

CHAPTER IV

EXPERIMENT



The experiments of the study of hydrogenation of rubber seed oil were divided into four parts: preparation of the nickel-supported catalysts, atomic absorption spectrophotometric determination of nickel contents of the catalysts, hydrogenation, and analysis of the resulting rubber seed wax. The details of the experiments were discussed in the followings.

4.1 Chemicals and Reagents

Chemicals used were of Analar grade except where specified.

Rubber seed oil from Phol Dhanya Co.,Ltd. The analytical results of the chemical properties which were analyzed by Department of Science Service, Ministry of Science, Technology and Energy are shown in Table 4.1.

Commercial catalysts were G53D and G95E from Nissan Girdler Catalyst Co.,Ltd., Tokyo, Japan; Nysel HK-4 or Ni 3609F from Harshaw Co.,Ltd., Cleveland, U.S.A.; and Kawaken catalyst from Kawaken Fine Chemicals Co.,Ltd.

G53D is a chemically precipitated nickel catalyst, supported on kieselguhr, dry-reduced and suspended in a protective medium of hardened tallow or vegetable oil, 20% Ni, 13-16% kieselguhr and 56-60% hardened oil. It is active and poison resistance. It is exceptionally well suited for rapid hydrogenation to low IV levels and for other difficult

Table 4.1 Rubber seed oil analysis data

Iodine value (Wijs)	141
Acid value, mgKOH/g oil	31.1
Cyanide	not found
Fatty acid composition (GLC), %	
Lauric	0.3
Myristic	0.3
Palmitic	12.4
Stearic	12.4
Oleic	26.9
Linoleic	30.4
Linolenic	15.9
Others	1.4

hydrogenations, such as those of tallow, marine oils and fatty acids. It is in flake-form and 100% passing through 4 mesh screen. Average particle size of catalysts is 3.0 μm .

G95E is a developed catalyst for use where high activity is required and where high linoleic/oleic selectivity is essential. It is a chemically precipitated nickel on kieselguhr catalyst, dry-reduced and suspended in a protective medium of hardened oil, 25% Ni, 9-12% kieselguhr and 61-65% hardened oil. It is in flake-form and 100% passing through 4 mesh screen. Average particle size of catalysts is 1.07 μm and specific gravity is 6.0 g/cm^3

Nysel HK-4 or Ni 3609F is a nickel flakes catalyst capable of superior selectivity for hydrogenation of corn, rapeseed, marine and other more difficult to harden oils. Twenty-five percent of

nickel is supported on a proprietary support, dry-reduced and is protected by 60% stearine. It is active and poison resistance.

Kawaken catalyst is the flake-form Raney nickel catalyst.

Hydrogen gas was bought from T.I.G. Trading limited.

4.2 Instruments and Apparatus

4.2.1 Preparation of the Nickel Catalysts

The instruments and apparatus for the preparation of nickel-supported catalysts are as the follows:

(1) Precipitator (Figure 4.1) It is used for precipitation method. A 2-L beaker as precipitating vessel, a pH meter, and a heating coil with stirrer were used for precipitating the precursor. The pH meter was used to control the pH during precipitation. The heating coil composed of a mercury thermometer for automatic controlling of temperature of the liquid in the beaker, and a stirrer which the speed can be controlled.

(2) Electric Oven The washed precipitate was dried in the electric oven at 110°C

(3) Electric Furnace (Figure 4.2) The dried precipitate was calcined in the Carbolite electric furnace type ESF 12/5 with a Eurotherm temperature controller/programmer type 812.

(4) Calcinator The calcined precursor was reduced in the calcinator which was specially fabricated for this study as shown in Figure 4.3.

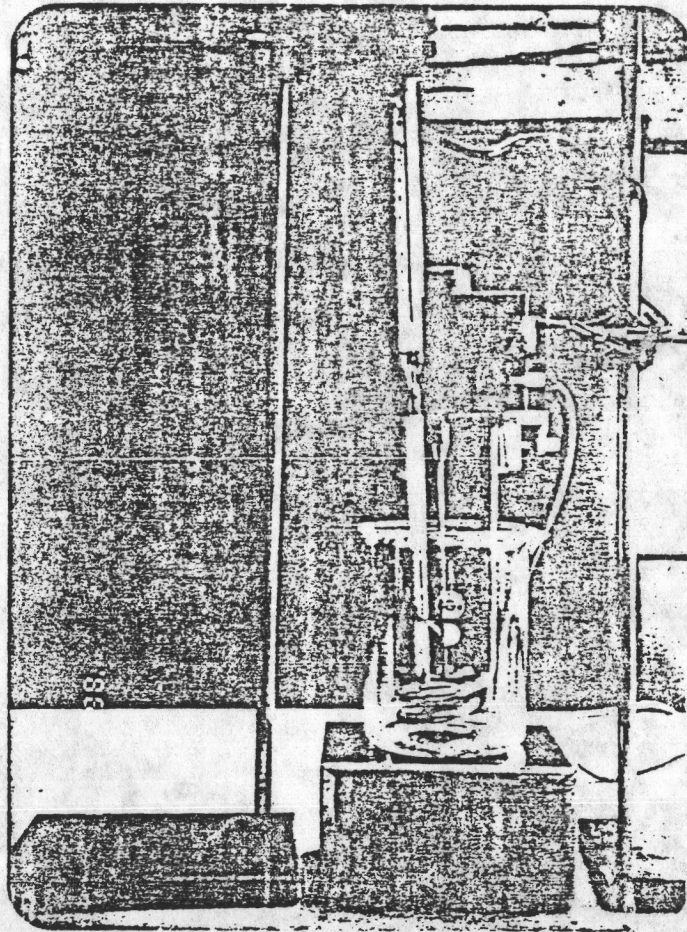


Figure 4.1 Precipitator

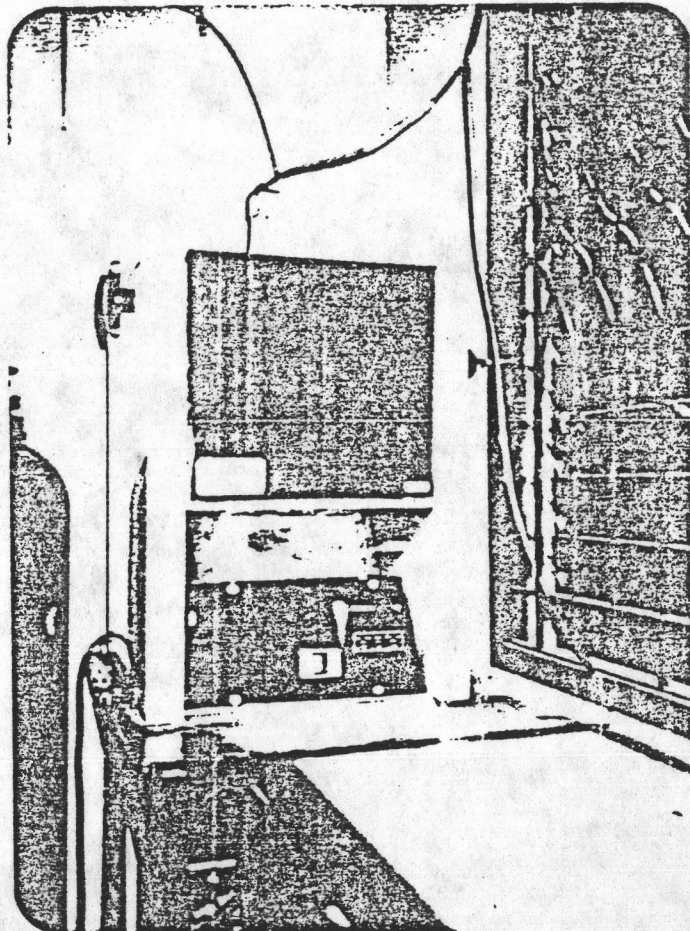


Figure 4.2 Electric furnace

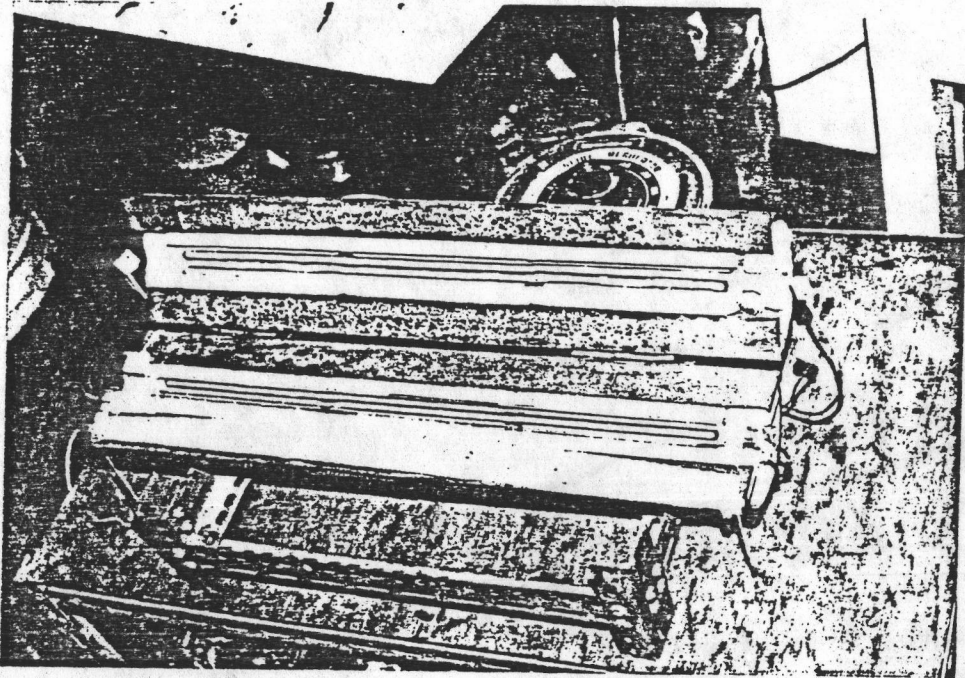


Figure 4.3 Calcinator

4.2.2 Determination of Nickel Contents of the Catalysts

The catalysts nickel loadings were determined by the atomic absorption spectrophotometer IL551 from the Instrumentation Laboratory Inc. (Figure 4.4)

4.2.3 Hydrogenation

The hydrogenation of rubber seed oil was studied in the hydrogenation apparatus which consisted of five parts as the followings:

(1) Reactor (Figure 4.5) The hydrogenation reactor is the high pressure stirred reactor model 4521 from the Parr Instrument Company. The reactor can work at the pressure range of 0-2000 psig and consists of a 1000-cm³ stainless steel 316 cylindrical bomb, a bomb head, a bomb heater, two stirrers and a spiral cooling coil.

(2) Adjustable Speed Motor Controller (Figure 4.6) The controller was model 64EEN of Parr Instrument Company. Its stirring speed can be adjusted in the range of 0-1000 rpm.

(3) Automatic Temperature Controller (Figure 4.7) It consists of a magnetic switch which connected to a Variac and a RKC model PF-8B1C-M temperature controller. It was operated in conjunction with a thermocouple installed in a thermowell attached to the bomb head to provide temperature read out. A dial setting established a set point at any temperature within the range from 0-400°C.

(4) Cooling System (Figure 4.8) It is composed of 2 parts for cooling, the reaction and the stirrer. It was found

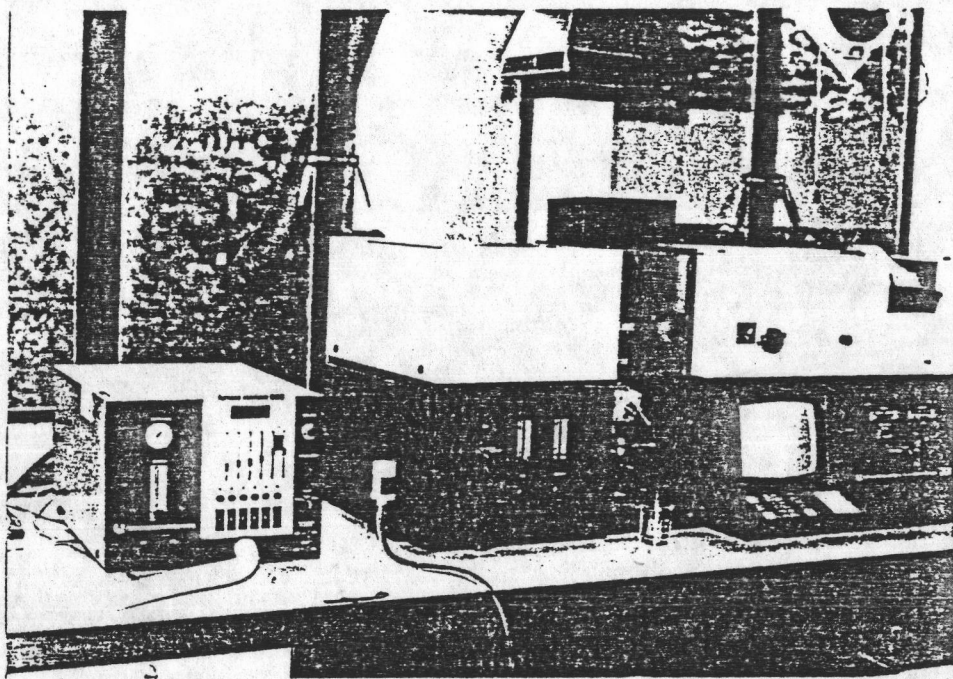


Figure 4.4 Atomic absorption spectrophotometer

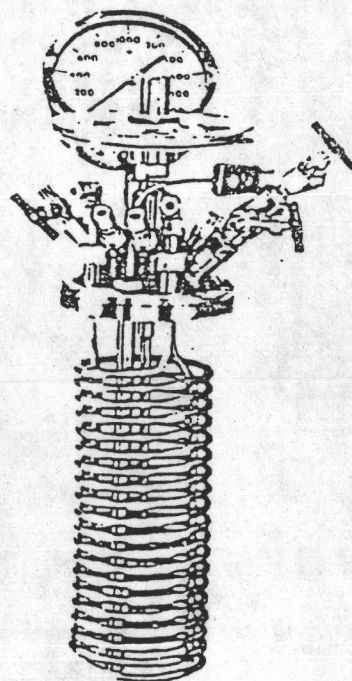
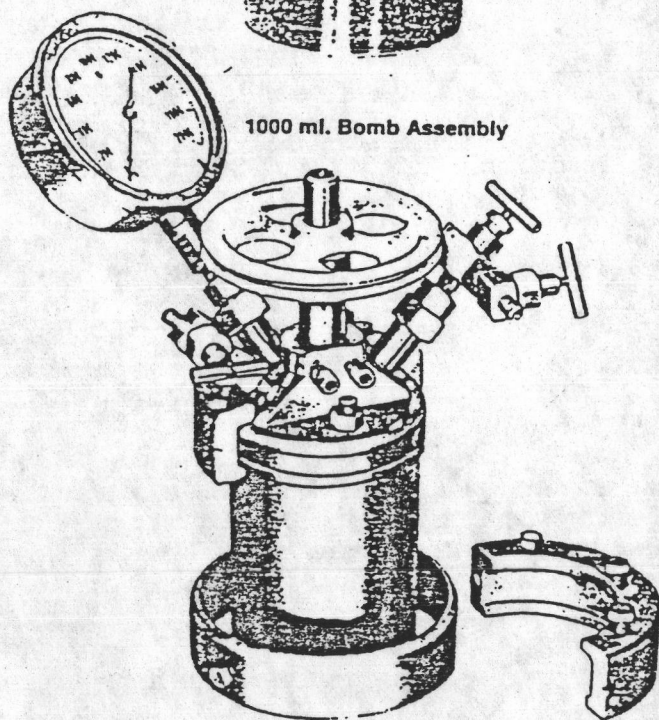
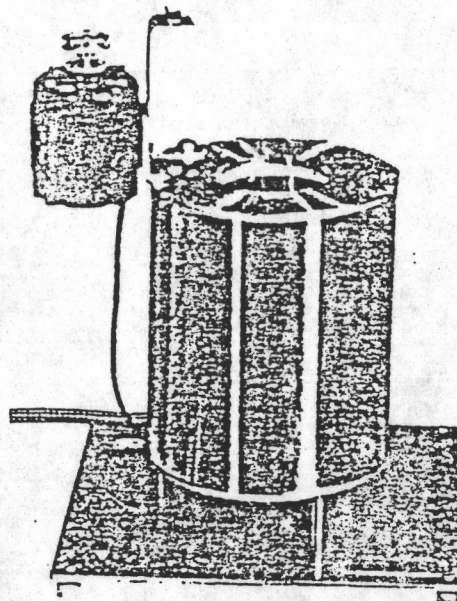
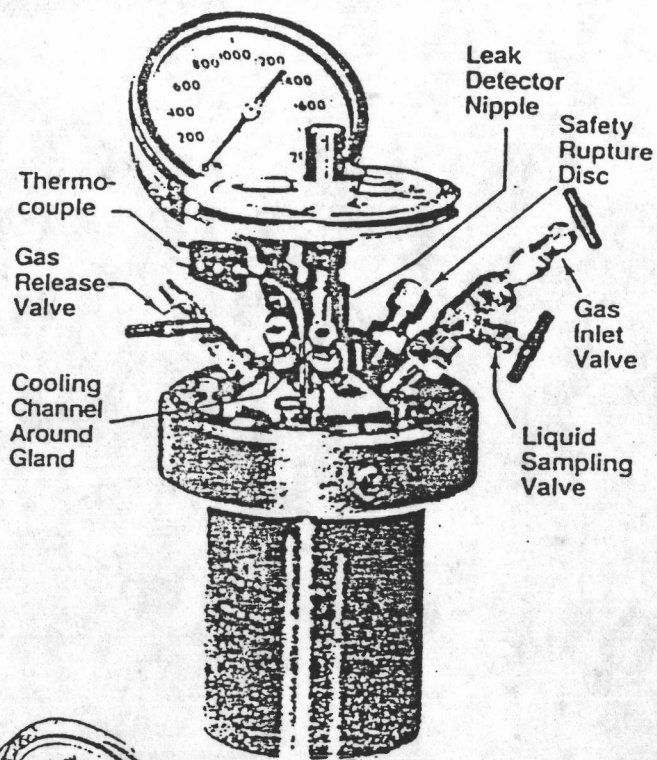


Figure 4.5 Reactor

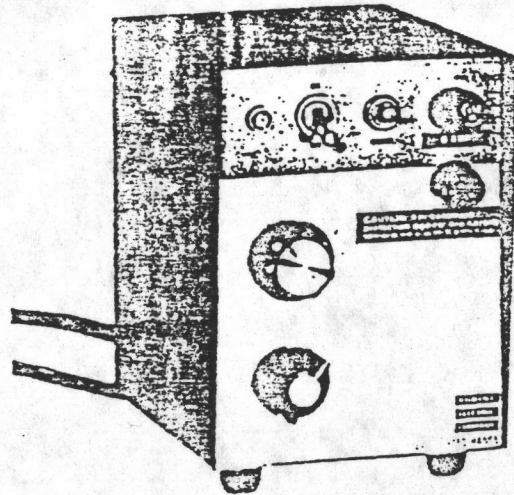


Figure 4.6 Adjustable speed motor controller

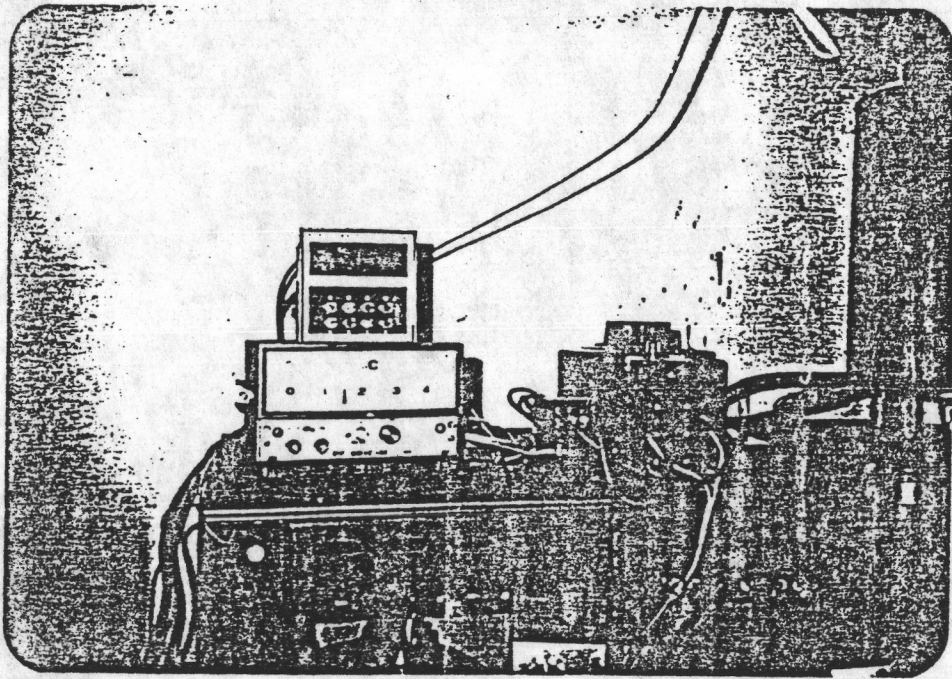


Figure 4.7 Automatic temperature controller

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. Then it must be cooled by the cooling 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 Eyela cooling bath.

(5) Gas Controlling System The system consists of:

- a hydrogen tank 1 equipped with a pressure regulator (0-400 psig) 2 and an on-off valve 3

- a supplied hydrogen tank 4 is used for supply hydrogen gas to the reactor. This tank is equipped with a pressure gauge 8 and a pressure regulator (0-350 psig) 9.

- an oxygen-free nitrogen tank 5 equipped with a pressure regulator (0-200 psig) 6, a three-way valve 7, pressure gauge 12, and on-off valves 10 and 11.

- an on-off valve 15 and a needle valve 13 were connected to the gas release tube.

The flow diagram of the hydrogenation system was shown in Figure 4.9.

Figure 4.10 showed all of the hydrogenation system.

4.2.4 Analysis of the Hydrogenated Rubber Seed Wax

The properties of the hydrogenated rubber seed wax were analyzed by using glasswares and chemicals.

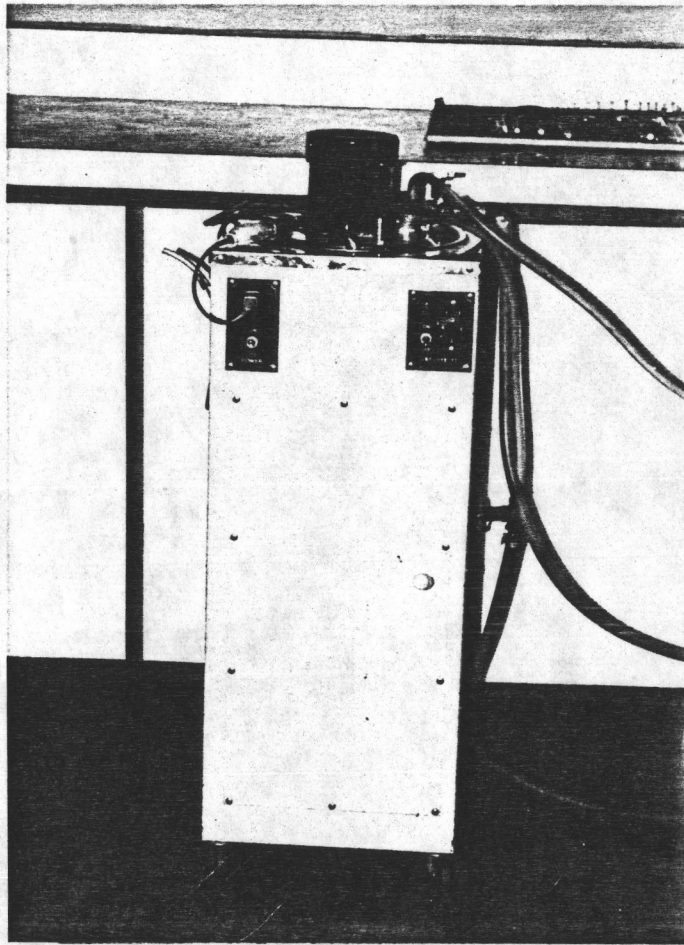


Figure 4.8 Cooling system

- | | | | |
|--------------------------------|----------------------|-------------------|--------------------------------------|
| 1 H ₂ tank | 6 Pressure regulator | 11 On-off valve | 16 Automatic temperature controller |
| 2 Pressure regulator | 7 Three-way valve | 12 Pressure gauge | 17 Thermocouple |
| 3 On-off valve | 8 Pressure gauge | 13 Needle valve | 18 Adjustable speed motor controller |
| 4 Supplied H ₂ tank | 9 Pressure regulator | 14 Reactor | |
| 5 N ₂ tank | 10 On-off valve | 15 On-off valve | |

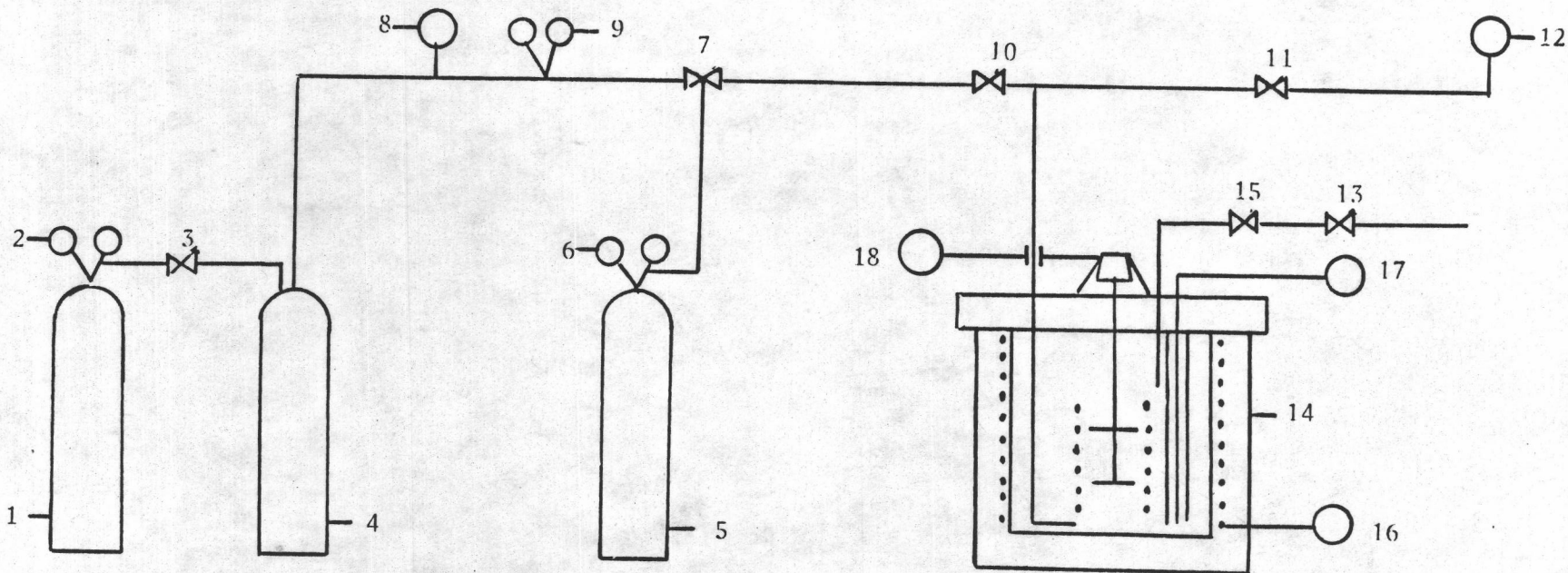


Figure 4.9 Flow diagram of the hydrogenation system

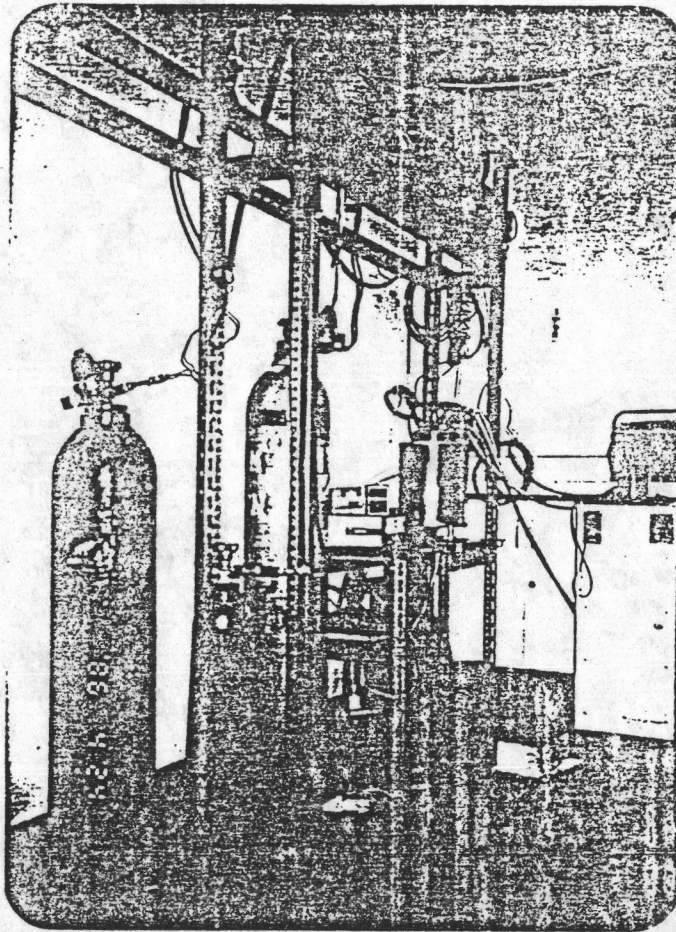


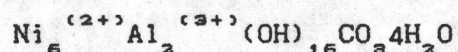
Figure 4.10 Hydrogenation system

4.3 Procedure

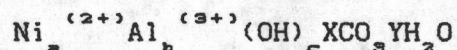
4.3.1 Preparation of the Nickel Catalysts

4.3.1.1 Precipitation Method

U.S. Patent No. 3,896,053 [45] was selected to be the instruction manual of this preparation. The precipitate or the precursor is parts of a series of mixed crystals which may be generally represented by the following formula:



If this instruction manual is followed, there will be only one nickel loading be prepared. For this study, the instruction manual was applied in order to vary the nickel loading. Then the formula of the nickel loading may be



The calculation of the amount of the nickel loading was based on the amount of alumina (Al_2O_3) and nickel metal (Ni) because it was supposed that after reduction the catalyst was nickel on alumina support. From the original formula, the nickel loading was about 77% and from the two applied formula, the nickel loadings were approximately 50 and 20%.

Table 4.2 showed the data of precipitation of nickel catalysts.

For the preparation of the precursor, the following solutions were prepared.

Table 4.2 Data of precipitation of nickel catalysts.

	Precipitated No. 1	Precipitated No. 2	Precipitated No. 3
Solution 1			
Ni(NO ₃) ₂ ·6H ₂ O, g	175.0	105.0	45.0
Al(NO ₃) ₃ ·9H ₂ O, g	75.0	154.5	267.6
Volume, cm ³	400	300	434
Solution 2			
Na ₂ CO ₃ , g	95.7	104	114
Volume, cm ³	452	490	535
Solution 3			
H ₂ O, cm ³	125	121	136
Precipitate color	green	green	green
After calcination	grey	grey	grey
After reduction	black	black	black

Solution 1: Ni(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O were dissolved in distilled water to give a 2M solution.

Solution 2: Na₂CO₃ was dissolved in distilled water to give a 2M solution.

Solution 3: Distilled water was placed in the precipitating vessel.

Solutions 1, 2 and 3 were separately heated to approximately 80 °C. Enough solution 1 was then added in the precipitating vessel with stirring until a pH of 5 was reached. The remainder of solution 1 was then added at a rate of approximately 8.9 cm³/s whilst solution 2 was added so as to maintain a pH of from 4.5 to 5.5. Not until all of the nitrate

solution had been added was the remainder of the soda solution added to give a pH of 6.5. The mixture of aqueous phase and precipitates was stirred for a further 15 minutes at 80 °C and the precipitate was then filtered off by Whatman filter No. 42 and washed until no more nitrate could be detected in the filtrate. Brown-ring test method was used to check nitrate.

The washed precipitate was dried at 110 °C for 12 hours and was ground through 200 mesh screen. The precursor thus obtained was transferred into a porcelain basin for calcination in the Carbolite electric furnace at 350 °C for 20 hours and ground through 400 mesh screen. The calcined precursor had dark grey or grey color depending on the nickel loading. Its form was NiO and Al₂O₃. It was transferred into a ceramic boat and reduced in a stream of hydrogen at 450 °C with a flow rate of 100 cm³/min for 7 hours. Finally, after reduction, the precursor was converted to active nickel metal (Ni) on alumina (Al₂O₃) supports.

The nickel contents of the precipitated catalyst obtained was determined by atomic absorption spectrophotometer.

4.3.1.2. Dry Impregnation Method

In order to compare with the prepared precipitated catalysts, dry impregnated nickel catalysts was prepared. Single impregnation was used in this procedure. NHK-3 Sumitomo Alumina support which particle size range 325-400 mesh was used. The support characteristics was shown in Table 4.3

The 26-cm³ nickel salt stock solution was prepared by dissolving 22.01 g of Ni(NO₃)₆H₂O in 15.3 cm³ distilled water. A 40.0 g of the 325-400 mesh alumina support was poured into a 500-cm³ suction flask equipped with a 50-cm³ burette through the

Table 4.3 Characteristics of the NHK-3 Sumitomo Alumina Support.

Shape	sphere
Color	white
Particle size, mm	4-6
Ignition loss, %	7.0
Fe ₂ O ₃ , %	0.02
SiO ₂ , %	0.02
Na ₂ O	0.08
Al ₂ O ₃ , %	92.8
Pack density, g/cm ³	0.62
Pore volume, cm ³ /g	0.65
BET surface area, m ² /g	340
Strength against the pressure, kg	14

mouth. Vacuum pump was connected to the flask in order to reduce the air pressure to 640 mm.Hg. The nickel stock solution was gradually dropped on the support while the flask containing the supports was swirled. After the solution was completely adsorbed on the support, the impregnated supports were transferred into a 250-cm³ beaker and dried in the oven at 50 °C for 6 hours, 75 °C for 6 hours, 100 °C for 8 hours, and finally 110 °C overnight. The dried impregnated support-nickel salt was transferred into a ceramic boat and calcined in the calcinator to convert the nickel salt to nickel oxide. The calcinator was set at 300 °C and N₂ flow rate of 80 cm³/min. The calcination period was 6 hours and the catalyst color was changed from green, Ni(NO₃)₂, to black NiO. The NiO-support was reduced in the calcinator at 450 °C with H₂ flow rate at 100 cm³/min for 5 hours to convert nickel (NiO) to active nickel metal (Ni).

4.3.2 Determination of Nickel Contents of the Catalysts

Addition method was used to determine the nickel content by atomic absorption spectrophotometer.

A catalyst sample was weighed accurately in order to prepare the solution of 0.2 mg Ni ion in 1 cm³ solution. The sample was placed in a 100 cm³-beaker and digested with 50 cm³ concentrated HNO₃ until the solution dried. The solution was cooled to room temperature, filtered on a Whatman filter paper No. 42 and washed with distilled water until it was salts-free. The solution was adjusted the volume to 250 cm³ in a volumetric flask.

Series of mixture solution of 3-7 mg Ni ion per litre of solution were prepared by diluting 1 cm³ of sample with 1,2,3,4 and 5 cm³ of the standard 100.00 mg/L stock solution of Ni ion with distilled water in the 100-cm³ volumetric flasks.

The atomic absorption spectrophotometer was set at the condition below:

Light Source	Hallow Cathod 1L Lamp No. 62819
Lamp Current	10 mA
Wavelength	232.0 nm
Slit Width	40 um
Bandpass	0.15 nm
Burner Head	Single Slot
Flame Description	Air-Acetylene Oxidizing, Fuel Lean, Blue

After the atomic absorption spectrophotometer was set, the mixture solutions were drawn to the flame and the detector responses were recorded. To obtain the concentration of

the samples, the detector responses against the concentrations of the mixture solution were plotted and least-square expression techniques were used. The point of intersection on the abscissa gave the concentration of the sample solution directly.

Vangmaneerat, B. [34] has described the detailed of this atomic absorption spectrophotometer in her work.

4.3.3 Hydrogenation

Rubber seed oil 200 g and the required quantity of catalyst were charged into a Parr high pressure hydrogenator of 1-L capacity provided with a Variac to control the heat input, thermocouple, mechanical stirrer, and pressure gauge. Before operation, the system was checked of leak by compressing with high-pressure oxygen-free nitrogen gas for half an hour. The reactor was heated keeping the stirrer on. Nitrogen gas was not vent. It took about an hour for the reactor to reach the desired temperature. If the hydrogenation was at low temperature such as 120 °C and 140 °C, the reactor would be heated to reach a value about 10 °C higher than the desired temperature because the temperature would decrease to the desired temperature when nitrogen gas was vent and hydrogen gas was supplied. If the reaction was taken at high temperature, 160 °C and 180 °C, the reactor would be heated to the desired value because of the exothermic reaction, the temperature would suddenly increase when the reaction occurred.

When the reaction temperature reached the desired value, hydrogen gas was introduced to the hydrogenator to displace nitrogen gas inside the reactor. The desired pressure was maintained constant throughout the run by means of a pressure-regulator. The temperature was maintained at the desired

value by the manual operation of the water-cooling coil and the magnetic switch connected with the temperature controller. The hydrogenation was run until the pressure-reading gauge constant but not more than 5 hours. The data of hydrogen pressure drop of the supplied tank 4 read from the pressure-reading gauge 8 versus time were recorded.

The rubber seed wax-catalyst mixture was transferred into a 250-cm³ beaker and filtered on Whatman filter paper No. 1 in an oven at 60-70 °C. The properties of the wax were determined.

Vangmaneerat, B. [34] has described the detailed of the operation of this hydrogenation system in her work.

The hydrogenation procedure consisted of as the followings:

4.3.3.1 Selection of the Suitable Temperature

The suitable temperature from this experiment was used for screening the best commercial catalyst. The hydrogenation condition was set at 150 psig, 0.2% Ni/oil of G95E catalyst, agitation 700 rpm and reaction period of 5 hours. The data were shown in Table A1.

4.3.3.2 Screening of Commercial Catalysts

To select the best commercial catalysts out of four which the hydrogenation data of hydrogen consumption with time were shown in Table A2. The hydrogenation condition was set at 160 °C, H₂ pressure in the reactor 150 psig, agitation 700 rpm, concentration of catalyst 0.2% Ni based on oil (weight per cent) and reaction period 5 hours.

4.3.3.3 Selection of the Optimum Operating Condition

From 4.3.3.2, the catalyst Nysel HK-4 and G95E gave the iodine value versus time curves (Figure 5.4) which showed better reaction rate than the others. Nysel HK-4 was selected for study the optimum operating condition. The reason of selection was given in Chapter 5.

The effect of reaction temperature, hydrogen pressure, catalyst concentration, and agitation were studied under the conditions which were shown in Table 4.4. The hydrogenation data were shown in Table A3 to Table A6.

4.3.3.4 Comparison of the In-house Catalysts with the Best Commercial Catalyst

For this study, the precipitated nickel-supported catalysts of various concentrations of nickel and impregnated 10% nickel catalysts were compared with the Nysel HK-4 nickel catalyst. The reaction condition was 160 °C, hydrogen pressure 150 psig, agitation 700 rpm, catalyst concentration 0.2% Ni/oil and reaction period 5 hours. The hydrogenation data were shown in Table A7.

4.3.4 Analysis of The Hydrogenated Rubber Seed Wax

The waxes from the study of the effects of temperature and pressure were analyzed in order to compare with the kinetic study. The analysis was done by Department of Science Service, Ministry of Science, Technology and Energy. The A.O.C.S. Methods, as shown in Appendix E, were used as the method of analysis. The A.O.C.S. Official Method Cd 1-25, the A.O.C.S.

Table 4.4 Study of the operating conditions.

Run no.	Parameter	Reaction temperature (°C)	Hydrogen pressure (psig)	Catalyst concentration (%Ni/oil)	Agitation (rpm)
1	Temperature	120	150	0.2	700
2		140	150	0.2	700
3		160	150	0.2	700
4		180	150	0.2	700
5	H ₂ pressure	160	60	0.2	700
6		160	90	0.2	700
7		160	120	0.2	700
8	Catalyst concentration	160	150	0.05	700
9		160	150	0.1	700
10		160	150	0.4	700
11	Agitation	160	150	0.2	200
12		160	150	0.2	400
13		160	150	0.2	600

Tentative Method 3a-63, the A.O.C.S. Official Method Ce 2-26 and Ce 1-62 were used for analysis of iodine value, acid value and composition of fatty acids, respectively.

The melting points of the products were determined by the A.O.C.S. Official Method Cc 3-25 (see Appendix E). This method is applicable to such fats as coconut oil, stearin, hydrogenated fats and hard tallows.