Research Article

Green Biodiesel Synthesis Using Waste Shells as Sustainable Catalysts with *Camelina sativa* Oil

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Waste utilization is an essential component of sustainable development and waste shells are rarely used to generate practical products and processes. Most waste shells are CaCO$_3$ rich, which are converted to CaO once calcined and can be employed as inexpensive and green catalysts for the synthesis of biodiesel. Herein, we utilized lobster and eggshells as green catalysts for the transesterification of *Camelina sativa* oil as feedstock into biodiesel. *Camelina sativa* oil is an appealing crop option as feedstock for biodiesel production because it has high tolerance of cold weather, drought, and low-quality soils and contains approximately 40% oil content. The catalysts from waste shells were characterized by X-ray powder diffraction, Fourier Transform Infrared Spectroscopy, and Scanning Electron Microscope. The product, biodiesel, was studied by $^1$H NMR and FTIR spectroscopy. The effects of methanol to oil ratio, reaction time, reaction temperature, and catalyst concentration were investigated. Optimum biodiesel yields were attained at a 12:1 (alcohol:oil) molar ratio with 1 wt.% heterogeneous catalysts in 3 hours at 65°C. The experimental results exhibited a first-order kinetics and rate constants and activation energy were calculated for the transesterification reaction at different temperatures. The fuel properties of the biodiesel produced from *Camelina sativa* oil and waste shells were compared with those of the petroleum-based diesel by using American Society for Testing and Materials (ASTM) standards.

1. Introduction

Development of alternative fuels has been widely studied because of the depletion of fossil fuels and increased concerns for environment. One of the most promising areas of renewable fuel development is the production of biodiesel. Biodiesel, which is a renewable, nontoxic, and biodegradable fuel, can be used in diesel engines without engine modifications. Biodiesel burns cleaner than conventional diesel fuel, substantially reduces carbon monoxide, hydrocarbons, particulate matter, and eliminates sulfur dioxide emissions [1]. It contributes no net carbon dioxide to the atmosphere and it reduces greenhouse gas emissions by 41% compared with diesel [2]. In addition, biodiesel has high cetane number, high flash point, and excellent lubricity and miscibility with petroleum diesel at all ratios [3].

Biodiesel, fatty acid methyl ester (FAME), is traditionally made by transesterification reaction from various types of oils and either ethanol or methanol in presence of a homogeneous catalyst [4]. Transesterification is a reversible process which requires a strong acid or a strong base. The main product of the transesterification reaction is biodiesel and glycerol is formed as a by-product. The transesterification reaction is shown in Figure 1 [5].

Most of the current biodiesel production comes from soybean as edible oil feedstock in the United States; as a result production of biodiesel competes for food. Worldwide demand for food is estimated to double within the fifty years and need for fuel is anticipated to increase even more rapidly [6]. There is a great need for biodiesel that does not cause significant environmental harm and does not compete with food supply. Biodiesel that can be produced from inedible crops on agriculturally marginal lands with minimal fertilizer, pesticide, and fossil energy inputs has potential to provide energy over the longer term [7]. *Camelina sativa* oil offers a valuable substitute for the edible oils, because *Camelina sativa* plant grows quickly in infertile grounds. *Camelina sativa* oil is high in erucic acid and glucosinolates which limits the usage as food [8]. It contains approximately 35–45% oil content and it has lower fertilizer, water, and
An initiating reagent for transesterification reaction, by mixing with methanol [16]. CaO has high basicity and low environmental impact due to its low solubility in methanol [17]. In addition, CaO is easy to handle, abundant, nontoxic, and economically feasible catalyst compared to its homogeneous counterpart, KOH. Both waste eggshell and lobster shells are composed of approximately 95% of calcium carbonate and the remaining components are magnesium carbonate, calcium phosphate, and organic matter [18, 19]. Since the shells mainly consist of CaCO₃, they decompose to CaO via calcination. Waste shells, including avian eggshells and seashells, are excellent raw materials for the preparation of the heterogeneous catalysts. For sustainable development, wastes should be recycled and reused towards the production of other goods. Over the years, it has become very costly to dispose the waste shells in landfills and the landfills are reaching their capacity. Waste shells remain largely unutilized as they are discarded wrongly. The waste shells are made up of calcium carbonate that can be used to produce heterogeneous catalysts for biodiesel synthesis. Figure 2 shows a flow diagram for transesterification process from Camelina oil and waste shells as heterogeneous catalysts.

Utilization of waste shells as catalysts will protect the environment by reducing the waste and create cost-effective biodiesel synthesis. In this paper, we utilized waste eggshells, lobster shells, and CaO as exemplary heterogeneous catalysts for the transesterification of Camelina sativa oil into biodiesel. The parameters such as methanol to oil ratio, reaction time; reaction temperature, and catalyst concentration were studied and a kinetic study was performed by using the data obtained from the optimization experiments. The study demonstrates several fundamental green principles including the use of renewable feedstocks, catalysis, and design for degradation.

2. Materials and Methods

Cold-pressed and unrefined Camelina sativa oil was obtained from Ole World Oils Company. Calcium oxide was purchased from Alfa Aesar. Waste eggshells and lobster shells were collected from college’s cafeteria and neighborhood restaurants. Anhydrous methanol was purchased from Fischer Scientific.

2.1. Catalyst Preparation. Calcium oxide was used as it was received. The eggshells and lobster shells were rinsed with tap water to remove organic materials and impurities and dried at 110°C for 2 hours. The dried waste shells were ground and calcined at 900°C in air atmosphere with a heating rate of 10°C per minute for 3 hours. All catalysts were kept in a desiccator to avoid the interaction with air. The raw and calcined samples of the shells were analyzed by X-ray powder diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscope (SEM). The XRD characterization was studied on Bruker X-Ray D-2 Phaser diffractometer over a 2θ range from 5° to 60° with a step size of 0.01° and FTIR spectroscopy was performed on Thermo Nexus 470 FTIR spectrometer. The spectra were obtained in the 500–4000 cm⁻¹ region and 32 scans were recorded.
Surface structure and the morphology of the heterogeneous catalysts were studied by Zeiss LEO Gemini 1550 Scanning Electron Microscope (SEM).

2.2. Characteristics of Camelina sativa Oil. Fatty acid composition of Camelina sativa oil, which was provided by the manufacturer, indicates 32.4%, 18.4%, 16.0%, and 15.1% as α-Linolenic Acid (18:3), Linoleic Acid (18:2), Oleic Acid (18:1), and cis-Eicosenoic Acid (20:1), respectively. The acid value of Camelina sativa oil was reported as 1.58% of free fatty acid [20]. As stated by the literature, the yield of biodiesel significantly decreases when the free fatty acid level exceeds 3% (w/w), since the soap formation inhibits the separation between the biodiesel and glycerol and decreases the yield of the final product [21]. Table 1 shows the properties of Camelina sativa oil.

2.3. Transesterification Reaction. The transesterification reaction was performed using 500 mL round bottom flask with a magnetic stirrer, thermometer, and reflux condenser. 100 mL of Camelina sativa oil was heated to 100°C for one hour to remove impurities before starting the transesterification reaction. The oil was allowed to cool down to 65°C. The reaction was carried out with a 12:1 molar ratio of methanol: oil ratio and 1% (w/w) of the chosen waste shell catalyst. Pulverized, calcined waste shell was stirred with methanol at 65°C for one hour to activate waste shell catalyst. The mixture was added to the oil and vigorously stirred at 65°C for 3 hours to ensure complete conversion of the oil into biodiesel. The waste shell catalyst was recovered through filtration and the reaction mixture transferred to separatory funnel was allowed to settle for 1 hour. The lower layer, which contains glycerol, was removed from the methyl esters. Due to the low solubility of glycerol in the esters, the separation takes place rapidly. The crude biodiesel remained in the top layer. Yellow color biodiesel was dried using anhydrous sodium sulfate. The yield of biodiesel was calculated by using the following equation:

\[
\% \text{ Yield} = \frac{\text{Weight of Biodiesel}}{\text{Weight of Camelina Oil}} \times 100.
\]

The conversion of oil to biodiesel was analyzed by \(^1\)H NMR and FTIR spectroscopies. An Eft-60 NMR spectrometer (Anasazi Instruments, Indianapolis, IN) and a Thermo Nicolet NEXUS 470 FTIR spectrometer (Thermo Scientific, Waltham, MA) were used for the analyses. The FTIR spectra of the samples were obtained in the 500–4000 cm\(^{-1}\) region after 32 scans were recorded for each sample. The quality of biodiesel product was analyzed according to American Society for Testing and Materials (ASTM) specifications designated in D-6751.

3. Results and Discussion

The percent conversions of Camelina oil with CaO, waste eggshell, and lobster shell catalysts to biodiesel are 99.1%, 97.2%, and 90.0%, for the given reaction conditions, respectively.

3.1. Catalyst Characterization

3.1.1. X-Ray Diffraction Analysis. The XRD patterns of raw and calcined lobster shell are given in Figure 3. The calcination at 900°C causes the removal of CO\(_2\) from CaCO\(_3\) in the
natural waste lobster shell and results in CaO [22]. Narrow and high intense peaks of the calcined catalyst define the well-crystallized structure of the CaO. Figure 4 shows the XRD patterns for calcined eggshell, lobster shell, and commercial CaO. The waste shell catalysts showed clear and sharp peaks which match the crystalline phase of CaO. The peaks for both calcined eggshell and lobster shell at 900°C show $2\theta$ values of 32.40, 37.50, and 54.10 which are the characteristic peaks for CaO [23].

3.1.2. FTIR Analysis. FTIR spectroscopy with Smart Diffuse Reflectance, which was used for characterization of the uncalcined (raw) and calcined lobster shells, is shown in Figure 5. KBr was used as infrared transparent matrix for characterization. The broad absorption band at around 3420 cm$^{-1}$ is most likely due to O-H vibrations in water molecules. The absorption bands of uncalcined lobster shell at 1425 cm$^{-1}$, 878 cm$^{-1}$, and 710 cm$^{-1}$ were attributed to asymmetric stretch, out-of-plane bend, and in-plane bend, respectively, of CO$_3^{2-}$ ions. The broad absorption band around 3420 cm$^{-1}$ disappears upon calcination at 900°C. Calcination causes the lobster shell to lose carbonate since CaCO$_3$ decomposes into CaO. While the intensity of CaCO$_3$ peaks decreases, a new sharp stretching band appears at 3630 cm$^{-1}$ which is corresponding to O-H stretching vibration. The peaks around 1450 cm$^{-1}$ correspond to the bending vibration of O-Ca-O group.

A detailed study about temperature effects on shells was published by Engin et al. and our results agree with the literature findings [24]. Figure 6 shows the FTIR spectra of calcined CaO, lobster, and eggshell. Both waste shells have the same absorption bands as the bands of CaO.

3.1.3. SEM Analysis. The surface morphology of uncalcined and calcined lobster shell catalysts is shown in Figure 7. The uncalcined shells display a typical layered architecture [25]. Both uncalcined and calcined shells contain various sized and shaped particles. The morphology of CaO, waste lobster, and waste eggshell calcined at 900°C is shown in Figure 8. Calcined lobster shell shows regular morphology of sphere particles with the size range from 1.20 to 5.0 μm in width. Upon calcination, the microstructures of the shells are changed from layered architecture to porous structure. The particle shape became more regular with smaller particles as a result of release of gaseous molecules. Calcination of the catalyst derived from the waste shells causes an increase in surface area, leading to better catalytic activity [26]. The small particles were combined together to yield agglomerates.
3.2. Analysis of Biodiesel

3.2.1. NMR Analysis. The conversion of *Camelina sativa* oil to biodiesel catalyzed by waste shells was analyzed by using $^1$H NMR spectroscopy. The spectra for starting *Camelina sativa* oil and biodiesel are shown in Figure 9. Starting oil has a 4.35 ppm signal which was lost during the transesterification reaction. The biodiesel spectra showed the characteristic peak of methoxy protons that was prominently indicated by a strong singlet at 3.68 ppm and $\alpha$-CH$_2$ protons as a triplet at 2.30 ppm. These two peaks confirm the presence of fatty acid methyl ester formation from starting oil. The other peaks were observed at 0.8 ppm due to terminal methyl protons; a strong peak at 1.3 ppm is related to the methylene protons of carbon chain, and multiplet at 2.1 ppm is due to $\beta$-carbonyl methylene protons, respectively. The peak at 5.4 ppm is solely due to olefinic protons on the carbon chain.

3.2.2. FTIR Analysis. FTIR spectroscopy was used to analyze biodiesel and the spectrum is shown in Figure 10. The most intense peak at 1745 cm$^{-1}$ is the characteristic of the ester carbonyl stretch, ester $\text{C}=\text{O}$. The absorption bands at 1248, 1198, and 1176 cm$^{-1}$ can be used to identify the methyl ester...
3.3. Effect of Parameters on Biodiesel Synthesis

3.3.1. Effect of Methanol to Camelina sativa Oil Molar Ratio on Biodiesel Yield. Methanol to oil molar ratio was varied from 6:1 to 18:1 while catalyst concentration and temperature were kept constant at 1% (w/w) and 65 °C, respectively. Figure II(a) shows the effect of methanol to oil molar ratio on biodiesel yield for CaO, eggshell, and lobster shell catalyzed transesterification reaction. While the transesterification of Camelina oil requires three moles of methanol for each mole of oil, excess methanol is required to shift the equilibrium towards the direction of biodiesel formation. The high amount of methanol promotes the formation of methoxy species which leads to higher yields. The biodiesel yield sharply increased while the molar ratio was increased from 6:1 to 12:1 and slightly decreased exceeding 12:1 methanol to oil ratio. According to literature, excess methanol inhibits the separation of glycerol since there is an increase in solubility [27]. Higher amount of glycerol drives the equilibrium back to the left and lowering the yield of biodiesel. The maximum yield was achieved at 12:1 molar ratio.

3.3.2. Effect of Reaction Time on Biodiesel Yield. The biodiesel yield was significantly affected by reaction time which was varied from 1 hour to 6 hours for experiments with three heterogeneous catalysts. During the trials, the methanol to oil molar ratio, catalyst concentration, and temperature were kept at 12:1 and 1% (w/w) and 65 °C, respectively. As shown in Figure II(b), as reaction time was increased from 1 to 3 hours, the yield increased for all catalysts. Longer reaction time may enhance the probability of contact between methanol and Camelina oil with catalysts’ basic sites which improve the biodiesel yield. The yield slightly decreased after 3 hours which may be attributed to hydrolysis of methyl esters.

3.3.3. Effect of Reaction Temperature on Biodiesel Yield. The effect of the reaction temperature on the product yield is shown in Figure II(c). Throughout the experiments, the methanol to oil molar ratio and catalyst concentration were kept at 12:1 and 1% (w/w), respectively. Reaction temperature was a significant factor in biodiesel synthesis as the yield increased significantly for all three catalysts between 25 °C and 65 °C. Addition of heterogeneous catalysts to reaction creates a triple phase system, oil-methanol-catalyst, and the interface of the triple phase probably accommodates the transesterification process [28]. Increasing reaction temperature reduces the viscosity of Camelina oil and enhances the product yield because of the inhibition of mass transfer resistance. For all catalysts, biodiesel yields were low at low temperatures. Optimum yields (99%, 97%, and 90% for CaO, eggshell, and lobster shell, resp.) were achieved when the reactions’ temperature was held at 65 °C. Further increase in temperature caused a decrease in biodiesel yield for all three catalysts which may be attributed to evaporation of methanol.

3.3.4. Effect of Catalyst Concentration on Biodiesel Yield. The yield of biodiesel was greatly dependent on the catalyst concentration. Reactions were carried out with different concentrations of catalysts, ranging from 0.25 to 2 weight%, and the results are illustrated in Figure II(d). The reactions were carried out at 65 °C for 3 hours with a methanol to oil ratio of 12:1. There was a significant increase in yield for all catalysts from 0.25% to 1.0% and optimum conversion was obtained for 1.0 wt.% catalyst concentration. Pretreating catalysts with methanol, a small amount of CaO was converted into Ca(OCH₃)₂, which acted as the initiating reagent for transesterification. The catalysts provide active basic sites that transform the methanol into methoxide...
which attacks the carbonyl carbon structure of oil. As the concentration of catalyst increases, the available active sites also increase leading to the improvement of biodiesel yield [29]. Beyond 1%, the yield was not greatly affected by catalysts’ concentration because the reaction mixture became more viscous and all active sites are loaded.

3.4. Kinetic Studies. Kinetic studies of the transesterification reaction of Camelina sativa oil were performed by lobster waste shell heterogeneous catalyst at three different temperatures, 50°C, 65°C, and 70°C, while the methanol to oil molar ratio and catalyst concentration were kept at 12:1 and 1% (w/w). As expected, decrease in temperature from 70°C to 50°C causes decrease in reaction rates. Rate expression of the reaction is shown as follows [30]:

$$\text{Rate} = -\frac{d [CS \text{ Oil}]}{dt} = k [CS \text{ Oil}] .$$

(2)
Table 2: Fuel properties of Camelina, petroleum diesel and the ASTM biodiesel standards.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Petroleum diesel</th>
<th>Camelina biodiesel</th>
<th>Biodiesel standards (ASTM D6751)</th>
<th>ASTM testing method</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity (40°C)</td>
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<td>3.1</td>
<td>1.9–6.0</td>
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<td>mm²/s</td>
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<tr>
<td>Specific gravity</td>
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<td>0.88</td>
<td>0.87–0.90</td>
<td>D287</td>
<td></td>
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<tr>
<td>Calorific value</td>
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<td>46</td>
<td></td>
<td>D240</td>
<td>MJ/kg</td>
</tr>
<tr>
<td>Pour point</td>
<td>−20</td>
<td>−10</td>
<td>−5 to 10</td>
<td>D97</td>
<td>°C</td>
</tr>
<tr>
<td>Cetane number</td>
<td>46</td>
<td>49</td>
<td>47–65</td>
<td>D613</td>
<td>min</td>
</tr>
</tbody>
</table>

Figure 12: Plot of \(\ln(1-X_{\text{FAME}})\) versus time of the transesterification reaction catalyzed by waste lobster shells.

\[
\ln [\text{CS Oil}]_0 - \ln [\text{CS Oil}]_t = k t. \tag{3}
\]

The initial concentration of Camelina oil and the concentration of Camelina oil at time, \(t\), are shown as \([\text{CS Oil}]_0\) and \([\text{CS Oil}]_t\), respectively. The fraction conversion of Camelina biodiesel, \(X_{\text{FAME}}\), can be cooperated into (3) as

\[
\frac{dX_{\text{FAME}}}{dt} = k (1 - X_{\text{FAME}}) \tag{4}
\]

and the integration of the equation becomes

\[-\ln(1 - X_{\text{FAME}}) = kt. \tag{5}\]

Figure 12 shows the graph between \(\ln(1 - X_{\text{FAME}})\) and time at the three temperatures to obtain rate constant values. The plots are linear plots at three temperatures which indicate that the transesterification reaction obeys first-order kinetics.

Arrhenius equation was utilized to calculate the activation energy and preexponential factor for the transesterification reaction of Camelina oil catalyzed by waste lobster shells.

\[
\text{Slope} = -7.52 \quad \text{Intercept} = 18.15
\]

The activation energy and preexponential factor were determined as 62.5 \(\text{kJ mol}^{-1}\) and \(7.62 \times 10^7 \text{ min}^{-1}\), respectively, by Arrhenius plot shown in Figure 13.

3.5. Fuel Properties of Camelina Biodiesel. Biodiesel was characterized for its fuel properties by ASTM D287, 445, 240, 613, and 97 methods. Table 2 shows the properties of the synthesized biodiesel and petroleum diesel. The comparison showed that most of the fuel properties of the Camelina biodiesel are quite comparable to those of ASTM petroleum diesel standards [32]. The kinematic viscosity of Camelina based biodiesel was similar to regular diesel fuel viscosity so no modifications of engine are required. The cetane number was found higher than regular diesel standards. Cetane number is a measure of a fuel’s autoignition quality characteristics. Since biodiesel is largely composed of aliphatic hydrocarbons, it usually has a higher cetane number than petroleum diesel [33]. Higher cetane number indicates more complete combustion of the fuel, better fuel efficiency, and quick ignition delay time of fuel. The pour point of Camelina biodiesel shows a good compatibility for places with cold climate.

4. Conclusion

Every year, enormous amount of waste shells are disposed of in landfills. Waste shells, such as eggshells or seashells, are rarely used to produce practical products and utilization
of the waste shells will help sustainable development. Waste shells can be utilized as economical and environmentally benign solid catalysts for the biodiesel synthesis. CaO, lobster, and eggshell catalysts were effectively employed for biodiesel synthesis from Camelina sativa oil and methanol at 60°C. The fuel properties of the biodiesel favorably match petroleum-based diesel counterparts. Biodiesel synthesis that employs waste shells and Camelina sativa oil will reduce waste disposal problem and cut the price of biodiesel, making biodiesel a viable fuel alternative compared to petroleum-derived biodiesel.

Competing Interests

The author declares that there is no competing interests regarding the publication of this paper.

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References


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