

# Steady States and Kinetic Modelling of Glucose, Cellulose, Xylan, Corn Cob, and Wheat Straw to Produce Butyl Levulinate

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## **Highlights**

- Kinetic modelling of the butanolysis of biomass based on a surrogate biochemical composition.
- Steady state times and concentrations of butyl levulinate production via alcoholysis.
- Acid-catalysed butanolysis of lignocellulosic biomass is not wholly catalytic.
- Butyl levulinate is produced from both cellulose and hemicellulose portions of the biomass.

## **1. Introduction**

The global transportation fleet is a significant contributor to anthropogenic greenhouse gas emissions. The substitution of fossil fuels with biofuels is a viable pathway to mitigate greenhouse gas emissions without the upheaval of existing transportation infrastructure. The industrial upscaling of biofuels is confronted by two primary challenges. Firstly, the dichotomy of using the crops for either food or fuel production. Additionally, expanding farmland for cultivating crops aiming to increase the production of the latter can pose indirect land-use issues. A feasible solution lies in advanced biofuels, which exclusively utilize non-food waste, residues, and by-products as raw materials. Alkyl levulinates have been identified as potential drop-in diesel and gasoline advanced biofuels [1] and are synthesized via alcoholysis processes. Upon alcoholysis, the carbohydrates of lignocellulosic biomass undergo a conversion process, forming esters (i.e., alkyl levulinate), while alcohols are converted to ethers (i.e., dialkyl ether)[2]. This study examines the fundamental reaction mechanism and kinetics of glucose, cellulose, xylan, and lignocellulosic biomass butanolysis using a combination of experiment and model. A parameterised study into the effect of various reaction conditions (reaction time, feedstock loading, acid concentration and temperature) on the product mixture is carried out and integrated into a hierarchical, mass-conserved chemical kinetic model capable of accurately predicting the relative abundance of the three primary components of the butanolysis reaction: n-butyl levulinate, di-n-butyl ether, and n-butanol, from the biochemical composition of the feedstock.

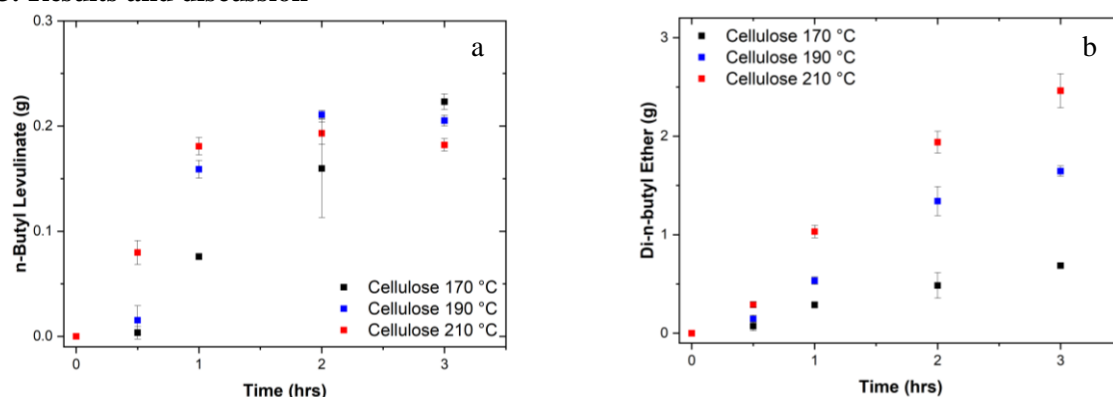
## **2. Methods**

Feedstock (glucose, cellulose, xylan, wheat straw or corn cob), butanol, and sulfuric acid are added to a 20 mL PTFE liner with a magnetic stirrer. The PTFE liner is placed into a metal autoclave which is sealed and placed into an insulated aluminium heating block preheated to the desired temperature. The mixture is centrifuged and neutralised using 50 milligram (mg) of sodium hydrogen carbonate. The product mixture is then diluted in dimethyl sulfoxide at a mass ratio of 400:1 and the product concentrations are determined via gas chromatography analysis. Two separate reactions were performed for each set of conditions and two gas chromatography samples were prepared for each reaction.

A chemical structure based kinetic model for the process is developed to provide a comprehension of the reaction rates in the system. The reaction mechanism is constructed hierarchically, one sub-model at a time in order of the chemical complexity of the feedstock, with the dehydration of ethanol to diethyl ether modelled in parallel. The kinetic model is implemented through Cantera [2]. All reactions progress according to an Arrhenius temperature dependence. The activation energy,  $E_A$ , of the reactions are defined as the value derived from an Arrhenius fit of the experimental data. All other kinetic constants are optimised to the time-resolved experimental data using the Phase 1 optimisation module of the MLOCK algorithm. [3] The sub-models are optimised to their corresponding experimental data in

hierarchical order based on the complexity of the feedstock molecule. Once derived, the rate constants for each sub-model are fixed in the overall system during subsequent optimisations.

### 3. Results and discussion



**Figure 1.** n-Butyl Levulinate (g) (a) and di-n-butyl ether (g) (b) produced from the acid catalysed (1 mass %) butanolysis of cellulose at 170 C, 190 C and 210 C.

Butyl levulinate concentrations are shown to increase with increasing feedstock loading and a constant acid concentration. This is true for synthetic feedstocks glucose, cellulose, and xylan. However, for the two real-world biomass, corn cob and wheat straw, at similar conditions, butyl levulinate concentrations do not scale with feedstock loading. This is due to the changing feedstock/acid mass ratio as the sulphuric acid catalyst concentration is kept constant. This shows that the hydrogen cations from the acid catalyst are being consumed in some irreversible process and the reaction is not wholly catalytic. Therefore, for maximum yields of ethyl levulinate from biomass, the acid concentration must be scaled with the feedstock concentration. This is further evidenced by the negligible quantities of di-n-butyl ether produced for the lower acid concentrations. The steady state yield of butyl levulinate is also shown to be independent of temperature. Maximum steady state butyl levulinate yields of 48 and 50 mass % are produced from glucose and cellulose respectively. Xylan, corn cob, and wheat straw butyl levulinate yields will be reported in the full submission. The chemical kinetic model's predicted product concentrations and deduced activation energies will also be reported in the full submission.

### 4. Conclusions

This work establishes the temperature dependence of the ethanolysis of glucose, cellulose, xylan, wheat straw, and corn cob toward the techno-economic-assessment of alcoholysis processes as a methodology to produce advanced biofuels. It is shown the conversion of synthetic feedstocks, glucose, cellulose and xylan, to butyl levulinate is a catalytic process. This is not true for real-world biomass as this process is not wholly catalytic and the acid concentration must be scaled with the feedstock concentration. Xylan, the main component of hemicellulose, is shown to produce butyl levulinate but at much lower yields compared to glucose and cellulose. This challenges the common assumption that all alkyl levulinates are produced from the cellulose content of the biomass alone. A self-consistent, hierarchical, and mass-conserved chemical kinetic model that accurately replicates experiment of the butanolysis of glucose, cellulose, xylan, wheat straw and corncob is elucidated and validated.

#### Keywords

“Butyl Levulinate”; “Advanced Biofuel”; “Alcoholysis”; “Surrogate Chemical Kinetic Model”.

#### References

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