

## Transesterification of Triglycerides in a New Ultrasonic-Assisted Mixing Device

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We adapted a media mill to house an ultrasonic horn to transesterify triglycerides to biodiesel. This configuration combines enhanced mass transfer from the acoustic cavitation of the ultrasonic probe with non-conventional mixing from the media mill. It ensures oil and methanol circulates in the vicinity of the ultrasonic tip. We tested methanol, ethanol and isopropanol as alcohols and KOH as a catalyst to transesterify canola oil. The branched isopropanol lowers the biodiesel cloud point by 10 °C compared to biodiesel produced with methanol (fatty acid methyl ester). We withdrew samples at regular intervals and analysed them in a GC according to EN14103-2011. The ultrasonic-assisted mixing device that we designed converts most of the triglycerides with methanol within one minute of pulsed ultrasonic irradiation. The reaction with ethanol and isopropanol is faster than in classical batch reactors.

### 1. Introduction

Biodiesel (BD) is biodegradable, lacks toxic aromatics, lowers automobile emissions and is carbon neutral (combusting BD generates as much CO<sub>2</sub> as what plants absorb). Compared to petro-diesel, BD produces from 75 % to 90 % less particulate matter (Antolin et al., 2002), unburned hydrocarbons, CO and sulphates (Lang et al., 2001).

In commercial BD facilities, methanol and basic catalysts transesterify triglycerides to methyl esters (Alves et al., 2013). Most of these plants operate in batch mode, for which the drawbacks include: multiple steps, long processing times, high raw material cost and it consumes catalyst that has to be disposed of (Perego and Ricci, 2012).

The production process and raw material costs make BD uneconomical versus petro-diesel. In fact, to produce 1 L of BD requires 3 kWh including separating the BD from glycerol and MONG (organic material other than glycerol) and purifying the BD (Radich, 2004). Besides the cost of the raw material, which can be up to 80 % of the total production process, the long reaction times translates to large equipment that consequently increases capital investment (Boffito et al., 2015).

To reach equilibrium can take 8 h. Poor mass transfer between the oil phase and MeOH phase contributes to the long residence time since methanol is only partially miscible in oil to between a mass fraction of 6 % and 8 % at room temperature (Pirola et al., 2014). Mass transfer is even poorer for crude vegetable oil or non-edible oils (Bianchi et al., 2011). Increasing mass transfer rates populate recent scientific literature, and include: acoustic cavitation with ultrasound (US), microwaves (Gole and Gogate, 2014), hydrodynamic cavitation, impeller blade design and other mixing devices (Boffito et al., 2013), reaction or extraction at supercritical pressure and temperature (Demirbas, 2008), dividing wall technology (Kiss, 2013) and liquid atomization into fluidized beds operating at high temperature and low pressure (Boffito et al., 2014).

Existing pilot-scale plants adopt US to accelerate BD synthesis. Tulsa Biofuels uses a Hielsher Ultrasonic device. The reaction mixture containing oil, MeOH and the catalyst passes through an ultrasonic chamber, where it remains 5 – 30 s. The mixture then enters a column for 1 h in which 99 % of the oil reacts (Hielsher,

2014). INCBIO applies US in both batch and continuous esterification and transesterification for a variety of feedstocks (Incbio, 2012).

The main hurdle to implement US in industrial processes relates to scaling up from 250 mL flasks to 500 m<sup>3</sup> vessels: ultrasonic horns scale with surface area whereas reactors scale volumetrically. The active area of the horn is near the tip that doesn't penetrate evenly across large vessels. Boffito et al. (2015) reviewed many US designs to address reactor scalability. They concluded that loop US reactors achieve the highest conversion of oil to BD in the shortest times. In loop technologies, oil and methanol re-circulate semi-continuously and react in small US chambers with higher US power/volume ratios.

Designing agitated vessels that integrate an ultrasonic chamber is an opportunity to innovate. Here, we installed a US horn in a laboratory scale media mill (which micronizes particles to submicron powder). This configuration ensures that oil and methanol circulate in the vicinity of the ultrasonic tip frequently.

The low cost and industrial availability makes methanol the preferred alcohol to produce BD (Leung et al., 2010). However, methyl esters have poor cold flow properties, with freezing points ranging from 0 °C to 10 °C depending on the raw material. Ethyl and isopropyl esters improve BD cold flow properties without comprising cetane number or oxidative stability (Knothe, 2008), but they cost more and their reaction rates are lower (Hanh et al., 2009).

The ultrasonic-assisted mixing device we propose increases the mass transfer between the dispersed phase (alcohol) and the dispersant (oil), particularly for C<sub>2+</sub> alcohols.

## 2. Experimental

### 2.1 Experimental Setup

We adapted a Mini-Fer media mill (Netzsch) to transesterify triglycerides. We modified the head of the ball mill (A) machining it to create an opening through which we inserted a 13 mm diameter ultrasonic thorn (B) (Figure 1). The ultrasound (US) probe (Vibra-cell VCX500 by Sonic and Materials) operates at a fixed frequency of 20 kHz and a nominal power of 500 W.



Figure 1: Mini-fer ball mill with an ultrasonic probe

### 2.2 Transesterification tests

In all experiments, KOH (a mass fraction of 5 % with respect to MeOH and 1 % with respect to oil) dissolved in methanol (a mass fraction of 20 % with respect to oil) catalysed the transesterification of the triglycerides. In a typical experiment, we charged 200 g of oil to the feed tank (1). After dissolving 2 g of KOH in 40 g of alcohol, we added the basic solution to the oil – 40 g of alcohol corresponds to 6.0, 3.8 and 3.0 moles of MeOH, EtOH and iPrOH, respectively. At time zero, we initiated the pump (2) to feed the reagents to the reaction chamber (3) as well as the micronizer motor (3) and the ultrasonic power (4). The pump sucked the reagents from the

bottom of the feed tank and fed them to the reaction chamber. After the reaction chamber, the reagents discharged (6) to the feed tank (1) and re-entered the reaction chamber. Cooling water (5) circulated around the reaction chamber for the duration of the experiment. The volume of the reaction chamber was 120 mL. The pump circulated the reactants at about 50 L/h in all the experiments. The micronizer shaft rotated at 1500 rpm and the pressure of the liquid circulating in the set-up was 1 bar (Table 1). We made two blank tests: i) tests with only the grinding mill operating ii) tests with only the US operating (only the feed pump operated and not the motor of the mill motor).

Table 1: Experiments

Test	Alcohol	US amplitude, %	Pulses, s on: s off	Micronizer	Catalyst, % <sub>wt</sub>
1	MeOH	0	-	✓	1
2	MeOH	20	0	✓	1
3	MeOH	20	1:1	✓	1
4	MeOH	20	1:1	-	1
5	MeOH	20	0	✓	5
6	MeOH	20	1:1	✓	5
7	MeOH	40	1:1	✓	1
8	MeOH	40	0	✓	1
9)	MeOH	40	1:1	✓	1
10	MeOH	60	0	✓	1
11	MeOH	60	1:1	✓	1
12	EtOH	0	-	✓	1
13	EtOH	20	0	✓	1
14	EtOH	20	1:1	✓	1
15	iPrOH	0	-	✓	1
16	iPrOH	20	0	✓	1
17	IPrOH	20	1:1	✓	1
18	iPrOH	20	1:1	-	1

We determined the biodiesel (BD) yields after separation of two phases. We followed the UNI EN 14103 norm to determine the alkyl esters concentration, corresponding to the BD yield. The internal standard was methyl nonadecanoate and toluene was the solvent. The column was a BR-Wax installed on a Varian CP 3800 Varian GC (FID).

The BD yield, expressed as a % mass fraction of alkyl esters, is

$$C_{FAAE} = \frac{\sum A - A_{C19}}{A_{C19}} \times \frac{C_{C19} \times V_{C19}}{m} \times 100 \quad (1)$$

where  $\sum A$  is the total peak area of the Fatty Acids Alkyl Esters (FAAE),  $A_{C19}$  is the peak area corresponding to methyl nonadecanoate;  $C_{C19}$  is the concentration ( $\text{mg mL}^{-1}$ ) 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.

We corrected the concentration of the methyl, ethyl and propyl esters taking into account that the response of the FID is proportional to the number of carbons atoms. The analysis of the methyl, ethyl and propyl esters was reproducible.

### 3. Results and Discussion

#### 3.1 Effect of mixing and ultrasound

The blank test – circulating oil and MeOH through the media mill – converted less than 2 % of the triglycerides to biodiesel (BD) after 1 h. We also tested the media mill independently of ultrasound (US) and US independent of the media mill. After 1 h and room temperature, the media mill converts more than 90 % of the triglycerides to methyl esters (with MeOH) and 27 % (with EtOH) and 10 % (with iPrOH) to ethyl and propyl esters, respectively (Figure 2a). The collection tank temperature was constant throughout the tests. In the second test (in which the media mill was not rotating), US converts over 90 % of the triglycerides in 1 min.

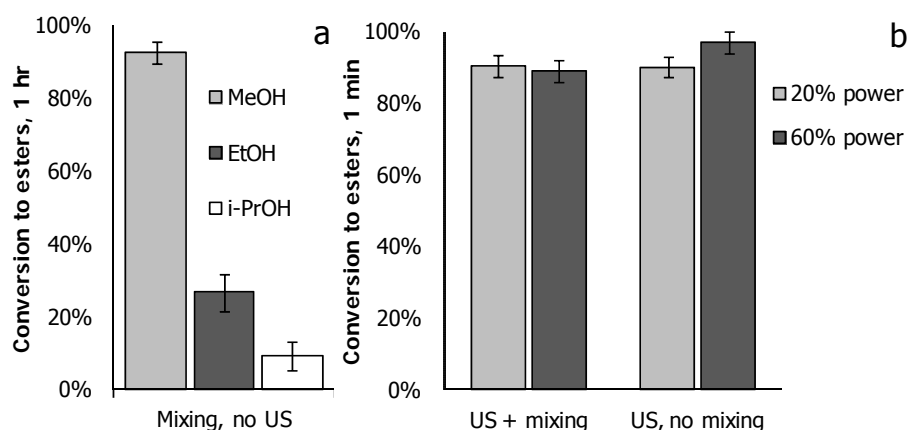


Figure 2: a) Conversion to esters b) Conversion to methyl esters with US pulses and a mass fraction of 1 % catalyst and 20 % alcohol/oil (room temperature).

The positive effect of US on triglycerides conversion to BD from vegetable oils consists of several phenomena associated with acoustic cavitation. Veljkovic et al. (2012) report both physical and chemical effects occurring in liquid heterogeneous systems due to cavitation. The implosion of the cavitation bubbles generated by US disrupts the phase boundary between MeOH and oil. This phenomenon emulsifies the methanol and oil phases that are otherwise poorly miscible and it forms a micro-emulsion. Georgianni et al. (2008) report that US-generated micro-emulsions have smaller droplet sizes and are more stable than emulsions formed by conventional mixing. The increased interfacial area between the micro-phases increases the reaction rates. Rotating the micronizer had no effect on conversion when the US was operating (Figure 2b). However, mixing (independent of US) contributes to the conversion of the triglycerides into esters (Figure 2a). At 60 % power amplitude the conversion to esters is slightly higher. A possible explanation might relate to the degasification of the system caused by the very high turbulence: degassed oil has less gas nuclei that are necessary for cavitation.

### 3.2 Effect of pulses and ultrasonic power

US pulses generally have a beneficial effect on the conversion into esters (Figure 3), which agrees with previous work (Boffito et al., 2013). US pulses reduce the temperature rise in the reaction medium to a certain extent. Overheating evaporates the alcohol and degasifies the system. Dissolved gases are necessary to promote acoustic cavitation. Moreover, US pulses are particularly interesting taking into account economical and energetic aspects. The conversion to esters at 60 % power amplitude is the same with and without pulses. The temperature rise promoted in the reaction media in both cases by the high power delivered to the system may account. On the other hand, high temperature lowers the viscosity of oil-alcohol systems, which makes acoustic cavitation more powerful (Mahamuni and Adewuyi, 2009). We attribute the high conversion to both of these effects.

The reason why a higher amount of catalyst dampens the yields remains unclear. We hypothesize that the amphiphilic nature of the products and co-products interact with the oil-MeOH interface in the micro-emulsion, which might hinder the contact between the two reagents. Future work will focus on quantifying the mono- and di-glyceride concentrations to assess this phenomenon.

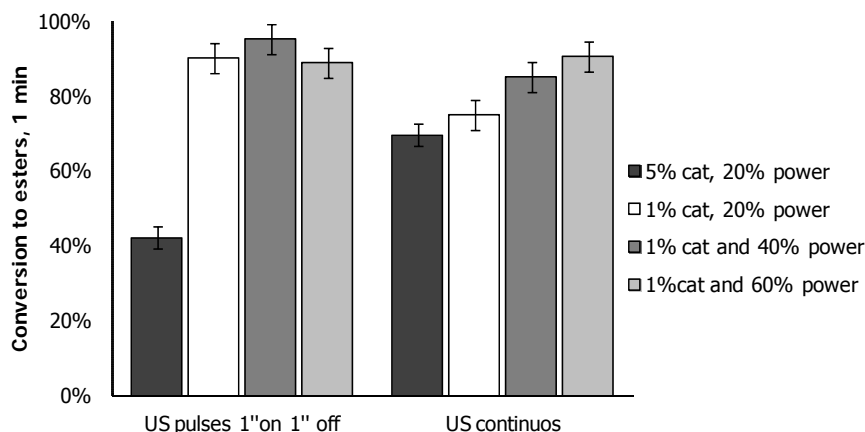


Figure 3: Conversion to methyl esters at 1 min for the US-assisted experiments in the micronizer,

US pulses have a positive effect in presence of all the alcohols (Figure 4). At a reaction time of 1 min, 65 % of the oil reacts to ethyl esters and 40 % reacts to propyl esters.

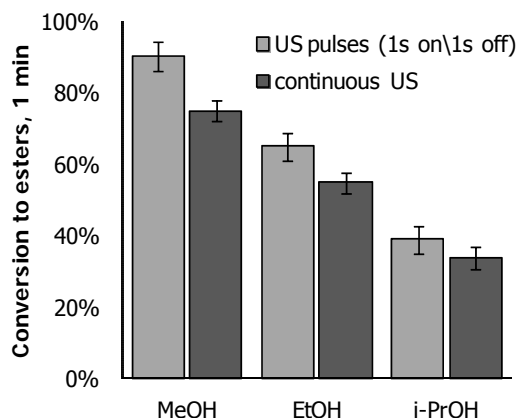


Figure 4: Conversion to alkyl esters at 1 min for the US-assisted experiments in the mixing device and a mass fraction of 1 % catalyst and 20 % alcohol/oil (room temperature).

Hanh et al. (2009) transesterified triolein with various n-alcohols at the same conditions as we adopted in this work, i.e. a mass fraction of 1 % KOH and an oil:alcohol ratio 1:6. They report that secondary alcohols, like isopropanol, give lower conversion with respect to primary alcohols. Moreover, it was harder to separate the ester and excess alcohol with longer chain alcohols. In the presence of iPrOH and under US irradiation, converted less the 25 % of the triolein in 25 min. This is not surprising considering that secondary alcohols are more sterically hindered and the nucleophilic attack to the carbon by the alkoxide anion is more difficult. We confirm that reaction rates are slower with longer chain alcohols but were able to quantify the methyl, ethyl and propyl esters easily.

#### 4. Conclusions

Ultrasonic-assisted oil transesterification in a micronizer converts 90 %, 40 % and 25 % of triglycerides to methyl, ethyl and isopropyl esters, respectively in only one minute. The micronizer, in the absence of US, converts 90 %, 27 % and 10 % of the triglycerides to methyl, ethyl and isopropyl esters, respectively in less than 1 h. The results of the combined system are worthy of scaling up to produce biodiesel with improved cold flow properties. Future work will be devoted to the optimization of the operating variables for the transesterification of triglycerides with isopropanol and examining stoichiometric ratios of alcohol and oil.

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