Chapter 7

Ultrasound Methods for Biodiesel Production and Analysis

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Additional information is available at the end of the chapter

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Abstract

Ultrasonic techniques have been widely used in biodiesel production, since the acoustic cavitation is a phenomenon capable of accelerating potentially the transesterification reactions. The equipment employed in such approach was simply equipment available in any regular laboratory of chemistry. Further developments introduced the ultrasound as an important tool to produce biodiesel. The main advantage is increasing the conversion of esters at reduced reaction times, with significantly lower production costs. As a method for characterization and analysis of materials, ultrasound has been used since several decades ago. However, ultrasonic analytical methods based on metrological principles are fairly recent investigated. Using ultrasound as physical principle to interrogate biodiesel is a promising field of research, with some remarkable outcomes produced so far. The aim of this chapter is to demonstrate advances of using ultrasonic techniques in production and characterization of biodiesel, as well as an appraisal of the current technology status, and provide insights into future developments.

Keywords: ultrasound, metrology, chemical kinetics, real-time reaction monitoring, biodiesel production

1. Introduction

Biodiesel production has achieved increasing importance worldwide due to the potential depletion of oil reserves and the environmental impacts caused by gases of fossil fuel. Biodiesel is a renewable fuel composed of alkyl esters of fatty acids, which are derived from triglycerides (vegetable oils or animal fats). There are several routes for biodiesel production, but the most

common is the transesterification, which is the reaction between triglycerides and a short chain alcohol in the presence of a catalyst, producing esters and glycerol [1].

The 3:1 molar ratio of alcohol/triglycerides is required for the complete transesterification. However, an excess of alcohol is usually added to displace the equilibrium of the reaction, ensuring the ester formation completely. Besides the molar ratio, there are other reaction variables such as temperature, type and quantity of catalyst and type of agitation, among others, that will affect the equilibrium and biodiesel production.

The conventional biodiesel production method uses mechanical agitation and high temperatures to facilitate mass transfer between the immiscible reagents (triglycerides and alcohol). Alternative methods were developed with the aim of increasing ester conversion with the decreasing of the reaction time [2].

The use of ultrasound in biodiesel production has gained emphasis over the years [3–6], since ultrasound can promote homogenization between the reagents through acoustic cavitation. Acoustic cavitation is the growth and violent collapse of cavitation bubbles, which, when exploded, generate an increase in temperature in the reaction medium. This phenomenon is able to increase the speed of the reaction, reduce the amount of catalyst and reduce the reaction time from hours to minutes [7]. In most of the cases, the reactions use simple ultrasonic baths or ultrasonic probes operating in the frequency range between 20 and 50 kHz and high output power (typically over 200 W). New developments introduced biodiesel as an important tool in biodiesel production, using more economical equipment and demonstrating satisfactory conversion values using powers as low as 50 W or even lower [8].

Not just as a way to accelerate the transesterification, the ultrasound is being studied as a tool to monitor the biodiesel reaction [9]. The use of low-power ultrasound to determine the end of the reaction in an inline method cannot just save time and energy, but also it can potentially avoid waste.

As a method for material characterization and analysis, ultrasound has been used for several decades in several applications. However, ultrasonic analytical methods for biodiesel production are quite recent. The aim of this chapter is to demonstrate advances of using ultrasonic techniques for the production and the characterization of biodiesel, as well as an appraisal of the current technology status, and to provide insights into future developments.

2. What is ultrasound?

2.1. Ultrasound basic concepts

According to IEC 60050-802:2011 [10], ultrasound is defined as “acoustic oscillation whose frequency is above the high-frequency limit of audible sound (about 20 kHz)” and has no difference from sound concerning its physical properties, except in that humans cannot hear it. In large spectrum, ultrasound devices operate with frequencies from 20 kHz up to several gigahertz. The most relevant physical properties are summarized hereafter.

Propagation direction. Considering ultrasonic waves propagating through matter, energy is transferred from one location to another, but this energy is not associated with mass transfer. Based on the relation between the wave propagation direction and the motion direction of the particles constituting the medium, the waves can be divided in two propagation types: longitudinal and transverse. In the longitudinal propagation, the direction of displacement for the medium's particles is parallel to the direction of wave propagation (**Figure 1**, top). For the transverse propagation, the direction of displacement for the medium's particles is perpendicular to the direction of wave propagation (**Figure 1**, bottom). Despite that this basic division is frequently used in ultrasound, it is important to have in mind that there are also wave types for which the direction of motion for the medium's particles is not fixed relative to the wave propagation direction. In surface waves, for example, the angle between the two directions changes continuously [11].

Wave front geometry. Another important classification is based on the wave front geometry. Using this approach, waves can be divided into planar, in which the wave front is located on a plane that propagates in space and spherical ones that propagates symmetrically around a reference point (**Figure 2**). However, in practice, intermediate type of waves can be found over the ultrasonic beam transmitted. Considering a disc-shaped transducer, planar wave characteristics are observed near the transducer particularly around its central region. However, as far as the propagation is from the transducer, the wave will have more and more spherical wave characteristics. Similarly, as the ratio between the transducer diameter and the wavelength is decreased, the same behavior is observed [11]. The general case is defined by Huygens' principle, in which

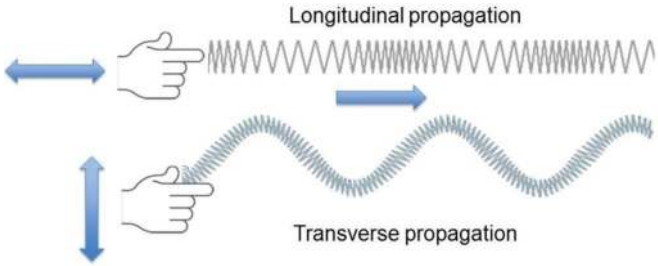

Figure 1. Example of longitudinal (top) and transverse (bottom) propagation.

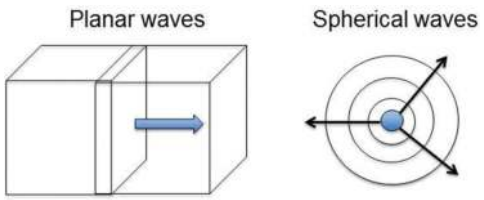

Figure 2. Diagram representing planar (left) and spherical (right) waves.

any wave source (or wave front) can be considered as an infinite collection of spherical wave sources (**Figure 3**).

Diffraction. It is a phenomenon by which a sound wave is changed in direction by an obstacle or other heterogeneity in the medium. This phenomenon is enhanced for wavelengths that are relatively long relative to the geometry of the obstacle [11]. The diffraction phenomenon is illustrated in **Figure 3**.

Interference. An important phenomenon occurs when two waves encounter each other in a propagation medium. It is called interference. The interference can be constructive, when the amplitudes of two waves enhance each other, or destructive, and their amplitudes attenuate each other. After passing through each other, if nonlinear effects are negligible (see "Nonlinear Propagation" section), the two waves proceed as though nothing has happened. Summarizing, within interference zone the result amplitude is the sum of all the interacting wave amplitudes, which is defined as the "superposition principle" [11].

Characteristic impedance of a medium. Product of the equilibrium density (ρ) and speed of sound (v) in a medium, as represented in (1). It can be understood as a measure of the impediment caused by a medium to the movement induced by a pressure applied to it. It is noteworthy that for a plane acoustic wave propagating in a non-dissipative medium, the specific acoustic impedance (at a specified surface, quotient of sound pressure (P) by volume velocity (U) through the surface) relative to this wave is equal to the characteristic impedance of the medium [11]:

$$Z = v \cdot \rho = \frac{P}{U} \tag{1}$$

Reflection and transmission. Given an incident wave at the interface between two media with different acoustic impedances, part of its energy is reflected, and part is transmitted to the adjacent medium, with or without a change in direction. The proportions of reflected (E_R) and transmitted (E_T) energies, relative to energy of the incident wave (E_I), can be estimated from the reflection (R) and transmission (T) coefficients. Eqs. (2) and (3) define these coefficients

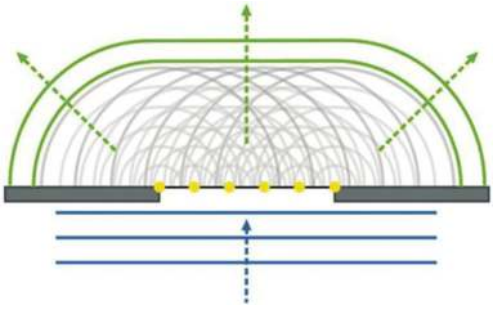

Figure 3. Schematic demonstration of Huygens' principle (left). Demonstration of the diffraction phenomenon for a planar wave propagating from the bottom toward the top and passing through a slot (right).

when the incidence at the interface of the media is perpendicular to the direction of wave propagation [11]:

$$R = \frac{I_R}{I_I} = \frac{(Z_2 - Z_1)^2}{(Z_2 + Z_1)^2} \tag{2}$$

$$T = \frac{I_T}{I_I} = \frac{(4 \cdot Z_2 \cdot Z_1)}{(Z_2 + Z_1)^2} \tag{3}$$

Propagation velocity. The propagation velocity of the wave in a medium (v) is dependent on the density and modulus of elasticity of the medium and can also be represented by the product of the ultrasonic frequency by wavelength as presented in (4):

$$v = \left(\frac{K}{\rho}\right)^{\frac{1}{2}} = f \times \lambda \tag{4}$$

in which f is the frequency of the ultrasound, λ is the wavelength, K is the modulus of elasticity (rigidity) and ρ is the density of the propagation medium [11]. Propagation velocity is named as speed of sound as well. Depending on some medium and the sound characteristics, phase velocity and group velocity are quantities more usable to physically describe the waveform displacement per unit of time.

Attenuation. In a planar wave propagating in a free field, the main causes of attenuation (loss of energy due to the distance traveled by the wave in a medium) of the ultrasound are scattering and absorption (mechanical energy conversion into thermal energy). Therefore, the attenuation of the signal is influenced by the characteristics of the medium [11].

2.2. Linear propagation

One of the most evident features in the shape of the ultrasonic beam generated by a piston, circular or not, is caused by the so-called edge effect [12]. This effect generates constructive and destructive interferences in a region known as near field, being observed in continuous waves. These interferences are not so evident in short-duration pulses [13, 14]. The edge effect is originated by the diffraction of the wave caused by the transducer because it has a finite aperture in relation to ultrasound wavelength.

Each element of the transducer surface can be considered an infinitely smaller point source and as such can generate spherical acoustic waves that create field interferences. In **Figure 4**, point A is distant from the transducer surface by a distance r, and it is apart from the symmetry axis by a distance r′. The lines d1 and d2 represent the distances from point A to the nearest and the farthest edges, respectively. Analytical expressions for pressure at A are available in the literature [14] and are relatively simple to derive because of the axial symmetry of a piston-like circular transducer. An even greater and possible simplification is the case where d1 = d2, i.e. the point A is on the symmetry axis of the transducer [15]. For this particular situation, Eq. 8.31b of Ref. [16], reproduced in (5), expresses the amplitude of the acoustic pressure as a

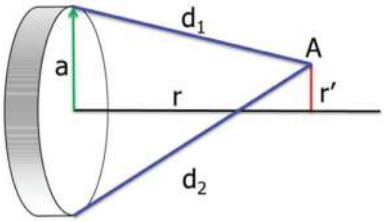

Figure 4. Representation of a point **A** positioned in the acoustic field generated by a flat piston with radius **a**.

function of the distance to the center of the piston, being valid for continuous waves or long tone bursts.

$$p(r) = 2\rho_0 c_0 U_0 \left| sen\left\{ \frac{1}{2} kr \left[\sqrt{1 + \left(\frac{a}{r}\right)^2} - 1 \right] \right\} \right| \tag{5}$$

In Eq. (5), $p(r)$ is the pressure amplitude along the symmetry axis as function of the distance; r, ρ_0 and c_0 denote the density and the phase velocity of the medium, respectively; U_0 is the transducer's surface velocity in the direction perpendicular to its face; and $k = \frac{2\pi}{\lambda}$ is the circular wavenumber ($\lambda = \frac{c_0}{f_0}$ and f_0 is the frequency). **Figure 2** shows the normalized amplitude $\frac{p(r)}{2\rho_0 c_0 U_0}$ plotted as a function of the normalized distance $\frac{r}{a}$ for the case in which $\frac{a}{\lambda} = 4$. The distance r_{Max}, described in (6), is the position of the last maximum in the increasing direction of r. It is considered the point of separation between the near field and the distant (or remote or far) field, from which the pressure amplitude decays with increasing r. In the example of **Figure 5**, $r_{Max} \cong 4a$:

$$r_{Max} = \frac{a^2}{\lambda} - \frac{\lambda}{4} \tag{6}$$

Another important position in the symmetry axis of a piston-like circular transducer is the last minimum, which Eq. (7) defines

$$r_{Min} = \frac{a^2 - \lambda^2}{2 \cdot \lambda} \tag{7}$$

According to [16], if $r > 6.41\frac{a}{\lambda}$, then (1) can be approximated to the far field equation $p(r) = \frac{k\rho_0 c_0 U_0}{2r}$, ensuring an error of less than 1% with that approximation. In general, measurements are taken in the far field, except when the effects of the near field are of interest in the measurement.

2.3. Nonlinear propagation

The theory adopted in the formulation of Eqs. (5) and (7) considers only the linear terms of the wave equation, so it is only an approximation of reality. The nonlinear effects of the

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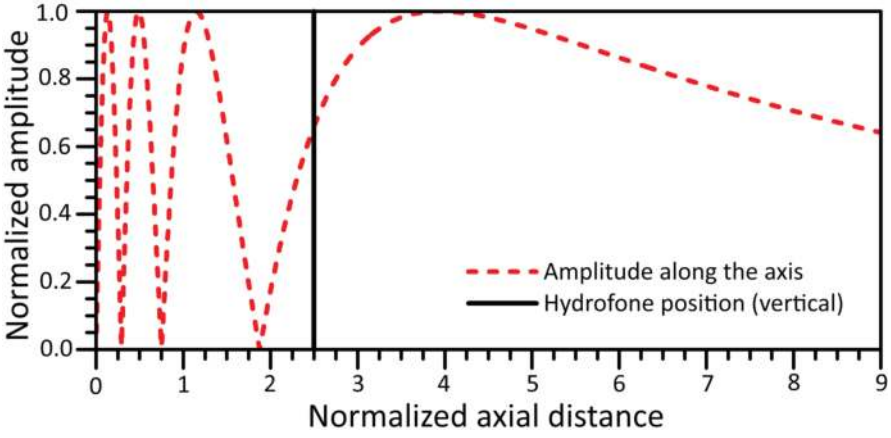

Figure 5. Pressure amplitude generated on the axis of symmetry of a plane circular piston-like transducer for $\frac{a}{\lambda} = 4$. The continuous vertical line simulates the position of a hydrophone in the field generated by the piston. In the example, the hydrophone is positioned at $r = 2.5a$, given a normalized pressure of 0.663.

propagation of the ultrasonic wave in fluid media cannot be arbitrarily neglected, under penalty of the theoretical model to present great discrepancies in relation to the realized measurements [17, 18], particularly in the ultrasonic fields generated by focused transducers [17, 19, 20]. Nonlinear effects can be observed even for small amplitudes [21, 22], from the propagation of only a few wavelengths [23, 24], in both water and other liquids [25, 26]. Essentially, the nonlinear propagation of the mono-frequency ultrasonic wave makes the power of the spectral component of the fundamental frequency to be gradually transferred to the higher harmonics, transforming an originally sine wave into a distorted or shock wave [27]. Despite that the shock wave profile is often compared to a sawtooth wave [22], in fact the negative peak of the wave is always smaller than the positive peak [17, 28], and the upward region of the wave has a curved and non-rectilinear profile (see **Figure 6**). The theory presented in [28] was used in the simulation of a distorted sine wave (burst) caused by the nonlinear propagation in water. The values of the relations between the harmonics, shown in the bottom graph of the figure, agree with [22] for a harmonic distortion parameter $\sigma \cong 5.7$, i.e. the wave of shock is completely developed—see Eq. (8). **Figure 7** shows the evolution of the composition of the harmonics as a function of the propagation distance.

Nonlinearity can be mathematically described by considering the higher-order terms in the resolution of the wave equation in which the wave propagation velocity becomes dependent on the velocity of the particle. During the compression (positive wave peak) the propagation velocity is higher than during rarefaction, and the waveform became distorted [22]. The shape of the beam is also changed, becoming more directional whilst the harmonics are being generated [29].

An effect resulting from the transfer of energy to high frequencies, particularly evident in organic medium such as fuel and biofuel, is the increase of absorption, since this effect is

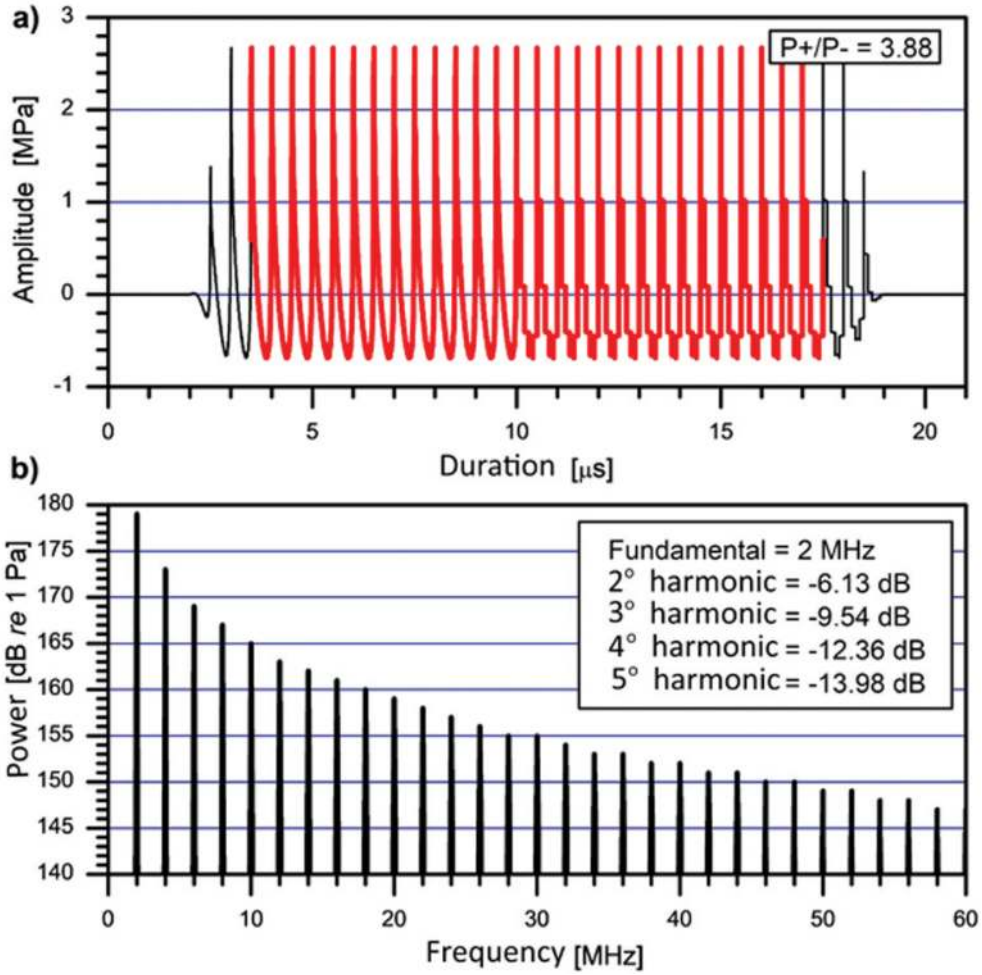

Figure 6. Example of a sine wave distorted by nonlinear propagation. (a) Graph of the wave in the time domain, showing the ratio between the positive and negative peaks (P+/P-). (b) Graph in the frequency domain, showing the ratio between the powers of the harmonics 2–5 in relation to the fundamental, in dB, which is related to the degree of wave distortion. For the example of the figure, $\sigma \cong 5.7$.

directly proportional to the frequency. In other words, the higher the energy at high frequencies, the greater the attenuation caused by propagation at these frequencies.

Although the waveform distortion mechanism is physically complex, involving the generation of harmonics and diffraction, dissipation and dispersion phenomena during the propagation of the acoustic wave in the fluid medium [28], mathematical models are available and are able to portray fairly accurately experimental results [30–33]. Of course, appropriate equipment allows reliable measurements capable of corroborating theoretical models [34], which was

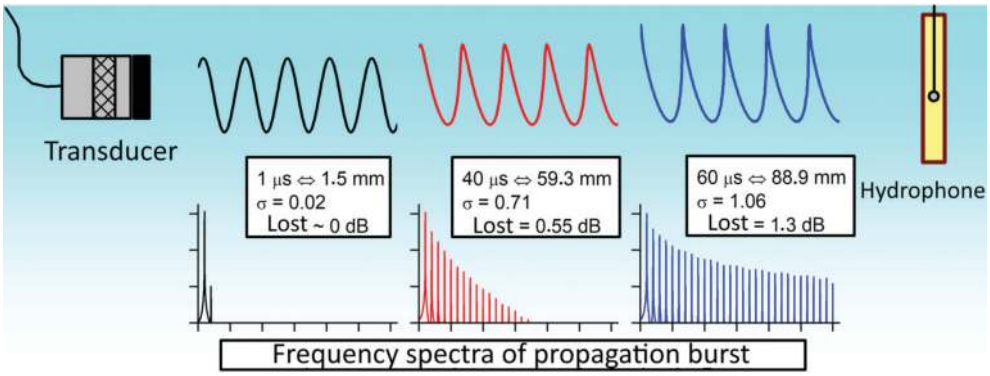

Figure 7. Sine wave distortion as a function of propagation distance.

more difficult to obtain in the past [35]. The theoretical model on which most of experimental applications are based today is described by Blackstock [30], which can be found in formulations of easy computational implementation [17, 22, 28].

A parameter used to describe the nonlinear deformation stage of the ultrasonic wave is called the degree of harmonic distortion σ, which for plane waves is defined as

$$\sigma = 2\pi\beta \frac{P_0 f_0 \Delta t}{\rho_0 c_0^2} \tag{8}$$

In Eq. (8), β is a dimensionless parameter dependent on the propagation medium (for water at 20°C, $\beta = 3.5$, according to [36]), P_0 is the effective pressure amplitude in the face of the generating transducer, Δt is the elapsed time since the waveform starts its propagation away from the transducer, and the other parameters are the same described previously.

2.4. Ultrasound industrial applications

Ultrasound is used in many different fields, and different devices have been constructed to specific applications. The most common uses include detecting objects and measuring distances; ultrasound imaging is used in medicine for diagnostic and in non-destructive testing of products, materials and structures to detect invisible flaws for raw eyes. Industrial applications of ultrasound include cleaning, mixing and accelerating chemical processes.

According to [37], sonicate is "to disrupt (something) by exposure to high-frequency sound waves", and sonication is "the act of applying sound energy to agitate particles in a sample, for various purposes". Hence, ultrasonication is a process in which ultrasonic frequencies are usually used to produce alternating low- and high-pressure waves in liquids, leading to the formation and violent collapse of small vacuum bubbles. This phenomenon is called cavitation and causes high-speed foist liquid jets and strong hydrodynamic shear forces. Ultrasonication proffers great potential in the processing of liquids, improving the mixing and chemical reactions in various industrial applications.

Industrial processes like the disintegration of cells or the mixing of reactants as well as the deagglomeration and milling of micrometer and nanometer-size materials are examples of ultrasonication application. Besides, chemical reactions benefit from the free radicals created by the cavitation, as well as from the energy input and the material transfer through boundary layers. For many processes, this sonochemical effect leads to a substantial reduction in the reaction time, like in the transesterification of oil into biodiesel.

In general, ultrasonic concepts of industrial processes are initially tested on laboratory scale to prove feasibility and establish the required operation ultrasonic parameters. The next step is to transfer the validated concept to a pilot scale for optimization and finally to an industrial scale. During the scale-up, it is important to guarantee that all exposure conditions (e.g. ultrasonic amplitude, working frequency, cavitation intensity, ultrasound exposure time, etc.) remain the same, in order to assure the final product quality, whilst the productivity is increased by a "scale-up factor".

2.5. Ultrasound parameter measurement

Considering some industrial applications, high ultrasonic power is required for many processes. On the other hand, when ultrasound is used to analyze the quality of chemical inputs [38] or the behavior of chemical reactions, low-power ultrasound is used to avoid any alteration in the chemical product or any interference in the chemical reaction.

In this direction, ultrasound parameters shall be calibrated to guarantee the adequate use of ultrasound at each specific industrial application. Herein, some parameters will be highlighted and how they are measured, as the output power and the working frequency, which are related to the device that generates the ultrasonic waves, and the propagation velocity and the attenuation, which are intrinsically correlated to the properties of the medium in which the ultrasonic waves are traveling.

According to IEC 61161 [39], output ultrasonic power (O_P) is defined as the "time-average ultrasonic power emitted by an ultrasonic transducer into an approximately free field under specified conditions in a specified medium, preferably water". The output power is expressed in watt (W). In general, ultrasonic power is measured in water, based on the measurement of the ultrasonic radiation force (F), which is the time-average force (expressed in N) acting on a target in an ultrasonic field and caused by the ultrasonic field. This force is typically measured using the radiation force balance that consists of a reflecting or absorbing target connected to a gravimetric microbalance. The ultrasonic beam is directed vertically upwards or downwards on the target, and the gravimetric balance measures the radiation force exerted by the ultrasonic beam. The radiation force component on the absorbing target in the propagation direction of the incident wave is related to the acoustic output power of the ultrasonic transducer as presented in (9):

$$O_P = v \cdot F \tag{9}$$

The ultrasonic power shall be determined from the difference between the force measured with and without ultrasonic radiation. The great advantage of radiation force measurements is that a value for the total radiated power is obtained without the need to integrate field data over the cross section of the radiated ultrasound beam.

The working frequency of an ultrasonic transducer is defined as the frequency of an ultrasonic signal based on the observation of the output of a hydrophone placed in an ultrasonic field at the position corresponding to the spatial-peak temporal-peak ultrasonic pressure [40]. The hydrophone is a transducer made from either polyvinylidene fluoride (PVDF) or piezoceramic (PZT) that produces electrical signals in response to surface input of ultrasonic signals [41]. Those signals are often measured using an oscilloscope, and the signal is analyzed using either the zero-crossing technique or a spectral analysis method [40].

The ultrasonic properties of materials within the megahertz frequency range are determined using techniques commonly referred to as the through-transmission substitution technique [42, 43] and as pulse-echo technique [44]. Using those techniques, it is possible to measure speed of sound and attenuation coefficient of the material under text. In general lines, the time of flight (related to the speed of sound) and the amplitude (related to attenuation) of the ultrasonic signal are measured in a reference medium, normally water. In the sequence, the time of flight and the amplitude are measured over the material under test. As the speed of sound and attenuation coefficient in the water are well known, and accurately determined based on measured temperature, the properties of the material under test are determined relative to water [45].

In more details, calculation of speed of sound is carried out by measuring the arrival time of the ultrasonic pulse both with (t_s) and without (t_0) the test sample in the ultrasonic beam. The difference in these times ($t = t_s - t_0$) is the time-shift caused by the different speed of sound in the material (v_s), which can be derived as [45]

$$v_s = \frac{l \cdot v_w}{v_w \cdot t + l} \tag{10}$$

in which v_w is the speed of sound in water at the temperature of interest and l is the sample thickness.

The ultrasonic transmission loss (TL) can be determined by measuring the frequency-dependent (f) change in amplitude of the electrical waveform through water ($V_0(f)$) and with the test sample in the ultrasonic beam ($V_s(f)$), which shall be positioned and aligned within the beam:

$$TL(dB) = -20 \cdot \log_{10} \frac{V_0(f)}{V_s(f)} \tag{11}$$

The attenuation coefficient of the test sample is obtained by dividing the TL by the sample thickness, after appropriately correcting for attenuation in water path and reflection of the incident wave at the interface between the water and the sample.

3. The past

It is known that biodiesel is typically obtained by the transesterification of the triglycerides of oils and fats with an alcohol in the presence of an acid or alkaline catalyst [46]. This reaction is

traditionally performed using mechanical stirring, but this process is limited by mass transfer between the different reactants. This limitation is normally overcome by increase stirring, temperature and reaction time to aid in solubility between the reactants.

Originally, the ultrasound was used in transesterification reactions to homogenize the two immiscible phases (triglyceride and alcohol). This homogenization is caused by acoustic cavitation. This phenomenon releases large amounts of energy resulting in very high temperatures and pressures [47].

In addition, there is another application which consists of the use of non-destructive ultrasound for characterization and analysis of materials. Ultrasound has been used for this purpose for several decades in various industrial applications, including chemistry reactions. However, in the past, methods were not addressed for the characterization and analysis of materials focused in the production of biodiesel. There is a study [46] that uses ultrasound to characterize the by-product (glycerol) formed in the transesterification reaction. The objective was not the ester formation, but the analyses of glycerol deposition instead.

That said, a systematic review of the use of ultrasound in biodiesel production will be presented in this section. Taking into account the importance of technology, the review will include a discussion about the notorious advantages of the technique, interaction with other methods and method limitations.

3.1. Ultrasound-assisted biodiesel production

According to [47], in 1927, Alfred L. Loomis was the first chemist to recognize the effect of intense sound waves propagating through the liquid, more known as sonochemical effect. Despite the discovery, research focused on the area started from 1980. In this context, since 2003, ultrasound has been a favorable tool in biodiesel production, due to the ability to eliminate the mass transfer resistance and for being an efficient and low-cost method.

WO2007/077302A1 [48] is the first patent that encompasses an ultrasound method and the production of biodiesel. This invention relates to equipment and process for producing biodiesel where ultrasound is used to destruct heated fat. The preheated fat is cracked in several tanks that are connected to each other in series or in parallel. The ultrasound device is situated inside the tank and uses ultrasonic frequency between 15 and 55 kHz.

Subsequently, two more patents were deposited. KR20100110678 [49] describes a reactor for biodiesel production, where the ultrasonic horn is exposed in the inside of the reactor. The reaction is performed under pressure from 100 to 350 bar, temperature between 35 and 60°C and ultrasonic power from 60 to 1.500 W. This invention aims to synthesize biodiesel with high reaction speed and high yield. The other invention US2012279111 [50] is a continuous process for producing biodiesel fuel. In this process, the reagents are fed into an ultrasonic cavitation reactor. After 5–30 s, the flow leaves the reactor and goes to an agitated-tank-type reactor. The mixture remains for about 1 h, which is the time needed to yield the final conversion of triglycerides of about 96%. The mechanical stirring is responsible for most of the reaction, and ultrasonic cavitation only assists the homogenization of the reagents.

Ultrasound methods for biodiesel production have developed continuously. **Table 1** compiles several papers published in the last decade, whether by irradiation ultrasonic indirect (bath) or direct (probe and transducer), in the presence of acid or basic catalysts, using the most diverse raw materials.

The main perspective in the past was the use of equipment available in any chemical laboratory, with ultrasonic waves of low frequency (up to 500 kHz) and high power [51].

The ultrasonic probe is a usual commercialized equipment that has high power output capability as it concentrates energy delivering. In this type of equipment, there is a distance (about 5 cm) between the transducer (responsible for irradiation) and the tip of the horn. The ultrasonic energy is provided to the liquid through the horn immersed in it, as shown in **Figure 8**.

Many studies using this equipment for producing biodiesel are found in the literature [3–6]. In the study by Lifka et al. [3], an ultrasonic processor (24 kHz; 200 W) known as ultrasonic probe was used in the transesterification reaction of canola oil with ethanol. After 30 min of reaction, a conversion of 87% was obtained to a molar ratio of 6:1 and 0.5–1% of the sodium hydroxide. A study of the energy balance was carried out comparing the three methods of agitation: magnetic, mechanical and by ultrasound. It was concluded that using ultrasound obtains lower energy costs. Georgogianni et al. [4] also performed biodiesel production with ultrasonic probe at low frequency (24 kHz; 200 W). They used sunflower oil and methanol at a molar ratio alcohol/oil of 7:1 and 2% sodium hydroxide. In 20 min of reaction, it reached 95% yield. In the presence of ethanol, using the same reaction parameters, the ultrasound led to high ester

Feedstock	Alcohol type; molar ratio	Catalyst type; (%)	Frequency; power	Time(min); conversion (%)	Refs.
Canola oil	Methanol 6:1	NaOH; 0.5	20 kHz; 200 W	30 min; 87	[3]
Sunflower oil	Methanol 7:1	NaOH; 2	24 kHz; 200 W	20 min; 95	[4]
Coconut oil	Ethanol 6:1	KOH; 0.75	24 kHz; 200 W	7 min; 98	[5]
Canola oil	Methanol 5:1	KOH; 0.7	20 kHz; 2000 W	50 min; 99	[6]
Synthetic oil	Methanol 6:1	NaOH; 0.5	40 kHz; 840 W	20 min; 98	[52]
Soybean oil	Ethanol 10:1	NaOH; 0.3	40 kHz;	30 min; 91.8	[53]
Oleic acid	Ethanol 3:1	H_2SO_4; 5	40 kHz; 700 W	120 min; 90	[54]
Fish oil	Methanol 9:1	H_2SO_4; 2	40 kHz; 60 W	90 min; 98.2	[55]
Waste cooking oil	Methanol 6:1	KOH; 1	20 kHz; 200 W	40 min; 89	[56]
Cottonseed oil	Methanol 6:1	KOH; 1	40 kHz;	5 min; 96.0	[57]
Palm acid	Methanol 7:1	H_2SO_4; 5	22 kHz; 120 W	200 min; >90	[58]
Waste cooking oil	Methanol 9:1	H_2SO_4; 3	40 kHz; 200 W	60 min; 99.9	[59]
Jatropha oil	Methanol 7:1	H_2SO_4; 4	210 W	60 min; 96.4	[60]

Table 1. Compilation of studies with typical parameters in ultrasound-assisted transesterifications.

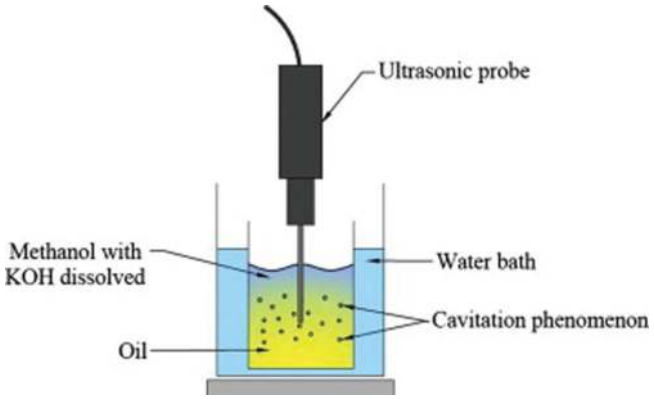

Figure 8. Schematic representation of the reaction using ultrasonic probe. Adapted from Sáez-Bastante et al. [7].

yields, about 98%. In only 40 min of reaction while using mechanical stirring it gave lower yields, about 88%, even after 4 h of reaction time.

Kumar et al. [5] used the same equipment as described in [3] in the transesterification of coconut oil to produce ethyl ester. A 98% conversion of the ethyl ester was obtained in 7 min of reaction at a molar ratio of 6:1. In these studies the ultrasonic probe was used as an alternative to the usual production process and resulted in high conversions. Thanh et al. [6] developed a pilot scale plant for biodiesel production from canola oil catalyzed by hydroxide potassium. An ultrasonic probe was used at low frequency (20 kHz). After 50 min of reaction, a maximum conversion of more than 99% was obtained with a methanol-to-oil molar ratio of 5:1, 0.7% catalyst concentration. The authors conclude that optimization of ultrasonic power and mode of delivery (pulsed ultrasound) can be carried out to minimize energy consumption while attaining high conversions.

Although it has been widely used, the ultrasonic probe has some disadvantages as it easily corrodes the horn tip [51] and presents low cavitation efficiency. In addition, the acoustic intensity is distributed in a concentrated and non-homogeneous fashion.

Another equipment commonly used in the production of biodiesel mainly because of its low cost and for being an equipment of easy acquisition is the ultrasonic bath. In this equipment, the ultrasonic transducers are positioned in the bottom or lateral position of the bath, and a reactor is fixed to the bottom, as shown in **Figure 9**.

There are several studies that performed transesterification reactions in ultrasonic baths. In these studies, the conversion results were greater than 90% [52–55]. Stavarache et al. [52] produced biodiesel using an ultrasonic bath with frequency of 40 kHz. The authors compared the profile of methyl esters of different vegetable oils produced under ultrasonic irradiation with conventional heating. The profile of methyl esters in the presence of potassium hydroxide was quite similar for both procedures. In the case of sodium hydroxide, the reaction with using ultrasound gave better results. In this study, the highest conversion obtained was 98% after 20 min of reaction at an alcohol-to-oil molar ratio of 6:1.

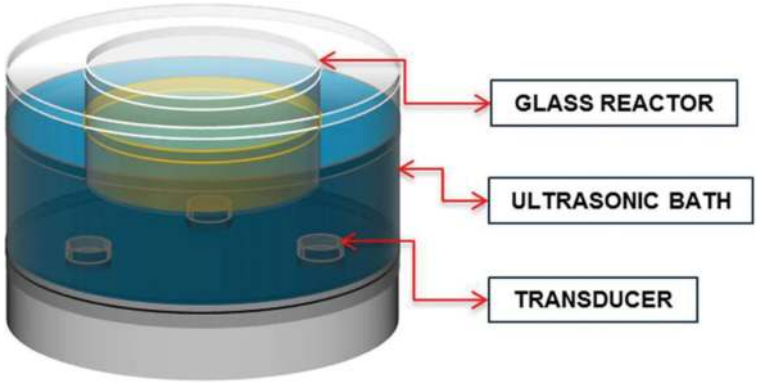

Figure 9. Schematic representation of the reaction using ultrasonic bath.

Rodrigues et al. [53] also produced biodiesel in an ultrasonic bath with low-frequency waves (40 kHz), using soybean oil as raw material and ethanol. The author reports that after 30 min of reaction, the conversion (91.8%) was greater than the conversion obtained using the conventional process. Studies from other research groups too have confirmed the high conversion by using the ultrasonic bath. In study of Hanh et al. [54], the reaction was carried out in an ultrasonic bath operating at 40 kHz and 700 W. The conversion obtained was 90% after 120 min of reaction, using oleic acid and ethanol at an alcohol-to-oil molar ratio of 3:1. Santos et al. [55] also used ultrasonic bath, operating at 40 kHz and 60 W. The biodiesel was produced from reaction fish oil with methanol by an ultrasound-assisted method. The reaction was carried out with molar ratio alcohol/oil of 9:1 and a catalyst concentration of 2.0%. A higher methyl ester yield was achieved as compared to mechanical stirring. The yield was equal to 98.2% in 90 min of reaction.

It may be noted that using an ultrasonic bath, it is possible to achieve high conversions. The ultrasonic bath was designed for cleaning and degassing and does not allow directional irradiation in the reaction medium. Therefore, a possible explanation for their performance is that these reactions are always conducted with external heating between 40 and 70°C, and heating facilitates transesterification of triglycerides. Despite the favorable results, this equipment has as disadvantage the low cavitation efficiency and distribution of the dispersed and non-homogeneous acoustic intensity and usually requires mechanical agitation [61].

In 2009, the use of ultrasonic transducer directly applied in the reaction media begins to be proposed. Different than the use of ultrasonic probe, in this application there is no separation between the transducer and the liquid surface; thus, the volume of wave propagation is more confined (see **Figure 10**).

Hingu et al. [56] synthesized biodiesel from waste cooking oil using a low-frequency ultrasonic reactor at 20 kHz with power of 200 W. The optimum conditions for the process have been molar ratio of alcohol to oil of 6:1, catalyst concentration of 1% and temperature of 45°C. The

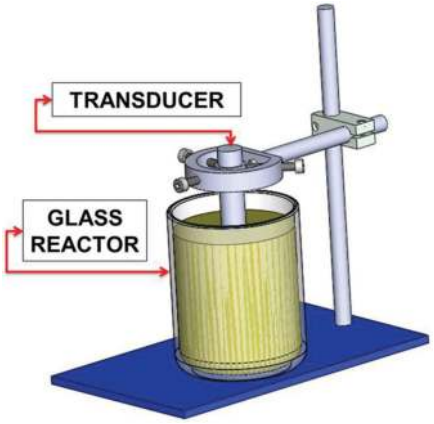

Figure 10. Schematic representation of the reaction using ultrasonic transducer.

power effect was studied, and the obtained conversion was around 66% at a power of 150 W. However, when the power was increased to 200 W, extent of conversion also increased to about 89%. On the other hand, an increase in the power dissipation from 200 to 250 W resulted in lower conversions. It was concluded that this can be attributed to the fact that at higher power levels, usually cushioning effect is observed which results in to decrease the transfer of energy into the system.

Fan et al. [57] used a transducer powered by a function generator to perform the transesterification of crude cottonseed oil with methanol in molar ratio of 6:1 in the presence of base catalyst. The reaction was conducted with low-frequency ultrasonic irradiation at room temperature. After 60 min of reaction, using the 40-kHz frequency waveform, a yield of approximately 90% yield was obtained. Four different frequencies were investigated: 400 Hz, 4 kHz, 40 kHz and 400 kHz. Significant difference in biodiesel yield among different frequencies was not observed. This suggests that there were no remarkable differences in the formation of the cavitation bubbles at the examined frequencies.

In the past, the use of ultrasound has proved to be an efficient technique to produce biodiesel. However, several ultrasonic parameters such as power, frequency and mode of operation can optimize the efficiency of this reaction. In this context, the development of new methods and equipment for ultrasound application must occur to make biodiesel production increasingly competitive.

4. The present

For the last 7 years, several studies showed the effective system optimization regarding the use of high-power and low-frequency (typically up to 50 kHz) ultrasound in the biodiesel production [7, 62–66]. These studies investigate the best procedure or configuration to achieve a better

yield. This improvement made this technique to be one of the most studied for the biodiesel production.

Although the use of ultrasound to improve the biofuel production has been used for decades, the literature about low-power ultrasound (less than 50 W), for this purpose, is rare.

When the question is "can we make better for the environment?" or "can we think in a greener procedure?", the use of high-power ultrasound for biodiesel production, even as it already demands less energy than the usual method, makes us reflect about the real energy necessary to produce a biofuel with quality. Within this approach, the Laboratory of Ultrasound of the Brazilian National Metrology Institute (Inmetro) has been developing different ways to produce biodiesel. The first results published about this study [8] used an ultrasonic transducer with 9 W to produce soybean biodiesel with methanol and potassium hydroxide as a catalyst. Despite that the results were considered good (conversion around 95%), the method used to analyze the conversion in that paper is not so well described in the literature regarding the reproducibility. In this way, the researches continued regarding the use of a lower-power and high-frequency ultrasound in the biofuel field production. Promising results have been obtained with the same equipment used in [8] (see **Figure 11**).

The optimization of the parameters and experimental setup were not the only changes in the study as shown in **Figure 11**. The monitoring of the conversion using the nuclear magnetic resonance of hydrogen (^{1}H NMR) gives more reliability to this study. The output power was calibrated according to the international standard [39], and 9.06 W was the effective acoustic power. The 85% of conversion supports the idea that reducing the delivered ultrasound energy is possible to produce biodiesel with a good conversion rate. Furthermore, it shows that the increase of the alcohol/oil ratio to 8:1 decrease the necessary time to achieve the maximum conversion rate.

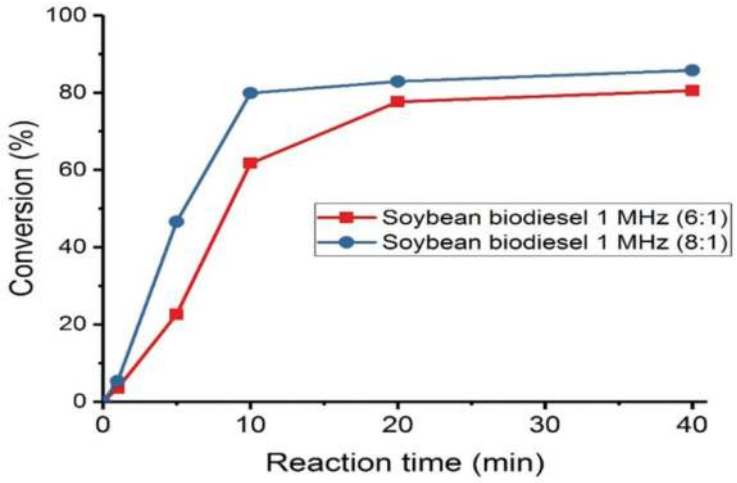

Figure 11. Soybean biodiesel by ultrasound using the 1 MHz transducer using an alcohol/oil ratio of 6:1 and 8:1.

The reactions described in **Figure 11** achieve 43°C without necessity of a heating system. This leads an energy saving, when you think that the most expensive part of the reaction is the heating. These first results aim not just the optimization of the ultrasound use in the transesterification but the current concerns about energy wasting.

However, the use of ultrasound to produce biofuels is not the only application of this versatile technique. The use of very low-power and high-frequency ultrasound to monitor the liquid properties has been used in several fields for many years [46, 67–72]. One of the first studies was in 1995, when Sheen et al. [73] showed a non-invasive and inline system capable to measure the density and viscosity of Newtonian liquids using a 1 MHz transducer. The inline applicability of the ultrasound techniques boosted the development of these techniques in the biofuel field. In the last 6 years, studies to detect the adulteration in biofuels [74, 75], to quantify oil and grease contents in biofuel wastewater [76] and to monitor the biodiesel reactions [77] were carried out with good results. The ethanol adulteration analyzed by Figueiredo et al. [75] introduced the idea of the importance of the metrology in the biofuel system. Not just the possibility of the use of ultrasound was proved to be simple and accurate but its feasibility as an auxiliary tool that can be applied in the line process.

In this way, the constant search for the improvement in ultrasound measurements is developing the real possibility of an ultimate ultrasound system to monitor not just the biodiesel production but its quality as well.

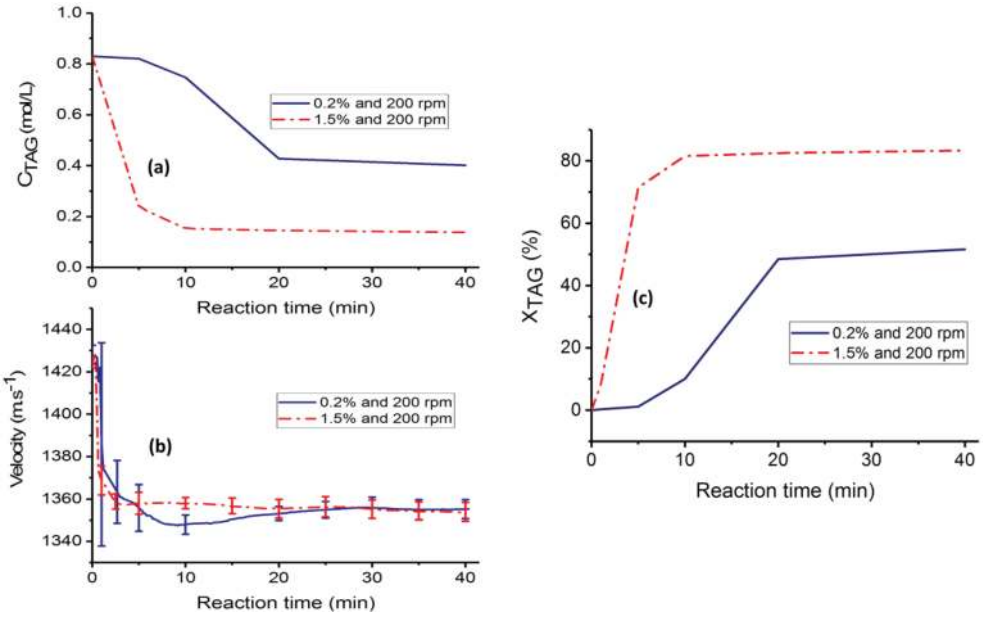

Figure 12. Variation of (a) TAG concentration, (b) propagation velocity and (c) TAG conversion for the reactions with 200 rpm of rotation. Reprinted from Baêsso et al. [9].

Considering the present worldwide biodiesel consumption, which increases every year, a new method for monitoring the production, helping to avoiding the waste of reagents, energy and time, is extremely necessary. The expensive and offline available methods can lead to accurate values but just in the end of each batch. This means that if something goes wrong during the process, the results would be noticed just after the end of the production. Thus, a low-cost and accurate technique, suitable to the process line, has been studied recently as a technological alternative way in the biodiesel industry.

Baesso et al. [9] disclose in their study that ultrasound can notice changes in the medium during transesterification reaction but can also monitor the kinetics behind the biodiesel production. That study analyzed four different reactions to produce biodiesel from commercial soybean oil. Methanol was the alcohol used, and potassium hydroxide was the catalyst. The changing of the catalyst concentration (0.2 or 1.5%) and the mechanical stirring (200 or 520 rpm) allowed the analyses of ultrasound capability to detect the real impact of changing these parameters. The study compared and related the oil consumption (CTAG), the biodiesel conversion rate (XTAG) and the propagation velocity. Both CTAG and XTAG were monitored by ^{1}H NMR, as an offline method. **Figures 12** and **13** show some results published in [9].

From the both figures reprinted from [9], it is possible to notice that ultrasound follows the results obtained by the ^{1}H NMR technique but in an inline mode. Baesso et al. [9] proved that for the four analyzed reactions, the ultrasound was capable to distinguish the end of

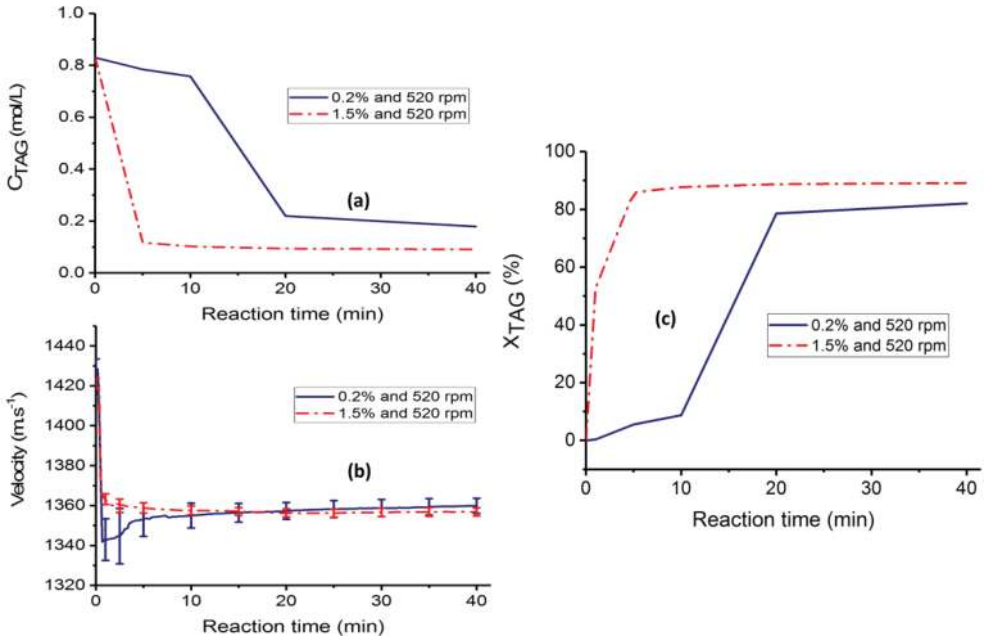

Figure 13. Variation of (a) TAG concentration, (b) propagation velocity and (c) TAG conversion for the reactions with 520 rpm of rotation. Reprinted from Baêsso et al. [9].

each one without any sample pretreatment. The use of the ultrasound in this study would allow the industry save not just energy with the reducing time but with the expensive techniques to analyze the final product. Not just the idea of using this kind of technology in biodiesel industry is remarkable, but the use of the metrology gives more reliability for the current technologies that aim the biofuel production optimization.

5. The future

Disclosing the future is not often considered science. Nevertheless, some clues can be gathered in the well-established state of the technique to point out some possible tracks to be followed. With respect to the use of ultrasound in biodiesel production and analysis, the future seems to be related to the use of broadband, frequency-modulated waveforms. Deconvolution techniques, both in time or frequency domains, are ready enough to be used in biodiesel analysis and production. Some recent achievement will be discussed in this section, and a sort of future prediction will be essayed.

Quantitative ultrasound (QUS) is a measurement approach for quantifying ultrasonic parameters of a medium. In general, the ultrasonic quantities are derived from two basic measuring quantities: time of flight and amplitude. Those quantities vary as function of frequency and physical-chemical properties of the interrogated medium, including density, temperature, viscosity, the presence of scatters, discontinuities and other interleaved structures or intercurrent phenomena. The aforementioned quantities are extracted from a time- or frequency-domain ultrasonic signal.

For inspection in liquid media, the most important aspects are the ultrasonic phase velocity and the scattering pattern [42, 43, 45]. The behavior of those derived quantities as function of frequency is deeply related to density and viscosity. Many studies have been demonstrating the relationship between QUS and fuel [9, 75, 76, 78]. Another approach to the use of ultrasound in the industry of fuel and biofuel is its use for production [1, 8, 54, 63, 64]. Ultrasound has been demonstrated to be useful to cell culture treatment [79], as well. In all cases, a proper evaluation of ultrasonic parameters or transducer characteristics plays an important role, and some basic metrological procedures shall be followed, including uncertainty determination [80–83].

Ultrasound propagation has intrinsic capability of generating nonlinear distortion, depending of some factors such as frequency, power and propagation distance [17, 23, 30]. It could even be of great interest as a disaster for ultrasound analysis. Fortunately, there is relatively simple way to deal with nonlinear distorted fields, which is the use of compensated frequency-modulated signals to identify systems and perform ultrasound measurements [84, 85]. The method described in those papers can be generalized for virtually any system to be measured, for instance, fuel and biofuel, including contaminants. The basis consists in constructing a waveform in the time domain from information previously known or experimentally obtained about the system frequency response. **Figure 14** was extracted and adapted from [84] and summarizes the signal construction method.

The system frequency response (FR) shall be previously determined or arbitrarily defined. After that, it is band-limited and pseudo-inverted, defining a bandwidth for the final signal. The group

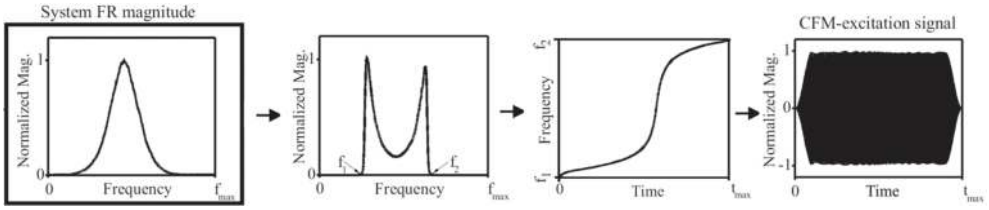

Figure 14. CFM construction forms a predetermined system frequency response. Adapted from Costa-Felix et al. [84].

delay is mathematically constructed based on the pseudo-inverted frequency spectrum, and the complex frequency spectrum is determined on sequence. Finally, the time-domain signal is constructed using the inverse Fourier transformation. Details of the processing can be found in the literature. The important concept here is that the system identification method developed as that has the intrinsic characteristic of putting apart any distortion caused by the system, including that one caused by nonlinear propagation. The distortion can even be evaluated separately, being the harmonics characterized or quantified individually. Such process has a completely unexploited capability to be used in fuel and biofuel analysis. It is our bet for the future of ultrasound methods on fuel identification, quantification and quality control.

6. Final remarks

Throughout this chapter, the past, the present and the future of biodiesel production and analyses using ultrasound methods were presented and discussed. The chapter was written aiming to let the not insider reader to be able to conquest the basis of ultrasound and biodiesel technical relationship.

The past was a remarkable assortment of attempts to make use of generic ultrasound systems to accelerate biodiesel production. The present brings several dedicated instruments, measurement systems and fabrications tools specially designed for the use of ultrasound in fuel and biofuel. In the future, who knows? The trend seems to be related to the use of digital signal processing for specially designed applications, using, for instance, online real-time signal design based on transfer function and system identification for manufacturing optimization. That is our best bet.

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