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Oxidative stability of biodiesel by mixture design and a four-component diagram

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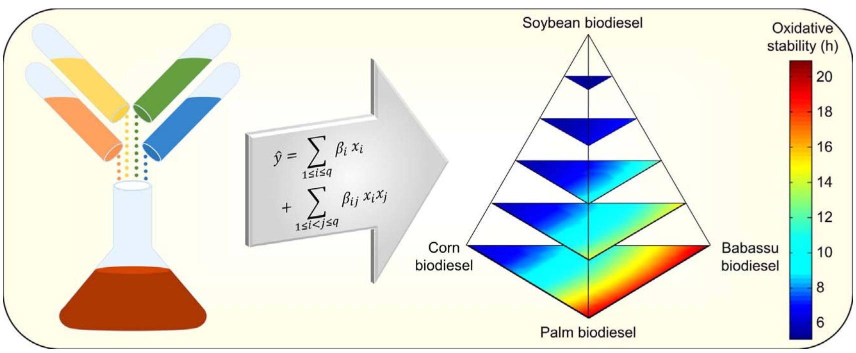
GRAPHICAL ABSTRACT



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ABSTRACT

Some biodiesels originating mainly from unsaturated feedstocks such as soybean, rapeseed, corn and sunflower do not reach the minimum oxidative stability of 8 h, as specified by standard EN 14214. An alternative to work with this type of biodiesels is to prepare their mixture with others biodiesels that are mainly saturated. This work presents a study employing binary, ternary and quaternary mixtures of biodiesels from soybean, corn, babassu and palm, aiming to improve the oxidative stability by using mixture design and polynomial modeling. For this, 71 mixtures were designed by simplex-lattice and simplex-centroid designs and divided into a calibration set (50 samples) and an external validation set (21 samples) employing the partitioning method based on joint **X-y** distances (algorithm SPXY). Six polynomials for quaternary mixtures models were built and statistically compared. The quadratic equation achieved the best results, with correlation coefficients (*r*) 0.9879 and 0.9569 for calibration and validation steps, respectively. Root mean square errors (RMSE) were 0.67 h for calibration and 0.71 h for validation and mean absolute percentage errors (MAPE) were 5.07% and 7.54% for calibration and validation, respectively. The quadratic equation was used to plot the contour maps for the oxidative stability resulting in a new way to represent four-component diagrams. In addition, a variety of possible biodiesel mixtures (binary, ternary and quaternary) are presented from babassu, soybean, corn and/or palm that meet any oxidative stability specifications within the range of 5.08 h–20.88 h, depending on the availability of the type and amount of the feedstock and target oxidative stability.

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1. Introduction

Due to climatic and environmental factors and to depletion of economically feasible oil resources, the search for new energy sources has been discussed worldwide with the goal of finding fuels that can gradually replace and thus reduce the demand for fossil fuels. For this purpose, biofuels are outstanding as they are renewable, biodegradable and environment-friendly, thus having a number of advantages over the petroleum derivative fuels [1,2].

Biodiesel is one of the most produced and sold biofuels worldwide. To ensure environmental and combustion quality, and safety in transportation and handling, the biodiesel needs to meet specifications for its quality parameters established by each country or region, such as EN 14214 (Europe) [3], ASTM D6751 (United States of America) [4] and RANP 45/2014 (Brazil) [5].

Some quality parameters of biodiesel are intrinsically related to its composition, varying according to the carbon chain size and to the saturation degree of its fatty acid esters. Since the transesterification process does not change the feedstock fatty acid composition, the compositional profile of the biodiesel is the same as the oil or fat of its origin [6].

One of the parameters related to biodiesel composition is its oxidative stability, which is associated to its resistance to oxidation. Biodiesel tends naturally to be less oxidation resistant than mineral diesel due to the presence of unsaturations in its ester chains: the higher the unsaturation degree, the lower the oxidation stability of biodiesel [7,8].

Oxidative degradation usually starts in double bonds that act as very reactive sites, susceptible to oxidation, especially when separated by a *bis*-allylic carbon [9]. Therefore, the oxidation rate is related not only to the amount of unsaturations, but also mainly to the positions of the double bonds [10].

The main compounds formed by biodiesel oxidation can lead to the formation of insoluble gums in the engine, to filter clogging, to injector coking, and to corrosion of engine metallic pieces [11–13]. In addition, biodiesel oxidation affects other properties such as kinematic viscosity, cetane number, acid value and density [12,14]. These aspects highlight the importance of the oxidative stability to the quality of the biodiesel.

As some pure biodiesels (made from a single feedstock) such as soybean, rapeseed, corn and sunflower do not reach the minimum oxidative stability of 8 h as specified by the standards EN 14214 and RANP 45/2014 [15], two alternatives have been developed to deal with this issue. One is the addition of antioxidants which, despite showing very promising results, implies higher cost and may be infeasible from an economic point of view [16,17]. Another alternative consists of blending unsaturated biodiesels with highly saturated biodiesels, resulting in a mixture that meets the specifications of oxidative stability [17,18].

It is important to note that there is no single oilseed with optimum composition that simultaneously favors all the quality parameters of biodiesel [6]. This indicates the need for studies on mixture design towards optimizing oxidative stability as well as other properties. The biodiesel sold in Brazil, for example, is a mixture mainly produced from soybean oil and beef tallow at a ratio of 4:1.

Experiments with mixtures are those in which the studied property is intensive, i.e., it depends only on the proportions of the components, and not upon the amount of material [19]. The general condition for a study with mixtures is that the sum of proportions of all the components must always to be 100% [20].

The methods of mixture design provide a complete and accurate scan of the factor space and allow exploring the influence of components and their interactions on the properties of the mixture [19,20]. In the literature, the two most widespread methods of mixture design reported are the simplex-lattice and the simplex-centroid designs, both developed by Scheffé [21,22].

The studied property, named response (*y*), can be properly visualized by means of a response surface perpendicular to the plane of the simplex representing the mixtures [19]. The response surface methodology involves two steps. In the first one, the modeling, mathematical models are adjusted to the responses obtained by the experimental design. The most used models are the polynomials. The second step is the displacement, which consists of establishment of the direction that leads to the optimal response [20].

In general, the degree of the polynomial function must be low so as not to extend the quantity of coefficients and render its application infeasible from a practical point of view, but it must be high enough to describe the behavior of even peculiar response functions adequately.

Studies employing biodiesel mixtures to optimize particular quality parameters related to their properties as biofuel are common in the literature [17,18,23–30]. Sarin et al. (2007) studied the effect of the composition and the use of antioxidants on biodiesels from palm, jatropha, pongamia, sunflower and soybean oils with the aim of obtaining a mixture with high oxidative stability and good performance at low temperatures in Asia. As jatropha and palm are the most predominant oilseeds in South Asian and South-East Asian countries, the authors optimized binary mixtures of these two feedstocks [17].

Carvalho et al. (2013) used a mixture design with constrains to evaluate the oxidative stability of soybean biodiesel samples containing different amounts of tallow and castor bean biodiesels. The authors provided a ternary diagram of mixtures and obtained a quadratic model based on response surface of the experimental data to predict optimal proportions of mixtures with high oxidative stability [18]. Up to the present, however, studies with mixtures for optimization of oxidative stability are limited to binary and/or ternary mixtures, even when the authors address more than three types of biodiesel feedstock [17,18,23,25–28].

In general, studies on quaternary mixtures are common in the literature [31–35], but works focusing on biodiesel are quite rare. Only one paper reports results of the influence of quaternary mixtures of biodiesels on quality parameters, but no equation or response surface were provided to estimate the parameters with better precision [30]. In 2012, Freire et al. developed a study with quaternary mixtures of vegetable oils (soybean, cotton, jatropha and babassu) for production of biodiesel with the aim of improving oxidative stability, kinematic viscosity and low temperature properties. Four samples of pure oils and five quaternary mixtures were prepared, but no direct application to biodiesel production was performed [24].

In addition, most studies do not employ a statistical methodology to design the mixtures and/or they use a very small quantity of samples, which may limit the generalization of equations to describe the behavior of the properties under study.

These shortcomings motivated the present study, which aims to optimize the oxidative stability of binary, ternary and quaternary mixtures of biodiesels from soybean, babassu, palm and corn oils designed by mixture design. Some polynomial equations were modeled for the mixtures, compared and statistically validated to plot diagrams representing the behavior of oxidative stability.

For this study, soybean (*Glycine* max) and palm (*Elaeis guineensis* J.) oils were selected because they are feedstocks widely employed for biodiesel production, especially in North and South American and Asian continents [36,37]. On the other hand, corn (*Zea mays*) oil has been extensively studied and reported in the literature as having great potential as biodiesel feedstock due to its high calorific value [6,37]. The babassu palm (*Attalea speciosa*), in turn, is a highly cultivated perennial plant in the North and Northeast of Brazil [38] whose oil has a mostly saturated composition and, therefore, contributes to improve the oxidative stability of the mixtures, as well as the palm oil.

Due to the opposing effects of FAMEs composition on oxidative stability and cold flow properties, which means that a saturated composition leads to a satisfactory oxidative stability and poor low-temperature properties (high values for these properties) [6], the use of the compositions of mixtures from this work has to be restricted to regions