

EXPERIMENTAL STUDY AND MECHANISTIC MODELING OF CATALYTIC EFFECTS OF SODIUM IONS ON FAST PYROLYSIS OF GLUCOSE-BASED CARBOHYDRATES

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Abstract

Sodium ions, one of the inorganic constituents that naturally exist in lignocellulosic biomass, significantly alter pyrolysis behavior and resulting chemical speciation. In this work, a mechanistic model that addressed the catalytic effects of NaCl on the quantitative pyrolysis product distribution was developed based on our previous model of fast pyrolysis of neat glucose-based carbohydrates. The model incorporated the interactions of Na⁺ with cellulosic chains and low molecular weight species formed in fast pyrolysis, reactions mediated by Na⁺ including dehydration, cyclic/Grob fragmentation, ring-opening/ring-closing, isomerization, and char formation, and a degradation network of levoglucosan in the presence of Na⁺. Kinetic parameters of each elementary step were specified in terms of the Arrhenius parameters. A computational framework based on continuous distribution kinetics and mass action kinetics was constructed to solve the mechanistic model. Agreement between model yields of various pyrolysis products with experimental data from fast pyrolysis of glucose-based carbohydrates dosed with NaCl ranging from 0–0.34 mmol/g at 500 °C validates the model and demonstrates the robustness and extendibility of the mechanistic model. The model was able to capture the yields of major and minor products as well as their trends across NaCl concentrations. Modeling results showed that Na⁺ accelerated the rate of decomposition and reduced the time for complete thermoconversion of carbohydrates. The sharp reduction in the yield of levoglucosan from fast pyrolysis of cellulose in the presence of NaCl was mainly caused by reduced decomposition of cellulose chains via endchain initiation and depropagation due to Na⁺ favoring competing dehydration reactions.

Keywords

Fast pyrolysis, Reaction mechanism, Kinetics, Mechanistic modeling, Sodium chloride.

Introduction

Fast pyrolysis of lignocellulosic biomass offers great potential for large-scale production of renewable liquid products that can be catalytically upgraded to transportation fuels and chemicals. Extensive studies have been conducted to understand the complexity of fast pyrolysis. One area of active research on fast pyrolysis is

the catalytic effect of naturally-occurring inorganic materials, and the past efforts in this field have been focused on experimental assessment of the impact of inorganic salts such as NaCl on the yields of global products (bio-oil, gases, and char) from fast pyrolysis of cellulose. Computational and modeling efforts have been

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primarily devoted to studying the catalytic effects of Na^+ on reactions of model compounds related to fast pyrolysis of cellulose or developing global kinetic models with a correlation factor to reflect the impact of inorganic salts on the yields of lumped products based on phases. However, a fundamental understanding of the chemistry and kinetics by which NaCl impacts fast pyrolysis and the quantification of the resulting product distribution at the mechanistic level are still not available. In this work, the first unified mechanistic model that incorporates the effects of Na^+ on fast pyrolysis of glucose-based carbohydrates was developed.

Methods and results

Previously, we developed a mechanistic model for fast pyrolysis of neat glucose-based carbohydrates based on continuous distribution kinetics.^{1,2} The model incorporates the following condensed phase reactions for the formation of various LMW products in bio-oil: glycosidic bond cleavage, retro-aldol, retro-Diels-Alder, dehydration, hydrolysis, cyclic/Grob fragmentation, isomerization, enol-keto transformation, ring-opening/ring-closing, and char formation reactions.^{1,2} We are now extending the model to incorporate the catalytic effects of Na^+ . As shown in Figure 1 for glucose as a representative example, reactions in which a sodium ion binds to a LMW species to form a complex were included. The complex can then undergo reactions analogous to those in the absence of a sodium ion, albeit governed by different kinetic parameters. Finally, the sodium ion can unbind from the LMW product. The model that includes the interactions of Na^+ with all relevant species and reactions mediated by Na^+ including dehydration, cyclic/Grob fragmentation, ring-opening/ring-closing, isomerization, and char formation, and a degradation network of levoglucosan in the presence of Na^+ , has been constructed.

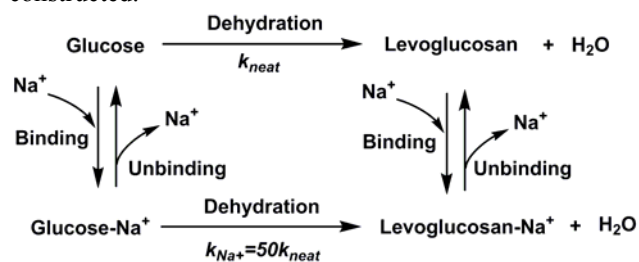


Figure 1. Modeling efforts to capture the effect of Na^+ on the product distribution involved adding interactions of Na^+ with species (e.g., glucose) and adding parallel reaction pathways (e.g., dehydration) mediated by sodium ion with different kinetic parameters.

Validation of the first mechanistic model was performed by comparing model yields with experimental data of fast pyrolysis of glucose-based carbohydrates dosed with NaCl ranging from 0–0.34 mmol/g at 500 °C using system of micro-pyrolyzer–GC–MS/FID. A single set of kinetic parameters was used for all chain lengths

ranging from glucose to long-chain cellulose. Figure 2 presents a respective comparison between experimental and model yields of levoglucosan (LVG) from pyrolysis of cellulose in the presence of NaCl . The model was able to capture the yields and trends of the major products such as LVG, LVG-furanose, 5-hydroxymethylfurfural, glycolaldehyde, char, H_2O , CO_2 , CO , and methyl glyoxal, and minor products like cyclic hydroxyl lactone, formaldehyde, acetaldehyde, levoglucosenone, furfural, furanmethanol, acetone, dihydroxyacetone, and propenal.

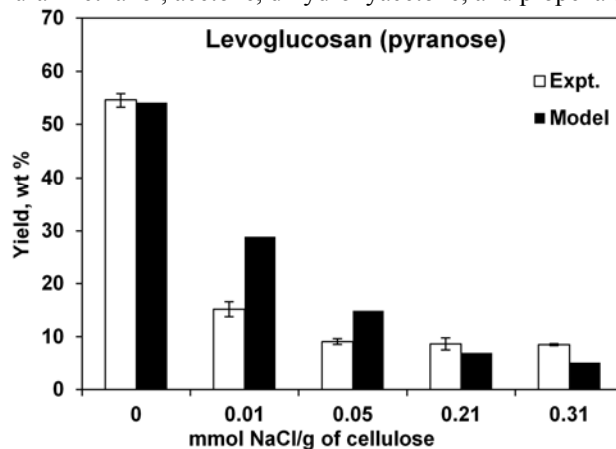


Figure 2. Comparisons of model and experimental yields of levoglucosan from fast pyrolysis of cellulose impregnated with different amounts of NaCl at 500 °C

Conclusions

The first mechanistic model that we developed for fast pyrolysis of glucose-based carbohydrates that incorporates the significant catalytic effects of NaCl was able to capture the yields and trends of various pyrolysis products. Dehydration reactions, especially midchain dehydration, that are favored by the presence of NaCl play a vital role in the reduction of LVG yield from cellulose pyrolysis.

Acknowledgments

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