Ultrasound Assisted Direct Transesterification of Algae for Biodiesel Production: Analysis of Emission Characteristics

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Recently, the algae-for-fuel concept has gained renewed interest with energy prices fluctuating widely. Due to some restrictions over the oil extraction from algae, direct transesterification may be considered as a good alternative. In this study, to improve the performance of direct transesterification, ultrasound induction was carried out. A sonicator probe was used to induce the direct transesterification of Cladophora fracta, a freshwater macro alga, which contains 14% lipid on dry biomass basis. Due to ultrasonication about 25% increased biodiesel yields were obtained and the biodiesel thus prepared was analyzed for emission characteristics. The analysis results showed that Cladophora biodiesel emits 18 mg/L of CO whereas petroleum diesel emits 50 mg/L. Similarly, the emission of NOx and particulate matter also were reduced to a considerable level. The Cladophora is a suitable source of biodiesel by ultrasound assisted direct transesterification in industrial level in the future.

1. Introduction : Since fossil fuel has become a finite energy source, in the last decades many efforts have been put into the production of renewable alternative energy sources. Among the existing renewable alternatives to fossil fuels, algae have raised great interest. Algae have long been considered as a promising alternative and renewable feedstock source for biofuels. Recently, the algae-for-fuel concept has gained renewed interest with energy prices fluctuating widely [1, 2]. In the algal biodiesel production processes, fatty acid methyl esters (FAME), the chemical composition of biodiesel, are commonly prepared by transesterification of algal oil using either acid or alkali as a catalyst [3 – 5]. Unlike terrestrial feedstock such as soybean or canola seed, from which oil can be extracted by crushing followed with solvent extraction, releasing oil from algal cells is hindered by rigid cell walls. Mechanically crushing algal biomass (in either a mudlike wet form or a powder-like dry form) to extract oil is also difficult to be implemented using the existing crushing equipment. Preparing biodiesel via the direct transesterification of raw oleaginous materials may overcome the limitations described above. The direct transesterification has shown an increased recovery of fatty acids from a variety of samples such as marine tissues, yeast and fungi, bacteria, and micro heterotrophs. The direct transesterification can be induced further by intensification techniques. Ultrasound treatment is a well-known intensification technique used to induce many chemical engineering unit operations. Hence, ultrasonication would induce the direct transesterification process [6, 7].

A number of studies with comparisons of diesel, natural gas, and diesel/biodiesel blend bus emissions have been published [8, 9]. Biodiesel has a good energy return because of the simplicity of its manufacturing process, has significant benefits in emissions as well, and could also play an important role in the energy economy if higher crop productivities are attained. The properties of biodiesel and diesel fuels, in general, show many similarities, and therefore biodiesel is rated as a realistic fuel as an alternative to diesel [10, 11]. This study deals with the production of biodiesel
from algae by ultrasound induced direct transesterification. The biodiesel derived by this method was further analyzed for the emissions.

2. Materials and Methods:

2.1 Collection of Algae and Pre-treatment: Algae samples were collected from a freshwater lake available at the town of “Maduranthagam” which is 80 km south to Chennai, Tamil Nadu. The collected algae were identified as Cladophora fracta. The algae were washed well in the running tap water and dried in a hot air oven for whole night. The dried algae were crushed in a ball mill and sieved using sieve shaker. Finer mesh particles were collected and stored in an air tight container for further use.

2.2 Direct Transesterification: Direct transesterification reactions were conducted in two modes: with and without ultrasonication. Dried algal biomass (10 g) was placed in a glass test tube and mixed with 40 mL of methanol and 5 mL of sulfuric acid. Hexane solvent was added to the tube (50 mL), the reaction mixture was heated at 90°C for 40 min and the samples were well-mixed during heating. After the reaction was completed, the tubes were allowed to cool to room temperature. For studying the effects of ultrasonication, the above said mixture was treated with ultrasonication process. The experimental set-up is shown in Figure (1).

Temperature of the ultrasound induced direct transesterification process was maintained at 60°C. Ultrasound having a frequency of 30 kHz was irradiated for 15 min. Then, 20 mL distilled water was added to the tube and mixed. The tubes were allowed to separate into two phases. The solvent layer that contained biodiesel (FAME) was collected. The composition of FAME contained in the crude biodiesel was further analyzed via gas chromatography (GC).

2.3 Emission Tests: The experimental work was conducted in a 4 cylinder, 4 – stroke, turbo charged, intercooled, direct injection, 2.2 L diesel engine. The exhaust gases were analyzed using online gas analyzer (Shimadzu) and for comparison of efficiency, experiments were carried out using biodiesel and petroleum diesel as well.

3. Results and Discussions:

3.1 Chemical Composition of Algae Biomass: The algae samples were analyzed for the fatty acid composition available. The results showed that per gram of dried algae contained 0.14 g of lipids and 0.15 g of carbohydrates. The fatty acid composition of the lipids available in Cladophora fracta is given in Table.1. From the fatty acid composition, the average molecular mass of the Cladophora oil was determined to be 282.29 g/mol.

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Molecular mass (g/mol)</th>
<th>% in sample</th>
<th>Molecular mass contribution (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16:0</td>
<td>256.43</td>
<td>3.35</td>
<td>8.59</td>
</tr>
<tr>
<td>C16:1</td>
<td>254.41</td>
<td>1.25</td>
<td>3.18</td>
</tr>
<tr>
<td>C18:1</td>
<td>282.46</td>
<td>55.6</td>
<td>157.05</td>
</tr>
<tr>
<td>C18:2</td>
<td>280.45</td>
<td>21.3</td>
<td>59.74</td>
</tr>
<tr>
<td>C18:3</td>
<td>278.43</td>
<td>11.57</td>
<td>32.21</td>
</tr>
<tr>
<td>C20:1</td>
<td>310.52</td>
<td>6.93</td>
<td>21.52</td>
</tr>
</tbody>
</table>

Table (1): Fatty Acid Composition of the Cladophora Oil.
Thus the extractable lipid content of Cladophora fracta was determined to be 14% of its dry weight.

3.2 Biodiesel Yields: Biodiesel yields during direct transesterification with and without sonication were studied and the results are shown in Figure (2).

![Figure (2): Biodiesel Yield in various processes (ET – Extraction and Transesterification; DT – Direct Transesterification; UDT – Ultrasound assisted Direct Transesterification)](image)

3.3 Emission Characteristics: Emission characteristics of biodiesel prepared by ultrasound assisted direct transesterification were analyzed and the results are showed in Figure (3). As illustrated by the figure, the amount of CO emitted was just 36% of CO emitted by petroleum diesel. This is mainly due to the availability of more molecular oxygen, which contributes to the complete combustion of biodiesel. Similarly, the NOx and particulate matter levels were also reduced by biodiesel.

4. Conclusions: This study deals with the improved biodiesel production of ultrasound assisted direct transesterification process. The following conclusions were made in this study:

- Cladophora fracta is a fresh water macroalgae which contains about 14% lipid on dry biomass basis.
- About 27% more biodiesel yield was obtained by ultrasound assisted direct transesterification process over normal direct transesterification process.
- Cladophora Biodiesel is an eco-friendly fuel that emits only 36% of the CO that emitted by Petroleum Diesel.

5. References:


