



Chapter II

Literature Review

A re-refining process is described as a process that effectively removes contaminants from used lubricating oil and returns the oil to a quality equivalent to oils produced from virgin stocks. Re-refining of used lubricating oil has existed as an industry since the late 1920's. A traditional re-refining process is acid-clay process (Figure 2.1). In acid-clay process, after water is removed, waste oil is contacted with strong sulfuric acid (98%) which extracts impurities and additives and forms an acidic tar that settles out. The slightly acidic oil that remains is mixed with active fuller's earth (a clay) to adsorb additional contaminants and to improve color. The oil is finally neutralized and distilled. The re-refined product is removed as overheads and the spent clay is separated from the bottoms by filtration.

Several problems were generated by this process. The sludge which was separated from the process contained sulfuric acid, combustion product, lead, organometallic sulfonates, etc. If the acid sludge was burnt, high concentration of sulfur oxides and fine metals would be emitted to environment. Beside the acid sludge, spent clay which produced by the process was basic. It consisted of polar compound such as organic compounds containing oxygen and nitrogen. Therefore, both acidic tar and spent clay posed disposal problem. In addition,

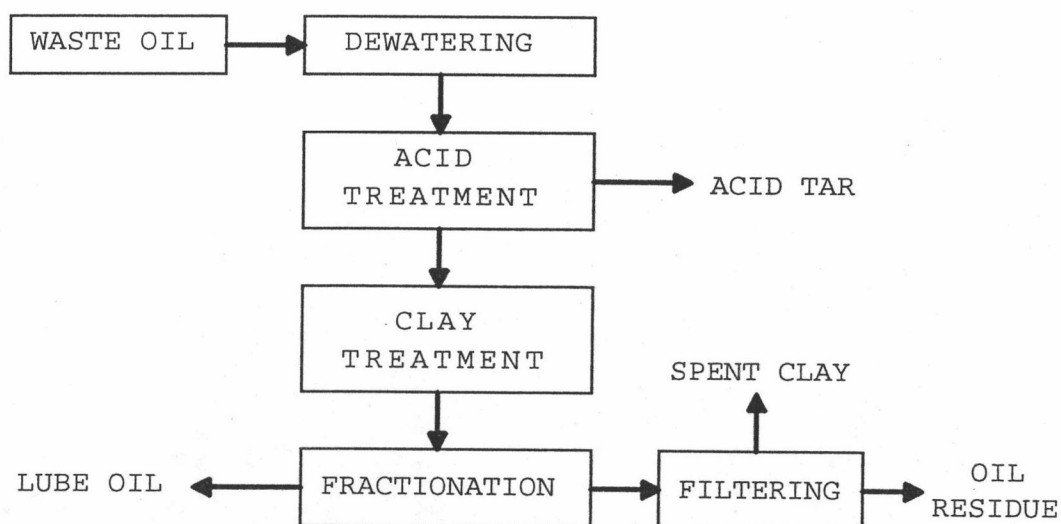


Figure 2.1 Acid-Clay Process

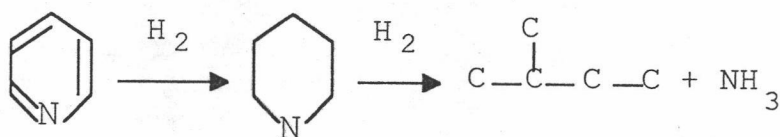
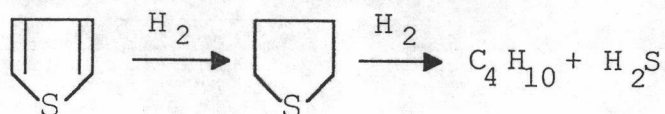
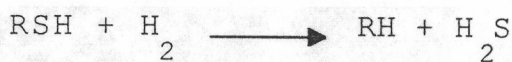
a desirable fraction of the oil was lost with the discharged residues. Today, automobile oils have a large number of additives, so more acid and more clay than ever are required to treat the used oil.

Several processes that have been under development for sometime seem ready to challenge the traditional acid-clay treatment technique. Details of new re-refining processes are described elsewhere (Whisman et al., 1978; David, 1978; Berry, 1979; Berry, 1981; Short et al., 1987; Brinkman, 1987; Mueller Associates, Inc., 1989). 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 product. Removal of water and light hydrocarbon usually uses flash distillation at temperature above 150°C (302°F). Removal of contaminants could be conducted via many methods such

as atmospheric distillation, vacuum distillation, evaporation, and reaction with chemicals. Both clay contacting and hydrofinishing have been used successfully in the finishing step to attain color and odor improvement. However, several processes that used clay contacting as finishing step still had high polychlorobiphenyls (PCB's) content (Muellur Associates, Inc., 1989). PCB's passed through clay contacting process with lube oil fraction and seriously damaged handling and marketing of re-refined oil (Brinkman, 1987). On the other hand, the processes which used hydrotreating could accept the used oil which contained PCB's (Muellur Associates, Inc., 1989). It was confirmed by O'Connell and Wozniak (1986) who patented a process which was used to remove halogenated polyphenyl compounds, especially polychlorinated biphenyls (PCB's) from used lubricating oil. In their study, the oil was subjected to mild catalytic hydrotreating after stream stripping and vacuum distillation. Then it was hydrotreated over NiMo catalyst at pressures of 4.48-5.71 MPa (650-750 psi), temperatures of 260-290°C and hydrogen flow rate of 1.13 kmol/m³ of oil stock (150 ft³/barrel). They reported that PCB content in the product was decreased from 50 ppm to less than 1 ppm. In addition, most hazardous materials were reportedly converted to relatively harmless substances during catalytic hydrotreating reaction (Surprenant and Fenelly, 1983).

Hydrotreatment

Hydrotreatment (hydrotreating or hydrofinishing) is a process commonly used in most modern oil refining operation (Satterfield, 1980). It is a process for stabilization of petroleum products and/or remove sulfur, nitrogen, oxygen, halides and metallic compounds from products or feedstocks by reaction with hydrogen on catalysts. It is employed in industry for one of the following reason: (1) to improve the quality of the downstream product, (2) to protect and improve the performance of catalyst used in downstream operations, (3) to reduce the sulfur content of the feed to meet environmental restriction, and (4) to improve the stability of the product. Hydrotreatment consists of several classes of reactions which occur simultaneously: hydrogenation, hydrodesulfurization (HDS), hydrodeoxygenation (HDO), hydrodenitrogenation (HDN) and hydrodemetallization. Some typical reactions taking place in hydrotreaters are shown below (Oblad et al., 1982):



The catalysts commonly used in hydrotreatment are Mo and W on alumina support. Ni and Co are also used as promoters to improve catalyst activities. The most common catalyst is CoMo oxides on alumina. Other catalysts, NiMo and NiW on alumina oxides, may also be used. Generally, these catalysts are converted to the sulfided form using some sources of hydrogen sulfide before use and a minimum concentration of hydrogen sulfide must be present in the reactor environment to maintain the catalyst in sulfided form. Hydrotreating is carried out in fixed bed reactors. Typical operating conditions employed are temperatures of 300 to 400°C, pressures of 2.03 to 4.05 MPa (20 to 40 atm) and liquid hourly space velocities of 1 to 5 hr⁻¹. A hydrogen/hydrocarbon mole ratio as high as 10 is used. Phases of operation may be vapor, liquid, or mixed.

Hydrotreating of used lubricating oil

Hydrotreating of used lubricating oil was first patented by Somogyi et al. (1967). The objective of their process was to improve recovery of used lubricating oil and to provide a regenerating process which made it possible to utilize the changed components. The used oil was subjected to treatment with sulfuric acid and followed by catalytic hydrotreating at a pressure of 4.05 MPa (40 atm), a temperature of 360°C, a liquid space velocity of 0.5 hr⁻¹ and a gas-to-liquid ratio of 0.1 Nm³/m³ in the presence of a sulfided hydrofining catalyst. The catalyst was nickel oxide and molybdenum trioxide on alumina support. They reported that their product had suitable viscosity, viscosity index, pour point, flash point, color and odor. The oxidation stability of the

product was better than the product which obtained by conventional method (acid-clay process).

However, the process which was patented by Somogyi et al. (1967) still produced acid sludge. Realizing that a more efficient re-refining process which produced minimum sludge and increased yields was demanded, Brownawell et al. (1972) proposed and patented a new re-refining process which removed contaminants and additives by solvent extraction and polished oil product by hydrotreating. They said that the reclaiming of used lubricating oils could be greatly improved if the used oil was first subjected to precipitation in an oxygenated polar liquid. The oxygenated compound which was used in their process was a mixture of normal butanol and pentane. After treated with solvent, the properties of the feedstock were a viscosity at 37.8°C (100°F) of 66.3 cSt., a viscosity index of 122 and an ASTM color of D8.0. A solvent-extracted oil was subjected to hydrotreating over Harshaw Ni-0104T, a nickel hydrotreating catalyst in a high pressure cell. Each experiment was conducted for 18 hours at a temperature of 300°C, pressures of 10.3 and 13.8 MPa (1500 and 2000 psig), catalyst to oil weight ratio of 1:4. The resulting re-refined oil had acceptable qualities that could be compared with 150 (31.9 cSt) and 200 SUS (43 cSt) viscosity. After hydrotreating, they found that the viscosity and the ASTM color decreased. At lower and higher temperature (200, 250 and 350°C), product oils which had higher ASTM color were produced.

After Brownawell et al. (1972)'s work, a more effective solvent process which provided high percentages of recovery and maintained the natural lubricity and

other desirable qualities of the base oil was patented by Whisman et al. (1978). Water and low-boiling contaminants were stripped from the used oils by vacuum distillation and dissolved in a solvent mixture of 1-butanol, 2-propanol and methylethyl ketone in a 2:1:1 ratio, by volume. The oil-solvent mixture was separated and the solvent was recovered. The separated oil was distilled and hydrotreated to effect odor and color improvement of the distilled oil. Typical conditions of hydrotreating included an operating temperature of 316°C (600°F), a hydrogen partial pressure of 4.48 MPa (650 psig), a space velocity of 1.0 hr⁻¹, and a hydrogen flow rate of 11.28 kmol/m³ (1500 SCFB). Typical catalysts were cobalt molybdate and nickel molybdate on alumina support. A viscosity of finished product at 38°C (100°F) was 35.33 cSt and a viscosity index was 99.8.

After several years of development work, The Bartlesville Energy Technology Center Solvent Extraction Process, a similar process was proposed by United State Department of Energy (DOE). Three volumes of solvent were needed for each volume of used oil. Dewatered, fuel-stripped oil was mixed with solvent in an inline mixer. The resulting sludge was separated from the oil-solvent mixture in enclosed (to prevent solvent loss) vertical solid-bowl centrifuges. The solvent was recovered in an atmospheric distillation column. Vacuum distillation of the treated oil was at 6.70×10^{-4} MPa (5 mmHg absolute) to minimize cracking. Blending-stock lube was the major product of vacuum distillation. Finishing could be accomplished by clay contacting or hydrotreating. For hydrotreating, the lube was heated to 316-343°C (600-650°F) and pumped into the top of a low-alloy-steel vessel. Nickel/cobalt catalyst was

required. Lube was flashed in two stages down to 0.69 MPa (100 psi), cooled, filtered and stored. The yield was 71% by volume.

Over the year, many firms had studied the use of propane as solvent. The first commercial propane extraction process was developed by the Institut Francais du Petrole (IFP). The used oil was first distilled to remove water and light hydrocarbon compounds. The oil was mixed with propane to selectively extract base lube oil from the used oil. The oil-mixture was sent to separation step where propane was separated from the mixture. After this step, the oil suffered an acid-clay treatment and filtration. Another propane extraction process, Snamprogetti, was similar to the IFP process but Snamprogetti process used two solvent-extraction stages, with a vacuum-fraction step in between.

Cutler et al. (1975) proposed a PVH (Propane-Vacuum-Hydrogen) process which required propane two to three times less than the conventional propane process (David, 1978). After passing through propane extraction and distillation, the lube oil cut was hydrotreated in a pressure vessel over Houdry HR-801 cobalt-molybdenum catalyst, 25% sulfided at a temperature of 343°C (650°F), a pressure of 4.48 MPa (650 psig) and a liquid space velocity of 1.0 hr⁻¹. They reported that hydrotreating removed impurities by chemically transforming into hydrocarbons having molecular weights equal to or less than oil, plus H₂S, H₂O, and NH₃. Impurities which were removed in this step consisted of low molecular weight additives, additive fragments, and oil oxidation products. A viscosity of the oil at 38°C (100°F) decreased from 68.75 cSt (319 SUS) to 36.33 cSt

(170 SUS). A viscosity index of the oil decreased from 141 to 101. A total acid number (TAN by ASTM D664) decreased from 5.80 to 0.06 mgKOH/g. ASTM color improved from D8.0 (black) to 1.5 and flash point increased from 182 to 229°C (360 to 445°F). The product oil was equal to or better than virgin lube oil in quality.

Another method to remove contaminants and additives was a reaction with chemicals. Nowack et al. (1979) from Phillips Petroleum Company patented a process which an aqueous ammonium salt treating agent such as ammonium sulfate, ammonium bisulfate, ammonium phosphate, diammonium phosphate, etc., was used as chemical substance. The pretreated oil was hydrotreated by contacting the oil with hydrogen on a hydrotreating catalyst at a temperature of 360°C, a pressure of 4.93 MPa (715 psig), and a hydrogen gas to oil ratio of 222 vol/vol oil. It was reported that hydrotreating removed unwanted compounds and unsaturated materials and decomposed residual sulfur, oxygen and nitrogen groups to yield an oil product suitable for further purification to a lube stock. Suitable catalysts were selected from group of catalysts which were used in conventional hydrodesulfurization process.

A two stage process, namely Phillips Re-refined Oil Process (PROP), which involved chemical demetallization and followed by hydrotreating as a finishing step was proposed by Phillips Petroleum Company. An aqueous solution of diammonium phosphate (DAP) was mixed with heated used oil and through a series of reactions, conducted at temperatures and pressures not exceeding 149°C (300°F) and 0.14 MPa (20 psig), metallic phosphates were formed. The metallic phosphates

precipitated and were filtered out. During the reaction, water and light ends were taken off as overheads.

The remaining oil was heated, mixed with hydrogen, percolated through a bed of clay (to remove trace inorganics) and passed over nickel-molybdate catalyst. This hydrotreating removed sulfur, nitrogen, oxygen and chlorine compounds and improved color. After hydrotreating, the oil was flashed, cooled, and subjected to a final stripping step to remove any remaining fuel from the lubricating oil. Phillips claimed that the process recovers over 90% of the waste oil.

A PROP process that was reviewed by Linnard and Henton (1979) showed that the viscosity of the oil decreased from 104 to 75.5 cSt. Sulfur content decreased from 0.44 to 0.04 wt%. ASTM color decreased from D8.0 to 3.5. Viscosity index was 104. They concluded that the basic product was a high quality base oil and suitable for marketing. The physical properties of the re-refined oil such as viscosity, viscosity index, pour point and paraffinicity were essentially the same as the 'virgin' base stock. In their review, the used oils were taken from different sources in the United State.

Kinetics Technology International, B.V. Process (KTI) used atmospheric distillation to remove water and gasoline and vacuum distillation to produce an overhead product in the lube oil range and heavy residue containing metals, polymerization products and asphaltenes.

Gulf's refinishing process was utilized to improve the color and odor of the overheads. The lube

oil was mixed with a hydrogen-rich gas, heated and passed through a reactor holding a fixed catalyst-bed. A product with the right specifications was obtained by stripping the treated oil with steam (any remaining light ends were removed) or fractionation it into different lube cuts and then dried in a vacuum column. Lube oil yield for a European spent-oil feed averaged 82% on dry basis. KTI stated that product specifications could be varied by changing hydrofinishing operating conditions (David, 1979; Berry, 1979; Short, 1987; Mueller Associates, Inc., 1989).

Falconer et al. (1986) from the Mohawk Oil used similar technology but a vacuum distillation unit in their process utilized two series connected wiped film evaporators. The hydrofinishing unit was operated at 370°C and 4.8 MPa over a metallic catalyst in the liquid phase. This unit was used to upgrade the color of the oil. Hydrofinishing also reduced the sulfur and nitrogen compounds contained in the oil and guaranteed that no heavy metal elements were present in the final product. They reported that the final product was a high-quality base lube oil and the finish base oil made by the re-refinery at Mohawk was blended into a wide range of specification engine oils, hydraulic oils and industrial oils.

A process which used a similar process to the KTI process and the Mohawk oil process was patented by Mead et al. (1984). After vacuum distillation, the overhead was hydrogenated over catalyst at pressure of 1.62 to 2.65 MPa (235 to 385 psig), temperatures of 252°C to 371°C (450 to 700°F), and liquid hourly space velocities of 0.6 to 1.5 hr⁻¹, to produce a lubricating base stock of ASTM

color less than 3.0. Their result showed a major products as a lubricating oil base stock suitable for blending. The bottoms residue was mixed with limestone and passed vacuum pyrolyzing to produce fuel oil.

Reid et al. (1985) patented a re-refining process which used many steps to remove contaminants and additives and used hydrotreating as the final step. The properties of process feedstock were a viscosity at 40°C of 50.4 cSt, a sulfur content of 0.39 wt%. After dewatering, defueling, heat soaking, wiped film evaporator distillation and alumina treating, the viscosity, viscosity index, sulfur content and ASTM color of the oil were 30.71 cSt., 98, 0.23 wt% and D8.0, respectively. The treated oil was hydrotreated over a conventional NiMo catalyst (CoMo catalyst can also be used). Temperatures of 260-300°C, hydrogen pressures of 3-5 MPa, liquid space velocities of 0.5-2.0 hr⁻¹ and hydrogen gas rates of 1.5-5.0 kmol/m³ were used. Two hydrotreating experiments was shown as example in their work. The temperatures and pressures were in the range of 284°C to 290°C and 3.5 to 5.6 MPa. A liquid space velocity of 1.0 hr⁻¹ and a gas flow rate of 7.5 kmol/m³ were used. The viscosity of liquid product decreased from 30.71 to 29.50 cSt. The sulfur contents decreased from 0.23 to 0.10 wt%. The ASTM colors decreased from D8 to L1.0. They said that a result of the improvements on the hydrofiner feedstock quality due to the previously recited processing steps, smooth hydrofiner operations and good quality base oils are secured. Their experiment was conducted for 1500 hours with no noticeable catalyst (NiMo) deactivation. Base oil target in their process was a 10 grade oil and the results indicated that the re-refined (280-300°C) oil closely matched the virgin base

oil in physical properties and chemical properties. Even though, they did not conclude that the pressure did not affect the hydrotreating performance but their result showed that the increasing operating pressure, the properties of resulted oils were not changed.

Khaltaeve et al. (1976) studied the hydrogenation of an asphalt-free lubricating oil at 400°C, 4.05 MPa (40 atm), liquid space velocity 1.5 hr⁻¹ in the presence of a catalyst. After hydrotreating, they reported that a viscosity index of the oil increased from 55 to 104 and 65 wt% of sulfur was removed.

Available research works on hydrotreating of used lubricating oil are very limited. Bethea et al. (1978) studied the re-refining process by using distillation and hydrotreating. The feedstock in their study was collected from different areas of United State. The feedstock had a viscosity at 38°C (100°F) of 51.00 cSt (237 SSU), a viscosity index of 166, color of black, a flash point of 93°C (200°F), a sulfur content of 0.30 wt%. After distillation, a distilled oil, boiling range 343-507°C (650-945°F), was hydrotreated over used Nalcomo 471 cobalt-molybdate commercial catalyst at temperature of 288, 316 and 343°C (550, 600 and 650°F) and a pressure of 4.48 Mpa (650 psig), a liquid space velocity of 1.0 hr⁻¹, and a hydrogen flow rate of 6.01 kmol/m³ (800 scf/Bbl). Hydrotreating at a temperature of 343°C (650°F) yielded a liquid product having acceptable quality of a 150 vis neutral lube base stock. Hydrotreating at lower temperatures, 388 and 316°C (550 and 600°F), produced oil with poor copper strip corrosion. Their experiments were conducted for 100 hours during which no significant catalyst deactivation was reported. Their result showed

that the sulfur content of resulted oils decreased as operating temperature increased.

The catalysts for hydrotreating of used lubricating oil was investigated by Wilson et al. (1983). Eight commercial catalysts were tested over a temperature range of 288 to 399°C (550 to 750°F) and a pressure range of 3.44 to 4.82 MPa (500 to 700 psig) in an autoclave reactor. Two commercial catalysts, American Cyanamid HDS-20A and Harshaw HT-500, were selected on the basis of their superior performance in the tests for further investigation in trickle-bed reactor. Product oil color of 1.5 was obtained for a hydrofinishing temperature of 349°C (660°F), pressure of 4.13 MPa (600 psig), and space time of approximately 5 hours, using the Harshaw HT-500 catalyst.

Similar study was conducted by Bahn et al. (1986) who tested activity of several commercial catalysts in hydrotreating of used lubricating oil. Light and heavy hydrocarbon compounds were removed from feedstock by vacuum distillation. A viscosity at 38°C (100°F), a ASTM color, a sulfur content of the distilled oil were 29.18 cSt, 8.0 and 0.3 wt%, respectively. Hydrotreating of distilled oil was conducted in two trickle-bed reactors placed in series. The top reactor contained the guard-bed material (high-surface-area alumina) and the bottom reactor contained the catalysts. The oil was hydrotreated over commercial Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts at a reactor temperature of 325°C, a pressure of 5.51 MPa (800 psig), a liquid space velocity of 1.0 hr⁻¹. Armark-840, a Ni-Mo/Al₂O₃ catalyst, showed the highest activity and stability for product liquid improvement and nitrogen removal. It was selected for additional study.

The effect of operating conditions on the product liquid color, viscosity, nitrogen and sulfur contents were discussed in study. The hydrofinishing reactor was operated at temperatures ranging from 285°C to 375°C, pressures between 4.14 to 6.89 MPa (600 to 1000 psig), liquid space velocity between 0.5 to 2.0 hr⁻¹ and hydrogen gas flow rate of 12.03 kmol/m³ (1600 SCF/Bbl). After hydrotreating, they found that ASTM color, viscosity at 38°C (100°F), sulfur and nitrogen content depended on operating temperature. ASTM color of the product oil decreased from 8.0 to 1.5 at temperature of 285°C and to 1.0 at temperature of 345°C. Both sulfur and nitrogen contents of the product oil decreased with increasing in temperature. Above 360°C, the temperature did not have a significant effect on sulfur and nitrogen contents. They reported that the operating pressure and the liquid space velocity did not affect product color significantly. They concluded that the optimum conditions for hydrotreating of the distilled oil were a temperature of 350°C, a pressure of 5.51 MPa (800 psig), and a liquid space velocity of 1.0 hr⁻¹.

Attempts had been made to identify kinetics and reaction order for hydrotreatment of used lubricating oil. First order and second order reactions were reported on hydrodesulfurization of the oil. No definite conclusion had yet been drawn. (Mohammad et al., 1986; Aragon et al., 1989)

Literature summary

1. The re-refining process consists of three major steps;

(1) removal of contaminated water and light hydrocarbon compounds from used oil

(2) removal of contaminants and additives from dehydrated oil

(3) finishing or polishing the oil product

2. Operating conditions for hydrotreating of the oil are temperatures of 260-430°C, pressures of 0.93-13.80 MPa, with liquid space velocity ranging from 0.5-2.5 hr⁻¹ and with gas flow rate 1.5-133.93 kmol/m³ or gas-to-oil ratio 34-3000 vol/vol oil.

3. Catalysts which used in hydrotreating of the oil are commercial hydrotreating catalysts such as nickel-molybdate and cobalt-molybdate on alumina support.

4. After re-refining used oil, some properties of used oil such as viscosity, ASTM color, sulfur and nitrogen content decreased.

5. Operating temperature of hydrotreater effected on some properties of the oil such as a viscosity, ASTM color, sulfur and nitrogen content. When increasing operating temperature, viscosity, ASTM color, sulfur and nitrogen content decreased.

6. Operating pressure and liquid space velocity did not affecte the product color significantly.