THERMOPHYSICAL PROPERTIES OF BIODIESEL OBTAINED FROM VEGETABLE OILS: CORN, SOY, CANOLA AND SUNFLOWER

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ABSTRACT

Biodiesel is biodegradable, renewable and obeys to the carbon cycle, being defined as mono-alkyl ester of fatty acids derived from renewable sources, such as vegetable oils and animal fat. For this work biodiesel was produced through transesterification reaction (methylic route) from sunflower, corn, soy and canola vegetable oils. From experimental data, it was possible to observe an inverse relation among temperature and viscosity/density. Among the four kinds of biodiesel (sunflower, corn, soy and canola), the one which has presented greater viscosity was canola, however all of them presented very similar behavior. Mathematic polynomial model used adjusted well to experimental data. Vegetable oils (sunflower, corn, soy and canola) are advantageous for biodiesel production. Experimental data were inside limits established by American Society for Testing and Materials, European Norm and Brazilian Agency of the Oil.
KEYWORD: Viscosity. Density. Biodiesel. Vegetable oils. Modeling.

PROPRIEDADES TERMOFÍSICAS DO BIODIESEL OBTIDO A PARTIR DE ÓLEOS VEGETAIS DE MILHO, SOJA, CANOLA E GIRASSOL

RESUMO

No presente trabalho o biodiesel foi produzido através da reação de transesterificação (rota metílica) a partir de óleos vegetais de girassol, milho, soja e canola. A partir de dados experimentais, foi possível observar uma relação inversa entre a temperatura e a viscosidade / densidade. Entre os quatro tipos de biodiesel (girassol, milho, soja e canola), o que apresentou maior viscosidade foi o biodiesel obtido de óleo de canola, porém todos apresentaram comportamento muito semelhante. O Modelo polinomial utilizado se ajustou bem aos dados experimentais.
PALAVRAS CHAVES: Viscosidade. Densidade. Biodiesel. Óleos vegetais. Modelagem.

1. INTRODUCTION

Concerns about international oil price rise associated to climatic change questions has lead humanity to a more rational use of energetic sources available nowadays, together with the development of energy production by renewable sources (ITURRA, 2003). In this scenario is highlighted biofuel, which bring incentives to agriculture by elevated demand of raw material, mainly present in ethanol production in Brazil, USA and E.U. – European Union biodiesel.

Brazil produces and has a consolidate market for ethanol; however the country is in the initial phase of biodiesel production, fostered by law requirement from the beginning of 2008 to add 2% biodiesel to mineral diesel. Even when adding only 1% biodiesel to diesel oil, it is possible to reduce greatly harmful effects of its combustion. Since January 1, 2010, biodiesel sold in Brazil contains 5% biodiesel (ANP, 2012). This little addition represents na important economy in oil importation, generating employments and profit in agricultural sector. It is expected that 150 million hectares agricultural area and diversity of edafo-climatic conditions may help Brazil to become a worldwide leader in biodiesel production (BORGES, 2008; HOLANDA, 2004).

Brazilian cultures potential for biodiesel production overcomes 200 species, involvolving annual cultivations, such as castor beans, sunflower, canola, cotton and peanut and also the perennial ones such as palm, babassu and other palm trees. Completing row material diversity for biodiesel there is also the use of tallow and residues from frying and domestic sewage, besides residues from crude vegetable oil refining. Brazil has potential to answer daily internal demand of 460.000 biodiesel barrels from oilseed species cultivation in 6 million ha, or else, only 18% of its deforested area (BODDEY, 1993).

Biodiesel is a generic term which refer to several fatty acid monoesters which may be used as diesel fuel. It is produced from the conversion of triglyceride (vegetable oil or animal fat) trough several sterification processes.[5] There are at least three preliminary ways to produce biodiesel: microemulsions, thermic cracking (pyrolysis) and transesterification. Most used method is vegetable oil and animal fat transesterification (FANGRUI, 1999). Not all vegetable oils and animal fat are appropriate for being used in biodiesel production, once they may present high amount of viscosity or a great number of instaurations in fatty acid carbonic chain which may constitute a biofuel (KNOTHE, 2005). Among several oilseed which are known in literature, the ones which present a high amount of oil in the seed, are advantageous for biodiesel production. Among these we may highlight oilseeds soy, peanut, sunflower, babassu, corn, colza, castor bean and cotton (VARGAS et al, 1999).

Knowing thermophysic properties: density, thermic conductivity, as well as rheological behavior is of great importance for scaling equipments used for controlling processes which involve energy production. The lack of biodiesel thermophysic properties data makes it difficult dimensioning equipments and processes, usually assuming approximate values. Physic and thermic properties, such as density and viscosity are much used in projects for pumps, engines, ducts, biodiesel factories and several other equipment moved by biofuel.

The present work was proposed for collecting biodiesel thermophysic properties data obtained by means of soy, canola, corn and sunflower vegetable oil transesterification reaction

2. MATERIALS AND METHODS

2.1 MATERIALS

Soy, corn, sunflower and canola vegetable oil (Bunge, Brazil) were purchased in the local market. For this experiment were used reagents of analytic degree and deionized water. Experimental data were analyzed using statistic package SAS®, (SAS, 1998).

2.2 METHODS

2.2.1 OBTAINING BIODIESEL

Biodiesel was obtained by means of transesterification reaction via methylic route, based in the methodology used by DANTAS (2006), and PEREIRA (2007). Initially potassium methoxide was produced mixing 40 mL methanol with 1 g KOH for each 100 mL vegetable oil into a beaker under shaking with the help of a magnetic shaker (Biomixer, Brazil) until the total dissolution of KOH. After that, potassium methoxide was added to respective vegetable oils.

The solution was submitted to a temperature of 45ºC under continuous agitation (180 rpm) with the help of an incubator shaker (Solab, Brazil), for making transesterification reaction for 60 minutes. After reaction, the mix was transferred to a decantation funnel, for phase separation. After 20 minutes it was possible to observe two distinct phases: one superior rich in methylic esters, less dense and clearer, and an inferior phase rich in glycerine, more dense and darker. After 24 hours resting, glycerine was collected into a beaker. Afterwards, the clearer one was submitted to washing process with the aim to neutralize basic excess, remove some undesired impurities and evaporate water residue.

2.2.2 DETERMINING DENSITY AND VISCOSITY

Kinematics viscosity and density were determined at different temperatures (283.15, 293.15, 303.15, 313.15 and 323.15) K. Biodiesel and ethanol mix were registered as follows: B100 – Pure Biodiesel; B75 – 75% Biodiesel + 25% Ethanol; B50 – 50% Biodiesel + 50% Ethanol; B25 – 25% Biodiesel + 75% Ethanol.

The density (ρ) was determined by using a standard volumetric pycnometer (~10 cm^3), with uncertainty of ± 0.01 $Kg \cdot m^{-3}$. The pycnometer was calibrated using double distilled water. Calibrated Cannon-Fenske glass capillary viscometer (sizes 50, 75, 100, and 150) was used to measure the kinematic viscosity (v) (Schott-Geräte, Germany) with an uncertainty of ± 0.01 $mPa \cdot s$. Viscometers were placed into a thermostatic water bath (Schott-Geräte, CT 53 HT, Germany) for temperature control, with estimated uncertainty of 0.1 K. Variation coefficients for experimental measurements may be estimated as being not higher than 5.0 %.

3. RESULTS AND DISCUSSION

3.1 THERMOPHYSIC PROPERTIES

Tables 1 to 4 present experimental data for density and kinematic viscosity of sunflower, corn, soy and canola biodiesel samples in function of variables analyzed (temperature and biodiesel concentration).

Table 1 – Density ρ , viscosity ν for sunflower biodiesel.

T / ºC	w_1	w_2	ρ / Kg . m^{-3}	ν / mm² . s^{-1}
283.15	0.25	0.75	829.772	3.248
293.15	0.25	0.75	828.535	2.563
303.15	0.25	0.75	825.134	2.074
313.15	0.25	0.75	820.126	1.701
323.15	0.25	0.75	816.655	1.484
283.15	0.5	0.5	847.247	4.711
293.15	0.5	0.5	845.777	3.566
303.15	0.5	0.5	842.213	2.875
313.15	0.5	0.5	837.374	2.333
323.15	0.5	0.5	833.995	1.926
283.15	0.75	0.25	868.402	6.471
293.15	0.75	0.25	864.902	4.857
303.15	0.75	0.25	860.647	3.815
313.15	0.75	0.25	858.004	3.161
323.15	0.75	0.25	853.172	2.586
283.15	1	0	887.599	9.926
293.15	1	0	883.410	7.441
303.15	1	0	879.324	5.546
313.15	1	0	874.962	4.571
323.15	1	0	871.035	3.827

w_1= Biodiesel (% v/v); w_2= ethanol (% v/v).

Table 2 - Density ρ , viscosity ν for corn biodiesel.

T / ºC	w_1	w_2	ρ / Kg . m^{-3}	ν / mm² . s^{-1}
283.15	0.25	0.75	829.391	3.264
293.15	0.25	0.75	827.960	2.598
303.15	0.25	0.75	826.171	2.077
313.15	0.25	0.75	821.161	1.715
323.15	0.25	0.75	817.566	1.437
283.15	0.5	0.5	850.079	4.751
293.15	0.5	0.5	846.229	3.575
303.15	0.5	0.5	842.385	2.911
313.15	0.5	0.5	837.412	2.379

323.15	0.5	0.5	834.579	1.936
283.15	0.75	0.25	866.850	6.406
293.15	0.75	0.25	864.811	4.806
303.15	0.75	0.25	860.124	3.793
313.15	0.75	0.25	856.715	3.163
323.15	0.75	0.25	853.437	2.595
283.15	1	0	885.860	9.542
293.15	1	0	880.947	7.162
303.15	1	0	877.259	5.580
313.15	1	0	873.728	4.329
323.15	1	0	869.248	3.674

w_1= Biodiesel (% v/v); w_2= ethanol (% v/v).

Table 3 - Density ρ , viscosity ν for soy biodiesel.

T / ºC	w_1	w_2	ρ / Kg . m^{-3}	v / mm² . s^{-1}
283.15	0.25	0.75	832.996	3.422
293.15	0.25	0.75	831.477	2.678
303.15	0.25	0.75	829.256	2.115
313.15	0.25	0.75	824.848	1.763
323.15	0.25	0.75	823.573	1.499
283.15	0.5	0.5	847.067	4.507
293.15	0.5	0.5	844.680	3.430
303.15	0.5	0.5	840.803	2.732
313.15	0.5	0.5	836.604	2.209
323.15	0.5	0.5	833.107	1.830
283.15	0.75	0.25	866.688	6.163
293.15	0.75	0.25	863.352	4.658
303.15	0.75	0.25	860.324	3.660
313.15	0.75	0.25	856.162	2.998
323.15	0.75	0.25	853.202	2.477
283.15	1	0	886.327	9.315
293.15	1	0	882.993	6.997
303.15	1	0	877.678	5.651
313.15	1	0	873.945	4.440
323.15	1	0	868.716	3.655

w_1= Biodiesel (% v/v); w_2= ethanol (% v/v).

Table 4 - Density ρ , viscosity ν for Canola biodiesel.

T / ºC	w_1	w_2	ρ / Kg . m^{-3}	v / mm² . s^{-1}
283.15	0.25	0.75	833.458	3.462
293.15	0.25	0.75	832.249	2.678
303.15	0.25	0.75	828.011	2.136

313.15	0.25	0.75	823.277	1.747
323.15	0.25	0.75	819.552	1.490
283.15	0.5	0.5	847.431	4.768
293.15	0.5	0.5	845.047	3.608
303.15	0.5	0.5	841.294	2.945
313.15	0.5	0.5	836.685	2.358
323.15	0.5	0.5	833.835	1.968
283.15	0.75	0.25	868.717	6.564
293.15	0.75	0.25	866.209	4.983
303.15	0.75	0.25	863.269	3.927
313.15	0.75	0.25	859.241	3.188
323.15	0.75	0.25	855.067	2.634
283.15	1	0	886.431	10.317
293.15	1	0	882.418	7.699
303.15	1	0	878.945	5.835
313.15	1	0	874.511	4.679
323.15	1	0	871.732	3.890

w_1= Biodiesel (% v/v); w_2= ethanol (% v/v).

Density and viscosity experimental values presented an inverse relation with temperature. The same tendency was observed by BAROUTIAN et al (2008) when analyzing palm tree biodiesel density, obtained to methylic route and by CERIANI et al (2008) when analyzing density and viscosity of vegetable oils babassu, buriti, brazil nuts, macadamia nut and grape seed. Highest cinematic viscosity values were noticed for canola biodiesel, however all samples presented values very close to one another. Density has presented a varied behavior, not revealing more dense biodiesel. BAROUTIAN et al (2008) has compared palm biodiesel density obtained via methylic route, and has concluded that, methylic esthers density is higher than ethylic esthers. For the author this tendency may be attributed to higher molecular weight of ethylic esthers and fatty acids. Samples densities depend on the molecular weight. Hence, according to molecular weight reduction there happens also an increase in density.

PEREIRA (2007), analyzed cinematic viscosity at 313.15 K of *Mabea fistulifera Mart* (canudo-de-pito) biodiesel, canudo de pito vegetable oil, diesel fuel and mix between biodiesel and diesel viscosity and has observed that biodiesel viscosity was lower than the one of vegetable oil, getting closer to values registered to diesel oil (a little superior, justifying the great advantage of using transesterification process for obtaining biodiesel derived from vegetable oil. Viscosity of diesel sample used in the works of PEREIRA (2007) was 3.327 $mm^2.s^{-1}$. The present work has obtained pure biodiesels cinematic viscosity values at 313.15K inferiors to 4.679 $mm^2.s^{-1}$. Viscosity is related to fuel optimization, as well as its flowing in the engine. For using biodiesel in diesel cycle engines (FELIZARDO et al, 2006), cinematic viscosity should be between 3.5 and 5.0 $mm^2.s^{-1}$. Brazilian Agency of the Oil (ANP), has determined as limit, interval between values ranging from 3.0 – 6.0 $mm^2.s^{-1}$ to 313.15 K. It is observed that great part of experimental data was inside this limit, except for some samples in certain temperatures. It is worth to observe that extension of reaction, as well as experimental circumstances used in biodiesel production has extremely influentiated fuel properties especially apparent viscosity.

CALAI e CLARK (2007), produced biodiesel from canola oil, obtaining cinematic viscosity at 313.15K between 4 and 6 $mm^2.s^{-1}$ value closer to 4.679 $mm^2.s^{-1}$ obtained with this work. Table 5 presents cinematic viscosity values at 313.15K biodiesel produced from different oilseed and also limits established by American Society for Testing and Materials (ASTM), European Norm (EN) and ANP.

Table 5 – Cinematic viscosity at 313.15K biodiesel from different raw materials.

Raw materials	**v** ($mm^2.s^{-1}$)	Limits ($mm^2.s^{-1}$)		
		USA *ASTM*	EU *EN*	BRA *ANP*
Sunflower	4.571	1.9-6.0	3.5-5.0	3.0-6.0
Corn	4.329			
Soy	4.440			
Canola	4.679			

DANTAS et al (2006) has studied biodiesel cinematic viscosity obtained from corn vegetable oil as well as diesel at 313.15, and obtained value 5.110 $mm^2.s^{-1}$ and also noticed a great similarity between biodiesel corn viscosity and diesel fuel. In this work at 313.15 K it was obtained value of 4.329 $mm^2.s^{-1}$, which is a little inferior value that reveals biodiesel higher quality once viscosity reduction may reflect positively during injection and biofuel burning inside the engine combustion chamber (PEREIRA, 2007).

It was possible to identify through data analysis (Table 1 to 4), a direct relation between viscosity our density and biodiesel concentration. The same behavior was observed by PEREIRA (2007), when studying canudo de pito biodiesel density and diesel fuel at 293.15 K obtained 892.8 and 864.7 $Kg.m^{-3}$, respectively. In this work, sunflower, corn, soy and canola biodiesels at 293.15 K were respectively: 883.410, 880.947, 882.993, 882.418 $Kg.m^{-3}$, comparatively quite similar. Limits specified by ANP for specific biodiesel mass at 313.15 K are among 850-950 $Kg.m^{-3}$. Only mix with 75 and 50% ethanol were lower than ANP specification; however this fact is explained by low ethanol density. Table 6 presents density values at 313.15K biodiesel produced from different oilseeds and also limits established by EN and ANP.

Table 6 – Density at 313.15 K biodiesel from different raw materials.

Raw materials	**ρ** ($Kg.m^{-3}$)	**Limits** ($Kg.m^{-3}$)	
		EU EN	BRA *ANP*
Sunflower	874.962	860-900	850-950
Corn	873.728		
Soy	873.945		
Canola	874.511		

3.2 MATHEMATICAL MODELLING

A polynomial model was used for relating viscosity data or density in function of temperature, biodiesel concentration and ethanol, respectively. General quadratic model, equation 1 was analyzed and non significative parameters were eliminated with base on *t* test (Student) and *p*>0.05. Table 7 shows predictive models based in equation model 1 for each oil used.

$$\Phi = y_0 + a \cdot x_1 + b \cdot x_2 + c \cdot x_3 + d \cdot x_1^2 + e \cdot x_2^2 + f \cdot x_3^2 + g \cdot x_1 \cdot x_2 + h \cdot x_1 \cdot x_3 + i \cdot x_2 \cdot x_3 \quad (1)$$

where Φ is viscosity ($mm^2 \cdot s^{-1}$) or density ($kg \cdot m^3$), x_1 corresponding to temperature (K), x_2 at biodiesel concentration (%v/v), x_3 ethanol concentration (%v/v) e *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h* and *i* correspond to parameters calculated by equation.

Table 7 – Model parameter (equation 1) employed for correlating a) sunflower, b) Corn, c) Soy, d) Canola biodiesel density and viscosity.

Parâmetros	ρ_a	ρ_b	ρ_c	ρ_d	ν_a	ν_b	ν_c	ν_d
yo	838.215	837.282	769.939	863.030	159.176	147.542	140.936	159.994
a	*	*	*	*	-1.035	-0.955	-0.904	-1.038
b	102.833	101.458	103.533	70.454	41.291	39.405	34.151	41.894
c	*	*	*	*	*	*	*	*
d	-0.0006	-0.0006	*	-0.0005	0.0017	0.0015	0.0014	0.0017
e	*	*	23.856	*	4.864	4.051	5.496	5.591
f	*	*	*	*	*	*	*	*
g	*	*	-0.2182	*	-0.138	-0.13	-0.119	5.591
h	*	*	*	*	*	*	*	*
i	*	*	*	*	*	*	*	*
R^2	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.98

* parâmetros não significativos (*p*>0.05)

In table 7 it is possible to observe that for viscosity, most significative variables (*p*>0.05) were temperature and biodiesel concentration in the mix. In case of density the variable which most significantly influenced (*p*>0.05) was biodiesel concentration in the mixture. In all cases studied correlation coefficient (R^2) was equal or superior to 0.98, demonstrating that model used adjusted well to behavior presented by viscosity and density experimental data.

4. CONCLUSION

Biodiesels density and viscosity biodiesel has presented an inverse relation with temperature. More viscous biodiesel was produced from canola vegetable oil; however all of them presented very similar behavior. Average biodiesel viscosity was closer to diesel fuel, demonstrating once more the relevance of transesterification process. Samples with 25% biodiesel presented smaller viscosity and density, showing that there is a direct relation between biodiesel concentration and viscosity/density. Polynomial mathematic model used adjusted well to experimental data.

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REFERENCES

ANP. Agência Nacional de Petróleo, Gás Natural e Biocombustíveis. **O biodiesel obrigatório**. Disponível em: <http://www.anp.gov.br>. Acesso em: 21 maio. 2012.

BAROUTIAN S, MOHAMED KA, ABDUL AAR, SULAIMAN NMN, **Densities of Ethyl Esters Produced from Different Vegetable Oils**. *J. Chem. Eng. Data*, v.53, p.2222-2225 2008b.

BAROUTIAN S. MOHAMED KA, ABDUL AAR, SULAIMAN NMN. **Density of Palm Oil-Based Methyl Ester**. *J. Chem. Eng. Data*, v.53, p**.**877-880,2008a.

BODDEY R, GREEN. **Energy from sugar cane**. *Chemistry and Industry, v.*17, p.355-358,1993.

BORGES, MC. **Protótipo de um Sistema Integrado de Apoio à Decisão sobre Investimentos Industriais e Agrícolas na Cadeia Produtiva do Biodiesel***.* Universidade Federal de Viçosa, Viçosa (2008).

CALAIS P., CLARK, T. **Métodos de determinação experimental da condutividade e difusidade térmica de materiais biológicos**. *Boletim SBCTA*, v.36 p**.**55-68, 2007.

CERIANI R, PAIVA FR, GONÇALVES CB, BATISTA EAC, MEIRELLES AJA, **Densities and viscosities of vegetable oils of nutritional value**. *J. Chem. Eng. Data,* v.53, p.1846-1853 2008.

DANTAS, HJ. **Estudo Termoanalítico, Cinético e Reológico de Biodiesel Derivado do Óleo de Algodão**. Universidade Federal da Paraíba. João Pessoa, (2006).

FANGRUI M, MILFORD AH, **Biodiesel production: a review**. *Bioresource Tecnology,v.*70, p.1-15,1999.

FELIZARDO P, CORREIA MJN, RAPOSO I, MENDES JF, BERKEMEIER R, BORDADO J, M. **Production of biodiesel from waste frying oil**. *Waste Management, v.*26, p.487-494, 2006.

HOLANDA, A. **Biodiesel e Inclusão Social**. *In:* Conselho de altos estudos e avaliação tecnológica da câmara dos deputados, Brasília (2004).

ITURRA A R. ***Análise Histórica do Biodiesel no Brasil**,* relatório apresentado ao Grupo de Trabalho Interministerial sobre Biodiesel, Brasília (2003).

JUNG H, KITTELSON, DB, ZACHARIAH MR, **Characteristics of SME Biodiesel-Fueled Diesel Particle Emissions and the Kinetics of Oxidation**. *Environ. Sci. Technol,v.*40, p. 4949-4955, 2006.

KNOTHE G, **Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters**. *Fuel Processing Technology*. v.86, p.1059-1070, 2005.

PEREIRA, FEA. ***Biodiesel produzido a partir do Óleo de Sementes***. Universidade Federal de Viçosa, Viçosa (2007).

SAS Institute, Inc SAS/STAT **user's guide release** 6.03.Cary, NC. (1998)

VARGAS RM, Schuchardt U, Sercheli, R. **Transesterification of vegetable oils: a review**. *Journal Brazilian Chemists Society*, v.9, p.199-210, 1999.