Reactive extraction of non-edible oil seeds for biodiesel production

Savita Kaul*, Richa Singhal, Babita Behera, Dinesh Bangwal and M. O. Garg
Council of Scientific and Industrial Research - Indian Institute of Petroleum, Dehradun- 248005, India

Received 23 August 2012; revised 16 September 2013; accepted 03 March 2014

Biodiesel is one of the potential global liquid transportation fuels that might replace diesel. Government of India had launched a national mission on Biofuels with the aim of achieving a target of 20% blending of biodiesel by 2012. For this purpose, economic and sustainable production of biodiesel is required. This paper studies the reactive extraction of biodiesel from two potential non-edible oil seeds (karanja and simarouba glauca). A statistical study was carried out to determine the influence of operating parameters on the biodiesel yield. The smallest seed size resulted in high biodiesel yield whereas the optimum methanol to oil ratio and catalyst concentration depended on the type of feed. Reaction temperature of 65°C was found to be optimum. The $^1$H-NMR and gas chromatographic analyses results were comparable. It was found from $^1$H-NMR analysis that biodiesel produced from reactive extraction of simarouba had better oxidation stability as compared to karanja.

Keywords: Reactive extraction, biodiesel, non-edible oil seeds, response surface methodology, $^1$H-NMR.

Introduction

Economic, environmental and energy security issues resulting from excessive reliance on petroleum are forcing countries the world over to shift to alternatives like biofuels$. The current energy situation has stimulated active research interest in non-petroleum based renewable, and non polluting fuels. At present, bioethanol and biodiesel are the two most potential global liquid transportation biofuels that might replace gasoline and diesel fuel because of their simplicity of production and price advantages$. Bioethanol/gasoline and biodiesel/diesel mixtures with 5 to 10% of the respective biofuel are already in use in some nations. It has been reported that in India blending of 5% biodiesel fuel to the diesel fuel can save about Rs. 4000 crore every year$^4$. India being deficient in oils imports 40% of its edible oil requirements and hence non-edible oils are the main resources for biodiesel production$. The common non-edible oil bearing plant species include Jatropha curcas (ratanjyot), Pongamia pinnata (karanj), Ricinus communis (castor), Cerbera odollam (sea mango), Hevea brasiliensis (rubber tree), Simarouba glauca, S. chinensis (jojoba), Madhuca indica (mahua) and Thevetia peruviana (yellow oleander), etc.$^4$.

The Government of India had launched a national mission on Biofuels with the aim of achieving a target of 20% blending of biodiesel by 2012 and it aimed to bring around 400,000 hectares of marginal land under cultivation of Jatropha Curcas as biodiesel feedstock. However, despite various advantages offered by Jatropha plantation, studies$^1,6$ have revealed this as not the best strategy in meeting the India’s biofuels goals. The yield of jatropha is highly variable depending upon the soil type, irrigation status and cultivation practices apart from its long gestation period. Hence, alternate plantation in wasteland with trees like Calophyllum inophyllum (undi) with 50-73% oil, Diploknema (Aisandra) with 60% oil and Simarouba glauca (Lakshmi tharu) with 60-75% oil may be explored$. Karanja (pongamia pinnata) another biodiesel feedstock though with long gestation period is also being explored.

In contrast to conventional transesterification process where biodiesel production from any oil seeds involve various stages such as oil extraction, purification (degumming, dewaxing, etc.) and subsequent esterification or transesterification, reactive extraction is a single step process where direct transesterification of oil seeds take place$. Reactive extraction is a new technique for viable production of biodiesel. The reactive extraction study on Jatropha curcas seeds is provided in literature$^7$ however, other non-edible oil seeds are not studied. This paper provides a comprehensive study on the
biodiesel production by alkali catalyzed reactive extraction of non-edible oil seeds important to Indian scenario. Pongamia pinnata (Karanja) and simarouba glauca were selected for the study. The response surface methodology coupled with Box-Behnken design was utilized to study the effect of process parameters on response variable, which provides more information in less number of experiments. The biodiesel yield was selected as the response variable. The reaction parameters were optimized for maximum biodiesel yield. The oil and biodiesel samples were then analyzed by ^1^H-NMR and the fatty acids present in biodiesel samples were quantified. The results of NMR were compared with gas chromatographic analyses.

**Experimental section**

**Materials**

The seeds of karanja and simarouba glauca (whole fruit) were obtained from Karnataka State Biofuel Development Board. Methanol (99.8% purity) and potassium hydroxide in the form of pellets (>84% pure) were purchased from MERCK.

**Physicochemical characterization of seeds**

Since the reactive extraction process involves direct transesterification of seeds; the physical and chemical characteristics of seeds such as moisture content, oil content, etc. are essential. The moisture content of seeds was determined by drying the seeds in an oven at 60 °C till constant weight is achieved. The oil content of the seeds was determined using the conventional solvent extraction method using a Soxhlet extractor with excess n-hexane as the solvent. After the extraction process, hexane was recovered using a rotary evaporator, and the amount of extracted oil was measured after removing traces of hexane under vacuum. Acid value of the extracted oil was measured using ASTM D 974 method. The fatty acid composition of the oil was determined by using gas chromatography.

**Reactive Extraction**

The seeds were crushed and sieved to three sizes: >2.46 mm, 0.85-2.46 mm, and <0.85 mm. Experiments were conducted in a laboratory-scale setup, which consisted of a 250 mL three-necked round bottom flask (reactor) equipped with a reflux system, heater and a mechanical stirrer. The known amount of methanol and potassium hydroxide were added to the reactor, mixed and preheated (40°C). 20 g of pre-dried seeds were then charged in the round bottom flask. The reaction mixture was heated to the desired temperature and continuously stirred for 1 hour (which was found to be sufficient for completion of alkali catalyzed reactions). Upon completion of reaction period, the reaction mixture was cooled and then filtered. The solid residue (seeds) was washed with methanol and the excess methanol was recovered in a rotary evaporator. The reaction mixture then separates into two layers of liquid. The lower layer containing glycerol was separated from the upper layer containing crude biodiesel. The upper layer was washed repeatedly with 1-2 ml of lukewarm water until the pH becomes neutral. The upper layer containing biodiesel was then weighed and analyzed with GC for composition of fatty acid methyl esters (FAME) in the biodiesel. GC analysis was performed on an Agilent Technologies 7890A GC System equipped with a flame ionization detector and a capillary column using nitrogen as carrier gas. The peaks were identified by measuring the retention time of the samples and comparing the same with standards analyzed under the same conditions. The yield of FAME in the samples was calculated as:

\[
\text{Yield (\%)} = \frac{(\text{Weight of biodiesel})}{(\text{total weight of oil})} \times 100\%
\]

\[
\text{Yield (\%)} = \frac{(\text{Weight of biodiesel})}{(\text{as determined from oil})} \times 100\%
\]

\[
\text{Yield (\%)} = \frac{(\text{Weight of biodiesel})}{(\text{content in the seeds})} \times 100\%
\]

\[
\text{Yield (\%)} = \frac{(\text{Weight of biodiesel})}{(\text{in the sample})} \times 100\%
\]

**Statistical Study**

Box-Behnken design (BBD) was used for designing of experiments. Design points are the midpoints of edges of the design space and at the center. The important parameters affecting biodiesel yield from reactive extraction process are seed size, reaction temperature, methanol to oil ratio, and catalyst concentration. The design factors (coded and un coded) used for the study are A: methanol to oil molar ratio (250, 500, 750), B: catalyst concentration, M (0.05, 0.125, 0.2), C: Reaction temperature°C (45, 55, 65), and D: seed size (>2.46, +0.85-2.46, <0.85).

**NMR Spectroscopy**

Solution state ^1^H-NMR spectra (in CDCl$_3$) were recorded on a 11.7T Bruker AVANCE III spectrometer operating at 500 MHz resonance frequency using a 5 mm BBFO probe. The conventional ^1^H-NMR experiment is carried out using 5% w/v sample solution in CDCl$_3$ (99.8%, Aldrich) with 64 number of scans, a Π/2 pulse length of 13.4 μs, 10s recycle delay, 64K time domain data.
The FID is exponentially multiplied and Fourier transformed with 0.3 Hz apodization and referenced to TMS at 0 ppm.

Results and discussion

The biodiesel yield (Yₖ for karanja and Yₛ for simarouba glauca respectively) obtained using reactive extraction with the combination of various process parameters. The results were analyzed using response surface regression procedure using second order polynomial equation. The model was tested for adequacy by analysis of variance (ANOVA) as shown in Tables 1 for karanja and simarouba biodiesel respectively. According to the ANOVA tables, the F value for regression was higher indicating that most of the variation in the response can be explained by the regression model equation. The significance of the model is estimated by the associated p-value. The p-value less than 0.05 indicate the significance of the respective model term for 95% confidence interval. The regressions for both the feeds were significant (p-value: 0) while residual error terms which measures the amount of variation in the response data left unexplained by the model given by lack-of-fit were insignificant (p-value: 0.131, 0.200). This means that second order polynomial explains the biodiesel yield for both the feeds.

The model equations obtained for the biodiesel yield from the reactive extraction of various feeds are given below. R² values close to 1 indicate the little variation between model and observed responses.

$$Y_k = 76.11 + 12.36A - 4.15B + 7.42C + 11.25D - 14.91A^2 - 27.9B^2 - 3.79C^2 - 8.41D^2 - 5.18AB + 10.51AC - 4.75AD + 19.02BC + 3.30BD + 4.39CD, \quad R^2 = 0.98$$

$$Y_s = 150.91 + 0.23A - 653.30B - 4.06C - 10.84D - 1712.82B^2 + 0.02C^2 - 3.87D^2 - 0.85AB + 0.02AD + 26.13BC + 103.29BD + 0.12C, \quad R^2 = 0.97$$

The individual or main effect of each of the reaction parameters on mean biodiesel yield is shown in Fig. 1. From Fig. 1(a), it is clear that seed size plays an important role in reactive extraction. The biodiesel yield increases significantly with decreasing seed size. The mean biodiesel yield from simarouba seeds is increased by 40 wt% and that of karanja by 22.5 wt% on decreasing seed size from >2.46 mm to <0.85 mm. This shows that mass transfer is important in the reactive extraction. As seed size decreases the mass transfer resistance for the transfer of oil from seed to methanol decreases and hence yield increases.

Fig. 1(b) shows the effect of temperature on mean biodiesel yield. There is a little increment in biodiesel yield on increasing temperature from 45 to 55 °C. However, the mean biodiesel yield is highest at 65 °C for reactive extraction of both karanja and simarouba. High temperature reduces mass transfer resistance and increases the rate of reaction. In conventional transesterification, Noureddini and Zhu observed that the temperature influenced both mass transfer as well as conversion.

Previous studies have shown that the required methanol to oil ratio in the case of reactive extraction is significantly high compared to conventional transesterification also confirmed in the present study. High amount of alcohol reduces the mass transfer resistances required to overcome the diffusion of alcohol into the particles or oil from particles to alcohol and hence for the reaction to proceed at an appreciable rate. However, too high molar ratio interferes with the separation of glycerin since there is an increase in solubility which drives the equilibrium in the reverse direction, lowering the yield of esters. Fig. 1(c) shows that the required methanol to oil molar ratio depends on the type of feed. For karanja, maximum yield is at molar ratio of 750, while for simarouba at 250 which is obvious due to different morphology of seeds.

<table>
<thead>
<tr>
<th>Variation</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>F</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KARANJA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regression</td>
<td>14</td>
<td>11114.5</td>
<td>793.89</td>
<td>37.15</td>
<td>0</td>
</tr>
<tr>
<td>Residual Error</td>
<td>12</td>
<td>256.4</td>
<td>21.37</td>
<td>7.04</td>
<td>0.131</td>
</tr>
<tr>
<td>Total</td>
<td>26</td>
<td>11370.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SIMAROUBA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regression</td>
<td>14</td>
<td>11005.2</td>
<td>786.09</td>
<td>27.97</td>
<td>0</td>
</tr>
<tr>
<td>Residual Error</td>
<td>12</td>
<td>337.3</td>
<td>28.11</td>
<td>4.39</td>
<td>0.2</td>
</tr>
<tr>
<td>Total</td>
<td>26</td>
<td>11342.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1(d) compares the effect of catalyst concentration on mean biodiesel yield. The biodiesel yield first increases with increasing catalyst concentration and then decreases as also observed for Jatropha curcas seeds\(^9\). The decrease in biodiesel yield is due to enhanced saponification reaction which is a competing reaction in alkali catalyzed transesterification.

The three dimensional response surface plots represented by Eqs. (1) and (2) are shown in Figs. 2 and 3 respectively. The process parameters were optimized to obtain the highest biodiesel yield for alkali catalyzed reactive extraction process. The desired target values of yield were set at 100% for each case. The optimized process parameters for maximum biodiesel yield as predicted by the model are given in Table 2. Comparing with literature data\(^7\), \(^9\), it is clear that the optimum reaction conditions are different for different feeds. The acid catalyzed process\(^7\) and supercritical fluid reactive extraction\(^15\) seem to be advantageous for high yield of biodiesel production. However, high reaction time for acid catalyzed process and very high operating reaction temperature and pressure are some of the demerits while considering scale up of the process for large scale production.

The \(^1\)H-NMR spectrum for the oil and biodiesel samples for karanja and simarouba are shown in Fig. 4. From the spectrum it is clear that the triglycerides are completely converted into fatty acid methyl esters as is shown by the absence of triglyceride protons peaks (peak no. 9) at 4.0-4.4 ppm and appearance of methyl ester protons peak (peak no. 7) at 3.5-3.8 ppm in the biodiesel samples. The \(^1\)H-NMR spectra was then used to quantify the fatty acids present in the biodiesel produced by reactive extraction of non-edible seeds by the method provided in literature\(^16\). This method is applicable to mixtures containing the triacylglycerol or alkyl esters of palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2) and linolenic (C18:3) acids. Hence, assuming the biodiesel of karanja and simarouba seeds contain only these fatty acids, the above method was applied. The integration values for the olefinic, allylic, and bis-allylic protons of C18:1, C18:2 and C18:3 fatty

![Fig. 1](image-url)

Fig. 1—Effect of process parameters (a) seed size, (b) reaction temperature, (c) methanol to oil molar ratio, and (d) catalyst concentration on mean biodiesel yield for different feeds.
acids from \(^1\)H-NMR spectra were determined thrice and the average value was used for further calculations. The results of integrated analytical approach for the present study are given in Table 3. Table 3 shows the amount of unsaturated and saturated fatty acids and the allylic position equivalents (APE) and bis-allylic position equivalents (BAPE) for the karanja and simarouba biodiesel respectively. The table also compares the physicochemical characterization of feedstock and fatty acid composition determined by GC analysis. The results from \(^1\)H-NMR and GC are in good agreement. GC results are reported in area-% equated with wt% while NMR data are reported in mol% which causes slight difference in results. Also, in GC analysis it was observed that the peaks of C18:3 and C18:2 were very close and mostly tend to overlap, hence the amount of C18:2 given by GC might contain C18:3 amount also. The APE and BAPE values determine the oxidation stability of the biodiesel. The BAPE index is more significant of the two values since the poly-unsaturation accompanied by bis-allylic positions impart greater reactivity\(^{17}\). The higher the BAPE value, greater is the tendency of a sample to oxidize. Hence, simarouba biodiesel has more oxidation stability than the karanja biodiesel.

Fig. 2—Surface Plots of Biodiesel Yield (Y\(_K\)) from karanja seeds.
Fig. 3—Surface Plots of Biodiesel Yield ($Y_3$) from simarouba seeds.

Table 2—Optimized process parameters

<table>
<thead>
<tr>
<th>Feed stock</th>
<th>Methanol to oil molar ratio</th>
<th>Catalyst conc., M</th>
<th>Reaction temp., °C</th>
<th>Seed size, mm</th>
<th>Reaction time, h</th>
<th>Predicted Yield, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karanja (present study)</td>
<td>649</td>
<td>0.1439</td>
<td>65</td>
<td>0.82</td>
<td>1</td>
<td>94.7</td>
</tr>
<tr>
<td>Simarouba glauca (present study)</td>
<td>250</td>
<td>0.2</td>
<td>65</td>
<td>&lt;0.85</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>Jatropha curcas (acid catalyzed)$^7$</td>
<td>10.5 ml/g$^a$</td>
<td>21.8 wt%</td>
<td>60</td>
<td>-</td>
<td>10</td>
<td>98.1</td>
</tr>
<tr>
<td>Jatropha curcas (alkali catalyzed)$^9$</td>
<td>400</td>
<td>0.15 N</td>
<td>30</td>
<td>&lt;0.71</td>
<td>1</td>
<td>81-88</td>
</tr>
<tr>
<td>Jatropha curcas (supercritical fluid reactive extraction)$^{15}$</td>
<td>10.0 ml/g$^a$</td>
<td>-</td>
<td>300 °C, 240 MPa</td>
<td>≤1.0</td>
<td>45-80 min</td>
<td>103.5</td>
</tr>
</tbody>
</table>

$^a$ Oil to seed ratio
Conclusion

The reactive extraction process is a suitable method for biodiesel production especially for local and small scale production. The cost of biodiesel production by reactive extraction can be reduced by using non-edible seeds from trees grown in wastelands which create no negative impact on environment and also generate employment for rural sector.

The biodiesel yield from reactive extraction process depends on acid value of the feed, seed size, reaction temperature, methanol to oil ratio and catalyst concentration. The optimum reaction conditions for the alkali catalyzed reactive extraction of karanja and simarouba were determined. Seed size, catalyst concentration and methanol to oil ratio strongly affect biodiesel yield. Smallest seed size
resulted in highest biodiesel yield. Optimum catalyst concentration and methanol to oil molar ratio depend on the type of feed. Reaction temperature of 65 °C was found to be optimum for both the feeds. The $^1$H-NMR analyses showed the complete conversion of triglycerides to methyl esters. The NMR results were in good agreement with gas chromatographic analyses. The BAPE values showed that biodiesel produced from reactive extraction of simarouba had higher oxidation stability than that of karanja.

Acknowledgement

The authors are grateful to the Director, Indian Institute of Petroleum, Dehradun, India for giving permission to publish this work.

References