

CHAPTER II

THEORETICAL CONSIDERATIONS

White Oil

White oil or white mineral oil called mineral oil is transparent, colorless or almost colorless, almost odorless, oily liquid obtained by the refining of crude petroleum feedstocks boiling point in the same range as the lubricating oil. In the production of white oil the petroleum feedstocks are refined to eliminate as completely as possible sulfur, nitrogen, and oxygen compounds, reactive hydrocarbons including aromatics, and any other impurities which would prevent use of the resulting white oil.

1. Classification and Specification [2,3]

There are three classes of white oils, recently defined by the UK white oil Association as follows:

1) Medicinal or Pharmaceutical grade- a highly refined transparent, colorless (Saybolt +30 minimum) mineral oil, almost odorless and tasteless, complying with the requirements for Liquid Paraffin (light, medium, heavy) of a relevant Pharmacopoeia.

2) Food grade- oil as described above, not necessarily complying with Pharmacopoeia requirements in respect of viscosity, although it should not be below 5 centistokes at 40°C.

3) Technical grade- a highly refined transparent, almost colorless (Saybolt +20 minimum) oil having a viscosity not below 5 centistokes at 40°C.

The specifications of each grade white oil of U.S. Food and Drug Administration (FDA) are shown in Table 2.1.

Table 2.1 Specifications of white oils.

Properties	Medicinal grade	Food grade	Technical grade
Saybolt color	+30 min.	+30 min.	+20 min.
Viscosity, cSt at 100°F (40°C)	38.1 min.	5.0 min.	5.0 min.
Density at 15.6°C, g/cm ³	0.845-0.905	0.845-0.905	-
Carbonizable substances	pass	pass	-
UV absorption of DMSO extract			
at 260-420 nm	0.1 max.	0.1 max.	-
280-299 nm	-	-	4.0 max.
290-299 nm	-	-	3.3 max.
300-329 nm	-	-	2.3 max.
330-350 nm	-	-	0.8 max.
Direct UV absorptivity ^a			
at 275 nm	1.60 max.	1.60 max.	-
295 nm	0.20 max.	0.20 max.	-
300 nm	0.15 max.	0.15 max.	-

^aspecification of Germany

2. Application

White oils are used in a wide range of applications and industries. Technical grade white oil is used in plastic industries as extender and plasticizer, in textile machineries as lubricating oil of synthetic fibre processing. Also used for leather processing, paper manufacture, wax polishes, agricultural spray boxes, mould release agents ect. Both food grade white oil and medicinal grade white oil are used in food industries as lubricate machinery and food packing materials, in cosmetics as a carrier or base for a wide variety of creams (beauty, cleaning, make-up, barrier, etc.), hair preparations, lipsticks, etc., and used as ingredient or processing aids in manufacture of industrial skin protections, toiletries and veterinary preparations. Moreover medicinal grade white oil is used in drag compositions which the well known are used as a laxative, and used in many preparations including balms, ointments paste bandages, etc.

3. Properties

3.1 Physical properties [4-6]

1) Specific gravity

Specific gravity of oil is defined as the ratio of its density to the density of water at a specified temperature. The standard temperature is 15.6°C or 60°F. In the petroleum industry the API gravity scale is almost universally used as the measure of the density of petroleum products. API

gravity is an arbitrary scale, calibrated in degree and related to specific gravity by

$$\text{API} = \frac{141.5}{\text{sp. gr.}} - 131.5$$

(at 15.6°C)

The API gravity value increases as the specific gravity decreases. Since both density and gravity change with the temperature, determinations are made at a controlled temperature and corrected to a standard temperature by using standard table.

2) Viscosity

Viscosity of fluid is a measure of its internal resistance to flow by reason of the forces of cohesion between molecules. It decreases with increasing temperature and decreasing pressure. The instrument used to determine the viscosity of oil is called the viscometer. Generally, two types are Saybolt and Kinetic viscometers. Kinetic viscosity is the more common and measured by timing the flow of a fixed amount of oil through a capillary tube under gravitational force at a standard temperature. Test temperatures are usually at 40°C and 100°C for centistokes unit.

3) Viscosity index

The viscosity index is an empirical number which indicates the effect of temperature changing on the viscosity of the oil. When the temperature is increased, oil films thin out or has lower viscosity. The higher the viscosity index, the smaller its change in viscosity for given change in temperature. The viscosity index of oil is calculated from viscosity determined at two temperatures by means of table published by ASTM.

4) Pour point

The pour point is the lowest temperature at which the oil will just flow under specified test condition, and is roughly equivalent to the tendency of oil to cease flowing from a gravity-fed system or container. Since the size and shape of the containers, the head of oil, and the physical structure of the solidified oil all influence the tendency of the oil to flow, the pour point of the oil is, and not an exact measure of, the temperature at which flow ceases under the service conditions of a specific system. The importance of the pour point is limited to application where low temperature are likely to influence oil flow.

5) Color [7,8]

White oil is colorless. Its color is measured as Saybolt color, a number related to the depth of a column of material which color is compared with specified glass standard. The range of number is +30 (lightest color) to -16 (darkest color). If oil is darker than the Saybolt color -16, its color is measured as Visual color. It is a number compared the color of the transmitted light with that transmitted by series of numbered glass standard. Color varies from partially clear or transparent to opaque or black. The range of the number is 0 to 8. The lower number is indicated that the color of oil is lighter.

3.2 Chemical properties [3,9,10,11]

The three most important tests are designed to determine the purity of white oil as follows.

1) Light absorption

This method is measurement of direct ultraviolet absorption over the range from 295 to 400 nm. It is a very sensitive means of detecting the presence of aromatic compounds. It is reported as the value of absorptivity, an absorbance per unit of the concentration of 1 g/L of white oil in iso-octane and of 1 cm of path length of cell. If the absorptive is low, the white oil is high purity. This test involves medicinal and food grade white oils of Germany.

2) Limit of polynuclear compounds

This method describes a procedure for the examination and evaluation of white oils. A mixture of 25 ml of white oil and 25 ml of hexane is extracted with 5 ml of dimethyl sulfoxide and the ultraviolet absorbance of the extract is determined in the range from 260 to 420 nm for food and medicinal grade white oils and from 280 to 350 nm for technical grade white oil. The absorbance specifications of white oils are shown in Table 2.1.

3) Carbonizable substances

It is necessary for food and pharmaceutical grade white oils to test carbonizable substances. White oil is shaken with an equal volume of acid of prescribed strength under specified conditions. It shall be reported as passing the test only when the oil layer shows no change in color and when the acid layer is not darker than the reference standard colorimetric solution. If the oil layer is discolored or if the acid layer is darker than the reference standard colorimetric solution, white oil shall be reported as not passing the test. It is considered an indication of purity, the purest products developing very little color.

4. Processing [3]

White oil can be produced from most types of crude oil, in varying yields and degrees of difficulty, by two types of process- acid treatment and hydrotreatment.

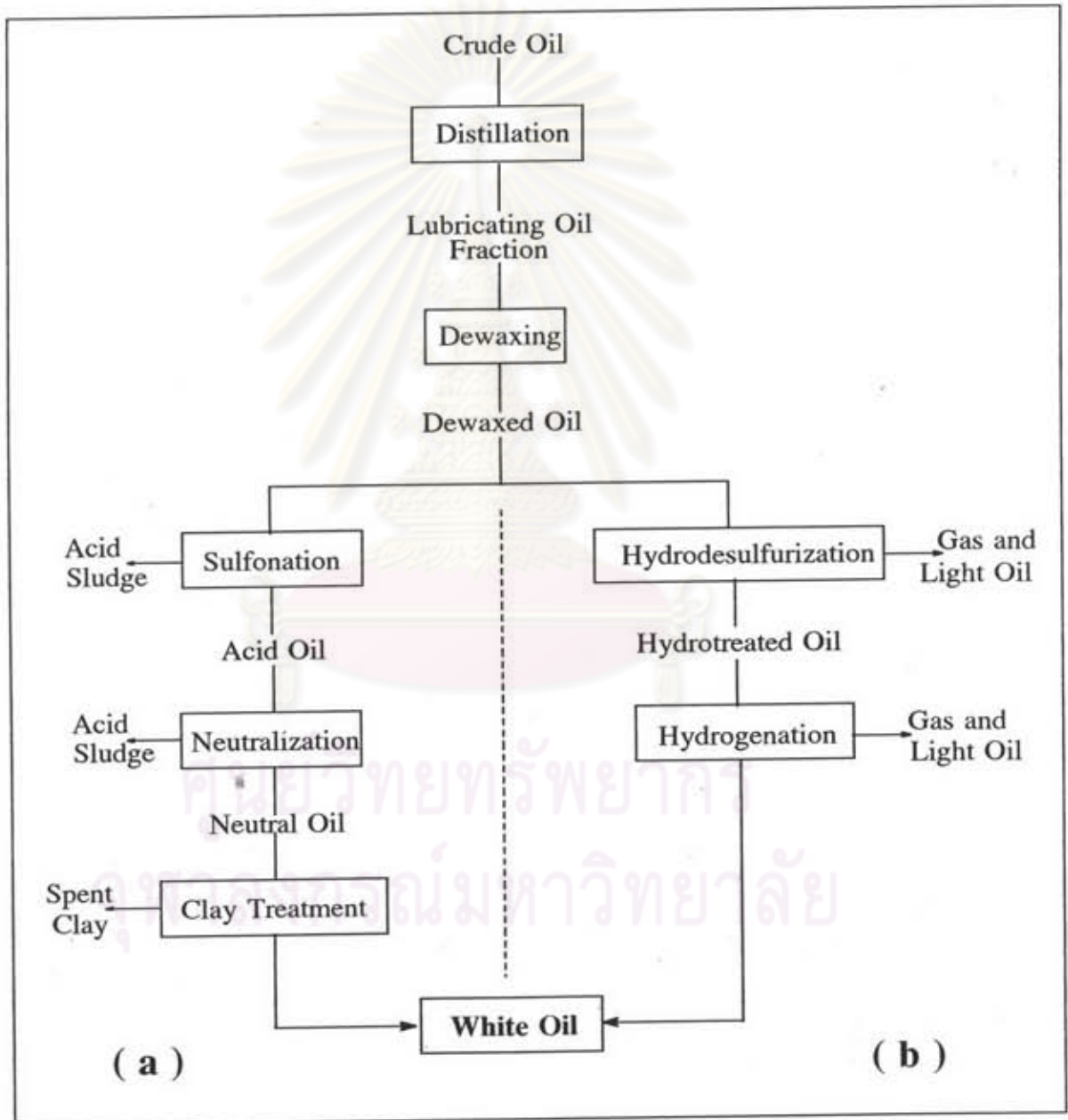


Figure 2.1 Processes for production of white oil

a) Acid treatment

b) Hydrotreatment

Generally, the first step of production of white oil in both processes has been the removal of lighter portions, such as gasoline, naphtha, kerosene, and light fraction, from crude oil by fractional distillation. If the crude oil contains wax, it is preferably dewaxed by using a solvent, such as methyl ethyl ketone, methyl iso-butyl ketone, toluene, etc., to obtain oils with a pour point below about -15°C . After dewaxing, it is necessary to determine the pour point by that required in the finished oils.

The first type process in the production of white oil is acid treatment. This process is essentially one of removal of compounds containing unsaturated and unstable aromatic compounds which comprised most of impurities present in the oily. The process involves the treatment of a suitable dewaxed crude oil or other feedstock with acidic compounds, such as sulfuric acid, gaseous sulfur trioxide and/or oleum, in a multi-stage process. Acid sludge is formed in the reaction, and has to be removed prior to neutralization step, which is carried out using an aqueous, alcoholic solution of sodium hydroxide. This removes the oil-soluble sulfonic acids formed in the operation, in the form of their sodium salts, which constitute a valuable by-product. The neutralized oil is finally contacted with activated bleaching earth, which produces the required white oil. The conventional methods of making white oil with acid, however, have been subject to objection in recent years since acid treatment is costly, low product yield, high sulfonate by-product, large quantities of acid sludge disposal and pollution problems. Furthermore, such processing of high viscosity fraction is very difficult because of emulsion and setting problems encountered during the operation.

some helium). The intermediate zone contains oil saturated with dissolved gas under the conditions of temperature and pressure prevailing in the reservoir rock; and the bottom zone is occupied by “connate” or “interstitial” water, traces of which are also present in the pore of reservoir rock in the oil and gas zones. Oilfield waters (or “brines”) contain relatively large amounts (frequently more than 10^4 ppm) of dissolved inorganic salts principally chlorides and sulfates of sodium, potassium, calcium, and magnesium.

The petroleum that flows from our wells today was formed many millions of years ago. It is believed to have been formed from the remains of tiny aquatic animals and plants that settled with mud and silt to the bottoms of ancient seas. As successive layers built up, those remains were subjected to high pressures and temperatures and underwent chemical transformations leading to the formation of the hydrocarbons and other constituents of crude oil.

2. Appearance and Composition [3,6,13]

Physically, crude oil is found in a variety of types ranging from light, mobile, straw-colored liquids containing a large proportion of easily distillable material to highly viscous, semi-solid black substances from which very little material can be removed by distillation before the onset of thermal decomposition. Densities generally lie in the range $0.79\text{-}0.95\text{ g/cm}^3$ under surface condition, and viscosity varies widely, from about 0.7 centipoise to more than 42000 centipoise.

highly-branched paraffins are high pour point and less good viscosity index. Both of them are lower in specific gravity, or higher in API gravity than the others.

- Olefins or alkenes

They are unsaturated molecules, but are comparatively rare in crude oil. Certain refinery process, however, do produce long amounts of paraffins by cracking or dehydrogenation. They are more chemically active than the others and subject to oxidation or polymerization forming gums.

- Naphthenes or cycloalkanes

They are saturated cyclic structures based on five- or six-member rings. They have rather high density and viscosity but low pour point and viscosity index. Also they are extremely stable compounds.

- Aromatics

They are cyclic structures with conjugated double bonds, based on the six-membered benzene ring. They have density and viscosity which are still higher. Viscosity index is in general rather poor but pour point is low.

2) Non-hydrocarbons

Non-hydrocarbons in crude oil incorporate other elements sometimes or as functional groups attached to hydrocarbon structures. Sulfur compounds are generally much more prevalent than nitrogen- or oxygen- contain in molecules. Within the boiling range appropriate to light distillate almost all of the sulfur and nitrogen compounds are heterocyclic molecules. In contrast, the principal oxygen contain molecules are carboxylic acid. In the production of white oil, these compounds, including olefins and aromatics, are removed.

The second type process is hydrotreatment. This process eliminates by-product disposal and pollution problems and advantageously is capable of handling high viscosity feedstocks. The first hydrotreating stage is a catalytic hydrodesulfurization, which, after removal of hydrogen sulfide, formed in take process is followed by topping operation which removes the low boiling compounds, and produces an oil of satisfactory volatility and viscosity. The second hydrotreating stage is a deep catalytic hydrogenation operation, which ensures the complete saturation of all aromatic hydrocarbons present. The process of this invention has been found to be particularly effective in providing technical, food and medical grade white oil of high quality and high yield greater than about 90%.

Crude Oil

1. Origin [3,12]

Petroleum is natural organic material composed principally of hydrocarbons which occur in the gaseous or liquid state in geological traps; the liquid part, after being freed from dissolved gas, is commonly referred to as crude oil. Underground reservoirs adopt various forms, and the oil is usually associated with natural gas and brines. In a typical dome-shaped formation, the fluids occupying the interstices in the rock are arranged in order of increasing density with ill-defined boundaries between zones. Uppermost is the gas zone or cap which contains so-called associated (i.e. with oil) natural gas; this comprises low molecular weight alkanes-methane (predominantly) plus its C_2 - C_7 homologous: ethane, propane, butanes, pentanes, hexanes, and heptanes)-together with inorganic gas (carbon dioxide, nitrogen, hydrogen sulfide, and

Crude oil consists of a very complex mixture of saturated and unsaturated hydrocarbons with minor amounts of non-hydrocarbons consisting chiefly of sulfur, nitrogen and oxygen. Also organometallics are usually present as traces. Examples of these types are shown in Figure 2.1

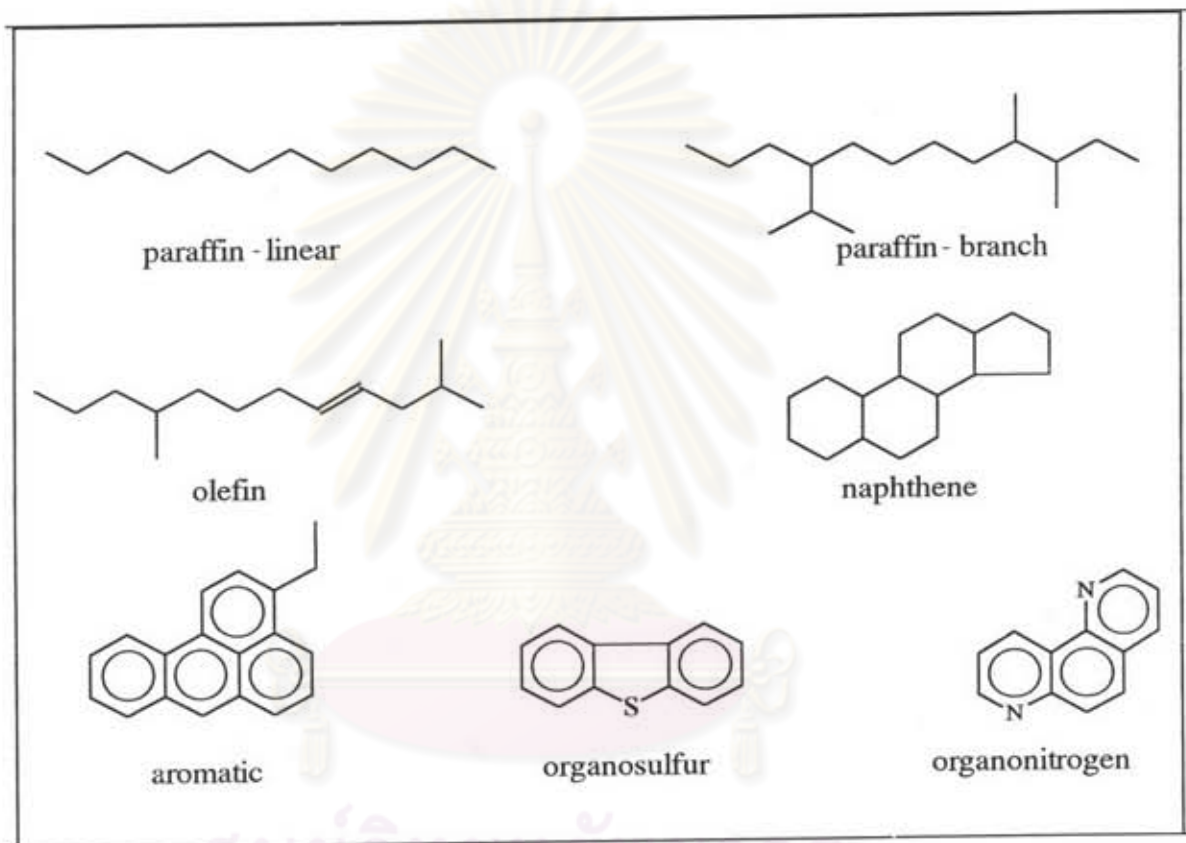


Figure 2.2 Typical organic compounds in crude oil.

In Figure 2.2, the following are the same of the different properties of these compounds.

1) Hydrocarbons

- Paraffins or alkanes

They are saturated linear or branched chain structures.

The linear paraffins have high viscosity index and low pour point. In contrast,

The boiling ranges of the compounds increase roughly with the number of carbon atoms:

- 1) Far below -18°C (0°F) for the light natural gas hydrocarbon with one to three carbon atoms.
- 2) About 27 to 204°C (80 - 400°F) for gasoline components.
- 3) 204 to 343°C (400 - 650°F) for diesel and home heating oils.
- 4) Higher ranges for lubricating oils and heavier fuels.

3. Refining Process [6,15,16]

Crude oil is sometimes used such as for fuel in power plants; but in most cases, it is separated into many fractions, which in turn require further processing to supply the larger number of petroleum products needs. In many cases, the first step is to remove from the crude certain inorganic salts suspended as minute crystals or dissolve in entrained water. These salts break down during processing to form acids that severely corrode refinery equipment, plug heat exchangers and other equipment, and poison catalysts used in subsequent process. Therefore, the crude is mixed with additional water to dissolve the salts and the resultant brine is removed by settling.

After desalting, the crude is pumped through a tubular furnace (Figure 2.2) where it is heated and partially vaporized. The refinery usually consists of connected lengths of pipe heated externally by gas or oil burners. The mixture of hot liquid and vapor from the furnace enters a fractionating column. This is a device that operates at a slightly above atmospheric pressure and separates groups of hydrocarbons according to their boiling ranges. The fractionating column works because there is a graduation in temperature from bottom to top so that, as the vapors rise toward the cooler upper portion, the

higher boiling components condense first. As the vapor stream moves up the column, lower boiling vapors are progressively condensed. Trays are inserted at various levels in the column to collect the liquids that condense at those levels. Naphtha, an industry term for raw gasoline that requires further processing, and light hydrocarbons are carried over the top of the column as vapor and are condensed to liquid by cooling. Kerosine, diesel fuel, home heating fuel, and heavy oils (called gas oils) are withdrawn as side cuts from the successively lower and hotter levels of the tower.

A heavy black, atmospheric residuum is drawn from the bottom of the column. Because the tendency of residuum to decompose at temperature about 371°C (700°F) heavier (higher boiling) oils must be distilled off in a separate vacuum fractionating tower. The greatly reduced pressure in the tower markedly lowers the boiling points of the desired hydrocarbons compounds. Bottom materials from the vacuum tower are for asphalt, or are further processed to make other products. The fraction separated by crude distillation are sometimes referred to as "straight run" products. The character of their hydrocarbon constituents is not changed by distillation.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

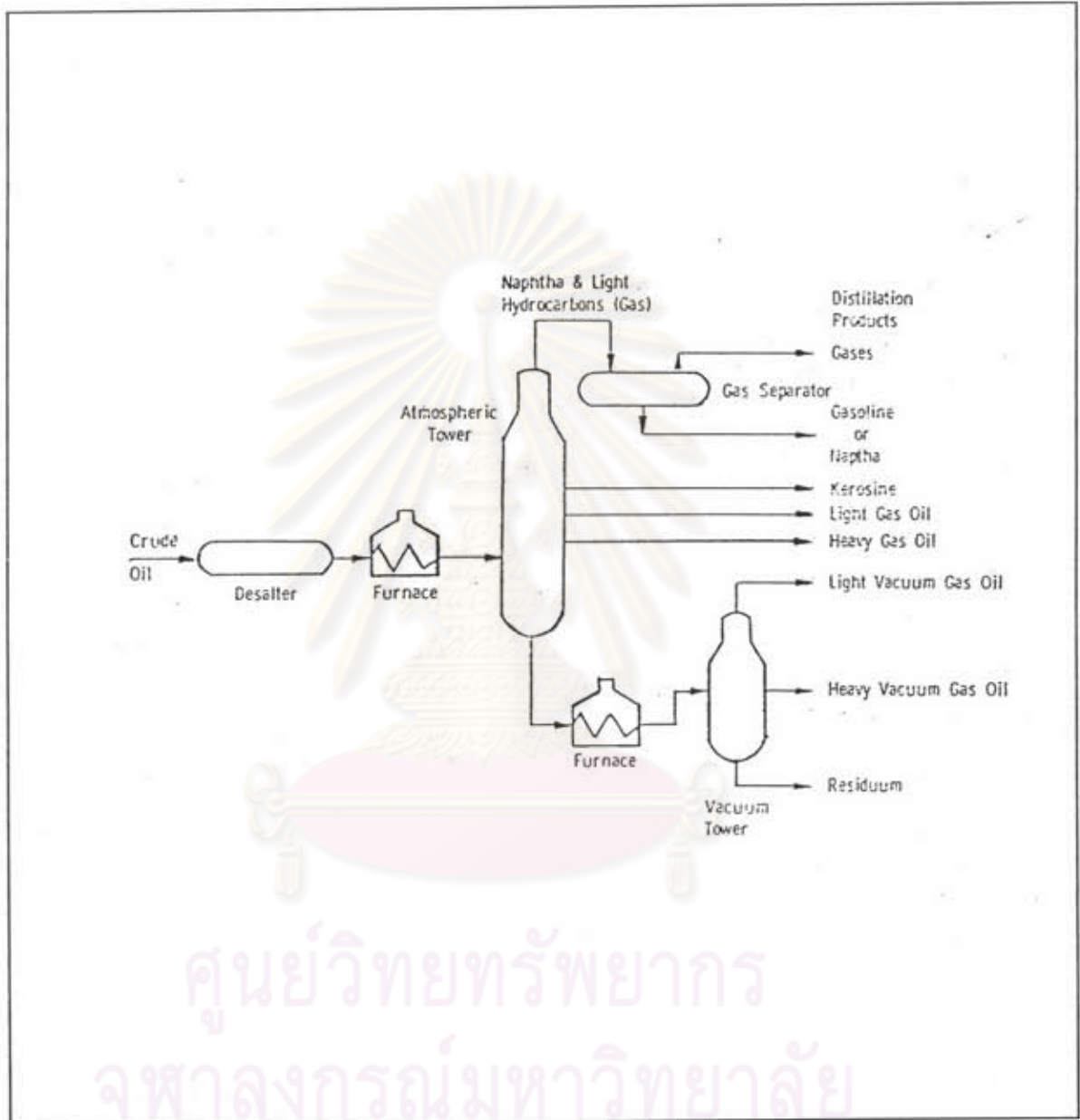


Figure 2.3 Crude distillation unit.

4. Fang Refinery [4,17]

Up to 1500 barrels of local crude oil can be refined at Fang Refinery per day. The refinery products are consisting of

- straight run oil 6%
- diesel 26%
- light distillate 17%
- heavy distillate 14%
- heavy fuel oil 37%

The process consists of several operation units including

Topping distillation unit

Vacuum distillation unit

Gasoline treating unit

Gasoline blending unit

Power unit

Facilities unit

Once crude oil from Mae Soon Huang is shipped to Fang Refinery, the water will be separated in the separation unit where treat-o-lite is used as an emulsifier. After that, the crude is pumped through a preheat exchanger and its temperature raised to about 120°C by exchanging with hot oil from the vacuum tower. It is then further heated to 340°C in an atmospheric heater (H-1) and charged to atmospheric fractions. The liquids withdrawn from this tower will contain straight run oil, kerosene and diesel. Reduced crude from the bottom of the atmospheric tower is sent to a vacuum heater (H-2) and its temperature raised to 365°C and is then charged to a vacuum tower where it is separated into light distillate, heavy distillate and heavy fuel oil.

Hydrotreating Process

Hydrotreating process involves the reaction of compounds with hydrogen in the presence of catalyst. The types of reaction that occur in this process are shown in Figure 2.4. [18]

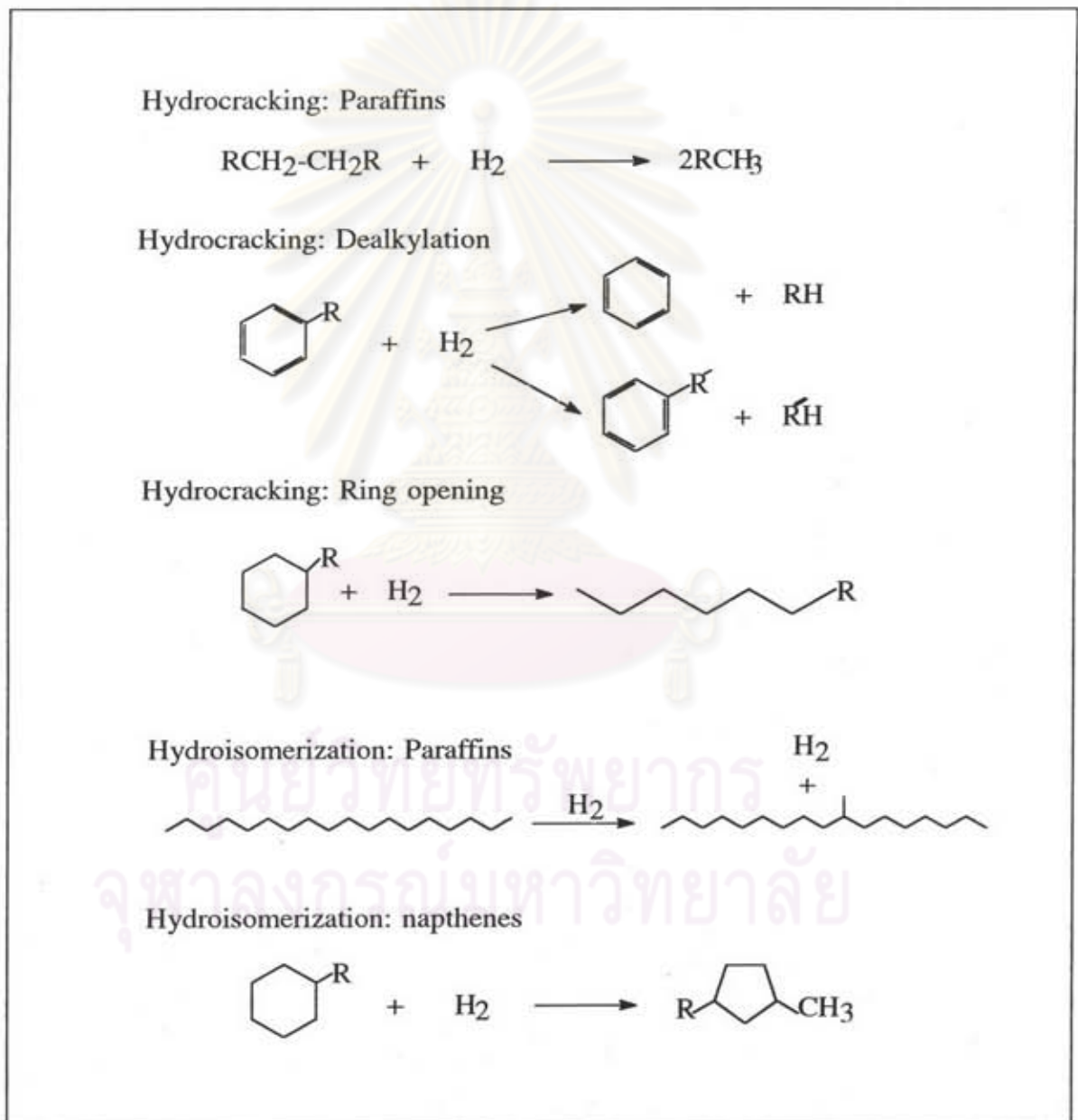
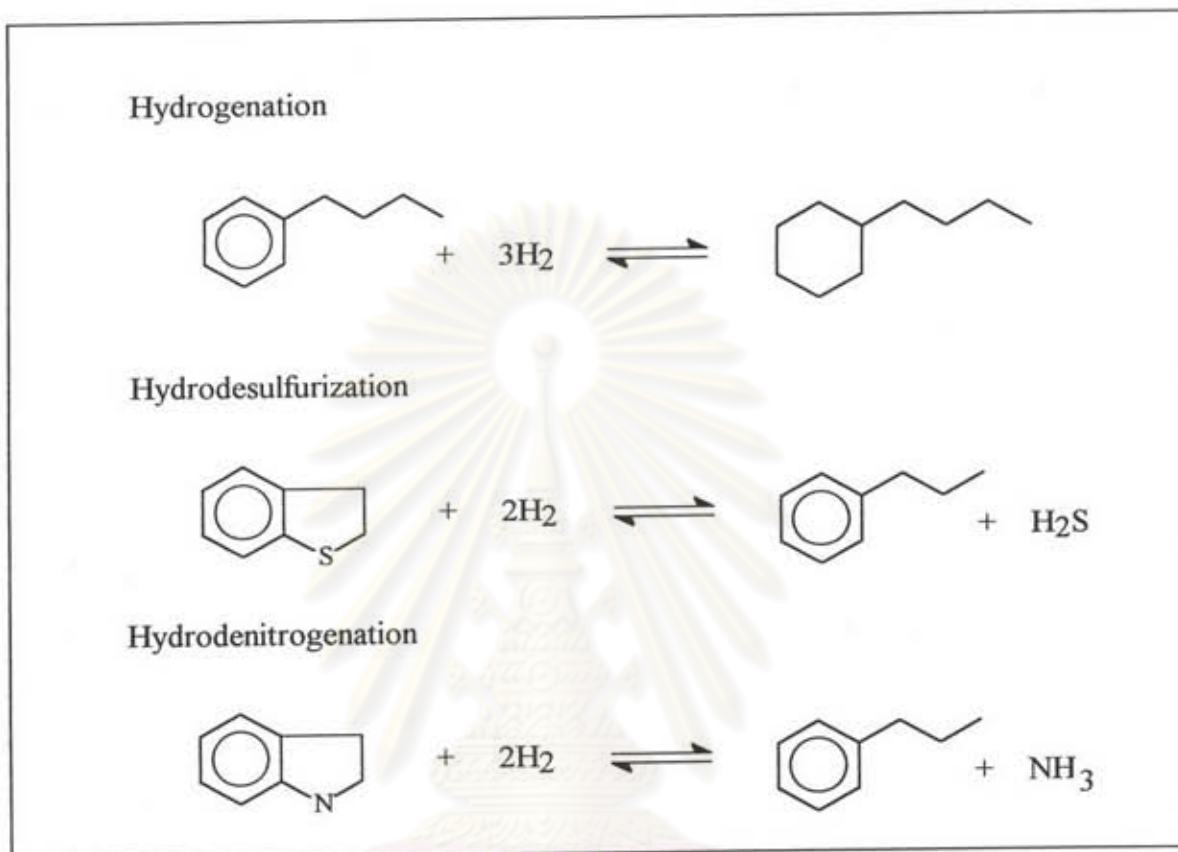


Figure 2.4 The types of reaction in hydrotreating process.

Figure 2.4 Continued.

White oil can be produced by hydrotreating process in two stages of hydrodesulfurization and hydrogenation.

1. Hydrodesulfurization Stage

1.1 Hydrodesulfurization Reaction [18,19]

Hydrodesulfurization is a reaction between sulfur compounds and hydrogen with the presence of a catalyst to produce hydrocarbons and hydrogen sulfide. Sulfur compounds in light distillate are mainly heterocyclic, having an aromatic character. The reaction of these compounds appears to start.

by the saturation of the heterocyclic. The ring is then cleaved to give hydrogen sulfide and the corresponding hydrocarbons. The following is examples illustrating some of reaction of sulfur compounds during hydrodesulfurization.

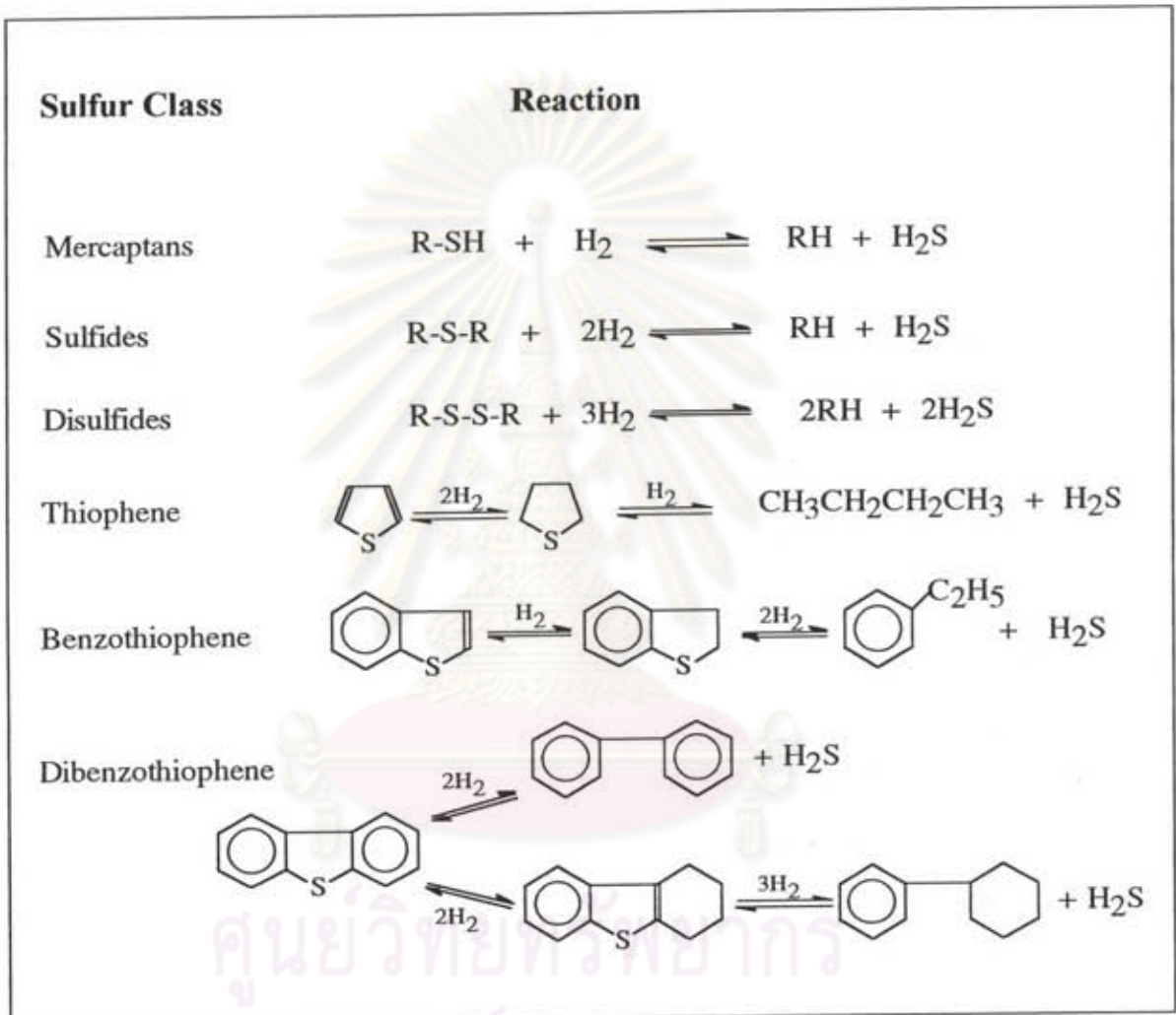


Figure 2.5 Hydrodesulfurization reaction.

The main objection in this stage is to remove sulfur compounds. However, hydrodenitrogenation, hydrooxygenation, and hydrogenation occur simultaneously. Generally, in light distillate, there are the amount of sulfur compounds more than other non-hydrocarbon compounds. This stage is called

hydrodesulfurization stage. To prevent the poison on catalyst in hydrogenation stage, sulfur content in feedstocks will be have dropped to less than 50 ppm and more preferably to less than 10 ppm. In plant run size practice, it is preferable to reduce the sulfur content down to less than 1 ppm. Catalyst poisoning typically results from strong chemisorption on the surface of metal. The adsorbed poison either blocks the chemisorption of reactants or blocks the desired reactions. Thus sulfur, oxygen, and nitrogen elements which form very stable compounds with the metal surface are typically severe poisons. Sulfur is the most prominent of these because of the great stability of metal sulfides. In addition cracking reaction can occur to a limited extent at start-of-cycle but become more important as temperatures are raised to maintain catalyst activity.

1.2 Hydrodesulfurization Catalyst [19-23]

The catalysts of hydrodesulfurization in the first stage can be of any of the sulfur resistant non-precious metal hydrotreatment catalysts some of which are conventionally employed in the hydrotreatment of both light and heavy petroleum oils. These catalysts typically comprise a major amount of a support and at least one non-precious metallic component in an amount effective to promote the hydrogenation of the mineral oil distillate. Examples of suitable catalytic ingredients are tin, vanadium, members of Group VI-B in the Periodic Table, i.e. chromium, molybdenum and tungsten, and metals of the iron group, i.e. iron, cobalt and nickel. These metals are often present in catalytically effects the specific examples below illustrate, these catalytic ingredients are generally employed while disposed on a suitable carrier of the solid oxide refractory type, e.g. a predominantly calcined or activated alumina. Commonly employed catalysts have about 1 to 10% of an iron group metal and

5 to 25% of a Group VI-B metal (calculated as the oxide). Advantageously, the catalyst is cobalt molybdenum (CoMo) or nickel molybdenum (NiMo) supported on alumina. CoMo catalyst is by far the most popular choice for hydrodesulfurization, particularly for straight-run petroleum fractions. NiMo is often chosen instead of CoMo when higher activity for polyaromatics saturation or nitrogen removal is required, or when more refractory sulfur compounds such as those in cracked stocks must be hydrodesulfurized. In some applications, nickel molybdenum cobalt (NiMoCo) catalyst appears to offer a useful balance of hydrotreating activity. Nickel tungsten catalyst (NiW) is usually chosen only when very high activity for aromatics saturation is required along with activity for sulfur and nitrogen removal. However, NiW catalyst has not had wide application because of its relatively high cost. The metallic component can be employed either as the metals or as the oxides or sulfide of such metals.

Although various solid refractory type carriers known in the art may be utilized as a support for the first and the second catalyst, the preferred support comprises a major amount of calcined, or otherwise activated, alumina. It is preferred that the alumina have a surface area of from about 25 m²/g to about 600 m²/g or more. The support comprises a major proportion of each catalyst, preferably at least about 60%, by weight of the first catalyst, and preferably at least about 80%, more preferably at least about 90%, by weight of the second catalyst. The alumina may be derived from hydrous alumina predominating in alumina trihydrate, alumina monohydrate, amorphous hydrous alumina and mixtures thereof, which alumina when formed as pellets and calcined, has an apparent bulk density of from about 0.60 g/ml to 0.85 g/ml, pore volume from about 0.45 ml/g to about 0.70 ml/g, and surface area from about 50 m²/g to about 500 m²/g. The alumina supports may contain,

in addition, minor proportions of other well-known refractory inorganic oxides such as silica, titania, zirconia, magnesia, natural or activated clays (such as kaolinite, monotonmorillonite, halloysite, etc.) and the like. However, the preferred supports are substantially pure alumina derived from hydrous alumina predominating in alumina monohydrate, amorphous hydrous alumina and mixtures thereof. More preferably, the alumina is derived from hydrous alumina predominating in alumina monohydrate.

1.3 Mechanism of Hydrodesulfurization Reaction [24]

The mechanism of hydrodesulfurization reaction based upon the remote control concept was the first proposed by Delmon. The concept distinguishes between the role of two types of species on the catalyst. One is active in creating spill-over hydrogen and the other is catalyzing the reactions. The spill-over hydrogen is created on the former phase(donor) and then migrates to the later phase(acceptor), where different types of active sites are created by the spill-over hydrogen. The donor is much less active than the acceptor in catalyzing the reactions.

For Co-Mo-S/alumina catalyst, the cobalt sulfide phase acts as donor of spill-over hydrogen, while the molybdenum sulfide phase acts as the acceptor. The activation of the catalyst consists of three steps: generation of spill-over hydrogen on the cobalt sulfide phase, migration of spill-over hydrogen from the cobalt sulfide phase to the molybdenum sulfide phase, and activation of the molybdenum sulfide phase by the spill-over hydrogen.

1) Generation of spill-over hydrogen on the cobalt sulfide phase

Spill-over hydrogen has been commonly accepted to be atomic hydrogen formed by the dissociative adsorption of molecular hydrogen. The atomic hydrogen may be an ionic, a radical or a bounded hydrogen, depending upon the circumstances. The hydrogen in the gas phase in the first dissociatively adsorbed on the cobalt sulfide phase. The atomic hydrogen then spill-over to the catalyst support and to the nearby molybdenum sulfide phase. This is considered to be intrinsically much slower than the former step.

2) Migration of spill-over hydrogen from the cobalt sulfide phase to the molybdenum sulfide phase

Spill-over hydrogen formed on the cobalt sulfide phase can migrate to the molybdenum sulfide phase. The driving force for this migration is the concentration difference of spill-over hydrogen between the two phases. The mass transfer rate also depends on the interfacial surface area of the two phases. The latter is a function of the dispersions of cobalt and molybdenum sulfide phases and the degree of contact between the two phases. The dispersion is reflected in the surface area, and the degree of contact is reflected in the size of interfacial area per unit product of unit surface areas. Therefore, the interfacial surface area between cobalt and molybdenum sulfide phases is proportional to the product of both unit surface area and the unit interfacial area.

3) Activation of the molybdenum sulfide phase by the spill-over hydrogen.

Delmon proposed the existence of three types of sites on the molybdenum sulfide phase during hydrodesulfurization: unreduced, weakly reduced, strongly reduced sites. Before the reduction by spill-over hydrogen, the unreduced site is only potentially active in the hydrodesulfurization reactions. It can be weakly reduced to a site, active in hydrogenation only, or strongly reduced a site, active in hydrogenolysis.

Spill-over hydrogen on the molybdenum sulfide phase may be involved in various types of reactions. Firstly, it is needed in the creation of hydrogenation sites and hydrogenolysis sites. The weakly reduced and strongly reduced sites are created by the reaction of unreduced and weakly reduced sites, respectively, with spill-over hydrogen on the molybdenum sulfide phase. During the site conversion, sulfur atoms of the molybdenum sulfide phase are rearranged and may be rejected into the gas phase as hydrogen sulfide.

The catalyst support plays an important role in the catalyst activity. It influences the dispersion and contact of cobalt and molybdenum sulfide phases and may interact with the cobalt and molybdenum sulfide phases. Spill-over hydrogen may be consumed on the catalyst support through the recombination and desorption of spill-over hydrogen.

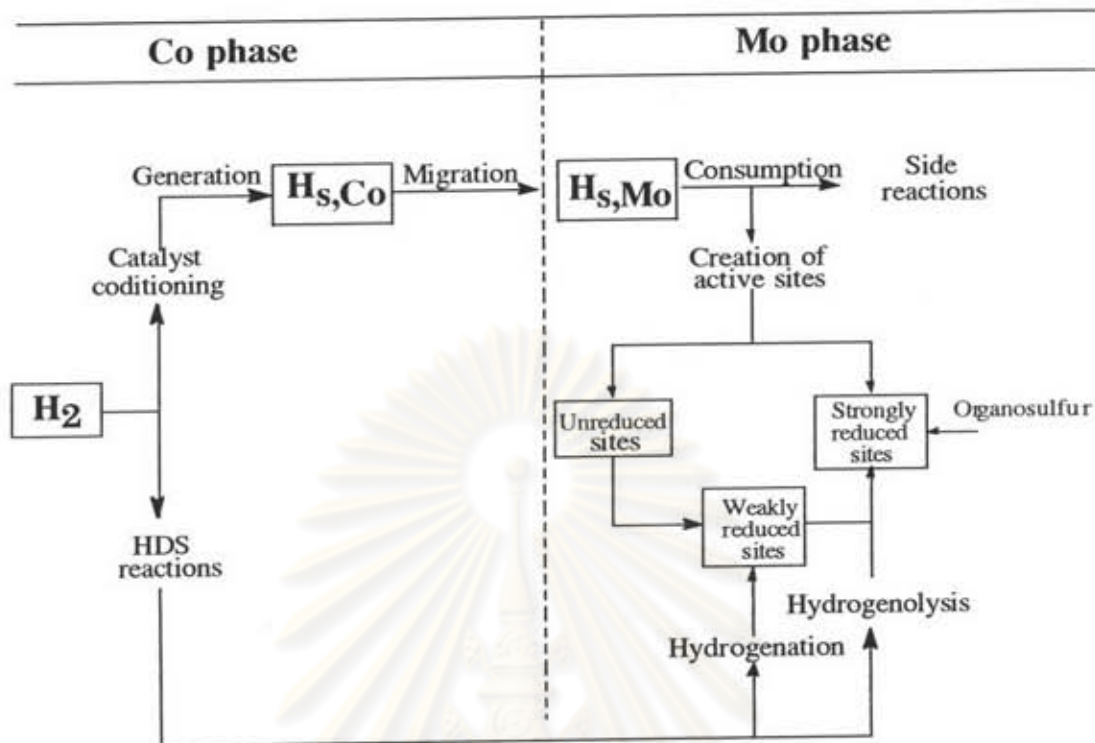


Figure 2.6 Flow diagram of the overall mechanism of hydrodesulfurization.

If NiW/alumina or NiMo/alumina is used as the catalyst for hydrodesulfurization, Ni can replace Co and W can replace Mo in these mechanisms.

2. Hydrogenation Stage

2.1 Hydrogenation Reaction [18,19]

In the hydrogenation stage, the product from the first stage is contacted with hydrogen in the presence of highly efficient hydrogenation catalyst such as platinum group metals to ensure the complete saturation of all aromatic hydrocarbon present. Example of hydrogenation reaction are shown

in Figure 2.7. However in hydrodesulfurization stage may produce saturated hydrocarbons.

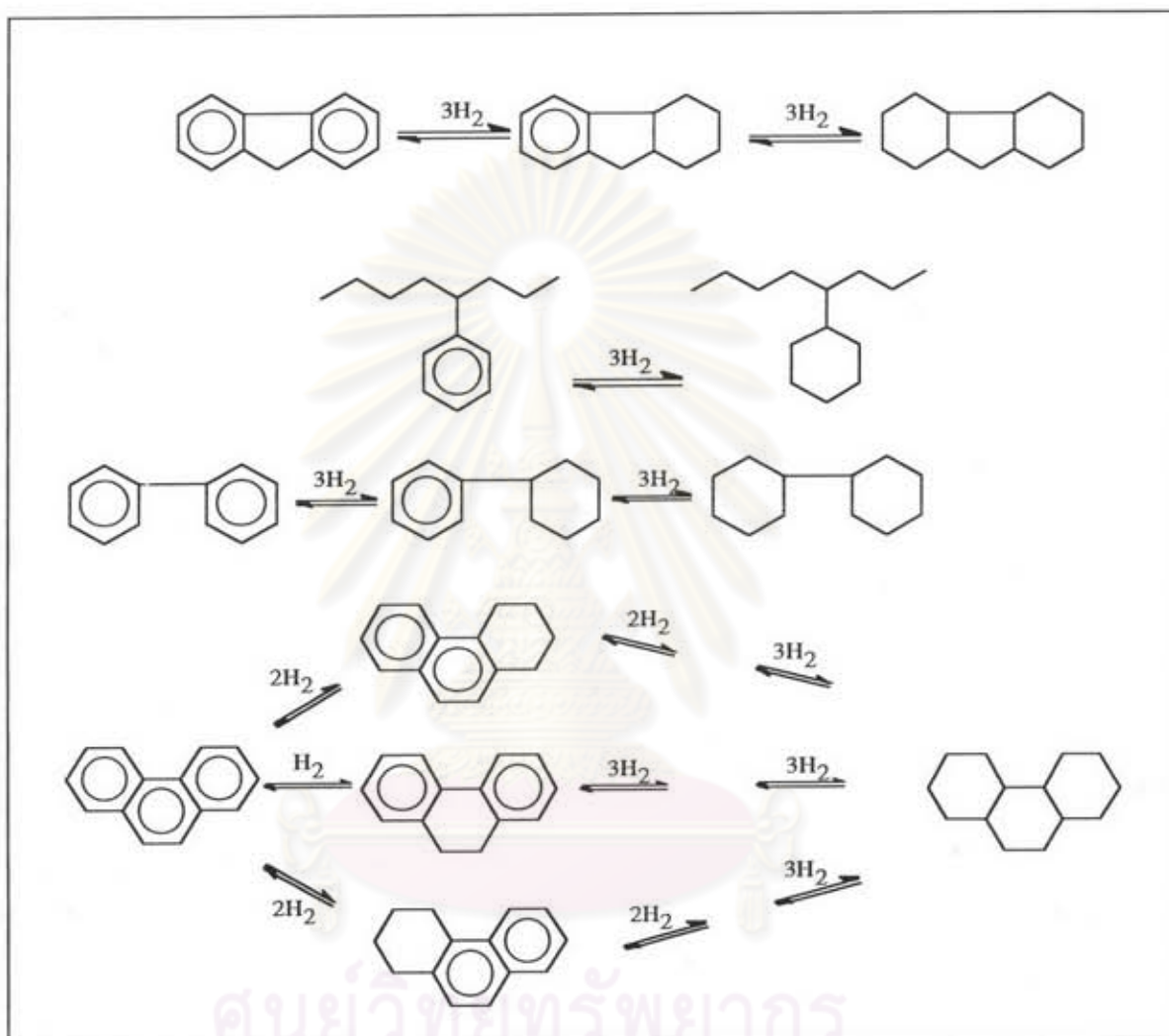


Figure 2.7 Hydrogenation of aromatic compounds.

2.2 Hydrogenation Catalyst [25]

The hydrogenation catalyst in the second stage comprises a major amount of a support, a catalytically effective amount of a platinum group metal component, and a minor amount of at least one halogen component

present in an amount sufficient to improve the hydrogenation activity of the catalyst. This second catalyst is to be distinguished from the first catalyst in that normally considered to be the sulfur-resistant catalyst. The catalyst includes catalytically effective amounts of the platinum group metals of Group VIII B, for instance platinum, palladium, rhodium or iridium, which are present in catalytically effective amounts, generally in the range of about 0.01 to 2 weight percent, preferably about 0.1 to 1 weight percent. The platinum group metal may be present in the metallic form or as a sulfide, oxide or other combined form. The metal may interact with other constituents of the catalyst but if during use the platinum group metal is present in metallic form, then it is preferred that it be so finely divided that it is not detectable by X-ray diffraction means, i.e. that it exists as crystallites of less than about 50 Å size. Of the platinum group metals, platinum is preferred.

An essential constituent of the second catalyst of the presence of invention is a halogen component.[25] Although the precise chemistry of the association of the halogen component with the support, e.g., alumina, is not entirely known, the halogen component may be referred to as being combined with the alumina support or with the other ingredients of the catalyst. This combined halogen may be fluorine, chlorine, bromine, and mixtures thereof, fluorine and, particularly, chlorine are preferred. The halogen may be added to the alumina support in any suitable manner, either during preparation of the support, or before or after the addition of the compounds of the platinum group metal. In any event, the halogen will be added in such a manner as to in a fully composed the second catalyst that contains from about 0.1% to about 4% and preferably from about 0.6% to about 2.5% by weight. During processing, i.e., the period during which hydrogenated oil in the presence of

hydrogen is being contacted with the second catalyst, the halogen content of catalyst can be maintained at or restored to the desired level by addition of halogen-containing compounds, such as carbon tetrachloride, ethyl trichloride, t-butyl chloride and the like, to the hydrogenated oil before such the second contacting.

2.2 Mechanism of Hydrogenation Reaction [26]

In hydrogenation stage, the platinum metals group are widely used as catalyst to completely convert aromatic compounds to be naphthenes. Although many details remain uncertain, a rudimentary understanding of the mechanism of catalytic hydrogenation has been developed. At high temperature, the working surface of metal is nearly clean; but at low temperature, it is largely covered with carbonaceous residues. It is possible that there are catalytic for hydrogenation in addition to those provided by the bare metal surface. Hydrogen is adsorbed on to metal surface and then carbon-carbon multiple bonds interact with the metal surface, forming intermediates in which the organic molecule is strongly adsorbed.

Figure 2.8 shows the intermediate of hydrogenation reaction of alkanes. The intermediate initially formed is adsorbed at both of carbon atoms of the Allen bond, as shown in B . The π -orbitals of the alkene are used for bonding to metal surface. Hydrogen adsorbed on the surface can be added to the organic residue leading to C, a monoadsorbed species attached to the metal surface by what approximates a sigma bond. This intermediate can react with adsorbed the other hydrogen atoms to give the saturated compounds.

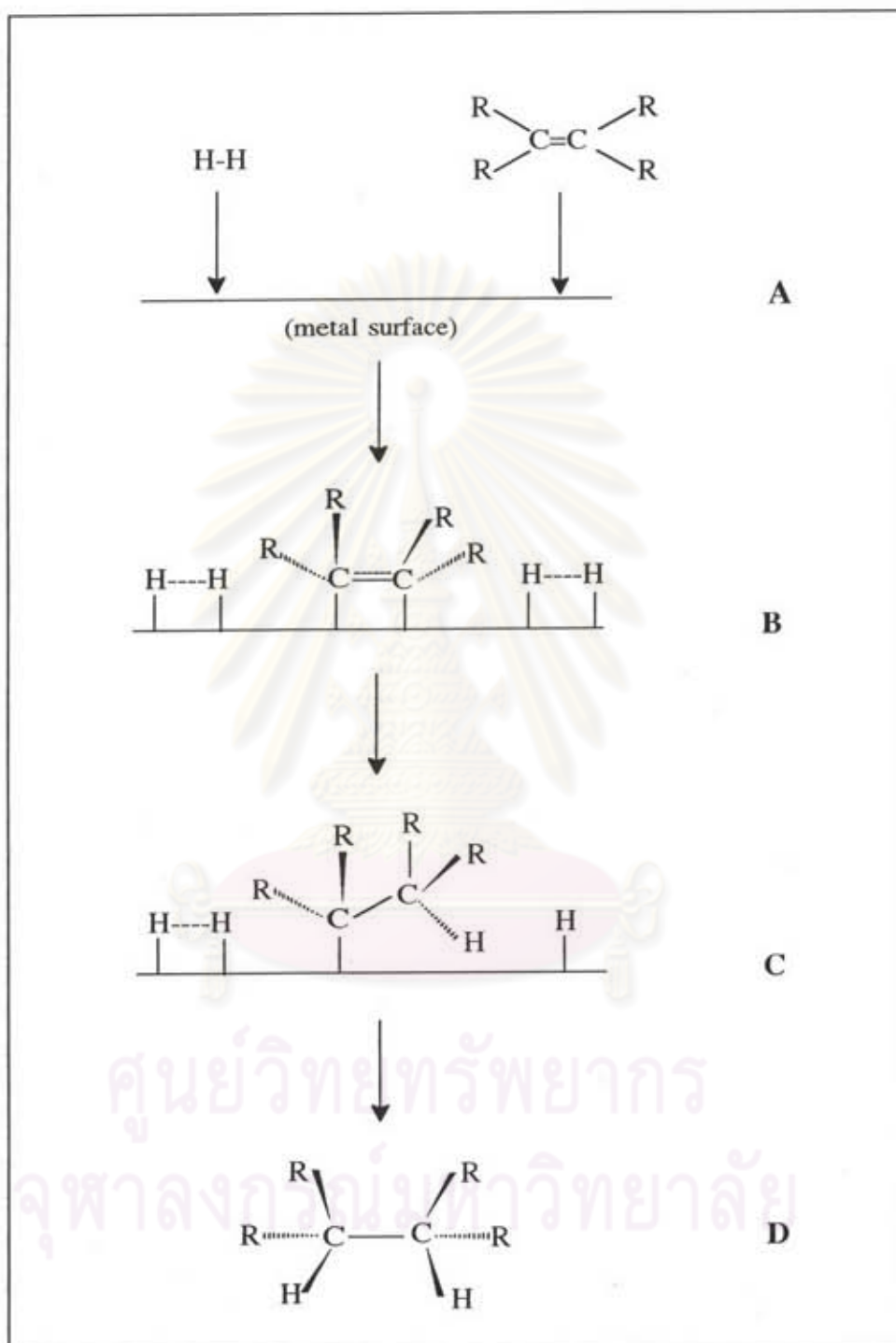


Figure 2.8 Mechanism of hydrogenation reaction.

3. Conditions of Hydrotreating Process [27-29]

In hydrodesulfurization stage, oil is conducted at temperatures of about 310 to 400°C, hydrogen pressures of about 1500 to 5000 Psig. The hydrodesulfurized oil from the first stage is then subjected to hydrogenation conditions, for example, at temperatures of about 230 to 330°C, hydrogen pressures of about 2200 to 5000 Psig. To provide the less severe reaction conditions, the average temperature of the hydrogenation stage is at least about 50°C than the hydrodesulfurization stage.

Hydrotreated oil may be distilled in a temperature range from 330 to 480°C to remove any hydrocracked or other light products.



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