

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

1. Soybean oil was obtained commercially.
2. Industrial hydrogen gas (H_2)
Thai Industrial Gas Trading Ltd.,
3. Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$)
Analytical grade; BDH chemicals Ltd.
4. Ball clay
Cernic internation Co Ltd.; Thailand
5. China clay
Cernic internation Co Ltd.; Thailand
6. Diatomite
Cernic internation Co Ltd.; Thailand
7. Kieselguhr acid washed
Analytical grade: Ajax Chemicals
8. Methyl alcohol (CH_3OH)
Analytical grade; Merck
9. Sodium Hydroxide ($NaOH$)
Analytical grade; Merck
10. Sulfuric acid (98%w/w)
Analytical grade; J.T. Baker

11. Glacial acetic acid (CH_3COOH)
Analytical grade; Carlo Erba
12. Carbon tetrachloride (CCl_4)
Analytical grade; Merck
13. Iodine trichloride (IOI_3)
Analytical grade; Fluka
14. Iodine (I_2)
Chemical grade; Fluka
15. Potassium iodide (KI)
Analytical grade; Merck
16. Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$)
Analytical grade; M&B
17. Starch granule ($\text{C}_6\text{H}_5\text{O}$)
Reagent grade; Sigma Chemicals Company
18. Sodium sulfate anhydrous (Na_2SO_4)
Chemical grade; Fluka
17. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)
Chemical grade, M&B

3.2 Apparatus and instruments

1. High Pressure Reactor, Parr model 4842

All experiments for the hydrogenation of soybean oils were carried out in a high pressure reactor, which consisted of four parts as follows:

1.1 Reactor (Figure 3.1)

The hydrogenation reactor was a batch high pressure stirred autoclave model from the Parr Instrument Company, consisting of 1,000 ml stainless steel, cylindrical bomb, bomb head, bomb heater, two stirrers and a cooling coil. The reactor could work at a pressure range of 0-2,000 psig and a temperature range of 0-350 °C.

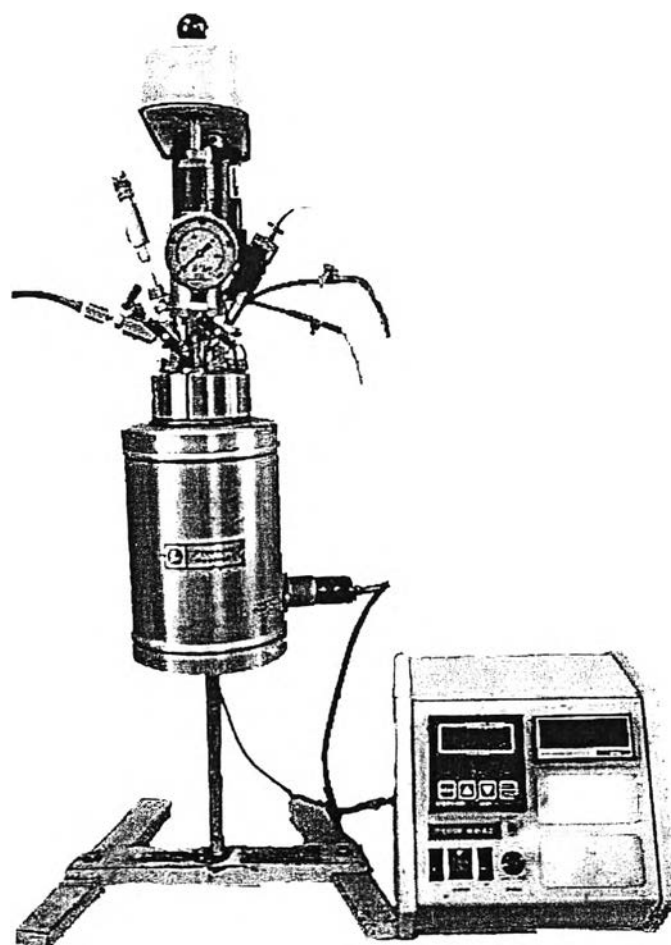


Figure 3.1 High pressure reactor

1.2 Reactor Fitting (Figure 3.2)

The stirred unit of the reactor was supplied with convenient fittings for hanging of various functions. The parts are indicated with the following letters.

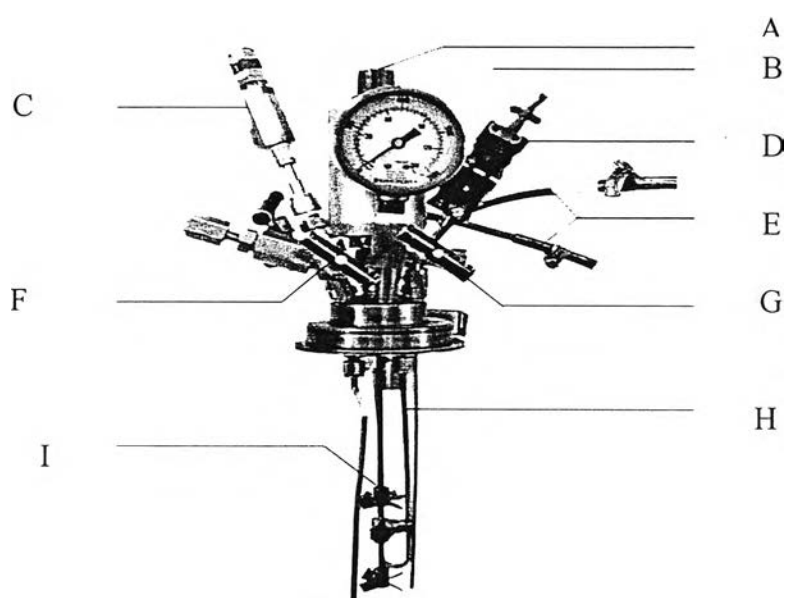


Figure 3.2 Reactor Fitting

- A. A stirrer magnetic drive system
- B. A pressurc gauge
- C. A safety rupture disc
- D. A dual thermocouple
- E. A water cooling channel
- F. A gas inlet value
- G. A gas release value
- H. A colling rod
- I. A stirring shaft with 6-blade turbine type impeller

1.3 High-speed motor

This part was attached to the reactor fitting.

1.4 Manual temperature controller

The temperature controller was model 4242 from the Parr Instrument Company. It was operated in association with a dual thermocouple. There were various improvability modules to support with monitoring and controlling of the temperature. A temperature setting on the controller established a set point temperature within the range of 0-350 °C.

1.5 Gas controller system

The system consisted of a hydrogen tank with regulator (0-2,000 psig).

1.6 Cooling system

It is composed of two parts, one for cooling the reaction and one for cooling the stirrer. It was found that at the beginning of the reaction, the rate of hydrogenation was so fast that the temperature controller could not keep the temperature at the desired value. Therefore, it had to be cooled by water in the cooling coil. The cooling coil was connected to the water pipe in the laboratory. The cooling system for the stirrer was connected to the reactor fitting.

2. Calcinator

Carbolite Furnaces, model GSM

3. Apparatus for determining the Iodine value (I.V.) of the oil

3.1 Burette in 50 ml.

3.2 Graduate pipette in 1, 5, 10 ml.

- 3.3 Glass stopper volumetric flask
- 3.4 Stand and clamp for supporting burette
- 4. Gas Chromatography (GC)
 - Hewlett Packard Instrument, GC 5890 SeriesII
- 5. Gas Chromatography – Mass Spectrometer (GC-MS)
 - Fisons Instrument, GC 800 Series; MS VG TRIO 2000
- 6. Fourier Transform Infrared Spectrophotometer (FTIR)
 - Nicolet (Impect 410)
- 7. Nuclear Magnetic Resonance Spectrometer (NMR)
 - Bruker, model AC-F 200
- 8. Atomic Absorption Spectroscopy (AAS)
 - Spectrophotometer IL 551, Laboratory model
- 9. Micro Pore Size according to Brunauer Emmett Teller (BET) method
 - Quantachrome, Autosorb1
- 10. Scanning Electron Microscopy (SEM)
 - JSM-6400, JEOL

3.3 Procedure

3.3.1 Determination of clay properties

1. Acidity [43]

The acidity was determined as following: clay (0.5 g) was dried at 120 °C for 6 hours. The clay was then treated with 0.1N NaOH (15 cm³) for 10 min. Excess NaOH was titrated with 0.1 N H₂SO₄. The acidity of clay was calculated according to the following equation:

$$\text{Acidity of clay} = (V1 - V2) \times [H_2SO_4] \times 100 / \text{amount of clay}$$

(mmol/100g clay)

V1 = Volume of NaOH

V2 = Volume of H₂SO₄

[H₂SO₄] = concentration of H₂SO₄

2. Morphology of clay

The surface of clay was characterized by Scanning Electron Microscopy (SEM).

3. Surface area and pore size

The surface area (BET method) and average pore radius of clay were characterized from N₂ adsorption-desorption isotherms at 77 K carried out in Autosorb-1 equipment from Micrometry. The amount of N₂ gas required to cover

the external and the accessible internal pore surfaces of a solid with complete monolayer of adsorbate was determined. This monolayer capacity was calculated from the adsorption isotherm by BET equation, as the surface area. Pore size distribution was determined from nitrogen desorption data with $p/p_o = 0.3$ and above.

3.3.2 Catalyst preparation

1. Preparation of 10% nickel on natural silicates

1.1 Preparation of 10%Ni on ball clay

Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (49.52 g) was dissolved in water (75 cm^3). The ball clay (90 g) was poured into the solution, which was left at room temperatures for 4 hours and stirred occasionally. Then the mixture was dried at 110 °C for 16 hours and then continually calcined at 500 °C for 4 hours to obtain the calcined solid.

1.2 Preparation of 10%Ni on china clay

The preparation procedure was carried out as in 1.1 but china clay was used in place of ball clay and the amount of water used to dissolve nickel salt was 59 cm^3 .

1.3 Preparation of 10%Ni on diatomite

The preparation procedure was carried out as in 1.1 but diatomite was used in place of ball clay and the amount of water used to dissolve nickel salt was 122 cm^3 .

1.4 Preparation of 10%Ni on kieselgurh

The preparation procedure was carried out as in 1.1 but kieselgurh was used in place of ball clay and the amount of water used to dissolve nickel salt was 155 cm³.

2. Activation of catalysts

The catalysts were activated by reduction with hydrogen before use. The activation of catalyst was carried out in a stainless steel reactor at 300 psig hydrogen pressure and 300 °C for 4 hours.

3.3.3 The catalysts characterization

1. Surface area and pore size analysis

The surface area and pore size of natural silicates was measured by Micro Pore Size according to Brunauer Emmett Teller (BET) method.

2. The determination of the catalyst composition [44]

Percentage of metal loading was analyzed by Atomic absorption spectroscopic method by the following procedure:

The catalyst (0.1 g) was weighed and placed into a 250-ml beaker, then 50 cm³ of concentrated HNO₃ was added and the beaker was heated on a hotplate. The solution mixture was heated continuously until the solvent was completely evaporated. Then the residue was dissolved in 50 cm³ of distilled water. The solution was warmed for 15 min and then filtered through a whatman filter paper No. 42. The paper was washed with distilled water until free from salts. The filtrate was then collected into 100 cm³ volumetric flask and the volume was made up to the

mark. The solution sample was then analyzed using an atomic absorption spectrophotometer.

The atomic absorption spectrophotometer used for this analysis was the Instrumentation Spectrophotometer IL 551, Laboratory model. The general condition can be summarized as follows:

Light source	Hollow cathode lamp for Ni
Lamp current	10 nm
Wavelength	232.0 nm
Slit width	40
Bandpass	0.15 nm
Burner head	Single slot
Flame description	Air-acetylene Oxidizing, fuel lean, blue

3.3.4 Hydrogenation

1. Hydrogenating process

The soybean oil (100g) was charged into the reactor and the required quantities of catalysts were added. The reactor was closed. After a thermocouple was inserted into the reactor, the stirring motor was connected and the water was passed into the cooling tube. Before starting the process, hydrogen gas was compressed into the reactor until desired pressure was obtained. The required conditions were set. After the reaction took place, heating was stopped and the reaction mixture was stirred until the mixture cooled to room temperature. The pressure was released and the catalyst was separated by filtration to give the hydrogenated soybean oil.

1.1 The effect of catalyst type on activity and selectivity for hydrogenating process.

The experiments were carried out using Ni catalysts on an ball clay, china clay and diatomite and kieselgurh. To test the activity and selectivity of the catalyst and select the best hydrogenating catalysts, the hydrogenation condition was set at a temperature 180°C, 200 psig. hydrogen pressure, 600 rpm. agitation speed, catalyst concentration of 0.05 %Ni /weight of oil, and various reaction time (30, 60, 90, 120, 150, 180 min).

1.2 The effect of temperature on hydrogenating process

The described procedure was operated at various temperatures (100, 120,150, and 180 °C) by using Ni catalysts on ball clay. The reaction mixture was worked up in the same manner as described in 1.1.

1.3 The effect of pressure on hydrogenating process

The hydrogen solubility in oil is directly proportional with pressure. Therefore, reaction rate could be increased when hydrogen pressure is increased. The described procedure was operated at various pressures (100, 150, and 200 psig) using the optimum temperature to produce the hydrogenated products, obtained from 1.2. The reaction mixture was worked up in the same manner as described in 1.1.

1.4 The effect of reaction time on hydrogenating process

The described procedure was operated at various reaction times (60, 100, 120, and 140 minutes) using the optimum temperature and the optimum pressure to produce the hydrogenated products, obtained from 1.2 and 1.3 respectively. The reaction mixture was worked up in the same manner as described in 1.1.

1.5 The effect of the catalyst concentration on hydrogenating process

The described procedure was operated at various catalyst concentration (0.025, 0.050, and 0.1 %by weight of oil) for the optimum temperature, pressure, and reaction time to produce the hydrogenated products, obtained from 1.2, 1.3 and 1.4, respectively. The reaction mixture was worked up in the same manner as described in 1.1.

3.3.5 Transesterification of soybean oil [45]

Soybean oil (about 150 mg) were placed into a screw cap vial. The sample was dissolved in 3 ml of diethyl ether. Using a graduated pipet 0.2 ml of the 20% tetramethylammonium hydroxide in methanol was added to the vial. The vial was capped and then shaken for 5 min. Then, 2 to 5 ml of deionized water was added to the vial and shaken to separate the top clear ether layer. Turbidity was formed almost immediately that settled into a lower layer after shaking. The clear upper ether layer contained the methyl ester formed from the glyceride fatty acids. An aliquot of this layer was injected into the gas chromatograph method to determine the fatty acid composition of the glyceride.

3.3.6 Analysis of chemical composition of soybean oil

1. Gas chromatograph (GC)

Gas chromatograph was used to quantitatively determine of the fatty acid components. The GC was performed using DBwax capillary column. The general conditions can be summerized as follows:

column	30 m.; 0.25 mm.
column packing	PEG (polyethyleneglycol); 0.25 microns
temperature of	
- injection port	240°C
- column	180°C – 220°C
temperature rate of	3 °C per min.
pressure	flow rate 5 psig
sample size	1 µl (splitl 1 ;50)

2. Gas chromatograph-Mass spectrometer (GC-MS)

Gas chromatograph-Mass spectrometer was used to identify the fatty acid components. The GC-MS was performed using BP20 capillary column. The general condition was the same as in GC analysis.

3. Iodine Value (I.V.) (Wij's method)

Iodine value is defined as the number of centigrams of iodine absorbed per gram of sample (% iodine absorbed). The method and reagents are shown in Appendix A.