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Reviving electrocatalytic reductive amination: a sustainable route from biogenic levulinic acid to 1,5-dimethyl-2-pyrrolidone

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PURPOSE OF THE ABSTRACT

Extending the tool case of sustainable techniques, electro-organic synthesis has attracted particular attention from academia and industry. The electrocatalytic reductive amination offers access to N-containing platform and fine chemicals in a green and sustainable way. However, systematic studies about suitable reaction conditions and the usage of biogenic substrates are rare. Here, we report the electrochemical transformation of levulinic acid to 1,5-dimethyl-2-pyrrolidone.[1]

As visualized in Figure 1, the used reaction system was based on previous experiments of Smirnov et al.[2] in 1992. Several ketones were aminated and reduction to the alcohol was detected as the main side reaction. Their experiments were validated and extended by investigating the impact of electrode material, solvent, electrolyte, pH value, current density, and substrate concentration on the conversion of the model compounds. The effect of the carbon chain length is discussed together with the importance of the preceding imine formation. This essential step is enabled by a high substrate concentration and alkaline pH. A selective transformation to the desired amines is performed on copper and silver electrodes limiting the alcohol formation to a small extent at current densities lower than 40 mA/cm2. The optimized system was successfully applied to levulinic acid as a biogenic substrate. Followed by a short heating procedure for ring closure, the reaction led to 1,5-dimethyl-2-pyrrolidone in 68(1)% NMR yield.

In a presentation, the systematic study with model compounds will be discussed comprehensively, followed by a detailed discussion of the transformation of levulinic acid. Here, the effects of industrially relevant current densities up to 200 mA/cm2 are shown as well as the influence of using more faraday equivalents. Finally, the latest findings about a fed-batch approach will be presented.[3]

Overall, the reported electrolysis allows sustainable access from biogenic feedstock to a pyrrolidone which can potentially replace N-methylpyrrolidone as a solvent, extractant, and detergent. Moreover, the systematic approach of this work offers a basis for applying this reaction in the synthesis of other N-containing species immediately.

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FIGURES

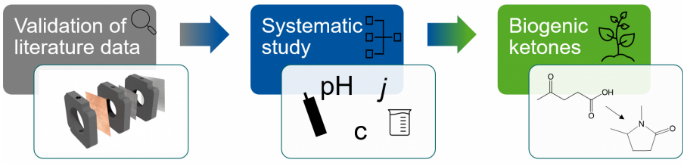

FIGURE 1
Schematic overview of focus and structure of the presentation.
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FIGURE 2

KEYWORDS
electro-organic synthesis | reductive amination | levulinic acid | condition screening for electrolysis

BIBLIOGRAPHY
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