Interfering factors in the oxidation of biodiesel and their mixtures

Oliveira, Carlos de Jesus de
Cremonez, Paulo André
Teleken , Joel Gustavo
Feroldi, Michael
Lima, Jamile Ribeiro Coelho de

Resumo

Atualmente, o biodiesel é apresentado como o principal substituto do combustível diesel derivado de hidrocarbonetos por ser um combustível similar ao diesel e menos danoso ao meio ambiente. No entanto, sua maior susceptibilidade aos processos oxidativos tem sido considerada um dos principais desafios a logística do biodiesel. Neste contexto, o presente trabalho estudou alguns fatores interferentes no processo de oxidação do biodiesel. Uma vez que a baixa estabilidade a processos oxidativos especialmente durante armazenamento prolongado é um dos principais problemas relacionados com a produção, distribuição e consequentemente com a representatividade do biodiesel no cenário energético brasileiro e mundial.

Palavras-chave: biodiesel; alternativa; oxidação; fatores; degradação.

Abstract

Currently, the biodiesel has been showing as the main diesel fuel substitute derived from hydrocarbons by be is a fuel like to diesel and less harmful to the environment. However, your greater susceptibility to oxidative processes have been considered one of the main challenges the logistics of biodiesel. In this context, the present work studied some interfering factors in the oxidation process of biodiesel. Once the low oxidative processes stability especially during extended storage is one of the main problems related to the production, distribution and consequently with the representativeness of biodiesel in the Brazilian and world energy scenario.

Keywords: biodiesel; alternative; oxidation; factors; degradation.

Resumen

En la actualidad, biodiesel se presenta como el principal combustible sustituto para derivado de hidrocarburos por ser un combustible similar al diesel y menos perjudicial para el medio ambiente. Sin embargo, su mayor susceptibilidad a los procesos de oxidativo ha sido considerado uno de los principales retos de la logística de biodiesel. En este contexto, el presente trabajo estudió algunos factores que interfieren en el proceso de oxidación del biodiesel. Una vez la estabilidad de los procesos oxidativos baja especialmente durante un almacenamiento prolongado es uno de los principales problemas relacionados con la producción, distribución y, en consecuencia, la representatividad del biodiesel en el brasileño y cenario de energía del mundo.

Palabras-clave: biodiesel; alternativa; oxidación; factores; degradación

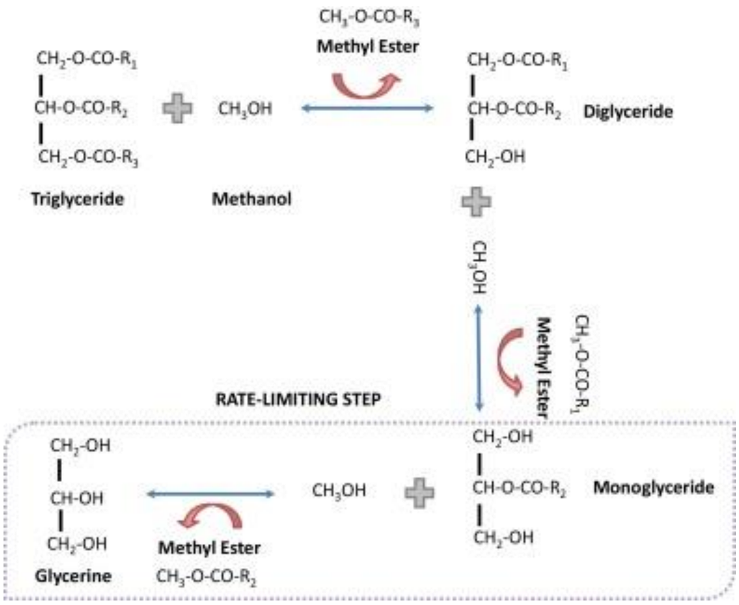
Introduction

The replacement of energy derived from fossil fuels is one of the most discussed current technological issues. This is due to the negative impact on the environment due to the burning of fossil fuels, as well as instability in demand and supply and the rising production cost of petroleum products (Fattah *et al*., 2014). This is a non-sustainable energy which has uneven geographical distribution. These facts have motivated by the world energy scene to seek alternative less environmentally harmful fuels (AHMED *et al*., 2014).

Among the various options researched, biodiesel, a mixture of fatty acid alkyl esters, which can be used in conventional diesel engines with almost none change (VELJKOVIć *et al*., 2015). Thus, biodiesel is gaining worldwide attention in recent years because of its physical and chemical characteristics like petrochemical diesel (LEUNG *et al*., 2010). Moreover, this biofuel has as main characteristics: (I) Lubricating action; (II) Higher cetane number; (III) Increased efficiency in the combustion process and consequently a lower emission of particulate matter and carbon monoxide in the atmosphere compared to diesel (BAMPI *et al*., 2013). These aspects have made biodiesel be considered a potential replacement for petrochemical diesel fuel (LEUNG *et al*., 2010).

Currently, biodiesel is primarily synthesized by transesterification of oils or fats together with short chain alcohol in the presence of a catalyst (methanol and ethanol), either sodium hydroxide (NaOH) or potassium hydroxide (KOH) which are the most commonly used (PASQUALINO *et al*., 2006; DEMIRBAS; DEMIRBAS, 2007; VELJKOVIć *et al*., 2015). In Figure 1 the mechanism of the methyl transesterification reaction is shown (using methanol as the short chain alcohol).

Figure 1. Mechanism of the transesterification reaction with methanol.



Source: (Salar-García et al., 2016).

Currently, refined or semi-refined vegetable oils are the raw materials predominantly used in the transesterification reaction (QIAN *et al.*, 2013). These sources provide numerous advantages to biodiesel, with renewability as its main feature (SCHLEICHER *et al.*, 2009).

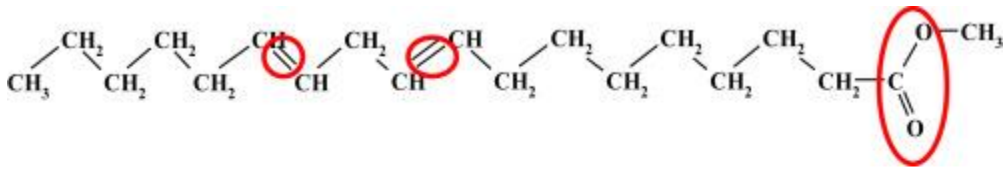
Although biodiesel has several important advantages, it is more prone to oxidation processes when compared to petrochemical diesel. This fact is due to the presence of unsaturated bonds in the molecules that biodiesel inherited from the original raw material. This susceptibility to oxidation has a significant impact on its quality during the storage process and long-term handling (FU *et al.*, 2016; MEYER *et al.*, 2012). The present work aimed to analyze the Interfering factors in the oxidation of biodiesel and their mixtures

1. MAIN BIODIESEL DISADVANTAGE

Currently the susceptible nature to oxidation due to the presence of unsaturated fatty acids is considered as the main biodiesel disadvantage (YAAKOB *et al.*, 2014). Since the profiles of the fatty acids (chain length and degree of unsaturation in the oil), influence the physicochemical properties of the mixture of esters produced from the same (FATTAH *et al.*, 2014; YAAKOB *et al.*, 2014). According to Santos *et al.* (2014) the oxidation process is characterized as an exothermic reaction.

Given that the presence of bis-allylic settings (-CH═CH-CH_2-CH═CH-), where the central methylene group is activated by two double bonds, contributes to increased susceptibility to oxidative processes of the chains in the presence of atmospheric oxygen, thus favoring polymerization reactions (MEIRA *et al.,* 2011). Figure 2 shows the double bonds in the molecule structure of a fatty acid methyl ester (methyl linoleate).

Figure 2. Structure of the fatty acid methyl ester molecule (methyl linoleate).



Source: (PÖLCZMANN *et al.*, 2016).

According to Karavalakis *et al.* (2010) polyunsaturated methyl esters are more vulnerable to oxidative processes when compared to monounsaturated esters, due to the greater presence of allylic methylene settings. By contrast, the saturated fatty acids are less unstable to oxidation processes (MEIRA *et al.,* 2011).

Thus, biodiesel is characterized as a fuel with diminished stability to oxidative processes when compared to petrochemical diesel (JAIN; SHARMA, 2012), as the main raw materials used for biodiesel production include mainly edible oils, inedible oils, waste oils and animal fats (AVHAD; MARCHETTI, 2015). Raw materials which generally have at least one methylene group in its composition. Then making the produced mixture of esters less stable to the oxidative process when compared with petrochemical diesel fuel, thereby reducing the biodiesel quality and hampering its commercialization.

The quality that in Brazil is defined by the National Agency of Petroleum, Natural Gas and Biofuels (ANP), which is based on the standards of the American Society for Testing and Materials (ASTM) D6751 and European standards (EN14214), base standards which have been adapted to meet the requirements of Brazilian raw materials (GOMES *et al.*, 2015).

Although the physicochemical properties of biodiesel have met the regulation since the composition of fatty acid methyl esters may be affected by numerous degradative processes such as: (A) autoxidation in the presence of atmospheric oxygen; (B) thermal degradation or thermal oxidative degradation; (C) hydrolysis and (d) microbial contamination of the fuel, they can deviate from the standard during the storage and handling process (FATTAH *et al*., 2014; JAKERIA *et al*., 2014).

Thus, the deterioration of biodiesel has been considered the greatest concern currently experienced by producers and distributors of this biofuel, as during storage biodiesel can deviate in their physicochemical properties causing significant impact on their quality. Accordingly, the oxidation has been increasingly studied since the typical storage conditions (exposure to air and temperature) promote oxidative biodiesel degradation (VEGA-LIZAMA *et al*., 2015).

2. OXIDATIVE PROCESS IN BIODIESEL

Oxidation, the leading cause of biodiesel degradation is a complex process in which numerous mechanisms are involved (FATTAH *et al*., 2014; KNOTHE, 2007).

According to Lapuerta *et al.* (2012), the biodiesel oxidation process can proceed by two mechanisms, autoxidation and photooxidation. However, according to the same authors mentioned above, the photo-oxidation mechanism usually occurs due to biodiesel exposure to ultraviolet light together with the presence of a photosensitizer. Therefore, it is almost unlikely to participate in biodiesel degradation. According to many authors use interchangeably the term oxidation and autoxidation as the main degradation processes in biodiesel (LAPUERTA *et al*., 2012). This degradation contributed by the presence of pro-oxidants, temperature, light exposure and dissolved oxygen rate (BELHAJ; ARAB-TEHRANY; LINDER, 2010). In the oxidation process, the unsaturated fatty acids, primarily the polyunsaturated are oxidized, forming odorless and tasteless hydroperoxides, which are decomposed into more stable secondary compounds (POYATO *et al*., 2014). Through a free radical mechanism this mechanism has been studied since the 1940s (CARVALHO *et al*., 2016).

Susceptibility increases when biodiesel is exposed to elevated temperatures in the presence of oxygen molecules. This combination influences a significant role in the degradation (LEUNG *et al*., 2006).

In biodiesel production the autoxidation is a crucial phenomenon because it affects the quality of this fuel (ZULETA *et al*., 2012). It has caused an increase in viscosity and acidity thereof since the low oxidative stability of biodiesel (SANTOS *et al*., 2014). This last characteristic probably because of the oxidation process which produces besides water, free fatty acids such as: formic acid, acetic acid, propionic acid, caproic acid, among others (HASEEB *et al*., 2010). In addition to also producing alcohols, aldehydes, peroxide, insoluble gum in water and sediments (JAIN; SHARMA, 2010).

In biodiesel oxidation stability depends on the susceptibility to degradation by oxidation reactions of the same, which has highly influenced by the composition of unsaturated esters (FU *et al*., 2016).

According Fu *et al.* (2016), there are two types of biodiesel stability: (I) Storage stability and (II) Oxidation stability.

2.1. Biodiesel oxidation stability

The oxidation stability refers to the tendency of the fuel to react with oxygen molecules in the atmosphere (FU *et al*., 2016). Since biodiesel resistance to oxidative processes is easily affected in contact with air especially during long-term storage periods (KNOTHE, 2005).

According to Yaakob *et al.* (2014) the composition and amount of ester molecules is the most important factor because it affects its properties, including, oxidation resistance, affecting the biofuel quality.

According to the last mentioned author the composition of fatty biodiesel acids, especially the position of the number of esters and bis-allylic methylene (adjacent portions to the double bond), determines the speed of the oxidation process.

A minimum stability to the oxidative process is necessary not only for newly manufactured biodiesel, but mainly for its long-term storage, handling and use (RAWAT *et al*., 2015). Thus, the low oxidation stability compared with petrochemical diesel fuel has been a major obstacle associated with biodiesel commercialization (AGARWAL *et al*., 2015).

2.2. Biodiesel storage stability

In accordance with Dwivedi; Sharma, (2015), Fu *et al.* (2016), storage stability is the resistance capacity of a liquid fuel to change in their physicochemical characteristics due to interaction with the environment. Changes which foster sediment formation, changes in pigmentation among other changes, thus contributing to reducing the purity of such fuel (DWIVEDI; SHARMA, 2015). According to Beck *et al.* (2014) biodiesel stability during storage is influenced by numerous factors, such: the molecular structure of the fatty acids, the presence of oxygen as well as partial pressure and the presence of peroxide compounds, metal ions, antioxidants, etc.

These compounds cause problems due to the deterioration process of biodiesel properties during the storage period.

Once in storage conditions, biodiesel is exposed to water molecules and oxygen, which contributes to the oxidative rate (OBADIAH *et al.*, 2012). Deteriorations which are characterized as striking in quality even when compared to diesel fuel derived from hydrocarbons (BOUAID; MARTINEZ; ARACIL, 2007).

2.3. Biodiesel degradation in the presence of oxygen

While there are increased trade prospects for biodiesel, concerns remain about resistance to oxidative processes which cause the degradation during storage BOUAID; MARTINEZ; ARACIL, 2007). In accordance with the last mentioned author this is justified due to the chemical structure of biodiesel (presence of the double bond in the molecule) that has a high level of reactivity with oxygen, especially when placed in contact with atmospheric air.

According to Jakeria *et al.* (2014) when biodiesel has exposed by oxygen molecules, it connects directly to the bis-allylic site adjacent to the double bonds of the molecule. At the same time, the autoxidation chain reaction starts and, finally, peroxide formation.

According to Yaakob *et al.* (2014) biodiesel degradation from autoxidation involves three phases: initiation, propagation and termination.
Autoxidation is the main cause of biodiesel degradation, which usually comprises three steps (Figure 3): (I) the release of hydrogen radicals by radical initiators; (II) Formation of peroxides and carbon radicals when hydrogen radicals interact with oxygen; (III) Subsequent reaction of carbon radicals with oxygen (FU et al., 2016).

Figure 3. Lipid oxidation mechanism. Where: unsaturated fatty acid (USFA); Free radical (R•); Peroxide radical (ROO•), and hydroperoxide (ROOH).

Initiation:	1) $\mathbf{RH + I \rightarrow R^{\bullet} + IR}$
Propagativos:	1) $\mathbf{R\bullet + O_2 \rightarrow ROO\bullet}$
	2) $\mathbf{ROO\bullet + RH \rightarrow ROOH\ R\bullet}$
Termination:	1) $\mathbf{R\bullet + R\bullet \rightarrow R - R}$
	2) $\mathbf{ROO\bullet + ROO\bullet \rightarrow ROOR + O_2}$

Source: adapted from Shahabuddin *et al.* (2012).

In accordance with Sarin *et al.* (2009) during the oxidation process the fatty acid methyl ester generally forms a double bond radical, which rapidly reacts with oxygen (biradical molecule) forming the peroxide compound. With the formation of peroxides, which are relatively unstable compounds, and react intramolecularly (acting on the double bond of the low molecular weight radicals) forming acids, aldehydes, ketones, alcohols, olefins, and alkanes, species. These are in turn may participate in reactions forming oligomeric compounds and polymeric products (CHRISTENSEN; MCCORMICK, 2014).

According to Sarin *et al.* (2009) during this degradative process up to 100 new radicals are quickly produced from one radical, characterizing that biodiesel decomposition occurs at an exponential rate and results in the formation of several byproducts.

In accordance with Knothe, (2005) esters exposure to oxygen molecules has determined a factor in the degradation process since the diminished biodiesel resistance to oxidation coupled with the presence of oxygen during its long term storage favors oxidation processes. This susceptibility is more significant when the biodiesel is exposed to high temperatures in conjunction with the presence of oxygen and water (LEUNG *et al.*, 2006).

2.4. Water content in biodiesel

Numerous alternative raw materials aimed at biodiesel production have been studied, but most of them have impurities, especially free fatty acids and water which hinders the transesterification reaction (PECHA *et al.*, 2016). Since the water molecules in the reaction system show a competition with alcohol molecules, thereby promoting the hydrolysis process of triglycerides (SOARES *et al.*, 2013).

Thus, decreasing the interaction between the lipid material and the short chain alcohol and consequently the rate of conversion of triglycerides to esters, because the hydrolysis reaction of ester (saponification) is a primary competitor of the transesterification reaction of lipid compounds (SOARES *et al.*, 2013). The saponification reaction favors the deactivation of the catalyst in addition to preventing the process of purification of the products (synthesized esters) (PECHA *et al.*, 2016).

Thus, the presence of water molecules has been undesirable in raw materials (oils/vegetable fats) for biodiesel synthesis since the presence of such a molecule has some negative effects on the synthesized biodiesel such as: (I) Reduction of calorific value generated during the combustion process; (II) Provides corrosion of the fuel pump and the fuel injection system and tubes; (III) Promotes biodiesel hydrolysis reaction to form free fatty acids (BHUIYA *et al.*, 2016). Besides contributing to the consumption of the catalyst (filling of the active site of the catalyst) reducing the efficiency for the reaction system (KUSDIANA; SAKA, 2004).

The increases in moisture content in biodiesel are often caused by three reasons: (I) Improper treatment after processing; (II) Absorption of atmospheric moisture during storage, or (III) Physical processes (condensation and precipitation) during the temperature variation of the storage period. Above all, the presence of water molecules in biodiesel is considered as an essential characteristic for the growth of microbial strains (SORIANO *et al.*, 2015).

Therefore, the volume of biodiesel applied in diesel blends is a critical factor that can determine the extent of biodeterioration and its impact on quality (SORIANO *et al.*, 2015). The removal of water molecules in fuel systems is extremely difficult, especially when a high percentage of biodiesel is added to fossil fuel due to the higher volume of water present in the biodiesel composition (SORIANO *et al.*, 2015).

However, according to Leung *et al.* (2006) the biodiesel hydrolysis effect is minor compared to the effect caused by the exposure of such biofuel with oxygen molecules and high temperatures. Thus, the authors suggest that biodiesel does not degrade so rapidly under high moisture, as exposure to oxygen and high temperatures, which are the main factors affecting the biodiesel degradation rate.

2.5. Microbial degradation in biodiesel

According to Pullen and Saeed (2012) the water molecules present in the biodiesel and petrochemical diesel blends can promote microbial growth and lead to corrosion of the tank. It participates in the formation of emulsions as well as contributes to hydrolysis reaction or hydrolytic oxidation of such mixtures.

This fact was favored since the main raw materials currently used in biodiesel synthesis, are characterized as more hygroscopic compared to petrochemical diesel (SORATE; BHALE 2015). Feature which also favors a greater susceptibility to biodegradations compared to fossil fuels (SORENSEN *et al.*, 2011). This degradative process, usually caused by changes in temperature and consequently in the medium (SORENSEN *et al.*, 2011). Besides the presence of free fatty acids and other water molecules.

However, the microbial biodegradation process in biodiesel has been slow since the microorganisms responsible for this degradation process, mostly show relatively slow growth kinetics. Thus, the problems related to this event will develop subsequently to numerous months after the fuel storage (BÜCKER *et al.*, 2011).

In the case of degradation from microorganisms in biodiesel, so far there are few studies on the response of microbiological populations, as well as research related to the corrosion process influenced microbiologically, which alter the chemical conditions of the fuel (SORENSEN *et al.*, 2011). Which according to the author above makes it difficult to predict and/or prevent this process. As such degradation process in biodiesel is about four times faster than the same process in diesel derived from hydrocarbons (DEMIRBAS, 2009).

According to Schleicher *et al.* (2009) the exact reasons for the great biodegradability of biodiesel have mostly still unknown. However, it has known that biodegradation of organic compounds by microorganisms occurs mostly with oxidation-reduction reactions in the presence of certain electron acceptors (GOMES, 2008).

Then, the high oxygen usually present content in biodiesel contributes to the biodegradation process (DEMIRBAS, 2009).

This degradation is also favored due to lower toxicity of biodiesel for some strains present in the soil. In the same context, Cyplik *et al.* (2011) cited in his studies that the microorganisms have showed a more intense rate of biodegradation in aerobic medium from biodiesel compared to the same degradative process with petrochemical diesel as the carbon source.

This increased degradative efficiency by microorganism strains with biodiesel as a source of energy and carbon. It is possibly a result of biofuel present as a carbon source more easily assimilable by some strains due to the presence of a carboxylic group that has attached to the aliphatic chain and has easily hydrolyzed enzymatically by some microorganisms (OWSIANIAK *et al.*, 2009; CYPLIK *et al.*, 2011).

Thus, these microorganisms get the essential nutrients for development more easily when compared to obtaining nutritional sources from the petrochemical diesel (OWSIANIAK *et al.,* 2009). According to Schleicher *et al.* (2009) the largest microbial degradative rate in biodiesel has directly influenced among other parameters by the supply of nutrients and oxygen in the biodiesel. Thus, microbial growth could be a consequence of biodiesel biodegradability (SCHLEICHER *et al.*, 2009).

During the biodiesel, auto-oxidation process the onset of water and oxygen molecules have been by the addition to the carbon source that is essential substance for the growth of some strains.

According to Pasqualino *et al.* (2006) the larger the amount of biodiesel added into the diesel will be generated a biodegradability of the remaining mixture. Since the higher the percentage of biodiesel in the blend (diesel/biodiesel), the higher the hygroscopic nature thereof, thus contributing to the growth of strains which may alter the physicochemical characteristics of the mixture. Given that many microorganisms have characterized by the potential consumers of methyl esters to obtain a source of energy and carbon (RON; ROSENBERG, 2002). Thus, Table 1 shows some microbial strains reported in the literature as potential biodegrades of biodiesel and mixtures thereof.

Table 1. Biodiesel biodegrading Microorganisms

Microorganisms	Species
Bacteria	• *Pseudomonas aeruginosa* • *Pseudomonas oleovarans* • *Pseudomonas gladioli* • *Burkolderia cepacia* • *Burkholderia gladioli* • *Escherichia coli* • *Bacillus subtilis* • *Marinomonas vaga*
Yeasts	▪ *Candida* ▪ *Pichia* ▪ *Rhodotorula* ▪ *Saccharomyces* ▪ *Sporobolomyces* ▪ *Rhodotorula*
Filamentous fungi	o *Aspergillus japonicas* o *Aspergillus terréus* o *Aspergillus niger* o *Aspergillus flavius* o *Aspergillus versicolor*

Source: adapted from Rocha, (2011).

2.6. Biodiesel thermal stability

According to Pullen; Saeed, (2012) the oxidation and elevated temperatures may result in degradation of biodiesel and consequently affect the engine performance. This author mentions that the fuel thermal stability has the same tendency of generating insoluble compounds when exposed to high temperature conditions.

Thus, many parameters may affect the stability of vegetable oils and biodiesel. Among these parameters the exposure to elevated temperature has a significant effect on biodiesel degradation due to increased degradative rate, playing an important role in biodiesel stability studies (JAIN; SHARMA 2012).

The temperature is an important role in the deterioration of the quality of the fuel (JAKERIA *et al*., 2014). It is responsible for the formation of dimers and polymers in biodiesel (LIN *et al*., 2014). These compounds can clog the fuel filter of the engine due to resinous generated as well the oil tar derived from hydrocarbons (JAKERIA *et al.,* 2014).

Consequently, despite extensive research aiming at biodiesel quality in this field the effects of thermal decomposition on biofuels properties have not yet been well established (LIN *et al*., 2014; JAIN; SHARMA, 2010). However, it is known that unsaturated fatty acids are more susceptible to thermal degradation (LIM; LEE, 2014).

In accordance with LI *et al.* (2015) the thermal degradation of biodiesel mainly involves the physical and chemical processes of dissociation and volatilization of the carbon present in the chain.

In the same context, Singer and Rühe (2014) cited that during the thermal decomposition of fatty acid methyl esters the following occurs: (I) Breakage of bonds and C — C, C— O bonds by β-scission reactions; (II) Subsequently, these connections have broken by two competing pathways, the deoxygenation (C—C bond cleavage) producing hydrocarbon radicals and concomitantly the cleavage of the C connection of the C—C chain hydrocarbons; and (III) Once again, the deoxygenation process provides the reduction of chains in the above formed molecule .

According to Jain; Sharma, (2010) biodiesel thermal instability have directly related by the increase of the oxidative rate even when exposed to high temperatures, which in turn contributes to an increase in the formation of insoluble products. Thus, contributing to increasing the density, viscosity, high surface tension, vapor pressure and heat of vaporization (vaporization enthalpy) from the mixture of esters (LIN *et al*., 2014).

According to Singer and Rühe (2014) when these changes in biodiesel characteristics are favorable there are numerous processes, such as corrosion, filter plugging, formation of deposits on injector parts can also possibly contribute to operational failure of such equipment.

The same author mentions that biodiesel degradation has also haven occurred due to recirculation of fuel molecules inside the engine, especially since the molecules which have not gone through a combustion process, can move up numerous times within the system fuel until they are eventually injected into the combustion chamber. The repeated exposure to high temperatures leads to a gradual thermoxidative degradation of these molecules. Moreover, such fuel can deteriorate during storage or in the tank system (SINGER; RÜHE 2014).

Thus, the aiming to predict the oxidative degradation for the duration of the storage process, there are standards available that discuss the minimum specification related to oxidation stability during use of biodiesel in the engine. However, at the same time there are no specifications available exclusively for the thermal stability. Specification for thermal stability can be developed from the relationship between oxidation and thermal stability (JAIN; SHARMA, 2012).

3. CHANGES IN BIODIESEL DURING THE DEGRADATIVE PROCESSES

According to Strömberg *et al.* (2013) the biodiesel oxidation process has directly related by an increase in acidity level due to the formation of compounds such as formic acid, acetic acid and propionic acid, which contributes to an increase in total acid number of the oxidized fuel.

According to Bücker *et al.* (2014), fuel biodeterioration has been proven by the accumulation of particulate matter, as well as the degradation of the fuel components such as hydrocarbons, fatty acid esters, etc. Given that, numerous biodiesel properties (viscosity, acidity and induction period) are directly influenced by a possible degradation (CANHA *et al.*, 2012). Thus, contributing to the forming of deposits inside the fuel tanks which causes clogging of fuel filters, injection systems, and encourage corrosion in the fuel system (FOCKE *et al.*, 2012).

In the same context, Leung *et al.* (2006), suggested from numerous studies that high temperature, coupled with exposure to air, considerably increase the degradation rate of biodiesel. Therefore, the biodiesel exposure to air or the temperature itself. However, it had little effect on the biodiesel degradation. According to the last mentioned author, the water content in biodiesel contributes to the degradation process of biodiesel due to hydrolysis, but its effect is minor compared to the effects of air exposure and high temperature.

According to Dinkov *et al.* (2009), the instability to oxidation processes has been characterized as one of the main obstacles to increased acceptance of biodiesel by manufacturers of equipment, engines and fuel injectors, and thus an expansionary barrier on the market for that fuel. In this context, there are numerous approaches aimed at preventing the biodiesel oxidation process as much as possible or even slowing down its rate. Among these measures, one of them can try to avoid contact between the fatty acids with air, pro-oxidants, high temperatures and the presence of light. However, these measures are not always feasible, so that the use of antioxidants is of significant interest (KNOTHE, 2007). In view of this, many researchers have been investigating and characterizing many antioxidants as a potential strategy to slow the oxidative degradation especially during biodiesel storage (PULLEN; SAEED (2012). This action is a practical solution for biodiesel to become more stable to autoxidative processes, without modifying the fuel properties (VELMURUGAN; SATHIYAGNANAM, 2016).

4. ANTIOXIDANT AGENTS USED IN BIODIESEL

Characterized as antioxidant compounds, substances that at considerably lower concentrations compared to oxidable substrates, delay the process of lipid autoxidation, reducing the oxidation rate or prolonging the induction period of the same (SILVA *et al.*, 1999). According to Carvalho *et al.* (2016) the use of antioxidants in biodiesel has increasing the stability index of oxidative processes, and thus meet or exceed the value specified by the rules.

According to Rashed *et al.* (2016) the antioxidants has been used as well as since the addition of a small number of antioxidants in the fuel inhibits the formation of free radicals by reaction with peroxyl radicals forming new inert radicals, thus obstructing the propagation step.

Thus, these antioxidants significantly retard the biodiesel degradation process (RASHED *et al.*, 2016).

However, in accordance with Agarwal *et al.* (2015) antioxidants are effective in very low concentrations. However, many of these compounds have demonstrated limited effectiveness with increasing its concentrations. Furthermore, the use of large concentrations of such additives makes the process economically unfeasible (RAWAT *et al.,* 2015).

According to Velmurugan; Sathiyagnanam, (2016) many compounds are classified according to their mode of action. Among these it can be cited the terminators of free radicals, chelating metal ions or oxygen scavengers. Free radical terminators are primary antioxidants. They donate one or more of an electron or hydrogen atom (ROO-) a derivative of free radicals (VELMURUGAN; SATHIYAGNANAM, 2016). Thus, Table 2 shows a comparison between some antioxidants and their mechanisms of action.

Table 2. Antioxidant agents and their mechanisms of action

Antioxidant type	Mechanism of action	Examples
Stabilizers of hydroperoxides	• kill switches from free radicals • Avoids the decomposition of hydroperoxides in free radicals	• Phenolic compounds
Synergists	• Promote the activity of antioxidants	• Citric acid, ascorbic acid
Metal Inactivators	• Bind heavy metals making them inactive	• Phosphoric acid, Maillard compounds, citric acid
Kill Switches O_2 Singlet	• Converts Singlet O_2 in O_2 triplet	• Carotenoids
Hydroperoxide-reducing substances	• Reduce hydroperoxide radical not roads	• Proteins, amino acids.

Source: adapted from Pokorný, (2007); Pereira, (2010).

According to Liang *et al.* (2006) most of the antioxidants used in biodiesel from numerous materials have different effects on the improvement in oxidative stability. However, many antioxidants (conventional butylated hydroxytoluene (BHT), butylated hydroxy anisole (BHA), tert-butylhydroquinone (TBHQ), propyl gallate (PG) and pyrogallol (PA), as well as some additives commonly are used in biodiesels to improve the oxidative stability, are usually phenolic compounds developed from petrochemical fuels (KREIVAITIS *et al.*, 2013).

According to the last cited author many synthetic antioxidants have a characteristically low biodegradability, high toxicity, and have little viability and efficiency in some applications. In accordance with Agarwal et al. (2015), the TBHQ antioxidant, PY and PG are highly effective for biodiesel produced from rapeseed oil, sunflower oil, frying oil and beef tallow while BHA and BHT demonstrated limited efficiency to such materials.

CONCLUSION

Among the liquid biofuels currently surveyed, biodiesel is still the one that faces the largest industrial barriers when it comes to increasing its representation in the global energy matrix in an economically viable way. Thus, the inclusion of such fuel with expressiveness in the global energy scenario is still quite far way.

Since the characteristics evident in the currently available raw materials require costly expenditures to obtain it (as the predominant raw material in the whole world is still mostly producing vegetable oils, which are also normally intended for other purposes). In addition to others the expensive antioxidants which undoubtedly are used in mixtures of esters produced to obtain the quality standards established by the competent agencies like ASTM US, EN in the European Union, and the National Agency of Petroleum, Natural Gas and Biofuels - ANP in Brazil. These factors are the main barriers to production and marketing of biodiesel highlighted by the industries.

REFERENCES

AGARWAL, A. K.; KHURANA, D.; DHAR, A. Improving Oxidation Stability of Biodiesels Derived from Karanja, Neem and Jatropha: Step Forward in the Direction of Commercialization. *Journal of Cleaner Production*, v. 107, p. 646–652, Nov. 2015.

AHMED, S.; HASSAN, M. H.; KALAM, M. A.; RAHMAN, S. M. A.; ABEDIN, J. M.; SHAHIR, A. An experimental investigation of biodiesel production, characterization, engine performance, emission and noise of Brassica juncea methyl ester and its blends. *Journal of Cleaner Production*, v. 79, p. 74-81, Sep. 2014.

AVHAD, M. R.; MARCHETTI, J. M. A review on recent advancement in catalytic materials for biodiesel production. *Renewable and Sustainable Energy Reviews*, v. 50, p. 696-718, Oct. 2015.

BAMPI, M.; SCHEER, A. P.; CASTILHOS, F. Application of near infrared spectroscopy to predict the average droplet size and water content in biodiesel emulsions. *Fuel*, v. 113, p. 546-552, Nov. 2013.

BECK, Á.; PÖLCZMANN, G.; ELLER, Z.; HANCSÓK, J. Investigation of the effect of detergent–dispersant additives on the oxidation stability of biodiesel, diesel fuel and their blends. *Biomass and Bioenergy*, v. 66, p. 328-336, Jul. 2014.

BELHAJ, N; ARAB-TEHRANY, E.; LINDER, M. Oxidative kinetics of salmon oil in bulk and in nanoemulsion stabilized by marine lecithin. *Process Biochemistry*, v. 45, p. 187-195, Feb. 2010.

BHUIYA, M. M. K.; RASUL, M. G.; KHAN, M. M. K.; ASHWATH, N.; AZAD, A. K.; HAZRAT, M. A.; PROSPECTS of 2nd generation biodiesel as a sustainable fuel – Part 2: Properties, performance and emission characteristics. *Renewable and Sustainable Energy Reviews*, v. 55, p. 1129-1146, Mar. 2016.

BOUAID, A.; MARTINEZ, M.; ARACIL, J. Long storage stability of biodiesel from vegetable and used frying oils. *Fuel*, v. 86, n. 16, p. 2596-2602, Nov. 2007.

BÜCKER, F.; BARBOSA, C. S.; QUADROS, P. D.; BUENO, M. K.; FIORI, P.; HUANG, C.; FRAZZON, A. P. G.; FERRÃO, M. F.; CAMARGO, F. A. O.; biodegradation and molecular characterization of microbial biofilms in stored diesel/biodiesel blend B10 and the effect of biocide. *International Biodeterioration Biodegradation*, v. 95, Part B, n. 1, p. 346-355, Nov. 2014.

BÜCKER, F.; SANTESTEVAN, N. A.; ROESCH, L. F.; JACQUES, R. J. S.; PERALBA, M. C. R.; CAMARGO, F. A. O.; BENTO, F. M. Impact of biodiesel on biodeterioration of stored Brazilian diesel oil. *International Biodeterioration & Biodegradation*, v. 65, p. 172-178, Jan. 2011.

CANHA, N.; FELIZARDO, P.; MENEZES, J. C.; CORREIA, M. J. N. Multivariate near infrared spectroscopy models for predicting the oxidative stability of biodiesel: Effect of antioxidants addition. *Fuel*, v. 97, p. 352-357, Jul. 2012.

CARVALHO, A. L.; CARDOSO, E. A.; ROCHA, G. O. TEIXEIRA, L. S. G.; PEPE, L. M.; GROSJEAN, D. M. Carboxylic acid emissions from soybean biodiesel oxidation in the EN14112 (Rancimat) stability test. *Fuel*, v. 173, p. 29-36, Jun. 2016.

CHRISTENSEN, E.; MCCORMICK, R. L. Long-term storage stability of biodiesel and biodiesel blends. *Fuel Processing Technology*, v. 128, p. 339-348, Dec. 2014.

CYPLIK, P.; SCHMIDT, M.; SZULC, A.; MARECIK, R.; LISIECKI, P.; HEIPIEPER, H. J.; OWSIANIAK, M.; VAINSHTEIN, M.; CHRZANOWSKI, L. Relative quantitative PCR to assess bacterial community dynamics during biodegradation of diesel and biodiesel fuels under various aeration conditions. *Bioresource Technology*, v. 102, p. 4347-4352, Mar. 2011.

DEMIRBAS, A. H.; DEMIRBAS, I. Importance of rural bioenergy for developing countries. *Energy Conversion and Management*, v. 48, p. 2386-2398, Aug. 2007.

DEMIRBAS, A. Progress and recent trends in biodiesel fuels. *Energy Conversion and Management*, v. 50, p. 14-34, Jan. 2009.

DINKOV, R.; HRISTOV, G.; STRATIEV, D.; ALDAYRI, V. B. Effect of commercially available antioxidants over biodiesel/diesel blends stability. *Fuel*, v. 88, n. 4, p. 732-737, Apr. 2009.

DWIVEDI, G.; SHARMA, M. P. Investigation of Oxidation stability of Pongamia Biodiesel and its blends with diesel. *Egyptian Journal of Petroleum*, Nov. 2015. doi.org/10.1016/j.ejpe.2015.06.005.

FATTAH, I.M. R.; MASJUKI, H.H.; KALAM, M.A.; HAZRAT, M.A.; MASUM, B.M.; IMTENAN, S.; ASHRAFUL, A. M. Effect of antioxidants on oxidation stability of biodiesel derived from vegetable and animal based feedstock's. *Renewable and Sustainable Energy Reviews,* v. 30, p. 356-370, Feb. 2014.

FOCKE, W. W.; WESTHUIZEN, I. V. D.; GROBLER, A. B. L.; NSHOANE, K. T.; REDDY, J. K.; LUYT, A. S. The effect of synthetic antioxidants on the oxidative stability of biodiesel. *Fuel,* v. 94, p. 227-233, Apr. 2012.

FU, J.; TURN, S. Q.; TAKUSHI, B. M.; KAWAMATA, C. L. Storage and oxidation stabilities of biodiesel derived from waste cooking oil. *Fuel*, v. 167, p. 89-97, Mar. 2016.

GOMES, A. P. N. *Biodegradação de biodiesel soja, mamoma e hidrocarbonetos monoaromáticos em ambientes aquáticos*. 2008. 88 f. Dissertação (Mestrado) - Curso de Pós-graduação em Engenharia Ambiental. Universidade Federal de Santa Catarina, Florianópolis – SC, 2008.

GOMES, M. C. S.; ARROYO, P. A.; PEREIRA, N. C. Influence of oil quality no biodiesel purification by ultrafiltration. *Journal of Membrane Science*, v. 496, p. 242-249, Dec. 2015.

HASEEB, A. S. M. A.; SIA, S. Y.; FAZAL, M. A.; Masjuki, H.H Effect of temperature on tribological properties of palm biodiesel. *Energy*, v. 35, p. 1460-1464, Mar. 2010.

JAIN, S.; SHARMA, M. P. Correlation development between the oxidation and thermal stability of biodiesel. *Fuel*, v. 102, p. 354-358, Dec. 2012.

JAIN, S.; SHARMA, M. P. Stability of biodiesel and its blends: A review. *Renewable and Sustainable Energy Reviews*, v. 14, p. 667-678, Feb. 2010.

JAKERIA, M. R.; FAZAL, M. A.; HASEEB, A. S. M. A. Influence of different factors on the stability of biodiesel: A review. *Renewable and Sustainable Energy Reviews*, v. 30, p. 154-163, Feb. 2014.

KARAVALAKIS, G.; STOURNAS, S.; KARONIS, D. Evaluation of the oxidation stability of diesel/biodiesel blends. *Fuel*, v. 89, p. 2483-2489, Sep. 2010.

KNOTHE, G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Processing Technology*, v. 86, n. 10, p. 1059-1070, Jun. 2005.

KNOTHE, G. Some aspects of biodiesel oxidative stability. *Fuel Processing Technology,* v. 88, n. 7, p. 669-677, Jun. 2007.

KREIVAITIS, R.; GUMBYTĖ, M.; KAZANCEV, K.; PADGURSKAS, P.; MAKAREVIČIENĖ, V. A comparison of pure and natural antioxidant modified rapeseed oil storage properties. *Industrial Crops and Products*, v. 43, p. 511-516, May 2013.

KUSDIANA, D.; SAKA, S. Effects of water on biodiesel fuel production by supercritical methanol treatment. *Bioresource Technology*, v. 91, n. 3, p. 289-295, Feb. 2004.

LAPUERTA, M.; RODRÍGUEZ-FERNÁNDEZ, J.; RAMOS, Á.; ÁLVAREZ, B. Effect of the test temperature and anti-oxidant addition on the oxidation stability of commercial biodiesel fuels. *Fuel,* v. 93, p. 391-396, Mar. 2012.

LEUNG, D. Y. C.; WU, X; LEUNG, M. K. H. A review on biodiesel production using catalyzed transesterification. *Applied Energy*, v. 87, p. 1083-1095, Abr. 2010.

LEUNG, D.Y.C.; KOO, B.C.P.; GUO, Y. Degradation of biodiesel under different storage conditions. *Bioresource Technology*, v. 97, n. 2, p. 250-256, Jan. 2006.

LI, H.; NIU, S.; LU, C.; Cheng, S. Comparative evaluation of thermal degradation for biodiesels derived from various feedstocks through transesterification. *Energy Conversion and Management,* v. 98, p. 81-88, Jul. 2015.

LIANG, Y. C.; MAY, C. Y.; FOON, C. S.; NGAN, A. M. et al. The effect of natural and synthetic antioxidants on the oxidative stability of palm diesel. *Fuel,* v. 85, p. 867-870, Mar. 2006.

LIM, S.; LEE, K. T. Investigation of impurity tolerance and thermal stability for biodiesel production from Jatropha curcas L. seeds using supercritical reactive extraction. *Energy,* v. 68, p. 71-79, Apr. 2014.

LIN, R.; ZHU, Y.; TAVLARIDES, L. L. Effect of thermal decomposition on biodiesel viscosity and cold flow property. *Fuel*, v. 117, p. 981-988, Jan. 2014.

MEYER, D. D.; SANTESTEVAN, N. A.; BÜCKER, F.; SALAMONI, S. P.; ANDREAZZA, R.; CAMARGO, F. A. O.; BENTO, F.M.; Capability of a selected bacterial consortium for degrading diesel/biodiesel blends (B20): Enzyme and biosurfactant production. *Journal of Environmental Science and Health*, Part A, v. 47, n. 12, p. 1776-1784, 4 Jul. 2012.

OBADIAH, A.; KANNAN, R.; RAMASUBBU, A.; KUMAR, S. V. Studies on the effect of antioxidants on the long-term storage and oxidation stability of Pongamia pinnata (L.) Pierre biodiesel. *Fuel Processing Technology*, v. 99, p. 56-63, Jul. 2012.

OWSIANIAK, M.; CHRZANOWSKI, Ł.; SZULC, A.; STANIEWSKI, J.; OLSZANOWSKI, A.; OLEJNIK-SCHMIDT, A. K.; HEIPIEPER, H. J. Biodegradation of diesel/biodiesel blends by a consortium of hydrocarbon degraders: Effect of the type of blend and the addition of biosurfactants. *Bioresource Technology*, v. 100, p. 1497-1500, Feb. 2009.

PASQUALINO, J. C.; MONTANÉ, D.; SALVADÓ, J. Synergic effects of biodiesel in the biodegradability of fossil-derived fuels. *Biomass and Bioenergy*, v. 30, p. 874-879, Oct. 2006.

PECHA, J.; ŠÁNEK, L.; FÜRST, T.; KOLOMAZNÍK, K. A kinetics study of the simultaneous methanolysis and hydrolysis of triglycerides. *Chemical Engineering Journal*, v. 288, p. 680-688, Mar. 2016.

PEREIRA, M. O. S. *Estudo comparativo de métodos de avaliação da capacidade antioxidante de compostos bioativos*. 2010. 40 f. Dissertação (Mestrado) - Curso de Engenharia Alimentar, Instituto Superior de Agronomia da Universidade Técnica de Lisboa, Lisboa, 2010.

POKORNÝ, J. Are natural antioxidants better – and safer – than synthetic antioxidants? *Eur. J. Lipid Sci. Technol.* 1, v. 109, p. 629-642, 2007.

PÖLCZMANN, G.; TÓTH, O.; BECK, Á.; Hancsók, J. Investigation of storage stability of diesel fuels containing biodiesel produced from waste cooking oil. *Journal of Cleaner Production,* v. 111, p. 85-92, Jan. 2016.

PULLEN, J.; SAEED, K. An overview of biodiesel oxidation stability. *Renewable and Sustainable Energy Reviews,* v. 16, n. 8, p. 5924-5950, Oct. 2012.

QIAN, J.; YANG, Q.; SUN, F.; HE, M.; CHEN, Q.; YUN, Z.; QIN, L. Cogeneration of biodiesel and nontoxic rapeseed meal from rapeseed through in-situ alkaline transesterification. *Bioresource Technology*, v. 128, p. 8-13, Jan. 2013.

RASHED, M. M.; MASJUKI, H. H.; KALAM, M. A.; ALABDULKAREM, A.; RAHMAN, M. M.; IMDADUL, H. K.; RASHEDUL, H. K. Study of the oxidation stability and exhaust emission analysis of Moringa olifera biodiesel in a multi-cylinder diesel engine with aromatic amine antioxidants. *Renewable Energy*, v. 94, p. 294-303, Aug. 2016.

RAWAT, D. S.; JOSHI, G.; LAMBA, B. Y.; TIWARI, A. K.; KUMAR, P. The effect of binary antioxidant proportions on antioxidant synergy and oxidation stability of Jatropha and Karanja biodiesels. *Energy,* v. 84, p. 643-655, May. 2015.

ROCHA, M. F. A. *Biodegradação de Biodiesel de Algodão em Ambiente Aquático.* 2011. 130 f. Dissertação (Mestrado) - Curso de Pós-graduação em Engenharia Química, Universidade Federal de Pernambuco, Recife-PB, 2011.

RON, E. Z.; ROSENBERG, E. Biosurfactants and oil bioremediation. *Current Opinion in Biotechnology,* v. 13, p. 249-252, Jun. 2002.

SALAR-GARCÍA, M. J.; ORTIZ-MARTÍNEZ, V. M.; OLIVARES-CARRILLO, P.; QUESADA-MEDINA, J.; DE LOS RÍOS, A. P.; HERNÁNDEZ-FERNÁNDEZ, F. J. Analysis of optimal conditions for biodiesel production from Jatropha oil in supercritical methanol: Quantification of thermal decomposition degree and analysis of fames. *The Journal of Supercritical Fluids*, Feb. 2016. DOI: 10.1016/j.supflu.2016.02.004.

SANTOS, A. G. D.; SOUZA, L. D.; CALDEIRA, V. P. S.; FARIAS, M. F.; FERNANDES, V. J. JR.; ARAUJO, A. S. Kinetic study and thermoxidative degradation of palm oil and biodiesel. *Thermochimica Acta*, v. 592, p. 18-22, Sep. 2014.

SARIN, A.; ARORA, R.; SINGH, N. P.; SHARMA, M.; MALHOTRA, R. K. Influence of metal contaminants on oxidation stability of Jatropha biodiesel. **Energy**, v. 34, n. 9, p. 1271-1275, Sep. 2009.

SCHLEICHER, T.; WERKMEISTER, R.; RUSS, W.; MEYER-PITTROFF, R. Microbiological stability of biodiesel–diesel-mixtures. *Bioresource Technology*, v. 100, p. 724-730, Jan. 2009.

SHAHABUDDIN, M.; KALAM, M.A.; MASJUKI, H.H.; BHUIYA, M. M. K.; MOFIJUR, M. An experimental investigation into biodiesel stability by means of oxidation and property determination. *Energy*, v. 44, n. 1, p. 616-622, Aug. 2012.

SILVA, F. A. M.; BORGES, M. F.M.; FERREIRA, M. A. Métodos para avaliação do grau de oxidação lipídica e da capacidade antioxidante. *Química Nova*, São Paulo, v. 22, p. 94-103, 1999.

SINGER, P.; RÜHE, J. On the mechanism of deposit formation during thermal oxidation of mineral diesel and diesel/biodiesel blends under accelerated conditions. *Fuel,* v. 133, p. 245-252, Oct. 2014.

SOARES, D.; PINTO, A. F.; GONÇALVES, A. G.; Mitchell, D. A.; Krieger, N. Biodiesel production from soybean soapstock acid oil by hydrolysis in subcritical water followed by lipase-catalyzed esterification using a fermented solid in a packed-bed reactor. *Biochemical Engineering Journal*, v. 81, p. 15-23, Dec. 2013.

SORATE, K. A.; BHALE, P. V. Biodiesel properties and automotive system compatibility issues. *Renewable and Sustainable Energy Reviews*, v. 41, p. 777-798, Jan. 2015.

SORENSEN, G.; PEDERSEN, D. V.; NØRGAARD, A. K.; SØRENSEN, K B.; NYGAARD, S. D.; Microbial growth studies in biodiesel blends. *Bioresource Technology,* v. 102, p. 5259-5264, Apr. 2011.

SORIANO, A. U.; MARTINS, L. F.; VENTURA, E. S. A.; LANDA, F. H. T. G.; VALONI, É. A.; FARIA, F. R. D.; FERREIRA, R. F.; FALLER, M. C. K.; VALÉRIO, R. R.; LEITE, D. C. A.; DO CARMO, F. L.; PEIXOTO, R. S. Microbiological aspects of biodiesel and biodiesel/diesel blends biodeterioration. *International Biodeterioration & Biodegradation,* v. 99, p. 102-114, Apr. 2015.

STRÖMBERG, N.; SARAMAT, A.; ERIKSSON, H. Biodiesel degradation rate after refueling. *Fuel*, v. 105, p. 301-305, Mar. 2013.

VEGA-LIZAMA, T.; DÍAZ-BALLOTE, L.; HERNÁNDEZ-MÉZQUITA, E.; MAY-CRESPO, F.; CASTRO-BORGES, P.; CASTILLO-ATOCHE, A.; GONZÁLEZ-GARCÍA, G.; MALDONADO, L. Thermogravimetric analysis as a rapid and simple method to determine the degradation degree of soy biodiesel. *Fuel*, v. 156, p. 158-162, Sep. 2015.

VELJKOVIć, V. B.; BANKOVIć-ILIć, I. B.; STAMENKOVIć, O. S. Purification of crude biodiesel obtained by heterogeneously-catalyzed transesterification. *Renewable and Sustainable Energy Reviews*, v. 49, p. 500-516, Sep. 2015.

VELMURUGAN, K.; SATHIYAGNANAM, A. P. Impact of antioxidants on NOx emissions from a mango seed biodiesel powered DI diesel engine. *Alexandria Engineering Journal,* v. 55, n. 1, p. 715-722, Mar. 2016.

YAAKOB, Z.; NARAYANAN, B. N.; PADIKKAPARAMBIL, S.; UNNI, S. K.; AKBAR, M P. A review on the oxidation stability of biodiesel. *Renewable and Sustainable Energy Reviews*, v. 35, p. 136-153, Jul. 2014.

ZULETA, E. C.; BAENA, L.; RIOS, L. A.; CALDERÓN, J. A. The oxidative stability of biodiesel and its impact on the deterioration of metallic and polymeric materials: a review. J. Braz. *Chem. Soc.,* v. 23, n. 12, p. 2159-2175, 2012.

1 Carlos de Jesus de OLIVEIRA. Possui graduação em Tecnologia em Biocombustíveis pela Universidade Federal do Paraná. Atuou nas áreas de produção e controle de qualidade de biocombustíveis líquidos (bioetanol de primeira geração e biodiesel por meio da transesterificação metílica alcalina), e estabilidade oxidativa de biodiesel a partir de óleos residuais. Atuou como bolsista CNPq na Embrapa - Agroenergia Brasília-DF, Brasil, na área de utilização de coprodutos agroindustriais para a síntese de químicos de maior valor agregado. Atualmente mestrando em Bioenergia pela Universidade Federal do Paraná - Setor Palotina. Atua na área de síntese e caracterização de catalisadores heterogêneos a partir de coprodutos agroindustriais para produção de biodiesel de segunda geração (óleos residuais) via reação de transesterificação metílica alcalina

2 Paulo André CREMONEZ. Graduado em Tecnologia em Biocombustíveis pela Universidade Federal do Paraná - Setor Palotina, Mestre em Engenharia de Energia na Agricultura pela Universidade Estadual do Oeste do Paraná, e doutorando em Engenharia Agrícola pela mesma instituição. Atua nas áreas de produção de biogás por degradação resíduos agroindustriais e polímeros biodegradáveis, além de pesquisas relacionadas a estabilidade oxidativa de biodiesel residual.

3 Joel Gustavo TELEKEN. Professor Adjunto Nível II da Universidade Federal do Paraná (UFPR). Atualmente é Chefe do Departamento de Engenharias e Exatas do Setor Palotina da UFPR. Possui Graduação em Engenharia Química (2007), Mestrado (2009) e Doutorado (2013) em Engenharia Química pela Universidade Federal de Santa Catarina na área de controle e simulação de processos de separação (Destilação). Atualmente é professor do Departamento de Engenharias e Exatas da Universidade Federal do Paraná (UFPR) - Setor Palotina, na área de produção de energias renováveis. Faz parte do quadro permanente dos Programas de Pós-Graduação em BioenergiA e Tecnologia de Bioprodutos Agroindustriais.

4 Michael FEROLDI. Graduado em Tecnologia em Biocombustíveis pela Universidade Federal do Paraná (UFPR) e integrante do Grupo de Pesquisa de Catálise e Produção de Biocombustíveis - GCatProBio. Atualmente trabalha com o uso de adsorventes no armazenamento de biometano à baixa pressão (GNA).

5 Jamile Ribeiro Coelho de LIMA. Pós-doutoranda da Empresa Brasileira de Pesquisa Agropecuária, unidade Agroenergia (CNPAE). Sendo bolsista CAPES-Embrapa no projeto; Aproveitamento da glicerina coproduto de biodiesel para obtenção de químicos visando agregar valor a cadeia do dendês. Doutora (2014) e mestre (2009) no Programa Tecnologia de Processos Químicos e Bioquímicos da Universidade Federal do Rio de Janeiro (UFRJ/EQ). Bióloga graduada pela Universidade do Estado Rio de Janeiro(2007). A experiência também contempla a atividade de docência no ensino médio. Revisora de três periódicos.