Production of biodiesel using the microwave technique

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Abstract Biodiesel production is worthy of continued study and optimization of production procedures because of its environmentally beneficial attributes and its renewable nature. Non-edible vegetable oils such as Jatropha oil, produced by seed-bearing shrubs, can provide an alternative and do not have competing food uses. However, these oils are characterized by their high free fatty acid contents. Using the conventional transesterification technique for the production of biodiesel is well established. In this study an alternative energy stimulant, “microwave irradiation”, was used for the production of the alternative energy source, biodiesel. The optimum parametric conditions obtained from the conventional technique were applied using microwave irradiation in order to compare the systems. The study showed that the application of radio frequency microwave energy offers a fast, easy route to this valuable biofuel with the advantages of enhancing the reaction rate (2 min instead of 150 min) and of improving the separation process. The methodology allows for the use of high free fatty acid content feedstock, including Jatropha oil. However, this emerging technology needs to be further investigated for possible scale-up for industrial application.

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Introduction

Biodiesel has many merits as a renewable energy resource including being derived from a renewable domestic resource, thereby relieving the reliance on petroleum fuel, and being bio-degradable and non-toxic. Further, compared to petroleum-based diesel, biodiesel has a more favorable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons [1]. Fuels derived from vegetable oils, due to their agricultural origin, are able to reduce net CO₂ emissions to the atmosphere along with import substitution of petroleum products [2]. They present a very promising alternative to diesel oil since they are renewable and have similar properties [3]. The use of non-edible vegetable oils compared to edible oils is very significant because of the tremendous demand for edible oils as food. Moreover, edible oils are far too expensive to be used as fuel at present [4].

The interest in using Jatropha curcas as a feedstock for the production of biodiesel is rapidly growing. The properties of the crop and its oil have persuaded investors, policy makers and clean development mechanism (CDM) project developers to consider Jatropha as a substitute for fossil fuels to tackle the
challenges of energy supply and GHG emission reduction [5]. The oil produced by this crop can be easily converted to liquid biofuel that meets the American and European standards [6]. Additionally, the press cake can be used as a fertilizer and the organic waste products can be digested to produce biogas (CH₄) [5]. The plant itself is believed to prevent and control soil erosion or can be used as a living fence or to reclaim waste-land [7].

Microwave irradiation, an unconventional energy source, has been used for a variety of applications including organic synthesis, wherein chemical reactions are accelerated because of selective absorption of MW energy by polar molecules, non-polar molecules being inert to the MW dielectric loss [8]. Microwaves, representing a non-ionizing radiation, influence molecular motions such as ion migration or dipole rotations without altering the molecular structure. Because the mixture of vegetable oil, methanol, and potassium hydroxide contains both polar and ionic components, rapid heating is observed upon microwave irradiation, and because the energy interacts with the sample on a molecular level, very efficient heating can be obtained. Microwave heating compares very favourably with conventional methods, where heating can be relatively slow and inefficient because transferring energy into a sample depends upon convection currents and the thermal conductivity of the reaction mixture [9]. To allow for a strict comparison between microwave irradiation and conventional heating under similar conditions (reaction medium, temperature and pressure), a monomode microwave reactor should be used. This ensures wave focusing (reliable homogeneity in the electric field) and accurate control of the temperature (using an optical fibre or infrared detection) throughout the reaction [10].

Several examples of microwave irradiated transesterification methods have been reported incorporating adapted domestic ovens for use as flow systems [11] or batch laboratory ovens [12] but only moderate conversions were obtained. A more recent study used homogeneous catalysis, both in a batch and in a flow system [13]. Leadbeater and Stencel reported the use of microwave heating as a fast, simple way to prepare biodiesel and in a flow system [13].

Helium was used as the carrier gas with a flow rate 1 mL/min and also as an auxiliary gas for FID. One micrometer of each diluted sample with analytical grade dichloromethane from BDH (England) was injected. The viscosity of the original oil and the produced biodiesel was measured using the Brookfield viscometer model DV-II.

As evident from the tables, the fatty acid composition of the oil is dominated by oleic acid (29%) and linoleic acid (48%) i.e., the oil contains about 77% unsaturated fatty acid, which is reflected on its pour and cloud points (−3 and 2 °C, respectively).

Materials

The main oil treated in this investigation is Jatropha oil. The fatty acid composition of the Jatropha oil used as a feedstock for biodiesel production is given in Table 1 and the oil characteristics are given in Table 2.

Experimental

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Determination of the composition of the oil was by gas chromatograph (Auto system XL, PerkinElmer type) using fused silica capillary column 60 m × 0.32 mm (ID) at the split ratio 1:5. The oven temperature was planned to remain at 150 °C for one min, then heated at 30 °C/min up to 240 °C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>mm²/s</td>
<td>46.6</td>
</tr>
<tr>
<td>Pour point</td>
<td>°C</td>
<td>−3</td>
</tr>
<tr>
<td>Cloud point</td>
<td>°C</td>
<td>2</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>235</td>
</tr>
<tr>
<td>Acid value</td>
<td>mg KOH g⁻¹</td>
<td>6.2</td>
</tr>
<tr>
<td>Iodine value</td>
<td>mg iodine g⁻¹</td>
<td>101</td>
</tr>
<tr>
<td>Calorific value</td>
<td>MJ kg⁻¹</td>
<td>39.54</td>
</tr>
</tbody>
</table>

Table 1 Fatty acid profile of feedstock.

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic</td>
<td>18.22</td>
</tr>
<tr>
<td>Stearic</td>
<td>5.14</td>
</tr>
<tr>
<td>Oleic</td>
<td>28.46</td>
</tr>
<tr>
<td>Linoleic</td>
<td>48.18</td>
</tr>
</tbody>
</table>

Table 2 Main characteristics of feedstock.

The method applied for the production of biodiesel from Jatropha oil in this research is base-catalyzed transesterification in a laboratory-scale setup. The reaction was performed using methanol as alcohol and KOH as catalyst. The transeste-
The optimum parametric conditions that were obtained from the conventional technique were applied using the microwave-assisted technique in order to compare the systems. In order to verify the advantages of microwave irradiation, the technique was applied on the oil without pretreatment. A scientific microwave with advanced vessel technology was used. This allowed fast vessel heating with homogeneous microwave distribution throughout the cavity. The oven used was the Start S (Milestone), manufactured by Milestone Inc., USA. A normal pressure glass reactor is equipped with a 500 mL flask and a reflux condenser. The oven is supplied with a colour touch screen controller that enables the creation, storage and use of time vs. temperature or time vs. power reaction profiles. The output microwave power is variable up to 1200 watts, controlled via a microprocessor.

The optimum parametric conditions obtained from the conventional technique were applied again using microwave irradiation in order to compare the systems. The temperature was adjusted to 65 °C, and the oil was preheated to the desired temperature of 65 °C using the microwave unit. The alcohol–catalyst mixture was then fed into the flask through the condenser, and the mixture was irradiated under reflux for different reaction times of 1, 2 and 3 min.

**Results and discussion**

**Results obtained by using the mechanical conventional technique**

**The effect of process variables on biodiesel yield**

The base-catalyzed transesterification result of Jatropha oil was investigated by changing catalyst (KOH) to oil ratios (% w/w) and alcohol to oil ratios (% w/w). The highest conversion was obtained with 1.5% of catalyst (KOH) to oil ratio and 7.5:1 of methanol to oil ratio for 60 min, and under these condition, the Jatropha oil methyl ester (JOME) yield was 99.8%.

Figs. 1 and 2 show biodiesel yield% with time for KOH 1% and KOH 1.5% at different alcohol/oil molar ratios.

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. In this study, a molar ratio of 7.5:1 has given a yield of over 98%.

Biodiesel with the best properties was obtained using potassium hydroxide as the catalyst in many studies. Methanolysis with 1 wt.% KOH catalyst resulted in successful conversion giving the best yields and viscosities of the esters in most of the literature reviewed. However, using a concentration of 1.5% showed better results in this study.

**Results obtained by using the microwave-assisted technique**

Applying the microwave technique as previously described in the Experimental section showed that the application of radio
frequency microwave energy enhances the reaction rate for the conversion of Jatropha oil to biodiesel, and drives the reaction equilibrium toward the production of biodiesel. Highest biodiesel yield (97.4%) was obtained by applying microwave irradiation for two minutes compared to 1 h with the conventional technique. The results are depicted in Fig. 3.

It should be pointed out, however, that these results were achieved by using Jatropha oil without pretreatment. It was also evident that exceeding the optimum reaction time will lead to deterioration of biodiesel yield. The interpretation of these results requires further investigation. The most accepted interpretation is that the exceeded time favours the equilibrium in the reverse direction. Attributing the decrease in yield after exceeding the optimum time to cracking followed by oxidizing of the formed fatty acid methyl esters to aldehydes, ketones and lower chained organic fractions could be excluded because the GC results do not show peaks of oxygenated compounds [33].

**Quality assessment of produced biodiesel**

Quality assessment was performed using physical parameters such as viscosity, flash point and calorific value, as shown in Table 3.

The viscosity difference forms the basis of an analytical method, viscometry, applied to determine the conversion of vegetable oil to methyl ester. The viscosity difference between component triacylglycerols of vegetable oils and their corresponding methyl esters resulting from transesterification is approximately one order of magnitude [34]. Kinematic viscosity has been included in biodiesel standards (1.9–6.0 mm²/s in ASTM D6751 and 3.5–5.0 mm²/s in EN 14214) [35].

The viscosity of the produced biodiesel was calculated using the Brookfield viscometer Model DV-II and was found to be 5.8 mm²/s. The result obtained is compatible with the reports from other studies on biodiesel from Jatropha oil. Kumar and Sharma reported a value of 5.65 mm²/s [36].

The flash point of the produced biodiesel was estimated to be 185 °C. This flash point is quite high compared to diesel. Hence, biodiesel is extremely safe to handle. The high flash point was referred to in many previous literature; Agarwal and Agarwal reported a flash point of 191 °C compared to 71 °C for mineral diesel [2], and Kumar and Sharma reported a flash point of 170 °C for Jatropha oil methyl ester (JOME) [36].

The calorific value (MJ/Kg) for the produced Jatropha biodiesel is 39.632 compared to 45.343 for mineral diesel.

Comparing the results with those obtained from neat and waste edible oils

The results obtained from this study on Jatropha-based biodiesel are confirming the results obtained in a previous study conducted by Refaat and co-workers on neat and waste edible vegetable oils [33] which also showed that no substantial differences were obtained from different oil origins. Hence, it can be concluded that biodiesel produced from Jatropha oil is at least not inferior to that produced from edible oils.

**Conclusion**

From the obtained results, using the conventional technique, the best yield % for the production of biodiesel from Jatropha oil was obtained using a methanol/oil molar ratio of 7.5:1, potassium hydroxide as catalyst (1.5%), and a reaction time.
of one hour with the reaction temperature maintained at 65 °C. The study also showed that the quality of the produced biodiesel satisfies the international American and European standards; hence, inedible vegetable oils such as Jatropha oil, produced by seed-bearing shrubs, can provide an alternative, and they do not have competing food uses.

The results showed that application of radio frequency microwave energy offers a fast, easy route to this valuable biofuel with advantages of enhancing the reaction rate and improving the separation process. The reaction time was reduced to 2 min instead of 150 minutes (90 min for the pretreatment process and 60 min for transesterification), because, by using the microwave technique, no pretreatment is required. The methodology also allows for the use of high free fatty acid content feedstock, including Jatropha oil. However, this will need time control, otherwise the yield may be affected.

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