

Editorial

Advances in the Catalytic Conversion of Biomass Components to Ester Derivatives: Challenges and Opportunities

Domenico Licursi 

Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy; domenico.licursi@unipi.it

Sustainable conversion of biomass feedstocks into valuable bio-fuels and bio-products plays a strategic role within modern industrial catalysis. However, despite the diversified possibilities already available and well developed on a laboratory scale, it is necessary to focus the potentially interesting bio-products at the next industrial scale, in the perspective of the concrete realization of the coming process intensification. The final application of a bio-product represents an essential prerequisite to define its potential industrial interest, but this is not enough to justify its effective production on a larger scale. To solve this bottleneck, one-pot biomass conversion approaches, carried out under the mildest conditions, using robust catalysts, and high biomass loadings, should be preferred. In this context, the esterification pathway fully fits all these requirements, and the exploitation of ester derivatives is already attractive in many fields of applied and industrial research. These aspects are of paramount importance and have been discussed more in-depth in the introductory Editorial of this Special Issue, focused on the identification of the main improvable key aspects for achieving the intensification of the esterification processes, but extendable to many other biomass conversion strategies [1].

In the first work of this Special Issue, de Oliveira et al. [2] have investigated the acetylation of eugenol with acetic anhydride, deepening the catalytic activity of a mesoporous catalyst, synthesized from 3-mercaptopropyltrimethoxysilane functionalized Amazonian *flint* kaolin, a kaolinitic waste residue disposed in the mine shortly after exploration. This work is well-supported by the value of the final product, eugenyl acetate, which can be used as a natural and efficient larvicide. In addition, the authors rightly claim some typical strengths, such as good stability, recyclability, and high catalytic activity of their catalyst, which was synthesized following the criteria of simplicity, low cost, and environmental sustainability. As a concluding remark, I highlight the well-developed discussion about the characterization of the synthesized catalyst.

Another valuable exploitation possibility of ester derivatives is certainly in the field of the oxygenated bio-fuels, and alkyl levulinates are attractive for this purpose. Antonetti et al. [3] have studied the one-pot butanolysis of the autohydrolyzed-delignified *Eucalyptus nitens* wood to *n*-butyl levulinate, adopting *n*-butanol as the green reagent/reaction medium, very dilute sulfuric acid as the homogeneous catalyst, and comparing microwave and traditional heating systems. To achieve the optimization of this reaction, the authors have developed a face-centered central composite design, experimentally validating their model at the optimal operating conditions for *n*-butyl levulinate production. In addition, a preliminary study of diesel engine performances and emissions for a model mixture with a composition analogous to that of the main components of the reaction mixture, has been proposed, to draw an indication of its potential application as an additive for diesel fuel, resulting in a relevant reduction in CO and soot emission. Certainly, the main strength of this work is the well-balanced synergy between catalysis and the development of the butyl levulinate application as a novel oxygenated bio-fuel, which is a topic of great interest and actuality. Moreover, the high biomass loading (20 wt%) adopted in the butanolysis reaction represents an eligible aspect from the perspective of the high gravity approach, which is



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conducive to the next process intensification. Similar conclusions have been claimed by Raspolli et al. [4] for the conversion to *n*-butyl levulinate of a *Cynara cardunculus* L. (cardoon) waste residue, obtained after seed removal for oil exploitation. Additionally, MW-assisted hydrolysis of the same biomass to levulinic acid was also investigated and optimized. In this context, an interesting section of the manuscript deals with the characterization of reaction by-products and the purification of the synthesized levulinic acid. The achieved results confirm that eco-friendly reaction conditions can be adopted for the conversion of low-cost residual cardoon both to the carboxylic acid or to its ester derivative.

Even cyclic esters, such as γ -valerolactone, are receiving considerable attention as bio-fuels, food additives, solvents, and drug intermediates. In the specific case of γ -valerolactone, its synthesis occurs via reduction and lactonization of the above mentioned levulinic acid, but it requires the development of low-cost, performing, and easily regenerable catalysts. Developing this approach, Luo et al. [5] have synthesized a series of Ni-Fe/SBA-15 catalysts, testing them for the catalytic hydrogenation of levulinic acid to γ -valerolactone, carried out in the presence of methanol as the only hydrogen donor, and investigating the synergism between Fe and Ni towards this reaction. The good catalytic performances/stability, the low cost, and the easy synthesis/regeneration of the synthesized Ni-Fe bimetallic catalysts are key aspects for the real development of γ -valerolactone production on a larger scale, thus contributing to fill the existing gap between the academic and industrial world.

From a different perspective, Wu et al. [6] have synthesized and characterized novel MgO–Al₂O₃ mixed metal oxides decorated with Ni nanoparticles (Ni–MgO–Al₂O₃), which have been tested on the Guerbet condensation reaction of ABE mixture into long-chain (C5–C15) ketones and alcohols, which are important bio-fuel precursors. Ni nanoparticles facilitate the dehydrogenation/hydrogenation process, whilst the activity of the condensation reactions is highly related to the acidity and basicity of the catalyst, which requires a careful balance and optimization, depending on the desired product(s) of interest. In their work, the authors have optimized the production of C5–C15 ketones and alcohols, after optimization of the Mg/Al ratio and Ni loading. However, the wide modularity of the involved ternary catalytic systems could be advantageously exploited to select the Guerbet reaction towards the selective production of aldo-esterification products.

Bio-diesel production certainly represents another very hot topic in the field of esterification reactions. It is a biodegradable and renewable fuel, showing chemical and physical properties similar to those of the petroleum-based fuels, and includes a mixture of fatty acid methyl esters (FAMES), but also other main other components, hitherto little exploited. Applying the fractionation concept on the lipid component, Di Bitonto et al. [7] have proposed the one-pot transesterification of methyl estolides extracted from the lipid component of the sewage scum with methanol, to give methyl 10-(R)-hydroxystearate and FAMES. Transesterification has been optimized by the authors developing a three-level and four factorial Box–Behnken experimental design, using AlCl₃·6H₂O or HCl as the catalyst. In both cases, a complete conversion of methyl estolides into methyl 10-(R)-hydroxystearate and FAMES, was ascertained. The products have been isolated, quantified, and fully characterized. At the end of the process, methyl 10-(R)-hydroxystearate was purified and well-characterized by NMR spectroscopy. The high enantiomeric excess (>92%) of the isolated R-enantiomer isomer opens a new scenario for the valorization of sewage scum towards a multi-product sustainable biorefinery, thus achieving the complete valorization of the lipid fraction present in the starting feedstock. In fact, in addition to FAMES, already well known as green and performing bio-fuels, methyl 10-(R)-hydroxystearate can be a valuable source of 10-(R)-hydroxystearic acid, a chemical used in the manufacturing of lubricants and cosmetics, and this new approach smartly solves the drawbacks of its current synthesis by enzymatic hydrolysis of edible vegetable oils.

In the last contribution, Kampars et al. [8] have proposed the use of MgO as the catalyst for bio-diesel synthesis. MgO synthesis was carried out starting from magnesium nitrate with ammonia, and calcination was performed at different temperatures in air, in

the presence of PEG as surfactant and fuel, leading to active catalysts towards this reaction. For most of these catalysts, FAME yield increased as the size of the crystallites of the catalyst decreased. FTIR spectra showed that deviations in this relationship may be due to the retention of incomplete calcination products on the surface of MgO. FAME and intermediate yield dependence on oil conversion confirmed that all catalysts had the same types of strong base sites that were necessary for the initialization of the transesterification reactions. In my opinion, the proposal of MgO as a catalyst for bio-diesel production well fits the general requirements and trends of the industrial catalysis, being eligible for activity, stability, wide availability, low cost, and environmental sustainability.

In summary, these eight papers highlight the relevance of obtaining ester derivatives for developing applications of great industrial interest, fully according to sustainability and cost-effectiveness criteria. I would like to thank all the authors of this Special Issue for their contributions, as well as all the reviewers for having improved the quality of the submitted papers with their valuable comments. I am also grateful to all the staff of the Catalysts Editorial Office for their helpful suggestions.

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