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Kinetic study and thermoxidative degradation of palm oil and biodiesel

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ABSTRACT

This work investigated the synthesis of biodiesel from palm oil, its thermal stability using the Ozawa–Flynn–Wall and Vyazovkin kinetic models and its thermoxidation using thermogravimetry. The obtained biodiesel was in accordance with the specifications of Resolution No. 7/2008 of the ANP. The 97.4% wt conversion of palm oil to methyl esters confirmed the efficiency of the conversion of fatty acids into esters. The thermal analysis was performed on a thermobalance using heating rates of 5, 10 and 20 °C min^{-1}. The oil exhibited two mass losses, and the biodiesel exhibited only one mass loss. The average values of the obtained apparent activation energies were 184.6 and 191.3 kJ mol^{-1} for palm oil and 64.1 and 65.3 kJ mol^{-1} for biodiesel. Additionally, the results indicate that thermal analysis can be used as a tool for monitoring the thermoxidation of biodiesel as a function of time.

1. Introduction

Biodiesel is a biodegradable fuel, and it is environmentally and socially friendly. This fuel can be produced from vegetable oils, waste oils and animal fats [1,2]. There are several advantages of using biodiesel as an alternative to fossil diesel: it is renewable and low polluting, it stimulates the economy and rural development, and it has a higher cetane number and a higher flash point than does fossil diesel [3]. The important disadvantages of biodiesel include its high feedstock cost, low storage and oxidative stabilities, increased socio-environmental costs (monoculture and deforestation), and in some cases, high NO_x exhaust emissions [4].

Vegetable oils and animal fats are the primary raw materials used for the production of biodiesel, and vegetable oils account for approximately 75% of biodiesel production [5]. Several oilseeds are being studied for the production of biodiesel, such as soybean, sunflower, rapeseed, colza, castor and palm. Among these oilseeds, palm has shown potential for this purpose because in Brazil, its production is quite strong, it is a perennial species and it possesses good features for the production of biofuels. Palm (*Elaeis guineensis*) produces fruits that consist of a hard core within a peel, which is surrounded by a fleshy mesocarp. This mesocarp contains approximately 49% palm oil, whereas the core contains approximately 50% palm oil [6]. This palm oil consists of different fatty acids, and the amounts of saturated and unsaturated compounds are practically identical [7]. Due to the current importance of biodiesel in the Brazilian and global energy matrices and due to the variety of raw materials that can be used to produce biodiesel, developing specifications for their commercial use is considered an essential step for the development success of biodiesel programs in the country. Currently, biodiesel produced from vegetable oils or animal fats must meet the specifications established by the ANP Technical Regulation No. 1/2008.

Among the various properties of biodiesel, its oxidative stability has been attracting increasing attention because the raw materials used for its production are susceptible to autoxidation; consequently, the produced biodiesels are susceptible to oxidation. The low oxidative stability causes an increase in viscosity and acidity, among other problems. The standard method for determining oxidative stability (induction period) is the Rancimat method. However, many researchers have attempted to use methods that are faster and more efficient than the standard method for determining the induction period. Many studies have employed differential scanning calorimetry (DSC) and pressure differential scanning calorimetry (PDSC) because the oxidation phenomenon is exothermic and the average analysis time (4 h) of these techniques is less than that of conventional methods [8–10]. Thus, alternative methods are desired for monitoring this oxidation process as functions of storage time and sample aging.

Different methods have been applied to study the thermal stability and kinetic parameters of biodiesel, particularly the Coats-Redfern, Madhusudanan and Ozawa methods [11], which

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are dependent on the temperature and on the extent of conversion. Using these methods, Conceição et al. [11] investigated the thermal decomposition of castor oil and its methyl and ethyl biodiesels. However, it is necessary to study other methods (such as isoconversional methods) to obtain a better understanding of the reaction mechanisms involved in the decomposition of oil and biodiesel. Studies focusing on the volatilization of sunflower oil and its respective biodiesel were performed using the Vyazovkin model-free kinetic approach [12], but it is necessary to work with different materials and methods to propose the best method that applies to the study of biodiesel [13,14]. Thus, the aim of this work was to investigate the thermal stabilities of palm oil and its biodiesel using isoconversional methods, such as the Vyazovkin model-free kinetic method [14–18] and the Ozawa–Flynn–Wall method [19,20], and to investigate the oxidation of biodiesel as a function of aging at room temperature and under accelerated conditions at a temperature of 70 °C.

2. Material and methods

Palm oil was converted to biodiesel through an alkaline transesterification using 2.5% wt potassium hydroxide as a catalyst and oil/methanol in a 1:12 molar ratio. The reaction consisted of adding the oil and potassium methoxide to an EROSTAR reactor (from IKA LABORTECHNIK) followed by continuous stirring for 4 h. At the end of the reaction, the mixture was transferred to a separatory funnel, in which the two phases were separated. Then, glycerine was removed, leaving only methyl esters, which were purified. The physico-chemical properties of the oil and its biodiesel were measured in accordance with the standards of the American Society for Testing and Materials (ASTM), Associação Brasileira de Normas Técnicas (ABNT) and the American Oil Chemists Society (AOCS), as indicated in Resolution No. 7 of the ANP [21].

The ester content was obtained according to EN 14103 using a gas chromatograph coupled with a flame ionisation detector (GC–FID) and equipped with a split injector and autosampler (Thermo mark, TRACE GC ULTRA model). The capillary column used for the analysis of polar compounds was a polyethylene glycol TR-WAX (Thermo). The carrier gas used was helium at flow rate of 1 mL min^{-1}, and the sample injection volume was 1 μL. The FID detector temperature was 250 °C, and the samples for the analysis weighed 0.05 g.

Thermogravimetric analyses (TGA) were performed using a Mettler-STGA 851 thermobalance over the temperature range of 30–600 °C under a helium atmosphere with a flow rate of 25 mL min^{-1} and heating rates of 5, 10 and 20 °C min^{-1}. Kinetic studies of palm oil and its biodiesel were conducted using data obtained from the thermogravimetric analyses. According to Vyazovkin et al. [14], all isoconversional methods are based on the isoconversional principle, which states that the reaction rate at a constant extent of conversion is only a function of temperature. Therefore, the temperature dependence of the isoconversional rate can be used to evaluate the isoconversional values of the activation energy (Ea), without assuming or determining any particular form of the reaction model. Isoconversion kinetic methods based on integral and approach calculations were used, such as the Ozawa–Flynn–Wall and Vyazovkin models. To apply the isoconversional methods, three runs with different heating rates were used to obtain thermoanalytical data. The activation energy (Ea) of the process was consequently determined to conversion range from 0.10 to 0.90. The equations used to obtain the activation energies are as follows [15,22].

For the Ozawa–Flynn–Wall model, the following equation was used:

$$\ln(\beta) = \text{Const.} - \left(\frac{\text{Ea}_\alpha}{R}\right) \times \frac{1}{T_\alpha} \quad (1)$$

For the Vyazovkin model, the following equation was used:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \text{Const.} - \left(\frac{\text{Ea}_\alpha}{R}\right) \times \frac{1}{T_\alpha} \quad (2)$$

The value of Ea is determined from the slope of the plot of ln (β) or ln (β/T^2) vs. $1/T$[18]. The Ozawa–Flynn–Wall and Vyazovkin methods are integral methods with distinct mathematical approaches. The Ozawa–Flynn–Wall method is limited to linear heating rate conditions; in contrast, Vyazovkin proposed a non-linear isoconversional method [14,16]. Regardless of the mathematical approaches used in each method, both of these methods are promising for use in studying the decomposition of oils and biodiesel.

For aging of the samples, thermogravimetric curves were obtained using a Shimadzu TGA 50 thermobalance. For these measurements, the samples were placed in a platinum crucible and heated from 25–600 °C with a heating rate of 10 °C min^{-1} under a dynamic nitrogen atmosphere with a flow rate of 25 mL min^{-1}. Biodiesel produced from palm oil was stored in a suitable container, which was composed of stainless steel and similar to commercial storage tanks, to minimize the oxidation process that occurs in this fuel. The measurements were performed for the following aging process: one year after the storage process, which is represented here as (0 h). The one year aging time was selected based on the Rancimat data; extrapolation of these data indicated that biodiesel stored at 25 °C has a resistance of 19 months (see Figs. S1 and S2 in the Supplementary material). Considering that the ambient temperature in northeast Brazil is 35–40 °C, the biodiesel was analyzed after one year.

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Subsequently, the oxidation process was accelerated in an oven at 70 °C, and measurements were performed after 24, 48, 72, 96, 120, 144 and 168 h.

3. Results and discussion

The results of the physico-chemical analyses of the palm oil and its biodiesel are shown in Table 1. The results obtained for some properties of palm oil were used to determine the optimal synthesis conditions. Among these properties, the acid value is one of the most important properties for the choice of material and for the type and amount of catalyst used. According to Knothe et al. [23], the acid value should be less than 1 mg KOH/g of oil or fat. This result was not obtained for the oil investigated in this study. To resolve this problem, a higher catalyst percentage was used. In this work, a basic catalyst was used due to its low cost. With respect to humidity, Silva [24] reported that all raw materials must be practically anhydrous; therefore, the water content values must be less than or equal to 0.5%. These values are ideal for the

Table 1
Physico-chemical properties of palm oil and its biodiesel obtained via the methanol route.

Property/Unit	Palm oil	Palm biodiesel	Limits[a] (ANP)
Kinematic viscosity/$mm^2\,s^{-1}$	42.4	4.7	3.0–6.0
Density/$kg\,m^{-3}$	912.0	882.3	850–900
Flash point/°C	264.0	180.0	≥100
Total sulphur/ppm	0.8	0.6	50
Acid value/mg KOH g^{-1}	2.39	0.61	≤0.5
Iodine value/g I_2 100 g^{-1}	60.7	62.6	–

[a] Specifications according to the Brazilian ANP.