REGENERATION OF USED PETROLEUM-BASED LUBRICANTS AND BIOLUBRICANTS BY A NOVEL GREEN AND SUSTAINABLE TECHNOLOGY

by

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DEDICATION

I dedicate this dissertation to the memory of my advisor, Professor Teh Fu Yen, and I wish to express my deepest gratitude for his guidance, support, encouragement, and patience.

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ABBREVIATIONS

CSEC System	Cold-Stage Energy Conversion System
NPG	Neopenthlglycol
PE	Pentaerythritol
S.M.	Solvent Mixture
TAG	Triacylglycerols
TMP	Trimethylol propane
U.L.	Used Lubricant
VI	Viscosity Index

ABSTRACT

Petroleum is an essential natural resource used as the source of energy and raw material for almost all industries. It is also a non-renewable resource and not easily accessible in most cases. Today, as the global petroleum reserves are becoming increasingly scarce due to the rapid industrialization, the price of petroleum and products used petroleum as base materials will inevitably escalate and negatively impact on our economy. Moreover, the environmental impacts associated with petroleum exploration have increasingly become critical issues of global concern. In order to conserve petroleum resource and reduce petroleum drilling, the regeneration of petroleum-based materials for beneficial reuse and the utilization of renewable resources as base materials to substitute petroleum are two necessary actions toward a sustainable earth.

Lubricants, either mineral-based or synthetic made, are the products derived from petroleum and developed through tribological research are essential elements for modern industries to perform not only for lubrication of moving parts in machines, engines, and vehicles; but also for many other functions, such as cooling, noise and vibration reduction, cleaning, corrosion protection, and power transfer.

However, lubricants require change after long service because the various impurities generated from the operation may degrade the efficiency of lubricants

and significantly contaminate lubricant. Each year over two billion gallons of used lubricants are generated around the world and expected to generate more due to worldwide increased demand in lubricants.

Many studies have confirmed that used petroleum-based lubricants collected from oil-change are slow in degradation and highly toxic to human health, fauna, and flora. Because the disposal of used lubricants is becoming a global concern, it is important to study the potential impacts of used lubricants on human health, animals, plants, and the environment in order to raise public awareness to proper handling in order to prevent them being released to the environment.

On the other hand, used lubricant also contains a significant amount of heating value. Hydrocarbon compounds in used lubricants can be regenerated into either lubricant base materials or an energy source. The regeneration of used lubricants has enormous benefits, including minimizing hazards, reducing waste, protecting the environment, conserving natural resources, and creating an energy source as the energy shortage is becoming a global problem.

The mission of this research is to (1) help the world to reduce used lubricants by regenerating them into an economically competitive energy resource through a sustainable technology and to (2) evaluate and promote the utilization of renewable source, such as plant oils, as green alternatives in lubricant applications. Both are essential to creating a sustainable earth as the ultimate goal of this research.

The binary solvent process, the binary system matrix, and the Cold-Stage Energy Conversion (CSEC) system are the newly developed technology and products during this four-year research endeavor. The engineering approach and the supporting concepts are presented along with the development of the process and products in this dissertation.

The potential of the binary solvent process in used lubricants purification and hydrocarbon compounds recovery is discussed and reviewed. It has been demonstrated to be a promising technology capable of removing up to 93% of impurities while recovering up to 99 % of hydrocarbon compounds from various types of used lubricants under atmospheric pressure and at a relatively low temperature. Moreover, environmental sustainability and economic feasibility are two significant designs in this process. All reagents used for this process can be recycled and reused indefinitely.

The binary system matrix is an analytical method designed to enhance the efficiency of the binary solvent process. CSEC system is built based on the concept of binary solvent process and capable of regenerating used lubricant in a continuous-flow fashion at relatively low temperature operated under atmospheric pressure. All these advantages lead to cost saving on less maintenance and easy to handle.

The benefits of new generation of lubricants made from the renewable resources is reviewed and discussed. This dissertation focus on the research of using plant oils as lubricant feedstock. The compositions of different plant oil are unique, many factors, such as climate, soil, and season, have played major contributing roles in the difference. Balancing the resources and the industrial use offers a major challenge in sustainable resource management. The adaptive management is becoming the key to achieving this balance. The adaptive management is becoming the key to achieving this balance. The use of animal fats or grease as lubricant base materials is no longer practical due to undesirable properties of most animal fats and the concern of society regarding animal welfare issues.

As the concern about the environment compatibility of petroleum-based lubricant is on the rise, lubricants made from plant oils are easily biodegradable; renewable and genetically changeable; less hazardous to human health, fauna, and flora; more stable with temperature change; and safer to use.

In the end, this dissertation presents the recommendations for the future improvements in CSEC system as well as the plans towards the future development of biodegradable lubricants derived from sources that do not compete with food sources, such as ocean phytoplankton or biomass waste.

CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 Research Background

The topics covered in this dissertation include green tribology, lubricant science and technology, environmental protection, energy source conservation and hazardous waste management by transforming used petroleum-based lubricants into an economically completive energy source, and overview of bio-based lubricants developed from renewable resources, such as plant oils.

Lubricant derived petroleum has played a significant role to improve efficiency as well as to reduce material loss for almost all industries throughout human history. According to 2009 Freedonia report, the worldwide consumption of lubricants is expected to increase 1.6 percent per year to 10.7 billion gallons in 2012. Only about two billion gallons of used lubricants are recycled around the world.

Many researches have confirmed that used petroleum-based lubricants collected from oil-exchange are slow in degradation, highly toxic to human health, fauna, and flora. The used petroleum-based lubricant risk assessment as well as the environmental impacts associated with used petroleum-based lubricants have been reviewed and discussed in the following chapters.

On the other hand, used petroleum-based lubricants are rich in hydrocarbon compounds, which can be regenerated by proper treatment technologies into lubricant base materials or economical energy sources after impurities are removed. Thus, the regeneration of used lubricants not only minimizes hazards and reduces waste, but also protects the environments as well as conserves energy and natural resources. However, many conventional technologies used today may create other environmental problems, such as inefficient use of energy and chemicals as well as the generation of harmful wastes during the process.

In order to make this practice truly practical and valuable, the system design must be environmentally sustainable and economically feasible. One of the major objectives of this research is to develop a green technology which is capable to convert used lubricants into an economically completive energy resource based on the principles of green tribology and sustainable design.

1.2 Research Objectives

In addition to the major objective as mentioned earlier, other objectives of this research are enumerated as follows:

- Assess human health and environmental impacts associated with used petroleum-based lubricants.

- Evaluate the conventional technologies currently used for the regeneration of used lubricants.
- Develop a new technology for the regeneration of used lubricants based on the principles of sustainable design.
- Design a reliable method to quantitate the impurities in used lubricant samples.
- Design a reliable method for quantification of hydrocarbon compounds in used lubricant samples.
- Design a reliable analytical method for the efficient use of reagents in the newly developed technology.
- Develop a new system based on the newly designed technology as well as the principles of sustainable design in a continuous-flow fashion.
- Promote the utilization of renewable resources which will ultimately reduce the consumption of petroleum and the problems associated with oil drilling; and encourage sustainability.

1.3 Research Approach

The supporting concepts and technologies for the design of a sustainable technology, such as green tribology and lubricant science, are introduced in the following chapters. The scientific approach used in this research consisted of following phases:

- **Phase 1- Identification of Role of Lubricants in Lubrication**

  Evaluate the role of lubricant through a review of literatures and documents in tribology as well as lubricant science and manufacturing technologies.

- **Phase 2 – Analysis of Used Lubricants**

  Identify the composition of used lubricants and the characteristics of its components by conducting a thorough literature review.

- **Phase 3 –Evaluation of the Existing Used Lubricant Regeneration Technologies.**

  Evaluate the existing used lubricant regeneration technologies by conducting a thorough literature review.

- **Phase 4 – Experimental Method Development**

  Establish criteria and procedures in the development of a new technology in energy conversion and regeneration of used lubricants. This phase also determines the reagents used in the newly developed technology based on the research in Phase1, 2, 3, and 4.

- **Phase 5 – Bench Testing and Data Analysis**

  Establish criteria and testing protocols for bench tests of the technology developed from Phase 4. Analyze the experimental data to confirm the feasibility and effectiveness of new technology.

- **Phase 6 –Sustainable System Design in a Continuous-Flow Fashion**

  Establish a systematic process of designing study to develop a system in a continuous-flow fashion based on the results and research from the previous phases and the principles of sustainable design. Confirm the feasibility and effectiveness of new system.

- **Phase 7 –Evaluation of Bio-Based Lubricants Derived From Renewable Resources**

  Evaluate the role of bio-based lubricants through a review of literatures and documents in green tribology. Identify the composition and the characteristics of components in bio-based lubricants through an analytic review of literatures and documents in green tribological science as well as the experimental data.

- **Phase 8 – Conclusion and Recommendations**

  Summarize the experimental results and research from Phase 1, 2, 3, 4, and 5 for the further improvements and research.

CHAPTER 2

GREEN TRIBOLOGY

2.1 Introduction

Tribology is a new science formally defined by a committee of the Organization for Economic Cooperation and Development in 1967. Trobology is the combination of science and technology in solid mechanics, surface engineering, fluid mechanics, thermodynamic, heat transfer, materials science, rheolgy, physic, chemistry, and applied mathematics (Bhushan, 2002).

Friction and wear resulting from inadequate lubrication on the interacting surfaces in relative motion may cause a significant loss in energy and materials or even a permanent damage.

The main objectives of green tribology are to save the energy and materials and enhance the environment and the quality of life (IET, 2009). The Institution of Engineering and Technology has defined green tribology as the science and technology of the tribological aspects of ecological balance and biological impacts.

Today green tribology is becoming an essential concept and knowledge for all modern industries, ranging from manufacturing to aerospace program, in order to optimize the energy efficiency as well as minimize the environmental impacts and the loss in materials.

The geometrical structure of metal surfaces as well as the concepts of friction, wear, lubricants, and lubrication in tribology are significantly important in the formulation of lubricants and the selection of lubricant materials and will be presentd in this chapter.

Lubricants, either petroleum based or synthetic made, are the products derived from petroleum and developed through tribological researches to perform not only for lubrication but also for many other functions, such as cooling, noise and vibration reduction, cleaning, corrosion protection, and power transferring (Khonsari, et al., 2008).

2.2 Topography of the Metal Surfaces

The investigation of topography of metal surfaces in nano- and microscale is essential for understanding the effects of friction and wear on metal surface as well as the functions of lubricant between two sliding parts in relative motion.

2.2.1 Surface Texture

The surface of metals and alloys is impossible to be completely smooth. A variety of irregularities and deviations of geometrical structure are naturally formed on the surface of metal and alloys as a result of forming process (Whitehouse, 1994; Thomas, 1999; Bhushan, 2002). Figure 2-1a shows the surface texture of an engine cylinder in microscale. Figure 2-1b shows that the surface of engine cylinder is still rough after UV treatment.

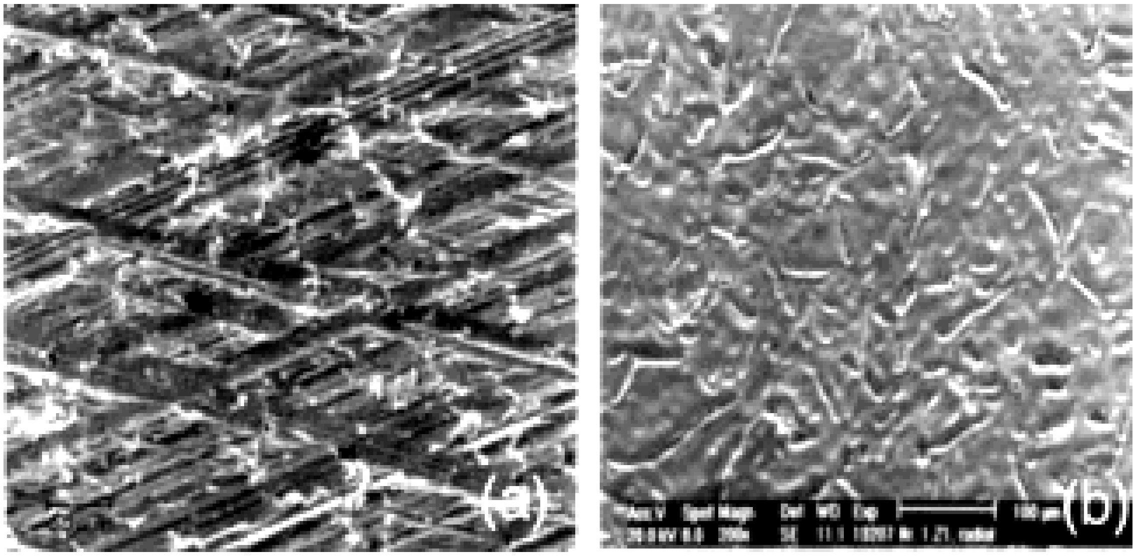


Figure 2-1. SEM Image of Engine Cylinder Surface: a) The Original Surface Texture, b) Surface Texture after UV Treatment.
(http://www.industrial-lasers.com/display_article/214247/39/none/none/Feat/Targeting-diesel-engine-efficiency)

2.2.2 Geometrical Structure

The geometrical structure on the surfaces of metals and alloys can be generally classified into: 1) roughness, 2) waviness, and 3) lay as illustrated in Figure 2-2. The total surface profile is the sum of roughness profile and waviness profile (Tarr, 2009; Khonsari, et al., 2008).

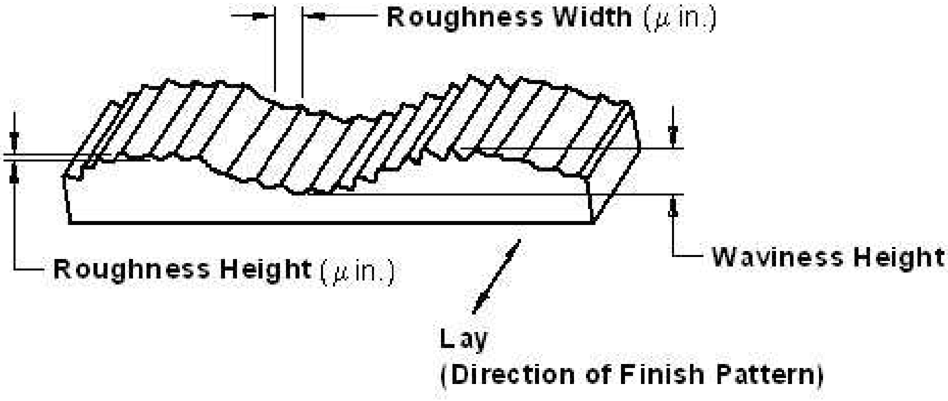


Figure 2-2. Characteristics of Surface Structure. (http://www.msitesting.com/assets/images/SurfaceRoughness.jpg)

2.3 Metal Surface Layers

The metal surface consists of various layers with different thickness depending on the production process, the temperature applied, and the degree of oxidation (Gatos, 1968; Haltner, 1969; Buckely, 1981; Bhushan, 2002). Figure 2-3 illustrates the typical layers on the metal surface.

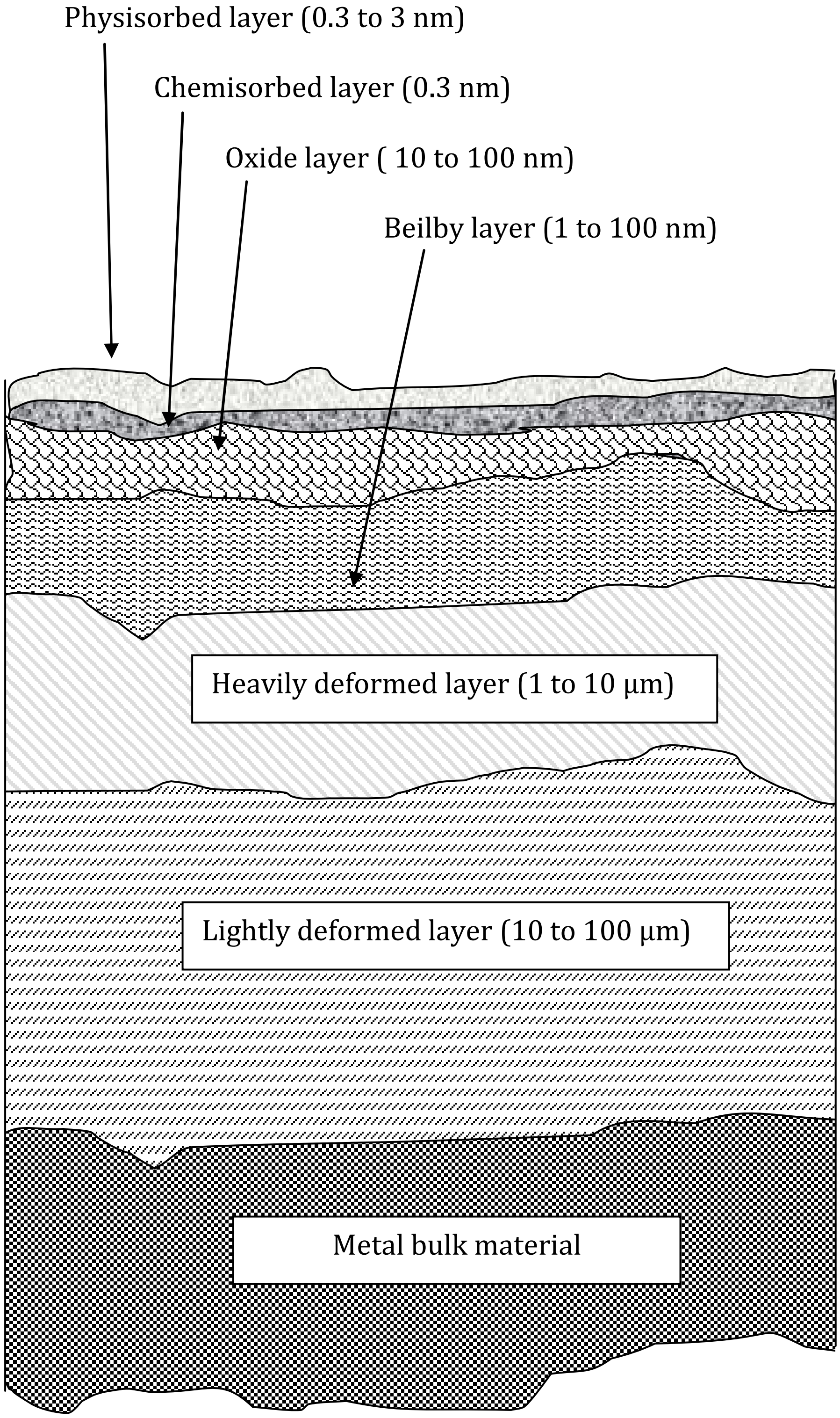


Figure 2-3. Typical Layers on Metal Surface.

2.3.1 Physisorbed Layer

A variety of molecules (e.g., water vapor, grease, and oxygen) can be easily adsorbed onto metal surface to form a layer (monomolecular or polymolecular) as a result of physical interaction due to van de Waals forces between adsorbed molecules and metal molecules (Haltner, 1969; Bhushan, 2002). Physisorbed layer can be easily removed since van de Waals force is a relatively weak force compared to the chemical bond of adsorbed molecules (Bhushan, 2002).

2.3.2 Chemisorbed Layer

Chemisorbed layer is a monomolecular layer which is bonded by covalent bonds between adsorbed molecules (e.g., water vapor, grease, and oxygen) and metal molecules on metal surface. A chemisorbed layer is commonly formed at high temperature (Bhushan, 2002). The bonding energy of chemisorbed layer is much higher (10 to 100 kcal/mole) than physical bond energy (1 to 2 kcal/mole) in physisorbed layer. Therefore, unlike physisorbed layer, it is more difficult to remove chemisorbed layer from metal surface.

2.3.3 Oxide Layer

Oxide layer formed on the surface of metals or alloys is normally resulting from either the friction process or the oxidative reaction between metal molecules and other reactive molecules depending on the environment (Bhushan, 2002). Oxide layer may consist of monoxide or mixed-oxides. The typical examples of oxide layer include ferrous oxides (e.g., FeO, Fe_2O_3, and Fe_2O_4) on iron; mixed-oxide of iron oxide and chromium oxide on the stainless steels; and the layers of nitrides, sulfides, and chlorides (Kubaschewski and Hopkins, 1953; Bhushan, 2002).

Most oxide layers, such as ferrous oxides and chromium oxide, are able to grow continually in a favorable environment. However, some metal oxides, such as aluminum oxide and titanium oxide, are stable and can even act as a protective layer on the surface (Bhurshan, 2002).

2.3.4 Beilby Layer

Beilby layer is formed as a result of quenching of molecular layers of metals and alloys during the process of melting, polishing, or lapping. It has either an amorphous or microcrystalline structure (Goswami, 1996; Bhushan, 2002).

2.3.5 Deformed Layer

Deformed layer is also known as strained layer. This strained zone in metals and alloys is commonly formed as result of a temperature gradient during grinding, machining, lapping, polishing, and friction process (Bhushan, 2002). The stretched part of material has completely different characteristics from the original material. The degree of deformation depends on the nature of materials and the amount of work applied to the material. In general, the area near the surface of metals and alloys, so called heavily deformed layer, are more likely to have higher degree of stretch than other parts of metals and alloys (Samuels, 1960; Shaw; 1997; .Bhushan, 2002).

2.4 Significance of Friction and Wear

Friction is the resistance force against the interface motion between two adjacent surfaces. Friction exists in engines or machines may lower energy efficiency, generate tremendous amount of heat, cause severe wear on moving parts, and increase the operating costs as a final result.

Two types of friction are greatly concerned in tribology: 1) sliding friction resulting from the interactions of two sliding surface, such as adhesion, deformation, and ploughing; 2) rolling friction, also known as rolling resistance, as a result of the interaction between two rolling surfaces, such as adhesion and deformation.

Energy loss as a result of rolling friction for a ball bearing in operation can be calculated by the equation 2.1 and 2.2 (Jenzurski and Jendzurski and Moyer, 1997; SKF, 2005; Khonsari and Booser, 2008):

$$\textbf{Energy loss} = 2\pi(n/60)M \tag{2.1}$$

where

n: bearing running speed (rpm)

M: bearing frictional moment (Nmm)

$$M = 0.5d\mu P \tag{2.2}$$

where

μ: coefficient of friction for the bearing

d: bearing bore diameter (mm)

P: bearing load (N)

As previously discussed in the section 2.2.1, the surface of metals and alloys are not completely smooth. Wear is a form of damage as a result of high friction on two rough surfaces in relative motion. Wear may increase noise, vibration, surface stresses, and fatigue damage (Khonsari and Booser, 2008).

Table 2- 1 summarizes types and cause of wear (Engel, 1976; Eyre, 1976; Rigney and Glaeser, 1978; Scott, 1979; Peterson and Winer, 1980; Suh and Saka, 1980; Buckley, 1981; Loomis, 1985, Suh, 1986; Zum Gahr, 1987; Hutchings, 1992; Bayer, 1994; Rabinowicz, 1995; Stachowiak and Batchelor, 2000; Bhushan, 1996, 2001a, 2001b, 2002).

Table 2-1. Types of Wear Commonly Found on the Surface of Metals and Alloys.

Wear Type	**Cause**
Adhesive wear	Adhesion between contacting surfaces
Fatigue wear	Repetitive stresses under sliding and rolling
Erosive wear	Repetitive impingement of solid particles
Percussion wear	Repetitive high speed solid impact
Corrosive wear	Oxidative reaction with corroding agents such as water
Abrasive wear	Repetitive scraping of hard particles
Electrical Induced wear	High electrical potential or plasma
Fretting wear	Low-amplitude oscillatory motion (vibration)

Wear increase linearly with service time. The wear life and total wear of a bearing can be determined by the following equations (Eschmann et al., 1985; Khonsari, and Booser, 2008):

Wear life (h)= k × fv **(6.3)**

where

fv: limiting wear factor (Appendix A)

k: environmental factor (Appendix B)

Total wear at bearing failure (μm) = fv /0.46d$^{2/3}$ (6.4)

where

d: bearing bore diameter (mm)

2.5 Lubricants and Lubrication

The total cost of energy waste and material loss resulting from frication and wear is approximately $40 billion a year for the various industries in the United States (Jost, 1981; Stachowik and Batchelor 2000; NASA, 2009). Thus, lubricants are essential elements used to improve the operating efficiency and reduce loss in energy and materials almost for all modern industries from manufacturing to space program.

The thickness of lubricant film between two sliding surfaces constantly changes in motion (Hamrock, 1994). The time taken for the thickness of lubricant film to change from one value to another can be determined by the following equation:

$$\frac{w}{\eta l^3}\int_{t1}^{t2} dt = \int_{h1}^{h2} \frac{1}{h^3} dh \qquad \text{or} \qquad \Delta t = \frac{\eta l^3}{2w}\left[\frac{1}{h_2^2} - \frac{1}{h_1^2}\right] \qquad \textbf{(6-5)}$$

where

w: load (N)

η: lubricant film viscosity (cP)

l: length

h1: lubricant film thickness at t1

h2: lubricant film thickness at t2

2.6 Summary

The surface of metals and alloys consists of various irregularities and deviations which is naturally formed as a result of the forming process. Friction and wear resulting from those roughnesses can cause large amount of loss in energy and materials. Triboloy is the science and technology used for the analysis of the problems associated with friction and wear and the development of lubricants to control those problems.

The concepts of friction, wear, and lubrication are significantly important in the formulation of lubricants and the selection of lubricant base materials. Lubricants developed from the tribological researches are essential elements for all modern industries to improve the efficiency of operations and save the energy costs.

CHAPTER 3

LUBRICANT SCIENCE AND TECHNOLOGY

3.1 Introduction

This chapter presents the overview of tribological science, such as lubricant origin, composition, functions, manufacturing technologies, and classifications. As previously discussed in chapter 2, friction can significantly reduce the efficiency of machines and engines as well as cause a significant loss in materials and energy. Thus, lubricant plays a significant role for all modern industries in controlling friction and wear, improving the operation efficiency, and reducing the operating cost resulting from the loss in energy and materials. It is estimated that the worldwide consumption of lubricants is expected to increase 1.6 percent per year to 10.7 billion gallons in 2012. Only about two billion gallons of used lubricants are recycled around the world (The Freedonia Group, 2009).

This section focus on the review and discussion in lubricants made of petroleum-based oils, mineral oils and synthetic long-chain hydrocarbons, which are the most popular lubricants used today. Bio-based lubricants will be reviewed and discussed Chapter 8.

3.2 Lubricant Functions and Types

The principal function of lubricants is to minimize friction and wear. The other functions of lubricant include:

- **Noise and Vibration Reduction**

  Noise and vibration results from friction between two sliding metal surfaces in contact can be minimized by lubricant film bonded on the metal surfaces.

- **Cleaning and Suspending Agent**

  Lubricant can act as a cleaning agent to prevent potentially harmful products such as varnish and lacquer, from depositing on the surface of pistons or cylinders in engines. Lubricants can protect machines and engines from cutting damages by acting as a medium to suspend hard and sharp impurities, such as metals from tear and wear of moving parts.

- **Corrosion Protection**

  Additives formulated in lubricants, such as rust and corrosion inhibitors, anti-oxidation agents, anti-wear agents, can protect engines and machines from rust and corrosion as a result of oxidation.

- **Cooling**

  Lubricant can act as a heatsink medium in engines or machines to dissipate the heat generated during the operation.

- **Power transferring**

  Lubricants can be used to transfer energy within a closed system, such as circulating systems, transmission systems, and hydraulic systems.

Lubricants, depending on the applications, could be formulated and produced in different forms such as soild, semi-solid, gas, or fluid. Lubricants are classified into two major groups: 1) automotive lubricants and 2) industrial lubricants. More than 60% of total lubricants sold around the world are used for vehicles (Singh, 2002).

Industrial lubricants can be subdivided into industrial oils and industrial specialty oils. Specialty oils include greases, metal working lubricants and solid lubricant films. The grades of specialty lubricants are standardized by Original Equipment Manufacturers (Singh, 2002).

Engine oils, also known as motor oils or crankcase oils, are the typical fluid-type automotive lubricants used for protecting internal combustion engines from intensive cycles of operation and constant combustion of fuels. Viscosity of motor oils is an essential factor to maintain engines operating at an optimal condition over a wide range of temperature and working conditions. Motor oils are classified by the Society of Automotive Engine (SAE) into different grades based on the viscosity of oils as shown in Table 3-1.

Table 3-1. Motor Oil Classification (Pirro, 2001).

SAE viscosity grade	Low temperature (°C) cranking viscosity (cP, max)[b]	Low temperature (°C) pumping viscosity (cP, max, with no yield stress)[c]	Kinematic viscosity (cSt) at 100°C min[d]	Kinematic viscosity (cSt) at 100°C max[d]	High shear viscosity (cP), at 150°C and $10^6 s^{-2}$, min[e]
0W	3250 at -30	60 000 at -40	3.8	—	—
5W	3500 at -25	60 000 at -35	3.8	—	—
10W	3500 at -20	60 000 at -30	4.1	—	—
15W	3500 at -25	60 000 at -25	5.6	—	—
20W	4500 at -20	60 000 at -20	5.6	—	—
25W	6000 at - 5	60 000 at -15	9.3	—	—
20	—	—	5.6	< 9.3	2.6
30	—	—	9.3	< 12.5	2.9
40	—	—	12.5	< 16.3	2.9[f]
40	—	—	12.5	< 16.3	3.7[g]
50	—	—	16.3	< 21.9	3.7
60	—	—	21.9	< 26.1	3.7

[a] All values are critical specifications as defined by ASTM D 3244.

[b] ASTM D 5293.

[c] ASTM D 4684. Note that the presence of any yield stress detectable by this method constitutes a failure regardless of viscosity.

[d] ASTM 445

[e] ASTM D 4683 or ASTM D 4741.

[f] 0W-40, 5W-40, and 10W-40 grades.

[g] 15W-40, 20W-40, 25W-40 and 40 grades.

API service label (Figure 3-1) shown on engine oil containers is used to identify the classification of specific engine oil (API, 2008). Figure 3-2 illustrates the interpretation of API service label.

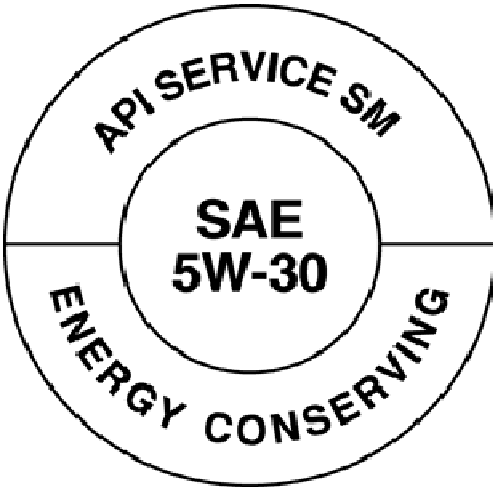


Figure 3-1. API Service Label Shown on Engine Oil Containers.

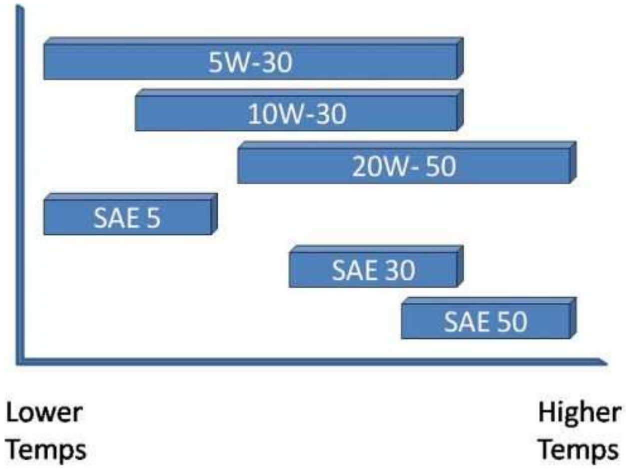


Figure 3-2. Interpretation of API Label.
(http://hubpages.com/hub/How-To-Read-A-Motor-Oil-Label)

3.3 Lubricant Composition

Modern industries need high performance lubricants to protect their machines from tear and wear. Engines used for modern vehicles are required to maintain their functions under a wide range of operating conditions. Thus, modern lubricants contain not only base material but also a variety of additives in order to enhance the specific performance which base material alone cannot achieve. Most lubricants used today consist of 80 to 95% of base oils and 5 to 20% of various additives (Pirro, 2001).

3.4 Lubricant Base Oils

The materials can be used for making lubricant base oils include: 1) the mineral oils derived from petroleum (crude oil); 2) the artificially made long-chain molecules, such as synthesized hydrocarbon fluids, organic esters, polyglyocols, phosphate esters, silicones, and silicate esters; and 3) oils extracted from plants or animal fat and grease (Singh, 2002).

The base stocks derived from the plants (e.g, canola, palm, castor, sunflower, grape seeds) are mainly triglyceride esters, which is composed of three fatty acids (stearic, oleic, and linoleic) and a glycerol (Schneider, 2006). The benefits of plant-based oils include low volatility, high additive solubility, high VI, and good environmental compatibility. Nevertheless, the oxidation stability of plant oils is poor compared to base oil 1) and 2).

The use of animal fats or grease as lubricant base oils is no longer practical due to undesirable properties of most animal fats and the essence of animal protection.

3.4.1 Lubricant Base Oil Classifications

The property of lubricants varies with base oils. The base oil is classified by the American Petroleum Institute (API) into different groups as follows depending on the sources and the characteristics of base stocks (LePera, 2000; Kramer et al., 2003a, 2003b, 2003c; Mobil, 2005; Denton, 2007; Randles et al., 2007). In general, group 1, 2, and 3 are different grades of mineral base oils. Group 4 and 5 are different types of synthetic oils.

- **Group 1 Conventional Base Oils**

  Group 1 base oils are conventional mineral oils derived from the selected fractions of crude oil distillation. Conventional mineral oils have been used as lubricant base oils since the 1930s. Group1 base oils have less than 90 % of saturated hydrocarbons and more than 300 ppm sulfur compounds (Kramer et al., 2003a; Mobil, 2005; Denton, 2007). Viscosity index (VI) of group 1 base oils is in the range of 80 to 119 (Kramer et al., 2003b).

- **Group 2 Modern Conventional Base Oils**

  Group 2 base oils are mineral oils produced by modern hydroprocessing technologies such as hydrotreating, hydrocracking, wax hydroisomrization, and hydrofinishing. Compared to group 1 convention mineral base oils, group 2 base oils have better performance, and the sulfur compounds and impurities of group 2 are lower. Furthermore, group 2 base oils are more stable than group 1 at high temperature. Group 2 base oils normally contain more than 90% of saturated hydrocarbon compounds and less than 300 ppm of sulfur compounds (Kramer et al., 2003b; Mobil, 2005; Denton, 2007). Viscosity index (VI) of group 2 base oils is also in the range of 80 to 119 (Kramer et al., 2003b).

- **Group 3 Unconventional Base Oils (UCBOS)**

  Group 3 base oils are also known as very high viscosity index (VHVI) base oils. VI of Group3 base oils is much higher than Group 1 and 2 base oils. The performance of group 3 bases oils is much better than Group 1 and 2 at low temperature. UCBOS are currently the most popular type of mineral base oils in North America. UCBOS contain more than 90% of saturated hydrocarbons and less than 300 ppm of sulfur compounds (Kramer et al., 2003b; Mobil, 2005; Denton, 2007). Viscosity index (VI) of group 3 base oils is normally greater than 120 (Kramer et al., 2003b).

- **Group 4 Traditional Synthetic Base Oils**

  Group 4 synthetic base oils are commonly referred to polymerized alpha olefins (PAOs). Compared to mineral base oils, PAOs have extremely low pour point so that they are suitable to use for the applications at very low temperature. Overall performance of group 4 synthetic base oils is similar to UCBOs. However, PAOs are still not as popular as UCBOs today due to their high cost. Today UCBOs are recognized as good as synthetic base oils by the National Advertising Department of the Better Business Bureau in North America (Kramer et al., 2003c; Mobil, 2005; Denton, 2007).

- **Group 5 Specialized Synthetic Base Oils**

  Group 5 are engineered-base oils which include synthesized hydrocarbon fluids (e.g, polyalphaolefins, polybutenes), organic esters (e.g., polyol ester, dibasic aid ester), and silicate esters, polyglycols (e.g., polyalkylene, polyoxyaklylene, polyethers, polyglyco esters), phosphate esters (e.g, triaryl phosphate ester, triakyl phosphate esters), silicones, and silicate esters (Bhushan, 2001; Pirro, et al., 2001).

Esters are the most popular synthetic base oils used today in the lubricant market because their boiling points are high, and their viscosities are relatively stable at high temperature (LePera, 2000; Denton, 2007).

3.5 Lubricant Additives

Lubricant base oils, either mineral base oils or synthetic base oils, may not have all of required properties to maintain their functions under a variety of conditions. Therefore, additives are the essential elements in the modern lubricants in order used to enhance the specific performance.

A variety of additives have been used as the performance enhancers for lubricants since the 1920s. The concentration of additives in lubricant ranges from one thousand to three hundred thousands ppm depending on the applications (Pirro, et al., 2001). The consumption of additives has enormously increased as the demand of lubricants has significantly increased around the world in recent decades. In 1997, the overall consumption of lubricant additives around the world was about 5.7 billion pounds (ASTM, 2009). In 2006, the demand for additives has increased to 6.6 billion pounds as a result of the fast growth of economies in Asia and Latin America (ASTM, 2009).

Most additives are chemical compounds. The possible chemical reactions between additives may create the negative effects to lubricant performance (Lepera, 2000). It is very important for lubricant manufactures to properly use additives in formulating lubricant in order to achieve the optimal performance. The following are the typical additives used today for enhancing lubricant performance:

3.5.1 Antioxidants or Oxidation Inhibitors

The oxidation of lubricant leads to the increase in viscosity and the formation of the corrosive products, such as organic acids (Pirro, et al., 2001; Audibert, 2006). The rate of oxidation process normally varies with temperature. When the temperature is below 200˚F (93˚C), the rate of oxidation is slow, and the oxidation process is initiated by the chain reaction of free radicals, such as peroxy radicals ($HO_2^{\cdot}$) resulting from the oxidation of unstable hydrocarbon molecules. Alkylated phenols (e.g., 2,6-ditertiary-butyl-4-methylphenol) and aromatic amines (e.g., N-phenyl-α-naphthylamine) are commonly used to hinder the chain reaction by neutralizing the free radicals to form inactive compounds (Mortier, et al., 1997; Pirro, et al., 2001).

When the temperature is above 200°F(93°C), the oxidation process is promoted by the catalytic effect of transition metal such as CO, Fe, Cr, CU, Mn, and V. The metallic ditiophosphates (e.g., Zn, Sb, and Mo) are commonly used as metal deactivators to form a layer of protective coating on the surface of metal parts (Audibert, 2006; Pirro, et al., 2001).

3.5.2 Antiwear Additives

Antiwear additives can form a protective film on the surfaces of metal parts to protect them from tear and wear. The examples of antiwear additives are polar organic compounds (e.g, alcohols), fatty esters, fatty amines, and organic compounds, containing sulfur, phosphorus, chlorine, nitrogen, lead, or zinc. Chemical compounds, such as zinc dithiophosphates, can be used as both antioxidant additive and antiwear additive (Mortier, et al., 1997; Pirro, et al., 2001; Audibert, 2006).

3.5.3 Viscosity Index (VI) Stabilizers

Viscosity index is one of most important characteristics of lubricants. It is a measure for the change in viscosity with temperature. In general, viscosity of oils changes inversely with temperature. If viscosity is too high, lubricant may lose its function and create negative effects to the machines or engines.

VI stabilizers are generally used to maintain the stability of lubricants viscosity in a wide range of operating temperature. The materials commonly used as VI stabilizers are the long-chain polymers which are capable to change the molecular structure with temperature (Pirro, et al., 2001).

The viscosity of lubricants decreases with increasing temperature. The long-chain polymers are capable to stretch out and interact with each other to maintain viscosity of lubricant at high temperature and vice versa at low temperature. The polymers, which can perform such effects, are hydrogenated styrene butadiene polymers, methacrylate polymers, acrylate polymers, and olefin polymers (Audibert, 2006; Pirro, et al., 2001).

3.5.4 Detergents and Dispersing Agents

Detergents and dispersing agents are added into lubricants to control the formation of varnish and lacquer, which may deposit on the surface of parts and combustion chamber in engine and reduce the efficiency of engine or even cause an engine a significant damage.

The salts of alkaline earth metals, such as calcium and magnesium sulfonates and calcium phenates, are commonly used today as detergents to keep engines clean and operate properly. Benzylamides and polymeric succinimides, such as alkenylsuccinimides, are usually used to destabilize the adsorption of varnish and lacquer (Audibert, 2006; Pirro, et al., 2001).

3.5.5 Antiforming Additives

Depending on the characteristics of lubricants, detergents and dispersing additives may cause the formation of air bubbles, so called forming, in lubricants. Forming may reduce the efficiency of lubricants and engine. Silicon polymers and alkyl polymetacrylate with low molecular weight are commonly used as antiforming additives to collapse the air bubbles by reducing the surface tension of air bubbles (Mortier, et al., 1997; Pirro, et al., 2001; Audibert, 2006).

3.5.6 Pour Point Improving Additives

Pour point is the lowest temperature at which a lubricant still can flow. Vehicle engines are required to work properly during the cold weather. Without the help of pour point improver, the formation of paraffin wax crystals in lubricants may reduce the mobility of lubricant at a low temperature.

Pour point improving additives, such as alkyaromatic polymers and polymethacrylate, are commonly used to hider the formation of paraffin wax crystals by reacting with wax crystals and preventing them from expanding (Pirro, et al. 2001).

3.5.7 Anticorrosion Additives

Metals and alloys used for making engine parts, such as cooper-lead or lead-bronze, can be easily corroded by the strong acids generated from the combustion of sulfur compounds or antiknock materials in fuels (Mortier, et al., 1997; Pirro, et al., 2001; Audibert, 2006).

Amine succinates and alkaline earth sulfonates are commonly used as anticorrosion additives to protect metal surfaces from corrosion by forming a protective film either physically adsorbing or chemically bonding to the surface of metal parts.

3.6 Mineral Base Oils Derived from Crude Oils

3.6.1 Crude Oils

Feedstock for making mineral base oils is originated from crude oil. The property and composition of crude oil vary with the geological conditions in the extracting location. Crude oils generally consist of various amounts of hydrocarbon compounds in different types, sulfur compounds, nitrogen compounds, oxygen compounds, and traces of metallic constituents (Sequeira, 1994; Speight, 2007). Table 3-2 summarizes the typical composition of crude oils around the world.

Table 3-2. Typical Components of Crude Oils.

Component	**Wt. %**
Hydrocarbons	
Carbon-rich compounds	83 to 87
Hydrogen-rich compounds	10 to 14
Non-Hydrocarbons	
Sulfur containing compounds	0.05 to 6
Nitrogen containing compounds	0.1 to 2
Oxygen containing compounds	0.05 to 1.5
Trace Metals (including organo-metallics)	0.1 and above
Asphaltene and resin	vary widely

3.6.2 Pure Hydrocarbon Constituents in Crude Oils

The pure hydrocarbon compounds found in crude oils are: 1) paraffins (alkanes); 2) olefins (alkenes); and 3) aromatic hydrocarbons (Zumdahl, et al., 2003; Speight,2007; Optima Energy, 2009; Mobil Oil, 2009).

Table 3-3. General Characteristics of Pure Hydrocarbon Compounds Found in Crude Oils.

Property	n-paraffin	iso-paraffin	Naphthene	Aromatic
Oxidative Stability	Good	Good	Fair	Poor
Thermal Stability	Good	Good	Fair	Poor
Viscosity Index (VI)	High	High	Medium	Low
Point Points, (F)	High	Low	Low	Low

3.6.2.1 Paraffins (Alkanes)

Alkanes are also known as saturated hydrocarbons. Linear paraffins include normal paraffins (n-paraffins) and branched paraffins (iso-paraffins) with a general formula C_nH_{2n+2}. Paraffin wax and asphalt are the alkanes with high value of n (Optima Energy, 2009). Naphthenes are alkanes with cyclical shape. Lubricant may contain napthenes up to six rings per molecule. The typical examples of napthenes are cyclohexane, cyclopentance, and their methyl derivatives (Optima Energy, 2009).

3.6.2.2 Olefins (Alkenes)

Alkenes are unsaturated hydrocarbons with one double bond. The general formula for alkenes is C_nH_{2n}. The total content of olefins in crude oil is small. Olefins are highly unstable. Thus, they are not suitable to use for making lubricant feedstock (Optima Energy, 2009).

3.6.2.3 Aromatic Hydrocarbons

Aromatic hydrocarbons are cyclic unsaturated hydrocarbons containing one or more benzene rings with a general formula $C_nH_{2n-6.}$ Aromatic hydrocarbon compounds are poor in oxidative stability and thermal stability and low in VI. Thus, aromatic hydrocarbon compounds are not suitable to use for making lubricant feedstock. However, benzenes can be combined with paraffins to provide desirable viscosity and temperature properties for making lubricant feedstock(Optima Energy, 2009).

3.6.3 Other Constituents in Crude Oils

3.6.3.1 Sulfur Containing Compounds

The content of sulfur generally varies with the density of the crude oil. Sulfur compounds, such as sulfide, disulfides, thiophenes, contribute corrosion and the formation of char in engine (Speight, 2007; Optima, 2009). The typical sulfur compounds found in crude oil are mercaptans (thiols), sulfides (thioethers), diosulfides, cyclic sulfides, thiophene, benzothiophene, dibenzothiophene, and naphobenzothiophene (Speight, 2007; Optima Energy, 2009).

3.6.3.2 Nitrogen Containing Compounds

Compared to paraffinic crude oils, the nitrogen concentration is high in naphehenic crude oils. The nitorgen compounds commonly found in crude oils include pyrrole (C_4H_5N), pyridine (C_5H_5N), indole (C_8H_7N), indoline (C_8H_9N), quinoline (C_9H_7N), carbazole ($C_{12}H_9N$), Benzo(f)quinoline ($C_{13}H_9N$), and Benzo(a)carbazole ($C_{16}H_{11}N$) (Speight, 2007; Optima Energy, 2009).

3.6.3.3 Oxygen Containing Compounds

The most abundant oxygen compounds found in crude oils are naptheric acids. Other oxygen compounds found in crude oils at low concentrations include ketones, amides, esters, and phenols (Speight, 2007; Optima Energy, 2009).

3.6.3.4 Trace Metals (Including Organo-Metallics)

Trace metals and organo-metallics commonly found in crude oils are either 1) inorganic water soluble salts, such as chlorides and sulfates of sodium, potassium, magnesium, and calcium, in the water phase of crude oil emulsions or 2) oil soluble compounds, such as vanadium, copper, part of the iron, and nickel (Sequeira, 1994; Speight, 2007). Table 3-4 shows the typical trace metals found in crude oils (Pirro, 2001; Speight, 2007).

Table 3-4. Typical Trace Metals Found in Crude Oils.

Metal	**Concentration (ppm)**
Copper	0.2 - 12.0
Calcium	1.0 - 2.5
Magnesium	1.0 - 2.5
Barium	0.001 - 0.1
Strontium	0.001 - 0.1
Zinc	0.05 - 1.0
Mercury	0.03 - 0.1
Cesium	0.001 - 0.6
Boron	0.001 - 0.1
Aluminum	0.5 - 1.0
Gallium	0.001 - 0.1
Titanium	0.001 - 0.4
Zirconium	0.001 - 0.4
Silicon	0.1 - 5.0
Tin	0.1 - 0.3
Lead	0.001 - 0.2
Vanadium	5.0 - 1500.0
Iron	0.04 - 120.0
Cobalt	0.001 - 12.0
Nickel	3 - 120.0

3.6.3.5 Asphatiene and Resin

Asphatiene and resin are natural occurring compounds during the formation of crude oils. They have compounds with multi-ring structure, which are undesirable for lubricants and required to be removed during the production of lubricants.

3.6.4 Selection of Crude Oil for Producing Lubricant Feedstock

The characteristics of crude oil, such as viscosity index, pour point, oxidative stability, and thermal stability are the essential factors required to be evaluated during the selection of crude oil for making lubricant feedstock (Sequeria, 1992; Ushio et al. 1992).

As previously discussed in this chapter, unsaturated olefins are highly unstable and low in crude oils. Thus, the selection of crude oils for making lubricant feedstock falls into two major groups: 1) paraffinic types, which mainly consist of n-paraffins or iso-paraffin hydrocarbons, and 2) naphthenic types, which mostly contain cycloparaffin hydrocarbons (Pirro, et al., 2001; Lynch, 2008). Table 3-5 shows the characteristics of these two groups. Compared to naphthenic type, paraffinic crude oils are more stable with many desirable characteristics for producing lubricant feedstock.

Table 3-5. Characteristics of Paraffinic and Naphthenic Crude oils.

Crude Type	**Paraffinic**	**Naphthenic**
Content	little asphalt, various amount of wax	little or no wax, little asphalt
Viscosity (cSt at 40°C)	20.53	20.53
Viscosity Index (VI)	100	15
Point Points, (F)	0	-50

3.6.5 Production of Lubricant Feedstock from Crude Oils

The first step in the production of mineral base oils is to obtain lubricant feedstock from crude oil as previously discussed. There are two major distillation processes involved in the production of lubricant feedstock (Pirro, et al., 2001; Audibert, 2006). First, crude oil is fractionated under atmospheric pressure by an atmospheric distillation unit (ADU) into various fractions, such as hydrocarbon gases, gasoline, kerosene, diesel fuel, and gas oils, based on the differences in their boiling point as shown in Figure 3-3a. The remaining heavy compounds are continually fractionated by a vacuum distillation unit (VDU) into lubricant feedstock as shown in Figure 3-3b.

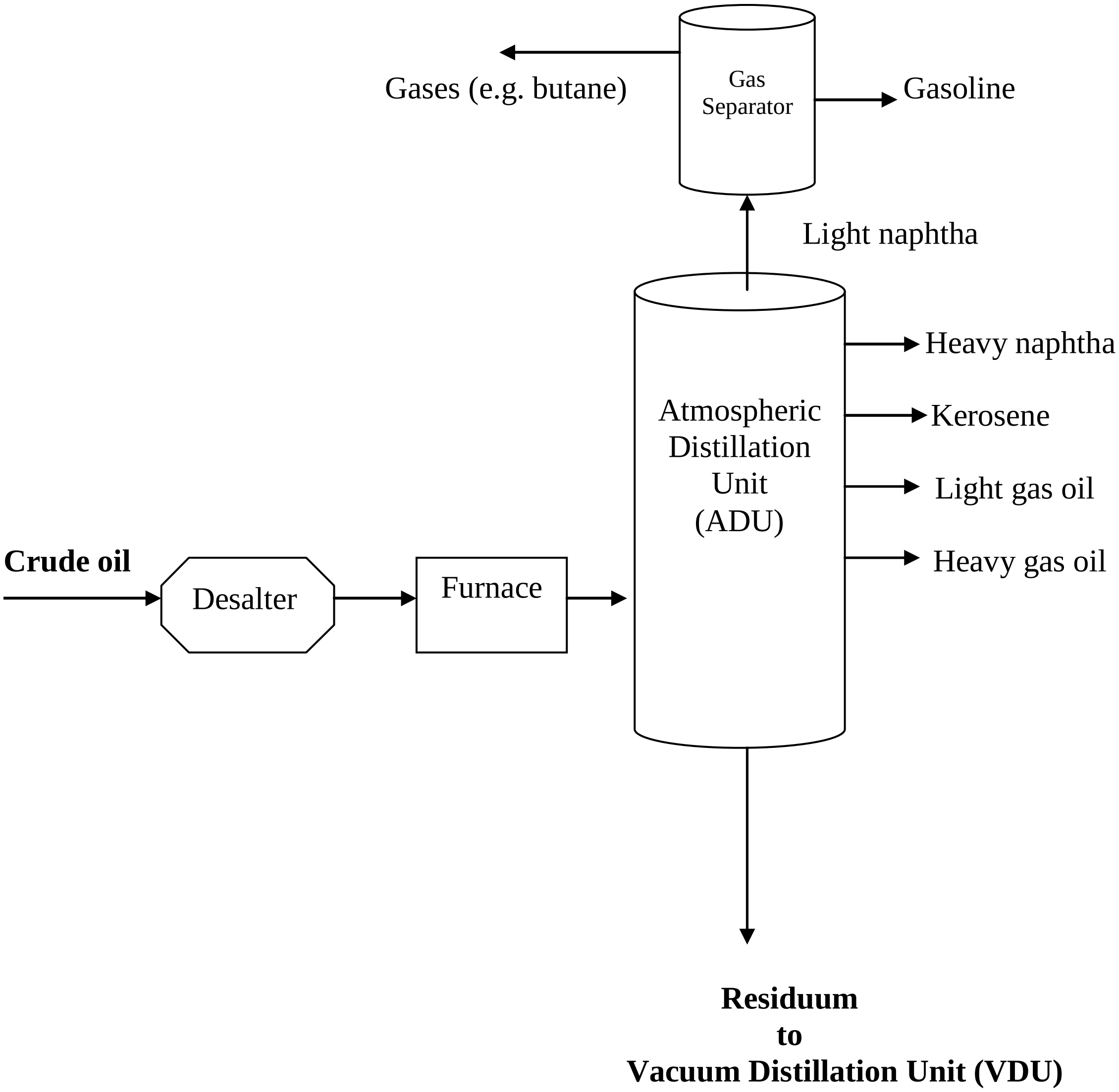


Figure 3-3a. Simplified Schematic Diagram of ADU Process.

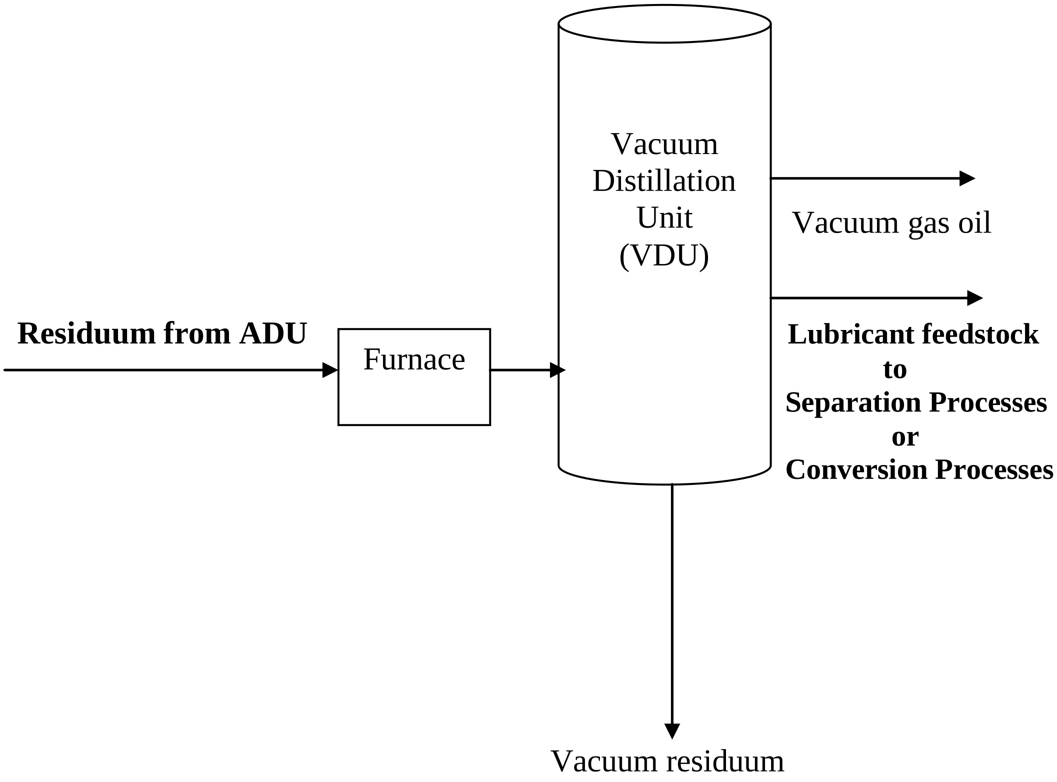


Figure 3-3b. Simplified Schematic Diagram of VDU Process.

3.6.6 Refining Processes of Mineral Base Oils

There are two well-known methods in refining lubricant feedstock into the lubricant base oils (Pirro, et al., 2001; Audibert, 2006): 1) separation processes and 2) conversion processes.

3.6.6.1 Separation Technology

Separation technology is the most popular method used today for producing mineral base oils around the world. Lubricant feedstock generated through ADU and VDU still contains various amounts of asphaltenes, resins, and wax, which are required to be removed. The first process in separation technology is deasphalting. Propane deasphalting is commonly used to separate asphaltenes and resins from wax based on the difference in the solubility of propane and the solubility of asphaltenes and resins. The deasphalted feedstock is called waxy raffinate, which is a long-chain hydrocarbon compounds (e.g. C38 and plus) which are continuously refined by the several different processes into mineral base oils (Pirro, et. Al., 2001; Speight, 2007; Lynch, 2008).

Aromatic hydrocarbon compounds in crude oils are the undesirable compounds for making lubricants as discussed earlier. The second process in separation technology is furfural extraction which is used to remove aromatic compounds.

The third stage is used to remove wax in feedstock. Methyl ethyl ketone (MEK) is commonly used for wax removal. The last stage of separation processes is hydrofinishing or clay treatment.

Traditional clay treatment has been gradually replaced by hydrofinishing because the later process is cost effective and simple. Figure 3-4 illustrates a simplified process flow diagram of the separation process.

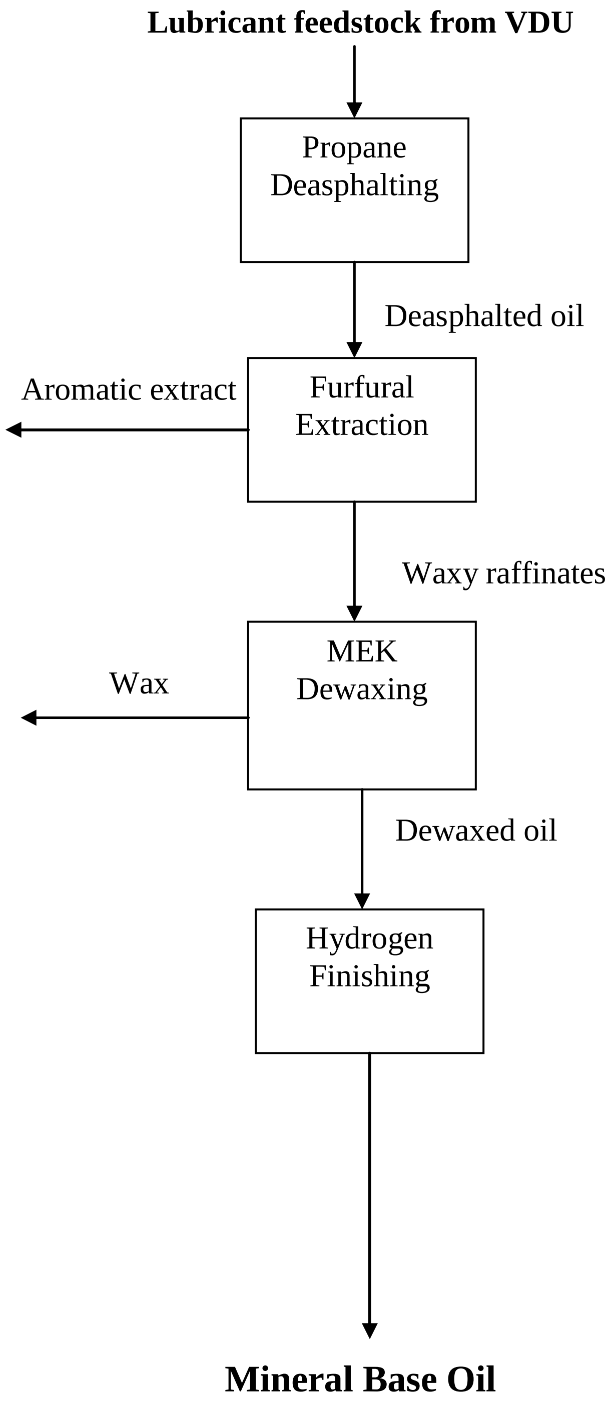


Figure 3-4. Simplified Flow Diagram of Separation System.

3.6.6.2 Conversion Technology

The processes in conversion technology include hydrogcracking, hydrodewaxing, and hydrofinishing. The concept of conversion method is totally different from separation process. Instead of taking out aromatic hydrocarbons from feedstock, hydrocracking unit (hydrocracker) catalytically cracks aromatic hydrocarbons and converts them into saturated paraffinic hydrocarbons in the presence of hydrogen and high pressure (3000psi). Hydrodewax is followed by hydrcracking to catalytically convert waxy n-paraffins into iso-paraffins in the presence of hydrogen.

The last process in conversion method is hydrofinishing, which involves the saturation of the remaining unsaturated hydrocarbons and the recovery of hydrogen from the first two processed. Figure 3-5 shows the simplified flow diagram for hydrogen conversion technology.

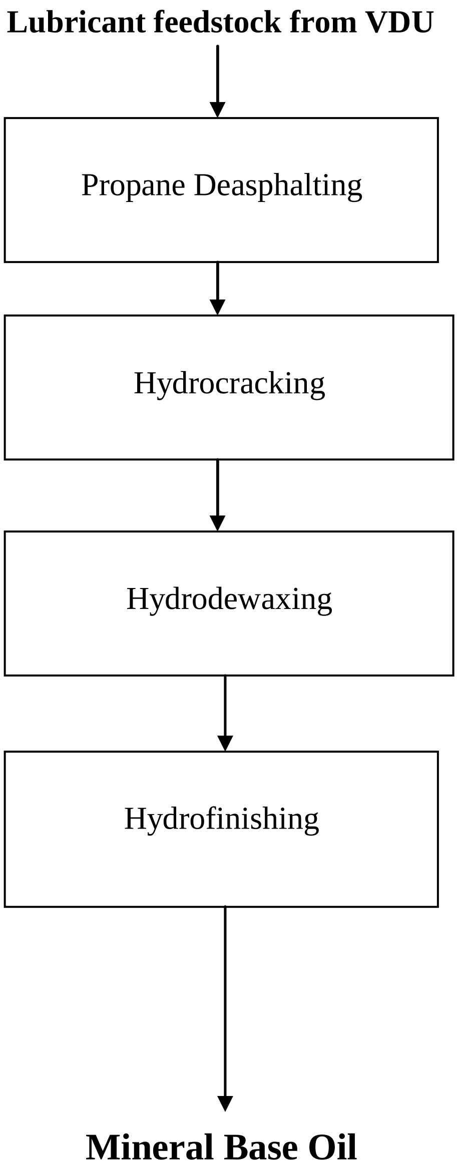


Figure 3-5. Simplified Flow Diagram of Conversion System.

3.7 Summary

Lubricants used today mostly consist of: 1) 80 to 95% of base Oils, such as mineral oils derived from petroleum (crude oil), artificially made long-chain molecules, and bio-based materials derived from renewable resources; and 2) 5 to 30% of various additives, such as antioxidants or oxidation Inhibitor, antiwear additives, viscosity Index (VI) stabilizer, detergents and dispersing additives, dntiforming additives, pour point improving additives, and antirust or anticorrosion additives. The grade of lubricant depends on the type of base oils formulated in the lubricant. Additives are the essential chemical compounds used to enhance the specific performance which base oil alone cannot achieve. The concentration of additives in lubricant ranges from one thousand to three hundred thousands ppm depending on the applications.

Crude oils used to produce base oils are normally consisted of pure hydrocarbon compounds (e.g. alkanes, alkenes, aromatic hydrocarbons) and non-hydrocarbon compounds (e.g. sulfur containing compounds, nitrogen containing compounds, oxygen containing compounds, traces of metallic constituents, asphatiene, and resin).

Paraffin feedstock derived from crude oils are the most popular materials used today for producing mineral based oils because they are more stable than aromatic and olefins. The feedstock can be further refined into different grades of base oils by either separation processes or conversion processes.

Separation process involves the removal of undesirable compounds in feedstock by a series of chemical treatments. Conversion processes convert non-useful compounds into desirable base materials through a series of hydroprocesses.

Compared to petroleum based lubricants, synthetic lubricants are more stable to temperature change. Thus, the service life of synthetic lubricants is generally longer than mineral-based lubricants. However, the cost of energy and materials required for manufacturing synthetic lubricants are high than mineral based lubricants.

As the concern about the environment compatibility of petroleum-based lubricant is on the rise, the development of lubricants with biodegradable material is becoming the future trend in lubricant industries. The details of bio-based lubricants will be reviewed and discussed in Chapter 8.

CHAPTER 4

OVERVIEW OF USED LUBRICANT

4.1 Introduction

Many researches have confirmed that used petroleum-based lubricants are slow in degradation, hazardous to the natural environments, and highly toxic to human health, fauna, and flora. The study of the potential impacts of used petroleum-based lubricants to human health, animals, plants, and the environment is important in raising public awareness to properly handle used lubricants in order to prevent used lubricants from releasing to the environment. This chapter presents the analysis of the general composition of most used lubricants, the evaluation of the biodegrability and toxicity of used lubricants, and the assessment of relative risk of used lubricants to human health and ecosystems.

As the petroleum shortage is becoming a global problem nowadays, the regeneration of used petroleum-based products is increasingly becoming more important than ever throughout human history. Most importantly, used lubricants regeneration has enormous benefits, including minimizing hazards; reducing waste; protecting the environment; and conserving energy and natural resources.

The technologies used today for regenerating of used lubricants are evaluated and discussed in this chapter.

4.2 Composition of Used Lubricants

The composition of used lubricants collected from engines and machines varies substantially from place to place. In addition to hydrocarbon compounds (C4 to C50) from base oils and unburned fuels, used lubricants also contain various additives from the original formulation as mentioned in the previous chapter and various amounts of contaminants such as metal fragments, soot gel networks, soot aggregates, dirt, organic compounds (e.g., benzene, toluene, xylene, PAHs), and heavy metals (e.g., cadmium, chromium, arsenic, barium, zinc, lead).

It is very difficult to characterize used lubricants because the composition of used lubricants varies widely with the type and age of vehicles and machines; the service life of lubricant; collecting places; and operating conditions.

4.2.1 Hydrocarbon Compounds

According to the study done by Elliot in 1986, approximately 50% of lubricant used in engines would be burned and released as exhaust emission during engine operation (CEPA 1994). The possible incomplete combustion of fuels, such as gasoline and diesel, has been the common situation for the internal combustion engines. Thus, the major hydrocarbon compounds found in used lubricants are the remaining unburned lubricants and fuels. Unburned fuels normally found in used lubricants are gasoline fuels and diesels. Diesels are different from gasoline in many ways. Table 4-1 shows the general characteristics of gasoline and diesel (Guibet, 1999; U.S. Department of Health and Human Services, 1999).

The general hydrocarbon compounds found in diesels are shown in Table 4-2 (Guibet, 1999; U.S. Department of Health and Human Services, 1999). Table 4-3 shows the general hydrocarbon compounds found in gasoline fuels (Guibet, 1999; U.S. Department of Health and Human Services, 1999).

Table 4-1. General Characteristics of Gasoline and Diesel.

General Characteristics	**Fuel**	
	Gasoline	**Diesel**
Density (15°C)	0.72-0.77	0.82-0.86
H/C Atomic Ratio	1.7-1.9	1.9-2.1
Parraffins[a]	40-65	50-65
Naphthenes[a]	0-5	20-30
Olefins[a]	0-20	0
Aromatics[a]	15 to 45	10 to 30

a. Composition of Organic Family (Volume %)

Table 4-2. Major Hydrocarbon Carbon Compounds in Diesels

Hydrocarbon Compounds	**Carbon Number**
Beneze	6
Toluene	7
Ethykbeneze	8
o-xylene	8
m-xylene	8
p-xylene	8
n-Undecane	11
n-Dodecane	12
n-Tridecane	13
n-Tetradecane	14
n-Pentadecane	15
n-Hexadecane	16
n-Heptadecane	17
n-Octadecane	18
n-Nonadecane	19
n-Eicoane	20

Table 4-3. Major Hydrocarbon Compounds in Gasoline.

Hydrocarbon Compounds	**Carbon Number**
n-Butane	4
Isopentane	5
n-Hexane	6
2,3-Dimethylbutane	6
2-Methylpentane	6
3-Methylpentane	6
Beneze	6
n-Heptane	7
2,4-Dimethylpentane	7
Toluene	7
n-Octane	8
Ethykbeneze	8
o-xylene	8
m-xylene	8
p-xylene	8
1-Methyl-4-ethyl-beneze	9
1-Methyl-3-ethyl-beneze	9
1,2,4-Trimethyl-beneze	9
1,3,5-Trimethyl-beneze	9
1,2,3,5-Tetramethyl-beneze	10

4.2.2 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are normally formed in gasoline engines due to the cyclization of low-molecular-weight unburned aromatic compounds in gasolines (Pruell and Quinn, 1998; Auibert, 2007). Diesels are high in paraffins and unlikely to form PAHs in diesel engines.

The concentration of PAHs in used motor oils varies widely from 0 to 4210 μg/g depending on the type of vehicle, age of vehicles, service life of lubricant, and driving conditions (Pruell and Quinn, 1998; Wong and Wang, 2001). In general, the longer use of lubricant, the higher concentration of PAHs was found in used lubricants (Pruell and Quinn, 1998). Many studies confirmed that PAHs are toxic to all orgnaisms (Donahues, et al., 1977; Bott, et al., 1978; Hedtke and Puglisi, 1980; CarMichael, et al., 1991, 1992; Borowsky, et al., 1993; Hewstone, 1994; Hellou, et al., 1997; Wong and Wang, 2009). The toxicity of PAHs is greatly affected by the structure of PAHs. PAHs with four or more rings are considered as carcinogens to human (Harvey, 1985; Wong and Wang 2001). Table 4-4 shows the typical PAHs found in used lubricants (Wong and Wang, 2001).

Table 4-4. Typical PAHs Found in Used Lubricants.

PAH	Structure (No. of Rings)
Naphthalene	2
Acenaphthylene	3
Acenaphthene	3
Fluorene	3
Phenanthrene	3
Anthracene	3
Fluoranthene	4
Pyrene	4
Benzo(a)an thracene	4
Chrysene	4
Benzo(b)fluoranthene	5
Benzo(f)fluoranthene	5
Benzo(a)pyrene	5
Dibenzo(a,h)anthracene	5
Indeno(I,2,3-cd)pyrene	6
Benzo(g,h,i)perylene	6

4.2.3 Additives from Lubricant and Fuels

Additives found in used lubricants normally come from either the original lubricant formulation or the unburned fuels. Additives used in lubricant formulation have previously discussed in Chapter 2. Table 4-5 shows the common additives used for gasoline (Guibet, 1999; Erdal, 2004).

Table 4-5. General Additives Used for Gasoline Fuels.

Gasoline Fuel Additives	
Antioxidants	Alkyl-p-phenylenediamines
	Alkyl-p-aminophenols
	Alkylphenols
Metal deactivators	N,N'-disalicylidene-1,2-propanediamine
Octane rating improver	Methyl cyclopentadienyl manganese tricarbonyl (MMT)
	Ethylene dibromide
	Iron pentacarborbonyl
	Lead alkyls
	Dicyclopentadienylirion
	Nickel carbonyl
	Tetraethyl tin
	Iodine
	Aniline
	N-methylaniline
	MTBE
Detergents	Propylenediamine amides
	Polyisobutenylsuccinic anhydride derivatives Polypropylphenol derivatives

Unlike gasoline, diesels need different types of additives because microorganisms, such as bacteria, yeasts, and fungi, are able to grow in diesel storage tank in case the tank is contaminated by water or moisture from the air (Guidet, 1999). The biocides or bacteriostats, are commonly added into diesels to control the growth of microbes. Table 4-6 shows the common additives used for gasoline Guibet, 1999; Erdal, 2004).

Table 4-6. General Additives Used for Diesels.

Diesel Fuel Additives	
Biocides	Quinoline
	Cyclic amines
	N-alkylpropanediamine
	Imidazolines
Antioxidants	N,N-dimethylcylo-hexylamine
Anti-forming	Polysiloxanes
Demulsifiers	Alkyloxypolyglycol
	Alrylsulfonates
Cetane improvers	2-ethylhexyl nitrate
	Triethyleneglycol dinitrates

4.2.4 Soot Gel Networks

Used lubricant is a unique colloidal system with a significant amount of suspended soot particles. Soot particles generated from the combustion of fuels are either released as exhaust emission to the air or retained in lubricant. According to the studies conducted by David Weiltz's group at Harvard University, soot particles retained in used lubricants tended to irreversibly transform into large aggregates as well as a number of soot gel networks at high temperature as a result of interactions between soot aggregates and dispersant additives in used lubricants (Won, et al., 2005; Osuji, C. and Weitz, D. 2009). The formation of high viscosity soot gel networks can significantly degrade the performance of lubricants. Figure 4-1 shows that the formation of soot aggregates and gel networks increases proportionally with the content of soot particles in oil at high temperature (Won, et al., 2005; Osuji, C. and Weitz, D. 2009).

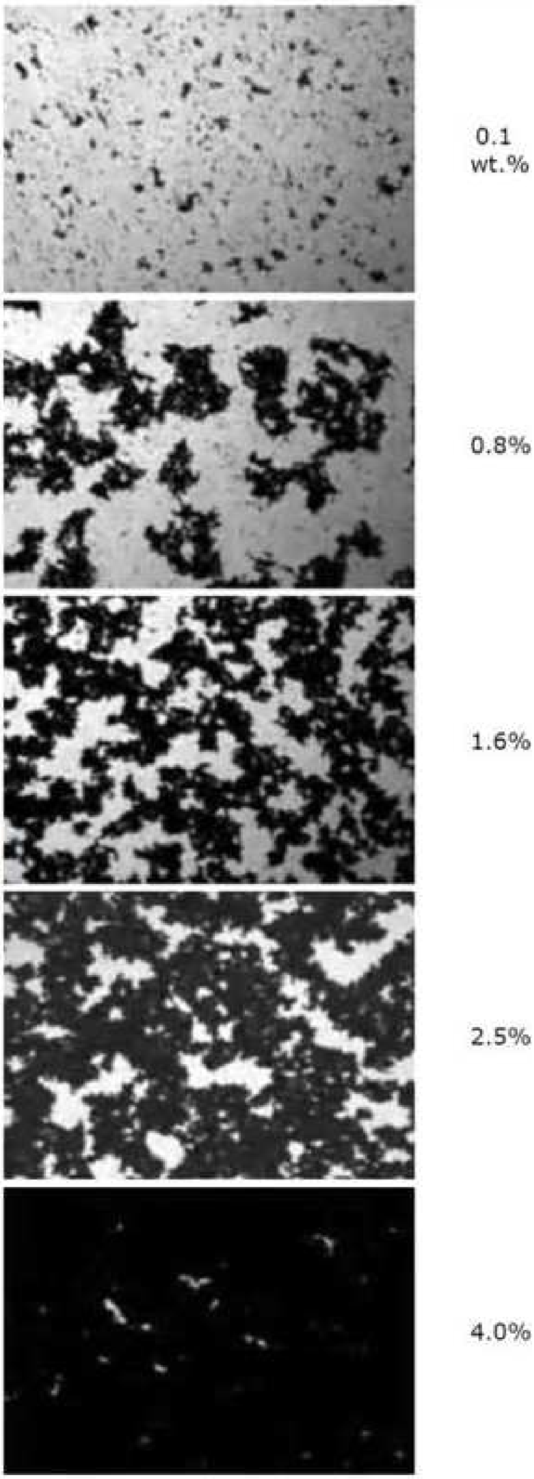


Figure 4-1. Formation of Soot Aggregates and Gel Networks Increases with Soot Content (Osuji, C. and Weitz, D. 2009).
(http://people.seas.harvard.edu/~cosuji/colloidal_aggregation.html)

4.2.5 Water

Water content in used lubricants is about 10 to 30% (Audibert, 2006). Water and moisture may be introduced into used lubricants by blowby vapors in the air, the leakage of the cooling system of vehicles, and the combustion of fuels (CEPA 1994; Yang, 2001; Awaja and Pavel, 2006).

4.2.6 Trace Metals and Metallic Fragments

Trace metals found in used lubricants possibly come from crude oils. Metallic fragments come from tear and wear of moving parts in engines or machines (Awaja and Pavel 2006).

4.2.7 Sand and Dirt

Sand and dirt are possibly introduced into used lubricans while in transit or waiting in refineries or collecting sites (Awaja and Pavel 2006).

4.3 Used Lubricant Impacts on Human Health and the Environment

"Used oils pose serious threat to human health and environment because of its ability to enter watersheds, pollute groundwater and drinking water."

U.S. EPA

Toxicity is one of most important characteristics of used lubricants required to consider in the assessment of relative risk to human health, animals, and plants.

4.3.1 Toxic Effects on Human Health

Used lubricants contain considerable amounts of polycyclic aromatic hydrocarbons (PAHs). PAHs with four or more rings are considered as carcinogens to human (Harvey, 1985; Wong and Wang 2001). The risk factors for PAHs are summarized in Appendix C which includes the route of exposure, intake dose, and the duration of exposure.

4.3.2 Toxic Effects on Animals

Used lubricants are very toxic to animals as well, especially for embryos and newborn animals. Laboratory studies have shown that the eggshells surface of mallard ducks and bobwhite quail were highly vulnerable to used lubricants. Even a low concentration of used lubricants (0.003 ml and 0.015ml) could cause 88% mortality in bobwhite quail embryos and 84% mortality in mallard duck embryos (Hoffman, 1990; CEPA, 1994). Other harmful effects include reduced growth, birth defects (e.g., subcutaneous edema, incomplete ossification, eye, and brain defects), and higher mortality (Albers, 1980; CEPA 1994).

Many studies have confirmed that water-soluable fractions of used lubricants are very toxic to aquatic organisms (U.S. EPA 1974; Byrne, et al.; Hedtke, et al. 1980; MacLean, et al, 1989; CEPA 1994). Table 4-7 shows the toxicity of water-soluble fractions of used lubricants. LC50 is used as a standard measure of toxicity to indicate the lethal concentration which is able to kill 50% of the population of experimental organism in a given time.

Table 4-7. Used Lubricant Toxic Effects on Aquatic Organisms.

Aquatic Species	**Concentration (mg/ L)**	**Time (Hr) to LC50**
<u>Fresh Water Species</u>		
American flagfish (*Jordanella floridae*)	1 to 9.5	96
Fathead minnow (*Pimephales promelas*)	1 to 9.5	96
Daphnia magna	4.65	48
<u>Marine Species</u>		
Clam (*Mercenaria*) embryo	0.04	48
Clam (*Mercenaria*) larvae	0.1	48

4.3.3 Toxic Effects on Plants

Plants are also vulnerable to used lubricants. Vegetables, such as radishes, turnips, beans, have been used to study for the effects of used lubricant on plant growth. Plants were seeded on various soils (e.g., sandy loam and clay loam) which were contaminated. The results indicated that none of them survived at silt loam and sandy loam after nine months. Although some of plants survived on the contaminated clay loam, they grew poorly with various abnormalities, such as yellow leaves and yellow stalk (Raymond et al., 1976; CEPA, 1994).

Used lubricants could greatly affect the growth of corn and sorghum. Corn decreased in growth by 46% on the contaminated soil (1300 ml/sq.m). The growth Sorghum also dropped to 76% at the end of the season (Giddens, 1976; CEPA, 1994).

Similar studies were done to assess the toxicity of used lubricants to fresh water algal communities and marine phytoplankton species. Study shown that the abundance of freshwater algae significantly dropped, and the photosynthetic rate of phytoplankton were inhibited as well (Bott, et al. 1978; Bate, et al. 1985; CEPA 1994).

4.3.4 Water Pollution

Water resources (surface water and ground water) can be polluted by used lubricant through the following ways:

- illegal disposal of used lubricants in sewers;
- dumping used lubricants with other wastes as trash; and
- leakage or spill of used lubricants entering to water body by stormwater runoff.

Used lubricants illegally disposed into stormwater sewer systems can significantly pollute surface water and cause harmful effects to the aquatic ecosystems. Stormwater runoff carries used lubricant spills into sewers is another possible route for used lubricants getting into surface water (CEPA, 1994). Five quarts of used lubricant can contaminate one million gallons of fresh water (L.A. County 2009). One pint of used lubricant can form oil film on the surface of water which can cover approximately one acre of the water surface (L.A. County, 2009). Used lubricant film may damage the water body and aquatic ecosystems by blocking sunlight for photosynthetic processes in water and impeding the cycle of dissolved oxygen (L.A. County, 2009; Ocean Planet, 2009). In addition to the oil film, metals like zinc, copper, and cadmium; and water soluable PAHs, such as benzo(a)pyrene, naphthalene, may dissolve into the water and cause considerable damages to aquatic organisms (Surprenant, et al. 1983; Payne et al., 1985).

In case used lubricant is disposed into sanitary sewer, they would most likely be transported into a wastewater treatment plant. The metal salts presented in used lubricant can seriously damage treatment plant (Mueller Associates Inc., 1987; 1989; American Petroleum Institute, 2009).

4.3.5 Soil Pollution

Used lubricants will most likely adsorb on organic wastes at landfills when used lubricants are disposed with other household wastes as trash and eventually end up to landfills (CEPA, 1994). For the landfills with permeable soils, water-soluble materials in used lubricants can easily penetrate refuses and end up polluting groundwater through runoff leaching and percolating (CH2M Hill Engineering Raymond, et al., 1976; LTD., 1992; CEPA, 1994).

4.4 Biodegradation of Used Lubricant

Biodegrability is another important characteristics of used lubricant required to consider in the assessment of used lubricant impacts to the environments. The rate of biodegradation for used lubricant in soil varies widely (30 to 410 days) depending on the composition of used lubricant; the structure and molecular weight of biodegrable materials in used lubricant; and the type of lubricant. In general, used synthetic lubricants could be degraded more rapidly in soil and water than mineral-based used lubricants (Denton, 2007). The other factors affect the rate of degradation including temperature and nitrogen availability in soil (Denton, 2007; Haigh, 1995)

Most of biodegrable compounds in used lubricant are hydrocarbon compounds. Many studies have confirmed that aromatic hydrocarbons and cyclic alkanes were degraded much slower than n-alkanes and branched alkanes (Atlas, 1981; CDM, 1986; Leahy et al., 1990; CEPA 1994). The compounds with high molecular weight tended to accumulate in the soil so the rate of degradation is much slower than the compounds with low molecular weight (Loehr et al., 1992, CEPA 1994). Service type also greatly affected the rate of degradation. About 55 to 82%of used lubricants collected from passenger cars could degrade in one year. Used lubricants collected from diesel trucks only degraded 23 to 53% within the same period of time (Raymond et al., 1976; CEPA 1994).

The light organic compounds (e.g., toluene, benzene) in oil films on the surface of water would gradually volatilize to the air. The remaining heavy hydrocarbons in used lubricant were usually converted by photo oxidation or biodegradation, either chemically or physically, into different compounds, such as such as aromatic acids, methyl esters, poly phenols, and peroxides. Those products and heavy metals originally suspended in oil film would stay in water and usually could cause a significant damage to aquatic organisms (Vaquez-Duhalt, et al., 1986).

4.5 Benefits of Used Lubricant Regeneration

Used lubricants can be regenerated into either lubricant base oils or an energy source. The benefits of used lubricant regeneration are outlined below:

- **Natural Resource conservation**

  As previously discussed, used lubricants contain considerable amounts of hydrocarbon compounds derived from the natural resources, such as crude oils. Thus, used lubricants recycle and reuse can reduce the consumption of natural resources.

- **Energy Conservation**

  Hydrocarbon compounds in used lubricants either from lubricant base materials or unburned fuels are considered as heating value and can be used as an energy source after used lubricant are purified.

- **Hazardous Waste Reduction**

  As previously discussed, used lubricants are highly toxic to human, animals, and plants. Used lubricant regeneration can reduce a significant amount of hazardous waste.

- **Environmental Protection**

  Used lubricants are hazardous to the environments as discussed in the previous section. Thus, regenerating used lubricants into either lubricant base material or an energy source can minimize the potential environmental hazards.

4.6 Used Lubricant Regeneration Technology

As previously discussed, over two billion gallons of used lubricants are generated around the world each year. The regeneration of used lubricants not only helps the world to reduce hazards and wastes but also conserves a signification amount of energy.

Most conventional processes for used lubricant regeneration involve physical and chemical treatments to remove the contaminants and impurities to reach a desirable level which is suitable for reuse as lubricant base oils or an energy source, such as heating oil.

Some technologies may generate liquid effluents, solid wastes, and air emissions during the regenerating process. The types of wastes, effluents, and wastes vary with the technology and processes used, and the environmental control methods (CEPA, 1994).

The sources of liquid effluents include 1) water separated from used lubricants and heat exchangers; 2) contaminated cooling water; 3) water from condensed steam; and 4) water from gas scrubbers. Liquid effluents are required additional treatments before they can be reused for cooling or discharged to a sewer system (Mueller Associates Inc., 1987; 1989; CEPA, 1994).

Solid wastes generated from the regenerating process of used lubricants include various types of sludge (e.g., acid sludge, soot sludge, used clays, and other impurities in used lubricants) depending on the process applied. Soot sludge can be mixed with asphalt and used as surfacing material and extender in paving the roads so that they become no longer hazardous to the environments (Weinstein et al., 1982; Mueller Associates Inc., 1989; CEPA, 1994). The technologies and processes commonly used today for the regeneration of used lubricant are summarized as follows:

4.6.1 Atmospheric Distillation

Atmospheric distillation (160 to180°C) is mainly used for the distillation of light hydrocarbon compounds in used lubricants such as gasoline, diesels, solvents, and water in used lubricants. The water separated from used lubricant can be further treated and used for cooling the plant or discharged into surface water (CEPA, 1994).

4.6.2 Vacuum Distillation

Vacuum distillation is commonly used to fractionate the hydrocarbon compounds that cannot be separated by atmospheric distillation. Those hydrocarbons usually have a molecular weight from medium to high and require a higher temperature for distillation. The typical pressure used in vacuum distillation is from 10 to 50 mm Hg. The hydrocarbon compounds distillated from this process can be sold as fuels or used as heating oils at the refineries (Byrant, 1989; U.S. DOE, 2006; Audibert, 2006).

4.6.3 Sulfuric Acid Process

Sulfuric acid has been used for refining oils (crude petroleum and animal oils) since the 1950s. In the case of used lubricants, the concentrated sulfuric acid (6 % to 98%) is used to oxidize the impurities in used lubricants (U.S. DOE, 1983). In order to prevent hydrocarbon compounds in used lubricants from oxidation, the operating parameters of acid treatment, such as temperature and resident time, have to be carefully controlled. The typical operating temperature for acid treatment is between 30 to 40°C. The resident time is controlled within 15 to 30 minutes (Audibert, 2006; California Integrated Waste Management Board., 2009).

Compared to other technologies, the cost of infrastructure and operation of acid treatment plant is low. The production yield of acid treatment plants is moderate. However, acid sludge and acid gas emission generated during the process of acid treatment are extremely hazardous to the environment (PEOTROF Refining Technologies, 2009; Mytol Petrotech, 2009; NHDC, 2009).

CaO or lime is commonly used to neutralize acid sludge. However, sludge usually cannot be completely neutralized and is still considered as a hazardous waste after neutralization (Hamad, et al., 2002). Other problems associated with this process include:

- The cost of the disposal of acid sludge is high.
- The locations for the storage of acid sludge are difficult to find.

These problems make this technology less favorable to the industries (U.S. DOE, 1983; Mytol, 2009).

4.6.4 Adsorption Process

Adsorbents, such as bauxite, silica gel, activated clay, are commonly used to separate either hydrocarbon compounds or impurities from used lubricants depending on the applications.

Activated clay is normally used to remove color and odor remaining in treated used lubricants after vacuum distillation or acid treatment. The resident time vary with the degree of contamination in used lubricants. Used clay can be recycled under the control of the temperature in the range of 150 to 330°C (Audibert, 2007).

The quality and yield of treated used lubricant may vary widely depending on the amount of contaminants in used lubricants. The adsorption efficiency may decline when adsorbent is saturated with impurities (MYTOL, 2009).

4.6.5 Hydroprocess

Combing hydrogen and solid catalysts under the control of the pressure (5 to 160 bar) is a common practice used to remove H_2S, NH_3, H_2O, and metals in petroleum refining (Auibert, 2007). Hydroproess also can be applied to the regeneration of used lubricants. Hydroprocess generally consists of two stages: 1) metals and metalloids removal and 2) sulfur and nitrogen compounds removal.

The first stage of hydro-treatment uses the similar concept as in refining of petroleum. Impurities are removed by mixing used lubricants with solid catalysts (CO-MO with alumina) in the presence of hydrogen. In order to minimize the saturation of catalyst, a pretrement is usually required in the first stage to reduce the impurities in used lubricants into an acceptable level (30-50 ppm). However, the recent improvement in catalyst structure (chestnut-bur structure) have made metal removal rate much higher (up to 60%) than the former design (up to 20%) (Auibert, 2007).

The second stage is used to remove sulfur and nitrogen compounds in used lubricants by alumina and Ni-Mo catalyst in spherical or extruded shape (Auibert, 2007).

4.6.6 Propane Extraction

Propane is commonly used to purify used lubricants by precipitating impurities out of oil phase under a high pressure (10 atm) (Mytol, 2009). Compared to other technology, propane extraction is economical because propane can be recycled and reused indefinitely. The quality of treated lubricants is relatively consistent.

A pretreatment is usually required for this process to remove large impurities in used lubricants in order to protect the plant from clogging (Auibert, 2007). Centrifugation is commonly combined with this process to settle the large impurities.

4.6.7 Thin Film Evaporation

In thin film evaporator, used lubricants are spread as a layer of solution over the hot surface. Oil phase in used lubricants is instantly evaporated from the hot surface and collected at the condenser next to evaporator or inside the evaporator depending on the design of system.

4.6.8 Centrifugation

Water and suspended impurities in used lubricants are difficult to settle by regular gravity due to the dispersive action of additives. Using the centrifugal force which is equivalent to thousand times of the gravitational force is one of the solutions to settle water and suspending impurities from used lubricants (Audibert 2006). However, centrifugation still cannot remove all impurities in used lubricants. Thus, centrifugation is commonly used as a pretreatment to eliminate large and heavy impurities in used lubricants, such as metal fragments from tear and wear of moving parts and sands.

Centrifugation is also employed to separate acid sludge in acid treatment process. Used clay used in acid treatment may soak up a considerable amount of treated lubricants which can be taken out by centrifugation in the finishing process.

4.7 Used Lubricant Regeneration Systems

Used lubricant is a complex mixture of various incompatible materials, such as liquid phase of hydrocarbons and solid phase of impurities. Thus, there is no single process or technology that can achieve all requirements needed for the regeneration of used lubricants. The conventional systems usually combine two or more processes as discussed in the previous section in order to regenerate used lubricants into an acceptable quality. Table 4-8 summaries the most popular systems used today for the regeneration of used lubricants.

Table 4-8. Systems for the Regeneration of Used Lubricants.

Process Name	Technologies
Clay bleaching	Atomospheric Distillation + Adsorption Process (Clay) + Centrifugation
Acid System	Atomospheric Distillation + Sulfuric Acid Process+ Adsorption Process (Clay or Activated carbon)+ Lime or CaO + Filteration or Centrifugation
Propane System	Atomospheric Distillation + Propane Extraction + Vacuum Distillation + Adsorption Process or Hydroprocess
Thermal System	Atomospheric Distillation + Thermal Process + Adsorption Process (Clay) or Hydroprocess
Hydrosystem	Atomospheric Distillation + Hydroprocess
Thin Film System	Atomospheric Distillation + Thin Film Evaporator (TFE) + Hydroprocess

4.8 Summary

It is very difficult to characterize used lubricants because the composition of used lubricants varies widely with the type and age of vehicles or machines, the service life of lubricants, the collecting places, and operating conditions. Impurities found in used lubricants may significantly affect the functions of lubricant and reduce the performance of engines or machines. The common impurities found in used lubricants are enumerated as follows:

- soot particles generated from frequent combustion of fuel;
- large soot aggregates irreversibly transformed from soot particles;
- large soot gel networks resulting from the interaction between dispersants in lubricant and soot aggregates;
- PAHs generated from the incombustible low-molecular-weight of aromatic hydrocarbon compounds;
- trace metals from the source of lubricant base oils, crude oils;
- metallic fragments from wear and tear of moving parts in engines or machines;
- oxidized metals from the corroded metal fragments in used lubricant;
- sand and dirt from collection places and during transit between collecting places; and
- water and moisture introduced into used lubricant by blowby vapors in the air, the leakage of the cooling system of vehicles, and the combustion of fuels

In addition to impurities mentioned above, used lubricants also contain considerable amounts of valuable hydrocarbon compounds, which can be regenerated by a proper treatment into energy sources or lubricant base materials.

Used lubricants are highly toxic to human health, animals, plants, and the natural environments. The study of the toxicity of used lubricants and the routes of exposure to them is the key to solve the associated problems as well as raise public awareness to proper handling in order to prevent them from being released to the environment.

Used lubricants can be regenerated into either lubricant base oils or an energy source. The benefits of used lubricant regeneration are enormous, including the conservation of natural resources and energy; the minimization of wastes and hazards; and the protection of human health and ecosystems.

CHAPTER 5

THEORETICAL BACKGROUND

5.1 Introduction

The major objective of this research is to develop a sustainable technology which is capable to effectively purify used lubricants and recover hydrocarbon compounds from used lubricants. "Environmentally friendly and cost effectiveness" are two important factors in the development of the new technology. The required criteria for this newly developed process are outlined below:

- The impurities need to be removed from used lubricants quickly and economically.
- The desirable hydrocarbon compounds need to be recovered from used lubricants quickly and economically.
- The regents used for used lubricants purification should be recyclable and reusable.
- The regents used for hydrocarbon compounds recovery should be recyclable and reusable.
- The energy consumption used for this system should be minimal.

This chapter covers the following topics: (1) the scientific approaches in used lubricant purification and hydrocarbon compounds recovery; (2) the selection of reagents used for the process; and (3) the sustainability design in the newly developed treatment system.

5.2 Scientific Theory and Approach

This novel treatment process is developed by a systematic approach based on experience, experimental results, and literature reviews. The following block diagram Figure 5-1 illustrates the phases involved in the process.

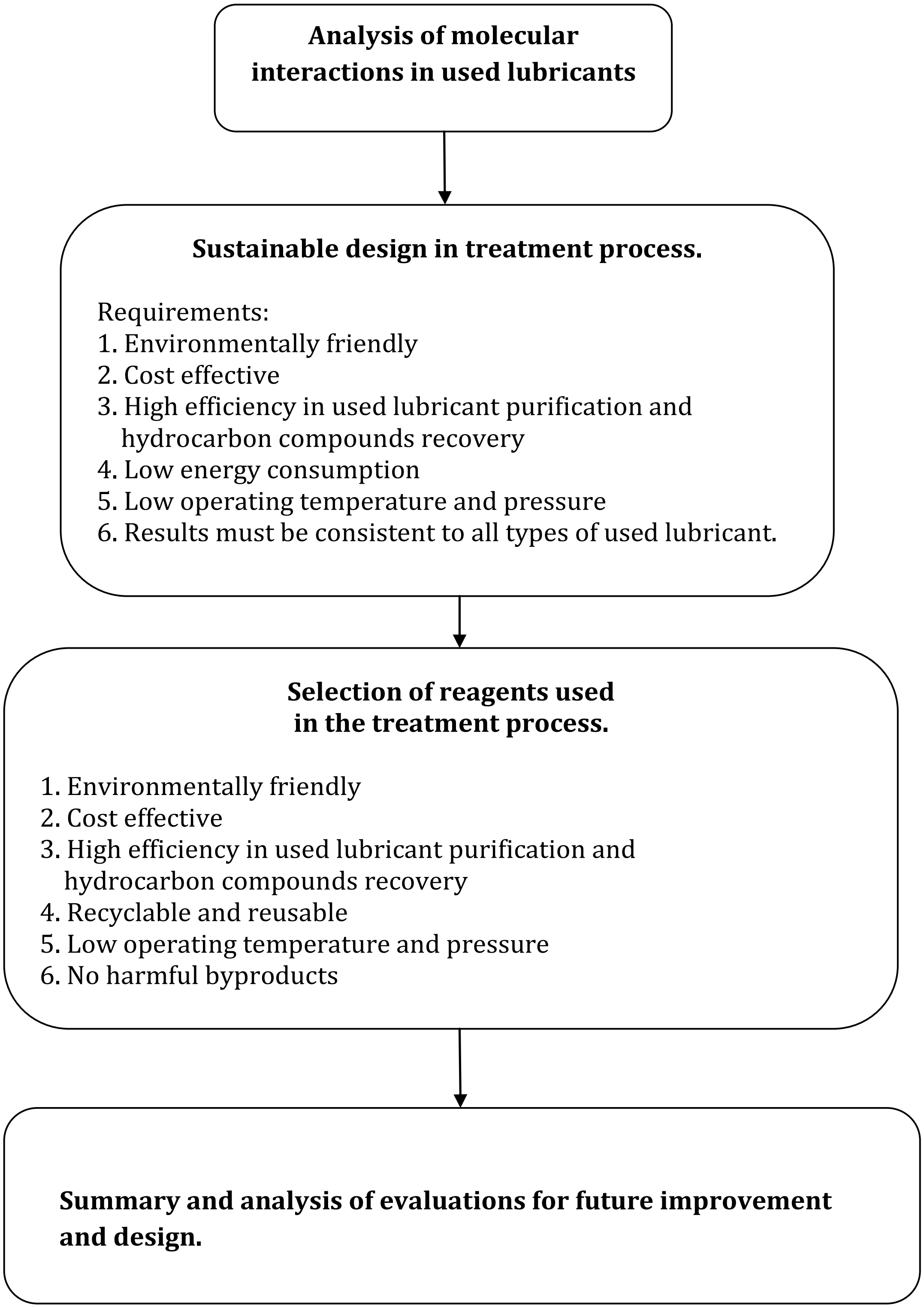


Figure 5-1. Scientific Approach in the Development of Used Lubricant Regeneration Process

5.2.1 Molecular Interactions in Used Lubricants

The analysis of molecular interactions between various components in used lubricants is an essential step in determining the treatment method as well as the selection of reagents in the newly developed treatment process.

As previously discussed in Chapter 4, used lubricant is a unique colloidal system which consists of a variety of impurities and various amounts of hydrocarbon compounds. The impurities must be removed before used lubricants can be regenerated into lubricant base materials or energy sources. Since used lubricant is a colloidal system, the destabilization of suspended impurities is the first logical step to do for purification. However, experiences have indicated that colloidal particles of used lubricants are different from those in water phase. Thus, coagulants used for water treatment didn't work for used lubricants. Since inorganic soot particles and organic hydrocarbon molecule are two incompatible materials; they should theoretically be placed in different categories based on their differences.

Experiences and experimental results indicate that utilizing the differences in solubility of organic solvents is a successful approach to separate them from each other. Furthermore, this approach follows the principles of sustainable design as mentioned in the previous section because organic solvents can be recycled and reused indefinitely.

5.2.2 Intermolecular Interaction and Solubility

The solubility of solute in solvent is determined by the intermolecular interaction between solvent and solute. The polar compounds normally have different intermolecular force from the non-polar compounds. The solubility of solute in solvent is greatly affected by the polarity of solvents and solutes as shown in Table 5-1 (Burke, 1984; Reichardt, C. 2003; Cheremisinoff, N.P. 2003).

Table 5-1. Solubility and Polarity of Solvent and Solute (Reichardt, C. 2003)

Solute	**Solvent**	**Interaction**			**Solubility of Solute in Solvent**
		Solute/ Solute	**Solvent/ Solvent**	**Solute/ Solvent**	
Non-Polar	**Non-Polar**	Weak	weak	weak	High
Non-Polar	**Polar**	Weak	strong	weak	Low
Polar	**Non-Polar**	Strong	weak	weak	Low
Polar	**Polar**	Strong	strong	strong	High

5.3 Solvent for Hydrocarbon Compounds Recovery

According to the principle shown in Table 5-2, utilizing the non-polar organic solvent to dissolve non-polar hydrocarbon compounds in used lubricants is considered as a logical and feasible approach for hydrocarbons recovery. However, since PAHs in used lubricants are not the target compounds for recovery in the study, the aromatic solvents have not been selected for this process.

Experimental results have confirmed that hexane (C_6H_{14}), as illustrated in Figure 5-2, is the most effective solvent used for hydrocarbons recovery because:

- It is inert to the dissolution condition.
- It is relatively economical.
- Most importantly, its boiling point, 156.2˚F (69˚C), is relatively low compared to other non-polar solvents so that it can be recycled at a lower temperature.
- It can be recycled and reused indefinitely.

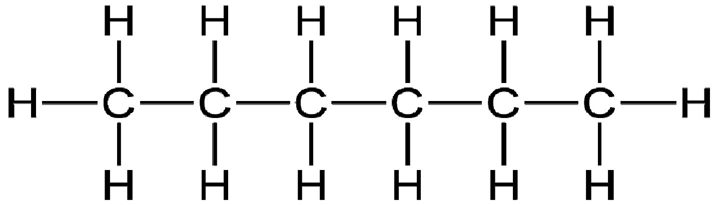


Figure 5-2. Molecular Structure of Hexane
(http://en.wikipedia.org/wiki/File:Hexane-2D-flat-B.png)

5.4 Solvent for Purification

Using hexane alone cannot settle the suspended impurities in used lubricant sample after used lubricant sample mixed with hexane as shown in Figure 5-3.

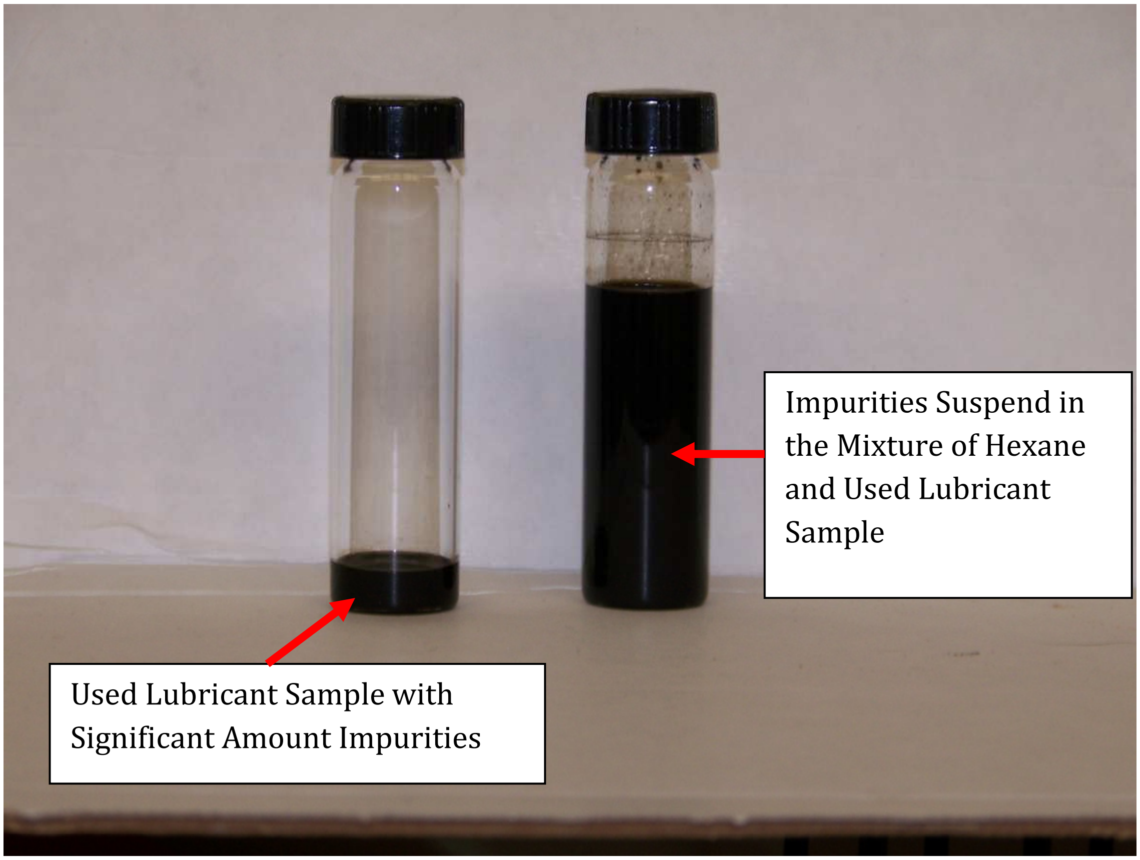


Figure 5-3. Hexane Could Not Settle the Impurities in Used Lubricant.

According to the theory of solubility and polarity as stated in Table 5, non-polar solutes are less likely to dissolve in polar solvents. Therefore, using polar solvents to control the suspended soot gel networks is a logical approach based on their incompatibility. Experimental results have confirmed that Dimethyl ketone (DMK) is the most effective polar solvent, which is capable to flocculate and settle impurities in used lubricants as shown in Figure 5-4.

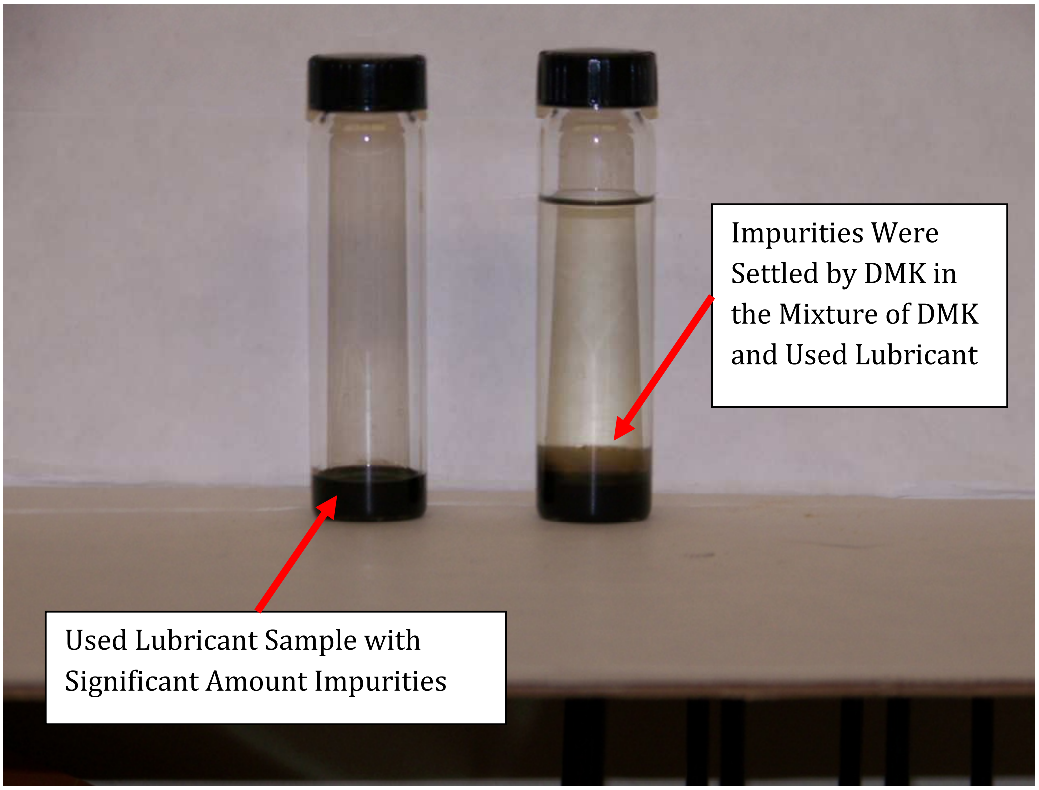


Figure 5-4. Impurities in Used Lubricant Are Settled by DMK.

DMK is a polar solvent with the formula (C_3H_6O) and has many advantages over other organic polar solvents.

- It is relatively economical.
- It is miscible with hexane.
- It is inert to the dissolution condition.
- Water is soluble in DMK so that water in used lubricants is simultaneously removed during the purification process.

- Its boiling point, 132.8°F (56°C), is relatively low so that it can be recycled at a lower temperature.
- It can be recycled and reused indefinitely.

Figure 5-5 illustrates the structure of DMK. The major intermolcular force involved in liqud include dipole-dipole interaction force and weak van der Waals between the methyl groups (Max, et al., 2007).

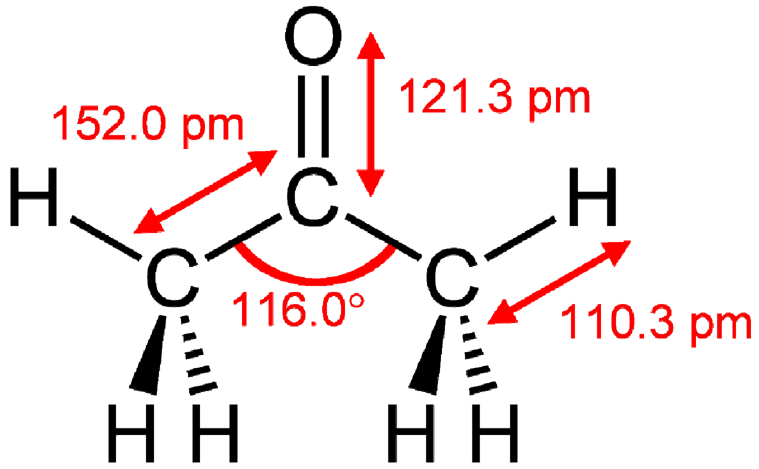
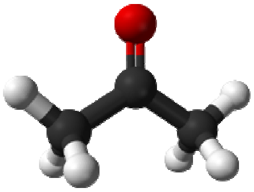
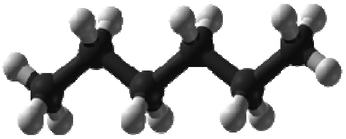


Figure 5-5. Molecular Structure of DMK.
(http://en.wikipedia.org/wiki/File:Acetone-CRC-MW-ED-dimensions-2D.png)

The general characteristics of DMK and hexane are summarized in Table 5-.2.

Table 5-2. General Characteristics of DMK and Hexane.

	Dimethyl Ketone (DMK)	**Hexane**
Chemical formula[a]	C_3H_6O	C_6H_{14}
Molecular weight[a] **(g/mole)**	58.0791	86.1754
Chemical structure[b]		
Other names[a]	2-Propanone; â-Ketopropane; Dimethylformaldehyde; Methyl ketone; Propanone; Pyroacetic ether; Dimethylketal; Ketone propane; Sasetone; Chevron acetone	n-Hexane; Skellysolve B; Esani; Heksan; Hexanen; Hexyl hydride; Gettysolve-B; NCI-C60571; UN1208; Exxsol hexane
Dielectric Constant[c]	20.7	2.02
Dipole Moment[c]	2.88	N/A
Boiling Point[c]	132.8˚F (56˚C)	156.2˚F (69˚C)

a. NIST, 2009
b. wikimedia, 2009
c. USM, 2009

5.5 Binary Solvent Process

In order to perform purification and energy recovery simultaneously, it is the best practice to mix hexane with DMK as one chemical system for both tasks. DMK and hexane are perfectly compatible to mix with each other in any ratios without having any negative effects. However, the dipole-dipole interactions changes inversely with the amount of hexane in the mixture.

5.6 Evaluation of Binary Solvent Process

Figure 5-6 confirms the result of binary solvent process as expected. Binary solvent process is capable to purifying used lubricants and recovering hydrocarbon compounds simultaneously under atmospheric pressure and at room temperature. Used organic solvents can be recycled and reused infinitely.

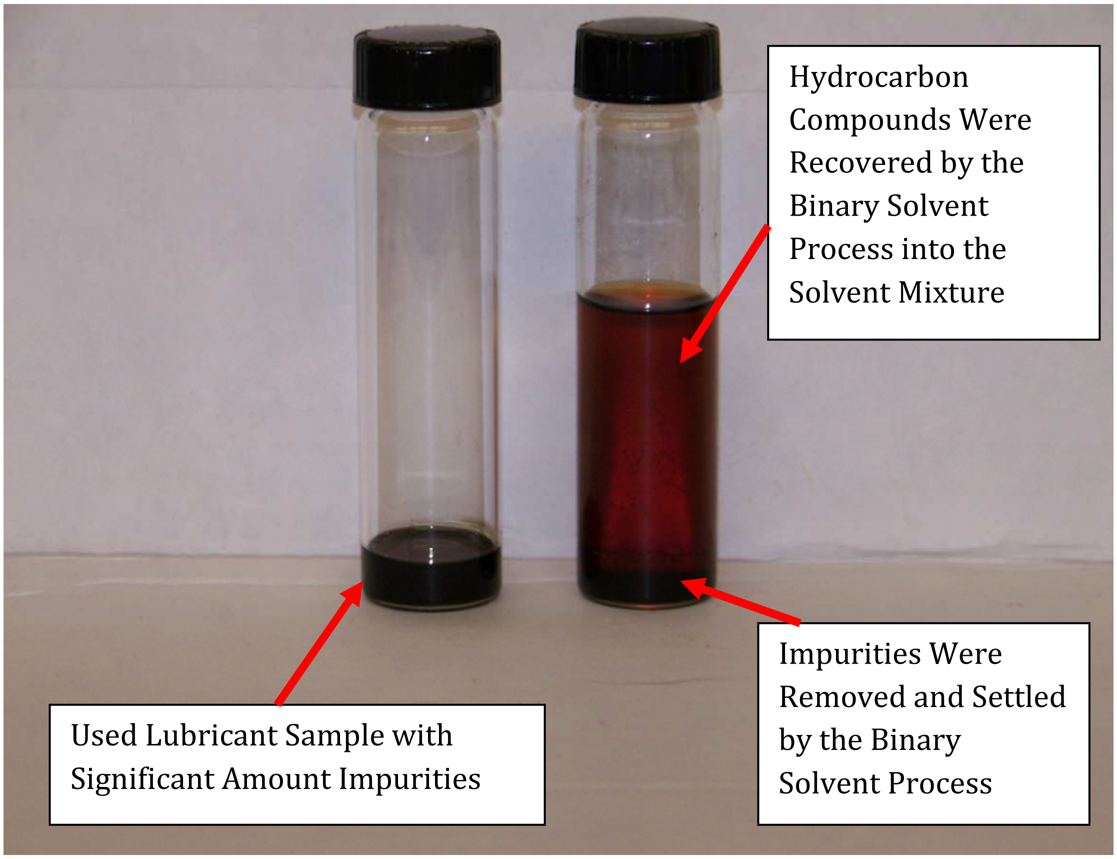


Figure 5-6. Binary Solvent Process Is Capable of Purifying Used Lubricants and Recovering Hydrocarbon Compounds from Used Lubricants Simultaneously under Atmospheric Pressure and Room Temperature.

The boiling point of solvent mixture, 156.2˚F (69˚C), is relatively low so that solvent mixture can be recycled at a low temperature, which follows the principle of sustainable design and the efficient use of energy. An added advantage of the binary solvent process is that water content of used lubricants is also removed. Water is dissolved in DMK through hydrogen bonding between the OH and carbonyl groups, C=O (Burke, 1984). Water and solvent mixture can be separated by distillation based on the difference between the boiling point of solvent mixture and the boiling point of water.

5.7 Summary

Understanding of intermolecular reactions between various molecules in used lubricants is essential for the development of effective treatment process for used lubricant purification and energy recovery.

Experiences and experimental results have confirmed that binary solvent process is capable of effectively settling suspended impurities in used lubricants and recovering hydrocarbon compounds under atmospheric pressure and at room temperature. Furthermore, organic solvents, DMK and hexane, used for this process can be recycled and reused indefinitely under atmospheric pressure and a relatively low temperature. Thus, the design of binary solvent process is sustainable, environmentally friendly, and cost effective.

CHAPTER 6

EXPERIMENTAL METHODS

6.1 Introduction

This chapter presents: 1) the bench-scale study of the binary solvent process in purification and hydrocarbon compounds recovery on three different compositions of used lubricants: mineral-based, synthetic, and mixed different types; and 2) the introduction of a binary system matrix, which is a newly designed analytic method used to determine the most effective combination in the binary solvent process in order to minimize the consumption of solvents and maximize the efficiency of binary solvent process.

The newly developed binary solvent process has been demonstrated as a promising technology capable of removing up to 93% of impurities while recovering up to 99 % of hydrocarbon compounds from various types of used lubricants under atmospheric pressure and room temperature. Furthermore, the binary solvent process is a sustainable technology. Organic solvents used in this process can be recycled and reused indefinitely. However, the use of excess amount of organic solvents is neither economically favorable nor environmentally friendly. Thus, how to effectively use organic solvents is the major concern in the binary solvent process.

The content of impurities and hydrocarbon compounds found in used lubricants vary widely. In order to effectively use organic solvents in the binary solvent process, the binary system matrix was designed as an analytical tool to determine the most effective utilization of organic solvents in the binary solvent process. This newly designed analytical method has successfully demonstrated as an accurate technique to enhance the binary solvent process to achieve the best result for different types of used lubricant samples. The optimal results in purification and hydrocarbon compounds recovery can be achieved as the mixing ratio (wt. %) of hexane and DMK is 1 to 3 for used mineral-based motor oils, 1 to 2 for used synthetic motor oils, and 1 to 3 for mixed used lubricants. The most effective mixing ratio (Wt. %) of used lubricant and solvent mixture is 1 to 9 for all samples.

6.2 Materials

6.2.1 Used Lubricant Samples

As previously discussed, the base oils used for making lubricants are generally derived from three different sources: petroleum or mineral-based oils, synthetic chemical compounds, and bio-based oils.

The binary solvent process developed from this research is primarily focusing on how to convert used motor oils, made by either petroleum-based oils or synthetic compounds, into an economically competitive energy source.

Mineral-based motor oils are the most popular engine oils used for most of service stations and car dealers today in the United States. Synthetic motor oils are more expensive and used upon special request only. Bio-based motor oils are more popular in European countries than the United States, where bio-based motor oils are very difficult to find at auto parts stores.

In order to confirm the versatile capability of the binary solvent process, a total of twenty different types of used lubricant samples were used for the feasibility study of binary solvent process. The samples were divided into three categories: 1) used mineral-based motor oils from various types of cars and manufactures, 2) used synthetic motor oils from different types of cars and manufactures, and 3) mixed used motor oils and lubricants collected from various sources of unknown types of cars and machines.

Table 6-1 shows used mineral based motor oil samples collocated from various types of vehicles and locations. Mineral-based motor oils used for this part of experiment were purchased from Auto Zone auto parts store.

Table 6-1. Used Mineral-Based Motor Oil Samples.

Sample	Sampling Place	Source	Year	Remark
A	Rowland Heights, CA	Passenger car	2009	Single source (American Cadilac)
B	Rowland Heights, CA	Passenger car	2009	Single source (Japanese Camary)
C	Rowland Heights, CA	SUV	2009	Single source (Japanese RAV 4)
D	USC, BHE 201A	Passenger cars	2009	Mixture of sample A and B
E	USC, BHE 201A	Passenger cars and SUV	2009	Mixture of sample C and D

Table 6-2 shows used synthetic motor oil samples collocated from various types of vehicles and locations. Synthetic motor oils used for this part of experiment were purchased from Pep Boy auto parts store.

Table 6-2. Used Synthetic Motor Oil Samples.

Sample	Sampling Place	Source	Year	Remark
F	Rowland Heights, CA	Passenger car	2009	Single source (American Cadilac)
G	Rowland Heights, CA	Passenger car	2009	Single source (Japanese Camary)
H	Rowland Heights, CA	SUV	2009	Single source (Japanese RAV 4)
I	USC, BHE 201A	Passenger cars	2009	Mixture of sample F and G
J	USC, BHE 201A	Passenger cars and SUV	2009	Mixture of sample H and I

In actuality, different types and classes of used lubricants are collected and mixed in storage containers, such as barrels or tanks, at collection centers, representing a more realistic composition of used lubricants than the sample from single source. Table 6-3 shows used lubricant samples collocated from various collection centers.

Table 6-3. Used Lubricant Samples Collected from Various Vehicles, Machines, and Places.

Sample	Sampling Place	Source	Year	Remark
K	Golden Eagle	Salt Lake City, Utah	2008	Mixture of different sources (locomotives)
L	Golden Eagle	Salt Lake City, Utah	2008	Mixture of different sources (locomotives and cars)
M	Golden Eagle	Salt Lake City, Utah	2008	Mixture of different sources (locomotives)
N	Golden Eagle	Salt Lake City, Utah	2008	Mixture of different sources (locomotives, cars, and machines)
O	Golden Eagle	Salt Lake City, Utah	2009	Mixture of different sources (locomotives)
P	Golden Eagle	Salt Lake City, Utah	2009	Mixture of different sources (locomotives and cars)
Q	Golden Eagle	Salt Lake City, Utah	2009	Mixture of different sources (locomotives, cars, and machines)

Table 6-3. (Continued)

Sample	Sampling Place	Source	Year	Remark
R	North State Environmental	Los Angeles, CA	2008	Mixture of different sources (passenger cars)
S	North State Environmental	Los Angeles, CA	2009	Mixture of different sources (passenger cars)
T	Jeffy Lube	Los Angeles, CA	2009	Mixture of different sources (cars)

6.2.2 Organic Solvents

As previously discussed in Chapter 5, Di-methyl ketone (DMK) was selected as the most effective polar organic solvent for used lubricant purification. Hexane was selected as the most suitable non-polar organic solvents for hydrocarbon compounds recovery. Both organic solvents were purchased from VWR Inc (USC, Los Angeles).

6.3 Experimental Methods

6.3.1 Binary Solvent Process

The binary solvent process utilizes solubility difference to achieve phase separation in used lubricants. In the process, DMK is used to control and settle suspended inorganic impurities in used lubricants, and hexane is used to recover the hydrocarbon compounds from used lubricants.

6.3.1.1 Hydrocarbon Compounds Recovery Mechanism

Non-polar hydrocarbon compounds in used lubricants are soluble in hexane. Inorganic impurities, such as soot particles, metals, dust, and sand are insoluble in hexane. Thus, hexane is used to separate hydrocarbon compounds from impurities based on the solubility difference to achieve phase separation in used lubricant.

6.3.1.2 Purification Mechanism

Using hexane alone cannot settle the suspended impurities in used lubricants after non-polar hydrocarbon compounds are dissolved in hexane. Thus, DMK is combined with hexane and utilized to settle the suspended impurities while non-polar hydrocarbon compounds are dissolving in hexane.

6.3.1.3 Solvents Recycle

Environmentally friendly and sustainability are two major requirements in the development of the binary solvent process. Both polar and non-polar solvents used in this process can be recycled and reused indefinitely by atmospheric distillation at a relatively low temperature, 156.2˚F (69˚C). The use of recyclable solvents and the operation at low temperature always lead to a low operation cost.

6.4 Analytical Methods for Efficiency Determination

Gravimetric method, EPA Method 9071B, was used to quantify the amount of hydrocarbon compounds and impurities in each used lubricant sample before and after the treatment process.

6.4.1 Purification Efficiency

Purification efficiency for each sample was calculated by using the following formula based on the percent removal from the original amount to the purification process.

$$Purification\ Efficiency(\%) = \left(\frac{Original\ \mathrm{Im}purty\ Concentration - \mathrm{Im}purty\ Concentration\ after\ Treatment}{Original\ \mathrm{Im}purty\ Concentration}\right)\times 100$$

where:

Original Impurities Concentration
= impurities (g) / 100g of used lubricant sample

Impurities Concentration after Treatment
= impurities (g) / 100g of used lubricant sample after treatment

6.4.2 Hydrocarbon Compounds Recovery Efficiency

Hydrocarbon compounds recovery efficiency for each sample was calculated by using the following equation based on the percent recovered from original concentration to the recovery process.

$$\mathrm{Recov}\mathit{ery\ Efficiency}(\%)$$
$$=\left(\frac{\mathit{Original\ Hydrocarbon\ Concentration} - \mathit{Hydrocarbon\ Concentration\ after\ Treatment}}{\mathit{Original\ Hydrocarbon\ Concentration}}\right)\times 100$$

where:

Original Hydrocarbon Concentration
= Hydrocarbons (g) / 100g of used lubricant sample

Hydrocarbon Concentration after Treatment
= Hydrocarbons (g) / 100g of used lubricant sample after treatment

6.5 Determination of the Most Effective Mixing Ratio

As previously discussed in Chapter 4, the content of impurities and hydrocarbon compounds found in used lubricants vary widely. Using excess amounts of solvents in binary solvent process is neither economically favorable nor environmentally friendly.

Thus, how to minimize the consumption of organic solvents and maximize the efficiency of process are the major concerns in binary solvent process.

6.5.1 Binary System Matrix

Binary system matrix as shown in Figure 6-1 is designed to determinate the most effective mixing ratio for solvents in the solvent mixture as well as the optimal efficiency in binary solvent process.

U.L. : S.M. (Wt. %)

1:9	1	2	3	4	5
1:4	6	7	8	9	10
1:3	11	12	13	14	15
1:2	16	17	18	19	20
	1:9	**1:4**	**1:3**	**1:2**	**1:1**

Hexane : DMK (Wt. %)

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-1. Binary System Matrix.

As illustrated in Figure 6-1, there are four components in a binary system matrix: 1) used lubricant, 2) solvent mixture, 3) hexane, and 4) DMK. The x-axis represents various mixing ratios (% wt.) for used lubricant and solvent mixture. The y-axis represents various mixing ratios (% wt.) for hexane and DMK. Each grid (1 to 20) will have either purification efficiency or hydrocarbon compounds recovery efficiency and a corresponsive mixing ratio of x and y, which is able to achieve that efficiency.

For each used lubricant sample, two matrixes are required to determine the most effective mixing ratio, which can achieve the optimal result for both purification and hydrocarbon compounds recovery. One is used to determinate the most effective mixing ratio for the optimal purification. Another is used for the determination of the most effective mixing ratio for the optimal result in hydrocarbon compounds recovery. As a result, the most effective mixing ratio for both tasks can be accurately determined by superimposing these two matrixes.

6.6 Results and Discussion

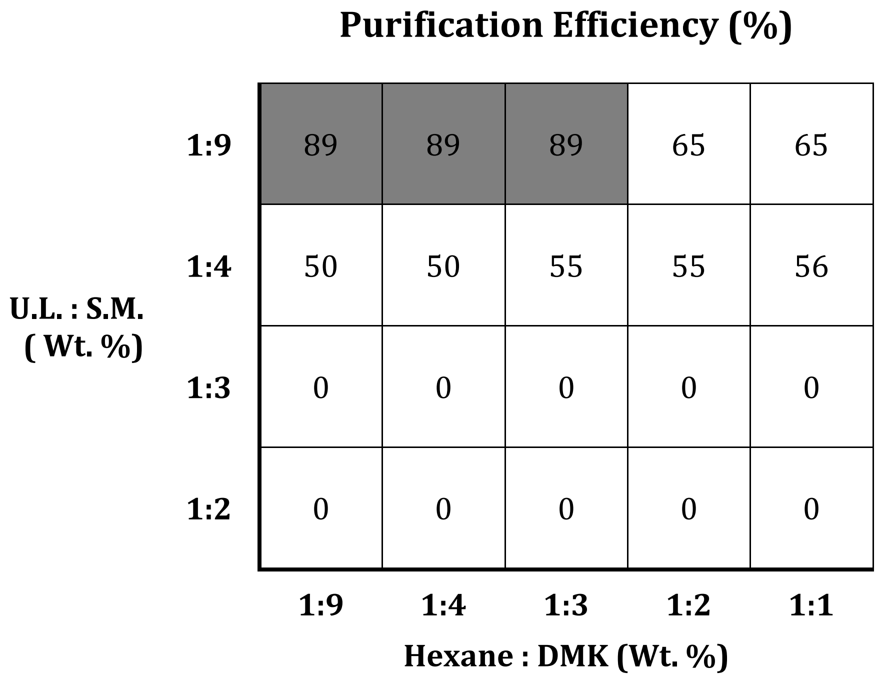
The composition of used motor oil sample is the most crucial factor that will affect the result of binary solvent. The base oil is the main component in each used lubricant sample that needs to be recycled by the binary solvent process. The manufacturing processes of base oils would determine the characteristics of different classes of lubricant. Therefore, the processes and property of each type of hydrocarbon compound will be briefly reviewed in the following sections.

6.6.1 Feasibility Study on Used Mineral-Based Motor Oils

Mineral-based motor oils are derived from petroleum feedstock into the lubricant base oils by either separation processes or conversion processes depending on the lubricant applications and specific requirements. Paraffin feedstock derived from crude oils are the most popular materials used today for producing mineral based oils because they are more stable than aromatic and olefins. The feedstock can be further refined into different grades of base oils by either separation processes or conversion processes, such as group 1, 2, and 3 mineral base oils as previously discussed in Chapter 3.

Group 1 base oils are conventional mineral oils derived from the selected fractions of crude oil distillation, a typical separation process; group 2 and 3 mineral base oils are commonly produced by modern hydroprocessing technologies (conversion processes), such as hydrotreating, hydrocracking, wax hydroisomrization, and hydrofinishing. Group 2 and 3 base oils normally contain more than 90% of saturated hydrocarbon compounds and less than 300 ppm of sulfur compounds.

Figure 6-2, 6-3, and 6-4 illustrate the analysis of the most effective mixing ratio for used lubricant sample A, a sample of used mineral-based motor oil from a single source. The optimal result in purification is 89% from the grid no. 1 to 3 as shown in Figure 6-2. The optimal result in hydrocarbon compounds recovery is 98% on the grid No. 3, 4, 5, 8, 9 and 10 as shown in Figure 6-3. The most effective ratio for both tasks is determined by superimposing Figure 6-2 and 6-3. As a result, the most effective mixing ratio for both tasks is on grid No.3 in which the most effective mixing ratio of hexane to DMK is 1:3, and the most effective used lubricant to solvent mixture is 1:9 as shown in Figure 6-4.



Purification Efficiency (%)

U.L. : S.M. (Wt. %)	1:9	1:4	1:3	1:2	1:1
1:9	89	89	89	65	65
1:4	50	50	55	55	56
1:3	0	0	0	0	0
1:2	0	0	0	0	0

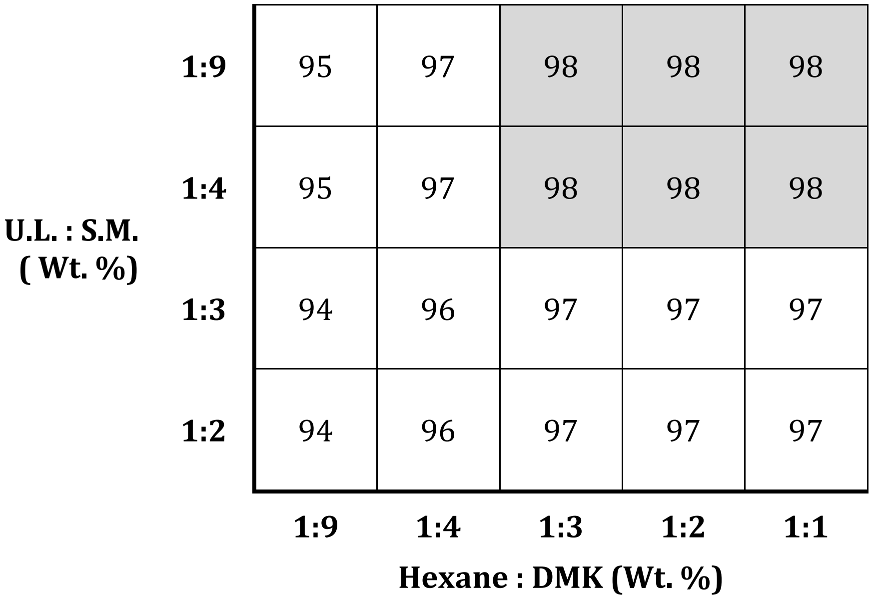
Hexane : DMK (Wt. %)

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-2. Most Effective Mixing Ratios for the Optimal Results in Purification for Sample A.

Hydrocarbon Compounds
Recovery Efficiency (%)

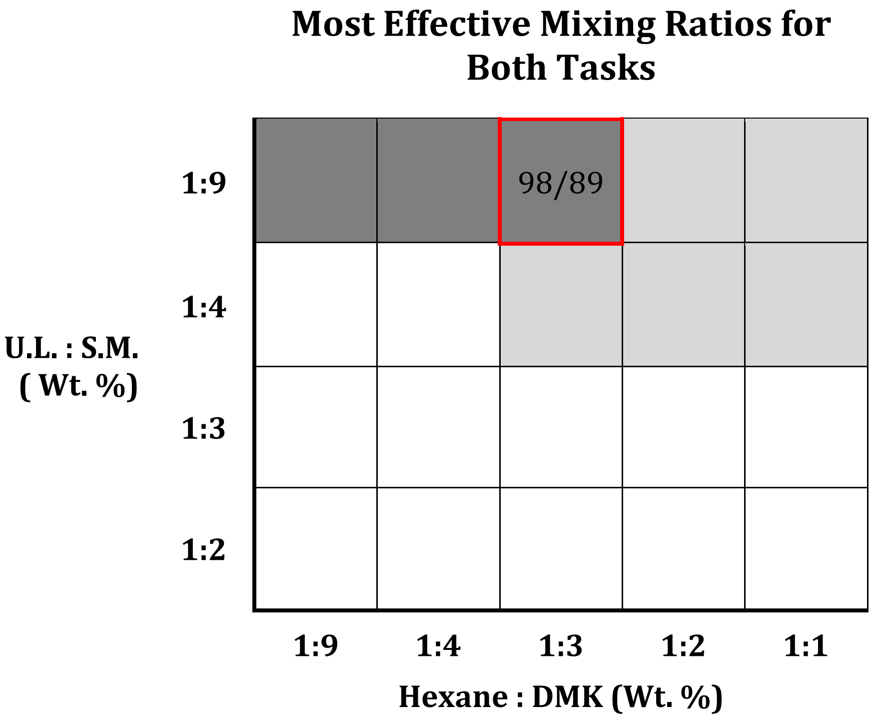


U.L. : S.M. (Wt. %) \ Hexane : DMK (Wt. %)	1:9	1:4	1:3	1:2	1:1
1:9	95	97	98	98	98
1:4	95	97	98	98	98
1:3	94	96	97	97	97
1:2	94	96	97	97	97

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-3. Most Effective Mixing Ratios for the Optimal Result in Hydrocarbon Compounds Recovery for Sample A.



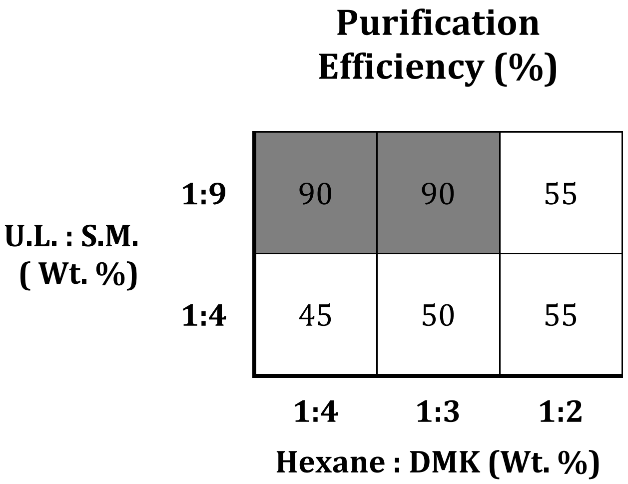
Remarks:

U.L. : Used Lubricant
S.M : Solvent Mixture

Figure 6-4. Most Effective Mixing Ratio Is Determined by Superimposing the Results of Figure 6-2 and 6-3.

The same analytical procedures were used for sample B to determine the most effective mixing ratio for used lubricant purification and hydrocarbon compounds recovery. However, this time binary system matrix was narrowed down to the area in which the most effective mixing ratio may locate based on the results of sample A as shown in Figure 6-4.

Figure 6-5, 6-6, and 6-7 illustrate the analytical procedures for sample B. The most effective ratio for both tasks is determined by superimposing Figure 6-5 and 6-6. As a result, the most effective mixing ratio is located at the grid no.3 in which the most effective mixing ratio of hexane to DMK is 1:3, and the most effective mixing ratio of used lubricant to solvent mixture is 1:9 as shown in Figure 6-7.



Purification Efficiency (%)

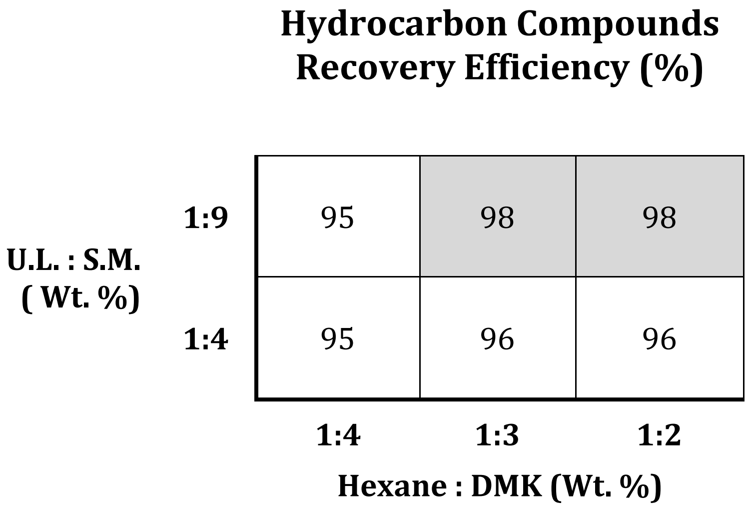
U.L. : S.M. (Wt. %)	1:4	1:3	1:2
1:9	90	90	55
1:4	45	50	55

Hexane : DMK (Wt. %)

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-5. Most Effective Mixing Ratios for the Optimal Result in Purification for Sample B.



Hydrocarbon Compounds Recovery Efficiency (%)

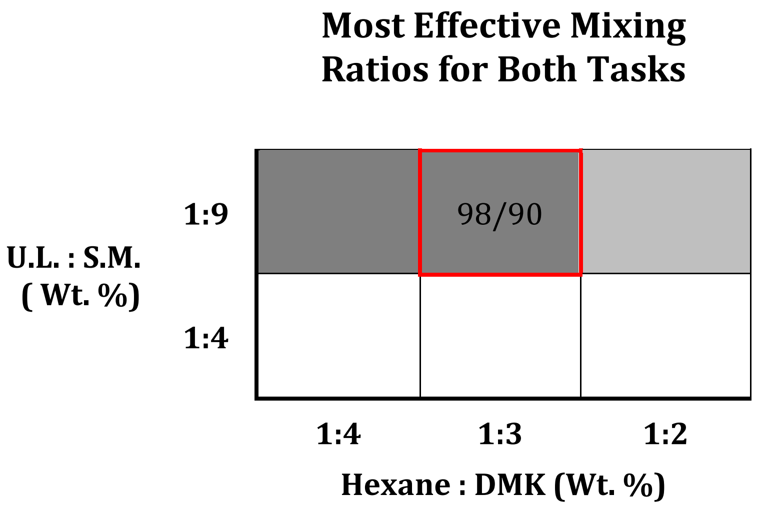
U.L. : S.M. (Wt. %)	1:4	1:3	1:2
1:9	95	98	98
1:4	95	96	96

Hexane : DMK (Wt. %)

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-6. Most Effective Mixing Ratios for the Optimal Result in Hydrocarbon Compounds Recovery for Sample B.



	1:4	1:3	1:2
1:9		98/90	
1:4			

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-7. Most Effective Mixing Ratio Is Determined by Superimposing the Results of Figure 6-5 and 6-6.

The same analysis was performed for sample C to E, used mineral-based motor oils. Table 6-4 shows the efficiency of purification on each sample.

Table 6-4. Impurity Removal Efficiency for Used Mineral-Based Motor Oil Samples.

Sample	**Impurities Concentration (g/100g of Sample)**		**Purification Efficiency (%)**
	Original	**After Treatment**	
A	10.7	1.6	85
B	30.5	2.7	91
C	19.4	1.9	90
D	17.4	1.8	90
E	16.0	1.5	91

Table 6-5 shows the efficiency of hydrocarbon compound recovery on each sample. Table 6-6 shows the most effective mixing ratios which can achieve the optimal results in used lubricant purification and hydrocarbon compounds recovery on each sample.

Table 6-5. Hydrocarbon Compounds Recovery Efficiency for Used Mineral-Based Motor Oil Samples.

Sample	**Hydrocarbon Compounds Concentration (g/100g of Sample)**		**Hydrocarbon Compounds Recovery Efficiency (%)**
	Original	**After Treatment**	
A	81.4	2.5	96.9
B	61.5	1.4	97.7
C	71.6	1.0	98.6
D	70.0	1.0	98.6
E	70.0	1.0	98.6

Table 6-6. Most Effective Mixing Ratios for Used Mineral-Based Motor Oil Samples to Achieve the Optimal Results in Used Lubricant Purification and Hydrocarbon Compounds Recovery.

Sample	**Mixing Ratio (wt. %)**	
	Used Lubricant/ Solvent Mixture	**Hexane/DMK**
A	1:9	1:3
B	1:9	1:3
C	1:9	1:3
D	1:9	1:3
E	1:9	1:3

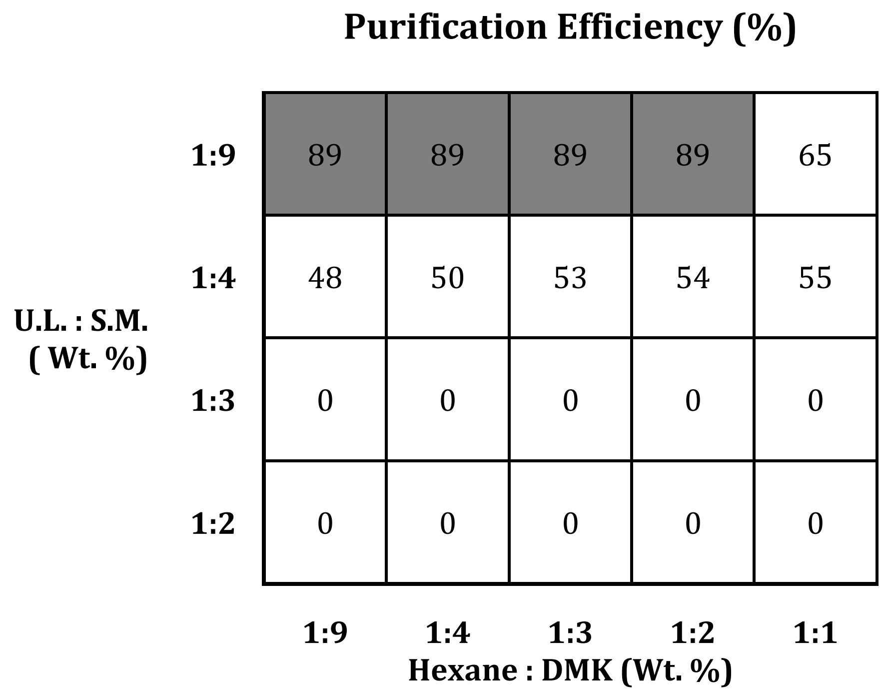
6.6.2 Feasibility Study on Used Synthetic Motor Oils

The same procedure was performed for used synthetic motor oils collected from various vehicles as shown Table 6-2. As its name suggested, synthetic motor oil is made of engineered based oil and various lubricant additives for the specific functions.

Synthetic based oils are commonly produced by chemically synthesizing low molecular weight compounds, which are primarily derived from petroleum. The molecular structures of synthetic base oils are usually specially made for specific lubricant applications, such as high boiling points and high temperature stability.

The typical examples of synthetic base oil include synthesized hydrocarbon fluids (e.g, polyalphaolefins, polybutenes), organic esters (e.g., polyol ester, dibasic aid ester), silicate esters, polyglycols (e.g., polyalkylene, polyoxyaklylene, polyethers, polyglyco esters), phosphate esters (e.g, triaryl phosphate ester, triakyl phosphate esters), silicones, and silicate esters. Esters are becoming the most popular synthetic base oils used today in the lubricant market due to their superior performance at high temperature.

The optimal results in purification and hydrocarbon compounds recovery for used synthetic motor oil sample F was determined as illustrated in Figure 6-8, 6-9, and 6-10. The optimal result in purification is 89% from the grid no. 1 to 4 as shown in Figure 6-8, while the optimal result in hydrocarbon compounds recovery is 98% on the grid no. 4, 5, 9, and 10 as shown in Figure 6-9. The most effective ratio for both tasks was determined by superimposing Figure 6-8 and 6-9 as illustrated in Figure 6-10. As a result, the most effective mixing ratio for both tasks falls into the grid no.4 in which the most effective mixing ratio of hexane to DMK is 1:3, and the most effective used lubricant to solvent mixture is 1:9 as shown in Figure 6-10.



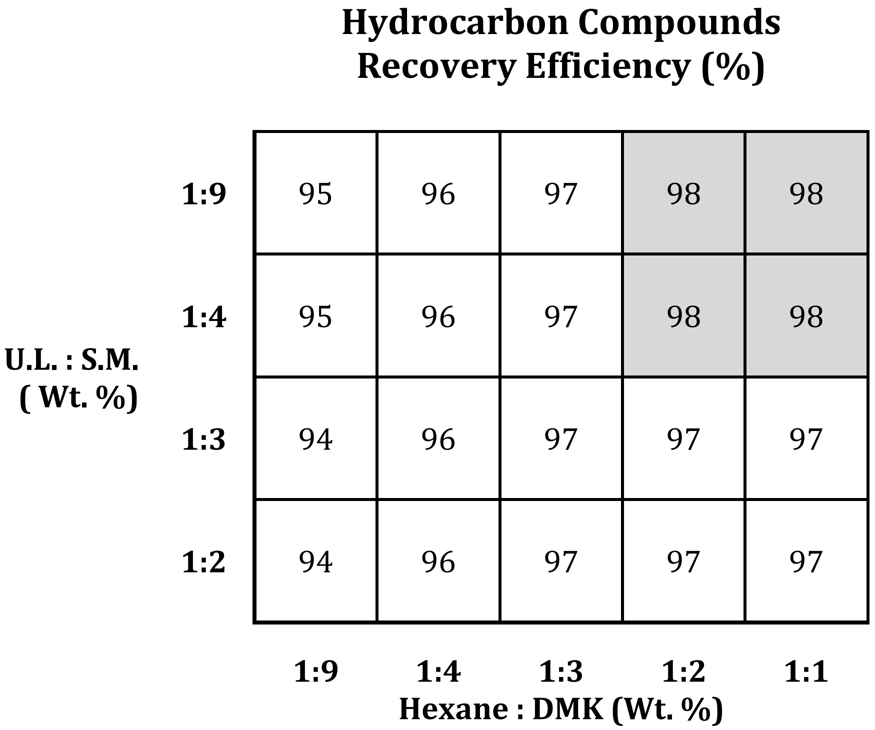
Purification Efficiency (%)

U.L. : S.M. (Wt. %) \ Hexane : DMK (Wt. %)	1:9	1:4	1:3	1:2	1:1
1:9	89	89	89	89	65
1:4	48	50	53	54	55
1:3	0	0	0	0	0
1:2	0	0	0	0	0

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-8. Most Effective Mixing Ratios for the Optimal Results in Purification for Sample F.



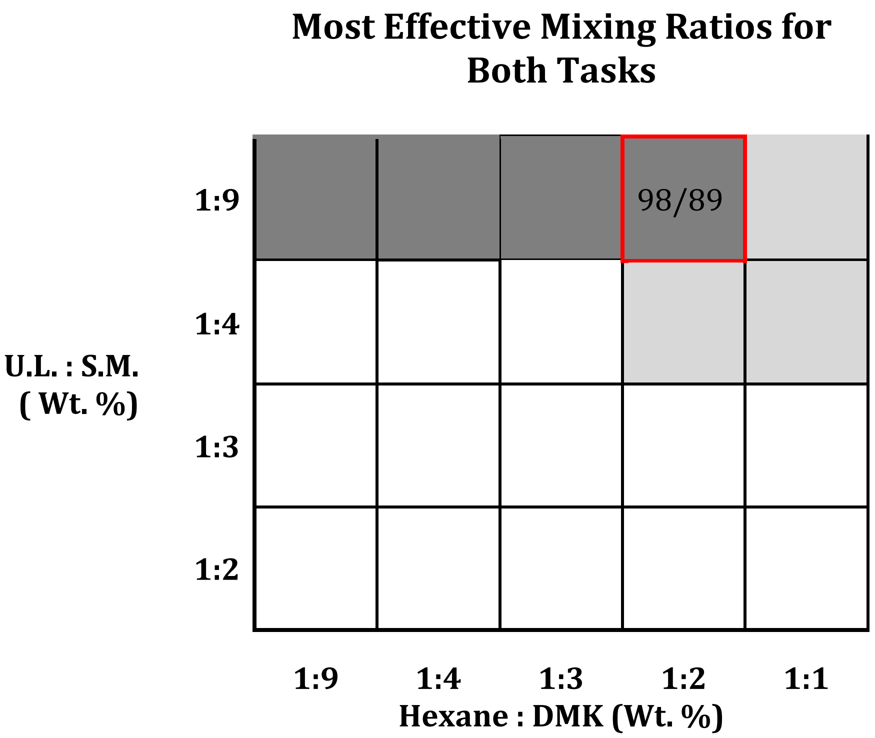
Hydrocarbon Compounds Recovery Efficiency (%)

U.L. : S.M. (Wt. %) \ Hexane : DMK (Wt. %)	1:9	1:4	1:3	1:2	1:1
1:9	95	96	97	98	98
1:4	95	96	97	98	98
1:3	94	96	97	97	97
1:2	94	96	97	97	97

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-9. Most Effective Mixing Ratios for the Optimal Result in Hydrocarbon Compounds Recovery for Sample F.



U.L. : S.M. (Wt. %)	1:9	1:4	1:3	1:2	1:1
1:9	▓	▓	▓	▓ 98/89	░
1:4				░	░
1:3					
1:2					

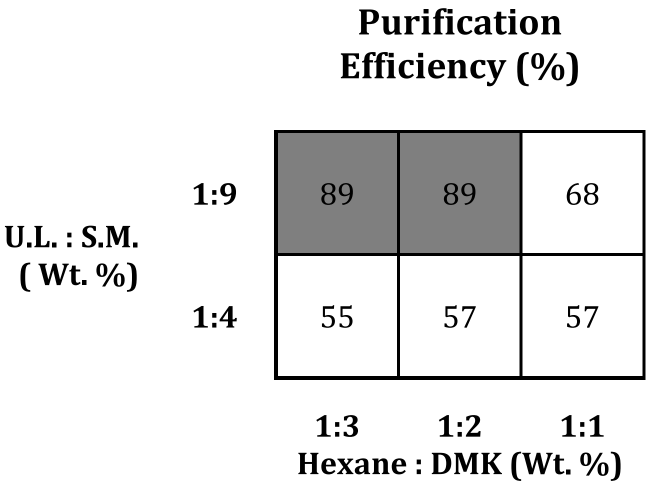
Remarks:

U.L. : Used Lubricant
S.M : Solvent Mixture

Figure 6-10. Most Effective Mixing Ratio Is Determined by Superimposing the Results of Figure 6-8 and 6-9.

The same analytical procedures were used for sample G to determine the most effective mixing ratio for purification and hydrocarbon compounds recovery. However, similar to the result of sample F, this binary system matrix was narrowed down to the area with the most effective mixing ratio, as shown in Figure 6-10.

Figure 6-11, 6-12, and 6-13illustrate the analytical procedures for sample G. The most effective ratio for both tasks is determined by superimposing Figure 6-11 and 6-12. As shown in Figure 6-13, the most effective mixing ratio is located at the grid no.4 in which the most effective mixing ratio of hexane to DMK is 1:3, and the most effective mixing ratio of used lubricant to solvent mixture is 1:9.



Purification Efficiency (%)

U.L. : S.M. (Wt. %) \ Hexane : DMK (Wt. %)	1:3	1:2	1:1
1:9	89	89	68
1:4	55	57	57

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-11. Most Effective Mixing Ratios for the Optimal Result in Purification for Sample G.

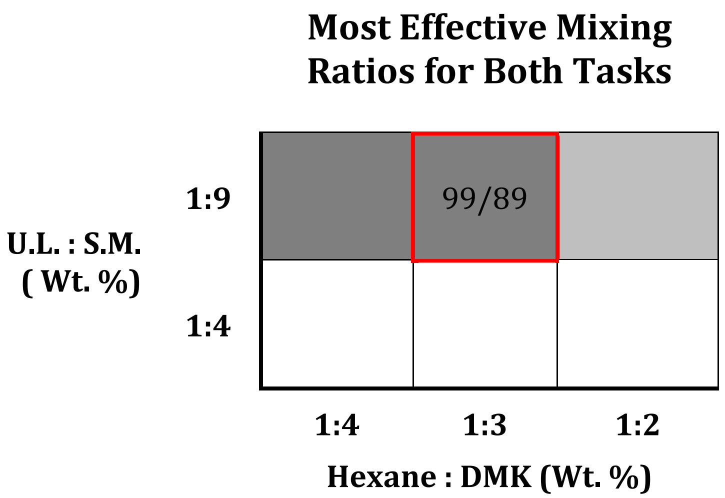
Hydrocarbon Compounds Recovery Efficiency (%)

U.L. : S.M. (Wt. %)	Hexane : DMK (Wt. %) 1:3	Hexane : DMK (Wt. %) 1:2	Hexane : DMK (Wt. %) 1:1
1:9	96	99	99
1:4	95	95	95

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-12. Most Effective Mixing Ratios for the Optimal Result in Hydrocarbon Compounds Recovery for Sample G.



Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-13. Most Effective Mixing Ratio Is Determined by Superimposing the Results of Figure 6-11 and 6-12.

The same analysis was performed for sample H to J, used mineral-based motor oils. Table 6-7 shows the efficiency of purification for each sample. Table 6-8 shows the efficiency of hydrocarbon compound recovery for each sample.

Table 6-7. Impurity Removal Efficiency for Used Synthetic Motor Oil Samples.

Sample	**Impurities Concentration (g/100g of Sample)**		**Purification Efficiency (%)**
	Original	**After Treatment**	
F	12.0	1.2	90
G	19.0	2.0	89
H	15.0	1.5	90
I	16.0	1.8	89
J	16.0	1.8	89

Table 6-8. Hydrocarbon Compounds Recovery Efficiency for Used Synthetic Motor Oil Samples.

Sample	**Hydrocarbon Compounds Concentration (g/100g of Sample)**		**Hydrocarbon Compounds Recovery Efficiency (%)**
	Original	**After Treatment**	
F	80.0	1.0	98.8
G	68.0	0.8	98.8
H	67.0	0.7	99.0
I	74.0	0.8	98.9
J	71.0	0.8	98.9

Table 6-9 shows the most effective mixing ratios that could achieve the optimal results in both purification and hydrocarbon compounds recovery for each sample.

Table 6-9. Most Effective Mixing Ratios for Used Synthetic Motor Oil Samples to Achieve the Optimal Results in Purification and Hydrocarbon Compounds Recovery.

Sample	**Mixing Ratio (wt. %)**	
	Used Lubricant/Solvent Mixture	**Hexane/DMK**
F	1:9	1:2
G	1:9	1:2
H	1:9	1:2
I	1:9	1:2
J	1:9	1:2

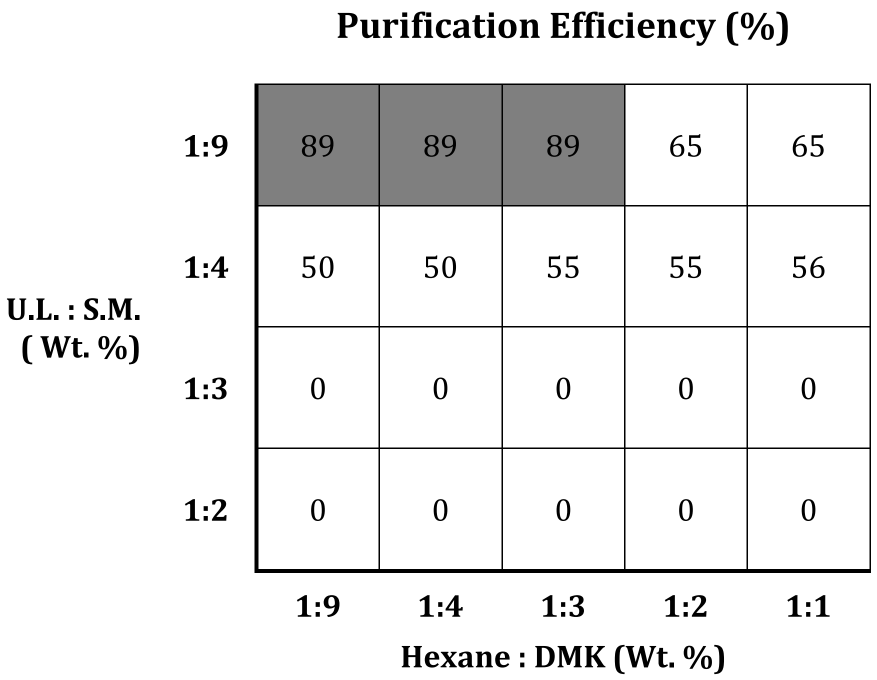
6.6.3 Feasibility Study on Mixed Used Lubricants

At the used lubricant collection centers, used lubricants of different types and for various applications are collected and mixed in storage containers, such as barrels or tanks. Indeed, used lubricants from the collection centers are mostly inconsistent from one sample to another and have much more complicated compounds than the samples collected from single source.

Used lubricant samples collected from the collection centers not only consisted of used mineral-based and synthetic motor oils, but also lubricant fluids, such as auto transmission fluids and machinery lubricants. In addition to hydrocarbon compounds (C4 to C50) from different types of lubricants and common impurities that could be found in used lubricants from single sources, these samples also contain various amounts of uncommon contaminants such as dirt and heavy metals, such as cadmium, chromium, arsenic, barium, zinc, and lead.

Figure 6-14, 6-15, and 6-16 illustrate the analysis of the most effective mixing ratio for used lubricant sample K, a sample of mixed used lubricants collected from Golden Eagle Refinery.

The best result in purification is 89% on the grid no. 1 to 3 as shown in Figure 6-14. The optimal result in hydrocarbon compounds recovery is 98% on the grid no. 3, 4, 5, 8, 9 and 10 as shown in Figure 6-15. The most effective ratio for both tasks is determined by superimposing Figure 6-14 and 6-15. As a result, the most effective mixing ratio for both tasks is on the grid no.3 in which the most effective mixing ratio of hexane to DMK is 1:3, and the most effective used lubricant to solvent mixture is 1:9 as shown in Figure 6-16.



Purification Efficiency (%)

U.L. : S.M. (Wt. %)

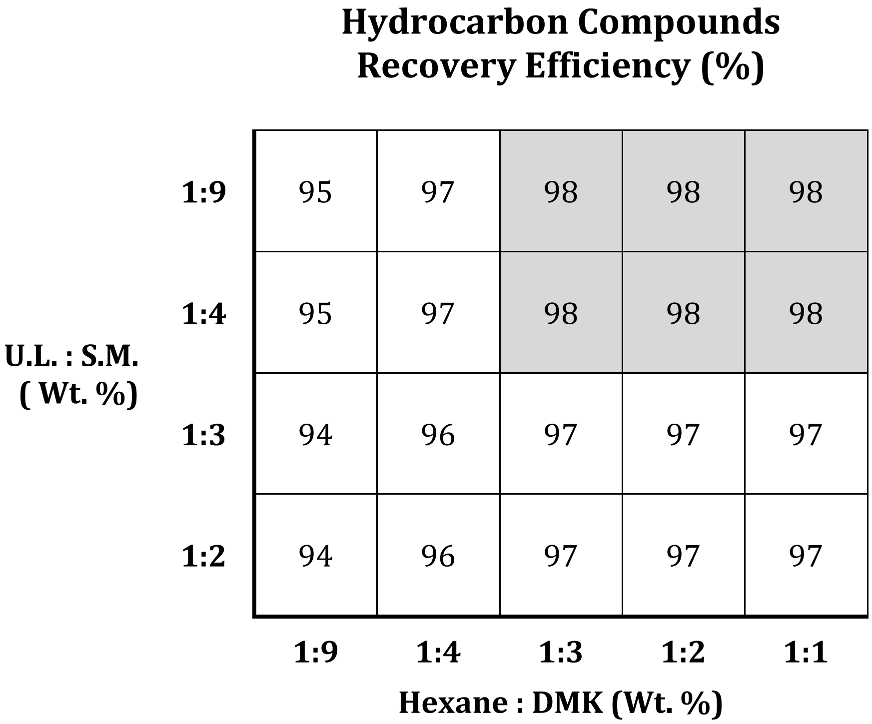
	1:9	**1:4**	**1:3**	**1:2**	**1:1**
1:9	89	89	89	65	65
1:4	50	50	55	55	56
1:3	0	0	0	0	0
1:2	0	0	0	0	0

Hexane : DMK (Wt. %)

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-14. Most Effective Mixing Ratios for the Optimal Results in Purification for Sample K.



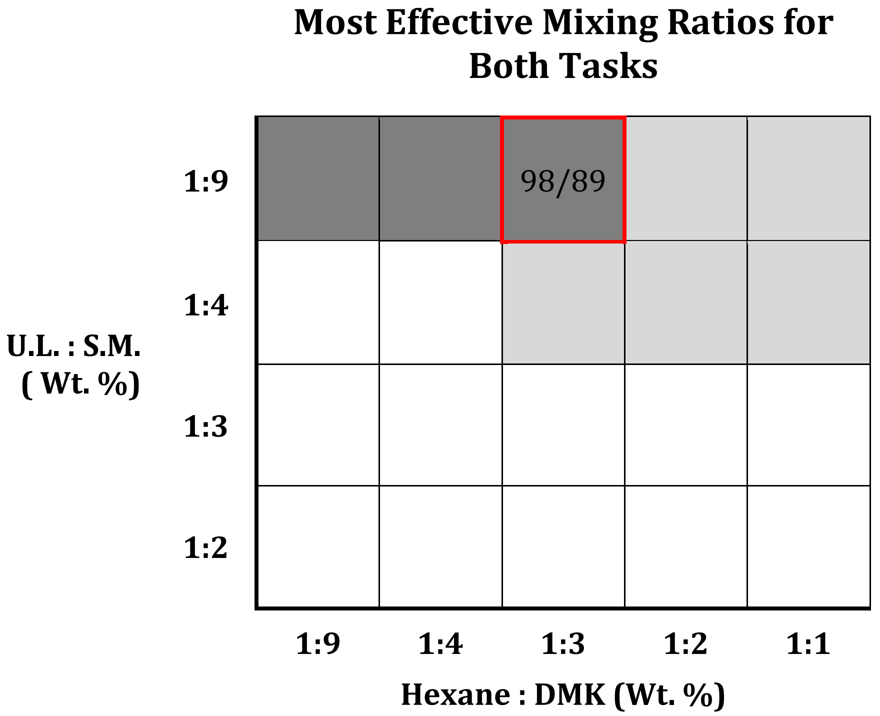
Hydrocarbon Compounds Recovery Efficiency (%)

U.L. : S.M. (Wt. %) \ Hexane : DMK (Wt. %)	1:9	1:4	1:3	1:2	1:1
1:9	95	97	98	98	98
1:4	95	97	98	98	98
1:3	94	96	97	97	97
1:2	94	96	97	97	97

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-15. Most Effective Mixing Ratios for the Optimal Result in Hydrocarbon Compounds Recovery for Sample K.



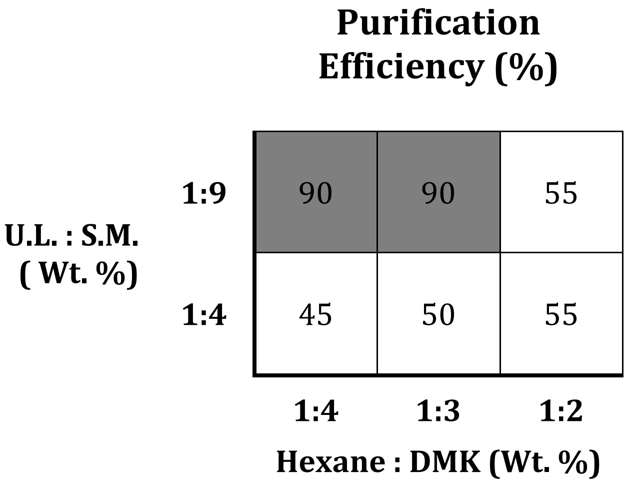
Remarks:

U.L. : Used Lubricant
S.M : Solvent Mixture

Figure 6-16. Most Effective Mixing Ratio Is Determined by Superimposing the Results of Figure 6-14 and 6-15.

The same analytical procedures were performed for sample L to determine the most effective mixing ratio for purification and hydrocarbon compounds recovery. However, this time binary matrix was narrowed down to the area in which the most effective mixing ratio might possibly locate based on the results of sample K as shown in Figure 6-16.

Figure 6-17, 6-18, and 6-19 illustrate the analytical procedures for sample L. Again, the most effective ratio for both tasks was determined by superimposing Figure 6-17 and 6-18. As shown in Figure 6-19, the most effective mixing ratio is located on the grid no.3 in which the most effective mixing ratio of hexane to DMK is 1:3, and the most effective mixing ratio of used lubricant to solvent mixture is 1:9.



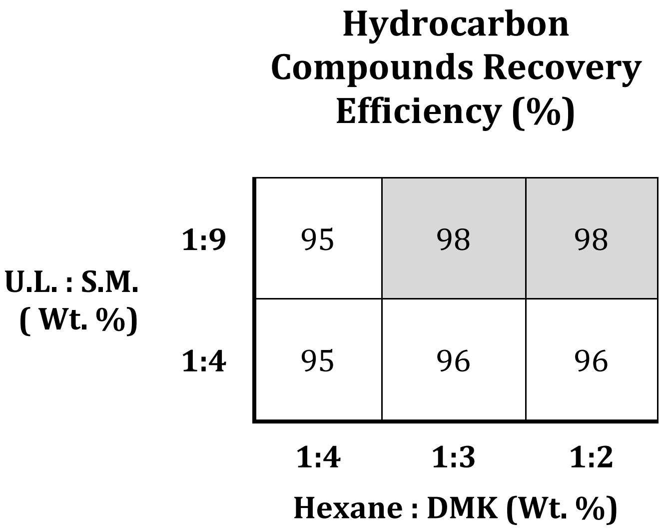
Purification Efficiency (%)

U.L. : S.M. (Wt. %) \ Hexane : DMK (Wt. %)	1:4	1:3	1:2
1:9	90	90	55
1:4	45	50	55

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-17. Most Effective Mixing Ratios for the Optimal Result in Purification for Sample L.



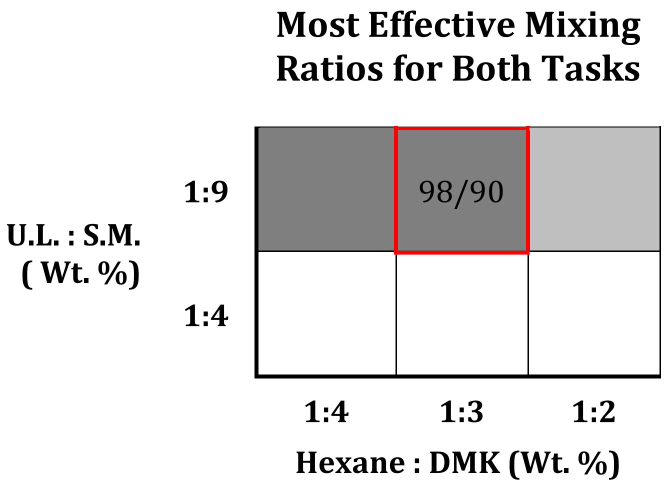
Hydrocarbon Compounds Recovery Efficiency (%)

U.L. : S.M. (Wt. %)	Hexane : DMK (Wt. %)		
	1:4	1:3	1:2
1:9	95	98	98
1:4	95	96	96

Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-18. Most Effective Mixing Ratios for the Optimal Result in Hydrocarbon Compounds Recovery for Sample L.



Remarks:

U.L. : Used Lubricant
S.M.: Solvent Mixture

Figure 6-19. Most Effective Mixing Ratio Is Determined by Superimposing the Results of Figure 6-17 and 6-18.

The same analysis and procedures were performed for sample M to T. The efficiency of purification and hydrocarbon compound recovery on each sample are shown in Table 6-10 and 6-11.

Table 6-10. Impurity Removal Efficiency for Mixed Used Lubricant Samples.

Sample	**Impurities Concentration (g/100g of Sample)**		**Purification Efficiency (%)**
	Original	**After Treatment**	
K	35.0	2.8	92
L	18.9	1.9	90
M	25.0	2.1	92
N	19.0	1.6	92
O	15.5	1.7	89
P	18.9	1.9	90
Q	30.0	2.0	93
R	13.9	2.1	85
S	17.9	1.6	91
T	20.0	1.6	92

Table 6-11. Hydrocarbon Compounds Recovery Efficiency for Mixed Used Lubricant Samples.

Sample	**Hydrocarbon Compounds Concentration (g/100g of Sample)**		**Hydrocarbon Compounds Recovery Efficiency (%)**
	Original	**After Treatment**	
K	55.0	1.0	98.2
L	70.0	1.9	97.3
M	60.0	1.0	98.3
N	72.0	1.8	97.5
O	70.8	1.7	97.6
P	69.2	1.2	98.3
Q	60.0	1.2	98.0
R	68.9	1.1	98.4
S	72.1	2.1	97.1
T	65.0	1.0	98.5

Table 6-12 shows the most effective mixing ratios that binary solvent process is capable to achieve for each sample in used lubricant purification and hydrocarbon compounds recovery.

Table 6-12. Most Effective Mixing Ratios for Used Mixed Lubricant Samples to Achieve the Optimal Results in Used Lubricant Purification and Hydrocarbon Compounds Recovery.

Sample	**Mixing Ratio (wt. %)**	
	Used Lubricant/Solvent Mixture	**Hexane/DMK**
K	1:9	1:3
L	1:9	1:3
M	1:9	1:3
N	1:9	1:3
O	1:9	1:3
P	1:9	1:3
Q	1:9	1:3
R	1:9	1:3
S	1:9	1:3
T	1:9	1:3

6.7 Summary and Results

The composition of used lubricants collected from engines and machines varies substantially with the point of source. In addition to hydrocarbon compounds (C4 to C50) from base oils and unburned fuels, used lubricants also contain various additives from the original formulation and various amounts of contaminants such as metal fragments, soot gel networks, soot aggregates, dirt, and heavy metals (e.g., cadmium, chromium, arsenic, barium, zinc, lead). Therefore, it is very difficult to characterize used lubricants because the composition of used lubricants varies widely with the type and age of vehicles and machines; the service life of lubricant; collecting places; and operating conditions.

Statistical analysis of multiple replications of experiments carried out in this research demonstrated acceptable standard deviations. The binary solvent system has demonstrated the viability of the process to simultaneously remove up to 93% of impurities (Table 6-13) and recover up to 99% hydrocarbon compounds (Table 6-14) from different types of used lubricant samples. Both purification and hydrocarbon recovery could operate under atmospheric pressure and at room temperature of 77°F (25°C). Furthermore, all reagents used in this process could be recycled and reused indefinitely under atmospheric pressure and at relatively low temperature of 156.2˚F (69˚C) compared to other conventional processes.

Table 6-13. Summary of Impurity Removal Efficiency for Each Used Lubricant Sample.

	Sample	Impurities Concentration (g/100g of Sample)		Purification Efficiency (%)
		Original	After Treatment	
Used Mineral-Base Motor Oil	**A**	10.7	1.6	85
	B	30.5	2.7	91
	C	19.4	1.9	90
	D	17.4	1.8	90
	E	16.0	1.5	91
Used Synthetic Motor Oil	**F**	11.0	1.2	89
	G	19.0	2.0	89
	H	15.0	1.5	90
	I	16.0	1.8	89
	J	16.0	1.8	89

Table 6-13. (Continued)

	Sample	Impurities Concentration (g/100g of Sample)		Purification Efficiency (%)
		Original	After Treatment	
Mixed Used Lubricant	**K**	35.0	2.8	92
	L	18.9	1.9	90
	M	25.0	2.1	92
	N	19.0	1.6	92
	O	15.5	1.7	89
	P	18.9	1.9	90
	Q	30.0	2.0	93
	R	13.9	2.1	85
	S	17.9	1.6	91
	T	20.0	1.6	92

Table 6-14. Summary of Hydrocarbon Recovery Efficiency for Each Used Lubricant Sample.

	Sample	**Hydocarbon Compound Concentration (g/100g of Sample)**		**Purification Efficiency (%)**
		Original	**After Treatment**	
Used Mineral-Base Motor Oil	**A**	81.4	2.5	97
	B	61.5	1.4	98
	C	71.6	1.0	99
	D	70.0	1.0	99
	E	70.0	1.0	99
Used Synthetic Motor Oil	**F**	80.0	1.2	99
	G	68.0	0.8	99
	H	67.0	0.7	99
	I	74.0	0.8	99
	J	71.0	0.8	99

Table 6-14. (Continued)

	Sample	**Hydocarbon Compound Concentration (g/100g of Sample)**		**Purification Efficiency (%)**
		Original	**After Treatment**	
Mixed Used Lubricant	**K**	55.0	1.0	98
	L	70.0	1.9	97
	M	60.0	1.0	98
	N	72.0	1.8	98
	O	70.8	1.7	98
	P	69.2	1.2	98
	Q	60.0	1.2	98
	R	68.9	1.1	98
	S	72.1	2.1	97
	T	65.0	1.0	98

The efficient use of solvents is one of the major requirements in the binary solvent process. The binary system matrix is designed to determine the most effective mixing ratio between solvent mixture and used lubricants as well as between organic solvents in solvent mixture. With the help of the binary solvent matrix, the organic solvents used in the binary solvent process could be efficiently used to achieve the best result of purification and hydrocarbon compounds recovery.

The binary system matrix has been demonstrated as a promising analytical method to conclude the most effective mixing ratios that work for all used lubricant samples experimented in this research. Statistical analysis of multiple replications of experiments have concluded that the best results could be achieved in purification and hydrocarbon compounds recovery by the following mixing ratios: the mixing ratio (wt. %) of hexane and DMK is 1) 1 to 3 for used mineral-based motor oils, 2) 1 to 2 for used synthetic motor oils, and 3) 1 to 3 for mixed used lubricants. The most effective mixing ratio (Wt.%) of used lubricant and solvent mixture is 1 to 9 for all samples as shown in Table 6-15.

Table 6-15. Most Effective Mixing Ratios for Each Sample to Achieve the Optimal Results in Used Lubricant Purification and Hydrocarbon Compounds Recovery.

	Sample	**Mixing Ratio (wt. %)**	
		Used Lubricant/ Solvent Mixture	**Hexane/ DMK**
Used Mineral-Base Motor Oil	**A**	1:9	1:3
	B	1:9	1:3
	C	1:9	1:3
	D	1:9	1:3
	E	1:9	1:3
Used Synthetic Motor Oil	**F**	1:9	1:2
	G	1:9	1:2
	H	1:9	1:2
	I	1:9	1:2
	J	1:9	1:2

Table 6-15. (Continued)

Sample		**Mixing Ratio (wt. %)**	
		Used Lubricant/Solvent Mixture	**Hexane/DMK**
Mixed Used Lubricant	**K**	1:9	1:3
	L	1:9	1:3
	M	1:9	1:3
	N	1:9	1:3
	O	1:9	1:3
	P	1:9	1:3
	Q	1:9	1:3
	R	1:9	1:3
	S	1:9	1:3
	T	1:9	1:3

CHAPTER 7

COLD-STAGE ENERGY CONVERSION SYSTEM

7.1 Introduction

This chapter covers the phase 7 in this research: 1) a systematic designing process and study in the development of new system in energy conversion and regeneration of used lubricants based on the concept of the binary solvent process, the results and research from the previous phases, and the principles of sustainable design; 2) the introduction of Cold-Stage Energy Conversion (CSEC) system and 3) the confirmation of the feasibility and effectiveness of new system in bench scale.

The newly developed CSEC system has been demonstrated as a promising engineering system capable of economically producing an energy source or petrochemical feedstock from used lubricants comprised of the following six major components: 1) solvent mixture unit, 2) used lubricant unit, 3) central reactor, 4) sedimentation unit, 5) hydrocarbons regenerator, and 6) used solvents regenerator. Each one of the units has its own specific function and role in the system. The system is able to operate in a continuous-flow fashion under atmospheric pressure and a relatively low temperature, 156.2˚F (69˚C). As a result, the low temperature; low pressure; low maintenance, and recyclable reagents lead to a low operation cost.

7.2 System Design Process

The development of CSEC system is a step-by-step designing process starting from setting the design goal to the final system implementation and testing. Figure 7-1 illustrates the schematic diagram of design process for CSEC system.

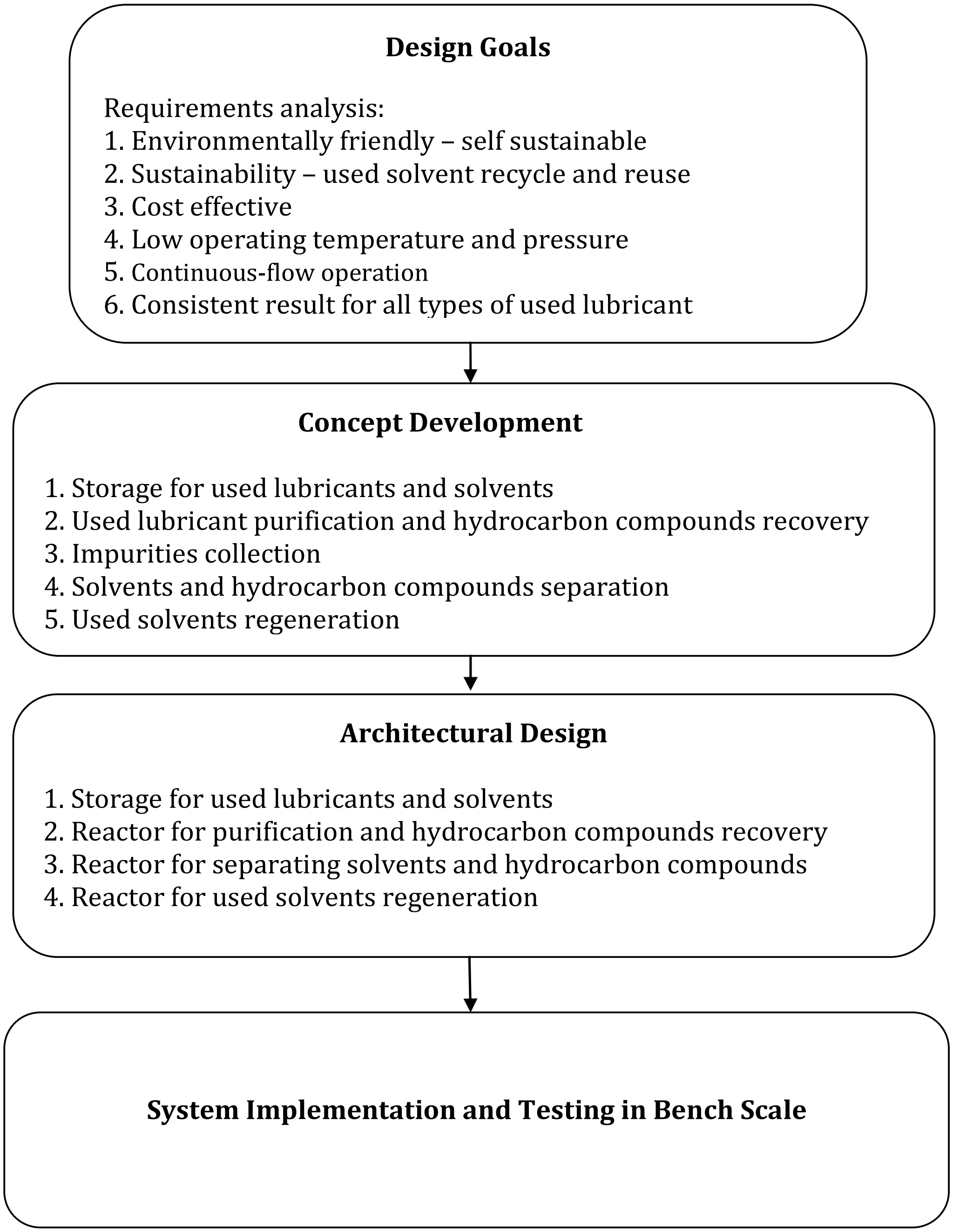


Figure 7-1. Scientific Approach in the Development of Cold-Stage Energy Conversion System.

7.3 Components of Cold-Stage Energy Conversion System

CSEC system consists of six major components: 1) solvent mixture unit, 2) used lubricant unit, 3) central reactor, 4) sedimentation unit, 5) hydrocarbon compounds collector, and 6) used reagents regenerator. Each one of the units has its own specific function and role in the system. The design concept and architectural design of each unit and the complete system are individually introduced in the following sections.

7.3.1 Solvent Mixture Unit

Solvent mixture unit is mainly used to store solvent mixture of DMK and hexane with the most effective mixing ratio determined by the binary solvent process and the binary system matrix in used lubricant purification and hydrocarbon recovery. Solvent mixture is gradually supplied into purification and hydrocarbon recovery reactor as shown in Figure 7-2.

7.3.2 Used Lubricant Unit

Used lubricant unit is mainly used to store used lubricants and to gradually supply used lubricant into purification and hydrocarbon recovery reactor as shown in Figure 7-2.

7.3.3 Central Reactor

In this reactor, used lubricant and solvent mixture chemically react to form two separated layers in the reactor as shown in Figure 7-2. DMK in solvent mixture flocculates and settles the impurities suspended in used lubricant at the bottom layer for further removal while hexane in the top layer is recovering hydrocarbon compounds (valuable energy sources) from used lubricant to the top layer.

Subsequently, the mixture of the recovered hydrocarbon compounds and solvents on the top layer transfers to solvent regeneration reactor for a separation process.

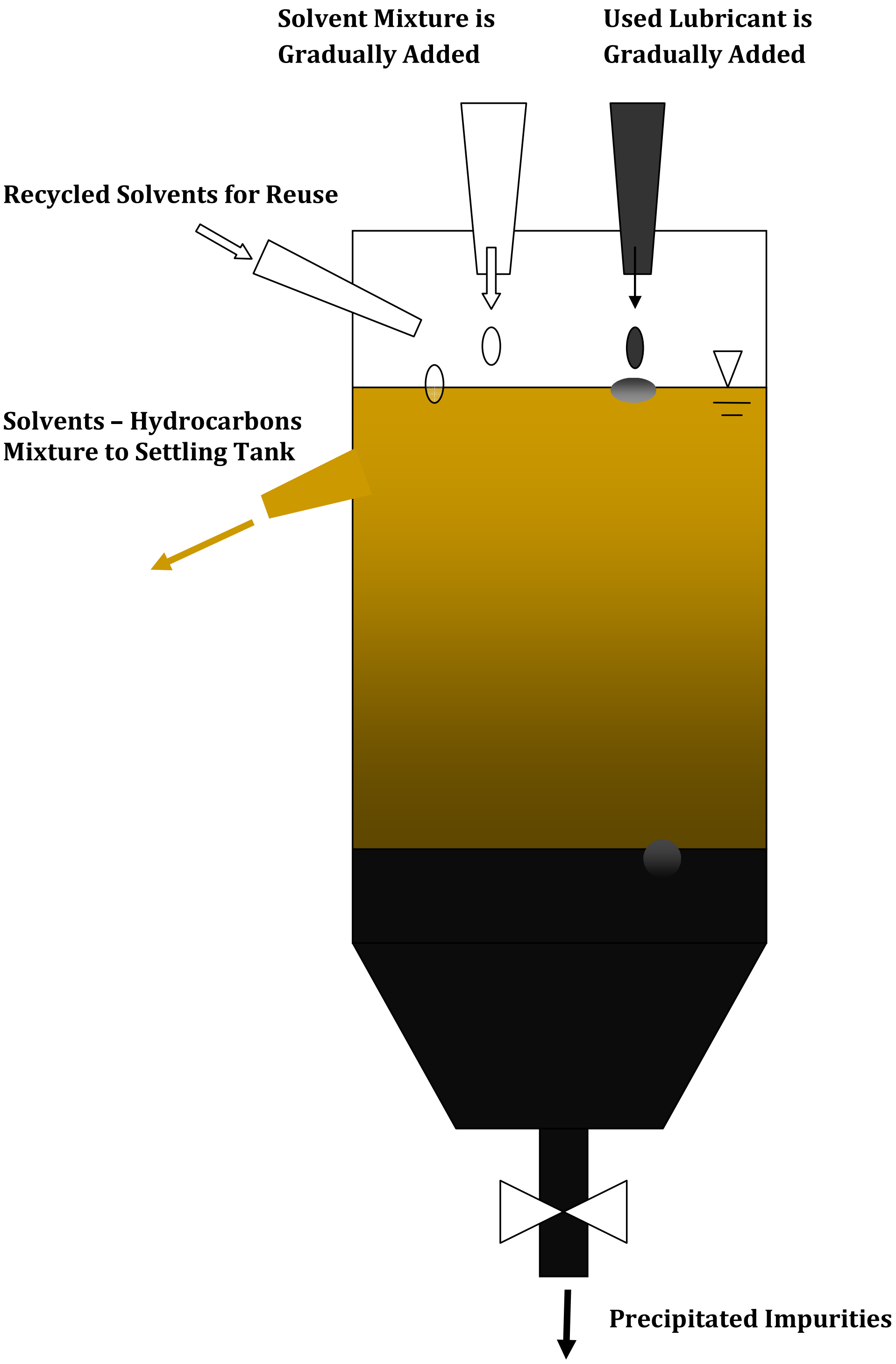


Figure 7-2. Solvent Mixture and Used Lubricant Are Gradually Supplied to the Central Reactor.

7.3.4 Sedimentation Unit

This is a supplementary unit in the system used to prevent any impurities removed at the purification and hydrocarbon compounds recovery reactor from flowing into the hydrocarbon compounds collector that follow this unit.

The impurities settled at this unit would flow to combine with the impurities previously collected at the bottom of purification and hydrocarbon recovery collector for further removal as illustrated in Figure 7-3.

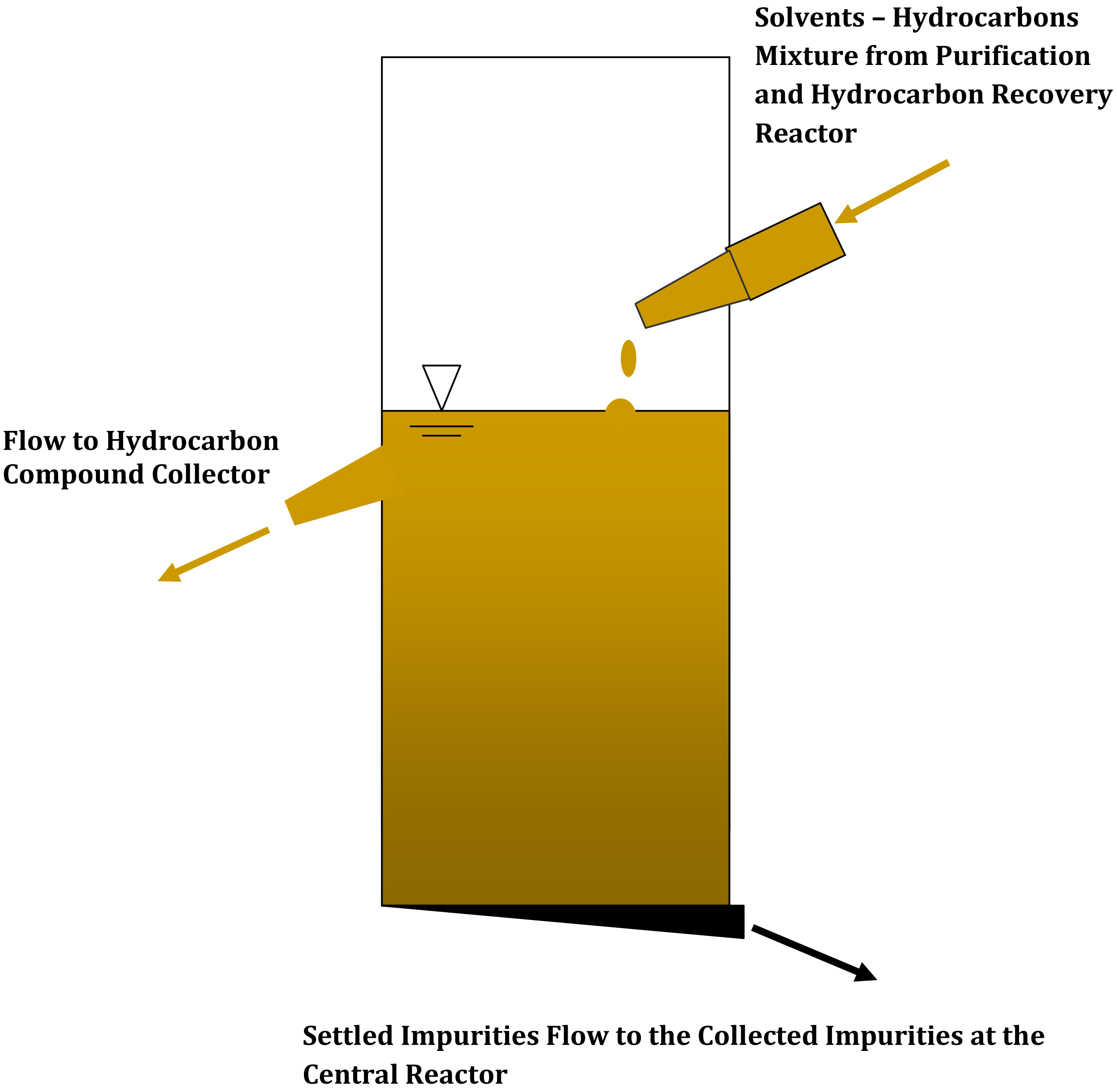


Figure 7-3. Sedimentation Unit Is Used To Settle Additional Impurities That Transferred From The Central Reactor.

7.3.5 Hydrocarbons Regenerator

The main function of this unit is to separate hydrocarbon compounds in solvent-hydrocarbons mixture that transferred from the sedimentation unit as shown in Figure 7-4. This unit performs two tasks based on the difference in the boiling points of compounds in the mixture. The boiling point of the recovered hydrocarbon compounds is in the range of 190°C to 300 °C. The boiling point of solvent mixture is 69 °C.

1) The regenerated hydrocarbon compounds are separated from the mixture by distillation and collected at the bottom of this reactor.
2) After the separation process, separated solvent mixture flows to the next unit, solvents regeneration unit.

Hydrocarbon compounds collected from this stage are ready for further treatment processes, such as color removal and desulfurization, depending on system user's requirements

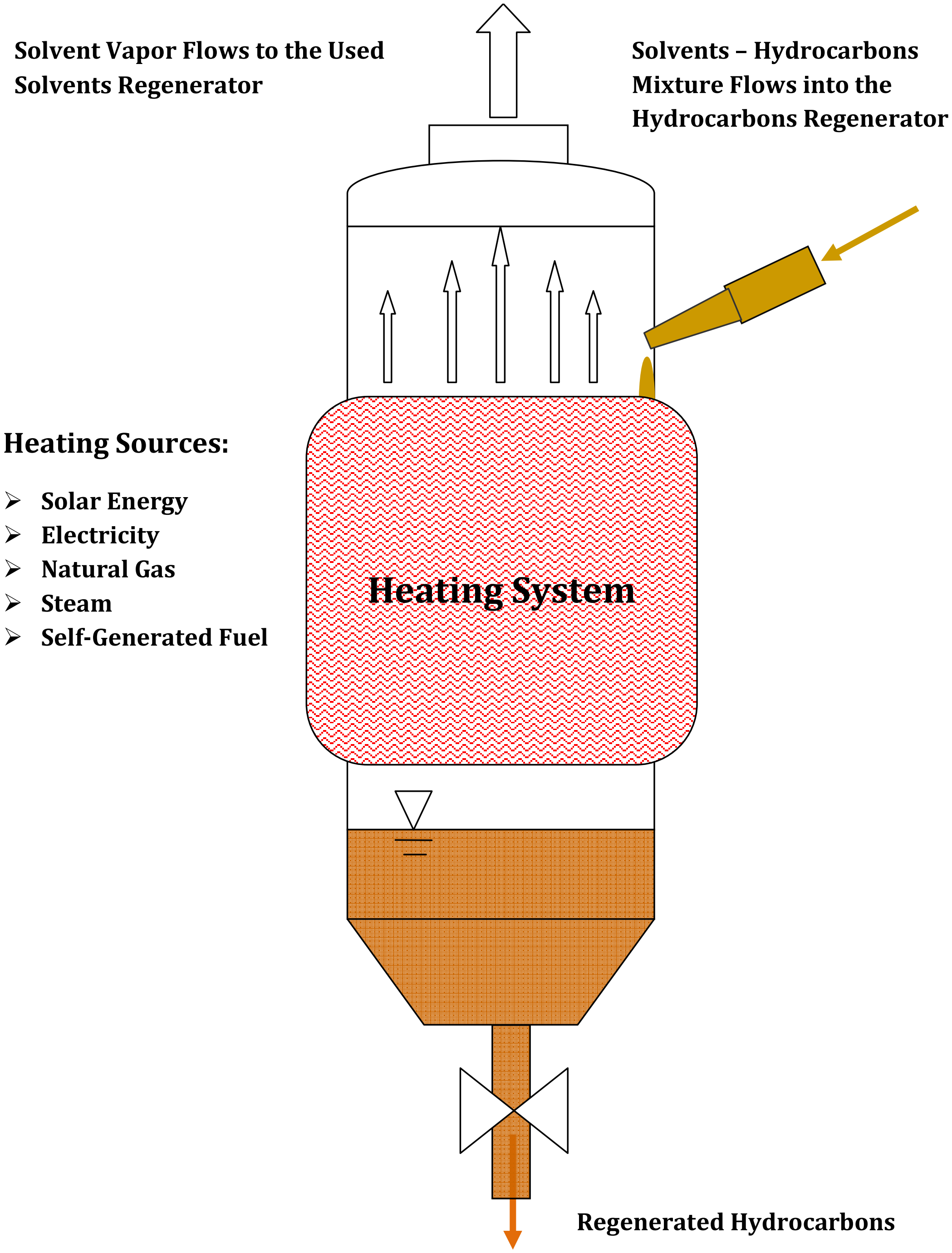


Figure 7-4. Hydrocarbon Regenerator Recovers Hydrocarbons from Solvent-Hydrocarbons Mixture.

7.3.6 Used Reagents Regenerator

Environmental sustainability and economical feasibility are the significant design factors in the CSEC system. All used reagents utilized in the system can be continuously rejuvenated for reuse without being released to the environment.

The main function of this unit is to regenerate used solvents by the condensation of used solvent vapor collected from the hydrocarbon compounds collector. The condensed solvents are recycled back to the purification and hydrocarbon compounds recovery reactor for reuse as shown in Figure 7-5.

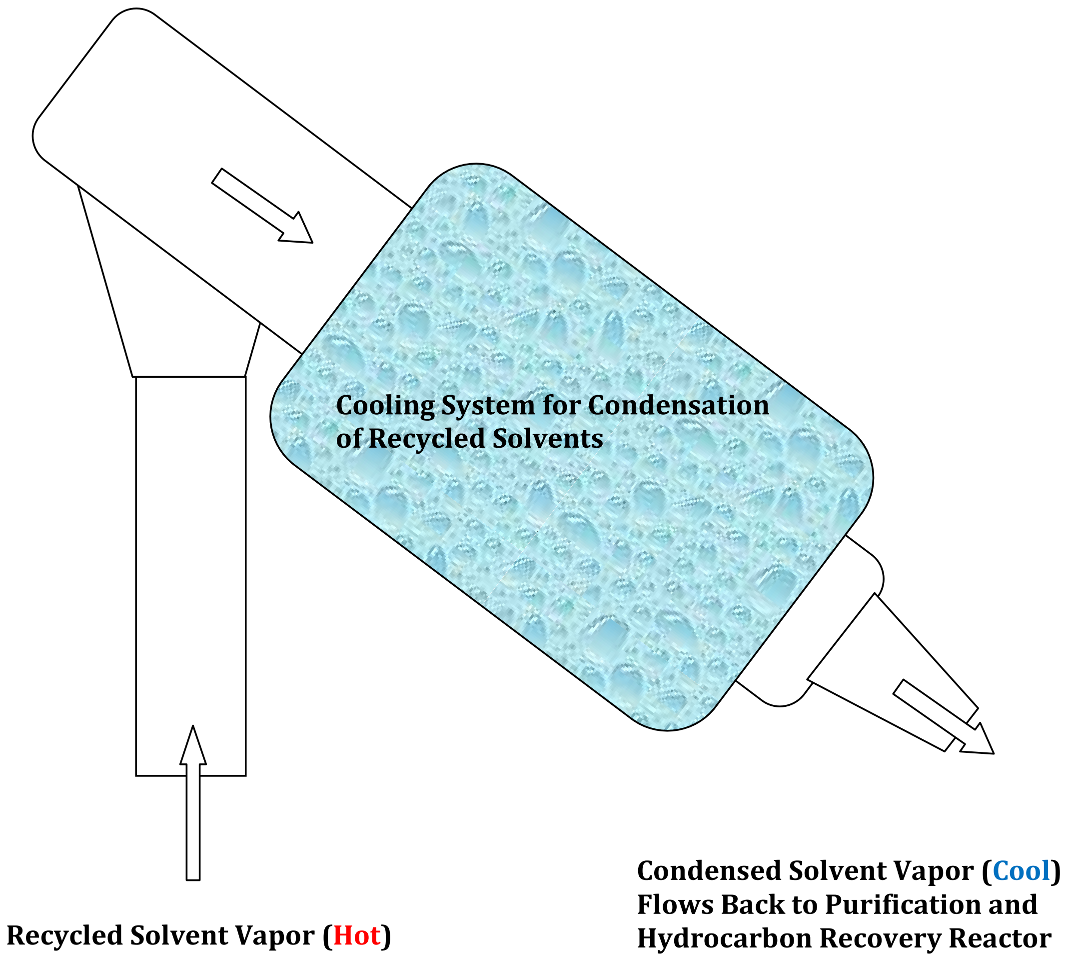


Figure 7-5. Used Solvents Is Regenerated at Used Solvent Regenerator for Reuse.

7.4 Cold-Stage Energy Conversion System in Bench Scale

Figure 7-6a illustrates the conjectural flow-diagram of the CSEC system and Figure 7-6b shows the bench-scale CSEC system in bench scale with a process loop for a feasibility study. Used lubricant and solvent mixtures are gradually added into the purification and hydrocarbon compounds recovery reactor and chemically react to each other to form two separated layers in the reactor. DMK in solvent mixture flocculates and settles the impurities suspended in used lubricant at the bottom layer for further removal while hexane in the top layer recovers hydrocarbon compounds (valuable energy sources) from used lubricant to the top layer. Solvents are recycled back to the purification and hydrocarbon compounds recovery reactor for reuse after the processes of hydrocarbon recovery and used solvent regeneration. Hydrocarbon compounds in used lubricant are regenerated and collected at the hydrocarbon compounds collector for further applications, such as energy use or recycled lubricant base oil. Subsequently, the mixture of the recovered hydrocarbon compounds and solvents on the top layer transfers to solvent

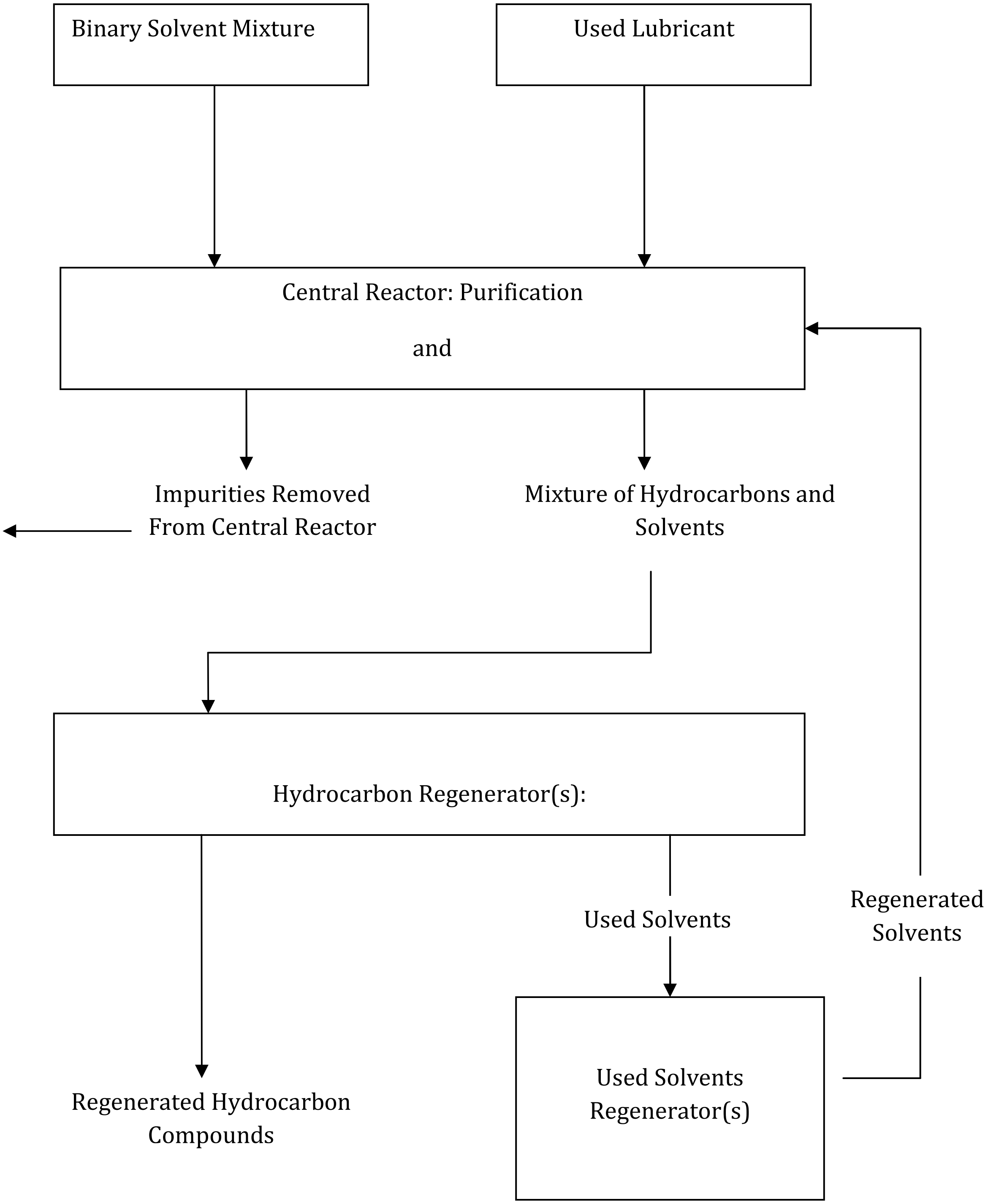


Figure 7-6a. Conceptual Flow-Diagram of CSEC System.

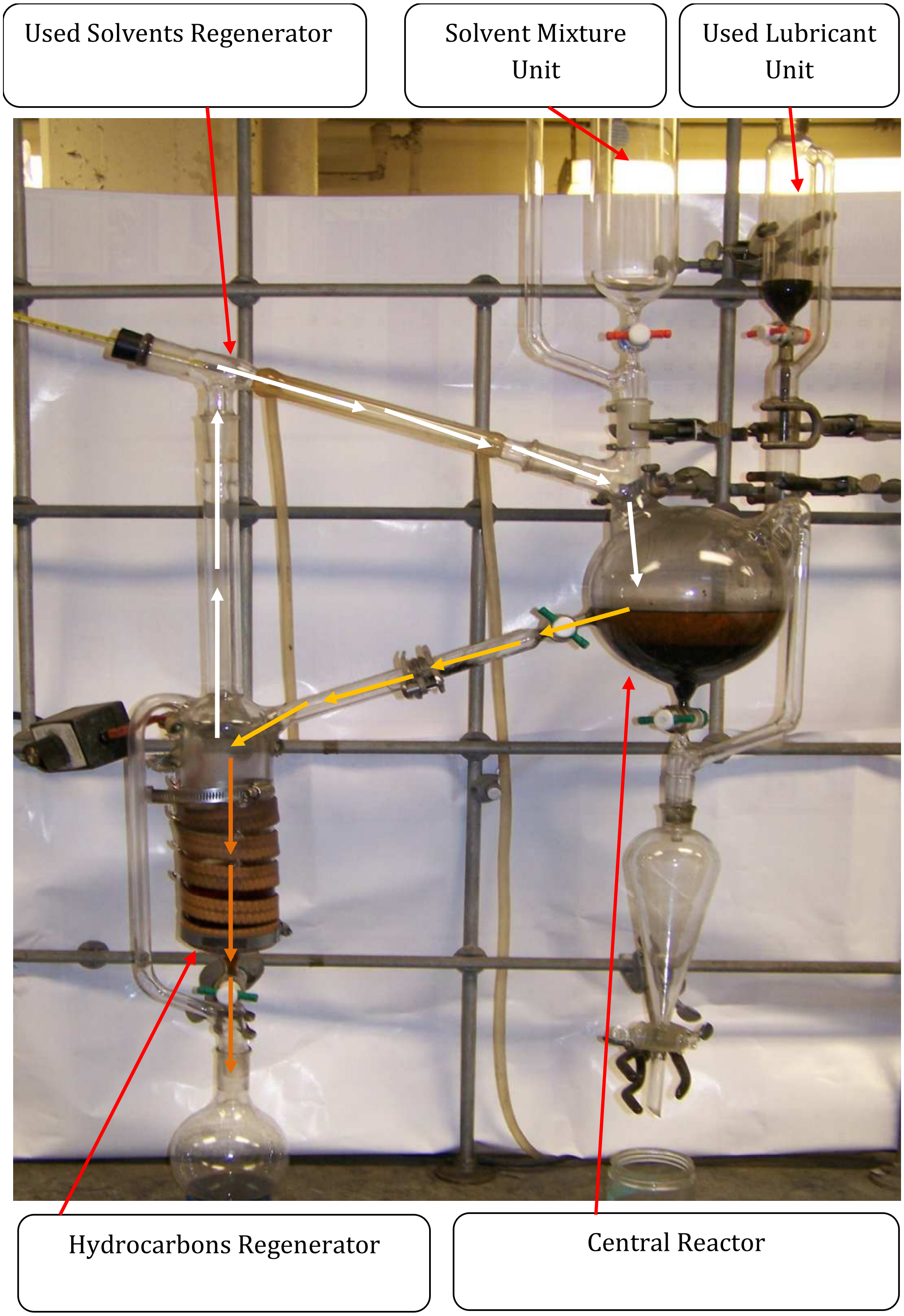


Figure 7-6b. Bench-Scale Cold-Stage Energy Conversion (CSEC) System Used for Feasibility Studies.

7.5 Preliminary Design of Cold-Stage Energy Conversion System in Full Scale

Figure 7-7 illustrates the overall schematics of CSEC system with multiple hydrocarbon compounds collectors in order to increase the recovery rate of hydrocarbon compounds. The heating source for the multiple hydrocarbon compounds collectors is flexible depending on the location and local resources, such as solar energy, electricity, or even heated water from burning of the recovered hydrocarbon compounds generated from the system itself, this would make the system “self-sustainable”. Figure 7-8 shows the top view of the CSEC system with multiple hydrocarbon compound collectors.

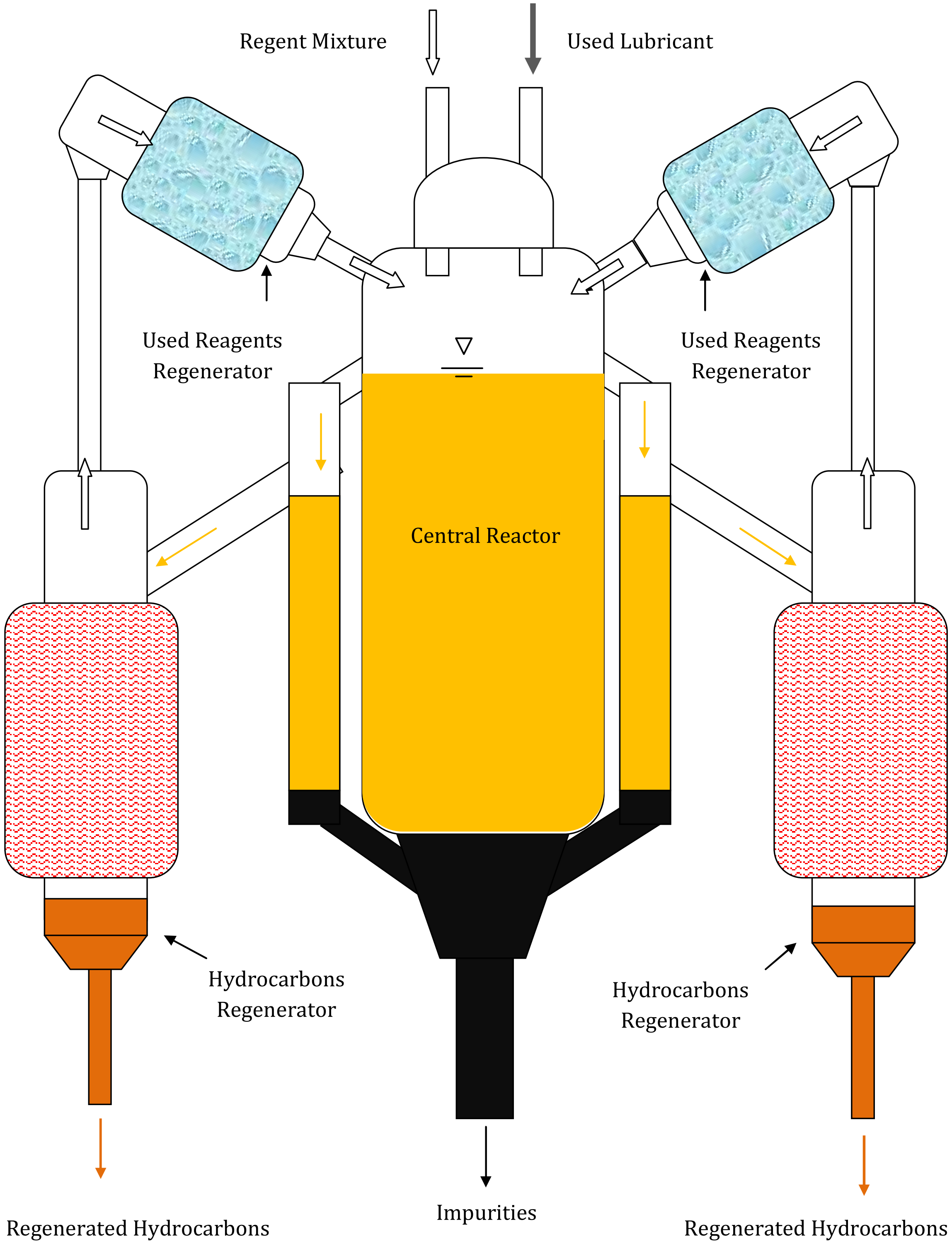


Figure 7-7. Cold-Stage Energy Conversion (CSEC) System with Multiple Hydrocarbons Regenerators.

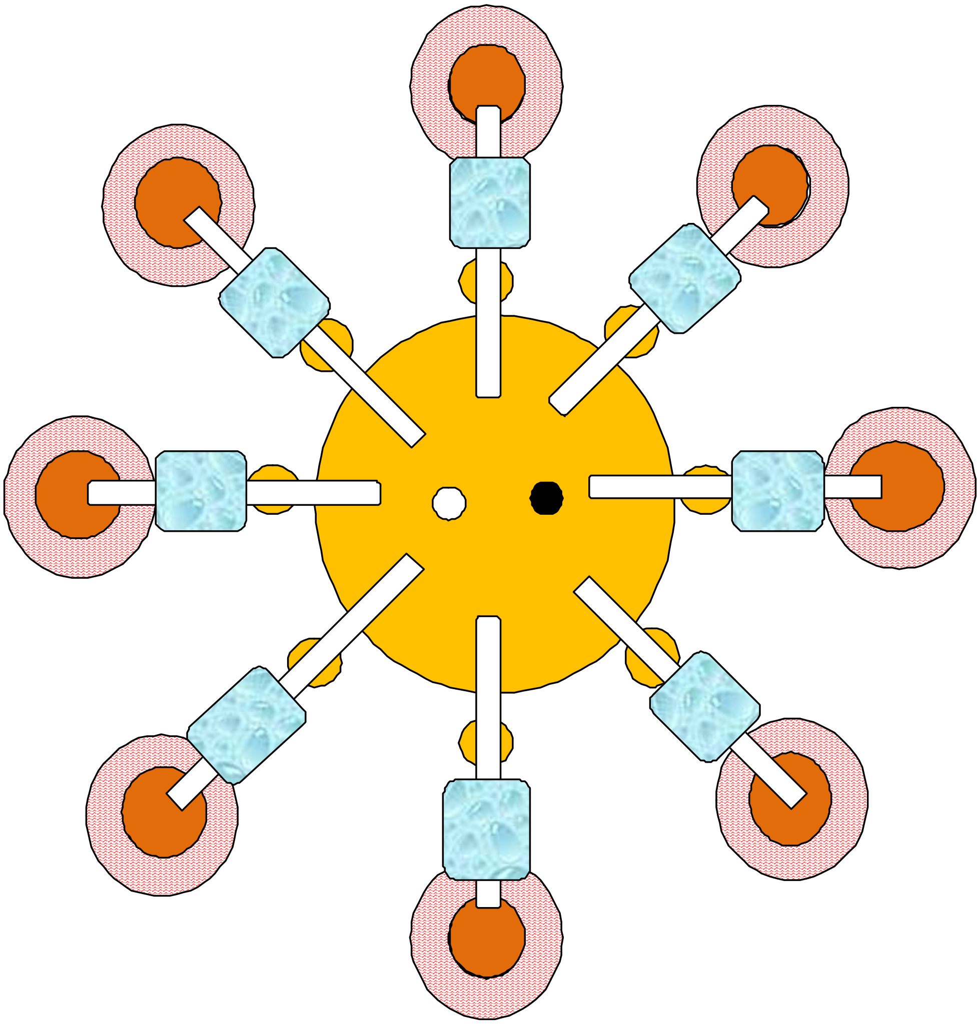


Figure 7-8. Top View of Cold-Stage Energy Conversion System with Multiple Hydrocarbons Regenerators.

7.6 Summary

Environmental sustainability and economical feasibility are two significant design factors in the development of CSEC system. The newly developed CSEC system is designed based on the concepts of the binary solvent process and the principles of sustainable design.

CSEC system has been demonstrated as a promising engineering system capable of producing an economically competitive energy source or petrochemical feedstock from used lubricants in a continuous flow fashion comprised of six major components: 1) solvent mixture unit, 2) used lubricant unit, 3) central reactor, 4) sedimentation unit, 5) hydrocarbons regenerator, and 6) used solvents regenerator. Each one of units has its own specific function and role in the system.

The operation of the CSEC System is economical. The system is able to continuously operate under atmospheric pressure and a relatively low temperature, 156.2˚F (69˚C). Furthermore, the system affords low maintenance in and used reagents can be continuously rejuvenated for reuse without releasing to the environment.

The CSEC system equipped with multiple hydrocarbons regenerators is able to increase the production rate in the recovery of hydrocarbon compounds. The heating source for the multiple hydrocarbon compounds collectors is flexible depending on the location and local resources, such as solar energy, electricity, or even heated derived from burning the recovered hydrocarbon compounds generated from the system itself to make this system truly self-sustainable. As a result, the system has the following advantages: 1) economically competitive, 2) environmentally sustainable, and 3) easy to operate and maintain. The overall benefits and the ultimate objective of CSEC system development are summarized and illustrated in as follows:

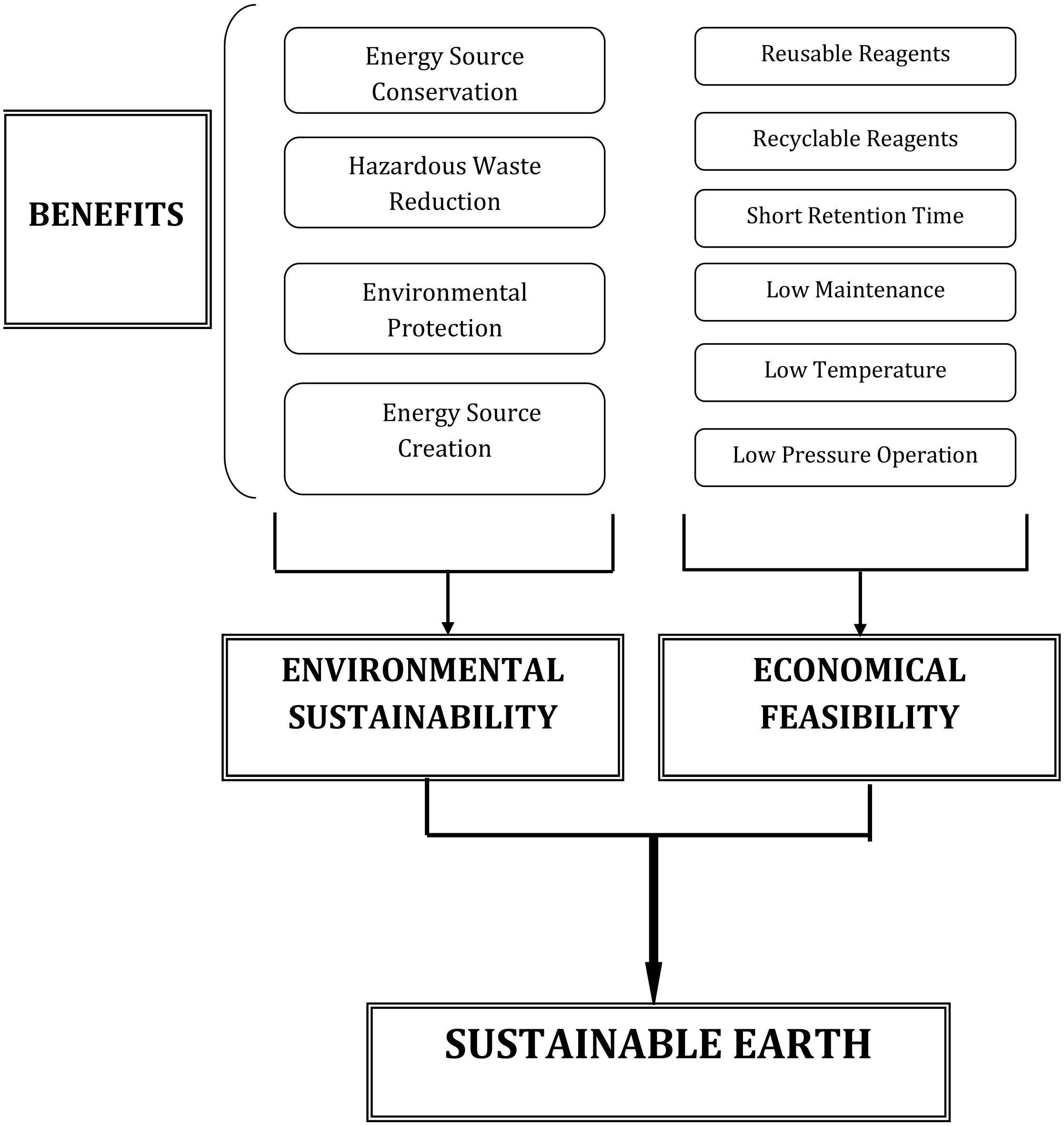


Figure 7-9. Summary of Benefits and Ultimate Objective of CSEC System.

CHAPTER 8

BIOLUBRICANTS FROM RENEWABLE RESOURCES

8.1 Introduction

Petroleum is a finite and non-renewable natural resource. Today the global petroleum reserves are becoming increasingly scarce due to the rapid industrialization. As a result, the price of petroleum and petroleum-based products, such as fuels and lubricants, will inevitably escalate and negatively impact our economy.

Plant oils are renewable natural resources. Researches have confirmed that oil extracted from many oil crops, such as soy bean, sunflower, castor bean, etc. are structurally similar to petroleum-based oils (long chain hydrocarbons) and posses many excellent properties, which are suitable for lubricant applications. The utilization of renewable source as green alternatives in lubricant science as well as an overview of market opportunity associated with biomass-based lubricants are reviewed and discussed in this chapter.

As the concern about the environment compatibility of used petroleum-based lubricants is on the rise, attention is being paid to plant-based lubricants that are easily biodegradable and less hazardous to human health, fauna, and flora.

The objective of this study is to support the use of plant oils in lubricant production. The ideal candidates should posses the following characteristics in order to ensure that the promotion of biomass-based lubricants is truly practical and meaningful (Rudnick, et al., 2006; Bremmer, et al., 2008):

- The source of selected biomass should be sustainable and without competing with food sources.
- The cost of selected biomass should be economically competitive.
- The composition of selected biomass should be environment and user friendly.

8.2 Bio-Based Lubricants

As its name implies, biolubricant is the lubricant made of biological products or renewable materials. In lubricant industry, biolubricants are consisted of rapidly biodegradable materials, which are nontoxic for humans and aquatic environments (Total, 2010).

According to law H.R.2646 Section 9001 of Farm Security and Rural Investment Act of 2002 (FSRIA), bi-based product is defined as follow:

“The term ‘biobased product’ means a product determined by the Secretary to be a commercial or industrial product (other than food or feed) that is composed, in whole or in significant part, of biological products or renewable domestic agricultural materials (including plant, animal, and marine materials) or forestry materials. “

Many studies have confirmed that the monounsaturated fatty acids in plants oils, such as oleic and palmitic, are considered as the best candidates for lubricants and hydraulic oils (Stymne, et al. 2006; Rudnick, et al. 2006). For any plant oils with a high concentration of saturated linear fatty acids are not desirable for lubricant production because they generally appear as solid form at room temperature.

Oleic acid has been proved by many studies as the most ideal mono-saturated fatty acid for biolubricant application. Many studies have also confirmed that the plant oils extracted from the crops with a high concentration of oleic acid, such as canola/rapseed and castor seeds, are the most desirable plants oils for biolubricant production (Bondioli, P., 2005; Ognniyi, 2006; Rudnick, et al., 2006; and Bremmer, et al., 2008).

8.3 Advantages of Biolubricants

One of the major objectives of this research is to promote the renewable biomass-based lubricants because using biolubricants or biohydraulic oils has many benefits over petroleum-based lubricants to the environment and human health (IENICA, 2004; Total Lubricants, 2010), as outlined below:

- The biomass used for producing bio-based oils is renewable and genetically changeable.
- Biolubricants are easily biodegradable, low in toxicity, and less hazardous to the environment because bio-based oils are totally free of aromatic compounds.

- Biolubricants have higher viscosity index (VI) and are more stable with temperature change because of lower viscosity of bio-based oils.
- Biolubricants are safer to use because they are not toxic to skin and low in evaporation losses, which leads to less inhalation of oil vapor into the lung.
- Biolubricants prolong the service life of equipments because the property of higher wetting tendency of polar esters in plant oils enhances the effectiveness of lubrication.
- Biolubricants are cost-effective, easy to handle, and afford less maintenance cost.

8.4 Biolubricants Market Overview

As the global lubricant demand is expected to reach 12 billion gallons in 2010 and continuously increase in the future. The depletion of petroleum reserves and the high cost of synthetic lubricants have made the development of lubricants derived renewable sources to replace petroleum-based lubricants inevitable. Thus, it is obviously the higher demand in lubricants, the higher potential market for biolubricants.

In recent years, many bio-based products, such as penetrating lubricants, diesel fuel additives, and mobile equipment hydraulic fluids, have been formally promoted by law in the United States to 1) protect the environment by reducing the negative environmental impacts caused by the use of petroleum-based products; 2) to create new job opportunities in biotechnology by increasing domestic energy and bio-based resources; 3) to enhance the national energy security by reducing the demand on imported petroleum-based products and natural gas (Bondioli, 2005; Bremmer, et al., 2008).

In Europe, biolubricants have been in the market for years. It is estimated that the annual overall use of biolubricant in the European Union (EU) is about 16 million gallons in recent years (Bremmer, et al., 2008).

In Asia, the country with rapid economic growth, such as China, is expected to be the major user of lubricants in the future (Bremmer, et al., 2008).

8.5 Applications of Biolubricants

Many studies have confirmed that biolubricants are able to provide the same performance as petroleum-based lubricants for various lubricant applications. Figure 8-1 illustrates the applicable applications for biolubricants (The Freedoina Group, 2009). Engine oils are the largest demand for the overall lubricant use in the world (The Freedoina Group, 2009; IENICA, 2004).

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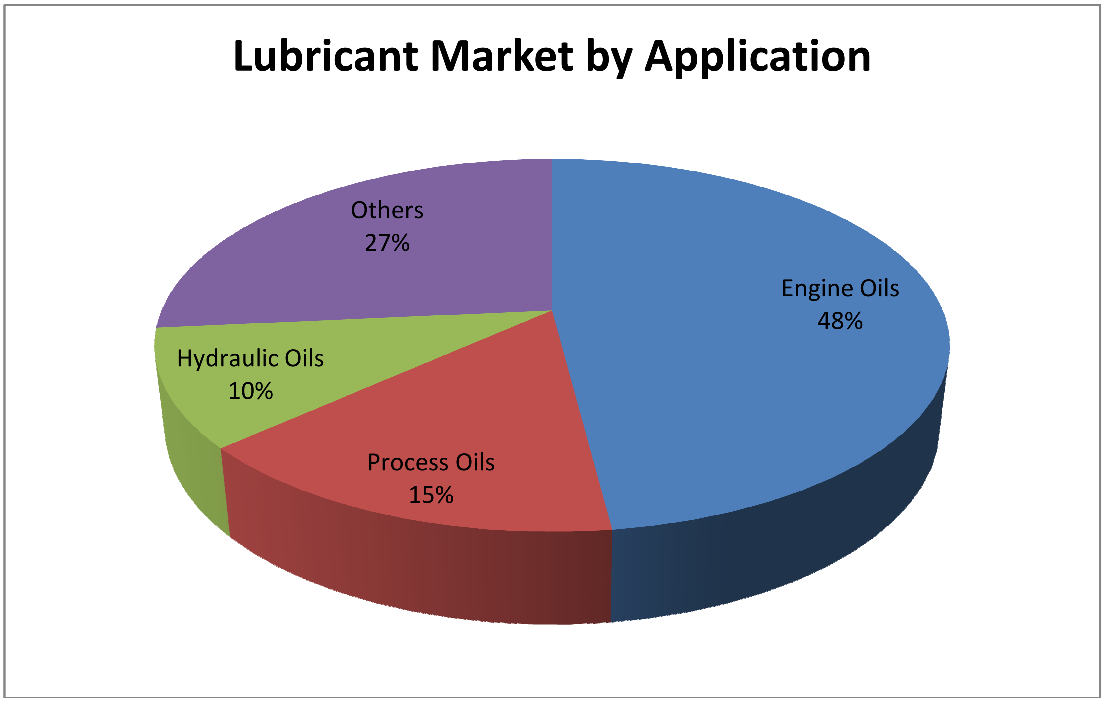

Figure 8-1. Applications of Biomass-Based Lubricants.

8.6 Biolubricant Composition

Modern engines, tools, machines, require high performance lubricants to reduce tear and wear in order to maintain a high efficiency and performance. Similar to petroleum-based lubricants, biolubricants contain not only base material but also a variety of additives in order to enhance the specific performance which base material alone cannot achieve (Stymne, et al. 2006; Rudnick, et al. 2006).

8.7 Biolubricant Base Oils

Biolubricant base oils are derived from biomass feedstocks. The following sections present the chemical properties of bio-based materials and the evaluation of various biomass sources in the production of biolubricants.

8.7.1 Biolubricant Feedstocks from Plant Oils

The concept of biolubricants is to replace petroleum lubricant feedstocks with crop oils, which is extracted from renewable biomass, such as plants or algae (Stymne, et al. 2006; Rudnick, et al. 2006).

8.7.1.1 Chemical Composition of Plant Oils

To understand the composition and structure of plant oils is the first step for the selection of the most suitable crop candidates. Although the composition of plant oils varies with the plants, the crop, soil types, climatic conditions, the season, and the amount of sunlight, oils extracted from oil crops are mostly consisted of triacylglycerols (TAG) with various composition of fatty acids and a variety of other compounds in a relatively low concentration as shown in Table 8-1 (Armstrong, W. P., 1999; Erhan, et al. 2006; and Ogunniyi, D.S., 2006)

Table 8-1. General Plant Oil Composition.

Plant Oil Composition	
Chemical Compound	**%**
Triacylglycerols	98
Diglycerols	0.5
Sterols	0.3
Free Fatty Acids	0.1
Tocopherols	0.1

Common fatty acids found in plant oils include: 1) saturated fatty acids, such as capric acid (C10:0), lauric acid (C12:0), myristic acid (C14:0) and palmitic acid (C16:0) as listed in Table 8-2a ; 2) mono-unsaturated fatty acid, oleic acid (18:1); and 3) poly-saturated fatty acids, such as ω6, linoleic acid (C18:2), and ω3, alpha linolenic acid (C18:3) as listed in Table 8-2b (Armstrong, W. P., 1999; Erhan, et al. 2006; Ogunniyi, D.S., 2006; Michael, et al. 2007).

Table 8-2a. Composition of Saturated Fatty Acids in Typical Oil Crops.

Plant Oil	Saturated Fatty Acids in Plant Oils (wt. %)				
	Capric Acid C10:0	Lauric Acid C12:0	Myristic Acid C14:0	Palmitic Acid C16:0	Stearic Acid C18:0
Corn	-	-	-	11	2
Soy bean	-	-	10	5	21
Castor Bean	-	2.4	2.4	2.4	2.4
New Rapeseed	-	-	0.5	4	1
Palm Kernel	-	50	15	7	2
Sunflower	-	-	-	6	4
Linseed	-	-	-	10	5

Table 8-2b. Composition of Unsaturated Fatty Acids in Typical Oil Crops.

	Unsaturated Fatty Acid in Plant Oils (wt. %)			
Plant Oil	**Mono**		**Poly**	
	Oleic Acid	**Ricinolenic Acid (ω9)**	**Linoleic Acid (ω6)**	**Alpha Linolenic Acid (ω3)**
	C18:1	**C18H34O3**	**C18:2**	**C18:3**
Corn	28	1	58	1
Soy bean	53	0.5	8	0.5
Castor Bean	7.4	87	3.1	-
New Rapeseed	60	9	20	9
Palm Kernel	15	-	1	-
Sunflower	28	-	61	-
Linseed	21	8	53	8

The content of triacylglycerols (TAG) in plants varies widely from one crop species to the other. The TAG content of yellow mustard is about 27%, which is very different from other mustard species, such as brown mustard that contains approximately 36 % TAG and some oriental mustard species which contain 50% TAG. Table 8-3 lists the average TAG content of common oil crops (PlantOils, 2010).

Table 8-3. Average TAG Content of Common Oil Crops.

Average TAG Content (% dry weight)

Plant	**%**
Corn	7
Soy bean	20
Canola/Rape seed	40
Safflower	40
Mustard	40
Castor	45
Flaxseed	45
Penut	50
Palm Kernel	50
Sunflower	55

8.7.1.2 Chemical Structure of Plant Oils

Triacylglycerols, also known as TAG, triglycerides, or triacylglycerides, is the natural long-chain fatty acid tri-esters of glycerol that is structurally similar to petroleum base oils. Thus, TAG, as shown in Figure 8-2, is the key component in plant oils ideally used for biolubricant feedstocks production.

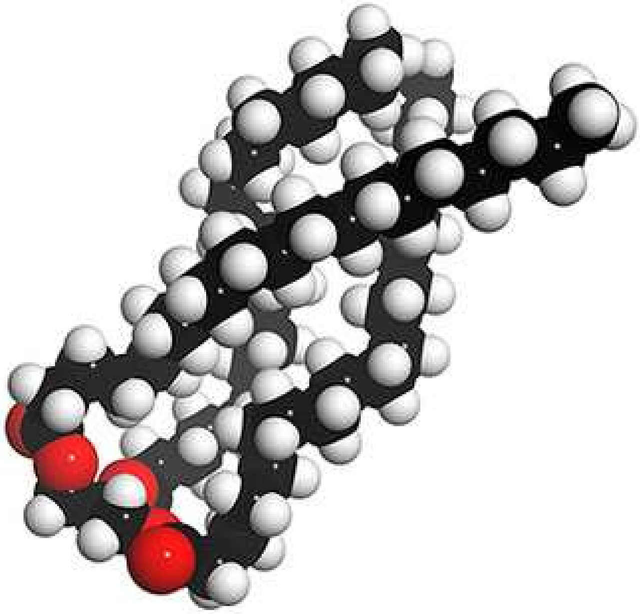

Figure 8-2. Structure of Triacylglycerols
(http://www.3dchem.com/moremolecules.asp?ID=320&othername=triacylglycerol#)

TAG are commonly divided into three general groups: 1) monoacid TAG, which contain only one type of fatty acid; 2) diacid TAG, which contain two types of fatty acids; and 3) triacid TAG, which have three different types of fatty acids.

Most plant oils are rich in long chain unsaturated hydrocarbons with even-numbered of carbon from 14 to 22. Unsaturated fatty acids with both the hydrogen atoms on the same side of the carbon double-bond are *cis*-unsaturated fatty acids. In contrary, *trans*-unsaturated fatty acids have hydrogen atoms on opposite sides of double bond. Both structures in *cis*- or *tran*- form can be found in plant oils. The symmetrical structure of *trans*-fatty acid usually has higher thermo-stability and melting point than *cis*-fatty acid (Rudnick et al. 2006). Figure 8-3 shows the typical fatty acids found in plant oils vary in shape that lead to the different prosperities of TAG.

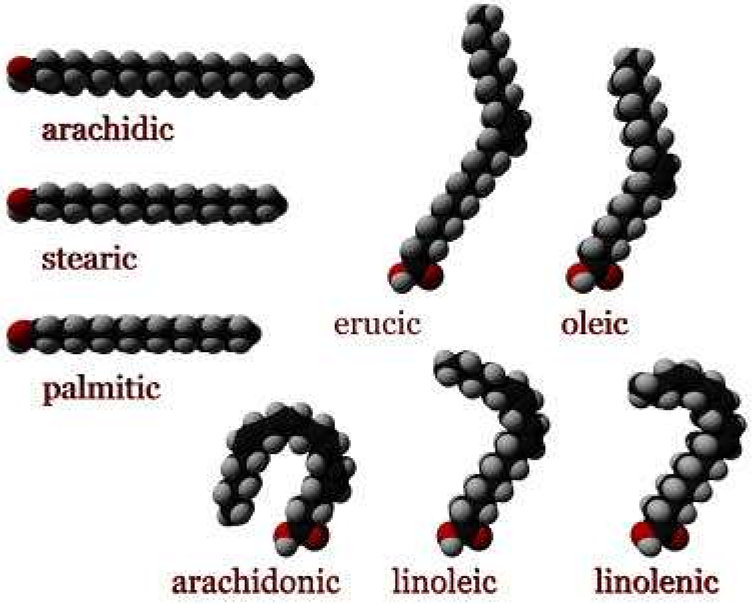

Figure 8-3. Common Fatty Acids Found in Plant Oils. (http://en.wikipedia.org/wiki/File:Rasyslami.jpg)

Attached fatty acids in TAG vary substantially from one crop species to another. The functions and performance characteristics of crop oils are commonly determined by the functional groups, length, and number of double bonds within fatty acids (Bondioli, P. 2005; Erhan, et al., 2006). Polar structure and high molecular weight TAG in plants oil possess many desirable lubricant properties, such as high viscosity index, low volatility, and high flash point (Dharma, 2002; Stymne, et al., 2006).

Oxidative stability of plant oils is directly related to the degree of unsaturated hydrocarbons presents in oils. Saturated fatty acids are high in cetane value and oxidative stability but low in cold stability. Polysaturated fatty acids are stable in cold condition but low in oxidative stability (Bondioli, 2005). Plant oils are low in oxidative stability due to its high content in unsaturated hydrocabons (Tupotilov, 2006; Stymne, 2006). The oxidation of plant oils generally involves the following two phases (Hamblin, 1999; Fox, et al. 2003; Rudnick, et al. 2006):

1. The formation of hydroperoxides on the fatty acid of plant oils.
2. The formation of alcohols, aldehydes, and ketones from hydroperoxides.

The operational temperature range of plant oils is between -40C to 120C, which is too narrow and another undesirable property of plant oils for the lubricant applications operated at high temperature, such as automotive lubricants.

In order to meet the challenge of lubricant applications, plant oils require additional antioxidants supplements, such as phenolic and arylamine antioxidants, to enhance the oxidative stability (Rudnick, et al. 2006). Another possible approach to improve the oxidative stability of the plants oils is to remove the double bonds by either genetically modification or chemical processes (Stymne, et al. 2006; Rudnick, et al. 2006).

8.7.1.3 Selection of Renewable Plant Oils

The composition and properties of various plant oils have been evaluated and indentified in the previous sections. Many studies have confirmed that plants oils containing a high concentration of monounsaturated fatty acid, oleic acid (18:1), is considered as the best candidates for lubricants and hydraulic oils due to its desirable lubrication properties. (Dharma, 2002; Stymne, et al., 2006; Maroto, 2009). Other criteria should be factored into the selection of suitable candidates for biolubricant production including (Rudnick, et al. 2006):

- Bio-based sources for oil extraction should be readily enough in order to avoid resource competition for foods.
- Bio-based oils should contain more mono-unsaturated fatty acid than poly-unsaturated fatty acids.
- The cost of bio-based sources should have a stable trading price that is lower than the cost of petroleum.

According to the summary in Table 8-2b and 8-3 and the requirements as previously discussed in this section, new rapeseed is one of ideal candidates used as renewable resource for the lubricant production. Corn and soy bean are not considered as significant oil resources due to their low oil content and competition over food sources.

Caster oil is rich in Ricinolic acid and has been widely used to produce motor oil for motorcycle engines and racing car, such as Catrol-R motor oil. Other applications of caster oil include soild lubricant, fuel additive, wax used for carbon paper and electrical condenser (Armstrong, 1999).

8.7.2 Plant Oil Production

The price of plant oil is substantially determined by the cultivation amount of oil crops. The selection of oil crops is most likely determined by the local climate and demand (The Freedoina Group, 2009).

In 2005, the total amount of plant oil extracted from oil crops in the world was estimated about 258 billion pounds from 1459 billion pounds of various oil crops (The Freedoina Group, 2009; Stymne, et al., 2006). Table 8-4 lists the most popular oil crops cultivated for oil extraction in the world.

Europe represents 71.4 % of the world production of olive oils. Poppy seed with 68% of the world production is the second most popular oil crop cultivated in Europe. Other common oil crops in Europe include poppy seed rape and mustard seed (32.7%) and hempseed (15.1%) (FAOSTAT, 2006; Stymne, et al., 2006).

Table 8-4. Most Popular Oil Crops in the World. (Sources: FAOSTAT data, 2006; Stymne, et al., 2006)

Oil Crop Production in 2005	
Corp	**Billion Pounds**
Soybeans	461
Oil Palm	382
Cocounts	121
Rape and Mustard Seeds	101
Cottonseed	91
Sunflower Seeds	68
Olives	32
Sesame Seeds	7
Castor Bean	3
Safflower Seeds	2

8.7.2.1 Technologies in Producing Biolubricant Feedstocks

Similar to the process in the production of petroleum-based lubricants, the first step in the production of biolubricants is to prepare feedstocks. Unlike feedstocks derived from petroleum, bio-based feedstocks are extracted from various biomass, such as oil crops and algae. The purpose of extraction is to separate fluid TAGs from the other constituents in biomass, such as polysaccharides, proteins, etc. Most importantly, the preservation of extracted TAG against oxidative degradation during the process and storage is even more challenging than the extraction process. In general, plant oils are more vulnerable to oxidation than petroleum-based oils, such as mineral oils and synthetic compounds, due to the high concentration of unsaturated compounds in plant oils (Tupotilov, et al., 2006; The Freedoina Group, 2009).

The two most common methods to extract TAG from oil crops are mechanical pressure and organic solvent extraction depending on the oil content of crops. Solvent extraction has been commonly used for the crop with low oil content, such as soybean and corn (Tupotilov, et al., 2006). The following sections present the processes in the preparation of bio-based feedstocks.

The non-polar solvents, such as diethyl ether or chloroform, are commonly used to extract neutral oils. The polar solvents, such as ethanol or methanol, are usually used to disrupt hydrogen bonding or electrostatic forces in membrane-associated oils (Cyberlipid Center, 2010).

For the production of industrial feedstocks, TAG molecules are further processed based on the requirement of applications into either free fatty acids (FFA) by fat splitting or methyl eters (ME) by methanolysis as illustrated in Figure 8-2 (Bondioli, 2005; Cyberlipid Center, 2010).

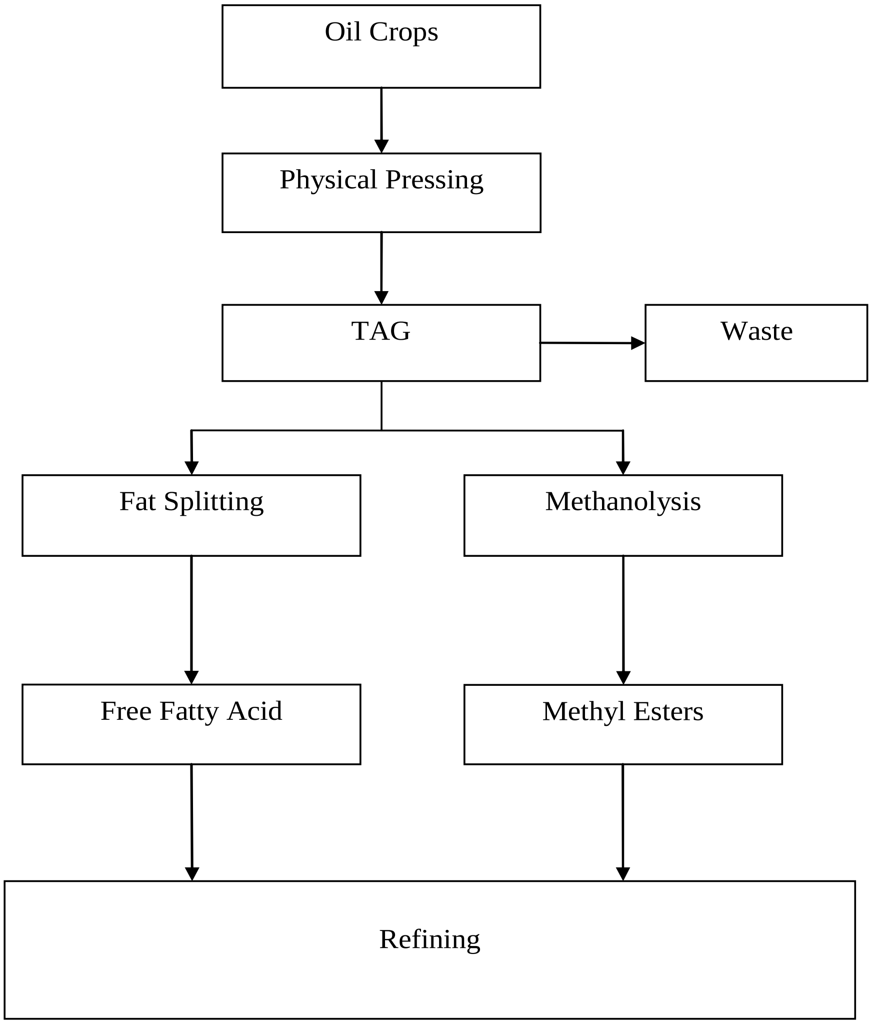

Figure 8-4. Processes in the Production of Bio-Lubricant Raw Materials.

Cold fractionation and vacuum distillation are commonly used as final steps to refine FAA and ME into different products with specific characteristics in order to be used for industrial feedstocks either as raw material or after chemical syntheses. Figure 8-3 illustrates a simplified flow diagram in the final step of refining processes (Bondioli, 2005; Cyberlipid Center, 2010).

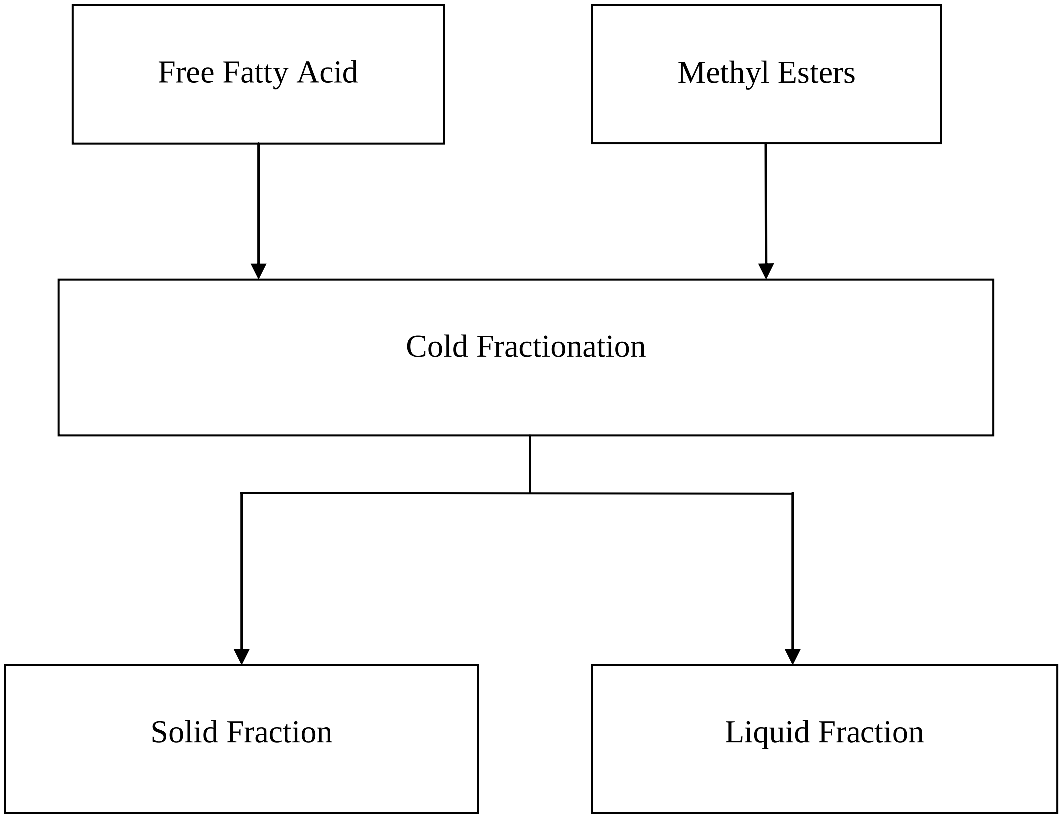

Figure 8-5. Refining Processes in the Production of Biolubricant Feedstock.

8.7.2.2 Technologies in Producing Biolubricant Base Oils

Similar to petroleum fractionation, liquid fraction can be further refined into various grade of hydrocarbons by vacuum distillation based on the requirements of industrial applications.

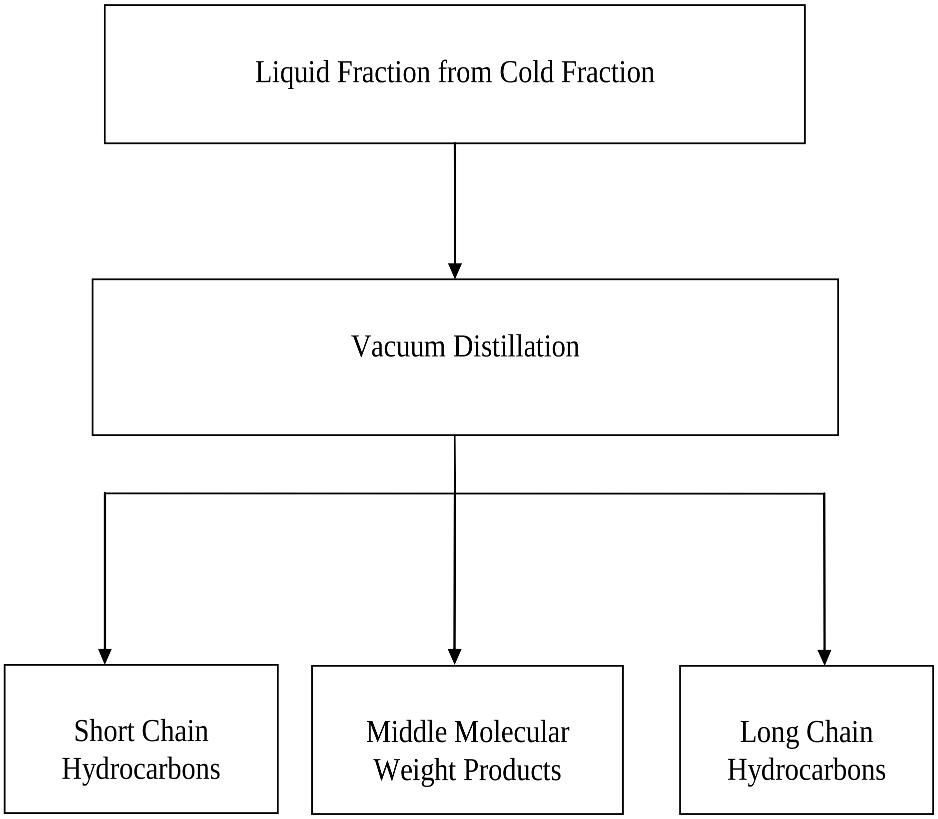

Figure 8-6. Production of Biolubricant Base Oils.

8.7.3 Plant Oil Enhancement Technologies

The saturated and monosaturated fatty acids, such as oleic acid, are the desirable compounds in plant oils required for the biolubricant applications. The fatty acids found in plant oils mostly poly-saturated fatty acids. Although the original composition of most plant oils is not perfect for biolubricant application, plant oils are still environmentally better than petroleum-based lubricants in the long run.

To meet that challenge, the problems associated with plant oils can be improved by either genetically block or chemically disrupt the genes responsible for the conversion of mono-saturated fatty acid to poly-saturated fatty acids.

8.7.3.1 Genetic Engineering Modification

Genetic engineering, also known as recombinant DNA technology, refers to the process of manipulating DNA of organisms. Plant developed by genetic modification into a new crop with a desired trait is refereed as a transgenic plant (Ross, et al. 2000).

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Poly-saturated fatty acids in plant oils are derived from oleic acid through a serious of enzyme-catalysis biochemical reactions. Since desaturase is formed through DNA transcription and followed by mRNA translation, the key to increase the concentration of oleic acid for biolubricant applications is either to disrupt the transcription of DNA or block translation of mRNA into enzyme (Ross, et al. 2000; Erhan, et al., 2006; David M. Mousdale. 2008).

In the case of desaturation improvement for soy bean, oleic fatty acid has been successfully increased 300 to 500% by genetic engineering modification (Erhan, et al., 2006).

8.7.3.2 Plant Bleeding

Plant bleeding is the process that enhances specific traits by mutations through either natural selection or artificial modification, such as chemicals or radiation. Plant bleeding techniques have been successfully used to produce soybean with a high concentration of oleic fatty acid by reducing 90% of linolenic fatty acid (Ross, et al. 2000; Schmidt, et al. 2006).

8.7.3.3 Chemical Alternation

Many studies have confirmed that the composition of plant oils can be transformed through various chemical processes to improve the specific performance characteristics for lubricant applications, such as oxidation stability and fluidity at low temperature. Most chemical alternations of plant oils used today involve either 1) chemical reactions of hydrocarbon chains in fatty acids, such as hydrogenation, ozonolysis, epoxidation, caboxylation, cyclization, alkaylation, acetylation, olefin metathesis, and catalytic cracking, or 2) modification of the carboxyl groups in fatty acids, such as transesterification and hydrolysis (Richtler and Knaut, 1984; Erhan, et al. 2006).

8.7.3.4 Ozonolysis

As the name of process implies, this process employs ozone to convert unsaturated fatty acid ester, such as oleic ester, in plant oils into either mono- or dialdehydes by reduction or mono- or dicarboxylic acids by oxidation (Dahlke, et al. 1995; Erhan, et al. 2006).

Ozonolysis is commonly used to improve 1) viscosity index of plant oils due to the linear diacid portion of the diester, 2) pour point because of the contribution of the branched ends, and 3) thermo-oxidative stability by converting the double bond into saturated single bond. However, the molecular weight of final product, diester, is much lower than the original fatty acid after oxidative scission. The esterification is commonly used to increase the viscosity and shear stability of the products of ozonolysis for lubricant applications. Figure 8-7 illustrates the simplified process of ozonolysis of oleic ester (Richtler and Knaut, 1984; Erhan, et al. 2006).

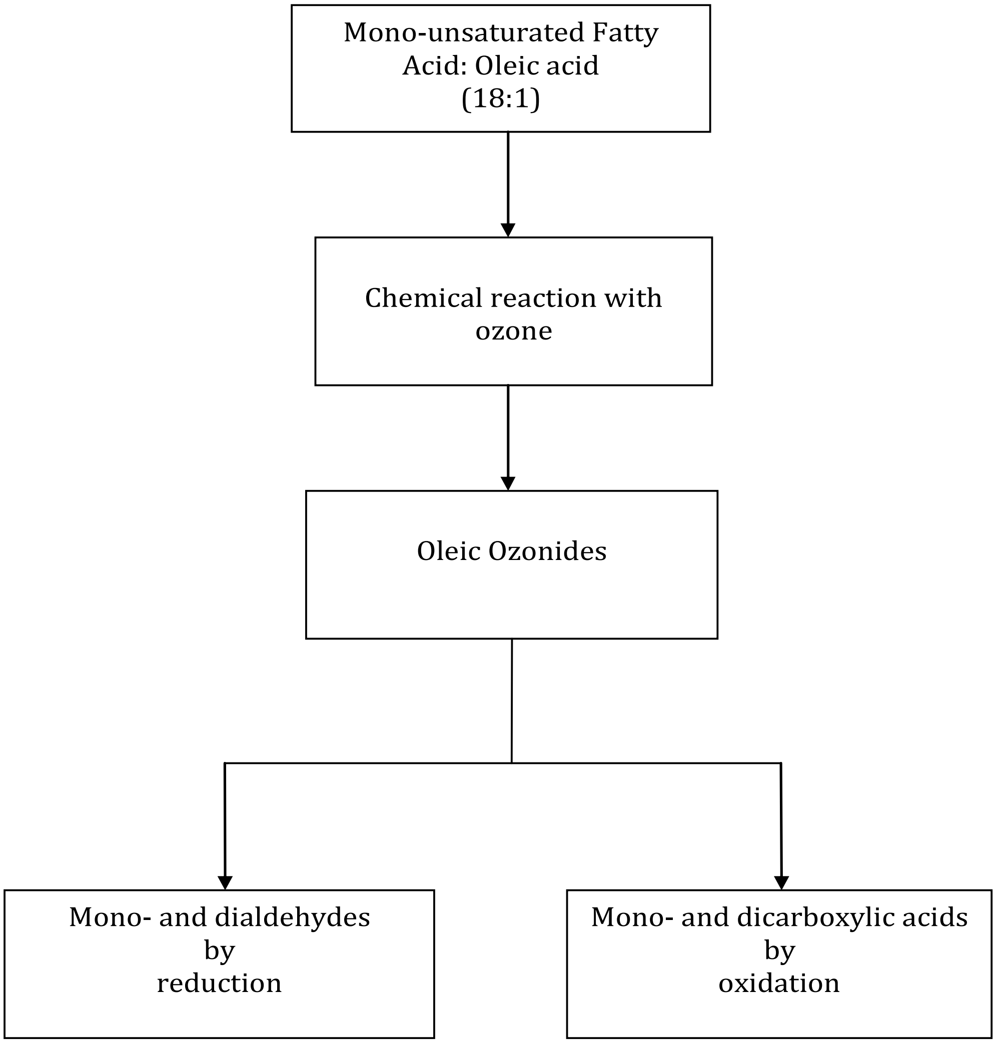

Figure 8-7. Ozonolysis of Oleic Fatty Acid.

8.7.3.5 Transesterification

Transesterification has been used for chemical modification of plant oils before World War II. This process originally invented by scientists E. Duffy and J. Patrick in the 18th century and used to convert plant oil into a high viscosity biofuel (Erhan, et al. 2006).

For lubricant applications, plant oils are commonly transesterified by high alcohols (C8 to C14) into high viscosity esters and followed by transesterification with polyhydric alcohols, such as neopenthlglycol (NPG), trimethylol propane (TMP), pentaerythritol (PE), and dipentawrythritol, to eliminate the byproduct from the first transesterification process, such as glycerol ß-carbon, in order to improve the stability of plant oils (Schuchardta, et al. 1998; Erhan, et al. 2006).

8.8 Summary

As the shortage of petroleum reserve and the environmental impact of petroleum based used lubricants are becoming a global concern, searching the alternative sources for the production of lubricants is inevitable and becomes very important and cannot be ignored for a scientific research.

A new generation of lubricants made from renewable resources, such as plant seeds, algae, and waste, have many benefits over conventional petroleum based lubricants and demonstrated as a feasible solution to meet worldwide increased demand in lubricants.

The utilization of renewable source, such as plant oils, as green alternatives in lubricant science is the key to promote a sustainable earth as the ultimate goal of this research. Many studies have confirmed that oils extracted from many plant seeds and algae are structurally similar to petroleum long-chain hydrocarbons and possess many excellent properties, which are suitable for lubricant applications. More importantly, the lubricants derived from plant oils extracted from oil crops, such as canola, sunflower seeds, soybeans, are 1) sustainable; 2) biodegradable; 3) less hazardous and to human health, fauna, and flora; 4) genetically changeable to the desirable traits and increase the production yield. Therefore, using oils extracted from crops is recently becoming a popular green solution for the production of feedstock, biolubricants, biofuels, and biochemical products.

The value of oil crops is greatly affected by the worldwide demands and industrial applications for either high yield of oil (biofuel and biolubricants) or high content of protein (animal feeds). Increase in the cultivation of crops has been become inevitable in order to support the demand for both food use and industrial applications. In order to meet the demands without causing any economical and environmental impacts, it is desirable to improve plant oil yields by production enhancement technologies, such as genetic engineering modification and plant bleeding techniques, instead of expanding the area of land for cultivation by destroying large areas of forests on earth for agriculture development.

The composition of plant oils varies with the plant, the crop, soil types, the climatic conditions, the season, and the amount of sunlight. Most plant oils extracted from oil crops consist mostly of triacylglycerols (TAG) with various compositions of fatty acids and minor amount of other compounds.

Generally plant oil with a high concentration of saturated linear fatty acids is not desirable for lubricant production because they generally appear as solid form at room temperature.

Many studies have confirmed that plant oil containing a high concentration of monounsaturated fatty acid, oleic acid (18:1), is considered as the best candidates for lubricants and hydraulic oils due to its desirable lubrication properties.

The concentration of oleic acid can be also improved by either genetically or chemically to block or disrupt genes for the conversion of mono-saturated fatty acid to poly-saturated fatty acids.

New rapeseed is rich in oleic acid and considered as one of ideal candidates used as renewable resource for the lubricant production. Corn and soy bean are not considered as significant oil resources due to their low oil content and competition over food sources. Castor oil contains a high concentration of ricinolic acid and has been widely used to produce fuel additive, wax, and motor oil for motorcycle engines and racing car, such as Castrol-R motor oil.

CHAPTER 9

SUMMARY AND RECOMMENDED FUTURE WORKS

9.1 Summary

9.1.1 Overview of Green Tribology and Lubricant Technology

Lubricants, either mineral-based or synthetic made, are the products derived from petroleum and developed through tribological researches to perform not only for lubrication but also for many other functions, such as cooling, noise and vibration reduction, cleaning, corrosion protection, and power transferring. However, the contamination of various impurities generated from the operation of machines or engines can significantly degrade the efficiency of lubricants and alter the composition of lubricants. Research have confirmed that used lubricants collected from oil exchange are highly toxic to human health, fauna, and flora, and illegal dumping of used lubricant has posed a risk to the natural environments. Each year over two billion gallons of used lubricants are generated around the world. Because the disposal of used lubricants is becoming a global concern, the study of the potential impacts of used lubricants to human health, animals, plants, and the environment is very important in raising public awareness to properly handle used lubricants in order to prevent this hazardous waste from releasing to the environment.

The analysis of used lubricants composition, the evaluation of the biodegrability and toxicity of used lubricants, and the assessment of relative risk of used lubricants to human health and ecosystems have been reviewed and discussed in this dissertation.

On the other hand, used lubricant also contains a significant amount of hydrocarbon compounds. Hydrocarbons found in used lubricants can be properly regenerated from used lubricants for many applications, such lubricant base materials and an energy source. The regeneration of used lubricants has enormous benefits, including minimizing hazards, reducing waste, protecting the environment, and conserving energy and natural resources as the energy shortage is becoming a global problem nowadays. The comparison of the conventional regeneration systems for used lubricants is summarized in Table 9-1.

Table 9-1. Comparison of Advantages and Disadvantages of Treatment Systems in Used Lubricants Regeneration.

System	Advantages	Disadvantages
Clay Bleaching	Simple, low capital cost	Low product quality, High temperature Environmental impact (clay sludge)
Acid System	Simple, low capital cost	Low product quality, Environmental impact (acid sludge), High Temperature
Propane System	Moderate yield, Good product quality, Recyclable and reusable sovent	Expensive, High temperature
Thermal System	Moderate yield, Simple	High temperature
Hydrosystem	High product quality	High Pressure
Thin Film System	Moderate yield, high product quality	High cost, high temperature, high pressure
CSEC System	Simple, low capital cost, Low operating temperature and pressure	Moderate yield

9.1.2 Development of Cold-Stage Energy Conversion System

To promote a sustainable earth and help the world to reduce used lubricants by converting them into an economically competitive energy resource are the major objectives in this research.

This dissertation presents the preliminary study of feasibility and effectiveness in 1) the binary solvent process, which is a newly developed technology used for lubricant purification and hydrocarbon compounds recovery under atmospheric process and room temperature; 2) the binary system matrix, is developed to enhance the efficiency of the binary solvent process; and 3) the Cold-Stage Energy Conversion (CSEC) System is a novel continuous flow system capable of regenerating used lubricants as well as rejuvenating used solvents which operates under atmospheric pressure at a relatively low temperature.

The binary solvent process has demonstrated to be a viable technology to simultaneously remove up to 93% of impurities (Table 9-1, 9-2, and 9-3) and recover up to 99% hydrocarbon compounds (Table 9-4, 9-5, and 9-6) from different types of used lubricant samples (mineral-based, synthetic made, and mixed sources). Both purification and hydrocarbon recovery could operate under atmospheric pressure at room temperature 77°F (25°C). Furthermore, all reagents used in this process could be recycled and reused indefinitely under atmospheric pressure and at a relatively low temperature, 156.2˚F (69˚C) compared to other conventional process.

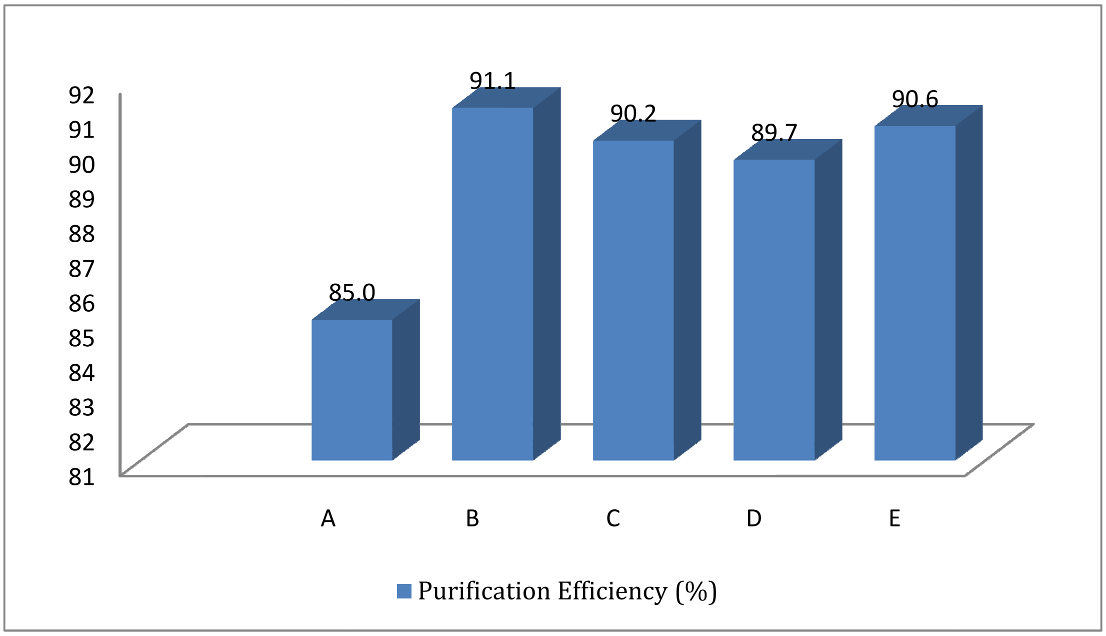

Figure 9-1. Purication Efficiency of Binary Solvent Process for Used Mineral-Based Lubricant Samples.

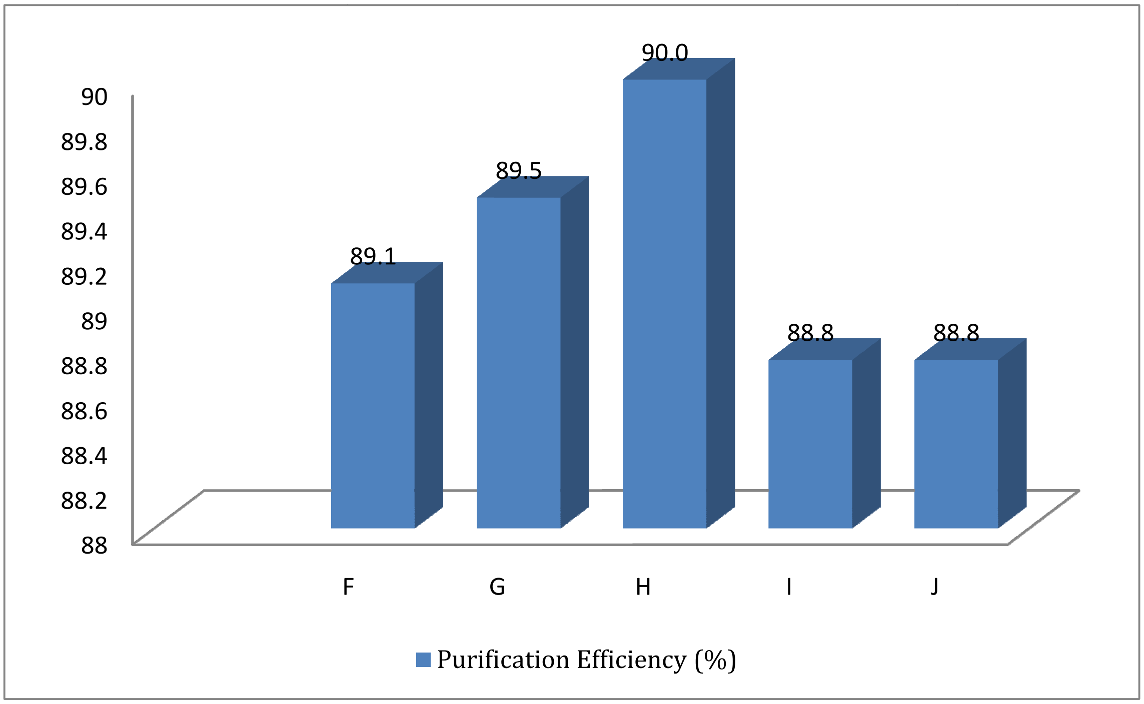

Figure 9-2. Purication Efficiency of Binary Solvent Process for Used Synthetic Lubricant Samples.

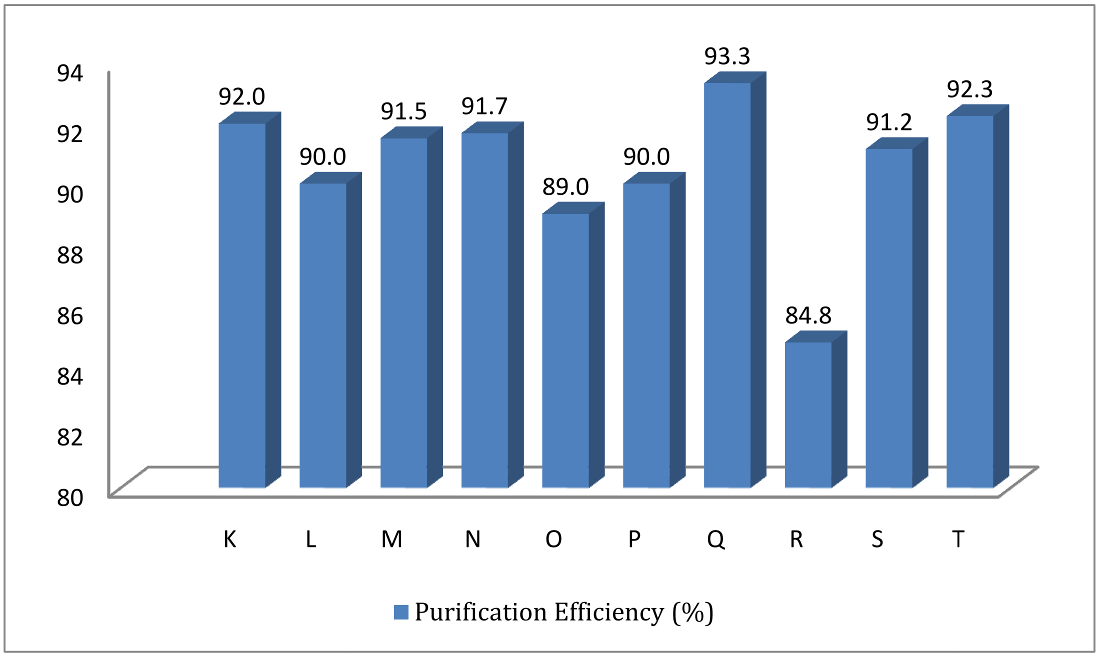

Figure 9-3. Purication Efficiency of Binary Solvent Process for Mixed Used Lubricant Samples

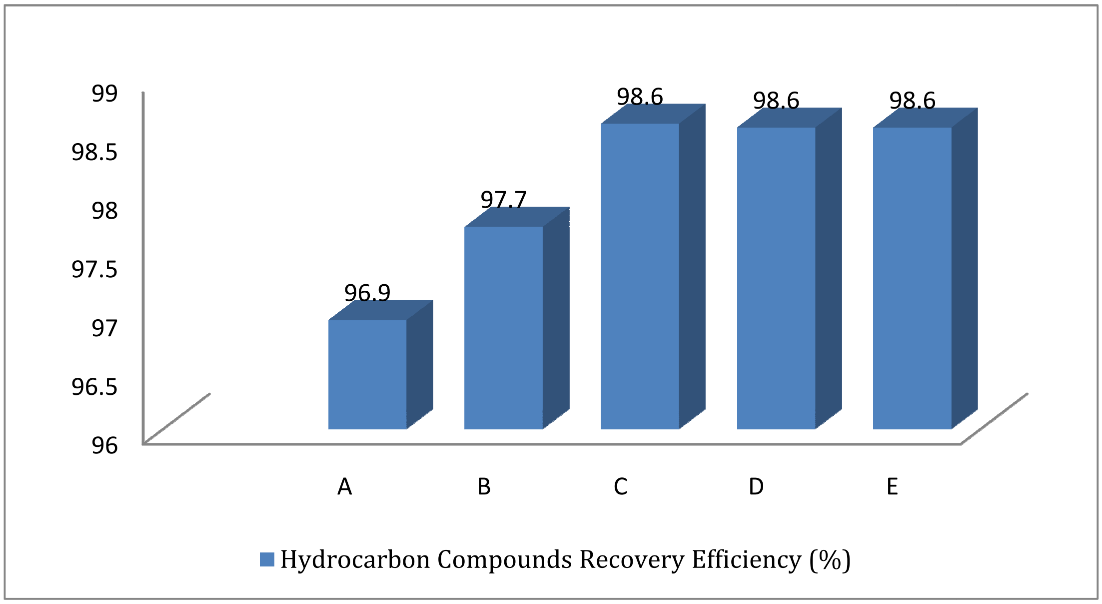

Figure 9-4. Hydrocarbon Compounds Recovery Efficiency of Binary Solvent Process for Used Mineral-Based Lubricant Samples.

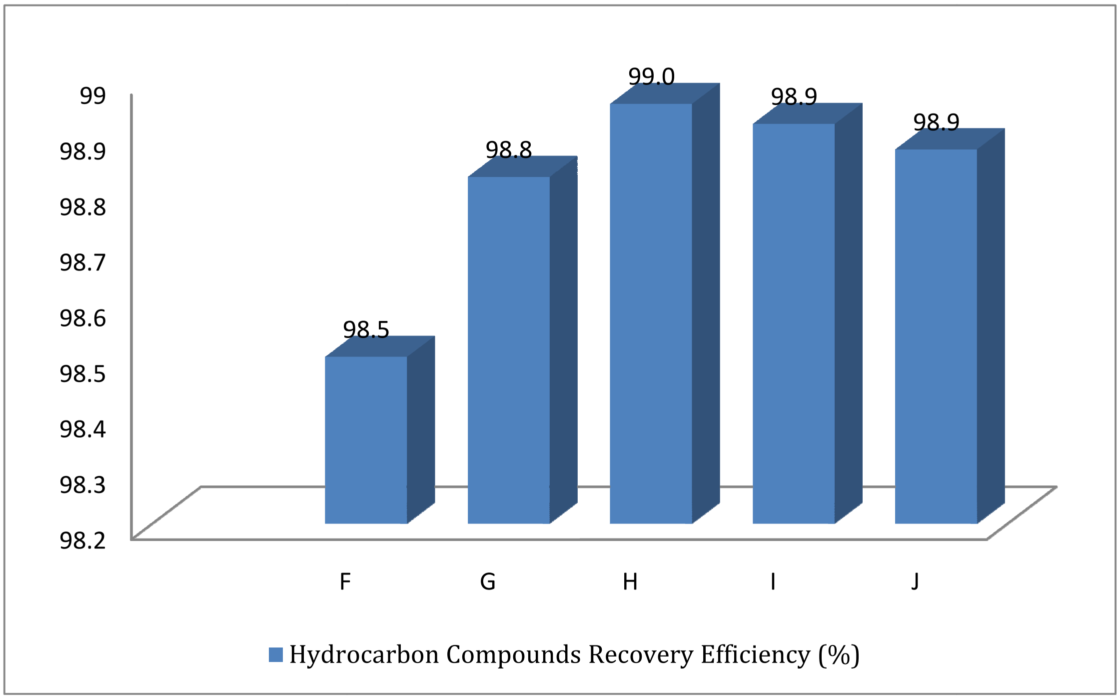

Figure 9-5. Hydrocarbon Compounds Recovery Efficiency of Binary Solvent Process for Used Synthetic Lubricant Samples.

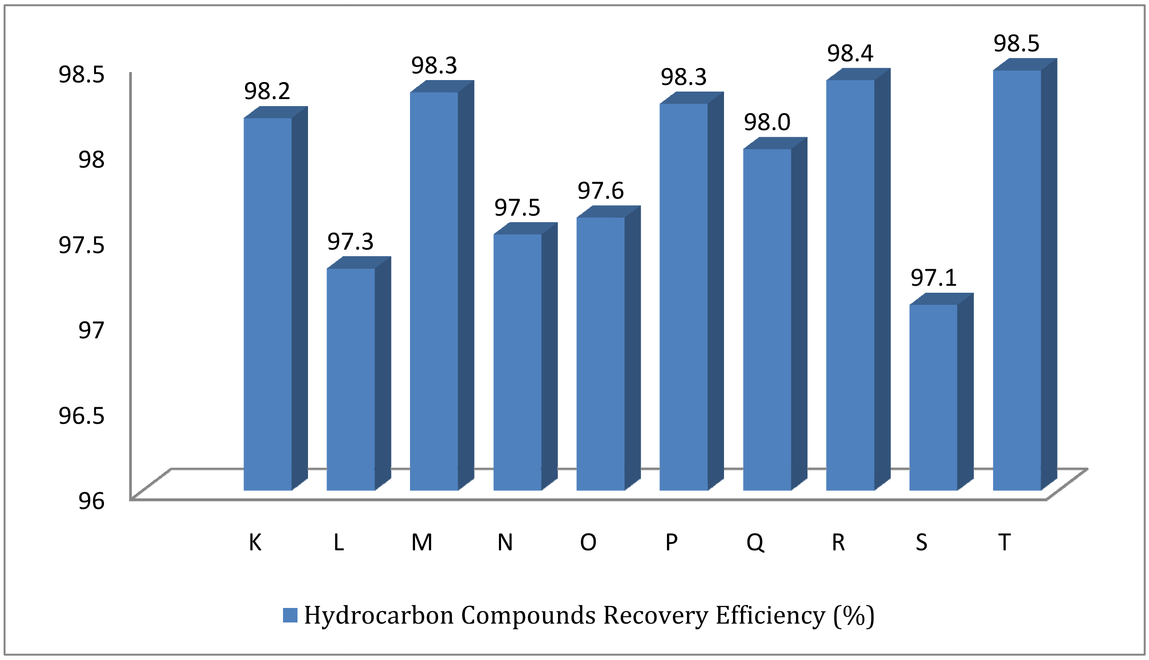

Figure 9-6. Hydrocarbon Compounds Recovery Efficiency of Binary Solvent Process for MixedUsed Lubricant Samples.

The efficient use of organic solvents is one of the major requirements for the binary solvent process because using excess amount of solvents is neither environmentally friendly nor economically favorable. In order to minimize the use of solvents in the process, the binary system matrix was designed to determine the most effective mixing ratio in the binary solvent process for solvent/solvent in solvent mixture as well as solvent mixture/used lubricant.

The binary system matrix has been demonstrated as a promising analytical method to conclude the most effective mixing ratios that work for all used lubricant samples.

The best results could be achieved in purification and hydrocarbon compounds recovery by the following mixing ratios: the mixing ratio (wt. %) of hexane v.s. DMK is a) 1 to 3 for used mineral-based motor oils, b) 1 to 2 for used synthetic motor oils, and c) 1 to 3 for mixed used lubricants. The most effective mixing ratio (Wt.%) of used lubricant /solvent mixture is 1 to 9 for all samples.

The engineering approach, the supporting concepts, and the technologies used for the design of a binary solvent process, binary system matrix, and CSEC system are outlined below:

- The composition of most lubricants, either mineral-based or synthetic based, includes 80 to 95% of base oils and 5 to 20% of various additives.

- Additives are the essential elements added into lubricants to enhance the functions which lubricant base materials cannot perform. The concentration of additives in lubricant ranges from one thousand to three hundred thousands ppm depending on the applications. The typical additives used for lubricants are: 1) antioxidants or oxidation Inhibitor, 2) antiwear additives, 3) viscosity index stabilizer, 4) detergents and dispersing additives, 5) antiforming additives, 6) pour point improving additives, and 7) antirust and anticorrosion additives.
- The composition of used lubricants varies widely depending on the vehicle types, the length of service, and the collection conditions. Used lubricants commonly consist of hydrocarbon compounds from the original base oils and unburned fuel as well as various concentration of impurities, such as soot from burning of lubricant and fuel; soot gel networks; metal fragments from tear and wear of engine and machine; and water.
- The utilization of the non-polar organic solvent to dissolve non-polar hydrocarbon compounds in used lubricants is considered as the most logical and feasible approach for hydrocarbons recovery. However, PAHs in used lubricants are not the target compounds for recovery. Thus, the aromatic solvents have not been selected for this process.
- According to the theory of solubility and polarity, non-polar solutes, such as hexane, are less likely to dissolve in polar solvents. Using non-polar solvent alone cannot settle the suspended impurities. Therefore, using polar solvents, such as DMK, to control and settle the suspended soot gel networks is most logical

approach based on their incompatibility. Most importantly, the selected solvents must not be reactive to each other.

9.1.3 Promotion of Biomass-Based Lubricants

Today green tribology is an essential concept and knowledge for all modern industries, ranging from manufacturing to aerospace program, in order to optimize the energy efficiency as well as minimize the environmental impacts and the loss in materials. The utilization of renewable source, such as plant oils, as green alternatives in lubricant science is the key to promote a sustainable earth as the ultimate goal of this research. However, balancing the resources and the industrial use offers a major challenge in sustainable resource management. The adaptive management is crucial to achieving this balance.

As the shortage of petroleum is becoming a global concern, the promotion of lubricants made of renewable biomass is another major objective of this research because using biolubricants has many benefits to the environment and human health:

- The biomass used for producing bio-based oils is renewable and genetically changeable.
- Biolubricants are easily biodegradable, low in toxicity, and less hazardous to the environment because bio-based oils are totally free of aromatic compounds.
- Biolubricants have higher VI and are more stable with temperature change because of lower viscosity of bio-based oils.

- Biolubicants are safer to use because they are not toxic to skin and low in evaporation losses, which leads to less inhalation of oil vapor into the lung.
- The service life of equipments can be increased with biolubicants because the property of higher wetting tendency of polar esters may enhance friction reduction, which lead to prolong intervals between changes;
- Biolubricants require less maintenance and are easy to handle.
- The applications of biolubricants lead to significant cost saving.

Figure 9-7 summarizes the overall objective and of this research to achieve a sustainable earth.

http://maxgladwell.ning.com/group/greenearthfriend

Figure 9-7. Sustainable Development Toward A Sustainable Earth.

9.2 Recommendations for Future Work

- Since the efficiency of purification and hydrocarbon recovery of used lubricants depend on the degree of mixing between organic solvents and the components in used lubricants, improving the mixing mechanism in the purification and hydrocarbon recovery reactor is required in the future scaled-up Cold Stage Energy Conversion (CSEC) system.
- Evaluate the feasibility of implementing other processes in the future scaled-up CSEC system, such as desulfurization, color removal, and auto-determination of the optimal mixing ratios of solvents and used lubricants by an advance electronic senor using organic markers.
- Evaluate the development of biomass-based lubricants from algae and biomass wastes.
- Evaluate the production of biomass-based lubricants by different microorganisms.

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APPENDIX A:

LIMITING WEAR FACTOR FOR VARIOUS APPLICATIONS

Table A-1. Limiting Wear Factor for Various Activities (Eschmann, et al., 1985; Khonsari, et al., 2008).

Application	Limiting Wear Factor
Agricultural machines	8 - 25
Consturction machinery	6 - 12
Crushers	8 - 12
Electric motors	3 – 5
Gears, general engineering	3 – 8
Machine tool spindles	0.5 - 1.5
Motor vehicles	3 - 5
Paper-making machines	5 - 10
Plastic processing	8 - 12
Pumps, fans, compressors	3 - 5
Rail vehicles	6 - 12
Textile machines	2 - 8

APPENDIX B:

ENVIRONMENTAL FACTOR FOR VARIOUS APPLICATIONS

Table B-1. Environmental Factor for Various Activities (Eschmann, et al., 1985; Khonsari, et al., 2008).

Application	Environmental Factor
Agricultural machines	100- 1500
Construction machinery	200 – 800
Crushers	700 – 2100
Electric motors	2200 – 12500
Gears, general engineering	1100 – 10400
Machine tool spindles	5000 – 45000
Motor vehicles	250 – 1000
Paper-making machines	6700 – 27000
Plastic processing	1100 – 7000
Pumps, fans, compressors	900 – 6800
Rail vehicles	1400 – 13300
Textile machines	1200 – 40000

APPENDIX C:

RISK FACTORS OF PAHS

Table C-1. Risk Factors of PAHs.

PAH	Route of Exposure	Health Hazards
Acenaphthene	Drinking contaminated water; eating food s grown in contaminated soil; skin contacts with contaminated water and foods (EPA, 2009; EWG, 2010)	Reproduction and fertility problem; gastrointestinal (including liver) problem (EPA, 2009)
Acenaphthylene	Drinking contaminated water; eating foods grown in contaminated soil; Skin contacts with contaminated water and foods (EPA, 2009; EWG, 2010)	Reproduction and fertility problem, accumulation in wildlife and people (EWG, 2010)
Anthracene	Drinking contaminated water; eating foods grown in contaminated soil; skin contacts with contaminated water and foods (EPA, 2009; scorecard, 2010)	Respiratory and skin toxicant, gastrointestinal toxicant, and endocrine toxicant (EPA 2009)
Benzo(a)an thracene	Drinking contaminated water; skin contacts with contaminated water (ATSDR, 2010)	Probable carcinogen (ATSDR, 2010)

Table C-1. (Continued)

PAH	Route of Exposure	Health Hazards
Benzo(a)pyrene	Breathing air containing it; skin contacts with contaminated air, water, soil, or food; drinking contaminated water or cow's milk; eating grilled or charred meats (DHSS, 2009)	Probable carcinogen (skin, lung, and bladder cancer in humans and animals) (DHSS, 2009)
Benzo(b)fluoranthene	Drinking contaminated water; skin contacts with contaminated water and soil (MSDS, 2009)	Probable carcinogen, very harmful to aquatic organisms, long term damage to the environment (MSDA, 2009)
Benzo(f)fluoranthene	Skin contacts with contaminated aerosol (INCHEM, 2009)	Probable carcinogen, genetic damage to humans(INCHEM, 2009)
Benzo(g,h,i)perylene	Breathing contaminated air; eating or drinking contaminated food or water; skin contacts with contaminated soil or products (EPA, 2009)	Effects found in laboratory animals only. Reproductive problems, birth defects, and skin problems (EPA, 2009)

Table C-1. (Continued)

PAH	Route of Exposure	Health Hazards
Chrysene	Drinking contaminated water; skin contacts with contaminated water or soil (ECO-USA, 2009)	Probable carcinogen to human and animals (ECO-USA, 2009)
Dibenzo(a,h)anthracene	Breathing contaminated air; skin contacts with contaminated products; ingesting contaminated fluids (INCHEM, 2009)	Probable carcinogen to human and animals (INCHEM, 2009)
Fluoranthene	Drinking contaminated water; eating food s grown in contaminated soil; Skin contacts with contaminated water and foods (SCORECARD, 2009)	Respiratory and skin toxicant, gastrointestinal (including liver) toxicant, endocrine toxicant, and carcinogen (SCORECARD, 2009)
Fluorene	Drinking contaminated water; eating foods grown in contaminated soil; Skin contacts with contaminated water and foods (EPA, 2010)	Gastrointestinal (including liver) toxicant (EPA, 2010)

Table C-1. (Continued)

PAH	Route of Exposure	Health Hazards
Indeno(I,2,3-cd)pyrene	Breathing contaminated aerosol; skin contacts with contaminated products (INCHEM, 2009)	Possibly carcinogenic to humans (INCHEM, 2009)
Naphthalene	Drinking contaminated water (ATSDR, 2009)	Hemolytic anemia, cancer, vomiting, nausea, diarrhea, blood in the urine, and yellow skin (ATSDR, 2009)
Phenanthrene	Drinking contaminated water; eating food s grown in contaminated soil; Skin contacts with contaminated water and foods (EPA, 2009; NIST, 2009)	Respiratory and skin toxicant (EPA, 2009; NIST, 2009)
Pyrene	Drinking contaminated water; eating food s grown in contaminated soil; Skin contacts with contaminated water and foods (EPA, 2010; Chemicalland21, 2010)	Respiratory and skin toxicant (EPA, 2010; Chemicalland21, 2010)