



Biodiesel production directly from oils with high acid value by magnetic $\text{Na}_2\text{SiO}_3@Fe_3O_4/C$ catalyst and ultrasound



Fan Zhang^{a,b}, Zhen Fang^{a,*}, Yi-Tong Wang^{a,b}

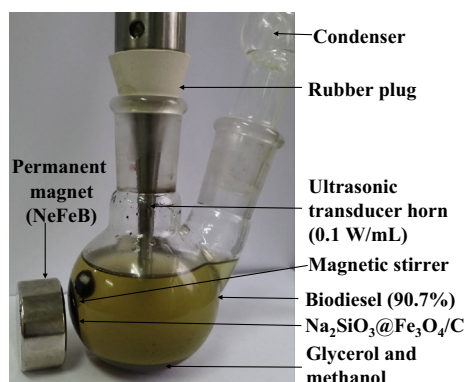
^a Chinese Academy of Sciences, Biomass Group, Key Laboratory of Tropical Plant Resources and Sustainable Use, Xishuangbanna Tropical Botanical Garden, 88 Xuefulu, Kunming, Yunnan Province 650223, China

^b University of Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100049, China

HIGHLIGHTS

- Low ultrasonic energy and magnetic $\text{Na}_2\text{SiO}_3@Fe_3O_4/C$ for biodiesel production.
- Soybean and *Jatropha* biodiesel yields reached 97.9% and 94.7%.
- The catalyst resisted high acid value (AV) oils under ultrasonic.
- 93.2% and 82.5% *Jatropha* biodiesel yield at AV of 4.8 and 7.3 mg KOH/g.
- The catalyst is stable for 5 cycles with biodiesel yield >70% at AV of 4.8.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 22 November 2014

Received in revised form 8 February 2015

Accepted 9 February 2015

Available online 19 February 2015

Keywords:

Ultrasonic

High acid value

Jatropha biodiesel

Magnetic catalyst

$\text{Na}_2\text{SiO}_3@Fe_3O_4/C$

ABSTRACT

Magnetic heterogeneous catalyst ($\text{Na}_2\text{SiO}_3@Fe_3O_4/C$) was prepared for the production of biodiesel from oils with high acid value (AV) under ultrasonic (US) irradiation and magnetic stirring (MS). With the catalyst and assisted by US, soybean biodiesel yield reached >90% in only 20 min (or at 318 K) and 97.9% under the optimal conditions. It was easily magnetically separated for 5 cycles with 94.9% recovery rate and biodiesel yield >80% with both US and MS. The catalyst transesterified *Jatropha* oil with biodiesel yields of 94.7%, 93.2% and 83.5% at AV of 1.3, 4.8 and 7.3 (mg KOH/g) with US, and was cycled 5 times with yield >70% at AV of 4.8 assisted by US and MS. High biodiesel yield (90.7%) was still achieved from high AV oil (4.8) at low US energy density (0.1 W/mL) and MS. The catalyst combined with US and MS can find practical application for direct production of biodiesel from oils with high AV.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

It is strategic important to convert renewable biomass to fuels due to limited fossil resources and the increasing atmospheric CO_2 concentration caused by the combustion of fossil fuels [1,2].

Biodiesel [3] is considered as a good alternative source for fossil fuels because it is clean, renewable and carbon neutral [4]. Biodiesel production by transesterification with homogeneous catalysts (e.g., sodium methoxide, sodium or potassium hydroxide) is one of the most common methods, but it is difficult to recycle because they are dissolved in methanol and glycerol mixture [5]. So, researchers have focused on finding suitable heterogeneous catalysts, such as K_2CO_3 supported activated carbon [6], CaO [7], Sr/MgO [8], MnO and TiO [9], to replace homogeneous catalysts.

* Corresponding author. Tel.: +86 871 65137468; fax: +86 871 65160916.

E-mail address: zhenfang@xtbg.ac.cn (Z. Fang).

URL: <http://brg.groups.xtbg.ac.cn/> (Z. Fang).

Solid Na_2SiO_3 was widely studied as a heterogeneous catalyst to synthesize biodiesel due to its excellent catalytic activity for transesterification [10–11], and the deactivated Na_2SiO_3 can be still used for the hydrothermal production of hydrogen from by-product glycerol [11]. However, parts of these heterogeneous catalysts are hard to be recovered during separation by filtration or centrifugation [12].

Magnetic heterogeneous catalysts can be separated easily from biodiesel and crude glycerol by an external magnetic field [13] with high recovery rate (mass of recovered catalyst/mass of fresh catalyst, wt%), e.g., the rate for $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4$ magnetic catalyst is 1.7 times that for Na_2SiO_3 catalyst (92.17% vs. 54.36%) [14]. But, biodiesel yield catalyzed by the reported catalyst $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4$ dropped rapidly from about 98.6% to 85% and 65% due to soap formation from free fatty acids (FFAs) when acid value (AV) of crude oil rose from 1.0 to 3.0 and 5.0 mg KOH/g [14]. So, $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4$ is not suitable to catalyze the transesterification of crude oils with high AV, such as waste frying oils [15], animal fats [16], and *Jatropha* oil [17]. Furthermore, long reaction time (e.g., 3 h) was required for biodiesel production with $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4$ under mechanical stirring [14], which was much longer than that with ultrasonic (US) irradiation [18]. US is an attractive and effective method to shorten reaction time [19] because it can promote the mixture and enhance the mass transfer of immiscible reactants, i.e., oil and methanol, as well as heterogeneous catalyst [20,21].

The purpose of this work is to prepare a novel magnetic solid catalyst that is easily separated for recycles and effectively used for biodiesel production from crude oils with high acid value. First, magnetic $\text{Na}_2\text{SiO}_3@\text{Fe}_3\text{O}_4/\text{C}$ catalyst is prepared. It is further used to transesterify both soybean and *Jatropha* oils (AV of 0.7–7.3 mg KOH/g) to biodiesel with ultrasonic and magnetic stirring (MS) assistances.

2. Experimental

2.1. Materials

The analytical reagents $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 98.5\%$), $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ($\geq 99.0\%$), dehydrated methanol ($\geq 99.5\%$), urea ($\geq 99.0\%$) and H_2SO_4 ($\geq 98.0\%$) were purchased from Xilong Chemical Factory Co., Ltd. (Shantou, Guangdong). Active carbon (powders, specific surface area: $216.1 \text{ m}^2/\text{g}$) was bought from Aladdin Factory Co., Ltd. (Shanghai). Standard heptadecanoic acid methyl ester (HDAM; $\text{C}_{17:0}$) and other methyl esters [palmitate ($\text{C}_{16:0}$), linolenate ($\text{C}_{16:1}$), stearate ($\text{C}_{18:0}$), oleate ($\text{C}_{18:1}$), linoleate ($\text{C}_{18:2}$) and linolenate ($\text{C}_{18:3}$)] ($\geq 99.0\%$) were purchased from Sigma (Shanghai). Soybean oil (refined, molecular weight of 880.0 g/mol , AV of 0.7 mg KOH/g) was purchased from COFCO Oils Co., Ltd. (Qinzhou, Guangxi). Crude *Jatropha* oil (stored for five years, AV of 17.2 mg KOH/g) was obtained from our Garden in Xishuangbanna (Yunnan).

2.2. Catalyst preparation

Aqueous solution (500 mL) of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.6 mol), solid urea (1.5 mol) and the active carbon (3.05 mol) were added into a three-neck flask (1 L) with a water-cooled condenser. The flask was submerged in an oil bath at 408 K with vigorous stirring for 10 h for reaction to form $\text{Fe}(\text{OH})_3$ by ammonium hydroxide caused by slow urea decomposition in hot water. The formed $\text{Fe}(\text{OH})_3$ precipitates together with solution were transferred to a conical beaker (1 L), and washed thoroughly with deionized water to remove residual urea. After filtered (pore size $1\text{--}3 \mu\text{m}$), the solid product was dried at 378 K to a consistent weight, and heated to 973 K (at 5.6 K/min heating rate) for 2 h calcination in a tubular furnace (SGL-1100, Shanghai Daheng Optics and Fine Mechanics Co., Ltd.)

under nitrogen flowing (200 mL/min) to form Fe_3O_4 by dehydration and reduction [$\text{Fe}(\text{OH})_3 \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3 + \text{C} \rightarrow \text{Fe}_3\text{O}_4 + \text{CO/CO}_2$]. Solid particles were obtained and identified as $\text{Fe}_3\text{O}_4/\text{C}$ by X-ray diffraction (XRD) (Fig. S1a) with strong magnetism (Fig. S2a). The magnetic $\text{Fe}_3\text{O}_4/\text{C}$ powders (20 g) were added into aqueous sodium silicate solution (300 wt% $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, 150 mL) in a flask (1 L) and stirred at 358 K in an oil bath to achieve a gel by evaporation. The dried gel was heated to 673 K (at 3.1 K/min heating rate) for 2 h calcination in the tubular furnace under nitrogen flowing (200 mL/min), and milled by a ball-mill with ZrO_2 balls (SHQM-0.4L, Chunlong Petroleum Instrument Co., Ltd., Lianyungang, Jiangsu) at spinning speed of 230 rpm for 12 h, and sieved by 200-mesh. The obtained catalyst (powders) was designated as fresh $\text{Na}_2\text{SiO}_3@\text{Fe}_3\text{O}_4/\text{C}$ catalyst (Fig. S1b) (containing 56 wt% Na_2SiO_3).

After transesterification, liquid products were removed and the used catalyst remained in the reactor by a permanent magnet (NeFeB, $\varnothing 37 \text{ mm} \times \text{H}18 \text{ mm}$) (Fig. 1b) and directly used for next runs without any treatment. At 5 cycles, the catalyst was washed by ethanol under MS thoroughly, and dried at 378 K to a consistent weight. The recovery rate of $\text{Na}_2\text{SiO}_3@\text{Fe}_3\text{O}_4/\text{C}$ catalyst was calculated by the equation:

$$\text{Recovery rate (wt\%)} = (\text{mass of recovered catalyst}) / (\text{mass of fresh catalyst}) \times 100\% \quad (1)$$

2.3. Catalyst characterization

Synthesized solid particles and prepared catalyst ($\text{Fe}_3\text{O}_4/\text{C}$ and $\text{Na}_2\text{SiO}_3@\text{Fe}_3\text{O}_4/\text{C}$) were analyzed by XRD (Rigaku Rotaflex RAD-C, Tokyo) using a $\text{Cu K}\alpha$ radiation source. Their morphologies were examined using a scanning electron microscope (SEM; Quanta 200, FEI, Hillsboro, OR). Temperature programmed desorption (TPD; Chemisorption analyzer, Quantachrome Instruments, Boynton Beach, FL) was used to assess their surface basicity. In TPD analysis, sample (about $50\text{--}100 \text{ mg}$) was preheated to 673 K at a heating rate of 5 K/min and cooled to 328 K exposed with He flowing (85 mL/min), and absorbed CO_2 by flushing pure CO_2 (85 mL/min) for 80 min. The sample was subsequently desorbed by heating to 673 K at a heating rate of 5 K/min and kept for $60\text{--}90 \text{ min}$ under a He flowing (85 mL/min). Four different volumes ($0.5, 1, 1.5, 2 \text{ mL}$) of a standard CO_2 gas ($10\% \text{ CO}_2$ and $90\% \text{ helium}$) were used to calibrate the basicity. The magnetic properties of catalyst were measured at room temperature by using a vibrating sample magnetometer (VSM; HH-15, Nanjing Nanda Instrument Plant, Jiangsu).

2.4. Biodiesel production and analysis

Refined soybean oil or pretreated *Jatropha* oil ($4.4\text{--}4.6 \text{ g}$), a relevant amount of dehydrated methanol and catalyst were added in a 40 mL special plastic reaction tube ($\varnothing 25 \text{ mm} \times \text{H}95 \text{ mm}$) (Fig. 1a). An ultrasonic generator (JY92-IIDN, $9\text{--}900 \text{ W}$, Ningbo Xinyi ultrasonic equipment Co., Ltd., Zhejiang) operated for 4 s per 5 s at power of $9\text{--}36 \text{ W}$ ($1.5\text{--}6 \text{ W/mL}$ energy density; about 6 mL sample) and frequency of $20\text{--}25 \text{ kHz}$ was fitted with the tube for biodiesel production. The transducer horn was immersed in reaction solution (up to $4\text{--}6 \text{ mm}$ deep) to transmit ultrasound from its tip into the reactants and catalyst (Fig. 1a) [22]. A magnetic bar at the bottom of the tube was stirred (200 or 400 rpm) to mix oil, methanol and catalyst for reaction heated by an oil bath at $323\text{--}338 \text{ K}$. All the experiments were repeated at least two times (except orthogonal runs), and the reported values are average of the individual runs. The experimental errors were within 5% of the value of extent of conversion.

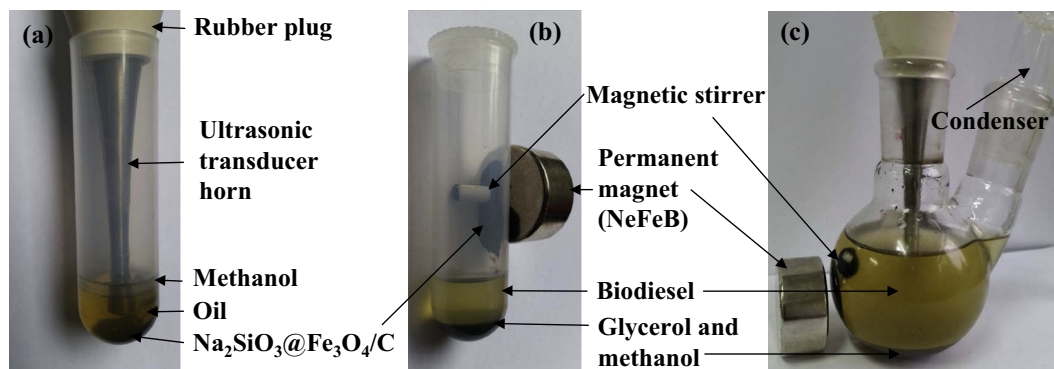


Fig. 1. Production of biodiesel with ultrasound (a) experimental setup (6-mL sample, 1.5–6 W/mL energy density), (b) separation of magnetic catalyst ($\text{Na}_2\text{SiO}_3@\text{Fe}_3\text{O}_4/\text{C}$), and (c) large reactor (90-mL sample) with low ultrasonic energy density of 0.1–4.5 W/mL.

After reaction, biodiesel at upper layer (Fig. 1b) was removed and filtered (pore size 0.22 μm) for analysis by Gas Chromatography (GC; GC-2014, Shimadzu, Kyoto) with a capillary column of Rtx-Wax (30 m \times 0.25 mm \times 0.25 μm) under analytical conditions of column temperature 493 K, injector temperature 533 K, detector temperature 553 K, carrier gas (helium) with flow rate of 1 mL/min and the split ratio 40/1. HDAM ($\text{C}_{17:0}$) was used as internal standard for quantitative analysis, according to the weights and GC peak areas of crude biodiesel and HDAM, biodiesel yield was calculated by the equation:

$$\text{Biodiesel yield (wt\%)} = \frac{\{(A_{\text{C16:0}}/f_{\text{C16:0}} + A_{\text{C16:1}}/f_{\text{C16:1}} + A_{\text{C18:0}}/f_{\text{C18:0}} + A_{\text{C18:1}}/f_{\text{C18:1}} + A_{\text{C18:2}}/f_{\text{C18:2}} + A_{\text{C18:3}}/f_{\text{C18:3}} + A_{\text{COthers}})/A_{\text{C17:0}}\} \times \text{weight of } \text{C}_{17:0}}{(\text{weight of crude biodiesel}) \times 100\%} \quad (2)$$

where f_{C_n} (1.014, 1.023, 1.076, 1.038, 1.019 and 0.926) ($n = 16:0, 16:1, 18:0, 18:1, 18:2, 18:3$) is the relative response factor of six standard methyl esters [palmitate ($\text{C}_{16:0}$), linolenate ($\text{C}_{16:1}$), stearate ($\text{C}_{18:0}$), oleate ($\text{C}_{18:1}$), linoleate ($\text{C}_{18:2}$) and linolenate ($\text{C}_{18:3}$)] to that of HDAM. It was separately calibrated for each GC peak in our previous work [23]. A_{C_n} is area for C_n peak. A_{COthers} is area for other components except A_{C_n} .

3. Results and discussion

Experimental setup and catalyst separation for biodiesel production with ultrasound are given in Fig. 1. The characteristic results of SEM, XRD, VSM and CO_2 -TPD for $\text{Fe}_3\text{O}_4/\text{C}$ and $\text{Na}_2\text{SiO}_3@\text{Fe}_3\text{O}_4/\text{C}$ are showed in Figs. 2, S1, S2 and S3, respectively.

Comparison results between US and MS for single-factor optimization of soybean biodiesel are presented in Figs. 3–6. An orthogonal experimental design and variance analysis for the transesterification of soybean oil are summarized in Tables 1 and 2. Catalyst cycles, stability and activity for oils with various AV are given in Figs. 7–9 and S4–S6.

Crude *Jatropha* oil was pretreated to various AV for experiments as follow: a three-neck flask (500 mL) with a water-cooled condenser was filled with 200-g crude oil, the esterification reaction was carried out with 0.60 w/w methanol to oil ratio in the presence of 1% w/w concentrated H_2SO_4 as catalyst at 323 K for 0.25, 0.5, 0.75, 1 and 1.25 h [24]. After reaction, the pretreated oil was washed with deionized water until the washing-water was neutral, dehydrated by centrifuging at 37,565 RCF (relative centrifugal force; 3–30 K, Sigma Laborzentrifugen GmbH, Osterode am Harz, Germany) for 20 min and dried at 378 K to a constant weight. According to the Chinese National standards (GBT 5530-2005 and 5534-2008), AV and SV (saponification value) of the pretreated *Jatropha* oil (for 0.25, 0.5, 0.75, 1 and 1.25 h) were measured by titration as (7.3, 4.8, 3.2, 2.1 and 1.3 mg KOH/g) and (193.2, 189.5, 188.9, 188.5 and 188.1 mg KOH/g). Their corresponding molecular weights were (923.7, 914.2, 907.8, 903.9, 901.0 g/mol), calculated by the formula $\{M = (56.1 \times 1000 \times 3)/(SV - AV)\}$ [25,26].

3.1. Catalyst characterization

The crystalline phases of Fe_3O_4 and Na_2SiO_3 in the solid particles and catalyst were determined by XRD (Fig. S1) as compared with the cards from Joint Committee on Powder Diffraction

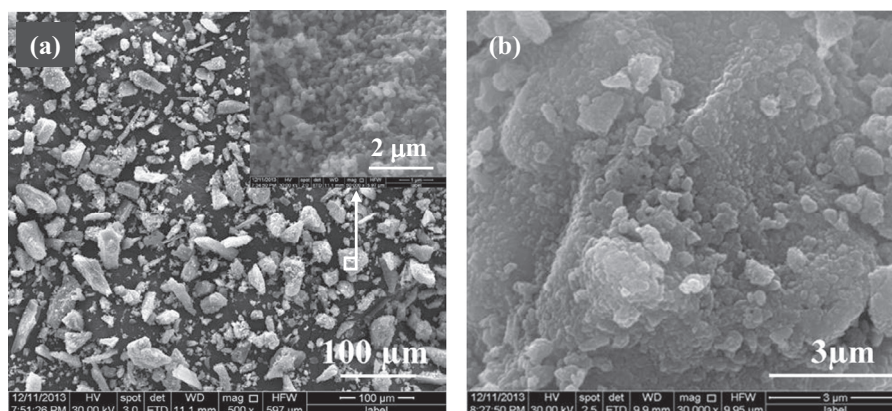


Fig. 2. SEM images of (a) magnetic $\text{Fe}_3\text{O}_4/\text{C}$ carrier, and (b) fresh magnetic $\text{Na}_2\text{SiO}_3@\text{Fe}_3\text{O}_4/\text{C}$ catalyst.

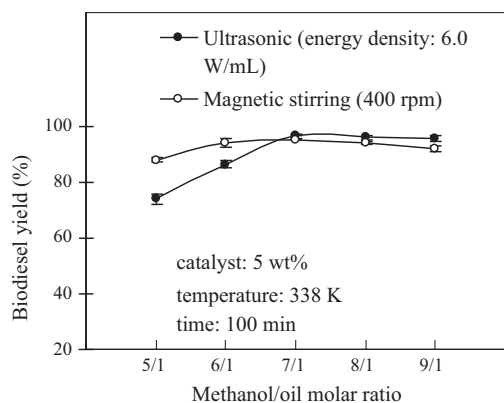


Fig. 3. Comparison of biodiesel yield under ultrasonic (6 W/mL) and magnetic stirring (400 rpm) conditions changed with methanol/oil molar ratio.

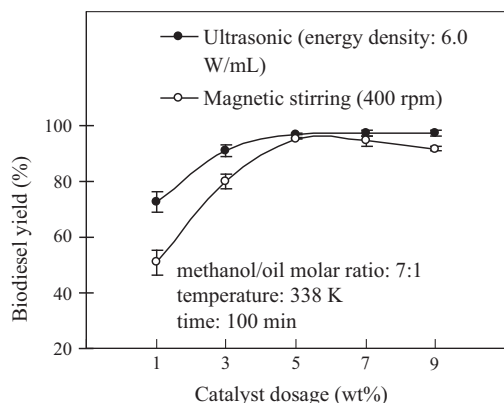


Fig. 4. Comparison of biodiesel yield under ultrasonic (6 W/mL) and magnetic stirring (400 rpm) conditions changed with catalyst dosage.

Standards (JCPDS: 74-0748, 16-0818). Fig. S1a shows that the solid particles have well-crystallized Fe_3O_4 structures with characteristic and symmetric reflections, and the average particle size is calculated as 14.0 nm by Scherer equation: $D_c = K\lambda/(\beta\cos\theta)$ [where D_c is the average particle size; K (0.89) is the Scherer constant; λ (0.1541 nm) is the X-ray wavelength of Cu $K\alpha$ radiation; β ($0.59 \times 3.14/180 = 0.0103$) is full-width at half-maximum; θ (at $35.47^\circ/2 = 17.735^\circ$ or $17.735 \times 3.14/180 = 0.31$) is the diffraction angle of the XRD reflection] [27]. Fig. S1b confirms that the fresh prepared catalyst has well-crystallized structures of Na_2SiO_3 and Fe_3O_4 (designated as $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4/\text{C}$). There is no peak from the active carbon.

Hysteresis loops measurement gives the specific magnetic saturation values (M_s) of 109 and $48.6 \text{ Am}^2 \text{ kg}^{-1}$ for $\text{Fe}_3\text{O}_4/\text{C}$ and fresh $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4/\text{C}$, respectively (Fig. S2a and b). The catalyst has stronger magnetism than that of the $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4$ catalyst prepared in previous work (48.6 vs. $0.5 \text{ Am}^2 \text{ kg}^{-1}$) [14] that is unable to be separated by a magnet. However, the prepared catalyst in this work is easily separated by a magnet for recycles (Fig. 1b and c).

SEM image illustrates that the $\text{Fe}_3\text{O}_4/\text{C}$ particles are composed of large carbon particles ($<50 \mu\text{m}$) with numerous spherical Fe_3O_4 nanoparticles (20–100 nm) on the surface (Fig. 2a). The nanoparticle size is a little bit larger than the above calculated datum by Scherer equation. The fresh $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4/\text{C}$ catalyst still remains the spherical Fe_3O_4 nanoparticles but is covered with Na_2SiO_3 gel after evaporating, drying, calcining and milling (Fig. 2b).

CO_2 -TPD profiles of $\text{Fe}_3\text{O}_4/\text{C}$ particles and fresh $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4/\text{C}$ catalyst are given in Fig. S3. Particles of $\text{Fe}_3\text{O}_4/\text{C}$ have no obvious CO_2 desorption (Fig. S3a) with a very weak basicity $<0.01 \text{ mmol/g}$. However, after loaded with Na_2SiO_3 , the catalyst has a strong peak at 400–500 K (Fig. S3b) for CO_2 desorption with basicity of 0.56 mmol/g .

3.2. Comparison experiments between US and MS

Comparison experiments between US (energy density: 6 W/mL) and MS (400 rpm) assistances were conducted to produce biodiesel from refined soybean oil (AV of 0.7 mg KOH/g) with catalyst ($\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4/\text{C}$) under different conditions of methanol/oil molar ratio, catalyst dosage, reaction temperature and reaction time (Figs. 3–6). The initial conditions set below for single-factor optimization are referred to the previous orthogonally optimized results (methanol/oil molar ratio of 6/1, catalyst of 5 wt%, reaction temperature of 338 K, and reaction time of 100 min) [14].

3.2.1. Methanol/oil molar ratio

Molar ratio of methanol/oil is one of the important factors that affect the conversion degree of transesterification. Each mole of oil requires 3 mol of methanol for complete reaction, excess methanol/oil molar ratio is usually needed, and values from 5/1 to 9/1 were used in this work. The effect of methanol/oil molar ratio on biodiesel yield assisted with US or MS is given in Fig. 3 under conditions of 338 K for 100 min with 5 wt% catalyst. When methanol/oil molar ratio rose from 5/1 to 7/1, biodiesel yield increased to the maximum of 96.3% from 73.5% with US, and 94.9% from 87.5% with MS, respectively. When the ratio reached 9/1, biodiesel yield with US decreased slightly to 95.1%, but dropped sharply to 91.5% with MS. The decline in biodiesel yield is possibly due to the relative low concentration of catalyst in the reaction system caused by excess methanol.

US was less efficient for transesterification than MS at low methanol/oil ratio ($<7/1$) and less sensitive to excess methanol ($>7/1$) because some of methanol was vaporized due to the effect of ultrasonic cavitation. Methanol/oil molar ratio of 7/1 with maximum biodiesel yields for both US and MS is selected as the best value for the next experiments.

3.2.2. Catalyst dosage

The effect of catalyst dosage from 1 to 9 wt% was studied for transesterification under fixed conditions of methanol/oil molar ratio of 7/1, reaction temperature of 338 K and reaction time of 100 min with US or MS. Much higher biodiesel yield was achieved by ultrasonic enhancement (72.1% and 90.4%) than that with MS

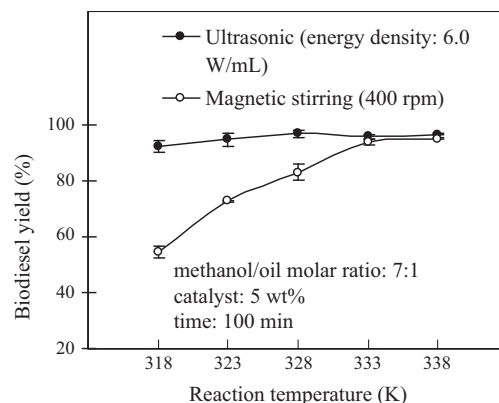


Fig. 5. Comparison of biodiesel yield under ultrasonic (6 W/mL) and magnetic stirring (400 rpm) conditions changed with reaction temperature.

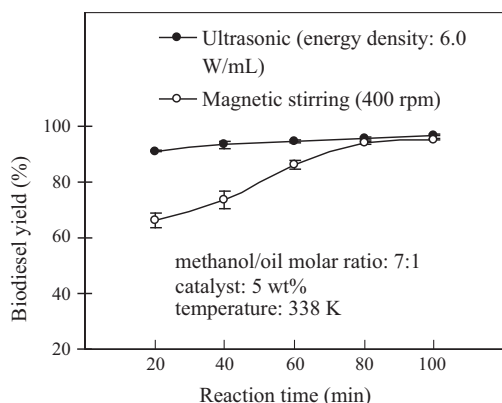


Fig. 6. Comparison of biodiesel yield under ultrasonic (6 W/mL) and magnetic stirring (400 rpm) conditions changed with reaction time.

(50.6% and 79.4%) with 1 and 3 wt% catalyst, respectively (Fig. 4). As catalyst grew further from 5 to 7 and 9 wt%, biodiesel yield changed little: slight growth with US (96.3%, 96.5% and 96.8%) but minor decline with MS (94.9%, 94.0% and 91.2%). US was more effective to mix liquid reactants and solid catalysts because it generated the emulsion droplets of methanol and oil that were easily contacted with the catalyst particles well-dispersed by US [28]. But high concentration of solid catalyst may cause difficult mixing of liquid reactants with the catalyst by MS [23]. So, 5 wt% catalyst is selected as the best value for the next experiments because biodiesel yield was high (>95%) and changed little for further increase in catalyst amount.

3.2.3. Reaction temperature

Five different reaction temperatures from 318 to 338 K were used for biodiesel production under conditions of methanol/oil molar ratio of 7/1, catalyst of 5 wt%, reaction time of 100 min with US or MS (Fig. 5). Overall, US was more effective than MS to promote biodiesel production, particularly at temperature <333 K, e.g., biodiesel yield of (91.8%, 94.4% and 96.6%) with US vs. (54.3%, 72.5% and 82.9%) with MS at (318, 323 and 328 K). As temperature grew further from 328 to 338 K, biodiesel yield declined

Table 1
Orthogonal experimental design $L_{16}(4)^5$ and results for the transesterification of soybean oil (only one experiment was done for each run).

No.	A Methanol/oil	B Catalyst (wt%)	C Temperature (K)	D Time (min)	E US (W/mL)	Biodiesel yield (%)
1	6/1	3	323	40	1.5	80.9
2	6/1	5	328	60	3	96.8
3	6/1	7	333	80	4.5	97.7
4	6/1	9	338	100	6	96.4
5	7/1	3	328	80	6	97.6
6	7/1	5	323	100	4.5	97.2
7	7/1	7	338	40	3	95.2
8	7/1	9	333	60	1.5	95.1
9	8/1	3	333	100	3	96.2
10	8/1	5	338	80	1.5	96.7
11	8/1	7	323	60	6	96.2
12	8/1	9	328	40	4.5	95.0
13	9/1	3	338	60	4.5	95.9
14	9/1	5	333	40	6	87.8
15	9/1	7	328	100	1.5	96.8
16	9/1	9	323	80	3	97.2
K_1	92.95	92.65	92.88	89.73	92.38	
K_2	96.28	94.63	96.55	96.00	96.35	
K_3	96.03	96.48	94.20	97.30	96.45	
K_4	94.43	95.93	96.05	96.65	94.50	
R	3.33	3.83	3.68	7.58	4.08	

slightly from the maximum of 96.6% to 96.3% with US, but increased from 82.9% to the maximum of 94.9% with MS. Using US, lower temperature was enough to achieve high biodiesel yield, e.g., 91.8% with US at 318 K vs. 93.5% with MS at 333 K. It is because the high temperature in the microenvironment could be reached by acoustic cavitation effect that gives additional energy to the reactants to counteract the detrimental effects of low temperature on the reaction kinetics [28,29]. Temperature of 338 K is selected as the best value for the next experiments because biodiesel yield reached the highest of 94.9% for MS and 96.3% remained for US.

3.2.4. Reaction time

The effect of reaction time on transesterification assisted with US or MS was studied from 20 to 100 min under conditions of methanol/oil molar ratio of 7/1, catalyst of 5 wt% and reaction temperature of 338 K. Similar trends for time to temperature were observed from 20 to 100 min with biodiesel yield increased from 90.6% to 96.3% with US, and 66.0% to 94.9% for MS (Fig. 6). Reaction was much faster assisted by US than MS with biodiesel yield of 90.6% vs. 66.0% for 20 min. The cavitation effect by US could accelerate the transesterification reactions as compared with MR assistance, but the introduction of US does not change the chemical mechanism of catalytic transesterification [28,30].

The best conditions for both US and MS are methanol/oil molar ratio of 7/1, catalyst of 5 wt%, reaction temperature of 338 K and reaction time 100 min with biodiesel yield of 96.3% with US and 94.9% with MS, respectively. Under US, the catalyst showed highly active with biodiesel yield >90% in only 20 min or with 3 wt% catalyst or at low temperature 318 K. However, at least 40 min, 5 wt% and 323 K conditions were required to produce high biodiesel yield for the catalyst $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4$ with MS [14].

It can be concluded that ultrasonic irradiation is much more efficient to promote biodiesel production as previous reported [31], particularly under mild conditions such as lower temperature, less catalyst and shorter reaction time. Therefore, a statistical experimental method was designed to further optimize biodiesel production assisted by US in the next Section.

3.3. Optimization of soybean biodiesel production with ultrasound

In order to optimize US effect on transesterification, biodiesel production from soybean oil was carried out according to an orthogonal experimental design $L_{16}(4)^5$ (Table 1) with 5 factors: methanol/oil molar ratio (A: methanol/oil: 6/1, 7/1, 8/1 and 9/1), catalyst dosage (B: catalyst: 3, 5, 7 and 9 wt%), reaction temperature (C: temperature: 323, 328, 333 and 338 K), reaction time (D: time: 40, 60, 80 and 100 min) and US energy density (E: US: 1.5, 3, 4.5 and 6 W/mL). K values (K_1 , K_2 , K_3 and K_4) of the 5 factors at different levels as well as biodiesel yield were calculated and listed in Table 1. The results show that the optimal reaction conditions were $A_2 B_3 C_2 D_3 E_2$ (methanol/oil molar ratio of 7/1, catalyst of 7 wt%, reaction temperature of 328 K, reaction time of 80 min and US energy density of 4.5 W/mL) with average biodiesel yield 97.9% (97.8% and 98.0% for two repeated runs). According to the R -square

Table 2
Variance analysis of orthogonal experimental results for the transesterification of soybean oil (Critical value of $F_{0.1}$ was 2.49).

Factor	R-square value	Freedom degrees	F value
(A) Methanol/oil	28.73	3	0.50
(B) Catalyst (wt%)	34.67	3	0.60
(C) Temperature (K)	34.54	3	0.60
(D) Time (min)	147.25	3	2.54
(E) US (W/mL)	44.16	3	0.76

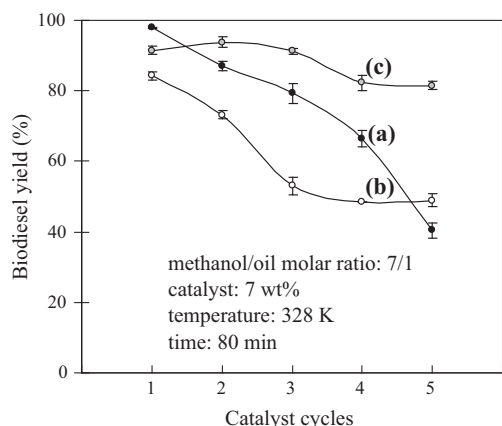


Fig. 7. Cycles of $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4/\text{C}$ catalyst used for soybean biodiesel production under (a) ultrasonic (4.5 W/mL), (b) magnetic stirring (400 rpm), and (c) both ultrasonic (3 W/mL) and magnetic stirring (200 rpm) conditions.

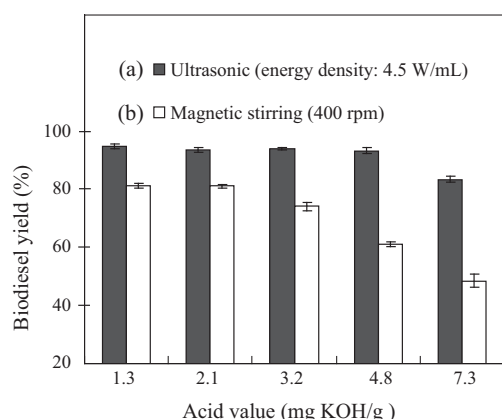


Fig. 8. *Jatropa* biodiesel production with $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4/\text{C}$ catalyst under (a) ultrasonic (4.5 W/mL), (b) magnetic stirring (400 rpm) conditions changed with acid value of pretreated *Jatropa* oil. Reaction conditions: 328 K for 80 min with 7/1 methanol/oil molar ratio and 7 wt% catalyst.

values in variance analysis (Table 2), the factors influenced biodiesel yield are listed in a decreasing order as follows: reaction time (147.25) \gg energy density (44.16) $>$ catalyst dosage (34.67) \approx reaction temperature (34.54) $>$ methanol/oil molar ratio (28.73). Reaction time is significant among the 5 factors. Methanol/oil molar ratio (6/1–9/1), catalyst (3–9 wt%), temperature (323–338 K) and US energy density (1.5–6 W/mL) are not significant at selected ranges because excess US energy density was used that could more effectively promote the mixture of methanol, oil and catalysts as well as increase local temperature. However, time is still important even high US energy was irradiated.

3.4. Catalyst cycles

Due to the reusability of catalyst is one of the important factors for its commercial application, so, $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4/\text{C}$ catalyst was recycled for soybean biodiesel production under the optimized conditions (328 K for 80 min with 7/1 methanol/oil molar ratio and 7 wt% catalyst) with US (energy density: 4.5 W/mL)/MS (400 rpm) (Fig. 7). Biodiesel yield was 97.9%, 87.0%, 79.3%, 66.5% and 40.4% with US (Fig. 7a), and 84.3%, 73.2%, 53.0%, 48.5% and 48.9% with MS (Fig. 7b) for 1–5 cycles. The catalyst can be cycled 3 times with US (biodiesel yield $>79\%$) and 2 times with MS (biodiesel yield $>73\%$) assistances, respectively. Biodiesel yield dropped

sharply at the fourth cycle with US and the third cycle with MS. After the fifth cycled, with US assistance, Na_2SiO_3 gel disappeared (Fig. S4a) with only 0.16 (vs. 0.56 for fresh catalyst) mmol/g basicity (Fig. S4b). However, the morphology of catalyst with MS changed little (Fig. S5a) with 0.45 mmol/g basicity (Fig. S5b). These results show that active component of Na_2SiO_3 was leached into reaction solution gradually by US [10,28]. Both the leached fragments and exposed active sites on the catalyst surface further promoted transesterification to result in higher biodiesel yield by US than MS. Recovery rate of catalyst after 5 cycles was 89.0% with US, and 96.1% with MS, respectively.

Since the catalyst was deactivated sharply by US with 4.5 W/mL after 3 cycles, lower US energy density may alleviate the deactivation. So, US with lower energy density (3.0 W/mL) combined with MS at lower stirring speed (200 rpm) was used to test catalyst cycles under the same optimized conditions. Results proved the catalyst was stable and could be cycled at least 5 times with biodiesel yield $>80\%$ (Fig. 7c; 91.5%, 93.8%, 91.3%, 82.4% and 81.5% for 1–5 cycles). After 5 cycles, SEM image and TPD analyses (Fig. S6) show that the catalyst still kept gel structure with strong basicity (0.42 mmol/g). Recovery rate of catalyst was 94.9% after 5 cycles, which is slightly higher than the value (92.2%) for the reported $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4$ catalyst after 1 cycle [14].

The prepared magnetic catalyst was easily recovered and showed highly active and stable for soybean biodiesel production assisted by US and MS. However, it is unknown its behavior for the oils with high AV. Pretreated *Jatropa* oil with different AV was used to test its activity and stability in the next Section.

3.5. *Jatropa* biodiesel production

$\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4/\text{C}$ catalyst was used to test its resistance to FFAs by using *Jatropa* oil with different AV (1.3, 2.1, 3.2, 4.8 and 7.3 mg KOH/g) pretreated from different times for biodiesel production assisted with US (4.5 W/mL), MS (400 rpm) as well as both US and MS (3.0 W/mL and 200 rpm) under the same optimized conditions obtained for soybean oil (i.e., 328 K for 80 min with 7 wt% catalyst and 7/1 methanol/oil).

When US was applied, the highest *Jatropa* biodiesel yield of 94.7% was obtained at AV of 1.3 mg KOH/g. The catalyst can resist high AV with biodiesel yield of 93.2% and 83.5% at AV of 4.8 and 7.3 mg KOH/g, respectively (Fig. 8a). However, only low-AV oil can be used for the MS production of biodiesel with yield of 81.3% and 81.1% at AV of 1.3 and 2.1 mg KOH/g. As AV increased to 7.3, biodiesel dipped rapidly to 48.5% (Fig. 8b). With previous

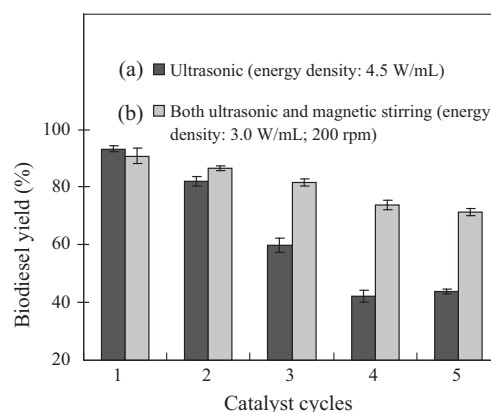


Fig. 9. *Jatropa* biodiesel production with $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4/\text{C}$ catalyst under (a) ultrasonic (4.5 W/mL), (b) both ultrasonic (3 W/mL) and magnetic stirring (200 rpm) conditions changed with catalyst cycles with oil at AV of 4.8 mg KOH/g. Reaction conditions: 328 K for 80 min with 7/1 methanol/oil molar ratio and 7 wt% catalyst.

reported $\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4$ catalyst assisted by MS, biodiesel yield was only about 85% and 65% at AV of 3.0 and 5.0 mg KOH/g, respectively [14]. Our catalyst under US showed strong resistance to FFAs with biodiesel yield of 93.2% at AV of 4.8, and 83.5% at high AV of 7.3 mg KOH/g.

The catalyst assisted with US resisted FFAs which could be due to two aspects: (i) The formation of free radicals caused by the breakdown of methanol and oil molecules on asymmetric cavitation bubble collapse [28,32] promotes the esterification of FFAs to fatty acid methyl esters (biodiesel) and inhibit the saponification of FFAs [33]; and (ii) extremely high temperature in the microenvironment caused by acoustic cavitation [28,32] would melt the saponified products that may form a semi-solidified or viscous substance at reaction temperatures, and transesterification reactions will proceed. Salamatinia et al. [33] also found that less soap formed and lower AV of biodiesel obtained by US than MS assistance.

Jatropha oil with AV of 4.8 mg KOH/g was used to test the catalyst stability (Fig. 9). It was found that under US (4.5 W/mL), the catalyst can be cycled 2 times with biodiesel yield of 93.2% and 82.1% for the first and second cycles but the yield sharply dropped to 60.0% at the third cycle (Fig. 9a). However, similar to Section 3.4, under both US and MS (3.0 W/mL and 200 rpm) assistances, the catalyst can be cycled 5 times with biodiesel yield gradual decreasing from 90.8% to 71.4% (Fig. 9b).

High US energy density (1.5–6 W/mL) was used in the above experiments due to the small volume of sample (about 6 mL) in the 40-mL plastic tubular reactor (Fig. 1a), so most of US energy was lost. In order to save energy for practical application, more reaction sample (90 mL) was used in a large flask (Fig. 1c). Five experiments with two repeated runs were conducted at US energy density of (4.5, 3, 1, 0.3 and 0.1 W/mL) with MS (at 200 rpm) for *Jatropha* oil with 4.8 AV under the optimized conditions (i.e., 328 K for 80 min with 7 wt% catalyst and 7/1 methanol/oil), surprisingly, biodiesel yields were very high with $95.2 \pm 0.9\%$, $93.0 \pm 1.0\%$, $95.8 \pm 1.0\%$, $92.7 \pm 0.6\%$ and $90.7 \pm 0.5\%$, respectively. Biodiesel yield reached the highest 95.8% at 1 W/mL, and still maintained 90.7% at 0.1 W/mL US energy density. The catalyst is expected to be damaged less and recycled more times at low US energy density (e.g., 0.1 W/mL) based on the above recycled experiments in Section 3.4. These results showed that low ultrasonic energy density was effective to resist high free fatty acids and promote biodiesel production. The energy density can be further optimized by reactor design (shape), volume of samples, position of transducer horn as well as combination with MS stirring.

4. Conclusions

Magnetic solid ($\text{Na}_2\text{SiO}_3/\text{Fe}_3\text{O}_4/\text{C}$) catalyst was obtained by precipitation, calcination and catalyst loading. It had strong magnetism with high recovery rate and presented active, stable, recyclable and resistant to free fatty acids for biodiesel production assisted by ultrasonic irradiation and magnetic stirring. Soybean biodiesel yield of 97.9% was achieved with 5 catalyst cycles (biodiesel yield >80%) and recovery rate of 94.9% under both ultrasonic and magnetic stirring conditions. *Jatropha* biodiesel yields were 93.2% and 83.5% at acid values of 4.8 and 7.3 (mg KOH/g) under ultrasound, respectively. It is also found that low ultrasonic energy density was effective to resist high free fatty acids and promote biodiesel production, with *Jatropha* biodiesel yield of 90.7% at acid value of 4.8 (mg KOH/g) and ultrasonic energy density of 0.1 W/mL. The catalyst can find practical application but further study is required to optimize ultrasonic energy density, ultrasonic frequency, reactor design (shape), volume of samples, position of transducer horn, magnetic stirring as well as reaction variables.

Acknowledgements

The authors wish to acknowledge the financial support from Chinese Academy of Sciences [Bairenjihua, CAS 135 program (XTBG-T02) and equipment R&D grant (No. YZ201260)], the Yunnan Provincial Government (Baiming Haiwai Gaocengci Rencai Jihua), and the Natural Science Foundation of China (No. 31400518). Thanks are also given to Dr. Lin Lin, Miss Wenyu Wu and Mr. Chunyu Sun (Jiangsu University) for VSM analysis.

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.fuel.2015.02.032>.

References

- [1] Jacobson MZ. Review of solutions to global warming, air pollution, and energy security. *Energy Environ Sci* 2009;2:148–73.
- [2] Sathre R. Comparing the heat of combustion of fossil fuels to the heat accumulated by their lifecycle greenhouse gases. *Fuel* 2014;115:674–7.
- [3] Lois E. Definition of biodiesel. *Fuel* 2007;86:1212–3.
- [4] Lin L, Zhou CS, Saritporn V, Shen XQ, Dong MD. Opportunities and challenges for biodiesel fuel. *Appl Energy* 2011;88:1020–31.
- [5] Deng X, Fang Z, Liu YH. Ultrasonic transesterification of *Jatropha curcas* L. oil to biodiesel by a two-step process. *Energy Conv Manag* 2010;51:2802–9.
- [6] Li XF, Zuo Y, Zhang Y, Fu Y, Guo QX. In situ preparation of K_2CO_3 supported Kraft lignin activated carbon as solid base catalyst for biodiesel production. *Fuel* 2013;113:435–42.
- [7] Kouzu M, Hidaka JS. Transesterification of vegetable oil into biodiesel catalyzed by CaO : a review. *Fuel* 2012;93:1–12.
- [8] Tantirungrotechai J, Thepwattee S, Yoosuk B. Biodiesel synthesis over Sr/MgO solid base catalyst. *Fuel* 2013;106:279–84.
- [9] Gombotz K, Parette R, Austic G, Kannan D, Matson JV. MnO and TiO solid catalysts with low-grade feedstocks for biodiesel production. *Fuel* 2012;92:9–15.
- [10] Guo F, Wei NN, Xiu ZL, Fang Z. Transesterification mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate. *Fuel* 2012;93:468–72.
- [11] Long YD, Fang Z, Su TC, Yang Q. Co-production of biodiesel and hydrogen from rapeseed and *Jatropha* oils with sodium silicate and Ni catalysts. *Appl Energy* 2014;113:1819–25.
- [12] Hu SY, Guan YP, Wang Y, Han HY. Nano-magnetic catalyst $\text{KF/CaO-Fe}_3\text{O}_4$ for biodiesel production. *Appl Energy* 2011;88:2685–90.
- [13] Lin L, Li XQ, Cui FJ, Zhou HN, Shen XQ, Dong MD. Transesterification of rapeseed oil to biodiesel on $\text{CaO}/\alpha\text{-Fe}$ hollow fiber catalyst: optimization by response surface methodology. *BioEnergy Res* 2012;5:949–57.
- [14] Guo PM, Huang FH, Zheng MM, Li WL, Huang QD. Magnetic solid base catalysts for the production of biodiesel. *J Am Oil Chem Soc* 2012;89:925–33.
- [15] Sanli H, Canakci M, Alptekin E. Predicting the higher heating values of waste frying oils as potential biodiesel feedstock. *Fuel* 2014;115:850–4.
- [16] Dias JM, Alvim-Ferraz MCM, Almeida MF, Díaz JDM, Polo MS, Utrilla JR. Selection of heterogeneous catalysts for biodiesel production from animal fat. *Fuel* 2012;94:418–25.
- [17] Teo SH, Rashid U, Taufiq-Yap YH. Biodiesel production from crude *Jatropha Curcas* oil using calcium based mixed oxide catalysts. *Fuel* 2014;136:244–52.
- [18] Chen GY, Shan R, Shi JF, Yan BB. Ultrasonic-assisted production of biodiesel from transesterification of palm oil over ostrich eggshell-derived CaO catalysts. *Bioresour Technol* 2014;171:428–32.
- [19] Takase M, Feng W, Wang W, Gu X, Zhu Y, Li T, et al. *Silybum marianum* oil as a new potential non-edible feedstock for biodiesel: a comparison of its production using conventional and ultrasonic assisted method. *Fuel Process Technol* 2014;123:19–26.
- [20] Badday AS, Abdullah AZ, Lee KT. Transesterification of crude *Jatropha* oil by activated carbon-supported heteropolyacid catalyst in an ultrasound-assisted reactor system. *Renew Energy* 2014;62:10–7.
- [21] Badday AS, Abdullah AZ, Lee KT, Khayoon MS. Intensification of biodiesel production via ultrasonic-assisted process: a critical review on fundamentals and recent development. *Renew Sustain Energy Rev* 2012;16:4574–87.
- [22] Worapun I, Piantong K, Thaiyavit P. Two-step biodiesel production from crude *Jatropha curcas* L. Oil using ultrasonic irradiation assisted. *J Oleo Sci* 2012;61:165–72.
- [23] Xue BJ, Luo J, Zhang F, Fang Z. Biodiesel production from soybean and *Jatropha* oils by magnetic $\text{CaFe}_2\text{O}_4\text{-Ca}_2\text{Fe}_2\text{O}_5$ -based catalyst. *Energy* 2014;68:584–91.
- [24] Berchmans HJ, Hirata S. Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. *Bioresour Technol* 2008;99:1716–21.
- [25] Hawash S, Diwani GE, Kader EA. Optimization of biodiesel production from *Jatropha* oil by heterogeneous base catalysed transesterification. *Int J Eng Sci* 2011;3:5242–51.

- [26] Anastopoulos G, Zannikou Y, Stournas S, Kalligeros S. Transesterification of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters. *Energies* 2009;2:362–76.
- [27] Liu XR. Catalyst characterization and evaluation. In: Huang ZT, editor. *Handbook of industrial catalyst*. Beijing: Chemical Industry Press; 2004. p. 187–9 [in Chinese].
- [28] Luo J, Fang Z, Smith RL. Ultrasound-enhanced conversion of biomass to biofuels. *Prog Energy Combust Sci* 2014;41:56–93.
- [29] Worapun I, Pianthong K, Thaiyasuit P. Optimization of biodiesel production from crude palm oil using ultrasonic irradiation assistance and response surface methodology. *J Chem Technol Biotechnol* 2012;87:189–97.
- [30] Gole VL, Gogate PR. Intensification of synthesis of biodiesel from nonedible oils using sonochemical reactors. *Ind Eng Chem Res* 2012;51:11866–74.
- [31] Boffito DC, Mansi S, Leveque JM, Pirola C, Bianchi CL, Patience GS. Ultrafast biodiesel production using ultrasound in batch and continuous reactors. *ACS Sustain Chem Eng* 2013;1:1432–9.
- [32] Fang Z, Smith Jr RL, Qi XH. *Production of biofuels and chemicals with ultrasound*. 1st ed. Heidelberg Berlin: Springer-Verlag; 2014. p. 3–86.
- [33] Salamatina B, Abdullah AZ, Bhatia S. Quality evaluation of biodiesel produced through ultrasound-assisted heterogeneous catalytic system. *Fuel Process Technol* 2012;97:1–8.