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Batch to batch variation study for biodiesel production by hydrothermal carbon catalyst: preparation, characterization and its application

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Abstract

In the present study, the esterification of oleic acid with methanol was studied in batch to batch method over hydrothermal carbon catalyst (HTCC) from Ziziphus Mauritiana L.. The synthesized catalyst was characterized by FT-IR, XRD, XPS, SEM, and BET analysis. The surface area and acid density of prepared HTCC were found to be 15.97 m² g⁻¹ and 2.53 mmol g⁻¹, respectively. Statistical analysis was performed by using ANOVA, mean, standard deviation and variance method. Statistically there is no significant difference among the means of the 4 variables at the 95% confidence level and the P-value of the F-test is equal to or greater than the 0.05. The maximum oleic acid conversions from methanol were obtained up to 91%. Furthermore, reusability and regeneration study were also carried out to assess catalytic performance. The study reveals that HTCC obtained from Ziziphus Mauritiana L. is an excellent catalyst and can be used for esterification of oleic acid to produce biodiesel.

1. Introduction

Biodiesel is an alternate form of fuel like conventional or fossil fuel. It can be prepared from animal fat, waste vegetable oil and/or residual oil by transesterification [1, 2]. The demand for biodiesel is continuously increasing due to the contamination, increased price and limited lifetime of fossil fuel. Moreover, biodiesel is widely and extensively accepted in modern era due to its excellent characteristics, i.e. biodegradability, renewability, non-toxic nature and high flash point [3, 4]. Biodiesel is obtained through transesterification process which is a simple process for conversion of fats and oils into respective esters. However, there are few factors affecting the transesterification process, for example; humidity, reaction temperature, mixing speed, type of catalyst, type of alcohol, reaction time and alcohol: oil molar ratio [5–8]. In the transesterification reaction, three types of catalysts are generally used, i.e. homogeneous or heterogeneous catalysts and biocatalysts [9]. Likewise, NaOH or KOH or sulfuric acid is used for the preparation of biodiesel as homogeneous catalyst [8]. Nonetheless, homogeneous catalysts have many limitations such as equipment corrosion and handling of the waste product obtained after the neutralization. Consequently, solid and reusable heterogeneous catalysts are widely employed to replace and overcome the difficulties related to homogeneous catalysts [10, 11]. Thus besides the reusability, heterogeneous catalysts have attracted much attention due to their green catalytic processes with benefits of no pollutants and easy separation. Many articles could be found in the literature and a series of heterogeneous catalysts have been reported, such as metal oxides (e.g. A1₂O₃), metal sulfides (e.g. CdS), zeolite molecular sieves (e.g. H-ZSM-five), heteropoly acids (e.g. H₅PW₁₂O₄₀), immobilized liquid acids (e.g. HF/AlCl₃), nanomaterial-based catalysts [12] cation exchange resins (e.g. Nafion-H), natural clay (e.g. bentonite) and strong super acid such as sulfated zirconia [13–15]. In fact, none of the above heterogeneous catalysts is ideal for all types of acid-catalyzed reactions. For example, studies dealing with the use of solid acid catalysts for biodiesel synthesis; it was observed that reaction rates were limited and few byproducts were also formed [16, 17]. Nevertheless, solid acid
catalysts are generally characterized by low acid density and strength. Thus, research in this field has focused on engineering catalysts with better acid density and strength as well as chemical stability. In recent years, carbon-based sulfonated catalysts (CBSCs) have been the focus of intense research activity. Subsequently, sulfonated carbon-based solid acids were reported to be efficient heterogeneous catalysts for many acid-catalyzed reactions [18, 19]. These heterogeneous catalysts are generally prepared through carbonization followed by sulfonation reaction using renewable biomass resources as carbon sources [20, 21]. They have shown good catalytic activity, particularly in acid catalyzed reactions such as esterification (e.g. biodiesel production) [22–24] and hydrolysis of cellulose [25–27].

In this work, we report the preparation of low-cost hydrothermal carbon catalyst (HTCC) from Ziziphus Mauritiana L. biomass by simple protocol and investigate its analytical applicability as a solid catalyst for biodiesel production, Ziziphus Mauritiana L. is generally known as ber in Pakistan and India. It is widely distributed in the tropical and subtropical regions of the world. It belongs to the Rhamnaceae family [28]. The pericarp of its fruit is consumed either fresh or dried, while its seeds are usually discarded as waste. Thus, the esterification of oleic acid with methanol was studied in batch to batch study over HTCC. The FT-IR results of HTCC confirm that catalyst has –SO3H and –COOH sites, which are responsible for the catalysis process. The statistical analysis also proves its high catalytic efficiency. The reproducibility, mesoporosity, surface area, acidic density and convenient synthesis protocol make the HTCC more efficient catalyst for the esterification of fatty acids to produce biodiesel.

2. Materials and methods

All the chemicals barium nitrate, sodium chloride, sodium hydroxide, methanol, oleic acid, and concentrated sulfuric acid were HPLC grade or AR grade and used directly as purchased.

2.1. Preparation of Hydrothermal Carbon Catalyst (HTCC1-HTCC4) from Ziziphus Mauritiana L.

Biomass was converted to solid carbonized material by hydrothermal carbonization of Ziziphus Mauritiana L. using a method described elsewhere [29]. The biomass of Ziziphus Mauritiana L. was collected from four different areas of Sindh to check the reliability of the catalyst. In a typical synthesis, 15 g of fresh Ziziphus Mauritiana L. (jujube) pulp were transferred in four 23 ml stainless steel Teflon-lined autoclaves and heated at 180 °C for 5 h. Finally, the solid products were washed separately with distilled water to get a neutral pH then dried at room temperature. The prepared four different HTCs were named as HTC1, HTC2, HTC3 and HTC4 and stored in glass bottles. The sulfonation of HTCs was carried out by refluxing 1.0 g of HTC in 10 ml of conc. H2SO4 in a round bottom flask at 150 °C for 15 h. The cold water was added after the sulfonation in the reaction mixture and through vacuum filtration, the black-brown product was collected. The resulting solid product was washed thoroughly with warm deionized (DI) water until the precipitates of barium sulfate were not formed when treated with 1 N barium nitrate. The prepared four different catalysts were named as HTCC1, HTCC2, HTCC3 and HTCC4 and stored in glass bottles for subsequent characterization and catalytic performance evaluation.

2.2. Acid density analysis

The total acid density of the catalysts was determined as follows: 0.05 g of HTCC was placed in 50 ml conical flask, and 15 ml of 2 M NaCl aqueous solution was added. The suspension was sonicated in ultrasound sonicator for 30 min. The solid was then filtered and the filtrate was titrated with 0.02 M aqueous NaOH solution using phenolphthalein as an indicator. The acid concentration was calculated as follows:

\[ C \text{ (H}^+\text{)} = C\text{(OH}^-\text{)} \times \Delta V/m \]

where \( V \) is the volume of titrant, ‘m’ mass of catalyst and OH\(^-\) indicates the concentration of NaOH.

2.3. Catalyst characterization

FT-IR (Thermo Scientific Nicolet TM iS10), was used to determined different surface functional groups of developed catalysts at room temperature and equipped with Diamond crystal, the spectra were recorded form a wave number of 500–4000 cm\(^{-1}\). Bruker-D2 phaser diffractometer was used to performed PXRD analysis, the operative voltage was set at 30 kV and current of 10 mA with Cu K\(\alpha\) radiation (\(\lambda = 1.5418 \AA\)), BET was used to determine the specific surface area and the pore volume of synthesized material by using (Autosorb-1 Quantachrome, ASiQwin). Before measurement, the degassing temperature for the sample was set at 150 °C for 20 h. Scanning electron microscopy (SEM) JSM-6491 LV, Joel, Japan, was used to study the morphology of synthesized HCT and HTCCs.
2.4. Catalytic activity analysis in batch method by FTIR

Esterification reaction in batch laboratory-scale setup: the experiment was designed sequentially in various batches by taking 50 ml of round bottom flask equipped with four different reflux condensers in a continuous manner and were placed in hotplates with a magnetic stirrer. The reaction was carried out at 65 °C with 150 rpm. The reaction mixture of oleic acid and methanol (1 ml: 10 ml) was initially heated until it reaches to the required temperature then about 0.1 g of catalysts which were prepared from different sources was raped in filter paper and added in each conical flask. Now, from the prepared mixture of the reaction, we have taken about (100 μL) of the sample after each hour. The samples were then purged with nitrogen to remove residual methanol and finally analyzed by ATR. Two absorbance bands (1710 cm⁻¹ and 1742 cm⁻¹) were used to monitor the progress of the esterification reaction. The peak at 1710 cm⁻¹ represents the carbonyl stretching frequency for oleic acid, and the peak at 1742 cm⁻¹ is due to the stretching frequency for the fatty acid methyl ester. The conversion of oleic acid into methyl esters was calculated by the following equation:

\[
\% \text{Yield} = \frac{A_i - A_f}{A_i} \times 100
\]

where as \(A_i\) is the initial concentration of Oleic acid and \(A_f\) is the final concentration of oleic acid.

3. Results and discussion

3.1. Structure and composition

The carbonization of Ziziphus Mauritiana L. biomass leads to 28% of HTC (conversion of wet biomass to solid hydrochar) and 84% yield of HTCC after sulfonation of HTC with conc. H₂SO₄. The different analytical techniques were used to characterize the prepared HTCC.

FT-IR spectroscopy was used to investigate the functional groups in Ziziphus Mauritiana L. biomass (dried pulp), HTC and HTCC which are shown in figures 1(a)–(c). In the spectrum of Ziziphus Mauritiana L. (figure 1(a)) the band observed at 3295.46 cm⁻¹ indicates the presence of O–H functional group. The band’s intensity decreases in the spectra of HTC and HTCC (figures 1(b) and (c)) due to the formation of hydrothermal carbon. The band observed at 2920.89 cm⁻¹ in the spectrum of Ziziphus Mauritiana L. corresponds to C–H stretching vibration in hemicellulose. This band completely disappears in HTC and HTCC indicating decomposition of hemicellulose [30]. The band at 1708.01 cm⁻¹ and 1598.02 cm⁻¹ could be assigned to C=C stretching of aromatic rings or the bending mode of adsorbed water. Only the biomass shows this band meaning that it is more hydrophilic than the HTC and HTCC. Aromatic rings are also observed in the spectra of HTC and HTCC [31]. The band at 1241.29 cm⁻¹ shows the presence of the CH₃ stretching in biomass but disappear in HTC and HTCC.

The bands at 1161.02 cm⁻¹ could be assigned to S=O double bond stretching vibration for CC–SO₃H in the spectrum of a sulfonated catalyst (HTCC-1 in this case) [32]. The band at 1027.25 cm⁻¹ is assigned to the vibration of C–O in hydroxyl group (C–O–H). FTIR spectra show that there are plentiful of oxygen-containing groups such as phenolic, hydroxyl, ether, carbonyl or carboxyl and sulphonic groups in these samples.
Table 1. Elemental analysis and BET surface area of HTC and HTCC.

| Sample | % C   | % H     | % N     | % S     | H/C   | O/C   | Surface area (m²/g) | Pore volume (c.c./g) | Pore diameter (nm) |
|--------|-------|---------|---------|---------|-------|-------|---------------------|---------------------|-------------------|
| HTC    | 63.42 | 5.49    | 1.06    | 0       | 30.03 | 0.086 | 0.473               | 4.716               | 0.014             | 3.410             |
| HTCC   | 47.13 | 3.98    | 0.72    | 5.46    | 42.71 | 0.081 | 0.889               | 15.978              | 0.020             | 9.564             |

Table 2. Comparison study of acid density with other carbon catalyst.

| S.No | Carbon catalyst          | Acid density (mmol g⁻¹) | % Yield | References |
|------|--------------------------|-------------------------|---------|------------|
| 1.   | Blank                    | —                       | 4.2     | [37]       |
| 2.   | H₂SO₄                    | 20.40                   | 71.3    | [37]       |
| 3.   | D-Glucose-derived catalyst | 1.60                  | 76.3    | [38]       |
| 4.   | Sucrose-derived catalyst  | 1.71                    | 84.4    | [38]       |
| 5.   | Cellulose-derived catalyst | 1.82                | 94.9    | [38]       |
| 6.   | Starch-derived catalyst   | 1.97                    | 86.6    | [38]       |
| 7.   | Sulphated zirconia       | 0.4                     | 80.5    | [39]       |
| 8.   | Niobic acid              | 0.3                     | 76.3    | [39]       |
| 9.   | Amberlyst-15             | 4.9                     | 58.2    | [40]       |
| 10.  | HTCC                     | 2.53                    | 91      | This work  |

Table 1 shows the results of elemental analysis of prepared HTC and HTCC material that confirms the presence of high contents of carbon and oxygen in HTC while HTCC indicates the presence of sulfur content and high content of oxygen. After sulfonation, the ratio between O/C ratios becomes increased while the H/C remained constant. It is reported that in the tough sulfonation environment more aromatic acid groups produced on the surface of carbonized material due to the incomplete oxidation of carbon [33, 34]. Furthermore, during the sulfonation process, some C–C bonding among the aromatic rings were removed which is present in the carbonized material structure [35].

By using the back titration method the total acid density of all acidic groups such as sulfonic, phenolic, and carboxylic groups in each catalyst was measured [36]. The total acid density of HTCC was also compared with other prepared materials as shown in table 2.

3.2. Textural characterization

The XRD diffraction pattern of HTC and HTCC shows two weak and broad diffraction peaks at 2θ = 20.086° and 2θ = 40.124°, 2θ = 22.463° and 2θ = 42.237° respectively as shown in figures 2(a) and (b). The broad diffraction pattern of HTC and HTCC at 2θ = 22.086° and 2θ = 23.463° confirms the amorphous structure of the carbon and for the catalytic activity amorphous nature of the carbon was important [41, 42]. The XRD diffraction peaks of HTC and HTCC are almost the same and have no observable difference except the latter angle was shifted to the right by a small amount. The process of introducing the sulfonic acid group (–SO₃H) on the surface of the HTC stimulated the additional conversion of the carbon structure [43].

SEM micrographs of HTC and HTCC are given in figure 3. Particularly the SEM analysis has been used to estimate the structural differences in carbonized and sulfonated materials. The physical structure would be useful to obtain accurate detail about the morphological structure of HTC and HTCC during the carbonization and sulfonation process. The surface of the HTC and HTCC was rough and porous and some globular agglomerated particles are seen in both images but in figure 3(a) the un-carbonized surface is also seen which tell us that the biomass is not completely carbonized in hydrothermal process whereas in figure 3(b) the almost all material was converted into the catalyst in sulfonation process and the size of particles was nearly same in HTC and HTCC which show that sulfonation does not alter the characteristics of the particles.

3.3. Surface area and porosity measurements

The physical properties such as surface morphology and surface area of Ziziphus Mauritiana L. explain that the sample structure was changed after carbonization and sulfonation [43]. The nitrogen adsorption–desorption isotherm of HTC and HTCC belongs type III of IUPAC classification which associated with the mesoporous structure and indicates the unrestricted multilayer formation [44] as shown in figure 4. The hysteresis loop of type III isotherms is H3 which associated with aggregates of plate-like particles forming slit-like pores [45].

Due to the removal of C–C attachment between the amorphous structures of HTC showed a very low surface area and negligible pore volume at 2.716 m² g⁻¹ and 0.014 c.c./g, whereas HTCC showed a small increase surface area and pore volume at about 7.978 m² g⁻¹ and 0.020 c.c./g [31, 39, 46]. The BJH method was used to...
Figure 2. XRD Spectra of HTC (a) and HTCC (b).

Figure 3. SEM images of HTC (a) and HTCC (b).

Figure 4. Nitrogen adsorption-desorption isotherms and Pore diameter for HTC and HTCC.
obtain the pore size distribution curve of HTC and HTCC. The pore volume and pore size of the prepared HTC and HTCC has the narrow distribution curves with a significant range less than 20 nm as shown in figure 4. The prepared HTCC confirms the mesoporous structure of the catalyst due to the less size range and pore volume. Table 1 represents the BET surface area, average pore size, and total pore volume of HTC and HTCC.

3.4. Esterification reaction of oleic acid with methanol over HTCC
The esterification reaction of oleic acid with methanol was used for biodiesel production over HTCC. The effects of the preparation variables on the esterification reaction of HTCC such as temperature, methanol to oleic acid molar ratio, catalyst loading and reaction time were studied as shown in table 3. The optimized parameters of methanol to oleic acid molar ratio of 1:10, catalyst loading of 10 wt% and the time of 5 h the maximum conversion yield of biodiesel increases from 59% to 91.5% as the temperature was increases from 40 to 70 °C due to the motion of molecules and the rate of mass transfer increases, as shown in table 3(a). When the reaction temperature increased to 70 °C, the yield of biodiesel decreased to 90%. Because a large number of bubbles are formed when the reaction temperature rises above the boiling point of the methanol as a result, the reaction yield was decreased. Therefore, it is conclude that the optimal reaction temperature was 65 °C. The effect of the methanol to oleic acid molar ratio from 5:1 to 20:1 was studied under the reaction conditions of 65 °C, 10 wt% catalyst, and 5 h as shown in table 3(b). The yield was increases as the methanol to oleic acid molar ratio was increases from 72.8 to 91.2% but the yield was decreases when the methanol to oil molar ratio was increases from 10:1 to 20:1. The reason behind them is that when an excess amount of methanol was used then unnecessary methanol molecules adsorbed on the catalyst surface and hindered the formation of methyl oleate [47]. Hence in this reaction the optimum methanol to oleic acid molar ratio was 10:1. The effect of catalyst loading from 5 wt% – 25 wt% was studied under the optimum reaction conditions of temperature 65 °C, 10:1 of methanol to oleic acid molar ratio and time of 5 h, the effect of catalyst loading was shown in table 3(c). The conversion of oleic acid into methyl oleate yield was increases as the catalyst loading increases within 10 wt% and the maximum conversion yield was about 92.5%. When the amount of catalyst increases from 10 wt% to 25 wt% the yield was decreases. So, it can be concluded that the optimum value of catalyst loading was about 10%. The effect of reaction time was also studied from 1 h to 12 h under the optimum reaction condition of temperature

| Table 3. Optimized factors for esterification of oleic acid via HTCC. |
|---|---|---|---|---|
| Temperature | Methanol: Oil | Catalyst loading (wt%) | Time (hrs.) | Conversion yield (%) |
| (A) | | | | |
| 40 | 10 | 10 | 5 | 59 |
| 45 | 10 | 10 | 5 | 61 |
| 50 | 10 | 10 | 5 | 67 |
| 55 | 10 | 10 | 5 | 71 |
| 60 | 10 | 10 | 5 | 82 |
| 65 | 10 | 10 | 5 | 91.5 |
| 70 | 10 | 10 | 5 | 90 |
| (B) | 65 | 5 | 10 | 5 | 72 |
| 65 | 10 | 5 | 5 | 92 |
| 65 | 15 | 5 | 5 | 87 |
| 65 | 20 | 5 | 5 | 76 |
| (C) | 65 | 10 | 5 | 5 | 86.4 |
| 65 | 10 | 10 | 5 | 92.5 |
| 65 | 10 | 15 | 5 | 84.7 |
| 65 | 10 | 20 | 5 | 81.2 |
| 65 | 10 | 25 | 5 | 79.7 |
| (D) | 65 | 10 | 10 | 1 | 36 |
| 65 | 10 | 10 | 2 | 49 |
| 65 | 10 | 10 | 3 | 57 |
| 65 | 10 | 10 | 4 | 71 |
| 65 | 10 | 10 | 5 | 87 |
| 65 | 10 | 10 | 6 | 92.6 |
| 65 | 10 | 10 | 7 | 91 |
| 65 | 10 | 10 | 12 | 90 |
| 65 | 10 | 0 | 6 | 5.2* |

*Blank performance test on esterification reaction.
65 °C, 10:1 of methanol to oleic acid molar ratio and catalyst amount was 10 wt% as shown in table 3(d). The conversion of oleic acid into methyl oleate was gradually increased from 36.9% to 91.2% by increasing the reaction time from 1 h to 12 h. The reaction reached near-equilibrium at 6 h and as the reaction time continued the oleic acid conversion remained unchanged. So, the appropriate reaction time was found to be 6 h. It is of particular interest to compare the catalytic activities of the hydrothermal carbon catalyst with blank and the conversion of oleic acid into methyl oleate was approximately 5.2% as shown in table 3. So it is concluded that the maximum conversion yield was about 92.5% under the optimized parameters for the esterification reaction of oleic acid were a reaction temperature of 65 °C, methanol to oleic acid molar ratio of 10:1, 10 wt% catalyst, and reaction time of 6 h.

3.5. Batch to batch variation study
The batch to batch variation studies of prepared HTCC was demonstrated through the esterification reaction of fatty acids with methanol. The catalysts (HTCC-1 to HTCC-4) prepared from various sources have applied in different batches. The results show that all catalysts have the same efficiency and give similar yield, i.e. about 90% after 6 h. Standard deviations and the mean of all measurements were calculated to test the variation in the catalytic activity of the samples and reliability of the results at different time intervals as shown in table 3.

Table 4 shows the comparison between the catalytic activities of the catalysts (HTCC1-HTCC4) prepared from various sources. The data show the standard deviation can measure the catalytic activity of the prepared catalyst by dividing the pooled standard deviation of samples with the square root of the number of observed values at each step.

ANOVA was also applied for statistical analysis, whereas table 5. Splits the variance of the data into two components: (i) between-group component and (ii) within-group component. The ratio of the between-group component to within-group component is the F-ratio which is equal to 2.36. Statistically there is no significant difference among the means of the 4 variables at the 95% confidence level and the P-value of the F-test is equal to or greater than the 0.05.

3.6. Reusability of the hydrothermal carbon catalyst
Usually, the reusability of the HTCC has a great influence on the production cost which is separated from the catalytic properties. The same catalyst was reused four times under optimal reaction conditions to determine the reusability of the HTCC. The catalyst was collected, washed with water and methanol after each use. The figure 5 shows the results of the recycled catalyst in which the optimum reaction conditions were: methanol/oleic acid molar ratio 10:1, catalyst loading 0.1 g (10%), reaction temperature 65 °C and reaction time 6 h. In the first run, the catalyst exhibits the good catalytic activity with a maximum yield of 91%. The catalyst can be reused 4 times after that the yield decreased gradually from 83%–54% afterwards four runs. The active sites (sulfonated groups) on the HTCC was leached out and the total acid density was decreases which cases the deactivation of the catalyst [48]. Though, it is concluded that reusability of the hydrothermal carbon catalysts was remained almost constant and relatively high the after 4 runs. After that, the catalyst was regenerated initially by 0.1 N and 1 N sulfuric acid and observed yield was found to be about 75.8%–87.6%. The regeneration of the catalyst was repeatedly done with conc. sulfuric acid and the obtained yield was observed to be about 90%.
4. Conclusion

The esterification reaction of oleic acid was performed by batch to batch method via HTCC and the maximum yield obtained is about 91% within 6 h. The HTCC was characterized by different analytical techniques such as FT-IR, XRD, SEM, XPS and BET. The prepared HTCC shows high surface area and acid density. Batch-to-batch variation study was also performed to check the reliability of the catalyst. The results show that all catalysts have the more or less the same efficiency and give similar yield, i.e. about 90% after 6 h. Statistical analysis was performed by using ANOVA, mean, standard deviation and variance method. Statistically there is no significant difference among the means of the 4 variables at the 95% confidence level and the P-value of the F-test is equal to or greater than the 0.05. The HTCC also exhibited the good reusability after 4 runs the small decrease in catalytic efficiency from 91%–65% then catalyst can be regenerated by treating with sulfuric acid. So, the prepared catalyst is non-corrosive, reusable and again regenerated and has the possibility to be used in industries for the production of biodiesel.

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Conflict of Interest

Authors declare ‘No Conflict of Interest’.

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