Evaluating the effect of potassium on cellulose pyrolysis reaction kinetics

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Abstract

This paper proposes modifications to an existing cellulose pyrolysis mechanism in order to include the effect of potassium on product yields and composition. The changes in activation energies and pre-exponential factors due to potassium were evaluated based on the experimental data collected from pyrolysis of cellulose samples treated with different levels of potassium (0-1% mass fraction). The experiments were performed in a pyrolysis reactor coupled to a molecular beam mass spectrometer (MBMS). Principal component analysis (PCA) performed on the collected data revealed that cellulose pyrolysis products could be divided into two groups: anhydrosugars and other fragmentation products (hydroxyacetaldehyde, 5-hydroxymethyl furfural, acetyl compounds). Multivariate curve resolution (MCR) was used to extract the time resolved concentration score profiles of principal components. Kinetic tests revealed that potassium apparently inhibits the formation of anhydrosugars and catalyzes char formation. Therefore, the oil yield

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predicted at 500°C decreased from 87.9 % from cellulose to 54.0 % from cellulose with 0.5 % mass fraction potassium treatment. The decrease in oil yield was accompanied by increased yield of char and gases produced via a catalyzed dehydration reaction. The predicted char and gas yield from cellulose were 3.7 % and 8.4 %, respectively. Introducing 0.5% mass fraction potassium treatment resulted in an increase of char yield to 12.1% and gas yield to 33.9%. The validation of the cellulose pyrolysis mechanism with experimental data from a fluidized-bed reactor, after this correction for potassium, showed good agreement with our results, with differences in product yields of up to 5%.

Keywords: cellulose, pyrolysis, potassium, kinetics, MBMS

1. Introduction

Biomass fast pyrolysis is a promising pathway for producing liquid fuels from a variety of solid biomass feedstocks [1, 2, 3]. In order to accelerate the development and commercialization of fast pyrolysis systems, it is important to be able to predict product yields and composition. Having a better estimate of biomass fast pyrolysis products allows more accurate techno-economic assessment of potential conversion processes. Therefore, biomass pyrolysis reactor modeling has been the subject of multiple studies [4, 5, 6, 7, 8]. However, modeling biomass fast pyrolysis is a challenging task because the reaction mechanism and the effects of feedstock composition on product yields are still not well understood.

Biomass composition and the amount of alkali metals present within its structure vary greatly depending on the environment of individual plants,

14 however, some general characteristics might be distinguished. The major
 15 inorganic elements found in biomass are sodium, potassium, magnesium and
 16 calcium [9]. They mostly ($>90\%$) exist in water soluble or ion exchangeable
 17 forms [10]. The mass fraction of inorganic compounds is typically obtained
 18 from ash analysis because it is difficult to directly determine the weight frac-
 19 tion of alkali metals in raw biomass. Ash content is typically low for woody
 20 biomass ($<0.5\%$) and increases for herbaceous species and organic waste (up
 21 to 30% ash) [9, 11]. For reference, the main constituents of ash typical of
 22 pine, oak and switchgrass feedstocks were measured via ICP-MS analysis of
 23 the ashed samples and are presented in Table 1. [Table 1 here] The mass
 24 fraction of ash in woody feedstocks is relatively low ($0.3 - 0.4\%$) compared
 25 to grassy feedstocks ($\sim 6.0\%$). The major components of the ash are silica,
 26 potassium and calcium. An extensive study of the ash compositions from
 27 86 biomass samples grouped into woody biomass, herbaceous and agricul-
 28 tural biomass, animal biomass, mixed biomass and contaminated biomass
 29 performed by Vassilev et al., [11] shows that the ash content and its chemical
 30 composition can vary over a wide range even for the same biomass type due
 31 to the dependence on plant origin and environment.

32 The effect of alkali/alkaline earth metals on biomass pyrolysis has been
 33 investigated by several researchers [9, 12, 13, 14, 15, 16]. Scott et al., [12]
 34 first observed that alkali metals cause reductions in oil yield. Varhegyi et
 35 al., [13] investigated the effect of magnesium, sodium, iron and zinc on cellu-
 36 lose and biomass pyrolysis. He observed that magnesium did not change the
 37 overall weight loss characteristics or the formation of water and carbon diox-
 38 ide. However, the yields of minor organic compounds (aldehydes, ketones,

etc.) were significantly lower. Sodium was found to increase the yields of char, water, carbon dioxide and carbon monoxide at the expense of the oil yield. Iron and zinc were found to promote water and char formation. These results were confirmed by Shimada et al. [17] who also found that potassium chloride and sodium chloride cause a reduced levoglucosan yield and increased yields of water, carbon monoxide and char. Calcium chloride and magnesium chloride were found to lower the pyrolysis onset temperature and have a large effect on the product composition. Patwardhan et al., [9] provided more details about the alterations in product composition caused by potassium and sodium, which cause a severe reduction of the levoglucosan yield and increased yield of formic acid, glycolaldehyde and acetol. They also found that calcium and magnesium had a much weaker effect on the levoglucosan yield and negligible effect on the yields of formic acid, glycolaldehyde or acetol [9]. Despite these studies the underlying kinetic mechanism causing the observed changes in product yields is still not well understood.

Some researchers have suggested that the catalytic cellulose pyrolysis mechanism might be either acidic or alkaline [18, 19]. According to this theory, acid catalysts promote dehydration reactions, thus causing increased formation of levoglucosenone, various furan derivatives and char. Alkaline catalysts promote fission and disproportionation reactions, causing increased formation of glyoxal, acetaldehyde, carbonyl compounds and char. However, it has been shown that neutral salts also caused reduced levoglucosan yield and increased char yield [20, 21]. Therefore, it was concluded that the catalytic mechanism was ionic and that alkalinity, acidity or neutrality was of secondary importance [15]. Piskorz et al., [22] found that levoglucosan for-

64 mation and aldehydes formation during cellulose pyrolysis were competing
65 reactions. The temperature had a weak influence on promoting either of the
66 pathways and it has been concluded that metals determined the product com-
67 position [16]. It was suggested that metal cations might inhibit levoglucosan
68 formation by capping the free ends of cellulose chain and thus preventing the
69 unzipping reactions from proceeding. Kawamoto et al. [23] investigated the
70 pyrolytic behavior of levoglucosan and they found that it can undergo sec-
71 ondary decomposition in the presence of other cellulose pyrolysis products.
72 There are several possible pathways for the secondary levoglucosan reactions
73 such as fragmentation into low molecular weight species or polymerization
74 into polysaccharides, which are subsequently converted to solid carbonized
75 products [24]. It is also possible for the secondary reactions to occur in a
76 liquid phase[25]. Williams and Horne [15] found that the weight loss curves
77 recorded during cellulose pyrolysis in the presence of salts were characterized
78 by several distinct slopes. As a result, several activation energies for different
79 temperature zones were reported, however the kinetic mechanism of cellulose
80 pyrolysis in the presence of alkali was not explained [15]. The findings on
81 the catalytic effect of alkali metals on the cellulose pyrolysis mechanism are
82 summarized in Table 2. [Table 2 here]

83 Despite the lack of an established mechanism, the general observations
84 are that inorganic compounds promote water and char formation and there-
85 fore, cause a reduced oil yield [9, 13]. Moreover, the composition of pyrolysis
86 oil is altered; the yield of levoglucosan decreases and the yield of glycolalde-
87 hyde, formic acid and acetol increase with an increased amount of salts [13].
88 However, it is not clear whether the observed changes in pyrolysis products

89 are due to alterations in primary reaction pathways, promotion of secondary
90 cracking reactions or a combination of both.

91 Most currently available cellulose and biomass pyrolysis reaction mecha-
92 nisms [26, 27, 28] do not capture the effect of inorganic compounds present
93 in the biomass feedstocks on the pyrolysis products because of poor under-
94 standing of this phenomenon and the lack of appropriate experimental data.

95 The first adaptation of a biomass pyrolysis reaction mechanism to account
96 for the catalytic effect of alkali was the incorporation of secondary cracking
97 reactions [29]. This adaptation is however only applicable when biomass par-
98 ticles are sufficiently large (1 cm). Therefore, there is still a need to develop
99 an experimental procedure and a data analysis methodology applicable to
100 smaller biomass particles that will allow to include the changes in kinetic pa-
101 rameters in the reaction mechanism. The goal of this work is to initiate this
102 process by evaluating the effect of potassium on cellulose pyrolysis kinetics
103 and incorporating the results into the cellulose pyrolysis reaction mechanism
104 [28]. Potassium could potentially serve as an engineering approximation for
105 all alkali metals due to its strong influence on levoglucosan and hydroxyac-
106 etaldehyde formation [14, 16], and its relatively large mass fraction in the
107 biomass structure compared to other metals, as shown in Table 1. This pa-
108 per explores the changes in reaction kinetics (reaction order, rate constants,
109 activation energy) and product yields by analyzing the experimental data
110 collected with a molecular beam mass spectrometer (MBMS) using statis-
111 tical tools (principal component analysis and multivariate curve resolution)
112 [30]. The results are incorporated into an existing reaction mechanism [28]
113 and validated with experimental data [31] from a fluidized-bed reactor at the

114 National Renewable Energy Laboratory (NREL).

115 2. Experimental

116 Experiments were performed with microcrystalline cellulose (Avicel) pur-
117 chased from Sigma Aldrich and cellulose treated with different levels of
118 potassium as K_2CO_3 (between 0.01% and 1%). This corresponds to molar
119 concentrations of potassium carbonate salt between 0.0013 and 0.13 mmol
120 K_2CO_3 /gram of cellulose. Previous work [30] has shown that the qualita-
121 tive changes in cellulose-derived pyrolysis products, which approximate that
122 found in biomass, could be affected by the addition of potassium carbonate
123 at concentrations of potassium that are found in woody biomass. Additions
124 of potassium as the chloride salt were not as effective in decreasing the lev-
125 oglucosan yield in favor of hydroxyacetaldehyde. The alkaline nature of the
126 carbonate salt may be an important part of the observed effect and a better
127 approximation of what is observed in biomass. Cellulose samples were pre-
128 pared by impregnating pure cellulose with aqueous solutions of potassium
129 carbonate. The created slurry was then dried in air at room temperature. In
130 order to ensure complete moisture removal, the samples were also dried in a
131 furnace at 120°C for 6 hours before the experiment. The sample weight was
132 4 mg, which was a minimum weight required for the equipment to obtain
133 an acceptable signal-to-noise ratio. Samples were pyrolyzed at five temper-
134 atures: 480°C, 490°C, 500°C, 510°C and 520°C in order to build a database
135 for evaluating the reaction rate constant. The experiments were performed
136 in a Frontier Laboratories 2020iD pyrolyzer (Fukushima, Japan) with an au-
137 to-sampler connected to the MBMS device, shown in Figure 1. [Figure 1 here]

138 The samples were placed in 80 cm³ stainless steel cups and pyrolyzed at a
139 cycle time of 90 s. The pyrolysis reactions were completed in less than 30
140 s in the considered temperature range. The vapors were swept with helium
141 gas at a flow rate of 15 cm³/s in order to ensure an inert environment for
142 pyrolysis processes. A small sample of the product stream was extracted by
143 the MBMS device through an orifice, where a nearly isentropic expansion
144 occurred. The rapid cooling of the product stream due to expansion helps
145 to eliminate the secondary cracking reactions. Next, the gases and vapors
146 passed through a three-stage vacuum system (p =13 Pa, 100 mPa and 100
147 μ Pa), where they were accelerated. The supersonic molecular beam was then
148 ionized with a low-energy (17.0 eV) electron beam. The ions were quantified
149 with an electron multiplier detector. The pyrolysis vapors mass spectra were
150 recorded with an Extrel mass spectrometer at a frequency of 500 mHz. Each
151 sample was analyzed in replicate. The MBMS was chosen for the experiments
152 due to the following advantages: i) collisionless flow, ii) preserved reactive
153 species (low temperature), iii) ability to record time-resolved processes, and
154 iv) quick data collection. However, MBMS data analysis can be challenging
155 due to the uncertainty about the parent compounds of the detected fragment
156 ions. Other factors which might influence the MBMS data are the electron
157 energy, quadrupole tuning, and so called "mass separation" [30].

158 The experimental data from a fluidized bed reactor at NREL [31] were
159 used for the purpose of validation of the modified cellulose pyrolysis mecha-
160 nism. The reactor system is presented in Figure 2. [Figure 2 here] Biomass
161 was supplied to the reactor through a feed hopper with a screw conveyor. Ni-
162 trogen gas was added in the feed system for pneumatic transport of biomass.

163 Additional 5 SLM of nitrogen were supplied to the reactor to ensure proper
164 fluidization. The fluidized bed material was olivine and the reactor inventory
165 was 400 g. The olivine was supplied by AGSCO with a particle size distri-
166 bution of 800 to 1000 μm and was 48% MgO, 41% SiO₂ and 8% Fe₂O₃ with
167 minor amounts of calcium, chromium, nickel and aluminum oxides. Pyrolysis
168 experiments were performed at 500°C with the residence time of 0.5 s. Pyrol-
169 ysis products were directed to a cyclone followed by a 2 μm hot filter, where
170 the char was separated from the pyrolysis gases and vapors. The reactor was
171 equipped with a two-step oil collection system. The first step was an electro-
172 static precipitator (ESP), where many lignin pyrolysis products and aerosols
173 were removed from the pyrolysis vapors. This is because lignin products have
174 higher molecular weights and higher condensation temperatures. Pyrolysis
175 vapors were cooled before the ESP to approximately 30°C in an air-cooled
176 heat exchanger. Therefore, the ESP was also a primary condenser. The sec-
177 ond condensation step was a dry ice condenser, which was the final liquid
178 collection step. In order to improve mass balance closure (to > 90%), the
179 amount of liquid collected in different condensation steps was determined by
180 weighing the entire condenser unit before and after the experiment.

181 3. Data Analysis Methodology

182 The recorded MBMS data presented in Figure 3 include the total ion
183 current (TIC) and the respective mass spectra. TIC is the sum of all ions
184 detected during the experiment and it provides the information about the
185 onset, progression and completion of the pyrolysis process. The mass spectra
186 show the relative contribution of individual fragment ions to the TIC at each

187 time step, thus providing the information about product composition. The
188 units of intensity have no direct physical meaning. [Figure 3 here]

189 The collected MBMS data were preprocessed in MS Excel for further
190 analysis in the UnscramblerX [32]. The preprocessing included normalizing
191 the data with the highest intensity in the dataset and scaling by a factor
192 of 1,000 in order to increase the numerical values for statistical calculations.
193 Only masses between $m/z=30-200$ were considered for further analysis as
194 the higher molecular weights accounted for a relatively low percentage of
195 the product mass ($\leq 2\%$). A principal component analysis (PCA) was per-
196 formed on the preprocessed data in order to reduce the dimensionality of the
197 dataset and describe the statistically significant trends with a small num-
198 ber of lumped product classes representative of major pyrolysis products,
199 as determined by the principal components. These principal components
200 were determined through the following mathematical process. Firstly, a co-
201 variance matrix was computed in order to evaluate the correlation between
202 the fragment ions. Next, the eigenvalues and eigenvectors were calculated.
203 The eigenvectors provide information about the correlation between samples
204 and the eigenvalues describe the strength of these correlations. The dataset
205 was then projected on a new set of orthogonal axes (determined by the eigen-
206 vectors) so that the variance explained was maximized by the fewest number
207 of principal components. The results were then displayed with a score plot
208 and a loading plot. A score plot shows the calculated values of principal com-
209 ponents for the samples and loadings typically show the grouping of clusters
210 of samples. A loading plot shows the relative contribution of individual mass
211 variance to each principal component. As a result, the correlated fragment

ions were grouped into clusters representative of chemical compounds or compound classes. Next, the multivariate curve resolution (MCR) (described in detail in [33]) was used to deconvolute the time-resolved data into evolving concentration score profiles of principal components. These concentration profiles were subjected to kinetic tests to determine reaction rate constants and reaction orders. The data were subjected to zeroth order, first order and a fractional order (n) kinetic tests by performing a linear fit of the following functions plotted against time:

$$f_0(t) = \frac{\int_0^t c_{PC}(t)dt}{c_o} \quad (1)$$

$$f_1(t) = \ln\left(\frac{\int_0^t c_{PC}(t)dt}{c_o}\right) \quad (2)$$

$$f_n(t) = \frac{1}{1-n} \cdot \left(\frac{\int_0^t c_{PC}(t)dt}{c_o}\right)^{1-n} \quad (3)$$

where $f_0(t)$, $f_1(t)$, $f_n(t)$ is the zero order, first order and n-th order kinetic test function respectively, t is time, c_{PC} is the concentration score of a principal component, and c_o is the total amount of products, so that the non-dimensional concentration score changes between zero and one. The slope of the linear fit is equal to the reaction rate constant. The initial and final data were excluded from the kinetic analysis as they were likely affected by heat transfer limitations. Although a rigorous quantification of the products was not performed in this study the time resolved intensity profiles of fragment ions provide useful information about the evolution of products and therefore can be used to evaluate the kinetics. The advantage of this method over a thermogravimetric analysis (TGA) is the fact that it is possible to evaluate the rate of formation of individual product classes.

235 4. Results and Discussion

236 The recorded mass spectra show that pure cellulose gives high yields of
237 levoglucosan ($m/z=162$) represented by characteristic fragment ions $m/z=57$,
238 60, 70, 73, 98 and 144, as illustrated in Figure 3 (b). The presence of potas-
239 sium causes an increased intensity of fragment ions $m/z=31$, 32 characteris-
240 tic of hydroxyacetaldehyde, $m/z=85$, 97, 126 representing 5-hydroxymethyl
241 furfural, $m/z=85$, and $m/z=43$ (C_2H_2O), which could be assigned to acetyl
242 compounds, as shown in Figure 3 (c). The relative intensity of anhydrosugars
243 decreases with the increased potassium treatment. The general characteris-
244 tics of these mass spectra are in accordance with previous studies [30, 34].
245 Therefore it is suspected that potassium is either inhibiting the formation
246 of levoglucosan or catalyzing the formation of other products. The major
247 characteristic fragment ions in the mass spectra and their possible sources
248 are summarized in Table 3. [Table 3 here]

249 PCA analysis performed on the collected MBMS data in the Unscram-
250 blerX software distinguishes the aforementioned product groups, which are
251 represented by two principal components PC1 and PC2. The two compo-
252 nent model explains 98 % of the variance in the dataset and it is determined
253 by the UnscramblerX as an optimal model for describing the dataset. Mass
254 spectra of the two principal components, shown in Figure 4, indicate that
255 PC1 represents anhydrosugars and PC2 represents fragmentation products
256 promoted by potassium carbonate (hydroxyacetaldehyde, acetyl compounds
257 and 5-hydroxymethyl furfural). [Figure 4 here]

258 MCR results provide the information about the changes in time resolved
259 concentration score profiles of the two principal components (PC1 and PC2)

260 in response to an increased amount of potassium in the sample. As shown
261 in Figure 5 (a), the concentration of anhydrosugars is much higher than the
262 concentration of the other products during the pyrolysis of untreated cellulose.
263 Figure 5 (c) shows that the concentration of the anhydrosugars and
264 other products are nearly equal at 0.5 % of potassium treatment, and Figure
265 5 (d) shows that there is significantly less anhydrosugars produced relative
266 to other products at 1 % potassium treatment. In addition, the total yield
267 of pyrolysis vapors decreases, which results in a decreased TIC. The scale in
268 Figure 5 (c) and (d) was adjusted for the decreased concentration score. The
269 presented results were obtained at 510°C, however, this trend was consistent
270 at all considered temperatures. The numerical values of the concentration
271 scores have no direct physical meaning. However, their relative changes in re-
272 sponse to increased potassium treatment provide valuable information about
273 changes in product composition. [Figure 5 here]

274 The obtained concentration score profiles were integrated in order to de-
275 termine isothermal mass loss curves. The obtained curves were next corrected
276 for the char yield. The comparison of the isothermal mass loss curves derived
277 through mathematical treatment of the experimental data at 510°C at differ-
278 ent levels of potassium treatment is provided in Figure 6. The results show
279 no significant changes in the mass loss curves due to the presence of potas-
280 sium. Slight differences are due to the noise in the experimental data and the
281 mathematical treatment of the dataset. [Figure 6 here]

282 The kinetic tests performed on the concentration score profiles of the two
283 principal components PC1 and PC2 reveal that the reaction order is not af-
284 fected by the presence of alkali metals, and all reactions are best represented

285 by first order. This also indicates that the data used were free from heat
286 transfer limitations. The activation energies for the formation of the prin-
287 cipal components PC1 and PC2 determined from kinetic tests are shown in
288 Figure 7. The addition of potassium strongly inhibits the formation of lev-
289 oglucosan, which manifests itself in an increased activation energy of PC1.
290 The activation energy for the formation of the other products represented
291 with PC2 also increases, however, at a much lower rate. The increased ac-
292 tivation energies for both reactions, result in decreased amount of condens-
293 ables. [Figure 7 here] These results are consistent with the decreased oil yield
294 from a fluidized-bed reactor reported by Scott et al., [12]. The strong inhi-
295 bition of levoglucosan formation results in the increased yield of acids and
296 aldehydes, as shown in Figure 5. The increased mass fraction of acids and
297 aldehydes caused by potassium has previously been reported by Patwardhan
298 et al., [35]. Higher activation energy also leads to the delay in the onset of
299 PC1 formation relative to PC2 formation (Figure 5 c and d).

300 The char yield was determined by weighing the solid residue after the ex-
301 periment. As shown in Figure 8, char yield increases from 3.7 % of the pure
302 cellulose sample to 14.0 % of the sample treated with 1 % potassium. The
303 temperature had a negligible effect on the char yield within the considered
304 range between 480-520°C. The char yield data were used to determine the
305 activation energy of the char formation reaction as a function of potassium
306 treatment. The activation energy for the char formation was calculated by
307 matching the predicted char yields with the experimental data. [Figure 8 here]

308 The determined activation energies and pre-exponential factors were in-
309 corporated into the cellulose pyrolysis mechanism developed by Ranzi et al.,

[28]. The original mechanism, shown in Figure 9 (a), is comprised of four reactions. Firstly, cellulose is partially depolymerized according to reaction (R1). Next, the active cellulose (at low degree of polymerization) undergoes either depolymerization leading to levoglucosan formation (R3) or fragmentation leading to the formation of acids, aldehydes, other volatiles and char (R2). In addition to this pathway, there is a competing dehydration reaction, which leads to formation of char (cross-linking) and water (R4). [Figure 9 here] The products of the dehydration reaction usually also include gases [27, 36], which are missing in the presented mechanism. Therefore an additional adjustment was made in the reaction stoichiometry to incorporate the produced CO, CO₂, and H₂, as shown in Figure 9 (b). The activation energies of reactions R2, R3 and R4 were adjusted, as functions of potassium treatment based on the experimental data. The activation energies of reactions R2 and R3 increase with the increased potassium treatment, since potassium strongly inhibits levoglucosan formation (R3) and mildly inhibits the fragmentation reaction (R2). The activation energy of the dehydration reaction (R4) decreases as it is catalyzed by potassium. The activation energies and pre-exponents of reactions R2, R3 and R4 for pure cellulose are summarized in Table 4. [Table 4 here] The adjusted activation energies are in the same order of magnitude compared with the original mechanism. The general trends are similar; the activation energy of transglycosylation is lower than the activation energy for fragmentation and for char formation; however it is noteworthy that the activation energy of transglycosylation approaches that of fragmentation. Moreover, the proposed activation energies are in a reasonable agreement with the values reported by Diebold [37]. However,

335 a direct comparison of the activation energies derived in this study with
336 other values reported in the literature might not be justified as those activa-
337 tion energies describe different reaction pathways. In addition, the activation
338 energies might vary due to the different experimental equipment, inability
339 to accurately determine the sample temperature during experiments, heat
340 and mass transfer limitations, compositional and size differences of biomass
341 samples or mathematical treatment of experimental data. The adaptation
342 of the pyrolysis mechanism proposed in this study is different from the ap-
343 proach presented by Anca-Couce et al. [29]. This is because in this study,
344 the particle size was very small ($50\ \mu\text{m}$) and the product vapors were im-
345 mediately removed from the pyrolyzer. Therefore, the authors think that it
346 is unlikely that secondary reactions were the dominant mechanism of char
347 formation in this study. Moreover, the char yield was determined by weighing
348 the residue after pyrolysis. The activation energy for charring reaction was
349 adjusted based on the collected yield data. Therefore, the available informa-
350 tion was not detailed enough to propose appropriate secondary reactions and
351 evaluate the respective kinetic parameters. The authors do not claim that the
352 proposed mechanism is the only possible explanation of the effect of potas-
353 sium. It might be desired to extend the model and incorporate secondary
354 reactions in the future. However, the proposed approach seems reasonable to
355 the authors based on the collected data.

356 Since the activation energies of reactions R2, R3, R4 change as functions
357 of the potassium treatment (% K), the following functions describing these
358 change were obtained by fitting the experimental data presented in Figure 7

359 and 8 (b):

$$E_{a,2}(\%K) = 100.16x^{0.0168} \quad (4)$$

$$E_{a,3}(\%K) = 118.99x^{0.056} \quad (5)$$

$$E_{a,4}(\%K) = 124.52x^{-0.03} \quad (6)$$

362 where E_a is the activation energy (kJ/mol), and x is the mass fraction of
363 potassium (%).

364 The modified cellulose pyrolysis mechanism was implemented in gPROMS
365 software [38]. Simulations were performed under isothermal conditions at
366 500°C and the residence time of 0.5 s in order to investigate the effect of
367 potassium on cellulose pyrolysis products in more details. Simulation results
368 show that the increased potassium treatment causes a dramatic reduction in
369 the oil yield from 87.9 % from untreated avicel to 54.0 % at 0.5 % potassium
370 treatment. Further increase in potassium treatment causes a further decrease
371 in the oil yield to 46.2 % at 1 % potassium treatment. The decrease of the oil
372 yield is accompanied by an increase of the gas and char yield. The predicted
373 char yield increases from 3.7 % from pure avicel to 14.0 % at 1 % potassium
374 treatment and the gas yield increases from 8.4 % from pure avicel to 39.8 %
375 at 1 % potassium treatment, as shown in Figure 10 (a). [Figure 10 here]

376 The composition of the produced pyrolysis oil is also altered in the pres-
377 ence of potassium. The predicted levoglucosan weight fraction decreases dra-
378 matically from 48.8 % of the produced oil from pure cellulose to only 5.6 % of
379 the oil at 0.5 % potassium treatment, as shown in Figure 10 (b). Further in-
380 crease in the potassium treatment causes further decrease in the levoglucosan
381 yield to 3.1 % at 1 % potassium treatment. Increasing the level of potas-
382 sium treatment is expected to eventually lead to zero levoglucosan yield.

383 The large initial drop of the predicted levoglucosan yield supports the theory
384 that potassium inhibits the unzipping reactions of cellulose molecules. The
385 inhibition of levoglucosan formation results in the increased yields of acids
386 and aldehydes produced in the competing fragmentation reaction. Moreover,
387 the heating value of the produced oil decreases with the increased potassium
388 treatment due to increased predicted weight fraction of water from 6.1 % of
389 the oil from pure cellulose to 21.9 % of the oil at 1 % potassium treatment.
390 The increased water yield is due to both decreased yield of organics and ad-
391 ditional water produced in the catalyzed dehydration reaction.

392 The simulation results were validated with the experimental data ob-
393 tained from the fluidized-bed reactor [31]. The experiments in the fluidized
394 bed reactor were performed with avicel and 0.1% potassium treated avicel.
395 Experimentally the addition of potassium caused a reduction of oil yield from
396 86.9% to 68.8%, an increase of gas yield from 13.0% to 22.9%, and an in-
397 crease of char yield from 0.1% to 8.3%. The comparison of the experimental
398 data with model results is given in Table 5. [Table 5 here] The model results
399 are in excellent agreement with the experimental yields, with the differences
400 in yields below 5% points. This is a very good result, given the uncertainty
401 related to the experimental data. The standard deviation in the oil yield
402 from the fluidized bed reactor was 7.1 % points. The mass balance closure
403 in the pure avicel experiment and the potassium treated avicel experiment
404 was 94.9% and 90.4% respectively. The mass imbalance was related to the
405 oil collection system and it was added to the oil yield in Table 5. The lower
406 than expected experimental char yield is not completely unexpected since
407 the experimental fluidized-bed reactor is susceptible to errors in the char

408 collection system.

409 **5. Conclusions**

410 An adjusted cellulose pyrolysis mechanism was proposed to account for
411 the effect of potassium, which causes severe reduction of oil yield and has
412 an adverse effect on the oil composition. The simulation results reveal that
413 potassium strongly inhibits levoglucosan formation and promotes the forma-
414 tion of char, water and gases. As a result the predicted oil yield decreases
415 from 87.9% achieved with pure avicel to 54.0% at 0.5% potassium treatment,
416 the predicted char yield increases from 3.7% to 12.1 % and the predicted
417 gas yield increases from 8.4% to 33.9%. Moreover, the heating value of the
418 produced oil decreases because of the increased predicted weight fraction of
419 water from 6.1% to 18.1%. The simulation results were in good agreement
420 with the experimental data from a fluidized-bed reactor. The differences
421 in product yields were below 5% on an absolute yield basis. This suggests
422 that the underlying model with the proposed adjustments may be extended
423 to derive practical value for predicting fast pyrolysis products in biorefinery
424 plant simulations, especially when there are variations in ash in the supplied
425 feedstock.

426 **6. Acknowledgements**

427 We thank the U.S. Department of Energy’s Bioenergy Technologies Office
428 (DOE-BETO) for supporting this work under Contract No. DE-AC36-08-
429 GO28308 with the National Renewable Energy Laboratory.

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Table 1: Composition of ash (mass fractions) obtained from pine, switchgrass and oak at NREL

Feedstock	Pine	Switchgrass	Oak
Ash (%)	0.44	6.02	0.27
SiO ₂ (%)	39.88	64.96	4.78
Al ₂ O ₃ (%)	3.87	3.28	2.15
TiO ₂ (%)	<0.01	0.13	<0.01
Fe ₂ O ₃ (%)	2.70	1.01	0.81
CaO (%)	21.60	9.35	32.40
MgO (%)	5.08	2.03	1.54
Na ₂ O (%)	1.58	0.52	0.71
K ₂ O (%)	12.10	7.21	20.40
P ₂ O ₅ (%)	3.36	4.46	2.12
SO ₃ (%)	1.56	0.77	0.79
Cl (%)	0.31	3.28	2.15
CO ₂ (%)	9.24	0.91	32.48

Table 2: Summary of the research findings on the catalytic effect of alkali metals on cellulose pyrolysis reaction mechanism

Research Paper	Proposed Catalytic Effect on Reaction Mechanism
Madorsky et al. [20]	neutral salts suppress levoglucosan formation and promote char formation
Shafizadeh [18], Antal [19]	acid catalysts promote the formation of glucosenone, furan derivatives and char; alkaline catalysts promote the formation of glyoxal, acetaldehyde, low molecular weight carbonyl compounds and char
Fung et al. [21]	acid, alkaline and neutral salts inhibit the formation of levoglucosan
Evans et al. [30]	alkali metals inhibit the formation of levoglucosan by disrupting the transglycosylation, they promote the formation of carbonyl groups, double bonds and substituted furans
Piskorz et al. [22]	alkali metals suppress levoglucosan formation by capping the free ends of cellulose chains and inhibiting the unzipping reaction; they promote the formation of glycolaldehyde via the alternative pathway
Williams and Horne [15]	the catalytic effect of alkali metals is likely through ionic catalysis with a negligible impact of the acidity, alkalinity or neutrality of the salts
Kawamoto et al. [24, 23, 25]	levoglucosan undergoes secondary reactions through either fragmentation or polymerization, the reactions can occur also in liquid phase
Patwardhan et al. [35]	inorganic salts/ash promote the formation of formic acid, glycolaldehyde and acetol; they suppress the competing reaction leading to levoglucosan formation

Table 3: Major characteristic fragment ions in cellulose pyrolysis product mass spectra and their possible sources

Ion (m/z)	Chemical Formula	Possible Source
31	CH_3O	hydroxyacetaldehyde
32	CH_4O	hydroxyacetaldehyde
43	$\text{C}_2\text{H}_3\text{O}$	acetyl
57	C_2HO_2 , $\text{C}_3\text{H}_5\text{O}$	levoglucosan
60	$\text{C}_2\text{H}_4\text{O}_2$	levoglucosan, acetic acid, hydroxyacetaldehyde
70	$\text{C}_4\text{H}_6\text{O}$	levoglucosan
73	$\text{C}_3\text{H}_5\text{O}_2$	levoglucosan
85	$\text{C}_4\text{H}_5\text{O}_2$	5-hydroxymethylfurfural, pentosan
97	$\text{C}_5\text{H}_4\text{O}_2$	5-hydroxymethylfurfural
98	$\text{C}_5\text{H}_6\text{O}_2$	levoglucosan, furfuryl alcohol
110	$\text{C}_6\text{H}_6\text{O}_2$	5-hydroxymethylfurfural, catechol, resorcinol
126	$\text{C}_6\text{H}_6\text{O}_3$	5-hydroxymethylfurfural, trihydroxybenzene, levoglucosenone
144	$\text{C}_6\text{H}_8\text{O}_3$	levoglucosan

Table 4: Activation energies and pre-exponents of reactions R2, R3, R4 for pure cellulose

Reaction	Activation Energy (kJ/mol)	Pre-exponent (1/s)
R2	93.6 $\pm$ 9.6	3.78 $\cdot$ 10 ⁹
R3	90.8 $\pm$ 0.8	2.61 $\cdot$ 10 ⁹
R4	142.3 $\pm$ 2.1	2.00 $\cdot$ 10 ⁹

Table 5: Comparison of avicel and potassium treated avicel pyrolysis product yields from model prediction with experimental data

Product Yield	Avicel (Simulation/Experiment)	Avicel + 0.1% K (Simulation/Experiment)
Oil (%)	87.9/86.9	71.2/68.6
Char (%)	3.7/0.1	8.0/8.3
Gas (%)	8.4/13.0	20.8/22.9