CHAPTER IV

RESULTS AND DISCUSSION

The hydrogenation of soybean oil was performed under various conditions in the presence of prepared catalysts. The goal of this research is to investigate the nickel supported on natural silicate catalysts that are more effective in selective hydrogenation of soybean oil. The temperature, pressure, and reaction time were optimized in order to achieve the required product.

The results from the experimental procedure mentioned in chapter III were presented in tables and figures. The results were also discussed as in the followings.

4.1 Properties and compositions of clays

The properties of clays (acidity, morphology, surface area, pore size and pore volume) were presented in Table 4.1. The morphology of clays was determined by SEM and shown in Figure B1-B4.

Table 4.1 Properties of clays

Clay	Acidity (meg/100g clay)	Morphology	Surface area (m^2/g)	Pore volume (cc/g)	Pore size (°A)
Ball clay	68	Sheet	48.33	0.83	39
Diatomite	54	Globule macroporous	39.07	1.35	52
China clay	33	Fibrous	20.82	0.64	36
Kieselghur	26	Globule macroporous	236.71	1.72	85

The composition of clays was presented in Table 4.2. (Information was obtained from Cernic Internation Co.Ltd.)

Table 4.2 Composition of clays

Composition (%)	Ball Clay	Diatomite	China clay	Kieselghur
SiO_2	51.50	74.35	66.05	77.94
Al_2O_3	23.00	16.35	22.55	10.56
TiO_2	0.63	-	0.02	-
Fe_2O_3	1.42	3.32	0.68	2.56
CaO	0.37	0.44	0.08	0.21
MgO	0.12	-	0.54	0..3
Na_2O	0.22	-	4.19	-
K_2O	0.92	-	0.41	-

From Table 4.1, the ball clay had the highest acidity and surface area (not to included kieselghur), among the Thai natural silicates used to support the catalyst in this investigation. However, kieselghur was reported to be use as a support in industrial process. In the present study kiselghur was used to compare the efficiency with natural silicates from Thailand.

4.2 Properties of the prepared catalysts

The catalysts were prepared by impregnation of nickel on ball clay, diatomite, china clay and kieselghur. BET method and AAS were used to characterize them. The results gave information on the surface area, pore size and the amount of nickel on catalysts, respectively. The properties of catalyst were presented in Table 4.3.

Table 4.3 Analytical results of the prepared catalysts.

Catalyst	% Ni	Surface area (m^2/g)	Pore size (°A)
NiB	10.86	35.43	31
NiD	11.09	24.67	35
NiC	9.92	16.52	30
NiK	10.43	142.20	69

Where **NiB = 10 % Ni on ball clay**

NiD = 10 % Ni on diatomite

NiC = 10 % Ni on china clay

NiK = 10 % Ni on kieselghur

From Table 4.3, the NiB catalyst had higher surface area than the NiC and the NiD catalysts, but they had similar pore size and concentration of nickel.

4.3 Hydrogenation process

The aim of this research was to study the activity and selectivity of prepared catalysts and found the suitable condition for hydrogenation of soybean oil. The original soybean oil was characterized and the results were shown in Table 4.4. All experiment.

Table 4.4 Fatty acid composition and iodine value of the original soybean oil.

Properties	**Soybean oil (%wt)**
Iodine Value (I.V.)	136
% Fatty acid composition	
C16:0 palmitic acid	10.56
C18:0 stearic acid	5.54
C18:1 oleic acid	26.47
C18:2 linoleic acid	52.40
C18:3 linolenic acid	5.02

4.3.1 Activity and selectivity of catalyst

The activity of the catalyst for hydrogenation of soybean oil was studied from the reaction conversion and iodine value. The selectivity in this reaction was defined as the preference shown for polyenoic acid over monoenic acids in the hydrogenation. The value obtained was quantified as the ratio between the oleic acid produced with the linoleic acid and linolenic acid being converted in the reaction.

The hydrogenation condition was chosen based on prior experiment [39]. This condition was 200 psig. of hydrogen pressure, 180 °C of reaction temperature, 600 rpm. of agitation speed, 0.05 % by weight of nickel per oil and various reaction time (30, 60, 90, 120, 150, 180 min). The properties of hydrogenated soybean oil are shown in Tables 4.5-4.8 and Figure 4.1.

Table 4.5 Analytical results of hydrogenated soybean oil using NiB catalyst: 180 °C reaction temperature, 200 psig. hydrogen pressure, various reaction time, 600 rpm. agitation speed, and catalyst concentration of 0.05 % by weight of oil.

Properties	Soybean oil	Reaction time (min)					
		30	60	90	120	150	180
Iodine value	136	117.83	101.33	92.33	82.67	75.83	73.83
% Fatty acid							
C16:0 palmitic acid	10.56	10.74	10.72	10.73	10.68	10.54	10.56
C18:0 steric acid	5.54	8.56	15.1	23.33	35.06	54.34	68.47
C18:1 oleic acid	26.47	39.63	51.87	58.24	51.79	35.12	20.98
C18:2 linoleic acid	52.40	38.86	21.33	7.7	2.47	0.00	0.00
C18:3 linolenic acid	5.02	2.34	1.56	0.00	0.00	0.00	0.00

Table 4.6 Analytical results of hydrogenated soybean oil using NiD catalyst: 180 °C reaction temperature, 200 psig. hydrogen pressure, various reaction time, 600 rpm. agitation speed, and catalyst concentration of 0.05 % by weight of oil.

Properties	Soybean	Reaction time (min)					
	Oil	30	60	90	120	150	180
Iodine value	136	121.83	101.33	96.83	90.83	83.17	79.67
% Fatty acid							
C16:0 palmitic acid	10.56	10.55	10.75	10.45	10.47	10.37	10.68
C18:0 steric acid	5.54	7.22	9.63	17.54	26.86	40.19	57.20
C18:1 oleic acid	26.47	36.42	44.25	50.77	53.76	45.54	32.06
C18:2 linoleic acid	52.40	42.17	33.02	20.11	8.94	3.98	0.00
C18:3 linolenic acid	5.02	3.65	2.47	1.14	0.00	0.00	0.00

Table 4.7 Analytical results of hydrogenated soybean oil using NiC catalyst: 180 °C reaction temperature, 200 psig. hydrogen pressure, various reaction time, 600 rpm. agitation speed, and catalyst concentration of 0.05 % by weight of oil.

Properties	Soybean	Reaction time (min)					
	Oil	30	60	90	120	150	180
Iodine value	136	125.33	117.33	105.00	98.17	93.50	91.67
% Fatty acid							
C16:0 palmitic acid	10.56	10.30	10.45	10.54	10.24	10.49	10.48
C18:0 steric acid	5.54	6.46	7.48	12.35	23.52	34.53	41.33
C18:1 oleic acid	26.47	31.44	41.04	49.03	55.73	50.77	48.15
C18:2 linoleic acid	52.40	47.99	37.53	25.66	9.92	3.59	0.00
C18:3 linolenic acid	5.02	3.81	3.21	2.50	1.26	0.38	0.00

Table 4.8 Analytical results of hydrogenated soybean oil using NiK catalyst: 180 °C reaction temperature, 200 psig. hydrogen pressure, various reaction time, 600 rpm. agitation speed, and catalyst concentration of 0.05 % by weight of oil.

Properties	Soybean Oil	Reaction time (min)					
		30	60	90	120	150	180
Iodine value	136	136.17	127.67	119.00	111.33	105.00	98.00
% Fatty acid							
C16:0 palmitic acid	10.56	10.34	10.34	10.70	10.36	10.78	10.64
C18:0 steric acid	5.54	7.73	7.73	9.83	13.02	19.89	21.11
C18:1 oleic acid	26.47	31.99	31.99	35.81	39.08	41.95	22.48
C18:2 linoleic acid	52.40	46.36	46.36	41.32	35.80	27.74	23.44
C18:3 linolenic acid	5.02	4.13	3.58	2.31	1.74	1.27	0.42

In Figure 4.1, the hydrogenation of soybean oil using various catalysts was shown as the variation of fatty acid composition and a function of time. From this experiment, it was concluded that the prepared NiB catalyst gave better performance than the other catalysts. With this catalyst, stearic acid was increased from 5.54% to 68.47% by weight of oil. While the other catalysts gave stearic acid content at 57.76%, 41.33%, and 21.11% by weight of total fatty acid, respectively. In the case of NiB catalyst, a small amount of *trans*-oleic acid (retention time 9.78 min.) was obtained at 180 min. reaction time, which was shown in Figure C12. In this experiment, the amount of oleic acid was included *cis*-oleic acid and *trans*-oleic acid. However, this condition was not aimed to produce oleic acid. The experiment was repeated twice.

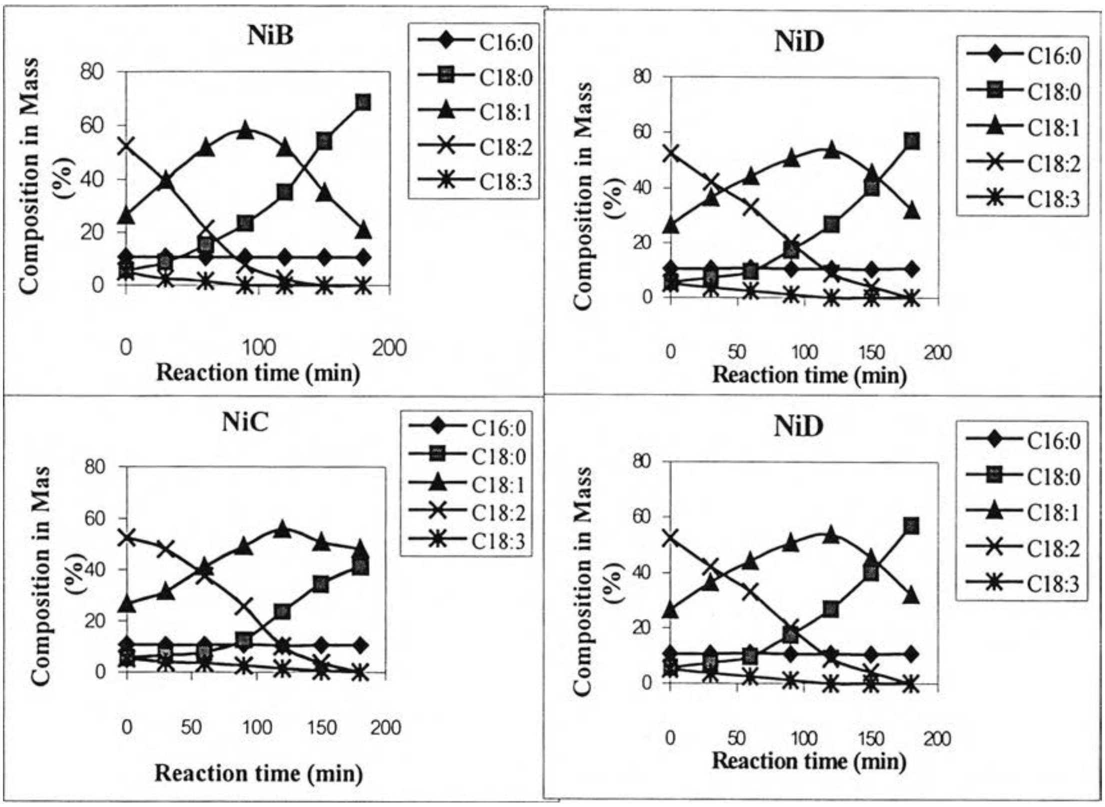

Figure 4.1 Relationship of fatty acid concentration (mass%) and reaction time of NiB, NiD, NiC and NiK catalysts: 180 °C reaction temperature, 200 psig. hydrogen pressure, various reaction time, 600 rpm. agitation speed, and catalyst concentration of 0.05 % by weight of oil.

4.3.1.1 Catalytic activity

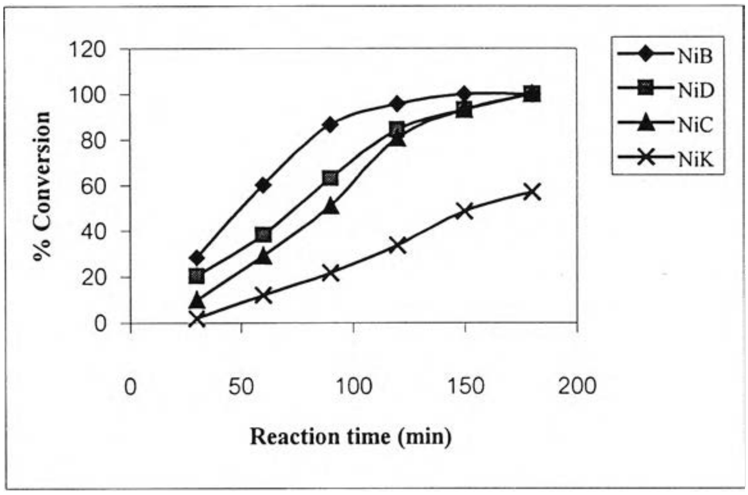

Figure 4.2 Relationship of reaction conversion and reaction time of various catalyst types.

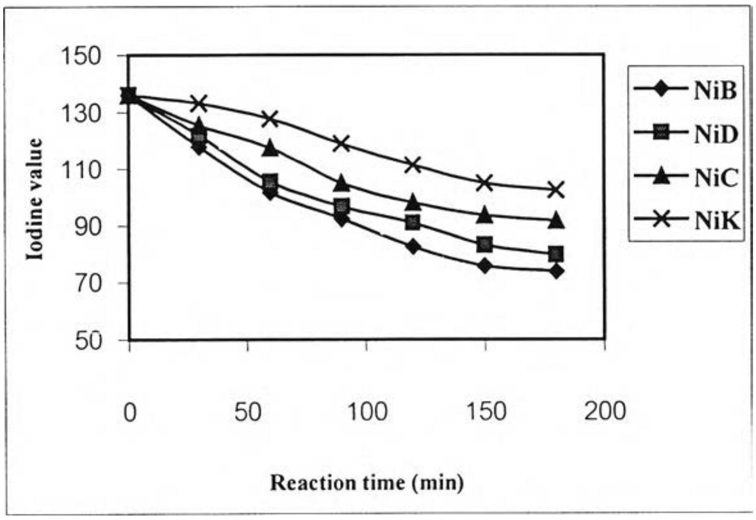

Figure 4.2 illustrated the conversion of linoleic acid and linolenic acid to oleic acid with reaction time and Figure 4.3 illustrated the iodine value with reaction time, for the four prepared catalysts. It was concluded that the NiB catalyst had the highest activity because it had the highest conversion and the lowest iodine value at various reaction times.

These differences in activity can be explained exclusively as a function of acidity and surface area of support (Table 4.2). Since adsorption of the unsaturated acid is first required to affect hydrogenation of the double bond and acid centers had been related with that function, therefore a prognosis of the acidic properties of the supports seems to be necessary [39]. The ball clay, which was used to prepare NiB catalyst, had high acidity and surface area. Thus the NiB catalyst revealed the activity. The actual acidity of the supports decreased in the series of ball clay> diatomite> china clay> kieselghur, which was also the sequence shown for their activities.

The NiK catalyst used for comparison under this experiment condition gave the lowest activity. Further more, kieselghur was the macroporous solid, therefor a major part of the nickel active phase must be occluded inside the macroporous and it is not accessible to the large triglyceride molecules [40]. In contrast, all the active phase was impregnated on ball clay (NiB), china clay (NiC) and diatomite (NiD) external surface, therefore, most of the nickel active site was accessible.

4.3.1.2 Selectivity of catalyst

In this research, selectivity to oleic acid, which is the desired product resulting from the hydrogenation of linoleic acid and linolenic acid in soybean oil, had been considered as shown in Figure 4.4.

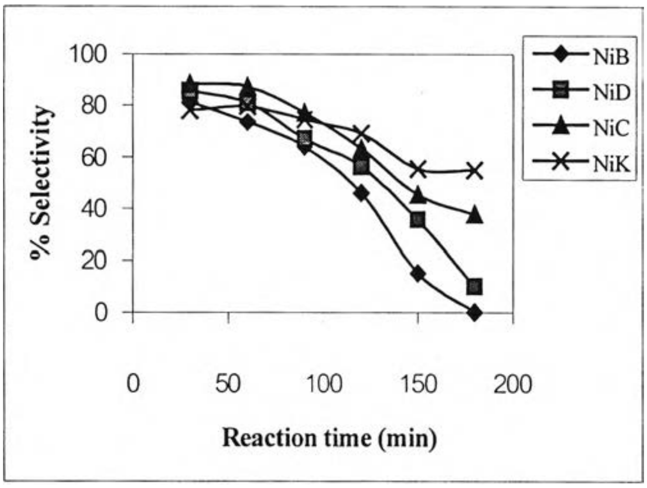

Figure 4.4 Relationship of % selectivity and reaction time of catalyst types

In Figure 4.4, the NiC catalyst had higher selectivity than NiB and NiD catalyst, but it had lower selectivity than NiK catalyst at high reaction time.

Furthermore, the morphology and especially the porosity of the support, plays an important role in the selectivity of the catalyst when determining the diffusion possibilities of the reactant molecule involved. Fibrous material (china clay) had the most selectivity towards oleic acid. Sheet material (ball clay) had high activity but low selectivity because the possibility exists of getting completely saturated products through successive active impacts of the unsaturated oil against the walls of the slit-shaped pores created by the swelling of the original clay [39].

Finally, globular macroporous solid such as diatomite and kieselghuhur used in conventional processes are very suitable as supports, but diatomite had low surface area results in a much less selective catalyst for oleic acid than kieselguhur.

A comparison of the results obtained when the hydrogenation was carried out at the same condition with different catalysts is presented in Figure 4.1-4.4. The most active catalyst that was selected for a process of partially and selectively hydrogenation of soybean oil was NiB catalyst. So this catalyst was used in order to find the optimized condition to produce oleic acid, which was the required product.

4.3.2 Selection of the optimum operating conditions

The NiB catalyst (high activity) and the NiC catalyst (high selectivity) were selected for determining the optimum operating conditions by varying these parameters: reaction temperature, hydrogen pressure, reaction time and concentration of nickel.

4.3.2.1 Effect of the reaction temperature

The effect of temperature on the rate of the reaction has been studied for a variety of hydrogenation. The exact observation is dependent on the nature of the substrate being hydrogenated and on the types of catalyst being used. For almost all hydrogenation the rate will approximately be double for every ten to twenty degree increase in temperature.[17]

In this section, the temperature of the experiments on hydrogenation of soybean oil was varied at different temperature of 100 °C, 120 °C, 150 °C, and 180 °C for both NiB and NiC catalysts.

4.3.2.1.1 Effect of reaction temperature on hydrogenation process using NiB catalyst

The results from the experiment carried out at different temperature are shown in Table 4.9. The fatty acids content changes as a function of the time lapse during the soybean oil hydrogenation reaction.

Table 4.9 Analytical results of hydrogenated soybean oil using NiB as a catalyst at various temperatures: 200 psig. hydrogen pressure, 90 min. reaction time, 500 rpm. agitation speed, catalyst concentration of 0.05% by weight of oil.

Properties	**Soybean oil**	**Reaction temperature (°C)**			
		100	**120**	**150**	**180**
Iodine value (I.V.)	136.0	132.83	121.83	99.00	92.33
%Fatty acid composition					
C16:0 palmitic acid	10.56	11.07	11.21	10.91	10.73
C18:0 stearic acid	5.54	6.80	8.02	20.03	23.33
C18:1 oleic acid	26.47	27.47	32.01	57.17	58.24
C18:2 linoleic acid	52.47	50.65	45.44	9.90	7.70
C18:3 linolenic acid	5.20	4.60	3.27	1.99	0.00

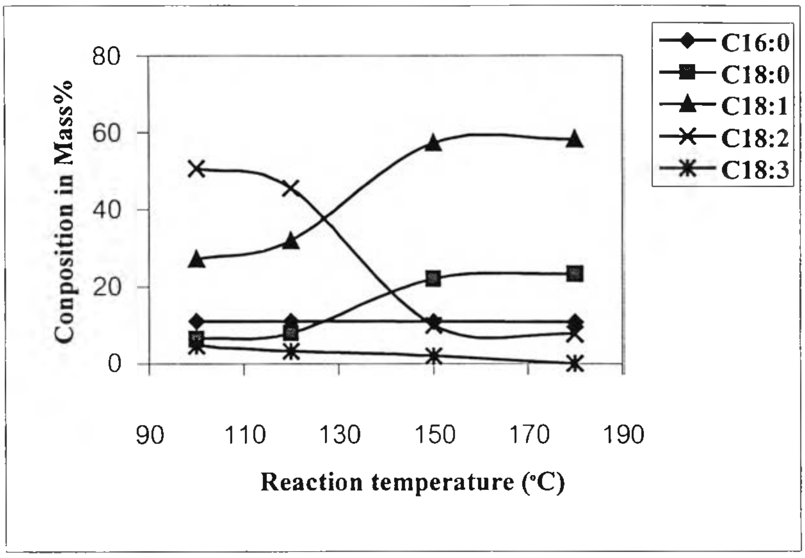

Figure 4.5 Relationship of fatty acid concentration (mass%) and reaction temperature (NiB catalyst).

From the experiment, it is observed that the fatty acid composition is important in changing the iodine value. In other words, the iodine value decreased from 132.83 to 92.83 with increasing temperature. From Figure 4.5, at 180 °C, the ratio of acid compositions was similar to the composition at 150 °C. It can be concluded that the optimum temperature for NiB catalyst should be 150 °C because it gave the highest amount of the oleic acid. Although, the amount of oleic acid at 180 °C was slightly different from that at temperature of 150 °C, the temperature at 150 °C was selected to be used in this study on ground of energy saving.

4.3.2.1.2 Effect of reaction temperature on hydrogenation process using NiC catalyst

The results from this experiment were derived from the test under the same conditions with NiB catalyst. The reaction temperature was varied from 100, 120, 150, and 180 °C, respectively. The operating conditions were carried out with hydrogen pressure at 200 psig.., reaction time at 90 min, agitation speed at 600 rpm., and catalyst concentration at 0.05% by weight of oil. The properties of hydrogenated oil are shown in Table 4.10 and Figure 4.6.

Table 4.11 Analytical results of hydrogenated soybean oil using NiC as a catalyst at various reaction temperatures: 200 psig. hydrogen pressure, 90 min. reaction time, 500 rpm. agitation speed, catalyst concentration of 0.05% by weight of oil.

Properties	**Soybean oil**	**Reaction temperature (°C)**			
		100	**120**	**150**	**180**
Iodine value (I.V.)	136.00	130.33	123.50	108.50	105.00
%Fatty acid composition					
C16:0 palmitic acid	10.56	10.91	11.32	12.04	10.54
C18:0 stearic acid	5.54	5.66	5.69	8.74	12.54
C18:1 oleic acid	26.47	28.00	29.80	35.04	49.03
C18:2 linoleic acid	52.40	50.91	49.09	40.69	25.66
C18:3 linolenic acid	5.02	4.53	4.09	3.50	2.50

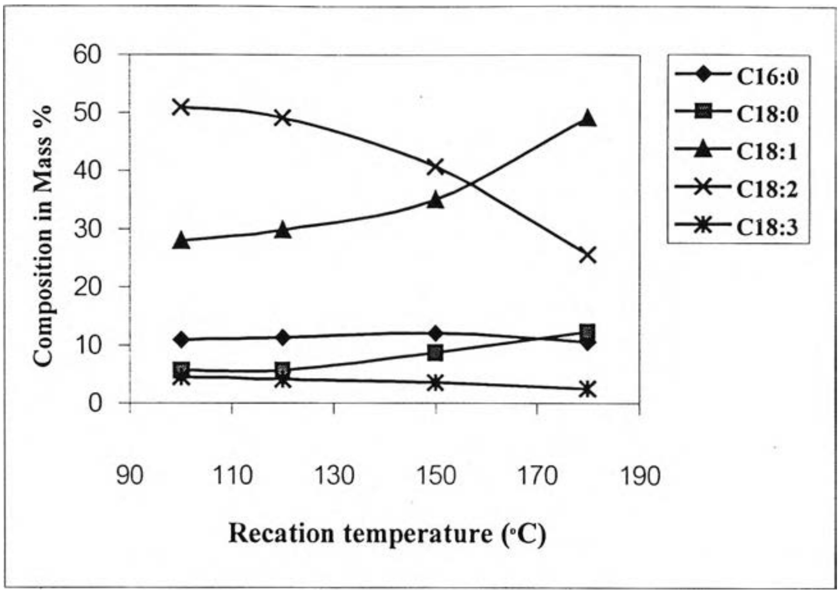

Figure 4.6 Relationship of fatty acid concentration (mass%) and reaction temperature (NiC catalyst).

The result showed that oleic acid in the hydrogenated oil increased when the temperature was increased from 150 °C to 180 °C. The reaction was operated at a higher temperature to increase the rate of hydrogenation and also to increase the higher molecular weight component.

In term of iodine value, the increasing of reaction temperature increased the rate of hydrogenation resulting in the increasing of higher molecule weight fatty acids. The hydrogenated soybean oil obtained from higher temperature had lower iodine value than the one at lower temperature.

This result revealed in Figure 4.6 that by using NiC catalyst, the hydrogenated oil obtained at a higher temperature had less amount of oleic acid than that at a lower temperature. It was expected that linoleic acid would be hydrogenated to oleic acid during hydrogenating process. However, the amount of oleic acid at 180 °C with NiC catalyst was less than that at 150 °C with NiB catalyst.

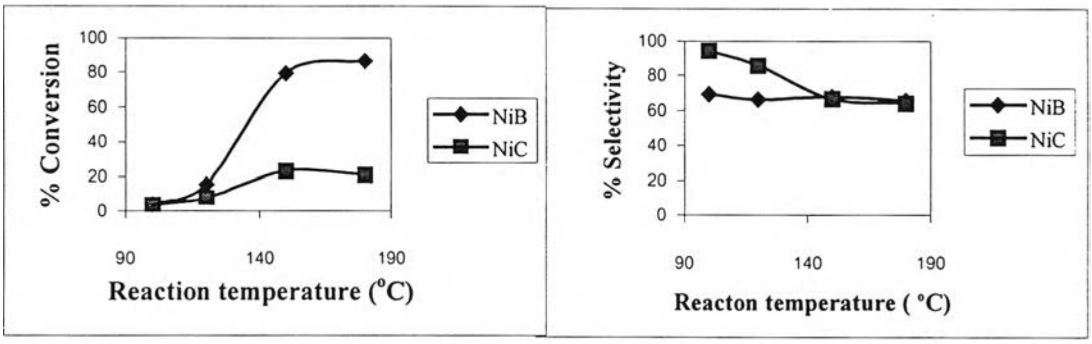

Figure 4.7 Relationship of % conversion and % selectivity of reaction with reaction temperature (NiB and NiC catalyst): 200 psig. hydrogen pressure, 90 min. reaction time, 500 rpm. agitation speed, catalyst concentration of 0.05% by weight of oil.

From Figure 4.7, it was obvious that NiB catalyst had better efficiency than NiC catalyst because NiB catalyst had more reaction conversion at temperature 120-180°C than NiC catalyst. The selectivity of the soybean oil hydrogenation is also dependent on the reaction temperature at which it was operating. The lower the temperature was the more selective the reaction was. The NiC had more selectivity than NiB catalyst at 100-150 °C but at 150-180 °C, they had similar selectivity.

4.3.2.2 Effect of the hydrogen pressure

The second parameter in the hydrogenating process was the hydrogen pressure. Generally, an increase in hydrogen pressure also results in a decrease in reaction selectivity. The hydrogen pressure on the hydrogenation of soybean oil with NiB and NiC catalysts was varied at different pressures of 100, 150, and 200 psig.. The operating conditions were carried out at the optimum temperature at 150 °C, reaction time at 90 min, agitation speed at 600 rpm., and catalyst concentration at 0.05% by weight of oil.

4.3.2.2.1 Effect of hydrogen pressure on hydrogenation process using NiB catalyst

The results from this experiment with different hydrogen pressure are shown in Table 4.11. It was evident from Figure 4.8 that hydrogenation rate increased with increasing hydrogen pressure. The increasing of hydrogen pressure affected the selectivity of soybean oil hydrogenation.

From the analytical result of the hydrogenated products, it was observed that some amount of oleic acid was converted to stearic acid. However the iodine value decreased from 128.00 to 99.00 when the hydrogen pressure was raised from 100 psig. to 200 psig..

Table 4.11 Analytical results of hydrogenated soybean oil using NiB as a catalyst at various hydrogen pressures: 150 °C reaction temperature, 90 min. reaction time, 600 rpm. agitation speed and catalyst concentration at 0.05% by weight of oil.

Properties	**Soybean oil**	**Hydrogen pressure (psig.)**		
		100	**150**	**200**
Iodine value (I.V.)	136.00	128.00	114.50	99.00
%Fatty acid composition				
C16:0 palmitic acid	10.56	10.89	11.05	10.91
C18:0 stearic acid	5.54	6.03	15.00	20.03
C18:1 oleic acid	26.47	30.98	58.48	57.19
C18:2 linoleic acid	52.40	47.97	13.14	9.90
C18:3 linolenic acid	5.02	4.17	2.45	1.99

In Figure 4.8, it showed that the amount of linoleic acid decreased in contrary to the increasing of oleic acid content. As hydrogen solubility in oil was directly in correlation to pressure, it was not surprising to see the higher reaction rate at 150 psig. than at 100 psig..

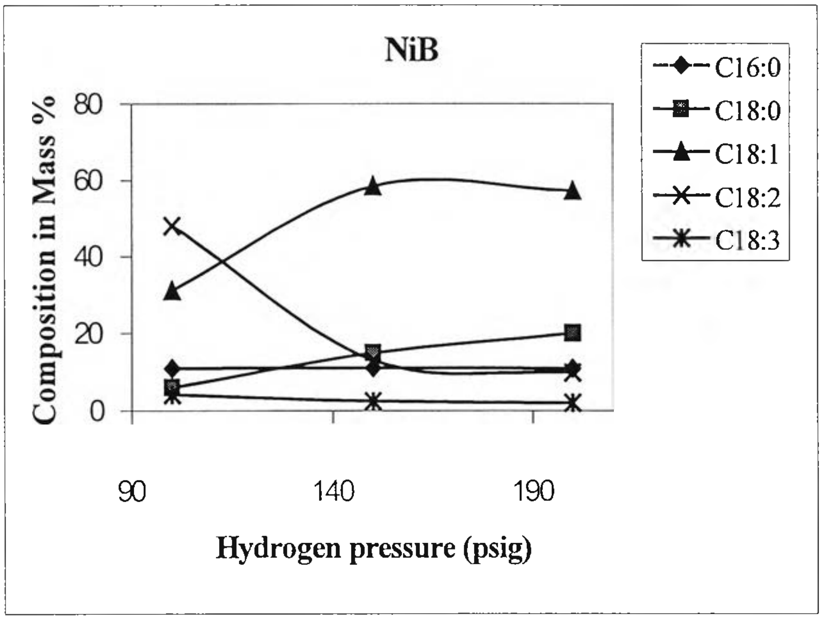

Figure 4.8 Relationship of fatty acid concentration (mass%) and hydrogen pressure. (NiB catalyst)

With respect to, for the higher amount of required product and the economic consideration, the suitable hydrogen pressure to be chosen is 150 psig..

4.3.2.2.2 Effect of hydrogen pressure on hydrogenation process using NiC catalyst

This parameter was studied for the hydrogenating process of soybean oil by using NiC catalyst. The reactions were performed with identical conditions with NiC catalyst. The results and the chromatograms are shown in Table 4.12, Figure 4.9.

Table 4.12 Analytical results of hydrogenated soybean oil using NiC as a catalyst at various hydrogen pressures: 150 °C reaction temperature, 90 min. reaction time, 600 rpm. agitation speed and catalyst concentration at 0.05% by weight of oil.

Properties	**Soybean oil**	**Hydrogen pressure (psig.)**		
		100	**150**	**200**
Iodine value (I.V.)	136.00	132.33	124.33	108.50
%Fatty acid composition				
C16:0 palmitic acid	10.56	11.05	10.95	12.04
C18:0 stearic acid	5.54	5.61	6.21	8.74
C18:1 oleic acid	26.47	27.52	31.09	35.04
C18:2 linoleic acid	52.40	51.21	47.76	40.69
C18:3 linolenic acid	5.02	4.62	3.70	3.50

From Figure 4.9, the properties of soybean oil were slightly changed between 150 psig. to 200 psig.. It was observed that when increasing the hydrogen pressure, the rate of hydrogenation of the unsaturated oil was increased, but was lower than those using NiB catalyst.

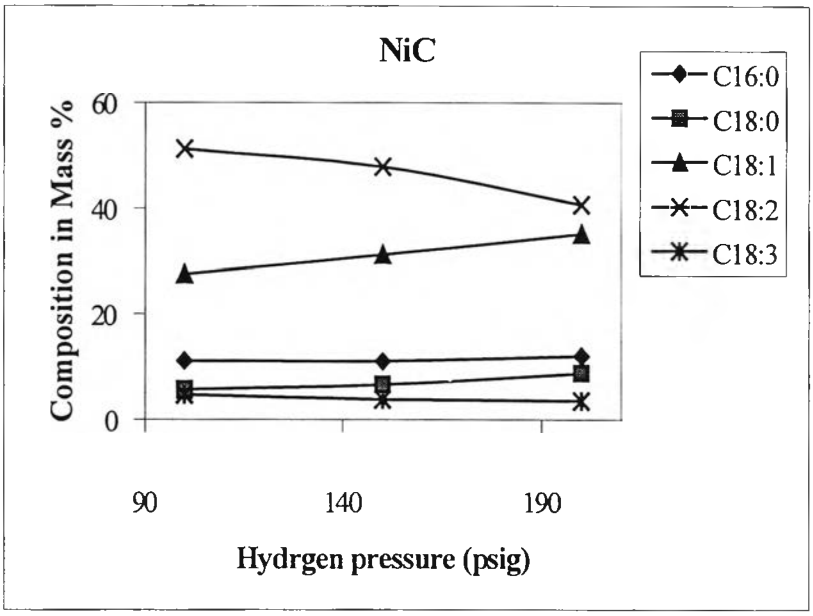

Figure 4.9 Relationship of fatty acid concentration (mass%) and hydrogen pressure. (NiC catalyst)

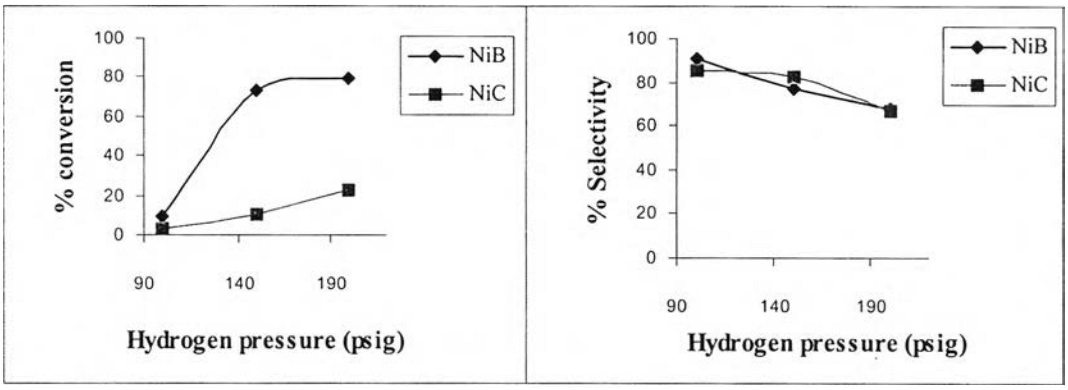

Figure 4.10 Relationship of % conversion and % selectivity of reaction with hydrogenation pressure (NiB and NiC catalyst): 150 °C reaction temperature, 90 min. reaction time, 600 rpm. agitation speed and catalyst concentration at 0.05% by weight of oil.

From Figure 4.10, it was obvious that NiB catalyst had better activity than NiC catalyst because NiB catalyst had more reaction conversion than NiC catalyst at hydrogen pressure 100-200 psig.. The selectivity of the hydrogenating soybean oil is also dependent on the hydrogen pressure at which it was operating. This due to the fact that when hydrogenation pressure was increased, the lower selective the reaction was. The NiC and NiB catalyst had shown no difference in selectivity.

4.3.2.3 Effect of the reaction time

The hydrogenation time was varied from 60, 100, 120, and 150 min, respectively. The NiB and NiC catalysts were used and the reaction was operated at 150 °C reaction temperature and 150 psig. hydrogen pressure.

4.3.2.3.1 Effect of reaction time on hydrogenation process using NiB catalyst

The results from this experimental section with different reaction times are shown in Table 4.13 and Figure 4.11.

Table 4.13 Analytical results of hydrogenated soybean oil using NiB as a catalyst at various reaction times: 150 °C reaction temperature, 150 psig. hydrogen pressure, 600 rpm. agitation speed and catalyst concentration at 0.05% by weight of oil.

Properties	**Soybean oil**	**Reaction time (min)**			
		60	**100**	**120**	**150**
Iodine value (I.V.)	136.00	121.67	114.50	108.67	93.00
%Fatty acid composition					
C16:0 palmitic acid	10.56	10.87	11..05	10.75	9.68
C18:0 stearic acid	5.54	9.03	15.00	16.11	24.52
C18:1 oleic acid	26.47	39.30	58.48	69.93	64.47
C18:2 linoleic acid	52.40	36.29	13.17	2.84	81.34
C18:3 linolenic acid	5.02	4.37	2.45	0.38	0.00

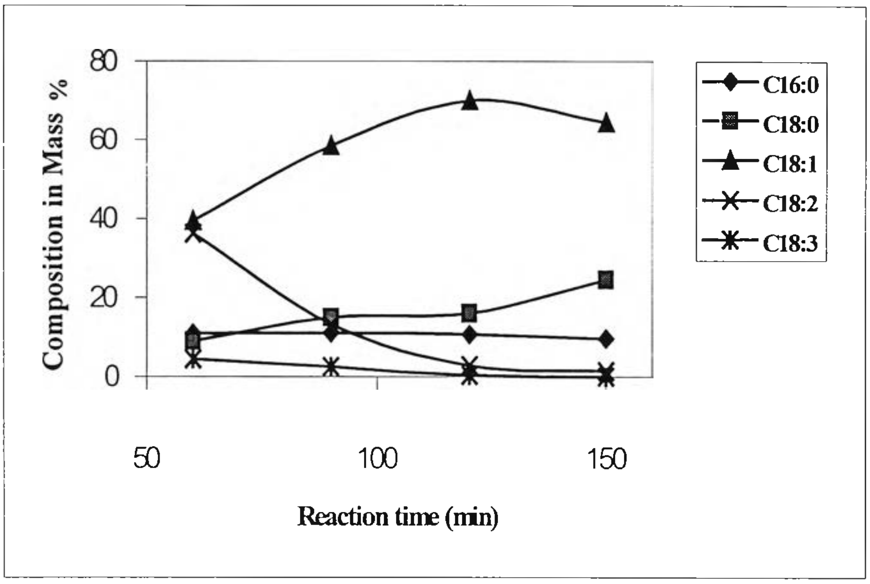

Figure 4.11 Relationship of fatty acid concentration (Mass%) and reaction time. (NiB catalyst)

The results from Table 4.13 and Figure 4.11 showed that the increasing of the reaction time from 30 to 120 min increased the amount of oleic acid. At 120 min, the increasing of hydrogenation rate was higher than the rate of reaction time, which increased from 60 to 100 min. This indicated that at a longer period of time, the increasing of reaction time caused much increase in the hydrogenating rate. However, if a longer reaction time was used (at 120 min), the required product would occur in higher quantity. However, at the reaction time of 150 min., some of oleic acid was hydrogenated to stearic acid. It was observed that the amount of stearic acid was slightly increased while the ratio of other fatty acid compositions was changed similarly. The iodine value decreased in accordance with the reaction time and the weight of oil.

4.3.2.3.2 Effect of reaction time on hydrogenation process using NiC catalyst

The NiC catalyst was used in the hydrogenation of soybean oil. At identical conditions as in the case of NiB catalyst, the results are shown in Table 4.14 and Figure 4.12.

Table 4.14 Analytical results of hydrogenated soybean oil using NiC as a catalyst at various reaction times: 150 °C reaction temperature, 90 min. reaction time, 600 rpm. agitation speed and catalyst concentration at 0.05% by weight of oil.

Properties	**Soybean oil**	**Reaction time (min)**			
		60	**100**	**120**	**150**
Iodine value (I.V.)	136.00	133.67	124.33	122.33	115.83
%Fatty acid composition					
C16:0 palmitic acid	10.65	11.10	10.95	10.67	10.66
C18:0 stearic acid	5.54	5.86	6.51	12.76	23.31
C18:1 oleic acid	26.47	27.53	31.09	34.02	42.22
C18:2 linoleic acid	52.40	51.36	47.76	40.35	22.46
C18:3 linolenic acid	5.02	4.21	3.70	2.29	1.37

In term of iodine value, the decreasing of reaction time increased the iodine value. This resulted in decreasing of lower molecular weight fatty acid components. Therefore, the hydrogenated soybean oil obbtained at a shorter reaction time had more iodine value than at longer reaction time. Oleic acid was increased when the reaction was performed at a longer reaction time. It was expected that the longer reaction time had a greater amount of oleic acid when NiC was used as a catalyst. But when comparing to the one with NiB catalyst, the oleic acid contents in reaction with NiC were lower at every reaction time.

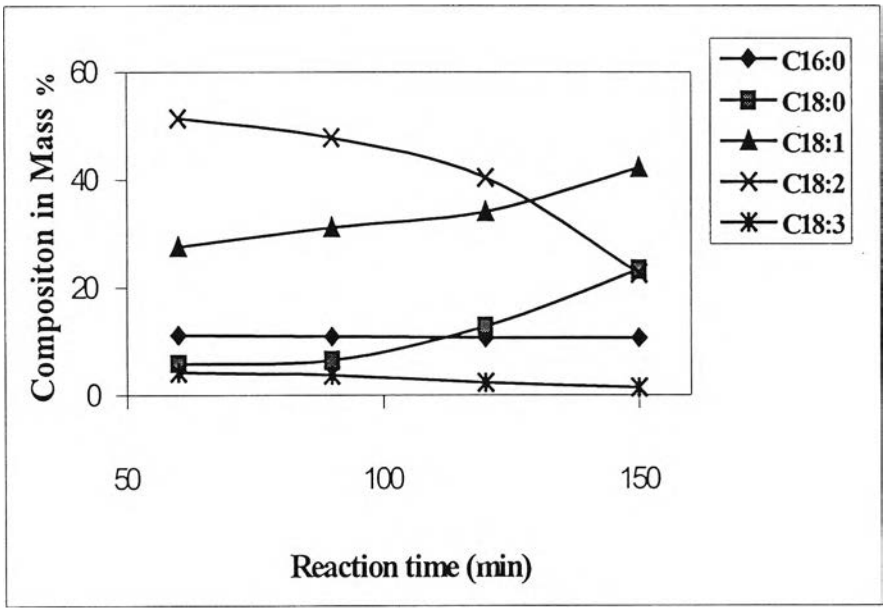

Figure 4.12 Relationship of fatty acid concentration (mass%) and reaction time. (NiC catalyst)

The observed data from Figure 4.12 indicated that the suitable reaction time was 150 min. If the reaction time was longer, the rate of hydrogenation would be increased.

The goal of this study was to find the minimum reaction time, which gave oil with high content of oleic acid. These observations suggested that the suitable reaction time was 120 min.

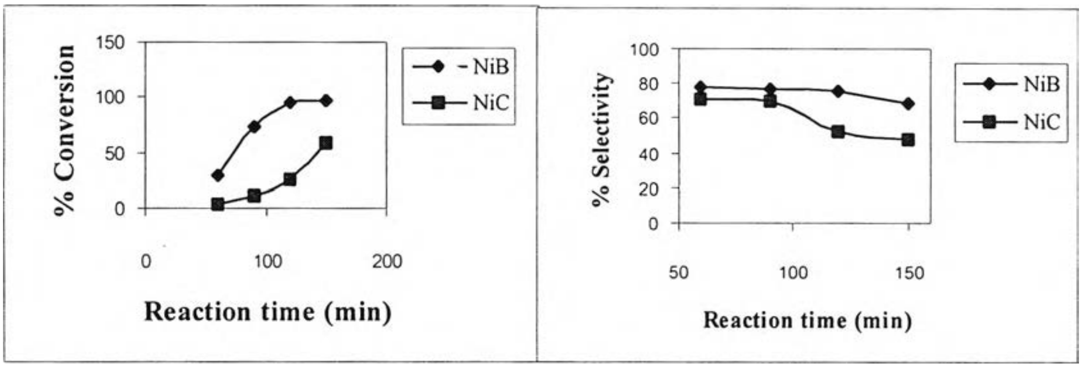

Figure 4.13 Relationship of % conversion and % selectivity of reaction with reaction time(NiB and NiC catalyst) : 150 °C reaction temperature, 90 min. reaction time, 600 rpm. agitation speed and catalyst concentration at 0.05% by weight of oil.

From Figure 4.13, it was obvious that NiB catalyst had better activity than NiC catalyst because NiB catalyst had higher reaction conversion than NiC catalyst at 60-150 min. reaction time. This due to the fact that when reaction time was increased, the selectivity the reaction was decreased. Then, the selectivity of the hydrogenating soybean oil was also dependent on the reaction time at which it was operated. The selectivity of NiC catalyst wasn't changed at 60-120 min. reaction time but at 120-150 min. reaction time the selectivity of it was decreased. The selectivity of NiB catalyst wasn't changed at 60-90 min. reaction time but at 90-120 min. reaction time the selectivity of it was rapidly decreased and at 90-120 min. reaction time the reaction gave little effect on the selectivity.

4.3.2.4 Effect of the concentration

The catalytic concentration was varied from 0.025, 0.05 and 0.10 % nickel by weight of oil

4.3.2.4.1 Effect of the concentration on hydrogenation process using NiB catalyst

The results in Table 4.15 and Figure 4.14 showed that increasing the concentration of catalyst from 0.025% to 0.10% nickel by weight of oil decreased the iodine value but increased the rate of hydrogenation. Then, the used concentration of catalyst at 0.05% nickel by weight of oil was used obtain in a required product.

Table 4.15 Analytical results of hydrogenated soybean oil using NiB as a catalyst at various catalyst concentration: 150 °C reaction temperature, 150 psig. hydrogen pressures, 120 min. reaction time, and 600 rpm. agitation speed.

Properties	**Soybean oil**	**Catalyst concentration (%Ni)**		
		0.025	**0.05**	**0.10**
Iodine value (I.V.)	136.00	127.83	108.67	87.83
%Fatty acid composition				
C16:0 palmitic acid	10.56	10.61	10.73	10.92
C18:0 stearic acid	5.54	6.53	16.11	48.73
C18:1 oleic acid	26.47	30.35	69.63	39.02
C18:2 linoleic acid	52.40	49..98	2.84	1.30
C18:3 linolenic acid	5.02	3.61	0.38	0.00

The results showed in Figure 4.14 that the amount of oleic acid was increased when the concentration of NiB catalyst was increased from 0.025 to 0.05% nickel by weight of oil, but it was decrease when the concentration of the catalyst was higher than 0.05%. Perhaps, at this concentration of catalyst, the oleic acid was rapidly converted to the stearic acid.

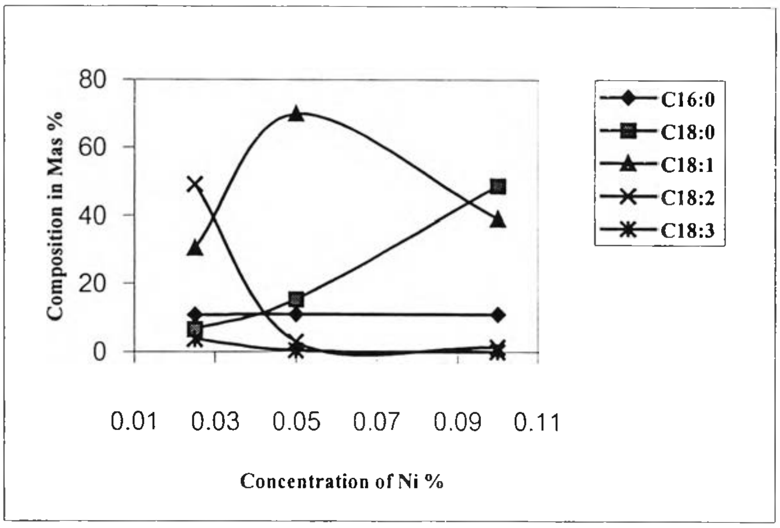

Figure 4.14 Relationship of fatty acid concentration (mass%) and concentration of nickel. (NiB catalyst)

4.3.2.4.2 Effect of the concentration on hydrogenation process using NiC catalyst

This parameter was studied on the hydrogenation process of soybean oil by NiC catalyst. The results are shown in Table 4.16 and Figure 4.15.

Table 4.16 Analytical results of hydrogenated soybean oil using NiC as a catalyst at various catalyst concentration: 150 °C reaction temperature, 150 psig. hydrogen pressures, 120 min. reaction time, and 600 rpm. agitation speed.

Properties	**Soybean oil**	**Catalyst concentration (%Ni)**		
		0.025	**0.05**	**0.10**
Iodine value (I.V.)	136.00	134.67	122.33	111.50
%Fatty acid composition				
C16:0 palmitic acid	10.56	11.01	10.67	11.77
C18:0 stearic acid	5.54	5.50	12.76	16.61
C18:1 oleic acid	26.47	27.33	34.02	41.70
C18:2 linoleic acid	52.40	51.42	40.35	28.32
C18:3 linolenic acid	5.02	4.73	2.29	1.61

From Table 4.16 and Figure 4.15, the result of hydrogenation process using NiC catalyst indicated that the increasing in concentration of catalyst was increased the amount of oleic acid. However, at the concentration of catalyst thus, the NiB catalyst gave more oleic acid than the NiC catalyst. The catalyst concentration at 0.05% nickel of NiB gave the highest the amount of oleic acid (69.93 % oleic acid).

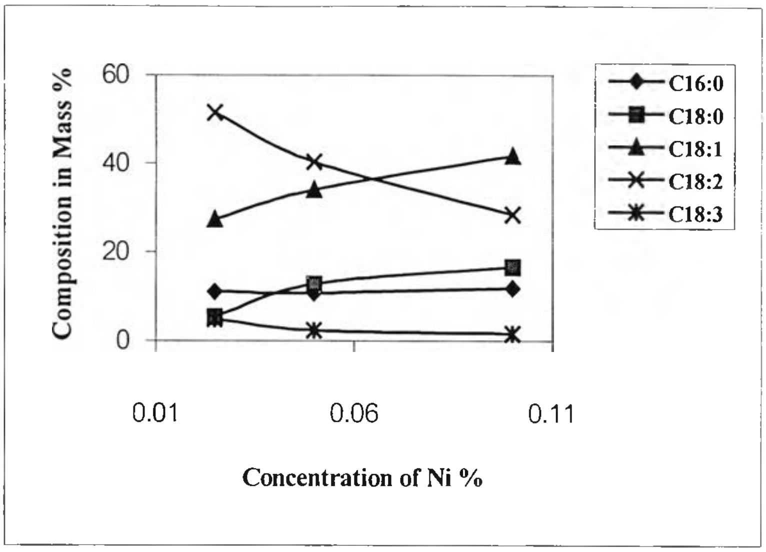

Figure 4.15 Relationship of fatty acid concentration (mass%) and concentration of nickel. (NiC catalyst)

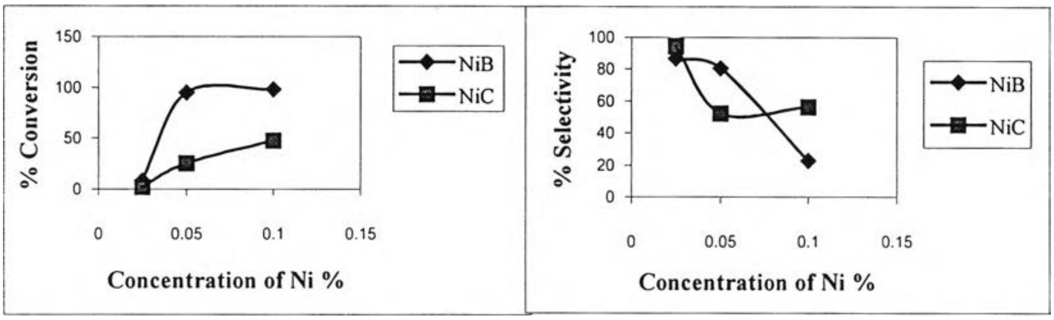

Figure 4.16 Relationship of % conversion and % selectivity of reaction with concentration of catalyst(NiB and NiC catalyst): 150 °C reaction temperature, 150 psig. hydrogen pressures, 120 min. reaction time, and 600 rpm. agitation speed.

From Figure 4.16, it was obvious that NiB catalyst had better activity than NiC catalyst because NiB catalyst had higher conversion than NiC catalyst at concentration of catalyst 0.025% to 0.10% nickel by weight of oil. The %conversion of the NiB catalyst was not changed at the concentration of catalyst between 0.05% to 0.10% nickel by weight of oil. When the concentration of catalyst was increased, the selectivity of the reaction was decreased. The selectivity of NiC catalyst was not changed at 0.05% to 0.10% nickel by weight of oil, but at 0.025% to 0.05% nickel by weight of oil the selectivity of was decreased.

4.3.5 Effect of the catalyst types

The effect of catalyst types on hydrogenation of soybean oil was studied using four types of catalysts under the same preparation conditions. The impregnated catalysts were 10%Ni on ball clay (NiB), on china clay (NiC), on diatomite (NiD), and on kieselghur (NiK).

The four types of catalysts were employed in the hydrogenation of soybean oil under the same condition including a temperature at 150 °C, 150 psig hydrogen pressure, 120 min. reaction time, 600 rpm agitation speed, and catalyst concentration of 0.05% by weight of oil. The results of the experiment at different catalyst types are shown in Table 4.17 and Figure 4.17.

Table 4.17 Analytical results of hydrogenated soybean oil using various catalyst types: 150 °C reaction temperature, 150 psig. hydrogen pressures, 120 min. reaction time, 600 rpm. agitation speed and catalyst concentration of 0.05 weight of oil.

Properties	**Soybean oil**	**Catalyst types**			
		NiB	**NiD**	**NiC**	**NiC**
Iodine value (I.V.)	136.00	108.60	111.17	122.33	131..33
%Fatty acid composition					
C16:0 palmitic acid	10.56	10.75	11.14	10.67	10.31
C18:0 stearic acid	5.54	16.11	15.30	15.76	7.98
C18:1 oleic acid	26.47	69.93	52.94	34.02	28.71
C18:2 linoleic acid	52.40	2.84	19.44	40.35	50.095
C18:3 linolenic acid	5.02	0.38	1.69	2.29	2.60

From the comparative results of the hydrogenation using different catalysts in Figure 4.17, it was clear that the hydrogenation using NiB catalyst (used ball clay to support catalyst) was faster than the other catalysts. Therefore, ball clay was the prefer catalyst in hydrogenation of soybean oil. At the same time, NiB catalyst gave more oleic acid than the other catalysts, it could give up to 69.93% oleic acid with higher selectivity.

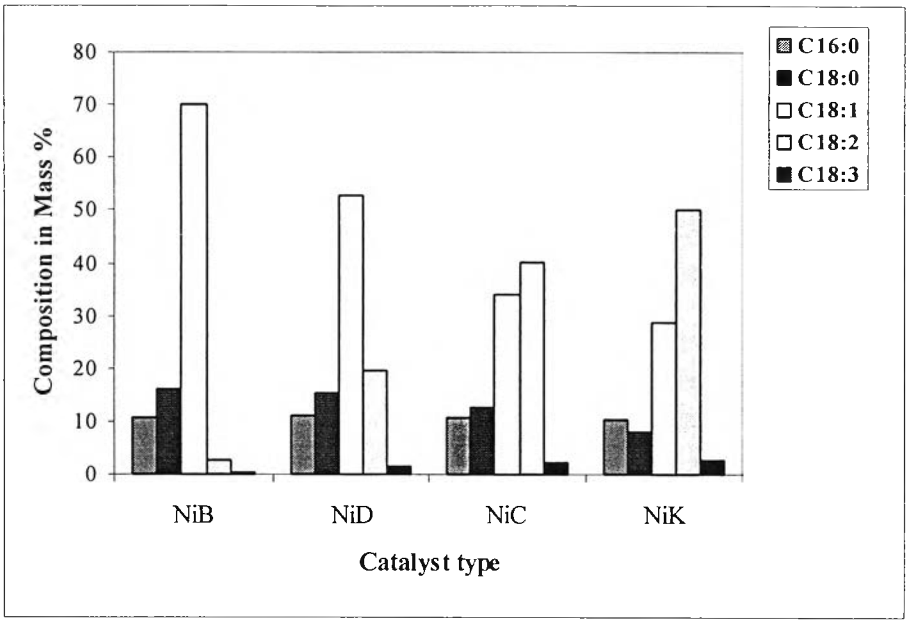

Figure 4.17 Relationship of fatty acid concentration (mass%) and catalyst types at the optimum condition.

From this study, it could be seen that the prepared NiB catalyst had better selectivity in hydrogenation of soybean oil than the other prepared catalysts. Therefore, the NiB catalyst was selected for a process of selective hydrogenation of soybean oil.

In the study of Rodigo et at.[39], they prepared catalyst that was a nickel deposited on a natural silicate support (sepiolite in Spain) used for hydrogenation of sunflower seed oil. In the study of Arpunda Pruckchrtsiri, she prepared catalyst that was a NiW/Al_2O_3 and CoW/Al_2O_3 used for selective hydrogenation of soybean oil. Their works were tabulated in Table 4.18.

Table 4.18 Comparison of the optimized condition to produce oleic acid between this research with Rodigo's work and Pruckchartsiri's work.

Subject	Reaction temperature (°C)	Hydrogen pressure (psig.)	% Metal of catalyst / wt of oil	Reaction time (min)	%wt of oleic acid
Rodigo	180	200	0.05	180	54.78
Pruckchatsiri	150	150	10	120	87.58
This work	150	150	0.05	120	69.93

Table 4.18 indicated that the amount of oleic acid obtained from this work was more than that obtained from Rodigo's work, and the condition of this work was less than that of Rodigo's work. Although, Rodigo's work used sunflower seed oil, but sunflower seed oil had the same composition with soybean oil. In Pruckchatsiri's work, the amount of oleic acid was higher than this work, but her work used 20 time the amount of catalyst than this work. Moreover, her catalyst was more expensive than the catalyst used in the present studied.

4.4 Determination of spectroscopic properties

The soybean oil was converted to fatty acid methyl esters and FTIR and ^{13}C-NMR as well as GC and GC-MS was used to characterize them.

4.4.1 Infrared spectra

The IR spectra were used to characterize original soybean oil and soybean oil fatty acid methyl ester (FAME). Their IR spectra are given in Figures C1 and C2 and the characteristic peaks are shown in Tables 4.19 and 4.20.

Table 4.19 The characteristic IR absorption of original soybean oil.

Absorption frequency (cm^{-1})	**Vibration assignment**
3006	=C–H stretching
2919,2847	aliphatic C–H stretching
1746	carbonyl (C=O) of triglyceride
1650	C=C bending
1460,1372	C–H bending
1163,1239	C–O stretching

Table 4.20 The characteristic IR absorption of soybean oil fatty acid methyl ester.

Absorption frequency (cm^{-1})	**Vibration assignment**
3006	=C–H stretching
2909,2847	aliphatic C–H stretching
1736	carbonyl C=O stretching
1460-1357	C–H bending
1250-1136	C–O stretching

4.4.2 ^{13}C-NMR spectra

Bruker, ACF 200 MHz nuclear magnetic resonance spectrometer was used for the characterization of original soybean oil fatty acid methyl ester. The ^{13}C-NMR spectra are shown in Figures C3 and C4, respectively.

The ^{13}C-NMR spectrum of original soybean oil is shown in Figure C3. It indicated the signals of triglycerides ($-CH_2-O-$) of soybean oil at 62.01 and 68.86 ppm, the signals of parafinic carbons (CH_2, CH_3) at 14..04 to 34.09 ppm, the signals of olefinic carbons (C=C) at 127.85 to 133.05 ppm, and the signals of the carboxylate (C=O) appeared at 172.61 to 173.01 ppm.

The ^{13}C-NMR spectrum of soybean oil fatty acid methyl ester shown in Figure C4 demonstrated the important signals of methyl ester (O-CH_3) and carbonyl (C=O) of methyl ester product at 51.26 and 174.07 ppm, respectively. The signals of parafinic carbons (CH_2, CH_3) were at 13.98 to 33.97 ppm and olefinic carbons (C=C) were at 127.66 to 130.10 ppm.

4.6.3 GC-MS technique

The composition and amount of fatty acid methyl esters at various conditions were determined by GC-MS. The GC-MS was performed using DB wax capillary column and the GC-MS chromatograms are shown in Figure C5 and mass spectra are shown in Figures C6-C10.

From Figure C11, GC chromatogram indicated that methyl ester of original soybean oil was a mixture of methyl ester of long chain fatty acid (C16 and C18). The main composition was methyl oleate. The total compositions of soybean oil fatty acid methylester are shown in Table 4.21.

Table 4.21 The retention time of each fatty acid methyl ester.

Retention time (min)	**Fatty acid methyl ester**
6.16	Hexadecanoic acid
9.23	Octadecanoic acid
9.68	9-octadecanoic acid
10.63	9,12-octadecanoic acid
11.77	9,12,15-octadecanoic acid

The peak area ratio of the GC chromatogram was determined and converted into the percentage of each composition of fatty acid.