Ultrasound assisted catalysis for biodiesel production

D.C. Boffito*, [1], G. Carvoli[1], S. Mansi[1], C. Pirola[1], S. Vitali[1], J.M. Leveque[2], C.L. Bianchi[1]

[1] Università degli Studi di Milano, via Golgi 19 20133 Milano (Italy)
[2] Sovoie University, 73376 Le Bourget du Lac cedex (France)

(*) daria.boffito@unimi.it

Keywords: heterogeneous catalysis, homogeneous catalysis, biodiesel, ultrasound

1 Introduction

The EU directive 2009/28/EC has set the targets of achieving in each member State, by 2020, a minimum share of 10% of energy consumption in transport sector from renewable sources. In this context special consideration is paid to the production of biofuels. The most recent challenges concerning biodiesel production (BD) deal with the use of non food-grade oilseeds and their standardization to make them suitable to be transformed into methyl esters (BD) through transesterification [1, 2]. In fact raw oils contain high acidities which, besides giving saponification problems during the BD production are also regulated by the European normative on BD (EN14214) [3].The aim of the present work is to conceive an efficient method able to perform both the standardization and the transformation into BD of raw oils. In this work heterogeneously acid-catalyzed esterification of free fatty acids (FFA) and homogeneously basic-catalysed transesterification are investigated in raw tobacco and rapeseed oils along with the use of ultrasound (US). The most outstanding result of this study concerns how US are able to increase reactions yields because of the occurrence of the acoustic cavitation in the liquid reaction medium as well as the occurrence of the surface cavitation which generates mechanical effects on the catalyst's surface.

2 Experimental

2.1 Heterogeneously acid-catalyzed esterification

Traditional and US assisted FFA esterifications were carried out in a raw tobacco oilseed. Both the processes were carried out in slurry modality, keeping the temperature at 63±2°C and at 18±1°C for the traditional and US esterification, respectively. The instrument adopted for the US reaction was a tip-type sonicator operating at the fixed frequency of 20 kHz and around 154 W of power. Reaction conditions for both the two kinds of process are given in Table 1.

Table 1. FFA esterification reaction conditions.

Method	Temp. (°C)	MeOH:oil wt ratio	Catalyst:oil wt ratio	Time (hr)
Traditional	63±2	16:100	10:100	6
US assisted	18±1	16:100	10:100	6

Ion exchange resin D5081 by Purolite® was used as a catalyst for all the tests being already selected as the best one among other kinds of similar products by the authors [3-5]. Its main features are given in Table 2.

Table 2. Features of the esterification catalyst D5081.

Matrix	Funct. Group	Ionic form	Acid capacity (mEq H^+/g)	Max. T (°C)
Styrene-DVB	$-SO_3H$	H^+	0.9-1.1	130

The main peculiarity of this catalyst lies in the location of all its active sites only on the external surface. Reaction progress was monitored through acid-base titrations as already reported in other authors' works [3-6].

2.2 Homogeneously base-catalyzed transesterification

For traditional and US assisted transesterification the same experimental setups already described for traditional and US esterification, respectively were used. Traditional synthesis was carried out on the raw tobacco and rapeseed oils deacidified with the traditional esterification. The common two steps procedure was used for the traditional transesterification [4, 5], while US assisted synthesis was performed in only one step on both raw and refined rapeseed oils. KOH was used as a catalyst for both the processes. Reaction conditions for the two kinds of synthesis are given in Table 3.

Table 3. Oil transesterification reaction conditions.

Method	Temp. (°C)	MeOH:oil wt ratio	Catalyst:oil wt ratio	Time (hr)
Traditional (2 steps)	1. 60±2 2. 60±2	1. 20:1 2. 5:1	1. 1:100 2. 0.5:100	1. 90 2. 60
US assisted (1 step)	18±1	20:1	1:100	30

The reaction yields and acidic compositions of the oils were calculated quantifying the methyl esters (BD) concentration through gas-chromatography.

3 Results and discussion

3.1 Heterogeneously catalyzed esterification

The results obtained from the deacidification of the tobacco oilseed are displayed in Figure 1. It can be noticed how all the adopted methods with the exception of the pulsed US with on/off ratio of 2 are able to lower the acidity below the 0.5% wt, i.e. the maximum amount of FFA required by both the transesterification and the EN 14214 (represented by the dotted line).

The best esterification method seems to be the continuous US assisted process. This result is particularly satisfying if it is moreover considered that the US assisted reaction was carried out at temperatures much lower than the traditional method and close to the room temperature. In addition, the catalyst was recycled for several uses for both the traditional and the ultrasound-

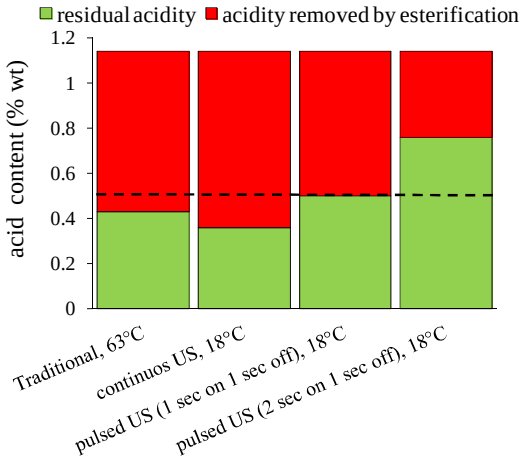

Fig. 1. Results of the FFA esterification reaction in a raw tobacco oilseed (6 hours).

assisted esterification. D5081 resulted to give a quite stable catalytic performance without showing any definitive deactivation. The stability of the performance is ascribable to the presence of the active sites exclusively on the catalyst's external surface. This minimizes the mass transfer limitations and gives practically no side products formation, as already experimented by the authors for similar catalysts [6].

The effects of US on chemical reactivity of FFA esterification reaction may be ascribable to the positive effects of the acoustic cavitation both in the liquid reaction medium and on the catalyst's surface. The homogeneous cavitation is in fact widely recognized to enable high-temperature (up to 5000 K) and high pressure (up to 100 atm) chemistry in liquid media [7], while surface cavitation is still poorly documented. Nevertheless, various papers available in literature seem to accept that when reactions are carried out in presence of US, a mechanical effect is developed on the surface of the catalyst [7-9]. This contributes to improve the mass transfer and hence high yields of reactions can be observed in very mild reaction conditions.

3.2 Homogeneously catalysed transesterification

The results obtained from the transesterification reaction of the different oils are displayed in Table 4.

Table 4. Results of the transesterification reaction.

Oil	Method of transesterification	Yield (%)	Methyl ester (BD) content (% wt)
Tobacco	Traditional	95.9	97.0
Raw rapeseed	Traditional	83.0	85.1
	US assisted	96.9	99.0
Refined rapeseed	Traditional	96.9	96.9
	US assisted	86.6	86.6

The yields reported in the table refer to the transesterification reaction, while the methyl esters content, i.e., the total BD yield, is the sum of the methyl esters obtained by the FFA esterification and transesterification reactions. As it can be noticed, the obtained conversions and the final BD contents are very high in all the cases. In particular, the result achieved by the US transesterification of the raw rapeseed oil is very satisfactory. It is moreover remarkable that much shorter times and lower reagents quantity are required to achieve very high triglycerides conversions. The positive effects of US on transesterification reactivity may be ascribable to the effects of the acoustic cavitation in a homogeneous medium, which generates high local temperatures and pressures as already described in the case of the FFA esterification. These phenomena result in increasing the reactivity due to the formation of radicals as a consequence of the very high temperatures developed inside the sonochemical reactor and in facilitating the mass transfer among the reagents and the catalyst.

4 Conclusions

The heterogeneous FFA esterification and homogenous catalysed transesterification reactions of not refined tobacco and rapeseed oils have been successfully performed with US assisted catalysis. An acidity below the 0.5% wt was obtained in 6 hours at 18°C with the use of continuous US in the esterification of an acid tobacco oilseed with catalyst D5081 (Purolite®). The positive effects of US in the case of heterogeneous catalysis are ascribable to the mechanical effects enabled by the US waves in the proximity of the catalyst's surface. Very satisfactory results were also obtained in the US assisted homogeneous transesterification of a raw rapeseed oil, where a final methyl ester content of 99% was obtained. In the case of homogeneously catalyzed reactions, the positive effects of US cavitation is mainly ascribable to the enhancement of the mass transfer among the reagents and the catalysts generated by the acoustic waves.

5 Acknowledgements

The authors would like to thank the Ministero delle Politiche Agricole Alimentari e Forestali (Italy) for funding SUSBIOFUEL project, Purolite company for providing the catalyst and Synetude Company (Chambery, France) for manufacturing some of the ultrasound reactors used in this work.

6 References

[1] C.L. Bianchi, C. Pirola, D.C. Boffito, V. Ragaini, Catal. Lett 134 (2010) 179

[2] M. Canakci, H. Sanli, J. Ind. Microbiol. Biotechnol., 35 (2008) 431

[3] D.C. Boffito, C. Pirola, C. L. Bianchi, Chemistry Today 30 (2012) 14

[4] C.L. Bianchi, D. C. Boffito, C. Pirola, S. Vitali, G. Carvoli, D. Barnabè, A. Rispoli, Biodiesel / Book 1 (2011), ISBN 978-953-307-713-0

[5] C. Pirola, D.C. Boffito, G. Carvoli, A. Di Fronzo, V. Ragaini, C.L. Bianchi, Soybean / Book 2 (2011) 321, ISBN 978-953-307-533-4

[6] C. Pirola, C.L. Bianchi, D.C. Boffito, G. Carvoli, V. Ragaini, Ind. Eng. Chem. Res., 10 (2010) 4601

[7] D.G. Shchukin, E. Skorb, V. Belova, H. Möhwald, Adv. Mater 23 (2011) 1922

[8] C. E. Brennen , Cavitation and Bubble Dynamics , Oxford University Press , New York 1995

[9] K.S. Suslick, S.J. Doktycz, Advances in Sonochemistry 1 (1990) 197