

CHAPTER VI

RESULT AND DISCUSSION

The results from the experiments in Chapter V were presented in Tables and Figures. The results were compared with commercial methyl 12-hydroxystearate showed in Table 6.9 and also discussed in the followings :

6.1 Screening Commercial Catalysts

The comparative results of hydrogenation with different commercial nickel catalysts present in Table 6.1 and Figure 6.1 showed the superiority of the Ni 3742D (Expt. No. 6) over other nickel catalysts. Two interesting catalysts, Ni 3712F and Ni 3609F, give hydrogenated products having low-iodine values, high hydroxy values and appropriate melting points but Ni 3742D, produced not only a product with a minimum iodine value of 1.85 and a maximum melting point of 48.5, which is comparable to commercial methyl ester wax in Table 6.9 (52.0 °C), but also the shortest induction time and reaction time to saturation. Therefore, it should be noted that the Ni 3742D catalyst was a suitable one for hydrogenation of methyl ricinoleate.

6.2 Determination of an Suitable Operating Condition

Twenty hydrogenation runs were made over a temperature range of 110 to 200 °C ; hydrogen pressure, 100 to 175 pounds per square inch gauge ; catalyst concentration, 0.01 to 0.50 % Nickel by weight ; agitation speed, 200 to 800 rpm. ; and

Table 6.1 The comparative result of hydrogenation of methyl ricinoleate with various commercial nickel catalysts

(Reaction temperature 150°C, hydrogen pressure 150 psig., reaction time 5 hrs., agitation speed 800 rpm., concentration of catalyst 0.20% Ni/oil)

Expt. No.	Type of Catalyst	Properties of Hydrogenated Product				Induction Time (min)	Hydrogen Consumption (psi.)
		I.V.	OH.V.	A.V.	m.p. (°C)		
1	Ni 3712 F	2.14	164.45	1.28	47.8	30	35.50
2	Ni 5132 F	5.89	162.58	1.41	46.9	54	33.50
3	Ni 0104 F	--	--	--	paste	115	11.50
4	Ni 3609 F	2.51	164.00	1.95	47.7	24	36.00
5	G 53 D	7.36	164.76	1.10	47.1	54	29.00
6	Ni 3742 D	1.85	162.78	1.25	48.5	0	36.50

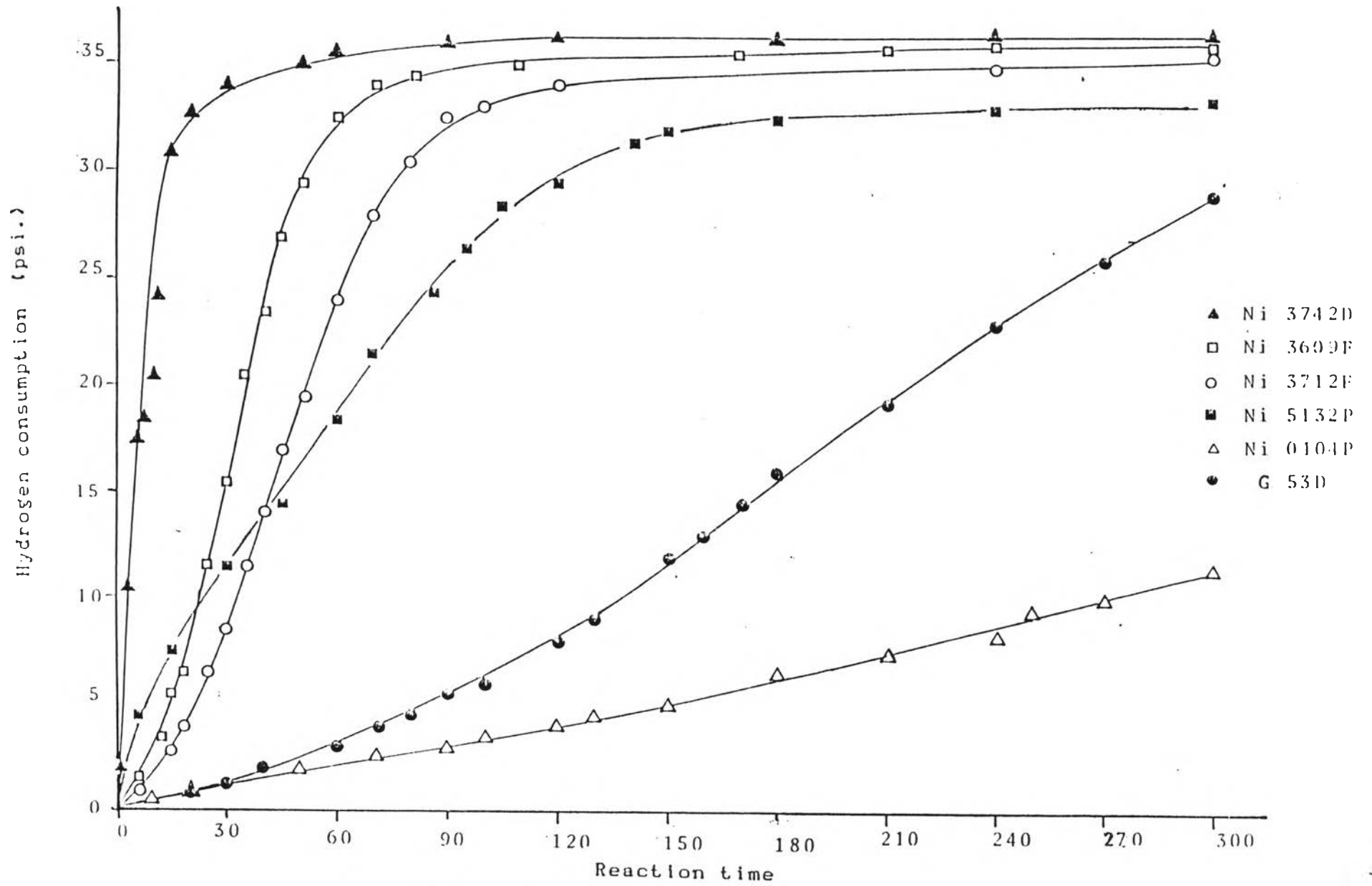


Figure 6.1 Hydrogen consumption curves of various commercial nickel catalysts

reaction time, 1 to 5 hours. When one operating parameter was being studied, all others were held constant. Because of its superior activity, Ni 3742D catalyst was used in determining the suitable operating condition. The results were shown by product properties and hydrogen consumption curves.

6.2.1 Effect of Reaction Temperature

Results of the experiments on hydrogenation of methyl ricinoleate at various temperatures given in Table 6.2, Figure 6.2 and Figure 6.3 showed that increasing the low reaction temperature range from 110 to 170 °C decreased both the iodine value from 10.60 to 2.80 and hydroxyl value from 166.74 to 163.12 but increased small amount of the acid value from 1.26 to 1.29. These values indicated that the rate of hydrogenation increased rapidly (see Figure 6.2) and of dehydroxylation increased slowly in this temperature range. At the reaction temperature over 170 °C (from 180 to 200 °C), rate of hydrogenation increased slower than the lower reaction temperature range (150-170 °C), while the rate of dehydroxylation and hydrolysis increased rapidly because of decreasing the hydroxyl value from 162.38 to 156.91 and of increasing the acid value from 1.35 to 2.45. This may be due to occurring the other kinetic and mechanism of hydrogenation on nickel catalyst surface. Although the higher temperature will lower the viscosity of the oil, the solubility of hydrogen actually increases slightly with temperature. In such a case, as the temperature increases, the overall reaction rate increases which results in drastically decreased hydrogen concentration at the catalyst surface. Because of a required product with high hydroxy value and maximum melting point of 48.4 °C, the suitable reaction temperature was 150 °C.

Table 6.2 Effect of reaction temperature on hydrogenation of methyl ricinoleate
 (Hydrogen pressure 150 psig., reaction time 2 hrs., agitation speed
 800 rpm., concentration of Ni 3742D catalyst 0.03% Ni/oil)

Expt. No.	Reaction Temperature (°C)	Properties of Hydrogenated Product				Induction Time (min)	Hydrogen Consumption (psi.)
		I.V.	DH.V.	A.V.	m.p. (°C)		
7	110	--	--	--	--	--	--
8	130	10.60	166.74	1.26	47.2	27	24.00
9	150	4.52	166.62	1.28	48.4	4	35.00
10	170	2.80	163.12	1.29	47.9	3	35.50
11	180	8.49	162.38	1.35	46.2	3	29.00
12	200	5.04	156.91	2.45	46.5	0	32.50

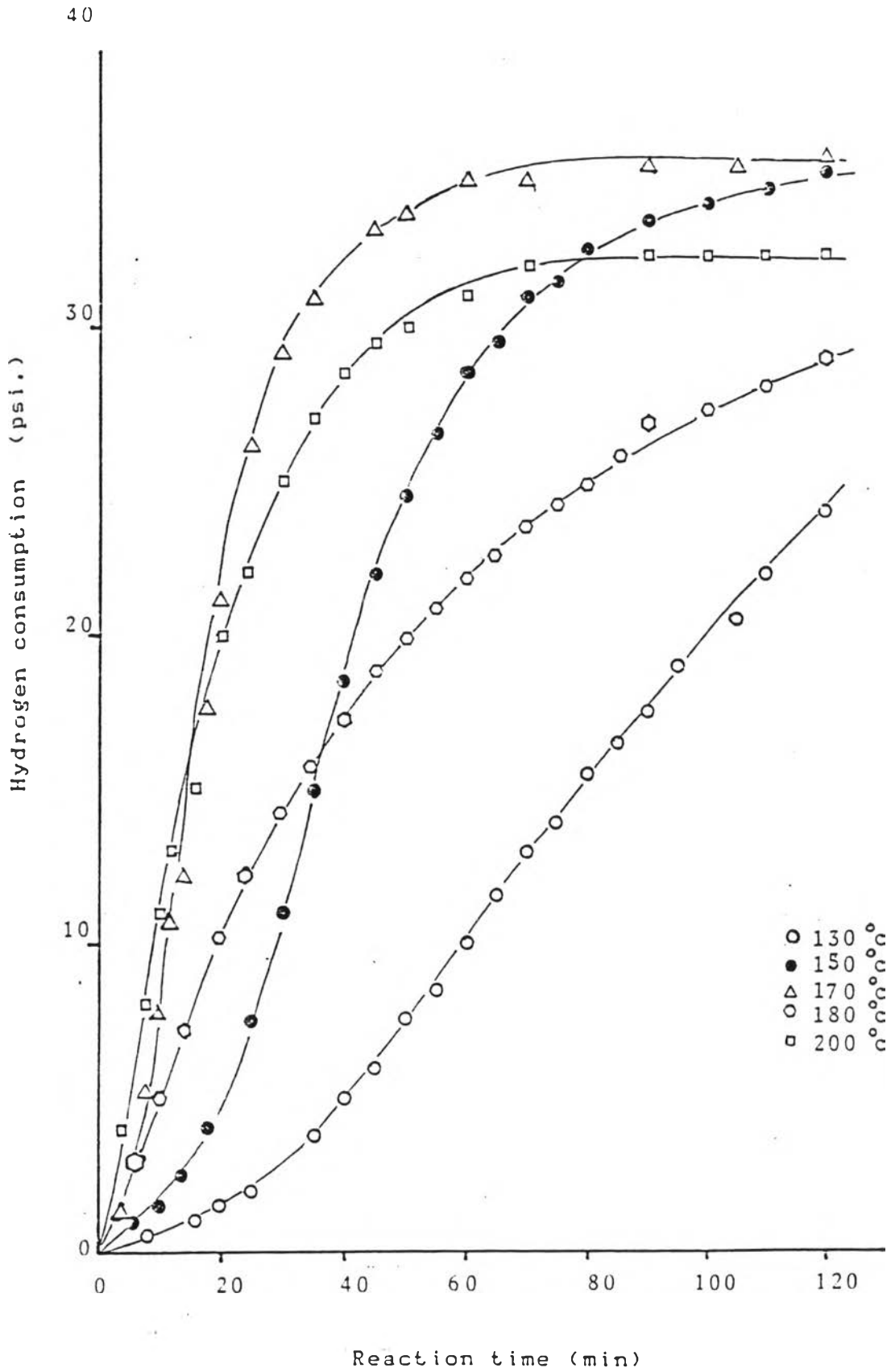


Figure 6.2 Hydrogen consumption curves at various reaction temperatures of Ni 3742D catalyst

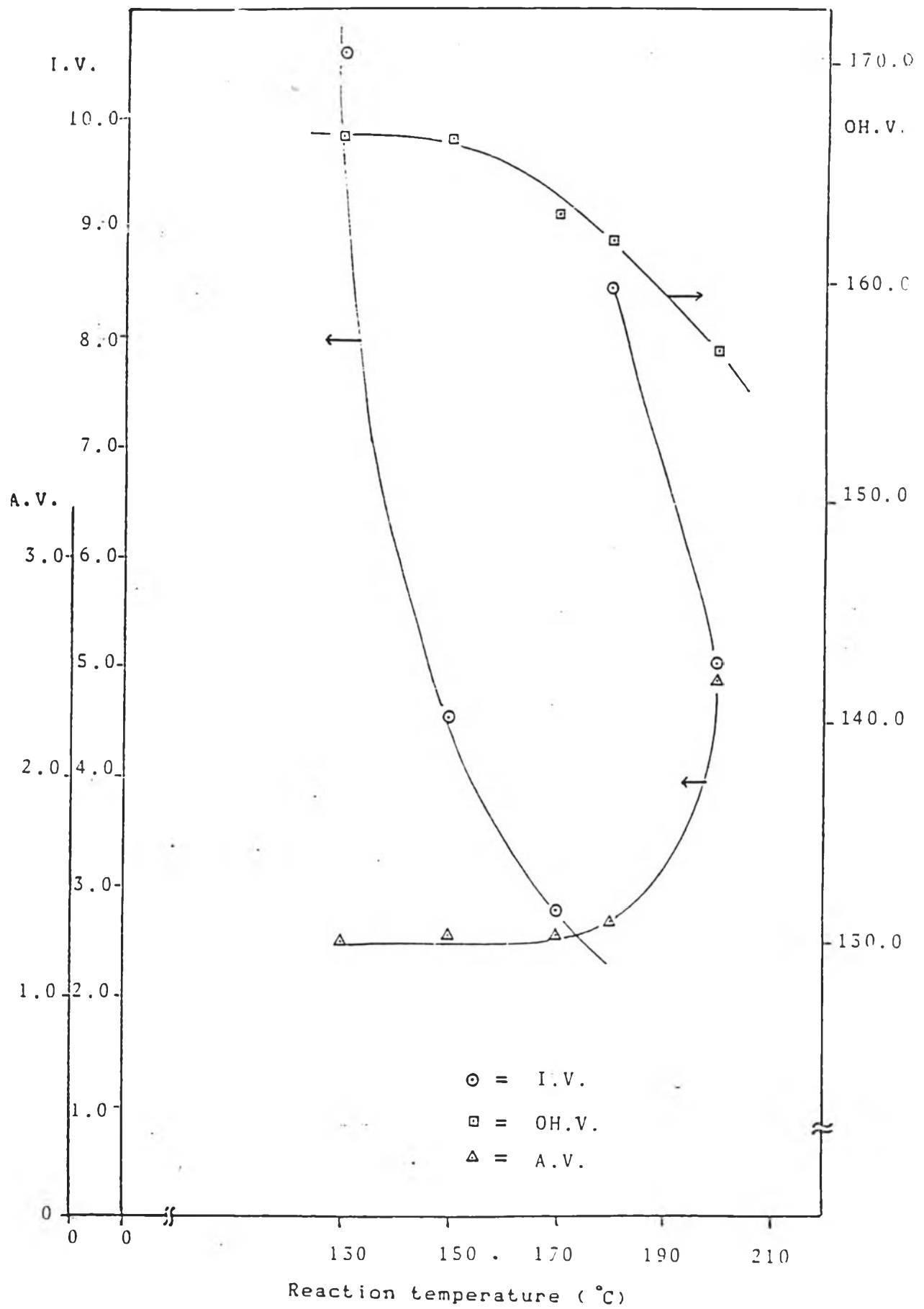


Figure 6.3 Effect of reaction temperature of Ni 3742D catalyst

6.2.2 Effect of Hydrogen Pressure

Results of the experiments on hydrogenation of methyl ricinoleate at various pressures, the pressure being maintained constant during each experiment, were illustrated in Table 6.3, Figure 6.4 and Figure 6.5 showed that increasing the hydrogen pressure from 100 to 150 psig. decreased the iodine value from 10.67 to 4.52 and the loss of hydroxyl value from 161.92 to 166.62 but the acid value unclearly changed. These values indicated that the rate of hydrogenation increased rapidly (see Figure 6.4) and the rate of dehydroxylation decreased with increasing hydrogen pressure. At hydrogen pressure 175 psig., the iodine value and the loss of hydroxyl value compared with these values at 150 psig were increased from 4.52 to 5.22 and 166.62 to 163.35, respectively. For increasing hydrogen pressure increase results in a large driving force to solubilize the hydrogen in the oil. As a result, the hydrogen concentrations were cover the catalyst surface. Thus, the rate of hydrogenation was increased but the rate of dehydroxylation was decreased. However at hydrogen pressure 175 psig, the iodine value that ought to be lower than the iodine value at hydrogen pressure 150 psig became value of 5.22. As a result, this may be due to accuring the rapid hydrogenation in the early more hydrogen covering on the catalyst surface (see Figure 5.4). Thus, the more heat of reaction occurred, the more rate of dehydrogenation was more dominant than the rate of hydrogenation. The suitable hydrogen pressure was 150 psig because of the hydrogenated product with high hydroxyl value and maximum melting point of 48.4°C .

Table 6.3 Effect of hydrogen pressure on hydrogenation of methyl ricinoleate
 (Reaction temperature 150 °C, reaction time 2 hrs., agitation speed
 800 rpm., concentration of Ni 3742D catalyst 0.03% Ni/oil)

Expt. No.	Hydrogen Pressure (psig.)	Properties of Hydrogenated Product				Induction Time (min)	Hydrogen Consumption (psi.)
		I.V.	OH.V.	A.V.	m.p. (°C)		
13	100	10.67	161.92	1.32	45.8	48	28.50
14	125	10.43	163.45	1.27	46.3	41	31.50
9	150	4.52	166.62	1.28	48.4	4	35.00
15	175	5.22	163.35	1.39	47.4	3	35.00

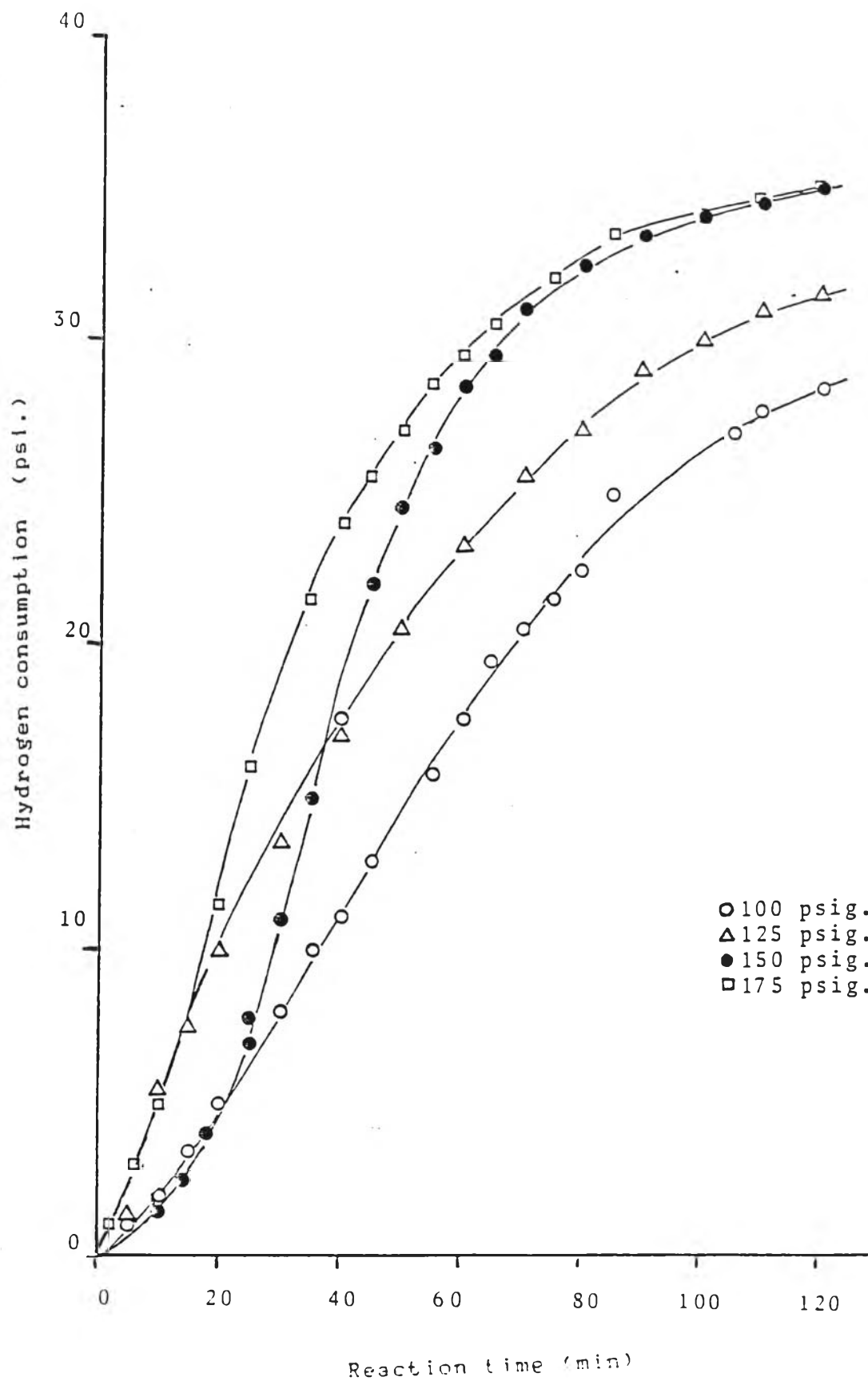


Figure 6.4 Hydrogen consumption curves at various hydrogen pressures of Ni 3742D catalyst

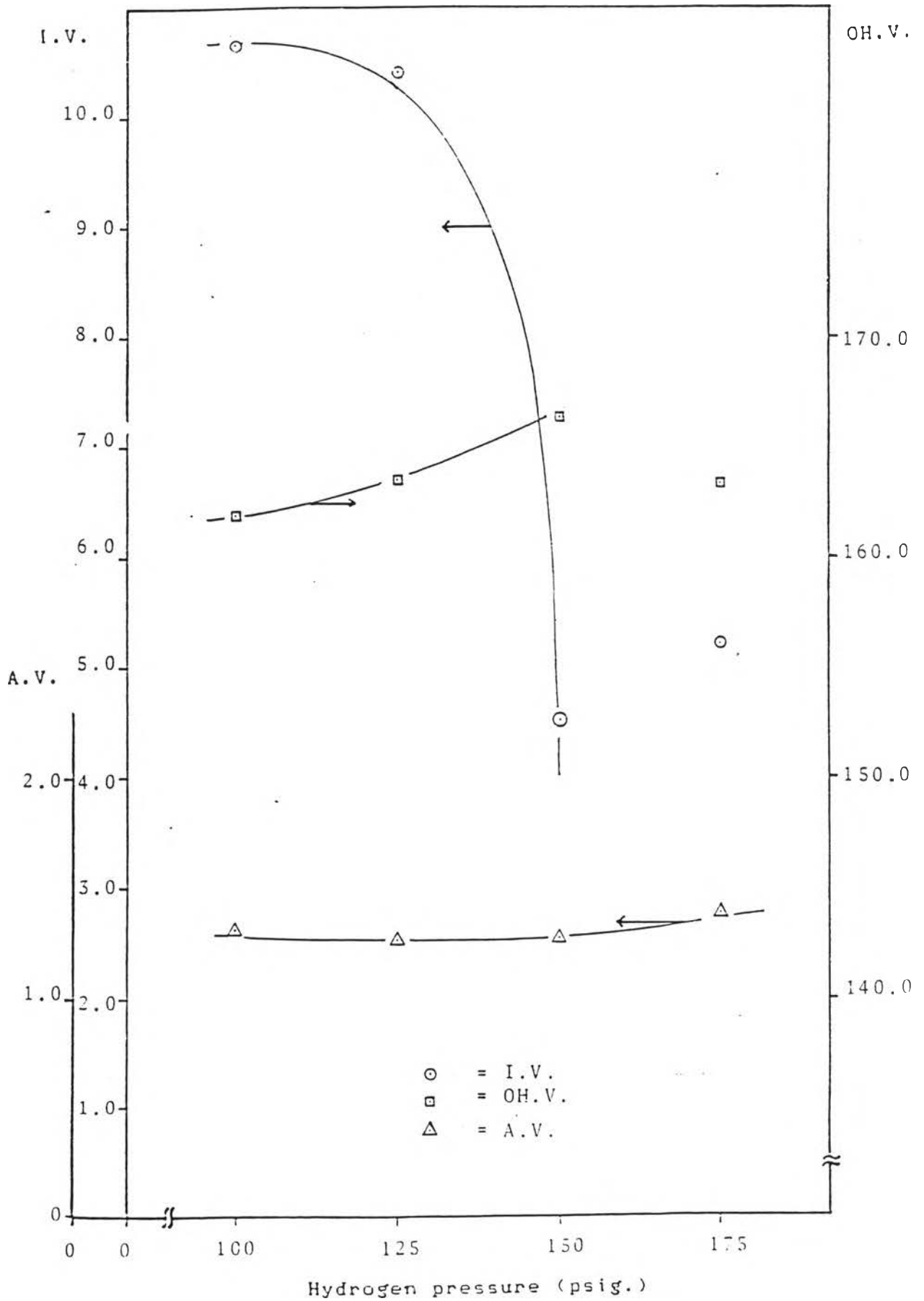


Figure 6.5 Effect of hydrogen pressure of Ni 3742D catalyst

6.2.3 Effect of Reaction time

The results given in Table 6.4 and Figure 6.6 showed that the main reduction of double bond in methyl ricinoleate took place in about 2 hours, after which the rate of hydrogenation processed slowly. Increasing the reaction time from 1 to 2 hours, the loss of the hydroxyl value and the acid value were unaffected but the iodine value was decreased rapidly. Increasing the reaction time from 2 to 5 hours, the iodine value and the hydroxyl value were decreased from 4.52 to 2.38 and from 166.62 to 164.01, respectively; and the melting point was decreased slightly from 48.4 to 48.0 °C. These values indicated that the rate of hydrogenation and of dehydroxylation increased with reaction time. The suitable reaction time, however, was not considered immediately because the other variables; such as temperature and catalyst concentration, are more significant. So this result showed the tendency of reaction time on the hydrogenation.

6.2.4 Effect of Agitation Speed

A comparison of the results given in Table 6.5, Figure 6.7 and Figure 6.8 showed that increasing agitation from 200 to 800 rpm. decreased the iodine value from 10.58 to 4.52 and the loss of the hydroxyl value from 156.23 to 166.62 but the acid value unclearly changed. The melting point of hydrogenated product was also increased from 45.5 to 48.4 °C. These values indicated that the rate of hydrogenation increased slowly (see Figure 6.7) and of dehydroxylation decreased while the agitation speed increased. Increasing agitation increased the dissolution rate and adsorption rate of hydrogen in oil on the catalyst

Table 6.4 Effect of reaction time on hydrogenation of methyl ricinoleate
 (Reaction temperature 150 °C, hydrogen pressure 150 psig., agitaion speed
 800 rpm., concentration of Ni 3742D catalyst 0.03% Ni/oil)

Expt. No.	Reaction Time (hr.)	Properties of Hydrogenated Product				Hydrogen Consumption (psi.)
		I.V.	OH.V.	A.V.	m.p. (°C)	
16	1	10.54	166.27	1.26	46.9	27.25
9	2	4.52	166.62	1.28	48.4	35.00
17	3	3.20	164.99	1.26	48.3	35.50
18	5	2.38	164.01	1.26	48.0	36.50

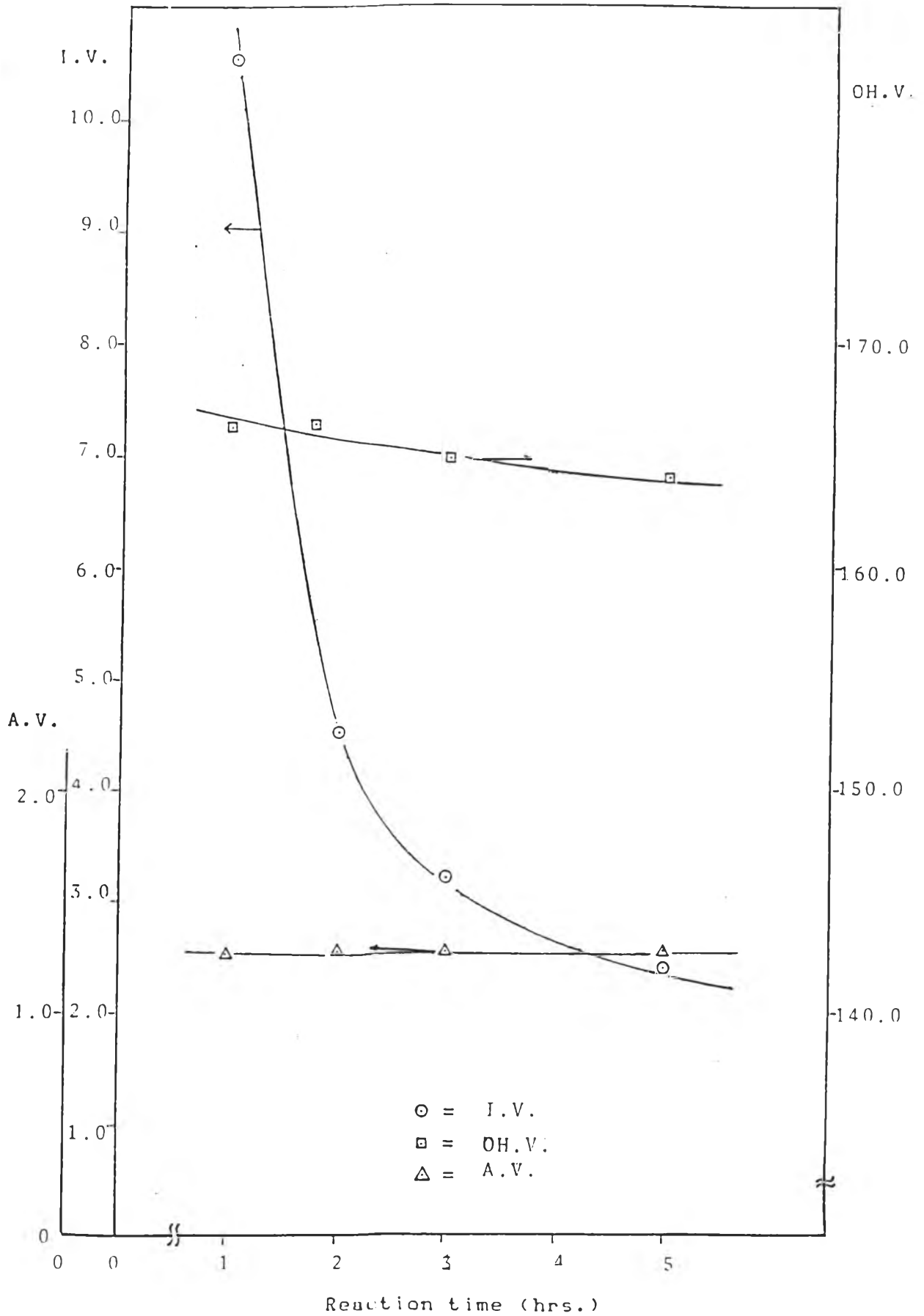


Figure 6.6 Effect of reaction time of Ni 3742D catalyst

Table 6.5 Effect of agitation speed on hydrogenation of methyl ricinoleate
 (Reaction temperature 150 °C, hydrogen pressure 150 psig., reaction
 time 2 hrs., concentration of Ni 3742D catalyst 0.03% Ni/oil)

Expt. No.	Agitation Speed (rpm.)	Properties of Hydrogenated Product				Induction Time (min)	Hydrogen Consumption (psi.)
		I.V.	OH.V.	A.V.	m.p. (°C)		
19	200	10.58	156.28	1.21	45.5	68	29.50
20	400	9.93	161.81	1.28	46.2	31	32.50
21	600	7.25	163.97	1.35	47.1	15	33.50
9	800	4.52	166.62	1.28	48.4	4	35.00

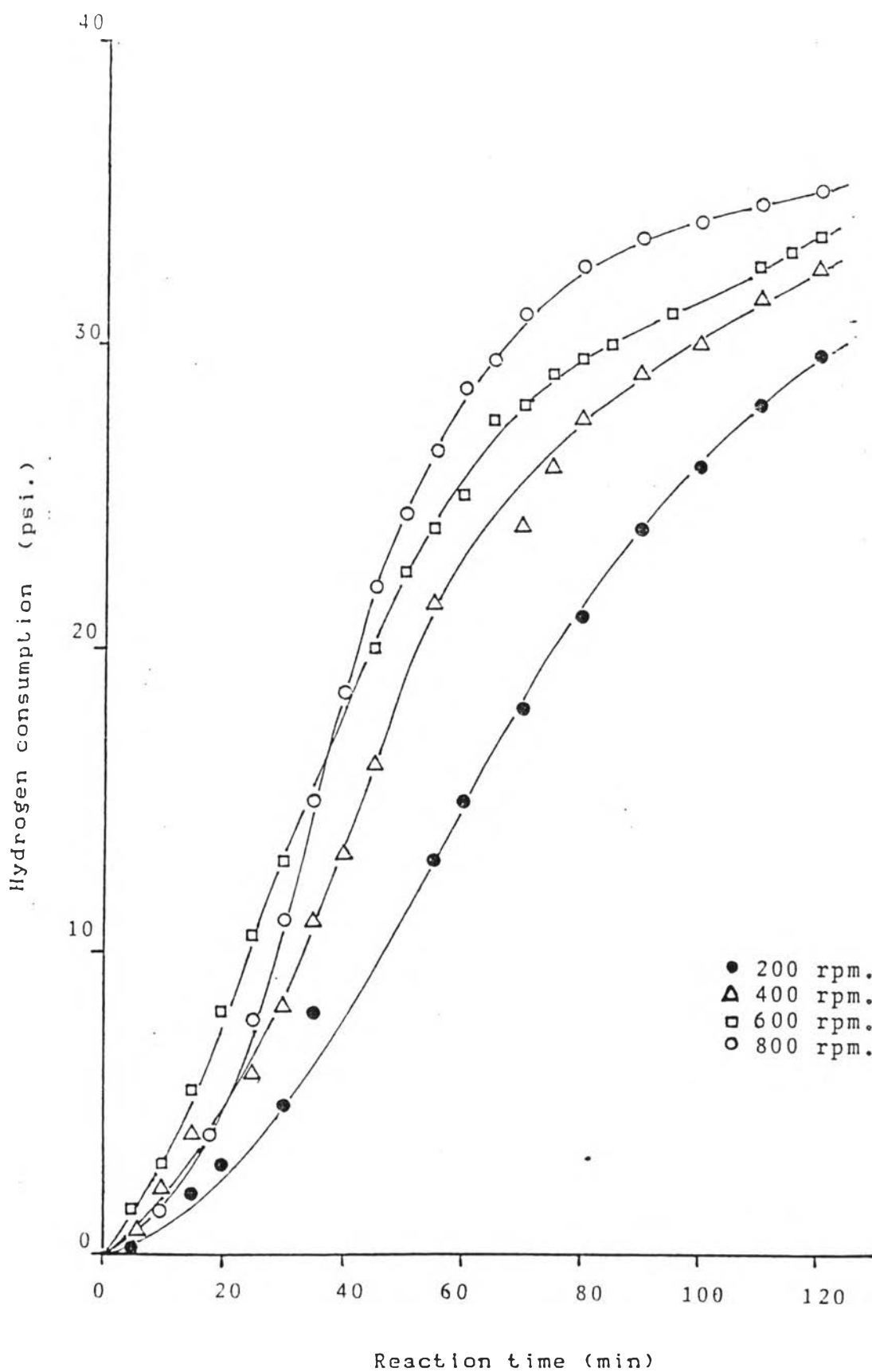


Figure 6.7 Hydrogen consumption curves at various agitation speeds of Ni 3742D catalyst

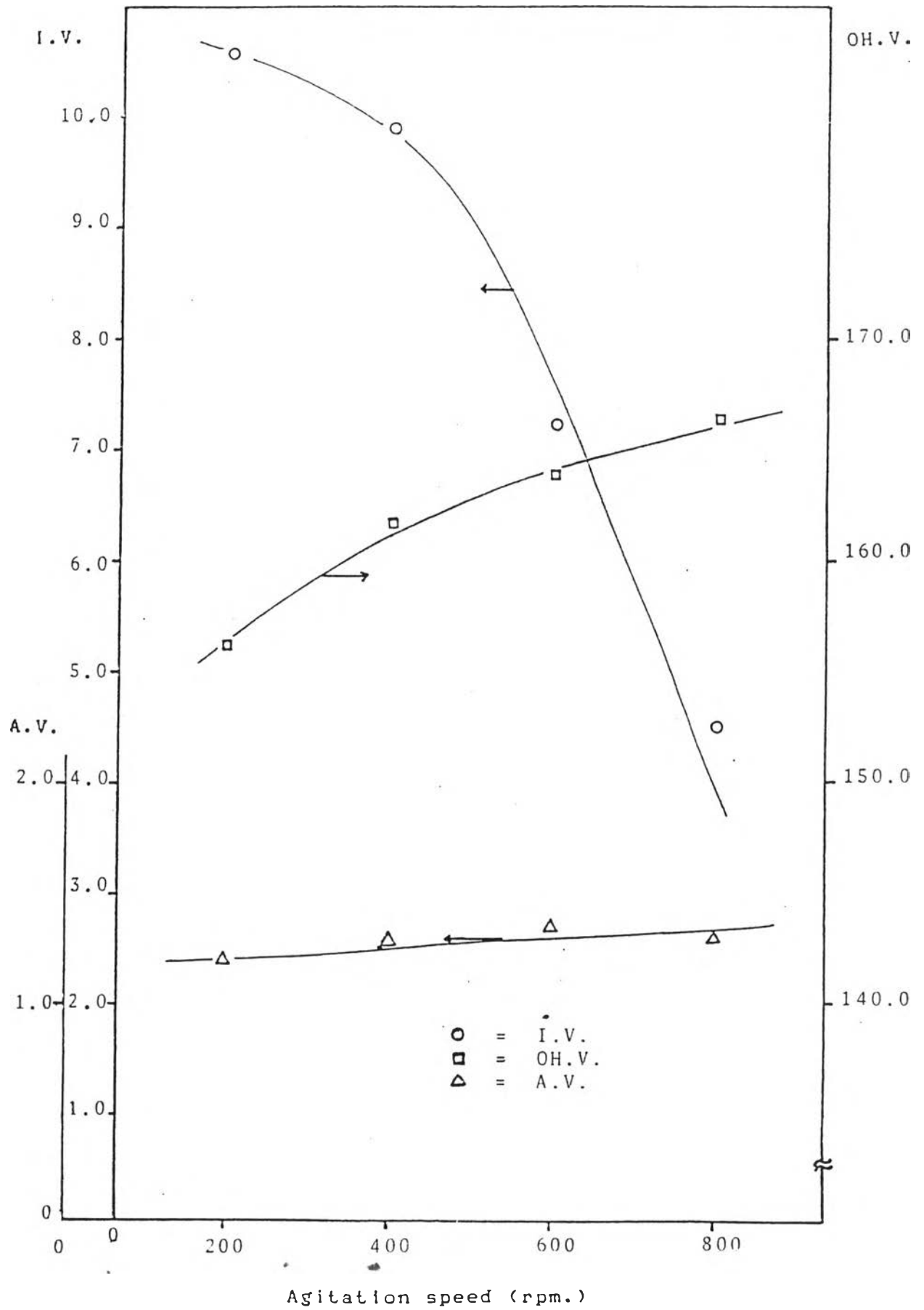


Figure 6.8 Effect of agitation speed of Ni 3742D catalyst

surface because it more quickly whipped the hydrogen from gas phase into the reaction mixture and decreased the film resistance of the mass and heat transfer around the catalyst particle so the rate of hydrogenation was increased. Increasing agitation not only increases hydrogenation but also decreases both dehydroxylation caused by hot spots or over heat on catalyst surface, and hydrolysis. The suitable agitation speed was 800 rpm. (For this equipment).

6.2.5 Effect of Concentration of Catalyst

The results given in Table 6.6, Figure 6.9 and Figure 6.10 showed that increasing the concentration of catalyst from 0.01 to 0.20% Ni/oil decreased the iodine value from 6.14 to 1.94 and the hydroxyl value from 168.36 to 162.47 but the acid value unclearly changed. These values indicated that the rate of hydrogenation and of dehydroxylation increased with this catalyst concentration range. Especially at 0.50% Ni/oil, the hydroxyl value was decreased from 162.47 (at 0.20% Ni/oil) to 141.07. This may be probably due to the fact that the hot spots from heat of reaction have taken place during the early hydrogenation because of having great amount of active catalyst surface. Thus, the rate of dehydroxylation was more dominant than the rate of hydrogenation. From Figure 6.10, the appropriate catalyst concentration for the iodine value below 3 and the hydroxyl value over 164.0 is the range between 0.07 and 0.08% Ni/oil.

Table 6.6 Effect of concentration of Ni 3742D catalyst on hydrogenation of methyl ricinoleate
 (Reaction temperature 150°C, hydrogen pressure 150 psig., reaction time 2 hrs., agitation speed 800 rpm.)

Expt. No.	Concentration of Catalyst (% Ni/oil, wt./wt.)	Properties of Hydrogenated Product				Hydrogen Consumption (psi.)
		I.V.	OH.V.	A.V.	m.p. (°C)	
22	0.50	2.58	141.07	0.95	44.7	39.00
23	0.20	1.94	162.47	1.07	47.9	36.50
24	0.10	2.26	163.65	1.55	48.3	36.25
25	0.06	3.84	164.25	1.22	47.5	36.00
9	0.03	4.52	166.62	1.28	48.4	35.00
26	0.01	6.14	168.36	1.29	48.1	23.00

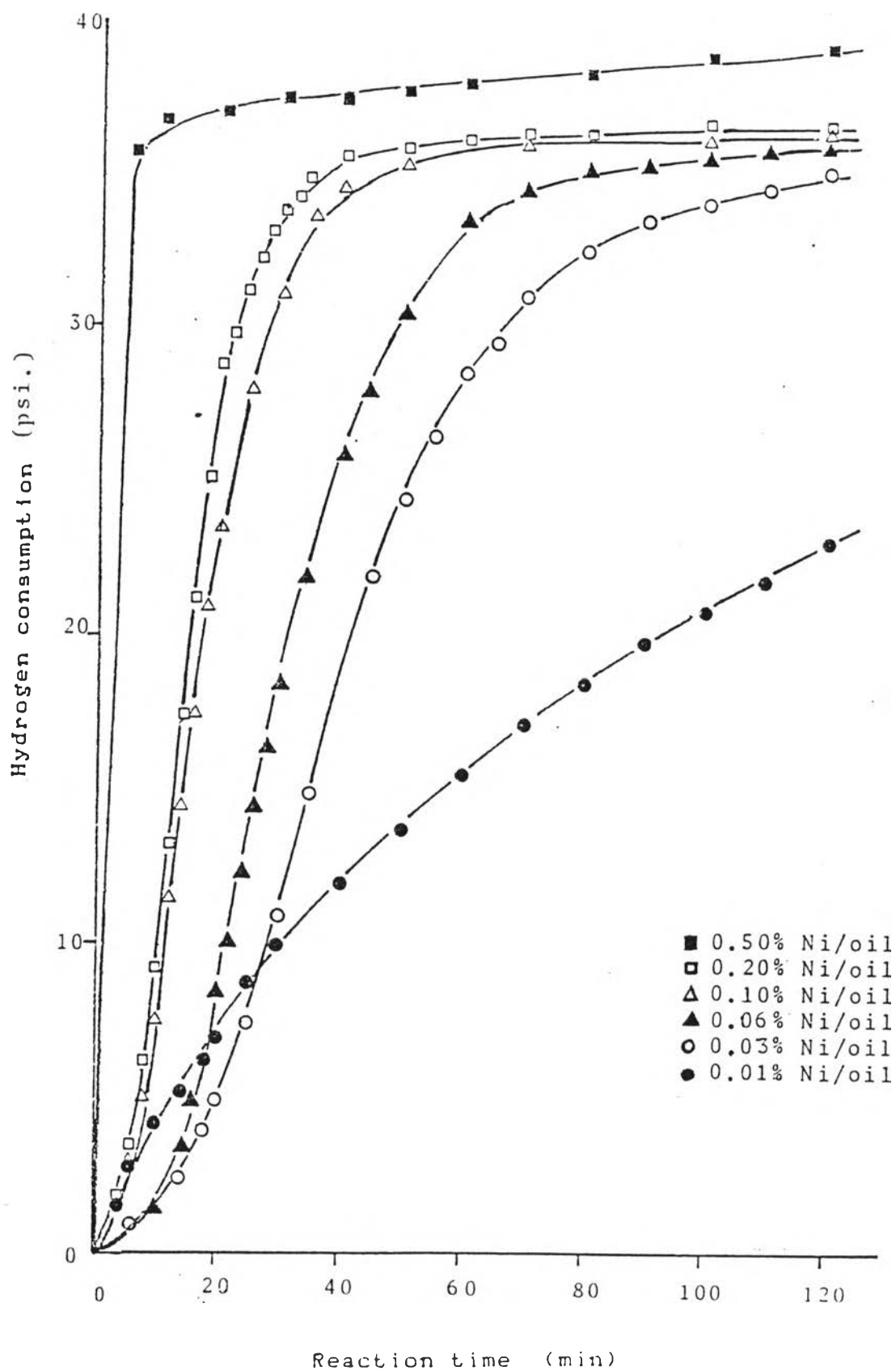


Figure 6.8 Hydrogen consumption curves at various concentrations of Ni 3742D catalyst

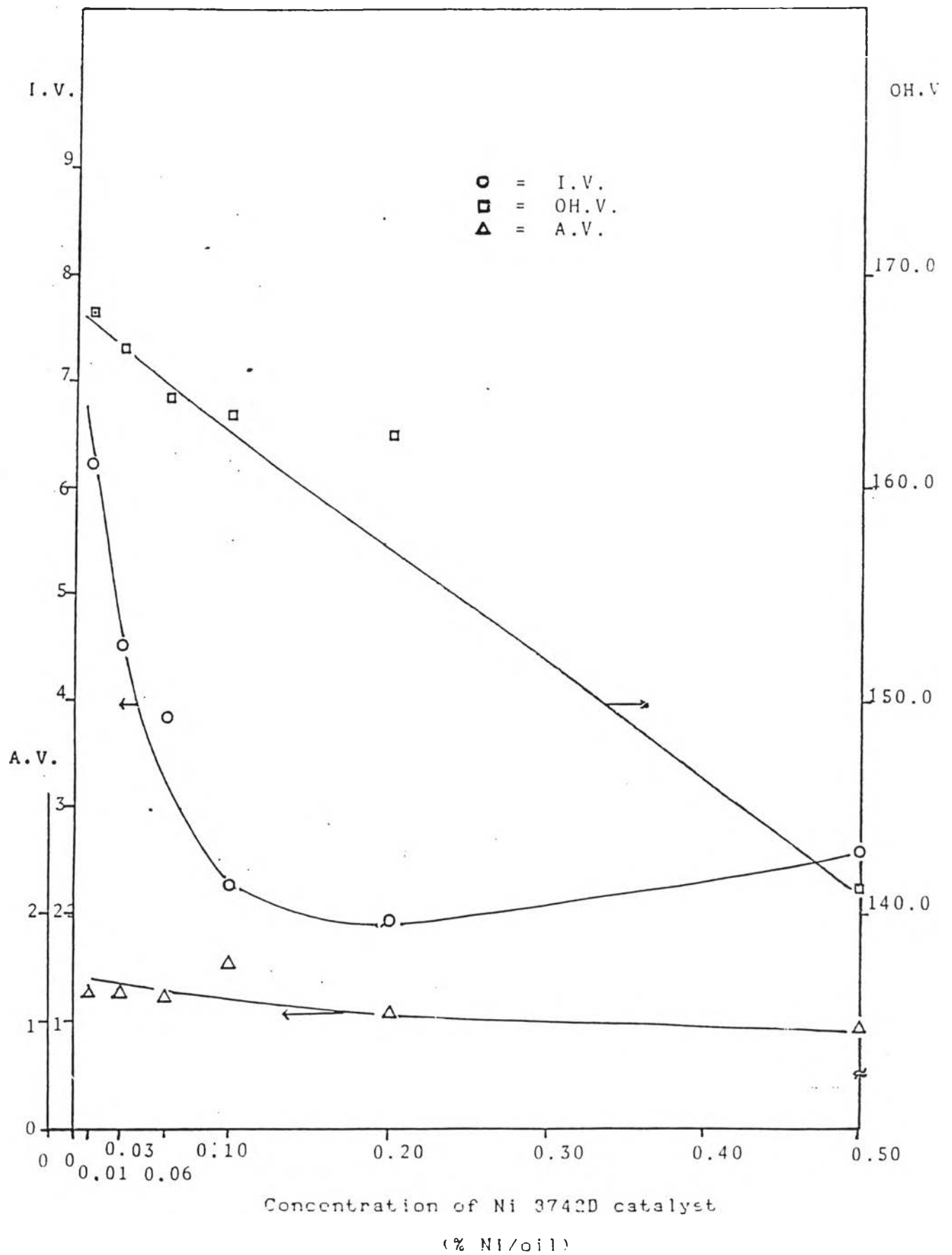


Figure 6.10 Effect of concentration of Ni 3742D catalyst



6.3 Effect of the Initial Hydrogen Feeding

Results of the experiment on hydrogenation of methyl ricinoleate at different time for hydrogen feeding illustrated in Table 6.7 showed that the initial hydrogen feeding (Procedure 2) gave better quality product than obtained with the initial nitrogen feeding (Procedure 1). Comparing the product obtained with the Procedure 1 and 2 at 0.03% Ni/oil, the iodine value was decreased from 4.52 to 2.57 and the melting point was slightly increased from 48.4 to 48.7 °C. For comparing the product obtained with the Procedure 1 and 2 at 0.07% Ni/oil, the iodine value was decreased from 2.72 to 2.05 and the melting point was slightly increased from 48.5 to 48.9. In the both cases, the hydroxyl values were slightly decreased and the acid values were almost constant. These values indicated that the rate of hydrogenation was increased and the rate of dehydroxylation was slightly increased when the Procedure 2 was used but the rate of hydrolysis is nearly constant. In addition the products from the procedure 2 were no more yellowish and higher melting point than from the Procedure 1. This may be due to occurring the deactivation of catalyst by these impurities ; such as carbonyl, quinone-type structure, and etc. occurred during processing crude oil or/and storing at atmospheric in drum. Thus, the iodine value of hydrogenated product ought to be higher than of product obtained with the normal active catalyst in the same operating condition. As a result, the hydrogen gas initially fed may cover the catalyst surface to prevent it from the impurities. From this experiments, the catalyst concentration of 0.03% Ni/oil at initial hydrogen feeding (Expt. No. 27) ought to be considered economically because of a desired product with the iodine value below 3 (2.57),

the hydroxyl value over 164.0 (165.86), and the melting point of 48.7 °C. If the desired product was also required in the better quality in colour, the catalyst concentration of 0.07% Ni/oil at suitable operating condition by using the initial hydrogen feeding (Expt. No. 29) would be considered (see Figure 6.11). In addition, the latter experiment produced the low iodine value of 2.05. Thus, to obtain the appropriate qualities of product for the iodine value below 3, hydroxyl value over 164.0, and good colour product, the parameter of Expt. No. 29 may be considered in reducing the reaction time.

6.4 Effect of the Storage Time

Results of the experiments on hydrogenation of methyl ricinoleate at the different storage time from 6 and 10 months, at catalyst concentration of 0.03% Ni./oil illustrated in Table 6.8 increased the iodine value and the loss of hydroxyl value of hydrogenated product from 4.52 to 8.87 and from 166.62 to 162.94 for the Procedure 1, respectively ; and from 2.57 to 5.60 and from 165.86 to 162.88 for Procedure 2, respectively. The acid values were increased in both cases. These values indicated that the storage time was important effective factor to hydrogenation for producing the desired product. This may be due to the fact that the atmospheric air over the liquid level in the storage drum contain the oxygen which is generally an oxidant to occur the auto-oxidation in oil. The oxidation products are aldehyde, ketone and other type structures. These structures may show deactivation the catalyst for hydrogenation of alkene compounds. In Figure 6.12 showed the hydrogenated at the different storage time.

Table 6.7 Effect of the initial hydrogen feeding on Hydrogenation of methyl ricinoleate
 (Reaction temperature 150 °C, hydrogen pressure 150 psig., agitation speed
 800 rpm., reaction time 2 hrs., Ni 3742D catalyst)

Expt. No.	Hydrogenation Procedure	Properties of Hydrogenated Product				Hydrogen Consumption (psi.)
		I.V.	OH.V.	A.V.	m.p. (°C)	
9*	1	4.52	166.62	1.28	48.4	35.00
27*	2	2.57	165.86	1.28	48.7	36.50
28**	1	2.72	163.12	1.47	48.5	38.50***
29**	2	2.05	162.34	1.49	48.9	36.00

* Catalyst concentration of 0.03 %Ni/oil

** Catalyst concentration of 0.07 %Ni/oil

*** Gas leaking

1 The initial nitrogen feeding

2 The initial hydrogen feeding

Table 6.8 Effect of the storage time on hydrogenation of methyl ricinoleate
 (Reaction temperature 150 °C, hydrogen pressure 150 psig., agitation
 speed 800 rpm., reaction time 2 hrs., concentration of Ni 3742D catalyst
 0.03% Ni/oil)

Expt. No.	Storage Time (months)	Properties of Hydrogenated Product				Hydrogen Consumption (psi.)
		I.V.	OH.V.	A.V.	m.p. (°C)	
9*	6	4.52	166.62	1.28	48.4	35.00
27**	6	2.57	165.86	1.28	48.7	36.50
30*	10	8.87	162.94	1.50	47.1	31.50
31**	10	5.60	162.88	1.50	47.7	36.00

* The initial nitrogen feeding

** The initial hydrogen feeding

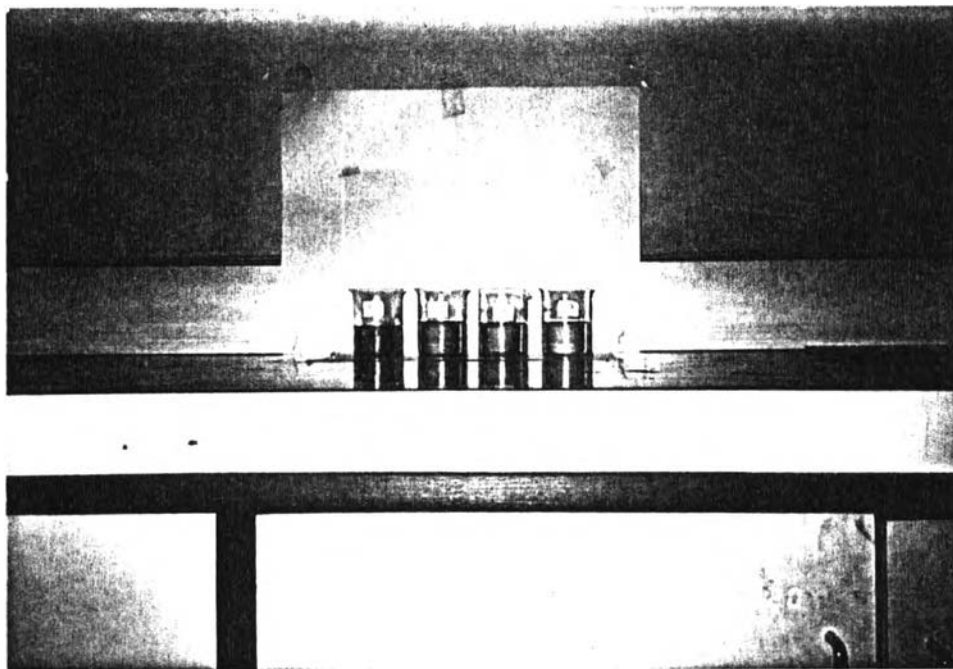


Figure 6.11 Comparing the hydrogenated products obtained by the different time of hydrogen feeding

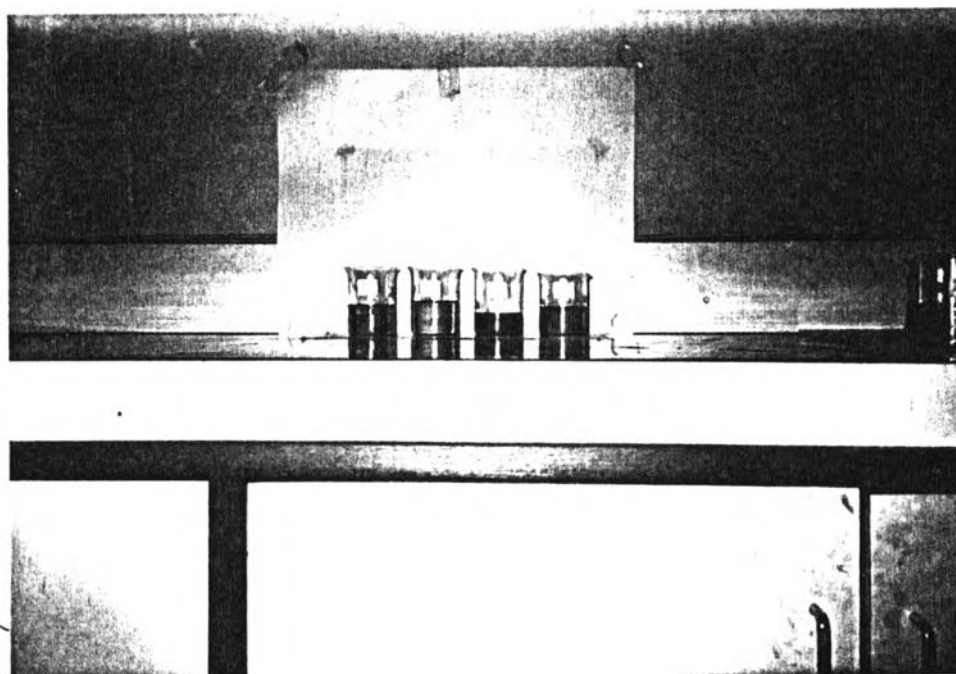


Figure 6.12 Comparing the hydrogenated products obtained by the different storage time of methyl ricinoleate

Table 6.9 Properties of commercial methyl 12-hydroxystearate wax and some resulting methyl ester waxes

Product Name	I.V.	OH.V.	A.V.	m.p. (°C)
Pericin 1 *	3.00	164.00	5.00	52.0
Methyl 12-hydroxy stearate **	5.00	--	--	48.0
Expt. No. 6	1.85	162.78	1.25	48.5
Expt. No. 9	4.52	166.62	1.28	48.4
Expt. No. 24	2.26	163.65	1.55	48.3
Expt. No. 27	2.57	165.86	1.28	48.7
Expt. No. 29	2.05	162.34	1.49	48.9

* From Baker Castor Oil Company

** From The Condensed Chemical Dictionary