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TÍTULO DO TRABALHO:

Model Proposals for Biodiesel Viscosity, Cetane Number and Heat Capacity in Terms of its Raw Materials

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Resumo

Biodiesel pode ser produzido a partir de diferentes óleos e gorduras, e é notório que diferenças nos perfis graxos dessas matérias-primas têm impacto em suas propriedades finais. Viscosidade (μ), número de cetano (CN) e capacidade calorífica (C_P) são três propriedades fundamentais para o bom funcionamento dos sistemas de alimentação de combustível e sua combustão, e exemplos de propriedades que são afetadas pelo perfil graxo do material utilizado para sua produção. Desse modo, a elaboração de modelos capazes de predizer o valor dessas propriedades em função da matéria-prima de origem se faz de grande valia, pois permitiria nortear medidas de adequação desses combustíveis ao mercado de interesse, bem como eventuais adaptações nos sistemas de combustão, e possivelmente a formulação de políticas mais assertivas. Portanto, o objetivo deste trabalho foi a proposição de modelos para predição de viscosidade, número de cetano e capacidade calorífica de biodiesel em função da matéria-prima de origem. Para isso, foi construída uma base de dados experimentais da literatura e foi realizada uma revisão acerca de propostas de modelos para essas três propriedades. Em seguida, foram selecionados os modelos mais promissores da literatura para fins de comparação com os modelos gerados neste trabalho: um modelo completamente preditivo para μ; um modelo baseado em composição para CN; e um modelo de estados correspondentes para C_P. Quando possível, os parâmetros destes modelos também foram reestimados para permitir uma análise mais justa dos resultados. A partir do conhecimento adquirido nestas etapas, foram propostas correlações em termos de grau de insaturação, fator acêntrico e temperatura crítica das moléculas constituintes do biodiesel de cada tipo, sendo as duas últimas propriedades calculadas por contribuição de grupos. Os parâmetros dos modelos foram estimados com metodologia Monte Carlo, e os modelos finais foram avaliados em termos de desvio padrão, erro médio absoluto e percentual, erro quadrático médio e teste χ^2. Como resultado, obteve-se erros médios percentuais de 10,33%, 2,62% e 1,18% para μ, CN, e C_P, respectivamente, com os modelos desenvolvidos, o que em todos os casos significou uma melhora com relação aos modelos da literatura originais e reajustados. Entretanto, os resultados obtidos no teste χ^2 apontam no sentido do desenvolvimento contínuo destes modelos, de modo que se possa evitar superparametrização. Estes resultados são aqui apresentados para que se possa promover o debate acerca das propostas apresentadas, visando a obtenção de formatos práticos para aplicação após desenvolvimento adicional.

Palavras-chave: biodiesel, composição, propriedades, estimação de parâmetros.

Abstract

Biodiesel can be produced from several oils and fats, and it is clear that differences in their fatty acid profiles have an impact on its final properties. Viscosity (μ), cetane number (CN) and heat capacity (C_P) are three fundamental properties for the proper functioning of fuel feeding and combustion systems, and examples of properties that are influenced by the fatty acid profile of the raw material used for its production. Therefore, the development of models for the prediction of these properties as a function of the raw material of origin is of great value, as it would allow guiding measures to adapt these fuels to the market of interest, as well as possible adaptations in the combustion systems, and possibly the formulation of more assertive policies. In this sense, the objective of this work was to propose models for predicting viscosity, cetane number and heat capacity of biodiesel in terms of its raw materials. For this, an experimental database from the literature was built and a review of model proposals for these three properties was carried out. Then, the most promising models from the literature were selected for

comparison with the models generated in this work: a completely predictive model for μ; a composition-based model for CN; and a corresponding states model for C_P. When possible, the parameters of these models were also re-estimated to allow a fairer comparison. Based on the knowledge acquired in these preliminary stages, correlations were proposed in terms of degree of unsaturation, acentric factor and critical temperature of the constituent molecules of the biodiesel of each type, with the last two properties being calculated through group contribution. The model parameters were estimated using a Monte Carlo methodology, and the final models were evaluated in terms of standard deviation, mean absolute and percentage error, mean squared error and χ^2 test. As a result, mean percentage errors of 10.33%, 2.62% and 1.18% were obtained for μ, CN, and C_P, respectively, with the developed models, which in all cases meant an improvement in relation to the original and readjusted literature models. However, the results obtained in the χ^2 tests point towards the continuous development of these models, so that overparameterization can be avoided. These results are presented here so that a debate can be promoted about the presented proposals, aiming to obtain practical formats for application after further development.

Keywords: biodiesel, composition, properties, parameter estimation.

Introduction

In a continental country like Brazil, the possibility of producing biodiesel from different raw materials is an important advantage, as this way the supply chain can be guaranteed in any region and at any time of the year, making use of alternatives that appear to be more competitive. However, the physicochemical properties of biodiesel, such as thermal capacity, cetane number and viscosity, may vary depending on the composition of the raw material used for its production and, evidently, this has an impact on both its application and regulation. For this reason, it is convenient to have assertive models for predicting these properties as a function of its raw materials.

Viscosity is a measure of friction in the internal layers of a fluid, which tends to oppose any dynamic variation in movement (POLING; PRAUSNITZ; O'CONNELL, 2004). It is a critical property because it affects injection behavior in diesel engines, so that high viscosities promote the formation of larger droplets with less vaporization, leading to poor combustion, with greater emissions (SAXENA; JAWALE; JOSHIPURA, 2013). Cetane number is a parameter used to measure ignition delay and the quality of combustion. The higher cetane number of biodiesel, compared to that of petroleum diesel, indicates that biodiesel is consumed in more efficient way, in addition to providing equal or greater power and torque than conventional diesel (BAJPAI; TYAGI, 2006). Heat capacity is a measure of the amount of energy required by a unit of matter of a substance to increase its temperature by one degree. This property is of great importance in the development of processes that involve heat transfer, such as the distillation and heating/cooling stages of biodiesel production (CERIANI; GANI; MEIRELLES, 2009). Therefore, its determination is fundamental in order to estimate the amount of energy in the production process - with effects also on fuel combustion -, especially in a scenario of increasing interest in quantifying its carbon footprint (i.e., RenovaBio).

There are several mathematical models capable of predicting the aforementioned properties of biodiesel, as a function of the fatty profile of the raw material used for its production. However, a robust bibliographical review, presented by Cardoso and da Fonseca (2023), demonstrated that there is a set of properties (namely the degree of unsaturation, the acentric factor and the critical temperature) that seem

to lead to better results in predicting the various properties of biodiesel, and they have never been tested together for these three specific properties.

Therefore, the objective of this work is to propose new models as a function of the degree of unsaturation, the acentric factor and the critical temperature of biodiesel. The proposed models were compared with some of the most successful models in the literature for each property. For this, the parameters of the proposed models and literature models were adjusted in an equivalent way, based on literature experimental data on biodiesel obtained for different types of oils and fats. Thus, it was possible to reproduce in these models the influence of their main constituents - via group contribution - , in addition to the evaluated input properties.

Methodology

The work started with a literature review of the types of models available for calculating each property. For viscosity, fully or partially predictive models can be found - in the latter case, the models require knowledge of the viscosity value at a reference temperature. For cetane number, it is possible to list compositional models, models based on properties of the fatty acid compounds - such as, for example, degree of unsaturation (DU) and chain length (CL) or molecular weight (MW) -, and models based on the cetane numbers of the pure species. And for heat capacity of the liquid phase, the models can be classified in theoretical models, thermodynamic cycle models, models based on the Principle of Corresponding States, and group contribution models. This complete review can be accessed in Cardoso and da Fonseca (2023). The thermodynamic determination of viscosity and heat capacity was also discussed in this reference, but was not subject of study in this work.

As a representative model from the literature for biodiesel dynamic viscosity, we selected the model by Ferreira et al. (2021), which is a fully predictive model:

$$\mu^{-0.65} = \mu_1^{-0.65} + \mu_2 T$$

$$\mu_1 = A + B.exp(C.DU) \qquad (1)$$

$$\mu_2 = D + E.exp(F.DU)$$

where DU is the degree of unsaturation of the biofuel, and A - F are the adjustable parameters. In this equation, temperature must be entered in K and the viscosity is obtained in mPa.s.

Among all the models evaluated for cetane number, we selected the model by Giakoumis and Sarakatsanis (2018), which is a compositional model:

$$CN = A + Bx_1 + Cx_2 + Dx_3 + Ex_4 - Fx_5 + Gx_6 - Hx_7 - Ix_8 \qquad (2)$$

where x_1 - x_8 are the mass fractions of the lauric, miristic, palmitic, estearic, palmitoleic, oleic, linoleic, and linolenic compounds, respectively, and A - I are the adjustable parameters.

And among the models evaluated for heat capacity, the model by do Carmo et al. (2020) - based on the Principle of Corresponding States - was selected:

$$\frac{C_P - C_P^{IG}}{R} = 1.586 + \frac{0.49}{1 - T_r} + \omega \left[A + \frac{B\left(1 - T_r\right)^{\frac{1}{3}}}{T_r} + \frac{C}{1 - T_r} \right] \qquad (3)$$

where R is the ideal gas constant, C_P^{IG} is the heat capacity of an ideal gas, the first two terms on the right-hand side refer to the simple fluid contribution, T_r is reduced temperature ($T_r = T/T_c$), ω is the acentric factor, and A - C are the adjustable parameters.

These models were evaluated in this work, when possible, both in their original form and with readjusted parameters, to allow a fair comparison with the proposed correlations. The values of the adjustable parameters of these models can be seen in Table 1. In this work, it was not possible to re-estimate the parameters of the Ferreira et al. (2021) model for biodiesel viscosity, because difficulties were found and were attributed to the exponential character of the model. To re-estimate the parameters of the model by do Carmo et al. (2020), the R value used was 8.3144621 $J.mol^{-1}.K^{-1}$, the T_r and ω values were calculated using the Constantinou-Gani group contribution method, while the C_P^{IG} values were obtained from the authors' work

Table 1 - Parameters of the literature models

Model		Parameters								
		A	B	C	D	E	F	G	H	I
μ - Ferreira et al. (2021)	Original	-1.4238	-0.6132	-2.6668	0.0059	0.0029	-3.4216			
	This work	-	-	-	-	-	-			
CN - Giakoumis & Sarakatsanis (2018)	Original	55.8700	0.0747	0.0980	0.1640	0.1760	-0.0500	0.0010	-0.1400	-0.2730
	This work	54.9005	0.5322	0.6140	1.1675	1.1671	-0.8062	1.1770	-1.1813	-0.9649
C_P - do Carmo et al. (2020)	Original	4.3164	5.5558	0.0506						
	This work	9.3673	5.1739	0.9862						

The second step of the methodology consisted of building an experimental database from the literature. This data was compiled into a Microsft Excel® spreadsheet, which can be provided to an interested reader. In total, this work encompassed 822 experimental points, divided for the three properties. 60% of the experimental data for viscosity and cetane number was used as model adjustment set, totaling 200 experimental points out of a total of 333 for μ, and 30 experimental points out of a total of 50 for CN. For C_P, the same adjustment set was used as in the work of do Carmo et al. (2020), representing 95 experimental points out of 439 compiled. Care was taken to avoid the formation of a bias towards FAMEs or FAEEs (fatty acid methyl esters and fatty acid ethyl esters, respectively). The remaining data was used to validate the models.

After that, we proceeded with an analysis of the literature models to define the physicochemical properties of biodiesel that should correlate with the three properties of interest in this work. Firstly, it was decided to use the degree of unsaturation (DU), which is directly obtained in terms of the biofuel composition and is very present in the literature models. Additionally, acentric factor (ω) and critical temperature (T_c) were added to the group. These are justified because they can be easily calculated for all types of biodiesel - via group contribution - and can be seen as complementary information to DU (chain size, polarization, criticality).

Then, the experimental data from the literature for μ, CN and C_P was plotted against DU, ω and T_c of the respective biofuels, in order to observe some type of correlation between these properties. The results can be seen in Figures 1 - 3. For μ, as it was decided since the beginning to proceed with an exponential format, only the way in which temperature should be inserted into the model was evaluated.

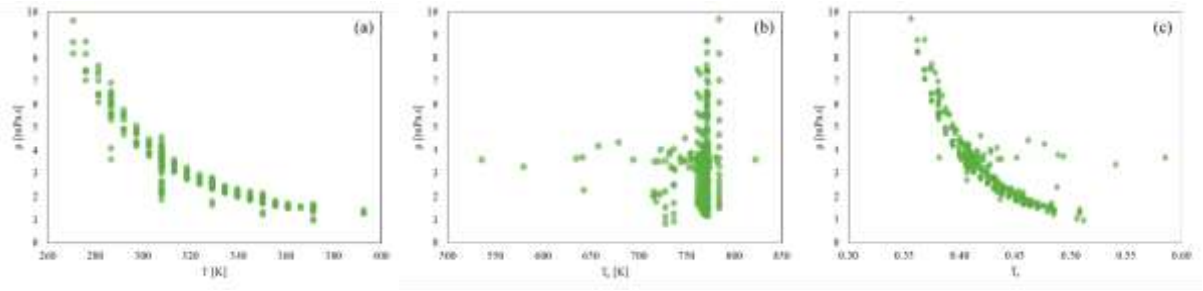

Figure 1 - Visual correlation between μ and: (a) T; (b) T_c; (c) T_r

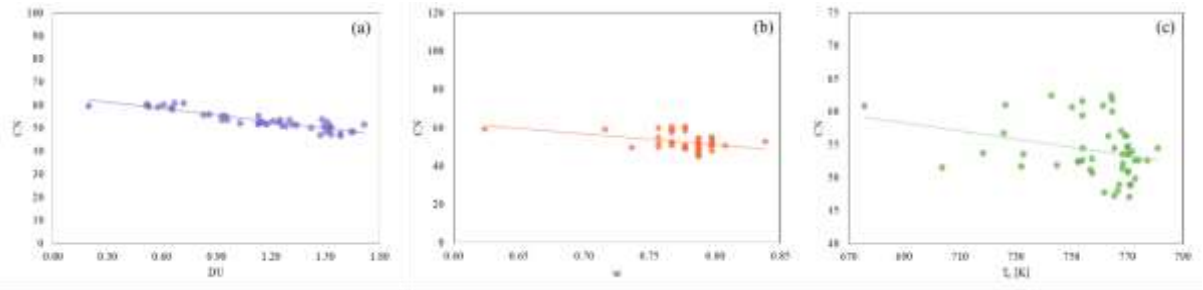

Figure 2 - Visual correlation between CN and: (a) DU; (b) ω; (c) T_c

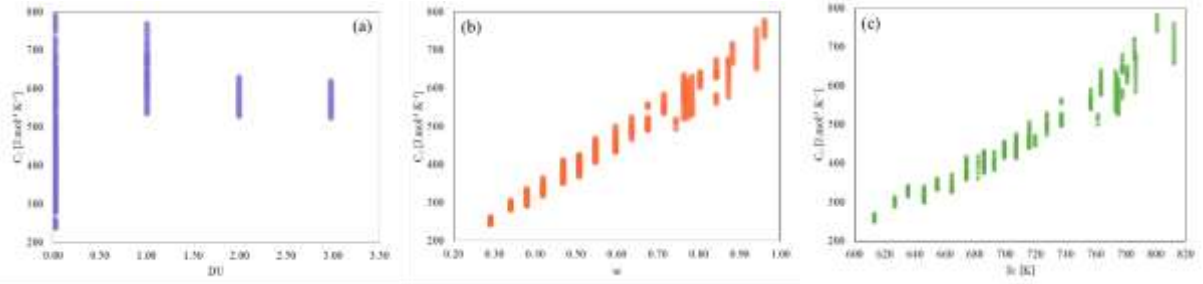

Figure 3 - Visual correlation between C_P and: (a) DU; (b) ω; (c) T_c

From the observation of the behaviors shown in Figures 1 - 3 and after some algebraic development, based on model proposals from the literature - and whose complete explanation can be found in Cardoso and da Fonseca (2023) -, the following proposals for new models were made:

$$ln\,\mu = A + B\,DU + \frac{C}{T} + D\,\frac{\omega}{T} \qquad (4)$$

$$CN = A - B\,DU - C\,T_c - D\,\omega \qquad (5)$$

$$C_P = A\left[\frac{\omega^{1.9}{T_r}^{\frac{1}{3}}}{\left(1-{T_r}^2\right)}\right]^B \qquad (6)$$

where A - D are the parameters to be adjusted. In these equations, temperature must be entered in K, viscosity is obtained in mPa.s, and heat capacity is obtained in $J.mol^{-1}.K^{-1}$. It should be noted that, with these formats, the number of parameters in each model is always lower than that of the literature models that are being used for comparison.

The parameters of all the models were estimated with a Monte Carlo methodology, aiming to minimize the following objective function:

$$F_{obj} = \frac{1}{N}\sum_{i=1}^{N}(y_i^E - y_i^C)^2 \qquad (7)$$

where N is the number of data points (experimental points) evaluated, y_i^E is the experimental value of the response variable, and y_i^C is the calculated value of the response variable. Here, the response variables are the evaluated biodiesel properties.

In addition to the mean squared error (MSE), in this work, standard deviation (θ), mean absolute error (MAE) and mean percentage error (MPE) were also evaluated for each model, and a χ^2 test was performed to evaluate the suitability of the models to the experimental data (SCHWAAB; PINTO, 2007). These metrics were applied to the portion of the data that was not used for model development, called validation set.

Results and Discussion

Table 2 shows the parameter values obtained for the models proposed in this work, and the results obtained for all models can be seen in Table 3.

Table 2 - Parameters of the proposed models

Model	Parameters						
	A	B	C	D	E	F	G
μ	-5.2812	-0.0844	1525.0300	755.3700			
CN	70.2755	11.4332	0.0011	2.0204			
C_P (version A)	834.8406	0.5164					
C_P (version B)	9.3673	5.1739	0.9862	-5.7855	4.1783	-1.9890	0.0350

The analysis of the μ prediction models over the validation set reveals that the model proposed in this work resulted in values of θ, MAE, MPE and MSE similar to those obtained with the model by Ferreira et al. (2021), although with a smaller number of parameters: 4 *vs* 6. It is concluded that the application of an exponential function appears to be quite reasonable for both T, DU and ω. Furthermore, the relationship between T and ω, accounted for in the last term of the developed model, appears to be appropriate. The model generated is less complex than that of Ferreira et al. (2021), facilitating

application. However, the χ^2 test resulted in values significantly below minimum for both models - in other words, a much better fit than expected due to the experimental error -, indicating that both formats may be overparameterized. This would justify an effort to further simplify the model.

Table 3 - Results

	Metric	Literature (original)	Literature (adjusted)	This work (A)	This work (B)
μ	θ	0.0300		0.0300	
	MAE	0.1100		0.1000	
	MPE	10.70%		10.33%	
	MSE	0.107		0.1033	
	χ^2 test	Reproved		Reproved	
CN	θ	1.0030	0.8803	0.4112	
	MAE	3.8307	3.3326	1.3699	
	MPE	7.37%	6.37%	2.62%	
	MSE	20.1215	15.4997	3.3822	
	χ^2 test	Reproved	Reproved	Reproved	
C_P	θ	1.2907	0.4459	0.6868	0.4224
	MAE	22.7565	5.9093	7.7618	5.6615
	MPE	4.82%	1.21%	1.51%	1.18%
	MSE	573.0928	68.3912	162.2727	61.3820
	χ^2 test	Approved	Reproved	Reproved	Reproved

For CN, the analysis reveals that the model proposed in this work resulted in values of θ, MAE, MPE and MSE lower than those obtained with the model by Giakoumis and Sarakatsanis (2018), both in its original and readjusted versions, indicating greater accuracy. And this was possible even with a significant reduction in the number of parameters, from 9 to 4. However, as for viscosity, the evaluation of the χ^2 test demonstrates the inadequacy of all the models evaluated, also in the direction of overparameterization. For the literature models, this result suggests that the consideration of the mass fraction of one or more FAME could be removed. In the model developed in this work, the analysis is more difficult, as a linear relationship with all variables was assumed. As it is less evident than for the other properties - Figure 2 -, it is suggested to remove or reevaluate the contribution of T_c to obtain a model that respects the quality limits established by the χ^2 test.

And finally, for C_P (version A, Equation 6), the results demonstrate that there was an improvement in relation to the original model by do Carmo et al. (2020), albeit with a reduction from 3 to 2 parameters. But there was a worsening in relation to the literature model readjusted over the database of this work. For this reason, we proceeded with the proposal of a second model for C_P:

$$C_P = \left\{1.586 + \frac{0.49}{1 - T_r} + \omega\left[\mathrm{A} + \frac{\mathrm{B}\left(1 - T_r\right)^{\frac{1}{3}}}{T_r} + \frac{\mathrm{C}}{1 - T_r}\right]\right\} R + C_P^{IG} + D\left[\frac{\omega^{1.9} {T_r}^{\frac{1}{3}}}{(1 - {T_r}^2)}\right]^{\mathrm{E}} + F.\mathrm{DU}\left[\frac{\omega^{1.9} {T_r}^{\frac{1}{3}}}{(1 - {T_r}^2)}\right]^{G} \quad (8)$$

The idea was simply to evaluate whether the relationship between C_P, ω and T_r presented in Equation 6 would contribute to a better fit. In fact, this new model (version B) obtained better results than the readjusted literature model, but at the expense of the inclusion of five additional parameters. As the χ^2 test indicated overparameterization for all models except the original one from the literature, additional effort is needed to develop a simpler format for predicting heat capacity as a function of the intended properties. Ultimately, it can also be concluded that the model by do Carmo et al. (2020) -

whose theoretical foundation is more rigorous than that of the models by Ferreira et al. (2021) and Giakoumis and Sarakatsanis (2018) - is a well-constructed model, although adjusting its parameters to a larger data set contributed to its improvement.

Conclusion

The models proposed in this work for viscosity, cetane number and heat capacity of biodiesel resulted in significant improvements in comparison to the literature models, especially when taking into account the reduction in the number of parameters and the associated complexity. However, the analysis of statistical metrics indicated that the development of new correlations is by no means finished. In any case, this work contributes to the enrichment of discussions regarding the calculation of these properties, since we investigated and could discern the effect of the most important variables in each case. At the end of the development process, it is important to obtain correlations with a practical format for application in the systems of interest. This must always be the goal.

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