



## Review

# Transformation of bio-derived acids into fuel-like alkanes via ketonic decarboxylation and hydrodeoxygenation: Design of multifunctional catalyst, kinetic and mechanistic aspects

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## ABSTRACT

The combination of a low cost source of Biofine's levulinic acid with available way of valeric acid synthesis opens up new opportunities for valeric acid as a promising bio-derived source for synthesis of valuable compounds for transportation sector. The present review illustrates the development of different approaches to one-pot synthesis of fuel-like alkanes from lignocellulose derived carboxylic acids where particular focus is given to valeric acid consecutive decarboxylative coupling (ketonization) and ketone hydrodeoxygenation in a single reactor over one catalyst bed. The key factors that influence the catalytic performance on both ketonization and hydrodeoxygenation steps as well as their cross-influence will be clarified to provide insights for the design of more efficient catalysts for the one-pot transformation. Valeric acid is considered as a potential acid source from viewpoint of cost effectiveness and feasibility of such transformation with reasonable alkane yield. The both reaction mechanisms and kinetics will also be discussed to understand deeply how the selective C–C coupling and following C=O hydrogenation can be achieved.

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## 1. Introduction

The biomass-based technologies have been acknowledged as becoming competitive options to convert bioresources into fuels/chemicals having the potential to replace at least a certain parts of the total fossil fuel consumption. The interest in biomass conversion to value-added chemicals increased constantly during the last 10 years in industry and academia. For the former it is a challenge to find alternative syntheses for substances that are currently obtained starting from petroleum. The challenge that might also be a chance is that bio-derived and petroleum-based feedstock involve diametrically opposite polarity characteristics. Petroleum consists of apolar hydrocarbons, immiscible with water, that have to be oxy-functionalized in many cases in industrial processes when chemicals rather than fuels are desired. On the contrary, biomass consists of highly oxy-functionalized molecules that have to be dehydrated and hydrogenated, especially if alkane-based fuels are the desired products [1,2]. In the transformation of lignocellulosic biomass into fuels and chemicals carbon–carbon bond

formations and increasing hydrophobicity are highly desired. Ketonic decarboxylation fits these requirements very well as in this reaction carboxylic acids are converted into ketones forming one carbon–carbon bond and eliminates three oxygen atoms as carbon dioxide and water. This reaction could be used in a cascade mode together with hydrogenation and dehydration catalysts to obtain hydrocarbons in the kerosene range from hexose-derived valeric acid (VA) [3]. In the case of chemicals alternative ways of synthesis are possible which might even be more economical when an advantage is taken from the molecule structure. This progress has to be supported by academia by developing and optimizing synthesis methods that accept biomass platform molecules as starting materials. Cost effective processes adapted to the molecular structure of highly functionalized biomass molecules have to be designed to make the quality and price of chemical compounds more competitive with respect to those obtained by traditional routes. A number of publications dedicated to biomass conversion into fuel and chemicals increased dramatically during the last years [4–9]. Extensive literature surveys covering this subject were published recently [10–17].

The present review illustrates one of the promising approaches for the synthesis of fuel-like alkanes from lignocellulose derived acids including consecutive decarboxylative coupling (ketonization)

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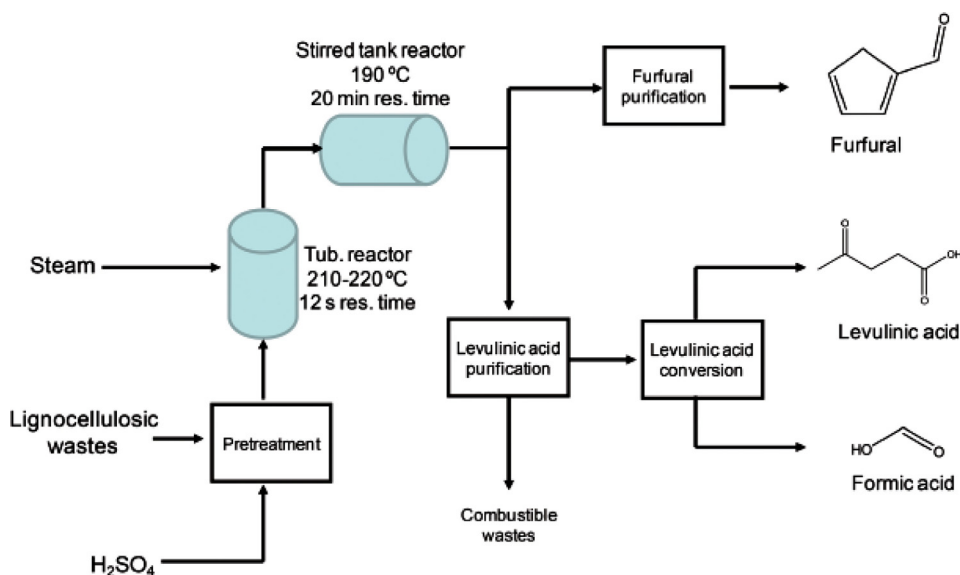


Fig. 1. Scheme of the Biofine process developed for the conversion of lignocellulosic wastes into levulinic acid [30]. Reproduced with permission from Royal Society of Chemistry.

and ketone hydrogenation in a single reactor. Valeric acid is viewed as a potential acid source for this process taking into account cost effectiveness and feasibility of such transformation through different ways with a reasonable alkane yield.

## 2. Alkanoic acids as a cost effective starting material

An interesting trend in current biomass conversion strategies involves utilization of biomass-derived alkanolic acids coming from cellulose, hemicellulose, tall oil and vegetable oil for production of valuable chemicals and motor fuel components [18–24]. Levulinic acid being one of important bio-derived platform molecules plays a predominant role in biomass transformations into fuels and chemicals when lignocellulose is considered as a raw material [25].

### 2.1. Synthesis of levulinic acid

Levulinic acid has been known as a versatile chemical for over 50 years, however earlier levulinic acid (LA, 4-oxopentanoic acid) has been often considered as an expensive and relatively small market specialty chemical (with about 1 million lb/year production at a selling price \$4.00–\$6.00/lb) [26–28]. Such high price has inhibited its widespread use, however, recent economic projections indicated that the LA production cost could fall as low as \$0.04–\$0.10/lb depending on the scale of the operation due to a new LA production process developed by Biofine Corporation [2,29,30] (Fig. 1). The technology has been demonstrated on a 1 ton/day scale at a facility in South Glens Falls, New York.

### 2.2. Synthesis of valeric acid

This cost effective production allows LA to be an economic starting material for production of fuel substitutes, monomers, novel pesticides and a wide range of commodity chemicals, such as  $\gamma$ -valerolactone (GVL), valeric acid (VA) and their derivatives. VA can be prepared from LA either through a single-step or two-stage process going first through GVL synthesis and its further conversion to VA. Kon et al. [31] were the first to report a highly selective single-step conversion of LA to VA or valeric acid esters over Pt/HMFI catalyst under low  $H_2$  pressure (0.2 or 0.8 MPa) conditions, with selectivity to VA or its esters being completely dependent on the solvent used. The reaction starts with hydrogenation

on Pt sites of LA to GVL, which undergoes ring-opening on Bronsted acid sites of H-MFI to give pentenoic acid. This intermediate is hydrogenated on Pt sites to yield VA. If the ring-opening Bronsted acid sites are not near the hydrogenation sites (Pt), pentenoic acid as an intermediate could undergo polymerization. This is a possible reason why a physical mixture of Pt/SiO<sub>2</sub> and HMFI gives a lower yield (~48%) than Pt/HMFI (~83% in toluene, 99% in solvent-free conditions and 19% in dioxane). Luo et al. also showed [32] that VA can be prepared directly by conversion of LA over 1 wt% Ru/H-ZSM5 at 4 MPa  $H_2$  and 473 K in dioxane with the yield of 91.3% after 10 h (Fig. 2). Direct synthesis, however, suffers from catalyst deactivation caused by carbon residue deposition on the strong acid sites. Thus a more effective way of VA synthesis includes two separately implemented transformations: first LA conversion to GVL followed by conversion of the latter into VA.

Different approaches to GVL synthesis from LA have been reported. The review [6] pinpointed the unique physical and chemical properties of GVL which makes it an ideal liquid for use as an intermediate in chemical industry or for energy storage [33].

As discussed in [6] GVL was obtained with 97% yield by hydrogenation of levulinic acid at 423 K over 5 wt% Ru/C catalyst. Hydrogenation was optimized by making a continuous process over Ru/SiO<sub>2</sub> catalyst in supercritical CO<sub>2</sub> resulting in 99% yield and an easy separation of GVL from water [6]. Pt/TiO<sub>2</sub> or Pt/ZrO<sub>2</sub> catalysts afforded continuous hydrogenation of levulinic acid with marginal deactivation over 100 h yielding 95% of GVL [6]. The direct synthesis of GVL from fructose aqueous solutions without isolation of levulinic acid was achieved with a 62% yield in an autoclave pressurized with hydrogen and loaded with water, trifluoroacetic acid and Ru/C catalyst [6]. Hydrogenation of levulinic acid to GVL was also performed using formic acid as a hydrogen donor in the presence of ruthenium catalysts [34]. Leitner and coworkers [35] conducted hydrogenation of levulinic acid in the presence of ruthenium complexes. Further improvement was achieved over Ni catalysts without any solvent, whereby the GVL yield increased to 92% at 100% levulinic acid conversion [36]. In the second stage of VA synthesis GVL could be effectively converted to VA by combining ring-opening over acid sites and hydrogenation reactions on metal sites (Fig. 3) using a water stable bifunctional Pd/Nb<sub>2</sub>O<sub>5</sub> catalyst at moderate temperatures and pressures [37] as well as a variety of other bifunctional metal–acid catalysts (Fig. 3) [38].

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