

CHAPTER III

EXPERIMENTATION

Materials

- Heavy distillate was obtained from Fang refinery plant.
- Alumina support, heterogeneous catalyst C20-7-06 (Al₂O₃+MoO₃+NiO) and heterogeneous catalyst T-2563 (Al₂O₃+WO₃+NiO) were obtained from United Catalyst Inc., USA. Their specifications are shown in Table 3.1.
- Methyl Ethyl Ketone (MEK) was obtained from Grand Chemical Inc. It was purified by simple distillation.
- Ammonium thiosulfate, (NH₄)₂S₂O₃, (AR grade) and Ammonium fluoride, NH₄F, (AR grade) were obtained from BDH Co., Ltd.
- Chloroplatinic acid, H₂PtCl₆·6H₂O, (AR grade) and Nickel chloride hexahydrate, NiCl₂·6H₂O, (AR grade) were obtained from Carlo Erba Co., Ltd.
- Ammonium molybdate, (NH₄)₆Mo₇O₂₄·4H₂O, (AR grade) was obtained from J.T. Baker, Inc.
- Cobalt chloride, CoCl₂·6H₂O, (AR grade) was obtained from Unilab company.
- Citric acid, C₆H₈O₇, (Lab grade) was obtained from M&B company.
- Industrial hydrogen was obtained from TIG Trading Limited.
- Raney nickel was obtained from Merck.
- Iso-octane (AR grade) was obtained from Mallinckrodt.

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

Types	Component	%
C-20-7-06	MoO ₃	15-20
	NiO	1-5
	Al ₂ O ₃	75-85
T-2563	WO ₃	< 10
	NiO	15-25
	Al ₂ O ₃	70-80

Apparatus and instruments

1. Apparatus for measuring pore volume of alumina support CS331-3[2] comprised of
 - Burette for charging deionized water.
 - Suction flask for charging alumina support.
 - Stand and clamp for supporting burette and suction flask.
 - Suction pump for removing trapped air from the pores of alumina supports before impregnating with solution.
2. Calcinator

The apparatus model GSM from Carbolite Furnaces Co., Ltd. was used.

3. Surface area analyzer

The apparatus model Flow SorbII 2300 from Micromeritics was used.

4. Press oil device [13]

5. Gas Chromatography-Mass Spectrometer (GC-MS)

The apparatus model GC 8000 and mass spectrometer model MD 800 from Fisons Instrument was used.

GC Condition

Column : DB-1 capillary column 30mx0.25mmIDx0.25 μ m

Carrier : Helium (flow velocity 50 cm/sec)

Oven : 80 °C (2min) to 300 °C (15min), rate 8 °C/min.

Injection temperature : 290 °C

Detector : MS (EI⁺ 70 eV)

6. Colorimeter

The Fisher ASTM Colorimeter was used. (ASTM D 1500)

7. Sulfur analyzer

The apparatus model SLFA-800 from Horiba was used.

8. Differential Scanning Calorimeter (DSC) and

Thermogravimetric Analyzer (TGA)

The apparatus model DSC 901s and TA 2950 from DuPont Instrument was used.

9. Viscometer

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

10. UV Spectrophotometer

The apparatus model 8950 from Hewlett Packard was used.

11. Nuclear Magnetic Resonance Spectrometer (NMR spectrometer)

The NMR model AC-F200 from Bruker (200 MHz) was used.

12. Pressure reactor (hydrogenator) from Parr Instrument Co., Ltd.

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

(1) Reactor (Figure 3.1)

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

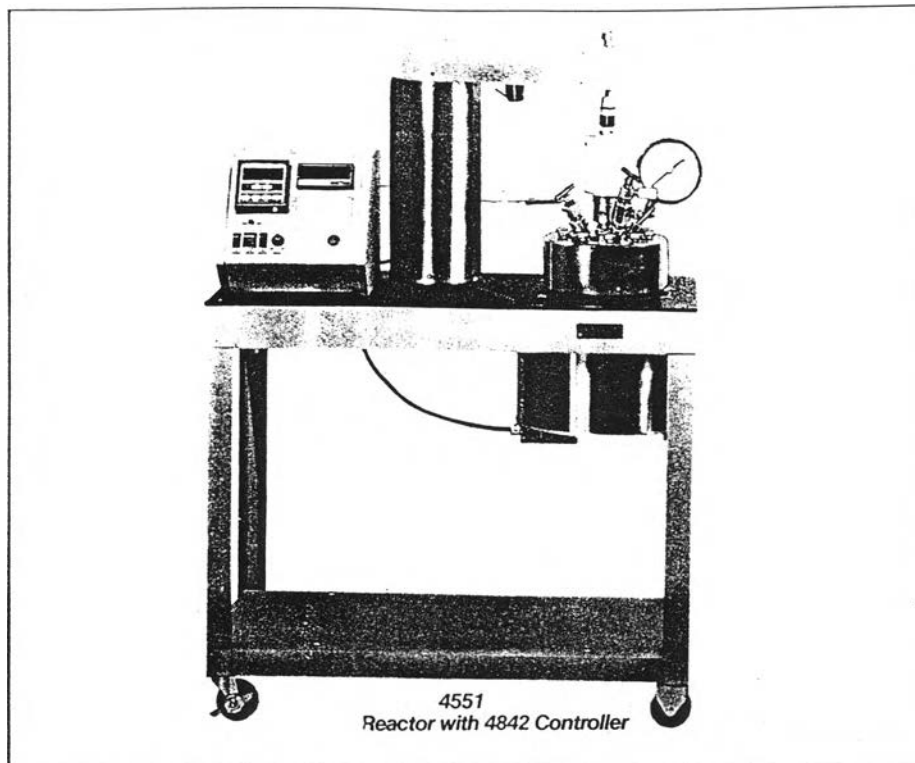
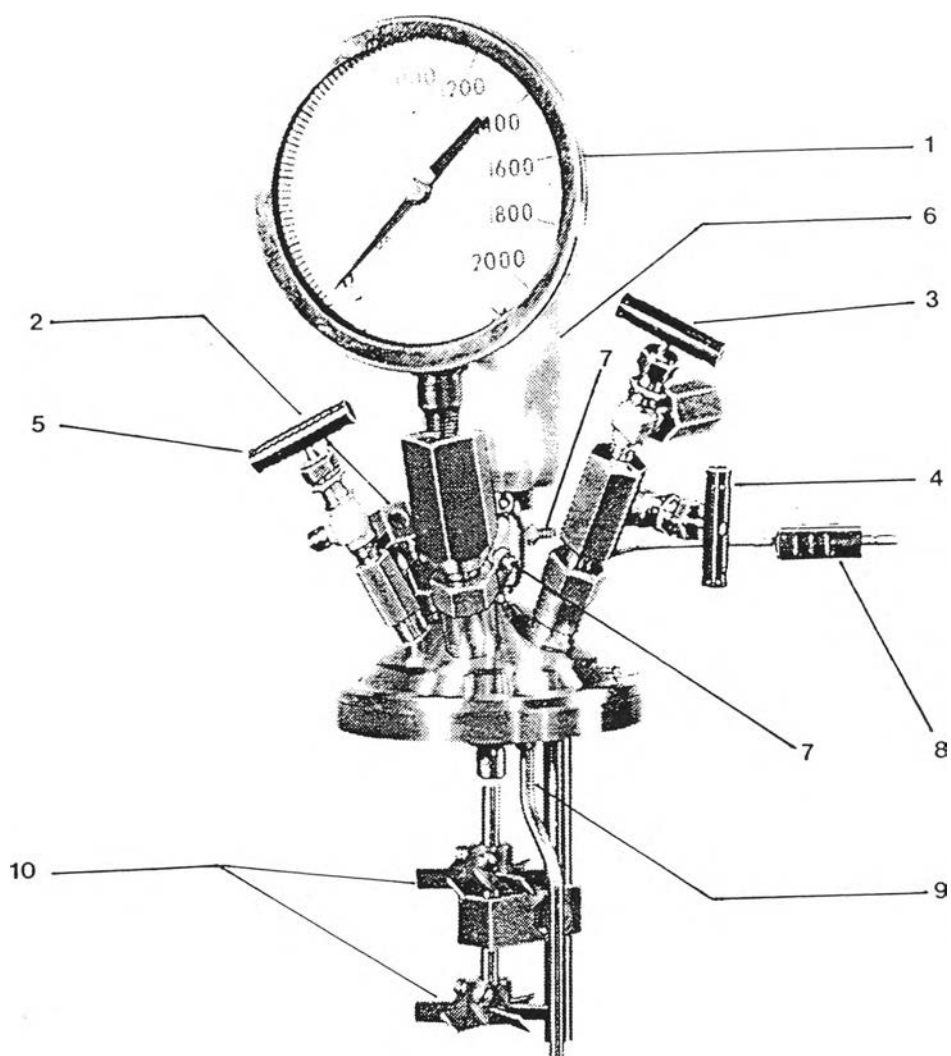


Figure 3.1 Floor Stand Reactor.

(2) Reactor fitting (Figure 3.2)

The reactor was equipped with stirrer and valves with fittings for handling various functions.



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

Figure 3.2 Reactor fitting

(3) Automatic temperature controller

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

(4) Gas controller system

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

Procedures

1. Deoiling of heavy distillate by methyl ethyl ketone (MEK) [2]

In this procedure 500 grams of heavy distillate was completely melted by heating slowly to a temperature of 60-70 °C and then was added to 1500 ml of MEK in a breaker. While vigorously stirring the mixture, the breaker was chilled to the deoiling temperature below 0°C by refrigerator. The mixture was then quickly filtered under reduced pressure through a Buchner funnel, which was cooled at 0 °C, the temperature of solution 0 °C. Suction was continued for several minutes until the oil was removed completely from the wax. The yield of wax was then determined by weighing.

2. Properties characterization

Physical and chemical properties of deoiled wax or slack wax from procedure 1 were determined using the following standard procedures:

Physical properties:

- a. Kinematics viscosity by ASTM D 445
- b. Color, Visual by ASTM D 1500
- c. Melting point by ASTM D 87
- d. Congealing point by ASTM D 938

Chemical properties:

- a. Sulfur content (%wt) by ASTM D 129
- b. The molecular weight distributions by GC-MS
- c. Aromatic content by UV spectrometer.

3. Oil content determination in slack wax [3]

Oil content of slack waxes was determined by the modified ASTM D 3235 procedure. The sample was dissolved in methyl ethyl ketone. With vigorously stirring of the mixture, the mixture was pressed by a pressing device, at ambient temperature (30 °C), to remove the solution of MEK and oil. Then the oil content in pressed waxes or slack waxes was determined by evaporating solvent from the pressed oil solution and weighing the residue. The procedure that described above was repeated until the weight of oil became unchanged.

4. Measuring pore volume of alumina support CS331-33 [2]

The alumina support (100 g) was charged in a suction flask equipped with a burette containing deionized water. The flask was connected to a vacuum pump and vacuum was applied to evacuate the air from the pores of the support. Deionized water from the burette was added to the support until it was moistened thoroughly. The volume of deionized water was determined. The procedure described above was

repeated until the water consumption by 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 support CS331-3 type was 0.64 ml/g.

5 Preparation of catalysts

a) Hydrodesulfurization catalyst: containing 10 % Mo, 5 % Co and 5 % Ni on alumina support [29,30,34]

The alumina support (100 g) was soaked about 15 minutes at room temperature in a pretreating solution, prepared by dissolving 40 g $(\text{NH}_4)_2\text{S}_2\text{O}_3$ in 200 ml deionized water. Excess pretreating solution was decanted. The pretreated alumina was dried at 120 °C, cooled and impregnated with 64 ml of an impregnating solution (pore volume of 100 g alumina support) containing 10 g citric acid, 18.41 g $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 20.18 g $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, and 20.24 g $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$. The impregnated alumina support was dried at 120 °C and then was calcined at 600 °C for 3 hours to give the hydrodesulfurization catalyst.

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

<i>Mo</i>	10 %
<i>Co</i>	5 %
<i>Ni</i>	5 %
<i>Surface area</i>	141.05 m ² /g

b) Hydroisomerization catalyst: containing 0.3 % Pt and 0.5 % F on alumina support [10-12]

An aqueous impregnating solution was prepared by dissolving 1 g of chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) 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 hours to obtain the calcined catalyst. That calcined catalyst was reimpregnated with 80 ml of aqueous solution containing NH_4F (1.22 g) (the aqueous volume equivalent to the pore volume of the alumina support), left at room temperature for one hour, and then dried at 120 °C for 16 hours to obtain the fluoride doped catalyst. This doped catalyst was calcined in air flow at the following condition (hold at 150 °C for 1 hour, raise temperature by 50 °C every 15 minutes to 400 °C, then hold at 400 °C for 1 hour) to obtain the hydroisomerization catalyst.

The components in this calcined catalyst were calculated and the surface area was determined. The results were as follows

:

<i>Pt</i>	0.3 %
<i>F</i>	0.5 %
<i>Surface area</i>	184.68 m ² /g

6 The hydrodesulfurization process

6.1 The effect of catalyst type on hydrodesulfurization

Slack wax (400 g) and the MoNiCo 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 the selected temperature (350 °C) and reaction time (4 hours). The stirring speed was set at 500 rpm. After the specified reaction time, heating was stopped and the reaction mixture was stirred until it had cooled to room temperature. The pressure was released and the gases in the reactor were trapped with 1% H₂O₂ solution. The reaction mixture was transferred to a 1 liter beaker and the catalyst was separated wax by filtration at 70 °C to give desulfurized. Sulfur content and color were measured by standard methods in procedure 2 and the results are shown in Table A2. The molecular weight distribution of the desulfurized wax was determined by GC/MS, the GC/MS chromatogram is shown in Figure A3 and the molecular weight distribution of components in the desulfurized wax is given in Table A3.

The desulfurized wax was deoiled following procedure 3. The percent oil content of desulfurized wax (or hydrotreated wax) was calculated. The result is shown in the Table A2.

Following the procedure described above except for MoNI/Al₂O₃, NiW/Al₂O₃ and Raney nickel catalysts. For each experiment, the reaction mixture was worked up in the same manner as above. The sulfur content and color of these samples were measured by standard methods in procedure 2 and the results are recorded in Table A2. The molecular weight distributions of these desulfurized waxes were determined by GC/MS. The GC/MS chromatograms are shown in Figure A3, and the molecular weight distributions of components in these waxes are collected in Table A3.

The percent oil content of the desulfurized waxes were determined following procedure 3. The results are shown in the Table A2.

6.2 The effect of temperature on hydrodesulfurization

Following the procedure in procedure 6.1 except the reaction was operated at various temperatures (200, 250, 300, 350 and 400 °C) using the optimum catalyst, MoCoNi, as determined from procedure 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 components are given in Table A5. The sulfur content and color of these waxes were measured by standard methods in procedure 2 and the results are given in Table A4.

The percent oil content of the desulfurized waxes were determined following procedure 3. The results are presented in Table A4.

6.3 The effect of hydrogen pressure on hydrodesulfurization

Following procedure similar to that in procedure 6.2 except the reaction was operated at various hydrogen pressures (300, 400, 500 and 600 psig) at the optimum temperature of 400 °C obtained from procedure 6.2. The reaction mixture was worked up in the same manner as described in procedure 6.1. The GC/MS chromatograms of the four products are shown in the Figure A5 and the molecular weight distributions of components are collected in Table A7. Sulfur content and color of these desulfurized waxes were measured by standard methods in procedure 2 and the results are given in Table A6.

The percent oil content of the desulfurized waxes were determined following procedure 3. The results are presented in Table A6.

6.4 The effect of reaction time on hydrodesulfurization

Following the procedure as described in procedure 6.3 except the reaction was operated at various reaction times (4, 6, 8 and 10 hours) at the optimum hydrogen pressure of 600 psig obtained from procedure 6.3. The reaction mixture was worked up in the same manner as described in procedure 6.1. The GC/MS chromatograms of the four products are shown in the Figure A6 and the molecular weight distributions of components are given in Table A9. The sulfur content and color of hydrodesulfurized waxes were measured by standard methods in procedure 2 and the results are shown in Table A8.

The percent oil content of the desulfurized waxes were determined following procedure 3. The results are presented in Table A8.

6.5 The effect of catalyst concentration on hydrodesulfurization

Following the procedure as described in procedure 6.4 except the reaction was operated at various catalyst concentrations (5.0, 2.0, 1.0, 0.5 and 0.2 % by weight of slack wax) at the optimum reaction time of 8 hours obtained from procedure 6.4. The reaction mixture was worked up in the same manner as described in procedure 6.1. The GC/MS chromatograms of the five products are shown in Figure A7 and the molecular weight distributions of components are given in Table A11. The sulfur content and color of desulfurized waxes were measured by standard methods in procedure 2 and the results are given in Table A10.

The percent oil content of the desulfurized waxes were determined following procedure 3. The results are recorded in Table A10.

7 Hydroisomerization process

7.1 The effect of temperature on hydroisomerization

Desulfurized wax (400 g), obtained from procedure 6.5 at the definable optimum operating condition and the Pt/F hydroisomerization catalyst (24 g, from procedure 5b) were placed in the stainless steel reactor. The gas in the reactor was replaced by hydrogen gas by successive dilution and the hydrogen gas pressure in the reactor was adjusted to 600 psig. The reaction was operated at the selected reaction time (4 hours) with stirring speed was set at 500 rpm for various reaction temperatures (250, 300, 350, and 400 °C). After 4 hours, heating was stopped and the reaction mixture was stirred until it had cooled to room temperature. The pressure was released and the gases in the reactor were trapped in 1% H₂O₂ solution. The reaction mixtures were transferred to 1 liter beakers and the catalysts were separated by filtration at 70 °C to give the isomerized waxes.

The molecular weight distributions of the four isomerized waxes were determined by GC/MS, the GC/MS chromatograms are shown in Figure A8, and the molecular weight distributions of components in these waxes are collected in Table A13. Color of the isomerized waxes were measured by ASTM D 1500 and the results are reported in Table A12.

The isomerized waxes were deoiled, according to the following procedure 3, to obtain a separated oil fraction. The percent oil content of each isomerized wax was calculated. The results are shown in the Table A12.

7.2 The effect of hydrogen pressure on hydroisomerization

Following a procedure similar to procedure 7.1 except various hydrogen pressures (300, 400, 500, and 600 psig) at the optimum temperature of 300 °C from procedure 7.1 were used. The reaction mixture was worked up in the same manner as described in procedure 7.1. The molecular weight distributions of the four isomerized waxes were determined by GC/MS. The GC/MS chromatograms are shown in Figure A9, and the molecular weight distributions of components in these waxes are given in Table A14. Color of isomerized waxes were measured by ASTM D 1500 and the results are shown in Table A12.

The percent oil content of the isomerized waxes were determined according to the following procedure 3. The results are recorded in Table A12.

7.3 The effect of catalyst concentration on hydroisomerization

Following a procedure similar to procedure 7.2 except various catalyst concentrations (1, 3, 4, 5, 6 and 7 % by wt of desulfurized wax) at the optimum hydrogen pressure of 600 psig from procedure 7.2. The reaction mixture was worked up in the same manner as described in procedure 7.1. The molecular weight distributions of the six isomerized waxes were determined by GC/MS. The GC/MS chromatograms are shown in Figure A10, and the molecular weight distributions of components in these waxes are collected in Table A15. Color of the hydroisomerized waxes were measured by ASTM D 1500 and the results are shown in Table A12.

The percent oil content of the isomerized waxes were determined following procedure 3. The results are recorded in Table A12.

7.4 The effect of reaction time on hydroisomerization

Following a procedure similar to procedure 7.3 except various reaction times (4, 6, 8, 10, and 12 hours) at the optimum catalyst concentration of 6 % by wt of desulfurized waxes from procedure 7.3 were used. The reaction mixture was worked up in the same manner as described in procedure 7.1. The molecular weight distributions of the five isomerized waxes were determined by GC/MS. The GC/MS chromatograms are shown in Figure A11, and the molecular weight distributions of components in these waxes are collected in Table A16. Color of the hydroisomerized waxes were measured and the results are reported in Table A12.

The percent oil contents of the isomerized waxes were determined following procedure 3. The results are given in Table A12.

8. Characterization of the properties of wax from hydrodesulfurization and hydroisomerization

Physical and chemical properties of wax at the suitable condition were determined following standard procedures :

- a. Kinematics viscosity by ASTM D 445.
- b. Melting point by ASTM D 87.
- c. The carbon distribution by GC/MS.
- d. Aromatic content by UV absorption.

9. Characterization of oil fractions from the hydrotreating process

The hydrotreated wax, obtained from the hydrotreatment process was distilled under reduced pressure to determine the light

fraction (boiling point less 330 °C). The light fraction was weighed and the determined values are reported in Table 4.5. The products with boiling point higher than 330 °C were deoiled following procedure 3. The oil fractions obtained from procedure 3 were dewaxed by MEK (at dewaxing temperature -10 °C) to obtain lube base oil. The lube base oil, after removing solvent, was weighed and the percent of lube base is reported in Table 4.5. After that, the properties of lube base oil were characterized by standard procedures as follows:

Physical properties :

- | | |
|-------------------------|----------------|
| a. Kinematics viscosity | by ASTM D 445 |
| b. Viscosity index | by ASTM D 2270 |
| c. Color, Visual | by ASTM D 1500 |
| d. Pour point | by ASTM D 97 |

Chemical properties :

- | | |
|--|---------------|
| a. Sulfur content, %wt | by ASTM D 129 |
| b. The percentage of oxidative compounds | by TGA |
| c. The molecular weight distributions | by GC/MS |