Chapter III

Experiment and Analysis Techniques

Experiment

General re-refining process utilized during the study consists of two major steps: solvent extraction of used oil and hydrotreating of the extracted stocks. Figure 3.1 shows a simplified process block diagram of various processing steps. Used lubricating oils were collected from several sources. Extraction was conducted by mixing one part of used lubricating oil with 4 parts of solvent and the mixture was allowed to settle for 24 hours at approximately 10°C. The solvents dissolved the oil while most of contaminants and additives present in the used oil precipitated out as a sludge. The oil-solvent phase was separated from precipitated sludge and was transferred to a batch distillation where the solvent was removed.

Hydrotreating of the extracted oils was conducted in a fixed-bed reactor system as shown in Figure 3.2. Details of the reactor system and experimental procedures are described elsewhere (Tanpichart, 1992 and Chantalaka, 1993). In this study, the reactor is 47 cm (18.5 inches) long, 1.90 cm (0.75 inch) outside diameter, and 0.165 cm (0.065 inch) thick.

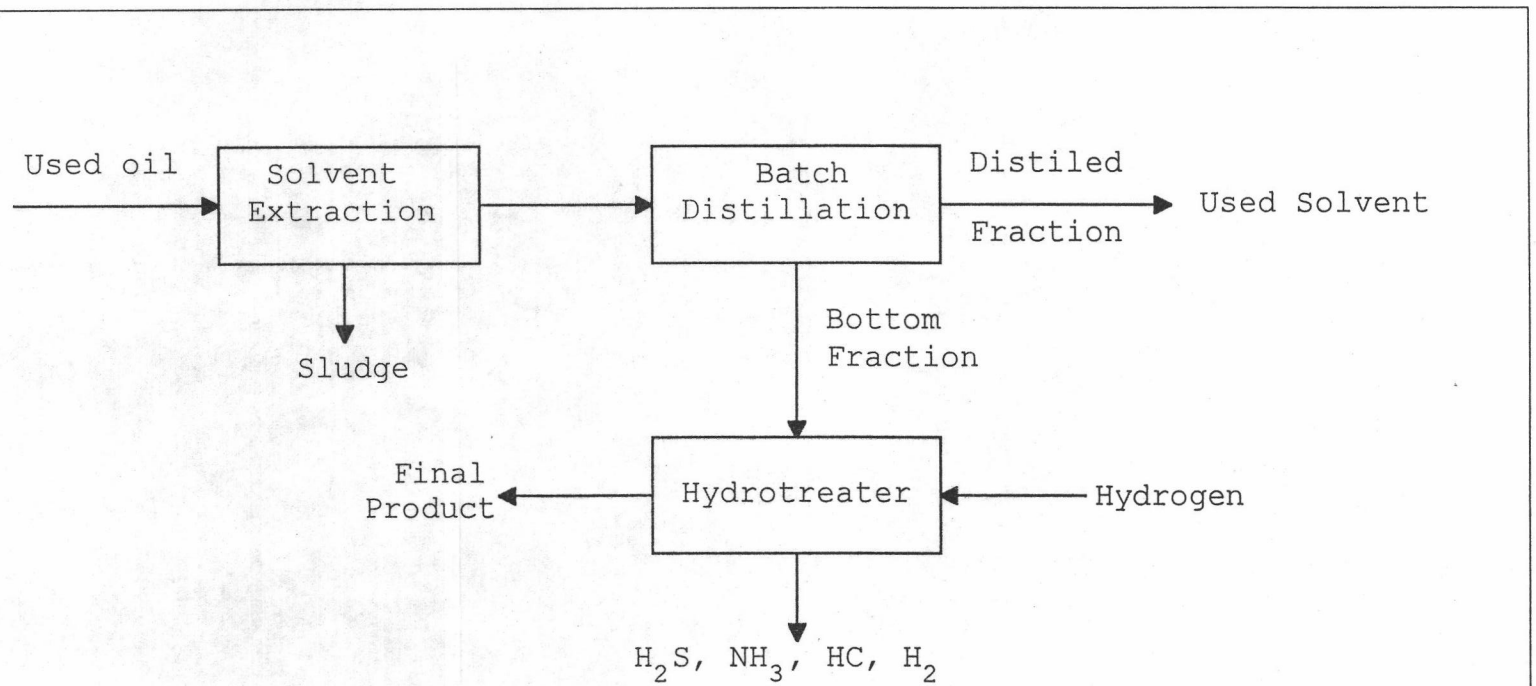

Figure 3.1 Process block diagram.

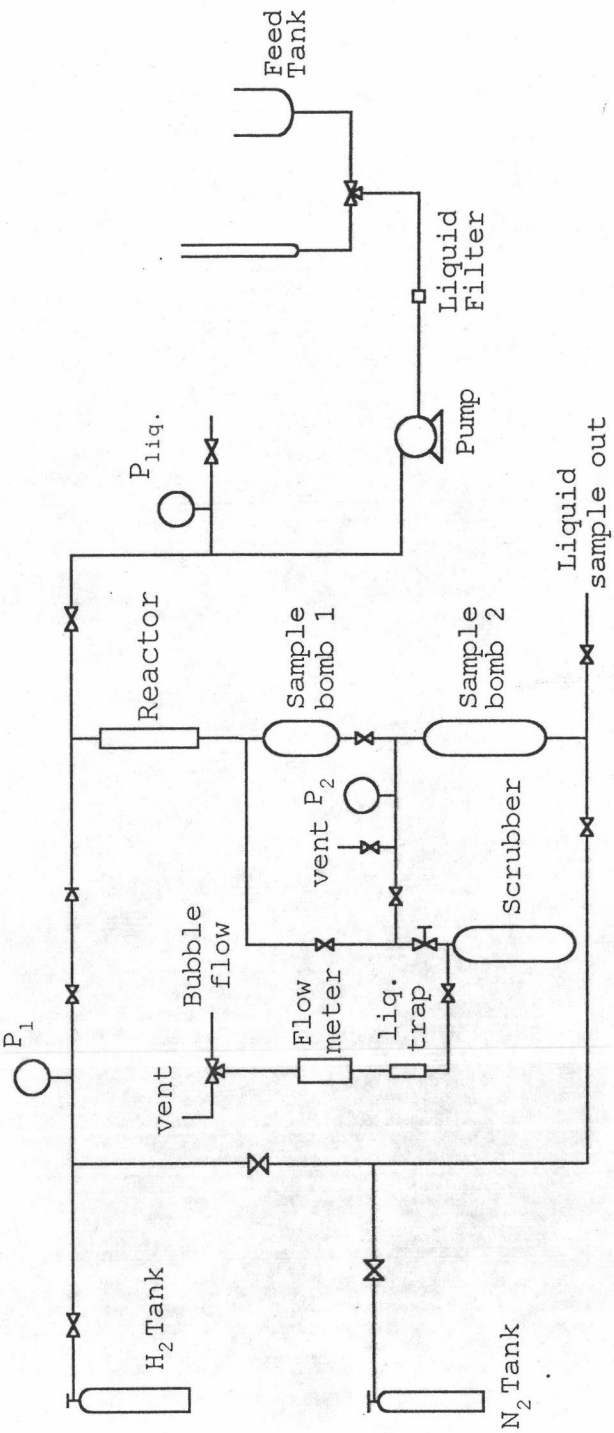

Figure 3.2 Simplified diagram of hydrotreating system

Three commercial hydrotreating catalysts, Co-Mo/Al_2O_3, Ni-Mo/Al_2O_3, and Ni-W/Al_2O_3, were evaluated for their hydrotreating services. Table 3.1 lists the chemical and physical properties of these catalysts. Table 3.2 shows the operating conditions of every experiment.

Table 3.1 The Chemical and Physical Properties of Catalyst.

Catalyst type	Co-Mo	Ni-Mo	Ni-W
	1/16	1/16	1/16
Chemical composition, wt% dry basis			
Cobalt	3.2	-	-
Nickel	-	3	3
Molybdenum	9.6	13	-
Tungsten	-	-	25
Phosphorus	-	-	2.5
Physical properties			
Surface area, m^2/g	230	162	135
Pore volume, cc/g	0.6	0.5	0.39
Side plate crush strength,[1] lb(kg)	18(8.2)	24(10.9)	25(11.3)
Bulk crushing strength,[2] kg/ml	15	16	16.7
Attrition Index[3]	99+	99+	98+
Compacted bulk density, lb/ft^3	48(0.77)	52(0.83)	61(0.98)

[1] 3/16-inch-long particles

[2] Pressure applied to produce 0.5% w fines< 40 mesh

[3] wt% retained on 20 mesh screen after tumbling 1 hour at 40 rpm

Table 3.2 The Experimental Operating Conditions.

Operating Condition		
Reactor Temperature, °C	:	320, 350, 380
Pressure, MPa	:	5.51
LHSV[1] , hr^{-1}	:	0.5, 1.0, 1.5
Oil flow rate, ml/hr	:	30, 60, 90
H_2 : Oil ratio	:	600 : 1
Hydrogen flow rate, ml/min	:	300, 600, 900
Time	:	48 Hrs.
Sampling	:	12 Hrs.
Catalyst	:	1/16" Extruded of Co-Mo/Al_2O_3
		1/16" Extruded of Ni-Mo/Al_2O_3
		1/16" Extruded of Ni-W/Al_2O_3
Catalyst Volume, ml	:	60
Catalyst Weight, g.	:	38.41 for Co-Mo/Al_2O_3
		40.00 for Ni-Mo/Al_2O_3
		58.45 for Ni-W/Al_2O_3

[1]LHSV is liquid hourly space velocity = volumetric feed rate of a liquid per volume of catalyst bed

Analysis Techniques

In each experiment, liquid product samples were collected and were analysed for viscosity, viscosity index, ASTM color, flash point, sulfur content and total acid number. All analytical methods followed the American Society for Testing and Materials (ASTM).

1. Viscosity

Viscosity is the most important physical property of lubricating oil. It is a measure of the lubricating oil's internal friction or the resistance of the flow. The viscosity of lubricating oil changes with temperatures; it increases as the temperature decreases and decreases as the temperature increases.

ASTM D445 is the Standard Test Method for kinematic viscosity of transparent and opaque liquid. This method covers the determination of the kinematic viscosity of liquid petroleum products, both transparent and opaque, by measuring the time of a volume of liquid that flows under gravity through a calibrated glass capillary viscometer. The dynamic viscosity can be obtained by multiplying the measured kinematic viscosity by the density of the liquid. The apparatus consists of viscometers, viscometer holders, viscometer thermostat and bath, thermometer and time device. In this test, Cannon-Fenske Routine viscometers (Figure 3.3) were used; 300 ml-size or 350 ml-size for test at 40°C and 150 ml-size for test at 100°C.

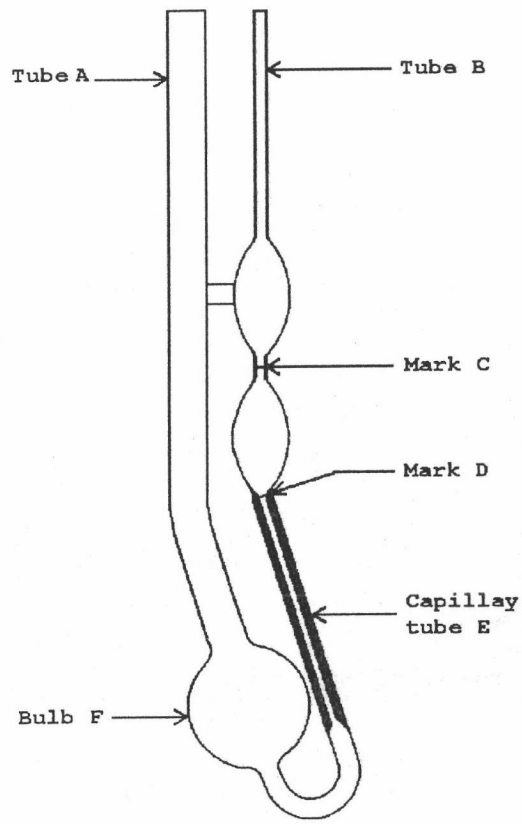

Figure 3.3 Cannon-Fenske Routine viscometer

The determination of viscosity starts with the selection of a clean dry, calibrated viscometer with a range of the estimated viscosity. The flow time should not be less than 200 seconds. The instrument is inverted and suction is applied to tube A. Tube B is dipped in the liquid sample and liquid is drew to mark D. Tube A is stopped suction and arm B is wiped clean. The instrument is turned to its normal vertical position. Next, the viscometer is placed into the holder and into the constant temperature bath. The sample is allowed to

flow through capillary tube E and is held in bulb F. The sample is allowed approximately 10 minutes at 40°C and 15 minutes at 100°C to come to bath temperature. Pressure is applied to tube A. Until liquid level is over mark C, tube A is stop pressurized. The sample is allowed to flow to mark C by gravity force. When liquid reach mark C, the efflux times is measured for the meniscus to pass from mark C to mark D. The kinematic viscosity of the sample is calculated by multiplying the efflux time (in seconds) for each bulb by the viscometer constant of each bulb.

2. Viscosity Index

The viscosity index is an arbitrary number indicating the effect of change of temperature on the kinematic viscosity of an oil. A high viscosity index signifies a relatively small change of kinematic viscosity with temperature. The viscosity index of an oil is calculated from its viscosities at 40°C and 100°C. The procedure for the calculation is given in ASTM Method D2270 for Calculating Viscosity Index for Kinematic Viscosity at 40°C and 100°C. In this study, the table in Viscosity Index Tables For Celsius Temperatures by American Society for Testing and Materials was used to find the viscosity index of the oil sample. The table in this book permits direct reading of the viscosity index of a petroleum product or lubricant if its kinematic viscosities at 40°C and 100°C are known. The accuracy of the calculated viscosity index obtained by the use of method D2270 or the table in the book depends on the accuracy of the viscosity determinations. It is recommended that the viscosity index be reported only in

whole numbers and that the use of decimal values be avoided.

3. ASTM Color

Color, ASTM, is the color of petroleum products that closely matches the color of a specified glass standard. ASTM D1500 is Standard Test Method for ASTM Color of Petroleum Products (ASTM Color Scale). This method covers the visual determination of the color of a wide variety of petroleum products such as lubricating oils, heating oils, diesel fuel oils, and petroleum waxes. In this study, the FISHER colorimeter is used to test the color number. The colorimeter consists of light source, glass color standards, sample container, sample container housing with cover, and viewing piece. The test began by placing a sample container filled to a depth of at least 50 mm with distilled water in the compartment of the colorimeter through which the standard glasses will be observed. The sample is placed in its container in the other compartment. Both containers are covered to eliminate all exterior light. The light source is switched on and the color of the sample is compared with that of the standard glasses. The glass which matches the color of the sample is determined; or if an exact match is not possible, then glass which possesses the next darker color is used. The color of the sample is reported by the designation of the matching color glass. If the color of the sample is intermediate between those of two standard glasses, the designation of the darker glass preceded by the letter "L" is recorded. The color is never reported as being darker than a given standard except those darker than 8.

4. Flash point

The flash point of oils is the temperature at which the oil releases enough vapor at its surface to ignite when an open flame is applied. The flash point of oils varies according to the degree of viscosity; higher viscosity oils have higher flash points.

In this study, ASTM D92 was used to find the flash point of liquid sample. ASTM D92 is the Standard Test Method for Flash and Fire Points by Cleveland Open Cup. This method covers determination of the flash and fire points of all petroleum products except fuel oils and those having an open cup flash below 79°C (175°F). The apparatus consists of a test cup, a heater flame type, a test flame applicator, a thermometer support, a thermometer and a stand to support the test cup. In testing the sample, the test cup is filled to a specified level with the sample. The test flame is lighted and is adjusted to a diameter of 3.2 to 4.8 mm. Heat is applied to the bottom of the test cup. At specified intervals a small test flame is passed across the cup. The lowest temperature at which application of the test flame causes the vapors above the surface of the liquid to ignite is taken as the flash point.

5. Sulfur content

Sulfur content is the weight percent of sulfur present in the sample. Analysis of sulfur content follows ASTM D4294 which is the Standard Test Method for Sulfur in Petroleum Products by Non-Dispersive X-Ray Fluorescence Spectrometry. This method covers the measurement of sulfur in hydrocarbons such as naphthas,

distillates, fuel oils, residues, lubricating base oils, and unleaded gasolines. The concentration range of sulfur in hydrocarbons, that can be measured by this method is within 0.01 and 5 weight%. In this study, HORIBA sulfur analyzer Model SLFA-800 was chosen to analyze the sample. The analyzer was calibrated using three standard sulfur solution which exact concentrations are known and the range of sulfur content in samples is covered. The sample cell must be thoroughly clean and dry before use. Window material is made of 60 μm polyester film. The sample cell is filled with sample to a minimum depth of 3 mm and is ensured that there is no air bubble between the window and the liquid. The sample cell is inserted into the analyzer and the three sequential test is obtained. The average concentration of the sample was calculated and was printed out by the analyzer.

6. Total Acid Number

Total acid number is the quantity of base, expressed in milligrams of potassium hydroxide (KOH), that is required to titrate all acidic constituents present in 1 gram of sample. The total acid number can be measured by several ASTM method. In this study, ASTM D974 was chosen to analyze the liquid sample. ASTM D974 is the Standard Test Method for Neutralization Number by Color-indicator Titration. This method covers the determination of acidic or basic constituents in petroleum product and lubricants soluble or nearly soluble in mixtures of toluene and isopropyl alcohol. The Metrohm Model 665 Dosimet and Metrohm Model E649 were used as titration instruments. The titration solution is the mixture of 500 ml of toluene, 5 ml of water and 495

ml of anhydrous isopropyl alcohol. The normality of standard KOH solution was 0.0739 N and p-Naphtholbenzene solution was used as an indicator. Approximately 0.5 gram of the sample is dissolved in 60 ml of the titration solution in 125 ml Erlenmeyer flask. Five drops of the indicator solution is added and, without stopping, swirl until the mixture is well-mixed. The color of the mixture is a yellow-orange color. The mixed solution is titrated at room temperature (25°C) with standard KOH solution. The end point is indicated by changing of yellow-orange color to green or green-brown and is considered definite if the color change persists for 15 second. A blank titration is also made on 60 ml of the titration solution and 5 drops of the indicator solution. The quantity of the standard KOH solution is recorded when the solution reachs the end point (orange to green). The total acid number is calculated as follows:

Total acid number, mg of KOH/g = [(A-B)Nx56.1]/W

Where:

A = millilitres of KOH solution required for titration of sample,

B = millilitres of KOH solution required for titration of blank,

N = normality of KOH solution, and

W = grams of sample used.