The solvent effect in direct conversion of cellulose to levulinic acid

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Highlights

- Use of sulfolane as solvent significantly increases reaction rate of cellulose conversion.
- Solvent composition does not affect selectivity of levulinic acid production.
- Solvent effect can be described by activity coefficients lumped with reaction rate parameters.
- Sulfolane prevents fouling of equipment by keeping by-products soluble.

1. Introduction

The increasing demand of chemicals and energy together with diminishing petroleum sources and global warming has led to major efforts in the development of renewable replacements for fossil raw materials. Thus, production of platform molecules from lignocellulosic biomass has a key role in developing alternatives for fossil-based chemicals. Levulinic acid is one of the promising platform molecules that can be produced from biomass [1]. The most suitable route in levulinic acid manufacturing starts from polymeric carbohydrates containing hexose sugars, mainly cellulose fraction of biomass. A well-known approach in levulinic acid production is acid catalysed treatment at elevated temperatures. At these conditions cellulose is first hydrolysed into glucose, which is then converted to 5-hydroxymethylfurfural (HMF), and further to levulinic acid and formic acid. [2] Most commonly water is used as solvent in these systems.

In this study the effect of the organic solvent to the production efficiency of the levulinic acid from cellulose was investigated and kinetic model was developed to describe the levulinic acid production. This work is a continuation to our previous study where the solvent effect of glucose conversion was investigated. [3].

2. Methods

The solvent used in this study was sulfolane which is a commonly known industrial solvent. The effect of sulfolane concentration in the reaction mixture was studied oved wide concentration range from 0 to 90 wt%. The raw material used was cellulose obtained from commercial Kraft-process. Sulphuric acid at concentration of 1 wt% was used as acid catalyst. Temperature was varied between 140 and 180 °C and time between 30 and 240 minutes. Experiments were conducted in zirconium batch reactors with the solution amount of 30 mL. The amount of the formed products was measured with HPLC. The conversion of cellulose was determined by measuring the cellulose amount in the residual solid material with total hydrolysis method [4].

The formed kinetic model is based on reaction scheme in which the cellulose firstly hydrolyses to glucose. After that glucose dehydrates to 5-HMF, and finally 5-HMF rehydrates to levulinic acid. Each step also includes a parallel side reaction in which undesired by-products, humins, are formed. Reaction kinetic modelling was carried out in Matlab environment. The systems of ODEs, representing the mass balances of the reacting components in batch reactor, were solved numerically (ode15s) and reaction rate parameters were estimated by non-linear regression analysis using the trust region reflective algorithm available within lsqcurvefit.

3. Results and discussion

Sulfolane solvent was found to have a significant effect to the conversion rate of cellulose as well as to production of levulinic acid. As an example, in Fig. 1. cellulose conversions (A) and levulinic acid yields (B) obtained at 160 °C are shown. It can be seen that with 90 wt% sulfolane total cellulose conversion is obtained already after 30 minutes whereas without sulfolane conversion after 4 hours is only 65 %.

The rate of levulinic acid production was increased in the same way as the conversion of cellulose. The rate increasing effect of the sulfolane is moderate with amounts up to 50 wt% but drastic with high amounts such as 70 or 90 wt%.

Whereas the effect of the sulfolane to the reaction rate is significant, the selectivity towards levulinic acid seems to remain quite similar independent of the used sulfolane amount. Similar levulinic acid yields can be achieved if the temperature is high and/or the time is long enough. The sulfolane solvent was also found to keep the formed by-products soluble. The formed humin by-products precipitates when using water as solvent causing fouling of the equipment.

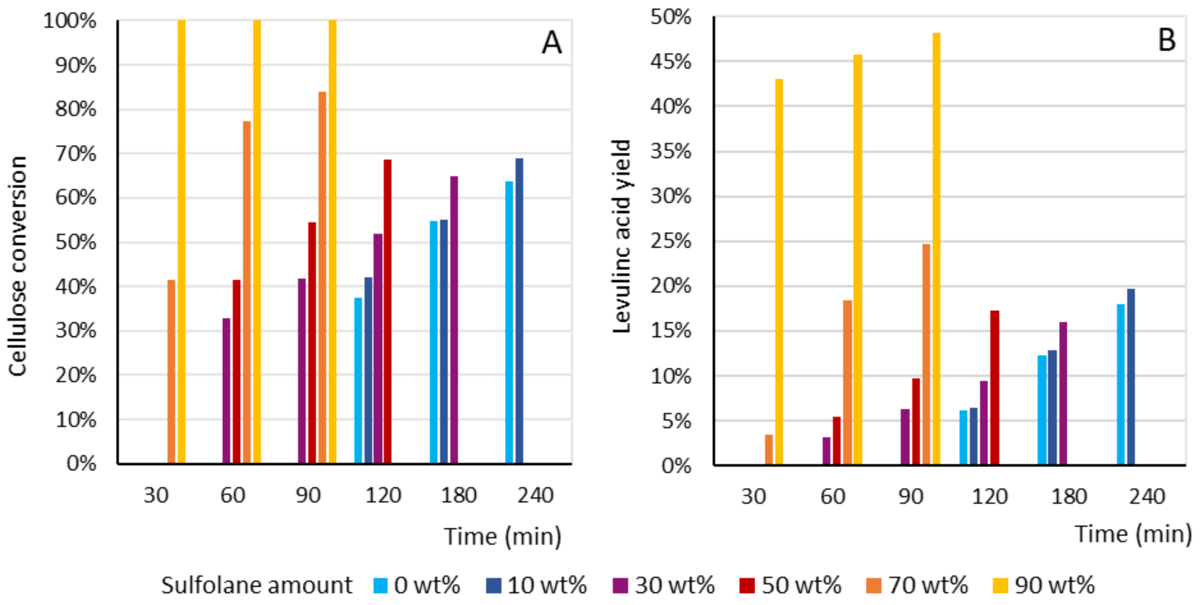

Figure 1. Cellulose conversion (A) and levulinic acid yield (B) at 160 °C.

The reaction kinetic modelling reveals that the straightforward kinetic model has an ability to explain the features of the chemical system; major part of the by-products is formed in glucose dehydration step; and sulfolane clearly increases the values of reaction rate coefficients (activities) of cellulose and glucose whereas effect to 5-HMF reactivity is lighter.

4. Conclusions

Using organic solvent in biomass conversion reactions instead of water offers multiple advantages. The increase of reaction rate is a big benefit since it enables the production at lower temperature in reasonable time without using massive amounts of acid catalyst, which recycling is often difficult. The ability of organic solvent to dissolve the formed by-products prevents the fouling of process equipment, which is a common cause of problems in practical operation of biorefining processes.

References

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Keywords
Levulinic acid; Cellulose; Solvent effect; Kinetic modelling