23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

PHYSICAL-CHEMICAL PROPRIETIES OF SOYBEAN AND SUNFLOWER BIODIESEL

Givan Martins Macedo Junior
Higor Henrique Tavares Silva
Julio Cesar C. Campos
Álvaro M. Bigonha Tibiriça
Henrique M. P. Rosa
Universidade Federal de Viçosa- Departamento de Engenharia de produção e Mecânica. Rua PH Rolfs s/n
givan.junior@ufv.br
higor.silva@ufv.br
julio.campos@ufv.br
alvaro.tibirica@ufv.br

Jane Selia dos Reis Coimbra
Raquel Moreira Maduro de Carvalho
Universidade Federal de Viçosa- Departamento de Tecnologia de Alimentos . Rua PH Rolfs s/n
jcoimbra@ufv.br
raquelmaduro@gmail.com

Abstract. *The objective of this work was to produce soybean and sunflower biodiesel in laboratory using a transesterification reaction and analyze the biodiesel quality parameters for its use in compression ignition engines. Environmental benefits achieved by using biofuels to drive machines has been increased their contribution in energetic matrixes. Biodiesel is a fuel composed by mono-alkyl ester of long chain fatty acids derivative from vegetable oil or animal fat. Similarities between physical-chemical characteristics of diesel and biodiesel make their mixture feasible. The physical-chemical properties of biodiesel measured in the present work were density, viscosity, cetane number, pour point, cloud point, and flash point. Such properties were within the limits established by Brazilian National Agency of Petroleum, Natural Gas and Biofuels. The produced biodiesel presented behavior similar to diesel proving its viability of use. Therefore, such detailed study allows us to compare some properties of soybean and sunflower biodiesel with petroleum diesel. This study is fundamental to the performance review of a compression ignition engine.*

Keywords**:** *biofuels, compression ignition engines, transesterification reaction*

1. INTRODUCTION

Most of all energy consumed in the world comes from oil, coal, and natural gas. These sources are limited and have estimated exhaustion time. Therefore, the search for alternative energy sources is important (Shuchrdt et al., 1998).

The industrial development associated with the increase in both vehicle numbers and global population has been increased the world energetic demand. Mineral oil remains as one of the most used source of energy. According to Empresa de Pesquisa Energética (EPE) oil supports 39.3% of Brazilian demand of energy. However, mineral oil is a non-renewable energetic source and emits high level of pollutants compounds.

The search for renewable fuels able to reduce or even replace petroleum-based fuels has been carried out worldwide. Brazil is a pioneer in biodiesel production being ranked as the biggest producer in the world (representing 22% of the world production).Several crops are used for its production, such as highlighting soybean, sunflower, palm oil, castor bean, and coconut among others(Bergmann et al., 2013).

The use of vegetable oil as fuel in diesel engines is considered inappropriate, since it presents a series of limitations due to its degradability, high viscosity, incomplete combustion, and low volatility. Such negative characteristics promote fouling formation in fuel injection pumps of the engines. The transesterification of vegetable oils is currently one of the most used method to produce biodiesel because the physical characteristics of fatty acid esters are very similar to diesel and thus does not requires change in the engines to work well (Ramadhas et al, 2003 and Carlos, 2014). In addition, the biodiesel is non-toxic, biodegradable, and reduces the emissions of most pollutant gases; however a problem of the biodiesel combustion is the increase of NOx emission (Can,2014). A study of gas emissions using fish oil biodiesel mixed with mineral diesel as fuel reveled an increase in NOx emissions with an increase of biodiesel percentage in fuel blends. Emissions of NOx also increased with the increment of engine loads (Varuvel et al., 2012).

Besides the increase in NOx emissions, other problems can also follow the use of biodiesel in diesel engines, such as low oxidation stability and higher viscosity causing cold flow problems. The biodiesel stability depends on its fatty

acid chains; feedstock with larger proportion of saturated fatty acids will be more stable than those having larger proportion of unsaturated fatty acids. On the other hand, higher content of saturated fatty acid reduces the low temperature properties such as cloud and pour points, thus there is an adjustment between the level of saturation of biodiesel and its cold flow properties (Sharma et al., 2008). However, such problems can be avoided appending additives in the fuel. Curcumin was used as an antioxidant for soybean biodiesel stored for 180 days. At the experiment end, biodiesel presented high efficiency and slow oxidation period, which is important since long fuel storage periods can affect biodiesel stability (Sousa et al. 2014).

Restrictions due to the use of biodiesel in engines tend to be overcome since investigations in renewable fuel area has been growing because sustainability ideas spreads fast in society, which reinforces the necessity of studies with biodiesel and its physical-chemical characterization.

This work aims to contribute to the research and study of biodiesel proprieties through the production of soybean and sunflower biodiesel in laboratory by using the transesterification method, and comparing the physical-chemical proprieties of these biodiesels with the petroleum diesel. Thus it can be noticed which proprieties are already satisfactory for the use of these fuels in diesel engines and which proprieties still need improvement.

2. METHODOLOGY

Samples of S10 diesel, soybean, and sunflower oils were selected, and the transesterification method was used for the soybean and sunflower oils to obtain correspondent biodiesels. The physical-chemical properties of S10 diesel and biodiesel were determined according to the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) methodology.

Figure 1 shows the biodiesel that was produced in laboratory, using potassium hydroxide (KOH) as catalyst and methanol anhydrous as transesterification agent. In the process, KOH(1% in relation to the oil mass) and methanol anhydrous (6:1 molar ratio) were mixed until dissolution, and then the oil was slowly added. The mixture of oil, methanol and KOH was kept under agitation for about 60 minutes at room temperature. After agitation the mixture was maintained under rest to phase splitting, the lower phase was glycerin and the upper phase was biodiesel. The process was similar for both soybean and sunflower oils.

Figure1.Biodiesel top phase and glycerin bottom phase (Carlos, 2014).

Figure 2 shows purified biodiesel after washing with citric acid solution (0.5% of oil mass), which was prepared by heating, at 90 ºC, a volume of water similar to the volume of biodiesel to be washed. The acid is added when water reaches 90 ºC. The acid solution was mixed with biodiesel and the mixture was put to rest for 5 minutes. During this process two phases were formed, the top phase (water +methanol) and the upper phase (biodiesel). After sequent washing steeps the water pH reaches initial pH of distilled water. Next, the biodiesel was transferred into a flask containing anhydrous sodium sulfate (1g/100 mL of oil used initially) aiming drying the sample and preventing contamination by water. The mixture was filtrated. Finally, the biodiesel was filtered under vacuum at 80°C.

Figure2. Biodiesel after acid washing (Carlos, 2014).

3. RESULTS AND DISCUSSION

The conversion rate of neutral soybean and sunflower oils in ethyl esters depends on the way that transesterification reaction is conducted as well as the process conditions. Thus, the transesterification reaction is influenced by several factors including the type of catalyst (acid or alkali), molar ratio alcohol/vegetable oil, temperature, purity of reagents (especially water content), and content of free fatty acids. In this research, alkaline catalysis was adopted due to its better performance, high selectivity, and to avoid problems with corrosion of engine components, which can occur in the presence of traces of acid (Encinar et al. 2002).

An automatic vacuum distiller HDV 632 was used in distillation test that consists of vaporization a standard volume of S10 diesel and biodiesel following along with the condensation of vapors in a way that it is possible to continually measure the boiling point and the distilled volume. So, the HDV 632 was used to determine the distillation characteristics of the S10 diesel and of both soybean and sunflower biodiesel. Distillations were carried out with pressures of 133.2 Pa for the biodiesel and 1333.2 Pa for diesel.

Table 1presents results of boiling points for distillation tests at atmospheric pressure, where AET is the boiling temperature corrected to atmospheric pressure. Boiling points are given at10%, 50% and 90% of recovered volumes of S10 diesel, soybean and sunflower biodiesels.

Table 1 reveals that the boiling point of 90% samples of recovered volume was not obtained for biodiesels. Biodiesels are long chain esters with a high content of instaurations due to the double bonds in carbon chains. Thus, distillation could occur only up to 50% in this work.

Table 1. Distillation test data.

AET	**Diesel** (°C)	**Soybean biodiesel** (°C)	**Sunflower biodiesel** (°C)
T (10 %)	240.1	359.2	361.5
T (50 %)	263.9	364.7	354.8
T (90 %)	416.4	-	-

Figure 3 represents the distillation test curve for S10 diesel (recovered volume from 10 to 90%), soybean, and sunflower biodiesel (recovered volume of 10 and 50 %). Distillation temperatures varied from 200°C to 400°C for S10 diesel and from 350°C to 360°C for biodiesel. It can be observed a small protuberance in S10 diesel distillation curve shape, which is probably caused by addition of 10% of biodiesel to diesel fuel. For the biodiesel a change in the distillation curve shape is not significantly evidenced.

The distillation process is important on ignition quality of diesel oil associated to soybean and sunflower biodiesels. Thus it is important to calculate the cetane number, because it has a direct influence on the engine start since its works with emissions (Brunetti,2009). Good relation between the cetane number and the cetane index are described in literature (Brunetti, 2009) (Sousa and Yamamoto, 2008). However, this work emphasizes the methodology to calculate the cetane index for the S10 diesel, soybean and sunflower biodiesel.

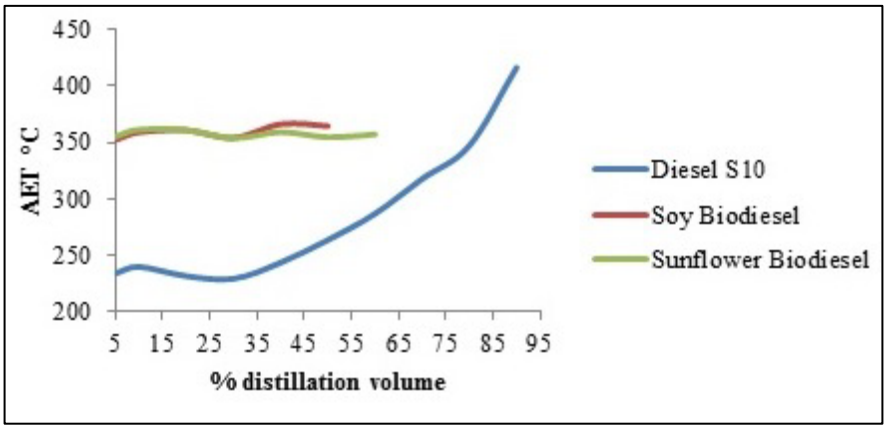

Figure 3. Distillation test curve

Calculated cetane index is connected with the ignition quality of the diesel and biodiesels. Actually, the cetane index is a mathematical correlation for the cetane number, allowing it to be estimated by calculation. This correlation reflects the cetane index influences on engine operation (Brunetti, 2009).

Thus, distillation results presented in Fig. 3 can be used to calculate the cetane index for diesel and biodiesels. Cetane index calculation is based on ATM D-4737 standard, in which four variables obtained in the distillation test at atmospheric pressure are used, as shown in Eq. 1:

$$\mathrm{CCI} = -386.26(\mathrm{D15}) + 0.1740(\mathrm{T10}) + 0.1215(\mathrm{T50}) + 0.01850(\mathrm{T90}) + 297.42 \quad (1)$$

where: CCI is the calculated cetane index; D(15) is the fuel density at 15 °C; T10, T50, and T90 are the vapor fraction temperatures when the fuel is distilled by 10%, 50% and 90% of their volumes respectively, as shown in Table 1.

Values of vapor temperature for distilled fractions of 10%, 50% e 90% were determined by ASTM D86 standard method and corrected at atmospheric pressure. The density D(15) was calculated according to ASTM D1298 standard. Table 2 presents cetane index calculated by using Eq. 1 for soybean and sunflower biodiesel. The cetane index for both biodiesel samples are similar showing that utilization of these types of biodiesel in association with diesel is technically viable.

In fact, the values shown in Table 2 are in according with ASTM D-4737 standard range. However the standard highlights the employment of Eq. 1for diesel oils with 90% of recovered values in temperatures up at382°C.It should be emphasized that the biodiesels used presented 10 % and 50 % of recovery volumes.

Table 2. Calculated cetane index for samples Eq.1 .

Sample	Calculated cetane index (CCI)
Diesel S-10	57.21
Soybean biodiesel	46.83
Sunflower biodiesel	48.74

In this context, the difference between the cetane index for S10 diesel and the biodiesel is approximately 15%, as shown in Table 2.

For the biodiesels, which distilled only up to 50% in recovered volume, the values of cetane index shown in Table 2 were not used. Therefore in this work Eq.2 was used for cetane index calculation of soybean and sunflower biodiesels, based on ASTM D 976 which uses only two variables (Souza, 2008).

.

$$\mathrm{CCI} = 454.74 - 1641.416(\mathrm{D}) + 774.74(\mathrm{D}^2) - 0.554(\mathrm{T50}) + 97.803(\log(\mathrm{T50}))^2 \quad (2)$$

where: CCI is the calculated cetane index; D is fuel relative density at 15°C according to ASTM D86,and T50 is the temperature of the vapor fraction when the fuel are 50% distilled. Table 3 presents cetane index calculated using Eq. 2. Such values are similar, which evidences the employment of these biodiesel in association with diesel.

Table 3. Calculated cetane index for biodiesel samples Eq. 2.

Sample	**Calculated Cetane Index (CCI)**
Soybean	53.88
Sunflower	55.66

In this context, the difference in cetane index between S10 diesel (Table 2) and biodiesels (Table 3) is approximately of 2.73%.By using data calculated by using Eq. 1 (more general)an error of 15% is observed. It can be noticed the cetane index was calculated here by using mathematical correlations. Somehow, this correlation can be used to obtain cetane index, a more realistic value is the cetane number measured in test engine. It is also important to evidence that the cetane index, in a general way is in the range of 40 to 60, the range observed in the present work.

Another relevant property in the study of fuels or biofuels is the flash point. In this work, flash point test was performed in the equipment FP93 5G2- Pensky-Martens flash point, operating according to ASTM D-93 standard. The results are shown in Table 4.

Table4. Experimental resultsfor flash point of samples.

Sample	**Temperature (**°C)
Sunflower biodiesel	135.6
Sunflower biodiesel-distilled fraction	142.0
Soybean biodiesel	187.0
Soybean biodiesel-distilled fraction	177.8
S10-diesel	61.8

For biodiesel the ASTM D-93 standard establishes a minimum expected value at100 °C, and of 38 °C for diesel. The S10 diesel, soybean and sunflower biodiesel samples exhibited flash point values according to the standard .In Table 4 it is evidenced values of flash point higher than 130°C for the biodiesels, which means there is no need to analyze the methanol content. The flash point does not influence the engine performance, however, it is important for the safety of handling and storage of the fuel.

Density was measured using a 10 mL pycnometer with sample at 20°C. The results are represented in Table 5. Soybean and sunflower biodiesel presented density according to the standard reference range (ASTM D-1298). The density values of biodiesels are lower than vegetable oil´s density used in transesterification and higher than S10 diesel density. Such behavior indicates that an increase of fuel injection mass in the engine can arise if biodiesel is used instead of diesel, generating more power. However, the increase in injection fuel mass can also lead to higher emissions of particulate matter, also called “black carbon”. Density of the non-distilled soybean and sunflower biodiesel are higher than the distilled fraction of both. Thus, the use of the non-distilled biodiesel will cause higher emission of particulate matter. Values of distilled biodiesel are approximate to the last value of the reference range for the S10 diesel, which is 850 kg/m^3.The ratio between biodiesel and diesel reference interval is 0.7% for sunflower biodiesel, and 1.2% for soybean biodiesel, whereas for the non-distilled fraction is 2.2% for the sunflower biodiesel and 2.5% for the soybean biodiesel. When comparing the non-distilled fraction with the distilled fraction these percentages evidenced an increase of three times for the sunflower biodiesel and two times for the soybean biodiesel.

Table5. Experimental results for density of samples.

Sample	**Density (kg/m³)**	
	Obtained value	**Reference value**
Sunflower oil	911	916-922
Sunflower biodiesel	860	850-900
Sunflower biodiesel distilled fraction	856	850-900
Sunflower biodiesel non-distilled fraction	869	850-900
Soybean oil	910	916-922
Soybean biodiesel	867	850-900
Soybean biodiesel distilled fraction	861	850-900
Soybean biodiesel non-distilled fraction	872	850-900
Diesel S10	833	820-850

Table 6 represents kinematic viscosity values of S10 diesel, soybean and sunflower biodiesel samples. Viscosity was determined by a reometer, which gives the dynamic viscosity of the samples through a Sheer Stress versus sheer rate graphic, at 40°C during 300s for each sample. The kinematic viscosity was calculated being the quotient between dynamic viscosity and density of the samples.

In Table 6 kinematic viscosity values calculated are according to the reference intervals of Associação Brasileira de Normas Técnicas (ABNT) except for the non-distilled fractions. It can be noticed in Table 6 that distilled fraction of both biodiesels show values of kinematic viscosity lowers than biodiesels without distillation. These values correspond to 15% and 16% for soybean and sunflower biodiesel, respectively. When used in compression ignition engines, high viscosity biodiesels can lead to atomization problems in fuel injection, as well as an increase in particulate matter and smoke emissions. Calculated kinematic viscosity values for the distilled biodiesels approximate to the last reference value of S10 diesel. The high values of kinematic viscosity of soybean and sunflower oils mean the presence of glycerol in these molecules.

Table 6. Kinematic viscosity of samples.

Sample	Dynamic viscosity (mPa.s)	Density at 40 °C	Kinematic viscosity (mm^2/s)	Reference values for kinematic viscosity (mm^2/s)
Diesel	2.76	833	3.31	2.0-4.5
Soybean oil	31.44	910	34.55	-
Sunflower oil	38.25	911	41.99	-
Soybean biodiesel	4.58	866	5.29	3.0-6.0
Soybean biodiesel distilled fraction	3.86	861	4.48	3.0-6.0
Soybean biodiesel non-distilled fraction	6.47	870	7.44	3.0-6.0
Sunflower biodiesel	4.55	859	5.30	3.0-6.0
Sunflower biodiesel distilled fraction	3.81	855	4.46	3.0-6.0
Sunflower biodiesel non-distilled fraction	5.86	869	6.74	3.0-6.0

Table 7 presents experimental data for samples cloud point and pour point. The tests were accomplished in the equipment HCP 852 and the properties were determined automatically according to ASTM standard. The cloud and pour point are physical properties associated to the cold flow characteristics of fuels. At cold temperatures fuels tend to partially solidify or lose their fluidity, compromising the fuel flow. The cloud point is the temperature in which liquid starts to get cloudy and it is connected to the starting of the engines in cold temperatures(Dwivediand Sharma, 2014). Both cloud and pour points vary according to the feedstock used in the biodiesel production, and with the alcohol type used in transesterification reaction. These properties are considered important with regard to the temperatures at which the fuel will be stored and used.

It is evidenced in Table 7 the cloud and pour point for the sunflower biodiesel are 13 °C and -2°C, respectively, which means that at temperatures under such values the biodiesel will get cloudy and its flow can be altered. However, in Brazil temperatures are mild from north to south, and fuel freezing is not a problem, mainly because it is intended to use biodiesel blended in diesel.

Table 1. Experimental results for the samples cloud and pour point.

Sample	Cloud point(°C)	Pur point(°C)
Diesel	8	-1
Sunflower biodiesel	13	-2
Soy biodiesel	-	-

4. CONCLUSIONS

The similarities in fluid and thermodynamics properties between diesel and biodiesel indicate these fuels are compatible, especially regarding cetane index in diesel cycle engines. Therefore, the performance and fuel consumption

of both fuels are practically equivalent. Moreover, there is no need to any modification or adaptation of the diesel engine so they can run with biodiesel. Because of this equivalence in physical-chemical properties, biodiesel and diesel are miscible, and it can be blended in any proportion. This condition is advantageous when compared with ethanol, once for biodiesel neither especial supply pumps nor different engines are required to work with different fuels or blends.

Another matter to consider is the use of a distilled biodiesel, where the physical-chemical properties are even more similar to diesel fuel. However, mathematical correlation of four variables should not be used to determine the cetane index for biodiesels.

5. ACKNOWLEDGEMENTS

The authors would like to thank FAPEMIG for the financial support and "Laboratório de Análises de Biocombustíveis" supported by Petrobrás.

6. REFERENCIAS

Bergmann J.C., Tupinambá D.D., Costa O.Y.A., Almeida J.R.M., BarretoC.C., Quirino B.F., 2013."Biodiesel production in Brazil and alternative biomass feedstocks". *Renewable and Sustainable Energy Reviews21 (2013)411–420.*

BRUNETTI, F., 2012. "Motores de combustão interna". *São Paulo: Blucher.*

Can O., 2014. "Combustion characteristics, performance and exhaust emissions of a diesel engine fueled with a waste cooking oil biodiesel mixture". *Energy Conversionand Management 87 (2014) 676–686.*

Carlos I.R.R., 2014. "Biodiesel: Produçãoe análise da prformance em motores diesel". *TCC engenharia mecânica Universidade Federal de Viçosa.*

Dwivedi G. and Sharma M.P., 2014. "Impact of cold flow properties of biodiesel on engine performance." *Renewable and Sustainable Energy Reviews 31(2014)650–656.*

Encinar, J.M., González, J.F., Rodríguez, J.J., Tejedor, A., 2002. "Biodiesel Fuels from Vegetable Oils: Transesterification of Cynara cardunculus L. Oils with Ethanol" *Energy Fuels (2002), 16, 443*.

Ramadhas, A.S., Jayraj, S., Muraleedharan, C., 2003. "Use of vegetable oils as I.C. engine fuels-A review". *Renew. Energy, v. 29, p. 727-742*

Sharma Y.C., Singh B., Upadhyay S.N., 2008."Advancements in development and characterization of biodiesel: A review". *Fuel 87 (2008) 2355–2373*

Sousa L.S., Moura C.V.R., Oliveira J.E, Moura E.M., 2014."Use of natural antioxidants in soybean biodiesel." *Fuel 134 (2014) 420–428.*

Sousa T.B. and Yamamoto C.I., 2008. "Revisão da equação de cálculo de índice de cetano para as características do diesel comercializado no paraná" *Dissertação de pós graduação Universidae Federal do Paraná, Curitiba, Brasil.*

Souza , T.B., 2008. "Revisão da equação de cálculo de índice de cetano para as características do diesel comercializado no Paraná". *Dissertação de Mestrado. Universidade Federal do Paraná, Curitiba, Brasil.*

Shuchrdt, U., Sercheli, R., Vargas, M., 1998. "Transesterification of Vegetable Oils: a Review" *J. Braz. Chem. Soc.(1998), 9, 190.*

Varuvel E.G., Mrad N., Tazerout M., Aloui F., 2012. "Experimental analysis of biofuel as an alternative fuel for diesel engines". *Applied Energy 94 (2012) 224–231*.

7. RESPONSABILITY NOTICE

The authors are the only responsible for the printed material included in this paper.