



## Chemical Characterization of Frying Oil Biodiesel and Relation with the Oxidation Stability

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The production of biodiesel from renewable sources is an important energy alternative to petroleum diesel. Even as the use of frying oil for biodiesel production is an environmentally friendly alternative. However, the oxidation stability is one of the properties that can affect the performance of a fuel. Thus, this work investigates the components responsible for this low oxidative stability. For this, biodiesels from soybean oil and frying oil were produced and analyzed according to methods determined by the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP). The results obtained were related to oxidation stability and show the influence of free fatty acids on the quality of frying oil biodiesel. When the sample presents short chain acids in the composition, as acetic and butyric acids, it can influence negatively the oxidation stability, reducing upon to 99.7%. In addition, it was observed that the caprylic, capric and lauric acids found in frying oil biodiesel contributed to the lower oxidation stability.

### 1. Introduction

Biodiesel is known as a potential candidate for replacing diesel oil (Demirbas (2008) and Gabriel et. al. (2015)). Generally, it is defined as an alkyl ester derived from long-chain carboxylic acids, produced from the reaction of transesterification or esterification of vegetable oils and animal fats. The Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) regulate the specifications for biodiesel commercialization in Brazil. Energetically, biodiesel production has become an alternative to the total or partial replacement of fossil fuel diesel. It can be used pure or in the form of blends with diesel without engine modifications. This year the mixture of biodiesel in diesel sold in Brazil rises from 11% to 12%, and the plan is to increase one point percent each year, reaching 15% in 2023 (ANP). While in Europe the content of the mixture varies according to the country, for instance in Italy and France this blend is B5 (Nersesian, 2010).

The use of residual frying oil for the production of biodiesel is an option to reduce costs since the raw material comprises around 88% of the costs of biodiesel production (Ghayal et al., 2013). In addition, the use of frying oil is an environmentally-friendly alternative for this residue (Da Silva and Neto, 2013). When improperly disposed, the frying oil reaches aquatic sources, forms layers on the surface of the water, avoiding the exchange of oxygen and causes alterations to the ecosystem. Frying oil could also clogs the sewer pipes, encouraging the formation of odors and increases the cost of water treatment (Montero and Stoytcheva, 2011, Correia et. al., 2017 and Zeleme and Barros, 2022)).

The frying oil is the one that has gone through the heating process, modifying their nutritional, functional (Corsini et al., 2008) and chemical properties (Akoh C. and Min, 2008). The chemical changes

that occur in frying oil are caused by hydrolytic degradation, polymerization and oxidation (Pullen and Saeed, 2012; Wang et al., 2016). Hydrolytic degradation occurs when water breaks the triglyceride molecule into diglyceride, monoglyceride and free fatty acid. Polymerization occurs when the products of the triglyceride decomposition react and form by-products of higher molecular mass (Zuleta et al., 2012a).

Within the quality parameters of biodiesel is the oxidation stability that is related to the time that a fuel is able to resist oxidation (*Biodiesel Handling and Use Guidelines (Second Edition)*, 2006). The biodiesel from frying oil has low stability to oxidation (Bouaid et al., 2007), fact that alters its properties and makes it difficult to use as fuel (Sorate and Bhale, 2015). Oxidation stability is one of the parameters for controlling the quality of biodiesel and it is related to the tendency of biodiesel to react with oxygen (Fu et al., 2016), thus changing its chemical and physical properties. It is a slow reaction, although it is fast when subject to high temperatures such as those of a vehicle engine (Pullen and Saeed, 2012).

Biodiesel tends to be less resistant to oxidation than petroleum diesel. Its low stability reduces storage time, increases viscosity and acidity, causing corrosion in the engine and forming deposits that lead to filter clogging or fuel injection failure (*Biodiesel Handling and Use Guidelines (Second Edition)*, 2006).

In some cases, oxidation alters the chemical structure of biodiesel to form polymers, aldehydes, short-chain acids and other products (Pullen and Saeed, 2012). The addition of antioxidants reduces the auto-oxidation of biodiesel. Vegetable oils have natural antioxidants such as tocopherols, sterols and tocotrienols. However, they are removed by distillation at the time of purification of the biodiesel manufacturing process. The addition of synthetic antioxidants

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ensures the stability of biodiesel by reacting with free radicals. The most used are butyl-hydroxytoluene (BHT), butylhydroxyanisol (BHA) and t-butyl-hydroxyquinone (TBHQ) (Domingos et al., 2007).

Several methods are used to measure oxidation stability. Currently, the reference method is the EN 14112 standard. This method is based on oxidizing the sample using a temperature of 110 °C and oxygen gas in the Rancimat device. The sample, when oxidized, forms volatile by-products that are discharged into a vat containing deionized water with a conductivity meter. The time it takes for the conductivity of deionized water to increase is the time corresponding to oxidation stability (Focke et al., 2016). Rancimat test is the most commonly used method, due to both rapid and economic method and also presents good repeatability. However, according to Saluja et al. (Saluja et al., 2016) this test it is not suitable for fat containing foods and oils because sometimes the temperature can interfere the oxidation of oils, especially at high temperatures.

Some researchers use thermogravimetric analysis, this technique consists of analyzing the thermal behavior of the samples based on the variation of the mass as a function of time or temperature. The sample is conditioned inside a crucible in a thermobalance, capable of measuring and recording the mass continuously, obtaining a thermogravimetric curve. Based on the generated graphic, percentage of mass lost versus temperature, the derivative of the thermogravimetric curve that corresponds to thermal stability, related to oxidation, is performed (Jain and Sharma, 2010).

The European standard EN 16091 determines the analysis of oxidation stability using the PetroOXY instrument. This method is

based on the oxidation of volatile and non-volatile compounds. Inside a closed chamber at a temperature of 140 °C, 5 mL of sample receives oxygen under a pressure of 700 kPa. The moment when the pressure decreases, it means that the oxygen gas has been consumed and the sample has reached the time required for (Neumann et al., 2008).

Another method is described in ASTM D5304, which measures oxidation stability using the differential scanning calorimetry technique at high pressures. In this procedure, the sample is subjected to temperatures of 155 °C to 210 °C at a pressure of 3.5 MPa. The induction time is the time required for the instrument to detect an exothermic reaction (Jain and Sharma, 2010). This method has the advantage of requiring small sample and it can determine other properties of oil, for instance specific heat, melting point, etc. However it has to use specialized equipment and it is not an economic method. Another limitation is the reproducibility of the results, according to Saluja et al. (Saluja et al., 2016) the presence of anti-oxidants can interfere in the result.

Table 1 shows acid index and oxidation stability data of vegetable, animal and residual oil. The acid index varies in a low range, typical for unused oil. For oxidative stability, a wide range of values was observed. This variation is a result of differences in the composition in terms of fatty acids (Focke et al., 2012; Yaakob et al., 2014) and the biodiesel produced will also be influenced by this. Among those raw materials the beef tallow presented the highest acid index, 2.77 mg KOH g<sup>-1</sup>. The lowest oxidative stability values were observed for frying oil, ranging from 0.2 to 2.6 h.

**Table 1.** Results found in the literature on acid index and oxidation stability for different raw materials.

Raw-material	Acid index (mg KOH g <sup>-1</sup> )	Oxidation stability (h)	References
Beef tallow	2.77	7.5	(Kleinberg et al., 2019) (Silva et al., 2015)
Cotton	0.27	3.6	(Serqueira et al., 2014)
Canola	0.22	11.0	(Giakoumis, 2013)
Corn	0.23	6.2	(Cremonez et al., 2016)
Fish	0.19	9.8	(Martins et al., 2015)
Frying oil	0.31	2.6	(Serqueira et al., 2014)
	0.18	0.2	(Y.-S. Hung et al., 2010)
	0.37	2.6	(Zhou et al., 2016)
	1.10	0.2	(Alberici et al., 2012)
	0.11	0.7	(De Souza Schneider et al., 2011)
Jatropha	0.41	3.3	(Zuleta et al., 2012b)
Linseed	0.70	2.2	(Pantoja et al., 2013)
Pequi	0.27	6.2	(Cremonez et al., 2016)
	0.17	8.1	(Serrano et al., 2014)
	0.17	9.2	(Serrano et al., 2013)
Rapeseed	0.22	11.2	(Serqueira et al., 2014)
	0.24	14.4	(Serrano et al., 2014)
Sunflower	0.15	4.9	(De Sousa et al., 2014)
	0.18	6.0	(Serrano et al., 2014)
	0.18	7.0	(Serrano et al., 2013)
	0.23	5.5	(Cremonez et al., 2016)
	0.23	4.4	(Damasceno et al., 2013)
	0.27	7.8	(Fernandes et al., 2013)
	0.32	5.0	(Giakoumis, 2013)
Soybean	0.37	3.7	(Roveda et al., 2016)
	0.49	3.6	(Beker et al., 2016)

The oxidation degradation has three stages: initiation, propagation and termination (Akoh C. and Min, 2008). Initiation is the reaction in which free radicals attack the allylic hydrogen of the lipid forming an

allylic radical and from this, propagation occurs. During this moment, the allylic radical reacts with oxygen and forms peroxide radical. This radical reacts with another hydrogen and forms a

hydroperoxide. Termination occurs when two radicals combine to form various products, such as organic acids, aldehydes, ketones, among others (Pullen and Saeed, 2012; Zuleta et al., 2012a).

The biodiesel composition in relation to the amounts of esters derived from fatty acids is the factor with the most impact on the properties of the fuel (Yaakob et al., 2014). Biodiesel containing higher number of double bonds has a tendency to react more with oxygen (De Sousa et al., 2014). While biodiesel produced from frying oil generally has higher acidity (Díaz and Borges, 2012), higher viscosity and can present lower stability to oxidation (Pullen and Saeed, 2012). This lower oxidation stability is one of the difficulties for the expansion of the use of biodiesel. In general, the effect of storage conditions is known to decrease the oxidative stability, especially when exposed to light and air. Besides that, Serrano et al. (Serrano et al., 2014) affirm that biodiesel oxidative stability is affected by content and position of double bonds in the fatty acids, presence of anti and pro-oxidant substances, production technology used. However, in this study the evaluation of oxidative stability was only focused on the influence of different chain size acids.

## 2. Methodology

### 2.1 Biodiesel production

Soybean oil was acquired from food suppliers (Soya<sup>®</sup>) while the frying oil was taken in a local restaurant in Blumenau - Santa Catarina State, Southern Brazil. Methanol and potassium hydroxide reactants were obtained from commercial sources (reagent-grade) and used without further purification. Biodiesel from soybean oil and frying oil were obtained from the alkaline transesterification reactions using methanol in a 1:6 molar ratio and with 0.6% (w/w) of potassium hydroxide (KOH) as catalyst (Knothe et al., 2006). The data for the transesterification reaction was presented in base mass rather than molar mass, aiming to broad the access and reproducibility of experiments. The reaction was carried out with 500 g of oil, 328.6 g of methanol and 3 g of potassium hydroxide in a round bottom flask, inserted into a water bath with controlled temperature and reflux, stirring for 1 hour at 65 °C. After the reaction time, the methanol was removed by simple distillation and the other products were put in a separation funnel. After 12 h, the formed glycerin was removed by decantation, the impurities of the

biodiesel were washed with water and the biodiesel was dried with desiccant sodium sulfate anhydrous.

### 2.2 Physical chemical analyses

The acid index (AI) was determined according to ASTM D 974. The method consists of titrating 5 g of sample dissolved in 50 mL of isopropanol with 0.01 M alcoholic potassium hydroxide and phenolphthalein as indicator. The iodine index (II) was determined by DS-EN14111. For the test, 0.14 g of sample, 25 mL of Wijs solution (iodine and chlorine commercial solution) and 20 mL of a solution of acetic acid and cyclohexane (1:1) were added to a flask and kept under absence of light for one hour. Subsequently, 20 mL of a 10% potassium iodide solution (w/v) and 150 mL of distilled water were added to the erlenmeyer flask. This mixture was titrated with 0.1 M sodium thiosulfate using starch as indicator.

The specific mass was determined by the method given in ABNT-NBR14065. The sample was transferred to a measuring cylinder at 20°C and a glass densimeter was inserted to read it directly. The method used for viscosity determination was ABNT-NBR10441, using an Ostwald viscometer and standard solution of viscosity S6. The S6 standard was inserted into the viscometer and was subjected to a bath at 40°C. In order to obtain the viscosity value, the sample density value was obtained beforehand at 40°C and the dynamic viscosity test was performed.

### 2.3 Chromatographic analysis

The biodiesels and oils were submitted to gas chromatography assay to enable compound identification. The samples were submitted to derivatization with sulfuric acid and the resultant organic phase was submitted to chromatographic analysis. A gas chromatograph with flame ionization detector (GC-FID), Shimadzu model GC-2010 with Stabilwax column (30 m x 0.25 mm x 0.25 µm) was used. Helium 5.0 was used as a carrier gas with 50 °C heating ramp for 2 min, heating at 10 °C/min to 200 °C maintained for 8 min, heating at 5 °C/min to 240°C maintained for 12 min. The temperature of both injector and detector temperature were 250 °C with 1:50 split ratio. The identification was obtained by comparison to the injected standards, methyl esters C<sub>7:0</sub>-C<sub>24:0</sub> and fatty acid standards C<sub>2:0</sub>, C<sub>4:0</sub>, C<sub>6:0</sub>, C<sub>8:0</sub>, C<sub>10:0</sub> and C<sub>12:0</sub>.

**Table 2.** Enrichment (m/m) of the soybean oil biodiesel with different compounds.

	Enrichment (%)	Description
B1	0	Pure soybean oil biodiesel sample
B2	0.1	C <sub>2:0</sub> , C <sub>4:0</sub> , C <sub>6:0</sub> , C <sub>8:0</sub> , C <sub>10:0</sub> , C <sub>12:0</sub>
B3	0.05	C <sub>2:0</sub> , C <sub>4:0</sub> , C <sub>6:0</sub> , C <sub>8:0</sub> , C <sub>10:0</sub> , C <sub>12:0</sub>
B4	0.02	C <sub>2:0</sub> , C <sub>4:0</sub> , C <sub>6:0</sub> , C <sub>8:0</sub> , C <sub>10:0</sub> , C <sub>12:0</sub>
B5	0.2, 0.02 and 0.1	C <sub>8:0</sub> , C <sub>10:0</sub> and C <sub>12:0</sub> , respectively
B6	0.06, 0.02 and 0.1	Methyl ester from C <sub>8:0</sub> , C <sub>10:0</sub> and C <sub>12:0</sub> , respectively
B7	0.05	
B8	0.1	
B9	0.2	
B10	0.3	Butyric acid (C <sub>4:0</sub> )
B11	0.4	
B12	0.5	
B13	0.6	
B14	0.1	Acetic acid (C <sub>2:0</sub> )
B15	0.1	Butyric acid (C <sub>4:0</sub> )
B16	0.1	Caproic acid (C <sub>6:0</sub> )
B17	0.1	Caprylic acid (C <sub>8:0</sub> )
B18	0.1	Capric acid (C <sub>10:0</sub> )
B19	0.1	Lauric acid (C <sub>12:0</sub> )

## 2.4 Oxidation stability

After analytical procedure to determine the chemical composition of soybean and frying biodiesel, the main differences were analyzed. In order to check if oxidation stability was affected by short chain acids ( $C_2$  to  $C_{12}$ ), these were added in soybean oil to check its behavior, the majority of those acids were present in the frying oil. Therefore, samples of biodiesel from soybean were enriched with different compounds (B1 to B6 samples) and were submitted to oxidation stability tests and acid index measurement in duplicate (Table 2). In order to evaluate the concentration effect, a sample of soybean biodiesel enriched with butyric acid in different concentrations, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6% (B7 to B13). Also, in order to verify which of the carboxylic acids with smaller chain size had more influence in the stability, samples of soybean biodiesel were again enriched with acids between  $C_{2:0}$  and  $C_{12:0}$  (B14 to B19) at 0.1% concentration.

The oxidation stability tests were carried out on Rancimat 873 equipment (Metrohm) following the standard DS EN 14112. For this procedure, 3 g of biodiesel was added in a 110 °C temperature cell with constant injection of oxygen. The volatile compounds formed were conducted to another cell containing deionized water with conductivity monitoring. A graph of conductivity versus time is formed. The inflection point corresponds to the induction time (Focke et al., 2016). The result of the oxidation stability is expressed in hours spent for degradation.

## 3. Results and Discussion

### 3.1 Oil analysis

The values of the oil analyses comprise the average of the duplicates and the results for acidity index were  $0.48 \pm 0.02$  mg KOH  $g^{-1}$  for soybean oil and  $6.03 \pm 0.11$  mg KOH  $g^{-1}$  for the frying oil. Oils with higher acid index indicate degradation tendency and directly influence the yield of the transesterification reaction (Díaz and Borges, 2012).

The iodine index showed an average value of  $126.41 \pm 0.01$  for soybean oil and  $95.9 \pm 0.71$  g  $I_2$  100  $g^{-1}$  for the frying oil. According to the maximum and minimum values for iodine index established by the MAPA (IT 49/2006), soybean oil should have iodine index between 124 to 139 g  $I_2$  100  $g^{-1}$ . The higher the iodine index, the higher the degree of unsaturation, whereas low iodine index may be indicative of the loss of these unsaturation by degradation or because they contain higher concentrations of saturated fatty acids (Zuleta et al., 2012a).

The technique of gas chromatography with flame ionization detector (GC-FID) showed peaks for soybean oil at retention times similar to those of frying oil, while frying oil presented higher amounts of peaks. Table 3 shows the retention values, the relative percentage of the area of the peaks and the composition found according to the inserted standards.

**Table 3.** Fatty acids composition for soybean oil and frying oil after GC-FID analyses.

Fatty acids	Soybean oil		Frying oil	
	RT* (min)	%	RT (min)	%
Caprylic acid ( $C_{8:0}$ )	NI**	NI	10.065	0.183
Capric acid ( $C_{10:0}$ )	NI	NI	12.783	0.027
Lauric acid ( $C_{12:0}$ )	NI	NI	15.229	0.11
Myristic acid ( $C_{14:0}$ )	NI	NI	17.298	0.10
Tetradecenoic acid ( $C_{14:1}$ )	NI	NI	17.466	0.51
Palmitic acid ( $C_{16:0}$ )	20.194	13.76	20.200	19.83
Palmitoleic acid ( $C_{16:1}$ )	20.633	0.29	20.667	0.44
Stearic acid ( $C_{18:0}$ )	24.514	4.25	24.519	6.00
Oleic acid ( $C_{18:1}$ cis <sup>9</sup> )	25.164	21.72	25.176	32.64
Elaidic acid ( $C_{18:1}$ n <sup>9</sup> )	25.338	1.31	25.325	4.10
Vaccinic acid ( $C_{18:1}$ n <sup>11</sup> )	NI	NI	25.521	2.90
Linoleic acid ( $C_{18:2}$ n <sup>9,12</sup> )	26.519	52.32	26.497	30.79
Linoleic acid ( $C_{18:2}$ n <sup>9,12</sup> )	NI	NI	26.787	0.39
Linolenic acid ( $C_{18:3}$ n <sup>9,12,15</sup> )	28.175	5.49	28.166	1.60
Arachidic acid ( $C_{20:4}$ n <sup>5,8,11,14</sup> )	29.777	0.37	29.778	0.37
Behenic acid ( $C_{22:0}$ )	30.843	0.51	NI	NI

\*RT = retention time and \*\*NI = not identified.

The main difference found in the frying oil were the presence of fatty acids with chain of 8, 10, 12 and 14 carbons in the frying oil and higher concentration of trans fatty acids, 7% for frying oil and 1.31% for soybean oil. The percentage of unsaturated compounds was 81.5% for soybean oil and 73.7% for frying oil, presenting

degradation. According to the literature, unsaturation should cause more oxidative instability, however our data indicates the opposite. This can be caused by the short chain carboxylic acids that are present in the frying oil composition. Therefore, to fulfill the need to

understand this behavior this study will assess enrichment with different acids and their effect in oxidative stability.

### 3.2 Biodiesel Analysis

The transesterification reaction of soybean oil with methanol produced 453.2 g of biodiesel, 65.3 g of glycerol and 214.1 g of recovered methanol, representing 90.9% recovery of soybean oil to biodiesel. And the transesterification reaction with the frying oil produced 420.6 g of biodiesel, 84.9 g of glycerol and 191.1 g of methanol recovered by distillation in 83.47% yield.

The results of the biodiesel analysis were carried out in triplicates according to the methods defined by the ANP. The specific mass presented close values for the frying oil and soybean oil,  $886.5 \pm 0.56 \text{ kg m}^{-3}$  and  $885.5 \pm 0.12 \text{ kg m}^{-3}$ , respectively. The specific mass is related to the structure of the molecule and it is a parameter that is influenced by oxidation (Knothe et al., 2006; Yaakob et al., 2014).

The viscosity test presented the highest value for frying oil biodiesel,  $4.83 \pm 0.01 \text{ mm}^2 \text{ s}^{-1}$ , while soybean biodiesel  $4.51 \pm 0.02 \text{ mm}^2 \text{ s}^{-1}$ . More unsaturated samples have a greater tendency to form products of high molecular mass or isomerization of the double bond of cis to trans (Yaakob et al., 2014).

In relation to the iodine index, the frying oil biodiesel had a lower value,  $98.8 \pm 1.45 \text{ g I}_2 100\text{g}^{-1}$  and the soybean  $133 \pm 0.31 \text{ g I}_2 100\text{g}^{-1}$ . The loss of the unsaturation is an indicative of degradation, since the double bonds undergo greater oxidation action (Demirbas, 2007; Zuleta et al., 2012a). In the case of the acid index, the frying oil biodiesel presented higher acidity,  $1.37 \pm 0.06 \text{ mg KOH g}^{-1}$  versus  $0.12 \pm 0.01 \text{ mg KOH g}^{-1}$  for soybean biodiesel. This value is justified by the excess acidity of the frying oil used as raw material and indicating the possible presence of free fatty acids.

The oxidation stability of soybean oil biodiesel was 4 h 52 min, whereas the frying oil biodiesel presented 99% reduction, lower than 1 min, thus indicating that it was already unstable. This oxidation stability can be attributed to acetic and butyric acids.

The gas chromatography technique performed on biodiesels showed differences in composition. Frying oil biodiesel had similar composition, however biodiesel from soybean oil does not presented caprylic acid (identified with letter e – 18.0 min), capric acid (identified with letter h – 21.4 min), lauric acid (identified with letter o – 26.3 min), as showed in Figure 1 chromatograms.

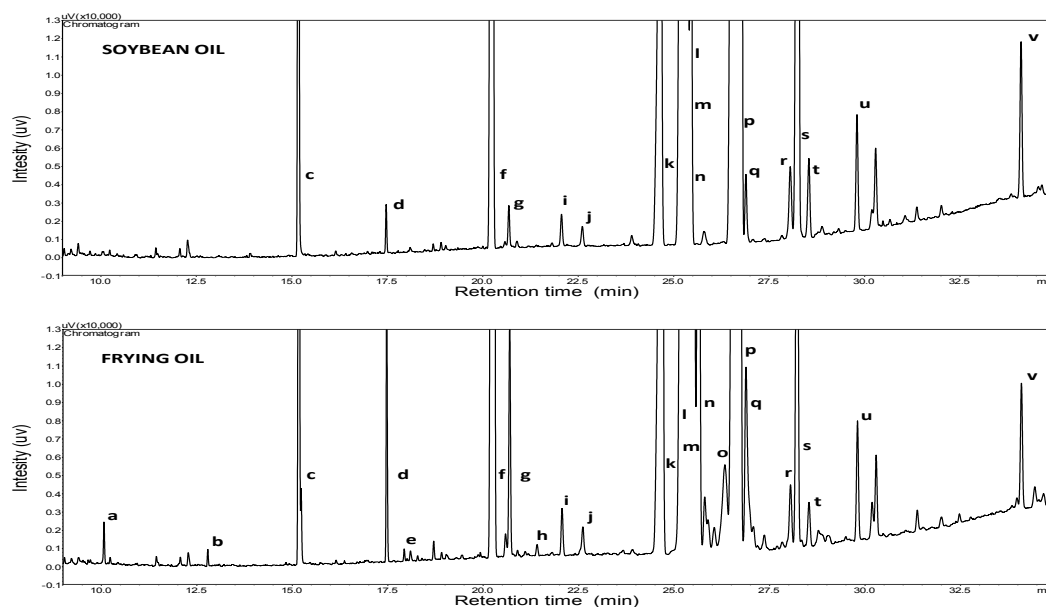


Figure 1. GC-FID chromatogram of soybean and frying oil biodiesels.

The values of retention times, the relative percentage of peak area and the composition found according to the inserted standards are listed in Table 4. The GC-FID analysis for biodiesel presented 85.6% of unsaturated methyl esters for soybean biodiesel and 78.51% for frying biodiesel. The trans isomers were in higher concentration for the frying biodiesel, 6.55%, while the soybean presented 1.55%.

It was observed that the composition of biodiesel from soybean oil and frying oil is similar. The main component present in frying oil biodiesel was methyl linoleate (35.13%), followed by methyl oleate (32.54%) and methyl palmitate (15.94%). The same trend was observed for soybean oil biodiesel with the corresponding components percentage of the 52.49, 25.23 and 10.83%,

respectively. Those values were similar with Sagioglu et al. (Sagioglu et al., 2011) results. The major difference found in the analysis of biodiesel from frying oil by GC-FID was the presence of methyl esters of 8, 10 and 12 carbons and the presence of free fatty acids, capric acid ( $C_{8:0}$ ), caprylic acid ( $C_{10:0}$ ) and lauric acid ( $C_{12:0}$ ), absent in biodiesel from soybean oil. Despite those compounds were being identified in small concentrations, summing approximately 0.77%. The presence of free fatty acids of 8, 10 and 12 carbons in biodiesel suggests a possible correlation with oxidative stability. In order to verify whether these acids have an effect on oxidative stability, enrichments were made in soybean oil (B5 from Table 2).

Table 4. Relative area composition for soybean oil and frying biodiesel after GC-FID analyses.

Compounds	Soybean oil biodiesel		Frying oil biodiesel	
	RT* (min)	%	RT (min)	%
a Methyl caprylate (C <sub>8:0</sub> )	NI**	NI	10.068	0.06
b Methyl capricate (C <sub>10:0</sub> )	NI	NI	12.786	0.02
c Methyl laurate (C <sub>12:0</sub> )	NI	NI	15.231	0.10
d Methyl myristate (C <sub>14:0</sub> )	17.471	0.07	17.473	0.42
e Caprylic acid (C <sub>8:0</sub> )	NI	NI	18.095	0.02
f Methyl palmitate (C <sub>16:0</sub> )	20.259	10.83	20.28	15.94
g Methyl palmitoleate (C <sub>16:1</sub> n <sup>9</sup> )	20.684	0.08	20.694	0.48
h Capric acid (C <sub>10:0</sub> )	NI	NI	21.412	0.02
i Methyl margarate (C <sub>17:0</sub> )	22.063	0.06	22.065	0.11
j Methyl heptadecanoate (C <sub>17:1</sub> n <sup>10</sup> )	22.609	0.05	22.610	0.08
k Methyl stearate (C <sub>18:0</sub> )	24.653	3.04	24.681	4.51
l Methyl oleate (C <sub>18:1</sub> n <sup>9</sup> )	25.363	25.23	25.388	32.54
m Methyl elaidate (C <sub>18:1</sub> n <sup>9</sup> )	25.452	1.50	25.484	3.71
n Methyl vaccenate (C <sub>18:1</sub> n <sup>11</sup> )	25.795	0.05	25.647	2.84
o Lauric acid (C <sub>12:0</sub> )	NI	NI	26.329	0.53
p Methyl linoleate (C <sub>18:2</sub> n <sup>9,12</sup> )	26.767	52.49	26.719	35.13
q Methyl linoleate (C <sub>18:2</sub> )	26.892	0.13	26.882	0.75
r Methyl linoleate (C <sub>18:3</sub> )	28.054	0.21	28.048	0.18
s Methyl linolenate (C <sub>18:3</sub> )	28.259	5.32	28.225	1.79
t Methyl arachidate (C <sub>20:4</sub> n <sup>5,8,11,14</sup> )	28.542	0.20	28.532	0.13
u Methyl arachidate (C <sub>20:4</sub> )	29.802	0.31	29.803	0.32
v Methyl behenate (C <sub>22:0</sub> )	34.100	0.43	34.096	0.33

\*RT = retention time and \*\*NI = not identified.

### 3.3. Oxidation stability evaluation

In order to verify the relationship between fatty acids and small chain methyl esters found in frying oil biodiesel with low oxidation stability, a sample of biodiesel from soybean oil was enriched with different compounds. The acid index in the different samples presented increase variation (Table 5). Soybean oil biodiesel (B1) showed an average value of 0.12 mg KOH g<sup>-1</sup>, while the average of biodiesels enriched with different fatty acids B2, B3 and B4 presented values higher than 2 mg KOH g<sup>-1</sup>, 2.68, 2.53 and 2.24 mg KOH g<sup>-1</sup>, respectively, therefore showing a decrease in the acid number as the enrichment decreased. Biodiesel B5, which refers to an enrichment closer to that found in frying biodiesel, had a value of 1.46 mg KOH g<sup>-1</sup>, higher value when compared to that found in frying biodiesel (1.37 mg KOH g<sup>-1</sup>). Biodiesel B6 enriched with methyl esters derived from C<sub>8:0</sub> fatty acids, C<sub>10:0</sub> and C<sub>12:0</sub> did not show an effective increase in acidity, 0.29 mg KOH g<sup>-1</sup>, indicating that the hydrocarbon chain size of the methyl ester does not effectively influence acidity. In order to evaluate those acids effect it was performed their enrichment in soybean oil. However, the presence of C8, C10 and C12 did not affect the oxidative stability.

The oxidation stability presented values that were decreasing with the increase of the free fatty acids. In concentrations higher than 0.1% the butyric acid present influence on oxidation stability. The

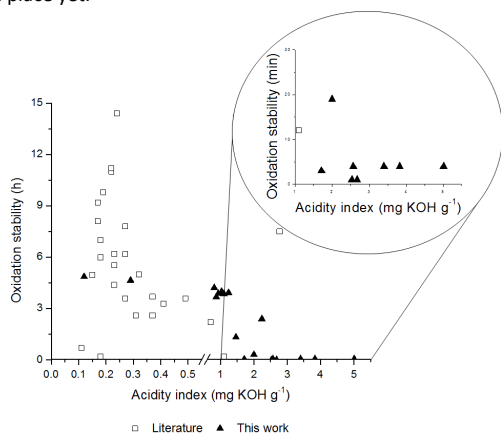
non-contaminated soybean biodiesel B1 presented 4 h 52 min of stability, the biodiesel enriched with 0.1% and 0.05% (B2 and B3) presented instability at the initial time (lower than 1 min). Biodiesels B4, B5 and B6 showed stability increase higher than 1h, B4 (0.02%) presented 2 h 24 min oxidation stability, B5 (enriched with the fatty acids found in the frying oil biodiesel) presented 1 h 20 min and B6 (enriched with methyl esters only) showed 4 h 39 min. In general, these oxidation stability tests with enriched biodiesels indicated that the methyl esters of 8, 10 and 12 carbon chains present oxidation stability similar to B1. From this assay it was possible to notice that the oxidation stability also depended on the acid type, as acetic acid influenced more on stability than the other higher chain acids. One possibility is that acetic acid, or any other short chain acids, when present in biodiesel, volatilize faster and show a shorter time of stability in Rancimat. The caprylic, capric, and lauric acids found in frying oil biodiesel contribute to low oxidation stability, but perhaps this low oxidation stability is not due to the fact that free fatty acids are able to degrade the biodiesel esters rapidly, but at the same time because they are capable of increasing the conductivity of the deionized water, indicating an induction point and low oxidation stability.

**Table 5.** Results of biodiesel from soybean oil enriched with different compounds.

Enrichment	Acid index (mg KOH g <sup>-1</sup> )	Oxidation stability
B1	0.12±0.01	4 h 52 min
B2	2.68±0.37	> 1 min
B3	2.53±0.00	> 2 min
B4	2.24±0.00	2 h 24 min
B5	1.46±0.00	1 h 20 min
B6	0.29±0.00	4 h 39 min
B7	0.81±0.05	4 h 13 min
B8	1.03±0.03	4 h
B9	1.71±0.03	3 min
B10	2.57±0.02	4 min
B11	3.40±0.05	4 min
B12	3.83±0.02	4 min
B13	5.01±0.04	4 min
B14	2.00±0.04	19 min
B15	1.03±0.03	4 h
B16	1.24±0.01	3 h 56 min
B17	0.87±0.03	3 h 41 min
B18	1.10±0.02	3 h 52 min
B19	0.93±0.07	3 h 53 min

Results found in the literature present values that indicate a relationship between the acid index and oxidation stability. Biodiesel with acid value less than 0.5 mg KOH g<sup>-1</sup> generally present oxidation stability of more than 3h, whereas frying oil biodiesel, also presents low values of oxidation stability. It was observed that the acid index increased with the enrichment with butyric acid, and the oxidation stability decreased. 1.71 mg KOH g<sup>-1</sup> was the maximum acidity limit for stability.

Comparing the results obtained in this work (Table 5) to the analyses of different raw materials and their respective values of oxidative stability and acidity index (Table 1), it was possible to infer that there is a tendency to increase the instability with the increase of acidity index, as showed in Figure 2. The method used to determine the oxidation stability was Rancimat test, which measures the degradation based on the production of the volatiles formed during the induced oxidation. More volatile compounds may contaminate deionized water before and increase conductivity, thus causing Rancimat results to be inaccurate. Therefore, there is the possibility that short-chain acids, due to their high volatility, contaminate the deionized water faster and more easily, thus indicating a false result of oxidation stability, whereas biodiesel degradation has not, in fact, taken place yet.

**Figure 2.** Relation between the acid index and the oxidation stability of the literature data (Table 1) and this work (Table 5).

The C<sub>2:0</sub> enriched biodiesel, sample B14, presented oxidation stability (Table 5) and the biodiesels enriched with the other carboxylic acids obtained similar values, with an average of approximately 3 h 52 min. The values of acid index did not change very much according to the added acid, the average value of the acidity index of all contaminated samples was 1.20 mg KOH g<sup>-1</sup>.

#### 4. Conclusions

Low oxidation stability is one of the problems that make frying oil biodiesel unviable as an option to substitute for petroleum diesel. This is due to the different compositions of the recycled oils, which have their physicochemical properties altered, varied or degraded by the heating process. Even after the transesterification reaction, those different compounds remain in the product and can influence the biodiesel quality. The relationship between acidity and oxidation stability is inversely proportional, so the biodiesel that present higher acidity generally present less oxidation stability. These parameters are influenced by the presence of free fatty acids, such as capric, caprylic and lauric acids. Assays with soybean biodiesel enriched with different fatty acids at different concentrations indicated that free fatty acids are able to effectively decrease oxidation stability without ester degradation.

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