

Note

OXIDATIVE STABILITY OF BIODIESEL FROM SOYBEAN OIL FATTY ACID ETHYL ESTERS

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ABSTRACT: Biodiesel consists of long-chain fatty acid esters, derived from renewable sources such as vegetable oils, and its utilization is associated to the substitution of the diesel oil in engines. Depending on the raw material, biodiesel can contain more or less unsaturated fatty acids in its composition, which are susceptible to oxidation reactions accelerated by exposition to oxygen and high temperatures, being able to change into polymerized compounds. The objective of this work was to determine the oxidative stability of biodiesel produced by transesterification of neutralized, refined, soybean frying oil waste, and partially hydrogenated soybean frying oil waste. The evaluation was conducted by means of the Rancimat[®] equipment, at temperatures of 100 and 105°C, with an air flow of 20 L h⁻¹. The fatty acid composition was determined by GC and the iodine value was calculated. It was observed that even though the neutralized, refined and waste frying soybean oils presented close comparable iodine values, biodiesel presented different oxidative stabilities. The biodiesel from neutralized soybean oil presented greater stability, followed by the refined and the frying waste. Due to the natural antioxidants in its composition, the neutralized soybean oil promoted a larger oxidative stability of the produced biodiesel. During the deodorization process, the vegetable oils lose part of these antioxidants, therefore the biodiesel from refined soybean oil presented a reduced stability. The thermal process degrades the antioxidants, thus the biodiesel from frying waste oil resulted in lower stability, the same occurring with the biodiesel from partially hydrogenated waste oil, even though having lower iodine values than the other.

Key words: Rancimat[®], transesterification, oxidation

ESTABILIDADE OXIDATIVA DE BIODIESEL DE ÉSTERES ETÍLICOS DE ÁCIDOS GRAXOS DE SOJA

RESUMO: Biodiesel consiste em ésteres de ácidos graxos de cadeia longa, proveniente de fontes renováveis como óleos vegetais, e sua utilização está associada à substituição do diesel em motores. Dependendo da matéria-prima, o biodiesel pode conter mais ou menos ácidos graxos insaturados em sua composição, que são suscetíveis a reações de oxidação aceleradas pela exposição ao oxigênio e altas temperaturas, podendo resultar em compostos poliméricos prejudiciais ao motor. O objetivo deste trabalho foi avaliar a estabilidade oxidativa do biodiesel obtido pela etanolise dos óleos de soja neutro, refinado, usado em fritura, e óleo parcialmente hidrogenado usado em fritura. A avaliação foi feita através do equipamento Rancimat[®], nas temperaturas de 100 e 105°C, com fluxo de ar de 20 L h⁻¹. A composição em ácidos graxos foi determinada por CG e o índice de iodo calculado. Embora os óleos de soja neutro, refinado e usado em fritura apresentassem índices de iodo próximos, a estabilidade oxidativa do biodiesel comportou-se de maneira distinta. O biodiesel de óleo neutro apresentou maior estabilidade, seguido pelo refinado e usado em fritura. Por conter antioxidantes naturais em sua composição, o óleo neutro de soja proporcionou uma estabilidade oxidativa maior ao biodiesel produzido. O proveniente de óleo refinado - que pelo processo de desodorização perde parte destes antioxidantes - apresentou menor estabilidade. O processo térmico degrada os antioxidantes, resultando em menor estabilidade ao biodiesel de óleo de fritura, ocorrendo o mesmo com o biodiesel de óleo hidrogenado usado em fritura, embora este apresentasse índice de iodo inferior aos demais.

Palavras-chave: Rancimat[®], transesterificação, oxidação

INTRODUCTION

There is an increasing interest in alternative energy sources since the major part of all energy consumed

worldwide comes from petroleum, charcoal and natural gas. These sources are limited, and will be exhausted in the near future (Schuchardt et al., 1998; Encinar et al., 1999; Nascimento et al., 2001). Historically, many bio-

mass and agricultural derived materials have been suggested as alternative energy sources and the use of biodiesel as fuel presents a promising potential (Al-Widyan & Al-Shyoukh, 2002; Mushrush et al., 2001b), being a market that grows rapidly (Harten, 2003). This is due to its great contribution to the environment (Bagley et al., 1998; Antolín et al., 2002) and to its role as a strategic source of renewable energy in substitution to diesel oil and other petroleum-based fuels (Wu et al., 1998; Cardone et al., 2002).

Biodiesel consists of long-chain fatty acid esters (Haas et al., 2001; Abreu et al., 2004) produced by transesterification reaction of vegetable oils with short chain alcohols (Noureddini et al., 1998; Encinar et al., 2002). It is compatible with conventional diesel fuel and already comprises a commercial fuel in Europe (Knothe et al., 2003; Dorado et al., 2003; Serdari et al., 1999). However, some chemical and physical properties of biodiesel can be affected by oxidation of the fuel during storage (Monyem et al., 2001). One drawback of biodiesel is that it is more prone to oxidation than petroleum-based fuels and, in its advanced stages, this can cause acidity in the fuel and form insoluble gums and sediments that can plug fuel filters (Monyem & Van Gerpen, 2001).

The rates of reactions in autoxidation schemes are dependent on hydrocarbon structure, heteroatom concentration, heteroatom speciation, oxygen concentration, and temperature. Fuel instability problems can be of two related types, short-term oxidative instability and long-term storage instability (Mushrush et al., 2000). Storage instability, is defined in terms of solid formation, which can plug nozzles, filters, and degrade engine performance (Mushrush et al., 2001a).

The objective of this work was to determine the oxidative stability of the ethyl esters manufactured by the transesterification of neutralized, refined, frying oil waste, and partially hydrogenated soybean frying oil waste.

MATERIAL AND METHODS

Preparation of the biodiesel samples

The reaction of transesterification was carried out with neutralized, refined, soybean frying oil waste, and partially hydrogenated frying oil waste samples under the same conditions in a 5 L spherical reactor, provided with temperature control and mechanical stirring. The system was kept at 50°C and then 3 L of oil were added. When the system reached 45°C, a solution of anhydrous ethanol and NaOH (catalyst) was added, in the ratio of 100:1 (g/g), taking this moment as zero time of the reaction. Each experiment lasted 5 min, after which the conversion to esters was complete. This point was evidenced by the rapid color alteration of the mixture. After that, 7.5% of glycerin, based on the weight of oil, was added, which

resulted in the formation of an upper phase consisting of ethyl esters and a lower phase consisting of the liberated and added glycerin, the excess of ethanol, the unreacted sodium hydroxide together with soaps formed during the reaction and some entrained ethyl esters and partial glycerides. After separating the two layers by decantation, the ethyl esters were purified by rinsing with a solution containing 1.5 L distilled water at 90°C and 0.5% (v/v) of HCl. With this the remaining catalyst of the reaction was neutralized, which was eliminated with the rinse water. Finally, the traces of water present in the esters was eliminated with anhydrous sodium sulphate by filtration. The lower phase was submitted to a distillation at 80°C under a moderate vacuum to recover the ethanol excess.

Oxidative stability determination

The oxidative stability of the biodiesel samples was evaluated by means of the Rancimat[®] equipment model 617, under temperatures of 100 and 105°C and air flow of 20 L h⁻¹. Samples of 5 g were utilized, weighed in the Rancimat[®] flask. The oxidation was then induced by the passage of the air flow through the sample, kept under constant temperature. The volatile products of the reaction, which were blown with the air, were collected in distilled water and measured by the change in electric conductivity of this water. They were expressed through a curve from which the induction period can be calculated by the interception of two lines: a tangent to the inclination and the another tangent to the curve level part. The method used was adapted from the American Oil Chemist's Society (1997) recommended method Cd 12b-92.

The cleanliness of the containers used in the Rancimat[®] apparatus is essential to get trustyful and safe results, therefore traces of oxidated fats or metals may have a harmful effect on the induction period. In order to avoid problems the cleaning practical procedures of the used material were performed according to Pacheco's (1991) specifications.

Fatty acids composition

The fatty acid composition of the biodiesel samples was determined by gas chromatography after preparation of fatty acid esters according to the Hartman & Lago (1973) method. The chromatograph was a Perkin Elmer Sigma 3B, equipped with FID detector and Silar 10C column (4 m × 1/8"i.d.). The injector and detector temperature was 225°C and the column temperature 175°C. Carrier gas: 35 mL N₂ per min, injection volume 1 mL. The identification of the peaks was carried out through the comparison with the retention time of standards Nu-Chek and the quantification by area normalization. The iodine value was calculated by the method Cd 1c-85 American Oil Chemist's Society (1997).

Statistical analysis

All determinations were carried out in triplicate and expressed as means. The experiment was repeated twice and compared by the Student t-test using the Statistica 5.0 Software.

RESULTS AND DISCUSSION

The fatty acid composition of the oils seems to have an important role in the performance of the biodiesel in diesel engine (Dorado et al., 2004). Based on the fatty acid composition and many other parameters, the EU biodiesel specifications will be mandatory to limit the oxidative stability, as it may be a crucial parameter for injection pump performance (Mittelbach & Gangl, 2001). Moreover, the stability of the fuel is a quality parameter established by the ANP – National Petroleum Agency in Brazil, being its evaluation and control necessary (Agência Nacional de Petróleo, 2003). The fatty acids composition determined for the different soybean oils is shown in Table 1.

Vegetable oils are natural products consisting of ester mixtures derived from glycerol (triglyceride), whose chains of fatty acid contain about 14 to 20 carbon atoms with different degrees of unsaturation. The transesterification reaction consists in the conversion of the triglyceride molecules, by means of the action of short chain alcohol, i.e., ethanol, into the corresponding fatty acids esters. According to the source of oilseed, variations in the chemical composition of the vegetable oil are expressed by variations in the molar ratio among different fatty acids in the structure.

The relative ratio of fatty acids present in the raw material is kept relatively constant after the transesterification reaction (Costa Neto et al., 2000). Therefore, in general the fatty acids ethyl esters profile obtained by transesterification is reflected by the composition in fatty acids of the employed raw material. This fact can be proven by comparing the fatty acid compositions in employed raw materials (Table 1), with the fatty acids composition in esters of the produced biodiesel (Table 2).

The duration of the induction period is a measure of its resistance to oxidation. The Rancimat[®] method is based on the fact that in oxidated oils or fats, volatiles are formed at the end of the induction period. In this method the oxidation is induced by the passage of a constant air flow through the sample that is kept under constant temperature. The volatile products of the reaction are collected in distilled or deionized water and are measured through the electric conductivity of these liquids. During the development of the reaction, due to an increase of the conductivity, a curve is drawn from which the induction period is inferred.

The most significant and undesirable instability change in liquid fuel with time is the formation of solids, also termed filterable sediments (Mushrush et al., 2001a). During long-term storage, oxidation due to contact with air (autoxidation) presents a legitimate concern with respect to maintaining fuel biodiesel quality (Dunn, 2002).

Table 3 shows the oxidative stability results of the biodiesel from neutralized, refined, soybean frying oil waste, and partially hydrogenated frying oil waste samples evaluated through the Rancimat[®].

Table 1 - Fatty acids composition of the different soybean oils used to produce biodiesel [% m/m].

Fatty acid*	Soybean oils			Partially Hydrogenated Frying Waste
	Neutralized	Refined	Frying Waste	
C12:0	nd**	nd	tr***	tr
C 14:0	tr	nd	0.36	0.60
C 16:0	11.22	11.76	12.40	21.48
C 16:1	nd	nd	0.72	tr
C 18:0	4.61	4.04	4.53	8.80
C 18:1 cis	22.75	24.98	24.30	62.01
C 18:1 trans	nd	nd	nd	1.83
C 18:2	54.45	55.41	51.97	5.28
C 18:3	6.97	3.80	5.48	tr
C 20:0	tr	tr	0.23	tr
C22:0	nd	tr	nd	nd
Σ saturated	15.83	15.80	17.52	30.88
Σ unsaturated	84.17	84.19	82.47	69.12
Iodine Value	129.50	133.13	131.60	66.92

*Mean of three analytical determinations **tr – traces < 0.1% ***nd – not detected

Table 2 - Fatty acids composition of the biodiesel from different soybean oil sources [% m/m].

Fatty acid*	Biodiesel from soybean oil			Biodiesel from
	Neutralized	Refined	Frying waste	
C12: 0	nd**	nd	0.38	0.53
C14:0	nd	nd	0.16	0.66
C16:0	11.29	11.62	12.67	20.81
C16:1	nd	nd	0.95	0.11
C18:0	3.54	3.39	3.56	9.83
C18:1cis	22.45	23.73	23.84	60.53
C18:1trans	nd	nd	nd	2.18
C18:2	54.62	54.36	51.27	5.36
C18:3	8.11	6.10	6.80	tr
C20:0	tr***	0.64	0.37	0.35
C22:0	nd	0.15	nd	nd
Σ Saturated	14.83	15.80	17.14	32.19
Σ Unsaturated	85.18	84.19	82.86	68.18
Iodine value	141.22	136.40	133.76	66.16

*Mean of three analytical determinations **nd – not detected ***tr – traces < 0.1%

Table 3 - Induction period of biodiesel from different vegetable oils obtained in Rancimat®.

Biodiesel	Induction period [min]*	
	105°C	100°C
Neutralized soybean oil	277	488
Refined soybean oil	132	238
Frying soybean oil waste	20	32
Partially hydrogenated frying waste	48	80

*Mean values of three analytical determinations.

The biodiesel from neutralized soybean oil presented greater stability, followed by biodiesel from refined and from frying waste. This can be explained by the fact that the neutralized soybean oil has in its composition natural antioxidants, as for example tocopherol (Hartman & Esteves, 1981), which increases the stability of the oil and also shows beneficial effects on retarding oxidative degradation of biodiesel produced from this oil. Otherwise, the refined soybean oil, because of the refining process, mainly in the stage of the deodorization, loses part of its natural antioxidants, which also decreases the stability of the biodiesel. The primary products from the deodorizer distillate are vitamin E (D- α -tocopherol) mixed tocopherols used as antioxidants (Erickson, 1995). Analysis of desodorizer distillates from soybean oil had indicated to contain about 11.1% of tocopherol.

Because of the heating process, soybean frying oil waste suffers oxidative and hydrolytic degradations, which are accelerated by the high temperature. It causes

the formation of oxidation products, which decrease the stability of the produced ethyl ester.

The highly saturated fatty acid level in fact proves to be advantageous in terms of storage stability as compared to the more unsaturated vegetable oil-based fuels, which are more susceptible to the chemical deterioration (e.g. autoxidation and polymerization) under certain conditions of storage temperature, moisture, ultraviolet radiation, and packaging materials (Wu et al., 1998). The results obtained for partially hydrogenated frying oil waste showed that it has greater percentage of unsaturated acids in its composition and it also presented lower iodine value, which should have provided a higher oxidative stability. However, when the partially hydrogenated frying oil waste was used for transesterification, the biodiesel obtained did not present a good stability probably because of the frying process to which it was submitted previously.

Methyl esters performed slightly better than ethyl esters during the storage test in stability studies carried by Du Plessis et al. (1985).

CONCLUSION

The biodiesel from neutralized soybean oil presented greater oxidative stability maybe due the presence of natural antioxidants in its composition. The biodiesel from refined soybean oil, due to the deodorization process, when part of these antioxidants are lost, presented less stability. Due to the thermal process which degrades antioxidants present in the oil, biodiesel from soybean frying oil waste showed lower stability. Biodiesel produced

from partially hydrogenated frying oil waste, even though it possessed low iodine value in comparison to the other, presented low oxidative stability possibly due to the thermal process to which it was submitted previously.

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