Fast pyrolysis of glucose-based carbohydrates with added NaCl part 2: Validation and evaluation of the mechanistic model

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Abstract
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Keywords
fast pyrolysis, reaction mechanism, kinetics, mechanistic modeling, sodium chloride

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Fast Pyrolysis of Glucose-Based Carbohydrates with Added NaCl Part 2: Validation and Evaluation of the Mechanistic Model‡

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ABSTRACT

A mechanistic model considering the significant catalytic effects of Na\textsuperscript{+} on fast pyrolysis of glucose-based carbohydrates was developed in Part 1 of this study. 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 validated the model and demonstrated 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\textsuperscript{+} 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\textsuperscript{+} favoring competing dehydration reactions. Analysis of the contributions of reaction pathways showed that the decomposition of levoglucosan made a minor contribution to its yield reduction and contributed less than 0.5 % to the final yield of glycolaldehyde from fast pyrolysis of glucose-based carbohydrates in the presence of NaCl.

**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.\textsuperscript{1,2} Extensive studies have been conducted to understand the complexity of fast pyrolysis.\textsuperscript{3-5} 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.\textsuperscript{6-19} On the other hand, computational and modeling efforts have been primarily devoted to studying the catalytic effects of Na\textsuperscript{+} on reactions of model compounds related to fast pyrolysis of cellulose\textsuperscript{20,21} 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\textsuperscript{22}. 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. Towards this end, in Part 1 of this study, we developed the first unified mechanistic model that incorporated the effects of Na\textsuperscript{+} on fast pyrolysis of glucose-based carbohydrates by integrating the interactions of Na\textsuperscript{+} with cellulosic polymer chains and low molecular weight (LMW) species, and reactions mediated by Na\textsuperscript{+} into our previous mechanistic model for fast pyrolysis of neat glucose-based carbohydrates\textsuperscript{23,24}.

The primary purpose of this paper is to validate and evaluate the mechanistic model. A computational framework based on continuous distribution kinetics for decomposition of cellulosic chains and mass action kinetics for reactions of LMW species was constructed to solve
the mechanistic model. Model results are compared against experimental results, which have been reported in Part 1 of this study for fast pyrolysis of cellulose, maltohexaose, cellobiose and glucose dosed with varying amounts of NaCl at 500 °C, to evaluate the quantitative and predictive performance of the model. Qualitative and quantitative analyses of the catalytic effects of NaCl on the overall thermal decomposition, competing reaction pathways, and pyrolysis product distribution were performed. Insights and information that the model provides lead to a better understanding of fast pyrolysis at the mechanistic level and the critical role that inorganic components play.

**Modeling Framework and Solution Approach**

In the first part of this study, we have specified the identities of the species in terms of neutral species and Na\(^+\)-complexes, polymeric chains (sorted according to different end-groups and mid-groups) and LMW compounds, and elementary reaction steps and their associated rate coefficients in terms of the Arrhenius parameters: activation energy (\(E_a\)) and frequency factor (\(A\)). The next step in the modeling approach is to generate rate equations and accompanying approximations to solve the model as well as validate and evaluate the model. The model includes three different types of reactions of the cellulosic chains, which are (i) unimolecular random cleavage of the chains, (ii) unimolecular unzipping of LMWPs from the chains and unbinding of Na\(^+\) from the Na\(^+\)-complex chains, and (iii) bimolecular thermohydrolysis and binding of Na\(^+\) to neutral chains. The rates of decomposition of cellulosic chains were modeled on the basis of continuous distribution kinetics, and the rate equations associated with these reaction types have been described in our previous work\(^{25}\). All the LMW species were assumed to react according to mass action kinetics with rate laws based on elementary steps and rate coefficients calculated using the Arrhenius equation, \(v_i\), \(k = A \cdot \exp(-E_a/RT)\). A semi-batch
reactor model that tracks the reduction in the volume of the melt phase caused by the
vaporization of LMWPs was established, in which all the \( \text{Na}^+ \)-complexes, various cellullosic
chains, C5 and C6 sugars, dehydrated sugars, and char were accounted for in the melt phase,
while all other neutral LMWPs were allowed to partition to the vapor phase. Programs were
developed using programming languages Perl and C++ to automatically generate the rate
equations and the associated algebraic equations, which were solved using DDASAC.\textsuperscript{26}

**Results and Discussion**

In this section, the mechanistic model that incorporates catalytic effects of \( \text{Na}^+ \) on fast
pyrolysis of glucose-based carbohydrates is validated and evaluated against experimental data
from fast pyrolysis of glucose-based carbohydrates dosed with varying amounts of NaCl at 500
\( ^\circ\text{C} \) that were reported in Part 1 of this study. Catalytic effects of NaCl on pyrolysis reactions and
the product distributions are discussed. Note that the mechanistic model of fast pyrolysis of neat
glucose-based carbohydrates, which the current model was built upon, was previously validated
against temperatures ranging from 400-600 \( ^\circ\text{C} \). Also note that the mechanistic model is validated
against the detailed yields of various pyrolysis products instead of the overall conversion of
carbohydrates. The final yields of pyrolysis products correspond to c.a. over 99 wt % conversion
of the initial carbohydrate samples.

Note that any fitting of kinetic parameters that was done was performed on the reactions
mediated by \( \text{Na}^+ \) and was carried out against the fast pyrolysis of glucose dosed with 0.03
mmol/g and 0.16 mmol/g and cellulose dosed with 0.01 mmol/g and 0.21 mmol/g. Therefore,
modeling results for fast pyrolysis of glucose dosed with 0.08 mmol/g and 0.34 mmol/g,
cellulose dosed with 0.05 mmol/g and 0.31 mmol/g, and for the different starting materials of
cellulbiose and maltohexaose in the presence of NaCl are pure predictions and were compared with experimental data to evaluate the predictive capability of the model.

**Fast pyrolysis of glucose in the presence of NaCl**

Figure 1 presents comparisons between the experimental and model yields for the major products from fast pyrolysis of glucose dosed with NaCl ranging from 0 to 0.34 mmol/g at 500 °C: (a) levoglucosan (LVG), (b) glycolaldehyde (GA), (c) levoglucosan-furanose, (d) 5-hydroxymethylfurfural (5-HMF), (e) char, and (f) CO₂. During fast pyrolysis of glucose, LVG was formed from dehydration of β-D-glucopyranose.²⁷ Although this dehydration reaction is accelerated by the presence of Na⁺, its competitive reaction, ring-opening of β-D-glucopyranose to D-glucose, is more facile with a rate coefficient that is much greater in the presence of Na⁺.²⁸ Moreover, Na⁺ assisted the decomposition of LVG. Therefore, a decreasing yield of LVG with increasing NaCl was observed in experiments, which was captured by the model as shown in Figure 1(a). Although GA formed from the decomposition of LVG increased in yield from 0 to 0.14 wt % as NaCl addition increased, it accounted for a very small portion (less than 0.25 %) of GA yield from glucose pyrolysis (Figure S1 in the Supporting Information). This result also indicated that the decomposition of LVG contributed little to the reduction in LVG yield from glucose pyrolysis in the presence of NaCl. The formation of LVG involved isomerization of β-D-glucopyranose to β-D-glucofuranose via ring-opening/ring-closing followed by dehydration.²³,²⁴ Decomposition of D-glucose via isomerization (reaction 19), Grob fragmentation (reactions 33 and 39), and dehydration (reactions 55 and 63) can also be greatly promoted by a higher level of NaCl.²⁸ Thus, the decomposition of D-glucose via ring-closing to β-D-glucofuranose (reaction 12) and via retro-aldo to give GA (reaction 44) would be retarded. The decomposition of levoglucosan-furanose via cyclic Grob fragmentation (reaction 15) and dehydration routes of
anhydro-glucose (reactions 58 and 64) also played a role in reducing the yields of GA and levoglucosan-furanose as the addition of NaCl increased, which were also captured by the model as shown in Figures 1(b) and 1(c), respectively.

NaCl promoted ring-opening, isomerization, and dehydration to different extents, all of which are involved in the formation of 5-HMF from glucose. On the other hand, NaCl also promoted the formation of char from intermediates anhydro-fructose and dianhydro-fructose, reducing the selectivity of 5-HMF. Furthermore, some 5-HMF decomposed into furfural and furanmethanol. Therefore, a non-monotonic trend of the yield of 5-HMF (Figure 1(d)) was captured by the model. As shown in Figures 1(e) and 1(f), the model gave strikingly good agreement with experimental data in terms of the final yields and the overall trends for char and CO₂ at all NaCl concentrations.

Figure 2 presents the comparisons between model output and experimental yields of (a) H₂O, (b) methylglyoxal, (c) levoglucosenone, (d) cyclic hydroxyl lactone, (e) furanmethanol, and (f) dihydroxyacetone. The model gives very good agreement for H₂O (Figure 2(a)), the pyrolysis product with the highest yield from glucose pyrolysis, in terms of the final yields and the overall trend across NaCl concentrations. As shown in Figure 2(b), the yields of methyl glyoxal varying with the amounts of NaCl added to glucose are predicted well in general. Although the yields of levoglucosenone are underestimated, the model yields follow a similar trend as experimentally observed (Figure 2(c)). The formation of levoglucosenone via multiple dehydration steps favored by Na⁺ leads to the increase in its yield, while char formation from anhydro-glucopyranose and dianhydro-glucopyranose is responsible for the declined yield at a high NaCl concentration of 0.34 mmol/g. The performance of the mechanistic model is further underscored by its ability to capture minor products with yields of less than 1 wt % or even lower. As shown in Figure 2(d),
the model captures well the decrease in the yield of cyclic hydroxyl lactone; this product is formed from 1,2-dehydration of β-D-glucopyranose to 1,2-anhydroglucopyranose, which becomes highly unfavored under the influence of NaCl. Noticeably, the model yields and their trends match well with experimental ones for minor products like furanmethanol (Figure 2(e)) and dihydroxyacetone (Figure 2(f)) that have yields of less than 0.2 wt %.

The good agreement between model yields and experimental data over such a wide range of NaCl concentrations indicates that the rate parameters being utilized for the reactions mediated by Na⁺ are reasonable representations of the transformations occurring for fast pyrolysis in the presence of NaCl.

**Fast pyrolysis of cellobiose in the presence of NaCl**

Cellobiose consists of two glucose molecules linked by a β-(1-4) glycosidic bond. Figure 3 depicts the comparisons between model output and experimental yields of major products (a) LVG, (b) GA, (c) levoglucosan-furanose, (d) 5-HMF, (e) char, and (f) CO₂ from fast pyrolysis of cellobiose in the presence of NaCl ranging from 0 to 0.21 mmol/g. As shown in Figures 3(a) and 3(b), the model matches the experimental yields of LVG and GA well in terms of the final yields and their overall decreasing trends across NaCl concentrations. The formation routes of LVG, glucose, and GA from cellobiose decomposition during fast pyrolysis compete with each other. The presence of NaCl in cellobiose pyrolysis promotes dehydration of cellobiose and LMW species, producing water vapor at a faster rate, and thus leading to faster thermohydrolysis that affords glucose (see our previous work 23-25 for more details on glucose being an important intermediate, the participation of water and the role of thermohydrolysis during fast pyrolysis of glucose-based carbohydrates). As a result, the yields of LVG and GA directly formed from cellobiose decrease from 21.1 to 3.41 wt % and from 2.21 to 1.60 wt %, respectively, as the
addition of NaCl increases from 0 to 0.21 mmol/g. Moreover, the contributions of pathways directly forming LVG and GA from cellobiose to their final yields decrease from 76.6 to 48.9 % and from 31.0 to 24.6 %, respectively (Figure 4). On the other hand, although the yield of LVG from glucose as an intermediate in cellobiose pyrolysis decreases from 6.46 to 3.57 wt %, the contribution of this route to the final yield of LVG increases from 23.4 to 51.1 % (Figure 4(a)). Note that the yield of GA formed via glucose remains around 4.9 wt %, and its contribution to the final yield of GA from cellobiose pyrolysis increases from 69 to 75.1 % (Figure 4(b)). This trend is strikingly different from the decreasing trends observed in glucose pyrolysis with increasing loadings of NaCl, where the decomposition of LVG contributes less than 0.43 % to the final yield of GA.

Although the yields of levogluconsan-furanose (Figure 3(c)) are overestimated, the model captures the trend as a function of NaCl concentration. The mechanistic model of cellobiose pyrolysis gives very good agreement with not only experimental yields of other major products such as 5-HMF (Figure 3(d)), char (Figure 3(e)), CO₂ (Figure 3(f)), and H₂O (Figure 5(a)), minor products like methyl glyoxal (Figure 5(b)) and CO (Figure 5(c)), and even dihydroxyacetone (Figure 5(d)) that has a yield less than 0.1 wt %, but also recapitulates their rising trends as NaCl concentration is increased from 0 to 0.21 mmol NaCl/g of cellobiose.

**Fast pyrolysis of maltohexaose in the presence of NaCl**

Comparisons between model output and experimental yields of major products (a) LVG, (b) GA, (c) H₂O, (d) 5-HMF, (e) char, and (f) CO₂ obtained from fast pyrolysis of maltohexaose impregnated with different amounts of NaCl at 500 °C are shown in Figure 6. Maltohexaose consists of six glucose molecules linked by α-(1-4) glycosidic bonds. In addition to glycosidic bond cleavage, dehydration, 1,2-dehydration, retro Diels-Alder and thermohydrolysis as were
included for cellobiose decomposition during fast pyrolysis, midchain dehydration that can be promoted by the presence of NaCl also occurs for maltohexaose during fast pyrolysis. As a result, the model accurately predicts a decreasing trend in LVG yield with increasing addition of NaCl (Figure 6(a)). It has been reported in our previous work there are three main pathways to form LVG from maltohexaose/cellulose: (1) end-chain initiation of cellulose with a NR-end, (2) depropagation of LVG-end chains, and (3) dehydration of glucose.\textsuperscript{23,24} Figure 7(a) shows the contributions of the three pathways to the final yield of LVG from maltohexaose pyrolysis as a function of NaCl loading. The contribution of glucose dehydration to the yield of LVG increased from 18.8 to 25.8\% as the dosage of NaCl was increased, which is attributed to the fact that more glucose is formed via thermohydrolysis with the addition of NaCl. The chains with dehydrated midgroups can further undergo midchain glycosidic bond cleavage to form LVG-end chains, and thus the yield of LVG formed from LVG-end chains via depropagation slightly decreases with the addition of NaCl. The yield of LVG from endchain initiation and its contribution to LVG yield drops from 24.4 to 10.6 wt\% and from 74.7 to 67.8\%, respectively, due to direct competition of endchain initiation with dehydration and thermohydrolysis, which are favored in the presence of NaCl.

As shown in Figure 7 (b), GA formed via intermediate glucose contributes the most to its final yield and increases from 61.9 to 78.1\% with an increase of NaCl added to maltohexaose from 0 to 0.21 mmol/g, while the final yield of GA directly formed from maltohexaose decreases from 2.87 to 1.52 wt\%, and its contribution to GA yield decreases from 38.2 to 21.8\%. GA formed from the decomposition of LVG accounts for less than 0.1\% of the GA yield. However, different behavior compared to that from fast pyrolysis of glucose or cellobiose in the presence of NaCl was observed for maltohexaose in that GA reaches a maximum in yield at a NaCl
concentration of 0.06 mmol NaCl/g. The increase in yield of GA at a lower NaCl concentration is caused by the addition of NaCl promoting midchain dehydration of the midgroups of maltohexaose, leading to greater formation of anhydroglucopyranose that produces GA. The subsequent decrease in GA yield at higher NaCl concentrations is attributed to the fact that char formation via anhydroglucopyranose is promoted by NaCl, and as a result, anhydroglucopyranose is consumed at a faster rate.

As shown in Figure 6(c), the yields of H$_2$O are slightly underpredicted, but their trend across NaCl concentrations is captured well. The model prediction of the yield of 5-HMF is reasonable, although the trend as a function of NaCl loading is not as satisfactory as that for other products, especially at a high NaCl concentration of 0.3 mmol/g. For char and CO$_2$, the model matches the experimental yields well. The model also captures well the experimental trend for formaldehyde (Figure 8(a)) with an increasing yield as NaCl concentration increased. For minor products with yields less than 1 wt %, the model again gives strikingly good agreement for the experimental yields of acetaldehyde (Figure 8(b)), propenal (Figure 8(c)), and dihydroxyacetone (Figure 8(d)) with slight deviations at a NaCl concentration of 0.3 mmol/g. Acetaldehyde is formed from 1,2-anhydroglucopyranose and 2,3-anhydroglucopyranose through retro Diels-Alder reactions (5) and (61). The formation of anhydroglucopyranose intermediates favored by the presence of NaCl leads to the increase in acetaldehyde yield. The catalytic effect of Na$^+$ promoting cyclic/Grob fragmentation (reactions 15 and 39) results in the increased yields of propenal and dihydroxyacetone with the addition of NaCl.

**Fast pyrolysis of cellulose in the presence of NaCl**

Figure 9 presents the comparisons between model output and experimental yields of major products (a) LVG, (b) GA, (c) formaldehyde, (d) char, (e) CO$_2$, and (f) CO obtained from fast...
pyrolysis of cellulose impregnated with different amounts of NaCl at 500 °C. The model captures the exponentially decreasing yield of LVG with the increasing addition of NaCl to cellulose. The yields of GA and formaldehyde as well as their trends were well captured with an outliner at NaCl concentration of 0.21. The yields of char and CO₂ are overestimated at higher NaCl concentrations of 0.21 and 0.31 mmol/g. This may be attributed to the model not making a fine enough distinction in the phase behaviour of various compounds, and efforts to more precisely capture the volatility of all species as a function of structure and reaction conditions represent a significant further advance in the model that is currently in progress. Thus, char and CO₂ were allowed to form from compounds that were assumed to stay in the melt phase. Figure 11 shows the comparison of model output with experimental yields of minor products. The model matches well with the experimental yields of formaldehyde (Figure 11(a)), cyclic hydroxyl lactone (Figure 11(c)), and acetone (Figure 11(d)). Although the yields of acetaldehyde (Figure 11(b)) were underestimated, the model captures the trend of acetaldehyde yield with a maximum at a NaCl concentration of 0.05 mmol/g.

Analysis of contributions of different pathways to the formation of LVG and GA was performed. Cellulose has many more midgroups than maltohexaose. Therefore, the reaction probability of midchain dehydration occurring to cellulose and its derived chains with dehydrated midgroups is much higher. As a result, the formation of glucose and 3,6-anhydroglucopyranose via thermohydrolysis in the initial stage of pyrolysis is greatly promoted by the addition of NaCl, leading to lower formation of LVG and thus a much sharper decrease in the yield of LVG from cellulose pyrolysis than from maltohexaose pyrolysis as NaCl concentration increases. As shown in Figure 10(a), LVG directly formed from decomposition of cellulosic chains through end-chain initiation and depropagation decreased from 28.3 to 2.44 wt
and from 22.2 to 0.68 wt %, respectively, as the NaCl concentration was increased from 0 to 0.31 mmol/g. However, these two pathways still account for the majority of the final yield of LVG, although the pathway of glucose dehydration contributes increasingly from 6.46 to 39.6 %. The formation routes for GA, LVG, and glucose from cellulose decomposition compete with each other in fast pyrolysis. Figure 10(b) presents the contributions of three different pathways to the formation of GA from cellulose. The decomposition of LVG plays an increasing role in producing GA with the increasing addition of NaCl, but still accounts for less than 0.25 % of its final yield. The yields of GA formed directly from cellulose and through glucose intermediates slightly decreased and increased, respectively, as the addition of NaCl increased. Furthermore, the pathway of directly forming GA from cellulose contributes more to its final yield than the pathway through glucose intermediates. Decomposition of LVG also makes a very minor contribution to the formation of char, less than 0.01 wt% in yield (Table S1)

Besides predicting the final yields of pyrolysis products, the mechanistic model also provides the evolution profile of the product distribution as the pyrolysis progresses. Representative evolution profiles of LVG and GA from fast pyrolysis of cellulose with different NaCl loadings (Figure 12). Net rate analysis is able to provide more insights. With the presence of NaCl in fast pyrolysis, Na$^+$ promotes dehydration reactions and the loss of water from cellulose, which in turn promotes thermohydrolysis. As shown in Figure 13 and Figure S2 in the Supporting Information, the initiation step dominates the initial stage of cellulose pyrolysis, but the rate of initiation decreases with increasing addition of NaCl from 0 to 0.31 mmol/g. Endchain initiation and depropagation are affected by the addition of NaCl in a similar way as initiation. Note that the time taken for initiation to lose its dominant role in the initial stage of pyrolysis and thermohydrolysis to take over is reduced by increasing addition of NaCl, as clearly shown in
Figure S2. Moreover, thermohydrolysis increases at a faster rate and reaches its first peak earlier with the increase in the addition of NaCl, which favors midchain dehydration and leading faster formation of intermediates glucose and 3, 6-anhydroglucopyranose, and their derived products, such as glycolaldehyde and char. In contrast, less competitive initiation, endchain initiation, and depredation in the presence of NaCl lead less formation of LVG-end chains species and LVG.

Wu et al.\textsuperscript{18} speculated that the reduction in the yield of LVG from cellulose pyrolysis was caused by the catalytic effect of NaCl on destruction of sugar ring structures in cellulose pyrolysis. Our modeling results show that this can be specifically attributed to the catalytic role of NaCl on dehydration reactions, especially midchain dehydration. Although the model is not able to give a quantitative prediction of the catalytic effects of K\textsuperscript{+} on fast pyrolysis of cellulose due to the difference in the interactions of K\textsuperscript{+} with species and the intensity of catalytic effects of K\textsuperscript{+} on individual elementary reactions from those of Na\textsuperscript{+}, the model is able to qualitatively predict the effects of K\textsuperscript{+} based on the modeling of the catalytic effects of Na\textsuperscript{+} on cellulose pyrolysis, as the effect would be expected to be similar. Indeed, the decreased yield of LVG and the increased yield of char and gaseous species from cellulose pyrolysis in the presence of KCl has reported in the literature based on experimental work\textsuperscript{17,19,29-32}. Also, given that alkaline earth metal chlorides such as MgCl\textsubscript{2}, CaCl\textsubscript{2}, and ZnCl\textsubscript{2} have also been reported to have high dehydration activity\textsuperscript{15-17}, the mechanistic model would thus predict a dramatic reduction in LVG yield from fast pyrolysis of cellulose in the presence of alkaline earth metal chlorides, which has been experimentally reported by Patwardhan et al.\textsuperscript{17} and other researchers\textsuperscript{15,16,19}.

\textit{Turnover frequency of Na\textsuperscript{+}}

Given that dynamic information is not collected experimentally and the network of possible reactions is large and intermeshed, the catalytic rates of Na\textsuperscript{+} on individual reactions in fast
pyrolysis of glucose-based carbohydrates can not be experimentally identified, and thus the experimental measurement of turnover frequency (TOF) of Na\(^+\) is impractical. In order to quantitatively evaluate the catalytic efficiency of Na\(^+\) on glucose-based carbohydrates pyrolysis, the turnover frequency of Na\(^+\) in this work was defined as the amount of H\(_2\)O produced by the reactions catalyzed by Na\(^+\)/the amount of Na\(^+\) × reaction time (s) (Eq. (1)) since dehydration, cyclic/Grob fragmentation and char formation that are catalyzed by Na\(^+\) involve the formation of H\(_2\)O.

\[
TOF = \frac{\text{mol of H}_2\text{O produced by reactions catalyzed by Na}^+}{\text{mol of Na}^+ \times \text{time}} \tag{1}
\]

TOF values of Na\(^+\) corresponding to the reaction time of 0.2 s were 25.1 s\(^{-1}\), 25.1 s\(^{-1}\), 24.9 s\(^{-1}\), and 23.9 s\(^{-1}\) for fast pyrolysis of glucose dosed with 0.03 mmol, 0.08 mmol, 0.16 mmol, and 0.34 mmol NaCl/g, respectively. Therefore, TOF of Na\(^+\) for glucose pyrolysis in the presence of NaCl is about 25 s\(^{-1}\).

It also should be underscored that it is extremely difficult to experimentally measure the dynamic product distribution (Figure 12), the reaction rates of individual reactions (Figure 13), and the contributions of different pathways to the formation of individual products during fast pyrolysis, as well as the pyrolysis timescale. On the other hand, this reflects the advantage of the mechanistic model because it is able to provide information and insights at the molecular level that a lumped model can not provide and that are difficult to obtain through experimental methods.

**Parameter sensitivity analysis**

While the model does a very good job overall capturing the behavior of the full range of glucose-based carbohydrates, the model gives less satisfactory results for fast pyrolysis of cellulose and maltohexaose than for celllobiose and glucose. This is potentially attributable to the
fitted kinetic parameters for reactions mediated by Na\textsuperscript{+} for which there was no data available, such as midchain dehydration mediated by Na\textsuperscript{+}, char formation mediated by Na\textsuperscript{+}, and cyclic/Grob fragmentation mediated by Na\textsuperscript{+}. In this section, parameter sensitivity analysis is performed to evaluate the impact of fitted kinetic parameters on the model output.

Decreasing the Gibbs free energy change in Na\textsuperscript{+} binding (reactions 101 and 102) to glucose and other LMW species from 3 to 1 kcal·mol\textsuperscript{-1} leads to less variation in the yields of pyrolysis products than increasing it from 3 to 7 kcal·mol\textsuperscript{-1} (Figure S3 in the Supporting Information). As similar trend is also observed for varying the Gibbs free energy change in Na\textsuperscript{+} binding to cellulose and LMW species (Figure S4 in the Supporting Information). The yields of levoglucosenone, char, CO, CO\textsubscript{2}, H\textsubscript{2}O, 5-HMF, and especially LVG are more sensitive to the binding energy of Na\textsuperscript{+} to neutral species than the other products.

Model results of fast pyrolysis of glucose dosed with 0.34 NaCl mmol/g show that the LVG yield decreases 9\% and increases 15\% when the rate of volatilization (reaction 100) is halved and doubled, respectively, while the yields of other pyrolysis products are much less affected (Figures S5 and S6 in the Supporting Information). The yields of char, CO, CO\textsubscript{2}, H\textsubscript{2}O, and 5-HMF are more sensitive to the rate of char formation from Na\textsuperscript{+}-complexes (reactions 70–99) than those of other products (Figures S7 and S8 in the Supporting Information). The model yields of minor LMW products such as formaldehyde, methyl glyoxal, propenal, dihydroxyacetone, and HCOOH decrease by \sim13\% and increase by \sim25\% when the rate of cyclic/Grob fragmentation mediated by Na\textsuperscript{+} (reactions 15, 30, 33, and 39) is halved and doubled, respectively, while the yields of major products like LVG, GA, 5-HMF, CO\textsubscript{2}, H\textsubscript{2}O, and char are changed within 4\% (Figures S9 and S10 in the Supporting Information). This result indicates the yields of minor LMW products are more sensitive to the kinetic parameters of cyclic/Grob
fragmentation mediated by Na\(^+\) than those of the major products. Figures S5-S10 also shows that model yields of cellulose pyrolysis are less sensitivity to those of glucose pyrolysis in the presence of NaCl. However, the yields of product especially, LVG and GA are sensitive to midchain dehydration mediated by Na\(^+\) (reactions i and iv). As shown in Figure S11 and S12, the model yield of LVG increases and decreases by \(~8\%\) and \(~12\%\) for other pyrolysis products when the rate of midchain dehydration mediated by Na\(^+\) (reactions i and iv) or the fit factor are halved and doubled, respectively, in fast pyrolysis of cellulose dosed with 0.01 mmol NaCl/g.

The above observations suggest that it would be valuable to carry out theoretical chemistry calculations or experimental efforts to obtain more accurate kinetic parameters. It would be expected to enhance the performance of the model by more precisely establishing kinetic parameters of pyrolysis reactions. Efforts to make a finer assessment of Na\(^+\) binding with cellulose and a more sophisticated yet still simplistic approach of modeling catalytic effects of Na\(^+\) on decomposition of chain species as well as incorporating phase behavior of species and sequential reactions of volatile species would further advance the model.

**Effects of NaCl on the reaction timescale of fast pyrolysis**

Compared to fast pyrolysis of neat glucose-based carbohydrates, the presence of NaCl reduces the activation energy required for dehydration, cyclic/Grob fragmentation, and char formation and speeds up the overall rate of degradation of carbohydrates. As a result, it takes less time for the complete conversion of carbohydrates in the presence of NaCl. The addition of NaCl (~0.3 mmol/g) to cellulose, maltohexaose, cellobiose, and glucose reduces the fast pyrolysis timescale from 5.0 to 3.7 s, from 3.6 to 2.8 s, from 3.5 to 2.3 s, and from 3.0 to 2.2 s, respectively. Figure 14 shows a representative plot of the timescale of fast pyrolysis of cellobiose varying with the addition of NaCl. As shown in Figure 14, the time taken for the complete conversion of
cellulbiose to dimeric intermediates, glucose, LVG, and other LMW intermediates and species is reduced from 0.59 to 0.27 s as the addition of NaCl increases from 0 to 0.21 mmol/g. Moreover, the time that is further required for complete conversion of glucose and other LMW intermediates into the final pyrolysis products is also reduced from 2.90 s for neat cellulbiose to 2.03 s for cellulbiose dosed with 0.21 mmol NaCl/g. These results are consistent with the experimental observation that fast pyrolysis of glucose-based carbohydrates dosed with NaCl occurs at a faster rate and requires reduced time to complete the thermoconversion of the initial carbohydrate samples.33-35

**Effects of NaCl on weight loss of carbohydrates and the yields of biooil and undesired gases and char during fast pyrolysis**

Despite the significant differences in the product distribution and the reaction timescale when NaCl is included in fast pyrolysis of glucose-based carbohydrates, the mass loss profiles of these carbohydrates during fast pyrolysis are all qualitatively similar, as shown in Figure S9 in the Supporting Information. Furthermore, the mechanistic model specifies the kinetic parameters for each elementary step in terms of activation energy and frequency factor, and thus has an obvious advantage over lumped kinetic models that use only apparent kinetic parameters based on experimental data for the overall weight loss of carbohydrate samples measured by thermogravimetric analyzers and the overall yields of global products. Moreover, the mechanistic model predicts the time at which the yield of the melt phase becomes constant, showing clearly that it shifts to earlier times as the addition of NaCl increases, as shown in Figure S9.

As shown in Figure 15, a higher loading of NaCl to cellulose resulted in a lower overall yield of biooil from fast pyrolysis of cellulose, which quantitatively supports the general assertion that
one way to achieve a higher yield of biooil from fast pyrolysis of native cellulose and biomass is to remove the alkali and alkaline earth metal salts.

As shown in Figure 16, the decomposition of the cellulose starting material and its derived polymeric chain species was completed at 1.5 s, and the yield of LMW products was essentially unchanged after 3 s, which suggests that the fast pyrolysis should be terminated at 3 s to reduce operating cost. Moreover, the yield of biooil reached its maximum value at 2.2 s, while the yields of gases and char continued to increase as the yield of biooil decreased as reaction proceeded, which further suggests that the fast pyrolysis should be terminated even earlier at 2.2 s in order to achieve the maximum yield of biooil and to mitigate the secondary degradation and charring of biooil into gases and char. Furthermore, the yields of sugars and anhydrosugars reached their peak values prior to that of biooil, which suggests that the fast pyrolysis should be terminated still earlier at 1.5 s or 2.0 s if the process is designed to maximize the yield of sugars or anhydrosugars, respectively. Therefore, the mechanistic model is not only able to advance the understanding of the composition of pyrolysis products at the molecular level and of the thermal degradation at the pathways level, but it is also able to provide information and insights that can be very useful for process engineers to better design a pyrolysis reactor and to better control the process.

Conclusions

Validation of the first mechanistic model that incorporated the significant catalytic effects of NaCl on fast pyrolysis of glucose-based carbohydrates was performed by comparing model yields with experimental data. A single set of kinetic parameters was used for all chain lengths ranging from glucose to long-chain cellulose. The agreement between model yields and experimental values for various products from fast pyrolysis of glucose-based carbohydrates in
the presence of varying amounts of NaCl supports the hypothesis that reactions occurring in the presence of NaCl follow the same mechanism as those taking place in fast pyrolysis of neat glucose-based carbohydrates, but with the kinetics altered. The model was able to capture the yields and trends of the major products such as LVG, levoglucosan-furanose, 5-HMF, GA, char, H₂O, CO₂, CO, and methyl glyoxal, and minor products like cyclic hydroxyl lactone, formaldehyde, acetaldehyde, levoglucosenone, furfural, furanmethanol, acetone, dihydroxyacetone, and propenal.

It should be underscored that the mechanistic model is able to provide information and insights at the molecular level that a lumped model can not provide and that are difficult to obtain through experimental methods, such as the dynamic product distribution, the reaction rates of individual reactions, TOF values of Na⁺, the contributions of different pathways to the formation of individual products during fast pyrolysis, and the pyrolysis timescale.

The model reveals that dehydration reactions, especially midchain dehydration, that are favored by the presence of NaCl play a vital role in the reduction of LVG yield from fast pyrolysis of cellulose. The competition among different decomposition pathways of carbohydrates contributes more significantly than decomposition of LVG to the reduction in LVG yield from fast pyrolysis of carbohydrates dosed with NaCl. Analysis of the contributions of reaction pathways showed that the decomposition of LVG made a minor contribution to its yield reduction and contributed less than 0.5 % to the final yield of GA from fast pyrolysis of glucose-based carbohydrates in the presence of NaCl. The addition of NaCl accelerates the thermal decomposition of carbohydrates and substantially reduces the time taken for complete conversion of carbohydrates into LMW pyrolysis products.
The mechanistic model for fast pyrolysis of glucose-based carbohydrates is robust and extendable. The modeling methodology can be applied for unraveling the decomposition kinetics and mechanism of fast pyrolysis of hemicelluloses and lignin, allowing for advances towards a mechanistic understanding of fast pyrolysis of real biomass.

Acknowledgment

The authors are grateful for financial support by the Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE) through the Office of Biomass Program, grant number DEEE0003044. The financial support of the National Science Foundation (CBET-1435228) is gratefully acknowledged. Funding from the Institute for Sustainability and Energy at Northwestern (ISEN) is also gratefully acknowledged. H. Mayes was supported by the DOE Computational Science Graduate Fellowship (CSGF), which is provided under grant number DE-FG02-97ER25308, and the ARCS Foundation Inc., Chicago Chapter. The authors thank Dr. R. Vinu and Abraham J. Yanez-McKay for fruitful discussions and useful suggestions. The authors also thank Prof. Dr. Jianliang Xiao and Dr. Jianjun Wu at University of Liverpool for discussions on catalysis. This contribution was identified by Richard West (Northeastern University) as the Best Presentation in the session “Reaction Path Analysis I” of the 2014 AIChE Annual Meeting in Atlanta, GA.” The authors are grateful to the anonymous reviewers for their constructive suggestions and comments.

Literature Cited


**Figure Captions**

**Figure 1.** Comparisons of model and experimental yields from fast pyrolysis of glucose impregnated with different amounts of NaCl at 500 °C for: (a) LVG, (b) GA, (c) levoglucosan-furanose, (d) 5-HMF, (e) char, and (f) CO2. The experimental error bars correspond to the standard deviation of triplicate pyrolysis runs.

**Figure 2.** Comparisons of model and experimental yields from fast pyrolysis of glucose impregnated with different amounts of NaCl at 500 °C for: (a) H2O, (b) methylglyoxal, (c) levoglucosenone, (d) cyclic hydroxyl lactone, (e) furanmethanol, and (f) dihydroxyacetone. The experimental error bars correspond to the standard deviation of triplicate pyrolysis runs.

**Figure 3.** Comparisons of model and experimental yields from fast pyrolysis of cellobiose impregnated with different amounts of NaCl at 500 °C for: (a) LVG, (b) GA, (c) levoglucosan-furanose, (d) 5-HMF, (e) char, and (f) CO2. The experimental error bars correspond to the standard deviation of triplicate pyrolysis runs.
Figure 4. Contributions of different pathways to the formation of (a) LVG and (b) GA in fast pyrolysis of cellobiose dosed with varying amounts of NaCl at 500 °C.

Figure 5. Comparisons of model and experimental yields from fast pyrolysis of cellobiose impregnated with different amounts of NaCl at 500 °C for: (a) H$_2$O, (b) methylglyoxal, (c) CO, and (d) dihydroxyacetone. The experimental error bars correspond to the standard deviation of triplicate pyrolysis runs.

Figure 6. Comparisons of model and experimental yields from fast pyrolysis of maltohexaose impregnated with different amounts of NaCl at 500 °C for: (a) LVG, (b) GA, (c) H$_2$O, (d) 5-HMF, (e) char, and (f) CO$_2$. The experimental error bars correspond to the standard deviation of triplicate pyrolysis runs.

Figure 7. Contributions of different pathways to the formation of (a) LVG and (b) GA in fast pyrolysis of maltohexaose dosed with varying amounts of NaCl at 500 °C.

Figure 8. Comparisons of model and experimental yields from fast pyrolysis of maltohexaose impregnated with different amounts of NaCl at 500 °C for: (a) formaldehyde, (b) acetaldehyde, (c) propenal, and (d) dihydroxyacetone. The experimental error bars correspond to the standard deviation of triplicate pyrolysis runs.

Figure 9. Comparisons of model and experimental yields from fast pyrolysis of cellulose impregnated with different amounts of NaCl at 500 °C for: (a) LVG, (b) GA, (c) formaldehyde, (d) char, (e) CO$_2$, and (f) CO. The experimental error bars correspond to the standard deviation of triplicate pyrolysis runs.

Figure 10. Contributions of different pathways to the formation of (a) LVG and (b) GA in fast pyrolysis of cellulose dosed with varying amounts of NaCl at 500 °C.
Figure 11. Comparisons of model and experimental yields from fast pyrolysis of cellulose impregnated with different amounts of NaCl at 500 °C for: (a) cyclic hydroxyl lactone, (b) acetaldehyde, (c) furanmethanol, and (d) acetone. The experimental error bars correspond to the standard deviation of triplicate pyrolysis runs.

Figure 12. Time evolution of (a) LVG and (b) GA during fast pyrolysis of cellulose dosed with varying amounts of NaCl at 500 °C.

Figure 13. Variation of net rates of initiation during fast pyrolysis of cellulose dosed with varying amounts of NaCl at 500 °C.

Figure 14. Timescale of fast pyrolysis of cellobiose and its intermediates in the presence of varying amounts of NaCl at 500 °C.

Figure 15. Variation of the yield of biooil from fast pyrolysis of cellulose dosed with varying amounts of NaCl at 500 °C.

Figure 16. Time evolution of lumped yields from fast pyrolysis of cellulose dosed with 0.31 mmol NaCl/g at 500 °C.

Figure Captions in the Supporting Information

Figure S1. Contributions of different pathways to the formation of GA in fast pyrolysis of glucose dosed with varying amounts of NaCl at 500 °C.

Figure S2. Variation of net rates of initiation, depropagation, end-chain initiation, and thermohydrolysis during fast pyrolysis of cellulose dosed with varying amounts of NaCl at 500 °C, obtained from the mechanistic model presented in this work.

Figure S3. Sensitivity of the model yields from fast pyrolysis of glucose dosed with 0.34 mmol NaCl/g to the binding energy of Na⁺ to neutral species at 500 °C.
Figure S4. Sensitivity of the model yields from fast pyrolysis of cellulose dosed with 0.01 mmol NaCl/g to the binding energy of Na\(^+\) to neutral species at 500 °C.

Figure S5. Sensitivity of the model yields from fast pyrolysis of glucose dosed with 0.34 mmol NaCl/g to volatilization of levoglucosan at 500 °C.

Figure S6. Sensitivity of the model yields from fast pyrolysis of cellulose dosed with 0.01 mmol NaCl/g to volatilization of levoglucosan at 500 °C.

Figure S7. Sensitivity of the model yields from fast pyrolysis of glucose dosed with 0.34 mmol NaCl/g to char formation mediated by Na\(^+\) at 500 °C.

Figure S8. Sensitivity of the model yields from fast pyrolysis of cellulose dosed with 0.05 mmol NaCl/g to char formation mediated by Na\(^+\) at 500 °C.

Figure S9. Sensitivity of the model yields from fast pyrolysis of glucose dosed with 0.34 mmol NaCl/g to cyclic/Grob fragmentation mediated by Na\(^+\) at 500 °C.

Figure S10. Sensitivity of the model yields from fast pyrolysis of cellulose dosed with 0.05 mmol NaCl/g to cyclic/Grob fragmentation mediated by Na\(^+\) at 500 °C.

Figure S11. Sensitivity of the model yields from fast pyrolysis of cellulose dosed with 0.01 mmol NaCl/g to midchain dehydration mediated by Na\(^+\) at 500 °C.

Figure S12. Sensitivity of the model yields from fast pyrolysis of cellulose dosed with 0.01 mmol NaCl/g to the fit factor of multiplying the preexponential factor of midchain dehydration mediated by Na\(^+\) at 500 °C.

Figure S13. Time evolution of overall weight loss obtained from the model of glucose, cellobiose, maltohexaose, and cellulose during fast pyrolysis in the presence of varying amounts of NaCl at 500 °C.
**Scheme Captions in the Supporting Information**

**Scheme S1.** Decomposition mechanisms of cellulose/maltohexaose chains involving end-groups.

**Scheme S2.** Decomposition mechanisms of cellulose/maltohexaose chains involving mid-groups.

**Scheme S3.** Reaction mechanism of β-D-glucopyranose to form a variety of C1-C6 compounds during fast pyrolysis.

**Scheme S4.** Continued mechanism of the formation of C1-C6 compounds.

**Scheme S5.** Char formation of various dehydrated species.

**Scheme S6.** Degradation mechanism of levoglucosan during fast pyrolysis in the presence of NaCl.

**Scheme S7.** Modeling approach to capture the effects of Na\(^+\) on the product distribution involved adding interactions of Na\(^+\) with cellulose and its derivative polymer chains (e.g., cellulose chain, NR-end chain, and LVG-end chain) and adding parallel reaction pathways (e.g., dehydration) mediated by Na\(^+\) with different kinetic parameters.

**Scheme S8.** Modeling approach to capture the effects of Na\(^+\) on the product distribution involved adding interactions of Na\(^+\) with low molecular weight species (e.g., glucose and levoglucosan) and adding parallel reaction pathways (e.g., dehydration) mediated by Na\(^+\) with different kinetic parameters.

**Table Caption in the Supporting Information**

**Table S1.** Contributions of levoglucosan degradation to the formation of levoglucosan in fast pyrolysis of cellulose dosed with varying amounts of NaCl at 500 °C.
Figure 1. Comparisons of model and experimental yields from fast pyrolysis of glucose impregnated with different amounts of NaCl at 500 °C for: (a) LVG, (b) GA, (c) levoglucosan-furanose, (d) 5-HMF, (e) char, and (f) CO₂. The experimental error bars correspond to the standard deviation of triplicate pyrolysis runs.
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Figure 6. Comparisons of model and experimental yields from fast pyrolysis of maltohexaose impregnated with different amounts of NaCl at 500 °C for: (a) LVG, (b) GA, (c) H₂O, (d) 5-HMF, (e) char, and (f) CO₂. The experimental error bars correspond to the standard deviation of triplicate pyrolysis runs.
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Figure 16. Time evolution of lumped yields from fast pyrolysis of cellulose dosed with 0.31 mmol NaCl/g at 500 °C.
(b) Glycolaldehyde

Yield, wt %

Expt.
Model

0 0.03 0.08 0.16 0.34
mmol NaCl/g of glucose

76x54mm (300 x 300 DPI)
(d) 5-Hydroxymethylfurfural

Yield, wt %

Expt.  
Model

0  
0.03  
0.08  
0.16  
0.34  

mmol NaCl/g of glucose

76x54mm (300 x 300 DPI)
76x54mm (300 x 300 DPI)
76x52mm (300 x 300 DPI)
(b) Methylglyoxal

<table>
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<tr>
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<td>0.34</td>
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mmol NaCl/g of glucose
(c) Levoglucosenone

![Graph showing yield of levoglucosenone with varying mmol NaCl/g of glucose. The x-axis represents the mmol NaCl/g of glucose with values 0, 0.03, 0.08, 0.16, and 0.34. The y-axis represents the yield, wt%, ranging from 0 to 2.5. Data points show the comparison between Expt. and Model.](image-url)

<table>
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<th>mmol NaCl/g of glucose</th>
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76x54mm (300 x 300 DPI)
(f) Dihydroxyacetone

![Graph showing yield vs. mmol NaCl/g of glucose for Dihydroxyacetone. The graph compares experimental (Expt.) and model results.](image)

Yield, wt %

<table>
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76x51mm (300 x 300 DPI)
(b) Glycolaldehyde

Yield, wt. %

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76x55mm (300 x 300 DPI)
(c) Levoglucosan (furanose)

![Graph showing yield vs. mmol NaCl/g of cellulose](image)

76x52mm (300 x 300 DPI)
(a) Levoglucosan-pyranose

- LVG from cellobiose
- LVG from glucose dehydration

Yield, wt %

mmol of NaCl/g of cellobiose
(b) Glycolaldehyde

Yield, wt %

0 2 4 6 8 10

0 0.02 0.04 0.11 0.21

mmol of NaCl/g of cellobiose

GA from LVG
GA from cellobiose
GA from glucose

86x66mm (300 x 300 DPI)
(b) Methylglyoxal

Yield, wt %

Expt.  
Model

0 0.02 0.04 0.11 0.21
mmol NaCl/g of cellubiose

76x51mm (300 x 300 DPI)
(d) Dihydroxyacetone

Expt.
Model

Yield, wt.

0 0.06 0.09 0.12 0.15

0 0.02 0.04 0.11 0.21
mmol NaCl/g of cellubiose

80x56mm (300 x 300 DPI)
(b) Glycolaldehyde

Yield, wt %

0 2 4 6 8 10

mmol NaCl/g of maltohexaose

Expt.
Model

0 0.01 0.06 0.18 0.3

76x54mm (300 x 300 DPI)
(c) H$_2$O

Yield, wt %

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76x51mm (300 x 300 DPI)
(d) 5-Hydroxymethylfurfural

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Yield, wt.

76x52mm (300 x 300 DPI)
(f) CO₂

Yield, wt.%

Expt.
Model

mmol NaCl/g of maltohexaose

0 0.01 0.06 0.18 0.3

76x55mm (300 x 300 DPI)
(a) Levoglucosan-pyranose

- LVG from endchain initiation
- LVG from chain depropagation
- LVG from glucose dehydration

Levoglucosan yield, wt %

mmol NaCl/g of maltohexaose

0 0.01 0.06 0.18 0.3

79x56mm (300 x 300 DPI)
(a) Formaldehyde

Yield, wt/
1.8
1.5
1.2
0.9
0.6
0.3
-2E-15
0
0.01
0.06
0.18
0.3
mmol NaCl/g of maltohexaose

Expt.
Model

76x52mm (300 x 300 DPI)
(b) Acetaldehyde

![Bar chart showing yield vs. mmol NaCl/g of maltohexaose](image)

Yield, wt %

Expt.  Model

0 0.01 0.06 0.18 0.3

mmol NaCl/g of maltohexaose

76x54mm (300 x 300 DPI)
(d) Dihydroxyacetone

Yield, wt. %

Expt.  Model

mmol NaCl/g of maltohexaose

0  0.01  0.06  0.18  0.3

0  0.03  0.06  0.09  0.12  0.15

76x51mm (300 x 300 DPI)
(c) Formaldehyde

Yield, wt %

Expt.
Model

mmol NaCl/g of cellulose

0 0.01 0.05 0.21 0.31

76x54mm (300 x 300 DPI)
(d) Char

Yield, wt %

Expt.
Model

mmol NaCl/g of cellulose

0, 0.01, 0.05, 0.21, 0.31

76x54mm (300 x 300 DPI)
(a) Levoglucosan-pyranose

- LVG from endchain initiation
- LVG from chain depopagation
- LVG from glucose dehydration

Yield, wt %

mmol NaCl/g of cellulose
### (b) Glycolaldehyde

- **GA from LVG**
- **GA from the chains**
- **GA from glucose**

<table>
<thead>
<tr>
<th>Yield, wt %</th>
<th>mmol NaCl/g of cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<tr>
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<td>3</td>
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<tr>
<td>0.05</td>
<td>6</td>
</tr>
<tr>
<td>0.21</td>
<td>12</td>
</tr>
<tr>
<td>0.31</td>
<td>18</td>
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</tbody>
</table>

75x54mm (300 x 300 DPI)
(a) Cyclic hydroxyl lactone

Yield, wt %

0 0.2 0.4 0.6 0.8

Expt.
Model

0 0.01 0.05 0.21 0.31 mmol NaCl/g of cellulose

76x53mm (300 x 300 DPI)
(b) Acetaldehyde

Yield, wt.%

<table>
<thead>
<tr>
<th>mmol NaCl/g of cellulose</th>
<th>Expt.</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.6</td>
<td>0.6</td>
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<tr>
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<tr>
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<tr>
<td>0.21</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>0.31</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

76x54mm (300 x 300 DPI)
(c) Furanmethanol

Yield, wt %

0 0.04 0.08 0.12 0.16 0.2

0 0.01 0.05 0.21 0.31 mmol NaCl/g of cellulose

Expt.  Model

76x52mm (300 x 300 DPI)
Initiation

- Neat cellulose
- 0.01 mmol NaCl/g of cellulose
- 0.05 mmol NaCl/g of cellulose
- 0.21 mmol NaCl/g of cellulose
- 0.31 mmol NaCl/g of cellulose

Rate of initiation, mol·L⁻¹·s⁻¹

Pyrolysis time, s

84x62mm (300 x 300 DPI)