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Using ultrasonic velocity for monitoring and analysing biodiesel production

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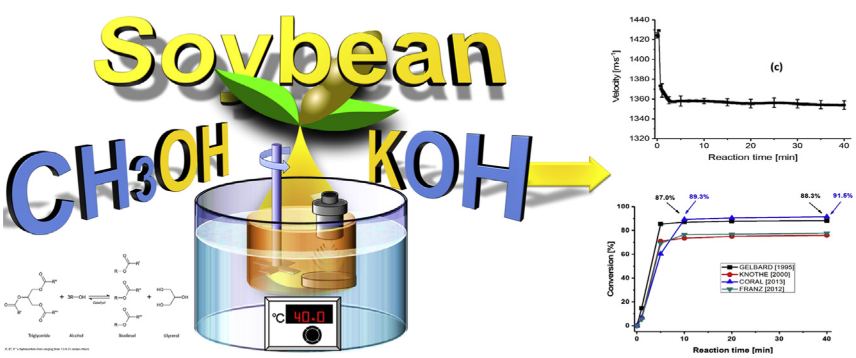
GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents an ultrasonic method capable of being applied in a process line for monitoring the soybean oil transesterification with methanol, catalysed by KOH. Four production routes had been studied, varying the concentration of catalyst (0.2% and 1.5% w/w) and the rotation period of the mechanical stirring (200 rpm and 520 rpm). A low-power, 1 MHz ultrasound signal was used with the pulse-echo method to interrogate the medium during the transesterification process, being the speed of sound the measurement quantity. Variation of this quantity was compared throughout the process with traditional and precise analytical methods (gas chromatography and nuclear magnetic resonance of hydrogen). Aliquots were collected every 5 min from the reactional medium, and the conversion rate was assessed thereafter. The measurement of ultrasonic velocity showed that the ultrasound could identify variations occurring in the reactional medium which are correlated to ester production. Complementary, results indicate that the ultrasonic velocity can aid in distinguishing among different biodiesels produced. Further, the reactional time of flight ratio is presented as an alternative method for monitoring the biodiesel synthesis in real time. As a final remark, it was possible to use the proposed ultrasonic method to monitor the transesterification reactions in real time, allowing this technique to be applied in the process line minimizing wastes of reagents and energy.

1. Introduction

Considering the current energy consumption scenario, in which the increase of demand for fossil fuel is much greater than the discovery of new sources, alternative energy began to appear as a way to supply the demand in sectors of transport, industrial activities and others. The

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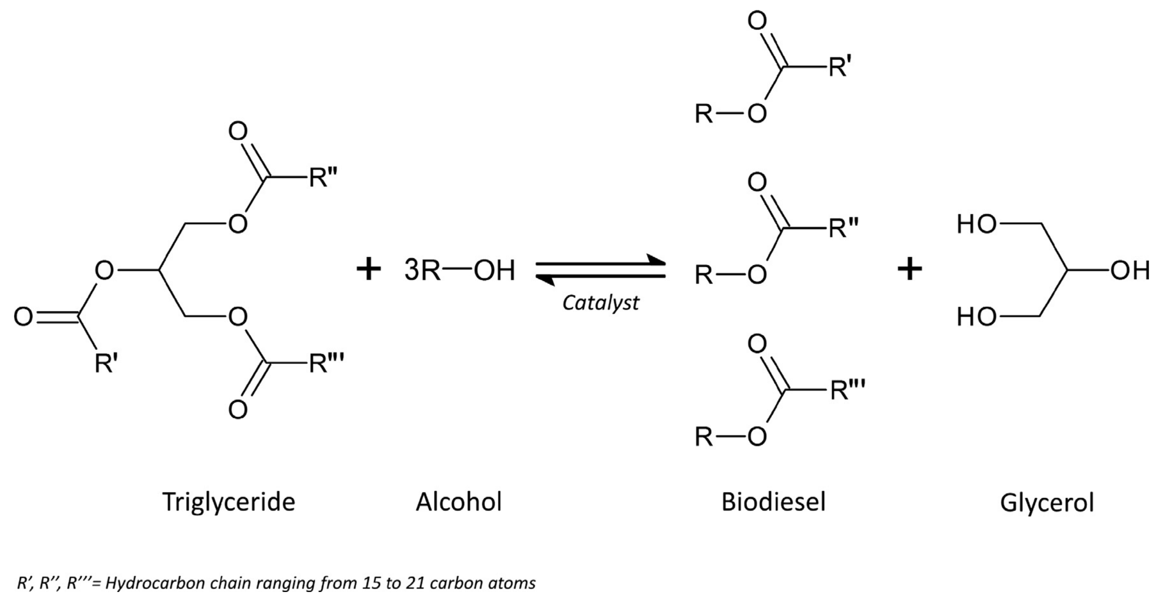

Fig. 1. Transesterification of vegetable oil.

high-energy consumption, directly linked to world population growth, deplete fossil fuel reserves, making oil prices unstable [1–5]. As a natural consequence, international trading and economic balance becomes unpredictable.

Greener fuels, such as ethanol and biodiesel, have been extensively studied, as they are known as less harmful on global warming and climate change. Biodiesel is considered a renewable, clean and biodegradable fuel. Chemically, biodiesel is composed of long chains of fatty acids of methyl esters (FAME), produced through the transesterification of renewable feedstock like oils and animal fats [5–8]. The most common method used to produce biodiesel is the transesterification via basic catalysis, using potassium hydroxide (KOH) or sodium hydroxide (NaOH) as the homogeneous catalyst and methanol (MeOH) as the short chain alcohol (Fig. 1).

The reaction is usually carried out in reactors and several factors can affect the process, such as the change of raw material, type of alcohol, concentration and type of catalyst, temperature, and velocity of agitation. Thus, to ensure the quality of biodiesel, international standards, such as the European Standard EN 14214 [9], establish parameters and quality control requirements for several biodiesel components. These requirements ensure stability within the period of storage, as well as prevent engine damage.

The most commonly used methods to verify the quality of biodiesel analyze it only at the end of each reaction, and always after the purification process. This off-line process is highly expensive [10], as it implies the need for reprocessing the entire batch if it's quality is not within the specifications. Several methods for monitoring of biodiesel production can be found in the literature for in-line and off-line approaches, being the most widely used based on spectroscopy gas chromatography [11–14], infrared [15–17], near-infrared [18–23], and nuclear magnetic resonance (NMR) [24,25]. Such analyzes have high precision and reliability, but require complex equipment and involve comparably high cost. The traditional analytical methods are fundamental to validate chemical kinetics as for instance the transesterification process [26–28]. Thus, it is important to develop robust, accurate, low-cost and non-destructive quality control methods. Ultrasound is a technique that could fulfill the requirements for the next generation of non-invasive analytical measurement method for biofuel analyses.

The use of ultrasound methods is interesting because they can be applied in the process line [29]. The literature discloses several works that show the possibility of using ultrasound to measure the physical and acoustic properties of liquids and solids [30–32]. Ultrasound has been extensively used in several stages of a chemical process, in the acceleration of the reaction [33], in the separation of compounds [30], and can also be used for identification and analysis [30,31,33–35]. However, considering metrological aspects, there is a lack of knowledge to be exploited [36].

The aim of this work was to develop a precise, robust and low-cost method that can be applied in a process line for monitoring the soybean oil transesterification with methanol, catalyzed by KOH. The monitoring of transesterification on-line allows the optimization of experimental parameters of the reaction in order to obtain better yields and to reduce overall costs of biodiesel production.

2. Material and methods

2.1. Uncertainties and statistical analyses

Throughout the whole work, all measurement uncertainties were assessed according to the internationally accepted Guide to the Expression of Uncertainty in Measurement (GUM) [37]. The terms and concepts about metrology are used in accordance with the international vocabulary [38]. Examples of detailed step-by-step uncertainty assessment for sound and ultrasound quantities can be found in [35,39–42]. All statistical analyses were done with the background detailed in [43].

2.2. Transesterification

Biodiesel was produced using the most common process, well known as a reliable way to achieve good quality products. According to the literature [44–49], the proportions of alcohol to oil must to be around 6:1 to obtain good yields during the homogeneous transesterification, while the catalyst concentration, in this case KOH, must be 1.5% (weight over weight, or w/w). The following products were chosen for biodiesel production: soybean oil as the esters' source, methanol as the alcohol, and KOH as the catalyst. The temperature was kept at 40 °C, while the stirring and catalyst concentration were varied to promote dissimilar production routes. For all different transesterification routes, an ultrasonic method was applied into the reactional medium in order to evaluate its sensitivity to evaluate the chemical process.

Four transesterification routes were defined *a priori* combining two stirring frequencies (200 rpm and 520 rpm) and two catalyst