CHAPTER 2

BACKGROUNDS AND LITERATURE REVIEW

2.1 Used Lubricating Oils

Lubricants are generally produced from base stocks refined from heavy fractions of crude oil or other hydrocarbons, into which various additives are blended. The components of lubricating oil are basic oil (crude oil or synthetic oil) and additives. Lubricants are used in a wide range of applications, including engine and transmission lubricants, hydraulic fluids, metal working fluids, insulating and process fluids and greases.

Part or all of the lubricant may be consumed during the process, which use these products. The balance tends to become contaminated with substances such as water, metal particles, rust, dirt, carbon and lead, and with other by-products of the combustion or the industrial process. The conditions and contaminants deteriorate the quality of the oil, and after some time it loses the ability as a lubricant and needs to be replaced. Generally, 70% of Lubricating Oil remain as waste or " Used Lubricating Oil, ULO". Characteristics and compositions of ULO varies based upon oil types, additives, generation sources, and collection methods [5-6].

ULO can be grouped into automotive and industrial sectors. Automotive lubricating oil includes engine oil, gear oil and break fluid. Industrial lubricating oil includes general use oil, special use oil, processing oil and Metalworking oil [6]. In Thailand, 68% of ULO is automotive where as 22 % is industrial [5]

2.2 Characteristics of ULO

The three most important aspects of ULO are contaminant content, energy value and hydrocarbon properties. Contamination of ULO makes it unsuitable for it original use due to the presence of contaminants or impurities or the loss of original properties. ULO contains hydrocarbons from additives and impurities due to physical contamination and chemical reactions occurring during its usage.

ULO contains various contaminants, depending on the nature of the process, such as heavy metals, by-products of thermal breakdown and substances associated with specific uses (lead, corrosion inhibitors). Examples are [6]:

- Used gasoline engine lubricating oil containing degraded additives, together with hazardous substances arising from combustion, particularly lead compounds and Polycyclic aromatics (PCAs)
- Used diesel engine lubricating oil containing PCAs and unburned fuel.
- Used metalworking fluids in either neat or emulsion form, which contain a wide range of additives including chlorinated paraffins.
- Used aviation lubes based on mineral oils containing PCAs and chlorinated solvents used in maintenance degreasing operation.
- Used transformer oil contaminated with Polychlorinated biphenyl (PCBs) and Polychlorinated terphenyl (PCTs) etc.

Polynuclear aromatics, halogenated organic and trace metals are compounds of potential concern in ULO. Several polynuclear aromatic hydrocarbon compounds are known carcinogens and mutagens such as PNAs and PCA, which are present in the petroleum base stock and can be produced during the use of the oil. Halogenated hydrocarbons may be produced in oil during normal usage cycles by the reaction of base-stack hydrocarbons halogenated compounds, typically inorganic chlorides from the additive package. Trace metals are introduced into the oil as part of the lubricating package or from external sources such as the wear of metal parts. Metals such as zinc, chromium, aluminium and barium are examples of contaminants that are introduced in this manner [7].

Table 2.1 summarizes the composition of hazardous materials in ULO using the following breakdown: mean, median (50th percentile), 75th and 90th percentile concentrations and range. Although ULO contains many hazardous components as described above, it also has other important properties, which might be of high value such as high flash point and remain energy content value.

Table 2.2 Physical properties of used lubricating oil [8].

Properties	No. of sample	Mean	Median	Range	
				Low	High
Flash Point	289	210	-	60	525
Viscosity, cSt @ 100 F° (37.78 C°)	70	71	47	1	513
API gravity, °API	48	28	27	13	80
Energy content, Btu/lb.	231	16,495	17,200	4,142	23,045
Bottom sediment and water, %	320	19	9	0	99
Water only, %	36	11	5	0	67

As shown in Table 2.2, the flash point of ULO ranges between 60-525 F° (15-274 C°) compared to virgin lubricating oil's of 100- 400 F° (37-204 C°); the lower value is probably due to the presence of high-ignitable chlorinated materials and organic solvents from engine blow. The energy content of ULO ranges between 4,142 and 23,045 Btu/lb., compared to virgin lube oil's of 20,000 Btu/lb [8].

Table 2.3 represent the composition of ULO varies considerably from of virgin lube oil and other virgin fuels. The similar properties of ULO compared with other fuel are specific gravity, flash point and pour point. Significant differences are observed with respect to ash, bottom sediment and water, and carbon contents, viscosity levels, as well as heavy metal concentrations

Table 2.1 Concentration of potential hazardous constituents in Used Lubricating Oil [8]

Contaminant	Total sample	Sample with detected contaminants		Mean Conc. (ppm)	Median Conc. (ppm)	Conc. at 75th percentile (ppm)	Conc. at 90th percentile (ppm)	Concentration range (ppm)	
		Number	%					Low	High
Metals									
Arsenic	537	135	25	17.26	5	5	18	< 0.01	100
Barium	752	675	89	131.92	48	120	251	0	3,906
Cadmium	744	271	36	3.11	3	8	10	0	57
Chromium	756	592	78	27.97	6.5	12	35	0	690
Lead	835	760	91	664.50	240	740	1200	0	21,700
Zinc	810	799	98	580.28	480	872	1130	< 0.5	8,610
Chlorinated Solvents									
Dichlorodifluoromethane	87	51	58	373.27	20	160	640	< 1	2,200
Trichlorotrifluoroethane	28	17	60	62,935.88	160	1,300	100,000	< 20	550,000
1,1,1-Trichloroethane	616	388	62	2,800.41	200	1,300	3,500	< 1	110,000
Trichloroethylene	608	259	42	1,387.63	100	200	800	< 1	40,000
Tetrachloroethylene	599	352	58	1,420.89	106	600	1,600	< 1	32,000
Total Chlorine	590	568	96	4,995	1,600	4,000	9,500	40	86,700
Other Organic									
Benzene	236	118	50	961.20	20	110	300	< 1	55,000
Toluene	242	198	81	2,200.48	380	1,400	4,500	< 1	55,000
Xylene	235	194	82	3,385.54	550	1,400	3,200	< 1	139,000
Benz(a)anthracene	27	20	74	71.30	12	30	40	< 5	660
Benzo(a)pyrene	65	38	58	24.55	10	12	16	< 1	405
Naphthalene	25	25	100	475.20	330	560	800	110	1,400
PCBs	753	142	18	108.51	5	15	50	0	3,800

Table 2.3 Properties of various oils and fuels [8].

Property	Fuel				
	ULO	Virgin lube	No.2 Fuel	No.6 Fuel	Coal
Physical Properties					
Specific gravity	0.91	0.882	0.836	0.979	-
Viscosity, SUS at 37.78 C°	324	-	36	-	-
Bottom sediment and water, % vol	12.3	0	0	1.0	-
Carbon residue, % wt	3.0	0.82	-	-	-
Ash, % wt	1.3	0.94	0.002	0.25	10.5
Flash point, C°	175	-	165	210	-
Pour point, C°	37	- 37	-20	40	-
Chemical Properties					
Saponification No.	12.7	3.94	-	-	-
Total acid No.	4.4	2.2	-	-	-
Total base No.	1.7	4.7	-	-	-
Nitrogen, % wt	0.428	0.05	-	-	-
Sulfur, % wt	0.42	0.32	0.30	2.15	3.0
Heavy metal contaminated, ppm					
Lead	7,535	0	0	2.9	71
Calcium	1,468	1,210	-	48	15,536
Zinc	1,097	1,664	-	-	123
Phosphorus	931	1,397	-	-	32
Magnesium	309	675	-	14	2,723
Barium	297	37	-	-	258
Iron	205	3	-	120	14,466
Sodium	118	4	-	241	469
Potassium	31	<1	-	-	-
Copper	29	0	-	0.5	64
Silicon	24	4	-	-	24,160
Chromium	15	0	-	13.7	24
Tin	13	0	-	-	276
Manganese	4	0	-	-	101
Molybdenum	-	-	-	2.3	16
Titanium	-	-	-	5.5	1,889
Vanadium	-	-	-	-	30

Characteristic of ULO in Thailand from the Guideline of Collecting Used Lubricating Oil Pilot Project represented in Table 2.4 [9].

Table 2.4 Characteristic of ULO in the Guideline for Collecting Used Lubricating Oil Pilot Project, Thailand [9].

Parameter	No. sample	Minimum	Maximum	Average
Flash point, C	35	126	265	227.6
Viscosity @ 50 C, cst.	35	46.34	182.11	83
Insoluble, %wt				
Pentane	35	0.04	75	7.65
Toluene	35	0.02	2,989	572
Water, % vol	30	0.1	2.7	0.52
Ash, %wt	5	0.11	1.35	0.75
Heating value, Kcal./Kg.	35	10,530	10,771	10646
Heavy metal, ppm				
Aluminum	35	2	46	12.74
Calcium	35	27	3796	1143
Copper	35	2	1194	190.46
Iron	35	12	1055	313
Magnesium	35	2	1055	261
Phosphorus	35	147	1121	805
Lead	35	0.05	24	3.82
Zinc	35	0.01	1158	538.17

Remark: Flash point; ASTM D 92, Kinematics Viscosity; ASTM 445, Water content; ASTM D95, Heating Value; ASTM 240, Insoluble; ASTM D 893-A, and Heavy metal; ICP-SCAN

2.3 Technology Options for Managing Used Lubricating Oils

The management of ULO is of particular importance due to their threat to the environment. The problem becomes serious as ULO is currently produced from various sources in large quantities, and they are not always handled properly. However, it is known that ULO has an inherent value and can be employed as an excellent source of energy. This has stirred worldwide research interests in the search of technologies for the recovery of valuable components from the ULO. These ULO managing technologies can generally be classified into two approaches, regeneration and recovery as fuel or as valuable products.

This section will provide a rough introduction to each of these technologies.

2.2.1 Regeneration

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

The most popular method for regeneration of ULO is re-refining which are advanced and complicated technology proven to be effective. The best feature of this technique is that ULO can be re-refined repeatedly. Normally, the conventional re-refining ULO process consists of 5 stages according to Table 3.1

Table 2.5 Conventional stage purpose of re-refining ULO

Stage purpose	Processes
1. Coarse removal of water and foreign solids	Sedimentation, Centrifugation
2. Removal of low-boiling fractions and residue water	Heating, Atmospheric distillation, Gas oil stripping
3. Removal of oxidation products, additives and ULO contaminate substances.	Sulfuric-acid treatment, Solvent extraction, Propane extraction, vacuum distillation or Wipe-film evaporation, Hydrotreatment, Chemical treatment, etc.
4. Separation of product and residue	Decanting, Filtration
5. Treatment of the by products and stabilization of the fractions	Treatment with bleaching clay, Hydrofinishing

The main stage which lead to be various technologies is the step to remove oxidation products, additives and contaminate substances. As shown in Table 3.1, there are many processes e.g. acid clay treatment, solvent extraction, propane extraction, vacuum distillation, hydrotreatment etc. In addition one process might not be enough in order to obtain the good quality product. Consequently, combinations of many processes are provided

A traditional re-refining ULO is an acid-clay process. This process is simple to design and operate. The principle of the process is the removal water from the waste oil before mixing with strong sulfuric acid (98%) to extract impurities and additives and acidic tar settles. The slightly acidic oil that remains is mixed with active clay to adsorb additional contaminants and to improve color. The oil is finally neutralized and distilled. The spent clay is separated from the bottom by filtration. It yields 45-75% of the feed oil. This process generates a clean oil which can be reused as a lubricant again. However, the acid sludge and spent clay from the process contains sulfuric acid combustion products, lead, organomatellic sultanates, etc. This causes a disposal problem because these waste products are toxic and must be handled as a hazardous waste. Besides, using clay contact as a finishing step still leaves high polychlorobiphenyls (PCB's) content in the ULO [8].

Over the years, several processes and technologies have been under development to meet the challenge of the traditional acid clay treatment. The new re-refining processes usually consist of three major steps; removal of water and light hydrocarbon compounds, removal of contaminants and additives, and finishing or polishing the products. The alternative technologies listed below are some modern re-refining processes [10]:

- Propane extraction/hydrotreatment (Institut Francais du Petrole: IFP, Snamprogretti)
- Demetallize with diammonium phosphate/filter/hydrotreatment (Phillips re-refined oil process, PROP)
- Solvent extraction/hydrotreatment (Bartlesville Energy Research Center, BERC)
- Metallic sodium treat/ vacuum distillation (Recyclon, Leybold Heraeus)
- Thin film vacuum distilltion/hydrotreatment (Kinetics Technology Inc., KTI)
- Thermal deasphaltining/ vacuum distillation (Viscolube-TDA)
- Pretreat/thin film vacuum distillation/ hydrotreatment (Mohawk, Evergreen, and Safety Kleen)

- Propane extraction/clay treatment (Interline) (a solvent is 25% isopropylalcohol, 25% methylethylketone, 50% n-butyl alcohol; BERC is Bartlesville Energy Research Center, part of US Dept. Of Energy)

Moreover, some reprocessing methods involve a treatment to separate solids and water, and to remove insoluble contaminants and oxidation products from ULO. These methods involve the following steps: heating, settling, filtering, dehydrating and centrifuging. Depending on the quality of the resulting material, these techniques can be followed by blending with reprocessed oil and additives to return original properties.

2.2.2 Recovery as fuel or valuable product

The inherent high-energy content of ULO and hydrocarbon properties, which illustrate in Table 2.2 may encourage their use as fuels or processing to other valuable petroleum products such as coke and gas lubricant feedstock. Consequently this approach is very favor one. From the data collection, direct burning, reprocessing in primary refinery and pyrolysis have found.

- Direct burning for heat

Direct burning means burning ULO without pretreatment/processing to remove contaminants such as water, solid particles, and heavy metals. Examples of unit operations that can accommodate the burning of ULO include space heaters, boilers, and industrial furnaces.

In most space heater designs, a low-pressure atomizing nozzle introduces oil into a burning chamber in which the oil is mixed with compressed air and burned. The performance of emission from space heaters depend on the frequency of maintenance, composition of ULO, height of the stack, and furnace settings that define the air-to-fuel ratio, oil droplet size, and flame temperature [7].

- Reclaiming fuel/Fuel Blend

In the UK, recovery as fuel is much simpler and cheaper than other methods. ULO is heated, treated with demulsifiers to counteract the emulsifiers which keep solids in suspension during use, solids are removed by settling, and the oil is filtered. The resultant oil is blended to achieve the required specification for a fuel or fuel extender. This has been widely applied around the world, in particular in cement kilns, asphalt plants, utility boilers, pulp and paper mills [10-11].

- Reprocessing in a primary refinery to produce petroleum products / Slipstreaming

This process uses reprocessed ULO (or sometimes not reprocessed) as feedstock in refineries with crude oils to produce virgin lube oil. With slipstreaming, used oil (approximately 1% of the feedstock material) is mixed with the virgin oil, and fed into the refining process which will remove contaminants in the ULO [11]. However, many refineries have not pursued this option because they are concerned about used oil contaminants, which have the potential to deactivate expensive refining catalysts. Literature search revealed that there were only 2 companies (Llondell and Texaco) who had successfully processed ULO in petroleum cokes [7].

- Pyrolysis to valuable products

Pyrolysis of ULO can produce valuable chemicals such as BTX, light olefins (ethylene and propylene), and light aromatics. The quality of the pyrolysis products varies significantly with the operating temperature and pressure. Location can sometimes play an important role in the decision about the optimal conditions for pyrolysis. For instance, if pyrolysis is carried out near a refinery, the pyrolysis products can be easily added to the refinery feedstocks. In this case, the production of light olefin is more favored and the best results are obtained at a temperature of 650°C and a pressure around 0.1 MPa. However, if the installation is independent, a so-called "hybrid" method is preferred where alkanes or BTX productions are the end products. This pyrolysis would then have to be operated at high temperature and pressure [12].

The co-pyrolysis of a ULO and coals has been reported. The co-utilization of coal and waste materials is nowadays a very powerful technology employed as a way of eliminating waste materials and producing at the same time valuable products for industry. Pyrolysis of coal is a good method for producing chemicals such as BTX and light olefins, but the yields of these products are limited because of the low hydrogen-to-carbon ratio in coal. For this reason, it is necessary to supply H_2 from other sources in order to improve the process performance, which renders ULO suitable for this technique [13].

Other options:

Some might directly reuse the ULO in "inappropriate" applications such as livestock oiling, oiling of equipment surface, weed killing, and road oiling etc However, this option is not recommended as it might have an uncontrolled pathway whereby the pollutants can use to contaminate the environment.

Disposal is undesirable and should be considered as a last resort for cases where ULO is highly contaminated and not cost-effective for collection, transportation and recycling. The recommended disposal options are the generally approved methods for the treatment of hazardous wastes or incineration, with solidification of the residual followed by disposal in a secure landfill [7].

2.4 Environmental Impacts

An environmental impact can be defined as a change in one or more of various socioeconomic and biophysical characteristics of the environment. Environmental assessment is, therefore, an evaluation of the probable changes, which may result from a proposed or impending action [14] This term is also used to imply the systematic identification and evaluation of the potential impacts (effects) of proposed projects, plans, programs or legislative actions relative to the physical-chemical, biological, cultural and socioeconomic component of the total environment, which is also commonly know as Environmental Impact Assessment (EIA). However, the scope of work for EIA is usually broader than the true meaning of environmental assessment as it includes as well the consideration of measures to mitigate undesirable impacts. The primary purpose of environmental impact assessment is to encourage consideration of the environment in planing and decision-making and ultimately to arrive at actions that are more environmentally compatible [15-16].

It is desirable to quantify impacts wherever possible. This may be accomplished through the use of instrumentation, data acquisition, and application of model or other quantification technique. There are specific numerical standards or criteria that can be used as a basis for impact interpretation [14-16]

2.5 Economic Analysis

In order to decide on alternative project or investment for the management of ULO, the important factor that must be evaluated is economic feasibility [17]. The proper application of economic principles to environmental problems is essential in order to identify and implement the most cost effectiveness solution. In this study *cost effectiveness analysis* will be employed as an economical tool for this purpose. Further detail for this analysis can be found elsewhere [18-20]. Fundamentally, the analysis will estimate and compare the performances of different alternatives in terms of some common indicators, such as average present unit cost of treatment ULO, average present unit cost of product and Revenue per cost.

2.6 Literature review

The management of ULO has been varied from time to time and from country to country. All countries around the world show the same trend or development by using develops countries such as the USA and Europe as models.

Muller Associates, Inc. [8] describe and assess the waste oil reclaiming technology. The assessment encompasses all aspects of technologies including the oil's generation, collection utilization and disposal. Examination the sources, properties and availability of waste oil as well as evaluates the collection and utilization infrastructure in terms of energy and environmental considerations, economic viability and regulatory constraints.

Graziano, D.J. and Daniels [7] conducted a study to identify and assess opportunities for the recovery and recycling of waste oils. The emphasis of the study was on establishing a consistent methodology that can be used to prioritize reduction, reuse, recycling and disposal options for waste oil on the basis of energy, environment, and economic impacts. This research reflects these priorities: 1.) Increase the availability and effectiveness of collection programs for do-it-yourself and off-road, used-oil generators, 2.) Reduce the volume of lubricating oil consumed or unrecovered and 3.) Increase the volume of re-refined oil manufactured and sold. For the third option, development of technologies for integrating re-refining into existing lubricating oil refineries is proposed.

Bill Wilson [9] defines the four main routes for reclaiming used oils recovery as fuel, reconditioning on site, oil laundering and re-refining. Places used oil re-refining in its historical context and present profiles of the two used oil re-refiners in UK, Orcol and Interline. The details of the Orcol are confidential but include dehydration and thin film vacuum distillation followed by molecular filtration. For the Interline operates a patented solvent extraction refining process.

Pyziak and Brinkman of Safety-kleen Corporation [21] rated used oil disposition techniques from the most improper to most of effective, are as follows: indiscriminate dumping, landfilling, road oiling and foliage control, burning for energy recovery, reclaiming and several types of re-refining processes such as introduction of waste oil into crude oil refining streams, acid/clay process and thin film evaporation. Heavy metals, chlorinated solvents and fused-ring combustion by products (e.g. PNAs) created used oil as a hazardous waste. When selecting a facility to process used oil, it is important to consider more than current cost. In the long run, it should be select the facility, which is financially stable, environmentally sound, and operationally clean should be selected

Ali, Farhat Mohammad and et al.[22] studied the secondary use of used automotive lubricating oils. The process technology of Meinken and Mohawk was selected for techno-economic evaluation. A plant size of 50000 TPA waste oil re-refining was chosen for economic study of these processes. The estimated production cost for the Meinken process was found to be $348.8 per ton and for the Mohawk process, assuming hydrogen supply to be made available from adjacent refinery, it was estimated to be $198.4 per ton. The Meinken process appears to be more popular but profitability was found to be lower than Mohawk. The Mohawk process is process is limited due to the location factor which requires hydrogen from an adjacent petrochemical plant.

In Thailand, United Nation Industrial Development Organization (UNIDO) [4] has studied the feasibility of Re-refining used lubricating oil. The conclusion from experience in industrialized countries found that production average for small re-refining is 15,000 ton/year and can save more than 60 million $ over 15 years of operation time. The brief results are shown as follows:

Pay back period	<	6 year
Internal Rate of Return		18 %
Benefit cost ratio		22 %

Pracha Nichapanuit [3] has studied a waste oil collection systems in Thailand : A case study in Bangkok Metropolitan Areas (BMP). It is also estimated that about 85 % of all ULO generated in BMP is collected for reuse and recycling, including 40% for burning, 30% for re-refining, 10% as a stripping mold agent, 5% for other uses. The remaining is suspected to be worst or dumped. Recommended utilization and disposal methods of ULO, ranked from best to worst in the case of BMA, are re-refining, energy recovery, transformation to refinery feedstock, and reconditioning of ULO.

Chanpen khumkeaw [4] studied situation and problems of used lubricating oil in Thailand. The result of this work shown that 50 percentage of lubricating oil used was turned into used lubricating oil. The collection system as well as treatment technologies currently used are not technical viable. The data from questionnaires in the industrial section, demonstrate that 78% of the factories studied had collection system for ULO, most of which commingle collected. Only 30.5 percentage collected with oil type. The utilization of ULO collected, in over all pictures, it can be sold off, used as fuel or use for other proposes, which percentages distribution of 54.9, 26.8 and 18.3 respectively. From this study it is suggested that there are 2 suitable ways to reuse the ULO. Firstly, re-refinery is recommended as it causes less environmental impact as well as reverses natural resources. The second method recommended is to use it as fuel in Cement kiln.

Rewadee Chuaykul [23] utilized the waste lubricating oil by mixing with wastewater sludge and burned the mixture in a fluidized bed in incinerator. The experiments used the ratio of lubricating oil and sludge waste at 1:5, 2:5 and 3:5, percent by weight. The flow rate of air was kept constant at 152.64 m^3/hr. The carbon and hydrogen contents in wastewater sludge were 44.64 and 11.21 %, respectively. A suitable ratio of air and fuel mixture were 6.3-7.4, 8-9.4 and 9.2-10.9 at the lubricating oil and sludge waste ratio 1:5, 2:5 and 3:5, respectively. The quantities of gaseous pollutants in the flue gas were lower than the emission standard of Pollution Control Department. In addition, the available heat in the flue gas was calculated to be 1402, 1765 and 1890 kJ/kg of the mixture at 1:5, 2:5 and 3:5, respectively.