Catalyst Development for Production of Biorenewable Chemicals Using Machine Learning and High-Throughput Experiments

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Furfural and 5-(hydroxymethyl)furfural (5HMF) are important value added bio-based chemicals produced from lignocellulosic biomass, which enable production of green and biorenewable chemicals and fuels. Therefore, these constitute a sustainable raw material with high potential in a carbon neutral future. Furfural and 5HMF are obtained by acid-catalysed dehydration of C5 and C6 sugars, respectively. Most studies have focused on model sugar compounds to determine precise reaction pathways [1] or screen limited catalyst composition spaces. In BioSPRINT, a BBI EU H2020 funded project, the main aim is the development of scalable processes for conversion of complex and realistic feedstocks, relying on recyclable heterogeneous catalysts and green solvents.

Heteropoly acids (HPAs) are acid catalysts composed of H, O, transition metals addenda atoms (*e.g*. Mo, W, V, Nb) and non-metals heteroatoms (*e.g*. P, Si, As) [2]. HPAs have stronger Brønsted acidity, better selectivity, and are more environmentally friendly and safer than conventional mineral acids. Nevertheless, HPAs are soluble in polar solvents [3], and have low surface area, which hinders recovery and activity [4]. Therefore, it is important to modify the HPA structures and composition to create true heterogeneous catalysts for dehydration of complex sugar matrices, while ensuring the catalyst formulation can be scaled up. In this study, HPA catalysts capable of selectively converting complex feedstocks were developed. HPAs precise composition allowed fine tunning of the catalyst properties for optimal performance. By screening a range of transition metals incorporated into the HPA structure, it was possible to tailor the Brønsted and Lewis acid densities for optimal selectivity. Silica, metal oxides and zeolites were used as supportive materials to overcome solubility and surface area issues. A machine learning (ML) approach

combined with high throughput (HTP) experiments was used to guide and streamline the development of the catalyst formulation.

The use of ML combined with HTP experiments allows correlation between catalyst properties and Figures of Merit (FOM) which quantitatively describe catalyst performance, increasing screening speed and enhancing catalyst synthesis [5]. However, predictions of catalytic FOMs are still in early stages and data are often incomplete, resulting in poor model predictions [5]. To overcome such challenges, this study combined fundamental and empirical modelling, focusing on systematic screening of variable selection algorithms and modelling methods. Linear, decision tree, ensemble, Support Vector Machine, and Gaussian Process Regression models were researched. In addition, ensemble tree model with hyperparameter optimization was tested, and reference methods (*e.g.* linear models, PLSR and regularization algorithms) were used. The modelling was done with subsets of descriptors selected by variable selection algorithms (Lasso and Ridge regression, elastic net, Genetic Algorithms and Floating Search algorithm).

Catalytic tests were conducted in parallel agitated reactors with automatic temperature and pressure control. Selected aqueous hemicellulose-derived monosaccharides (xylose, glucose and fructose) and solid catalyst were used. Activity tests were performed under N_2 at 5 bar, varying the temperature between 120-200 °C. The tests lasted 6 h and the quantification of samples was determined by Ultra-High Performance Liquid Chromatography. Gas phase products from selected reactions were analysed on-line by μ-GC. After defining the optimal reaction conditions (temperature 140-180°C) and catalyst:reactant ratios (2:1-1:10), 38% yield of furfural and 43% yield of HMF were obtained using xylose and fructose as starting material, respectively. Dehydration reactions utilizing mixtures representative of real biorefinery streams will also be presented. The kinetic model based on sugar model compounds will then be expanded to synthetic and realistic biorefinery streams.

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