CHAPTER II

THEORETICAL CONSIDERATIONS

Crude Oil [17-20]

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

Composition of Crude Oil

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

1. Paraffinic hydrocarbons are lower specific gravity or higher in API gravity than aromatics hydrocarbons of the same boiling point, which the naphthenic and olefinic compounds are intermediate in gravity or density. Oxidation stability of paraffinic hydrocarbons are 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 subject 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 27-204 °C (80-400 °F) for gasoline components.

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

4. Higher ranges for lubricating oils and heavier fuels.

The distribution of various sizes and types of hydrocarbons 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 of predominantly of gasoline and naphthas while the others contain asphalt as the principal constituent. Still other certain lubricating oil distillate as major constituents together with gasoline, naphtha, gas oil, wax, and asphalt in varying proportions.
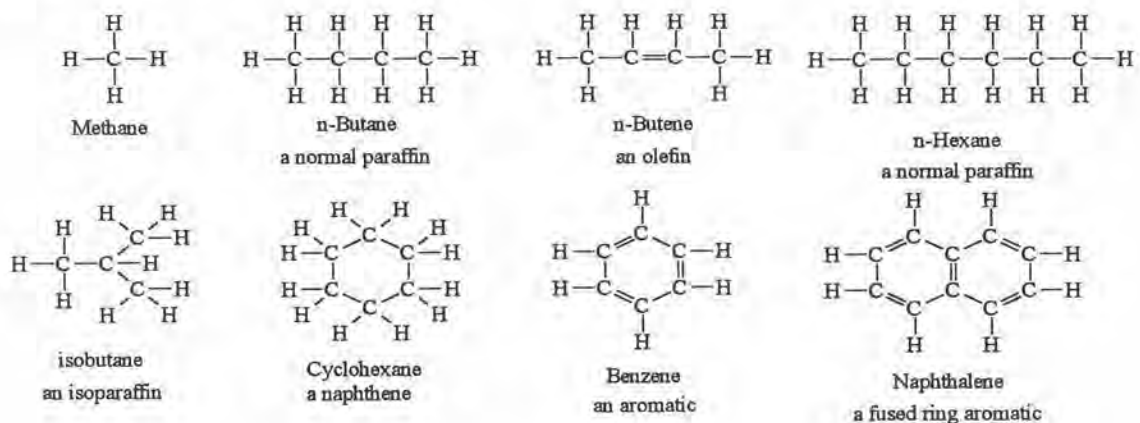

Figure 2.1 Typical hydrocarbons configuration in crude oil.

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

A. Refining Process of Crude Oil

The first step in 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.
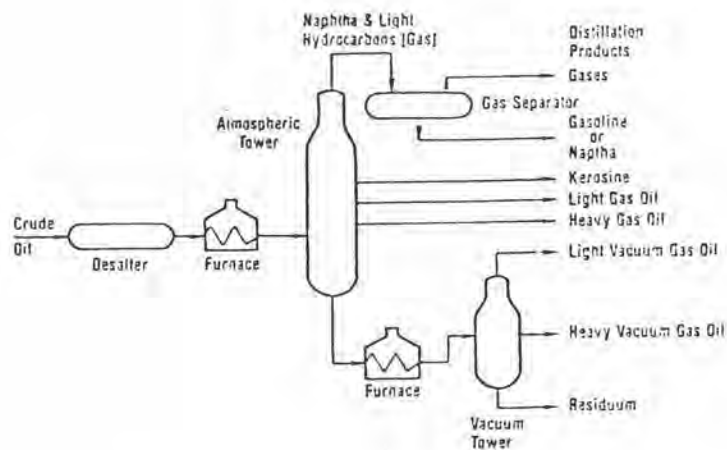
Figure 2.2 Crude distillation unit

Lubricating Base Oil

Source 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.

A. Refining of Petroleum Crude Oil

The manufacture of lubricating base stocks consist of a series of separation or subtractive processes which remove undesirable components from the feedstock leaving a lubricating base stock that meets performance requirements.
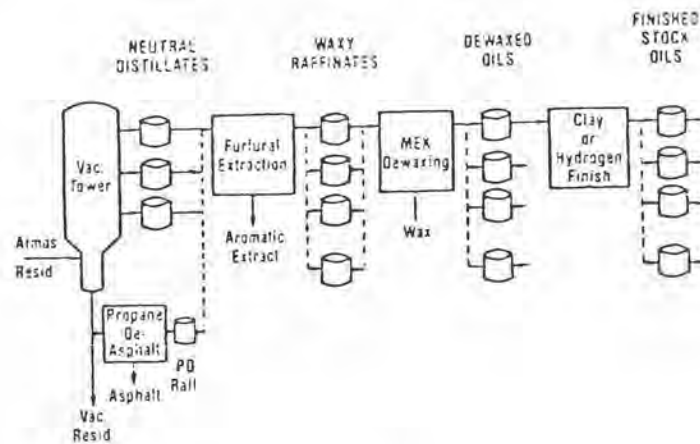
Figure 2.3 Lube Processing

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.

1. Vacuum distillation

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

2. Propane deasphalting

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

3. 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).

4. MEK dewaxing

This process is to remove wax to reduce pour point of the base stock. In this case illustrated, 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 °F) below the desired pour point. The wax crystals which form are ten removed from the oil by filtration.

5. Hydrofinishing

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

Some sticks, 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 psig 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 unsaturated to paraffinic wax-like materials.

Table 2.1 shows some inspection characteristics of some finished petroleum based 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	Sp.Gr. @ 60 °C	Sulfur wt %	Kin. Vis. cSt		VI	Pour Point, °C
			40 °C	100 °C		
Source 1						
100 N	0.860	0.065	20.39	4.11	101	-13
200 N	0.872	0.096	40.74	6.23	99	-20
350 N	0.877	0.126	65.59	8.39	97	-18
650 N	0.882	0.155	117.90	12.43	96	-18
150 BS	0.895	0.263	438.00	29.46	95	-18
Source 2						
150 N	0.861	0.036	24.38	4.55	98	-23
250 N	0.872	0.055	48.96	6.94	96	-21
600 N	0.878	0.099	108.00	11.64	95	-23
150 BS	0.892	0.147	473.00	30.90	95	-15
Source 3						
100 N	0.868	0.018	25.18	4.66	100	-20
200 N	0.869	0.012	39.78	6.19	101	-21
500 N	0.869	0.015	89.37	10.78	105	-21

B. 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. Olefins 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 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 which materially decrease its efficiency in this respect. Additives are generally imployed 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, acid combustion products, particulate matter, etc., which generally find their way into lubricating oils employed in various applications.

Properties

A. Physical property

1. Specific gravity   [21]

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   [21]

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

$$\text{API gravity, deg} = \frac{141.9}{\text{Sp.Gr. } 60/60\ ^\circ\text{F}} - 131.5$$

3. Pour point   [22]

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

4. Color   [23]

The color of lubricating 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 particle 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 [24]

Kinematic viscosity is a measure of the resistive flow of a fluid under gravity, the pressure head being proportional to the density,p, of the fluid : for gravity flow under a given hydrostatic head, the pressure head of a liquid is proportional to its density. For any particular viscometer, the time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity, $v = \eta/\rho$, 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 centimeter squared per second and is one stokes (symbol St). The St 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 cSt = 10^{-2} St = 1 mm ^{2}/s).

6. Viscosity index   [25]

Viscosity index 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 is the effect of temperature on its kinematic viscosity.

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

7. Sulfur content   [26]

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

B. Chemical property

1. Oxidation stability   [27]

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 exist for the evaluation of the thermooxidation stability of base oils or some of their additive blends. Some methods, require longer times and have low precision limits as seen in Table 2.2.

Table 2.2 Some standard oxidation test

Test Method	IP 48/67	IP 56/64	IP 307/80
Sample	Base oils	Transformer oils	Insulating oils
Catalyst	No catalyst	Copper sheet	Copper wire
Oxidizing Agent	Air (15L/h)	Air (2L/h)	O_2 (1L/h)
Temp, °C	200	150	100
Time	Two periods each of 6 them h	45 h	164 h
Sample Size	40 ml	100 g	25 g

The thermogravimetric balance (TG) is the one of recently 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, that 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 point can be used as an indication for base oil themooxidation stability.
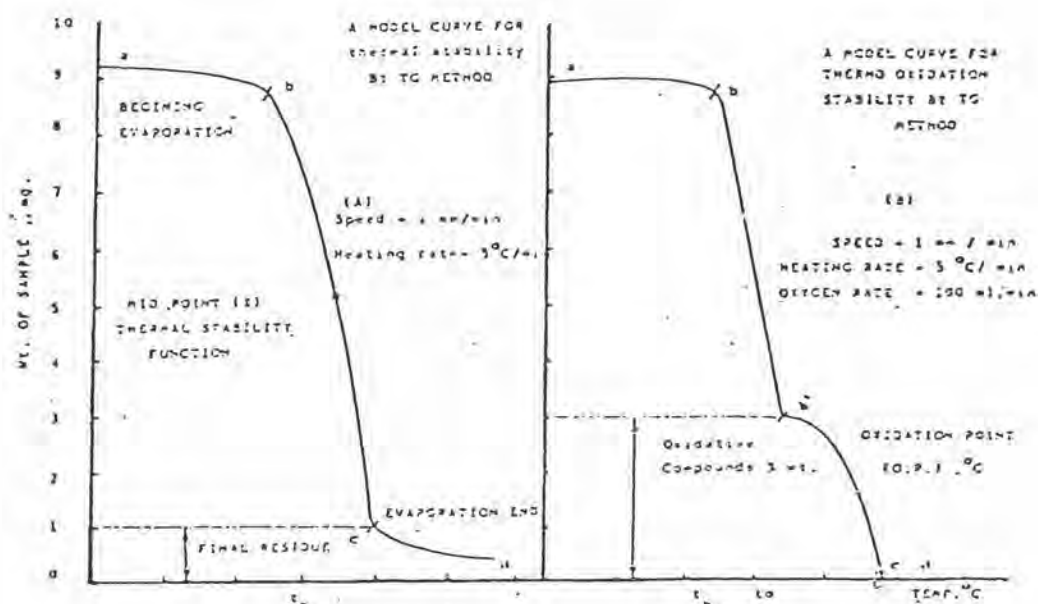
Figure 2.4 Comparison between typical model curves for both TG thermal and Thermooxidation stability.

From Figure 2.4, the difference between typical model curves for (TG) thermal and thermooxidation 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 state to carbonize and finally evaporate as CO_2.

2. C-13 NMR Spectroscopy   [28-29]

C-13 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 C-13 NMR of lubricating oil.
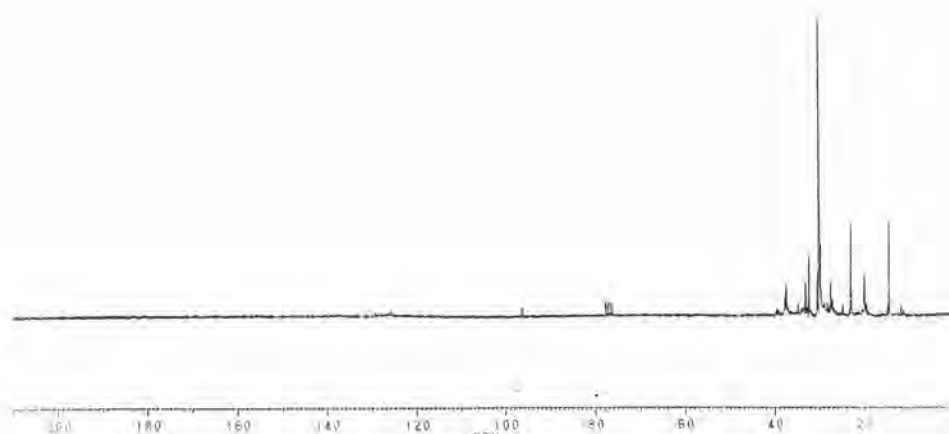
Figure 2.5 C-13 NMR spectrum of the lubricating base oil.

In the calculation, the percentages of aromatic carbon was obtained by summation of the intensities from 110 to 160 ppm devided 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 %Cp + %Cn + %Ca = 100, the percentage of the naphthenic carbon, %Cn can be obtained by difference.

Property and Structure Relationship   [30]

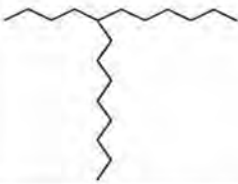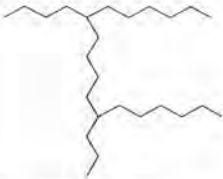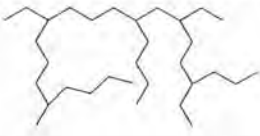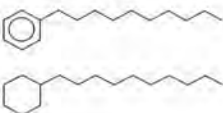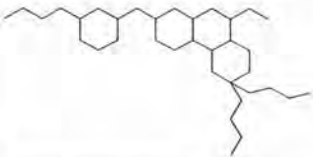The most important characteristics of oils are therefore their viscosity, viscosity index and pour point which must be compatible with climate conditions, the resistance to oxidation, and the ability to protect against corrosion. The base oil dose not usually have all these properties and must be improved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

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

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

Lubricating Oil Additives   [17]

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

A. 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 such as petroleum sulfonates, synthetic sulfonates, thiophosphonates, phenates, and phenol sulfide salts.

B. 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 these 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 succinimide, high molecular weight esters for examples.

C. 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.

D. 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.

E. Anti-Wear Additives

Wear is loss of metal with subsequent change in clearance between surfaces moving relative to each other. If continued, it will result in engine malfunction. Amount 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.

F. 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 pronounces at high temperatures which significantly improves the viscosity index of the lubricating oil.

G. 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.

Base Oils   (Marine Lubricants) [31]

Most modern marine lubricants are prepared from good quality paraffinic base oils although traditionally naphthenic base stocks were preferred. Paraffinic base oils have better oxidation resistance, a higher viscosity index and lower volatility but give harder carbon deposits. However, modern additive technology can modify the hard deposits allowing paraffinic base oils to be used and thereby gaining the advantage of their other superior properties.

Marine lubricants are supplied as monograde oils ranging from SAE 20 to SAE 60, with the SAE 30 and the 40 grades predominating for trunk piston engine oils and SAE 50 as the main cylinder oil grade (SAE J-300, 1987). System oils are invariably SAE 30. The complete ranges of viscosities can be blended from three base stocks which are generally 150SN, 500 SN and brightstock. All base oils are screened and approved by the marine lubricant supplier to ensure that the quality of their products is consistent worldwide.

Synthetic lubricants are starting to find limited specialized applications and trunk piston engine oils of 12 and 30 total base number (TBN) are available. They are currently based on polyalphaolefins with the inclusion of esters to improve additive solubility and seal compatibility.

Additives

The main types of additives used for formulating marine lubricants are:

1. Alkaline detergents
2. Dispersants

3. Antioxidants

4. Corrosion inhibitors

5. Anti-wear and extreme pressure additives

6. Pour point depressants

Many additives are multifunctional and their properties and functions, with particular reference to marine applications, are discussed below.

1. Alkaline detergents

Overbased calcium detergents, with total base numbers ranging from 250-400, from the backbone of the majority of marine lubricants. Although their principal function is to supply alkalinity to neutralize sulfur acids resulting from the sulfur fuels, they also contribute some detergency. Materials used include calcium sulphonates (natural and synthetic), phenates, salicylates, carboxylates and naphthenates. Except for calcium sulphonates, where all the alkalinity is in the form of micellar calcium carbonate, the alkalinity is built into the detergent molecule itself. Most formulations are based on a balanced blend of calcium sulphonates and phenates.

Low base detergents, such as calcium sulphonates, with a soap content of approximately 40 % and TBN of 5-25, are frequently include to maintain engine cleanliness and provide additional protection against rust and corrosion.

2. Dispersants

Ashless dispersant, like detergents, are included to improve engine cleanliness. Most are of the polyisobutylene-succinimide or polyisobutylene-succinate ester type and three basic structures can be identified; monosuccinimide, bis-succinimide and succinate esters. Bis-succinimide are normally used for marine applications because although they are less effective in peptizing low temperature sludge found in gasoline engines than mono-

succinimide, They give better diesel performance by reducing lacquer formation.

3. Oxidation inhibitors

Both chain terminating oxidation inhibitors, e.g. hindered phenols and amines, and peroxide destroying inhibitors, e.g. dithiophosphate and dithiocarbamates, can be included in marine formulations. Mixtures of phenols and amines are often used for synergy but they must have good high temperature performance. The sulfur-containing oxidation inhibitors also have extremely useful anti-wear properties. Oxidation inhibitors can be used advantageously in some base oils refined from low sulfur crudes and in synthetic base stocks.

4. Corrosion inhibitors

Not unexpectedly, marine crankcase oils are sometimes contaminated with water which is normally removed by the lubricating oil centrifuge. To assist further in protecting against rusting, inhibitors such as alkyl sulphonates, phosphonates, amines and alkyl succinic acids/esters are added. They work by forming a hydrophobic film on the metal but must be selected with due regard to the other additives present.

Non-ferrous metals, although resistant to attack by oxygen and water can be corroded by acids arising from the products of combustion and oxidation of the lubricating oil. Corrosion can be combated in two ways; neutralization with low base alkaline earth detergents and the formation of the protective barrier. Oxidation inhibitors can also assist by preventing the formation of acids through oxidation of the lubricant.

5. Load carrying

Load carrying requirements are generally less severe for marine than automotive applications, e.g. there are no specialized cam and tappet test requirements. Nevertheless, good load carrying properties are required particularly for crankcase oils. The requirements are achieved through the use of compounds such as zinc dithiophosphates, dithiocarbamates, sulphurised fatty esters, disulfides, sulphurised alkenes, etc.

6. Pour point depressants

The removal of wax in the refining of a base oil is moderately expensive and for this reason paraffinic base oils are normally only produced with pour points of no lower than -12 °C. Pour point of this level are not acceptable for many marine applications, e.g. oil used in deck machinery, and pour point depressants are therefore added, usually in the range 0.1-0.5 %. Materials used include polyalkylmethacrylates, alkyl naphthelenes and alkylated wax.

Properties and formulation of marine lubricants [31]

Typical properties of the three types of marine diesel engine lubricants are summarized in Table 2.4. The three types of oils have quite different performance requirements and these are summarized in Table 2.5.

There is no simple system for classifying marine engine lubricants comparable to the well known API system of CC, CD and CE for automotive diesel lubricants because they are used in such a range of designs, ratings and service applications on engines burning a wide range of fuels. Consequently, the lubricants are developed through a series of laboratory, rig and engine tests

culminating in shipboard trials. The results are shared with the engine builder when seeking formal approval.

Tests used in developing the various lubricants are outlined in the next three sections. Many of these tests are used for more than one type of oil.

Table 2.4 Typical properties of marine diesel engine lubricants

Properties	System oil	Cylinder oil	Trunk piston engine oil	Test method
Viscosity grade	SAE 30	SAE 50	SAE 40	-
Viscosity (cSt) @ 40 °C	103	218	138	ASTM D445
Viscosity (cSt) @ 100 °C	11.5	19.0	14.0	ASTM D445
Flash point, closed cup (°C)	225	210	220	ASTM D93
TBN (mg KOH/g)	5	70-100	20-40	ASTM D2896
Pour point (°C)	-18	-12	-18	ASTM D97

Table 2.5 Performance requirements of marine diesel engine lubricants.

Slow speed crosshead		Medium speed trunk piston
System oil	Cylinder oil	Crankcase oil
SAE 30	SAE 50	SAE 40
Good oxidation stability	Neutralize sulfur acids	Control piston deposits
High thermal stability	Prevent scuffing	Prevent ring sticking
Keep crankcase clean	Remove deposits	Neutralize sulfur acids
Release water and insoluble	Provide film strength Improve	Retain alkalinity
Aid load carrying	anti-wear	Protect bearings from corrosion
Low emulsibility	Compatible with system oil	Assist load carrying
Prevent rust and corrosion		Provide good filterability and demulsification

Collection of waste lubricant [1]

Waste lubricant that is collected is usually disposed of either by burning as fuel or incineration as waste, or is reclaimed. Some lubricants, such as industrial oils, can be treated relatively easily and recycled, whereas automotive engine oils require more sophisticated treatment to produce re-usable base fluid acceptable quality.

1. Used industrial lubricants

There are many potential sources of used industrial products but reprocessing is not option for a large number of these synthetic and fatty oil based products. Some products, such transformer oils and hydraulic oils, can be readily collected from large industrial concerns and segregated. Consequently, contamination can be avoided. These oils may be regenerated to a recognized standard and returned to the original source.

2. Used automotive lubricants

These will include mono- and multigrade crankcase oils from petrol and diesel engines, together with gear oils and transmission fluids. Used industrial lubricants that have been inadequately segregated will also be included. Apart from the degradation products from the in-service use of the oil, a wide range of contamination is possible. This includes:

- Water - combustion by-product, rain water/salt water ingress.

- Fuels - residual components of gasoline and diesel fuel.

- Solids - soot, additive and wear metals, rust, dirt, etc.

- Chemicals - used oil can be used as an unauthorized means of hazardous waste disposal.

- Industrial oils - inadequate segregation of oil types can allow contamination by fatty or naphthenic products.

There are many potential sources of used automotive oils, for example DIY motorists, service stations, company car or truck fleets and waste oil collection sites. There is also an equally wide range of commercial collectors. Good management of a used oil collection system is paramount to minimize both the variability of the material supplied to a re-refining plant, and the problems of contamination by toxic or hazardous materials.

Used oil analysis [31]

Regular testing of lubricants in service helps to safeguard the machinery. For maximum benefit, testing must be conducted rapidly and the tests are chosen to give the maximum information with a minimum number of tests. Supplementary tests can be carried out if the need arises.

Interpretation of results and, where necessary, a recommended course of action part of the lubricant suppliers responsibilities (Van der Horst,1987). The reasons for carrying out individual tests and the information they can give are outlined the following sections.

1. Density

Used for selecting the correct gravity disc for the lubricating oil centrifuge.

2. Viscosity

Changes in viscosity in service arise from either fuel dilution or suspended matter. Assuming no other adverse symptoms, changes in viscosity of ± 20-25 % can be tolerated. Contamination by marine diesel or distillate fuel

reduces viscosity; contamination by heavy fuel oil increases viscosity. In both cases the flash point of the lubricant is likely to be reduced. If increased viscosity is due to carbonaceous insoluble, both viscosity and insoluble can often be reduced by correct centrifuging.

3. Flash point

Both marine diesel and heavy fuel oil have low flash points compared with lubricating oil, e.g. 60-100 °C compared with over 200 °C. The relatively low flash point of heavy fuel oil is caused by the cutter stock, e.g. kerosene or gas oil used to give an acceptable viscosity from the extremely viscous vacuum residues, visbroken residues, etc. Contamination by diesel or heavy fuel oil therefore normally reduces the flash point of the lubricant, although with heavy fuel oil the small amount of volatile matter can be driven off from the lubricating system.

4. Insoluble

The majority of insoluble are derived from the combustion products of the fuel and lubricant. Insoluble can also contain spent additive from the lubricant and general debris such as rust, wear metals and contaminants from water ingress and air intakes.

Heavy duty detergent oils usually include ashless dispersants within their formulation to keep combustion contaminants in fine suspension in order to prevent damage to machinery. Warning limits for the insoluble content of trunk piston engine oils vary with the oil but in some cases level of 5 % can be tolerated. When high levels of insoluble are encountered, the fuel and fuel combustion systems should be examined.

5.Total base number

In service, the total base number, or reserve alkalinity, steadily declines until a plateau is reached. At this point the total base number of the new oil, used for topping up, balances the acidic products of combustion. The plateau is usually rather more than 50 % of the original TBN and must meet the minimum level set by the engine manufacturer. If TBN declines by more than say 60 %, countermeasures must be taken depending on the circumstances. In one-off situations, part of the charge can be replaced with a higher TBN oil, otherwise the continuous use of a higher TBN oil is recommended.

6. Water content

The water content of system and heavy duty of crankcase oils can generally be contained below 0.2 and 0.5 %, respectively. If water is detected, the first priority is to establish and correct the source of contamination. This is particularly true for sea water contamination because severe corrosion can occur very rapidly.

7. Wear metals

Inductively coupled plasma atomic emission spectroscopy has made the determination of wear metals very easy and used oil can be scanned for the presence of 20 elements in less than 1 minute. Wear trends can be obtained by comparing wear metals from a series of samples. However, it should be noted that the accuracy of the determination can be limited by the particle sizes present.

Environmental impact of 'consumed' lubricant [1]

Following the Exxon Valdez incident in Alaska, the time and effort spent on clean-up was considerable. One of the most spectacularly effective means of treating contaminated beaches was the addition, to the oil, of nutrients that allowed the indigenous bacteria to biodegrade the oil *in situ*. Land farming and oxygen addition to contaminated soil have also proved successful in dealing with hydrocarbon contamination. Oil dose biodegrade in aerobic conditions, albeit rather slowly. If a lubricant is subjected to one of the standard OECD tests for ready biodegradability, however, it will most probably fail to show more than 20-30 % degradation. There are many reasons for this; perhaps the most obvious, yet most often ignored, is that the test was probably designed to assesses a single water-soluble chemical, probably a surfactant, and not a complex mixture of poorly soluble hydrocarbons.

The environmental degradation of lubricating oils is less easily demonstrated. One of the problems is the complex and varied mixture of the used the material. Materials other than hydrocarbons can inhibit or influence the rate of degradation, which is of the greatest interest. Once released into the environment, there is a finite time before the waste lubricant is bound up in sediments or soils. Once there, due to the hydrophobic nature of the material, water is excluded and conditions are essentially anoxic. Anaerobic degradation of oils does not readily occur in nature--much to the relief of the oil exploration and refining industry. However, waste lubricant on the road, or in soil and sediments is not locked in place in the same ways as crude oil in rock formations. Heavy rain can wash surfaces, churn-up river beds and release sediments, while the action of animals and plants can oxygenate soils. One means of lessening the burden of the environment, and minimizing the

impact of 'consumed' lubricant, would be to use readily biodegradable lubricants.

Lubricants that are susceptible to microbial degradation were developed in the 1970s for use in outboard engines. These lubricants were based on synthetic esters, structurally similar to naturally occurring triglycerides, which increased their acceptability to the degrading organisms. In recent years, lubricants based on rape-seed oil have been developed for use in chain saws and the hydraulic systems of vehicles such as snowmobiles, which are used in environmentally sensitive areas. In order to develop a biodegradable lubricant, however, it is important to have a means of assessing biodegradability. This is by no means straight forward.

Treatment of collected lubricant

1. Production of fuel oil blending component

Used lubricant is an excellent source of energy, but contains contaminants which, when burnt, can create environmental pollution and operational problems. Simple processing (e.g. settling and filtration /centrifugation) is sufficient to remove coarse solids and water, and a mild chemical treatment (e.g. caustic soda solution) may also be used to reduce concentrations of other contaminants. Disposal of waste products may be a problem.

2. Reclamation of lubricating oils

Some specific types of industrial oils can be readily segregated and are suitable for relatively simple reprocessing before being returned to their original service. Typical processing methods involve filtration and removal of water or volatile decomposition products under vacuum.

Large industrial customers can arrange for on-site reprocessing (e.g. reconditioning of transformer oils at power generation plants), or can collect specific drain oils for off-site reprocessing and return (e.g. reclamation of railroad diesel engine oils). These types of consumer-specific reprocessing can be cost-effective compared to the expense of new oils.

3. Production of re-refined lubricant base oils

When dealing with oils from multiple sources, complex processes are needed to remove the wide range of contaminants and additives that will be present. The objective is to produce base oils that can then be used as substitutes or alternatives to virgin mineral base oils. The main re-refining technologies are summarized in sections 3.1 to 3.4. Most of these are continuous rather than batch processes and rely on receiving a reasonably homogeneous used oil feedstock if the product are to be consistent. One means of achieving consistency is to mix a complete month's supply of used oil and to use that to feed a continuous process appropriate to the characteristics of the resultant mixture. There is a risk that contamination will spoil a large batch, however, and quality checks on the feedstock are very important.

3.1 Acid/clay treatment

This has been the principal re-refining process in commercial use (e.g. Meinken process), but has the disadvantages that it generates large amount of hazardous waste and cannot effectively remove the high concentrations of additives used in modern engine oils. It is now being superseded by other, newer technologies.

In acid/clay process, the used oil of first treated with 98 % sulfuric acid; the resulting acid sludge is the separated and the remaining oil is clay treated, neutralized and filtered. Process yields from modern used engine oils are low (50-60 % of lube boiling range material), and large quantities of

acid sludge and oil soaked clay are generated. These wastes are difficult and costly to dispose of in an environmentally acceptable manner. Sometimes a thermal pre-treatment is use to degrade some of the additive and reduce the workload on the acid treatment stage. Base oils produced by the acid/clay process are usually dark in color, have a noticeable odor and are somewhat inferior in quality to virgin minerals oils.

3.2 Solvent extraction

Propane or other solvents can be used to selectively extract the base lube material from the used oil (e.g. IFP process). A high-boiling asphaltic residue, which contains most of the additives and other impurities, is recovered as a separate stream. (Note that this is not the same process as refinery furfural or phenol extraction, which uses solvent to selectively remove aromatics from lubricant fractions.) A further finishing treatment of the lube material is normally required any may involve low severity acid/clay treatment, clay treatment alone, or hydrofinishing. Solvent extraction plants are expensive to build and operate, and generate significant amounts of waste materials and hazardous by-products. Overall base oil yields are 70-80 %.

3.3 Distillation/clay treatment

Thin-film distillation under high vacuum (e.g. Luwa evaporators) allows the separation of gas oil, lube oil and an asphaltic residue containing most of the additives and contaminants from the used oil. The lube oil stream is finish by clay treatment. Overall base oil yields are again 70-80 % and significant amounts of spent clay must be disposed of.

3.4 Distillation/hydrotreatment

This technology is the most recent (e.g. KTI and Mohawk processes). After pre-treatment and thin film distillation, the base oil fraction is hydrotreated under moderate conditions. A final distillation step yields a range

of base oil streams of different viscosity. Process yields of base oil are high at 90-95 %. By-products are a low boiling distillate (used as fuel in the re-refining plant), gas oil and a non-hazardous asphaltic residue. Emission and waste streams are limited, therefore this process is capable of meeting very strict environmental controls. Base oils produced by this route tend to be of superior quality compared to the older technologies. The hydrotreatment process is comparatively sophisticated, capital intensive and requires skilled operation, although operating costs are not exceptionally high.

Reconditioning and Regeneration of Used Lubricating Oils [32]

Oxidation products, dirt or other contaminants that accumulate in the oil during use strongly reduce its quality. Lubricants with greater amounts of these products may not any more fully satisfy the demands and must be replaced. They are called waste oils and are collected and processed in order to prevent contamination of the environment, to preserve raw materials and in some cases for economical considerations. In cases where processing is not economical or reasonable or where it creates technical difficulties, waste oils are usually burned. In order to prevent environmental pollution, many countries have issued regulations for the treatment of waste oils; thus, the Federal Republic of Germany has issued the Waste Oil Law in 1968 and additional regulations in 1969 and 1971. As a result of this law and of steps for the preservation of the environment the amount of waste oil collected in the FRG has increased considerably and is now of the order of 90 % of the collectable volume. Considering the total lubricant consumption, it is to be regarded that certain amounts of used oils cannot be collected and recycled such as process oil (incorporated into rubbers, plastics, cosmetics, adhesives etc.), exported oil fillings, evaporation and leakage losses, oil fillings in car engines, gears, and axles to be scrapped etc.

A. Reconditioning

In some applications oils become contaminated without losing their effectiveness. This is the case with metalcutting oils and oils for hydraulic orcirculatory lubrication systems, as well as with oils for turbines and transformers, where, after prolonged use, aging products are precipitated as sludge and moisture and mechanical impurities are accumulated. Such oils are frequently purified by the user company by mechanical or adsorptive reconditioning and used again.

1. Mechanical Oil Purification

Undissolved contaminants and foreign matter are separated by sedimentation, filtration or centrifugation. Nondispersed coarse mechanical impurities, such as small shaving in metal cuttingoils, and coarse sludge or water can be removed by sedimentation in settling tanks which allow the separation of the clear oil from the sediment at the bottom. The separation can be accelerated considerably by heating of the oil to 50-80 °C. The procedure is time-consuming, the clarification of the oil is not always complete and the separated sludges still contain large amount of oil.

Separating centrifuges with a high settling efficiency and giving very good oil yields can be used for the removal of small amounts of solids as well as for the separation of water and sludge. Repeating the centrifugation two or three times further increases the purification effect. Small amount of water can be added to the oil in order to coagulate very fine impurities. However, this approach cannot be applied to oils with emulsion forming tendencies or which contain water-soluble components (formation of emulsions, leaching effect).

Filtration through paper and paper strip filters, precoated filters and recently also membrane filters can be used to remove finely dispersed solids or small quantities of sludge materials from large oil volumes.

Filtration or centrifugation is usually included in a side stream of large oil circulation systems and carried out during operation. Occasionally, both processes are used in combination with each other.

2. Adsorptive Purification

The treatment of oils which also contain dissolved aging products with adsorbents such as natural or activated bleaching clays (rarely active carbon) represents an efficient way of oil purification. Diatomaceous earth (kieselguhr) which is frequently used as filter aid must not be considered as an adsorbent.

After coarse removal of water (by sedimentation or centrifuging) 0.5-5 vol. % of adsorbent is added to the oil at 50-80 °C and the mixture stirred for 30 to 60 min. In most cases an adsorbent which has been separated from the oil on filter plates or precoated filters cannot be reused. Additives present in the oils are removed completely or partially by adsorption; they must replenished in a convenient way. Oil purification by adsorption is therefore preferably applied to additive-free products such as transformer oils in reconditioning systems within the user firm. Mobile purification aggregates can be connected directly to a transformer and may include an additional drying stage in the form of vacuum-spraying. Adsorptive cleaning processes are not suited for the purification of emulsions.

B. Regeneration [33]

Heavily contaminated and oxidized oils are usually subjected to regeneration in specialized plants (re-refining). The largest part of these oils are frequently reconditioned at the user plant.

The regeneration of waste oil includes a physical and a chemical treatment which remove practically completely the suspended as well as dissolved foreign matter, the aging products and products susceptible to aging, as well as the additives remaining in the oil.

Until recently, the waste oil regeneration has been carried out by a large number of small and medium companies with capacities varying from 5000 tons-20000 tons/year (130 to 500 bbl/d), which were usually located near waste oil accumulation centers. Recently, the number of these firms has been dropping showing a tendency towards and increase of the capacities to 40000-150000 tons/year (1000 to 4000 bbl/d).

The average yield of re-refined oil, obtained from a waste oil with ca. 10 % solid contaminants and containing water and fuel dilution of 2-4 %, is in the range of 70-85 %, depending on the process used. Problems arise from the varying composition of the raw materials which lead to different chemical structure of the regenerated oils.

Conventional Regeneration

The multi-stage process differs significantly from the primary refining of petroleum fractions. In most cases waste oils contain additives which must be removed from the oils since the decompose at the distillation temperatures used. For this reason the refining stage is carried out prior to the continuous still distillation. Cracking reaction may occur in older plants which

use direct heating without temperature control, thus creating the need for further treatment of the distillates and heavy residues. The refining consists of 6 stages (Table 2.6). The secondary raffinates (re-refined oils) obtained are used without further treatment as base oils for finished products.

Table 2.6 Conventional Regeneration of Waste Oils.

Stage	Purpose	Process
1	Coarse removal of water and foreign solids	Sedimentation
2	Removal of low-boiling fractions and residual water	Atmospheric distillation up to ca. 250 °C
3	Removal of oxidation products and additives	Sulfuric-acid treatment, followed by lime neutralization
4	Removal of refining sludge	Decanting, filtration
5	Separation into one or two light or medium viscosity distillates and a residue	Vacuum distillation (80-100 mbar)
6	Bleaching and stabilization of the fractions	Treatment with bleaching clay

The heavy naphthas, gas oils, and sludges obtained in the distillation are used as fuel for plant and for steam generation. The acid tar is neutralized with lime mixed with waste oil and burn in special installations. Where this is not possible due to the emission of sulfur dioxide, the tar can be processed as raw material in sulfate factories. The firm MEIKEN at Haltern/FRG has developed a process in which the acid tar is mixed with bleaching clay and used as fuel in cement production, without negative effects on the cement and the environment.

MEINKEN Process [34]

In the MEINKEN process the stages of conventional waste oil processing have been developed further with the aim to achieve a better product quality and energy utilization, to accumulate less acid tar and to minimize the labor requirements. A reduction in the sulfuric acid consumption and thus in the amount of acid tar accumulated is achieved by means of a patented intensive mixer. In order to avoid further treatment of the end products, the oil in the vacuum distillation id heated indirectly by a heat transfer fluid, thus protecting it from overheating and cracking reactions. By adding ca. 2% of bleaching clay to the raffinate the distillation is used at the same time as hot contact refining. The bleaching clay is removed from the still continuously together with the distillation residue and separated by filtration (Fig 2.6).

The process which consists of 5 stages (without the treatment of the byproducts) is partially automated; it is also optimized with respect to heat and labor requirements and can be run in single-shift operation with a start-up period of 1 h and a shut-down period of 1/2 h and a crew of 3-4 operators.

The quality of the secondary raffinates obtained in this way is satisfactory; the additives present in the raw material are practically completely removed from the regenerates. So far, more than 40 plants have been erected in Europe, Africa, in the Middle East and in the USA .
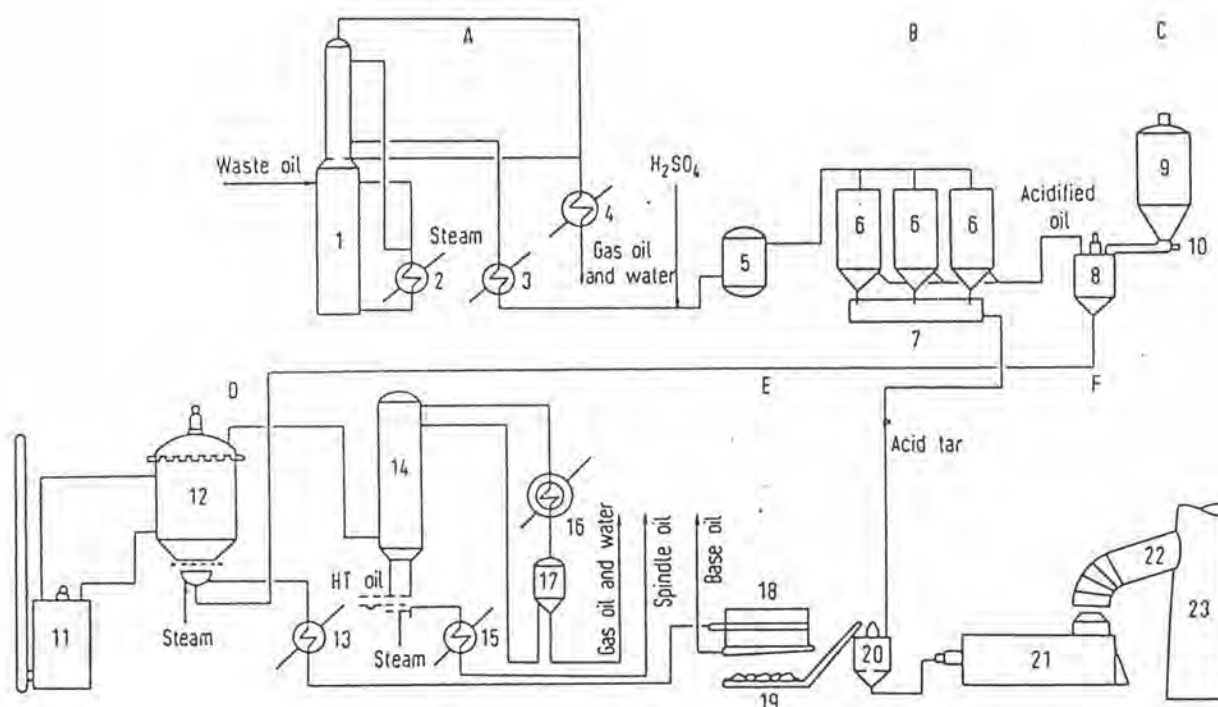
A. Dehydration unit: 1.dehydration column ; 2. heat exchanger ; 3. cooler ; 4. condenser

B. Refining unit: 5. reactor ; 6. settling tank ; 7. acid tar draining vessel

C. Bleaching clay mixing stage: 8. mixer ; 9. bleaching-clay hopper ; 10. dosage worm conveyer

D. Hot contact distillation: 11. high-temperature oil furnace ; 12. rapid evaporator ; 13. drain cooler ; 14. spindle oil column ; 15. drain cooler ; 16. condenser ; 17. separating tank

F. Filtration: 18. filter press or precoated filter ; 19. conveyer belt

Figure 2.6 Flow scheme of MEINKEN Process.

The IFP Process [35]

In the process developed by the INSTITUTE FRANCAIS DU PETROLE (IFP) the main bulk of the contaminants is removed prior to the refining stage by extraction with liquid propane. The result is a significant reduction of the sulfuric acid and bleaching clay consumption, a decrease in the accumulation of acid tar, and as increase of ca. 10% in the raffinate yield. The water-free waste oil from the atmospheric distillation is contacted in an extraction column with liquid propane at 75-95 °C. Dirt and insoluble sludge settle out and withdrawn at the bottom of the column. The clear propane is removed from the oil-propane mixture and the oil subjected to refining. Before depropanizing, the sediments are mixed with some fuel in order to keep the propane-free residue in a pumpable state, and are used for heating of the plant (Fig 2.7). At present, three plants using this process are in operation in Europe.
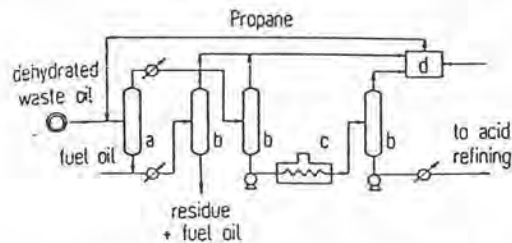

a. Extraction ; b. propane separation ; c. heater ; d. propane recovery

Figure 2.7 Flow scheme of IFP propane extraction

SNAMPROGETTI Process [36,37]

The SNAMPROGETTI S. P. A. (Italy) has further developed the
IFP process bu including a propane extraction before and after the vacuum
distillation and by adding the hydrofining step, thus converting the process to a
four-stage process without sulfuric acid treatment. The yield is significantly
higher than that obtainable with the addition of sulfuric acid and the
accumulation of difficult-to-dispose residues is eliminated. First, water and fuel
components are removed by atmospheric distillation. This is followed by the
first propane extraction in order to precipitate dirt, oxidation products and a
part of the additives. The depropanized oil is the distilled under vacuum into
three fractions : gas oil, spindle oil and light lubricating oil. After heating, the
residue is again extracted with propane to remove the remaining additives. All
lubricating oil fractions are the subjected to hydrofining (Figure 2.8).

The process is recommended primarily for motor oils, since
additives present in other lubricants may not be completely removed from the
oil by the propane extraction even after thermal treatment. One plant using this
process is at present in operation.
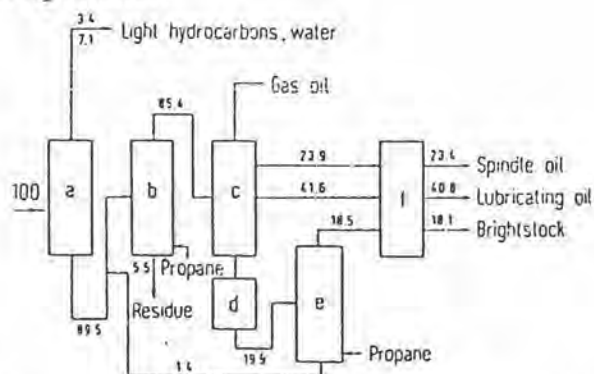
a. Atmospheric distillation ; b. depropanizing ; c. vacuum distillation ; d. heat
treatment ; e. depropanizing ; f. hydrofining

Figure 2.8 Flow scheme of SNAMPROGETTI process

KTI Process [38]

The process developed by KINETICS TECHNOLOGY INTERNATIONAL, The Hague (KTI) (in collaboration with GULF SCIENCE AND TECHNOLOGY) can be used to treat a large spectrum of waste oils. An acid treatment step is not included. Thus, additives or foreign matter must be removable by distillation (and remain in the residue) or must convertible to suitable products by hydrogenation. The additives must not affect the catalytic activity of the hydrogenation catalyst so that, for instance, cutting oil which contain halogenated hydrocarbons cannot be treated. The yields are said to lie between 80 and 85 %.
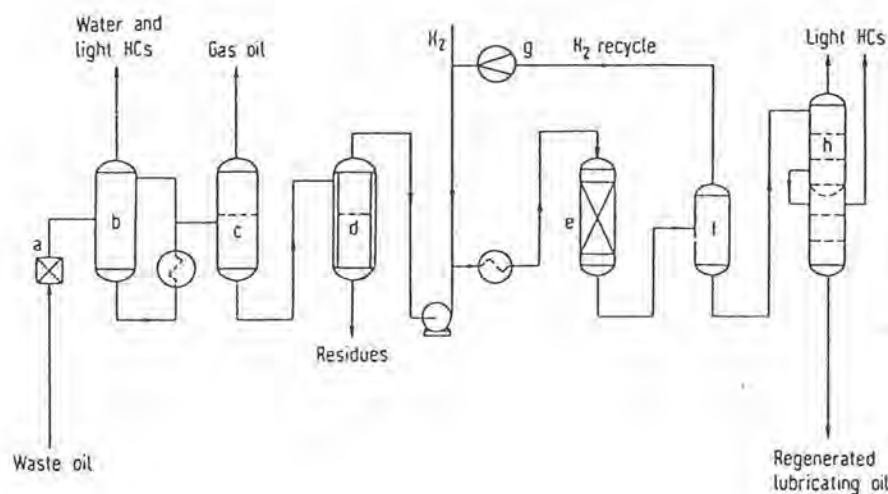
a. Sedimentation ; b. atmospheric distillation for the removal of remaining water and gasoline fractions ; c. gas oil distillation ; d. vacuum distillation ; e. hydrofining reactor ; f. gas separator ; g. compressor ; h. stripper

Figure 2.9 Flow scheme of the KTI process

The dirt and water is removed from the waste oil by sedimentation. Atmospheric distillation removes the remaining water and gasoline components and in a separate stage, the gas oil fraction. In the subsequent vacuum distillation the lubricating oils are vaporized and separated into fractions by fractional condensation; dirt, additives and a part of the oxidation products are removed as bottoms. The distillates are hydrofined and stripped and serve as starting material for finished products (Fig.2.9).

BERC Process [39]

The process, developed by the BARTLESVILLE ENERGY RESEARCH CENTER of the U.S. DEPARTMENT OF ENERGY, contains a noticeable technological step: the precipitation of contaminants with a mixture consisting of 50 % 1-butanol, 25 % i-propanol, and 25 % methylethyl ketone. One volume of the oil, from which water and light hydrocarbons have been removed by distillation, is diluted with three volumes of the mixture and centrifuged. The solvent is removed by distillation and the oil subjected to fractionation in vacuum and hydrofining or treatment with bleaching clay. There seem to be application limits to oils containing additives which cannot be removed by coagulation or distillation.

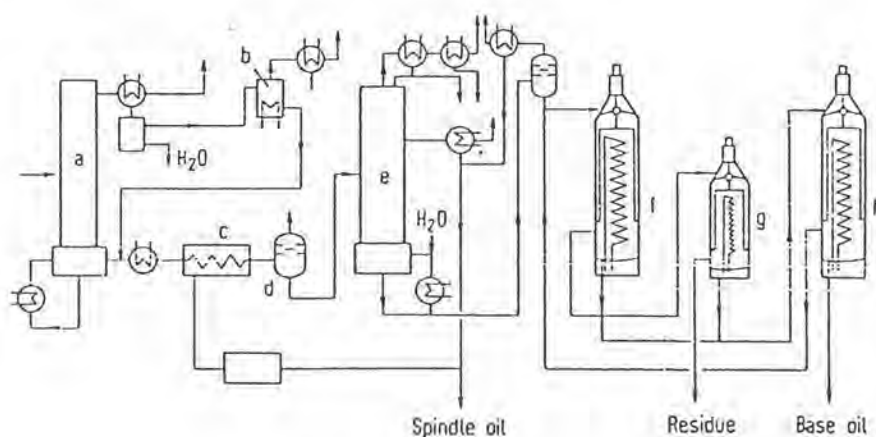### Recyclon Process [40]

In this new process the oxidation products and additives are removed by treatment with finely dispersed sodium, instead of with sulfuric acid. This leads either to the polymerization of these products or to conversion to their sodium salts, the boiling points of which are high enough so that the oil can be removed by distillation. This is carried out in two stages, the second

stage of which is designed as a thin film molecular vaporizer for the separation of the reaction products.

The waste oil is first freed from water and low-boiling hydrocarbons by distillation and then treated for a few minutes in reactor with max. 1 mass % of sodium metal, finely dispersed in oil (5-15 μm particle size). After the addition of small quantities of water, the gas oil and spindle oil fractions are distilled from the mixture at atmospheric pressure. The residue consisting of the lubricating oil and reaction products is then distilled at 1 mbar and under mild thermal conditions in thin-film molecular stills with rotating blades, arranged in series. With the aim to increase the yield, the residue of the preliminary distillation is redistilled in the third still; the distillate is again fractionated in the last still (Fig 2.10). The distillates are expected to be used as base oils without any further treatment; the yields are said to be significantly higher than those obtainable by conventional processes which include as acid treatment.

Figure 2.10 Flow scheme of Recyclon process

a. Dehydration and gasoline removal ; b. gasoline separation ; c. reactor ; d. gas separator ; e. atmospheric distillation ; f. preliminary distillation ; g. residue distillation ; h. after-distillation

New Physical Technological Steps

Ultrafiltration [41]

The INSTITUTE FRANCIAS DU PETROLE (IFP) has developed an ultrafiltration process on the industrial scale for the removal of solids and dirt from waste oils in order to reduce the amount of acid tar produced. The waste oil is dissolved in three volumes of hexane and filtered under pressure through special membrane filters made of acrylonitrile copolymers (RHONE-POULENC) and supported by PVC or polyacetate grids (Figure 2.11).

In the processing of waste oils the ultrafiltration is applied after water removal by distillation and prior to the refining or fractionation stage. The flow scheme of the filtration with hexane recovery is shown in Fig. 68. Filters are available with capacities of up to 15000 tons/year.
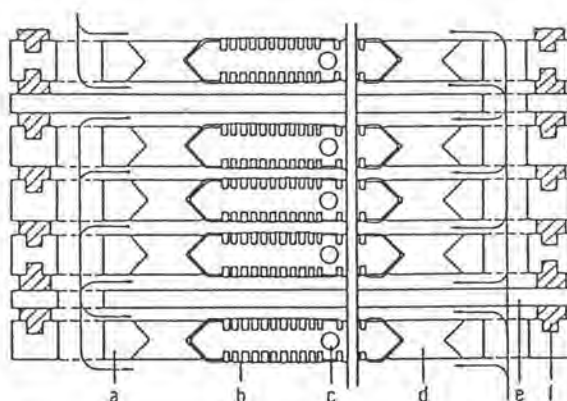
a. Membrane support plate ; b. membrane ; c. ultrafiltrate collector ; d. membrane support clamp ; e. spacer plate ; f. seals

Figure 2.11 Cross section of an IFP ultrafilter
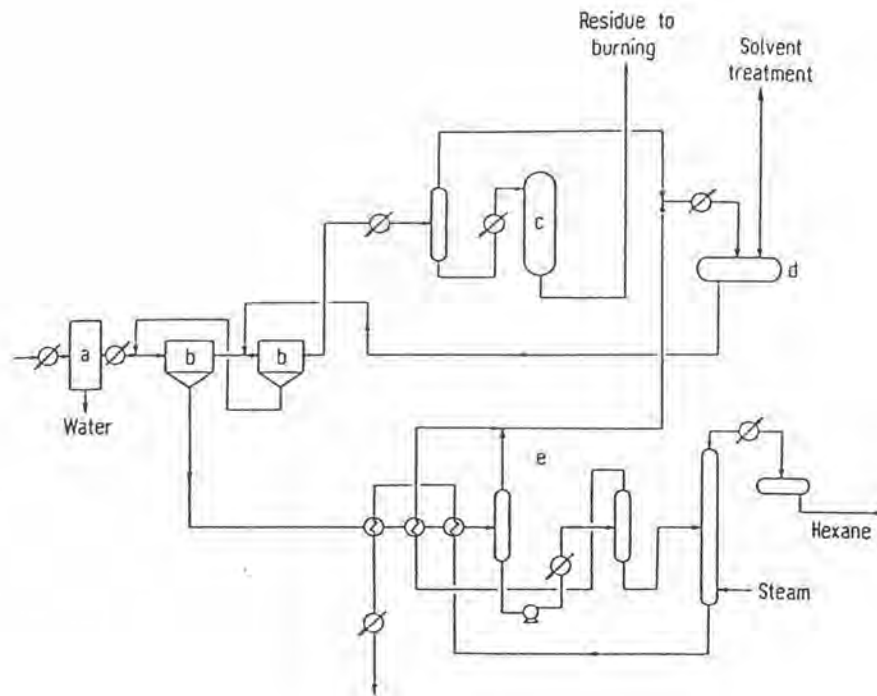
a. Drying ; b. ultrafiltration ; c. solvent recovery ; d. solvent storage ; e. solvent recovery

Figure 2.12 Waste oil regeneration by ultrafiltration with solvent recovery

Centrifuging [43]

Dirt and foreign matter can also be removed from the waste oils by centrifuging. In order to avoid the addition of a solvent to reduce the viscosity, the oil is passed through a separator centrifuge at ca. 180 °C and 7000 gm centrifugation is included in the process at the same point as the ultrafiltration (MATTHYS LUBRICANTS, France).

Molecular vaporization [41, 44-45]

In order to avoid excessive heating of the oil and thus to reduce the deposition of carbonaceous matter in the distillation units, to increase the yield and also to avoid an expensive and yield-reducing finishing treat molecular distillation has recently been introduced in the regeneration of waste oils (LEYBOLD-HERAEUS, Hanna; LUWA, Charlotte, North Carolina, USA PFAUDLER CORP., Rochester, USA). The best results have been obtained with molecular vaporizers with rotating blades, arranged in cascades or as single units. The inclusion of condensers after the vaporization stages allows separation of the distillation into fractions by fractional condensation (Figure 2.13 and 2.14). Depending on the design and size of the vaporizers, throughputs of up to 50000 tons/year can be reached. Analyses of the processed oils show that hardly any additive traces remain in the oils.
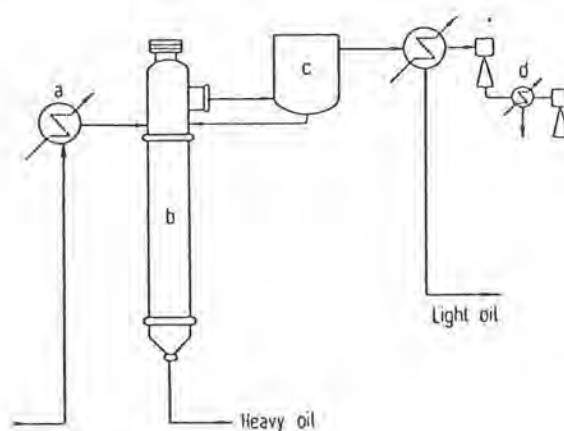
a. Preheater ; b. molecular vaporizer ; c. separation ; d. vacuum generation

Figure 2.13 Single-stage molecular vaporization
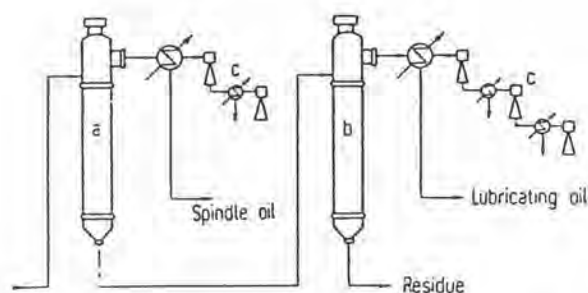
a. Molecular vaporizer for pre-fractionation ; b. molecular vaporizer for the main fractionation ; c. vacuum generation

Figure 2.14 Two-stage molecular vaporization

Secondary refining Products

Depending on the process, 2-3 base oil cuts are obtained in the regeneration of waste oils. Motor oils, gear oils, hydraulic oils and metal cutting oils and lubricating greases can be prepared from these cuts by blending and the addition of additives. When the secondary refining includes only the removal of water and light hydrocarbons including gas oils, the products can be used as flux oils for bitumen or similar products.

Quality of Secondary Raffinates

The quality of the secondary raffinates depends on various factors. As long as they have been treated thoroughly and with the sufficient quantities of refining agents so that the complete removal of all refining agents and additives present in the starting oils has been achieved through a mild thermal treatment, these raffinates can be considered as equal to the primary raffinates for many applications. The quality of additive-free oils is satisfactory for simple applications, some limitations will have to be observed for special

applications. Shortcoming of secondary raffinates can frequently be overcome by the addition of additives (Tables 2.7 and 2.8).

Table 2.7 Analysis of an Oil Regenerated by the MEINKEN Process

Properties		
Density	g/mL	0.89
Viscosity at 50 °C	mm²/s	56.1
Viscosity Index		94
Flash point	°C	249
Sulfur content	mass %	0.57
Carbon residue (CONRADSON)	mass %	0.13
Ash content	mass %	0.005

Lubricating base oils must meet certain, minimum performance characteristics; viscosity, viscosity index, pour point and volatility must all meet the required standard. When dealing with re-refined oils, additional characteristics such as color and odor must also be taken into account. Dark color or unusual odor are readily perceived by the customer as representing deficiencies in quality. Many re-refined oils, for example, have a definite, characteristic 'cracked or oxidized' odor, which may be totally unacceptable in some countries and markets. Table 2.9 provides quality guidelines for re-refined oil acceptance. [31]

Table 2.8 Comparison of Quality of Solvent-Refined Fresh Oils and IFP Regenerates

Properties		150 Neutral		350 Neutral		600 Neutral		Brightstock	
		Fresh oil	Regenerate	Fresh oil	Regenerate	Fresh oil	Regenerate	Fresh oil	Regenerate
Density	g/mL	0.875	0.874	0.835	0.882	0.895	0.888	0.910	0.882
Color (ASTM)		< 2	< 1.5	< 3	< 2	< 3.5	< 2.5	< 6.5	< 5.5
Viscosity at 50 °C	mm^2/s	19-21	18-20	40-46	37-41	60-74	60-64	242-272	226-242
Viscosity Index		97	95	95	95	95	95	95	95
Pour point	°C	-15	-9	-9	-12	-9	-12	-9	-9
Flash point	°C	200	215	215	245	240	255	290	275
Carbon residue	mass %	0.03	0.01	0.1	0.02	0.15	0.09	0.8	0.85
Ash	mass %	0	0	0	0	0	0	0	0

Due to the variety of potential sources of used lubricants, their differing histories of use, and their subsequent levels of possible contaminants, assessment of the quality of the resulting re-refined oil is major concern. Quality assurance must be applied, both to the used oil feedstock and, more particularly, to the product(s) of the re-refining process. Limits for the concentration of various contaminants in the finished base oil must be set and strictly adhered to. [1]

Table 2.9 Guidelines for quality acceptance of re-refined base oil

Properties	Grade	
	150	**500**
Viscosity at 100 °C (cSt)	5.0 + 0.2	11.0 + 0.4
Viscosity Index	90-110	90-100
Flash point (°C)	210	230
Pour point (°C)	-9	-9
Color (ASTM)	3	4.5
PAHs (ppm)	3	3
Sulfated ash (%)	0.01	0.01

Possible contaminants in re-refined base oils

1.1 Fuel and sovent residues

These can be present in varying amounts depending on the efficiency of the re-refining processes employed. Flash point and Noack volatility values in excess of those given in Table 2.9 indicate unacceptable contamination.

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1.2 Polycyclic aromatic hydrocarbons (PAHs)

These are primarily present as a result of the combustion process during previous of the lubricant, prior to re-refining. PAHs are found at varying concentrations in used oil, determined by factors such as drain interval, fuel type and sump size. Some PAHs are known to be carcinogenic, and the concentration of total PAHs in base fluids must be controlled.

1.3 Metals

Metals should not be present in re-refined base oils, either as wear metals or from previous use of metallic oil additives, or as clay or catalyst fines. Metals can be measured by determining total sulphated ash content or, individually, by atomic absorption spectroscopy.

1.4 Non-metallic impurities

Viscosity index (VI) improvers or polychlorinated biphenyls (PCBs) can be determined by dialysis or chlorine analysis, respectively. Indication of the presence of VI improver is given by unusually high viscosity index.

1.5 Water and untreated acid

These may be carried over from some processes. Total acid number and copper corrosion tests will indicate the presence of such contaminants in the re-refined oil.

1.6 Sulfur content

In virgin base oils this is seen as an index of inherent antioxidant capacity. With re-refined oils, those hydrocarbons that were inherently oxidatively unstable will have been oxidized during previous use. The function of the sulfur content of a re-refined base oil is not clear; more work is required to determine the need or concentration of sulfur required to meet minimum performance standards.

Health and safety aspects of re-refined oil [1]

Used engine oil is recognized as posing a carcinogenic risk to man. However, providing sensible precautions, such as good personal hygiene, are taken, the actual risks to health can be essentially eliminated. This is borne out by epidemiological studies on groups of mechanics where there has been no evidence of an increase in skin cancer.

The main carcinogenic agents in used oil are polycyclic aromatic hydrocarbons (PAHs) with 3-7 ring such as benzo(a)pyrene, benz(a)anthracene and chrysene. These chemicals, and many others like them, are found in used lubricant, having been formed during the combustion cycle in the engine. PAHs are also present in crude oil, and can be present in unused base fluids leaving the refinery. Refinery technologies, however, able to remove these harmful PAHs by hydrogenation and solvent extraction. Strict limits of 3 % on the DMSO extract of virgin base oil have been introduce by the oil industry; these limits are based on animal studies, which have shown that there no evidence of carcinogenic activity of DMSO extract levels below 3 %.

PAHs are found in re-refined oil samples at a higher level than those found in unused base oil. Interpretation of these results in relation to carcinogenic risk is not easy. The limits on total DMSO extractable materials (taken as a measure of PAH content) in virgin base stocks were set, base on a

knowledge of PAH distribution that is not applicable to the used oil situation. The probability is that re-refined base oils will present no significant risk to health, provided that normal precautionary measures of personal hygiene and handling are taken. However, until further biological studies are undertaken, the definitive position with regard to the carcinogenic potential of re-refined oil cannot be determined.

Environmental considerations of waste lubricant [1]

It is important to consider the total environmental costs and benefits of dealing with used lubricant. The previous section have indicated that the re-refined product is determined by the nature of feedstock, and by the treatment process. The total amount of energy consumed in the collection and re-refining of used oils to an acceptable standard must be balanced against the energy to be gained from utilizing the used oil as a fuel. Clearly, the choice between no lubricant or an inferior basestock is also a major consideration.

Of the three basic methods of disposal of used oil, the most efficient in terms of energy conservation, in that it displaces an equivalent amount of oil, is the use of the material as a fuel supplement. In heating processes where the fuel is supplied through a burner, some limited pre-treatment of the waste oils and blending with conventional fuels are necessary. Pre-treatment can range from simple settling and filtration, to heating, emulsion breaking, chemical treatment and centrifugation-- the amount of treatment will depend on the nature of the used oil and the required fuel specifications. The flue gas components of principal environmental concern are PCBs, PAHs, dioxins and heavy metals. Some treatment 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 treated accordingly. Waste oils can successfully be burnt in boilers, ranging in

size from electricity generating plants and industrial boilers to specially produced small furnace and boiler installations. An EC limit of 1 MW has recently been introduced, below which it is not advisable to burn used oil. Subject to control over metal content, one of the most satisfactory uses for waste oil is in cement production. The advantage of this disposal method is that wastes that would otherwise be vented to the atmosphere via the flue gases, are absorbed and contained within the product with no adverse environmental consequences. There are, of course, limits on the amount of cement production available to use such as fuel--particularly when the building industry is in recessing.

Disposal of waste oil as hazardous waste requires that it be incinerated at high temperature to ensure complete oxidation of PAHs, PCBs and PCTs (polychlorinated terphenyls). Such disposal is mandatory in many country if the content of some contaminant in the used oil exceeds predetermined concentrations, e.g. 20 ppm of PCB in Germany.

With regard to re-refining, providing the used oil is of a suitable quality and the process is able to generate the product of sufficiently high quality, the principal environmental consideration concerns the disposal of the by-products of the refinery process. The effluents/waste products from some re-refining processes can be highly toxic and/or potentially carcinogenic. If this wastes are not disposed of correctly, they represent a potential hazard to the environment, which is at least as severe as that of untreated used oils. The cost of safe disposal of these wastes is usually high.

Energy balance in terms of percent weight hydrocarbon feedstock for the three alternative disposal methods is as follows:

1. Disposal as toxic/hazardous waste 0 % energy gain; some additional energy input required to achieve high temperature combustion. Net loss = -X %.

2. Re-refining to produce base oils Net energy loss of 17 %, assuming 70 % recovery rate of lube oil.

3. Use as fuel Net energy gain of 90-95 %.

The use of re-refined base oils in the production of lubricants is being increasingly considered on a worldwide basis. The driving force behind this is the concept of recycling of resources, thus minimizing environmental impact.

These considerations, while commendable in principle, must not take precedence over the quality of the resulting lubricant. Full life-cycle analysis is required in each market to determine the true picture with regard to environmental impact. If lubricant quality is compromised, the results in terms of engine failure and loss of performance could lead to an overall environmental deficit when the cost of replacement parts and decrease efficiency are taken into account. The health consequences of increased PAH concentrations are also unknown, and must be considered if re-refined oils are used.

Quality control and process control should be able to produce a product of known and consistent quality, suitable for use as a lubricant basestock. In practice, however, oils that can meet the required performance characteristics tend to be expensive. For these reasons, the use of re-refined oil as a lubricant base fluid is not considered to represent a viable alternative to virgin base oils of consistent quality when these are readily available. In these circumstances, the most appropriate means of recycling used engine oil is as a fuel or fuel supplement. Recycling by re-refining should only be considered where alternative base oils are unavailable. In such cases, the use of re-refined oil in the production of lubricants represents the only viable alternative. Care must be taken to ensure that the re-refining process can produce an oil of acceptable quality.

Future trends [1]

As mentioned earlier, the largest proportion of lubricant enters the environment by virtue of its being used. Legislation can reduce unauthorized disposal, but this is a minor problem in terms of the overall situation. Engineering can minimize leaks and also increase the dependence on authorized waste disposal specialists to eliminate 'dumping', for example by using dry sump lubrication in car engines, with the lubricant in a replaceable canister that can be changed only at a service station.

The largest factor in minimizing environmental impact, however, will depend on the lubricant itself. As mentioned earlier, vegetable oil base fluids are being used in some applications, while readily biodegradable synthetic esters are used in outboard two-stroke engines. The choice of a biodegradable base fluid can aid the search for 'environmental friendliness'.

What, however, of the additive components? As described in earlier chapters, these materials are present in the formulation to perform a specific job. As engineering and fuel change, so does the need for additives. Does a low sulfur fuel (which is becoming the norm due to legislative pressure on acid emission) need a lubricant with as good a dispersant additive as a high sulfur fuel? The metallic and halogenated components of additives may eventually be replaced by easily biodegradable compounds that perform as effectively, if not better, than those currently in use.

It is said that conflict is one of the most effective stimuli to scientific research and new technology. Mankind has always been in conflict with the environment; it is only now that this realization has set in, and that acid rain, CFCs, pesticides, etc. are recognized as a major threat to the environment. The consequent need to minimize mankind's effects on the environment will drive technology forward at a pace undreamt of, even a few years ago.

Hydrogenation Process [13,14]

Hydrogenation is defined as the reaction between molecular hydrogen and an organic or an inorganic substrate. Hydrogenation reactions are exothermic but do not proceed at ordinary temperatures, except at negligible rates. The activation of hydrogen by the use of catalysts is among the oldest of chemical processes. Many metal oxides and metal complexes catalyze hydrogenation reactions. It may not be possible to list all hydrogenation reactions and the catalysts used, however, examples of industrial importance are discussed in this chapter. Although most commercial processes use heterogeneous catalysts, homogeneous systems are gaining in importance for the production of high-value chemicals.

Hydrogenation of Double Bonds :

$$-C=C- \quad + \quad H_2 \quad ----> \quad -CH-CH-$$

Most carbon-carbon double bonds, whether substituted by electron-donating or electorn-withdrawing substituents, can be catalytically hydrogenated, usually in quantitative or near-quantitative yields. Almost all known alkenes add hydrogen at temperatures between 0 and 275 °C. Many functional groups may be present in the molecule, e.g., OH, COOH, NH_2, CHO, COR, COOR, or CN. Some of these groups are also susceptible to catalytic reduction, but it is usually possible to find conditions under which double bonds can be reduced selectively. The catalysts used can be divided into two broad classes, Both of which mainly consist of transition metals and their compounds : (1) catalysts insoluble in the reaction medium (*heterogeneous*

catalysts). These have been the one traditionally used. Among the most effective are Raney nickel, palladium- of platinum-on-charcoal (perhaps the most common), $NaBH_4$-reduced nickel (also called nickel boride), platinum metal or its oxide, rhodium, ruthenium, $NaH-RONa-Ni(OAc)_2$, and zinc oxide, (2) Catalysts soluble in the reaction medium (*homogeneous catalysts*). These are of more recent discovery. The most important is chlorotris(triphenylphosphine)rhodium; $RhCl(Ph_3P)_3$, (Wilkinson's catalyst), which catalyzes the hydrogenation of many olefinic compounds without disturbing such groups as COOR, NO_2, CN, or COR present in the same molecule. Among other homogeneous catalyst

Catalytic Hydrogenation   [35-42]

Catalytic hydrogenation is a process to catalytically stabilize lubricating oils and/ or remove objectionable elements from the used oil or product 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 are removed by the process include sulfur, nitrogen, oxygen,halides and trace metals.

Generally, in practices, to treated used lubricating oils with the catalytic hydrogenation process, usually need the specific reaction as called hydrotreating process.

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

- 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 of stable polycyclic aromatics

The extend to which each of these reaction types occurs is determined by the types of 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 was employed specifically for sulfur removal it is usually called hydrodesulfurization or HDS.
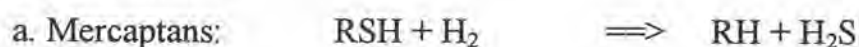
Hydrotreating Catalysts

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 catalysts generally is sulfides in situ prior to its use.
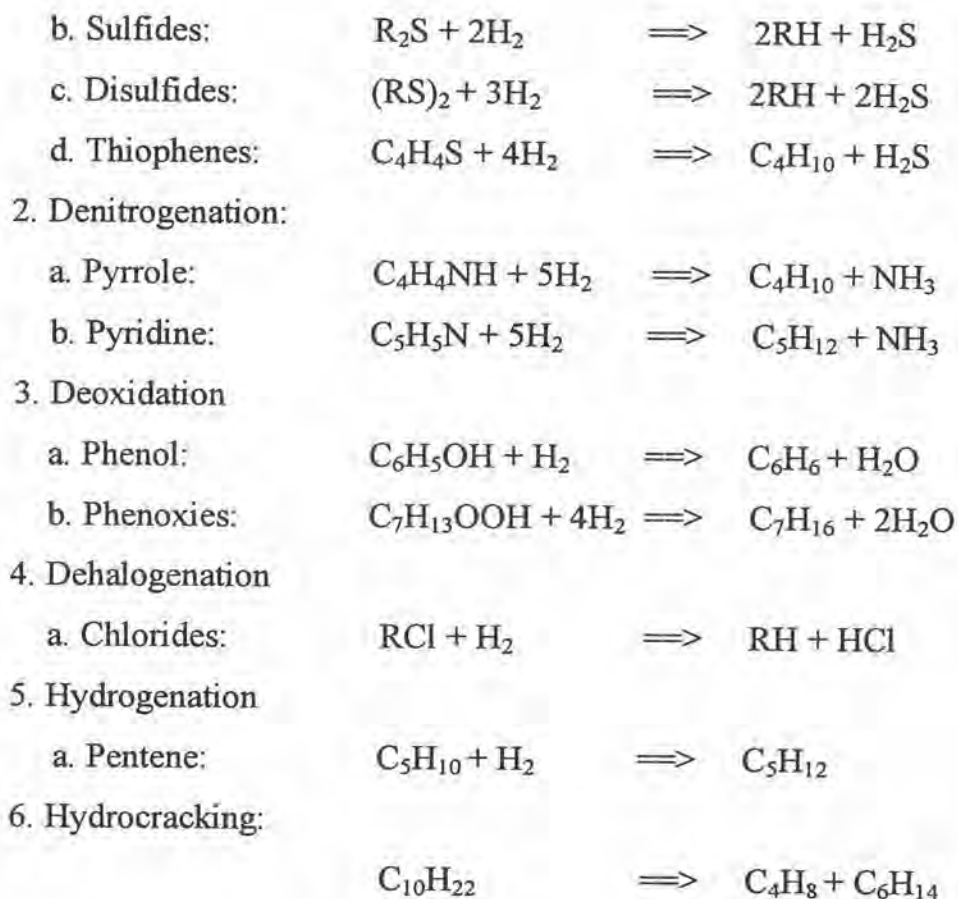
Reactions

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

1. Desulfurization

a. Mercaptans: $\qquad RSH + H_2 \implies RH + H_2S$

b. Sulfides:	$R_2S + 2H_2$	$\Longrightarrow$	$2RH + H_2S$
c. Disulfides:	$(RS)_2 + 3H_2$	$\Longrightarrow$	$2RH + 2H_2S$
d. Thiophenes:	$C_4H_4S + 4H_2$	$\Longrightarrow$	$C_4H_{10} + H_2S$

2. Denitrogenation:

a. Pyrrole:	$C_4H_4NH + 5H_2$	$\Longrightarrow$	$C_4H_{10} + NH_3$
b. Pyridine:	$C_5H_5N + 5H_2$	$\Longrightarrow$	$C_5H_{12} + NH_3$

3. Deoxidation

a. Phenol:	$C_6H_5OH + H_2$	$\Longrightarrow$	$C_6H_6 + H_2O$
b. Phenoxies:	$C_7H_{13}OOH + 4H_2$	$\Longrightarrow$	$C_7H_{16} + 2H_2O$

4. Dehalogenation

a. Chlorides:	$RCl + H_2$	$\Longrightarrow$	$RH + HCl$

5. Hydrogenation

a. Pentene:	$C_5H_{10} + H_2$	$\Longrightarrow$	C_5H_{12}

6. Hydrocracking:

	$C_{10}H_{22}$	$\Longrightarrow$	$C_4H_8 + C_6H_{14}$

Mechanism

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 atom 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 of butene by continued reaction with further hydrogen atoms.

Raney Nickel Desulfurization

Ni-Al alloy catalysts, either as powder or in lump form, frequently have characteristics making them superior for some hydrogenation. In the case of the powder, one of the advantages if 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 a first step, the chemisorption of the sulfur compound of the catalyst surface through unshared sulfur electrons. The carbon-sulfur bond is thus weakened and 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:

$$R\text{-}S\text{-}R + Ni \implies R + RS\text{-}Ni$$

$$R + H \text{ (surface bound)} \implies RH$$
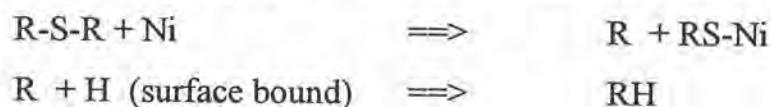
When there is no hydrogen available, such radicals may react in other ways. They may combine with one another,

$$R + R \implies R\text{-}R,$$

or they may form olefins.

$$RCH_2CH_2 \implies RCH{=}CH_2 + H$$

The Preferred Reactions

The preferred lubricating oil molecular structure were isoparaffins, single ring aromatics with long aliphatic chains, and naphthene with single ring, preferably having five carbon atoms on which aliphatic long chains are branched.

The desired reactions are generally as follow:

- hydrogenation of polycondensed aromatics into polycondensed naphthenes:
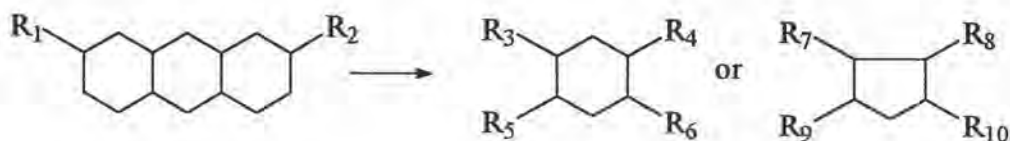

VI = -60	VI = 20
Freezing point > + 50 °C	Freezing point = > + 20 °C

- partial hydrogenation of polycondensed naphthenes:

VI = 20	VI = 110-140
Freezing point > +20 °C	Freezing point < 0 °C

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

$$C_{10}-C-C_{10}$$
$$\ \ \ \ \ |$$
$$C-C-C-C-C$$

$\longrightarrow$

$$C_{10}-C-C_{10}$$
$$\ \ \ \ \ C\overset{C_2}{\underset{C_2}{\diagup}}$$

VI = 125

Freezing point = 19 °C

VI = 119

Freezing point = - 40 °C

In general, 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 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 2.15) consisting of a hydrogenating, dehydrogenating function and acidic function.

The hydrogenation catalysts, especially hydrotreating catalysts which can be suitable applied for production of lubricating oil comprise at least one more metals, metal oxides, or metal sulfides or groups VIB and VIII on a carrier support which comprise 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 $NiO/MoO_3/Al_2O_3$ and

$NiO/WO_3/Al_2O_3$, 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, 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.
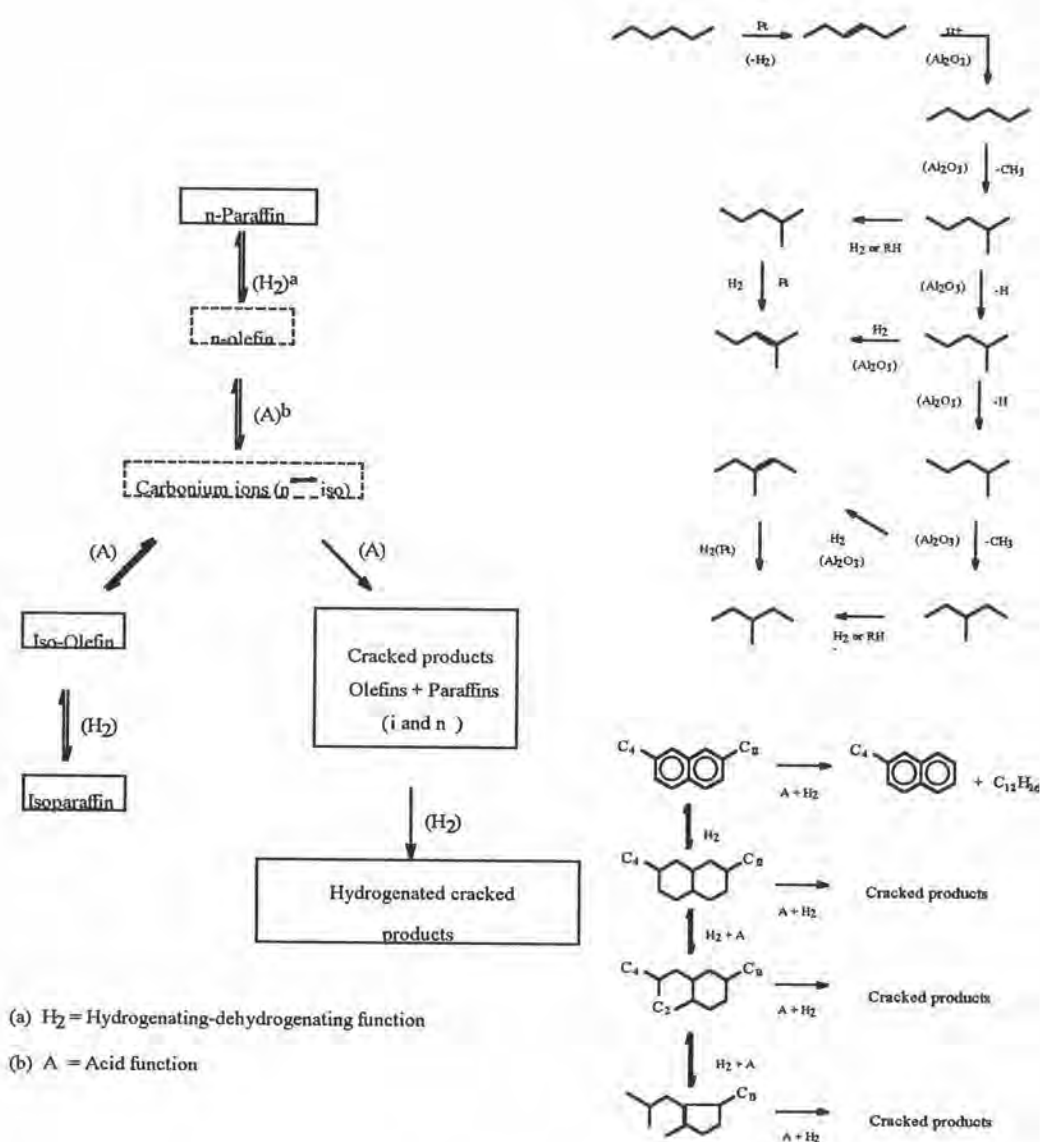
Figure 2.15 Reaction mechanism for bifunctional catalyst

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