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Synthesis of biodiesel from a model waste oil feedstock using a carbon-based solid acid catalyst: Reaction and separation

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ABSTRACT

A solid acid catalyst that can keep high activity and stability is necessary when low cost feedstocks are utilized for biodiesel synthesis because the reaction medium contains a large amount of water. Three solid acid catalysts were prepared by the sulfonation of carbonized vegetable oil asphalt and petroleum asphalt. The structure of these catalysts was characterized by a variety of techniques. A new process that used the coupling of the reaction and separation was employed, which greatly improved the conversion of cottonseed oil (triglyceride) and free fatty acids (FFA) when a model waste oil feedstock was used. The vegetable oil asphalt-based catalyst showed the highest catalytic activity. This was due to the high density and stability of its acid sites, its loose irregular network, its hydrophobicity that prevented the hydration of $-OH$ species, and large pores that provided more acid sites for the reactants.

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1. Introduction

Due to the potential shortage of fossil fuels and environmental concerns, the synthesis of biodiesel (fatty acid methyl ester, FAME) from the transesterification of triglycerides (the main component of vegetable oils or animal fats) and the esterification of free fatty acid (FFA) with methanol have drawn intense attention (Sharma et al., 2008; Canakci, 2007; Han et al., 2009). A wide variety of vegetable oils (e.g., soybean oil and rapeseed oil) can be employed as the raw material for the production of biodiesel. However, in China, there is a consumption need of approximately 22 million tonnes of edible oils annually (50% has to be imported) (Peng et al., 2008), so, vegetable oils are not favored as a feedstock. Only waste oils, such as used frying oil, trap grease and soapstock (byproduct of a vegetable oil refinery) that are available cheaply, can be considered as feedstocks for biodiesel (Felizardo et al., 2006; Mohamad and Ali, 2002; Zhang et al., 2003). However, waste oils are high in FFA. The base-catalyzed method is not suitable for these waste oils because soap is produced from the reaction of FFA with a base catalyst. The formation of soap not only consumes the catalyst, and it also can bring about the emulsification of FAME and glycerol (byproduct of biodiesel), which would make the separation of FAME–glycerol mixtures difficult.

A homogeneous acid such as H_2SO_4 can simultaneously catalyze esterification and transesterification, so it will have a better performance with waste oils than base catalysts (Georgogianni et al., 2008; Zhang and Jiang, 2008). However, it also suffers from several

drawbacks, such as corrosiveness, the difficulty of its separation from the reaction medium and the need to deal with the waste from the neutralization of H_2SO_4 . The use of heterogeneous acid catalysts to replace homogeneous ones has been considered to eliminate the problems associated with homogeneous acid catalysts. There are several reports about the use of heterogeneous acid catalysts to produce biodiesel, including zeolites (Ramos et al., 2008), La/zeolite beta (Shu et al., 2007), MCM-41 (Joaquín et al., 2003), silica-supported zirconium sulfate (Chen et al., 2007), Amberlyst-15 (Talukder et al., 2009) and Nafion (Ngaosuwan et al., 2009). However, the heterogeneous acid catalyst commonly is hydrophilic, and its activity will be decreased by the water produced from the esterification of FFA. This is because the acid catalysis over these inorganic oxide solid acids occurs at the acidic hydroxyl groups ($-OH$), which act as strong Brønsted acid sites, and the acid strength of these would be reduced by the hydration of $-OH$ when water is present (Nakajima et al., 2007). Park et al. studied the effects of water on the activity of Amberlyst-15 by adding different contents of FFA (50.0 and 99.8 wt.%), and found the activity greatly decreased at a high content of FFA (Park et al., 2009). Hence, it is important to find a solid acid catalyst that can maintain high stability and high density of strong protonic acid sites when waste oils with considerable amounts of FFAs are used as feedstock.

In recent years, the sulfonation of incompletely carbonized polymers (such as naphthalene) and carbon material (such as carbon nanotube) to synthesize carbon-based solid acid catalysts has received a great deal of research attention (Suganuma et al., 2008). Hara et al. reported obtaining an active and stable carbon-based solid catalyst by heating naphthalene in concentrated H_2SO_4 (at

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200–250 °C). It shows a good catalytic performance for the esterification of ethanol with acetic acid to form ethyl acetate (Hara et al., 2004). Unfortunately, this catalyst was only a soft aggregate of polycyclic aromatic hydrocarbons rather than a rigid carbon material. The sulfonic acid group ($-\text{SO}_3\text{H}$) is easily leached from the solid when it is used in liquid phase reactions over 100 °C or when the FFA acted as a surfactant, which resulted in the rapid loss of catalytic activity. Since the waste oil also contains triglycerides, it is also important to convert them into FAME. However, the protonation of the carbonyl group of a triglyceride to start the transesterification to produce biodiesel is difficult, and a high temperature is generally required at the range of 150–300 °C (Hara, 2009; Lotero et al., 2005). The carbon material that is a soft aggregate of polycyclic aromatic hydrocarbons will not be suitable for this high temperature reaction condition. Toda et al. employed D-glucose as a carbon precursor to prepare carbon-based solid sulfonic acid catalysts and investigated their catalytic properties. They found it can form a rigid carbon material composed of small polycyclic aromatic carbon sheets (a three-dimensional sp^3 -bonded structure) by carbonization (Toda et al., 2005). Sulfonation of such carbon materials can be expected to give a highly stable solid with a high density of active sites.

We have reported that the solid residue of vegetable oil asphalt can be employed as a raw material for the preparation of a carbon-based solid acid catalyst. It can maintain a high activity and stability when used to catalyze the transesterification of cottonseed oil with methanol at 260 °C (Shu et al., 2009a). The strong solid acid obtained probably consisted of a flexible carbon-based framework decorated with highly dispersed polycyclic aromatic hydrocarbons containing sulfonic acid groups. However, the carbon-based solid acid catalyst was only studied for catalyzing the esterification reaction to make biodiesel (Mo et al., 2008a; Liu et al., 2008; Zong et al., 2007). The utilization of these carbon-based solid acid catalysts to simultaneously catalyze transesterification and esterification for the production of biodiesel from waste oils with high contents of FFA has not been reported.

In this work, we prepared three carbon-based solid acid catalysts, including the sulfonation of an incompletely carbonized vegetable oil asphalt and petroleum asphalt, and compared their catalytic activities for the production of biodiesel from a model waste oil. Since the esterification proceeds faster than the transesterification when they are simultaneously catalyzed by an acid catalyst, we carried out the combination of esterification and transesterification in a sequential, two step process with the same catalyst at different reaction temperatures. This two step process is based on the assumption that the carbon-based solid acid catalyst can maintain high activity and stability at a high reaction temperature. Furthermore, since the conversion of cottonseed oil (triglyceride) will affect the conversion of FFA and vice versa, the conversion of a reactant will be limited by the proceeding high conversion of another reactant. In order to ensure that both the conversions of cottonseed oil and FFA are high, a new process that used the coupling of reaction and separation was used to improve the conversion of cottonseed oil and FFA. This study was designed to evaluate the feasibility of using this new two step catalytic process to produce biodiesel from waste oil feedstock.

2. Experimental

2.1. Catalyst preparation

The carbon-based solid acid catalyst precursors were obtained by carbonizing vegetable oil asphalt and petroleum asphalt. First, the vegetable oil asphalt from a biodiesel plant (Linyi Qingda New Energy Co., Ltd., China) was pre-treated to remove water

and residual esters. The pre-treated process was carried out as follows: the residual esters were converted to methyl ester, then the methyl ester and water were removed by the method of reduced pressure distillation. Second, batches of 10.0 g of extracted vegetable oil asphalt or petroleum asphalt were oxidized for 1.0 h at 280 °C in a stream of air (300 mL min^{-1}). Third, these were heated to 500–700 °C at a rate of 2 °C min^{-1} under an argon atmosphere (100 mL min^{-1}).

The sulfonation of the carbon precursors was performed as follows. Five grams of carbonized vegetable oil asphalt (or petroleum asphalt) and 100 mL concentrated H_2SO_4 (96 %) solution were put into a 250 mL flask controlled at 210 °C in an oil bath. This was kept under reflux and agitation for 10.0 h. After the treatment, the suspension was washed with hot deionized water ($>353 \text{ K}$) to remove any physically adsorbed species until the sulfate ions were no longer detected in the filtration water (sulfate ions were detected with $6 \text{ mol L}^{-1} \text{ Ba}(\text{NO}_3)_2$ solution). After the filtration, the samples were dried at 120 °C under vacuum for 4 h to obtain the sulfonated vegetable oil asphalt or petroleum asphalt catalyst.

2.2. Catalyst characterization

The morphology of the prepared vegetable oil asphalt and petroleum asphalt catalysts were characterized by a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS), while the structure of the catalyst were characterized by powder X-ray diffraction (XRD). The thermal stability of the catalysts was examined by thermo-gravimetric analysis (TGA). The amount of acid in the catalysts was assessed by temperature programmed desorption (TPD) of NH_3 . The Brunauer–Emmett–Teller (BET) surface area and pore size were measured by the multipoint N_2 adsorption–desorption method at liquid nitrogen temperature (-196 °C). The pore size distribution of the catalysts was measured by the method of Barrett–Joyner–Hallenda (BJH) pore size analysis. The graphitization degree was assessed by X-ray photoelectron spectroscopy (XPS).

2.3. Catalytic reaction procedure

In practical industrial production, waste vegetable oils used as feedstocks include rapeseed, cottonseed and soybean acidified oils (derived from soapstocks by acidification). In this work, a mixed oil was used as the feed that was made from adding 50 wt.% oleic acid (a common type of FFA in oils) to refined cottonseed oil. The molar ratio of methanol to mixed oil required was calculated by treating 3 mol of FFA as 1 mol of triglyceride. The refined cottonseed oil has the following characteristics: iodine value $114 \text{ mg I}_2/100 \text{ g}$, acid value 0.6 mg KOH/g , saponification value 199 mg KOH/g . The molecular weight of the cottonseed oil can be calculated from its saponification value which was defined as Eq. (1), and it was 845.7.

$$M = \frac{56.1 \times 3 \times 10^3}{SV} \quad (1)$$

where M was the molecular weight, SV was the saponification value (mg KOH/g).

The reaction was carried out in a 250 mL autoclave equipped with a magnetic stirrer. The mixed oil and a known amount of catalyst were charged into the reactor. When the required temperature was reached, methanol was added into the reactor by a pump. The reaction was started by stirring (at 240 rpm). The reaction process was divided into a sequential, two step process with the same catalyst at different reaction temperatures. In the first step (at a lower reaction temperature, 140 °C), a large amount of FFA and small amounts of triglyceride were converted into FAME.

In the second step (at a higher reaction temperature, 220 °C), the remaining large amount of triglyceride was converted into FAME.

For a typical run, after reaction for a fixed time, in order to get a higher conversion of FFA than was allowed by the reaction equilibrium, the methanol phase in the reactor was taken out to remove water from the reactant. This was done with the mixture of methanol and water distilled to recycle the methanol. This can substantially increase the conversion of esterification and effectively decreased the acid value of the product. After the first step, since a lot of FAME was produced from the esterification of oleic acid with methanol, in order to increase the conversion of triglyceride and inhibit the glycerolysis of FAME, the method of reduced pressure distillation was used to remove the FAME from the reaction medium. The reduced pressure distillation was carried out as follows: the reaction mixture was taken from the autoclave after the temperature was cooled to room temperature at first; and then the pressure over the reaction mixture was reduced to about 3 mm Hg and the whole was heated to 240 °C and kept at this temperature for 90 min to separate FAME. This helps the conversion of triglyceride. Finally, fresh methanol was added to the residual distillates to start the second step of the reaction. In this phase, most of the triglyceride was converted into FAME at a higher temperature. After several hours, the reaction mixture was cooled and separated by filtration. The filtrate was allowed to settle and separate into two layers. The oil phase consisted of methyl esters, while the aqueous phase mainly contained water, methanol and glycerol.

2.4. Product analysis

Samples for analysis were taken at different times during the run. A high performance liquid chromatograph (HPLC, Shimadzu LC-10A) equipped with an ultraviolet photometric detector was used for analyzing the samples. A spherisorb ODS 2 column (250 × 4.6 mm, 80 Å pore size and 5 µm particle size) was used for the separation. The mobile phase was a mixture of acetone and acetonitrile in the volumetric ratio of 50:50. The flow rate of the mobile phase was 1.0 mL/min. The column temperature was 40 °C. The components measured by HPLC included oleic acid, methyl esters, triglyceride, diglyceride and monoglyceride. Standard samples were used to establish a calibration graph. The calibration graph was used to calculate the weight percentage of the individual components by the integration of the peak areas using the external standard method.

As the molecular size of FFA and FAME is very close, some overlapping peaks will appear when these two substances were detected by the HPLC, resulting in peak area calculation error. In order to reduce this error, the acid value measurement was made as well. The conversion of FFA can be more accurately calculated by comparing the results from HPLC and acid value measurement. The measurement of acid value (ISO 1242:1999) was realized from using a KOH-ethanol solution. The acid value was defined as Eq. (2):

$$Y = \frac{C \times V \times 56.1}{m} \quad (2)$$

where Y was the acid value (mg KOH/g), V was the consumed volume of KOH (mL), C was the concentration of KOH (mol/L), and the m was the mass of tested sample (g).

The conversion of FFA was defined as Eq. (3):

$$X = \frac{Y_1 - Y_2}{Y_1} \quad (3)$$

where X was the conversion of FFA (wt.%), Y_1 was the acid value of initial FFA (mg KOH/g), and Y_2 was the acid value of the remaining FFA (mg KOH/g).

3. Results and discussion

3.1. Characterization of the catalyst

The morphology from SEM characterization of the vegetable oil asphalt catalyst V-C-600-S-210, the petroleum asphalt catalysts P-C-750-S-210 and P-C-950-S-210 (in the code V(P)-C-M-S-N, V is the vegetable oil asphalt, P is the petroleum asphalt, C is the carbonization, M is the carbonization temperature, S is the sulfonation, and N is the sulfonation temperature) are shown in Fig. 1. The elements present in the samples (O, C and S) from EDS characterization are given in Table 1.

The vegetable oil asphalt exhibited a loose irregular network structure after it was carbonized at 600 °C, and several closely linked pores in a shape similar to a net can be found (Fig. 1A). After the sulfonation treatment by concentrated H₂SO₄, the particle gets disintegrated to some extent and the pores became larger. In contrast, no obvious pores can be seen with the P-C-750-S-210 and P-C-950-S-210 catalysts. The big difference between the pores of the vegetable oil asphalt and petroleum asphalt-based catalysts can be explained as follows. Petroleum asphalt is a mixture of the heaviest hydrocarbons and the derivatives of non-metallic elements (mainly for the O, S, N, etc.). However, vegetable oil asphalt is a mixture of straight chain aliphatic hydrocarbon polymers. Since the main components of vegetable oil asphalt and petroleum asphalt have differences in their molecular structure, they would have different pathways to form carbon precursor during the carbonization process. The derivatives of non-metallic elements may be easy to be carbonized to form graphitic carbon, so there was more graphitic carbon in the P-C-750-S-210 and P-C-950-S-210 samples. Hence, their structures would be more compact than V-C-600-S-210 due to the higher degree of graphitization. As a result of this compact structure, there were no obvious pores found in the P-C-750-S-210 and P-C-950-S-210 samples. Since the vegetable oil asphalt has a loose irregular network structure after it was carbonized at 600 °C, the intercalation of concentrated H₂SO₄ with the carbon sheet will be easier than the case with a compact carbon structure. The pores of carbon derived from the vegetable oil asphalt are large, and it a high amounts of the sulfonic acid group (–SO₃H).

In order to estimate their acid site density, the sulfur content in the vegetable oil asphalt catalyst and petroleum asphalt catalyst was used. This was obtained from the EDS analysis (Table 1). The Brønsted acid site density of V-C-600-S-210 catalyst was 2.21 mmol g^{−1}. The acid site density of P-C-750-S-210 was 1.12 mmol g^{−1}. The acid site density of P-C-950-S-210 was 0.93 mmol g^{−1}. This indicated that a carbon material with a higher graphitization degree was more difficult to be sulfonated. This can be explained as follows: the –SO₃H can be attached only onto the edge of carbon sheets (Okamura et al., 2006). Non-graphitic carbon and graphitic carbon have different abilities to attach the –SO₃H. The non-graphitic carbon is easier to be attached with the –SO₃H group, so a carbon material with more non-graphitic carbon has more amounts of –SO₃H. When the carbon material was prepared from the same carbon source but was carbonized at different temperatures, the carbon sheet will grow with an increase in carbonization temperature. Therefore, the S content decreased with the increase in carbonization temperature.

The XRD patterns for the sulfonated vegetable oil asphalt and petroleum asphalt are shown in Fig. 2A. The TGA plots of the above carbon-based catalysts in air are shown in Fig. 2B. The NH₃-TPD profiles are shown in Fig. 2C. All the XRD patterns exhibited two diffraction peaks at 2θ angles of 10–30° and 35–50°, which were attributed to non-graphitic carbon. In the case of P-C-950-S-210, a distinct diffraction peak (2θ = 35–50°) due to the a axis of the graphite structure was seen. This indicated that this sample

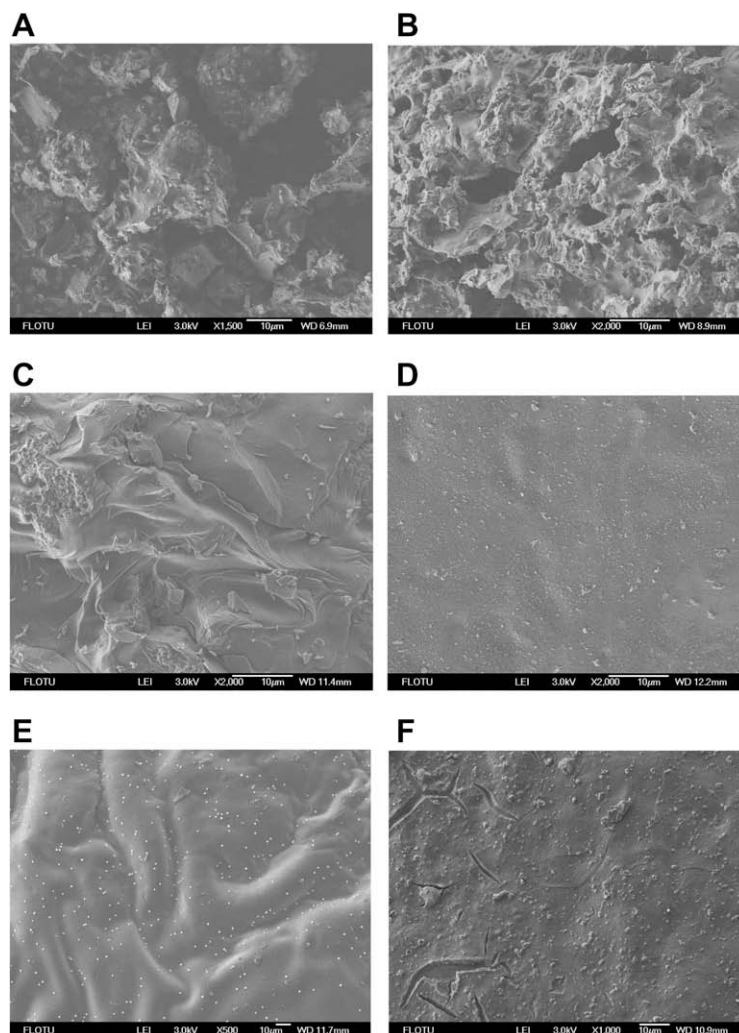


Fig. 1. SEM images (A) vegetable oil asphalt carbonized at 600 °C, (B) vegetable oil asphalt carbonized at 600 °C and sulfonated at 210 °C, (C) petroleum asphalt carbonized at 750 °C, (D) petroleum asphalt carbonized at 950 °C, (E) petroleum asphalt carbonized at 750 °C and sulfonated at 210 °C, (F) petroleum asphalt carbonized at 950 °C and sulfonated at 210 °C.

Table 1

The elements present in the different carbon-based solid acid catalysts.

Catalyst	Elements (wt.%)		
	C	O	S
Vegetable oil asphalt catalyst (V-C-600-S-210)	83.08	9.85	7.07
Petroleum asphalt catalyst (P-C-750-S-210)	87.71	8.70	3.59
Petroleum asphalt catalyst (P-C-950-S-210)	82.78	14.25	2.97

comprised a larger content of graphitic carbon than P-C-750-S-210 or V-C-600-S-210.

The TGA analysis showed the different levels of sulfonation and the stability of the acid site for the different carbon-based catalysts with different graphitization degrees. V-C-600-S-210 demonstrated a faster weight loss rate than the petroleum asphalt carbonized at 750 or 950 °C, which was ascribed to that V-C-600-S-210 consisted of more non-graphitic carbon in its carbon sheet than P-C-750-S-210 or P-C-950-S-210 (corroborated by the XRD analysis), and the oxidation rate of non-graphitic carbon was faster than graphitic carbon. V-C-600-S-210 and P-C-950-S-210 showed similar thermal behavior in the temperature range of 40–320 °C. However, P-C-950-S-210 showed a rapid weight loss up to 320 °C (about 8 wt.%). This was due to that the stability of the covalent bond between the acid site ($-\text{SO}_3\text{H}$) and the graphitic carbon was

lower than when it was covalently bonded with non-graphitic carbon.

The NH_3 -TPD profiles showed that all the catalysts had two distinct desorption peaks from 250 to 300 °C and 500 to 700 °C that were assigned to two types of acid sites. The low and high temperature peaks corresponded to weak and strong acid sites, respectively. The desorption characteristics of P-C-950-S-210 were quite different from V-C-600-S-210 and P-C-750-S-210. A desorption peak appeared at 50–250 °C, signifying that it had more weak acid sites. V-C-600-S-210 had the largest amount of desorbed NH_3 , indicating it had the largest number of acid sites, and the intensity of the desorption peak at 500–700 °C (strong acid sites) was also the highest. In general, it can be expected to give a higher activity for the production of biodiesel from waste oil with a high content of FFA because it has more acid sites and stronger acidity.

The different BET surface areas will give different amounts of acid sites on the exterior or in the interior of the solid catalyst, the BET surface area of the un-sulfonated and sulfonated carbon-based catalysts were measured. Since the pore size is also an important parameter for a porous material in a catalytic application to make biodiesel because this process involves large organic molecules. The pore size distribution was also measured. The BET surface areas and mean pore size of the un-sulfonated and sulfonated carbon-based catalysts are shown in Table 2. The BET

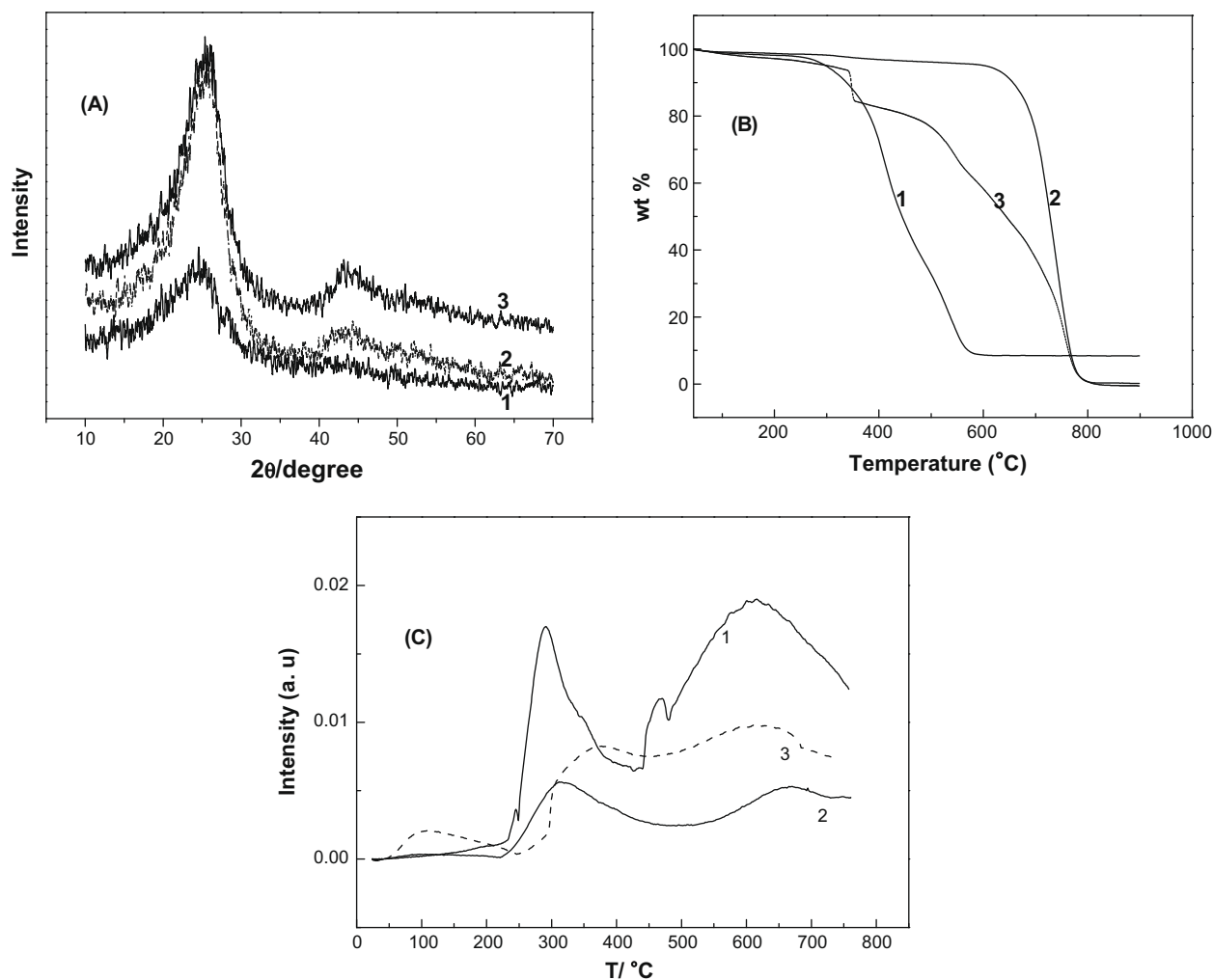


Fig. 2. (A) XRD of the carbon material catalyst; (B) TGA of the carbon material catalyst in air; (C) NH_3 -TPD profiles of the catalysts. (1) V-C-600-S-210. (2) P-C-750-S-210. (3) P-C-950-S-210.

surface areas ranged from 62.6 (P-C-950) to $24.1 \text{ m}^2 \text{ g}^{-1}$ (V-C-600), and the mean pore size ranged from 0.13 (P-C-950) to 12.5 nm (V-C-600) before these carbon-based catalysts were sulfonated. It can be seen that the surface area of the carbon-based catalysts decreased with increasing pore size. The sulfonation caused the pore size of the V-C-600 to increase greatly. However, the sulfonation caused the pore size of the P-C-750 and P-C-950 to increase slightly. Hence, it can be concluded that the different carbon sources lead the produced catalysts to be having different pore size after they were treated by the carbonization and sulfonation. The V-C-600-S-210 has the largest pore size, which is 43.9 nm . The low surface area ($7.48 \text{ m}^2 \text{ g}^{-1}$) and high $-\text{SO}_3\text{H}$ density (2.21 mmol g^{-1}) of the V-C-600-S-210 catalyst indicated that most of the $-\text{SO}_3\text{H}$ groups were in the interior of this catalyst. If the pore size of the catalyst was small, the entry of a bulky organic molecule

reactant will be obstructed. Since the average pore size of the sulfonated vegetable oil asphalt was large (43.90 nm), thus the reactants can easily diffuse into the interior of the catalyst. This allowed reactants to contact with more acid sites, and the catalyst had better activity.

These results from SEM, EDS, XRD, TGA, NH_3 -TPD, BET and pore size clearly indicated that V-C-600-S-210 can be expected to be a catalyst with good heat stability and high activity. Hence, additional XPS characterization was employed to investigate the chemical valences of the surface group on V-C-600-S-210. The data are shown in Fig. 3. The C_{1s} spectrum showed two peaks at 284.5 and 286.7 eV . The main peak centered at 284.5 eV was due to sp^2 -hybridized graphite carbon ($\text{C}=\text{C}$). The peak at 286.7 eV can be assigned as carbon atoms bound with sulfur in sulfonic groups. The O_{1s} spectra showed one main peak at 531.6 eV , which can be assigned as the oxygen atom in $\text{S}-\text{O}$ and $\text{S}-\text{OH}$. A S_{2p} photoelectron peak due to sulfur in $-\text{SO}_3\text{H}$ (168 eV) was also observed in the XPS spectrum for the sample. These results indicate that this carbon material contained $-\text{SO}_3\text{H}$, and all S atoms in the carbon material were contained in $-\text{SO}_3\text{H}$ groups.

Table 2

The BET and pore size of the un-sulfonated and sulfonated carbon-based catalysts.

Catalyst	BET ($\text{m}^2 \text{ g}^{-1}$)	Pore size (nm)
V-C-600	24.1	12.5
V-C-600-S-210	7.48	43.9
P-C-750	61.8	0.45
P-C-750-S-210	<10	2.2
P-C-950	62.6	0.13
P-C-950-S-210	<10	0.33

3.2. Two-step sequential reaction process

The three carbon-based solid acid catalysts, V-C-600-S-210, P-C-950-S-210 and P-C-750-S-210, were used to catalyze the

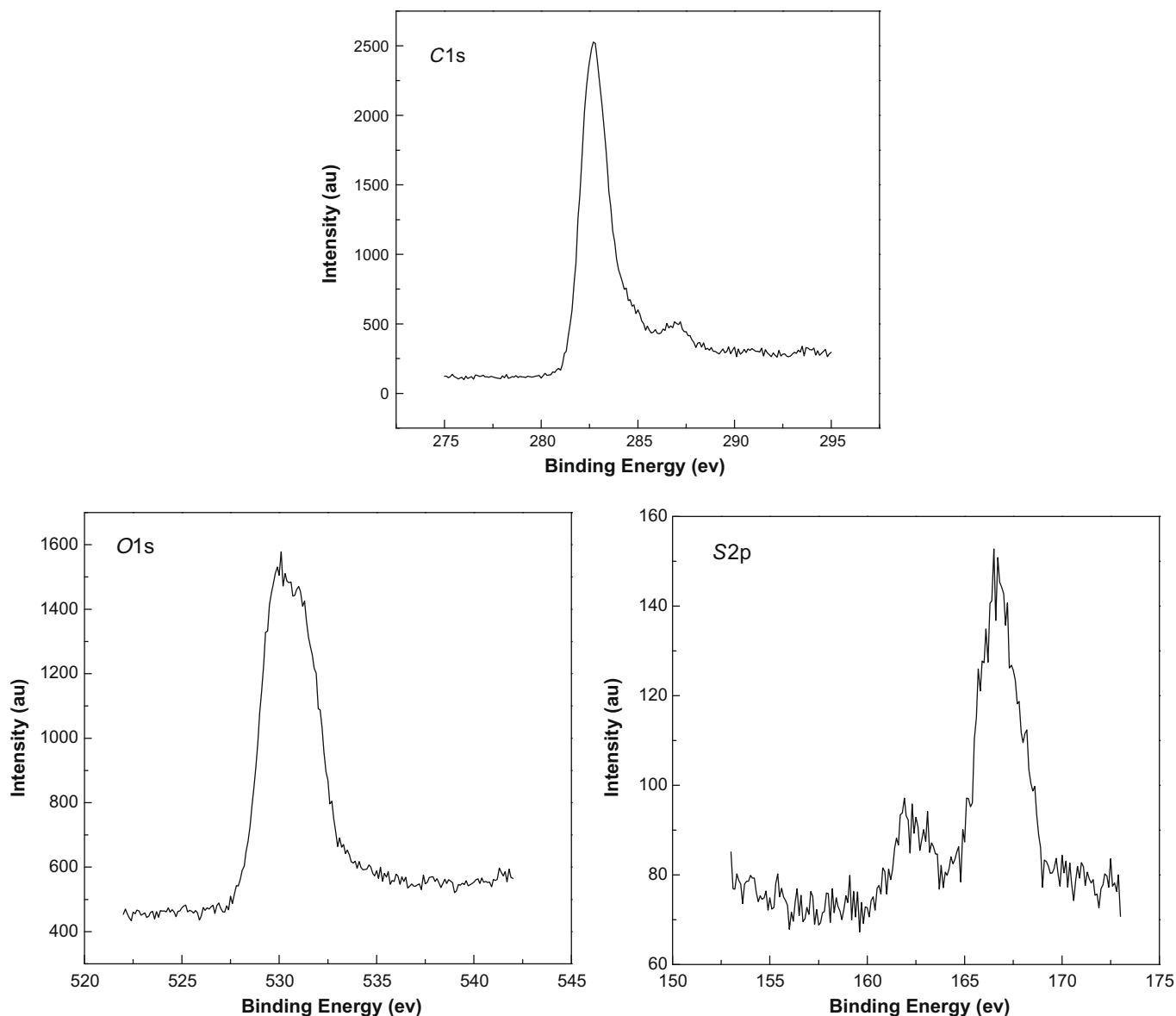


Fig. 3. The C_{1s}, O_{1s} and S_{2p} XPS spectra of V-C-600-S-210 catalyst.

esterification at 140 °C and the transesterification at 220 °C. Mixed oil (50% cottonseed oil and 50% oleic acid) was used to model the waste oil. Furthermore, a new process that coupled the reaction and separation was proposed to improve the conversion of triglyceride and FFA.

3.2.1. Comparison of the two processes

In our previous research we reported that 140 °C is a suitable reaction temperature for the esterification (Shu et al., 2009b) and 220 °C is suitable to transesterification (Shu et al., 2009a) when a carbon-based catalyst was used, respectively. In order to reduce the energy consumption, we carried out the experiments to validate the feasibility of a new process (reaction and separation) which combined esterification and transesterification in a two-step sequential process with the same catalyst at different reaction temperatures. The first step was performed at 140 °C. The second step was performed at 220 °C.

In order to examine if the process with the coupling of reaction and separation gives a better performance than the process that only had the reaction, so we carried out these two processes and

the conversions of FFA and triglyceride in them were compared. The comparison was carried out using V-C-600-S-210 as the catalyst. In the process that only had the reaction, the reaction temperature was 220 °C, catalyst/model waste oil mass ratio 0.3%, the molar ratio of methanol/model waste oil 20.9 and reaction time 5 h. In the new process that had the coupling of reaction and separation, the reaction temperature was varied from 140 °C (the first step) to 220 °C (the second step), and the other reaction conditions were the same as the process that only had the reaction.

The only process that was successful was a continuous process and consecutively reacted for 5 h. The new process with the coupling of reaction and separation was a sequential, two step process. First, the reaction was stopped after reacted for 2 h, and the methanol steam (at 0.8 MPa) was emptied out from the gas outlet to carry out the water that produced during the esterification from the reaction mixture; second, after the pressure had decreased back to atmospheric pressure, the fresh methanol was added into the reactor by a pump and the reaction was continued for another 3 h. The comparison of these two processes was made at the latter 3 h. The results are shown in Fig. 4.

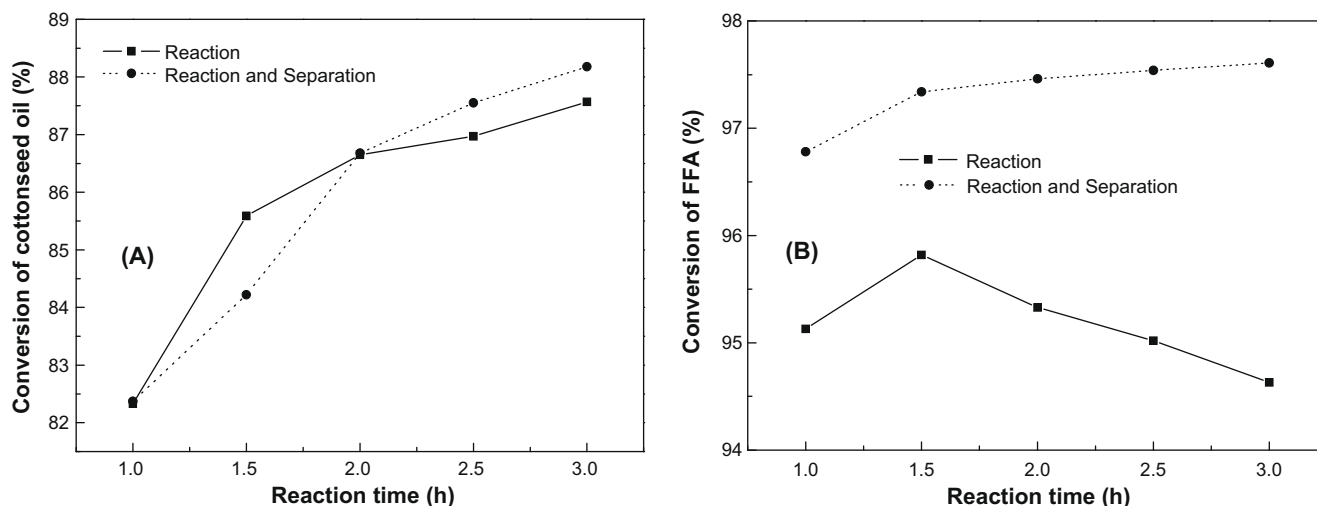


Fig. 4. Comparison of the two processes: process (1) only had the reaction and process (2) had the coupling of reaction and separation on the conversion of triglyceride (A) and FFA (B). The process (1): model waste oil (50% cottonseed oil and 50% oleic acid), catalyst/model waste oil mass ratio 0.3%, molar ratio of methanol/model waste oil 20.9, reaction temperature 220 °C and reaction time 5 h. The process (2): reaction temperature was varied from 140 °C (the first step) to 220 °C (the second step), and the other reaction conditions are the same as the process (1).

From Fig. 4 it can be seen that the new process with the coupling of the reaction and separation can greatly increase the conversion of FFA. For the process that only has the reaction, a conversion of FFA of 94.63 wt.% was obtained after 5 h. For the new process that coupled with the reaction and separation, a conversion of 97.61 wt.% was obtained after the re-started reaction for 3 h. Hence, it can be concluded that the chemical equilibrium conversion of FFA can be exceeded by the continuous removal of water from the reaction mixture, to give a high conversion. The conversion of triglyceride in the process that only has the reaction was higher than the new process when it was re-started and run for no longer than 2 h. However, with the time increased to 3 h, the conversion of triglyceride in the two step process was higher.

The above results can be explained as follows: (1) the FFA can act as a weak acid to catalyze the transesterification, and as more FFA was left in the process that only had the reaction than the two step process, this accelerated the conversion of triglycerides. (2) More monoglycerides and glycerol were also formed in the process that only had the reaction. This caused two problems: one is that the solubility of glycerol in FAME can be enhanced by the monoglycerides, so the glycerolysis of FAME will take place; the other is that esterification between the FFA with the glycerol and monoglycerides will occur, which decreased the conversion of the triglycerides. (3) Based on above analysis, if the disadvantaged influences such as the glycerolysis of FAME, the esterification between the FFA with the glycerol and monoglycerides exceed the advantaged influence of the catalysis effect of FFA, the conversion of triglycerides will decrease. From this comparison, it can be concluded that the process with the coupling of the reaction and separation is promising for the preparation of biodiesel from cheap feedstocks with large amounts of FFAs.

3.2.2. Use of a catalyst

FFA can act as a weak acid catalyst to catalyze the transesterification of triglyceride, and this catalysis effect has been previously reported (Wang et al., 2008; Minamia and Saka, 2006). In order to investigate the catalytic effect of FFA on the conversion of triglyceride, we carried out the simultaneous transesterification and esterification under two different reaction conditions: without a solid catalyst and with the addition of a solid catalyst. The conversions of FFA and triglyceride in these two processes were compared. The comparison was carried out with the use of V-C-600-

S-210 as the catalyst. The reaction conditions were reaction temperature 140 °C, catalyst/model waste oil mass ratio 0.3%, the molar ratio of methanol/model waste oil 20.9 and reaction time 2 h. The results are shown in Fig. 5A.

From Fig. 5A, it can be seen that the conversion of FFA with the addition of a solid catalyst was much higher than the process without a solid catalyst. It also can be noticed that the difference in FFA conversion for these two processes is obvious. For the triglyceride, the difference in the conversion was not obvious when the reaction time was less than 1 h. However, when the reaction time was increased to 2 h, the difference was obvious. Hence, it can be concluded that the FFA can catalyze the transesterification of triglyceride.

Since the concentration of the catalyst influences the conversion of FFA and triglyceride, this will lead to different remaining amounts of FFA when the same mass of FFA was added. Hence, the catalytic effect of FFA needs to be considered when a large amount of FFA remained. On the other hand, it has been reported that the leaching of acid sites occurred when a carbon-based catalyst was in contact with the liquid reactants, such as methanol and FFA, a period of time (Mo et al., 2008b). Hence, we also used the addition of equal amounts of the catalyst at the two steps. The difference between the adding of equal amounts of catalyst at two times and when the catalyst was added at one time was compared. The comparison was carried out using V-C-600-S-210 as the catalyst. The reaction temperature was varied from 140 °C (the first step) to 220 °C (the second step), and used a model waste oil (50% cottonseed oil and 50% oleic acid), catalyst/model waste oil mass ratio 0.3% and reaction time 5 h. The catalyst was added at one time in one process, and in the other process, the catalyst was added in equal amounts in two phases. Both processes were carried out using the method of reaction and separation. The process was stopped after 2 h (the first phase), and the FAME and water formed from the first phase reaction was separated from the mixture by the method of reduced pressure distillation. Then, fresh methanol was added to carry out the second phase reaction, and the reaction was continued for another 3 h. The comparison was made after the latter 3 h. The results are shown in Fig. 5B.

From Fig. 5B, it can be seen that the higher conversion of FFA was obtained for the process with the higher concentration of catalyst in the first step. It can be noted that the conversion of

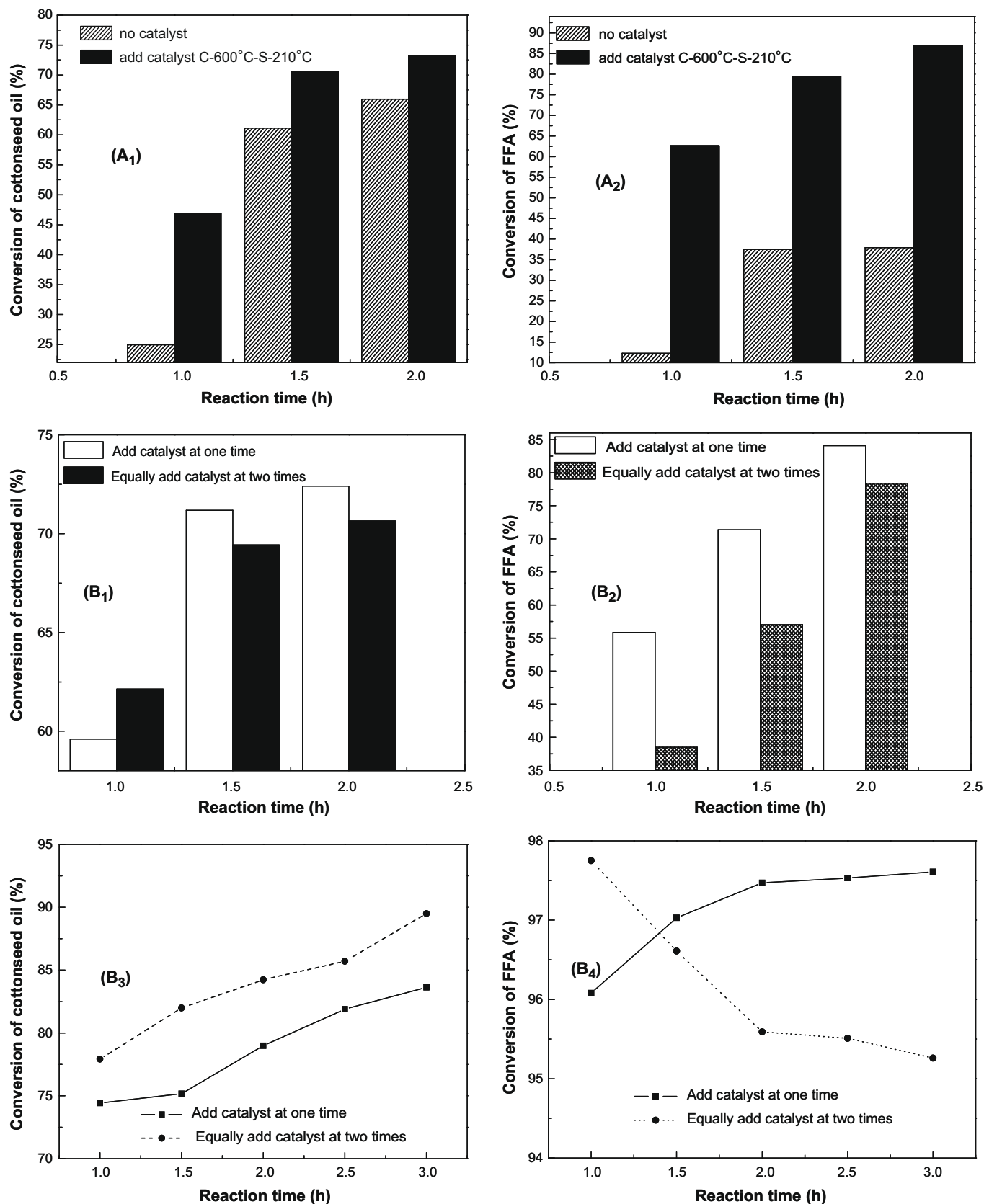


Fig. 5. (A) Comparison of the two processes (without a solid catalyst and with the addition of a solid catalyst V-C-600-S-210) on the conversion of triglyceride (A₁) and FFA (A₂): model waste oil (50% cottonseed oil and 50% oleic acid), reaction temperature 140 °C, catalyst/model waste oil mass ratio 0.3% and molar ratio of methanol/model waste oil 20.9 and reaction time 2 h. (B) Comparison of when the addition of all the catalyst was at one time and when equal amounts of catalyst were added at two times on the conversion of triglyceride (B₁: reaction temperature was 140 °C; B₃: reaction temperature was 220 °C) and FFA (B₂: reaction temperature was 140 °C; B₄: reaction temperature was 220 °C). The reaction time is 5 h, and the other reaction conditions are the same as the comparison (A).

triglyceride was higher when the reaction was catalyzed by a lower catalyst concentration at 1 h reaction time. However, when the reaction time was increased from 1 to 2 h, a higher conversion of triglyceride was obtained for the process with the higher concentration of catalyst. This can be ascribed to the larger catalytic effect of FFA when it was present in a higher concentration in the reaction medium. In the second step, a higher triglyceride conversion has obtained with the process where the catalyst was added in equal amounts at two times, and the chemical equilibrium of the esterification was also reached in a shorter time. Hence, it can be concluded the leaching of acid sites occurred when a carbon-based catalyst was contacted with the liquid reactants for a period of time.

3.2.3. Comparison of the activities of different carbon-based catalysts

The influence of the three solid acid catalysts (V-C-600-S-210, P-C-750-S-210 and P-C-950-S-210) on the conversion of triglyceride and FFA is shown in Fig. 6. The comparison was carried out as follows: the reaction temperature was varied from 140 °C (the first step) to 220 °C (the second step) using a model waste oil (50% cottonseed oil and 50% oleic acid), catalyst/model waste oil mass ratio 0.3% (equally added at two phases). The FAME and water formed from the first step reaction was separated from the mixture by the method of reduced pressure distillation by the method of reduced pressure distillation after 3 h. Then, fresh methanol was added to carry out the second step reaction, and the reaction was continued for another 3 h.

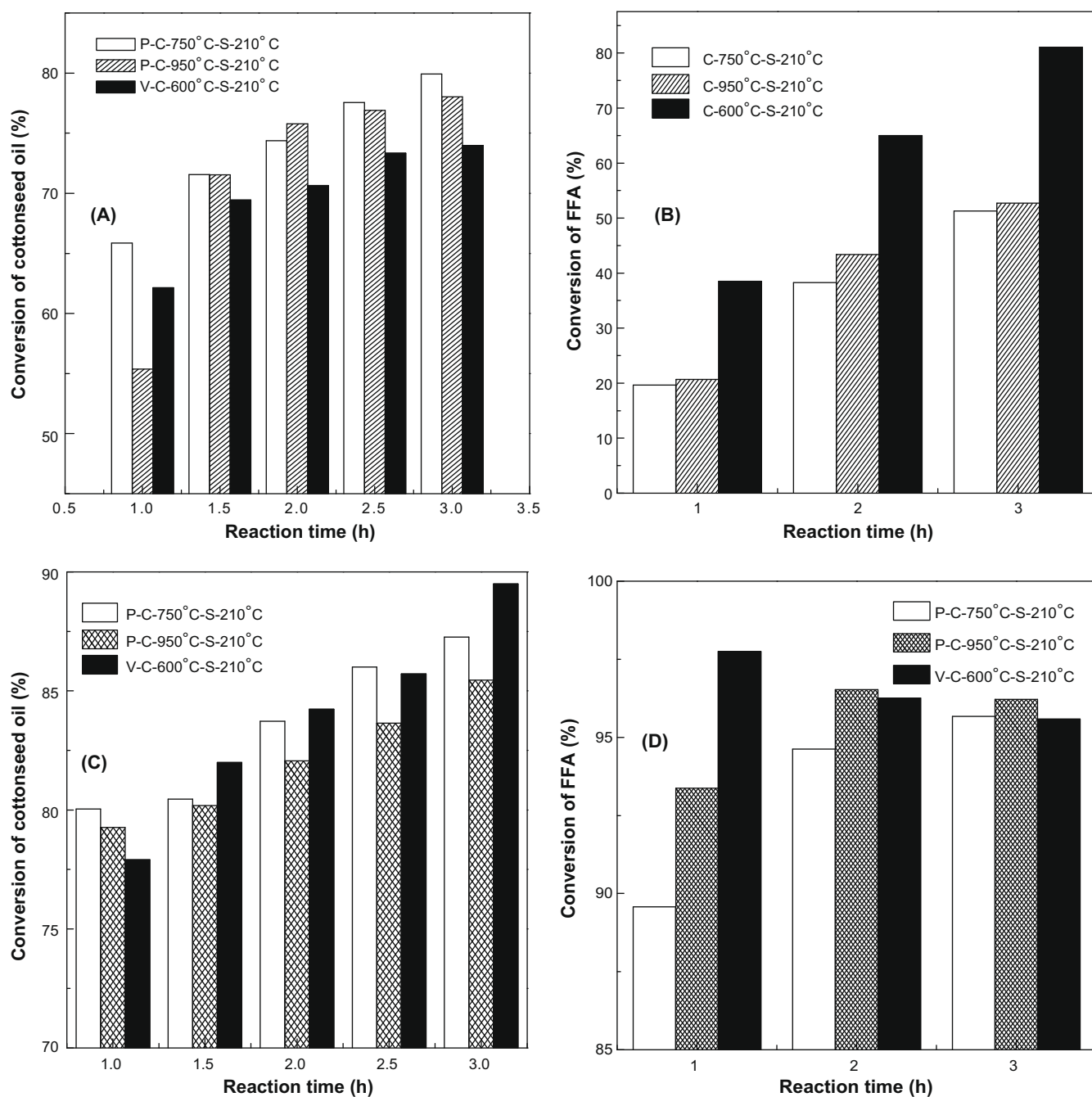


Fig. 6. Compare the activity of three experimental solid acid catalysts on the conversion of triglyceride (A: reaction temperature was 140 °C; C: reaction temperature was 220 °C) and FFA (B: reaction temperature was 140 °C; D: reaction temperature was 220 °C); model waste oil (50% cottonseed oil and 50% oleic acid), catalyst/model waste oil mass ratio 0.3% (equally added at two times), and molar ratio of methanol/model waste oil 20.9.

From Fig. 6, it can be seen that the V-C-600-S-210 catalyst gave the best activity for the conversion of triglyceride when the reaction time was 6 h. In the first step, the V-C-600-S-210 catalyst had the highest activity for the conversion of FFA. However, for the triglyceride, the difference on its conversion was not obvious with the three catalysts. This also can be ascribed to the catalytic effect of FFA. In the second step, because the amount of FFA was greatly decreased, the conversion of the residual triglyceride was mainly determined by the activity of the catalyst. Since the V-C-600-S-210 catalyst had a higher acid site concentration (2.21 mmol g^{-1}), a larger pore diameter (43.9 nm), and a higher stability of its acid site, it gave a better activity than the petroleum asphalt-based catalyst. However, the difference in the conversion of triglyceride was not very significant. This can be explained as follows. The sulfonated asphalt catalyst has a compact structure in the dry state due to strong hydrogen bonding in its structure, but it can become more flexible when it is made to swell in a swelling agent. However, the nature of the swelling agent can affect diffusion and swelling efficiency in polymers (Popli et al., 1991). It has been reported that the different hydrophilic reagents with different molecule sizes will produce different swelling effects to the sulfonated carbon catalysts, such as acetic acid and triacetin (Mo et al., 2008b). A similar swelling effect appears to be present here for the sulfonated carbon catalysts. Compared with smaller and more hydrophilic molecules, larger and more hydrophobic species like triglyceride would be less efficient swelling agents. However, the same swelling agent also can produce different swelling effects on different materials that have different structures. The vegetable oil asphalt catalyst illustrates a loose irregular network and large pores (Fig 1A and B). Hence, the improvement of its activity from the swelling effect will be less than the petroleum asphalt catalyst. However, due to the petroleum asphalt catalyst has a less flexible structure than the vegetable oil asphalt catalyst, the swelling effect maybe greatly ameliorate this inflexible structure, and thus to improve its catalytic activity. Since the activity of the petroleum asphalt catalyst can be improved by the swelling effect, it can be expected to compensate for its lower concentration and stability of its acid sites to some extent. Hence, there would only be small differences in the conversion of triglyceride. On the other hand, the different $-\text{SO}_3\text{H}$ concentrations on the different carbon-based catalysts will cause them to have different hydrophobicity since the $-\text{SO}_3\text{H}$ group is hydrophilic. Since the V-C-600-S-210 catalyst had a higher $-\text{SO}_3\text{H}$ concentration, it had the highest degree of hydrophilicity. The hydration of the $-\text{OH}$ groups will occur to a higher extent when water is present than with P-C-750-S-210 and P-C-950-S-210. The activity of V-C-600-S-210 will be affected because its $-\text{SO}_3\text{H}$ concentration was reduced to some extent. However, since the carbon-based catalyst was mainly composed of carbon sheets which were hydrophobic, these can be expected to have better hydrophobicity than other solid acid catalysts. Hence, these are suitable catalysts for the conversion of waste oils with high FFA concentrations to biodiesel in a two-step sequential catalytic process.

4. Conclusions

The carbon-based solid acid catalyst V-C-600-S-210 gave a high catalytic activity for biodiesel production from the model waste oil. This solid acid consisted of a flexible carbon-based framework that supported highly dispersed polycyclic aromatic hydrocarbons containing sulfonic acid groups. It can simultaneously catalyze transesterification and esterification, so it should potentially be useful for the conversion of waste oils with high FFA concentrations to biodiesel. The high activity can be ascribed to the high density and stability of its acid sites, loose irregular network, and the hydro-

phobic property of its carbon sheets that prevented the hydration of $-\text{OH}$ groups when water is present and large pores that can provide more acid sites to the reactants. The proposed new process (coupling of reaction and separation) can greatly improve the conversion of triglyceride and FFA. It offers a way to produce biodiesel that uses a recoverable solid acid catalyst, which would be more environmentally friendly than a liquid acid catalyst.

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References

- Canakci, M., 2007. The potential of restaurant waste lipids as biodiesel feedstocks. *Bioresour. Technol.* 98, 183–190.
- Chen, X.R., Ju, Y.H., Mou, C.Y., 2007. Direct synthesis of mesoporous sulfated silica-zirconia catalysts with high catalytic activity for biodiesel via esterification. *J. Phys. Chem. C* 111, 18731–18737.
- Felizardo, P., Correia, M.J.N., Raposo, I., 2006. Production of biodiesel from waste frying oils. *Waste Manage.* 26, 487–494.
- Georgianni, K.G., Kontominas, M.G., Pomonis, P.J., Avlonitis, D., Gergis, V., 2008. Conventional and in situ transesterification of sunflower seed oil for the production of biodiesel. *Fuel Process. Technol.* 89, 503–509.
- Han, M.H., Yi, W.L., Wu, Q., Liu, Y., Hong, Y.C., Wang, D.Z., 2009. Preparation of biodiesel from waste oils catalyzed by a Brønsted acidic ionic liquid. *Bioresour. Technol.* 100, 2308–2310.
- Hara, M., 2009. Environmentally benign production of biodiesel using heterogeneous catalysts. *Chem. Sus. Chem.* 2, 129–135.
- Hara, M., Yoshida, T., Takagaki, A., 2004. A carbon material as a strong protonic acid. *Angew. Chem. Int. Ed.* 43, 2955–2958.
- Joaquín, P.P., Isabel, D., Federico, M., Enrique, S., 2003. Selective synthesis of fatty monoglycerides by using functionalised mesoporous catalysts. *Appl. Catal. A-Gen.* 254, 173–188.
- Liu, R., Wang, X.Q., Zhao, X., Feng, P.Y., 2008. Sulfonated ordered mesoporous carbon for catalytic preparation of biodiesel. *Carbon* 46, 1664–1669.
- Lotero, E., Liu, Y.J., Lopez, D.E., Suwannakarn, K., Bruce, D.A., Goodwin, J.G., 2005. Synthesis of biodiesel via acid catalysis. *Ind. Eng. Chem. Res.* 44, 5353–5363.
- Minamia, E., Saka, S., 2006. Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process. *Fuel* 85, 2479–2483.
- Mo, X.H., Lotero, E., Lu, C.Q., 2008a. A novel sulfonated carbon composite solid acid catalyst for biodiesel synthesis. *Catal. Lett.* 123, 1–6.
- Mo, X.H., Lopez, D.E., Suwannakarn, K., Liu, Y., Lotero, E., Goodwin, J.G., Lu, C.Q., 2008b. Activation and deactivation characteristics of sulfonated carbon catalysts. *J. Catal.* 254, 332–338.
- Mohamad, I., Ali, O., 2002. Experimental evaluation of the transesterification of waste palm oil into biodiesel. *Bioresour. Technol.* 85, 253–256.
- Nakajima, K., Hara, M., Hayashi, S., 2007. Environmentally benign production of chemicals and energy using a carbon-based strong solid acid. *J. Am. Ceram. Soc.* 90, 3725–3734.
- Ngaosuwan, K., Lotero, E., Suwannakarn, K., Goodwin, J.G., Praserthdam, P., 2009. Hydrolysis of triglycerides using solid acid catalysts. *Ind. Eng. Chem. Res.* 48, 4757–4767.
- Okamura, M., Takagaki, A., Toda, M., Kondo, J.N., Domen, K., Tatsumi, T., Hara, M., Hayashi, S., 2006. Acid-catalyzed reactions on flexible polycyclic aromatic carbon in amorphous carbon. *Chem. Mater.* 18, 3039–3045.
- Park, J.Y., Kim, D.K., Lee, J.S., 2009. Esterification of free fatty acids using water-tolerable Amberlyst as a heterogeneous catalyst. *Bioresour. Technol.* 101, S62–S65.
- Peng, B.X., Shu, Q., Wang, J.F., Wang, G.R., Wang, D.Z., Han, M.H., 2008. Biodiesel production from waste oil feedstocks by solid acid catalysis. *Process. Saf. Environ. Protect.* 86, 441–447.
- Popli, R., Luccas, M.H., Tsaour, S.L., 1991. Swelling of latex particles by water-soluble solvents. 1. Experimental results. *Langmuir* 7, 69–72.
- Ramos, M.J., Casas, A., Rodriguez, L., Romero, R., Perez, A., 2008. Transesterification of sunflower oil over zeolites using different metal loading: a case of leaching and agglomeration studies. *Appl. Catal. A-Gen.* 346, 79–85.
- Sharma, Y.C., Singh, B., Upadhyay, S.N., 2008. Advancements in development and characterization of biodiesel: a review. *Fuel* 87, 2355–2373.
- Shu, Q., Yang, B.L., Yuan, H., Qing, S., Zhu, G.L., 2007. Synthesis of biodiesel from soybean oil and methanol catalyzed by zeolite beta modified with La^{3+} . *Catal. Commun.* 8, 2159–2165.
- Shu, Q., Zhang, Q., Xu, G.H., Nawaz, Z., Wang, D.Z., Wang, J.F., 2009a. Synthesis of biodiesel from cottonseed oil and methanol using a carbon-based solid acid catalyst. *Fuel Process. Technol.* 90, 1002–1008.

- Shu, Q., Zhang, Q., Xu, G.H., Wang, D.Z., Wang, J.F., 2009b. Preparation of biodiesel using s-MWCNT catalysts and the coupling of reaction and separation. *Food Bioprod. Process.* 87, 164–170.
- Suganuma, S., Nakajima, K., Kitano, M., Yamaguchi, D., Kato, H., Hayashi, S., Hara, M., 2008. Hydrolysis of cellulose by amorphous carbon bearing SO₃H, COOH, and OH groups. *J. Am. Chem. Soc.* 130, 12787–12793.
- Talukder, M.M.R., Wu, J.C., Lau, S.K., Cui, L.C., Shimin, G., Lim, A., 2009. Comparison of Novozym 435 and Amberlyst 15 as heterogeneous catalyst for production of biodiesel from palm fatty acid distillate. *Energy Fuels* 23, 1–4.
- Toda, M., Takagaki, A., Okamura, M., 2005. Green chemistry – biodiesel made with sugar catalyst. *Nature* 438, 178.
- Wang, C.W., Zhou, J.F., Chen, W., Wang, W.G., Wu, Y.X., Zhang, J.F., Chi, R.A., Ying, W.Y., 2008. Effect of weak acids as a catalyst on the transesterification of soybean oil in supercritical methanol. *Energy Fuels* 22, 3479–3483.
- Zhang, J.J., Jiang, L.F., 2008. Acid-catalyzed esterification of *Zanthoxylum bungeanum* seed oil with high free fatty acids for biodiesel production. *Bioresour. Technol.* 99, 8995–8998.
- Zhang, Y., Dube, M.A., McLean, D.D., Kates, M., 2003. Biodiesel production from waste cooking oil (1): process design and technological assessment. *Bioresour. Technol.* 89, 1–16.
- Zong, M.H., Duan, Z.Q., Lou, W.Y., Smith, T.J., Wu, H., 2007. Preparation of a sugar catalyst and its use for highly efficient production of biodiesel. *Green. Chem.* 9, 434–437.