

PETROLEUM REFINING
FOURTH CLASS
LECTURE (1)

INTRODUCTION

Petroleum (Latin *Petroleum* derived from Greek πέτρα (Latin *petra*) rock + έλαιον (Latin *oleum*) - oil) or **crude oil** is a naturally occurring liquid found in formations in the Earth consisting of a complex mixture of hydrocarbons (mostly alkanes) of various lengths. The approximate length range is C₅H₁₂ to C₁₈H₃₈. Any shorter hydrocarbons are considered natural gas or natural gas liquids, while long-chain hydrocarbons are more viscous, and the longest chains are paraffin wax. In its naturally occurring form, it may contain other nonmetallic elements such as sulfur, oxygen, and nitrogen. It is usually black or dark brown (although it may be yellowish or even greenish) but varies greatly in appearance, depending on its composition. Crude oil may also be found in semi-solid form mixed with sand, as in the Athabasca oil sands in Canada, where it may be referred to as crude bitumen.

Petroleum is used mostly, by volume, for producing fuel oil and gasoline (petrol), both important "primary energy" sources. 84% by volume of the hydrocarbons present in petroleum is converted into energy-rich fuels (petroleum-based fuels), including gasoline, diesel, jet, heating, and other fuel oils, and liquefied petroleum gas.

Due to its

- high energy density
- easy transportability

it has become the world's most important source of energy since the mid 1950s. Petroleum is also the raw material for many chemical products, including pharmaceuticals, solvents, fertilizers, pesticides, and plastics;

the 16% not used for energy production is converted into these other materials.

Petroleum is found in **porous rock formations** in the upper **strata** of some areas of the **Earth's crust**. There is also petroleum in **oil sands (tar sands)**. Known **reserves of petroleum** are typically estimated at around 1.2 trillion barrels without oil sands, or 3.74 trillion barrels with oil sands . However, oil production from oil sands is currently severely limited. Consumption is currently around 84 million barrels per day, or 3.6 trillion liters per year. Because of **reservoir engineering** difficulties, recoverable oil reserves are significantly less than total oil-in-place. At current consumption levels, and assuming that oil will be consumed only from reservoirs, known reserves would be gone around 2039, potentially leading to a global **energy crisis**. However, this ignores any new discoveries, rapidly increasing consumption in China & India, using oil sands, using synthetic petroleum, and other factors which may extend or reduce this estimate.

Formation

Formation of petroleum occurs in a variety of mostly **endothermic** reactions in high temperature and/or pressure. For example, a **kerogen** may break down into **hydrocarbons** of different lengths. **Geologists** view crude oil and **natural gas** as the product of **compression and heating** of ancient **organic materials** (i.e. **kerogen**) over **geological time**. Formation of petroleum occurs from **hydrocarbon pyrolysis**, in a variety of mostly **endothermic** reactions at high temperature and/or pressure. Today's oil formed from the preserved remains of **prehistoric zooplankton** and **algae**, which had settled to a sea or lake bottom in large quantities under **anoxic conditions**. Over geological time the organic matter mixed with **mud**, and was buried under heavy layers of **sediment** resulting in high levels of **heat**

and [pressure](#). This caused the organic matter to chemically change, first into a waxy material known as [kerogen](#) which is found in various [oil shales](#) around the world, and then with more heat into liquid and gaseous hydrocarbons in a process known as [catagenesis](#).

Geologists often refer to the temperature range in which oil forms as an "oil window"—below the minimum temperature oil remains trapped in the form of kerogen, and above the maximum temperature the oil is converted to [natural gas](#) through the process of [thermal cracking](#).

Although this temperature range is found at different depths below the surface throughout the world, a typical depth for the oil window is 4–6 km. Sometimes, oil which is formed at extreme depths may migrate and become trapped at much shallower depths than where it was formed.

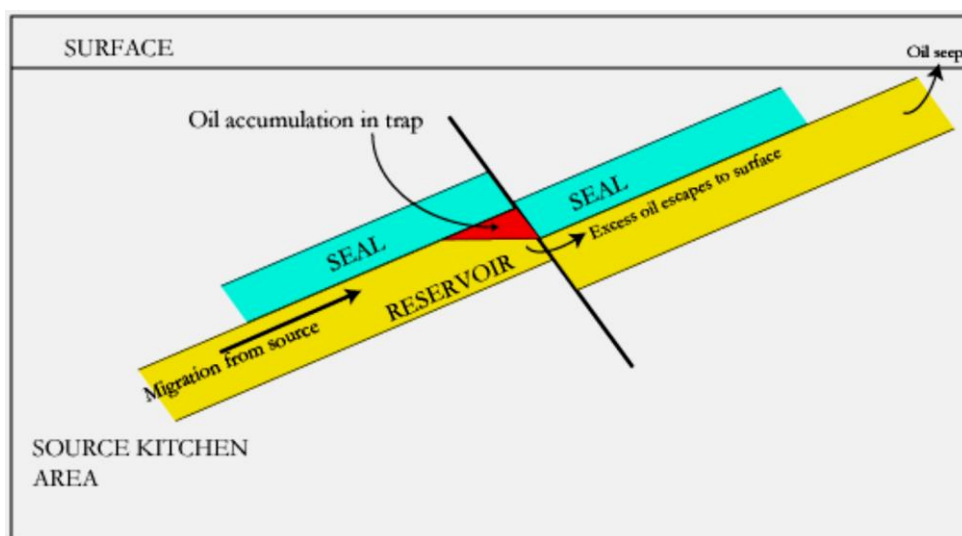
Oil forms at temperatures between about 50°C (120°F) and 175°C (350°F). At higher temperatures, gas is formed and any oil that has already been produced starts to turn into lighter oils and eventually into Methane gas, the lightest and simplest hydrocarbon. At temperatures above about 260°C (500°F),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

Crude oil reservoirs

Three conditions must be present for oil reservoirs to form:

1. A source rock rich in hydrocarbon material buried deep enough for subterranean heat to cook it into oil.
2. A [porous](#) and [permeable](#) reservoir rock for it to accumulate in.
3. A cap rock (seal) or other mechanism that prevents it from escaping to the surface.

Within these reservoirs, fluids will typically organize themselves like a three-layer cake with a layer of water below the oil layer and a layer of gas above it, although the different layers vary in size between reservoirs. Because most hydrocarbons are **lighter** than rock or water, they often migrate upward through adjacent rock layers until either reaching the surface or becoming trapped within porous rocks (known as **reservoirs**) by impermeable rocks above.



However, the process is influenced by underground water flows, causing oil to migrate hundreds of kilometers horizontally or even short distances downward before becoming trapped in a reservoir. When hydrocarbons are concentrated in a trap, an **oil field** forms, from which the liquid can be extracted by **drilling** and **pumping**. The reactions that produce oil and natural gas are often modeled as first order breakdown reactions, where hydrocarbons are broken down to oil and natural gas by a set of parallel reactions, and oil eventually breaks down to natural gas by another set of reactions. The latter set is regularly used in **petrochemical** plants and **oil refineries**.

Lecture Two

Chemical Composition of Petroleum:

The proportion of hydrocarbons in the mixture is highly variable and ranges from as much as 97% by weight in the lighter oils to as little as 50% in the heavier oils and bitumens. The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium.

The exact molecular composition varies widely from formation to formation but the proportion of chemical elements varies over fairly narrow limits as follows:

Composition by weight	
Element	Percent range
Carbon	83%
Hydrogen	10 to 14%
Nitrogen	0.1 to 2%
Oxygen	0.1 to 1.5%
Sulfur	0.5 to 6%
Metals	Less than 1000 ppm

Four different types of hydrocarbon molecules appear in crude oil. The relative percentage of each varies from oil to oil, determining the properties of each oil.

Composition by weight		
Hydrocarbon	Average %	Range %
Paraffins	30	15 to 60
Naphthenes	49	30 to 60
Aromatics	15	3 to 30
Asphaltics	6	Remainder

Petroleum is used mostly, by volume, for producing fuel oil and petrol, both important "primary energy" sources. 84 vol. % of the hydrocarbons present in petroleum is converted into energy-rich fuels (petroleum-based fuels), including petrol, diesel, jet, heating, and other fuel oils, and liquefied petroleum gas. The lighter grades of crude oil produce the best yields of these products, but as the world's reserves of light and medium oil are depleted, oil refineries are increasingly having to process heavy oil and bitumen, and use more complex and expensive methods to produce the products required.

Because heavier crude oils have too much carbon and not enough hydrogen, these processes generally involve removing carbon from or adding hydrogen to the molecules, and using fluid catalytic cracking to convert the longer, more complex molecules in the oil to the shorter, simpler ones in the fuels.

The crude oil mixture is composed of the following groups:

1. Hydrocarbon compounds (compounds made of carbon and hydrogen).
2. Non-hydrocarbon compounds.
3. Metallic compounds.

Crude oils contain many short, medium, and long-chain normal and branched paraffins. A naphtha fraction (obtained as a light liquid stream from crude fractionation) with a narrow boiling range. Crude oils contain many short, medium, and long-chain normal and branched paraffins. A naphtha fraction (obtained as a light liquid stream from crude fractionation) with a narrow boiling range may contain a limited but still large number of isomers.

Petroleum is a mixture of a very large number of different hydrocarbons; the most commonly found molecules are alkanes (linear or branched), cycloalkanes, aromatic hydrocarbons, or more complicated chemicals like asphaltenes. Each petroleum variety has a unique mix of molecules, which define its physical and chemical properties, like color and viscosity.

ALKANES / PARAFFINS

The alkanes (paraffins), are saturated hydrocarbons with straight (normal) or branched (iso) chains which contain only carbon and hydrogen and have the general formula C_nH_{2n+2} . They generally have from 5 to 40 carbon atoms per molecule, although trace amounts of shorter or longer molecules may be present in the mixture. - the alkanes from pentane (C_5H_{12}) to octane (C_8H_{18}) are refined into petrol, the ones from nonane (C_9H_{20}) to hexadecane ($C_{16}H_{34}$) into diesel fuel, kerosene and jet fuel. - alkanes with more than 16 carbon atoms can be refined into fuel oil and lubricating oil. - at the heavier end of the range, paraffin wax is an alkane with approximately 25 carbon atoms, while asphalt has 35 and up, although these are usually cracked by modern refineries into more valuable products. - the shortest molecules, those with four or fewer carbon atoms, are in a gaseous state at room temperature. They are the petroleum gases.

Depending on demand and the cost of recovery, these gases are either flared off, sold as liquified petroleum gas under pressure, or used to power the refinery's

own burners. During the winter, butane (C_4H_{10}), is blended into the petrol pool at high rates, because its high vapor pressure assists with cold starts. Petroleum Composition – Chemistry.

CYCLOPARAFFINS (NAPHTHENES)

Saturated cyclic hydrocarbons, normally known as naphthenes, are also part of the hydrocarbon constituents of crude oils. Their ratio, however, depends on the crude type. The lower members of naphthenes are cyclopentane, cyclohexane, and their mono-substituted compounds. They are normally present in the light and the heavy naphtha fractions. Cyclohexanes, substituted cyclopentanes, and substituted cyclohexanes are important precursors for aromatic hydrocarbons.

The cycloalkanes (naphthenes), are saturated hydrocarbons which have one or more carbon rings to which hydrogen atoms are attached according to the formula C_nH_{2n} . Cycloalkanes have similar properties to alkanes but have higher boiling points.

AROMATICS

The aromatic hydrocarbons are unsaturated hydrocarbons which have one or more planar six-carbon rings called benzene rings, to which hydrogen atoms are attached with the formula C_nH_n .

Lower members of aromatic compounds are present in small amounts in crude oils and light petroleum fractions. The simplest mononuclear aromatic compound is benzene (C_6H_6). Toluene (C_7H_8) and xylene (C_8H_{10}) are also mononuclear aromatic compounds found in variable amounts in crude oils. Benzene, toluene, and xylenes (BTX) are important petrochemical intermediates as well as valuable gasoline components. Separating BTX aromatics from crude oil distillates is not feasible because they are present in low concentrations. Enriching a naphtha fraction with these aromatics is possible through a catalytic

reforming process. Binuclear aromatic hydrocarbons are found in heavier fractions than naphtha. Trinuclear and polynuclear aromatic hydrocarbons, in combination with heterocyclic compounds, are major constituents of heavy crudes and crude residues. Asphaltenes are a complex mixture of aromatic and heterocyclic compounds.

Hydrocarbon (HC)	Formula	Phase	Examples
Paraffins	$C_n H_{2n+2}$ ☐ (n is a whole number, usually from(1 to 20). ☐ straight- or branched-chain molecules.	can be gasses or liquids at room temperature depending upon the molecule.	methane, ethane, propane, butane, isobutane, pentane, hexane.
Aromatics	☐ general formula: $C_6H_5 - Y$ (Y is a longer, straight molecule that connects to the benzene ring). ☐ ringed structures with one or more rings ☐ rings contain six carbon atoms, with alternating double and single bonds between the carbons.	typically liquids.	benzene, naphthalene.
Napthenes or Cycloalkanes	☐ general formula: $C_n H_{2n}$ (n is a whole number usually from 1 to 20). ☐ ringed structures with one or more rings. ☐ rings contain only single bonds between the carbon atoms.	typically liquids at room temperature.	cyclohexane, methyl cyclopentane.
Alkenes	☐ general formula: $C_n H_{2n}$ (n is a whole number, usually from (1 to 20). ☐ linear or branched chain molecules containing one carbon carbon double-bond.	can be liquid or gas.	ethylene, butene, isobutene.

Dienes & Alkynes	\general formula: $C_n H_{2n-2}$ (n is a whole number, usually from (1 to 20). linear or branched chain molecules containing two carbon carbon double-bonds.	can be liquid or gas.	acetylene, butadienes.
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OTHERS

❖ **Sulfur** – (hydrogen sulfide, sulfides, disulfides, elemental sulfur).

Hydrogen sulfide is a primary contributor to corrosion in refinery processing. Other corrosive substances are *elemental sulfur* and *mercaptans*. Moreover, the corrosive sulfur compounds have an obnoxious odor.

❖ **Nitrogen** - less than 1% (*basic compounds with amine groups*)

Nitrogen oxides can form in process furnaces. The decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides that can cause corrosion.

❖ **Oxygen** - less than 1%

(found in organic compounds such as carbon dioxide, phenols, ketones, carboxylic acids) occur in crude oils in varying amounts.

❖ **Metals** - less than 1%

(nickel, iron, vanadium, copper, arsenic) often found in crude oils in small quantities and are removed during the refining process

❖ **Salts** - less than 1%

Crude oils often contain inorganic salts such as sodium chloride, magnesium chloride, and calcium chloride in suspension or dissolved in entrained water (brine).

❖ **Carbon Dioxide**

Carbon dioxide may result from the decomposition of bicarbonates present in or added to crude, or from steam used in the distillation process.

❖ **Naphthenic Acids**

Some crude oils contain naphthenic (organic) acids, which may become corrosive at temperatures above 450° F when the acid value of the crude is above a certain level.

PHYSICAL & THERMODYNAMIC PROPERTIES OF PETROLEUM

On the basis of the production and refining processes, it may be said that the petroleum industry is involved with many types of equipment for production, transportation, and storage of intermediate or final petroleum products.

Some of the most important units are listed below:

- 1) Gravity decanter (to separate oil and water).
- 2) Separators to separate oil and gas.
- 3) Pumps, compressors, pipes, and valves.
- 4) Storage tanks.
- 5) Distillation, absorption, and stripping columns.
- 6) Boilers, evaporators, condensers, and heat exchangers.
- 7) Flashers (to separate light gases from a liquid).
- 8) Mixers.
- 9) Reactors (fixed and fluidized beds).
- 10) Online analyzers (to monitor the composition).
- 11) Flow and liquid level measurement devices.
- 12) Control units and control valves.

Optimum design and operation of such units as well as manufacture of products to meet market demands require a complete knowledge of properties and characteristics of hydrocarbons, petroleum fractions/products, crude oils.

Some of the most important characteristics and properties are listed

below:

❖ *Boiling-Point*

The boiling point of a pure compound at a given pressure is the temperature at which vapor and liquid exist together at equilibrium.

❖ *Flash Point*

Flash point, **T_f**, for a hydrocarbon or a fuel is the minimum temperature at which vapor pressure of the hydrocarbon is sufficient to produce the vapor needed for spontaneous ignition of the hydrocarbon with the air with the presence of an external source, i.e., spark or flame. **From this definition, it is clear that hydrocarbons with higher vapor pressures (lighter compounds) have lower flash points. Generally flash point increases with an increase in boiling point.** Flash point is an important parameter for safety considerations, especially during storage and transportation of volatile petroleum products (i.e., LPG, light naphtha, gasoline) in a high-temperature environment.

Flash point should not be mistaken with fire point, which is defined as the minimum temperature at which the hydrocarbon will continue to burn for at least 5 s after being ignited by a flame.

❖ *Autoignition Temperature*

This is the minimum temperature at which hydrocarbon vapor when mixed with air can spontaneously ignite without the presence of any external source. Values of autoignition temperature are generally higher than flash point. Values of autoignition temperature for gasoline is about **350°C (660°F)** and for alcohol is about **500°C (930 °F)**. With an increase in pressure the autoignition temperature decreases.

❖ *Freezing and Melting Points*

Petroleum and most petroleum products are in the form of a liquid or gas at ambient temperatures. However, for oils containing heavy compounds such as waxes or asphaltic oils, problems may arise from solidification, which cause the oil to lose its fluidity characteristics. For this reason knowledge of the freezing point, T_f , is important and it is one of the major specifications of jet fuels and kerosenes. For a pure compound the freezing point is the temperature at which liquid solidifies at 1 atm pressure. Similarly the melting point, T_M , is the temperature that a solid substance liquefies at 1 atm.

❖ *Pour Point*

Temperature at which the oil becomes “plastic” and will not flow. The pour point of the crude oil, in °F or °C, is a rough indicator of the relative paraffinic and aromaticity of the crude. **The lower the pour point, the lower the paraffin content and the greater the content of aromatics.**

It is measured by ASTM D-97 – temperature at which oil ceases to flow. Diesel may contain waxes, smaller than candle wax, which could solidify in cold weather.

❖ *Aniline Point*

The aniline point for a hydrocarbon or a petroleum fraction is defined as the minimum temperature at which equal volumes of liquid hydrocarbon and aniline are miscible. Aniline is an aromatic compound with a structure of a benzene molecule where one atom of hydrogen is replaced by the -NH₂ group (C₆H₅-NH₂). The aniline point is important in characterization of petroleum fractions and analysis of molecular type. The aniline point is also used as a characterization parameter for the ignition quality of diesel fuels. It is measured by the ASTM D 611 test method. **Within a hydrocarbon group, aniline point increases with molecular weight or carbon number, but for the same carbon number it increases from aromatics to paraffinic hydrocarbons. Aromatics have very low aniline points in comparison with paraffins, since aniline itself is an aromatic compound and it has better miscibility with aromatic hydrocarbons. Generally, oils with higher aniline points have lower aromatic content.**

❖ *Flammability Range*

To have a combustion, three elements are required: fuel (hydrocarbon vapor), oxygen (i.e., air), and a spark to initiate the combustion. One important parameter to have a good combustion is the ratio of air to hydrocarbon fuel. The

combustion does not occur if there is too much air (little fuel) or too little air (too much fuel). This suggests that combustion occurs when hydrocarbon concentration in the air is within a certain range. **This range is called flammability range and is usually expressed in terms of lower and upper volume percent in the mixture of hydrocarbon vapor and air. If the calculated vol% of hydrocarbon in the air is within the flammability range then the mixture is flammable by a spark or flame.**

❖ *Vapor Pressure*

Vapor Pressure in a closed container, the vapor pressure of a pure compound is the force exerted per unit area of walls by the vaporized portion of the liquid. **Vapor pressure, p^{vap}** , can also be defined as a pressure at which vapor and liquid phases of a pure substance are in equilibrium with each other. The vapor pressure is also called **saturation pressure, p^{sat}** , and the corresponding temperature is called **saturation temperature**. In an open air under atmospheric pressure, a liquid at any temperature below its boiling point has its own vapor pressure that is less than 1atm. When vapor pressure reaches 1atm, the saturation temperature becomes the normal boiling point.

It is measured by ASTM D-323. **Also know as Reid vapor pressure (RVP).**

True vapor pressure is usually 5-9% > RVP.

❖ *Carbon Residue, wt%*

Carbon residue is determined by distillation to a coke residue in the absence of air. The carbon residue is roughly related to the asphalt content

of the crude and to the quantity of the lubricating oil fraction that can be recovered. In most cases the lower the carbon residue, the more valuable the crude. This is expressed in terms of the weight percent carbon residue by either the *Ramsbottom (RCR) or Conradson (CCR)* ASTM test procedures (D-524 and D-189). The solid residue (%wt) remaining after heating to coking temperatures (700-800°C).

❖ *Salt Content, lb/1000 bbl*

If the salt content of the crude, when expressed as NaCl, is greater than 10 lb/1000 bbl, it is generally necessary to desalt the crude before processing. If the salt is not removed, severe corrosion problems may be encountered. If residua are processed catalytically, desalting is desirable at even lower salt contents of the crude. Although it is not possible to have an accurate conversion unit between lb/1000 bbl and ppm by weight because of the different densities of crude oils, 1lb/1000 bbl is approximately 3 ppm.

Measured by ASTM – 3230 (lb NaCl/1000 bbl).

Desalting is necessary because NaCl content > 10 lbs/1000 bbl leads to corrosion.

❖ *Sulfur Content*

Crude oil naturally contains sulfur compounds. **Crudes are classed as sweet or sour depending on their sulfur content.** If a crude has less than 0.5% sulfur in it, it is considered to be "sweet". If has greater than 2.5% sulfur,

it is "sour". A crude with a sulfur content between these two endpoints is called "intermediate".

Measured by ASTM D – 129, 1552, 2622.

Sour crudes > 0.5 wt% and sweet crudes < 0.5 wt%. Today it is difficult to find crudes below 1% sulfur.

❖ *Nitrogen Content, wt%*

A high nitrogen content is undesirable in crude oils because organic nitrogen compounds cause severe poisoning of catalysts used in processing and cause corrosion problems such as hydrogen blistering. Crudes containing nitrogen in amounts above **0.25%** by weight require special processing to remove the nitrogen.

❖ *Metals Content, ppm*

The metals content of crude oils can vary from a few parts per million to more than 1000 ppm and, in spite of their relatively low concentrations, are of considerable importance. Small quantities of some of these metals (nickel, vanadium, and copper) can severely affect the activities of catalysts and result in a lower value product distribution.

❖ *Sediment and Water*

Measured by ASTM D – 96 These inorganic particles can lead to operational problems.

❖ *Acidity*

Measured by ASTM – 664

❖ *TBP Distillation Data*

Butanes and lighter	55-175 °F
Light Gasoline	175-300 °F
Light naphtha	300-400 °F
Heavy naphtha	400-500 °F
Kerosene	500-650 °F
Atmosphere Gas Oil	650-800 °F
Light Vacuum Gas Oil	800-1000 °F
Heavy Vacuum Gas Oil	1000 °F
Vacuum Residue	> 1000 °F

❖ *Solubility*

Solubility of oil in water is generally very low ~ 5 ppm or one grain of sugar, out of a teaspoon of sugar, in a cup of water.

❖ *API*

Crude oils are also defined in terms of API (**American Petroleum Institute**) gravity. **The higher the API gravity, the lighter the crude.** For example, **light crude oils** have high API gravities, generally **exceed 38 °API** and low specific gravities. Crude oils with low carbon, high hydrogen, and high API gravity are usually rich in paraffins and tend to yield greater proportions of gasoline and light petroleum products.

Heavy crude oils are commonly with **API gravity of 22 degrees or lower.** Crude oils with high carbon, low hydrogen, and low API gravities are usually

rich in aromatics. **Intermediate crude oils** fall in range of **22 degree to 38 °API gravity**.

$$\text{°API} = (141.5/\text{Spgr } 15^\circ\text{F}) - 131.5$$

Crude Oils °API = 10 – 50

Higher °API, more paraffinic crude, higher yields of gasoline.

Lower °API, more aromatic crude, lower yields of gasoline.

❖ *Octane Number (ON)*

Octane number is a parameter defined to characterize antiknock characteristic of a fuel (gasoline) for spark ignition engines. Octane number is a measure of fuel's ability to resist auto-ignition during compression and prior to ignition.

Higher octane number fuels have better engine performance.

There are two methods of measuring octane number of a fuel in the laboratory:

- 1- **Motor Octane Number (MON)** which is indicative of high-speed performance (900 rpm) and is measured under heavy road conditions (ASTM D 357).
- 2- **Research Octane Number (RON)** which is indicative of normal road performance under low engine speed (600 rpm) city driving conditions (ASTM D 908).
- 3- **posted octane number (PON)**, which is the arithmetic average of the MON and RON:

$$[\text{PON} = (\text{MON} + \text{RON})/2].$$

Generally **isoparaffins** have higher octane number than do normal **paraffins**. **Naphthenes** have relatively higher octane number than **paraffins** and **aromatics** have very high octane numbers.

The octane number of a fuel can be improved by adding tetraethyl-lead (**TEL**) or methyl-tertiary-butyl-ether (**MTBE**). Use of lead (**Pb**) to improve octane number of fuels is limited in many industrial countries.

❖ *The Cetane Number*

measures the ease for self-ignition of a diesel fuel sample and is essentially an opposite of the octane number. It represents the percentage of pure cetane (n-hexadecane) in a blend of cetane and alpha methyl-naphthalene that matches the ignition quality of a diesel fuel sample. This quality is important for middle distillate fuels.

❖ *Refractive Index*

Refractive index or refractivity for a substance is defined as the ratio of velocity of light in a vacuum to the velocity of light in the substance (fluid) and is a dimensionless quantity shown by:

$$R_i = n \cdot (d/2)$$

Where:

R_i is the Refractive index or refractivity for a substance, **(n)** and **(d)** are refractive index and density of **liquid hydrocarbon at the reference state of 20 °C and 1atm in which density must be in g/cm³**. **R_i** is high for aromatics

and low for naphthenic compounds, while paraffins have intermediate/~ values.

❖ *Characterization Factors*

There are several correlations between yield and the aromaticity and paraffinicity of crude oils, but the two most widely used are **the UOP or Watson “characterization factor” (KW) and the U.S. Bureau of Mines “correlation index” (CI).**

This method is for calculating the UOP Characterization Factor of petroleum oils from API gravity and distillation data. The UOP **Characterization Factor, commonly called KUOP, is indicative of the general origin and nature of a petroleum stock.**

Watson characterization factor:

$$Kw = \frac{(Tb)^{\frac{1}{3}}}{SG_{15\text{ }^{\circ}C} (60\text{ }^{\circ}F)}$$

SG 15 °C: Specific Gravity at 15 °C (60 °F)

Tb: mean average boiling point (R) (MeABP)

The Watson characterization factor ranges from less than 10 for highly aromatic crudes to almost 15 for highly paraffinic crudes. Crude oils show a narrower range of K_w and vary from **10.5 for a highly naphthenic crudes to 12.9 for a paraffinic base crudes.**

UOP characterization factor:

Kuop has the same expression as **Kw**, but T_b transfer to **Volume average boiling point (VABP)** Additional notes related to the application of the above characterization factors:

- Aromatics would have lower Kuop.
- The use of boiling point indicates a relationship to the interactive forces between the molecules.
- The use of specific gravity relates to how tightly the molecules are packed (i.e. density).

❖ **The Correlation Index (C.I)**

It is useful in evaluating individual fractions from crude oils. The C.I scale is based upon straight-chain paraffins having a CI value of 0 and benzene having a C.I value of 100. The C.I values are not quantitative, but the lower the C.I value, the greater the concentrations of paraffin hydrocarbons in the fraction; and the higher the C.I value, the greater the concentrations of naphthenes and aromatics.

$$C.I = (48640/T_B) + 4737 S - 456.8$$

T_B : is the average molal boiling point (K)

S: is the specific gravity at 60 °F

C.I for Paraffin = 0

C.I for Benzene =100

C.I =0-15 Paraffin

C.I =15-50 either Naphtenes or mix (Paraffin + Naphtenes)

C.I = above 50 Aromatic.

❖ *Viscosity Index (V.I):*

The viscosity is a resistance to flow, usually measured @ 100 oF in centistokes (kinematic viscosity).

A series of numbers ranging from **0-100** which indicate the rate of change of viscosity with temperature.

For Paraffinic base crude oil (C.O), V.I =100

For Naphthenic base crude oil (C.O), V.I = 40

For Some Naphthenic base crude oil (C.O), V.I = 0

LECTURE (3)

PETROLEUM PRODUCTS

Crude oil is a naturally occurring liquid found in formations in the Earth consisting of a complex mixture of hydrocarbons (mostly alkanes) of various lengths. The approximate length range is C₅H₁₂ to C₁₈H₃₈. The first crude oil classification is by the types of hydrocarbons (paraffins, naphthenes, and aromatics).

This rating is important to the refinery since the value of the crude oil decreases from classification 1 to 6. Crude Classifications (in order of decreasing value) is shown in the following:

1- PARAFFINIC CRUDE:

- paraffins + naphthenes > 50%
- paraffins > naphthenes
- paraffins > 40%

2- NAPHTHENIC CRUDES

paraffins + naphthenes > 50%

naphthenes > paraffins

naphthenes > 40%

3- PARAFFINIC – NAPHTHENIC CRUDE

- aromatics < 50%
- paraffins < 40%
- naphthenes < 40%

4- AROMATIC – NAPHTHENIC CRUDE

aromatics > 50%

5- AROMATIC - INTERMEDIATE CRUDE

- aromatics > 50%
- paraffins >10%

6- AROMATIC – ASPHALTIC CRUDE

- naphthenes > 25%
- paraffins < 10%

The [petroleum industry](#) generally classifies crude oil by:

- 1) the geographic location it is produced in (e.g. [West Texas](#), [Brent](#), or [Oman](#)),
- 2) its [API gravity](#) (an oil industry measure of density).
- 3) by its sulfur content.

The geographic location is important because it affects transportation costs to the refinery. **Light** crude oil is more desirable than **heavy** oil since it produces a higher yield of gasoline, while **sweet** oil commands a higher price than **sour** oil because it has fewer environmental problems and requires less refining to meet sulfur standards imposed on fuels in consuming countries. Each crude oil has unique molecular characteristics which are understood by the use of [crude oil assay analysis](#) in petroleum laboratories.

[Barrels](#) from an area in which the crude oil's molecular characteristics have been determined and the oil has been classified are used as pricing [references](#) throughout the world.

Some of the common reference crudes are:

- 1- **West Texas Intermediate (WTI)**, a very high-quality, sweet, light oil delivered at **Cushing, Oklahoma** for North American oil.
- 2- **Brent Blend**, comprising 15 oils from fields in the **Brent** and **Ninian** systems in the **East Shetland Basin** of the **North Sea**
- 3- **Dubai-Oman**, used as benchmark for Middle East sour crude oil flowing to the **Asia-Pacific** region.
- 4- **Tapis** (from **Malaysia**, used as a reference for light Far East oil)
- 5- **Minas** (from **Indonesia**, used as a reference for heavy Far East oil)
- 6- The **OPEC Reference Basket**, a weighted average of oil blends from various **OPEC** (The Organization of the Petroleum Exporting Countries) countries.

The problem with crude oil is that it contains hundreds of different types of hydrocarbons all mixed together. You have to separate the different types of hydrocarbons to have anything useful. Fortunately there is an easy way to separate things, and this is what *oil refining* is all about.

Different hydrocarbon chain lengths all have progressively higher boiling points, so they can all be separated by distillation. This is what happens in an oil refinery - in one part of the process, crude oil is heated and the different chains are pulled out by their vaporization temperatures. Each different chain length has a different property that makes it useful in a different way. Table (1) shows the main products from crude oil.

Table (1): The main products from crude oil.

Product	Formula	Phase	B.P	Uses
Petroleum gas	<ul style="list-style-type: none"> □ small alkanes (1 to 4 carbon atoms). □ commonly known by the names methane, ethane, propane, butane. 	often liquified under pressure to create LPG (liquefied petroleum gas).	boiling range < 90 degrees Fahrenheit / <27 degrees Celsius.	for heating, cooking, making plastics.
Gasoline	mix. of alkanes and cycloalkanes (5 to 7 carbon atoms).	liquid	boiling range = 90-220 degrees Fahrenheit / 27-93 degrees Celsius.	motor fuel
Naphtha or Ligroin	mix. of 6 to 10 carbon atom alkanes	---	boiling range = 220-315 degrees Fahrenheit / 93-177degrees Celsius.	intermediate that will be further processed to make gasoline.
Kerosene	mix. of alkanes (10 to 15 carbons) and aromatics.	liquid	boiling range= 315-450 degrees Fahrenheit / 177-293degrees Celsius.	fuel for jet engines and tractors; starting material for making other products.
Gas oil or Diesel distillate	alkanes containing 13-18 carbon atoms.	liquid	boiling range = 450-650 degrees Fahrenheit / 293-315degrees Celsius.	used for diesel fuel and heating oil; starting material for making other products.
Lubricating oil	long chain (20 to 50 carbon atoms) alkanes, cycloalkanes, aromatics.	liquid	boiling range = 572 to 700 degrees Fahrenheit / 300 to 370 degrees Celsius.	used for motor oil, grease, other lubricants.
Heavy gas or Fuel oil	long chain (16 to 40 carbon atoms) alkanes, cycloalkanes, aromatics.	liquid	boiling range = 650-800 degrees Fahrenheit / 315-565 degrees Celsius.	used for industrial fuel; starting material for making other products

Residuals	multiple-ringed compounds with 40 or more carbon atoms.	solid	boiling range = greater than 800 degrees Fahrenheit / 565 degrees Celsius.	coke, asphalt, tar, waxes; starting material for making other products
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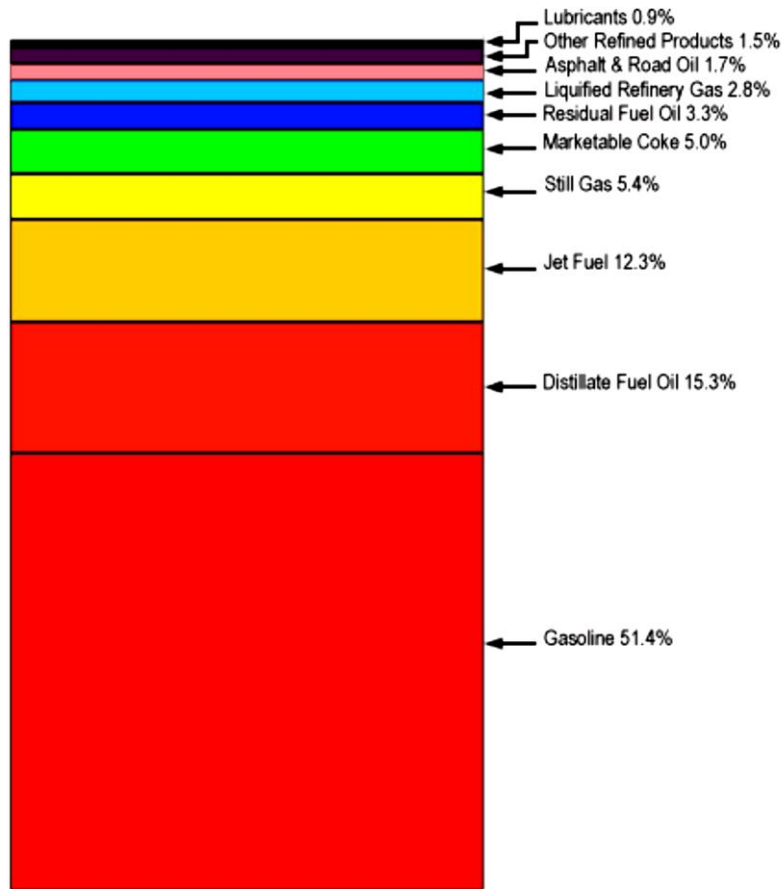


Figure (1): Petroleum Products Yielded from One Barrel of Crude Oil in California.

PETROLEUM REFINING PROCESSES

1. INTRODUCTION

The typical fuels refinery has as a goal the conversion of as much of the barrel of crude oil into transportation fuels as is economically practical. Although refineries produce many profitable products, the high-volume profitable products are the transportation fuels gasoline, diesel and turbine (jet) fuels, and the light heating oils, No. 1 and No. 2. These transportation fuels have boiling points between 0 and 345°C (30 to 650°F).

Light heating oils are not properly transportation fuels but the hydrocarbon components are interchangeable with those of diesel and jet fuels, only the additives are different. Although products such as lubricating oils, refrigeration and transformer oils, and petrochemical feedstocks are profitable, they amount to less than 5 percent of the total crude oil charged to U.S. refineries.

Crude oils with low API gravities (high specific gravities) and high sulfur contents require additional hydrotreating equipment. The greater densities will mean more of the crude oil will boil above 566°C (1050°F).

Historically this high-boiling material or residua has been used as heavy fuel oil but the demand for these heavy fuel oils has been decreasing because of stricter environmental requirements.

The environmental impacts of fuel preparation and consumption will require that a significant shift take place in product distribution (i.e., less conventional gasoline and more alternative fuels). This will have a major effect on refinery processing operations and will place a load on refinery construction in addition to the need to provide increased capacity for high sulfur and heavier crude oils.

Figure (1) shows the processing sequence in a modern refinery of high complexity, indicating major process flows between operations.

- 1- The crude oil** is heated in a furnace and charged to an **Atmospheric Distillation Tower**, where it is separated into butanes and lighter wet gas, unstabilized light naphtha, heavy naphtha, kerosine, atmospheric gas oil, and topped (reduced) crude (**Atmospheric Reduced Crude**) (**ARC**).
- 2-** The bottom crude is sent to the **Vacuum Distillation Tower** and separated into vacuum gas oil stream and **Vacuum Reduced Crude** bottoms (residua, resid, or **VRC**).
- 3- The reduced crude bottoms (VRC)** from the vacuum tower is then thermally cracked in a **Delayed Coker** to produce wet gas, coker gasoline, coker gas oil, and coke. Without a coker, this heavy resid would be sold for heavy fuel oil or (if the crude oil is suitable) asphalt. Historically, these heavy bottoms have sold for about 70 percent of the price of crude oil.
- 4-** The atmospheric and vacuum crude unit gas oils and coker gas oil are used as feedstocks for the **Catalytic Cracking or Hydrocracking** units.

These units crack the **heavy molecules** into lower molecular weight compounds boiling in the gasoline and distillate fuel ranges.

- 5- The products from the hydrocracker are saturated. The unsaturated catalytic cracker products are saturated and improved in quality by **Hydrotreating or Reforming**.
- 6- **The light naphtha streams** from the crude tower, coker and cracking units are sent to an **Isomerization** unit to convert straight-chain paraffins into isomers that have higher octane numbers.
- 7- **The heavy naphtha streams** from the crude tower, coker, and cracking units are fed to the **Catalytic Reformer** to improve their octane numbers.
- 8- The products from the catalytic reformer are **blended** into regular and premium gasolines for sale.
- 9- **The wet gas streams** from the crude unit, coker, and cracking units are separated in **the vapor recovery section (gas plant)** into fuel gas, liquefied petroleum gas (LPG), unsaturated hydrocarbons (propylene, butylenes, and pentenes), normal butane, and isobutane.
- 10- **The fuel gas** is burned as a fuel in refinery furnaces and the normal butane is **blended** into gasoline or LPG.
- 11- The unsaturated hydrocarbons and isobutane are sent to the **Alkylation** unit for processing. **The alkylation unit** uses either sulfuric or hydrofluoric acid as catalyst to react olefins with isobutane to form isoparaffins boiling in the gasoline range. The product is called **alkylate**,

and is a high-octane product **blended** into premium motor gasoline and aviation gasoline.

12- The middle distillates from the crude unit, coker, and cracking units are **blended** into diesel and jet fuels and furnace oils. In some refineries, the heavy vacuum gas oil and reduced crude from paraffinic or naphthenic base crude oils are processed into lubricating oils.

13- After removing the asphaltenes in a **Propane Deasphalting Unit**, **the reduced crude bottoms** is processed in a blocked operation with the vacuum gas oils to produce lubeoil base stocks.

14- The vacuum gas oils and deasphalted stocks are first **Solvent-Extracted** to remove the aromatic compounds and then **Dewaxed** to improve the pour point. They are then treated with special clays or high-severity **Hydrotreating** to improve their color and stability before being blended into lubricating oils.

Each refinery has its own unique processing scheme which is determined by the process equipment available, crude oil characteristics, operating costs, and product demand. The optimum flow pattern for any refinery is dictated by economic considerations and no two refineries are identical in their operations.

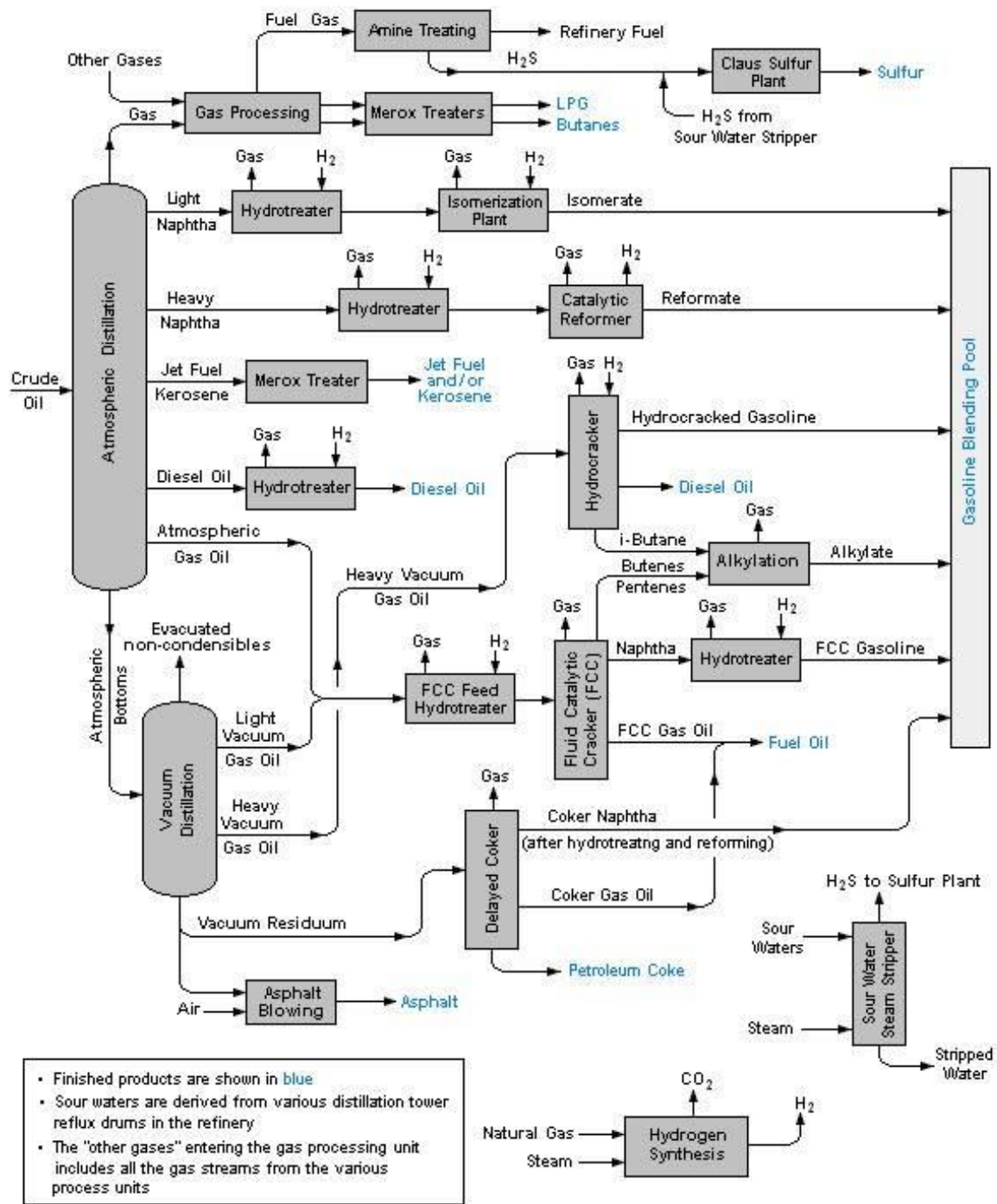


Figure (1): Over all Refinery Flow diagram

TREATING PROCESSES

The essential purpose of the **primary processes** is to produce the required amounts of the various products from the available crude. The products obtained are, as a general rule, unsuitable as such for immediate use, for the following reasons:

- 1) **Inadequate performance,**
- 2) **Instability in storage, and**
- 3) **Objectionable odor and appearance and contamination with water or particulate matter.**

Secondary Refining Processes (**Finishing or Treating Processes**), are required to give the products acceptable with respect to the above criteria.

MAIN FINISHING PROCESSES:

- 1) **The Removal of the Objectionable Gases (Acid Gas Removal).**
- 2) **The Removal of the Objectionable Odors (Sweetening Process).**
- 3) **The Removal of Water and Particulate Matter.**
- 4) **The Improvement in Storage Stability & Performance Characteristics.**

1) **The Removal of the Objectionable (unpleasable) Gases:**

Hydrogen Sulphide:

Has to be removed from products because:

- a) toxic,
- b) foul smelling,
- c) corrosive,

d) traces may seriously contaminate regenerative treating solvents used for final sweetening of the products.

PROCESSES:

- 1. Scrubbing with Caustic Soda.**
- 2. Girbotol process.**

1. Scrubbing with Caustic Soda:

It is still the most widely used process for the removal of H₂S, mainly because it simultaneously removes other constituents such as CO₂, carbonyl sulphide, lower aliphatic mercaptans, phenols fatty acids and naphthenic acids.

The disadvantage of this processes is that there is no known cheap method of regenerating the spent soda, and if H₂S is present in gross (big) amounts, as is frequently in crude gases, especially the C₂-C₃ fractions, a regenerative method of extraction such as the girbotol method is more generally used.

This method is more economical than caustic washing but caustic washing may still be required as a final cleaning-up operation for the removal of the last traces of H₂S.

The combination of the two processes not only provides a very low H₂S content but also safe guards against high sulfur contents in the treated products. In the caustic washing of gases rather weak solutions of 2-10%wt NaOH have to be used to prevent the deposition of sodium sulphide crystals. The reaction proceeds almost to the complete conversion of NaOH to NaHS.



Traces of H_2S often appear in fractions much heavier than $C_2 - C_3$ fraction because of a slight breakdown of sulfur compounds owing to pyrolysis during re-distillation or a similar operation. Caustic soda may be employed for its removal.

2. Girbotol process:

Hydrogen sulphide and carbon dioxide readily combine with aqueous solutions of certain alkanol amines at temperatures usually close to ambient, and may be driven off from the fat solutions by heating to about $100\text{ }^\circ\text{C}$.

The reaction with **hydrogen sulphide** is essentially:



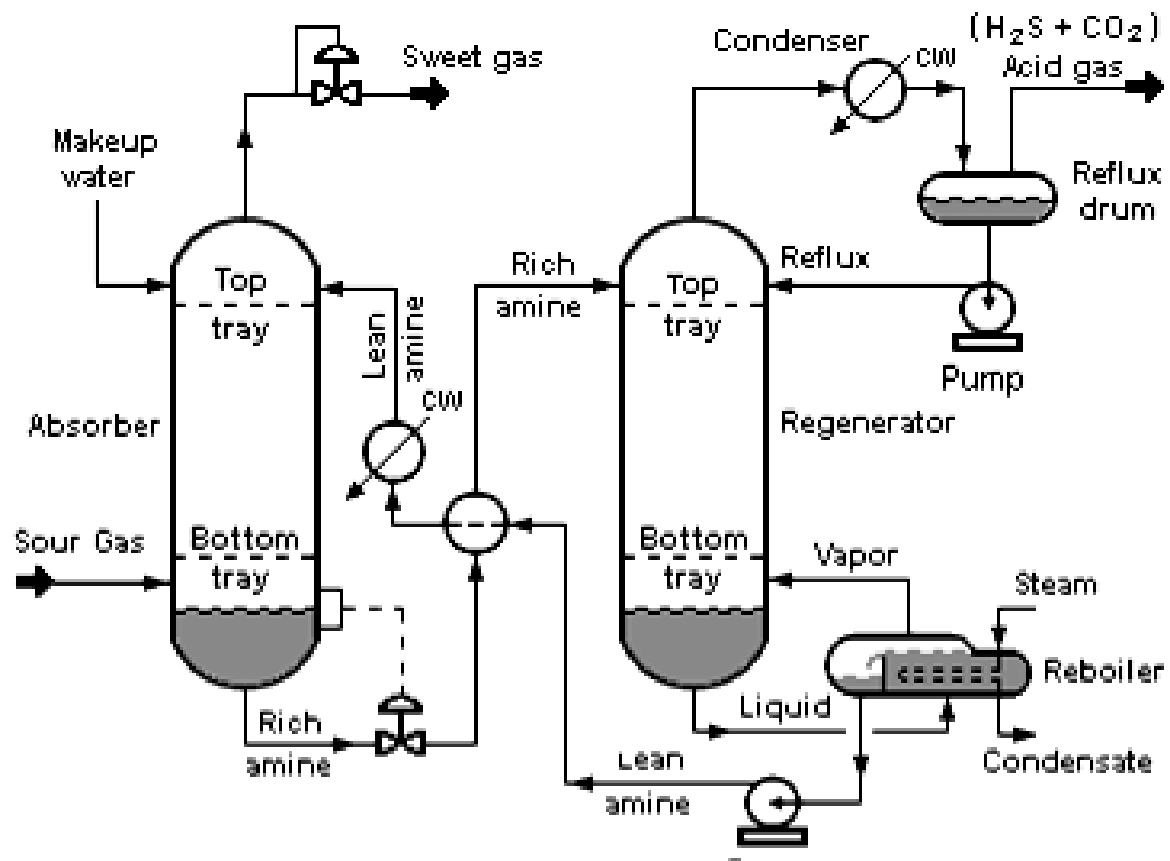
The conventional equipment, comprising a bubble- cup tower **together with a bubble cup tower for regeneration**. The treating temperature is **5 to 10 $^\circ\text{C}$ above the dew point of the gas** to ensure that no hydrocarbons liquid condenses out of the plant.

The girbotol process (fig.1) is the most widely used method for the regenerative removal of H_2S from both gases and liquids. Its use is not only in refineries but also for oilfield treatment of natural gases and LPG. **The choice of the proper amine and solution depends on the composition of the gas to be treated and the final purity desired.**

Carbon dioxide:

Carbon dioxide is frequently found in natural gas, and is also present in the products of catalytic crackers since regenerated catalyst always carries with it a small quantity of carbon dioxide. Its removal is rarely a direct aim but the major part of it will be removed by a caustic wash applied for the removal of H_2S .

When CO_2 removal is a direct aim, one of the regeneration processes such as Girbotol process would normally be used.



Figuer (1): Girbotol process

TREATIN PROCESSES (2)

2) The Removal of the Objectionable Odors (Sweetening Process)

The object of sweetening processes is to ensure that the finished products do not have objectionable odors. The objectionable odors are normally **attributed to traces of mercaptans**, and it is necessary either to remove them by **extractive processes** or by **hydrodesulphurization**, or to **convert them into disulphides**.

PROCESSES:

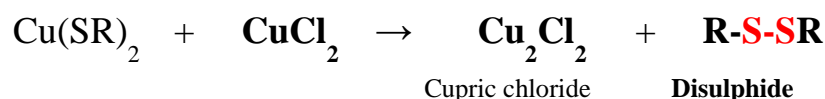
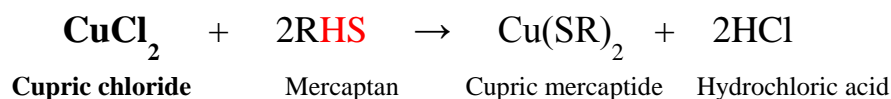
- 1) Copper Chloride Process.
- 2) Merox Process

1. Copper Chloride Process :

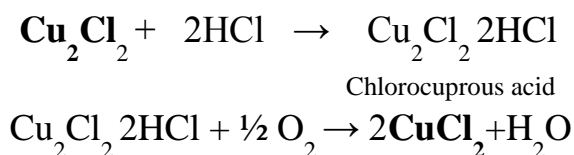
The copper chloride process is used to sweeten gasolines and kerosenes by the direct oxidation of mercaptans to disulphides, using cupric chloride as the oxidizing agent.

The basic reactions of the process may be expressed as follows :

Sweetening



Regeneration



- a) **The sour charge is caustic washed** to remove traces of hydrogen sulphide which would otherwise deactivate the cupric chloride.
- b) It then pass: **firstly through a sand coagulator** to remove any caustic and / or water and **secondly** remove the free water, which would adversely affect the water balance in the reactor.
- c) **After passing through a pre-heater** to raise the temperature sufficiently to dissolve the water formed during the process, **air or oxygen is injected into the line**, and the dried and oxygenated feed flows upwards through the reactor which contains a bed of fullers earth impregnated with cupric chloride.
- d) **The sweetened product is then water washed** to remove traces of acidity, clarified from water in an **up-flow sand coagulator** and passed to storage.

2. Merox Process :

The Merox process, Developed by UOP (Universal Oil Products), **is combination of mercaptan extraction and sweetening**. This **combined process** is applicable to all gasoline and lighter boiling range fractions; the **sweetening process** is applicable to many jet fuel and kerosenes.

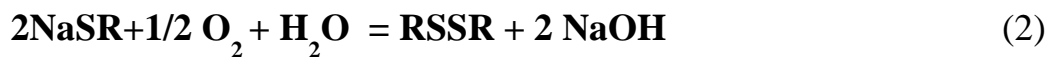
a) Merox Extraction:

- 1- **The mercaptans** are extracted by an aqueous solution of caustic soda according to the reaction :



Since the reaction is **reversible** it is impossible to get complete removal of mercaptans by extraction without the use of an excessive amount of caustic soda solution. The forward reaction is favored by low temperature, low molecular weight of mercaptan and high caustic concentration. It is also promoted by the use of compounds that increase the solubility of the mercaptan in the aqueous phase, of these methanol, isobutyric acid and cresols.

2- **The caustic is generated**, after separation from hydrocarbons **by blowing with air in the presence of a catalyst at ambient temperature** the reaction proceeding according to the reaction:



The disulphides so formed are insoluble in caustic soda and are removed in a **gravity separator**, the caustic is being re-circulated for further use.

The catalyst which consists of an iron group metal chelate (**a coordination compound in which a metal atom or ion is bound to a ligand at two or more points on the ligand, so as to form a heterocyclic ring containing a metal atom**), may be in solution in the caustic, in which case the caustic and air are brought into contact in a reactor such as an orifice column, a mechanically stirred reactor or some other type of gas/liquid contactor. Alternatively the

catalyst may be supported on a carrier, in which case the caustic and air are passed together over a packed bed.

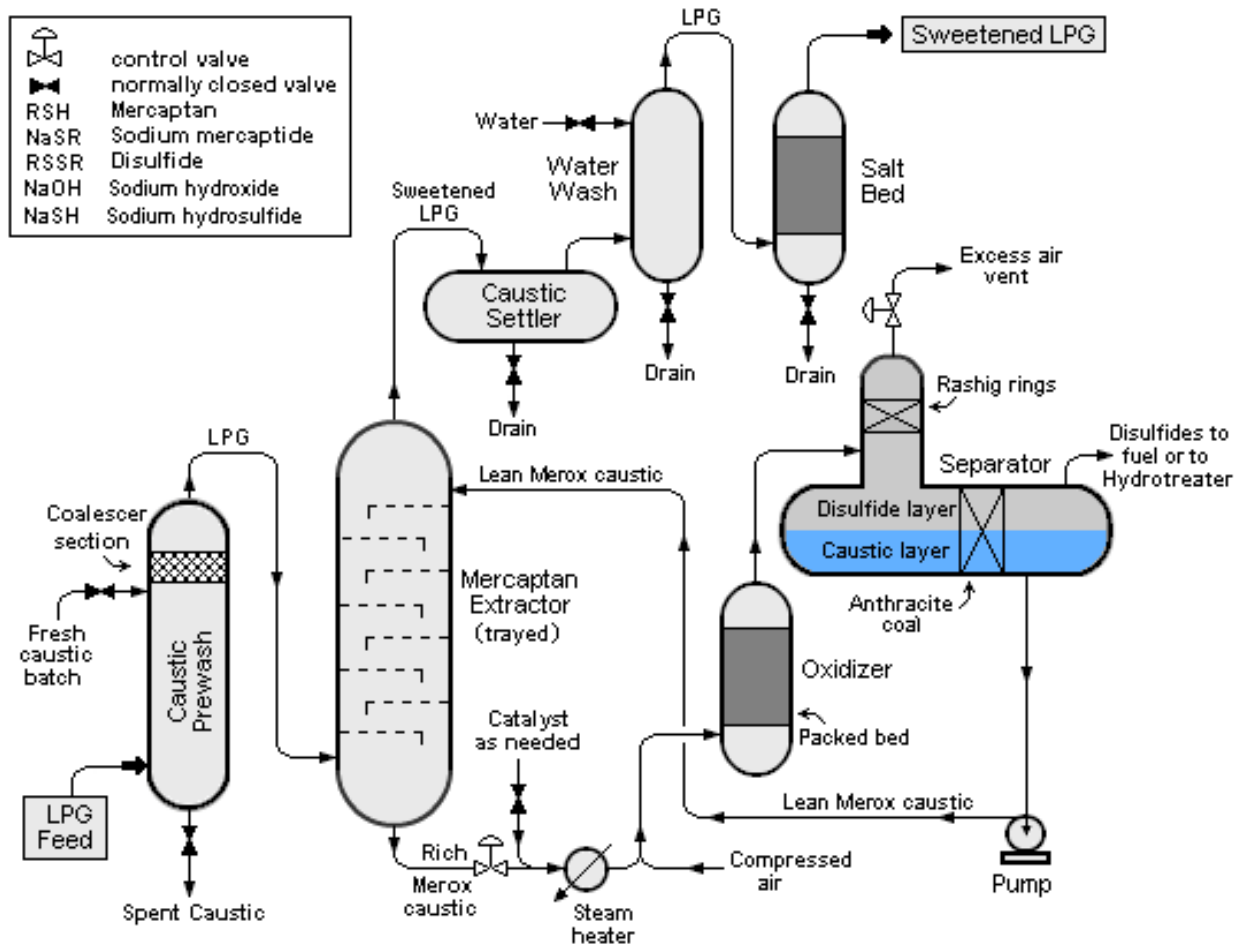


Figure (1): Merox Extraction

A coalescer is a technological device performing coalescence. They are primarily used to separate emulsions into their components via various processes; operating in reverse to an emulsifier.

b) Merox Sweetening

Sweetening is achieved by blowing a caustic hydrocarbon mixture with air in the presence of the catalyst where by disulphide are formed according to equation (2), and dissolve in the material being treated. As in the above

mentioned regeneration process, the catalyst may be in solution in the caustic or held on carrier, and the process is carried out as described.

c) **Combined Operation**

The combined extraction/ Sweetening operation is carried out by a combination of the extraction and sweetening processes.

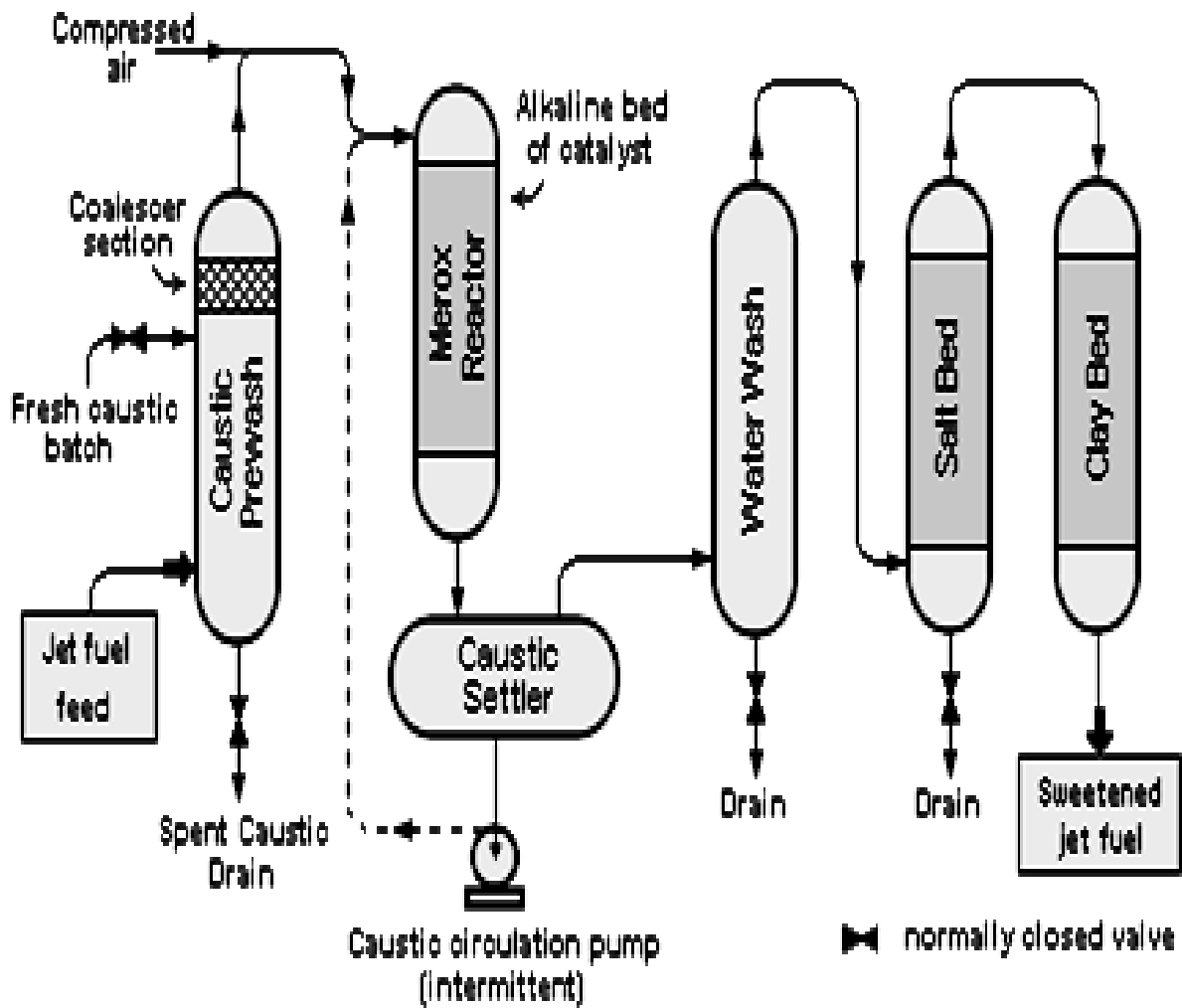


Figure (2): Merox Sweetening

TRAEING PROCESSES (3)

3) The Removal of Water and Particulate Matter:

1. Water and particulate matter in the fuel can have disastrous effects on gas turbine blades.
2. Free water may cause corrosion throughout a fuel distribution system.
3. Particulate matter may block filters or the fine orifices of fuel injection and burner.

Water may be removed by: 1) Physically 2) Chemically 3) Electro- statically

Particulate matter may be removed by: 1) Water washing 2) Filtration

Processes:

1) Salt Dryers:

Used to remove water from water primary distillation products and to control the water content both before and after secondary processing. The product is passed through a vertical drum filled with suitably graded rock salt. Rock salts are not powerful desiccants (مواد مجففة); it will remove the free water but not dissolved water. If more dissolved water has to be removed it is usual to use calcium chloride in the dryer.

2) Electrostatic Coalescers:

Uses electrical coalescing for the removal of free water and sodium chloride or calcium chloride for the removal of any residual traces of water. **The process is used for the dehydration of heating oil, kerosene, jet fuel, diesel fuel and**

solvents. The dehydration product contains no free water but may contain some dissolved water.

3) Sand Coagulators and Filters:

Vertical drums filled with fine sand are used for removal of particulate matter and water, this process have the advantage over salt dryers is not involving the use of chemicals. Down flow through the bed and up flow through a water separator will remove the water. For this purpose the oil must pass upward through the bed with a bottom water drain so that it can emerge clear, and bright from the top of the drum, 5 micron filter may be needed for turbo jet fuel.

4) Vacuum Flashing:

Where difficulties might be met in the removal of water from high-boiling or viscous products by the previous methods, water may be removed by passing the product through a vessel at a sufficiently reduced pressure to cause the water to evaporate, it is used sometimes for the clarification of lubrication oil.

4) The Improvement in Storage Stability & Performance:

Owing to their complex composition and the presence of small amounts of N_2 , S, organic acids, and oxygen, most petroleum products are subjected to **deterioration (weakening) in storage**. This storage instability may be noticed by:

- 1- a darkening in color,
- 2- the formation of gums, and

3- in some cases a significant deterioration in those characteristics that control the performance of the products.

Instability may be accompanied by a marked degree of corrosiveness due to the presence of organic and/ or inorganic acids.

The use of caustic soda for the removal of acidic gases and malodorous compounds as described earlier, is widely used for the removal of substances which cause instability and corrosion. The performance characteristics of products from primary refining processes are seldom in keeping with the demands of modern machinery and engines. It is therefore often necessary to subject the products to secondary refining processes to remove those compounds that have an adverse effect on performance.

Performance Improvement Processes:

1) SO₂ Extraction:

Liquid SO₂ is very selective solvent for removal of aromatic hydrocarbons.

SO₂ treatment removes aromatics and some polar compounds, including sulfur, gum and color constituents, as well as olefins. The removal of aromatics leads to better burning properties.

2) H₂SO₄ Treatment:

This process is used for the removal of sulfur and thiophene from aromatic streams. It is less applicable now a days as other treating methods are available.

This process may be applicable for the pretreatment of straight run naphtha that are to be reformed.

3) Hydrodesulphurization:

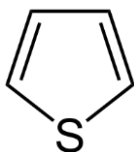
Hydrodesulphurization is the most modern and effective processes for the removal of sulfur from oil products and for general improvement in the

quality of refinery streams, including the pretreatment of catalytic reformer feed.

The process convert S to H₂S by reaction with hydrogen in the presence of catalyst. This process is used mainly for the processing of straight run and cracked medium and heavy distillates, while vapor phase hydro-treating is used for the processing of light distillates it operates at lower pressure.

Thiophen

Thiophen (XXII) and mono-methyl thiophens have been isolates (separate) from gasoline: alkyl-thiophens and benzo-thiophens (XXIII) have been isolates from kerosene. In gas oil range substituted thiophens, benzo-thiophens and higher polycyclic thiophens are present.



(XXII) Thiophen



(XXIII) Benzo Thiophen

Two general methods of reducing the amount of sulfur have been developed, those which involve:

- 1) solvent extraction of the sulfur compounds and
- 2) those by which most of the sulfur compounds are decomposed by the use of a catalyst into hydrogen sulfide and the remaining hydrocarbon part of the molecule.

The solvent extraction processes are not cheap or effective as the catalytic processes in the removal of sulfur because they remove the entire sulfur bearing molecule and at the same time certain hydrocarbons, particularly those with aromatic rings.

This when the removal of aromatic hydrocarbons as well as sulfur is desirable, the solvent process may be superior.

H_2SO_4 , HF are an effective solvents, but SO_2 and furfural are more frequently used. The solvent process tends to raise the pour point and moderately improve the Diesel Index, but the catalytic processes of desulphurization do not materially affect either of these properties. Yields by the catalytic processes may exceed 100% especially if outside hydrogen is used.

By the addition of H_2 from outside sources more vigorous reaction (decomposition) and hydrogenation can be undertaken, and in the extreme, whole crude oils and residues can be desulphurization.

Desulphurization is a mild selective hydrogenation, so mild that aromatic are not usually hydrogenation to naphthenes. Sulfur is removed as H_2S and the remaining part of the molecule is hydrogenated.

Mild decomposition result in an evolution of hydrogen which can be recycled for hydrogenation reactions but if higher boiling or refractory stocks are being treated, extra H_2 must be introduced from outside sources to maintain a higher concentration of hydrogen during the reaction. The decomposition leads to products of slightly lower boiling range than that of the parent material slightly API gravities.

Efficiency of desulphurization depends upon the charge stock and severity of treatment, ranging from as low as 50 to 60 % for mild operation to 80 to 99 % and 95 to 98% is not uncommon.

CRUDE DISTILLATION

1. INTRODUCTION

Separation the crude oils could be done by distillation into fractions according to boiling point so that each of the processing units following will have feedstocks that meet their particular specifications. Higher efficiencies and lower costs are achieved if the crude oil separation is accomplished in two steps: **first** by fractionating the total crude oil at essentially atmospheric pressure; **then** by feeding the high-boiling bottoms fraction (atmospheric reduced crude) from the atmospheric column to a second fractionator operated at a high vacuum.

The vacuum column is employed to separate the heavier portion of the crude oil into fractions because the high temperatures necessary to vaporize the topped crude at atmospheric pressure cause thermal cracking to occur, with the resulting loss to dry gas, discoloration of the product, and equipment fouling due to coke formation.

2. DESALTING CRUDE OILS

If the salt content of the crude oil is greater than 10 lb/1000 bbl (expressed as NaCl), the crude requires desalting to minimize fouling and corrosion caused by salt deposition on heat transfer surfaces and acids formed by decomposition of the chloride salts. In addition, some metals in inorganic compounds dissolved

in water emulsified with the crude oil, which can cause catalyst deactivation in catalytic processing units, are partially rejected in the desalting process.

The following analytical methods are used to determine the salt content of crude oils:

1. HACH titration with mercuric nitrate after water extraction of the salt
2. Potentiometric titration after water extraction
3. Mohr titration with silver nitrate after water extraction
4. Potentiometric titration in a mixed solvent
5. Conductivity

The two most typical methods of crude-oil desalting – **chemical and electrostatic separation** – use hot water to dissolve the salts and collect suspended solids. **In chemical desalting**, water and surfactants are added to the crude, heated to dissolve salts and other impurities, and then sent to a settling tank where the water and oil separate. **In electrostatic desalting**, chemicals are replaced with a strong electrostatic charge, which drives the separation of water from oil.

Two-stage desalting is used if the crude oil salt content is more than 20 lb/1000 bbl and, in the cases where residua are catalytically processed, there are some crudes for which **three-stage desalting** is used.

The salt in the crude is in the form of dissolved or suspended salt crystals in water emulsified with the crude oil.

The basic principles of desalting process are:

- 1- wash the salt from the crude oil with water.**
- 2- removal of suspended solids from the crude oil.**

The pH, gravity, and viscosity of the crude oil, as well as the volume of wash water used per volume of crude, affect the separation ease and efficiency. Total suspended solids removal should be 60% or better with 80% removal of particles greater than 0.8 micron in size.

Desalting is carried out by mixing the crude oil with from 3 to 10 vol% water at temperatures from 200 to 300°F (90 to 150°C).

Both the ratio of the water to oil and the temperature of operation are functions of the density of the oil. **Typical operating conditions are illustrated in the following table.**

Table 1: Typical Operating Conditions of Desalting Process.

API	Water Wash, Vol.%	Temp. °F (°C)
> 40	3–4	240–260 (115–125)
30-40	4–7	260–280 (125–140)
< 30	7–10	280–330 (140–150)

The salts are dissolved in the wash water and the oil and water phases separated in a settling vessel either by adding chemicals to assist in breaking the emulsion or by developing a high-potential electrical field across the settling vessel

(Fig.1). Either AC or DC fields may be used and potentials from 12,000 to 35,000 volts are used to promote coalescence.

For single-stage desalting units 90 to 95% efficiencies are obtained and two-stage processes achieve 99% or better efficiency. One process uses both AC and DC fields to provide high dewatering efficiency. An AC field is applied near the oil–water interface and a DC field in the oil phase above the interface. Efficiencies of up to 99% water removal in a single stage are claimed for the dual field process. About 90% of desalters use AC field separation only.

The dual field electrostatic process provides efficient water separation at temperatures lower than the other processes and, as a result, higher energy efficiencies are obtained.

Heavy naphthenic crudes form more stable emulsions than most other crude oils and desalters usually operate at lower efficiencies when handling them. The crude oil densities are close to the density of water and temperature above 280 °F(138 °C) are needed.

Make-up water averages 4 to 5% on crude oil charge and is added to the second stage of a two-stage desalter. For very heavy crude oils (<15 API), addition of gas oil as a diluent to the second stage is recommended to provide better separation efficiencies.

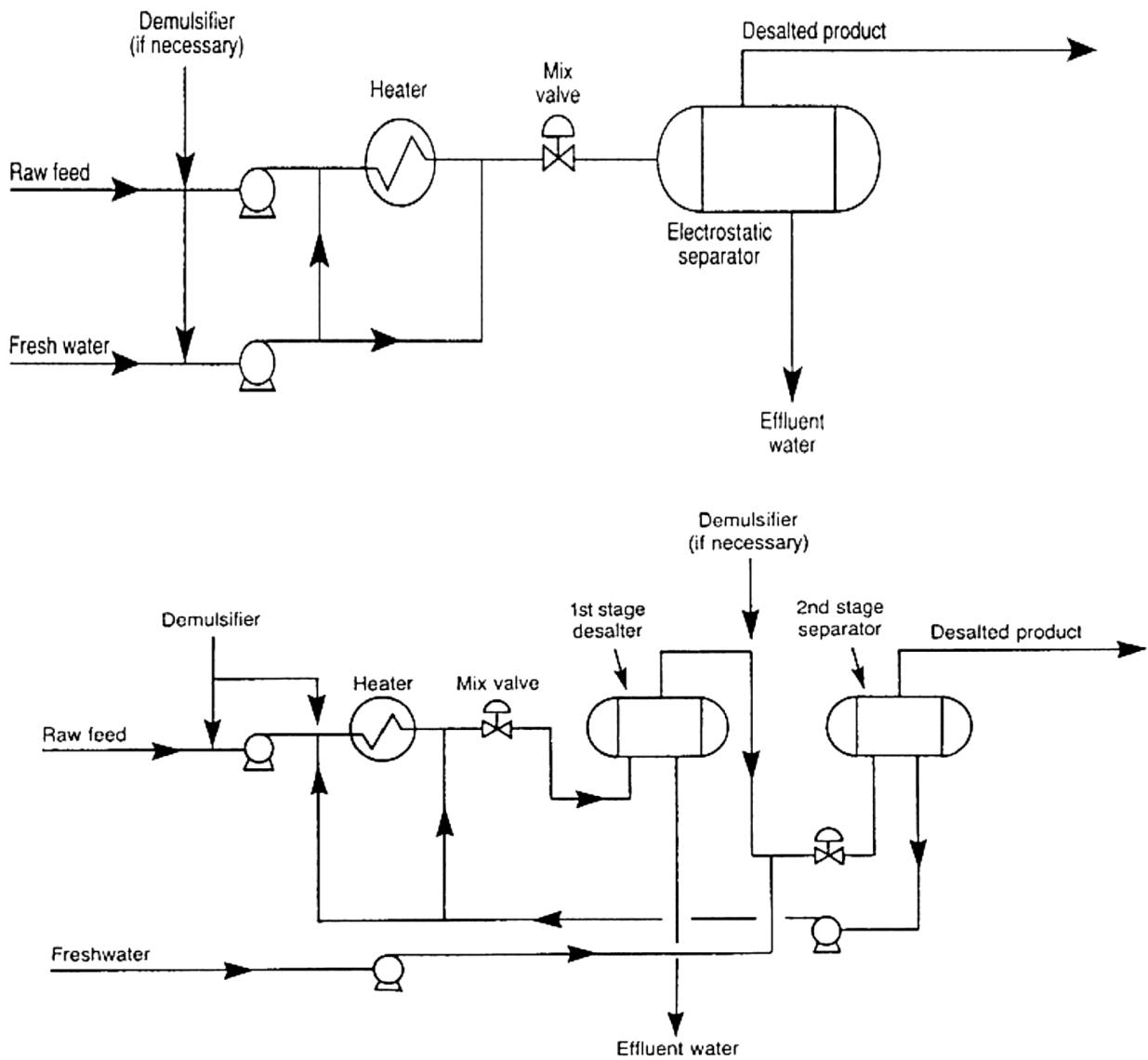


Figure 1: Single- and two-stage electrostatic desalting systems.

ATMOSPHERIC DISTILLATION

Distillation of crude oil is carried out at atmospheric pressure and under vacuum. Low boiling fractions vaporize at atmospheric pressure up to temperature below 400 °C without cracking the hydrocarbon compounds. High boiling fractions are vaporized under vacuum at a temperature much lower than 400 °C and thermal cracking is avoided. Thus, all the low and high boiling fractions of crude oil are separated by atmospheric distillation followed by vacuum distillation without cracking or degradation of the original hydrocarbons present in crude oil.

After the removal of oil fractions, the vacuum residue left requires solvent extraction (deasphalting) to recover the valuable petroleum fraction. Atmospheric distillates are the major sources of petroleum fuels and vacuum distillates are the source of fuel, wax, lubricating oil base stocks, bitumen, petroleum cokes, etc., mainly by secondary treatments like extraction, thermal and catalytic treatments.

Crude oil contains salts which can be harmful to downstream equipment and must be removed. To remove the salts, water is mixed with the crude oil and typically heated to temperatures between about 215 °F to about 280 °F and allowed to separate in the desalter. **It is then further heated to about 750 °F (399 °C) in a furnace (i.e., direct-fired heater or “pipe-still”).** The partially

vaporized crude is fed into the feed region (called flash zone) of the atmospheric column, where the vapor and liquid separate. The vapor includes all the components that comprise the products, while the liquid is the residue with a small amount of components in the range of gas oil.

These components are removed from the residue by steam stripping at the bottom of the column. Steam is added to enhance separation; it does so largely by decreasing vapor pressure in the column.

Products are withdrawn from the side of the column and side strippers are used to help controlling the composition of light components.

Reflux is provided by condensing the tower overhead vapors and returning a portion of the liquid to the top of the tower, and by pump-around and pump back streams lower in the tower. Each of the side stream products removed from the tower decreases the amount of reflux below the point of draw off.

Although crude towers do not normally use reboilers, several trays are generally incorporated below the flash zone and steam is introduced below the bottom tray to strip any remaining gas oil from the liquid in the flash zone and to produce a high-flash-point bottoms.

The atmospheric fractionator normally contains 30 to 50 fractionation trays. Separation of the complex mixtures in crude oils is relatively easy and generally five to eight trays are needed for each side stream product plus the same number above and below the feed plate. Thus, a crude oil

atmospheric fractionation tower with four liquid side stream draw offs will require from 30 to 42 trays.

The liquid side stream withdrawn from the tower will contain low-boiling components which lower the flashpoint, because the lighter products pass through the heavier products and are in equilibrium with them on every tray.

These “light ends” are stripped from each side stream in a separate small stripping tower containing four to ten trays with steam introduced under the bottom tray. The steam and stripped light ends are vented back into the vapor zone of the atmospheric fractionator above the corresponding side-draw tray (Fig.1).

The overhead condenser on the atmospheric tower condenses the pentane and heavier fraction of the vapors that passes out of the top of the tower. This is the light gasoline portion of the overhead, containing **some propane and butanes** and essentially all of the higher-boiling components in the tower overhead vapor. **Some of this condensate is returned to the top of the tower as reflux,** and the remainder is sent to **the stabilization section** of the refinery gas plant where the butanes and propane are separated from the **C5-180°F (C5-82°C) LSR (Light Straight-Run) gasoline.**

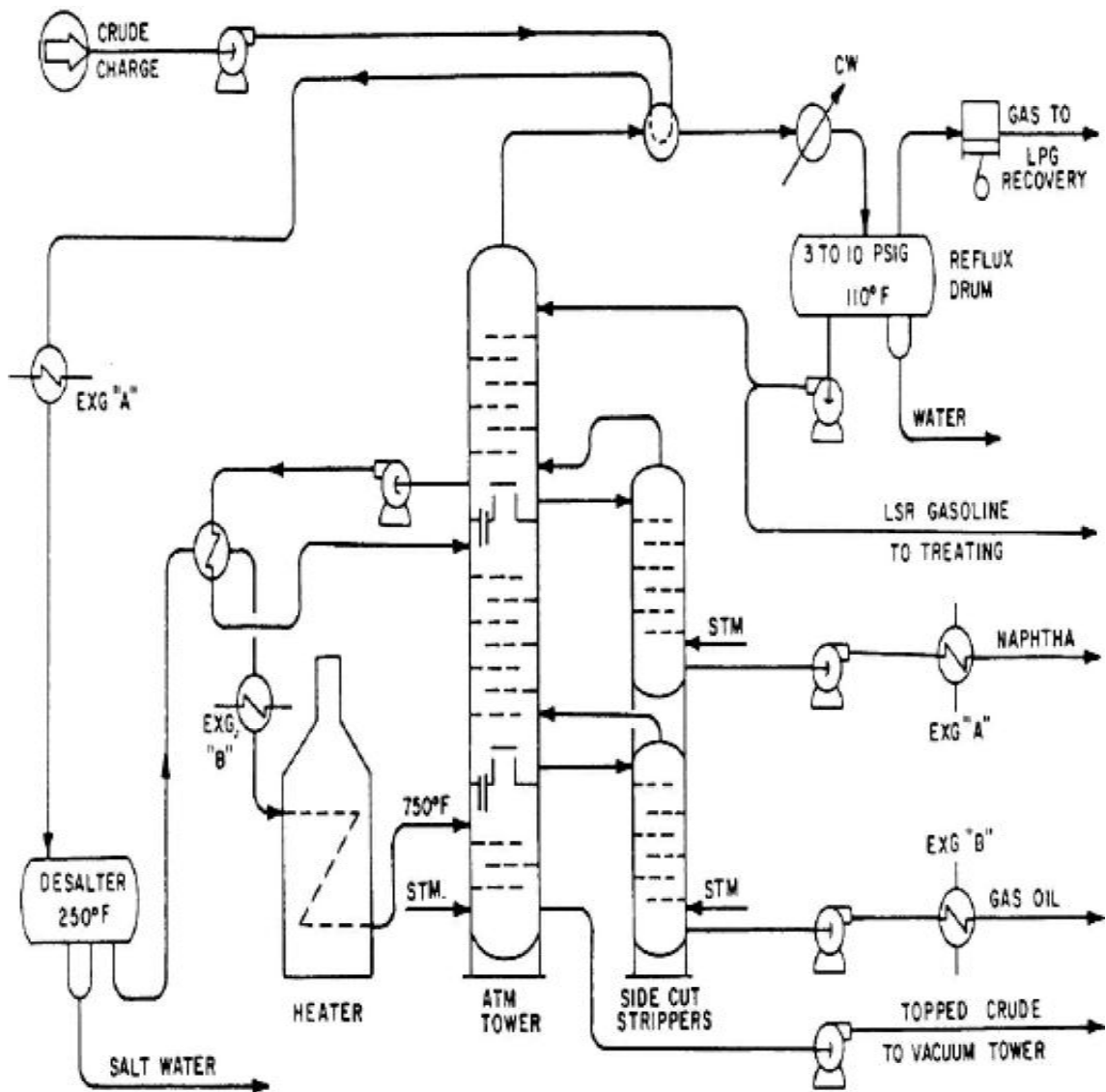


Figure 1: Atmospheric distillation. For simplicity, **only two side strippers are shown.** Usually at least four are provided to produce extra cuts such as kerosene and diesel.

VACUUM DISTILLATION

The furnace outlet temperatures required for atmospheric pressure distillation of the heavier fractions of crude oil are so high that thermal cracking would occur, with the resultant loss of product and equipment fouling (the temperature at which a crude oil begin to undergo thermal decomposition varies from crude to crude, depending on its composition (naphthenic, paraffinic, or aromatic base) and the trace metals present in the crude).

These materials are therefore distilled under vacuum because the boiling temperature decreases with a lowering of the pressure. **Distillation is carried out with absolute pressures in the tower flash zone area of 25 to 40 mmHg (Fig. 1).**

To improve vaporization, **the effective pressure is lowered** even further (to 10 mmHg or less) **by the addition of steam** to the furnace inlet and at the bottom of the vacuum tower. Addition of steam to the furnace inlet increases the furnace tube velocity and minimizes coke formation in the furnace as well as decreasing the total hydrocarbon partial pressure in the vacuum tower. The amount of stripping steam used is a function of the boiling range of the feed and the fraction vaporized, but generally ranges from 10 to 50 lb/bbl feed.

Furnace outlet temperatures are also a function of the boiling range of the feed and the fraction vaporized as well as of the feed coking characteristics. High tube velocities and steam addition minimize coke formation, and furnace outlet temperatures in the range of 730 to 850°F (388 to 454°C) are generally used.

Typically:

The highest furnace outlet temperatures are for “dry” operation of the vacuum unit; that is, no steam is added either to the furnace inlet or to the vacuum column.

The lowest furnace outlet temperatures are for “wet” operation when steam is added to both the furnace inlet and to the bottom of the vacuum tower.

Intermediate temperatures are used for “dump” operation of the vacuum unit when steam is added to the furnace inlet only. For most crude oils the furnaces can be operated from three to five years between turnarounds (restructuring).

The effective pressure (total absolute pressure–partial pressure of the steam) at the flash zone determines the fraction of the feed vaporized for a given furnace outlet temperature, so it is essential to design the fractionation tower, overhead lines, and condenser to minimize the pressure drop between the vacuum- inducing device and the flash zone.

A few millimeters decrease in pressure drop will save many dollars in operating costs. The lower operating pressures cause significant increases in the volume of vapor per barrel vaporized and, as a result, the vacuum distillation columns are much larger in diameter than atmospheric towers. **It is not unusual to have vacuum towers up to 40 feet in diameter.**

The desired operating pressure is maintained by the use of steam ejectors and barometric condensers or vacuum pumps and surface condensers. The size and number of ejectors and condensers used is determined by the vacuum needed and the quality of vapors handled.

For a flash zone pressure of 25 mmHg, three ejector stages are usually required. The first stage condenses the steam and compresses the noncondensable gases, while the second and third stages remove the noncondensable gases from the condensers. **The vacuum produced is limited to the vapor pressure of the water used in the condensers.**

If colder water is supplied to the condensers, a lower absolute pressure can be obtained in the vacuum tower. Although more costly than barometric condensers, a recent trend is the use of **vacuum pumps and surface condensers** in order to reduce the contamination of water with oil.

In many cases, a flash drum is installed between the feed-preheat heat exchangers and the atmospheric pipe-still furnace. The lower boiling fractions which are vaporized by heat supplied in the preheat exchangers are separated in the flash drum and flow directly to the flash zone of the fractionator.

The liquid is pumped through the furnace to the tower flash zone. This results in a smaller and lower cost furnace and lower furnace outlet temperatures for the same quantity of overhead streams produced.

A stabilizer is incorporated in the crude distillation section of some refineries instead of being placed with the refinery gas plant. The liquid condensed from the overhead vapor stream of the atmospheric pipe-still contains propane and butanes which make the vapor pressure much higher than is acceptable for gasoline blending. To remove these, the condensed liquid in excess of reflux requirements is charged to a **stabilizing tower** where the vapor pressure is adjusted by removing the propane and butanes from the LSR (**Light Straight-Run**) gasoline stream. **Later, in the product-blending section of the refinery, n-butane is added to the gasoline stream to provide the desired Reid vapor pressure.**

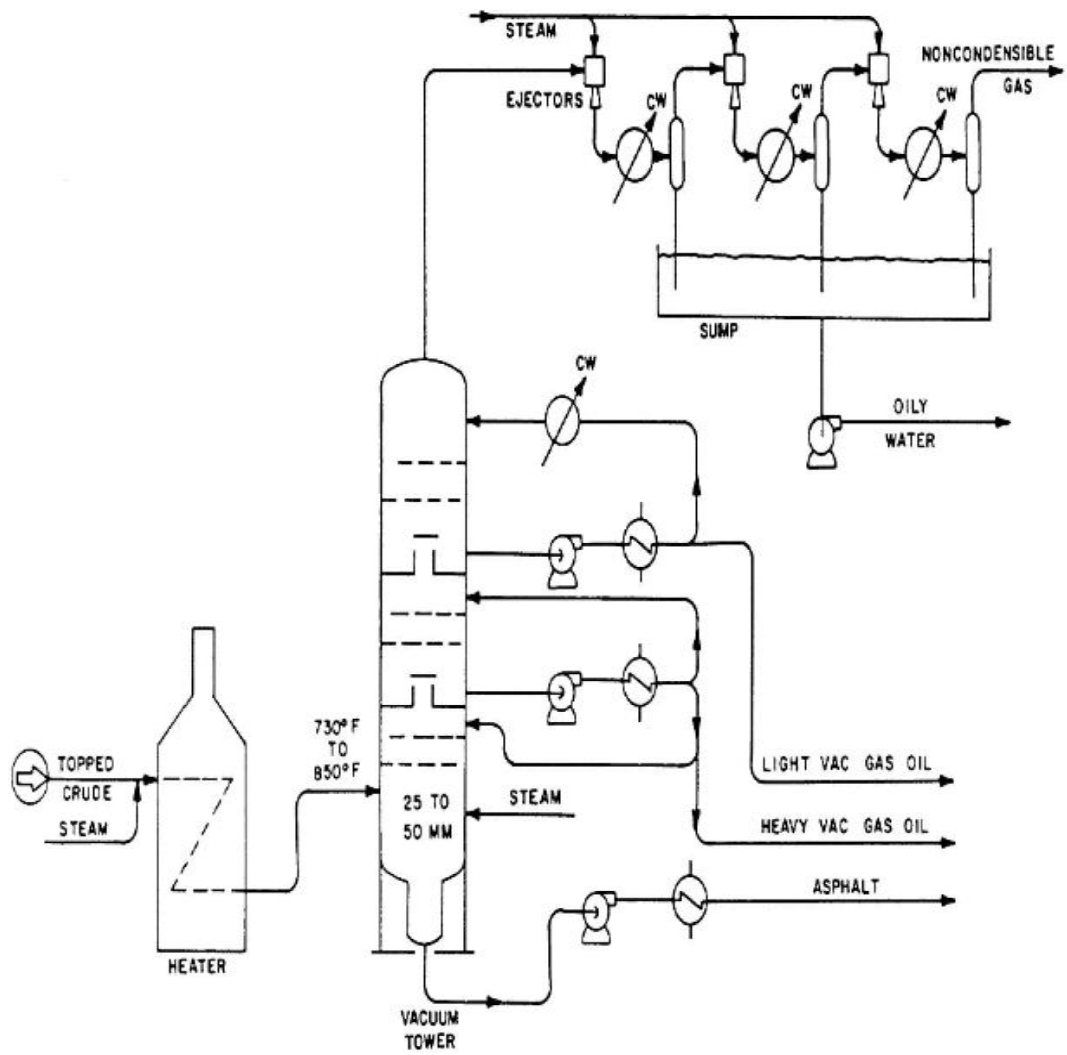


Figure (1): Vacuum distillation unit

UPGRADING (IMPROVING) PROCESSES:

COKING

The “bottom of the barrel” has become more of a problem for refiners because heavier crudes are being processed and the market for heavy residual fuel oils has been decreasing. Historically, the heavy residual fuel oils have been burned to produce electric power and to supply the energy needs of heavy industry, but more environmental restrictions (limitations) have caused many of these users to switch to natural gas. Thus when more heavy residuals are in the crude there is more difficulty in economically disposing of them. **The reduced crude bottoms (VRC) from the vacuum tower is thermally cracked in a Delayed Coker to produce wet gas, coker gasoline, coker gas oil, and coke. Coking units convert heavy feedstocks into a solid coke and lower boiling hydrocarbon products which are suitable as feedstocks to other refinery units for conversion into higher value transportation fuels.** From a chemical reaction viewpoint, coking can be considered as a severe (strict) thermal cracking process in which one of the end products is carbon (i.e., coke). Actually the coke formed contains some volatile matter or high-boiling hydrocarbons.

Delayed coking, fluid coking, and Flexicoking are the popular coking processes and the delayed coking is the most widely one. Petroleum coke characteristics are illustrated in Table (1).

Table (1): Characteristics of Petroleum Coke.

Process	Coke Type	Characteristics
Delayed	Sponge	Spongelike appearance Higher surface area Lower contaminants level Higher volatile content Higher Hardgrove grindability index (HGI) (~100) Typical size of 0–6 in. (0 -15 cm) Spherical appearance
	Shot	Lower surface area Lower volatiles Lower HGI ^a (<50) Tends to agglomerate
	Needle	Needlelike appearance Low volatiles High carbon content
Fluid	Fluid	Low volatiles Higher contaminants level Low HGI ^a (<40) Black sandlike particles
Flexicoker	Flexicoke	Highest metals level 80% <200 mesh

I. Needle petroleum coke:



II. Sponge petroleum coke:



III. Shot petroleum coke:



IV. Calcined Petroleum Coke (CPC) :



V. graphite petroleum coke (GPC) ,



The main uses of petroleum coke are as follows:

1. Fuel.
2. Manufacture of anodes for electrolytic cell reduction of alumina.
3. Direct use as chemical carbon source for manufacture of elemental phosphorus, calcium carbide, and silicon carbide.
4. Manufacture of electrodes for use in electric furnace production of elemental phosphorus, titanium dioxide, calcium carbide, and silicon carbide.
5. Manufacture of graphite.

The sulfur content of petroleum coke varies with the sulfur content of the coker feedstock. It is usually in the range of 0.3 to 1.5 wt%. It can sometimes, however, be as high as 8%. The sulfur content is not significantly reduced by calcining.

Delayed Coking:

The delayed coking process (Fig.1) was developed to minimize refinery yields of residual fuel oil by severe thermal cracking of stocks such as vacuum residuals, aromatic gas oils, and thermal tars.

It is called "delayed coking" because cracking takes place in a coke drum rather than in a furnace or reactor.

Typically furnace outlet temperatures range from 900–930°F (482–500°C).

The higher the outlet temperature, the greater the tendency to produce shot coke

and the shorter the time before the furnace tubes have to be **decoked**. **Usually furnace tubes have to be decoked every three to five months.**

This accomplishes (achieved by) the following:

- 1) Hot fresh liquid feed is charged to the fractionator two to four trays above the bottom vapor zone.
- 2) The hot vapors from the coke drum are quenched by the cooler feed liquid thus preventing any significant amount of coke formation in the fractionator and simultaneously condensing a portion of the heavy ends which are recycled.
- 3) **Any remaining material lighter than the desired coke drum feed is stripped (vaporized) from the fresh liquid feed.**
- 4) **The fresh feed liquid is further preheated making the process more energy efficient.**
- 5) **The gas oil side draw is a conventional configuration employing a six- to eight-tray stripper with steam** introduced under the bottom tray for vaporization of light ends to control the initial boiling point (IBP) of the gas oil.
- 6) **Steam and vaporized light ends** are returned from the top of the gas oil stripper to the fractionator one or two trays above the draw tray.
- 7) **A pump-around reflux system is provided at the draw tray** to recover heat at a high temperature level and minimize the low-

temperature-level heat removed by the overhead condenser. **This low-temperature-level heat cannot normally be recovered by heat exchange and is rejected to the atmosphere** through a water cooling tower or aerial coolers.

- 8) **Eight to ten trays are generally used between the gas-oil draw and the naphtha draw or column top.** If a naphtha side draw is employed, additional trays are required above the naphtha draw tray.

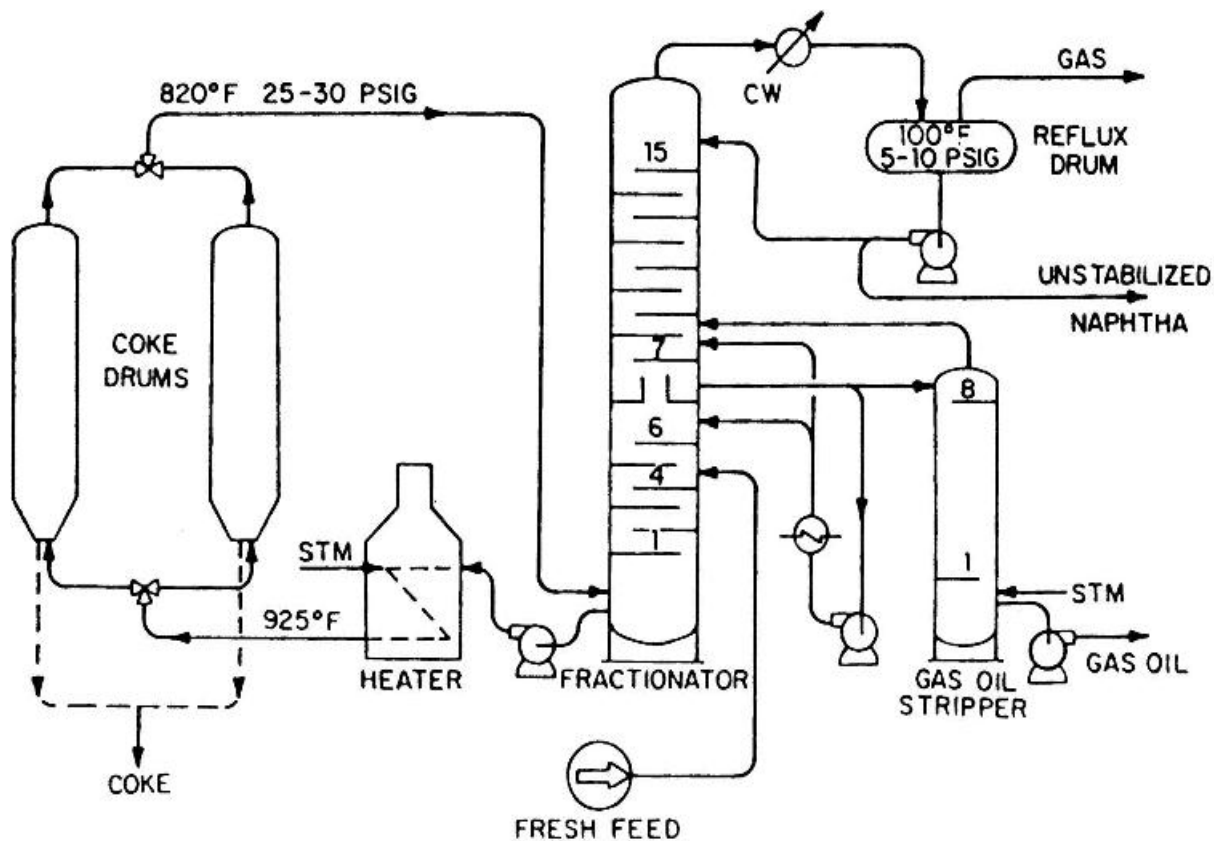


Figure (1): Delayed coking unit.

The naphtha or gasoline fraction may be split (crack) into light and heavy cuts. After hydrotreating for sulfur removal and olefin saturation, the light cut is

either isomerized to improve octane or blended directly into finished gasoline.

The heavy cut is hydrotreated and reformed.

A typical split (crack) of coker naphtha is as follows:

Light naphtha = 35.1 vol%, 65°API

Heavy naphtha = 64.9 vol%, 50°API

The gas-oil fraction is usually split into a light and heavy cut before further processing. The light fraction may be hydrotreated and subsequently fed to a FCC. The heavy fraction may be used as heavy fuel or sent to the vacuum distillation unit.

An approximate split of the coker gas oil can be estimated from the following:

Light gas oil (LCGO) = 67.3 vol%, 30°API

Heavy gas oil (HCGO) = 32.7 vol%, ~ 13°API

UPGRADING (IMPROVING) PROCESSES:

VISBREAKING

Visbreaking is a well-established noncatalytic thermal process that converts atmospheric or vacuum residues to gas, naphtha, distillates, and tar. Visbreaking reduces the quantity of cutter stock required to meet fuel oil specifications while reducing the overall quantity of fuel oil produced. The conversion of these residues is accomplished by heating the residue material to high temperatures in a furnace. The material is passed through a soaking zone, located either in the heater or in an external drum, under proper temperature and pressure constraints so as to produce the desired products. The heater effluent is then quenched with a quenching medium to stop the reaction.

With refineries today processing heavier crudes and having a greater demand for distillate products, visbreaking offers a low-cost conversion capability to produce incremental gas and distillate products while simultaneously reducing fuel oil viscosity. Visbreaking can be even more attractive if the refiner has idle equipment available that can be modified for this service.

When a visbreaking unit is considered for the upgrading of residual streams, the following objectives are typically identified:

- ✚ Viscosity reduction of residual streams which will reduce the quantity of high-quality distillates necessary to produce a fuel oil meeting commercial viscosity specifications.
- ✚ Conversion of a portion of the residual feed to distillate products, especially cracking feedstocks. This is achieved by operating a vacuum flasher downstream of a visbreaker to produce a vacuum gas oil cut.

- + Reduction of fuel oil production while at the same time reducing pour point and viscosity. This is achieved by utilizing a thermal cracking heater, in addition to a visbreaker heater, which destroys the high wax content of the feedstock.

Specific refining objectives must be defined before a visbreaker is integrated into a refinery, since the overall processing scheme can be varied, affecting the overall economics of the project.

Visbreaking is essentially a mild (moderate) thermal cracking operation at mild (moderate) conditions where in long chain molecules in heavy feed stocks are broken into short molecules thereby leading to a viscosity reduction of feedstock. Now all the new visbreaker units are of the soaker type. Soaker drum utilizes a soaker drum in conjunction with a fired heater to achieve conversion.

Visbreaking is a non-catalytic thermal process. It reduces the viscosity and pour point of heavy petroleum fractions so that product can be sold as fuel oil. It gives 80 - 85% yield of fuel oil and balance recovered as light and middle distillates. The unit produces gas, naphtha, heavy naphtha, visbreaker gas oil, visbreaker fuel oil (a mixture of visbreaker gas oil and visbreaker tar).

FEED:

Atmospheric Residues: To get gasoline and diesel oil.

Vacuum Residues: To reduce viscosity.

The degree of viscosity and pour point reduction is a function of the composition of the residua feed to the visbreaker. **Waxy feed stocks**

achieve pour point reductions from 15–35°F (-3 to 2°C) and final viscosities from 25–75% of the feed. **High asphaltene content in the feed** reduces the conversion ratio at which a stable fuel can be made, which results in smaller changes in the properties.

The Principal Reactions which occur during the Visbreaking Operation are:

1. **Cracking of the side chains** attached to cycloparaffin and aromatic rings at or close to the ring so the chains are either removed or shortened to methyl or ethyl groups.
2. **Cracking of resins** to light hydrocarbons (primarily olefins) and compounds which convert to asphaltenes.
3. At temperatures above 900°F (480°C), some **cracking of naphthene rings**. There is little cracking of naphthenic rings below 900°F (480°C).

A given conversion in visbreaker can be achieved by two ways:

- ✚ High temp., low residence time cracking: **Coil Visbreaking**.
- ✚ Low temp., high residence time cracking: **Soaker Visbreaking**

The feed is introduced into the furnace and heated to the desired temperature.

Coil cracking uses **higher furnace outlet temperatures** [885–930°F (473–500°C)] **and reaction times from one to three minutes**, while **soaker cracking** uses **lower furnace outlet temperatures** [800–830°F (427–443°C)] **and longer reaction times**.

Pressure is an important design and operating parameter with units being designed for pressures as high as 750 psig (5170 kPa) for liquid-phase

visbreaking and as low as 100–300 psig (690–2070 kPa) for 20–40% vaporization at the furnace outlet.

The desired cracking is achieved in the furnace at high temperature and the products of cracking are quenched and distilled in a downstream fractionator.

In Soaker Cracking, The furnace operates at a lower outlet temperature and a soaker drum is provided at the outlet of the furnace to give adequate residence time to obtain the desired conversion while producing a stable residue product, thereby increasing the heater run and reducing the frequency of unit shut down for heater decoking. The products from soaker drum are quenched and distilled in the downstream fractionator.

PRODUCTS:

The cracked product contains **gas, naphtha, gas oil and furnace oil**, the composition of which will depend upon the type of feedstock processed. A typical yield pattern may be **gas 1-2%, naphtha 2-3%, gas oil 5-7%, furnace oil 90-92%**.

The product yields and properties are similar, but the soaker operation with its lower furnace outlet temperatures has the advantages of lower energy consumption and longer run times before having to shut down to remove coke from the furnace tubes.

Many of the properties of the products of visbreaking vary with conversion and the characteristics of the feedstocks:

- 1- some properties, such as **diesel index and octane number**, are more closely related to feed qualities; and
- 2- others, such as **density and viscosity of the gas oil**, are relatively **independent** of both conversion and feedstock characteristics.

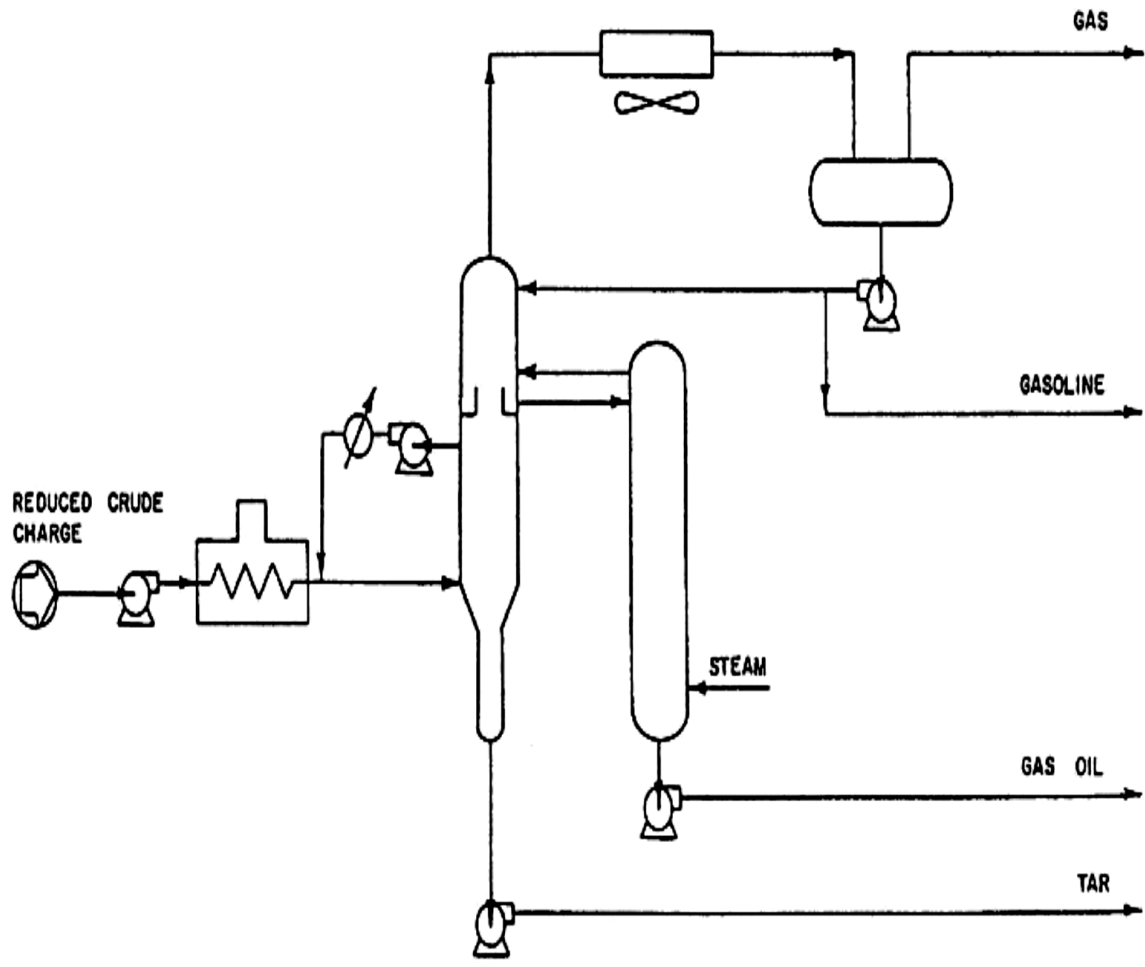


Figure 1: Coil Visbreaker

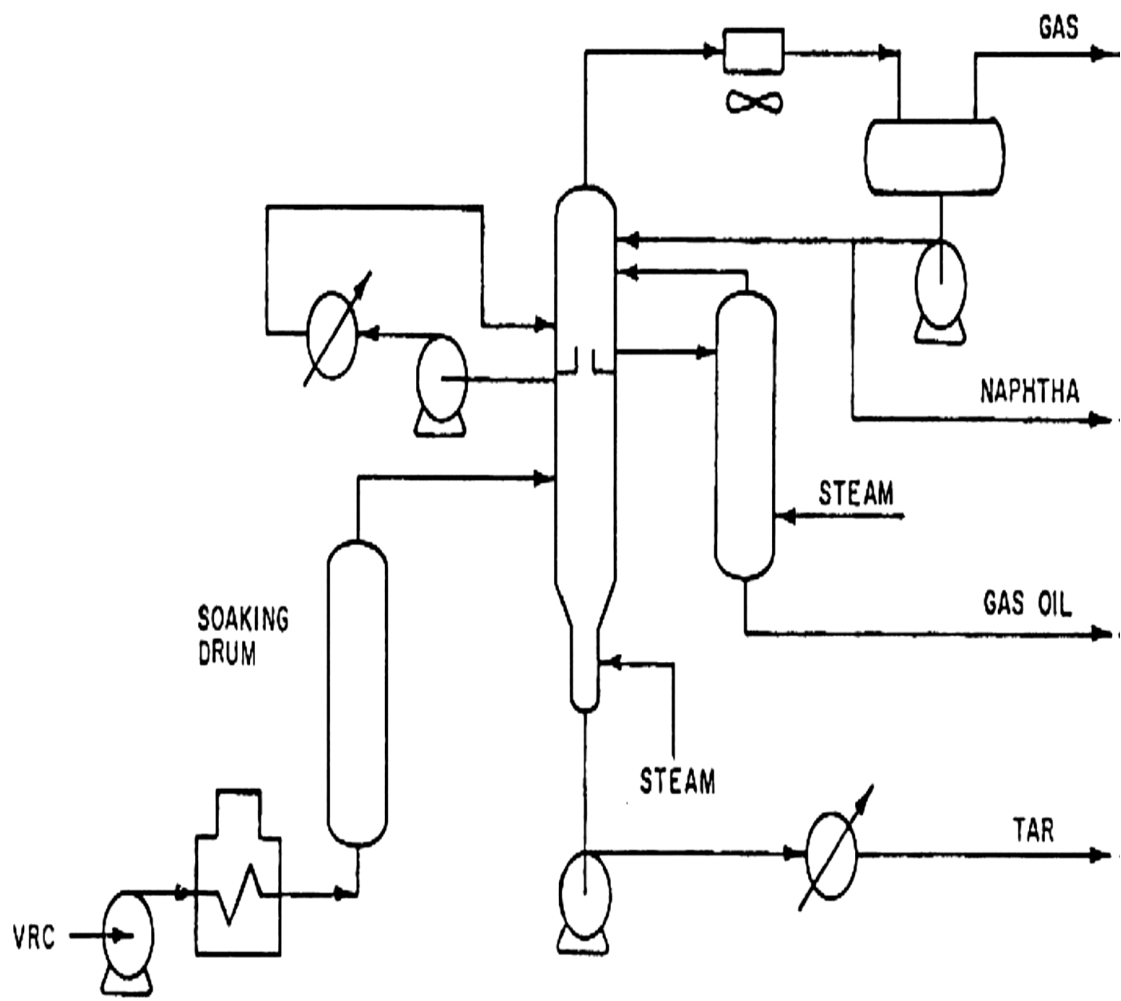


Figure 2: Soaker Visbreaker.