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Contributed Paper

Efficient Conversion of Oils to Biodiesel Catalyzed by Uncalcined Disodium Metasilicate Granules

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ABSTRACT

An efficient, simple conversion of oils to biodiesel catalyzed by uncalcined disodium metasilicate granules (0.3 mm-1 mm) is reported. Under optimum reaction conditions of catalyst content of 9 wt.%; methanol to oil molar ratio of 9:1; reaction temperature of 65 °C with a constant stirring of 200 rpm, many types of oils including waste cooking oil can be transesterified with methanol to biodiesel with a fatty acid methyl ester (FAME) yield over 97% in 40 min. The water contamination in oil of less than 4 wt.% has no effect on the activity of the catalyst. The catalyst can be easily removed from the reaction mixture by a simple filtration and can be reused several times with consistent results. The obtained biodiesel without any cleansing shows a high quality product in which fuel properties of the biodiesel congregate all ASTM and EN 14214 standards for biodiesel. Purification process with a cation-exchange resin efficiently removes all soluble ions to obtain high quality biodiesel product. Uncalcined disodium metasilicate granules showed excellent to be used as a low-cost, green, easy and high potential heterogeneous solid catalyst for biodiesel production.

Keywords: biodiesel, heterogeneous process, disodium metasilicate, solid catalyst

1. INTRODUCTION

Petroleum based-oil is the most important energy source which is consumed by the world's population. This power source is limited while the demand will be higher in

the future. In the recent years, there have been increasing worldwide concern in the protection environments and the growing shortage of non-renewable resources [1-3]. Biodiesel is an alternative source of renewable energy for diesel engines that is gaining greater attention in terms of depleting fossil fuel resources of the world and the mitigation of greenhouse effects due to carbon dioxide. Biodiesel composed of mono-alkyl ester of long chain fatty acid can be produced through transesterification of triglyceride (vegetable oils or animal fat) reacted with a small molecule of alcohol such as methanol in the presence of a catalyst [4-6]. Homogenization catalyzed by NaOH or KOH at 40-60 °C is a normal and effective process for biodiesel production and the reaction itself is easily performed [7]. However, subsequently neutralization and purification steps of biodiesel product are time-consuming and non-environmentally friendly due to the requirements of several washing stages that use a large amount of water [8].

Consequently, a considerable amount of highly contaminated water is inevitably produced. Therefore, major research has focused on the use of heterogeneous catalysts. They offer significant advantages of simple isolation from the reaction, which requires no water, is not polluted, and possible to be reused and recycled. Heterogeneous catalysts such as calcium oxide (CaO) [9] KOH/bentonite [10], calcined hydrotalcites [11], zeolites [12], lithium orthosilicate (Li_4SiO_4) [13] and cement [14] are attractive. These catalysts non-corrosive and environmentally benign, and they present fewer disposal problem which could solve the problems associated with the used of homogeneous catalysts. In addition, the use of disodium silicate in nano-powder obtained from calcined water-glass as a heterogeneous catalyst in biodiesel synthesis was recently

reported. Rapeseed oil and soybean oil were efficiently transformed to biodiesel in mild reaction conditions and short reaction time [15-17]. Since the heterogeneous catalyst are very active in powder form (nano-particle sizes), separation of this powder catalyst is very difficult. This issue makes the catalyst cannot be applied in industries. Therefore, the fabrication of powder catalysts to bulk or solid pellet is the way to solve these problems and make it possible to use in industrial processes [18, 19].

Recently, we have reported on the use of calcined coral fragments ($0.5\text{-}1.0\text{ cm}^3$) as an efficient bulk solid catalysts for transesterification of oils to biodiesel. A complete conversion of oil to biodiesel was attained in 2 h and the catalyst was easily removed by simple filtration. However, a large amount of catalyst (100 wt.%) was required to reach a high yield of biodiesel [20]. Since this work aimed to develop a heterogeneous catalyst for practical industrial applications, uncalcined disodium metasilicate in granular form was employed as a basic catalyst in the transesterification of oils with methanol. Several parameters, such as catalyst amount, methanol/oil molar ratio, reaction temperature, stirring rate, type of oil and free fatty acid (FFAs) quantity, water contamination and reusing of the catalyst are investigated. The removal of soluble ion in the biodiesel by cation exchange is studied. The fuel properties of the obtained biodiesel are evaluated using standard methods.

2. MATERIALS AND METHODS

2.1 Materials and Characterization

Disodium metasilicate (Na_2SiO_3) was purchased from Aldrich and used without any treatment. Many kinds of oils containing various amounts of FFAs including palm oil (acid value of 0.28 mg KOH/g oil), lard oil (acid value of 0.34 mg KOH/g oil),

coconut oil (acid value of 0.25 mg KOH/g oil), sunflower oil (acid value of 0.23 mg KOH/g oil), soybean oil (acid value of 0.18 mg KOH/g oil), rice bran oil (acid value of 0.10 mg KOH/g oil), jatropha oil (acid value of 0.45 mg KOH/g oil) and waste cooking oil (acid value of 2.25 mg KOH/g oil which equals to the FFAs content of 1.13%) were obtained from commercial sources in Thai market and were used without any purification. FFAs content in oils was determined following reported method by Virmani and Narula, 1995 [21]. The analytical grade methanol purchased from Fluka was used in this work.

X-ray diffraction (XRD) was examined by a PHILIPS X'Pert-MDP X-ray diffractometer using Cu K_{α} radiation ($\lambda = 1.5418 \text{ \AA}$) at 1,400 W, 40 kV and 35 mA in the scanning angle (2 theta) of 20-80° with a resolution of 0.04° at counting step of 1 s/step. X-ray fluorescence was analyzed by a PHILIPS MagiX wavelength dispersive X-ray Fluorescence (XRF) spectrophotometer with 1 kW Rh K_{α} radiation. Scanning electron micrograph (SEM) was operated using JEOL JSM 5410LV scanning electron microscope at an accelerated voltage of 20 kV. Brunauer Emmett Teller (BET) was employed on a Bel-sorp-mini II (Bel-Japan) to investigate surface area and pore volume of Na_2SiO_3 . Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer FTIR spectroscopy spectrum RXI spectrometer in the range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1} . Potassium bromide (KBr) was used as a matrix. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker AVANCE 300 MHz spectrometer with tetramethylsilane (TMS) as the internal reference using CDCl_3 as a solvent in all cases.

2.2 Transesterification of Oils

The transesterification was carried out in a batch reactor. A mixture of methanol and catalyst at a designated amount in a 250 mL 3-neck round bottom flask equipped with a reflux condenser was heated at a specific temperature for 2 h, and then a preheated oil (50 mL) was added. The reaction mixture was heated at a controlled temperature and a particular stirring rate. To follow the reaction progress, a solution mixture of 0.5 mL was sampled, and then excessive amount of methanol was evaporated in an oven at 80 °C for 3 h before analysis of biodiesel yield. For reused experiment, the solid catalyst recovered by filtration was directly used as the catalyst for the next reactions and all reactions were run under the same reaction conditions. The conversion of the oil to biodiesel was determined in term of %FAME as a function of time by nuclear magnetic resonance (NMR) technique. The % FAME was calculated from the ratio of the integrations of the ^1H -NMR signals [20].

The fuel properties of the obtained biodiesel were tested according to the American Society for Testing and Material (ASTM) methods and European Standard methods (EN14214) for bio-auto fuels [3, 5, 10, 13]. The amount of leaching sodium ion from the catalyst in the obtained biodiesel was analyzed by the atomic absorption spectrophotometric (AAs) method [22]. Removal of the soluble sodium ion in the obtained biodiesel was performed using commercially available cation exchange resins (Dowex[®] 50WX8). The resin was repeatedly immersed in methanol to remove moisture before use [20].

3. RESULTS AND DISCUSSION

3.1 Characterization of Catalyst

The basic strength of disodium metasilicate granules measured by Hammett indicator method is found to possess H_- values in the range of 15.0-18.4, as evidenced by its ability to effect a color change with 2,4-dinitroaniline ($pK_a = 15$). Elemental composition of the catalyst analyzed by XRF indicates that it composes of mainly SiO_2 as 58.71 wt%, Na_2O 40.54 wt%, Al_2O_3 0.28 wt% and other oxides 0.47 wt% (Table 1). As depicted in Figure 1a, the XRD pattern of the catalyst shows clear and sharp peaks agreeing to a single crystalline phase of Na_2SiO_3 [16]. The results can be confirmed by analysis of the functional group compositions by FT-IR technique (Figure 1b). The spectrum of the catalyst exhibits strong broad absorption bands at 982 cm^{-1} and 879 cm^{-1} assigning to the symmetric stretching modes of the Si-O and Si-O-Si, respectively, which confirm the three-dimensional Si-O-Si linking structure of Na_2SiO_3 . The absorption peaks at 507 cm^{-1} , 717 cm^{-1} , and 1459 cm^{-1} correspond to the Si-O bending, Si-O-Si bending, Si=O stretching modes, respectively, while broad peaks around $2800\text{--}3500\text{ cm}^{-1}$ and 1650 cm^{-1} relate to Si-O-H stretching of water molecules adsorbed on the catalyst surface [16, 17].

The BET surface area, total pore volume and mean pore diameter of the uncalcined disodium metasilicate were $4.93\text{ m}^2/\text{g}$, $1.08 \times 10^{-2}\text{ cm}^3/\text{g}$ and 8.79 nm , respectively. Corresponding to the image of the catalyst

in granule form obtained by SEM showed that it has a particle size in the range of 0.3 mm to 1 mm with a bumpy and pitted surface resulting in a large surface area (Figure 2a). This would allow more transesterification reaction to take place on the catalyst surface.

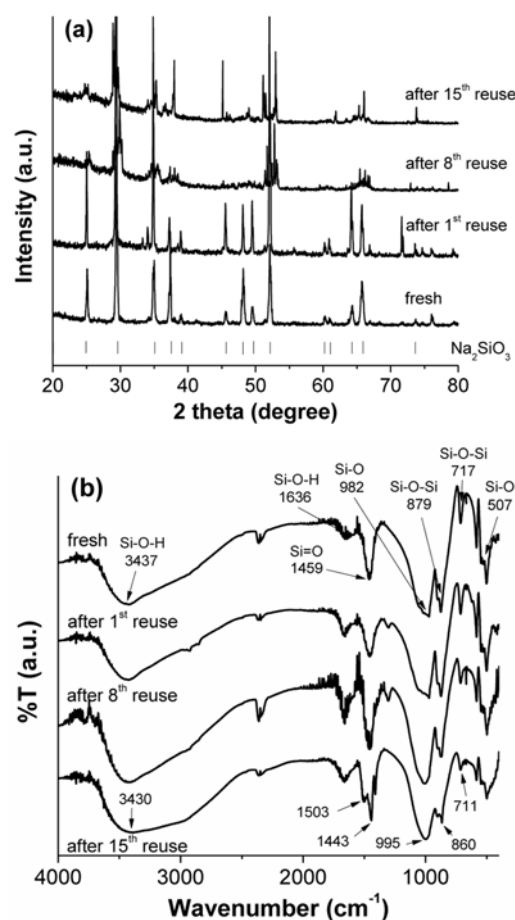


Figure 1. (a) powder XRD patterns and (b) IR spectra of the catalysts (fresh, after 1st, 8th and 15th reuse).

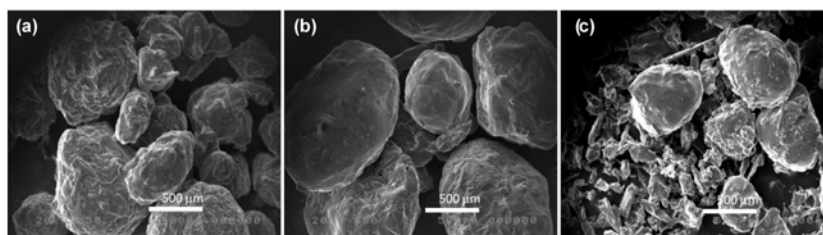


Figure 2. SEM images of the catalysts (a) fresh, (b) after 4th reuse and (c) after 15th reuse.

Table 1. The elemental compositions of the fresh and reused catalysts.

Elements	Mass (%) in catalyst				
	Fresh	after 1 st reuse	after 3 rd reuse	after 7 th reuse	after 15 th reuse
Na	30.07	30.04	29.99	29.96	29.77
Mg	0.30	0.51	0.20	0.51	0.52
Al	0.15	0.05	0.14	0.14	0.14
Si	27.44	27.33	27.51	27.29	27.40
O	41.98	42.01	42.07	42.01	42.07
other	0.06	0.06	0.09	0.09	0.10

3.2 Effect of Transesterification Process Parameters

Disodium metasilicate granules in the range of 0.5-11 wt.% of oil were used as catalysts to investigate the effect of the catalyst content on transesterification of palm oil to biodiesel. It is found that under the conditions: methanol/oil molar ratio of 9:1, reaction temperature of 65 °C, stirring rate of 200 rpm, reaction time of 40 min, the yield of FAME increases from about 12% to 96% as the catalyst content is increased from 0.5 wt.% to 7 wt.% (Figure 3a). However, there is no significant increase in the yield of biodiesel when the catalyst content increased from 7 wt.% to 11 wt.%. Taking into account the yield and the cost, catalyst contents of 7 wt.% and 9 wt.% are chosen for optimization of transesterification of palm oil.

The methanol to oil ratio is one of the most important factors affecting the yield of biodiesel and required to be optimized for each catalytic system. Though stoichiometric ratio needs three molar of methanol for each mole of oil (triglyceride), the base catalyzed transesterification is normally carried out with an extra amount of methanol in order to shift the equilibrium towards the direction of FAME by endorsing the creation of methoxide species on the catalyst surface [6, 13, 14]. The reactions performed with the catalyst contents of

7 wt.% and 9 wt.% and methanol/oil molar ratios of 7.5:1 to 10.5:1 indicate that the conversion of palm oil to FAME increases with increasing of molar ratio of methanol to oil. As shown in Figure 3b, the optimal catalyst content and methanol/oil ratio is determined to be 9 wt.% and 9:1, respectively. The higher molar ratio of methanol to oil of 10.5:1 does not help the transesterification. It is considered that the glycerol would largely dissolve in excessive methanol and then impede the reaction of methanol with oil and catalyst.

The effect of temperature on the transesterification of palm oil was studied by carrying out the reaction at different temperatures (room temperature, 50, 60, 65 and 70 °C). The rate of transesterification and yield of FAME increases with increasing reaction temperatures from room temperature to 65 °C, reaching over 96% of FAME at 65 °C and reaction time of 40 min (Figure 3c). As the transesterification reaction by using heterogeneous catalyst, the equilibrium constant of the reaction is generally influenced by temperature. Consequently, the reaction temperature increase an equilibrium rate is reached when compared with low temperature. However, at 70 °C which is above the boiling point of methanol (64.7 °C at 1 atm), methanol vaporized and caused a problem involving the three

phase interfaces namely methanol as gas phase, palm oil as liquid phase and disodium metasilicate granules catalyst as solid phase resulted in the slightly decreased biodiesel yield [15]. Running the reaction at above the optimal temperature of 65 °C results in a significant decrease in the rate of transesterification and the conversion of palm oil. This is expected due to the temperature dependent kinetic of the transesterification and also, in the latter case, due to methanol evaporation reducing the effective methanol to oil molar ratio around the catalyst [4, 14].

The rate of mixing of the reactants also plays an important role in transesterification since oil, methanol and disodium metasilicate granules are immiscible. It is, therefore, necessary to stir the reaction mixture to enhance the contact between oil and methanol

on a surface of the catalyst. The effect of stirring speed on the yield of FAME was investigated by stirring the reaction mixture at different rates (0, 100, 200 and 300 rpm). The rate of transesterification increases as the mixing speed increased (Figure 3d). A high stirring rate is a mass transfer of reactant molecules into the active surface of the catalyst. However, increasing the speed of stirring rate up to 300 rpm does not enhance the biodiesel yield but %FAME slightly decrease because it leads to the loss of methanol [16]. This suggests that the amount of methanol presence in the reaction mixture has more effect on the transesterification than the stirring speed. The complete conversion of oil to biodiesel with the maximal %FAME of over 96% is reached in 40 min by stirring the reaction mixture at 200 rpm.

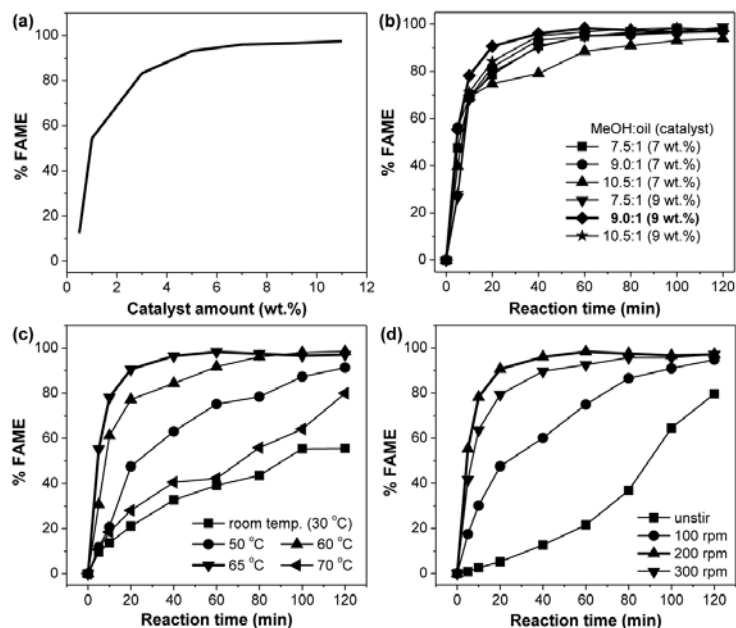


Figure 3. Effects of reaction parameters on the % FAME; **(a)** loading amount of the catalyst (methanol/oil molar ratio of 9:1; 65 °C, stirring rate of 200 rpm and 40 min), **(b)** methanol/oil molar ratio (catalyst content of 7 wt.% and 9 wt.%, 65 °C, stirring rate of 200 rpm), **(c)** reaction temperature (catalyst content of 9 wt.%, methanol/oil molar ratio of 9:1; stirring rate of 200 rpm) and **(d)** stirring rate (catalyst content of 9 wt.%, methanol/oil molar ratio of 9:1, and 65 °C).

3.3 Reusing of Catalyst

The reusability of the catalyst is an important factor in the economic applications of the heterogeneous catalysis process for biodiesel production. The reusability of disodium metasilicate granules was checked by reusing the catalyst without any further activation. As depicted in Figure 4a, the catalyst could be reused up to 8 times with no obvious loss in catalyst activity and more than 96% of FAME obtained within 40 min. After that, the catalytic activity of the disodium metasilicate granules is gradually reduced. The biodiesel yield at a reaction time of 40 min is reduced to 52% when the catalyst is reused for 15 times.

In an attempt to prove that such deactivation of the catalyst did not arise for the leakage of an active species (Na) from the catalyst, the quenching and leaching tests were done in which the reaction was performed in the same way. After a 5 min reaction, a hot liquid mixture was transferred carefully to another preheated flask, then the reaction was allowed to proceed under the same conditions and the yield of FAME

was monitored. As illustrated in Figure 4b, it was found that no significant increase in %FAME after the catalyst was removed from the reaction. The slight increase of yield of FAME in the early stage after removing of the catalyst, which reached a constant yield of 56% after 10 min, might come from the reaction of remaining methoxide anion formed during the presence of the catalyst with the triglycerides. This result indicates that the disodium metasilicate granules are the fairly stable catalyst. The origin of deactivation of the catalyst was further analyzed by monitoring the composition of the catalyst changes upon reusing of the catalyst using XRF technique. The results summarized in Table 1 reveal that the Si:Na ratios in the fresh and reused catalysts nearly remain unchanged after being reused for 15 times suggesting that there is no loss of an active species (Na) from the catalyst. The loss in catalytic activity of this catalyst, therefore, might be only due to a damage of the active sites on its surface.

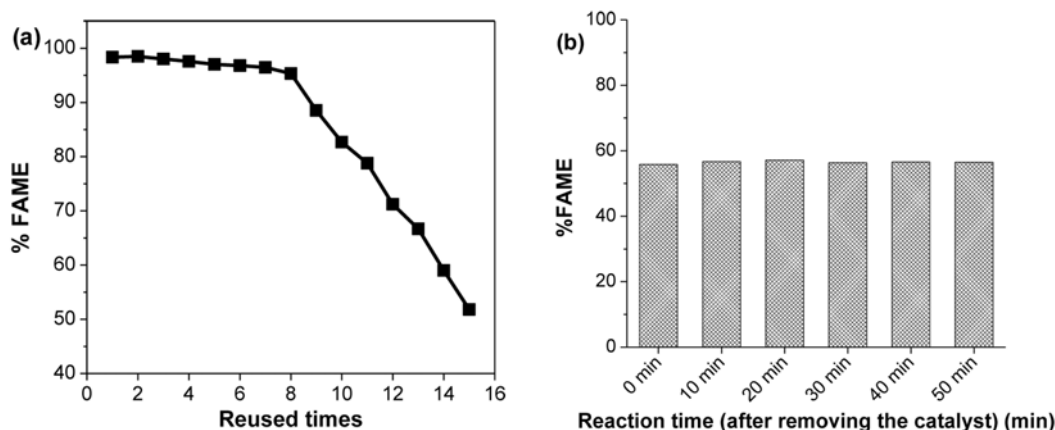


Figure 4. Effects of (a) reuse of the catalyst and (b) reaction time after removing the catalyst at 5 min on the FAME: (catalyst content of 9 wt.%, methanol/oil molar ratio of 9:1; reaction temperature of 65 °C, stirring rate of 200 rpm).

The FT-IR spectra of the catalyst reused for 15 times show that the absorption intensity of the peak at 717 cm^{-1} (Si-O-Si stretching) diminish, indicating that the content of Si-O-Si bonds has decreased. In contrast, the absorption peak at 995 cm^{-1} (Si-O bending) increases, which can be explained by the fact that some Si-O-Si bonds are broken down during the reusing processes of the catalyst (Figure 1b). The absorption band of Si-O-H at 3430 cm^{-1} also broadens indicating that the catalyst adsorbs some water molecules after 15th reuse. These chemical changes in

the catalyst are confirmed by XRD revealing a severe loss of the crystalline phase of Na_2SiO_3 in the catalyst after being reused for 15 times (Figure 1a). The SEM images also show that surface of the catalyst after numbers of reuses become smoother resulting in a decrease of the catalytic surface area (Figure 2b-c). This damage could come from water, glycerol by-product and also impurities in the reactants because the reactants contain a few impurities and the reaction is carried out in an open air.

Table 2. Comparison of transesterification conditions catalyzed by different solid particles.

Catalyst	Particle size	Transesterification parameters						Ref
		FAME	Catalyst content	Temperature (°C)	MeOH:oil molar ratio	Reaction time	Reuse (time)	
Na_2SiO_3	0.3-1mm	97%	9 wt.%	65	9:1	40 min	8	This work
Na_2SiO_3	1-5 μm	99.6%	3 wt.%	60	9:1	60 min	6	[15]
Na_2SiO_3	1-5 μm	100%	3 wt.%	60	7.5:1	60 min	5	[16]
KOH loaded pumice	1.4-3.0nm	>90%	20 wt.%	55	18:1	2 h	5	[18]
KOH loaded palm shell	0.55-0.81nm	98%	30.3 wt.%	64.1	24:1	60 min	2	[19]
Coral fragment	0.5-1.0cm	98%	100 wt.%	65	15:1	2 h	5	[20]
CaO based cockle shell	<1nm	97%	4.9 wt.%	>65	0.45:1 (mass ratio)	3 h	3	[23]
CaO/KF loaded cinder	0.9-2nm	99%	2.1 wt.%	65	12:1	20 min	4	[24]

Therefore, the optimal condition for conversion of palm oil to biodiesel catalyzed by disodium metasilicate granules is catalyst content of 9 wt.%, methanol/oil molar ratio of 9:1, a reaction temperature of $65\text{ }^\circ\text{C}$ with a constant stirring of 200 rpm, yielding FAME of more than 96% in 40 min. The catalyst could be reused for 8 times without loss of catalytic activity. Compared with other reported particulate solid catalysts,

uncalcined disodium metasilicate granules exhibit high catalytic efficiency in terms of both transesterification parameters and reuse of the catalyst as shown in Table 2. The transesterification catalyzed by disodium metasilicate granules give high yield of biodiesel at shorter reaction time, lower molar ratio of methanol/oil and higher number of reuse times of the catalyst compared with KOH loaded pumice [18],

KOH loaded palm shell activated carbon [19], coral fragment [20] and CaO based cockle shell [23]. Although the reaction time and catalyst content for CaO/KF loaded cinder [24] are lower, this catalyst could be reused for only 4 times and shows substantial low stability in water, methanol, and FFA due to the leakage of the loaded K and Ca or the occupation of the active sites. When comparing the results on %FAME from powder Na_2SiO_3 [16] against Na_2SiO_3 granule for transesterification of this work, the result found that powder Na_2SiO_3 catalyst showed lower catalyst loading amount, reaction temperature and methanol to oil molar ratio than Na_2SiO_3 granule for produce biodiesel product. This result can be described that the BET surface area of the powder calcined sodium silicate was $5.91 \text{ m}^2/\text{g}$ which higher than uncalcined disodium metasilicate. Higher surface areas of catalyst are correlated to the strong basic strength and high basicity of the catalysts which both properties usually affect to give higher biodiesel yield.

3.4 Effect of Type of Oils and Water

FFAs and water are usually considered as poisons to both acidic and basic catalyzed homogeneous transesterification as they consume the catalyst in the processes [25, 26]. In order to examine the effect of FFAs on the activity of disodium metasilicate granules in transesterification, many kinds of oils containing various amounts of FFAs including palm oil, lard oil, coconut oil, sunflower oil, soybean oil, rice bran oil, jatropha oil and waste cooking oil were used. As illustrated in Figure 5, it is found that the sources of oils (triglyceride) and the amount of free fatty acid (FFAs) in the oil have no effect on the conversion efficiency of the catalyst. In all cases, yields of FAME exceeding 96% are achieved within 40 min of a reaction time. Moreover, no soap

formation is observed in the transesterification of waste cooking oil (high FFAs oil).

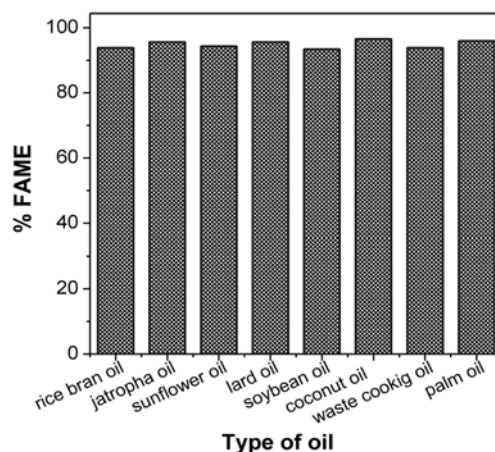


Figure 5. Effects of type of oils on the % FAME when FFAs of palm oil, lard oil, coconut oil, sunflower oil, soybean oil, rice bran oil, jatropha oil and waste cooking oil were 0.28, 0.34, 0.25, 0.23, 0.18, 0.10, 0.45 and 2.25 mg KOH/g of oil, respectively: (catalyst content of 9 wt.%, methanol/oil molar ratio of 9:1; reaction temperature of $65 \text{ }^\circ\text{C}$, stirring rate of 200 rpm and reaction time of 40 min).

The effect of water contamination in oil on the transesterification catalyzed by disodium metasilicate granules was investigated using palm oils with 0-9 wt.% of water. As depicted in Figure 6a, when the water content is in the range of 0-3 wt.%, the yield of FAME is remained as high as 97% at a reaction time of 40 min. This implies that the catalytic mechanism of the heterogeneous process is quite different from that of the traditional homogeneous process. However, with the further addition of water, the yield of biodiesel gradually decreases to 54% when the water content in oil was 9 wt.%. The result indicates that disodium metasilicate granule has a remarkable tolerance to water in the transesterification reaction in

comparison with NaOH and H₂SO₄ [27, 28]. This can be attributed to the fact that H₂O does not change the total basicity of the disodium metasilicate [16].

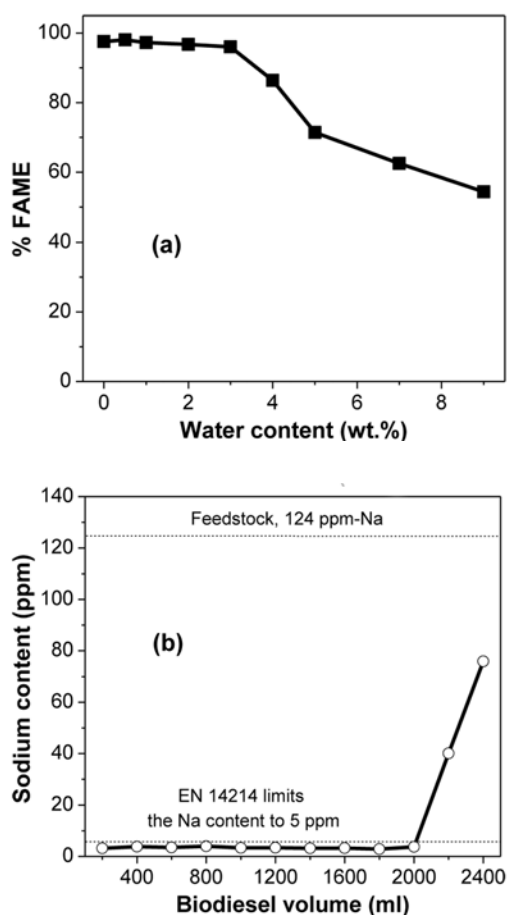


Figure 6. (a) Effect of water contamination on the % FAME: (catalyst content of 9 wt.%, methanol/oil molar ratio of 9:1; reaction temperature of 65 °C, stirring rate of 200 rpm and reaction time 40 min). **(b)** Variation in sodium content of biodiesel treated with sulfonated resin for 6 h.

3.5 Property of the Biodiesel

In the viewpoint of using disodium metasilicate granules in practical industrial biodiesel production, a primary investigation of medium scale biodiesel production from

palm oil (3 L scale) was carried out: catalyst content, 9 wt.%; methanol/oil molar ratio, 9:1; reaction temperature, 65 °C, stirring rate, 200 rpm. Under this condition, transesterification of palm oil progresses slightly slower than 50 mL scale reaction and a complete conversion with a yield of biodiesel over 97% was attained within 50-60 min. However, we consider that with optimum reaction conditions, the transesterification of oil to biodiesel would proceed faster. Moreover, it is essential to note that the solid catalyst can be removed from the reaction mixture by simple filtration. The liquid phase is heated in an oven (70-80 °C) or rotary evaporated to remove the excess methanol, and then settled in a separating funnel. The upper phase consists of biodiesel product (FAME) and the lower phase contains the glycerol by-product. Biodiesel is filtered through a cotton wool filter and corrected without any treatment and cleaning processes.

Fuel properties of the obtained biodiesel were evaluated according to the ASTM methods and compared with other catalysts, and the results are summarized in Table 3. The produced biodiesel has a density of 873 Kg/m³ which are slightly higher than that of diesel fuel (830 Kg/m³) but lower than jatropha oil biodiesel obtained from using acid-base CaO-La₂O₃ catalyst [29]. Referring to EN 14214 standards for bio-auto fuels, the obtained biodiesel is found to be within the standard limits in terms of methyl ester content, density, viscosity, flash point, acid value, total contamination, water content, oxidation stability and ion content (after treatment with the sulfonated resin). Consequently, we judge that the transesterification catalyzed by disodium metasilicate granules can be utilized for biodiesel production with the help of the purification technique by cation-exchange

resin. However, it is essential to prevent the soluble substance from being leached away by modifying the solid base catalyst and the work is now ongoing in our laboratory.

Table 3. Fuel properties of palm biodiesel obtained from the upper phase of the separation without any treatment and cleaning process (Performed by biodiesel testing unit, the National Science and Technology Development Agency, Thailand).

Fuel property	Standard value	This work	Biodiesel from palm oil catalyzed by		
			KOH loaded palm shell [19]	KF/Ca-Al hydrotalcite [30]	K loaded hydrotalcite [31]
Density@ 15°C (Kg m ⁻³)	860-900	873.8	877.2	-	877
Kinematic viscosity@ 40°C (cSt)	3.5-5.0	4.1	5.16	4.37	4.5
Flash point (°C)	>120	184.8	188	150	142
Acid number (mg KOH g ⁻¹ oil)	<0.5	0.086	0.33	0.3	0.2
Water content (%w/w oil)	<0.050	0.045	-	0.039	-
Copper strip corrosion	No. 1	No. 1	-	-	-
Methyl ester content (%)	96.5	97.7	-	99	96.9
Oxidation stability (h)	>6	14.5	-	-	-
Total contamination (ppm)	<24	4	-	-	-
Ion content (ppm g ⁻¹ oil)	5	124 (<3%*)	-	-	-

*after treatment with Dowex ion-exchange resin.

4. CONCLUSION

In summary, we have demonstrated that commercially available disodium metasilicate granules (uncalcined) can be utilized as an efficient heterogeneous solid catalyst for transesterification of many kinds of oils to biodiesel. The reaction under optimum conditions of catalyst content of 9 wt.%; methanol/oil molar ratio of 9:1; reaction temperature of 65 °C with a constant stirring

of 200 rpm yields biodiesel with a FAME exceeding 97% in 40 min. The catalyst can be easily removed from the reaction mixture by simple filtration and can be used several times with consistent activity. Biodiesel product without any cleaning processes shows high quality with fuel properties of the obtained biodiesel meet all EN 14214 standards and the help of the purification technique by cation-exchange resin all soluble ion can be

efficiently removed. The disodium metasilicate presents good catalytic activity, opening the possibility to perform a continuous catalytic process for biodiesel production with batch reactor. The utilization of this catalyst in granules form and the capability to use a residue as cooking oil as inexpensive feedstock would supplementary improve the economic aspect of overall biodiesel production based on this catalyst, producing cost-efficient biodiesel. The catalyst, therefore, exhibits high potential as a solid catalyst for practical, environmentally friendly, and low cost industrial biodiesel production.

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REFERENCES

- [1] Huang R., Cheng J., Qiu Y., Li T., Zhou J. and Cen K., *Energy Convers. Manage.*, 2015; **105**: 791-797. DOI 10.1016/j.enconman.2015.08.036.
- [2] Onoji E.S., Iyuke S.E., Igbafe A.I. and Nkazi D.B., *Energy Convers. Manage.*, 2016; **110**: 125-134. DOI 10.1016/j.enconman.2015.12.002.
- [3] Mathimani T., Uma L. and Prabakaran D., *Renew. Energy*, 2015; **81**: 523-533. DOI 10.1016/j.renene.2015.03.059.
- [4] Roschat W., Siritanon T., Yoosuk B. and Promarak V., *Energy Convers. Manage.*, 2016; **119**: 453-462. DOI 10.1016/j.enconman.2016.04.071.
- [5] Roschat W., Siritanon T., Yoosuk B., Sudyoosuk T. and Promarak V., *Renew. Energy*, 2017; **101**: 937-944. DOI 10.1016/j.renene.2016.09.057.
- [6] Dai Y.M., Chen K.T. and Chen C.C., *Chem. Eng. J.*, 2014; **250**: 267-273. DOI 10.1016/j.cej.2014.04.031.
- [7] Mahesh S.E., Ramanathan A., Begum K.M.M.S. and Narayanan A., *Energy Convers. Manage.*, 2015; **91**: 442-450. DOI 10.1016/j.enconman.2014.12.031.
- [8] Lee S.L., Wong Y.C., Tan Y.P. and Yew S.Y., *Energy Convers. Manage.*, 2015; **93**: 282-288. DOI 10.1016/j.enconman.2014.12.067
- [9] Kouzu M. and Hidaka J., *Fuel*, 2012; **93**: 1-12. DOI 10.1016/j.fuel.2011.09.015.
- [10] Soetaredjo F.E., Ayucitra A., Ismadji S. and Maukar A.L., *Appl. Clay Sci.*, 2011; **53**: 341-346. DOI 10.1016/j.clay.2010.12.018.
- [11] Silva C.C.C.M., Ribeiro N.F.P., Souza M.M.V.M. and Aranda D.A.G., *Fuel Process. Technol.*, 2010; **91**: 205-210. DOI 10.1016/j.fuproc.2009.09.019.
- [12] Carrero A., Vicente G., Rodriguez R., Peso M. and Linares G.L., *Catal. Today*, 2011; **167**: 148-153. DOI 10.1016/j.cattod.2010.11.058.
- [13] Wang J.X., Chen K.T., Wu J.S., Wang P.H., Huang S.T. and Chen C.C., *Fuel Process. Technol.*, 2012; **104**: 167-173. DOI 10.1016/j.fuproc.2012.05.009.
- [14] Wang J.X., Chen K.T., Wen B.Z., Liao Y.H.B. and Chen C.C., *J. Taiwan Inst. Chem. Eng.*, 2012; **43**: 215-219. DOI 10.1016/j.jtice.2011.08.002.
- [15] Long Y.D., Guo F., Fang Z., Tian X.F., Jiang L.Q. and Zhang F., *Bioresour. Technol.*, 2011; **102**: 6884-6886. DOI 10.1016/j.biortech.2011.04.007.
- [16] Guo F., Peng Z.G., Dai J.Y. and Xiu Z.L., *Fuel Process. Technol.*, 2010; **91**: 322-328. DOI 10.1016/j.fuproc.2009.11.003.

- [17] Guo F, Wei N.N., Xiu Z.L. and Fang Z., *Fuel*, 2012; **93**: 468-472. DOI 10.1016/j.fuel.2011.08.064.
- [18] Borges M.E., Diaz L., Alvarez-Galvan M.C. and Brito A., *Appl. Catal. B-Environ.*, 2011; **102**: 310-315. DOI 10.1016/j.apcatb.2010.12.018.
- [19] Baroutian S., Aroua M.K., Raman A.A.A. and Sulaiman N.M.N., *Fuel Process. Technol.*, 2010; **91**: 1378-1385. DOI 10.1016/j.fuproc.2010.05.009.
- [20] Roschat W., Kacha M., Yoosuk B., Sudyoadsuk T. and Promarak V., *Fuel*, 2012; **98**: 194-202. DOI 10.1016/j.fuel.2012.04.009.
- [21] Lianhua L., Pengmei L., Wen L., Zhongming W. and Zhenhong Y., *Biomass Bioeng.*, 2010; **34**: 496-499. DOI 10.1016/j.biombioe.2009.12.014.
- [22] Kouzu M., Yamanaka S., Hidaka J. and Tsunomori M., *Appl. Catal. A-Gen.*, 2009; **355**: 94-99. DOI 10.1016/j.apcata.2008.12.003.
- [23] Boey P.L., Maniam G.P., Hamid S.A. and Ali D.M.H., *Fuel*, 2011; **90**: 2353-2385. DOI 10.1016/j.fuel.2011.03.002.
- [24] Liu H., Su L., Shao Y. and Zou L., *Fuel*, 2012; **97**: 651-657. DOI 10.1016/j.fuel.2012.02.002.
- [25] Atadashi I.M., Aroua M.K., Abdul Aziz A.R. and Sulaiman M.N.M., *Renew. Sustain. Energ. Rev.*, 2012; **16**: 3456-3470. DOI 10.1016/j.rser.2012.03.004.
- [26] Fadhil A.B., Aziz A.M. and Al-Tamer M.H., *Energy Convers. Manage.*, 2016; **108**: 255-265. DOI 10.1016/j.enconman.2015.11.013.
- [27] Canakci M. and Gerpen J.V., *Trans Am. Soc. Agric. Eng.*, 1999; **42**: 1203-1210. 1999 American Society of Agricultural Engineers 0001-2351 / 99 / 4205-1203.
- [28] Roschat W., Siritanon T., Yoosuk B. and Promarak V., *Energy Convers. Manage.*, 2016; **108**: 459-467. DOI 10.1016/j.enconman.2015.11.036.
- [29] Lee H.V., Juan J.C. and Taufiq-Yap Y.H., *Renew. Energy*, 2015; **74**: 124-132. DOI 10.1016/j.renene.2014.07.017.
- [30] Gao L., Teng G., Xiao G. and Wei R., *Biomass Bioeng.*, 2010; **34**: 1283-1288. DOI 10.1016/j.biombioe.2010.03.023.
- [31] Trakarnpruk W. and Porntangjitlikit S., *Renew. Energy*, 2008; **33**: 1558-1563. DOI 10.1016/j.renene.2007.08.003.