



Feasibility study of various sulphonation methods for transforming carbon nanotubes into catalysts for the esterification of palm fatty acid distillate



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ABSTRACT

Sulphonated multi-walled carbon nanotubes were synthesised and utilised as catalysts to transform palm fatty acid distillate, the low-value by-product of palm oil refineries, into the more valuable product of biodiesel. The most common method to prepare carbon-based solid acid catalysts is thermal treatment with concentrated sulphuric acid, which is a time-consuming and energy-intensive process. Therefore, the feasibility of other sulphonation methods, such as the in situ polymerisation of acetic anhydride and sulphuric acid, the thermal decomposition of ammonium sulphate and the in situ polymerisation of poly(sodium4-styrenesulphonate), were examined in this study. The esterification reaction was performed at 170 °C for 3 h at a methanol to palm fatty acid distillate ratio of 20 and catalyst loading of 2 wt% in a pressurised reactor. The fatty acid methyl esters yields achieved by the sulphonated multi-walled carbon nanotubes prepared via thermal treatment with concentrated sulphuric acid, the in situ polymerisation of acetic anhydride and sulphuric acid, the thermal decomposition of ammonium sulphate and the in situ polymerisation of poly(sodium4-styrenesulphonate) were 78.1%, 85.8%, 88.0% and 93.4%, respectively. All catalysts could maintain a high catalytic activity even during the fifth cycle. Among the sulphonation methods, the in situ polymerisation of poly(sodium4-styrenesulphonate) produced the catalyst with the highest acid group density. In addition, the resonance structures of the benzenesulphonic acid groups attached to the surface of the multi-walled carbon nanotubes generated additional active sites for esterification that led to a higher biodiesel yield.

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1. Introduction

Fatty acid methyl esters (FAME), collectively known as biodiesel, have been hailed as a potential substitute fuel for petroleum-derived diesel due to their physical and chemical similarities to diesel. Biodiesel is superior to petroleum-derived diesel because it is biodegradable, renewable, clean and non-toxic, exhibits a low emission profile and is environmentally friendly [1,2]. Biodiesel is commonly produced from edible oils, such as palm, rapeseed, canola and sunflower oil. However, the major obstacles in this practice that prohibit the further development of biodiesel are the fluctuating price of refined vegetable oils and the food versus fuel issue [3]. In this regard, the production of biodiesel from non-edible oils, such as palm fatty acid distillate (PFAD) [4], *Jatropha curcas* L. seeds, karanja, castor [5], rubber seed, jojoba, waste animal fat [6] and sea mango (*Cerbera odollum*) [7] would be a solution to this problem. Among

these non-edible oils, PFAD represents a promising feedstock for biodiesel production because it is a low-value by-product generated during the fatty acid stripping and deodorisation stages of the purification process carried out in palm oil refineries [4]; thus, PFAD is much cheaper than other refined oils. Moreover, the high miscibility of free fatty acid (FFA) in methanol [8] makes PFAD even more suitable as a feedstock for biodiesel production because it can reduce the mass transfer limitation caused by the immiscibility between oil and methanol [1].

Homogeneous catalysts were the first generation of catalysts used in biodiesel production. However, the major drawbacks of using homogeneous catalysts in biodiesel production are the corrosion caused by the homogeneous acid catalysts (HCl and H₂SO₄), the difficulty to separate catalysts and the generation of wastewater [9,10]. Therefore, heterogeneous catalysts are preferred to homogeneous catalysts, because their products are easy to separate, the catalysts are reusable and the process is more environmentally friendly [11,12]. Common heterogeneous catalysts used in biodiesel production include mixed metal oxides, alkali metal oxides, ion-exchange resins and sulphated oxides. However, these

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conventional heterogeneous catalysts still feature limitations, such as mass transfer resistance, high catalyst cost and low catalyst stability because of leaching [11]. Due to the excellent catalyst stability induced by the covalent bonding between multi-walled carbon nanotubes (MWCNTs) with either basic or acidic functional groups and their high surface areas, MWCNTs can overcome the limitations faced by conventional heterogeneous catalysts and therefore seem to be good catalyst supports for biodiesel production. MWCNTs must be functionalised with acidic groups to convert PFAD, which contains mostly FFA, to biodiesel. The sulphonic group (SO_3H) has been identified as a promising acid catalyst for the catalysis of both transesterification and esterification processes because a high yield of biodiesel can be obtained [11].

The process of functionalising MWCNTs with SO_3H is known as sulphonation [13]. Among the studies reported on the sulphonation of MWCNTs, the process been applied to produce a catalyst for biodiesel production in two studies (the esterification of pure oleic acid and the transesterification of cottonseed oil) [14,15]. MWCNTs sulphonated by other sulphonation methods are usually used as catalysts for oxidation processes [16,17] or to enhance the metal utilisation in fuel cells [18]. Therefore, the main objective of this study was to compare and determine the feasibility of MWCNT-based catalysts produced by various sulphonation methods, including thermal treatment with concentrated sulphuric acid, the thermal decomposition of ammonium sulphate, the in situ polymerisation of acetic anhydride and sulphuric acid and the in situ polymerisation of poly(sodium 4-styrenesulphonate) for the esterification of the low-value industrial by-product PFAD.

2. Materials and methods

2.1. Materials

MWCNTs (Shenzhen Nanotechnologies Port Co.), PFAD (obtained from a local edible oil manufacturing company), nitric acid (HNO_3) (69–70%, JT Baker), sulphuric acid (H_2SO_4) (96%, Fisher Scientific), ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) (Fisher Scientific), methanol and n-hexane (Fisher Scientific), acetic anhydride ($(\text{CH}_3\text{CO})_2\text{O}$) (99%, Acros Organics), ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) (98%, Acros Organics), poly(sodium 4-styrenesulphonate) (PSS) (Sigma Aldrich) and methyl heptadecanoate (Sigma Aldrich) were used as received.

2.2. Purification of MWCNTs

The process used to purify MWCNTs in this study is similar to that reported elsewhere in the literature [13,19]. A mixture of pristine MWCNTs (1 g) and HNO_3 (100 ml) was subjected to 1 h of ultrasonication treatment before being heated to 80 °C for 8 h. The treated MWCNTs were then filtered, washed with distilled water until the pH of the filtrate was the same as the pH of the distilled water and then dried at 120 °C for 12 h to obtain MWCNTs-COOH, which were then subjected to sulphonation.

2.3. Sulphonation by in situ polymerisation of poly(sodium 4-styrenesulphonate)

This sulphonation method is similar to that reported elsewhere in the literature [18]. In this process, 0.4 g of MWCNTs-COOH was vigorously stirred in a mixture of 0.8 g PSS and 100 ml deionised water (DI) at room temperature for 10 h. Subsequently, 1.6 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was added, and the mixture was stirred and heated to 65 °C for 48 h to initiate polymerisation. After cooling to room temperature, the mixture was diluted with 100 ml of DI water, followed by sonication for 1 h, and then washed repeatedly with DI water. The mixture was filtered, mixed with 500 ml of 4 M

H_2SO_4 and then stirred at room temperature for 24 h. Finally, the mixture was filtered, washed with DI water until the pH of the filtrate was the same as that of the pH of distilled water and then dried at 120 °C for 12 h.

2.4. Sulphonation by in situ polymerisation of acetic anhydride and sulphuric acid

The sulphonation conditions and amount of chemicals used in this sulphonation method are based on those reported elsewhere in the literature [16,17]. In this process, 0.2 g MWCNTs-COOH was loaded into a mixture containing 300 ml $(\text{CH}_3\text{CO})_2\text{O}$ and 20 ml concentrated H_2SO_4 . The mixture was stirred and heated to 70 °C for 2 h. The mixture was then continuously stirred until reaching room temperature. The resultant product was filtered, washed with distilled water until the pH of the filtrate was same as the pH of distilled water and then dried at 120 °C for 12 h.

2.5. Sulphonation by thermal decomposition of ammonium sulphate

The sulphonation procedures and amount of chemicals used in this sulphonation method were modified according to those reported elsewhere in the literature [18,20]. In this process, 0.4 g of MWCNTs-COOH was mixed with 30 ml 10% $(\text{NH}_4)_2\text{SO}_4$ solution and sonicated for 10 min. The mixture was then heated to 235 °C for 30 min. The mixture was then washed with distilled water to remove excess $(\text{NH}_4)_2\text{SO}_4$ and dried at 120 °C for 12 h.

2.6. Sulphonation by thermal treatment with concentrated sulphuric acid

This sulphonation method is similar to those reported elsewhere in the literature [19]. In this process, 1 g of MWCNTs-COOH was mixed with 50 ml concentrated H_2SO_4 and sonicated for 30 min. The mixture was then stirred for 12 h at 250 °C under nitrogen flow (100 ml min^{-1}). After cooling to room temperature, the product was filtered, washed with distilled water until the pH of the filtrate was the same as the pH of distilled water and then dried at 120 °C for 12 h.

2.7. Esterification

The esterification of PFAD was carried out in a pressurised reactor under the following conditions: reaction temperature of 170 °C, reaction period of 3 h, methanol-to-PFAD ratio of 20 and catalyst loading of 2 wt%. These reaction conditions were selected based on the trial and error experimentation conducted prior to this study. Upon completion of the reaction period, the mixture was cooled to room temperature and filtered. The excess methanol was removed using a rotary evaporator. Two layers of liquids formed after the evaporation of methanol; the upper layer (dark yellow) was crude fatty acid methyl esters, whereas the bottom layer was water. The volume of the crude fatty acid methyl esters was measured and recorded.

2.8. FAME analysis

The composition and yield of FAME or biodiesel were analysed using a PerkinElmer Clarus 500 gas chromatograph equipped with a flame ionisation detector (FID) and a Nukol™ capillary column. n-Hexane was used as the solvent, and helium was used as the carrier gas. The oven temperature was set to 110 °C and then increased to 220 °C at a rate of 10 °C/min. The temperatures of the detector and injector were set to 220 and 250 °C, respectively. Methyl heptadecanoate was used as an internal standard [21,22]. The yield of FAME in the samples was calculated by the following equation:

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