Crambe abyssinica oil as an oxidative stability additive for soybean biodiesel

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Abstract: The quality of the biodiesel is of most importance for the success in the marketing of this fuel. Among the qualitative parameters there is the kinematic viscosity that can be affected due to the degradation of biofuel, which could be estimated as its stability. Such degradation occurs on account of the weather changing and also because of some catalytic agents. Because of that the stability to oxidation was denominated as a factor which relates the resistance level of the product to the different oxidizing agents. The present work aimed to study the inductive period of soybean biodiesel and its blends with crambe biodiesel. A Metrhom® Rancimat was used for getting data for this study. From the results it was observed that using crambe oil as an additive it could be viable for taking out the biodiesel producer dependency for chemistry industries for synthetic anti-oxidants. A 20% blend of crambe oil at the soybean biodiesel could elevate about 33,3% of the original biodiesel induction period with a low variation coefficient (1.52%) .

Key words: *Crambe abssynica* Hoechst; induction period; Rancimat.

Utilização de óleo de crambe como aditivo antioxidante para o biodiesel de soja

Resumo: A qualidade do biodiesel é de suma importância para o sucesso da comercialização deste biocombustível. Entre os parâmetros de qualidade está a viscosidade cinemática a qual pode ser afetada devido à degradação do biodiesel. Tal degradação acorre devido as condições climáticas a que este é submetido e pela presença de alguns agentes catalíticos. Com isto a estabilidade à oxidação foi denominada como um fator de relação entre o nível de resistência do produto e a presença de diferentes agentes catalizadores. O presente estudo teve como objetivo verificar o período de indução do biodiesel de soja e suas blendas com biodiesel de crambe. Para obter os dados um aparelho Rancimat da Metrhom foi utilizado. Pelos resultados observou-se que utilizar o óleo de crambe como aditivo antioxidante para o biodiesel de soja pode ser uma alternativa viável para diminuir a dependência do produtor de biodiesel pelas indústrias químicas produtoras de antioxidantes sintéticos. A blenda com 20% de biodiesel de crambe incrementou o período de indução original do biodiesel de soja em torno de 33,3% com baixo coeficiente de variação (1,52%).

Palavras-chaves: *Crambe abssynica* Hoechst; período de indução; Rancimat

Introduction

The environmental impacts caused by the use of fuels made out of fossil sources, and the concerns regarding the Crude Oil Inventories have been motivating studies and researches for renewable sources of biofuels, mostly for the replacement of diesel. According to Hill *et al.* (2006) in order to be a viable alternative the chain of the biofuel must have a positive energy balance, present environmental benefits, to be economically competitive and to be produced on a large scale without interfering in the food supply chain.

The used biofuel in the partial or in the total replacement of diesel in internal combustion engines, diesel cycle, can be obtained through the pyrolysis reaction, the cracking process and the transesterification process, the last one being the most used, of animal fat and vegetable oil. In a chemical matter, the biodiesel is nothing more than a mixture of alkyl esters of straight-chains, once its production also results in a co-product, the glycerol (Lôbo *et al.*, 2009).

As a result of its origin, the biodiesel, when compared to the fossil diesel, presents a degradability much higher in the environment, and for that same reason it is susceptible to oxidative and microbial degradation from its synthesis. The susceptibility to oxidation is a relevant aspect inside the existence cycle of the biodiesel, once that the fatty acids triglycerides, especially the unsaturated ones, present re-actives sites which are susceptible to oxidation (Monyem & Gerpen, 2001). One of the processes to which they are subjected is the oxidative degradation, also known as rancidification, and it causes serious implication to the consumer market.

According to Tang *et al.* (2008), among the negative implications of the oxidative degradation of the biodiesel, the increase of viscosity can be highlighted, the elevation of acidity and the formation of gums and undesirable polymeric compounds. Having in view that the main factors that affect the biodiesel characteristics are: the length of the chain (number of carbon atoms), the number of unsaturated chains and the occurrence of other chemical functions (Santos *et al.*, 2011), it is clear then, with this, that the properties of the raw materials are the ones that will result in a biofuel of a good or of a bad quality.

Crambe is an oleic plant that belongs to the *cruciferae* family, its origin is reported as from Etiopia. Is believed that it has been initially researched at Russia at the beginning of XX centuries, being introduced at United States by the 1940 years and research's intensified only by the 80's years (Pitol, Broch & Roscoe, 2010). At Brazil it's been reported productions between 1300 and 1500 kg.ha^{-1} (Rogério *et al.*, 2013; Pitol *et al.*, 2010) and at in adverse climate conditions means of 550 kg ha^{-1} (Santos & Vianna, 2011).

Material and Methods

The experiment was carried out in a laboratory belonging to the Western Paraná State University – Cascavel Campus/PR. The crambe crude oil was obtained from a research company which is located in Maracaju/MS. The oil was extracted from the grain by mechanical pressing, without addition of any solvent. As for the soybean oil, it was obtained from an agro-industry located in the city of Cascavel – PR and it was left in an incubator at 60ºC for 12 hours to remove any eventual excess of water.

The biodiesels were obtained by the transesterification reaction via methylic route with a basic catalyst KOH. The reaction was based on the stoichiometric ratio between the triglycerides and the chosen alcohol, as the amount of catalyst and alcohol was established as a percentage with regard to the volume of oil.

For the synthesis of the crambe biodiesel, a percent ratio of 25% alcohol (methanol) and of 0.8% catalyst (KOH) on the account of the oil volume (500 ml) was used. As for the soybean biodiesel, a higher percentage of catalyst (1%) and the same amount of alcohol (25%) were used. The oils were placed under constant mechanical stirring and they were heated at 60ºC, then the mixture alcohol + catalyst (potassium methoxide) was added in order to initiate the transesterification reaction. The temperature and the stirring were maintained for a period of 30 minutes to ensure the maximum efficiency of the reaction. At the end of the reaction time, all of the contents were transferred to two separation funnels, leaving the mixtures in decantation for 24 hours to ensure the total separation of the glycerin. After the separation of the biodiesel, it passed through a washing process, to remove the excess of catalyst and of any eventual triglycerides or free fatty acids that didn't react. The washing process was made with distilled water at a temperature of 80ºC in amounts of one third of the initial oil volume, and repeating as many times it was necessary so that the phenolphthalein indicator didn't show any reaction at the washing water. So the biodiesels were left in an incubator at 60ºC for 20 hours to remove the excess of water, and then they were left to reach room temperature in a desiccator.

To determine the induction period, a METRHOM® 857 Rancimat belonging to the Assis Gurgacz college laboratories was used. For this, samples of pure soybean biodiesel (0.05g) and with crambe blends (10%, 20%) were submitted to the stress test. The tests were carried out with duplicates, after all samples were submitted to stress all the data were statistically analyzed and the graphic were plotted.

Results and Discussion

From Table 1 we can see that crambe biodiesel has an induction period about 160% higher than pure soybean biodiesel. This could be explained because the oil obtained through the *Crambe abyssinica* features in its fatty acid profile more than 56% of erucic acid. This acid contains 22 carbon atoms and only one double bond (Laghetti *et al.*, 1995). And the soybean oil presents 54% of linoleic acid and 24% of oleic acid, both of which present 18 carbon atoms and, respectively, two and one double bonds (Sanibal & Mancini, 2004). Because of this drastic difference in the fatty acids profile, theoretically, the biodiesels obtained from these vegetable oils will show different stabilities to oxidation.

Table 1 – Biodiesel Induction Period (hours) for all blends and pure soybean and crambe

% Crambe Biodiesel	Induction Period (mean)(hours)	Variation Coefficient (%)
0	3.03	0.82
10	3.39	0.14
20	3.94	1.52
100	7.69	1.04

Schober and Mittelbach (2004) verified that the induction time of biodiesel oxidation depends on the biodiesel that is being studied and on the presence of antioxidant, considering that the best antioxidant to a given biodiesel does not guarantee that it will be the best antioxidant for another biodiesel. Studies of the oxidative stability of soybean biodiesel conducted by Ferrari *et al.* (2005) and by Guzman *et al.* (2009) showed that the oxidative stability of soybean biodiesel significantly alters when the oil passes through a purification process. The time of oxidative induction for the first author alters from 277 minutes to 132 minutes when it is deodorized and for the second author, alters from 2,68 hours to 0,17 hours when the oil is distilled, thus the presence of antioxidant compounds in oil in *natura* are removed by the purification process by altering its oxidative stability, this assumption was also proposed by Conceição *et al.* (2009). So small changes in the composition and in the purity of the oil cause significant alterations in the thermo-oxidative stability of biodiesel.

From Figure 1 we can observe that with the presence of 50% of crambe oil the soybean biodiesel induction period duplicates. This could be analyzed as viable alternative to synthetic addictive's putting out the biodiesel producer dependency for chemistry industries. Further economic studies should be done for seeking out the technical/economic point of viability for this oil be used as a stability additive.

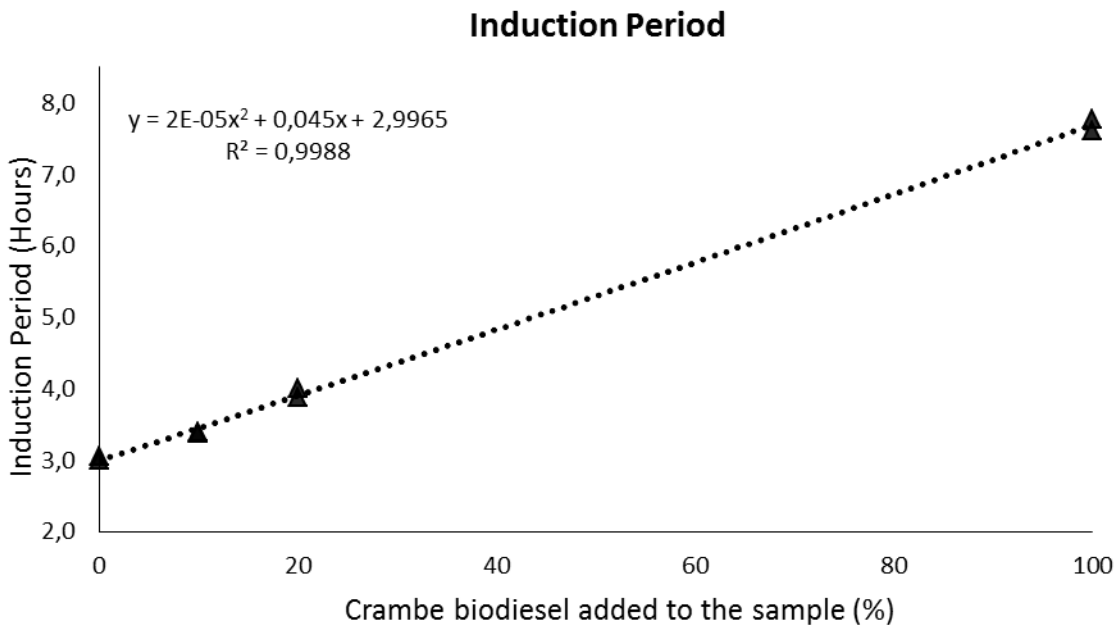

Figure 1 - Induction period obtained from Rancimat tests for pure soybean and crambe biodiesel and its blends.

Conclusions

Crambe biodiesel showed a high potential as an oxidative stabilizer for the soybean biodiesel.

The use of 20% of crambe oil could elevate about 33.3% of the original induction period of soybean biodiesel.

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