

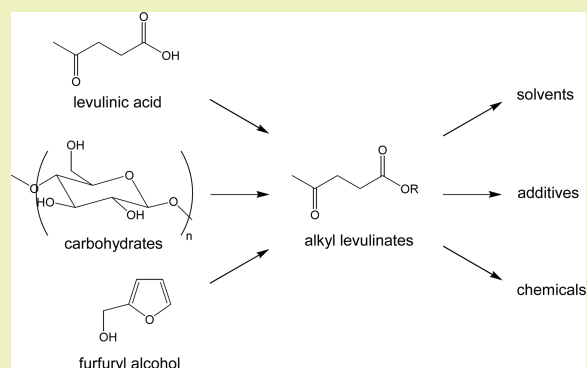
# Synthesis and Applications of Alkyl Levulinates

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**ABSTRACT:** Alkyl levulinates are biobased chemicals having a strong potential to be used in various applications, substituting current chemicals produced from petro-chemical routes. Dedicated literature has considerably increased in the past five years. This review describes state-of-the-art preparation routes and their main application fields. Alkyl levulinates are obtained in high yields and selectivities from simple biomass-derived products like levulinic acid or furfuryl alcohol. They are also obtained directly from lignocellulosic resources with generally limited yields. In all cases, the transformation needs a catalyst. Current efforts are now performed with developing efficient and recyclable catalysts. Alkyl levulinates found applications as solvents and additives as well as in the area of chemical synthesis. The development of new preparation routes and applications of alkyl levulinates are contributing to future greener and sustainable processes.

**KEYWORDS:** Biomass valorization, Alkyl levulinates, Catalysis, Levulinic acid, Cellulose, Saccharides, Biofuels, Biosolvents



## INTRODUCTION

Biomass is recognized as a possible resource for the sustainable production of chemicals and fuels. Recent literature reviews give an idea of the intense research activity currently performed on the production of chemical platforms from biomass, and many different routes give a wide variety of chemicals.<sup>1–5</sup> Lignocellulose is the most important source of biomass. It is mainly composed of lignin, cellulose, and hemicellulose. Lignin is a three-dimensional polymer formed of methoxylated phenyl propane structures. Therefore, lignin is regarded as source of aromatic molecules. Cellulose and hemicellulose are polymers composed of glucose or different carbohydrate units, respectively. Depolymerization of hemicellulose and cellulose can therefore give sugars (i.e., xylose, mannose, glucose) from nonedible and widely available renewable resources. Simple sugars and derivatives are of crucial importance due to their large potential for use and transformation to important commodity (e.g., sorbitol, furans) or platform chemicals.<sup>6–8</sup> Levulinic acid formed from deep hydrolysis of (ligno)cellulose belongs to this last class of compounds. Levulinic acid has been highlighted by the United States Department of Energy in 2004 and again in 2010 as a promising building block for chemistry.<sup>9</sup> Levulinic acid is industrially produced by the Biofine process.<sup>10</sup> Thanks to different functional groups, valorization of levulinic acid can lead to various important products for the polymer industry, to  $\gamma$ -valerolactone and its derivative methyl tetrahydrofuran for fuel and solvent applications and to alkyl levulinates (Figure 1).<sup>11</sup> Alkyl levulinates are of particular interest due to their specific physicochemical properties. Indeed, they could find applications as specialty chemicals and in the chemical and petrochemical industries.<sup>12,13</sup>

First reports concerning alkyl levulinates date from the 19th century (see below). However, the recent interest for biomass transformation and the discovery of new applications for biobased products have considerably increased this literature. Consequently, the majority of the publications have appeared during the last five years, similarly to those related to other biomass-issued, very important, sugar-derived compounds.<sup>14–17</sup> A couple of interesting papers describing advances in levulinic acid derivatives chemistry have therefore appeared very recently.<sup>11,18</sup> However, because they are not especially dedicated to the development of alkyl levulinates chemistry, we aim in the present review at detailing the synthetic methods that have been proposed for the production of alkyl levulinates and their upstream processing. The focus of this review is on the catalytic transformations while highlighting the importance of patent literature in this field of research.

## SYNTHESIS

Apart from a few exceptions,<sup>19–21</sup> starting materials consist of raw biomass (lignocellulose) or reactants derived from biomass (Figure 2). In general, all the preparations involve treatment of the reactant in alcohol and need the presence of an acid catalyst.

On one hand, the most evident reactant is levulinic acid, which can undergo a classical esterification with an alcohol under reflux conditions. Very high selectivity values are generally reported. On another hand, because levulinic acid is

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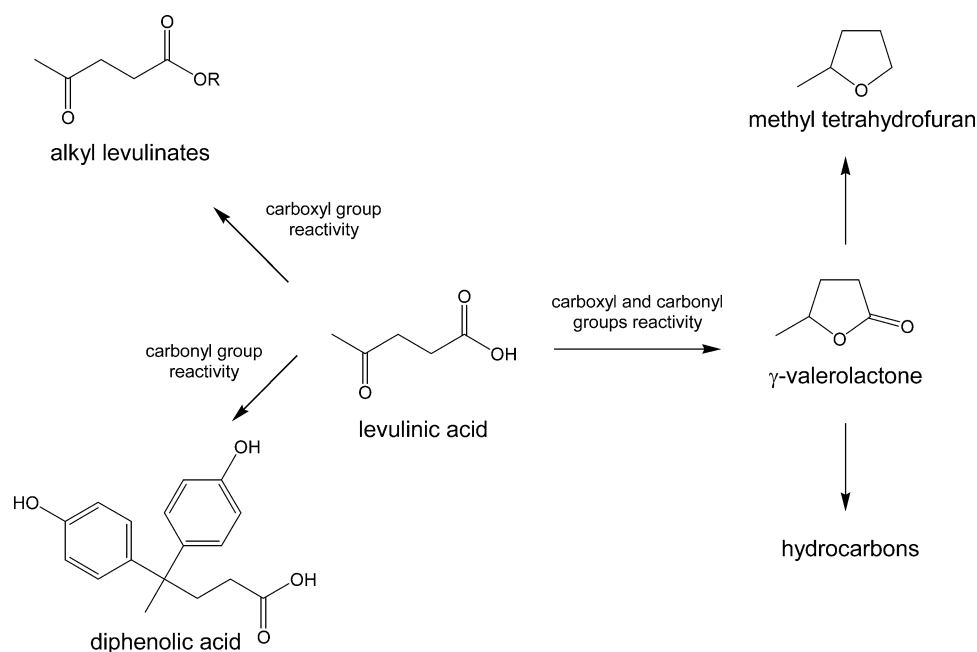


Figure 1. Examples of transformation of levulinic acid.

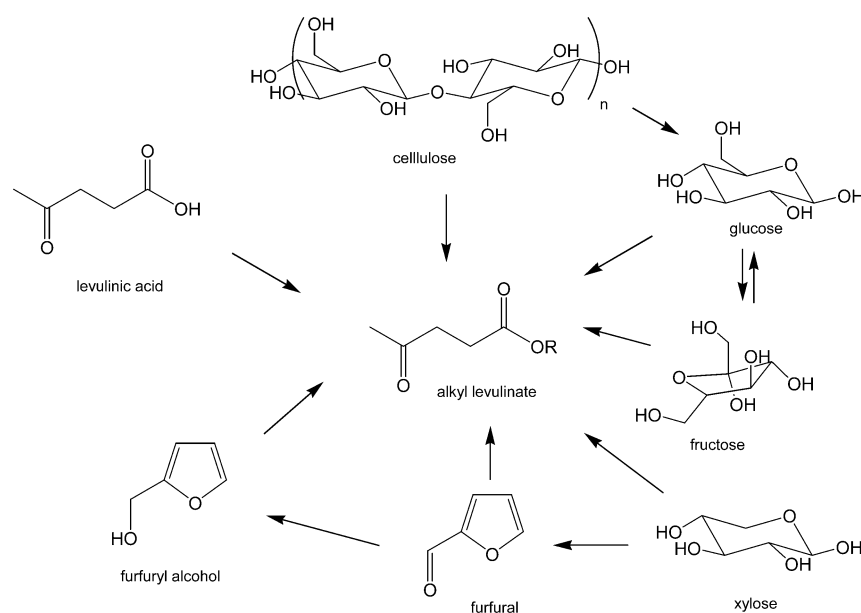


Figure 2. Synthesis of alkyl levulinates from various biomass reactants.

derived from carbohydrate biomass, (poly)saccharides have been obviously studied for the direct synthesis of alkyl levulinates. In the case of lignocellulosic materials, the recalcitrance and insolubility of the reactants in the reaction medium added to necessary steps of depolymerization, solvolysis, and thus dehydration, making the overall process require drastic conditions. This leads inevitably to selectivity issues. Nevertheless, reactions involving carbohydrates performed in alcohols, compared to those in water, show limited side reactions like humins formation. Indeed, introduction of an alkyl group from the alcohol can protect highly reactive intermediates and prevent unwanted polymerization reactions, leading to higher yields into target products.<sup>22</sup>

#### Synthesis of Alkyl Levulinates from Levulinic Acid.

About 150 years ago, a series of studies described the formation

of methyl to propyl levulinate from purified levulinic acid.<sup>23–25</sup> Forty years later, Sah<sup>26</sup> and then Schuette<sup>27</sup> et al. published the formation of several alkyl levulinates in the corresponding alcohol in the presence of HCl. After these early reports, the literature on levulinic acid esterification was revisited very recently. Heterogeneous catalysts are now the preferred catalysts giving moderate to high yields of alkyl levulinates (Table 1). One advantage of heterogeneous catalysts is that they can be easily separated from the reaction mixture for recyclability, regenerability, or reuse. In the case of acid catalysts, one other advantage is that the use of solid acids limits corrosion and disposal issues present when using liquid mineral acids.

Although it seems difficult to compare the yields reported by various studies because of very different reaction systems,

Table 1. Synthesis of Alkyl Levulinates from Levulinic Acid

conditions <sup>a</sup> (notes)	conversion (%)	alkyl group, yield (mol %)	ref
butanol, 6 equiv; 120 °C, 4 h, 20 wt % H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /K10, 10 wt % (3 runs with same efficiency)	97	Bu, 97	33
ethanol, 8 equiv; 78 °C, 4 h, 10 wt % H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /ZSM-5, 20 wt % (4 runs with same conversion)	94	Et, 94	34
ethanol, 15 equiv; 78 °C, 5 h, 34 wt % H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> -silica, 100 wt % (10% yield drop after first run then constant for 3 runs)	76	Et, 76	31
cyclohexane alcohol, > 20 equiv; 65 or 75 °C, 6 h, 20 wt % H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub> -SiO <sub>2</sub> , 50 wt %	79	Me, 73	36
	75	Et, 67	
alcohol, 7 equiv; reflux, 3 h, 7.6 wt % H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> -ZrO <sub>2</sub> -PMOS, 2 wt % (3 runs with same yield)	99	Me, 99	29,37
	–	Et, 91	
	–	Bu, 83	
alcohol, 5 equiv; 117 °C, 2–4 h, SBA-15-(CH <sub>2</sub> ) <sub>3</sub> -SO <sub>3</sub> H, 7 wt % (continuous conversion decrease from 95% to 93% over 4 runs due to surface poisoning)	95	Me, 95	30
	95	Et, 95	
	90	<i>i</i> Pr, 90	
	80	Bu, 80	
ethanol, 6 equiv; 78 °C, 5 h, bimodal porous H-BEA zeolites, 20 wt % (5 runs with same conversion)	40	Et, 39	28
ethanol, 5 equiv; 70 °C, 10 h, SnO <sub>2</sub> -SO <sub>3</sub> H, 2.5 wt % (catalyst not stable even after 1 run)	45	Et, 45	32
ethanol, 10 equiv; 70 °C, 24 h, ZrO <sub>2</sub> -SBA-15-SO <sub>3</sub> H, 5 wt % (continuous conversion decrease from 80% to 60% over 5 runs due to sulfate leaching and ZrO <sub>2</sub> particles sintering)	80	Et, 80	41
ethanol, 5 equiv; 70 °C, 5 h, sulfonated carbon nanotubes, 2.5 wt % (not catalyst recyclability due to poisoning by the reactant)	55	Et, 35	42
water, 50 equiv, ethanol, 30 equiv; 80 °C, 6 h, sulfonated carbon Starbon, 86 wt %	85	Et, 85	43
ethanol, 2.5 equiv; 105 °C, 3.5 h, sulfonated ZrO <sub>2</sub> -TiO <sub>2</sub> nanorods, 3 wt % (continuous conversion decrease from 90% to 60% over 5 runs due to sulfate leaching)	90	Et, –	44
dichloromethane, 3 equiv, iso-butene, 1.5 equiv; 25 °C, 5 days, H <sub>2</sub> SO <sub>4</sub> , 0.02 equiv	–	<i>t</i> Bu, 88	45
water, 3 equiv, 2-butene, 5 equiv; 80 °C, 2 h, H <sub>2</sub> SO <sub>4</sub> , 0.25 equiv	91	<i>sec</i> -Bu, 85	46
water or water–alkane, olefin, 7 bar; 75–150 °C, 0.5–5 h, H <sub>2</sub> SO <sub>4</sub> , 5 wt % or triflic acid, 2 wt % or H-ZSM, 15 wt %	–	Bu, pentyl, hexyl,-	47
CH <sub>2</sub> Cl <sub>2</sub> , 25 °C, 2 h, methylated polymer-supported triazene, 1.2 equiv	–	Me, 88	48
dimethylcarbonate, 20 equiv, K <sub>2</sub> CO <sub>3</sub> , 2 equiv; 160 °C, 4 h	100	Me, 99	49

<sup>a</sup>The equiv and wt % values (except catalyst composition) are referenced to the amount of levulinic acid.

general trends emerge from the data presented in Table 1. An example is the low molar ratio alcohol to levulinic acid, which falls in the range from 5 to 10. Such concentrated solutions are justified in the literature by the fact that a too diluted system could imply mass transfer limitations of the reactant to the solid catalyst and favor intermolecular alcohol dehydration.<sup>28–30</sup>

For heterogeneously catalyzed esterifications of levulinic acid, solids with Brønsted acidity are often used. Mechanisms proposed for the formation of alkyl levulinate on acidic surfaces involve adsorption through the protonated carbonyl group of the carboxylic function thus enabling a nucleophilic attack of the alcohol assisted by an oxygen atom from the oxide network rather than protonation of the hydroxyl group of the acid.<sup>31,32</sup>

Among acid catalysts, heteropoly acids (HPAs) and zeolites are the preferred choices. To overcome their intrinsic low specific surface areas, HPAs have been supported on metal oxides of high specific surface areas. Dharne et al.<sup>33</sup> demonstrated the importance of HPA loading for supported H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> or (NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> on montmorillonite K10. Similarly, Nandiwale et al.<sup>34,35</sup> deposited H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> on partially desilicated ZSM-5 zeolite forming a material with very enhanced textural and acidic properties allowing for high conversion of the substrate and higher selectivity to ethyl levulinate. Loss of activity due to HPA leaching was noticed after three runs. Besides, HPAs have been inserted within oxide matrixes to stabilize the active phase over leaching. Pasquale et al.<sup>31</sup> and Yan et al.<sup>36</sup> included H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> or H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> in silica frameworks to form mesoporous solids. The confinement of the HPA into mesopores facilitates the mass transport of reactant and products. Su et al.<sup>29,37</sup> reported the introduction of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> in a zirconia-modified mesoporous organic silica matrix. The organic moieties consist of benzene groups introduced by the co-condensation of 1,4-bis(triethoxysilyl)-benzene with zirconium alkoxide. The hydrophobicity given by

the benzene moieties contributed to the very high yield of alkyl levulinates by facilitating levulinic acid adsorption and water desorption. In contrast, the presence of surface hydroxyl groups on the benzene-free catalyst favors H<sub>2</sub>O adsorption and therefore inhibits the adsorption of levulinic acid. Several other studies demonstrated the importance of the mesostructure, pore and channel size, and geometry over acid sites density. For example, it has been shown that low diffusional limitations in mesostructured sulfonated SBA-15 silicas induced a catalytic efficiency close to that obtained with homogeneous *p*-toluenesulfonic acid.<sup>30</sup> A recent study showed a significant difference between micro- and mesoporous zeolites H-BEA for the synthesis of ethyl levulinate. The best activity was obtained with materials having a higher mesoporous volume while preserving a sufficient acid concentration.<sup>28</sup> Another report compared a series of classical zeolites that showed very poor or even no activity for the synthesis of ethyl levulinate. There was no correlation between the acid site density and the activity. In fact, it seems that the observed differences were mainly due to the structure (pores and channels size and geometry). It was concluded that the structure should be adequate to accommodate and stabilize the transition states and intermediates. In the case of nonporous materials (sulfonated oxides), the total amount of acid sites is a determining parameter to have a selective transformation, over, for example, the specific surface area.<sup>32</sup>

Biocatalytic esterifications of levulinic acid have been described.<sup>38–40</sup> Immobilized Novozym 435 (*Candida antarctica* lipase) in a macroporous polyacrylic resin was used for the production of butyl levulinate with 90% yield and full selectivity at low temperature (3 equiv butanol, *t*Bu-O-Me as a solvent).<sup>39</sup> Later, esterification with ethanol has been reported with the same catalytic system but in the absence of solvent. Under

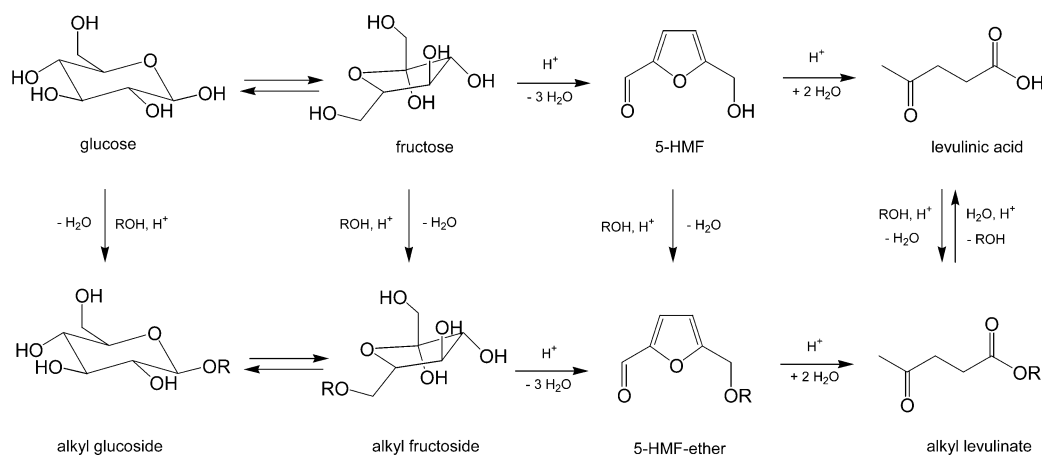


Figure 3. Different possible pathways for the formation of an alkyl levulinate from glucose or fructose.

Table 2. Synthesis of Alkyl Levulinates from Mono- and Disaccharides

conditions <sup>a</sup> (notes)	reactant, conversion (%)	alkyl group, yield (mol %)	ref
ethanol, 58 equiv; 140 °C, 24 h, [NEt <sub>3</sub> B-SO <sub>3</sub> H][HSO <sub>4</sub> ], 0.07 equiv (3 runs with same efficiency)	fructose, 99	Et, 74	64
ethanol, 58 equiv; 140 °C, 24 h, [NEt <sub>3</sub> B-SO <sub>3</sub> H][HSO <sub>4</sub> ], 0.07 equiv	glucose, 94	Et, 6	64
ethanol, 58 equiv; 140 °C, 24 h, [NEt <sub>3</sub> B-SO <sub>3</sub> H][HSO <sub>4</sub> ], 0.07 equiv	sucrose, 97	Et, 41	64
ethanol, 58 equiv; 140 °C, 24 h, [NEt <sub>3</sub> B-SO <sub>3</sub> H][HSO <sub>4</sub> ], 0.07 equiv	cellulose, 95	Et, 2	64
alcohol, 124 equiv; 160 °C, 20 h, H-USY 60 wt %	fructose, 99	Me, 51	66
		Et, 40	
alcohol, 124 equiv; 160 °C, 20 h, H-USY 60 wt % (5 runs with same yield)	glucose, 99	Me, 49	66
		Et, 41	
methanol, 90 equiv; 200 °C, 2 h, TiO <sub>2</sub> -SO <sub>3</sub> H, 2.5 wt %	fructose, –	Me, 59	51
methanol, 90 equiv; 200 °C, 2 h, TiO <sub>2</sub> -SO <sub>3</sub> H, 2.5 wt % (continuous yield decrease from 33 to 10% over 7 runs due to sulfate leaching)	glucose, –	Me, 33	51
methanol, 90 equiv; 200 °C, 2 h, TiO <sub>2</sub> -SO <sub>3</sub> H, 2.5 wt %	sucrose, –	Me, 43	51
ethanol, 230 equiv; 120 °C, 24 h, <i>p</i> -styrenesulfonic acid grafted on nanotubes, 40 wt % (continuous yield decrease from 84% to 69% over 5 runs due to <i>p</i> -styrenesulfonic acid leaching)	fructose, 99	Et, 84	58
methanol, 500 equiv; 175 °C, 1 h, TiO <sub>2</sub> -SO <sub>3</sub> H nanoparticles, 55 wt % (continuous yield decrease from 80% to 70% over 6 runs)	fructose, 99	Me, 80	59
ethanol, 57 equiv, water, 3 equiv; 200 °C, 3 h, ZrO <sub>2</sub> -SO <sub>3</sub> H, 5 wt % (5 runs with same yield)	glucose, 99	Et, 30	52
methanol, 10 equiv; 100 °C, 4 h, H <sub>2</sub> SO <sub>4</sub> , 0.005 M (kinetic modeling, corrosion studies)	glucose, 100	Me, 50	50
methanol, 175 equiv; 130 °C, 2 h, Fe-exchanged H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> , 55 wt % (5 runs with same efficiency)	fructose, 100	Me, 74	54
alcohol, 17–80 equiv; 120–140 °C, 5–15 h, H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub> , 37 wt %	fructose, –	Me, 80	68
		Bu, 60	
alcohol, 30 equiv; 120 °C, 30 h, H <sub>2</sub> SO <sub>4</sub> , 10 equiv	fructose, –	Et, 56	67
		Bu, 64	
methanol, 100 equiv; 170 °C, 3 h, Amberlyst-70, 5 wt %	glucose, 95	Me, 90	61
ethanol, 28 equiv; 170 °C, 30 min microwaves (1000 W), Amberlyst-35, 100 wt %	glucose, >75	Et, 49	62
alcohol, 50 equiv; H <sub>2</sub> , 70 bar; 155–175 °C, 2 h, Amberlyst-70, 5 wt %, Pd/Al <sub>2</sub> O <sub>3</sub> , 9.1 wt %	xylose, 100	Me, 23	63
		Et, 18	

<sup>a</sup>The equiv and wt % values (except catalyst composition) are referenced to the amount of monosaccharide.

optimized conditions obtained by experimental design, a 96% yield was achieved.<sup>40</sup>

**Synthesis of Alkyl Levulinates from Mono- and Disaccharides.** Despite the inconvenience of the insolubility of such reactants in alcohols, the main described method involves the treatment of the saccharide directly in the alcohol. As exemplified in Figure 3, two routes are possible with glucose and fructose: transformation into levulinic acid through the formation of 5-HMF followed by a final esterification or formation of ether species that then undergo dehydration/rehydration to the final ester.

As shown in the following, selectivity depends on factors such as reaction time, temperature, presence of water, and acid catalyst concentration.

Here, significantly higher temperatures in the range of 120–200 °C with greater equivalents of alcohol are needed (Table 2). Nonetheless, these conditions are more favorable for alcohol dehydration into the corresponding dialkyl ether by acid catalysis (Figure 4).

The formation of dialkyl ether in these conditions seems unavoidable. This renders problematic possible industrial developments for the commercialization of alkyl levulinates following these synthetic routes. Not only alcohol over consuming would hamper its recycling, but also necessary



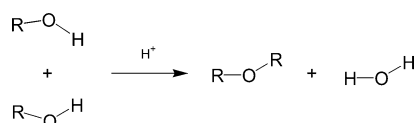


Figure 4. Dialkyl ether formation from alcohol dehydration.

separation and elimination or recycling of dialkyl ether would inevitably lead to complex processes. Reports rarely mentioned the presence of dialkyl ethers when describing alkyl levulinates preparation. However, in some studies, the formation of dialkyl ethers is reported and limited by using solid catalysts or working at very low acid concentrations. For example, Peng et al. showed that during methanolysis of glucose in the presence of  $0.1 \text{ mol L}^{-1}$  of  $\text{H}_2\text{SO}_4$  at  $200 \text{ }^\circ\text{C}$ , up to 58% of methanol was lost in the form of  $\text{Me}_2\text{O}$ , while this transformation was limited to acceptable 2.5% under more diluted conditions ( $0.005 \text{ mol L}^{-1}$ ). Also, the same authors showed the importance of solid acid type of catalysts. Using ZSM-5 zeolites led to important  $\text{Me}_2\text{O}$  formation (50%), which was shown to be almost negligible in same conditions with sulfated titania materials. Also, sulfated zirconia has been shown to give less dialkyl ether than sulfated titania during glucose ethanolysis. Deng et al. observed a significant conversion of methanol to  $\text{Me}_2\text{O}$  (28%) during the methanolysis of cellulose at  $195 \text{ }^\circ\text{C}$  using heteropoly acids.<sup>50–56</sup>

Among the most studied monosaccharides, glucose is supposed to be less reactive than fructose. However, these reactants do not show a great difference in conversion. The difference is noticeable concerning the alkyl levulinate yields that are significantly lower from glucose. The critical step is proposed to occur during the isomerization from glucose to fructose, when side reactions (e.g., polymerization) may take place.<sup>57</sup> Concerning the catalysts, efforts are made toward the development of solid acids. The direct transformation of saccharides into alkyl levulinates has been described with sulfonated catalysts presenting high acid sites densities in addition to high thermal stability under the reaction conditions. Different types of sulfonated materials have been proposed, from metal oxides to carbons, and also sulfonated ionic liquids, acting in this case as catalysts rather than as solvents. Despite their low thermal stability, Amberlyst resins have been used in a couple of examples for fructose,<sup>58–60</sup> glucose,<sup>61,62</sup> and xylose.<sup>63</sup>

In a comparative study, Saravanamurugan et al.<sup>64</sup> evaluated the reactivity of different carbohydrates in ethanol in the presence of small quantities of acidic ionic liquids as catalysts. Fructose gave good yields of ethyl levulinate at  $140 \text{ }^\circ\text{C}$  (74%), while the reaction with glucose stopped at the alkyl glucoside step for almost full conversion. Under these conditions, most likely glucose was not able to isomerize into fructose. Here, the important role of acid strength was pointed out to allow successive steps of cyclo-dehydration and especially final rehydration. The ionic liquids were shown to be reusable after separation. Same authors assessed the influence of various solid acid catalysts by reacting fructose and glucose in ethanol.<sup>65</sup> With zeolites, the conversion of fructose mainly stopped at the HMF-ether stage with low selectivity, and some ethyl levulinate (<10%) seems to only form with large-pore zeolites. The authors stated that HMF-ether, once formed, rapidly diffused out of the pores. Medium-pore zeolites were not able to reaccommodate HMF-ether and thus could not form alkyl levulinate. Therefore, the size of the HMF intermediate seems to be the determining factor for the

selectivity. Sulfonated SBA-15 materials of similar acidic features, but with mesoporosity, gave good yields ( $\sim 50\%$ ) into ethyl levulinate from fructose. Nevertheless, glucose gave selectively the alkyl glucoside. In fact, it seems that only sulfonated zirconia gave a significant quantity of ethyl levulinate, probably due to its Lewis acid sites that can promote glucose isomerization into fructose, as shown by Peng et al.<sup>52</sup> Therefore, the use of zeolites was reported and H-USY was able to form methyl and ethyl levulinate from glucose with interesting yields ( $\sim 50\%$ ) at  $160 \text{ }^\circ\text{C}$  similar to those obtained from fructose.<sup>66</sup> Note that running the reaction in alcohol allowed the zeolite to maintain its structure and enabled recyclability after a calcination step. Peng et al.<sup>51</sup> reported results in line with the above observation comparing the relative reactivity of the two monomers in methanol at  $200 \text{ }^\circ\text{C}$  in the presence of zeolites and sulfonated or phosphated metal oxides. An example of using heteropoly acids was reported for fructose transformation with Fe-exchanged  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (having both Brønsted and Lewis acid sites). The study highlighted the importance of fine-tuning these two acid types. It was proposed that fructose, rather than etherification (see below), undergoes dehydration to 5-HMF that is etherified before rehydration.<sup>54</sup>

Alcoholysis of fructose at  $120 \text{ }^\circ\text{C}$  with acidified porous carbons was studied by Liu et al.<sup>58</sup> Two types of catalysts were assessed. The first one was formed from CMK-5 or carbon nanotubes, modified with grafted sulfonated benzyl groups. They were prepared by treating the carbon precursor with 4-benzene-diazoniumsulfonate in the presence of hypophosphorous acid. The second type consisted of carbon nanotubes copolymerized with *p*-styrenesulfonate and a HCl treatment. The authors reported high yield of alkyl levulinate correlating with the acid strength of the different carbons. A low, but existing, deactivation was observed as usual with this kind of sulfonated material. Concerning formation pathway, the important effect of the reaction temperature and time to allow the transformation of the supposed HMF-ether intermediate to the final levulinate was noticed, as already observed with soluble acids by Balakrishnan et al.<sup>67</sup> A related study on glucose ethanolysis showed that increasing temperature and time led to an increase in formation rate of byproducts greater than that of ethyl levulinate.<sup>53</sup> Other studies from Peng et al.<sup>50–52</sup> suggested this route via HMF-ether for glucose alcoholysis using sulfonated metal oxides. Interestingly, the best alkyl levulinates yields were obtained in the presence of single oxides that however showed limited recyclability even after calcination. Mixed oxides apparently disfavored levulinate formation by stopping the transformation to alkyl glucoside. A very recent study from Kuo et al.<sup>59</sup> on fructose methanolysis using  $\text{TiO}_2$  nanoparticles suggests that the alkoxy group addition may only take place on levulinic acid at the end of the process. Therefore, no HMF-ether was produced. These nanoparticles showed good recyclability after a calcination step at  $400 \text{ }^\circ\text{C}$ .

Very recently, Hu et al.<sup>63</sup> reported the first direct synthesis of alkyl levulinates ( $\sim 20\%$  yield) from a five-carbon carbohydrate, xylose. They showed that the co-presence of Amberlyst-70 and  $\text{Pd}/\text{Al}_2\text{O}_3$  under  $\text{H}_2$  pressure allows hydrogenation of furfural into furfuryl alcohol leading to alkyl levulinate. The fast and selective reduction of furfural limited unwanted polymerization of substrate and intermediates.

**Synthesis of Alkyl Levulinates from Polysaccharides and Biomass.** The general trends described for simple carbohydrates in terms of selectivity are obviously also true

Table 3. Synthesis of Alkyl Levulinates from Cellulose and Lignocellulose in the Presence of Soluble Catalysts

conditions <sup>a</sup> (notes)	reactant, conversion (%) <sup>b</sup>	alkyl group, yield (mol %)	ref
alcohol, > 15 equiv; 179–211 °C, 15 min, concentrated H <sub>2</sub> SO <sub>4</sub> , 20 wt %	cellulose (powder), –	Me, 46 Et, 44 Pr, 37 iBu, 33	73,74
methanol, 200 equiv, N <sub>2</sub> , 50 bar; 180 °C, 5 h, 2-naphtanelesulfonic acid, 4 mol %, In(OTf) <sub>3</sub> , 0.8 mol % (2 runs with same yield)	cellulose (microcrystalline), 98	Me, 75	75
butanol, 117 equiv; 1 bar; 130 °C, 5 h, H <sub>2</sub> SO <sub>4</sub> , 3000 wt %	cellulose (particles 0.075–0.15 mm), 100	Bu, 60	81
ethanol; 200 °C, H <sub>2</sub> SO <sub>4</sub> (part of a global method for fuel production)	cellulose (fibers), –	Et, 40	82
ethanol or water; 185 or 200 °C, H <sub>2</sub> SO <sub>4</sub> (part of a global method for fuel production)	ethyl-cellulose, –	Et, 13 to 20	82
2-butene; 170 °C, 100 bar, 2 h, H <sub>2</sub> SO <sub>4</sub> (supercritical conditions)	cellulose (microcrystalline), 83	sec-Bu, 13	83
methanol, 190 equiv; 190 °C, 5 h, H <sub>2</sub> SO <sub>4</sub> , 17 mol % (near-critical conditions)	cellulose (microcrystalline, particles 50 μm), –	Me, 55	76
alcohol, > 33 equiv; 200 °C, 4 h, 2-naphtanelesulfonic acid, 40 wt %	coniferous wood (particles <1 mm, cellulose 50 wt %), –	Et, 97 Pr, 89 Bu, 85	77
ethanol; 190 °C, 10 min, H <sub>2</sub> SO <sub>4</sub> , 20 mol %	pine wood chips (cellulose 42 wt %), –	Et, 37	84
ethanol; 190 °C, 10 min, H <sub>2</sub> SO <sub>4</sub> , 20 mol %	grass (cellulose 35 wt %), –	Et, 38	84
ethanol; 190 °C, 10 min, H <sub>2</sub> SO <sub>4</sub> , 20 mol %	paper pulp (cellulose 78 wt %), –	Et, 31	84
ethanol, 44 equiv; 183 °C, 36 min, H <sub>2</sub> SO <sub>4</sub> , 2.5 wt % (optimization using experimental design)	wheat straw (particles 0.4–0.8 mm, cellulose 39.5 wt %), –	Et, 51	85

<sup>a</sup>The equiv, mol %, and wt % values are referenced to the amount of glucoside units in cellulose. <sup>b</sup>Conversion is given by reference to cellulose. The wt % values are referenced to the fraction of cellulose.

Table 4. Synthesis of Alkyl Levulinates from Cellulose in the Presence of Solid Catalysts

conditions <sup>a</sup> (notes)	reactant, conversion (%) <sup>b</sup>	alkyl group, yield (mol %)	ref
methanol 90%, 230 equiv, 100 bar; 300 °C, 1 min, C <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> , 43 wt % (supercritical conditions)	cellulose (microcrystalline, particles 20 μm), 90	Me, 20	90
methanol, 400 equiv; 180 °C, 4 h, Fe <sub>2</sub> O <sub>3</sub> or CuO or TiO <sub>2</sub> or Amberlyst-35 (near-critical conditions)	cellulose (microcrystalline, particles 50 μm), –	Me, 5–10	76
methanol, 85 equiv; 200 °C, 2 h, TiO <sub>2</sub> -SO <sub>3</sub> H, 50 wt % (near-critical conditions)	cellulose, –	Me, 10	51
methanol, 500 equiv, N <sub>2</sub> , 20 bar; 175 °C, 20 h TiO <sub>2</sub> -SO <sub>3</sub> H nanoparticles, 55 wt %	cellulose, 72	Me, 58	59
methanol, 170 equiv; 200 °C, 75 min, sulfonated carbon, 50 wt % (continuous conversion decrease from 100 to 80% over 5 runs)	cellulose powder (microcrystalline), 100	Me, 30	89
methanol, 180 equiv, Ar, 20 bar; 200 °C, 20 h, H-USY, 67 wt %	cellulose, –	Me, 13	66
methanol, 175 equiv, N <sub>2</sub> 20 bar; 220 °C, 2 h, Fe-exchanged H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> , 55 wt %	cellulose, –	Me, 14	54

<sup>a</sup>The equiv and wt % values are referenced to the amount of glucoside units in cellulose. <sup>b</sup>Conversion is given by reference to cellulose.

for the transformation of polysaccharides and more generally biomass. Concerning lignocellulose, one could expect higher yields due to the presence in some cases of hemicellulose that can also be transformed into alkyl levulinates. Although they could have an impact on the transformation, important features of these reactants (e.g., morphology, particle size, crystallinity) are rarely mentioned. This lack of information makes data comparison difficult. High temperatures (190–250 °C) under pressure are used (Tables 3 and 4). Concerning the catalytic systems, liquid acids are still the most studied ones. The use of solid catalysts is relatively less developed. This fact can be partly explained by the need of conditions under which the stability of usual solid catalysts becomes really limited. Surprisingly, ionic liquids, widely studied as solvents for low temperature hydrolysis of cellulose,<sup>69–71</sup> have not yet been applied to alkyl levulinates synthesis.

Although some studies reported the formation of alkyl levulinates from starch or inulin,<sup>72</sup> the formation of alkyl levulinates from various lignocellulosic resources was first reported by Garves.<sup>73,74</sup> Powder cellulose was treated in alcohols with concentrated H<sub>2</sub>SO<sub>4</sub> giving methyl to isobutyl levulinates at temperatures of 180–210 °C. Tominaga et al.<sup>75</sup>

treated cellulose in methanol at 180 °C using 2-naphtalene-sulfonic acid with the co-presence of catalytic amounts of In(OTf)<sub>3</sub> and obtained a very good yield of 75%. Lewis acid sites of the triflate complex were proposed to promote the transformation of the methyl glucoside intermediate to methyl levulinate. The catalytic system could be reused after product distillation. An interesting study by Wu et al.<sup>76</sup> compared a large series of catalysts for methanolysis of cellulose, including acids that were merely used. They showed as expected that best results were obtained with H<sub>2</sub>SO<sub>4</sub> and *para*-toluenesulfonic acid, while other soluble acids like H<sub>3</sub>PO<sub>4</sub> or carboxylic acids gave poor yields. Methylated glucosides were shown to be the intermediates, and their transformation is the rate limiting step.

Concerning lignocellulosic materials, the procedure developed by Garves was also applied to the formation of methyl levulinate from more complex biomass (e.g., beechwood, bagasse, straw, and even paper waste) with yields in the 17–37 wt % range. On the basis of Garves studies in which *para*-toluenesulfonic acid was also exemplified, Bianchi et al.<sup>77</sup> patented much later the use of recyclable sulfonated naphthalenes for direct transformation of ground coniferous wood into various alkyl levulinates at 200 °C. Impressive yields

Table 5. Synthesis of Alkyl Levulinates from Furfuryl Alcohol

conditions <sup>a</sup> (notes)	conversion (mol %)	alkyl group, yield (mol %)	ref
alcohol, > 4 equiv; 90 °C, HBr or HCl, 0.3 wt %	–	Me to decyl, 52 to 98	91
alcohol, 4 equiv; CCl <sub>4</sub> , 2 equiv; 70 °C, 4 h, Fe(acac) <sub>3</sub> , <sup>b</sup> 9 wt % (HCl formed in situ from CCl <sub>4</sub> and alcohol)	100	Me to <i>i</i> Pr, 80 to 98	102
ethanol, 2.7 equiv; 125 °C, Amberlyst-35, 20 wt %	–	Et, 91	95
ethanol, 2.7 equiv; 125 °C, H-ZSM-5 (30), 20 wt %	100	Et, 80	94
ethanol, 60 equiv; 140 °C, 24 h, Al-TUD-1 zeolite, 30 wt % (3 runs with same yield)	100	Et, 80	96
butanol, 50 equiv; water, 1 equiv; 110 °C, 12 h, [MIMBS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> , <sup>b</sup> 180 wt % (other alcohols were tested)	100	Bu, 93	97
alcohol, > 25 equiv; 130 °C, 2 h, [BMIm-SH][HSO <sub>4</sub> ], <sup>b</sup> 8 wt % (selectivity decrease over 4 runs)	99	Me to Bu, 73 to 91	98
ethanol, 44 equiv; 110 °C, 2 h, [(HSO <sub>3</sub> -p)im][HSO <sub>4</sub> ], <sup>b</sup> 12 wt % (correlation Hammet acidity and activity)	–	Et to pentyl, 80 to 95	100

<sup>a</sup>The equiv and wt % values are referenced to the amount of furfuryl alcohol. <sup>b</sup>acac = acetylacetonate; MIMBS = BMIm-SH = 1-butyl sulfonic acid, 3-methyl imidazolium; [(HSO<sub>3</sub>-p)im][HSO<sub>4</sub>] = 1,3-bis(sulfopropyl)1H-imidazol-3-ium hydrogensulfate.

were claimed for isolated levulinates (~90%). The naphthalene-based catalysts were described to be more selective by limiting side reactions usually occurring with H<sub>2</sub>SO<sub>4</sub>. Given these excellent results, Mascal et al.<sup>78</sup> attempted to reproduce these data but obtained a limited yield of ~20% in ethyl levulinate. They stated that this seemed to be the order of magnitude with which this compound can be obtained directly from lignocellulosic biomass at this date. Le Van Mao et al.<sup>79,80</sup> have developed a concept to increase the yields of esters that can be obtained from alcoholysis of biomass. They stated that the amount of these esters depends on the amount of the corresponding carboxylic acid intermediates. Therefore, their strategy was to perform the reaction in oxidative conditions to maximize the formation of carboxylic acid from earlier solvolysis intermediates. Thus, they treated raw biomass (e.g., pine wood, paper pulp) at 140–160 °C in ethanol in the presence of H<sub>2</sub>SO<sub>4</sub> and a Fenton-like reagent consisting of a mixture of Fe(SO<sub>4</sub>) and H<sub>2</sub>O<sub>2</sub> to obtain ~20% yield of ethyl levulinate. The presence of Na<sub>2</sub>SO<sub>4</sub> led to a significant reduction of tar formation by limiting polymerization of the intermediates.

Solid catalysts currently widely studied for cellulose/wood reactivity in water<sup>7,86–88</sup> find new interest for treatments in alcohols. There are some examples for the formation of alkyl levulinates from cellulose (Table 4). Interestingly, it seems that the related literature reports to date only include examples of the treatment of cellulose in methanol. Generally yields in methyl levulinates remain lower than those obtained from monosaccharides or using soluble acids. Moreover, catalyst recyclability was rarely mentioned certainly due to the presence of remaining reactant in the solid phase that can prevent catalyst regeneration.

Deng et al.<sup>55</sup> investigated the efficiency of several solid acids like sulfated zirconia and sulfonated carbons, resins, and soluble heteropoly acids (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>) for treatment of cellulose in methanol and ethanol at 180 °C. They aimed at forming the corresponding alkyl glucosides. The alkyl levulinates were obtained only as byproducts, but their yield could be increased (~20%) with time or temperature at the expense of the alkyl glucosides, confirming a consecutive reactions pathway. With the same goal, Dora et al.<sup>89</sup> reported the use of sulfonated carbon obtained from biochar. In some conditions of time and temperature, an interesting yield (30%) of methyl levulinate was obtained from methyl glucoside transformation. The authors stated that 98 wt % of the carbon catalyst can be recovered. Five cycles of reuse showed a continuous conversion decrease from 100% to 80%. Methyl glucoside yields were constant, while no methyl levulinate formed after the third cycle. With the objective to transform

cellulose directly into methyl levulinate, our group<sup>90</sup> reported the use of insoluble catalysts, for example, C<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub>, in supercritical methanol–water (300 °C), and yields up to 20% after 1 min of reaction were obtained. The overall process was shown to combine cellulose solubilization in the supercritical solvent and catalytic formation of methyl levulinate. Later, Wu et al.<sup>76</sup> treated cellulose in near-critical methanol in the presence of various catalysts from metal oxides to Amberlyst-35 resin. Much lower yields (10%) were obtained compared to sulfonated liquid acid catalysts. It is interesting to compare the data obtained by Peng<sup>51</sup> and Kuo<sup>59</sup> et al. In these two studies, sulfonated TiO<sub>2</sub> was used but with a difference in the solid morphology (bulk or particles). In the first case, a 10% yield of methyl levulinate was obtained after 2 h at 200 °C (bulk, BET surface 128 m<sup>2</sup> g<sup>-1</sup>, acid sites 630 μmol g<sup>-1</sup>), while in the second case, nearly 40% were obtained after 1 h at 175 °C (nanoparticles, BET surface 238 m<sup>2</sup> g<sup>-1</sup>, acid sites 303 μmol g<sup>-1</sup>), with a similar concentration of catalyst. Here, in the absence of important data concerning the reactant that could impact the final yields, it seems that the morphology of the catalyst plays a more important role over the amount of acid sites, and a much higher yield could be obtained with the nanosized materials despite lower temperature, reaction time, and acid sites concentration.

#### Synthesis of Alkyl Levulinates from Furfuryl Alcohol.

Furfuryl alcohol is formed by the reduction of furfural, obtained from the xylan hemicellulose component of lignocellulosic biomass (Figure 2). The conversion of furfuryl alcohol in water in the presence of an acid forms levulinic acid, and consequently, treatment in alcohols can lead to alkyl levulinates. The conditions for this transformation are similar to those used for levulinic acid (Table 5). High selectivities are also generally obtained. This route is therefore an alternative to that involving cellulose-derived reactants.

The first reports are found in patent literature.<sup>91–93</sup> Reports published in scientific literature specifically dedicated to this reaction seem to have appeared only very recently, introducing the use of solid catalysts and ionic liquids. The first examples of using a solid acid catalyst were reported by van de Graaf et al.<sup>94,95</sup> who studied the efficiency of resins (macroreticular type-Amberlyst and gel-type Dowex series) and zeolites (H-ZSM, Beta, mordenite of various compositions) for large-scale ethanolysis of furfuryl alcohol. A flow of an ethanol–furfuryl alcohol mixture was introduced in a reactor containing an excess of ethanol. The important general parameters are temperature (which has to be higher than that with liquid acid catalysts) and flow rate. A low flow rate improves the reaction efficiency by diminishing the formation of byproducts, including diethyl ether. Concerning the catalysts, the authors



showed that the crucial factor is the accessibility of furfuryl alcohol to the acid sites and that the acid strength seemingly does not play an important role there. Gel-type resins possess active sites more accessible to ethanol than less polar furfuryl alcohol, limiting therefore its reactivity at the benefit of formation of undesired diethyl ether. General relationships between the texture of various zeolites or Amberlyst resins and the efficiency for ethyl levulinate formation were reported very recently by Neves et al.<sup>96</sup> It was basically concluded that a synergy between the acid sites density, strength, and porosity is necessary, but the main parameter is suggested to be the accessibility of active sites to the reactants. Moreover, this paper reported a comprehensive identification of possible intermediates and byproducts using advanced two-dimensional GC-MS techniques. As from simple carbohydrates, the use of ionic liquids with acidic features has been proposed. The first example was provided by Zhang et al.<sup>97</sup> They used an ionic liquid with a counteranion based on a heteropolyanion, leading to the organic–inorganic hybrid solid catalyst [MIM-BS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. The authors proposed a mechanism for the overall transformation and concluded a rapid formation of an alkoxyethylfuran intermediate subject to slower transformation by successive addition and then release of another equivalent of alcohol, followed by a final hydration. Later, the same ionic liquid core was used for various alcoholysis of furfuryl alcohol, and the nature of the counteranion was highlighted. Associated with Ru/C under H<sub>2</sub> atmosphere, this catalytic system led to  $\gamma$ -valerolactone (see Applications section).<sup>98</sup> Note that this system showed recyclability with same efficiency over four runs. Here also, 2-alkoxyethylfurans were described as first intermediates. González Maldonado et al.<sup>99</sup> studied the ethanolysis of furfuryl alcohol using *ab initio* quantum chemical calculations. They reported that 2-ethoxymethyl furan formed but was not the intermediate involved in the main reaction pathway. Indeed, as confirmed very recently by Wang et al.,<sup>100</sup> the formation of ethyl levulinate can follow parallel routes involving other intermediates. More recently, Chen et al.<sup>101</sup> reported the direct use of more available furfural for its first one-pot transformation into levulinates (Figure 2). The catalyst was composed of platinum supported on mesoporous-phosphonated mixed oxides. Thus, treating furfural in ethanol in the presence of 2 wt % Pt/ZrNbPO<sub>4</sub> under H<sub>2</sub> led through a selective hydrogenation to furfuryl alcohol to ethyl levulinate with 76% yield at 92% of conversion (130 °C, 50 bar H<sub>2</sub>, 6 h, 11 equiv ethanol, 15 wt % catalyst). The stoichiometric presence of zirconium oxide was essential to have this good selectivity.

## ■ APPLICATIONS

**Solvents and Additives.** The first specific studies on properties of alkyl levulinates go back to the first part of last century. Sah<sup>26</sup> and Schuette<sup>27</sup> et al. published basic properties of methyl to hexyl levulinates prepared by HCl-catalyzed esterification of levulinic acid (see Synthesis section). They reported the boiling point (190–270 °C), density (0.89–1.05), and refractive index (1.42) of these faintly smelling colorless liquids, all soluble in classical solvents (e.g., alcohols, ethers, and chloroform) but insoluble in water (methyl levulinate excepted).

The use of alkyl levulinates was patented later for mineral oil refining.<sup>103</sup> A distillate oil was treated with ethyl levulinate to extract low viscosity constituents, leading to a refined oil with an increased viscosity index. At that time, reports on their

possible utility remained scarce. Only very recently have more focused studies appeared on their properties for new applications.

For example, Lomba et al.<sup>104–106</sup> studied physicochemical characteristics of biobased liquids, such as furfural, levulinic acid, and methyl, ethyl, and butyl levulinates, for green solvents application. Properties like surface tension, density, refractive index, viscosity, vapor pressure, and static permittivity were evaluated at temperatures from 5 to 65 °C. They showed that these liquids possess similar characteristics to those of most fluids with, for instance, isobaric thermal expansion and isothermal compressibility increasing with temperature and decreasing with pressure, respectively. Levulinates were shown to be more compressible due to internal organization of molecules (hydrogen bond network) and to possess much lower vapor pressures compared to usual solvents. For example, vapor pressures measured at 100 °C were 5.96, 4.69, and 1.56 kPa for methyl, ethyl, and butyl levulinates, respectively, against more than 400 kPa for chlorinated solvents. On the basis of this, Bayarri Ferrer et al.<sup>107</sup> patented the use of alkyl levulinates for metallic surface degreasing processes. They claimed a degreasing efficiency equivalent to that obtained with industrially used harmful trichloroethylene. Interestingly, this report also includes data of cytotoxicity and mutagenicity and VOC classification for butyl and pentyl levulinates confirming their potential to be considered as green solvents.

Other possible applications of alkyl levulinates concern the use as additives. Although levulinic acid esters or their ketal adducts<sup>12</sup> could find interest, for example, in polymers, perfume, or flavouring preparations and latex coating compositions,<sup>108–112</sup> the main potential application seems to concern at the moment fuel formulations.

Initial communications in this field can be found mainly in patent literature. Alkyl levulinates are proposed as additives to conventional diesel<sup>47,113–115</sup> or gasoline<sup>47,113,114,116</sup> fuels, (Fischer–Tropsch) gas oil-based fuels,<sup>117,118</sup> and even biodiesels.<sup>47,113,119–121</sup> Among possible candidates, long alkyl chain levulinates (4–10 carbons) are currently mainly studied due to greater solubility in the hydrocarbonated fraction concomitant to lower water solubility.<sup>122</sup> However, a compromise between above properties and other requirements like density, viscosity, boiling, flash, and cloud points of the final mixture has to be found.<sup>115</sup> For that, ethyl to butyl levulinates seem to be the main studied esters, and the addition ratio (alkyl levulinate/fuel) falls in the range of 0.5–20 vol %. The advantage of introducing alkyl levulinates in transportation fuel mixtures can be, for example, the substitution of conventional additives (ethanol, methyl-tert-butylether) by biomass-derived products.<sup>113,115</sup> It has been shown that the presence of these oxygenated compounds leads to cleaner combustion processes with fewer smoke or NO<sub>x</sub> (nitrogen oxides) emissions.<sup>118</sup> Another reported advantage is that butyl levulinates cause lower degradations to some elastomeric constituents of the engine (swelling) than other additives.<sup>117</sup> Some comprehensive studies with practical data can also be found in this patent literature. Examples concern miscibility of ethyl to butyl levulinates with various diesel fuels, along with phase separation temperature determination,<sup>117</sup> fuel consumption, particles, NO<sub>x</sub> emissions, cetane number, lubricity, miscibility, and stability of ethyl levulinate blending with biodiesel or conventional diesel (ULSD).<sup>120</sup>

After these reports, some more fundamental studies appeared in the conventional literature to provide additional information



Table 6. Synthesis of  $\gamma$ -Valerolactone from Alkyl Levulinates

conditions <sup>a</sup> (notes)	alkyl group, conversion (mol %)	yield (mol %)	ref
dichlorobenzene, H <sub>2</sub> , 57 bar; 90 °C, 12 h, [Cp*Ru(CO) <sub>2</sub> ] <sub>2</sub> ( $\mu$ -H)OTf, <sup>b</sup> 1 equiv	Me, –	>90	131
gas phase, H <sub>2</sub> , < 1 bar; 70 °C Ni	Me, 100	100	133
gas phase, H <sub>2</sub> , < 1 bar; 70 °C Ni, (R,R) tartaric acid	Me, –	22 (~5% ee) <sup>c</sup>	133
ethanol, H <sub>2</sub> , 60 bar; 60 °C, 5 h, Ru, 0.005 equiv; BINAP, <sup>d</sup> 0.005 equiv, HCl, 0.05 equiv	Et, 100	95 (99% ee)	132
methanol, H <sub>2</sub> , 12 bar; 130 °C, 2 h, 5% Ru/C, 4.5 wt %	Me, 98	87	130
	Bu, 91	75	
alcohol, H <sub>2</sub> , 35 bar; 130 °C, 2 h, 5% Ru/C, 13 wt % (5 runs with same efficiency)	Me, 98	86	129
	Et, 98	80	
	Bu, 98	60	
methanol, H <sub>2</sub> , 34 bar; 200 °C, 5 h, Cu-ZrO <sub>2</sub> , 13 wt %	Me, 95	87	136
methanol–water, H <sub>2</sub> , 30 bar; 90 °C, 10 h, levulinic acid, 18 equiv, 5% Ru/C, 1.2 wt %	Me, 100	100	137
water, H <sub>2</sub> , 30 bar; 70 °C, 4 h, 1% Ru/C, 6 wt % H-ZSM-5, 6 wt %	Me, 100	92	138
2-butanol, 20 bar; 180 °C, 16 h, ZrO <sub>2</sub> , 80 wt % (continuous flow experiments)	Bu, 100	85	140
EtOH; 250 °C, 3 h, ZrO <sub>2</sub> (supercritical conditions)	Et, 96	81	141
2-propanol; 200 °C, 1 h, Zr(OH) <sub>4</sub> , 50 wt % (10 runs with same efficiency)	Et, 94	88	142
2-propanol; 25 °C, 2 h, Ni <sub>Raney</sub> , 70 wt %	Et, 100	99	143
formic acid, water, 3 equiv, 35 bar; 150 °C, 10% Pd/C, 5% Ru/C	sec-Bu, 91	89	46,145
butyl formate, 1 equiv; water, 4 equiv, 10 bar; 170 °C, 15 h, Au/ZrO <sub>2</sub> , 0.1 equiv Au (3 runs with same efficiency)	Bu, 98	95	146

<sup>a</sup>The equiv and wt % values (except catalyst composition) and are given by reference to the amount of alkyl levulinate. Pressure is total pressure of the system. <sup>b</sup>Cp\* = pentamethylcyclopentadiene. <sup>c</sup>ee = enantiomeric excess. <sup>d</sup>BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl.

on the possibility of using alkyl levulinates in fuel mixtures. A computer-based study from Kashinath et al.<sup>123</sup> confirmed that butyl levulinate possesses characteristics like density (1.091), viscosity (4.5 cSt), and cetane number (48) close to those of diesel and can be acceptable for such application. On the basis of cost, sulfur content, and CO<sub>2</sub> emission, the authors calculated that it can be blended along with butanol in diesel in an optimum proportion of 1/6.6/82.4, respectively. Windom et al.<sup>124</sup> studied the volatility of fuel compositions made of ethyl levulinate and a biodiesel formed with fatty acid ethyl esters, or ULSD, in various proportions. They showed that mixtures containing modest 2.5 vol % did not change the volatility of USLD. For biodiesel mixtures, a decrease in enthalpies of combustion was noticed. Studies from Wang et al.<sup>125,126</sup> demonstrated a decrease in smoke emission in the presence of ethyl levulinate in diesel, and this phenomenon is related to levulinate content. Another study from Christensen et al.<sup>122</sup> compared the relative stability of such mixtures. It was importantly shown that if added in a 33 vol % proportion in diesel, crude ethyl levulinate separates from the blend at low temperature (10 °C), but this phenomenon can be limited in the presence of a biodiesel that serves as a co-solvent. This observation is less marked with crude butyl levulinate giving diesel mixtures stability until –10 °C. The authors concluded that although these two compounds improved the lubricity and conductivity of fuel, their low cetane number and poor diesel solubility would limit their use for this application.

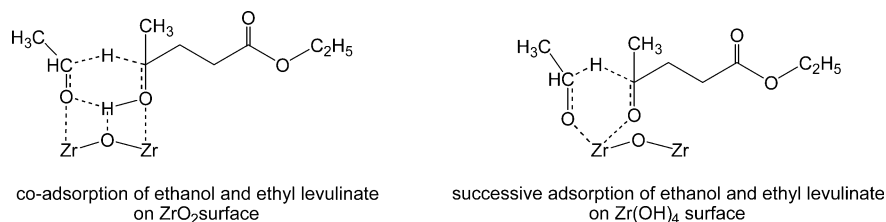
**Synthesis of  $\gamma$ -Valerolactone.** Besides the applications described above, a different and important field of application of alkyl levulinates concerns the use as building blocks for chemical transformations. The most described reaction in the literature involving alkyl levulinates concerns the transformation into  $\gamma$ -valerolactone (Figure 1).  $\gamma$ -Valerolactone (GVL) is a cyclic ester that can find, among others, applications in the perfumes and food industries or as a solvent or fuel additive.<sup>16,127,128</sup> The synthesis of  $\gamma$ -valerolactone from levulinic acid occurs in the presence of a hydrogenating metal catalyst under H<sub>2</sub>.  $\gamma$ -Hydroxyvaleric acid intermediate forms first and is

then subject to ring closing. In the case of alkyl levulinates as reactants, this last step releases an equivalent of alcohol.

Starting from alkyl levulinates instead of levulinic acid can possess certain advantages. For example, using the ester would limit metal leaching from the catalyst by the carboxylic function of levulinic acid. This is why  $\gamma$ -valerolactone formation is now actively considered from alkyl levulinates (Table 6). Apart from a few exceptions, conditions are similar to those reported for levulinic acid. Due to a higher selectivity, ruthenium is the most studied metal. It seems that palladium or platinum can over hydrogenate GVL giving undesired products.<sup>129,130</sup> Although some examples with homogeneous catalysts exist,<sup>131,132</sup> most of the studies involve solid catalysts in alcohols.

The first works concern the enantioselective version of this reaction. In early studies, Yokozeki et al.<sup>133</sup> aimed at forming chiral  $\gamma$ -hydroxyvaleric ester (GHVE) from methyl levulinate on a nickel surface modified by optically active acids in gas phase (at low temperature but under vacuum conditions). While a nonmodified surface gave pure achiral GVL, the presence of preadsorbed chiral tartaric acid led to two different types of active sites: one being selective toward (R)-GHVE formation and one nonselective giving (R)-GVL from (R)-GHVE. More recently, Starodubtseva et al.<sup>132,134,135</sup> showed the formation of (R)-GVL from ethyl levulinate at 60 °C by a catalytic system formed of [Ru(COD)(MA)<sub>2</sub>] (COD = cyclooctadiene, MA = 2-methylallyl) in the presence of a (R)-BINAP ligand in HCl-containing ethanol. The determinant step was the cyclization of GHVE without loss of chirality. HCl was shown to participate in the formation of the active species.

Concerning the use of supported Ru catalysts, in their study on levulinic acid conversion into GVL with Ru/C in alcohols, Al-Shaal et al.<sup>130</sup> evaluated the potential of methyl and butyl levulinates as reactants, with similar yields to those obtained from levulinic acid (75–85%). Under close conditions, Hengne et al.<sup>129</sup> obtained similar results from methyl, ethyl, and butyl levulinate. A noticeable decrease in product selectivity was observed from methyl to butyl due to the different leaving ability of the alkyl group. The authors pointed out the



**Figure 5.** Transition states proposed for the hydrogenation of ethyl levulinate with  $\text{ZrO}_2$  or  $\text{Zr(OH)}_4$  in EtOH (adapted from Tang et al.).

importance of having a high reduced Ru density on the support surface. Note that the same group reported recently the one-pot formation of GVL from furfuryl alcohol with Ru/C in various alcohols and in the presence of acidic ionic liquid. The acidic sites of the ionic liquid promoted full conversion to the corresponding levulinate that was then hydrogenated to lactones by the supported metal (see Synthesis section).<sup>98</sup> The same authors reported also for the first time an efficient transformation of levulinic acid or its methyl ester into GVL with the use of nonprecious metal catalysts, like  $\text{Cu}^0\text{-ZrO}_2$ , but at a relatively high temperature. The authors suggested that the  $\text{ZrO}_2$  phase played also a role in the hydrogenation step by dissociating  $\text{H}_2$ .<sup>136</sup>

Nadgeri et al.<sup>137,138</sup> developed a low-temperature process for methyl levulinate hydrogenation in the presence of the Ru/C catalyst. They showed that addition of levulinic acid and water or zeolites led to exclusive formation of GVL (90–100% yield) at the expense of the GHVE intermediate at a temperature of 90 °C. The authors evoked the presence of additional protons brought by the acids and water systems allowing cyclization of GHVE at this temperature.

A different approach is proposed in literature by replacing  $\text{H}_2$  for other hydrogen donors (catalytic transfer hydrogenation). An example is the Meerwein–Ponndorf–Verley type reduction using alcohols as the hydrogen source, which is very selective to carbonyl groups.<sup>139</sup>

The advantage here, is that reactions can be performed in the absence of precious metals and are catalyzed by simple metal oxides. The drawback is the need of higher temperatures. Chia et al.<sup>140</sup> first reported the use of 2-propanol or 2-butanol to transform butyl levulinate into GLV in the presence of  $\text{ZrO}_2$  with a high relative amount of catalyst (85% yield). They pointed out that secondary alcohols gave better selectivity into GVL than primary ones. The possibility of using a continuous flow reactor was also demonstrated, with a relative stability of the catalyst. Tang et al.<sup>141</sup> reported the use of supercritical ethanol (250 °C) as the hydrogen donor and reaction medium for the hydrogenation of ethyl levulinate also in the presence of  $\text{ZrO}_2$ . Formation of the GHVE intermediate was proposed through a six-member ring transition state from co-adsorption of ethanol and ethyl levulinate on the  $\text{ZrO}_2$  surface (Figure 5). The same group showed that noncalcinated  $\text{Zr(OH)}_4$  was more efficient than metal oxides, and a moderate basicity was necessary. It seems that, in this case, two equivalents of ethanol are necessary to fully reduce the carbonyl function of the alkyl levulinate due to successive adsorption of the reactants (Figure 5).<sup>142</sup> Note that this catalyst showed exceptional stability over 10 runs, despite a slight loss of activity after the first run.

A room-temperature process for the formation of GVL from ethyl levulinate with 2-propanol was recently reported in the presence of  $\text{Ni}_{\text{Raney}}$  by Yang et al.<sup>143</sup> To be efficient, this reaction has to be performed under an inert atmosphere and dry conditions. Extension to biomass-derived substrates like

fructose in ethanol and in the co-presence of Amberlyst-15 was attempted, but low yields of GVL were obtained due to fast poisoning of  $\text{Ni}_{\text{Raney}}$  by humins. A very recent thermodynamic study by Rinaldi et al.<sup>144</sup> showed that with the same system it is possible to determine the selectivity into GHVE or GVL by tuning conditions. Particularly, GHVE would form preferentially at low temperature, and results are in contrast to those described above. The authors also proposed a continuous flow process using propyl levulinate and 2-propanol as reactants to produce either GHVE or GVL if in the presence of Amberlyst-15 to help cyclization.

Other sources of hydrogen than alcohols were explored, for example, formic acid or esters, which are always present as co-products during the synthesis of levulinic acid or ester from carbohydrate reactants. The feasibility of using formic acid was demonstrated by Gürbüz et al.<sup>46,145</sup> in a process based on extraction/separation/recycling steps. They treated a mixture of levulinic and formic acids with 2-butene (in the presence of  $\text{H}_2\text{SO}_4$ , see Synthesis section) to form *sec*-butyl levulinate (and formate) that was then hydrogenated in situ into GVL by formic acid formed upstream. This was possible using a dual-catalyst bed formed of Pd/C for dehydrogenation of formic ester and Ru/C for transformation of *sec*-butyl levulinate to GVL. Du et al.<sup>146</sup> treated a mixture of butyl levulinate and formate in the presence of Au/ $\text{ZrO}_2$ . One-pot transformation was attempted from cellulose hydrolysate, but low activity was observed due to metal poisoning similar to the Yang et al.<sup>143</sup> study with  $\text{Ni}_{\text{Raney}}$ .

## CONCLUSIONS AND OUTLOOK

In this article, we reported the literature associated with the synthesis and applications of alkyl levulinates. These compounds can be obtained in high yields from biomass-derived simple molecules like levulinic acid and furfuryl alcohol at relatively low temperatures (e.g., 80–130 °C) with solid acid catalysts, and it seems that the morphology of the solid is more important than acidic features. Starting from raw lignocellulose requires more demanding conditions (e.g., 150–300 °C). Here, although the use of soluble acid catalysts remains of topical interest, efforts are being made to introduce solid acid catalysts. This results to date in limited yields due to selectivity issues. Therefore, improvements are necessary to develop valuable alkyl levulinate formation routes from raw resources. This will be possible only using efficient, selective, and robust solid catalysts associated with innovative reaction media to minimize byproducts formation. Concerning the application of alkyl levulinates, many studies on transformation into  $\gamma$ -valerolactone are reported. Good results can be obtained using solid catalysts, and alkyl levulinates can be regarded as a potential alternative to levulinic acid reactant. Due to their physicochemical properties, the literature mainly cites fuel additives and biobased solvents as other applications, but the number of reports in these fields remains relatively limited and concerns

principally patent literature. However, some studies recently available from open literature provide useful data confirming the interest of using these compounds for such applications. These need to be further investigated with, for example, practical studies of the use of alkyl levulinates as green solvents for chemical synthesis while developing toxicity studies. To conclude, the recent increase in literature data concerning alkyl levulinates confirms that they have the potential to form an unavoidable biosourced class of compounds that can participate in the development of green and sustainable chemistry and processes.

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### Notes

The authors declare no competing financial interest.

### Biographies



Alexandre Démolis studied chemistry at the University of Bourget du lac (France). During the course of his master degree, he spent six months at the University of Laval, Quebec, working with Prof. T. Ollevier. He then started his Ph.D. in 2013 at the Institute for Research on Catalysis and Environment of Lyon working on the catalytic formation of levulinates from lignocellulosic biomass.



Dr. Nadine Essayem is CNRS Director of Research at the Institute for Research on Catalysis and Environment of Lyon (IRCELYON) at the University of Lyon. After a degree as a chemical engineer, she obtained in 1991 a Ph.D. from the University of Poitiers (France) on the catalytic hydrogenation of fatty nitriles. She then got a permanent position at CNRS first in charge of solid acid catalysis for hydrocarbons conversion. She did pioneering studies in aliphatic alkylation in supercritical phase using a continuous flow reactor. Her

main current research activities concern biomass conversion by means of solid acid/base catalysis. Nadine Essayem is coauthor of 18 patents and more than 80 publications.



Dr. Franck Rataboul graduated in chemistry from the University of Toulouse (France) working for his research project with B. Chaudret. He obtained his Ph.D. from the University of Lyon (France) working with J.-M. Basset on heterogeneous catalysis for alkane transformations. After one year of postdoctoral research with M. Beller (Rostock, Germany), he spent two years as a research associate at Imperial College London (U.K.) in the group of P. D. Lickiss. In October 2007, he joined the Institute for Research on Catalysis and Environment of Lyon with a permanent CNRS research position. His current projects include the transformation of polysaccharides using heterogeneous catalysis.

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