

## OC-1: Sonochemical Production of Fatty Alkyl Methyl Esters from Raw Oils

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In this study the use of ultrasound (US) and microwave (MW) for the production of Fatty Alkyl Methyl Esters (FAME), i.e. biodiesel (BD) is investigated in both the heterogeneously catalyzed esterification of Free Fatty Acids (FFA) and the homogeneously catalyzed transesterification of triglycerides (TG). The use of US appears to enhance the reactivity of the homogeneous reaction, whereas it does not bring advantages to the ion exchange resins-catalyzed esterification with respect to the traditional method. On the contrary, MW leads to a remarkable increase in the FAME production.

### 1. Introduction

The most recent challenge concerning the BD production deals with the processing of non-food, raw oils to make them suitable to be used as biofuels. Very often these oils require several standardization processes, which raise the overall cost for biodiesel manufacturing. The search for high efficiency transformation methods it is therefore a key issue in this context.

In this work the use of US and MW is investigated for the production of BD from raw feedstock. All the oils were first deacidified by FFA esterification (Pirola, 2010) to yield FAME, using ion exchange resins as catalysts, and then fully transformed into ME by transesterification (Bianchi, 2011).

### 2. Experimental Details

Ion Exchange resins Amberlyst<sup>®</sup>46 (A46) by Dow Chemical or Purolite D5081 (described by Boffito, 2012) and NaOH or CH<sub>3</sub>ONa were used as esterification and transesterification catalysts, respectively. Both type-type sonicators operating at frequencies from 20 to 500 kHz and US baths were used. US equipments were provided by Bandelin (Germany) and Syntude (France). MW emitter (Alter, Mod. TM A09-51), connected to the MW applicator (Andrew Corp, Rolando Park, IL USA, model HST2-50), was operated at the 30% of the maximum frequency. Full description of this equipment can be found in the work of Ragaini and coauthors. Reaction conditions for both the two kinds of process are given in Table 1. ME yields were monitored through acid base titrations and gas chromatographic analyses, respectively (Pirola, 2011).

### 3. Results and Discussion

In Table 1 the results of both the esterification and transesterification reactions are displayed for traditional and US-assisted methods.

Table 1

**Conversion of an acid rapeseed oil: operative conditions and achieved results. Esterification catalyst: D5081, transesterification catalyst: KOH.**

Reaction	Method	T (K)	MeOH:oil (g/100g)	catalyst:oil (g/100g)	Time (min)	Conv. to ME (% wt)
Esterification	Traditional	313 <sup>a</sup>	16	10	360	52.8
		336 <sup>b</sup>	16	10	360	71.2
	US	313 <sup>a</sup>	16	10	360	77.3
		336 <sup>b</sup>	16	10	360	76.1
	MW	333	16	10	360	92.5
Transesterification	Traditional (2 steps)	333 <sub>1step</sub>	20	1	90	96.9
		333 <sub>2step</sub>	5	0.5	60	
	US (1 step- horn)	303	20	1	5	82.7
		303	20	1	30	86.6
		303	20	1	90	93.4

As it can be noticed, the use of US allows achieving higher ME conversions in the esterification at lower temperatures and in the transesterification. In the latter case shorter times and lower amounts of reagents are required. In particular it is noteworthy that just after 5 minutes of reaction at 303 K, transesterification conversion into methyl esters is already around 80%. Very high yields, around 90%, can be achieved after 90 minutes of reaction.

In Figure 1 some of the results of the esterification are reported.

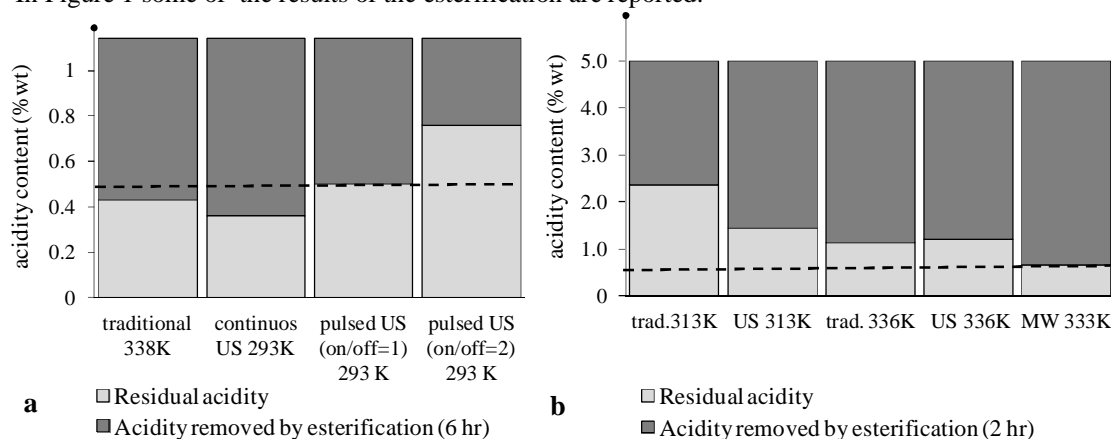


Figure 1. a) Results of the FFA esterification reaction performed on a) raw tobacco oilseed, catalyst: D5081 b) acid rapeseed oil (5% oleic acid), catalyst: A46

The dotted line represents the maximum FFA content tolerated by the European normative on BD (EN14214). As it can be observed MW are able to bring the acid content down to the required limit within just 2 hours. The positive effect of MW may be not just described in terms of thermal activation but also in terms of the microwave absorption by the catalytic material. The more the absorptive the material, the more the effect of MW hot spots is improved (Yuan, 2009).

The positive effect of US is more pronounced at lower temperatures, whereas at higher temperatures it does not seem to bring any advantage with respect to the traditional method. This suggests that at lower temperatures the acoustic cavitation effects are enhanced: it has in fact already been observed the existence of an optimum temperature for the occurrence of the acoustic cavitation in different reactive systems, oilseeds included (Lu, 2009). In the case of the homogeneously catalyzed transesterification, the high reactivity observed with the use of US may be ascribable to the effects caused by the acoustic cavitation in a homogenous medium, which generates very high local temperatures and pressures.

### Aknowledgements

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