Ultrasound-assisted C=C bond activation

Ana Luisa Soutelo Maria
Department of Drug Science and Technology, University of Turin and Centre de Recherche Rhône-Alpes ARKEMA, Pierre-Bénite-France
ana.soutelomaria@edu.unito.it;
Tutors: Giancarlo Cravotto (UniTO), Jean-Luc Dubois, Jean-Luc Couturier (ARKEMA)

The doctoral study arose from the COSMIC (European Training Network for Continuous Sonication) project. The main goals of ultrasound application covered 1) the oxidative cleavage of unsaturated fatty acids to obtain bifunctional monomers and 2) the catalyst reactivation of hydrogenation of bifunctional monomers to obtain suitable building blocks for polyamides synthesis. Mono Unsaturated Fatty Acids (MUFAs) from bio-sourced oils, as castor oil, have attracted a growing interest as a specialty monomer precursor, motivated not only by its renewability, but also by the outstanding polymer technical properties [1].

Oxidative cleavage of fatty acids and derivatives proved to be an attractive way to obtain bifunctional monomers, which can be used for polycondensation reactions to obtain specialty polymers[1]. Among all the oxidants, hydrogen peroxide proved to be easier to handle than ozone, but the kinetics of the catalyzed reactions remain slow. The time-consuming reaction (24h) requires high temperatures (85-95°C) to cleave C-C bonds (347-356 kJ/mole, at 298 K) to recover the monomers. In addition, several studies highlighted major limitations in mass transfer leading to undesired by-products and lack of reproducibility at larger scale[2]. Arkema has selected mono-unsaturated fatty nitriles from MUFAs as precursors of a new synthetic route to obtain monomers for PA11 and PA12 using hydrogen peroxide [2]. The solventless multiphasic system requires a phase transfer agent to promote the difficult mass transfer as reported in the literature [3].

Since 1927 ultrasound technology confirmed its potential in a variety of catalytic processes. It has been also proved that mass transfer across the phase boundary of a multiphasic system is substantially enhanced by acoustic emulsification [4]. The aim of our work was to exploit sonochemical methods to overcome mass transfer and time limitation of conventional oxidative cleavage reaction in MUFAs and derivatives. Experimental data obtained in ultrasonic tank and with ultrasonic horn were compared with results obtained in a conventional batch reactor. Significant improvements were achieved with an ultrasonic horn (25 kHz, 100 W input power). With this system we were could **1)** shorten the reaction time from 24h to 5h, **2)** reduce the concentration of H_2O_2 from 70% to 35% *wt*, **3)** reduce the working temperature from 90°C to 60°C, **4)** to isolate the expected monomers in higher yields without emulsifier. Studies with an ultrasonic reactor designed for continuous processes provides additional data for further industrial implementation.

The application of ultrasound in Ru-based and Raney-Nickel® catalyst reactivation after the hydrogenation of mono unsaturated nitrile esters to amino-esters was also compared with conventional methodologies.

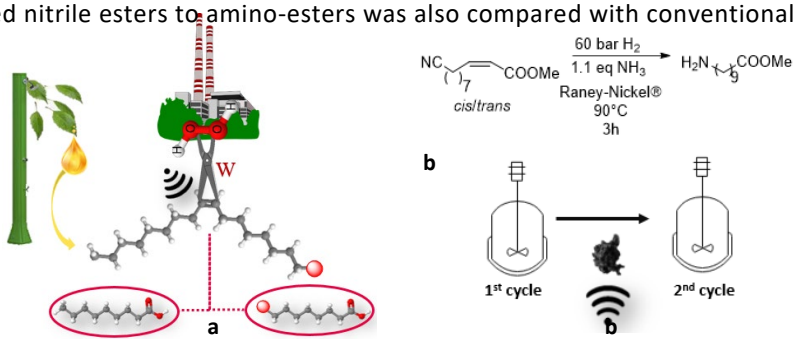

Figure 1. a- Ultrasound-assisted oxidative cleavage of fatty acids with H_2O_2 to obtain bifunctional monomers, **b-** Application of ultrasound technology in Raney-Nickel® catalyst regeneration in the hydrogenation of unsaturated nitrile-esters.

Acknowledgements
This project has received funding from the European Union's Framework Program for Research and Innovation Horizon 2020 under Grant Agreement N° 71290.

[1] Rilsan® Polyamide Family. https://www.arkema.com/en/products/product-finder/range-viewer/Rilsan-Polyamide-Family/
[2] A. Soutelo-Maria, J.L. Dubois, J.L.Couturier, G. Cravotto, *Oxidative cleavage of Fatty acid Derivatives for Monomer Synthesis* **2018**, p 464.
[3] R. Noyori, M. Aoki, K. Sato, *Green oxidation with aqueous hydrogen peroxide* **2003** p 1977-86.
[4] D; Radwiuk, H. Mohwald, *Ultrasonically treated liquid interfaces for progress in cleaning and separation processes* **2015**, p 21-46.