CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Heavy distillate was obtained from Fang Refinery Plant.

3.1.2 Methyl ethyl ketone (MEK) (commercial grade) was obtained from Grand Chemical Inc. It was purified by simple distillation.

3.1.3 Industrial hydrogen gas was obtained from TIG Trading Limited.

3.1.4 Nickel chloride hexahydrate ($NiCl_2.6H_2O$) and chloroplatinic acid ($H_2PtCl_6.6H_2O$) (analytical grade) were obtained from Carlo Erba.

3.1.5 Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$) (analytical grade) was obtained from J.T. Baker Inc.

3.1.6 Cobalt chloride hexahydrate ($CoCl_2.6H_2O$) (analytical grade) was obtained from Unilab.

3.1.7 Citric acid ($C_6H_8O_7$) (laboratory grade) was obtained from May & Baker Company Co., Ltd.

3.1.8 Ammonium fluoride (NH_4F) and ammonium thiosulfate $(NH_4)_2S_2O_3$ (analytical grade) were obtained from BDH Ltd.

3.1.9 Raney nickel was available from Merck.

3.1.10 Alumina support (CS331-3 type) and heterogeneous catalysts (C20-7-06 (MoO_3+NiO+Al_2O_3) and T-2563 (WO_3+NiO+Al_2O_3)) were obtained from United Catalyst Inc., USA. Their specifications are shown in Table 3.1.

Table 3.1 Specifications of the C20-7-06 and T-2563 heterogeneous catalysts

Types	Components	Percent
C20-7-06	MoO_3	15-20
	NiO	1-5
	Al_2O_3	75-85
T-2563	WO_3	<10
	NiO	15-25
	Al_2O_3	70-80

3.2 Apparatus and Instruments

3.2.1 Apparatus for measuring pore volume of alumina support CS331-3 comprised of:

- Buret for charging deionized water.
- Suction flask for charging alumina support.
- Stand and clamp for supporting buret and suction flask.
- Suction pump for removing trapped air from the pores of alumina supports before impregnating the solution.

3.2.2 Calcinator

The apparatus model GSM from CARBOLITE FURNACES was used.

3.2.3 Nuclear Magnetic Resonance Spectrometer (NMR Spectrometer)

The NMR model AC-F 200 from Bruker operation at 200 MHz was used. The solution of oil (0.1 g) in $CDCl_3$ (3 ml) was subjected to ^{13}C-NMR analysis.

3.2.4 Gas Chromatrography-Mass Spectrometer (GC-MS)

The apparatus model GC 8000 series and Mass detector model

MD 800 from Fison Instrument were used.

Concentration of sample: 1000 ppm of oil in hexane

GC conditions:

Column: DB-1 capillary column 30m x 0.25mm ID. x 0.25μm

Carrier: Helium, 40 cm /sec

Oven: 80 °C (2 min) to 300 °C (15 min) at rate 4 °C/min

Injection temperature: 290 °C

Detector: MS (EI^+ 70 ev)

3.2.5 High Pressure Reactor

All experiments for the hydrodesulfurization and hydroisomerization studies of lubricating base oils were carried out in the hydrogenation apparatus which consisted of four parts as follows:

3.2.5.1 Reactor (Figure 3.1)

The hydrogenation floor stand reactor was a high pressure batch stirred autoclave model 4551 from Parr Instrument Company with a 3750 cubic centimeter stainless steel 316 cylindrical bomb, split ring closures and a bomb heater. The reactor could work in a pressure range from 0-2000 psig and a temperature range of 0-450 °C.

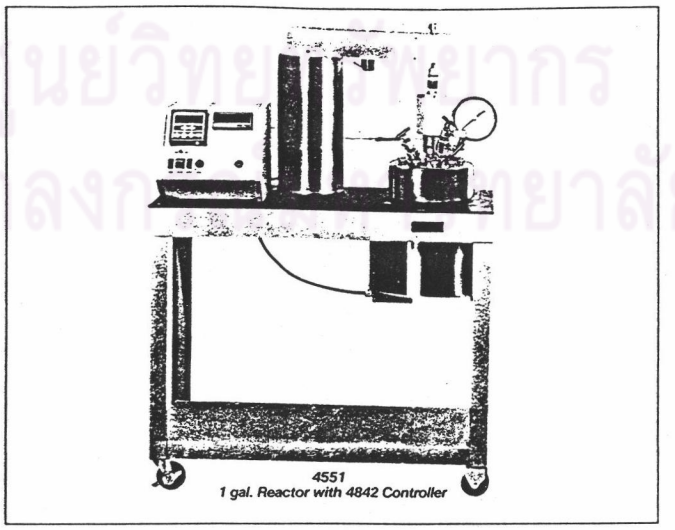
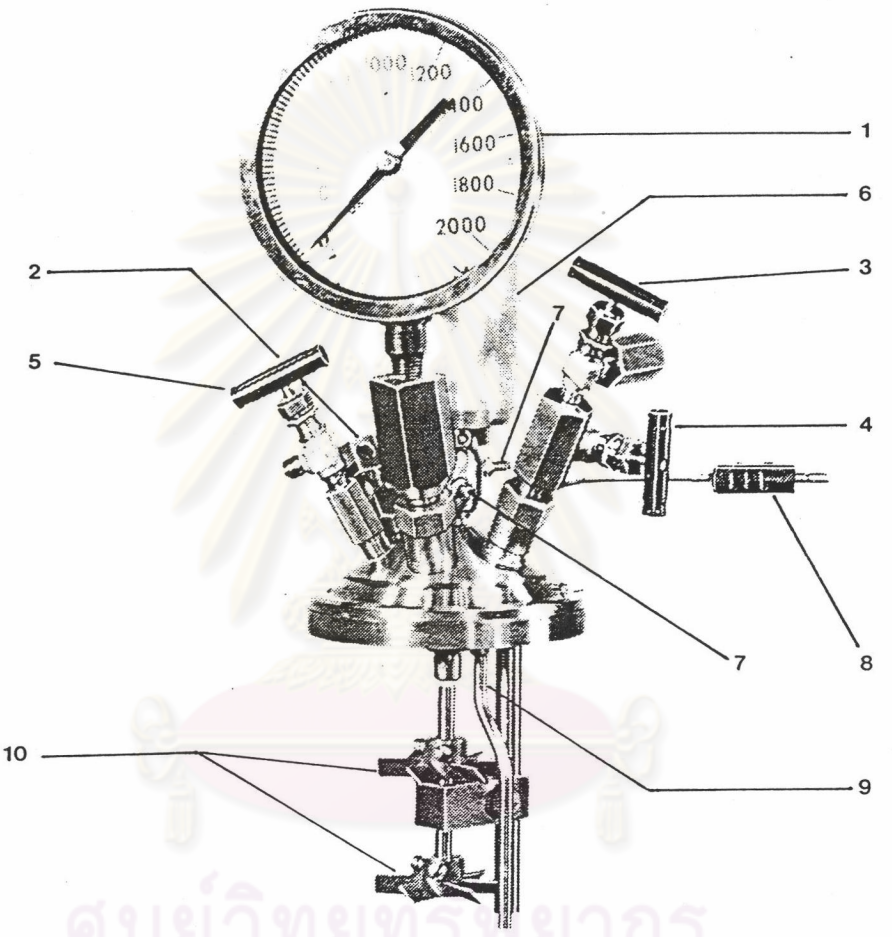


Figure 3.1 Floor Stand Reactor

3.2.5.2 Reactor Fitting (Figure 3.2)

The stirring unit of reactor was equipped with convenient valves and fittings for handling the various functions. The parts were indicated with the following number.



1. a pressure gauge
2. a safety rupture disc
3. a gas inlet valve
4. a liquid sampling valve
5. a gas release valve
6. a stirrer magnetic drive system
7. a water cooling channel
8. a thermocouple
9. a dip tube
10. a stirring shaft with 6-blade turbine type impellers

Figure 3.2 Reactor Fitting

3.2.5.3 Automatic Temperature Controller

The controller used was model 4842 PID controller from the Parr Instrument Company. It was operated in conjunction with a dual thermocouple. There were various enhancement modules to assist in monitoring and controlling the temperature, pressure and stirring speed. Stirring speed could be adjusted in the range of 0-1000 rpm.

3.2.5.4 Gas Controllers System

The system consisted of a hydrogen tank with a pressure regulator (0-2000 psig).

3.2.6 Viscometer

The apparatus model K-234 A from Hochler Instrument Co., Inc. was used.

3.2.7 Pour Point Tester

The apparatus model A 82 from Haake was used.

3.2.8 Sulfur Analyzer

The apparatus model SLFA-800 from Horiba was used.

3.2.9 Colorimeter

The Fisher ASTM Colorimeter was used.

3.2.10 Thermogravimetric Analyzer

The TGA model TA 2950 from DuPont Instrument was used.

3.2.11 Flash Point Tester

The cleveland open cup semi-automatic apparatus from Herzog was used.

3.2.12 Surface Area Analyzer

The instrument model Micromeritics Flow Sorb II 2300 was used.

3.3 Procedure

3.3.1 Dewaxing of Heavy Distillate by Methyl Ethyl Ketone [3,4]

There are three main parts for solvent dewaxing process – precipitation, filtration and solvent recovery. Beginning with precipitation, heavy distillate (749 g) was heated slowly to a temperature of 60-70 °C until the wax was dissolved completely. Methyl ethyl ketone (2700 ml) was added with stirring. The ratio by volume between solvent and oil was 3:1. The solvent and oil mixture was chilled to the dewaxing temperature of 0 °C by refrigeration. The mixture was then quickly filtered through a Buchner funnel under reduced pressure to separate the crystallized wax. The temperature of the solution remained below 5 °C. Suction was continued for several minutes until the oil was removed completely from the wax. The filtrate was collected and the oil was recovered from the filtrate by simple distillation to obtain dewaxed oil.

3.3.2 The Physical and Chemical Properties Determination of Dewaxed Oil

The physical and chemical properties of dewaxed oil were determined using the following standard procedure as follow:

Physical properties:

a. Kinematic viscosity	by	ASTM D-445
b. Viscosity Index (VI)	by	ASTM D-2270
c. Colour, Visual	by	ASTM D-1500
d. Pour point	by	ASTM D-97
e. Flash point	by	ASTM D-92
f. API gravity	by	ASTM D-1298

Chemical properties:

a. Sulfur content, %wt by ASTM D-129
b. The percentages of oxidative compounds were determined by TGA.
c. The composition ($\%C_a$, $\%C_n$, $\%C_p$) was determined by ^{13}C-NMR.
d. The molecular weight distribution was determined by GC-MS.

3.3.3 Oil yields determination in dewaxed oil

Oil yields of dewaxed oil were determined by the modified ASTM D3235 procedure. The sample was dissolved in methyl ethyl ketone. The solution was cooled to -10 °C for precipitating wax, then filtered. The oil content in the combined filtrate was determined by evaporating solvent from the filtrate and weighing the residue.

3.3.4 Measuring Pore Volume of Alumina Support CS331-3 Type [3]

The alumina support (100 g) was placed in a suction flask which equipped with a buret containing deionized water. The flask was connected to a vacuum pump. The vacuum pump was applied to evacuate the air from the pores of the support. Deionized water from the buret was added to the support until thoroughly. The volume of deionized water was determined. The procedure described above was repeated until the water consumption by the support became constant. The pore volume of the support was calculated from the volume of consumed water. The result of this experiment indicated that the pore volume of the support CS331-3 type was 0.64 ml/g.

3.3.5 Preparation of Catalysts

3.3.5.1 Hydrodesulfurization Catalyst: containing 10% Mo , 5% Ni and 5% Co on alumina support. [24,27]

The alumina support (100 g) was soaked for about 15 minutes at room temperature in a pretreating solution, prepared by dissolving $(NH_4)_2S_2O_3$ (40 g) in deionized water (200 ml). The excess pretreating solution was drained off. The pretreated alumina support was dried at 120 °C, cooled, and added to an impregnating solution (64 ml), prepared by dissolving 18.41 g of $(NH_4)_2Mo_7O_{24}.4H_2O$, 20.18 g of $CoCl_2.6H_2O$, 20.24 g of $NiCl_2.6H_2O$ and 10 g of citric acid in a sufficient amount of water to give 64 ml of acid impregnating solution (pore volume of 100 g of alumina support). The impregnated alumina support was dried at 120 °C and then calcined at 600 °C for 3 hours to give the Mo/Ni/Co hydrodesulfurization catalyst.

The metal components in this prepared catalyst were calculated and the surface area was determined. The results are shown as follow:

Molybdenum	10 %
Nickel	5 %
Cobalt	5 %
Surface area	141.05 m^2/g

3.3.5.2 Hydroisomerization Catalyst: containing 0.3% Pt and 0.5% F on alumina support. [17-19]

An aqueous impregnating solution was prepared by dissolving 1 g of chloroplatinic acid ($H_2PtCl_6.6H_2O$) in 80 ml of deionized water. The alumina support (125.55 g) was impregnated with this prepared

solution. The impregnated support was dried at 120 °C and then calcined at 450 °C for 3 hrs to obtain the calcined catalyst. That calcined catalyst was reimpregnated with 80 ml of aqueous solution containing NH_4F (1.22 g) (the volume of aqueous solution equivalent to the pore volume of the alumina support) and then was left at room temperature for one hour, dried at 120 °C for 16 hrs to obtain the fluoride doped catalyst. This fluoride doped catalyst was calcined in a continuous current of air at the following condition (hold at 150 °C for 1 hr , raise temperature by 50 °C every 15 minutes to 400 °C, then hold at 400 °C for 1 hr) to obtain the Pt/F hydroisomerization catalyst.

The metal components in this calcined catalyst were calculated and the surface area was determined. The results are shown as follow:

Platinum	0.3 %
Fluoride	0.5 %
Surface area	184.68 m^2/g

3.3.6 Hydrodesulfurization Process

3.3.6.1 The Effect of Catalyst Type on Hydrodesulfurization

Dewaxed oil (400 g) and the Mo/Ni/Co hydrodesulfurization catalyst (20 g) were placed in the stainless steel reactor. The gas in the reactor was replaced by hydrogen gas by successive dilution and then the hydrogen gas pressure in the reactor was adjusted to 500 psig. The reaction was operated at selected temperature (350 °C) and reaction time (4 hours). The stirring speed was set at 500 rpm. After the reaction took place, heating was stopped and the reaction mixture was stirred until the mixture was cooled to room temperature. The pressure was released and the reaction mixture was transferred to a 1 litre beaker and the catalyst was separated by suction filtration to give desulfurized

oil. The molecular weight distribution of this desulfurized oil was determined by GC-MS, the GC-MS chromatogram is shown in Figure A3 and the molecular weight distribution of this oil is tabulated in Table A2. The sulfur content was measured as described in 3.3.2 and the result is shown in Table A3.

The desulfurized oil was further distilled under reduced pressure to obtain a lube cut (≥ 330 °C) and distillate cut (< 330 °C). The physical properties (color, VI and pour point) of the lube cut were determined by the procedures listed in 3.3.2. and % yield was calculated. The results are shown in the Table A3.

The experiment was repeated according to the procedure described above for CS20-7-06, T-2563, and Raney nickel catalysts. For each experiment the reaction mixture was worked up in the same manner as above to give the desired products. The molecular weight distributions of these desulfurized oils were determined by GC-MS. The GC-MS chromatograms are shown in Figure A3 and the molecular weight distributions of the components in these oils are tabulated in Table A2. Physical and chemical properties listed in section 3.3.2 were determined by the methods listed therein. Results of these determination are presented in Table A3.

3.3.6.2 The Effect of Temperature on Hydrodesulfurization

Following the procedure as in experiment 3.3.6.1 except the reaction was operated at various temperatures (200, 250, 300, 350 and 400 °C) using the optimum catalyst, (Mo/Ni/Co catalyst), as determined from 3.3.6.1. The reaction mixture was worked up in the same manner as above. The GC-MS chromatograms of the five products are shown in the Figure A4 and the molecular weight distributions of the components are tabulated in Table A4. Physical and chemical properties listed in section 3.3.2 were determined by the

methods listed therein. Results of these determination are presented in Table A5.

3.3.6.3 The Effect of Hydrogen Pressure on Hydrodesulfurization

Following the procedure similar to that in experiment 3.3.6.2 except the reaction was operated at various hydrogen pressures (200, 300, 400, 500 and 600 psig) at the optimum temperature of 400 °C obtained from 3.3.6.2. The reaction mixture was worked up in the same manner as described in 3.3.6.1. The GC-MS chromatograms of the five products are illustrated in the Figure A5 and the molecular weight distributions of the components are tabulated in Table A6. Physical and chemical properties listed in section 3.3.2 were determined by the methods listed therein. Results of these determination are presented in Table A7.

3.3.6.4 The Effect of Reaction Time on Hydrodesulfurization

Following the same procedure as described in experiment 3.3.6.3 except the reaction was operated at various reaction times (2, 4, 6, 8 and 10 hours) with the optimum hydrogen pressure of 600 psig obtained from 3.3.6.3. The reaction mixture was worked up in the same manner as described in 3.3.6.1. The GC-MS chromatograms of each products are illustrated in Figure A6 and the molecular weight distributions of the components are tabulated in Table A8. Physical and chemical properties listed in section 3.3.2 were determined by the methods listed therein. Results of these determination are presented in Table A9.

3.3.6.5 The Effect of Catalyst Concentration on Hydrodesulfurization

Following the same procedure as described in experiment 3.3.6.4 except the reaction was operated at various catalyst concentrations (1, 2, 3, 4 and 5 % by weight of oil) for the optimum reaction time of 6 hours obtained from 3.3.6.4. After the reaction, the mixture was worked up in the same manner described in 3.3.6.1 to give the desired products. The GC-MS chromatograms of the five products are shown in the Figure A7 and the molecular weight distributions of the components are tabulated in Table A10. Physical and chemical properties listed in section 3.3.2 were determined by the methods listed therein. Results of these determination are presented in Table A11.

3.3.7 Hydroisomerization Process

3.3.7.1 The Effect of Temperature on Hydroisomerization

Desulfurized oil (400 g), obtained from 3.3.6.5 at the define optimum operating condition and the Pt/F hydroisomerization catalyst (24 g) (from 3.3.5.2) were placed in the stainless steel reactor. The gas in the reactor was replaced by hydrogen gas by successive dilution and then the hydrogen gas pressure in the reactor was adjusted to 600 psig. The reaction was operated at selected reaction time (4 hours) with stirring speed set at 500 rpm for various reaction tempertures (250, 300, 350 and 400 °C, respectively). After 4 hours heating was stopped and the reaction mixture was stirred until the mixture cooled to room temperature, the pressure was released, and the reaction mixture was transferred to a 1 litre beaker and the catalyst was separated by suction filtration to give isomerized oil.

The molecular weight distributions of the four isomerized oils were determined by GC-MS. The GC-MS chromatograms are shown in Figure A10, and the molecular weight distributions of the components in these oils are tabulated in Table A12.

The isomerized oil was further distilled under reduced pressure to obtain a lube cut (≥ 330 °C) and distillate cut (< 330 °C). The physical properties of the lube cut as well as % yield were determined by the methods identified in 3.3.2. The results are presented in Table A13.

3.3.7.2 The Effect of Hydrogen Pressure on Hydroisomerization

Following the procedure similar to that described in experiment 3.3.7.1 except various hydrogen pressures (300, 400, 500 and 600 psig) and the optimum temperature of 350 °C from 3.3.7.1 were used. The reaction mixture was worked up in the same manner to give the desired products. The molecular weight distributions of each isomerized oils were determined by GC-MS. The GC-MS chromatograms are shown in Figure A11, and the molecular weight distributions of components in these oils are tabulated in Table A14.

The physical properties of lube cut were determined in the same manner as described in 3.3.2 and % yield was calculated. The results are presented in Table A15.

3.3.7.3 The Effect of Reaction Time on Hydroisomerization

Following the procedure similar to that described in experiment 3.3.7.2 except various reaction times (4, 8, 12, and 16) and the selected hydrogen pressure of 600 psig from 3.3.7.2 were used. After the reaction, the mixture was worked up in the same manner as 3.3.7.1 to give the

desired products. The molecular weight distributions of each isomerized oils were determined by GC-MS. The GC-MS chromatograms are illustrated in Figure A12, and the molecular weight distributions of components in these oils are tabulated in Table A16.

The physical properties of lube cut were determined in the same manner as described in 3.3.2 and % yield was calculated. The results are shown in Table A17.

3.3.7.4 The Effect of Catalyst Concentration on Hydroisomerization

Following the procedure similar to that described in experiment 3.3.7.3 except various catalyst concentrations (2, 4, 6 and 8% by weight of oil) and the optimum reaction time of from 3.3.7.3 was used. The reaction mixture was worked up in the same manner as 3.3.7.1 to give the desired products. The molecular weight distributions of each isomerized oils were determined by GC-MS. The GC-MS chromatograms are shown in Figure A13, and the molecular weight distributions of components in these oils are tabulated in Table A18.

The physical properties of lube cut were determined in the same manner as described in 3.3.2 and % yield was calculated. The results are presented in Table A19.