Utilization of waste seashells and *Camelina sativa* oil for biodiesel synthesis

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**ABSTRACT**

The seafood industry produces over 100 million pounds of seashell waste every year. With landfill space diminishing quickly, ways to recycle waste materials are becoming more sought for. Herein, we utilized waste mussel, clam and oyster shells as heterogeneous catalysts for the transesterification of *Camelina sativa* oil as a feedstock into biodiesel. *Camelina sativa* oil provides a reliable solution for biodiesel production because it has high tolerance of cold weather, drought, low-fertility soils and contains approximately 40% oil content. The catalysts from waste seashells were characterized by X-ray powder diffraction and Fourier transform infrared (FTIR) spectroscopy. High biodiesel yields were achieved at a 12:1 (alcohol:oil) molar ratio with 1 wt.% waste seashell catalysts in 2 h at 65°C. Biodiesel was analyzed by 1H NMR and FTIR spectroscopy and the fuel properties of the biodiesel produced from *Camelina sativa* oil and waste seashells were compared with American Society for Testing and Materials standards.

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**1. Introduction**

Mussel, clam and other seashell farming is a fast growing industry around the world and the increase in the production of shellfish generates a large amount of shell waste. Every year, the seafood industry produces over 100 million pounds of waste from shellfish and crustaceans (1). Much of the waste that is generated from the industry is simply sent to landfills and this leads to the need to burn the shells which is an environmentally costly activity. Finding ways to recycle the waste seashells is becoming more sought after. The utilization of waste materials as heterogeneous catalysts has been of recent interest in the search for sustainable processes (2). Waste shells are a calcium-rich resource that can be used to produce calcium oxide which is an excellent source of heterogeneous-based catalyst (3).

One of the ways to utilize calcium oxide as heterogeneous catalyst is in the production of biodiesel (4, 5). The pursuit of sustainable energy sources in the view of the environmental problems has resulted in increasing global support of biodiesel production as an alternative energy source. Biodiesel has been considered as the best candidate for petroleum-based diesel fuel substitution because it can be used in any compression ignition engine without modification and its superb fuel properties. Biodiesel is nontoxic, biodegradable, renewable and environmentally benign fuel (6). Moreover, biodiesel is better than petroleum-based diesel fuel in terms of sulfur content, flash point, aromatic content and cetane number (7). Biodiesel accounts for significantly less carbon emissions as compared to standard diesel, in some cases lowering the amount of emissions by more than 70% (8).

The most widely used method for the production of biodiesel is a transesterification reaction using KOH as a homogeneous catalyst, vegetable oil and methanol to produce fatty acid methyl esters (FAME) as biodiesel.
the waste seashells creates a less expensive and more environmentally friendly biodiesel production. Employment of natural calcium sources from waste shells as heterogeneous catalyst for biodiesel production is an excellent example of green chemistry.

2. Experimental section

2.1. Cold-pressed and unrefined

Camelina sativa oil was obtained from Ole World Oils Company. Waste shells were collected from the college’s cafeteria and neighborhood restaurants. Anhydrous methanol was purchased from Fischer Scientific.

2.2. Catalyst preparation

The waste seashells were washed thoroughly to remove any organic leftover materials and dried at 100°C for 1 h. The dried waste shells were pulverized before calcination at 900°C in air with a heating rate of 10°C per minute for 2 h. A Thermo Scientific Thermolyne™ Benchtop Muffle Furnace was used for the calcination of the waste shells. All catalysts were kept in a closed vessel to avoid interaction with air. The raw and calcined samples of the shells were analyzed by X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The XRD characterization was performed on a 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 a Thermo Nicolet Nexus 470 FTIR spectrometer. The attenuated total reflection method was employed to study the characteristics of the raw and calcined waste shells. The spectra were obtained in the 500–4000 cm⁻¹ region and 32 scans were recorded.

2.3. Transesterification reaction

About 100 mL of Camelina sativa oil was heated to 100°C for 1 h to remove impurities and it was allowed to cool down to 65°C. About 1% of selected calcined seashell was mixed with 70 mL methanol at 65°C for 1 h to activate the catalyst. Methanol:oil ratio was kept constant at 12:1. Shell:Methanol mixture was added to the Camelina sativa oil and vigorously stirred at 65°C for 2 h. After completion of the transesterification reaction, the seashell catalyst was recovered by filtration. The reaction mixture was allowed to separate for 30 min and glycerol was removed from the product as the bottom layer. Biodiesel was dried using anhydrous sodium sulfate. The conversion of oil to biodiesel was analyzed by 1H NMR and FTIR spectroscopy. 1H NMR spectroscopy was performed on an Anasazi EFT-60 spectrometer. The FTIR analysis of FAME was done on a Thermo Nexus 470 FTIR spectrometer using a KBr pellet method.
The physical and chemical properties of biodiesel including kinematic viscosity, density, flash point, cloud point, pour point, acid value and water content were analyzed according to the American Society for Testing and Materials (ASTM) methods.

### Table 1. Fatty acid composition (% as methyl esters) of *Camelina sativa* oil (19).

| Fatty acid                  | Percentage |
|----------------------------|------------|
| Palmitic acid (16:0)       | 5.3        |
| Stearic acid (18:0)        | 2.2        |
| Oleic acid (18:1)          | 16.0       |
| Linoleic acid (18:2)       | 18.4       |
| α-Linolenic acid (18:3)    | 32.4       |
| Arachidic acid (20:0)      | 1.6        |
| cis-Eicosenoic acid (20:1) | 15.1       |
| Eicosadienoic acid (20:2)  | 1.7        |
| Eicosatrienoic acid (20:3) | 1.2        |
| Behenic acid (22:0)        | 0.4        |
| Erucic acid (22:1)         | 3.7        |
| Docosadienoic acid (22:2)  | 0.2        |
| Docosatrienoic acid (22:3) | 0.4        |
| Lignoceric acid (24:0)     | 0.2        |
| Nervonic acid (24:1)       | 0.7        |

### Table 2. Yields of transesterification reaction of *Camelina sativa* oil.

| Waste shell catalyst | Percent yield (%) |
|----------------------|-------------------|
| Mussel shell         | 95                |
| Clam shell           | 93                |
| Oyster shell         | 91                |

### 3. Results and discussion

#### 3.1. Catalyst characterization

The main component of waste seashells is CaCO₃ and when it is calcined, it decomposes to CaO. CaO is a basic heterogeneous catalyst that has a higher basicity, lower solubility and is easier to handle than KOH (7). When using CaO for biodiesel production, CaO should be pretreated with methanol, because a small amount of CaO gets converted into Ca(OCH₃)₂ that acts as an initiating reagent for the transesterification reaction (9).

The XRD patterns of natural and calcined mussel shell as a representative of waste shells are given in Figure 2. CaCO₃ in the natural waste seashell completely transforms into CaO by evolving CO₂ at 900°C (16). Narrow and high intense peaks of the calcined catalyst define the well-crystallized structure of the CaO (17). The peaks for calcined shell at 900°C show 2θ values of 32.30, 37.38 and 54.10 for all waste shells which are the characteristic peaks for CaO (17).

The FTIR spectra of raw and calcined waste mussel shell as a representative are shown in Figure 3. The absorption bands of raw seashells at 1415 and 880 cm⁻¹ were attributed to the vibration of CO₂⁻ ions. A broad absorption around 3400 cm⁻¹ is due to O─H stretching vibration which decreases upon calcination at 900°C. On the other hand, a sharp OH⁻ stretching band at 3625 cm⁻¹ emerges followed by calcination. The peaks around...
1450 cm\(^{-1}\) correspond to the bending vibration of the 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 (18).

3.2. Analysis of biodiesel

Fatty acid composition of the *Camelina sativa* oil is given in Table 1. The acid value of *Camelina sativa* oil showed 1.58\% of free fatty acid (19). According to the literature, transesterification reaction would not take place if the amount of free fatty acid was above 3\% (20).

Previous research on *Camelina sativa* oil indicated lower reaction yields by utilizing heterogeneous catalysts such as BaO and SrO. The reactions were completed at 100°C in 2 h and yields were 84\% and 82\% for BaO and SrO, respectively (10, 21). Because of their toxicity and harmful properties, BaO and SrO have limitations in usage. CaO shows a great potential and several reports have been published on CaO-catalyzed transesterification using laboratory grade CaO (22). In this paper, reaction time of 2 h at 65°C was found to yield the optimum biodiesel as a product. Conversion yields of transesterification reaction of *Camelina sativa* oil with waste seashell heterogeneous catalysts and methanol are shown in Table 2. The minor differences in reaction yields are due to experimental variability. In addition, the catalyst generated from the waste seashells opens the door for renewable green catalysts and at the same time recycles the seashell waste generated.
FTIR spectra of Camelina oil and biodiesel are shown in Figure 4. A sharp absorption band at 1742 cm\(^{-1}\) is the characteristic of the aliphatic ester –C=O bond. The stretching vibrations of CH\(_3\), CH\(_2\) and CH appear at 2850, 2925–2975 and 3050 cm\(^{-1}\) whereas 720, 1150–1350 and 1350–1475 cm\(^{-1}\) shows the bending vibrations of these groups. There are several differences between FTIR spectra of Camelina sativa oil and biodiesel. There is a new signal at 1435 cm\(^{-1}\) which is an indication of the methyl ester group, –OCH\(_3\) group. The next visible transformation is in the ester signal area at 1200 cm\(^{-1}\). The strong, broad signal at 1150 cm\(^{-1}\) in Camelina oil will separate into two concrete signals at 1168 and 1195 cm\(^{-1}\) in the biodiesel spectrum.

The conversion of Camelina sativa oil to biodiesel catalyzed by waste seashells was analyzed by using \(^1\)H NMR spectroscopy and the spectra for starting oil and biodiesel are shown in Figure 5. The spectra showed that the terminal methyl ester moiety was prominently indicated by a strong singlet at 3.67 ppm and \(\alpha\)-CH\(_2\) protons as a triplet at 2.34 ppm. These peaks confirm the presence of FAME formation from starting oil. The other peaks were observed at 0.8 ppm due to terminal methyl protons; a strong signal at 1.3 ppm is related to the methylene protons of carbon chain, multiplet at 2.1 ppm is due to \(\beta\)-carbonyl methylene protons and the peak around 5.4 ppm is related to olefin hydrogens, respectively.

One of the most important advantages of employing a heterogeneous catalyst is its reusability. As shown in Figure 6, high biodiesel yields were obtained for all 10 cycles with 1% of selected heterogeneous catalyst and methanol:oil ratio of 12:1 at 65°C for 2 h. After each reaction, the waste catalyst was separated from the reaction mixture by simple filtration and washed with methanol and recalcined.

| Fuel properties | Camelina oil | Camelina biodiesel | Regular diesel | Method (ASTM) |
|-----------------|-------------|-------------------|---------------|---------------|
| Specific gravity | 0.91        | 0.88              | 0.85          | D4052         |
| Viscosity at 40°C (mm\(^2\)/s) | 14.0        | 4.0               | 2.6           | D445          |
| Calorific value (MJ/kg) | 44.5        | 45.0              | 42.0          | D240          |
| Pour point (°C) | −23         | −10               | −20           | D613          |
| Cetane number | 35          | 49                | 46            | D97           |

Figure 6. Reusability of waste seashell catalyst for biodiesel synthesis from Camelina sativa oil.

Figure 5. \(^1\)H NMR spectra of Camelina oil and synthesized biodiesel catalyzed by waste seashells.
Fuel properties of Camelina biodiesel

The fuel properties of biodiesel from *Camelina sativa* oil with testing methods are given in Table 3. The viscosity of biodiesel from *Camelina sativa* oil was comparable to regular diesel fuel viscosity so there is no need for modification of the engine to utilize the biodiesel. The cetane number was found higher than the ASTM biodiesel standards. A higher cetane number means more complete combustion of the fuel, better fuel efficiency, good ignition quality of fuel, reduction of harmful emissions and faster pumping of protective lubricating fluids throughout the system. The pour point of biodiesel from *Camelina sativa* oil is lower than the standards which might create incomplete combustion of the fuel, better fuel efficiency, good ignition quality of fuel, reduction of harmful emissions and faster pumping of protective lubricating fluids throughout the system. This problem could be solved by addition of fuel additives to improve the cold flow properties.

### 4. Conclusion

*Camelina sativa* oil shows excellent promise as a renewable feedstock for the synthesis of biodiesel. Waste seashells such as mussel, clam and oyster were utilized as cost-effective and environment-friendly heterogeneous catalysts for the production of biodiesel. The experimental results showed that the waste sea-shell heterogeneous catalysts had high catalytic activity and excellent thermal and chemical stability during transesterification. The catalysts were utilized for 10 cycles with no apparent loss of activity. The fuel properties of the biodiesel were compared to the ASTM standards and physiochemical properties meet ASTM specifications. Biodiesel synthesis that employs waste seashells as heterogeneous catalysts will minimize pollution and decrease the cost of biodiesel and the steps of purification, making biodiesel competitive with petroleum-derived biodiesel.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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