

## Study of the Kinetics of Formation of Carboxylic Acids Using Ion Chromatography during Oxidation Induced by Rancimat of the Oleic Acid, Linoleic Acid, Linolenic Acid, and Biodiesel

**Authors :** Patrícia T. Souza, Marina Ansolin, Eduardo A. C. Batista, Antonio J. A. Meirelles, Matthieu Tubino

**Abstract :** Lipid oxidation is a major cause of the deterioration of the quality of the biodiesel, because the waste generated damages the engines. Among the main undesirable effects are the increase of viscosity and acidity, leading to the formation of insoluble gums and sediments which cause the blockage of fuel filters. The auto-oxidation is defined as the spontaneous reaction of atmospheric oxygen with lipids. Unsaturated fatty acids are usually the components affected by such reactions. They are present as free fatty acids, fatty esters and glycerides. To determine the oxidative stability of biodiesels, through the induction period, IP, the Rancimat method is used, which allows continuous monitoring of the induced oxidation process of the samples. During the oxidation of the lipids, volatile organic acids are produced as byproducts, in addition, other byproducts, including alcohols and carbonyl compounds, may be further oxidized to carboxylic acids. By the methodology developed in this work using ion chromatography, IC, analyzing the water contained in the conductimetric vessel, were quantified organic anions of carboxylic acids in samples subjected to oxidation induced by Rancimat. The optimized chromatographic conditions were: eluent water:acetone (80:20 v/v) with 0.5 mM sulfuric acid; flow rate 0.4 mL min<sup>-1</sup>; injection volume 20 µL; eluent suppressor 20 mM LiCl; analytical curve from 1 to 400 ppm. The samples studied were methyl biodiesel from soybean oil and unsaturated fatty acids standards: oleic, linoleic and linolenic. The induced oxidation kinetics curves were constructed by analyzing the water contained in the conductimetric vessels which were removed, each one, from the Rancimat apparatus at prefixed intervals of time. About 3 g of sample were used under the conditions of 110 °C and air flow rate of 10 L h<sup>-1</sup>. The water of each conductimetric Rancimat measuring vessel, where the volatile compounds were collected, was filtered through a 0.45 µm filter and analyzed by IC. Through the kinetic data of the formation of the organic anions of carboxylic acids, the formation rates of the same were calculated. The observed order of the rates of formation of the anions was: formate >>> acetate > hexanoate > valerate for the oleic acid; formate > hexanoate > acetate > valerate for the linoleic acid; formate >>> valerate > acetate > propionate > butyrate for the linolenic acid. It is possible to suppose that propionate and butyrate are obtained mainly from linolenic acid and that hexanoate is originated from oleic and linoleic acid. For the methyl biodiesel the order of formation of anions was: formate >>> acetate > valerate > hexanoate > propionate. According to the total rate of formation these anions produced during the induced degradation of the fatty acids can be assigned the order of reactivity: linolenic acid > linoleic acid >>> oleic acid.

**Keywords :** anions of carboxylic acids, biodiesel, ion chromatography, oxidation

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