Comparing the lubricity of biofuels obtained from pyrolysis and alcoholysis of soybean oil and their blends with petroleum diesel

Paulo A.Z. Suarez a,*, Bryan R. Moser a, Brajendra K. Sharma a,b, Sevim Z. Erhan a

a Food and Industrial Oil Research Unit, National Center for Agricultural Utilization Research, United States Department of Agriculture, Agricultural Research Service, 1815 N. University St., Peoria, IL 61604, USA

b The Pennsylvania State University, Chemical Engineering Department, University Park, PA 16802, USA

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A diesel-like fuel, pyrodiesel (PD), was synthesized by a pyrolysis method using soybean oil as starting material. Some physical properties of the material were studied, both neat and in blends with high-sulfur (HSD) and low-sulfur (LSD) diesel fuels, and compared with blends of biodiesel (BD) in fossil fuels. It was observed using different methods that the lubricity of biobased fuels obtained after the transesterification or pyrolysis of soybean oil is superior to LSD and HSD and also that the lubricity of diesel fuels are enhanced when either BD or PD are added. Based on the results reported herein, PD is a viable alternative to BD for use in compression-ignition engines.

1. Introduction

Since the development of the diesel engine, the use of fatty materials and their derivatives have been pointed out as possible fuels. Indeed, the use of neat fats and oils as well as fatty acid mono-alcohol esters (biodiesel, BD) and hydrocarbons (pyrodiesel, PD) obtained after the cracking of fatty materials have been proposed as suitable fuels for these engines [1]. Note that, although direct use of vegetable oil was demonstrated as feasible in the first half of the 20th century [2], due to their high viscosity, density, and deposit buildup, engine failure can occur in modern engines. However, the higher price of these materials and the low price of petroleum and its derivatives did not encourage the use of fatty materials as, except in periods when crude petroleum was in short supply [3].

More recently, concerns about petroleum supply in the forthcoming years and global warming in the last few years have led several governments around the world to encourage the use of BD. For instance, the US government has encouraged the use of bio-based products [4] through various regulations and tax incentives, making a dramatic increase in recent years in the production and use of biobased fuels [5,6] and in the number of BD production plants in operation and under construction [7]. Another example is the Brazilian Government, who has launched a BD program that aims to substitute through mandate all diesel consumed with B2 (blend of 2% BD in fossil diesel) after January, 2008, and B5 after January, 2013 [3]. This program has also stimulated the production of biodiesel and the construction of several plants around the country [3].

There are different methods to produce fuels from vegetable oil. The most common method is alcoholysis, also known as transesterification, where the triacylglyceride structures of oil are reacted with a mono-alcohol to produce BD. This reaction can be carried out using Bronsted [8] or Lewis [9–11] acids [9], Bronsted [12,13] or Lewis [14] bases, or enzymatic [15], or heterogeneous [16–18] catalysis, or under supercritical conditions [19]. Although BD is the most popular route, it has some drawbacks, such as high quality raw-material is needed and also the requirement of a large amount of alcohol. The presence of water in the reaction leads to hydrolysis of the different esters, with is critical in base catalysis because of the possibility of soap formation. On the other hand, at least 3 mol of alcohol are consumed for every mol of triacylglyceride reacted, and an excess is usually used to obtain a complete reaction.

* Corresponding author. Present address: LMC-IQ, Universidade de Brasilia, CP 4478, CEP 70919-970, Brasilia-DF, Brazil.
E-mail addresses: psuarez@unb.br (P.A.Z. Suarez), Sevim.erhan@ars.usda.gov (S.Z. Erhan).

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For these reasons, alternative routes to a biobased fuel have been studied, such as the cracking of fatty materials. Pyrolysis or cracking of oils and fats is well studied [20–23], and a recent report described a method for the synthesis of PD with physical and chemical properties that match diesel fuel specifications [24]. The main advantage of this process is that it is possible to use a variety of feedstocks, both edible and inedible. The process has shown its industrial applicability as well. Indeed, the use of the products as fuels dates back 60 years [25,26]. More recently, fuel of this type made from animal fats may soon be incorporated into a large industrial scale process in a joint collaboration between a food industry giant and a large petrochemical producer in USA [27], and has already been done by a large petroleum company in Brazil [28].

As already observed elsewhere, the main products of the cracking reaction is a mixture of hydrocarbons and oxygenated compounds, like carboxylic acids, ketones, aldehydes, as well as water and carbon mono- and di-oxides [24]. However, there are other studies which should be performed before the product can be used as fuel.

An important property of the fuel is the lubricity. In the last few decades, due to environmental concerns, more rigid regulations have been implemented in several countries about the emissions of diesel engines. To minimize the SO\(_2\) emissions the sulfur content in diesel was decreased, which has lead to failure of engine parts, as indicated by several reports in the literature [29–33]. For these reasons, the low-sulfur diesel had to be blended with additives or other fuels with superior lubricity in order to regain lubricity [29]. In this sense, BD and other fatty materials have been proposed as excellent alternatives to enhance the lubricity of low-sulfur diesel, as indicated by several reports in the literature [29–33].

Herein we report our study on the lubricity of PD made from a pyrolysis process which was reported earlier utilizing as feedstock refined soybean oil and its blends with low- and high-sulfur diesel (respectively, LSD and HSD). The results are compared to a similar set of experiments done using commercially available soybean oil methyl esters (BD). The density and viscosity, which are other properties related to the proper function of the injectors and pumps, were also studied and are related here.

## 2. Experimental

### 2.1. Materials

Alkali refined soybean oil was obtained from ADM packed oils (Decatur, IL) and was used as received without further purification. BD (methyl soyate; trade name SoyGold) was obtained from Ag environmental products (Lenexa, KS). Low- and high-sulfur petrodiesel fuel (respectively, up to 15 ppm for LSD and 50 ppm for HSD) were obtained from Chevron-Phillips (Pascagoula, MS). All other materials were acquired from Aldrich Chemical Company (Milwaukee, WI).

### 2.2. Pyrolysis experiments

Diesel-like pyrolytic fuel (PD) was obtained after pyrolysis of soybean oil followed by atmospheric distillation of the product, using an adapted method from one published elsewhere [24]. Pyrolysis experiments were carried out at temperatures ranging from 350 to 400 °C using a round bottomed three neck 5 L flask equipped with a side condenser. The soybean oil (2 L) was introduced in the flask and then heated by an external electric resistance heating mantle. When the temperature inside the reactor achieved 350 °C, the vegetable oil was pyrolyzed, vaporized, and a vapor feed left the flask by the upper neck adapted to the side condenser at temperatures ranging from 200 to 250 °C. Next, the vaporous feed was passed through the condenser and, as a result, two liquid fractions were obtained in the collector: an aqueous fraction and an organic fraction. The yield in the organic fraction was approximately 80% related to starting soybean oil. These fractions were separated by decantation and the organic phase was distilled using standard laboratory techniques. The fractions that distilled bellow 200 °C were discharged and those that distilled above this temperature, approximately 60% of the starting material, were recovered and used as PD.

### 2.3. Samples preparation

Twenty-four samples corresponding to BD and PD blends in petroleum diesels HSD and LSD, were prepared at room temperature using a balance (Mettler PM2000, ±0.01 g) and their compositions are displayed in Table 1.

### 2.4. Viscosity and density measurements

Kinematic and absolute viscosities and density, at 20 and 40 °C, were determined following ASTM method D7042 using an Anton Paar Stabinger Viscometer model SVM3000 (Ashland, VA, USA). Each sample was run in triplicate and an average value is reported. The precision is with in the limits of ASTM method specification.

#### 2.4.1. High frequency reciprocating rig (HFRR) method

Lubricity determinations were made at 60 °C (controlled to less than ±1 °C), according to ASTM D 6079 using a PCS Instruments (London, UK) Model HFRC80 high frequency reciprocating rig (HFRR) lubricity tester. At the conclusion of each test the ball was visually inspected for wear and the dimensions of an observed wear scar (\(\mu\text{m}\)) on the ball were averaged. All wear scar data are the averages of two replicates.

### 2.5. Friction measurement by ball-on-disk method

Boundary lubrication properties of the different blends described in Table 1 were studied using a multi-specimen friction

<table>
<thead>
<tr>
<th>Sample</th>
<th>BD (g)</th>
<th>PD (g)</th>
<th>SD (g)</th>
<th>LSD (g)</th>
<th>HSD (g)</th>
</tr>
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<tr>
<td>BD</td>
<td>200</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
<td>200</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>LSD</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>200</td>
<td>–</td>
</tr>
<tr>
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<td>–</td>
<td>–</td>
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</tr>
<tr>
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<td>–</td>
<td>190.28</td>
<td>–</td>
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<tr>
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<td>–</td>
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<tr>
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<td>–</td>
<td>100.27</td>
<td>–</td>
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<td>–</td>
<td>179.96</td>
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<td>4.00</td>
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<td>159.96</td>
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</tr>
<tr>
<td>LSD/BD50</td>
<td>–</td>
<td>100.34</td>
<td>–</td>
<td>100.00</td>
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</tbody>
</table>

Table 1: Blends (% w/w) prepared and used in this work: high-sulfur and low-sulfur content diesel (HSD and LSD, respectively); biodiesel (BD) and diesel-like fuel prepared from soybean oil (PD).
measurement apparatus of FALEX (Sugar Grove, IL). Ball-on-disk experiments (1018 steel disk, Rc 15–25) were carried out under low speed 6.22 mm s\(^{-1}\) (5 rpm) and high load 181.44 kg at 25 °C. Measurements of coefficient of friction (CoF) and torque were made in each case. The CoF values reported are averages of two or three independent experiments and the standard deviation observed was ±0.02.

3. Results and discussion

Refined soybean oil was pyrolyzed and distilled using a method previously reported and the results gave a material (PD) similar to that obtained in the past [24]. The density of BD and PD and their blends with LSD and HSD at 20 and 40 °C are shown, respectively, in Fig. 1a and b. As can be seen, both BD and PD have densities higher than LSD and HSD and the densities of the biofuel/fossil fuel blends grows linearly with increasing composition of PD or PB in LSD or HSD. It is worth mentioning that at both temperatures PD presents a lower density than BD and that the density of PD is very close to the density of HSD.

The dynamic viscosity (\(\eta\)) and the kinematic viscosity (\(\nu\)) of BD and PD and their blends with LSD and HSD at 20 and 40 °C are shown, respectively, in Figs. 2 and 3. As can be seen, both PD and BD have \(\eta\) and \(\nu\) higher than LSD and HSD and are considerably higher than the standard value (\(\nu\): 1.3–2.4 mm\(^2\)/s at 40 °C) for petrochemical diesel contained within ASTM D 975 [34], but both biofuels meet the ASTM D 6751 requirement (\(\nu\): 1.9–6.0 mm\(^2\)/s at 40 °C) set for biodiesel [35]. However, it is worth mentioning that
blends with up to 50% biobased fuels match the standard for diesel fuel [34]. Contrary to the behavior of density, the viscosities did not grow linearly with the composition of PD or PB for all blends. It is important to highlight that at 20°C and low biofuel content, a discontinuity was observed in the slope for both η and ν, but this behavior was not observed at 40°C.

The high frequency reciprocating rig (HFRR) data (60°C and 50% humidity) of BD and PD and their blends with LSD and HSD are shown in Fig. 4. As expected, LSD exhibited inferior lubricity in comparison to HSD, as evidenced by longer wear scar lengths for LSD in comparison to HSD. Both BD and PD have superior lubricity to HSD, and PD exhibited a longer wear scar than BD, which was expected since these biofuels, especially BD, present high oxygen content in their compositions. Obviously, all biofuels and blends match the ASTM standard for diesel fuel [34]. Wear scar data behaves differently when comparing BD and PD blends in either LSD or HSD. Indeed, whereas wear scar length continuously decreased with increasing amount of BD in LSD or HSD, for PD blends in LSD or HSD was observed a significant decrease for blends containing less than 10% of biofuel and then the value increased with increasing amount of PD. However, unexpectedly, blends of BD and PD in LSD had smaller wear scar lengths than the corresponding blends in HSD. Logically, the opposite should be true, i.e., blends of HSD should have smaller wear scar lengths than similar blends with LSD. It was noticed that HSD and blends thereof in either biodiesel or pyrodiesel tended to deposit a small amount of black residue in the sample well during the experiment. The HFRR method holds the sample at 60°C for 75 min. Perhaps elevated temperature for extended times results in sample decomposition, thus compromising data integrity. However, this hypothesis seems unlikely, as one would imagine that HSD should possess sufficient thermal stability to survive the experiment unscathed.

In Fig. 5 are shown the coefficient of friction data for HSD, LSD, BP, PD and the different fossil/biobased fuels blends. As can be seen, friction measurement by the ball-on-disk method also showed that PD and BD present better lubricity than either HSD or LSD. Different from the results obtained using the HFFR method, similar behavior was exhibited by BD and PD blends in either LSD or HSD. Indeed, for all cases was observed a accentuated decrease in the coefficient of friction (CF) for low biobased fuel content blends and then the CF gently increased or stayed constant with increasing amount of BD or PD in LSD or HSD.

4. Conclusion

In summary, we have shown using different methods that the lubricity of biobased fuels obtained after the transesterification or pyrolysis of soybean oil are superior to either LSD or HSD. We have also observed that the lubricity of diesel fuels are enhanced when either BD or PD are added, strongly suggesting that both biofuels are suitable as additives for improving this property in fossil fuels. Thus, it is possible to assume after this work that the use of fuels from biomass has great potential, at least blended with fossil fuels. It is also interesting to note that the use of pyrolysis products has a couple of potential advantages, being the biggest advantage the fact that there is no requirement for a large amount of alcohol and correspondingly no production of waste glycerol.
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References


