Recycling of Used Lube Oil by Alcohol Extraction

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ABSTRACT

The aim of this work is to study the variables which are expected to affect recycling used lube oil by liquid extraction using alcohols. The variables which are kind of solvents 1-butanol, 1-pentanol, *n*-hexanol and cyclohexanol solvent-to-oil ratios 1:1, 2:1, 3:1 and 4:1 working temperature 25°C and 70°C for time of residues settlement and also find percent of asphaltenes removed. The results were shown that the best of solvent type was 1-butanol, because it can extract more asphaltenes from lubricating oil compared to others. Solvent-to-oil ratio of 4:1 gave the best extraction efficiency. The higher the extraction temperature (70°C), the more the percentage of asphaltenes, and the better the extraction efficiency compared to that at room temperature. A suitable time for extraction in this experiment was 5 days since no more asphaltene was collected.

Key words: Recycling, Used lube oil, Liquid extraction, Alcohols, Asphaltenes

หัวข้อวิทยานิพนธ์ : **การนำน้ำมันหล่อลื่นใช้แล้วกลับมาใช้ใหม่โดยการสกัดด้วยตัวทำละลายแอลกอฮอล์**

นักศึกษา : **นางสาว ปิยะนุช จันทวสุ**
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บทคัดย่อ

การทดลองนี้มีจุดประสงค์คือศึกษาค่าตัวแปรที่มีผลกระทบต่อวิธีการนำน้ำมันหล่อลื่นใช้แล้วกลับมาใช้ใหม่โดยการสกัดด้วยตัวทำละลายแอกกอฮอล์ภายใต้เงื่อนไขต่างๆ โดยค่าตัวแปรที่คาดว่าน่าจะมีผลกระทบได้แก่ ชนิดของตัวทำละลาย 1-บิวทานอล, 1-เพนทานอล, *n*-เฮกซานอล, ไซโคลเฮกซานอล อัตราส่วนระหว่างตัวทำละลายต่อน้ำมันหล่อลื่นใช้แล้ว 1:1, 2:1, 3:1, 4:1 อุณหภูมิที่ อุณหภูมิห้อง และ 70 องศาเซลเซียส เวลาการตกตะกอนของไฮโดรคาร์บอนหนัก และนอกจากนี้ยังสามารถหาเปอร์เซ็นต์ไฮโดรคาร์บอนหนักที่สกัดออกได้ จากผลการทดลองที่ได้แสดงให้เห็นว่า ตัวทำละลายที่ดีที่สุดคือ 1-บิวทานอล เพราะตัวทำละลายชนิดนี้สามารถแยกไฮโดรคาร์บอนหนักจากน้ำมันหล่อลื่นใช้แล้วได้มากที่สุด อัตราส่วนที่เหมาะสมระหว่างตัวทำละลายต่อน้ำมันหล่อลื่นใช้แล้ว คือ 4:1 เพราะ ตัวทำละลายสามารถแยกไฮโดรคาร์บอนหนักออกจากน้ำมันหล่อลื่นใช้แล้วได้มากที่สุด อุณหภูมิที่เหมาะสม คือ 70 องศาเซลเซียส เพราะได้ปริมาณของไฮโดรคาร์บอนหนักมากที่สุด และ เวลาที่เหมาะสมคือ 120 ชั่วโมง (5 วัน) เพราะว่าไม่มีไฮโดรคาร์บอนหนักตกแล้ว

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Chapter I
Introduction

1.1 Motivation

The term “lubricant” or lubricating oil applies to products based predominantly on mineral oil or partly or entirely on synthetic oils, which are intended as lubricants, power and heat transmission media dielectrics, and process oils. World consumption of lubricants and related products is about 0.8% of total petroleum consumed. It is high especially in very industrialized countries [1]. Lubricating oil is produced increasingly every year to satisfy the demand. Waste lubricating oil is produced increasingly likewise. Nowadays, methods to eliminate waste lubricating oils still affect the environment because wastes may contain small quantities of hazardous substances that can be a threat to air, soil and ground water. Examples of impurities in waste lubricating oil include:

- Glycols and water
- Polynuclear aromatic hydrocarbons
- Trace metals
- Products from incomplete combustion, etc.

If used lubricating oil is dumped in landfills, it may cause toxicity in ground water. This sewage will create oil sheens that are negative on aquatic animals. If it is burnt, it may cause toxic gases from impurities. If used lubricating oil is recycled properly, it can help to preserve our valuable resources as well as to reduce its environmental impacts. Two gallons of used motor oil can provide enough electricity (energy) to run an average household for about a day. It is estimated that each gallon of used oil contains 140,000 Btu (Holmes et al., 1993)[2]. A purpose to recover used lubricating oil is to reduce processes of lubricating oil and to reuse used lubricating oil as crankcases oil. There are several ways to restore used lubricating oil with virgin lubricating oil properties.

Recycling of used lubricating oil varies from simple cleaning to complex refining process. Different techniques have been practiced for recycling used lubricating oils. Solvent extraction is a simple process in which used oil and solvent are mixed in appropriate proportions to complete miscibility of the base oil in the solvent. The extracting solvent should also reject the additives and carbonaceous impurities normally found in used oils. Solvent extraction should have the capability of separating the maximum amount of sludge particles from used oil and, at the same time, losing the minimum amount of base oil in the sludge phase [3].

In this research, treatment of used lube oils by solvent extraction was investigated. Factors affecting the treatment were studied, i.e., types of alcohols (1-butanol, 1-pentanol, *n*-hexanol and cyclohexanol), solvent to oil ratios, temperatures (room temperature and 70°C) and time. Optimum conditions for efficient oil recovery would be investigated.

1.2 Objectives

1. To study a recycling method for used lube oil by using solvent extraction.
2. To study the effect of types of alcohol, solvent to oil ratios, temperatures, and time on extraction efficiency.

1.3 Scopes of Study

1. Determination of an appropriate alcohol from 4 types of alcohol, namely 1-butanol, 1-pentanol, *n*-hexanol and cyclohexanol.
2. Determination of an appropriate solvent to oil ratio by varying the ratio from 1:1, 2:1, 3:1 to 4:1.
3. Determination of an appropriate temperature by changing the temperature from room temperature to 70°C.
4. Determination of an appropriate time for the extraction of used lube oil in 7 days.
5. Comparative study of oil properties before and after treatment, namely ash contents and density.

1.4 Expected Results

1. Decrease metal contents in used lubricating oil to a minimum level
2. Improve physical properties of used lube oil, i.e., color, viscosity
3. Remove most of contaminants and water in used lubricating oil
4. Reduction of the environmental impact

Chapter II
Theory and Literature Review

2.1 Lubricants [4]

The most important function of lubricants is the reduction of friction and wear and in some case, the relative movement of two bearing surfaces is only possible if a lubricant is present. In times when saving energy and resources and cutting emission have become central environmental matters, lubricants are increasingly attracting public awareness. Scientific research has shown that 0.4% of gross domestic product could be saved in terms of energy in Western industrialized countries if current tribological knowledge, i.e. the science of friction, wear and lubrication, was just applied to lubricated processes.

Apart from important applications in internal combustion engines, vehicle and industrial gearboxes, compressors, turbines or hydraulic systems, there are a vast number of other applications which mostly require specifically tailored lubricants. This is illustrated by the numerous types of greases or the different lubricants for chip-forming and chip-free metalworking operations which are available. Between 5000 and 10,000 different lubricant formulations are necessary to satisfy more than 90% of all lubricant applications.

2.1.1 Lubricating Base Oils [4]

Base oils are the most important components of lubricants. As a weighted average of all lubricants, they account for more than 95% of lubricant formulations. There are lubricant families (e.g. some hydraulic and compressor oils) in which chemical additives only account for 1% while the remaining 99% are base oils. On the other hand, other lubricants (e.g. some metalworking fluids, greases, or gear lubricants) can contain up to 30% additives.

The origin of the overwhelming quantity of mineral lubricant base oils has led to lubricants being viewed as a part of the petroleum industry and this is underlined by their inclusion in petroleum statistics. In the last few years, lubricants have increasingly become a separate discipline with clear differences from petroleum mass product segment along with the fact that many high-performance lubricants no longer contain petroleum base oil.

2.1.1.1 Mineral Base Oil Processing [4]

Since the beginning of the petroleum industry, mineral oils have been used for lubricant base oils. The process of converting crude oil into a finished base oil is referred to as refining. As far as base oil manufacturing is concerned, the actual refining process begins only after the distillation stages. Refining is thus the term often used to describe all the manufacturing stages after vacuum distillation.

Lubricant refineries are divided into integrated and non-intergrated plants (Figure 2.1). Integrated refineries are linked to primary crude oil refineries and are fed with vacuum distillate by pipeline. Non-integrated refineries purchase vacuum distillate on the open market or buy atmospheric residues and perform their own vacuum distillation. Occasionally they perform vacuum distillation on crude oil.

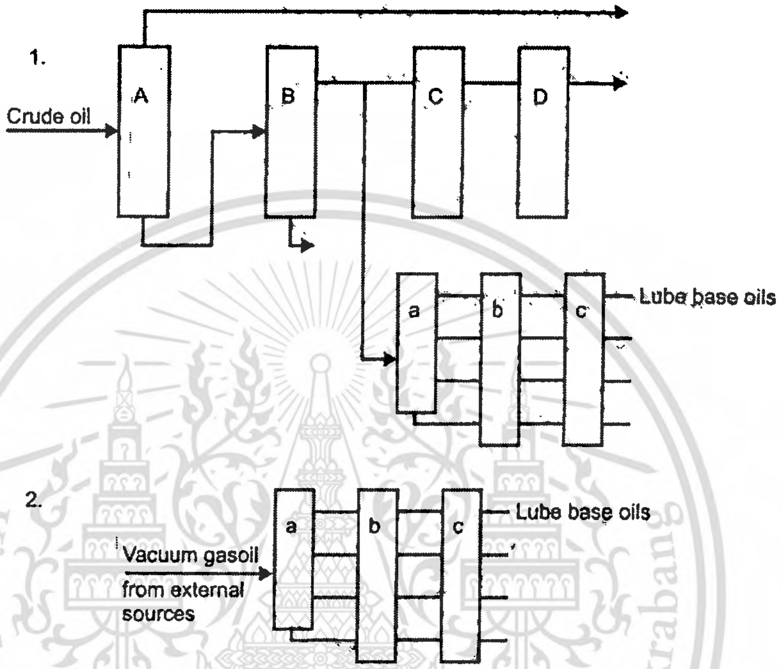
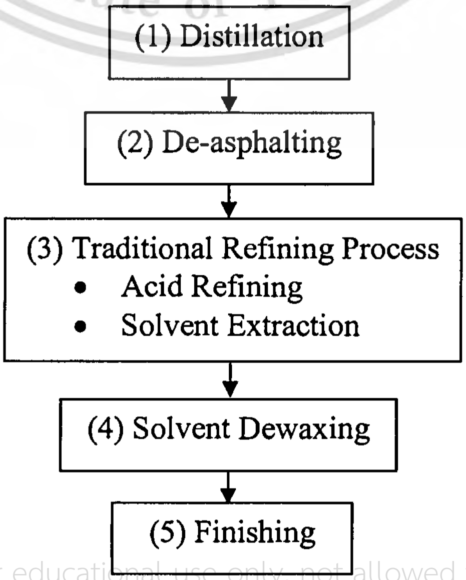


Figure 2.1 Integrated (1) and not integrated (2) lube refinery. A. Atmospheric distillation; B.Vacuum distillation; C,D. Processing of vacuum distillates for non-lube production. a. Fractionating vacuum distillation; b,c. Lube refining processes [4].

Refining Steps.



(1) Distillation

The fractional distillation, product are removed from crude oil which approximately meet the viscosity grades ultimately required. Often only four or five cuts suffice to fulfil lubricant requirements. The viscosity of the primary vacuum distillate is independent of the finished base oils in hydrocracking processes because the hydrocracking process creates new molecule dimension.

After the corresponding separation of the lighter components from the crude oil by atmospheric distillation, the lubricants are in the atmospheric residue. Figure 2.2 shows the yields of the various cuts in conventional lube oil refining with the corresponding boiling ranges of a typical lube crude. The atmospheric residue is now subjected to vacuum distillation to remove the components required for lubricants. In a vacuum, the boiling points of the heavier cuts fall so that distillation without thermal destruction (cracking) is possible.

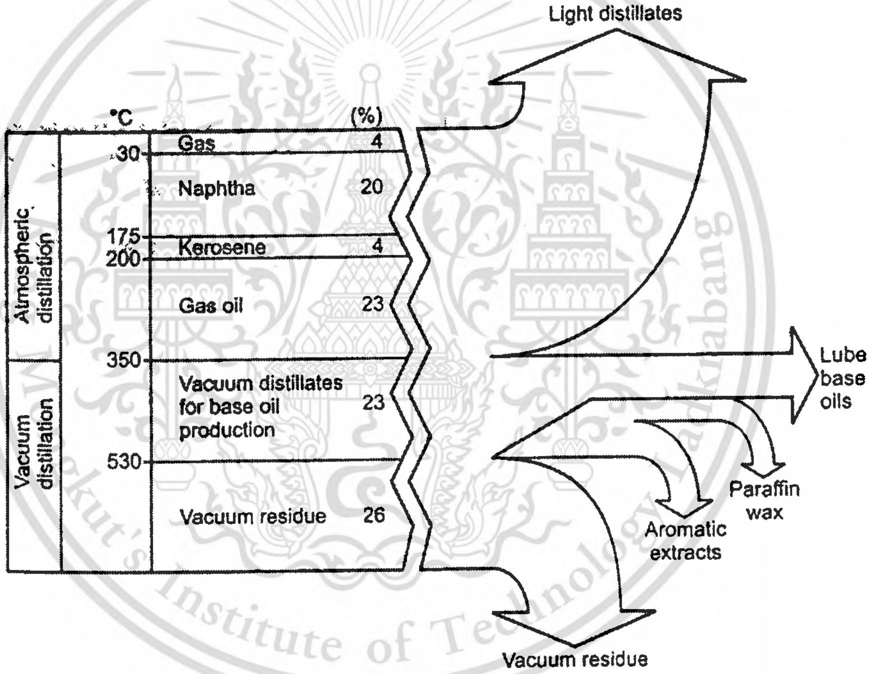


Figure 2.2 Yield of the various cuts in conventional lube oil refining of a typical lube crude [4].

(2) De-asphalting

Although the vacuum residue still contains highly viscous hydrocarbons which can supply valuable components for lube base oils, distillation cannot separate these from the asphalt which is also present and extraction processes must be used to separate these highly viscous base oils, commonly known as brightstocks. Brighstocks are produced in lube oil refineries when the use of the manufacture of high quality bitumen depends on the crude oil. Extractive separation uses light hydrocarbons (propane to heptane), of which propane is the leading product for de-asphalting.

Figure 2.3 shows a flow chart for the manufacture of suitable feeds for lube oil refining by distillation and propane de-asphalting. Figure 2.4 shows the de-asphalting process.

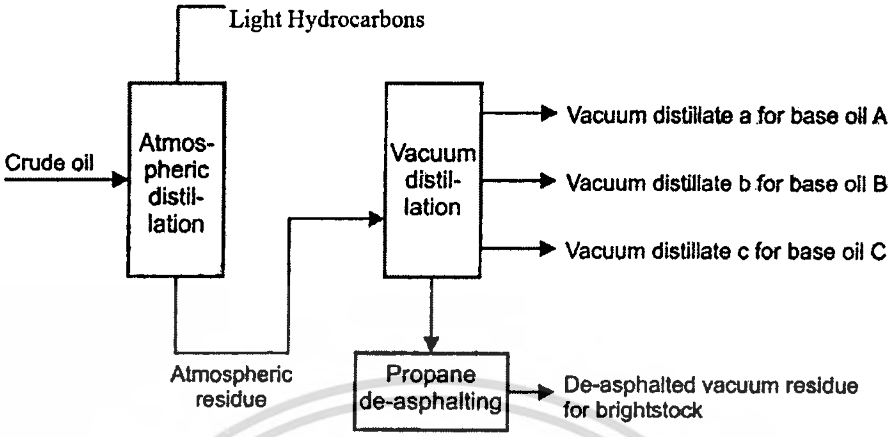


Figure 2.3 Flow chart for the manufacture of suitable feeds for lube oil refining by distillation and propane de-asphalting [4].

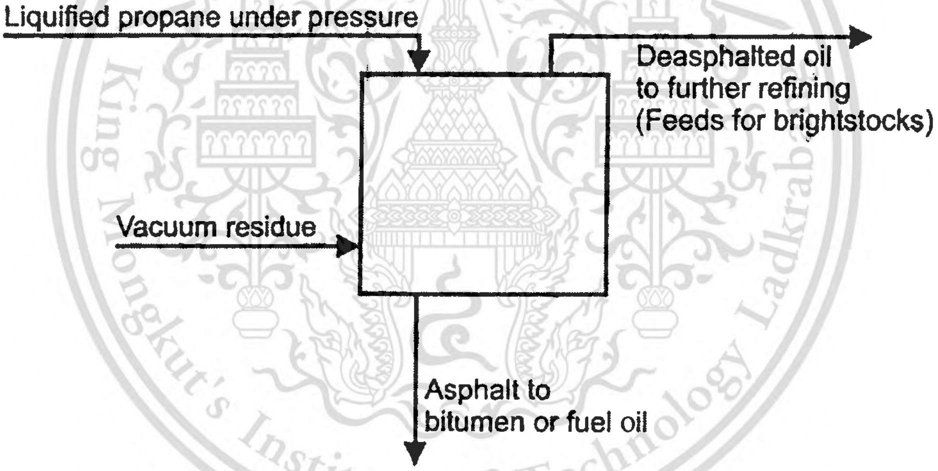


Figure 2.4 Flow chart of the de-asphalting process[4].

(3) Traditional Refining Processes

Vacuum distillation cuts determine the viscosity and flashpoint of later base oils. The precision of the fraction at the lower boiling limits of a cut are of great importance.

The distillates still contain components which can detrimentally affect aging, viscosity-temperature behavior and flowing characteristics, and components which are hazardous to health. To eliminate these disadvantages, several refining methods were developed.

- **Acid Refining**

Acid refining has become less popular because the acid sludge waste produced is difficult to dispose of. This method has been replaced by solvent extraction. Acid refining is still used to some extents for the re-refining of used lubricating oils and for the production of very light-colored technical or pharmarceutical white oils and petroleum sulfonates as by-products.

When the distillates are treated with concentrated sulfuric acid or fuming sulfuric acid (oleum), substances which accelerated oil aging are removed. Oleum treatment (wet refining) has a greater chemical effect on the structure of aromatics and not only readily removes reactive oil components such as olefins but also reduces the aromatic content, which in turn increases the viscosity index of the product. Reaction with saturated paraffinic structures lead to refining losses. Acid-refined oils require complex neutralization and absorption follow-up treatment to remove all traces of acid and undesirable by-products. Some lubricant specifications still require base oil to be free of acid even though modern base oils no longer come into contact with acids.

- **Solvent Extraction**

Whereas acid refining uses chemical reaction to reduce aromatic content and to eliminate reactive, oil-aging accelerators, solvent extraction is based on physicochemical separation (Figure 2.5). Solvent extraction creates base oils which are known as solvent raffinates or solvent neutrals (SN). Extraction processes using solvents create both a base oil and, after evaporation of the solvent, an aromatic-rich extract.

Many processes use solvent such as furfural, NMP (N-methyl-2-pyrrolidone), and phenol also sulfurdioxide (SO_2) for the refining of naphthenic distillates. Normally use NMP because non-toxic solvent and can be used in a low solvent-to-oil ratio with high selectivity.

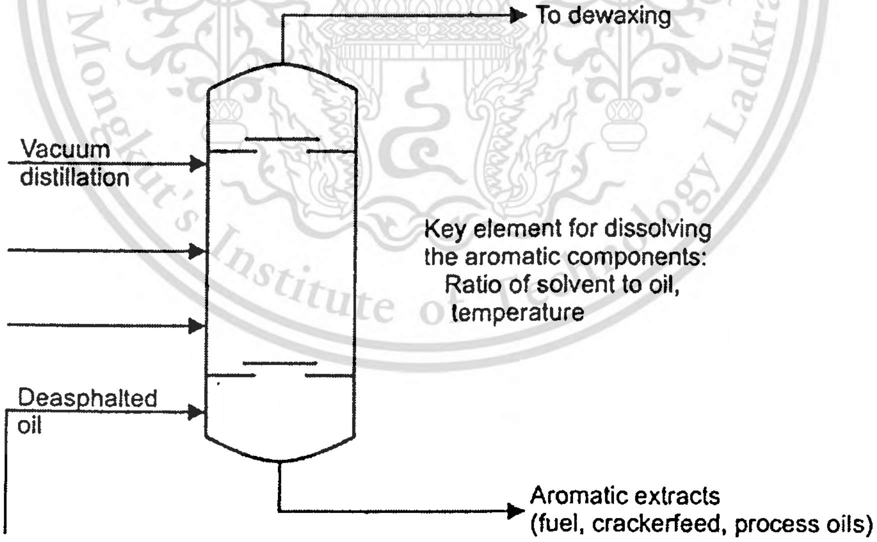


Figure 2.5 Solvent extraction [4].

The selectivity of the extraction media for aromatic is an important selection parameter. A higher proportion of aromatic and naphthenic hydrocarbons in the distillates require greater extraction severity and thus a larger quantity of extract. In general, extracts can only be used as products which are of lower value than the finished base oil.

(4) Solvent Dewaxing

Solvent extraction is followed by solvent dewaxing. Long-chain, high melting point paraffins negatively affect the cold flow properties of lube oil distillates and lead to a high pour point. This is caused by the crystallization of waxy substances at low temperatures which results in turbidity and an increase in viscosity.

Dewaxing by crystallization of paraffins at low temperatures and separation by filtration are the principal processes in traditional refining. Crystallization methods involve mixing the solvent with the oil; this improves filtration, as a result of dilution, and promotes the growth of large crystal formations. The important solvents are ketones and chlorinated hydrocarbons. Figure 2.6 illustrates a conventional solvent dewaxing process.

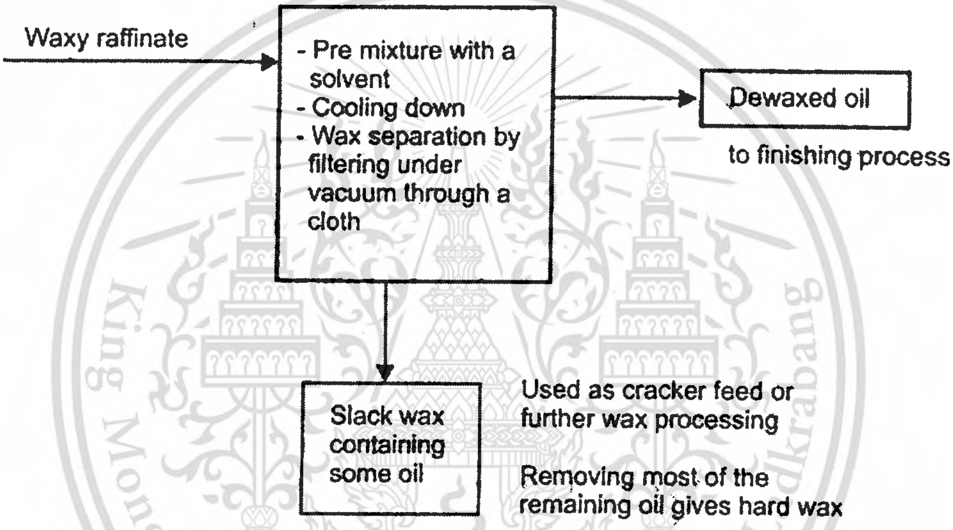


Figure 2.6 Illustrates a conventional solvent dewaxing process [4].

(5) Finishing

In the past, methods which employed absorbents were often used but these days the processes almost all use hydrogen (hydrofinishing). Finishing should improve the color of the product and remove surface-active substances which can negatively affect the air-release or demulsifying properties of a lubricating oil. In general, the hydrofinishing process is referred to as mild hydrotreating and focuses on improving color, odor, and ultra-violet stability.

Additional finishing with absorbent (bleaching clays, bauxite) is sometimes used for the manufacture of refrigerator, transformer, or turbine oils.

2.1.1.2 Synthetic Base Oil [5]

The synthetic base oils usually are prepared by reaction of a few defined and distilled compounds. Synthetic base oils in many cases are also based on petroleum. These lubricants make up the majority of the commercially available lubricants in the marketplace today. Applications of this type of lubricants are engine oil, hydraulic oil, turbine oil, gear oil, air compressor oil, etc. Synthetic base oils can be many different types of compounds with many being limited to one specific application. The majors push synthetic base oil lubricants because the primary synthetic is PAO (polyalpha-olefin). These lubricants are formulated for superior performance in a specific range of applications without limitations to the base oil type or performance additives used. If the high performance lubricant manufacturer believes that synthetic base oil with additives is needed for the application. This is why the lubricant is looking at a synthetic in the first place, because of their desire for a superior performance lubricant.

2.1.2 Additives of Lubricants [4, 6]

Additives are synthetic chemical substances that can improve lots of different parameters of lubricants. They can boost existing properties, suppress undesirable properties and introduce new properties in the base fluids.

Additives are used for increase rate of engine revolution. Also additives have a very big influence on the performance of lubricants that make it possible to fulfil new performance levels, of cause there are some properties that cannot be influenced by additives, e.g. volatility, air release properties, thermal stability, thermal conductivity, compressibility, boiling point etc.

Also well balanced and optimized additive systems can improve the performance of lubricants enormously the formulation of high performance lubricants requires also excellent high quality base fluids.

(1) Antioxidants

Even highly refined base oils contain some organic compounds that can decompose in the presence of heat. This destroys an ability of oil to lubricate and results in severe engine deposits. Antioxidants retard this process.

(2) Viscosity Modifiers

Temperature affects viscosity grade, making an oil either thicker or thinner. This hurts its ability to protect engine parts at temperature extremes. Viscosity modifiers allow the oil structure to adapt to temperature changes, maintain its grade, and retain its lubricating effectiveness.

(3) Pourpoint Depressants (PPD)

Pourpoint Depressants (PPD) are special additives that allow mineral oil lubricants to keep flowing at lower ambient temperatures. Engine oils, transmission oils, gear oils and other lubricants designed for year-round use outdoors contain PPDs as part of the formulation. Lubricants containing PPDs protect equipment better because they flow more readily during cold start up to reach critical parts more quickly when the potential for wear is greatest.

(4) Detergents and Dispersants

Detergents: They neutralize impurities in the oil to prevent deposit formation on engine parts. Available in different strengths, they can either prevent further deposits from forming or clean up deposits that have already formed.

Dispersants: These molecules bond to contaminants in the oil to keep them from clumping together. Contaminants are then kept suspended in the oil until they can be removed by a filter or oil change.

(5) Antifoam Agents

Retard the formation of foam in oil that can result from the mechanical action of the engine. Foam reduces an oil's ability to lubricate effectively.

(6) Demulsfiers and Emulsifiers

Most of the industrial oils in circulation systems (hydraulic, gear, turbine and compressor oils) require good or excellent demulsification or emulsification properties to separate water contamination from the lubricating system. Without demulsifiers or emulsifier, lubricating oils can form relatively stable water-in-oil emulsions.

(7) Dyes

For marketing, identification or leak detection purpose, some lubricants contain dyes which are classified according to the International Color Index.

(8) Antiwear (AW) and Extreme Pressure (EP) Additives

These agents bond to metal surfaces to create a strong lubricant film between moving metal parts. This film can withstand extreme heat and mechanical pressure to keep metal parts separated, protecting them from scoring and seizing.

(9) Friction modifier (FM)

In effect, they make oil more slippery by reducing the friction between moving parts. This both reduces wear and improves fuel efficiency.

(10) Corrosion Inhibitors

Corrosion inhibitors are used in nearly every lubricant to protect the metal surface of any machinery, metalworking tool or work piece from the attack of oxygen, moisture and aggressive products.

2.1.3 Properties of Lubricating Oils [7]

The large number of natural lubricating and specialty oils sold today are produced by blending a small number of lubricating oil base stocks and additives. The lube oil base stocks are prepared from selected crude oils by distillation and special processing to meet the desired qualifications. The additives are chemicals used to give the base stocks desirable characteristics which they lack or to enhance and improve existing properties. The properties considered important are:

1. Viscosity
2. Viscosity change with temperature (viscosity index)
3. Pour point
4. Oxidation resistance

5. Flash point
6. Boiling temperature
7. Acidity (neutralization number)

Viscosity. The viscosity of a fluid is a measure of its internal resistance to flow. The higher the viscosity, the thicker the oil and the thicker the film of the oil that clings to a surface. Depending upon the service for which it is used, the oil needs to be very thin and free-flowing or thick with a high resistance to flow. From a given crude oil, the higher the boiling point range of a fraction the greater the viscosity of the fraction. Therefore the viscosity of a blending stock can be selected by the distillation boiling range of the cut.

Viscosity index. The rate of change of viscosity with temperature is expressed by the viscosity index (VI) of the oil. The higher the VI, the smaller its change in viscosity for a given change in temperature. The VIs of natural oils range from negative values for oils from naphthenic crudes to about 100 for paraffinic crudes. Specially processed oils and chemical additives can have VIs of 130 and higher. Additives, such as polyisobutylenes and polymethacrylic acid esters, are frequently mixed with lube blending stocks to improve the viscosity temperature properties of the finished oils. Motor oils must be thin enough at low temperature to permit easy starting and viscous at engine operating temperatures [180 to 250°F (80 to 120°C)] to reduce friction and wear by providing a continuous liquid film between metal surface.

Pour Point. The lowest temperature at which a oil will flow under standardized test conditions is reported in 5°F or 3°C increments as the pour point of the oil. For motor oils, a low pour point is very important to obtain ease of starting and proper start-up lubricating on cold days.

These are two types of pour points, i.e., a viscosity pour point and a wax pour point. The viscosity pour point is approached gradually as the temperature is lowered and the viscosity of the oil increase until it will not flow under the standardized test conditions. The wax pour point occurs abruptly as the paraffin wax crystals precipitate from solution and the oil solidifies. Additives that affect wax crystal properties can be used to lower the pour point of a paraffin base oil.

A related test is the cloud point, which reports the temperature at which wax or other solid materials begin to separate from solution. For paraffinic oils, this is the starting temperature of crystallization of paraffin waxes.

Oxidation resistance. The higher temperatures encountered in internal combustion engine operation promote the rapid oxidation of motor oils. This is especially true for oil coming in contact with the piston heads where temperatures can range from 500 to 750°F (260 to 400°C). Oxidation causes the formation of coke and vanishlike asphaltic materials from paraffin-base oils and sludge from naphthenic-base oils. Antioxidant additives, such as phenolic compounds and zince dithiophosphosphates, are added to oil blends to suppress oxidation and its effects.

Flash point. The flash point of an oil has little significance with respect to engine performance and serves mainly to give an indication of hydrocarbon emission or of the source of the oils in the blend; for example, whether it is a blend of high and low viscosity oils to give an intermediate viscosity or is comprised of a blend of center cut oils. Low flash points indicate greater hydrocarbon emission during use.

Boiling temperature. The higher boiling temperature range of a fraction, the higher the molecular weight of the components and, for a given crude oil, the greater the viscosity. The boiling ranges and viscosities of the fractions are the major factors in selecting the cut points for the lube oil blending stocks on the vacuum distillation unit.

Acidity. The corrosion of bearing metals is largely due to acid attack on the oxides of the bearing metals. These organic acids are formed by the oxidation of lube oil hydrocarbons under engine operating conditions and by acids produced as by-products of the combustion process which are introduced into the crankcase by piston blow-by. Motor oils contain buffering materials to neutralize these corrosive acids. Usually the dispersant and detergent additives are formulated to include alkaline materials which serve to neutralize the acid contaminants. Lube oil blending stocks from paraffinic crude oils have excellent thermal and oxidation stability and exhibit lower acidities than do oils from naphthenic crude oils. The neutralization number is used as the measure of the organic acidity of an oil. The higher the number, the greater the acidity.

2.1.4 Lubricants for Internal Combustion Engines [4]

Fundamental Principles

Engine oils have to fulfil a wide range of functions in engines. The purely tribological task consists of guaranteeing the functional reliability of all friction points in all operating conditions (Figure 2.7). Apart from this classical tribological task, engine oils have to perform a number of additional functions. This begins with the sealing the cylinder and ends with the transport of sludge, soot and abraded particles to the oil filter.

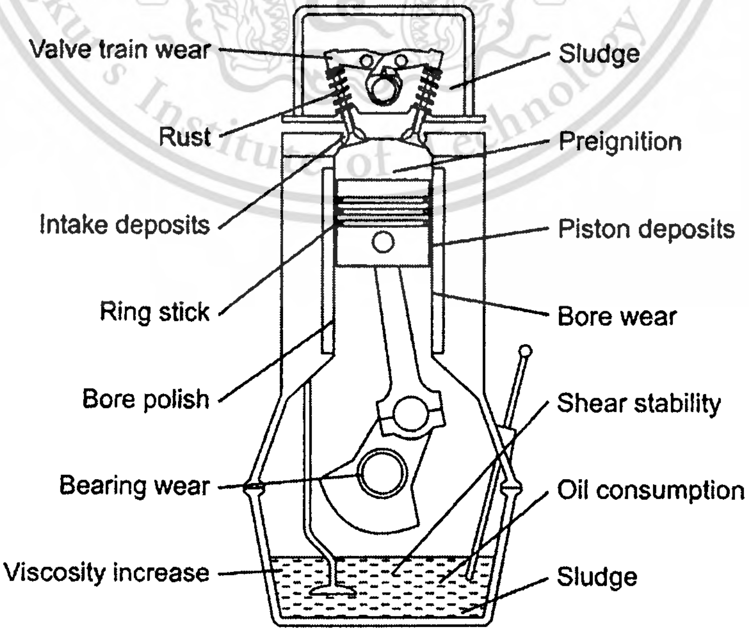


Figure 2.7 Scheme of lubrication points in an engine. [4]

Starting with the tribological functions, three classic sections of the Stribeck graph are satisfied, from hydrodynamic full lubrication to the elasto-hydrodynamic (EHD) area in bearings to the boundary friction conditions at top dead center (TDC) and bottom dead center (BDC). All friction pairings and a whole series of parameters are covered. Sliding friction speeds from simple linear up-and-down movement of the piston in the cylinder through to extreme rotational movements in floating needle roller bearings found in advanced turbochargers rotating at speeds of up to 200,000 rpm with micron tolerances. The temperatures encountered range from ambient in the Arctic (-40°C) to sump temperatures of 100°C to peak values of over 300°C under the piston crown.

During the combustion process, the engine oil helps to seal the piston and cylinder. At the same time, it should burn off the cylinder wall without leaving any residue. As for the piston itself, the engine oil dissipates heat from the piston and thus cools it. The blow-by gases formed when fuel is burned and their reaction by-products have to be neutralized and held in suspension. The same applied to the soot and sludge particles caused by incomplete combustion. The oil also transports dirt and any abraded particles to the oil filter and ensures its filterability. In addition, any water formed during the combustion process should be emulsified and even higher concentrations are present and when the phases separate as temperature falls, the oil should protect against corrosion.

Engine oils should reduce friction and wear during extreme, low-temperature start-ups as well as when the lubricating film is subjected to high temperatures and pressures in bearings and around the piston rings. While the oil should still flow well and be pumpable without aeration at low temperatures (down to -40°C) to avoid metal-to-metal contact during cold start-ups, the lubricating film must perform satisfactorily in bearings and hydraulic tappets. At low temperatures, additives must not precipitate and the oil must not gel. At the upper end of the temperature scale, the oil must offer far-reaching resistance to thermal and mechanical aging. And finally, the stability of the lubricating film should not be diminished by fuel dilution of up to 10%.

2.2 Used lubricating oil [4, 8]

Used lubricants represent a problem for the environment created when all mechanical possibilities in a machine or at the user's premises no longer suffice to maintain the performance of the lubricant and especially when chemical additives have been used-up and aging by-products are present in the oil. In fact, lubricants lose value during use and re-refining, at best, can only restore the value of base oil. In the case of conventional mineral oils, this value is only slightly higher than fuels or heating oils. From a global competition point of view, other disposal options include the direct incineration of untreated waste oils, the simple pre-treatment (cleaning) and alternative uses such as flux oils for bitumen or for the manufacture of secondary feeds in sec-feed plants for catalytic crackers and as blending stock for high-sulfur fuels.

Used lubricating oils are usually significantly contaminated. Besides normal degradation compounds/products, a wide range of contaminants can be encountered, including [8]:

1. residual components of engine fuels (gasoline and diesel fuel)
2. solids from wear processes and additives, along with corrosion products and dirt
3. soot
4. combustion products (water, acids)
5. various chemicals.

2.2.1 Generation of used lubricating oils

Used oil generation is strictly related to lubricating oil consumption. On average, 50% of lube oil consumed can be regenerated for reuse. Automotive gasoline and diesel engine oils, together with railroad diesel engine oils, are the major lubricant products. Most of them are mono- and multigrade crankcase lubricants, along with gear lubricants and transmission fluids. There are several potential sources of used motor oils, including service stations, do-it-yourself (DIY) motorists, company fleets, and specialised used oil collection points.

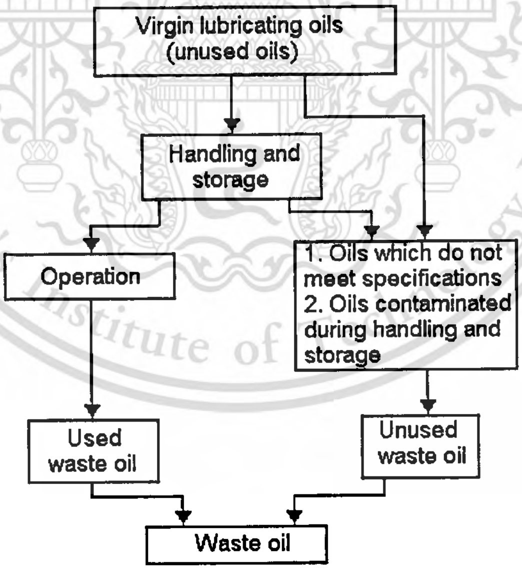


Figure 2.8 Generation of used (waste) oil [8].

Figure 2.8 is a scheme representing the generation of waste oil. The terms used here, defined include:

Used waste oil is mineral or synthetic lubricating oil that physical and chemical properties have changed in use such that it is not fit for its original purpose.

Unused waste oil is unused virgin oil that has become contaminated when spilled or mixed with other waste, or that has failed to meet specifications.

Waste oil is oil that becomes contaminated during storage, handling, or use. It is made up of both used and unused waste oils.

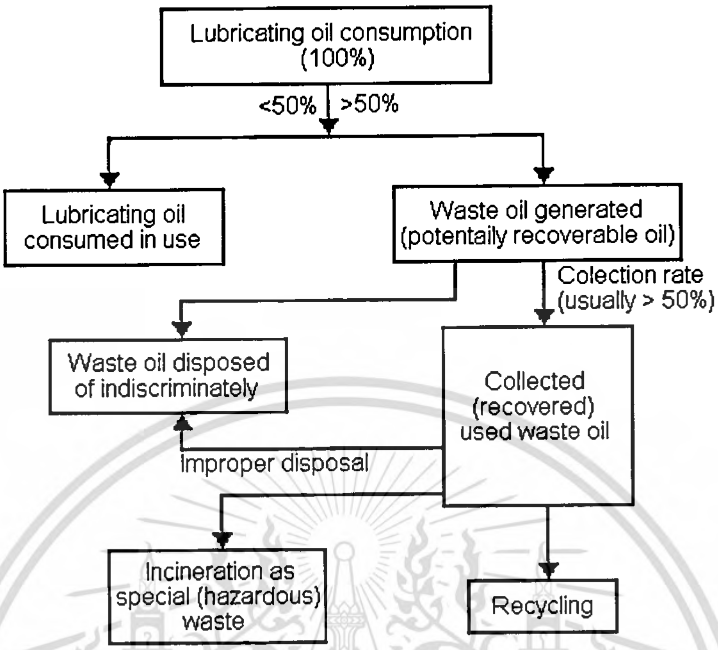


Figure 2.9 Used oil generation and collection [8]

Figure 2.9 provides an indication of the paths to the generation and collection of used waste oil. By and large, the availability of used waste oil relates directly to lubricating oil usage. The greater the usage, the larger the quantity of potentially recoverable waste oil for reutilization, which amount equals the fraction available for collection in the waste oil management system, and does not include the oil in waste water treatment sludge at industrial sites.

2.2.2 Recycling of Used Lubricating Oils

Recycling of used oil relates to passing it through a cycle of changes or treatment which provides products or materials for reuse, and usually employs one or more of the three methods for commercial regeneration of used oils:

- reclaiming (not widely use)
- reprocessing (not widely use)
- re-refining

2.2.2.1 Reclaiming or reconditioning

Reclaiming or reconditioning is the processing that mostly removes solids and water by simple physical methods (settling, heating, filtration, centrifuging) but does not remove unwanted oil-soluble contaminants.

2.2.2.2 Reprocessing

Reprocessing process removes solids, water, and some soluble contaminants using chemicals. Use of adsorbents may also be part of reprocessing. Reprocessing also relates to fuel oil production from waste oil with mild cleaning.

2.2.2.3 Re-refining

The principal reasons why re-refining is unable to find acceptance are: high selling prices compared to relatively low virgin oil prices, in adequate removal of carcinogenic polycyclic aromatics, the negative image of such oils in most markets and the increasing complexity of base oil blends in engine and other lubricants.

In general, the process stages are common to all the different methods, i.e.,

1. Separation of larger solid impurities along with most of the water. This is normally achieved by sedimentation.
2. Separation of the volatile parts (fuel residues in engine oils, solvents and low boiling-point lubricant components). This normally happens by atmospheric distillation. The separated light hydrocarbons can usually be used in-house for energy creation.
3. Separation of the additives and aging by-products. This can occur by acid refining. Solvent (propane) extraction, vacuum distillation or partly also by hydrogenation.
4. Finishing process to separate any remaining additives, aging by-products and refining reaction products. This normally happens by hydrofinishing, with absorbents such as bleaching clay or mild, selective solvent extraction (e.g. Furfural).

- **Sulfuric Acid Refining (Meinken)**

The sulfuric acid refining process was mostly developed by Meinken. Due to the acidic sludge problem, acid refining has largely been replaced by other methods. However, numerous such plants were still in operation in 1999. Figure 2.10 shows a Meinken flow plan.

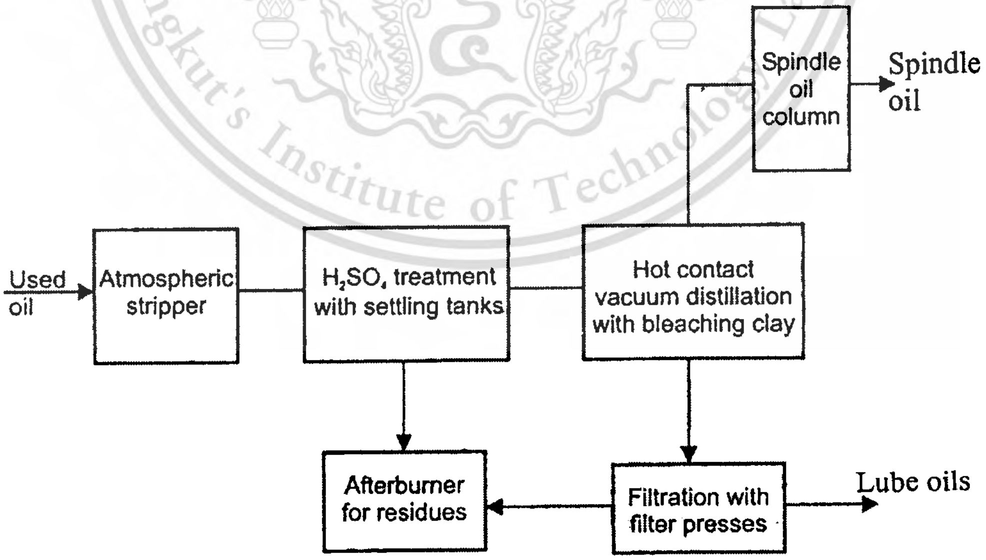


Figure 2.10 Sulfuric acid re-refining (flow chart of the Meinken process) [4].

- **Propane Extraction Process (IFP, Snamprogetti)**

This initially used propane extraction together with acid refining and later together with hydrofinishing. Propane extraction is also used by Snamprogetti (Italy) as the main refining step before and after vacuum distillation. Figure 2.11 shows the process with propane extraction.

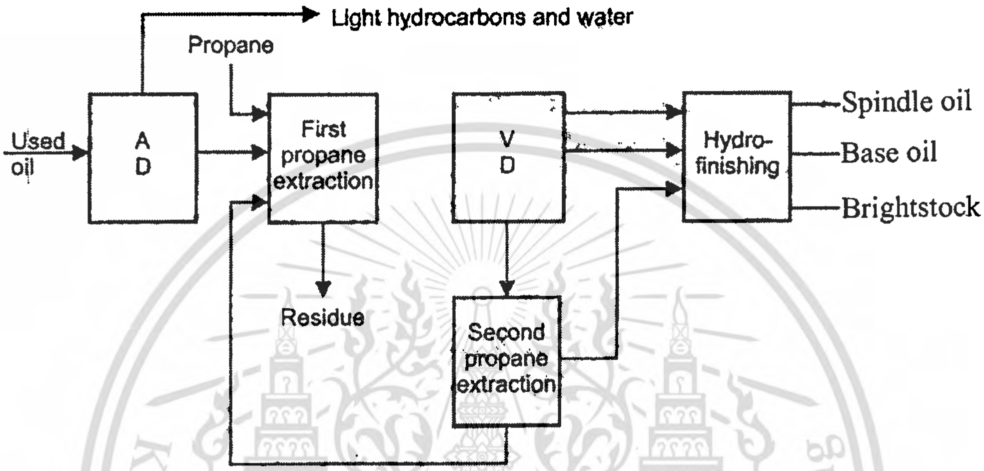


Figure 2.11 Re-refining by propane extraction (IFP, Snamprogetti). AD Atmospheric distillation; VD.Vacuum distillation [4].

- **Mohawk Technology (CEP-Mohawk)**

The Mohawk Process (subsequently CEP-Mohawk) using high pressure hydrogenating. The process begins with thin-film vacuum distillation (after flashing the light hydrocarbons and water). This is followed by hydrogenation of the distillate at 1000 psi over a standard catalyst. Special steps realized catalyst life of 8 to 12 months, which was essential for the economy of the process.

- **KTI Process**

The KTI (Kinetics Technology International) process combines vacuum distillation and hydrofinishing to remove most of the contamination and additives. The key to the process is the thin-film vacuum distillation to minimize thermal stress through mild temperatures not exceeding 250°C.

The hydrofinisher removes sulfur, nitrogen and oxygen. The yield of finished base oils is high (82% on a dry waste oil basis). Figure 2.12 shows the flow chart of this process.

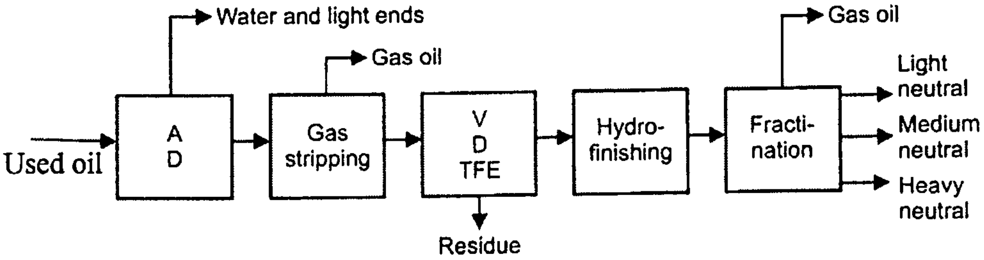


Figure 2.12 Flow chart of the KTI Process: thin film evaporator (TFE) with hydrotreatment AD Atmospheric distillation; VD.Vacuum distillation [4].

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- **PROP Process**

The key elements of the process are the chemical demetalization (mixing an aqueous solution of diammonium phosphate with heated base oils) and a hydrogenation process. A bed of clay is used to adsorb the remaining traces of contaminants to avoid poisoning of the Ni/Mo catalyst. Figure 2.13 shows the PROP Process

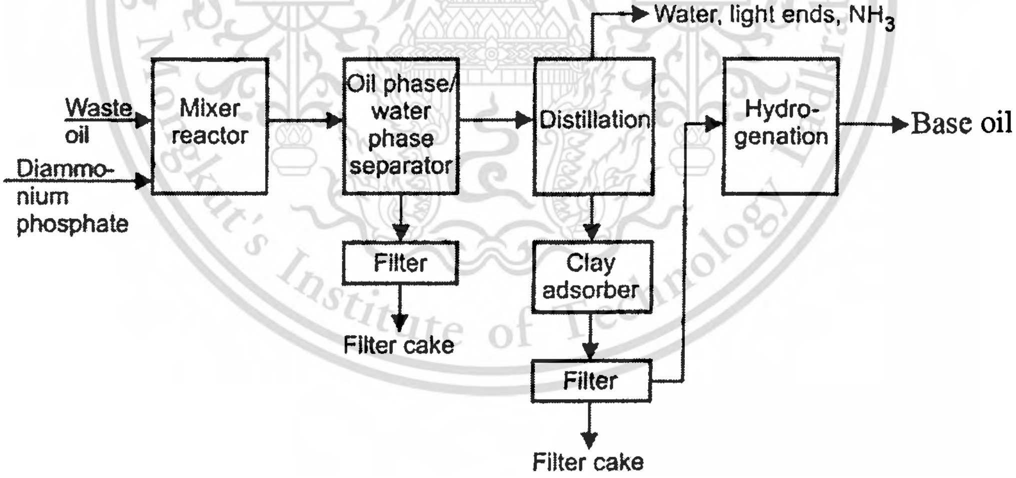


Figure 2.13 Flow chart of the PROP Process [4].

- **Safety Kleen Process**

This process uses atmospheric flash for removing water and solvents, a vacuum fuel stripper, vacuum distillation with two thin-film evaporators, hydrotreater with fixed bed Ni/Mo catalyst. When using high severity the hydrotreater is in the position to reduce polynuclear aromatics; it also removes higher boiling chlorinated paraffins. Figure 2.14 shows a simplified block diagram.

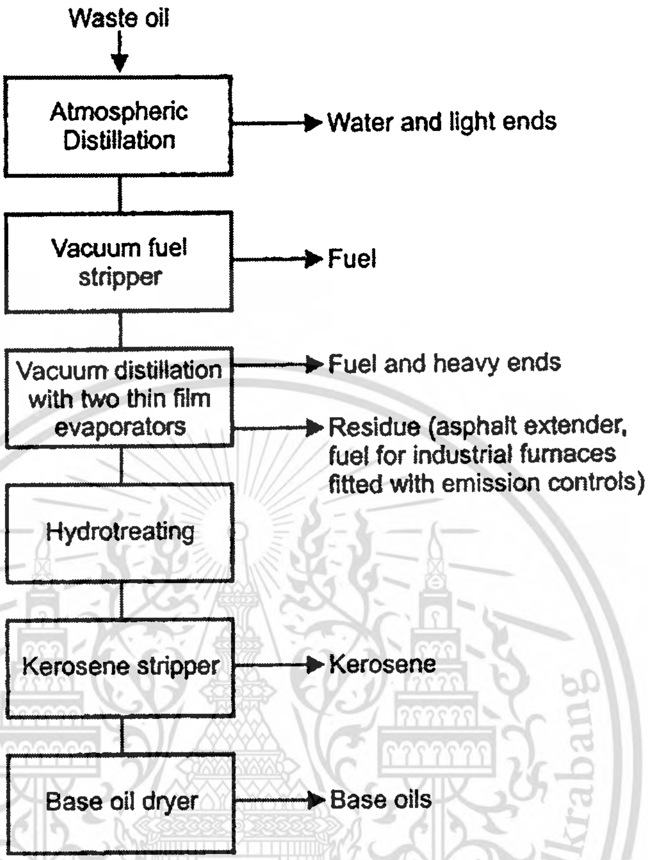


Figure 2.14 The Safety Kleen process [4].

- **DEA Technology**

In this process, the distillate from vacuum thin-film distillation towers equipment at re-refinery (Dollbergen/Germany) are finally treated in a lube refinery solvent extraction plant followed by hydrofinishing (DEA, Hamburg/Germany). After this extraction process, the PAH (Polycyclic aromatic hudrocarbon) content is lower than that of virgin solvent neutrals. Figure 2.15 shows the corresponding flow-chart.

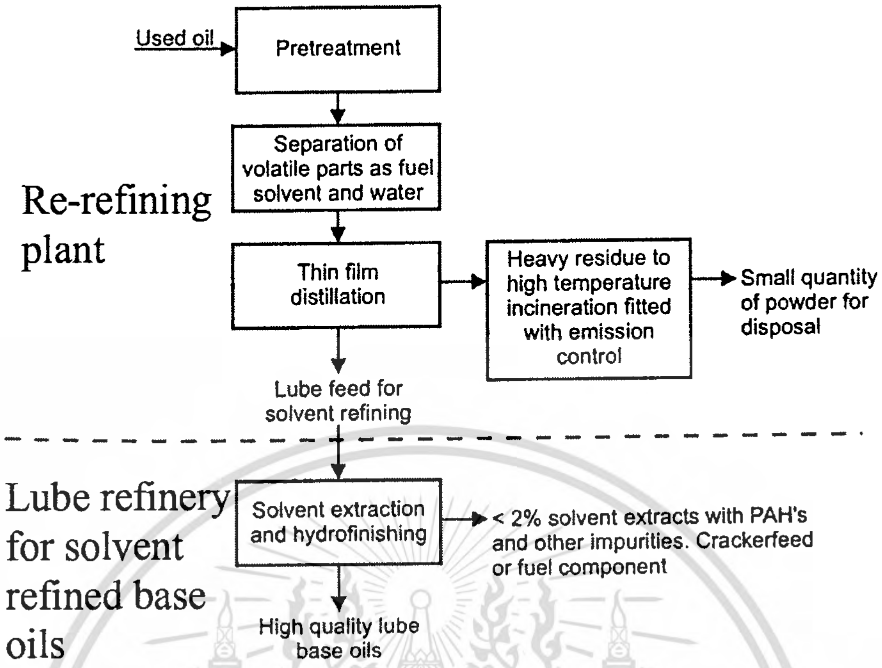


Figure 2.15 Introduction of selectivity solvent extraction in the re-refining process (DEA/Mineralöl-Raffinierie Dollbergen, Germany) [4].

2.3 Solvent Extraction [9]

A method of separating the constituents of a mixture utilizing preferential solubility of one or more components in a second phase. Commonly, this added phase is a liquid, while the mixture to be separated may be either solid or liquid. As a mundane example, the preparation of tea or coffee is a process of liquid/solid extraction whereby water selectively dissolves certain components of the mixture, leaving behind the insoluble residue (as tea leaves or coffee grounds). If the starting mixture is a liquid, then the added solvent must be immiscible or only partially miscible with the original and of such a nature that the components to be separated have different relative solubility in the two liquid phases.

Solvent extraction is a selective separation procedure for isolating and concentrating a valuable substance from an aqueous solutions with the aid of an organic solution. In the procedure the aqueous solution containing the substance of interest, often at a low concentration and together with other dissolved substances, is mixed (extraction) with an organic solvent containing a reagent. The substance of interest reacts with the reagent to form a chemical compound, which is more soluble in the organic than in the aqueous solution. As a consequence, the substance of interest is transferred to the organic solution.

Subsequently, in order to recover the extracted substance, the organic solution is mixed (stripping) with an aqueous solution whose composition is such that the chemical compound between the substance and the reagent is split and, thus, the substance is recovered in the "new" aqueous solution, in a pure form. The concentration of the substance in the "new" aqueous solution may be increased, often to 10-100 times that of the original aqueous solution, through adjustment of the liquid flow rates. Freed from the substance of interest, the organic solution is returned for further extraction, either directly or after a fraction of it has been cleansed of impurities.

Extraction processes are divided to 3 kinds, i.e.,

1. Liquid/solid extraction
2. Liquid/liquid extraction
3. Supercritical fluid extraction

For **liquid/liquid** extraction separates the components of a homogeneous liquid mixture on the basis of differing solubility in another liquid phase. Because it depends on differences in chemical potential, liquid/liquid extraction is more sensitive to chemical type than to molecular size. This makes it complementary to distillation as a separation technique. One of the first large-scale uses was in the petroleum industry for the separation of aromatic from aliphatic compounds. The original process employed liquid sulfur dioxide as solvent. More recently, sulfolane (thio-cyclopentane-1, 1-dioxide) has replaced sulfur dioxide for extraction of lighter aromatics due to its greater selectivity and ease of recovery. For selective separation of higher-molecular weight aromatics and aliphatics as in lubricating oil manufacture, phenol and furfural are the most widely used solvents.

Liquid/liquid extraction has found application for many years in the coal tar industry. The recovery of tar acids from crude tar oil by washing with an aqueous solution of alkali is an example where chemical interaction between solute and solvent determines differential solubility.

On a smaller scale, extraction is a key process in the pharmaceutical industry for recovery of antibiotics from fermentation broths. Penicillin is obtained by extraction into solvents such as amyl acetate at relatively low pH value (2 to 2.5) and is then stripped from the organic phase by treatment with a buffered aqueous solution at about pH 7 to 7.5. Other examples in this field are the recovery and separation of vitamins and the production of alkaloids from natural products.

2.4 Applications [10]

Used oil, or 'sump oil' as it is sometimes called, should not be thrown away. Although it gets dirty, used oil can be cleaned of contaminants so it can be recycled again and again. There are many uses for recycled used oil. These include:

- Industrial burner oil, where the used oil is dewatered, filtered and demineralised for use in industrial burners;
- Mould oil to help release products from their moulds (e.g. pressed metal products, concrete);
- Hydraulic oil;

- Bitumen based products;
- An additive in manufactured products; or
- Re-refined base oil for use as a lubricant, hydraulic or transformer oil.

2.5 Literature Reviews

Ahmad Hamada, Essam Al-Zubaidya and Muhammad E. Fayed [2] investigated new extraction solvents used to treat lubricant used oil. The solvents used were liquified petroleum gas (LPG) and stabilized condensate. A demulsifier was used to enhance the treatment process. The treatment process was carried out at ambient conditions. The results shown that the stabilized condensate at solvent to oil ratio equal to four demonstrated a high removal asphaltene ratio compared to LPG. Stabilized condensate solvent was able to reduce the asphaltene content of the treated lubricating oil to 0.106% (w/w), the ash content to 0.108%, and the carbon residue to 0.315% with very low levels of contaminant metals. The overall yield of oil was 79%. The major disadvantage of this work is the high temperature of solvent recovery.

N.O. Elbashir , S.M. Al-Zahrani , M.I. Abdul Mutalib and A.E. Abasaeed [3] studied the performance of three extracting solvents (2-propanol, 1-butanol, and methyl-ethyl-ketone (MEK) in recycling used oil. The parameters that they concerned are types of solvent, solvent to oil ratio, and extraction temperature. They used the solubility parameter to select the best solvent with regard to the percent oil losses and determining the effective extraction parameters, are solvent to oil ratio and extraction temperature. The results showed MEK achieved the best performance with the lowest percent oil losses, followed by 2-propanol and 1-butanol. An extraction temperature increased the percent oil losses decreased.

Chandra W. Angle, Yicheng Long, Hassan Hamza, Leo Lue [11] studied the ratios of n-heptane (hep) to toluene (tol) affected the solubility of the asphaltenes in heavy oil extraction processes, the kinetics of phase change when n-heptane was added to toluene-diluted heavy oils, and the thermodynamic properties of partially deasphalted heavy oils. The methods used were monitoring precipitation in time using light microscopy, quantitative asphaltenes analysis by near infrared spectroscopy, refractive index and densities measurements, and calculated solubility parameters of mixtures. At critical mass ratios of hep/tol from 1.37 to 2.0 in diluted heavy oil the precipitated asphaltene particles were observed under the microscope after lag times from 2 hrs to instantly. Lag times were longer at low initial oil concentration. The floc growth time decreased as heavy oil concentration in toluene increased. The results showed that the amount of precipitated asphaltenes depended on the concentration of the starting material after equilibrium was established. Precipitation kinetics near onset point depended on the initial concentration of the heavy oil in toluene. Even at similar heptol values, lag (delay) time before precipitation decreased with increasing starting oil concentrations. A lag time was confirmed by visual evidence of precipitation by microscopy when observed by optical microscopy, the structures of asphaltene precipitated during formation and growth depended on time as well as both mass ratio of initial heavy oil/toluene and n-heptane added. The most diluted oil showed the most detailed time-dependent deposition and growth response.

Murat Erol, Belma Demlrel, Taner Togrul, Ayla Calimli [12] analyzed separation of organic matter from asphaltite with supercritical fluid mixtures and described supercritical fluid extraction (SFE) of Turkish asphaltite with toluene mixtures. The experiments were performed in a stirred batch autoclave at 613 K. Organic matter recovered from the SFE were fractionated into oils, asphaltenes and preasphaltenes by solvent extraction. The results showed the yield of extract obtained from SFE of asphaltite was 15.1% with toluene, but about 17% with toluene mixtures.

Teresa Rauckytea, Douglas J. Hargreaves, Zenon Pawlak [13] studied determination of heavy metals and volatile aromatic compounds in used engine oils and sludges. Results of the study examining a toxic metal leachability from used engine oil and sludge samples employing leaching test (TCLP). The leaching test indicated that lead in oil samples exceeded 5-ppm concentration level what qualified them as a toxic waste. The samples of contaminated sludge were found to contain high concentration of total lead, barium and chromium, but the leaching test showed concentration below regulatory limit. The total content of benzene, ethylbenzene, toluene, and xylenes (BETX), and naphthalene in used oil and sludge samples was also determined and was found not to be a significant factor to contamination.

Thallada Bhaskar, Md Azhar Uddin, Akinori Mutoa, Yusaku Sakata, Yoji Omura, Kenji Kimura, Yasuhisa Kawakami [14] prepared Silica (SiO_2), alumina (Al_2O_3), silica–alumina (SiO_2–Al_2O_3) supported iron oxide (10 wt% Fe) catalysts by wet impregnation method and used for the desulfurization of waste lubricant oil into fuel oil and also used X-ray diffraction, Gas chromatography with thermal conductivity detector analysis. The thermal and catalytic treatments of waste lubricant oil with silica, silica–alumina, alumina supported iron oxide catalysts were performed at 400°C at atmospheric pressure. The results showed that Fe/SiO_2 catalyst decreased the sulfur content from 1640 to 90 ppm and produced low molecular weight hydrocarbons by cracking the high molecular weight hydrocarbons. Fe_2O_3 crystalline size was found to be smaller in Fe/SiO_2 catalyst than Fe/Al_2O_3 and Fe/SiO_2–Al_2O_3 catalysts. The Fe/SiO_2–Al_2O_3 (86%) and Fe/Alumina (90%) catalysts could decrease the sulfur content, but increase of reaction time, the desulfurization activity was found to decrease.

P.K. Wong , J. Wang [15] compared supercritical fluid (SFE) and liquid-liquid extraction (LLE) methods to accumulate polycyclic aromatic hydrocarbons in lubricating oil. The results showed that recovery of polycyclic aromatic hydrocarbons (PAHs) extracted by SFE from the used lubricating oil were higher than those by LLE. The concentrations of total PAH in lubricating oils collected from both automobiles increased rapidly after oil change. And finally, extraction temperature from 60 to 150°C could effectively increase the recovery of all 16 certified PAHs.

Hong E, Paul Watkinson [16] studied of asphaltenes solubility and precipitation. The Cold Lake vacuum residue and Athabasca atmospheric tower bottoms were determined using the hot filtration method at 60–85 °C. For selected mixtures the temperature range was extended to 300 °C and the diluents are pure n-alkanes, a lube oil base-stock, heavy vacuum gas oil and a resin-enriched fraction recovered from Cold Lake vacuum residue by supercritical fluid extraction and fractionation. The results showed that the amount of asphaltene precipitation decreased as the molecular mass of n-alkanes increased and the increased of diluent-to-residue ratios R; the amount of precipitated asphaltene increased sharply at first and then leveled off, the solubility of asphaltenes in selected mixtures increased with temperature over the range of 60 to 300 °C.

Chapter III
Experiment Detail

3.1 Materials

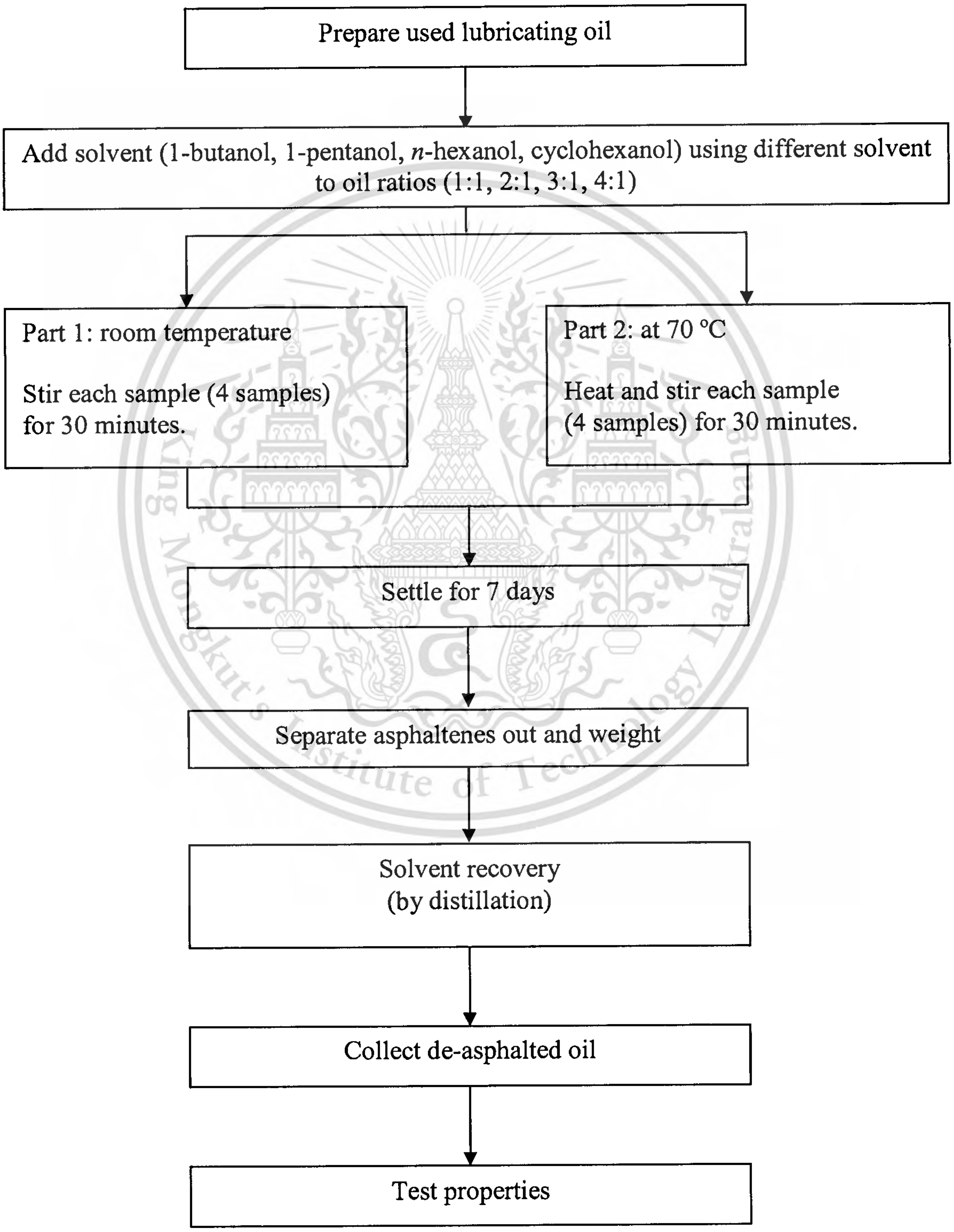
1. Used lubricating oil received from Shell petrol station
2. 1-butanol, Italma Co,Ltd. Laboratory grade
3. 1-pentanol, Labsystems Co,Ltd. Laboratory grade
4. *n*-hexanol, Labsystems Co,Ltd. Laboratory grade
5. cyclohexanol, Labsystems Co,Ltd. Laboratory grade
6. hexane, Lab Scan Co,Ltd. Commercial grade

3.2 Equipments

1. Distillation set
2. Reflux set
3. Laboratory glass wares
4. Thermometer
5. Crucible
6. Furnace
7. Desicators
8. Oven
9. Bunsen burner
10. Stirrer
11. Hot plate
12. Heating mental
13. Magnetic bar
14. Rubber grove
15. Stand and Clamp
16. Tong
17. Balance

3.3 Experimental Procedures

Flow Chart



3.3.1 Sample Preparation.

Figure 3.1 Filtration of used lube oil by filter cloth

1. Pour used lubricating oil to sift on filter cloth.
2. Weight 20 ml for each one of 8 used lubricating oil sample

3.3.2 Study of the Effect of Temperature on %w/w of Accumulated Asphaltenes.

Part 1 At room temperature

Figure 3.2 Extraction at room temperature

1. Mix used lubricating oil (20 ml) with solvent (1-butanol, 1-pentanol, *n*-hexanol and cyclohexanol) using varied solvent to oil ratio (1:1, 2:1, 3:1 and 4:1)
2. Stir at 3 rpm on Fisher scientific stirrer for 30 minutes
3. Leave to settle. Filter and weight accumulated asphaltenes every 24 hours for 7 days

Part 2 At 70 Degree Celsius

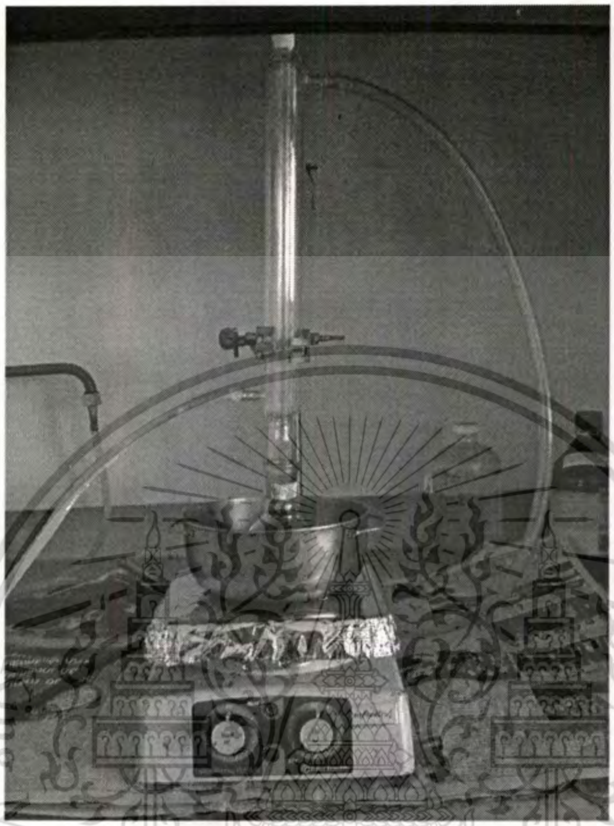


Figure 3.3 Extraction at 70 degree celsius

1. Mix used lubricating oil (20 ml) with solvent (1-butanol, 1-pentanol, *n*-hexanol and cyclohexanol) using varied solvent to oil ratio (1:1, 2:1, 3:1 and 4:1)
2. Boil water in water bath to 70°C using hot plate and stirrer. Set stirrer at 3 rpm
3. Heat and stir the sample in water bath for 30 minutes
4. Cool it down to room temperature
5. Leave to settle. Filter and weight accumulated asphaltenes every 24 hours for 7 days

3.3.3 Determination of Percent Ash Content.

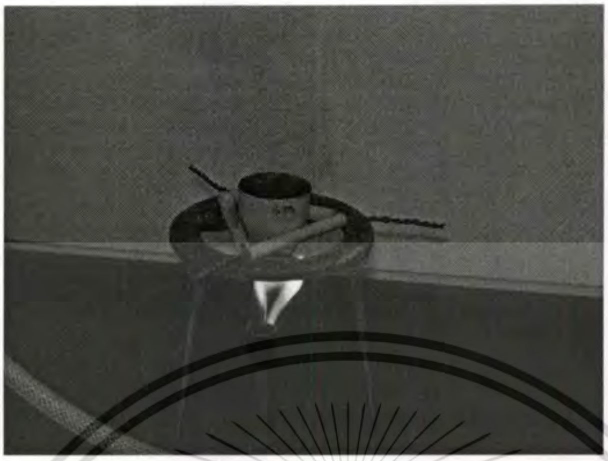


Figure 3.4 Combustion of de-asphalted oil

1. Prepare a crucible by place it in the furnace and heat it at 750°C for 2 hours. Wait until the temperature drops to 100°C. Remove it from the furnace and cool it down in a desiccator. Weight the crucible
2. Weight 5 g of the de-asphalted oil for each sample. Pour it into the crucible
3. Burn the extracted oil with Bunsen burner until no smoke is detected.
4. Place the sample into the furnace at 750°C for 2 hours. Wait until the temperature drops to 100°C. Remove it from the furnace and cool it down in a desiccator. Weight the crucible
5. Weight the sample and calculate percent ash content

3.3.4 Determination %w/w of Accumulated Asphaltenes

1. Collect and weight the recovered accumulated asphaltenes
2. Find percent of accumulated asphaltenes using the equation below

$$\%\text{ accumulated asphaltenes} = \frac{\text{Weight of accumulated residue} \times 100}{\text{Weight of used oil sample}}$$

3.3.5 Determination of the Density

1. Place a 10 ml cylinder on a balance and set to zero
2. Pour oil into the cylinder to an exact volume
3. Record weight of oil
4. Calculate the density using the equation below

$$\text{Density (D)} = \frac{\text{Mass (g)}}{\text{Volume (ml)}}$$

Chapter Ⅳ
Results and Discussion

The objective of this project was to study recycling of used lubricating oil by liquid-liquid extraction process. Some variables which play important roles in the quantity and quality of treated lubricating oil were investigated. Those are type of solvents (1-butanol, 1-pentanol, *n*-hexanol, cyclohexanol), solvent-to-oil ratios (1:1, 2:1, 3:1, 4:1), working temperature (room temperature vs. 70°C) and time of asphaltenes settlement (1 to 7 days). The percent of asphaltenes removed was also calculated.

4.1 Effects of Solvent Types

The solvents used in this project were 1-butanol, 1-pentanol, n-hexanol and cyclohexanol. Table 4.1 and Figure 4.1 show %w/w accumulated asphaltenes extracted from used lubricating oil using above solvents at room temperature after 7 days with varied solvent to oil ratios.

Table 4.1 %w/w accumulated asphaltenes after 7 days using alcohols as solvent at room temperature

Solvents	**%w/w accumulated asphaltenes with varied solvent:oil ratios**			
	1:1	**2:1**	**3:1**	**4:1**
1-butanol	3.01	9.33	13.08	17.35
1-pentanol	3.44	10.98	12.48	8.75
n-hexanol	0.80	1.13	1.58	3.51
cyclohexanol	0.73	1.00	1.34	2.09

At room temperature, the solvent which gave the best performance of setting more of asphaltenes was 1-butanol. The result was similar to that reported by Chandra W. Angle, Yicheng Long, Hassan Hamza, Leo Lue [11]. Since the polarity of 1-butanol is higher than 1-pentanol, it tends to reject the higher molecular weight hydrocarbons. As a consequence, 1-butanol gave the lowest yield of de-asphalted oil of the highest quality. On the other hand, cyclohexanol gave the highest oil yield, unfortunately, with low quality. This is because the polarity and structure of cyclohexanol are more compatible with those of asphaltenes, so the solution contained more of the high molecular weight hydrocarbons.

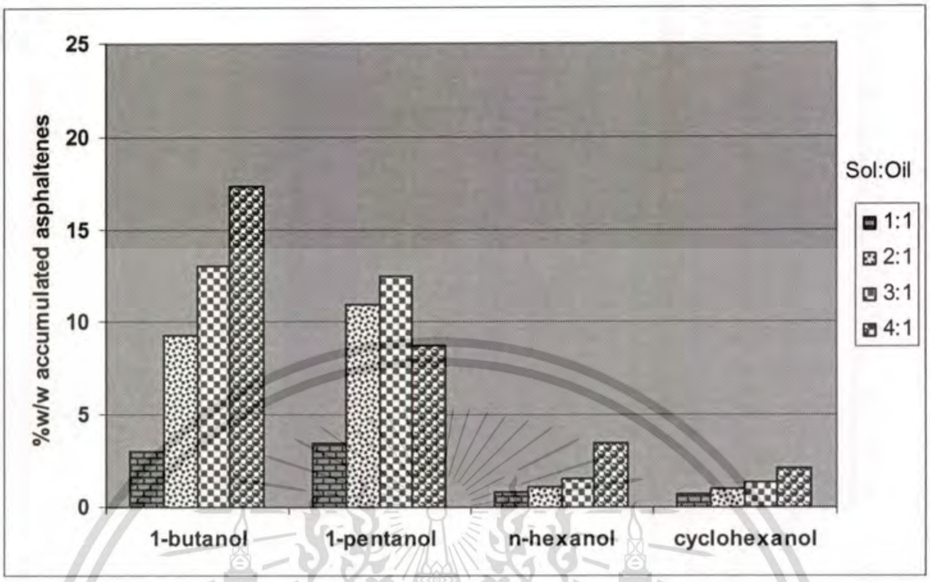


Figure 4.1 %w/w accumulated asphaltenes after 7 days using various types of alcohols as solvent at room temperature

Table 4.2 and Figure 4.2 show %w/w accumulated asphaltenes removed from used lubricating oil after 7 days with those solvents and solvent to oil ratios at an alternative temperature of 70°C.

Table 4.2 %w/w accumulated asphaltenes after 7 days using alcohols as solvent at 70°C

Solvents	**%w/w accumulated asphaltenes with varied solvent to oil ratios**			
	1:1	**2:1**	**3:1**	**4:1**
1-butanol	9.21	13.67	20.99	22.39
1-pentanol	4.55	16.81	17.38	15.97
n-hexanol	4.75	5.74	12.26	12.39
cyclohexanol	2.67	3.10	4.01	4.94

At 70°C, the same trend as that at room temperature was detected as shown in Figure 4.2. 1-butanol was still the best solvent followed by 1-pentanol, *n*-hexanol and cyclohexanol, respectively. The result can also be explained as mentioned earlier with the extraction at room temperature.

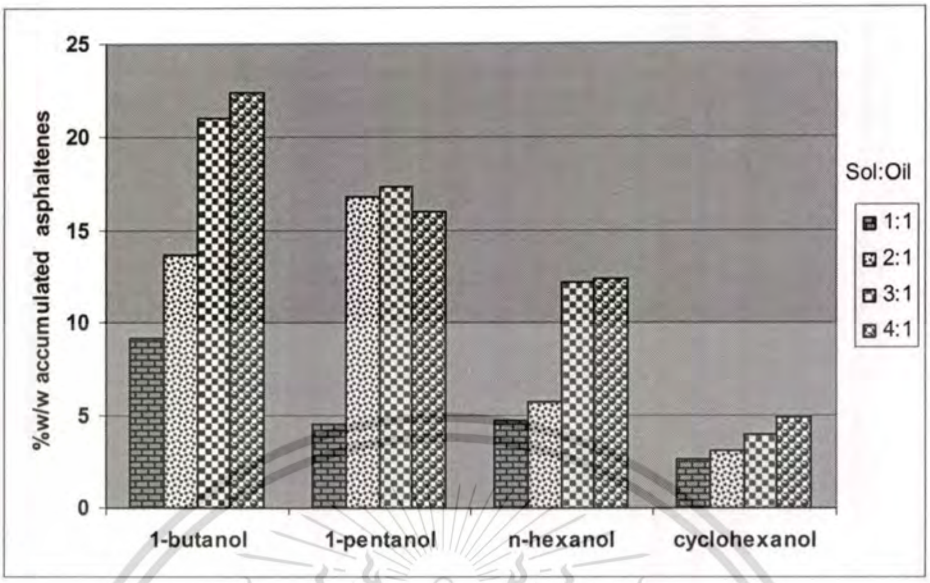


Figure 4.2 %w/w accumulated asphaltenes after 7 days using various types of alcohols as solvent at 70°C

4.2 Effects of Solvent-to-Oil Ratio

The effects of solvent-to-oil ratios were studied by changing the ratios from 1:1, 2:1, 3:1 to 4:1. The experiments were carried out both at room temperature and at 70°C. The amounts of accumulated asphaltenes after 7 days of extraction using each solvent at room temperature and at 70°C are reported in Tables 4.3 and 4.4, respectively.

Table 4.3 %w/w accumulated asphaltenes after 7 days by varied solvent-to-oil ratio at room temperature

Solvents to oil ratio	**Solvent types**			
	1-butanol	**1-pentanol**	***n*-hexanol**	**cyclohexanol**
1:1	3.01	3.44	0.80	0.73
2:1	9.33	10.98	1.13	1.00
3:1	13.08	12.84	1.58	1.34
4:1	17.35	8.75	3.51	2.09

The above data is graphically displayed for comparing the varied solvent-to-oil ratios with various solvent types at room temperature. The results are shown in Figure 4.3.

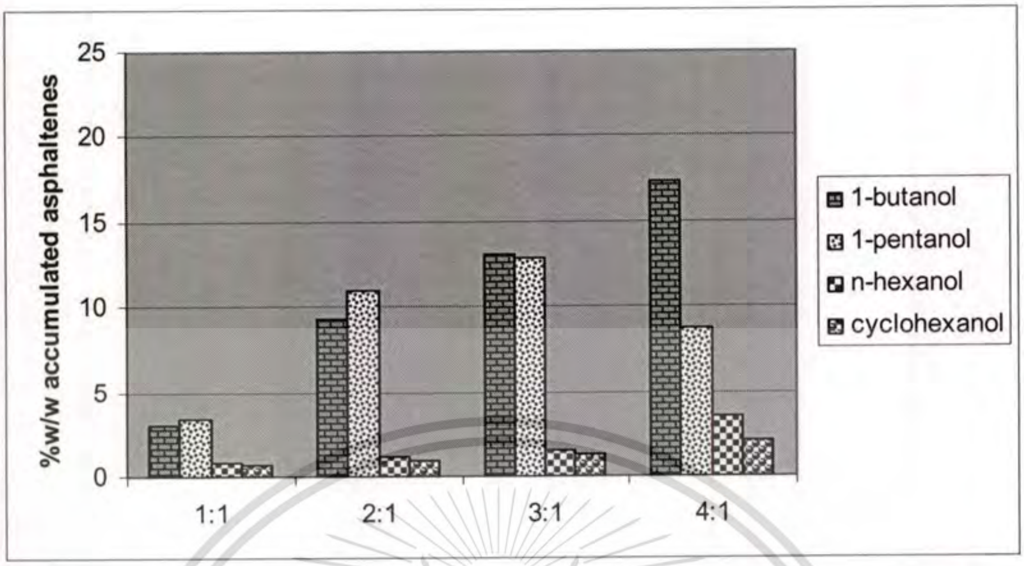


Figure 4.3 %w/w accumulated asphaltenes after 7 days using varied solvent-to-oil ratios with various types of alcohol as solvent at room temperature.

At room temperature, an appropriate solvent-to-oil ratio which gave the highest amount of accumulated asphaltenes was 4:1. The result was similar to that reported by Ahmad Hamada, Essam Al-Zubaidya and Muhammad E. Fayed [2].

By comparing the solubility of 1-butanol and 1-pentanol, they are quite similar. However, at a solvent-to-oil ratio of 4:1, 1-pentanol showed better solubility toward asphaltenes, and less de-asphalted oil was obtained. This is probably because 1-pentanol, with lower polarity, tends to separately form a phase with asphaltene than to interact with lighter hydrocarbons at high solvent-to-oil ratios. As a consequence, 4:1 solvent-to-oil ratio gave the lowest quantity of de-asphalted oil but with the highest quality. Thus, it can be concluded that 1-butanol with 4:1 solvent-to-oil ratio is by far the most selective system for asphaltenes removal using one extraction. On the other hand, using 1-pentanol, 1:1 solvent-to-oil ratio would probably give a better performance over that of 4:1 solvent-to-oil ratio if more than one extraction is carried out.

Table 4.4 %w/w accumulated asphaltenes after 7 days by varied solvent-to-oil ratio at 70ºC

Solvents to oil ratio	**Solvent types**			
	1-butanol	**1-pentanol**	***n*-hexanol**	**cyclohexanol**
1:1	9.21	4.55	4.75	2.68
2:1	13.67	16.81	5.74	3.10
3:1	20.99	17.38	12.26	4.01
4:1	22.39	15.97	12.39	4.94

Using the data from Table 4.4, the results can be illustrated to compare the effect of varied solvent-to-oil ratios at 70℃ and shown in Figure 4.4.

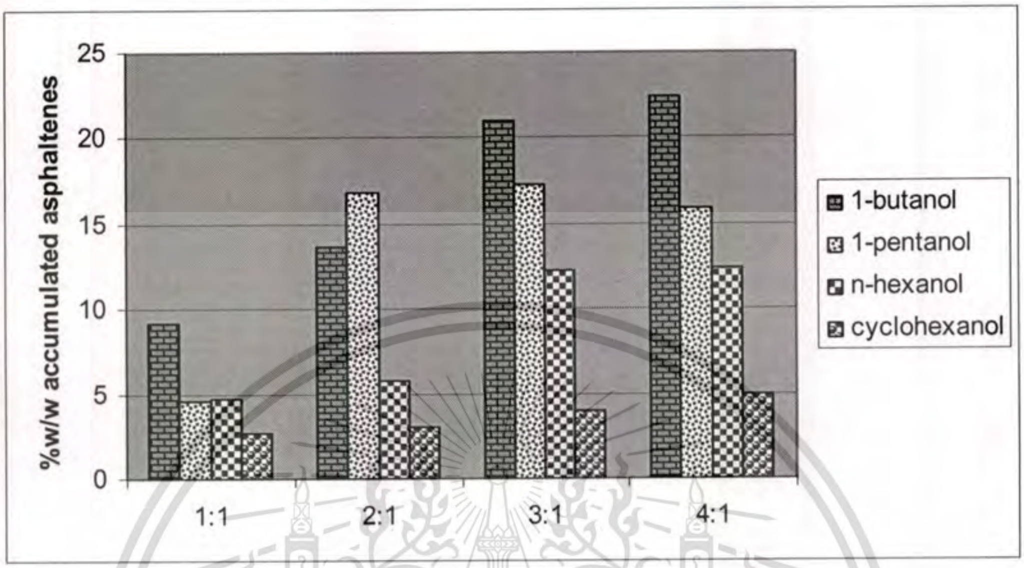


Figure 4.4 %w/w accumulated asphaltenes after 7 days using varied solvent-to-oil ratios with various types of alcohol as solvent at 70°C.

At 70°C, the similar results as that at room temperature were obtained. Again, 4:1 solvent-to-oil ratio gave the highest yield of asphaltenes followed by 3:1, 2:1, and 1:1, respectively. 1-butanol was also the most efficient one compared to the others.

4.3 Effects of Temperature

The extraction was attempted at room temperature and at 70°C. Tables 4.5–4.8 show %w/w accumulated asphatlenes removed at both temperatures after 7 days with various alcohols as solvent using varied solvent-to-oil ratios.

Table 4.5 %w/w accumulated asphatlenes after 7 days at room temperature and 70°C using 1:1 solvent-to-oil ratio

Solvents	**%w/w accumulated asphaltenes with 1:1 solvent to oil ratio**	
	Room temperature	**70 °C**
1-butanol	3.01	9.21
1-pentanol	3.44	4.55
n-hexanol	0.80	4.75
cyclohexanol	0.73	2.68

Table 4.6 %w/w accumulated asphaltenes after 7 days at room temperature and 70°C using 2:1 solvent-to-oil ratio

Solvents	**%w/w accumulated asphaltenes with 2:1 solvent to oil ratio**	
	Room temperature	**70 °C**
1-butanol	9.33	13.67
1-pentanol	10.98	16.81
n-hexanol	1.13	5.74
cyclohexanol	1.00	3.10

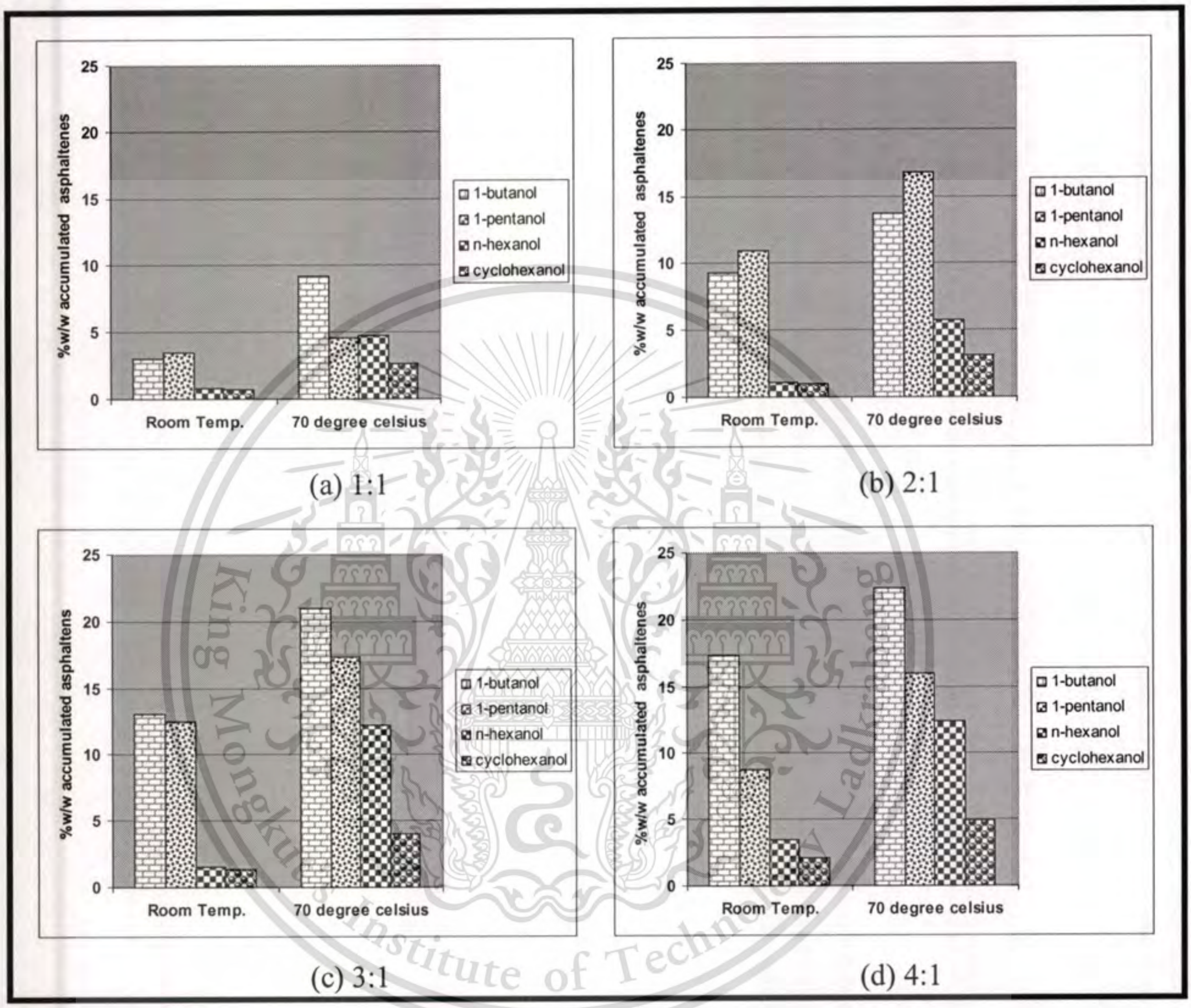
Table 4.7 %w/w accumulated asphaltenes after 7 days at room temperature and 70°C using 3:1 solvent-to-oil ratio

Solvents	**%w/w accumulated asphaltenes with 3:1 solvent to oil raio**	
	Room temperature	**70 °C**
1-butanol	13.08	20.99
1-pentanol	12.48	17.38
n-hexanol	1.58	12.26
cyclohexanol	1.34	4.94

Table 4.8 %w/w accumulated asphaltenes after 7 days at room temperature and 70°C using 4:1 solvent-to-oil ratio

Solvents	**%w/w accumulated asphaltenes with 4:1 solvent to oil ratio**	
	Room temperature	**70 °C**
1-butanol	17.35	22.39
1-pentanol	8.75	15.97
n-hexanol	3.51	12.39
cyclohexanol	2.09	4.94

The impact from temperature differences which affects the extraction results is displayed in Figure 4.5.



(a) 1:1

(b) 2:1

(c) 3:1

(d) 4:1

Figure 4.5 %w/w accumulated asphaltenes after 7 days at room temperature and at 70 °C with various solvents using varied solvent-to-oil ratios; (a) 1:1, (b) 2:1, (c) 3:1 and (d) 4:1

From the results, it can be depicted that %w/w asphaltenes removed at 70 °C was higher than at room temperature. The result was similar to that reported by P.K.Wong, J. Wang [15]. As the solvent tended to eject more of the higher molecular hydrocarbons at higher temperatures than at room temperature, so the asphaltenes was almost extracted out at 70 °C. Accordingly, increasing in temperature affects the solubility of heavy hydrocarbons to decrease [7].

4.4 Effects of Time

The settling time to examine the asphaltenes precipitated with various alcohols as solvent at various solvent-to-oil ratios at both room temperature and 70 °C was 7 days. The precipitated asphaltenes was determined everyday. The data is presented in Tables 4.9 to 4.16.

Table 4.9 %w/w accumulated asphaltenes at room temperature with various alcohols as solvents at 1:1 solvent-to-oil ratio

Days	1-butanol	1-pentanol	*n*-hexanol	cyclohexanol
1	1.81	2.67	0.80	0.73
2	3.01	3.44	0.80	0.73
3	3.01	3.44	0.80	0.73
4	3.01	3.44	0.80	0.73
5	3.01	3.44	0.80	0.73
6	3.01	3.44	0.80	0.73
7	3.01	3.44	0.80	0.73

Table 4.10 %w/w accumulated asphaltenes at 70°C with various alcohols as solvents at 1:1 solvent-to-oil ratio

Days	1-butanol	1-pentanol	*n*-hexanol	cyclohexanol
1	7.16	3.01	4.75	2.68
2	9.21	4.55	4.75	2.68
3	9.21	4.55	4.75	2.68
4	9.21	4.55	4.75	2.68
5	9.21	4.55	4.75	2.68
6	9.21	4.55	4.75	2.68
7	9.21	4.55	4.75	2.68

From the Tables 4.9 and 4.10, the settling time as comparable to the observed temperatures (room temperature and 70°C) for 1:1 solvent-to-oil ratio is shown in Figure 4.6.

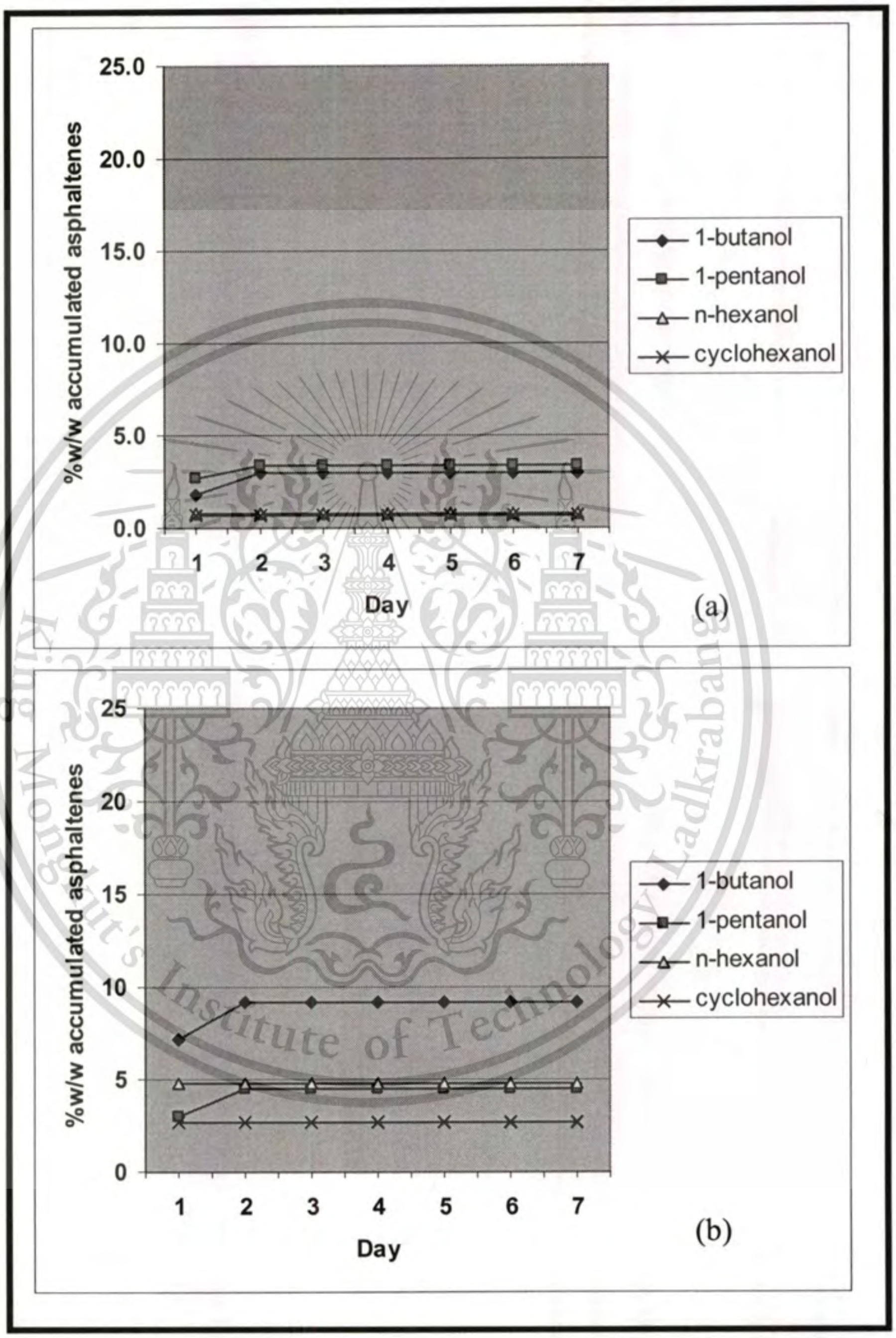


Figure 4.6 The settling times using 1:1 solvent-to-oil ratio at (a) room temperature and (b) 70°C

Table 4.11 %w/w accumulated asphaltenes at room temperature with various alcohols as solvents at 2:1 solvent-to-oil ratio

Days	1-butanol	1-pentanol	*n*-hexanol	cyclohexanol
1	7.56	10.12	1.13	1.00
2	8.75	10.98	1.13	1.00
3	9.33	10.98	1.13	1.00
4	9.33	10.98	1.13	1.00
5	9.33	10.98	1.13	1.00
6	9.33	10.98	1.13	1.00
7	9.33	10.98	1.13	1.00

Table 4.12 %w/w accumulated asphaltenes at 70°C with various alcohols as solvents at 2:1 solvent-to-oil ratio

Days	1-butanol	1-pentanol	*n*-hexanol	cyclohexanol
1	7.84	12.22	5.74	3.10
2	9.72	13.23	5.74	3.10
3	11.68	15.47	5.74	3.10
4	12.78	16.81	5.74	3.10
5	13.67	16.81	5.74	3.10
6	13.67	16.81	5.74	3.10
7	13.67	16.81	5.74	3.10

From the Tables 4.11 and 4.12, the settling time as comparable to the observed temperatures (room temperature and 70°C) for 2:1 solvent-to-oil ratio is shown in Figure 4.7.

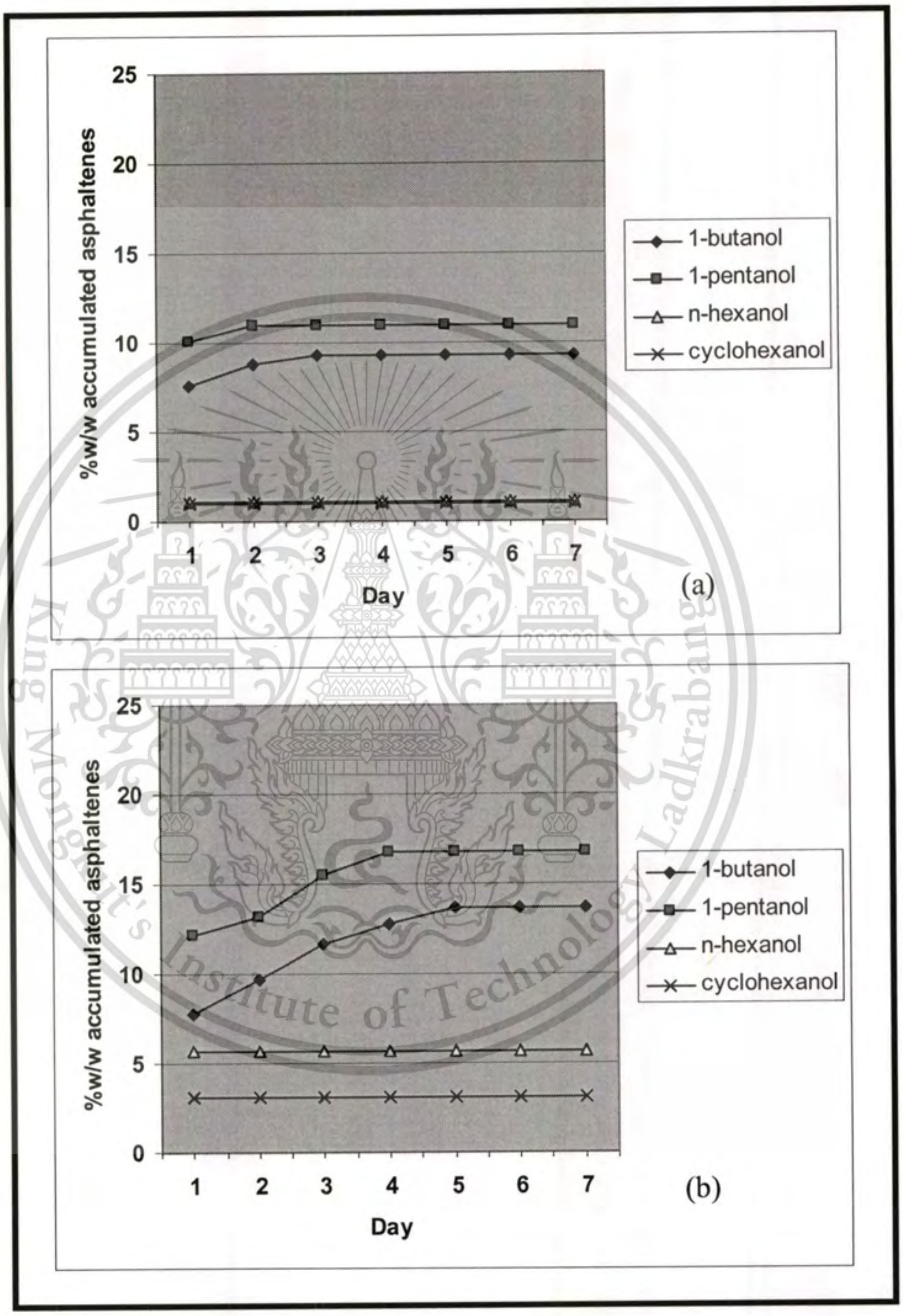


Figure 4.7 The settling times using 2:1 solvent-to-oil ratio at (a) room temperature and (b) 70°C

Table 4.13 %w/w accumulated asphaltenes at room temperature with various alcohols as solvents at 3:1 solvent-to-oil ratio

Days	**1-butanol**	**1-pentanol**	***n*-hexanol**	**cyclohexanol**
1	11.38	11.83	1.58	1.34
2	12.31	12.48	1.58	1.34
3	13.08	12.48	1.58	1.34
4	13.08	12.48	1.58	1.34
5	13.08	12.48	1.58	1.34
6	13.08	12.48	1.58	1.34
7	13.08	12.48	1.58	1.34

Table 4.14 %w/w accumulated asphaltenes at 70°C temperature with various alcohols as solvents at 3:1 solvent-to-oil ratio

Days	**1-butanol**	**1-pentanol**	***n*-hexanol**	**cyclohexanol**
1	10.70	13.13	12.26	4.01
2	13.30	14.52	12.26	4.01
3	16.21	15.92	12.26	4.01
4	19.60	17.38	12.26	4.01
5	20.99	17.38	12.26	4.01
6	20.99	17.38	12.26	4.01
7	20.99	17.38	12.26	4.01

From the Tables 4.13 and 4.14, the settling time as comparable to the observed temperatures (room temperature and 70°C) for 3:1 solvent-to-oil ratio is shown in Figure 4.8.

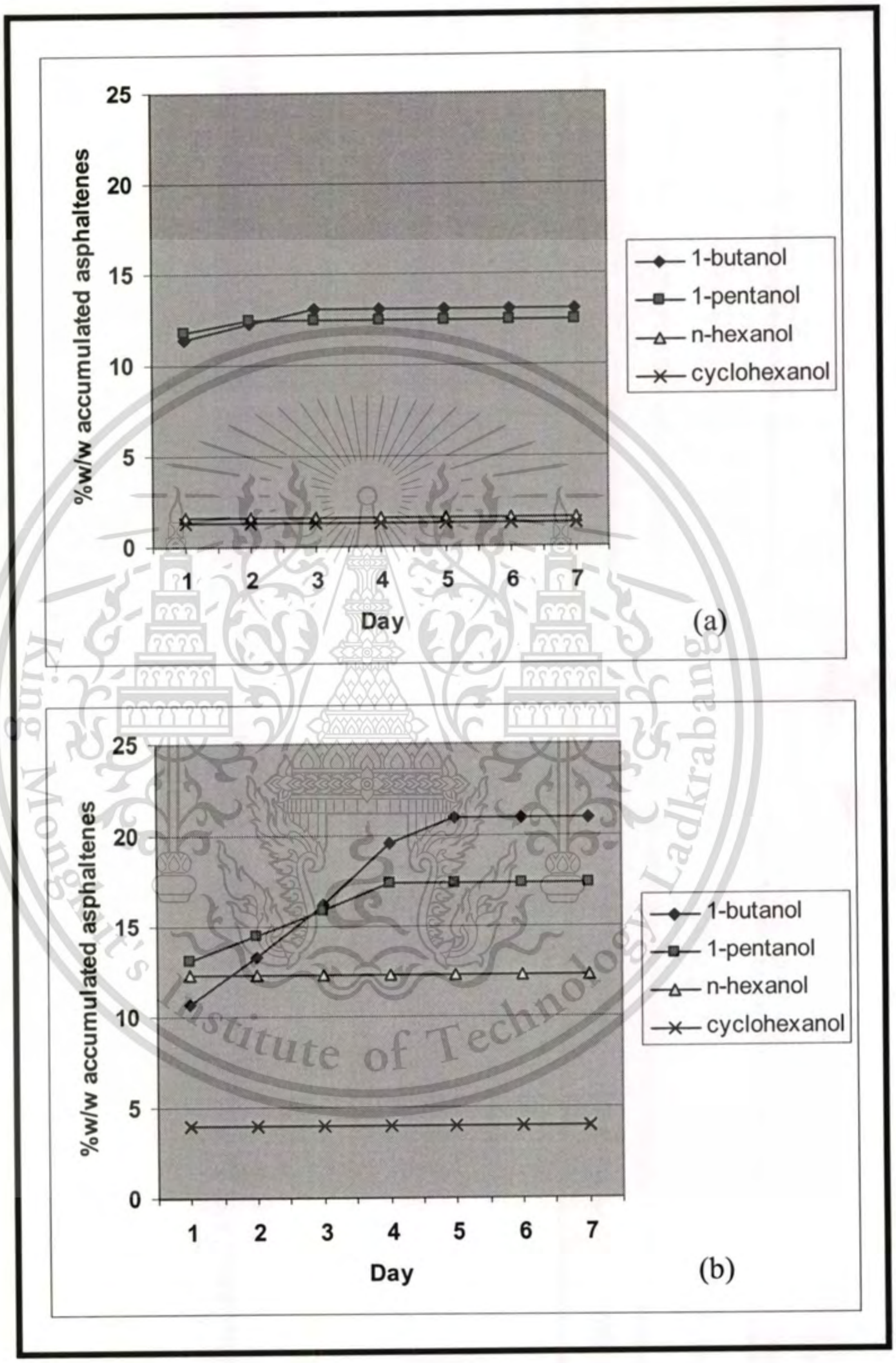


Figure 4.8 The settling times using 3:1 solvent-to-oil ratio at (a) room temperature and (b) 70°C

Table 4.15 %w/w accumulated asphaltenes at room temperature with various alcohols as solvents at 4:1 solvent-to-oil ratio

Days	**1-butanol**	**1-pentanol**	***n*-hexanol**	**cyclohexanol**
1	16.30	8.27	3.51	2.09
2	16.75	8.75	3.51	2.09
3	17.35	8.75	3.51	2.09
4	17.35	8.75	3.51	2.09
5	17.35	8.75	3.51	2.09
6	17.35	8.75	3.51	2.09
7	17.35	8.75	3.51	2.09

Table 4.16 %w/w accumulated asphaltenes at 70°C temperature with various alcohols as solvents at 4:1 solvent-to-oil ratio

Days	**1-butanol**	**1-pentanol**	***n*-hexanol**	**cyclohexanol**
1	15.40	11.82	12.39	4.94
2	16.61	12.90	12.39	4.94
3	18.97	15.34	12.39	4.94
4	20.16	15.97	12.39	4.94
5	22.39	15.97	12.39	4.94
6	22.39	15.97	12.39	4.94
7	22.39	15.97	12.39	4.94

From the Tables 4.15 and 4.16, the settling time as comparable to the observed temperatures (room temperature and 70°C) for 4:1 solvent-to-oil ratio is shown in Figure 4.9.

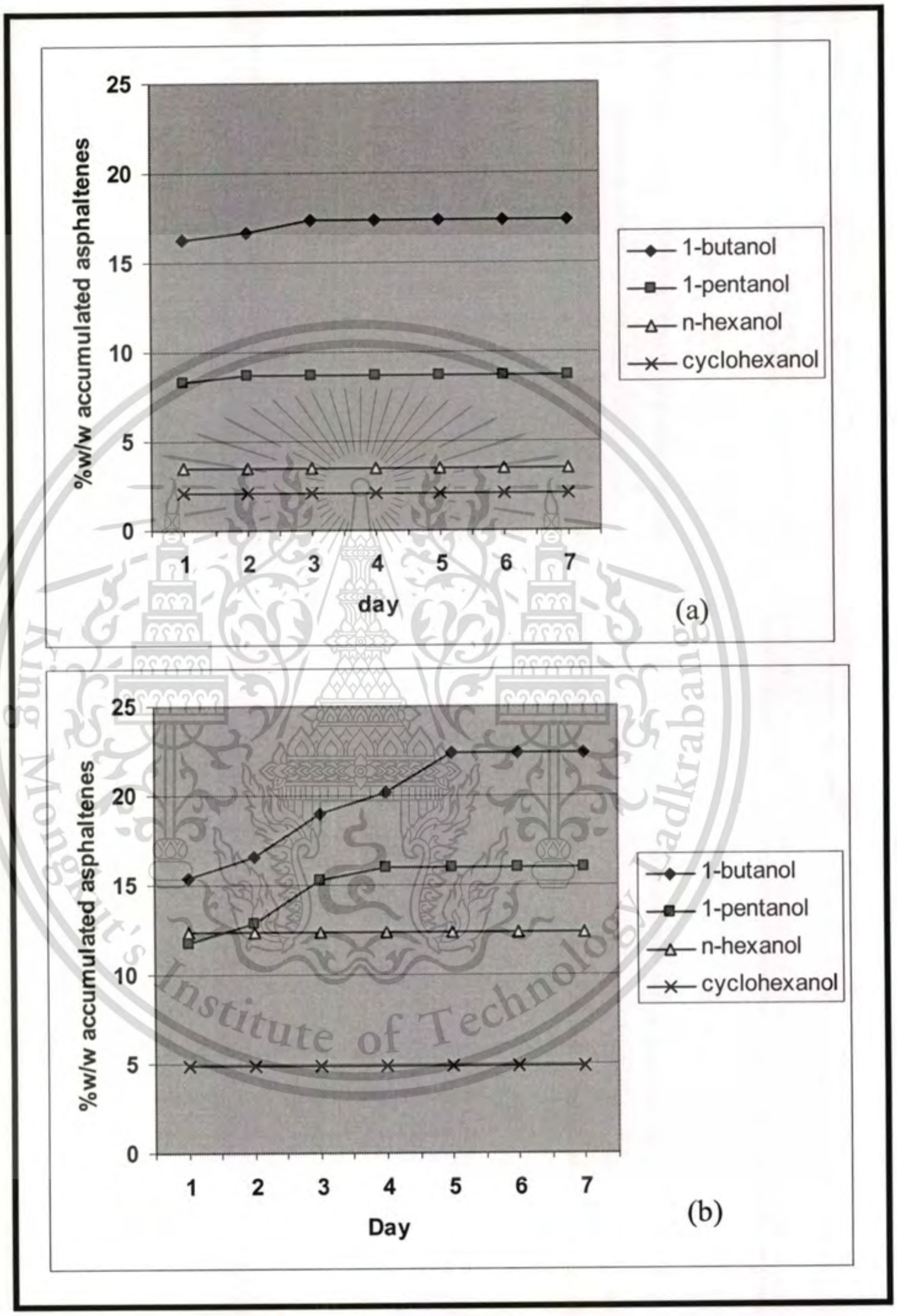


Figure 4.9 The settling times using 4:1 solvent-to-oil ratio at (a) room temperature and (b) 70°C

The proper time which gave the best result was three days at room temperature, and five days at 70°C. The result was similar to that reported by Ahmad Hamada, Essam Al-Zubaidya and Muhammad E.Fayed [2]. The time for settling was shown to be dependent on the temperature. At high temperature, the time used for settling the asphaltenes is longer than the asphaltenes at room temperature. This is because some types of asphaltenes that normally can not precipitate out at room temperature can precipitate at 70°C. As a result, the higher amount of asphaltenes can be accumulated at 70°C.

4.5 Determination of Percent Ash Content

The results from the examination of percent ash content of de-asphalted oil extracted with various alcohols as solvent using varied solvent-to-oil ratios at room temperature and 70°C were shown in Tables 4.17 and 4.18.

Table 4.17 % Ash content of de-asphalted oil at room temperature

Solvent-to-Oil Ratio	% Ash Content			
	1-butanol	1-pentanol	*n*-hexanol	cyclohexanol
1:1	1.249	1.255	1.288	1.300
2:1	1.074	1.406	1.226	1.284
3:1	0.945	0.948	1.139	1.283
4:1	0.726	0.806	1.021	1.278

Table 4.18 % Ash content of de-asphalted oil at 70°C

Solvent-to-Oil Ratio	% Ash Content			
	1-butanol	1-pentanol	*n*-hexanol	cyclohexanol
1:1	1.134	1.139	1.183	1.285
2:1	0.994	1.055	1.147	1.276
3:1	0.734	0.899	1.130	1.280
4:1	0.502	0.693	0.918	1.277

The %Ash content of used lube oil was 1.3953%

Comparison of percent ash content in asphaltenes extracted by various types of alcohols using varied solvent-to-oil ratios at room temperature and 70°C after 7 days are also illustrated in Figure 4.10. The lowest amount of %ash contents was obtained by using 1-butanol as solvent at 4:1 solvent-to-oil ratio which operating at 70°C. This was according to the less solubility of solvent towards accumulated asphaltenes at higher temperature and its higher polarity characteristic over the other alcohols which affected the higher ability to eliminate the metal contents obtained in the oil fraction. As a consequence, % ash contents of used lubricating oil after extraction processes were certainly decreased.

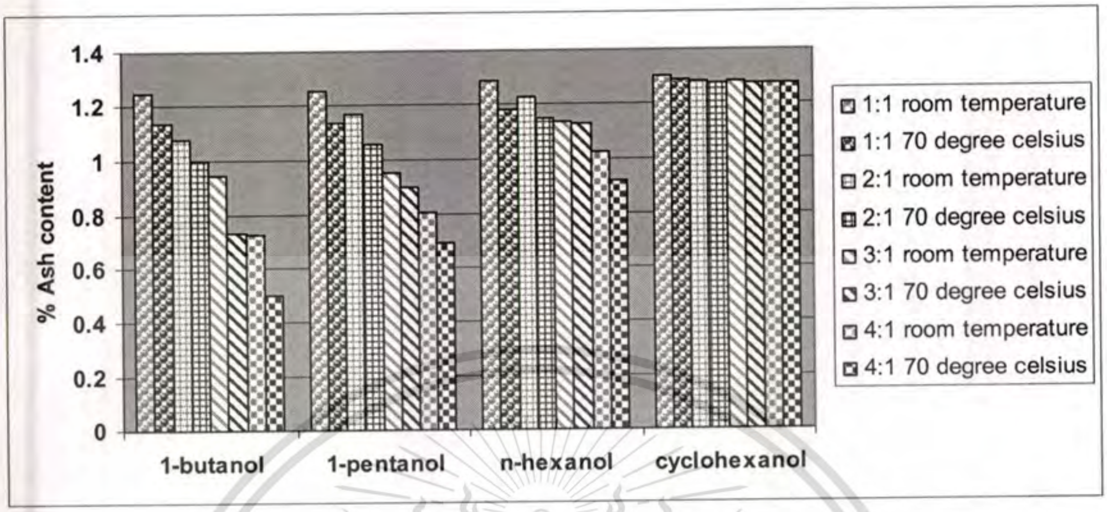


Figure 4.10 % Ash content of de-asphalted oils

4.6 Determination of Density

The scrutiny of de-asphalted oil's density which was extracted from used lubricating oil by using various types of alcohol as solvents with varied solvent-to-oil ratios in both observed temperatures (room temperature and 70°C) after 7 days are shown in Tables 4.19 to 4.20.

Table 4.19 Density of de-asphalted oil at room temperature

Solvent-to-Oil Ratio	**Density of de-asphalted oil (g/ml)**			
	1-butanol	**1-pentanol**	***n*-hexanol**	**cyclohexanol**
1:1	0.7671	0.7799	0.8111	0.8179
2:1	0.7569	0.7694	0.7739	0.7880
3:1	0.7503	0.7533	0.7612	0.7721
4:1	0.7385	0.7432	0.7451	0.7688

Table 4.20 Density of de-asphalted oil at 70°C

Solvent-to-Oil Ratio	Density of de-asphalted oil (g/ml)			
	1-butanol	**1-pentanol**	***n*-hexanol**	**cyclohexanol**
1:1	0.6888	0.7388	0.7480	0.7887
2:1	0.6760	0.7017	0.7067	0.7832
3:1	0.6357	0.6539	0.6886	0.7174
4:1	0.6185	0.6329	0.6704	0.6949

The results from the determination of density were illustrated to see the effect of types of alcohol using varied solvent-to-oil ratios at both temperatures after 7 days, as shown in Figure 4.11.

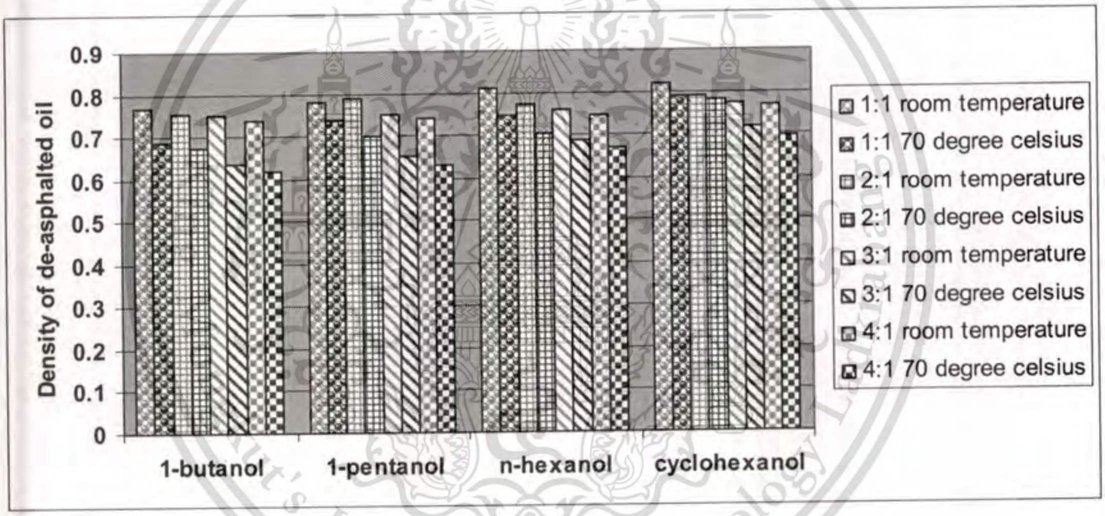


Figure 4.11 Density of de-asphalted oil

The density of used lube oil was 0.8302 g/ml

The experiment showed that the lowest density of de-asphalted oil was upshot with 1-butanol using 4:1 solvent-to-oil ratio at 70°C. The trend declined with the change of types of solvent to 1-pentanol, *n*-hexanol and cyclohexanol, and of solvent-to-oil ratio to 3:1, 2:1, and 4:1, respectively. As a consequence, the proficiency of solvents used with an appropriate solvent-to-oil ratio and correct operating temperature will cause the better selectivity toward the removal of asphaltenes. The highest quality of de-asphalted oil would have the lowest amount of percent ash contents.

Chapter V
Conclusions and Suggestion

5.1 Conclusions

This special project studied the effect of types of alcohol, the effects of solvent-to-oil ratio, the effects of temperature and times for the extraction of oil from used lubricating oil. Experiment was divided into two parts, at room temperature and at 70°C. It was found that:

1. 1-butanol gave the best performance. The highest amount of settling asphaltenes was obtained with de-asphalted oil of the best quality. The worst alcohol was cyclohexanol. Even though it gave the highest amount of oil but with the lowest quality. This was due to its structure and polarity which were more compatible with the asphaltenes.

2. The most suitable solvent-to-oil ratio operating on both observed temperatures was 4:1. The amount of accumulated asphaltenes was declined by using the ratio of 3:1, 2:1 and 1:1, respectively. According to the results, the difference in solubility of the oil in solvents, the polarity of the solvents, and the number of extraction are the keys to the explanation.

3. Temperatures that were used in this work are room temperature and 70°C. The prefered temperature was the higher temperature (70°C) because the solubility of asphaltenes decreased when temperature increased.

4. The suitable time for asphaltene accumulation was five days at 70°C and three days at room temperature. This was due to the more quantity of asphaltenes that was capable of being precipitated at high temperature.

5.2 Suggestion for Future Works

1. Use of other types of solvent; for example; esters, which have a similar polarity could be attempted.

2. Operating temperature could be changed to the boiling point of solvents for gaining the best quality of de-asphalted oil.

3. The solvent to oil ratio can be optimized to a more narrow ratio.

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APPENDIX A

Experimental Datas

Table 1 Weight used oil at room temperature

Solvents	Weight of used oil (g)							
	1st times				2nd times			
	1:1	2:1	3:1	4:1	1:1	2:1	3:1	4:1
1-butanol	14.7113	14.8461	14.9763	15.0771	14.3860	14.1860	15.2910	14.4450
1-pentanol	14.8712	14.0073	14.9316	14.7112	14.5500	14.4120	14.5360	14.7819
n-hexanol	14.7932	14.1238	14.6531	14.6531	15.0638	14.6382	15.1142	14.8632
cyclohexanol	14.2441	15.0123	14.7132	14.8113	15.1062	14.7113	14.1960	14.7135

Table 2 Weight used oil at 70°C

Solvents	Weight of used oil (g)							
	1st times				2nd times			
	1:1	2:1	3:1	4:1	1:1	2:1	3:1	4:1
1-butanol	15.7123	14.7513	14.1662	15.0118	15.8670	14.6440	14.4870	15.6220
1-pentanol	14.6112	14.8712	14.1073	14.9769	14.3780	14.5090	14.4320	14.7100
n-hexanol	14.9712	14.9981	14.6973	14.6835	14.1872	14.6932	14.7312	15.0872
cyclohexanol	14.8663	14.6536	14.6112	15.0038	15.0861	14.7631	14.6936	14.6998

Table 3 Weight of residues 1:1 at room temperature

Day	Weight of residues (g)							
	1-butanol		**1-pentanol**		***n*-hexanol**		**cyclohexanol**	
	1st times	2nd times	1st times	2nd times	1st times	2nd times	1st times	2nd times
1	0.2748	0.2516	0.4034	0.3829	0.1120	0.1204	0.1060	0.1075
2	0.2842	0.0690	0.1352	0.0921	0.0000	0.0000	0.0000	0.0000
3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4 Weight of residues 1:1 at 70°C

Day	Weight of residues (g)							
	1-butanol		**1-pentanol**		***n*-hexanol**		**cyclohexanol**	
	1st times	2nd times	1st times	2nd times	1st times	2nd times	1st times	2nd times
1	1.1620	1.0905	0.4674	0.4061	0.7051	0.7042	0.3882	0.4140
2	0.3284	0.1587	0.2194	0.2260	0.0000	0.0000	0.0000	0.0000
3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 5 Weight of residues 2:1 at room temperature

Day	Weight of residues (g)							
	1-butanol		**1-pentanol**		***n*-hexanol**		**cyclohexanol**	
	1st times	2nd times	1st times	2nd times	1st times	2nd times	1st times	2nd times
1	1.1429	1.0544	1.4651	1.4090	0.1552	0.1702	0.1420	0.1473
2	0.1838	0.1616	0.1315	0.1143	0.0000	0.0000	0.0000	0.0000
3	0.1003	0.0685	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 6 Weight of residues 2:1 at 70°C

Day	Weight of residues (g)							
	1-butanol		**1-pentanol**		***n*-hexanol**		**cyclohexanol**	
	1st times	2nd times	1st times	2nd times	1st times	2nd times	1st times	2nd times
1	1.1722	1.1324	1.9946	1.6017	0.8716	0.8344	0.4411	0.4712
2	0.3342	0.2202	0.1138	0.1615	0.0000	0.0000	0.0000	0.0000
3	0.3371	0.2387	0.4218	0.2369	0.0000	0.0000	0.0000	0.0000
4	0.0906	0.2303	0.0739	0.3176	0.0000	0.0000	0.0000	0.0000
5	0.2361	0.0268	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 7 Weight of residues 3:1 at room temperature

Day	Weight of residues (g)							
	1-butanol		**1-pentanol**		***n*-hexanol**		**cyclohexanol**	
	1st times	2nd times	1st times	2nd times	1st times	2nd times	1st times	2nd times
1	1.9441	1.4960	1.9433	1.5481	0.2415	0.2353	0.2091	0.1473
2	0.0050	0.2793	0.0747	0.1160	0.0000	0.0000	0.0000	0.0000
3	0.1519	0.0790	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 8 Weight of residues 3:1 at 70°C

Day	Weight of residues (g)							
	1-butanol		**1-pentanol**		***n*-hexanol**		**cyclohexanol**	
	1st times	2nd times	1st times	2nd times	1st times	2nd times	1st times	2nd times
1	1.6148	1.4499	2.0594	1.6843	1.7812	1.8276	0.5891	0.5860
2	0.3940	0.1449	0.1580	0.0011	0.0000	0.0000	0.0000	0.0000
3	0.4489	0.3836	0.1824	0.2191	0.0000	0.0000	0.0000	0.0000
4	0.4007	0.5712	0.2098	0.2039	0.0000	0.0000	0.0000	0.0000
5	0.3148	0.0820	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 9 Weight of residues 4:1 at room temperature

Day	**Weight of residues (g)**							
	1-butanol		**1-pentanol**		***n*-hexanol**		**cyclohexanol**	
	1^{st} times	2^{nd} times	1^{st} times	2^{nd} times	1^{st} times	2^{nd} times	1^{st} times	2^{nd} times
1	2.6252	2.1948	1.2639	1.1744	0.5000	0.5364	0.3130	0.3037
2	0.0634	0.0674	0.1074	0.0342	0.0000	0.0000	0.0000	0.0000
3	0.0723	0.1065	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 10 Weight of residues 4:1 at 70°C

Day	**Weight of residues (g)**							
	1-butanol		**1-pentanol**		***n*-hexanol**		**cyclohexanol**	
	1^{st} times	2^{nd} times	1^{st} times	2^{nd} times	1^{st} times	2^{nd} times	1^{st} times	2^{nd} times
1	2.3691	2.3449	1.7411	1.6966	1.8261	1.8624	0.8121	0.6581
2	0.2570	0.1118	0.2100	0.1106	0.0000	0.0000	0.0000	0.0000
3	0.2883	0.4393	0.1438	0.3513	0.0000	0.0000	0.0000	0.0000
4	0.2398	0.1120	0.0070	0.1127	0.0000	0.0000	0.0000	0.0000
5	0.3753	0.3089	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 11 Ash content of used oil

1st times		2nd times	
Weight oil (g)	**Weight ash (g)**	**Weight oil (g)**	**Weight ash (g)**
2.0081	0.0262	2.3016	0.0342

Table 12 Ash content of extracted oil at room temperature; W_O = weight of extracted oil, W_A = weight of ash

Ratios	**1-butanol**				**1-pentanol**				***n*-hexanol**				**cyclohexanol**			
	1st times		**2nd times**		**1st times**		**2nd times**		**1st times**		**2nd times**		**1st times**		**2nd times**	
	W_O	W_A	W_O	W_A	W_O	W_A	W_O	W_A	W_O	W_A	W_O	W_A	W_O	W_A	W_O	W_A
1:1	2.0067	0.0250	2.0319	0.0254	2.0367	0.0256	2.0457	0.0257	2.0834	0.0268	2.0967	0.0270	2.0476	0.0266	2.0312	0.0264
2:1	2.0783	0.0218	2.0030	0.0221	2.0967	0.0246	2.1074	0.0245	2.0915	0.0253	2.0035	0.0249	2.2001	0.0279	2.0186	0.0262
3:1	2.0134	0.0168	2.0170	0.0213	2.0978	0.0189	2.0147	0.0200	2.0456	0.0226	2.0070	0.0236	2.1098	0.0270	2.0185	0.0259
4:1	2.0080	0.0143	2.0040	0.0149	2.1084	0.0171	2.0567	0.0165	2.1587	0.0205	2.0617	0.0226	2.0356	0.0260	2.0035	0.0257

Table 13 Ash content of extracted oil at 70°C; W_O = weight of extracted oil, W_A = weight of ash

Ratios	1-butanol				1-pentanol				*n*-hexanol				cyclohexanol			
	1st times		2nd times		1st times		2nd times		1st times		2nd times		1st times		2nd times	
	W_O	W_A	W_O	W_A	W_O	W_A	W_O	W_A	W_O	W_A	W_O	W_A	W_O	W_A	W_O	W_A
1:1	2.0661	0.0234	2.0938	0.0238	2.0678	0.0235	2.1009	0.0240	2.0989	0.0252	2.1209	0.0248	2.0546	0.0262	2.1875	0.0283
2:1	2.0669	0.0204	2.0112	0.0201	2.0014	0.0212	2.0835	0.0218	2.0014	0.0230	2.0147	0.0231	2.0878	0.0264	2.0987	0.0270
3:1	2.0137	0.0128	2.0038	0.0167	2.0367	0.0183	2.0018	0.0232	2.0184	0.0223	2.0165	0.0233	2.0142	0.0258	2.6587	0.0340
4:1	2.0167	0.0099	2.0154	0.0103	2.0689	0.0139	2.0665	0.0193	2.0361	0.0184	2.1054	0.0196	2.2009	0.0280	2.0356	0.0260

Table 14 Density of used oil

1st times		2nd times	
Mass (g)	Volume (g)	Mass (g)	Volume (g)
4.1523	5.00	4.1489	5.00

Table 15 Density of extracted oil at room temperature; M = mass (g), V = volume (ml)

Ratios	1-butanol				1-pentanol				*n*-hexanol				cyclohexanol			
	1st times		2nd times		1st times		2nd times		1st times		2nd times		1st times		2nd times	
	M	V	M	V	M	V	M	V	M	V	M	V	M	V	M	V
1:1	1.5388	2.00	1.5298	2.00	1.5714	2.00	1.5482	2.00	1.6246	2.00	1.6198	2.00	1.6500	2.00	1.6218	2.00
2:1	1.5092	2.00	1.5186	2.00	1.5382	2.00	1.5396	2.00	1.5572	2.00	1.5386	2.00	1.5858	2.00	1.5662	2.00
3:1	1.4870	2.00	1.4942	2.00	1.5168	2.00	1.4966	2.00	1.5386	2.00	1.5064	2.00	1.5682	2.00	1.5202	2.00
4:1	1.4764	2.00	1.4778	2.00	1.4936	2.00	1.4792	2.00	1.4974	2.00	1.4842	2.00	1.5278	2.00	1.5464	2.00

Table 16 Density of extracted oil at 70°C; M = mass (g), V = volume (ml)

Ratios	1-butanol				1-pentanol				*n*-hexanol				cyclohexanol			
	1st times		2nd times		1st times		2nd times		1st times		2nd times		1st times		2nd times	
	M	V	M	V	M	V	M	V	M	V	M	V	M	V	M	V
1:1	1.3742	2.00	1.3812	2.00	1.4278	2.00	1.5274	2.00	1.5138	2.00	1.4824	2.00	1.5862	2.00	1.5686	2.00
2:1	1.3378	2.00	1.3664	2.00	1.4064	2.00	1.4004	2.00	1.4392	2.00	1.3876	2.00	1.5664	2.00	1.5662	2.00
3:1	1.2628	2.00	1.2802	2.00	1.3162	2.00	1.2996	2.00	1.3878	2.00	1.3664	2.00	1.4268	2.00	1.4428	2.00
4:1	1.2232	2.00	1.2476	2.00	1.2654	2.00	1.2662	2.00	1.3426	2.00	1.3390	2.00	1.3996	2.00	1.3798	2.00

APPENDIX B

Properties of solvents

Table 1 Physical properties of 1-butanol

Properties	
Appearance	Colourless liquid
Melting point	-89 °C
Boiling point	118 °C
Vapour density	2.6 (air = 1)
Vapour pressure	4 mm Hg at 20 °C
Specific gravity	0.81
Flash point	35 °C

Table 2 Physical properties of 1-pentanol

Properties	
Appearance	colourless liquid
Melting point	-78 °C
Boiling point	136-138°C
Specific gravity	0.814
Density (g cm^3):	0.811
Flash point	49°C

Table 3 Physical properties of *n*-hexanol

Properties	
Appearance	Colourless liquid (odour recognition threshold 0.09ppm)
Melting point	-52 °C
Boiling point	156.5 °C
Specific gravity	0.814
Vapour pressure	55 mm Hg at 37 °C
Flash point	140°C

Table 4 Physical Properties of cyclohexanol

Properties	
Appearance	colourless liquid
Melting point	20-22 °C
Boiling point	160-161 °C
Vapour density	3.5 g/l
Vapour pressure	0.98 mm Hg at 25 °C
Specific gravity	0.948
Flash point	67°C

Calculations

1. Calculate %w/w of accumulated asphaltenes

$$\%\text{w/w of accumulated asphaltenes} = \frac{\text{Weight of accumulated asphaltenes} \times 100}{\text{Weight of used oil}}$$

2. Calculate % ash content

$$\%\text{ ash content} = \frac{\text{Weight of ash} \times 100}{\text{Weight of oil}}$$

3. Calculate Density (D)

$$\text{Density (D)} = \frac{\text{Mass (g)}}{\text{Volume (ml)}}$$