A Surrogate Approach to Model the Effects of Compositional Variations in Lignocellulosic Biomass on the Acid Catalysed Ethanolysis Process

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Highlights
- Kinetic and steady state yields of ethyl levulinate, diethyl ether, ethanol and humins are quantified for the ethanolysis of glucose, cellulose, xylan, and lignocellulosic biomass.
- The apparent activation energies of the global reactions to ethyl levulinate and diethyl ether are empirically derived from temperature dependent data.
- A hierarchical kinetic model describes the ethanolysis reactivity of lignocellulosic biomass as a chemically discrete surrogate composed of cellulose, hemicellulose, and lignin.

1. Introduction
Advanced biofuels are required to play a key role in the transition to a sustainable global fuel economy. It has previously been shown that gasoline and diesel compatible drop-in advanced biofuel additives can be produced via the acid catalysed hydrolysis of lignocellulosic biomass in ethanol solvent. Under these conditions, the carbohydrate is converted to an ethyl levulinate, and ethanol is converted to diethyl ether. [1]

This study examines the fundamental reaction mechanism and kinetics of glucose, cellulose, xylan, and lignocellulosic biomass ethanolysis 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 chemical composition of the advanced biofuel products is reported with the aim of informing reaction kinetics in the process simulation.

2. Methods
Feedstock (glucose, cellulose, xylan, or biomass), ethanol, and sulfuric acid are added to 20 mL PTFE liners with a magnetic stirrer. The PTFE liner is placed into a metal autoclave which is sealed and placed in an insulated aluminium heating block preheated to the reaction temperature for the given reaction time. After being cooled to room temperature, the supernatant is separated by centrifuge and neutralised with $NaHCO_3$. The products are analysed using an Agilent 8860, GC-FID, equipped with an Agilent DB-624 column. Duplicate experiments are performed for every set of reaction conditions.

A chemical structure based kinetic model for the process is developed to provide a comprehension of the reaction rates in the system. Due to the unknown nature of the system, a reaction mechanism is proposed based on the analogous hydrolysis system and major species detected in experiment. The reaction mechanism (Figure 1) 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], where the rates of formation and consumption of species and the physical and chemical state of the system are used to calculate the concentration of species as a function of time. 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, where applicable. 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

For a constant concentration of acid, the yield of the ethyl levulinate increases with increasing feedstock concentrations and with increasing reaction times, until a steady state is reached. This is true for the model compounds, glucose, cellulose, and xylan. However, the yield of ethyl levulinate does not scale linearly with feedstock concentration for the biomasses. Further investigation concluded that this effect is due to the changing feedstock/acid mass ratio as the feedstock loading in increased. It is observed that for a maximum yield of ethyl levulinate from biomass, the acid concentration must be scaled with the feedstock concentration. It is hypothesised that this is due to the hydrogen cation from the acid catalyst being consumed in some irreversible process so that the reaction cannot proceed. This is consistent with observations of increased rate and yield when the mass ratio of biomass:acid is fixed. The steady state yield of ethyl levulinate is independent of temperature. Maximum steady state yields of 39.3%, 39.1%, 7.9%, and 18.6% are produced from glucose, cellulose, xylan, and corncob, respectively. The steady state yield of diethyl ether is not reached at the conditions investigated. The apparent E_A of the global reaction of glucose to ethyl levulinate is 21.5 kcal mol^{-1} and the apparent E_A of the global reaction of ethanol to diethyl ether is 23.0 kcal mol^{-1}.

The chemical kinetic model describes the relative concentrations of ethyl levulinate, diethyl ether, and ethanol as a function of the reaction parameters for each feedstock. As the essential monosaccharide chemical structure is general to all biomasses, the concept of hierarchy is appropriate. In this way, the information learned from the chemically discrete glucose is transferred to the more complex but also chemically discrete cellulose, and those self-consistent learnings are transferred to the less chemically discrete and much more complex lignocelluloses. A range of lignocellulosic biomasses are experimentally characterised to both train and validate the surrogate model concept.
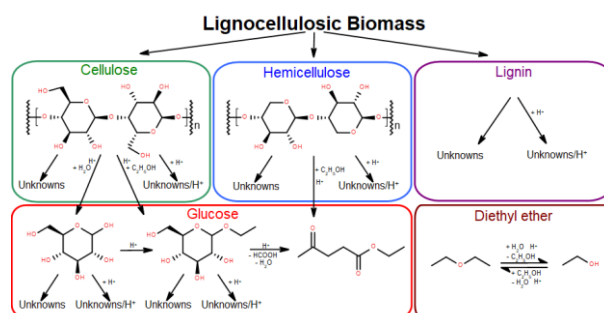

Figure 1. Reaction mechanism described by the chemical kinetic model, depicting reaction pathways and the hierarchical sub-models.

4. Conclusions

This work establishes the temperature dependence of the ethanolysis of glucose, cellulose, xylan, and lignocellulosic biomass toward the assessment of the techno-economic viability of the process as a methodology to produce advanced biofuels. The sulfuric acid catalysed ethanolysis of xylan forms ethyl levulinate in a one-pot process. This indicates that the hemicellulose portion of biomass contributes to the total yield of ethyl levulinate. The reactivity of lignocellulosic biomass is modelled as a chemically discrete surrogate as a function of the cellulose, hemicellulose, and lignin composition. The implementation of a surrogate modelling strategy based on model compounds allows for the model to be readily applied to a range of lignocellulosic biomasses and thus for this process of advanced biofuel production to be considered techno-economically.

References

[1]   M. Howard, G. Issayev, N. Naser, S. Sarathy, A. Farooq, S. Dooley, Sust. Energy & Fuels 3 (2019) 409-421
[2]   D.G. Goodwin, H.K. Moffat, I. Schoegl, R.L. Speth, and B.W. Weber, Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes (2023)
[3]   M. Kelly, M. Fortune, G. Bourque, S. Dooley, Combustion and Flame 253 (2023) 112755.