

CHAPTER II

THEORETICAL CONSIDERATIONS

Crude Oil [15-18]

Crude oil is an extremely complex mixture of organic chemicals ranging in size from simple gaseous molecules, such as methane, to very high molecular weight asphaltic components.

Physical Characteristics of Crude Oil

color	:	red,brown or black
viscosity	:	from fluid as water to tar-like
odor	:	from nil to rotten eggs
pour point	:	0 to 100 °F
specific gravity	:	15-45 API

Compositions of Crude Oil

There are four types of hydrocarbons in crude oil as follow:

1) Paraffinic hydrocarbons are lower in specific gravity, or higher in API gravity than aromatic hydrocarbons of the same boiling point, of which the naphthenic and olefinic compounds are intermediate in gravity or density. Oxidative stability of paraffinic hydrocarbons is very good.

2) Aromatic hydrocarbons posses a much higher specific gravity, or lower API gravity than the other three classes. They are very stable under heat, and are chemically active to a moderate degree.

3) Naphthenic hydrocarbons are extremely stable compounds.

4) Olefinic hydrocarbons are more chemically active than the other three classes. They are subjected to oxidation or polymerization forming gums.

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°C to 204°C (80 - 400°F) for gasoline components.

3) About 204°C to 343°C (400 - 650°F) for diesel and home heating oils.

4) Higher ranges for lubricating oils and heavier fuels.

The distribution of various sizes and types of hydrocarbon and hence the amount of potential lubricating oil present in a given crude oil varies widely with the source of the crude. Some crudes consist predominantly of gasoline and naphthas while the others contain asphalt as the principal constituent.

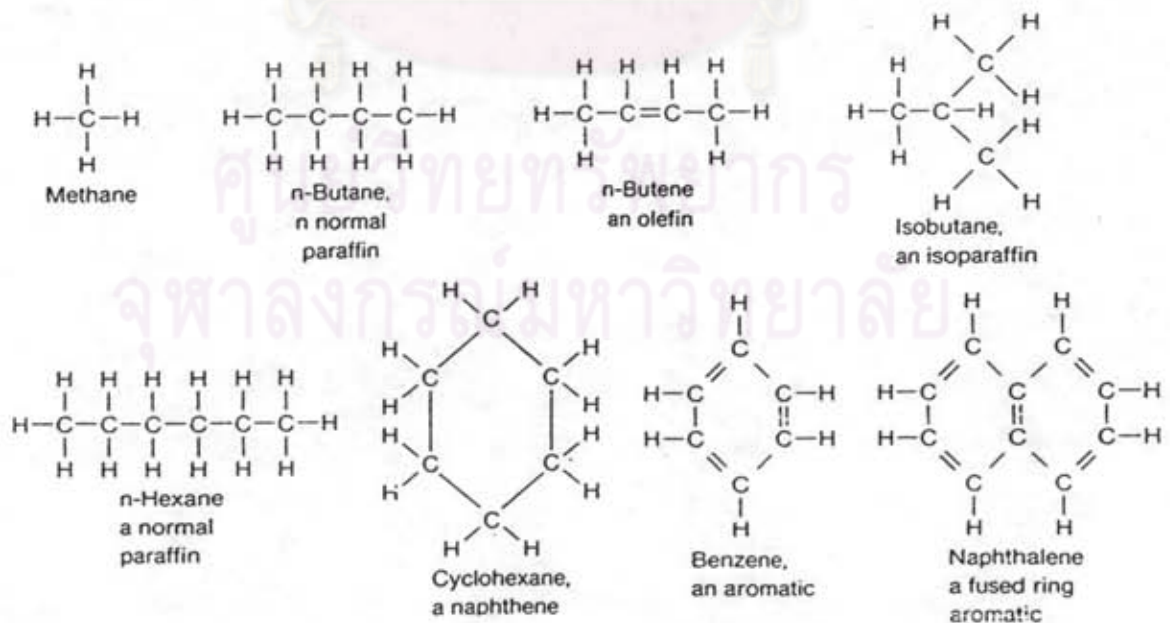


Figure 2.1 Typical hydrocarbon configuration in crude oil

Crude oils also contain varying amounts of compounds of sulfur, nitrogen, oxygen, trace metals such as vanadium, nickel, water and salts.

Refining Process of Crude Oil

The first step in the refining of petroleum is usually a desalting operation followed by heating in a tubular furnace. The mixture of hot liquid and vapor enters a fractionating column operating slightly above atmospheric pressure. This device separates groups of hydrocarbons according to their boiling range. A heavy black residuum is drawn from the bottom of column and crude oil is separated by vacuum distillation unit.

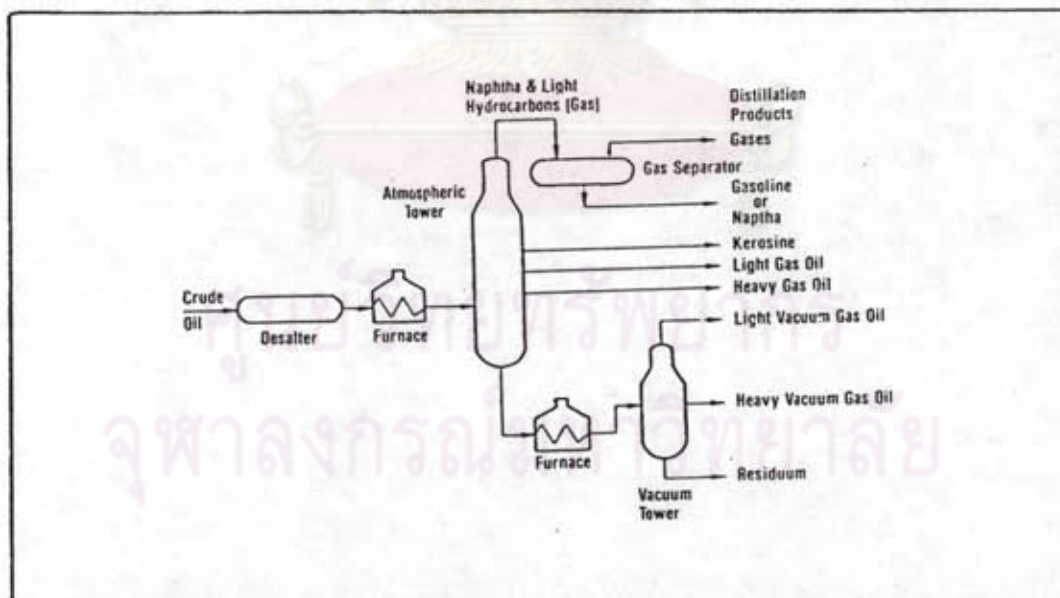


Figure 2.2 Crude distillation unit

Lubricating Base Oil

Sources of Lubricating Base Oil

There are essentially two sources from which the base lubricant fluids are obtained. These are (A) the refining of petroleum crude oil and (B) the synthesis of relatively pure compounds with properties which are suitable for lubricant purposes.

Refining of Petroleum Crude Oil

The manufacture of lubricating base stocks consists of a series of separation or subtractive processes which remove undesirable components from the feedstock leaving a lubricating base stock that meets performance requirements.

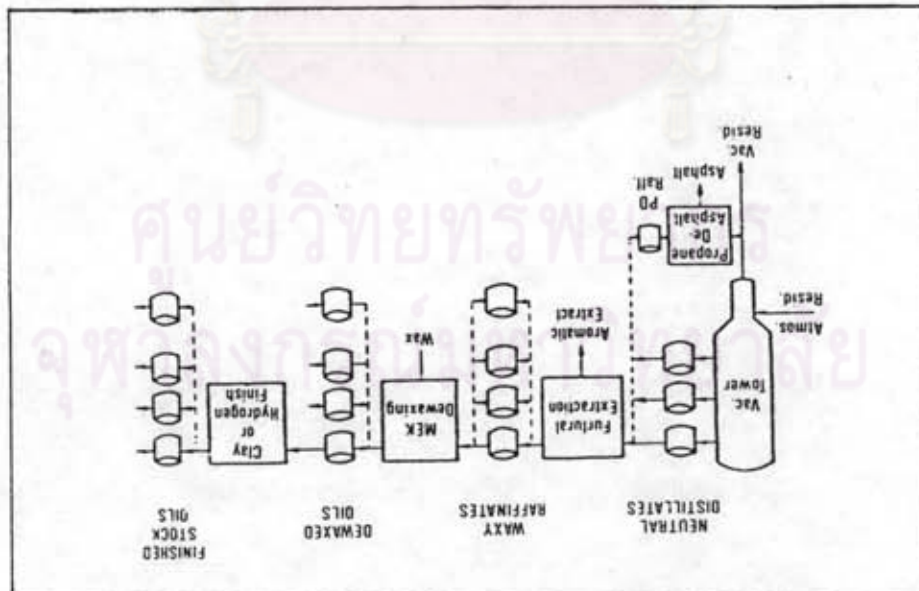


Figure 2.3 Lube processing

The simplified block flow diagram (Figure 2.3) indicates the five processes in lube oil refining:

- 1) vacuum distillation
- 2) propane deasphalting
- 3) furfural extraction
- 4) methyl ethyl ketone (MEK) dewaxing
- 5) hydrofinishing

The first four items are separation processes. The fifth, hydrofinishing, is a catalytic hydrogenation. The purpose of these processes is to remove materials that are undesirable in the final product.

Vacuum distillation

This process separates the atmospheric residue mixture into a series of fractions representing different molecular weight ranges or viscosity ranges from the 90-100 neutrals to the 500 neutrals (500 SUS @ 210 °F). The residue contains the heavier base oils such as the bright stocks (150-250 SUS @210 °F)

Propane deasphalting

The highest boiling portions of most crude oils contain resins and asphaltens. These materials must be removed in order to provide an oil with acceptable performance.

Furfural extraction

Furfural extraction separates aromatic compounds from nonaromatic compounds. The resultant product shows an increase in thermal and oxidative stability as well as an improvement in viscosity and temperature characteristics, as measured by a higher viscosity index (VI).

MEK dewaxing

This process is to remove wax to reduce pour point of the base stock. In this illustrated case, methyl ethyl ketone (MEK) is mixed with the waxy oil. The mixture is then cooled to a temperature between 10 °F (-12 °C) and 20 °F (-6 °C) below the desired pour point. The resulting wax crystals are then removed from the oil by filtration.

Hydrofinishing

For many bases, dewaxing is the final process. The stocks are then shipped to a blending plant where the final products are made by blending the base stocks with additives.

Some stocks, particularly premium stocks, require a finishing process to improve the color, oxidation, or thermal stability of the base stock.

Oil is contacted with hydrogen in the presence of a catalyst at about 600 psi and 500-600 °F. Sulfur is removed as hydrogen sulfide and oxygen from naphthenic acids as water. A slight increase in pour point may occur after hydrofinishing due to conversion of unsaturates to paraffinic wax-like materials.

Table 2.1 shows some inspection characteristics of some finished petroleum base oils obtained from various crude oils using processes described in the foregoing paragraphs.

Table 2.1 Inspection characteristics of some finished petroleum base oils

Source	Sulfur % wt	Kin. Vis., cSt		VI	Pour Point, °C
		40°C	100°C		
Source 1					
100N	0.065	20.39	4.11	101	-13
200N	0.095	40.74	6.23	99	-20
350N	0.126	65.59	8.39	97	-18
650N	0.155	117.90	12.43	96	-18
150BS	0.263	438.00	29.46	95	-18
Source 2					
150N	0.036	24.38	4.55	98	-23
250N	0.055	48.96	6.94	96	-21
600N	0.099	108.00	11.64	95	-23
150BS	0.147	473.00	30.90	95	-15
Source 3					
100N	0.018	25.18	4.66	100	-20
200N	0.012	39.78	6.19	101	-21
500N	0.015	89.37	10.78	105	-21

Synthetic Lubricating Base Oil

Another source of base fluids for lubricants is via the synthetic route. Commercial synthetic fluids are not confined to a single chemical type. Among those of current commercial interest are the following classes:

1. Alkylated aromatics
2. Olefin oligomers
3. Esters of dibasic acids
4. Neopentyl polyol esters
5. Polyglycols
6. Phosphate esters

7. Silicate esters
8. Silicones
9. Polyphenyl ethers

Basic Function of Lubricating Oil

The basic functions of a lubricating oil are: A) Friction reduction, B) Heat removal, and C) Containment of contaminants.

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 in contact and subsequently causing surface damage.

In heat removal, lubricating oil acts as coolant, removing heat generated either by friction or other sources such as via combustion process or by transfer from contact with substances at a higher temperature. In performing this function, it is important that the lubricating oil remains in a relatively unchanged condition. Changes in thermal and oxidative stability materially decrease its efficiency in this respect. Additives are generally employed for the solution of such problems.

Another function of lubricating oil is to remain effective in the presence of outside contaminants. These contaminants are water, acidic combustion products, particulate matter, etc., which generally find their way into lubricating oils employed in various applications.

Properties

Physical property

1. Specific gravity [19]

Specific gravity is the ratio of the mass of a given volume of liquid at 15 °C (60 °F) to mass of an equal volume of pure water at the same temperature. When reporting results, explicitly state the standard reference temperature, for example, specific gravity 60/60 °F.

2. API gravity [19]

API gravity is a special function of specific gravity 60/60 °F, represented by:

$$\text{API gravity, deg} = \frac{141.5}{\text{Sp.Gr. 60/60 } ^\circ\text{F}} - 131.5$$

3. Pour point [20]

Pour point is the lowest temperature at which the movement of the oil is observed. The pour point of lubricating oil is an index of the lowest temperature of its utility for certain applications.

4. Color [21]

The color of lubricating oil is measured in a standard glass container by comparing the color of the transmitted light with that transmitted by a series of numbered glass standard. Color varied from partially clear or transparent to opaque or black. This test is used for manufacturing control purposes and is important since the color is readily observed by the customer.

5. Kinematic viscosity [22]

Kinematic viscosity is a measure of the resistive flow of a fluid under gravity, the pressure head being proportional to the density, ρ , of the fluid : for gravity flow under a given hydrostatic head, the pressure head of a liquid is proportional to its density, ρ . For any particular viscometer, the time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity, $\nu = \eta/\rho$, where η is the dynamic viscosity coefficient. The kinematic viscosity coefficient has the dimension L^2/T , where L is a length, and T is a time. The cgs unit of kinematic viscosity is one centimetre squared per second and is one stokes (symbol St).

The SI unit of kinematic viscosity is one metre squared per second and is equivalent to 10^{-2} St. Frequently, the centistokes (symbol cSt) is used ($1 \text{ cSt} = 10^{-2} \text{ St} = 1 \text{ mm}^2/\text{s}$).

6. Viscosity index [23]

Viscosity index (VI) of lubricating oil is the results obtained from the calculation from their kinematic viscosities determined at 40 and 100 °C.

Viscosity index is an arbitrary number used to characterize the variation of the kinematic viscosity of lubricating oil with temperature. For oils of similar kinematic viscosity, the higher the viscosity index the smaller the effect of temperature on its kinematic viscosity.

The viscosity index is a widely used and accepted measurement of the variation in kinematic viscosity due to change in the temperature of a lubricating oil between 40 to 100 °C.

7. Sulfur content [24]

Sulfur content in lubricating oil will vary to some extent with the instrumentation used and the nature of the oils. Sulfur content is measured by using x-ray fluorescence spectrometric method.

Chemical property

1. Oxidative stability [25]

The most important chemical aspect of lubrication is the degree to which atmospheric oxygen can react with lubricants under various operating conditions. Since the degradation of lubricants by oxidation can be lead to the development of corrosive organic acids and insoluble resinous matter, and a marked increase in viscosity of the lubricant, all of which seriously impair the efficiency of the lubricant.

There are several standard methods existed for the evaluation of the thermooxidation stability of base oils or some of their additive blends. Some methods require longer time and have low precision limits as seen in Table 2.2 .

Table 2.2 Some standard oxidation test

Test Method	IP 56/64	IP 307/80
sample	transformer oils	insulating oils
catalyst	copper sheet	copper wire
oxidizing agent	air (2L/h)	oxygen (1L/h)
temp., °C	150	100
time	45 h	164 h
sample size, g	100	25

The thermogravimetric balance (TG) is one of recent technique developed to evaluate thermal behavior of different chemical compounds.

Loss in weight for most of the tested samples was found to be negligible up to a temperature of 300 °C. Higher than 300 °C , the sample weight begins a rapid and continuous loss. In the presence of oxygen, decomposition reaction occurred, the reaction observed at temperature around 350 °C or higher which leads to retard decreasing in weight loss. These temperatures can be named oxidation points.

At higher temperatures than these oxidation points, weight loss was rapid and continuous again until the complete decomposition and oxygenated resins remains nearly constant with further increase in temperature. The oxidation points can be used as an indication for base oil thermooxidative stability.

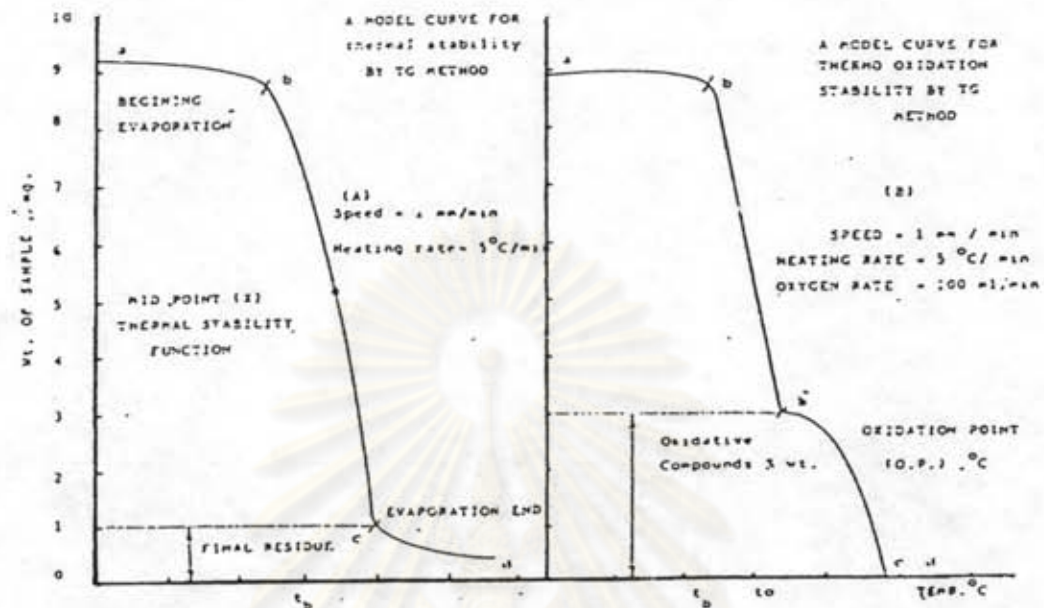


Figure 2.4 Comparison between typical model curves for both TG thermal and thermooxidative stabilities

From Figure 2.4 , the difference between typical model curves for (TG) thermal and thermooxidative stability of lubricating oils usually include the following variable or parameters.

- oxidation points; i.e., temperature at which the rate of weight loss decreases due to the formation of high molecular weight oxygenated compounds.

- oxidative compounds ; i.e., weight of oxygenated compounds in milligrams which remains in the pan of balance at the oxidation point. Higher than that point, the oxidative compounds start to carbonize and finally evaporate as CO_2 .

^{13}C -NMR Spectroscopy [26-27]

^{13}C -NMR method is one of the most important features in separation of paraffinic, naphthenic and aromatic carbon percentages. All the accurate result of carbon types can be directly observed by this technique. Figure 2.5 is spectrum of ^{13}C -NMR of lubricating oil.

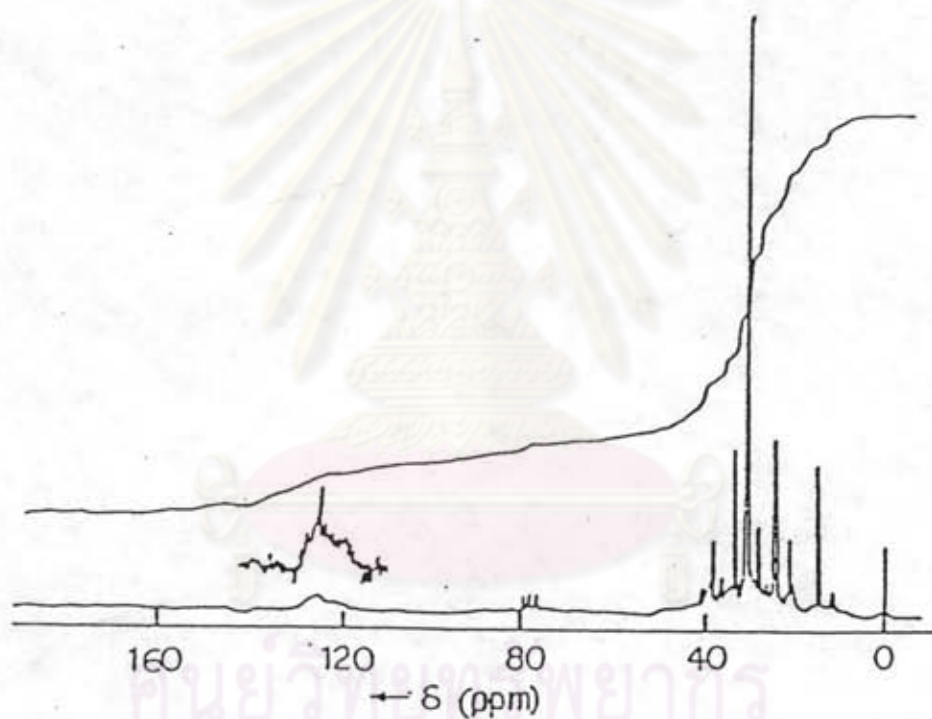


Figure 2.5 ^{13}C -NMR spectrum of the lubricating base oil

In the calculation, the percentage of aromatic carbon was obtained by summation of the intensities from 110 to 160 ppm divided by total integrated area (excluding the area of solvent), while the percentage of the

paraffinic carbon was calculated in similar manner but involving only the intensities from 0-25 ppm and the resolved intensities from 25-60 ppm.

Since $\%C_p + \%C_n + \%C_a = 100$, the percentage of the naphthenic carbon, $\%C_n$, can be obtained by subtraction.





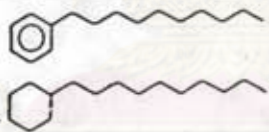
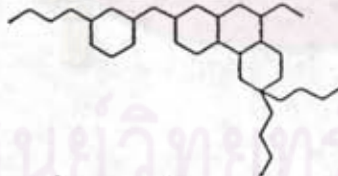

Property and Structure Relationship [28]

The most important characteristics of oils are therefore their viscosity and viscosity index, pour point which must be compatible with climate conditions, the resistance to oxidation, and the ability to protect against corrosion. The base oil does not usually have all these properties and must be improved with appropriate additives.

The effect of difference types of compounds on the properties of lubricating oil can be seen from Table 2.3.

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Table 2.3 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 chains 	High	Medium	Good	Medium
Isoparaffin with isomerized chain 	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

From Table 2.3, the straight , long-chain paraffins are wax-like and therefore their concentrations must be minimized, especially in those oils for application at low temperature. On the other hand, branched chain paraffins can be very desired constituents in a lubricant because of their good stability and viscosity/ temperature characteristics. The longer the side chains in the molecule, the more do these attractive fraction become.

These desirable properties still exist in those naphthenes in which the number of rings per molecule is low, but the side chains and connecting links are long and paraffinic. With increasing ring condensation and shortening of paraffinic chains, the viscosity/ temperature characteristics of hydrocarbons progressively worsen in respect of their stability of lubricants.

Lubricating Oil Additives [15]

Additives can be classified as materials which either impart or enhance a desirable property of the lubricant into which they may be incorporated.

Dispersants-Metallic Types

These compounds have been described in the literature as “detergent”. Since their function appears to be one of affecting a dispersion of particulate matter rather than one of “cleaning up” any existing dirt and debris, it is more appropriate to categorize them as dispersants.

Materials of this type are generally molecules having a large hydrocarbon “tail” and a polar group head. The tail section, oleophilic group, serves as a solubilizer in the base fluid while the polar group serves as the element which is attracted to particulate contaminants in the lubricant.

These additives are, for example, petroleum sulfonates, synthetic sulfonates, thiophosphonates, phenates, and phenol sulfide salts.

Dispersants-Ashless Types

A development of major importance in the additive field has been the discovery and use of ashless dispersants. These materials may be categorized into two broad types : high molecular weight polymeric dispersants for the formulation of multigrade oils and lower molecular weight additives for use where viscosity improvement is not necessary.

These additives are much more effective than the metallic dispersants in controlling sludge and varnish deposits which are involved in intermittent and low-temperature gasoline engine operation.

The compounds useful for this purpose are again characterized by a "polar" group attached to a relatively high molecular weight hydrocarbon chain.

These compounds are N-substituted long chain alkenyl succinimides, high molecular weight esters for examples.

Polymeric Dispersant Additives

These ashless dispersants may serve a dual function. They can be both a viscosity index improver and a dispersant and consist of two general types of molecular configurations, i.e., those whose structure is similar to the ones employed as viscosity index improvers to insure oil solubility, and those containing "polar" compounds to impart the dispersancy characteristic.

Oxidation and Bearing Corrosion Inhibitors

The function of an oxidation inhibitor is the prevention of deterioration associated with oxygen attack on the lubricant base fluid. These inhibitors function either to destroy free radicals (chain breaking) or to interact with peroxides which are involved in the oxidation mechanism.

These compounds are phenolic inhibitors, zinc dithiophosphates for examples.

Anti-Wear Additives

Wear is a loss of metal with subsequent change in clearance between surfaces moving relative to each other. If continued, it will result in engine malfunction. Among the principal factors causing wear are metal to metal contact, presence of abrasive particulate matter, and attack of corrosive acids.

Metal to metal contact can be prevented by addition of film-forming compounds which protect the surface either by physical absorption or by chemical reaction. Abrasive wear can be prevented by effective removal of particulate matter by filtration of both the air entering the engine and the lubricant during operation. Corrosive wear by acidic blow-by products, can be controlled by the use of alkaline additives.

Viscosity Improvers

Viscosity improvers or viscosity index improvers, as they are quite often referred to, comprise a class of materials which improve the viscosity-temperature characteristics of the lubricating oil. This modification of the

rheological property results in an increase in viscosity at all temperatures. The increase in viscosity, however, is more pronounced at high temperatures which significantly improves the viscosity index of the lubricating oil.

Pour Point Depressants

Pour point depressants prevent the congelation of the oil at low temperature. This phenomenon is associated with the crystallization of the paraffin wax which is most often present in the mineral oil fractions.

The pour point depressants do not prevent wax from crystallizing from the oil, but amount of oil occluded on the crystal. The reduction in volume of the crystal permits flow of the lubricating oil.

Industrial Lubricating Oil [29]

Industrial lubricating oil comprises a wide variety of products which, depending on their application, differs widely in their chemical and physical properties. So-called general machinery oil classified according to ISO 3448 viscosity grades (Table 2.4).

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Table 2.4 ISO standard classification of industrial lubricating oils

ISO VG	Kinematic Viscosity @ 40 °C, cSt	
	Min.	Max.
2	1.98	2.42
3	2.88	3.52
5	4.14	5.06
7	6.12	7.48
10	9.00	11.00
15	13.50	16.50
22	19.80	24.20
32	28.80	35.20
46	41.40	50.60
68	61.20	74.80
100	90.00	110.00
150	135.00	165.00
220	198.00	242.00
320	288.00	352.00
460	414.00	506.00
680	612.00	748.00
1000	900.00	1100.00
1500	1350.00	1650.00

This work aims to re-refine used industrial lubricating oil which obtained by collecting mainly as a mixture of hydraulic and gear oils. Thus, in the following contents, only two kinds of industrial lubricating oils, are described.

Industrial Hydraulic Oils [29]

Hydraulic oils represent one of the most important groups of industrial lubricating oils, being widely used in industrial hydraulic systems, particularly machine tools, steering gears, etc. The ISO 6743/4 classification (Table 2.5) classifies hydraulic fluids according to type.

Table 2.5 ISO standard 6743/4 classification of industrial hydraulic fluids

Fluid symbol	General fluid characteristic
HH	Non-inhibited refined mineral oil
HL	Rust and oxidation inhibited refined mineral oil
HM	HL type with improved anti-wear properties
HR	HL type with improved viscosity index
HV	HM type with improved viscosity index
HG	HM type with antistick-slip properties
HS	Synthetic fluids with no specific fire-resistant properties
HFAE	Fire-resistant oil-in-water emulsions containing maximum 20 % of combustible materials
HFAS	Fire-resistant solutions of chemical in water containing minimum 80 mass % water
HFB	Fire-resistant water-in-oil emulsions
HFC	Fire-resistant water polymer solutions containing minimum 35 mass % water
HFDR	Fire-resistant synthetic fluids based on phosphoric acid esters
HFDS	Fire-resistant synthetic fluids based on chlorinated hydrocarbon
HFDT	Fire-resistant synthetic fluids consisting of mixtures of HFDR and HFDS
HFDU	Fire-resistant synthetic fluids of other types

The selection of the hydraulic lubricating oils and the specifically required properties depends on the hydraulic system operating conditions.

Besides, hydraulic oils may be classified in three types :

a) oil based hydraulic fluids which can be divided into three subgroups:

- antiwear fluids
- rust and oxidation inhibited fluids
- invert emulsions

b) water based hydraulic fluids

c) synthetic hydraulic fluids

In applications, hydraulic oils require :

- containment of contaminants, by using appropriated additives such as dispersants, anti-wear additives, anti-rust additives, anti-oxidants, bearing corrosion inhibitors.

- removal of heat, by using appropriated additives such as anti-oxidants, VI improvers.

- reduction of frictional effects, by using appropriated additives such as anti-wear additives, VI improvers, pour depressants, anti-foam agents, friction modifiers.

Industrial Gear Oils

Gear oils are high viscosity index oils, generally compounded with extreme pressure additives to meet the unique requirements of gear lubrication. In applications, gear lubricating oil functions are used to reduce friction, control wear, dissipate heat , prevent rust and corrosion, control foam and to reduce power consumption.

The American Gear Manufacturers Association (AGMA) classified industrial gear oils as shown in the following Table:

Table 2.6 AGMA classification of industrial gear oils

AGMA No.	Kinematic Viscosity @ 40 °C, cSt	
	Min.	Max.
1	41.40	50.60
2	61.20	74.80
3	90.00	110.00
4	135.00	165.00
5	198.00	242.00
6	288.00	352.00
7	414.00	506.00
8	612.00	748.00
8A	900.00	1100.00

The principal types of additives employed for various gear lubricant functions are as follow:

- containment of contaminants, by using some appropriated additives such as anti-rust additives, anti-oxidants.
- removal of heat, by using some appropriated additives such as anti-oxidants, anti-foam agents.
- reduction of frictional effects, by using some appropriated additives such as anti-wear and extreme pressure additives, anti-foam agents.

Used Lubricating Oils [30]

Characteristics of Used Lubricating Oils

As shown in Table 2.8, the composition of used oils vary considerably from that of virgin lubricating oils and other virgin fuels.

Significant differences are observed with respect to ash, bottom sediment and water, carbon contents, viscosity levels. These differences relate primarily to the sources of the used oils.

In general, lubricating oils become contaminated during service or use as well as through mismanagement.

The principal source of contamination during oil usage is the chemical breakdown of additives and the subsequent interaction among the resultant components to produce corrosive acids and other undesired substances.

Physical and Chemical Properties of Used lubricating oil

Physical and chemical properties of used oils wide variations which could be the result of many factors including the characteristics of the virgin oils and their use, as well as the collection/ handling process associated with the used oils.

Table 2.7 is an example of used lubricating oil properties

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Table 2.7 Summary of used lubricating oil analyses

Property or Test	Motor Oils	Industrial Oils
Viscosity @ 40°C,SUS	87-837	143-330
API gravity@ 15.6°C	19.1-31.3	25.7-26.2
Water, vol %	0.2-33.8	0.1-4.6
Benzene insolubles, wt %	0.56-3.33	
Gasoline dilution, vol %	2.0-9.7	
Flash point,°C	79-220	157-179
Heating value, MJ/kg	31.56-44.88	40.12-41.84
Ash,sulfated,wt %	0.03-6.43	3.2-5.9
Carbon residue, wt %	1.82-4.43	
Chlorine, wt %	0.17-0.47	<0.1-0.83
Sulfur, wt %	0.17-1.09	0.54-1.03
Zinc, ppm	260-1,787	
Calcium, ppm	211-2,291	
Barium, ppm	9-3,906	
Phosphorus, ppm	319-1,550	
Lead, ppm	85-21,676	
Aluminium,ppm	<0.5-758	
Iron, ppm	97-2,401	

Technologies of Used Lubricating Oil Recycling [1,31-32]

There are three main recycling technologies of used oils :

- 1) used oil recycled as burner fuel
- 2) reclaiming
- 3) re-refining

Used oil recycled as burner fuel

Processing techniques for the recycling of used oil into fuel include pretreatment of the used oil to remove all or most of the contaminants which pollute the environment or use of specialized facilities with acceptable environmental control. This technique has often been condemned because it destroys a valuable resource and it can cause substantial environmental pollution through widely dispersed distribution of metal oxides and stable organic contaminants. Further, these contaminants may cause scaling of heat-transfer surfaces and fouling of burners and fuel-transfer lines if not handled properly.

Reclaiming

This technique may include any or all of the following : removal of solid particles by settling, centrifuging , or filtering; neutralization of acidic components with clay or alkali, and removal of resulting soaps by washing; heating-distillation to remove volatile solvents, gasoline, and water; clay contacting to remove oxygenated components and spent additives or for decolorization; aeration and use of biocides to reduce bacterial levels; and replenishment of additives.

Re-refining

This process was employed for used lubricating oil to produce clean, high quality, lubricating base oil. Re-refining processes often include a pretreatment to reduce the impurity content by one or more of these methods : application of heat, filtration, acid, caustic, solvents, or

other chemicals. The pretreatment is usually followed by one or more of the following refining processes : vacuum distillation with clay or hydrogen finishing, acid-clay treatment followed by hydrotreating, solvent extraction with clay or hydrogen finishing, and extensive treatment with only clay; the latter is limited to highly segregated used oils.

Four modern re-refining processes were shown schematically in Figure 2.6-2.9.

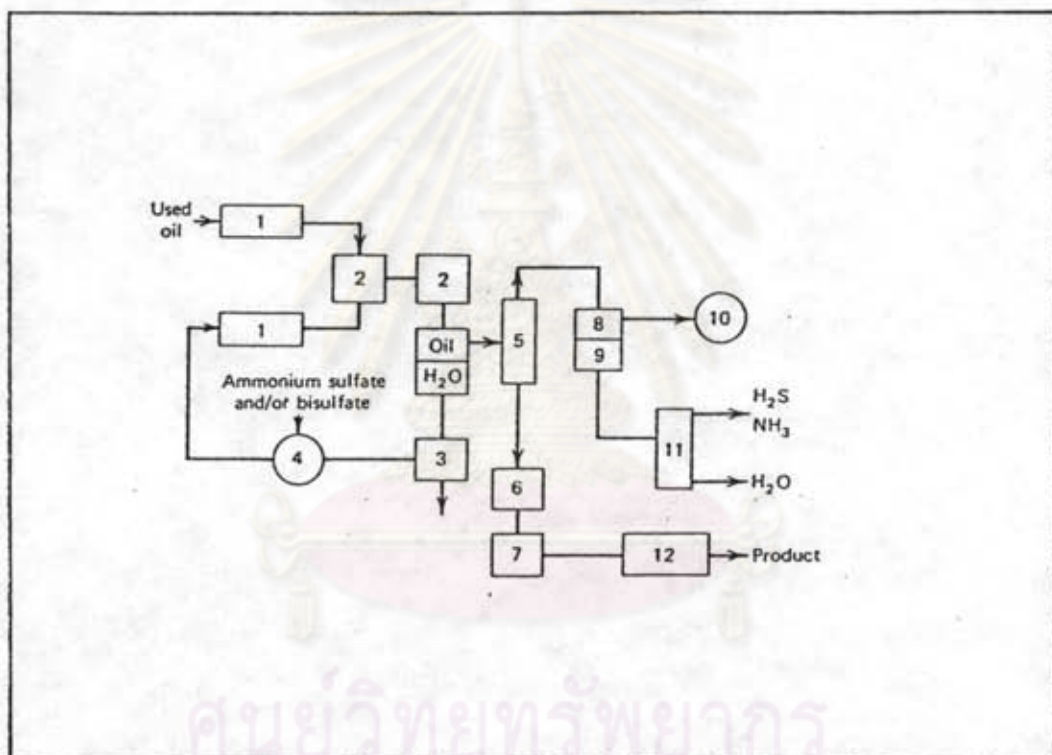


Figure 2.6 Flow chart of the Phillips PROP process(Phillips Petroleum, Bartlesville, Okla.) for re-refining used oil. 1, preheater; 2, reactor; 3, filter; 4, mixing; 5, flash; 6, adsorbent(clay); 7, filter; 8, gasoline; 9, water; 10, storage; 11, stripper; 12, hydrotreater

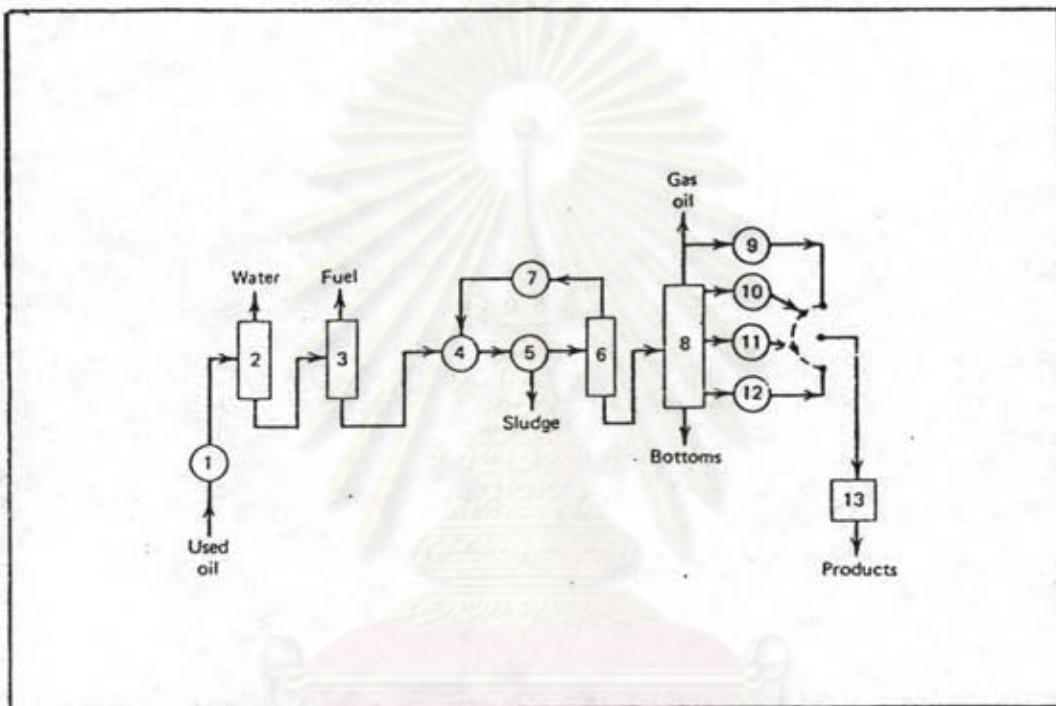


Figure 2.7 Flow diagram of BETC solvent-distillation re-refining process (Bartlesville Energy Technology Center, U.S.DOE). SN=solvent neutral. 1, preheater; 2, atmospheric distillation; 3, vacuum distillation; 4, mixer-solvents/oil; 5, centrifuge or settlers; 6, stripper(vacuum); 7, solvent storage; 8, fractional distillation; 9-12, different distillate fractions; 13, hydrofinishing or clay contactor

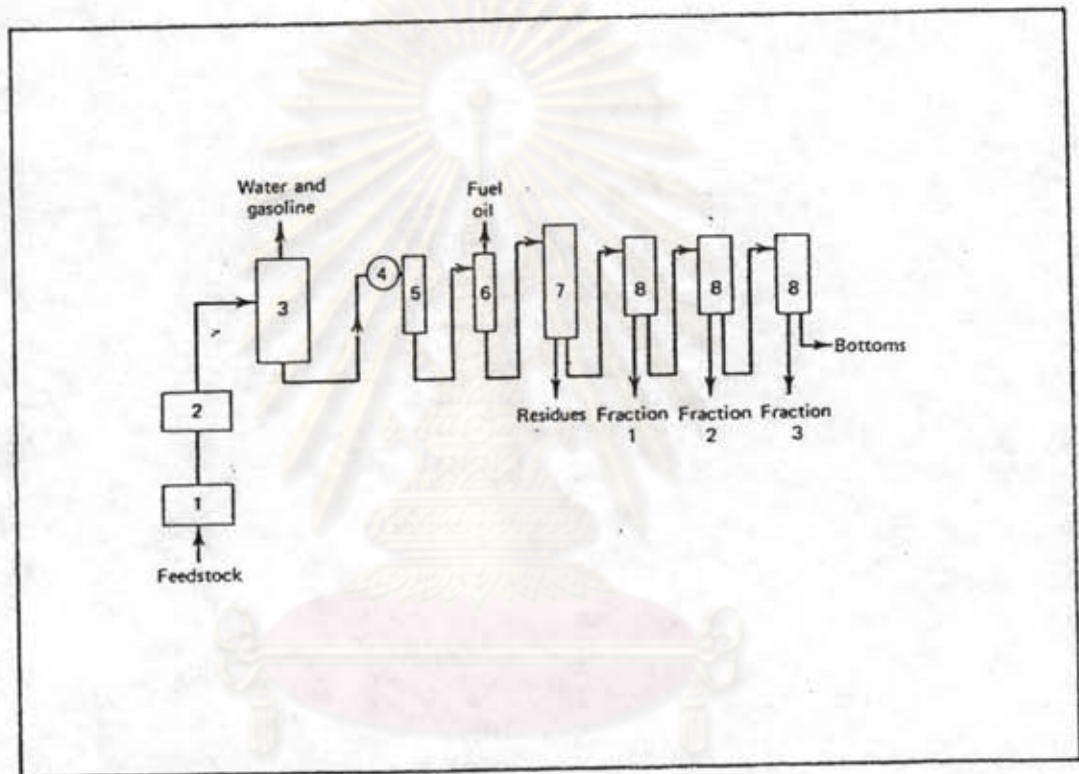


Figure 2.8 Flowchart of the Recyclon process (Leyhold-Heraeus/Adolf Schmits Erban/Degussa, Federal Republic of Germany) for the re-refining of used oils. 1, filter; 2, preheater; 3, dehydration; 4, gasoline separation; 4, sodium emulsion; 5, mixer; 6, flasher; 7, short-path distillation total evaporation; 8, wiped-film evaporators.

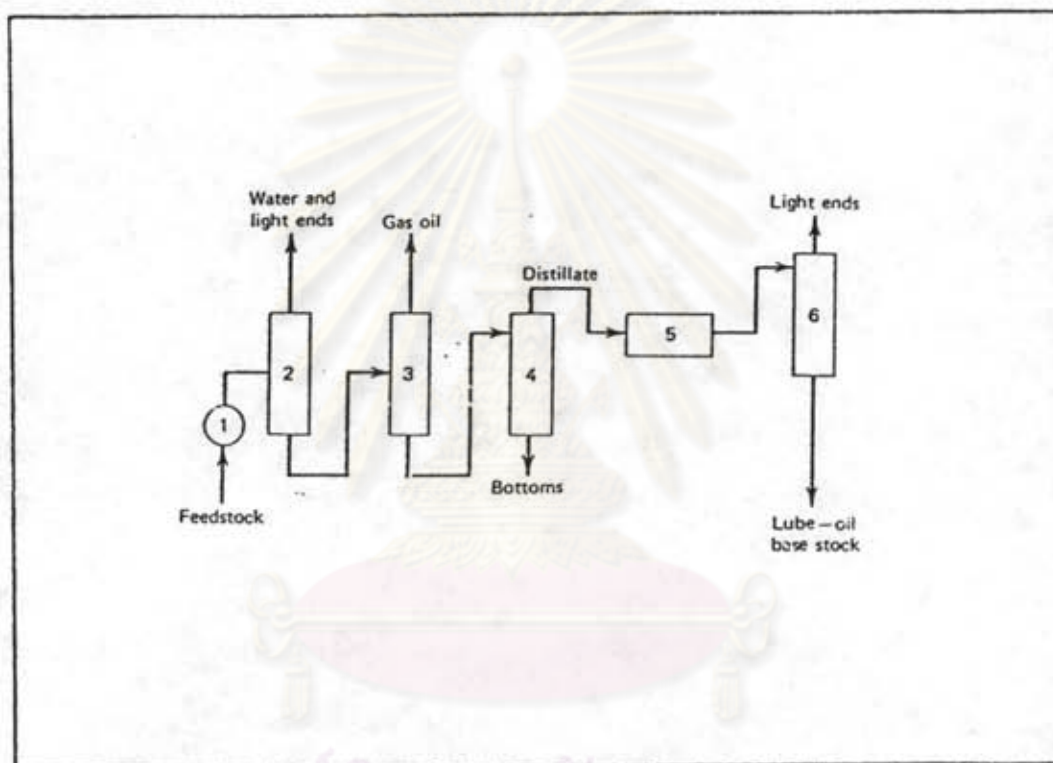


Figure 2.9 KTI process (Kinetics Technology International/Gulf S and T, The Netherlands). 1, preheater; 2, atmospheric distillation dehydration; 3, vacuum distillation; 4, distillation; 5, hydrofinishing; 6, fractional distillation

These processes have been selected for inclusion because of the substantial differences between them, and no implications as to the suitability or quality of the processes or the products is expressed or implied. The principal concern with many of these new re-refining technologies is the lack of technical data and long-term experience establishing the quality of the re-refined base-oil product.

The major objective of this work, as described in chapter I, is to study recycling of used oil by means of two methods : physical and chemical treatment method and catalytic hydrogenation method. The following paragraphs, closely described the two recycling methods.

Physical and Chemical Treatment [33-34]

Physical and chemical treatment method is concerned with two treatments:

- acid treatment
- clay treatment

Acid Treatment

The acid treatment process consist essentially of treating the used oil with concentrated sulfuric acid or oleum. The sludge formed is allowed to settle and removed. The acidic oil is then neutralized with alkali usually soda ash. The neutralized oil is washed with water to remove sodium sulfate, oil-soluble sulfonates recovered as byproducts. The oil is extracted with a solvent such as ethyl alcohol and isopropyl alcohol. The solvent, usually isopropyl alcohol, removes sodium petroleum sulfonats, sodium sulfate and other impurities.

The reaction of concentrated sulfuric acid with oil constituents is an exothermic and irreversible reaction. Acid acts like an acidic sulfonating, polymerizing, alkylating, precipitating, oxidizing and solvent refining agent.

Lubricating oil is acid treated for the following reasons:

- to remove straight chain unsaturated compounds,
- to remove aromatic compounds,
- to remove sulfur, nitrogen and oxygen containing compounds,
- to remove waxes,
- to remove asphaltic and resinous products.

The purpose of acid treatment is to remove all reactive and unsaturated hydrocarbons and impurities which would cause the oil to be darken.

Acid treatment improves color, decreases viscosity, increases viscosity index, electrical properties, oxidative and chemical stability.

Clay Treatment

After neutralization and washing, the acid treated oil is usually treated with clay or other adsorbents. The purpose of the clay treatment is to decolorize the oil and to remove carbon, coke, resinous and asphaltic substances, water and suspended matter. A large portion of coloring matter is removed in the acid treatment process but traces of oil-soluble coloring matters still remain. Trace amounts of inorganic materials such as sodium sulfate and sodium carbonate are also present in the oil. Clay treatment and filtration process is necessary for removing such substances.

Great losses occur in the process of oils as a result of exhaustive treatment with acid for the following reasons:

- polymerization of some hydrocarbons,
- formation of sulfonic acids,

- absorption of oil by the acid sludge.

The physical and chemical treatment has been drastically reduced recently because of the high costs and difficulty associated with disposing large amount of the acid and clay waste byproducts produced by the process.

For further treatment which is the main purpose of this work, to diminish the disposal problem of waste byproducts and to reduce the environmental impact which used oil was treated directly by the catalytic hydrogenation method by using various catalysts.

Catalytic Hydrogenation [35-42]

Catalytic hydrogenation is a process to catalytically stabilize lubricating oils and/ or remove objectionable elements from the used oil or products by reacting them with hydrogen. Stabilization involves converting unsaturated hydrocarbons such as olefins and gum-forming unstable diolefins to saturated materials such as paraffins. Objectionable elements removed by the process include sulfur, nitrogen, oxygen, halides and trace metals.

Generally, in practice, to treat used lubricating oils with the catalytic hydrogenation process, usually need the specific reaction called hydrotreating process.

Hydrotreating is a process to catalytically stabilize petroleum products and/or remove objectionable elements from products or feedstocks by reacting them with hydrogen. Stabilization involves converting unsaturated hydrocarbons such as olefins and gum-forming unstable diolefins to paraffins. Objectionable elements removed by hydrotreating include oxygen, halides, and trace metals.

The main objective of the hydrotreating reaction is desulfurization but many others take place to a degree proportional to the severity of the operation. Typical reactions are:

- hydrogenation of aromatics and other unsaturated molecules,
- ring-opening, especially of multi-ring molecules,
- cracking to lower molecular weight products,
- isomerization of alkanes and alkyl side-chains,
- desulfurization,
- denitrogenation,
- reorganization of reactive intermediates, e.g., to form traces amount of stable polycyclic aromatics.

The extend to which each of these reaction types occurs is determined by the type of the catalyst used, the process conditions and the basestock composition. In general, to handle catalyst in use, more comfortable, and can be recycled well, the supported catalyst should be considered.

Hydrotreating is applied to a wide range of feedstocks from naphtha to reduced crude. When the process is employed specifically for sulfur removal it is usually called hydrodesulfurization or HDS.

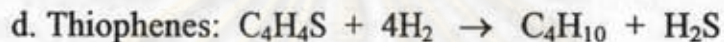
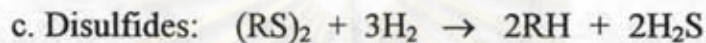
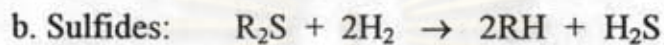
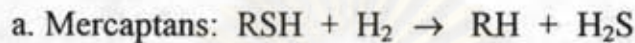
Hydrotreating Catalysts

Catalysts developed for hydrotreating include cobalt and molybdenum oxides on alumina, nickel oxide, nickel thiomolybdate, tungsten and nickel sulfides, and vanadium oxide. The cobalt and molybdenum oxides on alumina catalysts are in most general use today because they have proven to be highly selective, easy to regenerate, and resistant to poisons. The catalyst generally is sulfided in situ prior to its use.

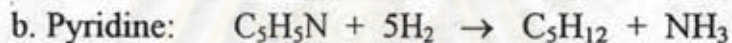
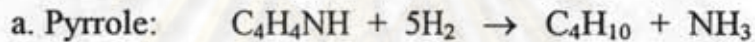
Reactions

The main hydrotreating reaction is desulfurization but many others take place to a degree proportional to the severity of the operation. Typical reactions are:

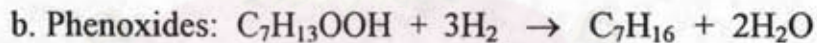
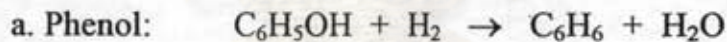
1. Desulfurization



2. Denitrogenation:



3. Deoxidation:



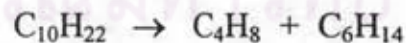
4. Dehalogenation



5. Hydrogenation:



6. Hydrocracking:



Mechanism

1. Molybdenum Sulfide Desulfurization

Griffith, Marsh and Newling proposed mechanisms for hydrogenation of thiophene over the catalysts which they employed. It was thought that the reaction proceeded over molybdenum sulfide catalyst according to the following sequence:

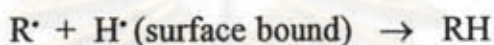
- a. Two-point adsorption of thiophene on a pair of adjacent Mo atoms in an exposed plane of the MoS_2 layer lattice.
- b. Conversion to the half-hydrogenated state by reaction with a hydrogen atom adsorbed on an adjacent Mo atom.
- c. Rupture of the carbon-sulfur bond by reaction of more hydrogen atoms with the half-hydrogenated molecule in which the sulfur atom has become linked to a molybdenum atom.
- d. Conversion of the adsorbed molecule to butane or butene by continued reaction with further hydrogen atoms.

2. Raney Nickel Desulfurization

Ni-Al alloy catalysts, either as powder or in lump form, frequently have characteristics making them superior for some hydrogenations. In the case of the powder, one of the advantages is that it is extremely active and also has a high settling rate so that a reaction can be conducted and the catalyst allowed to settle, then the product can be decanted from the catalyst which can be used in the next batch.

Bougault, Cattelain and Chabrier had proposed the mechanism of desulfurization over Raney nickel that the reaction occurs through the free

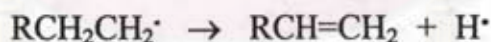
radical involving, as the first step, the chemisorption of the sulfur compound on the catalyst surface through unshared sulfur electrons. The carbon-sulfur bond is thus weakened and a free radical is detached. The hydrogen present on the catalyst surface then reduces the radical to the corresponding hydrocarbon. A simplified mechanism is roughly schematized as follows:



When there is no hydrogen available, such radicals may react in other ways. They may combine with one another,



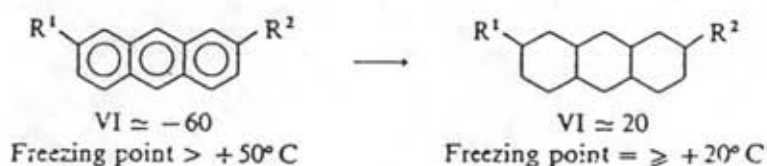
or they may form olefins.



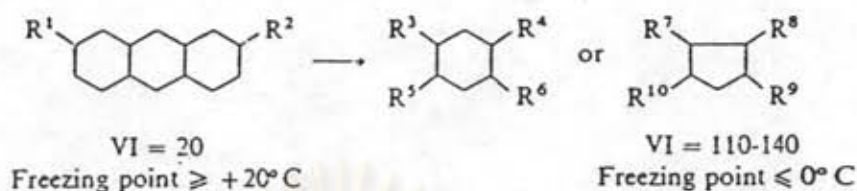
The Preferred Reactions

The desired reactions are generally as follow :

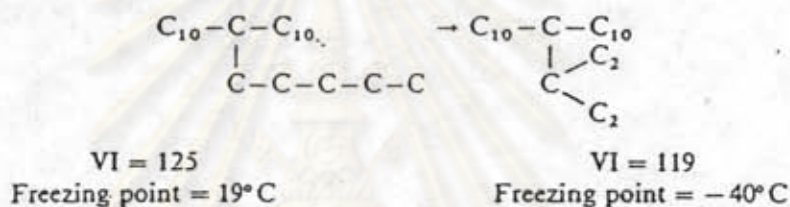
- hydrogenation of polycondensed aromatics into polycondensed naphthenes:



- partial hydrogenation of polycondensed naphthenes :



- hydroisomerization of normal or slightly branched paraffins into highly branched isoparaffins.



In general, the reactions to avoid are cracking reactions such as paraffin and isoparaffin hydrocracking and acid hydrodealkylation of alkylaromatics and alkyl naphthenes. These reactions lead to lower yields of lubricating base oils, lower viscosity, and higher consumption of hydrogen.

The desired reactions indicate that the catalyst should simultaneously activate :

- a) hydrogenation of aromatics
- b) hydrodecyclization of naphthenes plus hydroisomerization of paraffins and naphthenes.

A combination of reactions require a bifunctional mechanism (Figure 2.10) consisting of a hydrogenating, dehydrogenating function and acidic function.

The hydrogenation catalysts, especially hydrotreating catalysts which can be suitably applied for production of lubricating oil comprise at

least one or more metals, metal oxides, or metal sulfides of groups VIB and VIII on a carrier support which comprises one or more oxides of elements of groups II, III and IV.

Because of an economic aspects of the catalyst costs, thus , this work , the reactions ,not only used hydrotreating catalysts such as NiO/MoO₃/ Al₂O₃ and NiO/WO₃/Al₂O₃ , but also studied the reaction of Raney nickel catalyst. In comparison, though Raney nickel catalyst is not hydrotreating catalyst, but it can work as well in hydrogenation reation, and its price is quite more cheaper than those hydrotreating catalysts.

This process has more advantages than the conventional physical and chemical process, such as acid treatment which were messy and gave waste disposal problems. Yields of base oil from the process are higher and costs are quite lower.



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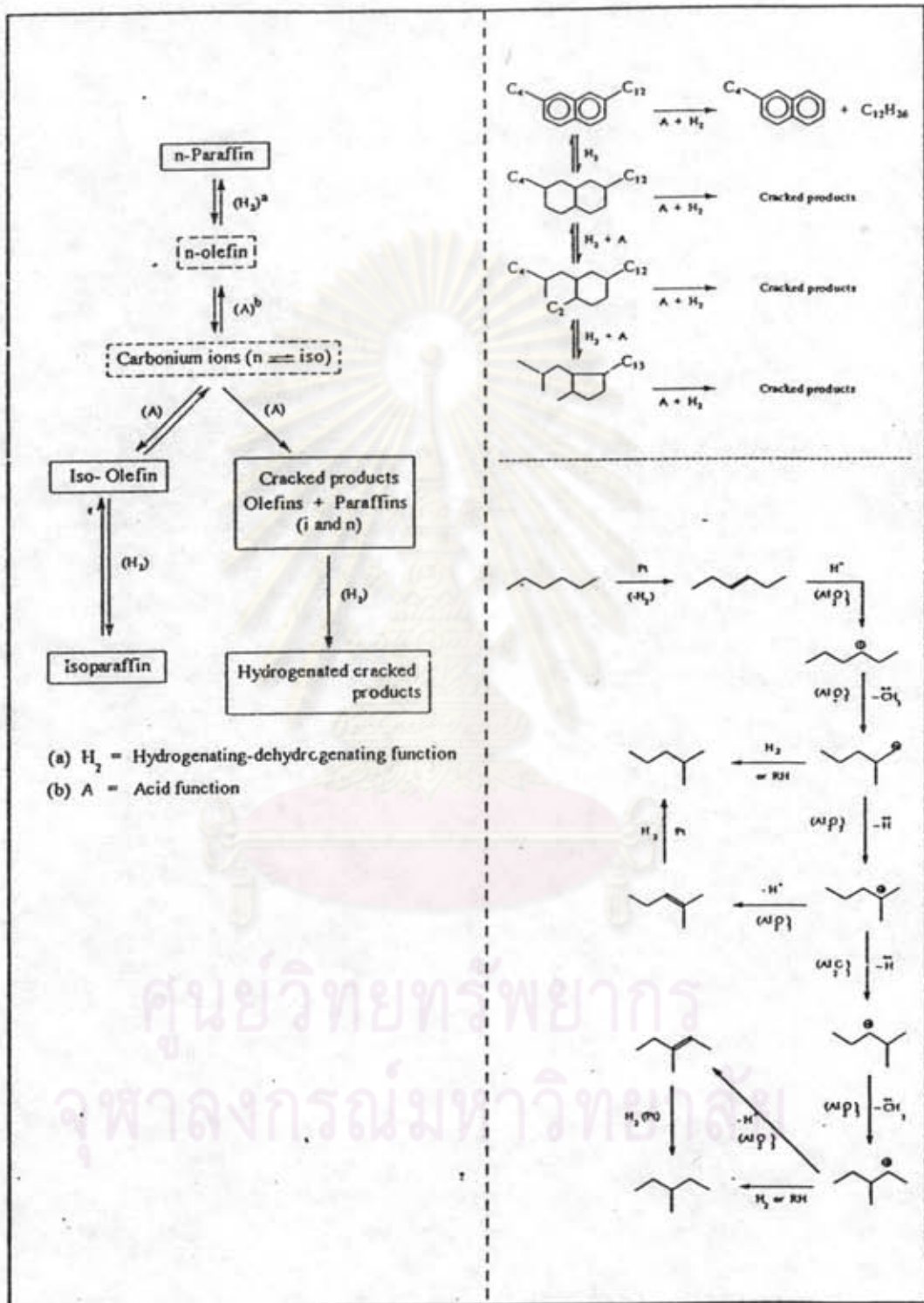


Figure 2.10 Reaction mechanism for bifunctional catalyst

Under much more severe operating conditions, hydrogenation of aromatics and ring opening reactions become important and the aromatic content of the lube base oils is substantially reduced.

Environmental considerations of used lubricating oil [1]

There are three basic disposal methods for used lubricating oils:

- disposal as toxic/ hazardous waste
- re-refining to produce base oils
- use as fuel

Of the three basic methods of disposal or recycling of used oils, the most efficient in term of energy conservation, in that it displaces an equivalent amount of oil, is the use of the material as a fuel. The flue gas components of principal environmental concern are PCBs, PAHs, dioxins and heavy metals. Some pretreatment of the oil will be required to ensure that emission standards for these materials are not exceeded when waste oil is used as fuel. Should this not be possible, the oil must be considered a hazardous waste and treated accordingly.

Disposal of waste oil as hazardous waste requires that it be incinerated at high temperature to ensure complete oxidation of PAHs, PCBs and PCTs.

With regard to re-refining, the process is able to generate a product of sufficiently high quality, the principal environmental consideration concerns the disposal of the byproducts of the refinery process. The effluents/ waste products from some re-refining process can be highly toxic and / or potentially carcinogenic. If these wastes are not disposal properly, they represent a potential hazard to the environment, which is at least as serve as that of untreated used oils.

Economic Aspects of Lubricating Oil Need of Thailand [43]

As the growth of industries in Thailand, lubricating oil is a choice of demands for a necessary chemical used in the production processes. The more productions, the more quantity of oil is needed. Thailand's economic data can be shown in the following Tables.

Table 2.8 Monthly import of petroleum crude oils in 1993 and in 1994

Month	Quantity (million liters)	
	1993	1994
January	1,241.554	1,525.074
February	1,424.711	1,563.849
March	1,092.631	1,854.683
April	1,541.105	1,711.741
May	1,821.550	1,830.552
June	1,446.689	1,616.529
July	1,294.918	1,992.417
August	no data	1,779.680
September	1,802.473	no data
October	1,682.746	1,924.344
November	1,626.195	1,817.978
December	1,892.675	2,085.282

Table 2.9 Monthly import of lubricating oil in 1993 and in 1994

Month	Quantity (million liters)	
	1993	1994
January	6.397	6.482
February	4.792	7.863
March	12.454	7.548
April	10.503	14.169
May	5.793	5.795
June	8.337	10.853
July	10.192	8.414
August	8.897	7.200
September	2.673	5.885
October	8.146	16.635
November	7.197	0.675
December	10.005	13.465

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Table 2.10 Monthly domestic sales of finished oils in 1993 and in 1994

Month	Quantity (million liters)	
	1993	1994
January	21.887	21.975
February	24.480	19.464
March	24.026	26.205
April	21.877	21.649
May	22.258	23.780
June	25.520	25.738
July	22.251	21.465
August	21.271	25.909
September	23.397	23.209
October	20.858	22.836
November	21.116	24.915
December	25.604	27.311

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Table 2.11 Monthly export of finished oils in 1993 and in 1994

Month	Quantity (million liters)	
	1993	1994
January	0.229	0.624
February	0.059	0.346
March	0.355	0.489
April	0.351	0.207
May	0.208	0.317
June	0.226	0.279
July	0.122	0.308
August	0.298	0.106
September	0.174	0.338
October	0.225	0.185
November	0.468	0.311
December	0.178	0.244

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Forecast of Lubricating Base Oil Demand

Table 2.12 Forecast of lubricating base oil demand

Year	Quantity (million liters)
1989	272.3
1990	326.4
1991	345.3
1992	382.0
1993	417.6
1994	458.0
1995	504.4
1996	547.3
1997	593.9
1998	644.2
1999	699.0
2000	758.4

From these Tables, it can say that the more growth in industrial productions, the more demand of lubricating oil in Thailand. Then,if some used lubricating oil can be recycled to the new process, we can save some quantities of oil in use.