Synthesis of Novel Magnetic Carbon Microtube-Based Solid Acid and Its Catalytic Activities for Biodiesel Synthesis

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Abstract: Novel magnetic carbon microtube-based solid acid was synthesized via the carbonization of FeCl₃-doped willow catkin and benzenediazoniumsulfonate acid-based sulfonation. The biomass willow catkin provided the special microtube structure and the high surface area of 215 m²/g for the novel solid acid. The microtube structure was well conserved during the mild carbonization (400 °C) and sulfonation process. The large number of acidic sites (2.3 mmol/g) on the microtube surface was quite accessible to reactants. Its magnetic properties offered a simple separation process. The novel solid acid showed very high activity for biodiesel synthesis, using cooking oils as raw material, which gave a total yield of 99% and free fatty acid conversion of 98.7% under mild conditions (70 °C). The facile synthetic process, high activity, high stability, and high recovery simplicity were the main properties of the novel magnetic solid acid, which is one of the best choices for biodiesel synthesis.

Keywords: magnetic carbon microtube-based solid acid; willow catkin; biodiesel synthesis

1. Introduction

Acid catalysts are of great importance in the chemical industry in producing many chemicals [1]. Solid acid catalysts also attract a lot of attention due to their easy recovery and high reusability [2]. Among the various solid acidic catalysts, carbon-based solid acids have high thermostability and catalytic activity, and are regarded as the optimal substitute for liquid acids [3]. However, traditional carbonaceous solid acid is restricted by its extremely low surface area (<2 m²/g) and high polarity, which greatly prevent hydrophobic molecules from reaching the active sites. Furthermore, their amorphous structure adds to the difficulty of catalyst recycling [4]. There is great demand to increase the surface area and simplify the catalyst recovery. Mesoporous materials, such as mesoporous molecule sieve SBA-15 [5], were applied as hard templates to increase the surface area. However, the use of templates added to the cost of the catalyst. In addition, the removal process of the templates was a tedious task. Magnetic materials have wide applications in numerous areas for their unique magnetism, low biological toxicity, and an easily modified surface [6]. Magnetic separation is superior to filtration, which is an additional advantage of magnetic solid acid [7]. Carbon nanotubes have wide applications in catalysis and catalyst supports [8]. Compared to nanotubes, carbon microtubes, with their larger tube diameter, decrease the mass diffusion hindrance, especially for large molecules. Carbon microtubes are generally synthesized through the complicated hard-template method, or by chemical vapor deposition under tedious conditions [9]. Therefore, a facile and convenient process for carbon microtube synthesis is in high demand. Biomass, especially plants, has abundant microstructures, which could be suitable structure suppliers [10]. Catkin is the typical biomass from willow and poplar, which causes damage to the human respiratory system. Catkin forms in the spring and blows around in the wind, which causes serious trouble. Catkin was used as a carbon resource to prepare the carbon microtube-based solid acid [11]. However, the microtube structure was easily destroyed during the harsh sulfonation conditions, which added to the difficulty of catalyst recovery. Here, catkin was first soaked with FeCl₃ solution.
Then, the FeCl$_3$-doped catkin was treated at 400 $^\circ$C to form the magnetic carbon microtubes. Finally, benzenediazoniumsulfonate-acid-based sulfonation was carried out to introduce the functional sulfonic acid groups (Scheme 1). Biodiesel is one of the most important renewable resources, and has excellent ignition properties in compression-ignition (diesel) engines, with almost no modifications [12–14]. Here, the catalytic activity of the novel magnetic carbon microtube-based solid acid was examined via biodiesel synthesis, using cooking oil as the raw material.

![Scheme 1. The synthesis of magnetic carbon microtube-based solid acid.](image)

2. Results and Discussion

2.1. Characterization of the Novel Magnetic Carbon Microtube-Based Solid Acid

The acidity of the magnetic carbon microtube-based solid acid was 2.3 mmol/g, which was calculated based on neutralization titration. The sulfonic acid groups were introduced via benzenediazoniumsulfonate acid instead of sulfuric acid, which avoided corrosion of the magnetic particles [15]. The microtube structure was well kept during the mild sulfonation process. In addition, the acidity could be adjusted by the usage ratio of carbon microtubes and benzenediazoniumsulfonate acid. When the benzenediazoniumsulfonate acid amount was reduced to 2 g, the solid acid only had a low acidity of 0.5 mmol/g. A lower amount of benzenediazoniumsulfonate acid reduced the acidity, for there were not enough sulfonation reagents. The acidity of the solid acid increased with the amount of benzenediazoniumsulfonate acid. The acidity increased very quickly in the initial stage. The acidity increased to 2.3 mmol/g when 6 g of benzenediazoniumsulfonate acid was used. On the other hand, the acidity increased to 2.5 mmol/g when the benzenediazoniumsulfonate acid was further increased to 12 g. The slight increase in acidity indicated that the most active sites on the carbon microtubes were substituted by benzenesulfonic acids. Further increasing the amount of benzenediazoniumsulfonate acid would add to the cost of the catalyst [7]. As a result, a novel solid acid with an acidity of 2.3 mmol/g was chosen for further investigation.

The FT-IR spectra of the magnetic carbon microtube intermediate and the novel solid acid showed almost the same peaks (Figure 1), which further confirmed the mild sulfonation process. The novel solid acid gave similar IR adsorption peaks to traditional carbon-based solid acid [16]. The peak at 540 cm$^{-1}$ was the characteristic vibration absorption of Fe-O, which confirmed the magnetic Fe$_3$O$_4$. The Fe-O adsorption hardly changed in solid acid, which further confirmed that the mild sulfonation condition was quite suitable for magnetic Fe$_3$O$_4$ [17]. The peak located at 1576 cm$^{-1}$ was assigned to the C=C stretching vibration from the aromatic ring, which indicated the aromatic structures in the carbon microtubes. The peaks ranging from 750 to 860 cm$^{-1}$ were the multi-substituted aromatic rings. Here, the carbon was mainly amorphous, with a low extent of carbonization due to the low temperature (400 $^\circ$C). The C-H (1425 cm$^{-1}$) and C-O (1130 cm$^{-1}$) absorption peaks indicate that the carbon microtubes were not completely carbonized with abundant active sites for the following sulfonation. The benzenediazoniumsulfonate acid brought about both the benzene ring and the sulfonic acid groups; therefore, the C-H and C=C (Ar) adsorptions were not greatly decreased for the solid acid. Compared to the carbon microtube intermediate, the novel solid acid showed additional S=O absorption at 1045 cm$^{-1}$, which was covered by the C-O peak and the small peak. The S=O absorption and O-H peak
at 3400 cm$^{-1}$ indicates that the sulfonic acid groups were introduced onto the solid acid successfully [18].

![Figure 1](image1.png)

**Figure 1.** The IR spectra of magnetic carbon microtubes and solid acid.

The XRD pattern (Figure 2) of the solid acid showed the obvious diffraction peaks at 18.37° (111), 30.16° (220), 35.50° (311), 37.12° (222), 43.12° (400), 53.50° (422), 57.01° (511), and 62.58° (440), which fitted well with the pure Fe$_3$O$_4$ (JCPDS:00-003-0862) [7]. This indicates that the magnetic Fe$_3$O$_4$ cores retained their magnetite crystalline structure after sulfonation. The Fe$_3$O$_4$ structure was well kept during the mild sulfonation conditions. Furthermore, the baseline was quite uneven, which accounted for the amorphous carbon microtubes due to the low extent of carbonization [16]. There was a broad peak at around 2θ (8°), which further confirmed the amorphous carbon microtube structure. The magnetite crystalline structure offered the convenient magnetic recovery of the novel solid acid, which added to its simple reusability [18].

![Figure 2](image2.png)

**Figure 2.** The XRD pattern of the magnetic carbon microtube-based solid acid.

The SEM image of the novel solid acid showed the typical microtube morphology in Figure 3a. The microtube structure of catkin was well kept during the synthetic process due to the mild reaction condition. The TG analysis showed the sharp weight loss of catkin at 350–400 °C [11]. Therefore, 400 °C was chosen as the carbonization temperature. The microtubes shrank during the carbonization process, which made the round tubes distorted. Some shrinkages were very obvious on the walls of the microtubes [16]. The
microtubes had a diameter between 1.6 and 4.8 µm with a pore wall thickness of 250 nm. Besides the shrinkage, some tubes were broken during the carbonization, which could be observed in Figure 3a. The diameters of the microtubes were not equally distorted during the carbonization process. The magnetic particles were mainly deposited on the inner surface of the microtubes, which can be seen in the TEM images in Figure 3b. The magnetic particle size was 200 nm, which provided the magnetic property for the solid acid. The magnetism was weak when the FeCl$_3$ amount was reduced to 0.001 mol. The solid acid was hardly attracted by the external magnet. On the other hand, the microtubes were covered by iron oxide with few sites for sulfonation when 0.1 mol FeCl$_3$ was used. A solid acid with strong magnetism and low acidity (0.3 mmol/g) was obtained.

Figure 3. The SEM (a) and TEM (b) images of the novel magnetic solid acid.

The BET surface area of the novel magnetic solid acid was as high as 215 m$^2$/g. Compared to the low surface area of the traditional carbon-based solid acid (2.5 m$^2$/g), the novel solid acid provided a large space for the reactants, which greatly reduced the mass transfer hindrance. The microtube structure of catkin was the main factor for the high BET surface area of the solid acid [11]. Moreover, the big benzenediazoniumsulfonate acid molecules easily attached onto the external surface of the microtubes. Therefore, sulfonic acid groups were mainly dispersed on the external surface due to the occupation of the inner surface by magnetic particles, which made the active sites easily accessible to the reactants [16].

2.2. The Catalytic Activities of the Novel Solid Acid for Biodiesel Synthesis

The catalytic activities of the magnetic carbon microtube-based solid acids were investigated via biodiesel synthesis using waste oils as raw material (Figure 4). Here, the novel solid acid gave high activity for both esterification and transesterification, with a total yield of 99% under mild conditions. FFAs and triglycerides were both converted to the biodiesel product. For the traditional carbon-based solid acid, the high yield was only obtained under harsh conditions (250 °C), which formed the highly activated supercritical methanol [19]. The novel magnetic solid acid had a high surface area of 215 m$^2$/g, which greatly improved the mass transfer efficiency. Furthermore, the active sites on the external microtube surfaces made them easily accessible to the bulky waste oil molecules [16]. The acidic sites on the microtube’s outer surface interacted easily with the big triglyceride molecules. Compared to triglycerides, the smaller FFA molecules with lower steric hindrance interacted more easily with the acidic sites. As a result, the FFAs converted more quickly than the triglycerides at the beginning of the reaction. The reaction for biodiesel synthesis from triglycerides contains three steps [18]. In the first stage, the hydrophobic oils did not mix well with the methanol, which increased the mass transfer hindrance. Therefore, the reaction rate was very low at first. During the reaction process, intermediate diglycerides and monoglycerides with hydroxyl groups were produced. The intermediates had affinity with both the oils and with the methanol. The reactants gradually dissolved together and became a homogeneous solution, which greatly increased the mass transfer efficiency [19]. The reaction rate increased during the middle process of the reaction. The
magnetic solid acid had a high BET surface area and a special microtube structure, which was important to the high catalytic activity. The novel solid acid was well dispersed in the upper hydrophobic biodiesel layer after setting for 12 h, which indicated the hydrophobic surface of the novel solid acid. The polar byproducts of water and glycerol were effectively separated from the acidic sites, which promoted the forward reactions. The high yield of 99% was obtained after 9 h. Further prolonging the reaction time actually led to a slightly reduced yield, which might be caused by a reaction equilibrium shift. Therefore, 9 h was chosen as the optimal reaction time.

Figure 4. The catalytic activity of the novel magnetic carbon microtube-based solid acid\textsuperscript{a,b}. \textsuperscript{a} The reaction conditions: cooking oil—5 g, methanol—3.01 g, catalyst usage—0.04 g, 70 °C; \textsuperscript{b} The yield was calculated on GC using internal standard method.

The catalyst usage determined the number of active sites, which was a key factor for the reaction (Table 1). There were not enough active sites when the catalyst usage was low \cite{17}. The novel solid acid had quite high activity in the reactions. The high total yield of 93.2% was reached only when the 0.01 g catalyst was used. Both the FFAs and triglycerides were converted to biodiesel with high conversion. The yield increased with catalyst usage, which provided more acidic sites for the reaction. The yield achieved the peak value of 99% when the catalyst usage was 0.04 g. The yield then decreased when the catalyst usage was increased further. The acidic sites catalyzed both the biodiesel synthesis and the hydrolysis reactions \cite{15}. Too much catalyst usage accelerated the reverse hydrolysis, which lowered the yield. The optimal catalyst usage was 0.04 g.

Table 1. The effect of the catalyst usage on the reaction.

| Catalyst Usage/g | 0.01 | 0.02 | 0.04 | 0.06 | 0.08 |
|------------------|------|------|------|------|------|
| FFA conversion/% | 92.1 | 95.6 | 98.7 | 98.6 | 98.4 |
| Yield/% \textsuperscript{a,b} | 93.2 | 96.6 | 99.0 | 98.9 | 98.8 |

\textsuperscript{a} The reaction conditions: cooking oil—5 g, methanol—3.01 g, 70 °C, 9 h; \textsuperscript{b} The yield was calculated on GC using internal standard method.

Besides the catalyst usage, the methanol amount was also investigated (Table 2). More methanol increased the interactions between waste oil and methanol molecules, which increased the efficiency of esterification and transesterification \cite{11}. As a result, the conversion and yield of the FFAs increased when more methanol was used in the reaction. The peak yield of 99% was reached when 3.01 g of methanol was used in the reaction. The yield even reduced a little when the methanol amount was further increased to 3.49 g. Too much methanol may have caused a dilution effect, which reduced the reaction rate instead \cite{17}. Therefore, 3.01 g of methanol was chosen as the optimal amount.
Table 2. The influence of the amount of methanol on the reaction.

| Methanol Amount/g | 1.82 | 2.22 | 2.62 | 3.01 | 3.41 |
|-------------------|------|------|------|------|------|
| FFA conversion/%  | 88.5 | 93.6 | 97.4 | 98.7 | 98.6 |
| Yield/%           | 87.6 | 95.8 | 97.9 | 99.0 | 98.8 |

a The reaction conditions: cooking oil—5 g, catalyst usage—0.04 g, 70 °C, 9 h; b The yield was calculated on GC using internal standard method.

The reaction temperature was also investigated for the reactions. A high reaction temperature was generally used to obtain a satisfactory yield for the traditional solid acid catalysts [20]. The reaction temperature also greatly affected the catalytic activity of the magnetic carbon microtube-based solid acid (Table 3). The yield was quite low at a low temperature (25 °C), with a very low yield of 25%. The activity slowly increased when the reaction temperature rose to 50 °C. Evidently, the temperature was not high enough for the activation process [11]. The high yield of 99% was achieved at 70 °C, while the low yield of only 46.2% was achieved at 50 °C. In accordance with the boiling point of methanol, the reaction temperature was restricted to 70 °C to assure the mild condition (atmosphere pressure). Here, the high temperature of 140 °C was also investigated in the autoclave reactor. A higher yield of 99.2% was achieved with an even shorter reaction time of 4 h. The magnetic carbon microtube-based solid acid had even higher activity for the reactions than the common carbon-based solid acid catalysts [4], with a lower temperature and a shorter time. Furthermore, the reaction at 250 °C showed even a higher yield within 2 h. These results further confirm that the novel solid acid has superior activity to traditional carbon-based solid acids.

Table 3. The influence of the reaction temperature on the reaction.

| T/°C  | 25   | 50   | 70   | 140 c | 250 c |
|-------|------|------|------|-------|-------|
| FFA conversion/% | 21.3 | 35.7 | 98.7 | 99.1  | 99.3  |
| Total yield/%      | 25.4 | 46.2 | 99.0 | 99.2  | 99.5  |

a The reaction conditions: cooking oil 5 g, methanol 3.01 g, catalyst usage 0.04 g, 9 h; b The yield was calculated on GC using internal standard method; c The reaction was carried out in an autoclave reactor for 4 h and 2 h respectively.

2.3. The Recycled Activity of the Magnetic Carbon Microtube-Based Solid Acid

The recovery of the novel magnetic solid acid was quite simple with external magnets. The recycled activity was investigated (Figure 5). The results show that the novel magnetic solid acid had very high stability for the reaction, with little decrease in yield even after 10 runs. In order to confirm the acidic site leaking, the filtrate of the recycled reaction mixture was analyzed. The results show no existence of S, which confirms that no sulfonic acid groups were released during the reaction [11]. The slight decrease in acidity of the recycled catalyst further confirms the high stability of the novel solid acid. The catalytic process of the recycled catalyst was also carefully investigated. The middle yield of 31.1% was obtained after 3 h, with a yield of 32.4% for the fresh solid acid. This result further confirms the high stability and reusability of the novel magnetic solid acid [16].
A comparative study on the catalytic activities of other solid acids was carried out (Table 4). The Lewis acidic ionic liquid [Et$_3$NH]Cl-AlCl$_3$, with high activity for rapeseed oil, was not efficient for the cooking oils [21]. The cooking oil contained high FFA content, which esterificated with methanol to form the byproduct water. Water decomposed the Lewis acidic IL, which caused the low activity. H$_2$SO$_4$ had the strongest acidic sites; however, the activity was not very high. The strong acidic sites from H$_2$SO$_4$ totally dissociated, which made H$^+$ ions interact quite easily with the polar byproduct water. As a result, the biodiesel product was hydrolyzed in the late stage of the reaction, which caused relatively low yield [17]. The traditional carbon-based solid acid [4] has a very low surface area (2 m$^2$/g), which has high activity only under harsh reaction conditions (>220 °C). The activity was very low (79.6%) at 70 °C because of the low surface area and rich polar groups on the surface. The acidic sites on traditional carbon-based solid acid were quite hydrophilic, which meant that the waste oil hardly reached the active sites [11]. When the surface area increased, the catalytic activity was greatly improved [5]. For the porous solid acid (563 m$^2$/g), the yield increased to 91.3% because of the lower steric hindrance. The acid sites on the porous surface were quite accessible to the cooking oils. The novel magnetic carbon-based solid acid with the microtube structure gave the highest activity for the reaction (99%). Although the acidity of the novel solid acid was not the highest, the acidic sites on the external microtube surface were easily accessible to the reactants. The microtube surface gave hydrophobicity to the novel solid acid. The byproduct water was effectively released from the active sites, avoiding a hydrolysis reaction [16]. Therefore, the reverse reaction was restricted and high activity was obtained. The porous carbon-based solid acid with a high BET surface area of 563 m$^2$/g also showed relatively low yield (90.3%). Furthermore, the magnetic recovery increased the advantages of the novel catalyst.

### Table 4. The comparative study on other acid catalysts.

| Catalyst                        | Catalyst Usage/mg | Reaction Time/h | FFA Conversion/% | Yield/% $^{a,b}$ |
|--------------------------------|-------------------|-----------------|-----------------|-----------------|
| Novel magnetic solid acid      | 40                | 9               | 98.7            | 99.0            |
| Carbon-based solid acid [4]    | 50                | 12              | 83.2            | 88.7            |
| Porous carbon-based solid acid [5] | 55              | 12              | 89.5            | 90.3            |
| [Et$_3$NH]Cl-AlCl$_3$          | 60                | 24              | 86.2            | 78.8            |
| H$_2$SO$_4$                    | 70                | 18              | 88.5            | 89.7            |

$^a$ The reaction conditions: cooking oil—5 g, methanol—3.01 g, 70 °C. $^b$ The yield was calculated on GC using internal standard method.
3. Experimental

All organic chemical reagents were bought from commercial reagent companies. They were of high purity (>98%) and were used directly in the reaction without pretreatment.

3.1. Preparation of the Magnetic Carbon Microtube-Based Solid Acid

Carbonization procedure: Catkin (1.0 g) was soaked in the solution of FeCl$_3$·6H$_2$O (0.01 mol, 2.7 g) and ethanol (99%, 10 mL) for 12 h. Then, the mixture was filtered and the catkin was washed with ethanol (99%) to remove the residue of FeCl$_3$ from the external surface. The FeCl$_3$-doped catkin was carbonized in a quartz tube furnace at 400 °C for 12 h under N$_2$ atmosphere to form the magnetic carbon microtubes.

Sulfonation: Firstly, diazotization of p-sulfonilic acid was carried out [15]. P-sulfonilic acid (0.075 mol, 12.99 g) was dispersed in 750 mL of 1 M HCl. The suspension was cooled down to 3–5 °C in an ice-water bath. Then, 1 M aqueous solution of NaNO$_2$ (83 mL) was added dropwise. The mixture was stirred at the speed of 100 rpm for an additional 1 h. Benzenediazoniumsulfonate acid was obtained after filtering, washing, and drying. Benzenediazoniumsulfonate acid (6.0 g) was dissolved in the mixture of ethanol (99%, 200 mL) and water (10 mL). Then, the magnetic carbon microtubes (0.5 g) were added to the solution. The mixture was mechanically stirred (160 rpm) at 50 °C for 2 h. After magnetic separation, washing with ethanol (99%), and drying in an oven (80 °C), the magnetic carbon microtube-based solid acid was obtained. The exact synthetic flowchart is shown in Scheme 2.

3.2. Biodiesel Synthetic Procedure Using Waste Oils as Raw Material

Waste cooking oil with an acidity of 45 mgKOH/g was used as the raw material. The waste oil was provided by Shaoxing Restaurant. The waste oil was simply pretreated by dehydration under reduced pressure (110 °C, 1.33 KPa) and decolorization with active carbon. The composition of the fatty acids in free fatty acids (FFAs) and triglycerides were analyzed using total esterification with methanol according to ISO 5509:2000. The results are given in Table 5. The free fatty acid content in the waste oil was about 21 wt%. Here, 3 mol FFAs were treated as 1 mol of triglyceride when calculating the molar ratio of methanol to waste oil. The waste oil was mixed with methanol and catalyst. The mixture was stirred at 70 °C for a certain time. The reaction was traced by chromatographic (GC) analysis using a Shimadzu (GC-14C) gas chromatograph, following the method provided by Alcantara [22]. After the reactions, the catalyst was magnetically recycled and reused directly. Here, other methods, such as NMR and hydroxyl value analysis, were also compared with GC analysis, and the results show a high agreement with GC analysis, with a difference of 1%. Furthermore, the isolated biodiesel yield was obtained under optimal conditions, which fit well with the GC results. The FFAs conversion was calculated based on the acidity. The total biodiesel yield was calculated based on GC analysis using the following equation. The average molecular weights of biodiesel products and waste oil were calculated based on the FFAs composition [17].

\[
\text{Yield(\%)} = \frac{\text{weight of biodiesel produced}}{\text{Mw of biodiesel} \times \text{biodiesel conc}} \times \frac{\text{weight of oil}}{\text{Mw of oil} \times 3} \times 100
\]
Table 5. The fatty acid content in cooking oil.

| Fatty Acid                  | Palmitic Acid (C16:0) | Stearic Acid (C18:0) | Oleic Acid (C18:1) | Linolenic Acid (C18:3) | Linoleic Acid (C18:2) |
|-----------------------------|-----------------------|----------------------|--------------------|------------------------|-----------------------|
| FFAs/%                      | 27                    | 31                   | 29                 | 7                      | 6                     |
| Triglycerides/%             | 22                    | 28                   | 33                 | 7                      | 10                    |

3.3. Characterization

The thermogravimetric (TG) analysis was taken under N\textsubscript{2} atmosphere from 25 °C to 800 °C with a heating rate of 10 °C/min using a Mettler-Toledo (TGA/SDTA851\textsuperscript{\textregistered}STAR, Italy) DTA-TG instrument. The Fourier transform infrared (FT-IR) spectra were carried out on a Nicolet Nexus 670 by a pressing potassium bromide troche. The Brunauer–Emmett–Teller (BET) surface area was measured on a Micromeritics Empyrean instrument. Scanning electron microscopy (SEM) studies were carried out on a JEOLJSM-6360LV instrument. A transmission electron microscope (TEM) was used on a JEOL 2011 operating at 200 kV. Powder X-ray diffraction patterns were analyzed on a Bruker D8 Advance diffractometer fitted with a Lynx eye high-speed strip detector and Cu-Ka radiation source.

4. Conclusions

The novel magnetic carbon microtube-based solid acid was prepared from the FeCl\textsubscript{3}-doped biomass waste catkin and mild benzenediazoniumsulfonate-acid-based sulfonation. The magnetic solid acid had a special microtube structure and a high BET surface area of 215 m\textsuperscript{2}/g, which provided the easily accessible hydrophobic active sites. The magnetic property was added to ensure recovery simplicity. The novel solid acid showed much higher activity than the traditional carbon-based solid acids and H\textsubscript{2}SO\textsubscript{4} for biodiesel synthesis from cooking oil. The optimal reaction condition for biodiesel synthesis from waste oil was obtained. Furthermore, 5 g of waste oil, 3.01 g of methanol, and 0.04 g of catalyst were mixed and stirred at 70 °C for 9 h, which gave a high total yield of 99%. High activity, stability, and reusability were the key characteristics of the novel magnetic carbon microtube-based solid acid.

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References
1. Anastas, P.; Kirchhoff, M.M. Origins, Current Status, and Future Challenges of Green Chemistry. *Accounts Chem. Res.* 2002, 35, 686–694. [CrossRef] [PubMed]
2. Clark, J.H. Solid Acids for Green Chemistry. *Accounts Chem. Res.* 2002, 35, 791–797. [CrossRef] [PubMed]
3. Toda, M.; Takagaki, A.; Okamura, M.; Kondo, J.; Hayashi, S.; Domen, K.; Har and M. Green chemistry: Biodiesel made with sugar catalyst. *Nature* 2005, 438, 178. [CrossRef]
4. Okamura, M.; Takagaki, A.; Toda, M.; Kondo, J.N.; Domen, K.; Tatsumi, T.; Har and M.; Hayashi, S. Acid-Catalyzed Reactions on Flexible Polycyclic Aromatic Carbon in Amorphous Carbon. *Chem. Mater.* 2006, 18, 3039–3045. [CrossRef]
5. Nakajima, K.; Okamura, M.; Kondo, J.N.; Domen, K.; Tatsumi, T.; Har and S.; Hayashi, M. Amorphous Carbon Bearing Sulfonic Acid Groups in Mesoporous Silica as a Selective Catalyst. *Chem. Mater.* 2009, 21, 186–193. [CrossRef]
6. Yuan, S.M.; Li, J.X.; Yang, L.T.; Su, L.W.; Liu, L.; Zhou, Z. Preparation and Lithium Storage Performances of Mesoporous Fe\textsubscript{3}O\textsubscript{4}@C Microcapsules. *ACS Appl. Mater. Interfaces* 2011, 3, 705–709. [CrossRef]
7. Gill, C.S.; Price, B.A.; Jones, C.W. Sulfonic acid-functionalized silica-coated magnetic nanoparticle catalysts. *J. Catal.* 2007, 251, 145–152. [CrossRef]
8. Jänes, A.; Kurig, H.; Lust, E. Characterisation of activated nanoporous carbon for supercapacitor electrode materials. *Carbon* 2007, 45, 1226–1233. [CrossRef]

9. Meduri, P.; Kim, J.H.; Russell, H.B. Thin-Walled Carbon Microtubes as High-Capacity and High-Rate Anodes in Lithium-Ion Batteries. *J. Phys. Chem. C* 2010, 114, 10621–10627. [CrossRef]

10. Reza, M.; Samaneh, K.; Siavash, I.; Rajender, S.V. Plant-derived nanostructures: Types and applications. *Green Chem.* 2016, 18, 20–52. [CrossRef]

11. Shi, Y.; Kevin, M.-W.; Liang, X. Facile synthesis of novel porous carbon based solid acid with microtube structure and its catalytic activities for biodiesel synthesis. *J. Environ. Chem. Eng.* 2018, 6, 6633–6640. [CrossRef]

12. Ranganatha, S.L.; Banapurmath, N.R.; Chandrashekar, T.K.; Soudagar, M.E.M.; Gul, M.; Nik-Ghazali, N.-N.; Mujtaba, M.A.; Shahapurkar, K.; Agbulut, U.; Alshershi, S.M.; et al. Effect of injection timing and duration on the performance of diesel engine fueled with port injection of oxygenated fuels. *Chem. Eng. Commun.* 2021. epub ahead of printing. [CrossRef]

13. Khan, H.; Soudagar, M.E.M.; Kumar, R.H.; Safaei, M.R.; Farooq, M.; Khidmatgar, A.; Banapurmath, N.R.; Parade, R.A.; Abbas, M.M.; Azfal, A.; et al. Effect of Nano-Graphene Oxide and n-Butanol Fuel Additives Blended with Diesel—Nigella sativa Biodiesel Fuel Emulsion on Diesel Engine Characteristics. *Symmetry* 2020, 12, 961. [CrossRef]

14. Gavhane, R.S.; Kate, A.M.; Pawar, A.; Safaei, M.R.; Soudagar, M.E.M.; Abbas, M.M.; Ali, H.M.; Banapurmath, N.R.; Goodarzi, M.; Badruddin, I.A.; et al. Effect of Zinc Oxide Nano-Additives and Soybean Biodiesel at Varying Loads and Compression Ratios on VCR Diesel Engine Characteristics. *Symmetry* 2020, 12, 1042. [CrossRef]

15. Bouchet, M.J.; Rendon, A.; Wermuth, C.G.; Goeldner, M.; Hirth, C. Aryl diazo compounds and diazonium salts as potential irreversible probes of the GABA receptor. *J. Med. Chem.* 2016, 30, 2222–2227. [CrossRef] [PubMed]

16. Li, J.; Liang, X. Magnetic solid acid catalyst for biodiesel synthesis from waste oil. *Energy Convers. Manag.* 2017, 141, 126–132. [CrossRef]

17. Shi, Y.; Liang, X. Novel carbon microtube based solid acid from pampas grass stick for biodiesel synthesis from waste oils. *J. Saudi Chem. Soc.* 2019, 23, 515–524. [CrossRef]

18. Liang, X. Novel Efficient Procedure for Biodiesel Synthesis from Waste Oils Using Solid Acidic Ionic Liquid Polymer as the Catalyst. *Ind. Eng. Chem. Res.* 2013, 52, 6894–6900. [CrossRef]

19. Shu, Q.; Gao, J.; Nawaz, Z.; Liao, Y.; Wang, D.; Wang, J. Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon-based solid acid catalyst. *Appl. Energy* 2010, 87, 2589–2596. [CrossRef]

20. Melero, J.A.; Bautista, L.; Iglesias, J.; Morales, G.; Sánchez-Vázquez, R. Zr-SBA-15 acid catalyst: Optimization of the synthesis and reaction conditions for biodiesel production from low-grade oils and fats. *Catal. Today* 2012, 195, 44–53. [CrossRef]

21. Liang, X.; Gong, G.; Wu, H.; Yang, J. Highly efficient procedure for the synthesis of biodiesel from soybean oil using chloroaluminate ionic liquid as catalyst. *Fuel* 2009, 88, 613–616. [CrossRef]

22. Alcantara, R.; Amores, J.; Canoira, L.; Fidalgo, E.; Franco, M.J.; Navarro, A. Catalytic production of biodiesel from soy-bean oil, used frying oil and tallow. *Biomass Bioenergy* 2000, 18, 515–527. [CrossRef]