Ultrasonic characterisation of soybean biodiesel produced from different molar ratios

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Abstract. The ultrasonic characterisation of soybean biodiesel produced from different alcohols and molar ratios was performed at 1 MHz. The measurement of the speed of sound of the biodiesel samples was performed using the pulse-echo technique. It was possible to observe that samples of biodiesel produced from different alcohols under the same molar ratio present a non-equivalent speed of sound. Samples produced at a molar ratio of 6:1 have the lowest speed of sound. The ultrasound could differentiate the biodiesel samples evaluated through the speed of sound parameter.

1. Introduction

The global search for alternative energy sources to supply energy demand in the industrial and transport sectors has promoted excessive growth in the production of biofuels. Biodiesel is an alternative fuel similar to conventional diesel, being as less environment-damaging [1]. Also known as fatty acid methyl ester (FAME), it can be produced from animal fat, vegetable oil and waste oil through transesterification [2].

Quality control of the produced biodiesel is essential. Some physical properties influence this quality of the fuel and, consequently, the injection process and engine efficiency [3][4]. Thus, to guarantee the efficiency of the engine's injection timing and combustion rate, the fuel must meet the pre-established specifications in quality standards[5][6]. It is essential to identify compositional variations of biodiesel to ensure compliance with regulatory specifications.

In recent years, ultrasound technique has been extensively used to monitor chemical reactions and characterise liquids. In this sense, papers have been published on the characterisation of fluids such as oils [7][8][9] and biodiesel [10][11][12] by ultrasound. Studies report the ultrasound characterisation of biodiesel produced from different sources of oils and fats. However, no studies were found that evaluated the influence of the molar ratio and the type of alcohol on the speed of sound of the produced biodiesel. Including measurement uncertainty and normalised error provide enough reliability to differentiate biodiesel samples [9][10].

This work aims to evaluate the speed of sound of biodiesels produced from different alcohols (methanol and ethanol) using the molar ratios of 6:1, 8:1 and 10:1. Speed of sound measurements was performed at frequency of 1 MHz. The present work demonstrated the ultrasound technique as an alternative tool to evaluate different biodiesel types.

2. Materials and methods

2.1. Biodiesel samples

Biodiesel samples were produced through the transesterification of soybean oil. Methanol and ethanol were used in different molar ratios such as 6:1; 8:1 e 10:1, while KOH was used as catalyst at a fixed proportion of 1.5%. The temperature was maintained at 40 °C, and the mechanical stirring was at 400 rpm throughout the transesterification process. Table 1 shows the six routes used in this study to produce the biodiesel samples: I, II, III, IV, V and VI.

Table 1. Biodiesel samples.

Sample	Alcohol type	Molar ratio
I	Methanol	6:1
II	Methanol	8:1
III	Methanol	10:1
IV	Ethanol	6:1
V	Ethanol	8:1
VI	Ethanol	10:1

2.2. Speed of sound

The speed of sound (SoS) in biodiesel produced with different types of alcohol and different molar ratios (samples A, B, C, D, E and F) was measured at 1 MHz. The measurement of the speed of sound of the biodiesel samples was performed using the experimental setup described in [9][13]. The measurement setup includes a thermal bath, a cell containing the biodiesel sample, and an ultrasonic transducer of each frequency mentioned previously (NDT-Panametrics, Olympus Corporation, Japan). The ultrasonic transducer acted as a transmitter and a receiver and was excited through a wave generator model 33250A (Agilent Technologies, CA, USA). The acquired signals were digitised with an oscilloscope model DSO-X 3012A (Agilent Technologies, CA, USA) and transferred to a computer through a program developed in LabView (National Instruments, TX, USA). Five replicates were performed under repeatability conditions.

2.3. Uncertainty analysis

The expanded uncertainty was calculated according to the Guide of the Expression of Uncertainty in Measurements [12], with a coverage factor k that considers the t-distribution with probability of 0.95, and the effective degrees of freedom. The results of speed of sound and their respective uncertainties of the produced biodiesel were statistically compared by calculating the normalised error [14].

3. Results and discussion

The results of SoS for the investigated samples and their respective expanded (U) and relative (Urel) uncertainties obtained from five replications are presented in Table 2 and Table 3. When increasing the molar ratio from 6:1 to 10:1, the SoS did not show significant variation in all investigated samples. For the frequencies studied, the SoS values varied between 1422.1m·s^{-1} and 1417.7 m·s^{-1} for methyl biodiesel (I, II and III) and between 1409.6 m·s^{-1} and 1395.6 m·s^{-1} for ethyl biodiesel (IV, V and VI). The uncertainties found were lower than 2.1 m·s^{-1} (0.15 %). Table 4 shows the results of the normalised error to evaluate the equivalence between the results presented in Table 2 and Table 3.

Table 2. Speed of sound as a function of frequency for biodiesel samples produced with methanol and different molar ratios.

METHYL BIODIESEL			
Sample	SoS[m·s^{-1}]	U[m·s^{-1}]	U_{rel}[%]
I [6:1]	1417.7	1.8	0.13
II [8:1]	1422.1	1.8	0.12
III [10:1]	1419.8	1.6	0.11

Table 3. Speed of sound as a function of frequency for biodiesel samples produced with ethanol and different molar ratios.

ETHYL BIODIESEL			
Sample	SoS[m·s^{-1}]	U[m·s^{-1}]	U_{rel}[%]
IV [6:1]	1395.6	1.6	0.11
V [8:1]	1401.8	1.7	0.12
VI [10:1]	1409.6	1.6	0.11

Table 4 - Normalised error for methyl and ethyl biodiesel samples.

Frequency [MHz]	METHYL BIODIESEL			ETHYL BIODIESEL		
	E_n [I - II]	E_n [I – III]	E_n [II – III]	E_n [IV – V]	E_n [IV – VI]	E_n [V – VI]
1	1.7	0.88	0.93	4.9	8.5	3.4

From Table 4, it is observed that at a frequency of 1 MHz, it was not possible to statistically differentiate the speed of sound between samples I and III (E_n= 0.88) and between samples II and III (E_n= 0.93). However, samples I (6:1) and II (8:1) were considered non-equivalent (E_n= 1.7), demonstrating that the ultrasonic technique can distinguish samples of methyl biodiesel produced from different molar ratios at 1 MHz frequency.

In addition, analysing Table 2, it is noted that for all evaluated molar ratios, the sample that presented the lowest speed of sound was the sample I being equal to 1417.7 m·s^{-1} ± 1.8 m·s^{-1} at 1 MHz. Studies in the literature [15][16] show that biodiesel with higher conversion rates of triglycerides into esters has a lower speed of sound due to its composition. Based on this, biodiesel produced with alcohol:oil molar ratio of 6:1 has a lower speed of sound and possibly a higher conversion rate. It is essential to highlight that the 6:1 molar ratio is the most described and studied in literature due to its optimal conversion rate.

Unlike the results presented for methyl biodiesel, Table 3 shows that at a frequency of 1 MHz, it was possible to observe a statistical difference in the speed of sound between samples IV, V and VI ($E_n > 1$, for all pairs). The obtained results demonstrated that it is possible to differentiate the three samples of ethylic biodiesel produced from different molar ratios at 1 MHz. In the same way, as observed in methyl biodiesel, for ethyl biodiesel, the sample that presented the lowest speed of sound was the sample produced with a molar ratio of 6:1 (IV).

Normalised error values were calculated between pairs of biodiesels produced from different types of alcohol to statistically identify which samples can be considered equivalent in terms of propagation velocity values.

One can observe that the biodiesel samples produced from different alcohols and the same molar ratio (I-IV), (II-V) and (III-VI) presented a normalised error more significant than 1 for all the investigated frequencies. Being equal to 11.1 for (I-IV) samples, 8.2 for (II-V) samples and 4.5 for (III-VI) samples Even after the purification process, biodiesel produced with ethanol showed a lower speed of sound. The decrease in viscosity could explain this. These results demonstrate that the proposed technique is a promising tool to help identify biodiesel produced by different routes.

4. Conclusions

Biodiesel samples obtained from different types of alcohol and molar ratios were characterised using low-power ultrasound. The speed of sound was measured at the frequency of 1 MHz. Methyl biodiesel samples were differentiated only in molar ratios of 6:1 and 8:1 using the 1 MHz frequency, whereas ethyl biodiesel all samples were distinguished. The results demonstrated that biodiesels produced with different alcohols have a non-equivalent speed of sound. Regarding the molar ratio, using methanol and ethanol, the sample that presented the lowest speed of sound was the sample produced in the molar ratio of 6:1. In this work, the ultrasound could differentiate the biodiesel samples evaluated through the speed of sound parameter. It could be used as a solvent-free technique for biodiesel quality assessment.

References

[1] Ambat, I.; Srivastava, V.; Sillanpaa, M. 2018 *Renewable ans Sustainable Energy Reviews*. v.90, p.356-369.

[2] Karmakar, B.; Halder, G. 2019 *Energy Conversion Management* reference. v.182, p.307-339.

[3] Lopes, A.F.G.; Talavera-Pietro, M.C.; Ferreira, A.G.M.; Santos, J.B.; Santos, M.J.; Portugal, A.T.G. *Fuel.* v.116, p.242-254.

[4] Shameer, P.M.; Ramesh, K.; *Renew Sustain Energy Rev.* v.61, p.45-61.

[5] ASTM – *American Society for Testing and Materials*. ASTM D6751. URL:

[6] EUROPEAN STANDARDS - EN 14214:2014+A2:2019 Liquid petroleum products – Fatty acid methyl esters (FAME) for use in diesel engines and heating applications – Requirements and test methods (includes Amendment A1:2014).

[7] Alouache, B.; Laux, D.; Hamitouche, A.; Bachari, K.; Boutkedjirt. 2018 *Applied Acoustics.* v. 131, 70-78.

[8] Alouache, B.; Khechena, F.K.; Lecheb, F.; Boutkedjirt, T. 2015 *Physics* Procedia. v.70, p. 1061–1065.

[9] Oliveira, P.A.; Silva, R.M.B; Morais, G.C.; Alvarenga, A.V.; Costa-Félix, R.P.B. 2016 *Journal of Physics: Conference Series.* v.733, 012040.

[10] Baesso, R.M.; Costa-Félix, R.P.B.; Miloro, P.; Zeqiri, B. 2019 *Fuel.* v.241, p.155-163.

[11] Freitas, S.V.D.; Paredes, M.L.L.; Daridon, J-L.; Lima, A.S.; Coutinho, J.A.P. 2013 Fuel v.103,

p.1018-1022.
[12] Lopes, A. F.G.; Talavera-Pietro, M.C.; Ferrira, A.G.M.; Santos, J.B.; Santos, M.J.; Portugal, A.T.G. 2014 *Fuel* v.116, 242-254.
[13] Costa-Júnior, J.F.S; Cortela, G.A.; Maggi, L.E.; Costa-Félix, R.P.B.; Alvarenga, A.V. 2018 *Measurement: Journal of the International Measurement Confederation*. v.122, p.45-56.
[14] Steele, A.G.; Douglas R.J.; 2006 *Metrologia.* v.43, p.S235-243.
[15] Laesecke, A.; Fortin, T.J.; Splett, J.D.; 2012 *Energy Fuel.* v.26, p. 1844-1861.
[16] Oliveira, P.A.; Silva, R.M.B; Morais, G.C.; Alvarenga, A.V.; Costa-Félix, R.P.B 2018 IOP Conf. Series: Journal of Physics: Conf. Series 975, 012019.

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