

CHAPTER V

RESULTS AND DISCUSSION

The hydrogenation of triglyceride oils is obviously a complicated reaction. It involves not only several simultaneous and consecutive chemical steps but also physical transfer steps of reactants and products on the catalyst surface. The experimental data in Chapter IV are shown in Appendix A. The results were calculated and shown in Tables C1 to C11. The results, illustrated in Figures 5.1 to 5.23, are also discussed in this chapter.

The properties of the in-house catalysts were shown in section 5.1 and the comparison of the reaction between them and the best commercial catalyst was discussed in section 5.4. The selection of the best commercial catalyst for study the effects of the parameters were explained in section 5.2 and the details about the effects of the parameters were in section 5.3. The order of the reaction and the reaction rate constants were described in section 5.5 while the applications of rubber seed wax were stated in the last section.

All the samples of calculation are shown in Appendix B.

5.1 Properties of the In-house Catalysts

The properties of the in-house catalysts are presented in Table 5.1.

The precipitated catalysts were prepared with three nickel loadings of 56.1%, 41.8% and 15.2%. They were pulverized through

Table 5.1 Properties of the in-house catalysts

Catalyst No.	Type of catalyst	Support	% Ni	Particle size (mesh)
PC1	Precipitated Ni	alumina	56.1	<400
PC2	Precipitated Ni	alumina	41.8	<400
PC3	Precipitated Ni	alumina	15.2	<400
IC	Impregnated Ni	alumina	9.3	325-400

400-mesh screen before reduction. After reduction these catalysts were nickel on alumina support. The impregnated catalyst with 9.3% nickel loading was prepared in order to compare the hydrogenation rate with the in-house precipitated catalysts. It was nickel catalyst on the NHK-3 Sumitomo Alumina support with particle size in the range of 325-400 mesh.

5.2 Screening of Commercial Catalysts

The hydrogenation condition was set from prior experiment [34]. This condition was 150 psig of hydrogen pressure and 0.2% Ni in oil. The maximum speed of agitation, about 700 rpm, is used in order to neglect the mass transfer effect. Firstly, the G95E catalyst was chosen for evaluation of the suitable temperature. The data and results of hydrogenation rate at various temperatures are shown in Table A1, Table C1, Figure 5.1 and Figure 5.2, respectively. The suitable temperature is 160 °C as the reaction rate is not too fast or too slow. The reaction rate at 180 °C is so fast that the temperature of the reactor can not be controlled well. At 120 °C and 140 °C, the reaction rates are so

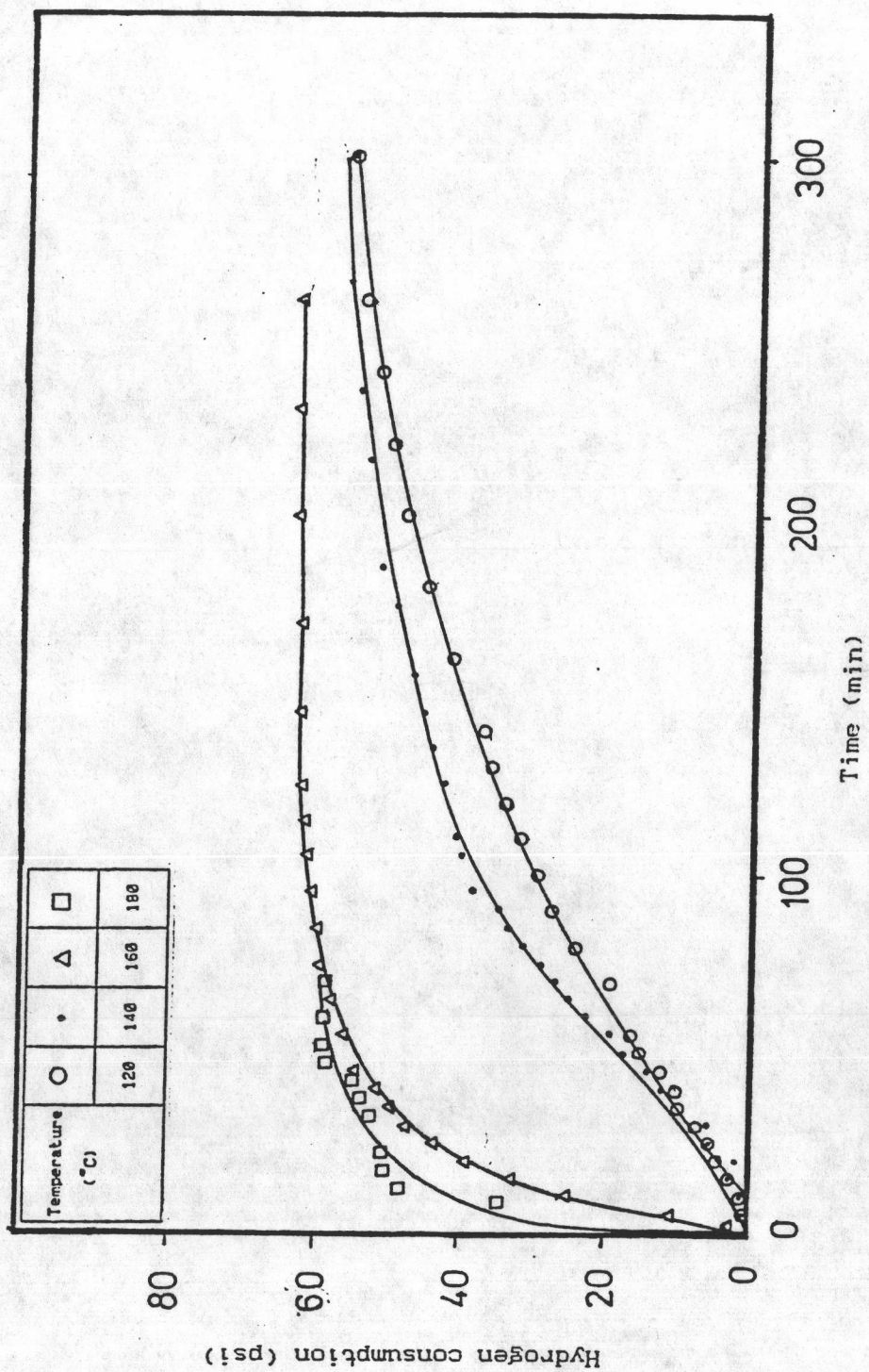


Figure 5.1 Hydrogen consumption curves at various reaction temperatures of G95E catalyst: 150 psig, 700 rpm and 0.2% Ni in oil.

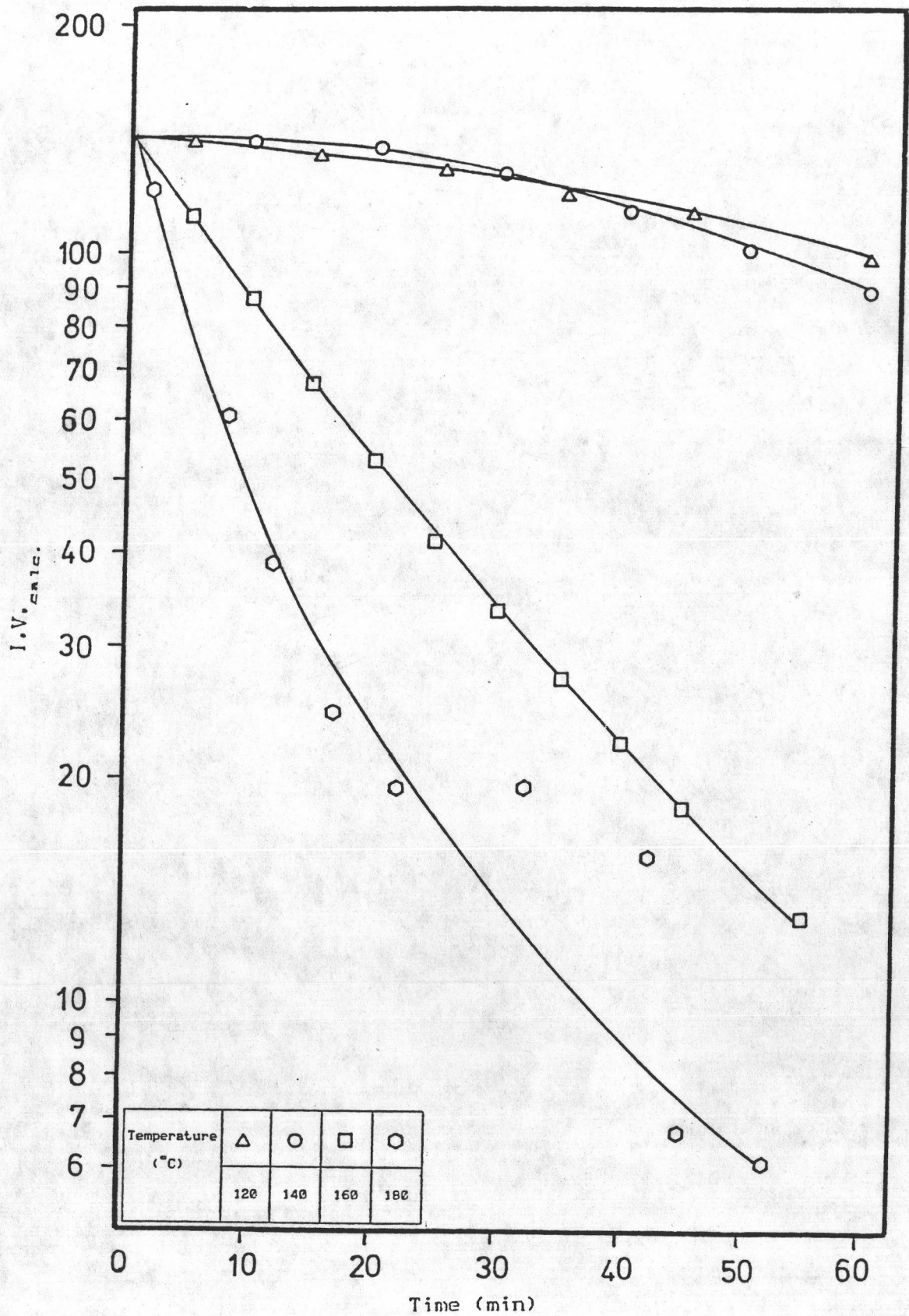


Figure 5.2 Plot of calculated I.V. versus time at various temperatures of G95E : 150 psig, 0.2% Ni/oil and 700 rpm.

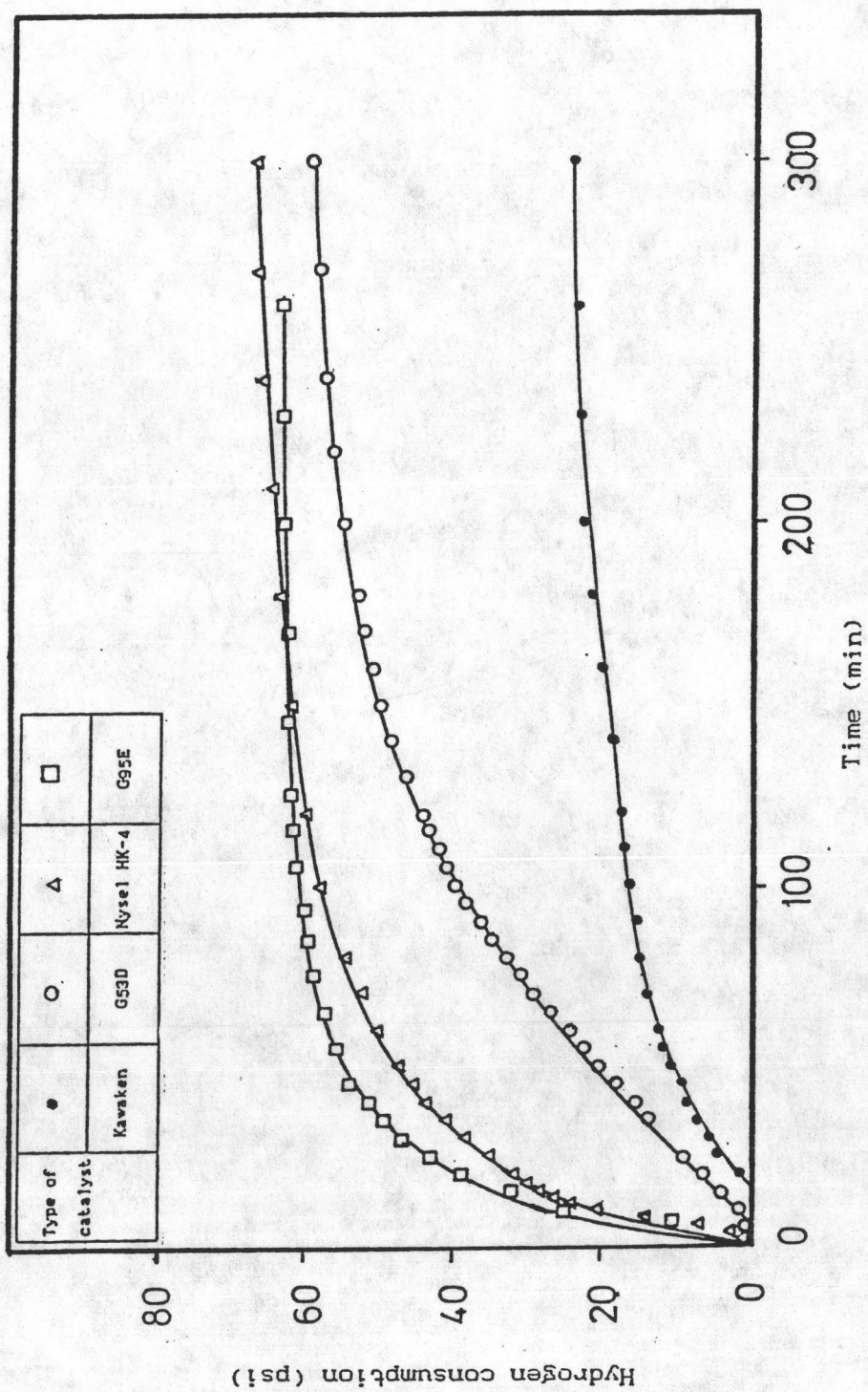


Figure 5.3 Hydrogen consumption curves of various commercial catalysts: 160°C, 150 psig, 700 rpm and 0.2% Ni in oil

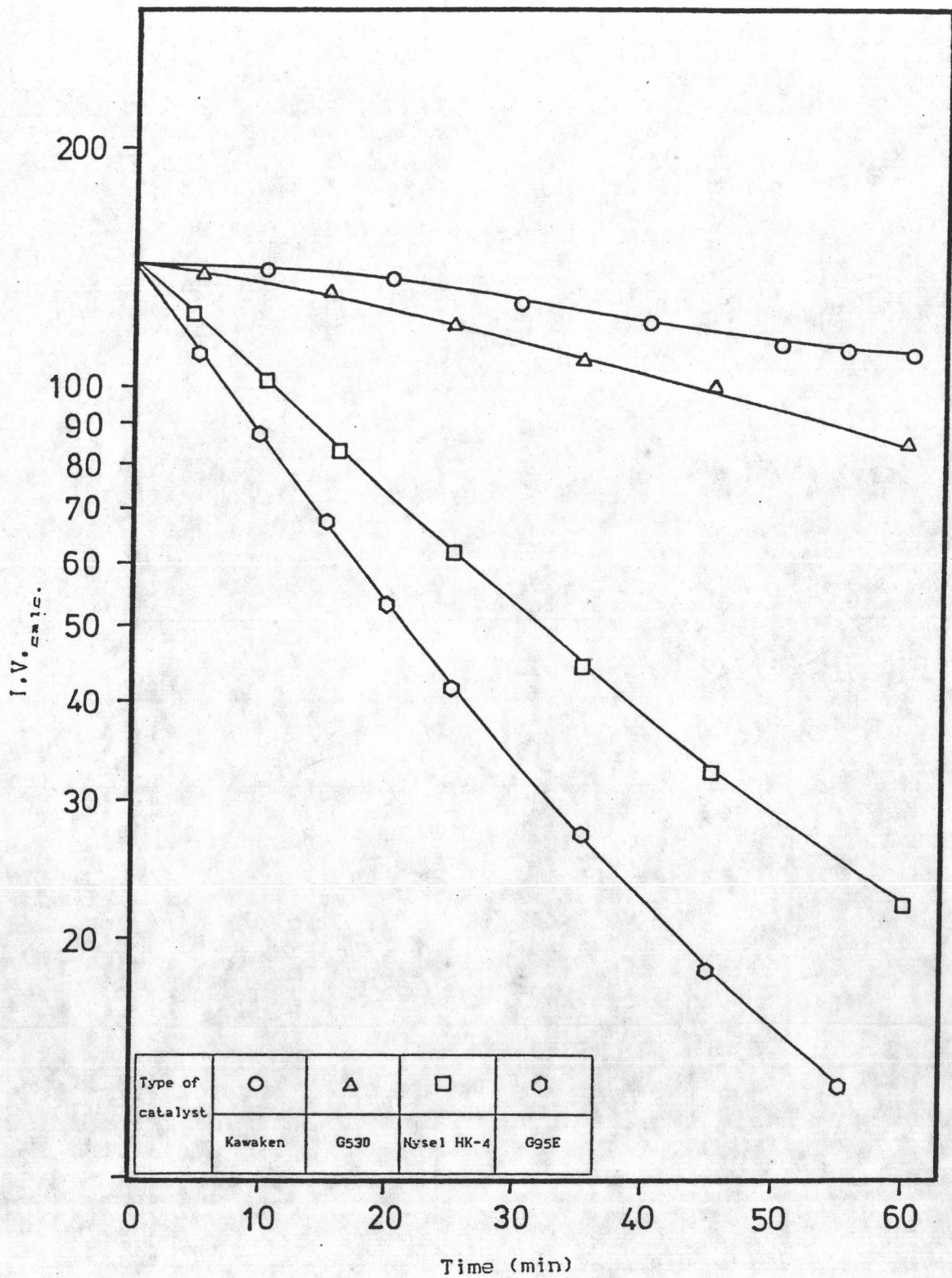


Figure 5.4 Plot of calculated I.V. versus time of various commercial catalysts : 160°C , 150 psig, 0.2% Ni/oil and 700 rpm.

slow that so much time was waste on hydrogenation.

The commercial catalysts which were used for screening were Kawaken, G53D, G95E and Nysel HK-4. A comparison of the results obtained when the hydrogenation is carried out at the same condition with different commercial catalysts is presented in Table C2, Figure 5.3 and Figure 5.4. From Figures 5.3 and 5.4 it is found that the rate of hydrogenation with the Kawaken catalyst is very slow and the product after 5-hour hydrogenation is semisolid which is more liquidlike. The rate of hydrogenation with the G53D catalyst is faster than that with the Kawaken catalyst and the product is solid. The hydrogenation rate with the G95E at 180°C is so fast that the temperature is very difficult to control but at 120°C and 140°C the rates were too slow. The initial hydrogenation rate with the G95E catalyst is faster than that with the Nysel HK-4 catalyst but their products are similar. Therefore, the Nysel HK-4 catalyst is used to run at various temperatures, as shown in Figure 5.5, for comparing with the G95E catalyst. From Figures 5.1 and 5.5 we can see that the hydrogenation rates of the Nysel HK-4 catalyst vary more smoothly with temperature than those of the G95E catalyst. Thus, the Nysel HK-4 is more suitable for study the reaction kinetics.

5.3 Selection of the Optimum Operating Condition

The Nysel HK-4 catalyst is selected for determining the optimum operating condition by varying these parameters - reaction temperature, hydrogen pressure or reactor pressure, catalyst concentration and agitation.

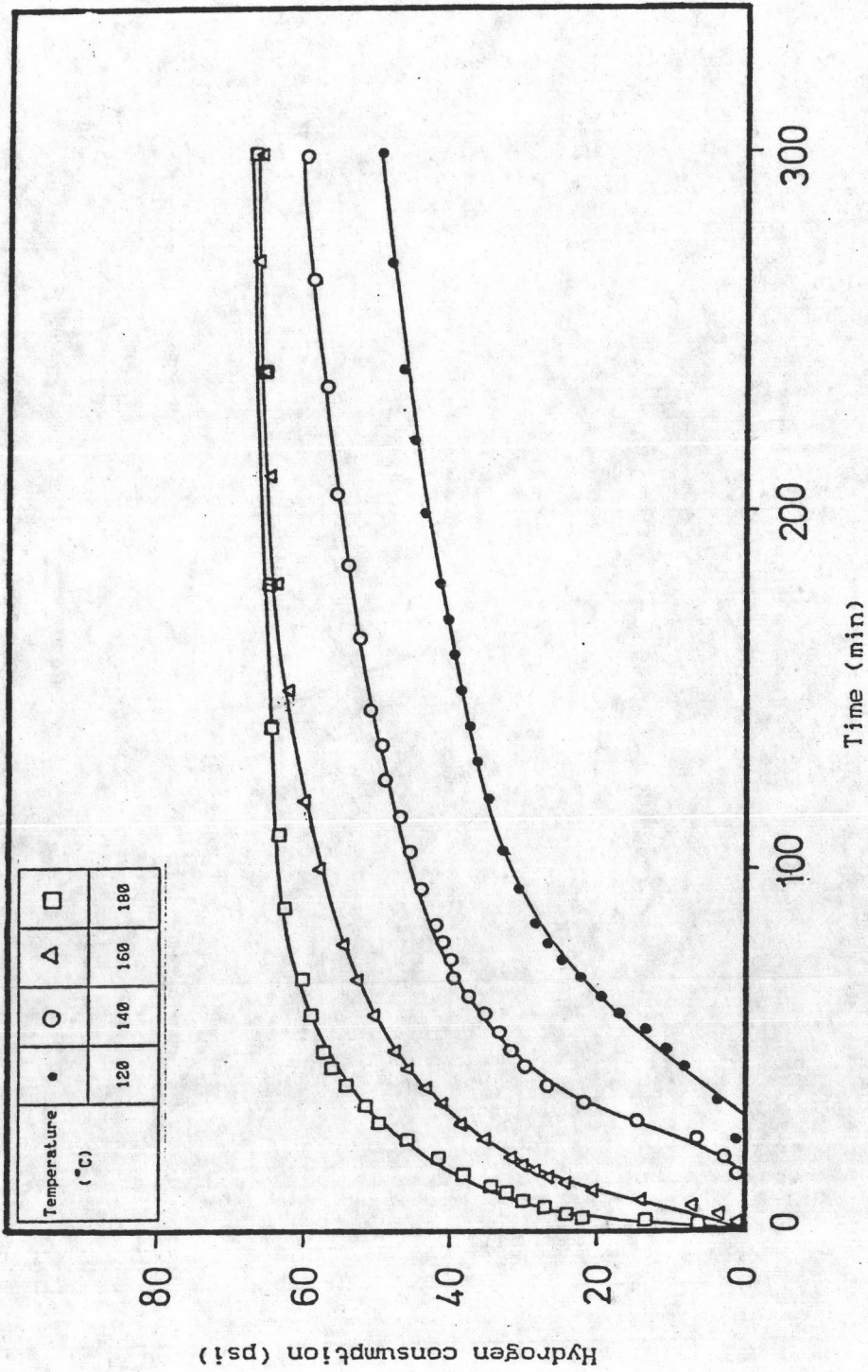


Figure 5.5 Hydrogen consumption curves at various reaction temperatures of Nysel HK-4: 150 psi, 700 rpm, and 0.2% Ni in oil.

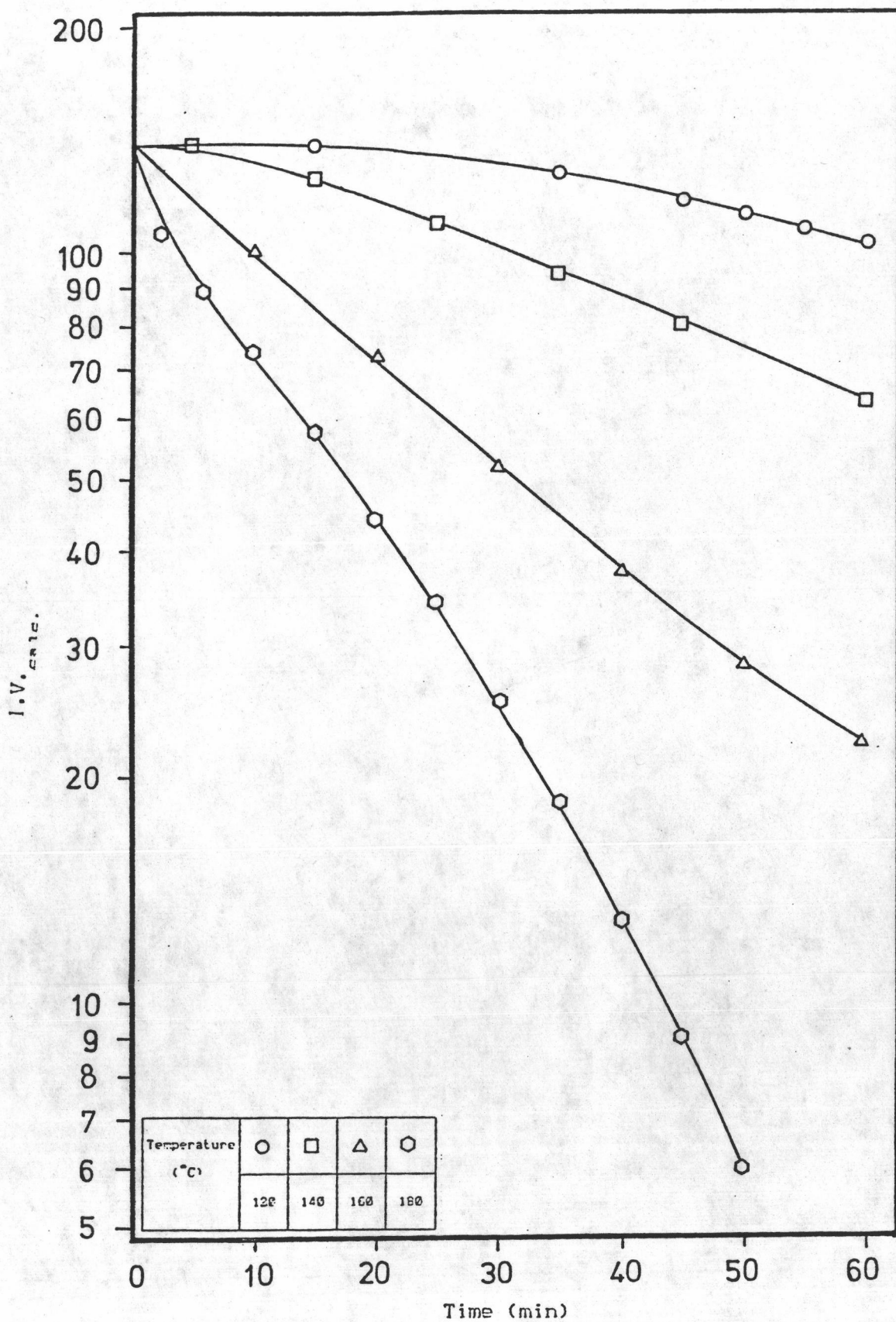


Figure 5.6 Effect of reaction temperature on hydrogenation with Nysel HK-4 : 150 psig, 700 rpm and 0.2% Ni in oil.

5.3.1 Effect of Reaction Temperature

The data and results of the experiments on hydrogenation of rubber seed oil at different temperatures of 120 °C, 140 °C, 160 °C, and 180 °C are shown in Table A3, Table C3, Figure 5.5 and Figure 5.6, respectively. From Figure 5.6 it shows that the hydrogenation rate increases apparently with temperature in the range of 120 °C to 180 °C.

Table 5.2 lists the analytical results of the hydrogenated products. It is obvious that the increasing reaction temperature from 120 °C to 180 °C decreases the iodine value from 40 to 5 and increases the melting point from 47.8 to 55.8. There is only little difference in melting point between 160 °C and 180 °C hydrogenation. This may be due to the differences in their compositions. The hydrogenated wax is composed of different kinds of fatty acids which cause the different melting point.

Table 5.2 Analytical results of hydrogenated rubber seed wax with the Nysel HK-4 catalyst at various temperatures: 150 psig, 0.2% Ni/oil, 700 rpm, and 5 hours of reaction time.

Run no.	Reaction temperature (°C)	Properties of rubber seed wax			Induction Time (min)	Total H ₂ Consumption (psi)
		I.V.	A.V.	m.p.(°C)		
1	120	40	31.1	47.8	20	49.5
2	140	16	29.9	53.5	10	61.0
3	160	7	30.2	56.0	-	67.0
4	180	5	29.9	55.8	-	66.0

During the operation, the induction periods which occurred at 120°C and 140°C, were 20 and 10 minutes, respectively. However, at both 160°C and 180°C the induction periods were not noticeable. The cause of induction period is not known definitely, but it is probably related to some extent at least with selective adsorption of the trace-quantity polar materials of the oil.

5.3.2 Effect of Hydrogen Pressure

The data and results of the experiments on the hydrogenation of rubber seed oil at different pressures of 60, 90, 120, and 150 psig, with the constant pressure during each experiment, are illustrated in Table A4, Table C4, Figure 5.7, and Figure 5.8. It is evident from the figures that the rate of the hydrogenation increases with increasing pressure. The increasing hydrogen pressure affects a large driving force to solubilize the hydrogen into the oil, thus, increases the hydrogen concentrations on the catalyst surface and the rate of hydrogenation. However, from Figures 5.7 and 5.8, the rates of hydrogenation at 120 psig and 150 psig are almost similar. This may result from the saturated solubility of hydrogen at 120 psig or from sintering which reduces the rate of hydrogenation at 150 psig.

The analytical results of the hydrogenated products are shown in Table 5.3. The iodine value decreases from 19 to 7 and the melting point increases from 52.5 to 57.5 while increasing hydrogen pressure ranges from 60 to 120 psig. At 120 psig the iodine value is equal to the value at 150 psig, but the melting point is a little higher. It may be because of the difference in their compositions. There are little decrease in acid value with increasing pressure. Thus, the effect of pressure on the acid value may be neglected.

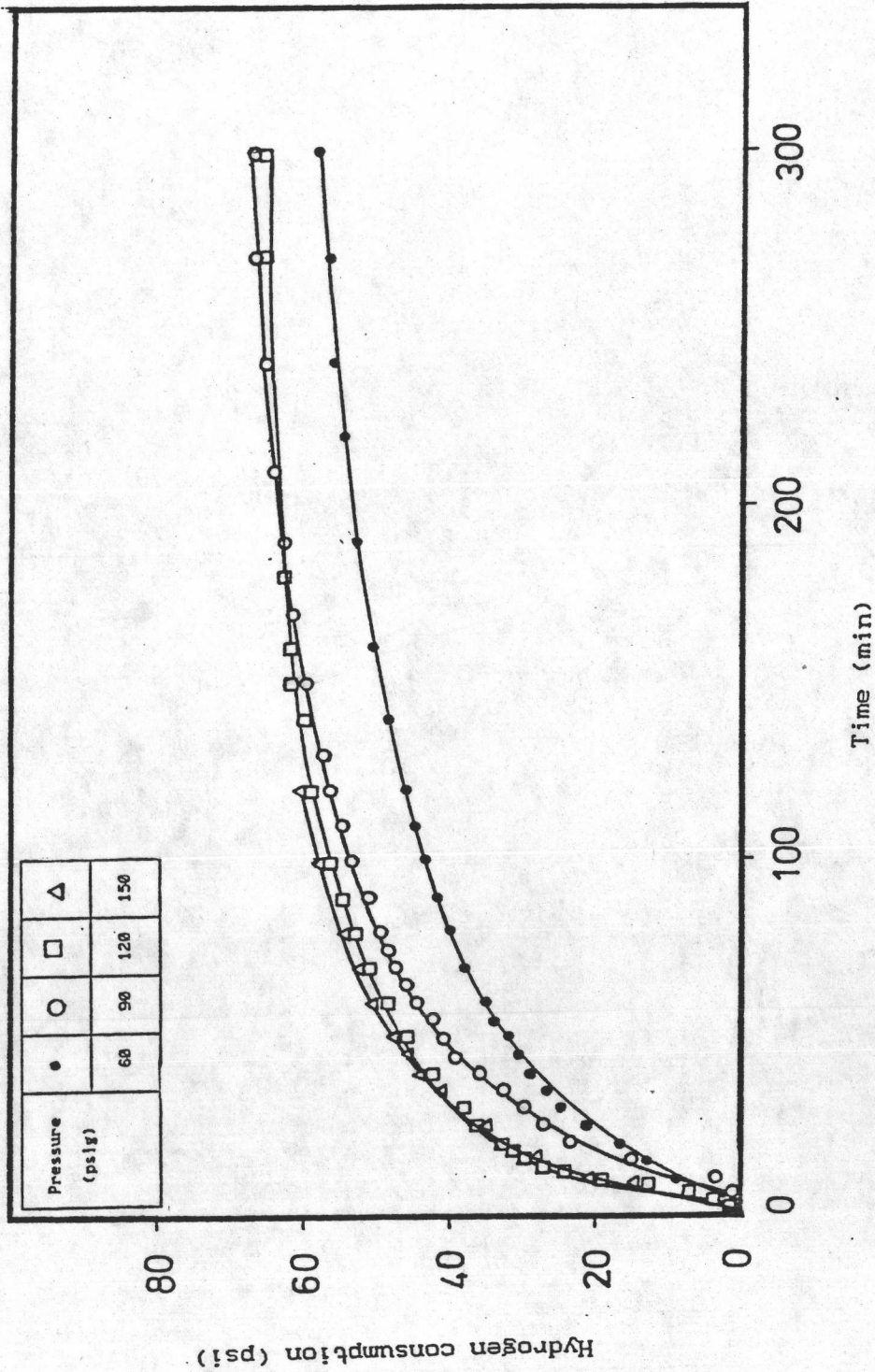


Figure 5.7 Hydrogen consumption curves at various hydrogen pressures of Nysel HK-4: 160°C, 700 rpm. and 0.2% Ni in oil.

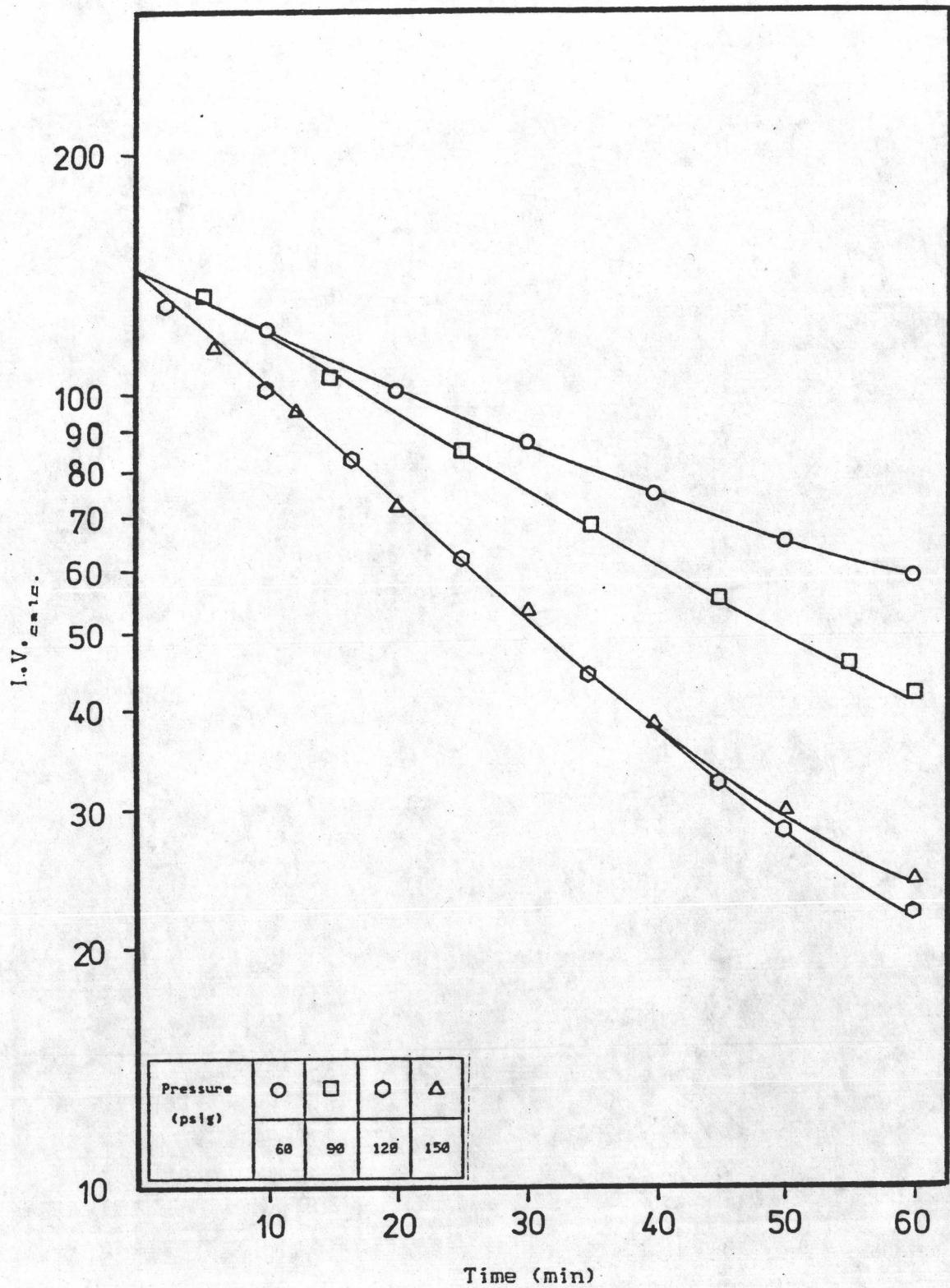


Figure 5.8 Effect of hydrogen pressure on hydrogenation with Nysel HK-4 : 160°C, 700 rpm and 0.2% Ni in oil.

Table 5.3 Analytical results of hydrogenated rubber seed wax with the Nysel HK-4 catalyst at various hydrogen pressures: 160 °C, 0.2% Ni/oil, 700 rpm, and 5 hours of reaction time.

Run no.	Hydrogen Pressure (psig)	Properties of rubber seed wax			Total H ₂ consumption (psi)
		I.V.	A.V.	m.p.(°C)	
5	60	19	30.7	52.5	58.5
6	90	10	30.4	56.8	67.5
7	120	7	30.4	57.5	66.0
3	150	7	30.2	56.0	67.0

The induction periods were not noticeable during the study of hydrogen pressure effect.

In this research, from the better quality products and the economic considerations, the suitable hydrogen pressure is 120 psig.

5.3.3 Effect of Catalyst Concentration

The results from Figures 5.9 and 5.10 show that the increasing of the catalyst concentration from 0.05% to 0.40% Ni in oil increases the hydrogenation rate. Figure 5.10 shows that an increasing in the catalyst concentration from 0.05% to 0.1% Ni in oil and from 0.1% to 0.2% Ni in oil, the increasing reaction rates are faster than that of the increasing catalyst concentration from 0.2% to 0.4% Ni in oil. This shows that at low level of catalyst, the increasing of catalyst concentration causes much increase in the rate of hydrogenation. However, if more

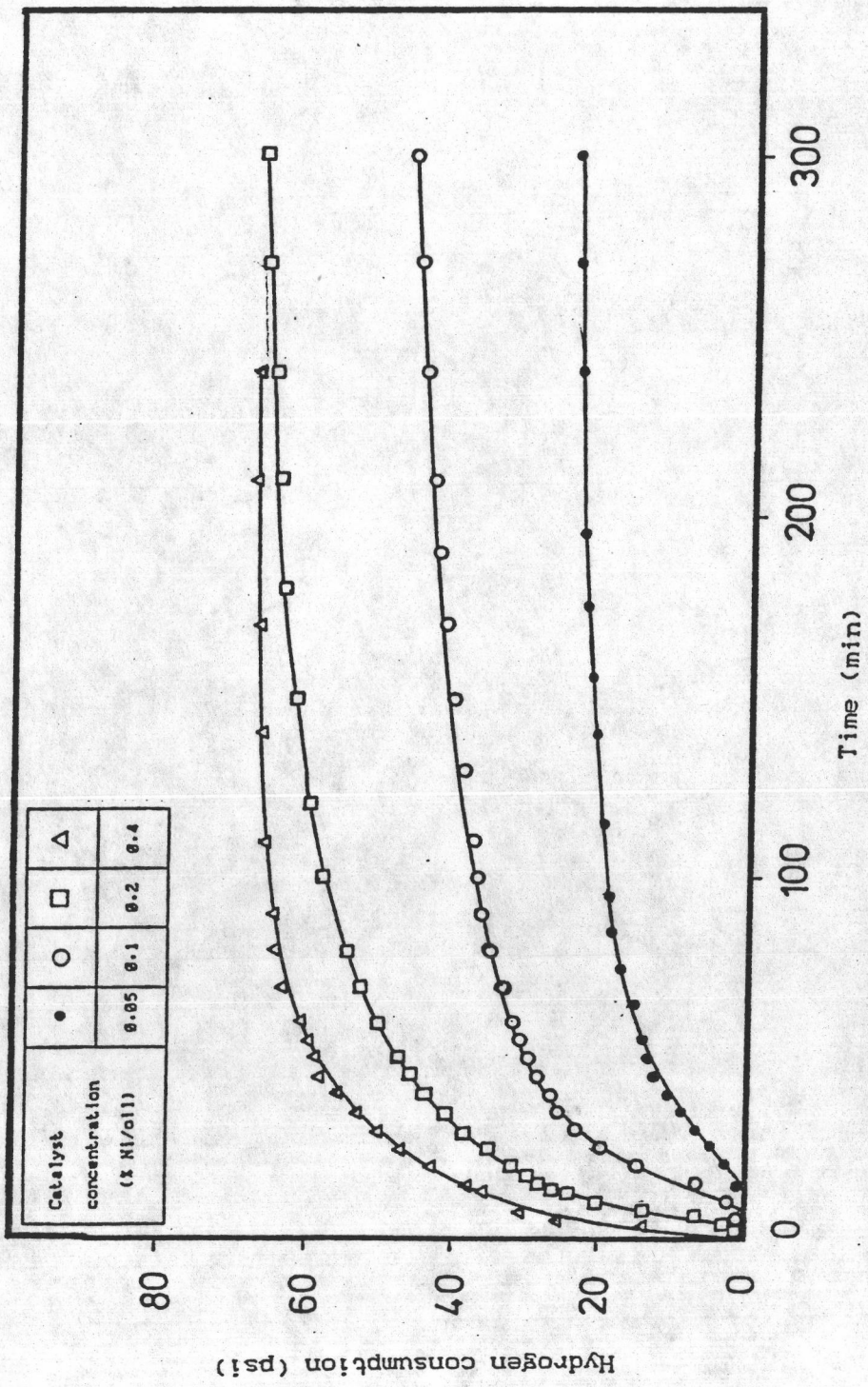


Figure 5.9 Hydrogen consumption curves at various catalyst concentrations of Nysel HK-4: 160°C, 150 psig, and 700 rpm.

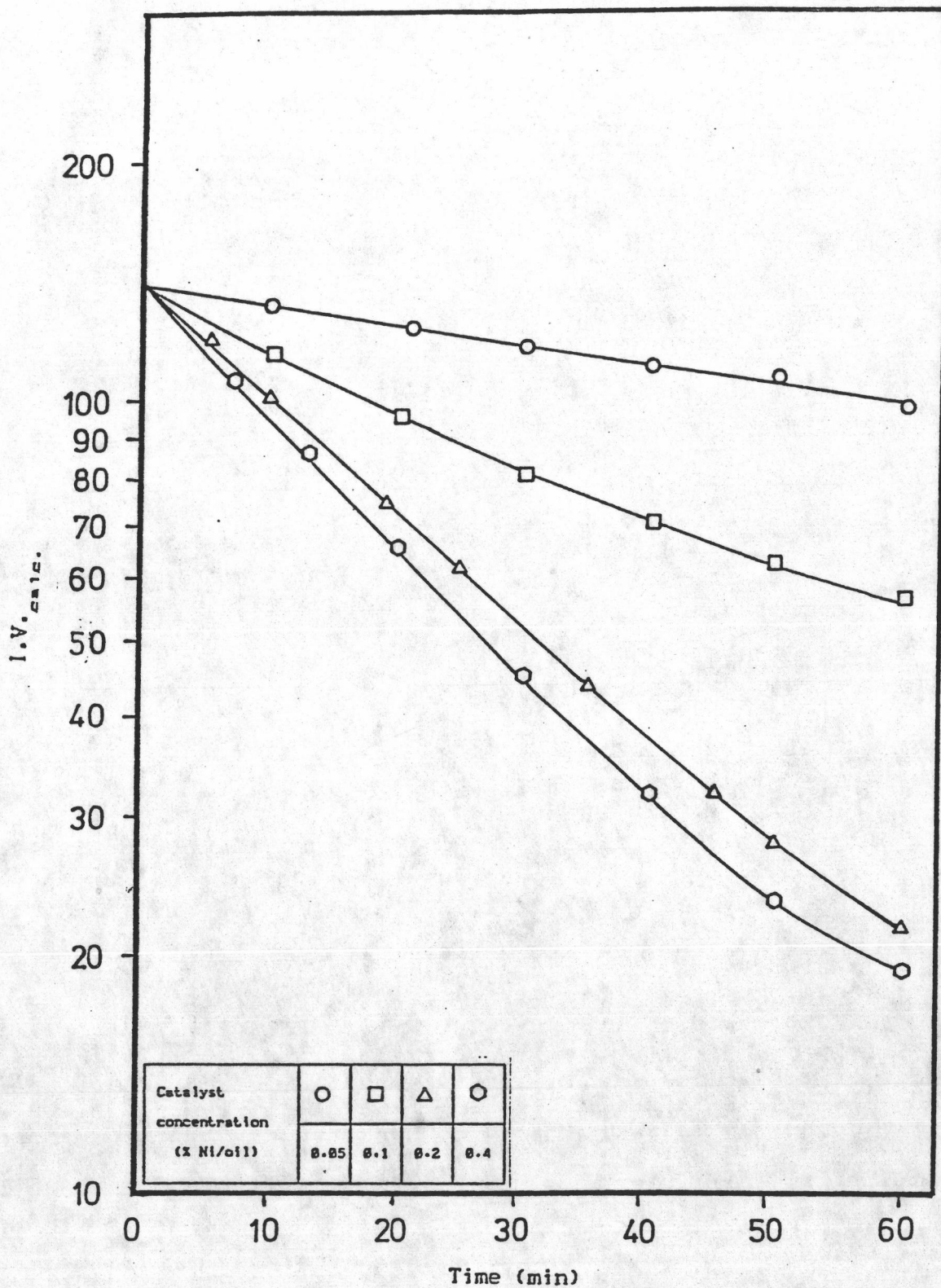


Figure 5.10 Effect of catalyst concentration on hydrogenation with Nysel HK-4 : 160°C, 150 psig and 700 rpm.

catalyst is used (as 0.4% Ni), the increasing in the rate is decreased. Thus, from the economic considerations, 0.2% Ni in the rubber seed oil is more suitable.

The induction period of 12 minutes occurred at 0.05% Ni in the oil but at 0.1%, 0.2%, and 0.4% Ni in oil were not noticeable.

5.3.4 Effect of Agitation

A comparison of the results from Figures 5.11 and 5.12 illustrates that the increasing agitation from 200 to 600 rpm increases the reaction rate. The main function of agitation is to supply dissolved hydrogen to the catalyst surface. Then, increasing agitation increases the dissolution rate and the adsorption rate of hydrogen into the oil and on the catalyst surface because the hydrogen was much quickly transferred and decreased the film resistance of the mass and heat transfer around the catalyst particle and finally increased the rate of hydrogenation. From Figures 5.11 and 5.12, the rate of hydrogenation at 600 and 700 rpm are similar. (In Figure 5.11, if the hydrogen consumption curves are normalized, based on the same weight of rubber seed oil, the hydrogen consumption curves at 600 and 700 rpm will overlap. This may due to that at high rate of agitation in which the resistances for all transfer steps are eliminated, further increasing of agitation has no effect on rate. The iodine value is calculated from the hydrogen consumption and the weight of oil, as shown in Appendix B.

The induction period were not noticeable during the study of the effect of agitation.

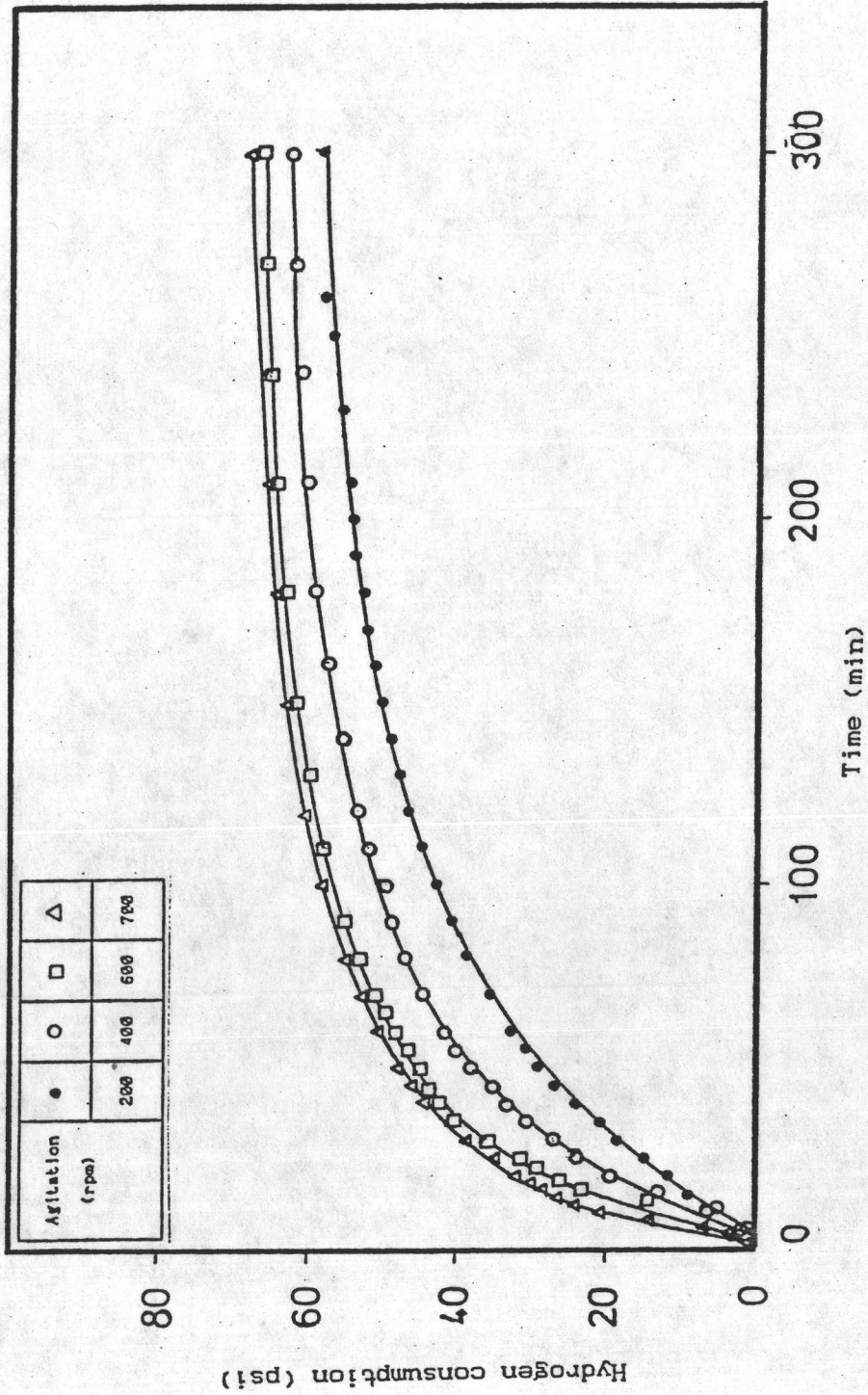


Figure 5.11 Hydrogen consumption curves at various agitations of Nysel HK-4: 160°C, 150 psig, and 0.2% Ni in oil.

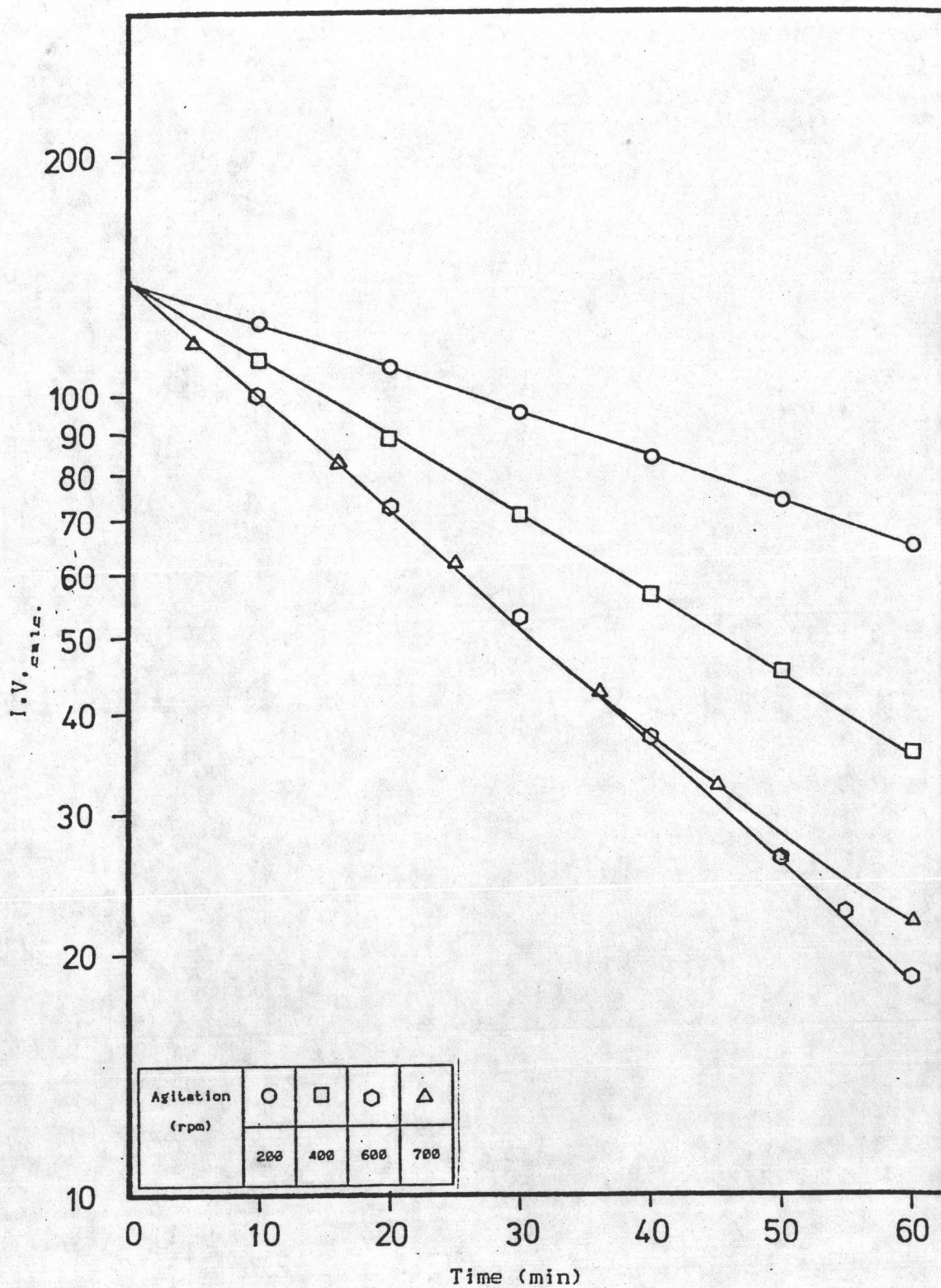


Figure 5.12 Effect of agitation on hydrogenation with Nysel HK-4 :
 160°C , 150 psig and 0.2% Ni/oil.

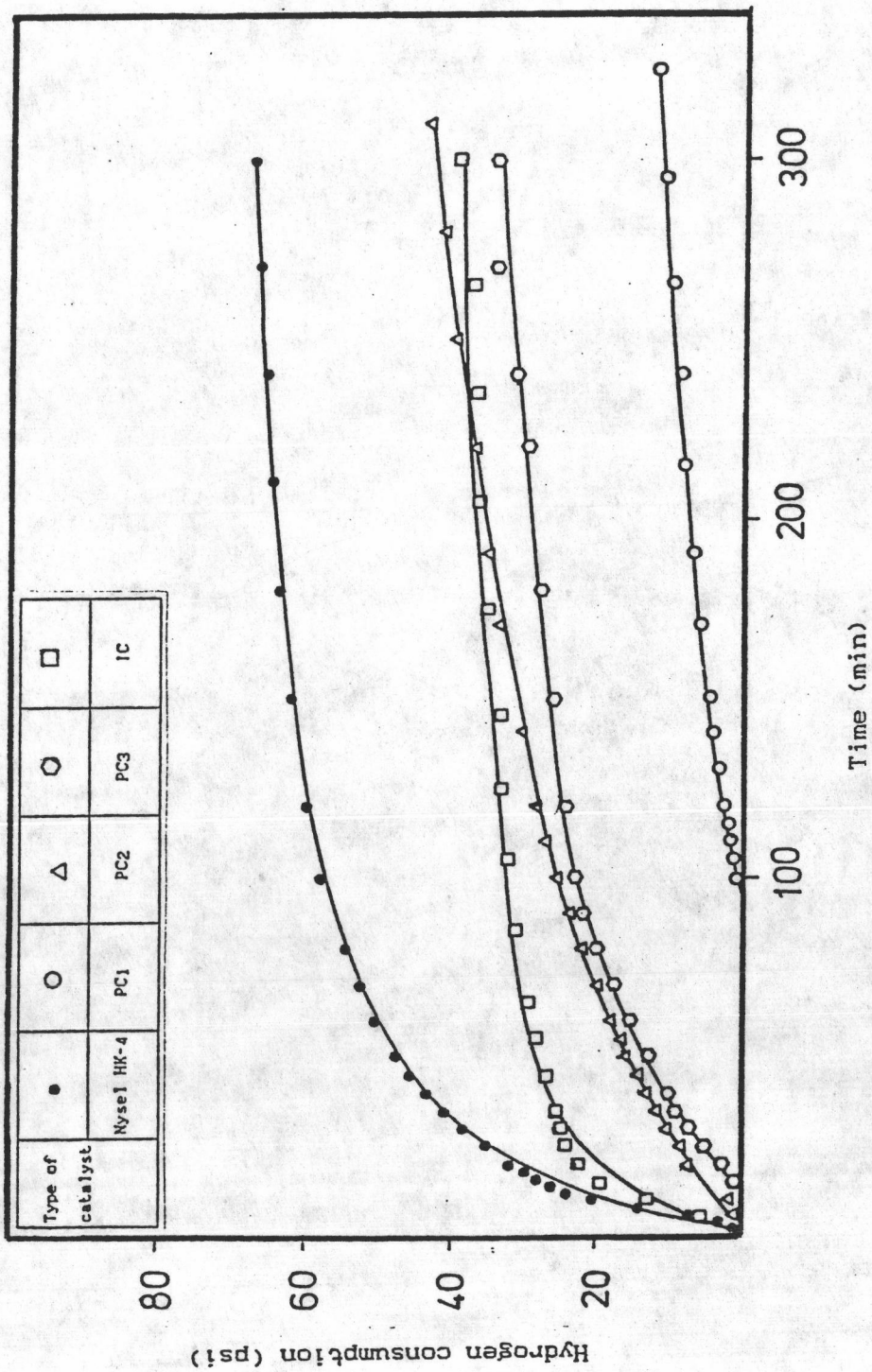


Figure 5.13 Hydrogen consumption curves of various in-house catalysts and Nysel HK-4: 160°C, 150 psig, 700 rpm. and 0.2% Ni in oil..

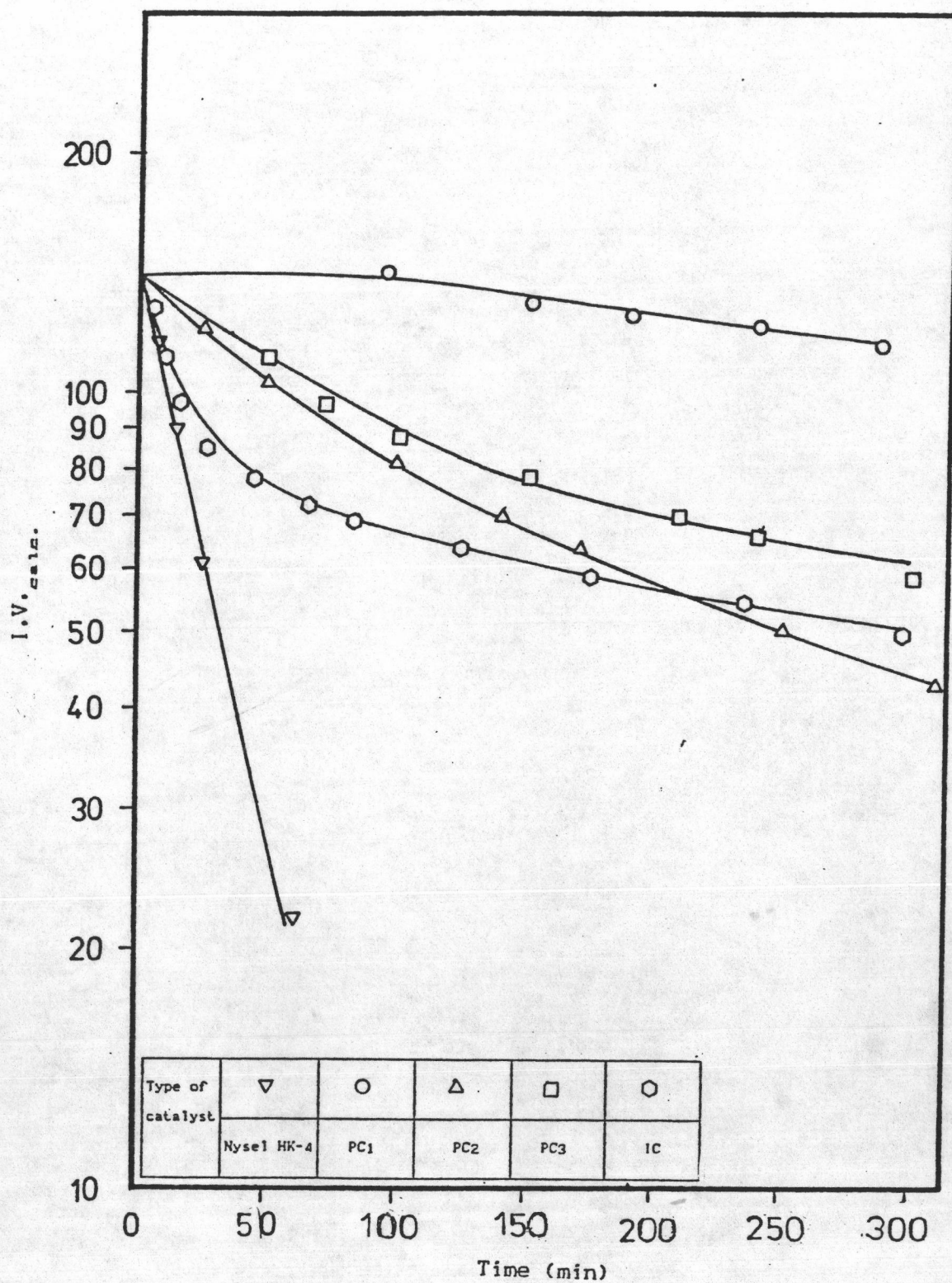


Figure 5.14 Comparing the hydrogenation rate of the in-house catalysts with Nysel HK-4 : 160°C, 150 psig, 700 rpm and 0.2% Ni in oil.

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

From the comparative results of the hydrogenation using different catalysts from Figure 5.13 and Figure 5.14, it is evident that the hydrogenation rate of all the in-house catalysts are very slow. It may result from catalyst poison. The hydrocyanic acid of the cyanogenic glucoside may poison the catalyst. The in-house catalysts were prepared without any prevention from poison. The comparative results of Figure 5.3, the reaction rates with the G95E and the Nysel HK-4 catalysts which are poison-resistance catalysts, are fast. The Kawaken catalyst and the G53D are prepared for castor oil and edible oils. But they may be not poison-resistance to the rubber seed oil, so their rates are slow. The other reason may be a lower intrinsic activity resulted from the step of reduction. The in-house catalysts are reduced in the calcinator (Figure 4.3). The nickel loading of PC1, PC2, and PC3, which are the precipitated catalysts, are high at 56.1%, 41.8%, and 15.2%, respectively. After reduction, oxidation occurred when they left the calcinator. It may be this oxidation that causes the catalyst sintering. PC2 is the best in-house catalyst from the comparison of PC1, PC2, and PC3. The impregnated catalyst (IC), which is prepared for comparing with the in-house precipitated catalyst, has higher reaction rate than the PC2 at the beginning until about 220 min. (3.40 hours), then becomes slower. This may due to different induction period between the two catalysts or to different sintering rates or both.

The hydrogenated products after 5-hour-hydrogenation using the catalysts PC2, PC3, and IC are semisolid waxes. The products using PC1 has a little solid appears in the oil.

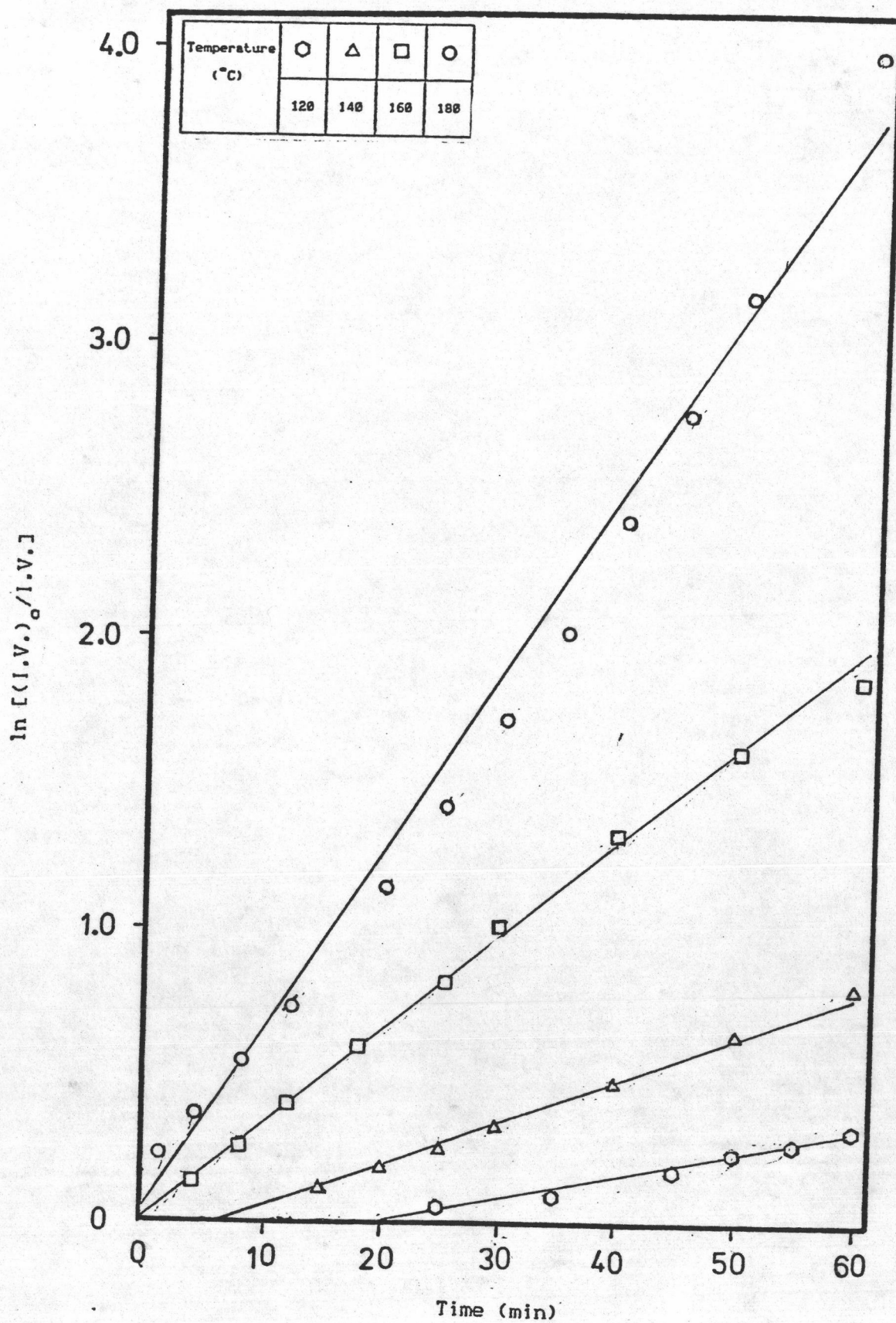


Figure 5.15 Determination of overall rate constant at various temperatures: 150 psig, 700 rpm, and 0.2% Ni in oil.

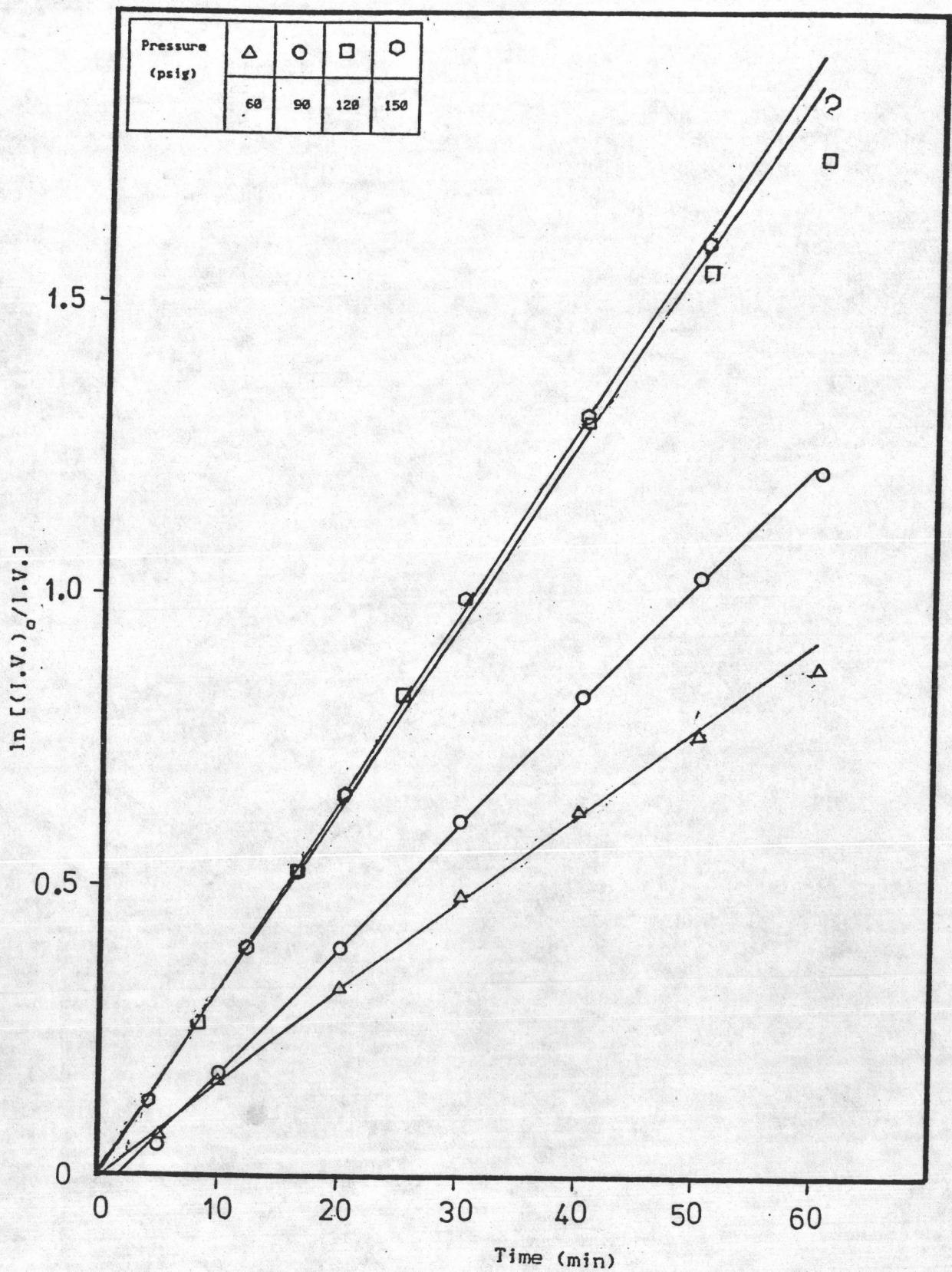


Figure 5.16 Determination of overall rate constant at various pressures : 160°C, 700 rpm, and 0.2% Ni in oil.

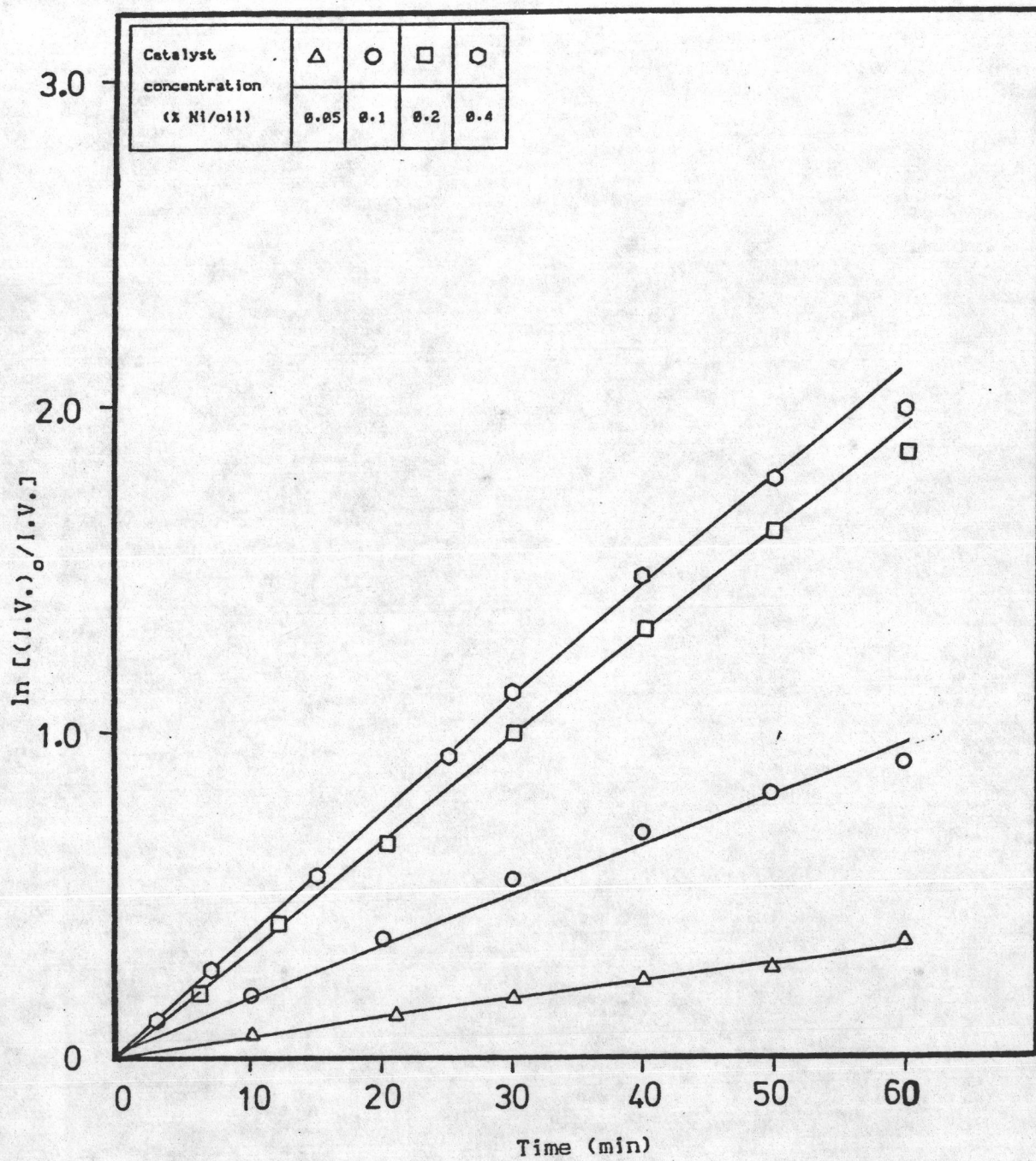


Figure 5.17 Determination of overall rate constant at various catalyst concentrations : 160°C , 150 psig, and 700 rpm.

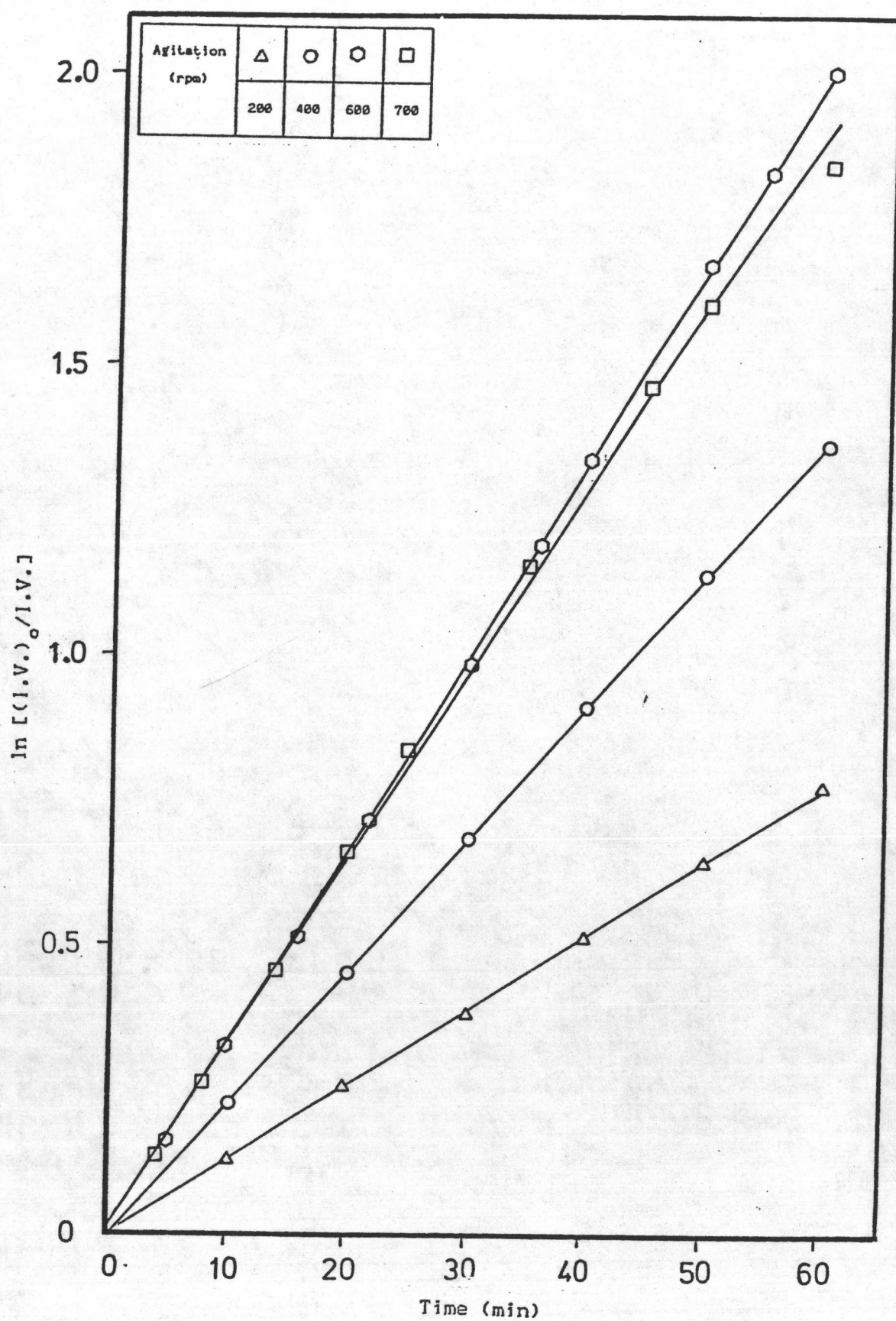


Figure 5.18 Determination of overall rate constant at various agitations : 160°C, 150 psig, and 0.2% Ni in oil.

From the comparison of PC2, PC3, and IC with the Kawaken and the G95E catalysts in Figures 5.9 and 5.13, it is obvious that the rates of hydrogenation of these in-house catalysts are higher than the Kawaken catalyst. The initial rate of the IC is higher than the G53D catalyst but after 70 minutes the rate of the G53D catalyst is higher. This may be due to a high sintering rate on the IC catalyst and, thus, the in-house catalysts should be prepared on various supports in order to reduce sintering. In addition the precipitated catalyst should be prepared under various conditions and the effects of promoters should also be studied.

5.5 Order of Reaction and Overall Reaction Rate Constants

For obtaining the order of the reaction and the overall reaction rate constant of the hydrogenation of rubber seed oil, the data obtained from the experiments are tested for the first-order reaction by plotting $\ln [(I.V.)_t / I.V.]$ versus time as shown in Figure 5.15 to Figure 5.18, where I.V. is the iodine value at time t and $(I.V.)_0$ is the initial iodine value of rubber seed oil. These plots give straight lines. The linear relationship is found to be statistically significant with correlation coefficient varying from 0.946 to 0.999. The slopes of the straight lines are equal to the first-order overall reaction rate constant, k , in the equation [46].

$$-r = k(I.V.)$$

$$\begin{aligned} \text{where } r &= \text{reaction rate, I.V./min} \\ &= \frac{d(I.V.)}{dt} \end{aligned}$$

The experimental values of k are shown in Table 5.4.

From the Arrhenius equation, the values of the apparent activation energy and the apparent frequency factor of Run no.1 to 4

Table 5.4 First-order reaction rate constants

Run no.	Reaction temperature (°C)	Hydrogen pressure (psig)	Catalyst concentration (%Ni/oil)	Agitation (rpm)	k (min ⁻¹)
1	120	150	0.2	700	0.0055
2	140	150	0.2	700	0.0140
3	160	150	0.2	700	0.0319
4	180	150	0.2	700	0.0609
5	160	60	0.2	700	0.0150
6	160	90	0.2	700	0.0210
7	160	120	0.2	700	0.0304
3	160	150	0.2	700	0.0319
8	160	150	0.05	700	0.0054
9	160	150	0.1	700	0.0152
3	160	150	0.2	700	0.0319
10	160	150	0.4	700	0.0346
11	160	150	0.2	200	0.0129
12	160	150	0.2	400	0.0229
13	160	150	0.2	600	0.0337
3	160	150	0.2	700	0.0319

are calculated (as shown in Appendix B and Figure 5.19). The apparent activation energy is 14.5 kcal/mole. The apparent frequency factors are shown in Table 5.5. The average value of A is $6.39 \times 10^5 \text{ min}^{-1}$ and from the Polyfit program is $6.31 \times 10^5 \text{ min}^{-1}$.

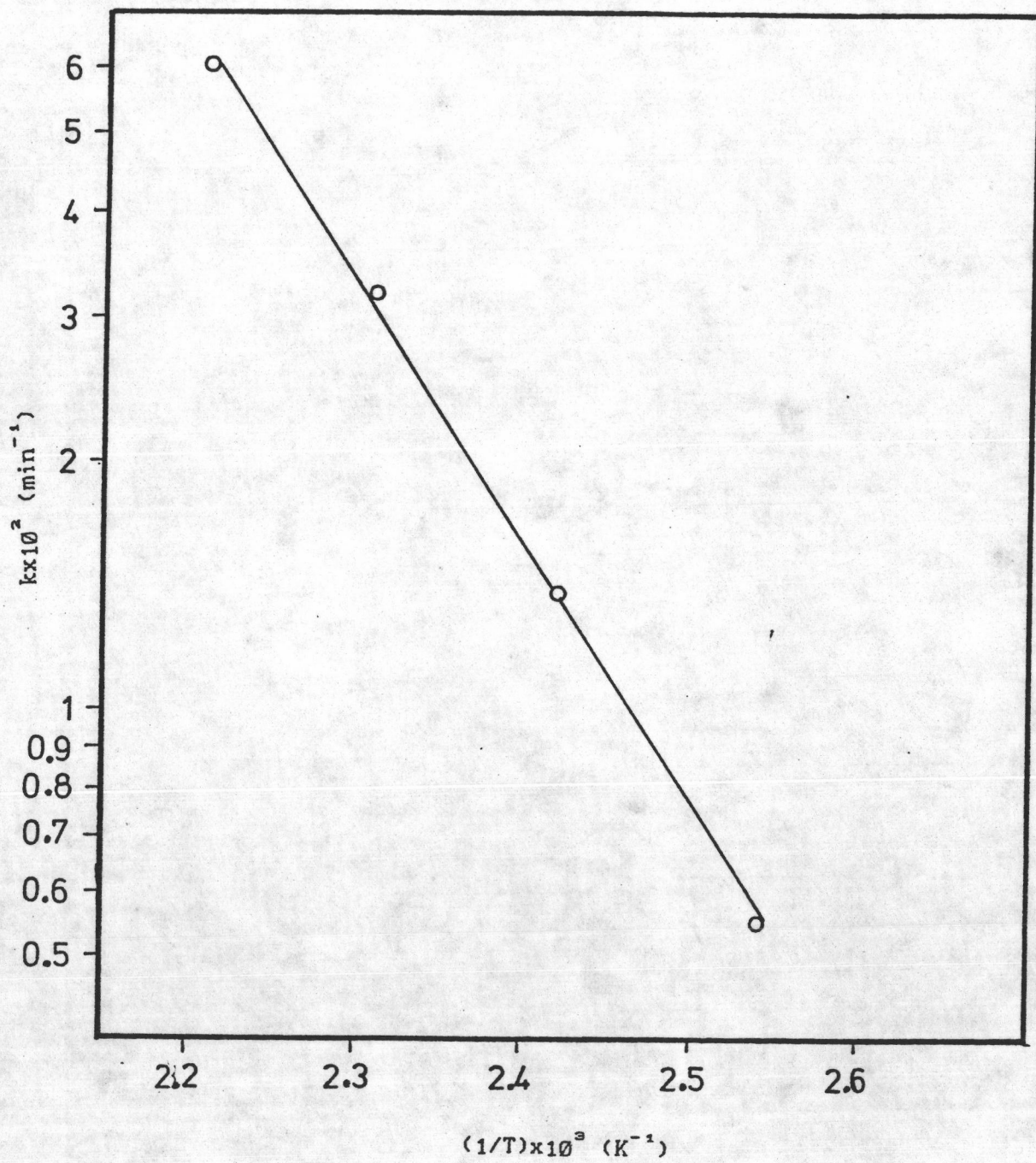


Figure 5.19 Arrhenius plot for the hydrogenation of rubber seed oil with Nysel HK-4 : 150 psig, 700 rpm, and 0.2% Ni in oil.

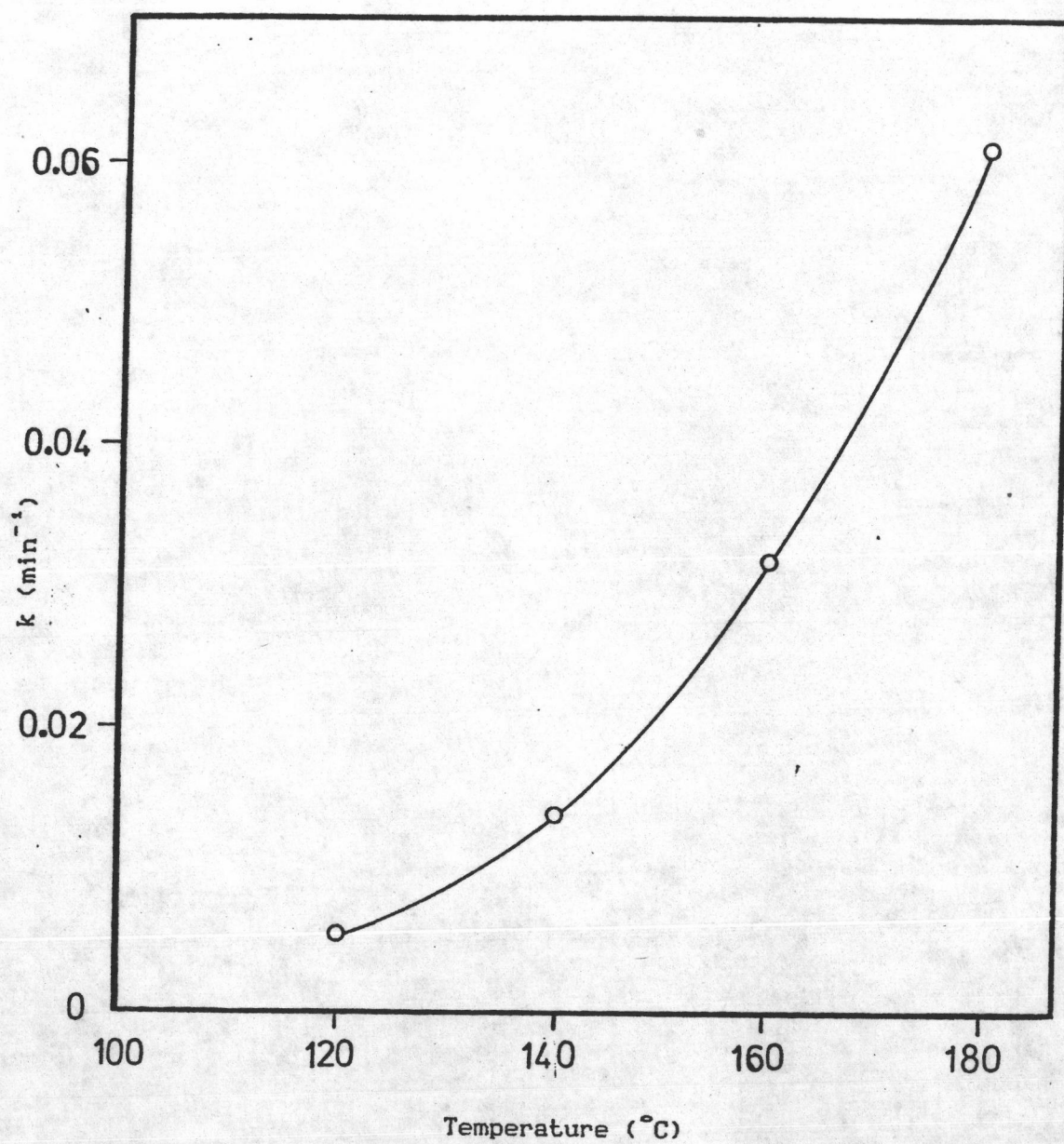


Figure 5.20 Effect of temperature on the overall rate constant:
150 psig, 700 rpm, and 0.2% Ni in oil.

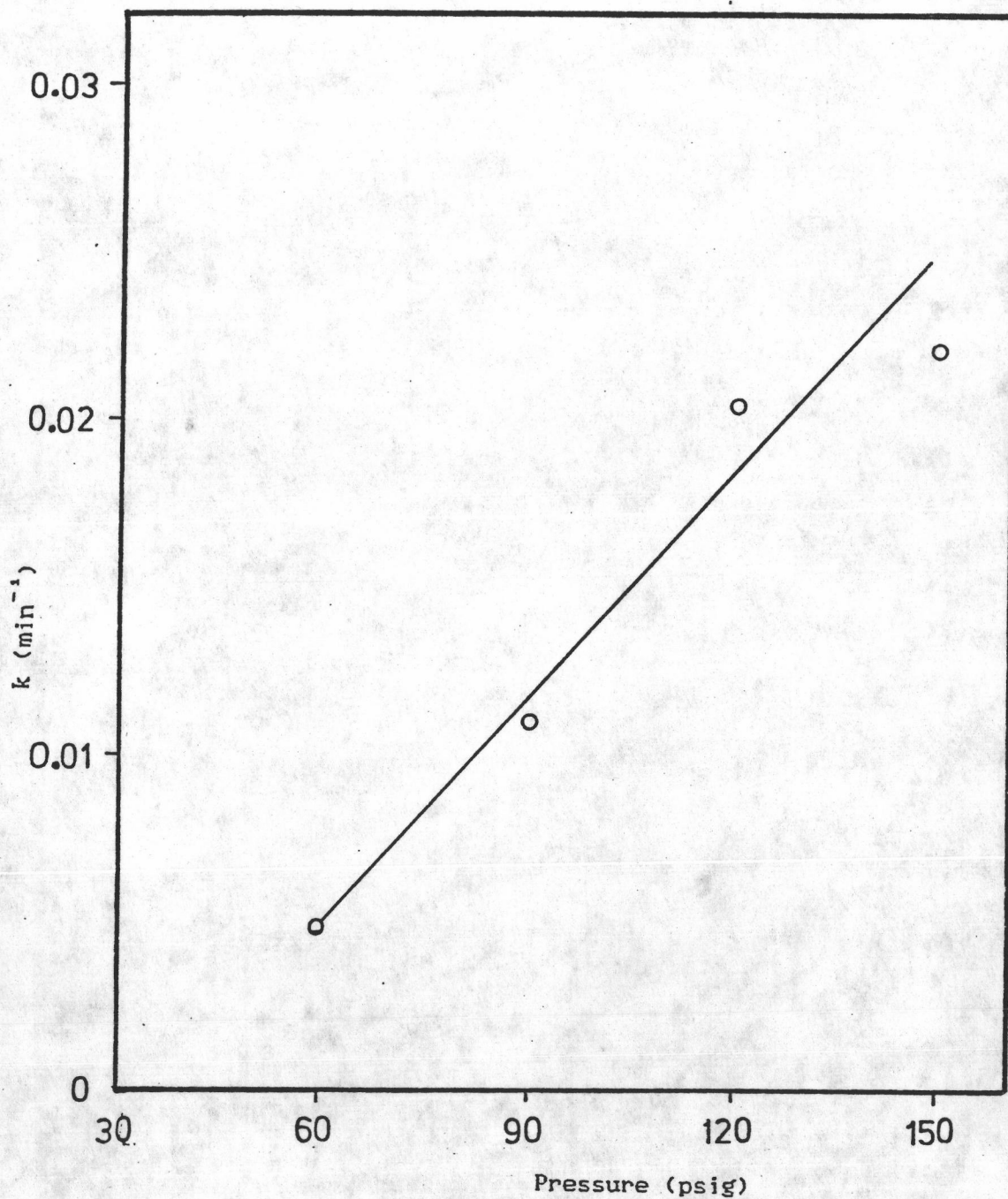


Figure 5.21 Effect of pressure on the overall rate constant :
160°C, 700 rpm, and 0.2% Ni in oil.

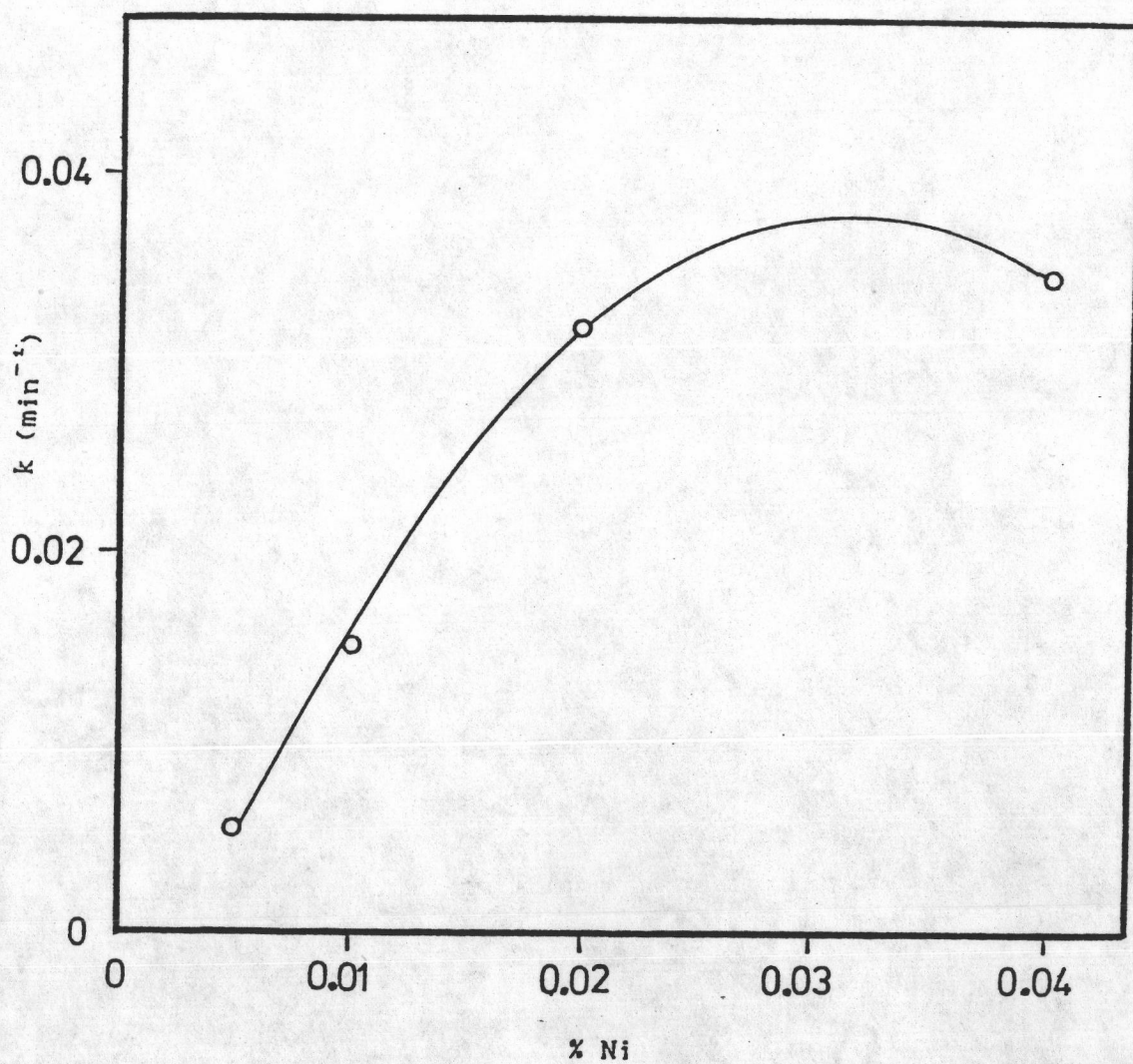


Figure 5.22 Effect of catalyst concentration on the overall rate constant : 160°C , 150 psig, and 700 rpm.

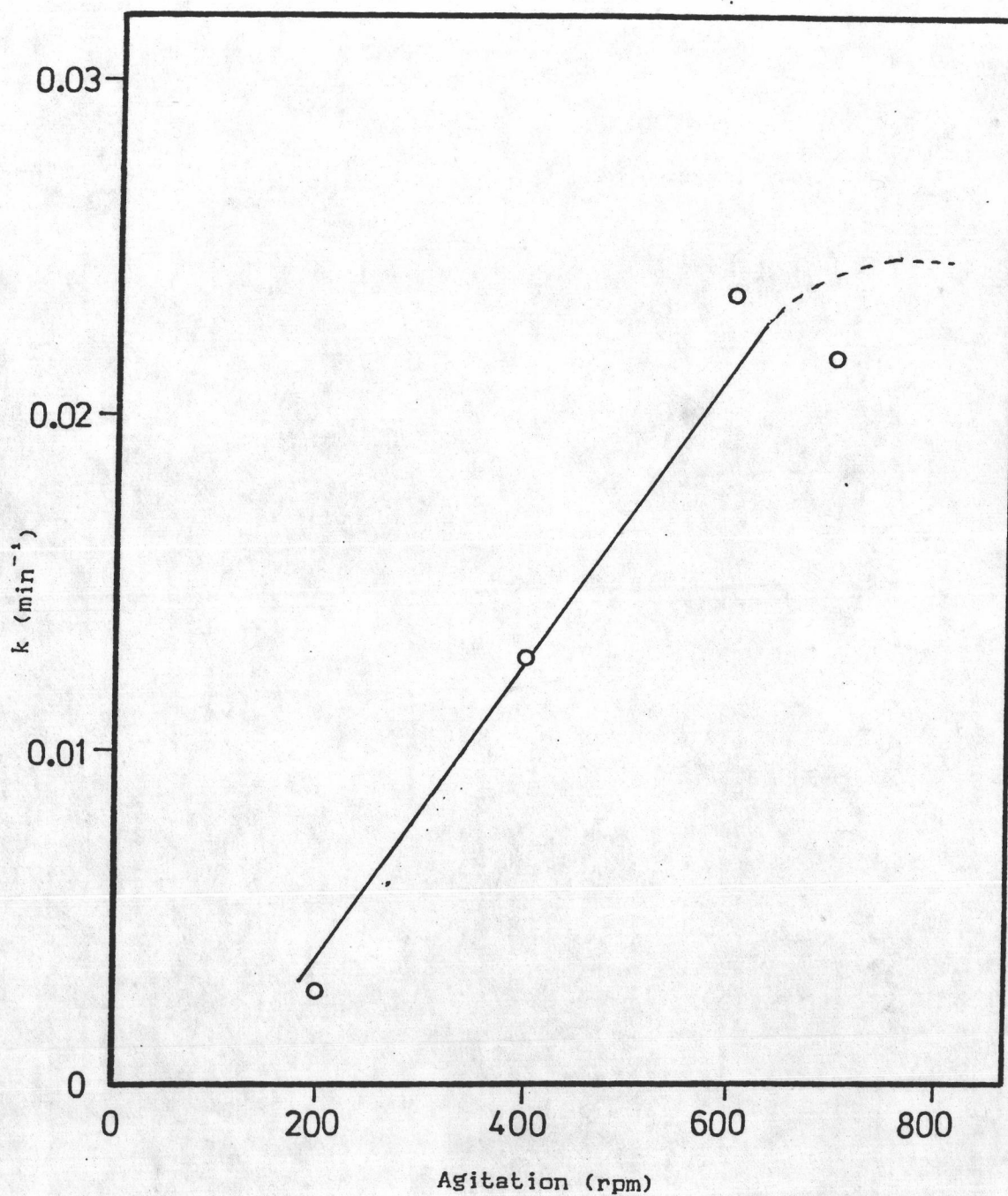


Figure 5.23 Effect of agitation on the overall rate constant :
 160°C , 150 psig, and 0.2% Ni in oil.

Figures 5.20 to 5.23 indicate the relationships between the overall reaction rate constant and reaction temperature, hydrogen pressure, catalyst concentration, and agitation, respectively. They show that the k values are proportional to these parameters. The constants k vary directly proportional to hydrogen pressure and agitation. From this research, at the agitation speed higher than 600 rpm, it may be no effect of agitation to the rate of hydrogenation, thus, the k may be constant which is shown as the dotted line in Figure 5.23. There is little decrease in the value of k at 600 and 700 rpm. At low catalyst concentration, the increasing rate of k is higher than at high concentration, but at low temperature, the increasing rate of k is lower than at high temperature.

Table 5.5 Apparent frequency factors of the hydrogenation rate of rubber seed oil with the Nysel HK-4 catalyst at various temperatures: 150 psig, 0.2% Ni/oil, and 700 rpm.

Run no.	Reaction temperature ($^{\circ}$ C)	$A \times 10^{-5}$ (min^{-1})
1	120	6.39
2	140	6.56
3	160	6.61
4	180	6.00

5.6 Properties and Applications of the Rubber Seed Wax.

The hydrogenation of rubber seed oil yields waxlike substances. The color of wax is light-yellow. When it melts, it is clear, transparent, and yellow-colored. The completely hydrogenated rubber seed wax is a hard and brittle product. It is

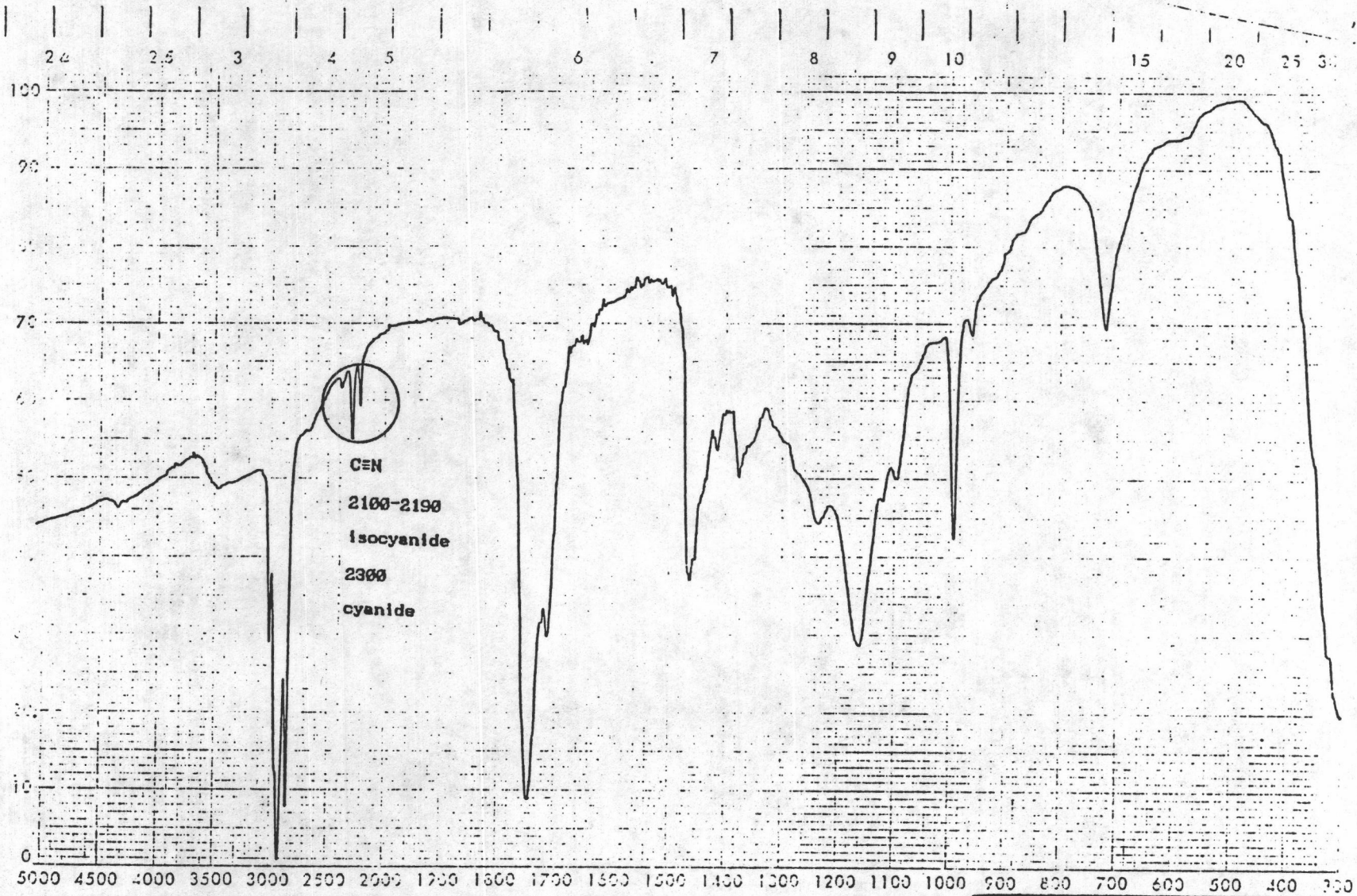
Table 5.6 Analysis data of rubber seed oil and rubber seed wax.

	Rubber seed oil	Rubber seed wax
Iodine value (Wijs)	141	7
Acid value, mg KOH/g oil	31.1	30.2
Cyanide	not found	not found
Fatty acid composition, (GLC), %		
Lauric	0.3	0.2
Myristic	0.3	0.2
Palmitic	12.4	9.6
Stearic	12.4	89.0
Oleic	26.9	0.2
Linoleic	30.4	0.6
Linolenic	15.9	not found
Others	1.4	0.2

tough and soft when it is partially hydrogenated.

Table 5.6 shows the chemical properties of rubber seed oil and rubber seed wax. The wax is from Run no. 3 with the condition of 160 °C, 150 psig, 0.2% Ni in oil, and 700 rpm. It can be seen that the principal constituent of the wax is stearic acid (89%). Most of the linolenic acid, linoleic acid and oleic acid are hydrogenated. In the oil, there are 15.9%, 30.4%, and 26.9%, respectively, but in the wax, linolenic is not found, linoleic and oleic acid have left only 0.6 and 0.2%, respectively.

From Table 5.6, cyanide which is analyzed by quantitative method is not found both in the oil and in the wax. But from



<p>Figure 5.24 Infrared spectrum of rubber seed oil.</p>	<p>REMARKS KBr demountable cells</p> <p>DATE <u>24/01/89</u></p> <p>OPERATOR <u>[Signature]</u></p>
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<p>ศูนย์เครื่องมือวิจัยวิทยาศาสตร์และเทคโนโลยี</p> <p>PART NO. 264-52392</p> <p>จุฬาลงกรณ์มหาวิทยาลัย</p>

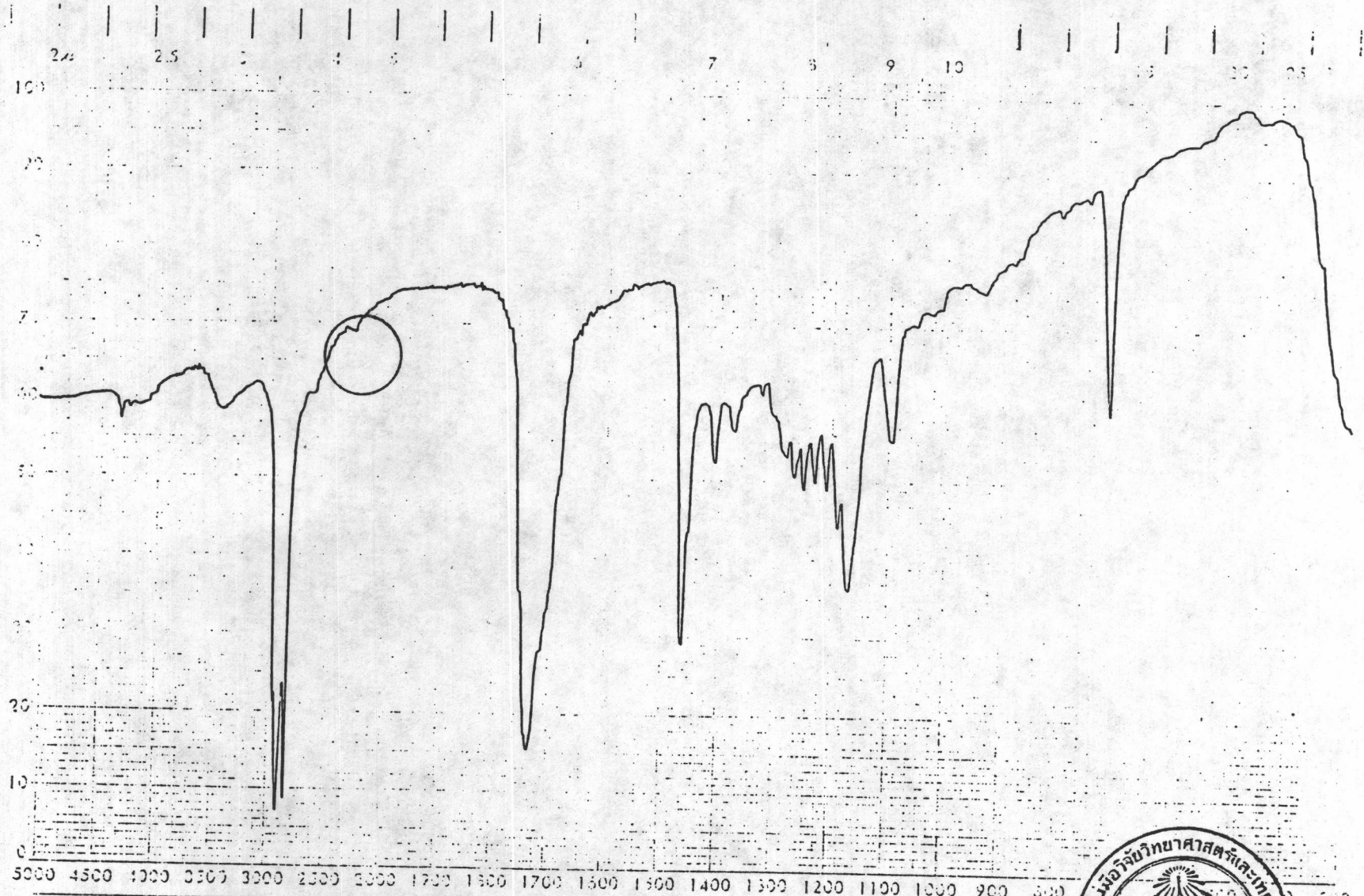


Figure 5.25 Infrared spectrum of
 rubber seed wax from
 run no.31

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KBr demountable cells	Feb 187
	OPERATOR
	Paulson



literature survey, cyanide is the substance in cyanogenic glucoside, then, the infrared (IR) spectrophotometer is used to analyze the cyanide. Figures 5.24 and 5.25 illustrate the spectrums from IR spectrophotometer of rubber seed oil and rubber seed wax of Run no. 3. From Figure 5.24, the isocyanide and the cyanide (CN^-) peaks appear at the wavelengths of 2190 cm^{-1} and 2300 cm^{-1} , respectively. These cyanide peaks disappear in Figure 5.25. This shows that the hydrogen cyanide is decomposed. It can be show that rubber seed wax is relatively non-toxic.

The properties of the rubber seed wax as compared with other commercial hydrogenated waxes [47], as shown in Appendix F, such as melting point, iodine value, and acid value, are in the same range as those waxes.

Since rubber seed oil is triglycerides, its completely hydrogenated product is tristearin. The applications of tristearin are soap, candles, adhesive pastes, metal polishes, water-proofing paper, textile sizes, leather stuffing and manufactured of stearic acid. Stearic acid is produced from tristearin by hydrolysis. Esterification of tristearin produces stearate. The applications of stearic acid are chemical (especially stearate and stearate driers), lubricants, soaps, pharmaceuticals, cosmetics, accelerator activator, dispersing agent, softener in rubber compounds, shoes and metal polishes, coatings, and food packaging.

From the properties of the rubber seed wax, which are illustrated before, the rubber seed oil is potential for hydrogenation to be a useful product.