Renewable resources for the synthesis of novel ester biofuels employed as diesel blendstocks

Claudia Antonetti[a], Nicola Di Fidio[a], Stefano Frigo[b], Domenico Licursi[a], Rosaria Lorè[a], Marco Martinelli[a], Luca Mussi[a], Gianluca Pasini[b], Anna Maria Raspolli Galletti[a]

[a] Dipartimento di Chimica e Chimica Industriale - Università di Pisa, Italy. [b]Dipartimento di Ingegneria dell'Energia, dei Sistemi, del Territorio e delle Costruzioni – Università di Pisa, Italy

In these last years increasing attention has been devoted to biofuels, due to the novel regulations requiring the improvement of renewables in fuel composition. The addition of low net-carbon biofuels reduces the carbon footprint of Diesel combustion and can significantly improve the characteristics of both the engine performances and combustion emissions. Biofuels are forecast to grow more than 70 percent with increasing demand for lower-carbon liquid fuels and technology advancements that reduce costs and land-use, while global Diesel demand is forecast to have a significant growth through 2040, becoming the single largest liquid fuel segment [1]. The sustainability of the adoption of novel advanced biofuels is strictly related to the characteristics of the starting biomass as well as to the feasibility of the conversion process. Products obtained from waste or not edible cheap biomasses with a simple, high yield process represent effective renewable components of the fuel. In this perspective two different reactions have been optimized: the direct butanolysis of biomass to butyl levulinate (BL) [2] and the hydrogenation of hexanoic acid obtained from biomass anaerobic fermentation to give hexanol/hexyl hexanoate (HeOH/HeHe).

BL was obtained by one-pot butanolysis of various feedstocks having low or negative value (such as defatted cardoon, giant reed, papermill wastes) employing *n*-butanol as green reagent/reaction medium, very dilute proton acid as a homogeneous catalyst and different heating systems. Significant optimization of the reaction conditions has been carried out starting from the above raw or waste biomasses: under the optimized reaction conditions yields higher than 40 mol %, evaluated respect to the units of glucose in the starting materials, were reached, while the formation of dibutyl ether can be suppressed. Remarkably, these results were analogous to the best ones obtained under the same reaction conditions in the butanolysis of a pure valuable substrate as microcrystalline cellulose. The solid residue recovered from the alcoholysis has been characterized and proposed for different exploitation routes in the context of a more sustainable and integrated process.

HeOH/HeHe mixtures can be obtained with tunable composition and high selectivity by hydrogenation of bio-hexanoic acid. This research was performed in the framework of the PRIN 2017 "VISION" project, devoted to the exploitation of levulinic acid and carboxylate platforms [3]. Commercial Re/C resulted an active catalytic system whose selectivity and activity were tailored by changing the main reaction conditions, as hydrogen pressure, temperature and reaction time.

The reaction products obtained in the two processes were tested as effective renewable components in a mixture with Diesel fuel in a small single-cylinder air-cooled Diesel engine, evaluating the performances of different blend compositions [4]. The obtained results, compared with those obtained fuelling the engine with a conventional Diesel fuel, confirmed the significant potentiality of these novel mixtures to reduce the emissions of particulate without increasing NO_x emissions or worsening engine performances.

[1] ExxonMobil, "*2019 Outlook for Energy: A View to 2040*" **2019**.
[2] A.M. Raspolli Galletti, C. Antonetti, S. Fulignati, D. Licursi, *Catalysts* **2020,** *10*, 1221.
[3] https://www.prin-vision.it/.
[4] S. Frigo, G. Pasini, G. Caposciutti, M. Antonelli, A.M. Raspolli Galletti, S. Gori, R. Costi, L. Arnone, *Fuel* **2021** , *297*, 120742.