Evaluation On The Use Of Some Synthetic And Natural Materials For Treatment And Recycling Of Used Lubricating Oils

By

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B.Sc.Biochemistry,Faculty Of Science,Ain Shams University,2000

A Thesis Submitted in Partial Fulfillment

Of

The Requirement for the Master Degree

In

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Approval Sheet

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CHAPTER (I) - INTRODUCTION

I-1-Crude Oil Components *(Pirro andWessol, 2001)*

Petroleum is one of the naturally occurring hydrocarbons that frequently include natural gas, natural bitumen and natural wax.

The name " petroleum" is derived from the latin petra (rock) and oleum (oil).

Petroleum was formed by the decomposition of organic refuse, aided by high temperatures and pressures over a vast period of geological time.

Petroleum or crude oil is refined to make many essential products as gasoline, kerosene, solvents, fuel oils, diesel fuel, lubricating products and industrial specialty products (waxes, chemicals, asphalt and coke).

Crude oil is refined into 2 stages:-

1) refining of light products .
2) refining of lubricating oils and waxes.

At approximately 700ºF (371ºC) the residuum from light products refining has to decompose, thus the refining of lubricating oils and waxes takes place under vacuum conditions and at temperatures under the decomposition point.

There are 2 basic refining processes :-

1) separation.
2) conversion.

Separation process : selects certain desirable components by distillation, solvent extraction and solvent dewaxing.

Conversion process: involves changing the chemical structure of certain undesirable crude oil components into desirable components and a degree of removal of nondesirable species.

I.1.1- Crude Oil Origin and Sources

It is believed to have been formed from the remains of tiny aquatic animals and plants that settled with mud and silt to the bottoms of ancient seas.

As successive layers built up those remains were subjected to high pressures and temperatures and underwent chemical transformations, leading to the formation of the hydrocarbons and other constituents of crude oil.

I.1.2- Crude Oil Production

The crude oil frequently comes to the surface under great pressure and in combination with large volumes of gas. Present practice is to separate the gas from the oil and process the gas to remove from it additional liquids of high volatility to form what is called **" natural gasoline".**

I.1.3- Crude Oil Types and Composition

Crude oils are found in a variety of types ranging from light-colored oils consisting mainly of gasoline to black nearly solid asphalts.

Crude oils are very complex mixtures consisting and containing many individual hydrocarbons or compounds of H and C. These range from methane ,the main constituent to compounds containing 50 or more carbon atoms.

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

I.2- Crude Oil Selection for Base Oils Manufacturing

One way to understand the extreme differences that can exist among crude oils is to examine some of the products that are made from different types of crude. Crude range from "paraffin" types which are high in paraffin hydrocarbons ,through the " intermediate" or " mixed base" types to the naphthenic types, which are high in hydrocarbons containing ring structures. Asphalt content varies in crudes of different types.

Naphthenic type of crude is unusual because it contains essentially no wax (very low pour point) -50ºF (-46ºC).

The viscosity of the naphthenic oil will change with temperature much more than the viscosity of the paraffin stock. This is reflected in the lower viscosity index (VI) of the naphthenic oil.

I.3- Oil Refinery Processes

I.3.1- CDU Process (Crude Distillation Unit) *(Colwell,2009)*

Process Objective:

By this process, it is possible to separate valuable distillates (naphtha, kerosene, diesel) and atmospheric gas oil (AGO) from the crude feedstock.

In this process, fractional distillation is applied under normal pressure.

Table (1): Typical Yields and Dispositions of CDU process

Product	Yield, wt% of Crude	Disposition
Light Ends	2.3	LPG
Light Naphtha	6.3	Naphtha Hydrotreating
Medium Naphtha	14.4	Naphtha Hydrotreating
Heavy Naphtha	9.4	Distillate Hydrotreating
Kerosene	9.9	Distillate Hydrotreating
Atmospheric Gas Oil	15.1	Fluid Catalytic Cracking
Reduced Crude	42.6	Vacuum Distillation Unit

I.3.2- Vacuum Distillation Unit (VDU Process)

Process Objective:

This process is applied to recover valuable gas oils from reduced crude via vacuum distillation.

Table (2): Typical Yields and Dispositionsof VDU process

Product	Yield, wt% of Crude	Disposition
Light Ends	< 1	LPG
Light VGO	17.6	Distillate Hydrotreating
Heavy VGO	12.7	Fluid Catalytic Cracking
Vacuum residue	12.3	Coking

I.3.3- Solvent Extraction (Sequira,1992;Soudek,1971;Hournac1981, Lache et al ,1984).

In the early days of oil refining sulphuric acid treatment was applied to improve the quality of the vacuum distillates, followed by clay-treatment as a neutralization step and to improve color. This expensive and polluting operation was abandoned to be replaced by solvent extraction whereby solvents such as phenol, furfural or N-methylpyrrolidone (NMP) are used to selectively extract unstable and undesirable components from the vacuum distillates. From these solvents, furfural is most widely used, whereas new refineries use NMP in view of its somewhat greater overall efficiency. Solvent extraction is the most important operation to remove undesirable components. The furfural (or other solvent) is miscible with the aromatic components which are unstable and undesirable from a viewpoint of health hazards.

This process yields the highly paraffinic raffinates for further processing the aromatic extracts which are mainly used as fuel or thermal cracker feedstock at the refinery and also as rubber process oils for the tire industry.

The residue from the vacuum distillation can be also used for lube oil production after removal of asphaltenic components. This is carried out by solvent treatment using propane, in which these high molecular materials are not dissolved.

The raffinate from this propane precipitation or deasphalting process is further treated in the same processes as the vacuum distillates, to yield bright stock base oil.

I.3.4 Dewaxing

To improve the cold flow properties of the paraffinic type base oils, the waxy raffinates or hydrofinishing raffinates are dewaxed by filtration of a chilled mixture of oil-methyl ethyl ketone and toluene. The pour point of the finished base oil can be well controlled by this process. The crude wax or slack wax, which contains normal paraffins and paraffins with minor branching, is scraped from filters and further used by the wax industry for production of candles and refined waxes.

Alternatively, a newer process, catalytic dewaxing can be used. In this process, the straight chain paraffins are being cracked to lighter components. This process may even provide base oils with a very low pour point matching those of naphthenic base oils, albeit at a loss of viscosity index. **Chevron** was the first to combine catalytic dewaxing with hydrocracking and hydrofinishing in its Richmond, Calif. Base oil plant in 1984. In 1993, the first modern wax isomerization-dewaxing process was commercialized by **Chevron**. This was a huge improvement over earlier catalytic dewaxing because the pour point of the base oil was lowered by isomerzing (reshaping) the n-paraffins (wax) and other molecules with waxy side chains into desirable branched compounds with superior lubricating qualities rather than cracking them away. This process greatly improves dewaxing yields and base oil performance(Wilson et al ,1994;Zakarian et al ,1994).

I.3.5 Hydrofinishing

The final step in modern base oil plants is hydrofinishing which utilizes sophisticated catalysts and pressures above 1000 Psi to give a final polishing to the base oil. Such hydrofinishing step is meant as a purification step and results in improvement of color and removal of remaining polar compounds containing nitrogen, oxygen and/or sulphur.

In some refineries such hydrofinishing step is not carried out, but additional clay percolation treatment is performed for those applications where these polar materials need to be removed. As an example, in manufacture of turbine oil it is essential that the base oil meets high standards of demulsibility and air release characteristics, which means that such polar components need to be absent. Even if hydrofinishing is used, clay treatment followed by candle filtration can still be an optional process to remove contaminants due to transport ***(David et al,2003)*** .

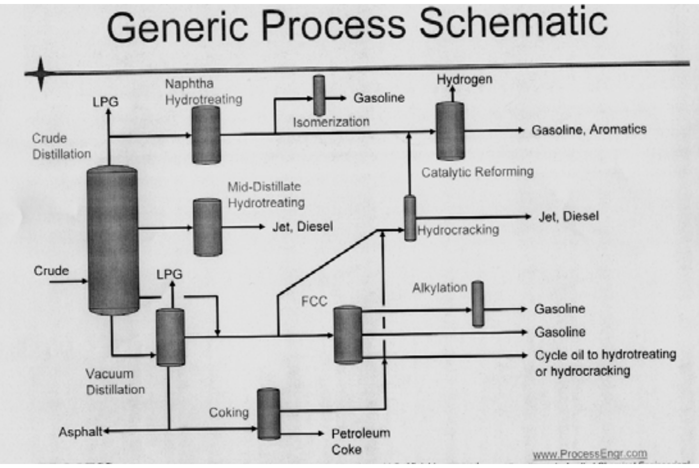

Fig.1: Generic Process Schematic

I-4-Base Oil Categories

The major component of lubricants is mineral(petroleum) base oil. which may comprise greater than 90% of the formulation. Nowadays synthetic base oils are used to achieve certain desired properties and additives are used to enhance their performance in amount ranging from less than 1% to 25% or more.

Modern engine oils contain a wide range of additives which are blended with base oils to form a complete package capable of meeting demanding performance requirements ***(Havet et al,2001; Pirro andWessol,2001)***.

Base oils are mainly derived from distillation of crude petroleum and are classified as refined or synthetic. Paraffinic and naphthenic oils are refined from crude oil and synthetic oils are manufactured from chemically-derived precursors. Base oils derived from vegetable oils still only make up a small part of the total volume. However, for certain applications they do capture a distinct portion of the market and have a growing presence.

I-4-1 Mineral base oils

Paraffinic

The molecular structure of paraffinic oils consists of long linear chains of hydrocarbons. They contain paraffinic wax and are the most widely used base stock for lubricating oils. Paraffinic oils are characterised by ***(US Army Corps of Engineers,1999)***:-

- Excellent stability (higher resistance to oxidation)
- Higher pour point

- Higher viscosity indexes
- Low volatility that gives a high flash point
- Low specific gravities

They are preferentially used for manufacturing lubricants such as:
engine oils, transmission fluid and gear oils.

Naphthenic

Naphthenic oils do not contain wax and behave differently from paraffinic oils. This is because they consist of cycloalkanes. These oils are used for applications with narrow temperature ranges and where a low pour point is required. In comparison to paraffinic oils naphthenic oils have (***US Army Corps of Engineers,1999)***:-

- Good stability
- Lower pour point due to the absence of wax
- Lower viscosity indexes
- High volatility (lower flash point)
- Higher specific gravities

The lower pour point and good solvency characteristics of naphthenic oils make them ideal for manufacturing of low temperature hydraulic oils, refrigeration oils, rubber process oils, metal working oils and greases.

I-4-2 Synthetic base oils

Synthetic oils are composed of oil components that have been synthesized rather than refined from petroleum or vegetable oils. Because their compositions are much more precise synthetic oils are generally superior to the refined oils. They perform better than the previous two in the following respects (***US Army Corps of Engineers,1999)***:-

- Better oxidation stability or resistance
- Better viscosity indexes
- Much lower pour point, as low as -46°C
- Lower coefficient of friction

The qualities of synthetic oils are especially noticeable at either very low or very high temperatures. Their improved oxidative stability and lower coefficient of friction permit extended operation at high temperatures. The better viscosity index and lower pour point allow for smooth operation at low temperature. The main disadvantage of synthetic oils is that they are approximately three times more expensive to purchase than mineral-based refined oils(***US Army Corps of Engineers,1999)***. However, this is somewhat balanced with their longer lifetime compared to conventional lubricants. But because of their high cost, synthetic oils should not be considered for high leakage or total loss applications. There are several categories of synthetic oils of which some are listed below:

- Synthesized hydrocarbons - These synthetic oils have functions and qualities much like mineral oil-derived lubricants. Polyalfaolefins (PAO) and dialkylated benzenes are two examples and applications where synthesized hydrocarbons are used include engine and turbine oils, hydraulic fluids, gear and bearing oils and compressor oils.
- Organic esters - Dibasic acid and polyolesters are the most common types and applications include crankcase oils and compressor oils.
- Phosphate esters - These are used in applications where fire-resistance is needed.
- Polyglycols - These are used for applications such as gear,

bearings and compressors for hydrocarbons gases.

I-4-3 Vegetable-based base oils

Vegetable oils have very good tribological properties. With few exceptions such as the waxes of jojoba oil, they consist of triacylglycerol esters containing 3 fatty acids with chain lengths of C_8 to C_{24}, with C_{16} and C_{18} as the dominating carbon chains. Due to their relatively inert hydrocarbon structures their positive properties are:

- Good boundary lubrication
- General wear protection
- High viscosity index
- High flash point
- Low volatility

Studies on the tribological properties of vegetable oils have revealed that ***(Bhuyan et al,2006)***

- Oils with longer carbon chains show lower friction and lower wear than shorter ones.
- Oils containing saturated compounds show improved oxidative stability in high temperature/pressure applications in comparison to oils containing unsaturated ones.
- Free fatty acids have a high degree of polarity and will react readily with metal surfaces to form a protective layer. They exhibit better tribological properties (improved boundary lubrication, lower friction and anti-wear abilities) compared to alcohols and methyl esters, as well as, triacylglycerol esters whose polarity is less.