Catalytic production of *Jatropha* biodiesel and hydrogen with magnetic carbonaceous acid and base synthesized from *Jatropha* hulls

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1. Introduction

As more and more intensive oil supply and the serious pollution of vehicle emissions [1,2], biodiesel (fatty acids methyl esters, FAMEs) [3], ethanol [4], and hydrogen [5] have become the focus of development of renewable and clean transportation fuels. Biodiesel is produced with high yield through the transesterification of triglycerides with bases including homogenous catalysts of diesel is produced with high yield through the transesterification of triglycerides with bases including homogenous catalysts of sodium and potassium methoxides [6], and heterogeneous catalysts [7]. For biodiesel production from crude oils with high FFAs or high acid values (AV), solid acid catalysts such as Nafion [11], supported heteropolyacid [12], and carbon nanotube-based solid sulfonic acids [13] were directly applied for catalyst recycles [18]. Alternatively, a two-step biodiesel production method was developed, in which high FFAs in crude oils could be firstly esterified by acids followed by transesterification of the oils catalyzed by base catalysts [16,17]. Heterogeneous catalysis of the two-step biodiesel production became a popular technique with significant advantages of high biodiesel yield and easiness for catalyst recycles [18].

The recovery of solid catalysts was usually performed by filtration or centrifugation methods that were time-consuming with low energy efficiency [15]. The development of magnetic solid catalysts would benefit the easiness of catalyst separation by a magnet attraction. Magnetic carbonaceous solid acid (Fe/C-SO₃H) was successfully applied in the esterification of oleic acid [19].

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Magnetic carbonaceous solid base (Na2SiO3@FeO4/C) also possessed high activities in catalyzing transesterification reactions in biodiesel production [10]. Na2SiO3@FeO4/C catalyst after five cycles could still achieve a 1.8-times recovery rate as that using sole Na2SiO3 particles (96.1 vs. 54.4 wt%) [10,20] due to the high separation efficiency by a magnet. Although these magnetic solid catalysts showed promising advantages in biodiesel production, source of their carbonaceous supporters were from expensive edible sugars or commercial active carbons [10,19]. Any potential application of the reported Na2SiO3@FeO4/C catalyst for H2 production was not possible due to the lack of necessary active elements such as Ni [10,21].

The drought-resistant perennial Jatropha trees grow well in marginal/poor soils [22]. Jatropha oil has attracted great attention as a promising crude oil resource for biodiesel production [23]. By 2008, the global plantation of Jatropha trees has reached about 9.0 × 107 ha in Asia, Africa and Latin America [24] including about 1.5 × 107 ha in China [23]. The state forestry administration of China declared to expand the Jatropha tree plantation (including natural forests) to 1.45 × 107 ha in southwest of China until 2020 [25]. As reported [26], producing 1000 L of Jatropha oil could generate 6.86 t Jatropha-hull waste. After transesterification, the reaction mixture contained approximately 10 wt% by-product glycerol [27]. With a growth of Jatropha biodiesel production, large quantities of Jatropha-hulls and glycerol will be generated. It is important to make full use of these Jatropha wastes.

In this study, magnetic carbonaceous solid acid and base catalysts were synthesized by loading active groups on the carbonaceous supporters derived from Jatropha-hull hydrolysate and hydrolysis residue. They were applied in the two-step biodiesel production with high-AV Jatropha oil as feedstock. The crude glycerol generated from biodiesel production was further hydrothermally gasified for H2 production that was catalyzed by the deactivated base catalyst.

2. Experimental

2.1. Material

Jatropha-hull powders (48.6 C, 7.23 H and 41.1 O, wt%; particle size <200 μm) were provided by Yunnan Shenyu New Energy Co., Ltd. (Chuxiong, Yunnan). Crude Jatropha oil (AV of 17.2 mg KOH/g, molecular weight of 942.9 g/mol, Scheme 1a) was supplied by Xishuangbanna Tropical Botanical Garden (Mengla, Yunnan). FeCl3·6H2O (81.1 g), solid urea (30.0 g) and Jatropha-hull hydrolysate (0.3 L) were mixed in the autoclave and heated to 180 °C within 36 min. The reaction was conducted for 14 h with a stirring speed of 500 rpm. After reaction, the solid residual produced from the hydrolysate polymerization and iron precipitation [CO(NH)2 + H2O → NH3↑ + CO2↑ + NH4OH; FeCl3 + NH4OH → Fe(OH)3↓ + NH4Cl] was separated from the reaction mixture and washed with deionized water and ethanol for several times until reaching neutral. After freeze-dried at −47 °C for 24 h, the residual was submitted in a tubular furnace for pyrolysis at 700 °C (with heating rate of 7.4 °C/min) for 1.5 h. N2 was used as the protect gas with a flowing rate of 200 mL/min. During the pyrolysis, the magnetic core (Fe3JHC) was formed through dehydration and reduction reactions [Fe(OH)3 → Fe2O3 + H2O; Fe3O4 + C → Fe2O3 + Fe + CO/CO2].

Because the dissolution of Fe2O3/Fe in H2SO4 [14] led to an extremely weak magnetism (0.56 Am²/kg) after sulfonation, pre-coating of carbon layers on the magnetic core was performed with the Jatropha-hull hydrolysate (Scheme 2ii). JRC/JHC powders (20 g) were dispersed in Jatropha-hull hydrolysate (0.3 L). The mixture was incubated at 180 °C for 14 h with a stirring speed of 500 rpm. After reaction, the coated magnetic carbon (C@Fe/JHC) was collected by a magnet and washed with deionized water and ethanol. The carbon coating was stabilized through pyrolysis at 600 °C (heating rate of 6.3 °C/min) for 1.5 h.

In the sulfonation (Scheme 2iii), a 500-mL three-neck flask containing 10 g C@Fe/JHC particles and 200 mL concentrated H2SO4 (98%, w/w) was incubated at 150 °C for 16 h with a nitrogen flow rate of 100 mL/min. After washed with hot distilled water (80 °C), the solid acid catalyst (C-SO3H@Fe/JHC) was obtained. Freeze-dried and screen through a 200-mesh sieve for the esterification of Jatropha oil.

2.2. Preparation of Jatropha-hull hydrolysate and residue

Jatropha-hull hydrolysate was prepared in a 500-mL ZrO2-coated autoclave (FCD03-50, Jianbang Chemical Mechanical Co. Ltd., Yantai, Shandong) containing 15 g Jatropha hulls, 200 mL H2O and 6 g concentrated H2SO4 (98%, w/w). The hydrolysate was performed at 150 °C for 1.5 h with a stirring speed of 300 rpm. After reaction, the solid residue was collected by filtration through a filter (RW19, pore size of 1.2 μm, Merck Millipore Ltd., Cork, Ireland). The hydrolysate was neutralized with saturated Ca(OH)2 solution and concentrated through vacuum evaporation at 65 °C until reaching the total organic carbon (TOC) of 61 g/L. The collected solid residue was washed twice with hot distilled water (80 °C) and dried at 75 °C until reaching a constant weight. The dried Jatropha hull hydrolysate residue (JR) was sieved through a 200-mesh (particle size ≤75 μm) before use.

2.3. Catalyst preparation

2.3.1. Magnetic carbonaceous acid (C-SO3H@Fe/JHC)

Solid acid was synthesized by a 3-step method (Scheme 2) based on the previous study [14]. Firstly (Scheme 2i), FeCl3·6H2O (81.1 g), solid urea (30.0 g) and Jatropha-hull hydrolysate (0.3 L) were mixed in the autoclave and heated to 180 °C within 36 min. The reaction was conducted for 14 h with a stirring speed of 500 rpm. After reaction, the solid residual produced from the hydrolysate polymerization and iron precipitation [CO(NH)2 + H2O → NH3 ↑ + CO2 ↑ + NH4OH; FeCl3 + NH4OH → Fe(OH)3↓ + NH4Cl] was separated from the reaction mixture and washed with deionized water and ethanol for several times until reaching neutral. After freeze-dried at −47 °C for 24 h, the residual was submitted in a tubular furnace for pyrolysis at 700 °C (with heating rate of 7.4 °C/min) for 1.5 h. N2 was used as the protect gas with a flowing rate of 200 mL/min. During the pyrolysis, the magnetic core (Fe3JHC) was formed through dehydration and reduction reactions [Fe(OH)3 → Fe2O3 + H2O; Fe3O4 + C → Fe2O3 + Fe + CO/CO2].

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In the sulfonation (Scheme 2iii), a 500-mL three-neck flask containing 10 g C@Fe/JHC particles and 200 mL concentrated H2SO4 (98%, w/w) was incubated at 150 °C for 16 h with a nitrogen flow rate of 100 mL/min. After washed with hot distilled water (80 °C), the solid acid catalyst (C-SO3H@Fe/JHC) was obtained, freeze-dried and screen through a 200-mesh sieve for the esterification of Jatropha oil.

2.3.2. Magnetic solid base (Na2SiO3@Ni/JRC)

A 500 mL reaction solution containing 145.5 g Ni(NO3)2·6H2O, 60 g solid urea and 24 g Jatropha residue (JR) was loaded in a 1-L three-neck flask equipped with a condenser. The flask was incubated at 135 °C in oil bath for 10 h with a stirring speed of 500 rpm. After reaction, the solid product with Ni(OH)2 precipitate was collected by filtration (1.2 μm) and washed with deionized water. For the synthesis of Ni/JRC (JRC: Jatropha residue carbon) supporter, the solid product was submitted to calcination at 700 °C for 2 h with a nitrogen flow rate of 200 mL/min.

Ni/JRC supporter (20 g) and Na2SiO3@H2O (120 g) were loaded in a 1-L flask containing 150 mL water. The solution was stirred and evaporated at 85 °C to form a gel. Followed by calcination at 400 °C for 2 h, the solid was processed by ball milling with ZrO2 balls for 12 h at a spinning speed of 230 rpm and screen through a 200-mesh sieve. The prepared Na2SiO3@Ni/JRC base contained 72.0 wt% Na2SiO3.
2.4. Instrumentation

The crystal forms, magnitude of magnetism, morphologies and total acid/base contents of the synthesized supporters/catalysts were characterized by X-ray diffraction (XRD; Rigaku Rotaflex RAD-C, Tokyo with Cu Kα radiation source), vibrating sample magnetometer (VSM; lakeshore7407, Lake Shore Cryotronics, Inc., Westerville, OH), scanning electron microscope (SEM; ZEISS EVO LS10, Cambridge, UK) and temperature programmed desorption (TPD; Chemisorption analyzer, Quantachrome Instruments, Boynton Beach, FL), respectively. Specific surface area and pore volume were determined by Bruner Emmett and Teller (BET) method (Tristar II 3020, Micromeritics Instrument Co., Ltd., Northcross, GA). Chemical bonds were analyzed by Fourier transform-infrared spectroscopy (FT-IR; Nicolet iS10, Thermo Fisher Scientific Co., Ltd., Waltham, MA) from 4000 to 400 cm⁻¹ with the resolution of 0.4–4 cm⁻¹. Inorganic compositions contained in crude glycerol and catalysts were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES; Optima 5300 DV, Perkin-Elmer Inc., Waltham, MA). Before ICP analysis, catalysts and crude glycerol were dissolved in concentrated HCl.

Contents of acidic groups on the derived carbonaceous supporters were determined according to the modified acid-base titration method using phenolphthalein as an indicator [28,29]. Each 0.50 g sample was mixed with 25.0 mL of (a) NaHCO₃ (0.05 M, 99.7%), (b) Na₂CO₃ (0.05 M, 99.99%), (c) NaOH (0.05 M, 99.99%) and (d) Na₂SO₄ (0.1 M, 99.99%) for acid groups (a. carboxylic, b. phenols, c. lacarbonctones groups and d. sulfonic group) with stirring for 24 h, respectively [28,29]. The extracted solutions (a–c) after filtration were acidified by 10–15 mL HCl (0.05 M, 99.0%), placed in a sealed tube, and bubbled with nitrogen for 2 h at 80°C for 30 min. The acid group contents (carboxylic, phenols, lactones groups) were determined by back potentiometric titration with 0.05 M NaOH solution [28,29]. The sulfonic group content was determined from solution d by direct titration with a NaOH (0.05 M) solution [28]. Measurement of
each sample was conducted in triplicate and the average values were reported.

2.5. Jatropha biodiesel production and analysis

Jatropha oil was esterified with solid acid, and subsequently transesterified to biodiesel with solid base. The synthesized biodiesel was analyzed by gas chromatography (GC).

2.5.1. Pretreatment (esterification) of crude Jatropha oil

Crude oil (27.9 g or 0.03 mol) was mixed with the magnetic C-SO3H@Fe/JHC acid (2.5–12.5 wt%) in a 50-mL reactor lined with a quartz cup (YZPR-50, Shanghai Yanzheng Experimental Instrument Co., Ltd.). The reactor was filled by N2 with initial pressure of 1.9–2.1 MPa to avoid methanol evaporation to its dead volume (9.6 mL) during reaction. The esterification was conducted at 60–100°C for 30–150 min with a stirring speed of 750 rpm. After reaction, catalyst was isolated by an NdFeB magnet (Scheme 1b) and submitted for cycles without washing. The esterified Jatropha oil (EJO) was collected and filtered through a 0.22-μm filter. The AV and saponification value (SV) of oils were measured by titration according to the standard methods of American Society for Testing and Materials (ASTM, D1990-87(1998) and D5558-95(2011)), respectively. The molecular weight (M) was calculated by the equation of 

\[
M = 3.5 \times 10^{3} \text{AV} \text{mg} / 3 \text{SV} \text{AV} \text{mg} \text{g}^{-1}
\]

After 3 or 5 reaction cycles for C-SO3H@Fe/JHC, the catalysts (designated as C-SO3H@Fe/JHC-3 or C-SO3H@Fe/JHC-5) were recovered by a 3-time washing with 20 mL ethanol followed by drying at 85°C for 2 h with a nitrogen flow rate of 200 mL/min. The washed recovered catalysts were recycled further, similarly, C-SO3H@Fe/JHC-R6 and C-SO3H@Fe/JHC-R9 were recovered catalysts after 6 and 9 cycles for esterification, respectively. The recovery yield of catalyst was defined as:

\[
\text{Catalyst recovery (\%)} = \frac{\text{mass of recovered catalyst (g)}}{\text{mass of catalyst submitted to the reaction (g)}} \times 100\% \quad (1)
\]

2.5.2. Production of Jatropha biodiesel

EJO (0.3 mol) and related dehydrated methanol were loaded in the YZPR-50 reactor containing certain amount of the magnetic base Na2SiO3@Ni/JRC for transesterification at 55–75°C for 60–140 min with a stirring speed of 750 rpm. After reaction, the magnetic base catalyst was separated for cycles (Scheme 1c) without washing. The upper-layer (biodiesel product) was analyzed using GC (GC-2014, Shimadzu, Kyoto) equipped with a capillary column (Rtx-Wax, 30 m × 0.25 mm × 0.25 μm, Restek Corporation, Bellefonte, PA) and a flame ionization detector (FID, 221-70162-9, Shimadzu). The crude biodiesel was diluted with CH2Cl2. The injection volume was 1.0 μL with a split ratio 40/1. Temperatures of column, injector and detector were set at 220°C, 260°C and 280°C, respectively. Helium (1 mL/min, 99.999% purity) was used as the carrier gas. To quantify the FAMEs composition, C17:0 was used as an internal standard with calibrated relative response factors of 1.014, 1.023, 1.076, 1.038, 1.019 and 0.926 for the methyl esters of C16:0, C16:1, C18:0, C18:1, C18:2 and C18:3, respectively [31]. Biodiesel yield was defined as the weight percentage of all the FAMES in the crude biodiesel [31].

After 3 or 5 reaction cycles for Na2SiO3@Ni/JRC, the catalysts (similarly designated as Na2SiO3@Ni/JRC-3 or Na2SiO3@Ni/JRC-5) were recovered and washed by the method described above. The washed recovered base catalysts were recycled further, similarly, Na2SiO3@Ni/JRC-R6 and Na2SiO3@Ni/JRC-R9 were recovered base catalysts after 6 and 9 cycles for transesterification, respectively.

2.6. Hydrothermal gasification of glycerol and analysis

A 15 g water, 0.43–0.48 g glycerol and the appropriate amount of the ethanol-washed deactivated base catalyst were loaded in a 25-mL Hastelloy autoclave (HC-276, Parr Instrument Co., Moline, IL) with an 8.4 mL headspace. Before reaction, the autoclave was sealed and filled with 8.0 MPa N2 (99.999% purity). The autoclave was gradually heated up to 350°C in a 54–56 min period with a stirring speed of 250 rpm. When reached 350°C, temperature was retained for 24–26 min under pressure of 21.5–22.0 MPa.

The gas produced was collected in a gasbag after the autoclave was cooling down to low temperatures (25–35°C) in 2–2.5 h (Scheme 1d). A wet gas meter (LMF-1, Shanghai A.K. Instruments Co., Ltd.) was used for determination of the gas volume. The aqueous phase was centrifuged and submitted to TOC and inorganic carbon (IC) analyses using a TOC analyzer (TOC-VCPN, Shimadzu). C2H2(COOK)(COOH) and Na2CO3 were used as calibrating standards. Gas compositions were analyzed by GC (7820A, Agilent, Palo Alto, CA) equipped with a thermal conductivity detector (TCD), and a packed Porapak N column (3 ft × 1/8 in. for H2, CO2, C2H6, C2H4, C2H2 and molecular sieve 5A (6 ft × 1/8 in. for CH4 and CO). The conditions for analysis were followed by Ref. [21].

The glucose, xylose, 5-hydroxymethylfurfural (HMF), furfural, methanol and formaldehyde in the Jatropha-hull hydrolysate or liquid products after gasification were determined by a high performance liquid chromatography (HPLC; LC-20A, Shimadzu). Gasification yield and glycerol conversion yield were calculated as below:

Gasification yield (mol%) = \left(\frac{\text{mol of inorganic carbon in the aqueous}}{\text{mol of carbon in glycerol}}\right) \times 100\%
\]

Conversion yield (wt%) = \left(\frac{\text{mass of residual glycerol after reaction. mg}}{\text{mass of glycerol before reaction. mg}}\right) \times 100\%
\]

3. Results and discussion

3.1. Catalyst characterization

3.1.1. SEM and BET

The magnetic supporter (C@Fe/JHC) showed a morphology of agglomerated rough particles (<30 μm) with tiny porous on the particle surface (Fig. 1A-a). It had a reduced size (about 2 vs. 10 μm) against the AC-600@Fe/C supporter prepared using glucose as the carbon source and pyrolyzed at 600°C [14]. After the sulphonation process, specific surface area and pore volume of the magnetic C-SO3H@Fe/JHC acid increased from 53.7 and 0.091 to 15.6 m2/g and 0.121 cm3/g, respectively (Fig. S1A-a vs. b). It was inferred that catalyst size could increase may be caused by the formation of numerous spherical particles after gasification were determined by a high performance liquid chromatography (HPLC; LC-20A, Shimadzu). Gasification yield and glycerol conversion yield were calculated as below:

Gasification yield (mol%) = \left(\frac{\text{mol of inorganic carbon in the aqueous}}{\text{mol of carbon in glycerol}}\right) \times 100\%
\]

Conversion yield (wt%) = \left(\frac{\text{mass of residual glycerol after reaction. mg}}{\text{mass of glycerol before reaction. mg}}\right) \times 100\%
\]
Jatropha-hull powders. Ni/JRC as base support showed a similar fibrous shape with numerous spherical Ni particles (<1.5 \( \mu \)m) well deposited on the surface (Fig. 1B-a). The size of Na\(_2\)SiO\(_3\)@Ni/JRC base was <100 \( \mu \)m but with small particles (about 3 \( \mu \)m) agglomerated on the catalyst surface with Na\(_2\)SiO\(_3\) gel (Fig. 1B-b). After loading of Na\(_2\)SiO\(_3\) gel on Ni/JRC, the specific surface area and pore volume of Na\(_2\)SiO\(_3\)@Ni/JRC declined from 76.1 to 12.2 \( m^2/g \), and from 0.101 to 0.018 \( cm^3/g \), respectively (Fig. S1B-a vs. b) [21].

3.1.2. XRD, VSM and ICP-OES

The crystalline phases of Fe, Fe\(_3\)C, FeO\(_2\), Ni, Na\(_2\)SiO\(_3\) as well as the aromatic carbon sheets [14,33] on the magnetic supporters or catalysts were identified separately according to the Powder Diffraction Standards (06-0696, 72-1110, 39-1346, 04-0850 and 16-0818) and Refs. [14,33], respectively. It was revealed that the formation of Fe and Fe\(_3\)C crystalline structures in C@Fe/JHC supporter through reactions of \([Fe_3O_4 + C \rightarrow Fe + CO_2/CO]\), \(Fe + C \rightarrow Fe_3C\) [14] by the symmetric XRD reflections (Fig. S2A-a). The average size of the crystal Fe was about 106 nm calculated with the Scherer equation [34]. After sulfonation, the XRD pattern of C-SO\(_3\)H@Fe/JHC was dramatically changed for the reduction of Fe size to 42.5 nm from 106 nm as well as with an appearance of Fe\(_3\)O\(_2\) phase (Fig. S2A-b) [14]. However, the formation of Fe\(_3\)O\(_2\) [Fe + H\(_2\)SO\(_4\) \( \rightarrow \) Fe\(_2\)O\(_3\) + H\(_2\)O + SO\(_2\)] on the surface could protect the Fe component from further corrosion in concentrated H\(_2\)SO\(_4\) [14]. The formation of an amorphous aromatic carbon sheet structure with random orientations could be confirmed in C-SO\(_3\)H@Fe/JHC by a strong but broad diffraction peak signal at 2-theta of 20–30 [33,35]. Both magnetic Ni/JRC and Na\(_2\)SiO\(_3\)@Ni/JRC contained Ni structure. Moreover, there was an additional Na\(_2\)SiO\(_3\) symmetric reflection in the XRD pattern of Na\(_2\)SiO\(_3\)@Ni/JRC, indicating a successful loading of Na\(_2\)SiO\(_3\) component on Ni/JRC supporter.

The existence of Fe and Fe\(_3\)C (Fig. S2A-a) promoted the magnetic saturation (Ms) of C@Fe/JHC supporter to 83.9 Am\(^2/\)kg (Fig. S3A-a) [36]. However, Ms of C-SO\(_3\)H@Fe/JHC declined to 11.2 Am\(^2/\)kg (Fig. S3A-b). It could be attributed by the dissolution of Fe and Fe\(_3\)C compositions during sulfonation [14]. The Na\(_2\)SiO\(_3\) coating on Ni/JRC particles reduced Ms of Na\(_2\)SiO\(_3\)@Ni/JRC form 59.9 to 15.0 Am\(^2/\)kg (Fig. S3B a and b). The synthesized Na\(_2\)SiO\(_3\)@Ni/JRC base in this study had a higher magnetism than the reported Na\(_2\)SiO\(_3\)/Fe\(_3\)O\(_4\) catalyst with Ms of only 0.5 Am\(^2/\)kg [20]. The higher Ms would benefit an improved efficiency on magnetic separation of Na\(_2\)SiO\(_3\)@Ni/JRC from biodiesel products (Scheme 1c).

ICP-OES analysis showed a composition (w/w) of 91.6% Ni and 8.40% char with trace elements of 0.03% Na and 0.07% Si in Ni/JRC (Table S1). In Na\(_2\)SiO\(_3\)@Ni/JRC, Ni content dropped from 91.6 to 25.6 wt% with increased Na, Si and O contents to 27.7, 16.5 and 28.2–28.9 wt%, respectively [21]. After 3 cycles, Ni content increased to 30.2 wt% while Na and Si contents declined to 18.4 and 11.3 wt%, respectively. It could be explained by the release of Na\(_2\)SiO\(_3\) from the catalyst in the reaction media [6,21]. In the crude glycerol, the determined contents of Na and Si were 3.12 and 1.67 wt% with trace 0.130 wt% Ni.

3.1.3. FT-IR, TPD and acid-group titration

Both C@Fe/JHC and C-SO\(_3\)H@Fe/JHC catalysts showed similar infrared absorptions at 3460 and 1610 cm\(^{-1}\) (Fig. S4A) that demonstrate the \(\text{O}\text{-H}\) and \(\text{C}\text{-O}\text{H}\) stretching vibrations in phenolic \(\text{O}\text{-H}\) or \(\text{C}\text{-O}\text{H}\) groups [18], respectively. Absorbances of \(\text{C}\text{-O}\text{S}\) and \(\text{O}\text{-S}\text{O}\) stretching vibrations at 1060 and 1180 cm\(^{-1}\) indicated the existence of \(-\text{SO}_3\text{H}\) groups in C-SO\(_3\)H@Fe/JHC (Fig. S4A-b). Through NH\(_3\)-TPD analysis, the total acid content of C@Fe/JHC was only 0.83 mmol/g but it was promoted to 2.96 mmol/g after sulfonation (Fig. 2A). The value was lower than the total acid content determined by the titration method, which was 3.78 mmol/g (Table S2).

Compared to the reported AC-600-SO\(_3\)H@Fe/C acid derived from glucose [14], C-SO\(_3\)H@Fe/JHC acid showed a larger specific surface area (99.8 vs. 88.9 \( m^2/g \), attributed to the existence of smaller particles (about 20 nm vs. 5 \( \mu \)m) on the catalyst surface.
On the other hand, C-SO₃H@Fe/JHC acid possessed higher contents of carboxylic and sulfonic groups (1.13 and 1.65 mmol/g vs. 0.92 and 1.27 mmol/g) than that of AC-600-SO₃H@Fe/C. The differences of acid-group density between the two carbon solid acids may not only rely on their distinct specific surface areas but also their origins from different carbon resources [37]. Li et al. [38] showed that furfural produced from xylose or Jatropha hulls [39] could be subsequently converted to γ-butyrolactone with a high conversion yield in hydrolysates. The soluble carbon sources such as 26.7 g/L xylose, 11.8 g/L HMF and 7.90 g/L furfural that were found in the Jatropha-hull hydrolysate might have played key roles in generating additional lactonic groups on C@Fe/JHC supporter. A higher content of lactonic groups (1.41 vs. 0.59 mmol/g) could lead to the formation of extra phenols, carboxylic and sulfonic groups on C@Fe/JHC through the reactions (Fig. S5) [28], which could have contributed to the promoted content of acid groups on the C-SO₃H@Fe/JHC catalyst.

Other than the -OH group, there was no significant FT-IR absorbance of functional groups in Ni/JRC (Fig. S4B-a), indicating a complete reduction of NiO in Ni/JRC [40,41]. After loading of Na₂SiO₃, Na₂SiO₃@Ni/JRC catalyst showed several FT-IR absorbance peaks from wave-numbers of 710 to 1025 cm⁻¹ (Fig. S4 B-b), such as Si—O bending, Si—O—Na, Si—O—H and Si—O—Si stretching vibrations [42]. In addition, the absorbances at 745 and 467 cm⁻¹ were attributed to the symmetric stretching and bending vibrations of Si—O—Si bond [43]. The absorbance at 1462 cm⁻¹ was for the CO²⁻ group, which could be formed by absorption of CO₂ in the air through reactions of [Na₂SiO₃ + CO₂ + H₂O → Na₂CO₃ + H₂SiO₃] [44]. This phenomenon revealed a high sensitivity of Na₂SiO₃@Ni/JRC to CO₂. TPD analysis showed that loading of Na₂SiO₃ significantly promoted the total alkal content of Ni/JRC from 0.17 to 3.24 mmol/g of Na₂SiO₃@Ni/JRC (Fig. 2B). It was also observed an agglomeration of the Na₂SiO₃ gel (~3 μm in size) on Na₂SiO₃@Ni/JRC (Fig. 1B-b). The solid base catalyst synthesized in this study showed a higher total alkal content against the Na₂SiO₃@Ni/C derived from bamboo powders (3.24 vs. 3.18 mmol/g) [21].

### 3.2. Esterification of crude Jatropha oil using solid acid

The synthesized C-SO₃H@Fe/JHC was applied in the esterification of crude Jatropha oil with a high AV of 17.2 mg KOH/g. Effects of catalyst dosage (2.5–12.5 wt% of oil), reaction temperature (60–100 ºC), reaction time (30–150 min) and molar ratio of methanol/oil (6/1–18/1) on the AV reduction were investigated using a single factor test design (Fig. S6).

#### 3.2.1. Catalyst dosage

Under the reaction conditions of 80 ºC and 90 min with methanol/oil ratio of 12/1, a gradual increase of catalyst from 2.5 to 10 wt % led to a remarkable decline of AV from 15.4 to 6.05 mg KOH/g (Fig. S5a). However, a further increase in catalyst to 12.5 wt% had AV slightly increased to 6.15 mg KOH/g. The disproportionate correlation between catalyst dosage and AV indicated a great challenge in fully mixing liquid reactants with heterogeneous catalyst in the magnetically stirred reactor [14,21]. Therefore, 10 wt% catalyst was selected to be used in the following experiments.

#### 3.2.2. Reaction temperature

Under the conditions of 90 min and 10 wt% catalyst with 12/1 methanol/oil ratio, AV decreased sharply from 16.9 to 2.05 mg KOH/g with an increase of temperature from 60 to 90 ºC (Fig. S6b). As higher temperature (100 ºC) only contributed a slight reduction in AV to 1.95 mg KOH/g, 90 ºC was selected as reaction temperature in the following experiments [15].

#### 3.2.3. Reaction time

Reacted at 12/1 methanol/oil molar ratio and 90 ºC, AV decreased from 10.5 to 1.3 mg KOH/g when time was prolonged from 30 to 120 min. The further extension of time to 150 min only achieved an AV of 1.1 mg KOH/g (Fig. S6c) [15]. Since there was little change of AV from 120 to 150 min, 120 min was used as the reaction time in the following experiments.

#### 3.2.4. Methanol/oil molar ratio

As methanol possesses a boiling point (64.7 ºC) below most of the reaction temperatures applied in this study, excessive methanol was usually supplied (with methanol/oil ratio from 6/1 to 18/1) to compensate the methanol evaporated to the dead volume of the reactor (Fig. S6d). When methanol/oil molar ratio increased from 6/1 to 12/1, AV remarkably decreased from 11.5 to 1.30 mg KOH/g. However, a further increase in methanol/oil molar ratio from 15/1 to 18/1 could have the relative consistency of catalyst intensively diluted in the reacting mixture and led to a slight increase of AV from 1.5 to 1.8 mg KOH/g, respectively [14]. The value of 12/1 methanol/oil molar ratio was selected.

Under the reaction conditions of 90 ºC, 120 min, 10 wt% catalyst and 12/1 methanol/oil molar ratio, crude Jatropha oil could be efficiently esterified using C-SO₃H@Fe/JHC acid. The AV of the oil decreased from 17.2 to 1.3 mg KOH/g, with a reduction by 92.44%. The low AV oil was used for the base transesterification to produce biodiesel.
3.3. Biodiesel production with solid base

The esterified oil with an AV of 1.3 mg KOH/g was reacted with methanol catalyzed with base Na$_2$SiO$_3$@Ni/JRC. Effects of methanol/oil molar ratio (3/1–15/1), catalyst dosage (3–11, wt%), reaction temperature (55–75 °C), and reaction time (60–140 min) on biodiesel yield were investigated using a single-factor test design (Fig. S7).

3.3.1. Methanol/oil molar ratio

When applying 5 wt% catalyst at 65 °C for 100 min with theoretical methanol/oil ratio of 3/1, methanol evaporation caused insufficient alcohol for the transesterification reaction [31], only 56.7% biodiesel yield was produced. As methanol/oil molar ratio increased from 6/1 to 9/1, biodiesel yield was promoted to 83.3% and further reached the peak value of 91.3% (Fig. S7a). However, an intensive increase of methanol had a negative effect on biodiesel yield. With methanol/oil molar ratio increased from 12/1 to 15/1, biodiesel yield dropped from 89.2% to 88.1%, respectively [31]. Methanol/oil molar ratio was selected as 9/1.

3.3.2. Catalyst dosage

In Fig. S7b, when catalyst increased from 3 to 7 wt%, biodiesel yield reached the highest value of 94.7%. However, further increase of catalyst from 9 to 11 wt% led to a slight decline of biodiesel yield from 93.2% to 92.3%. It could be explained by an insufficient distri-

![Graph](image1.png)

Fig. 3. Cycle of catalysts for (a) crude Jatropha oil esterified with C-SO$_3$H@Fe/JHC acid and (b) biodiesel production with Na$_2$SiO$_3$@Ni/JRC base. [Reaction conditions: (a) 10 wt% catalyst loading with 12/1 methanol/oil molar ratio, at 90 °C for 120 min; and (b) 7 wt% catalyst loading with 9/1 methanol/oil molar ratio, at 65 °C for 120 min.]

![Graph](image2.png)

Fig. 4. (a) SEM images and (b) EDX graphics of (A) unwashed magnetic Na$_2$SiO$_3$@Ni/JRC-3 catalyst and (B) washed magnetic Na$_2$SiO$_3$@Ni/JRC-R3 catalyst.
bution of catalyst in the reaction system with the magnetic stirring method [21]. Catalyst dosage was selected as 7 wt%.

### 3.3.3. Reaction temperature

With reaction time of 100 min, biodiesel yield was only 78.0% at 55 °C. An increase in temperature to 65 °C achieved the highest biodiesel yield of 94.7% (Fig. S7c). A higher temperature at 75 °C had the biodiesel yield declined to 87.2%. Although high temperature promoted chemical reaction rate, evaporation of methanol that could result in lowering biodiesel yield should also be considered [45]. For balancing a high reaction rate with less methanol evaporation, 65 °C was recognized as the relative optimal temperature for biodiesel production in this study.

### 3.3.4. Reaction time

Biodiesel yield continuously increased from 87.4% to 96.7% with reaction time increased from 60 to 120 min (Fig. S7d). As the transesterification is a reversible conversion reaction [21], biodiesel yield slightly decreased to 95.6% with a prolonged reaction time to 140 min. Reaction time was selected as 120 min.

In total, the relative optimal conditions for biodiesel production with Na2SiO3@Ni/JRC base were: 7 wt% catalyst at 65 °C for 120 min with 9/1 methanol/oil molar ratio. Under these conditions, biodiesel yield reached 96.7%.

### 3.4. Catalyst cycles

Under the optimal conditions obtained above, the recycle of both C-SO3H@Fe/JHC for esterification and Na2SiO3@Ni/JRC for transesterification was performed, respectively (Fig. 3).

Both solid acid and base catalysts showed a decline in catalyzing efficiencies after several cycles. With an average recovery yield of 90.3 ± 3.17 wt%, a 5-cycle use of C-SO3H@Fe/JHC acid in esterifying the crude *Jatropha* oil led to the AV reduced to 1.30, 1.10, 1.70, 2.45 and 3.20 mg KOH/g, respectively (Fig. 3a). Na2SiO3@Ni/JRC base was also recycled in the transesterification of EJO for biodiesel production. There were no significant differences in biodiesel yields among the 1st, 2nd and 3rd cycle of the solid base, with 96.7%, 97.5% and 96.5% yields, respectively (Fig. 3b) [10]. However, biodiesel yield dropped to 85.6% and 75.3% in the 4th and 5th cycle, respectively [21]. The average recovery yield of the solid base was 86.7 ± 2.56 wt% for the 5 cycles.

For C-SO3H@Fe/JHC-3, the calculated content of sulfonic group (–SO3H) was 0.506 mmol/g assuming that all S atoms were only associated in the –SO3H group. Compared to the original C-SO3H@Fe/JHC acid, the content (wt%) of S in the unwashed C-SO3H@Fe/JHC-3 showed a remarkable decrease from 3.56 to 1.62 wt% (Table S3). At the meantime, the C and H contents (wt%) increased from 38.6 to 45.9, and 2.10 to 5.37, respectively. The N and Fe contents (wt%) decreased from 1.14 to 0.71, and 26.7 to 17.4, respectively. After washed, the recovered C-SO3H@Fe/JHC-3 acid had similar elemental compositions of C, H, N, S and Fe to that for the original C-SO3H@Fe/JHC catalyst (wt%, 39.6, 2.63, 1.08, 3.39 and 25.6 vs. 38.6, 2.10, 1.14, 3.56 and 26.7) because organics were removed that have high content of C and H.

As for the solid base, compared to the original Na2SiO3@Ni/JRC (Fig. 1B-b), a dramatic change in morphology was observed for the unwashed Na2SiO3@Ni/JRC-3 base (Fig. 4A-a) possibly due to being covered by oil and formed soap (Fig. 4A-a). But, the washed Na2SiO3@Ni/JRC-R3 base (Fig. 4B-a) had some cracks or minor fragments on the surface, similar to that of the original Na2SiO3@Ni/JRC base (vs. Fig. 1B-b). EDX analysis showed an elementary composition (wt%) of C (23.7), O (16.6), Na (18.3), Si (26.5) and Ni (14.9) on the unwashed Na2SiO3@Ni/JRC-3 surface (Fig. 4A-b). Compared to the washed Na2SiO3@Ni/JRC-R3, the higher contents of C and O on the unwashed Na2SiO3@Ni/JRC-3 (23.7 and 16.6 vs. 7.80 and 12.5) could be caused by the existence of glycerol, biodiesel or oil residuals deposited within the interior structure of the catalyst. The washed recovered C-SO3H@Fe/JHC-R3 acid and Na2SiO3@Ni/JRC-R3 base were cycled in the esterification and transesterification, respectively. Results showed that the average AV of EJO was ≤1.80 mg KOH/g (1.53, 1.44 and 1.80) with C-SO3H@Fe/JHC-R3 and biodiesel yield was >92.0% (95.5, 94.8 and 92.4%) with Na2SiO3@Ni/JRC-R3 in 3 cycles (Fig. 3).

Both C-SO3H@Fe/JHC and Na2SiO3@Ni/JRC catalysts possessed a good reusability. It was revealed that the binding of active sites by the crude glycerol or other residuals from the oil was the main cause of the catalyst deactivation [21]. An ethanol-wash could simply realize the recovery of catalyst activities. With an intensive recycle of the recovered catalysts for 10 cycles, AV of the EJO was still below 2.0 mg KOH/g with biodiesel yield remained above 85% (Fig. 3).

### Table 1 Gasification yields (mmol) and gas compositions (mol%) in the hydrothermal gasification of glycerol with Ni/JRC or the washed Na2SiO3@Ni/JRC-R3.

<table>
<thead>
<tr>
<th>Gas products</th>
<th>Ni/JRC</th>
<th>Na2SiO3@Ni/JRC-R3</th>
<th>Ni/JRC</th>
<th>Na2SiO3@Ni/JRC-R3</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>8.07</td>
<td>58.8 ± 0.89</td>
<td>12.5</td>
<td>73.5 ± 2.09</td>
</tr>
<tr>
<td>CO</td>
<td>0.00777</td>
<td>0.06 ± 0.01</td>
<td>0.0154</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td>CH4</td>
<td>0.851</td>
<td>6.20 ± 0.70</td>
<td>1.17</td>
<td>6.91 ± 0.23</td>
</tr>
<tr>
<td>CO2</td>
<td>4.79</td>
<td>34.9 ± 2.96</td>
<td>3.30</td>
<td>19.3 ± 1.99</td>
</tr>
<tr>
<td>C2H2, C2H6, C3H8</td>
<td>&lt;0.01 &lt;0.01</td>
<td>&lt;0.01 &lt;0.01</td>
<td>3.71</td>
<td>25.5 ± 2.77</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.46 g glycerol (total carbon 15 mmol), 15 g H2O and 33 wt% Ni/JRC or 100 wt% Na2SiO3@Ni/JRC-R3 in the autoclave with 8.0 MPa N2. Reaction was conducted at 350 °C for 4–6 min at 22.0 MPa. Using *pure* glycerol or *crude* glycerol as the reaction substrate.
3.5. Hydrothermal gasification of the glycerol by-product

The Ni/JRC supporter and washed deactivated Na2SiO3@Ni/JRC-R3 base were used for the hydrothermal gasification of glycerol for H2 production. The reaction was conducted at 350 °C for 24–26 min (Fig. S8). Without adding any catalyst, gasification yield was extremely low with 0.102 H2, 0.00352 CO, 0.0702 CH4, and 0.468 CO2 (mmol) produced from pure glycerol with a total carbon loading of 15 mmol. When using Ni/JRC, the H2, CO, CH4 and CO2 yields were promoted remarkably to 8.07, 0.00777, 0.851 and 4.79 (mmol), respectively (Table 1). It could be explained by the high activity of Ni/JRC in catalyzing the water-gash shift reaction (C3H8O3 + H2O → CO2 + CO + H2) and the methanation reaction (CO + H2 → CH4 + H2O) [46,47].

With the deactivated Na2SiO3@Ni/JRC-R3 base (containing 30.2 wt% Ni, Table S1), H2-rich gas (13.2 H2, 0.0208 CO, 0.978 CH4 and 1.97 CO2, mmol, Table 1) was produced from the crude glycerol. Compared to the deactivated Na2SiO3@Ni/JC catalyst derived from bamboo in previous work [21], the deactivated Na2SiO3@Ni/JRC-R3 base had more Na2SO3 remained on the catalyst (18.4 and 11.3 Na and Si wt% vs. 8.21 and 5.09, Table S1). It provided a higher activity in catalyzing glycerol gasification in the absence of additional Na2CO3. It was found that using the crude glycerol could achieve a higher gas yield as well as a higher glycerol conversion yield than the pure glycerol (Table 1).

The conversion yield of pure glycerol was only between 0 to 16.7 wt% when temperature was raised up from 114 to 318 °C with the deactivated Na2SiO3@Ni/JRC-R3 base (Fig. S5a). As temperature increased to 350 °C, a sharp increase in conversion yield (85.6 wt% achieved with gasification yield of 72.6 mol%) and H2 purification of 73.5 mol% (Table 1). As time extended to 10 and 20 min, conversion yield reached 93.7% and 95.5%, respectively. Similarly, Samad et al. [49] reported that glycerol degradation and methanol production was enhanced by increasing temperature up to 300 °C. The dramatic promotion on conversion yield could be attributed to high temperature, as well as the high concentration of OH− and H+ from water as the decrease in the dielectric constant at temperature close to the critical point of water (>374 °C and 22.1 MPa) [46,48]. Methanol also played a role for the rise.

It was found that using the crude glycerol produced from the catalytic transesterification achieved a higher gas yield with a higher glycerol conversion yield than using pure glycerol (Table 1). On one hand, it was indicated that the leached Na+ and Si4+ ions (3.12 wt% Na and 1.67 wt% Si, Table S1) in the crude glycerol had played a positive role in promoting the hydrothermal gasification reaction (Table 2) [21]. When using Na2SO3@Ni/JRC for the transesterification, the leached free Na2SO3 could form Na2CO3 in the crude glycerol by reacting with CO2 from the air through reaction of [CO2 + H2O + Na2SO3 → Na2CO3 + H2SO4]. In this reaction, the Na2SO3 could be a catalyst to facilitate the gasification.

When using a Ni/JRC catalyst (Table 2), the methanol was still less than that for the crude glycerol, which was 93.4 wt%, which confirmed the importance of the Na+ and Si4+ ions leached from Na2SiO3@Ni/JRC-R3 into the crude glycerol to facilitate the gasification.

### Table 2

<table>
<thead>
<tr>
<th>Components (mol%)</th>
<th>Ni/JRCa</th>
<th>Na2SiO3@Ni/JRC-R3a</th>
<th>Ni/JRCb</th>
<th>Na2SiO3@Ni/JRC-R3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon in aqueous-phase</td>
<td>56.7</td>
<td>73.3</td>
<td>66.1</td>
<td>78.9</td>
</tr>
<tr>
<td>Inorganic carbon</td>
<td>4.30 ± 0.15</td>
<td>46.1 ± 1.26</td>
<td>20.3 ± 0.78</td>
<td>62.7 ± 2.13</td>
</tr>
<tr>
<td>Organic carbon</td>
<td>52.4 ± 1.73</td>
<td>27.2 ± 0.84</td>
<td>45.8 ± 1.21</td>
<td>16.2 ± 0.76</td>
</tr>
<tr>
<td>Carbon in gas-phase</td>
<td>41.2</td>
<td>26.5</td>
<td>32.6</td>
<td>18.3</td>
</tr>
<tr>
<td>Total carbon</td>
<td>97.9</td>
<td>99.8</td>
<td>98.7</td>
<td>97.2</td>
</tr>
<tr>
<td>Glycerol gasification yield</td>
<td>45.5</td>
<td>72.6</td>
<td>52.9</td>
<td>81.0</td>
</tr>
</tbody>
</table>

Reaction condition was the same as Table 1.

Using pure glycerol or crude glycerol as the reaction substrate.

4. Conclusions

Solid C-SO3H@Fe/JHC acid and Na2SiO3@Ni/JRC base, with strong magnetism (Ms of 11.2 and 15.0 Am2/kg) and high content of acid/base sites (2.96 and 3.24 mmol/g) were prepared from Jatropha hulls and applied in a two-step biodiesel production by catalyzing the esterification and subsequent transesterification of Jatropha oil, respectively. Compared to traditional carbon resources such as glucose and bamboo powders, Jatropha-hull hydrolysate or hydrolyzed residue led to a promising carbonaceous supporting structure with abundant functional groups, or high specific surface area and pore volume. The catalysts showed advantages of less corrosion, high recovery as well as stability for at least 10 cycles. Through the hydrothermal gasification with the deactivated Na2SiO3@Ni/JRC-R3 base, H2 was produced from the crude glycerol by-product. The research demonstrated a comprehensive green approach to fully utilize the Jatropha seeds for the co-production of biodiesel and H2.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.enconman.2017.03.026.

References


