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Preparation of biodiesel using s-MWCNT catalysts and the coupling of reaction and separation

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ABSTRACT

A new process that coupled the reaction and separation in the production of biodiesel from feedstocks with Free Fatty Acids (FFAs) was studied. A novel solid acid catalyst, sulfonated-multiwalled carbon nanotubes (s-MWCNTs), was used in the synthesis of biodiesel from methanol and oleic acid in a 250 mL autoclave. s-MWCNTs with different concentrations of $-SO_3H$ were produced from the treatment of MWCNTs with concentrated H_2SO_4 (96%) at 120–210 °C, and were characterized by SEM/EDS and FTIR analysis. Recycling of the methanol phase was used to separate the water produced from the reaction mixture, which increased the esterification conversion substantially and decreased the acidity of the product. A conversion of oleic acid of 95.46 wt.% was obtained with a catalyst/oleic acid mass ratio of 0.20%, methanol/oleic acid molar ratio of 5.8, temperature of 135 °C, and reaction time of 1.5 h. By removing water from the reaction mixture and adding the recycling of the methanol steam, the conversion of oleic acid was increased to 99.10 wt.% after 1 h.

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Keywords: Sulfonated-multiwalled carbon nanotube; Free fatty acids; Biodiesel; Reaction and separation

1. Introduction

Biodiesel is a clean and renewable biomass energy that can be used as an alternative to diesel because it is similar to petroleum-based diesel. Biodiesel can be produced from either the transesterification of triglycerides (vegetable oils or animal fats) or the esterification of Free Fatty Acids (FFAs) with a short chain alcohol such as methanol or ethanol in the presence of a catalyst (Ma and Hanna, 1999; Behzadi and Farid, 2007). As the alcohol, methanol is the least expensive and readily available from syngas. Therefore, biodiesel is often referred to as fatty acids methyl esters (FAME).

The major drawback in the commercialization of biodiesel from vegetable-origin oil primarily lies in the high raw material cost when compared with petroleum-based diesel fuel. In recent years, China annually consumed approximately 22 million tons of refined edible oils, and 50% of the consumed oils needed be imported to meet this consumption requirement. Therefore, it is unfeasible to produce biodiesel using refined edible oils as feedstocks in China. The use of cheap raw feedstocks such as waste cooking oils, soapstock (byproduct of

vegetable oil refinery) and non-edible oils, which are available cheaply, is a possible solution in improving the economical feasibility of biodiesel in China (Felizardo et al., 2006; Zhang et al., 2003). However, these feedstocks are challenging due to the presence of considerable amounts of FFAs that interfere with the transesterification process. The FFAs must first be converted into their corresponding esters through esterification.

There are several comprehensive studies of base-catalyzed transesterification to produce FAME and a higher conversion of vegetable oil has been reported using strong basic solutions such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) (Vicente et al., 2004). However, a small amount of moisture can initiate oil hydrolysis to form FFA and glycerol. The FFA produced would react with the base catalyst to form soaps, and these soaps can bring about the emulsification of FAME and glycerol. This will make the separation of the FAME-glycerol mixture more difficult when the water washing method is used, only refined crude oils have acid value less than 1 could be used in a base-catalyzed process (Zhang et al., 2003; Felizardo et al., 2006).

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Nomenclature

C	concentration of KOH (mol/L)
<i>m</i>	mass of tested sample (g)
M_1	mass of initial oleic acid (g)
M_2	mass of remained oleic acid (g)
<i>V</i>	volume of KOH (mL)
<i>X</i>	conversion of oleic acid (wt.%)
<i>Y</i>	acid value (mgKOH/g)

For the homogeneous acid-catalyzed system, H_2SO_4 has been the most investigated catalyst. However, it requires special neutralization and a costly separation processing. The consumption of sulfuric acid, the separation of sulfates (from the neutralization processing) and the purification of the product also give rise to substantial energy and material use. Therefore, the development of solid acid catalysts has gained much attention in order to improve the environmental safety of chemical and energy production. Among the heterogeneous acid catalysts studied to date for trans/esterification are zeolites (Machado et al., 2000), MCM-41 (Joaquín et al., 2003), tungstated zirconia (Furuta et al., 2004), silica-supported zirconium sulfate (Juan et al., 2007), Amberlyst-15 (Bozek and Gmehling, 2006) and Nafion (Heidekum et al., 1999). Some common problems with solid acid catalysts have been: low acid site concentrations, microporosity, hydrophilic character of catalyst surfaces, and active site leaching. And further, the major obstacle in using the recyclable solid acid as the substitute of H_2SO_4 lies in the lack of a solid acid that is as active, stable and inexpensive as sulfuric acid.

An ideal solid acid catalyst for the preparation of biodiesel from a feedstock with considerable amounts of FFAs should have high stability and a high density of strong protonic acid sites in the presence of water (which is produced from the esterification of FFAs by methanol). Unfortunately, the inorganic oxide solid acids such as Al_2O_3 , zeolites and niobic acid have a low density of strong protonic acid sites and readily lose their activities in the presence of water. This is because the acid catalysis over these inorganic oxide solid acids occurs at acidic hydroxyl groups (–OH), which act as strong Brønsted acid sites, but the acid strength of these are reduced due to the hydration of –OH when water is present (Nakajima and Hara, 2007). Although strong acidic cation-exchangeable resins and Nafion have large amounts of sulfonic acid group (– SO_3H) Brønsted acid sites, and have been studied extensively as promising choices for the solid acids, they are expensive and their catalytic activities are still much lower than that of sulfuric acid.

For the esterification, carbon-based solid acid catalysts have been reported as promising catalysts (Hara et al., 2004; Toda et al., 2005; Takagaki et al., 2006; Zong et al., 2007). The catalyst can be either produced from the carbonization of sulfopolycyclic aromatic hydrocarbons (such as the sulfonate derivative produced by reaction of anthracene with concentrated H_2SO_4) or the sulfonation of the carbonized inorganic/organic compound. The former is simple and straightforward. Recently, carbon nanotubes have become seen as an attractive material because of many unique properties originating from the small size, cylindrical structure, and high aspect ratio of length to diameter. Single-walled carbon nanotubes (SWCNTs) consist of a single graphite sheet wrapped around to form a cylindrical tube. Multiwalled carbon

nanotubes (MWCNTs) comprise an array of such nanotubes that are concentrically nested like the rings of a tree trunk. H_2SO_4 can be intercalated among the layers of the graphite to serve as an acid catalyst. Recently, various kinds of nanotubes, including agglomerated SWCNTs, few walled CNTs, MWCNTs, and aligned MWCNTs has been mass produced at a relatively low price (Wang et al., 2002; Zhang et al., 2008b,c; Wei et al., 2008). The CNTs showed various new performances in catalysis and find more and more application as new kinds of high performance catalyst (Serp et al., 2003; Li et al., 2007, 2008; Pan et al., 2007; Zhang et al., 2008a). Recently, SWCNTs have been sulfonated and employed as solid acid in the preparation of ethyl acetate (Yu et al., 2008).

The MWCNTs have a more lamellar structure and H_2SO_4 can be intercalated among the layers of the graphitic structure. It can be expected that MWCNTs could be used as an effective precursor to synthesize a solid acid. The covalent functionalization of MWCNTs with sulfonic groups should provide stability, considerable solubility and strong surface acidity. However, the use of such catalysts to produce biodiesel has not yet been reported in current literatures.

Based on the considerations above, and that the soapstock commonly contains 85–90 wt.% fatty acid, we used oleic acid as a model substitute soapstock. A new process that used the coupling of the reaction and separation was used. The recycling of the methanol steam was used to directly separate water from the reactant, which increased the esterification conversion substantially and effectively decreased the acid value of the product.

This study was aimed at the application of s-MWCNT catalysts in the esterification of oleic acid with methanol. The reaction conditions with respect to catalytic activities have been individually optimized by changing the experimental conditions of reaction temperature, reaction time, catalyst/oleic acid mass ratio, and methanol/oleic acid molar ratio. The new process with the coupling of the reaction and separation was compared with the process that only comprises the reaction, and shown to have better performance.

2. Experimental

2.1. Catalyst preparation

A fluidized bed reactor was used to synthesis the MWCNTs (Wang et al., 2002; Wei et al., 2008). The inside diameter and height of this reactor were 0.250 m and 1 m, respectively. Fe/Mo/ Al_2O_3 was used as the catalyst and fed into the reactor before reaction. Propylene was used as the carbon source. This entered from the bottom vessel of the reactor, and then passed through the gas distributor, the fluidized bed unit, and finally flowed out into the atmosphere. The flow of propylene was 5–10 m^3/h diluted with a 1–3.5 m^3/h mixture of nitrogen and hydrogen at atmospheric pressure and ambient temperature. The reaction temperature was maintained at 500–700 °C, and synthesis times were between 30 and 60 min. Reaction occurred within the catalyst particles which are the sites of growing MWCNTs. Both the catalyst and the MWCNTs were smoothly fluidized in the reactor via proper self-agglomeration.

The s-MWCNTs were prepared as follows: 1 g MWCNT was dipped in 50 mL concentrated H_2SO_4 (96%) solution at 120–210 °C under reflux and agitation for 10 h. After the treat-

ment, the suspension was diluted by deionized water and dried at 115 °C for 2 h to give s-MWCNTs.

2.2. Catalyst characterization

The samples were characterized by a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). The structure and chemical compositions of the samples (O, C and S) were obtained using a HRSEM JSM 7401F SEM and EDS analyzer, respectively. The characterization of the sulfonic acid group $-SO_3H$ in the s-MWCNTs was recorded with a FTIR-spectrometer (Nicolet Magna 550 II FTIR). The particle size distribution of the s-MWCNT catalyst was determined using the ZetaPALS analyzer.

2.3. Material and reaction procedure

In an industrial production, waste vegetable oils such as corn, cottonseed, rapeseed and soybean acidified oils (derived from soapstocks by acidification) would be used as feedstocks. In this research, oleic acid (Analytical Reagent, 99%) was used as the model substitute soapstock to react with methanol (Analytical Reagent, 99.5%) to investigate the influence of the reaction parameters. The reaction was carried out in a 250 mL autoclave equipped with a magnetic stirrer that can recirculate the vapors inside the liquid at 240 rpm. An electronic temperature controller was used to maintain the reaction temperature by introducing a thermoelement into the liquid and reflux condenser. The reaction was carried out in a two phase system, and the working pressure in the autoclave is 0.4–0.8 MPa.

In the first phase, the oleic acid and fresh catalyst were added into the reactor first. When the required temperature was reached, methanol was heated to 50 °C and then added into the reactor by a pump, and the reaction was started by stirring.

After reaction for a certain time, in order to exceed the reaction equilibrium to improve the conversion of oleic acid, the methanol phase in the reactor was taken out to remove the water from the reactant, during which the mixture of methanol and water was distilled to recycle the methanol. The second phase comprised the mixture of the product (oleic acid methyl ester) and unconverted oleic acid from the above reaction. This was heated to the same temperature as the first phase and then added into the recycled methanol by a pump, and the reaction was re-started with stirring.

2.4. Product analysis

Sampling analysis was manually carried out at different times during the run. After reaching the reaction time, the reaction mixture was cooled and separated by filtration. The filtrate was allowed to separate into two layers that are the different phases. The oil phase consisted of methyl esters and oleic acid, while the aqueous phase mainly contained water and methanol.

High performance liquid chromatography (HPLC, Shimadzu LC-10A) equipped with an ultraviolet photometric detector was used for analyzing the withdrawn samples. A ppherisorb ODS 2 column (250 mm × 4.6 mm with 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 mL/min, and the column temperature was 40 °C. The components measured by the HPLC included methyl esters and oleic acids. Standard samples were used to establish the calibration charts. The calibration charts were used to calculate the weight percentage of the individual components from integrated peak areas. The oleic acid conversion is defined as Eq. (1):

$$X = \frac{M_1 - M_2}{M_1} \quad (1)$$

where, X is the conversion of oleic acid (wt.%), M_1 is the mass of initial oleic acid (g), and M_2 is the mass of remained oleic acid (g).

The acidity of the product is quantified by the measurement of its acid value (mgKOH/g) according to ISO 1242:1999. The acid value is defined as Eq. (2):

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

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

3. Results and discussion

3.1. Characterization of the catalyst

The SEM microphotographs that depicted the structures of untreated and H_2SO_4 -treated MWCNTs are shown in Fig. 1. The

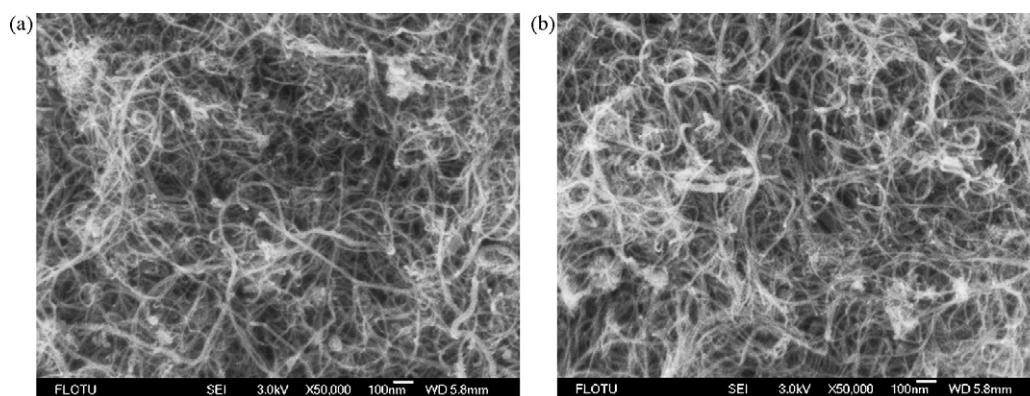


Fig. 1 – SEM microphotograph (a) before and (b) after H_2SO_4 -treated MWCNTs at 210 °C.

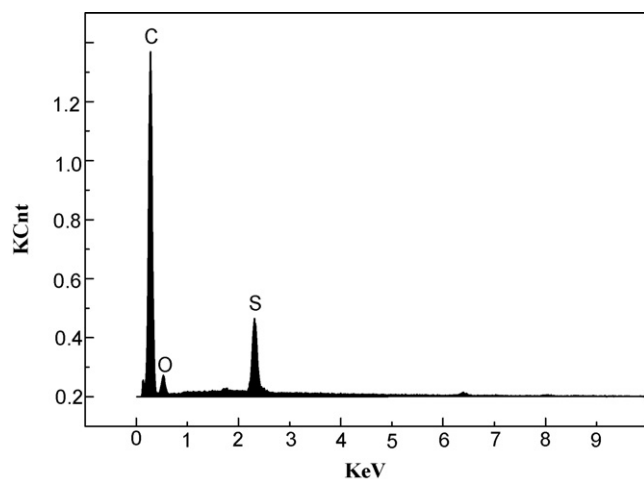


Fig. 2 – The EDS spectrogram of H₂SO₄-treated MWCNTs at 210 °C.

EDS spectrogram of H₂SO₄-treated MWCNTs is shown in Fig. 2.

The SEM photograph revealed that the morphology and structure of the MWCNTs did not change after sulfonation with concentrated H₂SO₄ at 210 °C. This indicated the MWCNTs have a stable structure, which can be ascribed to that the CNTs were entangled with each other to form a multistage agglomerated-structure (Wang et al., 2003; Wei et al., 2008; Liu et al., 2008a,b). It is a stable structure that will ensure the MWCNTs have good stability both in the sulfonation and when used as a catalyst in the esterification. EDS results showed that the content of sulfur and oxygen were 7.2 and 9.9% (mass ratio) in the s-MWCNTs. The content of sulfur in the s-SWCNTs was 5.3 wt.% (Peng et al., 2005). Hence, it can be concluded that the more lamellar structure provided more space for H₂SO₄ intercalation.

FTIR spectroscopy was employed to investigate the functional groups in the s-MWCNTs. As shown in Fig. 3, two bands appeared at 1040 and 1179 cm⁻¹, which can be assigned to the SO₂ asymmetric and symmetric stretching modes (Wilson et al., 2002). This is evidence that the H₂SO₄ treatment at 210 °C enabled the intensive covalent sulfonation of the MWCNTs. All these data indicated the solid acid catalyst s-MWCNTs would have high catalytic activity.

The particle size distribution of s-MWCNTs is shown in Fig. 4. It is evident from the results that about 75% (w/w) of the

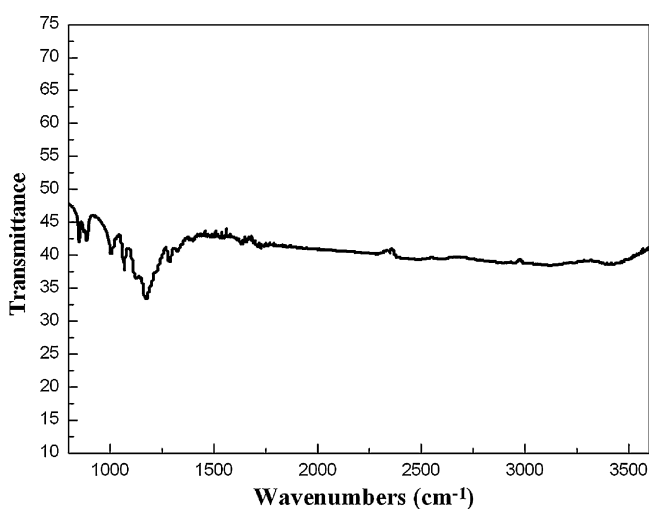


Fig. 3 – FTIR spectroscopy of H₂SO₄-treated MWCNTs at 210 °C.

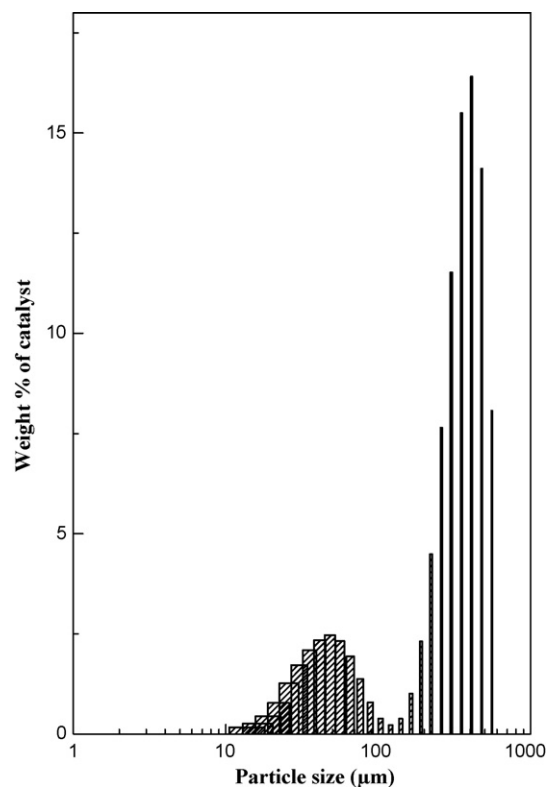


Fig. 4 – The particle size distribution of s-MWCNTs catalyst.

catalyst particles are within the size range 259–556 µm, and the remainder is within the range 14–223 µm. The average particle size of this catalyst is 314 µm. The particles with different sizes were separated from using standard-sized sieves (600 µm down to 180 µm), and the effect of particle size on the conversion of oleic acid was studied from 180–600 µm. For a specified catalyst loading, it was observed that there was no effect of the variation in the particle size from 180–600 µm. This endorses that intraparticle diffusional resistances of the reactant in the s-MWCNTs are not important. Hence, all further experiments were conducted directly with the s-MWCNTs (without any size screening).

The preliminary experiments were also conducted varying the stirring speed, to quantify the influence of external resistances to heat and mass transfer. These experiments showed that there was very little effect of speed of agitation in the range 180–300 rpm on the overall rate of the reaction. Hence, all further experiments were conducted at a stirrer speed of 240 rpm, ensuring that there were no external mass transfer resistances.

3.2. Catalytic activity for the esterification of oleic acid

3.2.1. s-MWCNTs from different sulfonation temperature

The effect of the sulfonation level on the conversion of oleic acid was studied. Catalysts produced from different sulfonation temperatures of 120, 150, 180 and 210 °C were used for the esterification reaction. For a typical run, the reaction temperature was controlled at 135 °C and the reaction time was 1.5 or 2 h, molar ratio of methanol to oleic acid 6.4:1, and catalyst/oleic acid 0.19 wt.%. The results are shown in Fig. 5.

Fig. 5 shows that the sulfonation level of s-MWCNTs has a positive effect on the conversion of oleic acid. From this figure, it can be seen that the s-MWCNTs (prepared from the MWCNTs after H₂SO₄ treatment at 210 °C) had the best catalytic

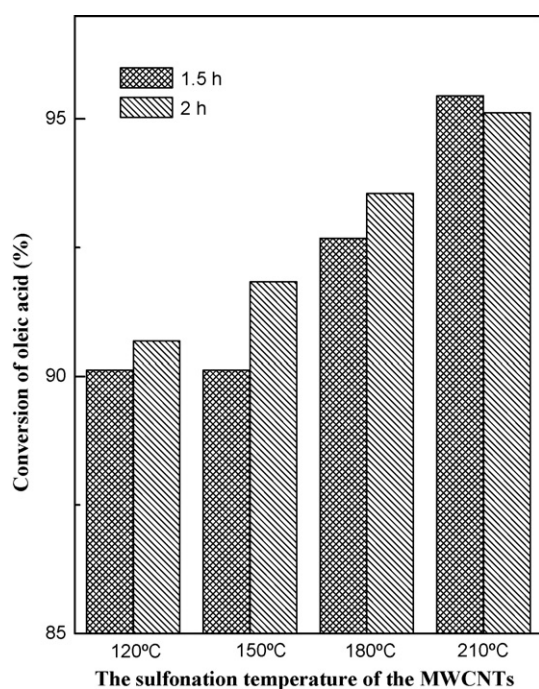


Fig. 5 – Influence of the sulfonation level of the s-MWCNTs on the conversion of oleic acid. The reaction temperature was controlled at 135 °C and the reaction time was 1.5 and 2 h, molar ratio of methanol to oleic acid 6.4:1, and catalyst/oleic acid 0.19 wt.%.

activity. With an increase in the reaction time from 1.5 to 2 h, the conversion of oleic acid changed from 83.49 to 90.68, 90.12 to 91.83, 92.68 to 93.55, 95.45 to 95.12 wt.% when using the s-MWCNTs (prepared from the MWCNTs after H₂SO₄ treatment at 120, 150, 180 and 210 °C, respectively) as catalyst, respectively. It also can be concluded that the reaction equilibrium had been reached after 1.5 h when using the s-MWCNTs (sulfonated at 210 °C) as catalyst. Thus, 1.5 h was chosen as a suitable reaction time for the production of FAME. The probable reason why the s-MWCNTs (sulfonated at 210 °C) had the best catalytic activity is that H₂SO₄ will be better intercalated into the MWCNTs at the higher sulfonation temperature. From the experiments, it can be concluded that s-MWCNTs are well adapted for the preparation of biodiesel from cheap feedstocks with high contents of FFAs.

3.2.2. Effect of reaction temperature

In order to study the influence of the reaction temperature on the conversion of oleic acid, experiments using the s-MWCNTs (sulfonated at 210 °C) catalyst were conducted at 120, 130, 135, 140 and 145 °C. The results are shown in Fig. 6.

From Fig. 6 it can be seen that the conversion of oleic acid increased with an increase in temperature. The highest conversion of oleic acid was 96 wt.% when the reaction temperature was 145 °C and the reaction time was 1 h. When the reaction time was increased to 1.5 h, the conversion of oleic acid also increased except when the reaction temperature was 145 °C when it decreased to 95%. This implied the reaction equilibrium had been reached after 1 h when the reaction temperature was 145 °C. Due to that methanol is less soluble in oleic acid, and that it is important to ensure that the reaction takes place in the oleic acid phase, a high temperature and pressure would be needed, but this will increase the biodiesel production cost. Due to that the increase in the reaction temperature from 120 to 135 °C caused a marked increase in the

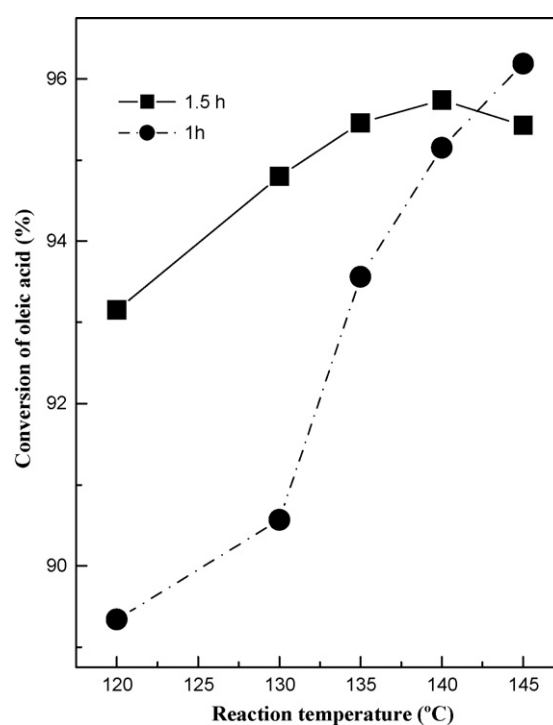


Fig. 6 – Influence of the reaction temperature on the conversion of oleic acid. The catalyst/oleic acid mass ratio was 0.20%, the methanol/oleic acid molar ratio was 5.8.

conversion of oleic acid from 93.15 to 95.46 wt.% at 1.5 h, and that the further increase in the reaction temperature from 135 to 145 °C caused an insignificant decrease of conversion of oleic acid from 95.46 to 95.43 wt.% at 1.5 h, the optimum temperature for this reaction was 135 °C.

3.2.3. Effect of catalyst loading

The amount of catalyst also will affect the conversion of this process. The s-MWCNTs (sulfonated at 210 °C) was used as the catalyst and the effect of the catalyst loading (0.14, 0.16, 0.20 and 0.24 wt.%) on the conversion of oleic acid was studied. The results are shown in Fig. 7.

From Fig. 7, it can be seen that the conversion of oleic acid increased with increase in catalyst loading. The highest conversion of oleic acid was 95.95 wt.% when the catalyst loading was 0.24 wt.% and the reaction time was 1.5 h. Due to that the increase in the catalyst loading from 0.14 to 0.20 wt.% caused a marked increase in the conversion of oleic acid from 93.58 to 95.44 wt.% at 1.5 h, and the further increase in the catalyst loading from 0.20 to 0.24 wt.% gave an insignificant increase of conversion of oleic acid from 95.44 to 95.95 wt.% at 1.5 h, the optimum catalyst loading for this reaction was 0.20 wt.%.

3.2.4. Effect of molar ratio of methanol/oleic acid

Since the esterification is a reversible reaction, in the reaction mixture, the amount of methanol must be in excess to force the reaction towards the formation of the FAME. The effect of the molar ratio of methanol to oleic acid on the conversion of FAME was examined by varying the amount of methanol with a fixed amount of oleic acid of 60 g in the reactions at 135 °C. The initial amounts of methanol were set at 45, 50, 55, 60 and 65 mL respectively, corresponding to the molar ratios of methanol/oleic acid at 5.2, 5.8, 6.4, 7.0 and 7.6. The results are shown in Fig. 8.

From Fig. 8 it can be seen that the highest conversion of oleic acid was 96.10 wt.% when the molar ratio of

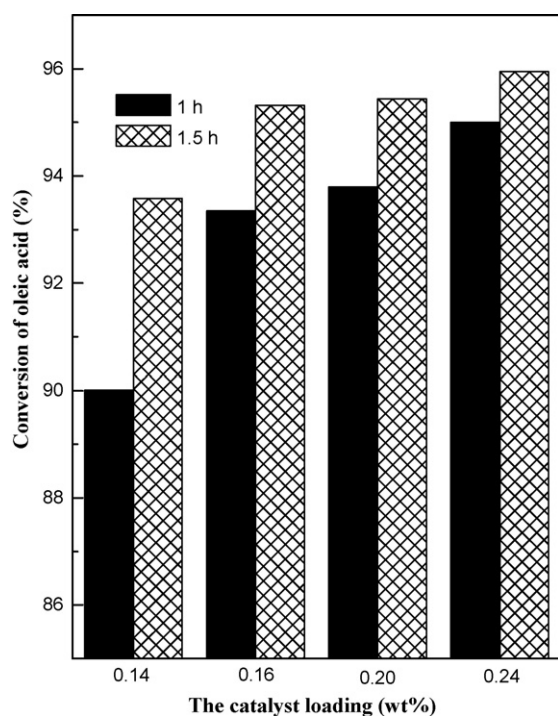


Fig. 7 – Influence of the catalyst loading on the conversion of oleic acid. The reaction temperature was 135 °C, the methanol/oleic acid molar ratio was 6.4.

methanol/oleic acid was 7.6. However, the more in excess the methanol amount, the more methanol would be needed to be removed from the product, which would increase the cost of the biodiesel production. Due to that the increase in the molar ratio from 5.2 to 6.4 gave an increase of conversion of oleic acid from 94.36 to 95.90 wt.%, but a further increase in the molar ratio of methanol to 7.6 showed a very limited effect on the conversion of oleic acid, a molar ratio of methanol/oleic acid

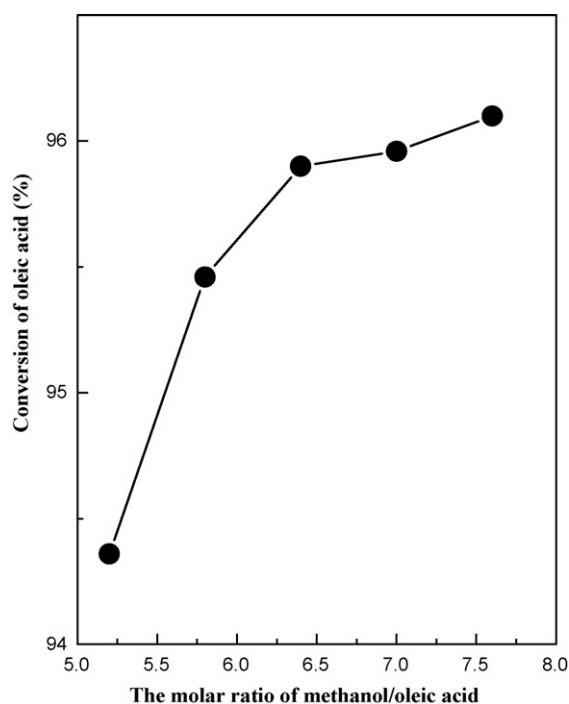


Fig. 8 – Influence of the molar ratio of methanol/oleic acid on the conversion of oleic acid. The reaction temperature was 135 °C, the catalyst/oleic acid mass ratio was 0.20%, the reaction time was 1.5 h.

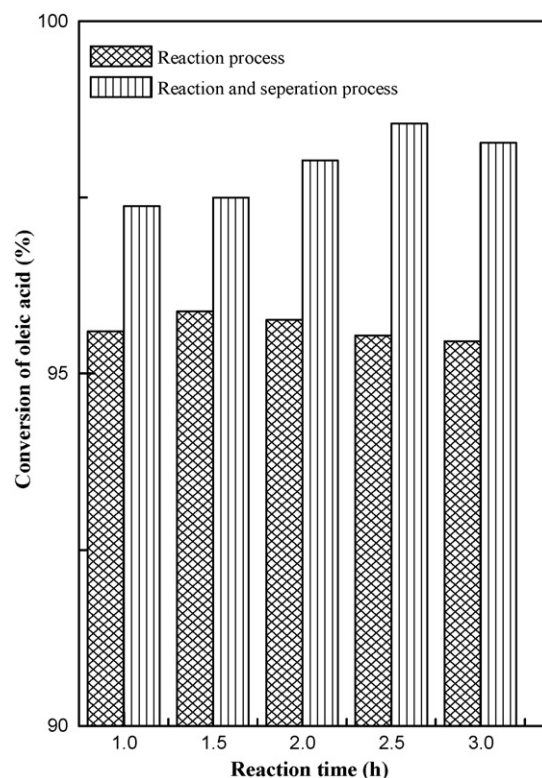


Fig. 9 – Comparison of the two processes using the conversion of oleic acid. The methanol/oleic acid molar ratio was 5.8, the reaction temperature was 130 °C, the catalyst/oleic acid mass ratio was 0.20%, and the reaction time was 4.5 h.

6.4 is appropriate for this reaction.

It also must be pointed out, the occur of esterification was started from the oleic acid chemisorbed on the active sites, and then protonated the carbonyl group to give an carbocation ion, which can undergo the attack by the methanol to form esters. When the amount of methanol is high to some extent, the approach of methanol molecules to the carbocation will be enhanced and increased the conversion. However, when the amount of methanol is much high, it will lead to the flooding of active sites by methanol molecule rather than oleic acid. Therefore, increase of molar ratio will hinder the completion of oleic acid being protonated at the active sites.

3.2.5. Comparison of two reaction process

From the results in Figs. 5 and 6, it is obvious that the conversion of oleic acid was limited by the reaction equilibrium. Hence, the influence of emptying the methanol phase to remove the water product from the reaction mixture, thus, to shift the reaction equilibrium to improve the conversion of oleic acid was studied.

In order to examine if the new process with the coupling of the reaction and separation has a better performance than the process that only has the reaction, the conversions of oleic acid in these two processes were compared. The comparison was carried out using the s-MWCNTs (sulfonated at 210 °C) as catalyst, and the reaction temperature was 130 °C, the catalyst/oleic acid mass ratio was 0.20%, the reaction time was 1.5 h and the methanol/oleic acid molar ratio was 5.8. The process that only has the reaction was continued for 4.5 h. The new process with the coupling of the reaction and separation was stopped after 1.5 h, and the methanol phase was emptied

out to remove the water produced from the reaction mixture. Then, after the pressure had decreased back to atmospheric pressure, the recycled methanol was added into the reactor by a pump and the reaction was continued for another 3 h. The comparison was made after the latter 3 h. The results are shown in Fig. 9.

From Fig. 9 it can be seen that the new process with the coupling of the reaction and separation can greatly increase the conversion of oleic acid. For the process that only has the reaction, the conversion of oleic acid of 95.46 wt.% was obtained for 4.5 h. For the new process that coupled with the reaction and separation, the conversion of 98.28 wt.% was obtained after re-started the reaction for 3 h. When the reaction temperature was increased to 135 °C and the other conditions were not changed, the conversion of oleic acid of 95.46 wt.% was obtained after 1.5 h (only reaction). After re-started the reaction for 1 h, the conversion of oleic acid can reach 99.10 wt.% (coupling of the reaction and separation). The acid value of the product is 1.8 when the conversion of oleic acid approached to 99.10 wt.%. Hence, it can be concluded that the chemical equilibrium can be overcome from the continuous removal of the water from the reaction mixture, and to reach a high conversion.

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 high contents of FFAs.

4. Conclusion

The present study showed that the solid acid catalyst, s-MWCNTs, has a high catalytic activity for biodiesel production from cheap raw feedstocks with high concentrations of FFAs. It offers a possible way to produce biodiesel that use a recoverable solid acid catalyst, which would be more environmentally friendly than a liquid acid catalyst. A new process with the coupling of the reaction and separation has the potential for the production of biodiesel on an industrial scale.

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