Palm Fatty Acid Distillate based biodiesel: characterization and Emission analysis

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Biodiesel obtained from the acid catalyzed esterification and trans-esterification of palm fatty acid distillate (PFAD) was characterized using gas chromatographic and Fourier transform infrared spectroscopic analyses. Physico-chemical and thermal properties of the biodiesel were evaluated and compared in relation to that of conventional petro-diesel following ASTM and Indian standards. The PFAD-biodiesel blended with different proportion of petro-diesel was also subjected to performance and emission tests at varying loads in order to evaluate its actual performance, when used in a four stroke diesel engine. Exhaust gas analysis showed appreciable reduction of CO₂ and hydrocarbons as against the unblended petrodiesel, although reduction of CO was marginal.

Keywords: Biodiesel; FFA; PFAD; esterification; emission.

Introduction
A plethora of feed stocks including most common vegetable oils (e.g., soybean, cottonseed, palm, peanut, rapeseed/canola, sunflower, safflower, coconut) and animal fats (usually tallow) can be used for the production biodiesel¹,². However, due to the higher cost of raw vegetable oils, the production cost of biodiesel gets exorbitantly high posing a deterrent towards its commercial viability. Palm oil is one of the most widely used and versatile vegetable oils in the world. During the fatty acid stripping and deodorization stages of the palm oil refining process, a lower-value by-product, known as Palm Fatty Acid Distillate (PFAD) is generated. PFAD consists of 85–95% fatty acids and 5–15% triglycerides, both of which are available for biodiesel production. A number of works with PFAD as the feed stock for biodiesel are cited in literature using catalytic³, ⁴ as well as non catalytic esterification⁵,⁶. The price of PFAD is much cheaper than other refined oils which are currently the major feed stocks for most of the biodiesel plants. Besides, the quality control of biodiesel is of paramount importance in view of its commercialization and market acceptance. American Society of Testing Methods (ASTM) has prescribed certain tests and their limits for diesel fuel to be used in CI engines. For any alternative fuel to be suitable for long-term engine operation without engine modifications, it must be in conformity or within close range to these ASTM permissible limits. Production of biodiesel from PFAD via esterification using a novel catalyst, superphophoric acid, and effect of various physico-chemical parameters thereon have been reported elsewhere by the authors⁷. Hence, in the present work, we report the characterization of PFAD-biodiesel in terms of various physical, chemical and thermal properties. Gas chromatographic and infrared spectroscopic analyses were carried out. The fuel properties were critically analyzed and compared with the American standards as well as Indian petro-diesel standards. The PFAD-biodiesel was blended with petrodiesel in different proportions and tested in an engine to evaluate the emission profile for assessing its suitability as a fuel in diesel engines.

Materials and Methods

Chemicals used

PFAD (FFA: < 90, moisture content 0.50 %, density 870 kg/m³ and saponification value 210.37 mg KOH/g ) was procured from Gujarat Ambuja Exports Limited, Kadi, Gujarat. Super phosphoric acid and methanol were purchased from S. D. Fine Chemicals Limited, Baroda, Gujarat, India. The super phosphoric acid used was a concentrated grade of phosphoric acid (85% P₂O₅) with density 2.05 g/cm³ and boiling point 530°C. All other chemicals used in this study were of AR grade, supplied by Merck, India and were used as received without further purification. Deionized
water (resistivity 18 MΩ·cm$^{-1}$ at 25 °C) was used for preparing stock solution.

**Fatty acid profile of the PFAD**
The fatty acid profile of the PFAD and PFAD-biodiesel was determined by gas chromatography (Model: GC-2010 Shimadzu, Japan) with flame ionization detector (FID) and capillary column (ZB-5HT Inferno, 15 m × 0.32 mm × 0.10 µm). The formed methyl ester was identified by comparing its retention time to the retention time of standard methyl ester of fatty acid. The relative percentage of the fatty acid was calculated on the basis of the peak area of a fatty acid species to the total peak area of all the fatty acids in the oil sample.

**Fourier transform infrared spectroscopy**
The surface organic functional groups of PFAD and PFAD-biodiesel were studied by the Fourier transform infrared spectroscopy (Perkin Elmer Spectrum GX). The spectra were recorded from a wave number of 400 – 4000 cm$^{-1}$ at a resolution of 4.0 cm$^{-1}$ with an acquisition time of 1 min. At least 2 replicates were obtained for every sample type without applying any baseline corrections.

**Experimental details**
The schematic of experimental set up and the procedure have been described elsewhere. Different oil to methanol ratios ranging from 1:8 to 1:12 were employed, and the catalyst amount was varied between 5 to 9% by weight and temperature in the range 50 to 70°C. The progress of the reaction was monitored by measuring the elimination of the FFAs by way of acid value using American Oil Chemists’ Society Official Method (AOCS Ca 3a–63 for Acid Value, AOCS, 1990). Each experiment was conducted in triplicate and the data reported as mean ± standard deviation.

**Exhaust gas analysis of biodiesel blends**
Biodiesel blends of different combination were used in a four-stroke diesel engine (Model VW2, single cylinder, 5 hp, 1500 rpm; fuel injection pressure:185 kg/cm$^2$) and the exhaust gases were analyzed using a Technovation gas analyzer by measuring gas concentrations in the sample cell by using the unique Infra Non-Dispersive-Red (NDIR) absorption spectra of each particular gas of interest.

**Results and Discussion**

**GC and FTIR analysis**
The chromatograms of the GC analysis of PFAD oil and PFAD-Biodiesel (not shown) indicate the distinct presence of three major and several minor peaks. The major peaks correspond to the presence of palmitic acid (40.31%), oleic acid (41.01%) and Linoleic acid (9.99%), whereas the minor peak stands for stearic (3.26%). In general, there are three main types of fatty acids that can be present in a triglyceride: saturated (Cn: 0), monounsaturated (Cn: 1) and polyunsaturated with two or three double bonds (Cn: 2, 3). The chromatogram in the present study reveals that PFAD predominantly contains saturated palmitic acid (C16:0) and stearic acid (C18:0); and monosaturated oleic acid (C18:1) along with polysaturated linoleic acids (C18:3). The initial acid value, a measure of the FFA content of the oil, was found to be 177.49 mg KOH/g corresponding to FFA level of 89.19%, which was far above the 1% limit for satisfactory transesterification reaction using alkaline catalyst. Therefore, FFAs were first converted to esters in a pretreatment process with methanol using super phosphoric acid as an acid catalyst. Esterification and trans-esterification does not alter the fatty acid composition of the feedstock and this composition plays an important role in some critical parameters of the biodiesel, as cetane number and cold flow properties. This has been discussed little later.

The biodiesel produced from palm fatty acid distillate was characterized using FT-IR spectroscopy. FTIR spectra showed characteristic bands of fatty acid methyl ester at 3000–2853 cm$^{-1}$ equivalent respectively to asymmetric and symmetric CH$_3$ stretching vibration (–CO–O–CH$_3$), 1459 cm$^{-1}$ equivalent respectively to asymmetric CH$_3$
deformation vibration, 1169 cm\(^{-1}\) corresponding to rocking CH\(_3\) vibration and 1244 – 1015 cm\(^{-1}\) equivalent to stretching vibration of the C–O ester groups\(^{17-19}\). This result reflects the conversion of fatty acid and triglycerides to methyl esters. FTIR determination of FFAs may be based on measurement of their characteristic functional group absorption at 1711 cm\(^{-1}\) \(\nu(C = O)\) of dimerized carboxylic acid groups.

PFAD Biodiesel characterization

Comparison of various characteristics of PFAD biodiesel with petro-diesel and ASTM D6751 standard are presented in Table 1. Some general parameters like specific gravity, API gravity, kinematic viscosity and content of sulfur, mainly depend on the choice of vegetable oil and cannot be influenced by different production methods or purification steps. The process of esterification brings about a radical change in the density of PFAD as a result the obtained biodiesel has almost similar density to that of petrodiesel\(^{21}\). PFAD biodiesel was miscible in any proportion with that of mineral diesel oil. The optimized blend of biodiesel has density very close of diesel oil. Among the general parameters for biodiesel, viscosity controls the characteristics of the injection from the diesel injector. The viscosity of fatty acid methyl esters is important to control within an acceptable level to avoid negative impacts on fuel injector system performance. The process of esterification and transesterification reduced the viscosity from 10.75 to 5.4 mm\(^2\)/s. This achievement paved the way to use the produced biodiesel without any engine modifications. The flash point, however, strictly corresponds to the content of methanol and the viscosity correlates with the content of unreacted triglycerides\(^{22}\). Table 2 reveals that PFAD-biodiesel obtained in present study has a higher cetane number than petroleum diesel oil. Even 20 percent blend of biodiesel showed improvement in cetane number. It is well known that biodiesel cetane number depends on the feedstock used for its production\(^{24}\).

### Table 1–Property comparison of PFAD biodiesel with petro-diesel and ASTM D6751 standard

<table>
<thead>
<tr>
<th>Fuel properties</th>
<th>PFAD Biodiesel (present study)</th>
<th>Petro-diesel (IS 1460-2005(^{1}))</th>
<th>ASTM D6751</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity (kg/m(^3) at 15°C)</td>
<td>862</td>
<td>820-860</td>
<td>860-900</td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C (mm(^2)/s)</td>
<td>5.4</td>
<td>2.0-5.0</td>
<td>4-6</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>190</td>
<td>66</td>
<td>100-170</td>
</tr>
<tr>
<td>Cloud point, °C</td>
<td>18</td>
<td>-</td>
<td>–3 to 12</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>16</td>
<td>3-15</td>
<td>–15 to 10</td>
</tr>
<tr>
<td>Acid value (mg KOH/g)</td>
<td>0.91</td>
<td>0.01-0.2</td>
<td>0.8 max.</td>
</tr>
<tr>
<td>Carbon residue wt%</td>
<td>1</td>
<td>0.3-1.5</td>
<td>0.77</td>
</tr>
<tr>
<td>Degree API</td>
<td>32.65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Saponification Value (mg KOH/g)</td>
<td>210.375</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Iodine Value (Wijs gm/100gm)</td>
<td>55.835</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>59.37</td>
<td>45-51</td>
<td>48-60</td>
</tr>
</tbody>
</table>

\(^{1}\) Indian Standard, Automotive Diesel Fuel specifications, IS 1460-2005.

### Table 2–Physico-chemical properties of PFAD biodiesel and its blend with petro-diesel

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flash Point °C</th>
<th>Fire point °C</th>
<th>Density (kg/m(^3))</th>
<th>Kinematic Viscosity (mm(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel</td>
<td>56</td>
<td>58</td>
<td>831</td>
<td>2.11</td>
</tr>
<tr>
<td>PFAD Biodiesel</td>
<td>186</td>
<td>190</td>
<td>862</td>
<td>5.4</td>
</tr>
<tr>
<td>B10</td>
<td>74.5</td>
<td>75.1</td>
<td>834</td>
<td>2.55</td>
</tr>
<tr>
<td>B20</td>
<td>86.4</td>
<td>89.3</td>
<td>838</td>
<td>2.67</td>
</tr>
<tr>
<td>B30</td>
<td>99</td>
<td>105.4</td>
<td>842</td>
<td>2.99</td>
</tr>
<tr>
<td>B40</td>
<td>118.6</td>
<td>125.5</td>
<td>847</td>
<td>3.21</td>
</tr>
<tr>
<td>B50</td>
<td>130</td>
<td>138.5</td>
<td>850</td>
<td>3.51</td>
</tr>
</tbody>
</table>
flash point much above that of diesel oil, making it a preferable choice as far as safety is concerned. Table 2 shows the Physico-chemical properties of PFAD biodiesel and its blend with petro-diesel.

**Emission analysis**

Exhaust gas analysis was carried out on an engine using diesel and biodiesel blends separately as fuels at 1500 rpm. Emission test was conducted on various biodiesel blends to assess the emission level of CO₂, CO and hydrocarbons (HC). Five different combination of diesel-biodiesel blends, namely B-0, B-10, B-20, B-30 and B-50 were used in the present study. The baseline data were generated using unblended petro-diesel. It was observed that percentage emission of CO₂ increased with the increase in engine load for all the combinations of biodiesel blends as well as unblended petro-diesel. However, the magnitude of CO₂ emission was appreciably less in all blends tested compared to the unblended petro-diesel regardless of engine load. Among all the blends, B-30 had the least percent emission of CO₂ in the exhaust gas. CO₂ emissions of B-10 were close to petro-diesel. On the other hand, no significant trend could be observed in the emission profile of CO, which largely remained same for most of the blends, although there was marginal increase in CO content of B-10 blend (data not shown). Factors causing combustion deterioration (such as high latent heat of evaporation) could be responsible for the increased CO emission. CO emission increases gradually with blending of higher concentration of biodiesel to diesel. It is worth mentioning that the impact of diesel–biodiesel blends on CO emissions varies with engine operating conditions and was not conclusive. Emission profile of hydrocarbons with different blends of PFAD-biodiesel and petro-diesel as a function of engine load revealed that there was considerable reduction of hydrocarbon emission for all the blends compared to unblended petro-diesel. At the highest engine load (3 kw) under the present experimental conditions, the maximum reduction of hydrocarbon was roughly 66% for B-50, 50% for B-30 and 44% for B-20. Biodiesel contains oxygen in its structure. When biodiesel is added to diesel fuel, the oxygen content of fuel blend is increased and thus less oxygen is needed for combustion. The reduction in HC is mainly due to the result of improved combustion of biodiesel blends within the combustion period due to the presence of excess oxygen atom in biodiesel²⁹.

**Conclusion**

The high FFA level of PFAD could be reduced to the acceptable value by its pretreatment with methanol (0.08 molar ratio) using super phosphoric acid as catalyst (7% w/w) at 70°C temperature. The methyl ester which produced at optimum conditions had acceptable fuel properties and compared well with petro-diesel. It had lower carbon residue and acid number than petro-diesel, but kinematic viscosity, cetane number and flash point of biodiesel were higher as compared to petrodiesel. Analysis of exhaust gas from engine with different blends of PFAD-biodiesel and petrodiesel showed appreciable reduction of CO₂ and hydrocarbons as against the unblended petrodiesel, however reduction of CO was marginal. Production of biofuels from edible oils could result in inevitable displacement of food crops, leading to possible food scarcity and inflation of food prices. In line with the argument, palm fatty acid distillates, from palm kernel oil refinery and methanol used in this work are not edible, enabling them better raw materials to be used for biodiesel production to avoid soaring of food prices.

**Acknowledgement**

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**References**

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