Valorization of Lignocellulosic Wastes for Solid Acid Catalyst Production and Its Application in Biodiesel Production from Algal Oil

Benan İnan¹, Anıl Tevfik Koçer¹, Didem Özçimen¹

Abstract

Today, the use of solid acid catalysts (SACs) in biodiesel production process is considered as a sustainable and cost effective approach. SACs are reusable products that can be easily recovered after the reaction. Since they are not consumed in the process, they increase the biodiesel yield, and allows easy separation of the final products. Recently, carbon-based SACs have come into prominence among different types of SACs in biodiesel production. They can be derived from a variety of carbon precursors, including waste biomass, at low cost. Reuse of abundant waste biomass, which is generally dumped or burnt, for SACs preparation helps in solid waste management and minimizes the possible greenhouse gas emissions. Since algal biodiesel production is not so economical and needs to be improve, using SACs produced from waste biomass can be promising for making the process more cost effective. In this study, walnut shell and olive stone were utilized to produce biochar based solid acid catalyst, and produced catalysts were used for biodiesel production from algal oil. According to the obtained results, it was found that lignocellulosic wastes can be valorized not only as biochar also as solid acid catalyst and provide a cost-effective biodiesel production.

Keywords: Solid acid catalyst, waste biomass, biochar, algae, biodiesel

1. INTRODUCTION

Algae have come into prominence over the last two decade as third generation biofuel feedstock with their appropriate structural properties and high production capacity [1]. They are photosynthetic organisms which can use solar energy to fix carbon dioxide in the atmosphere and produce glucose as a main product, then convert it to other important components such as lipids. However, despite of their great potential, obtaining algal biofuels and other products requires more energy and input and their production processes are quite expensive. In order to overcome production cost, researchers are investigating cost effective downstream processes or reusable materials to use in algal biofuel production [2], [3]. In recent years, researchers evaluate the heterogeneous solid acid catalyst which was produced via sulfonation of biochar, in biodiesel production. Biodiesel is a biofuel obtained after transesterification of raw materials such as vegetable oils, waste frying oils, and algal oils, using homogenous or heterogeneous catalysts and monohydric alcohols [4]. Heterogeneous catalysis using a solid base catalyst for the transesterification shows similar properties as the homogeneous base

Corresponding author: Yildiz Technical University Department of Bioengineering, 34220, Esenler/Istanbul
benaninan@gmail.com
catalysis such as mild operating conditions, a fast rate of reaction and a high conversion. However, heterogeneous base catalysis has a significant advantage over the traditional homogeneous base catalysis. The heterogeneous nature of the reaction means that no separation is required and that the catalyst has the potential to be reused multiple times. Heterogeneous acid catalysis is a promising alternative to conventional biodiesel production due to the simplistic and environmentally friendly nature of the process [5].

Biochar is a solid product having high carbon content and obtained by thermal decomposition of organic material subjected to low temperature (<700 °C), in the absence of air [2], [6]. Various organic materials can be used for biochar production, such as woody material, algae, grasses, corn stover, straw, peanut shells, sorghum, olive pits, bark, and sewage wastes. Although being a solid biofuel, biochar has many application areas such as environmental and agricultural practices such as soil amendment and water contaminant removal [7]. Biochar can be also utilized as catalyst for certain catalytic reactions such as transesterification and hydrolysis which require strong acid sites. To carry out the process, biochar is sulfonated using a general procedure for liquid sulfonation via the addition of concentrated H₂SO₄ (> 95%) to biochar. The mixture is stirred at temperatures between 90 and 150 °C followed by washing until the solution is neutral without sulfate ion and then dried [7]–[9]. Instead of traditional liquid acid catalysts such as H₂SO₄ which may cause corrosion of facilities and increase difficulty for subsequent treatment and recycling, economical solid catalysts, allowing easy separation from the reaction system with good performance, are highly desirable [10].

In this study, common lignocellulosic wastes from Turkey were valorized for solid acid catalyst production, and then utilized in biodiesel production from algal oil. In this context, olive stone and walnut shell were chosen for solid acid catalyst production and biodiesel production using solid acid catalyst were investigated statistically.

2. MATERIALS AND METHODS

2.1. Materials

In the experimental work, olive stones and walnut shells were used as raw materials for solid acid catalyst production. Microalgae oil was used as a feedstock for biodiesel production. All the chemicals used for catalyst production, biodiesel production and analytical measurements were supplied from Merck, Germany.

2.2. Carbonization Process

Olive stones and walnut shells were dried in an oven at the temperature of 100°C for 24 h. After drying process, biomass was stored in air-tight container. The carbonization experiments were performed in “Protherm” model split type reactor which is a horizontal flow pipe type reactor with an inner diameter of 10 cm. Experiments were carried out under temperature of 500°C and 600°C, heating rate of 20°C/min, and nitrogen gas flow of 300 ml/min conditions. Before the carbonization process, raw materials were weighed and then samples were loaded in a porcelain crucible placed into the reactor. Before heating, the system was swept with nitrogen gas for 15 min to provide an inert media and nitrogen gas was continuously supplied during carbonization. When the temperature of the inside of reactor reached the final temperature, reactor was kept at the final temperature for 10 min and after that, reactor was allowed to cool. At the end of carbonization, samples were collected from the system and weighed on analytical balance to calculate the yield of biochar. FTIR and proximate analysis of biochar were carried out for characterization of biochar. Proximate analyses of the materials were conducted using the thermogravimetric analyser (TA Instrument, SDT Q600). Moisture, volatile, fixed carbon and ash contents were determined according to the Garcia et al. [11].

2.3. Preparation and Characterization of Acidic Biochar

Biochar obtained from carbonization process were subjected to sulfonation by applying sulfuric acid to the biochars. Sulfonation was performed by subjecting 1 gr of biochar with 10 ml of 98% purity sulfuric acid. The mixture was heated at the temperature of 100°C for 5 h. Then, mixture was cooled to room temperature and washed with hot deionized water to remove the free sulfate ions. Washing was carried out until the pH of the filtrate becomes 7.

FTIR was used to detect the functional groups on the surface of sulfonated biochar and absorbance values of functional groups were recorded at between 4000 and 500 cm⁻¹ for both biochar and sulfonated biochar. Sulfonic acid density was determined using the titration method described by [12] (Fig 1). The catalyst which have highest acid density was utilized as a catalyst for the biodiesel production from algal oil.
2.4. Biodiesel Production from Algal Oil

Experiments were performed using the solid acid catalyst with the amount of catalyst varying from 1% and 5% and having methanol: oil ratio ranging from 6:1 to 12:1 at the temperature of 65 °C for 30-60 min using an ultrasound bath. An ice bath was used to cool the product that composed of methyl ester-glycerine mixture obtained at the end of the reaction. After the cooling, centrifugation was performed at 5000 rpm for 5 minutes and created two phases as bottom and supernatant. Glycerin, soap, methanol and impurities were separated from the product as bottom phase and methyl ester product was separated as supernatant. The yield of methyl esters was calculated on the basis of the amount of methyl esters obtained and the amount of oil used, and was estimated using Eq. (1) [13].

\[
\text{Methyl ester yield (\%)} = \frac{\text{Mass of methyl ester produced (g)}}{\text{Mass of oil used (g)}} \times 100
\]  

(1)

3. RESULTS AND DISCUSSION

3.1. Characterization of Biochar and Acidic Biochar

Biochar production yield and proximate analysis of olive stone and walnut shells biochar were given in the Table 1. As can be seen from the results of the Table 1, it can be said that, increasing temperature decreased the biochar yield. This was expected result because secondary decompositions which starts in high carbonization temperatures and therefore solid product yield decreases. In literature studies about biochar production of olive stone [6], apricot stone, hazelnut shell, grapeseed and chestnut shell [14], hybrid poplar [15] also show that biochar yield is decreased by temperature increasing and our results were consistent with the results of these studies. According to proximate analysis results, after carbonization process, a decrease in volatile substance content and an increase in fixed carbon content were observed. The volatile substance content in solid products after the carbonization process indicates that the thermal decomposition in the carbonization process does not occur completely [6]. In the case of ash content, it was seen that after carbonization process there is an increase in ash content. Ash content is a measure of non-volatile and inflammable substance of biochar. Increase in ash content occurred due to removing volatile compounds after carbonization. Results obtained from this analysis are in agreement with literature studies [6].

Table 1. Biochar yield and proximate analysis of olive stone and walnut shell

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
<th>Moisture (%)</th>
<th>Volatile (%)</th>
<th>Ash (%)</th>
<th>Fixed carbon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olive stone</td>
<td>500</td>
<td>30.3</td>
<td>4.26</td>
<td>20.12</td>
<td>3.26</td>
<td>72.36</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>28.8</td>
<td>2.54</td>
<td>10.57</td>
<td>4.26</td>
<td>82.63</td>
</tr>
<tr>
<td>Walnut shell</td>
<td>500</td>
<td>30.2</td>
<td>6.64</td>
<td>35.94</td>
<td>2.58</td>
<td>54.84</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>29.5</td>
<td>4.2</td>
<td>22.24</td>
<td>3.78</td>
<td>69.78</td>
</tr>
</tbody>
</table>

Table 2. Sulfonic acid density of olive stone and walnut shell biochars

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Sulfonic density of biochar (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Olive stone</td>
</tr>
<tr>
<td>500</td>
<td>0.15</td>
</tr>
<tr>
<td>600</td>
<td>0.12</td>
</tr>
</tbody>
</table>
The sulfonic acid density of biochar carbonized at different temperatures was represented in Table 2. The highest sulfonic acid density of 0.35 mmol/g was obtained for the walnut shell carbonized at 500 °C. With an increase in pyrolysis temperature, the sulfonic acid density decline was observed irrespective of the feedstock, as complete combustion and aromatization at high temperature, often results in lesser number of acidic functional groups on the surface [16]. In addition to that, high pyrolysis temperature results in increased crosslinking and enhanced degree of polymerization that might not result in formation of polycyclic aromatic sheets, to trap the sulfonic acid sites.

FTIR instrument (Bruker, Alpha) was used to determine functional groups of biochars and solid acid catalyst, absorbance values of functional groups were recorded at between 4000 and 500 cm⁻¹ for all samples. Sample of olive stone biochar and olive stone acidic catalyst and, walnut shell biochar and walnut shell acidic catalyst were shown in spectrum, respectively (Fig 2 and 3). Biochar samples of olive stone and walnut shell have similar functional groups. During the carbonization process, deformation of CH₃ and adjacent H deformation were observed. The aromatic structure of biochar causes presence of adjacent aromatic hydrogen bonds [17].
Aromatic C=C stretching at 1563 and 1565 cm\(^{-1}\) in the spectrum of biochar samples can be explained with degradation of lignin. It also indicates the presence of alkenes. Bands between 750-950 cm\(^{-1}\) indicate the presence of aromatic compounds [18]. Asymmetric and symmetric stretching of SO\(_2\) was confirmed by the presence of sharp peaks at an intensity of 1031 cm\(^{-1}\) and 1029 cm\(^{-1}\) compared to the corresponding biochar. This was also observed by Behera et al., for peanut shell acidic catalyst [19]. Ido et al. also reported that the presence of peaks at 1073 cm\(^{-1}\) and 1044 cm\(^{-1}\) in the sulfonated moringa leaves acidic catalyst corresponding to the stretching of C-O and S=O respectively [20].

### 3.2. Biodiesel Production from Algal Oil

In this step of this study, effects of different solid acid catalyst amount, methanol:oil ratio and reaction time on methyl ester yield were investigated. In ultrasound assisted process, alcohol reacts quite rapidly due to an increased mass transfer in the presence of ultrasound. Ultrasounds make methanol to cavitate and disperse as nano-droplets into the oil, form a fine emulsion of methanol in oil, so the contact surface between reagents increases dramatically and consequently accelerates the reaction rate [21]. Since walnut shell acidic biochar have higher sulfonic acid density than olive stone catalyst, was evaluated in the biodiesel production. In the Table 3, results of the experiments were presented. As can be seen that, methyl ester yield increased with the solid acid catalyst amount, methanol:oil ratio and reaction time. In this study, the highest methyl ester yield was obtained with 5\% catalyst amount, 12:1 methanol:oil ratio and 60 min reaction time. Since the larger amounts of alcohol can enhance the reaction to result in the equilibrium favorable to the FAME formation, the results from this study is in agreement with the literature. In addition to that, similar to this study, Behera et al. also reported that the highest methyl ester yield was obtained with 5\% solid acid catalyst amount [19]. Higher concentration of solid acid catalyst can result in an increase in mass transfer resistance due to an increase in viscosity of the reaction mixture, thereby declining the transesterification efficiency [22]. Results obtained from this experiment were also analyzed statistically and a regression equation (2) was obtained for this bioprocess.

\[
Y=51.88+4.63*X_1+5.87*X_2+11.63*X_3
\] (2)

The experimental variables for biodiesel production were given as below:

- \(X_1\): Methanol/oil molar ratio: 12:1 (Superior level), 6:1 (Inferior level)
- \(X_2\): Catalyst/oil ratio (wt\%): 5 (Superior level), 3 (Inferior level)
- \(X_3\): Reaction time (min): 60 (Superior level), 30 (Inferior level)

\(Y\): Methyl ester yield (%)

It can be seen from the regression equation (Eq.2) derived for this bioprocess which is given above, \(X_3\) (coefficient of reaction time) is the highest among all other variables and it can also be indicated that its effect on methyl ester yield is the strongest. Moreover, it can be seen that the alcohol/oil molar ratio and the catalyst/oil ratio also have positive influence on the methyl ester yield. The coefficient of determination for regression Eq. (2) was determined as 0.90. ANOVA values were given in the Table 4.

### Table 3. Methyl ester yields at different reaction conditions

<table>
<thead>
<tr>
<th>Experimental number</th>
<th>Methanol/oil molar ratio</th>
<th>Catalyst oil ratio (wt.%)</th>
<th>Time (min)</th>
<th>Methyl ester yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6:1</td>
<td>3</td>
<td>30</td>
<td>34%</td>
</tr>
<tr>
<td>2</td>
<td>6:1</td>
<td>5</td>
<td>60</td>
<td>52%</td>
</tr>
<tr>
<td>3</td>
<td>6:1</td>
<td>3</td>
<td>30</td>
<td>39%</td>
</tr>
<tr>
<td>4</td>
<td>6:1</td>
<td>5</td>
<td>60</td>
<td>64%</td>
</tr>
<tr>
<td>5</td>
<td>12:1</td>
<td>3</td>
<td>30</td>
<td>42%</td>
</tr>
<tr>
<td>6</td>
<td>12:1</td>
<td>3</td>
<td>60</td>
<td>56%</td>
</tr>
<tr>
<td>7</td>
<td>12:1</td>
<td>5</td>
<td>30</td>
<td>46%</td>
</tr>
<tr>
<td>8</td>
<td>12:1</td>
<td>5</td>
<td>60</td>
<td>82%</td>
</tr>
</tbody>
</table>
In this study, olive stone and walnut shell were valorized for solid acid catalyst production which have higher sulfonic acid density than olive stone catalyst, was evaluated in the biodiesel production from algal oil. Since these materials are commonly found wastes, valorization of them as biochar, activated carbon and solid acid catalyst for the usage in fuel production, water treatment or agricultural application is very important. Solid acid catalyst can reduce the biodiesel production costs as well as the environmental impacts associated with the corrosive chemicals.

REFERENCES


BIOGRAPHY

Dr. Benan İNAN was graduated from Yıldız Technical University in 2012. She finished her Ph.D study on the algal bioprocess and nanoparticle production in Yıldız Technical University, at Bioengineering Department in 2019. She is interested in the algal bioprocesses, algal biofuels, nanotechnology thermal conversion technologies, energy and environment, and biotechnological applications.

She may be contacted at benaninan@gmail.com