

CHAPTER II

THEORETICAL CONSIDERATIONS

Lubricating Base Oils

2.1 Sources [5]

There are essentially two sources from which the base lubricant fluids are obtained. These are the refining of petroleum crude oil and the synthesis of relatively pure compounds with properties which are suitable for lubricant purposes. The lower cost of lubricating oils produced from petroleum makes these the most widely used of all the available lubricants.

2.1.1 Crude Oil and Its Components [5-8]

Crude oils are the end result of physical and chemical processes acting over many millions of years on the buried remains of plants and animals. They are found in a variety of types ranging from light colored oils, consisting mainly of gasoline, to black, nearly solid asphalts. These crudes are extremely complex mixtures of hydrocarbons ranging from methane with one carbon atom to compounds containing 50 or more carbon atoms. The principle hydrocarbon classes of the mixture are:

- (a) Paraffins (alkanes): These have saturated straight- and branched- chain structures.
- (b) Olefins (alkenes): These are unsaturated molecules.

(c) Naphthenes (alicyclics): These are polycyclic and fused-ring saturated hydrocarbons based on cyclopentane and cyclohexane prototype ring structures.

(d) Aromatics: These are both mono and polynuclear hydrocarbons based on unsaturated ring structures.

Olefinic compounds are essentially not present in crude oils, depending on the origin of crude oil and on the conditions under which it is formed. In addition to the hydrocarbons, crude oils may contain small quantities of sulfur and nitrogen compounds and inorganic salts, along with trace amounts of organometallic compounds such as vanadium and nickel compounds. The presence of these nonhydrocarbon compounds can cause problems in refining or in subsequent product applications. Examples of hydrocarbons and nonhydrocarbons are shown in Figure 2.1 and 2.2 respectively.

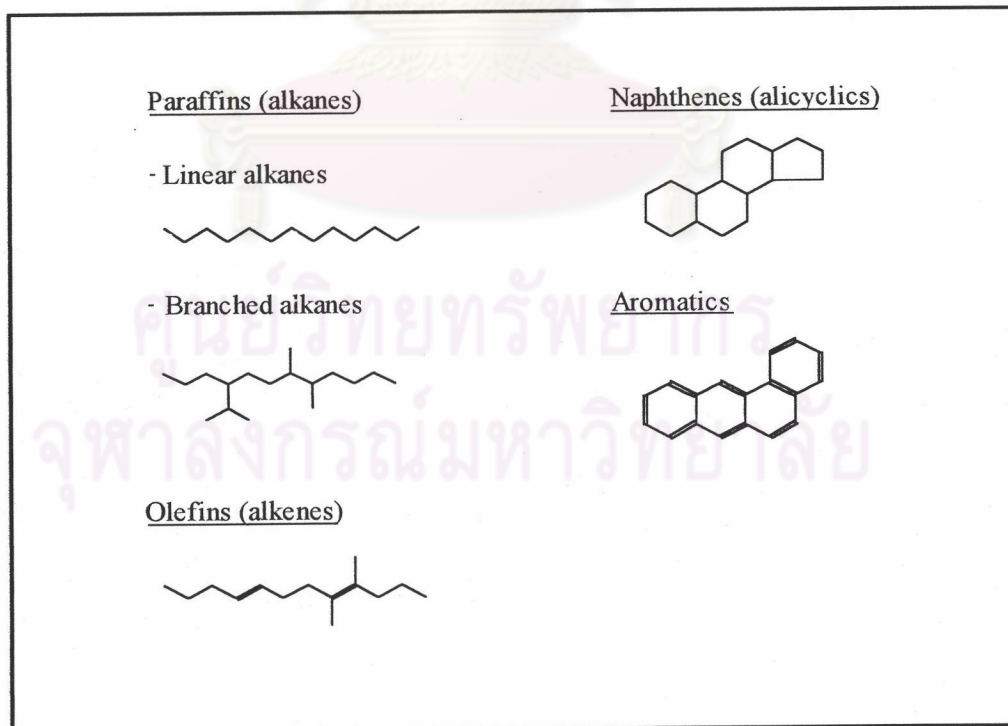


Figure 2.1 Examples of hydrocarbons

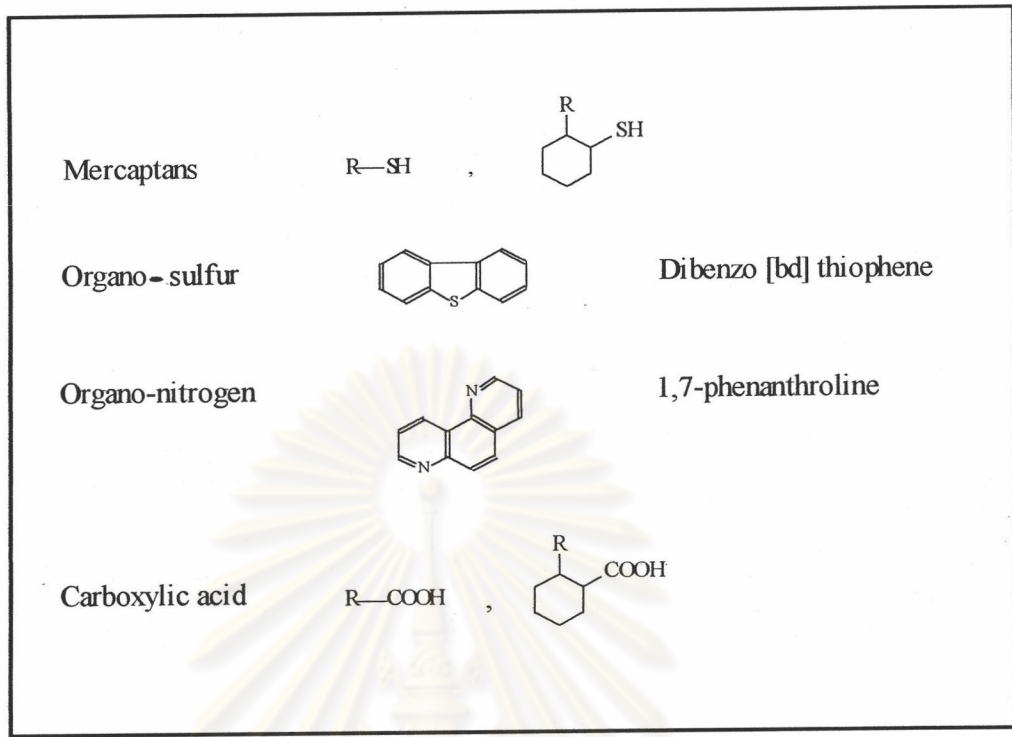


Figure 2.2 Examples of nonhydrocarbons

2.1.2 Refining Process

2.1.2.1 Crude Oil Distillation [5,9,10]

Crude oil distillation is the process whereby crude oil is fractionated into a series of products based on boiling ranges. The precedable step before the distillation is usually a desalting operation followed by heating in a tubular furnace where the crude oil is partially vaporized (Figure 2.3).

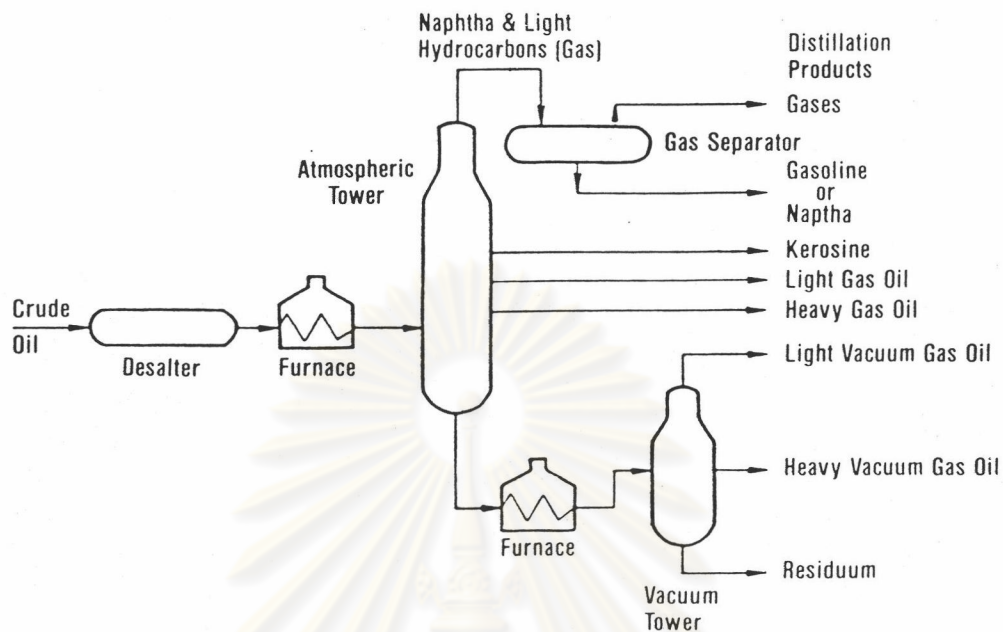


Figure 2.3 Crude distillation unit [5]

The mixture of hot liquid and vapor enters a fractionating column operating slightly above atmospheric pressure. A heavy black residuum is drawn from the bottom of the column. Because of the tendency of residuum to decompose at temperatures above 700 °F (371 °C), higher boiling oils such as lubricating 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 oil components. Bottom materials from the vacuum tower are either used for asphalt or are further processed for other materials such as bright stocks. The fractions separated by crude distillation are referred to as “straight run” products. The character of their hydrocarbon constituents is not changed by distillation. These products are usually not suitable for disposition as finished products but require further processing, which may be simple or complex according to the nature of the crude oil, the requirement of the market, or the economics of the downstream

operations. Small refineries are often quite simple, but large ones not at all so; there are a variety of conversion and finishing operations needed to increase the commercial value of the petroleum fractions. However, a crude is divisible into the product categories as shown in Table 2.1.

Table 2.1 Petroleum fractions

Products	Boiling range (°F)	API
Gas, light ends	C ₁ - C ₄	-
Light naphtha	50-200	70
Heavy naphtha	200-375	53
Kerosine	375-450	43
Diesel, heating oil	450-550	37
Atmospheric gas oil	550-650	32
Reduced crude loss, slop	650+	
Light vacuum gas oil	650-750	30
Heavy vacuum gas oil	750-1000	23
Residuum	1000+ (large molecule)	

2.1.2.2 Fang Refinery [2,3]

For over 30 years, Fang refinery has been in operation under the supervision of the Defence Energy Department (DED), Ministry of Defence. All of its crude supplies come from the nearby Fang basin area, where the production level is now at 1,500 barrels per day. The refinery which runs at capacity consumes 1,000 barrels of crude oil per day.

The process consists of several operation units including topping distillation unit, vacuum distillation unit, gasoline trading

unit, gasoline blending unit, power unit and 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 a demulsifier. After that, the crude is pumped through preheat exchanger and its temperature raised to about 120 °C by heat exchange with hot oil from the vacuum tower. It is then further heated to 340 °C in atmospheric heater (H-1) and charged to the atmospheric fractionators. The liquids withdrawn from this tower will contain straight run oil, kerosine, and diesel. Reduced crude from the bottom of the atmospheric tower is sent to vacuum heater (H-2) and its temperature raised to 365 °C afterwhich it is charged to a vacuum tower where it is separated into light distillate, heavy distillate and heavy fuel oil. The refinery products consist of straight run oil 6%, diesel 26%, light distillate 17%, heavy distillate 14% and heavy fuel oil 37%.

In general, lubricants are derived from distillates having boiling points of at least 315 °C and usually above 345 °C and are separated by vacuum distillation and then treated and refined to meet quality requirements (see 2.4).

2.2 The Basic Functions of Lubricant [5]

2.2.1 The Reduction of Friction

Simply stated, friction reduction is accomplished by maintaining a film of lubricant between surfaces which are moving with respect to each other, thereby preventing these surfaces from coming into direct contact and thus preventing surface damage.

One of the most important properties of a lubricating oil is its viscosity. It is a factor in the formation of lubricating films under both thick and thin film conditions. Viscosity, as it relates to fluid internal friction, affects heat

generation in bearings, cylinders and gears. It governs the sealing effect of oils and the rate of oil consumption. It determines whether machines may be started under varying temperature conditions, particularly at cold temperature. For any given piece of equipment satisfactory results are obtained only with the use of an oil of proper viscosity under the operating conditions.

The basic concept of viscosity is shown in Figure 2.4 where a plate is being drawn at uniform speed over a film of oil. The oil adheres to both the moving surface and the stationary surface. Oil in contact with the moving surface travels at the same velocity (U) as that on surface, while oil at contact with the stationary surface is at zero velocity.

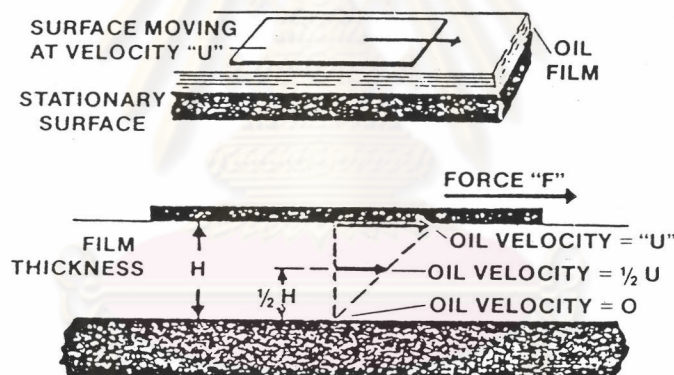


Figure 2.4 Concept of dynamic viscosity [5]

In between, the oil film may be visualized as made up of many layers, each being drawn by the layer above it at a fraction of velocity U that is proportional to its distance above the stationary plate (Figure 2.4 - Lower view). A force (F) must be applied to the moving plate to overcome the friction between the fluid layers. Since the friction is the result of viscosity, the force is proportional to the viscosity of the fluid.

2.2.2 Heat Removal

Another important function of a lubricant is to act as a coolant, removing heat generated by friction or from other sources such as the combustion process or transferred by contacting with substances at a higher temperature. In performing this function it is important that the lubricant remain in a relatively unchanged condition. Changes in thermal and oxidation stability which affect its ability to reach the involved areas will materially decrease its efficiency in this respect.

2.2.3 Containment of Contaminants

The ability of a lubricant to remain effective in the presence of outside contaminants is quite important. Among these contaminants are water, acidic combustion products, particulate matter, etc., which generally find their way into lubricants employed in various applications. Additives are generally the answer in accomplishing these objectives.

2.3 Necessary Properties of a Lubricant [6,11]

Lubricants are formulated by blending base oils and additives to meet a series of performance specifications. These specifications relate to the physical and chemical properties of the oil. Base oils have a range of properties that can be measured and used to predict performance. Analysis and testing of lubricants and related products are based on standards [International Organisation for Standardisation (ISO), American Society for Testing and Materials (ASTM), Institute of Petroleum (IP), Deutsches Institut für Normung (DIN), etc.] which are often identical.

2.3.1 Physical Properties [3,10-12]

A. Viscosity

Viscosity is the most significant property of a lubricating oil. The primary purpose of a lubricant is to reduce friction and minimize wear by separating lubricated surfaces with an oil film. Viscosity is a measure of resistance to flow. It decreases with increasing temperature and increases with large increasing pressure. The extent of the viscosity change depends on the crude source of the oil and the molecular weights of the constituent components.

The instrument used to determine the viscosity of an oil is called a viscometer. In general two types are used: the Saybolt and kinematic viscometers. Kinematic viscosity is the more common and is measured by the time required for a given volume of an oil at a specified temperature to flow through a capillary tube under gravitational force. Test temperatures are usually at 40 and 100 °C for centistokes unit.

B. Viscosity Index (VI)

Viscosity index is a reflection of an oil's resistance to viscosity change with fluctuation in temperature. The higher the viscosity index of an oil, the more resistant it is to a viscosity change caused by temperature fluctuation. All lubricating oils thin out or have lower viscosity as the temperature is increased. Likewise, oils become thicker or more viscous as the temperature is reduced. However, not all oils respond to the same degree to temperature changes.

Lubricating oils are subjected to wide variations of temperature in service. At high temperatures the viscosity can drop to a point where the oil is so thin that the oil film may break, allowing metal surfaces to touch, resulting in excessive wear. At the other extreme, the temperature can be so low that the

oil becomes viscous and does not allow proper circulation to the parts being lubricated.

Take an automobile, for example. During startup the oil can be quite cold, particularly during winter. But the oil must not be so viscous that the drag on the engine makes starting difficult. During warm-up the oil must be able to flow to all the moving parts. Finally, after the engine has reached its normal operating temperature, the oil must not be so thin that oil consumption is high or the lubricating film can no longer carry the load. Most motor oils have a viscosity index of 100 or higher. Where temperature variations are less or for continuous operation at constant temperature, viscosity index is less critical.

C. Specific Gravity

Specific gravity is defined as the ratio of the mass (weight) of a given volume of product to the mass of an equal volume of water, usually at 60 °F for each. The density is the absolute value and can be expressed as lb/gal or lb/ft³ in English units or as kg/m³ in the SI system of units.

In the petroleum industry the API gravity scale is almost universally used as the measure of the density of a petroleum product. API gravity is an arbitrary scale, calibrated in degrees and related to the specific gravity by

$$\text{API gravity (degrees)} = \frac{141.5}{\text{specific gravity at } 60/60^{\circ}\text{F}} - 131.5$$

The higher the specific gravity or density, the lower the °API gravity. Water, by definition, has an API gravity of 10°.

The specific gravity (or API) is an important parameter which is sometimes used to indicate crude oil quality. A low density crude (high API) has a higher percentage of the more valuable light and middle distillates. Oils with a high sulfur content are less in demand than those with a low sulfur content hence lower density since fractions from the former oils have to be subjected to further treatment to remove these sulfur compounds.

D. Pour Point

As a lubricating oil is chilled, it eventually reaches a point where it will no longer flow under the influence of gravity. This condition is brought about either by the thickening (more viscous) that always accompanies a reduction in temperature or by crystallization of wax dissolved in the oil, restricting the flow of the liquid portion. The lowest temperature to which an oil can be chilled and still be poured from a container is called the "pour point".

The pour point is related to the ability of the oil to start lubricating when a cold machine is placed into operation. Engines that are stopped and started under low-temperature conditions require an oil that will flow readily when cold.

E. Flash Point

The flash point is a measurement of the flammability of a petroleum product. The flash point is the temperature at which enough vapor is produced to be burned in an instantaneous flash when exposed to a source of ignition. Normally, this test is used to determine the storage and operating temperatures and the type of storage that will preclude the possibility of a fire.

Flash point is also useful in evaluating used oils. A drop in flash point indicates contamination by dilution of the motor oil with unburned fuel. An increase indicates evaporation of the oil. This property is determined by the

open-cup method, usually called the Cleveland Open Cup method and abbreviated COC.

F. Color Test, ASTM D 1500

The color test was performed by following the ASTM D 1500 method. The oil's color is normally not an indication of its lubricating properties. It is, however, a guide to the presence of contaminants or to the degree of deterioration in storage. It is also an indication of the intensity of refining. Absence of color (water white) is important in certain applications such as in textile machinery lubrication to avoid indelible staining of the textile. Absence of color is also important to users of waxes, petrolatums, and white oils where extremely high purity is required.

2.3.2 Chemical Properties [3,12]

All petroleum products are subject to chemical attack by oxygen. Attack is promoted by high temperatures, catalysts, and the presence of water or acids. Oil oxidation results in two general classes of degradation products:

1. Oil-insoluble materials, i.e., resins, varnish, or sludge
2. Oil-soluble products, primarily acids and peroxides

Resistance to oxidation is important in the performance of a lubricant. Acids formed may be corrosive to metals. Varnish may deposit on sliding surfaces, causing them to stick or wear. Sludge may plug screens or passages or the rings on cylinders, causing them to be ineffective. Resistance to oxidation is extremely important for a steam-turbine oil because of the serious consequences of a bearing failure. Transformer oils, gear oils, hydraulic fluids, heat transfer oils, and crankcase oils also require a high degree of oxidation stability to ensure a satisfactory service life.

There are several accelerated tests to measure an oils' resistance to oxidation which are designed to correlate with field performance.

2.4 Base Oil Composition, Properties and Structure Relationship [3,6,13]

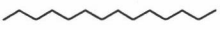
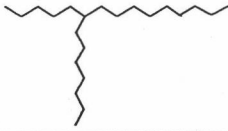
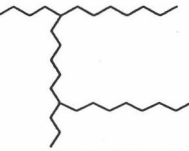
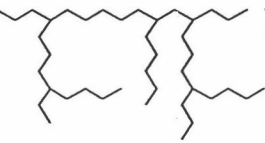
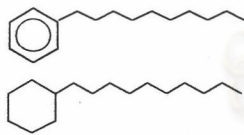
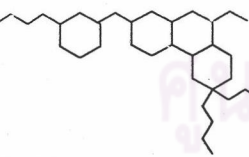
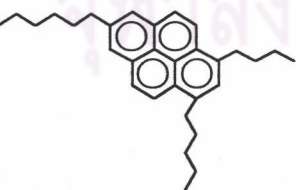
The petroleum fraction used as lubricant generally contains compounds containing 18 or more carbon atoms. The lubricating base oil fraction is a complex mixture consisting primarily of five characteristic classes -- paraffin naphthenes, condensed naphthenes, aromatic naphthenes, naphthalenes (two ring aromatics) and multi-ring aromatics. It also contains small amounts of heterocyclic compounds containing sulfur and nitrogen atoms (e.g. thionaphthene, indole, quinoline and carbazoles) and various oxygen containing compounds, including naphthenic acids, which account for most of the chemically bound oxygen in petroleum fractions.

Alkanes, alicyclics and aromatics of the same molecular weight have markedly different physical and chemical properties. Physical characteristics will affect the viscometrics of the lubricant. The chemical stability of each class to oxidation and degradation while in use will also be very important. The effect of different types of compounds on a lubricating oil's properties can be seen in Table 2.2.

Table 2.2 shows qualitatively that the highly desirable structures for lubricant base oils are the highly branched isoparaffin and monocyclic hydrocarbons, saturated or unsaturated, with long aliphatic chains and preferably five carbon atoms in the ring.

The linear alkanes (normal paraffins) have good viscosity/temperature characteristics but their high melting points cause them to crystallise out of solution as wax. On the other hand, branched-chain paraffins are not waxy and have good stability and viscosity/temperature properties.

Table 2.2 Lubricating oil properties of some typical hydrocarbon structures

Structures	VI	Freezing point	Resistance to oxidation	Value as base oil
Linear paraffin 	Very high	High	Good	Nil
Isoparaffin with linear chain 	High	Medium	Good	Medium
Isoparaffin with isomerized chains 	High	Low	Good	High
Highly substituted isoparaffin 	Medium	Low	Good	Medium
Single ring with long aliphatic chain 	High	Low	Good	High
Polycondensed naphthenes 	Low	Low	Medium	Nil
Polycondensed aromatics 	Very low (< 0)	Low	Weak	Nil

Alicyclics and aromatics have rather higher density and viscosity for their molecular weight compared to the alkanes. They tend to have low melting points and so do not contribute to wax. However, their viscosity/temperature characteristics and oxidation stability are in general rather poor. Single ring alicyclics or single ring aromatics with long alkyl side chains, in contrast, share many properties with branched alkanes and can in fact be very desirable base oil components.

2.5 Base Oil Manufacturing Methods

2.5.1 Conventional Methods [5,6,12]

In conventional mineral lubricating oil manufacture, the base stock will be produced from the crude oil by distillation of the crude in atmospheric and vacuum distillation towers to remove both the components of too low boiling point and too high boiling point, leaving the lubricant boiling range distillates. Distillation is followed by separation of undesirable aromatic components which lead to high viscosity and extremely poor viscosity index, and finally, by dewaxing and various finishing steps. The dewaxing step is normally necessary in order for the lubricant to have a satisfactorily low pour point and cloud point, so that less soluble paraffinic components will not solidify or precipitate under the influence of low temperature. A number of dewaxing processes are known in the petroleum refining industry. Of these solvent dewaxing with solvents such as methyl ethyl ketone (MEK) and liquid propane, have achieved the widest use in the industry. Hydrofinishing differs from all the process steps described so far because it is not a physical separation procedure. It depends on the selective, catalysed hydrogenation of the impurities to form harmless products and is carried out under relatively mild conditions.

Figure 2.5 is a simplified processing diagram illustrating one way these processes are combined to manufacture lube base stocks and by-products. The finished lube base stocks are blended with each other and /or with additives using batch and continuous methods to prepare fully formulated lubricants.

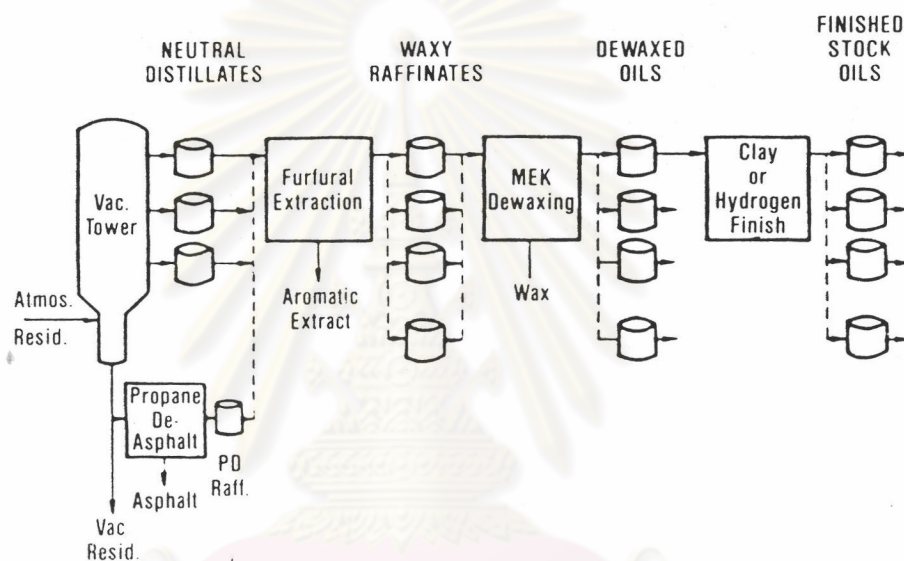


Figure 2.5 Lube processing

The effect of lube processes on the chemical constituents and physical properties of lube base stocks are summarized in Table 2.3. It should be noted that each process is generally used for one purpose and that any accompanying change must be accepted to obtain the desired change in physical properties or chemical composition. For example, solvent extraction is used to increase the viscosity index and to improve the quality of lube base stocks by extracting aromatics. Accompanying this change are a reduction in sulfur and nitrogen content, an increase in API gravity, a decrease in viscosity, and improvement in color.

Table 2.3 Effect of processes on properties and chemical composition of lubricating oil base stocks^a

	Process									
	PDA	Refining			Dewaxing			Finishing		
		Solvent	Hydrogen	Chemical	Solvent	Catalyst	Urea	Hydrogen	Acid	Clay
Property:										
API gravity	+	+	+	+	-	-	-	N	N	N
Flash point	N	N	N	N	N	N	N	N	N	N
Viscosity	-	-	-	-	+	+	+	N	N	N
Viscosity index	+	+	+	+	-	-	-	N/+	N/+	N
Pour point	+/-	+	+	+	-	-	-	N/+	N/+	N
Color	-	-	-	-	+	-	+	-	-	-
Thermal stability	+	+	+/-	+/-	N	N	N	+/-	+/-	+
Oxidation stability	+	+	+/-	+/-	N	N	N	+/-	+/-	+
Inhibitor response	+	+	+	+	N	+/-	N	+	+	+
Constituent:										
Asphaltenes	-	-	-	-	+	N/-	+	N/-	-	-
Resins	-	-	-	-	+	N/-	+	N/-	-	-
Aromatics	-	-	-	-	+	+	+	N/-	-	-
Naphthenes	+	+	+	+	+	+	+	N/+	+	+
Paraffins	+	+	+	+	-	-	-	N/+	+	+
Wax	+	+	+	+	-	-	-	N/+	+	+
Nitrogen	-	-	-	-	+	N/-	+	-	-	-
Oxygen	-	-	-	-	+	-	+	-	-	-
Sulfur	-	-	-	-	+	N/-	N	-	-	-

^a N = nil (min), + = increase, - = decrease on severity, +/- = depends on severity, PDA = propane deasphalting.

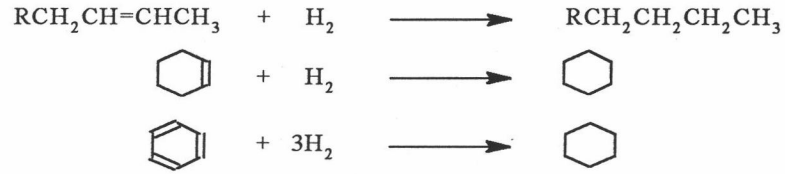
2.5.2 Modern Catalytic Process [6,13,14]

Recently, various catalytic hydrogenation or hydrotreating purification processes have been developed and introduced to replace of the conventional solvent refining technology which relies on physical separation processes. As a result the performance of mineral oil type base oil has been improved greatly. Hydrogenation may offer economic advantages over solvent processes and some of the processes can create new and highly desirable components. The types of reaction that occur in catalytic hydrogenation processes are shown in Figure 2.6.

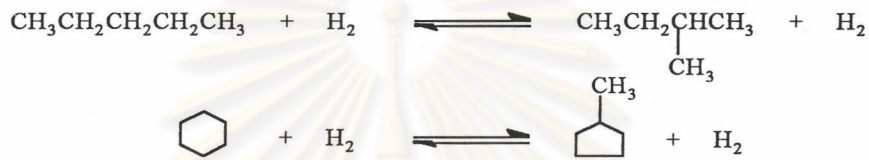
The extent to which each of these reaction types occurs is determined by the type of catalyst used, the process conditions and the feedstock composition. Normally, for commercial operation, temperature is limited to a maximum of about 532 °C and pressure to a maximum of about 10,000 psig.

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1. Saturation: Hydrogenation of aromatics and other unsaturated molecules



2. Hydroisomerization: Isomerization of alkanes, alkyl side-chains and naphthenes



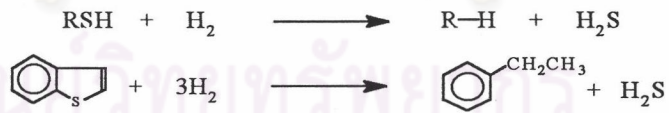
3. Hydrocracking: Ring-opening, especially of multi-ring molecules



: Cracking to lower molecular weight product



4. Desulfurization:



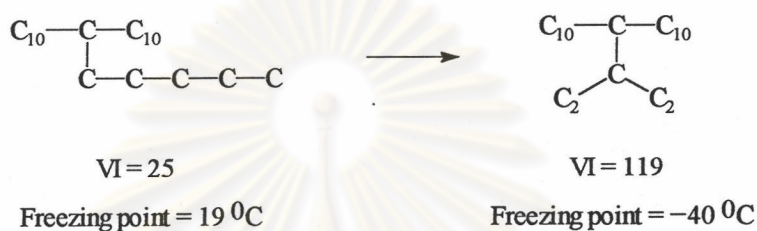
5. Denitrogenation:



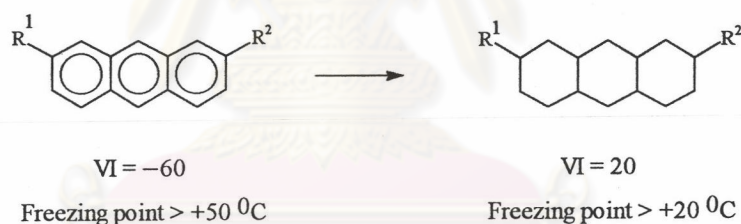
Figure 2.6 Typical hydrogenation reactions [5,6]

Knowledge of the natural structures available plus the desired reactions, enables one to make a list of desired reactions for high quality base oil manufacture. These reactions are generally as follows:

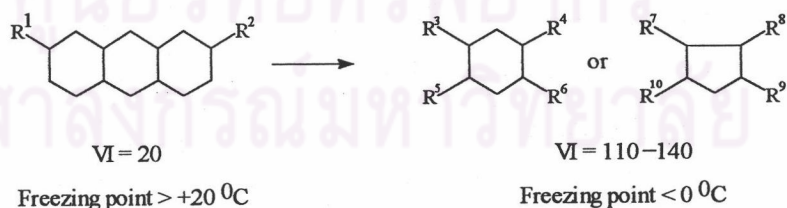
-- Hydroisomerization of normal or slightly branched paraffins into highly branched isoparaffin.



-- Hydrogenation of polycondensed aromatics into polycondensed naphthenes.



-- Partial hydrogenation of polycondensed naphthenes.



For base oil manufacture, the reactions to avoid are cracking reactions such as paraffin and isoparaffin hydrocracking and acid hydrodealkylation of alkylaromatics and alkylnaphthenes. These reactions lead to lower yields of lubricating oil stocks, lower viscosity, and higher

consumption of hydrogen. It is also necessary to limit as much as possible the condensation of condensed polyaromatic hydrocarbons, since this leads to coking and a drastic reduction in catalyst life.

2.5.2.1 Special Base Oil by Wax Isomerization [6,7]

One of the most important application of the severe hydrotreatment process is the substitution of waxes for lube distillate as feedstock. These waxes can be divided into three categories:

Paraffin waxes, boiling in the range of about 300-580 °C, are mixtures of saturated paraffinic hydrocarbons (alkanes), straight-chain or "normal" paraffinic hydrocarbons (alkanes) being by far the major components of the mixtures, but with varying proportions of paraffinic hydrocarbons having some degree of branching in their chains (isoalkanes) also present, together with a small cycloalkane content. The chain length of the individual alkanes ranges from about 18-45 carbon atoms. Alkane mixtures with higher average molecular weight are likely to have a higher proportion of isoalkane.

Intermediate waxes are very similar to paraffin waxes, with individual alkane chain lengths of up to 60 carbon atoms, higher average molecular weights, and up to 50% branched-chain components.

Microcrystalline waxes also are mixtures of saturated alkanes, but with a much greater preponderance of branched-chain or cyclic molecules. The carbon atom content per molecule can vary from the mid-thirties to well over eighty, the average molecular weight thus being much higher than in the case of the distillate waxes. The complex branched-chain structure prevents any degree of close packing and macrocrystallization, giving rise to the original name of "amorphous" waxes, and later, rather more accurately, to the current nomenclature of "microcrystalline" waxes.

Petroleum streams containing a high proportion of waxy hydrocarbons are not easily dewaxed using conventional solvent dewaxing techniques. High wax content leads to an overload in the solvent handling and recovery systems. With these types of feedstock appropriate operating conditions can be selected such that the isomerization reaction predominates over cracking reactions. If hydrocracking is allowed to become the dominant mechanism the yield of material within the useful lube boiling range falls from 40-70% to 5-15%. After hydrotreatment, unconverted wax can be removed by conventional methods to yield a base oil that is exclusively composed of isoalkanes having a wider spread of isomers and a broader band of molecular weights than the original feedstock.

A process flow scheme for making these base oils is shown in Figure 2.7. The wax feedstock reacts over a catalyst in a hydrogen atmosphere but, despite control of conditions to favour isomerization, a significant amount of cracking to lighter products is inevitable. Products are separated by distillation and the lube boiling range material is dewaxed by conventional methods. It is possible to recycle the unconverted wax to increase the overall base oil yield.

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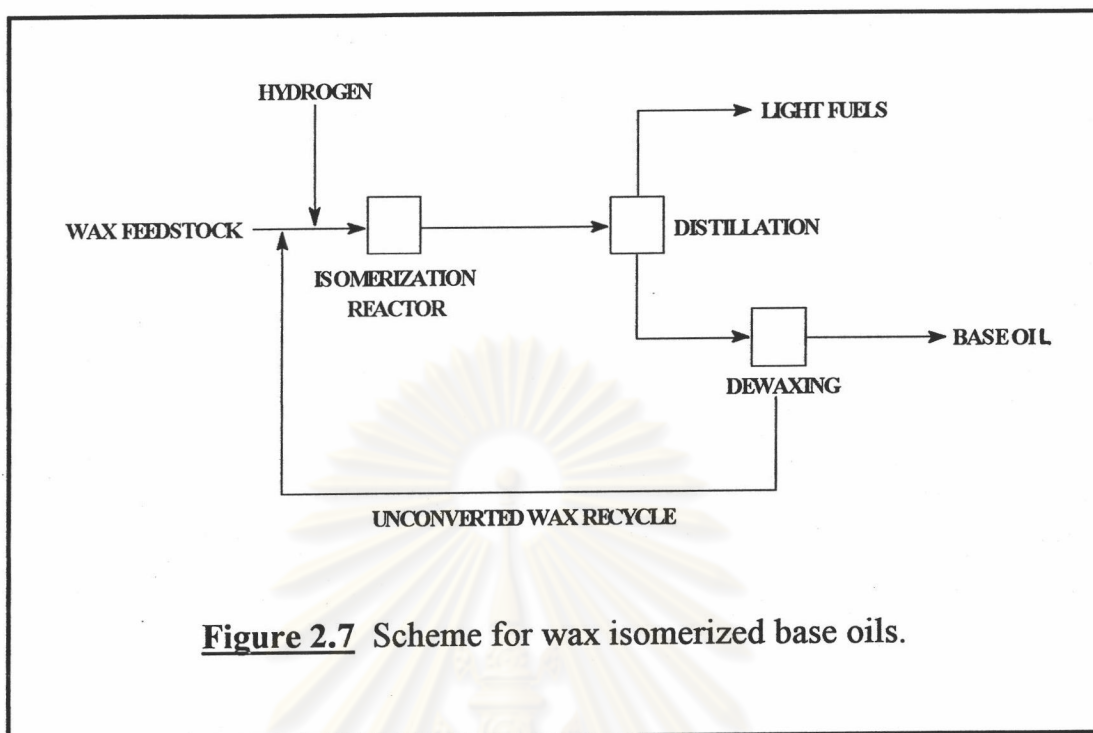


Figure 2.7 Scheme for wax isomerized base oils.

-- Catalyst and Chemistry of Hydroisomerization [7,15-20]

The desired reactions indicate that the catalyst should simultaneously activate: (a) hydroisomerization of paraffins and naphthenes plus hydrodeacyclization of naphthenes and (b) hydrogenation of aromatics. These very different reactions require a bifunctional catalyst system consisting of a metal functionality which catalyzes hydrogenation-dehydrogenation reactions and an acidic or hydrocracking functionality provided by the support which catalyzes isomerization reactions through carbonium ion mechanisms. The two functions interact through the olefins, which are the key intermediates in the reaction network (Figure 2.8). In the first reaction in the pathway, n-paraffin is rapidly dehydrogenated on the metal surface, the resulting n-olefin is easily protonated by the acidic sites on the support to give a carbonium ion, which can then isomerize and desorb isoolefin which migrates to the metal function, where it can be adsorbed and hydrogenated to give an isoparaffin. Alternatively, the secondary carbonium ion can react to form cracked products

(iso- or n- olefins and paraffins), which can react further to form hydrogenated cracked products.

Isomerization also occurs on a pure platinum surface, but the rates are slow compared with those of dual-function catalysts, so the contribution of the metal induced isomerization route is probably minor.

Generally, isomerization is conducted over a catalyst containing a hydrogenating metal component typically one from Group VI or Group VIII or a mixture thereof, preferably Group VIII, more preferably noble Group VIII most preferably platinum on a halogenated refractory metal oxide support. Pt is the metal of choice because it is the only one that has activity for the desired reactions without being more than moderately active for undesired reactions such as hydrogenolysis of paraffins. The catalyst typically contains from 0.1-5.0 wt% metal, preferably 0.1-1.0 wt% metal, most preferably 0.2-0.6 wt% metal. The refractory metal oxide support is typically a transition e.g. gamma or eta alumina. Alumina is the support of choice because it is inexpensive, is easily prepared with the desired physical properties, and interacts strongly enough with the aggregates of Pt to maintain a high metal dispersion. The halogen, most usually fluorine, acts as a promoter by increasing the acidity of the acidic function.

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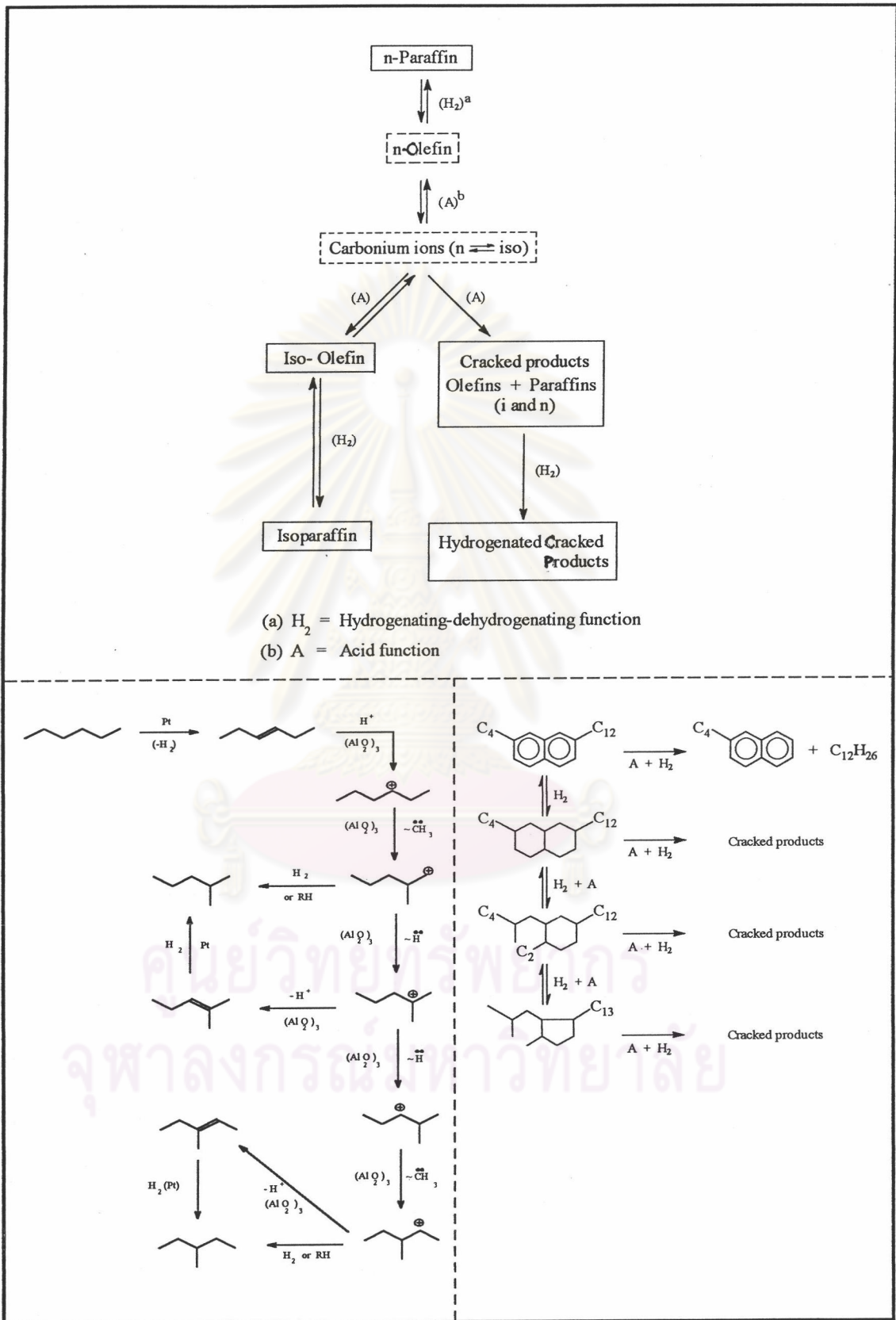
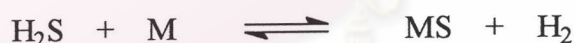


Figure 2.8 Reaction mechanism for bifunctional catalysts [7,13]

2.5.2.2 Hydrodesulfurization [15,16,21-23]

Catalytic hydrodesulfurization of petroleum feedstocks, sometimes called catalytic hydrotreating, is widely applied to prepare charge for catalytic reforming and isomerization processes. It is carried out with several objectives, among them pretreatment of catalytic reformer or isomerization feeds to prevent sulfur poisoning of the platinum containing catalysts, and treatment to provide sweetened and stabilized products.

Catalyst poisoning typically results from strong chemisorption on the surface of the metal. The adsorbed poison either blocks the chemisorption of reactants or blocks the desired reactions. Catalyst poisoning is most appropriately considered from the surface-compounds approach, discussed above. Thus those 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, the equilibrium position of the reaction is far to the right for most metals.



The hydrogenation process involves the reaction of sulfur compounds with hydrogen in the presence of a catalyst, resulting in their decomposition into hydrogen sulfide and hydrocarbon remnants of the original sulfur compounds.

The sulfur content of crude oils ranges from virtually nil to as high as 7 or 8 wt% in extreme cases, depending upon the source of the crude. The organic sulfur in petroleum fractions ranges from very simple identifiable compounds in the lightest fractions to much more complicated compounds in heavier fractions. Desulfurization of residues is considerably more difficult than lighter oil desulfurization because many more contaminants

are presented and very large complex molecules are involved (see Figure 2.9) The thiophenic sulfur in this case is much more difficult to remove because the aliphatic groups interfere with the adsorption of the sulfur compound on the reactive sites of the catalyst. The size of the molecule itself can also inhibit adsorption on the catalyst. This helps explain why residues are more difficult to desulfurize than lighter oils.

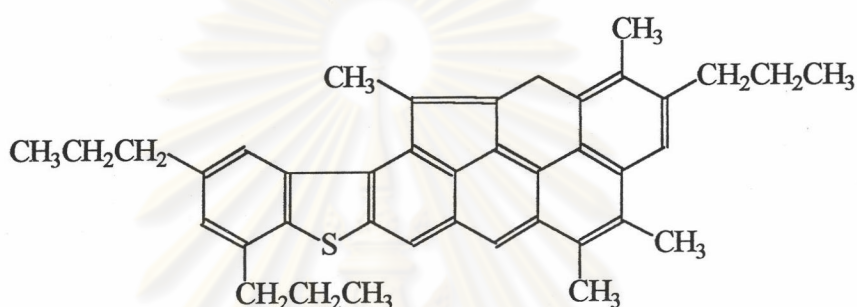


Figure 2.9 Typical residue molecule

The main purpose in most of the residue desulfurization processes is to remove sulfur, but denitrogenation, deoxygenation, and olefin saturation reactions occur simultaneously. These reactions are also beneficial since the noble metal catalysts used in reforming and isomerization can be poisoned by oxygen and nitrogen compounds, and olefins as well as by sulfur in the feedstocks. Sulfur and nitrogen limitations can in the isomerization of waxy lube stream feed be less than about 500 ppm and more preferably to less than 50 ppm (typically less 10 ppm). In addition, hydrocracking and thermal cracking reactions occur to a limited extent at start-of-cycle but become more important as temperatures are raised to maintain catalyst activity.


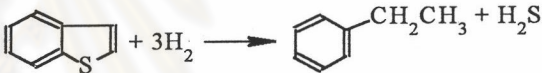
-- Hydrodesulfurization Catalyst and Its Chemistry [20-26]

Generally, the metals employed will be chromium (Cr), molybdenum (Mo) or tungsten (W) metals of Group VI, and iron (Fe), cobalt (Co) or nickel (Ni) metals of Group VIII. Mo is generally regarded as the active desulfurization component, with Co or Ni acting as a promoter which increases catalytic activity. CoMo catalysts are by far the most popular choice for desulfurization, 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 desulfurized. In some applications, nickel-cobalt-molybdenum (NiCoMo) catalysts appear to offer a useful balance of hydrotreating activity. NiW is usually chosen only when very high activity for aromatics saturation is required along with activity for sulfur and nitrogen removal. However, NiW catalysts have not had wide application because of their relatively high cost. The metallic component can be employed either as the metals or as the oxides or sulfides of such metals.

The different types of sulfur compounds and the basic desulfurization reaction for each type are listed in Table 2.4.

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Table 2.4 Desulfurization reactions of sulfur compounds

Type of Sulfur Compound	Desulfurization Reaction
1. H ₂ S	None-usually separated by stripping
2. Mercaptans (R-SH)	$R-SH + H_2 \longrightarrow R-H + H_2S$
3. Sulfides (R-S-R')	$R-S-R' + 2H_2 \longrightarrow R-H + R'-H + H_2S$
4. Disulfides (R-S-S-R')	$R-S-S-R' + 3H_2 \longrightarrow R-H + R'-H + 2H_2S$
5. Cyclic sulfides	 $\text{C}_5\text{H}_{10}\text{S} + 2H_2 \longrightarrow C_5H_{12} + H_2S$
6. Benzothiophene	 $\text{Benzothiophene} + 3H_2 \longrightarrow \text{Ethylbenzene} + H_2S$

These reaction equations illustrate that desulfurization is accomplished by the cleavage of carbon-sulfur bonds. These bonds are replaced by C-H and S-H bonds. The activation of the Co/Mo/alumina desulfurization catalyst consists of three steps:

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

The hydrogen in the gas phase is first dissociatively adsorbed on the cobalt sulfide phase. The atomic hydrogen then spills over to the catalyst support and to the nearby molybdenum sulfide phase. The cobalt sulfide phase itself may be reduced by atomic hydrogen, (which may be an ionic species, a radical, or a bound hydrogen, depending upon the circumstances) or by the molecular hydrogen from the gas phase thus becoming inactive in the production of spill-over hydrogen.

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.

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

Spill-over hydrogen on the molybdenum sulfide phase may be involved in various types of reactions. First, it is needed in the creation of hydrogenation (weakly reduced; τ) sites and hydrogenolysis (strongly reduced; σ) sites. The τ and σ sites are created by the reaction of π (unreduced sites) and τ 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 flow diagram of the overall mechanism, including the generation, migration and consumption of spill-over hydrogen, the creation and interconversion of active sites and the hydrogenolysis and hydrogenation reaction, is presented in Figure 2.10.

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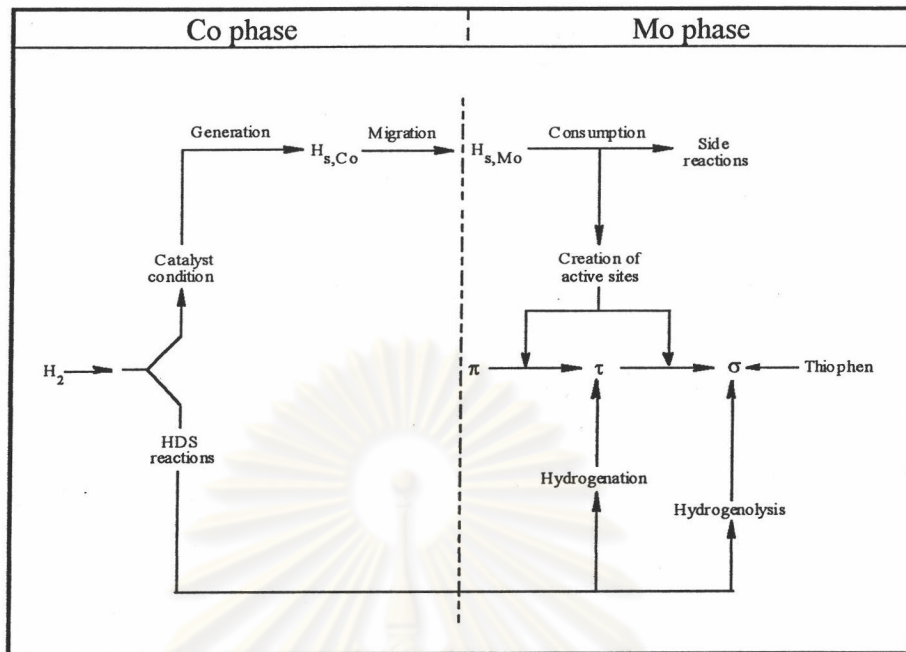


Figure 2.10 The activation of Mo/Co/Al₂O₃ desulfurization catalyst

The steps of the desulfurization on molybdenum are shown in Fig. 2.11. The first step is the cleavage of the sulfur hydrogen bond. This step occurs very rapidly and is favored because both sulfur and hydrogen form strong bonds to the molybdenum surface. In subsequent steps, the carbon-sulfur bond must break, and one carbon-hydrogen bond is either formed or broken to yield the hydrocarbon products from the thiol. For example, ethanethiol bonds to the catalyst breaking the sulfur-hydrogen bond and becoming ethyl thiolate (CH₃(CH₂)S). The carbon-sulfur bond is broken next. Finally, the formation of a carbon-hydrogen bond yields ethane, whereas the breaking of such a bond leads to ethene. Sulfur atoms of the molybdenum sulfide phase are rearranged and may be rejected into the gas phase as hydrogen sulfide.

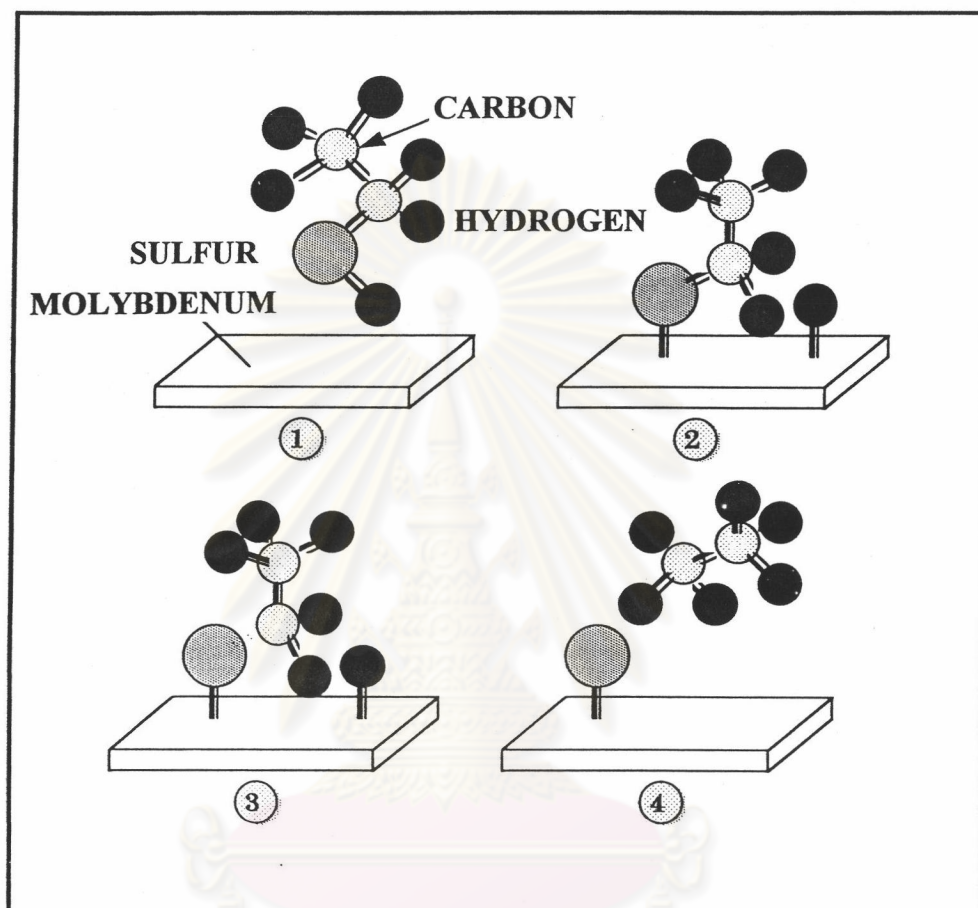


Figure 2.11 The steps of the desulfurization of thiol on molybdenum

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