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INSIDE THE MECHANISM FOR TRANSFORMING CELLULOSE INTO BIOFUELS: KINETIC AND CALORIMETRY INVESTIGATION OF 5-HMF ALCOHOLYSIS TO N-BUTYL LEVULINATE OVER SOLID CATALYST

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PURPOSE OF THE ABSTRACT

The goal of carbon neutrality and the complete energy transition to renewable energy are still far away due to industrial dependence on non-renewable sources. In the fight against pollution and greenhouse gas emission, lignocellulosic biomass (LCB) is a strong ally, since it is an abundant renewable raw material, not in competition with alimentary sector, and particularly rich in building blocks. [1] The conversion of lignocellulosic matrix leads to valuable compounds for the refining and chemical industries, as furans, Levulinic acid (LA) and Levulinate esters (LE). [2] Levulinate esters are commercially used in mineral oil refining, polymer application, and as promising blending with commercial diesel. In particular, butyl levulinate (BL) has been identified as one of the most promising blends thanks to its water solubility and cetane number properties. [2,3] The synthesis of butyl levulinate can occur through acid-catalysed alcoholysis in butanol of biomass-derived precursors as 5-(Hydroxymethyl)furfural (5-HMF), which may turn into butyl levulinate via hydration to levulinic acid, then esterified, or through its corresponding ether (5-(butoxymethyl)furfural, BMF). [2,4,5] Furthermore, furans tend to undergo acid-degradation, determining side-products, as humins, and hindering BL product selectivity. [2,4,5] Major control of conversion steps and side-reactions occurrence can be achieved by using solvent in the alcoholic medium. In particular, aprotic polar solvents have been remarked as stabilisers of positively charged intermediates. [6] Among these, ?-Valerolactone (GVL) is particularly promising, not only for its green footprint but also for stabilising intermediates and solubilising humins, avoiding their accumulation and catalyst fouling. [6] The use of heterogeneous acid catalysts should be preferred due to their greater sustainability. Ion exchange resins show high recyclability and efficiency under mild conditions [2,4] and therefore Amberlite IR120 resin was selected in this study. Different catalyst loading and 5-HMF initial concentrations have been tested in the optimised mixture butanol-GVL (75/25 v/v%).

The conversion of furans is a key step in the upgrading of LCB-derivatives and its study in kinetic and thermodynamic aspects is essential in the perspective of extending the study to the direct production of butyl levulinate from lignocellulosic biomass.

To the best of our knowledge, there is not kinetic model for the alcoholysis of 5-HMF to butyl levulinate via heterogeneous catalyst in solvent system butanol-GVL. Therefore, we have assessed different kinetic models for these crucial reaction steps. From an industrial viewpoint, it is important to know the amount of energy released or absorbed by a chemical system, and from a fundamental standpoint the thermodynamic knowledge can aid to have a better understanding. Therefore, a calorimetry analysis was also done.

Considering different initial 5-HMF concentration (0.08 - 0.31 mol/L), effect of temperature and catalyst loading have been considered on the reaction kinetic. The kinetic model developed fits well the experimental trends, also in case of high initial substrate concentration (Fig.1). Fig. 1 shows the fitting of the model to the experimental data for one of the experiments at high initial concentration of 5-HMF.

In this work, we are developing a kinetic model using Bayesian inference, and considering the side-reaction of humins production. Kinetics in butanol-GVL medium will be compared with those in pure butanol to better elucidate the effect of aprotic polar additives.

FIGURES

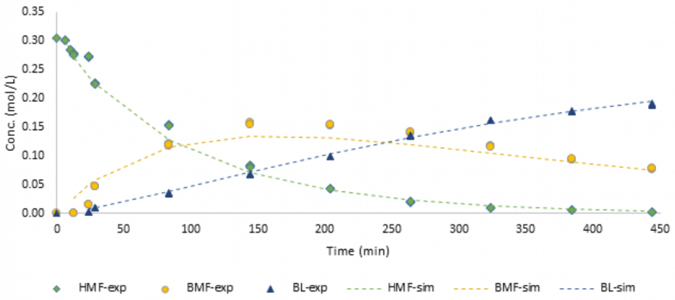

FIGURE 1

Fig. 1

Experimental and simulated trends of 5-HMF, BMF and BL. (T=110°C, p=20bar of N2, 800 rpm, 8 g of catalyst).

FIGURE 2

KEYWORDS

Butyl levulinate | Kinetic model | Bayesian statistics | Solid catalyst

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