CHAPTER III

EXPERIMENTAL

3.1 Apparatus and Instruments

1. Apparatus for measuring pore volume of alumina support 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. Gas Chromatography-Mass Spectrometer (GC/MS)

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

GC condition

Column : DB-1HT capillary column 30m x 0.25 mm ID. x 0.1 μm film thickness

Carrier : Helium with flow rate of 0.8 ml/min

Oven : 60 °C (1 min) to 150 °C (3 min) at rate 20 °C/min
150 °C (3 min) to 200 °C (3 min) at rate 8 °C/min

Injection temperature : 250 °C

Detector : MS (EI^+ 70 ev)

4. Pressure reactor (hydrogenation) from Parr Instrument Co.,Ltd.

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

(1) Reactor (Figure 3.1)

The hydrogenation floor stand reactor consisted of an autoclaves 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 from ambient to 450 °C.

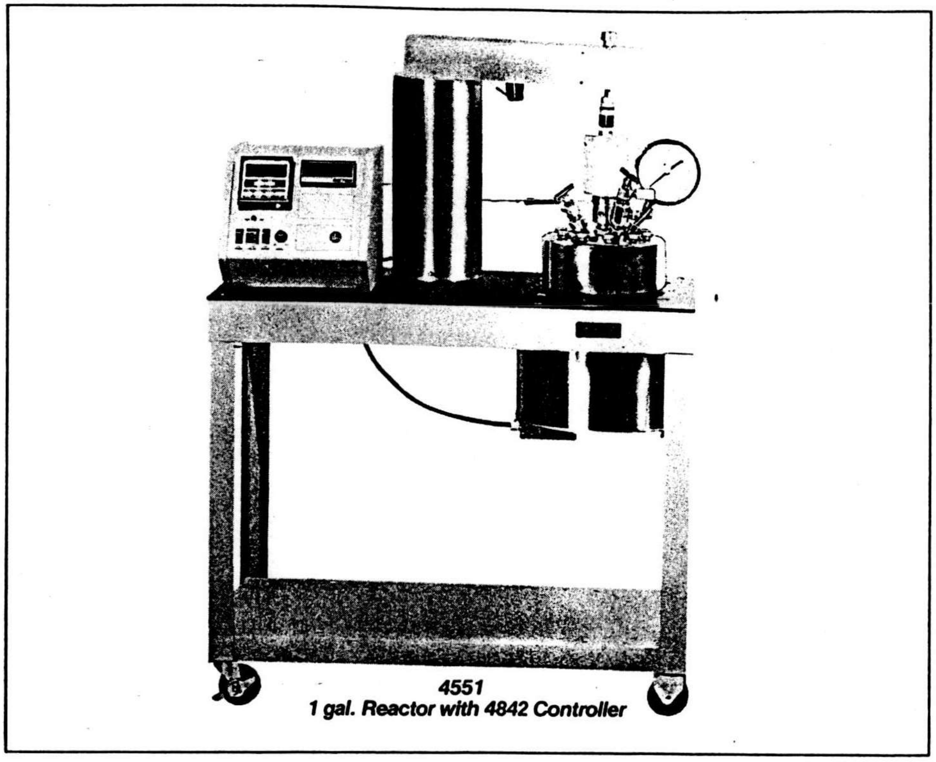
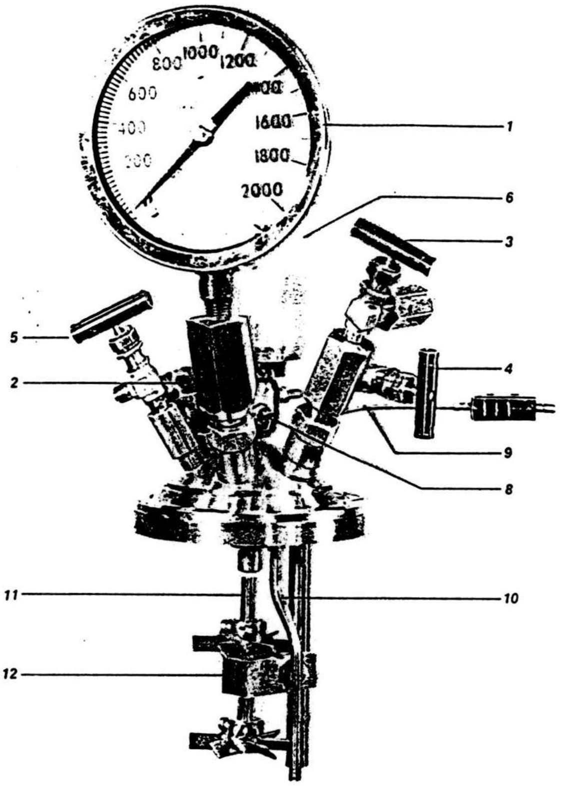


Figure 3.1 Floor Stand Reactor

(2) Reactor fitting (Figure 3.2)

The reactor was equipped with stirrer and valves with fitting for handling various as follows



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 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 and a pressure gauge (0-2000 psig).

3.2 Materials

1. HDPE wax was obtained from Thai Petrochemical Industry (TPI)
2. Chloroplatinic Acid ($H_2PtCl_6 \times 6H_2O$) was obtained from Merck.
3. Alumina Support CS 331-3 was obtained from United Catalyst Inc.,USA.
4. Industrial grade hydrogen gas was obtained from TIG Trading Limited
5. Chloroform was obtained from Carlo Erba.

3.3 Preparation of Catalysts

3.3.1 Measuring pore volume of alumina support CS 331-3

The suction flask was equipped with a burette containing deionized water and connected to a vacuum pump. A vacuum was applied to evacuate the air from the pores of the support (100 g) in a suction flask. 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 CS 331-3 type was 0.64 ml/g.

3.3.2 Impregnation of Platinum and Fluoride on Alumina Support : containing 0.3% Pt and 0.5% F on alumina support.

The alumina support (125.55 g) was impregnated in an aqueous impregnating solution. This solution was prepared by dissolving 1 g of chloroplatinic acid ($H_2PtCl_6.6H_2O$) in 80 ml of deionized water (the volume of water equivalent to the pore volume of the alumina support). The impregnated support was dried at 120 °C for 3 hours and then was calcined at 450 °C for 3 hours to obtain the calcined catalyst. The calcined catalyst was reimpregnated with 80 ml of aqueous solution containing NH_4F (1.22 g), left at room temperature for 1 hour and then dried at 120 °C for 16 hours to obtain the fluorided catalyst. This fluorided catalyst was calcined 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.

3.3.3 Activation of platinum fluoride on alumina catalyst

Platinum fluoride on alumina was introduced into the stainless steel reactor. The latter was closed and gas in the reactor was replaced by 400 psig hydrogen gas. Then, the high pressure reactor was heated at 400 °C for 6 hrs to obtained the activated catalyst.

3.4 Characterization of platinum fluoride on alumina catalyst

Platinum fluoride on alumina catalyst was characterized by x-ray diffraction and scanning electron microscopy.

3.5 Hydroisomerization process

3.5.1 Reaction procedure

HDPE wax (400 g) and Pt/F hydroisomerization catalyst were introduced into the stainless steel reactor. The latter was closed and air in the reactor was replaced by hydrogen gas. The reaction was operated at various conditions in procedure 3.5.2-3.5.5 with stirring speed set at 500 rpm. At the end of the reaction, the reactor was cooled down to room temperature and depressurized. Products were removed from the reactor and separated from the catalyst by centrifugation and filtration. Liquid products were analyzed by GC/MS.

3.5.2 The effect of catalyst concentration on hydroisomerization

Following a procedure similar to procedure 3.5.1. The effect of catalyst concentration was studied by varying catalyst concentrations (5, 6, 7, 8, and 9 % by wt). The reaction was operated at the reaction temperature of 350 °C and selected reaction time (2 hours). The hydrogen gas pressure in the reactor was adjusted to 400 psig.

3.5.3 The effect of temperature on hydroisomerization

Following a procedure similar to procedure 3.5.1. The effect of temperature was studied by varying temperatures (400, 350 and 300 °C). The selected catalyst concentration was 5 % by wt. The reaction was operated under 400 psig hydrogen pressure and selected reaction time (2 hours).

3.5.4 The effect of hydrogen pressure on hydroisomerization

Following a procedure similar to procedure 3.5.1. The effect of hydrogen pressure was studied by varying hydrogen pressures (500, 400, and 300 psig), The selected catalyst concentration was 5 % by wt. The reaction was operated at reaction temperature of 300 °C and selected reaction time (2 hrs).

3.5.5 The effect of reaction time on hydroisomerization

Following a procedure similar to procedure 3.5.1. The effect of reaction time was studied by varying reaction times (4, 3, 2, 1 hr and 10 min.).The selected catalyst concentration was 5 % by wt. The reaction was operated at reaction temperature 300 °C and under 300 psig hydrogen pressure.

3.6 Determination of product properties

The spectroscopic and physical properties of the hydroisomerization product, obtained at optimum condition, were determined.

3.6.1 Spectroscopic properties

Product obtained from hydroisomerization process at optimum condition was characterized by ^{13}C NMR.

3.6.2 Physical properties

Products obtained from hydroisomerization process were characterized by standard procedures as follow :

a. Specific gravity	by	ASTM	D 1298
b. Kinematics viscosity	by	ASTM	D 445
c. Flash point	by	ASTM	D 93
d. Pour point	by	ASTM	D 97
e. Distillation	by	ASTM	D 86
f. Color visual	by	ASTM	D 1500
g. Sulfur content	by	ASTM	D 4294
h. Cetane Index	by	ASTM	D 976