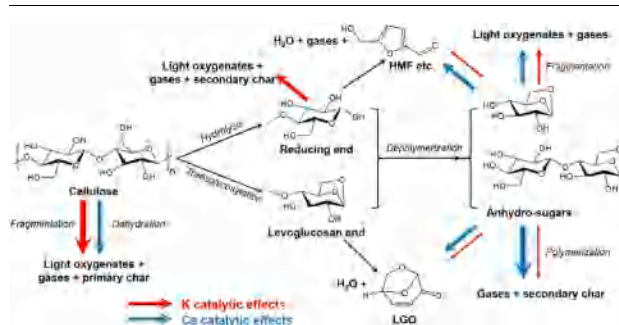Full Length Article

Effects of KCl and CaCl$_2$ on the evolution of anhydro sugars in reaction intermediates during cellulose fast pyrolysis

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GRAPHICAL ABSTRACT

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ABSTRACT

Reaction intermediates mainly consisting of anhydro sugars are the crucial transitional stage connecting the cellulose feedstock and the three phases of products during pyrolysis. For the first time, the effects of KCl and CaCl$_2$ on the evolution of anhydro sugars in reaction intermediates were examined by using levoglucosan pyranose (LGA_Pyran), maltosan and cyclodextrin as model compounds. These compounds were subjected to fast pyrolysis on a Py-GC/MS, where dry samples were heated at a heating rate of 10 °C/s to 500 °C with a holding time of 20 s at 500 °C. The results indicated that KCl had a stronger inhibitory effect than CaCl$_2$ on LGA_Pyran formation during cellulose fast pyrolysis. However, during the pyrolysis of the oligosaccharides, the catalytic effects of KCl were weakened by the low degree of polymerization and the lack of reducing ends, while the catalytic effects of CaCl$_2$ were enhanced by a better distribution. This led to the reverse order of their effects on LGA_Pyran formation. Furthermore, much higher char yields from oligosaccharides under catalysis of CaCl$_2$ than under the catalysis of KCl indicate the prominent influence of CaCl$_2$ on the secondary reactions of reaction intermediates leading to secondary char.

1. Introduction

The extensive use of traditional fossil fuels brings about various concerns with regard to energy shortage and environmental pollutants [1–4]. Biomass, which is a promising carbon-based clean substitute resource for fossil fuels, can provide bio-fuels, chemicals and carbon materials through thermochemical or biochemical conversion processes [5–7]. Among them, the fast pyrolysis of biomass is a promising technology for the production of bio-fuels, whose characteristics depend on the type of feedstock [8,9]. It is known that indigenous alkaline and

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alkaline earth metals (AAEM) in biomass can strongly influence the products distribution of the fast pyrolysis of biomass [10–14]. Therefore, an understanding of the effects of AAEM on biomass pyrolysis is of crucial importance for biomass commercialization. Cellulose is one of the three main components of biomass, whose evolution during pyrolysis can be strongly influenced by the AAEM. It was proposed that AAEM can favour the degradation of cellulose and strongly promote the formation of char and low molecular weight (LMW) species at the expense of anhydro sugars [15–19]. For LMW species, alkaline metals can promote the formation of hydroxyacetaldehyde (HAA) and acetol, while alkaline earth metals are beneficial for the formation of furans such as furfural [10], with the effects depending on the loading level of AAEM. However, due to the numerous reactions related to these chemicals during cellulose pyrolysis, the role of the AAEM, especially the different catalytic mechanisms of the four cations, are still poorly understood.

According to the Broido-Shafizadeh model [20], the evolution of cellulose can be divided into two steps: the formation of reaction intermediates (or active cellulose) through depolymerization reactions, and their subsequent degradation, involving numerous reactions, e.g., dehydration, depolymerization, isomerization, fragmentation and so forth. The reaction intermediates were proposed to consist of anhydro sugars and oligosaccharides [21,22], and levoglucosan pyranose (LGA_Pyran) and cellobiosan are the prominent anhydro sugars in the reaction intermediates [23]. Yu et al. [24] suggested that $MgCl_2$ is more effective in promoting the formation of water-soluble intermediates than NaCl through the weakening of hydrogen bonds and the cleavage of glycosidic bonds. This result was attributed to the stronger Lewis acidity of Mg^{2+} than Na^+. In a previous work [23], we explored the effects of KCl and $CaCl_2$ during the first step and concluded that at low temperatures, AAEM can improve the depolymerization of cellulose leading to more reaction intermediates. However, as the temperature increases, the yield of reaction intermediates is reduced, leading to less anhydro sugars in tar. In addition, at different temperature intervals, the AAEM affect the pyrolysis of cellulose in different ways. Considering that the AAEM have similar effects as secondary reactions, researchers tried to separate the effects of AAEM on the primary and secondary reactions [23,25–28]. A review paper from Dauenhauer's group emphasized the importance of revealing the roles of the natural catalysts in the formation of reaction intermediate liquids [29]. Recently, Zhu et al. [27] examined the pyrolysis of thin-film and powder samples of cellulose loaded with magnesium and calcium. They suggested that alkaline earth metals mainly influence the secondary (diffusion-limited) reactions of volatile species within molten cellulose, i.e. reaction intermediates, where Ca^{2+} performed more effectively than Mg^{2+}. In addition, it seems that the effects of the AAEM on the primary and secondary reactions are strongly related to their loading levels [28]. By comparing the pyrolysis in the vacuum and atmospheric pressure, it was found that the low content of potassium mainly catalysed the secondary degradation of the volatiles, while increasing the potassium remarkably promoted CO and CO_2 formation from the reacting sample. Therefore, it can be concluded that the effects of the AAEM on the degradation of reaction intermediates vary with the type of feedstock and pyrolysis conditions, which makes them complex. To simplify the research of intermediates degradation, model compounds are frequently used. Zhou et al. [30,31] conducted experiments and detailed kinetic modelling on the pyrolysis of glucose-based carbohydrates including glucose, cellobiose, maltohexaose, and cellulose with NaCl added. Their model included > 300 components and 200 elemental reactions to consider the interactions of Na^+ with neutral species and the reactions of Na^+-complexes. The model results show that the strong reduction of LGA_Pyran under the catalysis of NaCl is due to the promoted dehydration reactions at the expense of the depolymerization via end-chain initiation and depropagation rather than the secondary degradation of LGA_Pyran. In addition, the quantum chemical calculation of cellobiose with AAEM was also conducted [32,33].

It was proposed that alkali metals can interact with the oxygens of hydroxyl and ether groups to form a complex, which stabilizes the glycosidic bonds and favours ring opening [32]. However, Arora et al. [33] suggested that different from the negligible effects of alkali metals, inhibitory effects of Mg^{2+} and Ca^{2+} were obtained for the dehydration pathway (i.e. end-chain initiation) leading to LGA_Pyran, while Mg^{2+} can also strongly accelerate glycosylation, ring contraction and the mannose pathway.

Despite the above experimental and numerous studies using reducible carbohydrates, limited work has been performed with regard to about the pyrolysis of anhydro sugars, which actually are the dominant component of reaction intermediates during cellulose pyrolysis. In this work, the effects of KCl and $CaCl_2$ on the degradation of reaction intermediates (mainly anhydro sugars) are explored. LGA_Pyran and maltosan were selected as representatives. Furthermore, given that anhydro sugars with high degree of depolymerization (DP > 3) are inaccessible, α-cyclodextrin (DP = 6), which has no reducing end such as anhydro sugars, was also applied as the representative of high DP anhydro sugars in reaction intermediates. To the best of our knowledge, this is the first study that explores the different catalytic effects of the AAEM on the pyrolysis of the anhydro sugar part of the reaction intermediates. The fast pyrolysis of the carbohydrates (i.e. LGA_Pyran, maltosan, maltose, cyclodextrin and cellulose) containing KCl or $CaCl_2$ was conducted on a Py–GC/MS.

2. Materials and methods

2.1. Materials

Cellulose (Avicel PH-101), α-cyclodextrin, maltose and LGA_Pyran (1,6-anhydro-β-D-glucopyranose) were all obtained from Sigma-Aldrich (USA). Maltosan was purchased from Carbosynth Ltd. (England) with negligible amounts of impurities. KCl and $CaCl_2$ were purchased from Sinopharm Chemical Reagent (China) as AR grade chemicals. Table 1 shows the chemical structures of the samples in this work.

2.2. Loading method and Py–GC/MS experiments

Fast pyrolysis experiments of carbohydrates were conducted on a CDS5200 Pyroprobe (CDS Analytical, USA) with a 7890A/5975C GC/MS (Agilent Technologies, USA). In each experiment, ~0.3 μl of the aqueous mixture of the sample (10 wt%) with KCl or $CaCl_2$ was loaded in the middle of a quartz-tube between two layers of quartz wool. Subsequently, the quartz-tube was heated at 75 °C for 12 h to dry the sample. In addition, the quartz-tube was weighed before and after the loading process to determine the sample amount. The loading levels of K or Ca were 0.0, 0.001, 0.005, 0.025 and 0.1 mol/mol of glucose units. FTIR analysis (Fig. S1) revealed that the chemical structure of the samples did not change during the loading process. The tube with the dried sample was loaded in Py and heated at a heating rate of 10 °C/s–500 °C with a holding time of 20 s. More details regarding the setting of the Py–GC/MS are available elsewhere [23,35]. After pyrolysis, the tube was weighed again to determine the char yield based on the weight. By regarding the char as 100% carbon, we can obtain the yield of char based on carbon. Each experiment was repeated three times to assess the repeatability of the data.

2.3. Quantification of components

In this work, according to the method used in previous works [34,36], 27 compounds, monitored by MS, were determined according to the NIST library database, among which 12 main compounds were quantified by standards and the remaining 15 compounds were just identified by MS and standards with similar molecular weight and structure. It is noteworthy that standard curves of LGA_Pyran and HAA were established by the pyrolysis of pure LGA_Pyran and HAA dimer,

Table 1
Chemical structure of samples used in this work [34].

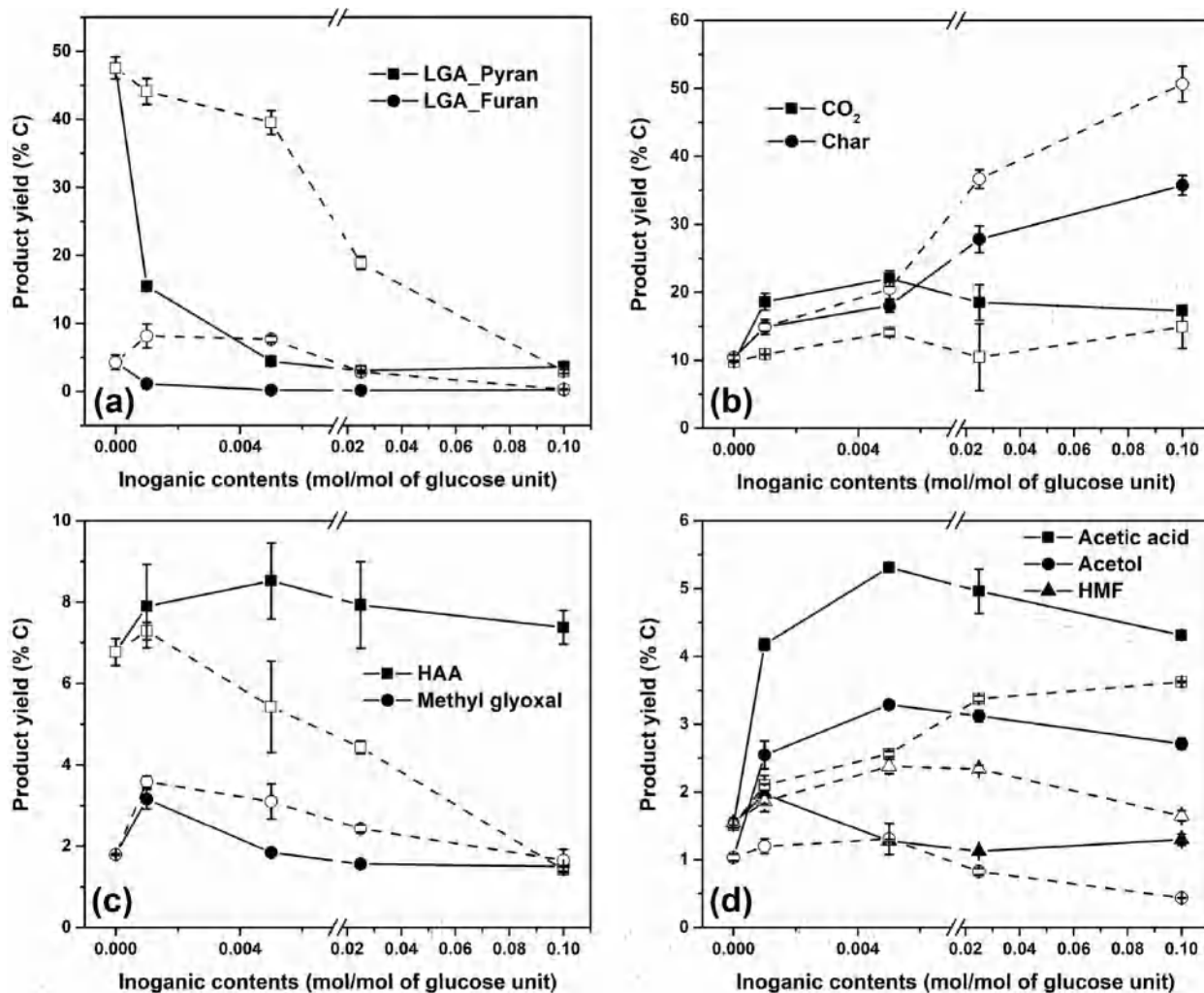| Compound	DP	Glycosidic bond	Reducing end/DP	Structure
LGA_Pyran	1	None	0	
Maltose	2	α-1, 4	0.5	
Maltosan	2	α-1, 4	0	
Cyclodextrin	6	α-1, 4	0	
Cellulose	~ 200	β-1, 4	~ 0.005	

Fig. 1. Effects of KCl (solid symbols) and $CaCl_2$ (hollow symbols) with different loading levels on the main products distribution of cellulose pyrolysis.
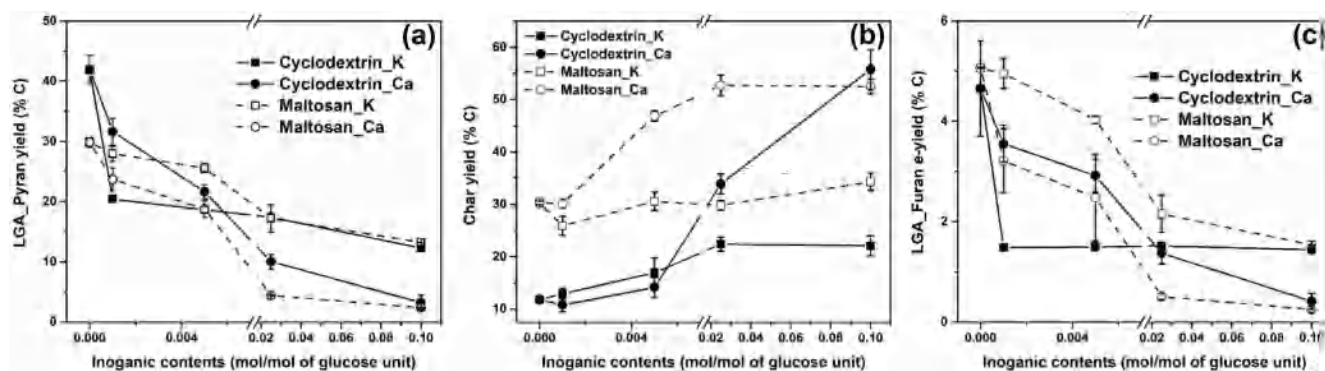
Fig. 2. Effects of KCl and CaCl$_2$ with different loading levels on the formation of LGA_Pyran (a), char (b), and LGA_Furan (c) during cyclodextrin (solid symbols) and maltosan (hollow symbols) pyrolysis.

while other standard curves depended on the direct injection of the acetone solutions of standards into the GC/MS. Details of the standard curves and quantification of the components are listed in Table S1. It needs to be stated that different from our previous work [34], the present study used the standard of acetol instead of HAA to determine methyl glyoxal. In consideration of that H$_2$O was not quantified in this work, all of the yields were presented in the form based on carbon (% C), i.e. the carbon ratio of a certain product to the total carbon of the loaded cellulose.

3. Results and discussion

In our previous work [34], the product distributions of the glucose-based anhydro sugars and oligosaccharides were compared to explore the evolution of reaction intermediates and the role of different chain ends during this process. The data of the pure samples was also used in this work together with the products distribution of the samples loaded with KCl or CaCl$_2$, with the aim of examining the effects of the two salts on the evolution of the reaction intermediates. The detailed product distributions of different samples are listed in Tables S2–6. For the closures of the total yield of determined products based on carbon, two observations should be made. First, it is related with the closure of 100.2% in the cellulose pyrolysis with 0.005 mol CaCl$_2$/mol of glucose units. This is perhaps due to the quantification of the CO$_2$ using the standard curve of HAA, which overestimates the yield. For example, the yield of CO$_2$ (10.43% C) during the pyrolysis of pure cellulose determined in this work is much higher than the value of 2.19% C obtained under similar conditions in a previous work [30]. Therefore, in this work, the quantitative results are not accurate for those products quantified according to the standard curves of other compounds with similar a chemical structure and molecular mass. Then in consideration of this inaccuracy, the estimated yield (e-yield) is used for them instead of the yield. Second, it is related with the much weaker closures of the pyrolysis of cyclodextrin and maltosan compared with cellulose under catalysis, which is discussed below (Section 3.2.3).

3.1. Effects of KCl and CaCl$_2$ on the products distribution of cellulose pyrolysis.

As shown in Table S2, compared with the pyrolysis of pure cellulose, cellulose with catalyst did not yield additional main products. Fig. 1 shows the variation of the yields of the main products (> 1% C) in cellulose pyrolysis under catalysis. Compared with CaCl$_2$, KCl presents a much stronger inhibitory effect on the formation of LGA_Pyran, as shown in Fig. 1a. In addition, as shown in Fig. 1b–d, KCl generally favoured light oxygenates including CO$_2$, HAA, acetic acid and acetol, except methyl glyoxal, while CaCl$_2$ favoured 5-Hydroxymethylfurfural (HMF). These results are in line with a previous work [10]. In addition, with the increase of the catalyst loading, the yields or the e-yields of

volatile products decreased and the char yield increased, indicating the strongly catalysed char formation reactions. Fig. 1a also shows the e-yield of levoglucosan furanose (LGA_Furan), which is an isomer of LGA_Pyran with a furan ring. It is seen that the e-yield of LGA_Furan follows a similar tendency as that of LGA_Pyran under the catalysis of KCl or CaCl$_2$, except that different from the completely inhibitory effect of KCl, an obvious positive effect with a low amount of CaCl$_2$ was observed.

Previous works suggested that volatiles obtained during the cellulose pyrolysis result from the direct decomposition of the cellulose chain and the secondary reactions of reaction intermediates formed by end-chain initiation and depropagation [37,38]. The catalysis of KCl and CaCl$_2$ can alter the kinetic parameters of the reactions involved in the two mechanisms and result in different products distribution [30,39]. Here, α-cyclodextrin (DP = 6), maltosan (DP = 2) and LGA_-Pyran (DP = 1) were selected as model compounds of reaction intermediates.

3.2. Effects of KCl and CaCl$_2$ on the products distribution of cyclodextrin and maltosan pyrolysis

Cyclodextrin was found to result in a similar products distribution during pyrolysis to that cellulose because of their close ratios of reducing ends [40]. Due to its simpler and smaller structure compared with cellulose, it was used as surrogate of cellulose in research of the chemical kinetics and molecular dynamics modelling [40,41]. However, as for the catalytic effects of KCl and CaCl$_2$, significant differences were observed between them.

3.2.1. LGA_Pyran, LGA_Furan and char formation

The most prominent difference is the change of the inhibiting effect order of two catalysts on LGA_Pyran. The effect of CaCl$_2$ on LGA_Pyran was remarkably enhanced during the pyrolysis of cyclodextrin compared with cellulose, while that of KCl was reduced, especially at higher loading levels. For example, in Fig. 1a and Fig. 2a, as KCl increases from 0.0 to 0.1 (0.005) mol/mol of glucose units, the yields of LGA_Pyran from cellulose and cyclodextrin decrease by 92.3 (67.4)% and 70.6 (51.3)%, respectively. For CaCl$_2$, the decrease of the LGA_Pyran yield is remarkably accelerated during the cyclodextrin pyrolysis. For example, with 0.025 mol/mol of glucose, cellulose and cyclodextrin yielded 39.7% and 23.9% of the LGA_Pyran maximum yield, respectively. This led to the lower yield of LGA_Pyran under the catalysis of CaCl$_2$ compared with KCl at 0.1 mol/mol of glucose units. Generally, the change of the effects of two salts on LGA_Pyran may be attributed to two mechanisms, a chemical mechanism and a physical mechanism. The chemical mechanism is mainly related with the different DP of the two samples, while the physical one is linked to the diffusion of the two salts in the samples during pyrolysis. For amorphous cyclodextrin, the two salts can distribute well after the loading process in this work, while the

crystalline region of the cellulose with a compact hydrogen bonds network is inaccessible to aqueous salt solution [42]. This may restrict its distribution during the salt loading process and its diffusion during pyrolysis, which together alter the catalytic effect. With regard to this issue, the pyrolysis of maltosan, which is water-soluble but with a lower DP, provided interesting results.

As shown in Fig. 2a, during the maltosan pyrolysis, with the KCl loading increasing from 0.0 to 0.1 mol/mol of glucose units, the yield of LGA_Pyran gradually decreased by 55.7% from 29.85 to 13.23%C, a value much lower than the value of 92.3% obtained for cellulose and 70.6% obtained for cyclodextrin. It is thus obvious that the effects of KCl on LGA_Pyran formation from the different feedstocks follow the order cellulose > cyclodextrin > maltosan. Thus, it seems that the effect of KCl on LGA_Pyran has a strong relationship with the DP. Furthermore, the char yields shown in Fig. 1b and Fig. 2b follow a similar tendency, increasing by 243.5%, 87.2% and 13.1% (based on the char yield from pure samples) during the pyrolysis of cellulose, cyclodextrin and maltosan respectively. This indicates the weak effect of KCl on the secondary reactions of reaction intermediates yielding secondary char. Correspondingly, as shown in Fig. 2b, $CaCl_2$ exhibits a positive effect on the secondary char formation in reaction intermediates. Moreover, in Fig. 2a, under the catalysis of different amounts of $CaCl_2$, the yields of LGA_Pyran from maltosan, divided by the initial maximum value, are 0.79, 0.63, 0.15 and 0.08, which are close to those from cyclodextrin (0.75, 0.51, 0.24 and 0.08). As mentioned above, a chemical mechanism (i.e. DP) or a physical mechanism (i.e. diffusion) may be responsible for the effects of the two salts on LGA_Pyran from different feedstocks. Then, in consideration of the similar effects of $CaCl_2$ on cyclodextrin and maltosan pyrolysis, which are stronger than those on cellulose pyrolysis, it seems that the effect of $CaCl_2$ is highly related to its distribution within the feedstock. These results support the conclusion in our previous work that KCl can catalyse the cleavage of glycosidic bonds and ring opening directly, while $CaCl_2$ is more effective on dehydration reactions and cross-linking reactions [23,24].

Fig. 2c also shows the yields of LGA_Furan during the pyrolysis of cyclodextrin and maltosan. Previous works [37,40,43,44] proposed a mechanism for the conversion of β-D-glucofuranose to LGA_Furan through the opening of D-glucose. As shown in Fig. 2c, LGA_Furan follows a similar tendency as that of LGA_Pyran during the cyclodextrin and maltosan pyrolysis. During the pyrolysis of glucose-based carbohydrates (glucose, cellobiose, and so forth) under the catalysis of NaCl [30,31], a similar strong relationship was also obtained between these two types of levoglucosan. This suggests that LGA_Furan may be a by-product produced simultaneously during the depolymerization reaction leading to LGA_Pyran.

3.2.2. HMF and levoglucosenone (LGO) formation

Given the high value of furans for the synthesis of a broad range of chemicals and fuels [45], various earlier studies concentrated on their formation mechanism. Since glucose is the intermediate from cellulose to furans during hydrolysis, this mechanism was also used for furans formation in cellulose pyrolysis and related kinetic modelling [44,46–48]. However, this mechanism as the main process is uncertain because of the limited amount of glucose present during cellulose pyrolysis [21]. Shen and Gu [49] suggested another two possible mechanisms for furans, i.e., the direct opening of pyran rings followed by rearrangement reactions or the secondary transformation of LGA_Pyran. Using CPMD simulation, Mettler et al. [40] proposed the direct formation of furans from the cellulose chain without intermediates such as LGA_Pyran and glucose. In the present work, KCl and $CaCl_2$ showed quite different effects on HMF formation during the pyrolysis of cyclodextrin and maltosan compared with cellulose. As shown in Fig. 3a, when KCl increased from 0.0 to 0.1 mol/mol of glucose units, the yield of HMF from cyclodextrin first decreased from 1.92 ± 0.01 to 1.19 ± 0.01% C and then gradually increased to a maximum of 2.18 ± 0.12% C. For the $CaCl_2$, lower yields of HMF were obtained for

all of the loading levels compared with pure cyclodextrin. In regard to the maltosan pyrolysis, the two salts showed similar positive effects on HMF formation. Hence, it seems that the promotion of HMF formation during the cellulose pyrolysis by a low amount of $CaCl_2$ is due to the direct influence of $CaCl_2$ on the cellulose chain rather than on the reaction intermediates.

LGO is an important chiral synthon for chemical synthesis [30]. In our previous work [34], it was concluded that the levoglucosan end of maltosan strongly promotes LGO formation. As shown in Fig. 3b, the addition of both salts almost suppressed the formation of LGO. In contrast, the trace amounts of LGO obtained through the pyrolysis of pure cyclodextrin are obviously improved by $CaCl_2$, which is in line with the result for cellulose shown in Table S2. It was proposed that the formation of LGO is related to the dehydration reactions [50], which can be strongly catalysed by $CaCl_2$ [23].

3.2.3. Formation of light oxygenates

Fig. 4 shows the yields of light oxygenates during the pyrolysis of cyclodextrin and maltosan. As shown in Fig. 4a–c, the formation of HAA, acetol and methyl glyoxal was generally suppressed by both KCl and $CaCl_2$, especially at high loading levels, with $CaCl_2$ being more active than KCl. Meanwhile, the yields of char and CO_2 improved for high loadings of KCl and $CaCl_2$, as shown in Figs. 2b and 4e. It seems therefore that the decreases of these light oxygenates during the cyclodextrin and maltosan pyrolysis can be attributed to the improved repolymerisation reactions and cross-linking reactions under catalysis [25,51]. Here, the abovementioned weaker closures of cyclodextrin and maltosan compared with cellulose can be attributed to the oligomers captured by the transfer line, which are gases undetectable by GC/MS, generated during the repolymerisation and cross-linking reactions [30]. During the cellulose pyrolysis, such as for HMF, light oxygenates can also be generated from the direct decomposition of the cellulose chain and the secondary degradation of reaction intermediates [40,52]. As shown in Fig. 1, the initial increase of light oxygenates may be due to the improved decomposition of the cellulose chain with low amounts of KCl or $CaCl_2$. However, a greater catalyst loading can affect the reaction intermediates, which improves char and non-condensable gas formation at the expense of light oxygenates [28]. Different from other oxygenates, the acetic acid shown in Fig. 4d can be obviously promoted by the two catalysts during maltosan pyrolysis, indicating another mechanism.

3.3. Effects of KCl and $CaCl_2$ on the products distribution of LGA_Pyran pyrolysis

LGA_Pyran is the uppermost product and the most prominent anhydrosugar in reaction intermediates obtained during pure cellulose pyrolysis [22]. The secondary degradation and repolymerisation of it play a crucial role in the pyrolysis of cellulose, especially with limited heat and mass transfer. Numerous papers studied the effects of the AAEM on its secondary degradation and repolymerisation [25,27,30,31,51]. It was proposed that the AAEM favour the degradation and polymerization of LGA_Pyran, respectively, leading to LMW species and char. Compared with alkali metals, alkaline earth metals have stronger catalytic activities on the LGA_Pyran polymerization leading to higher yields of secondary char [25]. In this work, the effects of KCl and $CaCl_2$ on LGA_Pyran pyrolysis were compared directly. As seen in Fig. 5a, a recovery of almost 100% of LGA_Pyran was obtained after its pyrolysis with no metals involved. After the loading of KCl or $CaCl_2$, LGA_Pyran was consumed with the production of char and LMW species, mainly consisting of HMF, HAA, LGO, furfural, methyl glyoxal, acetic acid and CO_2. As shown in Fig. 5b–e, amounts of $CaCl_2$ below 0.005 mol/mol of glucose units show strong positive effects, which decreased for higher loading levels, especially with regard to the formation of HAA and methyl glyoxal. Correspondingly, KCl shows weaker effects in regard to both LGA_Pyran and LMW species, and the effects
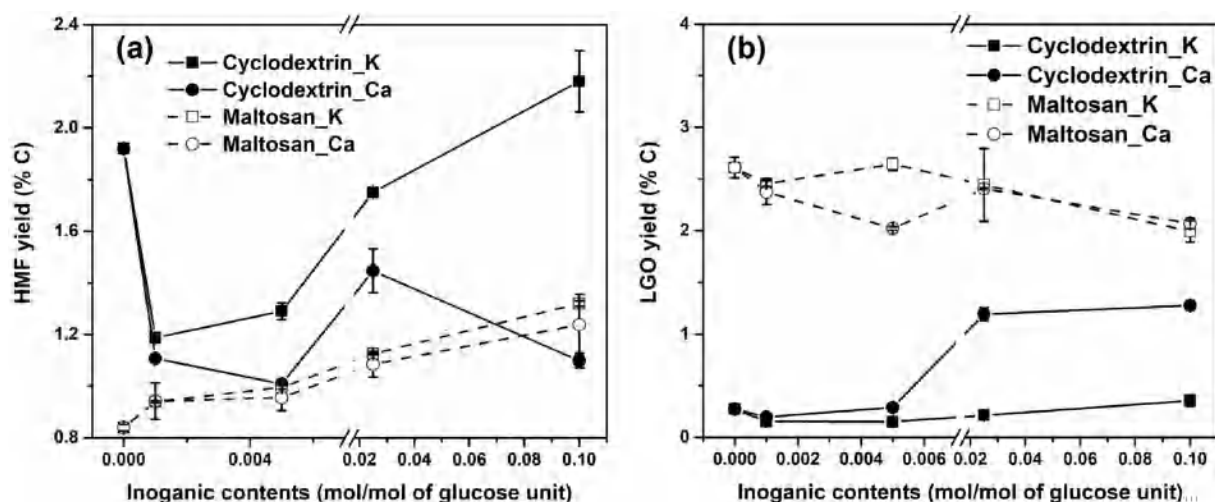
Fig. 3. Effects of KCl and CaCl$_2$ with different loading levels on the formation of HMF (a) and LGO (b) during cyclodextrin (solid) and maltosan (empty) pyrolysis.
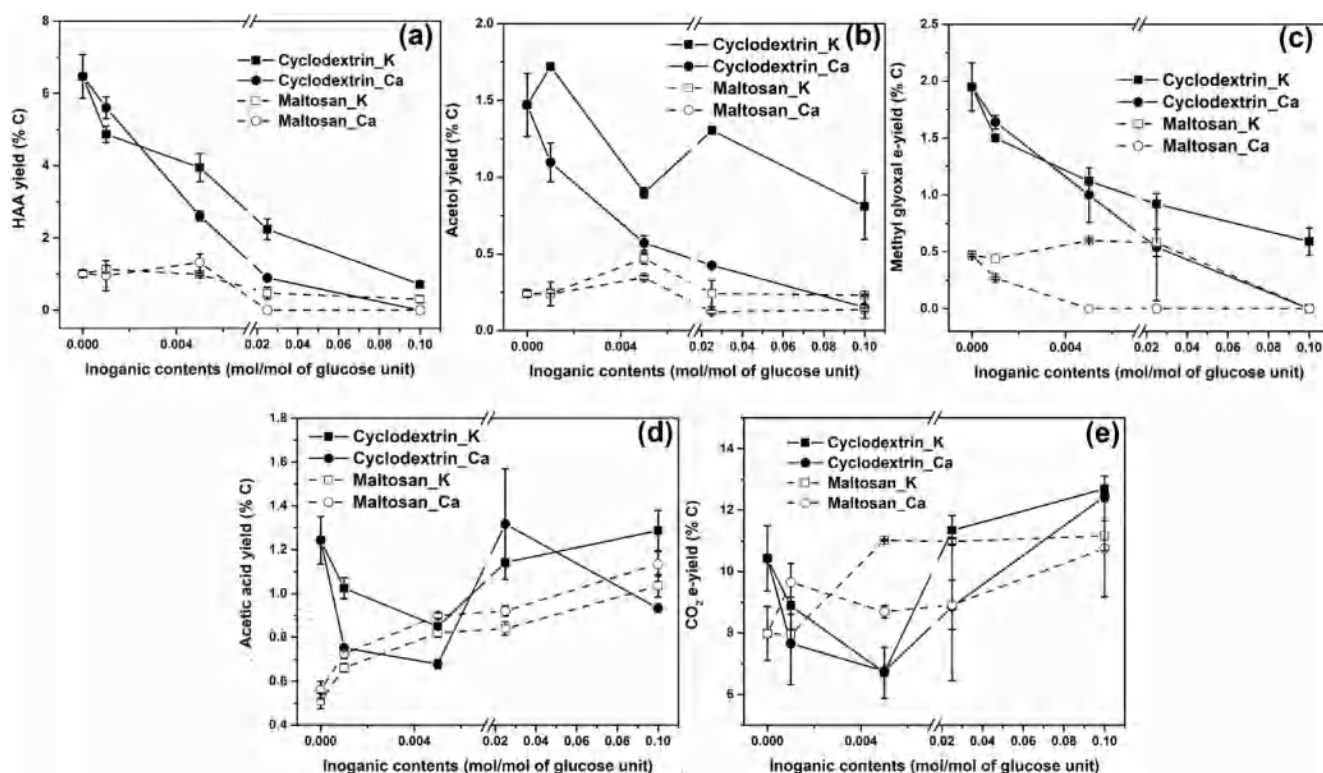

Fig. 4. Effects of KCl and CaCl$_2$ with different loading levels on the formation of light oxygenates (a. HAA, b. acetol, c. methyl glyoxal, d. acetic acid and e. CO$_2$) during cyclodextrin (solid symbols) and maltosan (hollow symbols) pyrolysis.

increased synchronously with the catalyst loading. These results are in agreement with the conclusion discussed above that CaCl$_2$ has a stronger catalytic effect on the secondary reactions of reaction intermediates than KCl. In addition, considering the reduced yield of LGA_Pyran during the cellulose pyrolysis, as shown in Fig. 1a, and the promoted amount of LMW species, as shown in Fig. 5, the decomposition of LGA_Pyran by catalysts cannot account for the total increase of LMW species during the cellulose pyrolysis.

3.4. Catalytic mechanism of KCl and CaCl$_2$

Several mechanisms have been provided for the inhibitory effects of inorganic species on the depolymerization of cellulose forming LGA_Pyran. As mentioned above, Saddawi et al. [32] conducted the ab

initio modelling of cellobiose degradation with K$^+$ and Na$^+$. The results showed that the interactions between cations and the oxygens of hydroxyls and glycosidic bonds can prevent the glycosidic bonds from depolymerization. Compared with cations, anions were proposed to be less active in forming salt-carbohydrate complexes [53]. Their effects mainly depend on the different affinities with cations [39]. Furthermore, chlorine seems to start to release at low temperatures such as 200 °C and have limited direct effects on the pyrolysis of biomass [54]. Conversely, as a favourable catalyst for gasification, potassium was proposed to enhance the homolytic scission of pyran rings leading to the formation of LMW species [55,56]. In addition, it was also proposed that inorganic ions could cap ionic or free chain ends during the cellulose depolymerization and restrain the 'unzipping' process forming LGA_Pyran [52,57]. However, recent studies argued that
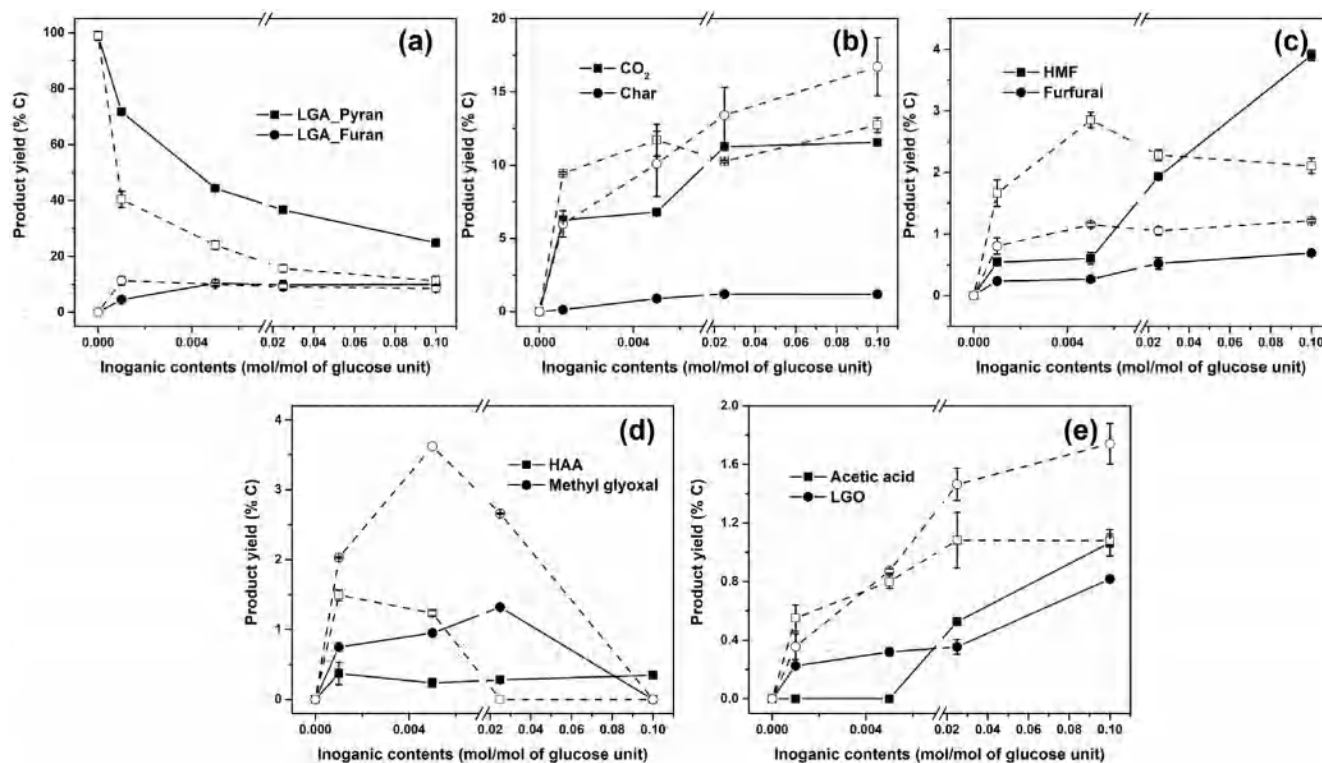
Fig. 5. Effects of KCl (solid symbols) and CaCl₂ (hollow symbols) with different loading levels on the main products distribution of LGA_Pyran pyrolysis.

transglycosylation and hydrolysis, which lead to levoglucosan and reducing ends, respectively, seem more reasonable than homolytic and heterolytic cleavage [41,58]. Therefore, in this work, by comparing the products distribution of maltosan and maltose under catalysis, the clear effect of inorganic species on the different chain ends can be obtained, which can perhaps provide another catalytic mechanism.

As shown in Fig. 6, under the catalysis of CaCl₂ (0.025 mol/mol of glucose units), the yield of LGA_Pyran decreased by 85.1% (from 29.8% C to 4.4% C) and 82.4% (from 26.4% C to 4.6% C) during the pyrolysis of maltosan and maltose respectively. Correspondingly, for KCl, the yield respectively decreased by 42.3% (from 29.8% C to 17.2% C) and 67.8% (from 26.4% C to 8.5% C). It can thus be concluded that the reducing ends enhance the catalytic effect of KCl, but have a negligible

influence on CaCl₂. This conclusion is also supported by the increased char and CO_2 yields during the maltose pyrolysis with KCl. During the pyrolysis of cellulose with loaded KCl, as shown in Fig. 1, the higher DP can provide more reducing ends through hydrolysis before the volatiles, and these ends probably interact with the KCl. However, more research is needed for the detailed reaction mechanism of the interactions. With regard to CaCl₂, its similar effects on cyclodextrin, maltosan and maltose indicate the negligible influence of DP and the chain ends on the catalytic the effect of CaCl₂. Therefore, the distinguishable improvement of the effect of it (especially with low loading levels) on LGA formation during the pyrolysis compared with cellulose is probably attributed to its distribution during the loading process and the diffusion during pyrolysis. In a previous work [59], it was proposed that alkaline earth metals can be passive during the interaction with liquid intermediates, which indicates the poor diffusion of alkaline earth metals during cellulose pyrolysis. The conclusions about the different mechanisms of KCl and CaCl₂ are also supported by the influence of the loading level on the catalytic effects of KCl and CaCl₂. As shown in Figs. 1a and 2a, the effect of the KCl levels off with loading amounts above 0.005 mol/mol of glucose units for cellulose and cyclodextrin, which perhaps indicate the dependence of the effect on the initial DP of the feedstock. In contrast, the inhibitory effect of CaCl₂ gradually increases with an increased loading level.

As the competing reaction of LGA_Pyran formation, the formation of LMW species (including LGO, furans and light oxygenates) and char can be catalysed by KCl and CaCl₂ through direct interactions with the cellulose chain or the secondary reactions of reaction intermediates [10,60]. Here, depending on different pathways, the char is divided into primary and secondary char. During the pyrolysis of cellulose, 0.025 mol of KCl or CaCl₂/mol of glucose units increased the char yield by 2.43 (10.4% C to 35.7% C) and 3.87 (10.4% C to 50.6% C) times, respectively. Correspondingly, the values for cyclodextrin and maltosan were 0.87 (KCl), 3.72 (CaCl₂) and 0.14 (KCl), 0.73 (CaCl₂), respectively. Obviously, the promotion effects of the two salts on char formation are reduced during the pyrolysis of the two oligosaccharides as compared with cellulose. Furthermore, the maximum char yield of the
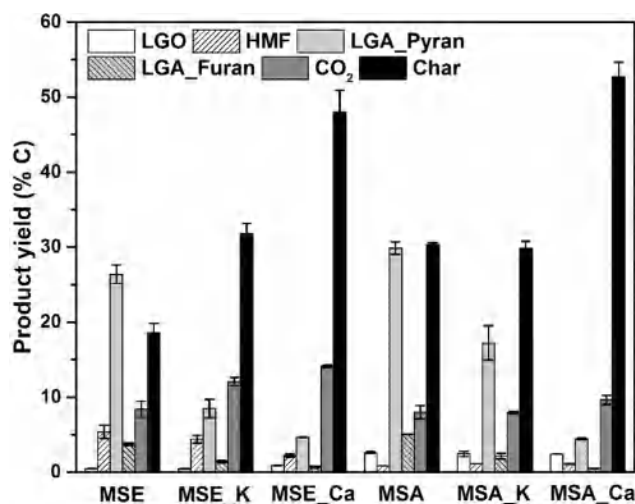

Fig. 6. Main products distribution (based on carbon) of the pyrolysis of maltosan (MSA) and maltose (MSE) under the catalysis of KCl (0.025 mol/mol of glucose units) or CaCl₂ (0.025 mol/mol of glucose units).
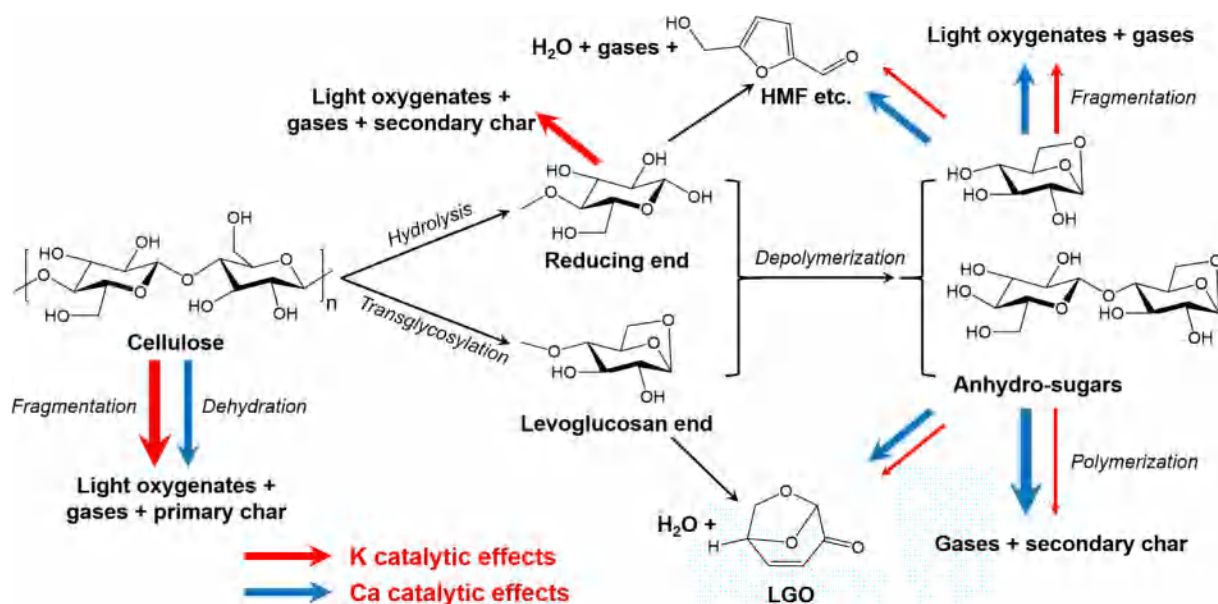
Fig. 7. Summary of the effects of KCl and CaCl$_2$ on primary (direct decomposition of cellulose) and secondary (evolution of reaction intermediates) reactions during cellulose pyrolysis. The different widths of the blue and red lines represent the different strengths of the effects of KCl and CaCl$_2$.

LGA_Pyran pyrolysis under the catalysis of KCl and CaCl$_2$ were 1.2% C and 16.7% C, respectively. Given the maximum decrease of LGA_Pyran during the cellulose pyrolysis under catalysis (43.94% C for KCl and 44.64% C for CaCl$_2$), the increase of the char yield cannot be all attributed to the promoted secondary reactions of LGA_Pyran by the two salts.

Based on the above discussion and our previous work [34], the effects of KCl and CaCl$_2$ on the cellulose pyrolysis are summarized in Fig. 7. The different widths of the blue and red lines present the different strengths of the effects of K and Ca. During pyrolysis, cellulose produces reducing and levoglucosan ends through hydrolysis and transglycosylation, respectively, and further depolymerizes into reaction intermediates, mainly composed of anhydro sugars. KCl can strongly promote the direct dehydration and fragmentation of the cellulose chain leading to light oxygenates, gases and primary char, perhaps through interactions with the reducing ends, which strongly decreases the yields of sugars and bio-oil even with a low content of KCl. In contrast, CaCl$_2$ has strong effects on both primary and secondary reactions, especially on the polymerization of anhydro sugars in reaction intermediates, which lead to a high yield of char. Moreover, the effects of CaCl$_2$ are strongly related to the amount of CaCl$_2$ in the feedstock.

4. Conclusions

LGA_Pyran, maltosan and cyclodextrin were selected as the representative model components for the anhydro sugars in reaction intermediates during cellulose pyrolysis. Fast pyrolysis experiments of these samples and cellulose were conducted on a Py-GC/MS with different loading amounts of KCl and CaCl$_2$, aiming to examine the effects of AAEM on the secondary evolution of reaction intermediates. The main products obtained during the fast pyrolysis experiments were quantified by the standards, and other products were determined by MS analysis.

The results indicate that the inhibitory effect of KCl on LGA_Pyran is strongly related to the DP and reducing end. The strong effect of KCl during the cellulose pyrolysis is remarkably weakened during the pyrolysis of cyclodextrin and maltosan, which have much lower DP than cellulose. Furthermore, the reducing chain end in maltose can interact with the KCl to suppress the yield of LGA_Pyran. Correspondingly, CaCl$_2$ presents a stronger activity on oligosaccharide pyrolysis than on

cellulose pyrolysis regarding the LGA_Pyran formation, which may be due to the better distribution of the catalyst in oligosaccharides. For the char and LMW species, CaCl$_2$ can promote their direct formation from the cellulose chain and the secondary reaction of anhydro sugars in reaction intermediates, while KCl mainly accelerates the direct decomposition of cellulose into primary char and LMW species and has a limited effect on secondary char from reaction intermediates. Due to their different effects, a low KCl content can obviously promote the formation of gas at the expense of bio-oil, while the promotion effect of CaCl$_2$ on char formation highly depends on its content in the feedstock. Therefore, in the biomass industry, the evaluation of the interaction between the inorganic salt composition and reaction intermediates in biomass particles is crucial for bio-oil and chemical production.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2019.04.006.

References

[1] Kuang M, Li Z. Review of gas/particle flow, coal combustion, and NOx emission characteristics within down-fired boilers. Energy 2014;69:144–78.

[2] Zhou Z, Liu X, Hu Y, Liao Z, Cheng S, Xu M. An efficient sorbent based on CuCl2 loaded CeO2-ZrO2 for elemental mercury removal from chlorine-free flue gas. Fuel 2018;216:356–63.

[3] Yang Y, Liu W, Hu Y, Sun J, Tong X, Chen Q, et al. One-step synthesis of porous Li4SiO4-based adsorbent pellets via graphite moulding method for cyclic CO2 capture. Chem Eng J 2018;353:92–9.

[4] Han J, Yu D, Yu X, Liu F, Wu J, Zeng X, et al. Effect of the torrefaction on the emission of PM10 from combustion of rice husk and its blends with a lignite. Proc Combust Inst 2018.

[5] Wang S, Dai G, Yang H, Luo Z. Lignocellulosic biomass pyrolysis mechanism: a

state-of-the-art review. Prog Energy Combust Sci 2017;62:33–86.

[6] Anupam K, Sharma AK, Lal PS, Dutta S, Maity S. Preparation, characterization and optimization for upgrading Leucaena leucocephala bark to biochar fuel with high energy yielding. Energy 2016;106:743–56.

[7] Anupam K, Swaroop V, Deepika, Lal PS, Bist V. Turning Leucaena leucocephala bark to biochar for soil application via statistical modelling and optimization technique. Ecol Eng 2015;82:26–39.

[8] Leng E, Zhang Y, Peng Y, Gong X, Mao M, Li X, et al. In situ structural changes of crystalline and amorphous cellulose during slow pyrolysis at low temperatures. Fuel 2018;216:313–21.

[9] Lv D, Xu M, Liu X, Zhan Z, Li Z, Yao H. Effect of cellulose, lignin, alkali and alkaline earth metallic species on biomass pyrolysis and gasification. Fuel Process Technol 2010;91(8):903–9.

[10] Patwardhan PR, Satrio JA, Brown RC, Shanks BH. Influence of inorganic salts on the primary pyrolysis products of cellulose. Bioresour Technol 2010;101(12):4646–55.

[11] Zhang H, Ma Y, Shao S, Xiao R. The effects of potassium on distributions of bio-oils obtained from fast pyrolysis of agricultural and forest biomass in a fluidized bed. Appl Energy 2017;208(Supplement C):867–77.

[12] Le Brech Y, Ghislain T, Leclerc S, Bouroukba M, Delmotte L, Brosse N, et al. Effect of potassium on the mechanisms of biomass pyrolysis studied using complementary analytical techniques. ChemSusChem 2016;9(8):863–72.

[13] Feng D, Zhang Y, Zhao Y, Sun S. Catalytic effects of ion-exchangeable K+ and Ca2+ on rice husk pyrolysis behavior and its gas-liquid-solid product properties. Energy 2018;152:166–77.

[14] Yin L, Leng E, Gong X, Zhang Y, Li X. Pyrolysis mechanism of β-O-4 type lignin model polymers with different oxygen functional groups on Cα. J Anal Appl Pyrol 2018.

[15] Nowakowski DJ, Jones JM. Uncatalysed and potassium-catalysed pyrolysis of the cell-wall constituents of biomass and their model compounds. J Anal Appl Pyrol 2008;83(1):12–25.

[16] Shimada N, Kawamoto H, Saka S. Different action of alkali/alkaline earth metal chlorides on cellulose pyrolysis. J Anal Appl Pyrol 2008;81(1):80–7.

[17] Eom I-Y, Kim J-Y, Kim T-S, Lee S-M, Choi D, Choi I-G, et al. Effect of essential inorganic metals on primary thermal degradation of lignocellulosic biomass. Bioresour Technol 2012;104:687–94.

[18] Trendewicz A, Evans R, Dutta A, Sykes R, Carpenter D, Braun R. Evaluating the effect of potassium on cellulose pyrolysis reaction kinetics. Biomass Bioenergy 2015;74:15–25.

[19] Ferreiro AI, Rabaçal M, Costa M, Giudicianni P, Grottola CM, Ragucci R. Modeling the impact of the presence of KCl on the slow pyrolysis of cellulose. Fuel 2018;215(Supplement C):57–65.

[20] Bradbury AGW, Sakai Y, Shafizadeh F. A Kinetic model for pyrolysis of cellulose. J Appl Polym Sci (United States) 1979;23:11.

[21] Yu Y, Liu D, Wu H. Characterization of water-soluble intermediates from slow pyrolysis of cellulose at low temperatures. Energy Fuels 2012;26(12):7331–9.

[22] Gong X, Yu Y, Gao X, Qiao Y, Xu M, Wu H. Formation of anhydro-sugars in the primary volatiles and solid residues from cellulose fast pyrolysis in a wire-mesh reactor. Energy Fuels 2014;28(8):5204–11.

[23] Leng E, Wang Y, Gong X, Zhang B, Zhang Y, Xu M. Effect of KCl and CaCl2 loading on the formation of reaction intermediates during cellulose fast pyrolysis. Proc Combust Inst 2017;36(2):2263–70.

[24] Yu Y, Liu D, Wu H. Formation and characteristics of reaction intermediates from the fast pyrolysis of NaCl- and MgCl2-loaded celluloses. Energy Fuels 2014;28(1):245–53.

[25] Kawamoto H, Yamamoto D, Saka S. Influence of neutral inorganic chlorides on primary and secondary char formation from cellulose. J Wood Sci 2008;54(3):242–6.

[26] Patwardhan PR, Dalluge DL, Shanks BH, Brown RC. Distinguishing primary and secondary reactions of cellulose pyrolysis. Bioresour Technol 2011;102(8):5265–9.

[27] Zhu C, Maduskar S, Paulsen AD, Dauenhauer PJ. Alkaline-earth-metal-catalyzed thin-film pyrolysis of cellulose. ChemCatChem 2016;8(4):818–29.

[28] Marathe PS, Oudenhoven SRG, Heerspink PW, Kersten SRA, Westerhof RJM. Fast pyrolysis of cellulose in vacuum: the effect of potassium salts on the primary re-actions. Chem Eng J 2017;329(Supplement C):187–97.

[29] Mettler MS, Vlachos DG, Dauenhauer PJ. Top ten fundamental challenges of bio-mass pyrolysis for biofuels. Energy Environ Sci 2012;5(7):7797–809.

[30] Zhou X, Mayes HB, Broadbelt LJ, Nolte MW, Shanks BH. Fast pyrolysis of glucose-based carbohydrates with added NaCl part 1: experiments and development of a mechanistic model. AIChE J 2016;62(3):766–77.

[31] Zhou X, Mayes HB, Broadbelt LJ, Nolte MW, Shanks BH. Fast pyrolysis of glucose-based carbohydrates with added NaCl part 2: validation and evaluation of the mechanistic model. AIChE J 2016;62(3):778–91.

[32] Saddawi A, Jones JM, Williams A. Influence of alkali metals on the kinetics of the thermal decomposition of biomass. Fuel Process Technol 2012;104:189–97.

[33] Arora JS, Chew JW, Mushrif SH. Influence of alkali and alkaline-earth metals on the cleavage of glycosidic bond in biomass pyrolysis: a DFT study using cellobiose as a

[34] Leng E, Costa M, Peng Y, Zhang Y, Gong X, Zheng A, et al. Role of different chain end types in pyrolysis of glucose-based anhydro-sugars and oligosaccharides. Fuel 2018;234:738–45.

[35] Zhang B, Leng E, Wang P, Gong X, Zhang J, Zhang Y, et al. Effect of reducing ends on the pyrolysis characteristics and product distribution of cellulose. J Anal Appl Pyrol 2015;114:119–26.

[36] Paulsen AD, Mettler MS, Dauenhauer PJ. The role of sample dimension and tem-perature in cellulose pyrolysis. Energy Fuels 2013;27(4):2126–34.

[37] Zhou X, Nolte MW, Mayes HB, Shanks BH, Broadbelt LJ. Experimental and me-chanistic modeling of fast pyrolysis of neat glucose-based carbohydrates. 1. Experiments and development of a detailed mechanistic model. Ind Eng Chem Res 2014;53(34):13274–89.

[38] Zhou X, Nolte MW, Shanks BH, Broadbelt LJ. Experimental and mechanistic mod-eling of fast pyrolysis of neat glucose-based carbohydrates. 2. Validation and eval-uation of the mechanistic model. Ind Eng Chem Res 2014;53(34):13290–301.

[39] Mayes HB, Nolte MW, Beckham GT, Shanks BH, Broadbelt LJ. The alpha–bet(a) of salty glucose pyrolysis: computational investigations reveal carbohydrate pyrolysis catalytic action by sodium ions. ACS Catal 2015;5(1):192–202.

[40] Mettler MS, Mushrif SH, Paulsen AD, Javadekar AD, Vlachos DG, Dauenhauer PJ. Revealing pyrolysis chemistry for biofuels production: conversion of cellulose to furans and small oxygenates. Energy Environ Sci 2012;5(1):5414–24.

[41] Zhu C, Krumm C, Facas GG, Neurock M, Dauenhauer PJ. Energetics of cellulose and cyclodextrin glycosidic bond cleavage. React Chem Eng 2017;2(2):201–14.

[42] Heiner AP, Kuutti L, Teleman O. Comparison of the interface between water and four surfaces of native crystalline cellulose by molecular dynamics simulations. Carbohydr Res 1998;306(1):205–20.

[43] Mayes HB, Nolte MW, Beckham GT, Shanks BH, Broadbelt LJ. The alpha–bet(a) of glucose pyrolysis: computational and experimental investigations of 5-hydro-xymethylfurfural and levoglucosan formation reveal implications for cellulose pyrolysis. ACS Sust Chem Eng 2014;2(6):1461–73.

[44] Seshadri V, Westmoreland PR. Concerted reactions and mechanism of glucose pyrolysis and implications for cellulose kinetics. J Phys Chem A 2012;116(49):11997–2013.

[45] van Putten R-J, van der Waal JC, de Jong E, Rasrendra CB, Heeres HJ, de Vries JG. Hydroxymethylfurfural, a versatile platform chemical made from renewable re-sources. Chem Rev 2013;113(3):1499–597.

[46] Vinu R, Broadbelt LJ. A mechanistic model of fast pyrolysis of glucose-based car-bohydrates to predict bio-oil composition. Energy Environ Sci 2012;5(12):9808–26.

[47] Liu Q, Wang S, Wang K, Guo X, Luo Z, Cen K. Mechanism of formation and con-sequent evolution of active cellulose during cellulose pyrolysis. Acta Phys Chim Sin 2008;24(11):1957–63.

[48] Wang S, Guo X, Liang T, Zhou Y, Luo Z. Mechanism research on cellulose pyrolysis by Py-GC/MS and subsequent density functional theory studies. Bioresour Technol 2012;104:722–8.

[49] Shen DK, Gu S. The mechanism for thermal decomposition of cellulose and its main products. Bioresour Technol 2009;100(24):6496–504.

[50] Lu Q, Zhang Y, Dong C-q, Yang Y-p, Yu H-z. The mechanism for the formation of levoglucosenone during pyrolysis of β-d-glucopyranose and cellobiose: a density functional theory study. J Anal Appl Pyrol 2014;110:34–43.

[51] Kawamoto H, Morisaki H, Saka S. Secondary decomposition of levoglucosan in pyrolytic production from cellulosic biomass. J Anal Appl Pyrol 2009;85(1–2):247–51.

[52] Piskorz J, Radlein DSA, Scott DS, Czernik S. Pretreatment of wood and cellulose for production of sugars by fast pyrolysis. J Anal Appl Pyrol 1989;16(2):127–42.

[53] Mayes HB, Tian J, Nolte MW, Shanks BH, Beckham GT, Gnanakaran S, et al. Sodium ion interactions with aqueous glucose: insights from quantum mechanics, molecular dynamics, and experiment. J Phys Chem B 2014;118(8):1990–2000.

[54] Björkman E, Strömberg B. Release of chlorine from biomass at pyrolysis and gasi-fication conditions 1. Energy Fuels 1997;11(5):1026–32.

[55] Kuzhiyil N, Dalluge D, Bai X, Kim KH, Brown RC. Pyrolytic sugars from cellulosic biomass. ChemSusChem 2012;5(11):2228–36.

[56] Jensen A, Dam-Johansen K, Wójtowicz MA, Serio MA. TG-FTIR study of the influ-ence of potassium chloride on wheat straw pyrolysis. Energy Fuels 1998;12(5):929–38.

[57] Ponder GR, Richards GN, Stevenson TT. Influence of linkage position and orienta-tion in pyrolysis of polysaccharides: a study of several glucans. J Anal Appl Pyrol 1992;22(92):217–29.

[58] Zhang X, Yang W, Blasiak W. Kinetics of levoglucosan and formaldehyde formation during cellulose pyrolysis process. Fuel 2012;96:383–91.

[59] Liu D, Yu Y, Long Y, Wu H. Effect of MgCl2 loading on the evolution of reaction intermediates during cellulose fast pyrolysis at 325 °C. Proc Combust Inst 2015;35(2):2381–8.

[60] Patwardhan PR, Satrio JA, Brown RC, Shanks BH. Product distribution from fast pyrolysis of glucose-based carbohydrates. J Anal Appl Pyrol 2009;86(2):323–30.