Cellulose Alcoholysis to Alkyl-levulinate Biofuels

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Alkyl levulinates (ALs) represent outstanding bio-fuels and strategic bio-products within the context of the marketing of levulinic acid derivatives. In order to promote the market for these bio-products and, concurrently, the immediate development of new applications, it is necessary to speed up the intensification of their production processes. In this regard, today, it is possible to achieve this important issue only by using low-cost or, even better, waste biomasses, as starting feedstocks. Thus, the transition to the real biomass now represents a necessary choice for allowing the next ALs production on a larger scale. The improvement of the available synthetic strategies, the use of raw materials and the development of new applications for ALs can contribute to develop more intensified, greener and sustainable processes.

Keywords: Alkyl levulinates ; One-pot alcoholysis ; Solvothermal processes ; Levulinic acid ; Bio-fuels ; Process intensification

1. Introduction

Alkyl levulinates (ALs) are valuable chemicals having strong market potential, mainly as oxygenated bio-fuels. ALs can be produced via dehydration of C6 carbohydrates, such as glucose or fructose, carried out in the presence of acid catalyst and alcohols as reaction medium.[1] In this context, also the direct transformation of model and real cellulose-based feedstocks into ALs has been proposed and demonstrated, the last one resulting certainly more advantageous than that of simpler pure carbohydrates, especially when low-cost or waste biomasses are used as starting feedstock.[2] The overall C6-pathway occurs via etherification of the starting C6 carbohydrates, their next transformation into the corresponding 5-hydroxymethylfurfural-ether derivative, and subsequent rehydration of the latter to give the desired AL.[3] In the presence of alcohol medium, the formation of furanic by-products, known as humins, is greatly reduced respect to the corresponding hydrothermal process for levulinic acid production, thus leading to higher yields and selectivities to ALs.[4] C6-pathway is certainly more performing starting from simpler model sugars (rather than cellulose or real biomass), homogeneous catalysts (rather than heterogeneous ones) and shorter-chain alcohols. For example, in the case of methyl levulinate production, the highest yield of about 90 mol% was obtained by Feng et al.[5] starting from fructose and adopting sulfuric acid as homogeneous catalyst. On the other hand, lower yields (up to 70 mol%) were obtained by other authors starting from glucose or cellulose, due to the greater difficulty of their conversion, caused by the additional isomerization step from glucose to fructose, which is generally favoured by Lewis acids, and by the greater recalcitrance of cellulose.[6] To a greater complexity, lignocellulosic biomass (such as bamboo, straw, eucalyptus, poplar, pine and bagasse) is even more difficult to convert, mainly due to the presence of the lignin component, leading to methyl levulinate (ML) yields up to 35 mol%.[5] On this basis, many homogeneous/heterogeneous catalysts have been proposed, such as sulfonic acids, sulfonate salts (in particular, triflates), polyoxometalates, zeolites, montmorillonites and metal oxides, by alone or in some combinations, in order to balance the Brønsted-Lewis acidities, thus directing the reaction towards the AL production, rather than those of other reaction products, such as humins, alkyl lactate and 1,1,2-trialkoxyethane.[2]

In addition to the alcoholysis of C6-feedstocks, occurring in the presence of alcohols and acid catalysts, synthetic strategies via 5-chloromethylfurfural and subsequent heating in the desired alcohol or utilizing furfuryl alcohol as starting feedstocks, have been proposed and demonstrated.[7] While 5-chloromethylfurfural may be obtained in one-step from cellulose, furfuryl alcohol pathway employs hemicellulose as starting feedstock, thus bridging the C5 and C6 carbohydrate value chain, very promising in a biorefinery perspective.

2. Possible ALs Applications

Regarding the possible applications of ALs, in principle, they can be used as biofuels, biofuel additives, green solvents, flavoring agents, lubricants, fragrances and polymer plasticizer.[8][9] The use of short-chain ALs, in particular, ML and ethyl levulinate (EL), as sustainable oxygenated fuel-additives, has been deeply investigated, resulting in being really promising for this purpose.[8][9] Shrivastav et al.[10] blended C1-C4 ALs with conventional gasoline fuel maintaining up to 18 mol%,

density, viscosity and compressibility within the recommended limits. The tested ALs showed good octane ratings, similar C/H ratio to that of aromatics and better local oxygen concentration than that of traditional methyl *tert*-butyl ether. The authors increased the amount of the blended ALs up to 35 mol%, reducing the aromatic content of gasoline. However, low-chain ALs suffer from some limitations, including high oxygen content, good water solubility and low-energy density. For this reason, new research trends are rather directed towards the synthesis of longer-chain ALs with higher carbon content and stronger hydrophobicity, thus improving the energy density and water insolubility. These “biodiesel-like” ALs result in being more appropriate as oxygenated additives for diesel blends.[11][12][13][14][15] However, given the more difficult synthesis of the levulinates with increasing length of the alcohol residue, only a few papers are reported for these esters, mostly synthesized starting from the more costly and pure levulinic acid, often preferring elegant catalysts, which have been synthesized *ad hoc* on the laboratory scale. In order to increase the development of high-volume automotive applications, it is necessary to find a compromise between the synthesis of these bio-products, which should be easily achievable, and their motor performances, which should be (at least) satisfactory. Up to now, butyl levulinate (BL) meets both of these requirements, due to its feasible synthesis, even starting from real biomasses, and to the related good diesel performances, also allowing for a significant reduction of both CO and soot emissions.[16] In this context, Kremeret al.[17] have discussed in detail the engineering aspects that are related to the motor applications of this levulinate, also positively re-evaluating those of the di-*n*-butyl ether. This last compound, which is obtained as the main by-product from the same alcoholysis process, can be used, in addition to a pure diesel alternative, as an ignition enhancer for low-cetane biofuels, due to its high self-ignitability (Cetane Number = 100). In principle, alcoholysis can be applied as mild biomass pre-treatment, in a biorefinery perspective, such as for the selective depolymerization/liquefaction of its main components, cellulose, hemicellulose, and lignin. All of them can be effectively fractionated and converted into valuable bioproducts, such as not only ALs but also alkyl glucosides/xylosides and soluble aromatics to be used for niche added-value applications.[18][19][20] In particular, the use of long-chain alkyl glucosides as bio-surfactants has been widely demonstrated, showing the remarkable advantages of performance, biodegradability, low-toxicity and environmental compatibility.[21][22] On the other hand, alcoholysis also enables the breakdown of ether linkages of lignin, in order to give smaller aromatics,[23][24] which can be isolated and further functionalized to more value-added products, such as polymer building blocks/pharmaceuticals, or defunctionalized to simpler *drop-in* molecules (BTX, phenol, catechol, and cyclohexane), which have a large market potential.[25]

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