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OXIDATIVE STABILITY OF FATTY ACID ALKYL ESTERS: A REVIEW

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ABSTRACT

The purpose of this study was to investigate and to process the current literary knowledge of the physico-chemical properties of vegetable oil raw used for biodiesel production in terms of its qualitative stability. An object of investigation was oxidative stability of biodiesel. In the study, we focused on the qualitative physico-chemical properties of vegetable oils used for biodiesel production, oxidative degradation and its mechanisms, oxidation of lipids, mechanisms of autooxidation, effectivennes of different synthetic antioxidants in relation to oxidative stability of biodiesel and methods of oxidative stability determination. Knowledge of the physical and chemical properties of vegetable oil as raw material and the factors affecting these properties is critical for the production of quality biodiesel and its sustainability. According to the source of oilseed, variations in the chemical composition of the vegetable oil are expressed by variations in the molar ratio among different fatty acids in the structure. The relative ratio of fatty acids present in the raw material is kept relatively constant after the transesterification reaction. The quality of biodiesel physico-chemical properties is influenced by the chain length and the level of unsaturation of the produced fatty acid alkyl esters. A biodiesel is thermodynamically stable. Its instability primarily occurs from contact of oxygen present in the ambient air that is referred to as oxidative instability. For biodiesel is oxidation stability a general term. It is necessary to distinguish 'storage stability' and 'thermal stability', in relation to oxidative degradation, which may occur during extended periods of storage, transportation and end use. Fuel instability problems can be of two related types, short-term oxidative instability and long-term storage instability. Storage instability is defined in terms of solid formation, which can plug nozzles, filters, and degrade engine performance. Biodiesels are more susceptible to degradation compared to fossil diesel because of the presence of unsaturated fatty acid chain in it. The mechanisms of oxidative degradation are autoxidation in presence of atmospheric oxygen; thermal or thermal-oxidative degradation from excess heat; hydrolysis in presence of moisture or water during storage and in fuel lines; and microbial contamination from contact with dust particles or water droplets containing fungi or bacteria into the fuel. The oxidation of lipids is a complex process in which unsaturated fatty acids are reacted with molecular oxygen by means of free radicals. The radicals react with lipids, and cause oxidative destruction of unsaturated, polyunsaturated fatty acids, therefore, known as lipid peroxidation. The factors such as heat, oxygen, light, and some metal ions, especially iron and copper, also play a significant role in creating oxidation. Oxidative products formed in biodiesel affect fuel storage life, contribute to deposit formation in tanks, and they may cause clogging of fuel filters and injection systems. The volatile organic acids formed as secondary by products of the oxidative degradation, may stimulate corrosion in the fuel system. Poor stability can lead to increasing acid numbers, increasing fuel viscosity, and the formation of gums and sediments. In general, antioxidants can prevent oxidation. Biodiesel, because it contains large numbers of molecules with double bonds, is much less oxidatively stable than petroleum-based diesel fuel. Oxidation stability is the important parameter to determine the storage of biodiesel for longer period of time. Biodiesel samples were evaluated according to methods on the base of kept in contact with pure oxygen at elevated temperatures and pressures. The results show that the performance antioxidants variation is observed for biodiesel. The most commonly used primary synthetic antioxidants.

Key words: biodiesel; vegetable oil; fatty acid; oxidation; stability

INTRODUCTION

Traditionally, oil and fat consumption was shared between food, feed, and industrial use in the ratio 80:6:14. But with growing production of biodiesel this ratio is probably now closer to 74:6:20 **(Gunstone, 2008)**.

Palm and rapeseed oils contribute most to the growing industrial use, palm oil mainly because of the development of the oleochemical industry in southeast Asia and rapeseed oil mainly because of the biodiesel industry in Europe **(Gunstone, 2009)**.

In 2008 biodiesel production and capacity amounted globally to 11.1 and 32.6 million tonnes, respectively **(Biodiesel 2020: A global market survey, 2008)**. The huge gap between capacity and production is most likely due the fluctuation of subsidies. This situation could offer an opportunity for the chemical industry, since biodiesel (a mixture of C_{16} and C_{18} fatty acid methyl esters) should be considered as a potential chemical feedstock. For instance, applications of biodiesel as a polymerization solvent have already been studied **(Salehpour and Dube, 2008; Salehpour et al., 2009)**.

The production of fatty acids is the highest volume oleochemical process and accounts for about 52% of industrially used oils and fats **(Gunstone, 2001)**.

Biodiesel is chemically fatty acid alkyl esters (FAAEs) of long-chain fatty acids derived from renewable sources such as vegetable oils, animal fats, waste greases, recycled cooking oils etc., through the esterification and transesterification reactions of free fatty acids (FFAs) and triglycerides, respectively **(Borugadda and Goud, 2012; Atabani et al., 2013; Ong et al., 2013; Sanjid et al., 2013; Silitonga et al., 2013)**.

Biodiesel also has a much lower oxidative stability than mineral diesel **(Bouaid et al., 2007; Knothe, 2007; Santos et al., 2007; Araújo et al., 2009; Jain and Sharma, 2011; Karavalakis et al., 2011)**.

Biodiesel also has a much lower oxidative stability than mineral diesel **(Bouaid et al., 2007; Knothe, 2007; Santos et al., 2007; Araújo et al., 2009; Jain and Sharma, 2011; Karavalakis et al., 2011)**.

Previous literature **(Dunn, 2000; Litwinienko et al., 2000; Litwinienko and Kasprzycka-Guttman, 2000; (Haas et al., 2001; Abreu et al., 2004)** produced by transesterification reaction of vegetable oils with short **(Litwinienko, 2001; Dunn, 2002; Dunn, 2005a)** on the oxidative stability of oleochemicals utilizing DSC studied a variety of vegetable oils and biodiesel, along with selected fatty acids and their corresponding ethyl esters. However, individual fatty acid alkyl ester was not investigated. Other reports **(Dunn, 2000; Knothe and Dunn, 2003a; Dunn, 2005b; Dunn, 2008b)** on the oil stability index of various fatty acid alkyl esters (including biodiesel) and vegetable oils were accomplished following the American Oil Chemists' Society (AOCS) official method Cd 12b-92 at a variety of block temperatures (50–110 °C). These studies did not include a number of fatty acid alkyl ester commonly found in biodiesel, nor were EN 14112 or differential scanning calorimetry (DSC) methods utilized. A more recent report **(Knote, 2008)** on the oil stability index of selected fatty acid alkyl ester employed both EN 14112 and the American Oil Chemists' Society official method Cd 12b-92 at 110 °C, but once again did not include a number of fatty acid alkyl ester commonly found in biodiesel, nor were the effects of chain length, double bond location or orientation investigated.

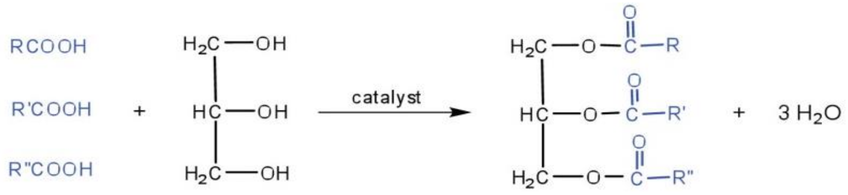
The purpose of this study was to investigate and to process the current literary knowledge of the physico-chemical properties of vegetable oil raw used for biodiesel production in terms of its qualitative stability.

An object of investigation was oxidative stability of biodiesel. In the study, we focused on the qualitative physico-chemical properties of vegetable oils used for biodiesel production, oxidative degradation and its mechanisms, oxidation of lipids, mechanisms of autooxidation, effectivennes of different synthetic antioxidants in relation to oxidative stability of biodiesel and methods of oxidative stability determination.

Vegetable oils and biodiesel

The main constituents of vegetable oils are triglyceride molecules. If the vegetable oil allowed to be reacted with methanol in the presence of a catalyst, the result is biodiesel and glycerol. Triglyceride molecules are tranesterified to form fatty acid alkyl esters **(Marchetti et al., 2007; Gui, 2008; Atadashi et al., 2012; Motasemi and Ani, 2012; Atabani et al., 2013; Yaakob et al., 2013)**.

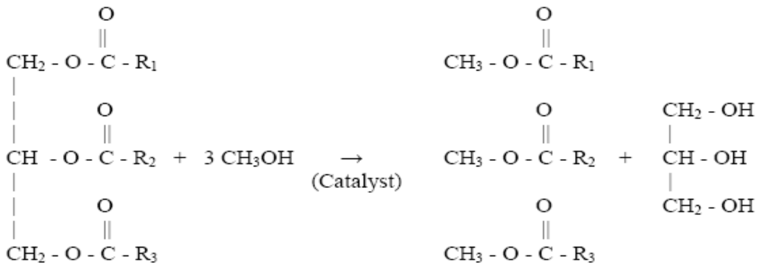
Transesterification reaction can be catalyzed by both homogeneous (alkalies and acids) and heterogeneous



triglyceride *free fatty acids* *glycerol*

R_1, R_2, and R_3 represent hydrocarbon groups (also known as chains or radicals)

Figure 1 A triglyceride is the condensation product of one molecule of glycerol with three molecules of fatty acids **(Blagdon, 2007)**.



triglyceride *methanol* *mixture of fatty esters* *glycerol*

Figure 2 Transesterification reaction **(Van Gerpen et al., 2004)**.

catalysts. The most commonly used alkali catalysts are sodium hydroxide (NaOH), sodium methoxide (CH_3ONa), and potassium hydroxide (KOH) **(Encinar et al., 2010)**.

Thus the biodiesel consists of long-chain fatty acid esters **(Haas et al., 2001; Abreu et al., 2004)** produced by transesterification reaction of vegetable oils with short chain alcohols **(Noureddini et al., 1998; Encinar et al., 2002)**.

Biodiesel typically comprises alkyl fatty acid (chain length C_{14}-C_{22}) esters of short-chain alcohols, primarily, methanol or ethanol **(Ma and Hanna, 1999; Demirbas, 2009)**.

The transesterification reaction consists in the conversion of the triglyceride molecules, by means of the action of short chain alcohol, i.e., ethanol, into the corresponding fatty acids esters. According to the source of oilseed, variations in the chemical composition of the vegetable oil are expressed by variations in the molar ratio among different fatty acids in the structure. The relative ratio of fatty acids present in the raw material is kept relatively constant after the transesterification reaction **(Costa Neto et al., 2000)**.

Currently, more than 95% of the world biodiesel is produced from edible oils which are easily available on large scale from the agricultural industry **(Gui, 2008)**.

However, continuous and large-scale production of biodiesel from edible oils has recently been of great concern because they compete with food materials, the food versus fuel dispute **(Refaat, 2010)**.

Biodiesel physico-chemical properties

The quality of biodiesel physico-chemical properties is influenced by the chain length and the level of unsaturation of the produced fatty acid alkyl esters. According to **Schuchardt et al. (1998)** the chain length and the level of unsaturation of the produced fatty acid alkyl ester correspond to that of parent oil. Therefore, in general the fatty acids ethyl esters profile obtained by transesterification is reflected by the composition in fatty acids of the employed raw material. This fact can be proven by comparing the fatty acid compositions in employed raw materials, with the fatty acids composition in esters of the produced biodiesel **(Ferrari et al., 2005)**.

Knothe and Dunn (2003a) reported that biodiesel is thermodynamically stable. Its instability primarily occurs from contact of oxygen present in the ambient air that is referred to as oxidative instability. The term 'oxidation stability' is a general term. It is necessary to distinguish 'storage stability' and 'thermal stability', in relation to oxidative degradation, which may occur during extended periods of storage, transportation and end use. **Monyem et al. (2001)** reported also that some chemical and physical properties of biodiesel can be affected by oxidation of the fuel during storage.

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

Oxidative degradation

Oxidative degradation during transport and storage causes deterioration of the physical properties of the biodiesel making it unstable and unusable **(Bouaid et al., 2007; Hoshino et al, 2007)**.

Biodiesels are more susceptible to degradation compared to fossil diesel because of the presence of unsaturated fatty acid chain in it (carbon double binds C=C) **(Prankl and Schindlbauer, 1998; Pullen and Saeed, 2012)**.

The mechanisms of degradation are: autoxidation in presence of atmospheric oxygen; thermal or thermaloxidative degradation from excess heat; hydrolysis in presence of moisture or water during storage and in fuel lines; and microbial contamination from contact with dust particles or water droplets containing fungi or bacteria into the fuel **(Dunn, 2008; Pullen and Saeed, 2012; Obadiah et al., 2012)**.

This degradation is exasperated if there is at least two or higher number of carbon double bonds (polyunsaturation) are extant in their fatty acid chains **(Graboski and McCormick, 1998)**.

More than half of a century has been elapsed after the establishment of autoxidation mechanism of polyunsaturated fatty acids as a radical chain reaction **(Bolland, 1949; Bergström et al., 1950)**. This was followed by interpretation on role of antioxidants as inhibiting agent **(Ingold, 1961)**.

Oxidation

The oxidation of lipids is a complex process in which unsaturated fatty acids are reacted with mlecular oxygen by means of free radicals **(Gray, 1978)**. The radicals react with lipids, and cause oxidative destruction of unsaturated, polyunsaturated fatty acids, therefore, known as lipid peroxidation. Lipid peroxidation is chain reaction **(Sakac and Sakac, 2002)**.

The factors such as heat, oxygen, light, and some metal ions, especially iron and copper, also play a significant role in creating oxidation **(Ozturk and Cakmakcib, 2006)**.

The oxidation of biodiesel is due to the unsaturation in fatty acid chain and presence of double bond in the molecule which offers high level of reactivity with O_2, especially, when it is placed in contact with air/water. The primary oxidation products of double bonds are unstable allylic hydroperoxides which are unstable and easily form a variety of secondary oxidation products. This includes the rearrangement of product of similar molecular weights to give short chain aldehydes, acids compounds and high molecular weight materials.The oxidation reactivity is related to the degree of C=C bonds in the fuel, increased content of the C=C bonds correlates to decreased oxidative stability of the fuel. The increase in instability of a given diesel fuel molecule is generally directly proportional to the number of C=C bonds in the molecule (i.e., a molecule containing two C=C bonds has half the stability of a molecule containing one C=C bond) **(Berman et al., 2011)**. The methylene groups adjacent to double bonds have turned out to be particularly susceptible to radical attack as the first step of fuel oxidation **(Knothe and Dunn, 2003b)**. The rate of oxidation of fatty compounds depends on the number of double bonds and their position **(Knothe, 2005)**. The oxidation chain reaction is usually initiated at the positions allylic to double bonds **(Hoshino et al., 2007)**. The oxidation can be described in terms of initiation reactions as a tree phases **(Formo et al., 1979; Kemin and Industries Inc., 2010)**.

In the start-up phase are highly active free radicals formed due to temperature, light or metal ions. The second step in the process is called phase oxidation promotion, in each reaction, because the new, reactive radicals are formed, followed by of the two radicals may be combined and mutually neutralized, resulting in the formation of stable oxidation formed, followed by a chain reaction. During the final products stages of the two radicals may be combined and mutually neutralized, resulting in the formation of stable oxidation products **(Jain and Sharma, 2011)**.

The mechanism of autooxidation of lipids describes **Kanner and Rosenthal (1992), Choe and Min (2006)** as a free radical chain reaction that involves three stages: initiation, propagation and termination.

Autoxidation of oils requires fatty acids or acylglycerols to be in radical forms. Fatty acids or acylglycerols are in nonradical singlet states, and the reaction of fatty acids with radical state atmospheric $^3O_2$ is thermodynamically unfavorable due to electronic spin conservation **(Min and Bradley, 1992)**.

The oxidation products formed in biodiesel affect fuel storage life, contribute to deposit formation in tanks, and they may cause clogging of fuel filters and injection systems **(McCormick et al., 2007)**. The volatile organic acids formed as secondary by products of the oxidative degradation, may stimulate corrosion in the fuel system **(Araújo et al., 2009)**.

Antioxidants

The antioxidants can be generally categorized into primary and secondary types **(Dubey, 2015)**. Stability of the biodiesel is an important attribute if the biodiesel is to be stored for a prolonged period. Poor stability can lead to increasing acid numbers, increasing fuel viscosity, and the formation of gums and sediments. Information about the stability of the stored biodiesel can be achieved by monitoring the acid number and viscosity. Storage stability of biodiesel has not been extensively examined relative to its composition. Therefore, the current best practice involves not storing biodiesel or biodiesel blends for more than six months. The stability of stored diesel fuels can be enhanced by using antioxidants **(Van Gerpen et al., 2004)**.

In general, antioxidants can prevent oxidation **(Ozturk and Cakmakcib, 2006)**. **Tkačová et al. (2015)** reported that they could be on a natural basis. Oxidation cannot be entirely prevented but can be significantly slowed down by the use of antioxidants which are chemicals that inhibit the oxidation process **(Pospisil and Klemchuk, 1990)**. One area where the biodiesel producer needs to give serious consideration is oxidative stability. Biodiesel, because it contains large numbers of molecules with double bonds, is much less oxidatively stable than petroleum-based diesel fuel. Fortunately, stability-enhancing additive technology is well-developed in the food industry and many of these additives can be carried over to stabilizing biodiesel **(Van Gerpen et al., 2004)**. Naturally occurring antioxidants were shown to provide relatively poor oxidation stabilization of biodiesels compared to synthetic antioxidants **(Ball et al., 2009)**. Two types of antioxidants are generally known: chain breakers and hydroperoxide decom- posers **(Pospisil and Klemchuk, 1990)**. Literature related to hydroperoxide decomposers is very scarce. The two most common types of chain breaking antioxidants are phenolic and amine-types. Almost all the work related to stability of fatty oil and ester applications is limited to the phenolic type of antioxidant **(Natarajan, 2012)**.

According to **Dubay (2015)**, primary, or chain-breaking antioxidant, are free radical scavengers that delay or inhibit the initiation step of autooxidation or interrupt the propagation step.

$$ROO\cdot + AH \rightarrow A\cdot + ROOH \qquad (6)$$

$$RO\cdot + AH \rightarrow A\cdot + ROH \qquad (7)$$

$$R\cdot \rightarrow A\cdot + RH \text{ (stable product)} \qquad (8)$$

Where: ROO·=peroxyl radical, AH=primary antioxidant, ROOH=hydroperoxide, A·=antioxidant radical.

Initiation	$RH + ?$	$\rightarrow$	R
	$R'\text{-}CH\text{=}CH\text{-}R'' + O_2 + ?$	$\rightarrow$	ROOH
Propagácia	$R\cdot + O_2$	$\rightarrow$	$ROO\cdot$
	$ROO\cdot +$	$\rightarrow$	$ROOH + R\cdot$
	ROOH	$\rightarrow$	$RO\cdot + OH$
Termination	$R\cdot + R\cdot$	$\rightarrow$	nonradical product
	2 ROO	$\rightarrow$	$R_1\text{-}CO\text{-}R_2 + R_1\text{-}CHOH\text{-}R_2 + O_2$
	Other free radical rearrangements		

where:

RH=hydrogen containing compound
R·=alkyl radical
R'-CH=CH-R"=reactive alkene
O_2=air oxygen, triplet
ROOH=hydroperoxide
ROO·=peroxyl radical
RO·= alkoxyl radical
OH·=hydroxyl radical.

Figure 3 Mechanism of lipid autoxidation as a free radical chain reaction involving initiation, propagation and termination **(Min and Bradley, 1992)**.

Antioxidants significantly slow down the biodiesel degradation process. According to their mode of action, antioxidants could be classified in to various groups: free radical terminators, metal ion chelators capable of catalyzing lipid oxidation, or as oxygen scavengers that react with oxygen in closed systems **(Shahidi et al., 1992)**. The antioxidants sú described in papers by **Manura (1994), Imahara et al. (2008), Jain and Sharma (2013), Atabani et al. (2013), Dwivedi and Sharma (2014a)**.

The study by **Dwivedi and Sharma (2014b)** shows that oxidation stability is the important parameter to determine the storage of biodiesel for longer period of time. The study also shows that out of various natural and synthetic antioxidants Pyrogallol is best for storage of biodiesel. There are various type of metal and alloys containers are used for storage of biodiesel. Out of various metal and alloys iron and aluminium alloy is best for storage of biodiesel. The future scope of study includes the thermal stability of various biodiesel and the long term effect of various antioxidant, metal and alloys on biodiesel.

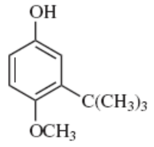
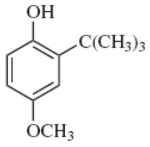
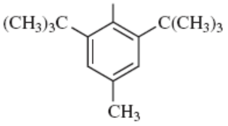
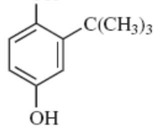
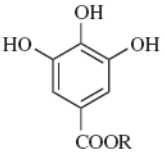
Determination of lipid oxidative stability

It is believed according to **Wąsowicz et al. (2004)** that for the determination of oxidative stability and shelf life, methods for the determination of lipid oxidation can be ranked in the following order: sensory analysis > headspace analysis of volatiles > oxygen absorption > peroxide value > thiobarbituric acid reactive substances (TBARS) > carotene bleaching by cooxidation with linoleic acid > Rancimat test **(Frankel, 1993)**. The diversity and abundance of methods used to monitor lipid oxidation reflect the complexity of this issue and confirm the fact that multiple methods should be applied to get the maximum information available.

Method for determine of the biodiesel oxidative stability

Method for determine of the biodiesel oxidative stability according to **Ferrari et al. (2005)** can be evaluated by means of the Rancimat® equipment model 617, under temperatures of 100 and 105 ºC and air flow of 20 $L.h^{-1}$. Samples of 5.0 g are utilized, weighed in the Rancimat® flask. The oxidation is then induced by the passage of the air flow through the sample, kept under constant temperature. The volatile products of the reaction, which are blown with the air, are collected in distilled water and measured by the change in electric conductivity of this water. They are expressed through a curve from which the induction period can be calculated by the interception of two lines: a tangent to the inclination and the another tangent to the curve level part. The method used is adapted from the **American Oil Chemist's Society (1997)** recommended method Cd 12b-92. The cleanliness of the containers used in the Rancimat® apparatus is essential to get truthful and save results, therefore traces of oxidized fats or metals may have a harmful effect on the induction period. In order to avoid problems the cleaning practical procedures of the used material were performed according to **Pacheco's (1991)** specifically. Moreover, **Angelovič et al. (2013)** reported that no comprehensive risk assessment for diesel engine emissions from biodiesel and its blends is possible in regard to a comprehensive hazard characterization it is urged to develop a panel

Table 1 The most commonly used primary synthetic antioxidants **(Dubay, 2015)**.

Name	Chemical structure	
Butylated ydroxyanisole (BHA) Molecular formule: $C_{11}H_{16}O_2$	 	(**Shahidi and Zhong, 2005**)
Butylated hydroxytoluene (BHT) Molecular formule: $C_{15}H_{24}O$		(**Shahidi and Zhong, 2005**)
tert-Butylhydroquinone (TBHQ) Molecular formule: $C_{10}H_{14}O_2$		(**Shahidi and Zhong, 2005**)
Different alkyl gallate: Propyl gallate (PG) $C_{10}H_{12}O_5$ Octyl gallate (OG) $C_{15}H_{22}O_5$ Dodecyl gallate (DG) $C_{19}H_{30}O_5$, most of them propyl gallate (PG)		(**Shahidi and Zhong, 2005**) (**Dubay, 2015**)

of standardized and internationally accepted protocols which allow a reliable assessment also of possible health hazards which may arise from the combustion of new fuels compared to conventional diesel fuel.

The effectiveness of various antioxidants and biodiesel oxidative stability

Biodiesel samples were evaluated according to methods on the base of kept in contact with pure oxygen at elevated temperatures and pressures. The results show that the performance antioxidants variation is observed for biodiesel. **Karavalakis et al. (2011)** reported that butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) displays the lowest effectiveness in neat biodiesel. Propyl gallate (PG) and pyrogallol (PY) additives showed the strongest effectiveness in both the neat biodiesel and the biodiesel blends.

Stability was enhanced in canola biodiesel with antioxidant 2,5-di-tert-butylhydroquinone (DTBHQ) or poly(1,2-dihydro-2,2,4-trimethylquinoline) (Orox PK) **(Focke et al., 2012)**.

Accordingly, the review by **Jain and Sharma (2010)** focussed on data for eight representatives of the class phenolic antioxidants. Overall, propyl gallate (PG), pyrogallol (PA) and tert-butyl hydroquinone (TBHQ) were considered the most effective additives in both the neat biodiesel and the biodiesel blends. The superior performance of propyl gallate (PG) and pyrogallol (PA) was confirmed by **Karavalakis et al. (2011)**. These authors reported that butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) displays the lowest effectiveness in neat biodiesel. Propyl gallate (PG) and pyrogallol (PY) additives showed the strongest effectiveness in both the neat biodiesel and the biodiesel blends. **Schober and Mittelbach (2004)** used a Rancimat instrument at 110 °C and investigated the potential of 11 synthetic phenolic antioxidants to improve the oxidation stability of four biodiesel samples derived from different feedstocks. 2,5-di-tert-butylhydroquinone (DTBHQ) was found to be a very effective antioxidant even at low concentrations. **Focke et al. (2012)** prepared biodiesel samples using base-catalyzed methanolysis of sunflower, soybean and canola oils. Fatty acid methyl ester analysis results, in conjunction with Fourier Transform Infrared (FTIR) spectroscopy (FTIR spectra), confirmed the absence of water and methanol but indicated that the fuels contained unreacted vegetable oils. The stability of the neat oils correlated with the degree of unsaturation of the fatty acid methyl esters. The Rancimat induction periods were 0.61 h, 3.3 h and 7.1 h for the neat (and fresh) sunflower, soybean and canola fuels respectively. The measured Rancimat induction periods decreased by about 25% when the neat oils were exposed to air for 12 days. The neat canola biodiesel already conformed to the European Rancimat specification **EN 14214** or biodiesel stability of > 6 h. Its stability was further improved by the addition of the synthetic antioxidants di-tert-butylhydroquinone (DTBHQ) or poly(1,2-dihydro-2,2,4-trimethylquinoline) (Orox PK). Surprisingly it was found that low additions of the synthetic antioxidant tris(nonylphenyl) phosphite (Naugard P) to canola oil actually resulted in an apparent decrease in the oxidative stability as quantified by Rancimat. Such an effect was also observed, albeit to a lesser extent, with DTBHQ as inhibitor in sunflower and canola biodiesels.

CONCLUSION

Biodiesel is chemically fatty acid alkyl esters of long-chain fatty acids derived from renewable sources, which include also the vegetable oils. The quality of biodiesel physico-chemical properties is influenced by the chain length and the level of unsaturation of the produced fatty acid alkyl esters. A biodiesel is thermodynamically stable. Its instability primarily occurs from contact of oxygen present in the ambient air that is referred to as oxidative instability.

The great deal of knowledge accumulated on the general chemistry of oxidation of lipids suggests that further efforts should be directed to a detailed understanding of the effects of this process in biodiesel.

Potential targets for future research would be based on the following:

- For biodiesel is oxidation stability a general term. It is necessary to distinguish ‘storage stability’ and ‘thermal stability’, in relation to oxidative degradation, which may occur during extended periods of storage, transportation and end use.
- Fuel instability problems can be of two related types, short-term oxidative instability and long-term storage instability. Storage instability is defined in terms of solid formation, which can plug nozzles, filters, and degrade engine performance. Biodiesels are more susceptible to degradation compared to fossil diesel because of the presence of unsaturated fatty acid chain in it.
- The mechanisms of oxidative degradation are autoxidation in presence of atmospheric oxygen; thermal or thermal-oxidative degradation from excess heat; hydrolysis in presence of moisture or water during storage and in fuel lines; and microbial contamination from contact with dust particles or water droplets containing fungi or bacteria into the fuel.
- The factors such as heat, oxygen, light, and some metal ions, especially iron and copper, also play a significant role in creating oxidation.
- Oxidative products formed in biodiesel affect fuel
- Storagelife, contribute to deposit formation in tanks, and they may cause clogging of fuel filters and injection systems.
- The volatile organic acids formed as secondary by products of the oxidative degradation, may stimulate corrosion in the fuel system.
- Poor stability can lead to increasing acid numbers, increasing fuel viscosity, and the formation of gums and sediments.
- Oxidation stability of biodiesel is the important parameter to determine the storage of biodiesel for longer period of time. Biodiesel samples were evaluated according to methods on the base of kept in contact with pure oxygen at elevated temperatures and pressures. Antioxidants showed preventive effects on oxidative stability of biodiesel, especially primary synthetic.

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