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Electro- and Chemocatalytic Conversion of Biogenic 3-Hydroxy Decanoic Acid into Green Fuels

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PURPOSE OF THE ABSTRACT

The increase of atmospheric CO2 levels due to anthropogenic emissions leading to global warming is a matter of serious concern, forcing us to rethink the use of fossil fuels. Currently, worldwide endeavors are made to finding sustainable alternatives, overcoming the high degree of dependence on fossil feedstocks for the supply of energy and chemicals. In this regard, two highly promising approaches have evolved: The first is renewable electric power generated from e.g. the sun, wind, or water, whose share has increased recently. Secondly, biomass can serve as feedstock for the supply of fuels and platform chemicals. For the former approach efficient ways for the storage of the produced electrical energy are required due to the fluctuating feed of renewable energy. Here, electrochemistry shows a strong potential to fill this technology gap through the production of platform chemicals and fuels from overproduced green electricity. As regards the second, a biotechnological fermentation of glucose enables the production of hydroxy-fatty acid esters (e.g. 3-(3-hydroxy-alkanoyloxy)alkanoates (HAAs)),[1] which may serve as raw material for renewable hydrocarbons.

In this work we report the study of an electrocatalytic (non-Kolbe electrolysis) and chemocatalytic (deoxygenation) route for the production of green fuels and additives starting from bio-derivable 3-hydroxy decanoic acid (3-HDA). 3-HDA can be readily produced from HAAs through hydrolysis in water at mild conditions.

In our electrochemical setup we have used a 3D-printed support to which the respective electrodes were attached. Electrochemical conversion was performed with a fittingly sliced graphite electrode as anode and titanium as cathode. The highest overall yields (86%) were achieved in methanol with an inorganic base as electrolyte at ambient temperature, overcoming the long existing lack of protocols for the efficient conversion of 3-hydroxy acids via non-Kolbe electrolysis. A thorough study of the reaction network revealed that 3-HDA is oxidatively decarboxylated into a radical species followed by an additional oxidation leading to the formation of a carbonium ion. Subsequently, the latter further reacts to various C9-based products. Noteworthy, product selectivity is tunable from carbonyls to alcohols by choosing 0.5 M NEt3 over 0.5 M KOH as electrolyte.[2] The afforded liquid C9-oxygenate product mixture shows highly promising physical properties besides good combustion characteristics for a direct application as diesel fuel. The herein electrochemically synthesized fuel fulfills the EN 590 diesel norm, forming the basis for the realization of high blending rates and providing immediate CO2 reduction potential in a well-to-wheel perspective.[3]

The chemocatalytic conversion of 3-HDA in water over Ru/C was performed in aqueous phase at a temperature of 200 °C using 40 bar of hydrogen in batch-autoclaves. A careful study of the reaction network enabled us to identify the four deoxygenation pathways, namely hydrodeoxygenation, decarboxylation, decarbonylation, and dehydration leading to three different compounds of high interest for fuel applications. Catalytic tests for an unoptimized system revealed nonane (37%), decane (13%), and 2-nonanol (14%) as main products after 6 h. The alkanes are already well-established fuel compounds as principal part in diesel and jet fuel, while the secondary alcohol is to be evaluated in its performance as additive in a blend with nonane and decane in the near future.

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FIGURES

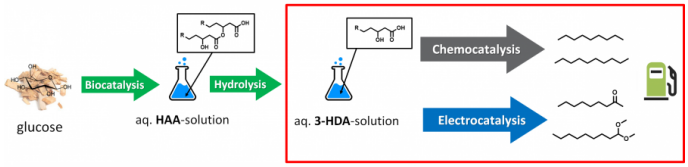

FIGURE 1

FIGURE 2

KEYWORDS

Biofuels | Biomass | Electrochemistry | Heterogeneous Catalysis

BIBLIOGRAPHY