

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Abstract

Biodiesel or fatty acid methyl ester (FAME) is considered one of the most promising alternative fuels. It has a higher cetane number than diesel; however, there are some problems related to oxidative stability and the cold flow properties. These properties depend on the degree of unsaturation in the FAME chains. Therefore, the quality of biodiesel can be improved by partial hydrogenation. The main objectives of this work were to study the effect of metal type; Pd, Pt, and Ni, and also study the effect of sulfur compound on different metal types in the partial hydrogenation of soybean oil based-biodiesel. The catalytic activity of all catalysts dropped after adding additional sulfur. The highest catalytic activity of hydrogenated biodiesel both before and after adding additional sulfur was represented by Pd/SiO₂. However, the highest sulfur tolerance was exhibited by Pt/SiO₂ (37.05% loss activity). The results indicated that partial hydrogenation reaction was the efficient method to improve the biodiesel properties by increasing the oxidative stability.

Keywords: Partial Hydrogenation/ Biodiesel/ Metal Type/ Oxidative Stability

4.2 Introduction

Petroleum or oil plays the most important role in developing everything. In the past few years, however, many researchers found that oil have finite resources, which are not sufficient to sustain the increasing rate of the world's fuel consumption. Therefore, alternative energy becomes a popular solving way. For agricultural countries such as Thailand, biodiesel seems appropriate because there are plenty of resources that can be used to produce biodiesel.

Biodiesel or fatty acid methyl ester (FAME) can be manufactured from vegetable oils and animal fats with methanol via the transesterification reaction. Biodiesel has similar fuel properties as diesel; however, there are some problem

associated with biodiesel properties such as oxidative stability and cold flow. Therefore, the quality of biodiesel especially oxidative stability can be improved by partial hydrogenation.

Partial hydrogenation is the reaction that hydrogen atoms take place in the double bond of unsaturated FAME. It helps to saturate the molecule of oil and increases the oxidative stability. In general, noble metals (Ni, Mo, Pd, Pt, Rh, and etc.) are applied in the catalytic partial hydrogenation because of their high activity and selectivity.

Therefore, the goal of this research was to upgrade soybean oil based-biodiesel properties by partial hydrogenation of polyunsaturated FAMES using different metals: Ni, Pd, and Pt, supported on mesoporous SiO₂ support. Soybean oil was used as biodiesel feedstock because of its compositions. There are higher percentage of diunsaturated FAME than the other types of vegetable oil which help to clearly study the proceeding of partial hydrogenation reaction. In addition, the effect of sulfur content on catalytic activity in this reaction was also concerned. There was adding additional sulfur content into original biodiesel in order to compare the activity of catalysts before and after adding additional sulfur.

4.3 Experiment

4.3.1 Transesterification of Soybean Oil

A 50 g of soybean oil is added to 500 ml three-necked round bottom flask and is heated on hot plate which is set to be 60 °C. Then the mixture of methanol and KOH catalyst is prepared by using 16.9 g methanol (9:1 methanol to oil molar ratio) and 0.5 g KOH (1 wt.% of soybean oil). The mixture is stirred until it is completely mixed. Heated soybean oil is observed until its temperature reaches 60 °C and then the solution mixture is added and stirred together at 300 rpm. Its container is connected to a condenser for 1 hour for transesterification of soybean oil. After that the container is taken off the condenser and hot plate and then it is left to cool down. Afterwards, the soybean oil solution is poured into a separatory funnel. The oil separates into 2 phases after leave it for 1 night; the lower glycerine phase will be removed, and the upper biodiesel phase will be kept in volumetric flask.

4.3.2 Catalyst Preparation

The main method used for preparing catalysts used in this experiment is incipient wetness impregnation. Three types of metals that are Ni, Pd, and Pt were used. At the beginning, Pd on SiO₂ catalysts were impregnated with an aqueous solution containing appropriate amounts of Pd(NH₃)₄.Cl₂. The total amount of Pd loading was 1 wt.%. After impregnation, the catalyst was dried by a rotary evaporator at room temperature for 2 hours, then at 60 °C for 2 hours, and finally by a vacuum pump at 60 °C for 2 hours. Then, the catalyst is calcined under an oxygen stream at 300 °C with a heating rate of 0.5 °C/min and 1 L/min of oxygen flow rate. Lastly, the catalyst is reduced by heating it to 300 °C for 2 hours with a heating rate of 5 °C/min and 100 ml/min hydrogen flow rate prior to using in partial hydrogenation reaction. The same procedure is applied for preparation of Ni catalyst (loading 10 wt.%) and also Pt catalyst (loading 1.82 wt.%). The precursors which were used for both catalysts are Ni(NO₃)₂.6H₂O and Pt(NH₃)₄.Cl₂.

4.3.3 Partial Hydrogenation

The reaction is carried out in a batch reactor with operating conditions of 120 °C and 4 bar. Firstly, 150 ml of biodiesel is poured into the reactor. Then, catalyst is placed in the reactor (1 wt.% of catalyst compared with starting oil) and the system is purged with nitrogen to remove remaining air. Hydrogen is then flowed into the reactor with the flow rate of 150 ml/min and the partial hydrogenation reaction occurs. After that, the temperature and pressure is increased up to a desired point. During partial hydrogenation step, the stirrer is used at 1000 rpm to mix the biodiesel, catalyst, and hydrogen thoroughly to prevent external mass transfer. In addition, the sample is collected at every 30 minutes. The Hewlett Packard gas chromatography 5890 Series II equipped with a FID detector is applied to analyze the product by using n-heptane as a solvent.

4.3.4 Sulfur Tolerance

Allyl Isothiocyanate is added into biodiesel before partial hydrogenation reaction in order to observe sulfur tolerance of each catalyst. Prior to

study sulfur tolerance, soybean oil based-biodiesel is tested for sulfur concentration. The initial sulfur concentration is 0.64 ppm. For this experiment, the sulfur concentration is doubled to be 1.28 ppm for study the effect of sulfur to catalyst activity.

4.3.5 Biodiesel Analysis

Biodiesel and partial hydrogenated biodiesel will be identified the composition of C12:0, C14:0, C16:0, C18:0, C18:1, C18:2 and C22:0 by Hewlett Packard gas chromatograph 5890 Series II. The GC equipped with a flame ionization detector (FID) and a DB-WAX (30 m x 0.25 mm) fused-silica capillary column coated with a 0.1 μm film will be used. A carrier gas will be helium (99.99%) with a flow rate of 70 ml/min. The fatty acids will be quantified by injecting 0.2 μl of each sample. The injector and detector temperatures will be set at 200 $^{\circ}\text{C}$ with a split ratio of 75:1 and 230 $^{\circ}\text{C}$, respectively. The oven temperature will be initially at 130 $^{\circ}\text{C}$ after an isothermal period of 2 min, then increased to 220 $^{\circ}\text{C}$ with a rate of 2 $^{\circ}\text{C}/\text{min}$ and held for 15 min with the total analysis time of 62 min. FAME composition will be identified from the fraction of the area under the peak at different retention times.

Oxidative stability is an important criterion for evaluating biodiesel quality. Because of its content of polyunsaturated methyl esters (FAME), which have several double bonds and oxidize easily so it effects on vehicle system. Oxidative stability will be analyzed according to European standard UNE-EN 14212:2003 method using a Metrohm 743 Rancimat instrument (Herisau, Switzerland). Sample of 3 g will be analyzed at a heating block temperature of 110 $^{\circ}\text{C}$ with the temperature correction factor (ΔT) of 0.98 $^{\circ}\text{C}$, and a constant air flow of 10 L/h. The volatile compounds formed will be collected in the conductivity cell of 50 ml of DI water. The inflection point of the derivative curve of conductivity as a function of time will be reported as the induction period (IP, h). All the measurements will be performed in duplicate (Wadumesthrige et al., 2009).

The cloud point of a liquid FAME mixture, which usually occurs at a higher temperature than the pour point. The cloud point is the temperature at which fuel become cloudy due to formation of crystals and solidification of saturates. Biodiesel sample will be first poured into a test jar to a level approximately half full.

Then, the entire test subject will be placed in a constant temperature cooling bath. At every 1 °C, the sample will be taken out and inspected for cloud. In accordance with ASTM D2500, the oil is required to be transparent in layers 40 mm in thickness. The cloud point is the temperature at which the milky cloud crystals first appear.

Most biodiesel fuels are inherently composed of little or no sulfur compound which is a potential catalyst poison. In ASTM D6751, biodiesel fuels will be determined by D5453 which is applied for sulfur content determination. The sample is tested by using UV fluorescence during its combustion. SO₂ which is produced during sample combustion is then converted to excited SO₂*. After that, the excited SO₂* try itself to return to the stable SO₂ state which cause the fluorescence emission. This emission is detected with the signal indicating the amount of sulfur in the sample (Knothe, 2006).

4.3.6 Catalyst Characterization

A Bruker D8 Advance X-ray diffractometer system (XRD) is used to characterize and identify the internal structure, bulk phase, crystallinity and composition in crystalline phases of the catalysts. A 2.2 kW Cu anode long with fine focus ceramic X-ray tube which generates CuK α radiation (1.5405 Å) is used as an X-ray source to obtain the XRD patterns at running conditions for the X-Ray tube of 40 kV and 30 mA. The prepared sample will be held in the X-ray beam and the detector will scan the intensity of diffracted radiation from the sample as a function of 2 θ in the range of 5° to 90° and a scan speed used is 5°/second. Finally, the obtained XRD patterns will be compared to the standard file to identify the crystalline phases of the catalysts.

The method used for measuring the specific surface area and pore size distribution is Quantachrome Autosorb-1 MP surface area analyzer. Prior to performing the test, the volatile species that are adsorbed on the catalyst surface must be eliminated by heating the catalyst under vacuum atmosphere at 250 °C overnight. Helium gas is used as an adsorbate for blank analysis and nitrogen gas is used as an adsorbate for actual analysis. The specific surface area and pore size distribution of the catalyst will be calculated by the software.

4.4 Results and Discussion

4.4.1 Feed Biodiesel Analysis

For FAME composition of the feed biodiesel determination, a gas chromatograph (GC) equipped with a flame ionization detector (FID) was applied. The FAMEs composition of feed biodiesel was shown in Table 4.1. In addition, the overall FAME composition of feed biodiesel was exhibited by GC chromatogram, as presented in Figure 4.1.

The highest composition in soybean oil based-biodiesel was methyl linoleate (51.00%) which led to easy oxidize. The *cis*-methyl oleate remained the higher percentage up to 25.92%. This composition occurs naturally and reduces the melting point which relates to cold flow properties of biodiesel (Moser, 2009). From this point, biodiesel need to have higher percentage of this composition. In addition, there was 10.90% of methyl palmitate that need to hold this composition constantly because of cold flow properties as well. Although there was a little percentage of methyl linolenate (5.16%), it had greater effect on autoxidation than the other compositions. Methyl linolenate (C18:3) can be oxidize about two times more easily than methyl linoleate (C18:2) and almost hundred times than methyl oleate (C18:1) (Knothe, 2007).

Table 4.1 FAME composition of feed biodiesel

FAME	Structure	%
methyl myristate	C14:0	0.08
methyl palmitate	C16:0	10.90
methyl palmitelaidate	<i>trans</i> -C16:1	0.05
methyl palmitoleate	<i>cis</i> -C16:1	0.12
methyl heptadecanoate	C17:0	0.11
methyl stearate	C18:0	3.38
<i>trans</i> -methyl elaidate	<i>trans</i> -C18:1	0.14
<i>cis</i> -methyl oleate	<i>cis</i> -C18:1	25.92
methyl linoleate	C18:2	51.00
methyl linolenate	C18:3	5.16
methyl arachidate	C20:0	1.10
methyl <i>trans</i> -eicosenoate	<i>trans</i> -C20:1	0.25
methyl <i>cis</i> -eicosenoate	<i>cis</i> -C20:1	0.04
methyl behenate	C22:0	0.53
methyl lignocerate	C24:0	0.19

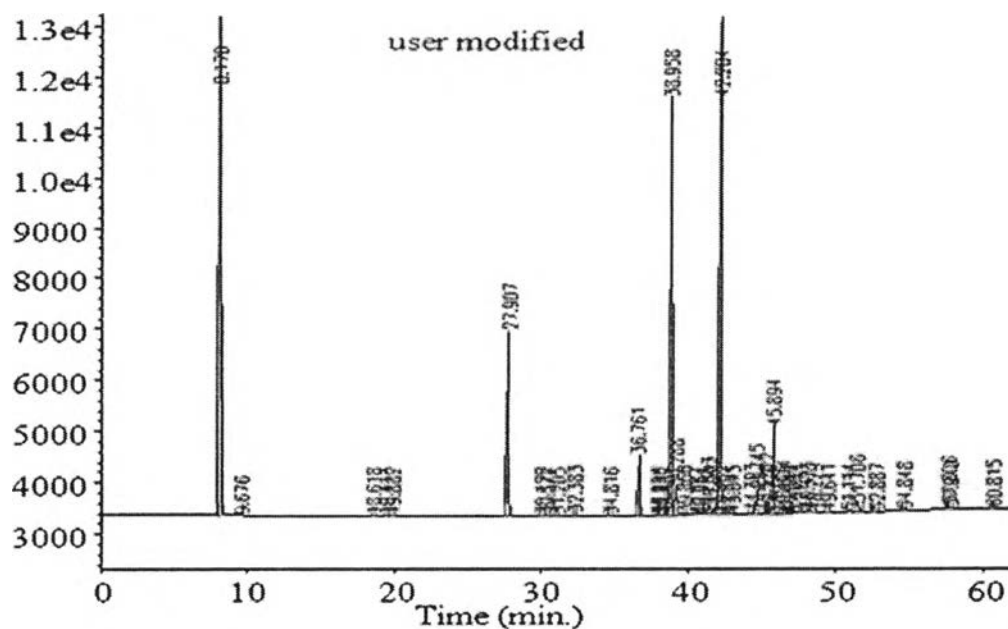
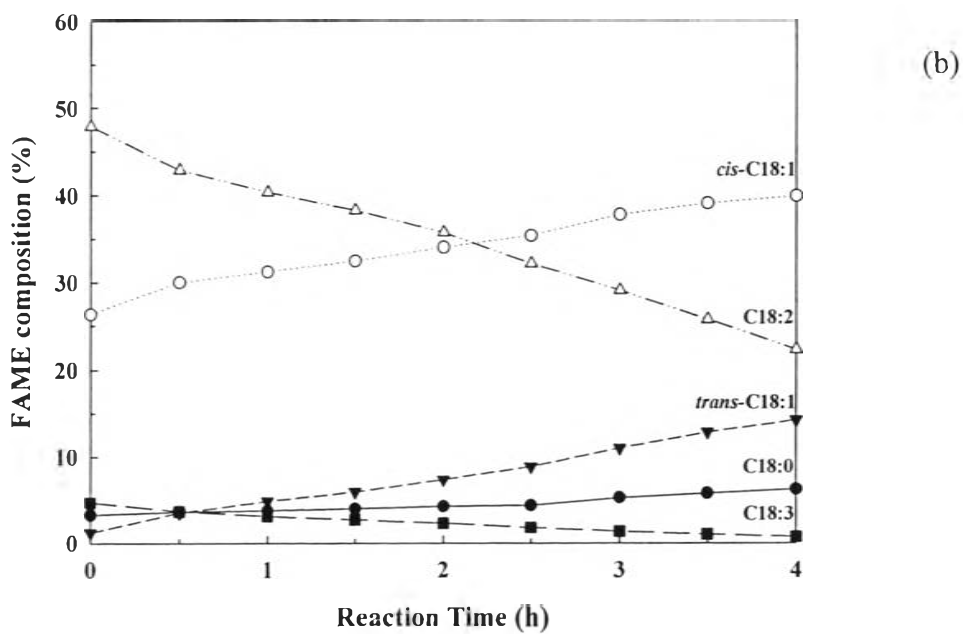
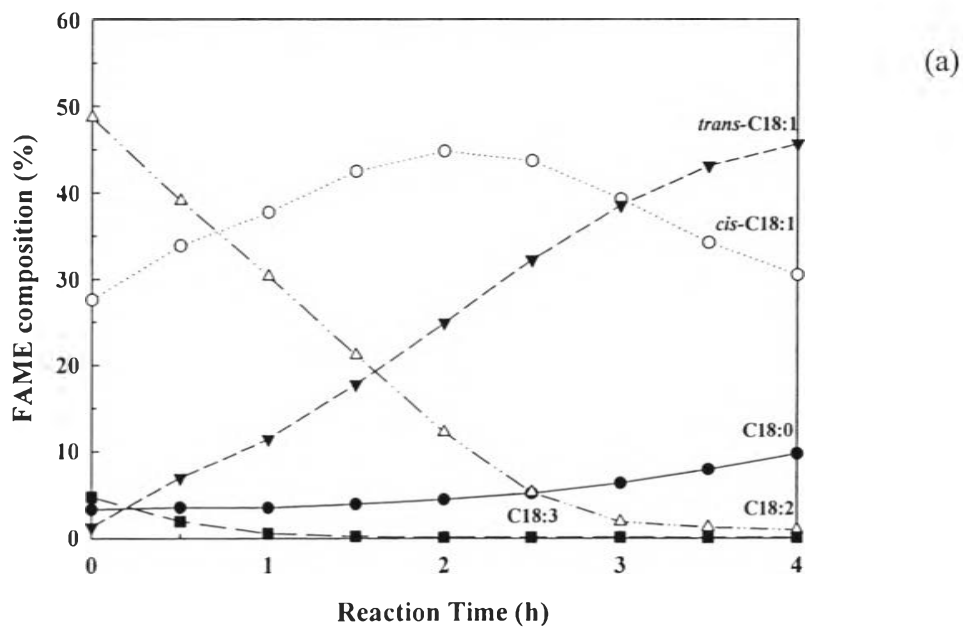


Figure 4.1 Overall FAME composition of feed biodiesel from gas chromatograph.

4.4.2 Effect of Metal Type on Partial Hydrogenation

Partial hydrogenation of soybean oil-based biodiesel was carried out as a reaction to compare the partial hydrogenation activity of different catalysts; Pd/SiO₂, Pt/SiO₂, and Ni/SiO₂. The reaction was performed under mild condition of 120 °C, 4 bar, 150 ml/min of hydrogen flow rate, 1000 rpm of stirring rate, and 1 wt.% of catalyst compared to 130.395 g of biodiesel (150 ml).

The results of each catalyst; Pd/SiO₂, Pt/SiO₂, and Ni/SiO₂, are presented below, respectively. Since, the other compositions consist of C14:0, C16:0, trans-C15:1, cis-C16:1, C17:0, C20:0, *trans*-C20:1, *cis*-C20:1, C22:0, and C24:0 relatively kept constant along the reaction time. Therefore, all C18 compositions would be focused in this study.



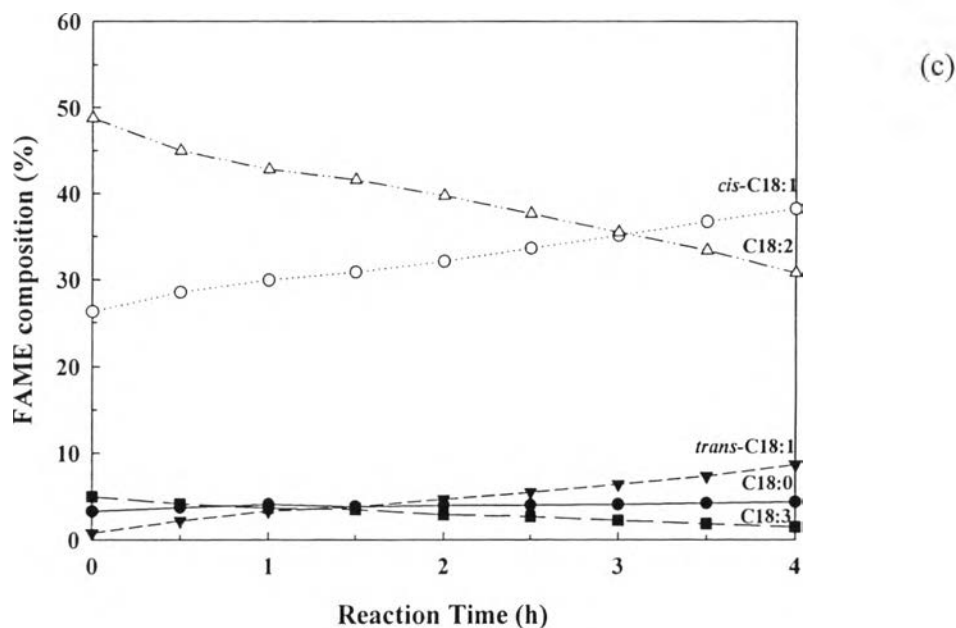


Figure 4.2 Effect of metal type: (a) 1 wt.% Pd/SiO₂ (b) 1.82 wt.% Pt/SiO₂ (c) 10 wt.% Ni/SiO₂ on FAME composition of biodiesel after partial hydrogenation reaction using catalyst reduced under H₂ at 300°C (for Pd/SiO₂ and Pt/SiO₂) and 400°C (for Ni/SiO₂) (Reaction condition: 120°C, 4 bar, 150 ml/min of H₂ flow rate, 1000 rpm of stirring rate, and 1 wt.% of catalysts compared with 130.395 g of biodiesel).

The catalytic activity of these catalysts were investigated by using GC chromatography in order to identify FAME composition in the partial hydrogenated biodiesel. The results represented that the higher the reaction time, the higher the conversion of unsaturated FAMES (C18:3, C18:2 and C18:1) while the other FAMES composition was quite stable. These results are in agreement with previous study (Numwong *et al.*, 2012). For partial hydrogenation reaction using Pd/SiO₂ as a catalyst, the FAMES composition is shown in Figure 4.2(a), it exhibited that C18:3 decreased from 4.77% to 0.08% and C18:2 decreased from 48.72% to 0.96%. The amount of *cis*-C18:1 slowly increased from 27.60% to 44.80% within 2 hours and then it gradually decreased to 30.51% within 4 hours of the reaction. While *trans*-C18:1 rapidly increased from 1.31% at initial and reached 45.63% after 4 hours of the reaction. The C18:0 content slowly increased from 3.35% to final values at

9.75% after 4 hours of reaction because of the conversion of *cis*-C18:1. And the partial hydrogenation by using Pt/SiO₂ as a catalyst, the FAMEs composition is shown in Figure 4.2(b); C18:3 decreased from 4.72% to 0.76% and C18:2 decreased from 47.90% to 22.31% after 4 hours of reaction time, whereas *cis*-C18:1 slowly increased from 26.35% to 39.91%. Then *trans*-C18:1 continually increased from 1.24% to 14.23% at 4 hours of the reaction time. In addition, the composition of C18:0 gradually increased from 3% at starting time to 6% at the end of reaction. For partial hydrogenation reaction using Ni/SiO₂ as a catalyst, the FAMEs composition is shown in Figure 4.2(c); C18:3 and C18:2 gradually decreased from 4.97% to 1.49% and 48.78% to 30.80%, respectively. While *cis*-C18:1 increased from 26.29% to 38.25%, the level of *trans*-C18:1 also increased from 0.78% to 8.70% after 4 hours of the reaction. However, the amount of C18:0 still relatively kept constant through whole reaction time.

The comparison between each catalyst are represented in Figure 6.3. This bar chart obviously indicated that Pd catalyst could converted the most of C18:3 and also the highest content of C18:2. In addition, the amount of both *trans*-C18:1 and *cis*-C18:1 much increased. Moreover, C18:0 contents slightly increased as compared to the feed biodiesel. For the other catalysts, they also presented the similar trend of activity, however, Pt catalyst gave the higher catalytic activity than Ni catalyst.

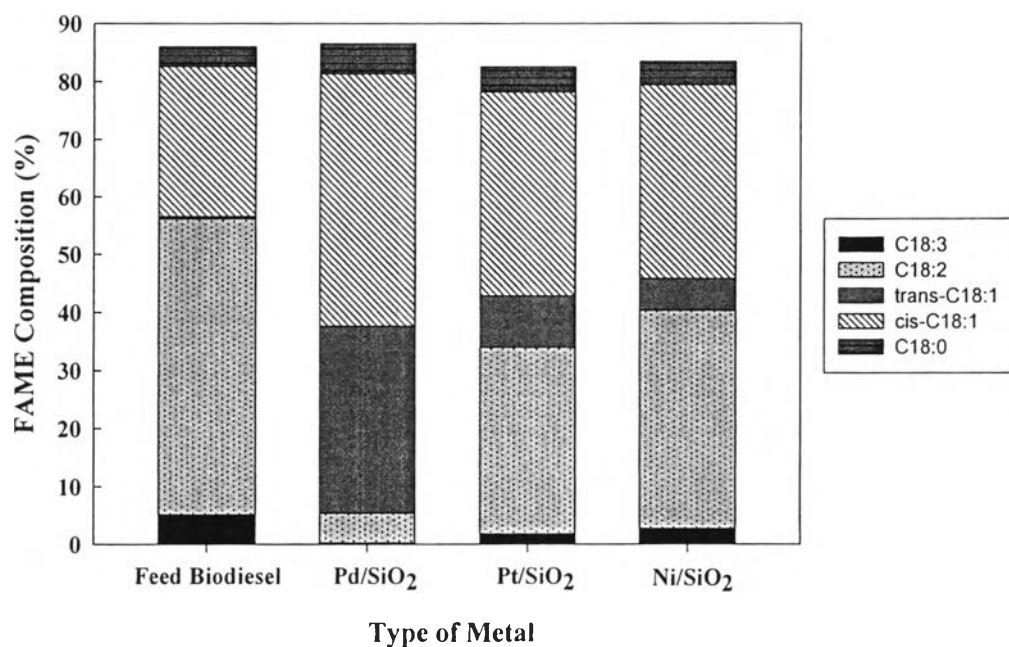


Figure 4.3 Comparison of C18 FAME composition of biodiesel after hydrogenation reaction (2.5 h) in conditions : 120°C, 4 bar, 150 ml/min of H₂ flow rate, 1000 rpm of stirring rate, 1 wt.% of Palladium loading , 1.82 wt.% of Platinum loading, 10 wt.% of Ni loading, and 1 wt.% of silica catalyst.

In addition, turnover frequency (TOF) which calculate from C18:2 conversion within 0.5 hour of reaction time was applied in order to confirm the catalytic activity of each catalyst. The turnover frequency equation are shown below;

$$TOF (h^{-1}) = \left[\frac{\frac{\%conversion}{100} \times \text{Amount of biodiesel (g)}}{\frac{wt.\%metal}{100} \times \frac{\%metal\ dispersion}{100} \times W_{catalyst}(g)} \right] \div time$$

By

$$\%conversion = C18:2_{t=0hr} - C18:2_{t=0.5hr}$$

$$\text{Amount of biodiesel} = 130.395 \text{ g}$$

$$W_{catalyst} = 1.30395 \text{ g (1 wt. \%catalyst compared to amount of biodiesel (g))}$$

$$\text{Time} = 0.5 \text{ hour}$$

The percentage of metal dispersion which was obtained by using hydrogen chemisorption and TOF of each catalyst were represented in Table 6.2

Table 4.2 Metal Dispersion and Turnover Frequency (TOF)

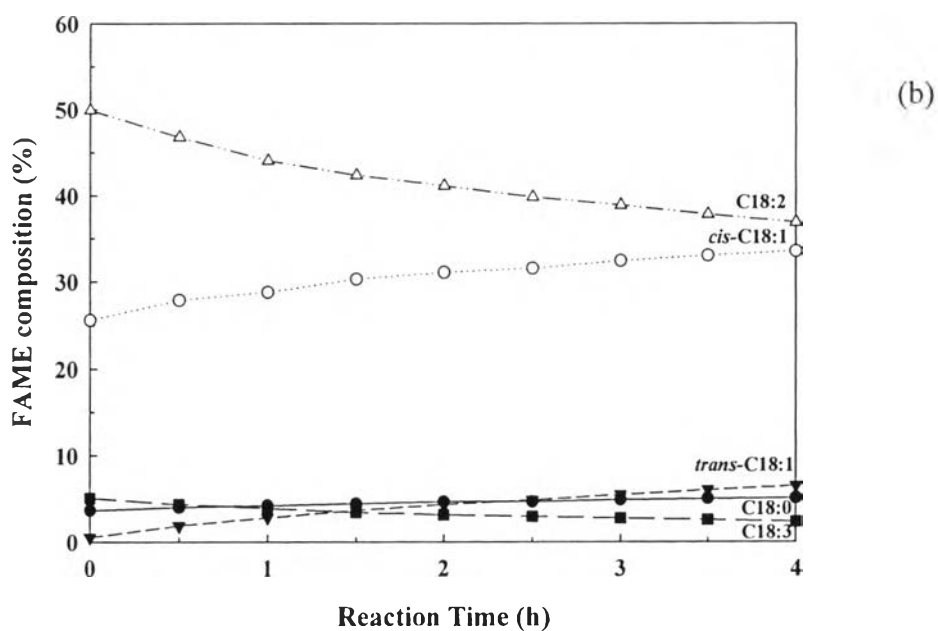
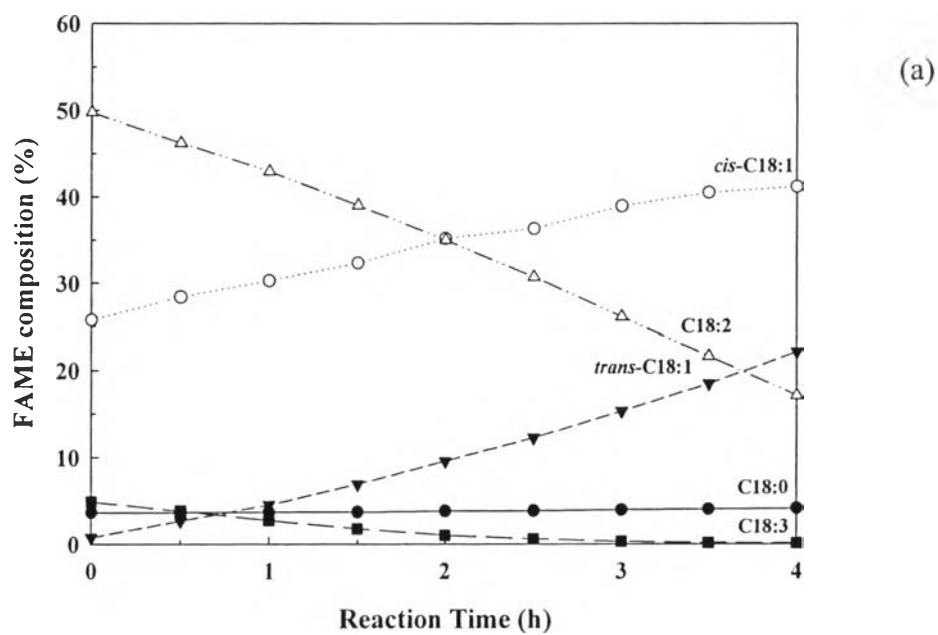
Catalyst	Dispersion (%)	TOF (h⁻¹)
Pd/SiO ₂	6.88	28,050.09
Pt/SiO ₂	7.49	7,365.13
Ni/SiO ₂	5.82	1,298.97

The percentage of metal dispersion showed that Pt (1.82 wt.% loading) had the highest value which indicated that the Pt metal well dispersed on silica support and had less cluster forming than the others. While metal dispersion of Ni (10 wt.% loading) showed the lowest value, it meant that there were large metal cluster forming. In addition, the TOF presented that the Pd catalyst gave the highest TOF. It meant that Pd catalyst could be the most suddenly converted C18:2 within 0.5 hour of reaction time and followed by Pt and Ni catalyst, respectively. This value supported the results that obtained from Gas Chromatography (GC). Moreover, these results was consistent with McArdel and co-workers' research (2011). They purposed that Pd based catalysts are more active than the conventional Ni catalyst and Pt based catalysts for the hydrogenation of vegetable oil. Moreover, these study also conformed to Numwong and co-workers' work (2012). The authors purposed that Pd/SiO₂ gave the highest catalytic activity in partial hydrogenation reaction of rapeseed oil based-biodiesel and followed by Pt/SiO₂ and Ni/SiO₂, respectively.

4.4.3 Effect of Sulfur Compound on Catalysts in Partial Hydrogenation

Apart from effect of metal type of catalysts used in partial hydrogenation, effect of sulfur compound was also studied. In this part, the partial hydrogenation conditions are the same as used in effect of metal type. Ally isothiocyanate was applied as sulfur compound because this compound is generally used as insecticide and bactericide. It was added into biodiesel in order to study the

effect of sulfur content on each catalysts. The results of each catalyst; Pd/SiO₂, Pt/SiO₂, and Ni/SiO₂ are shown in Figure 4.4(a-c), respectively.



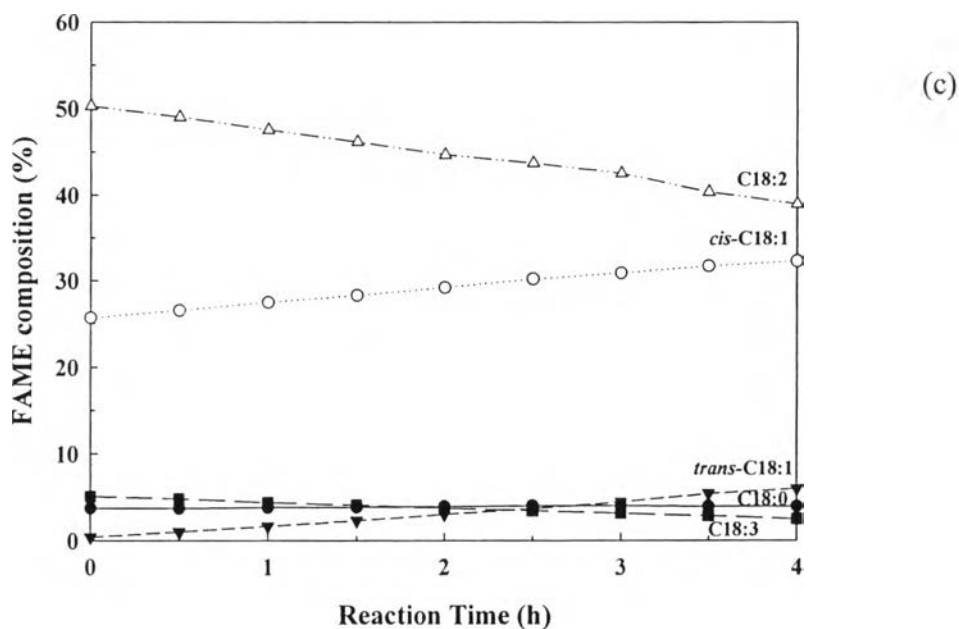


Figure 4.4 Effect of sulfur compound: (a) 1 wt.% Pd/SiO₂ (b) 1.82 wt.% Pt/SiO₂ (c) 10 wt.% Ni/SiO₂ on FAME composition of biodiesel after partial hydrogenation reaction using catalyst reduced under air at 300°C (for Pd/SiO₂ and Pt/SiO₂) and 400°C (for Ni/SiO₂) (Reaction condition: 120°C, 4 bar, 150 ml/min of H₂ flow rate, 1000 rpm of stirring rate, and 1 wt.% of catalysts compared with 130.395 g of biodiesel).

In order to compare the catalytic activity of each catalyst, bar chart was applied and shown in Figure 4.5. Similar to the previous effect, Pd catalyst presented the highest catalytic activity. Since, it could convert both C18:3 and C18:2 rapidly within 2.5 hour of reaction time, and also increased the amount of C18:1. For Pt catalyst and Ni catalyst, they followed the concept of partial hydrogenation. However, Ni catalyst showed the lowest catalytic activity as same as used in biodiesel without adding additional sulfur.

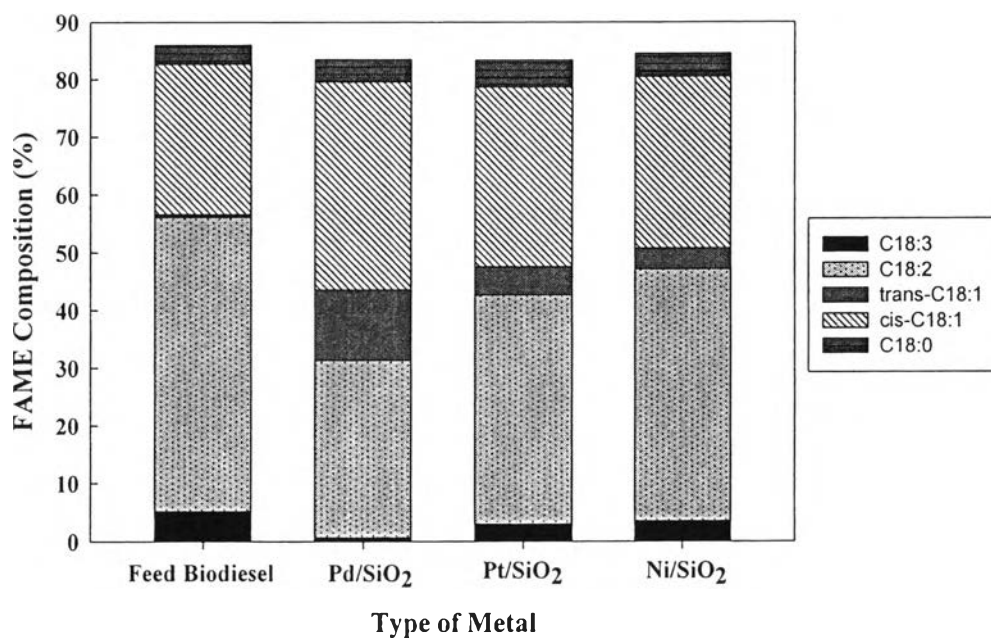


Figure 4.5 Comparison of C18 FAME composition of hydrogenated biodiesel (2.5 h) with adding additional sulfur compound in conditions : 120°C, 4 bar, 150 ml/min of H₂ flow rate, 1000 rpm of stirring rate, 1 wt.% of Palladium loading , 1.82 wt.% of Platinum loading, 10 wt.% of Ni loading, and 1 wt.% of silica catalyst.

Similar to the effect of metal type used in original biodiesel, the catalytic activity was shown by TOF which calculated from C18:2 conversion within 2.5 hour of reaction time. These values were represented in Table 4.3, it also indicated that Pd catalyst gave the highest catalytic activity and follow by Pt and Ni catalyst, respectively.

Table 4.3 Turnover Frequency (TOF) after adding additional sulfur

Catalyst	TOF (h ⁻¹)
Pd/SiO ₂	10,380.28
Pt/SiO ₂	4,636.22
Ni/SiO ₂	429.55

Apart from these studies, the comparison between catalytic activity of each catalyst which were used in partial hydrogenation reaction before and after adding additional sulfur compound were also concerned. The percentage of all FAME compositions of feed biodiesel and hydrogenated biodiesel; with and without adding additional sulfur compound, were compared as exhibited in Table 4.4.

This table exhibited that after partial hydrogenation reaction, hydrogenated biodiesel contained lower triunsaturated FAME and diunsaturated FAME, while increased the amount of monounsaturated FAME (both cis- and trans-isomers) and also slightly increased saturated FAME as compared to feed biodiesel. These results were occurred in the similar way for all metal types. After adding additional sulfur compound, however, triunsaturated FAME and diunsaturated FAME conversion occurred in lower rate as compared to the original hydrogenated biodiesel. And there were also less amount of both monounsaturated and saturated FAME.

Table 4.4 FAME composition (%) of soybean BDF and hydrogenated BDF with and without additional sulfur, after 2.5 hours of reaction using Pd/SiO₂, Pt/SiO₂, and Ni/SiO₂ (in parenthesis is the composition of C18 FAME)

	Soybean BDF	Pd/SiO ₂		Pt/SiO ₂		Ni/SiO ₂	
		w/o S	with S	w/o S	with S	w/o S	with S
Saturated FAME	16.31 (3.38)	17.53 (5.18)	17.78 (3.89)	19.58 (4.40)	18.82 (4.69)	19.13 (4.03)	17.18 (4.02)
<i>trans</i> - Monounsaturated FAME	0.43 (0.13)	32.27 (32.19)	12.29 (12.20)	8.88 (8.60)	4.88 (4.82)	5.46 (5.24)	3.68 (3.60)
<i>cis</i> - Monounsaturated FAME	26.07 (25.92)	43.70 (43.46)	36.34 (36.05)	35.36 (35.15)	31.55 (31.10)	33.64 (33.44)	30.20 (29.73)
Diunsaturated FAME	51.00	5.28	30.74	32.16	39.78	37.67	43.73
Triunsaturated FAME	5.16	0.13	0.62	1.83	2.97	2.69	3.45

In addition, Figure 4.6 also represented the comparison of only C18 FAME composition of both feed biodiesel and hydrogenated biodiesel; with and without adding additional sulfur compound. It also indicated that the catalytic activity of each catalyst dropped after adding additional sulfur compound.

According to these results, it can be summarized that sulfur compound showed a significant effect on the catalytic activity. It was supported by Numwong *et al.*, 2012's work and Yu *et al.*, 2012's work. They proposed that the activity of catalysts decreased after adding additional sulfur compound and lower composition of *trans*-isomers was obtained as well.

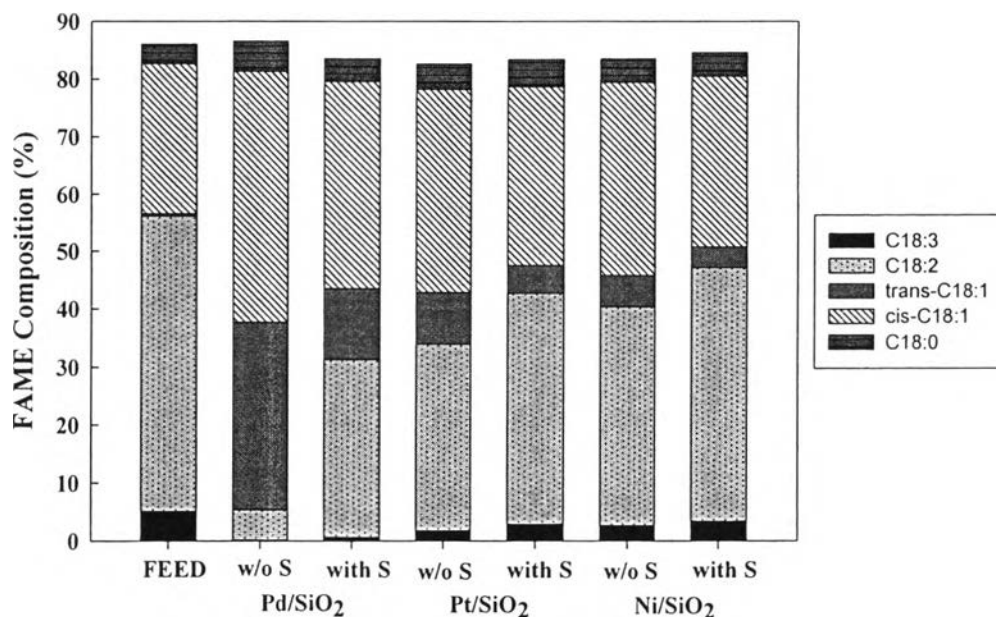


Figure 4.6 Comparison of C18 FAME composition between feed biodiesel and hydrogenated biodiesel with and without adding additional sulfur compound after 2.5 hour of reaction time in conditions : 120°C, 4 bar, 150 ml/min of H₂ flow rate, 1000 rpm of stirring rate, 1 wt.% of Palladium loading , 1.82 wt.% of Platinum loading, 10 wt.% of Ni loading, and 1 wt.% of silica catalyst.

In addition, the sulfur tolerance of catalyst was also concerned by using percentage of loss activity which was calculated from difference of TOF before and after adding additional sulfur compound. For this study, Pt catalyst presented the highest sulfur tolerance with was shown by the lowest percentage of loss activity (37.05%). While, Pd catalyst had relatively high percentage of loss activity (62.99%) after adding additional sulfur compound. However, it still be lower than that of Ni catalyst (66.93%). Therefore, the sulfur tolerance of catalyst in partial hydrogenation of soybean oil based-biodiesel was exhibited in this order; Pt/SiO₂ > Pd/SiO₂ > Ni/SiO₂.

$$\text{Percentage of loss activity} = \left[\frac{TOF_{\text{before adding S}} - TOF_{\text{after adding S}}}{TOF_{\text{before adding S}}} \right] \times 100$$

Table 4.5 Percentage of loss activity

Catalyst	TOF (h ⁻¹)		% Loss activity
	Without S	With S	
Pd/SiO ₂	28,050.09	10,380.28	62.99
Pt/SiO ₂	7,365.13	4,636.22	37.05
Ni/SiO ₂	1,298.97	429.55	66.93

This result is consistent with Matsui and co-worker's work (2005). They exhibited that Pt catalyst could resist sulfur effect than Pd catalyst. They purposed the reason that particle size had greater effect on sulfur tolerance. Because of larger particle size, faster metal sulfidation.

The important information were represented in Table 4.6 in order to explained the sulfur tolerance which occurred in the similar way as the other author's work. For Ni metal, although it had the smallest size (8.47 nm), it was loaded with the highest percentage (10 wt.% metal loading). This caused the high metal cluster formation as shown by the lowest percentage of metal dispersion. For Pd metal, it had the biggest particle size (32.14 nm), however, it was loaded on support just 1 wt.% metal loading and the relatively high percentage of metal dispersion. From this point, it could be indicated that the metal dispersed separately or there was little cluster formation which caused the smaller particle size than Ni metal. This might be the reason that Pd catalyst obtained the higher sulfur tolerance than Ni catalyst. For the highest sulfur tolerance in this study, Pt metal, it had 3 times smaller size than Pd metal and slightly larger than Ni metal. Although it was loaded on support with 1.82 wt.% metal loading, there was highest metal dispersion. That caused the lower metal cluster and also the small size of metal, that led to this metal type had the slowest metal sulfidation.

Therefore, it can be conclude that metal particle size had the significant effect on catalytic activity in partial hydrogenation reaction of soybean oil based-biodiesel.

Table 4.6 Percentage of metal loading and metal dispersion and metal particle size of each catalyst

Metal	%Metal loading	Particle size (nm)	%Metal dispersion
Pd	1	32.14	6.88
Pt	1.82	10.67	7.49
Ni	10	8.47	5.82

4.4.4 Catalyst Characterization

The characteristics of the catalysts were obtained using various analysis tools.

4.4.4.1 *X-ray Diffraction (XRD)*

The X-ray diffraction patterns of 1wt.% Pd/SiO₂, 1.82 wt.% Pt/SiO₂, and 10 wt.% Ni/SiO₂ catalysts are shown in Figure 4.7-9, respectively. These catalysts prepared by incipient wetness impregnation (IWI) using Pd(NH₃)₄.Cl₂, Pt(NH₃)₄.Cl₂, and Ni(NO₃)₂.6H₂O precursor. For drying state of Pd/SiO₂ catalyst, the strongest peak for Pd(NH₃)₄.Cl₂ was observed at 19.13° 2 θ . According to Panpranot and co-workers' work (2004), they purposed that diffraction peaks for palladium oxide (PdO) were detectable at 33.8° and less so at 42.0°, 54.8°, 60.7°, and 71.4° 2 θ in calcination state. From Figure 4.7(b), the main characteristic peaks for PdO were found at 33.89°, 41.95°, 54.76°, 60.21°, and 71.48° 2 θ , respectively. These peaks were indicated that the catalyst was formed to be palladium oxide (PdO) after calcination state. In addition, Pd/SiO₂ catalyst was then reduced at 300°C for 2 hours and XRD patterns showed that the four main characteristic peaks of crystalline Pd including plane (1 1 1), (2 0 0), (2 2 0), and (3 1 1) at 2 θ of 40.12, 46.66, 68.12, and 82.10, respectively, were observed. The presence of crystalline Pd in reduction state was confirmed by Numwong *et al.*, (2012). It was meant that this catalyst was reduced to be crystalline Pd before used in

partial hydrogenation reaction. However, the peaks for Pd/SiO₂ catalyst in XRD patterns were not shown obviously. The reasons were few amount of Pd loading and well-dispersed nature of the catalyst.

XRD analysis of the Pt/SiO₂ catalyst was represented in Fig. 4.8. In drying state, there were 3 main peaks at 12.02°, 24.44°, and 27.34° 2 θ . These peaks generally indicated to Pt(NH₃)₄.Cl₂.H₂O. After calcination state at 300°C for 3 hours, XRD patterns changed, there were characteristic peaks of platinum metal (Pt⁰) instead of the peaks corresponding to the phases of PtO₂ or PtCl₄ which ensuring the complete reduction to Pt⁰ during the catalyst preparation (Telkar *et al.*, 2005). Therefore, there were three main peaks appeared in the 2 θ range of 10° to 80° and these peaks were the same in both calcination and reduction state. The three Pt reflections at 2 θ of 39.77°, 46.24°, and 67.46° were assigned to face-centered cubic (f.c.c.) Pt (1 1 1), Pt (2 0 0), and Pt (2 2 0), respectively. This peak analysis was supported by McArdle's work who purposed that the Pt reflections of their work occurred at 39.8°, 46.6°, and 67.5° 2 θ .

For Ni/SiO₂ catalyst, the XRD patterns of catalyst dried at room temperature and 60°C are shown in Figure 4.9(a). No distinct XRD peaks were observed for this state. This result indicated the highly dispersed nickel species in the dried catalyst (Chen *et al.*, 2012). After looking in detail, however, there was peak at 21.03° 2 θ , probably belonging to Ni(NO₃)₂. In addition, there was some peak at 2 θ of 16.16° which indicated to Ni(NO₃)₂.6H₂O. This might be the result from incomplete drying which led to have some water molecules in catalyst after drying state. According to Chen and co-workers' work (2012), they displayed that in calcination state at 450°C, the diffraction peaks the diffraction peaks at 37°, 43°, and 63° might belong to MgO, NiO or the solid solution formed between NiO and MgO. The XRD pattern as shown in Figure 6.8(b) represented three main peaks at 2 θ of 37.25°, 43.28°, and 62.88°. After reduction state, the XRD patterns were changed from calcination which meant that NiO was formed to be metallic Ni. The two distinct peaks at 2 θ of 44.51° and 51.85° were attributed to f.c.c. Ni (1 1 1), and Ni (2 0 0), respectively. This analysis results were also confirm by Chen and co-workers' work (2012).

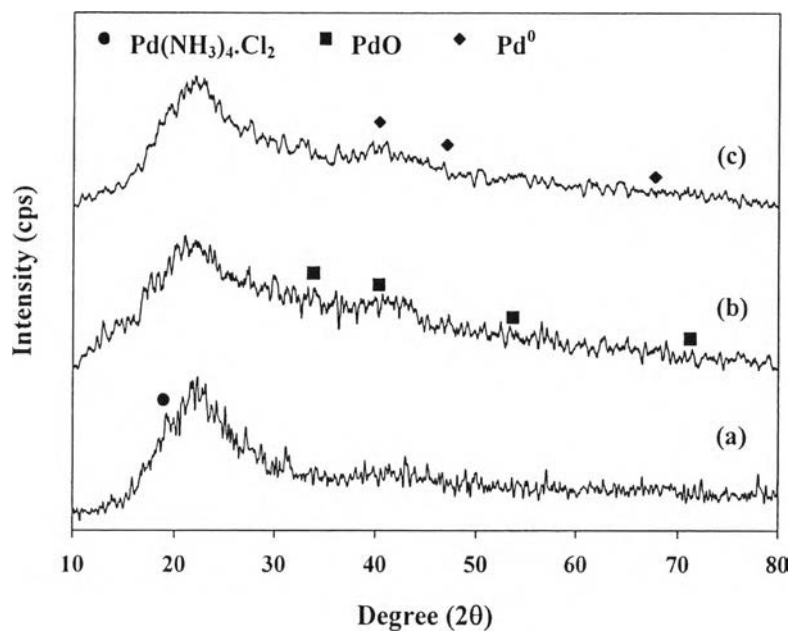


Figure 4.7 XRD patterns of spent 1 wt.% Pd supported on silica, (a) Dried (b) Calcined (c) Reduced.

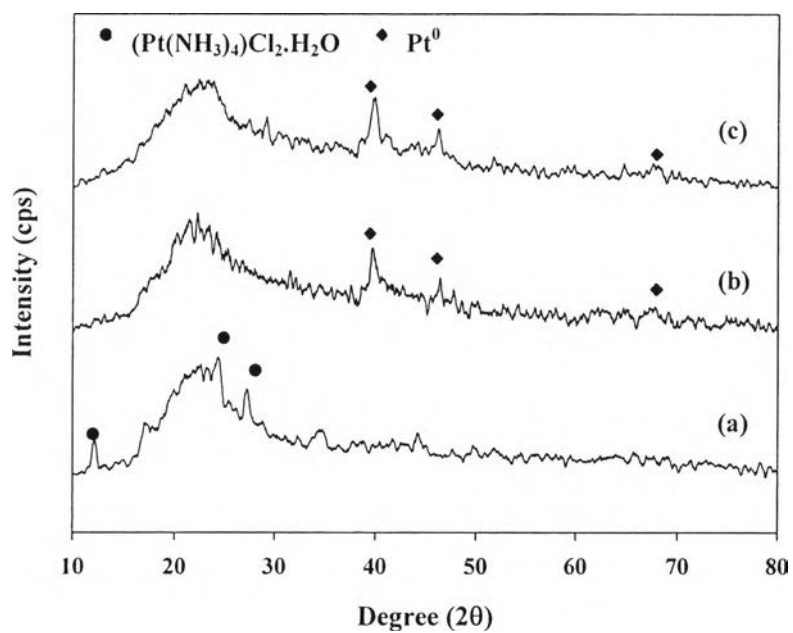


Figure 4.8 XRD patterns of spent 1.82 wt.% Pt supported on silica, (a) Dried (b) Calcined (c) Reduced.

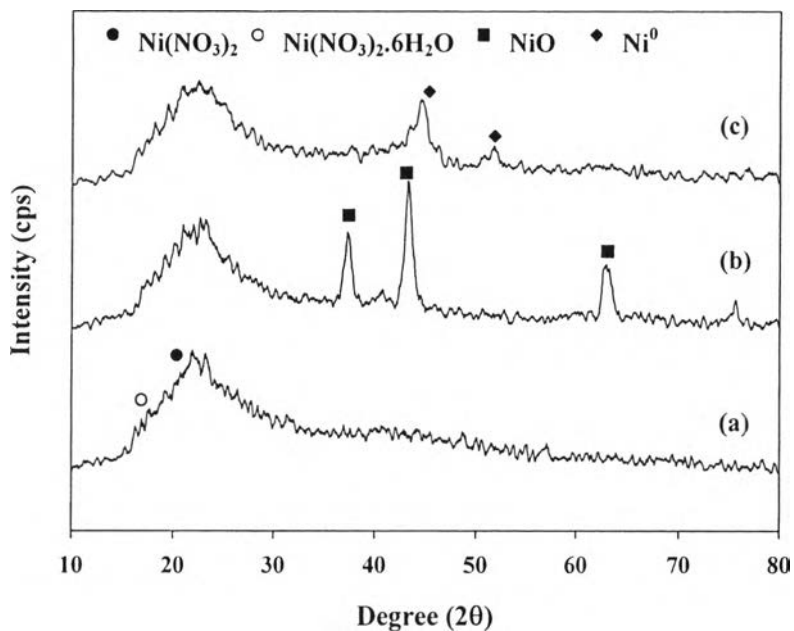


Figure 4.9 XRD patterns of spent 10 wt.% Ni supported on silica, (a) Dried (b) Calcined (c) Reduced.

For all catalysts, the crystallite sizes for the reduced samples were calculated from the peak width at half height of the diffraction peak by applying Scherrer's equation (Mehta *et al.*, 2012). In addition, the metal particle sizes were presented in Table 4.7.

$$t = \frac{K \times L}{B \times \cos\theta_B}$$

By

t = thickness of crystallite

K = constant dependent on crystallite shape (0.89)

L = 1.54 of Cu (°Å)

B = FWHM (full width at half max) or integral breadth

θ_B = Bragg Angle ($\pi = 180$)

Table 4.7 Particle size estimated by XRD

Metal	Particle size (nm)
Pd (1 1 1)	32.14
Pt (1 1 1)	10.67
Ni (1 1 1)	8.47

4.4.4.2 Surface Area Analyzer (SAA)

The BET surface area, total pore volume, and average pore diameter of SiO₂, Pd/SiO₂, Pt/SiO₂, and Ni/SiO₂ analyzed by using Autosorb-1 MP surface area analyzer were given in Table 4.8. After palladium impregnation on SiO₂, the BET surface area total was slightly increased. On the contrary, total pore volume and average pore diameter of Pd/SiO₂ were decreased as compared to the SiO₂. It can be suggested that palladium was deposited on some pores of the support. For Pt/SiO₂ and Ni/SiO₂ catalysts, the BET surface area, total pore volume, and average pore diameter were decreased. It can also be concluded that both platinum and nickel were accessed in some pores of the SiO₂ support.

Since the surface area of each catalyst just slightly change as compared to silica support. While both total pore volume and average pore diameter were decreased insignificantly that the results from some metal deposition in pores of support. It can be suggested that these properties do not the significant factor for the catalytic activity.

Table 4.8 Characteristics of SiO₂, Pd/SiO₂, Pt/SiO₂, and Ni/SiO₂ catalyst

	Surface area (m ² /g)	Total pore volume (ml/g)	Average pore diameter (nm)
SiO ₂	112.25	1.29	45.83
Pd/SiO ₂	116.56	1.26	43.09
Pt/SiO ₂	110.64	1.19	43.14
Ni/SiO ₂	105.47	1.08	40.77

4.4.5 Properties of Biodiesel

The properties of biodiesel before and after partial hydrogenation (with and without additional sulfur content) are presented in Table 4.9. These properties were analyzed by EN 14112:2003, ASTM D 2500-02, and ASTM D 6371-05 method for oxidation stability, cloud point, and cold filter plugging point, respectively.

These data showed that after reaction, the hydrogenated biodiesel gave higher oxidative stability. On the contrary, cloud point and cold filter plugging point were also increased which the result from increasing saturated FAME in hydrogenated biodiesel. However, these three properties of hydrogenated biodiesel with adding additional sulfur compound were lower than that of without adding sulfur content. These were results from lower catalytic activity in partial hydrogenation reaction.

For conclusion, the partial hydrogenation reaction can improve the biodiesel properties of soybean oil based-biodiesel especially oxidative stability. This was the result from decreasing amount of polyunsaturated FAME particularly C18:3 and C18:2. In addition, it also slightly increased the cold flow properties as the result from increasing the contents of saturated FAME.

Table 4.9 Biodiesel properties before and after partial hydrogenation

	Oxidative Stability (hr)	Cloud point (°C)	Cold Filter Plugging Point (°C)
Feed Biodiesel	1.4	1	-6
Pd/SiO₂			
• Hydrogenated Biodiesel	30.4	6	0
• Hydrogenated Biodiesel with adding sulfur	7.7	4	-2
Pt/SiO₂			
• Hydrogenated Biodiesel	5.0	4	-2
• Hydrogenated Biodiesel with adding sulfur	3.6	3	-2
Ni/SiO₂			
• Hydrogenated Biodiesel	3.6	3	-2
• Hydrogenated Biodiesel with adding sulfur	3.5	1	-4

4.5 Conclusion

Partial Hydrogenation reaction was the effective way which used to improve the biodiesel properties especially oxidative stability. For this work, all of three metal types; Pd, Pt, and Ni, exhibited good partial hydrogenation of soybean oil based-biodiesel. They could decrease the contents of C18:3 and C18:2 and also increase

monounsaturated FAME and saturated FAME particularly C18:1 (both *cis*- and *trans*-isomers) and C18:0 contents, respectively. As compared between these catalysts, Pd catalyst presented the highest catalytic activity as presented by TOF of C18:2 conversion. In addition, this result was consistent with several authors such as McArdel *et al.*, 2011 and Numwong *et al.*, 2012. After adding additional sulfur, Pd catalyst gave the highest catalytic activity; however, Pt catalyst could resist the effect of sulfur compound more than the others. In the same way, the highest sulfur tolerance was Pt catalyst. The significant factor for sulfur tolerance was metal particle size. The larger particle size gave the faster metal sulfidation. Although, Ni metal had the smallest size, there were large cluster formation. This caused the lowest sulfur tolerance. Pd metal was the relatively large particle size; however, it was loaded on support with the lowest percentage and also well dispersed. There were little cluster formation as compared to Ni metal. For Pt metal, the particle size was 3 times smaller than Pd metal and exhibited the highest metal dispersion which caused the lowest metal cluster formation than the others and showed the highest sulfur tolerance in this study.

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4.7 References

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