CHAPTER 3

EXPERIMENT

3.1 Materials

- Alumina support was bought from United Catalyst Inc.,. It was CS-303 type and its specification are shown in table 3.1.

Table 3.1 The chemical composition and physical properties of support type CS-303 from United Catalysts Inc.,.(18)

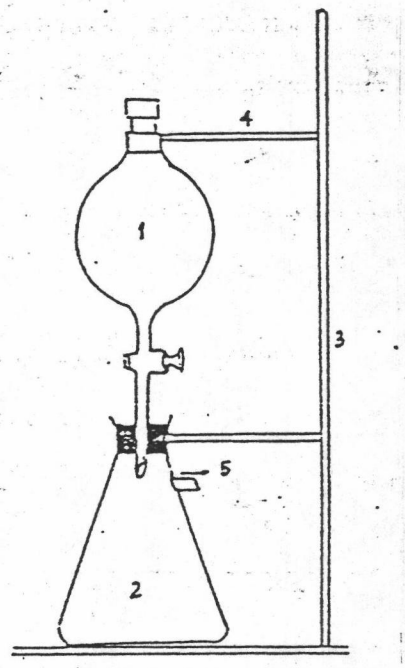
Chemical Composition	Weight Percent
Al_2O_3	80-86%
CaO	< 0.10%
MgO	< 0.10%
SiO_2	< 0.05%
TiO_2	< 0.05%
C	< 0.10%
Na	< 0.15%
S	< 0.05%
Cl	< 0.02%
B	< 0.02%
K_2O	< 0.05%
Other Alkali Metals	< 0.05%
Other Heavy Metals	< 0.05%

Physical Properties	
A. Bulk Density (lb./Cu.ft.)	77+/-5
B. Surfaces Area (m^2/gm)	3-10
C. Pore Volume (cc/gm)	0.15-0.30
D. Fusion Point (°F)	3000 °F
E. Particle Size	
Normal	5/8"
Normal Height	3/8"
Normal Hole Diameter	5/16"
Form Variation:	
Diameter Range	0.584-0.656
Height Range	0.337-0.413
Hole Diameter Range	0.285-0.342

- Hydrogen and Nitrogen gas were bought from T.I.G. Trading Limited.
- Lubricating Base Oil,150 BS Mobil ahsrf No. 23 B, from Petroleum Authority of Thailand.
- Lubricating Oil: Shell, PTT.
- Nickel nitrate hexahydrate ($NiNO_3.6H_2O$) was bought from Carlo Erba.
- Cyclohexene was bought from Fluka.

3.2 APPARATUS

3.2.1 Apparatus for preparing nickel catalyst by dry impregnation



1. Separating funnel
2. Suction flask
3. Stand
4. Clamp
5. Suction pump

Figure 3.1 The apparatus for preparing nickel catalyst by impregnation method

The important apparatus

1. Separating funnel for charging nickel nitrate solution
2. Suction flask for charging alumina supports
3,4. Stand and clamp for tighting separating funnel and suction flask
5. Suction pump for trapping air in the pores of alumina supports before impregnating nickel nitrate solution

3.2.2 Calcinator

1 Calcinator (Fig 3.2)

2 Bubble Flow Meter (Fig 3.3)

3.2.3 Infrared Spectrophotometer model 780 from Perkin Elmer was used.

3.2.4 Atomic Absorption model AA-670 from Shimadsu was used.

3.2.5 Hydrogenator

All experiments for the hydrogenation study of lubricating base oils were carried out in the hydrogenation apparatus which consists 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 can work in a pressure range of 0-2000 psig and in temperature 0-450 °C.

2. Reactor Fitting (Figure 3.5)

The stirred reactor are 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 can 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-234A from Hoehler 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

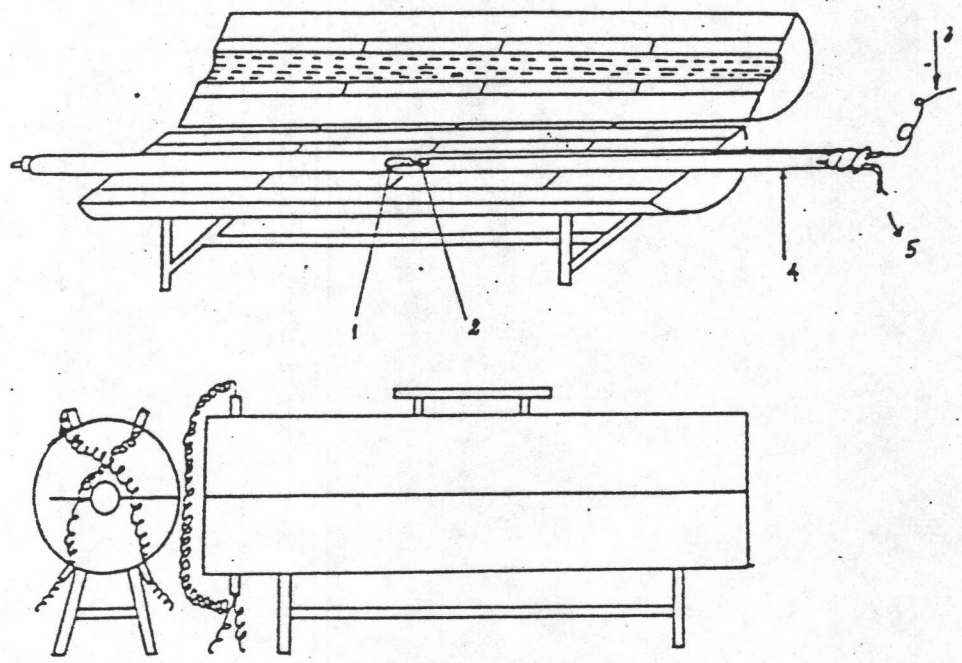
The apparatus model SLFA-800 from HORIBA was used.

3.2.10 C^{13}-Nuclear Magnetic Resonance spectrometer

The NMR model AC-F 200 from Bruker operating at 50.32 MHz was used.

3.2.11 Thermal Gravimetry Analyzer

The TGA model DT-30 from Shimadzu was used.



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

Figure 3.2 Calcinator

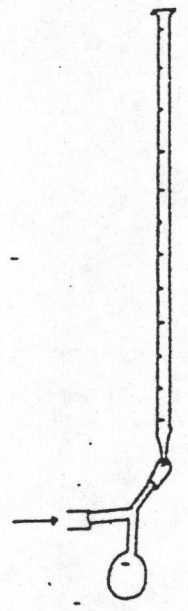


Figure 3.3 Bubble Flow Meter

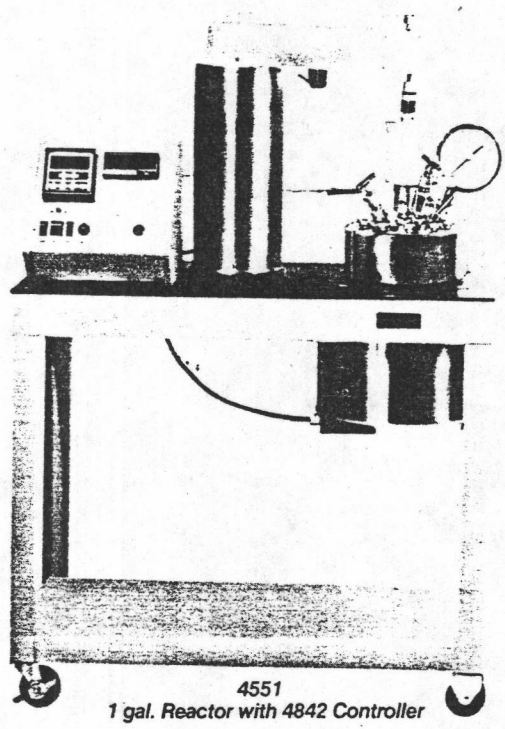
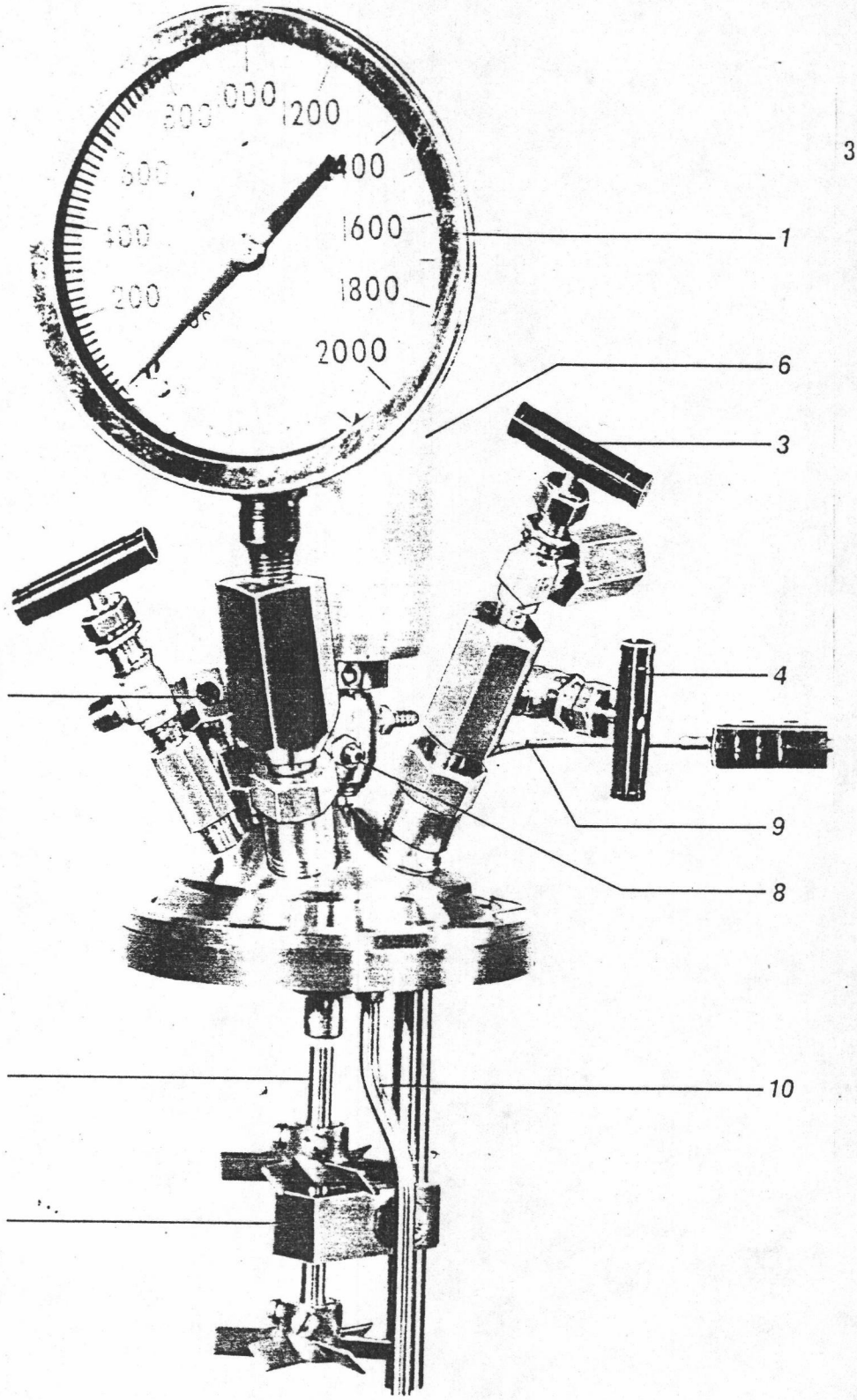


Figure 3.4 Floor Stand Reactor



1. a pressure gage
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 Fittings

3.3 Procedure

3.3.1 Measuring pore volume of alumina support CS-303 as follow:

The alumina supports (20 grams) 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 supports was impregnated by continuously adding distilled water from the buret. The water was allowed to contact the supports thoroughly. The volume of water was recorded and the procedure was repeated until the volume of water was constant.

3.3.2 Preparing nickel nitrate solution

An aqueous impregnating solution was prepared by dissolving 2, 5.44, 10.87, 13.34 and 17.27 grams of nickel nitrate hexahydrate ($NiNO_3.6H_2O$) in 5.28 ml. of distilled water. The solution was diluted with water to 50 ml. by using volumetric flask. The solution had nickel 2, 5, 10, 12 and 15% respectively.

3.3.3 Preparing nickel catalyst by dry impregnation method

The alumina supports was crushed to give the particle with a diameter about 0.5 cm. and was charged into the suction

flask. The apparatus was set as shown in figure 3.1. The side arm of the flask was attached to a vacuum pump. Nickel nitrate solution was placed in the separatory funnel which was equivalent to the total pore volume of the supports. The flask was evacuated, then the solution was admitted into the flask while the supports was shaking. The impregnated supports was dried overnight in an oven at 100 °C and then calcined at 300 °C.

3.3.4 The amount of nickle in the catalyst were analyzed by atomic absorption.

Table 3.2 The percentages of nickel were analyzed by atomic absorption

% Ni/Al_2O_3	%Ni/Al_2O_3 analyzed by atomic absorption
2	1.85
5	4.83
10	9.87
12	11.86
15	14.85

3.3.5 The catalyst activity was tested by hydrogenation of cyclohexene. Cyclohexene 300 grams and nickle catalyst 6 grams were charged into the reactor. The amount of nickel in the catalyst was 10%. The reactor was pressurized at ambient temperature to 200 psig with hydrogen and then was heated to 100 °C for 2 hours. The products were tested by Infrared Spectrophotometer.

3.3.6 Determination of the physical and chemical properties of lubricating oil as follow: API gravity, color, flash point, kinematic viscosity, pour point, % sulfur, $\%C_A$, $\%C_P$, $\%C_N$ and oxidative compound (% by weight).

Table 3.3 The physical and chemical properties of lubricating base oil (150 BS) and lubricating oil (Shell, PTT).

Type of oil	150 BS	SHELL	PTT
Physical Properties:			
API gravity@15.6 °C	29.5	29.5	29.5
Flash point, °C	>243	>243	>243
Pour point, °C	-9	-9	-9
colour,Visual	3.5	Std.red	Std.green
Kinematic Viscosity			
@ 40 °C,cSt	485.69	137.99	144.27
@100 °C,cSt	32.09	13.89	14.32
Viscosity Index	97	95	96
Sulpher,% wt	1.137	1.037	0.934
% C_A	18.41	19.23	18.81
% C_P	47.14	52.23	51.49
% C_N	34.45	28.54	29.70
Oxidative Compound			
% wt.	38	27.5	27.0

3.3.7 Hydrogenation

The lubricating oil 300 grams and required quantity of catalyst were charged into the reactor. A reactor was closed and split ring closures were moved into position from the sides and cap screws were tighted with the bomb in the heater. A thermocouple was inserted into a sturdy thermowell attached to the underside of the bomb head and was extended to a point near the bottom of the reactor cavity. The stirring motor was connected to the reactor through an overarm drive and then water was passed into the cooling channel. A power button and a motor button were switched on and the speed was adjusted to 100 rpm.

All oxygen gas was removed from the reactor by opening a gas inlet valve and a gas release valve. A valve of a hydrogen tank was opened and adjusted at ambient temperature until the pressure gauge indicated about 10 psig. A gas release valve was closed after charging gas about 2 minutes.

The desired temperature was set at the temperature controller. The valve of the hydrogen tank was adjusted until the pressure was reached 200 psig and then a valve of the hydrogen tank and a gas inlet valve were closed. The stirring speed was adjusted to 300 rpm. A heater was switched on.

When hydrogenating time equalled the desired time, the reaction was stopped. A heater was switched off and stirring rate was adjusted to minimum speed and then a motor was switched off. A liquid sampling valve was opened for withdrawing oil from the reactor into a 500 cc beaker. A gas release valve was opened until the pressure was reduced to atmospheric pressure. The overarm drive was disconnectted from the stirring motor. The water was stopped flowing into the cooling channel when the temperature in the reactor was about 105 °C. A thermocouple was pulled out of the bomb head and the reactor was opened. The reactor was taken from the heater. The remaining hydrogenated oil was poured into a beaker and then the catalysts was seperated from catalyst oil mixture by filtration through a Whatman filter paper No.1 in an oven at 100 °C.

3.3.8 Selecting an Suitable Operating Condition

The effect of percentages of nickel on alumina supports, reaction temperature, reaction time and catalyst concentration were studied under different conditions which were shown in Table 3.2

3.3.9 Lubricating oils (SHELL, PTT) were hydrogenated under suitable operating condition from 3.3.8

3.3.10 Determination of physical and chemical properties of lubricating oil after hydrogenation as follow:

Physical Properties

1) Colour, Visual by ASTM D 1500

2) Flash Point, (C.O.C.) by ASTM D 92

3) Kinematic Viscosity by ASTM D 445

4) Viscosity Index by ASTM D 2270

5) % Sulfur by weight by ASTM D 129

Chemical Properties

1) The percentages of oxidative compounds by Thermogravimetric balance.

2) The composition of lubricating oil ($\%C_A$, $\%C_P$, $\%C_N$) by C^{13}-NMR.

Table 3.4 The various operating conditions for the experiment at constant reaction pressure 200 Psig. and agitation speed 300 rpm.

Parameters Studied	Reaction Temperature (°C)	Reaction Time (hrs)	Conc. of Catalyst (% by wt.of oil)	% Ni on alumina support
% Ni on alumina support	200	1	1	2
	200	1	1	5
	200	1	1	10
	200	1	1	12
	200	1	1	15
Conc. of Catalyst	200	1	1.0	10
	200	1	1.5	10
	200	1	2.0	10
	200	1	2.5	10
	200	1	3.0	10

Parameters Studied	Reaction Temperature (°C)	Reaction Time (hrs)	Conc. of Catalyst (% by wt.of oil)	% Ni on alumina support
Reaction time	200	1	2.0	10
	200	2	2.0	10
	200	3	2.0	10
	200	4	2.0	10
Reaction Temperature	200	3	2.0	10
	250	3	2.0	10
	300	3	2.0	10
	350	3	2.0	10