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Low temperature behavior of poultry fat biodiesel:diesel blends

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ABSTRACT

As the worldwide consumption of poultry meat rises the use of poultry fat as a feedstock for biodiesel production becomes attractive considering economical and environmental reasons. However, poultry fat biodiesel still faces some restrictions due to its poor flow properties at low temperatures. In this study ethylic and methylic poultry fat biodiesels and their blends with diesel were evaluated in terms of flow properties. Modulated Temperature Differential Scanning Calorimetry (MT-DSC) was used to understand the physical meaning of properties as Cold Filter Plugging Point (CFPP), Pour Point (PP) and Cloud Point (CP), widely used in biodiesel characterization. Based on the MT-DSC studies, it was observed that the first crystallization peak temperature had values similar to CFPP and CP. This way CP was found to be associated with the first solidified material and not with the early formation of the first nuclei, as normally reported. On the other hand, these crystals already lead to the flow decrease, as indicate by the CFPP results. PP values were close to the second crystallization peak temperature, not being related to the complete solidification of the fuel.

1. Introduction

Brazil occupies the third world position in the poultry meat production, after China and United States, with an average production estimated at 10.9 million tons per year. Occupying a leader position in terms of overseas exportation, Brazil is responsible for supplying 40% of the poultry meat world market.

Such position favors the availability of a high amount of inedible residual fats. This by-product is usually not reused by industries and traders enhancing solid waste problems and environmental pollution. The use of poultry residues as a fatty acid-rich feedstock of biodiesel production is promising since this sort of raw material is of relatively low cost, readily available, very rich in lipids and exhibits very attractive physico-chemical properties, such as high calorific power and cetane number [1–7].

The use of poultry fat biodiesel is however of limited application, mainly due to its solidification tendency, particularly in cold weathers. The presence of a high amount of saturated fatty acids in its composition is responsible for such low temperature performance as it tends to solidify even at room temperatures in cold regions. Thus, it becomes essential to evaluate the low temperature properties of biodiesel in order to gain a further insight into this problem and develop new ways to overcome these difficulties which lead to engine damage due to the presence of micro-crystals in the fuel.

Geller et al. [1] studied the viscosity variation of poultry fat biodiesel and their biodiesel/diesel blends (B20, B40, B60 and B80) after a 12-month storage period under varied temperature ranges. Viscosity alterations have been noticed particularly for B80 blends while no meaningful changes in viscosity for blends up to B60 were observed. Sediment formation was found in all blends whose amount increased with biodiesel concentration.

Rheological properties of biodiesels from poultry fat, beef tallow, lard and yellow grease were already evaluated [2,3]. It was observed that all fats showed liquid–solid transitions between 40 and 48 °C being completely liquid at 50 °C. These studies also indicated that this sort of fats exhibited pseudo-plastic behavior.

Cold flow properties, such as Cold Filter Plugging Point (CFPP), Pour Point (PP) and Cloud Point (CP) were determined in order to investigate the formation of precipitates in biodiesel/diesel blends produced from poultry fat (PFB), soybean oil and cottonseed oil. Cold flow performance is related to the saturation and unsaturation degree of fatty acids. Saturated acids were found in higher proportion in PFB comparing with soybean and cotton biodiesels leading to lower flow at higher temperatures [7].

The crystallization temperature is a very important factor to be considered for applications in low temperature environments. Differential

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Scanning Calorimetry (DSC) has been shown to be an efficient method to investigate liquid–solid transitions, crystallization and melting characteristics including the crystallization temperature of biodiesel [8]. This technique has been used to characterize biodiesels from babassu, soybean, tallow, corn and linseed [8–10] but no works were found related to poultry fat.

In the present work, poultry fat ethylic and methylic biodiesel's (PFEB and PFMB, respectively) and their corresponding binary biodiesel–diesel blends (B5, B10, B15, B20 and B50) were studied. An attempt was made to gain a better understanding of their rheological and cold flow properties by associating these results with informations obtained from Modulated Temperature Differential Scanning Calorimetry (MT-DSC) and from Gas Chromatography/Mass Spectrometry (GCMS).

2. Experimental

2.1. Sample preparation

The pieces of poultry waste were locally supplied. Heating was done in an oven at 70–80 °C for fat extraction followed by occasional stirring for 2 h to complete liquefaction. Subsequently, the fatty blend was subjected to vacuum filtration to remove impurities.

The biodiesel samples were obtained by alkali-catalyzed (KOH) transesterification of the poultry fat, using methanol and ethanol routes [10,11]. A molar ratio of poultry fat:alcohol of 1:6 and 1.0% of catalyst were employed. The blends were prepared by addition of 5, 10, 15, 20, and 50% (v/v) of pure PFMB and PFEB into diesel (0.02% sulfur).

2.2. Chemical characterization

The poultry fat (PF) and the biodiesel samples (PFMB and PFEB, for the methylic and ethylic poultry fat biodiesels', respectively) were analyzed by Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR) and Gas Chromatography/Mass Spectrometry (GCMS).

The results of ^{1}H NMR (200 MHz) were obtained in a VARIAN MERCURY spectrometer. Tetramethylsilane (TMS) was used as the internal standard and deuterated chloroform ($CDCl_3$) as the solvent.

GCMS analysis were done in a Shimadzu, model GCMS-QP2010, spectrometer, equipped with split injector and with auto-sampler. The capillary column used was Durabond – DB-SHT (Agilent Technologies). The carrier gas used was helium, using a flow rate of 3 mL min^{-1} and an injection volume of 1 mL. The MS detector temperature of 250 °C was used. The characterization of the fatty acid occurred by comparing the mass spectra with existing patterns in the software library of the equipment (Mass Spectral Database NIST/EPA/NIH).

2.3. Physicochemical characterization

The cold flow properties and MT-DSC analyses were determined for biodiesel samples, diesel and their blends. Dynamic and kinematic viscosities were determined for all samples.

Regarding the cold flow properties, Cold Filter Plugging Point (CFPP), Pour Point (PP) and Cloud Point (CP) were determined. For CFPP analyses a TANAKA Model AFP-102 equipment was employed according to ASTM Test Method D6371-05 [12]. For CP and PP a TANAKA Model MPC – 102 L equipment was used. CP measurements were done according to ASTM D2500-09 [13] while PP measurements were done according to ASTM D 97-09 [14].

The dynamic viscosity measurements were conducted in a Brookfield LV-DVII viscometer, with a small sample adapter, using an isothermal bath at 25 °C. The kinematic viscosity determinations were performed in accordance to the ASTM D445-97 [15] Test Method, using a Cannon Fenske calibrated viscometer.

The MT-DSC curves were obtained in non-isothermal conditions in a TA Instruments DSC 2920 using 10 mg of sample in nitrogen atmosphere heated from 40 to −60 °C and from −60 to 100 °C with a temperature modulation of ±1 °C min^{-1}.

3. Results and discussion

Fig. 1 shows ^{1}H NMR spectra. The triplet at δ = 2.32–2.24 appeared in all fatty acid esters with small shifts to higher or lower values according to the chain attached to the ester oxygen. The signal at δ = 2.74 was assigned to the bis-allylic hydrogens being specific of linoleic and linolenic fatty chains. The double doublet at δ = 4.31–4.23 and from 4.15 to 4.06 was related to the H of the glyceride portion of the triglycerides. The signals at δ = 5.35–5.24 were associated to the olefin protons confirming the presence of unsaturated C=C in all fatty chains.

As expected, the ^{1}H NMR spectrum of methyl and ethyl esters presented a profile similar to PF in the region of the hydrogens of the hydrocarbon chains (δ ~0.83 to 3.00) considering the structural permanence of the chains after the transesterification reactions. The most characteristic sign of the methyl ester was the methoxyl singlet located at δ = 3.64 distinguishing it from the PF and the ethyl ester.

The ^{1}H NMR spectrum of ethanol biodiesel confirmed the formation of ethyl ester by the presence of a quartet at 4.15 ppm that is assigned to the ethylene group protons of the alcohol ester. Almost no glycerides were found.

The fatty acid compositions of PF, PFEB and PFMB are shown in Table 1. Comparing with other animal fats such as lard and beef tallow, the fatty acid composition of poultry fat showed a higher proportion of unsaturated and polyunsaturated fatty acids in agreement with the literature [16]. The saturation degree of fatty acids may vary especially when the poultry feed diet composition contains a high percentage of saturated or unsaturated fats [17].

The chromatogram profiles of methanol and ethanol biodiesels displayed some quantitative differences. For instance, the linoleic acid content (C18:2) present in PFMB and especially in PFEB was significantly smaller than in PF while a higher amount of stearic acid (C18:0) was obtained. This indicates that the proportion of unsaturated chains reduced significantly after the transesterification reaction, especially in ethanol route.

Comparing the chromatograms with ^{1}H NMR spectra, similar results were obtained suggesting that the reduction in the chain size and in the unsaturation degree occurred making PF biodiesels more prone to crystallization.

Previous studies [7] demonstrated that several factors may affect the precipitated formation in biodiesel–diesel blends, such as storage temperature, storage time, biodiesel blend level, and

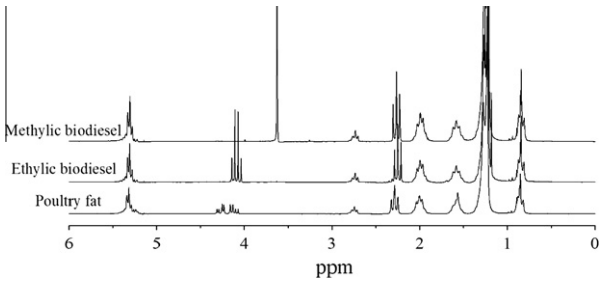

Fig. 1. ^{1}H NMR spectra of poultry fat and ethanol and methanol poultry fat biodiesels.