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Conversion of Bio-based Levulinic Acid and its Derivatives to Methyl-N-ethyl-Pyrrolidone: High Throughput Screening and Reaction Network Analysis

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PURPOSE OF THE ABSTRACT

Introduction

Pyrrolidones represent an example of the fine chemicals that can be prepared from biomass-derived sugars. Pyrrolidones find application in various sectors ranging from polymers, to pharmaceuticals, to battery materials, to downstream industries. [Ref 1] Industrially, N-vinylpyrrolidone synthesis, for examples, involves vinylation of 2-pyrrolidone, which is based on acetylene chemistry and can be prepared from ?-butyrolactone and ammonia. [Ref 2]

Recently, much research has focused on alternative routes for pyrrolidone synthesis starting from biogenic acid (e.g. itaconic acid, lactic acid, levulinic acid). [Ref 3] Herein we employ levulinic acid (LA) and ethylamine as substrates in a reductive amination reaction targeting methyl-N-ethyl-pyrrolidone (MNEP). Using throughput catalyst screening technology and a design of experiment study, based on 45 references, we identified the best catalyst systems and the most effective factors and the ideal parameters for pyrrolidone synthesis from levulinic acid. A reaction network analysis provided insight into the reaction mechanism and on the effect of the reaction medium on the reaction outcome.

In addition to levulinic acid, ?-valerolactone (GVL), ethyl levulinate, and butyl levulinate were also used to prepare MNEP. The reaction was conducted in the aqueous phase or in ethanol and over heterogeneous catalysts.

In total 24 catalysts including Ru, Pt, Ni, and Cu impregnated on $Al2O3$, $ZrO2$, and $TiO2$ supports using incipient wetness impregnation were prepared and tested in this study.

An eight-fold parallelized and fully automated high throughput screening unit equipped with 300 mL reactors was used for this study. The reaction mixtures were analyzed using offline GC/GC-MS.

Results and Discussion

High throughput experimentation methodology and two design of experiment techniques, namely full factorial design and surface screening, were considered in catalysts synthesis and catalyst testing, respectively. We have found that Pt and Ni show higher catalytic activity than Ru and Cu, respectively. The study of the support effect reveals calcined Al2O3 to be the best support for the reductive amination reaction. For Pt catalysts, the reaction temperature founds to be the most effective factor in the reductive amination of LA, while both T and P influence the productivity and pyrrolidone selectivity for Ni catalysts. Ultimately, Pt/ Al_2O_3 catalyst proved to be best at 75% NMEP yield at [T and P].

A detailed reaction network analysis of LA reductive amination was carried as function of temperature. Already at room temperature and without catalyst we found 50% conversion of LA to the imine intermediate; no other products than the imine were seen under these conditions, also at increased temperatures. GVL, a hydrogenation product of LA and a side product of the reductive amination, has been tested as a starting material and we found that GVL can undergo ring opening reactions to give amide and amine intermediates and pyrrolidone as a final product. Water influence, as a reaction medium, was also investigated, and we found that water can suppress the dehydration step of amine to pyrrolidone and affect the selectivity of GVL ring opening. Conducting the reaction with minimum amount of water, by using ethanol as a solvent, results in significant increase in pyrrolidone yield and remarkable improvement in the kinetics. Using alkyl levulinate as a substrate and ethanol as a solvent show high catalytic activity and yield of pyrrolidone and the results are comparable to LA reductive amination in ethanol. Overall, our study highlights the influence of the reaction medium on the reductive amination of LA and demonstrates that the hydrogenation side reaction results in pyrrolidone alongside the reductive amination pathway.

FIGURES

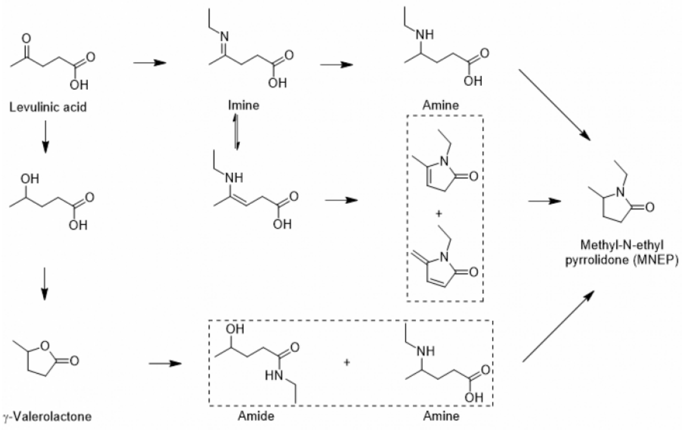

FIGURE 1

Reductive amination of levulinic acid

Figure 1. Reaction network analysis of the reductive amination of levulinic acid with ethyl amine to methyl-N-ethyl pyrrolidone. The dashed boxes indicates that the products were found as a mixture and react further to give MNEP

FIGURE 2

KEYWORDS

reductive amination | High throughput experimentation | Pyrrolidones | heterogenous catalysts

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