Biofuels

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Pentenoic Acid Pathways for Cellulosic Biofuels**

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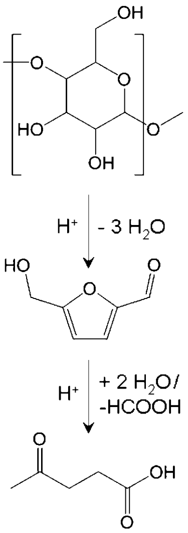
The depletion of fossil fuels, climate change, growing world population, and future energy supplies are certainly important challenges to tackle these days. While several options exist to cover energy supplies of the future, including solar, wind, and water power, individual mobility, aviation, and heavy duty vehicles will for some time continue to require fuels of high energy density to guarantee sufficient drive capacity and cruising range.

Bioethanol and biodiesel were the first biofuels and have certainly been valuable in developing the biofuel market. However, their production from sugars, starches, and vegetable oils induces competition with food production and can thus hardly deliver the large volumes required for worldwide transportation. Current expectations concentrate on lignocellulose, which is available in large amounts, potentially not in competition with the food chain, and could serve as an alternative feedstock for fuels and chemicals.

Biomass gasification along with Fischer–Tropsch technology or pyrolysis of biomass to bio-oils would deliver hydrocarbons which could be integrated easily in today's refineries, but have rather high energy demands, mostly require hydrogen, and do not use the defined chemical structures of lignocellulose.

The chemocatalytic synthesis of defined target molecules as building blocks for fuels and chemicals is an alternative approach and could be realized in a biorefinery concept to integrate complete value chains. Potential biofuels should ideally be suited to today's engines, exhibit a high energy density, require little energy in their production, be nontoxic, and result in reduced emissions during combustion. Fuel platforms based on glucose, 5-hydroxymethylfurfural (5-HMF), and levulinic acid (LA) were described in previous publications. The latter two fuels may be derived by dehydration of hexoses to 5-HMF, followed by rehydration to yield LA along with formic acid (Scheme 1).



Scheme 1. Dehydration of hexoses to 5-hydroxymethylfurfural and rehydration to yield formic and levulinic acid.

Aldol condensation of 5-HMF with acetone and subsequent hydrogenation produces C_9 or C_{15} alkanes, while hydrogenation of glucose to sorbitol followed by hydrodeoxygenation could yield hexane.[1,2] Both routes, however, require lots of external hydrogen, which is to a large extent "lost" as water. With regard to real "bio"fuels, esters of LA have been considered along with γ-valerolactone (gVl) and methyltetrahydrofuran (mTHF), which can be obtained by hydrogenation of LA.[3] Lactones, diols, and cyclic ethers could be thus obtained by controlled transformation of LA and itaconic acid by utilizing a single multifunctional molecular catalyst.[4] Although suitable in terms of combustion properties and energy content, their polarity and high tendency to swell and dissolve conventional polymer materials complicate their application in today's combustion systems.

Recently, two new directions have been proposed, both establishing a value chain based on pentenoic acid.[5,6] This acid can be obtained by hydrogenation of LA to gVl and subsequent ring opening catalyzed by solid acids. The hydrogen required for the production of gVl can be supplied by transfer hydrogenation from formic acid.[7,8]

Dumesic and co-workers reported an integrated approach based on gVl for the synthesis of C_{8+} alkenes for fuel application without the need for external hydrogen (Scheme 2).[5] gVl is converted into pentenoic acid, which

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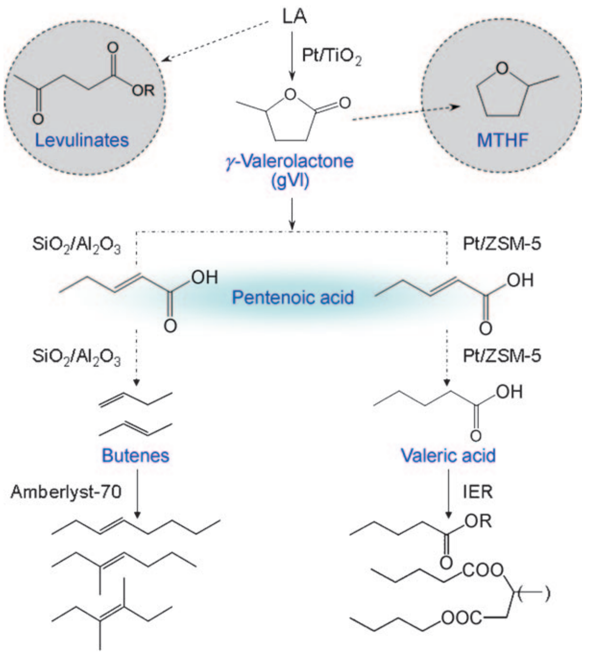

Scheme 2. Potential pathways to biofuels starting from levulinic acid, with a focus on pentenoic acid as a potential platform (IER = acidic ion exchange resin).[5,6]

undergoes decarboxylation to butene and is subsequently oligomerized to yield C_{8+} alkenes.

Starting from an aqueous solution of gVl, an isomeric mixture of pentenoic acids is formed and subsequently decarboxylated to *n*-butenes and an equimolar amount of CO_2. Both transformations are catalyzed by solid acids, for example, SiO_2/Al_2O_3, and can be integrated in a single fixed-bed reactor.

With regard to the mechanism, decarboxylation is proposed to proceed through an acid-catalyzed protonation to cleave the cyclic ether linkage followed by proton transfer, which leads to C−C bond scission, and deprotonation to yield butene and CO_2. The pressure, temperature, and space velocity have to be balanced to achieve an optimum yield of butene. Although gVl conversion appears to be pressure-independent, the decarboxylation is hindered at elevated pressures and the selectivity shifts to the formation of pentenoic acid. An increase in the temperature improves the selectivity for butene, but leads to the formation of coke and thus reduces the stability of the catalyst. In combination, operating at 648 K and 36 bar with a reduced weight hourly space velocity (WHSV) allows complete conversion of a 60 wt% gVl feed with a 93% yield of butene and negligible deactivation of the catalyst. Pentenoic acid is not detected under these conditions, but a certain amount of C_{8+} alkenes and aromatic compounds are formed.

The effect of CO_2 and water on the oligomerization was studied so as to allow integration of butene production and further oligomerization. While oligomerization can be carried out under elevated pressure and in the presence of CO_2, the inhibitory effect of water necessitates its removal by condensation before the butene/CO_2 mixture from the first reactor is oligomerized over solid acids such as ZSM-5 or Amberlyst-70. Interestingly, the latter showed superior activity at lower temperature, higher WHSV, and in the presence of both CO_2 and small amounts of water a 90% conversion of butene and a 86% yield of C_{8+} alkenes was achieved at 443 K, 17 bar pressure, and 0.63 h^{-1}.

The reaction conditions have to be adapted to integrate both reactions in a single process. The whole process is carried out at 36 bar and 648 K in the first and 443 K in the second reactor unit, thereby avoiding the need for compression or thermal energy. Two additional separation units, one before and one after the second reactor, allow removal of water before the oligomerization reactor and separation of the final products from CO_2. Starting from gVl, yields of 77% of the C_{8+} alkenes are produced, with C_8–C_{16} alkenes as the main fraction.

The described transformation of lignocellulose would not require any external hydrogen or other substrates and could be carried out as a closed process. Moderate reaction conditions and simple solid acids without any precious metals are advantageous with regard to economic issues. Noteworthy, CO_2 is released with up to 36 bar and could be utilized for sequestration or chemical synthesis without any need for additional compression energy.

Almost simultaneously, Lange et al. focused on a comparable value chain, and published a comprehensive investigation on alkyl valerate esters as potential biofuels for application in gasoline or diesel.[6] They revisited the complete value chain starting from acid-catalyzed hydrolysis of lignocellulose to LA, hydrogenation to gVl, and further hydrogenation to valeric acid—a transformation which was not reported before. This was followed by esterification to generate alkyl valerate esters as potential fuel compounds (Scheme 2).

With regard to the hydrogenation of LA to gVl, catalyst screening and stability tests show that Pt supported on TiO_2 or ZrO_2 are the most suitable. These catalysts result in over 95% selectivity to gVl at a differential productivity of 10 h^{-1} with negligible deactivation over 100 h at 473 K and 40 bar H_2 pressure.

The one-step transformation of gVl to valeric acid is catalyzed by bifunctional catalysts with acid and hydrogenation functions, for example, a Pt-loaded SiO_2-bound H-ZSM-5. The reaction is not structure-selective, but a balanced acid and hydrogenation activity of the catalyst is important to exclude the formation of pentenoic acid at low hydrogenation or over-hydrogenation to mTHF, alcohols, and alkanes at high metal concentrations. The reaction appears to proceed by acid-catalyzed ring opening of gVl to pentenoic acid followed by hydrogenation to valeric acid. Over a Pt/ZSM-5 catalyst, the selectivity reaches 90% for a WHSV of 2 h^{-1}, 523 K, and 10 bar H_2, and can be kept for more than 1500 h with routine regeneration by hot H_2 strips at 673 K and 10 bar H_2.

Ethyl esters are promising fuels for gasoline and pentyl, ethylene, and propylene glycol esters for diesel applications. They meet all the fuel requirements, including suitable energy density and polarity, and are obtained with above 95% selectivity by esterification of valeric acid with the appropriate alcohol over acidic ion-exchange resins.

With regard to process integration, one-step conversion of gVl into pentyl valerate with 20–50 % selectivity is reached over Pt or Pd/TiO_2 at 275–300 °C. Therein, the metal content of the catalyst has to be enhanced to increase the formation of products from overhydrogenation, such as mTHF or pentanol, which are reacted in situ with valeric acid to yield pentyl valerate.

Assessment of the fuel properties supports the superior properties of alkyl valerates for gasoline and diesel applications. A 250 000 km road trial run on 15 % vol ethyl valerate in gasoline could further substantiate the results. Remarkably, pentenoic acid esters also proved to have promising properties; thus, the hydrogenation to valeric acid could be dispensable.

Both approaches integrate promising value chains and would not require external hydrogen if pentenoic acid esters prove to be suitable fuels. The first approach additionally yields C_4 building blocks which fit well in today's value chains, while the latter could not only yield target biofuels but could open up efficient synthesis routes to pentenoic and valeric acid as future building blocks. By combining these routes with the hydrolysis of (ligno)cellulose to LA,[9] complete process integration becomes feasible and could facilitate commercialization.

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