Functionalization of MWCNT by –SO$_3$H and –COOH Groups and Their Application as Solid Acidic Catalysts for Esterification of Waste Chicken Fat

A. Shokuhi Rad,[a,*] M. lotfinezhad,[b] E. Ganjian,[c] S. Afrashteh,[d] and H. Reza Ghorbani[a]

[a]Department of Chemical Engineering, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran

[b]Department of Chemical Engineering, Science and research Branch, Islamic Azad University, Tehran, Iran

[c]Department of Chemical Engineering, Babol University of Technology, Babol, Iran

[d]Department of Textile Engineering, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran

In the present research, the esterification of waste chicken fat (WCF) by two different homogeneous and heterogeneous catalysts has been studied. Sulfonate and carboxylate functionalized multiwall carbon nanotubes (MWCNT-SO$_3$H, MWCNT-COOH) were applied as useful heterogeneous acidic catalysts during esterification of WCF. According to the experimental results, sulfonate-modified MWCNT showed more effective catalytic activity than did carboxylate-modified MWCNT. It was found that free fatty acid (FFA) of WCF in the single stage esterification of WCF had decreased down to less than 1 % in the presence of 25 % MWCNT-SO$_3$H catalyst (according to the amount of FFA), reactor temperature of 90 °C with contact time of 3 h, and methanol/FFA molar ratio of 30:1.

Key words:

waste chicken fat, biodiesel, MWCNT-SO$_3$H, MWCNT-COOH, esterification, transesterification

Introduction

There are two major categories of fuels – fossil fuels and biofuels. Fossil fuels are extracted from coal which is not renewable, and biofuels are a derivative of plant or animal waste which is renewable[1,2]. About 80 % of required energy in the world is supplied by fossil fuels. In manufacturing industries, products are generated by machines that consume diesel fuel. Every day, worldwide, the consumption of diesel and gasoline in public transportation, shipment transportation and private vehicles is considerable. This proves the role of fossil fuels in everyday life of every person in the world. On the other hand, energy can be supplied from some natural sources such as agricultural and biological wastes and crops like oil seed wastes, straw, wood, human wastes and animal fats[3].

Due to the toxic nature of fossil fuel wastes, new sources of energy have been considered for the substitution of fossil fuels. Some common raw materials used in biodiesel (BD) production are animal fats, vegetable oils and waste oils in the presence of various catalysts and alcohols[4]. Generally, production of BD is performed by the transesterification method, which is a common procedure and contains various oils and alcohols together with proper catalysts. Methanol is a low-cost alcohol, so it is used as a prevalent alcohol for production of BD.

Bhatti *et al.*[5] studied the production of BD from waste tallow as a low-cost sustainable raw material, by investigating the effects of some important parameters, such as catalyst dosage, contact time, and temperature. The single stage and catalyst-free transesterification reaction of Karanja oil with supercritical methanol was investigated by Ortiz-Martinez *et al.*[6] In addition, Salar-Garcia *et al.*[7] optimized the operating conditions for BD production from Jatropha oil in supercritical methanol. Their study had been concentrated on the optimum conditions for production of second-generation BD from Jatropha oil.

Sodium and potassium hydroxides are two well-known homogeneous base catalysts, which are commonly applied in BD production. These catalysts boost the transesterification reaction to a short

*Corresponding author: a.shokuhi@gmail.com, a.shokuhi@qaemiau.ac.ir

reaction time under mild operating conditions. Thus, soap formation during the esterification reaction reduces the yield of BD production due to the use of the catalyst. Therefore, the content of water and FFA, which are the source of soap formation, should be kept at a low level. (Scheme 1). Application of low-cost and non-edible raw materials, such as vegetable oils and waste animal fats, is an effective plan to reduce the cost of BD productions. On the other hand, consumption of these low-cost materials including major fraction of FFA causes an increase in catalyst dosage, purification costs, and decline in BD efficiency[8,9]. These problems can be solved by transesterification reaction with acidic catalyst, which takes a long time to be completed[10]. The transesterification reaction with acidic catalyst followed by alkali catalyst is an enhanced procedure for high FFA content oils. Some researchers have investigated the transesterification reaction using this technique considering either homogeneous or heterogeneous acid[11–15].

Esterification and transesterification of triglyceride, especially oils having high content of FFA, can be performed by homogeneous acidic catalysts such as sulfuric and hydrochloric acid. These processes need a high molar ratio of methanol to oil and a long time for reaction completion[16]. In addition, all the tools require protection against corrosion due to the acidic environment[17]. Since homogeneous catalysts are consumed when the reaction occurs, they are not reusable and cannot be regenerated, and this is the major disadvantage of homogeneous catalysts. Moreover, catalyst separation from the final mixture is too difficult and requires excess equipment that leads to the increase in operating and capital costs[18].

Esterification reactions using solid acidic catalysts have been investigated by many researchers[19–23]. For instance, ferric sulfate was applied for esterification of FFA in waste frying oil, and this solid acid catalyst exhibited a high performance[24–25].

Corrosion of equipment and the separation process are the significant problems of the esterification reaction by homogeneous liquid acidic catalysts such as sulfuric acid. These problems can be eliminated by using solid acidic catalysts.

Application of heterogeneous catalysts in the esterification reaction has been restricted because of the low level of active sites. It is well known the use of solid nano-catalyst accomplishes great catalytic activity and easy separation.

By controlling the surface chemistry of nanotubes, new types of sensors based on nanotubes and new light composites with high catalytic activity and suitable mechanical characteristics (thermal, electrical, etc.) can be designed. Chemical modification is an easy way to functionalize nanotubes to-

ward enhancing their catalytic activity[26]. Many studies have been conducted on the functionalization of carbon nanotubes (CNT) as an effective catalyst. This process is performed by strong oxidizing-acid solutions. For instance, sulfuric and nitric acids have been applied for functionalization of carbon nanotubes surfaces with e carboxylic acid groups[27]. Recently, Sobati *et al*. have investigated ultrasound irradiation esterification of fish oil by sulfonate modified activated carbon catalyst[28]. Esterification of palm oil for BD production with sulfonate modified MWCNT was studied by Shuit *et al*.[29]. In their research, esterification of animal fats containing high value of FFA was not investigated.

The aim of the present study was to investigate the application and comparison of MWCNT-SO_3H and MWCNT-COOH catalysts for the esterification process. Thus, a new powerful protonic acidic catalyst is formed with high catalytic performance for the esterification process, which is a suitable replacement for non-recyclable liquid acidic catalysts.

$$RCOOR' \ + \ H_2O \ \rightleftarrows \ RCOOH \ + \ R'OH$$

$$RCOOH \ + \ NaOH \ \rightleftarrows \ RCOONa \ + \ H_2O$$

S c h e m e 1 – *Saponification of fatty acid alkyl ester*

Experimental

Materials

All materials and reagents with analytical grade were bought from Merck Company (German). These materials were used without purification. WCF with acid amount of 23.8 mg KOH g^{-1} (11.9 % FFA) was prepared from the local market (Qaemshahr, Iran). Some properties of WCF are listed in Table 1. The composition of different fatty acids of WCF, analyzed by GC chromatography, is presented in Table 2. The liquid WCF was filtered with 50-micron fuel filter before transmission to the esterification reactor.

The reduction of the FFA percentage in WCF down to less than 1 % was the first aim of the esterification reaction.

T a b l e 1 – *Some physical properties of the WCF*

Property	Unit	WCF
Density	kg m^{-3}	964.1
Water content	% mass	0.5
Acid amount	mg KOH g^{-1}	23.8

Table 2 – *Fatty acid content of WCF obtained by GC chromatography analysis*

Fatty acid	Fatty acid content (g per 100 g sample)
Palmitic acid	12.65 ± 0.17
Stearic acid	3.98 ± 0.03
Oleic acid	38.10 ± 0.89
Linoleic acid	46.78 ± 011
Linolenic acid	4.12 ± 0.22
Arachidonic acid	0.0
Eicosadienoic acid	0.0

Chromatography apparatus

To analyse the feedstocks and determine the composition of different fatty acids, the chromatography technique was applied with Hewlett Packard's (HP) Gas Chromatography Mass Spectrometry (GC/MS) model HP6890 and HP5973 (mass selective detector) equipped with a flame-ionization detector and a 60 m× 0.25 mm i.d. column coated with a 0.25 μm film of HP-23. Split injection (split ratio 1:50) was performed using H_2 as carrier gas at a flow rate of 45 m s^{-1}. The column temperature was fixed at 160 °C for 1 min following injection, then automated at 2.75 °C min^{-1} to 215 °C, which was fixed for 2 min, and finally at 40 °C min^{-1} to 230 °C, which was kept for 2 min. The injection port and detector temperatures were 270 °C. Calculations were based on analysis of standard mixtures and calculation of distinct correction coefficients.

Synthesis of MWCNT-SO$_3$H and MWCNT-COOH

The amount of 5 g pristine MWNTs and 250 mL sulfuric acid (98 wt %) were stirred for 20 h at 250 °C with nitrogen gas flow. The prepared product was then washed twice with distilled water, and oven-dried at 120 °C for 12 h to obtain sulfonate modified MWCNT (named MWCNT-SO$_3$H).

In addition, for preparation of carboxylate modified MWCNT (MWCNT-COOH), 5 g of pristine MWNTs were added to a mixture of HNO_3/H_2SO_4 (volume ratio of 1:3, 250 mL) and kept for 2 h in an ultrasonic bath at 30 °C, according to the procedure previously studied[30]. The resulting dispersed solution was washed with deionized water and decanted for one week to separate the acid modified MWCNT. Thereupon, both acid modified carbon nanotubes were washed with distilled water to obtain a neutral pH. Scanning electron microscopy images (SEM-XL30 Philips Electron Microscope) was applied to characterise the surface morphology of the pristine and functionalized MWCNTs.

Design of experiments

The significant factors influencing the esterification process were designed by the one-factor-at-a-time method. Three major parameters, including methanol to oil molar ratio, reaction time, and catalyst dosage for optimization and experiments of the esterification reaction were evaluated. The selected values of the main parameters are presented in Figures 3–5.

Esterification parameters

For esterification of the WCF, a combination of modified MWCNTs catalyst (MWCNT-SO$_3$H or MWCNT-COOH) and methanol was applied at appropriate situations. About 100 g of vacuum-dried raw WCF (to remove water content) was poured into a separate 250-mL flat-bottom one-neck reactor containing solid catalyst, fed by a reflux condenser. To adjust the reactor to the favourable temperature (90 °C), a warm water bath was provided. The reaction was carried out without stirring due to the boiling of methanol. During the reaction, evaporated methanol condensed continually and returned to the reactor. After the completion of the esterification reaction, the mixture was left overnight to settle, after which the supernatant (methanol–water) was separated. For the separation of the insoluble catalyst and purification, a filtration process was then applied. The residual methanol in the lower layer of the mixture was also separated using a rotational evaporator under vacuum conditions at 50 °C.

The parameters influencing the esterification reaction in the presence of acidic catalysts were selected as follows: 12, 18, 24, and 30 % methanol ratio (based on FFA), 2, 4, 10, 20 % (based on FFA) of sulfuric acid (regarding homogeneous catalyst), 5, 10, 18, 25 % (based on FFA) of solid catalyst (regarding heterogeneous catalyst), and three different contact times of 1, 2, and 3 h. For calculation of the amount of FFA in WCF, the mean of acid value (AV) of the oil layer was titrated by 0.1 equivalent per liter KOH.

Results and discussion

Fig. 1 shows the scheme of the synthesis path of both MWCNT-COOH and MWCNT-SO$_3$H. The first stage was to modify pure MWCNT by HNO_3/H_2SO_4 at 30 °C with short contact time of 2 h. The second step was to functionalize MWCNT by only sulfuric acid at 250 °C with long contact time of 20 h.

Characterization of MWCNT-SO$_3$H

The surface morphology of the samples was investigated by SEM images. As can be seen in

HNO3/H2SO4
1:3
30 °C /2h

-COOH
-COOH
-COOH
-OH
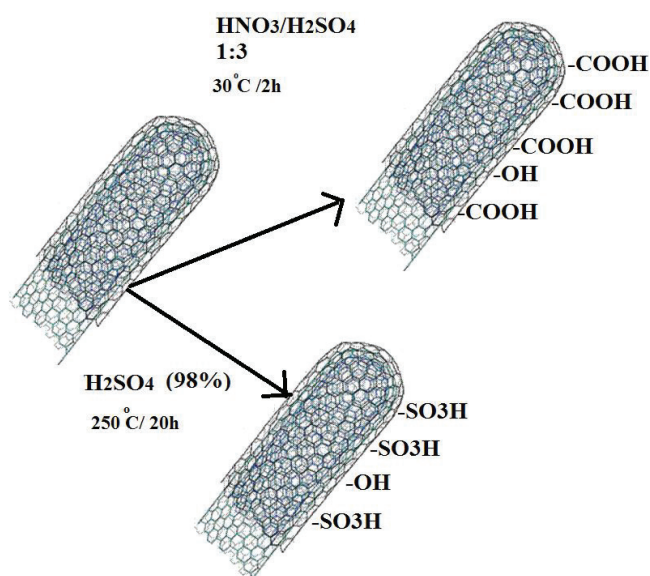-COOH

H2SO4 (98%)
250 °C/ 20h

-SO3H
-SO3H
-OH
-SO3H

F i g . 1 – *Scheme of –COOH and –SO$_3$H functionalization of MWCNT*

Fig. 2a, the sidewalls of the MWCNTs are not damaged and the surface is smooth without oxidation. As Figs. 2b and 2c exhibit, in comparison with Fig. 2a, the sidewalls of MWCNTs are significantly damaged. This is because of the ruinous impacts of the oxidizing agents on the outer layer of MWCNTs walls.

Pre-treatment of WCF

The acid value of the applied WCF was 23.8 mg KOH g^{-1}, which is equal to 11.9 % of FFA. As mentioned previously, the FFA content of oil should be lower than 1 % before application of alkaline catalysis[31]. In the present study, for the esterification reaction of WCF, three acidic catalysts were applied; sulfuric acid as homogeneous catalyst, sulfonate modified MWCNT (MWCNT-SO$_3$H) and carboxylate modified MWCNT (MWCNT-COOH) as heterogeneous catalysts. In order to decrease the high content of FFA, two-stage pre-treatment processes have been reported by some researchers[11,32]. It should be noted that the increase in pre-treatment stages leads to the reduction in ester yield because

of the ester solubility in methanol[33]. Therefore, one-stage pre-treatment was applied for reduction of the FFA content during the esterification reaction. After esterification of each sample, the whole mixture was washed twice with hot and distilled water to eliminate any remaining acid.

Esterification of the WCF with sulfuric acid

For homogeneous catalyst, the esterification reaction was performed with four different methanol molar ratios of 12:1, 18:1, 24:1, and 30:1, four various catalyst amounts of 2 %, 4 %, 10 % and 20 % (based on the FFA) during 2 h reaction time at 90 °C. As can be seen in Fig. 3, low amounts of sulfuric acid do not obtain good results. At methanol/FFA molar ratio of 30:1 and in the presence of 2 and 4 % sulfuric acid, the percentages of FFA were decreased only to 8.5 and 4.8 %, respectively, which is not suitable for transesterification processing. In addition, Fig. 3 shows that with the increase in sulfuric acid and the methanol ratio, the FFA percentages of the WCF will decrease. In the presence of 20 % and 10 % sulfuric acid and methanol molar ratio of 24:1, the FFA amounts of WCF decreased down to 1 % and 3.2 %, respectively. The increase in methanol ratio from 24:1 to 30:1 had no significant effect on the reduction of FFA percentage. Whereas, the main objective of esterification is to reduce the FFA content from 11.9 % to less than 1 %; therefore, 20 % sulfuric acid and a methanol ratio of 24:1 are the optimum conditions to decrease the FFA percentage down to less than 1 %. From the results, it can be stated that the increase in the methanol/FFA molar ratio makes the esterification reaction easier; however, the esterification reaction depends on the concentration of sulfuric acid as predicted.

Esterification of WCF with solid catalysts

The esterification reaction was performed for both solid catalysts with methanol molar ratios of 12:1, 18:1, 24:1, and 30:1, and different catalyst amounts of 5 %, 10 %, 18 %, and 25 % (according
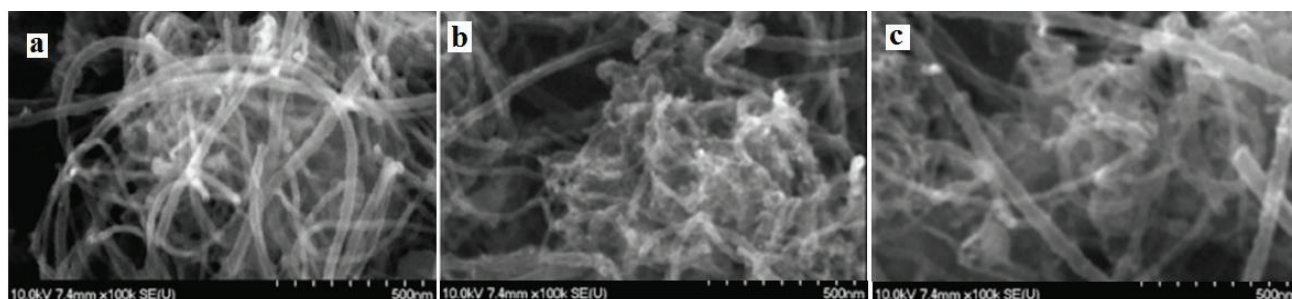

F i g . 2 – *SEM of pristine MWCNT (a), MWCNT-SO$_3$H (b), and MWCNT-COOH (c)*

to FFA) for 2 h reaction time at 90 °C. As Fig. 4 illustrates, sulfonate modified MWCNT has higher catalyst activity than that of carboxylate modified MWCNT in similar conditions. The results also show that the reduction of FFA level by MWCNT-COOH catalyst at high methanol/FFA ratio and high catalyst dosage (25 %) is not favourable, showing

that this catalyst is not suitable for esterification reactions in solitary. In addition, sulfonate modified MWCNT did not generate suitable results at its lower dosages (5 % and 10 %) and methanol molar ratios of 12:1 to 30:1 for 2 h esterification at 90 °C.

In addition, Fig. 4 exhibits that the amounts of FFA in the presence of 18 % MWCNT-SO$_3$H reduced to 3.5 % and 3.1 % for methanol molar ratio of 20:1 and 30:1, respectively. As predicted, mass transfer resistances in the presence of solid catalyst reduce the efficiency of esterification; however, the mass transfer resistances can be rectified with the increase in solid catalyst dosage. In addition, the enhancement of methanol/oil ratio improves the mass transfer resistance problem. Therefore, the amount of 25 % sulfonate modified MWCNT and the methanol/FFA ratio of 30:1 is the optimum condition that causes the reduction of FFA percentage down to about 1.1 %. Comparing the results of Figs. 3 and 4, suggests that, in order to obtain the 1 % of FFA, a higher amount of sulfonate modified MWCNT than homogeneous catalyst should be used. However, it is important to stress that the application of the heterogeneous catalyst is favourable, because it enables easy production and refining processes, and decreases the amount of basic waste and the process cost.
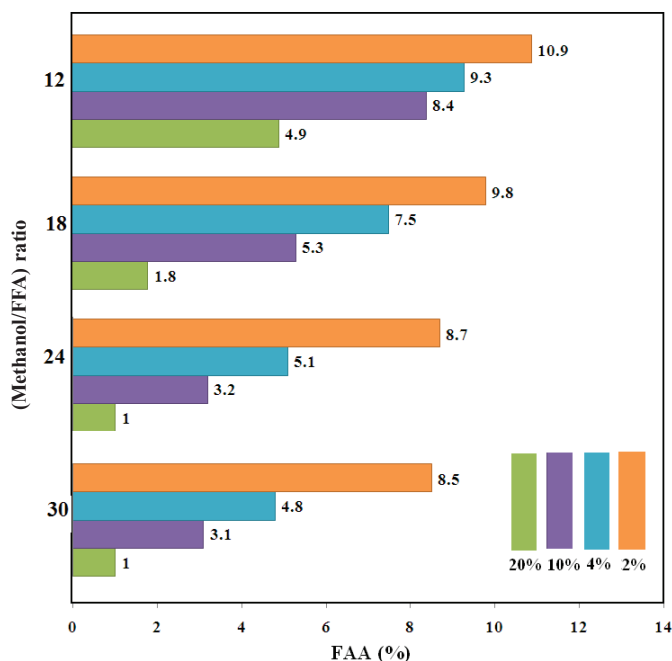
The effect of reaction time

To assess the time effect on the esterification process, 25 % of both sulfonate and carboxylate

F i g. 3 – *FFA content using different amounts of H$_2$SO$_4$ at various methanol/FFA ratios (time = 2 h and temperature 90 °C)*
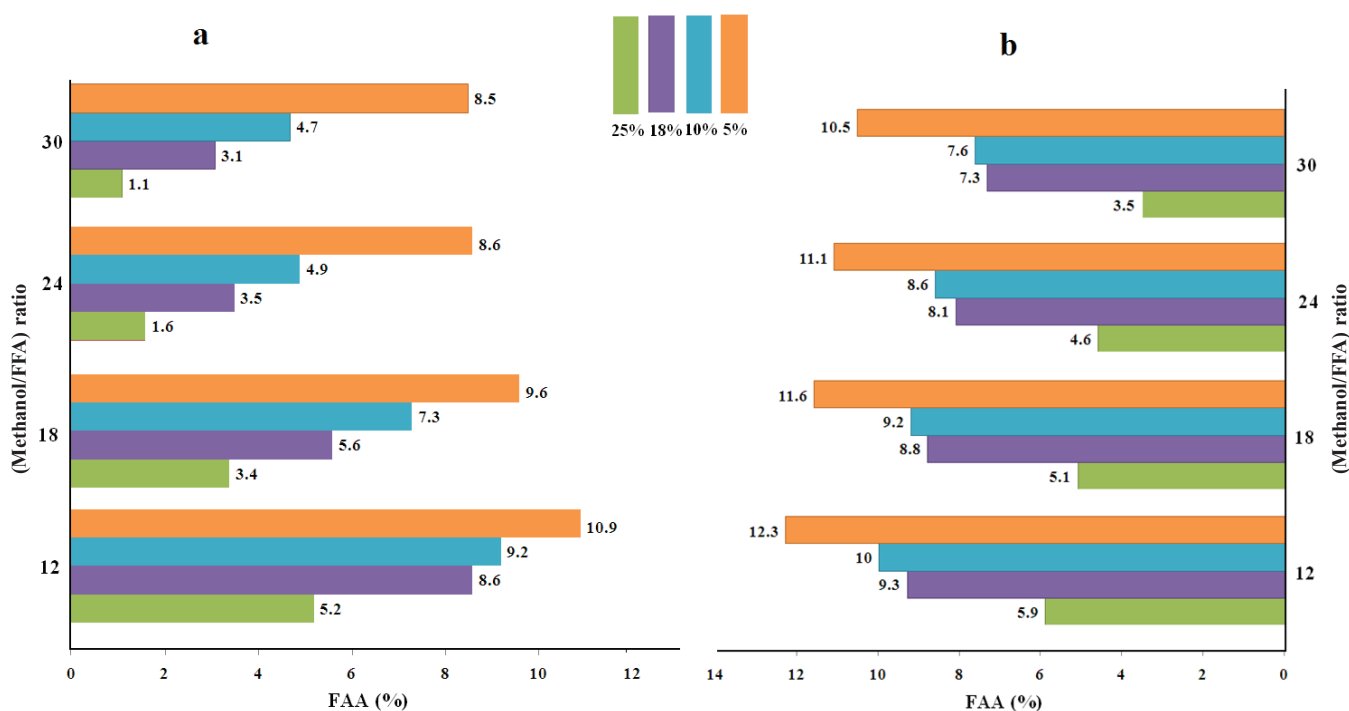

F i g. 4 – *FFA content using different amounts of MWCNT-SO$_3$H (a) or MWCNT-COOH (b) at various methanol/FFA ratios (time = 2 h and temperature 90 °C)*
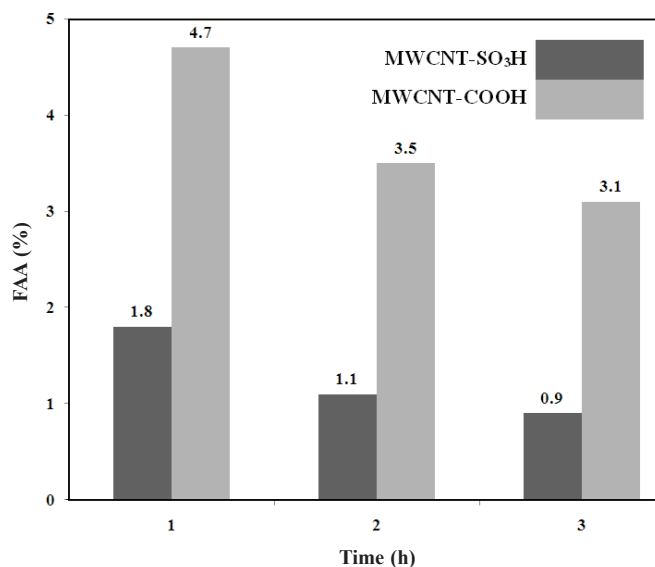
Fig. 5 – *Effect of reaction times on FFA content of heterogeneous acid catalyzed esterification*

modified MWCNTs were chosen, while the methanol molar ratio was enhanced up to 30:1 for the reduction of FFA percentage to less than 1 %. Three different reaction times of 1, 2, and 3 h at 90 °C were selected. Fig. 5 demonstrates the FFA percentages for 1, 2, and 3 h pre-treatment in the presence of 25 % solid catalysts and methanol/FFA molar ratio of 30:1. In the presence of 25 % of each catalyst and methanol/FFA molar ratio of 30:1 with 1, 2, and 3 hours of esterification reaction, the FFA amounts in the WCF were measured to be 1.8 %, 1.1 %, 0.9 % MWCNT-SO$_3$H and 4.7 %, 3.5 %, 3.1 % for MWCNT-COOH, respectively. The comparison of these results verifies that catalytic performance of MWCNT-SO$_3$H is higher than that of MWCNT-COOH. Thus, the MWCNT-SO$_3$H catalyst is found to be effective in reducing the FFA percentage down to less than 1 % in order to obtain a high ester yield during transesterification.

Conclusions

In this research, sulfonate and carboxylate modified multiwall carbon nanotubes (MWCNT-SO$_3$H, MWCNT-COOH) as two solid heterogeneous acidic catalysts were applied for esterification of WCF. The surface morphology of the synthesized catalysts was characterized by SEM technique. Higher catalytic performance of MWCNT-SO$_3$H than that of MWCNT-COOH was verified. The FFA percentage in the presence of 25 % MWCNT-SO$_3$H (regarding FFA) decreases down to less than 1 % by a one-stage esterification reaction with methanol/FFA molar ratio of 30:1 at 90 °C and 3 h reaction time. These optimum values provide suitable conditions for transesterification.

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