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Research Article

Biodiesel Production from Raw Tunisian Castor Oil and Its Application as Alternative Fuel

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Abstract

Commercialized biodiesel has been intensively produced from edible-grade sources, thus raising some critical environmental concerns. Aiming at the latter's reduction, alternative oilseeds, as biodiesel feed stocks, are being considered. Castor (*Ricinus communis* L.) is deemed to be one of the most promising non-edible oil crops. Nevertheless, and to the best of our knowledge, a few research works pertaining to its fuel-related properties in its pure form or as a blend with petro diesel, have been undertaken, mainly due to its extremely high content of Ricinoleic acid. In this study, Tunisian castor oil was characterized then converted into methyl esters Ca ME and ethyl esters Ca EE. The high transesterification yield was obtained with ethanol, in the presence of H_2SO_4 as catalyst. The specifications in ASTM D6751 and EN 14214 of pure Ca EE and its blend with petro diesel in a different volume ratio were investigated. Despite the various benefits of biodiesel and its blend with petro diesel, the density, viscosity and distillation temperature still remain the main obstacle of their application as Fuel. Only B10 and, in the first time B20, can meet all the specifications.

Keywords: Biodiesel; Castor oil; Fuel properties; Petro diesel; Ricinoleic acid

Introduction

In order to lessen the dependence of fossil fuels, renewable biofuels are receiving growing attention. In fact, biodiesel is an alternative diesel fuel derived from vegetable oils or animal fats [1], whose main components are triglycerides, also identified as esters of fatty acids attached to a glycerol. Generally, these triglycerides consist of many fatty acids that have physically and chemically different properties. Actually, the composition of these fatty acids will be the most important parameters influencing the corresponding properties of vegetable oils and animal fats [2], whose direct use as inflammable fuel is not appropriate because of their high kinematic viscosity and low volatility. Furthermore, its long-term use has been proven to pose serious problems such as deposition, ring sticking and injector chocking in engine [3]. Therefore, to reduce the oils viscosity, vegetable oils and animal fats have to be exposed to chemical reactions, as transesterification, in which triglycerides are converted into Fatty Acid Methyl Ester (FAME), in the presence of short chain alcohol such as methanol or ethanol, and a catalyst such as alkali or acid, with glycerol as a byproduct [1].

The worldwide biodiesel production had risen from 0.8 to nearly 4 h m^3 from 2001 to 2007. Actually, edible-grade vegetable oils particularly rapeseed, sunflower and soy are presently the main biodiesel feed stocks. Since commercialized biodiesel has been intensively produced some critical environmental concerns have risen. Indeed, its large-scale production may lead to disequilibrium in the worldwide food market by the dramatic increase of the consumption oil prices, which mainly affects developing countries. The rivalry for land with food crops and especially land availability are also considered as the fundamental restraints [5]. Unconventional oilseeds are being studied as alternative feed stocks so as to diminish these environmental impacts. Castor (*Ricinus communis* L.) is a significant non-edible oil crop, deemed as crucial industrial

raw material. Although absent from the oil itself, the toxic protein ricin found in castor's seeds are poisonous to humans and animals [6]. Castor is cultivated on 12 600 km^2 around the world, with an annual seed production of 1.14 Mt and an average seed yield of 902 kg ha^{-1} [7]. It is available at low prices and the plant is recognized to tolerate various weather conditions. In addition, castor can be grown on peripheral lands that are commonly inappropriate for food crops. Therefore, all castors' features make it a promising alternative of biodiesel feedstock. In the northeast of Brazil, castor oil has been identified as a considerable potential source of raw material for the local production of biodiesel [8].

Castor oil is made up almost exclusively (ca. 90%) of triglycerides of Ricinoleic acid (12-hydroxy-cis-octadec-9-enoic acid) in which several unique chemical and physical properties were imparted by the presence of a hydroxyl group at C-12. Hence, castor oil and its derivatives are totally soluble in alcohols and display viscosities that are up to 7-fold higher than those of other vegetable oils [9]. These properties are deployed in several industrial applications of castor oil, namely the production of coatings, plastics and cosmetics. The elevated level of this hydroxylated fatty acid conveys distinctive properties to the oil and biodiesel produced from it. The use of Biodiesel can be in its pure (B100) or blended form at any level with petro diesel to produce a blend. Blends are denoted as "BXX", where "XX" designates the biodiesel fraction (i.e., B20 is 20% biodiesel and 80% petro diesel). To guarantee good vehicle performance, official standards were set up. ASTM D6751 (American Society for Testing and Materials) is a prevalent international standard of pure biodiesel (B100) [10]. Practically, more common BXX blends have been legislated in Europe and US. This work reports a systematic and comparative study of the transesterification of Tunisian castor oil with ethanol and methanol as transesterification agents in the presence of various conventional catalysts. Before biodiesel conversion, some foremost properties of Tunisian castor oil were identified and compared to Rapeseed oil. The specifications related to the FA composition of pure Ca EE (B100) and its blend with petro diesel in a 10, 20, 40, 60 and 80% vol ratio (B10-B80) were investigated according to ASTM D6751 in the United States and EN 14214 in Europe [10, 11].

Materials and Methods

Reagents

Castor seeds were obtained from a Tunisian company. Seeds were oven dried at 70°C for 72 h before oil extraction to get rid of excess moisture. With an industrial extruder, castor oil was extracted by cold-pressing castor seeds. The crude oil was filtered with a plate filter press (three plates, final pore size 0.5 mm). All the other chemical reagents used in this study were of analytical grade. Sodium hydroxide pellets (97%), sulfuric acid (purity 99%), methanol and absolute ethanol were purchased from Prolabo (France).

Characterization of castor oil

The determination of the fatty acids composition was carried out by the use of capillary column gas chromatography. The methyl esters were prepared according to a standard protocol: vigorous shaking of the solution of oil in n/heptane (0.1 g in 2 mL) with 0.2 mL of 2 N Methanolic potassium hydroxide [12,13]. Prior to analysis, it was necessary to introduce a silanization reagent to block the hydroxyl group of Ricinoleic acid, the major component of castor oil. The gas chromatographic analysis of Ca ME was performed on an Auto System Gas chromatograph equipped with capillary injection system operating at 250°C, with a split ratio of 100:1 and sample size of 1 μL. The capillary Agilent CP-Sil88 column (cyanopropyl polysiloxane), with 50 m in length, 0.25 mm in internal diameter and 0.2 µm in film thickness, was employed. Besides, the column temperature program was the initial temperatures of 60°C (1 min), 15°C/min to 180°C, 7°C/min to 340°C. The detection system was equipped with a Flame Ionization Detector (FID) operating at 350°C. The carrier gas was high-purity hydrogen.

Biodiesel production

Biodiesel was prepared in glass rector submerged on a thermostatic bath, capable of maintaining the required temperature and equipped with a reflux condenser and a magnetic stirrer. The oil was heated at 100°C to remove the residual water, cooled to the reaction temperature, weighed and then added to the reactor. The reaction started when alcohol pre-mixed with the catalyst was added to the reactor. The reaction mixture containing methanol or ethanol, castor oil with a molar ratio 6:1, and KOH or H_2SO_4 as catalyst (1% w/w based on the raw material weight), was refluxed at the boiling point of the respective alcohol for an appropriate time. Towards the end of the reaction, the products were left to settle in a separatory pipe overnight for the separation between biodiesel and glycerol. After separation, the excess of methanol was recovered from using an oven working at a temperature around 100°C. The purification of biodiesel was achieved by washing to get rid of residual catalyst and after drying to obtain the final product. Gas chromatography was used to determine the biodiesel yield which expressed in terms of weight percentage of FAEEs or FAMEs formed. The mixture was dried before the chromatographic characterization in the presence of $MgSO_4$ and centrifuged.

Pure and blended biodiesel quality evaluation

Concerning the density measurements, they were taken according to EN ISO 3675 / ISO 12185 / EN12185, and the value found at 15°C was converted using the density table ASTM 1250. As for the kinematic viscosity KV, it was determined at 40°C in accordance with EN ISO 3104 / EN 1410, using a Model M-1 Viscometer (Cannon, USA). The viscometer was maintained in a bath at 40°C. The kinematic viscosity is determined by the flow time

multiplied by the capillary constant. With respect to the flashpoint, it was identified according to EN ISO 2719 / EN ISO 3679. At the time of the first distinctive sparkle, the temperature was recorded as being the flashpoint. The distillation characteristics were evaluated by vacuum distillation unit and semi automated distillation apparatus according to ASTM D86.

The cetane number CN is about the determination of the temperatures corresponding to each of these percentages: 0%, 10%, 50%, 80%, 95%, and 100% with 0.5°C precision. CN was determined according to EN ISO 5165; it was calculated from the distillation temperatures according to the following formula:

$IC = 45.2 + 0.00892\ T10N + (0.131 + 0.901\ B)\ T50N + (0.0523 - 0.42B)\ T90N + 0.00049\ (T^2 10N - T^2 90N) + 107\ B + 60\ B^2$

Sulfur content was determined according to ASTM D4294 by fluorescence Px.

Results and Discussion

Characterization of Tunisian Castor oil

As shown in Table 1, the fatty acid profile of Tunisian castor oil was similar to the Brazilian one. In fact, it is clear that the Ricinoleic acid is the major compound with a percentage higher than 88% in both oils.

Fatty acid	Brazilian castor oil	Tunisian castor oil
Palmitic $C_{16:0}$	1.4	1.15
Stearic $C_{18:0}$	0.9	0.97
Oleic $C_{18:1}$	3.5	3.08
Linoleic $C_{18:2}$	4.9	3.85
Linolenic $C_{18:3}$	0.3	0.45
Ricinoleic $C_{18:1\ –OH}$	88.9	88.85
Dihydroxystearic $C_{18:0\ –2(OH)}$	-	0.65

Table 1: Fatty acid profile of Brazilian and Tunisian castor oils.

The oleic and linoleic acids are the other significant compounds, although present in much smaller quantities of approximately 3 and 4%, respectively. The other compounds representing a very small minority are palmitic, stearic and linoleic, each of which is less than 1%. Rapeseed oil which was chosen as reference in this work was frequently used in the biodiesel production [13-17]. Like all other vegetable oils, castor oil has different physical -properties. The principal properties of castor oil were identified and compared to Rapeseed oil properties (Table 2). Both oils displayed low acid values, rendering any acid pre-treatment that is unnecessary for conversion into the methyl esters. As shown in Table 2.

Oil	Acid index (mg KOH/g)	Iodine index (g I-/100 g)	Density (Kg/m^3) (15°C)	Viscosity (mm^2/s) 40°C
Castor	1	89	965	256.7
Rapeseed	0.6	110	920	44.9

Table 2: Properties of castor and rapeseed oils.

Castor oil has the smallest iodine value, indicating less unsaturated chains, and consequently a good oxidative stability. The hydroxyl group in the Ricinoleic acid causes strong intermolecular interactions by hydrogen bonds, which increases the density and, especially, the kinematic viscosity which was 6-fold higher than that of rapeseed oil. This property leads to difficulties in pumping and drainage through filters and pipes. Furthermore, its long-term use posed serious problems such as deposition, ring sticking and injector chocking in engine [3]. To circumvent this problem, a transesterification reaction should be preceding [18].

Transesterification of castor oil

The quantification of biodiesel were conducted after the separation and purification steps in terms of the yield in CaME or CaEE, obtained by the Trans Esterfication of castor oil with methanol and ethanol, respectively, in the presence of KOH and H_2SO_4 as conventional catalysts (Figure 1). The methanolysis of castor oil is effectively catalyzed by an acid with a very good yield similar to that obtained by basic catalyst, as clearly shown in Figure 1.

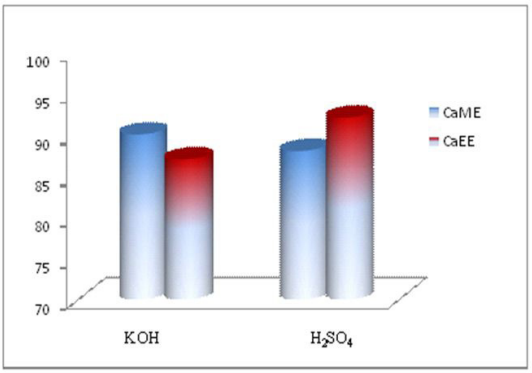

Figure 1: Yield of CaME and CaEE by acid and basic catalysts.

Moreover, the performance of the acid catalyst is better than the basic one in the case of Ethanolysis. It is stated that the acid catalyzed transesterification reaction continues at rates that are ca. 4000 times slower than the equivalent base-catalyzed reactions and so have not been considered commercially practical. Such conclusions, however, are associated with conventional vegetable oils having heterogeneous triglycerides, without or with a very

low content of derivatives of hydroxyl fatty acid, which are clearly not applicable with castor oil as the substrate. A significant feature should be taken into consideration in the acid or basic catalytic castor oil transesterification. In fact, in both conditions, the reaction takes place in a homogeneous phase due to the high solubility of the reagents in the castor oil, which is not observed with other typical vegetable oils. In addition, in basic condition, it has been perceived that there are some disadvantages that do not occur in the acid one. Firstly, a part of the used catalyst may neutralise the free fatty acids present in the castor oil hence decreasing the formation of ethoxides and producing soaps within the reaction medium. The formation of soaps would reduce the mass transfer during the reaction and exacerbate the problem of phase separation [19]. Secondly, the hydroxyl group at C-12 of Ricinoleic acid may be converted, into an alkoxide, in basic medium. The production of this anionic species may compete with the ethoxides species formation; thus, reducing the ester yields [20]. In the present study, the best reaction to produce biodiesel from raw Tunisian castor oil was by the use of ethanol and H_2SO_4 as catalyst.

Characterization of biodiesel

The various parameters specified in ASTM D6751 and EN14214 can be divided into processes and oil/petro diesel-related parameters. Concerning the former, it can be controlled by altering the conditions of the reaction, including sediment and water, carbon residue sulfated ash, glycerin content, copper strip corrosion and metals content. As for the category of oil/petro diesel-related parameters, which is the focus of this study, it encompasses parameters that are essentially dependent on the composition of the chosen oil Fatty Acid (FA) or quality of the petro diesel fuel, including Kinematic Viscosity (KV), Cetane Number (CN), Density and Distillation Temperature (DT). Several other parameters also depend on the quality of the oil, though not directly linked to the FA composition, including flash point, acid number and sulfur content. Some interesting properties of the castor oil and the produced biodiesel in optimum condition were measured by ASTM or standard EN methods then recapitulated in (Table 3).

	CaEE	Castor oil	Standard EN14214	ASTM D6751
Density(Kg/m3) 15°C	930	965	860-900	-
Viscosity (mm^2/s) 40°C	16.9	256.7	3.5-5.0	1.9-6.0
Flashpoint (°C)	109	270	>101	>130
Cetane number	56.23	30	>51.0	>47
Sulfur content (%)	0.0416	-	-	-

Table 3: Fuel properties of castor oil and CaEE with comparison to biodiesel standards.

Density

Density is specified in EN 14214 with a range of 860-900 kg/m3 at 15°C. Neither castor oil nor ethyl esters meets this specification, although CaEE is closer to the prescribed maximum value. Values similar to those in Table 3 have been reported in the literature for CaEE such as 924.4 kg/m3 [21] This may be explained by the fact that the hydroxyl group of Ricinoleic acid causes a strong intermolecular interaction by the presence of hydrogen bonding which increases the density of the castor oil [22].

Kinematic viscosity

The viscosity affects the atomization of fuel during injection into combustion chamber, as well as the formation of engine deposits. In general, viscosity increases with the number of CH2 groups in FAEE's chain and decreases with the increase in the number of oil instauration [23]. Reducing the kinematic viscosity is the main reason for the transesterification of oils. The results show that the viscosity of CaEE is less than the initial oil .

However, these values are far from the norm EN 14214 or ASTM D6751. Only the mixture of these esters with petroleum diesel would be possible. The obtained KV value is close to that of methyl Ricinoleate (15.44mm2/s) [24]. This high viscosity may be due to the intermolecular hydrogen bonding of molecules methyl Ricinoleate.

Flash point

The flash point is a security criteria imposed by norms to prevent the risk of flammability of enormous quantities of biofuels during storage. This is the temperature at which the vapors burn spontaneously in the presence of a flame. The obtained results have shown that the flash point is high compared with that of diesel set by ASTM between 55-120°C, thus giving the biodiesel a greater security handling. This increase is explained by the high molecular weight of the castor oil [25]. These values directly affect the diesel engine i.e., the higher the point is, the slower the inflammation completion is. During the flash point's determination, false sparks were obtained when the temperature is equal to that of the boiling ethanol. This is due to residual alcohol. Indeed, after the separation of the glycerol and biodiesel, excess alcohol is removed by evaporation using rotary vap. This is not sufficient to remove all alcohol because Ricinoleate oil retains most of the alcohol due to its bonding with the methyl Ricinoleate by the hydrogen bonds [23]. The alcohol residue drops the temperature to 107°C compared to 165°C for the rapeseed oil [26].

Distillation

This property enables the measurement of temperature range in which fuel is volatilized. Distillation proceeds to separating the constituents of a homogeneous mixture under the heat effect. The substances vaporize successively, and the resulting vapor is lique-

fied to give distillate. DT determines the distillation curve of a fuel and specifies the maximum temperature of distillation for 90% of its components. To the best of our knowledge, the distillation temperature has not been of much interest to researchers. In fact, the reason behind this is probably linked to the fact that this test specification is excluded from the European standard (EN 14214), and necessitates costly specialized equipment. Besides, the initial distillation temperature of biodiesel is considerably more elevated than that of petro diesel. For instance, while the DT limits of rapeseed biodiesel are 299-346°C, those of petro diesel are 177.8-345-°C [27]. The biodiesel fuel evaporation temperature is dependent on the length of chain of the fatty acid ester carbon and has practically no dependence on the saturation degree.

Figure 2 shows the distillation curve of biodiesel using the ASTM D86 method. As expected, the high content of Ricinoleic acid (which has the same number of carbons as oleic and linoleic acids) leads to very high distillation temperature (398°C), thus not meeting the standard limit. This can significantly affect the degree of formation solid deposits of combustion.

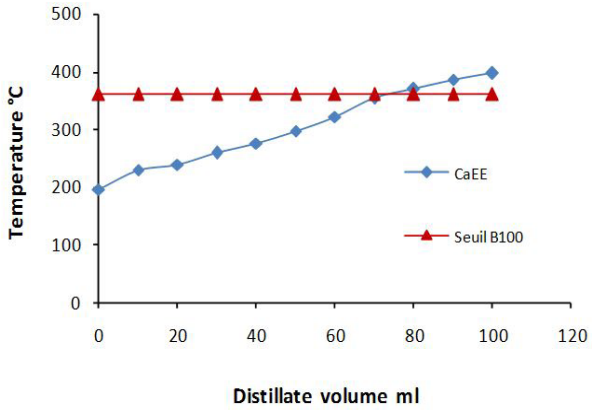

Figure 2: Distillation curve of Biodiesel.

Cetane number

Cetane number is a dimensionless descriptor of biodiesel explosion quality, which affected by the chain length and that of branching and unsaturation. The decrease of these variables leads to the decrease of the cetane number. The latter is a measure of the biodiesel's ignition delay, with higher CNs, mentioning less time between the initiation of ignition and fuel injection [28]. The good performance of the engine and the reduction of NOx emissions are related to high cetane number values [29]. Compared to diesel fuels, biodiesels hold higher cetane number. Despite the importance of CN as a critical parameter for evaluating the fuel quality, this fact is not mentioned in the literature. For instance, Know the [30] measured the CN of pure methyl Ricinoleate (37.38), and Cvengros et al [21] used an extrapolation for CaME (43.9) as well as (43.8) for castor ethyl esters. Though the CN of CAEE (52.23) is low, it was found in this study that it is somewhat above the lower limit of the standard and this is probably caused by the branching of the hydroxyl group in Ricinoleic acid [31].

Sulfur content

Because of firm environmental restrictions, sulfur content in petro diesel has been considerably declined during the past few years. As a consequence, the reduced fuel lubricity can be detrimental to the engine [32]. In this study, the sulfur content of CaEE determined by referring to the standard ASTM D4294, which is still in norms. This low value is one of biodiesel advantages compared to diesel, indicating the reduction of gas emissions and pollution.

The prevailing levels of Ricinoleic acid (89.15%, Table 1) primarily affected the physical properties of CaEE discussed above. The most harmful impact, based on intermolecular interactions imparted by the hydroxyl moiety, was found on KV and DT, which surpassed, the international standard limits. Such parameters are directly detected by the choice of feedstock for biodiesel production, because no KV and DT improvers are found. To increase the range of feed stocks for the biodiesel industry there exist two probable solutions. The first one would involve the reduction of the Ricinoleic acid content in castor seeds by means of genetic engineering or breeding selection programs. Indeed, although Rojas-Barros et al. [33] have already discovered such a mutant with 71.4% Ricinoleic acid, his program takes time to materialize entirely. The second solution, most interesting, involves blending CaEE in petro diesel. In this context, the performance of a diesel engine fueled with different CaEE blends (B0-B80) were examined according to the European standard.

Characterization of Blend biodiesel / diesel

Although it is out of the standard norm, biodiesel is usually mixed with petroleum diesel (petro diesel). Blends are denoted as "BXX", where "XX" represents the biodiesel fraction for example: B20 is 20% biodiesel and 80% petro diesel, while a B100 is a pure biodiesel. Several types of blend are marketed; the most common of which are B2, B5, B20 and B100. The intermolecular hydrogen bonding of alkyl Ricinoleate molecules is the major obstacle for the pure use of B100 as engines fuel, the dissolution of biodiesel in petroleum diesel minimizes intramolecular interactions responsible for this property. (Figure 3) shows the distillation curves for B10, B20, B40, B60 and B80. It is clear that only B10 and B20 were found to very closely meet the maximum temperature limit for 90% distillation.

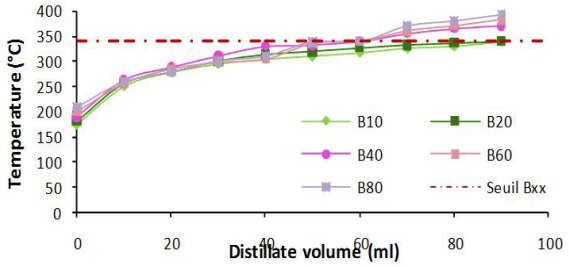

Figure 3: The distillation curves for B10, B20, B40, B60 and B80.

While other blends B40, B60 and B80 like B100 (Figure 2) exceed the standard limit. To complete this study, it is interesting to examine the other fuel properties. In this context, (Table 4) summarizes the values found on the density, viscosity, flash point, cetane number and sulfur content from petro diesel, blends up to pure biodiesel. As shown in (Table 4), there are some advantages for biodiesel and its blends to the petro diesel.

	CaEE / diesel (volume %)							EN 590
	0/100	10/90	20/80	40/60	60/40	80/20	100/0	
Density (Kg/m²) 15°C	823	834	841	855	862	897	926	820-845
Viscosity (mm²/s) 40°C	2.35	2.8	3.27	4.7	5.29	8.67	12.14	2.00- 4.5
Flash point (°C)	62	69	72	80	89	96	105	>55
Cetane Number	45	58.66	60.1	60.7	61.91	62.51	63.82	>51
Sulfur content (%)	0.2	0.144	0.0834	0.0616	0.0534	0.0434	0.0334	-

Table 4: Propriety of blend Biodiesel/Diesel.

The sulfur content of biodiesel and its blends are very low; it is insignificant compared to diesel. Moreover, the high flash point of biodiesel and its blends compared with that of diesel give the biodiesel greater security handling. Another important advantage of B100 or blends compared to petro diesel is the higher cetane number. A high index leads to complete fuel combustion, which is correlated with a lower gas emission. In spite of the various benefits of biodiesel and its blends with petro diesel, the density and viscosity still remains the main obstacle of their application as Fuel. Indeed, the density and viscosity of the blends biodiesel/diesel to about 20% by volume is within the limits of standard.

Although we cannot exceed B20 to stay within the limits required by the standard, the results are found to be very interesting. It is important to note that, to the best of our knowledge, this is the first time we obtain a blend with 20% biodiesel. In fact, a new research inspected the performance of a diesel engine fuelled with various CaME blends (B0-B20) and resolved that B10 develops better power than diesel [34].

Conclusion

The search for alternative feed stocks for biodiesel as a partial replacement for petro diesel has recently extended to castor oil. The castor oil ethyl esters were prepared with high yield using H_2SO_4 as acid catalyst. The complexity and chemical diversity of biodiesel (mixed esters) requires that it should be certified according to several quality criteria (ASTMD6751 in North America or Europe EN 14214) before being marketed. The high values of KV and DT due to the intermolecular hydrogen bonding of molecules methyl Ricinoleate limit the direct application of pure Biodiesel. Only the mixture of these esters with petroleum diesel would be possible. The performance of a diesel engine fueled with different CaEE blends (B10-B80) show that B20 is the best one that can respect all standard limits.

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