Applied Energy xxx (2012) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst

Feng Guo [a,b], Zhi-Long Xiu [a,*], Zhi-Xia Liang [a]

[a] *Department of Bioscience and Biotechnology, School of Environmental and Biological Science and Technology, Dalian University of Technology, Dalian 116024, China*
[b] *Biomass Group, Laboratory of Tropical Plant Resource Science, Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, 88 Xuefu Road, Kunming 650223, China*

ARTICLE INFO

Article history:
Received 25 October 2011
Received in revised form 21 February 2012
Accepted 27 February 2012
Available online xxxx

Keywords:
Biodiesel
Lignin-derived carbonaceous catalyst
Soybean soapstock
Esterification

ABSTRACT

Biodiesel was produced from acidified soybean soapstocks by using lignin-derived carbonaceous catalyst (LCC). LCC was a solid acidic catalyst prepared by direct sulfonation of residual lignin from *Xanthoceras sorbifolia* Bunge hulls. The textural properties of the catalyst were characterized by ^{13}C MAS NMR, X-ray diffraction, FT-IR, elemental analysis and BET surface area measurement. When 7 wt.% of LCC was used in the esterification, the maximum free fatty acids (FFAs) conversion (above 97%) could be achieved at a molar ratio of methanol/oil of 1:9 and a reaction temperature of 70 °C for 5 h. A comparison of catalytic activity between sulfuric acid and LCC revealed that LCC performed 3.5 times higher activity than sulfuric acid with the equivalent active group ($-SO_3H$). Additionally, LCC could be reused at least three times with high FFAs conversion (>80%).

1. Introduction

Biodiesel has gained significant attention in recent years because of its renewability and environment-friendliness comparing with fossil diesel. Exploitation of vegetable oils and animal fats as energy sources plays an important role in our energy, economy and environment system. Transesterification is by far the most common method to produce biodiesel, and the commercial process is catalytically transesterified by homogeneous acid or base [1]. Refined vegetable oils are glyceride-based materials that can be used for biodiesel production. Instead, low-cost oils are fostered to be used as feedstock for biodiesel production, such as inedible oils or fats, unrefined vegetable oils and waste oils [2]. Non-edible soybean soapstock is found to be a better raw material for the synthesis of biodiesel, because it is relatively centralized [3]. However, such oils usually contain some amounts of water and free fatty acids (FFAs). The FFAs are not converted to esters but soap when homogeneous base catalysts are used [4]. As for feed stocks with high level of FFAs, immobilized lipase or acid was usually used to catalyze simultaneous transesterification and esterification [3–6]. The high-cost for immobilized lipase, corrosion behavior for acid and a long reaction time for both catalysts limit their commercial industrial application [7,8].

The development and research of novel and efficient ways using solid catalysts for the transesterification of inedible oil into biodiesel are the key industrial challenges. Solid acid catalysts have gained considerable attention due to their advantages of non-corrosion, non-toxicity, water tolerance, and easy separation for recycling [4,9–13]. Novel solid acid catalysts derived from sulfonation of carbonized D-glucose and sucrose was reported and studied extensively [14–20]. These catalysts were typically prepared from carbohydrates by carbonizing at 400 °C under N_2 and then sulponating at 150 °C. The carbon in the catalysts was in amorphous forms consisting of polycyclic aromatic carbon sheets [15]. All S atoms in the catalysts were in SO_3H groups, which were the active sites [15,17]. However, the high density of hydrophilic functional groups bound to the flexible carbon sheets, led to poor access for the glyceride to the SO_3H groups [20]. Generally, in porous materials, most of the catalytic sites were inside the pore catalyst [21], a hydrophobic carrier is needed for synthesizing an ideal solid acid catalyst. Furthermore, it is commonly known that carbohydrates can be carbonized with sulfuric acid under N_2 [22,23]. Although lignin is a non-carbohydrate biopolymer with cross-linked aromatic structure, it can be carbonized in a similar way. Herein, we proposed a one-step method to synthesize solid catalyst by simultaneous carbonization and sulfonation of lignin materials with concentrated sulfuric acid.

In this work, residual lignin from the hydrolysis of *Xanthoceras sorbifolia* Bunge was collected, and used as starting material for preparing lignin-derived carbonaceous catalyst by simultaneous carbonization and sulfonation with concentrated sulfuric acid under N_2. The textural properties of the prepared catalyst were

---

* Corresponding author. Address: Department of Bioscience and Biotechnology, Dalian University of Technology, Linggong Road 2, Dalian 116024, China. Tel./fax: +86 411 84706369.
E-mail address: zhlxiu@dlut.edu.cn (Z.-L. Xiu).

0306-2619/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.apenergy.2012.02.071

Please cite this article in press as: Guo F et al. Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst. Appl Energy (2012), doi:10.1016/j.apenergy.2012.02.071

characterized and then compared with the reported catalyst. Furthermore, the prepared catalyst was evaluated for biodiesel production from acidified soybean soapstock containing 56 wt.% FFAs. Effect factors of esterification and catalyst recycles were also investigated.

2. Methods

2.1. Materials

Industrial oleic acid (purity 99%), dehydrated methanol (purity 99.5%) and H_2SO_4 (purity 98%) used in this study were obtained from Kermel Corp., Tianjin, China. Soybean soapstock was purchased from Huiliang Soybean Technology Corp., Dalian, China. *X. sorbifolia* Bunge was collected from Huhehaote, China.

2.2. Preparation of lignin-derived carbonaceous catalyst

2.2.1. X. sorbifolia

Bunge was recently considered as oil plant in China, and is planed to plant on a commercial scale. If oil from *X. sorbifolia* Bunge was used to produce biodiesel, a large amount of nutshells would be produced. Bioconversion of lignocellulosic materials to ethanol has been recognized as one of the promising routes of producing competitive substitutes to gasoline. Lignin residual remained after hydrolysis of hulls of *X. sorbifolia* Bunge. Using the residual lignin as starting materials for preparing solid acid is undoubtedly an attractive method for comprehensive uses of biomass.

Hulls of *X. sorbifolia* Bunge were firstly grounded to powders and pretreated to remove the soluble components according to the method of Van Soest [24]. The obtained solid mixture, including cellulose, hemicelluloses and lignin, was hydrolyzed by cellulase after pretreatment in diluted sulfuric acid solution. After filtration, the hydrolyzates were used for ethanol fermentation, and the residue was dried and then carbonized and sulfonated by concentrated sulfuric acid. A typical preparation process of sulphonated amorphous carbon from lignin was as follows: Ten grams of the residue was put into a 250 ml three-necked round-bottomed flask. The flask was immersed in a thermostat-controlled oil-bath controlled at 150 °C. After aerated by nitrogen for 30 min, 5 ml of concentrated H_2SO_4 (98%) solution was added to the flask to start carbonization and sulfonation. After 60 min, the mixture was cooled to room temperature, filtered and washed by deionized water until the wash water to reach pH of 7.0. Finally, the obtained LCC was dried at 150 °C for 2 h. In order to find out the structural differences, carbonaceous solid acid was also prepared according to the reported two-step method [22,23]. Lignin powders were pyrolyzed at 400 °C for 1 h under nitrogen gas flow. The pyrolyzed char was then washed several times with hot water to remove residual chemicals, mineral matter and impurities, and oven-dried overnight at 105 °C. Sulfonation was carried out at 150 °C for 2 h with 10-g char immersed and stirred in 5-ml concentrated sulfuric acid (98%). The sulfonated sample was rigorously washed with hot distilled water to remove any physically adsorbed species until free of sulfate ions. The resulting sample was dried in an oven at 105 °C for 48 h and used as the catalyst.

2.3. Catalyst characterization

Spectrum of ^{13}C MAS NMR was recorded on a Bruker MSL 400 M spectrometer (BRUKER, CH). X-ray diffraction (XRD) was conducted using Cu Kα ($\lambda = 0.154$ nm) as radiation source in an automatic X-ray diffractometer (RIGAKU DENKI, JPN). The sample was scanned in the range of 2θ of 5–80°at a scanning speed of 2°/min. Scans were collected by an MDI XRD diffractometer control and data acquisition system (MDI, US). Forier-Transform Infrared (FT-IR) spectra (EQUINOX55, GER) were applied to characterize the structure of the catalyst, with a scanning range from 900 to 1900 cm^{-1}. Elemental composition of the prepared catalyst was determined by elemental analysis (EA) using VARIO EL III apparatus (ELEMENTAR, GER). Furthermore, the acid density of SO_3H groups was examined by EA. The BET surface area of the prepared catalyst was measured with AUTOSORB-1-MP (QUANTACHROME, US).

2.4. Reaction procedure

Composition and characteristics of soybean soapstock, such as soap content, acid value, moisture, content of phospholipids and glyceride, were determined according to the National Standards of PR China: GB 5533-85, GB/T 14489.3-93, GB/T 14489.1-93, GB/5537-85 and GB/T 14488.1-93, respectively. The acid oil was prepared according to modification of the published methods [25]: In a typical procedure, the soybean soapstock (500 g) was mixed with 50 ml of saturated NaCl solution and 200 ml of petroleum ether (bp 40–60 °C, reagent grade) and maintained at room temperature for 12 h. After centrifugation, the phospholipid contained in the upper phase was removed by acetone. The soap phase was acidified using 50% sulfuric acid in a 250 ml three-necked round-bottom flask. The acidification was carried out at 60 °C for 2 h. The brown crude oil was further treated with active clay to absorb the residues, and settled in separation funnel and washed to pH 4–5. Then it was centrifuged at 5000 r/min for 15 min to remove the solid impurities and dried using vacuum distillation. The concentration of FFAs in the obtained oil was 56.2%.

Esterification was conducted in a 250 ml three-necked round-bottomed flask, equipped with reflux condenser, thermostat and mechanical stirrer. After the acid oil (26.3 g; 0.097 mol) was mixed with freshly prepared solid acid catalyst and maintained at the required temperature, a relevant amount of methanol was added to start the esterification. Experiment was carried out at 50–80 °C for 5 h. The molar ratio of methanol to oil ranged from 3:1 to 9:1 while the amount of LCC varied from 1.0 wt.% to 7.0 wt.% of the acid oil. The samples were regularly collected for analysis every 60 min.

During recycling, the solid catalysts were recovered by centrifugation at 3000 r/min for 5 min after one batch of experiment. The recovered catalyst was washed with n-butanol, dried to remove the absorbed water, and then used for the next reaction under the optimal reaction conditions. The excess methanol was recovered by vacuum distillation and also used for the next batch of esterification reaction.

2.5. Products analysis

At the end of esterification, the samples were centrifuged at 3000 r/min for 5 min, and separated to three layers. They were the top (oil) phase, the middle (aqueous) phase and the bottom phase (solid catalyst), respectively. Compositions of methyl esters were analyzed by using gas chromatography–mass spectrometry (GC–MS) (HP 6890/5976 MS, US). The conversion of FFAs into methyl esters was determined by titration using a modification of GB/T 14489.3-93. The percentage of conversion was calculated as follows [26]:

$$\text{FFAs conversion (wt.\%)} = [(AV_0 - AV_N)/AV_0] \times 100\% \quad (1)$$

where AV_0 is the initial acid value of acid oil; AV_N is the instant acid value at N (N = 1, 2, 3, 4, or 5) h.

The average molecular weight of FFAs was calculated as follows:

Please cite this article in press as: Guo F et al. Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst. Appl Energy (2012), doi:10.1016/j.apenergy.2012.02.071

$$\begin{aligned}M_{\mathrm{FFAs}} = {} & (M_{\text{methyl palmitate}} \times 11.79\%) + (M_{\text{methyl linoleate}} \times 59.85\%) \\ & + (M_{\text{methyl oleate}} \times 21.73\%) + (M_{\text{methyl linolenate}} \times 0.11\%) \\ & + (M_{\text{methyl stearate}} \times 3.67\%)\end{aligned}$$

M is the molecular weight of FFAs. The percentages of FAMEs derived from the acid oil obtained from soybean soapstock were measured by GC–MS. The average molecular weight of FFAs by this equation is 270.3 g/mol.

3. Results and discussion

3.1. Characterization of the catalyst

The ^{13}C MAS NMR spectrum for the catalyst was given in Fig. 1. The resonance peaks at 129 and 148 ppm were attributed to aromatic carbon atoms with and without —SO_3H groups, respectively. The directly prepared catalyst contains amorphous carbon consisting of polycyclic aromatic carbon sheets, which are similar to those of carbon-based solid acids [15]. The XRD diffraction peaks of LCC (Fig. 2a) showed a broad diffraction peak ($2\theta = 20–25°$), which were attributed to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion [7]. This indicates that the catalyst prepared by direct sulfonation of the hydrolyzed residue of hulls has an amorphous structure. Furthermore, the results were similar to those of amorphous carbon prepared by carbonization and sulfonation except for a weak diffraction peak at about 45° (Fig. 2b). Therefore, the lignin and cellulose were simultaneously carbonized and sulfonated by sulfuric acid. As a result, amorphous structure can be obtained by direct sulfonation of lignocellulosic biomass. This will simplify the preparation process and greatly reduce the cost of carbonaceous solid acid catalyst.

The FT-IR spectra of carbonaceous catalysts prepared by different methods were shown in Fig. 3. A peak at 810 cm^{-1} is attributed to C—O—S stretching vibration. The strong band at 1040 cm^{-1} and 1160 cm^{-1} are attributed to the S=O symmetric and asymmetric stretching vibrations, respectively. This indicated that the SO_3H groups are linked to amorphous structure in the form of C—O—SO_3H. The above two kind of catalysts showed similar absorption peaks at the labeled three wave-numbers, indicating they have the same functional groups. The —SO_3H groups are the active sites of the LCC [16]. Furthermore, the absorption of C=O stretching vibration was found at 1720 cm^{-1}. Absorption band occurring at 1610 cm^{-1} is attributed to the spectra of substituted benzenes, indicating the formation of polycyclic aromatic carbons. The acid density of —SO_3H groups could be calculated according to the S content in the catalyst [17]. Fig. 3 shows that carbonaceous catalysts prepared by different methods have similar functional groups. In this study, the content of S was 3.89 wt.% of the catalyst. The composition, surface area and acid density of LCC were given in Table 1. Compared with other solid acid catalysts prepared by sulfonation following carbonization of various carbohydrates, the LCC had similar textural properties, but accommodated fewer —SO_3H groups, because the catalyst has higher oxygen content. The possible reason was that lignin was not completely carbonized.

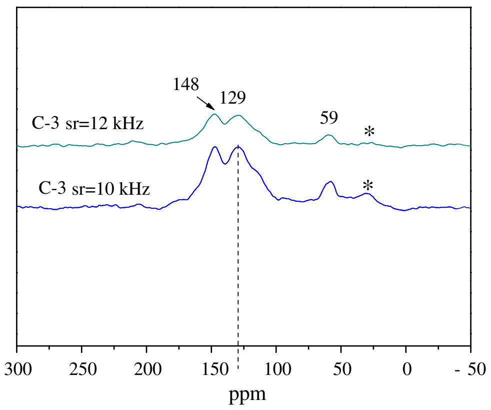

Fig. 1. ^{13}C MAS NMR spectra for the lignin-derived carbonaceous solid acid catalyst prepared from hull of *Xanthoceras sorbifolia* Bunge.

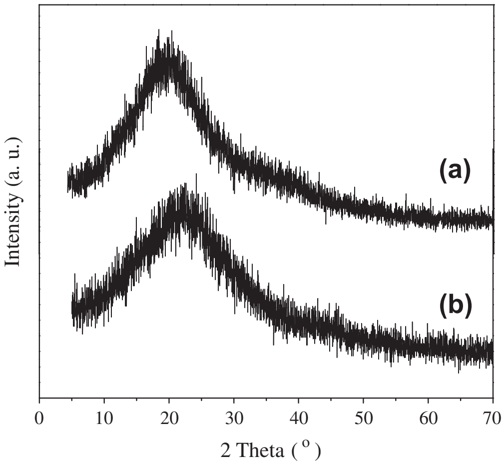

Fig. 2. XRD pattern of sulphonated carbonaceous catalyst ((a) carbonaceous catalyst prepared by direct sulfonation and (b) carbonaceous catalyst prepared by carbonization and sulfonation).

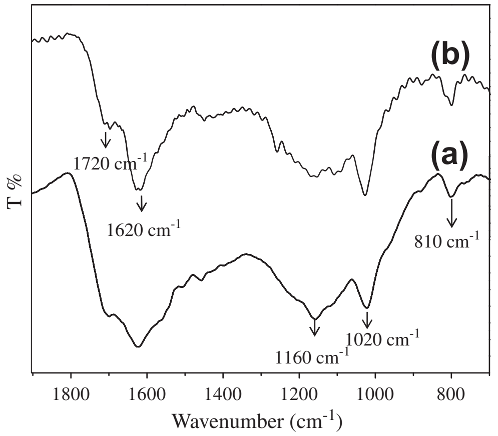

Fig. 3. FT-IR spectrum of the LCC ((a) carbonaceous catalyst prepared by direct sulfonation and (b) carbonaceous catalyst prepared by carbonization and sulfonation).

3.2. Catalytic mechanism of lignin-derived carbonaceous catalyst in esterification

According to the structural characterization, carbonaceous catalysts have hydrophilic and hydrophobic groups, such as hydroxyl group and polycyclic aromatic carbon. Therefore, methanol and oleic acid are easily absorbed on the surface of solid acids to contact reactants and active sites. This is one of the reasons why such carbonaceous catalyst performed higher activity than some other solid acids [15,16]. Furthermore, the reaction kinetic was studied experimentally at optimum conditions. The kinetic results are given in Fig. 4, which reveal a linear relation between the reaction time and $-\ln(1-x)$ (x, FFAs conversion). The regression coefficients of the straight line show good fits to first-order kinetics.

Please cite this article in press as: Guo F et al. Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst. Appl Energy (2012), doi:10.1016/j.apenergy.2012.02.071

Table 1
Comparison of textural properties of solid acid catalysts prepared by different methods and starting materials.

Catalyst	Composition	Surface area (m^2/g)	Acid density (mmol/g)		Refs.
			Total	SO_3H	
Carbon (H_2SO_4)	$CH_{0.45}O_{0.39}S_{0.01}$	2	1.4	0.7	Takagaki et al. [15]
Sugar catalyst	$CH_{1.14}{}^{\circ}{}_{0.39}S_{0.03}$	–	4.13	1.5	Zong et al. [17]
Starch-derived catalyst	$CH_{0.85}O_{0.23}S_{0.032}$	7.2	1.97	1.83	Lou et al. [18]
Sulfonated vegetable oil pitch	–	7.5	2.04	2.21	Shu et al. [19]
In this study	$CH_{0.78}O_{0.50}S_{0.027}N_{0.033}$	4.7	1.71	0.86	In this study

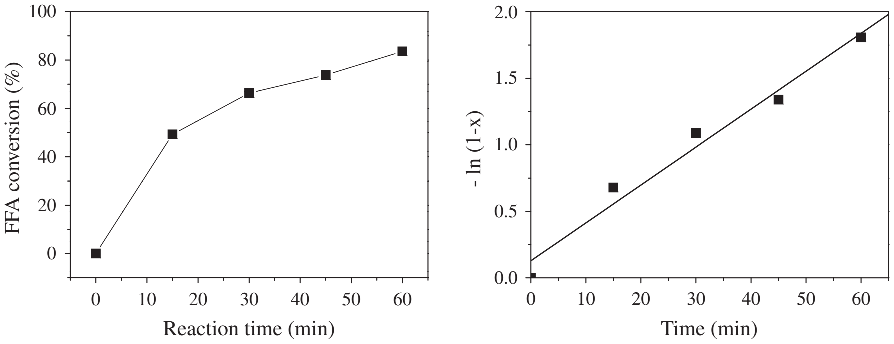

Fig. 4. Esterification of oleic acid with methanol. Reaction fitting to first-order kinetics.

The active sites of —SO_3H groups play the role of Brønsted acid as proton donor in the reaction. The esterification is assumed to finish in the following route presented in Fig. 5: Step (1): A positive carbon ion and a $-SO_3^-$ were produced by the action of —SO_3H on carbonyl of oleic acid when the FFAs were absorbed on the surface of solid acid; Step (2): A tetrahedral intermediate (I) was generated under the nucleophilic attack of methanol on the positive carbon ion; Step (3): The proton of methanol hydroxyl was rearranged and transferred to the carbonyl oxygen of FFAs; Step (4): The tetrahedral intermediate (II) was dehydrated; and Step (5): The proton of tetrahedral intermediate (II) was transferred to $-SO_3^-$. Methyl esters were formed and active sites of —SO_3H were restored.

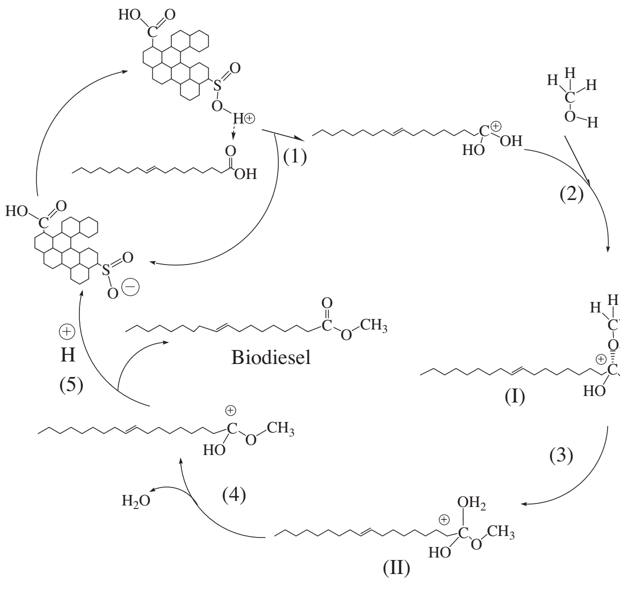

Fig. 5. The reaction mechanism for esterification catalyzed by LCC.

3.3. Esterification of acidified soybean soapstocks

The compositions of FAMEs derived from the acid oil obtained from soybean soapstock were measured by GC–MS, including methyl palmitate (11.79 wt.%), methyl linoleate (59.85 wt.%), methyl oleate (21.73 wt.%), methyl linolenate (0.11 wt.%) and methyl stearate (3.67 wt.%). Methyl linoleate and methyl oleate together made up a major portion of the total fatty acid methyl esters (FAMEs) fraction. In this study, transesterification of pure soybean oil were also performed at 70 °C for 5 h, only <1% of triglycerides was transesterified into FAMEs. Herein the transesterification of triglycerides present in the oil (~44-wt.%) is not taking into account.

The acid-catalyzed reaction is about 3 orders of magnitude slower than that of base-catalyzed one [16]. Furthermore, the mass transfer of solid acid catalysts is poor, and more LCC is needed to gain a high FFAs conversion. The esterification performed with a catalyst content of 1.0–7.0 wt.% at 70 °C for 5 h. In Fig. 6a, the FFAs conversion increased as the catalyst content was increased. The initial reaction rate was high, but the rate reduced significantly when the reaction time was over 1 h. There was no substantial increase in the FFAs conversion when the catalyst content was higher than 5.0 wt.%. The FFAs conversion was 97.2% with 7.0 wt.% catalyst (to acid oils) at 70 °C for 5 h.

The solid acid-catalyzed esterification of fatty acids with methanol exhibits similar kinetic behavior to the homogeneous acid-catalyzed reaction [7]. The molar ratio of methanol to acid oil is one of the most important variables affecting the FFAs conversion. Because esterification is an equilibrium reaction, the amount of methanol is usually excessive to force the reaction towards the formation of FAMEs. There is a big gap between the behavior at 6 and 7.5 of methanol/substrate molar ratio (Fig. 6b). This may be partially due to the vaporization of methanol when the methanol/oil molar ratio was less than 7.5, only little methanol was existed in liquid phase in a flask equipped with reflux condenser. A high FFAs conversion of 93.4% was obtained at the molar ratio of 9:1 and 12:1. For molar ratios less than 9:1, the reaction was incomplete.

Please cite this article in press as: Guo F et al. Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst. Appl Energy (2012), doi:10.1016/j.apenergy.2012.02.071

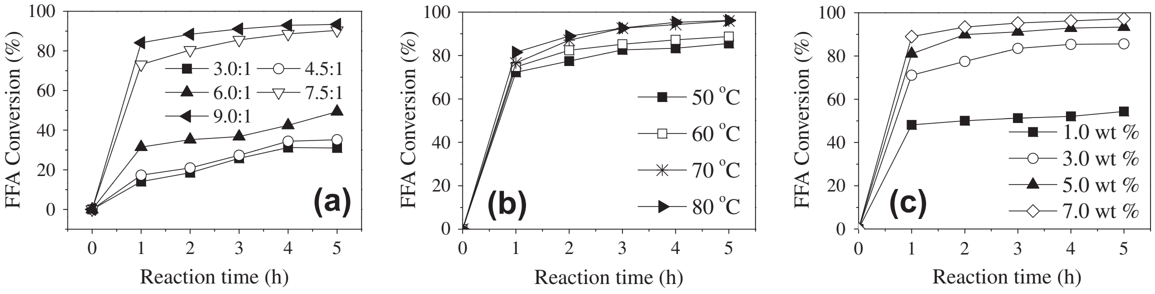

Fig. 6. Effect of reaction variables ((a) molar ratio of methanol/oil; (b) reaction temperatures; and (c) catalyst content).

Because high molar ratio of methanol to the oil would increase the energy consumption of separation process, molar ratio of 9:1 seems to be the most appropriate. This catalyst displayed similar high efficiency with the solid acid catalysts derived from various carbohydrates in esterification [17]. At the end of the reaction, the excess methanol could be recovered by distillation and recycled in latter reaction.

Esterification can occur at different temperatures, depending on the oil used. The effect of reaction temperature on esterification was investigated at different temperatures (50, 60, 70, and 80 °C, respectively) for 5 h. Temperature clearly influenced the reaction rate. In the first 1 h, the formation of FAMEs was similar at all temperatures (Fig. 6c). After 2 h, the FFAs conversion showed different trends. The FFAs conversions at 50 °C and 60 °C for 5 h were all lower than those at 70 and 80 °C for 2 h. The phenomenon was different from base-catalyzed transesterification, where high temperature enhances both transeterification and saponification reactions [27]. The esterification rate was 96.0% at 70 °C for 5 h.

After the esterification reaction, the acid value of products was less than 2.2 mg KOH/g. The remained triglycerides can be transesterified into FAMEs by directly adding a solid base to the products. In our previous work, calcined sodium silicate could tolerate 2.5 wt.% FFAs contained in soybean oil [28,29]. The biodiesel yield was maintained at 98% when the FFAs content was 2.5 wt.%. Therefore, LCC is an efficient solid acid catalyst for production of biodiesel from waste oil with high-acid value by a two-step process.

3.4. Comparison of catalytic activity in esterification

To compare the catalytic activity in esterification of low-quality acidified oil, LCC and sulfuric acid were used as acid catalysts. The amount of LCC was 5.0 wt.% of acidified oil. The loading of —SO_3H on the solid acid was 0.86 mmol/g. The content of —SO_3H in acidified oil matches 0.42 wt.% of H_2SO_4. The amount of sulfuric acid used in esterification was usually ranged from 1.0 wt.% to 3.0 wt.%. In control experiments, the sulfuric acid concentration was chosen at 1.5 wt.% and 0.42 wt.%. Other reaction conditions were methanol/oil ratio of 9.0:1, reaction temperature of 70 °C and stirring speed of 200 r/min. In Fig. 7, the catalytic activity in esterification catalyzed by LCC was significantly higher than that of 0.42 wt.% of H_2SO_4, but was similar to that of 1.5 wt.% of H_2SO_4. These results indicate that the lignin-derived carbonaceous catalyst is suitable to catalyze low-quality oils to produce biodiesel. According to the equivalent active group (—SO_3H), the solid-acid LCC performed 3.5 times higher activity than sulfuric acid in esterification. This may be contributed to the fact that the solid-acid catalyst provides much contact between reactants and active sites as described in Section 3.2.

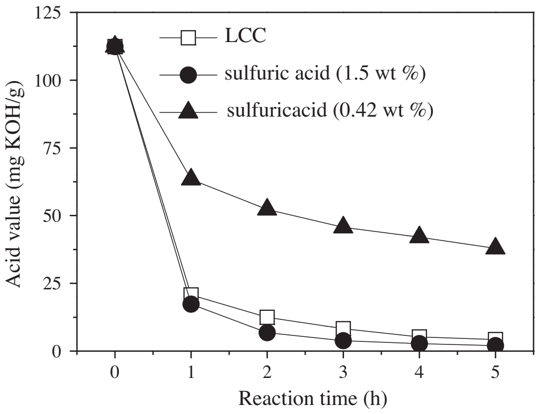

Fig. 7. Comparison of catalytic activity between LCC and sulfuric acid in esterification.

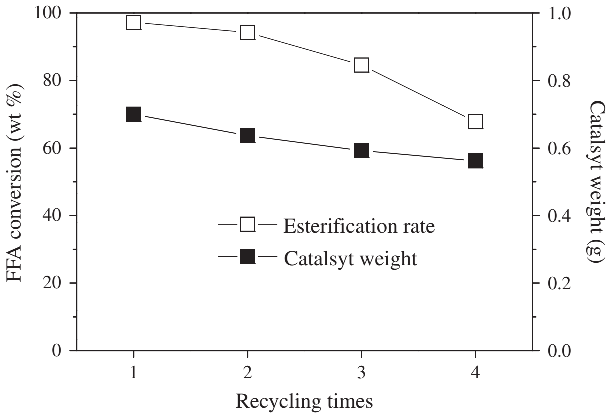

Fig. 8. Effect of the recycling of catalyst on FFAs conversions.

3.5. Recycling of catalyst

The reaction conditions of catalyst recycling were solid catalyst of 5.0 wt.%, molar ratio of methanol/acidified oil of 9:1, reaction temperature 70 °C, reaction time of 5 h and stirring speed of 200 r/min. It can be observed that FFAs conversion decreased as recycling times increased (Fig. 8). The FFAs conversion of the forth batch was reduced to 67.8%. At the end of recycling, the solid catalyst was recovered, and its content of S was analyzed by EA. The S content of recovered catalyst was 3.56%. Compared with freshly prepared catalyst, it was reduced by about 8.5%. However, the qualities of catalysts have also shown a similar decline trend, indicating a drop in FFAs conversion was mainly caused by the loss of catalyst amount.

4. Conclusions

LCC was prepared from lignocellulosic residue through direct sulfonation. Compared with carbohydrate-derived solid acid

Please cite this article in press as: Guo F et al. Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst. Appl Energy (2012), doi:10.1016/j.apenergy.2012.02.071

catalysts prepared by sulfonation after carbonization, it had similar textural properties. The solid acid catalyst displayed high catalytic activity in catalyzing esterification of acidified soybean soapstock with methanol. The maximum free fatty acids (FFAs) conversion (97.2%) was achieved under the following optimal esterification conditions: LCC content of 7.0 wt.%, reaction temperature of 70 °C and molar ratio of methanol to acidified oil of 9:1. This preparation method was not only reduce the cost and simplify the process, but also made full use of biomass waste. In the preparation of FAMEs from acidified soybean soapstock, LCC obtained similar catalytic activity to that of 1.5 wt.% of H_2SO_4. There was little decline in —SO_3H content in the catalyst during the recycling.

Acknowledgements

The authors wish to acknowledge the Major State Basic Research Development Program of China (973 Program) (No. 2007 CB714306), the 863 project (No. 2007AA02Z208) from the Ministry of Science and Technology of China and the Fundamental Research Grant (2011FB111) from Yunnan Provincial Government.

References

[1] Semwal S, Arora AK, Badoni RP. Biodiesel production using heterogeneous catalysts. Bioresour Technol 2011;102(3):2151–61.
[2] Lin L, Zhou C, Saritporn V, Shen XQ, Dong MD. Opportunities and challenges for biodiesel fuel. Appl Energy 2011;88:1020–31.
[3] Moser BR. Biodiesel production, properties, and feedstocks. In: Tomes D, Lakshmanan P, Songstad D, editors. Global impact on renewable energy, production agriculture, and technological advancements. New York: Springer; 2011. p. 285–347.
[4] Li Q, Yan YJ. Production of biodiesel catalyzed by immobilized *Pseudomonas cepacia* lipase from *Sapium sebiferum* oil in micro-aqueous phase. Appl Energy 2010;87:3148–54.
[5] Lotero E, Liu YJ, Lopez DE, Suwannakarn K, Bruce DA, Goodwin JG. Synthesis of biodiesel via acid catalysis. Ind Eng Chem Res 2005;44:5353–63.
[6] Nigam PS, Singh A. Production of liquid biofuels from renewable resources. Prog Energy Combust 2011;37:52–68.
[7] Yin X, Ma H, You Q, Wang Z, Chang J. Comparison of four different enhancing methods for preparing biodiesel through transesterification of sunflowers oil. Appl Energy 2012;91:320–5.
[8] Balat M, Balat H. Progress in biodiesel processing. Appl Energy 2010;87:1815–35.
[9] Melero JA, Iglesias J, Morales G. Heterogeneous acid catalysts for biodiesel production: current status and future challenges. Green Chem 2009;11:1285–308.
[10] Li Y, Zhang XD, Sun L, Xu M, Zhou WG, Liang XH. Solid superacid catalyzed fatty acid methyl esters production from acid oil. Appl Energy 2010;87:2369–73.
[11] Wen ZZ, Yu XH, Tu ST, Yan JY, Dahlquist E. Synthesis of biodiesel from vegetable oil with methanol catalyzed by Li-doped magnesium oxide catalysts. Appl Energy 2010;87:743–8.
[12] Lam MK, Lee MT, Mohamed AR. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. Biotechnol Adv 2010;28:500–18.
[13] Sharma YC, Singh B, Korstad J. Advancements in solid acid catalysts for ecofriendly and economically viable synthesis of biodiesel. Biofuel Bioprod Bio 2011;5:69–92.
[14] Toda M, Takagaki A, Okamura M, Kondo JN, Hayashi S, Domen K, et al. Biodiesel made with a sugar catalyst. Nature 2005;438:178.
[15] Takagaki A, Toda M, Okamura M, Kondo JN, Hayashi S, Domen K, et al. Esterification of higher fatty acids by a novel strong solid acid. Catal Today 2006;116:157–61.
[16] Nakajima K, Hara M. Environmentally benign production of chemicals and energy using a carbon-based strong solid acid. J Am Ceram Soc 2007;90:3725–34.
[17] Zong MH, Duan ZQ, Lou WY, Smith TJ, Wu H. Preparation of a sugar catalyst and its use for highly efficient production of biodiesel. Green Chem 2007;7:434–7.
[18] Lou WY, Zong MH, Duan ZQ. Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts. Bioresour Technol 2008;99:8752–8.
[19] Shu Q, Gao JX, Nawaz Z, Liao YH, Wang DZ, Wang JF. Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon-based solid acid catalyst. Appl Energy 2010;87:2589–96.
[20] Fukuhara K, Nakajima K, Kitano M, Kato H, Hayashi S, Hara M. Structure and catalysis of cellulose-derived amorphous carbon bearing SO_3H groups. ChemSusChem 2011;4:778–84.
[21] Rinaldi R, Schüth F. Design of solid catalysts for the conversion of biomass. Energy Environ Sci 2009;2:610–26.
[22] Kim DY, Nishiyama Y, Wada M, Kuga S. High-yield carbonization of cellulose by sulfuric acid impregnation. Cellulose 2001;8:29–33.
[23] Joo SH, Jun S, Ryoo R. Synthesis of ordered mesoporous carbon molecular sieves CMK-1. Micropor Mesopor Mat 2001;44–45:153–8.
[24] Van Soest PJ, Robertson JB, Lewis BA. Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition. J Dairy Sci 1991;74:3583–97.
[25] Diaz-Felix W, Riley MR, Zimmt W, Kazz M. Pretreatment of yellow grease for efficient production of fatty acid methyl esters. Biomass Bioenerg 2009;33:558–63.
[26] Hara M, Yoshda T, Takagaki A, Kondo JN, Hayashi S. A carbon material as a strong protonic acid. Angew Chem Int Edit 2004;43:2955–8.
[27] Phan AN, Phan TM. Biodiesel production from waste cooking oils. Fuel 2008;87:3490–6.
[28] Guo F, Peng ZG, Dai JY, Xiu ZL. Calcined sodium silicate as solid base catalyst for biodiesel production. Fuel Process Technol 2010;91:322–8.
[29] 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.

Please cite this article in press as: Guo F et al. Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst. Appl Energy (2012), doi:10.1016/j.apenergy.2012.02.071