Full Length Article

Modeling viscosity of butanol and ethanol blends with diesel and biodiesel fuels

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HIGHLIGHTS

- Alcohols in diesel or biodiesel cause a strong non-linear decrease of viscosity.
- Viscosity of all butanol-diesel blends remains within a permissible range.
- Grunberg-Nissan equation fits well ethanol-biodiesel and butanol blends viscosity.
- Interaction parameters are proposed and related to polarity of the species involved.
- A 3-parameter model is needed to fit viscosity of gel-like ethanol-diesel blends.

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ABSTRACT

Kinematic viscosities were measured for ethanol and n-butanol blends with diesel and biodiesel fuels, showing that increasing alcohol contents contributed to a non-linear decrease in the viscosity. Only ethanol blends with alcohol content lower than 36% (volume basis) fulfill diesel fuel quality standard, whereas the whole range of n-butanol blends fulfills this standard. Generalized correlations were tested for the estimation of the viscosity of ethanol and butanol blends with diesel and biodiesel fuels in the whole range of alcohol contents. Interaction coefficients were required for an adequate estimation due to strong molecular interactions. Two-parameter equations did not improve, and three-parameter equations improved only slightly, the estimations with respect to the Grunberg-Nissan equation, with only one interaction coefficient. This interaction coefficient decreases when the number of carbon atoms in the n-alcohol molecule increases for both diesel blends and biodiesel blends because the non-polar part of the molecule becomes dominant against the polar hydroxyl group. Original correlations were proposed for the modeling of the interaction coefficient in alcohol-diesel and alcohol biodiesel fuels as a function of the carbon number of the alcohol. Other n-alcohols (methanol, propanol and n-pentanol) were also tested to extend the validity of the correlation proposed. These correlations are useful for the design of transport equipment or pipelines in a scenario where alcohols may constitute a fuel component in diesel blends. Also the decision on feasible blends that fulfill the narrow viscosity ranges set by fuel standards (to avoid loss of vehicle operability) will benefit from the proposed correlations.

1. Introduction

Oxygenated fuels such as alcohols are recognized as an effective way to reduce soot emissions and to improve the combustion process [1,2]. Among the alcohols, ethanol has been suggested as one of the most promising blending components for diesel fuel. However, the higher viscosity of butanol with respect to ethanol, together with its higher heating value, better miscibility and lower hydrophilic nature, suggest that n-butanol is a better renewable component than ethanol in diesel blends.

Alcohols have been widely used in chemical and petroleum industries. Therefore, accurate and reliable knowledge of their viscosity is required for the design of transport equipment or pipelines [3]. In a diesel engine, the liquid fuel is sprayed into compressed air and atomized into small droplets near the nozzle exit. The viscosity affects the atomization of a fuel when it is injected into the combustion chamber, the size of the fuel droplets, the formation of engine emissions and deposits [4,5] and the lubricity of the fuel [6].

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Nomenclature

μ	absolute viscosity	M	molecular weight
B	biodiesel	n	number of carbon atoms
Bu	butanol	v	kinematic viscosity
D	diesel	v'	interaction coefficient for McAllister equations
db	number of double bonds	x	mole fraction
Et	ethanol	z	volume fraction
G	interaction coefficient for Grunberg-Nissan equation	ρ	liquid density

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Fuels with high viscosity tend to form larger droplets in the injection which leads to a poor fuel atomization that increases the spray tip penetration and decreases the spray angle, deriving into a poor combustion. This finally increases the exhaust emissions and smoke opacity, and tends to form engine deposits [7]. Moreover, long-term durability problems may be related to the use of high viscosity fuels, and carbon deposits may dilute in the engine lubricant leading to engine damage. Also, high-viscosity fuels require more energy in the fuel pump and increase wear in the injection system [8]. At low temperature, filter plugging problems may occur because the viscosity increases with decreasing temperature [9]. On the contrary, fuels with excessively low viscosity may not provide sufficient lubrication for the injection system leading to greater pump and injector leakage, reducing maximum fuel delivery, and thus decreasing power output [7]. The addition of alcohol (ethanol or butanol) to diesel reduces fuel viscosity. However, it can be compensated by adding biodiesel, which is likely to yield the viscosity close to that of diesel fuel [10].

Generalized correlations for the prediction of the viscosity of liquid mixtures are needed for the design of combustion equipment. If the viscosity of hydrocarbon blends is to be predicted, the interaction between components can usually be considered as negligible. In these cases, it can be assumed that the viscosity is additive and it can be modeled through ideal additivity. In the case of biodiesel fuels, small interaction coefficients have been used to account for the interactions between methyl esters [11] and the same occurs for diesel-biodiesel blends [4,12,13]. However, for alcohol blends with diesel and biodiesel fuels, species interact strongly between them and interaction parameters obtained from experimental data are needed to correct the ideal model [14]. For this reason, in this study, the viscosity of butanol and ethanol blends with diesel and biodiesel fuels have been measured and modeled using the correlations proposed by Arrhenius [15], Kendall-Monroe [16], Bingham [17], Grunberg-Nissan [18] and McAllister [19]. Other n-alcohols were also tested to propose a correlation for the interaction coefficient of the Grunberg-Nissan equation.

2. Experimental procedure and fuels

2.1. Fuel properties and blends

The main characteristics of pure alcohols and reference fuels (diesel and biodiesel) are shown in Table 1.

Diesel fuel used for this study was supplied by Repsol (Madrid, Spain) and it follows the European standard EN 590 [27]. It has no oxygen content and its main properties fall in the range of most of the diesel fuels supplied by petrol stations in Europe in winter. The biodiesel fuel was donated by Bio Oils (Huelva, Spain). It was produced from soybean oil (around 80%) and palm oil (around 20%) and it fulfills the European standard EN 14214 [28]. The methyl ester profile of the biodiesel fuel tested is shown in Table 2. Its saturated-ester content amounts 20.64%, which is not far from an average saturation content of biodiesel fuels used in Europe and

the iodine number amounts 119 which is slightly below the upper limit established in standard EN 14214 [28]. In this table the number of carbon atoms of the acid chain (n) and the number of double bonds (db) is indicated. Although both diesel and biodiesel fuels, as any other commercial fuel, are batch-dependent, they were selected to represent the typical winter diesel and biodiesel fuels used in Europe to be further blended in order to comply with the renewable energy targets in European transport. Butanol was supplied by Green Biologics Ltd., as a member of the Consortium of ButaNexT Project (see aknowledgements) and methanol, ethanol, propanol and pentanol were purchased from PanReac AppliChem. All the properties were measured in the authors' laboratory except purities (for alcohols) and mono-, di- and triglycerides, and glycerol contents (for the biodiesel fuel), which were measured by the supplying companies.

For this study, blends with diesel and biodiesel as reference fuels have been tested. Diesel blends with alcohol (ethanol or n-butanol) at 2.5%, 5%, 7.5%, 10%, 15%, 20%, 30%, 40%, 50%, 75% (volume basis), and biodiesel blends with alcohol (ethanol or n-butanol) at 2.5%, 5%, 10%, 20%, 40% and 75% (volume basis) were tested. Most of the blends were defined with low alcohol content because the low cetane number of high alcohol-content blends is unfeasible in diesel engines. No stabilizing additives were used in any of the blends. The use of additives would be expected to modify the viscosity trends observed hereinafter as far as they improve the miscibility of the blends.

Furthermore, to obtain an equation for modeling the viscosity of alcohol-biodiesel blends, additional biodiesel blends with other n-alcohols (methanol, propanol and n-pentanol) at 2.5%, 5%, 10%, 20%, 40%, 75%, 90% and 95% (volume basis) were tested.

2.2. Equipment

The kinematic viscosity of the blends was measured at 40 °C following the EN ISO 3104 standard. Every experiment was replicated twice, and the standard desviation was ±0.008 cSt. Cannon-Fenske viscosimeters were used in order to measure the kinematic viscosity of blends. The temperature was maintained at 40 °C, according to standard EN ISO 3104, for all samples using a thermostatted bath Tamson TV 2000 purchased from Fisher Scientific.

2.3. Equations for viscosity modeling

The equations used for modeling the viscosity of the liquid mixtures tested are summarized in Table 3, where x_i, z_i, ρ_i and υ_i are the mole fraction, volume fraction, density and kinematic viscosity, respectively, of component i (i = 1 or 2) in the binary blends.

Linear, Arrhenius, Kendall-Monroe and Bingham equations predict the viscosity of binary mixtures without using any adjustable parameter. Linear equation is the application of the Kay's mixing rule (i.e., mole fraction average) to the dynamic viscosity. Arrhenius equation is a logarithmic-scale average of the dynamic viscosities. Kendall-Monroe equation estimates the viscosity as a

Table 1
Properties of the fuels used for blends.

Properties	Method	Diesel	Biodiesel	Methanol	Ethanol	Propanol	Butanol	Pentanol
Purity (%, v/v)		–	–	99.8	99.5	99.5	99.5	98
Density at 15 °C (kg/m3)	EN ISO 3675	842.0	883.5	791.3	792.0	803.7	811.5	814.8
Kinematic viscosity at 40 °C (cSt)	EN ISO 3104	3.00	4.19	0.58	1.13	1.74	2.27	2.89
Gross heating value (MJ/kg)	UNE 51123	45.77	40.19	22.31	29.67	33.52	36.11	37.60
Lower heating value (MJ/kg)	UNE 51123	42.93	37.64	19.58	26.84	30.63	33.20	34.65
C (wt%)		86.74	77.08	37.48	52.14	59.96	64.86	68.13
H (wt%)		13.26	11.91	12.58	13.13	13.42	13.51	13.72
O (wt%)		0	11.00	49.93	34.73	26.62	21.62	18.15
Water content (mg/kg)	EN ISO 12937	41.70	352.10	1382	2024	309	1146	2970
Molecular weight (kg/kmol)		208.20	291.26	32.04	46.07	60.09	74.12	88.15
Boiling point (°C)	ASTM D86	149–385	190–340	64.7	78.37	97.1	117.4	137.9
Freezing point (°C)				−97.7	−114.1	−126.2	−89.8	−78.9
Standard enthalpy of vaporization (kJ/kg)			353.56[a]	1237.96[a]	943.78[a]	748.28[a]	619.82[a]	542.35[a]
Stoichiometric fuel/air ratio		1/14.51	1/12.50	1/6.47	1/9.01	1/10.35	1/11.15	1/11.77
CFPP (°C)	EN 116	−20	−1					
Cloud Point (°C)	EN 23015	−4.3	1.9					
Pour Point (°C)	ASTM D97	−21	0					
Lubricity (WS1.4) (μm)	EN ISO 12156–1	371	143	1100	966	624	529	670.5
Filterability	ASTM D2068	1.02	2.35		1.00		1.00	
Derived cetane number	ASTM D7668-14	52.65	52.48	5[b]	8[c]	12[d]	15.92	18.2[e]
Mono/di/triglyceride content (% m/m)	EN 14105		0.26/0.10/0.05					
Free/total glycerol content (% m/m)	EN 14105		0.009/0.096					

[a] Estimated from the corresponding-state correlation proposed by Pitzer [20] with modified exponents as proposed in [21];
[b] taken from references [22,23];
[c] taken from references [24,25];
[d] taken from reference [25];
[e] taken from reference [26].

Table 2
Methyl ester profile of biodiesel.

Methyl ester	Cn:db	%w/w
Lauric	C12:0	0.03
Myristic	C14:0	0.21
Palmitic	C16:0	15.62
Palmitoleic	C16:1	0.11
Margaric	C17:0	0.08
Margaroleic	C17:1	0.04
Stearic	C18:0	3.77
Oleic	C18:1	26.22
Linoleic	C18:2	47.26
α-linolenic	C18:3	5.39
Arachidic	C20:0	0.37
Gadoleic	C20:1	0.25
Behenic	C22:0	0.40
Lignoceric	C24:0	0.16

cubic average of the dynamic viscosities. Finally, Bingham proposed an inverse mixing law. Differently to the mentioned mixing rules, Grunberg-Nissan equation uses one interaction parameter to estimate changes in the dynamic viscosity of binary liquid mixtures caused by molecular interactions.

The McAllister viscosity equation used for liquid mixtures is based on Eyring's theory of absolute reaction rates. McAllister's three-body interaction model is applicable for liquid mixtures in which two different types of molecules interact between them in one plane. This type of interactions is simulated in the model with an equation including two interaction parameters. However, if the two types of molecules in the blend are different in size (radius) by more than a factor of 1.5 (as it is the case of the blends studied here), considering more complex equations may become necessary. With this aim, the four-body interaction model from McAllister was also tested. This model uses three interaction parameters and considers multiple molecular interactions, not simply in a plane but in a three-dimensional space.

3. Results and discussion

3.1. Experimental results

As shown in Fig. 1, viscosity values decrease when alcohol content increases in all cases. The reduction is more significant for alcohols with shorter carbon chain (ethanol). This decreasing trend is not linear with respect to the volumetric, mass or molar content.
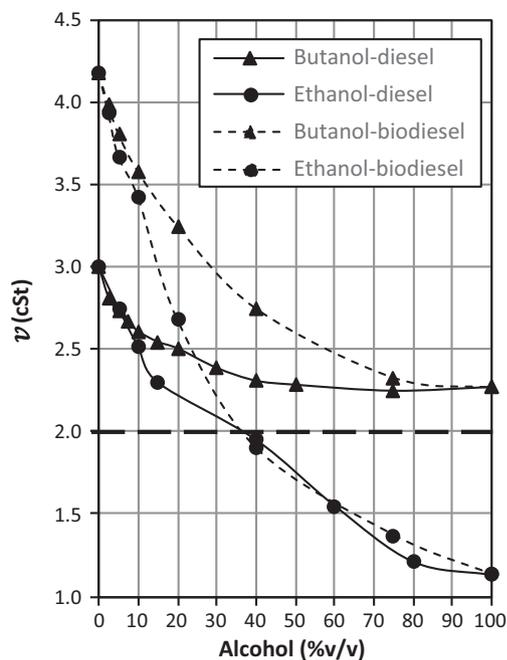
Table 3
Viscosity modeling equations.

Model	Ref	Equation
Linear		$\upsilon = \frac{x_1 \upsilon_1 \rho_1 + x_2 \upsilon_2 \rho_2}{z_1 \rho_1 + z_2 \rho_2}$
Arrhenius (1887)	[12]	$\upsilon = \frac{10^{[x_1 \log(\rho_1 \upsilon_1) + x_2 \log(\rho_2 \upsilon_2)]}}{z_1 \rho_1 + z_2 \rho_2}$
Kendall-Monroe (1917)	[13]	$\upsilon = \frac{(x_1(\upsilon_1 \rho_1)^{1/3} + x_2(\upsilon_2 \rho_2)^{1/3})^3}{(z_1 \rho_1 + z_2 \rho_2)}$
Bingham (1914)	[14]	$\upsilon^{-1} = (z_1 \rho_1 + z_2 \rho_2)\left(\frac{x_1}{\rho_1 \upsilon_1} + \frac{x_2}{\rho_2 \upsilon_2}\right)$
Grunberg-Nissan (1949)	[15]	$\upsilon = \frac{\exp(x_1 \ln \rho_1 \upsilon_1 + x_2 \ln \rho_2 \upsilon_2 + x_1 x_2 G_{12})}{z_1 \rho_1 + z_2 \rho_2}$
MacAllister-3B (1960)	[16]	$\ln(\upsilon) = x_1^3 \ln \upsilon_1 + 3x_1^2 x_2 \ln \upsilon_{12} + 3x_1 x_2^2 \ln \upsilon_{21} + x_2^3 \ln \upsilon_2 - \ln\left[x_1 + x_2 \frac{M_2}{M_1}\right] + 3x_1^2 x_2 \ln\left[\frac{2}{3} + \frac{M_2}{3M_1}\right] + 3x_1 x_2^2 \ln\left[\frac{1}{3} + \frac{2M_2}{3M_1}\right] + x_2^3 \ln\left[\frac{M_2}{M_1}\right]$
MacAllister-4B (1960)	[16]	$\ln(\upsilon) = x_1^4 \ln \upsilon_1 + 4x_1^3 x_2 \ln \upsilon_{1112} + 6x_1^2 x_2^2 \ln \upsilon_{1122} + 4x_1 x_2^3 \ln \upsilon_{2221} + x_2^4 \ln \upsilon_2 - \ln\left[x_1 + x_2 \frac{M_2}{M_1}\right] + 4x_1^3 x_2 \ln\left[\frac{3}{4} + \frac{M_2}{4M_1}\right] +$ $6x_1^2 x_2^2 \ln\left[\frac{1}{2} + \frac{M_2}{3M_1}\right] + 4x_1 x_2^3 \ln\left[\frac{1}{4} + \frac{3M_2}{4M_1}\right] + x_2^4 \ln\left[\frac{M_2}{M_1}\right]$

Fig. 1. Viscosity for alcohol-diesel and alcohol-biodiesel blends (horizontal line indicates the lower limit established in EN-590 for diesel blends).

In the case of ethanol-diesel blends with ethanol contents from 15% up to 80%, the viscosity is affected by their poor miscibility, which leads to a gel formation, thus increasing viscosity close to the values of ethanol-biodiesel blends with the same ethanol content range.

According to the diesel fuel standard (EN 590) [27], requiring viscosity values higher than 2 cSt, only ethanol blends with alcohol content lower than 36% (volume basis) fulfill this requirement. However, the whole range of butanol blends fulfills this standard (see horizontal dashed line in Fig. 1). In some cases, due to the interaction between alcohol and diesel, some synergistic effects are observed. In fact, diesel blends with high butanol content have lower viscosity values than pure butanol [29].

The use of biodiesel as base fuel increases the viscosity values of the blends, consistently with the higher viscosity of biodiesel,

which has been reported to increase in a non-linear manner with the biodiesel content in biodiesel-diesel blends [12,30].

3.2. Modeling results

3.2.1. Comparison of equations

Optimal modeling for different equations has been obtained with MS Excel Solver. Linear equation models the mixture viscosity weighting with mole fraction. As observed in Fig. 2, where volume fraction is represented instead, this fit is weak, which proves that the viscosity trend is not linear with the molar content.

Other models such as Arrhenius, Bingham and Kendall-Monroe were used to quantitatively analyse the interactions and to model viscosity [31]. However, since these equations have no interaction parameters, they do not predict accurately the viscosity of binary blends [32].

Among the correlations used for predicting the viscosity of the blends tested, the Grunberg-Nissan equation for binary blends showed an accurate fit for butanol-diesel, butanol-biodiesel and ethanol-biodiesel blends. Nevertheless, the fit is not good enough for ethanol-diesel blends because the formation of a gelatinous phase, as a consequence of the weak miscibility between 15% and 80% of ethanol, hinders the internal mobility of the fluid, thus disrupting the expected trend.

As experimental data shows large deviation from ideal behavior for ethanol-diesel blends, other equations with a larger number of interaction parameters such as the three-body correlation proposed by McAllister should be used [19,33]. The three-body interaction model from McAllister has two interaction parameters. Despite the additional parameter, the fit achieved for ethanol-diesel blends using this model is only better than that achieved with Grunberg-Nissan for intermediate ethanol contents, but it is worse for low ethanol contents. Since only blends with limited ethanol content have interest for diesel engines to avoid excessive cetane number reduction [34], a different model should be used instead. Furthermore, when the difference between molecule sizes (radius) is higher than a factor of 1.5, an additional interaction parameter must be included to simulate interations in a three-dimensional space [19]. Only the four-body interaction model of McAllister, which has higher number of interaction parameters (three), achieves a reasonably good fit for ethanol-diesel blends, because it fits the model for low, high and intermediate concentrations of alcohol. Also in the case of alcohol-biodiesel blends the
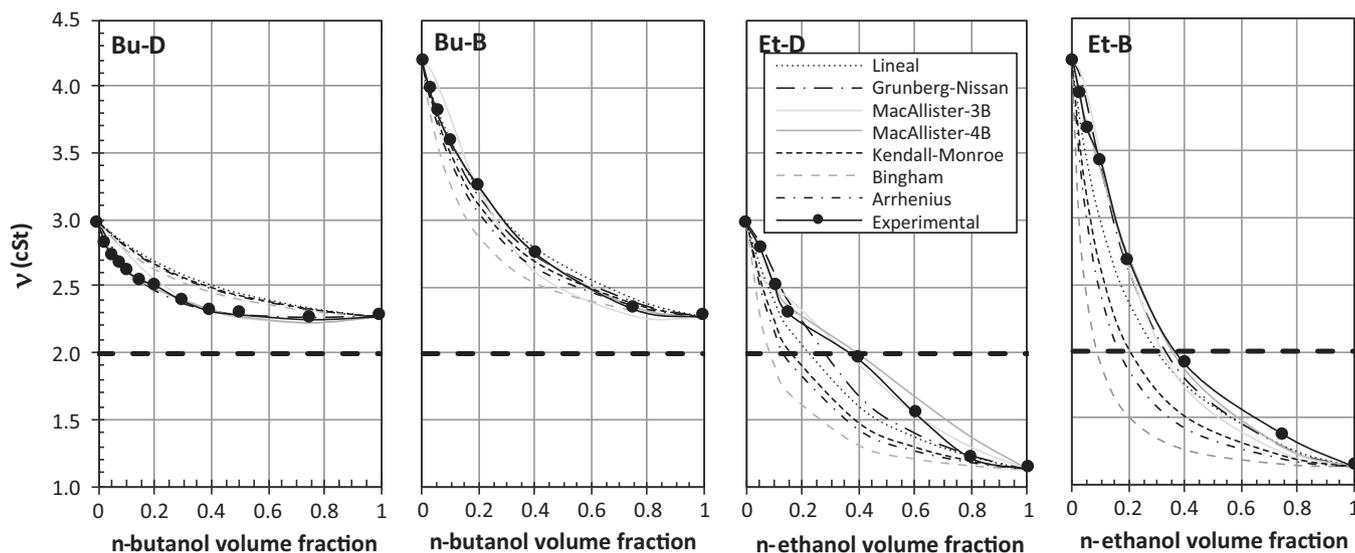

Fig. 2. Modeled viscosities for alcohol-diesel and alcohol-biodiesel blends.

four-body interaction model of McAllister provides the best fit. Similar conclusion has been obtained by other authors for blends of alcohols and esters [35].

The coefficient of determination (R^2) has been used to assess the adjustment achieved for each model (Table 4). Despite the best fit being achieved with the four-body interaction model of McAllister for all cases, the Grunberg-Nissan equation was selected as that providing the best compromise in general between the complexity and the accuracy of the modeling equation, and thus, it was used in the following section for modeling the viscosity of alcohol blends with diesel and biodiesel fuels.

3.2.2. Grunberg-Nissan equation

In the Grunberg-Nissan equation [18], the content of each component is quantified by its mole fraction, x_r for reference fuel (diesel or biodiesel) and x_i for alcohols, with $i = 2,4$ for ethanol and butanol, respectively. When the reference fuel is diesel fuel, x_r is replaced with x_d, and when it is biodiesel fuel, it is replaced with x_b. Eq. (1) defines the absolute viscosity of a blend (μ) following the Grunberg-Nissan equation for binary blends.

$$\ln \mu = x_r \ln \mu_r + x_i \ln \mu_i + x_r x_i G_{ri} \tag{1}$$

Despite some minor positive excess volume found in alcohol-ester solutions [35], the density of alcohol blends with diesel and biodiesel fuels (ρ) has been proven to vary approximately linearly with the alcohol volume fraction (z_i) [29,30]. Therefore, Eq. (1) was transformed into Eq. (2) to model the kinematic viscosity.

$$\nu = \frac{\exp(x_r \ln \rho_r \nu_r + x_i \ln \rho_i \nu_i + x_r x_i G_{ri})}{z_r \rho_r + z_i \rho_i} \tag{2}$$

Interaction coefficients providing an optimal adjustment of the kinematic viscosity are $G_{d2} = 0.85$ for ethanol-diesel blends, $G_{d4} = -0.32$ for butanol-diesel blends, $G_{b2} = 1.40$ for ethanol-biodiesel blends and $G_{b4} = 0.16$ for butanol-biodiesel blends.

The equation used to adjust the interaction coefficient for diesel blends was taken from Lapuerta, et al. [29]. The parameter n_i represents the number of carbon atoms in the alcohol molecule.

$$G_{di} = 0.11 n_i^2 - 1.242 n_i + 2.897 \tag{3}$$

To obtain a Grunberg Nissan equation for alcohol biodiesel blends, methanol, propanol and n-pentanol were also tested blended with biodiesel fuel. As shown Fig. 3, the viscosity is sharply reduced with a small content of any alcohol. This decreasing trend is not linear with respect to the volumetric, mass or molar content. The reduction is inversely proportional to the alcohol carbon chain, this trend being consistent with the viscosity of pure alcohols (Table 1). Some synergistic effect is observed for pentanol-biodiesel blends as a consequence to the interaction between pentanol and biodiesel molecules. Fig. 3 shows that blends with high pentanol content have lower viscosity values than pure pentanol.

The Grunberg Nissan interaction coefficients providing an optimal fit between measured and modeled viscosities are shown in
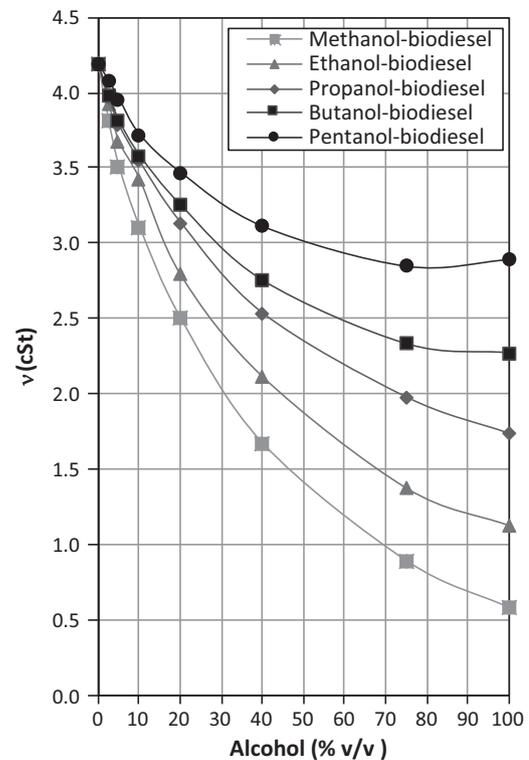
Fig. 3. Viscosity of alcohol-biodiesel blends.

Fig. 4. These coefficients were obtained for methanol, ethanol, propanol, n-butanol and n-pentanol blends with both reference fuels (diesel and biodiesel).

Alcohol's polarity is induced by the hydroxyl group (–OH), which is one of the most polar chemical groups, regardless the polarity index used [36]. In general, biodiesel fuels have lower mean polarity, with only the ester functional group (–COO–) providing polarity to the molecule while the aliphatic chain of the molecule is roughly non-polar. In alcohol-biodiesel blends, the polar group of both components attract each other and form permanent dipoles. Furthermore, the intensity of these interactions is enhanced by the formation of hydrogen bonds (attractive forces between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule) [37]. The diesel fuel is a complex mixture of different chemical compounds, from highly non-polar n-alkanes to moderately polar aromatic hydrocarbons. In alcohol-diesel blends, these aromatic structures may interact slightly with the hydroxyl group of the alcohol forming transient dipoles (intermolecular forces weaker than the hydrogen bond) [37]. Consequently, as shown in Fig. 4, positive Grunberg-Nissan coefficients are higher for alcohol-biodiesel blends than for alcohol-diesel blends because in the first ones, the attraction between the hydroxyl group of the alcohol

Table 4
R^2 coefficients of determination describing the quality of models for the viscosity of alcohol-diesel and alcohol-biodiesel blends.

R^2 coefficient	Blends			
Model	Butanol-diesel	Butanol-biodiesel	Ethanol-diesel	Ethanol-biodiesel
Linear	0.9052	0.9984	0.9475	0.9846
Arrhenius	0.9289	0.9900	0.8959	0.9074
Kendall-Monroe	0.9214	0.9950	0.9160	0.9417
Bingham	0.9491	0.9631	0.8134	0.7602
Grunberg-Nissan	0.9894	0.9978	0.9510	0.9944
MacAllister-3B	0.9649	0.9849	0.9757	0.9924
MacAllister-4B	0.9972	0.9998	0.9910	0.9988
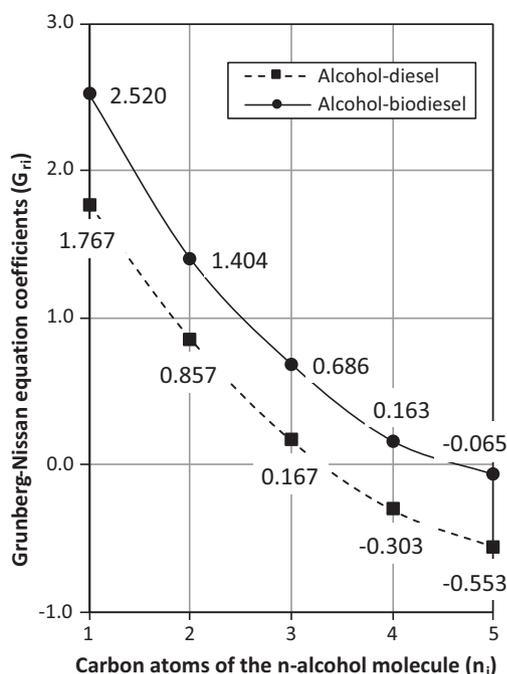
Fig. 4. Interaction coefficients for Grunberg-Nissan equation.

- Among the correlations used for predicting the viscosity of binary blends, Grunberg-Nissan equation shows an accurate fit for butanol-diesel, butanol-biodiesel and ethanol-biodiesel blends. However, this fit is not good enough for ethanol-diesel blends, where the formation of a gel disrupts the trend. The four-body interaction model of McAllister, with three interaction parameters, achieves a reasonably good fit for ethanol-diesel blends.
- Positive Grunberg-Nissan coefficients are higher for alcohol-biodiesel blends than for alcohol-diesel blends because the attraction between the hydroxyl group of the alcohol molecule and the carboxyl group of the biodiesel is stronger than that between the hydroxyl group and the aromatic hydrocarbons of diesel fuel. Interaction coefficients become negative for long-chain alcohol-diesel blends.
- Grunberg Nissan interaction coefficients decrease when the number of carbon atoms in the n-alcohol molecule increases for both diesel blends and biodiesel blends because when the chain length increases, the non-polar part of the molecule dominates against the hydroxyl group.
- A previous work, in which alcohol-diesel blends were modeled with Grunberg-Nissan equation, has been completed using the same type of second-order equation to model the Grunberg-Nissan interaction coefficients for alcohol-biodiesel blends.

Acknowledgements

molecule and the carboxyl group of the biodiesel fuel is stronger than that between the hydroxyl group and the aromatic hydrocarbons of diesel fuel.

Fig. 4 also shows that Grunberg Nissan interaction coefficients decrease when the number of carbon atoms in the n-alcohol molecule increases for both, diesel blends and biodiesel blends. When the alcohol chain length increases, the non-polar part of the molecule becomes increasingly dominant and, consequently, alcohols with high carbon chain lengths have lower Grunberg-Nissan interaction coefficients than alcohol with low carbon chain lengths. For alcohols with 5 carbon atoms, Grunberg-Nissan interaction coefficients become negative, and in this case, the interaction between alcohol-diesel blends becomes higher (higher absolute values for the interaction coefficient) than for alcohol-biodiesel blends. This could be explained because both large alcohols and diesel fuel have higher affinity as a consequence of their basically non-polar character.

Similarly as for alcohol-diesel blends, the interaction coefficients obtained for alcohol-biodiesel blends have also been fitted to a second order equation (Eq. (4)) where n_i is the number of carbon atoms in the alcohol molecule, leading to:

$$G_{bi} = 0.141n_i^2 - 1.486n_i + 3.851 \qquad (4)$$

From Eqs. (3) and (4) a good and fast estimation of the viscosity of blends of alcohols and diesel and biodiesel fuels can be achieved, which is useful for researchers, fuel producers and engine, pump and pipeline designers.

4. Conclusions

From this study, the following conclusions can be obtained:

- Viscosity values decrease when alcohol content (ethanol or butanol) increases for both, diesel and biodiesel blends. However, this decreasing trend is higher for ethanol blends.
- While only ethanol blends with alcohol content lower than 36% (volume basis) fulfill the diesel fuel standard (EN 590), the whole range of butanol blends fulfills this standard.

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