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Oxidative stability and cold flow behavior of palm, sacha-inchi, jatropha and castor oil biodiesel blends

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ABSTRACT

Oxidative stability and cold-filter plugging points (CFPP) of blends of biodiesel from palm, sacha-inchi, jatropha and castor oils were evaluated. Blends were made as a strategy to obtain a biodiesel with a better performance. These properties of biodiesel depend on the type of methyl-ester constituents and they are generally opposed, i.e., a biodiesel with good oxidative stability exhibits bad CFPP. Biodiesel was produced through KOH-catalyzed methanolysis of the oils. Binary blends of biodiesel from castor-jatropha, palm-castor and palm-sacha inchi were made, in proportions of 25:75, 50:50 and 75:25. The oxidative stability was evaluated following the standard EN 14112. CFPP of pure biodiesels and binary blends were evaluated according to ASTM D6371. An induction time greater than 6 hours and a CFPP below 0 °C were set as quality criteria. Among the pure biodiesels, only castor oil biodiesel achieved this quality because its induction time and CFPP were 31 h and −7 °C, respectively. The best biodiesel blend was made of 75% jatropha and 25% castor. This blend achieved an induction time of 7.56 h and a CFPP of −12 °C. However, this blend has a viscosity higher than the required by international standards. The oxidative stability (induction time) and the CFPP were correlated with the structural indices APE (allylic position equivalent), BAPE (bis-allylic position equivalent), SME (saturated methyl esters content), MUME (mono-unsaturated methyl esters content) and PUME (poly-unsaturated methyl esters content); it was found that BAPE and PUME correlate with IT, while CFPP does not correlate with any of these indices.

1. Introduction

Properties of biodiesel such as cetane number, viscosity, calorific value, cold flow, oxidative stability and lubricity are determined by the structure of their alkyl esters [1], in such a way that for a certain biodiesel composition some of these properties are adequate while others are not. For instance, palm biodiesel has good oxidative stability but very poor cold-flow properties, while soy biodiesel has good cold-flow properties but poor oxidative stability. Among the strategies that have been developed to solve the technical problems linked to the biodiesel composition are the mixing of biodiesel with traditional fossil diesel in different proportions to achieve an optimal blend [2,3], the use of additives to correct the negative properties of biodiesel [4,5], changing the chemical structure of esters that comprise biodiesel [6,7] and the change in the composition of biodiesel [7].

Blending of biodiesel from different oils is another technique that has been recently studied to improve the properties of this biofuel. Park et al. studied blends of biodiesel from palm, rapeseed and soybean, and determined their oxidative stability and CFPP [8]. Moser evaluated some fuel properties of soy biodiesel (oxidative stability, CFPP, cloud point, kinematic viscosity, lubricity, acid value and iodine value) and its mixture with methyl esters of palm, canola and sunflower [9]. Sarin et al. examined blends of jatropha and palm biodiesel in order to study their physicochemical properties and to achieve an optimal blend in terms of cold flow properties and oxidative stability [10].

The autoxidation of lipids is a very studied process due to its relevance to chemical, biological and food fields [11]. In biodiesel industry, the autoxidation is a very critical issue because it affects the quality as fuel. Autoxidation is a very complex process that involves the stages of initiation, propagation and termination (Fig. 1).

Double allylic positions in polyunsaturated fatty acids, such as linoleic acid (one double allylic position) and linolenic acid (two double allylic position), make them more prone to autoxidation than monounsaturated fatty acids such as oleic, which have only one allylic position. It has been established that the relative rates of oxidation for the methyl esters and ethyl esters of oleic, linoleic and linolenic acids are 1, 41 and 98 respectively [12]. Therefore, chemical composition of biodiesel is crucial to determine its oxidation stability.

Cold flow properties of a fuel define its behavior in a given climate conditions. Partial solidification that a fuel may have in cold weather can cause clogged fuel supply lines and filters, which creates problems for engine ignition [1,13]. The most frequently used parameters to determine the cold flow properties of diesel are cloud point (CP), pour point (PP) and cold-filter plugging point (CFPP). In general, these

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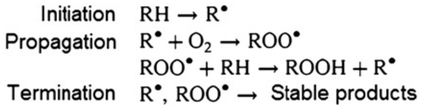

Fig. 1. Stages involved in oxidation of lipids.

parameters measure the temperature at which the fuel begins to have changes in its liquid phase and it gets crystallized, producing changes in its fluidity and leading to performance problems.

Cold flow properties of biodiesel also depend on the structure of the alkyl esters. The melting point increases with chain length and decreases with the increase of double bonds. Saturated fatty acids with 10 or more carbons are solid at room temperature and their melting point increase with chain length, whereas unsaturated fatty acids are liquid [4]. Among the saturated acids, odd-chain acids have lower melting points than even-chain acids. The *cis* configurations and/or the presence of —OH groups in the chain significantly reduce the melting point [14]. Biodiesel behaves as a multicomponent system where the first components of the system beginning to crystallize are those with the highest melting points. A biodiesel made from an oil with large amounts of fatty acids with low melting points, such as sunflower (<73.73% linoleic acid, methylester melting point of −35 °C) will have a low cloud point (1 °C) [15,16]. A biodiesel produced from an oil with high concentrations of fatty acids with high melting points, such as palm oil (<43.9% palmitic acid, methylester melting point of 30.5 °C), will have a high cloud point (16 °C) [17].

The African oil palm (*Elais guinehensis*) is the oilseed species with the highest oil production per hectare (4 ton/ha year) [18], making it the main source of biodiesel in tropical countries. Biodiesel from this oil has very good oxidative stability due to the high content of saturated fatty acids and natural antioxidants. Unfortunately, this high content of saturated fatty acids causes poor cold flow properties. The use of palm oil for biodiesel production has been questioned in some countries because it can compete for food use. However, it has been argued that production volumes of this oil, present and future, can meet both requirements.

Jatropha oil (*Jatropha curcas*) is a very interesting raw material for the production of oleochemicals because it has ca. 80% of unsaturated compounds and it is a non-edible oil. Therefore, this oil could lead to a lower consumption of edible oils for chemical purposes, which is currently a very hot discussion topic. Besides, jatropha plants grow under non-very stringent conditions. Owing all these attributes, production of jatropha is currently being undertaken by some developing countries [19].

Castor oil (*Ricinus communis)* is widely used in oleochemical industry. It is used in the production of lubricating oils, bases for inks and varnishes as well as in the production of resins and polymers. This oil is considered a good source for biodiesel production because it is not used as food and does not require demanding agricultural conditions [20]. Castor oil is chemically quite different from the other oils because it has a hydroxyl group (—OH) attached to the hydrocarbon chain; the presence of this —OH group leads to a lower melting point [14] and to a better oxidation stability [21]. Sacha inchi (*Plukenetia volubilis*) is a climbing plant that grows in wild regions of South America, where its seeds are used as food and to extract its oil. Sacha inchi oil has a high content of unsaturated fatty acids [22–24], which affect its oxidative stability but lowers its crystallization temperature. It is considered a promising resource for the oleochemical industry, including its use in biodiesel production, in rural areas of high humidity.

In this study, the oxidative stability and CFPP of palm (P), castor (C), jatropha (J) and sacha inchi (S) biodiesel blends were evaluated as a strategy to achieve a biodiesel with better performance. According to its composition, some of these biodiesels have good cold flow properties but poor oxidative stability, and vice versa, that is why this research aimed to develop a biodiesel blend with an induction time higher than 6 hours and a CFPP lower than 0 °C. Besides, the oxidative stability (IT-induction time) and the CFPP were correlated with the structural indices APE (allylic position equivalent), BAPE (bis-allylic position equivalent), SME (saturated methyl esters content), MUME (mono-unsaturated methyl esters content) and PUME (poly-unsaturated methyl esters content) to find out which one accurately describes the behavior of IT and CFPP.

2. Materials and methods

2.1. Biodiesel production and characterization

Biodiesel was produced by transesterification of refined oils with methanol (methanol/oil molar ratio 6/1) and using KOH as catalyst (0.7% w/w based on oil). This reaction was carried out in round-bottom flasks connected to a reflux condenser, heating at 60 °C under magnetic stirring for 1 hour. The final product was transferred to a funnel to separate biodiesel and glycerin. Excess methanol was removed from the ester phase using a roto-evaporador, then the biodiesel was washed with hot water until neutral pH. Ultimately, residual moisture was removed from biodiesel adding anhydrous sodium sulfate followed by a filtration step [30].

Biodiesels thus prepared were tested for acid value, peroxide and methyl ester content. The acid value and peroxide value were assessed by titration, which was conducted using a Titrino Plus 848 automatic titrator (Metrohm). Methyl esters content was determined by gas chromatography following the standard EN 14103 [25], using gas chromatograph (Agilent 7890A) with a capillary column (Agilent J & W HP-Innowax), flame ionization detector and tetradecanoic acid as internal standard. The viscosities of biodiesels were measured following the standard ASTM D 445 [26].

Binary blends were made from castor-jatropha, palm-castor, and palm-sacha inchi biodiesels in proportions of 25:75, 50:50 and 75:25 (w/w). These blends are called C25/J75, C50/J50, C75/J25, P25/C75, P50/C50, P75/C25, P25/S75, P50/S50 and P75/S25 (C = castor, J = jatropha, P = palm, S = sacha-inchi, the number denotes the percentage of each oil). Among the possible binary biodiesel blends, only the above were evaluated, taking into account that the blends castor-sacha inchi and jatropha-sacha inchi would have a very high content of unsaturated methyl esters (therefore poor oxidative stability), while the blend palm-jatropha would have a very high content of saturated methyl esters (therefore poor cold-flow properties).

2.2. Evaluation of the oxidative stability

Oxidative stability was evaluated using a Rancimat 873 (Metrohm), following the standard EN 14112 [27]. The variation of conductivity with time was recorded in a PC connected to the Rancimat and induction times (IT) were automatically measured. Induction time is the time when the maximum increase in electrical conductivity occurs.

2.3. Evaluation of the cold-filter plugging point

Cold-filter plugging point (CFPP) was evaluated according to ASTM D 6371 [28]. This point is the highest temperature at which

Table 1
Characterization of biodiesels.

Test	Biodiesel			
	Palm	Castor	Jatropha	Sacha inchi
Acid value (mg KOH/g)	0.28	0.80	0.41	0.39
Peroxide value (mmol O_2/kg)	2.03	0.71	7.40	10.95
Methyl-esters content (weight %)	98.10	89.90	97.40	97.40
Viscosity (mm^2/s, 40 °C)	4.10	13.34	4.44	4.66