Co-production of biodiesel and hydrogen from rapeseed and *Jatropha* oils with sodium silicate and Ni catalysts

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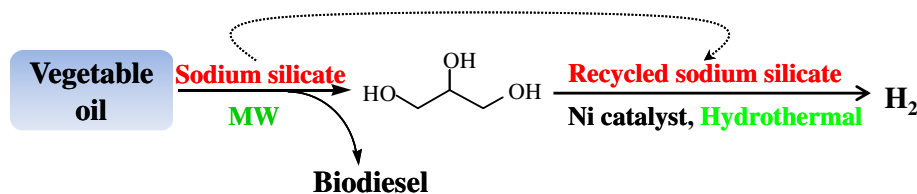[b] University of Science and Technology of China, School of Life Science, 443 Huangshan Road, Hefei, Anhui Province 230027, China

HIGHLIGHTS

► Calcined sodium silicate was used for microwave-irradiated transesterification.
► Biodiesel yield of 95.8% was achieved from rapeseed oil at 400 W in 5 min.
► Biodiesel yield of 92.8% was achieved from *Jatropha* oil at 400 W in 5 min.
► The fourth cycled catalyst was utilized to gasify by-product glycerol at 350 °C.
► H_2 yield of 82.8% (purity 73.6%) was achieved with the used and Ni catalysts.

GRAPHICAL ABSTRACT

Sodium silicate was an effective catalyst for the microwave-irradiated production of biodiesel and hydrothermal production of hydrogen from by-product glycerol combined with Ni catalyst.

ABSTRACT

Calcined sodium silicate was used to rapidly catalyze the transesterification of rapeseed and *Jatropha* oils to biodiesel under microwave irradiation. Biodiesel yields of 95.8% and 92.8% were achieved from rapeseed and *Jatropha* oils, respectively (microwave power of 400 W, methanol/oil molar ratio of 11/1, catalyst amount of 4 wt.% and reaction time of 5 min). The catalyst was recycled, and biodiesel yield reduced to 83.6% at the fourth cycle. Fresh and reused sodium silicate catalysts were charaterized by BET (Brunauer, Emmett and Teller) surface area, XRD (X-ray diffraction), SEM (scanning electron microscope) and CO_2-TPD (temperature programmed desorption), and it was found that the agglomeration and leaching of basic species resulted in the loss of catalytic activity. The reused catalyst was collected and utilized for hydrothermal gasification of glycerol to hydrogen. A maximum H_2 yield of 82.8% with a concentration of 73.6% was obtained in the presence of the fourth-cycled sodium silicate and Ni catalysts at 350 °C. Sodium silicate was an effective catalyst for the microwave-irradiated production of biodiesel and hydrothermal production of hydrogen from by-product glycerol combined with Ni catalyst.

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1. Introduction

As fossil fuel resources are running out, biodiesel, as a promising alternative fuel, is receiving extensive attention because it is biodegradable and renewable, and suitable for use in existing vehicles and distribution infrastructures [1]. Biodiesel production is a simple catalytic transesterification process of vegetable oils (e.g., rapeseed and *Jatropha* oils) or animal fats to fatty acid methyl esters (FAMEs) [2,3]. Generally, homogeneous catalysts such as sodium hydroxide are used for its production [4]. However, the removal of these homogeneous catalysts is difficult, which leads to pollution and high production cost. Moreover, use of homogeneous base catalysts will result in the saponification of biodiesel and the decrease of biodiesel yield when high acid value (AV) crude oils are used [4,5]. Compared with

homogeneous catalysts, heterogeneous ones have significant advantages in catalytic transesterification, such as easy separation for recycles, simple purification steps without neutralization process [6] and less corrosion to reactors. However, their major drawbacks are severe reaction conditions (e.g., high reaction temperatures and long reaction times) [7], moisture sensitivity [8] and high cost for preparation [9]. Besides, they will be gradually deactivated due to the leaching of active species during cycles. On the other hand, both basic homogeneous and heterogeneous catalysts are not suitable for high AV feedstocks because of the formation of soaps. So, such feedstocks (e.g., Jatropha oil) need to be acid-pretreated to remove free fatty acids (FFAs) before base-catalytic transesterification [10]. In all, low-cost, high-active and stable heterogeneous catalysts still need to be developed. Previous studies showed that sodium silicate was highly-active and recyclable with little deactivation as a heterogeneous catalyst in converting vegetable oils to biodiesel [11,12].

Recently, microwave irradiation was used in the transesterification of vegetable oils to biodiesel [13–15], because of its high product selectivity, significant energy-saving and drastic reaction acceleration as compared with conventional heating systems [16–18]. Therefore, the aim of this study was to examine the effect of sodium silicate on the transesterification of rapeseed oil and non-edible Jatropha oil under microwave irradiation conditions. Reaction process was examined and the catalyst was recycled to test its reusability.

On the other hand, as biodiesel output increases, glycerol, the main by-product (approximately 10 wt.% in products) rises too. The overproduction resulted in its market price dropping sharply [19]. The conversion of excessive glycerol to value-added chemicals and biofuels becomes crucially significant for biodiesel industry. Hydrogen, widely used in fuel cells nowadays [20], can be produced from catalytic gasification of glycerol according to the following equation [21]:

$$C_3H_8O_3 + 3H_2O \overset{Cat.}{\rightarrow} 3CO_2 + 7H_2 \qquad (1)$$

Hydrothermal gasification is a promising technology to covert biomass including glycerol, to hydrogen by thermochemical reaction [Eq. (1)] using the unique properties of subcritical water [<critical point of water (CP): 374 °C, 22.1 MPa] or supercritical water (SCW > CP) [22,23]. Subcritical hydrothermal gasification operates at lower temperatures (e.g., 200–350 °C) and under sufficient pressures to maintain a liquid phase [24]. Addition of catalysts is always required under subcritical hydrothermal conditions [22]. Generally, soluble alkali, such as NaOH, KOH, Na$_2$CO$_3$, K$_2$CO$_3$ and NaHCO$_3$ [25–27], and heterogeneous catalysts including Pt, Ru, Co and Ni [28–30], are used to promote biomass hydrothermal liquefaction and gasification. Ni catalysts are mostly utilized due to their lower cost as compared with noble metal catalysts. Catalytic hydrothermal gasification of biomass in the presence of Ni and NaOH catalysts was studied before [31], but no work was reported about using sodium silicate to gasify glycerol. Therefore, in order to make full use of the deactivated sodium silicate from biodiesel production, another objective of this work was to study hydrogen generation from glycerol in subcritical water with the reused sodium silicate and Ni catalyst. In addition, the effects of combination of Ni catalyst and sodium silicate on hydrogen production were also examined.

2. Materials and methods

2.1. Materials

Sodium silicate nonahydrate (Na$_2$SiO$_3$·9H$_2$O, 19.3–22.8 wt.% Na$_2$O, the weight ratio of Na$_2$O/SiO$_2$ = 1.03 ± 0.03) and methanol (99.5%) were purchased from Xilong Chemical Corp., Shantou, China. Sodium silicate was firstly dehydrated at 200 °C for 20 min, then calcined at 400 °C for 2 h, and passed through a 100-mesh sieve as catalyst for biodiesel production. Ni catalyst (66 ± 5% Ni on silica–alumina, powder <150 μm) was purchased from Alfa Aesar (Tianjin). High-purified glycerol (99.9%) and heptadecanoic acid methyl ester (HDAME) were obtained from Sigma–Aldrich (Shanghai). Crude glycerol was from the biodiesel production. Refined rapeseed oil was obtained from a supermarket. Crude Jatropha oil with high AV (12.8 mg KOH/g) was obtained from Xishuangbanna Tropical Botanical Garden, Menglun, Yunnan. The crude Jatropha oil was acid-pretreated to remove the excessive FFAs. First, 200-mL Jatropha oil, 40-mL methanol and 4-mL sulfuric acid (98.0%) were added to a three-neck flask with a water-cooled condenser. The mixture was heated to 45 °C and held for 1.5 h with ultrasonic radiation and vigorous stirring. After pretreatment, the mixture was moved to a separating funnel to separate oil. The oil was washed three times with water. After dried using anhydrous sodium sulfate and centrifuged, the pretreated Jatropha oil with low AV (1.1 mg KOH/g) was obtained. Deionized water was used in all experiments.

2.2. Catalyst characterization

Fresh and reused sodium silicate catalysts were characterized by several techniques. Their surface areas were measured with a Brunauer, Emmett and Teller (BET) analyzer (Tristar II 3020, Micromeritics Instruments, Atlanta, GA). The morphology was examined using a scanning electron microscope (SEM; Quanta 200, Hillsboro, OR). X-ray diffraction (XRD) analysis was conducted using a Rigaku TTR3 (Rigaku Co., Tokyo) with a Cu Kα radiation (40 kV and 200 mA). The basicity of the samples was evaluated by CO$_2$ temperature programmed desorption (CO$_2$-TPD) using a ChemBET Pulsar TPR/TPD (Quanta, Hillsboro, OR). Catalyst powder (0.1 g) was pretreated in He flow (50 mL/min) at 150 °C for 0.5 h. Then it was flushed with pure CO$_2$ gas (50 mL/min) at 100 °C for 1 h. After that, the sample was cooled to room temperature and subsequently desorbed by heating to 900 °C at a rate of 10 °C/min in He flow (50 mL/min). And the samples were calibrated with a pure CO$_2$ gas.

2.3. Experimental procedure

2.3.1. Biodiesel production

The transesterification of rapeseed and Jatropha oils to biodiesel was carried out in a commercial microwave apparatus (MC8S-1000, Nanjing Huiyan Microwave Co., Ltd., Nanjing). A Teflon reactor (60 mL) fitted with a thermocouple and a magnetic stirrer was used for the microwave-assisted transesterification. In a typical experiment, 15-g oil, and desired amounts of methanol and catalyst were added to the reactor. Then, it was closed and put into the microwave apparatus under continuous microwave-heating with magnetic stirring. After one batch of experiment, the product mixture was removed to a tube and centrifuged at 15,000 rpm for 10 min with a centrifugal machine (3–30 K, SIGMA, Osterode am Harz, Germany), and three layers were formed (Fig. 1A-b and C-b). The upper layer (crude biodiesel) was sampled by a pipettor for gas chromatography (GC) analysis. The middle layer (glycerol and methanol) was distilled to remove methanol, and then crude glycerol was obtained for gasification experiments. The bottom solid layer (catalyst) was recovered for recycles.

2.3.2. Hydrothermal gasification of glycerol

Subcritical water gasification of glycerol was conducted in a Hastc alloy (HC-276) autoclave (25 mL with 17 mL headspace, Parr Instrument Co., Moline, IL). The autoclave has a maximum
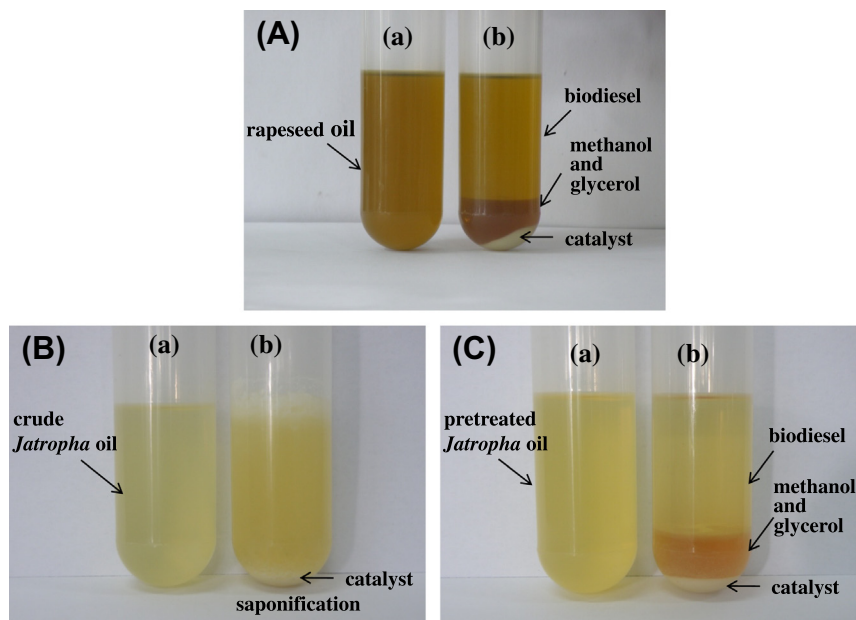
Fig. 1. Images of (a) oils, and (b) their products (biodiesel and glycerol) and catalyst after transesterification and centrifugation for (A) rapeseed oil, (B) crude *Jatropha* oil, and (C) pretreated *Jatropha* oil.

operating temperature and pressure of 500 °C and 34.5 MPa, respectively. In each experiment, 10-mL water, glycerol (3 mmol) and sodium silicate (40–200 wt.% based on glycerol)/Ni catalyst (5–80 wt.% based on glycerol) were added to the autoclave and sealed. Then, nitrogen (99.999% purity) was added and purged for three times to remove air, and an initial nitrogen pressure of 12 MPa was used to avoid water vaporization during gasification. The autoclave was heated at a heating rate of 11 °C/min from room temperature to 350 °C and 18.6–19.9 MPa with a magnetic stirring rate of 250 rpm, then it was immediately cooled down to room temperature by an electric fan. After reaction, gas volume (about 6600–7114 mL) was measured using a wet gas meter (LMF-1, Shanghai A.K. Instruments Co., Ltd.), where water was saturated by NaHCO$_3$ to avoid absorption of CO$_2$. Gas was collected in a gas bag for GC analysis. The aqueous sample was collected and centrifuged for further analyses.

2.4. Product analysis

Biodiesel was analyzed by GC (GC-2014, Shimadzu, Kyoto) equipped with a capillary column Rtx-Wax (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID). Helium (99.999% purity) was used as carrier gas. The temperatures of injector, column oven and detector were 260, 220 and 280 °C, respectively. HDAME was used as internal standard for quantitative analysis. According to the areas of FAMEs and HDAME in GC graph, and the weights of HDAME and crude biodiesel measured, biodiesel yield was calculated by the following definition [15]:

Biodiesel yield (wt.%)

$$= \frac{(\text{area of FAMEs/area of HDAME}) \times \text{weight of HDAME}}{\text{weight of crude biodiesel}} \times 100\%$$

Produced gases (H$_2$, CO$_2$, C$_2$H$_6$, C$_2$H$_4$ and C$_2$H$_2$) were analyzed by GC (7820A, Agilent, Palo Alto, CA) with a packed column Porapak N ((3 ft × 1/8 in.) and a thermal conductivity detector (TCD). CH$_4$ and CO were analyzed by the same GC with a packed column Molecular Sieve 5A (6 ft × 1/8 in.) and a TCD. Helium (99.999% purity) was used as carrier gas. Gas sample was calibrated with a

standard gas mixture (9.082% H$_2$, 6.063% CO, 6.013% CH$_4$, 6.029% CO$_2$, 0.100% C$_2$H$_6$, 0.106% C$_2$H$_4$ and 0.100% C$_2$H$_2$; v/v) (Yunnan Messer Co., Ltd., Kunming). Hydrogen yield was defined as:

$$\text{Hydrogen yield (mol.\%)} = \frac{H_2 \text{moles produced}}{H_2 \text{moles in glycerol}} \times 100\%$$

Inorganic carbon (IC) and total organic carbon (TOC) of aqueous products were measured with a TOC analyzer (TOC-5000A, Shimadzu). Glycerol was determined with a high performance liquid chromatography (HPLC; LC-20A, Shimadzu) fitted with an HPX-87H column and a reflex index (RI) detector.

3. Results and discussion

3.1. Biodiesel production

The effects of variables, i.e., microwave power (100–500 W), methanol/oil molar ratio (7/1–15/1) and catalyst amount (1–5 wt.%) on the transesterification of rapeseed oil by continuous microwave-heating were studied to obtain reaction conditions. *Jatropha* oil was then used for the production of biodiesel under the obtained conditions. Furthermore, catalyst was recycled to determine its stability.

3.1.1. Effects of microwave power

At given conditions (9/1 methanol/oil molar ratio and 3 wt.% catalyst) based on the previous work [12], biodiesel was synthesized at a constant microwave power (100, 200, 300, 400 and 500 W) for 5 min. Temperature profiles with time (15-g oil, methanol/oil molar ratio 9/1) at different microwave powers are given in Fig. 2 (curves 1–5: <201 °C). The measured temperature at initial stage for 500 W microwave-heating (<89 s, curve 5 vs. 4) was lower than that for 400 W, which was most likely caused by thermocouples contact problem of the instrument itself. Fig. 3a shows the effect of microwave power on biodiesel yield. Biodiesel yield jumped from 17.5% to 75.6% when microwave power increased from 100 to 300 W, and reached to 83.1% at 400 W. These results showed that strong microwave irradiation accelerated the transesterification process, and high biodiesel yield was achieved within a short time.
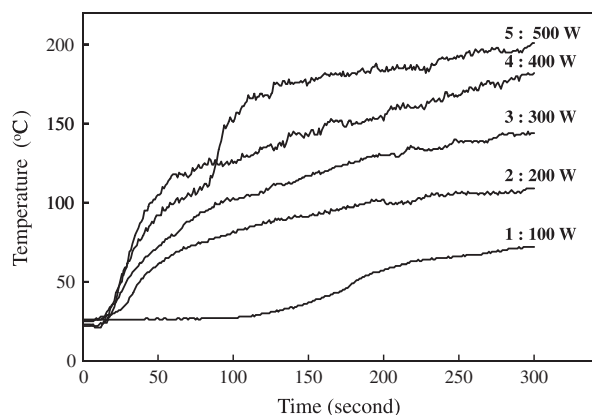
Fig. 2. Temperature profiles with time (15-g oil, methanol/oil molar ratio 9/1) at different microwave powers (100–500 W).

Microwave irradiation enhances the molecular friction and collision of reactants which give rise to intense localized heating to promote reactions. On the other hand, microwave provides immediate agitation and rapid mixing of reactants to accelerate reactions as compared with conventional thermal heatings [32]. Considering biodiesel yield and production cost, microwave at 400 W was chosen for the subsequent experiments.

3.1.2. Effects of methanol/oil molar ratio

Five different methanol/oil molar ratios, namely 7/1, 9/1, 11/1, 13/1 and 15/1, were used for biodiesel production at given conditions (microwave power 400 W, catalyst amount 3 wt.% and reaction time 5 min). Biodiesel yield increased with methanol/oil molar ratio, and reached 90.5% at the molar ratio of 11/1. As the molar ratio rose further to 15/1, biodiesel yield increased slightly to 93.2% (Fig. 3b). Adding more methanol can promote reactions, however, excessive methanol will increase glycerol solubility in oil to enhance reverse reactions, and form emulsion that will cause

the difficulty in biodiesel separation [33]. Therefore, the methanol/oil molar ratio of 11/1 was selected.

3.1.3. Effects of catalyst amount

The effect of catalyst amount (1–5 wt.%) on the transesterification reaction was studied at given conditions (microwave power 400 W, methanol/oil molar ratio 11/1 and reaction time 5 min). Biodiesel yield increased from 33.1% to 95.8% as the catalyst rose from 1 to 4 wt.% (Fig. 3c). When the catalyst rose further to 5 wt.%, however, biodiesel yield increased slightly to 96.9%. These results showed that 4 wt.% catalyst was suitable for the transesterification reaction under the given conditions.

In this study, each variable was optimized one by one under given conditions. Orthogonal or other statistic methods [34,35] will be used in experimental design in our next study. Therefore, the conditions were chosen as: methanol/oil molar ratio of 11/1, catalyst amount of 4 wt.%, microwave power of 400 W and reaction time of 5 min, under which biodiesel yield of 95.8% was achieved. The results demonstrated that microwave-assisted transesterification significantly increased reaction rate and drastically reduced reaction time to 5 min from 60 min for the conventional heating [11].

3.1.4. Jatropha biodiesel production

Under the above conditions (11/1 methanol/oil molar ratio, 4 wt.% catalyst, 400 W microwave power and 5 min reaction time), *Jatropha* oil was used to produce biodiesel. Only 11.6% biodiesel yield without glycerol layer formation was obtained if crude *Jatropha* oil (AV of 12.8 mg KOH/g) was used as raw material due to severe saponification (Fig. 1B-b). However, when pretreated *Jatropha* oil (AV of 1.1 mg KOH/g) was used, a high biodiesel yield of 92.8% was achieved with a reddish glycerol layer (Fig. 1C-b).

3.1.5. Recycle experiments

The stability and reusability of catalysts are vital for their commercialization. Consequently, recycle studies were carried out under the conditions (i.e., methanol/oil molar ratio of 11/1, catalyst amount of 4 wt.%, microwave power of 400 W and reaction time
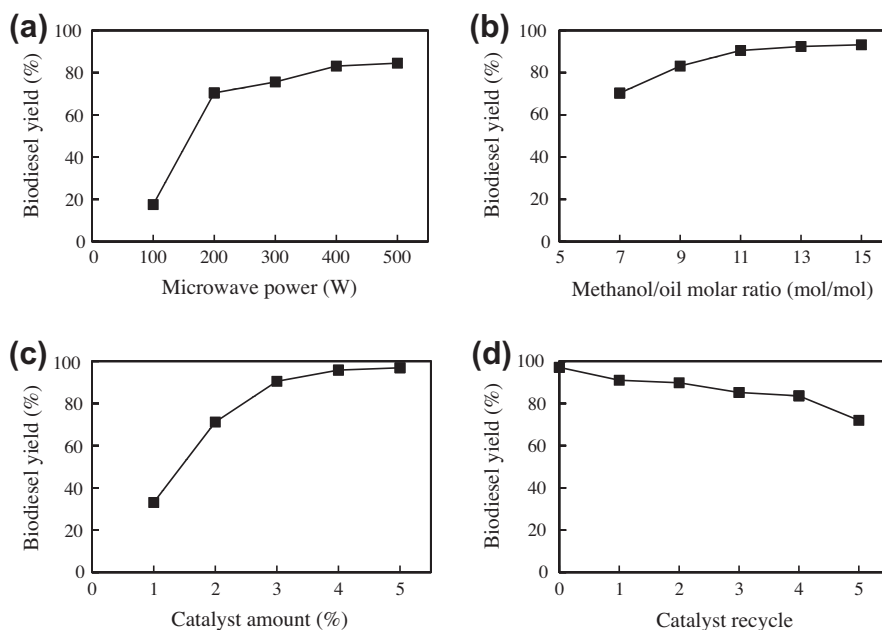

Fig. 3. Effects of variables on the transesterification of rapeseed oil: (a) microwave power (9/1 methanol/oil molar ratio, 3 wt.% catalyst, and 5 min reaction time), (b) methanol/oil molar ratio (400 W microwave power, 3 wt.% catalyst, and 5 min reaction time), (c) catalyst amount (400 W microwave power, 11/1 methanol/oil molar ratio, and 5 min reaction time), and (d) catalyst recycle (400 W microwave power, 11/1 methanol/oil molar ratio, 4 wt.% catalyst, and 5 min reaction time).

of 5 min). After each reaction, the solid catalyst was recovered by centrifugation. Then, it was washed with methanol under ultrasonic for 10 min, and dried at 80 °C for 2 h before the next batch of experiment. Biodiesel yield was more than 80.0% for the first four recycles (Fig. 3d). However, a significant catalytic loss was found at the fifth cycle with only 72.0% biodiesel yield.

After four recycles, the reused catalyst was collected. Both fresh and fourth-cycled sodium silicate catalysts were characterized. XRD patterns (Fig. 4) show that the structure of sodium silicate was assigned to Na_2SiO_3. The identical intensity of diffraction peaks indicated that the crystal phase of catalysts changed little. BET surface area of the fresh and fourth-cycled catalysts was 2.40 and 2.96 m^2/g, respectively. The slight change had little effect on the loss of activity. SEM images (Fig. 5) show that the fourth-cycled catalyst agglomerated to large blocks leading to the loss of activity due to its less contact to reactants. The agglomeration was possibly caused by the absorption of trace water which might come from methanol (99.5%) and crude oil. In the presence of small amount of water, some Si—O—Si or Si—O—Na bonds were broken into Si—O—H bonds and formed H_4SiO_4 monomers which can conglutinate the catalyst [36]. CO_2-TPD measurements were carried out to determine the base strength of the catalysts (Fig. 6). The catalysts exhibited three desorption ranges: weak (200–500 °C), medium (500–700 °C) and strong (700–900 °C) basic sites. The basicity (at 700–900 °C region) of the fresh catalyst was reduced from 0.32 to 0.10 mmol/g after four cycles, indicating that leaching of strong basic species into methanol occurred in reaction and washing processes [36]. In order to fully utilize the deactivated catalyst, it was
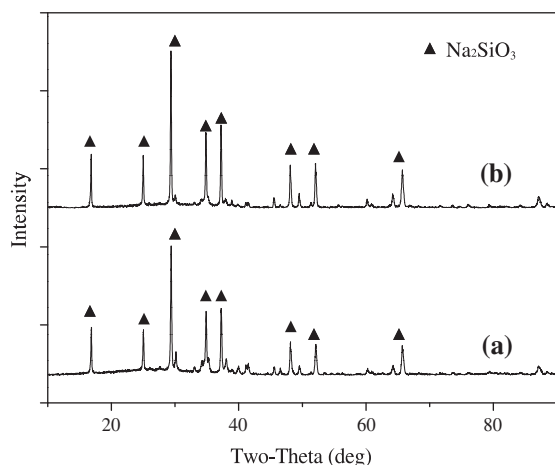

Fig. 6. CO_2-TPD profiles of sodium silicate: (a) fresh and (b) fourth-cycled.

collected to catalyze subsequent hydrothermal gasification of by-product glycerol to hydrogen.

3.2. Hydrothermal gasification

3.2.1. Pure glycerol as raw material

Pure glycerol sample (3 mmol) was subjected to the hydrothermal gasification process in the presence of sodium silicate/Ni catalyst, respectively. When only sodium silicate was added, hydrogen yield was very low. So, Ni catalyst was used in all gasification experiments. Fig. 7 shows the separate effects of Ni and sodium silicate as well as Ni catalyst on the yield of produced gases including H_2, CO, CH_4 and CO_2. It should be noted that other gas species, such as C_2H_2, C_2H_4 and C_2H_6, were not shown in the figure because of their ignorable concentration levels (each C_2 gas concentration <500 ppm). In Fig. 7a with a fixed amount of Ni (40 wt.%) and different amounts of sodium silicate catalyst, hydrogen increased from 8.79% to 10.22% mmol (or concentration from 51.9% to 86.2%) as sodium silicate increased from 40 to 160 wt.%. At the same time, CO_2 gradually decreased from 4.29 to 0.21 mmol (or concentration from 25.3% to 1.8%) due to its dissolution into the basic hydrothermal solution. Actually, the process of hydration of sodium silicate proceeded in the following three steps [37]:

$$\equiv Si-O-Na + H_2O \rightarrow \equiv Si-O-H + NaOH \qquad (2)$$

$$\equiv Si-O-Si\equiv + [OH^-] \rightarrow \equiv Si-O-H + \equiv Si-O^- \qquad (3)$$

$$\equiv Si-O^- + H_2O \rightarrow \equiv Si-O-H + [OH^-] \qquad (4)$$

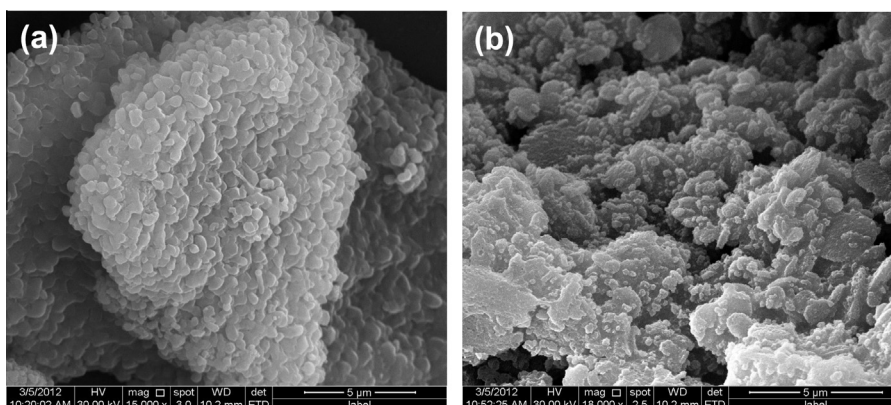**Fig. 4.** XRD patterns of sodium silicate: (a) fresh and (b) fourth-cycled.

Fig. 5. SEM images of sodium silicate: (a) fresh and (b) fourth-cycled.
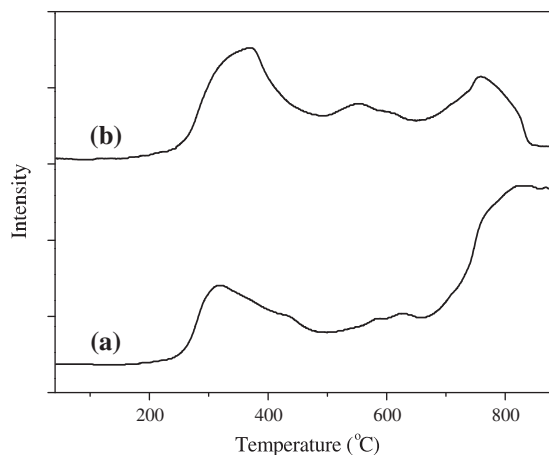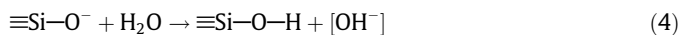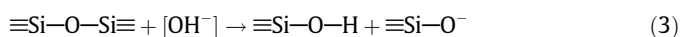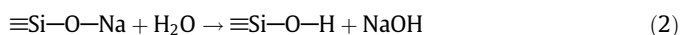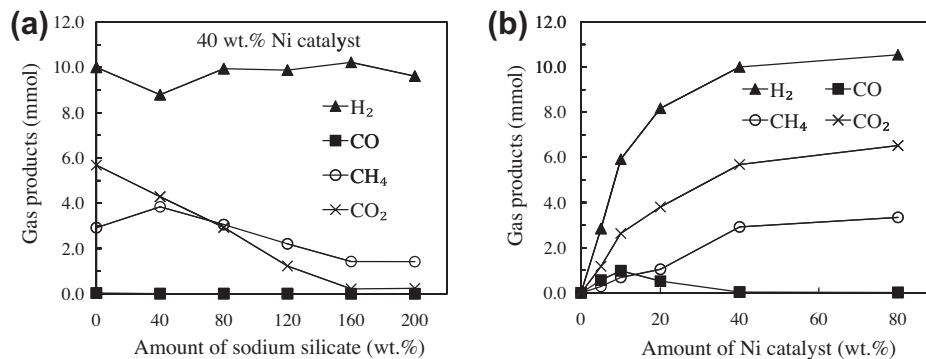
Fig. 7. Yield of gas products from hydrothermal gasification of pure glycerol (3 mmol) with (a) sodium silicate and Ni catalyst (40 wt.%), and (b) Ni catalyst.

Such series of reactions produced [OH⁻] that accounted for the basic medium to absorb CO_2 [27]:

$$2OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O \tag{5}$$

$$CO_3^{2-} + CO_2 + H_2O \rightarrow 2HCO_3^- \tag{6}$$

In addition, CH_4 decreased to yield H_2 when sodium silicate increased due to the following reaction occurred:

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \tag{7}$$

Effects of Ni catalyst ($Ni/Al_2O_3-SiO_2$) on the hydrothermal gasification of glycerol were also studied (Fig. 7b). Hydrogen gas substantially increased when Ni catalyst was added from 5 to 80 wt.%. A maximum yield (10.54 mmol or 51.6% concentration) was achieved with 80 wt.% Ni catalyst. These results indicated that hydrothermal gasification was efficiently promoted by the addition of Ni catalyst that had a good activity for C—C scission followed by water–gas shift reaction. The yield of CH_4, however, increased from 0.28 to 3.34 mmol as catalyst rose from 5 to 80 wt.%. This observation suggested that methanation reaction occurred under the hydrothermal gasification conditions:

$$\text{Methanation reaction}: \ CO + 3H_2 \rightarrow CH_4 + H_2O \tag{8}$$
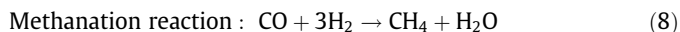
The combination of sodium silicate and Ni catalyst was used for hydrothermal gasification of glycerol under the optimized amounts of sodium silicate (160 wt.%) and Ni catalyst (40 wt.%) (Fig. 8). Hydrogen increased to 10.22 mmol (or 85.2% yield) as compared with that obtained with addition of either sodium silicate (1.55 mmol or 12.4% yield) or Ni catalyst (10 mmol or 83.4% yield). In addition, CO_2 decreased significantly to 0.21 mmol (or 1.8% concentration) as compared with that obtained with Ni catalyst (5.68 mmol or 30.5% concentration). Therefore, the addition of
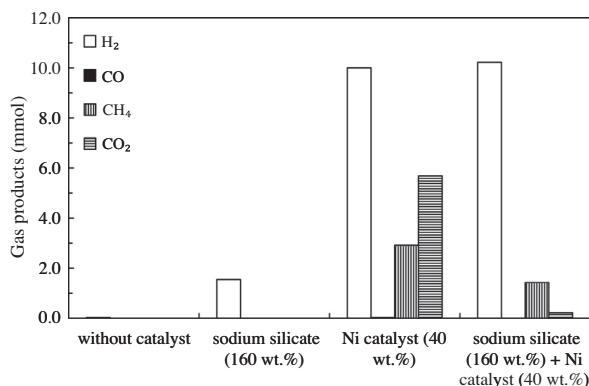
both sodium silicate and Ni catalysts resulted in highly efficient hydrogen production by promoting the reaction (Eq. (7)) and increasing the hydrogen concentration due to CO_2 absorption. The analysis results of carbon balance are shown in Table 1. IC analysis data with addition of Ni catalyst (0.5% IC), as well as both sodium silicate and Ni catalysts (36.5% IC) also confirmed that CO_2 was captured significantly by [OH⁻] from the dissolution of sodium silicate in water during gasification (Eqs. (5) and (6)). On the other hand, carbon gasification was inhibited when sodium silicate was added, resulting in TOC being increased from 4.1% to 41.6% (Table 1) and only a slight increase in H_2 yield (Fig. 7a).

Hydrothermal gasification of glycerol using the fourth-cycled sodium silicate combined with Ni catalyst was also carried out (Table 2). Compared with the hydrogen molar yield (85.2%) and concentration (86.2%) that obtained with fresh sodium silicate and Ni catalysts, a decrease in the hydrogen molar yield (82.8%) and concentration (73.6%) but higher concentration of CO_2 (9.9% vs. 1.8%) in gas-phase was observed by using reused sodium silicate and Ni catalyst. These results showed that reused sodium silicate had similar activity but lower CO_2 absorption ability to fresh one due to its complete dissolution in water to form alkaline

Table 1
Carbon balance in hydrothermal gasification of glycerol.

	Ni catalyst	Sodium silicate and Ni catalysts
Carbon in aqueous-phase (wt.%)	4.6	78.1
Inorganic carbon	0.5	36.5
Organic carbon	4.1	41.6
Carbon in gas-phase (wt.%)	95.0	18.4
Total (wt.%)	99.6	96.5

Experimental conditions: 350 °C and 19.2–19.7 MPa, heating time 30 min (Ni catalyst 40 wt.%, sodium silicate 160 wt.% based on glycerol).

Table 2
Yields and concentrations of gas products from hydrothermal gasification of glycerol with sodium silicate and Ni catalysts.

	Na_2SiO_3[a] and Ni catalyst	Na_2SiO_3[b] and Ni catalyst
Gas-phase composition (mol.%)		
H_2	86.2	73.6
CO	<0.02	0.1
CH_4	12.0	16.4
CO_2	1.8	9.9
C_2 (C_2H_2, C_2H_4, C_2H_6)	<0.01	<0.01
H_2 yield (mol.%)	85.2	82.8

Experimental conditions: 350 °C and 19.2–19.5 MPa, heating time 30 min (Na_2SiO_3 160 wt.%, Ni catalyst 40 wt.% based on glycerol).
[a] Na_2SiO_3 fresh sodium silicate.
[b] Na_2SiO_3 used sodium silicate after transesterification of rapeseed oil for four recycles.

Fig. 8. Yield of gas products from hydrothermal gasification of pure glycerol (3 mmol) with both sodium silicate and Ni catalysts.

solution with weaker strength through the hydration processes (Eqs. (2)–(4)). The loss of basic species of reused catalyst during transesterification cycles was confirmed by the higher concentration of CO_2 (9.9% vs. 1.8%) absorbed by its weaker alkaline solution (Eqs. (5) and (6)).

3.2.2. Crude glycerol as raw material

Crude glycerol (90.0 wt.% glycerol; 0.5 wt.% methanol; 9.5 wt.% unreacted oil, biodiesel and water) from biodiesel production after distillation was used as raw material for the hydrothermal gasification under the optimized amounts of sodium silicate (160 wt.%) and Ni catalysts (40 wt.%). Elemental compositions of the crude glycerol (50.56 C, 8.71 H, 40.45 O, 0.03 N and 0.19 S; wt.%) were analyzed by a CHNOS Elemental Analyzer (vario MICRO cube, Elementar, Hanau, Germany). When the crude glycerol sample was used as raw material (glycerol accounted for 70.3 wt.% carbon), a gasification yield of 51.3% (carbon in gas-phase and inorganic compounds) with a hydrogen concentration of 85.3% was achieved. There was no significant change in gas compositions between crude glycerol (H_2: 85.3%; CH_4: 12.8% and CO_2: 1.9%) and pure glycerol (H_2: 86.2%; CH_4: 12.0% and CO_2: 1.8%), because glycerol was mainly responsible for gas products at relatively low temperature (e.g., 350 °C) [38]. These results indicated that crude glycerol can be used as a low-cost substitute for pure glycerol in hydrothermal hydrogen production. However, more researches should be further investigated to gasify the other components (e.g., methanol, oil) except glycerol in crude glycerol. In this case, higher temperature and longer reaction time would be required.

4. Conclusions

Microwave irradiation was proved to be efficient for biodiesel production catalyzed by calcined sodium silicate. Biodiesel yields of 95.8% from rapeseed oil and 92.8% from Jatropha oil were achieved under the conditions: 11/1 methanol/oil molar ratio of, 4 wt.% catalyst and 400 W microwave power for 5 min reaction time. Therefore, microwave-assisted transesterification of vegetable oil with sodium silicate is an effective and economical method for the rapid production of biodiesel.

The reused catalyst after transesterification process for four recycles was recovered and utilized for hydrothermal gasification of by-product glycerol together with Ni catalyst. A high selective hydrogen yield of 82.8% (with 73.6% concentration) was obtained from pure glycerol with the reused sodium silicate and Ni catalysts at 350 °C. A hydrogen concentration (85.3%) was achieved by using crude glycerol as raw material. Overall, sodium silicate was fully used in biodiesel production and glycerol gasification, and this co-production process provided a novel green method in biodiesel production and glycerol utilization.

Acknowledgements

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