BRIEFING NOTE

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KINETIC STUDY OF FURFURAL PRODUCTION AND DEGRADATION

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KEY FINDINGS

Kinetic study of xylan and xylose conversion to furfural was conducted and separate kinetic models were developed to interpret the experimental results. The kinetic study demonstrated that only temperature and acid concentration contribute to conversion processes significantly. The comparison of the kinetic behavior of xylan and xylose to furfural resulted in fundamental knowledge, which can be useful for the industry dealing with furfural production. Furthermore, furfural degradation was investigated in the absence of sugar (xylose) to generate an industrially relevant understanding of the contribution of resinification and fragmentation to furfural degradation. Degradation reactions result in Humin formation which can be combusted to produce 1.3% of the energy required for steam generation in the furfural production process.

INTRODUCTION

Since fossil oil resources are exhaustible, in the near future an all-embracing alternative is required for the supply of fuels and chemicals. A biorefinery is such an alternative, with its ability to provide both (liquid) energy carriers and platform chemicals. While the cellulose part of a biomass is easily fermented to bioethanol, the hemicellulose part can be used for the production of value-added chemicals, as can be the lignin part. Furfural is such a chemical rated among the top ten valuable platform chemicals with extensive industrial applications as a bio alternative to petrochemicals.

Over the course of the second half of the previous century, the kinetics of the formation of furfural both from pure pentoses and from biomass resources has been studied extensively. Traditional production processes employ the direct furfural production method, which utilizes whole, untreated, xylan-rich biomass materials such as corn cob and sugarcane bagasse as feed to the furfural production reactor. The alternative to the direct method is the indirect furfural method that employs a pretreated or fractionated lignocellulose feed, where only the resulting hemicellulose-rich hydrolysates, typically consisting of polymeric xylan and/or monomeric xylose, are fed to the furfural reactor.

METHODOLOGY

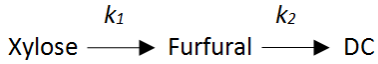
The main goal of this study was to investigate and compare the kinetics of furfural production from monomeric xylose and polymeric xylan at selected operating conditions. To achieve this goal, separate experiments were conducted for each of xylan and xylose to examine their conversion process to furfural. The experimental data was used to develop a model that sufficiently explained the interactions of the process variables and their effect on the production process, within the confines of the selected experimental conditions. In addition, furfural degradation was investigated at similar condition and the data were fitted to kinetic model and mechanisms reported by literature to determine the best kinetic representing the collected data.

MAIN RESULTS

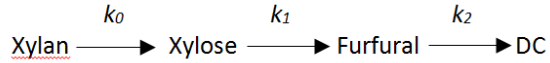
The statistical analysis of the experimental results demonstrated that only temperature and acid concentration affect the conversion processes significantly for both xylose and xylan conversion. However, furfural degradation was found to be a function of temperature and initial furfural concentration, whereas sulfuric acid concentration had no significant effect on the degradation.

The modelling results demonstrated that direct conversion of xylose and xylan to furfural without the

formation of any side products was the best mechanism fitting the experimental data.



Where k_1 and k_2 are first order reaction rates constants for xylose and furfural decomposition, respectively and DC the lump sum of degradation products formed in reaction.



Where k_0 and k_1 are first order reaction rates constants for xylose formation and xylose conversation, respectively.

On the other hand, furfural degradation under the investigated reaction conditions showed an average reaction order with respect to furfural.

During conversion of xylan, the xylose formation pattern at different temperatures demonstrated that xylose accumulation occurs within the first five minutes of the reaction, showing that the hydrolysis reaction is very fast relative to the simultaneous xylose dehydration to furfural reaction (Figure 1).

Higher rate of resinification degradation was recorded for xylose conversion compared to xylan conversions that resulted in higher furfural yields for xylan compared to xylose conversions.

From the selected models, xylose degradation and condensation degradation reactions were found to be negligible in the range of condition investigated in this study. The furfural degradation experiments (in absence of xylose) also investigated resinification reactions and humin formations. The mechanism responsible for humin formation was fond to be Sanchez mechanism which involves bifurylic and trifurylic structures.

In a conventional furfural production plant, humins are generated amongst the (pentosan containing) biomass fibres and combusting these humins alone (instead of coal) produces 1.3% of the energy required to generate steam for the furfural production process. When humins are generated in biorefinery pre-treatment stages or from processing pulp mill pre-hydrolysis liquor. A valorisation method should be explored so that humins do not remain in the system, blocking up pipes and adhering to reactor walls. Humins can be combined with PFA to give a lower cost resin composite with decreased brittleness and higher tensile strength compared to pure PFA resins.

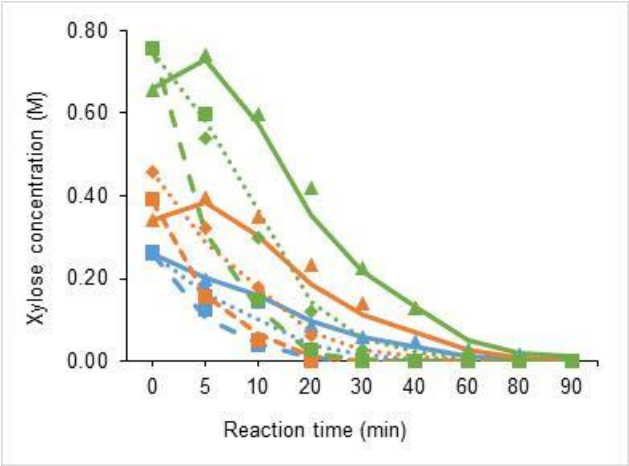


Figure 1. Experimental and predicted values for xylan conversion (xylose-equivalent) with varying solids loading (■ 4 wt% ■ 8 wt%, ■ 14 wt%), acid concentration (Δ 0.5wt%, ◊ 1wt% and □ 2wt%) at 170°C

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