Kinetic modelling and process simulation of hydroxy carboxylic acids production by alkaline degradation of cellulosic waste

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Highlights

- New information on cellulose alkaline degradation at elevated temperatures.
- The reactions involved in hydroxy acids formation were identified.
- Monosaccharides degrade as soon as they are produced.
- Degradation of GISA is not significant under the conditions studied in this work.

1. Introduction

The kinetics of alkaline degradation of cellulosic materials at elevated temperatures was studied and a rigorous mathematical model was developed to simulate and optimize the process. This is of great importance since cellulosic materials comprise a substantial portion of biobased wastes produced globally that is improperly discarded, leading to a waste management problem [1]. Eventually, also cellulosic wastes reach a stage where they cannot be reused or recycled by preserving the structure. This research focuses on the chemical conversion of such low-grade cellulosic wastes into valuable products. A major class of such products could be hydroxycarboxylic acids (hydroxy acids in short) such as isosaccharinic acids that are not readily available from any other route (e.g., anaerobic digestion). Earlier research has focused on studying the kinetics of alkaline degradation of cellulosic materials, at temperatures below 170 °C and in the realm of pulping processes and radioactive waste repositories emphasizing preservation of cellulose. While the investigation of kinetic modeling at higher temperatures, aiming to destruction and valorization of these materials, remains a research gap. The present study aims to develop a detailed kinetic model for disaccharides and polysaccharides cleavages and conversion into hydroxy acids. This novel kinetic model gives a better understanding of involved reactions, rate constants, production costs (using pulp mill primary sludge as the feed stream), and optimum operating conditions. The main hypothesis is that both macroscopic transformations (crystalline cellulose into amorphous form) and microscopic transformations (cleavage of glycosidic bonds) must be considered in the kinetic model. The crystalline structure of cellulosic materials, the large number of monomer units constructing the polysaccharide molecules, unknown reactions resulting in hydroxy acids formation, and the dynamic behavior of the reactor make it more challenging to mathematically model the whole process.

2. Methods

This work is a numerical study that was carried out using the experimental data taken from Laine [2]. The model species were crystalline cellulose, individual dissolved polysaccharide molecules of different chain length, disaccharides (D), monosaccharides (M), glucoisosaccharinic acid (GISA), and smaller hydroxy acids (SHA). Only two types of hydroxy acids were considered; GISA is the desired product, and all hydroxy acids with lower molecular weight than GISA were lumped into a pseudo-component SHA. In the reaction pathways conversion of crystalline cellulose to amorphous cellulose, peeling off, hydrolysis or random scission producing GISA, and conversion of monosaccharides and GISA into SHA were considered. The ODE system, resulting from the mass balances derived for hundreds of components in a batch reactor and with the assumption of first order reactions, was solved using MATLAB software. Nonlinear regression was done to minimize the error between the experimental data and the model results. Aspen Plus software is used to carry out the computer-aided simulations.

3. Results and discussion

As seen in Figure 1, the kinetic model which considers both macroscopic and microscopic transformations describe the cellobiose and cellulose degradation very well.

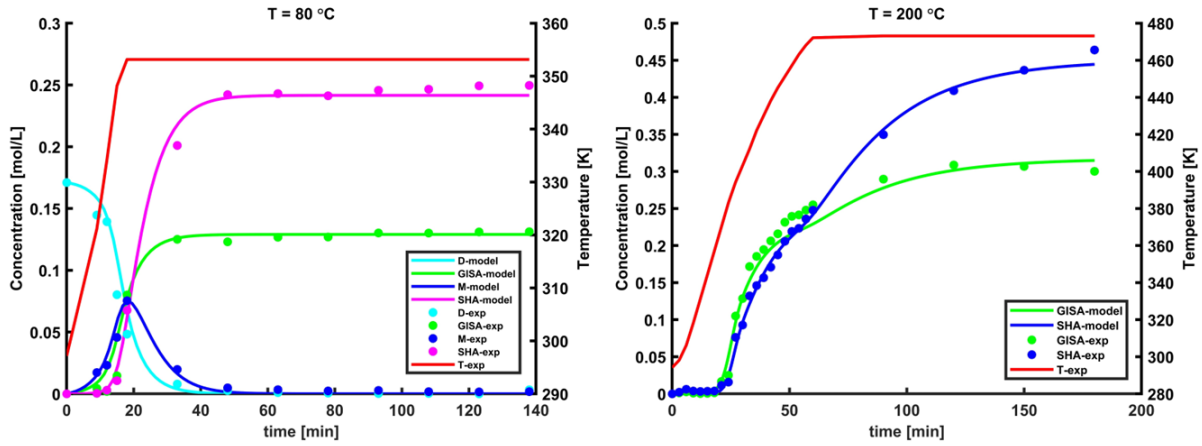

Figure 1. Degradation results in a batch reactor. Cellobiose with 5 wt-% NaOH and 80 °C (left) and Cellulose with 10 wt-% NaOH and 200 °C (right), experimental data from [2]

Based on the results, a large part of degradation occurs during the reactor warming up (about 20 and 50 minutes for cellobiose and cellulose, respectively). The high value of the rate constant of degradation of monosaccharides to SHA (2.02×10^{-1}) obtained through cellobiose degradation kinetic model showed that monosaccharides are converted into SHA as soon as they are produced. Also, the small value of the rate constant of GISA degradation equal to 1.38×10^{-7} (estimated by cellobiose degradation kinetic model at reference temperature of 80 °C) confirmed that GISA degradation does not occur even at 200 °C. The extrapolation of its rate constant in cellobiose kinetic model to 200 °C giving a value in the order of 10^{-5} confirms this claim. In case of cellulose, the data could not be reproduced without considering the transformation of crystalline cellulose into the more reactive amorphous and dissolved forms (macroscopic level). Moreover, it is found that decrystallization of cellulose having the lowest rate constant is the rate determining step. The agreement between the model results and the experimental data confirmed that the processes obey the proposed reaction pathways.

4. Conclusions

It is found that almost 80% of degradation occurs during the reactor warming up period, which varies based on the final temperature. Decrystallization of cellulose was concluded to limit the rate of hydroxy acids production at temperatures below 85 °C. The very small rate constant of GISA degradation obtained suggests that degradation of GISA is not significant at least at temperature range and conditions studied in this work. Monosaccharides are converted into SHA instantly as they are produced. The presented kinetic model gives new information about the phenomena of cellulose alkaline degradation at high temperatures and involved reactions in hydroxy acids production. This enables other researchers to investigate similar techniques for other applications. The new knowledge obtained in this study could be used to estimate the energy consumption and costs of production of hydroxy acids from low-grade waste celluloses such as pulp mill primary sludges. This also helps to find the optimum operating conditions of the process to make it feasible at large scale.

References

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Keywords
Cellulose degradation, Hydroxy carboxylic acids, Reaction kinetics, Chemical conversion, Waste cellulose