THE FEASIBILITY STUDIES ON SONOCHEMICAL PROCESSES
FOR TREATING USED OIL:
TOXIN REDUCTION FOR ELIMINATING RECYCLE INTERFERENCE

by

Chia-Yu (Iris) Yang

A Dissertation Presented to the
FACULTY OF THE GRADUATE SCHOOL
UNIVERSITY OF SOUTHERN CALIFORNIA
In Partial Fulfillment of the
Requirements for the Degree
DOCTOR OF PHILOSOPHY
ENVIRONMENTAL ENGINEERING

December 2008

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ACKNOWLEDGEMENTS

I am deeply grateful to my advisor, Prof. T. F. Yen, for his consistent support and encouragement during my unexpected long period of study at USC. Thanks are also due to my other committee members: Prof. M. M. Pirbazari and Prof. K. S. Shing for their invaluable comments and suggestions. To other professors from whom I have taken courses and consulted, I would like to express my appreciation as well.

I wish to express my sincere appreciation to all my colleagues and associates in Dr. Yen’s group, particularly Dr. Jason Chen, who help me to initiate my interest in research during the early years of my study here. And I also wish to thank Dr. Jau Ren Chen, Dr. Frank Shiu, Dr. Joon Park, Mr. Ricky Li, and Dr. Kai Dunn. Their kind assistance and discussion often inspire me and help me finish my research work. I also feel an immense gratitude to some wonderful close friends in ENE program at USC, to Dr. Ann Chang, Dr. Jesse Tu, Dr. Eric Wu, and Dr. Walter Den for their friendships and companionships.

Finally, I sincerely express my gratitude to my family from the heart, especially my parents for their generous support over the years, to my sister and brothers for their love, patience, understanding, and encouragement. This dissertation would not mean nearly as much to me if it were not for the joy that I know it would bring to them. I dedicate this dissertation to them.
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ABSTRACT

Biochemical processes are well known for their superior performances in the upgrading of heavy crude oils. Based on a similar experimental strategy, a new technology was developed using biochemical process for the conversion of fossil fuel wastes into valuable biomaterials. The technology, developed by Brookhaven National Laboratory and based on a well-developed “Hydrocarbon to Protein” technology, is able to convert used oils to commercially valuable products through a biochemical process.

Production and utilization of fossil fuels generate wastes that contain EPA priority pollutants, such as polyaromatic hydrocarbons (PAH) and toxic metals. Used oil, which often contains metals, chlorinated hydrocarbons and other organic compounds, including many that are listed as EPA priority pollutants, is a good example that is generated at a rate of more than 1.5 billions gallons per year in the U.S. As a result, the associated impact to the environment is huge when there is uncontrolled dumping and landfilling of used oil in the environment. Used oil is a valuable resource and a vital source of energy; it still has lubricating value and heat value. Following the proper treatment to remove contaminants, used oil can be re-refined into base lube oil, reprocessed as fuel oil, or used as feedstock to produce petroleum-based products or other commercially valuable products via different processes. The high contamination levels in some used oils, however, increase the difficulties in the operations and generate hazardous byproducts as secondary pollutants. A large portion of the recycled used oil is combusted for energy utilization (often creates air pollution problems) or thermally destroyed by incineration (only when the oil has a high concentration of toxic contaminants that makes recycling
impractical or unsafe).

For BNL’s process, preliminary results showed that biomass generated from used oil contains 90% delipidated biomass and 10% lipids. The live biomass, delipidated biomass, and lipid have been proved successful in many applications and have high market values. However, there are problems encountered in the process, such as the poor quality and inconsistency of the bioproducts. The contaminants in the used oil are toxic to the bacteria strains used in the biochemical process and lower product yields. Another concern is the potential bioaccumulation of these toxins in the bioproducts. A proper pretreatment process is necessary to remove these toxins from the used oil stock to enhance the yield efficiency of the bioconversion process and improve the quality of the bioproducts.

A chemical-aided ultrasonic irradiation method is proposed to remove/degrade the toxins from used oil. Target contaminants that need to remove from used oil include heavy metals, chlorinated hydrocarbons, BTEX compounds, PAHs, and PCBs. Ultrasound irradiation is widely used in environmental cleanup applications to remove/degrade many toxic compounds in contaminated soils and waters; it is proven to be effective on many fossil fuel related applications, including upgrading and recovery. Free radical chain reaction is believed to be the dominant reaction to cause the effects in these systems. Ultrasonic irradiation has the ability to initiate and enhance the free radical generation from both water molecules and hydrocarbons. Hence, it could effectively remove/degrade the toxins in used oil with appropriate chemical additions. If technically and economically proven feasible, the chemical-aided ultrasonic irradiation process may be used not only as the pretreatment step for BNL’s biochemical process,
but could also become a pretreatment package in other used oil recycling and reprocessing options.

To develop a pretreatment package for BNL’s process (biocoversion of used oil), the chemical-aided ultrasonic irradiation is server as the basic terminology. Accompanied by destructive adsorption process, the removal efficiency for the decontamination of used oil is greatly enhanced. Optimal operating conditions will be examined and from the results of this study, it seems that this process is a feasible option to pre-treat toxic contaminants before further recycle or reuse options are applied to used oil.
CHAPTER 1

Introduction

Used oil is a valuable resource and a vital source of energy. Oil does not wear out; it just gets dirty after use. Thus, used oil still has lubricating value and heat value. Following the proper treatment to remove contaminants, used oil can be re-refined into base lube oil, reprocessed as fuel oil, or used as feedstock to produce petroleum-based products or other commercially valuable products via different processes.

Why is the proper management of used oil such an important issue? It is important because used oil often contain metals, chlorinated hydrocarbons and other organic compounds, including many that are listed as priority pollutants by the U.S. EPA. If used oil is mismanaged, the effects upon the environment will be detrimental. Since used oil is generated in large quantities, estimating more than 1.5 billions gallons per year in the U.S., that the associated impact to the environment is huge when there is uncontrolled dumping and landfilling of used oil in the environment. Spilled or dumped used oil on land can reduce soil productivity and seep into the groundwater to contaminate our water sources. According to EPA, just one quart of used oil can make 1 million gallons of water undrinkable. When used oil enters surface water, oil films will block sunlight, impair photosynthesis, and prevent the replenishment of dissolved oxygen, which lead to the death of aquatic plants and animals. When used oil is dumped down the drain and enters a sewage treatment plant, very small concentrations of oil in the wastewater (50 to 100 ppm) can foul sewage treatment processes. Used oil drainage has
been reported to account for more than 40% of the total oil pollution (the largest single source) to American waterways. In addition, both used oil and used oil filters are not regulated as hazardous waste in most states and allowed to be disposed in municipal landfills. Hence, the associated environmental problems are unquestionable.

Two major sources of used oil are automotive and industrial used oil. Automotive used oil tends to have a high concentration of potentially hazardous heavy metals, usually as the result of the engine or bearing wear, or the inclusion of these metals in oil additives. Industrial used oil tends to have a high level of chlorinated hydrocarbons and PCBs through careless management practices. The presence of other toxic organic compounds like benzene or naphthalene is usually associated with the oil formulation itself.

Currently, the recycling and reuse of used oil are limited to a few options. From the standpoint of energy conservation, recycling used oil efficiently saves a precious, nonrenewable resource. The most encouraged option, even by governments, for reuse of the used oil generated by consumers, is to recycle it back to base lube oil. It does not only save a tremendous amount of time and money, but more importantly helps to conserve our natural resources. Used oil can be combusted for energy utilization or thermally destroyed by incineration. Due to the economic benefit of recycling used oil, only a very small quantity of used oil is currently incinerated. The oil that is incinerated generally has a high concentration of toxic contaminants that makes recycling impractical or unsafe. One of the most common applications for recycled oils is reprocessing them to be used as fuels. In some cases, however, the contamination levels in used oil are too high. As a result, it increases the difficulties in the reprocessing operations. Moreover,
the hazardous byproducts generated in the recycling processes become secondary pollutants that are even more difficult to handle.

Production and utilization of fossil fuels generate wastes that contain EPA priority pollutants, such as polyaromatic hydrocarbons (PAH) and toxic metals. These wastes can be used as feedstock for biochemical processes. For example, studies showed that biological methods are capable of recovering metals, especially strategic metals, from fossil fuel effluents and wastes; the fossil fuel effluents include those derived from coal, geothermal, oil sand, oil shales and heavy/light petroleum. The recovery of uranium from black shale was proven feasible, as was the recovery of vanadium and nickel from petroleum, germanium and molybdenum from coal, and titanium from tar sands. Thus, biochemical processes can alleviate environmental problems associated with fossil fuel wastes and produce valuable bioproducts at the same time. Bacteria grown on oil wastes can be used as biosorbent materials, which is selective and efficient for environmental clean-up works including radionuclides removal from contaminated water. In addition, biosurfactants and biopolymers can be produced from oil waste cultures as byproducts. The produced biopolymers have demonstrated to be effective in enhancing oil recovery from oil reservoirs. The process is based on using biopolymers to control the sweeping front in oil recovery.

Biochemical upgrading of petroleum on some crude oils has been proven to cause: (1) qualitative and quantitative changes in the light and heavy fractions of crudes; (2) a decrease in asphaltene fraction with a concurrent increase in the concentration of saturates, aromatics, and resins; (3) a decrease in organic sulfur and nitrogen content with
a concurrent biochemical conversion of polar compounds into lighter molecular weight ones; and (4) a decrease in trace metals concentration, such as V, Ni, As, and Se.

The above findings initiated the development and/or modification of biochemical processes for the conversion of fossil fuel wastes into valuable biomaterials. The experimental strategy, based on the experiences gained in the past which deal with the biochemical upgrading of heavy crude oils, serves as a model in the development of the new technology. Since 1994, we here at USC have worked with Brookhaven National Laboratory on a project sponsored by DOE to develop a biochemical process that converts used oils to commercially valuable products. The basis of the process is adapted from a well-developed “Hydrocarbon to Protein” technology. Preliminary results showed that the biomass generated from used oil contains 10% lipids and 90% delipidated biomass. The live biomass concentrate has been successfully demonstrated in the bioremediation of oil waste contaminated soil. The delipidated biomass (rich in protein) is projected to be sold as high protein animal feed. Also, its ability as ion-exchange materials in uptaking and adsorbing heavy metals has been confirmed. The purity and properties of the 10% lipids from the process have not yet been evaluated, but potential markets for these natural and biodegradable lipids are raw material for surfactants, cosmetics, and medicine.

The change in virgin crude oil price directly affects recycling options for used oils. If higher-value products other than petroleum products can be recovered or produced from used oils by some new technologies, larger profit margins could be generated than those from reprocessed oil or re-refined oil. Unfortunately, not many research studies are
making developments for new recycling options of used oils. It is the uniqueness as well as the superiority of the biochemical process that converts used oils into commercially valuable products.

The contaminants in the used oils may be toxic to the bacteria strains that are used in the process and may lower product yields. Another concern is the potential bioaccumulation of these toxins in the bioproducts. A proper pretreatment process is necessary to remove these toxins from the used oil stock before it was sent to the fermentor. Not only the yield efficiency of the bioconversion process would be higher, but the quality of products can also be improved. When this process is upscaled to a commercial-size plant, the plant can accept a broader range of used oils as the feedstock for the process.

At the same time, efforts were made to compare other recycling and reprocessing options for used oils, and how the toxins were removed from their processes. Unfortunately, toxin problems are not treated as important issues in most cases. It is found out that toxins either end up in wastestreams as secondary pollutants to be treated or simply are released into our environment to cause other problems; they are seldom destroyed during the process. From environmental point of view, it is not solving the problem, but rather just passing the problem to another.

A chemical-aided ultrasonic irradiation method is proposed to remove/degrade the toxins from the used oil. Target contaminants that need to remove from used oil include heavy metals, chlorinated hydrocarbons, BTEX compounds, PAHs, and PCBs. Ultrasound irradiation is widely used in environmental cleanup applications to
remove/degrade many toxic compounds in contaminated soils and waters; and it is also proven to be effective on many fossil fuel related applications, including upgrading and recovery. Free radical chain reaction is believed to be the dominant reaction to cause the effects in these systems. Ultrasonic irradiation has the ability to initiate and enhance the free radical generation from both water molecules and hydrocarbons. Hence, it could effectively remove/degrade the toxins in used oil with appropriate chemical additions. If technically and economically proven feasible, the chemical-aided ultrasonic irradiation process may be used not only as the pretreatment step for BNL’s biochemical process, but could also become a pretreatment package in other used oil recycling and reprocessing options.

Previous joint efforts with BNL on the biochemical conversion process include survey on bacteria for bioconverting oil into bioproducts, evaluation on the properties of bioproducts for capacity and selectivity, and survey on potential markets for bioproducts.

For future work focused on toxin removal/destruction to enhance product yield and to improve product quality, kinetic studies on the toxins and oil properties analyses will be the basis for process design in scale-up and pilot-plant studies. By conducting specific analytic techniques on oil components to assure the adequacy and quality of the optimal used oil feedstock for the process, product yield and product quality can then be optimized. Economic analysis for an industrial scale operation will be conducted based on the modification of the current technology and the add-on pretreatment process. The outlines of the objects of this study and the research scopes include: (1) proper selection of used oil samples and optimization of their variations in oil to water ratio;
(2) preparation of used oil samples suitable for this research study; (3) choice of specific analytical techniques for oil components; (4) identification of all the factors for the chemical-aided ultrasonic irradiation reactions on used oil and optimization of the best operating conditions; (5) tests on other treatment options in combination with the chemical-aided ultrasonic irradiation process for better efficiency.

For the limited amount of used oil recycled each year in the United States, current options for reuse are mainly: reprocessing to fuels or re-refining into base lube oil. These two options, however, are not creating big profit margins to attract investors into the business because the profit margins largely depend on the price of crude oils, which is at a quite steady low in recent years. New technologies to convert used oil into value-added products are necessary to encourage the recycling of used oil instead of illegal dumping or disposing the used oil into the environment. The biochemical process developed at Brookhaven National Laboratory proved to generate various bioproducts from used oil for many applications and markets. Toxic materials, however, are widely found in used oil, especially many that are from EPA priority pollutant list. These toxins are creating problems in the recycling and reprocessing operations; they sometimes are concentrated and released to the environment to become secondary hazardous wastes. It is essential to develop a pretreatment process to remove the undesirable toxins for the existing biochemical process or other used oil recycle and reuse options.

In this research, a chemical-aided ultrasonic irradiation process is proposed for the decontamination of used oil. Its ability to degrade (not only remove) toxins commonly found in used oil, such as heavy metals (e.g., As, Ba, Cd, Cr, Pb, and Zn), chlorinated
hydrocarbons (CFC-12, CFC-113, and TCE), PAHs and PCBs, is evaluated. Factors that may affect the feasibility and efficiency of the proposed method will be identified and optimized in future studies. Besides batch type reactions, continuous flow system will also be suggested for a better approach, similar to an industrial scale operation.

In this study, different recycling and reprocessing options for used oil that are currently in practice, are studied. The method by which the contaminants are removed from their processes is also identified if possible. The proposed method, combined with simple polishing steps, may also be used as a pretreatment process for other options as well as for BNL’s biochemical process if technically and economically proven feasible.

The chemical-aided ultrasonic irradiation method is designed to investigate the feasibility in the decontamination of used oil, i.e., remove or degrade the toxic compounds. Initial studies will focus on a better understanding of used oil characteristics, water-in-oil emulsions, and vesicles/micelles. Actual used oil samples collected from commercial recyclers were used in this study. Specific analytical techniques for the characterization of used oil components and evaluation of the degradation performances was also being studied.

The entire dissertation is divided into six chapters. In Chapter 2, the general reviews on the background as well as properties of both used lube oils and possible contaminants found in used lube oil. And some of their current treatment alternatives will be described. Chapter 3 is the theoretical discussion. It begins with the introduction of ultrasound techniques and followed by adsorption process and destructive adsorption process, which are used in later research. In Chapter 4, the destruction of heavy metals
from used oil samples by ultrasound irradiation, adsorption, destructive adsorption is described. In Chapter 5, the destruction of BTEX compounds from used oil samples by ultrasound irradiation, adsorption, destructive adsorption is described. The last chapter, Chapter 6, contains important conclusions in this dissertation, and recommendations for future research.
CHAPTER 2

Overview of Toxins in Used Lube Oils

2.1 Lubricant Oils

2.1.1 Base Oils from Petroleum

Modern lubricants are mostly formulated from a wide range of base fluids and different packages of chemical additives. The majority of the base fluids is produced from the refining of crude oil since large crude oil refining operations can produce base oils with high quality and excellent performance at an economical price. Base oil composition may vary depending on the crude oil it is made from. For different applications, lubricants are formulated by blending different base oils and additives to meet a series of performance specifications. Hence, formulations and performance specifications for automotive lubricants, industrial lubricants, aviation lubricants, and marine lubricants are greatly different.

In a modern refinery, base oil plants (lube plants) are integrated with the mainstream refinery process. Overall production capacity for lubricant base oils is only a very small part (about 1 percent) of the total refinery production lines. Figure 2-1 indicates where a lube plant fits into a typical refinery process scheme and the inter-relationship between each step. Figure 2-2 is a typical process scheme for base oil production in which the numbers roughly indicate the relative amount of the intermediates and final products throughout the manufacturing process.
Figure 2-1. Simplified Schematic Diagram of a Typical Refinery. (Source: Mortier, 1997)
Figure 2-2. Schematic Diagram of Base Oil Production. (Source: Mortier, 1997)
The feedstock for this process is the residue from atmospheric distillation, which represents only about 50% of the original crude oil in a mainstream refinery process.

2.1.2 Automotive Lube Oil

For special performance specifications, automotive lube oil has unique characteristics different from industrial lube oils. The most important responsibility of the automotive lube oil is to form a layer between metal surfaces of various engine parts so that friction and wear is minimized. It also serves as a sealant to fill the microscopic ridges and valleys in any metal surfaces to increase the engine’s efficiency.

Lube oil also acts as the coolant in the automatic transmission and engine. It helps to take away the heat from the combustion of fuel as well as from friction. In addition, it serves as a cleaning agent to carry away dirt or other debris that may damage the bearings or other parts that are operated in tight tolerance. Debris is removed through the engine oil filter or the transmission filter. The detergent additives in the auto lube oil can combat the combustion by-products. Burning gasoline or diesel fuel produces acids, moisture, soda, ash and other contaminants. Hence, detergent would fight these by-products and inhibit their buildup as sludge or varnishes.

In order to meet the performance specification as mentioned above, a specific additive package is required to prolong the oil’s life and improve oil’s protective qualities. The major additives in automotive lube oils are listed as follows:

★ Detergents: to keep high temperature engine parts clean and free from deposits.
★ Dispersants: to suspend and disperse sludge- and varnishes-forming materials and prevent them to clog the engine.

★ Anti-wear: to add film strength to prevent wear of heavily loaded surfaces.

★ Friction modifiers: to reduce the friction losses throughout the engine.

★ Corrosion inhibitors: to fight the rust and wear caused by acids and moisture.

★ Oxidation inhibitors: to prevent oil and oxygen combination (produces damaging materials) and to reduce thickening of the oil and sludge formation.

★ Foam inhibitors: to limit the growth of bubbles and break them up quickly in the oil, allow the oil pump to only circulate oil, not oil and air throughout the engine.

★ Viscosity Index (VI) improver: to fight viscosity change with temperature variations.

★ Pour point depressant: to improve the oil’s ability in winter to flow at very low temperature.

2.1.3 Used Lube Oil

Additive packages blended into base oils range from 10 to 20 percent, by volume, of the finished lubricants. Performance of the lubricants deteriorates over time as the additives are chemically changed and the oil becomes contaminated (Mueller Associates, 1989). Contamination sources could be:

(1) the breakdown of the additives and their subsequent reaction;

(2) soot and lead from engine blowby;

(3) dirt and dust; metal particles from engine wear;
(4) residual gasoline or diesel fuels from incomplete combustion;

(5) water from combustion, blowby vapors, and rain water/salt water ingress;

(6) the mixing or dumping of other materials (chemicals or other oil types) into used oil.

Some industrial lubricants, such as transformer oils and hydraulic fluids, can be treated relatively easily and recycled. They can be readily collected and segregated without potential cross contamination. These oils may be regenerated to a recognized standard and returned to the original source while automotive engine oils often require a more sophisticated treatment to regenerate usable base fluids to acceptable quality.

Automotive used oils tend to have high concentrations of potentially hazardous heavy metals. Industrial oils tend to have high levels of chlorinated hydrocarbons and PCBs. The contaminants typically found in used oils are listed in Table 2-1 (Energy and Environmental Research Corp., 1989). It should be noted that most of these contaminants are known to be carcinogenic and listed as priority pollutants by the U.S. EPA. More detailed information about the physical and health-hazard properties for these contaminants can be found in Appendix B.
Table 2-1. Typical Contaminants Found in Used Oils.

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<tr>
<th>Metals</th>
<th>Chlorinated Hydrocarbons</th>
<th>Other Organic Compounds</th>
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<tbody>
<tr>
<td>Cadmium</td>
<td>Dichlorodifluoromethane</td>
<td>Benzene</td>
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<td>Arsenic</td>
<td>Tetrachloroethylene</td>
<td>Xylene</td>
</tr>
<tr>
<td>Barium</td>
<td>1,1,1-Trichloroethane</td>
<td>Benzo(a)anthracene</td>
</tr>
<tr>
<td>Zinc</td>
<td>Trichloroethene</td>
<td>Benzo(a)pyrene</td>
</tr>
<tr>
<td>Lead</td>
<td>Total chlorine</td>
<td>Naphthalene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PCBs</td>
</tr>
</tbody>
</table>

2.2 Used Lube Oils and Their Impacts on Human Health and the Environment

2.2.1 Introduction to Used Oil

What is used oil? According to Chapter 40 of the Code of Federal Regulations (40 CFR), Part 279 (Standards for the Management of Used Oil), the definition of used oil is any oil that has been refined from crude oil, or any synthetic oil, that has been used and as a result of such use is contaminated by physical or chemical impurities. According to the California Integrated Waste Management Board, any oil that has been refined from crude oil and has been put to use is “used oil”. The term “used oil” also applies to any oil that is no longer useful to the original purchaser as a consequence of extended storage, spillage or contamination with non-hazardous impurities such as dirt.
and water. On May 20, 1992, EPA published a listing decision for used oils destined for disposal. EPA decided not to list these used oils as hazardous wastes according to the technical criteria for listing in Sections 1004 and 3001 of the Resource Conservation and Recovery Act (RCRA) and Sections 26.1.1 I(1)(1) and (3) of 40 CFR. Used oil handlers must determine whether the used oil exhibits a characteristic of hazardous waste. If so, the handlers must dispose of the waste in accordance with the hazardous waste regulations in 40 CFR. Disposal of non-hazardous used oil must be performed in accordance with the Criteria for Classification of Solid Waste Disposal Facilities and Practices (40 CFR, Part 257) and the Criteria for Municipal Solid Waste Landfills (40 CFR, Part 258). In California and four other states, used oil is listed as a hazardous waste (Cal. IWMB, 1998). The hazards associated with the used oil come from the various additives used in its manufacture and from contaminants picked up from use in the internal combustion engine. More information about used oil will follow in Section 4.

According to Robert Arner of the Northern Virginia Planning District Commission, in 1994 approximately 90% of the used oil filters in the United States were disposed of in landfills. This resulted in 17.8 million gallons of oil and 161,500 tons of steel going to waste. Both of these resources could have been recycled instead.

EPA has exempted used oil filters from hazardous waste requirements since May of 1992, as long as they are not constructed of terne plate steel (a lead/tin alloy). They believed that a hazardous waste listing might discourage recycling and result in more uncontrolled disposals. The basis of the ruling was made from a study of the toxicity characteristics (TC) of 46 used oil filters. This study found that none of the 35 light-duty
vehicle filters that were tested exhibited TC; however, low levels of lead, chromium, cadmium, and benzene were detected (Peaslee, 1994). On the other hand, it was determined that five out of the 11 heavy-duty vehicle filters (terne-plated) exhibited TC for lead. Once the oil filters are collected, they are sent to processing facilities to be drained of oil (regulations require that filters be hot drained). The filters are then crushed into flat pucks, compressed into cubes or hemispheres, shredded, or dismantled. This steel is then available for recycling and re-manufacturing into many different products. Today, more people are aimed at promoting researches in the field of recycling oil filters (Peaslee, 1995) so that further pollution, caused by used oil filters which end up in the landfills, can be stopped.

Non-hazardous used oil (at most states) and sorbent mixtures, by federal law, can be disposed in landfills as long as they pass the Paint Filter Test. Free liquids, including oil, have been prohibited in the hazardous waste landfill since RCRA promulgated in 1980. Effective on Oct. 9, 1993, municipal landfills can no longer accept liquid wastes, including used oil. EPA requires sorbent materials that contain hazardous liquids to be mechanically processed using a centrifuge or wringer to remove free liquids for land disposal. Disposal procedures consist of combining conventional used sorbent material with used oil in a 55-gal steel drum and sending it to a landfill; the cost per drum is between $150-$350. Many used oil generators are seeking a new sorbent technology in order to reduce their disposal expenses (Mouche, 1995).
2.2.2 Proper Management of Used Oil

If managed properly, used oil is a valuable resource that can be reused either as a base stock for new lubricants or as a fuel. Only when mismanaged, used oil can threaten human’s health, damage the environment, and cause long-term liability for the costs of environmental cleanup upon generator or subsequent handlers.

On May 20, 1992, EPA decided that used oil destined for disposal is not a listed hazardous waste (U.S. EPA, 1992a). Federal regulations mandate that used oil must be tested to determine if the used oil is hazardous before it is disposed. If testing or other procedures find that the oil is hazardous, it must be disposed of as a hazardous waste under RCRA Subtitle C (U.S. EPA, 1996b). If the used oil is not hazardous, it must be disposed of in accordance with other federal regulations, such as RCRA Subtitle D (U.S. EPA, 1996a). In either case, the regulatory requirements are designed to prevent used oil from endangering human health and the environment.

Furthermore, on September 10, 1992, EPA decided not to list used oil destined for recycling as a hazardous waste (U.S. EPA, 1992b). EPA determined that used oils that are properly managed and recycled do not significantly threaten human health or the environment. Since EPA’s Used Oil Management Standard requires used oil to be managed in an environment ally safe manner, listing used oil that is to be recycled as a hazardous waste is not necessary. It is very important, however, to keep used oil from being contaminated with other hazardous wastes, otherwise, the risks to human health and the environment will greatly increase, and the costs for proper management will significantly rise.
2.2.3 Consequences of Releasing Used Oil to the Environment

According to EPA, just one quart of used oil is able to make 1 million gallons of water undrinkable. When used oil enters surface water, oil films will block sunlight, impair photosynthesis, and prevent the replenishment of dissolved oxygen, which lead to the death of aquatic plants and animals. When used oil is dumped down the drain and enters a sewage treatment plant, very small concentrations of oil in the wastewater (50 to 100 ppm) can foul sewage treatment processes. Used oil drainage has been reported to account for more than 40% of the total oil pollution (the largest single source) to American waterways (API, 1996). Used oil filters are not regulated as hazardous waste for most states and are allowed to be disposed in municipal landfills. Serious problems for the groundwater supplies surrounding the landfills are caused by residual oils from the filters that leach into the ground. Hence, practicing a good used oil recycling management is an important step for municipal solid waste reduction (Tchobanoglous, 1993).

Used oil that is dumped onto soil can be washed into surface water by rain or snow, or it can seep through the soil into groundwater to contaminate our water sources. Used oil in the soil can also evaporate into the air. The contaminants in used oil that enter the air through evaporation or improper burning can then settle, or be washed by rain or melting snow, into surface water or onto soil. The only way to make sure that used oil will not contaminate either water, soil, or air is to make sure that it is not released into the environment at all.
Since used oil is generated in such large quantities, estimating more than 1.5 billion gallons per year in the U.S., the associated impact to the environment is tremendously serious when there is uncontrolled dumping and landfilling of used oil in the environment. EPA data show that more than 33% of used oils generated each year in the U.S. are illegally dumped. The most uncontrollable used oil source is those do-it-yourself oil changers (DIYers). According to EPA, only 5 percent of used oil generated by DIYers is recycled, and the rest is either burned onsite (4 percent), disposed of in trash (30 percent) or illegally dumped (61 percent). Lack of public education and awareness and shortage of convenient recycling centers are main reasons why many DIYers do not participate in the used oil collection program. Of course, they don’t mean to harm the environment, most just simply don’t realize the damage they may cause through the improper handling of used oil.

As shown in Table 2-1, there are many harmful constituents in the used oil that may cause cancer or other health problems if they are inhaled or ingested. For example, it was reported that burning used oil tagged as the top source of airborne lead emissions (J. Air Waste Manage. Assoc., 1992), especially in those states where used oil is not listed as hazardous waste and lead concentration in used oil is not regulated. Used oil, therefore, is not prohibited for open burning even if lead is present at high concentrations. Typical levels of contaminants found in used oils are summarized in Table 2-2.

These contaminants not only cause problems when they are released into the environment through improper management, but sometimes also interfere with the recycling/reusing operations of used oils. At other times, they are found to be
concentrated in the waste streams of the reprocessing or re-refining plants and can cause further disposal problems.

2.3  Review on Existing Recycling and Reuse Options for Used Oils

2.3.1  The Importance of Recycling and Reusing Used Oils

Used oil is definitely a vital source of energy. Oil doesn’t wear out; it just gets dirty after use. Used oil can be re-refined into base lube oil, reprocessed as fuel oil, or used to as feedstock to produce petroleum-based products or other commercially valuable products via different methods. There are some facts about conserving resources by proper handling of used oil. Re-refining used oil takes about 1/3 of the energy needed to refine crude oil to lubricant quality; and one gallon of used lube oil that is re-refined produces the same 2.5 quarts of lubricating oil as 42 gallons of crude oil does (API, 1996). Collecting and recycling used oil, therefore, not only protects our environment from used oil contamination, but also conserves a valuable non-renewable resource.

From the standpoint of energy conservation, recycling used oil efficiently saves a precious, nonrenewable resource. Only one out of 70 barrels of crude oil is processed into virgin lube stock. That’s why many oil companies spend billions of dollars on exploring, recovering, and refining crude oil into quality lube oil. If the used oil generated by consumers can be recycled back to useful products such as pure lube oil again and again, tremendous time and money can be saved. More importantly, our natural resources will be conserved.
Table 2-2. Typical Levels of Contaminants Found in Used Oils.

<table>
<thead>
<tr>
<th>Categories</th>
<th>Automotive Used Oil Concentrations (ppm)</th>
<th>Industrial Used Oil Concentrations (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metal</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>5-25 ppm</td>
<td>NG</td>
</tr>
<tr>
<td>Barium</td>
<td>50-500 ppm</td>
<td>NG</td>
</tr>
<tr>
<td>Cadmium</td>
<td>2 ppm</td>
<td>NG</td>
</tr>
<tr>
<td>Chromium</td>
<td>3-30 ppm</td>
<td>NG</td>
</tr>
<tr>
<td>Lead</td>
<td>100-1200 ppm</td>
<td>NG</td>
</tr>
<tr>
<td>Zinc</td>
<td>100-1200 ppm</td>
<td>NG</td>
</tr>
<tr>
<td><strong>Chlorinated Hydrocarbons</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dichlorodifluoromethane</td>
<td></td>
<td>NG</td>
</tr>
<tr>
<td>Trichlorotrifluoroethane</td>
<td></td>
<td>NG</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>( \Rightarrow 1000\text{-}4000 \text{ ppm} )</td>
<td></td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>( \Rightarrow 1000\text{-}6000 \text{ ppm} )</td>
<td></td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total chlorine</td>
<td>1000-4000 ppm</td>
<td>1000-6000 ppm</td>
</tr>
<tr>
<td><strong>Other Organic Compounds</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>100-300 ppm</td>
<td>100-300 ppm</td>
</tr>
<tr>
<td>Toluene</td>
<td>500-5000 ppm</td>
<td>500-5000 ppm</td>
</tr>
<tr>
<td>Xylene</td>
<td>500-5000 ppm</td>
<td>500-5000 ppm</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>10-50 ppm</td>
<td>NG</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>5-20 ppm</td>
<td>NG</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>100-1400 ppm</td>
<td>NG</td>
</tr>
<tr>
<td>PCBs</td>
<td>NG(^*)-20 ppm</td>
<td>100 -1000 ppm</td>
</tr>
</tbody>
</table>

Note: \(^*\) NG indicates negligible amount detected
Many industries found that the capital investment on on-site used oil regeneration or reuse in the plant returns at a comparable rate, therefore, eliminates a lot of disposal costs (Nemerow, 1991).

2.3.2 Burning for Energy Recovery

Used oil can be thermally destroyed by incineration or combusted for energy utilization. Due to the economic benefit of recycling used oil, only a very small quantity of used oil is currently incinerated. The used oil that is incinerated generally has high concentrations of toxic contaminants that make recycling impractical or unsafe. Burning used oil is to utilize oil’s heating value and reduces the consumption of the non-renewable fossil fuels. It can create significant environmental problems however, by releasing major and trace elements and organic contaminants to the atmosphere. Proper flue gas pollution control equipment should be equipped with the cement kilns or industrial/utility boilers to minimize this problem. Otherwise, only the used oil that meets specified standards for maximum contaminant levels and minimum heating values can be burned. According to 40 CFR Part 266, all used oil collectors for the purpose of resale as fuel must document whether or not the waste meets the standards as outlined in Table 2-3.

EPA has to regulate used oil burning because toxic contaminants can end up in the smoke and ashes. A service station, county garage or other small site user does not need a regulatory permit for burning used oil if ALL the following conditions are met:

★ The heater is designed to have a maximum capacity of not more than 500,000 BTUs per hour.
The heater burns only used oil that the owner or operator generates or that is received from do-it-yourselfers who changed their oil at home.

Absolutely nothing has been added to the used motor oil -- no antifreeze, no solvents, and no other liquids.

The heater is vented to the outdoors.

Table 2-3. Used Oil not Exceeding any Specification Level is not Subject to this Part When Burned for Energy Recovery*. (from 40 CFR, Part 279.11)

<table>
<thead>
<tr>
<th>Constituent/Property</th>
<th>Allowable Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; 2 ppm</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt; 100 ppm</td>
</tr>
<tr>
<td>Halogens</td>
<td>&lt; 4000 ppm**</td>
</tr>
<tr>
<td>Flash Point</td>
<td>100° F minimum</td>
</tr>
<tr>
<td>PCBs</td>
<td>&lt; 50 ppm</td>
</tr>
</tbody>
</table>

Note: * The specification does not apply to mixture of used oil and hazardous waste that continue to be regulated as hazardous waste.

** Used oil containing more than 1000 ppm total halogens is presumed as hazardous waste unless analyses indicate otherwise.
2.3.3 Reprocessing

One of the economically attractive ways to manage used oil is to burn it as fuel. Thus, most used oil being reprocessed is utilized as fuel. Compared to direct burning, the major advantage from reprocessing used oil is that it improves the burning quality of used oil by removing/reducing some contaminants. A typical used oil reprocessing system is simplified as shown in Figure 2-3. Processes such as adding chemicals, heating, filtration, and centrifugation or combinations of the above can separate the undesirable constituents from valuable portions. Odor produced from nitrogen and sulfur species is the greatest concern in operating these facilities. Severe corrosion may occur in the equipment when acidic gases from additive elements and water vapors combine during the process. In reality, processing used oil is a widespread industry in the U.S., although mostly in small operations. There are more than 200 reprocessors around the country (Arner, 1992). Reprocessors and re-refiners often have to compete with each other to acquire used oil stock from independent transporters. Reprocessing, however, is a much more readily available recycling option than re-refining.

2.3.4 Re-refining

Used oil can be re-refined into base lube oil. Lube oil is a premium substance that can be re-refined and reused again and again. In general, water and dissolved low boiling point organic are removed by atmospheric or moderate vacuum distillation. Lube oil is then recovered and fractionated by distillation. Light ends byproducts are commonly used for plant combustion fuels. Diesel fraction and gas oil fractions can be recovered as high
Air, Water Emmissions; Sludge from Tank Bottoms

Figure 2.3. Simplified Used Oil Reprocessing System. (Source: Arner, 1992)
quality byproducts after further advanced treatment. Residual streams from distillation can be used by asphalt industry as an asphalt flux to produce roofing asphalt, paving asphalt, insulating materials, and other asphalt based products.

The major differences among all the processes are in how additives, impurities and sludges are removed. Considering technical feasibility, economical profitability, and operational easiness, re-refining processes are narrowed down to combinations of solvent treatment, distillation, hydrotreating, vacuum distillation, clay polishing, chemical treatment, and demetallization. Marketability of products and byproducts will affect the combination choices of the processes. Processes, which do not generate hazardous wastes that are difficult to handle, will be preferred in the future. Another problem is that the retail acceptance of recycled refined base oils in their blends, not because of quality issues, but mainly because of public acceptance. The public needs to learn that re-refining of used motor oil is a very sophisticated process that produces high quality base lube oil. Re-refined oil carrying the API logo meets the same high quality standards as lube oil made from crude oils.

Although there are many companies devoting their efforts to developing technologies for re-refining used oils, profitable used oil re-refining has not been so widespread due to the high capital and operating cost. The two major base oil re-refiners in the U.S. are Safety-Kleen (Chicago, IL) and Evergreen Oil (Newark, CA).

Safety-Kleen collected approximately 155 million gallons of used oil, oily water, and anti-freeze through its branches in 1996. From this total, the collection fee averaged approximately $0.26 per gallon. Customers begin to recognize the benefits of re-refining
and are willing to pay a higher price to have their used oil removed and processed for reuse. During this year, Safety-Kleen increased its re-refining capacity at its facilities in East Chicago, Indiana, and Breslau, Canada, to a combined annual capacity of 135 million gallons.

For Evergreen Oil, the current capacity of the re-refinery is 15 million gallons per year of used lubricating oil feed, which is converted to a high-quality distillate to be used as Secondary Feed to fluid catalytic cracking plants at nearby refineries (Oil & Gas J., 1997). The distillate is also suitable for hydrofinishing to produce high-quality lube base oils. The capacity is planned to double during 1998. The plant is also able to process 30 million gallons per year of oil-contaminated water. This capacity will be increased to 50 million gallons during 1998.

Both Safety-Kleen and Evergreen Oil are using the most recent and advanced technology -- distillation/hydrotreatment. The process is as shown in Figure 2-4. Not all available used oil streams are selected to proceed through this process. The better feedstocks include automotive and railroad crankcase oils, hydraulic and transmission fluids, and other high quality used oil streams. Potential feedstocks with high water, excessive contamination, or animal fats are processed as fuel. After pretreatment and thin-film distillation, the base oil fraction is then hydrotreated under moderate conditions and yields a range of base oil streams with different viscosities. By-products from this process are low boiling distillates, gas oils, and non-hazardous asphaltic residues. Metals are removed in the distillation step while higher-boiling halogenates and polar compounds are removed in hydrotreating step, thereby reducing the acid number
(Brinkman, 1991). Table 2-4 shows the typical re-refinery process stream characteristics (Pyziak, 1993). Emissions and waste streams from this type of process are limited in comparison to other older technologies (e.g., treatments by acid/clay, solvent extraction, and distillation/clay). That’s the reason why recent researches relating re-refining used oil technologies are mostly concentrating on how to improve the hydrotreating processes (Bhan, 1986; Brinkman, 1987). Safety-Kleen and Evergreen Oil both distribute re-refined lubricants, and sell the base oils to be blended by other lubricant marketers in the United States. Three major oil companies are blending premium quality additive packages with re-refined base oils, Lyondell Lubricants (Enviroline line), Unocal (Firebird line), and Chevron (ECO line, Environmentally Conscious Oil line). On June 30, 1988, EPA issued procurement guidelines for re-refined oil. All federal agencies, and all state and local government agencies and contractors that use federal funds to purchase such products, are required to implement a preference program favoring the purchase of re-refined oil to the maximum extent practicable. President Clinton’s Executive Order on Recycling further require that by April 20, 1994, federal agencies implement guidelines for the procurement of re-refined oil-base lubricants for all government vehicles. Increased consumer, industrial, and government demand taking the lead in the “buy recycled” movement can create and expand the market for the re-refined oil. The government can lead the way in building the market for this critical environmental product and demonstrate that the obstacles of price and performance are proven to be overcome. A growing market can also successfully overcome distribution and availability problems.
Figure 2-4. Simplified Schematic Diagram of a Re-Refining Process for Used Oil.
(Modified from Safety-Kleen Oil Recovery Co.)
Table 2-4. Typical Re-refinery Process Stream Characteristics.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Distillation Feed</th>
<th>Hydrotreat Feed</th>
<th>Final Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Light</td>
<td>Heavy</td>
<td>Light</td>
</tr>
<tr>
<td>Water %</td>
<td>20</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Flash pt. °C</td>
<td>&gt; 100</td>
<td>215</td>
<td>154</td>
</tr>
<tr>
<td>Cl, ppm</td>
<td>2800</td>
<td>2700</td>
<td>1150</td>
</tr>
<tr>
<td>S, ppm</td>
<td>4000</td>
<td>4000</td>
<td>3000</td>
</tr>
<tr>
<td>Zn, ppm</td>
<td>550</td>
<td>550</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Pb, ppm</td>
<td>70</td>
<td>70</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

Re-refined lube oil has to meet strict standards and must be approved by API. It has to contain at least 40% by volume re-refined oil in the base stock and contain limited amounts of certain toxic chemicals in base stock:

★ Organic halide < 5ppm total

★ PCBs < 1 ppm total

★ RCRA solvent waste < 1 ppm

★ Metals (Cd, As, Cr, Pb, Ba, Zn < 10 ppm, individual < 2 ppm)

★ Benzo(a)pyrene and benzo(a)anthracene < 5 ppm each

The re-refining of used motor oil is a very efficient process. According to Evergreen Oil Refinery, 1.41 gallons of wet used motor oil can yield 1 gallon of re-refined motor oil. Comparing this value to crude oil refining, it would take about 84
gallons of crude to yield 1 gallon of motor oil (data from American Petroleum Industry based on 1995 average yields for U.S. refiners). Of course, we cannot simply compare those ratios and conclude that refining from crude oil is inefficient. Refining crude oil obtains a large amount of fuels of various types. Below is the comparison of refining from used motor oil and refining from crude oil.

<table>
<thead>
<tr>
<th>Refining one unit of crude oil yields:</th>
<th>Re-refining one unit of used motor oil yields:</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 84% fuels (46% gasoline, 38% others)</td>
<td>• 5% fuels</td>
</tr>
<tr>
<td>• 9% gases</td>
<td>• 14% asphalt</td>
</tr>
<tr>
<td>• 4% coke</td>
<td>• 10% water</td>
</tr>
<tr>
<td>• 3% asphalt and road oil</td>
<td>• 71% lube oil</td>
</tr>
<tr>
<td>• 3% petrochemical feedstocks</td>
<td></td>
</tr>
<tr>
<td>• 1% lube oil</td>
<td></td>
</tr>
</tbody>
</table>

2.3.5 Reclaiming

The use of waste lubricants for alternate, less strenuous lubricant applications is a common practice. Some specific types of industrial oils can be readily segregated and are suitable for relatively simple reprocessing before being returned to their original service. Both of these types of recycling are referred to as reclaiming. Typical processing methods involve filtration and removal of water and volatile decomposition products under vacuum.

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

2.3.6 Biochemically-Converting into Valuable Bioproducts

The change in virgin crude oil price can directly affect the used oil recycling options. If the crude oil prices drop, petroleum product prices will fall accordingly. Gasoline and fuel oil prices track crude oil prices very closely, while lubricating oil prices react very slow with crude oil price changes since lube oil contains many additives and other components that add to the final product cost. A drop in crude oil price will decrease the value of reprocessed oil sold as a fuel supplement and as well as lower the re-refiners’ revenues. If higher-value products other than petroleum products can be recovered or produced from the used oil by some new technologies, larger profit margins could be generated than reprocessed oil or re-refined oil as expected. Unfortunately, almost no research studies are related to the field that is exploring other recycle/reuse options for used oils. It is the uniqueness and superiority of the biochemical process to convert used oils to commercially valuable products.

2.3.7 Survey on Used Oil Markets and Current Recycle/Reuse Programs

Used oil is not only a big problem for the United States; it also creates problems in every single country since it generates such large quantities of waste. In the process of evaluating the feasibility of adaptation of the biochemical process for the used oil
worldwide, efforts were done in surveying annual quantities of used oil generated and existing recycle/reuse programs in different countries (API, 1997). Regulatory structure and enforcement ability on used oil management differs with the country’s size and political structure. Facilities in each country may also be significantly different from one another. There were studies stating that used oils may have unique geological characteristics from place to place (Information Transfer Inc., 1974). It is important for an individual to acknowledge that it’s not good enough for an individual only not pollute his own backyard and that everyone must learn to protect the entire environment, no matter where they are standing on this earth. That’s why we feel that it is crucial for every country to understand the importance of recycling/reusing the used oils (it counts one of the biggest waste streams in many countries). The survey on used oil market and current recycle or reuse programs in some selected countries is attached as Appendix C.

2.4 Toxin Reduction and Their Interference in Recycle/Reuse Practices

2.4.1 Techno-Economic Evaluation

The price of virgin oil dramatically affects the used oil management system because used oil competes with virgin oil as a source of fuel and as a base stock for lubricating oil. Like all recycling markets, recycled oil products must be sold at a lower price than virgin oil products in order to compete. Used oil recyclers must cover the costs of collecting and recycling used oil, as well as maintain a profit to stay in business. When the virgin oil price is high, the used oil recyclers make large enough profits that they can pay generators for the used oil they produce or the transporters for the used oil
they collect. When the virgin oil price drops, the used oil recyclers can then have a little profit margin to pay (or must charge) generators or transporters. Figure 2-5 shows how the price of virgin fuel oil can affect the used oil generators.

When recyclers and transporters pay for used oil, the service stations, quick-lube shops, fleet operations, and DIY collection centers have an incentive to have their used oil recycled off site. As a result, high virgin oil price encourages used oil processing and re-refining. Conversely, low virgin oil price encourages the onsite burning of used oil (U.S. EPA, 1994). How to choose a cost-effective recycling option, therefore, depends on the projected price of virgin oil. Other than that, protecting human health and the environment must always be the main concern. Choosing the most environmentally sound used oil management method will minimize potential liability costs and eliminate fines and other costs associated with enforcement actions for violating environmental regulations.

Re-refined base oil from used lube oil in general, in comparison to the quality and technology of virgin base oil, is proven to be economically viable when payments for feed, production costs, by-product credits and product sell price are all accounted for (McKeagan, 1992). In some cases, re-refiners have a pay back period as low as 1.4 years (Ali, 1995), which is more profitable than virgin lube producers and would definitely be attractive to potential investors.

In order to make BNL’s biochemical process become techno-economically feasible and fully commercialized, there are some important scopes to achieve. First of all, improvement on the quality of the bioproducts (live biomass, lipidic biomass, and
Figure 2-5. The Effect of Virgin Oil Prices on Payments Made to Generators for Used Oil. (Source: Nolan, 1990)
delipidated biomass) will help to ensure these products can be sold to the markets at higher prices to create larger profit margins. Secondly, if possible, used oil stock from either generators or transporters needs to be acquired at reasonable price. Large used oil reprocessors or re-refiners always have their own fleet or collection system to lower the operation cost on feedstock. The commercialized biochemical plant would have to compete with these existing facilities in acquiring used oil stock. Lastly, since the market/application for the bioproducts are not limited to only one option, more profits actually, should be expected instead of other options.

2.4.2 Problems with Contaminants and Associated Hazardous Byproducts

When the chemical-aided ultrasonic irradiation method was proposed as the pretreatment process for BNL’s biochemical process, we looked into the possibility to adopt this method as the pretreatment step for other used oil recycling/reusing processes if it proves to be economically feasible. Since the undesirable toxic contaminants in used oil that cause problems in other reclaiming, reprocessing or re-refining operations are the same.

For reclaiming operation, since only a minimum simple step is applied on the used oil, the remaining fuel dilution and cracked hydrocarbon molecules often limit lubricant performance. Acids and metals that are not completely removed may act as catalysts and may further degrade or shorten the useful life of oil. Additional costs and long-term liability of the water, fuels, sludges, and residues generated by the drying and
filtering process must be considered. These new wastes may need to be further treated onsite or sent to landfills or incineration plants.

For reprocessing operation, as mentioned earlier, odor produced from nitrogen and sulfur species is the greatest concern. Severe corrosion may occur in the equipment when acidic gases from additive elements and water vapors combine during the process. These problems can be avoided and eliminated if the trouble-making components removed from the process as early as possible. Wastes generated from each step also need further handling.

For re-refining operation, less problems are presented. Heavy metals are removed from the dewatered oil components at the distillation step and then ended in asphalt flux, while higher-boiling-point halogenates and polar compounds are expected to be removed in the hydrotreating step. Refer to Table 2-4, it is obvious that chlorinated and sulfur compounds are not removed until the last hydrotreating step. Unfortunately, data on how other organic toxins are removed during each step or the concentrations in the final products are not publicly available. It was claimed by Evergreen Oil that all those organic contaminants are removed from the distillation step, however, it is really hard to make believe. Refer to Appendix B, it is obvious that many contaminants have very high boiling points, which make them end up either in the asphalt flux or gas oil to become the problem for the byproducts or possibly still stay in the lube oil distillates and go through the process. According to data compiled from PAHs analyses on many re-refined oils from different sources/countries (by Biochemisches Institut für Umweltcarcionogene in Hamburg), PAHs are found in re-refined oil samples at a higher level than those found in
unused base oil (see Table 2-5). Some of them do not meet the API standards for allowable PAHs (individual PAHs < 5ppm) in re-refined base oil (however, the guidelines for quality acceptance of re-refined base oil in Europe is less stringent compared to in U.S., for example, 3% for PAH). This may indicate that current re-refining techniques are not effective enough to remove all PAHs from used oil. The remaining levels of other organic contaminants in the final re-refined base oil products are not determined or emphasized for some sensible reasons.

2.4.3 Destruction or Removal of Toxins

From the above comparison, it should be fully understood that, no matter for what recycling/reusing option, there are many benefits if toxic materials are removed in the early steps of the entire process. Not only are there fewer problems to interfere the operation, but a better product quality can also be achieved.

From the environmental point of view, however, the “destruction of toxins” is a better option than just a “removal of toxins” option. Since toxins removed from used oils are eventually generated into wastes in some form with their original hazardous characteristics, further treatment or handling of these hazardous wastes (air, water, sludge) is still needed. In fact, this sometimes creates other problems in almost all recycling/reusing operations. Thus, a process that can “degrade” or “decompose” these toxins to less toxic materials would be favorable because it will eliminate any further potential environmental hazards.
Table 2-5. PAH Analysis of Re-refined Oil. (Source: Mortier, 1997)

<table>
<thead>
<tr>
<th>Individual PAH</th>
<th>Virgin reference oil</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoranthene</td>
<td>0.02</td>
<td>6.74</td>
<td>1.64</td>
<td>2.77</td>
<td>3.26</td>
<td>0.14</td>
<td>1.42</td>
<td>1.78</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.42</td>
<td>5.33</td>
<td>2.75</td>
<td>7.16</td>
<td>9.19</td>
<td>0.42</td>
<td>0.60</td>
<td>20.66</td>
<td>0.26</td>
<td>0.36</td>
</tr>
<tr>
<td>Benzo(b)naphtho(2,1-d)thiophene</td>
<td>0.34</td>
<td>0.89</td>
<td>1.02</td>
<td>2.29</td>
<td>0.60</td>
<td>0.07</td>
<td>1.24</td>
<td>0.38</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>Benzo(ghi)fluoranthene + benzo(c)phenanthrene</td>
<td>0.01</td>
<td>1.02</td>
<td>0.11</td>
<td>0.37</td>
<td>0.21</td>
<td>0.12</td>
<td>0.19</td>
<td>0.29</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>Cyclopenta(cd)pyrene</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>0.13</td>
<td>0.05</td>
<td>0.06</td>
<td>&lt;0.01</td>
<td>0.11</td>
<td>0.08</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Benz(a)anthracene</td>
<td>0.08</td>
<td>5.39</td>
<td>1.05</td>
<td>1.62</td>
<td>2.84</td>
<td>1.13</td>
<td>0.30</td>
<td>0.34</td>
<td>0.07</td>
<td>0.08</td>
</tr>
<tr>
<td>Chrysene + triphenylene</td>
<td>2.10</td>
<td>9.47</td>
<td>2.89</td>
<td>4.16</td>
<td>12.65</td>
<td>1.73</td>
<td>6.65</td>
<td>6.26</td>
<td>1.23</td>
<td>1.36</td>
</tr>
<tr>
<td>Benzofluoranatenes (b+j+k)</td>
<td>0.28</td>
<td>6.84</td>
<td>0.98</td>
<td>1.20</td>
<td>12.32</td>
<td>4.37</td>
<td>2.34</td>
<td>4.93</td>
<td>4.53</td>
<td>5.36</td>
</tr>
<tr>
<td>Benzo(e)pyrene</td>
<td>0.41</td>
<td>3.56</td>
<td>1.04</td>
<td>1.41</td>
<td>14.46</td>
<td>6.28</td>
<td>0.65</td>
<td>6.51</td>
<td>11.25</td>
<td>11.20</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>0.01</td>
<td>0.83</td>
<td>0.53</td>
<td>0.60</td>
<td>1.65</td>
<td>2.82</td>
<td>0.13</td>
<td>0.31</td>
<td>0.47</td>
<td>0.47</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>0.06</td>
<td>0.31</td>
<td>0.22</td>
<td>0.30</td>
<td>2.37</td>
<td>2.30</td>
<td>0.08</td>
<td>1.40</td>
<td>6.10</td>
<td>9.33</td>
</tr>
<tr>
<td>Dibenz(a,h)anthracene</td>
<td>&lt;0.01</td>
<td>0.26</td>
<td>0.05</td>
<td>0.09</td>
<td>0.12</td>
<td>0.76</td>
<td>0.04</td>
<td>0.04</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>Benzo(ghi)perylene</td>
<td>0.53</td>
<td>1.63</td>
<td>0.86</td>
<td>1.14</td>
<td>5.05</td>
<td>11.49</td>
<td>0.40</td>
<td>5.97</td>
<td>38.50</td>
<td>36.30</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.03</td>
<td>1.21</td>
<td>0.09</td>
<td>0.21</td>
<td>0.11</td>
<td>0.16</td>
<td>0.11</td>
<td>0.08</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>Coronene</td>
<td>0.13</td>
<td>0.19</td>
<td>0.10</td>
<td>0.35</td>
<td>1.19</td>
<td>2.30</td>
<td>0.09</td>
<td>0.24</td>
<td>11.40</td>
<td>12.60</td>
</tr>
<tr>
<td>Known or suspect carcinogen</td>
<td>4.44</td>
<td>42.49</td>
<td>13.46</td>
<td>3.72</td>
<td>66.08</td>
<td>34.10</td>
<td>19.84</td>
<td>49.27</td>
<td>74.74</td>
<td>77.47</td>
</tr>
<tr>
<td>Total PAH content (3-7 rings)</td>
<td>7.5</td>
<td>87.3</td>
<td>22.6</td>
<td>52.5</td>
<td>93.5</td>
<td>49.5</td>
<td>30.2</td>
<td>112.0</td>
<td>67.7</td>
<td>126</td>
</tr>
</tbody>
</table>
2.5 A Biochemical Process that Converts Used Oils into Valuable Products

2.5.1 Hydrocarbon to Protein Technology

Prior to the early 1970s, Hydrocarbon to Protein Technology has been fully developed and commercialized. In 1975, there were three major oil groups in the world which distributed products of proteins from hydrocarbons over 100 million lb/yr, the worldwide Hydrocarbon to Protein Production in 1975 is as shown below in Table 2-6 (Fong, 1975):

Products from the Standard Oil Company (India) plant were marketed as a human food supplement, whereas that of BP plants were sold as an animal feed supplement, a replacement for skimmed milk. Besides gas oil, n-paraffins, ethanol, methanol and methane (natural gas) were chosen as the feedstock of hydrocarbon to protein process. This process is especially popular in countries that heavily rely on corn or soybean imports, for example, western European countries and Japan. Economic feasibility depends on the price of the hydrocarbons and end use of the products. The most important step in this technology is fermentation, since the product properties would depend not only on the choice of feedstock, but also on the choice of microorganisms (bacterium and yeast) used in the fermentation section. The individual process may be somewhat different, yet quite similar. A simplified flow diagram of this $H \rightarrow P$ process is shown in Figure 2-6. A more detailed engineering design for Hydrocarbon to Protein Technology can be found in Appendix A.
Table 2-6. The worldwide Hydrocarbon to Protein Production in 1975.

<table>
<thead>
<tr>
<th></th>
<th>Capacity</th>
<th>Feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Million lb/yr</td>
<td>1000 Tons/yr</td>
</tr>
<tr>
<td>British Petroleum (UK)</td>
<td>33</td>
<td>24.0</td>
</tr>
<tr>
<td></td>
<td>Gas oil, n-Paraffins</td>
<td></td>
</tr>
<tr>
<td>USSR</td>
<td>44</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>n-Paraffins</td>
<td></td>
</tr>
<tr>
<td>Standard Oil Co. (India)</td>
<td>10</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>107</td>
<td>48.5</td>
</tr>
</tbody>
</table>

2.5.2 Process Modification and Adjustment by Brookhaven National Laboratory

The idea brought up in 1994 at Brookhaven National Laboratory (Biosystems and Process Sciences Division, Department of Applied Science), Long Island, NY that to utilize used oil as the starting material in the $H \rightarrow P$ process was ingenious. No similar research, using biological methods to recycle used oil into higher value products, was performed before. However, bioremediation technology is not an uncommon practice in clean up of oil polluted sites. It is worthwhile to make an effort to generate something valuable out of dirty waste. Although the conversion rate or efficiency from used oil may be lower than that of pure materials such as gas oil, paraffins, natural gas, or methanol. The advantage is that used oil stock can be obtained for almost “free”. The government encourages the recycling business by paying commercial collectors incentives for picking up and managing used oils. In reality, the utilization of used oil as the feed would reduce
Figure 2-6. The Flow Diagram of the Hydrocarbon to Protein (H \rightarrow P) Process.
production costs. At the same time, our environment would have less of an opportunity to become polluted.

Brookhaven National Laboratory (BNL) has developed a simplified lab-scale process from H → P technology starting with used oil as feed (see Figure 2-7). The product yield for each step is presented in Figure 2-8.

Live biomass concentrate was first directly used for the bioremediation of oil waste contaminated soil. The tests show positive results in the degradation of oil waste but the process is slow. Oxygen, water, organic fertilizer and inorganic elements such as N, P, K and Mg may be added to maintain the process.

Biomass generated from the process can be separated into two categories: 10% lipids, and 90% delipidated biomass. The analysis of the constituents is as follows:

- Delipidated Biomass (90%)
  - Crude protein: 66%
  - Crude carbohydrate: 27%
  - Crude lipid: 6.7%
- Lipid (10%)
  - Steroid esters: 15%
  - Fatty acids: 40%
  - Phosphatidyle-ethanolamine: 10%
  - Phosphatidyle-serine: 15%
  - Phospholipids: 10%

The delipidated biomass rich in protein can be sold as high protein animal feed for $1000/ton. Its ability in the adsorption of heavy metals has also been tested. Adsorption capacities of metals such as Be, Cr, Co, Cu, As, Cd, and Hg by the raw delipidated biomass produced from different used oils proved that this product can replace high-cost
Figure 2-7. Current BNL Process at Laboratory Scale.
1 kg of Used Oil → 100 liters

Bioconverted: 450 g = 45%

Unreacted: 55%

Crude Dried Biomass

Lipid: 45 g = 10%

Delipidated Biomass: 400 g = 90%

Solvent Recycle

Figure 2-8. Product Yield from Current BNL Process.
ion exchange resin as an absorbent for metal ions. Although the adsorption capacity of the delipidated biomass is only 1 meq/gram compared to 5 meq/gram for common ion exchange resin, its $1/kg cost makes it very competitive in comparison to $200/kg for resin. The distinctions between common ion exchange resin and the delipidated biomass are listed in Table 2-7.

Table 2-7. Comparisons between Ion Exchange Resin and Biomass from H→P Process.

<table>
<thead>
<tr>
<th></th>
<th>Ion Exchange Resin</th>
<th>Biomass from H→P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>synthetic polymer</td>
<td>natural polymer</td>
</tr>
<tr>
<td>Adsorption capacity</td>
<td>5 meq/gram</td>
<td>1 meq/gram</td>
</tr>
<tr>
<td>Selectivity toward ions</td>
<td>highly selective</td>
<td>highly selective</td>
</tr>
<tr>
<td>Stability for recycle use</td>
<td>very stable</td>
<td>moderate stable</td>
</tr>
<tr>
<td>Size (diameter)</td>
<td>&gt; 1000 μm</td>
<td>1 ~ 2 μm</td>
</tr>
<tr>
<td>Cost ($/kg)</td>
<td>200</td>
<td>1</td>
</tr>
</tbody>
</table>

Other potential markets, which include known applications in mining & metal concentration and environmental heavy metal pollution cleanup, still need more research.

The purity and properties of the 10% lipids from the process has not yet been evaluated. Potential markets for these natural and biodegradable lipids could be raw materials for surfactants (i.e., soap and detergent), cosmetics (i.e., body and facial cream)
and medicines (i.e., drug delivery). Market values will depend on the quality and purity of the lipid biomass.

2.5.3 Problems Encountered in BNL Process

A laboratory pilot plant (50-gal capacity) has been successfully tested at BNL using H→P technology. Economics evaluation and process design for the full-scaled plant with 100,000 ton/yr biomass production are now in progress and seeking cooperative partners. At this capacity, the plant can treat up to 10% of the annual used oil currently dumped in the U.S. illegally. However, there are still some problems in this pilot-scale stage that need to be solved before upscale work can proceed further. Problems encountered during the development of the technology are explained below:

2.5.3.1 Products with Poor Quality

Some simple physico-chemical methods have been developed to convert any used oil into a chemical form suitable for this biochemical process. Two used oil samples were sent from the Los Angeles area to BNL for initial tests. Table 2-8 lists the elemental analysis of these two used oil samples. It can be seen that some metal concentrations are amazingly high. Pretreatment processes such as with celite, filtration, or washing with filtration have been proven by Brookhaven Laboratory to effectively remove most toxic metals up to 90-100%. In this manner, a broader spectrum of used oil can be used as the feedstock of this process.
Table 2-8. Elemental Analysis for Two Original Used Oil Samples.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>KS-1 Oil</th>
<th>KS-2 Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>N in %</td>
<td>0.41</td>
<td>0.04</td>
</tr>
<tr>
<td>P2O5</td>
<td>1240</td>
<td>120</td>
</tr>
<tr>
<td>K</td>
<td>628</td>
<td>105</td>
</tr>
<tr>
<td>Na</td>
<td>1955</td>
<td>419</td>
</tr>
<tr>
<td>Ca</td>
<td>3597</td>
<td>523</td>
</tr>
<tr>
<td>Mg</td>
<td>960</td>
<td>593</td>
</tr>
<tr>
<td>Fe</td>
<td>55475</td>
<td>5967</td>
</tr>
<tr>
<td>Mn</td>
<td>428</td>
<td>65</td>
</tr>
<tr>
<td>Zn</td>
<td>1466</td>
<td>264</td>
</tr>
<tr>
<td>Cu</td>
<td>26</td>
<td>15.6</td>
</tr>
<tr>
<td>Pb</td>
<td>9.7</td>
<td>7.2</td>
</tr>
<tr>
<td>Cd</td>
<td>1.2</td>
<td>0.12</td>
</tr>
<tr>
<td>Co</td>
<td>5.1</td>
<td>3.1</td>
</tr>
<tr>
<td>Ni</td>
<td>33</td>
<td>41</td>
</tr>
<tr>
<td>Cr</td>
<td>9.7</td>
<td>5.3</td>
</tr>
<tr>
<td>Hg</td>
<td>44.4</td>
<td>22.2</td>
</tr>
</tbody>
</table>
Pretreatment techniques to remove other toxic organic constituents like chlorinated hydrocarbons, BTEX, or PAHs, however, were not studied. Although the possibility of the bioaccumulation effects attributed from these toxic organic compounds was not well studied, concerns were raised about whether the bioaccumulation of these toxic materials would affect the quality and public acceptance of the bioproducts.

In effect, it would be better to develop a pretreatment process or a combination of pretreatment processes that can remove every undesirable compound that is toxic to the bacteria strains in this process, and at the same time lower the possibility of bioaccumulation in order to improve the product quality. The important part of this work is to obtain the characteristics of used oil that is going to be the feedstock of this process so that an appropriate pretreatment process can be decided. Another noticeable problem is the unpleasant dark color of the bioproducts, especially since the market of these bioproducts is aimed towards cosmetics or pharmaceutical applications (for lipidic biomass). Hence, it greatly lowers the buyers’ interest. Since most used oil looks dirty because the oil gets dirty after use, unless the color-causing compounds can be identified and removed prior to the fermentation step, it may be difficult to improve the color from the final products. For other applications, color may not be a very important issue, but it is a better add-on benefit if the pretreatment process can also improve the color of the products.

KS-1 Oil and KS-2 Oil were used oil samples collected from Los Angeles region and shipped to Brookhaven Laboratory for fermentation tests. From Brookhaven’s data, 100% of metals like Cr, Mn, Co, Ni, Cu, Cd, Hg in used oils KS-1 and KS-2 can be
removed by one of the three pretreatment methods mentioned. Removal efficiency for Fe, Zn, Sr, Ba, Pb in used oils KS-1 and KS-2 can reach 83% - 99.3% (see Table 2-9). However, to separate the added washing water from oil after the pretreatment was a big challenge for BNL and not yet successful. Water dispersed in used oil is quite stable and it is hard to break the emulsion since used oil itself contains surfactants from the additive packages. This would also be an important issue when we consider other pretreatment methods.

2.5.3.2 Inconsistency of the Products

Several microbial strains were tested to grow on used oil KS-1 and KS-2 to compare biomass yield from each strain in order to decide the better strain which produced higher biomass yield for further use (see Table 2-10). Although most of the metal contents were removed prior to the fermentation step, microbial strains with a higher tolerance on heavy metals were considered for the initial studies. It should be noted that even the same strain of microbes still possibly generate a different biomass yield when it grows on different used oil. It is difficult to optimize conditions for fermentation step here since the feedstock of used oil, in reality, may differ from batch to batch depending on the sources. In the future, it will be important to know how to pretreat the bulk-size feedstock to become a comparatively consistent source for microbial strains to grow at the best condition and produce a maximum yield of biomass.
Table 2-9. Removal of Toxic Metals from Used Oil KS1 and KS2 (in %).
Treatments: A (Celite), B (Filtration), C (Washing and Filtration)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Mn</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Fe</td>
<td>98.3</td>
<td>99.3</td>
<td>99.3</td>
<td>94.6</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>Co</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Ni</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Cu</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zn</td>
<td>98</td>
<td>98.9</td>
<td>98.9</td>
<td>92.4</td>
<td>99</td>
<td>98.7</td>
</tr>
<tr>
<td>Sr</td>
<td>97</td>
<td>98.8</td>
<td>99</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Cd</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Ba</td>
<td>86</td>
<td>90.5</td>
<td>89</td>
<td>90.2</td>
<td>93.8</td>
<td>94</td>
</tr>
<tr>
<td>Hg</td>
<td>98.5</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Pb</td>
<td>83</td>
<td>96.6</td>
<td>86.7</td>
<td>94.3</td>
<td>97</td>
<td>95.7</td>
</tr>
</tbody>
</table>
Table 2-10. Biomass Growth on Used Oils.

(yield, gram of biomass/liter of culture)

<table>
<thead>
<tr>
<th>Microbial Strains</th>
<th>KS-1 Oil</th>
<th>KS-2 Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acinetobacter sp.</td>
<td></td>
<td>0.62</td>
</tr>
<tr>
<td>Pseudomonas sp. (1)</td>
<td>0.20</td>
<td>1.07</td>
</tr>
<tr>
<td>Pseudomonas sp. (1) with detergent</td>
<td>0.09</td>
<td>1.07</td>
</tr>
<tr>
<td>Pseudomonas sp. (2)</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Candida sp.</td>
<td></td>
<td>1.20</td>
</tr>
</tbody>
</table>

2.5.4 Proposed Solutions for Problems Encountered in BNL Process

Initially, the responsibility shared in this research project with Brookhaven National Laboratory is to gather information on worldwide markets of used oil and current recycle/reuse options available, then to collect some used oil samples for the initial tests on \( H \rightarrow P \) process conducted in BNL. More efforts involved later include survey on proper microbial strains, evaluation of the bioproducts, and survey on potential markets for bioproducts. Problems arose when the bioproducts produced were not of satisfactory quality concerns. Further worries and considerations about the toxic materials originally present in used oil made an add-on pretreatment step a necessary and crucial part of the biochemical process. Until these problems can be solved substantially, any intention for scale-up and commercialization of the process is not possible to carry on.
So we were consulted to develop a pretreatment process in order to remove all toxic constituents from the used oil before it is fed to the microorganisms. After reviewing the problems encountered in BNL’s process and other reprocessing/re-refining techniques for current used oil recycling, we have the following suggestions:

2.5.4.1 Selection of Appropriate Used Oil Feedstock

Used oil could come from different sources, though the two major categories are automotive used oil and industrial used oil. They may contain a very wide range of contaminants at various levels, and this makes the quality control and homogeneity of the used oil feedstock more difficult to achieve. We have also reviewed the two most popular technologies for used oil recycle/reuse options – reprocessing and re-refining, and we found out that a screening procedure is necessary to guard and reject any inappropriate feedstock before it enters the system. In this way, the performance of the system and the quality of the products can be assured. So we would suggest developing a screening method to select appropriate used oil feedstock. Although it’s impossible to completely reject used oil feedstock that contains toxic contaminants (then there won’t be any used oil bulk qualifying), we can still make the pretreatment process more feasible and efficient by accepting better feedstock of the used oil. Furthermore, it would reduce the unnecessary cost for excess pretreatment.
2.5.4.2 Pretreatment by Chemical-Aided Ultrasonic Irradiation

Although the pretreatment methods such as celite treatment, filtration, or washing with filtration developed by BNL were claimed to efficiently remove most of the heavy metal contents from used oil, these methods may not be useful to remove other toxic organic constituents. From an economic point of view, it is better to develop one pretreatment process that can remove all undesirable materials all together. Thus, a chemical-aided ultrasonic irradiation process is proposed as the pretreatment method. Ultrasound technology is well known for its applications in destruction of toxins. And not only limited to lab-scale studies, many clean-up works of pilot-scale operation in real contaminated sites are proven to be feasible for both technology and economic considerations. The proposed chemical-aided ultrasonic irradiation method may be a combined process with many steps, and using adsorption to remove toxic heavy metals may be one of those steps. A detailed description of this method is illustrated in next Chapter.

2.6. Sources of Used Oil Samples

Automotive used oils, including engine crankcase oil, diesel engine oil, and hydraulic brake, transmission, power steering fluids, constitute a large portion of used oils. Sources of used automotive oils are do-it-yourself oil changers (DIYers), service stations, repair and maintenance shops, vehicle dealers, truck and taxi fleets, military installations, and industrial/manufacturing facilities. Another main category of used oils is industrial used oils, which include lubricating oil, hydraulic fluids, grease, and process oils. In most
lubricating and industrial applications, the oil must be replaced by new oil when the performance of the oil deteriorates over time as additives break down and contaminants build up. The fraction of the new oil that becomes used oil varies widely for different applications. For example, only 10 percent of industrial process oils sold, in comparison to 90 percent of electrical transformer oils, are generated as used oil. The used oil generation rate for automotive oils is about 60 percent, which is a little bit higher than 52 percent for industrial oils. The recycling rate for automotive oils ($\approx 60$ to $70$ percent), however, is much higher than that for industrial oils ($\approx 25$ to $40$ percent).

From the experiences, many industrial used oils can be easily recycled and reused onsite through simple processing steps. In another way, automotive used oils mostly are collected by commercial recyclers and could become the major source for this research. However, since used oil is categorized as hazardous waste in California, it’s not easy to request used oil samples from commercial recyclers or reproprocessors/re-refiners. In order to get representative used oil samples; however, we still tried to acquire samples from big recyclers or reproprocessors/re-refiners. Unfortunately, most of them were not willing to be involved in situations where they would be in trouble from legal liability. Some simply rejected the request at once and refused to reveal any information while others would ask us to provide formal document and permission from their supervising governmental agencies. The collection of used oil samples really brought some difficulties for this research study after many frustrated phone requests. Finally, we had to just get a mixed used lube oil sample by the help of a service station for some initial tests, which, in our mind, was not so representative. Finally, a mid-size commercial used oil recycler (Leach
Co., Compton, CA) kindly provided some used oil samples from its big storage tanks. However, it was identified later that those were just constituted of used automotive oils.

Used automotive lube oil sample was tested as the feedstock for the biomass production. Since the characteristics of automotive used oils may be very similar from batch to batch (need to be verified, of course), it could make the optimal pretreatment process much simpler to decide.

Another good source of used oil is the used cooking oil. According to the market research, recycled used cooking oil mostly came from the frying basins of restaurants, fast food chain stores, and some deep-fat frying snack manufacturers. Used cooking oil is always collected and recycled in order to process to make soap, paint, feed, fertilizer, or fuel. Few studies have investigated the possibility of converting used sunflower oil to diesel fuels (Nye, 1983, Karaosmanolu, 1996 and Cigizoglu, 1997). Used cooking oil may be another good source for this biochemical process since it may contain good nutrients for bacteria strains, though it’s presence in solid state at room temperature may make people think that used cooking oil is not easily re-used. At high fermentation temperature, however, it should not be difficult to process. Vegetable oil (corn oil, olive oil…) consists mostly of unsaturated hydrocarbons, while vegetable shortening is consisted of mostly saturated hydrocarbons through hydrogenation process. Unsaturated hydrocarbons are very active during excess heating process and easily oxidized into toxic compounds (color-causing materials). The target undesirable compounds we should be careful about are amines, hindered phenols, etc., which not only reduce the useful life of the oil but also are responsible for human health problems (for example, acne formation).
It is claimed that fat or oil must be discarded when its polar fraction is more than 25% (Cuesta, 1993). The manager of the fast food store on campus kindly explained how to decide if the oil is unfit to use — by a color comparison method (see Figure 2-9). It is a common practice for individual restaurant owners to filter oil used for deep-fat frying to remove food debris, which may accelerate the decomposition of the oil. Together with the adsorption of soluble impurities, it will extend the life of the oil and provide higher-quality fried food (Yates, 1992). The number and variety of products in the frying process are great, but the nutritional and toxicological consequences of their consumption remain largely unknown. If we want to utilize used cooking oil as the feedstock of the biochemical process, then these toxic materials are also suggested to be removed prior to the fermentation stage to avoid any adverse effect. Since no research has been done on this area, further study is needed.
Figure 2-9. The Method Used in Fast Food Chain Stores to Determine the Remaining Useful Life of the Cooking Oil in Deep-Fat Frying. (Source: Carl’s Jr., USC main campus.)
CHAPTER 3

Theoretical Background

3.1 Ultrasound

3.1.1 Introduction

Ultrasound is the sound wave in which frequencies are beyond the human audible limit (human hearing range is from 16 Hz to 16 kHz). The upper limit of ultrasound frequency is not well defined, but is usually 500 MHz for liquids and solids and 5 MHz for gases. High energy (low frequency) waves, which are known as the power ultrasound between 20 and 100 kHz, are used mostly for cleaning, plastic welding, and more recent applications to affect chemical reactivity (Mason, 1988). For a 20kHz ultrasonic unit, the time period per cycle is $5.0 \times 10^{-5}$ second. The collision of water molecules occurs in less than one quarter of the cycle. Thus, the collision time should have a magnitude of less than $1.3 \times 10^{-3}$ seconds. As a result, there is high pressure and temperature. Ultrasound radiation can generate a very high temperature (up to 5000°C) and pressure (up to 500 atm) at many localized centers (cavitation bubbles) in aqueous solutions. The effective lifetime of these localized hot spots may be only a few microseconds (Suslick, 1986; and Suslick, 1990). It’s these extreme conditions (high temperature and pressure), however, that provide an unusual chemical environment (Suslick, 1989). Experimentally, the actual cavitation temperature has been measured at $5200 \pm 560$K for alkane solvents (Suslick, 1986) and $5075 \pm 156$K for silicone oil (Flint, 1991).
In aqueous sonochemistry, chemical reactions occur at three different regions as (Chen, 1998): (1) Interiors of collapsing bubbles where extreme conditions of temperature and pressure exist transiently, which induces chemical reactions yielding products that are typical of pyrolysis or combustion reactions in the gas phase. (2) Interfacial regions between the cavitation bubbles and bulk solution where a high temperature (lower than that of the bubbles) and a high gradient is present. The nonvolatile solute that accumulates in this region can undergo thermal decomposition and induce radical reactions. This interfacial reaction zone is estimated to be about 200nm thick (Suslick, 1990). (3) Bulk solution where the radicals, being produced in the interior of bubble and in the interfacial region, that survive migration from the interface can undergo radical reactions with solute present in the bulk solution.

Table 3-1 summarizes some important physical parameters that affect cavitation.

3.1.2 Free Radicals by Ultrasound

3.1.2.1 Aqueous System

Many examples of reactions of hydrated electrons, hydrogen atoms, and hydrated radicals with substrates have been reviewed (Fendler, 1982). The primary cavitation reaction under ultrasound is the homolytic dissociation of water molecules into atomic hydrogen (H) and hydroxyl (OH) radicals. This has been verified by Del Duca et al. (Del Duca, 1958) using the isotopic exchange method to establish the formation. The principle products from the ultrasonic irradiation of pure water are $H_2O_2$ and $H_2$.

$$\text{H}_2\text{O} \xrightarrow{\text{\textbullet\textbullet\textbullet}} \text{H}^* + \text{OH}^* \xrightarrow{\text{\textbullet\textbullet\textbullet}} \text{H}_2\text{O}_2 + \text{H}_2 \quad (\text{Eq. 3-1})$$
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Property</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acoustic intensity</td>
<td>Period of collapse</td>
<td>Resonant bubble radius, probability of cavitation events per unit time</td>
</tr>
<tr>
<td>Acoustic frequency</td>
<td>Size of cavitation zone</td>
<td>Probability of cavitation events per unit volume</td>
</tr>
<tr>
<td>Bulk temperature</td>
<td>Liquid vapor pressure, gas solubility</td>
<td>Bubble content, intensity of collapse</td>
</tr>
<tr>
<td></td>
<td>Thermal activation</td>
<td>Enhanced secondary reaction rates</td>
</tr>
<tr>
<td>Static pressure</td>
<td>Total applied pressure</td>
<td>Intensity of collapse</td>
</tr>
<tr>
<td></td>
<td>Gas solubility</td>
<td>Bubble content</td>
</tr>
<tr>
<td>Nature of gas</td>
<td>Polytropic ratio</td>
<td>Intensity of collapse</td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity</td>
<td>Intensity of collapse</td>
</tr>
<tr>
<td></td>
<td>Gas solubility</td>
<td>Bubble content</td>
</tr>
<tr>
<td></td>
<td>Chemical reactivity</td>
<td>Primary or secondary sonochemistry</td>
</tr>
<tr>
<td>Nature of liquid</td>
<td>Vapor pressure</td>
<td>Intensity of collapse</td>
</tr>
<tr>
<td></td>
<td>Surface tension</td>
<td>Transient cavitation threshold</td>
</tr>
<tr>
<td></td>
<td>Viscosity</td>
<td>Transient cavitation threshold</td>
</tr>
<tr>
<td></td>
<td>Chemical reactivity</td>
<td>Primary or secondary sonochemistry</td>
</tr>
<tr>
<td></td>
<td>Compressibility of liquid</td>
<td>Gas bubble dynamics</td>
</tr>
<tr>
<td>Petreatment of liquid</td>
<td>Size distribution of cavitation nuclei</td>
<td>Cavitation threshold</td>
</tr>
<tr>
<td>Time of ultrasound</td>
<td>Total energy input</td>
<td>Extent of reaction, heat dissipation</td>
</tr>
</tbody>
</table>
Since hydrogen peroxide is quite active and dissociates easily, its formation is extremely unstable in the solution. Hence, the collision of two hydroxyl radicals will not terminate the reaction (Chen, 1990). Hydroxyl radical has a very high oxidizing power (with potential of 2.80 volts), which is only second to fluorine as oxidants. Hydroxyl radical is particularly reactive with carbon-carbon double bonds and carbon-chlorine bonds and is capable of aromatic ring cleavage.

Although applying ultrasound to dilute aqueous solution alone could produce hydrogen peroxide, the amount is too small to be significant. Saturation of various gases in the water is proven to enhance the production of hydrogen peroxide to different levels. Additional hydrogen peroxide may be added to increase free radical concentration in aqueous solution. Since the bond strength of hydrogen-oxygen (119 kcal mole\(^{-1}\)) is much higher than that of oxygen-oxygen (ca. 37 kcal mole\(^{-1}\)) in hydrogen peroxide molecule, the main effect of ultrasound on hydrogen peroxide results in the cleavage of the O-O bond and the formation of hydroxyl radicals (Chen, 1998). In ultrasonic cavitation studies the most common media used are aqueous solutions, because they are good as solvents for gases and other solutes (e.g., methanol).

When the medium is kept at a reducing environment, hydrogen in water produces hydrogen atoms. This is supported by the fact that, in the presence of N\(_2\) and H\(_2\) gas, ammonia is formed; formaldehyde is formed when CO and H\(_2\) are present in water (Suslick, 1988). A convenient and constant source of hydrogen in the laboratory is sodium borohydride. The reaction is expressed in Equation 3-2.

\[
\text{NaBH}_4 + 2\text{H}_2\text{O} \longrightarrow 4\text{H}_2 + \text{NaBO}_2
\]  
(Eq. 3-2)
As for an industrial scale, it is suggested that hydrogen gas bubbles be finely dispersed to the reactor at a constant rate and appropriate sizes.

3.1.2.2 Non-Aqueous System

Very few studies have been reported for sonolysis of nonaqueous solution. Although some pioneer studies demonstrated that cavitation effect could occur outside of water, sonochemistry, in general, had not been popularly observed in most common volatile organic solvents (or aqueous solutions with volatile organics). The problem may simply be that many organic liquids have high vapor pressures, which greatly diminish the intensity of cavitational collapse (Suslick, 1988).

The most famous example for sonolysis of hydrocarbon is the Rice radical-chain mechanism for alkane pyrolysis (Suslick, 1983). A similar mechanism is usually derived accordingly for the sonolysis of other hydrocarbons. Ultrasound energy can split substituted hydrocarbons into alkyl or aryl radicals. These radicals together with the radicals from water-splitting (if any) can propagate through chain transfer or termination steps. Polymerization or polycondensation is a consequence of energetic radical attack when two alkyl radicals collide (Lian, 1994).

3.1.3 Ultrasonic Applications in Environmental Studies

3.1.3.1 Decomposition and Degradation of Pollutants at Laboratory Scale

The use of ultrasound is not limited to more recognized processes such as cleaning, homogenization, emulsification, sterilization, plastic welding, biological cell
disruption, and crystallization (Frederick, 1965; and Gooberman, 1968). In addition, ultrasound technique has been used in the decomposition of environmental pollutants for several years, which includes phenols, halogenated hydrocarbons, pesticides, herbicides, humic acids, PAHs and H₂S. Degradation and modeling studies are mostly conducted in dilute aqueous systems; selected examples are summarized in Table 3-2.

From Table 3-2, it can obviously be seen that most studies are conducted in batch-type reaction systems and with 20 kHz ultrasound frequency. Appropriate reaction time for enough degradation varies from 30 minutes to 10 hours depending on the nature of the pollutants. Using argon (Ar) as the purged gas is proved to achieve faster results. In these cases, ultrasound energy produces atomic OH• and H• radicals. When oxygen is the saturation gas, sonication leads to HOO• obtained at the expenses of H• (Eq. 3-3). The chance for recombination of OH• and H• radicals is lowered (Eq. 3-4).

\[
\text{H}^* + \text{O}_2 \rightarrow \text{HOO}^* \quad \text{(Eq. 3-3)}
\]
\[
\text{H}^* + \text{OH}^* \rightarrow \text{H}_2\text{O} \quad \text{(Eq. 3-4)}
\]

In argon atmosphere, roughly 80% of the H atoms and OH radicals initially produced during the ultrasonic irradiation of water recombine. The combination reactions predominantly form H₂, H₂O₂, and H₂O. These reactive species are available in the medium to react with dissolved target compounds. However, all these studies are conducted in dilute aqueous system. Almost no study was found related to pollutant reduction in pure solvent system, or in complex hydrocarbon system.
Table 3-2. Selected Examples for Ultrasonic Treatment on Aqueous Pollutants.

<table>
<thead>
<tr>
<th>Target Compounds</th>
<th>System</th>
<th>Gas Purged</th>
<th>Reaction Time</th>
<th>Operating pH</th>
<th>Hydrogen Source</th>
<th>Efficiency</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Phenols</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Chlorophenol</td>
<td>Batch, 20kHz, 38.1 W/cm²</td>
<td>O₂/N₂/air</td>
<td>2-40 hrs</td>
<td>3</td>
<td>No</td>
<td>126 μM → 0 μM</td>
<td>Ku, 1997</td>
</tr>
<tr>
<td>2-, 3-, 4-Chlorophenol</td>
<td>Batch, 20kHz, 52.1 W/cm²</td>
<td>air</td>
<td>10-15 hrs</td>
<td>--</td>
<td>No</td>
<td>80-90 μM → 0 μM</td>
<td>Serpone, 1994</td>
</tr>
<tr>
<td>p-Nitrophenol</td>
<td>Batch, 20kHz, 84 W</td>
<td>air</td>
<td>2 hrs</td>
<td>5</td>
<td>No</td>
<td>100 μM → 10 μM</td>
<td>Kotronarou, 1991</td>
</tr>
<tr>
<td><strong>Halogenated Hydrocarbons</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>batch, 40 kHz, 300 W</td>
<td>No</td>
<td>120 min</td>
<td>3.5</td>
<td>H₂O₂</td>
<td>94% removal</td>
<td>Chen, 1990</td>
</tr>
<tr>
<td>Phentachlorophenate</td>
<td>batch, 530 kHz, 20 W</td>
<td>O₂/N₂/air</td>
<td>200 min</td>
<td>7</td>
<td>No</td>
<td>100 μM → 0 μM</td>
<td>Petrier, 1992b</td>
</tr>
<tr>
<td>Chlorinated C1/C2 VOCs</td>
<td>batch, 20 kHz, 200 W</td>
<td>No</td>
<td>40 min</td>
<td>6 → 3</td>
<td>No</td>
<td>72-100% removal</td>
<td>Bhatnagar, 1994</td>
</tr>
<tr>
<td>CFCs</td>
<td>batch/flow, 20 kHz, 160 W</td>
<td>No</td>
<td>40 min</td>
<td>7.4 → 5.4</td>
<td>No</td>
<td>90% removal</td>
<td>Cheung, 1994</td>
</tr>
<tr>
<td>Chlorinated mixture</td>
<td>batch, ?</td>
<td>Ar</td>
<td>6-10 hrs</td>
<td>--</td>
<td>No</td>
<td>---</td>
<td>Catallo, 1995</td>
</tr>
<tr>
<td>CCl₄</td>
<td>batch, 20 kHz, 113 W/cm²</td>
<td>Ar/Ar-O₃</td>
<td>90 min</td>
<td>6.5</td>
<td>No</td>
<td>400 μM → 4 μM</td>
<td>Hua, 1996</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>batch, 20/500 kHz, 30W</td>
<td>air</td>
<td>5 hrs</td>
<td>--</td>
<td>No</td>
<td>500 μM → 0 μM</td>
<td>Petrier, 1998</td>
</tr>
<tr>
<td><strong>Pesticides and Herbicides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parathion</td>
<td>batch, 20 kHz, 75 W/cm²</td>
<td>air</td>
<td>120 min</td>
<td>6.1 → 3.1</td>
<td>No</td>
<td>82 μM → 0 μM</td>
<td>Kotronarou, 1992a</td>
</tr>
<tr>
<td><strong>Humic Acids</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxybenzoic/tanic acid</td>
<td>batch, 200 kHz, 200 W</td>
<td>Ar/air</td>
<td>60 min</td>
<td>--</td>
<td>No</td>
<td>100 μM → 0-35 μM</td>
<td>Nagata, 1996</td>
</tr>
<tr>
<td><strong>Other Compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAHs</td>
<td>batch, 20 kHz, 35 W/cm²</td>
<td>Ar</td>
<td>60-120 min</td>
<td>2</td>
<td>NaBH₄, H₂O₂</td>
<td>≈ 80% reduction</td>
<td>Park, 1995</td>
</tr>
<tr>
<td>H₂S</td>
<td>batch, 20 kHz, 75 W/cm²</td>
<td>air</td>
<td>30 min</td>
<td>10</td>
<td>No</td>
<td>196 μM → 0 μM</td>
<td>Kotronarou, 1992b</td>
</tr>
<tr>
<td>Chlorobenzene, phenols</td>
<td>batch, 20 kHz, 130 W</td>
<td>Ar</td>
<td>60 min</td>
<td>--</td>
<td>No</td>
<td>20-30% removal</td>
<td>Seymour, 1997a</td>
</tr>
</tbody>
</table>
Many researches have been focused on how to enhance ultrasonic irradiation efficiency, different reaction parameters such as temperature, pH, static pressure, ultrasound frequency, solvent choice, and dissolved gas have been studied in depth. Addition of chemicals, such as NaCl salt, also proved to enhance the oxidation rate by several folds (Seymour, 1997a) due to hydrophobic interactions.

Higher frequencies (e.g., > 500 kHz) also achieved significant improvement by producing smaller bubble size and forming larger amounts of hydrogen peroxide (Petrier, 1992a). Another study by Cum and co-workers conducting a model chemical reaction (iodide to iodine oxidation) at different ultrasonic frequencies, i.e. 20, 40, 60 and 80 kHz, illustrated the relationship between resonance frequency and bubble radius. They concluded that selecting an appropriate frequency value of ultrasound is able to drive a sonochemical reaction to its maximum yield (Cum, 1992).

A straightforward interpretation of the fundamental role played by frequency indicates that such an effect occurs when bubbles are excited with a radius value at the center of a statistical distribution curve. Such an event is also made possible by driving the bubble’s field from its equilibrium distribution state to a different one suitable for the occurrence of transient cavitation.

While the chemical effects of acoustic cavitation have been extensively investigated during recent years, little is known about the chemical consequences when hydrodynamic cavitation is created during the turbulent flow of liquids. One important exception comes from W. R. Moser and co-workers (Moser, 1995). They utilized commercially available high-pressure jet fluidizers (capable of pressure drops as high as
2 kBar and jet velocities approaching 200 m/s) to prepare nanostructured catalytic materials. Moser speculated that the unusual properties of his catalysts resulted from hydrodynamic cavitation within the fluidizer. Suslick and his co-workers (Suslick, 1997) then use this jet fluidizer to study the chemical reactions caused by hydrodynamic cavitation within. They found that the chemical effects of hydrodynamic cavitation and acoustic cavitation respond identically to experimental parameters, especially to the bulk temperature and nature of the dissolved gas. Another research was done by Moholkar and his co-workers. They studied the bubble behavior in a hydrodynamic cavitation under the effect of turbulence (Moholkar, 1997). Before them, it was believed that hydrodynamically generated cavities were in a stable cavitation mode and hence, not very useful for the desired sonochemical effects. But Moholkar concluded that the bubble behavior under turbulent conditions was transient and resembled the behavior of a cavity under acoustic cavitation. This is an interesting result and opens up a number of possibilities for the design of cavitating reactors to enhance sonochemical effects.

Recently, there was a study (Seymour, 1997b) that involved the improvement of reactor configurations (proper focusing and reflection of ultrasound), which was tested on the oxidation of KI in a batch system (640 kHz, 258 W) saturated with air. A 100% enhancement was achieved with the newly developed reactor configuration. We discovered, however, that there are some drawbacks in their design after evaluation. First of all, the material for the reactor is not very corrosion resistant. Secondly, extensive cooling with ice bath is strongly required because the reactor would heat up rapidly only after a few minutes of irradiation.
3.1.3.2 Environmental Cleanup Applications — Case Studies

A lot of environmental cleanup work has utilized sonochemical treatment or ultrasonic-aided treatment at industrial scale or commercially-available services. Some of the applications are introduced below.

Water, wastewater and biosolids disinfection using ultrasonic technology has been studied for a long time in many countries. The TechnoWater Co. in Germany has developed a commercialized ultrasonic post treatment, which is a patented solution to avoid the precipitation of lime and rust in drinking water pipes in inhouse-services for cold and hot water. This process is especially suitable in plants where softening or dosing is uneconomical or chemical post treatment is not allowed. The main advantages for this treatment package include low investment costs, low operational costs (power consumption 5W), good drinking water quality without chemical additives, service needed once in 4 years, and no excess charges for industrial design.

Atomic Energy of Canada, Ltd. of Chalk River Laboratories, Canada, has developed and tested a pilot-scale unit to treat acidic soil leachate solution containing low levels of metals and radionuclides by ultrasonic-aided treatment (as shown in Figure 3-1). The major difference between this technology and conventional processes is the use of ultrasonic mixing instead of mechanical agitation within large tanks. The research on this pilot scale unit was co-supported by U.S. DOE and EPA and tested at EPA sites.

There were many projects sponsored by U.S. EPA and DOE to develop ultrasonically-assisted chemical destruction process for detoxification of hazardous
Figure 3-1. Schematic Remediation of the Ultrasonic-Aided Leachate Treatment System.
(Source: Chalk River Laboratory)
materials from contaminated soils. By applying ultrasound energy in-situ coupled with soil fracturing technology, one successful example is the enhanced destruction PCBs-contaminated soil cleanup (as shown in Figure 3-2).

Sonication has also been used to study the strength and structure of the sludges (both anaerobic and activated) in wastewater treatment plant (Morgan, 1992). It gives useful information about the characterization and desintegration of the sludges. Hence, the dewaterbility of the sludges can be easily understood.

3.1.4 Ultrasonic Applications in Fossil Fuel Related Studies

Studies involving fossil fuel related fields using ultrasound technique include tar sand recovery (Sadeghi, 1992), upgrading of heavy oil (Lin, 1993), and upgrading of asphalt, coal liquid, and oil shale (Sadeghi, 1994). In these cases, free radicals are generated in organic phase by ultrasound irradiation as illustrated by the Rice radical-chain mechanism and follow the conventional free radical propagation, inhibition and termination steps. The addition of radicals ($\text{H}_2\text{O}_2$, benzoyl peroxide, AIBN) into the reaction has been proven to shorten the reaction time.

3.1.5 Proposed Chemical-Aided Ultrasonic Treatment on Used Oil

It is surprising to know that there have been very few basic researches conducted or currently in progress related to the treatment of used oil. Most studies are targeted on improving the efficiency or quality of re-refining and reprocessing technologies.
Figure 3-2. PCB Soil Detoxification Process. (Source: Trinity Environmental Technologies, Inc.)
One study shows the decontamination of low-level radioactive used oil (generated as waste in a nuclear power plant) by a combined filtration, centrifugation, and chelation process (Simiele, 1987). Another specific study directly focused on the dechlorination and ash-removal of used oil (machine oil, automotive oil, and diesel oil) by a combined chemical-thermal method, total chlorine content in used oil sample was greatly reduced (Wentz, 1991). The treatment time, however, requires as long as 35 hours to remove 10,000 ppm total chlorine down to 300 ppm for machine oil. The samples also have to be heated and kept at 280 °C at all times, which is not too economically feasible.

In this study, the method proposed is to utilize a chemical-aided ultrasonic irradiation process to decontaminate used oil. Since the objective is to remove the contaminants from used oil or degrade the contaminants in the used oil, the mechanism for the destruction/removal of an individual group of contaminants under ultrasonic irradiation can be hypothesized according to many previous studies. Experimental work, however, is necessary to prove these hypotheses.

One important benefit from using ultrasonic irradiation for toxin reduction is that the reactions are usually carried at an ambient temperature and pressure, which not only saves a lot of energy, but also reduces the environmental impact from released toxins.

3.1.5.1 Micelle and Reverse Micelle in Water-in-Oil Emulsions

When water phase and organic phase mix together with the presence of surfactant (the emulsifying agent), emulsion or even microemulsion is formed. For used lube oil sample, organic phase volume is much larger than water phase volume, so it is a water-
in-oil (W/O) emulsion case. Oil is the continuous phase as water droplets are dispersed in oil. By definition, micellar aggregates often occur when amphiphilic molecules (amphiphiles) dissolve in solution and form micelles. The spherical form of micelle (structure of micellar aggregates) is now generally accepted as approximating the actual structure (Moroi, 1992), outcomes the lamellar form (proposed by McBain) or rod-like form (proposed by Debye). According to SARA analyses (by TLC-FID method), the constituents of unused lube oil or used lube oil are very similar, with approximately > 98% aromatics, <1% resins, <1% asphaltenes, and no saturates. A Hartley micelle (i.e., polar-external spherical micelle) will form when the surfactant molecules migrate into the reversed (oil external-water internal) micelle and disrupt the polar structure. Micelle reversion caused by ultrasonic irradiation is illustrated in Figure 3-3.

When water is the dispersed phase in organic phase, the center of the reversed micelle can be metals, trace water, or other heteroatoms (e.g., S, N compounds). Sonication-induced cavitation causes the metals, polar and non-polar components to reorganize into a continuous, single-phase micelle in polar external form (Hartley micelle). When polar ends face towards the outside, attached molecules, such as metals and heteroatoms, can easily be removed by effective contact when they are brought outside as the micelle is reversed. The bondings between surfaces are greatly reduced (chelation for metals and hydrogen bonding for heteroatoms) so that these molecules can be removed. Metals are expected to separate from organic phase and stay in the water phase while heteroatoms may not only separate from the oil phase, but may possibly break down into smaller molecules by free radical attack.
Figure 3-3. Micelle Reversion under Ultrasonic Irradiation (after Sadeghi, 1992).
Catalysts or chelating agents may be added into the system to enhance the dissolution rate of metal molecules in water phase. Some catalysts also have the ability to initiate or enhance free radical formation, thus further enhance the decontaminating rate in the process.

Another option in order to enhance the removal of metals and heteroatoms may be the adjustment of the pH of the water phase. Acidic water may help to extract more metals from organic phase to water phase. pH effect on the ultrasonic cavitation is also widely discussed in many studies since it can alter the free radical reactions.

Purging argon gas or other gases into the system under ultrasonic irradiation is often practiced as a physical enhancement method. This is due to their ability to create more cavitation bubbles with optimal size. Argon itself does not participate in the reaction in any chemical way since it is an inert gas. However, when a solution is saturated with Ar gas, free radicals’ combination route may be different from the route where O$_2$ is present.

3.1.5.2 Free Radical Reactions

As mentioned in Section 3.1.2.2, when hydrocarbons in the oil samples are subjected to ultrasonic irradiation, they can be affected in two different ways. First, some alkyl or aryl radicals may be generated directly from hydrocarbons, and these radicals together with the radicals from water-splitting (if any) can propagate through chain transfer or termination steps. In this manner, the constituents of the oil may change due to the recombination of molecules. FT-IR or SARA analysis can be used to confirm the
transformation. Second, free radicals (from water or from hydrocarbons) are able to attack molecules at positions where there is weaker bonding. The scission or bond breaking will lead to fused rings in some aromatic compounds. The destruction of PAHs, PCBs, or BTEX compounds is possible. It is reported in many studies that ultrasonic energy is effective in breaking C=C and C-Cl bonds; hence, chlorinated compounds can be degraded accordingly. At the bubble/water interface, thermal decomposition may occur as one of the degradation pathways for the organic contaminants.

Chemicals, such as H$_2$O$_2$ or NaBH$_4$, can be added into the system to enhance the degradation efficiency. The effects, however, may be totally opposite. The addition of H$_2$O$_2$ directly supplies more hydroxyl radicals to initiate more free radical chain reactions and may possibly reduce the reaction time. Oxidation reactions are expected to occur on aromatic hydrocarbons. On the other hand, the addition of NaBH$_4$ produces a reducing environment. This is true when an abundant amount of H$_2$ gas is formed in the system (eq. 3-2); and consequently, the number of hydroxyl radicals in the system is far less than that of hydrogen radicals. Hydrogenation reaction will be the major reaction under reducing environment since the probability for small alkyl radicals to be captured by hydrogen radicals is increased, forming lighter hydrocarbons. Both chemicals are to be tested in order to verify which reaction environment is more efficient for decontaminating used oil.
3.2 Adsorption

3.2.1 Introduction

Adsorption phenomena have been known to mankind for a quite long time, and they are mostly utilized to perform desired bulk separation or purification purposes. The heart of a adsorption process is usually the porous solid medium. The use of porous solid is simply that it can provide a very high surface area or high micropore volume and it is this high surface area or micropore volume that high adsorptive capacity can be achieved. Since the porous medium is usually associated with very small pores and adsorbate molecules have to find their way to the interior surface area or micropore volume. This “finding the way” does give rise to the so-called diffusional resistance towards molecule flow. Hence, in order to properly understand both the adsorptive capacity and the diffusional resistance of the adsorption process, we must first understand these basic components: equilibria and kinetics.

Some of the principal terms and properties associated with adsorption and porous solids are defined in Table 3-3, Table 3-4, and Table 3-5. These definitions are consistent with those proposed by the International Union of Pure and Applied Chemistry (IUPAC) and by the British Standards Institution, and other official organizations.

The term “adsorption” is universally understood to mean the enrichment if one or more of the components in the region between two bulk phases (i.e. the interfacial layer). In the present context, one of these phases is necessarily a solid and the other a fluid (i.e. gas or liquid). The term “adsorption” and “desorption” are often used to indicate the
<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Enrichment of one or more components in an interfacial layer</td>
</tr>
<tr>
<td>Adsorbate</td>
<td>Substance in the adsorbed state</td>
</tr>
<tr>
<td>Adsorptive</td>
<td>Adsorbable substance in the fluid phase</td>
</tr>
<tr>
<td>Adsorbent</td>
<td>Solid material on which adsorption occurs</td>
</tr>
<tr>
<td>Chemisorption</td>
<td>Adsorption involving chemical bonding</td>
</tr>
<tr>
<td>Physisorption</td>
<td>Adsorption without chemical bonding</td>
</tr>
<tr>
<td>Monolayer capacity</td>
<td>either Chemisorbed amount required to occupy all surface sites or Physisorbed amount required to cover surface</td>
</tr>
<tr>
<td>Surface coverage</td>
<td>Ratio of amount of adsorbed substance to monolayer capacity</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Powder</td>
<td>Dry material composed of discrete particles with maximum dimension less than about 1 mm</td>
</tr>
<tr>
<td>Fine powder</td>
<td>Powder with particle size below about 1 μm</td>
</tr>
<tr>
<td>Aggregate</td>
<td>Loose, unconsolidated assemblage of particles</td>
</tr>
<tr>
<td>Agglomerate</td>
<td>Rigid, consolidated assemblage or particles</td>
</tr>
<tr>
<td>Compact</td>
<td>Agglomerate formed by compression of powder</td>
</tr>
<tr>
<td>Acicular</td>
<td>Needle-shaped</td>
</tr>
<tr>
<td>Surface area</td>
<td>Extent of available surface as determined by a given method under stated conditions</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>Surface area of unit mass of powder, as determined under stated conditions</td>
</tr>
<tr>
<td>External surface</td>
<td>Area of external surface of particles, as taking account of roughness (i.e. all cavities which are wider than they are deep), but not porosity</td>
</tr>
<tr>
<td>Roughness factor</td>
<td>Ration of external surface area to area of smoothed envelope around particles</td>
</tr>
<tr>
<td>Divided solid</td>
<td>Solid made up of more or less independent particles which may be in the form of a powder, aggregate or agglomerate</td>
</tr>
</tbody>
</table>
Table 3-5. Definitions: Porous Solids. (Rouquerol, 1999)

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous solid</td>
<td>Solid with cavities or channels which are deeper than their width</td>
</tr>
<tr>
<td>Open pore</td>
<td>Cavity or channel with access to the surface</td>
</tr>
<tr>
<td>Interconnected pore</td>
<td>Pore which communicates with other pores</td>
</tr>
<tr>
<td>Blind pore (Dead-end pore)</td>
<td>Pore with a single connection to the surface</td>
</tr>
<tr>
<td>Closed pore</td>
<td>Cavity not connected to the surface</td>
</tr>
<tr>
<td>Void</td>
<td>Space between particles</td>
</tr>
<tr>
<td>Micropore</td>
<td>Pore of internal width less than 2 nm</td>
</tr>
<tr>
<td>Mesopore</td>
<td>Pore of internal width between 2 and 50 nm</td>
</tr>
<tr>
<td>Macropore</td>
<td>Pore of internal width greater than 50 nm</td>
</tr>
<tr>
<td>Pore size</td>
<td>Pore width (diameter of cylindrical pore or distance between opposite walls of slit)</td>
</tr>
<tr>
<td>Pore volume</td>
<td>Volume of pores determined by stated method</td>
</tr>
<tr>
<td>Porosity</td>
<td>Ratio of total pore volume to apparent volume of particle or powder</td>
</tr>
<tr>
<td>Total porosity</td>
<td>Ratio of volume of voids and pores (open and closed) to volume occupied by solid</td>
</tr>
<tr>
<td>Open porosity</td>
<td>Ratio of volume of voids and open pores to volume occupied by solid</td>
</tr>
<tr>
<td>Surface area</td>
<td>Extent of total surface area as determined by given method under stated conditions</td>
</tr>
<tr>
<td>External surface area</td>
<td>Area of surface outside pores</td>
</tr>
<tr>
<td>Internal surface area</td>
<td>Area of pore walls</td>
</tr>
<tr>
<td>True density</td>
<td>Density of solid, excluding pores and voids</td>
</tr>
<tr>
<td>Apparent density</td>
<td>Density of material including closed and inaccessible pores, as determined by stated method</td>
</tr>
</tbody>
</table>
direction from which the equilibrium states have been approached. Adsorption hysteresis arises when the amount of adsorbed is not brought to the same level by the adsorption and desorption approach to a given “equilibrium” pressure or bulk concentration. The relation, at constant temperature, between the amount adsorbed and equilibrium pressure, or concentration, is known as the “adsorption isotherm”.

A powder is easily recognized as a mass of small dry particles. And it is reasonable to apply the term “fine powder” to a material consisting of particles less than 1 μm. This unit mass of a fine powder contains a large number of small particles and hence exhibits an appreciable surface area. For example, in the simplest case of an assemblage of spherical particles, all with the same diameter, $d$, the specific surface area, $a$, is given by the relation

$$a = 6/\rho d$$  \hspace{1cm} (Eq. 3-5)

where $\rho$ is the particle absolute density. The same calculation would apply to cubic particles, but in this case $d$ would be the edge length of the cube.

It is evident that it is more difficult to define particle size if the particle shape is not spherical or cubic. With some other simple geometric forms, a single linear dimension, $d_x$, may be used to calculate the surface area. In particular, when the particle aspect ratio is sufficiently large, $d_x$ is taken as the minimum dimension. Thus, if the particles are thin or long (i.e. plates or rods), it is the thickness that mainly determines the magnitude of the specific surface area.
The individual particles in a fine powder are usually clustered together in the form of aggregates or agglomerates. Loosely bonder aggregates are unconsolidated and non-rigid, but they may be converted into more rigid, consolidated agglomerates as a result of sintering or ageing. The breakdown, or particle breakdown, of the consolidated material can be achieved by grinding. The process of agglomeration involved the bridging or cementation of particles. An agglomerate may be regarded as a “secondary” particle, which always contains within it some internal surface. In many cases, the internal surface area is much larger than the external surface area and the agglomerate then possesses a well-defined pore structure.

The hypothetical types of pores shown in Figure 3-4 relate to the definitions in Table 3-4. In addition to closed pores and open pores, it is reasonable to distinguish between blind pores (or dead-end pores) and interconnected pores. Pores which are open at both sides of a membrane or porous plug are termed “through pores”.

Porosity is usually defined as the ratio of the volume of pores and voids to the volume occupied by the solid. However, it should be kept in mind that the recorded value of porosity is not always a simple characteristic property of the material, since it is likely to depend also on the methods used to assess both the pore volume and the volume of the solid. The pore volume us usually regarded as the volume of open pores, but it may include the volume of closed pores.
3.2.2 Physisorption and Chemisorption

When adsorption is about the interactions between the solid and the molecules in the fluid phase, two kinds of forces are involved, namely, either physisorption or chemisorption. Physisorption forces are the same as those responsible for the condensation of vapors and the deviations from ideal gas behavior, whereas chemisorption interactions are essentially those responsible for the formation of chemical compounds.

Figure 3-4. Cross Section of a Hypothetical Porous Grain Showing Various Types of Pores: closed (C), blind (B), through (T), interconnected (I), together with some roughness (R). (Rouquerol, 1990)
The most important distinguishing features may be summarized as follows:

(1) Physisorption is a general phenomenon with a relatively low degree of specificity whereas chemisorption is dependent on the reactivity of the adsorbent and adsorptive.

(2) Chemisorbed molecules are linked to reactive parts of the surface and the adsorption is necessarily confined to a monolayer. At high relative pressures, physisorption generally occurs as a multilayer.

(3) A physisorbed molecule keeps its identity and on desorption returns to the fluid phase in its original form. If a chemisorbed molecule undergoes reaction of dissociation, it loses its identity and cannot be recovered by desorption.

(4) The energy of chemisorption is the same order of magnitude as the energy change in a comparable chemical reaction. Physisorption is always exothermic, but the energy involved is generally not much larger than the energy of condensation of the adsorptive. However, it is appreciably enhanced when physisorption takes place in very narrow pores.

(5) An activation energy is often involved in chemisorption and at low temperature the system may not have sufficient thermal energy to attain thermodynamic equilibrium. Physisorption systems generally attain equilibrium fairly rapidly, but equilibrium may be slow if the transport process is rate-determining.

3.2.3. Adsorbents

The porous solid of a given adsorption process is surely a critical variable. The success or failure of the process depends on how the solid performs in both equilibrium...
and kinetics. A solid with good capacity but slow kinetics is not a good choice as it takes adsorbate molecules too long a time to reach the interior of particles. On the other hand, a solid with fast kinetics but low capacity is not good either as a large amount of solid is required for a given throughput. Thus, a good solid is the one that provides good adsorptive capacity as well as good kinetics. To satisfy these two requirements, the following aspects must be followed:

1. the solid must have reasonably high surface area or micropore volume
2. the solid must have relatively large pore network for the transport of molecules to the interior.

Hence, the porous solid must have small pore size with a reasonable porosity, better have a combination of two pore ranges: the micropore range and macropore range.

3.2.4 Destructive Adsorption

It is reported by Koper and his co-workers (Koper, 1997a and 1997b) that, ultrafine calcium oxide particles were employed as destructive adsorbents (high surface area solids that dissociatively chemisorb and immobilize all or fragments of incoming adsorbates) for three of the most common solvents: trichloroethene (TCE), chloroform, and tetrachloroethene.

As a one-step approach to the safe destruction of carbon tetrachloride with ultrafine calcium oxide to give calcium chloride and carbon dioxide (CCl₄(g) + 2CaO(s) \rightarrow CO₂(g) + 2CaCl₂(s)) has also been studied in detail. It also found that calcium oxide prepared by an aerogel/hypercritical drying method (AP-CaO) is superior to a
conventional prepared (CP-CaO) sample, and both are vastly superior to commercial CaO (CM-CaO). Reaction temperature were about 300 - 500 °C and would altered reaction efficiencies.

Since ultrasound can also provide locally high temperature and pressure in the solutions, similar situation would be possible to be observed. It is reasonable to make the assumption that if ultrasonic irradiation is applied following the adsorption process, to the samples with adsorbents still inside, we would have the following advantages:

(1) Greater chance for radicals or sonic energy wave to hit the target molecules that are adsorbed tightly inside the pores. Bond cleavage will occur within a thin film distance from the solid surface by free radicals attack or sonic energy. This is called “destructive adsorption”. (see Figure 3-5)

(2) Carefully selecting appropriate adsorbents depending on their characteristics and surface properties, destruction efficiency of the specific molecules or compounds could be enhanced.

(3) Modification of the surface can enhance or alter the adsorption as well as destruction of selected molecules or compounds.
Figure 3-5. Possible Schematic Expression for the Destructive Adsorption Reaction.
3.3 Water Separation Techniques

Water is considered as a contaminant species that invades lube oil during use. For any used oil recycling/reuse option, water has to be removed as a waste. For example, in re-refining process, water is removed in the early dehydration step by flashing the processing oil at near atmospheric condition. Water vapor is condensed and collected for treatment. In most cases, phenolic compounds and oil residues are two major concerns in the wastewater stream that have to be removed according to discharge standards prior to their discharge to POTW. According to Ms. Burn, a field operating engineer in Evergreen Oil, the size of the dehydration tower is about 30ft high in order to treat 43,000 gal/day oil during a 24 hr/day operation (the average water content in their used oil feedstock is 7-8%). For industrial-size operation, flashing/distillation may be a good choice for the separation of water from lube oil.

For this research, water separation is an important task. After ultrasonic irradiation treatment, water phase and organic phase in the emulsion samples have to be separated for individual analyses. Although we are more interested in the concentration level of pollutants left in the organic phase, it is necessary to determine the wastewater quality for the purpose of material balance study and for future suggestion of wastewater treatment options. Furthermore, if water phase can be separated from the organic phase in pretreatment steps, any consequent treatment in the recycling/reuse process will be simplified. It is crucial, however, not to alter the characteristics of both water and oil phase and not to lose targeted contaminants during water separating process. Otherwise, the results will be highly affected.
3.3.1 General Consideration

Demulsification is important for many production or refining industries. The basic philosophies followed in commercial emulsion breaking include: provide a density differential between immiscible liquids, increase droplet size, alter the stable emulsion environment, and remove emulsifying agents. All these actions can enhance the separation of the phases. Although a stable emulsion is able to separate naturally with age, immediate separation (made possible by external actions) is often required when necessary. The selection of demulsification method and proper practice are important in terms of quality issues, operative issues, and energy conservation concerns. Some techniques currently practiced are introduced below. An investigation about applying each technique on used lube oil W/O emulsion samples will be conducted in order to decide an appropriate demulsification technique.

3.3.2 Membrane Filtration Technique

When oil phase is dispersed in water phase, an oil-in-water emulsion is formed. Reported by Lin, 1998, it is possible to separate water and oil by membrane processes (RO or UF) followed a prefiltration step using a microfilter (woven cotton threads to retain particulates). This technique is successfully demonstrated for the treatment of waste drawing oil (an O/W emulsion in the cable and wire manufacturing processes). This method, however, may not be appropriate for W/O demulsification since transmembrane pressure buildup will be too high to operate feasibly.
3.3.3 Centrifugation Technique

For the reprocessing of used lube oil, centrifugation (or combined with fine filtration) refers to the method in which water is removed from the lube oil phase (see Fig. 4-3). In the study for removing radionuclides from waste lubricating oil, centrifugation is also used for water separation (Simiele, 1987). It was reported, however, that a long centrifuging time may be needed for complete separation, depending on the nature of the emulsions and the performance of the centrifuge.

3.3.4 Heating/Microwave Heating Technique

Increasing the temperature of the emulsion is commonly used in refining and oil-field industries to enhance emulsion breaking. Heat addition, however, is usually based on the overall economic picture of a treatment facility, minimum heat input is favored to avoid the lost of light end products and to save the consumption of flue gas.

Microwave heating emulsification technology is currently used in many chemical plants and has been successfully demonstrated as effective on crude oil/water emulsions. A study (Fang, 1995) utilized a domestic microwave oven to successfully separate synthetic lube oil/water emulsions. From their results, small temperature gradients through the body of irradiated emulsion proved that viscous water-in-oil emulsions are heated more quickly and uniformly by microwaves than by conventional convective heating, providing a faster water-oil separation. Operation of microwave energy at industrial scale is already proven possible. However, the energy consumption, has to be minimized to be economically feasible.
3.3.5 Chemical & Electrical Methods

Chemicals designed to eliminate or neutralize the effects of emulsifying agents can effectively resolve emulsions. It is commonly combined with heat or electric field to shorten the time. The function of the electrical field is to disturb the surface tension of each droplet, probably by causing polar molecules to reorient themselves, or to provide induced and oriented charges to adjacent emulsion particles in order to create mutual attraction. The chemicals used, however, will probably lead to a secondary pollutant since the separated water may contain high levels of chemicals for discharge. For this research, since trace level determination of some contaminants is needed, chemical addition is not strongly considered since it may interfere with the analytical work.

3.4 Specific Analytical Techniques for Oil Components

A series of specific analytical procedures have been established to characterize used oil. According to Section 5, what we are concerned about in used oil are contaminants targeted to be removed, especially heavy metals, BTEX compounds, chlorinated hydrocarbons, PAHs, and PCBs. The analytical techniques to determine these components and other oil properties are summarized below:

3.4.1 Moisture Content

Moisture content is also considered as one of the contaminants in used lube oil since virgin lube oil does not contain detectable amount of moisture. Water contamination is an economic concern for everyone dealing with used oil because of the
added cost associated with handling the water (e.g., dehydrating step in re-refining). In our proposed treatment process, however, a certain amount of water may be needed to create an optimum water/oil ratio for perfect emulsion. Thus, we have to measure the water content in the original used oil sample, sometimes we may need to add some water (distilled water or other waters with specific properties) to make the sample needed for the treatment.

However, laboratory methods for quantitatively determining water content in oil are mostly expensive (such as Karl Fisher method), time consuming and give a poor accuracy result, such as the distillation method. Hence, a convenient test kit “HydroScout™” developed by Dexsil Corporation (Hamden, CT) is used in the study.

The HydroScout™ system is designed to accurately and quickly measure the water (especially the dissolved water) content in used oil (or in other petroleum oil products). The test uses a specially formulated CaH₂ reagent to quantitatively convert all water contained in the oil sample to H₂ gas. The reaction is carried out in a sealed tube and the resulting pressure is measured using a specially designed meter. The results are displayed directly in percent and it takes only two minutes to finish one measurement. The measuring ranges are 0-20 v/v% (mode A) and 20-100 v/v% (mode B) with a detection limit of 0.15 v/v%.

3.4.2 Organic Hydrocarbons (BTEX, chlorinated compounds, PAHs, and PCBs)

The concentration of individual BTEX compounds (benzene, toluene, ethylbenzene, and xylene) and chlorinated compounds (dichlorodifluoromethane,
trichlorotrifluoroethane, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethene, and total chlorine) in either oil or in water sample is determined by GC-MS (EPA Method 8260, with purge and trap).

The concentration of individual PAH compounds in either oil or in water sample is determined by GC-FID (EPA Method 8100).

The concentration of PCBs (individual Aroclor species) in either oil or in water sample is determined by GC-ECD (EPA Method 8080). Due to the high sulfur content in the oil phase as interference, pretreatment cleanup for the oil samples is necessary.

3.4.3 Heavy Metals

Individual metal concentration in oil or in water is determined by ICP-MS. After proper dilution (for oil phase, 10 or 20mg oil to 1ml ultra-pure HNO₃), samples are placed in small teflon tubes and subjected to acid digestion while heated at >100°C under pressure for at least 24 hours and later washed with 1% dilute HNO₃. Metal concentration is then determined by ICP-MS (Fission, Model PQII-Plus). Although more than 60 elements can be determined for every sample in one scan, As, Ba, Cd, Cr, Pb, and Zn will be our major concerns. Any metal with an exceptionally high concentration also needs special attention.

3.4.4 Sulfur Content

Sulfur is viewed as an index of inherent antioxidant capacity in virgin lube oil. With re-refined oils, hydrocarbons that were inherently oxidatively unstable would have
been oxidized during previous use. It is necessary to identify the types of sulfur content, both in virgin lube oil and used oil, in order to better understand the role that sulfur plays.

Total sulfur content in an oil sample is determined by a sulfur-in-oil analyzer, Model SLFA-20/20T manufactured by Horiba Ltd., Japan. The measuring principle for this unit is the non-dispersive x-ray fluorescent (NDXRF) analysis, with a measuring range of 0-5 m/m%, repeatability of 15 ppm, and a detection limit of 20 ppm. It also uses the automatic C/H ratio compensation function to solve the problem of measurement error, which is caused by different types of oil. Any oil sample with water content more than 1v/v%, however, is not recommended to determine its total sulfur content with this instrument since noticeable deviation from actual concentration is expected to occur.

Different organo-sulfur type can be determined by GC-MS. The type of sulfur compounds in lube oil may change after use and may change further after ultrasonic irradiation. It’s important, therefore, to differentiate the sulfur type as well as measure the total sulfur content. Although the total sulfur content in the used oil sample may not change after treatment, but the individual sulfur species may change.

After ultrasonic treatment, some sulfur may be present in water phase as sulfate or sulfide. Sulfate concentration in water can be determined by turbidimetric method (Standard Method 4500-SO\text{4}^{2-}, Part E). Sulfide concentration in water can be determined by iodometric method (Standard Method 4500-S^{2-}, Part F).
3.4.5 Information of Water/Oil Emulsions

The crucial point about applying ultrasound energy to destroy or decompose the pollutants in the oil-based sample is to make good water/oil emulsions. It is important to define, therefore, what is a good water/oil emulsion. Both light microscope and scanning electron microscope (SEM) have been used to study the size distribution of emulsion by direct observation. The resolution and depth of field from SEM are significantly better than in comparison to what can be achieved through optical microscopy. The optical and electron microscopic techniques, however, are quite complimentary in terms of the information that they can provide. Optical microscopy, in fluorescence mode or with polarized light, can provide information about the organic phases in the emulsion. Electron microscopy, through the X-rays excited in the sample, can provide information about the inorganic and mineral phases present (Schramm, 1992). The practical lower limit of emulsion sizing with optical microscopy is at the level of 0.5 μm, with the limit as low as 0.1 μm or less for electron microscopy with direct observation of the frozen sample. Even lower limit such as 0.01 μm or less can be achieved with replicas and transmission electron microscopy.

Light polarizing microscopy (Leitz, model SM-LUX-POL) is initially used to observe the emulsion. First, we only checked if water and oil were in good emulsifying state. Later, we measure the micelle size if necessary, which may be needed for determining optimized ultrasound frequency. Since preparation of suitable emulsion samples for SEM observation is difficult, there is no intention to utilize SEM as a tool at
3.4.6 Other Evaluation Techniques

PCBs content in used oil is essential for determining how the used oil is going to be recycled or treated. Hence, it’s important to screen PCBs content in bulk used oil. If PCBs content is too high, then the used oil cannot be reprocessed or re-refined. Many screening techniques have been developed for PCBs in used oil, such as total organic halide methods, simplified chromatographic procedures, x-ray fluorescence, or total chlorine determination. The last method is the basis for many commercial colorimetric kits in field test use; unfortunately, these kits only give semiquantitative results. For lower regulatory limits of 50ppm, there is always some uncertainty about the accuracy. A new technique using thermal neutron activation analysis (ITAN) was proposed (Sutcliffe, 1989). Although it produces faster and more accurate PCBs results at a very low cost, it requires access to a reactor and trained personnel, which does not seem very applicable and convenient.

The techniques mentioned above are mostly adapted from determination methods of common oil samples. Since it’s not popular or necessary to characterize used oil samples; it’s rare to see a specific method developed mainly for used oil analysis. However, there are still some interesting techniques available. For example, FT-IR technique can be used to monitor lube oil condition coupled with an automated Spectrum™ Used Oil Analyzer (by Perkin-Elmer). When used oil is compared to fresh
oil with parameters (shown at different wavelengths) such as soot, hydroxyl, glycol, NOx/carboxylate, sulfate, antiwear loss, ester breakdown, and fuel contaminants in FT-IR spectrums, it provides information on the state of the oil itself and the engine from which the oil comes and ensures that an engine is operating with optimum efficiency.

Another technique used to evaluate the remaining useful life (RUL) of lubricant in the engine/equipment is the Remaining Useful Life Evaluation Routine (RULER™). This method utilizes voltammetric technique to indicate how much additive depletion has occurred (Jefferies, 1998). By tracking the readings over operating time, the user is able to identify abnormal operating conditions and predict necessary oil changes.
CHAPTER 4
Destruction of Heavy Metals in Used Lube Oils

4.1 Introduction

This chapter deals with the study on destruction of heavy metals in various used lube oil samples. Factors such as surfactant type, H\textsubscript{2} source, radical source, water content, reaction time, purging gas, catalysts that could possibly affect the destruction efficiencies were studied. Sonochemical process, adsorption process, and combined destructive adsorption process will be evaluated individually and the destruction efficiencies will be compared.

4.2 Preliminary Test Runs

4.2.1 Factors Affecting the Sonochemical Process

The initial study for applying the sonochemical process on the treatment of used oil is concentrated to investigate some factors that may affect the feasibility as well as the efficiency of the sonochemical process. Factors include:

- surfactant type/concentration, if needed
- H\textsubscript{2} source type and concentration, if needed
- radical source type and concentration, if needed
There are many other factors will also affect the sonochemical process, the optimum condition for these factors will be determined in future studies. Here are some potential parameters that need to be determined:

- optimum amount of water in water/oil emulsions
- optimal reaction time
- optimal reaction temperature
- pH/conductivity/OPR of the water in the emulsions
- purging gas type and optimal flow rate
- energy level and frequency of ultrasound
- additional catalysts or chemicals

The reaction kinetics for individual contaminant would be different as expected, thus, the optimization design, therefore, should consider every single contaminant involved, and tries to get the balance from all aspects.

4.2.2 Experimental Design – Sonochemical Process

Since the size of the used oil sample acquired from different source is individually different, it is important to decide how to take representative subsamples each time from the original big sample bottles (at least with volume size of one gallon) before conducting any experiment. A procedure was determined — the big sample bottles were shaken with inversion for 30 seconds and then allowed to settle for 15 seconds. This allowed the coarsest particles (if any) to settle, but included a representative sample of the other
constituents at most homogeneous state. Then, appropriate amounts of used oil samples were quickly poured out from the big bottles directly to smaller bottles (125mL) for ultrasonic irradiation treatment or to the blender to make emulsion samples.

The experimental design for the preliminary studies is illustrated in Figure 4-1. The experiments were conducted in a way to study how the factors, mentioned in previous section, would affect the feasibility or efficiency of the reaction.

For each different used oil sample, in order to know if the emulsifying condition is good enough for effective ultrasonic irradiation reaction, the water-in-oil emulsion state first has to be observed under microscope ($S_0$). Also the water content in original used oil sample has to be measured first ($S_0$). According to information from many sources, water content reported in used oil ranges from 5% to 20%. The four used oil samples acquired for this study, however, all contain very low water content, e.g., below detection limit of 0.15v/v% for the two automotive used oil samples and the hydraulic fluid sample, and merely 3.99v/v% for the mixed used oil sample. It is very possible that when we acquired the samples from the sources, the samples were just taken randomly from their big holding towers. Depending on from what level or what position they were drawn, the oil samples may not be so representative already. Ideally, we need to have an optimal water content to form effective-size vesicles and micelles in the water-in-oil emulsions so that the ultrasonic irradiation is then able to separate or break down toxins. Since water is considered as a contaminant for any used oil reuse process, extra water should be added as little as possible in order not to create too much trouble in water/oil separation step later on. From this point of view, 20m/m% is the maximum amount of water
Figure 4-1. Experimental Design for Preliminary Studies.
considered to add into original used oil samples for making emulsions \( (S_1) \). (It is easier to prepare a specific weight of used oil samples than a specific volume of used oil. Hence, in this study, oil samples are all prepared by weight.) If samples that are more representative could be acquired in the future (with higher average water content), then more efforts will be made on this subject.

Since the water-in-oil emulsion samples are quite different than any samples ever studied with ultrasonic irradiation (mostly dilute aqueous system, or heavy fossil fuels), there are still some factors that are not clearly known which will affect our system. For example, the gas environment or the addition of different chemicals (hydrogen source or radical sources) may have different effects in our system from in other systems. Thus, experiments should be designed in a way to identify the effects made by those factors, positively or negatively.

To make water/oil emulsion samples, a domestic blender (Hamilton Beach/Proctor-Silex, Inc., Model 56200) with 16 speed selection and a LO/HI power range was used. The maximum motor power is 425 Watt. Emulsion samples were prepared with different selections of speed and time. Microscopic examination was used to check the stability of the emulsion. An optimal speed/time combination will be decided for preparation of future samples.

For each test run, 75g of raw used oil sample or emulsified sample was transferred into 125-mL reaction bottle and subjected to ultrasonic irradiation. The schematic of the batch system for ultrasonic irradiation reactions used in initial test runs is shown in Figure 4-2.
Figure 4-2. Schematic Diagram of the Batch System for Ultrasonic Irradiation Reactions.
The ultrasound instrument is manufactured from Sonics & Materials, Inc. (Model VCX-600). This model has an operating frequency of 20kHz and an estimated intensity, with a titanium tip of 0.25-in (0.6-cm) sonication probe, of about 35 W/cm². A big water bath was used to keep the operating temperature at 25 ± 5ºC. During the sonication irradiation process, 5 m³/min of 99% compressed argon was applied to the sample. Although a higher degradation rate is expected with purged argon (Park, 1995), its effect in this new type of samples is not yet clear. Presently, argon is the only gas tested in the initial studies and other types of dissolved gas may be studied later.

Two different chemicals were separately added in different runs. A solution of 1 wt% hydrogen peroxide (Mallinckrodt Chemical Co.) was applied in one shot to the samples before the irradiation reaction was initiated. Also, 0.5 wt% sodium borohydride (Wilshire Chemical Co.) was added in two different ways: once before the irradiation reaction, or four times after every 15 minutes during the irradiation reaction. This is to avoid H₂ gas being released from the samples too quickly to generate a sufficient amount of radicals in the system. The results from the two different ways and the effects from adding two different chemicals will be compared. Then, the possible radical chain reaction pathway and the preferred operating system (oxidizing or reducing environment) can be identified.
4.2.3 Experimental Design – Adsorption Process and Destructive Adsorption Process

Four different adsorbent materials were selected in the adsorption test runs: alumina (Al₂O₃), silica gel (SiO₂), GAC (Calgon BPL) and PAC (Calgon WPH). The first two are widely used in column chromatography as adsorption and filtration media, and they are also very good catalysts. GAC and PAC are commonly used adsorbents in environmental applications. The simple comparison about the size, pore size, and surface area for these adsorbents is shown Table 4-1.

Adsorption Reaction was carried in 125mL bottles subjects to 2 hrs constant shaking at 20°C. The amount of adsorbents used is in 20% wt.

Samples were then subject to ultrasonic irradiation under the following conditions:

1) 5 m³/min Ar gas
2) 25 ± 5 °C
3) 60 min irradiation time
4) Sodium borohydride @1wt% was added every 15 min
Table 4-1. Comparison of Particle size, Pore Size and Surface Area for Various Absorbents.

<table>
<thead>
<tr>
<th></th>
<th>Particle size</th>
<th>Pore size (Å)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>75 – 180 μm</td>
<td>58</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td>80-200 mesh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica Gel (SiO₂)</td>
<td>75 – 250 μm</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>60-200 mesh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAC (Calgon BPL)</td>
<td>4.75mm × 2mm</td>
<td>20 – hundreds</td>
<td>800-1000</td>
</tr>
<tr>
<td></td>
<td>4 × 10 mesh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAC (Calgon WPH)</td>
<td>45 μm (90%+)</td>
<td>20 – hundreds</td>
<td>800-1000</td>
</tr>
<tr>
<td></td>
<td>325 mesh</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.2.4 Characteristics of the Used Oil Samples in This Study

Four different used oil samples were in this study, they are:

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Sample Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA-UO1</td>
<td>Used automotive lube oil from recycler in L.A. area</td>
</tr>
<tr>
<td>LA-UO2</td>
<td>Mixed used lube oil from a bug re-refining facility</td>
</tr>
<tr>
<td>BNL-UO1</td>
<td>Used automotive lube oil from Brookhaven Laboratory</td>
</tr>
<tr>
<td>BNL-UO2</td>
<td>Used hydraulic fluids from Brookhaven Laboratory</td>
</tr>
</tbody>
</table>

Besides these used oil samples, two different brands of clean lube oil, Pennzoil 10W-30 (labeled P-10W-30) and Valvoline 10W-30 (labeled V-10W-30) are purchased from Target store for the purpose of blank study. The reason for choosing 10W-30 grade for comparison is because it is the most popular used one, especially with Southern California’s weather condition.

The characteristics of the four original used oil samples and two unused automotive lube oil samples are listed in Table 4-2. It is obvious that there are some problems encountered with the acquired used oil samples.

First, the water content in the four used oil samples is too low when compared to reported values (possible 5%-20%, with average 7%-8% most common). In addition to conducting reactions with the original used oil samples, some samples were prepared by adding about 20% distilled water by weight (about 17% by volume, confirmed by water content measurement) — the maximum water content ever reported, and mechanically
Table 4-2. Characteristics of Oil Samples Used in This Study.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Water (v/v%)</th>
<th>Sulfur (m/m%)</th>
<th>Benzene (ppm)</th>
<th>Toluene (ppm)</th>
<th>EthylBzne (ppm)</th>
<th>Xylene (ppm)</th>
<th>PAHs&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PCBs&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Chlorinated&lt;sup&gt;c&lt;/sup&gt; Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA-UO1</td>
<td>0.05</td>
<td>0.3139</td>
<td>ND</td>
<td>136</td>
<td>116</td>
<td>535</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>LA-UO2</td>
<td>3.99</td>
<td>0.3442</td>
<td>23.2</td>
<td>406</td>
<td>393</td>
<td>823</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>BNL-UO1</td>
<td>0.05</td>
<td>0.3138</td>
<td>13.4</td>
<td>305</td>
<td>113</td>
<td>591</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>BNL-UO2</td>
<td>0.11</td>
<td>0.1399</td>
<td>ND</td>
<td>9.28</td>
<td>11.8</td>
<td>25</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>P-10W-30</td>
<td>0</td>
<td>0.3721</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>V-10W-30</td>
<td>0</td>
<td>0.2895</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>As (ppm)</th>
<th>Ba (ppm)</th>
<th>Cd (ppm)</th>
<th>Cr (ppm)</th>
<th>Pb (ppm)</th>
<th>Zn (ppm)</th>
<th>Al (ppm)</th>
<th>B (ppm)</th>
<th>Ca (ppm)</th>
<th>Cu (ppm)</th>
<th>Mg (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA-UO1</td>
<td>0.02</td>
<td>3.04</td>
<td>0.10</td>
<td>8.63</td>
<td>10.65</td>
<td>388.14</td>
<td>46.00</td>
<td>109.36</td>
<td>171.28</td>
<td>34.49</td>
<td>441.94</td>
</tr>
<tr>
<td>LA-UO2</td>
<td>0.21</td>
<td>14.42</td>
<td>0.51</td>
<td>19.85</td>
<td>24.24</td>
<td>403.96</td>
<td>57.93</td>
<td>118.42</td>
<td>204.94</td>
<td>37.20</td>
<td>422.21</td>
</tr>
<tr>
<td>BNL-UO1</td>
<td>0.17</td>
<td>0.08</td>
<td>0.03</td>
<td>21.52</td>
<td>4.26</td>
<td>906.24</td>
<td>40.36</td>
<td>239.48</td>
<td>203.43</td>
<td>101.27</td>
<td>969.16</td>
</tr>
<tr>
<td>BNL-UO2</td>
<td>0.03</td>
<td>0.06</td>
<td>0.01</td>
<td>9.90</td>
<td>0.15</td>
<td>88.95</td>
<td>14.67</td>
<td>54.57</td>
<td>58.04</td>
<td>1.84</td>
<td>7.65</td>
</tr>
<tr>
<td>P-10W-30</td>
<td>ND</td>
<td>0.05</td>
<td>0.00</td>
<td>4.81</td>
<td>0.16</td>
<td>140.99</td>
<td>13.40</td>
<td>65.19</td>
<td>67.86</td>
<td>1.04</td>
<td>279.38</td>
</tr>
<tr>
<td>V-10W-30</td>
<td>ND</td>
<td>0.75</td>
<td>ND</td>
<td>4.77</td>
<td>0.18</td>
<td>175.95</td>
<td>17.45</td>
<td>49.07</td>
<td>82.33</td>
<td>1.42</td>
<td>164.41</td>
</tr>
</tbody>
</table>

<sup>a</sup>PAHs compounds measured include 14 different individual PAH listed in Table 2-5.

<sup>b</sup>PCBs compounds measured include: Aroclor 1016, 1221, 1232, 1242, 1248, 1254.

<sup>c</sup>Chlorinated compounds measured include: dichlorodifluoromethane, trichlorotrifluoroethane, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethene.
mixed by the blender. It is expected when finer and more homogeneously dispersed vesicles are formed, more interfacial contacts between the two phases will occur, which can enhance the ultrasonic irradiation reactions. The mechanical force (blender) used to make the emulsion, however, may create an emulsion state in the emulsified sample which is a lot different from its natural form.

Secondly, many contaminants such as PAHs, PCBs, and chlorinated compounds were not found in any of the four used oil samples as predicted. BTEX compounds and heavy metals did present in these four used oil samples, however, the levels of concentrations were mostly much lower than typical values (Refer to Table 2-2). The reason for why such deviated and not-so-representative samples were acquired probably was due to the fact that these samples were taken from some upper levels of the holding towers. Thus, they were already cleaner than the average condition. Contaminants tend to settle at the bottom of the big holding tower with particulates or colloids after a period of holding time. It is possible that the water was already separated out and stayed at the bottom of the holding tower, so very low water content was found in original four used oil samples. The lack of PAHs, PCBs, and chlorinated compounds is hard to explain. It may be because the cross contamination did not occur in the sources of the four used oil samples. It is obvious that these samples may not be representative enough for the feasibility studies about ultrasound’s ability to decompose every potential contaminant in used oil. On the other hand, it could also be the fact that it is just too difficult to acquire used oil samples containing all potential contaminants within; if this is the case, then the current four used oil samples may still tell us some stories. In the first few test runs
applying ultrasonic irradiation on the four used oil samples, only heavy metals and BTEX compounds could be investigated. For future studies, synthetic used oil samples with known constituents will be prepared in order to systematically control the consistency of the experimental samples.

For sulfur determination, total sulfur measured in the unused lube oil or used lube oil is about 0.3wt% or even to 0.4wt%. Sulfur is added to base lube oil (contains total sulfur at only 0.05wt% for 100 neutral base oil and 0.07wt% for 300 neutral base oil) from the additive packages and should be removed during the recycling operations. In most cases, sulfur compounds produce acidic gases to cause corrosion problems in the treatment facilities. Thus, it is better to remove sulfur compounds early from the process flow. Unfortunately, they are always not removed until the last step (Refer to Table 2-4, in re-refining system), or only release as acidic gases (in reprocessing system) to create problems. Total sulfur content in treated samples is not determined due to incomplete water separation. The samples valid for total sulfur measurement by Horiba SLFA-20 are limited for whose water content is under 1%. The procedure for identifying different sulfur compounds in any oil phase by GC-MS is still under development in BNL and will be ready to routinely conduct the determination of different types of sulfur compounds after the database is completely set up.

4.2.5 Water-in-Oil Emulsions

When the original used oil sample was observed under light microscope, a well-dispersed water-in-oil emulsifying state was clearly seen. Oil immersion technique and
both regular/polarized light modes were used to focus beyond the cover slide and prevent the interference from trapped air bubbles. Since used oil must have certain levels of surfactants carried from its additive package, it seems that a good emulsion is naturally formed without further addition of surfactants. After extra water was added into used oil and mechanically mixed by the blender, the emulsion sample was also observed under light microscope. Finer and more homogeneously dispersed vesicles were observed. Emulsion samples were prepared with different selections of speed and time. The stability of the emulsion was checked by microscopic examination. However, the size of the vesicles is not measured at this time due to instrumental unavailability but will be determined for comparison later. An optimal speed/time combination will be decided for preparation of future samples.

4.2.6 Difficulties Encountered in Analytical Work

There were several problems encountered during the analytical procedures. First, it was discovered that the inhomogeneity of the used oil samples could cause inconsistent results unless the samples were prepared with special care at each step. The bulk sample had to be continuously stirred and the representative portion had to be carefully transferred to make emulsions or used as it is for the test runs. When water and oil are separated after the reaction, representative samples have to be taken from each phase for analysis. For analysis conducted by GC (e.g., PAHs, PCBs, BTEX, and chlorinated hydrocarbons), the amount of sample taken for preparation of the dilution is no more than one gram. For metal analysis by ICP-MS, only 20 mg or even 10 mg was taken from
each sample for preparation. It is obvious that if a sample taken for analysis is not from a homogeneous solution, replicated results cannot even be anticipated for the same sample matrix. Thus, it is critical to develop a secure sampling procedure for both water and oil phase samples in order to obtain reliable and reproducible results. Especially, homogeneity for oil phase samples needs more efforts to achieve due to the viscous property of oil. For the analyses that are performed in other facilities (BNL analytical lab, or other commercial labs), specific instruction should be given to the technicians involved to use same sampling techniques and procedures.

Secondly, it should be noted that used oil samples may be aged through time and some of the constituents may change or be released. A blank sample, therefore, has to be prepared in each set of test runs for analysis; it will serve as the new baseline to compare the degradation efficiency.

Lastly, the dirty and complex nature of the used oil samples makes the trace level analyses a little difficult. For example, a cleaning procedure to remove some interference factors is required for all samples; otherwise, PCBs peaks cannot be clearly identified and quantified. The detection limit for determining the organic contaminants (PCBs, PAHs, and chlorinated compounds) in the oil phase is very high since further concentration of these components in oil phase is very difficult and there is too much interference from the samples themselves.
4.2.7 Results from Preliminary Tests on Reduction of Heavy Metals from Used Oil

The experimental data from preliminary tests showing ultrasonic irradiation effect on heavy metals are presented in Figures 4-3 to 4-7. The experiments were conducted by varying the operating conditions as mentioned in the last section. Metal determination by ICP-MS has a very low detection limit of ppb level, however, a big variation could be observed even in the same sample matrix when the sample that is taken and prepared for acid digestion is not taken from a homogeneous bulk.

The results depicted in Figure 4-3 correspond to the ultrasonic irradiation experiments for identifying the effects of ultrasound and hydrogen peroxide on heavy metals, such as Ba, Cd, Cr, Pb, and Zn. Arsenic is not discussed here since it presented a very low concentration level in the original four used oil samples. In these experimental runs, the greatest reduction in metal content was observed when hydrogen peroxide was added to emulsified sample (A1-W-OH-US60).

The effects of water (for creating emulsion) and hydrogen peroxide on heavy metal removal from used oil by ultrasonic irradiation are presented in Figure 4-4. The results indicate that the addition of hydrogen peroxide could only enhance heavy metal removal rate when extra water was added to the original used lube oil and mechanically emulsified. Extra water alone could not enhance the removal of heavy metal without adding hydrogen peroxide. The results also indicate that hydrogen peroxide is effective only when a certain amount of water is present.
Operating Condition:

(1) 5 m³/min Ar gas
(2) 25±5°C

A1: LA-UO1 automotive used oil sample
W: distilled water 20wt% added and emulsified
OH: hydrogen peroxide 1wt% added
US60: ultrasonic irradiation for 60 minutes

Figure 4-3. The Effects of Ultrasound and H₂O₂ on Heavy Metals in Used Oil.
Figure 4-4. The Effects of Ultrasound and Water (under Oxidizing or Reducing Environment) on Heavy Metals in Used Oil.
The comparison of the effects of ultrasound under oxidative and reduced environment is depicted in Figure 4-5. It indicates that hydrogen peroxide seemed to better in removing heavy metals than sodium borohydride (i.e., under reducing environment).

For the set of experiments conducted using alkaline water (with addition of Na$_2$SiO$_3$) instead of distilled water to emulsify the used oil samples, the results, as shown in Figure 4-6 indicate that alkaline condition had very little effect in enhancing the removal of heavy metals from used oil.

The results from the destructive adsorption process of removing heavy metals from used oils were depicted in Figure 4-7. Only Zn was selected as the target for measurement at this preliminary test run. It is clearly to see that either GAC or PAC is not a good selection for removing heavy metals from used oil. Both of them alone seemed not only unable to remove the heavy metals from used oil. When they combined with subsequent ultrasonic irradiation, the GAC test run can merely approach the same efficiency as ultrasonic irradiation run alone, however, the PAC test run indicates that the usage of PAC can alter the efficiency of heavy metal removal from used oil in a very undesirable direction.

Though alumina alone can remove about 30% of Zn from used oil, however, when subsequent ultrasonic irradiation was applied, it did not improve the removal efficiency in a noticeable way compared to ultrasonic irradiation test run alone. Overall, silica gel seemed to perform superiorly in this destructive adsorption case since though
Operating Condition:
(1) 5 m³/min Ar gas
(2) 25±5°C

A1: LA-UO1 automotive used oil sample
W: distilled water 20wt% added and emulsified
OH: hydrogen peroxide 1wt% added
US60: ultrasonic irradiation for 60 minutes

Figure 4-5. The Effects of Water and H₂O₂ on Heavy Metals in Used Oil.
Figure 4-6. The Effects of Ultrasound and Alkaline Solution on Heavy Metals in Used Oil.
Adsorption Reaction was carried in 125mL bottles subjected to 2 hrs shaking at 20ºC. Adsorbent used: 20 wt%

Operating Condition for Ultrasound Reaction:
1. 5 m³/min Ar gas
2. 25 ± 5 ºC
3. 60 minutes irradiation time
4. Sodium borohydride 1 wt% was added every 15 minutes

Figure 4-7. The Effects of Different Adsorbent Following Ultrasonic Irradiation on Zn Removal from Used Oil.
itself alone cannot remove metal constituent from used oil, when subsequent ultrasonic irradiation was applied with silica gel still inside the used oil samples, it can enhance the removal efficiency of metal constituent from used oil almost 20% more.

4.3 Optimal Conditions for Destructive Adsorption of Heavy Metals from Used Oil

According to the results from the preliminary test runs, the operating conditions that gave better performance in destructive adsorption reaction of heavy metal removal from used oil are:

(1) with hydrogen peroxide present in the emulsified sample
(2) oxidative environment is better
(3) silica gel is the best adsorbent candidate

Thus, with this information in mind, we can optimize the reaction conditions for Heavy metal removal from used oil.

4.3.1 Water Effect

The study of the effects of water content on heavy metal removal is depicted in Figure 4-8. The proper amount of water added is crucial to the emulsification of the oil samples to gain better heavy metal removal rate. However, too much water added to the oil sample would increase the difficulty later on to separate the water from oil sample. Hence, from Figure 4-8, we may suggest 20% water content is good enough as the optimal water content in emulsification of used oil samples.
Figure 4-8. The Effects of Water Content on Heavy Metal Removal from Used Oil.
4.3.2 Hydrogen Peroxide Effect

The study of the effects of hydrogen peroxide content on heavy metal removal is shown in Figure 4-9. Though 1.5% of hydrogen peroxide can give slightly better removal efficiencies on heavy metals from used oil than 1.0% of hydrogen peroxide used in the preliminary test runs. However, if we consider from the economic point of view when this application expands to large scale, it would be more cost-effective using 1.0% of hydrogen peroxide as the optimal condition.

4.3.3 Oxidative vs. Reducing Environment

In preliminary study, we only use sodium borohydride as the catalysis in the destructive adsorption reaction since the removal efficiencies for BTEX is much better under reducing environment. However, it is still worthwhile to study if the removal efficiencies for heavy metals could be better under oxidative environment. From Figure 4-10, it is clearly to see that when sodium borohydride is added into the used oil sample every 15 min during the 1-hr reaction, actually it would give very similar result that hydrogen peroxide can achieve in heavy metal removal from used oil. Hence, for optimal operating conditions, we can go for either way. However, BTEX compounds removal efficiency as well as heavy metal removal efficiency from used oil, both should be considered equally important. Thus, reducing environment may be still the better choice for destructive adsorption process in used oil de-toxification.
Figure 4-9. The Effects of Hydrogen Peroxide Content on Heavy Metal Removal from Used Oil.
Operating Condition:
(1) 5 m³/min Ar gas
(2) 25±5°C
LA-UO1 automotive used oil sample
OH: Hydrogen peroxide 1wt% added
H(4): Sodium borohydride 1wt% added every 15 min
Ultrasonic irradiation for 60 minutes

Figure 4-10. The Effects of Oxidative or Reducing Environment on Destructive Adsorption of Heavy Metal Removal from Used Oil.
4.4 Concluding Remarks

Based on the limited results from this Chapter, several conclusions can be drawn as follow:

(1) The destructive adsorption process, using silica gel as the adsorbent, aided with following ultrasonic irradiation for heavy metal removal from used lube oil samples is feasible.

(2) The optimal operating conditions for this proposed process are: 20% water as the emulsifier, 1wt% of sodium borohydride is added every 15 min for the 1-hr reaction time to keep the reaction environment under a reducing condition for better removal efficiency.
CHAPTER 5

Destruction of BTEX Compounds in Used Lube Oils

5.1 Introduction

This chapter deals with the study on destruction of BTEX compounds in various used lube oil samples. Same factors such as surfactant type, H₂ source, radical source, water content, reaction time, purging gas, catalysts that could possibly affect the destruction efficiencies were studied as in last chapter. Sonochemical process, adsorption process, and combined destructive adsorption process will be also evaluated individually and the destruction efficiencies will be compared.

5.2 Preliminary Test Runs

Same experimental approach and design were carried as in last chapter for the removal of BTEX compounds from used oil samples.

5.2.1 Factors and Experimental Design

Please refer to Section 4.2.1 through Section 4.2.3.

5.2.2 Materials and Methods

Please refer to Section 4.2.4 through Section 4.2.6.
5.2.3 Results of Preliminary Tests on Reduction of BTEX Compounds from Used Oil

The experimental data showing ultrasonic irradiation effect on BTEX compounds are presented in Figures 5-1 to 5-7. The experiments were conducted by varying the operating conditions including water content, irradiation time, and addition of chemicals such as hydrogen peroxide, sodium borohydride, and sodium ortho-silicate. Since benzene is not detected in any of the four original used oil samples, so only three other compounds, toluene, ethylbenzene, and xylene are discussed in the results. (BTEX compounds – mentioned later in this section and in all the figures, represents only these three compounds.)

For blank sample run, the original sample was placed in the apparatus setup and subjected to the same operating condition as others: it was purged 5 m³/min argon gas at 25 ± 5℃ for 60 minutes without turning off the power of ultrasound. The analytical data for this sample will be the basis to compare the removal efficiency, eliminating the effect from purged argon gas.

The results depicted in Figure 5-1 correspond to the ultrasonic irradiation experiments for identifying the effects of ultrasound and hydrogen peroxide on BTEX compounds in used lube oil samples collected in Los Angeles area (LA-UO1, in short of A1). Among these experimental runs, the greatest reduction in BTEX compounds was observed when hydrogen peroxide was added to the emulsified sample (A1-W-OH-US60 run).
Operating Condition:
(1) 5 m³/min Ar gas
(2) 25±5°C

A1: LA-UO1 automotive used oil sample
W: distilled water 20wt% added and emulsified
OH: hydrogen peroxide 1wt% added
US60: ultrasonic irradiation for 60 minutes

Figure 5-1. The Effects of Ultrasound and H₂O₂ on BTEX Compounds in Used Oil.
To study the effect of irradiation time, experimental runs were conducted with two different irradiation duration times. The results depicted in Figure 5-2 indicate that a greater BTEX removal rate was achieved with longer irradiation time.

The effects of water (for creating emulsion) and hydrogen peroxide on BTEX compounds removal from used oil by ultrasonic irradiation are presented in Figure 5-3. The results indicate that when no hydrogen peroxide was added, extra water and enhanced emulsification alone could not increase the removal rate for BTEX compounds under ultrasonic irradiation. The results, however, also indicate that the addition of hydrogen peroxide could only enhance BTEX removal rate when extra water was added to the original used lube oil and mechanically emulsified. An opposite effect (low removal rate) was even observed when hydrogen peroxide was added to the original used lube oil samples, which were directly subject to ultrasonic irradiation without further emulsification. This may suggest that hydrogen peroxide is effective only when a certain amount of water is present.

The results depicted in Figure 5–4 correspond to the ultrasonic irradiation experiments for different used oil samples. The data also indicate that hydrogen peroxide could promote the removal rate of BTEX compounds from different used oils that are in an enhanced emulsified state.

The comparison of the effects of ultrasound under oxidative and reduced environments is depicted in Figure 5-5 and 5-6. The results in Figure 5-5 indicate that the periodical addition of sodium borohydride achieved a better BTEX removal efficiency than single addition prior to the irradiation. Extra water and enhanced emulsification, however, seemed unnecessary for sodium borohydride to be effective.
Figure 5-2. The Effect of Ultrasonic Irradiation Time on BTEX Compounds in Used Oil.
Operating Condition:
(1) 5 m³/min Ar gas
(2) 25±5°C
A1: LA-UO1 automotive used oil sample
W: distilled water 20wt% added and emulsified
OH: hydrogen peroxide 1wt% added
US60: ultrasonic irradiation for 60 minutes

Figure 5-3. The Effects of Water and H₂O₂ on BTEX Compounds in Used Oil.
Figure 5-4. The Effects of Ultrasound and Water on BTEX Compounds in Different Used Oils.
Operating Condition:  
(1) 5 m³/min Ar gas  
(2) 25±5°C  
A1: LA-UO1 automotive used oil sample  
W: distilled water 20wt% added and emulsified  
H2(1): sodium borohydride 0.5wt%, added once  
H2(4): sodium borohydride 0.5wt%, added four times  
US60: ultrasonic irradiation for 60 minutes

Figure 5-5. The Effects of Ultrasound and Water (under Reducing Environment) on BTEX Compounds in Used Oil.
Operating Condition:
(1) 5 m³/min Ar gas
(2) 25±5°C
A1: LA-UO1 automotive used oil sample
W: distilled water 20wt% added and emulsified
OH: hydrogen peroxide 1wt% added
H2(1): sodium borohydride 0.5wt%, added once
H2(4): sodium borohydride 0.5wt%, added four times
US60: ultrasonic irradiation for 60 minutes

Figure 5-6. The Effects of Ultrasound and Water (under Oxidizing or Reducing Environment) on BTEX Compounds in Used Oil.
From Figure 5-6, it can be concluded that sodium borohydride seemed more effective in removing BTEX compounds than hydrogen peroxide when it is periodically added to the reaction system.

One set of experiments was conducted using alkaline water (with addition Na₂SiO₃) instead of distilled water to emulsify the used oil samples. The results depicted in Figure 5-7 indicate that alkaline condition had a poor effect on the removal of BTEX compounds from used oil samples.

The results from the destructive adsorption process of removing BTEX compounds from used oils were depicted in Figure 5-8. Alumina is out of question the one that gives the poorest performance. And it is also clearly to see that either GAC or PAC alone is a good selection for removing BTEX compounds from used oil, especially GAC can remove as high as 98% of BTEX compounds from used oil. However, when they combined with subsequent ultrasonic irradiation, the GAC test run indicate that around 20 – 30% adsorbed BTEX compounds was released from GAC and get back into the used oil. Though PAC test run does not show any desorption of BTEX compounds after further ultrasound irradiation, its overall removal efficiency is not as good as what silica gel performs.

Overall, silica gel seemed to perform superiorly again in this destructive adsorption case as it did in last Chapter. Though itself alone cannot remove BTEX compounds from used oil as GAC can, when subsequent ultrasonic irradiation was applied with silica gel still inside the used oil samples, it can enhance the removal efficiency of BTEX compounds from used oil almost 30% more.
Operating Condition:
(1) 5 m³/min Ar gas
(2) 25±5°C
A1: LA-UO1 automotive used oil sample
DW: distilled water 50wt% added and emulsified
NaSi: Na₂SiO₃ 10wt% added
US30: ultrasonic irradiation for 30 minutes

Figure 5-7. The Effects of Ultrasound and Alkaline Solution on BTEX Compounds in Used Oil.
Operating Condition for Ultrasound Reaction:
(1) 5 m³/min Ar gas
(2) 25±5°C
(3) 60 minutes irradiation time
(4) Sodium borohydride 1wt% was added every 15 minutes

Adsorption Reaction was carried in 125mL bottles subjected to 2 hrs shaking at 20°C.
Adsorbent used: 20wt%
5.3 Optimal Conditions for Destructive Adsorption of BTEX Compounds from Used Oil

In order to meet the consistency with the optimal conditions for destructive adsorption of heavy metals from used oil, not only the results from the preliminary test runs have to evaluated, also the conclusion from Section 4.3 is necessarily to the operating conditions that gave better performance in destructive adsorption reaction of BTEX Compounds removal from used oil.

5.3.1 Water Effect

The study of the effects of water content on BTEX compounds removal is depicted in Figure 5-9. Very similar result to the heavy metal removal can be concluded, we may still suggest 20% water content is good enough as the optimal water content in emulsification of used oil samples.

5.3.2 Sodium Borohydride Effect

The study of the effects of sodium borohydride content on BTEX compounds removal from used oil is shown in Figure 5-10. Though 1.5% of sodium borohydride can give slightly better removal efficiencies on heavy metals from used oil than 1.0% of hydrogen peroxide used in the preliminary test runs. Same consideration could be applied here as in Section 4.3.2, from the economic point of view when this application expands to large scale, it would be more cost-effective using 1.0% of sodium borohydride as the optimal condition.
Operating Condition:
(1) 5 m³/min Ar gas
(2) 25±5°C
LA-UO1 automotive used oil sample
Sodium borohydride 1wt% added every 15 min
Ultrasonic irradiation for 60 minutes

Figure 5-9. The Effects of Water Content on BTEX Compounds Removal from Used Oil.
Figure 5-10. The Effects of Sodium Borohydride on BTEX Compounds Removal from Used Oil.
5.3.3 Oxidative vs. Reducing Environment

In preliminary study, we only use sodium borohydride as the catalysis in the destructive adsorption reaction since the removal efficiencies for BTEX compounds subject to ultrasonic irradiation reaction alone is much better under reducing environment. However, it is necessary to study if the removal efficiencies for BTEX compounds could be better under oxidative environment undergoing destructive desorption reaction. From Figure 5-11, it is clearly to see that when sodium borohydride is added into the used oil sample every 15 min during the 1-hr reaction, actually it would give a better result that hydrogen peroxide can achieve in BTEX compounds removal from used oil. Hence, for optimal operating conditions, reducing environment may be still the better choice for destructive adsorption process in used oil de-toxification for both heavy metals as well as BTEX compounds.
Figure 5-11. The Effects of Oxidative or Reducing Environment on Destructive Adsorption of BTEX Compounds Removal from Used Oil.
5.4 Concluding Remarks

Based on the limited results from this Chapter, several conclusions can be drawn as follow:

(1) The destructive adsorption process, using silica gel as the adsorbent, aided with following ultrasonic irradiation for BTEX Compounds removal from used lube oil samples is feasible.

(2) The optimal operating conditions for this proposed process are: 20% water as the emulsifier, 1wt% of sodium borohydride is added every 15 min for the 1-hr reaction time to keep the reaction environment under an reducing condition for better removal efficiency.
CHAPTER 6

Conclusions and Recommended Future Work

6.1 Summary and Conclusions

This dissertation is the preliminary study of sonochemical process and destructive desorption process enhanced by sonochemical process for the toxin reduction of used oil. The main two categories of toxins focused in this study are heavy metals and BTEX compounds. These two categories of toxic contaminants intruded into lube oil during its usage will eventually end up in the used lube oil bulk and cause severe problems in any current options for recycling and reuse of used lube oils. Thus it is

The following summarizes some of the important conclusions which are based on the work and materials presented in this dissertation. Also, some recommendations that could improve the understanding the applicability of these processes are made for future study.

(1) Used oil is a valuable resource and a vital source of energy. Oil does not wear out; it just gets dirty after use. Thus, used oil still has lubricating value and heat value. Following the proper treatment to remove contaminants, used oil can be re-refined into base lube oil, reproessed as fuel oil, or used as feedstock to produce petroleum-based products or other commercially valuable products via different processes.
The proper management of used oil is a very important issue because used oil often contains metals, chlorinated hydrocarbons and other organic compounds, including many that are listed as priority pollutants by the U.S. EPA. If used oil is mismanaged, the effects upon the environment will be detrimental. Since used oil is generated in large quantities, estimating more than 1.5 billions gallons per year in the U.S., that the associated impact to the environment is huge when there is uncontrolled dumping and landfilling of used oil in the environment.

Two major sources of used oil are automotive and industrial used oil. Automotive used oil tends to have a high concentration of potentially hazardous heavy metals, usually as the result of the engine or bearing wear, or the inclusion of these metals in oil additives. Industrial used oil tends to have a high level of chlorinated hydrocarbons and PCBs through careless management practices. The presence of other toxic organic compounds like benzene or naphthalene is usually associated with the oil formulation itself.

The destructive adsorption process, using silica gel as the adsorbent, aided with following ultrasonic irradiation for both heavy metal removal as well as BTEX compounds removal from used lube oil samples is feasible. And the removal efficiencies for both categories of toxic contaminants are better than undergone ultrasonic irradiation alone.

The proper amount of water added is crucial to the emulsification of the used oil samples to gain better heavy metal removal or BTEX compounds removal efficiencies. However, too much water added to the used oil sample would
increase the difficulty in separating water from oil and may cause unexpected problems to the following recycle or reuse options.

(6) The optimal operating conditions for this proposed process are: 20% water as the emulsifier, 1wt% of sodium borohydride is added every 15 min for the 1-hr reaction time to keep the reaction environment under an reducing condition for better removal efficiency.

(7) Cost estimation or techno-economic evaluation for this proposed process has not been considered in this thesis due to the insufficient information. And it has to be compared against some other currently readily-in-use options in this industry in order to evaluate both the economic and technical feasibility to expand this application to used oil recycle industry.

6.2 Recommended Future Work

(1) The intensity of ultrasound would affect the degree of chemical reaction. The use of high power and continuous-type ultrasound need to be studied. They may enhance the removal efficiencies of the process.

(2) Though it is preferred to conduct the reaction process under room temperature from the energy-saving point of view, however, the effect of temperature on the removal efficiency also needs to be determined.

(3) Destructive adsorption reaction is reported feasible on the destruction of some chlorinated hydrocarbons at reaction temperature of 300-500°C. Since chlorinated hydrocarbon is also a potential contaminant category in used oil (especially used
industrial lube oil), this could be interest research direction. Because though ultrasonic reaction is often carried out at near room temperature, but the sample under ultrasonic irradiation is actually contains many many high-temperature and high-pressure spots locally, thus maybe similar results could be drawn as other destructive adsorption of reported chlorinated compounds.
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Mr. Sean Campbell, Cal. Int. Waste Manage. Board, Sacramento, CA. 1-800-466-4744.
Mr. James Prado, Rosemead Oil, Santa Fe Spring, CA. 1-562-941-3261
Mr. Greg Hutchison, Safety-Kleen, Chicago, IL. 1-800-535-5407.


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Appendix A

Detailed Engineering Layout for the Hydrocarbon to Protein Process

Biomass Production from Oil Wastes:

(1) Fermentation Section
(2) Lipid Extraction and Product Drying Section
(3) Detergent Wash Section
Figure A-1. Biomass Production from Oil Wastes: Fermentation Section.
Figure A-2. Biomass Production from Oil Wastes: Lipid Extraction and Product Drying Section.
Figure A-3. Biomass Production from Oil Wastes: Detergent Wash Section.
Appendix B

Physical and Health Hazard Properties of Selected Target Compounds

(1) Heavy Metals  
(As, Ba, Cd, Cr, Pb, Zn)

(2) BTEX Compounds  
(benzene, toluene, xylene)

(3) Chlorinated Hydrocarbons  
(dichlorodifluoromethane, trichlorotrifluoroethane,  
trichloroethene, tetrachloroethylene, 1,1,1-trichloroethane)

(4) PAHs  
(benzo(a)anthracene, benzo(a)pyrene, naphthalene)

(5) PCBs
Table B-1. Physical and Health Hazard Properties of Heavy Metals

<table>
<thead>
<tr>
<th>Name and Symbol</th>
<th>m.p. (°C)</th>
<th>b.p. (°C)</th>
<th>Carcinogenic</th>
<th>RCRA Waste? MCL (mg/L)</th>
<th>EPA Priority Pollutant?</th>
<th>Health Hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic As</td>
<td>650</td>
<td>1380</td>
<td>Yes</td>
<td>Yes, 5.0</td>
<td>Yes</td>
<td>All arsenic compounds are toxic, the toxicity varying with the oxidation state of the metal and the solubilities.</td>
</tr>
<tr>
<td>Barium Ba</td>
<td>710</td>
<td>1600</td>
<td>No</td>
<td>Yes, 100</td>
<td>No</td>
<td>Toxic routes include inhalation and ingestion. Ingestion of barium salts can be lethal to humans.</td>
</tr>
<tr>
<td>Cadmium Cd</td>
<td>321</td>
<td>767</td>
<td>Yes</td>
<td>Yes, 1.0</td>
<td>Yes</td>
<td>Toxic routes are inhalation or ingestion. Cadmium is a poison that is accumulated in liver and kidneys.</td>
</tr>
<tr>
<td>Chromium Cr</td>
<td>1900</td>
<td>2642</td>
<td>Yes</td>
<td>Yes, 5.0</td>
<td>Yes</td>
<td>Among all chromium compounds, only the hexavalent salts are a prime health hazard.</td>
</tr>
<tr>
<td>Lead Pb</td>
<td>327.5</td>
<td>1740</td>
<td>No</td>
<td>Yes, 5.0</td>
<td>Yes</td>
<td>Toxic routes of exposure are food, water, and air. Toxic effects depend on the dose and nature of lead salts.</td>
</tr>
<tr>
<td>Zinc Zn</td>
<td>419.5</td>
<td>908</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Inhalation of fumes and ingestion of sol salts may result in fever, nausea, skin irritation, and vomiting.</td>
</tr>
</tbody>
</table>
### Table B-2. Physical and Health Hazard Properties of BTEX Compounds.

<table>
<thead>
<tr>
<th>Name and Structure</th>
<th>b.p. (°C)</th>
<th>Carcinogenic</th>
<th>RCRA Waste (#)</th>
<th>EPA Priority Pollutants?</th>
<th>Health Hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benzene</strong></td>
<td>80.1</td>
<td>suspected</td>
<td>Yes (U019)</td>
<td>Yes</td>
<td>Toxic effects from inhalation, ingestion and skin contact. Symptoms are distorted perception, nausea, vomiting and headache. Irritant to eyes, nose, and respiratory tract. Target organs are blood, bone marrow, central nervous and respiratory system, skin, and eyes.</td>
</tr>
<tr>
<td><img src="image" alt="Benzene Structure" /></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Toluene</strong></td>
<td>110.7</td>
<td>No</td>
<td>Yes (U220)</td>
<td>Yes</td>
<td>Exposure routes are inhalation, ingestion and skin absorption. Affected Organs are central nervous system, liver, kidneys, and skin. Symptoms are distorted perception, euphoria, confusion, headache, and dizziness. May be accumulated in fatty tissues, cause bone marrow depression or anemia.</td>
</tr>
<tr>
<td><img src="image" alt="Toluene Structure" /></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Xylene</strong></td>
<td>137-140</td>
<td>No</td>
<td>Yes (U239)</td>
<td>Yes</td>
<td>Target organs are central nervous system, eyes, gastrointestinal tract, kidneys, liver, blood, and skin. Irritates eyes, nose, throat, causes nausea, vomiting, headache, dizziness, abdominal pain, and dermatitis. Inhalation and skin absorption are major route of exposures. May accumulate in adipose tissue and blood.</td>
</tr>
<tr>
<td><img src="image" alt="Xylene Structure" /></td>
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<td></td>
</tr>
<tr>
<td>Compound Name (Other Common Name)</td>
<td>Structure</td>
<td>b.p. (°C)</td>
<td>Carcinogenic ?</td>
<td>RCRA (#)</td>
<td>EPA Priority Pollutants?</td>
</tr>
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<td>--------------------------</td>
</tr>
<tr>
<td>Dichlorodifluoromethane (Freon-12, CFC-12)</td>
<td>CCl₂F₂</td>
<td>-29.8</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Trichlorotrifluoroethane (Freon-113, CFC-113)</td>
<td>ClCF₂CCl₂F</td>
<td>46-48</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Trichloroethene (Trichloroethylene, trichloride, trielene)</td>
<td>CCl₂=CHCl</td>
<td>86.7</td>
<td>Yes</td>
<td>Yes (U228)</td>
<td>Yes</td>
</tr>
<tr>
<td>Tetrachloroethylene (Perchloroethylene, Ethylenetetrachloride)</td>
<td>Cl₂C=C Cl₂</td>
<td>121</td>
<td>Yes</td>
<td>Yes (U210)</td>
<td>Yes</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane (Methylchloroform, Chlorothene)</td>
<td>CH₃CCl₃</td>
<td>74.1</td>
<td>No</td>
<td>Yes (U226)</td>
<td>Yes</td>
</tr>
<tr>
<td>Name and Structure</td>
<td>m.p./b.p. (°C)</td>
<td>Carcinogenic</td>
<td>RCRA Waste (#)</td>
<td>EPA Priority Pollutants?</td>
<td>Health Hazards</td>
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<td>----------------</td>
</tr>
<tr>
<td>Benzo[a]Anthracene</td>
<td>160</td>
<td>Yes</td>
<td>Yes (U108)</td>
<td>Yes</td>
<td>No report on oral toxicity, but highly toxic by intravenous procedures. Carcinogenicity is correlated to its bioalkylation at the site of injection.</td>
</tr>
<tr>
<td></td>
<td><img src="image1" alt="Benzo[a]Anthracene" /></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Benzo[a]Pyrene</td>
<td>179 / 311</td>
<td>Yes</td>
<td>Yes (U022)</td>
<td>Yes</td>
<td>Poor absorption by gastrointestinal tract. Carcinogenicity affects lungs, skin, liver, kidney, and blood. Exhibits teratogenic effect. A mutagen, showed positive in a histidine reversion-Ames test and in-vitro SCE human lymphocytes.</td>
</tr>
<tr>
<td></td>
<td><img src="image2" alt="Benzo[a]Pyrene" /></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>80.2 / 218</td>
<td>No</td>
<td>Yes (U165)</td>
<td>Yes</td>
<td>Irritation to eyes, skin, respiratory tract, injury to cornea, headache, nausea, through inhalation or indigestion or skin absorption. Damage to liver, kidney, blood, and central nervous system.</td>
</tr>
<tr>
<td></td>
<td><img src="image3" alt="Naphthalene" /></td>
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Table B-5. Physical and Health Hazard Properties of PCBs.

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</thead>
<tbody>
<tr>
<td>Biphenyl</td>
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<td></td>
<td></td>
<td>PCBs are moderately toxic substances that have been found to cause cancers and to induce birth defects. Occupational exposures to PCBs exhibit a broad range of adverse health effects on the skin, eyes, mucous membranes, and digestive and neurological systems. The severity of the health hazard depends on the concentration and chlorine content of the PCBs. PCBs with higher chlorine contents are more toxic than are the lower ones.</td>
</tr>
<tr>
<td>2,2',6,6': ortho position</td>
<td>275 to 450</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>3,3',5,5': meta position</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4,4': para position</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(halogen atoms are attached to the biphenyl ring)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix C

Survey on Used Oil Markets and Current Recycle/Reuse Programs in Selected Countries

(1) State of California
(2) USA
(3) France
(4) Sweden
(5) United Kingdom
(6) Germany
(7) Mexico
(8) Brazil
(9) Japan
(10) New Zealand
(1) State of California

The data shown next page is from the report of the California Integrated Waste Management Board (Cal. IWMB, 1997). To account for oil consumed during usage, including leakage or combustion, the recycling rate must be adjusted first according to the estimation that 60 percent of all lubricating oils and 52% of industrial oils are generated as used oil. And after adjusting proportionate share of California oil recycled out of state, adjusted lubricating oil recycling rate is between 64% and 75%, and adjusted industrial oil recycling rate is only between 27% and 46%.

<table>
<thead>
<tr>
<th>Year</th>
<th>Lubricating Oil</th>
<th>Industrial Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sales</td>
<td>Recycled</td>
</tr>
<tr>
<td>1993</td>
<td>139.4</td>
<td>60.8</td>
</tr>
<tr>
<td>1994</td>
<td>141.9</td>
<td>59.1</td>
</tr>
<tr>
<td>1995</td>
<td>141.7</td>
<td>52.0</td>
</tr>
<tr>
<td>1996</td>
<td>136.2</td>
<td>54.3</td>
</tr>
<tr>
<td>1997 (Jan-Jun)</td>
<td>71.3</td>
<td>28.3</td>
</tr>
</tbody>
</table>

(unit: in millions of gallons)

(2) USA

In May of 1992, the United States Environmental Protection Administration (U.S. EPA) issued standards establishing a presumption that all used oil is to be recycled unless a used oil handler disposes of used oil or sends used oil for disposal. Specific requirements and exemptions are listed in 40 CFR Part 279. Currently most states have adopted the federal used oil management standards, though some states have made some reversions. Five states including California have adopted a more stringent approach to used oil management by defining used oil as a hazardous waste.

Estimated by U.S. EPA, about 1.5 billion gallons used oil is generated per year.

Of that total, 12 % recycled into high quality products

56 % burned

32 % disposed illegally
It is surprising to know that approximately only 12 percent are recycled into high
quality products while the rest is either burned (56 percent) as low-grade fuel primary for
space heaters, commercial and industrial boilers; or disposed illegally (32 percent) by
landfilling, burning, or dumping. Since the used oil that is burned is only minimally
cleaned, as a result, harmful metals and other contaminants in the used oil could be
released into our environment. Furthermore, burning used oil is not recycling used oil to
its highest and best value.

(3) France

France imposes a very active used motor oil management program in order to
conserve the nation’s oil supply and to protect the environment by recycle and reuse the
used oil. The used oil collection program in France is currently administered by Agence
de l’Environnement et de la Maîtrise de l’Energie (ADEME).

In 1990, a report by ADEME indicated that a total of 945,576 kilotons of oil is
sold annually in France (most recent data available) and more than half of this oil is for
automotive uses. The amount of used motor oil that has been collected for recycling or
reuse has increased from about 50 percent in 1990 to 78 percent in 1995. Used oil
treatment facilities in France are re-refining plants, combustion plants, reclaiming plants,
or reprocessing plants. Direct burning, combustion accounts for more than 50 percent of
used oil disposal. Re-refining of used oil then accounts for about 42 percent, while about
6 percent oil used oil is reclaimed. The most concern for the used oil management in
France is the toxic contaminants like PCBs, chlorine, and heavy metals in used oil.

(4) Sweden

There is no national used motor oil recycling program in Sweden, but used motor
oil is classified and managed as hazardous waste. Since no national collection system is
available to regulate the collection work, some gas stations offer environmental services
such as used oil and used battery collection. About 70 percent of used motor oil in
Sweden is collected and delivered to the cement industry to be used as fuel and
incinerated effectively under controlled conditions.
(5) United Kingdom

Total used oil production is 1 billion liters (≈ 264.20 million gallons) per year. Of that total, about 500 millions liters (≈132.10 million gallons) of the used oil are collected. And among the collected used oil, about 240 millions liters (≈ 63.41 million gallons) are recycled.

(6) Germany

Germany regulates the collection, transportation, and disposal of used oil. And it is remarkable that of the 690 kilotons of used motor oil produced annually (Feb. 1996 data); the government reported that 94 percent is collected and is either reprocessed (diesel, ship or gas oils) or burned (in cement kilns or as special waste).

(7) Mexico

A proposal for updated used oil management program in Mexico is currently under active development and will be soon reviewed and approved by Secretariat of Social Development (Secretaría de Desarrollo Social – SEDESOL). Used motor oil has been regulated as hazardous waste in Mexico since 1988. The hierarchy for the treatment of used oils and lubricants established in the rule is in the following order: (1) re-refining, (2) combustion, (3) incineration, and (4) confinement. In 1996, an estimated 300 million liters of used motor oil was generated in Mexico. But the information about the end uses of used oil remained uncertain.

(8) Brazil

Resolution Number 9, of August 31, 1993, is the national legislation on used motor oil recycling in Brazil. In the resolution, recycling is described as either recycling through regeneration or recycling through use. Discarding lubricant oils into the environment and the production/sale of unrecyclable new oil of both domestic and imported origin are prohibited. The law requires all used lubricant oil to be recycled. Recycle or reuse of used oil could be through re-refining, combustion for power
generation, or incineration. The gas stations (marketers) collect used oil and sell to the reprocessing companies, who then recycle the oil and sell it back to the marketers.

(9) Japan

Used oil recycling program in Japan is not at national level, nor major legislation is specifying the requirements for the management. However, though there are more than 40 million passenger cars and over 21 million trucks, buses, and other special purpose vehicles in Japan, almost no motor oil is changed by DIYers. Thus the collection and recycle percentage for used motor oil is very high.

<table>
<thead>
<tr>
<th></th>
<th>Collected</th>
<th>Recycled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lubricating oil [ton]</td>
<td>1,588,000</td>
<td>900,000</td>
</tr>
<tr>
<td>Cooking oil [kliter]</td>
<td>400,000</td>
<td>250,000</td>
</tr>
</tbody>
</table>

The percentages for the option of the collected used lubricating oil are as follow: 60.1% burned as fuel, 1.5% reprocessed for lubricating oil, 38.4% incinerated.

The end uses of the recycled cooking oil are soap, paint, feed, fertilizer, and fuel. Due to lack of DIY motor oil changers in Japan, it is expected that there is very little public awareness or knowledge about used motor oil issues. Also, the information about the contaminants in used oil is not reported publicly. The technologies for reclamation or recycle are comparatively low and can be improved. Most reclaimers are having business only at small-scale.

(10) New Zealand

Each year, between 60 and 70 million liters of lubricating oil is used in New Zealand and 40-60% of this amount is consumed during use. The rest, estimated about 30 million liters are generated annually as waste. Of this 30 million liters, 7 million liters of used oil are re-refined by Dominion Oil and sold in the marketplace as motor oil. The remaining 23 million liters are currently disposed of in ways that may be harmful to the environment.