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Ultrasound as a Metrological Tool for Monitoring Transesterification Kinetics

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Additional information is available at the end of the chapter

Abstract

Ultrasound has been widely used as a technological alternative way to analyse non-invasively an assortment of materials. It includes liquids with dissimilar physical characteristics, including mono- and multi-phasic mixtures, suspension formation and dissolution, in-line processing, among other practical applications. Regardless the huge spread of uses, so far ultrasound has not been proved to be able to quantify transesterification kinetics with a metrological approach. The aim of this chapter is to demonstrate that a properly designed ultrasonic experiment can be developed to identify remarkable stages of a transesterification reaction to produce biodiesel. The method was compared both with gas chromatography and hydrogen nuclear magnetic resonance (^{1}H NMR). For an in-line application, ultrasound has been proved to work properly as a monitoring tool for chemical reaction kinetics.

Keywords: ultrasound, metrology, chemical kinetics, monitoring, biodiesel production

1. Introduction

Currently, in the chemical, food, petrochemical and other industries, there is a considerable demand for measuring instruments that are able to characterize liquids with high sensitivity, robustness and precision. An instrument that is able to perform the process accurately, ranging from chemical reactions (production) to quality control (final product), is necessary. Due to the automation of processes, in-line measurements are increasingly being studied to ensure that the product is in conformity to technical requirements [1–5].

The competitiveness of companies for which the core business is the production of consumer goods is directly linked to their production process. Quality and productivity, once seen as dissociated elements, now are joined together, strongly impacting business competitiveness, improving process performance, product quality and reducing costs. In this way, the study of the kinetics of chemical processes allows the optimization of the process, avoiding the waste not only of raw materials, but also of energy and time [6].

Establishing the kinetics of a chemical reaction can be very complex depending on the chemical route. An in-depth study requires a series of experiments and simulations that can predict when the reaction has reached the optimal state. For reactions in which the converting mechanism is not well established, several kinetic models may be proposed, arising from countless reaction monitoring techniques. Thus, the combination of techniques, well described in the literature and easily accessible, allows a more precise conclusion of the object of study [6, 7].

To illustrate, let us take one of the chemical reactions responsible for biodiesel production, the transesterification reaction, disclosed in **Figure 1**.

Figure 1 discloses that an oil can react with a small chain alcohol in the presence of a catalyst and produce biodiesel. Biodiesel, also known as fatty acid methyl ester (FAME), is nothing more than a mixture of esters.

The transesterification reaction to produce biodiesel is reversible and, therefore, usually works with excess of alcohol. A typical proportion is 6:1 (alcohol:oil) ratio, so that the equilibrium displacement is forced towards the conversion of biodiesel. However, the oil and alcohol are not miscible, establishing two phases. In this stage, when there are two phases within the mixture, one can say that the mass transfer controls the kinetics of the reaction. Nevertheless, as biodiesel (methyl ester) is formed, it works as a co-solvent, facilitating the miscibility. Upon reaching the homogeneity of the system, the chemical reaction starts to control the system. A reaction in which an exchange of mechanism occurs makes difficult to define the kinetics and, consequently, the establishment of optimal reaction conditions [7–12].
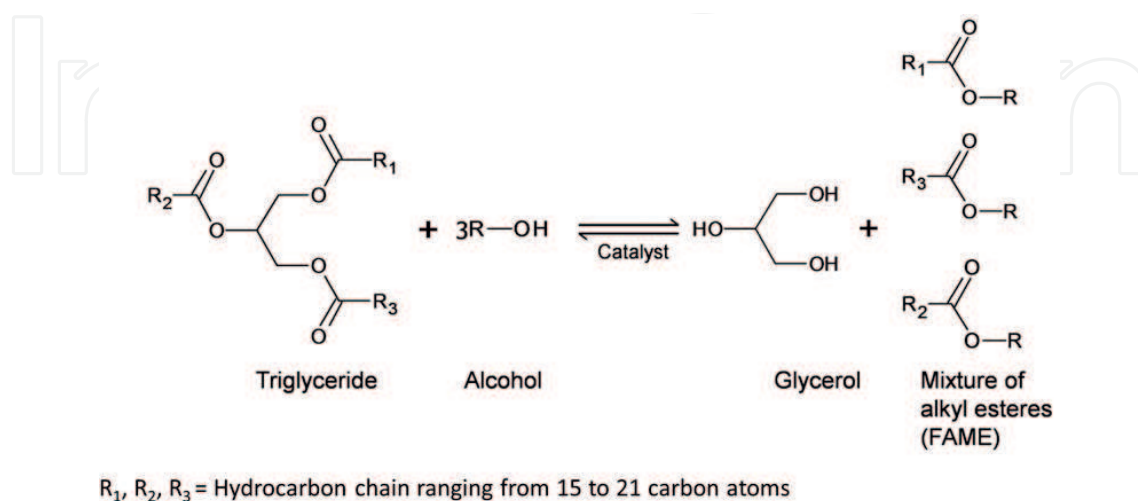

Figure 1. Transesterification of vegetable oil for biodiesel production.

Within this chapter, we will disclose the recent outcomes of a research in which ultrasound has been used as a way of monitoring the progress of the reaction of transesterification of soybean oil with methanol in the presence of KOH as basic catalyst. The pulse/echo technique was used to monitor acoustic velocity throughout the reaction, composed as an in-line scheme. The results were related to the reference method based on gas chromatography (EN 14103 standard) and to the ^{1}H NMR technique [13–18].

2. Fundamental of the transesterification reaction

Let us consider the reaction TAG + 6 MeOH → 3 FAME + G, where TAG (triglyceride) is soybean oil, MeOH is methanol, FAME is the ester mixture and G is glycerol. To simplify the study, there are some considerations before starting the process of monitoring the transesterification reaction by ultrasound. As there is excess alcohol, we can consider TAG as a limiting reagent, i.e., when it is totally consumed the reaction will finish. With the excess of methanol, the reaction becomes irreversible, which means that the whole equilibrium of the reaction is displaced to produce biodiesel. Another important consideration is to admit a batch reactor in which reagents are mixed at the beginning of the reaction, without any inlet or outlet flow of reagents further than those mixed at time 0.

Thus, we determine the amount of TAG consumed (N_{TAG_c}), quantified in mol, through Eq. (1), in which N_{TAG_0} represents the amount of TAG inserted in the reactor at time 0 (in mol), and X is the relationship between the TAG that reacted with the TAG inserted into the reactor at time 0.

$$N_{TAG_c} = N_{TAG_0} \cdot X \tag{1}$$

The TAG in a given time (N_{TAG_t}) is obtained by the difference of the TAG inserted in the reactor and the TAG consumed, according to Eq. (2) (all values expressed in mol).

$$N_{TAG_t} = N_{TAG_0} - N_{TAG_0} \cdot X \tag{2}$$

Thus, Eqs. (1) and (2) lead to Eq. (3), as depicted elsewhere [6, 9].

$$N_{TAG_t} = N_{TAG_0}(1 - X) \tag{3}$$

From stoichiometry, one can derive to $C_{TAG} = \frac{N_{TAG}}{V}$, and for liquids $V = V_0$ (volume is constant), evolving to Eq. (4).

$$C_{TAG} = C_{TAG_0}(1 - X) \tag{4}$$

The disappearance of the TAG must be accompanied by the appearance of the FAME. However, a question arises: how the actual concentration of FAME throughout the reaction can be assessed? Complementary, one could ask how to know that in fact the reaction has ended and it has already reached the maximum conversion? There are several techniques proposed in the literature, but few can make this determination in an in-line scheme with an accurate way

without demanding exorbitant expenses. To sort out that drawback, ultrasound methods emerge as a tool capable of assisting in the biodiesel manufacturing process.

3. Ultrasound as a tool for liquid characterization

Ultrasound is a mechanical wave that propagates in fluids or solid materials at frequencies greater than 20 kHz, i.e., out of the audible range for healthy humans [19–25].

An often used ultrasonic measurement method consists on a pulse/echo arrangement. Basically, it consists on

$$EMISSION \rightarrow PROPAGATION \rightarrow REFLECTION \rightarrow PROPAGATION \rightarrow RECEPTION$$

Two important quantities are easily assessed from the pulse/echo ultrasonic measurement method: time of flight and pulse (or signal) amplitude. Both are measured after the reception of the ultrasound wave. Whenever an acoustic impedance mismatch occurs, the ultrasonic wave is partially reflected in the discontinuity boundary. The amount of reflection depends on the acoustic impedance difference between the two media, due to what is called the reflection coefficient of the interface. In a typical pulse/echo experimental set-up in sonochemistry, the propagation medium is fluid and the reflection takes place in an interface with a solid object, generically denominated reflecting target. Similarly, the liquid-air interface is a reflecting target, as well.

Throughout the propagation, other physical phenomena diminish the ultrasonic amplitude due to different mechanisms. Mainly, scattering and absorption are in charge for ultrasonic attenuation, mitigating the capability of free propagation. All those phenomena are natural and unavoidable. Nevertheless, a proper experimental ultrasonic set-up will either concern on its quantification, or will deal with other quantities that are not undesirably affected.

The speed of sound is a quantity that is not related to attenuation phenomena, or at least is not the case in a linear range of frequencies and in infinite-like three-dimensional propagation medium, even if there is a constraint in one dimension. In the linear range of ultrasonic propagation, the sound velocity in any determined medium or material varies as a function of the temperature, density and viscosity. As a matter of fact, those quantities are not absolutely correlated to each other, what makes the establishment of a mathematical function a virtually unrealisable task for complex mixtures of fluids. For monophasic simple liquids, such as pure water or hydro carbonates, it is easier to define a function relating those quantities, but it is not the case for a transesterification process.

To assess the speed of sound, the typical approach is to measure the time of flight of an ultrasonic pulse within a vessel with a pre-determined distance from the surface to the emitting ultrasonic transducer and a properly designed reflecting target. It is the so-called pulse/echo experimental method. Materials in different macrophysics states transmit ultrasonic waves with different velocities. In general, but not in a universal way, the more rigid is a

material, the faster the ultrasonic wave will propagate within it. It is important to keep in mind that the ultrasonic velocity changes significantly with temperature [26–29].

Mathematically, the speed of sound is computed dividing the distance travelled by the pulse by the time spent to travel it (time of flight), as disclosed in Eq. (5).

$$v = \frac{2 \cdot \Delta s}{t} \tag{5}$$

Here, Δs is the distance separating the ultrasonic surface and the reflecting interface (the travelling distance is twice this value) and t is the time required for the ultrasonic pulse to transpose that distance and return to the transducer. This process can be repeated many times, depending on the attenuation and the distance from the transducer and the reflecting surface. After each subsequent reflection, the pulse amplitude will decrease, as a consequence of attenuation. The multiple reflections will remain until the sound energy is completely absorbed in the process. **Figure 2** exhibits that multi-reflection behaviour.

While planning the experimental set-up for the pulse/echo method, one must be aware about the absorption of the liquid under investigation, as well as the distance between the transducer and the reflecting surface. The pulse frequency plays a key role, as ultrasonic attenuation is exponentially proportional to the frequency. In general, water is used as reference once its behaviour both for attenuation and ultrasonic velocity are very well known [26–29].
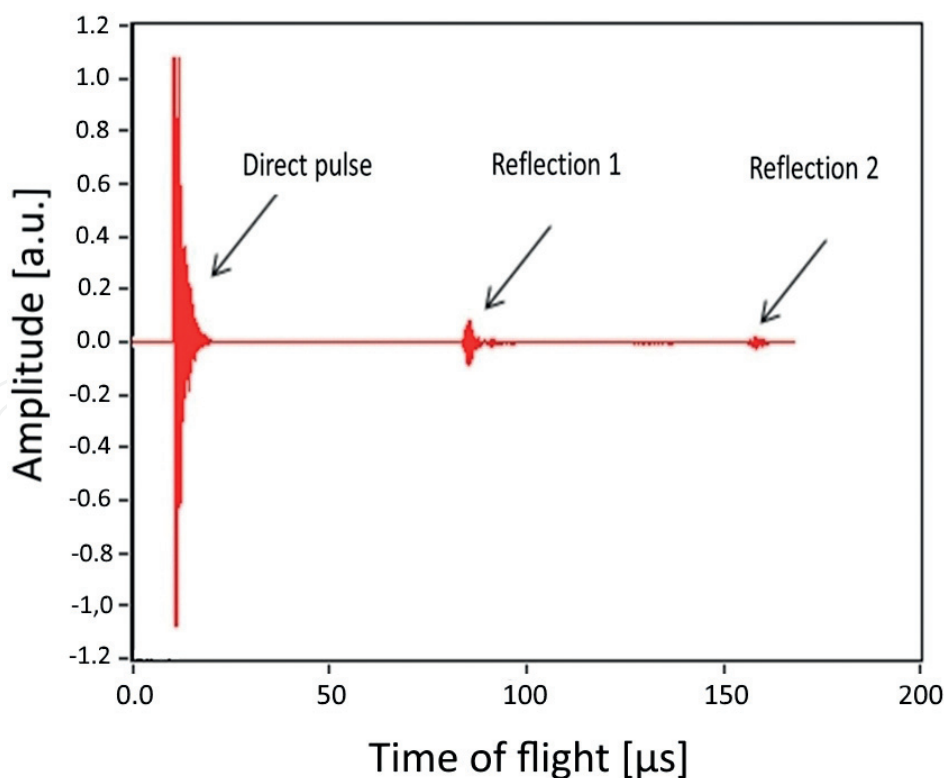

Figure 2. Ultrasonic pulse and reflections.

4. Validation of the experimental ultrasonic method

In previous studies, the value of the propagation speed in soybean oil in a range of 20–50°C was determined [20]. For the practical application presented within this paper, all reactions were performed at 40°C. At this temperature, soybean oil has a velocity of 1418.3 m s^{-1}, with expanded uncertainty (p = 0.95) U_{exp} = 5.2 m s^{-1} [21]. As soon as the oil starts to react with methanol and the catalyst, variation on the speed of sound will indicate that something is happening within the medium. Despite it is easy to measure speed of sound, it is not trivial to relate this variation with anything that is going on in the reaction. The chemical kinetics is not directly assessed, unless some methodological study is conducted. That was the case, insofar we conducted an experimental method validation. The idea was to compare the speed of sound measured throughout the transesterification process with a quantification of the reaction stoichiometric situation at different moments. The worldwide accepted reference method for determination of ester content is based on gas chromatography (GC), according to the standard EN 14103. However, this method, besides being time-consuming, it is not applicable in the process line and demands expensive equipment, supplies, and specific technical training. Thus, less costly methods have emerged as an alternative for determining the conversion, as is the case with ^{1}H NMR. Despite it is not a cheap technique, it is much less time-consuming than the GC analysis [13, 14, 21, 22, 30–32].

In establishing parameters for the reactions that will be analysed, an isothermal batch reactor (T = 40°C) is chosen. The validation experiment was restricted to two concentrations for the catalyst (0.2% and 1.5% w/w) and two mechanical stirring rotational speeds (200 and 520 rpm). The reaction time was set to a limit of 40 min.

There are several studies that propose equations that take into account the number of hydrogens present in the molecules consumed (TAG) in relation to the number of hydrogens present in the formed molecule (FAME). **Figures 3** and **4** disclose the ^{1}H NMR spectra for the pure soybean oil and the biodiesel made from this oil, respectively.

The formation of methyl ester (methylic biodiesel) can be noticed by the appearance of the signal of the methylic hydrogen from the methoxyl group at 3.7 ppm (chemical shift represented per B in **Figure 4**), while occurs the disappearance of the methylene hydrogens from glycerol in the triacylglycerol from 4.0 to 4.4 ppm (chemical shift represented per B in **Figure 3**). Eq. (6) presents a method described in the literature [14] used to determine the conversion of TAG.

$$X_{TAG}(\%) = 100 \cdot \left(\frac{2A_1}{3A_2}\right) \tag{6}$$

Here, X_{TAG} (%) is the amount of TAG that has been converted into biodiesel, A_1 and A_2 are areas of the methylic hydrogens (δ = 3.7 ppm) of methoxyl group, the methyl ester and the glycerol methylene hydrogens (δ = 4–4.4 ppm), respectively. Calculation of the ^{1}H NMR conversion was compared to the reference method (GC) for the two reactions with 200 rpm (see **Figure 5**).
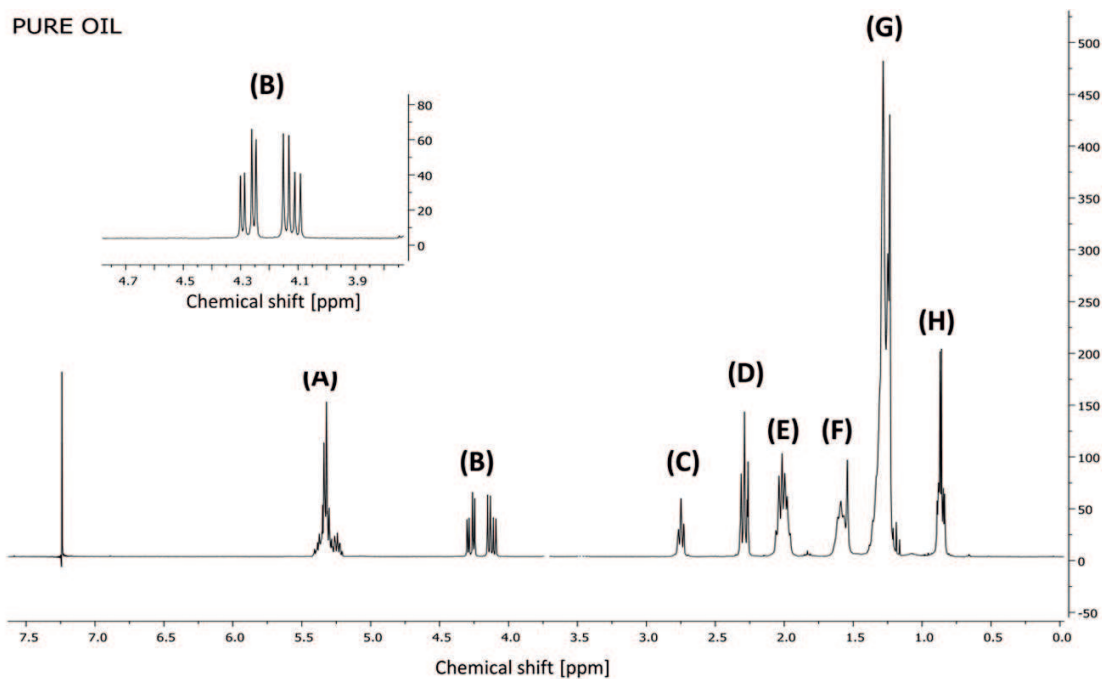
Figure 3. ^{1}H NMR spectra for pure soybean oil: (A) HC=CH; (B) CH$_2$—O; (C) C=C—CH$_2$—C=C; (D) CH$_2$—C=O; (E) CH$_2$—C=C; (F) CH$_2$—C—C=O; and (G) —CH$_2$—; (H) CH$_3$.
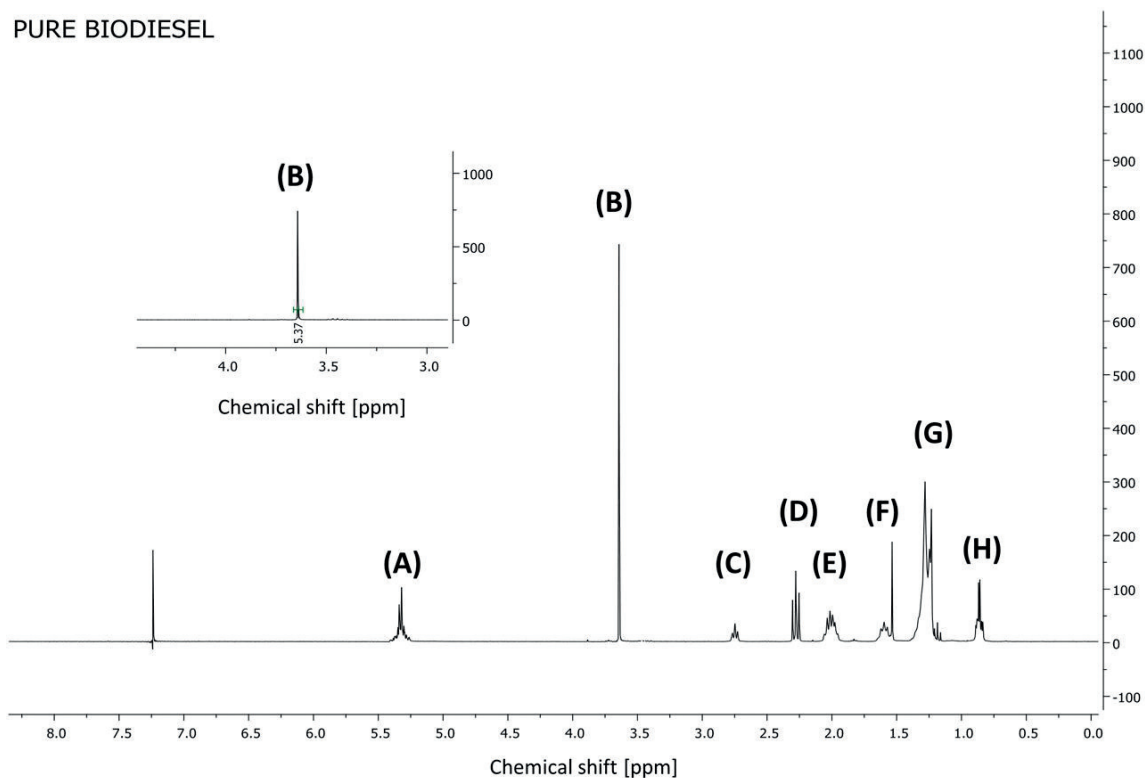

Figure 4. ^{1}H NMR spectra of methyl biodiesel obtained on the homogeneous transesterification of soybean oil: (A) HC=CH; (B) CH$_3$—O; (C) C=C—CH$_2$—C=C; (D) CH$_2$—C=O; (E) CH$_2$—C=C; (F) CH$_2$—C—C=O; and (G) —CH$_2$—; (H) CH$_3$.

Figure 5 shows that the ^{1}H NMR method is very similar to the reference method (GC). After this straightforward validation, comparing both technics, we used ^{1}H NMR to assess the conversion of analytical curves as described in Eq. (6) for the four reactions (see **Figure 6**).

As disclosed in **Figure 6**, one can note that each reaction reaches the maximum conversion at a given moment. But how to know during the reaction that the maximum conversion has already been reached and there is no longer any need to continue the process? NMR analyses, as well as GC, require the sample to be pure, which means free of other substances that may interfere with the analysis. In this way, ultrasonic monitoring stands out, being able to determine the maximum point of the reaction even in the presence of excess reagents and by-products. **Figures 7** and **8** depict a set of results for all chemical routes employed in the present study.

Figure 7 shows that each reaction has a propagation velocity configuration. They all start with a value close to the pure soybean oil velocity. However, during the reaction time, the speed of
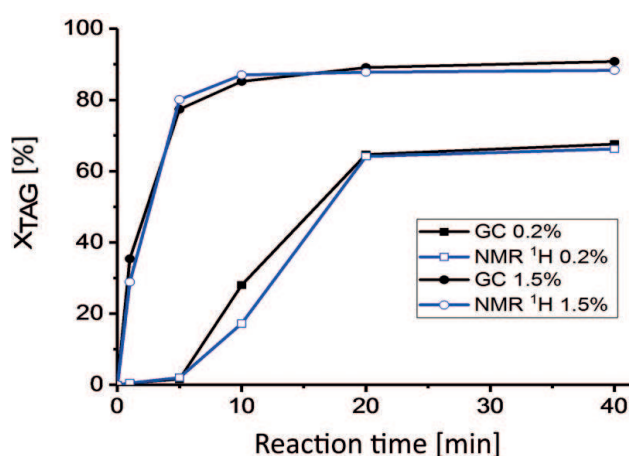

Figure 5. Variation of biodiesel conversion during the homogeneous transesterification of soybean oil with methanol and 200 rpm of mechanical stirring.
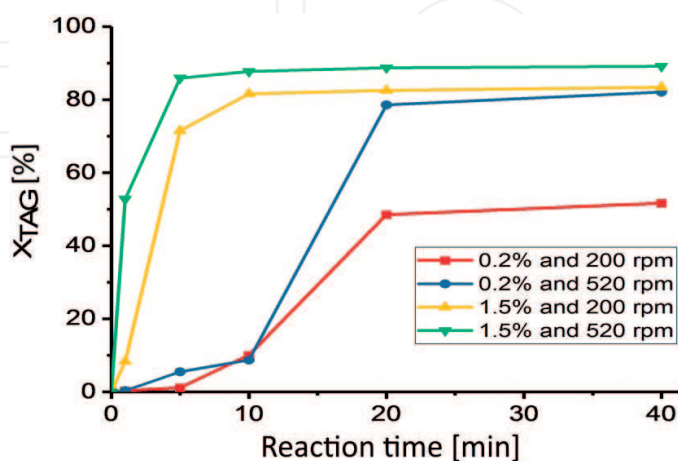

Figure 6. Conversion rate calculated by ^{1}H NMR for four transesterification reactions of soybean oil using KOH as the basic catalyst.
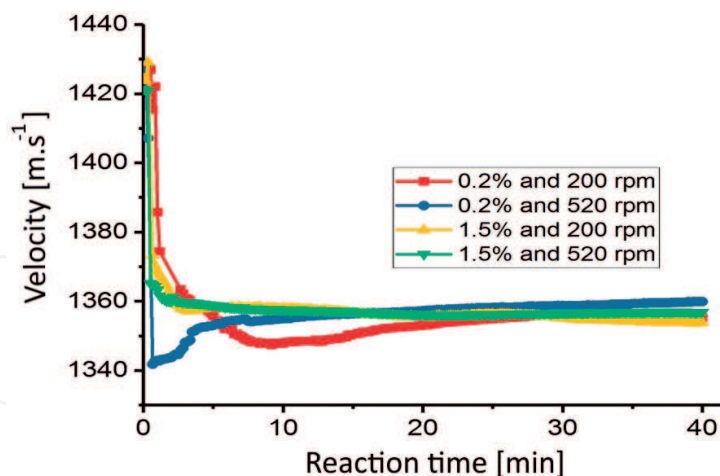
Figure 7. Variation of the propagation velocity along the transesterification reaction of soybean oil with methanol in the presence of KOH.
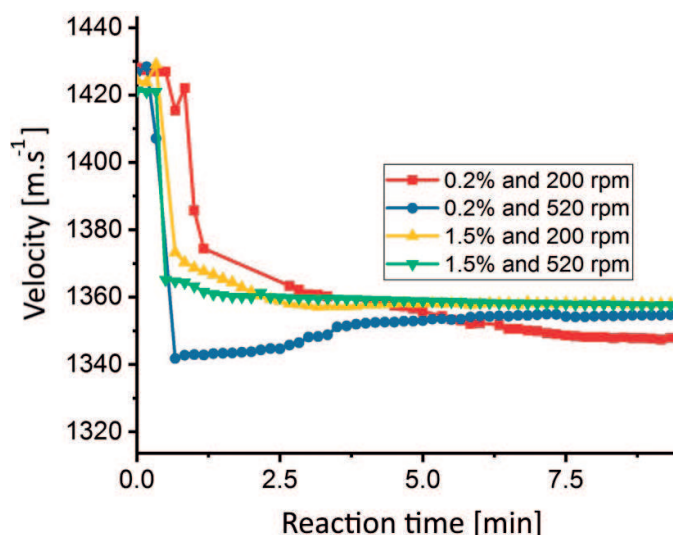

Figure 8. First 7.5 min of the variation of the propagation velocity along the transesterification of soybean oil with methanol in the presence of KOH.

sound decreases until stabilized, demonstrating that the maximum conversion was reached. This variation can be better observed in **Figure 8**, which is a zoomed part of **Figure 7** restricted to the first few minutes. Considering that the idea is to obtain pure biodiesel, independent of the reaction conditions, it is quite natural that the final velocities (when the highest concentration of biodiesel is present) are close to each other.

5. Looking into the results in details

Let us analyse the effect of each parameter (catalyst and rotation) on the final biodiesel conversion.

5.1. Analysis of the effect of catalyst concentration

The presence of catalyst helps to accelerate the reaction, reducing the activation energy required to start it. Thus, catalyst concentration is one of the main factors that can affect the reaction kinetics.

In order to analyse the effect of the variation of the catalyst concentration, it is necessary to separately analyse different rotation values.

For an initial concentration of soybean oil equal to 0.83 mol L^{-1} and by the Eqs. (4) and (6), the consumption of TAG and conversion into FAME were calculated. The velocity (υ) was calculated according to Eq. (5).

Table 1 and **Figure 9** disclose the results for the reactions with 200 rpm of rotational speed.

	0.2% and 200 rpm			1.5% and 200 rpm		
Time [min]	X_{TAG} [%]	C_{TAG} [mol L^{-1}]	υ [m s^{-1}]	X_{TAG} [%]	C_{TAG} [mol L^{-1}]	υ [m s^{-1}]
0	0	0.83	1428.1	0	0.83	1424.3
1	0.3	0.83	1385.7	8.3	0.75	1368.7
5	1.1	0.82	1355.8	71.5	0.24	1358.0
10	10.0	0.75	1347.9	81.6	0.15	1356.1
20	48.5	0.43	1353.2	82.5	0.15	1355.4
40	51.6	0.40	1355.2	83.4	0.14	1353.9

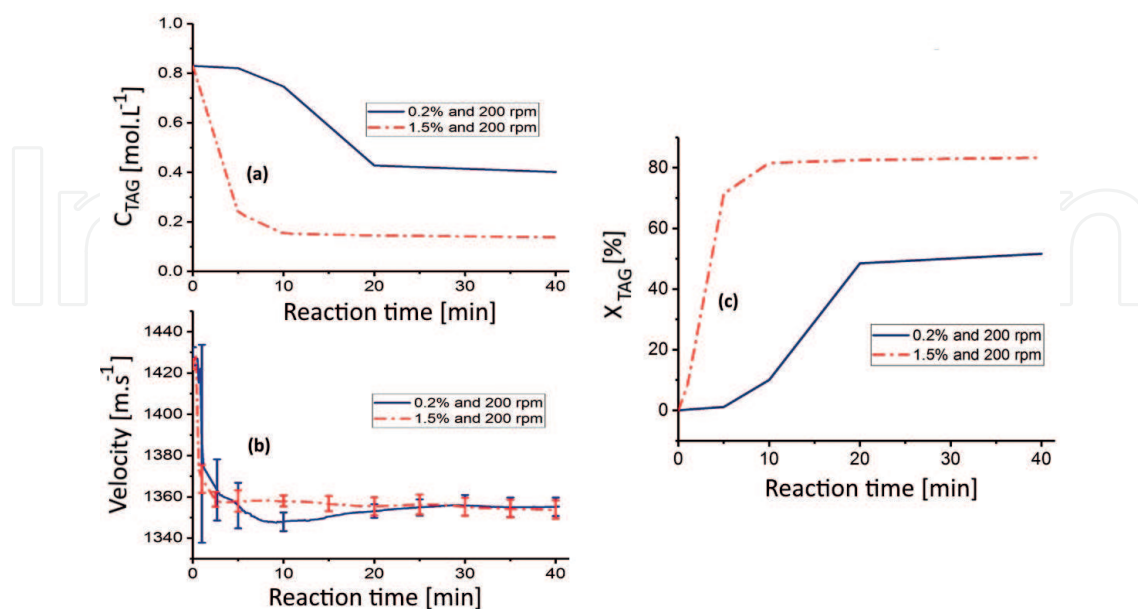**Table 1.** Results for reactions at 200 rpm.

Figure 9. Variation of (a) TAG concentration, (b) propagation velocity and (c) TAG conversion for the reactions with 200 rpm of rotation.

Looking at **Table 1** and **Figure 9**, one can note that there is a large difference in C_{TAG} and υ decay between both reactions, what reflects in the conversion rate (X_{TAG}). The uncertainty bars calculated for the velocity are disclosed to determine the accuracy of the study [33]. The behaviour observed in the reaction with 0.2% KOH and 200 rpm presents a slow decay in the concentration of TAG in the first 10 min of reaction, which is expected for reactions in which mechanism exchange occurs. That region on the graphics of **Figure 9** (first 10 minutes of reaction) is in which the rate of consumption and conversion rate are slow, and it occurs due to the low miscibility between alcohol and oil. Thus, as the methyl ester is produced, the chemical reaction starts to control the kinetics of the reaction and, therefore, a large jump between 10 and 20 min of reaction is observed. After 20 min of reaction, it is clearly noticeable that there is stability between the conversion values and propagation velocity. This result indicates that the ultrasound can determine the maximum point of conversion even in the presence of secondary substances (by-products).

On the other hand, when the reaction with 1.5% KOH and 200 rpm is on focus, yet in **Figure 9**, it is observed an expressive consumption of TAG in the first 10 min of reaction. After that time, the stability in the values of the conversion as well as in the propagation velocity is evident. Reactions like that, in which there is a rapid conversion, the region controlled by mass transfer can be considered insignificant. Here, it is observed that for reactions with 200 rpm stirring, the increase in catalyst concentration not only accelerates the transesterification process but also increases the final conversion as well, and consequently decreases the remaining TAG in the reaction medium.

Let us check if the same will occur analysing the results presented in **Table 2** and **Figure 10**, in which the rotation speed was increased to 520 rpm.

For the reaction with 0.2% of KOH and 520 rpm of stirring, it is noticeable that there is a slow decrease in the TAG concentration in the first 10 min and stability of the values after 20 min. On the other hand, the reaction with 1.5% of KOH and 520 rpm reaches the maximum conversion as fast as 5 min after the reaction had begun. In the same way as observed in **Figure 9**, the mass transfer controls the start of the reaction for the reaction with 0.2% of catalyst, independently of the rotational speed employed. With the increase of KOH concentration by 7.5 times, there is a 300% decrease in reaction time for the reaction with 520 rpm of

	0.2% and 520 rpm			1.5% and 520 rpm		
Time [min]	X_{TAG} [%]	C_{TAG} [mol L^{-1}]	υ [m s^{-1}]	X_{TAG} [%]	C_{TAG} [mol L^{-1}]	υ [m s^{-1}]
0	0	0.83	1426.8	0	0.83	1421.3
1	0.3	0.81	1342.9	52.8	0.65	1363.2
5	5.5	0.78	1353.0	85.9	0.12	1358.8
10	8.7	0.76	1354.0	87.7	0.10	1357.6
20	78.6	0.22	1357.3	88.7	0.09	1356.3
40	82.1	0.18	1360.0	89.1	0.09	1356.9

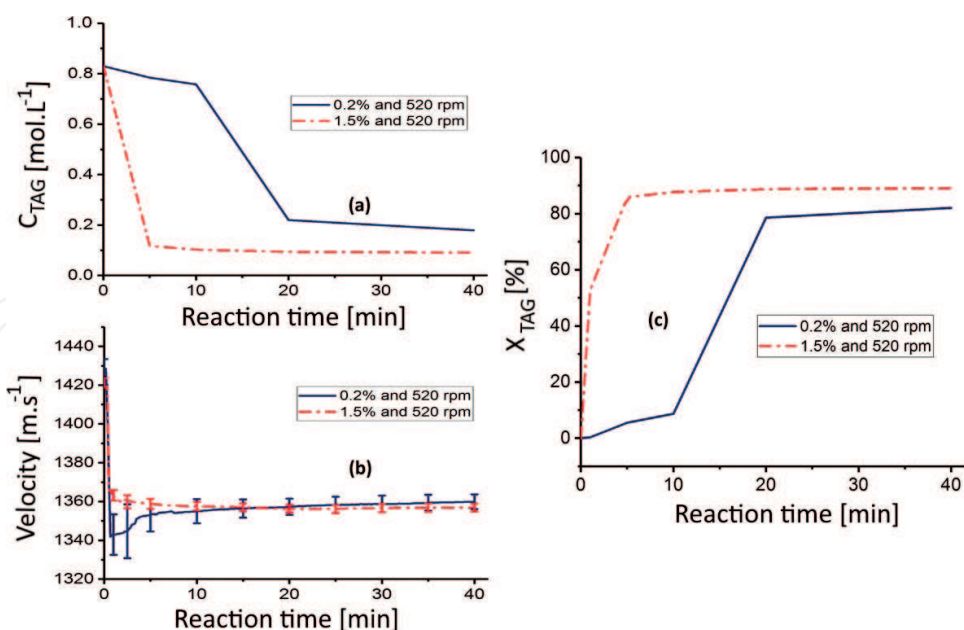**Table 2.** Results for reactions at 520 rpm.

Figure 10. Variation of (a) TAG concentration, (b) propagation velocity and (c) TAG conversion for the reactions with 520 rpm of rotation.

rotation. However, the maximum values reached by the conversion for the two reactions described in **Figure 10** are very close (89 and 82%).

5.2. Analysis of the effect of system stirring

If the same concentration of catalyst is used, would the stirring of the system interfere with the kinetics of the reaction? The answer is: Surely enough!

Firstly, the lowest catalyst concentration, 0.2% KOH, will be analysed. The impact due the change in rotational speed will be variable in those reactions. **Table 3** and **Figure 11** show the results for the reactions with 0.2% catalyst.

From **Table 3** and **Figure 11**, we note that the two reactions with 0.2% of catalyst need the same reaction time to reach their maximum conversion, regardless of the rotation applied to the

	0.2% and 200 rpm			0.2% and 520 rpm		
Time [min]	X_{TAG} [%]	C_{TAG} [mol L^{-1}]	υ [m s^{-1}]	X_{TAG} [%]	C_{TAG} [mol L^{-1}]	υ [m s^{-1}]
0	0	0.83	1428.1	0	0.83	1426.8
1	0.3	0.83	1385.7	0.3	0.81	1342.9
5	1.1	0.82	1355.8	5.5	0.78	1353.0
10	10.0	0.75	1347.9	8.7	0.76	1354.0
20	48.5	0.43	1353.2	78.6	0.22	1357.3
40	51.6	0.40	1355.2	82.1	0.18	1360.0

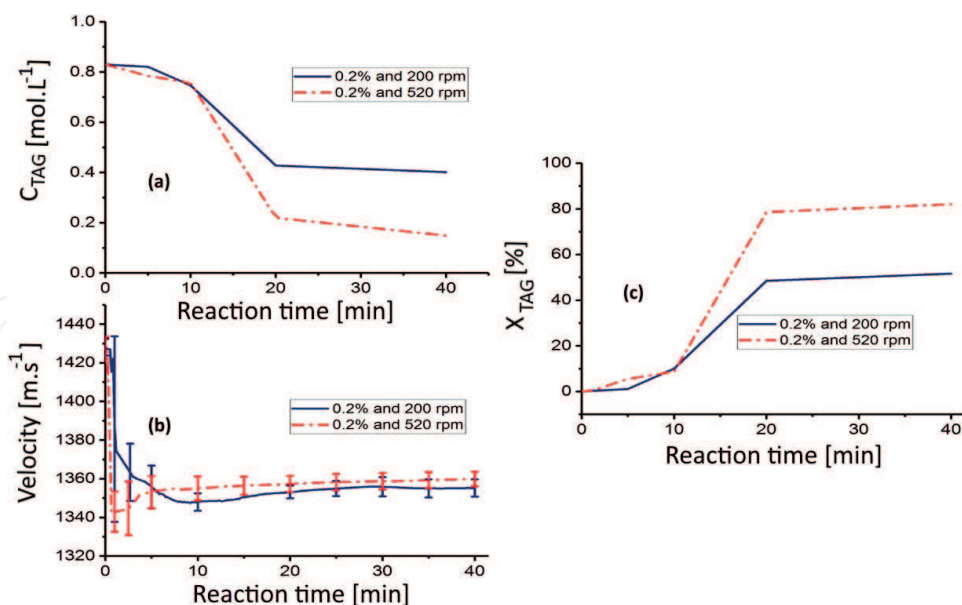**Table 3.** Results for 0.2% (w/w) of KOH reactions.

Figure 11. Variation of (a) TAG concentration, (b) propagation velocity and (c) TAG conversion for the reactions with 0.2% (w/w) of KOH.

system. However, there is a significant increase in the conversion value from 52% (200 rpm) to 82% (520 rpm), which shows that for reactions like those, with low catalyst concentration, the rotation does not interfere in the reaction velocity, but at the maximum conversion value.

And what happens increasing 7.5 times the concentration of the catalyst? Does this pattern hold? **Table 4** and **Figure 12** show the answers.

Increasing the concentration of KOH clearly increases the rate of TAG consumption and, consequently, formation of FAME. While the reaction with 200 rpm reaches the maximum conversion and the equilibrium with 10 min of reaction, the reaction at 520 rpm only requires half the time, 5 min. However, despite the decrease in time, we observed that the values for the maximum conversion are very close.

	1.5% and 200 rpm			1.5% and 520 rpm		
Time [min]	X_{TAG} [%]	C_{TAG} [mol L^{-1}]	v [m s^{-1}]	X_{TAG} [%]	C_{TAG} [mol L^{-1}]	v [m s^{-1}]
0	0	0.83	1424.3	0	0.83	1421.3
1	8.3	0.75	1368.7	52.8	0.65	1363.2
5	71.5	0.24	1358.0	85.9	0.12	1358.8
10	81.6	0.15	1356.1	87.7	0.10	1357.6
20	82.5	0.15	1355.4	88.7	0.09	1356.3
40	83.4	0.14	1353.9	89.1	0.09	1356.9

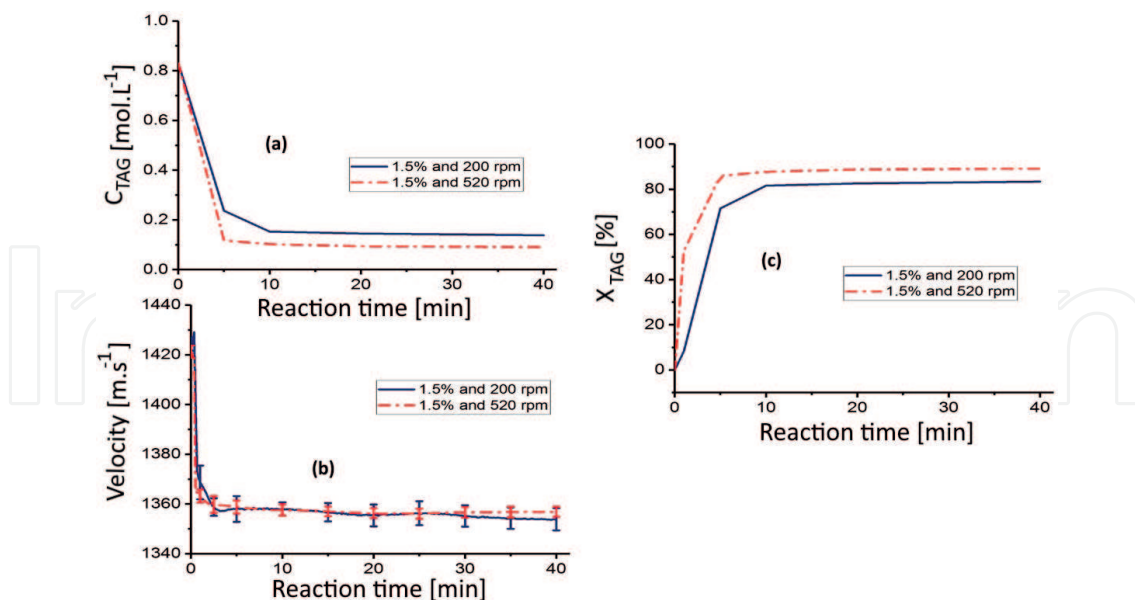**Table 4.** Results for 1.5% (w/w) of KOH reactions.

Figure 12. Variation of (a) TAG concentration, (b) propagation velocity and (c) TAG conversion for the reactions with 1.5% (w/w) of KOH.

Thus, an economic analysis is necessary to evaluate to what extent an increase of the rotation used, or of the catalyst concentration, to the detriment of the reduction in the reaction time, is economically feasible. But the use of ultrasound as a tool for monitoring chemical reactions has been shown to be efficient [33].

6. Final remarks

Ultrasound is widely used for more than a century for diagnosis applications. The state of the technology is vast on applications for non-destructive testing and biomedical equipment. The use of ultrasound in chemistry is more common as a tool to accelerate reactions or enhance the performance of established methods. However, the technology is not so widely developed and spread around regarding the use of ultrasound as a monitoring tool for chemical reactions.

As a tool, ultrasound is remarkably simple to use. Nevertheless, one must be aware that the apparent straightforwardness undercovers a complex physical process that takes place in the generation, propagations, reflection and reception of ultrasound in both the transmit/receive and pulse/echo approaches. Unless an experiment is carefully designed, carried out, and analysed, the outcome of any ultrasonic proposed method could be of no technical usefulness.

In the present chapter, the use of an ultrasound pulse/echo scheme was validated as a monitoring procedure of the transesterification kinetics of soybean oil into biodiesel. The sensibility of the method was good enough to compare different catalyst concentrations (0.2 and 1.5%) and different rotational speed of mechanical stirring (200 and 520 rpm). The comparison was done using as gold standard the gas chromatography and ^{1}H RMN. The validation leads to quite interesting outcomes.

It was possible to observe purely from the ultrasonic velocity measurement that the faster the mechanical stirring acts, the faster is the transesterification kinetics. Moreover, it is possible to identify the elapsed time when the reaction reaches its maximum possible conversion, dictated by the amount of catalyst. For all cases, ultrasonic monitoring has disclosed a causal relation to the gold standard analytical methods.

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References

[1] Greenwood MS, Bamberger JA. Measurement of viscosity and shear wave velocity or slurry for on-line process control. Ultrasonics. 2002;**39**(9):623-630. DOI: https://doi.org/10.1016/S0041-624X(02)00372-4

[2] Saggin R, Coupland JN. Oil viscosity measurement by ultrasonic reflectance. Journal of the American Oil Chemists' Society. 2001;**78**(5):509-511. DOI: https://doi.org/10.1007/s11746-001-0294-z

[3] Saggin R, Coupland JN. Concentration measurement by acoustic reflectance. Journal of Food Science. 2001;**66**(5):681-685. DOI: https://doi.org/10.1111/j.1365-621.2001.tb04621.x

[4] Richard R, Li Y, Dubreuil B, Thiebaud-Roux S, Prat L. On-line monitoring of the transesterification reaction between triglycerides and ethanol using near infrared spectroscopy combined with gas chromatography. Bioresource Technology. 2011;**102**(2):6702-6709. DOI: https://doi.org/10.1016/j.biortech.2011.03.111

[5] Dubé MA, Zheng S, McLean DD, Kates M. A comparison of attenuated total reflectance-FTIR spectroscopy and GPC for monitoring biodiesel production. Journal of the American Oil Chemists' Society. 2004;**81**(6):599-603. DOI: https://doi.org/10.1007/s11746-006-0948-x

[6] Fogler HS. Elementos de Engenharia das Reações Químicas. 4th ed. São Paulo, SP: Editora LTC; 2009

[7] Kusdiana D, Saka S. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. Fuel. 2001;**80**:693-698. DOI: https://doi.org/10.1016/S0016-2361(00)00140-X

[8] Galvan D, Orives JR, Coppo RL, Silva ET, Angilelli KG, Borsato D. Determination of the kinetics and thermodynamics parameters of biodiesel oxidation reaction obtained from an optimized mixture of vegetable oil and animal fat. Energy Fuels. 2013;**27**(11):6866-6871. DOI: https://doi.org/10.1021/ef401927x

[9] Vicente G, Martínez M, Aracil J, Esteban A. Kinetics of sunflower oil methanolysis. Industrial & Engineering Chemistry Research. 2005;**44**(15):5447-5454. DOI: https://doi.org/10.1021/ie040208j

[10] Stamenkovic OS, Todorovic ZB, Lazic LM, Veljkovic VB, Skala DU. Kinetics of sunflower oil methanolysis at low temperatures. Bioresource Technology. 2008;**99**(5):1131-1140. DOI: https://doi.org/10.1016/j.biortech.2007.02.028

[11] Clark WM, Medeiros NJ, Boyd DJ, Snell JR. Biodiesel transesterification kinetics monitored by pH measurement. Bioresource Technology. 2013;**136**:771-774. DOI: https://doi.org/10.1016/j.biortech.2013.03.089

[12] Tapanes NCO, Aranda DAG, Carneiro JWM, Antunes OAC. Transesterification of Jatropha curcas oil glycerides: Theoretical and experimental studies of biodiesel reaction. Fuel. 2008;**87**(10-11):2286-2295. DOI: https://doi.org/10.1016/j.fuel.2007.12.006

[13] EUROPEAN COMMITTEE FOR STANDARDIZATION. CSN EN 14103 – Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of ester and linolenic acid methyl ester contents. Brussels: CEN. 2011

[14] Gelbard G, Brès O, Vargas RM, Vielfaure F, Schuchardt UF. 1H nuclear magnetic resonance determination of the yield of the transesterification of rapeseed oil with methanol. Journal of the American Oil Chemists' Society. 1995;**72**:1239-1241. DOI: https://doi.org/10.1007/BF02540998

[15] Nehdi IA, Sbihi HM, Al-Resayes S.I. Rhazya stricta Decne seed oil as an alternative, non-conventionalfeedstock for biodiesel production. Energy Conversion and Management. 2014;**81**:400-406. DOI: http://dx.doi.org/10.1016/j.enconman.2014.02.038

[16] Kumar R, Bansal V, Patel VMB, Sarpal AS. 1H Nuclear magnetic resonance (NMR) determination of the iodine value in biodiesel produced from algal and vegetable oils. Energy Fuels. 2012;**26**:7005-7008. DOI: https://doi.org/10.1021/ef300991n

[17] Kouame S-D B, Perez J, Eser S, Benesi A. 1H-NMR monitoring of the transesterification process of Jatropha oil. Fuel Processing Technology. 2012;**97**:60-64. DOI: https://doi.org/10.1016/j.fuproc.2012.01.006

[18] Farobie O, Matsumura Y. A comparative study of biodiesel production using methanol, ethanol, and tert-butyl methyl ether (MTBE) under supercritical conditions. Bioresource Technology. 2015;**191**:306-311. DOI: https://doi.org/10.1016/j.biortech.2015.04.102

[19] Killner MHM, Rohwedder JJR, Pasquini C. A PLS regression model using NIR spectroscopy for on-line monitoring of the biodiesel production reaction. Fuel. 2011;**90**:3268-3273. DOI: https://doi.org/10.1016/j.fuel.2011.06.025

[20] Oliveira PA, Baêsso RM, Morais GC, Alvarenga AV, Costa-Félix RPB. Speed of sound as a function of temperature for ultrasonic propagation in soybean oil. Journal of Physics Conference Series (Online). 2016;**733**:012040. DOI: http://dx.doi.org/10.1088/1742-6596/733/1/012040

[21] Baêsso RM, Oliveira PA, Morais GC, Alvarenga AV, Costa-Félix RPB. Use of ultrasound to monitor physical properties of soybean oil. Journal of Physics Conference Series (Online). 2016;**733**:012042. DOI: https://doi.org/10.1088/1742-6596/733/1/012042

[22] Reddy SR, Titu D, Chadha A. A Novel method for monitoring the transesterification reaction of oil in biodiesel production by estimation of glycerol. Journal of the American Oil Chemists' Society. 2010;**87**(7):747-754. DOI: https://doi.org/10.1007/s11746-010-1549-2

[23] Koc AB. Ultrasonic monitoring of glycerol settling during transesterification of soybean oil. Bioresource Technology. 2009;**100**:19-24. DOI: https://doi.org/10.1016/j.biortech.2008.05.037

[24] Georgogianni KG, Kontominas MG, Pomonis PJ, Avlonitis D, Gergis V. Conventional and in situ transesterification of sunflower seed oil for the production of biodiesel. Fuel Processing Technology. 2008;**89**(5):503-509. DOI: https://doi.org/10.1016/j.fuproc.2007.10.004

[25] Figueiredo MK-K, Alvarenga AV, Costa-Félix RPB. Ultrasonic attenuation and sound velocity assessment for mixtures of gasoline and organic compounds. Fuel. 2017;**191**:170-175. DOI: https://doi.org/10.1016/j.fuel.2016.11.076

[26] Alouache B, Khechena FK, Lecheb F, Boutkedjirt T. Characterization of olive oil by ultrasonic and physico-chemical methods. Physics Procedia. 2015;**70**:106-1065. DOI: https://doi.org/10.1016/j.phpro.2015.08.226

[27] Meier K, Hawary AE. Measurements of the speed of sound in liquid and supercritical ethane. Fluid Phase Equilibria. 2016;**418**:125-132. DOI: https://doi.org/10.1016/j.fluid.2015.11.019

[28] Del Grosso VA, Mader CW. Speed of sound in pure water. The Journal of the Acoustical Society of America. 1972;**52**:1442. DOI: http://dx.doi.org/10.1121/1.1913258

[29] Monteiro MR, Ambrozin ARP, Lião LM, Ferreira AG. Critical review on analytical methods for biodiesel characterization. Talanta. 2008;**77**(2):593-605. DOI: https://doi.org/10.1016/j.talanta.2008.07.001

[30] Nagy M, Foston M, Ragauskas AJ. Rapid quantitative analytical tool for characterizing the preparation of biodiesel. The Journal of Physical Chemistry, A. 2010;**114**(11):3883-3887. DOI: https://doi.org/10.1021/jp906543g

[31] Sáez-Bastante J, Ortega-Román C, Pinzi S, Lara-Raya FR, Leiva-Candia DE, Dorado MP. Ultrasound-assisted biodiesel production from Camelina sativa oil. Bioresource Technology. 2015;**185**:116-124. DOI: http://dx.doi.org/10.1016/j.biortech.2015.02.090

[32] Joint Committee for Guides in Metrology. Evaluation of Measurement data – Guide to the Expression of Uncertainty in Measurement – JCGM 100:2008 [Internet]. 2008. Available from: http://www.bipm.org/en/publications/guides/gum.html [Accessed: 13 January 2017]

[33] Gaeta-Bernardi A, Parente V. Organic municipal solid waste (MSW) as feedstock for biodiesel production: A financial feasibility analysis. Renewable Energy. 2016;**86**:1422-1432. DOI: https://doi.org/10.1016/j.renene.2015.08.025