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Ultrafast Biodiesel Production Using Ultrasound in Batch and Continuous Reactors

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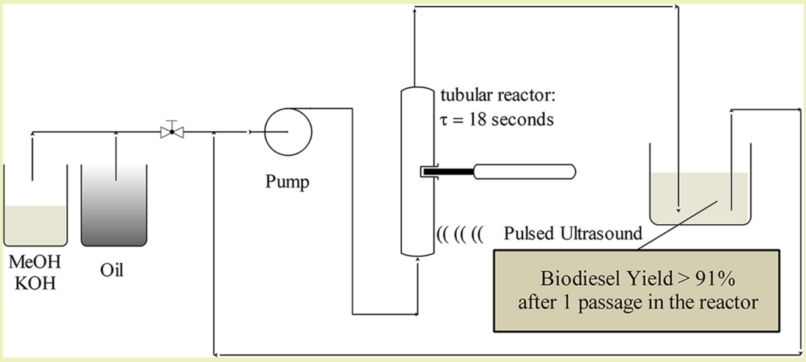

ABSTRACT: Biodiesel is produced in multi-stage batch reactors in which mass transfer is a rate limiting step. Mass transfer rates may be accelerated with ultrasound (US). In this paper, the performance of continuous flow US reactors, a Rosett US cell reactor, and a batch US reactor are compared to a conventional mechanically stirred batch reactor. The Rosett cell reactor combines acoustic cavitation and turbulence and achieved biodiesel yields greater than 90% in 5 min, whereas the same level of performance in the conventional reactor took more than 90 min. The most significant result of this work lies in achieving biodiesel yields greater than 90% after a single passage of the reagents in a continuous flow reactor in the presence of pulsed ultrasound. This corresponds to a reaction time of 18 s and a rate 300 times faster than the conventional process.

KEYWORDS: *Biodiesel production, Transesterification, Hydrodynamic cavitation, Acoustic cavitation, Rosett cell, Continuous reactor*

INTRODUCTION

Environmental concerns are driving scientific research to seek alternatives to fossil fuels. Biodiesel (BD) is a liquid biofuel that can be produced on a large scale[1] and used in compression ignition engines without major modifications.[2] It is a mixture of fatty acids methyl esters (FAME) obtained through the transesterification of triglycerides.[3−5] Lower toxicity, better biodegradability, absence of aromatics, and up to 90% fewer toxins (particulate matter, unburned hydrocarbons, carbon monoxide, and sulfur oxides) when combusted are advantages versus petroleum-based diesel.[6,7]

The EU directive 2009/28/EC targeted a 20% share of energy from renewable energy sources in the EU's overall energy consumption and a 10% share of energy from renewable sources in each member state's transport sector by 2020. In this context, special consideration is paid to the role of sustainable and responsible biofuels production, with no impact on the food chain, that can be produced at a cost lower than petrodiesel. The challenges are both technological and economic. The pursuit for highly efficient transformation methods is therefore key to developing a sustainable BD production. Most BD is produced through triglycerides transesterification of edible oils with methanol in the presence of an alkaline catalyst.[5,6,8]

The technology involves multi-stage reactors with homogeneous basic catalysts such as NaOH, KOH, or CH_3ONa. The acids are neutralized after the completion of the reaction and the salts are disposed of. Other limitations of the present technologies include large equipment, long reaction times, use of excess methanol (a health hazard because it is not entirely contained), and high cost of the raw materials (up to 80% of the variable cost).[9] Homogeneously base-catalyzed transesterification is known to suffer from mass transfer limitations in the initial period of the reaction due to the high viscosity of the triglycerides.[10] Different intensification methods such as ultrasonic (US) and microwave (MW) irradiation, hydrodynamic cavitation, addition of co-solvents, and application of supercritical conditions have been tested to eliminate or minimize mass transfer limitations.[8]

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Sonochemistry applies ultrasonic irradiation as a new more efficient mixing tool in BD production. Veljković[8] reviews the state of the art and perspectives of BD production by US-assisted transesterification and asserts that low frequency US (LFU) has several advantages over the classical synthesis process.

Continuous processes exploiting ultrasound are a commercial reality. Tulsa Biofuels uses a Hielsher Ultrasonic device to accelerate the transesterification of oil. The oil/MeOH/catalyst mixture passes a flow cell, where it is exposed to ultrasonic cavitation for 5 to 30 s. The mixture then enters a reaction column where it remains for 1 h.[11] Ultrasonic Power Corporation also provides ultrasonic reactors operating at high powers (from 0.5 to 2.0 kW) for continuous processing of oils.[12] Incbio[13] applies ultrasound to promote both batch and continuous esterification and transesterification of acidic oils.

Academics have contributed widely to the design of BD reactors. Vinatoru[14] describes the ultrasonic synthesis of biodiesel in a continuous reactor using a push−pull US emitter. Conversion surpassed 90% after 20 min. Cintas et al.[15] used a flow US reactor consisting of three transducers and reported complete BD conversion in 1 h.

We examine BD process intensification with US in both batch and continuous flow reactors. The novelty of the present work is related to comparing a conventional mechanically stirred vessel and a Rosett cell reactor. In the Rosett cell, US promotes turbulence around the loops. The turbulence might generate hydrodynamic cavitation. Classical hydrodynamic cavitation is generated by passing a liquid through a constriction, such as an orifice plate, as in the case of the characteristic loops of the Rosett cell reactor.[16] The cavitation is produced by pressure variations due to the system geometry that subsequently creates a velocity variation.[17] Hydrodynamic cavitation is able to generate flow energy at an intensity that is suitable for physical and chemical processing.[16,17]

Besides the batch studies, we also examined BD production in continuous flow reactors using different power inputs and continuous or pulsed US.

EXPERIMENTAL SECTION

Materials. Commercial rapeseed oil was used as a feedstock for all the experiments. The oil was analyzed by acid−base titration to quantify the amount of free fatty acids (FFA). The procedure to determine the acidity has been reported by the authors elsewhere.[17−20] The initial acidity of the oil is important because FFA reacts with the transesterification catalyst (KOH) and forms soap. Soap can affect reaction yields and the quality of the finished products.[18−22] An FFA concentration higher than 0.5% wt affects BD yield.[23] The acidity of the oil in this study was 0.1% wt, and therefore, the effect of soap on yield is negligible.

Methanol (>99% purity, Fluka) was used for all experiments with potassium hydroxide (>99% purity, Fluka) as the transesterification catalyst.

Table 1. Reaction Conditions

method	reactor	step	g_{MeOH}/100 g_{oil}	g_{KOH}/100 g_{oil}	T (°C)	t (min)
mechanical stirring	batch	1	20	1.0	60	90
		2	5.0	0.5	60	60
ultrasound-assisted	batch	1	20	1.0	40, 60	30
ultrasound-assisted	continuous	1	20	1.0	65	30

Conventional Mechanically Stirred Experiments. The traditional mechanically stirred transesterification experiments were conducted in a 250 mL three-necked glass flask at 60 °C (Table 1). A thermocouple was placed through one neck to monitor temperature, and a coil condenser passed through the second neck. The third neck was reserved for sampling. The reaction was performed in two steps.[5] In a typical experiment, 1 g of catalyst (KOH) was dissolved in 20 g of MeOH and charged to the flask together with 100 g of oil. The two fluids were then charged to the reactor, and the temperature was increased until the set-point (60 °C), which took several minutes. When the set-point temperature was reached, the mechanical stirrer was activated as well as the timer. After 90 min, the mixture was allowed to decant in a separating funnel (Step 1). The bottom phase contained excess methanol, KOH, and glycerol, and the top phase contained the reaction products. The top phase (~95 g) was transferred back to the reactor for Step II in which 5 g of MeOH containing 0.5 g of KOH was added and allowed to react for 60 min at 60 °C ± 1 °C. Afterward, the mixture was separated again, and the top biodiesel (BD) phase analyzed. The temperature was maintained with a thermostat, and the stirring rate was kept constant at 100 rpm. The reaction conditions were identical for the conventional reactor as for the tests conducted with US.

Ultrasound-Assisted Batch Experiments. Tables 2a and 2b lists the conditions adopted for the ultrasound-assisted batch experiments.

Table 2a. Ultrasound-Assisted Batch Transesterification Experiments: Conventional Reactor

test	D_{tip}(mm)	power (W)	mode	T (°C)
1	13	17.6 (low)	continuous	40
1a			pulsed	40
2			continuous	60
3		21.7 (high)	continuous	40
4				60
5	20	19.0 (low)	continuous	40
6				60
7		27.1 (high)	continuous	40
8				60

Table 2b. Ultrasound-Assisted Batch Transesterification Experiments: Rosett Cell

test	D_{tip}, mm	power (W)	mode	T (°C)
9	13	16.9 (low)	continuous	40
9a			pulsed	40
10			continuous	60
11		20.3 (high)	continuous	40
12				60
13	20	17.6 (low)	continuous	40
14				60
15		24.4 (high)	continuous	40
16				60

US experiments were conducted in both a conventional cylindrical vessel and a Rosett cell. The Rosett cell consists of a vessel equipped with four loops at the bottom, designed to generate turbulence (leading to hydrodynamic cavitation) inside the reaction medium (Figure 1). The volume of both the Rosett cell and the conventional vessel was 0.0680 L.

Experiments were carried out using two 20 kHz US cylindrical tips. The maximum nominal power emission of the 13 mm diameter tip was 400 W, and the 20 mm diameter tip had a power emission of 500 W. The amplitude was varied at 60% and 80% of the maximum nominal power. In the tables and figures, 60% of amplitude refers to "low power" and 80% refers to "high power". The power reported in Tables 2a and 2b were determined through a standard calorimetric[18] calibration (correlation factors $R^2 > 0.99$).

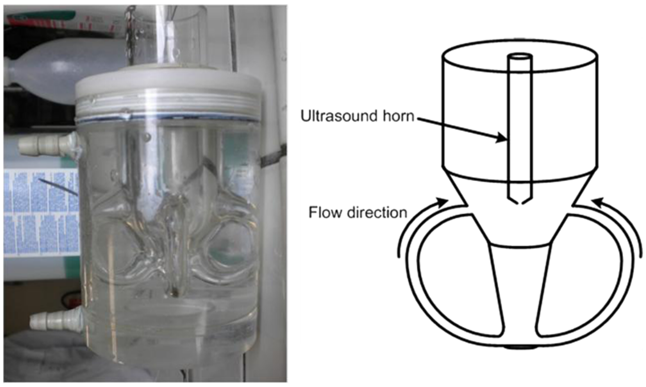

Figure 1. Rosett cell reactor.

In the US batch experiments only one reaction step was performed. The conditions, reported in Table 1, are the same as the ones adopted in the first step of the mechanically stirred experiments. The temperature was maintained by a thermostat connected to the reactor jacket. In a typical experiment, ∼0.55 g of catalyst (KOH) was dissolved into ∼11 mL of MeOH and charged to the vessel together with 55 g of oil at ambient temperature. Sonication increased the temperature of the fluids to 40 °C within seconds without any external heat source, which demonstrates a tremendously high reaction rate. To achieve 60 °C, the bath was heated to 40 °C after which the sonication was initiated and the reagent temperature increased to 60 °C. Approximately 10 min after the reaction was complete, the biodiesel phase was withdrawn directly from the reactor, centrifuged and analyzed. The US horns were provided by the Synetude Company (Chambery, France).

Ultrasound-Assisted Continuous Experiments. Both a 0.700 L (20 kHz) and a 0.070 L (35 kHz) tubular Sonitube reactor (Synetude) were used for the ultrasound-assisted continuous experiments. Both sonicators were operated at 85% of their maximum nominal power, corresponding to 1500 and 400 W for the 0.700 and the 0.070 L reactor, respectively. The power at the sonnicator tips in the reaction mixture was estimated with a standard calorimetric method,[18] and the power was 68 W in Test 1 and 19 W for the other tests (Table 3). The experiments in the continuous reactors were carried out either using the same volume of the reagents (Tests 1 and 2, Table 3) or keeping the power/volume ratio constant for both the small and big reactor (Tests 1 and 3, Table 3). The experiment conducted in the smaller reactor at high power/volume ratio was also carried out using pulsed US (2 s on and 2 s off; Test 4, Table 3). The residence time τ (equal to the ratio between the tubular reactor volume and the total flow of reagents) is reported together with the "reagents time", i.e. the time required for the whole treated volume of the reagents (2.40 or 0.68 L) to pass through the tubular reactor.

The continuous reactor system consisted of a beaker to store the oil, another for the MeOH/KOH, a pump, tubular reactor, and a collecting tank (Figure 2). Initially, the transfer lines, reactor, and collecting bath were empty. The reagents and catalyst were pumped at a rate of 38 mL s^{-1} to the tubular reactor (first passage represented by the dotted line in Figure 2). Note that when 2.4 L of the reagents were charged to the system, the average residence time to complete a loop through the system is close to 1 min, and a 30 min test represents circulating the fluid through the reactor 30 times. The collecting bath was maintained at a constant temperature with a thermostat. After the vessels containing the MeOH and oil emptied, the fluid from the collecting bath was recirculated to the reactor. The second passage from the collecting bath to the reactor is illustrated with a solid line in Figure 2. The transesterification conditions correspond to the ones used for the ultrasonic batch experiments as well as in the first step of the mechanically stirred experiments (Table 1).

Biodiesel Analysis. All the BD samples were centrifuged before the analysis of the fatty acids methyl esters (FAME).

The BD yield, corresponding to the FAME concentration, was determined by gas chromatography according to the UNI EN 14103 norm. About 250 mg of the sample was dissolved in 5.0 mL of a standard 0.1 M solution of methylnonadecanoate. Methyl nonadecanoate (>99%, Fluka product) was used as an internal standard and heptane as a solvent. An OmegaWax capillary GC column (Sigma Aldrich) was installed in a PerkinElmer AutoSystem XLGas Chromatograph, operating isothermally at 210 °C to separate the compounds. He was used as a carrier at 70 kPa. The BD yield, expressed as a % mass fraction of FAME, was calculated according to eq 1.

$$C_{\mathrm{FAME}} = \frac{(\sum A) - A_{\mathrm{C19}}}{A_{\mathrm{C19}}} \times \frac{C_{\mathrm{C19}} \times V_{\mathrm{C19}}}{m} \times 100 \qquad (1)$$

where $\sum A$ is the total peak area of the FAME, A_{C19} is the peak area corresponding to methylnonadecanoate; C_{C19} is the concentration (mg mL^{-1}) of the methyl nonadecanoate solution; V_{C19} is the volume (mL) of the methyl nonadecanoate solution; and m is the mass, in mg, of the sample.

RESULTS AND DISCUSSION

Comparison between Conventional and Ultrasound-Assisted Batch Transesterification. The biodiesel (BD) yield as a function of time is reported for the batch experiments—Rosett Cells and the conventional "vessel" at 40 and 60 °C—together with the control experiment conducted with mechanical stirring. The data at low power for both the Rosett cell and the conventional vessel are illustrated in Figure 3 (the actual powers are reported in Tables 2a and 2b). BD yield was 40% after 30 min in the conventional mechanically stirred reactor, which is significantly lower than the yield in the US experiments. As mentioned in the Experimental Section, the temperature of the reagents increased within seconds of initiating sonication. BD yield of the first sample, withdrawn after 1 min of sonication, ranged from 40% to 90%. This level of performance was only reached after 90 min in the mechanically stirred reactor. Transesterification of oil is limited by equilibrium; therefore, it is usually performed in two steps, as described in the Experimental Section. The second step is necessary to convert the unreacted mono- and di-glycerides to glycerol and methyl esters. BD yield was 90% at the end of Step I (90 min) using the mechanically stirred traditional method (results not reported in Figure 3). This agrees with the results of Gole[24] and Çaylı[25] who adopted the same experimental conditions in their work. After the first step, the separation of glycerol and the addition of fresh catalyst and

Table 3. Ultrasound-Assisted Batch Transesterification Experiments[a]

test	reactor volume (L)	mode	frequency (kHz)	power (W)	treated vol. (L)	τ (s)	reagents time (s)	US time (s)	power density (Wcm^{-3})
1	0.700	continuous US	20	68.2	2.4	19	66	66	0.28
2	0.070	continuous US	35	19.3	2.4	19	66	66	0.081
3	0.070	continuous US	35	19.3	0.68	1.9	18	18	0.28
4	0.070	pulsed US	35	19.3	0.68	1.9	18	9	0.28

[a] τ = residence time; reagents time = time required for the whole treated volume of the reagents to pass through the tubular reactor; T = 40−65°C.

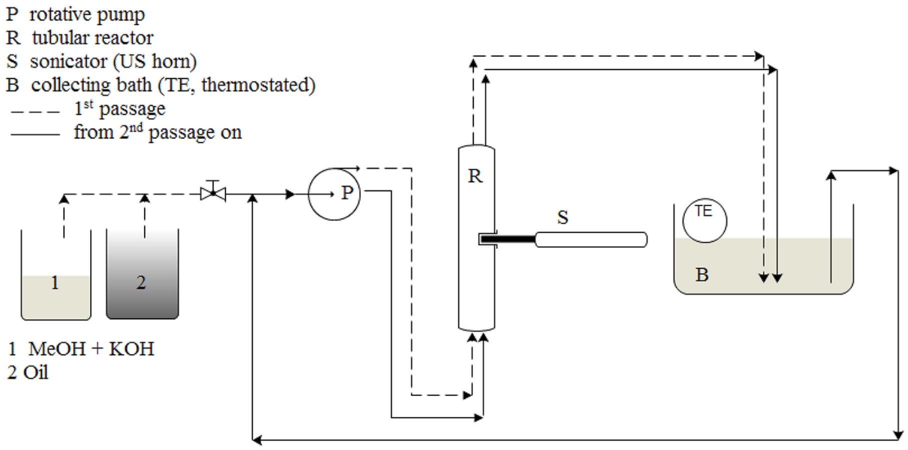

Figure 2. Schematic of the continuous reactors.

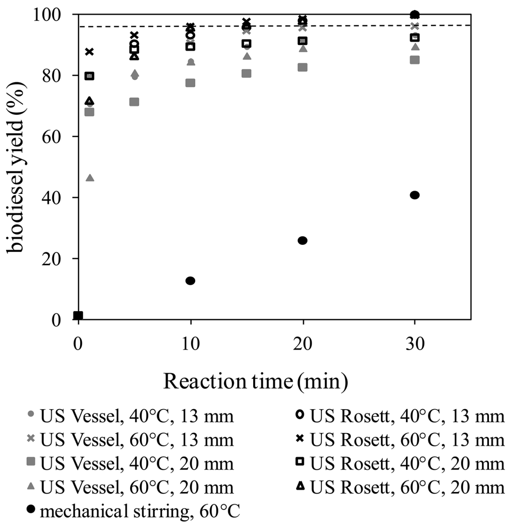

Figure 3. Results of the transesterification batch experiments: Triglycerides conversion into FAME (biodiesel) vs reaction time.

methanol are required to shift the reaction equilibrium toward the products (Table 1). The second step (results not shown in Figure 3) was carried out for an additional hour to achieve BD yields higher than 96.5%, which is the minimum FAME concentration required by the European Norm on BD.

In 10 min with US in the Rosett cell, oil conversion is the same as with the traditional process with 2 steps and 150 min of reaction time. Moreover, less methanol and catalyst are required to achieve yields greater than 96.5% (compared with the experimental conditions reported in Table 1). As shown in the paper of Kelkar on transesterification of virgin sunflower oil and palm oil,[26] the conventional approach is about 10 times slower compared to acoustic and hydrodynamic cavitation. In this work, it is about 15 times slower than the US powered in the Rosett cell at 60 °C or at 40 °C (but with the use of pulses).

The positive effect of US on BD production from vegetable oils via transesterification may be ascribable to different phenomena associated with acoustic cavitation inside the reaction medium. Veljkovi and co-authors[8] explain the effects caused by the acoustic cavitation occurring during the transesterification.

US can have physical and chemical effects on heterogeneous reaction systems through cavitation bubbles.[27] The physical effects are related to the formation of an emulsion between the liquid reactants that are usually immiscible, such as oil and methanol. The micro-turbulence generated by the collapse of the cavitation bubbles disrupts the phase boundary leading to the formation of a micro-emulsion. The increased interfacial area between the micro-phases of the triglycerides and methanol enhances the reaction rates even more than a vigorously mechanically agitated reactor. These emulsions are reported to have smaller drops and to be more stable than those generated using conventional techniques, which is beneficial for liquid−liquid reaction systems.[28] The positive effect of oil−MeOH emulsions to yield FAME has been reported by the authors.[22] In this case, stable emulsions formed with an emulsificator endowed with five coaxial rotating-ring gears that broke the biphasic mixture into very small drops.

The chemical effects are due to radical formation caused by the collapse of the transient cavitation bubbles. Transesterification may be governed by the in situ generation of methoxy radicals, provided that the temperature generated by the collapse of the cavitation bubbles is high enough to allow their formation.[29] However, according to Kalva and coauthors,[30] free radicals play a minor role, if any, in the base-catalyzed methanolysis of soybean oil. Some researchers also reported that ultrasonic cavitation can lower the activation energy required for initiatingtransesterification.[31]

The role of the temperature in the US-assisted experiments is difficult to assess. On the one hand, transesterification of vegetable oil is exothermic, but high temperatures (up to 65 °C) are usually adopted to favor the kinetics and the solubility of methanol in the oil.[24] Moreover, as reported by Mahamuni,[32] increasing the temperature decreases the viscosity of the reaction medium, which makes cavitation easier. On the other hand, it is well known that high temperatures dampen acoustic cavitation effects due to the lower concentration of dissolved gases. Colucci et al.[33] observed the maximum FAME formation at 40 °C. Gole[25] reported that increasing temperature had no significant affect on BD yield beyond 40 °C for US-assisted methods compared to the traditional method. In this work, US methods performed better than the conventional method at all tested conditions, but higher temperatures were not necessarily favorable to increasing BD yields (Figure 3).

Ultrasound-Assisted Batch Experiments: Comparison between Rosett Cell and Vessel. In Figure 4a and b, the BD yields obtained with the 20 mm US horn after 1 and 30 min, respectively, are reported. Similarly, in Figure 4c and d, the biodiesel yields obtained with the 13 mm US horn after 1 and

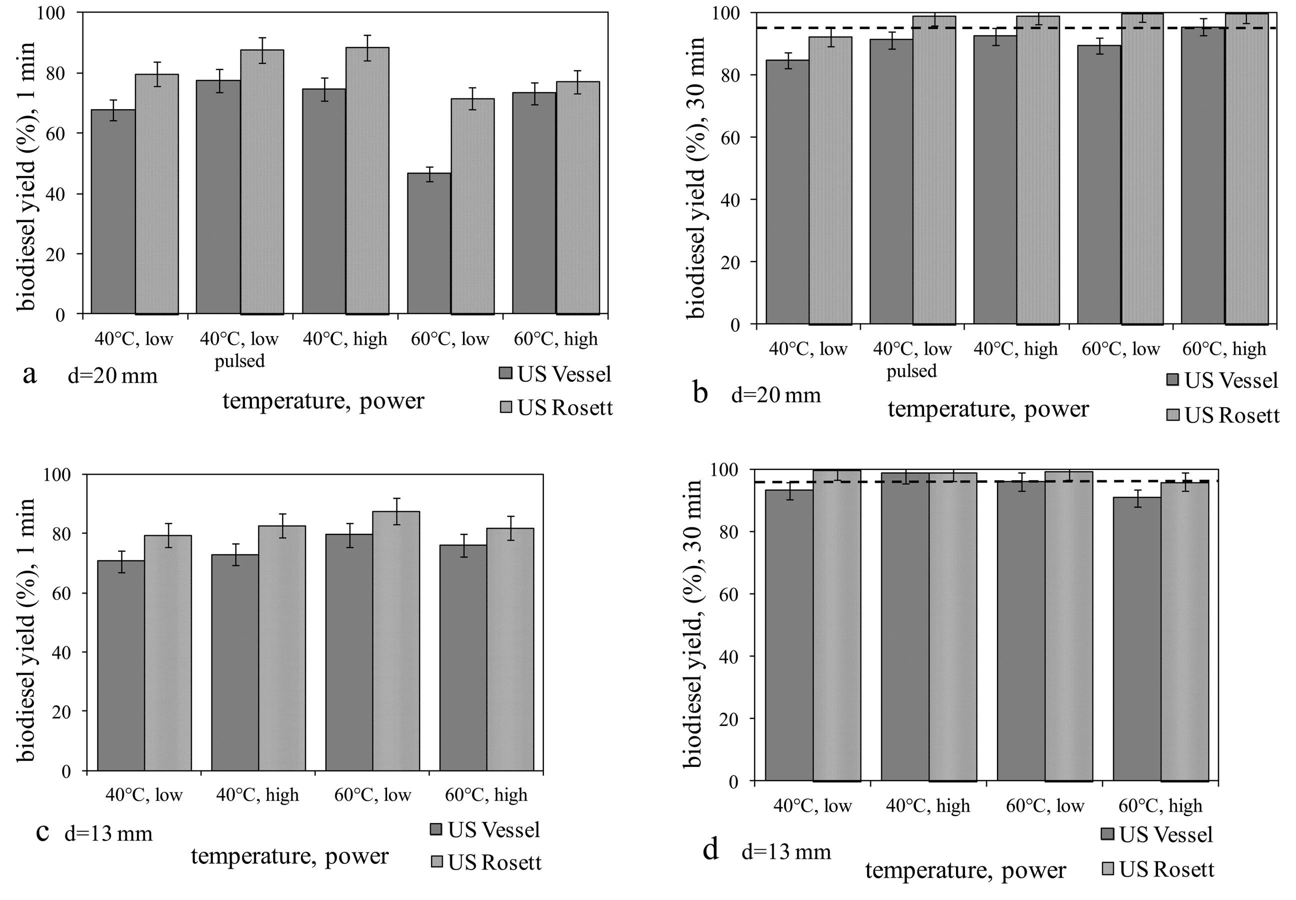

Figure 4. Results of the transesterification batch experiments. Biodiesel conversion at different powers and temperatures: (a) after 1 min and (b) after 30 min of reaction for the 20 diameter tip (400W); (c) after 1 min and (d) after 30 min of reaction for the 13 diameter tip (500 W). The dotted lines represent a FAME (biodiesel) concentration corresponding to 96.5%, (minimum limit required by the European norm 14214).

30 min, respectively, are shown. The error bars in the figure represent one sigma from the mean based on three and four repeat measurements.

In Figure.4b and d, the dotted lines represent a FAME concentration corresponding to 96.5%, i.e., the minimum limit required by the European Norm on BD EN 14214.

Other conditions being equal, the Rosett cell reactor always exhibits higher BD yield than the traditional vessel. The design of the cell allows the irradiated reaction mixture to be sonically propelled from the end of a probe around the loops of the vessel. The sudden increase in pressure at the entrance of the loops, which propagates throughout their length, causes substantial turbulence inside the reactor, which promotes efficient mixing. Hydrodynamic cavitation might also occur but remains to be quantified. The Rosett cell reactor is therefore able to provide both optimal temperature control within the reactor and enhanced mass transfer.

The higher yields in the Rosett cell reactor are attributable to the combined effect of the acoustic cavitation and turbulence due to the presence of the loops. The loops are designed to generate hydrodynamic cavitation. Hydrodynamic cavitation is already reported to contribute to process BD intensification.[34] Kelkar et al.[34] reviewed the separate use of ultrasonic and hydrodynamic cavitation for methyl esters production.

As already mentioned in the Introduction, hydrodynamic cavitation consists of pressure variations, which are generated from the geometry of the system to create velocity variations.[17] Hydrodynamic cavitation is therefore able to generate flow energy at an intensity that is suitable for physical and chemical processing.[16,17] However, the Rosett cell reactor remains to be characterized and is the subject of a subsequent paper. The occurrence of hydrodynamic cavitation is therefore just hypothesized and cannot be state with certainty.

BD yields are high in the Rosett cell reactor with ultrasound (Figure 4b,c), i.e., FAME concentrations higher than 96.5%, at all conditions, with the exception of the low temperature (40 °C), low power, and with the 20 mm diameter US tip.

To demonstrate the extent of the beneficial effects introduced by the Rosett cell reactor compared to the traditional vessel, the BD yields were plotted against the power density expressed as measured power over unit of ultrasonic emitter surface area and volume of the treated reagents (Figure 5).

When low power intensities are delivered to the system, higher conversion is obtained with the Rosett cell compared to the traditional vessel. Moreover, the difference between FAME conversion obtained at lower power intensities and higher power intensities is more remarkable for the traditional vessel, while in the case of the Rosett cell there is an insignificant difference, meaning that this reactor is optimized also to work at lower power intensities. This effect is attributable to the benefits brought by the turbulence generated in the Rosett cell reactor for which we hypothesize that hydrodynamic cavitation is likely to occur.

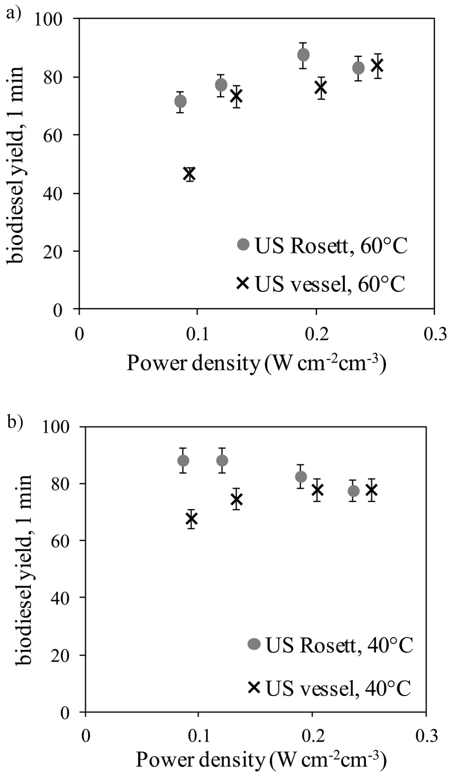

Figure 5. Biodiesel conversion as a function of the power density per unit of US emitter surface area and reagent volume at (a) 60 °C and (b) 40 °C.

In conclusion, temperatures of 60 or 40 °C were optimal for the ultrasound-assisted batch transesterification with pulsed US in the Rosett cell reactor, providing a reaction time 15X faster than the conventional process.

Ultrasound-Assisted Batch Experiments: Effect of Pulses. US pulses have a beneficial effect on the BD yield for both the traditional reaction vessel as well as the Rosett cell reactor (Figure 4a,b) and has also been extensively reported for transesterification.[34−36]

In particular, Chand et al.[34] reported that the temperature rise in the reaction medium was lower with pulses. Excessive heating during transesterification might lead to methanol evaporation resulting in a lower reaction rate.

Moreover, it is well known that excessive heating might also lead to the loss dissolved gases in the medium that are necessary to initiate acoustic cavitation. Pulses may reduce the loss of dissolved gases.

The beneficial effects of pulses were found to be of the same extent in both the traditional reaction vessel and in the Rosett cell reactor. Moreover, the use of pulses is particularly interesting in the case of electrical energy saving considerations.

Ultrasound-Assisted Batch Experiments: Effect of Tip Diameter and Power. Other conditions being equal, increasing the power generally enhances the conversion to FAME at both 40 and 60 °C and with both the horns (Figure 4a,c). Experiments performed at high power exhibit higher conversion than the corresponding experiments carried out at low power; the actual power is given in Tables 2a and 2b.

The increase in the FAME yields as the power increases has already been reported at different frequencies.[37] When the intensity (i.e., ultrasonic power/irradiation area) is increased, the acoustic amplitude increases and a more violent collapse of the cavitation bubble will occur.[37]

Nevertheless, this does not happen for experiments performed with the 13 mm US horn at 60 °C and high powers. The result is consistent with the general view that there is an optimum power density (or acoustic intensity) that can be applied in an US process to obtain maximum reaction rates before reaching a point of diminishing returns.[37] Singh et al.[38] have also observed an optimum energy input for BD formation from soybean oil in the presence of US. However, we hypothesized that too high temperatures generated inside the reaction medium at the high power using the 13 mm diameter tip (500W) might have led to the methanol evaporation and the removal of dissolved, thereby reducing the transesterification reaction rate and acoustic cavitation phenomena, respectively.

The difference in the 13 mm (500 W) and 20 mm (400 W) horns is evident by comparing Figure 4a with c and 4b with d. In general, at equivalent conditions, BD yield achieved with the small tip is higher than for the larger one. In particular, using the 13 mm tip, BD yields higher than 96.5% are achieved within 30 min in most of the cases also in the classical reaction vessel, as displayed in Figure 4d. This may be attributable to the higher power density.

Ultrasound-Assisted Continuous Experiments. Continuous experiments were performed using a 0.700 L and a 0.070 L tubular reactor, equipped with two different horns working at different powers as displayed in Table 3. First, the same total volume of reagents, corresponding to 2.40 L was fed to both reactors (Tests 1 and 2 in Table 3). Afterward, for the sake of comparison, 0.68 L of reagents was fed to the smaller reactor in order to have the same power density in the 0.700 L as in the 0.070 L reactor. This last experiment was performed using both continuous and pulsed ultrasound in the smaller reactor (Tests 3 and 4, Table 3).

The reaction rates are extremely high in the continuous reactors. Within 10 min, BD yields exceed 80% at all the conditions tested (Figure 6). The dotted lines in Figure 6 represent a FAME concentration corresponding to 96.5%, i.e., the minimum limit required by the European norm on biodiesel EN 14214.

When the same volume of reagents is charged to each reactor (0.70 and 0.07 L), BD yield in the larger reactor is higher than

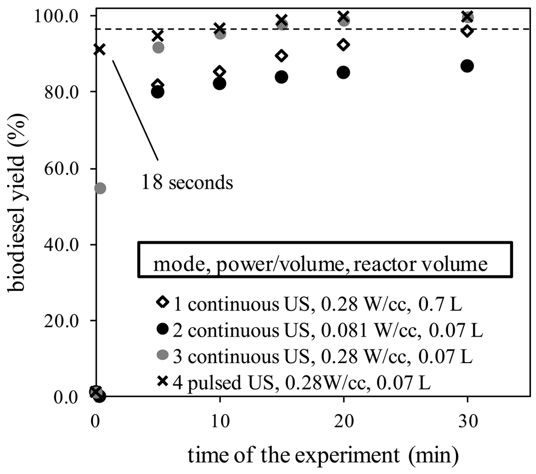

Figure 6. Results of the ultrasound-assisted continuous transesterification experiments: Biodiesel yield vs time.

in the smaller reactor (compare series 1 and 2, Figure 6). This may be attributable to the higher powers delivered by the ultrasound horn operating in the larger reactor against the one used in the smaller reactor (Table 3). Experiments carried out in the smaller reactor, lowering the total volume of treated reagents are indicated as series 3 and 4 in Figure 6; high yields are achieved within very short times. A remarkable result was achieved when pulses were adopted. BD yield higher than 90% was attained after just one passage in the reactor, equivalent to 18 s and to a reaction time 300X faster than the conventional process. Note that because pulses (2 s on and 2 s off) are adopted, the total time of sonication during one pass through the reactor equals just 9 s. To the best of the authors' knowledge, this result has never been reported.

The positive effect of pulses has been discussed previously for the ultrasound-assisted batch experiments. Another positive effect of the use of pulses in the continuous reactors might be related to the reduction in the evaporation of methanol. Also, the gases may remain dissolved with pulsed ultrasound versus continuous due to the lower heat generated.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

Notes

The authors declare no competing financial interest.

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