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Research article

Study of kinetics and thermodynamic parameters of the degradation process of biodiesel produced from fish viscera oil

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ABSTRACT

The present study determines the kinetic and thermodynamic parameters of the degradation process of the biodiesel produced from fish viscera oil. The analyses were performed through the accelerated trials of oxidation of biodiesel (EN 14112) at different temperatures (100, 105, 110, 115, 120 e 125 °C). Through the analyses of the results of the induction period, the reaction was considered to be of the first order. It was determined by the rate constants (K) varying from 0.0868 to 0.42271 h^{-1}, activation energy (E_a) of 81.99 $kJ \cdot mol^{-1}$, the pre-exponential factor (A) of $2.61 \times 10^{10}\ h^{-1}$, enthalpy of activation ($\Delta H^{\neq}$) of 78.79 $kJ \cdot mol^{-1}$, entropy of activation ($\Delta S^{\neq}$) – 55.94 $J \cdot k^{-1} \cdot mol^{-1}$ and Gibb's free energy of activation ($\Delta G^{\neq}$) average of 100.25 $kJ \cdot mol^{-1}$. The results showed that biodiesel oxidation reaction is non-spontaneous ($\Delta G^{\neq} > 0$), endothermic ($\Delta H^{\neq} > 0$), and that the temperature and the oxidation concentration influences significantly the degradation process of methyl esters.

1. Introduction

Biodiesel is a renewable and biodegradable fuel produced from vegetable oil or animal fat [1,2]. This fuel is presented as an alternative to replace diesel oil derived from petroleum. Once it causes less environmental problems when compared to diesel oil such as sulfur compounds reduction during combustion, more lubricity and higher flash point, what attaches more safety in both handling and storage [3,4].

However, this fuel presents some disadvantages because unlike fossil fuels, which are relatively inert and maintain their essential characteristics little altered in storage period, biodiesel degrades more easily when exposed to the action of light, atmospheric air, temperature and humidity [5].

Biodiesel degradation process may occur in three different ways: Enzymatic oxidation, photo-oxidation and autoxidation [6,7]. Being the last one the main responsible for methyl esters degradation process. Its mechanism is divided into three stages, at the first stage, named initiation, the formation of free radical occurs due to the scavenging of the hydrogen from the allylic carbon in the molecule in favorable conditions of heat and temperature [5]. At the second stage, it occurs the propagation of the radicals that react with the atmospheric oxygen forming the peroxides and hydroperoxides, which are the primary products of oxidation, and the formation of other radical, resulting in a high catalytic process. At the third stage, it occurs the end of the reaction, with the appearance of the secondary products of oxidation, obtained from split and rearrangement of peroxides (epoxides, volatile and nonvolatile compounds) [8,9].

With the purpose of inhibiting or delaying biodiesel lipid oxidation are used antioxidants [10]. The use of antioxidants and their mechanisms have been widely studied and are classified into primary, synergistic, oxygen scavenging, biological and chelating agents [9,4]. The primary antioxidants are composed of phenolic chemical substances that promote the scavenging or the inactivation of free radicals formed during the initiation or propagation of the reaction, interrupting the chain reaction [9].

Vegetable oils present natural antioxidants that provides a good oxidative stability and the most commons are the tocopherols. The antioxidant activity of tocopherols is mainly due to the ability of donating their phenolic hydrogens to lipid free radicals [8,4,11]. However, the oils produced from fish viscera do not present natural antioxidant, and added to the large amount of unsaturation present in their carbon chains, they present a low oxidative stability [1,12]. For this it is used synthetic antioxidants as butylhydroxyanisole (BHA), butylhydroxytoluene (BHT), *tert*-butylhydroquinone (TBHQ) and propyl gallate (PG) [6,10,9]. The

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phenolic structure of these compounds allows donation of a hydrogen to free radical, regenerating, this way, the ester molecule and interrupting the oxidation mechanism by free radicals. These antioxidants present the ability of stabilizing the charge formed by resonance, preventing the propagation of biodiesel oxidation reaction [13,9].

One of the greatest challenges in the use of waste of fishing industries is the low oxidative stability of biodiesel produced from this alternative raw material, becoming necessary the study of degradation kinetics, as well as its thermodynamic parameters [14,12,15–17]. Then, this work aimed to study the degradation process of biodiesel produced from fish viscera, determining the influence of temperature and the concentration of antioxidant BHA in the induction period of the samples, allowing, this way to ensure its quality during storage period until its commercialization.

2. Methodology

2.1. Materials

The reagents used were: potassium hydroxide (Vetec, 85%), sodium sulfate anhydrous (Sigma-Aldrich, ≥99%), methanol (Vetec, 99%), butylhydroxyanisole (BHA).

2.2. Biodiesel from fish viscera oil

Biodiesel from tilapia viscera oil was obtained from transesterification reaction performed according to Kiliç [18]. It was added 450 g from fish viscera oil in a round flask (1 L) and mixed with 93 mL of methanol and 4,5 g of KOH. The reaction conditions were: temperature of 60 °C, magnetic stirring of 900 rpm for 60 min. After the end of the reaction, the sample was placed in a separatory funnel, where glycerin was separated from the methyl esters. The biodiesel was purified by successive washing with warm distilled water (3 × 45 mL) until to remove all catalyst (KOH), soaps and glycerol. Finally, the washed biodiesel was heated at 50 °C for 30 min under vacuum to remove the residual moisture, after mixed with anhydrous sodium sulfate followed by filtration to eliminate traces of water.

2.3. Determination of fatty acids

For the determination of methyl esters from fish viscera oil was used the European Standard EN 14103. The analyses were carried out in Shimadzu it equipment 17th model, with Supelco capillary column 5% of phenyl and 95% of dimetilpolisiloxane (100 m × 0.25 mm and 0.25 μm). The drag gas used was nitro gen. The operating conditions were: initial column temperature 150 °C, detector temperature of 280 °C, column temperature programming: of 15 °C/min until 240 °C and maintained for 2 min and then 20 °C/min to 260 °C maintained for 21 min. The other chromatographic parameters were operated as it follows: Split mode 1:30, pressure of 206 atm, gas flow of 1.5 mL/min, linear rate of 32.6 mL/min and total flow of 55 mL/min [19].

2.4. Physical-chemical analyses of biodiesel

The physical-chemical properties evaluated were: iodine value by volumetry using Wijs reagent according to the norm EN 14111; Kinematic viscosity determined by the norm ASTM D 445-97; Specific weight 20 °C according to the norm ABNT NBR 14065; Flash point using the norm EN ISO 3679; Water content by the norm EN ISO 12937; Total esters using the norm EN 1410; Acid value determined by the norm EN 14104.

2.5. Oxidative stability

The biodiesel was separated in seven amber bottles (100 ml) and subsequently it was added the antioxidant obtaining samples with different concentrations of BHA receiving the following nomenclatures BP100 (0 ppm), BP-BHA-250 (250 ppm), BP-BHA-500 (500 ppm), BP-BHA-750 (750 ppm), BP-BHA-1000 (1000 ppm), BP-BHA-2000 (2000 ppm) and BP-BHA-3000 (3000 ppm). These samples were studied in Rancimat equipment 843 model (Metrohm) according to the norm EN 14112. The test consisted in weighing approximately 3 g of the sample in a test tube and bound it to an oxidation system that presents a heating block with programmable temperature, in this study the temperature ranged from 100 to 125 °C. The upper part of the test tube presents a connector that allows the air flow rate (6 L/h) that contacts the biodiesel by a glass capillary. The gases generated in the degradation process of the sample in the test tube are sent to a cuvette that contains deionized water and a conductivity meter that registers the conductivity throughout the biodiesel degradation process. The data obtained from oxidative stability were used to analyze the chemical kinetics and the thermodynamic parameters of biodiesel degradation process.

3. Result

3.1. Physical-chemical properties and fatty acid composition

Fatty acids of fish biodiesel showed the following chemical composition: myristic acid C14:0 (3.11%), palmitic acid C16:0 (25.53%), palmitoleic acid C16:1 (6.14%), stearic acid C18:0 (6.17%), oleic acid C18:1 (39.01%), linoleic acid C18:2 (15.61%), linolenic acid C18:3 (2.38%) and gadoleic acid C20:1 (2.03%). These results were compared with literature works [14,15] and they presented similar results having a higher amount of unsaturated fatty acids in relation to the saturated ones. Table 1 shows the results of physical-chemical properties of biodiesel. The determined values were compared with the work described by Martins [14] who also evaluated the physical-chemical properties of biodiesel from fish oil produced in Brazil. Both results were within the specifications outlined by the Brazilian National Agency of Oil, Natural Gas and Biofuels (ANP) showing that oil from the fishing industry waste is an excellent alternative in biodiesel production.

3.2. The effect of temperature and antioxidant concentration on the oxidative stability of biodiesel

The influence of the concentration on the oxidative stability of biodiesel oil from fish viscera at different temperatures tested (100, 105, 110,115, 120 and 125 °C) is shown in Table 2. It was verified that all concentrations of antioxidant BHA analyzed in the biodiesel increased significantly its oxidative stability at all temperatures tested, and that the increase in temperature influences negatively the oxidative stability of biodiesel, that is, the higher the temperature, the lower the oxidative stability of the sample. Evaluating the control sample (BP100), it was verified that the induction period was very below the value established by ANP specification. However, all samples with different antioxidant concentrations were above the minimum value established by the norm EN 14112. The influence of different concentrations of the

Table 1
Physical-chemical properties of fish viscera oil biodiesel.

Analyses	FOME	FOME[a]	ANP	
Acidity value	0.17	0.19	Max. 0.5	mg KOH/g
Specif mass 20 °C	876.02	877	850–900	Kg/m^3
Iodine value	81.54	–	Anotar	100 mg I_2/g
Water content	150.01	95	Max. 200	mg/Kg
Flash point	145.00	145	Min. 100	°C
Viscosity 40 °C	4.69	5.34	3–6	mm^2/s^2
Total esters	97.20	–	Min. 96.5	%m/m

[a] Martins et al. 2015 [14].