December 11-15, 2017

4TH INTERNATIONAL CONGRESS ON CATALYSIS FOR BIOREFINERIES

Lyon, France

PB53
Process intensification in biodiesel production under non-conventional techniques

Emanuela Calcio Gaudino,[a] **Giorgio Grillo,** [a] **Xinyu Ge,** [a] **Giancarlo Cravotto** [a,*]

[a]*Dipartimento di Scienza e Tecnologia del Farmaco, and NIS e Centre for Nanostructured Interfaces and Surfaces, University of Turin, Via P. Giuria 9, 10125, Turin, Italy*

**Corresponding author: giancarlo.cravotto@unito.it*

1. Introduction

Biodiesel or fatty acid alkyl ester (FAAE), a clean and renewable fuel, is widely considered to be an attractive and sustainable fuel. Biodiesel is commonly produced *via* the transesterification of lipid feedstocks with methanol, promoted by alkaline or acidic catalysis. Inefficient mass and heat transfer is one of the main limitations of transesterification reactions to form biodiesel ($R'CO_2R$) and glycerol (GL).[1] A huge gap currently exists between classic production processes and the most recent generation of enabling technologies such as microwaves (MW) and ultrasound (US) which provide process intensification, higher efficiency and sustainability.[2] Dielectric heating has been proved to dramatically enhance transesterification reaction because it provides improved heat transfer over the conventional methods.[3] Sonochemical effects, instead, arise from the action of ultrasound (US) waves and/or hydrodynamic cavitation (HC). The use of sound energy can result in significant gains in transesterification process by enhance mass transfer.[4] A concerned effort has been made by our group to research new highly efficient reactors to produce biodiesel while saving time and energy. Moreover, the high cost of vegetable oils and the ethical issues that surround competition with the food industry for oil crops leads us to start also from non-edible oils or frying oils as renewable source for biodiesel production.[5]

2. Experimental

Rotor stator reactor: the transesterification of refined or bleached palm oil and WCO was performed by means of a double hydrodynamic cavitation steps in a rotor-stator reactor (E-PIC S.r.l.) by dosing 75% (by volume) of the methoxide solution in the first step and the remaining 25% in the second step (after glycerol recovery). In both step the two hydrodynamic treatments (15 min) were performed at 55°C, under a flow rate of 390 L/h.
Flow MW reactor: continuous production of biodiesel from palm oil was exploited using a commercial MW reactor (FlowSynth, Milestone S.r.l.) at 70°C (400 W) using an NaOH catalyst loading of 1%wt and a methanol to oil molar ratio of 12.
Integrated flow reactor: the combination of two commercial reactors, a High-Shear Mixer (HSM, Magic-Lab e IKA) and a multimode MW reactor (MicroSynth, Milestone Srl) was exploited for biodiesel production using an NaOH catalyst loading of 1%wt and a methanol/oil mole ratio of 6. Feed flow rate was fixed at 250 cm^3 min–1 and MW irradiation at 400 W.

3. Results and discussion

With the aim of reducing energy consumption in biodiesel production, and addressing the mass and heat transfer issue of the overall process, over the last few years, we have thoroughly investigated different enabling technologies suitable for transesterification process: both acoustic and HC,[6] high-speed mixers[7] and MW irradiation.[8] We have also investigated combinations of different technologies both in batch and flow processes (figure 1). Waste cooking oil (WCO) was finally exploited as starting material. The overall production costs (reagents, electric energy, purification, wastes) are the real driving force of this investigation.

Hydrodinamic cavitation treatment for biodiesel production: The HC unit used is a continuous rotor-stator type reactor in which reagents are directly fed into the controlled cavitation chamber. The high-speed rotation of the reactor creates micron-sized droplets of the immiscible reacting mixture leading to outstanding mass and heat transfer and enhancing the kinetics of the transesterification reaction, which completes much more quickly than traditional methods. All the biodiesel samples obtained respect the ASTM standard and present fatty acid methyl ester contents of >99% m/m in both feedstocks. The electrical energy consumption was 0.030 kWh/L, making HC technology really competitive.

Continuous MW irradiation treatment for biodiesel production: The optimal flow MW conditions for biodiesel production (70°C, 400W) entail a methanol to oil molar ratio of 12 and a NaOH loading of 1%wt of oil. Biodiesel yield of 99.4% was achieved from palm oil in only 1.75 min of residence time. Energy consumption was 0.1167 kWh/L, which is the half of conventional processes. This confirms the benefits of using MW heating for biodiesel production also in large scale.

Integrated MW and high-shear mixing treatment for biodiesel production: This work proposes a new flow system for oil transesterification that combines a commercial HSM and a MW reactor. Such a combination dramatically enhances both mass and heat transfer during the NaOH-catalyzed transesterification of refined palm oil and a high biodiesel yield of 99.80% was obtained in 5 circulation cycles (corresponding to 5 min of reaction time). Moreover, the total energy consumption required for this hybrid reactor was noticeably lower (0.109 kWh/L of biodiesel) than a conventional process.

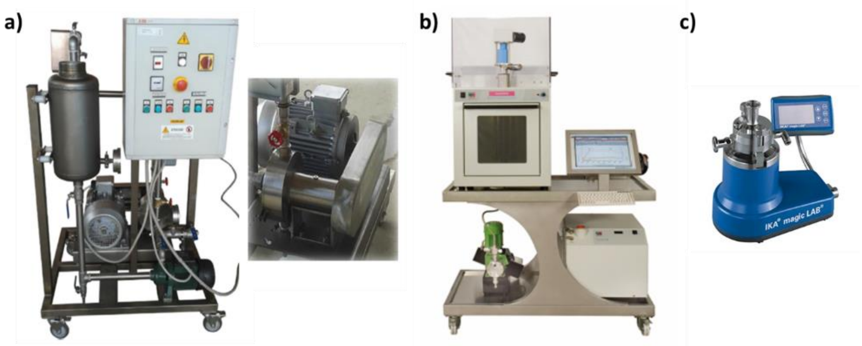

Figure 1. **a)** Rotor-stator generator of hydrodynamic cavitation _E-PIC S.r.l. (Turin, Italy). **b)** The configuration of FlowSynth Microwave system (Milestone S.r.l.). **c)** High-Shear Mixing (Magic-Lab, IKA).

4. Conclusions

The enabling technologies presented for biodiesel production are competitive in terms of electric energy consumption and their scalability. We believe that cavitational reactors and their synergistic combination with other nonconventional technologies such as MW irradiation will gain still further recognition as a powerful ally to green chemistry and beyond.

References

[1] T. Tan, J. Lu, K. Nie, L. Deng, F.Wang, *Biotechnol Adv* 28 (2010) 628-634.
[2] C. Lafleur, Jr H. Bouknight, SrH. Bouknight. System for creating a biofuel. United States Pat., US7452515.
[3] F. Motasemi, F.N. Ani, *Renew Sust Energy Rev,* 16 (2012) 4719-4733.
[4] P. Cintas, S. Mantegna, E. Calcio Gaudino, G. Cravotto, *Ultrason. Sonochem*. 17 (2010) 985-989.
[5] A. Kumar, S. Sharma, *Renew Sust Energy Rev*. 15 (2011) 1791–1800.
[6] D. Crudo, G. Cravotto *et al.* / *Ultrason Sonochem.* 33 (2016) 220–225.
[7] I. Choedkiatsakul, G. Cravotto *et al.* *Biomass and Bioenergy* 77 (2015) 186-191.
[8] I. Choedkiatsakul, G. Cravotto *et al.* *Renew Energy* 83 (2015) 25-29.