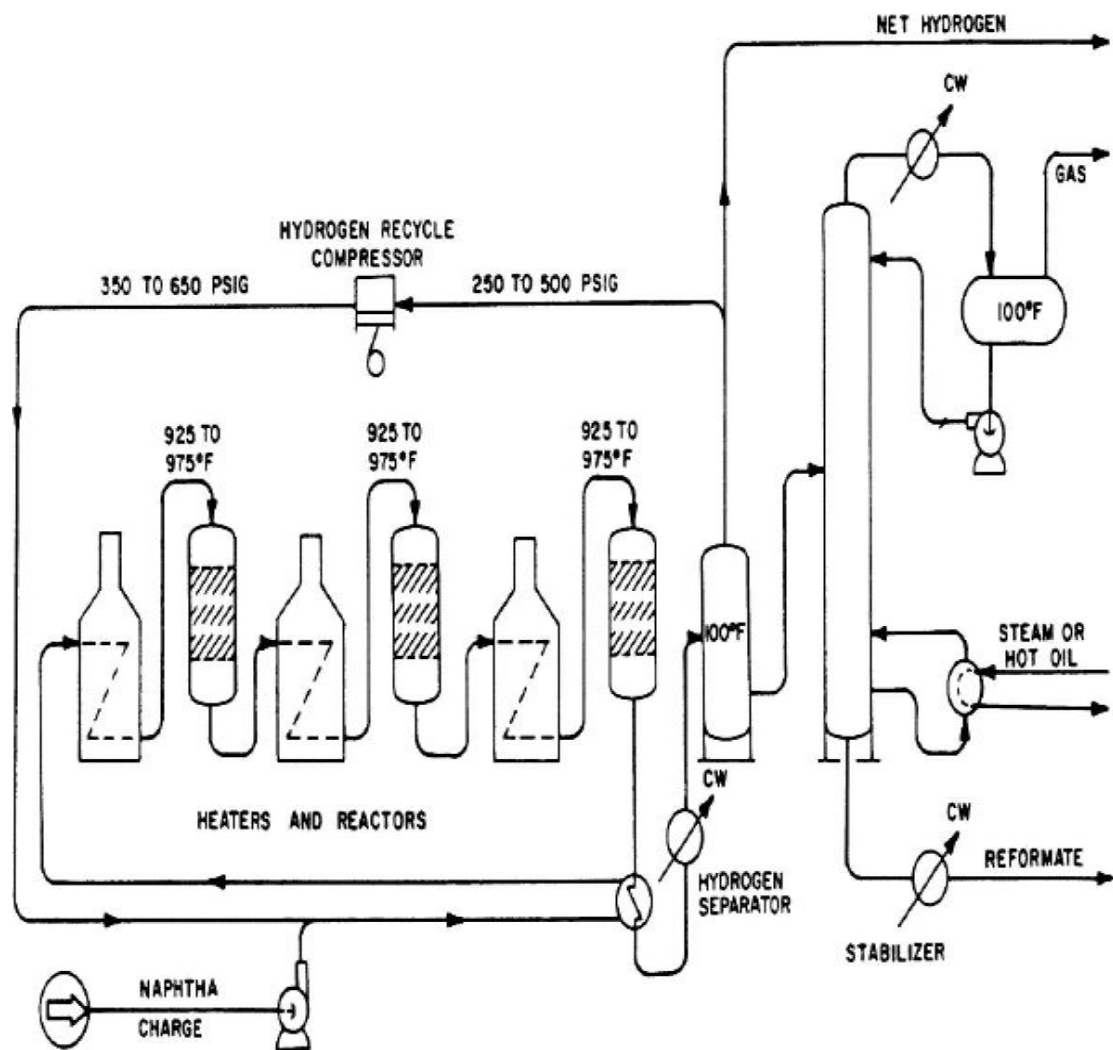
The **SEMIREGENERATIVE** is considered as a typical fixed-bed reactor reforming operation with advantage of minimum capital costs.

1. The pretreated feed and recycle hydrogen are heated to (925 - 975°F) (498–524°C) before entering the first reactor.
2. IN THE FIRST REACTOR, the major reaction is the dehydrogenation of naphthenes to aromatics and, as this is strongly endothermic, a large drop in temperature occurs.
3. To maintain the reaction rate, the gases are reheated before being passed over the catalyst in the second reactor. As the charge proceeds through the reactors, the reaction rates decrease and the reactors become larger, and the preheat needed becomes less.

USUALLY THREE or FOUR REACTORS are SUFFICIENT to provide the desired degree of reaction and heaters are needed before each reactor to bring the mixture up to reaction temperature. In practice, either separate heaters can be used or one heater can contain several separate coils.

4. **The reaction mixture from the last reactor** is cooled and the liquid products condensed.
5. **The hydrogen-rich gases** are separated from the liquid phase in a **DRUM SEPARATOR**, and the liquid from the separator is sent to a fractionator to be debutanized.
6. **The hydrogen-rich gas stream** is split into a hydrogen recycle stream and a net hydrogen by-product which is used in hydrotreating or hydrocracking operations or as fuel.

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



Catalytic reforming, **SEMIREGENERATIVE** process.

UPGRADING PROCESSES

HYDROTREATING

Hydrotreating of residual oils was a natural extension of hydrotreating distillate oils and VGOs to remove sulfur. CLG's first commercial RDS Hydrotreater was commissioned in 1969. Typical of many early residuum hydrotreaters, CLG's first RDS Hydrotreater was designed to remove sulfur to produce low-sulfur fuel oil (LSFO). CLG's first VRDS Hydrotreater, commissioned in 1977, was also designed to produce LSFO. In 1984 Okinawa Sekiyu Seisei, a Japanese refiner, first reported⁴ the operation of a CLG RDS Hydrotreater in "conversion mode. In this operation, the reactor temperature was raised fairly high early in the run—much higher than required to simply produce lowsulfur fuel oil—and held high until the end of run. This operation hydrocracked as much VR as possible to lighter boiling products (VR was "converted" to light products). It also shortened the run length because of higher catalyst deactivation from coke deposited on the catalyst through more of the run.

Conversion mode operation has been favored by many RDS/VRDS Hydrotreater operators in recent years to minimize the production of fuel oil. An alternative to destroying low-value fuel oil has been to convert it to higher value fuel oil. During the late 1970s and through the 1980s and 1990s, the demand for and value of high-sulfur (3 percent) fuel oil and low-sulfur (1 percent) fuel oil dropped. In some cases, power plant operators have been willing to pay higher prices for fuel oils with much lower sulfur content (0.1 to 0.5 wt %). RDS/VRDS Hydrotreating enabled refiners to produce these lower-sulfur fuel oils.

The lowest-sulfur fuel oil commercially produced from sour crudes (about 3 wt % sulfur in the AR) was 0.1 wt %. This fuel oil was produced by the CLG RDS Hydrotreater at Idemitsu Kosan's refinery in Aichi, Japan. The ability of residuum hydrotreaters to improve the economics of conversion units by pretreating their feeds has been understood for many years. The most noticeable economic impact of feed pretreatment is to lower the sulfur content of the feed to the conversion unit. For example, pretreatment of RFCC feed to reduce its sulfur to less than 0.5 wt % eliminates the need to install costly flue gas desulfurization facilities. Addition of hydrogen to the feed by the hydrotreater also improves the product yields and product qualities of the downstream conversion unit. The 50,000 barrel per day (BPD) RDS Hydrotreater was designed to achieve 92 percent hydrodesulfurization (HDS) and 91 percent hydrodemetallization (HDM) from a mixed domestic and Arabian Heavy AR for a 1-year cycle. In addition to its contribution toward meeting environmental requirements and reducing catalyst usage, the feed pretreatment significantly increased the gasoline yield from the RFCC.

The hydrotreater was originally designed to remove sulfur and metals from the feed to the coker so that the coke would have less sulfur and metals and be easier to sell. Coke production has been reduced and the proportion of light products is higher than it would have been without the RDS. This includes converting VR (which would otherwise be fed to the coker) to VGO, diesel, and naphtha in the RDS Hydrotreater. In addition, the hydrotreated VR from the RDS produces lower weight percent coke in the coker than the straight-run VR. Both of these effects lead to lower coke production and more light products from the refinery. Fixed-bed residuum hydrotreating continues to be a popular route to residuum conversion.

HYDROTREATING refers to a relatively mild operation whose primary purpose is to saturate olefins and/or reduce the sulfur and/or nitrogen content (and not to change the boiling range) of the feed. **HYDROCRACKING** refers to processes whose primary purpose is to reduce the boiling range and in which most of the feed is converted to products with boiling ranges lower than that of the feed.

HYDROTREATING is a process to **catalytically stabilize** petroleum products and/or remove objectionable elements from products or feedstocks **by reacting them with hydrogen**. Stabilization usually involves converting unsaturated hydrocarbons such as olefins to paraffins. Objectionable elements removed by hydrotreating include sulfur, nitrogen, oxygen, halides, and trace metals.

HYDROTREATING is applied to a **wide range of feedstocks, from naphtha to reduced crude**. When the process is employed specifically for sulfur removal it is usually called **hydrodesulfurization, or HDS**. To meet environmental objectives it also may be necessary to hydrogenate aromatic rings to reduce aromatic content by converting aromatics to paraffins.

THE MAIN HYDROTREATING REACTION is that of **DESULFURIZATION**:

- a. Mercaptans: $\text{RSH} + \text{H}_2 \rightarrow \text{RH} + \text{H}_2\text{S}$
- b. Sulfides: $\text{R}_2\text{S} + 2\text{H}_2 \rightarrow 2\text{RH} + \text{H}_2\text{S}$
- c. Disulfides: $(\text{RS})_2 + 3\text{H}_2 \rightarrow 2\text{RH} + 2\text{H}_2\text{S}$

The principal operating variables are:

- a. temperature,
- b. hydrogen partial pressure, and
- c. space velocity.

1- Increasing temperature and hydrogen partial pressure

increases sulfur and nitrogen removal and hydrogen consumption. Although increasing temperature improves sulfur and nitrogen removal, excessive temperatures must be avoided because of the increased coke formation.

2- Increasing pressure also increases hydrogen saturation and reduces coke formation.

3- Increasing space velocity reduces conversion, hydrogen consumption, and coke formation.

Typical ranges of process variables in hydrotreating operations are:

Temperature of 520–645 °F (270–340 °C), Pressure of 100–3,000 psig (690–20,700 kPag).

CATALYSTS developed for hydrotreating include:

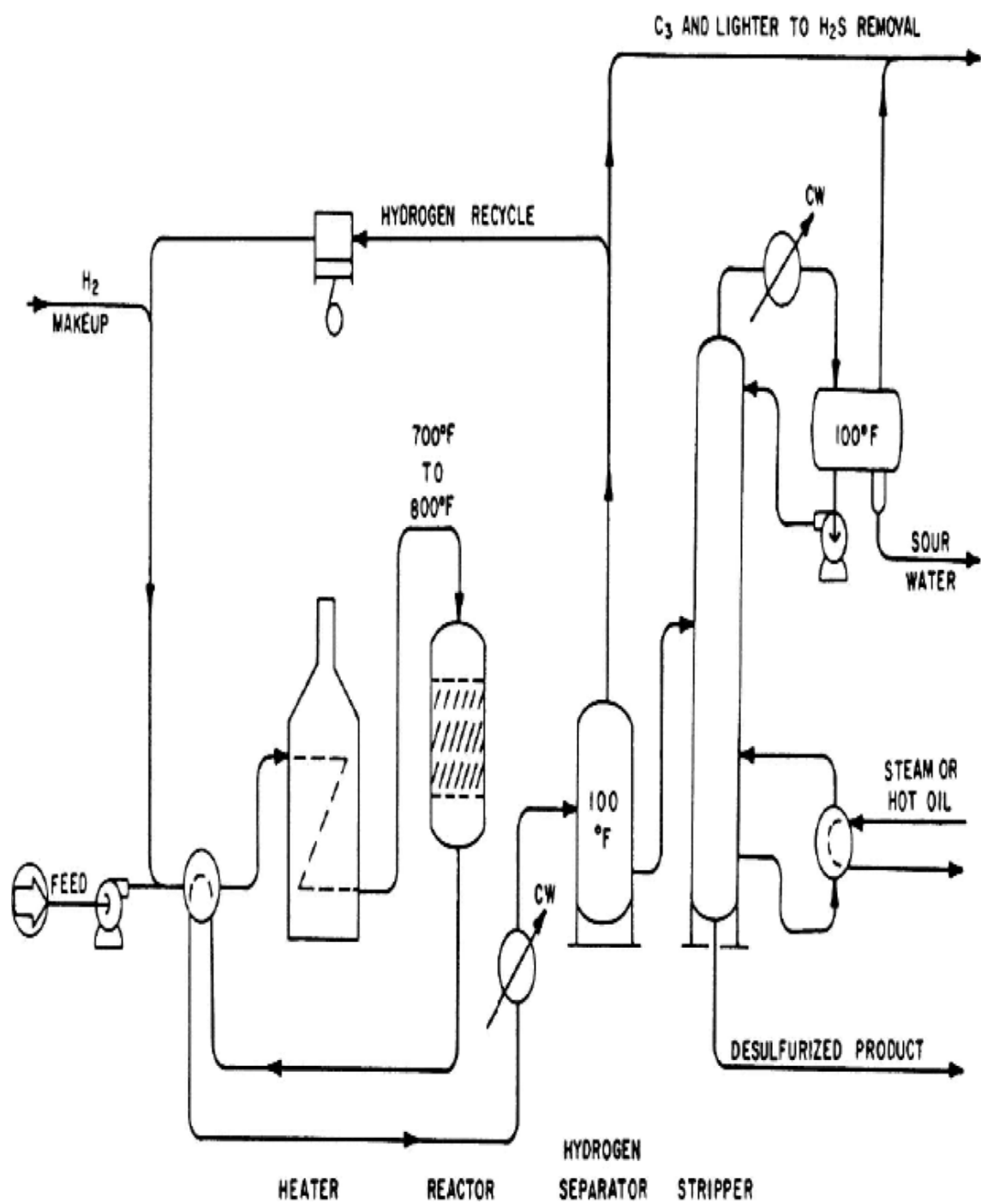
- 1- **cobalt and molybdenum oxides on alumina,**
- 2- **nickel oxide,**
- 3- **nickel thiomolybdate,**
- 4- **tungsten and nickel sulfides, and**
- 5- **vanadium oxide.**

The cobalt and molybdenum oxides on alumina catalysts are in most general use today because: they have proven to be **highly selective, easy**

to regenerate, and resistant to poisons. They must be activated by converting the hydrogenation metals from the oxide to the sulfide form.

Although there are about 30 hydrotreating processes available, most of them have essentially the same process flow for a given application.

- 1- The oil feed is mixed with hydrogen-rich gas either before or after it is preheated to the proper reactor inlet temperature.**
Most hydrotreating reactions are carried out below 800 °F (427 °C) to minimize cracking, and the feed is usually heated to between 500 and 800 °F (260–427 °C).
- 2- The oil feed combined with the hydrogen-rich gas enters the top of the fixed-bed reactor.**
- 3- In the presence of the metal-oxide catalyst,** the hydrogen reacts with the oil to produce: hydrogen sulfide, ammonia, saturated hydrocarbons, and free metals.
- 4- The metals remain on the surface of the catalyst and other products leave the reactor with the oil–hydrogen stream.**
- 5- The reactor effluent** is cooled before separating the oil from the hydrogen-rich gas. The oil is stripped of any remaining hydrogen sulfide and light ends in a stripper.
- 6- The gas may be treated to remove hydrogen sulfide and recycled to the reactor.**



Catalytic hydrodesulfurizer

UPGRADING PROCESSES

ALKYLATION

The addition of an alkyl group to any compound is an alkylation reaction but **in petroleum refining terminology the term alkylation is used for the reaction of low molecular weight olefins with an isoparaffin to form higher molecular weight isoparaffins.** Although alkylation can take place at high temperatures and pressures without catalysts, **the only processes of commercial importance involve low temperature alkylation conducted in the presence of either sulfuric or hydrofluoric acid.** The reactions occurring in both processes are complex and the product has a rather wide boiling range. **By proper choice of operating conditions,** most of the product can be made to fall within the gasoline boiling range with **Motor Octane Numbers (MON)** from 88 to 94 and **Research Octane Numbers (RON)** from 94 to 99.

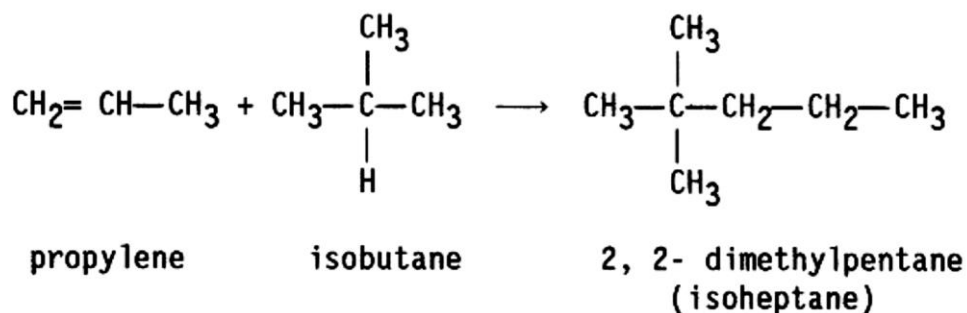
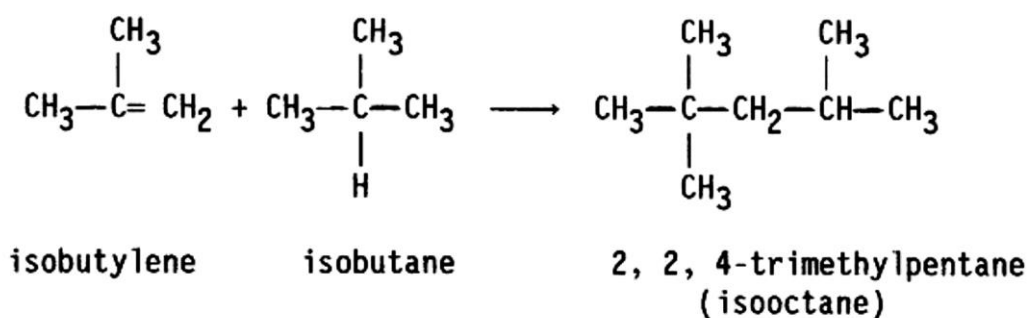
ALKYLATION REACTIONS

In alkylation processes using hydrofluoric or sulfuric acids as catalysts, **only isoparaffins with tertiary carbon atoms, such as isobutane or isopentane,** react with the olefins. In practice only isobutane is used because isopentane has a sufficiently high octane number and low vapor pressure to allow it to be effectively blended directly into finished gasolines.

The process **using sulfuric acid** (See Fig. 20-11 Page 739 Nelson) as a catalyst is much more sensitive to temperature than the **hydrofluoric acid** (See Fig. 20-12 Page 739 Nelson) process.

With sulfuric acid it is necessary to carry out the reactions at 40 to 70°F (5 to 21°C) or lower, to minimize oxidation reduction reactions which result in the formation of tars and the evolution of sulfur dioxide. **When anhydrous hydrofluoric acid is the catalyst**, the temperature is usually limited to 100°F (38°C) or below.

THE PRINCIPAL REACTIONS which occur in alkylation are the combinations of olefins with isoparaffins as follows:



ALKYLATION FEEDSTOCKS

Olefins and isobutane are used as alkylation unit feedstocks. The chief sources of olefins are catalytic cracking and coking operations. Butenes and propene are the most common olefins used, but pentenes are included in some cases.

Some refineries include pentenes in alkylation unit feed to lower the FCC gasoline vapor pressure and reduce the bromine number in the final gasoline blend. Alkylation of pentenes is also considered as a way to reduce the C5 olefin content of final gasoline blends and reduce its effects on ozone reduction and visual pollution in the atmosphere. Olefins can be produced by dehydrogenation of paraffins, and isobutane is cracked commercially to provide alkylation unit feed. Hydrocrackers and catalytic crackers produce a great deal of the isobutene used in alkylation but it is also obtained from catalytic reformers, crude distillation, and natural gas processing. In some cases, normal butane is isomerized to produce additional isobutane for alkylation unit feed.

ALKYLATION PRODUCTS

In addition to the alkylate stream, the products leaving the alkylation unit include the propane and normal butane that enter with the saturated and unsaturated feed streams as well as a small quantity of tar produced by polymerization reactions.

The product streams leaving an alkylation unit are: **LPG grade propane liquid, Normal butane liquid, C5-alkylate, and Tar.**

CATALYSTS

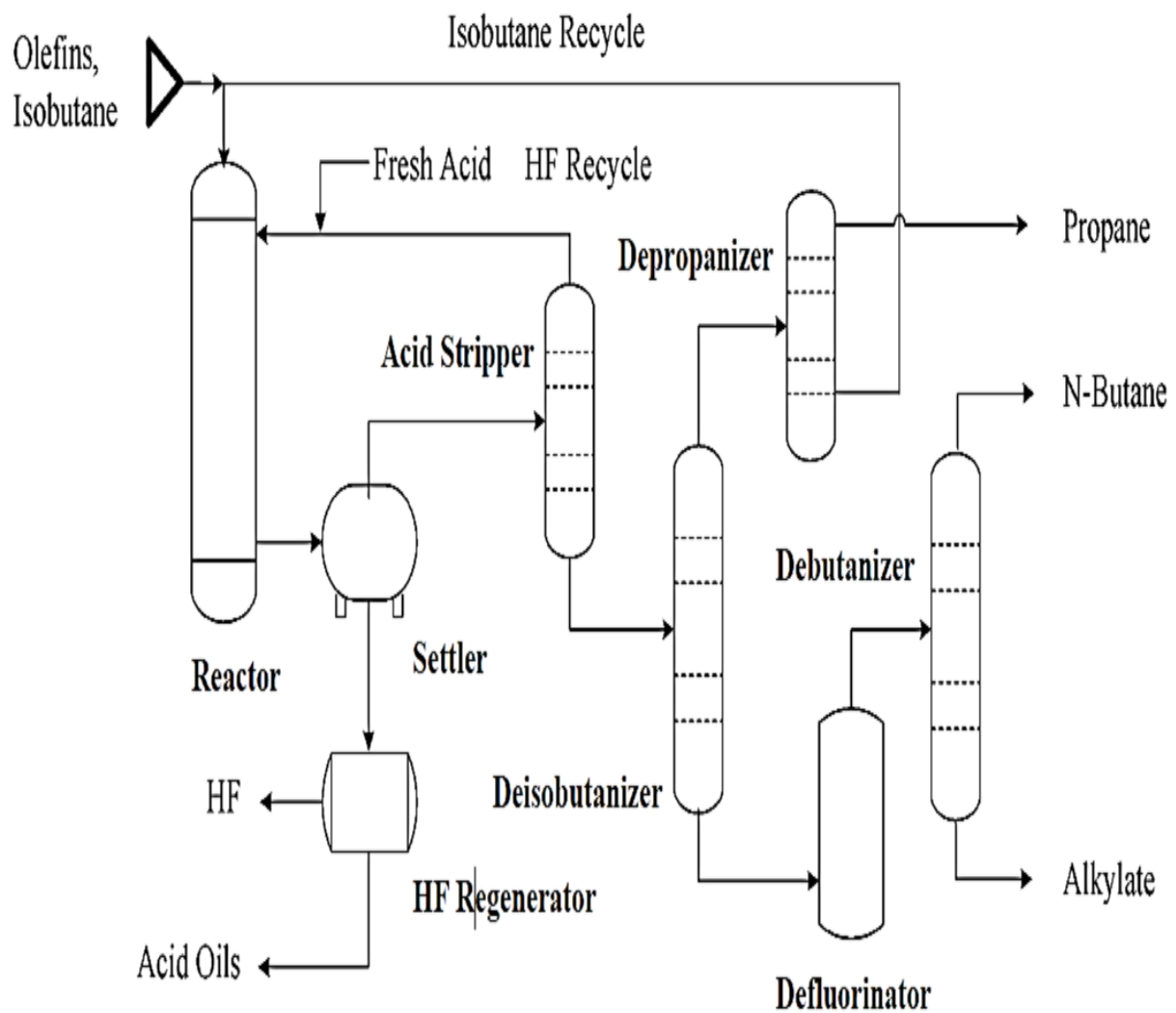
Concentrated sulfuric and hydrofluoric acids are the only catalysts used commercially today for the production of high octane alkylate gasoline but other catalysts are used to produce ethylbenzene, cumene, and long-chain (C12 to C16) alkylated benzenes.

PROCESS FLOW: SULFURIC ACID ALKYLATION

- 1) **The feeds – propylene, butylene, amylene, and fresh isobutane** enter the reactor and contact sulfuric acid with a concentration of 85 to 95%.
- 2) **The reactor is divided into zones.** Olefins are fed through distributors to each zone, and sulfuric acid and isobutanes flow over baffles from one zone to the next.
- 3) **The reactor effluent goes to a settler,** in which hydrocarbons separate from the acid. The acid is returned to the reactor.
- 4) **The hydrocarbons** are washed with caustic and sent to fractionation.
- 5) **The fractionation section** comprises a depropanizer, a deisobutanizer, and a debutanizer.
- 6) **Alkylate from the deisobutanizer** can go directly to motor-fuel blending, or it can be reprocessed to produce aviation-grade gasoline. Isobutane is recycled.

PROCESS FLOW:
HF ALKYLATION

- 1) **Olefins and isobutane are dried and fed to a reactor**, where the alkylation reaction takes place over the HF catalyst.
- 2) **The reactor effluent flows to a settler**, where the acid phase separates from the hydrocarbon phase.
- 3) **The acid is drawn off** and recycled.
- 4) **The hydrocarbon phase** goes to a deisobutanizer (DIB).
- 5) **The overhead stream**, containing propane, isobutane, and residual HF, goes to a depropanizer (DeC3).
- 6) **The depropanizer (DeC3) overhead** goes to an HF stripper. It is then treated with caustic and sent to storage.
- 7) **Isobutane from the deisobutanizer (DIB) main fractionator** is recycled.
- 8) **The bottom stream from the debutanizer** goes to product blending.



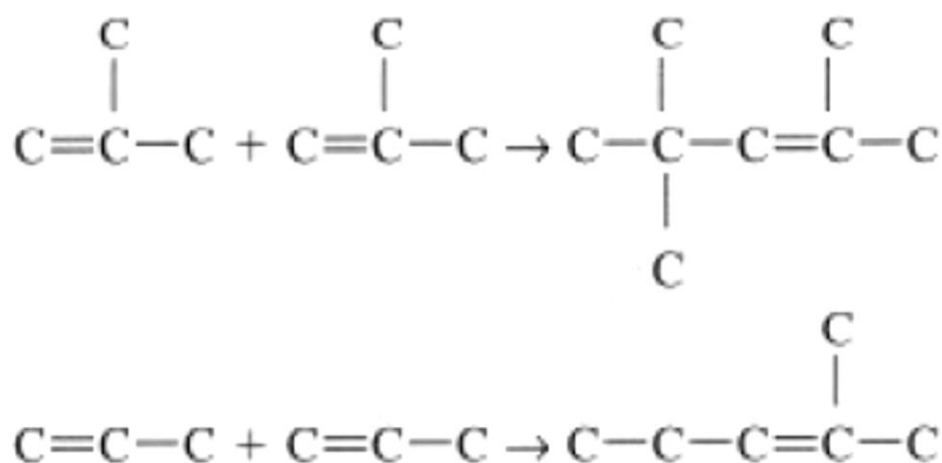
Hydrofluoric acid (HF) alkylation

POLYMERIZATION

Propene and butenes can be polymerized to form a high-octane product boiling in the gasoline boiling range. The product is an olefin having unleaded octane numbers of 97 RON and 83 MON.

Polymerization produces about 0.7 barrels of polymer gasoline per barrel of olefin feed as compared with about 1.5 barrels of alkylate by alkylation, and the product has a high octane sensitivity, but capital and operating costs are much lower than for alkylation. As a result, polymerization processes are being added to some refineries.

The polymerization reaction is highly exothermic and temperature is controlled either by injecting a cold propane quench or by generating steam:

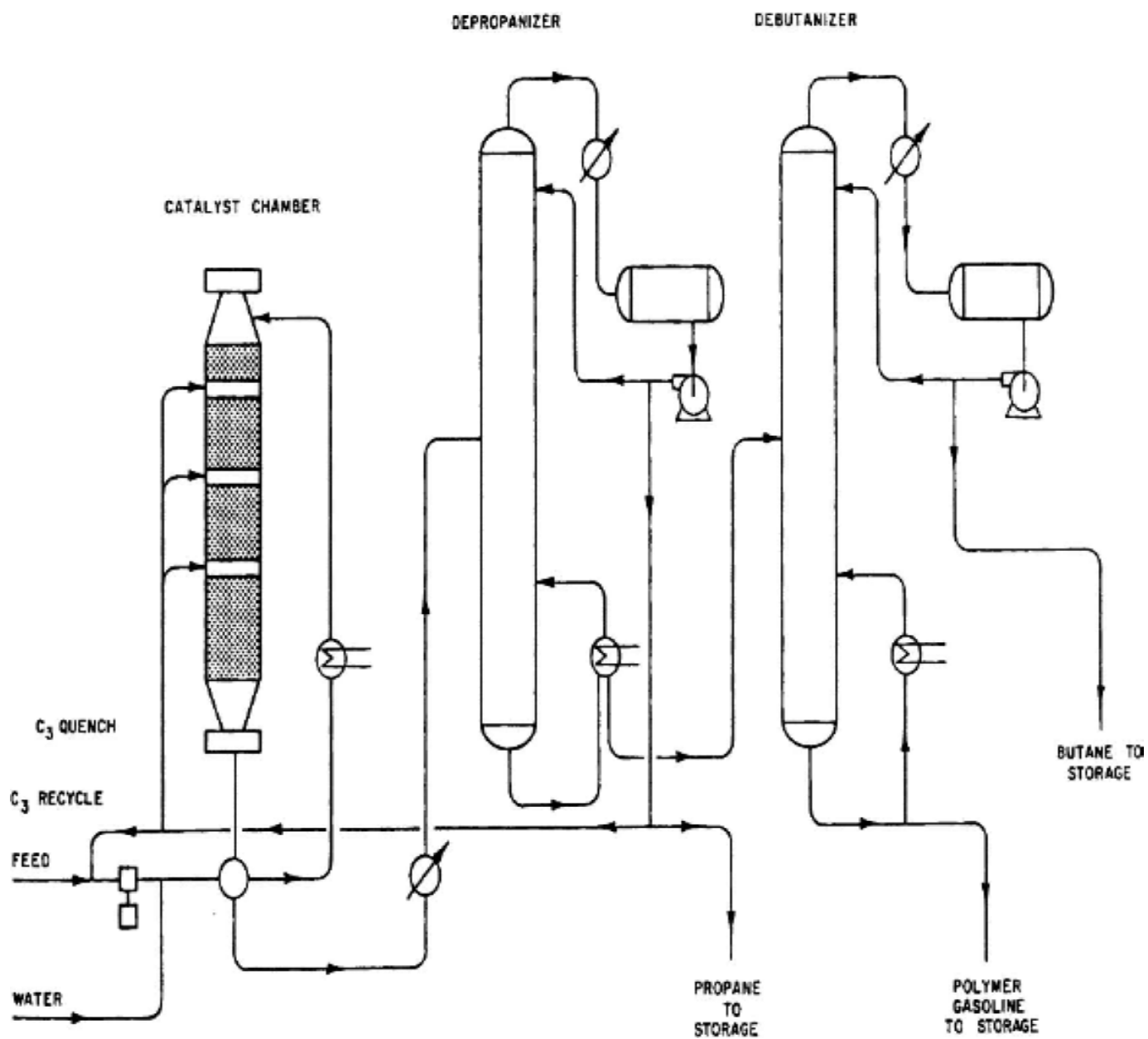


The most widely used catalyst is phosphoric acid on an inert support. This can be in the form of phosphoric acid mixed with a natural clay or a film of liquid phosphoric acid on crushed quartz. Sulfur in the feed poisons the catalyst and any basic materials neutralize the acid and increase catalyst consumption. Oxygen dissolved in the feed adversely affects the reactions and must be removed.

PROCESS DESCRIPTION

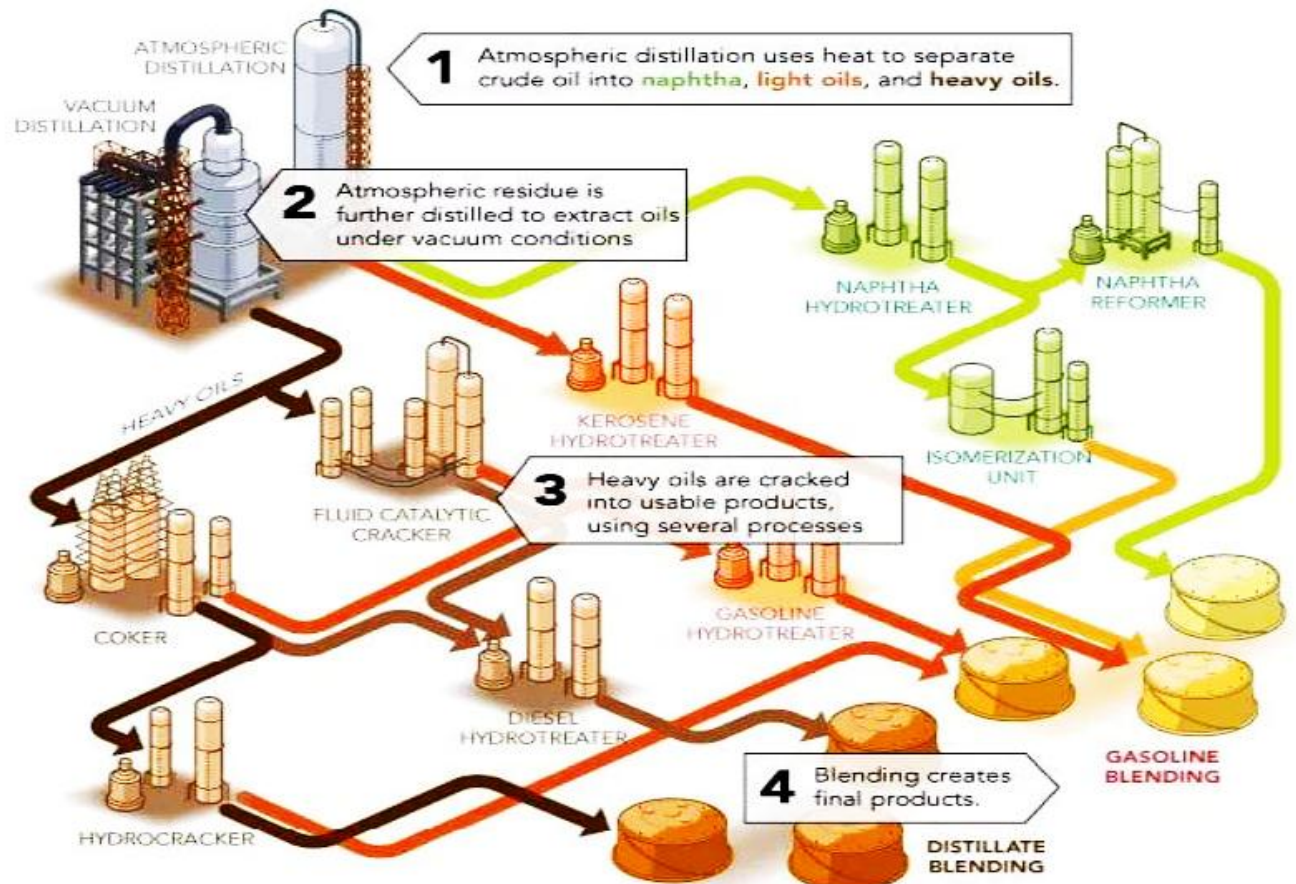
- 1- **The feed**, consisting of propane and butane as well as propene and butene, is contacted with an amine solution to remove hydrogen sulfide and caustic washed to remove mercaptans.
- 2- It is then scrubbed with water to remove any caustic or amines and then dried by passing through a silica gel or molecular sieve bed.
- 3- Finally, a small amount of water (350–400 ppm) is added to promote ionization of the acid before the olefin feed steam is heated to about 400°F (204°C) and passed over the catalyst bed.
- 4- Reactor pressures are about 500 psig (3450 kPa).
- 5- **After leaving the reactor** the product is fractionated to separate the butane and lighter material from the polymer gasoline. Gasoline boiling

range polymer production is normally 90–97 wt% on olefin feed or about 0.7 barrel of polymer per barrel of olefin feed.



UOP solid phosphoric acid polymerization unit.

Crude Oil Refining



LUBRICATING OILS

The large number of natural lubricating and specialty oils sold today are produced by blending a small number of lubricating oil base stocks and additives.

➤ **The lube oil base stocks are prepared from selected crude oils by distillation and special processing to meet the desired qualifications.**

➤ **The additives are chemicals used to give the base stocks desirable characteristics or to enhance and improve existing properties.**

The properties considered important are:

- 1) Viscosity**
- 2) Viscosity Change with Temperature
(Viscosity Index)**
- 3) Pour Point**
- 4) Oxidation Resistance**
- 5) Flash Point**
- 6) Boiling Temperature**
- 7) Acidity (Neutralization Number)**

LUBE OIL PROCESSING:

➤ **The first step in the processing of lubricating oils is the separation on the crude oil distillation units of the fractions according to viscosity and boiling range specifications.**

➤ **The heavier lube oil raw stocks are included in the vacuum fractionating tower bottoms with the ASPHALTENES, RESINS, and OTHER UNDESIRABLE MATERIALS.**

The undesirable characteristics include:

- 1. high pour points,**
- 2. large viscosity changes with temperature (low VI),**
- 3. poor oxygen stability,**
- 4. Poor color,**
- 5. high cloud points,**
- 6. high organic acidity, and**
- 7. high carbon- and sludge-forming tendencies.**

**The Processes used to Change these
Characteristics are:**

(H.W)

(See Fig. 11.1 W.L. NELSON, page 349)

1. Solvent deasphalting to reduce carbon- and sludge-forming tendencies.

2. Solvent extraction & hydrocracking to improve viscosity index.

3. Solvent dewaxing & selective hydrocracking to lower cloud and pour points.

4. Hydrotreating and clay treating to improve color and oxygen stability

5. Hydrotreating and clay treating to lower organic acidity

Although the main effects of the processes are as described above, there are also secondary effects.

For example, the main result of **solvent dewaxing** is the lowering of the cloud and pour points of the oil, solvent dewaxing **also slightly reduces the VI of the oil.**

For Economic Reasons, the Process Sequence (Series) is usually in the order of:

- 1- Deasphalting,**
- 2- Solvent Extraction,**
- 3- Dewaxing, and**
- 4- Finishing.**

1- PROPANE DEASPHALTING

➤ **The lighter distillate feedstocks for producing lubricating oil base stocks can be sent directly to the SOLVENT EXTRACTION units.**

➤ **The atmospheric and vacuum bottoms require :**

1- DEASPHALTING to remove the asphaltenes and resins then to

2- SOLVENT EXTRACTION.

PROPANE is usually used as the solvent in deasphalting but it may also be used with ethane or butane in order to obtain the desired solvent properties.

Table (11-2) (**W.L. NELSON, page 351**) lists the Principal Properties of Extraction Solvents.

➤ **Propane has unusual solvent properties** in that from 100 to 140°F (40 to 60°C).

➤ **Paraffins are very soluble in propane**, but the solubility decreases with an increase in temperature until at the critical temperature of propane [206°F (96.8°C)] all hydrocarbons become insoluble.

➤ **In the range of 100 to 206°F (40 to 96.8°C)** the high molecular weight asphaltenes and resins are largely insoluble in propane.

➤ Separation by distillation is generally by molecular weight of the components and solvent extraction is by type of molecule.

➤ Propane Deasphalting Falls in between these categories because separation is a function of both molecular weight and type of molecular structure.

➤ **The FEEDSTOCK** is contacted with 4 to 8 volumes of liquid propane at the desired operating temperature.

➤ **The EXTRACT phase** contains from 15 to 20% by weight of **oil with the remainder solvent**. The heavier the feed stock, the higher the ratio of propane to oil required

➤ **The RAFFINATE phase** contains from 30 to 50% propane by volume and is not a true solution but an emulsion of precipitated asphaltic material in propane.

PROCESS DESCRIPTION:

1- A typical propane deasphalting unit (Fig.) injects propane into the bottom of the treater tower, and the vacuum tower bottoms feed enters near the top of the tower.

2- As the propane rises through the tower, it dissolves the oil from the residuum and carries it out of the top of the tower.

3- Between the residuum feed point and the top of the tower, heating coils increase the temperature of the propane–oil extract phase thus reducing the solubility of the oil in the propane. This causes some of the oil to be expelled (separated) from the extract phase creating a reflux stream.

4- The reflux flows down the tower and increases the sharpness of separation between the oil portion of the residuum and the asphaltene and resin portion.

5- The asphaltene and resin phase leaving the bottom of the tower is the **RAFFINATE** and the propane–oil mixture leaving the top is the **EXTRACT**.

6- In the flash system, the first stages are operated at pressures high enough to condense the propane vapors with cooling water as the heat exchange medium.

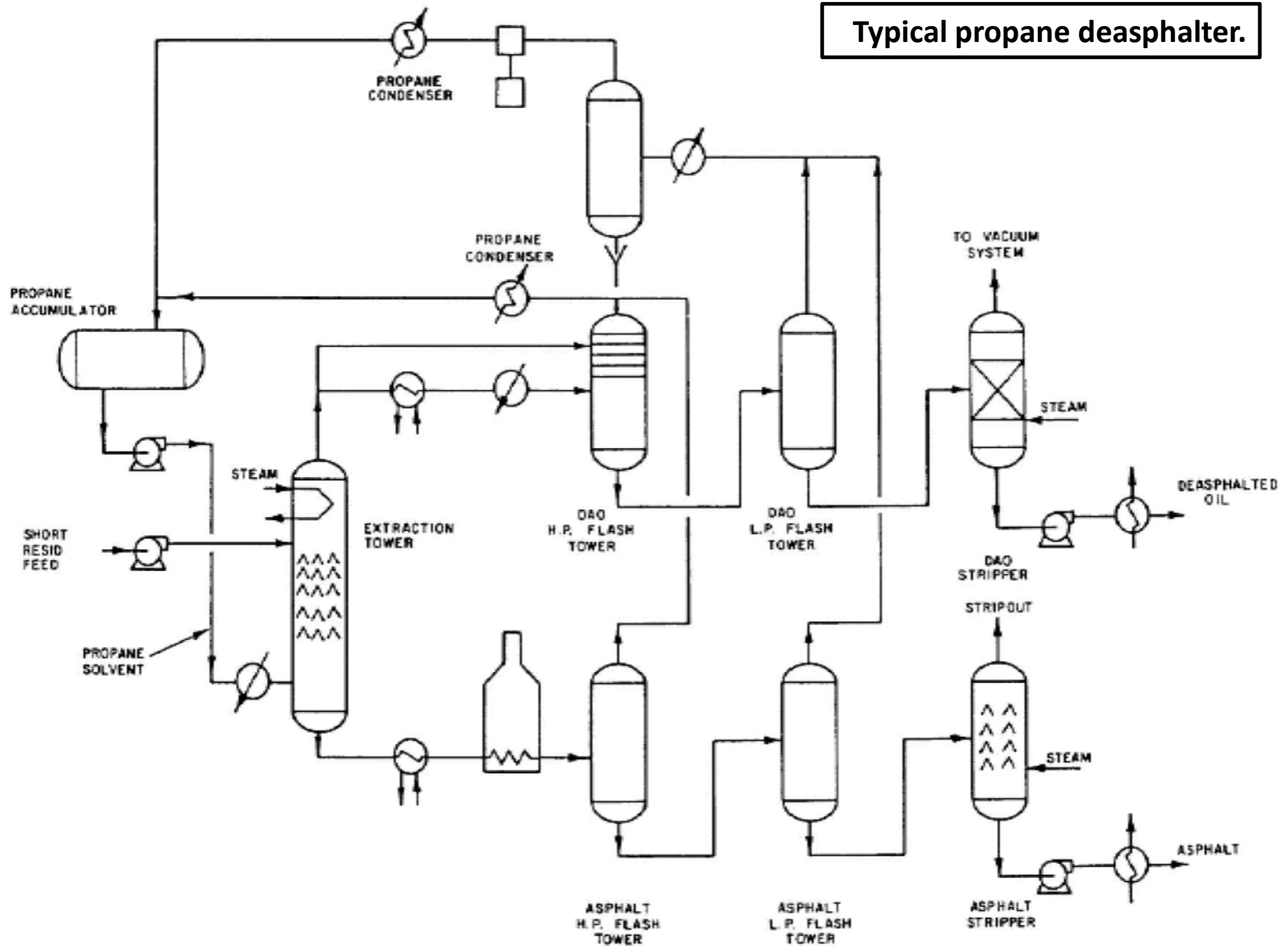
7- In the high pressure raffinate flash tower, foaming and asphalt entrainment can be a major problem. To minimize this, the flash tower is operated at about 550°F (290°C) to keep the asphalt viscosity at a low level.

8- The second stages strip the remaining propane from the raffinate and extract **at near atmospheric pressure.**

9-This propane is compressed and condensed before being returned to the propane accumulator drum.

The propane deasphalting tower is operated at a **pressure sufficiently high** to maintain the solvent in the liquid phase. This is usually about **500 psig (3448 kPa).**

Typical propane deasphalter.



2. Viscosity Index Improvement & Solvent Extraction

2. Viscosity Index Improvement & Solvent Extraction

There are **three solvents** used for the extraction of aromatics from lube oil feed stocks and the solvent recovery portions of the systems are different for each.

These are:

- 1- Furfural,
- 2- Phenol, and
- 3- N-methyl-2-pyrrolidone (NMP).

2.1. Furfural Extraction:

The process flow through the furfural extraction unit is similar to that of the propane deasphalting unit **EXCEPT for the solvent recovery section, which is more complex.**

The oil feedstock is introduced into a

**Continuous Counter-current
Extractor**

at a temperature which is a function of the viscosity of the feed; the greater the viscosity, the higher the temperature used.

**The extraction unit is usually
a Raschig Ring-packed
Tower or a Rotating Disc
Contactor (RDC) with a
temperature gradient from
top to bottom of 60 to 90°F
(30 to 50°C).**

The temperature at the top of the tower is a function of the miscibility temperature of the furfural and oil. It is usually in the range 220 to 300°F (105 to 150°C).

The oil phase is the continuous phase, and the furfural-dispersed phase passes downward through the oil.

2.2. Phenol Extraction:

The process flow for the **phenol extraction unit** is somewhat similar to that of the **furfural extraction unit** but **differs in the solvent recovery section** because **phenol is easier to recover than is furfural.**

The important Extraction Tower Operating Variables are:

- **Phenol-to-oil ratio (treat rate),**
- **Extraction temperature, and**
- **Percent water in phenol.**

➤ **Treat rates** vary from 1:1 to 2.5:1 depending upon the quality and viscosity of the feed and the quality of the product desired.

➤ **Increasing the treat rate** for a given stock improves the VI of the product and decreases the yield.

➤ **Phenol** is recovered from the Extract and Raffinate streams by distillation and gas or steam stripping.

2.3. NMP-Extraction:

The NMP Extraction Process
uses N-methyl-pyrrolidone
(NMP) as the solvent to remove
the condensed ring aromatics
and polar components from the
lubricating oil distillates and
bright stocks.

This process was developed as a replacement for phenol extraction because of:

- the safety, health, and**
- environmental problems associated with the use of phenol.**

Several differences between the characteristics of NMP and phenol make it necessary to modify the phenol plant design.

These differences include:

- 1- higher boiling point for NMP,**
- 2- lower melting point,**
- 3- complete miscibility of NMP with water,**
- 4- no azeotrope formation of NMP with water, and**
- 5- 69% lower viscosity than phenol at 122°F (50°C).**

3. VISCOSITY INDEX IMPROVEMENT & HYDROCRACKING

Components of lubricating oil fractions which have high viscosity indexes are:

- 1- the mononaphthalenes and**
- 2- isoparaffins.**

Hydrocracking of vacuum gas oils:

- 1- increases the paraffin concentration.**
- 2- increases the viscosity index of a lube oil feedstock.**
- 3- produces increasing quantities of the mononaphthalenes and isoparaffins.**

Hydrogenation of polyaromatic aromatic compounds to polynaphthenic ring compounds,

1- **breaking (cracking)** of polynaphthenic rings, and

2- **isomerization** of n-paraffins are promoted by high conversion, low space velocity, and low reaction temperature.

3.1. DEWAXING

3.1. DEWAXING

All lube stocks, except those from a relatively few highly naphthenic crude oils, must be dewaxed or they will not flow properly at ambient temperatures.

There are two types of processes in use today:

1- One uses refrigeration to crystallize the wax and solvent to dilute the oil portion sufficiently to permit rapid filtration to separate the wax from the oil.

2- The other uses a selective hydrocracking process to crack the wax molecules to light hydrocarbons.

3.1.1. Solvent Dewaxing:

There are two principal solvents used in the United States in solvent dewaxing processes:

1- Propane.

2- Ketones.

3- Dichloroethane-methylene is also used in some other countries.

About 85% of the dewaxing installations use ketones as the solvent and the other 15% use propane.

The comparative advantages and disadvantages of the processes are:

Propane	Ketones
Readily available, less expensive, and easier to recover.	
Direct chilling can be accomplished by vaporization of the solvent, thus reducing the capital and maintenance costs of scraped-surface chillers.	Fast chilling rate. Shock chilling can be used to improve process operations.
High filtration rates can be obtained because of its low viscosity at very low temperatures.	Good filtration rates but lower than for propane.
Rejects asphaltenes and resins in the feed.	
Large differences between filtration temperatures and pour point of finished oils [25 to 45°F (15 to 25°C)].	Small difference between filtration temperature and pour point of dewaxed oil [9 to 18°F (5 to 10°C)].

3.1.2. Selective Hydrocracking.

The feed to the selective hydrocracking unit **is** solvent-extracted oil from the aromatic extraction units.

There are two types of selective hydrocracking processes for dewaxing oil:

- **one uses** a single catalyst for pour point reduction only and
- **the other uses** two catalysts to reduce the pour point and improve the oxygen stability of the product.

The advantages claimed over conventional solvent dewaxing units include:

- 1. Production of very low pour and cloud point oils from paraffinic stocks.**
- 2. Lower capital investment.**
- 3. Improved lube oils base stock yields.**
- 4. A separate hydrofinishing operation is not necessary.**

4- HYDROFINISHING

➤ **Hydrotreating of dewaxed lube oil stocks is needed to remove chemically active compounds that affect the color and color stability of lube oils.**

➤ **Most hydrotreating operations use cobalt–molybdate catalysts and are operated at a severity set by the color improvement needed.**

5- FINISHING BY CLAY CONTACTING

➤ Many older lube oil processing plants use **contacting of the dewaxed oil with activated clays** at elevated temperatures to improve the stability of the finished oils in engine service.

➤ **Polar compounds** (aromatic and sulfur and nitrogen containing molecules) are adsorbed on the clay and removed by filtration.

تمهيد

محاضرة تعريفية عن الغاز الطبيعي

الغاز الطبيعي أحد مصادر الطاقة البديلة عن النفط من المحروقات عالية الكفاءة قليلة الكلفة قليلة الانبعاثات الملوثة للبيئة. الغاز الطبيعي مورد طاقة أولية مهمة للصناعة الكيماوية .

تكوينه

يتكون الغاز الطبيعي من **العوالق (Plankton)** ، وهي كائنات مجهرية تتضمن الطحالب و الكائنات الأولية ماتت و تراكمت في طبقات المحيطات و الأرض ، و انضغطت البقايا تحت طبقات رسوبية . و عبر آلاف السنين قام الضغط و الحرارة الناتجان عن الطبقات الرسوبية بتحويل هذه المواد العضوية إلى غاز طبيعي ، و لا يختلف الغاز الطبيعي في تكوينه كثيراً عن أنواع الوقود الحفري الأخرى مثل الفحم و البترول . وحيث أن البترول و الغاز الطبيعي يتكونان تحت نفس الظروف الطبيعية ، فإن هذين المركبين الهيدروكربونيين عادةً ما يتواجدان معاً في حقول تحت الأرض أو الماء ، و عموماً الطبقات الرسوبية العضوية المدفونة في أعماق تتراوح بين 1000 إلى 6000 متر (عند درجات حرارة تتراوح بين 50 إلى 175 درجة مئوية) تنتج بترولاً بينما تلك المدفونة أعمق و عند درجات حرارة أعلى تنتج غاز طبيعي ، وكلما زاد عمق المصدر كلما كان أكثر جفافاً (أى تقل نسبة المتكثفات في الغاز) . بعد التكون التدريجي في القشرة الأرضية يتسرب الغاز الطبيعي و البترول ببطء إلى حفر صغيرة في الصخور المسامية القريبة التي تعمل كمستودعات لحفظ الخام ، ولأن هذه الصخور تكون عادةً مملوءة بالمياه ، فإن البترول و الغاز الطبيعي – و كلاهما أخف من الماء و أقل كثافة من الصخور المحيطة – ينتقلان لأعلى عبر القشرة الأرضية لمسافات طويلة أحياناً . في النهاية تُحبس بعض هذه المواد الهيدروكربونية المنقلة لأعلى في طبقة لا مسامية (غير منفذة للماء) من الصخور تُعرف بـ **صخور الغطاء (Cap Rock)** ، و لأن الغاز الطبيعي أخف من البترول فيقوم بتكوين طبقة فوق البترول تسمى **غطاء الغاز (Gas Cap)** . ولا بد أن يصاحب البترول غاز يسمى بـ **الغاز المصاحب (Associated Gas)** ، كذلك تحتوى مناجم الفحم على كميات من الميثان – المكون الرئيسي للغاز الطبيعي - ، و في طبقات الفحم الرسوبية يتشتت الميثان غالباً خلال مسام و شقوق المنجم ، يسمى هذا النوع عادة بـ ميثان مناجم الفحم .

الاحتياطيات العالمية من الغاز الطبيعي

نظراً لارتفاع المستوى المادي للبشر في العالم فقد زاد استهلاكهم من الطاقة بشدة من أجل تسيير السيارات التي تحملهم لأعمالهم ، ومن أجل الكهرباء التي صارت لا غنى عنها في الحضارة الحديثة ، و غير ذلك كثير . وحيث أن مصادر الطاقة في العالم ناضبة و غير متجددة يُعرّف **الاحتياطي المؤكد** – من البترول أو الغاز الطبيعي - لحقل ما بأنه **الكمية القابلة للاستخلاص على مدى عمر الحقل في ظل التكنولوجيا والاعتبارات الاقتصادية السائدة** .

و طبقاً لتعريف **مجلة البترول و الغاز (Oil And Gas Journal)** الأميركية المتخصصة يتم تعريف **الاحتياطي المؤكد من الغاز الطبيعي بأنه : الكميات التي يمكن استخراجها في ظل ما هو معروف حالياً من الأسعار و التكنولوجيا** .

أما هيئة سيديجاز (Cedigas) الفرنسية فتُعرِّفه بأنه : الكميات المكتشفة التي يتأكد بقدر معقول من اليقين إمكانية إنتاجها في ظل الظروف الاقتصادية و الفنية السائدة .

و يُعدّ التعريف الأول الأكثر تحفظاً لذا نجد أن احتياطات الغاز الطبيعي العالمية في أول يناير عام 1999 طبقاً لتقدير مجلة البترول و الغاز تقل بنسبة 7 % عن تقديرات سيديجاز ، بل إن احتياطات الغاز الطبيعي لمنطقة الشرق الأقصى كانت طبقاً للمجلة تقل بنسبة 30 % عن تقديرات سيديجاز ! . وكلا التعريفين يخضع للتقدير الشخصي أكثر منه لمعايير موضوعية ثابتة يمكن قياسها بدقة. وقد بلغت الاحتياطات العالمية من الغاز الطبيعي في بداية هذا العام حوالي 6504 تريليون قدم مكعب قياسي أو مايكافى 180 تريليون متر مكعب . ويفيد تقرير إحصائي لشركة برتش بتروليوم أن العالم لديه احتياطات مؤكدة من الغاز الطبيعي تكفي استهلاكه لمدة 64 عاما بالمقارنة مع احتياطات تكفي 40 عاما فقط من النفط الخام. لكن أغلب الاحتياطات العالمية من الغاز الطبيعي توجد في المياه العميقة أو في الصحارى الشاسعة أو في دول يصعب التكهن بالتحويلات السياسية فيها. وتملك روسيا 27% من احتياطات الغاز العالمية وإيران 15% وقطر 14%. ويوجد نحو 58% من إجمالي الاحتياطات في الجمهوريات السوفياتية السابقة.

انتاج الغاز الطبيعي ومعالجته

يستخرج الغاز الطبيعي من ابار شبيهة بآبار النفط و يوجد الكثير من تجمعات الغاز على مبعدة من الشاطئ ويتم نقل الغاز بالانابيب من منصات الانتاج إلى نقطة تجميع على الشاطئ ومنها إلى معمل تكرير حيث ينقى.

أنواع الغاز الطبيعي

الغاز الطبيعي : هو عبارة عن مزيج من المواد الهيدروكربونية التي تتواجد في مكامن صخرية تحت سطح الأرض و غالباً ما يكون الغاز الطبيعي متواجداً مع النفط الخام , إما مذاباً او طافياً على سطحه و في هذه الحالة يسمى هذا النوع من الغاز " غاز مصاحب " (Associated Gas) كما توجد كذلك حقول تحتوي فقط على الغاز الطبيعي و هو ما يسمى " الغاز الحر " (Free Gas) و جميع المكونات الهيدروكربونية للغاز الطبيعي هي من نوع البرافينات الخفيفة القابلة للاشتعال بسهولة بوجود الهواء و يعتبر غاز الميثان أكثر مكونات الغاز الطبيعي توفراً إذ تزيد نسبته عن 80% في أغلب الأحيان يليه الإيثان فالبروبان فالبيوتان . ويسمى الغاز الطبيعي " جافاً " (Dry Gas) عندما تكون كمية المكونات الهيدروكربونية السائلة المستخلصة منه تحت الظروف القياسية من الحرارة و الضغط أقل من 0.1 غالون لكل قدم مكعب من الغاز المعالج أما إذا تراوحت هذه الكمية بين 0.1-0.3 غالون لكل قدم مكعب فإن الغاز يعتبر " متوسط الرطوبة " أما إذا زادت كمية السوائل عن 0.3 غالون لكل قدم مكعب فإن الغاز يعتبر " رطباً " (Wet Gas) أي أنه يحتوي على كمية من السوائل الغازية التي يمكن فصلها والاستفادة منها في المجالات العديدة .

و بالإضافة إلى الهيدروكربونات القابلة للاحتراق توجد كميات متفاوتة من الغازات الأخرى غير القابلة للاحتراق . إن بعض هذه الغازات غير القابلة للاحتراق يكون متواجداً بكميات عالية نسبياً كما هو الحال بالنسبة لغازات النيتروجين " N_2 " و كبريتيد الهيدروجين " H_2S " و ثاني أكسيد الكربون " CO_2 " في حين أن بعض الغازات الخاملة مثل الأرجون " Ar " و الهيليوم " He " عادةً ما تكون متوفرة و لكن بكميات قليلة جداً.

إزالة الغازات الحامضية (Sour Gases) من الغاز الطبيعي يعد من أهم التحديات التي تواجه العاملين في شركات صناعة الغاز الطبيعي. وجود الغاز الحمضي في مكونات الغاز الطبيعي يسبب مشاكل في تكلفة عمليات تسهيل الغاز والبيئة في آن واحد. الطرق المتوفرة هي

الامتصاص الكيميائي (Absorption) باستخدام مذيب كيميائي ، الإدمصاص (Adsorption) باستخدام مواد صلبة نشطة كيميائياً ، التفاعل البيولوجي باستخدام بكتيريا صديقة للبيئة. و اتضح من خلال الدراسات شيوع استخدام مذيبيات كيميائية تنتمي لعائلة " الكان أمين " التي تحسن من عملية إزالة الغاز الحمضي.

4 مستقبل الغاز الطبيعي

شق الغاز الطبيعي طريقه بصعوبة ، لكن بثبات، خلال العقود الأربعة الماضية ، ليصبح ثالث مصدر أحفوري في مزيج الطاقة العالمي، بعد النفط والفحم، ونظراً لتسارع وتائر الطلب عليه ، وتطور تقنيات معالجة وتحويله إلى سوائل، يتوقع له أن يغدو مزاحماً جدياً للفحم على المرتبة الثانية بعد النفط الذي سيظل مصدر الطاقة الأول بلا منازع لعقود عديدة قادمة. وبومها ستبلغ حصة الغاز في مزيج الطاقة العالمي نحو 26% حيث سيبلغ إستهلاكه عالمياً نحو 4.7 تريليون م³ في عام 2030، مرتفعاً من نحو 2.8 تريليون م³ حالياً .

ويعرف بعض المراقبين الغاز بأنه «**فارس على ظهر جواد أخضر**» ، بسبب نظافته وما يتمتع به من ميزات بيئية وبسبب مكانته كوقود مثالي في توليد الكهرباء عن طريق شبكات دوامات الغاز ذات الدورة المدمجة. وطالما ظل المنتجون والموردون قادرين على توفير كميات كبيرة من هذه الزيادة فسوف تنتعش الآمال العالمية بخصوص الغاز الطبيعي، إلى درجة أنه قد يهدد قوة التأثير التي يتمتع به النفط الخام، خاصة بعد أن استطاع الغاز الاستقلال عنه بتطور القدرة التقنية على استكشاف الغاز (غير المصاحب) للنفط وإنتاجه وتسويقه.

وبعد أن كان الغاز الطبيعي المصاحب للنفط الخام، وحتى بداية السبعينيات من القرن الماضي يتم إهداره بالكامل أثناء عمليات الإنتاج أو التكرير، فإنه بات اليوم البديل الأهم للنفط خاصة بعد ظهور مؤشرات دولية عن بداية نضوب النفط وهبوط معدلات إنتاجه من مواقع مهمة مثل الولايات المتحدة وبحر الشمال مع وجود إشارات مماثلة تبشر بارتفاع سريع في استهلاك واستكشاف الغاز. فقد ازداد الطلب العالمي على الغاز خلال العشر السنوات الماضية من 190 مليار قدم مكعب قياسي في اليوم إلى أكثر من 235 مليار قدم مكعب قياسي بزيادة سنوية قدرها 2.2 في المائة كمتوسط. ويتوقع أن تستمر الزيادة على طلب الغاز خلال السنوات العشر القادمة بنحو 100 مليار قدم مكعب قياسي في اليوم، لتبلغ نسبة الزيادة السنوية نحو 3.2 في المائة سنوياً. وطبقاً للوكالة الدولية للطاقة، فسوف يزيد إسهام الغاز في الطاقة العالمية من 24 في المائة إلى 30 في المائة بحلول عام 2020.

وفي حال استمرت معدلات زيادة الطلب على ما هي عليه أو ارتفعت، ومن المرجح أنها سوف ترتفع، فإن ذلك يعني أن الغاز، قد يصبح مصدر الطاقة الأهم في العالم خلال العقود القليلة القادمة فيما يتقلص تأثير النفط الخام.

لذلك أولت أسواق الطاقة اهتماماً متزايداً للغاز الطبيعي نظراً لسمعته البيئية كوقود نظيف، ووفرة المؤكد من احتياطياته، ولأنه غداً لقيماً أساسياً للصناعات البتروكيمياوية، ووقوداً رئيسياً في محطات توليد الطاقة الكهربائية وتحلية المياه ، ناهيك عن استخدامه في المنازل للطبخ والتدفئة ، وأضحى ووقود للسيارات – وإن على نطاق لايزال ضيقاً .

لقد تطورت تكنولوجيا تسهيل الغاز التي أستخدمت لأول مرة في المنطقة العربية وفي العالم في الجزائر قبل نحو 43 سنة ، وأصبحت تستخدم اليوم في خمسة أقطار عربية أخرى هي قطر والإمارات ومصر وليبيا وعمان . أما إستخداماتها في **تحويل الغاز إلى سوائل GTL** لكي يغدو

لقيمًا ومكثفات تدخل في الصناعة البتروكيمياوية وفي التكرير ، فتتفرد به الآن دولة قطر . وساهمت التكنولوجيا كذلك في خفض تكاليف مد أنابيب نقل الغاز العابرة للحدود والبحار ، وأسعار ناقلات المسيل منه ، وصار بالإمكان بناء ناقلات عملاقة تتجاوز حمولاتها 200 ألف طن ، بسعر يقل بنحو 20% عن أسعارها السابقة ، وبمواصفات سلامة وأمان أكثر تطوراً . وإستغلالاً لهذه المنحى الإيجابي لنمو الطلب العالمي على الغاز ، إتجه منتجوه في المنطقة العربية والعالم إلى تنفيذ مشاريع ضخمة لتسييله، ومد انابيب برية وبحرية، لإمداد مناطق الإستهلاك الرئيسية . ولعل المشاريع العربية التي تمت أو تتم إقامتها ، إنطلاقاً من هذا المنظور ، في كل من الجزائر ومصر ودول الخليج العربية سوف تلبي تزايد الطلب العالمي على غاز المنطقة العربية . ومن جهتها شرعت البلدان المستهلكة للغاز الطبيعي ، في بناء مرافئ منشآت لإستقبال كميات متزايدة من الغاز المسيل وإعادة تغويزه . وسيساهم ذلك في فتح مزيد من لفرص أمام الغاز الطبيعي المسيل ، والعربي منه خاصة .ومن المتوقع أن تظل نسبة نمو الطلب العالمي على الغاز الطبيعي شبه ثابتة عند مستوى 2% سنوياً . وستستحوذ محطات توليد الكهرباء على ما بين 50 و70% من كميات الغاز المسوقة ، فيما تستأثر بالبقية قطاعات الصناعة والتجارة والسكن . وستظل البلدان الصناعية في أوروبا وأمريكا الشمالية ومنطقة آسيا/ الهادي مستهلكاً رئيسياً للغاز الطبيعي ، فيما ستشهد مناطق العالم الأخرى في كل من آسيا (خصوصاً الصين والهند واندونيسيا) وأفريقيا ، وكذلك المنطقة العربية إرتفاعاً ملحوظاً في طلبها عليه ، بفعل النمو الإقتصادي الذي تحققه ، وإتجاه مجتمعاتها إلى مزيد من التمدن . يمثل الجدول التالي احتياطات الغاز الطبيعي في الدول العربية.

Definitions

Pipeline Gas: Gas that has the quality to be used as a domestic or industrial fuel. It meets the specifications set by a pipeline transmission company, and/or distributing company.

Sour Gas: Gas that contains more than 1 grain of H_2S /100 SCF.

Sweet Gas: Gas in which the H_2S content is less than 1 grain /100 SCF.

Wet Gas: Gas that contains more than 0.1 gallons (U.S.) of condensate per 1000 CF of gas.

Dry Gas: Gas that contains less than 0.1 gallons (U.S.) of condensate per 1000 CF of gas.

Rich Gas: Gas containing a lot of compounds heavier than ethane., about 0.7 US gallons of C₃+ per 1000 CF of feed to an absorber.

Lean Gas: Gas containing very little propane and heavier – or the effluent gas from an absorption unit.

Pentanes+: The pentane and heavier fraction of hydrocarbon liquid.

Condensates: The hydrocarbon liquid fraction obtained from a gas stream containing essentially pentanes.

Lean Oil: Absorption oil sent to an absorber.

Rich Oil: Absorption oil containing absorber material. The effluent from an absorber.

Lean Solution: A stripped sweetening solution.

Rich Solution: A sweetening solution containing absorbed acid gases.

Liquefied natural gas (LNG): When natural gas is cooled to a temperature of approximately –260 °F (–160 °C) at atmospheric pressure it condenses to a liquid called liquefied natural gas (LNG). One volume of this liquid takes up about 1/600th the volume of natural gas at a stove burner tip. LNG is only about 45% the density of water. LNG is odorless, colorless, non-corrosive, and non-toxic. When vaporized it burns only in concentrations of 5% to 15% when mixed with air. Neither LNG, nor its vapor, can explode in an unconfined environment.

Natural gas is composed primarily of methane (typically, at least 90%), but may also contain ethane, propane and heavier hydrocarbons. Small quantities of nitrogen, oxygen, carbon dioxide, sulfur compounds, and water may also be found in "pipeline" natural gas. The liquefaction process removes the oxygen, carbon dioxide, sulfur compounds, and water. The process can also be designed to purify the LNG to almost 100% methane.

Compressed natural gas (CNG): Is natural gas pressurized and stored in welding bottle-like tanks at pressures up to 3,600 psig (25 MPa). Typically, it is same composition of the local "pipeline" gas, with some of the water removed. CNG and LNG are both delivered to gas engines as low pressure vapor (ozf/in² to 300 psig, up to 2.1 MPa). CNG is often misrepresented as the only form natural gas can be used as vehicle fuel. LNG can be used to make CNG. This process requires much less capital intensive equipment and about 15% of the operating and maintenance costs.

Liquid petroleum gas (LPG): and sometimes called propane) is often confused with LNG and vice versa. They are not the same and the differences are significant. Varieties of LPG bought and sold include mixes that are primarily propane, mixes that are primarily butane, and mixes including propane, propylene, n-butane, butylene and iso-butane. Depending on the season—in winter more propane, in summer more butane. Vapor pressures, at 30 °C, are for commercial propane in the range 10-12 barg (1 to 1.2 MPa), for commercial butane, 2-4 barg (0.2 to 0.4 MPa). In some countries LPG is composed primarily of propane (upwards to 95%) and smaller quantities of butane.

LPG compared to natural gas has a significantly higher heating value and requires a different air-to-gas mixture (propane: 24:1, butane: 30:1) for good combustion.

LPG can be stored as a liquid in tanks by applying pressure alone. While the distribution of LNG requires heavy infrastructure investments (pipelines, etc.), LPG is portable. This fact makes LPG very interesting for developing countries and rural areas. LPG (sometimes called autogas) has also been used as fuel in light duty vehicles for many years. An increasing number of petrol stations around the world offer LPG pumps as well. A final example that should not be forgotten is that the "bottled gas" can often be found under barbecue grills.

Gaseous Fuels

Classification of Gaseous Fuels

The following is a list of the types of gaseous fuel:

(A) Fuels naturally found in nature:

1. Natural gas
2. Methane from coal mines

(B) Fuel gases made from solid fuel

1. Gases derived from Coal
2. Gases derived from waste and Biomass
3. From other industrial processes (Blast furnace gas)

(C) Gases made from petroleum

1. Liquefied Petroleum gas (LPG)
2. Refinery gases
3. Gases from oil gasification

(D) Gases from some fermentation processes.

The Importance of Gaseous Fuel

- ❖ Generally VERY clean burning. Little soot. Operate with low XSA
- ❖ Easy to burn - No grinding or atomization. Excellent mixing
- ❖ No problems with erosion or corrosion
- ❖ No ash
- ❖ The gas is easy to clean. E.g. if sulphur is present, it may be easily removed prior to combustion.
- ❖ Simplest combustion plant of all - Burners
- ❖ Control system
- ❖ No ash problems
- ❖ Heat exchangers
- ❖ Can be started up and shut down very easily and quickly.

The disadvantages of gaseous fuels are;

- Problems with distribution and storage
- Explosion risk - very volatile.
- Relatively costly. Offset by cheaper and more efficient plant.

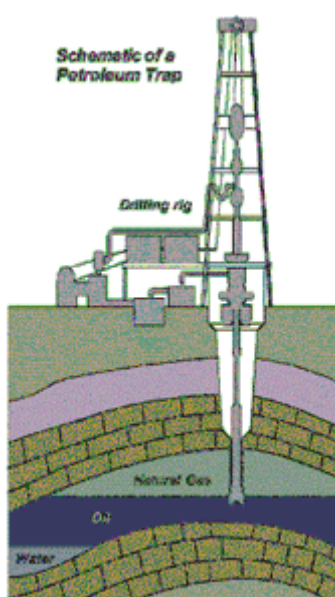
Natural Gas

Origin & World Reserves

Natural gas is generally considered a *nonrenewable* fossil fuel. Natural gas is called a fossil fuel because most scientists believe that natural gas was formed from the remains of tiny sea animals and plants that died 200-400 million years ago.

Several differing theories attempt to explain the true origin of natural gas, though the most widely accepted explanation is that natural gas forms from the remains of ancient microorganisms as well as plant and animal matter that have undergone conditions of extreme heat and pressure over very long periods of time. As such organic matter is buried by increasing amounts of mud and sediment over time, the resulting pressure forces it further underground, compressing the matter and subjecting it to the high temperatures that exist deep within the earth. Intense compression and

high temperature conditions cause carbon bonds in the organic matter to break down, a chemical transformation resulting in the formation of natural gas and other fossil fuels.



Another way natural gas is formed is by microorganisms known as *methanogens*. Methanogens are microscopic organisms which live in environments devoid of oxygen and chemically decompose organic matter, creating methane as a byproduct. Contrary to the natural gas formed by compression of organic matter under intense pressure at great depths, methane created by methanogens is typically found closer to the earth's surface where the organisms live.

Once natural gas forms within the earth, its low density causes it to rise through the path of least resistance, often escaping the earth's crust and dissipating into the atmosphere. But natural gas deposits that are sought for extraction form when impermeable rock "traps" the natural gas within the earth, preventing it from escaping and causing it to collect, creating a *reservoir*.

Natural gas is usually located within such reservoirs floating atop oil deposits, which have formed reservoirs in much the same way. However, deposits containing only natural gas are not unusual. Both the oil and natural gas may be extracted by drilling into the impermeable rock restricting the fossil fuels to the reservoir. The natural pressure already present within the reservoir allows the fossil fuels to escape on their own once the rock containing them is penetrated.

Once natural gas is extracted from the earth, it is treated (if necessary) and distributed to supply the energy on which much of the world relies.

Oil forms at temperatures between about 50°C (120°F) and 175°C (350°F). At higher temperatures, gas is formed and any oil that has already been produced starts to turn into lighter oils and eventually into Methane gas, the lightest and simplest hydrocarbon. At temperatures above about 260°C (500°F), plant and animal remains turn completely to carbon and no more oil or gas are produced. Figure (2) shows the world natural gas reserves.

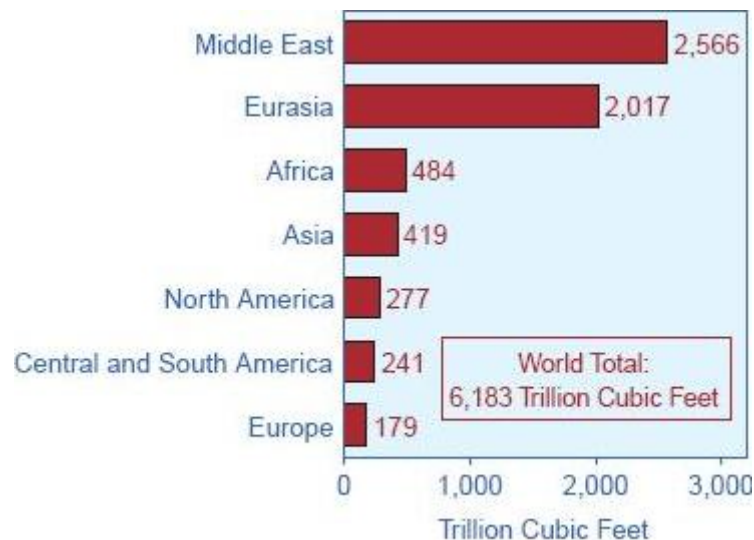


Fig (2); World Natural Gas Reserves - 2006

Oil Wells

Raw natural gas comes primarily from any one of three types of gas wells.

- 1) crude oil wells
- 2) gas wells
- 3) condensate wells.

Natural gas wells average 6000 feet deep.

Natural gas that comes from crude oil wells is typically termed **associated gas**. This gas can exist separate from the crude oil in the underground formation, or dissolved in the crude oil.

Natural gas from gas wells and from condensate wells, in which there is little or no crude oil, is termed **non-associated gas**. Gas wells typically

produce only raw natural gas, while condensate wells produce raw natural gas along with a very low density liquid hydrocarbon called *natural gas condensate* (sometimes also called *natural gasoline* or simply *condensate*).

Raw natural gas can also come from methane deposits in the pores of coal seams. Such gas is referred to as *coalbed gas* and it is also called *sweet gas* because it is relatively free of hydrogen sulfide.

Another source of natural gas is the gas produced in landfills. Landfill gas is considered a *renewable* source of natural gas since it comes from decaying garbage.

The gas from coal beds and landfills accounts for three percent of the total gas supply today, yet their contribution could double by the year 2010.

Composition of natural gas

Natural gas is a complex mixture of *hydrocarbon* and *non-hydrocarbon* constituents and exist as a gas under atmospheric conditions.

The composition of natural gas is never constant, however, the primary component of natural gas is *methane* (typically, at least 90%).

Methane is highly flammable, burns easily and almost completely, while it emits very little air pollution.

It also contains heavier gaseous hydrocarbons such as *ethane* (C_2H_6), *propane* (C_3H_8) and *butane* (C_4H_{10}), in.

Also, in the raw state it often contains non hydrocarbons such as *nitrogen*, *hydrogen sulfide* and *carbon dioxide*. There are traces of such compounds as *helium*, *carbonyl sulfide* and various *mercaptans*. It is also generally saturated with *water*.

Typical Composition of Natural Gas

<i>Methane</i>	CH_4	70-90%
<i>Ethane</i>	C_2H_6	0-20%
<i>Propane</i>	C_3H_8	
<i>Butane</i>	C_4H_{10}	

<i>Carbon Dioxide</i>	<i>CO₂</i>	<i>0-8%</i>
<i>Oxygen</i>	<i>O₂</i>	<i>0-0.2%</i>
<i>Nitrogen</i>	<i>N₂</i>	<i>0-5%</i>
<i>Hydrogen sulphide</i>	<i>H₂S</i>	<i>0-5%</i>
<i>Rare gases</i>	<i>A, He, Ne, Xe</i>	<i>trace</i>

Energy content

Combustion of 100 ft³ of commercial quality natural gas typically yields approximately 1 therm (100,000 BTU, 30 kWh). One m³ yields 38 MJ (10.6 kWh).

Important Facts About Natural Gas:

- Flammability range 5% to 15%
- No color, odor or taste
- Mercaptan is added for odor
- Nontoxic
- Burns with a blue flame
- Liquefies at - 200 °F
- Heating Value 800 to 1200 BTU's per cubic foot.

Storage And Transport

The major difficulty in the use of natural gas is **transportation** and **storage** because of its low density. Natural gas **pipelines** are economical, but are impractical across oceans.

LNG carriers can be used to transport liquefied natural gas (LNG) across oceans, while **tank trucks** can carry liquefied or compressed natural gas (CNG) over shorter distances. They may transport natural gas directly to end-users, or to distribution points such as pipelines for further transport. These may have a higher cost, requiring additional facilities for liquefaction or compression at the production point, and then gasification or decompression at end-use facilities or into a pipeline.

USES

- Power generation
- Hydrogen production
- Vehicles
- Residential domestic use
- Fertilizer
- Aviation
- Natural gas is also used in the manufacture of fabrics, glass, steel, plastics, paint, and other products.

Fig.(3) shows the natural gas uses.

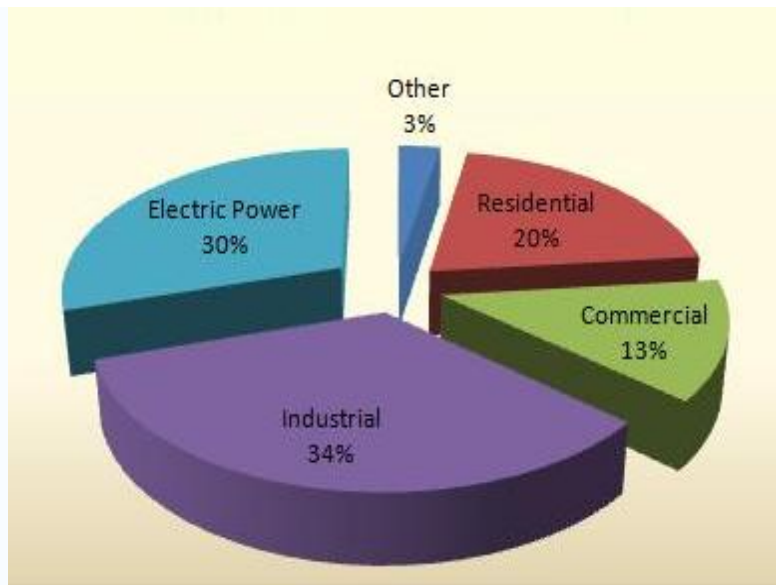


Fig. (3): Natural Gas Uses by Sector (2007)

Syngas (from *synthesis gas*) is the name given to a gas mixture that contains varying amounts of carbon monoxide and hydrogen generated by the gasification of a carbon containing fuel to a gaseous product with a heating value. Examples include;

- The gasification of coal and in some types of waste-to-energy gasification facilities.
- Steam reforming of natural gas or liquid hydrocarbons to produce hydrogen,

The name comes from their use as;

- intermediates in creating synthetic natural gas (SNG).
- for producing ammonia or methanol.
- Syngas is also used as an intermediate in producing synthetic petroleum for use as a fuel or lubricant via Fischer-Tropsch synthesis and previously the Mobil methanol to gasoline process.

Gasification

Gasification is a process that converts carbonaceous materials, such as coal, petroleum, or biomass, into carbon monoxide and hydrogen by reacting the raw material at high temperatures $> 700\text{ }^{\circ}\text{C}$ with a controlled amount of oxygen (partial combustion). The resulting gas mixture is called synthesis gas or syngas and is itself a fuel. Gasification is a very efficient method for extracting energy from many different types of organic materials, and also has applications as a clean waste disposal technique.

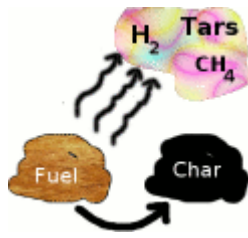
The advantage of gasification is that;

- using the syngas is more efficient than direct combustion of the original fuel; more of the energy contained in the fuel is extracted.
- Syngas may be burned directly in internal combustion engines, used to produce methanol and hydrogen, or converted via the Fischer-Tropsch process into synthetic fuel.
- Gasification can also begin with materials that are not otherwise useful fuels, such as biomass or organic waste.
- In addition, the high-temperature combustion refines out corrosive ash elements such as chloride and potassium, allowing clean gas production from otherwise problematic fuels.

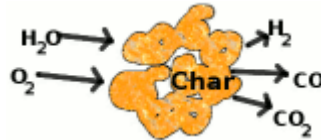
Gasification of fossil fuels is currently widely used on industrial scales to generate electricity. However, almost any type of organic material can be used as the raw material for gasification, such as wood, biomass, or even plastic waste. Thus, gasification may be an important technology for renewable energy.

Chemistry

In a gasifier, the carbonaceous material undergoes several different processes:



Pyrolysis of carbonaceous fuels



Gasification of char

- The pyrolysis (or devolatilization) process occurs as the carbonaceous particle heats up. Volatiles are released and char is produced, resulting in up to 70% weight loss for coal. The process is dependent on the properties of the carbonaceous material and determines the structure and composition of the char, which will then undergo gasification reactions.
- The combustion process occurs as the volatile products and some of the char reacts with oxygen to form carbon dioxide and carbon monoxide, which provides heat for the subsequent gasification reactions. Letting C represent a carbon-containing organic compound, the basic reaction here is;



- The gasification process occurs as the char reacts with carbon dioxide and steam to produce carbon monoxide and hydrogen, via the reaction;



In addition, the reversible gas phase water gas shift reaction reaches equilibrium very fast at the temperatures in a gasifier. This balances the concentrations of carbon monoxide, steam, carbon dioxide and hydrogen.

Hydrogen production

Hydrogen is used for the hydrotreating and hydrocracking processes. The hydrogen from reformer is often not sufficient for hydrotreating process.

Hydrogen is commonly produced from hydrocarbon fossil fuels via a chemical path. Hydrogen may also be extracted from water via biological production in an algae bioreactor, or using electricity (by **electrolysis**) or heat (by **thermolysis**); these methods are presently not cost effective for bulk generation in comparison to chemical paths derived from hydrocarbons. Cheap bulk production of hydrogen is a requirement for a healthy hydrogen economy.

Hydrogen can be generated from natural gas with approximately 80% efficiency or other hydrocarbons to a varying degree of efficiency.

1. Steam reforming of natural gas

Commercial bulk hydrogen is usually produced by the steam reforming of natural gas as shown in Fig.(1). At high temperatures (700–1100 °C), steam (H₂O) reacts with methane (CH₄) to yield syngas.



25-40% NiO/low SiO₂/Al₂O₃ catalyst, (760-816°C)

The heat required to drive the process is generally supplied by burning some portion of the methane.

• Shift Conversion

Additional hydrogen can be recovered from the carbon monoxide (CO) through the lower-temperature water gas shift reaction, performed at about 130 °C:



Cr₂O₃ and Fe₂O₃ as catalyst

• Gas Purification:

The Shift Converter product stream is then scrubbed, usually through absorption with a potassium carbonate solution to remove the carbon dioxide.

The potassium carbonate solution is regenerated in a Carbon Dioxide Still by applying reboiler heat to the tower bottoms. This heat drives off the carbon dioxide from the solution which is then re-circulated.

- **Methanation**

Since carbon monoxide (CO) and carbon dioxide (CO₂) are poisons to the catalysts of some of the hydrogen consuming refinery processes. Methanation is employed as the final step to remove any remaining CO and CO₂ in the hydrogen stream.

The methanation reaction takes place in a fixed-bed reactor consisting of a nickel-based catalyst. The resulting hydrogen product stream is typically approximately 95% hydrogen and the balance methane with only trace amounts of CO and CO₂. The Methanation reactions are:



Reaction conditions are at 425°F over Ni/Al₂O₃ catalyst.

Trace amounts of CH₄ can be present in the H₂ stream.

Refinery Gasses

In refinery, gas is formed in **cracking** and **reforming** operations due to the thermal degradation of liquid hydrocarbons. During **stabilization** of **wild gasolines** or **processed gasolines**, the gases are vented. This forms a major source of heat energy for refinery, as well as feed stock for petrochemicals. All the gasses contain impurities like **CO₂**, **N₂**, **mercaptans**, **H₂S**, **water vapor**, **suspended impurities**. First three paraffins are gases at room temperature. The mixture of methane and ethane is called **dry gas**. Propane and butane mixture is called **wet gas**.

Biogas, Landfill gas, and Methane Hydrates

Methanogenic archaea are responsible for all biological sources of methane. Methane released directly into the atmosphere would be considered a pollutant, however, methane in the atmosphere is oxidized, producing carbon dioxide and water. Methane in the atmosphere has a half life of seven years, meaning that every seven years, half of the methane present is converted to carbon dioxide and water.

Future sources of methane, the principal component of natural gas, include **landfill gas**, **biogas** and **methane hydrate**. Biogas, and especially landfill gas, are already used in some areas, but their use could be greatly expanded. Landfill gas is a type of biogas, but biogas usually refers to gas produced from organic material that has not been mixed with other waste.

Biogas: Typically refers to a gas produced by the biological breakdown of organic matter in the absence of oxygen. Biogas originates from biogenic material and is a type of **biofuel**.

One type of biogas is produced by anaerobic digestion or fermentation of biodegradable materials such as biomass, manure or sewage, municipal waste, green waste and energy crops. This type of biogas comprises primarily methane and carbon dioxide. The other principal type of biogas is wood gas which is created by gasification of wood or other biomass. This type of biogas is comprised primarily of nitrogen, hydrogen, and carbon monoxide, with trace amounts of methane.

The gases methane, hydrogen and carbon monoxide can be combusted or oxidized with oxygen. Air contains 21% oxygen. This energy release allows biogas to be used as a fuel. Biogas can be used as a low-cost fuel

in any country for any heating purpose, such as cooking. It can also be used in modern waste management facilities where it can be used to run any type of heat engine, to generate either mechanical or electrical power. Biogas can be compressed, much like natural gas, and used to power motor vehicles. Biogas is a renewable fuel, so it qualifies for renewable energy subsidies in some parts of the world.

Landfill Gases: When the organic portion of landfill waste decomposes under anaerobic (without oxygen) conditions, a gas is produced that is typically composed of 40-60% methane, with the remainder being mostly carbon dioxide (CO₂). Landfill gas also contains varying amounts of nitrogen, oxygen, water vapor, sulfur and a hundreds of other contaminants -- most of which are known as "non-methane organic compounds" or **NMOCs**. Inorganic contaminants like mercury are also known to be present in landfill gas. Sometimes, even radioactive contaminants such as tritium (radioactive hydrogen) have been found in landfill gas.

NMOCs usually make up less than 1% of landfill gas. Many of these compounds are toxic chemicals like benzene, toluene, chloroform, vinyl chloride, carbon tetrachloride, and 1,1,1 trichloroethane. At least 41 of these are halogenated compounds. Many others are non-halogenated toxic chemicals. When halogenated chemicals (chemicals containing halogens - typically chlorine, fluorine, or bromine) are combusted in the presence of hydrocarbons, they can recombine into highly toxic compounds such as dioxins and furans, the most toxic chemicals ever studied.

The general options for dealing with landfill gas (once collected) are as follows:

1. flare it
2. boiler - makes heat
3. internal combustion engine - makes electricity
4. gas turbine - makes electricity
5. fuel cell - makes electricity
6. convert the methane to methyl alcohol
7. clean it up enough to pipe it to other industries or into the natural gas lines

Hydrates: A speculative source of enormous quantities of methane is from methane hydrate, found under sediments in the oceans. However, as of 2008 no technology has been developed to recover it economically.