CHAPTER V

RESULTS AND DISCUSSIONS

Due to many conflicting statements about conditions in the preparation of Raney nickel catalysts, it was necessary to study the effects when the conditions were changed. When considerations were taken about the preparation procedure, it could be seen that the activity of the catalyst might be affected by various parameters; period of time of digestion, temperature of digestion, concentration of NaOH solution and the ratio of Ni-Al alloy to NaOH (anhydrous). These parameters were varied and the catalysts thus obtained were tested in the hydrogenation of castor oil. The results, plots of the amount of hydrogen consumed versus time during reaction or "curves of hydrogen consumption", are illustrated in part 5.1 of this chapter.

The best catalyst obtained from part 5.1 was used to find the optimum operating conditions for the hydrogenation of castor oil. To achieve this, the concentration as Ni/oil of catalyst used in the reaction, temperature and pressure were varied. The results are explained in part 5.2.

The incorporation of palladium compound into Raney nickel catalysts was consequently carried out. By varying the percentage of Pd/Ni (metal/metal), the effects of the presence of palladium and of the amount of palladium loaded might be shown. This is elucidated in part 5.3.

5.1 Effects of Parameters in the Preparation Procedure of Raney Nickel Catalyst.

Several catalysts were prepared according to various parameters and then tested by hydrogenating castor oil at 150 °C, under a pressure of 150 psig and a catalyst concentration as Ni/oil of 0.1%.

The effect of each parameter is separately shown as follows:

5.1.1 Effect of Digestion Time Period.

In the preparation of Raney nickel catalysts, the digestion temperature was fixed at 110 °C, the concentration of NaOH at 25% and the ratio of Ni-Al alloy to NaOH (anhydrous) at 1:5. The digestion time periods were 1, 2 and 3 hours and the catalysts obtained were designated T1, T2 and T3, respectively.

From the results shown in Fig.5.1, it is apparent that the hydrogen consumption for T2 and T3 was nearly the same, but higher than that for T1. That meant the former two catalysts had the same activity and were more active than T1.

From thermodynamic point of view, it might be concluded that the reaction between NaOH and Ni-Al alloy requires 3 hours to reach its equilibrium. Therefore, a digestion period of 3 hours should be selected. However, a digestion period of 2 hours was chosen in subsequent preparations of the catalyst in order to minimize time.

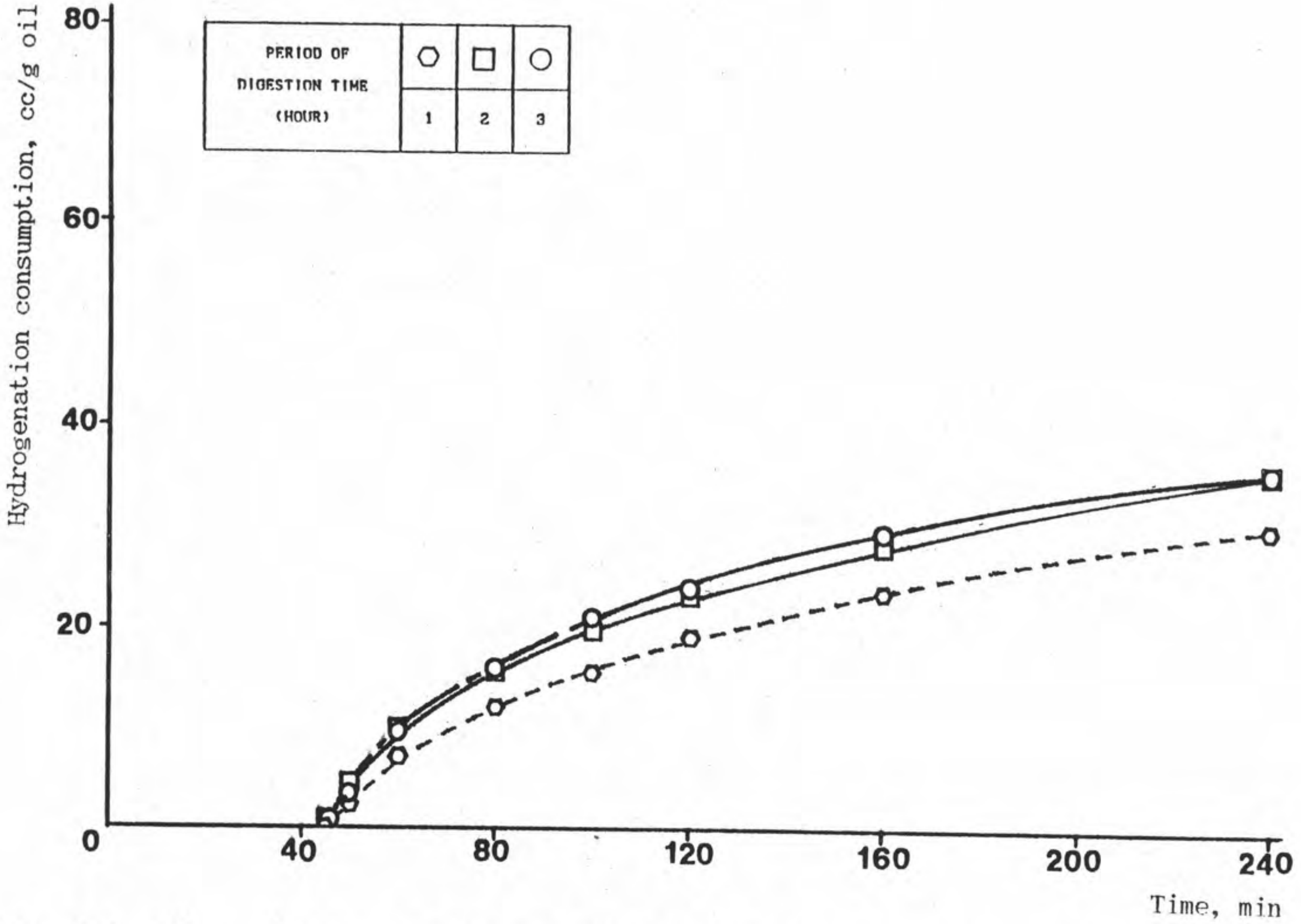

Fig. 5.1 Effect of Digestion Time on Activity of Catalyst for the Hydrogenation:
Alloy:NaOH = 1:5 ; Conc. of NaOH = 25 % (wt/wt) ; Digestion Temp. = 110 °C.
Reaction : Temp. = 150 °C ; H_2 Press. = 150 psig.; 800 rpm.; Cat. Conc. = 0.1 % Ni/oil.

5.1.2 Effect of Digestion Temperature.

The reaction between NaOH and Ni-Al alloy took 2 hours, using an NaOH concentration of 25% and a ratio of alloy to NaOH being 1:5. The digestion temperature was varied to 90°, 110°, 130° and 150°C and the catalysts obtained were named as TE1, TE2, TE3 and TE4, respectively.

The results are shown in Fig.5.2 with the catalyst that showed maximum activity referred to as TE2. This meant that the optimum temperature for the preparation of the Raney catalyst was 110°C. This phenomenon could be justified as follows:

The reaction between NaOH and Ni-Al alloy, like many other reactions, was dependent upon temperature; the higher the temperature of reaction, the better the rate of reaction. So, the catalyst digested at a higher temperature was likely to be more active. However, if the digestion temperature was too high, the porous structure of the Raney nickel, and the product of the reaction, would be destroyed [49], and the activity of the catalyst would be reduced due to a reduction of surface area caused by the destruction. The higher the temperature, the more structure destruction of the catalyst. An optimum temperature was thus chosen.

5.1.3 Effect of Concentration of NaOH Solution.

The reaction between NaOH and Ni-Al alloy was carried out for 2 hours at 110° C with a ratio of the alloy to NaOH equal to 1:5. The concentrations of NaOH solution were 12.5, 16.7 and 25% and the catalysts obtained were designated as C1, C2 and C3, respectively. (The upper limit was 25% because, when the concentration was greater than 25%, NaOH was not completely

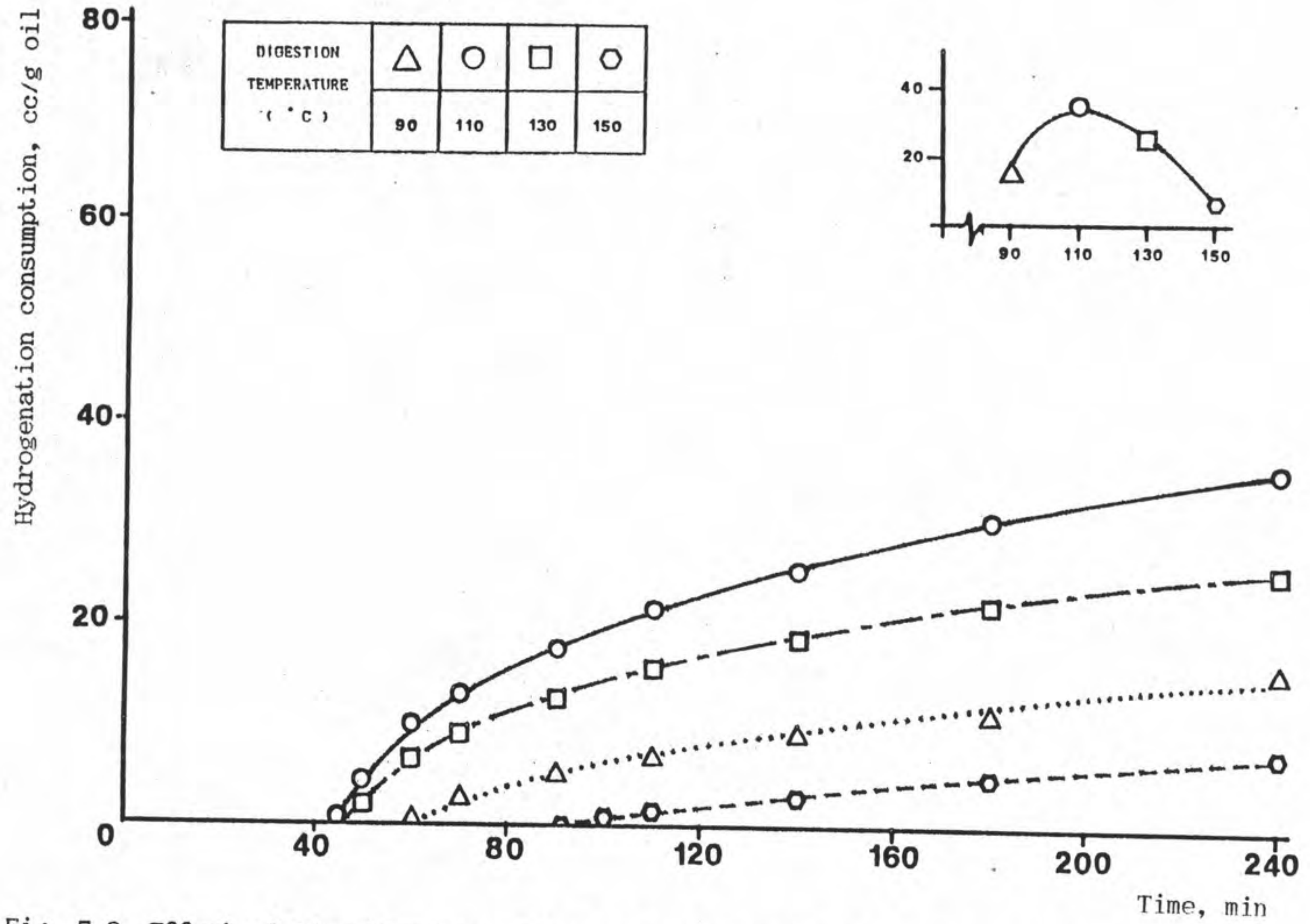

Fig. 5.2 Effect of Digestion Temperature on Activity of Catalyst for the Hydrogenation: Alloy:NaOH = 1:5 ; Conc. of NaOH = 25 %(wt/wt) ; Digestion Time = 2 hr. Reaction : Temp. = 150 °C ; H_2 Press. = 150 psig.; 800 rpm.; Cat. Conc. = 0.1% Ni/oil.

dissolved in water.

The curves of hydrogen consumption were shown in Fig.5.3. It can be seen that the higher the concentration of NaOH solution, the greater the activity of the catalyst (C1 > C2 > C3).

This can be easily explained by the number of times, in a limited time, for the reactant molecules to collide and react with each other, as follows:

Consider a constant volume, it can be justified that when the concentration is dilute, the density of the molecules to be reacted is reduced. As a consequence, the number of times of reactant molecules colliding with each other is lower. So, in a limited time, the reaction rate, for lower concentration, is not high enough to approach equilibrium.

5.1.4 Effect of the Ratio of Ni-Al Alloy to NaOH (anhydrous).

The reaction between NaOH and Ni-Al alloy took place at 110°C for 2 hours, using an NaOH concentration of 25%. The ratio of Ni-Al alloy to NaOH (anhydrous) was 1:3, 1:5 and 1:7.5 and the catalysts obtained were designated as R1, R2 and R3.

The curves of hydrogen consumption were shown in Fig.5.4. The curves were nearly the same. It can be concluded that, considering the chemical equation below, there is no effect of ratio of the alloy to NaOH as long as NaOH is present in excess.

The chemical equation is:

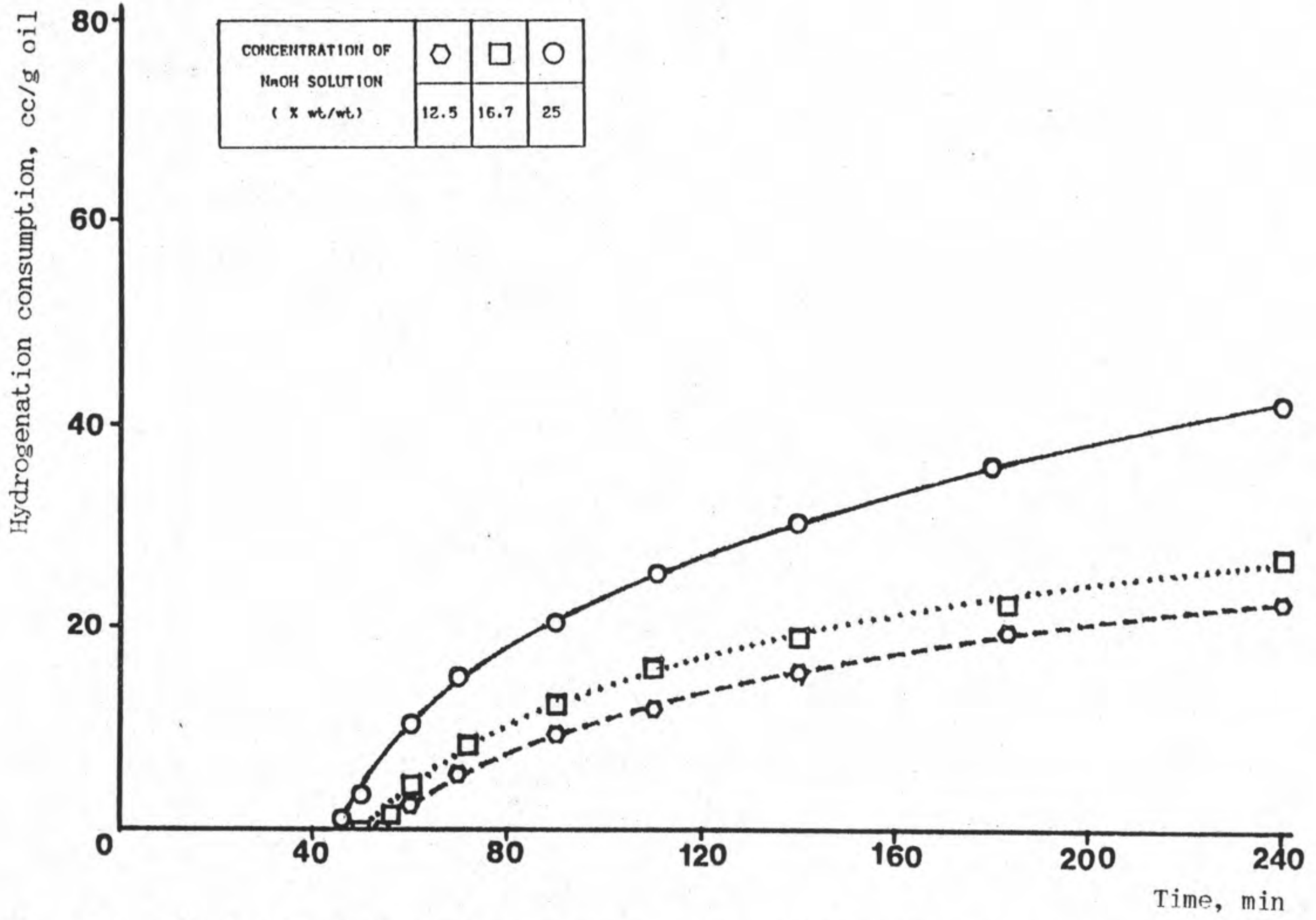

Fig. 5.3 Effect of NaOH Concentration on Activity of Catalyst for the Hydrogenation:
Alloy:NaOH = 1:5 ; Digestion Time = 2 hr.; Digestion Temp. = 110 °C.
Reaction : Temp. = 150 °C ; H_2 Press. = 150 psig.; 800 rpm.; Cat. conc. = 0.1 % Ni/oil.

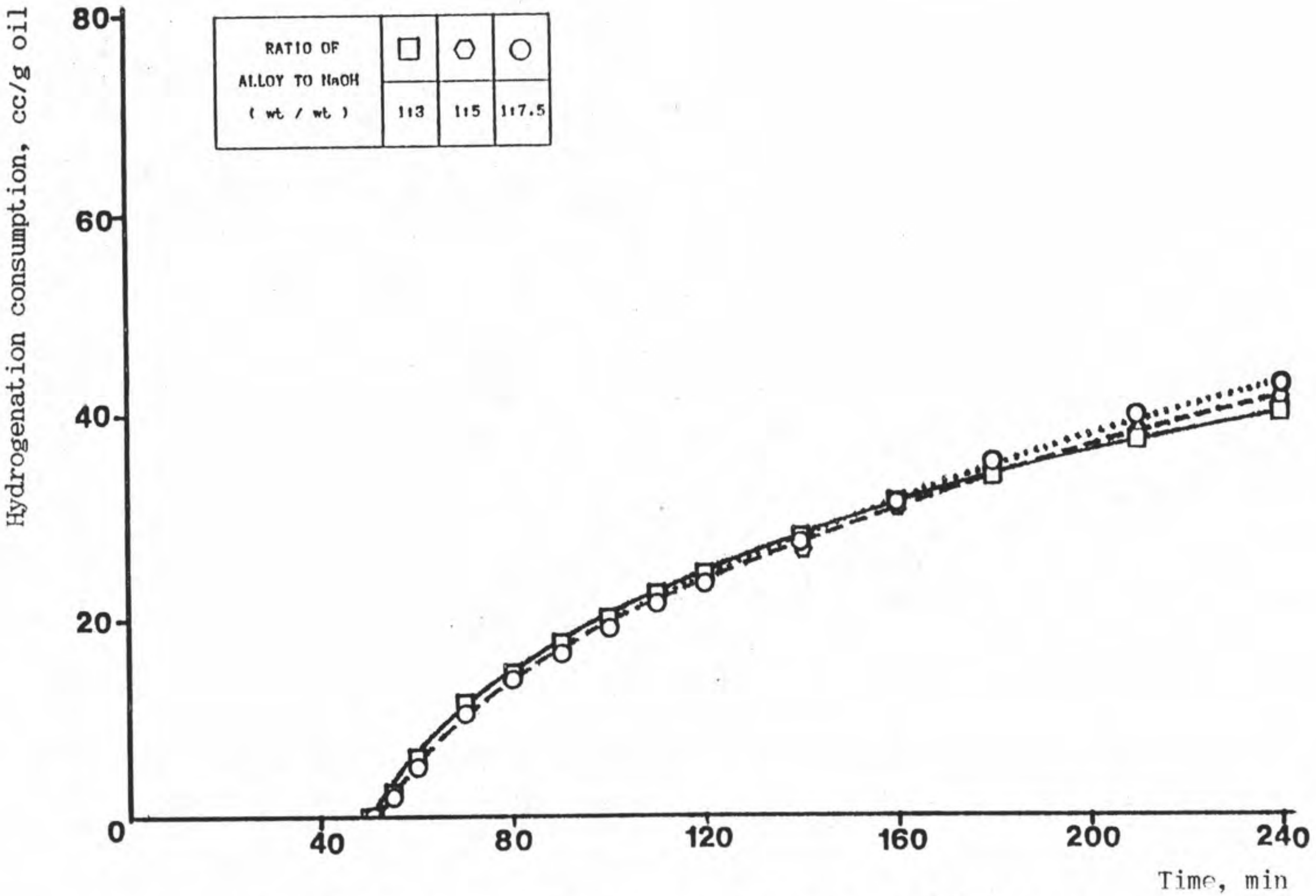

Fig. 5.4 Effect of Alloy to NaOH Ratio on Activity of Catalyst for the Hydrogenation: Conc. of NaOH = 25 % ; Digestion Time = 2 hr.; Digestion Temp. = 110 °C. Reaction : Temp. = 150 °C ; H_2 Press. = 150 psig.; 800 rpm.; Cat. Conc. = 0.1%.

$$Al + 3NaOH \longrightarrow Na_3AlO_3 + 3/2\ H_2$$

So far, it can be concluded that the best conditions for preparation of the Raney nickel are at a digestion temperature of 110 °C, a digestion time of 2 hours, a concentration of NaOH solution of 25% and a ratio of Ni-Al alloy to NaOH of 1:3.

5.2 Optimum Hydrogenation Conditions of Raney Nickel Catalyst.

The Raney nickel catalysts were prepared, using the best conditions obtained from part 5.1, and used in the hydrogenation reaction. The reaction conditions, such as catalyst concentration, temperature and pressure, were changed The results are presented as follows :

5.2.1 Variation of the Amount of the Catalyst.

The hydrogenation of castor oil at 150 °C, under a pressure of 150 psig and a reaction time of 4 hours was studied. The concentration of catalyst, as Ni/oil, was varied to 0.1, 0.2, 0.3 and 0.4%. The curves of hydrogen consumption were shown in Fig.5.5.

From Fig.5.5, it can be seen that when the concentration of catalyst used for the hydrogenation is higher, the induction period is shorter. The rate of reaction is significantly increased as the concentration of the catalyst, as Ni/oil, is changed from 0.1 to 0.3%. However, when the percentage of Ni/oil is raised from 0.3% to 0.4%, the rate is only slightly increased. This phenomenon can be explained as follows:

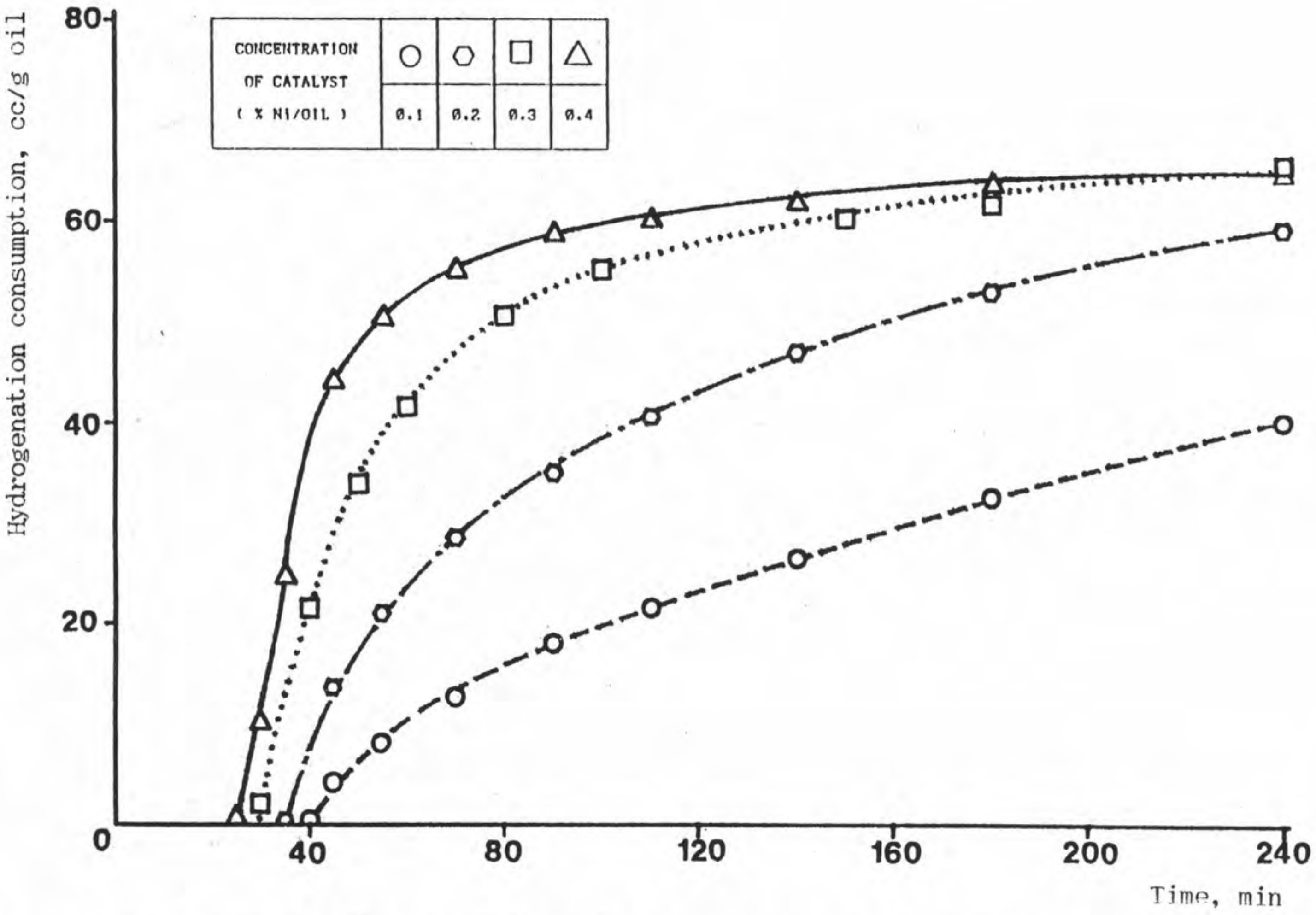

Fig. 5.5 **Effect of Catalyst Amount for the Hydrogenation of Castor Oil:**

Preparation : Alloy:NaOH = 1:3 ; Conc. of NaOH = 25 % ; Digestion Time = 2 hr.;

Digestion Temp. = 110°C. Reaction : Temp. = 150°C ; H_2 Press. = 150 psig.; 800 rpm.

Consider a certain amount of catalyst, when used for a hydrogenation reaction, what happens will be:

(1) A fraction of active sites will be poisoned by the impurities in the castor oil. The poisoning is usually random.

(2) the other fraction will be adsorbed by molecules of the oil and hydrogen gas, and if they adsorb on the adjacent sites, reaction will occur.

Then if the amount of catalyst used is low, and a number of the active sites are poisoned, the probability of finding groups of adjacent sites for the oil and hydrogen to adsorb and subsequently react with each other is low. Also, the number of groups of adjacent sites is low. This can be justified for the case of hydrogenating castor oil using low concentration of catalyst, Ni/oil = 0.1% in this case, which shows long induction period and low rate of reaction.

When the amount of catalyst is larger, both the probability of finding groups of adjacent sites and the number of groups of adjacent sites are higher. This reflects in the shorter induction periods and higher rates of reaction for the cases of hydrogenating castor oil using Ni/oil of 0.2, 0.3 and 0.4%, respectively.

From this study during the variation of concentration of catalyst in the hydrogenation of castor oil, the decision was made to select an Ni/oil ratio of 0.3% as the optimum concentration due to economic aspects.

5.2.2 Variation of Temperature of Hydrogenation Reaction.

The hydrogenation reaction was carried out under a pressure of 150 psig and a reaction time of 4 hours, using a catalyst concentration as Ni/oil of 0.3%. The temperature of reaction was varied to 130°, 150° and 170°C. The results as curves of hydrogen consumption are shown in Fig.5.6.

In Fig.5.6, the curve of hydrogen consumption at 170 °C is above that at 150°C, which in turn is over the curve of hydrogen consumption at 130°C. This means that the Raney Nickel has a better activity at higher temperature.

However, in the selection of a suitable temperature of hydrogenation, other things must be considered. It had been shown in the prior studies [35,48] that the higher the temperature of hydrogenation was raised, the more the hydroxyl value would be lowered. In their studies, it had been suggested that the temperature of hydrogenation should not exceed 150°C.

According to Fig.5.6, it is apparent that, though the activity of Raney Nickel for hydrogenation at 170°C is better, it is not much more than that for hydrogenation at 150 °C. So, the suitable temperature chosen still be 150°C.

5.2.3 Variation of pressure of hydrogenation reaction.

The hydrogenation of castor oil was carried out at 150°C for 4 hours, using a catalyst concentration as Ni/oil of 0.3%. The pressure of reaction was varied to 100, 125, 150 and 175 psig. The curves of hydrogen consumption are shown in Fig.5.7.

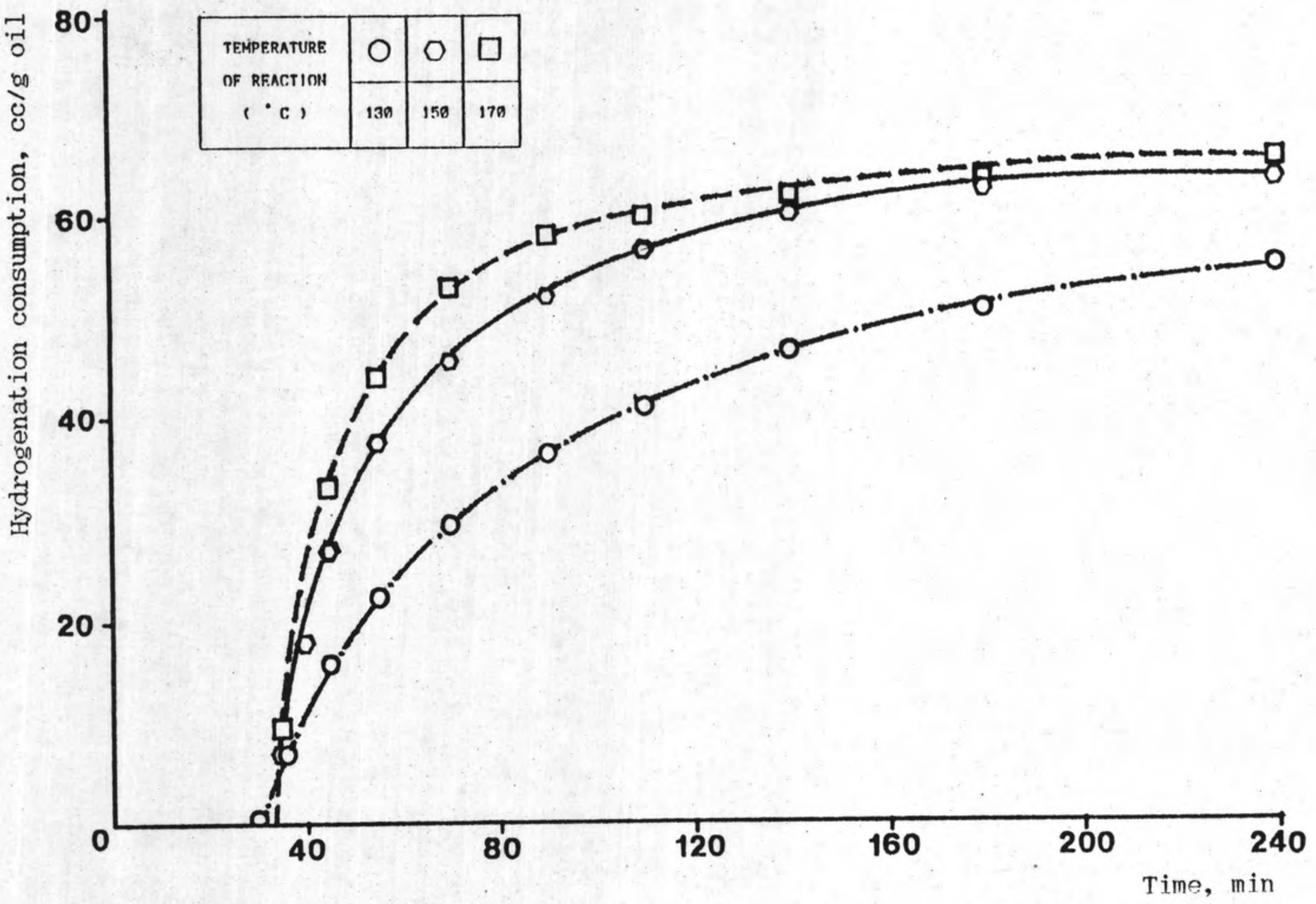

Fig. 5.6 Effect of Reaction Temperature on Activity of Catalyst for the Hydrogenation: Preparation : Alloy:NaOH = 1:3 ; Conc. of NaOH = 25 % ; Digestion Time = 2 hrs.; Digestion Temp.=110 °C. Reaction : Cat. Conc.=0.3 % ; H_2 Press.=150 psig.; 800 rpm.

In Fig.5.7, Raney nickel catalyst shows maximum activity at 125 psig. However, the activities of Raney nickel catalysts at 125, 150 and 175 psig are not much different.

The pressure selected as the best is 125 psig.

In conclusion, the best conditions for the hydrogenation of castor oil using the Raney nickel as catalyst are a temperature of 150 °C, a pressure of 125 psig and a concentration of catalyst as Ni/oil of 0.3%. The hydrogenated castor wax obtained from reaction under these conditions had an iodine value of 5.80, a hydroxyl value of 160.80 and an acid value of 1.00.

5.3 Effects of Palladium Incorporation into Raney Nickel Catalysts.

Several Raney nickel catalysts were prepared following the procedure described in Sec.4.1.3.1 (see Chapter 4) using the best conditions inferred from Sec.5.1. The catalysts were then incorporated with palladium compound, $Pd(NO_3)_2.2H_2O$, following the procedure shown in Sec.4.1.3.2. The ratios of Pd/Ni (metal/metal) were varied to 0.5, 1.0, 1.5 and 2.0%. The catalysts obtained were designated as Pd1, Pd2, Pd3 and Pd4, respectively. When these catalyst were analyzed by ICPS (Inductively Coupled Plasma Spectrometry), the measured values of Pd/Ni were shown in Table 5.1. The catalysts were tested in the hydrogenation of castor oil to find out whether the activities of Raney nickel catalysts were affected or not.

The conditions used in the hydrogenation reaction were: the concentration of catalyst as Ni/oil = 0.2%; a hydrogen pressure of 150 psig; the temperature controlled at 150 °C.

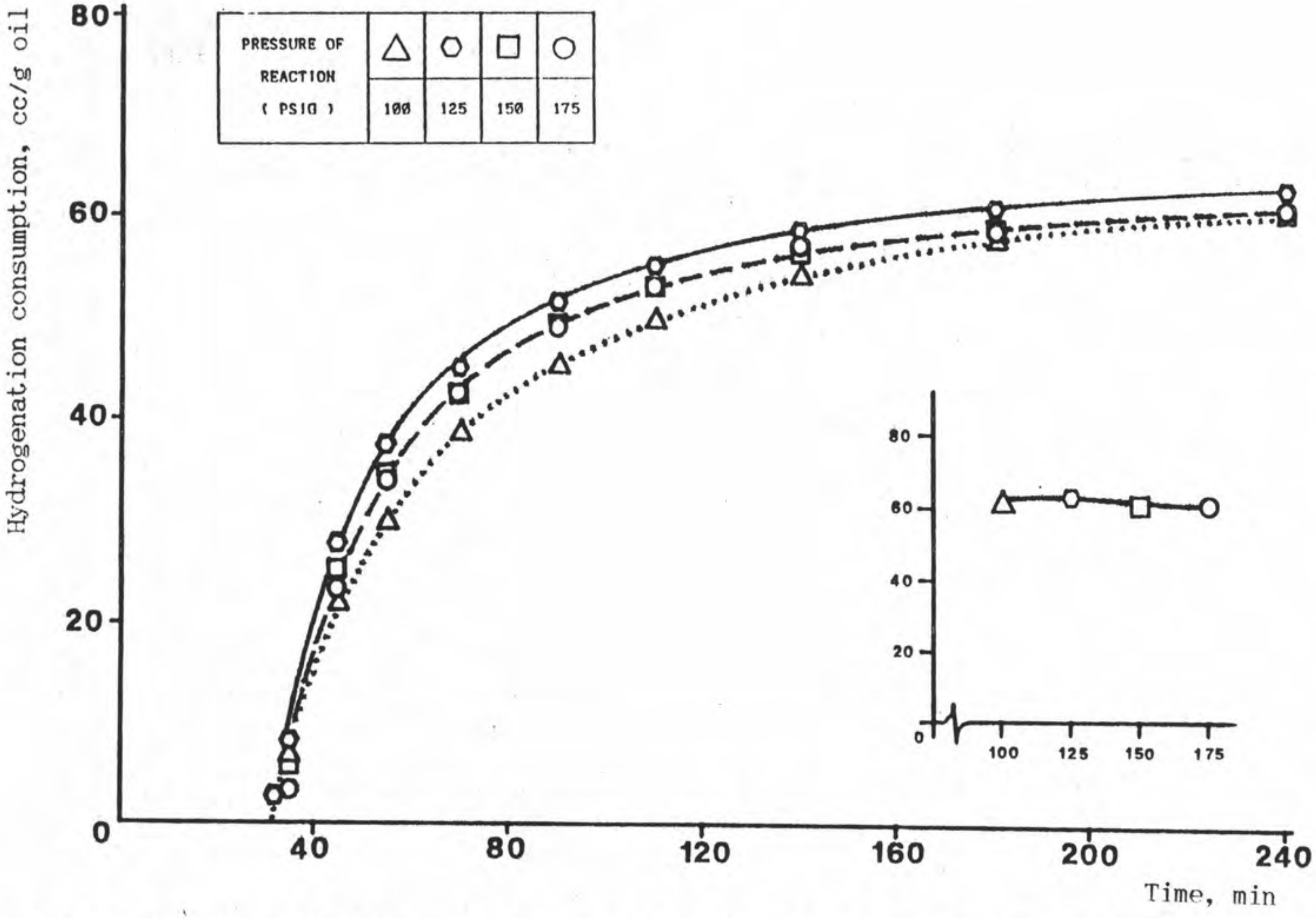

Fig. 5.7 Effect of Hydrogen Pressure on Activity of Catalyst for the Hydrogenation:
Alloy:NaOH=1:3 ; Conc. of NaOH=25 % ; Digestion Time=2 hr.; Digestion Temp.=110 °C.
Reaction : Cat. Conc. = 0.3 % ; Temp. = 150 °C ; 800 rpm.

The concentration of catalyst used is 0.2%, instead of 0.3%, it can be justified as follows:

From Section 5.2.1, it was apparent that when the concentration of catalyst as Ni/oil exceeded 0.3%, the effect of the increased rate of reaction would not be clearly seen. So, the concentration of catalyst of 0.2% was selected.

The effects of Raney nickel catalysts incorporated with palladium compound are shown in Fig.5.8. In this figure, the curves of hydrogen consumption of Pd1, Pd2, Pd3 and Pd4 are plotted in comparison with that of Raney nickel catalyst.

It is apparent that the activity of Raney nickel catalysts when incorporated with palladium (up to 1.0%) was higher than that of pure Raney nickel catalyst. This was concluded owing to the following results:

(1) The rate of hydrogenation reaction when using Raney nickel catalyst incorporated with palladium compound (up to 1.0%) was considerably higher than that when pure Raney nickel catalyst was used.

(2) The induction period of the reaction was also shorter.

(3) The asymptotes of hydrogen consumption curves of Pd1 and Pd2 were raised to higher position. The iodine values (I.V.) of final castor waxes obtained when using Pd1 and Pd2 as catalysts were also lower than that when pure Raney nickel was used, while hydroxyl values and acid values were almost the same (See Table 5.1). These meant that when using Raney nickel catalyst incorporated with palladium (up to 1.0%), only the desired hydrogenation of double

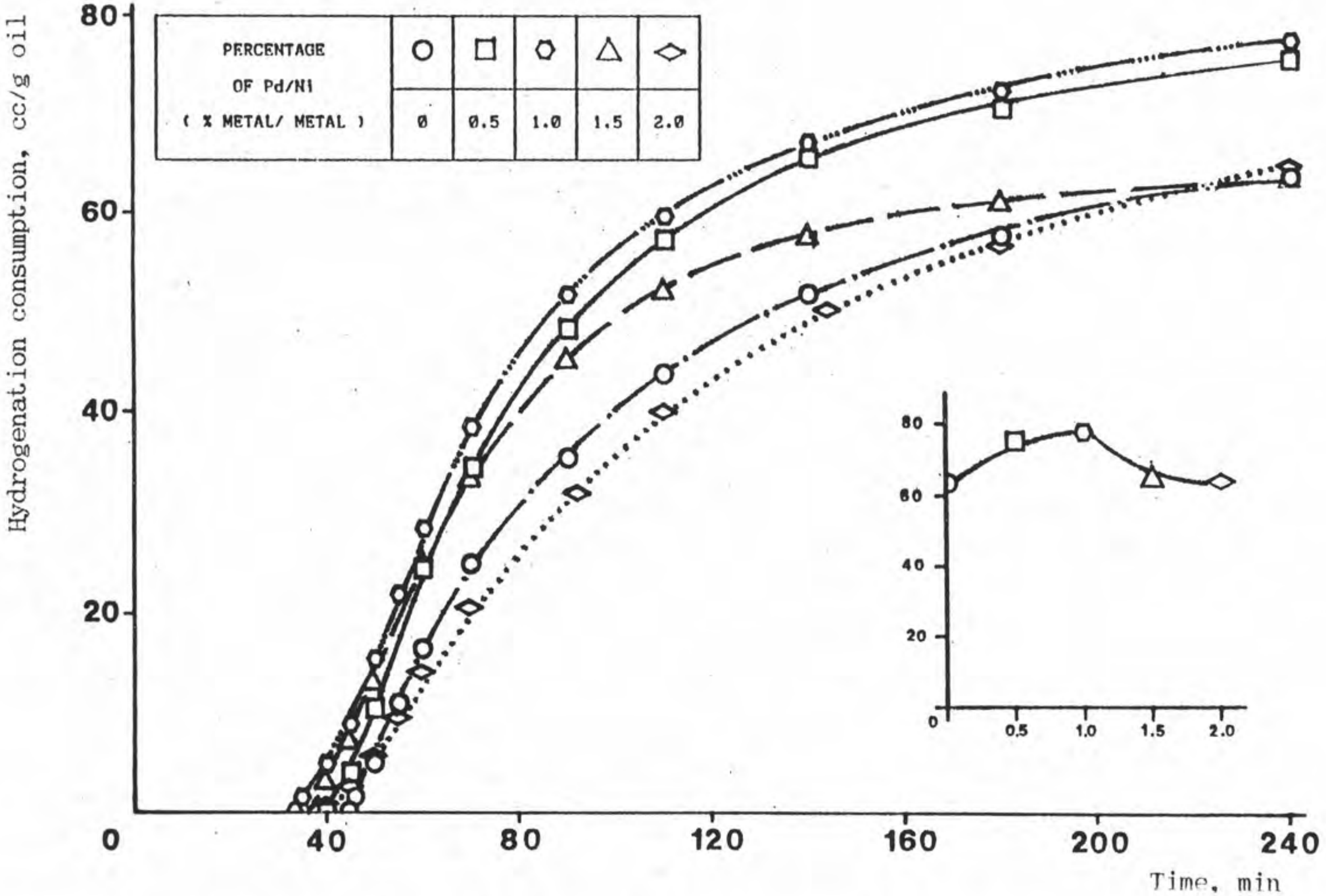

Fig. 5.8 Effect of Palladium on Activity of Catalyst for the Hydrogenation:

Alloy:NaOH=1:3 ; Conc. of NaOH=25 % ; Digestion Time=2 hr.; Digestion Temp.=110 °C.

Reaction : Cat. Conc. = 0.2 % ; Temp. = 150 °C ; H_2 Press. = 150 psig. ; 800 rpm.

bonds in castor oil was accelerated.

When a comparison was made between the activities of Pd1 and Pd2, it could be justified that Pd2 was more active than Pd1 due to a shorter induction time and lower iodine value while the rates and asymptotes of hydrogen consumption curves being the same.

Table 5.1 Properties of Castor Waxes obtained when using various catalysts

Type of catalyst	measured value of Pd/Ni (%)	Properties of Castor Waxes		
		I.V.	OH.V.	A.V.
		87.31^{*}	165.77^{*}	0.69^{*}
Raney nickel		5.56	160.78	0.99
Pd1	0.42	3.54	160.28	1.00
Pd2	0.81	3.29	160.83	0.96
Pd3	0.94	4.17	157.15	1.12
Pd4	1.45	6.01	152.67	0.97

(*) means the properties of castor oil before hydrogenated.

However, when the ratio of Pd/Ni was over 1.0% (Pd3 and Pd4), the curves of hydrogen consumption did not show the same tendency. The results were as follows:

When Raney nickel catalysts were incorporated with palladium compounds in the ratio of Pd/Ni exceeding 1.0%, the asymptotes of hydrogen consumption curves were the same as that of pure Raney nickel catalyst while the hydroxyl values were significantly lowered. Inversely, the iodine value was progressively increased. These implied that the rate of dehydroxylation became competitive with the rate of hydrogenation of the double bond. The catalysts, instead of accelerating the addition of hydrogen to double bonds in castor oil, caused the hydroxyl group in the oil molecule to react with adjacent hydrogen, and thereby leaving a new double bond in the molecule.

So far, it might be concluded that the activity and selectivity of Raney nickel catalyst to the hydrogenation of the double bond in castor oil was improved by the incorporation of palladium compounds in the ratio of Pd/Ni (metal/metal) up to 1.0%. However, if the palladium compound was present in the ratio of Pd/Ni exceeding 1.0%, the activity of Raney nickel would be adversely affected and the selectivity changed to the dehydroxylation reaction.

The five catalysts were further characterized by H_2 adsorption measurement and BET analyzer. The results were shown in Appendix B.