Artigo

Volumetric Property for Tankage of Biodiesel from Residual Oil

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Propriedade Volumétrica para Tancagem do Biodiesel de Óleo Residual

Resumo: A reciclagem do óleo de fritura para produção de biodiesel não só retira um composto indesejado do ambiente, mas também permite a geração de uma fonte de energia alternativa aos derivados de petróleo, renovável e menos poluente. Uma propriedade física conhecida como coeficiente de expansão volumétrica é importante para tancagem de combustíveis e é determinada para o diesel e o biodiesel de óleo residual obtido pela catálise básica homogênea. Este estudo teve como objetivo determinar este coeficiente de expansão a partir de dados experimentais da massa específica em função da temperatura de biodiesel metílico e etílico de óleo residual e compará-lo com o diesel. Todas as propriedades físico-químicas do biodiesel analisado encontram-se dentro das especificações brasileiras. O coeficiente de expansão volumétrica para o óleo diesel, biodiesel etílico e metílico são $8.36 \times 10^{-4}\,{}^{\circ}C^{-1}$, $8.37 \times 10^{-4}\,{}^{\circ}C^{-1}$ e $8.35 \times 10^{-4}\,{}^{\circ}C^{-1}$, respectivamente, sendo os valores encontrados com 95% de confiança. Os dados estatísticos mostram uma excelente correlação do modelo linear com valores experimentais. Variação no coeficiente de expansão implica em diferentes intensidades das interações intermoleculares.

Palavras-Chave: Biodiesel; óleo residual; coeficiente de expansão volumétrica.

Abstract

The recycling of frying oil for biodiesel production not only removes an undesirable compound of the environment, but it also allows the generation of an alternative energy source to petroleum derivatives, renewable and less pollutant. A physical property known as the coefficient of volumetric expansion is important to fuel tankage and is determined for diesel and biodiesel of residual oil obtained by the basic homogeneous catalysis. This study aims to determine this expansion coefficient from experimental data of specific mass as a function of temperature of methylic and ethylic biodiesel of residual oil and compare it with diesel. All physical-chemistry properties analyzed are in accordance with specification from Brazil. The coefficient of volumetric expansion for diesel oil, ethylic and methyl biodiesel are $8.36 \times 10^{-4}\,{}^{\circ}C^{-1}$, $8.37 \times 10^{-4}\,{}^{\circ}C^{-1}$ and $8.35 \times 10^{-4}\,{}^{\circ}C^{-1}$, respectively, and the values were found with 95% confidence. Statistical data show an excellent correlation of the linear model with experimental values. Variation in the coefficient of expansion implies in different intensities of intermolecular interactions.

Keywords: Biodiesel; residual oil; coefficient of volumetric expansion.

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1. Introduction

The substitution of fossil fuels in order to ensure energy supplies in the future and to preserve the environment remains a major concern. Increased global demand for liquid fuels, global warming, energy security, political development in the fields of agriculture, social and also energy are points that open new areas of interest and opportunities for research and development in academia and industry, as are the driving forces responsible for the renewed interest in biofuel production.[1-4]

In the literature, the technology[1] most commonly used for biodiesel production worldwide is the methylic transesterification in which vegetable oils or residues are mixed with methanol and combined with a catalyst to produce biodiesel. The choice of methanol is due to the high cost of ethanol and also by the ease of phase separation process.[5-8]

Advantages of biodiesel include domestic, renewable and biodegradable source, it presents higher flash point, inherent lubricity, reduction of exhaust emissions, as well as miscibility with diesel fuel (petrodiesel).

The cost reduction in the production of biodiesel becomes essential. Therefore, raw materials such as residual oils and fats have attracted the attention of biodiesel producers due to its low cost. The recycling of frying oil as biofuel not only removes an

unwanted compound from the environment, but also allows the generation of an alternative energy source.[9]

Through the inclusion of biodiesel into Brazil's energy matrix, it becomes necessary to obtain information about the physical and chemical properties of such biofuel, as it can affect significantly the parameters of lubrication, wear of engine components, carbon deposits, the process of injection and atomization, the transformation of chemical energy into mechanical energy and so on.[10] Not all of these properties were included as standard specifications of biodiesel, as the coefficient of volumetric expansion, important information in which concerns the biodiesel tankage. With heating, there is an increase in the frequency of atoms vibration. Consequently, there is an increase of repulsive forces which increases the average distance between the atoms. Each material reacts differently to a temperature change. Some materials exhibit a great variation in size with temperature increase, while others practically do not change its dimensions.[11] This fact is explained by the coefficient of volumetric expansion, also called coefficient of volumetric thermal expansivity or expandability, indicating the change in volume caused by the temperature.[12] This property is of great importance for the transport and storage of biodiesel due to the fact that the capacity of tanks is not designed considering the specific volume change of each biofuel.

The Equation 1, defined as the coefficient of volumetric expansion (β), undergoes variation in volume (V) caused by varying the temperature (T) while the pressure (P) remains constant.[13]

$$\beta = \left(\frac{1}{V} \right) \times \frac{\partial V}{\partial T}$$ Equation 1

The thermal expansion is related to the variation, in strength, of binding with the distance between atoms. So, the coefficient of thermal expansion is low when the intermolecular interaction is strong (*e.g*, more polar molecules). The materials tend to swell when exposed to heat. It increases the vibration of atoms or molecules so that the average distance between them also increases.[13]

This study aims to determine the thermal expansion coefficient from experimental data of specific mass as a function of temperature of methylic and ethylic biodiesel of residual oil and compare it with diesel.

2. Experimental

2.1. Biodiesel production and physicochemical properties

Residual oil samples, as feedstock, were collected from local restaurants and then filtered to remove any inorganic residues and suspended matters. The water was removed by rotary evaporation. All the chemicals used in experiments were purchased from Merck chemicals®.

Biodiesel was obtained by alkaline transesterification reaction with ethanol and methanol, using as raw material the residual oil (see diagram in Figure 1). The reaction conditions were: rotating at 80 rpm with the alcohol: oil molar ratio 7:1, potassium hydroxide as the catalyst at a concentration of 1.7 wt%, temperature of 35 ^{o}C and reaction time of 30 minutes for ethylic procedure and temperature of 48 ^{o}C and reaction time of 60 minutes for methylic procedure.[14-16] After the alkaline transesterification reaction, the system resulted in two phases with impure biodiesel being formed at the top and glycerin at the bottom. The biodiesel was removed from the mixture, adjusted the pH to near 7 and then washed 3 times with water at 80 ^{o}C. A high temperature of the washing water was necessary to solubilize and remove impurities. Residual water was removed by rotary evaporation. The conversion of raw

material to biodiesel is above 99% using this methodology.[17,18]

The methods used to analyze the biodiesel were: acidity ASTM D-664, humidity ASTM D-6304, viscosity ASTM D-445 e D-446, oxidative stability EN 14112, flash point ASTM D-93, specific gravity ASTM D-4052, peroxide index NBR 9678, free glycerol NBR 15771 and carbon residue ASTM 4730.[19] The specific mass was determined on a Kyoto density/specific mass meter (model DA-500), according to ASTM D-4052, within the temperature range of 10 to 50 ^{o}C at intervals of 5 ^{o}C. The calibration was performed with water, the default uncertainty of expanded of which is $\pm^o$0.01 kg m^{-3}, in order to ensure the reliability of the metrological experiments.[20]
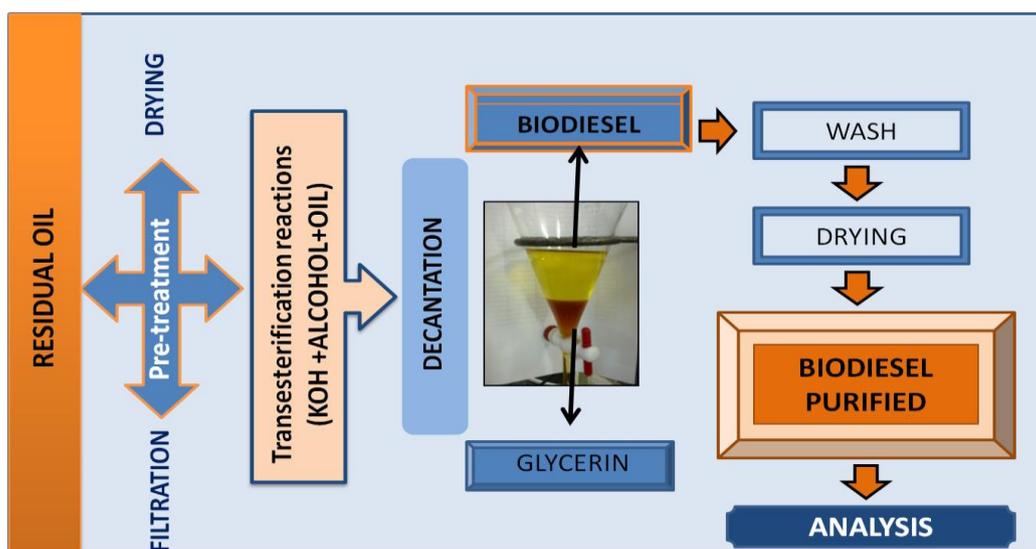
Figure 1. Diagram of biodiesel production from residual oil

2.2. Determining the coefficient of volumetric expansion

Using simple linear regression of ln (μ_0/μ) *versus* (T-T$_0$), with μ_0 and T$_0$ being respectively the initial specific mass and initial temperature and μ and T being the final specific mass and final temperature, it was possible to calculate the slope of the line, which is numerically equal to the thermal expansion coefficient of the diesel, and of the methylic (BMR) and ethylic (BER) biodiesels obtained from residual oil. The Statistica 7.0 StatSoft program was used to analyze the results.[21,22]

3. Results and Discussion

3.1. Physicochemical properties of biodiesel

The physicochemical properties of ethylic and methylic biodiesel from residual oil were analyzed. These properties are directly related to the quality of biofuel.[2] The characterization analyzes are shown in Table 1.

Table 1. Physicochemical properties of BMR and BER

PROPERTIES	UNITS	BMR	BER	ANP	METHOD
Water	mg kg^{-1}	127.8	129.5	<500	ASTM D-6304
Acidity	mg KOH g^{-1}	0.27	0.37	<0.50	ASTM D-664
Free glycerol	% mass	8.55×10^{-5}	1.07×10^{-4}	< 0.02	NBR 15771
Specific mass	kg m^{-3}	880.7	877.1	850 – 900	ASTM D-4052
Flash Point	^{o}C	176	175	>100	ASTM D-93
Viscosity	mm^2 s^{-1}	4.2	4.5	3.0 – 6.0	ASTM D-445 and 446
Carbon residue	wt %	0.003	0.011	< 0.050	ASTM 4730
Peroxide value	meq kg^{-1}	4.11	3.70	---	NBR 9678
Oxidative Stability	hours	6.36	7.19	>6.00	EN 14112

All results meet the specification of National Agency of Petroleum, Natural Gas and Biofuels (ANP).[23] The methylic and ethylic biodiesel have slightly different values due to the slight difference in the structure of such esters.

Moisture is a very important parameter for the quality of biodiesel, since water can cause an unwanted reaction (hydrolysis), decomposing the biodiesel and producing free fatty acids which can cause the development of engine problems. As the moisture content, the acidity of a fuel is an essential factor control since the presence of free fatty acids may trigger a whole oxidation of the fuel and is also responsible for oxidation of the internal engine parts, causing corrosion and deposit formation. The acidity is also within the specification.[24]

According to the results, the washing procedure was effective to remove free glycerin. Fuels with excess of free glycerin may cause clogging of fuel filters, deposition of glycerol in the storage tanks and, therefore, problems in the combustion engine. Moreover, the burning of glycerin generates, among other toxic compounds, acrolein, a carcinogen aldehyde that can cause respiratory problems if breathed for long periods, as frequently occurs in inside tunnels, in the middle of a traffic jam.[24]

The fluid dynamic properties of a fuel, which are important as regards the operation of injection compression engines (diesel engines), are the viscosity and specific mass. These properties have a great influence on the movement and fuel injection.[26-27] A major aim of biodiesel production is to reduce the viscosity of triglycerides to values close to the diesel. Both biodiesels meet the specification stating different viscosity of diesel oil.

The specific mass is within the limits accepted by ANP for both ethylic and methylic biodiesel of residual oil. The specific mass is an essential property which affects the development of the engine, since fuel air ratio in the combustion chamber is directly affected.[28] The flash point is the temperature at which a flammable liquid catches fire in the presence of a flame or sparks. This property is of importance only as regards the safety of transport, handling and storage and may indicate contamination by alcohol. Methylic biodiesel flash point was lower than that of ethylic biodiesel probably due to the smaller carbon length.[30]

The burning of these esters was almost complete, with only minimal residual, somewhat lower than the maximum accepted by ANP, providing fuel quality. These residues can cause the formation of sludge in the region of the nozzle, which can cause problems in operation and, in severe cases, irreparable damage to internal parts.

Although not a requirement of the fuel analysis, the peroxide analysis have proven to be an interesting study object, since the oxidation reaction is often suggested by the

increase in peroxide value over the storage period.

The biodiesel showed good oxidative stability. Fuel can lead to unstable increased viscosity and the formation of gums, sediment or other deposits. More ideas on these degradation processes are provided in recently published reviews.[31]

3.2. Coefficient of volumetric expansion for biodiesel

In Table 2, there are the values obtained for specific mass in function of temperature for methylic (BMR) and ethylic (BER) biodiesels. The density, at 20 ^{o}C, for BMR and BER are 880.7 kg m^{-3}, and 877.1 kg m^{-3}, respectively. The density of 855.2 kg m^{-3} is respective to diesel oil at 20 ^{o}C. These values found for both biofuels are close to values found in literature for different materials, ranging from 873 to 883 kg m^{-3}. The slight difference is due to the change of the raw material used, with different variations in volume, according to each molecule of biodiesel.

Applying integral on both sides of equation 1, substituting the variable volume for specific mass, adjusting and operating by linear regression, one obtains Figure 2 from the Table 2 data and thus the coefficient of volumetric expansion, for each biodiesel and diesel oils, could be determined.

Table 2. Measured values of specific mass in function of temperature for BMR and BER and diesel oil

T/°C	BER (kg m^{-3})	BMR (kg m^{-3})	DIESEL (kg m^{-3})
10	884.4	888.1	862.2
15	880.8	884.4	858.7
20	877.1	880.7	855.2
25	873.4	877.0	851.7
30	869.8	873.5	848.1
35	866.2	869.8	844.6
40	862.6	866.2	841.0
45	858.9	862.5	837.5
50	855.3	858.9	833.9
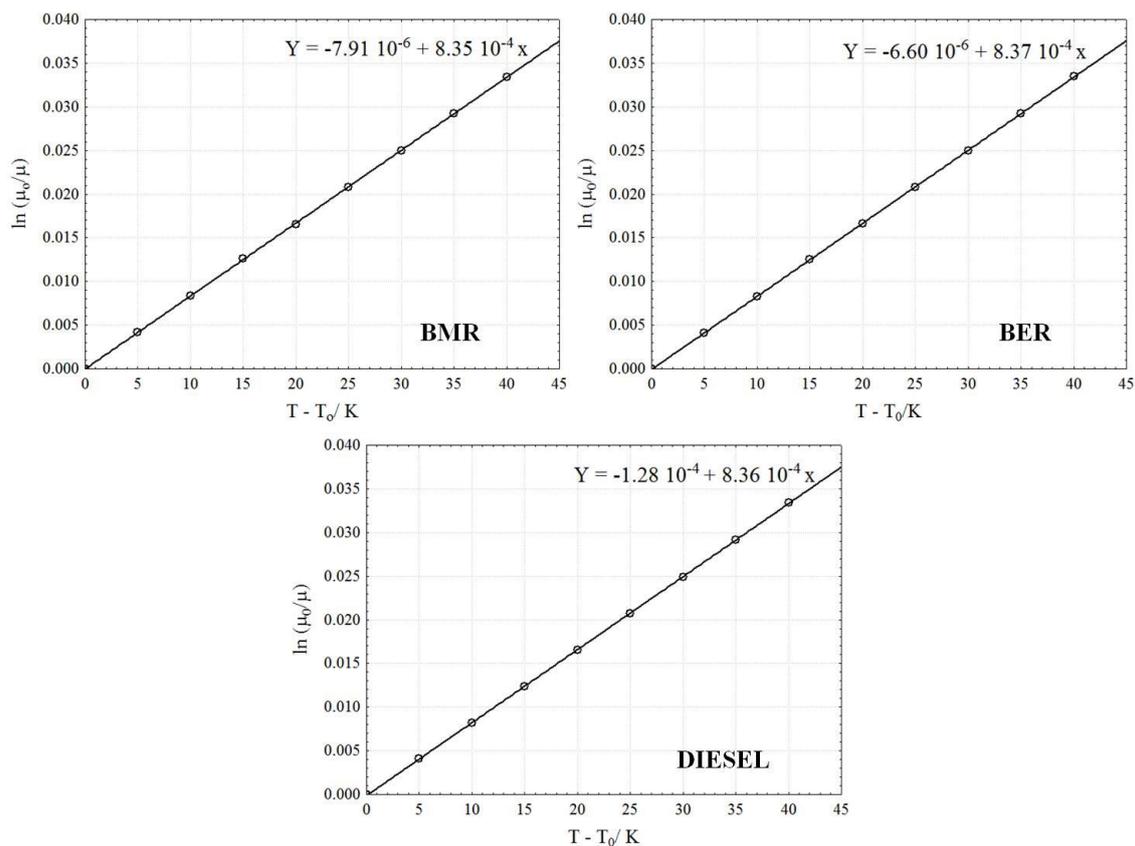
Figure 2. The graph for determining the coefficient of thermal expansion of BMR and BER and diesel oil

Statistical methods allows the characterization of the data obtained and the evaluation of the quality of such data on the assumption that the random errors contained in the analytical results follow in most cases a gaussian or normal distribution. Through statistical analysis of linear regression of the specific mass, data is possible to accept the mathematical algorithm and provide through an F-test if the regression is significant within a confidence level.[30]

According to the equation, the coefficient of volumetric expansion is numerically equal to the slope and the values found with 95% confidence are 8.36×10^{-4} °C^{-1} ± 0.06×10^{-4}, 8.37×10^{-4} °C^{-1} ± 0.01×10^{-4} and 8.35×10^{-4} °C^{-1} ± 0.02×10^{-4} for diesel, BMR and BER biodiesel, respectively.[20-22] The percentage of explained variance for this model was 99.99%, showing an excellent correlation of the linear model with experimental data. The F value provides an indication of the significance of the regression and all calculated F was greater than the F tabulated in Table 3, which have a regression statistically significant at 95% confidence. Comparing the data of biodiesel with diesel fuel will provide the information necessary to adapt engines and tankage in a near future.

Table 3. Linear regression data to diesel fuel, BMR and BER to determine the coefficient of volumetric expansion

SAMPLE	DATA REGRESSION		R^2	$F_{calculated}$	$F_{tabulated}$	p-value
	Linear Coefficient	Slope				
Diesel	-1.28×10^{-4}	8.36×10^{-4}	99.99%	1.25×10^5	5.59	3.33×10^{-16}
BER	-6.60×10^{-5}	8.37×10^{-4}	99.99%	3.46×10^5	5.59	1.07×10^{-17}
BMR	-7.91×10^{-6}	8.35×10^{-4}	99.99%	2.67×10^5	5.59	2.69×10^{-17}

The study of the effect of temperature on some physical properties such as specific mass and viscosity have been conducted in order to know such variations and to enhance mechanical ignition by developing methods and empirical models, and thus to extend the possibilities of biodiesel application. The use of specific mass obtained through experimental data according to the temperature associated with the concepts of thermodynamics, predict the possible thermal expansion coefficient of diesel fuel, ethylic and methylic biodiesel from residual oil. An increased coefficient of cubic expansion means in a lower specific mass when the temperature is increased, which causes a higher loss of engine power as a result of fuel heating. [31]

The study of thermal expansion to determine the volume, changes with temperature. The coefficient of thermal expansion of the BMR and BER is: 8.37×10^{-4} $^{o}C^{-1}$ and 8.35×10^{-4} $^{o}C^{-1}$, respectively. Considering that for the commercialization of fuel in Brazil the reference temperature is used in sales of 20.0 ^{o}C, the conversion to the correct volume discharged at other temperatures, without prejudice to the buyer, it is necessary to know the coefficient of expansion. According to the determined coefficient, a tank loaded with residual biodiesel oil to 30.0 ^{o}C corresponds to a volume increase of about 83 liters per 1,000 liters of biodiesel and, thus, will be paid a larger volume than if conversion to the reference temperature had been done. Thus, the volume occupied by biodiesel into the tank or truck is strongly influenced by temperature.

To determine the confidence in the experiment and to verify conformity with the mathematical model studied, the Figures 3 and 4 were prepared for both biodiesels. Residual analysis is essential to evaluate the fit of any model. A model that leaves much waste is a bad model. In an ideal model would be no waste, ie, the results observed were equal to those.[32] Through the Figure 3 one can see alternating of the vertical deviations of points about the straight line (residues), which can be concluded that the variance of errors is constant and that there are systematic errors.
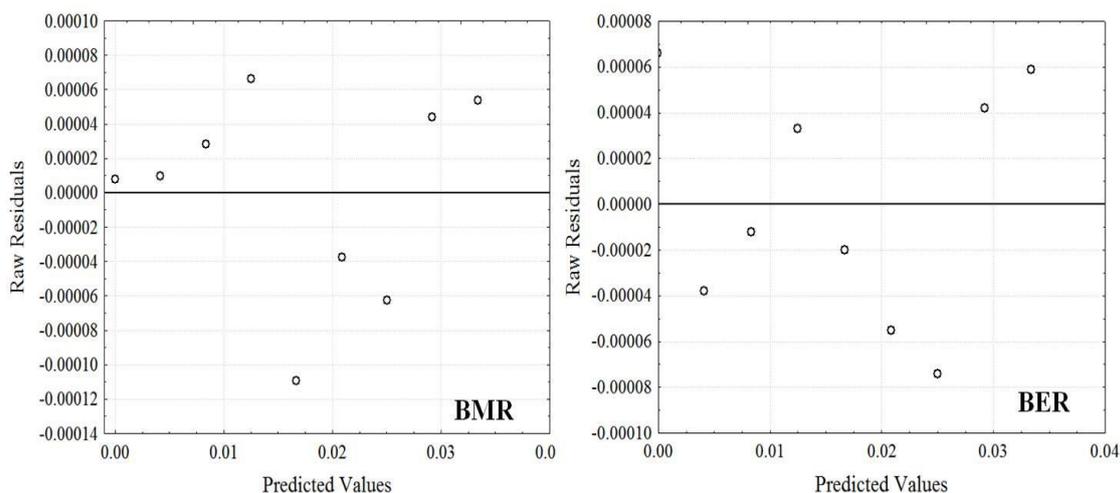
Figure 3. Residue ln (specific mass) *versus* predicted value for BMR and BER
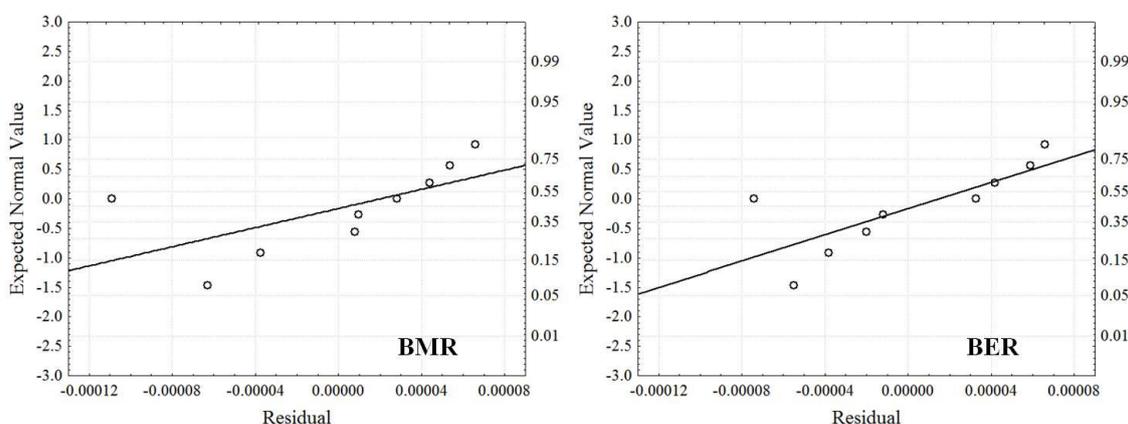
Figure 4. Distribution of residuals about the line that indicates normality of ln (specific mass) for the BMR and BER

Data from methylic and ethylic biodiesel behave near normal distribution, according to Figure 4, showed adaptation of the mathematical model in the studied system.

4. Conclusions

All parameters for the quality of biodiesel analyzed meet the specifications of ANP. These physicochemical properties are very important and can influence the degradation of biofuel, the oxidation of internal engine parts and fuel injection system.

Through this work it was possible to determine the volumetric property called coefficient of volumetric expansion by specific mass of biodiesel from residual oil and diesel. This property is an extremely important parameter in order to estimate other physicochemical properties, including heat of vaporization.[12]

The coefficient of volumetric expansion showed a value of 8.36×10^{-4} $^{o}C^{-1}$, 8.37×10^{-4} $^{o}C^{-1}$ and 8.35×10^{-4} $^{o}C^{-1}$ for diesel, BMR and BER, respectively. The results showed the regression statistically significant at 95% confidence. A normal distribution and variance for this model was 99.99% for both. The increase of 10 ^{o}C in temperature causes an increase of 83 liters in volume of 1000 liters of biodiesel.

Thus, the volume occupied by the biodiesel inside the tanks has strong

temperature influence. In order to enable tankage and trading of biodiesel, enhance all business operations and set prices to the volumes referred to temperature of 20.0 ^{o}C as reference temperature in Brazil, it is necessary to know how much volume expanded with temperature increase using the coefficient of volumetric expansion.

Acknowledgment

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