Comparative Study of Biodiesels Produced from Unrefined Vegetable Oils

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Abstract: Biodiesels were prepared according to standard methods from unrefined oils of cashew nut and palm kernel cultivars and compared for differences in physical properties important for fuel performance. Dynamic viscosity, kinematic viscosity and density were measured from 100 to 15 ^{o}C, and differences in these physical properties occurred more frequently at lower temperatures when comparing the different cultivars. It was observed that their was no meaningful correlation among the biodiesels fatty acid profiles and either fuel viscosity or density as opposed to what was obtained for data of oil feedstocks. The cultivars data were also compared to biodiesel from soy. Biodiesel produced from cashew nut cultivar gives the best performance for use in diesel engines.

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1. Introduction

Biodiesel can be produced by the transesterification of a feedstock containing triglyceride with short-chained alcohols (Fukuda et al. 2001; Ma and Hanna, 1999). The alkyl esters of fatty acids produced during this reaction is referred to as biodiesel. In the reaction, glycerin is obtained as a byproduct. Biodiesel has wide applications as alternative fuel for use in unmodified, standard diesel engines. In many of these applications biodiesel can be used alone, or blended with petroleum based diesel.

Some of the important benefits derivable from biodiesel are: (1) renewability of the fuel, (2) clean burning in most emission engines, (3) compatibility with current fuel engine systems, (4) lubricity of diesel blends containing biodiesel, and (5) reduction on petroleum dependence for fuel while potentially creating domestic jobs (Fukuda et al. 2001; Goodrum and Geller, 2005).

Industries that produce biodiesel have as their pressing concern a stable supply of low-cost oil feedstocks capable of yielding a quality biodiesel product competitive in price with petroleum based diesel fuels. Palm kernel and cashew nuts represent some of the vegetable oil sources available in abundant commercial quantities for investigative exploitations for biodiesel generation. Meaningful results obtained may serve as tools for decision making regarding the production of biodiesel. The goal of the present study is on the performance of biodiesel produced from unrefined oils of palm kernel and cashew nuts cultivars. Essentially, farmers would be able to grow, harvest, crush, and transesterify these cultivars into usable fuel sources to offset petroleum consumption.

Comparison of the results evaluated for variation in important physical properties such as viscosity and density is made with oils from soy and their corresponding biodiesels. Significant variation was noted among these parameters. As such, the current study allows for a unique opportunity to directly compare oil feedstock quality factors with the corresponding biodiesel quality factors.

2. Materials and Methods.

Vegetable Oil Extraction

Palm kernel and cashew nuts were collected from fields located in Ogbomoso and Okitipupa, Nigeria, during the 2007 cropping season. The samples were PK-01GB, PK-02OK and CA-01GB. Refined soy oil was purchased locally. Shells of the palm kernel and cashew cultivars were removed from each sample with the aid of a sheller-separator (Hattaway, Model 4-AH). Seeds of these fruits that has been sized to ride a 0.72 cm slotted screen but not a 0.84 cm screen were kept separate for oil analysis. The seeds were preheated between 95 and 100 ^{o}C to improve efficiency of oil expression and thereafter, processed in a screw-type oil expeller (Hander, Model N52OJ). Oil was collected in 9.5 L plastic containers and allowed to settle for 48 hours at 30 ± 2 ^{o}C. Vacuum filtration was applied to the bilayer of oil to remove any unsettled particulates in preparation for further testing.

Biodiesel Production

Biodiesel was produced from 500 mL each of palm kernel and cashew nuts oil, 100 mL of methanol and 4.6 g of potassium hydroxide as a catalyst. The acid number of the oil was determined by simple colorimetric titration and excess KOH was added at proper concentration to neutralize any free fatty acids. KOH and methanol were mixed in separate containers. Oils were contained in 1 L flasks and heated to a reaction temperature of 60 ^oC, at which time the methanol/KOH solution was added and the mixture subsequently stirred for 90 min at 120 rpm. After the reaction time was complete, the mixture was transferred to a 1 L separatory funnel for 3 hours. The glycerol layer was decanted and the biodiesel was heated to 65 ^oC to remove excess methanol. The product was washed 5 times with 100 mL warm water. The final, washed product was polished by heating to 100 ^oC to remove water until boiling ceased.

Measurements

The measurements taken were the dynamic and kinematic viscosities of the biodiesels, their densities, and the fatty acid methyl ester (FAME) profile analyses. Dynamic viscosity and density were determined with the aid of a dual viscometer/density meter (Anton-Paar, SVM3000) from 100 to 15 ^oC. Density is measured to allow for the automatic calculation of kinematic viscosity. Dynamic viscosity and density were measured as a function of temperature which was automatically adjusted beginning at 100 to 15 ^oC.

The method of analyzing biodiesel has been described by Bannon et al. (1982). Samples of biodiesel from the present study were submitted to this method. Samples were diluted into hexane and analyzed by gas chromatography (GC) using an autosampler XL GC (Perkin Elmer Instruments) with a flame ionization detector (FID) and an SGE capillary column containing 70 % cyanopropyl polysil-phenylene-siloxane as the stationary phase (30 m length 0.25 mm i.d., 0.25 µm film thickness). Helium was used as the carrier gas at 1.85 mL/min. A temperature program was used with an initial temperature of 60 ^oC held for 2 min. The temperature was increased to 180 ^oC at 10 ^oC/min, then to a final temperature of 235 ^oC at 4 ^oC/min. The injector was heated to 265 ^oC and the split flow was 76.9 mL/min. The detector temperature was 265 ^oC.

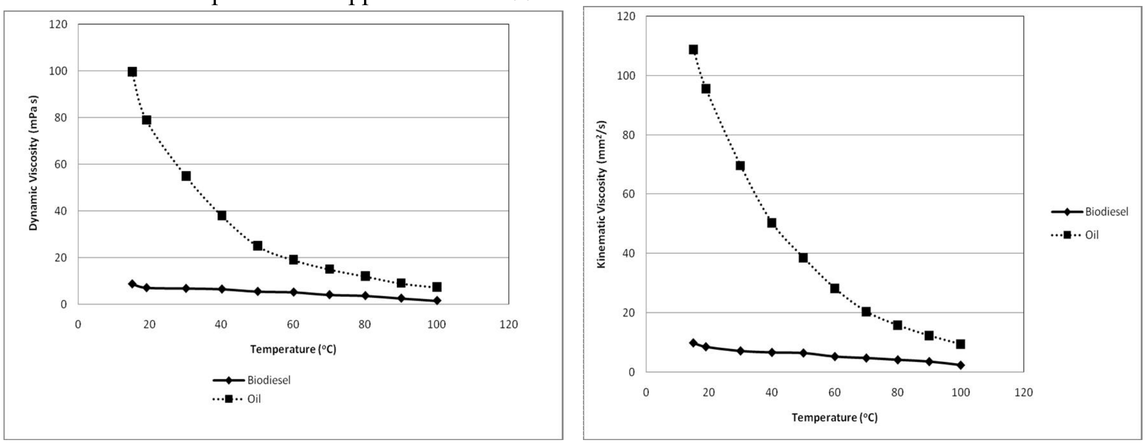
3.Results and Discussions

In this study, we have shown the fatty acid methyl esters profiles for the biodiesels produced from oils of palm kernel, cashew nuts and soy (Table 1). The cultivars PK-01GB and PK-02OK from which biodiesel were produced contain high oleic content which was approximately 80 % compared to CA-01GB which contain 60 % of oleic acid. The category “others” accounts for any trace FAMEs found in the biodiesels and is simply computed by subtracting from 100 % the summation of all the other FAME categories. For soy the relative percentage of “others” was 7.3. Soy contain roughly 8 % of C18:3 (Canakci and Sanli, 2008), which is not typically found in palm kernel and cashew nuts oils at any appreciable amount, thus 18:3 comprises the majority of the “others” category for soy.

Table 1: Average relative percentage of fatty acid methyl esters found in biodiesels prepared from oils of various vegetable cultivars and soy.

Cultivars	C16:0	C18:0	C18:1	C18:2	C20:0	C20:1	C22:0	C24:0	Others
CA-01GB	9.6	2.4	55.0	29.0	1.3	1.5	3.5	1.7	0.8
PK-01GB	5.1	1.8	80.4	4.0	1.0	2.3	2.5	1.7	1.2
PK-02OK	6.0	2.0	79.8	2.6	1.2	2.2	2.9	2.0	1.3
Soy	10.0	4.0	22.3	55.8	0.2	0.0	0.4	0.0	7.3

Seed oils are not directly utilized in unmodified diesel engines because the relatively viscous oils (as compared to standard diesel fuel) do not fully combust leading to carbon deposition in diesel engines (Geller and Goodrum, 2000; Tat and Van Gerpen, 1999). Accordingly, seed oils are converted to biodiesel essentially to reduce fuel viscosity, thereby increasing combustibility. The viscosity of a biodiesel is approximately an order of magnitude less than the corresponding oil feedstock from which the biodiesel was prepared (Joshi and Pegg, 2007; Krisnangkura et al., 2006; Tate et al., 2006). This can be illustrated for palm kernel and cashew nuts based fuel, by plotting dynamic viscosity (A) and kinematic viscosity (B) each as function of temperature for oil and biodiesel from cashew nuts CA-01GB which is depicted in Figure 1. Figure 2 and 3 show the corresponding results for oil and biodiesel from palm kernel sources (PK-01GB, PK-02OK). It should be noted that the kinematic viscosity has units of mm^2/s and is simply the dynamic viscosity divide by the density. As seen in Figures 1, 2 and 3, trends for dynamic and kinematic viscosities as a function of temperature were the same, although the magnitudes of kinematic viscosity were slightly greater when compared at the same temperature. At 15 ^oC, dynamic and kinematic viscosities for oils CA-01GB, PK-01GB, and PK-02OK were approximately 99.8 mPa s and 108.9 mm^2/s, 101.3 mPa s and 110.2 mm^2/s, 107.6 mPa s and 113.4 mm^2/s, respectively (Figures 1, 2, 3), whereas the dynamic and kinematic viscosities of the biodiesel were approximately 8.7 mPa s and 9.9 mm^2/s, 10.2 mPa s and 12.3 mm^2/s, 10.8 mPa s and 13.1 mm2/s, respectively (Figures 2, 3). Differences in oil and biodiesel viscosities (either dynamic or kinematic) were greater at lower temperatures with an approximate 91 % reduction upon biodiesel conversion at 15 ^{o}C for CA-01GB as compared to an approximate 78 % reduction at 100 ^{o}C.



A B

Figure 1: Dynamic (A) and Kinematic (B) Viscosity Response as a function of Temperature for an unrefined Cashew nut oil (CA-01GB) and the corresponding Biodiesel produced from the same oil.

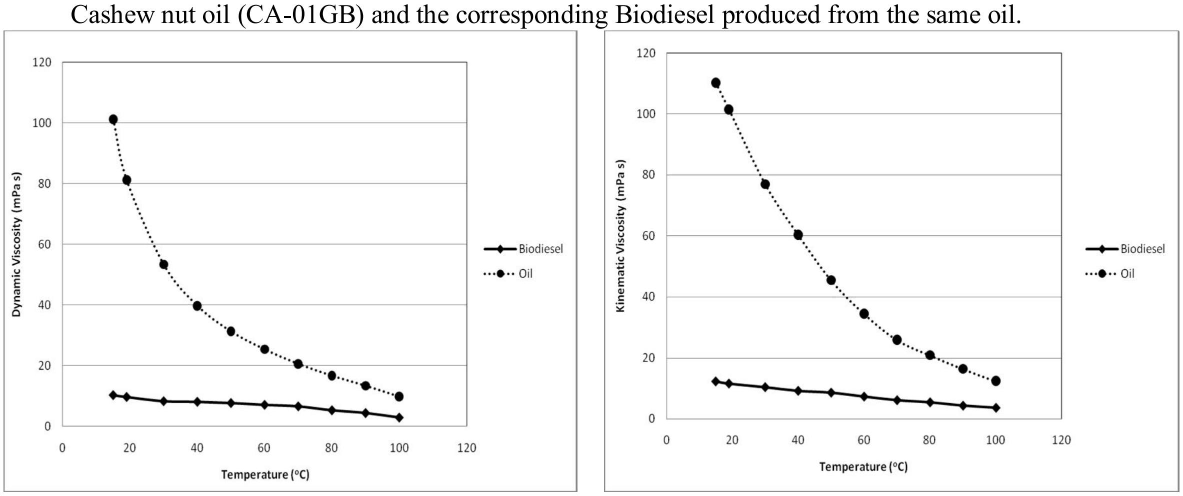


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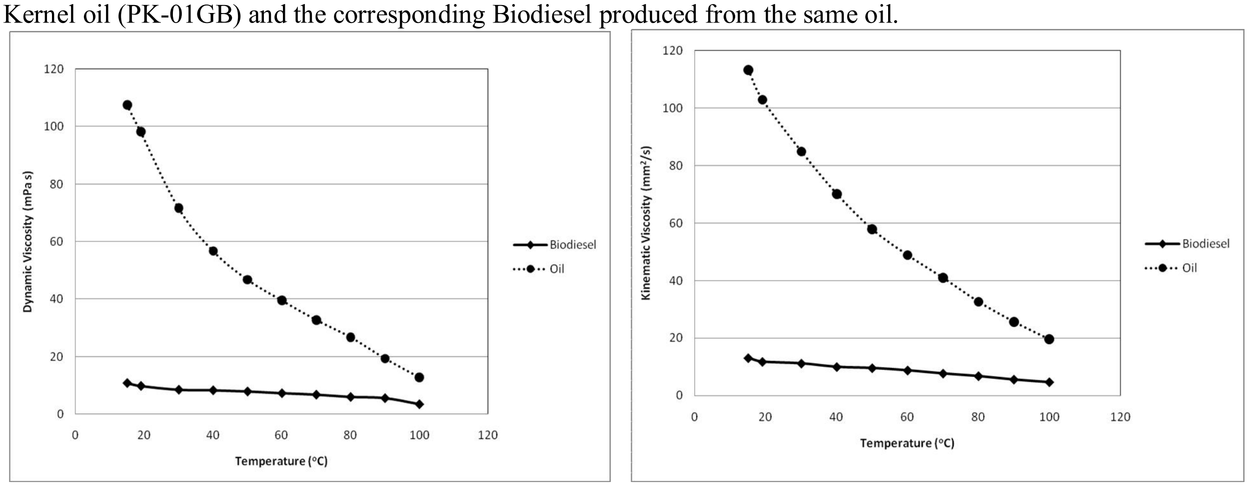
Figure 2: Dynamic (A) and Kinematic (B) Viscosity Response as a function of Temperature for an unrefined Palm Kernel oil (PK-01GB) and the corresponding Biodiesel produced from the same oil.



A B

Figure 3: Dynamic (A) and Kinematic (B) Viscosity Response as a function of Temperature for an unrefined Palm Kernel oil (PK-02OK) and the corresponding Biodiesel produced from the same oil.

Table 2: Comparison of unrefined oil and resulting biodiesel physical properties for different cultivars of vegetable fruits

	Cultivars	Oil Viscosity (mPa s)	Oil Density (g/cm^3)	Biodiesel Viscosity (mPa s)	Biodiesel Density (g/cm^3)	% Viscosity reduction	% Density reduction
100 °C	CA-01GB	7.3	0.8605	1.6	0.8205	78	5
	PK-01GB	7.5	0.8580	1.6	0.8178	79	5
	PK-02OK	7.6	0.8580	1.8	0.8216	76	4
40 °C	CA-01GB	34.5	0.8999	4.5	0.8636	87	4
	PK-01GB	36.7	0.8975	4.5	0.8612	88	4
	PK-02OK	37.2	0.8973	5.3	0.8645	86	4
15 °C	CA-01GB	99.8	0.9169	8.7	0.8818	91	4
	PK-01GB	108.9	0.9145	9.5	0.8793	91	4
	PK-02OK	110.7	0.9143	15.8	0.8842	86	3

Table 2 summarizes dynamic viscosity and density data for the three cultivars, both for the unrefined feedstocks and the corresponding biodiesels produced from the same oils. Differences in biodiesel viscosity among the cultivars were more pronounced at lower temperatures with values at 15 °C ranging from 15.8 to 8.7 mPa s for PK-02OK and CA-01GB, respectively (Table 2). Further, the reduction in viscosity upon conversion of the oils to biodiesels was approximately 90 % for all cultivars at 15 °C, whereas at 100 °C this reduction was closer to 80 % (Table 2). The densities of all the cultivars biodiesels were lower than the corresponding feedstocks; however, these differences were minor, with a typical 3 - 4 % density reduction observed at 100 °C (Table 2).

ASTM Biodiesel Standard D6751-07b states that 100 % biodiesel at 40 °C should have a kinematic viscosity between 1.9 and 6.0 mm^2/s. Kinematic viscosity is the dynamic viscosity divided by density, so for the cultivars biodiesels at 40 °C, the kinematic viscosities ranged from 6.5 (CA-01GB) to 8.1 (PK-01GB, PK-02OK).

Viscosity and density data for all the cultivars biodiesels were compared to biodiesels produced from soy, as the feedstocks is more typical within the biodiesel industry. Average kinematic viscosity for soy biodiesel at 40 °C was 4.3 mm^2/s. This indicates that a significantly lower value than all cultivars biodiesels. It is important to note that the soy biodiesel was prepared from refined oils. In contrast, all cultivars biodiesels were prepared from unrefined oils. Typical seed oil refining steps remove a number of impurities from the crude oils, namely phospholipids, which were present in the cultivars oils upon biodiesel production. Phospholipids are known to inhibit the transesterification reaction central to biodiesel production (Watanabe et al., 2002), which would likely increase the types of impurities in the final biodiesel products and potentially contribute to a higher viscosity. However, as oils were intentionally left unrefined prior to biodiesel production to replicate biodiesel production as it would occur in a small-scale production

Conclusion

The production of biodiesel from different cultivars namely cashew nut and palm kernel have been investigated. Unrefined oil from these cultivars found in different locations in Nigeria was used in the preparation of the biodiesel. The biodiesel produced have low values of dynamic and kinematic viscosities for those obtained from cashew nut oil, while the viscosities of the biodiesel from palm kernel sources were slightly higher. The viscosities of the biodiesel from cashew nut oil were within the range suitable for use in diesel engines. The present will be helpful for decision making regarding the production of biodiesel.

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