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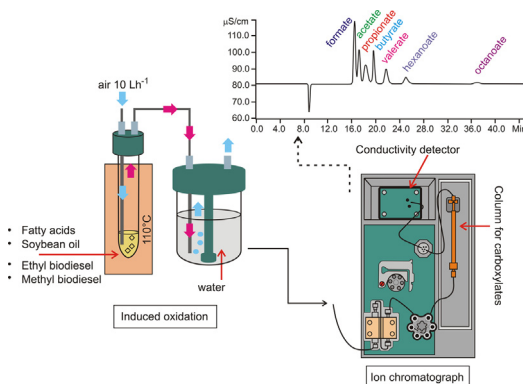
Kinetic of the formation of short-chain carboxylic acids during the induced oxidation of different lipid samples using ion chromatography

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HIGHLIGHTS

- Short-chain acids generation during induced lipid oxidation by Rancimat was noted.
- The short-chain acids were identified in their anionic forms using ion chromatography.
- The lipid samples were: free fatty acids, soybean oil, methyl and ethyl biodiesels.
- Found: formic, acetic, valeric and hexanoic acids come from oleic and linoleic acids.
- Found: formic, acetic, valeric, propionic, and butyric acids come from linolenic acid.

GRAPHICAL ABSTRACT



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ABSTRACT

Short-chain carboxylic acids are commonly formed in the oxidation of vegetable oils, long carbon-chain fatty acids and biodiesel. The formation of short-chain (up to six carbons) carboxylic acids during induced oxidation in the Rancimat procedure for oleic acid (OA), linoleic acid (LA), linolenic acid (LnA), soybean oil (SO), methyl biodiesel from soybean oil (MBSO) and ethyl biodiesel from soybean oil (EBSO) was studied. Samples of OA, LA and LnA were submitted to oxidation, and the short-chain carboxylic acids formed were identified in their anionic forms using ion chromatography (IC). Formate, acetate, valerate and hexanoate were identified in the OA and LA samples. For the LnA sample formate, acetate, valerate, propionate and butyrate were found. For the MBSO, EBSO and SO, formate, acetate, propionate, valerate and hexanoate were identified. The rate of formation of formic acid was highest for each sample. The quantitative analysis of short-chain carboxylic acids present in lipid samples can help in determining product age, degree of oxidation, oxidative stability and corrosiveness.

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1. Introduction

The molecules of the majority of the natural fatty acids do not present ramifications and have a pair number of carbon atoms in their molecular structures, due to the biochemical route of synthe-

sis. Among them, they differ by the number of carbon atoms and also by the number of double carbon to carbon bonds in their carbonic chain. Commonly, when there are double bonds, the molecules are in the *cis* form [1,2].

The vegetable oils and the animal fats can be used to produce biodiesel which is synthesized through a transesterification reaction with a short-chain alcohol in the presence of a catalyzer. Methanol is mainly employed in this reaction because it presents

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higher reactivity and also due to its lower cost among the other alcohols. However, other alcohols, as for example ethanol, can be employed [3–5].

The lipid oxidation is a main cause of the deterioration of fatty acids. This is a problem in the case of biodiesel because the burning of the products resulting from the oxidation of such biofuel, during storage, damages the motors [1,3]. Among the main consequences of the biodiesel oxidation can be highlighted the increase of viscosity, the increase in the acidity and the formation of insoluble gums and sediments which provoke the clogging of the fuel filter of the motor [6]. The auto-oxidation is considered the most common process which conducts to the oxidative deterioration. It is defined as being the spontaneous reaction of the atmospheric oxygen with lipids [7].

The oxidation reaction of lipids is constituted by the following steps: (i) Formation of free radicals begins the oxidation process and during this step the oxidation rate is small; (ii) Formation of hydroperoxides as products of primary reactions, a step during which the rate of oxidation increases; on the other hand, the decomposition rate of the hydroperoxides is significantly small in this stage and a very small quantity of oxidation products is formed; (iii) Formation of secondary products, in this step the rate of degradation of hydroperoxides is higher than the rate of their formation and an exponential increase in the formation of secondary products of oxidation is observed. The understanding of the mechanisms of these reactions is very important in order to choose the adequate method for the analysis of the formed products [7–10].

To determine the oxidative stability of oils and biodiesels, their oxidation process is accelerated by submitting the samples to 110 °C in the presence of a flow of air or oxygen. The Rancimat equipment is commonly employed for the determination of the induction period. In this essay, the volatile compounds formed during the accelerated oxidation are collected in distilled water, increasing its conductivity which is continuously and automatically monitored [3,9,11,12].

Along the oxidation of lipids, volatile organic acids, mainly formic and acetic acids, are produced simultaneously with the hydroperoxides, as secondary products of the oxidation. Also, other formed secondary products, including alcohols and carbonyl compounds, can be oxidized to carboxylic acids [1,7,9].

The studies which have been performed on the auto-oxidation of vegetable oils and biodiesels indicate the presence of the formate as the main organic anion formed, followed by acetate. The analytical methodologies which have been employed in the monitoring of such anions use capillary electrophoresis [13] and ion chromatography [14,15].

The oxidative stability of biodiesel is a parameter experimentally determined through the procedure established by the norm EN 14112 [16] and for oils by the method AOCS Cd 12b-92 [17].

Fritsch and Deatherage [18] studied the induced oxidation of oleic acid and methyl oleate and found as degradation products formic and acetic acids, having formic acid the higher concentration. The formation of short-chain carboxylic acids as degradation products of the induced oxidation of vegetable oils was reported by deMan et al. [19]. The following acids were detected: formic, acetic, propionic, butyric, valeric and caproic. The concentration of each one was dependent of the oil, however formic acid was always preponderant, representing between 58 and 81% of the total formed in each case. Flitsch et al. [20] determined formic and acetic acids in the induced oxidation of methyl biodiesel from canola oil. They correlated the sum of the acids' concentrations, i.e., the total concentration of the acids formed, with the curve of the induction period (IP), finding that the main acid formed was the formic one. Carvalho et al. [21] studied the short-chain carboxylic acids formed in the induced oxidation of the methyl biodiesel from soybean oil

and also found that the most concentrated was formic acid, followed by acetic and by propionic acid.

The acid number, which gives the total acidity, is an important parameter related to the quality of biodiesels [22] and oils [23]. However, it does not inform about the nature of the acids presents in the samples.

Strömberg and Sahlin [24] determined, before and after the induced oxidation, the total acidity (Total Acid Number – TAN) of methyl biodiesel from rapeseed oil and the molar fraction of formic, acetic and propionic acids. Before the induced oxidation procedure, the sum of the quantities, in mol%, of these three acids was 20.4% of the TAN. After the oxidation procedure, this sum passed to 52.4% (formic acid 41.6 mol%; acetic acid 7.5 mol%; propionic acid 3.3 mol%) of the TAN. Strömberg et al. [25] reported a similar study on samples obtained before and after the refueling of fuel containers and did not find any difference of the acidity which could be attributed to the replenishment.

Other important parameter of biodiesel is its corrosiveness in relation to copper, according to EN ISO 2160 [26]. This kind of corrosion has been associated to the short-chain carboxylic acids, particularly to the formic and acetic acids components that at concentration between 10 mgL⁻¹ and 300 mgL⁻¹, in presence of humidity, show important aggressiveness with respect to copper [27,28]. Lower corrosion effects were also found with propionic acid [29].

Despite the fact that the concentration of short-chain carboxylic acids in biodiesel and vegetable oils is not regulated by law, it should be considered important to determine their presence as, on one hand, they indicate, the oxidation degree of the matrices and, on the other hand, they can damage the metallic surfaces of the engines due to their acid character. Also, the study of the formation of such acids, during the oxidation process of the matrices, can help in the understanding of the related chemical reactions.

In the present work it was employed an ion chromatography method for the quantification of organic anions of short-chain carboxylic acids containing from one to eight carbons. The determination of such anions was performed analyzing the distilled water which receives the volatile compounds, in the Rancimat procedure. The formation rate of these anions were calculated in the same conditions and the studied samples were: oleic acid (OA), linoleic acid (LA), linolenic acid (LnA); soybean oil (SO); methyl biodiesel from soybean oil (MBSO) and ethyl biodiesel from soybean oil (EBSO). With the data obtained for the different fatty chains was possible to propose routes for the formation of some anions (short-chain carboxylic acids) detected in the Rancimat procedure. With the data obtained for the different lipid molecule classes it was possible to compare their availability to suffer oxidation. To what is known both, data and routes, are still unpublished in the literature.

2. Experimental methods

2.1. Materials and reagents

Fatty acids (purity indicated on the label): oleic acid (90%), linoleic acid (60–74%), linolenic acid (70%) from Sigma–Aldrich, St. Louis, MO, USA, which were analyzed by gas chromatography (GC) before the execution of the oxidation experiments. Refined soybean oil, Soya, from Bunge, SP, Brazil. Methyl biodiesel from soybean oil (MBSO) and ethyl biodiesel from soybean oil (EBSO). The biodiesels used in the experiments were produced following the method already reported by Silva et al. [5]. The soybean oil and the biodiesels were analyzed by GC before the execution of the oxidation experiments. These samples were selected in order to study different fatty chains and lipid molecule classes. Short-chain carboxylic acids: valeric acid (>99%), heptanoic acid (>99%)

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