Obtaining Biodiesel with High Oxidation Stability from the Oil Blend Extracted from Seeds of *Citrullus lanatus* and *Vitis vinifera*

MIHAELA GABRIELA DUMITRU*
University of Craiova, Faculty of Science, Department of Chemistry, 107i Calea Bucuresti, 200585, Craiova, Romania

The increase of energy demand associated with stringent worldwide emission legislation and the depletion of fossil resources has led to the use of biodiesel and biodiesel blends from various feedstocks. One of the main problems with biodiesel is the susceptibility to oxidation and degradability due to the environmental factors. The oxidation process is complex affecting the fuel quality resulting in choking of injector and formation of deposits in fuel system. Antioxidants are used to limit the oxidative degradation. The present paper review some attempts to use natural and synthetic antioxidants form different papers available in the public domain. Two types of biodiesel from oils of Citrullus lanatus and Vitis vinifera were obtained by base catalyzed transesterification. Peroxide value, iodine value, acid value and induction period were determined monthly to observe the degradation process for biodiesel samples. The biodiesel from Citrullus lanatus 90% and oil of Vitis vinifera 10% exhibits presented the best oxidation stability over a period of 12 months. A single cylinder diesel engine setup was used to determine the performance and gas emissions for biodiesel samples. The results show that biodiesel can be used without engine modification with results comparable with diesel fuel.

Keywords: biodiesel, Citrullus lanatus, Vitis vinifera, oxidation stability

Currently the alternative fuels have become a solution to the depletion of the fossil fuels. Various percentages of biofules in the blend are used depending of the regulation norms of each country. The demand for biofuels has raised the price of crude oil due to the use of biodiesel not only in agriculture but also in transport and industrial sector. Therefore researchers and authorities are keenly looking to increase the biodiesel production from new sources and to reduce dependability of conventional fuels [1]. Various vegetable oils such as soybean, sunûower, palm, rape, jatropha, mustard, karanja, cotton and neem were used to produce biodiesel. Biodiesel is composed by or methyl esters of long chain fatty acids obtained from various feedstocks [2, 3]. Despite his many advantages such as renewability, non toxicity and biodegrability the drawbacks are that cost more than fossil diesel, deteriorates rubber compounds and suffers a oxidative degradation [4]. The oxidation process change the physico-chemical and tribological properties during biodiesel storage or use. This process produces insoluble deposits and increase in the values of peroxide value, kinematic viscosity, iodine value, density and acid number. The formed products affect the engine by formation of deposits, obstructions of the injection system, corrosion etc. [5]. Antioxidant substances as ketones, peroxides, dimmers and aldehydes can prevent the formation of compounds from thermal oxidation processes. Also some substances from natural sources such phenolic compounds, vitamins and nitrogenous (alkaloids, amino acids etc.) can be used as antioxidants [6, 7]. Bouaid et al. [8] investigated the oxidative stability of biodiesel from sunflower oil, Erucic Brassica Carinata and used frying oil under various conditions for a period of 30 months. The authors found that the increase in temperature accelerates the oxidation process and the process accelerates with the increase of storage time. During oxidation process are formed volatile products such as ketones, alcohols, aldehydes and peroxides. Bondioli et al. [9] investigated the biodiesel of rapeseed under different conditions and found that the oxidation process was influenced by the temperature and the characteristics of the storage container. Berrios et al. [10] found that the temperature play an important role in the oxidation process and the degradation is more intense with the rise of temperature.

They recommend that biodiesel must be placed in underground storage tanks to keep his properties. Aquino et al. [11] reported that oxidation of biodiesel is accelerated by the presence of light and high temperature. The authors recommended that biodiesel should be storage in rooms without light. Researches show that autoxidation is a critical phenomenon that affects the properties of the fuel. The process of oxidations has three main stages: initiation, propagation and termination [12-14], (fig. 1).

Although the process cannot be stopped, there are some methods that may be taken to slow down this process. Addition of antioxidants in the oils may help to slow oxidation, (fig. 2) or degradation processes and increase their oxidation stability. The literature shows the oil extracted from the *Vitis vinifera* seeds compared to other oils as a source of antioxidants directly related to the high concentration in tocopherol and tocotrienol isomers of vitamin E, vitamin E that is rarely found in other oils (the literature shows the oil extracted from the *Vitis vinifera* seeds compared to other oils as a source of antioxidants directly related to the high concentration in tocopherol and tocotrienol isomers of vitamin E, vitamin E that is rarely found in other oils [15-23]. In table 1, are shown the main chemical components contained in the oil extracted from Vitis vinifera seeds [14].

In addition, grape seed oil contains tannins in higher concentrations than other seed oils [24] such as Gallic acid, catechin, epicatechin, and a large amount of procyanidins [25]. In this context we used the oil extracted from roasted *Vitis vinifera* seeds in supplementing the oil extracted from *Citrullus lanatus* to obtain biodiesel with high stability to oxidation.

** email: dummgs@yahoo.com; Phone: +40 251597048*

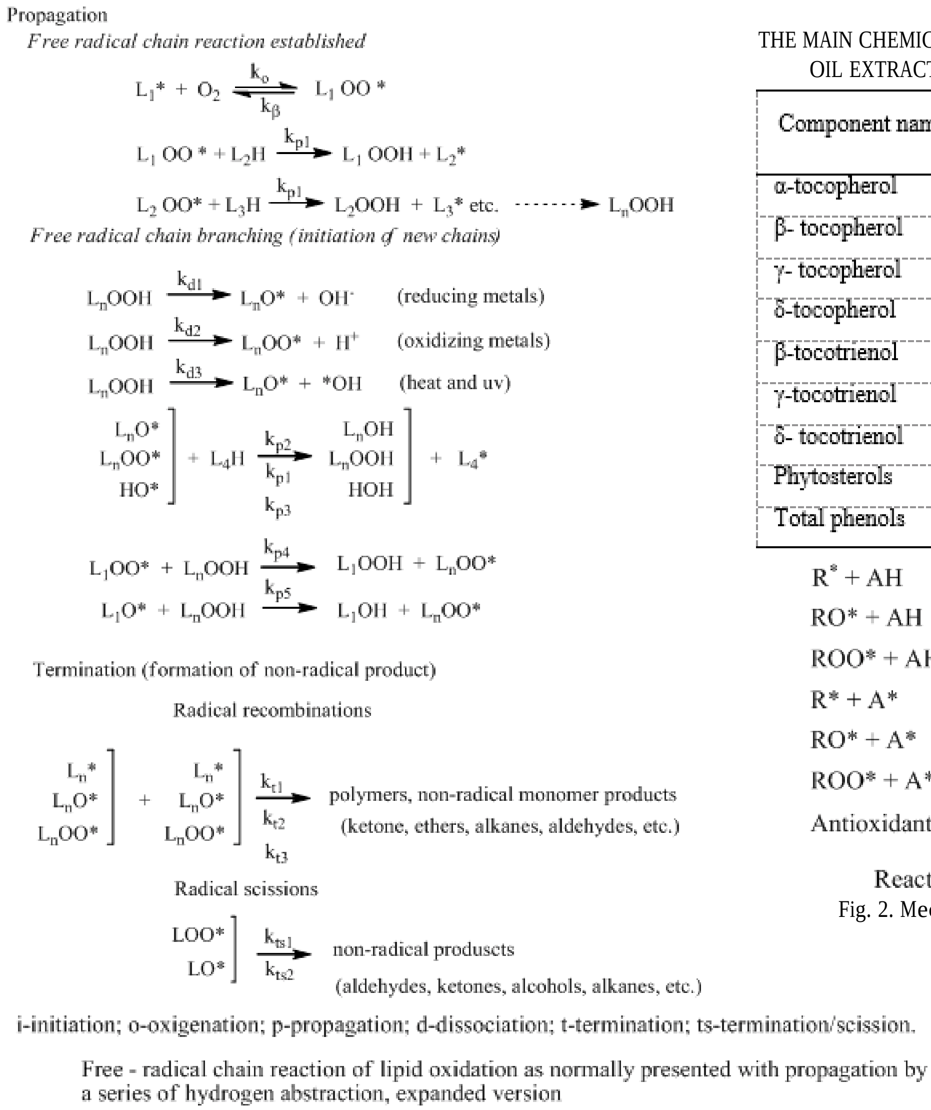

Fig. 1. Stages of the oxidation process

Table 1
THE MAIN CHEMICAL COMPONENTS CONTAINED IN THE OIL EXTRACTED FROM *VITIS VINIFERA* SEEDS

Component name	Concentration mg Kg^{-1} oil	Source
α-tocopherol	36-325	16; 18-22
β- tocopherol	25-48	16; 18; 19; 23
γ- tocopherol	3-39	18; 19; 20-23
δ-tocopherol	0.6-163	16
β-tocotrienol	4-18	20
γ-tocotrienol	261-1575	18; 19; 20; 23
δ- tocotrienol	6-17	18; 19; 22; 23
Phytosterols	82-136	20
Total phenols	100-238	16

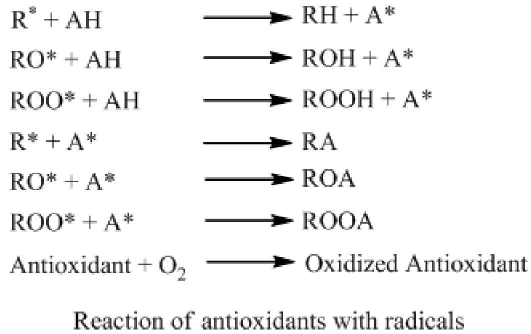

Fig. 2. Mechanism of action of the antioxidant

Experimental part

Biodiesel production

Oil content of *Citrullus lanatus* seed and *Vitis vinifera* seed were determined after Soxhlet extraction with petroleum ether at 70-80°C as solvent for 6 h. Two types of biodiesel were obtained:

- biodiesel obtained from the oil extracted from seeds of *Citrullus lanatus*;
- biodiesel obtained from the oil extracted from seeds of *Citrullus lanatus* 90 % and oil extracted from seeds of *Vitis vinifera* 10 %.

The biodiesel was produced by alkali catalyzed transesterification process, figure 3 and 4 in biochemistry laboratory of Chemistry Department of University of Craiova. The peroxide value (mEqO_2 kg^{-1} oil), iodine value (gI_2 100 g^{-1} oil), acid value (mgNaOH g^{-1} oil) and induction period (h) was determined monthly according to [14, 26, 27].

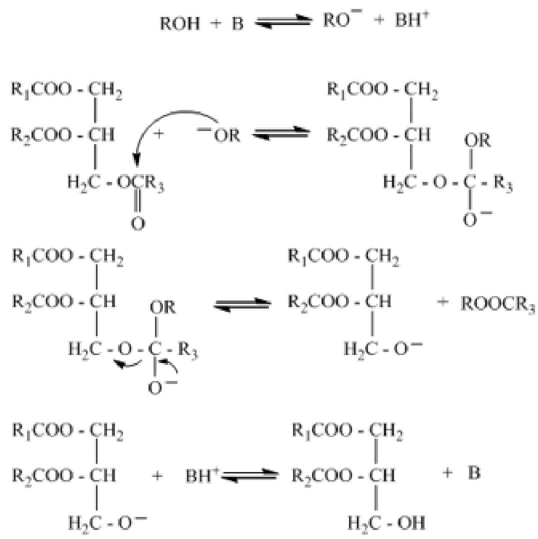

Fig.3 Mechanism of transesterification (base catalyzed) of vegetable oils [28]

Determination of Peroxide value.

The standard method prescribed by the Association of Official Analytical Chemists [29] was performed to measure the peroxide value. In this procedure, the biodiesel samples weighing 2 g were taken individually in different conical flasks and then a solution of acetic acid and chloroform in the ratio 3:2 is added. Later, the solution of saturated potassium iodide of 0.5 mL is mixed up with samples in every flask. All the flasks are then undisturbed for 5 minutes. Now the distilled water measuring 15 mL is added to each flask and then titrated with a sodium thiosulfate solution of 0.1N until the yellowish color disappears. Finally, 0.5 mL of starch is added and the titration is continued till the end point where the mixture turns colorless. The peroxide values are calculated from the expression [30]:

$$PV = \frac{(V_2 - V_1) \times T \times 1000}{m}$$

where: V_1 = volume of 0.1 N blank;
V_2 - volum of 0.1 N $Na_2S_2O_3$;
T - normality of $Na_2S_2O_3$ (0.1N);
m = mass of oil taken.

Determination of Iodine value

The iodine value represents the quantity of iodine expressed into grams, which is added by 100 g of lipids. It is a measure of the unsaturated fatty acids grade which enters in the structure of animal and vegetal lipids. The iodine value was calculated using the Hanus method. The iodine value was calculated according to the formula [26]

$$I_i = \frac{(V_m - V_p) \times t \times f \times 100}{m_p} \quad \mathrm{g\,I/100g}$$

where:

V_m - volume of the solution of sodium thiosulphate 0.1 N used in the titration of sample control, mL;

V_p - volume of the solution of sodium thiosulphate 0.1 N used in the titration of analysed sample, mL;

t - titre of the solution of sodium thiosulphate 0.1 N in relation with the iodine (0.01269 mg/mL);

f - factor of the solution of sodium thiosulphate 0.1 N;

m_p - mass of the analyzed sample.

Determination of acid value

The acid value of the oil sample was determined using ASTM method [31]. Twenty five milliliter diethyl ether with 25 mL alcohol and 1 mL phenolphthalein solution (1 %) was mixed and carefully neutralized with 0.1 m NaOH. One to ten gram of the biodiesel was dissolved in the mixed neutral solvent and titrated with aqueous 0.1 m NaOH, shaken constantly until a pink color which persists for 15 s was obtained. The acid value was calculated calculated according to the formula [32]:

$$\text{Acid value} = \frac{\text{Titre (mL)} \times 5.6}{\text{Weight of sample}}$$

Determination of Induction period stability through the Hadorn-Zürcher method (Rancimat)

This method consists in the biodiesel oxidation in accelerate conditions. The method permits the establishment of the induction period, which corresponds, with the initiation step of the biodiesel auto-oxidation. To determine the stability in oxidation it was used an installation, which used oxidized oil samples (10 g) at a temperature of 110 °C [14; 33, 34]. Through the oil samples, it was bubbled air with a debit of 8 L h^{-1}. Because of the oxidation reactions, which take place in a reactor, the formed volatile acids are trained by the air current and absorbed in the measurement cell where there is bidistilled water. The measurement of the solution conductibility is done with a conductometer of Radelkis type. In the beginning, we notice a slow increasing of the solution conductibility, after that it appears a sudden increasing of this because of the formation of volatile acids. The induction period is considered the interval until the moment of the suddenly curve's change.

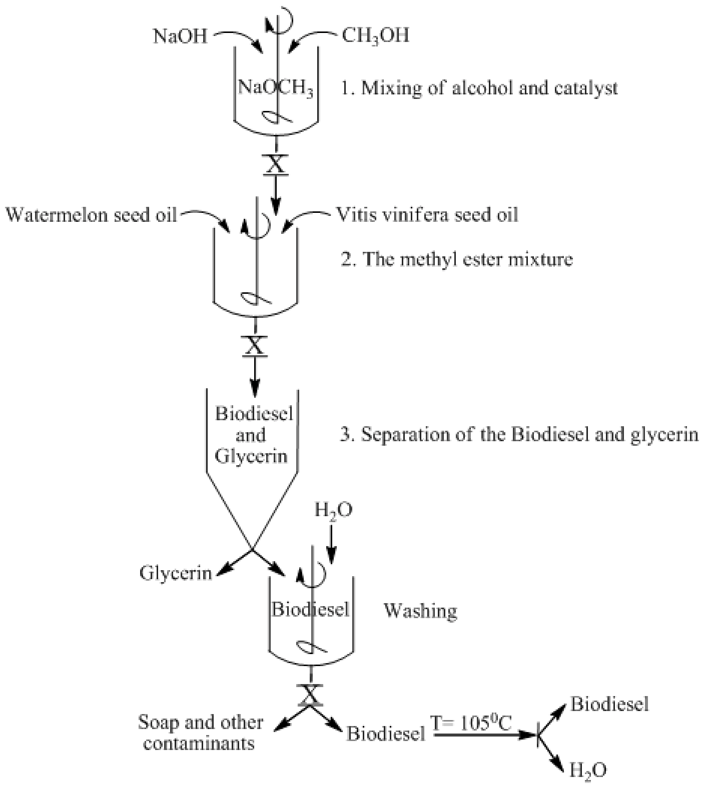

Fig. 4. Transesterification process

Table 2
ENGINE SPECIFICATIONS

Manufacturer	WUXI WORLDBEST KAMA POWER CO., LTD
Model	KM186FA/E
Configuration	Single cylinder vertical
Type	Direct injection diesel
Displacement	418 cm^3
Bore	86 mm
Stroke	72 mm
Compression ratio	19:1
Power	7,35 kW
Speed	3600 rpm
Type of cooling	Air cooling

Engine testing

The performance and emission test were conducted in a single cylinder air cooled four stroke engine. The technical specifications and main characteristics are presented in table 2. The engine was coupled with a generator and a resistive load bank was used to load the engine. Exhaust gas emissions were measured with a gas analyzer type Stargas 898. This analyzer measures CO, CO_2, HC, O_2 and NOx in the exhaust gas. The ambient conditions were monitored by a barometer and a thermometer. The engine was started and allowed to warm-up for about 30 minutes with diesel fuel. Figure 5 shows the schematic diagram of the experimental setup.

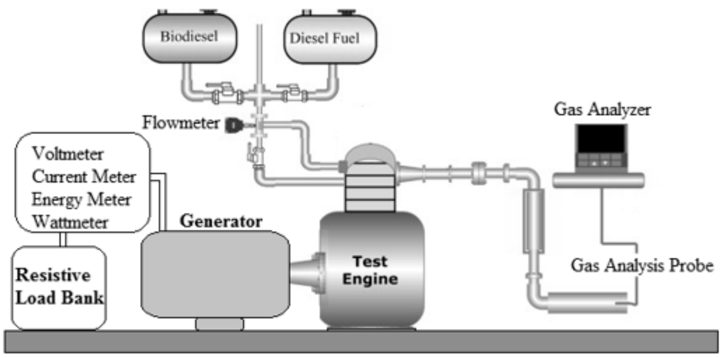

Fig. 5. Schematic diagram of the experimental setup

Results and discussions

Characterization of biodiesel

Peroxide value is a parameter used to determine the oxidation of biodiesel and measures only primary oxidation products, hydroperoxides. The peroxide value is not always specified in the Standards that characterize biodiesel but it is a parameter that influences cetane number (parameter is specified in the standards) [35]. An increase in peroxide value implies a rise in the cetane number and therefore may reduce ignition. The determination of the presence of hydroperoxides in biodiesel helps in assessing the degradation level of this biodiesel, which can occur mainly due to exposure to high temperatures. The oxidation process in the case of biodiesel is especially due to the radical chain reaction which causes the formation of hydroperoxides. Through the initial period of storage, the formation of hydroperoxides is very low. This period of time is named the induction period (IP). Once the induction period is reached, the level of hydroperoxide, ROOH increases rapidly and results in a fast overall oxidation process. Once the induction period is reached, the level of hydroperoxide, ROOH increases rapidly and results in a fast overall oxidation process. Following the induction period, oxidation reactions proceed, decomposition of primary oxidation products (hydroperoxides) produce a mixture of secondary products including short-chain carboxylic acids, etones, aldehydes, ono- and dihydroxy compounds and also polymers or sediments [36, 37]. As an effect, after induction period, not only the key properties of biodiesel degrade quickly, but also engine operation problems come forth. To slow down the oxidation reaction, antioxidants are used. Antioxidants are substances that delay the lipid oxidation by interrupting propagation of the free radical by one (or more) of several mechanisms or by preventing the formation of free radicals: (1) chelating metal ions such that they are unable to generate reactive species or decompose lipid peroxides, (2) scavenging species that initiate peroxidation, (3) quenching O_{2-} preventing formation of peroxides, (4) breaking the autoxidative chain reaction, and/or (5) reducing localized O_2 concentrations [38]. The most efficient antioxidants used for biofuels are those that interrupt the free radical chain reaction. Frequently having phenolic or aromatic rings, these antioxidants giving H^+ to the free radicals constituted during oxidation becoming a radical themselves. Then the radical intermediates are stabilized by the resonance delocalization of the electron within the aromatic ring and formation of quinone structures [39]. The experimental data presented in figure 6 shows the dynamics of the oxidation process of biodiesel samples for a period of 12 months. Changes in peroxide values are observed which show a slight increase at the start of storage. After 180 days of storage, the biodiesel samples obtained from *Citrullus lanatus* oil show a peroxide value of 23.8 $mEqO_2\,Kg^{-1}$. After this period the increase of the peroxide value is significant, reaching the final value of 57.3 $mEqO_2\,Kg^{-1}$. During this period oxidation compounds are formed which have the effect of modifying the acidity value, the refractive value, the induction period, the iodine value etc. The peroxide values of biodiesel samples obtained from oil of *Citrullus lanatus* 90 % and oil of *Vitis vinifera* 10 % are between 11.2 $mEqO_2\,Kg^{-1}$ after 180 days of storage and 41.0 $mEqO_2\,Kg^{-1}$ at the end of storage. These results highlight the role played by antioxidant compounds (polyphenolic compounds, carotenes etc.) form the oil of *Vitis vinifera* which act on the free radicals formed by slowing the reaction rate of lipid oxidation.

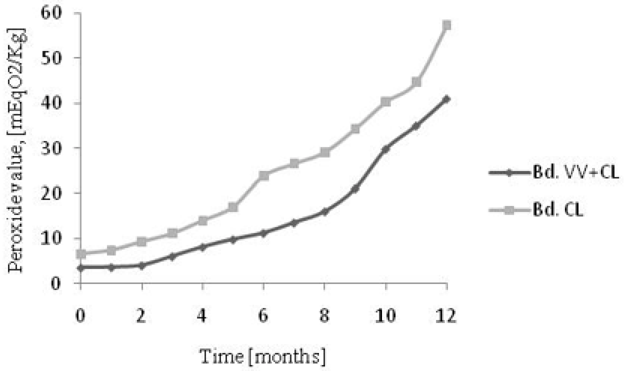

Fig. 6. Peroxide value

Iodine number is a measure of total unsaturation (double bonds) within the FAME product. It is expressed as the grams iodine required to react with 100 g of FAME sample. High Iodine value is related to polymerization of fuels, leading to injector fouling. It is also linked to poor storage stability [40]. The iodine value is in context with the number of the double bonds of the hydrocarbons. In case of biodiesels shows how the material is prone to polymerization and form deposits in the storage vessels and in the engines [41]. The Iodine Value can be important because many biodiesel fuel standards specify an upper limit for fuel that meets the specification. For example, Europe's EN14214 [42] specification allows a maximum of 120 gI_2 100 g^{-1} for the Iodine number. In figure 7 are presented the values of iodine value the tested samples. All samples showed a decrease of the initial value of the iodine with a higher decrease in the samples of biodiesel obtained from oil of *Citrullus lanatus*. The samples of biodiesel obtained from oil of *Citrullus lanatus* have a iodine value between 110 gI_2 100 g^{-1} at the start of the experiment and 58 gI_2 100 g^{-1} at the end comparative with biodiesel obtained from oil of *Citrullus lanatus* and *Vitis vinifera* with values between 118 and 89 gI_2 100 g^{-1}.

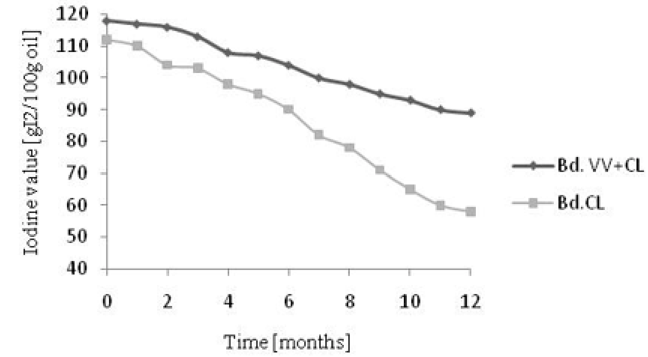

Fig. 7. Iodine value

Acid value

Another parameter used to understand biodiesel degradation is the acid value (AV) because it is directly related to stability to oxidation. This parameter is a measure of the amount of carboxylic acid groups in a chemical compound and can be used to quantify the amount of acid present. The AV is the quantity of base, expressed in milligrams of potassium hydroxide that is required to neutralize the acidic constituents in one gram of the sample. The acid value is a parameter regulated by international standards for biodiesel. European [42] According to the standard, the acid value should not exceed 0.5 mgKOH g^{-1} biodiesel. Formally, the acid value was not used for the evaluation of degradation but is useful for assessing the quality of stored biodiesel and is included in the standards [43]. Figure 8 shows the effect of storage period on the acid value of the biodiesel. From the figure, it is observed that the acid value of the biodiesel increase with the increase in storage period. This is because of formation and decomposition of peroxides which results in the formation of aldehydes and higher acidity. The increasing peroxide formation during the oxidation of biodiesel will eventually increase the AV as the peroxides experience complex reactions, including a split into more reactive aldehydes, which further oxidize to form acids. In figure 7 the acid values for the test samples are presented. Biodiesel samples obtained from oil of Citrullus lanatus show a slow increase of acid value over a period of 120 days after storage reaching a value of 0.22 mgKOH g^{-1} after which it recorded a faster growth of it reaching the end of the experiment at 0.55 mgKOH g^{-1}, value which exceed the standard (EN 14214). The acidity value of the biodiesel samples obtained from the mixture of oil extracted from *Citrullus lanatus* and *Vitis vinifera* has a much slower acidification increase over the entire storage period, reaching the end of the experiment 0.43 mgKOH g^{-1} of biodiesel, a value that is in the standard. The acid value of biodiesel samples obtained from oil of *Citrullus lanatus* and *Vitis vinifera* have a much slower increase of acid value over the entire storage period, reaching the end of the experiment at 0.43 mgKOH g^{-1}, a value that is in the standard.

Induction period.

Biodiesel oxidation is mainly the result of a radical chain reaction that causes the formation of hydroperoxides. During the initial period of storage, the formation of hydroperoxides is very low. This characteristic time period is named the induction period (IP). On the the induction period is reached, the level of hydroperoxide, ROOH increases rapidly and results in a fast overall oxidation process. Once the induction period is reached, the level of hydroperoxide, ROOH increases rapidly and results in a fast overall oxidation process. Following the induction period, oxidation reactions proceed, decomposition of primary oxidation products (hydroperoxides) yield a mixture of secondary products including short -chain carboxylic acids, etones, aldehydes, ono-and dihydroxy compounds and also polymers or sediments [36, 37]. As a result, after induction period, not only the key properties of biodiesel degrade quickly, but also engine operation problems come forth. The oxidation stability is one of the major issues for implementing the use of biodiesel as an alternate fuel to petrodiesel. To increase the oxidative stability of biodiesel, the most active and commercial method is the use of antioxidants, which are also effective for the biodiesel blends. Antioxidants have an enhanced role in the delay of oxidation by the extension of the induction period. The resistance of biodiesel to oxidation degradation during storage is a key issue for the sustainability and viability of biodiesel and biodiesel blends. From the values presented in figure 9 it is observed the role that antioxidants contained in the oil extracted from *Vitis vinifera* have on the induction period of the biodiesel. It was recorded an increase in the induction period from 4.8 h to 8.5 h. The induction period at the end of the experiment was 0.2 h for the biodiesel samples obtained from oil of *Citrullus lanatus* and 4.1 h for the biodiesel samples obtained from oil of *Citrullus lanatus* and *Vitis vinifera.*

The oxidation stability of biodiesel is referred and regulated in international standards with what is known as the induction time. In practice there are only a few type of biodiesel that meet the regulated minimum values (6 h in the EN 14214) and is necessary to add antioxidants to meet the standards. The antioxidants contains a highly

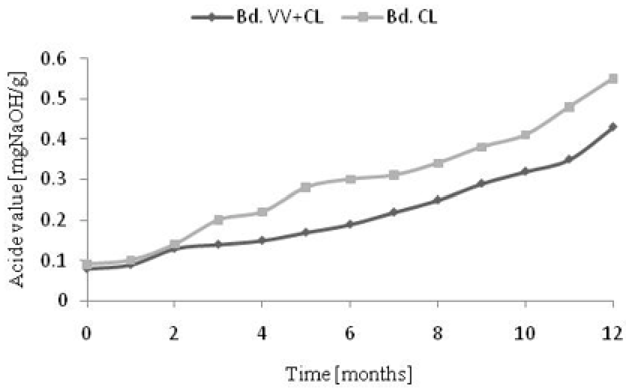

Fig.8. Acid value

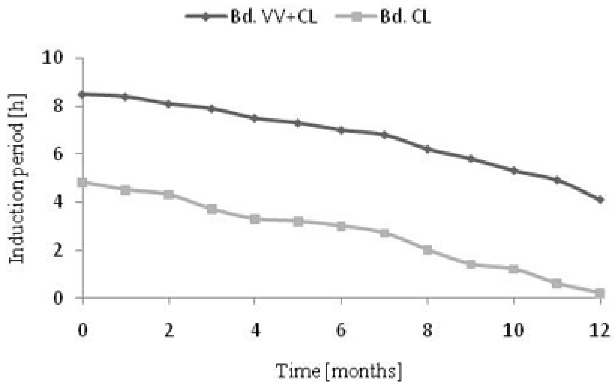

Fig. 9. Induction period

labile hydrogen that is more easily abstracted by a peroxy radical than fatty oil or ester hydrogen. The resulting antioxidant free radical is either stable or can further react to form a stable molecule which is further resistant to chain oxidation process. In figure 10 and 11 is represented the mechanism of action of α-tocopherol [44] and primary antioxidants [45] existing in appreciable quantities in the oil extracted from *Vitis vinifera* (table 1).

Engine experiments

Figure 11 shows the variation of Brake Thermal Efficiency (BTE) with load of the engine for biodiesel and diesel fuel. For all the samples tested in the engine BTE increases with increase in load up to 80 and decrease when reach the maximum load due to the incomplete combustion. The decrease in BTE for biodiesel can be due to the high value of viscosity and density which affects the vaporization and atomization of the fuel in the combustion chamber of the engine. Figure 12 shows the variation of Brake Specific Fuel Consumption (BSFC) with load of the engine. As the load increases the BSFC presented a decrease for all tested fuels. It was observed that BSFC values are higher for biodiesel due to the lower calorific value which affects the fuel evaporation. Hence the slower evaporation rates leads to higher brake specific fuel consumption. From the figure 13 the Exhaust Gas Temperature (EGT) increases with the increase in load for all tested samples. The EGT is parameter that indicates the heat during combustion period. Biodiesel shows higher temperature due to the high oxygen content which leads to better combustion.

The variation of Carbon Monoxide (CO) emissions with load of the engine is shown in figure 14. The neat biodiesel exhibits lower emissions of CO comparative with diesel fuel for all loads. CO emissions are dependent of carbon and oxygen content and combustion efficiency of the fuel. The higher oxygen content aids the combustion process leading to the decrease of emissions in the case of

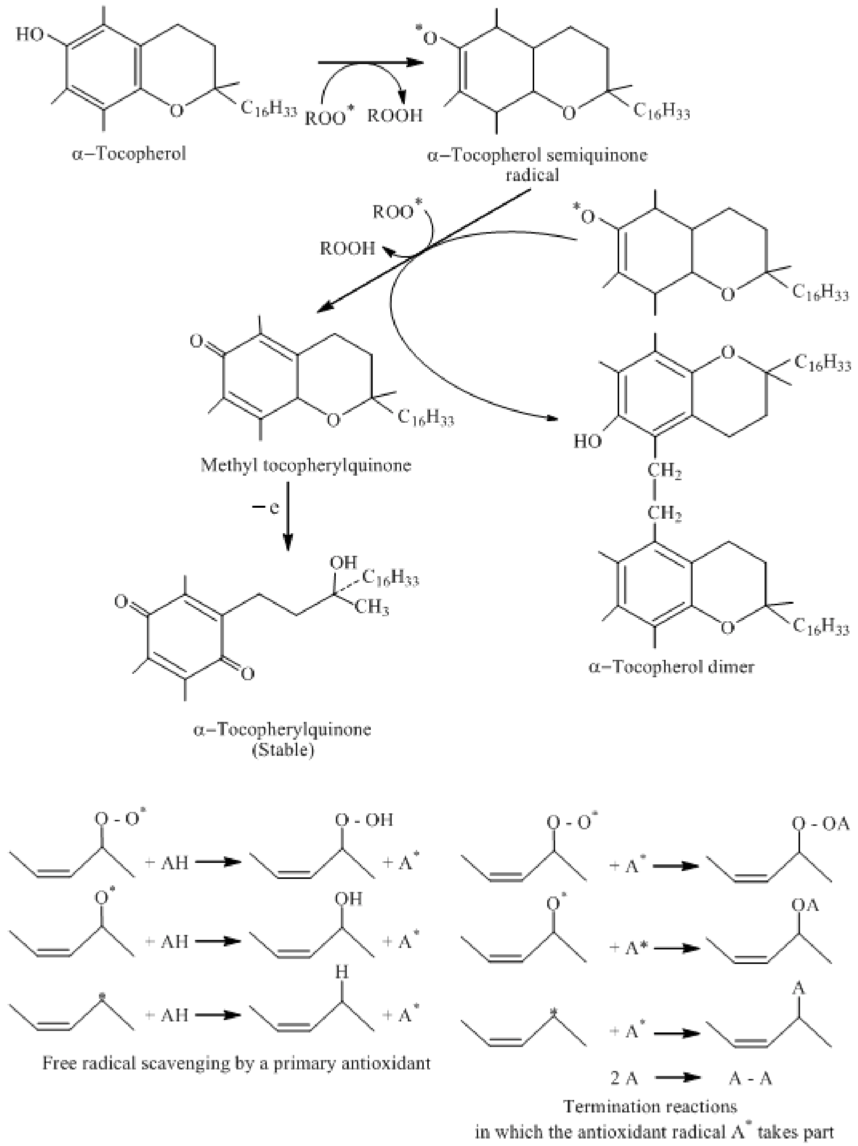

Fig.10. The mechanism of action of α-tocopherol [44] and primary antioxidants [45] existing in appreciable quantities in the oil extracted from *Vitis vinifera*

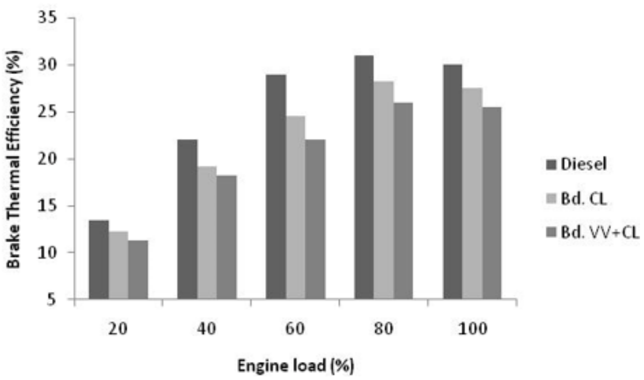

Fig. 11. Variation in brake thermal efficiency with load

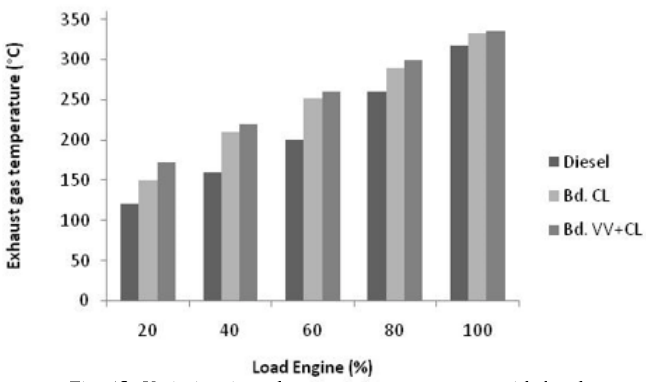

Fig. 13. Variation in exhaust gas temperature with load

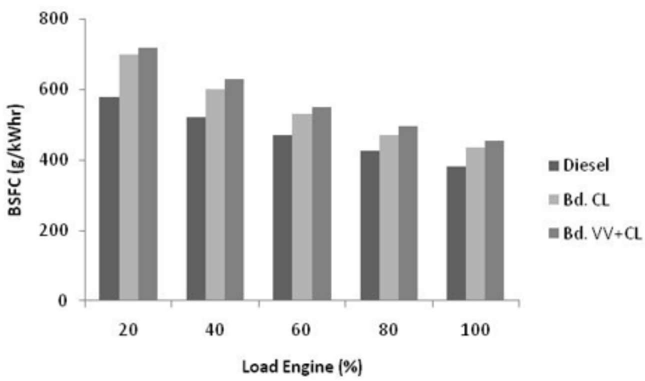

Fig. 12. Variation in brake specific fuel consumption with load

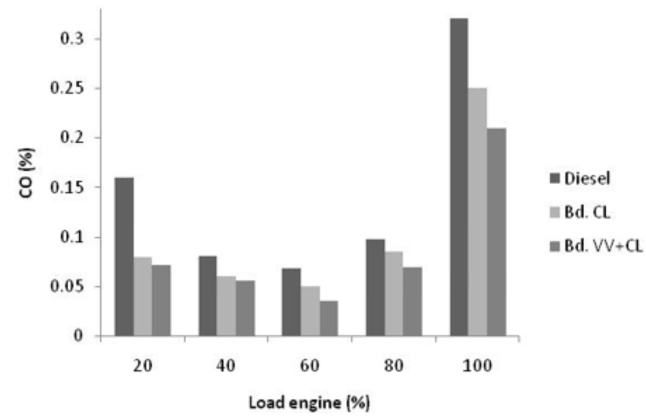

Fig.14. Variation in CO emission with load

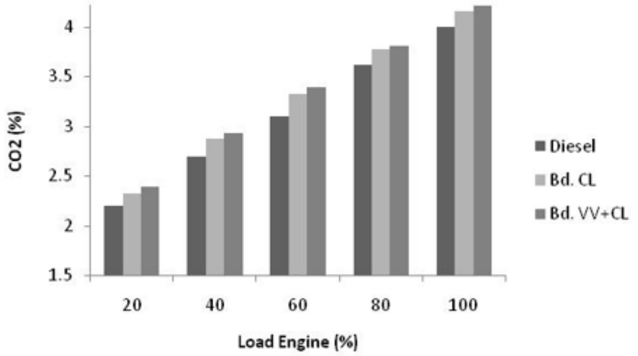

Fig.15. Variation in CO_2 emission with load

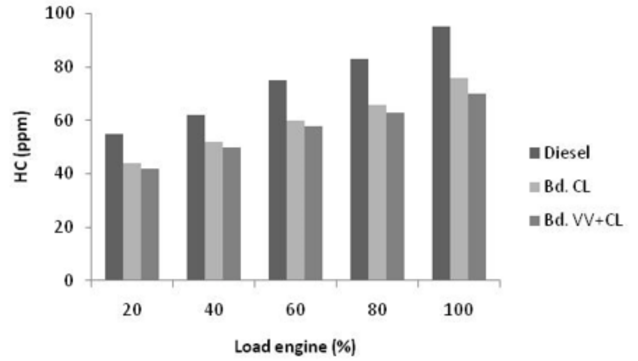

Fig.16. Variation in HC emission with load

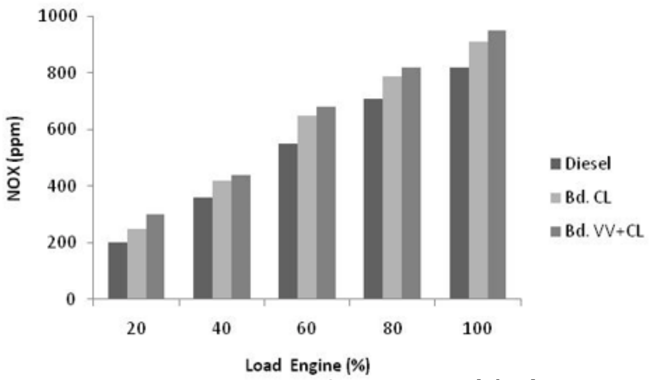

Fig.17. Variation in NOx emission with load

biodiesel samples. Figure 15 shows the variation of carbon dioxide (CO_2) emissions with engine load. CO_2 is an indicator of the complete combustion and in general of the fuel efficiency inside the combustion chamber. Biodiesel present CO_2 emission higher than diesel fuel due to the higher oxygen content. The completeness of the combustion affects the unburned hydrocarbon (HC) emissions (fig.16). The emission of HC decreases for biodiesel due to the higher cetane number and oxygen content. Figure 17 shows the variation of Nitrogen Oxide (NO_x) emissions with engine load. The rise of NO_x content in the case of neat biodiesel is mainly due to the increased temperature in the combustion chamber and the complete combustion process.

Conclusions

The oxidation stability of biodiesel is one of the most important issues that affect the biodiesel usage and performances in compression ignition engines. The oxidation cannot be entirely prevented but can be significantly slowed down by using antioxidants which are chemicals that inhibit the process. The high content of antioxidant substances contained in the oil extracted from Vitis vinifera is indicated for use in blending with other low antioxidant oils to produce a high-stability biodiesel. Biodiesel tests in the engine show a reduction in Brake Thermal Efficiency comparative with diesel fuel. Emissions are lower than diesel fuel with the exception of NO_x which present a slight increase due to the complete combustions that take place in the combustion chamber increasing the temperature.

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