



## Effect of temperature on the oxidation of soybean biodiesel

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**SUMMARY:** This paper proposes to examine the effect of temperature on the oxidation behavior of biodiesel. Soybean biodiesel was oxidized at different temperatures (room temperature, 60, and 110 °C), and the increase in primary and secondary oxidation products was determined based on the peroxide and anisidine values, respectively, during the induction period (IP). The results indicated that the evolution of hydroperoxides followed zero-order reaction kinetics during the IP at all temperatures, and their rate of formation was exponentially affected by temperature. It was also deduced that temperature influenced the ratio between primary and secondary oxidation products formation, which decreased as the temperature increased. Additionally, it was possible to predict the oxidation behavior of the soybean biodiesel at room temperature by an exponential model fitted to the IP values at different temperatures (70, 80, 90, 100, and 110 °C) using the Rancimat apparatus.

**KEYWORDS:** *Oxidation kinetic; Oxidation products; Soybean biodiesel; Temperature; Tocopherols*

**RESUMEN:** *Influencia de la temperatura en la oxidación de biodiesel de soja.* El propósito de este trabajo es evaluar el efecto de la temperatura en el comportamiento oxidativo del biodiesel. Biodiesel derivado de aceite de soja fue oxidado a diferentes temperaturas (temperatura ambiente, 60 y 110 °C) y se evaluaron el contenido de compuestos primarios y secundarios de oxidación mediante el índice de peróxidos y de anisidina, respectivamente, a lo largo del periodo de inducción. Los resultados indicaron que el contenido de hidroperóxidos evolucionó siguiendo una cinética de orden cero a lo largo del periodo de inducción a todas las temperaturas y que su velocidad de formación cambió exponencialmente con la temperatura. También se dedujo que la temperatura influyó en la relación entre la formación de los productos de oxidación primarios y secundarios, disminuyendo a medida que aumentaba la temperatura. Además, fue posible predecir el comportamiento oxidativo del biodiesel de soja a temperatura ambiente ajustando a un modelo exponencial los valores de periodo de inducción obtenidos a diferentes temperaturas (70, 80, 90, 100 y 110 °C) mediante un equipo Rancimat.

**PALABRAS CLAVE:** *Biodiesel de soja; Cinética de oxidación; Productos de oxidación; Temperatura; Tocoferoles*

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## 1. INTRODUCTION

Interest in new energy sources, especially for partially replacing fossil fuel, has drawn attention to biodiesel research (Nigam and Sing, 2011). Biodiesel comprises a mixture of alkyl esters obtained by transesterification between a lipid-based feedstock, such as vegetable oils, animal fats, and/or waste cooking oils, and a short-chain alcohol using a catalyst (Giordani *et al.*, 2008). In addition to the status of renewable energy resources, biodiesel presents some advantages compared to fossil fuel, such as its biodegradability, reduced exhaust emissions, higher cetane number, greater lubricity, and safer distribution and storage due to its higher flash point (Hoshino, 2007; Knothe, 2007; Monyem and Van Gerpen, 2001). Furthermore, the production and use of biodiesel has also focused on social inclusion and regional development by generating employment and income, as is the case in Brazil (Suarez, 2006).

An essential feature of a fuel is its ability to resist chemical and physical changes during distribution and storage. Accordingly, biodiesel is more prone to degradation *via* oxidation than conventional fossil-based fuels due to its content in unsaturated fatty acid chains (Knothe, 2007). Oxidation is a complex autocatalytic reaction that produces a high number of new products. In this context, hydroperoxides, the primary oxidation compounds, are the main compounds formed in the earlier stages of oxidative degradation, which is during the induction period (Jain and Sharma, 2010; Pereira *et al.*, 2013). However, hydroperoxides are quite unstable and easily form secondary oxidation products in the advanced stages of oxidation. These secondary products can originate from rearrangements in monomeric products (keto, hydroxy, and epoxy functional groups), from decomposition into lower-mass products (aldehydes, alcohols and hydrocarbons), or from polymerization (dimers and oligomers) (Frankel, 1984; Knothe, 2007). In this stage of the oxidation process, biodiesel does not fulfill the main quality specifications (Lacoste and Lagardere, 2003) and therefore is not suitable for use. The formation of oxidation compounds negatively affects the mechanical components of engines. For example, hydroperoxides can attack elastomers, acid products formed from hydroperoxide cleavage cause the corrosion of metal systems, and gums and sediments of high-molecular mass can clog injection pumps and filters (Fazal *et al.*, 2010; Monyem and Van Gerpen, 2001; Sorate and Bhale, 2013).

The rates of these oxidation reactions depend on several factors inherent to the biodiesel nature as well as on the external environment and storage conditions. The major constituents of biodiesels are unsaturated fatty acid esters because they are typically produced from vegetable oils, such as soybean and rapeseed (Knothe, 2007; McCormick *et al.*, 2007).

In fact, di- and tri-unsaturated fatty acid chains contain the most reactive sites for hydrogen atom abstraction, making biodiesels with high contents of linolenic and linoleic acids more susceptible to degradation (Knothe and Dunn, 2003). On the other hand, the presence of natural or synthetic antioxidants increases the stability of biodiesel by reducing the rate of free radical propagation (Fröhlich and Schober, 2007). The oxidative degradation of biodiesel occurs primarily as a result of contact with metal, light, air and/or heat during its storage and distribution. Metal and light are pro-oxidants that affect the oxidation rate (Aquino *et al.*, 2012), but contact with air and elevated temperature are the most deleterious parameters related to biodiesel degradation (Godoy *et al.*, 2013). It is recognized that, in general, the rate of a chemical reaction approximately doubles for every 10 °C increase (Stoker, 2010). For this reason, oxidative stability is even more crucial for biodiesel quality in countries where there are high annual average temperatures, such as Brazil.

It is noteworthy that, in spite of the complex specification of biodiesel, there is no analytical parameter to evaluate their oxidative quality, with the exception of oxidative stability. However, oxidative stability is not a method that measures oxidation status. In this context, in a previous study our research group investigated the evolution of oxidation in soybean oil and its biodiesel under the standard conditions of oxidative stability (110 °C), using a pool of analytical methods. Here, we aimed to expand the research related to biodiesel oxidation, focusing on the effect of temperature on the formation of primary and secondary oxidation products. We further aimed to predict the end of the stability at storage conditions from the results obtained in the accelerated oxidation experiments.

## 2. MATERIAL AND METHODS

### 2.1. Biodiesel production

Soybean oil used in biodiesel production was supplied by Koipe S.A. (Andújar, Jaén, Spain). Transesterification of the oil involved mixing, under constant stirring, 100 g of soybean oil and 35 mL of sodium methoxide solution (1.5 M in methanol) at ambient temperature for 30 minutes. After the reaction, the medium was washed with water to remove impurities, such as glycerol, soaps, catalysts, and methanol residues. The ester fraction was filtered with anhydrous sodium sulfate to eliminate traces of moisture (Tomasevic and Siler-Marinkovic, 2003).

### 2.2. Physicochemical characterization of biodiesel

Fresh soybean biodiesel was characterized by standard methods of oxidation and quality. Fatty acid methyl esters were determined by gas

chromatography according to the IUPAC method 2.302 (IUPAC, 1992). Mono-, di-, triacylglycerol, and glycerol residues in the fresh soybean biodiesel were determined according to method EN 14105 (CEN, 2003a). The content of nonpolar and polar compounds was determined gravimetrically by IUPAC method 2.507 (IUPAC, 1992) with a slight modification. 150 mL of hexane/diethyl ether (95:5) were used to elute the nonpolar fraction due to the lower polarity of fatty acid methyl esters compared to that of triacylglycerols. The kinematic viscosity was determined by the method ASTM D7042 (ASTM, 2012). Finally, acid value and oxidative stability were determined following the methods EN 14104 (CEN, 2003b) and EN 14112 (CEN, 2003c), respectively. Oxidative stability is expressed by the induction period, which is the time (in hours) that elapses until the primary and secondary oxidation products increase significantly. This value indicates the resistance of biodiesel to oxidation.

### 2.3. Oxidation procedures

The soybean biodiesel was submitted to three different oxidation procedures, at room temperature, 60 °C, and 110 °C. The conditions for the oxidation procedures were as follows.

#### 2.3.1. Room temperature

Samples containing 40 g of soybean biodiesel were placed in 200 mL open amber glass containers and kept in the laboratory with exposure to indoor air. Samples were collected for analysis every 10 days, approximately, over a period of 340 days. Average temperatures ranging from 15 to 25 °C were measured throughout this storage time.

#### 2.3.2. Oven at 60 °C

Samples containing 10 g of soybean biodiesel were placed in Petri dishes with a surface-to-volume ratio of 13 cm<sup>-1</sup> and stored in an oven at 60 °C without exposure to light. Samples were collected for analysis at the following time intervals: 0, 2, 3, 4, 5, 7, and 8 days.

#### 2.3.3. Rancimat at 110 °C

Samples containing 10 g of soybean biodiesel were placed in Rancimat tubes and then inserted into a Rancimat apparatus (Metrohm, Herisau, Switzerland) with the block temperature set to 110 °C and with an air flow rate of 20 L·h<sup>-1</sup>. Samples were collected for analysis at the following time intervals: 0, 1, 2, 3, 4, 5, and 6 h.

In each procedure, samples were collected for analysis at different time intervals until the induction

period was exceeded. All the experiments were performed in duplicate.

### 2.4. Analysis of biodiesel oxidation

The oxidation evolution of the soybean biodiesel samples was analyzed by standard methods to determine the primary and secondary oxidation compounds; *via* the peroxide (AOCS Cd 8b-90) and *p*-anisidine values (AOCS Cd 18-90) (AOCS, 1997). Changes in the tocopherol contents were also monitored by normal high-performance liquid chromatography with fluorescence detection (excitation at 290 nm and emission at 330 nm) according to the IUPAC method 2.432 (IUPAC, 1992). In addition, the useful life of the fresh soybean biodiesel samples was predicted by fitting an exponential equation to the oxidative stability data obtained under the same conditions defined by EN 14112 at different temperatures (70, 80, 90, 100, and 110 °C).

### 2.5. Statistical analysis

Regression analyses were performed using Excel 2007 software (Microsoft Co., USA).

## 3. RESULTS AND DISCUSSION

The physicochemical characterization data for the fresh soybean biodiesel are given in Table 1. In general, the biodiesel showed good oxidative quality, as verified by the low values of peroxide, anisidine, and polar compounds. In addition, all the parameters, except the acid number and oxidative stability, were in accordance with the European specifications (EN 14214). Although the sample does not meet the specifications for oxidative stability, it is recognized that most of the biodiesels produced from polyunsaturated vegetable oils present low oxidative stability when no antioxidants have been added (Dantas *et al.*, 2011; Jain and Sharma, 2011; Maia *et al.*, 2011). This was also true for the soybean biodiesel used in this study, as evidenced by its major fatty acid methyl esters (C16: 0–10.7%, C18: 0–3.3%, C18: 1–21.5%, C18: 2–51.2%, and C18: 3–5.9%). However, the value found for oxidative stability (5.5 h) met the less rigorous ASTM D 6751 specification (min. 3 h).

Figure 1 shows the evolution of hydroperoxides in the soybean biodiesel measured by the peroxide value at the three different temperatures (110 °C, 60 °C, and room temperature) as well as the parallel loss of total tocopherols. As can be observed, the peroxide value increased moderately during the induction period (IP); however, a marked increase in the oxidation rate was observed when the IP was exceeded. Interestingly, the sharp increase in the primary oxidation products coincided with the loss of natural tocopherols. It can also be observed that, despite the enormous differences in the IP of the soybean biodiesel samples at different

TABLE 1. Quality and oxidative parameters of soybean biodiesel compared with the EN and ASTM specification limits

Physicochemical parameters	ASTM D 6751 limits	EN 14214 limits	Soybean biodiesel
Oxidative stability (h)	Min. 3	Min. 8	5.5
Peroxide value (meq O <sub>2</sub> ·Kg <sup>-1</sup> )	–	–	5
Acid number (mg KOH·g <sup>-1</sup> )	Max. 0.5	Max. 0.5	0.9
Anisidine value	–	–	0.4
Total tocopherol (mg·Kg <sup>-1</sup> )	–	–	785
FAME content <sup>a</sup> (%)	–	Min. 96.5	97.2
Polar compounds (%)	–	–	2.8
Kinematic viscosity (mm <sup>2</sup> ·s <sup>-1</sup> )	1.9–6.0	3.5–5.0	4.2
Total glycerol (%)	Max. 0.24	Max. 0.25	0.10
Free glycerol (%)	Max. 0.02	Max. 0.02	0.02
Monoacylglycerol (%)	–	Max. 0.8	0.22
Diacylglycerol (%)	–	Max. 0.2	0.07
Triacylglycerol (%)	–	Max. 0.2	0.16

<sup>a</sup>Measured by IUPAC method 2.507 (IUPAC, 1992).

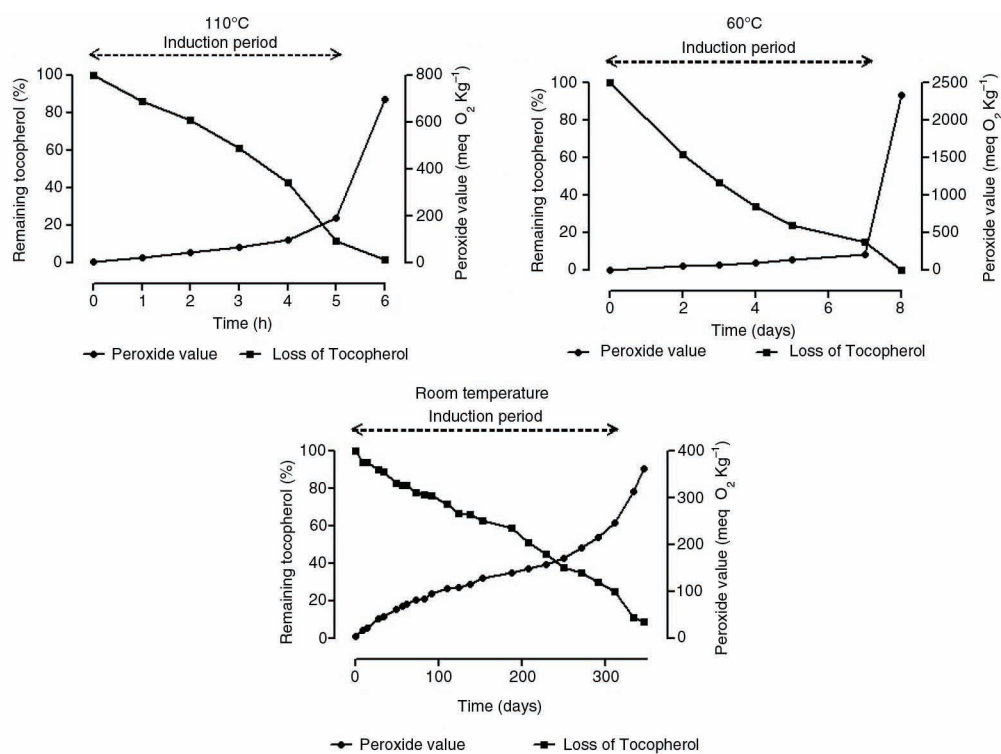


FIGURE 1. Evolution of the peroxide value and remaining tocopherol content in soybean biodiesel at different temperatures\*. \*Samples were collected for analysis at different time intervals until the induction period was exceeded.

temperatures (5–6 hours, 7–8 days, and approximately 10 months at 110 °C, 60 °C, and room temperature, respectively), the levels of natural antioxidants were approximately 15% for samples close to the end of the IP. Thus, an acceleration in the oxidative degradation of the biodiesel appeared to take place when the level of antioxidants was too low to delay oxidation.

Figure 1 also shows that the peroxide values at the end of the IP decreased as the assay temperature

increased. Thus, the last samples before the end of the IP had peroxide values of 191, 212, and 314 meq O<sub>2</sub>·Kg<sup>-1</sup> at 110 °C, 60 °C, and at room temperature, respectively. This may be due to the instability of tocopherols (Márquez-Ruiz *et al.*, 2003) or hydroperoxides at higher temperatures.

The instability of the hydroperoxides was confirmed by determining the anisidine value as a measure of the presence of secondary oxidation

TABLE 2. Influence of temperature on the formation of primary and secondary oxidation compounds

Temperature (°C)	Peroxide value (PV) meq O <sub>2</sub> ·Kg <sup>-1</sup>	Anisidine value (AV)	PV/AV
110	67	7.3	9.2
	99	10.1	9.8
	191	21.2	9.0
60	76	3.1	24.8
	104	4.1	25.4
	140	5.7	24.6
	212	9.0	23.6

compounds, specifically aldehydes. Table 2 shows the peroxide and anisidine values as well as the ratio between the two indices for selected samples before the end of the IP at 110 °C and 60 °C. It can be clearly observed that the formation of secondary oxidation compounds, as determined by the increases in the anisidine value, was much higher at 110 °C than at 60 °C for similar levels of hydroperoxides. This fact can be explained by the decomposition of the hydroperoxides, which occurred in a fast rate at 110 °C. Additionally, it is interesting to observe that the ratios between the indices were similar throughout the IP at each temperature, i.e. around 9 and 24 at 110 and 60 °C, respectively.

Figure 1 also shows that hydroperoxide formation appears to follow zero-order reaction kinetics during the IP. This behavior was confirmed in Figure 2, where the peroxide values were fit to a linear model

with high coefficients of correlation ( $r > 0.98$ ). The linear model follows equation 1:

$$PV = k \cdot t + b \quad (1)$$

where PV=peroxide value (meq O<sub>2</sub> Kg<sup>-1</sup>), k=the rate of hydroperoxide formation (meq O<sub>2</sub>·Kg<sup>-1</sup> h<sup>-1</sup>), t=the time of oxidation (h), and b=the intercept of the PV-axis. It is interesting to note that the poorer fit of the equation to the room conditions was due to the variable temperature (15–25 °C), with the high initial slope corresponding to the summer season (approximately 25 °C). From the slopes of the equations (k), it was possible to obtain the rates of hydroperoxide formation, which were calculated to be 23.1, 1.23, and 0.027 meq O<sub>2</sub>·Kg<sup>-1</sup> h<sup>-1</sup> at 110 °C, 60 °C, and ambient conditions, respectively (Figure 2). Therefore, increasing the temperature to 60 °C and 110 °C accelerated the oxidation rate 45- and 855-fold, respectively, relative to the ambient conditions. These results indicate that temperature has an exponential influence on the oxidation rate of the soybean biodiesel. Accordingly, the storage and distribution temperatures of biodiesel are critical variables that determine its quality and useful life.

We further aimed to determine whether the end of the IP at storage conditions could be deduced from the results obtained from the accelerated oxidation experiments. For this purpose, we determined the IP using a Rancimat apparatus under the same conditions defined by EN 14112 at different temperatures (70–110 °C). Figure 3 shows that the IP and temperature followed an exponential

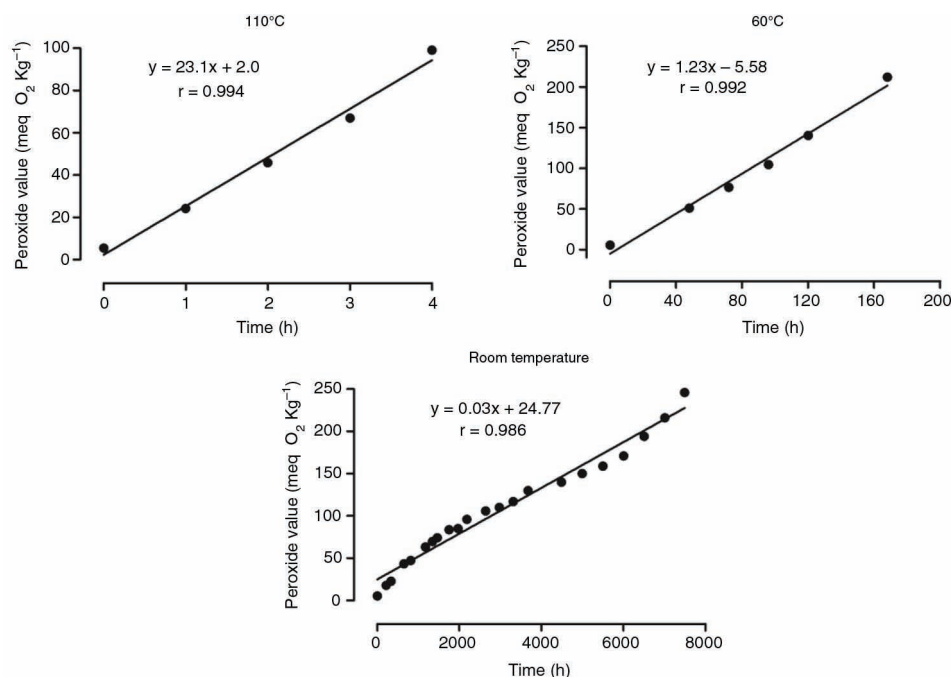


FIGURE 2. Kinetics of hydroperoxide formation in soybean biodiesel samples oxidized at different temperatures\*. \*Samples were collected for analysis at different time intervals until the induction period.

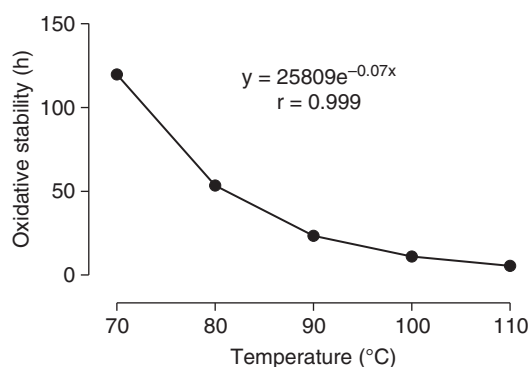


FIGURE 3. Exponential relationship between the induction period (IP) and the temperature obtained by a Rancimat apparatus\*.

\*Oxidative stability data at different temperatures: 70 °C=120 h, 80 °C=53 h, 90 °C=23 h, 100 °C=11 h, and 110 °C=5.5 h.

model with an excellent coefficient of correlation ( $r=0.999$ ). The end of the IP, as extrapolated by the exponential model at room temperature (15–25 °C), occurred between 186 and 376 days. From the experimental data, this event occurred at approximately 314 days, as can be observed by the sharp increase in the peroxide value (Figure 1). Consequently, it is noteworthy that the end of the IP under ambient conditions could be predicted by an exponential model similar to that proposed in Figure 3. Although the end of IP depends on the different variables of the biodiesel sample and storage conditions, its determination by accelerated condition tests may be a practical tool in the routine analysis of biodiesel.

#### 4. CONCLUSIONS

In conclusion, the results obtained in this paper indicate that the oxidation behavior of soybean biodiesel followed a general pattern. Temperature negatively affected the biodiesel quality, reducing its oxidative stability and consequently accelerating the formation of oxidation products. In this context, elevated temperatures increased the rate of hydroperoxide formation and also favored the emergence of secondary products, which are harmful to engine and fuel systems. Finally, we verified the usefulness of an exponential model fit to the IP values at different temperatures to predict the end of the induction period of a biodiesel during storage.

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#### REFERENCES

- AOCS. 1997. American Oil Chemists' Society. *Official methods and recommended practices of the AOCS*. AOCS, Champaign.
- ASTM. 2012. American Society for Testing and Materials. *Method ASTM D7042 – Standard test method for dynamic viscosity and density of liquids by Stabinger viscosimeter (and calculation of kinematic viscosity)*. ASTM, West Conshohocken.
- Aquino IP, Hernandez RPB, Chicoma DL, Pinto HPF, Aoki IV. 2012. Influence of light, temperature and metallic ions on biodiesel degradation and corrosiveness to copper and brass. *Fuel* **102**, 795–807. <http://dx.doi.org/10.1016/j.fuel.2012.06.011>.
- Dantas MB, Albuquerque AR, Barros AK, Rodrigues Filho MG, Antoniosi Filho NR, Sinfrônio FSM, Rosenhaim R, Soledade LEB, Santos IMG, Souza AG. 2011. Evaluation of the oxidative stability of corn biodiesel. *Fuel* **90**, 773–778. <http://dx.doi.org/10.1016/j.fuel.2010.09.014>.
- CEN. 2003a. European Committee for Standardization. *Method EN 14105 – Determination of free and total glycerol and mono-, di-, triglyceride contents*. CEN, Brussels.
- CEN. 2003b. European Committee for Standardization. *Method EN 14104 – Determination of acid value*. CEN, Brussels.
- CEN. 2003c. European Committee for Standardization. *Method EN 14112 – Determination of oxidation stability*. CEN, Brussels.
- Fazal MA, Haseeb ASMA, Masjuki HH. 2010. Comparative corrosive characteristics of petroleum diesel and palm biodiesel for automotive materials. *Fuel Process. Technol.* **91**, 1308–1315. <http://dx.doi.org/10.1016/j.fuproc.2010.04.016>.
- Frankel EN. 1984. Lipid oxidation: mechanisms, products and biological significance. *J. Am. Oil Chem. Soc.* **61**, 1908–1917. <http://dx.doi.org/10.1007/BF02540830>.
- Fröhlich A, Schober S. 2007. The influence of tocopherols on the oxidation stability of methyl esters. *J. Am. Oil Chem. Soc.* **84**, 579–585. <http://dx.doi.org/10.1007/s11746-007-1075-z>.
- Giordani DS, Siqueira AF, Silva MLCP, Oliveira PC, Castro HF. 2008. Identification of the biodiesel source using an electronic nose. *Energy Fuels* **22**, 2743–2747. <http://dx.doi.org/10.1021/ef700760b>.
- Godoy AT, Pereira GG, Ferreira LL, Cunha IBS, Barrera-Arellano D, Daroda RJ, Eberlin MN, Alberici RM. 2013. Biodiesel oxidation monitored by ambient desorption/ionization mass spectrometry. *Energy Fuels* **27**, 7455–7459. <http://dx.doi.org/10.1021/ef401542z>.
- Hoshino T, Iwata Y, Koseki H. 2007. Oxidation stability and risk evaluation of biodiesel. *Therm. Sci.* **11**, 87–100. <http://dx.doi.org/10.2298/TSC10702087H>.
- IUPAC. 1992. International Union of Pure and Applied Chemistry. *Standard Methods for the Analysis of Oils, Fats and Derivates*. 7. ed. International Union of Pure Applied Chemistry, Blackwell Scientific, Oxford.
- Jain S, Sharma MP. 2010. Stability of biodiesel and its blends: a review. *Renew. Sustain. Energy Rev.* **14**, 667–678. <http://dx.doi.org/10.1016/j.fuel.2011.05.003>.
- Jain S, Sharma MP. 2011. Oxidation stability of blends of *jatropha* biodiesel with diesel. *Fuel* **90**, 3014–3020.
- Knothe G, Dunn RO. 2003. Dependence of oil stability index of fatty compounds on their structure and concentration and presence of metals. *J. Am. Oil Chem. Soc.* **80**, 1021–1026. <http://dx.doi.org/10.1007/s11746-003-0814-x>.
- Knothe G. 2007. Some aspects of biodiesel oxidative stability. *Fuel Process. Technol.* **88**, 669–677. <http://dx.doi.org/10.1016/j.fuproc.2007.01.005>.
- Lacoste F, Lagardere L. 2003. Quality parameters evolution during biodiesel oxidation using rancimat test. *Eur. J. Lipid. Sci. Technol.* **105**, 149–155. <http://dx.doi.org/10.1002/ejlt.200390030>.
- Maia ECR, Borsato D, Moreira I, Spacino KR, Rodrigues PRP, Gallina AL. 2011. Study of the biodiesel B100 oxidative stability in mixture with antioxidants. *Fuel Process. Technol.* **92**, 1750–1755. <http://dx.doi.org/10.1016/j.fuproc.2011.04.028>.

- Márquez-Ruiz G, Martín-Polvillo M, Dobarganes C. 2003. Effect of temperature and addition of alpha-tocopherol on the oxidation of trilinolein model systems. *Lipids* **38**, 233–40. <http://dx.doi.org/10.1007/s11745-003-1056-2>.
- McCormick RL, Ratcliff M, Moens L, Lawrence R. 2007. Several factors affecting the stability of biodiesel in standard accelerated tests. *Fuel Process. Technol.* **88**, 651–657. <http://dx.doi.org/10.1016/j.fuproc.2007.01.006>.
- Monyem A, Van Gerpen JH. 2001. The effect of biodiesel oxidation on engine performance and emissions. *Biomass Bioenergy* **20**, 317–325. [http://dx.doi.org/10.1016/S0961-9534\(00\)00095-7](http://dx.doi.org/10.1016/S0961-9534(00)00095-7).
- Nigam PS, Singh A. 2011. Production of liquid biofuels from renewable resources. *Prog. Energy Combust. Sci.* **37**, 52–68. <http://dx.doi.org/10.1016/j.peccs.2010.01.003>.
- Pereira GG, Marmesat S, Barrera-Arellano D, Dobarganes MC. 2013. Evolution of oxidation in soybean oil and its biodiesel under the conditions of the oxidation stability test. *Grasas Aceites* **64**, 482–488. <http://dx.doi.org/10.3989/gya.036913>.
- Sorate KA, Bhale PV. 2013. Impact of biodiesel on fuel system materials durability. *J. Sci. Ind. Res.* **72**, 48–57.
- Stoker HS. 2010. *General, organic, and biological chemistry*. Cengage Learning, Belmont.
- Suarez PAZ. 2006. O biodiesel e a política de C & T brasileira. *Quim. Nova* **29**, 1157–1157. <http://dx.doi.org/10.1590/S0100-40422006000600001>.
- Tomasevic AV, Siler-Marinkovic SS. 2003. Methanolysis of used frying oil. *Fuel Process. Technol.* **81**, 1–6. [http://dx.doi.org/10.1016/S0378-3820\(02\)00096-6](http://dx.doi.org/10.1016/S0378-3820(02)00096-6).