

## 6.5 Petroleum Refinery

### 6.5.1 Petroleum <sup>1) 2)</sup>

Petroleum is generally considered to be formed by the sedimentation of organic materials originated from ancient animals buried under the seabed, but there are many different theories. In 1890, a Russian N.V. Sokoloff proposed a theory of space origin for petroleum in which he insisted that hydrocarbons in the petroleum has been existing since the early stage of the space formation because trace methane is found in the meteorite. A volcanic theory has been also proposed because there are volcanic eruptions in the oil well regions and hydrocarbons are present in the volcanic gases. Furthermore, a theory of earth's depth origin was presented in which petroleum is thought to be made as carbon dioxide solved in the water deep underground of the earth reacts with alkaline metals to form acetylene and then petroleum. Although those inorganic theories of petroleum origin had some rationality in reasoning, they didn't correspond with the conditions of petroleum turn out, and the theory of organic origin attracted general supports. The theory of land plant origin, in which the difference in the formation of petroleum and coal was explained by the difference in heat and pressure subjected to buried plants, has little ground concerning to chemical proofs.

Further, the theory of coal origin was not supported because coal and oil were not found simultaneously. The theory of oil shale origin had been attracted some support, but it required an explanation of the origin of oil shale itself. Also, there are many supporters of the theory of sea weeds origin, in which sea weeds are transformed to petroleum by heat and pressure. The theory of animal origin insisted that fish, shellfish, and microorganism have been transformed to petroleum. The theory of fish origin proposes that petroleum was formed as ancient marine animals were buried underground and their protein was dissolved by decomposition and fermentation action and the fats remained formed petroleum. In 1880, Engler in Germany produced petroleum by dry distillation of fishes at 10 atm and 320°C. K. Kobayashi in Japan proved experimentally that petroleum could be easily formed under atmospheric pressure by mixing Japanese acid clay and fishes, and claimed that Japanese acid clay has some relationship with the formation of petroleum. Many theories and experimental results have been reported about the origin of petroleum, and the existence of organic nitrogen compounds in the petroleum is considered to be a strong basis for the animal origin theory and fish origin one is now widely supported.<sup>1)</sup> In this theory, the organic material sediments on the seabed is considered to be decomposed by anaerobic bacteria, releasing most of their oxygen, sulfur, and nitrogen. Hydrocarbons formed by decomposition is then considered to dissolve into water and condensed in the sedimentation rock. The theory explains that those were gradually accumulated in the space of rock dome and formed an oil field. As for the natural gas, it is considered that there are two kinds of gas, namely that formed simultaneously with petroleum in the rock dome and that formed from anaerobic decomposition of plants. The former is thought to be a main resource.

Petroleum is a mixture of hydrocarbons which could be classified by the molecular structure and number of carbons, and contains small amount of organic nitrogen and sulfur compounds. Hydrocarbons in petroleum include paraffins, expressed as a general chemical formula of  $C_{2n}H_{2n+2}$ , naphthenes  $C_nH_{2n-6} + 6H$ , olefins  $C_nH_{2n}$  and benzenes  $C_nH_{2n-6}$ . Also, the structure of various hydrocarbons is very complex as there are compounds with straight or

branched carbon chain, ring structure of five or six elements, or multiple union <sup>1)</sup>.

Hydrocarbons in the petroleum can be separated by distillation utilizing the difference of molecular weight.

Table 6.5.1 summarizes the composition of each petroleum distillate <sup>2) 3)</sup>.

Table 6.5.1 Composition and Boiling Point of Various Oil Distillates <sup>2) 3)</sup>

Distillate	Typical Hydrocarbon	Boiling Point (°C)
Natural Gas	CH <sub>4</sub>	-161
Liquefied Gas	C <sub>3</sub> H <sub>8</sub> , C <sub>4</sub> H <sub>10</sub>	-44 ~ +1
Petroleum Ether	C <sub>5</sub> H <sub>12</sub> , C <sub>6</sub> H <sub>14</sub>	30 ~ 60
Aviation Gasoline	C <sub>5</sub> ~ C <sub>9</sub>	32 ~ 150
Automotive Gasoline	C <sub>5</sub> ~ C <sub>12</sub>	32 ~ 210
Naphtha	C <sub>7</sub> ~ C <sub>12</sub>	100 ~ 200
Kerosene	C <sub>10</sub> ~ C <sub>16</sub>	177 ~ 290
Light Oil	C <sub>12</sub> ~ C <sub>18</sub>	205 ~ 316
Lubricating Oil	C <sub>15</sub> ~ C <sub>24</sub>	250 ~ 400
Heavy Oil		300 ~

## 6.5.2 Petroleum Refinery

### (1) Outline

Crude oil is distilled to separate each hydrocarbon component by the difference of boiling point into similar groups because of the convenience of usage. The distillation is a process to separate mixed liquid into its component by utilizing the difference of boiling point and volatility. Also, in the production process of fuels and lubricating oils, the conversion of some components, which have little value in the aspect of demand, into other products of higher value by chemical reaction, as well as a refinery process to remove impurities and hazardous components from the product, is performed to maintain the balance of demand and supply for different distillate <sup>4) 5)</sup>.

### (2) Oil Refinery

The structure of oil refinery is roughly divided into a refinery facility and an utility facility. Facilities for the normal pressure distillation (topping), normal/reduced pressure combination, reduced pressure distillation (vacuum flash, vacuum distillation), catalytic reforming, cracking, coking, visbreaking, hydrogenation refinery of kerosene, desulfurization of heavy oil, solvent dewaxing, solvent extraction, cleaning of naphtha, cleaning of kerosene, cleaning of lubrication oil, recovery of sulfur (desulfurization) belong to the former. The facilities for harbor, boiler and oil storage belong to the latter. The scale of oil factory is now very large, and a typical capacity of a single oil refinery is almost 300 thousand barrels (1 barrel is 159 liter) per operating day <sup>3)</sup>.

### (3) Oil Storage

As the oil refineries in Japan depend their supply of crude oil on the import, they have port facilities and store imported oil in the outdoor tanks. The storage tank is divided into a fixed roof tank and a floating roof tank. Incidentally, the salt component is removed from crude oil before the distillation process by the electric demineralization or chemical demineralization process <sup>4)</sup>.

#### (4) Distillation

The distillation is a basic operation of the oil refinery, and divided into the natural pressure distillation and reduced pressure distillation (vacuum distillation, vacuum flash). The natural pressure distillation is the first stage of oil refinery, and is called topping. Crude oil is heated by the heating furnace (pipe still), but maintains a liquid state without being vaporized because the pressure in pipe still is high. It is then blown into the flash zone of the fractionator (rectification column) which has a dozen stepped racks with many bubble-caps and holes, in 45-90 cm intervals. As its pressure is atmospheric, crude oil except for its heavy components is vaporized and the heavy components descends the tower and are taken out from the bottom. The vaporized oil ascending the fractionator is gradually condensed at each step rack, in the order of higher boiling point components, and flows down to lower step racks, because the temperature is lower as it goes upward inside the column. As the temperature of lower step rack is higher than that of upper step racks, light components are again transferred to upper racks. Inside the fractionator, the volatilization and liquefaction of oil are repeated and the same effect as re-distillation is realized. Various different distillates can be obtained by extracting the distilled liquid from the appropriate part of the rack and cooling it by the heat exchanger. For heavy oil, it is distilled at reduced pressure because it will be decomposed thermally if distilled in the normal pressure. When the pressure is reduced, the boiling point is also reduced and the distillation can be performed at relatively low temperature to prevent thermal decomposition. The principle of reduced pressure distillation is similar as that of natural pressure distillation, and a similar type of fractionator is used in which the pressure is reduced to 30-80 mm by a steam ejector. In this case, the fractionator becomes generally large in diameter and shows a short and thick appearance<sup>4)</sup>. The outline of crude oil distillation process is shown in Fig.6.5.1<sup>5)</sup>.

#### (5) Conversion

If the oil is sent directly to the market as distilled, the ratio of oil products is restricted by the composition of crude oil. Then, the supply could not always respond to the demand, and the demand and supply will not be balanced appropriately. Lack or excess of supply will occur for certain products. Therefore, it is desirable to convert some oil distillates (fraction) that could be excessive in supply into more useful products by chemical reaction. This process is called the oil conversion. The conversion had been started since when the demand for gasoline increased and the direct distillate gasoline (straight run gasoline) alone could not fill the demand. The oil conversion process includes, for instance, the thermal cracking that produce gasoline by pressurized decomposition of heavy oil at a temperature of about 500°C, catalytic reforming that produce high octane gasoline by catalytic decomposition of high boiling point distillates heavier than kerosene, hydrogenating decomposition (hydrofinishing) that converts unsaturated hydrocarbons to saturated hydrocarbons or removes sulfur and nitrogen compounds<sup>4)</sup>. The hydrogenating decomposition will be described more in detail later, because it is very important in the measures for air pollution.

#### (6) Treating

As impurities and hazardous materials are contained in the crude oil distillates, the substances such as compounds of sulfur, nitrogen and oxygen, resins, asphalt, and aromatic compounds should be removed from them. This process is called the treating, and includes such operations as cleaning by acid/alkali, absorption refining, solvent extraction, and hydrogenation refining<sup>4)</sup>.

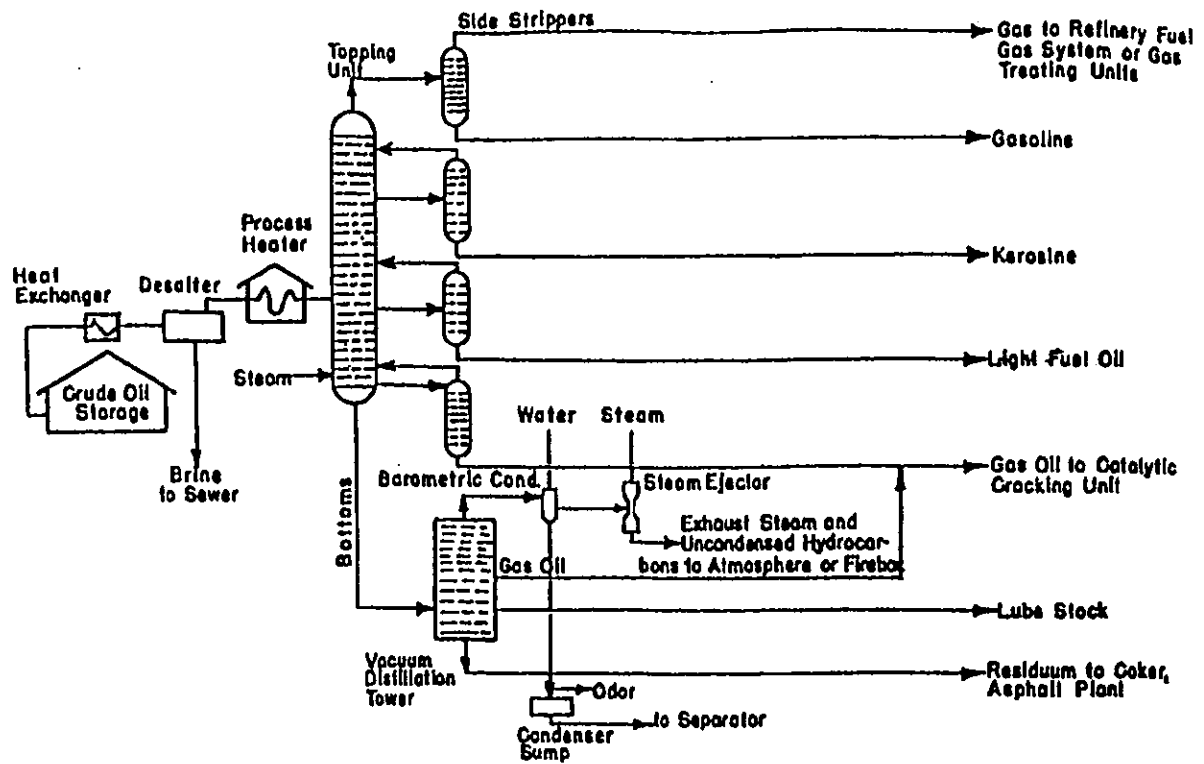


Fig.6.5.1 Outline of Crude Oil Distillation Process

(7) Petroleum Products and Shipping

Many kinds of petroleum product are existing including fuels such as gasoline, kerosene, light oil, jet fuel, heavy oil, and liquefied petroleum gas, lubricating oil, grease, and oil pitch. Fuels are shipped by tankers, tank train, and tank lorries, while lubricating oil and grease are shipped in cans <sup>4) 6)</sup>.

6.5.3 Desulfurization of Heavy Oil

(1) Hydrogenating Desulfurization

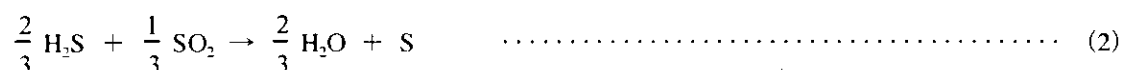
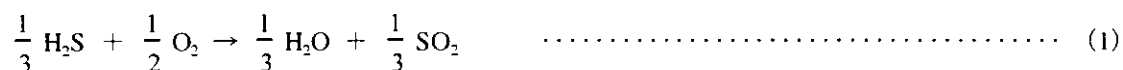
The hydrogenating desulfurization process performed to remove sulfur from heavy oil is very important in the oil refinery operation as a measure for the air pollution control. Compounds of sulfur based on thioalcohol (mercaptane), sulfide and thiophene are contained in the crude oil. Generally, the oil produced in the Middle East contains more sulfur than that produced in Southeast Asia. Also, distillates with higher boiling point contains more sulfur, and more than 80% of sulfur in the crude oil remains in the residual oil at natural pressure. Of course, sulfur remains in every class of distillate (fraction) and is desulfured, but the most important process for air pollution control purposes is the hydrogenating desulfurization of residual oil obtained by topping. This process utilizes the reaction of sulfur compounds and hydrogen at high pressure to form hydrogen sulfide, under the action of catalyst such as Co-Mo/Al<sub>2</sub>O<sub>3</sub>. The hydrogenating desulfurization of heavy oil, which is the most important among the hydrogenating desulfurization, is divided into a direct desulfurization and an indirect desulfurization. The former method desulfurs the entire residual oil and is currently possible to reduce the sulfur content to as small as 0.1%. In

the latter method, the residual oil is separated into reduced pressure light oil and reduced pressure residual oil by a reduced pressure so that the metal contamination of desulfurizing catalyst could be reduced, and only the reduced pressure light oil is desulfured by hydrogenation.

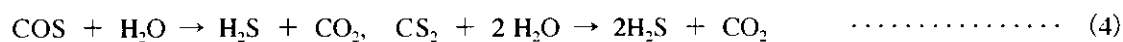
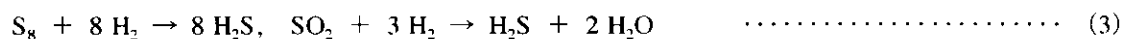
Therefore, the efficiency of desulfurization for the entire natural pressure residual oil is relatively low, and the sulfur content of desulfured heavy oil could be reduced to only about 1% or so. Presently, the technology of direct hydrogenating desulfurization of reduced pressure residual oil is already established.

## (2) Gas Cleaning and Sulfur Recovery

Although most of the gas released from the hydrogenating desulfurization equipment is hydrogen, some hydrogen sulfide and hydrocarbons are also contained. Accordingly, hydrogen sulfide is absorbed by the substance such as aliphatic alkanol amine and recovered after performing separation and condensation processes. A typical process of converting the recovered hydrogen sulfide into elemental sulfur is the Claus method. In this method, one third of hydrogen sulfide is burned in the combustion reaction furnace to form sulfur dioxide and then it is reduced to elemental sulfur by hydrogen sulfide, as shown in Eq.(1) and (2). As the conversion ratio of sulfur in the combustion reaction furnace is relatively low with 60-70%, the unreacted gas is further reacted in the subsequent 2-3 stages of catalytic reactors.



Several thousands ppm of hydrogen sulfide and sulfur dioxide are contained in the tail gas discharged from the Claus equipment, and small amount of COS, CS<sub>2</sub>, and sulfuric acid mist are also contained. The SCOT (Shell Claus Off-gas Treater) process is used to remove those substances. In this process, sulfur dioxide and others are reduced by hydrogen as shown in Eq.(3), and COS and others are decomposed by hydrolysis to recover hydrogen sulfide as shown in Eq.(4), and to recycle the latter to the Claus equipment.



The concentration of unreacted hydrogen sulfide in the exhaust gas from the absorption tower is about 300 ppm, and it is emitted from the combustion furnace as sulfur dioxide. Using the above described Claus process and tail gas treatment process in combination, the recovery efficiency of elemental sulfur from hydrogen sulfide reaches to 99.5-99.8%<sup>7)</sup>.

#### 6.5.4 Air Pollutants

The sources of air pollutant in the oil refinery to be noted are the storage tanks for crude oil and its products. The tanks are classified into a fixed roof type and a floating roof type, and both types of tank release hydrocarbon vapor as a result of the evaporation of oil. In the former type of tank, a roof equipped with internal pressure control valve is fixed to a top of cylindrical steel shell. The oil vapor is filled in the space between the oil surface and roof, and it is released to the atmosphere as the valve opens when the atmospheric temperature, and thus pressure of the space, increases. Also, when the temperature decreases, the gas inside the tank contracts to draw in the outside air. At the same time, the oil vaporizes to saturate the gas phase and the loss occurs. In the fixed roof tank, a certain amount of stored oil is lost by internal gas expansion and contraction caused by daily temperature change, and it is called the breathing loss. The vapor release from the fixed roof tank is also caused by the change in oil level which occurs when oil is supplied to or discharged from the tank. The loss caused by those operations is called the working loss. The floating roof tank has been constructed to prevent this working loss, and all the large crude oil storage tanks now used in the oil refinery belong to this type. The floating roof tank has a cylindrical steel shell and a floating roof that floats on the surface of stored oil. The floating roof that contacts with outside air covers the oil surface completely, and the roof and inside wall of the tank are sealed. The floating roof moves up and down following the movement of oil surface caused by supply and discharge of the stored oil. Evaporation of oil is minimized by the seal against the inside wall and the amount of evaporation is reduced to about 0.2-0.1% of that for the fixed roof tank. Major evaporation loss is caused by the wind around the tank and the evaporation of oil adhered to the inside wall remained when the oil surface lowers as the stored oil is discharged. There is data that about  $0.48 \times 10^{-3}$  kg of oil per 1 kl of discharged oil is released in the air through this loss <sup>6)</sup>.

Such an evaporation loss occurs during the process of loading of the oil fuels, and the oil vapor leaks through flanges, valves and pumps of oil pipeline in the oil refinery facilities. Generally, the evaporation loss is said to differ depending on the maintenance of oil refinery facilities <sup>5)</sup>.

Furthermore, air pollutants are generated in the combustion process of heating furnace (pipe still), catalyst recovery furnace and boiler in the oil refinery. Particularly, carbon particles and fine particulate metal salts could be contained in the exhaust gas of the catalyst recovery furnace. The source substance of offensive odor in the oil refinery is mainly hydrogen sulfide and mercaptane. The sources and counter measures for these substances are shown in Table 6.5.2 <sup>8)</sup>.

Table 6.5.2 Sources and Counter Measures for Offensive Odor in Oil Refinery

Equipment/Facility	Source	Counter Measure
Refining Facility	Offensive odor occurs at steam purge for the open inspection of the facility.	Condensation→Separation of Gas Phase→Gas Phase→Combustion→Liquid Phase→Drain
Tank	<p>① Offensive odor substances evaporate associated with evaporation loss from the fixed roof tank. Crude oil and crude naphtha containing offensive odor substances are generally stored in the floating roof tank.</p> <p>② Hydrogen sulfide is generated from the liquid sulfur tank.</p> <p>③ Characteristic smell is generated from the vent of asphalt tank.</p>	<p>① Absorption, adsorption, etc.</p> <p>② Absorption by sodium hydroxide solution.</p> <p>③ Combustion, absorption, etc.</p>
Shipping Facility	<p>① Hydrocarbon smell is generated at the loading of gasoline to the lorry.</p> <p>② Offensive odor is generated from hold and vent of the ship at oil loading works.</p>	<p>① Condensation, absorption balance line, etc.</p> <p>② Absorption by sodium hydroxide or kerosene.</p>
Drain Treatment Facility	Offensive odor substances dissolved into the drainage come up from oil separator, pressurized float up tank, and activated sludge aeration tank.	Attachment of cover to the tank, absorption or adsorption after sucking in by blower.