Rational optimisation of biomass-derived γ-valerolactone cascade synthesis

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Significance and Relevance

This work presents a promising framework for tackling the development of complex processes, particularly for converting biomass-derived molecules into relevant products. A series of Aquivion/Zirconia (Aq/ZrO_2) composite catalysts were developed via spray freeze-drying (SFD), and then a Design-of-Experiment approach was employed to study the process parameters to identify optimal conditions to achieve conversion of biomass-derived furfuryl alcohol (FAL) into γ-valerolactone (GVL). This approach led to an increase in GVL productivity from 4'500 µmol h^{-1} g^{-1} to 18'000 µmol h^{-1} g^{-1}, demonstrating the potential of this approach.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion, Circular economy
Preferred presentation: Oral preferred

Introduction and Motivations

The development of biorefineries and the transition of the industrial landscape towards a future wherein fossil feedstocks are replaced with biomass-derived ones hinges on the invention and optimization of industrially relevant processes for the conversion of biomasses and biomass-derived feedstocks into desirable target products. Among such processes, the synthesis of γ-valerolactone (GVL) from biomass-derived feedstocks such as furfuryl alcohol (FAL) is of great interest for the potential application of the product in the production of chemicals, fuels and plastics.[1] This process involves a cascade reaction, the optimization of which requires proper tuning of multiple parameters, the interactions among which are not always predictable. The most common One-Variable-At-a-Time (OVAT) approach can elucidate the effect of the single parameters but is unable to provide insight into the interaction between different ones, if any. To overcome this limitation, Design-of-Experiment (DoE) can maximize information from the chemical data by variating the main parameters within their relevant ranges and enabling inferring a multivariate, data-driven regression model to predict the interaction of the different parameters within the desired domain. In addition, these goals are generally achievable with a lower number of experiments than OVAT.[2]
In this work, DoE was employed to rationalize the effect of five different parameters on the cascade synthesis of GVL. To carry out the reaction, Spray-Freeze Drying (SFD)[3] was employed to combine the Brønsted Acid Sites (BAS) of Aquivion and the Lewis Acid Sites of zirconia into bifunctional catalysts capable of converting FAL into GVL. Then, batch reactions were carried out following the experimental design to develop a data-driven model capable of predicting the effects of all five variables considered.

Materials and methods

High surface area zirconia was synthesized via precipitation at controlled pH, then was employed in conjunction with Aquivion water suspension (D79-25BS) for the SFD synthesis of the composite catalysts. The reactions were carried out in a batch reactor using FAL as a substrate and isopropanol as both solvent and hydrogen donor. The tests were carried out following a Face-Centered Design model with replicates wherein each parameter was normalized to three levels as reported in Table 1.

Table 1. DoE variables and levels

Level	Temperature (°C)	Time (h)	FAL Conc. (mmol L^{-1})	BAS/FAL (mol%)	Polymer Content (wt%)
1	180	3	200	1.5	30
0	165	2	133	1	20
-1	150	1	67	0.5	10

Results and Discussion

A set of 48 tests was defined and carried out in a random order to avoid systematic errors, investigating the effect that the five independent variables have on the catalytic performances, measured as both GVL productivity and selectivity. The obtained results were elaborated via MATLAB, building a quadratic regression model.

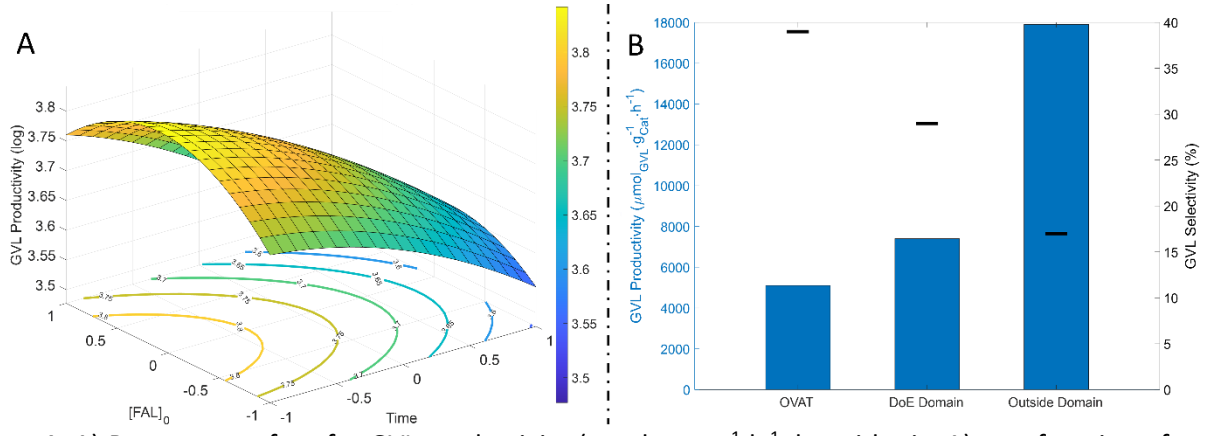

Figure 1. A) Response surface for GVL productivity ($\mu mol_{GVL}\ g_{Cat}^{-1}\ h^{-1}$, logarithmic, A) as a function of substrate concentration and reaction time. B) Results obtained from the investigation outside the experimental domain of the first DoE.

From the regression model, vast insight was gained on the behaviour of the system, especially on the interaction between the process variables. While reaction temperature showed the expected positive influence on both productivity and selectivity, reaction time showed a positive effect on selectivity and a negative effect on productivity (Figure 1A). More interestingly, the interactions between temperature and time, as well as between temperature and catalyst loading, were found to be negative. This is due to substrate degradation, which is more prominent when both reaction temperature and reaction time or catalytic loading are high.

While the regression model provided valuable insight into the behaviour of this complex system, it also indicated that maximization of catalytic performances would require an expansion of the experimental domain. Proper control of the interactions with other process parameters could allow further increase of the reaction temperature without causing excessive substrate degradation. Using the insight gained from the first study, new tests were carried out outside the initial experimental domain, increasing the reaction temperature, decreasing reaction time and keeping low catalytic loadings to prevent decomposition of molecules of interest. These tests yielded the result presented in Figure 1B; while the exploration of the initial experimental domain led to a 45% increase in GVL productivity over the initial OVAT studies, using the regression model as a guideline for further exploration increased productivity by a further 145% (corresponding to a 250% increase compared to the OVAT results).

References

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