

CHAPTER 3

EXPERIMENTATION

3.1 Material

- Heavy distillate was supported from Fang Refinery.
- Alumina support was commercial available from United Catalyst Inc.,. It was CS-303 type and its specifications were shown in table 3.1 and table 3.2 [19]
- Methyl Ethyl Ketone (MEK) was commercial available from Grand Chemical Inc.,.
- Hydrogen, oxygen and air gas were available from T.I.G. Trading Limited.
- Nickel nitrate hexahydrate ($\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$) was available from Carlo Erba.
- Ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) was available from Carlo Erba.
- Sulfuric acid was available from BDH.
- Sodium hydroxide was available from Fluka.
- Fuller's earth was available from Fluka.
- Cyclohexene was available from Fluka.
- Universalindikator pH 0-14 was available from Merck.

Table 3.1 Typical chemical properties of support
type CS-303 from United Catalyst Inc.,

Chemical Composition	Weight Percent
Aluminium Oxide	99.2
Silica Oxide	< 0.05
Iron Oxide	< 0.05
Calcium Oxide	< 0.01
Magnesium Oxide	< 0.01
Titanium Oxide	< 0.05
Potassium Oxide	< 0.05
Sodium Oxide	< 0.15
Sulfur	< 0.15
Chlorides	< 0.02

Table 3.2 Typical physical properties of support
type CS-303 from United Catalyst Inc.,

Physical Properties	
Surface Area m^2/g	3
Pore Volume cc/g	0.15-0.30
Density lbs/CF	65

3.2 Apparatus

3.2.1 Apparatus for preparing catalyst by dry impregnation

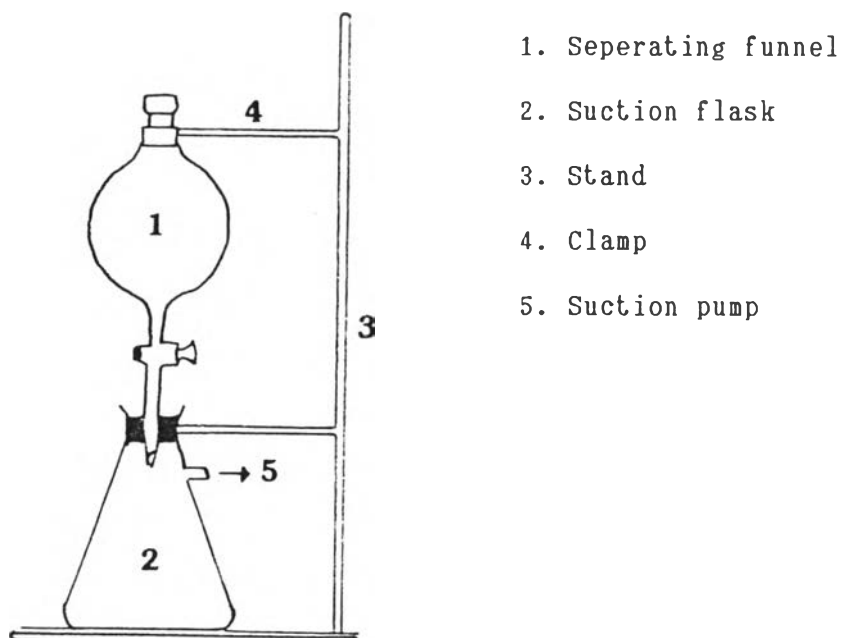


Figure 3.1 The apparatus for preparing catalyst by dry impregnation method

The important apparatus

1. Separating funnel for charging precursor salt solutions.

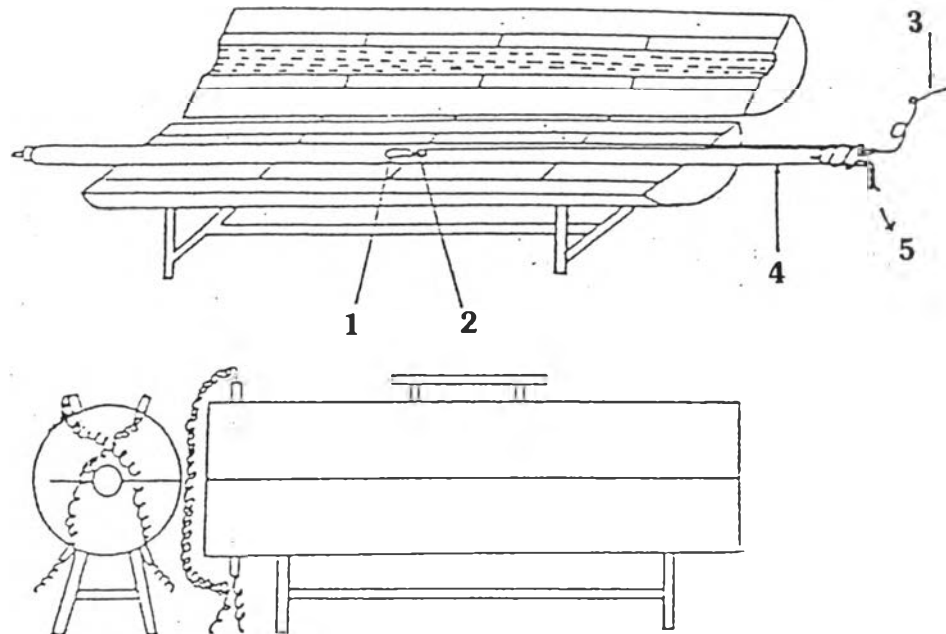
2. Suction flask for charging alumina support.

3,4 Stand and clamp for tightening separatory funnel and suction flask.

5. Suction pump for trapping air in the pores of alumina supports before impregnating the solution.

3.2.2 Apparatus for calcination [20]

1. Calcinator



- | | |
|--------------------------------------|----------------|
| 1. A tunnel kiln | 2. Catalyst |
| 3. Thermocouple | 4. Quartz Tube |
| 5. Tube connect to bubble flow meter | |

Figure 3.2 Calcinator

2. Bubble flow meter



Figure 3.3 Bubble flow meter

3.2.3 Infrared Spectrophotometer

The apparatus model 780 from Perkin Elmer was used.

3.2.4 Inductively Coupled Plasma Emission Spectrometer

The apparatus model 1000 from Perkin Elmer Plasma was used.

3.2.5 Hydrogenator

All experiments for the hydrogenation study of lubricating base oils were carried out in the hydrogenation apparatus which consisted of four parts as follow:

1. Reactor (figure 3.4)

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 of 0-2000 psig and in temperature 0-450 °C.

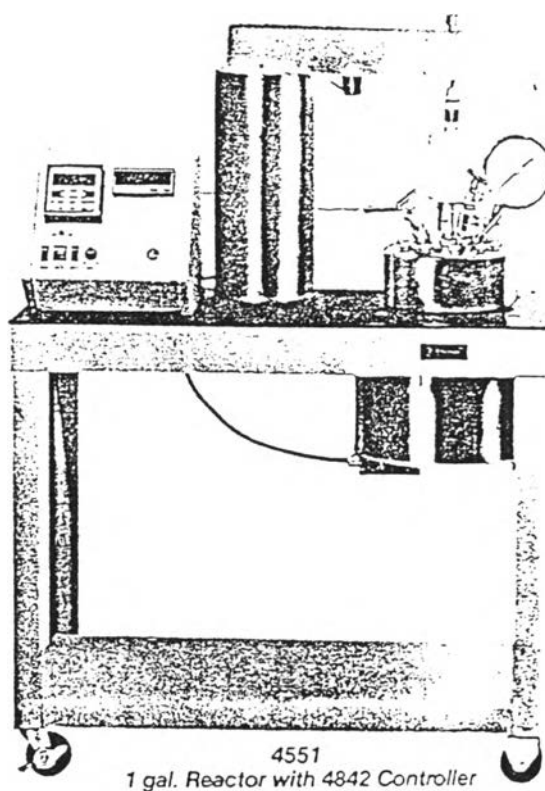


Figure 3.4 Floor Stand Reactor

2. Reactor fitting (figure 3.5)

The stirred reactor was equipped with convenient valves and fittings for handling the various functions.

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 motoring 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).

3.2.6 Viscosity

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

3.2.7 Pour Point

The apparatus model A 82 from HAAKE was used.

3.2.8 Color

The Fisher ASTM Colorimeter was used.

3.2.9 % Sulfur

The apparatus model SLFA-800 from HORIBA was used.

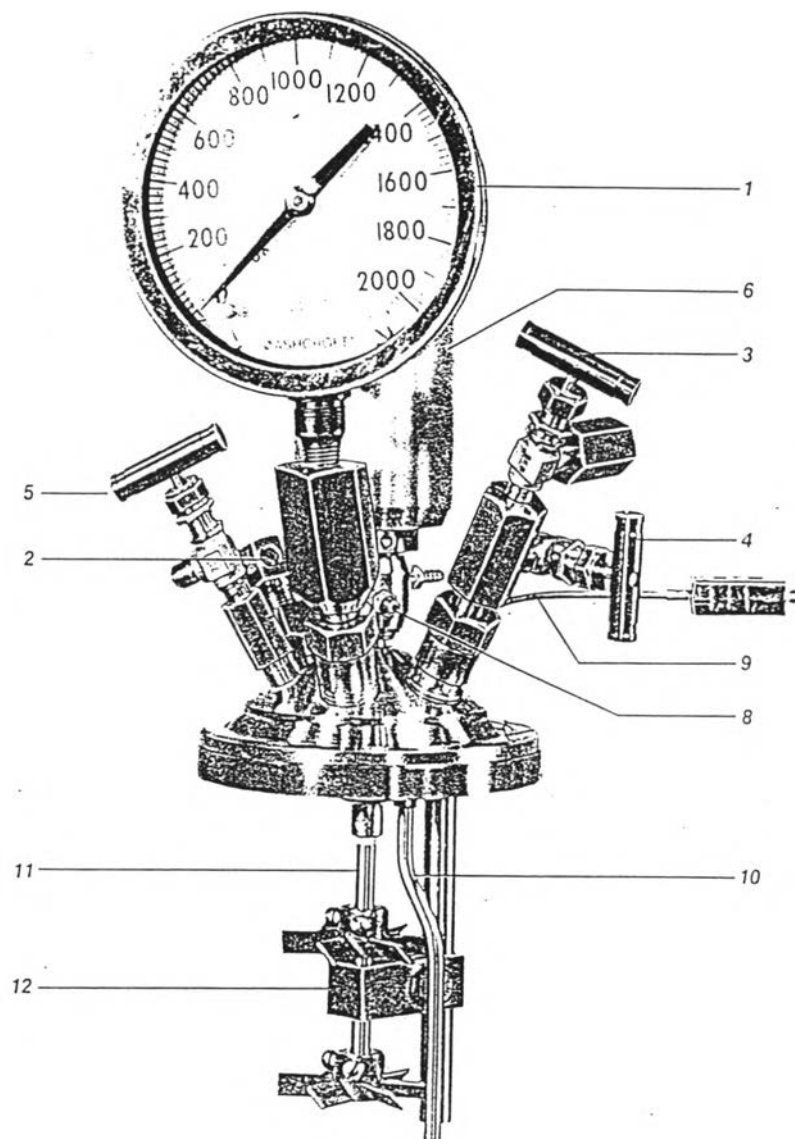
3.2.10 C^{13} -Nuclear Magnetic Resonance Spectrometer

The NMR model AC-F 200 from Bruker operation at

50.32 MHz was used.

3.2.11 Thermogravimetric Analyzer

The TGA model TA 2950 from Du Pont Instrument was used.



- | | |
|----------------------------------------------------------|------------------------------------|
| 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 3.5 Reactor fitting

3.3 Procedure

3.3.1 Dewaxing of heavy distillate by methyl ethyl ketone [5]

Dewaxing temperature = -15°C

Solvent/oil ratio by volume = 3:1

This process consists of three main segments-precipitation, filtration and solvent recovery. Precipitation began with slowly heating of heavy distillate (749 g) to temperature of 45°C to completely dissolve wax before adding cooled methyl ethyl ketone (2700 ml). The solvent oil mixture was chilled to the dewaxing temperature of -15°C by refrigeration. The wax crystals were then filtered through a buchner funnel under reduced pressure. The mixture was quickly filtered before the temperature had a chance to rise much above 5°C and allowed suction to continue for several minutes to completely remove oil from the wax. The filtrate was collected and the oil was recovered from the filtrate by simple distillation.

3.3.2 Determination of the physical and chemical properties of dewaxed oil as follow:

Physical properties

1. Colour, Visual by ASTM D 1500

2. Kinematic viscosity by ASTM D 445
3. Viscosity index by ASTM D 2270
4. Pour point by ASTM D 92
5. % Sulfur (by weight) by ASTM D 129

Chemical properties

1. The percentages of oxidative compounds were determined by Thermogravimetric Analyzer.
2. The composition ($\%C_A, \%C_P, C_N$) of dewaxed oil was determined by C^{13} -NMR

3.3.3 Acid-Clay Treatment [22]

The dewaxed oil (408 ml) was heated to 30 °C to reduce its viscosity, so as to assist mixing with acid. Concentrated sulfuric acid (10% by volume of oil) was added to the oil while vigorously agitated was required to divide the acid into minute particles which was necessary to increase its active surface. After mixing for 20 seconds, distilled water (the same volume as acid) was added to provide coagulation of the acid sludge and continued agitation for a few minute before allowing the mixture to settle down at least 7 hours. After removal the sludge, the oil was then neutralized with caustic soda.

After treating with acid, the neutral oil was treated with fuller's earth (30% by weight of oil). A neutral oil was heated to approximately 50 °C and fuller's earth was added. The mixture was stirred for 45 minutes at temperature

of 150 °C. The oil and activated clay were then separated by vacuum filtration.

3.3.4 Determination of the physical and chemical properties of acid-clay treated oil as follow:

Physical properties

1. Colour, Visual by ASTM D 1500
2. Kinematic viscosity by ASTM D 445
3. Viscosity index by ASTM D 2270
4. Pour point by ASTM D 92
5. % Sulfur (by weight) by ASTM D 129

Chemical properties

1. The percentages of oxidative compounds were determined by Thermogravimetric Analyzer.
2. The composition ($\%C_a, \%C_b, C_n$) of acid-clay treated oil was determined by C^{13} -NMR

3.3.5 Measuring pore volume of alumina support
CS-303 [20]

The alumina support (100 g) was charged into the suction flask. The apparatus was set as shown in figure 3.1 but using buret instead of separatory funnel. The vacuum pump was switched on for trapping air from the pores of the supports. The support was then impregnated by continuously adding the distilled water from the buret and

allowed the water to contact the supports thoroughly. The volume of water was recorded and repeated the procedure until the volume of the water was constant before calculating the pore volume of the support.

3.3.6 Preparation of catalyst containing 10% MoO₃ and 5% NiO on alumina support [17]

Ammonium molybdate (NH₄)₂MoO₄ (13.77 g) was added slowly to 25.46 ml of water with agitation. This solution was used to impregnate 100 g of alumina support. The impregnated supported was dried overnight at 125 °C and thereafter calcined at 450 °C with air for one hour.

A solution contained 20.70 g of nickel nitrate hexahydrate in 25.46 ml of water was prepared with agitation and this solution was used to impregnate the calcined molybdenum impregnated support. The support was dried overnight at 125 °C and calcined with air at 450 °C for one hour.

The hydrotreating catalyst prepared in this manner contained 5% of nickel oxide and 10% of molybdenum trioxide.

3.3.7 Analysis of molybdenum trioxide and nickel oxide amount in the catalyst by Inductively Coupled Plasma (ICP) Emission Spectrometer.

The prepared catalyst (0.1 g) was digested with the mixture of concentrated hydrochloric acid and concentrated nitric acid and analyzed by ICP.

3.3.8 The catalyst activity was tested by hydrogenation of cyclohexene. [21]

Cyclohexene (300 g) and catalyst (6 g) were charged into the reactor. The reactor was pressurized at ambient temperature to 400 psig with hydrogen and was then heated to 100 °C for 2 hours. The product was tested by Infrared Spectrophotometer.

3.3.9 Hydrotreating Process

The prepared base oil(300 g) was charged into the reactor and the required quantity of catalyst was added. The reactor was then closed and split ring closures were moved into the position from the sides and cap screws were tightened with the bomb in the heater.

Next, a thermocouple was inserted into a sturdy thermowell attached to the underside of the bomb head and extended to a point near the bottom of the reactor cavity followed by connecting the stirring motor and passing water into the cooling channel. A power button and a motor button were switched on with the speed 100 rpm.

In order to remove all oxygen gas in the reactor,

a gas inlet valve and a gas release valve had to be open as well as a valve of hydrogen tank. The regulator was also adjusted until pressure gauge indicated 10 psig. After charging for 2 minutes, a gas release valve was closed.

The desired temperature was setted at the temperature controller. The regulator was adjusted to the desired pressure and then the valve of hydrogen tank and a gas inlet valve were closed respectively. The stirring speed was adjusted to 300 rpm. The heater was switched on.

The reaction was allowed to occur for the desired time before the motor and the heater were switched off to stop the reaction. The liquid sampling valve was opened in order to remove hydrotreated oil from the reactor into 500 ml beaker. After a gas release valve was opened, the pressure was reduced to atmospheric pressure. Stirring motor was disconnected and when the reactor temperature reached 50 °C. A thermowell was pulled out of the bomb head and the reactor was opened. The remaining oil was poured into a beaker. Finally, the catalyst was separated from the mixture by filtering with a Whatman filter NO.1 in an oven at temperature of 60 °C.

3.3.10 Selecting a suitable operating conditions

The effect of reaction temperature, hydrogen partial pressure, reaction time and catalyst concentration were studied under conditions which were shown in table 3.3.

3.3.11 Determination of the physical and chemical properties of hydrotreated oils as follow:

Physical properties

1. Colour, Visual by ASTM D 1500
2. Kinematic viscosity by ASTM D 445
3. Viscosity index by ASTM D 2270
4. Pour point by ASTM D 92
5. % Sulfur (by weight) by ASTM D 129

Chemical properties

1. The percentages of oxidative compounds were determined by Thermogravimetric Analyzer.
2. The composition ($\%C_n, \%C_m, \%C_n$) of hydrotreated oils were determined by C^{13} -NMR

Table 3.3 The various operating conditions for the experiment at a constant agitation 300 rpm

Parameters Studied	Temperature (°C)	Concentration of catalyst (% by wt. of oil)	Time (hrs)	Partial pressure of H ₂ (psig)
Temperature	150	3	2	529
	200	3	2	529
	250	3	2	529
	300	3	2	529
	350	3	2	529
Catalyst Concentration	350	1	2	529
	350	2	2	529
	350	3	2	529
	350	4	2	529
	350	5	2	529

Table 3.3 The various operating conditions for the
(cont.) experiment at a constant agitation 300 rpm

Parameters Studied	Temperature (°C)	Concentration of catalyst (% by wt. of oil)	Time (hrs)	Partial pressure of H ₂ (psig)
Reaction	350	4	1	529
Time	350	4	1.5	529
	350	4	2	529
	350	4	2.5	529
	350	4	3	529
	350	4	3	529
Pressure	350	4	2.5	129
	350	4	2.5	229
	350	4	2.5	329
	350	4	2.5	429
	350	4	2.5	529