ความว่องไวของ Ni/SiO_2 ในกระบวนการไฮโดรจิเนชันบางส่วนของไบโอดีเซลจากน้ำมันพืชใช้แล้ว

Catalytic Activity of Ni/SiO_2 Supported on Partial Hydrogenation of Biodiesel from Waste Cooking Oil

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บทคัดย่อ

กระบวนการไฮโดรจิเนชันบางส่วนช่วยปรับปรุงคุณสมบัติของไบโอดีเซล โดยการเปลี่ยนโครงสร้างกรดไขมันไม่อิ่มตัวไปเป็นสารอิ่มตัว วัตถุประสงค์ของงานวิจัยนี้ คือศึกษาความว่องไวของตัวเร่งปฏิกิริยา Ni/SiO_2 ศึกษาความสามารถในการเลือกสรรการเกิด *cis-trans* ของตัวเร่งปฏิกิริยาผ่านกระบวนการไฮโดรจิเนชันบางส่วน โดยไบโอดีเซลสังเคราะห์จากน้ำมันพืชใช้แล้วด้วยปฏิกิริยาทรานส์เอสเทอริฟิเคชันในเครื่องไมโครเวฟ ส่วนกระบวนการไฮโดรจิเนชันบางส่วนทดลองที่อุณหภูมิ 100 องศาเซลเซียส ความดันของไฮโดรเจน 4 บาร์ โดยใช้ตัวเร่งปฏิกิริยา Ni/SiO_2 ซึ่งสังเคราะห์ด้วยวิธีทำให้ชุ่ม ไบโอดีเซลวิเคราะห์ด้วยก๊าซโครมาโตกราฟีและฟูเรียร์ทรานสฟอร์มอินฟราเรดสเปคโตรมิเตอร์ (FTIR) ตัวเร่งปฏิกิริยาวิเคราะห์จากการเลี้ยวเบนรังสีเอกซ์ การกระจายตัวของตัวเร่งปฏิกิริยา (CO pulse chemisorption) จากผลการทดลองพบว่า Ni/SiO_2 ช่วยปรับปรุงผลผลิตไบโอดีเซลให้มีปริมาณ *cis*-C18:1 และ *trans*-C18:1 เพิ่มขึ้น ซึ่งความว่องไวของตัวเร่งปฏิกิริยาแสดงผลในค่า TOF โดยคำนวณจากค่าการเปลี่ยนแปลงของ C18:2 พบว่าที่ 1 ชั่วโมงของการทำปฏิกิริยา มีค่า TOF สูงสุด เท่ากับ 486 h^{-1} แสดงให้เห็นว่าช่วงแรกของปฏิกิริยามีโลหะนิกเกิลที่มีความว่องไวในการเร่งปฏิกิริยาไฮโรจิเนชันในปริมาณมาก อย่างไรก็ตาม TOF มีค่าลดลงที่ 4 ชั่วโมงของปฏิกิริยา มีค่าเท่ากับ 203 h^{-1}

คำสำคัญ: ไบโอดีเซล น้ำมันพืชใช้แล้ว ตัวเร่งปฏิกิริยา กระบวนการไฮโดรจิเนชันบางส่วน นิกเกิล

Abstract

Partial hydrogenation can be used to improve biodiesel properties by transforming the polyunsaturated fatty acid methyl ester (FAME) to the saturated FAME. The aim of this research was to study the effect of catalytic performance of Ni supported on SiO_2 (Ni/SiO_2) catalyst on the partial hydrogenation of polyunsaturated FAME. The effect of hydrogenation activity on *cis-trans* selectivity of the catalyst was also investigated. Biodiesel was synthesized by

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using waste cooking oil (WCO) as a feedstock via a transesterification with a microwave irradiation. Partial hydrogenation was performed with operating conditions of 100 °C and 4 bar hydrogen pressure. The Ni/SiO_2 catalyst was prepared by incipient wetness impregnation. Biodiesel was characterized by gas chromatography (GC-FID) and Fourier transform infrared absorption spectroscopy (FTIR). The catalyst was determined by X-ray diffraction (XRD) and CO pulse chemisorption. The results showed that the Ni/SiO_2 catalyst enhance the formation of both *cis*-monounsaturated and *trans*-monounsaturated FAME. The catalytic activity was represented by turnover frequency (TOF) as exhibited by C18:2 conversions. The highest TOF (486 h^{-1}) was exhibited at 1 h of hydrogenation, indicating that the abundance of Ni active sites. Nevertheless, TOF decreased within 4 h of reaction time (TOF; 203 h^{-1}).

Keywords: Biodiesel, Waste Cooking Oil, Catalyst, Partial Hydrogenation, Ni

Introduction

Nowadays, the energy demand rapidly increases since it dramatically rise of the population, industrial development, and transportation, which need to find an alternative fuels [1-2]. To solve these problems, biodiesel fuel seem appropriate for replace fossil fuel because of its biodegradability, non-toxicity, renewability, lower exhaust emissions, and higher cetane number as compared to petroleum based diesel [3-5]. Biodiesel or fatty acid methyl ester (FAME) synthesis is carried out from vegetable based oil or animal fats via transesterification in the presence of alcohol by means of alkaline or alkaline combined acid catalyst [6]. Due to the higher cost of the raw materials, waste cooking oil (WCO) have suggested as alternatives, compared to expensive first generation edible oils and also prevents environmental pollution [7-8]. In addition, biodiesel production was synthesized by microwave irradiation processes can accelerate the chemical reaction of transesterification, decrease the reaction time and also reduce the net energy [9-10].

The properties of biodiesel depend on the fatty acid composition of the feedstock. The highly amount of polyunsaturated fatty acid causes low oxidative stability and low cetane number of biodiesel. On the other hand, biodiesel with fully saturated fatty acid consequently influences to cold flow properties, which give poor quality biodiesel. Many researchers reported that the oil contains high content of monounsaturated fatty acid are the great feedstock for production of excellent quality biodiesel. Therefore, partial hydrogenation processes of polyunsaturated FAME to monounsaturated FAME especially the *cis*-isomer in biodiesel are a promising solution to solve this problem [4-5, 11-13]. The noble metal e.g. palladium (Pd) [4, 12-14] and platinum (Pt) [12-13, 15] are often used for catalyzed the hydrogenation of oil and FAME. Nevertheless, nickel catalyst (Ni) supported on silica was studied since it is cheaper than noble metal catalysts [12-13]. Silica (SiO_2) is mainly used as a support-catalyzed in partial hydrogenation, as it has high surface area, large pore volume, and has higher stability to reduction [13].

This paper was mainly focused on the catalytic activity of Ni/SiO_2 catalyst on the partial hydrogenation of biodiesel derived from WCO via transesterification reaction with a microwave irradiation. Additionally, the effect of hydrogenation activity on *cis-trans* selectivity of the catalyst was thoroughly discussed. The properties of biodiesel before and after partial hydrogenation and the characteristic of catalyst were determined by GC-FID, FTIR, XRD, and CO pulse chemisorption.

Materials and Methodology

Materials

WCO from the local areas of Songkhla, Thailand was used as a raw material for biodiesel production. WCO was heated in order to remove the leftover water. After that the residues matters in WCO were refined by filtration. The free fatty acid (FFA) content of the WCO was less than 2 mg KOH/oil. Silica with a mesoporous (pore diameter of 30 nm) procured from Fuji Silysia Chemical Company Ltd. was used as a solid support. The Nickel (II) nitrate hexahydrate (99.9 %) was applied as Ni precursor was purchased from Wako Pure Chemicals Industries Limited. All chemical reagents were of analytical grades obtained from RCI Labscan Company Ltd.

Transesterification of Waste Cooking Oil via Microwave Irradiation

WCO (200 mL) was carried out in 500 mL glass equipped and then placed on the hot plate, which was heated to 60 ± 5 °C. The solution of 2 g KOH and 40 mL methanol were mixed together under vigorous stirring. Heated WCO was reaches to desired temperature and then mixed solution of KOH and commercial methanol was added into the flask, it was vigorously stirred at 300 rpm for 10 min. The transesterification was operated under a microwave irradiation with a power of 300W for 3 min. After the reaction was completed, the resultant mixture was separated in a separatory funnel for one night. The mixture was separated into two phase: biodiesel (top) and glycerin (bottom). The biodiesel phase was decanted into a flask, which was washed with 65 °C of distillated water for several times in order to remove the residuals. The obtained pure biodiesel was kept in a glass bottle and the residual water was removed over anhydrous Na_2SO_4.

Synthesis of Ni/SiO_2 Catalyst

The incipient wetness impregnation method was conducted to prepare the catalyst. The commercial silica (SiO_2) support was dried in an oven over night to remove adsorbed water. An aqueous solution of $Ni(NO_3)_2.6H_2O$ used as a Ni precursor was prepared by 10 wt % of Ni impregnated into the silica support and kept under vacuum for 24 h. The catalyst was dried at 60 °C for 6 h. After drying, the catalyst was calcined at 450 °C under an oxygen stream flow of 500 mL/min for 3 h. Finally, the catalyst was reduced at 400 °C under hydrogen gas flow of 5°C/min for 2 h.

Catalyst and Biodiesel Analysis

The chemical composition of catalyst was analyzed by using x-ray diffraction (XRD) measurement at 2 theta between 10º and 90º with a scanning speed of 1º/s. The XRD was carried out using Cu-Kα radiation and operated at 40 kV and 30 mA. The XRD data was recorded on Rigaku DMAX 2200 HV.

The nickel dispersion was characterized by CO pulse adsorption method using temperature-programmed desorption/reduction/oxidation (TPD/R/O), Ohkura R6015 model. The catalyst was reduced with hydrogen gas at 400° C for 1 h and helium gas was purged at the same condition for 10 min. The Ni dispersion was determined by assuming a stoichiometry of CO:Ni was 1:1.

The FAME compositions of the feed biodiesel (WCO) and partially hydrogenation biodiesel were determined by gas chromatography (Hewlett Packard 5890 Series II) equipped with FID detector (GC-FID). A HP-88 silica capillary column (100 m X 0.25 nm) was examined. GC-FID conditions were helium as a carrier gas with a flow rate of 70 ml/min; injector temperature at 200°C with a split ratio of 75:1; detector temperature at 230°C. Sample was

injected into an oven temperature at 130°C. After 2 min of isothermal period, the GC oven was heated to 220°C with a heating rate of 2°C/min and held for 15 min. The running time of one cycle was 62 min.

In addition, the chemical functional group of the partial hydrogenated biodiesel was analyzed by Fourier Transform Infrared Spectroscopy (FTIR). The sample was placed on a Zn-Se crystal plate with a condition was as follows a 4 cm^{-1} resolution over a scanning range of 650-4000 cm^{-1}.

Partial Hydrogenation of WCO Biodiesel

One hundred fifty milliliter of WCO-biodiesel and 1.30 g Ni-catalyst were placed in a batch reactor. Then, the nitrogen gas was purged in order to remove any residual air from the reactor. Subsequently 150 ml/min of hydrogen gas was flowed into the reactor and pressure was set at 4 bars. When the temperature was reached to 100°C, the stirrer was started at 500 rpm to mix biodiesel and catalyst. The biodiesel products were collected every 30 min, and reaction was carried out for 4 h.

Results and Discussion

Feed WCO Biodiesel Analysis

The fatty acid composition of feed WCO-biodiesel is given in Table 1. The carbon chain lengths of fatty acid were methyl myristate (C14:0) to methyl lignocerate (C24:0). The properties of biodiesel depend on the FAME composition. The saturated fatty acid found in WCO-biodiesel was 1.14 % C14:0, 33.31 % C16:0, and 4.72 % C18:0 which provide high oxidative stability but presents poor cold flow properties biodiesel [12-14, 16]. The mono-unsaturated fatty acid was methyl palmitoleate (2.59 %) and methyl oleate (33.56 %), which provided more stable against oxidative and cold flow properties. The content of *trans*-C18:1 (1.01 %), which is less favorable due to causes an increase in melting point [12-13]. The di- and triunsaturated fatty acid methyl ester was C18:2 (16.30 %) and C18:3 (3.10 %), exhibit low resistance to oxidation since it high oxidation rate [5, 12-13]. In addition, small amount (< 1 %) of *trans*-C16:1, C17:0, C20:0, *trans*-C20:1, *cis*-C20:1, C22:0, and C24:0 were also found in WCO-biodiesel.

The FTIR spectrum of WCO is shown in Fig. 1. The detected band at 3003 cm^{-1} was the C-H stretching of CH=CH referred to tri-, di-, and monounsaturated FAME. The wavenumber at 2922 and 2853 cm^{-1} related directly to the presence of aliphatic CH stretching of CH_2. The methyl esters was observed at 1741 cm^{-1} (C=O ester), confirms the presence of WCO-based biodiesel via transesterification. The vibration at 1457 and 1361 cm^{-1} were determined the -CH_2 scissor and -CH_3 anti symmetric, respectively. The absorbance peak at 1169 cm^{-1} was characteristic of the C-O symmetric stretching band. The vibration peaks at 1015 and 721 cm^{-1}, which corresponding to C-O anti-symmetric stretching and *cis*-isomers of -CH, respectively.

Catalyst Characterization

An XRD was studied to identify the crystalline phase of catalyst. The Ni/SiO_2 catalyst was prepared by incipient wetness impregnation (IWI) method which was calcined and reduced at 450 °C and 400 °C, respectively. The XRD spectrum that was characterized peaks at 2 theta is illustrated in Fig. 2. The amorphous silica using as a supporting material was detected at 22.10°. As expected, the characteristic line of nickel metallic (44.60°, 51.92° and 76.16°) was appeared, which is in agreement with the data presented by Thunyaratchatanon *et al.* [12-13]. The metal dispersion was

recorded by using the pulse CO chemisorption technique to characterize the catalytic activity of Ni catalyst. Table 2 shows the Ni loading (10 wt % of Ni/SiO_2 catalyst) and Ni dispersion on the silica support (5.60 %) (Agree well with data characterized by XRD [13]).

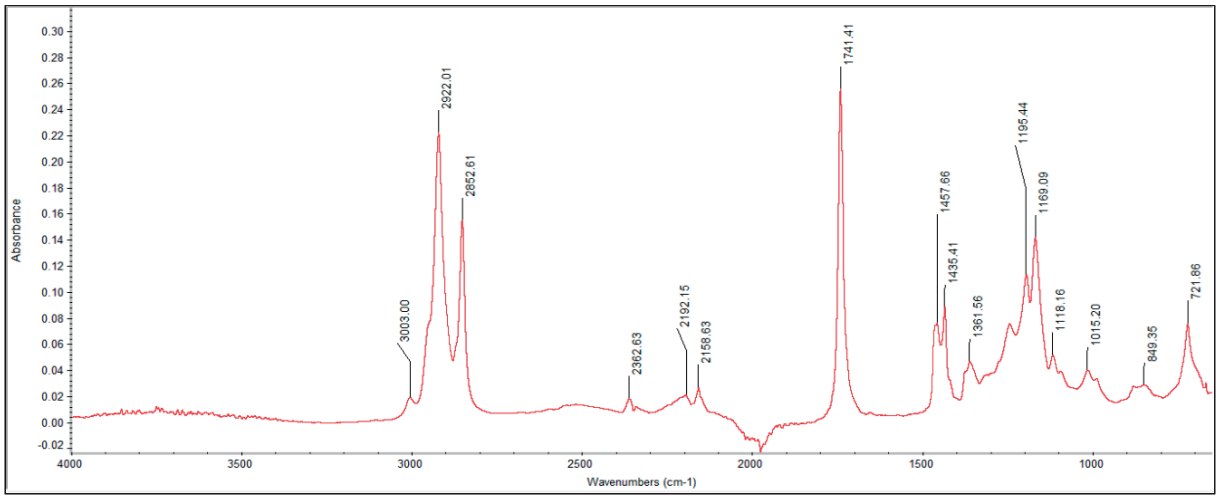

Figure 1 FTIR spectra of WCO-based biodiesel

Table 1 FAME Composition of Feed Biodiesel from WCO.

FAME	**Structure**	**%**
Methyl myristate	C14:0	1.14
Methyl palmitate	C16:0	33.31
Methyl palmitelaidate	*trans*-C16:1	0.29
Methyl palmitoleate	*cis*-C16:1	2.59
Methyl heptadecanoate	C17:0	0.20
Methyl stearate	C18:0	4.72
Methyl elaidate	*trans*-C18:1	1.01
Methyl oleate	*cis*-C18:1	33.56
Methyl linoleate	C18:2	16.30
Methyl linolenate	C18:3	3.10
Methyl arachidate	C20:0	0.34
Methyl *trans*-eicosenoate	*trans*-C20:1	0.38
Methyl *cis*-eicosenoate	*cis*-C20:1	0.11
Methyl behenate	C22:0	0.45
Methyl lignocerate	C24:0	0.06

Effect of Catalytic Activity and *cis-trans* Selectivity of Ni/SiO_2 Catalyst

The catalytic activity of Ni/SiO_2 catalyst was determined from the composition of FAME after partial hydrogenation 100 °C for 1 h and 4 h (Table 2). At these times, the conversions of diunsaturated FAME were about 7 and 23 %, respectively. It can be observed that, at 7 % of C18:2 conversion the total amount of saturated FAME and

monounsaturated FAME were raised to approximately 41.39 % and 39.24 %, respectively. While, the amounts of di- and triunsaturated were decreased. The similar trend of all fatty acid composition was also observed in the 23 % conversion of diunsaturated FAME. However, only 0.75 % triunsaturated FAME was detected indicating that C18:3 was more quickly hydrogenated than other unsaturated FAME.

The turnover frequency (TOF) of catalyst was calculated from the C18:2 conversion at 1 and 4 h of reaction time according to Hongmanorom et al and Thunyaratchatanon *et al.* [5, 13]. Surprisingly, the highest catalytic activity was obtained at 1 h (TOF=486 h^{-1}) since at the initial reaction, the Ni catalyst had high active sites and well dispersed. Hence, TOF value was decreased at the end of reaction (TOF=203 h^{-1}). It is worth to note that, the amount of catalyst at the beginning of hydrogenation reaction has a large number of vacant Ni active sites that are accessible to the reactant, after that; catalytic performance slightly deactivated.

The methyl elaidate (*trans*-C18:1) and methyl oleate (*cis*-C18:1) content determined by GC-FID was extensively compared between 1 and 4 h of hydrogenation (Fig. 3). The contents of *cis*-C18:1 was continuously increased from 35.50 % at 1 h to 38.68 % at 4 h of partial hydrogenation. Whereas, the amounts of *trans*-C18:1 was gradually raised from 1.23 % at 1 h to 1.39 % at 4 h of partial hydrogenation. Evidently, the ratio of *cis*-C18:1/total C18:1 of feed WCO-biodiesel and partially hydrogenated products does not change (approximately 0.97).

Table 2 FAME Composition and Turnover Frequency (TOF) of C18:2 in Partially Hydrogenated Biodiesel

FAME	**Feed WCO**	**Ni/SiO_2**	
		Ni/SiO_2 [a]	**Ni/SiO_2** [b]
Saturated FAME	40.22	41.39	41.63
Monounsarurated FAME	37.94	39.24	43.12
Diunsaturated FAME	16.30	15.19	12.59
Triunsaturated FAME	3.10	2.89	0.75
Total FAME	97.56	98.71	98.09
Ratio of *cis*-C18:1/total C18:1	0.965	0.967	0.970
TOF (h^{-1})	-	486	203

[a] When diunsaturated fatty acid methyl ester conversion was approximately 7 %.

[b] When diunsaturated fatty acid methyl ester conversion was approximately 23 %.

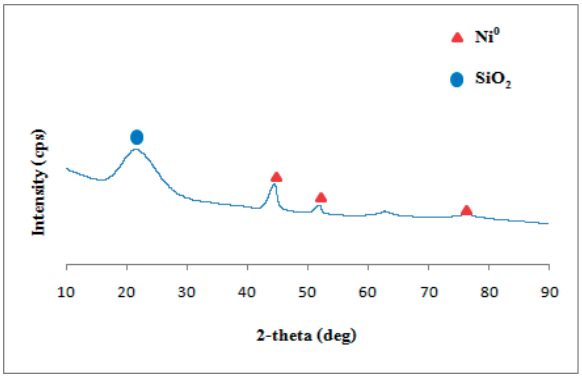

Figure 2 XRD Pattern of Reduced Ni Catalyst.

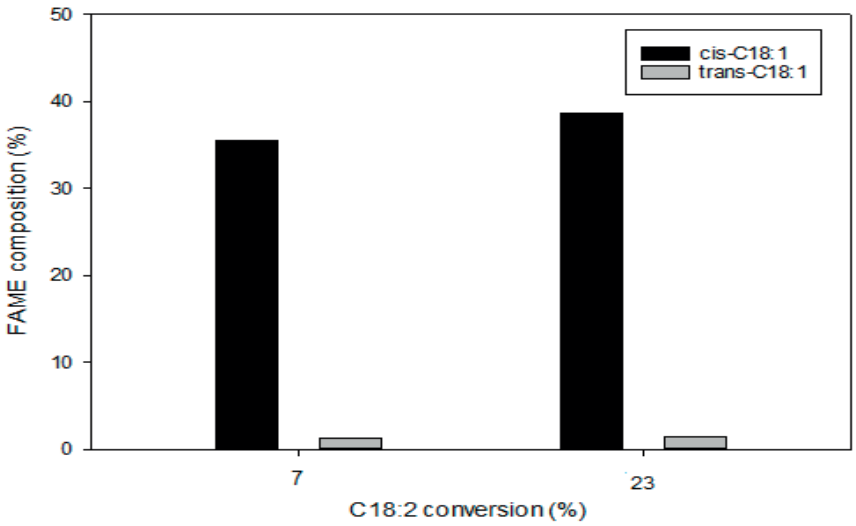

Figure 3 FAME Compositions of Both Percentage of Methyl *cis*-C18:1 and Methyl *trans*-C18:1 in Partial Hydrogenated Biodiesel at 1 and 4 h Reaction.

Conclusion

The Ni/SiO_2 catalyst prepared by incipient wetness impregnation was used to catalyst in partial hydrogenation for improving the WCO-based biodiesel. It was found that the Ni catalyst could enhance the formation of both *cis*-monounsaturated and *trans*-monounsaturated FAME. The highest turnover frequency was found at 1 h of reaction time due to abundance of active sites. Moreover, the biodiesel yield could be improved from 97.56 % of non-hydrogenated FAME to 98.09 % of hydrogenated FAME by using the prepared Ni/SiO_2 as catalyst.

Acknowledgments

The authors gratefully acknowledge Rajamangala University of Technology Srivijaya and The Petroleum and Petrochemical College, Chulalongkorn University was financially supported. We also deeply thank National Institute of Advanced Industrial Science and Technology, Japan for providing material and instrumental analysis. And sincerely thankful to Ms. Chachchaya Thunyaratchatanon and Ms. Chatrawee Direksilp, PhD students at the Petroleum and Petrochemical College, Chulalongkorn University, Thailand for their helps on instrumental analysis.

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