Production of biodiesel from *Jatropha* oil catalyzed by nanosized solid basic catalyst

Xin Deng [a], Zhen Fang [a,*], Yun-hu Liu [a], Chang-Liu Yu [b]

[a] Biomass Group, Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, 88 Xufulu, Kunming, Yunnan province 650223, China
[b] Perochemical Company, Dagang Oilfield Group, Tianjin 300280, China

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ABSTRACT

In this work, hydrotalcite-derived particles with Mg/Al molar ratio of 3/1 were synthesized by a coprecipitation method using urea as precipitating agent, subsequently with (MHT) microwave-hydrothermal treatment, and followed by calcination at 773 K for 6 h. These particles were micro-sized mixed Mg/Al oxides as characterized by SEM and AFM. But actually they were nanosized according to the calculations from XRD data. Because of their strong basicity, the nanoparticles were further used as catalyst for biodiesel production from *Jatropha* oil after pretreatment. Experiments were conducted with the solid basic catalyst in an ultrasonic reactor under different conditions. At the optimized condition, biodiesel yield of 95.2% was achieved, and the biodiesel properties were close to those of the German standard. The catalyst can be reused for 8 times.

1. Introduction

Biodiesel has drawn more and more attention in recent years because it is renewable and has less detrimental effects on environment as compared with conventional diesel derived from petroleum [1]. Biodiesel obtained from renewable biomass feedstocks can be used in diesel engines or blended at various proportions with petroleum diesel as fuel [2]. It consists of mono-alkyl esters that are usually produced by transesterification of plant oil with methanol or ethanol. It has similar and sometimes better physical and chemical properties than petroleum diesel, such as higher flash point, ultra-lower sulphur concentration, better lubricating efficiency and few pollutants produced [3–6]. However, biodiesel is expensive due to the high price of plant oil and some processing technological issues, such as catalyst and equipment. Therefore, little commercial biodiesel is used in China. The raw materials exploited commercially by some developed countries are edible oils such as, rapeseed, soybean, palm, sunflower, coconut and linseed oils [3,7]. The fraction of raw materials for world commercial biodiesel production is rapeseed oil 84%, sunflower oil 13%, palm oil 1%, soybean oil and others 2% [7]. Using edible oils to produce biodiesel in developing countries such as China with limited arable land per capita is not feasible and is banned. Therefore, only non-edible plants are considered as favorable resources for biodiesel production, such as Chinese tallow [8] and *Jatropha curcas L.* trees [9,10], which are producing non-edible oil in appreciable quantity and can be grown in a large-scale on non-cropped marginal lands and wastelands. *Jatropha curcas L.*, a drought-resistant shrub or tree, is widely distributed in the wild in semi-cultivated tropical or subtropical areas in Central and South America, Africa, India, and South China. It has a productive lifespan in excess of 30 years. The fatty acid composition of *Jatropha* oil is similar to other edible oils, but the presence of some toxic materials in kernel (e.g., curcin) renders the oil unsuitable for cooking purposes [11,12]. The oil content in *Jatropha* seed ranges from 25% to 40% by weight and in the kernel itself ranges from 45% to 60% [10]. Nowadays, *Jatropha* trees, as a potential alternative biodiesel crop, are widely cultivated in Southwest of China such as Yunnan, Sichuan, and Guangxi provinces [9]. In the near future, it will supply part of crude oil for commercial biodiesel production in China.

The conventional industrial production of biodiesel is through transesterification of crude oil with a homogeneous strong base catalyst such as NaOH and KOH [1,3,13]. After reaction, recovery of glycerol, removal of base catalyst from products, and treatment of alkaline wastewater are costly and non-environmental. Furthermore, a homogeneous base catalyst is ineffective for production biodiesel from high acid-value crude oils due to the formation of soap. Tan et al. [14] reported a catalyst-free biodiesel production method, using waste palm cooking oil as raw material and

* Corresponding author. Tel.: +86 871 5163360; fax: +86 871 5160916.
E-mail address: zhenfang@xtbg.ac.cn (Z. Fang).
URL: http://brg.groups.xtbg.cn/

supercritical methanol. But the method has a high cost in reactor and operation (due to high pressures and high temperatures), and high methanol consumption (e.g., high methanol/crude-oil molar ratio of 40/1). Therefore, heterogeneous solid catalysts were used for the transesterification process, where a better separation and reuse of the catalysts without saponification were achieved [15].

Preparation and application of solid superbase catalysts are an emerging area that is attracting more and more attention, because the catalysts are easily separated for reuse and possess a high activity for various reactions under mild conditions. They can replace homogeneous base catalysts in order to minimize the production of pollutants. LDHs (Layered double hydroxides) are important inorganic materials with layered structure and anion exchanged capacity. As classical solid base materials, calcined LDHs are widely used as catalyst in the production of biodiesel [16—18]. In previous work [17], transesterification process was carried out with reflux of methanol, methanol/soybean-oil molar ratio of 15/1, reaction time of 9 h and catalyst amount of 7.5%, and oil conversion rate was only 67%. In the work of Brito et al. [18], waste oil as feedstock, biodiesel production was performed at high temperatures ranging from 353 to 433 K, methanol/oil molar ratio from 12/1 to 48/1 and catalyst concentration from 3 to 12%, respectively, and 90% biodiesel yield was achieved. Ultrasonic radiation is a relative new technique that results in the formation and collapse of microscale bubbles in liquid to generate local high temperature and high pressure. So, it can be used as an alternative energy source to promote reactions. It enormously reduces reaction time, methanol/oil molar ratio and catalyst concentration. Therefore, biodiesel production with calcined hydrotalcite catalyst coupled with ultrasonic radiation is likely to become a new effective method.

The purpose of this work is to synthesize hydrotalcite particles and subsequently to calcine them as catalyst for biodiesel production. Hydrotalcite particles were prepared in an ultrasonic reactor by coprecipitation of aqueous nitrate solutions of Mg and Al using urea as precipitating agent, and subsequently with MHT (microwave-hydrothermal treatment). The synthesized particles, after calcination, were used as solid basic catalyst in the transesterification of *Jatropha* oil to test their activities in the ultrasonic reactor. Experiments under different reaction conditions, such as methanol/*Jatropha*-oil molar ratio, catalyst concentration, reaction temperature and ultrasonic power, were performed in order to optimize biodiesel yield. The reasons for catalyst deactivation were also studied.

2. Experimental

2.1. Materials

Nitrates of Mg and Al (99.8% purity) used in the synthesis were obtained from Chengdou Fine Chemical Co. Ltd. Urea (99.0% purity) and methanol (99.0% purity) were purchased from Shanghai Fine Chemical Co. Ltd. *Jatropha* oil with high FFAs (free-fatty-acids) was obtained from our institute in Xishuangbanna, Yunnan province, Southwest of China [9]. According to the Chinese National standards GB 9014.2-88 and GB 164-64, *AV* (acid value) and *SV* (saponification value) of the *Jatropha* oil were measured as 10.5 mg KOH/g and 191.0 mg KOH/g, respectively. So its molecular weight was calculated as 932 g/mol by the formula: $M = (56.1 \times 1000 \times 3)/(SV - AV)$ [19].

2.2. Catalyst preparation

Hydrotalcite particles with Mg/Al molar ratio of 3/1 were synthesized by a coprecipitation method using urea as precipitating agent, and with MHT. In this method, a solution (0.15 M Mg nitrate and 0.05 M Al nitrate) was made in a three-neck flask by dissolving the two solid nitrates in deionized water. Urea {[urea]/[NO_3^-] molar ratio of 4/1} was then added into the flask. The flask was submerged in an oil bath at 373 K with stirring about 500 rpm in the ultrasonic reactor for 2 h. The slurry obtained was subsequently submitted to MHT in the mother liquor for 2 h at 393 K. After filtered, washed thoroughly with deionized water and dried at 373 K for 10 h at a vacuum condition, solid hydrotalcite particles were obtained. They were characterized by powder XRD (X-Ray Diffraction). Catalytic activity of hydrotalcite was studied by the transesterification of *Jatropha* oil with methanol to biodiesel. Without calcination, hydrotalcite displayed no particular catalytic activity in the reaction. But, after calcined, hydrotalcite was in the form of OH contained mixed Al-Mg oxides which had heterogeneous surface basicity with basic sites of low (OH-groups), medium (Mg-O pairs), and strong (O^{2-} anions) basicity and exhibited a significant activity [20]. So, hydrotalcite particles were calcined at 773 K for 6 h in a muffle furnace and used as catalyst for the following biodiesel production.
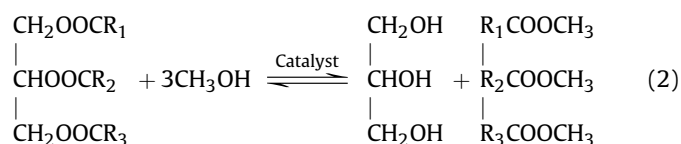
2.3. Biodiesel production

Biodiesel production process is strongly influenced by the fatty acid composition and FFAs content of crude oil. The *AV* of fresh *Jatropha* oil in Xishuangbanna, Yunnan province, is from 5 to 12 mg KOH/g. Owing to its high FFAs, the transesterification of *Jatropha* oil to biodiesel catalyzed directly by solid catalyst had a low conversion rate. Even using longer reaction time, only 80.4% biodiesel yield was achieved. In order to increase biodiesel yield, FFAs in *Jatropha* oil need to remove. A two-step process of *Jatropha* oil to biodiesel was used to resolve the problem [10].

First, an acid-esterification pretreatment was performed with concentrated sulfuric acid as catalyst. The three-neck flask with a water-cooled condenser was filled with 200-mL *Jatropha* oil, 40-mL anhydrous methanol and 4-mL sulfuric acid. The mixture was vigorously stirred and refluxed at 318 K in an ultrasonic reactor for 1.5 h. After reaction, the mixture was filtered, and the unreacted methanol was separated from the liquid phase via rotary evaporation. The oil was washed three times with sodium chloride solution then dried using anhydrous sodium sulfate. After the pretreatment, the *AV* of the pretreated oil was reduced to only 0.7 mg KOH/g with 93.3% esterification rate. The reaction equation was described as below:

$$RCOOH + CH_3OH \rightarrow RCOOCH_3 + H_2O \qquad (1)$$
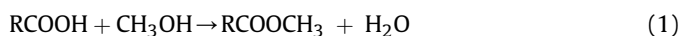
The second step, a base-catalyzed transesterification reaction (Eq. (2)) was carried out in the same ultrasonic reactor with the calcined hydrotalcite catalyst:

$$\begin{array}{ccc} CH_2OOCR_1 & & CH_2OH \quad R_1COOCH_3 \\ | & & | \qquad\qquad | \\ CHOOCR_2 \;+\; 3CH_3OH \underset{}{\overset{Catalyst}{\rightleftharpoons}} & CHOH \;+\; R_2COOCH_3 \quad (2) \\ | & & | \qquad\qquad | \\ CH_2OOCR_3 & & CH_2OH \quad R_3COOCH_3 \end{array}$$

Biodiesel yield was calculated as:

$$\text{Biodiesel yield}(\%) = (\text{total actual weight of methyl esters} \times 100)/(\text{total theoretical weight of methyl esters}) \qquad (3)$$

where, total weight of methyl esters were produced from both steps, total theoretical weight was obtained assuming 100% conversion of fatty acids in *Jatropha* oil according to Eqs. 1 and 2.

The reaction procedure was as follows: first, the catalyst was dispersed in methanol with mechanical stirring (about 600 rpm).

Then, the above pretreated oil was added into the mixture and heated to 318 K by water bath. After reaction, excessive methanol was distilled off under a vacuum condition while catalyst was separated by high-speed centrifugation. After removal of the glycerol layer, biodiesel was collected and ready for Chromatographic analyses.

2.4. Jatropha oil and biodiesel analyses

2.4.1. Jatropha oil

The composition of crude oil was analyzed by Gas Chromatography (GC, Shimadzu, GC-2014) with a flame ionization detector and a capillary column (Rtx-Wax 30 m × 0.25 mm × 0.25 μm). Oxygen-free nitrogen was used as a carrier gas at a flow rate of 1.4 mL/min. Other conditions were as follows: initial oven temperature of 443 K (2 min), ramp at 5.0 K/min, final temperature of 503 K (4 min), injector temperature of 523 K, detector temperature of 553 K, and a split ratio of 39/1. The analysis was carried out by injecting 1-μL sample solution (0.25-mL crude Jatropha-oil dissolved in 9.75-mL n-hexane) into the GC. Undecanoic acid methyl ester was used as the internal standard. The fatty acids in Jatropha oil were identified and quantified by comparing their retention times and peak areas to those of standard fatty acids. Fig. 1 shows six fatty acids were identified and quantified as: palmitic acid (C16:0) 15.18%, palmitoleic acid (C16:1) 0.99%, stearic acid (C18:0) 6.25%, oleic acid (C18:1) 41.17%, linoleic acid (C18:2) 31.25%, and linolenic acid (C18:3) 0.08%.

2.4.2. Biodiesel

Biodiesel was also analyzed by the above GC method under similar conditions. The prepared biodiesel (5 mL) was dissolved in 20-mL dichloromethane and 1-mL internal standard solution for GC analysis. Sample solutions (1 μL) were injected by a sampler at an oven temperature of 493 K. Helium was used as carrier gas at a flow rate of 0.8 mL/min. Identification of methyl ester peaks was done by comparing the retention times between the samples and the standard compounds. Methyl esters (biodiesel) were quantified by comparing the peak areas between the samples and the standard compounds.

2.5. Characterization of hydrotalcite particles

XRD analyses were conducted on a Siemens D-5000 diffractometer with a CuKα radiation source at voltage of 40 kV and current of 30 mA, Ni-filtered and a graphite secondary monochromater. Samples were analyzed in a continuous scan mode between 5° and 70° (2θ). Scanning Electron Microscope (SEM, Hitachi S-520) measurements were carried out at 11 kV. AFM (Atomic Force Microscope) images were obtained using WET-SPM-9500-J3 instrument (Shimadzu Co. Ltd.). Samples for AFM observation were dispersed in an alcohol solution for 8 h in an ultrasonic reactor. Nitrogen physisorption was conducted on a Micromeritics ASAP-2020 surface area and porosimetry system. The elemental analyses were determined by wavelength dispersive XRF (X-Ray Fluorescence) spectrometer (Bruker AXS).

2.6. Physicochemical properties of biodiesel

Flash point, pour point, viscosity, AV and cetane number of biodiesel were measured according to the Chinese national standards GB 267-64, GB 265-64, GB 164-64 and GB 386-64. Other physicochemical properties of biodiesel were obtained according to references [19] and [21].

3. Results and discussion

3.1. Characterization of hydrotalcite and calcined hydrotalcite

XRD patterns of hydrotalcite particles with Mg/Al molar ratio of 3/1 were given in Fig. 2. In Fig. 2a, the particles exhibited a single phase, corresponding to a typical hydrotalcite structure (JCPDS file 70-2151) with strong, sharp, and symmetric peaks for the (003), (006), (110), and (113) planes as well as broad and symmetric peaks for the (009), (015), and (018) planes [22]. The average particle size was calculated as 7.3 nm by the Scherer equation [$Dc = k((\lambda/\beta) \bullet \cos \theta)$; where Dc is the average particle size; k is the Scherer constant (0.89); λ is the X-ray wavelength, (CuKα) = 0.1541 nm; β is the FWHM (full-width at half-maximum); θ is the diffraction angle] in the XRD (003) reflection [23,24]. After calcined at 773 K for 6 h, hydrotalcite particles were decomposed to mixed Mg-Al complex oxides, which were confirmed by the XRD pattern in Fig. 2b. For the calcined particles, the characteristic reflections were observed clearly at 2θ of 43° and 63°, corresponding to an MgO-like phase or magnesia-alumina solid phase. The peaks of Al_2O_3 phase were very small, indicating that Al^{3+} cations were dispersed in the structure of MgO without the formation of spinel species [15,25].

SEM images of hydrotalcite and calcined hydrotalcite were given in Fig. 3. Hydrotalcite had a relatively uniform hexagonal
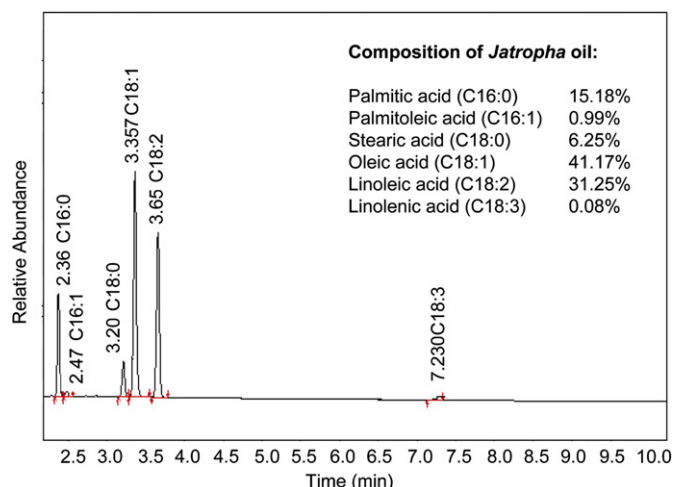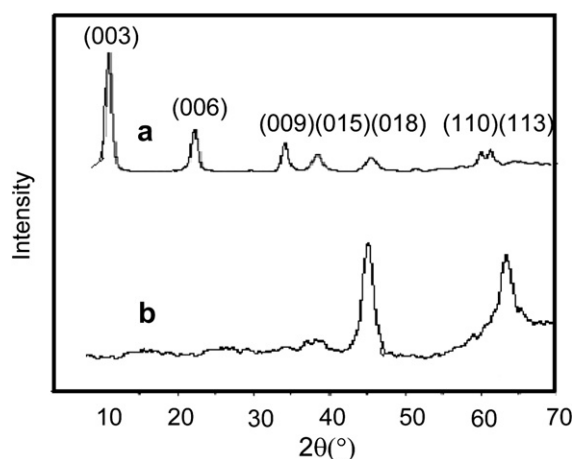

Fig. 1. GC graph for crude Jatropha oil.

Fig. 2. XRD patterns of hydrotalcite: (a) without calcination, and (b) after calcined at 773 K for 6 h.
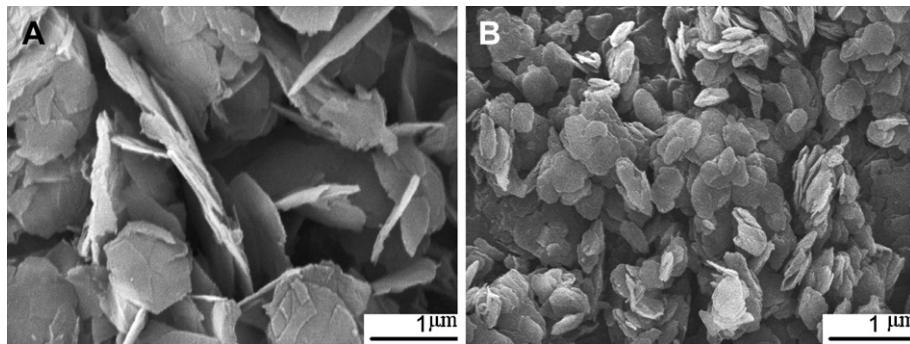
Fig. 3. SEM images of (A) hydrotalcite, and (B) calcined hydrotalcite at 773 K for 6 h.

platelet-like structure, but partly destroyed at the calcined temperature of 773 K. Before calcination, hydrotalcite had a well-developed platelet structure of a typical layered material with a uniform size of 1 μm width and 72 nm thickness (Fig. 3A) that is much larger than the above calculated value (7.3 nm). The possible reason is that the platelets were formed by agglomeration with numerous fine nanoparticles. After calcined at 773 K, the uniform hexagonal platelet structure was partly destroyed due to the removal of hydroxyl groups in the metal hydroxide layers and carbon dioxides production from the decomposition of CO_3^{2-} existed in the interlayer space as charge-balancing anion. But it still kept sheet structure with a smaller size of 372 nm width and 72 nm thickness (Fig. 3B).

AFM images of the calcined hydrotalcite particles at 773 K for 6 h with the solid structure, diameter and thickness were given in Fig. 4. The particles of the metal hydroxide layers were congregated to form a large layered structure with the size of 941 nm width and 381 nm thickness. However, the average particle size was only 372 nm width and 72 nm thickness in Fig. 3B, which indicated that large particles were formed by agglomeration that were hard to separate for AFM analyses even after ultrasonic dispersion treatment.

The Mg/Al atomic ratio in the mixed metal oxide sample was verified by XRF spectroscopy. The actual Mg/Al atomic ratio was 2.78/1, that is close to 3/1 of the starting Mg and Al nitrates. Physical-chemical properties of calcined hydrotalcite were given in Table 1, and they agreed well with the earlier measurements by Tantir-ungrotechai et al. [16]. The Mg-Al mixed metal oxide sample exhibited high surface area of 218 m^2/g with pore volume and pore diameter of 0.17 cm^3/g and 3.9 nm, respectively. The basic strength of it was determined by Hammett indicator. Calcined hydrotalcite contained surface basic sites of low (OH$^-$ group), medium (Mg-O pairs) and strong (O^{2-}) basicities. The main basic sites with H_ were in the range of 7.2–9.8 and the other sites with H_ were in the range of 9.8–15. The similar results were obtained by Xie et al. [17,26].

3.2. Transesterification reaction

Biodiesel was produced by a two-step process. The first step-pretreatment (acid-esterification) of *Jatropha* oil was studied in our previous work [10], so in this paper only the second step solid base catalytic transesterification experiments were introduced and discussed.
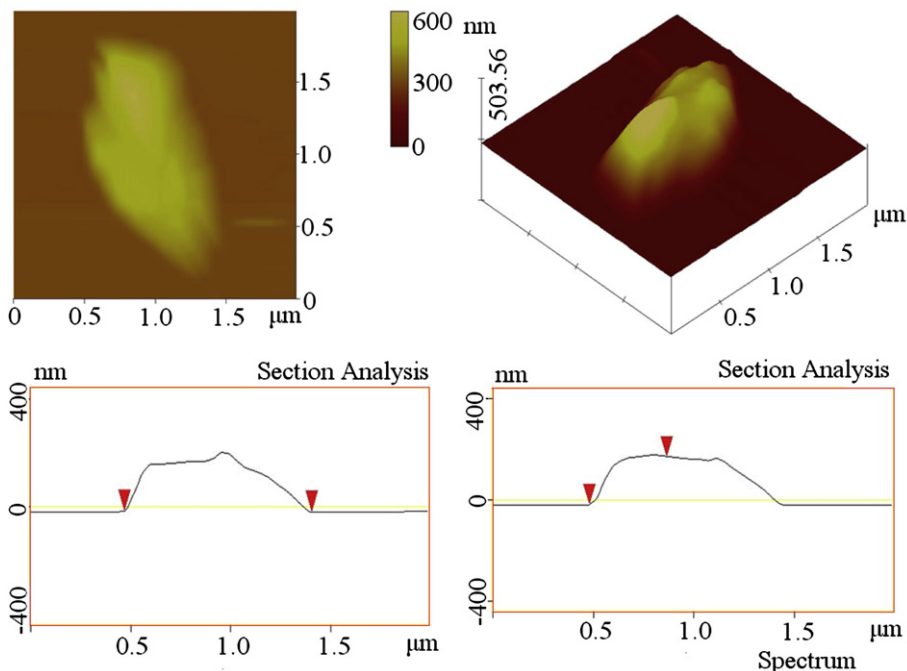

Fig. 4. AFM images of the calcined hydrotalcite at 773 K for 6 h.

Table 1
Physical-chemical properties of calcined hydrotalcite at 773K for 6 h.

sample	Mg/Al molar ratio (actual)	Surface area (m²/g)	Pore volume (cm³/g)	Pore diameter (nm)	Basicity (mmol/g)
Mg-Al (3/1)	2.78	218	0.17	3.9	3.4

The transesterification process consisted of three consecutive reversible reactions, wherein *Jatropha* oil was successively converted into diglyceride and monoglyceride, and finally into glycerin and FAMEs (fatty acid methyl esters) [26,27]. Fig. 5 gave the produced biodiesel consisting of six FAMEs: palmitic acid (C16:0) 13.79%, palmitoleic acid (C16:1) 0.95%, stearic acid (C18:0) 6.33%, oleic acid (C18:1) 42.61%, linoleic acid (C18:2) 26.34%, and linolenic acid (C18:3) 0.06%.
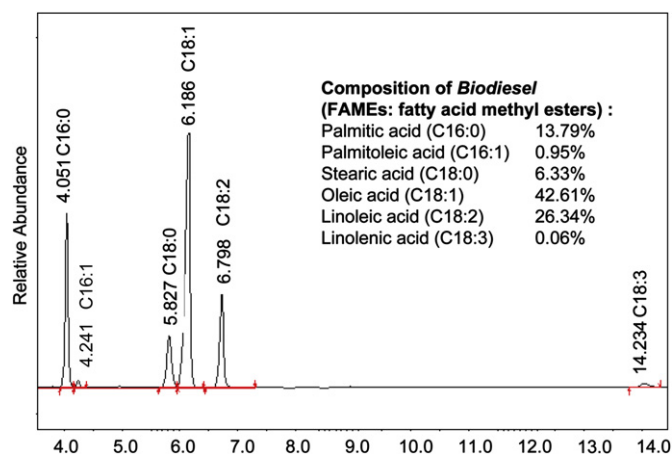

Fig. 5. GC graph for biodiesel.

The molar ratio of methanol/*Jatropha*-oil was one of the important factors that affected the yield of methyl esters. Stoichiometrically, 3 mol of methanol were required for each mole of *Jatropha* oil (Eq. (2)). However, in practice, methanol/oil molar ratio should be higher than that of stoichiometry in order to drive the reaction toward completion and produce more methyl esters. The effects of methanol/*Jatropha*-oil molar ratio on biodiesel yield were given in Fig. 6a. When the ratio increased from 3/1 to 4/1, the yield of methyl esters rose considerably from 63.0 to 94.7%. Because *Jatropha* oil was immiscible with methanol, the reaction was incomplete and limited by diffusion and thermodynamic process. So, excessive methanol should be used to promote the reaction (Eq. (2)). The maximum yield of 94.7% was achieved when the molar ratio was close to 4/1. Higher molar ratio over the stoichiometric value resulted in a high rate of esters formation and could ensure complete reaction [28]. However, it was observed that at molar ratios above 4/1, excessive methanol had no significant effect on the yield. Conversely, a longer time was required for the subsequent separation stage because separation of the esters layer from glycerol was difficult due to the fact that methanol with one polar hydroxyl group could emulsify the products [29]. Hence, the best methanol/oil molar ratio was selected as 4/1.

The calcined nanoparticles as catalyst exhibited high activity because they possessed strong basic sites and a large surface area. The transesterification reaction was strongly affected by catalyst concentration. Without adding catalyst, little reaction occurred. The effect of catalyst concentration on biodiesel yield was given in Fig. 6b. When the catalyst concentration increased from 0.5 to 1.0 wt%, esters yield was raised from 53.8% to the maximum yield of 93.9%. The reason was that catalyst concentration rose from 0.5 to 1.0 wt% could increase contact between reactants and catalyst. However, when the catalyst concentration increased further above 1.0 wt%, biodiesel yield dropped, which was possibly due to a mixing problem involving reactants, products and solid catalyst. Furthermore, when excessive catalyst was used, the transesterification process was easily emulsified and resulted in hard separation of products. So the optimized catalyst concentration was 1.0 wt%.
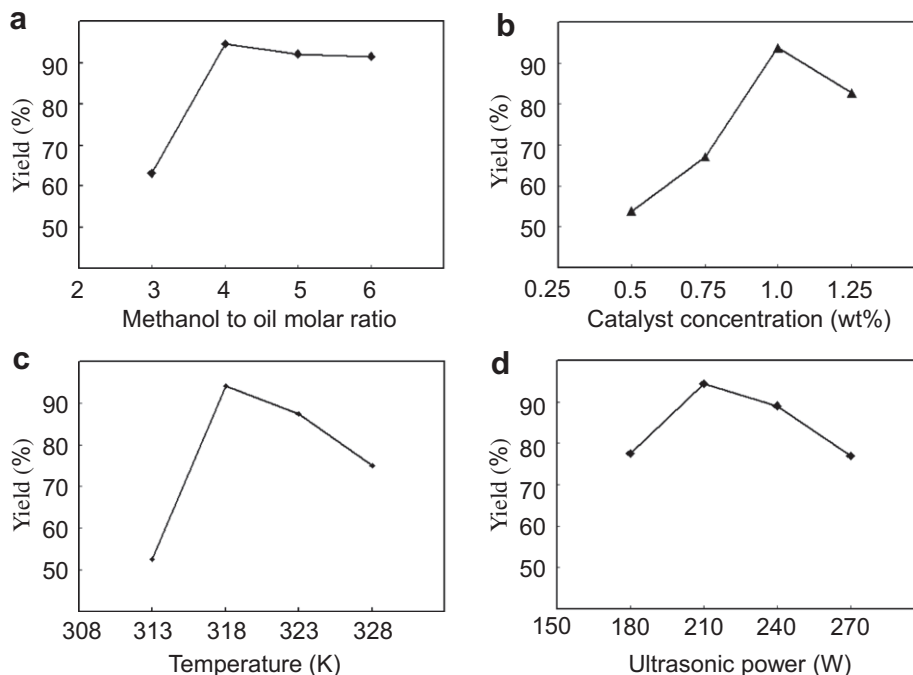

Fig. 6. Effects of variables on biodiesel yield: (a) methanol to oil molar ratio; (b) catalyst concentration; (c) temperature; and (d) ultrasonic power.

Reaction temperature was also an important factor that influenced biodiesel yield. Each experiment was run for 1.5 h with 1 wt% catalyst and 4/1 molar ratio of methanol/oil. The results (Fig. 6c) indicated that biodiesel yield was low at low temperatures with only 52.4% yield at 303 K for 1.5 h. Biodiesel yield increased sharply as temperature rose, and reached 94.2% at 318 K. However, the yield decreased as temperature increased further. When temperature was higher than 318 K, methanol would vaporize and form a lot of bubbles, which could inhibit reactions on the three-phase interface. Therefore, the optimized temperature was around 318 K.

Effect of ultrasonic power on biodiesel yield was investigated with methanol/Jatropha-oil molar ratio of 4/1, 1 wt% catalyst and temperature of 318K (Fig. 6d). Biodiesel yield increased from 77.7% to 94.5% as ultrasonic power rose from 180 to 210 W. In biodiesel production, Jatropha oil, methanol and solid catalyst formed a three-phase reaction mixture due to their immiscibility. Ultrasonic irradiation promoted sufficient mixing, helped the formation and collapse of micro-scale bubbles to generate local high temperature and high pressure, and also provided alternative energy source to promote reactions [30]. However, as the ultrasonic power increased further from 210 to 270 W, biodiesel yield dropped from 94.5 to 76.9%. The possible reason was that methanol was vaporized that it was seen fog formed on the liquid surface at higher ultrasonic power.

At the optimized condition, i.e., methanol/oil molar ratio of 4/1, catalyst concentration of 1.0 wt %, reaction temperature of 318 K, and ultrasonic power of 210 W, three repeated tests were conducted and an average biodiesel yield of 95.2 ± 0.6% was achieved in 1.5 h. The yield (95.2%) is higher than previous works reported (e.g., 67%, 90%) that were conducted at severer reaction conditions (e.g., 9 h, 353−433 K) [17,18]. The possible reason for the high conversion rate is due to ultrasonic radiation that helps mixing reactants with catalyst and promotes reactions, and the highly active nanocatalysts synthesized by using urea as precipitator and with MHT.

3.3. Properties of biodiesel

Owing to the high FFAs, without pretreatment, direct transesterification of Jatropha oil was easily emulsified and the biodiesel produced was not stable. After stored for 1 year, the biodiesel precipitated at the bottom of the container. The two-step process was successfully used to produce high qualified biodiesel. Its properties such as density, flash point, viscosity, AV and cetane number, were close to those of the German standard (DIN V 51606; Table 2). The similar results were obtained by Jain and Sharma [31], De Oliveira et al. [32] and Tiwari et al. [33].

3.4. Stability of biodiesel

Biodiesel was synthesized from Jatropha oil by the two-step process. The AV, viscosity, density and chemical composition of the fresh biodiesel and the stored biodiesel for 1 year were shown in Table 3. After stored for 1 year, the AV, viscosity and density increased slightly, from 0.154, 3.89 and 0.886 to 0.36, 4.05 and 0.887, respectively. However, they were still close to those of the German standard (DIN V 51606; Table 2). The chemical composition indicated that biodiesel stored for 1 year, saturated fatty acids increased slightly, palmitic acid from 13.79% to 15.20% and stearic acid from 6.33% to 8.37%, respectively. Unsaturated fatty acids were decreased, palmitoleic acid from 0.98% to 0.87%, oleic acid from 42.61% to 38.96% and linoleic acid from 26.34% to 25.41%, respectively. The possible reason was unsaturated fatty acids were unstable and oxidized after stored for long time. Linolenic acid was

Table 2
Properties of Jatropha biodiesel.

Parameter	Jatropha oil	Biodiesel	The German Standard (DIN V 51606: 1997)
Density (g/mL, 289 K)	0.892	0.886	0.875−0.900
Flash point (K)	498	459	≥373
Viscosity (mm^2/s, 313 K)	24.5	3.89	3.5−5.0
Acid value (mg KOH/g)	10.5	0.154	≤0.5
Free methanol content (wt%)	−	0.2	≤0.3
Free glycerol content (wt%)	−	0.16	≤0.2
Total glycerol content (wt%)	−	0.18	≤0.25
Sulphur content (wt%)	−	0.003	≤0.01
Cetane number	51	58	≥49
Water content/(mg/kg)	5200	172	≤300
Ash content (wt%)	−	0.024	≤0.05
Pour point (K)	271	268	−
Carbon residue (%)	1.0	0.2	≤0.05
Copper strip corrosion	1a	1a	≤1a
Calorific value (MJ/kg)	38.65	41.72	−
Color	yellow	buff	−

not detected by GC after stored 1 year. It could be concluded that the biodiesel was stable and qualified for use.

3.5. Catalyst deactivation

Deactivation of solid basic catalyst for biodiesel production was caused by the three main reasons. Firstly, products and by-products were absorbed on the surface of the catalyst that would decrease the contact between basic sites and reactants. Secondly, the activity sites were leached partly into solutions. The last reason was that the catalyst structure collapsed. Biodiesel yield was 95.2% if the catalyst was first-time used. After reaction, the used catalyst was separated by high-speed centrifugation, and reused as catalyst for the second time. Biodiesel yield was decreased to 90.4%. For the third time used, biodiesel yield was only 80.7%. The service life of the calcined hydrotalcite for biodiesel production was only 3 times. After the catalyst was separated, we found that viscous liquid was absorbed on the surface of the catalyst. FT-IR (Fourier Transform Infrared) spectrum (Fig. 7) showed that the liquid was glycerol that deactivated the catalyst. Therefore, the viscous liquid on the catalyst was removed by washing with ethanol, and the catalyst was reused. At the 8th time reused, biodiesel yield was 89.1%. But at the 9th time, biodiesel yield sharply decreased to about 43.7%. The catalyst was deactivated but without leachability of Mg^{2+} and Al^{3+} in the liquid products as confirmed by ICP (Inductively Coupled Plasma) [34]. SEM image of the deactivated catalyst was shown in Fig. 8. The catalyst had a platelet-like structure (402 nm width and 64 nm thickness), but it was not as uniform as the initial calcined hydrotalcite (Fig. 3B). It was found that the active sites of the deactivated catalyst disappeared due to its structure collapsed identified by XRD [35].

Table 3
Stability of Jatropha biodiesel.

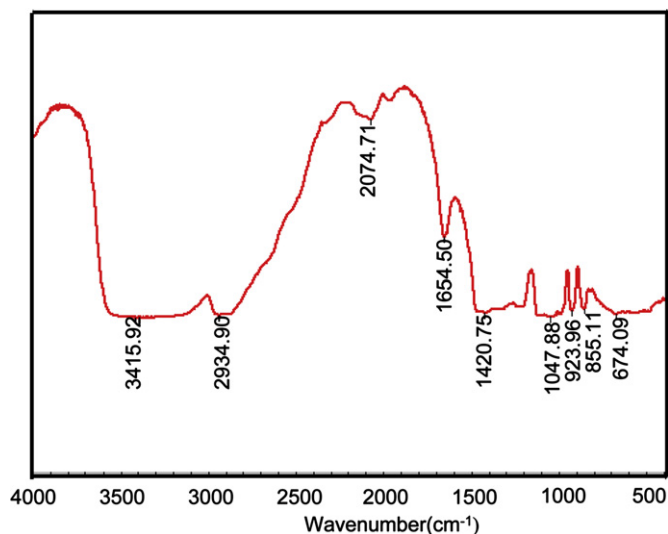| Parameter	Biodiesel (fresh produced)	Biodiesel (stored for 1 year)
Density (g/mL, 289 K)	0.886	0.887
Viscosity (mm^2/s, 313 K)	3.89	4.05
Acid value (mg KOH/g)	0.154	0.36
palmitic acid	13.79%	15.2%
palmitoleic acid	0.95%	0.87%
stearic acid	6.33%	8.37%
oleic acid	42.61%	38.96%
linoleic acid	26.34%	25.41%
linolenic acid	0.06%	−

Fig. 7. FT-IR spectrum of the viscous liquid on the surface of the used catalyst.
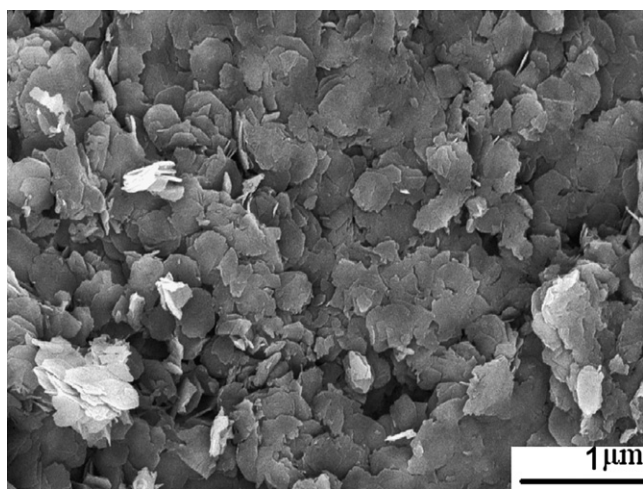

Fig. 8. SEM image of the deactivated catalyst.

4. Conclusion

Solid base nanocatalyst derived from hydrotalcites with Mg/Al molar ratio of 3/1 was synthesized by coprecipitation method using urea as precipitator and with MHT, followed by calcination. The catalyst was only 7.3 nm by calculation, but according to AMF analysis, they congregated to form a layered structure with size as large as 0.941-μm width and 381-nm thickness. Owing to its strong basicity, the catalyst was used for the transesterification of *Jatropha* oil containing 5-12 *AV*s to biodiesel after pretreatment. It was found that at 210 W ultrasonic power, when methanol reacted with the oil (4/1 molar ratio) mixed with 1.0 wt % catalyst at 318 K for 1.5 h, biodiesel yield of 95.2% was obtained that was higher than previous reported, the biodiesel properties were close to those of the German standard (DIN V 51606). The main reasons for catalyst deactivation were the surface absorption of by-product glycerol as well as the collapse of the layered structure. After removing the glycerol on the surface, the catalyst was reused for 8 times. It could be concluded that the calcined hydrotalcite nanocatalyst combined with ultrasonic radiation is an effective method for the production of biodiesel from *Jatropha* oil.

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