

CHAPTER III

EXPERIMENTAL

Materials

1. Heavy distillate was supplied from Fang Refinery Plant.
2. Methyl Ethyl Ketone (MEK) was commercial grade and available from Grand Chemical Inc.,. It was purified by distillation.
3. Industrial hydrogen gas was available from TIG Trading Ltd..
4. Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) were analytical grades and available from Carlo Erba.
5. Ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) was analytical grade and available from J.T. Baker Inc.,.
6. Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was analytical grade and available from Unilab.
7. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was laboratory grade available from May & Baker Company Co., Ltd..
8. Ammonium fluoride (NH_4F) and ammonium thiosulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_3$) were analytical grades and available from BDH Ltd..
9. Iso-octane was analytical grade and available from Mallinckroat.
10. Dimethyl sulfoxide ($(\text{CH}_3)_2\text{SO}$) was spectrophotometric grade and available from Fluka Chemika.
11. Raney nickel was available from Merck.

12. Alumina support (CS331-3 type) and heterogeneous catalysts T-2563 (WO_3/NiO on alumina) and C20-7-06 (MoO_3/NiO on alumina) were supplied from United Catalyst Inc.,. The approximate amount of component in these catalysts are shown in Table 3.1.

Table 3.1 The approximate amount of components in C20-7-06 and T-2563 catalysts.

Catalyst Types	Components	% by weight
C20-7-60	MoO_3	15-20
	NiO	1-5
T-25263	WO_3	< 10
	NiO	15-25

13. Shell Risella White Oil 15 is technical grade white oil and was supplied from Shell Thailand Ltd.. The specification of this white oil is shown in Table 3.2.

Table 3.2 Specifications of Shell Risella White Oil 15.

Properties	Specification
Color, Saybolt	+30
Viscosity, cst, at 40°C	15
API	31.1

Apparatus and Instruments

1. Apparatus for Measuring Pore Volume of Alumina Support CS331-3
 - Buret for charging deionized water.
 - Suction flask for charging alumina support.
 - Stand and clamp for tightening buret and suction flask.
 - Suction pump for trapping air in the pores of alumina supports before impregnating the solution.
2. Calcinator
The apparatus model GSM from Cabolite Furnaces was used.
3. Nuclear Magnetic Resonance Spectrometer (NMR Spectrometer)
The NMR model AC-F 200 from Bruker (200 MHz) was used.
4. Gas Chromatograph-Mass Spectrometer (GC-MS)
The apparatus model GC 8000 series and Mass spectrometer model MD 800 from Fison Instrument were used.
5. UV Spectrophotometer
The apparatus model 8452A from Hewlett Packard was used.
6. Viscometer
The apparatus model K-234 A from Hochler Instrument Co., Inc. was used.
7. Pour Point Tester
The apparatus model A 82 from HAAKE was used.
8. Sulfur Analyzer
The apparatus model SLFA-800 from HORIBA was used.
9. Colorimeter
The Fisher ASTM Colorimeter was used.
10. Surface Area Analyzer
The instrument model Micromeritics Flow Sorb II 2300 was used.

11. High Pressure Reactor

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

1) Reactor (Figure 3.1)

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

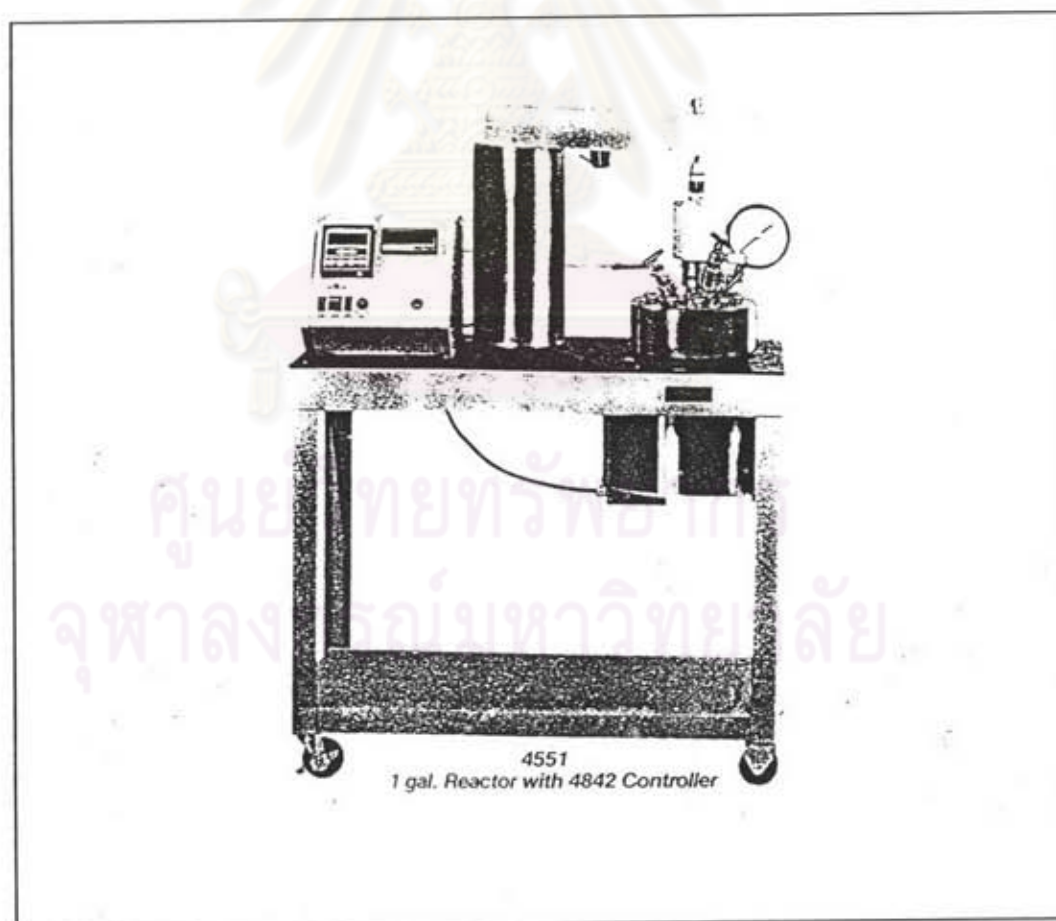


Figure 3.1 Floor stand reactor.

2) Reactor Fitting (Figure 3.2)

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

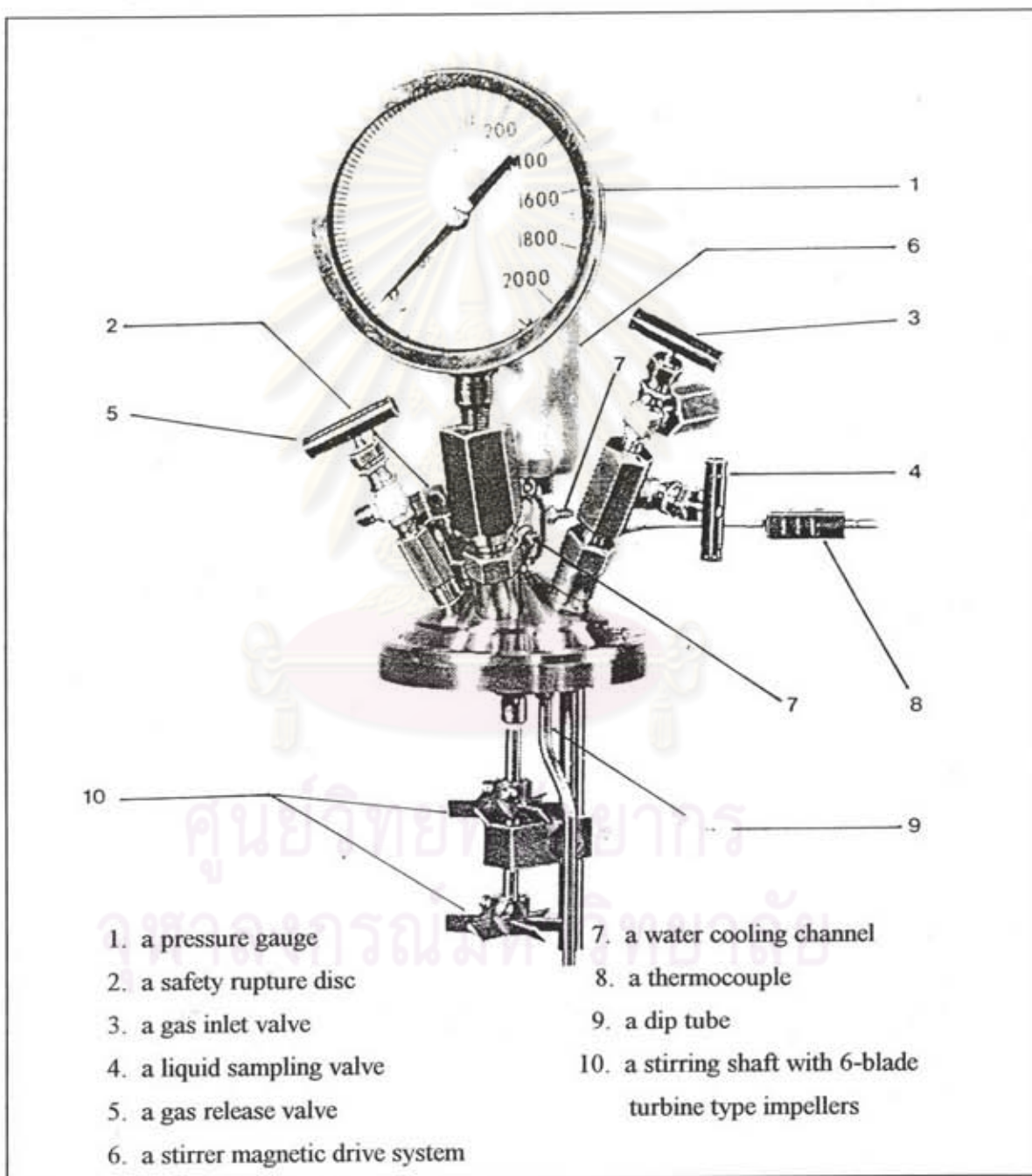


Figure 3.2 Reactor fitting.

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. Its stirring speed could be adjusted in the range of 0-1000 rpm.

4) Gas Controllers System

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

Procedure

1. Dewaxing Process [3,4]

The three main steps for solvent dewaxing process were precipitation, filtration and solvent recovery. Beginning with precipitation, light distillate (600 g) was heated slowly to temperature of 60-70°C until wax was liquefied completely then cool methyl ethyl ketone (1800 ml) was added. The ratio by volume between solvent and oil was 3:1. The solvent oil mixture was chilled to temperature of 0°C by refrigeration. The wax crystals were then filtered through a buchner funnel under reduced pressure. The mixture was quickly filtered with suction before the temperature had a chance to rise much above 5 °C and the suction was allowed for several minutes until 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.

2. Determination of Properties of Dewaxed Oil

2.1 Physical properties:

- 1) Kinematic viscosity by ASTM D-445
- 2) Viscosity Index (VI) by ASTM D-2270
- 3) Color, Visual by ASTM D-1500
- 4) Color, Saybolt by ASTM D-156
- 5) Pour point by ASTM D-97
- 6) API gravity by ASTM D-1298

2.2 Chemical properties:

- 1) Sulfur content, %wt by ASTM D-129
- 2) Aromatic content, %by mole atom of carbon was determined by ^{13}C -NMR

The solution of about 0.1 g of oil in 3 ml of CDCl_3 was subjected to ^{13}C -NMR analysis.

- 3) The carbon distribution was determined by GC-MS.

Concentration of Sample: 1000 ppm of oil in hexane

GC Conditions:

Capillary Column: DB1, 30 m x 0.25 mm ID, 0.25 μm

Temperature Program: 80°C(1 min) to 200°C(1 min) at rate 8°C/min and to 300(15min) at rate 3°C/min

Carrier Gas : Helium at flow rate of 55 cm/sec

Injector Temperature: 280°C

Split Ratio: 50:1

Detector: MS (EI⁺ 70 eV)

4) UV absorption of DMSO extract of oil by ASTM D 2269-73

A mixture of 25 ml of oil and 25 ml of hexane was extracted with 5 ml of DMSO. Then the DMSO extract of oil was determined the absorbance compared to the solvent control (DMSO extract of 25 ml of hexane) through the range 250 to 450 nm by using 1 cm of cell path length.

5) Direct UV absorptivity of oil in iso-octane by ASTM D 2008

The solution of 1g/l of oil in iso-octane was subjected to UV absorption measurement compared to iso-octane through the range 250 to 450 nm by using 1 cm of cell path length. The absorptivity of solution of oil is calculated by $a = A/(bC)$. (a = absorptivity, A = absorbance, b = cell path length in unit of cm, C = concentration of oil in iso-octane in unit of g/l) In this study, the absorptivity is equal absorbance.

The percentages of dewaxed oil and wax fractions are shown in Figure 4.1. The ^{13}C -NMR spectrum and the GC-MS chromatogram of dewaxed oil are shown in Figure A1 and Figure A2, respectively. The UV spectra of the solution of dewaxed oil in iso-octane and DMSO extract of dewaxed oil are shown in Figure A2. The properties of dewaxed oil are recorded in Table 4.1.

3. Measuring Pore Volume of Alumina Support [3]

The alumina supports (100 g) were subjected into the suction flask which equipped with a buret containing deionized water. These apparatuses were connected with vacuum pump. Then the vacuum pump was applied to evacuate an air from the pore of those supports. Deionized water from buret was added to the supports thoroughly. The volume of deionized water was

determined. The procedure that described above was repeated until the water consumption by support became constant. The pore volume of 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.

4. Preparation of Catalysts

4.1 Hydrodesulfurized Catalyst:

(5%Ni-10%Mo-5%Co/Al₂O₃) [24,27]

The alumina support (100 g) was soaked in a pretreating solution, prepared by dissolving (NH₄)₂S₂O₃ (40 g) in deionized water (200 ml), for about 15 minutes at room temperature. The excess pretreating solution was drained off. The pretreated alumina support was dried at 120°C and then was added to an impregnating solution (64 ml) comprising 18.41 g of (NH₄)₂Mo₇O₂₄.4H₂O, 20.24 g of NiCl₂.6H₂O, 20.18 g of CoCl₂.6H₂O, and 10 g of citric acid in a sufficient amount of water to give 64 ml of solution (pore volume of alumina support (100 g) was proportional to 64 ml). 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 shown as follow:

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

4.2 Hydrogenation Catalyst: 0.3%Pt/Al₂O₃ [17-19]

An aqueous impregnating solution was prepared by dissolving 1 g of chloroplatinic acid (H₂PtCl₆.6H₂O) 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 was calcined at 450 °C for 3 hours to obtain the hydrogenation catalyst.

The platinum content in this calcined catalyst was calculated and the surface area was determined. The results are shown as follow:

Platinum	0.3%
Surface area	190.52 m ² /g

5. Hydrodesulfurization Stage

5.1 The Effect of Catalyst on Hydrodesulfurization

Dewaxed oil (400.0 g) and the NiMo/AlO₃ catalyst (20 g) were placed in a stainless steel reactor. The gas in the reactor was replaced by hydrogen gas for several times and then hydrogen gas pressure in this reactor was adjusted to 500 Psi. The reaction was operated at selected temperature (350 °C) and reaction time (3 hours). The stirring speed was maintained at 500 rpm. After the reaction took place, heating was stopped and the reaction mixture was stirred until that mixture was cooled to room temperature. Next, the pressure was released and the content in reactor was transferred to a 1 liter beaker and the catalyst was separated by suction filtration to give 392.2 g of hydrodesulfurized oil.

The molecular weight distribution of hydrodesulfurized oil was analyzed by GC-MS. The sulfur content and the color of hydrodesulfurized oil were measured as described in the procedure 2 (p.39). The low boiling point products were separated by reduced pressure distillation to obtain the hydrodesulfurized oil with a boiling range above 330°C. The yield of hydrodesulfurized oil was 96.0%

Following the procedure similar to that described above except various types of catalyst (NiW, NiMoCo, and Raney nickel) were used. After that the reaction mixture was worked up in the same manner to give the desired products. These oils were analyzed above.

The GC-MS chromatograms of these hydrodesulfurized oils are shown in Figure A4. The sulfur content, the color and the percent yield of hydrodesulfurized oils are presented in Table 4.3. The effect of catalyst type on sulfur content, color and percent yield of hydrodesulfurized oil are shown in Figure 4.2-4.4, respectively.

5.2 The Effect of Reaction Temperature on Hydrodesulfurization

Following the same procedure as referred in the experiment 5.1 except the various reaction temperatures (250, 300, 350 and 400 °C) and the suitable catalyst obtained from the experiment 5.1 were used. After the reaction was completed, the mixture was worked up in the same manner to give the desired products. The properties of these hydrodesulfurized oils were determined as described in the experiment 5.1.

The GC-MS chromatograms of hydrodesulfurized oils at various temperatures are shown in Figure A5. The sulfur content, the color and

the percent yield of hydrodesulfurized oils are presented in Table 4.4. The effect of reaction temperature on sulfur content, color and percent yield of hydrodesulfurized oil are shown in Figure 4.5-4.7, respectively.

5.3 The Effect of Hydrogen Pressure on Hydrodesulfurization

Following the same procedure similar to that described in the experiment 5.2 except various hydrogen pressures (300, 400, 500 and 600 Psig) and the optimum temperature obtained from the experiment 5.2 were used. After the reaction was completed, the mixture was worked up in the same manner to give the desired products. The properties of these hydrodesulfurized oils were determined that described in the experiment 5.1.

The GC-MS chromatograms of hydrodesulfurized oils at various hydrogen pressures are shown in Figure A6. The sulfur content, the color and the percent yield of hydrodesulfurized oils are presented in Table 4.5. The effect of hydrogen pressure on sulfur content, color and percent yield of hydrodesulfurized oil are shown in Figure 4.8-4.10, respectively.

5.4 The Effect of Catalyst Concentration on Hydrodesulfurization

Following the same procedure as described in the experiment 5.3 except the various catalyst concentrations (1, 3, 5, and 7 % by weight of oil) and the optimum hydrogen pressure obtained from the experiment 5.3 were used. After the reaction was complete, the mixture was worked up in the same

manner to give the desired products. The properties of these hydrodesulfurized oils were determined as described in the experiment 5.1.

The GC-MS chromatograms of hydrodesulfurized oils at various catalyst concentrations are shown in Figure A7. The sulfur content, the color and the percent yield of hydrodesulfurized oils are presented in Table 4.6. The effect of catalyst concentration on sulfur content, color and percent yield of hydrodesulfurized oil are shown in Figure 4.11-4.13, respectively.

5.5 The Effect of Reaction Time on Hydrodesulfurization

Following the same procedure as described in the experiment 5.4 except the various reaction times (2, 3, 4, 5 and 6 hours) and the optimum catalyst concentration obtained from the experiment 5.4 were used. After the reaction was completed, the mixture was worked up in the same manner to give the desired products. The properties of these hydrodesulfurized oils were determined as described in the experiment 5.1.

The GC-MS chromatograms of hydrodesulfurized oils at various reaction times are shown in Figure A8. The sulfur content, the color and the percent yield of hydrodesulfurized oils are presented in Table 4.7. The effect of reaction time on sulfur content, color and percent yield of hydrodesulfurized oil are shown in Figure 4.14-4.16, respectively.

5.6 The Effect of Double Hydrodesulfurization

In the first hydrodesulfurized step, dewaxed oil (400.0 g) was carried out, following the same procedure as described in the experiment 5.5 at reaction time of 3 hours and other optimum conditions in the experiment 5.1-5.4. After the reaction was completed, the mixture was worked up as usual, heating was stopped and the reaction mixture was stirred until that mixture was cooled to room temperature. The pressure in the reactor was then released. The second hydrodesulfurization step was begun by replacing residual hydrogen sulfide in the reactor with hydrogen gas for several times, then hydrogen gas pressure in this reactor was adjusted to desired pressure. The reaction was heated to as same temperature and time as the first hydrodesulfurization step, to give 392.5 g of the second hydrodesulfurized oil.

Following the procedure similar to that described above except various reaction times of both steps were set at 2 and 4 hours, respectively. After the reaction was completed, the mixture was worked up in the same manner to obtain the desired second hydrodesulfurized oils which properties were determined as described in the experiment 5.1.

The sulfur content and the color of the second hydrodesulfurized oils are presented in Table 4.8. The effect of double hydrodesulfurization on sulfur content and color of the second hydrodesulfurized oils compared with the first hydrodesulfurized oil operated at 5 and 6 hours are shown in Figure 4.17-4.18, respectively.

5.7 Determination of Properties of Hydrodesulfurized Oil

The hydrodesulfurization oil of the optimum conditions in the experiment 5.6 was distilled by reduced pressure distillation to obtain the products with a boiling range of 330 to 450°C for hydrogenation stage. The properties of this hydrodesulfurized oil were determined as same as dewaxed oil that described in the procedure 2 (p.39).

The GC-MS chromatogram and the ^{13}C -NMR spectrum of this hydrodesulfurized oil are shown in Figure A9 and A10, respectively. The UV spectra of DMSO extract of hydrodesulfurized oil and of dewaxed oil are compared in Figure A11. The UV spectra of solutions of hydrodesulfurized oil in iso-octane and of dewaxed oil in iso-octane are compared in Figure A12. The properties of hydrodesulfurized oil compared with dewaxed oil are recorded in Table 4.9.

6. Hydrogenation Stage

6.1 The Effect of Temperature on Hydrogenation

The hydrodesulfurized oil (400 g), in boiling range of 330 to 450°C, which obtained from the experiment 5.6 at the optimum conditions and $\text{Pt}/\text{Al}_2\text{O}_3$ (20g) as hydrogenation catalyst were placed in a stainless steel reactor. The gas in reactor was replaced by hydrogen gas for several times and then hydrogen gas pressure in this reactor was adjusted to 600 Psig. The reaction was operated at 3 hours by various reaction temperatures (275, 300, and 350°C, respectively) and the stirring speed was maintained at 500 rpm.

After the reaction took place, heating was stopped and the reaction mixture was stirred until that mixture was cooled to room temperature. Next, the pressure was released and the content in the reactor was transferred to a 1 liter beaker and the catalyst was separated by suction filtration to give oil products. The low boiling products were separated by reduced pressure distillation to obtain hydrogenated oil in a boiling range above 330°C. The color of these hydrogenated oils were measured as Saybolt color following ASTM D-156. The sulfur content, UV absorption of DMSO extract and UV absorptivity of solution of hydrogenated oil in iso-octane were determined.

The UV spectra of DMSO extracts of hydrogenated oils at various temperatures are shown Figure A13. The UV spectra of solutions of hydrogenated oils in iso-octane are shown in Figure A14. The color, the sulfur content and the percent yield of hydrogenated oils are recorded in Table 4.10. The effect of reaction temperature on UV absorption of DMSO extract and direct absorptivity of hydrogenated oil are presented in Figure 4.19 and 4.20, respectively.

6.2 The Effect of Reaction Time on Hydrogenation

Following the procedure similar to the experiment 6.1 except the various reaction times (3, 6, and 9 hours) and the suitable reaction temperature obtained from the experiment 6.1 were used. After the reaction was completed, the mixture was worked up in the same manner to give the desired products. The properties of hydrogenated oils were determined in the same way as hydrogenated oils in the experiment 6.1.

The UV spectra of DMSO extracts of hydrogenated oils at various reaction times are shown Figure A15. The UV spectra of solutions of hydrogenated oils in iso-octane are shown in Figure A16. The color, sulfur content and percent yield of hydrogenated oils are recorded in Table 4.11. The effect of reaction time on UV absorption of DMSO extract and direct absorptivity of hydrogenated oil are presented in Figure 4.21 and 4.22, respectively.

6.3 The Effect of Multiple Hydrogenation

Following the procedure of the first hydrogenation step similar to the experiment 6.2 at temperature of 300°C under hydrogen pressure of 600 Psi for 3 hours. After the reaction mixture was worked out, heating was stopped and the reaction mixture was stirred until that mixture was cooled to room temperature. Next, the pressure was released which keeping the content in reactor. The second hydrogenation step was begun by replacing residual hydrogen sulfide in reactor with hydrogen gas for several times, then hydrogen gas pressure in this reactor was adjusted to 600 Psig. The reaction was then heated to the temperature and time as in the first hydrodesulfurization step. After that heating was stopped and the reaction mixture was stirred until that mixture was cooled to room temperature. Next, the pressure was released. About 50 g of the second hydrogenated oil were collected and were distilled to test the properties in the same way as the hydrogenated oil with a boiling range above 330°C following the experiment 3.3.7.2. The remain hydrogenated oils were still in the reactor and then hydrogenated in the third and the forth steps, respectively.

The UV spectra of DMSO extracts of hydrogenated oils at each step are shown in Figure A17. The UV spectra of solutions of hydrogenated oils in iso-octane are shown in Figure A18. The color, the sulfur content and the percent yield of hydrogenated oils are recorded in Table 4.12. The effect of multiple hydrogenation on UV absorption of DMSO extract and Direct absorptivity of hydrogenated oil are presented in Figure 4.23 and 4.24, respectively.

6.4 Determination of Properties of White Oil

The hydrogenated oil that passed the color and the UV absorption specifications of white oil was used to determined other properties as same as dewaxed oil and hydrogenated oil.

The ^{13}C -NMR spectrum of white oil thus obtained and that of Shell Risella White oil 15 (commercial technical grade white oil) are shown in Figure A19, A20, respectively. The GC-MS chromatograms of white oil and Shell Risella White oil 15 are shown in Figure A21. The UV spectrum of DMSO extract of white oil, and the UV spectrum of solution of white oil in iso-octane, compared with Shell Risella White Oil 15 are shown in Figure A22, A23, respectively.