Palash Seed Oil - Potential Feedstock for Biodiesel Preparation

Ch. Bindhu, M.S.L. Karuna, P.P. Chakrabarti, Sanjit Kanjilal and R.B.N. Prasad

Centre for Lipid Research, Indian Institute of Chemical Technology, Hyderabad 500 007, India

(bindhu.chem@gmail.com, karuna@iict.res.in, pradosh@iict.res.in, sanjit@iict.res.in, rbnprasad@iict.res.in)

‡Corresponding Author; R.B.N. Prasad, Centre for Lipid Research, Indian Institute of Chemical Technology, Hyderabad 500 007, India, Tel.: +91-40-27193179; fax: +91-40-27193370, rbnprasad@iict.res.in

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Abstract- Palash (Butea monosperma) seed oil is a non-edible, minor oil, being produced in India. The present investigation aims at optimizing a process for the preparation of biodiesel from palash seed oil. As the oil contains high phosphorous content (557 ppm), the oil was pretreated by degumming process. The degummed oil with 4% FFA was converted into biodiesel employing acid esterification followed by alkaline transesterification. The biodiesel exhibited physico-chemical and fuel properties within the ASTM and EN specifications. Palash biodiesel was reported for the first time and found to be a potential feedstock for biodiesel preparation.

Keywords- Biodiesel, Degumming, Pretreatment, Soxhlet extraction, Acid esterification, Alkaline transesterification

1. Introduction

Due to the shortage of edible oils, it is not affordable to prepare biodiesel from cleaner edible oils and so, depend on the non-edible sources like jatropha [1,2,3,4,5,6], [7,8,9,10,11,12,13], castor [14], neem [15], rubber [16], Sterculia foetida [17] etc., seed oils. There are review reports where few non-conventional oils have been explored as potential feed stocks for biodiesel production [18, 19]. In this study, a non-edible, tree borne minor seed palash (Butea frondosa) was chosen to screen its suitability as raw material for biodiesel preparation.

Palash (Butea frondosa) is synonymous with Butea monosperma or flame of the forest. The tree is native to the Indian subcontinent, Burma, Ceylon [20] and South Asian peninsula [21, 22]. It is a slow growing tree that reaches a height of 40 to 50 feet. Each part of the palash tree is being utilized both medicinally and commercially. The tree provides wood, gum and dye. Wood is used to make well curbs and water scoops. The wood pulp is useful in newsprint manufacturing. Gums are used in leather industry, drugs and in some food preparations. All parts of the trees like flowers, bark, seed, gum, leaves and root possess anti-inflammatory, antimicrobial, antifungal, antibacterial, antidiabetic and antiestrogenic properties. The tree is extensively used in ayurvedic, unani and homeopathic medicine. The palash seed oil exhibits significant bactericidal and fungicidal effects. Overall, only few isolated reports are available which are mostly on phytochemical and pharmacological studies of Butea monosperma [23, 24, 25], biodiesel preparation from this oil is being reported for the first time. As the tree grows widely in India and a source of tribal wealth, an attempt was made to explore for the first time, the potentiality of the seed oil as a source of biodiesel.

2. Materials and Methods

The seeds of palash were procured from M/S. Sanjeevani Herbal Health Society, Hyderabad, India. All the chemicals, reagents and solvents used were purchased from S.D. Fine Chemicals, Mumbai, India. Palash seed oil was extracted from palash seeds (1000 g) using soxhlet extraction method. Hexane (3.5 lit) was used as solvent. Extraction was carried out for 8 h. Palash oil (200 g, 20%) was obtained by evaporating hexane using rotary evaporator after passing over anhydrous sodium sulfate. The oil was dried under reduced pressure and determined for physico-chemical properties like free fatty acid [26], iodine value [27], saponification value [28], unsaponifiable matter [29], phosphorous content [30], density [31], viscosity [32] and calorific value [33] were determined using standard
The fatty acid composition of palash seed oil was determined using GC by converting into fatty acid methyl esters. An Agilent 6890 Gas Chromatograph fitted with an flame ionization detector (FID) detector and split injector was used for the determination of fatty acid composition of oil. A non-bonded cyano silicone column (DB-225, 30m × 0.25 mm × 0.2µm) was employed for gas chromatographic analysis. The oven temperature was kept at 160 ºC for 2 min and programmed for 15 min from 160 to 180º C at 6º C/min, kept for 2 min at 180º C and finally raised to 230º C at 4º C/min and maintained for 15 min at 230º C. The injector and detector temperature were set at 250º C.

2.1. Experimental Procedure

2.1.1. Fatty acid composition of palash seed oil

Fatty acid composition of the palash seed oil was determined by converting to fatty acid methyl esters using 2% sulphuric acid in methanol. The reflux was carried out for 4 hr at 70º C. The methyl esters thus produced were further extracted using ethyl acetate and dried. The ethyl acetate extract was then used for GC analysis. The fatty acid composition of palash seed oil is given in Table 2.

2.2. Degumming of Palash Oil

Palash oil (150 g) was heated to 75 ºC. Distilled water (4.5 ml, 3% wt. of palash oil) was added to the oil. The contents were stirred for 30 min. After half an hour, oil was centrifuged to separate the gums from the oil. The degummed oil was dried under reduced pressure and the weight of the degummed oil was 145 g (97%). The phosphorous content was reduced to 156 ppm.

2.3. Biodiesel Preparation from Degummed Palash Seed Oil

Degummed Palash seed oil with FFA 4%, was converted into biodiesel by using the standard two-step process, acid esterification followed by alkaline transesterification.

2.3.1. Esterification

Degummed Palash seed oil (FFA, 4.0%; 250 g) was taken into a 1000 ml round bottom flask and 1.5% methanolic sulfuric acid was added (FFA: Methanol; 1:6 mol/mol). The contents were stirred for 3 hr under reflux at 65 ºC. The reaction was monitored by determining acid value of the product at different intervals until the acid value reached less than 1.0. After 3 hr, product was washed with water to remove the excess acid, dried under reduced pressure to obtain 240 g of esterified product and the FFA of the esterified product was found to be 0.4.

2.3.2. Transesterification

The esterified product (240 g) was transesterified using methanolic NaOH in two stages. Esterified product was taken into a solution of NaOH (1.5% wt of oil) in methanol (oil to methanol; 1:6 mol/mol ratio) and stirred for one hour at 65ºC. The reaction was monitored by TLC till the oil was completely converted to fatty acid methyl esters. The product was poured into separating funnel to separate the glycerol layer. The upper layer containing methyl ester was taken and a solution of NaOH (0.5% wt of oil) in methanol (oil to methanol; 1:3 mol/mol ratio) was added and stirred at 65 ºC for complete conversion. The product was washed and dried following the standard procedure. The weight of product was 242.5 g (97%). Transesterification was carried out thrice and the yields obtained are 97±0.5%.

3. Results and Discussions

Palash seeds were soxhlet extracted using hexane as solvent. The oil content was found to be 20%. The physico-chemical properties of the oil were determined using standard procedures like AOCS, ASTM and IUPAC. The free fatty acid content of palash seed oil was about 4.0%. Phosphorous content of palash oil was found to be 557 ppm which accounted for higher content of phospholipids. The physico-chemical properties of palash seed oil is given in Table 1. Palash seed oil contains of 32.8% of saturated fatty acids comprising of palmitic, stearic, arachidic, behenic and lignoceric acids. 65.4 % of unsaturation comprising of oleic, linoleic and linolenic acids. The fatty acid composition is tabulated in Table 2. The GC chromatogram of palash seed oil is given in Fig 1.

Table 1. Physico-chemical properties of palash seed oil

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free fatty acids (wt %)</td>
<td>4.0</td>
<td>AOCS Ca 5a-40</td>
</tr>
<tr>
<td>Iodine value (g/100g)</td>
<td>75.3</td>
<td>AOCS Cd 1-25</td>
</tr>
<tr>
<td>Saponification value</td>
<td>171.4</td>
<td>AOCS Cd 3-25</td>
</tr>
<tr>
<td>Unsaponifiable matter (wt %)</td>
<td>1.17</td>
<td>AOCS Ja 6a-40</td>
</tr>
<tr>
<td>Phosphorous content (ppm)</td>
<td>557.0</td>
<td>IUPAC 2.421</td>
</tr>
<tr>
<td>Density (g/cm³) at 40 ºC</td>
<td>0.8978</td>
<td>ASTM D4052</td>
</tr>
<tr>
<td>Viscosity (cSt) at 40 ºC</td>
<td>42.3</td>
<td>ASTM D445</td>
</tr>
<tr>
<td>Calorific value (K cal/kg)</td>
<td>8358</td>
<td>ASTM D240</td>
</tr>
</tbody>
</table>

Table 2. Fatty acid composition of palash seed oil

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Composition (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic (16:0)</td>
<td>24.4</td>
</tr>
<tr>
<td>Stearic (18:0)</td>
<td>4.7</td>
</tr>
<tr>
<td>Oleic (18:1)</td>
<td>23.8</td>
</tr>
<tr>
<td>Linoleic (18:2)</td>
<td>40.4</td>
</tr>
<tr>
<td>Linolenic (18:3)</td>
<td>0.6</td>
</tr>
<tr>
<td>Arachidic (20:0)</td>
<td>0.8</td>
</tr>
<tr>
<td>Gondoic (20:1)</td>
<td>0.6</td>
</tr>
<tr>
<td>Behenic (22:0)</td>
<td>2.9</td>
</tr>
<tr>
<td>Lignoceric (24:0)</td>
<td>1.0</td>
</tr>
</tbody>
</table>
The fatty acid composition was found comparable with that reported by Prasad et al. [34], but the saturated fatty acid content was found less compared to that reported by Bringi [35].

The oil being high in phosphorous content (557 ppm) was subjected to degumming to obtain degummed oil with low content of phospholipids. Degumming helps in reducing the problem of emulsification during the removal of glycerol from biodiesel. As the oil contained 4% FFA, a two stage process acid esterification followed by alkaline transesterification, was employed to produce biodiesel.

The biodiesel prepared from degummed palash seed oil, was evaluated for physico-chemical and fuel properties like methyl ester content [36], acid number [26], phosphorous content [30], iodine value [27], kinematic viscosity [32], density [31], flash point [37], micro carbon residue [38], presence of Na & K metals [39], calorific value [33], oxidation stability [40] and copper strip corrosion [41] by following standard methods (Table 3). The properties were compared with standard specifications recommended by ASTM D 6751 and EN 14214. Methyl ester content of biodiesel showed 96.7%. Acid value of the biodiesel was found to be 0.45.

Table 3. Physico-chemical and fuel properties of biodiesel prepared from degummed palash seed oil in comparison with ASTM and EN standard specifications

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
<th>ASTM D6751</th>
<th>EN 14214</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl ester content (wt %)</td>
<td>96.7</td>
<td>-</td>
<td>96.5 min</td>
<td>EN 14103</td>
</tr>
<tr>
<td>Acid number</td>
<td>0.45</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>AOCS Ca 5a-40</td>
</tr>
<tr>
<td>Phosphorous content (ppm)</td>
<td>2.4</td>
<td>≤10</td>
<td>≤10</td>
<td>IUPAC 2.421</td>
</tr>
<tr>
<td>Iodine value (g/100g)</td>
<td>74.9</td>
<td>-</td>
<td>≤120</td>
<td>AOCS Cd 1-25</td>
</tr>
<tr>
<td>Kinematic viscosity at 40 °C (cSt)</td>
<td>4.8</td>
<td>1.9 to 6.0</td>
<td>3.5 to 5.0</td>
<td>ASTM D445</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.86</td>
<td>-</td>
<td>0.86 to 0.90</td>
<td>ASTM D4052</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>149.5</td>
<td>&gt;130</td>
<td>&gt;120</td>
<td>ASTM D93</td>
</tr>
<tr>
<td>Micro carbon residue (%)</td>
<td>Nil</td>
<td>0.05 max</td>
<td>0.3 max</td>
<td>ASTM D 4530</td>
</tr>
<tr>
<td>Group I (Na and K) (ppm)</td>
<td>4.52</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>EN 14538</td>
</tr>
<tr>
<td>Calorific value (K Cal/Kg)</td>
<td>8174</td>
<td>-</td>
<td>-</td>
<td>ASTM D240</td>
</tr>
<tr>
<td>Oxidation stability (h)</td>
<td>3.81</td>
<td>3 h min</td>
<td>6 h min</td>
<td>EN 14112</td>
</tr>
<tr>
<td>Copper strip corrosion</td>
<td>1a</td>
<td>No. 3 max</td>
<td>No. 1 max</td>
<td>ASTM D130</td>
</tr>
</tbody>
</table>

The properties like ‘P’ content (2.4 ppm), iodine value (74.9), kinematic viscosity (4.8 cSt), density (0.86 g/cm³) and flash point (149.5 °C) were well within the range of standard specifications recommended by ASTM and EN. Microcarbon residue is an important property which indicates the choking tendency of engines. This is the measure of residual carbon that remains after combustion. Hence, the oil was analysed for micro carbon residue and found to be nil. Oxidative stability is an important issue which affects the biodiesel quality during extended storage [42]. Oxidative stability was determined using rancimat and was found to be 3.81 h, well within the range of ASTM specifications, however, the value was found lower compared to EN specifications. Copper corrosion is another important property which is used to detect the corrosiveness to copper for fuels and solvents. The corrosiveness of the biodiesel (1a) was found to be well within the ASTM and EN specifications. The remaining properties like presence of Na and K metals (4.52 ppm) and calorific value (8174 K cal/Kg) were also determined using standard methods and found to be in the required range. Though there are reports on biodiesel preparation from non-conventional oils [18, 19], there is no literature on the use of palash seed oil for biodiesel preparation. Overall, the physico-chemical and fuel properties (Table 3) were well within the range of standard specifications.

4. Conclusion

Biodiesel was prepared from degummed palash seed oil using a two-step process, acid catalyzed esterification followed by base catalyzed transesterification. The physicochemical and fuel properties of palash biodiesel were critically evaluated using standard methods specified by AOCS, ASTM and EN. The properties were compared with ASTM D 6751 and EN 14214 standard specifications and found to be within the specified limits. However, the oxidation stability of palash biodiesel is 3.81 h, which lies well within the ASTM Specifications but does not match with EN Specifications. Therefore based on the properties, palash seed oil can be exploited as a potential feedstock for biodiesel preparation.

Acknowledgements

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References


[34] R.B.N. Prasad, Y. Nagender Rao, S. Venkob Rao, “Phospholipids of palash (Butea monosperma), papaya (Carica papaya), Jangli badam (Sterculia foetida), coriander (Coriandrum sativum) and carrot (Daucus carota) seeds”, J. Amer. Oil Chemists’ Society, vol. 64, 1424-1427.


