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Production and characterization of cold-flow quality biofuel from soybean oil using different alky and benzyl alcohols

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ABSTRACT

Biodiesel is an alternative fuel that has been used for partial or total substitution of diesel to reduce its environmental impacts. In Brazil, the main industrial technique used to produce biodiesel is via transesterification of soybean oil with methanol under sodium methoxide as a homogenous catalyst. Some studies on this topic have focused on improving the cold properties of biodiesel for use in cold climate countries. This research focused on the comparison of the cold properties of the biofuel produced from the transesterification of soybean oil with different alcohols. The alcohols used vary according to the size of the carbon chain and its nature: methyl, ethyl, isopropyl, isoamyl and benzyl alcohol. The chemical composition of the esters formed were studied by means of ^{1}H NMR, HPLC, FTIR, sodium and sulphur content. The ^{1}H NMR spectra showed that only the methyl and ethyl esters reached the minimum value of ester content established for the international specifications for biodiesel. Despite the greater difficulty in removing the excess of the reactant alcohol at the end of the reaction and having an ester content above requirements, the esters obtained from the alcohol isopropyl and isoamyl presented the best results in terms of their cold properties. However, the presence of the benzyl in the structure of the ester did not show any change in its CFPP, compared to the respective methyl ester. In addition to the cold properties, studies of some other physicochemical properties have also been made to show the maintenance of international specifications.

1. Introduction

Biodiesel is a renewable fuel resource that can be used in its pure form or mixed with diesel oil 'as is' because they are miscible and have similar physicochemical properties [1]. Brazil, along with Germany and the United States, is one of the world's largest biodiesel markets, both with regard to production and consumption. Other important markets are France, Spain, Italy and Argentina.

In addition to the various environmental advantages presented by biodiesel, it can also be produced from a wide variety of oleaginous substances and various short chain alkyl alcohols. As a result of these numerous combinations of esters and alcohols, the resulting biodiesel might exhibit varying physicochemical and combustion properties. To standardize these properties, authorization to use this fuel must meet stringent quality specifications to ensure trouble-free performance. These specifications include the American Society for Testing and Materials (ASTM) D6751 in the USA, EN 14214 in Europe, and CNS 15072 in Taiwan. In Brazil, biodiesel specifications must comply with ANP Resolution N° 30, defined by the Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP).

One of the major technical obstacles for the use of biodiesel fuel is its cold flow properties, which can be critical, depending on the climate and seasonal conditions of the region in which the fuel will be used. Several methods have been developed to measure low-temperature properties of diesel fuels and to estimate their effects on low temperature operability of vehicles. Common tests include the Cloud Point and the Pour Point methods. A number of filterability methods are also used, including cold filter plugging point (CFPP), low-temperature flow test (LTFT) and Simulated Filter Plugging Point (SFPP). Among these parameters, the CFPP (applied in countries outside North America) is a direct and reliable indicator for low-temperature engine operability. The maximum limit set by the European standard EN 14214-12 is 0 °C whereas the American standard ASTM D6751 does not stipulate limits. In Brazil, the ANP tolerates limits ranging from 0 to +12 °C, depending on the time of year and the region of the country. Despite the fact that the predominant weather in Brazil is moderate, the use of this biofuel is compromised during the winter in some regions in the south of the country because it has a high freezing point. The same thing happens in

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several other countries that consume biodiesel.

To meet the most stringent specifications, we believe that when the value of CFPP is lower, the biodiesel will be better. Ideally, it should not exceed 0 °C. The literature proposes different production or processing conditions for the final product to improve the cold properties of the biodiesel generally obtained with methanol. Among them, we can highlight the addition of additives based on aromatic compounds [2], the use of short chain oleaginous substances [3], winterization processes [4,5] and the use of branched-chain alcohols [6].

Regardless of these restrictions, several studies have been conducted in which the alcohol employed in the synthesis of biofuels is changed. The effects on cold properties and the manner in which this change affects the other physicochemical properties so as to meet other international standards have been studied. Considering the alternative of choosing new alcohols as reagents in the transesterification reaction, one of the limiting factors is the European standard for biodiesel specifications, EN 14214, which determines that biodiesel should be composed of methyl esters of fatty acids (FAME), that is, only methanol is allowed in the reactions. The American standards, ASTM D6751, are less stringent and allow other alkyl alcohols to be used. In addition to meeting both international standards, methanol is widely used in biodiesel production despite its toxicity because of its superior reactivity, low cost, and availability [7]. Much is said about the use of different alkyl alcohols for the production of biodiesel, but nothing is discussed in the literature regarding the use of alcohols with aromatic chains, except in the work performed by our group [3,4]. The proposal for studying the biodiesel produced with benzyl alcohol was based on the use of aromatic additives in biodiesel as a pour point depressant and thermal stabilizer [2].

Ethanol has been widely studied, especially in Brazil and Spain [8], perhaps due to its value as a renewable commodity, with low toxicity and environmental impact [9]. Knothe et al. studied the biodiesel obtained from methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *sec*-butyl and 2-ethylhexyl alcohols, evaluating, among other properties, the cetane number of the esters produced [10]. Sanli and Canakci, in addition to studying different oils, produced biodiesel from various alcohols such methyl, ethyl, isopropyl and *n*-butyl alcohols [7]. Foglia et al. published a study of the cold properties of methyl, ethyl, propyl, isopropyl, butyl, isobutyl and *sec*-butyl esters, as well as their respective blends with diesel [11]. In another study, Foglia, together with Wu et al., studied the effects of methyl, ethyl and isopropyl alcohols on the performance of their respective esters in engines [12]. Furthermore, Lee et al. evaluated the decrease in the crystallization temperature of methyl, ethyl, propyl, isopropyl, *sec*-butyl, *terc*-butyl and neopentyl esters obtained from soybean oil and canola oil, among others [6].

Other than the work already performed by our group involving benzyl esters from palm oil, there are no other reports in the literature regarding transesterification reactions using this alcohol, despite its low cost [3,4]. Up to the present moment, there is also no knowledge of research using isoamyl alcohol to produce biodiesel, which, therefore, makes the present study innovative. It is worth mentioning that isoamyl alcohol is a residue from the fermentation process in the production of ethanol [13] and can be used to produce a fully renewable biodiesel.

Previous studies have shown that the fatty acid profile of the feedstock influences the CFPP of biodiesel samples because of the different melting points of individual FAMEs [14]. Unsaturated FAMEs have melting points lower than those of saturated FAMEs. Consequently, biodiesels with a higher concentration of unsaturated FAMEs such as that produced from the soybean oil tend to have lower CFPP. In spite of the various oilseeds studied in the production of biodiesel, production in Brazil mostly focuses on processing soybean oil with methanol [15,16]. Nevertheless, ethanol has been widely studied, especially in Brazil and Spain [8], perhaps because of its value as a renewable commodity with a low toxicity and environmental impact [9]. The foregoing is a justification for exploring the particularity with regard to the cold properties of the esters obtained from soybean oil transesterified with methyl, ethyl, isopropyl, isoamyl and benzyl alcohols.

2. Materials and methods

2.1. Materials

Commercial soybean oil (Liza®) was used without further purification. All reagents were of analytical grade: Methanol (99.8%, VETEC®, Brazil), ethanol (99.5%, VETEC®, Brazil), isopropyl alcohol (99.5%, VETEC®, Brazil), isoamyl alcohol (99.36%, NEON®, Brazil), Benzyl alcohol (99.0%, SYNTH®, Brazil), sodium methoxide in 30% methanol (VETEC®, Brazil), potassium biphthalate (99.95-100.05%, VETEC®, Brazil) and $CDCl_3$ containing 1% TMS (D, 99.8%, CIL®, USA). HPLC grade methanol (J.T. Baker®), isopropyl alcohol (J.T. Baker®) and hexane (Mallinckodt®) were used as eluents for HPLC analysis.

2.2. Biodiesel synthesis

Alkyl and benzyl esters were prepared by transesterification of 100 g of soybean oil with 6:1 alcohol: oil molar ratio of methyl, ethyl, isopropyl, isoamyl or benzyl alcohol and 1% (w/w) sodium methoxide catalyst to oil were used, discounting the acidity of the raw material in each case, as previously described in the literature [17].

The mixture was stirred and heated at 65 °C for methanol preparation and at 85 °C for preparation with other alcohols. After 1 h, The phases that formed as reaction products were separated, and the organic fraction was neutralised with 0.1% $HCl_{(aq)}$, then washed with distilled warm water (40 °C). For the reaction performed with isoamyl and benzyl alcohol, an extra step was added to remove the remaining alcohol after washing the ester layer with water [4]. The resulting organic layer was dried over Na_2SO_4, and excess alcohol was removed at reduced pressure. Excess isopropyl alcohol was removed at a reduced pressure at 90 °C for more than 1 h, due to its higher boiling point. The biofuel was cooled to 18 °C for 24 h then rapidly subjected to vacuum filtration using a Buchner funnel with a sintered glass plate with 16–40 μm pores in order to remove possible insoluble impurities.

2.3. Analytical methods

All the analyses were done in triplicate. The biofuels were characterised based on their density (Anton Paar DMA 4500 automatic density meter, according to ASTM D4052), kinematic viscosity (Precitech Haake rheometer, according to ASTM D445), sodium content (Perkin Elmer Analyst 400, according to ABNT NBR 15553), higher and lower heating values (PARR 1241 adiabatic calorimeter, according to ABNT MB-2850 and ABNT NBR 8628), CFPP (TANAKA equipment with LAUDA RK8 CS – EDITION 2000 bath cooler, according to ASTM D6371), oxidation stability (Metrohm Biodiesel Rancimat instrument, according to EN 14112:2003), acid values (AT500N automatic potentiometric titrator, according to ASTM-D664), lubricity (PCS Instruments High-Frequency Reciprocating Rig and Meiji Techno ML7000 microscope, according to ASTM D6079) and the sulphur content (Antek 9000NS ultraviolet fluorescence analyser, according to ASTM D5453).

Fourier Transformed Infrared Spectra (FTIR) were obtained on an ARIS-ZONE ABB Bomem-MS Series spectrometer with 16 scans and a resolution of 4 cm^{-1}. Attenuated Total Reflection spectroscopy (ATR) was used with a diamond accessory. FTIR spectra were acquired between 4000 and 1000 cm^{-1}.

HPLC was used to detect the presence of fatty acids (FA), monoacylglycerides (MG), diacylglycerides (DG), triacylglycerides (TG), and the alkyl and benzyl esters using a Shimadzu LC-20AT chromatography system [SIL-20A HT automatic sampler, DGU-20A5 degasser, CTO-20A column oven, SPD-M20A UV − vis detector, SIL- 20HT pump, and Shimadzu CLC−ODS C18 column (M) (25 × 4.6 mm)] at 40 °C, with a