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Release and transformation of chlorine and potassium during pyrolysis of KCl doped biomass

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1 **Abstract**

2 The formation of CH₃Cl and the transformation of chlorine and potassium during pyrolysis of biomass
3 were investigated. Model biomass compounds (i.e. cellulose, xylan, lignin and pectin) and pine wood
4 doped with KCl were pyrolysed in a TGA at different heating rates (10-1000°C/min), temperatures (300-
5 850°C), and KCl contents (0-5 wt%). The volatiles were collected and analyzed for CH₃Cl concentration
6 by GC-MS. The solid residue was analyzed by ICP-OES for the contents of total and water soluble K
7 and Cl. Considerable amounts of CH₃Cl, corresponding to 20-50% of the fuel chlorine, were formed in
8 pyrolysis of KCl doped pine wood, lignin and pectin samples, suggesting a methylation ability of these
9 biomass on KCl by their methoxyl groups. Lignin and pine wood could supply methoxyl groups for
10 reaction with as much as about 2% KCl doping, and pectin had an even greater capacity. Organic K was
11 found in the solid residue of all samples, further supporting the occurrence of reactions between KCl and
12 the organic matrix in biomass. With a holding temperature of 500°C, an increase of heating rate from
13 10°C/min to 500°C/min significantly reduced the yield of CH₃Cl from KCl doped wood/lignin/pectin,
14 while no further reduction effect was observed at 1000°C/min. For a heating rate of 500°C/min, an
15 increase of holding temperature from 300°C to 850°C caused a decrease in the yield of CH₃Cl.

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17 **Keywords:** biomass pyrolysis, model compounds, KCl, CH₃Cl, release, ash transformation

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2 **1. Introduction**

3 Biomass is becoming important in heat and power production because of its renewable and CO₂-neutral
4 characteristics. However, utilization of biomass in high temperature processes is challenged by ash-
5 related problems, such as deposition and corrosion [1–4]. The release of Cl and K is a main concern due
6 to the relatively high content of Cl and K in biomass (especially in annual biomass) and their adverse
7 effect on biomass combustion and gasification processes, such as deposition [5,6], corrosion [7],
8 deactivation of SCR catalysts [8], and emission of HCl and CH₃Cl [9–12]. To minimize these
9 operational problems, a good understanding of the Cl and K release and transformation during high
10 temperature utilizations of biomass is required.

11 The concentration and association of Cl and K vary in different biomass [13,14]. In woody biomass, the
12 concentration of Cl is typically very low (<0.01%) and more than 90% of the Cl is water soluble [15]. In
13 annual biomass like rice and wheat straw, the concentration of Cl is much higher (0.1-0.6%), and the
14 water soluble Cl constitutes an important part of the total Cl (typically above 50%) [16]. Potassium
15 normally has the second largest concentration among all inorganic elements in biomass (lower than Si or
16 Ca depending on fuel type), ranging from 0.02% to 1.5% depending on fuel type (low in woody biomass
17 and high in annual biomass) [13–16]. More than 50% of the total K in biomass may exist in a form of
18 water soluble K [16]. Water soluble Cl and K are largely present as KCl, which is proposed as a major
19 inorganic constituent in biomass [17]. Therefore, understanding the interactions between KCl and
20 biomass during thermochemical conversion processes is of importance.

21 In biomass thermochemical conversion processes, Cl is primarily released during the devolatilization
22 stage. Van Lith et al. [18,19] investigated the Cl release of several woody biomass in a fixed bed reactor
23 at a heating rate of about 30°C/min and reactor temperatures of 500-800°C. They found that 60-80% of
24 the Cl release took place during the devolatilization phase. Rahim et al.[20] observed that little Cl was

1 retained in char during pyrolysis of bark wood at a temperature of 400°C. For annual biomass with a
2 high Cl content, Johansen et al. [21,22], Knudsen et al. [23] and Jensen et al. [24] found a release of 40-
3 60% of the Cl during pyrolysis at 500-800°C. Since KCl is considered as main Cl species in biomass, it
4 is hypothesized that the KCl in biomass reacts with organic groups during devolatilization, releasing Cl
5 to gas phase and fixing K in the char [18,19]. The hypothesis is supported by the observation that a
6 relatively smaller amount of K is released compared to Cl in the temperature range of 200-700°C during
7 pyrolysis [18,19,21–24]. The difference in Cl release during pyrolysis of different biomasses is
8 presumably caused by the speciation and availability of functional groups in the biomass that can react
9 with KCl [18]. For biomass with a low Cl content, a large fraction of Cl has the opportunity to react with
10 the organic matrix, thus resulting in the release of a larger fraction of Cl [18,19].

11 Hydrogen chloride and CH₃Cl are the two main gas phase Cl species released during devolatilization.
12 Dayton et al. [25] observed HCl release with molecular beam mass spectrometry (MBMS) in
13 switchgrass combustion at 1100°C. Strömberg et al. [26] suggested that KCl can react with chain-
14 bonded carboxylic groups in the temperature range of 200-700°C and yield HCl. They also studied the
15 reactions between KCl and other functional groups [9], and found that ester, acetal, hemiacetal and
16 hydroxymethyl also reacted with KCl and released HCl, even though the reactivity varied. Hamilton et
17 al. [10] reported significant CH₃Cl release in biomass combustion at temperatures of 150-350°C and
18 ascribed it to the methylation of Cl⁻ by lignin and pectin. Saleh et al. [27] found that CH₃Cl is the
19 predominant form of gaseous chlorine released in straw pyrolysis at 250-500°C, and the release of
20 CH₃Cl decreases with increasing pyrolysis temperature. Sailaukhanuly et al. [28] and Czegeny et al. [29]
21 found methylation ability of Cl⁻ in pectin and lignin, respectively, in the temperature range of 200-
22 300°C.

23 In spite of the progress, there are still some unresolved issues about the reaction between biomass and
24 KCl, such as the influences of heating rate and different biomass components on the release of chlorine
25 and the formation of CH₃Cl. To address these issues, four model compounds of biomass (cellulose,

1 xylan, lignin and pectin) and a pine wood, were chosen in this work to investigate their reactions with
2 KCl during pyrolysis. The experiments were carried out in a TGA under well-controlled heating rate
3 (10-1000°C/min) and temperature (300-850°C) conditions that are relevant for gasification/combustion
4 of biomass in fluidized bed and fixed bed systems. The focuses are on the impacts of heating rate,
5 temperature and KCl concentration in biomass on the release of chlorine and the formation of CH₃Cl.

6 **2. Experimental**

7 *2.1 Reactants*

8 Cellulose (CAS No. 9004-34-6), xylan (CAS No. 9014-63-5), lignin (CAS No. 8068-05-1) and pectin
9 (apple) (CAS No. 9000-69-5) were obtained from Sigma Aldrich (Germany). The model biomass
10 compounds and the pine wood particles were prepared and analyzed according to CEN/TS 14780 and
11 CEN/TS 15290 respectively. The inorganic elemental compositions are shown in Table 1. The Cl
12 content in all fuels was negligible (<0.01%). The K content was slightly higher, taking up 0.095% and
13 0.12% for lignin and pectin respectively.

14 *2.2 Sample preparation*

15 The KCl doping procedure used in [30] was chosen to produce KCl doped biomass. As an example,
16 cellulose doped with 2% KCl was prepared in the following way: 3.92g cellulose and 0.08g KCl were
17 weighted separately and put into a dry empty beaker. The mixed sample was then dissolved in 100 ml
18 distilled water and stirred for 12 h before being dried in a muffle furnace at 105°C.

19 *2.3 Instrumentation*

20 *2.3.1 TGA*

21 A high heating rate (up to 1000°C/min) TGA (STA 449 F1 Jupiter) was applied as the reactor. 30
22 ml/min of N₂ was used in the TGA to provide a pyrolysis atmosphere. To collect sufficient amount of

1 solid residue for further analysis, the sample mass was approximately 300 mg. A holding time of 50 min
2 was kept for each measurement to ensure complete reaction. The influences of holding temperature,
3 heating rate and KCl content were studied in different experimental conditions, as shown in Table 2. To
4 reduce the experimental work, the influence of the KCl content was only investigated under
5 experimental condition (3), i.e., at a heating rate of 500°C/min and a holding temperature of 500°C. This
6 condition has been chosen for the following reasons: 1) a high heating rate of 500°C/min is close to the
7 conditions in fixed bed/fluidized bed; 2) compared to 1000°C/min, the temperature control in the TGA
8 performs much better at 500°C/min; 3) with a holding temperature 500°C, the release results obtained
9 are not influenced by KCl vaporization.

10 2.3.2 GC-MS

11 The gas samples produced in pyrolysis were collected in gasbags and analyzed for CH₃Cl in a GC-MS
12 (a Varian 3400 gas chromatograph interfaced to a Saturn II ion trap mass spectrometer). Specified
13 amounts of CH₃Cl were prepared by injecting known volumes (100 to 1000 µL) of 1000 ppm of CH₃Cl
14 in N₂ and a standard curve was generated and used for CH₃Cl quantification. A 100 µL gas sample was
15 taken out from each gasbag and injected manually into the GC-MS system with a Pressure-Lok syringe
16 (VICI Precision Sampling, Inc., USA), and introduced in split mode (approximately 1:50) at 150°C. The
17 GC to MS transfer line and the manifold of the mass spectrometer were kept at 200°C. Separation was
18 achieved by a 0.32mm i.d.×25m fused silica column coated with 10µm PoraPLOT U (Analytical,
19 Denmark). Appropriate separations were achieved isothermally at 80°C. Full mass spectra were recorded
20 every 0.5s (mass range m/z 35-m/z 100). From repeating analyses, the uncertainties of the GC-MS
21 analysis were found within 5%.

22 2.3.3 ICP-OES

1 ICP-OES was applied to determine the contents of total K, water soluble K, total Cl and water soluble Cl
2 in the solid residue according to the standard CEN/TS 15290. The washing procedure consisted of
3 adding water to a liquid/solid ratio of 200. The solution was then placed in an oven at 120°C for 1 h. The
4 liquid was analyzed using ICP-OES to quantify the contents of water soluble K and Cl. The uncertainty
5 of the ICP-OES analysis of K and Cl was 8% and 10%, respectively.

6 *2.4 Calculation method in the balance of Cl and K*

7 The fraction of Cl (other than CH₃Cl) and K released could not be quantified directly in this system.
8 Therefore, a mass balance method based on the amount of K and Cl found in the raw fuel and the solid
9 residue [18], was applied to analyze the Cl and K release at various conditions.

10

11 **3. Results and discussion**

12 *3.1 TG curves*

13 In pyrolysis of biomass, significant amounts of organic vapors or gases (e.g., CO, CO₂, H₂O, CH₄ and
14 CH₃OH) are released because of the thermal decomposition of the organic matrix during heating. Some
15 ash-related elements are also released in this phase [31]. The solid residue is char, which is mainly
16 composed of carbon.

17 As shown in Figure 1(a), KCl had an obvious effect of increasing the char yield (here defined as the
18 weight percentage of the residue compared to the raw fuel) during pyrolysis of pine wood, and the
19 impact was beyond the amount of KCl added to the biomass. Similar results were obtained for the
20 biomass model compounds cellulose, xylan and lignin (see Supplemental Material for the detailed
21 results). The char yield increased with the KCl content. Jensen et al. [30] studied the effects of KCl on
22 the pyrolysis products of cellulose, xylan and lignin in TG-FTIR, and also found that KCl can enhance

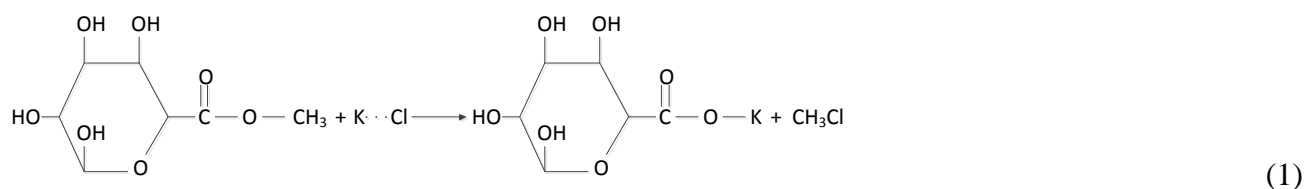
1 the char yield. The higher char yield in KCl doped fuels suggests that KCl is involved in reactions with
2 organics, and/or that KCl can catalyze the char formation.

3 The heating rate and the holding temperature have significant influences on the char yield. As shown in
4 Figure 1(b), increasing the heating rate from 10°C/min to 500°C/min lead to much faster decomposition
5 and lower char yield of pure or KCl doped wood. Increasing the holding temperature also lead to more
6 thorough decomposition and lower char yield.

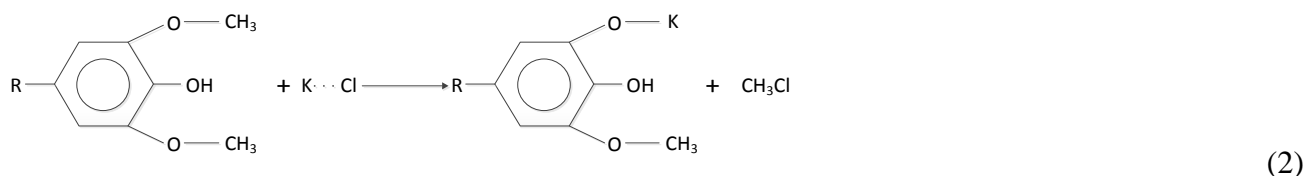
7 *3.2 Release of Cl as CH₃Cl*

8 *3.2.1 The impact of biomass type*

9 Figure 2 shows the fraction of total released Cl and the Cl released as CH₃Cl in all 2% KCl doped
10 samples at 500°C with a heating rate of 10°C/min. Repetitions were conducted on several samples,
11 showing good repeatability. For KCl doped cellulose and xylan, negligible amounts of CH₃Cl were
12 produced. However, a significant amount of Cl (25-50%) was released as CH₃Cl during pyrolysis of
13 KCl-doped pine wood, lignin and pectin, with the KCl-doped pectin releasing the most CH₃Cl. The total
14 Cl release of KCl-doped wood, cellulose and pectin were generally more than 10% higher than the Cl
15 released as CH₃Cl, implying that also other forms of Cl (presumably HCl or tar-Cl) were released during
16 pyrolysis. In KCl-doped lignin, the total release of Cl was close to that of CH₃Cl, indicating that Cl is
17 predominantly released as CH₃Cl in lignin. Only a small amount of Cl was released in KCl doped xylan.
18 The monomer structures of the model biomass compounds in Figure 3 indicate that the methylation
19 ability of lignin and pectin on Cl⁻ may be attributed to the methoxyl groups on rings [28,29,32,33].
20 Sailaukhanuly et al. [28] studied the nucleophilic substitution of pectin on the formation of CH₃Cl and
21 proposed the reaction mechanism shown in Eq. (1).



1
 2
 3 Czegeny et al. [29] conducted pyrolysis of lignin in a HCl atmosphere (produced by PVC), and observed
 4 formation of CH₃Cl. The results in the present study prove that KCl can also react with lignin and form
 5 CH₃Cl, presumably according to the reaction shown in Eq. (2).



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 9 The CH₃Cl produced from pine wood (a softwood) is presumably partly related to its lignin content,
 10 because lignin takes up about 20% in total in woody biomass while the content of pectin is very low
 11 [14]. The lignin used in this study is from hardwood, which typically has about twice as many methoxyl
 12 groups compared to the softwood lignin from pinewood. The similar amounts of CH₃Cl released in KCl
 13 doped wood and lignin imply that the number of methoxyl groups are similar in the two samples, and/or
 14 that the methoxyl groups in the pine wood are more reactive than those of the lignin.

15 3.2.2 The impact of holding temperature

16 As shown in Figure 4, increasing the holding temperature has a negative effect on CH₃Cl release. At a
 17 heating rate of 500°C/min, CH₃Cl produced from KCl doped wood, lignin and pectin are highest at
 18 300°C and lowest at 850°C. This is in agreement with the observations of Saleh et al. [27]. In their straw
 19 pyrolysis experiments, CH₃Cl was found to be the only form of gas phase released Cl at the holding
 20 temperature of 250°C, a small amount of other Cl containing species such as HCl were formed at 350°C
 21 and the fraction of CH₃Cl released decreased with increasing temperature [27]. In our experiments, for
 22 holding temperatures of 300°C and 500°C with a heating rate of 500°C/min the samples experienced the
 23 same temperature history until 300°C was reached. The difference in CH₃Cl yield indicates that a

1 considerable amount of CH₃Cl is released during the 50 min holding time at 300°C. This is supported by
2 the considerable mass loss of the sample during holding at 300°C (27.6%), while it was only 5.2% at the
3 holding temperature of 500°C. The mass loss of the sample during the holding temperature at 850°C
4 (3.3%) was close to that of 500°C. However, a decrease on CH₃Cl yield was still observed when the
5 holding temperature increased from 500°C to 850°C. This may be attributed to secondary reactions
6 between CH₃Cl and char at high temperatures, as a considerable amount of samples (~300 mg) was used
7 in our TGA experiments. Knudsen et al. [34] found that a substantial amount of HCl could be captured
8 by char of wheat straw by secondary reactions at 400-800°C and found a maximum in the char capture
9 efficiency at about 600°C. However, little is known about the reaction of CH₃Cl with char/ash.

10 3.2.3 The impact of heating rate

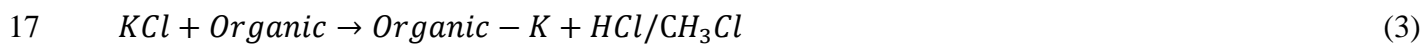
11 As shown in Figure 5, an increasing heating rate has also a negative influence on the release of CH₃Cl,
12 especially when the heating rate is below 500°C/min. During pyrolysis at a holding temperature of
13 500°C, a low heating rate of 10°C/min lead to the highest release of CH₃Cl in doped pine wood, lignin
14 and pectin. Increasing the heating rate lowered the fraction of CH₃Cl produced in pyrolysis. When the
15 heating rate was 100°C/min, the CH₃Cl produced was less than but close to that of 10°C/min. However,
16 for a heating rate of 500°C/min, the CH₃Cl produced was more than 20% lower than that of 10°C/min. A
17 further increase of the heating rate to 1000°C/min showed little further reduction of the yield of CH₃Cl.
18 The effect of heating rate on the release of CH₃Cl is explained by this hypothesis: CH₃Cl is mainly
19 formed at low temperatures (e.g. 200-350°C), and a shorter residence time of the particles in this
20 temperature range due to a higher heating rate inhibits the reactions between KCl and organic groups,
21 thus leading to a lower production of CH₃Cl. Conceivably a higher heating rate can also enhance the
22 secondary reactions between CH₃Cl with char, thus reducing the CH₃Cl yield, but this is not proved
23 directly by experiments.

24 3.2.4 The impact of doped KCl content

1 Figure 6 (a) and (b) show the mass (mg/g-fuel) and fraction of Cl released as CH₃Cl during pyrolysis of
 2 different samples at 500°C with a heating rate of 500°C/min. The mass of CH₃Cl released from doped
 3 pine wood increased with the concentration of KCl up to a level of about 2 wt%, and then it kept almost
 4 stable with increasing KCl. This indicates that the CH₃-donating groups in pine wood can offer reaction
 5 sites for as much as 2 wt% of KCl (Cl: 0.95 wt%). The percentage release of Cl as CH₃Cl in doped pine
 6 wood reached the highest level (about 54%) when the concentration of KCl was about 1 wt% (Cl: 0.48
 7 wt%) and then started to decrease. The results for KCl doped lignin were similar to those of doped pine
 8 wood. The amount of CH₃Cl produced from doped pectin was even higher than those from doped wood
 9 and lignin, and the mass continued to increase until the concentration of KCl reached 5 wt%, suggesting
 10 that more methoxyl can be supplied for the formation of CH₃Cl in pectin than in pine wood and
 11 hardwood lignin.

12 3.3 Cl and K balance

13 The current hypothesis about the reaction mechanism between KCl and organics is shown in Eq. (3).
 14 KCl reacts with the organic matrix and release HCl or CH₃Cl, and at the same time bind the K in the
 15 char. Released gas phase Cl can be captured by char via secondary reactions, forming organically
 16 associated Cl [35] or KCl [22,34], in Eqs. (4) and (5).



20 According to this hypothesis, the fraction of water soluble K should be equal to that of water soluble Cl
 21 in the residue (i.e., KCl). Table 3 shows that the molar ratio of water soluble K/Cl is not equal in all of
 22 the samples, and the ratio varies depending on fuel type. In most cases, K/Cl is above 1. One possible
 23 explanation is that some reaction products, i.e. organic-K and organic-Cl, are also water soluble (e.g.
 24 CH₃COOK [36]). Another possibility is the formation of water soluble K-salts, e.g. K₂CO₃ and K₂SO₄.

1 The transformation and release of K in pyrolysis is complicated. Organic K may decompose at increased
2 temperature and the primary released K (maybe even as atomic K [37]) may undergo secondary
3 reactions with ash species and char, forming KCl, K₂CO₃, K₂SO₄ and K-minerals, etc. These reactions
4 limit the amount of K released to the environment. In the temperature range 700-800°C, KCl starts to
5 evaporate [25]. Potassium in K₂CO₃ and K₂SO₄ is released by dissociation and vaporization at higher
6 temperatures (depending on fuel type [38] and water concentration) or incorporated into K-minerals.

7 Figure 7 (a) and (b) show the balance of Cl and K, respectively, in 2% KCl doped model compounds and
8 pine wood at 500°C with a heating rate of 10°C /min. The release of K and Cl in forms other than CH₃Cl
9 (in HCl and tar-Cl, etc.) is calculated from a mass balance. Of the five samples, water insoluble Cl and
10 water insoluble K were both highest in doped lignin, lowest in doped cellulose, and in similar levels in
11 the remaining 3 samples. This suggests that the extent of reaction in Eq. (3) and Eq. (4) varies for
12 different samples. It seems that lignin, compared to other fuels, has a higher capability to react with KCl
13 and produce organically bound K and Cl.

14 Chlorine released as CH₃Cl in both doped cellulose and xylan is very low and can be ignored. The
15 remaining Cl in doped cellulose is mainly released in other forms (20%), and almost no Cl is retained in
16 residue as water insoluble. Rahim et al. [39] studied the release of Cl from the slow pyrolysis of NaCl-
17 loaded cellulose at low temperatures. They observed that Cl is mainly released as HCl at temperatures
18 below 300°C. A part of the primary released HCl would react with char and form organic Cl, which can
19 be released in the form of tar-Cl at temperatures higher than 300°C. A very low content of organic Cl
20 was found in the residue produced at temperatures above 400°C and HCl was found to be the only Cl
21 containing gas released during the process [39]. The results of the present study are in agreement with
22 these observations. Chlorine released in other forms is lower in doped xylan, taking up less than 10%.
23 However, due to the lack of data for the release of HCl, the mechanism of the reaction between KCl and
24 xylan still remains in question. In KCl-doped pine wood, lignin and pectin, CH₃Cl is the main form of

1 Cl in the balance, taking up more than 50% in each sample. Chlorine released in other forms is very low
2 for all of the 3 samples.

3 Very little K release is observed for all of the samples, consistent with results in literature [18,19,21–24].
4 According to the hypothesis in Eq. (3), K in KCl is mainly transformed into organically bound K during
5 pyrolysis. The formation of organic-K is supported by SEM-EDX analyses, shown in Figure 11. In
6 Figure 11 (b), the K/Cl ratios of Area 1 and 4 are much higher than 1, implying a considerable excess of
7 K compared to Cl in the char. Moreover, in Figure 11 (c), only K can be found in the char washed by
8 deionized water, suggesting the K is organically bounded.

9 The molar ratio of water soluble K/Cl in the residue of doped cellulose, shown in Table 3, is about 1.11,
10 illustrating that KCl is not the only form of water soluble K left in the char residue. Chen et al. [35]
11 found a similar result from pyrolysis of KCl doped cellulose. According to the hypotheses above, water
12 soluble organic-K (e.g. CH_3COOK) and water soluble K salts (e.g. K_2CO_3 and K_2SO_4) can be formed
13 during pyrolysis. The formation of water soluble K salts is supported by XRD analysis, shown in Figure
14 10. For similar reasons, the content of water soluble K is higher than that of water soluble Cl in the
15 residue of doped pine wood, lignin and pectin. The molar ratio of water soluble K/Cl is higher (1.83,
16 1.55, 2.61) in these samples than in doped cellulose, which is probably due to variations in the extent of
17 the reaction in Eq. (3). However, in doped xylan the molar ratio of water soluble K/Cl is 0.80, indicating
18 water soluble Cl is higher than water soluble K in the residue. This is in agreement with the observations
19 by Chen et al. [35], and is probably due to the different structure of xylan.

20 The results for the same samples at 500°C with a heating rate of 500°C/min are shown in Figure 8 (a)
21 and (b). The fractions of water soluble K and water soluble Cl increase for all samples at high heating
22 rate, supporting the hypothesis that the reaction in Eq. (3) is inhibited by a high heating rate. This is also
23 supported by the change in the molar ratio of water soluble K/Cl in the residue. As shown in Table 3,
24 compared to the low heating rate of 10°C/min, the molar ratio of water soluble K/Cl for all samples at

1 the high heating rate of 500°C/min is closer to 1, suggesting a smaller fraction of KCl has participated in
2 the reaction with the organic matrix during pyrolysis.

3 In KCl-doped pine wood, lignin and pectin, the fraction of Cl released as CH₃Cl decreases for all three
4 samples compared to that of the low heating rate, as explained in section 3.2.3. For KCl-doped cellulose
5 and xylan, little difference is found in their Cl balance from the low heating rate of 10°C/min. This
6 means that the release and the potential secondary reactions of Cl are not sensitive towards the heating
7 rate.

8 The release of K is influenced only to a very limited extent by the high heating rate. It is probably
9 because organic K usually decomposes at temperatures higher than 500°C and limited K is released at
10 temperatures below 500°C. The pyrolysis results by Okuno et al. [37] and Keown et al. [40] support that
11 the influence of heating rate on the release of K is more pronounced at temperatures above 600°C.

12 Figure 9 (a) and (b) show the Cl and K balance of the same samples at 850°C with a heating rate of
13 500°C/min. The fractions of water soluble K and water soluble Cl decrease for all samples at the high
14 holding temperature, probably due to vaporization of KCl. For this reason, the molar ratio of water
15 soluble K/Cl increases for all samples, as shown in Table 3. In the residue of KCl doped xylan, the
16 molar ratio of water soluble K/Cl increase from 0.83 at 500°C to 1.42 at 850°C, suggesting that a higher
17 fraction of water soluble organic-Cl than water soluble organic-K, or K salts decompose in the
18 temperature range of 500-850°C in KCl doped xylan.

19 For all samples, a small reduction in CH₃Cl release was observed with the temperature increasing from
20 500°C to 850°C, as discussed in section 3.2.2. Because of the decomposition of organic-Cl, the fraction
21 of Cl released in other forms (HCl, tar and KCl, etc) increases for all samples at 850°C.

1 Water insoluble K in all samples also decreases at the high temperature of 850°C, while the fraction of
2 released K increases. The K release in the KCl-doped wood sample is about 36%, while it is more than
3 50% in KCl-doped cellulose and less than 20% in the remaining samples.

4 *3.4 XRD and SEX-EDX analysis of residues*

5 XRD was applied to study the crystallized mineral species in char. Figure 10 shows the XRD peaks of
6 char from pyrolysis of KCl-doped pine wood, cellulose, xylan, lignin and pectin at 500°C with a heating
7 rate of 500°C/min. All peaks showed presence of KCl, and it was almost the only mineral in the char of
8 pine wood and cellulose. Due to the high content of Na in xylan and pectin, Na salts (e.g. NaCl and
9 Na₂CO₃) were found in their chars. K₂SO₄ was found in the char of lignin, consistent with its high
10 content of S. K₂SO₄ is water soluble and thus it supports the hypothesis that salts other than KCl
11 contribute to the water soluble K. K₂CO₃ was not detected in any of the samples in Figure 10.
12 Presumably it is not produced in pyrolysis, or it has been decomposed or reacted with other substances.

13 Figure 11 (a) shows the morphology and composition of 2% KCl-doped pine wood sample before
14 pyrolysis. Part of the doped KCl (e.g., area 2) was distributed uniformly in the wood, and part of the
15 doped KCl (e.g., area 3) was present as KCl particles on the wood surface. However, the KCl particles
16 were still observed in the char of the same sample after pyrolysis, as shown in Figure 11 (b). The K/Cl
17 ratios of Area 1 and 2 in Figure 11 (b) suggest that the big particle (Area 2) is KCl, while Area 1 may
18 contain organic-K in addition to KCl (maybe as small particles). Figure 11 (c) shows the same char after
19 washing by deionized water. All of the KCl particles were washed away and the elemental composition
20 of Area 1 proves that part of K was fixed in char during pyrolysis.

21 *3.5 Practical implication*

22 The results from the present work have some practical implications for biomass combustion/gasification
23 in fluidized bed or fixed bed systems:

- 1 1) During biomass pyrolysis under low and moderate heating rate (e.g. $<1000^{\circ}\text{C}/\text{min}$) conditions, the
2 reactions between KCl and organics with methoxyl groups (e.g. lignin and pectin) may result in a
3 considerable fraction of chlorine released to gas phase as CH_3Cl . The presence of CH_3Cl may
4 become a concern for gas purification in gasification systems.
- 5 2) After the chlorine in KCl is released as CH_3Cl during biomass pyrolysis, the potassium is primarily
6 converted to organic bounded K in char. The oxidation of organic bounded K may results in the
7 formation of KOH or K_2CO_3 which may induce bed agglomeration in fluidized bed systems.
- 8 3) Shortening the residence time of biomass particles at temperatures below 500°C could inhibit the
9 release of chlorine as CH_3Cl and the formation of organic bounded K in char. This provides
10 possibilities of reducing the formation of CH_3Cl and Char-K through modification of reactor design
11 and change of operation parameters.
- 12 4) For biomass with a large amount of KCl, the formation of CH_3Cl during pyrolysis may be limited by
13 the amount of methoxyl groups available in biomass. This may provide a possibility to predict the
14 formation of CH_3Cl and Char-K based on the fuel properties and reaction conditions.

15 **4. Conclusion**

16 The present study shows that during pyrolysis at low and moderate heating rates ($<1000^{\circ}\text{C}/\text{min}$), a
17 significant amount of CH_3Cl can be released from KCl-doped pine wood, lignin and pectin, while the
18 release of CH_3Cl from KCl-doped cellulose and xylan is negligible. The formation of CH_3Cl takes place
19 mainly below 500°C , and can be inhibited by increasing the heating rate of the biomass particles. It is
20 suggested that the methoxyl groups in pine wood, lignin and pectin are responsible for the reaction with
21 KCl and the formation of CH_3Cl . For pine wood and lignin, the amount of CH_3Cl formed is not
22 increased further when the doped KCl content is larger than 2%, implying a limitation of the
23 methylation ability. On the other hand, pectin can convert more KCl to CH_3Cl , suggesting a better
24 methylation ability than that of pine wood and lignin. Analyses of the pyrolysis residues by ICP-OES

1 and SEM-EDX reveal that the reactions of KCl with pine wood and model biomass compounds (except
2 for xylan) result in a considerable formation of organically bounded K in the char.

3

4

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11

12 **Reference**

- 13 [1] Miles TR, Baxter LL, Bryers RW, Jenkins BM, Oden LL. Alkali deposits found in biomass power
14 plants, Vol 2 1995;II:1–122.
- 15 [2] Wang L, Wu H, Jensen PA, Dam-johansen K, Hustad JE, Engineering B. Ash Transformation and
16 Deposition Behavior During Co-Firing Biomass Fuels With Sewage sludge. Impact of Fuel
17 Quality on Power Production & Environment 2012.
- 18 [3] Bartolomé C, Gil A. Ash deposition and fouling tendency of two energy crops (cynara and poplar)
19 and a forest residue (pine chips) co-fired with coal in a pulverized fuel pilot plant. Energy Fuels
20 2013;27:5878–5889.

- 1 [4] Wang L, Hustad JE, Skreiberg Ø, Skjevraak G, Grønli M. A critical review on additives to reduce
2 ash related operation problems in biomass combustion applications. *Energy Procedia* 2012;20:20–
3 29.
- 4 [5] Åmand LE, Leckner B, Eskilsson D, Tullin C. Deposits on heat transfer tubes during co-
5 combustion of biofuels and sewage sludge. *Fuel* 2006;85:1313–1322.
- 6 [6] Jensen P a., Stenholm M, Hald P. Deposition Investigation in Straw-Fired Boilers. *Energy Fuels*
7 1997;11:1048–1055.
- 8 [7] Michelsen HP, Frandsen F, Dam-Johansen K, Larsen OH. Deposition and high temperature
9 corrosion in a 10 MW straw fired boiler. *Fuel Process Technol* 1998;54:95–108.
- 10 [8] Zheng Y, Jensen AD, Johnsson JE. Deactivation of V_2O_5 - WO_3 - TiO_2 SCR catalyst at a biomass-
11 fired combined heat and power plant. *Appl Catal B Environ* 2005;60:253–264.
- 12 [9] Strömberg B, Zintl F. Release of Chlorine from Biomass and Model Compounds at Pyrolysis and
13 Gasification Conditions. *Prog Thermochem Biomass Convers* 2008;624:1234–1245.
- 14 [10] Hamilton JTG, McRoberts WC, Keppler F, Kalin RM, Harper DB. Chloride methylation by plant
15 pectin: an efficient environmentally significant process. *Science* 2003;301:206–209.
- 16 [11] Zhao H, Song Q, Yao Q. HCl Capture by Rice Straw Char and Its Influence on the
17 Transformation of Alkali and Alkaline Earth Metallic Species during Pyrolysis. *Energy Fuels*
18 2016;30:5854–5861.
- 19 [12] Narayan V, Jensen PA, Henriksen UB, Egsgaard H, Nielsen RG, Glarborg P. Behavior of Alkali
20 Metals and Ash in a Low-Temperature Circulating Fluidized Bed (LTCFB) Gasifier. *Energy*
21 *Fuels* 2016;30:1050–1061.
- 22 [13] Jenkins B., Baxter L., Miles T., Miles T. Combustion properties of biomass. *Fuel Process Technol*
23 1998;54:17–46.
- 24 [14] Demirbas A. Combustion characteristics of different biomass fuels. *Prog Energy Combust Sci*
25 2004;30:219–230.

- 1 [15] Werkelin J, Skrifvars B-J, Zevenhoven M, Holmbom B, Hupa M. Chemical forms of ash-forming
2 elements in woody biomass fuels. *Fuel* 2010;89:481–493.
- 3 [16] Werkelin J. Ash-forming elements and their chemical forms in woody biomass fuels elements.
4 PhD thesis 2008.
- 5 [17] Zevenhoven-Onderwater M. Ash-forming matter in biomass fuels. PhD thesis 2001.
- 6 [18] van Lith SC, Alonso-Ramírez V, Jensen P a., Frandsen FJ, Glarborg P. Release to the gas phase
7 of inorganic elements during wood combustion. Part 1: Development and evaluation of
8 quantification methods. *Energy Fuels* 2006;20:964–978.
- 9 [19] Frandsen F, Frandsen F, Glarborg P, Glarborg P, Jensen PA, Jensen PA, et al. Release to the Gas
10 Phase of Inorganic Elements during Wood Combustion. Part 2: Influence of Fuel Composition.
11 *Energy Fuels* 2008;22:1598–1609.
- 12 [20] Rahim MU, Gao X, Garcia-Perez M, Li Y, Wu H. Release of chlorine during mallee bark
13 pyrolysis. *Energy Fuels* 2013;27:310–317.
- 14 [21] Johansen JM, Jakobsen JG, Frandsen FJ, Glarborg P. Release of K, Cl, and S during pyrolysis and
15 combustion of high-chlorine biomass. *Energy Fuels* 2011;25:4961–4971.
- 16 [22] Johansen JM, Aho M, Paakkinen K, Taipale R, Egsgaard H, Jakobsen JG, et al. Release of K, Cl,
17 and S during combustion and co-combustion with wood of high-chlorine biomass in bench and
18 pilot scale fuel beds. *Proc Combust Inst* 2013;34:2363–2372.
- 19 [23] Knudsen JN, Jensen P a., Dam-Johansen K. Transformation and release to the gas phase of Cl, K,
20 and S during combustion of annual biomass. *Energy Fuels* 2004;18:1385–1399.
- 21 [24] Jensen P, Frandsen F. Experimental investigation of the transformation and release to gas phase
22 of potassium and chlorine during straw pyrolysis. *Energy Fuels* 2000;14:1280–1285.
- 23 [25] Dayton DC, French RJ, Milne T a. Direct Observation of Alkali Vapor Release during Biomass
24 Combustion and Gasification. 1. Application of Direct Observation of Alkali Vapor Release
25 during. *Energy Fuels* 1995;9:855–865.

- 1 [26] Björkman E, Strömberg B. Release of Chlorine from Biomass at Pyrolysis and Gasification
2 Conditions. *Energy Fuels* 1997;11:1026–1032.
- 3 [27] Saleh SB, Flensburg JP, Shoulaifar TK, Sárossy Z, Hansen BB, Egsgaard H, et al. Release of
4 chlorine and sulfur during biomass torrefaction and pyrolysis. *Energy Fuels* 2014;28:3738–3746.
- 5 [28] Sailaukhanuly Y, Sárossy Z, Carlsen L, Egsgaard H. Mechanistic aspects of the nucleophilic
6 substitution of pectin. On the formation of chloromethane. *Chemosphere* 2014;111:575–579.
- 7 [29] Czégény Z, Jakab E, Bozi J, Blazsó M. Pyrolysis of wood-PVC mixtures. Formation of
8 chloromethane from lignocellulosic materials in the presence of PVC. *J Anal Appl Pyrolysis*
9 2015;113:123–132.
- 10 [30] Jensen A, Dam-Johansen K, Wójtowicz M a., Serio M a. TG-FTIR Study of the Influence of
11 Potassium Chloride on Wheat Straw Pyrolysis. *Energy Fuels* 1998;12:929–938.
- 12 [31] Hupa M. Ash-related issues in fluidized-bed combustion of biomasses: Recent research highlights.
13 *Energy Fuels* 2012;26:4–14.
- 14 [32] OSullivan AC. Cellulose: the structure slowly unravels. *Cellulose* 1997;4:173–207.
- 15 [33] Bastawde KB. Xylan structure, microbial xylanases, and their mode of action. *World J Microbiol*
16 *Biotechnol* 1992;8:353–368.
- 17 [34] Knudsen JN, Jensen PA, Lin W, Dam-johansen K. Secondary Capture of Chlorine and Sulfur
18 during Thermal Conversion of Biomass. *Energy Fuels* 2005;19:606–617.
- 19 [35] Chen H, Chen X, Qiao Z, Liu H. Release and transformation characteristics of K and Cl during
20 straw torrefaction and mild pyrolysis. *Fuel* 2016;167:31–39.
- 21 [36] Hou H, Wang S, Jin W, Jiang Q, Sun L, Jiang L, et al. KOH modified Nafion112 membrane for
22 high performance alkaline direct ethanol fuel cell. *Int J Hydrogen Energy* 2011;36:5104–5109.
- 23 [37] Okuno T, Sonoyama N, Hayashi JI, Li CZ, Sathe C, Chiba T. Primary release of alkali and
24 alkaline earth metallic species during the pyrolysis of pulverized biomass. *Energy Fuels*
25 2005;19:2164–2171.

- 1 [38] Misra MK, Ragland KW, Baker AJ. Wood ash composition as a function of furnace temperature.
2 Biomass and Bioenergy 1993;4:103–116.
- 3 [39] Rahim MU, Gao X, Wu H. Release of chlorine from the slow pyrolysis of NaCl-loaded cellulose
4 at low temperatures. Proc Combust Inst 2015;35:2891–2896.
- 5 [40] Keown DM, Favas G, Hayashi JI, Li CZ. Volatilisation of alkali and alkaline earth metallic
6 species during the pyrolysis of biomass: differences between sugar cane bagasse and cane trash.
7 Bioresource technology 2005; 96(14): 1570-1577.
- 8 [41] Sathe C, Pang Y, Li CZ. Effects of heating rate and ion-exchangeable cations on the pyrolysis
9 yields from a Victorian brown coal. Energy Fuels 1999;13:748–755.

10

Table 1

Inorganic elemental composition of the model biomass compounds and pine wood (dry basis)

Parameter	Unit	Cellulose	Xylan	Lignin	Pectin	Pine wood
Al	mg/kg	<10	50±4	150±12	18±1	32±12
Ca	mg/kg	<10	5800±460	160±13	1400±110	950±60
Cl	mg/kg	<100	<100	<100	<100	160±20
Fe	mg/kg	<10	80±6	43±3	12±1	26±5
K	mg/kg	<150	180±14	950±76	1200±96	480±30
Mg	mg/kg	<10	79±6	170±12	380±30	140±10
Na	mg/kg	13±1	19000±1500	6500±520	20000±1600	95±10
P	mg/kg	<20	160±13	<20	110±9	52±8
S	mg/kg	<20	160±13	16000±1280	470±38	70±30
Si	mg/kg	<100	200±16	300±24	<100	<200
Ti	mg/kg	<3	<4	<3	<3	<5

Table 2

Table 2 Experimental conditions and samples

Experiment condition	Content of doped KCl
(1): Temperature: 500°C Heating rate: 10°C/min	Pine wood: 2% KCl, Cellulose: 2% KCl, Xylan: 2% KCl Lignin: 2% KCl, Pectin: 2% KCl.
(2): Temperature: 500°C Heating rate: 100°C/min	Pine wood: 2% KCl, Cellulose: 2% KCl, Xylan: 2% KCl Lignin: 2% KCl, Pectin: 2% KCl.
(3): Temperature: 500°C Heating rate: 500°C/min	Pine wood: 0%, 0.5%, 1%, 2%, 3%, 4%, 5%, 6% KCl, Cellulose: 2% KCl, Xylan: 2% KCl, Lignin: 0%, 1%, 2%, 5% KCl, Pectin: 0%, 1%, 2%, 5% KCl
(4): Temperature: 500°C Heating rate: 1000°C/min	Pine wood: 2% KCl, Lignin: 2% KCl
(5): Temperature: 300°C Heating rate: 500°C/min	Pine wood: 2% KCl, Cellulose: 2% KCl, Xylan: 2% KCl Lignin: 2% KCl, Pectin: 2% KCl.
(6): Temperature: 850°C Heating rate: 500°C/min	Pine wood: 2% KCl, Cellulose: 2% KCl, Xylan: 2% KCl Lignin: 2% KCl, Pectin: 2% KCl.

Table 3

The molar ratio of water soluble K/Cl in residue at different conditions

2%KCl doped samples	500°C, 10°C/min	500°C, 500°C/min	850°C, 500°C/min
Wood	1.83	1.28	2.21
Cellulose	1.11	1.07	2.44
Xylan	0.80	0.83	1.42
Lignin	1.55	1.09	4.17
Pectin	2.61	2.55	3.20

Figure captions

Figure 1 (a): Impact of KCl contents on char yield during pyrolysis of pine wood (heating rate 500°C/min, and holding temperature 500°C); (b): Impact of heating rate and holding temperature on char yield during pyrolysis of pure or KCl doped pine wood (“10-500” means heating rate 10°C/min and holding temperature 500°C)

Figure 2 Fraction of total released Cl and CH₃Cl in 2%KCl doped model compounds and pine wood at 500°C with a heating rate of 10°C/min

Figure 3 Monomer structures of cellulose, xylan, lignin and pectin

Figure 4 Influence of holding temperature on the release of Cl as CH₃Cl (heating rate: 500°C/min)

Figure 5 Influence of heating rate on the release of Cl as CH₃Cl (holding temperature: 500°C)

Figure 6 Mass (a) and Fraction (b) of Cl released as CH₃Cl in pyrolysis of wood/lignin/pectin doped with different percentages of KCl. The pyrolysis was carried out at a heating rate of 500 °C/min, a holding temperature of 500 °C and a holding time of 50min.

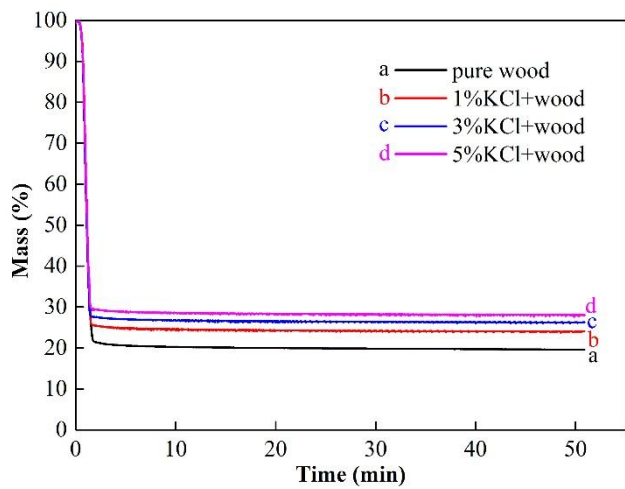
Figure 7 Cl (a) and K (b) balance of 2%KCl doped model compounds and pine wood at 500°C with a heating rate of 10°C/min

Figure 8 Cl (a) and K (b) balance of 2%KCl doped model compounds and pine wood at 500°C with a heating rate of 500°C/min

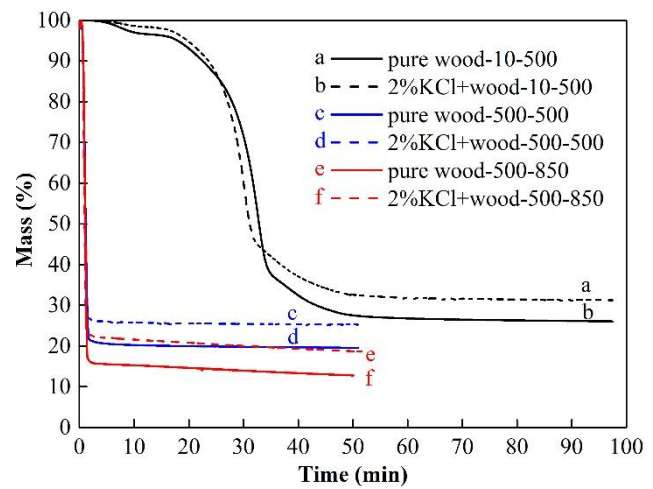
Figure 9 Cl (a) and K (b) balance of 2%KCl doped model compounds and pine wood at 850°C with a heating rate of 500°C/min

Figure 10 XRD peaks of char from pyrolysis of pine wood (a), cellulose (b), xylan (c), lignin (d) and pectin (e) at 500°C with the heating rate of 500°C/min

Figure 11 Morphology and composition of: 2% KCl doped wood (a); char of 2% KCl doped wood from pyrolysis at 500°C with the heating rate of 500°C/min (b); washed char of 2% KCl doped wood from pyrolysis at 500°C with the heating rate of 500°C/min (c). The remaining elements not shown in the figure are C and O.



(a)



(b)

Figure 1 (a): Impact of KCl contents on char yield during pyrolysis of pine wood (heating rate $500^{\circ}\text{C}/\text{min}$, and holding temperature 500°C); (b): Impact of heating rate and holding temperature on char yield during pyrolysis of pure or KCl doped pine wood (“10-500” means heating rate $10^{\circ}\text{C}/\text{min}$ and holding temperature 500°C)

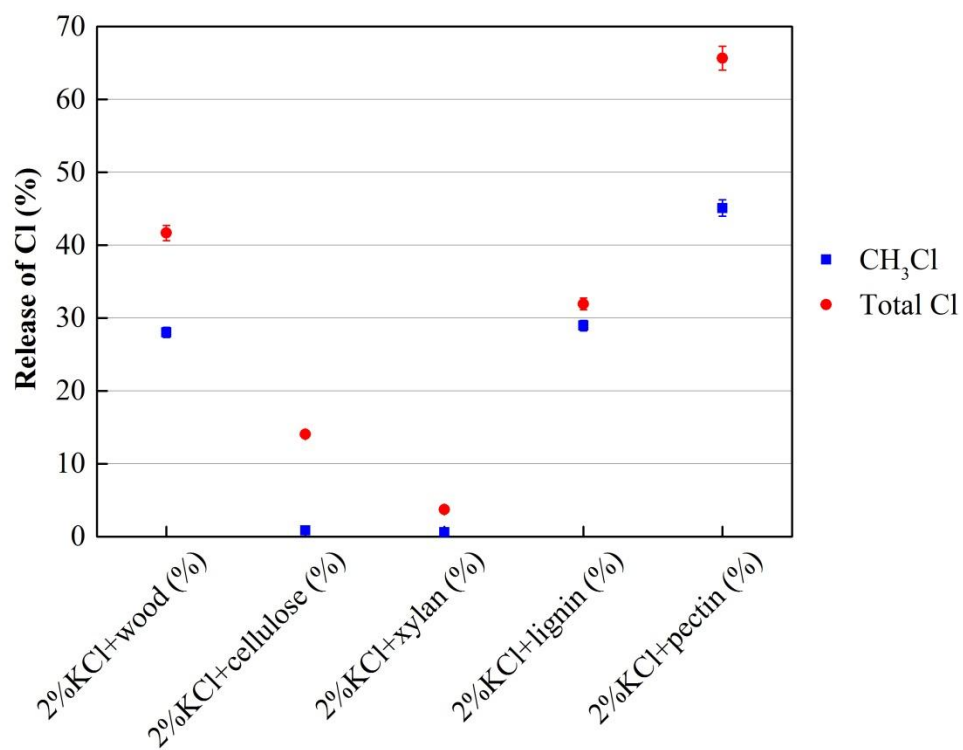
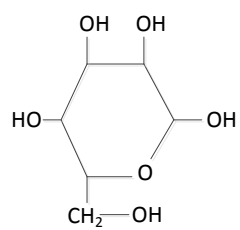
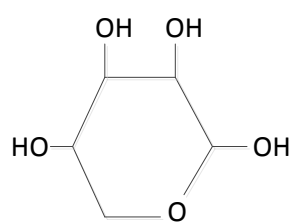


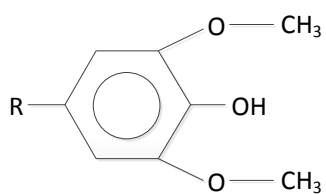
Figure 2 Fraction of total released Cl and CH₃Cl in 2%KCl doped model compounds and pine wood at 500°C with a heating rate of 10°C/min



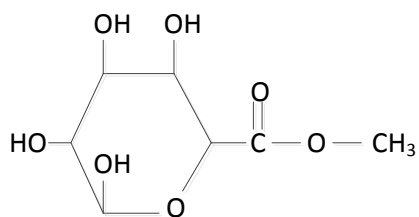
(a) Cellulose



(b) Xylan



(c) Lignin



(d) Pectin

Figure 3 Monomer structures of cellulose, xylan, lignin and pectin [28, 29, 32, 33]

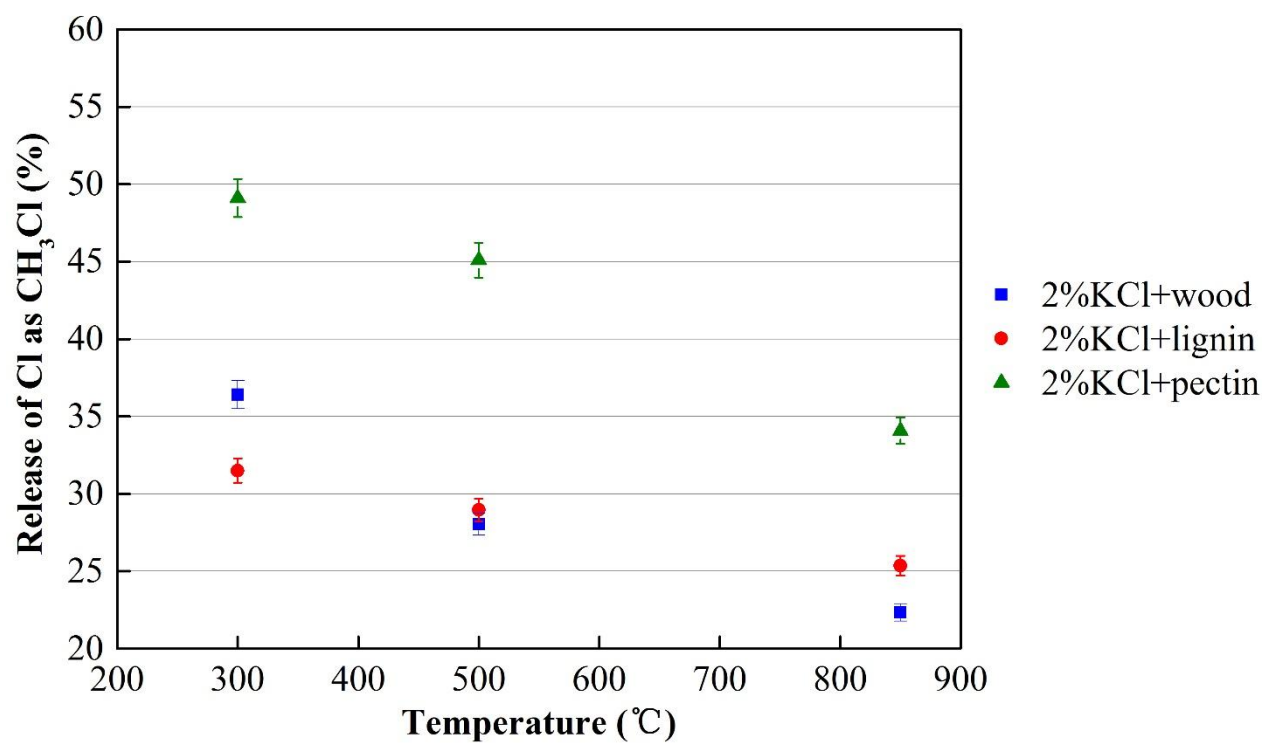


Figure 4 Influence of holding temperature on the release of Cl as CH₃Cl (heating rate: 500°C/min).

Sample mass in each case is 300mg.

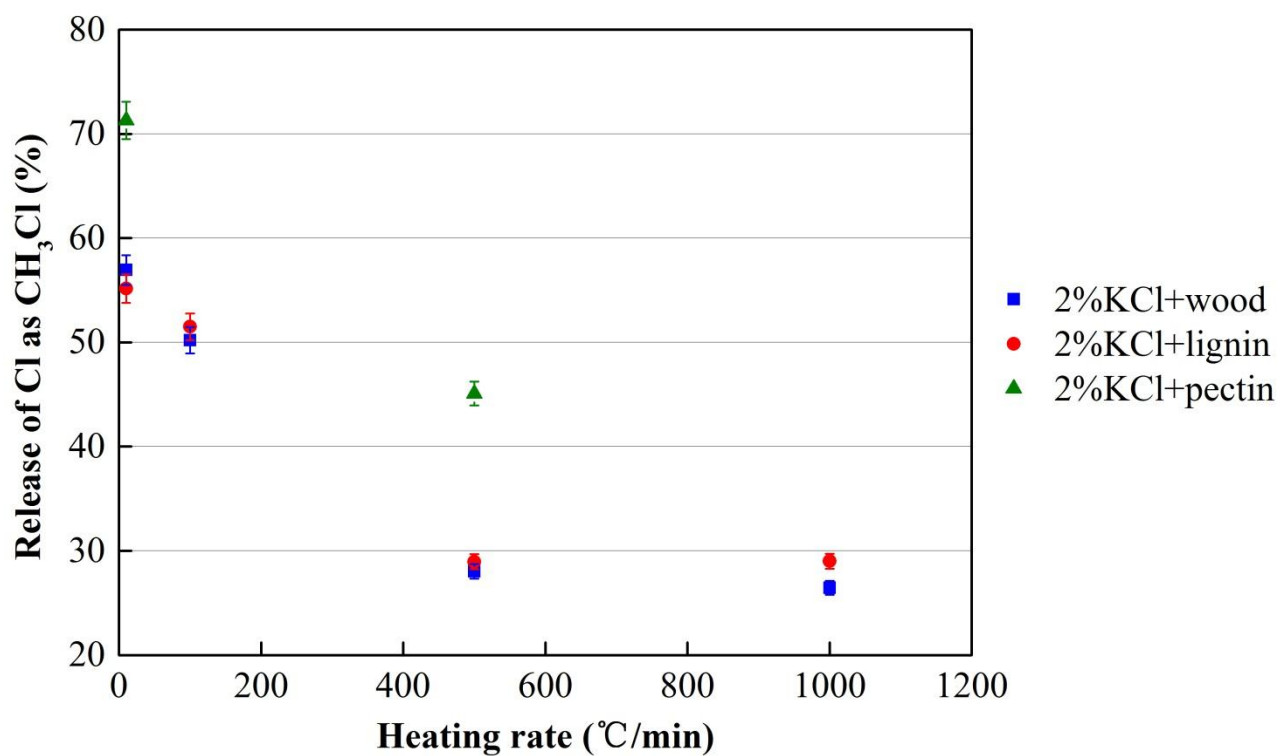
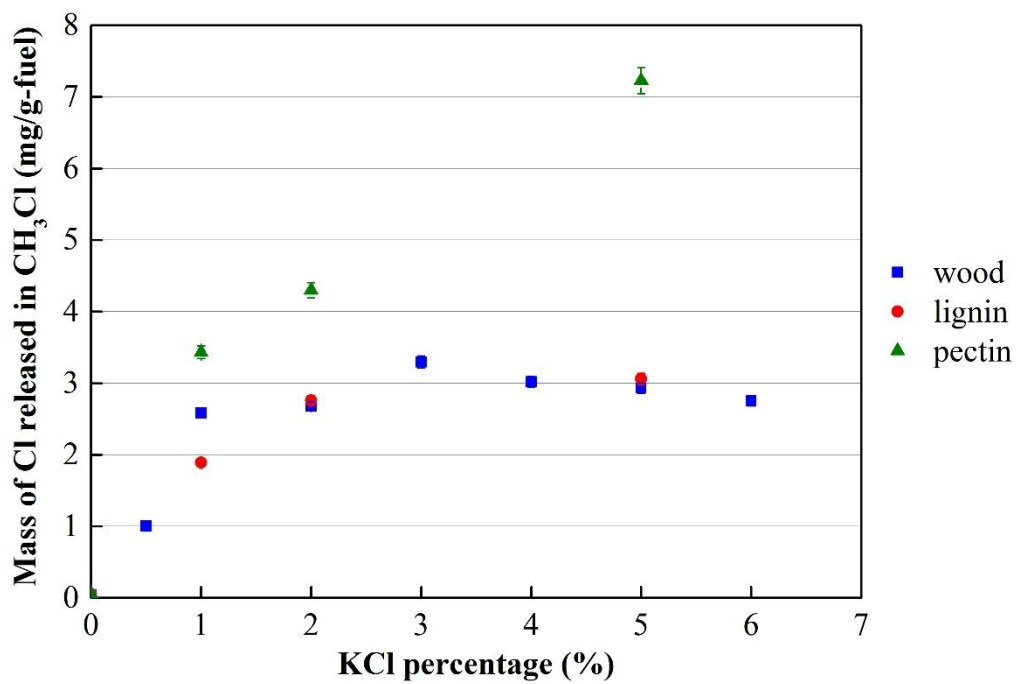
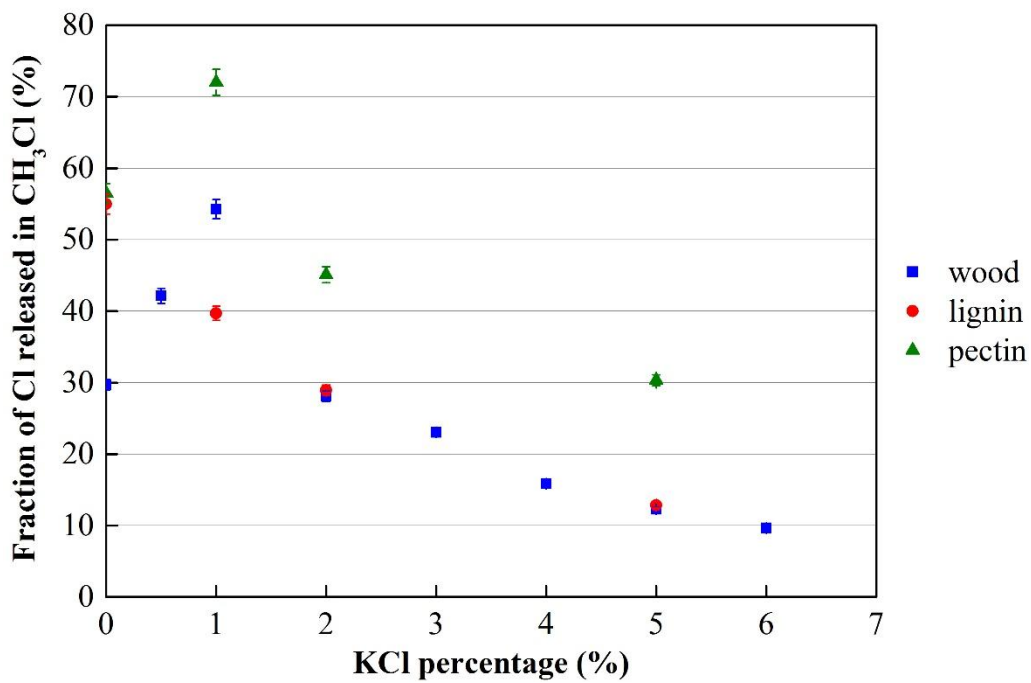


Figure 5 Influence of heating rate on the release of Cl as CH₃Cl (holding temperature: 500°C)

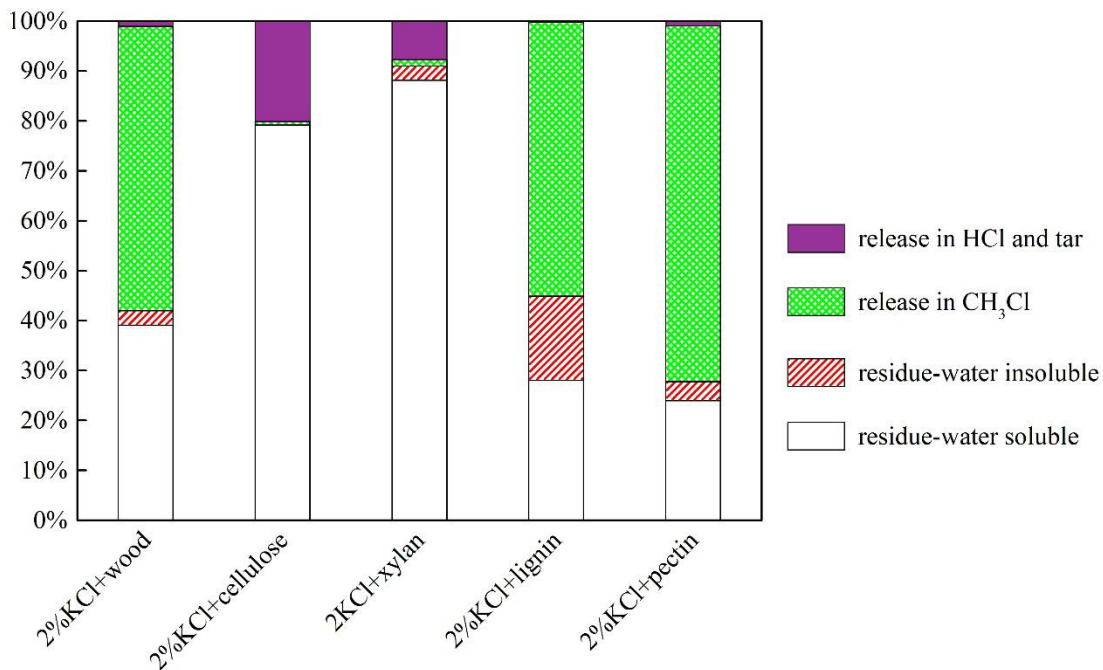


(a)

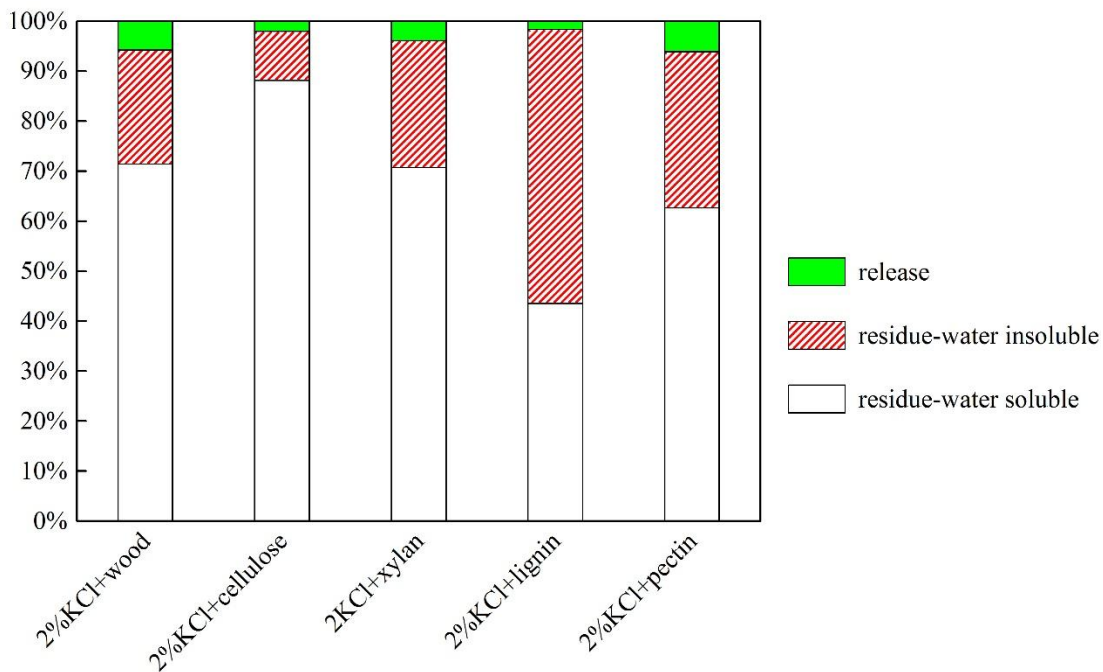


(b)

Figure 6 Mass (a) and Fraction (b) of Cl released as CH₃Cl in pyrolysis of wood/lignin/pectin doped with different percentages of KCl. The pyrolysis was carried out at a heating rate of 500 °C/min, a holding temperature of 500 °C and a holding time of 50min.

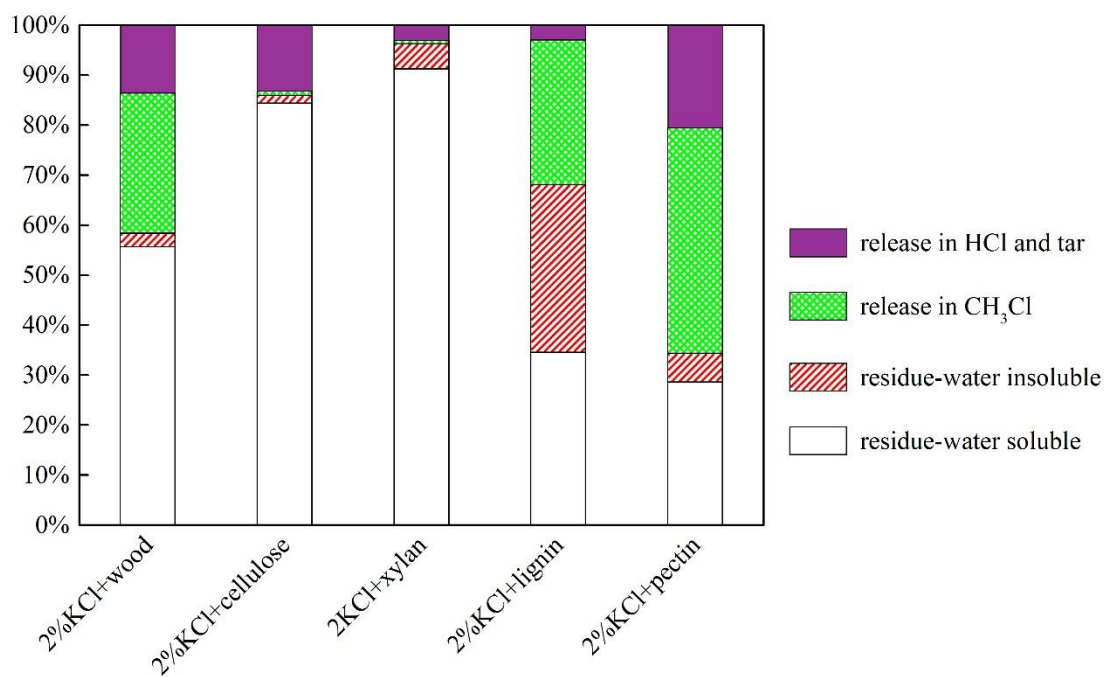


(a)

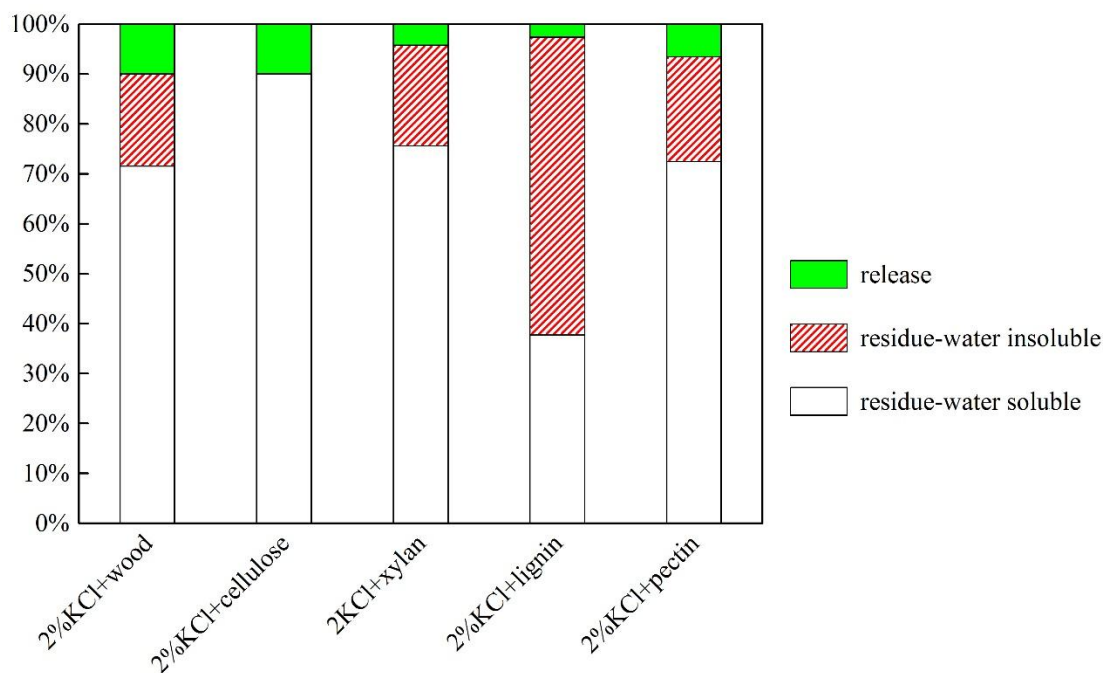


(b)

Figure 7 Cl (a) and K (b) balance of 2% KCl doped model compounds and pine wood at 500°C with a heating rate of 10°C/min

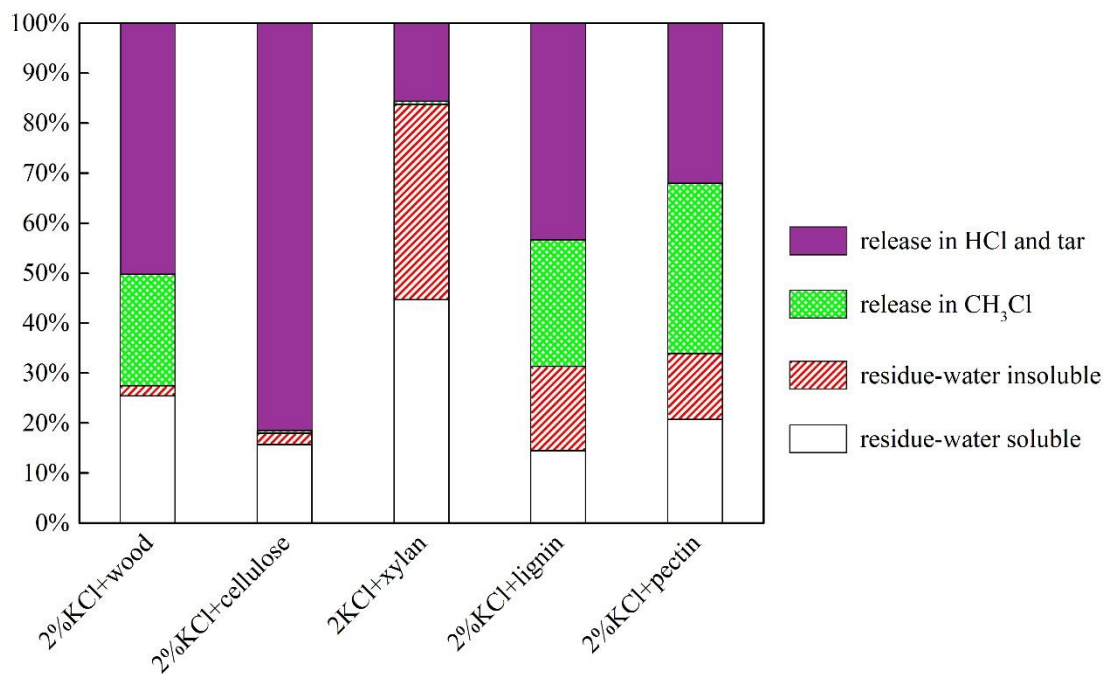


(a)

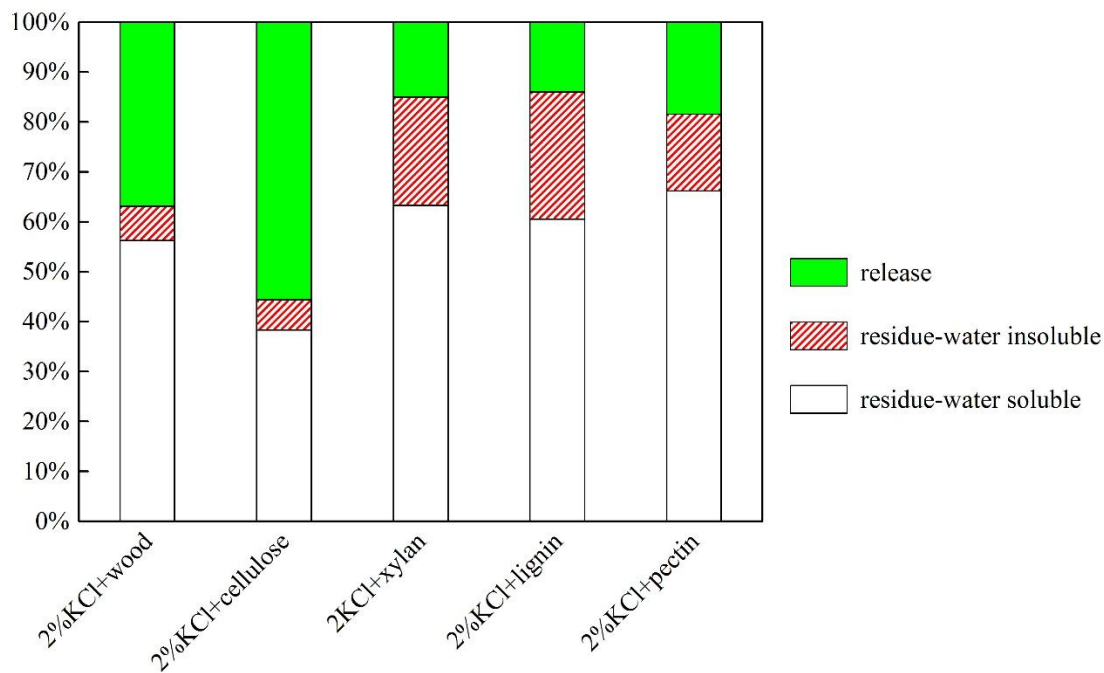


(b)

Figure 8 Cl (a) and K (b) balance of 2%KCl doped model compounds and pine wood at 500°C with a heating rate of 500°C/min



(a)



(b)

Figure 9 Cl (a) and K (b) balance of 2%KCl doped model compounds and pine wood at 850°C with a heating rate of 500°C/min

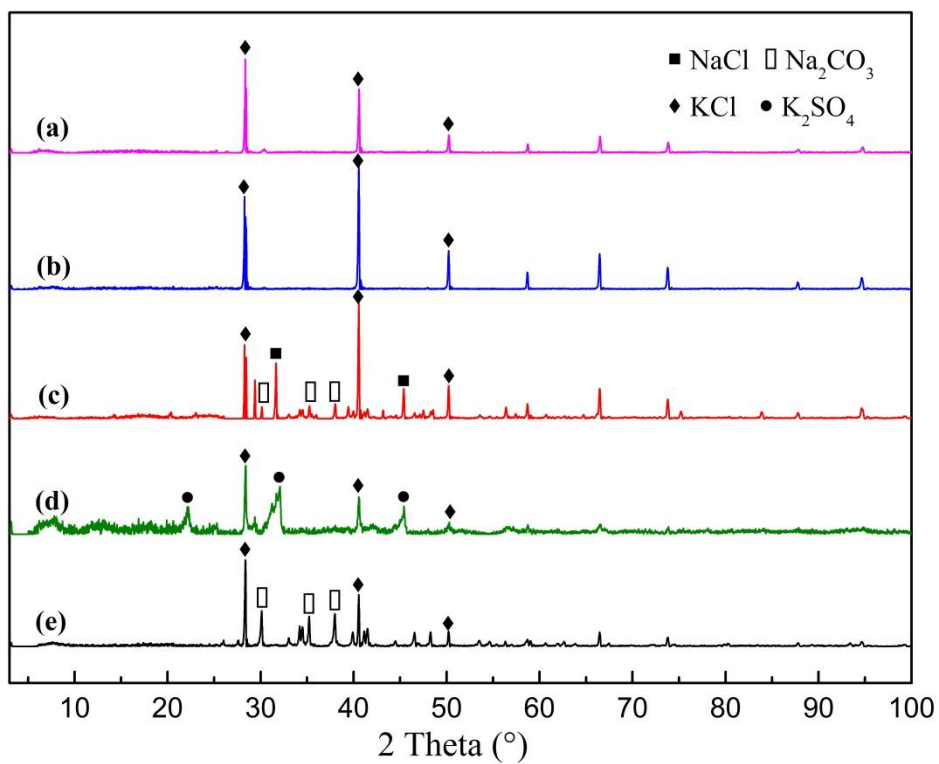


Figure 10 XRD peaks of char from pyrolysis of pine wood (a), cellulose (b), xylan (c), lignin (d) and pectin (e) at 500°C with the heating rate of 500°C/min

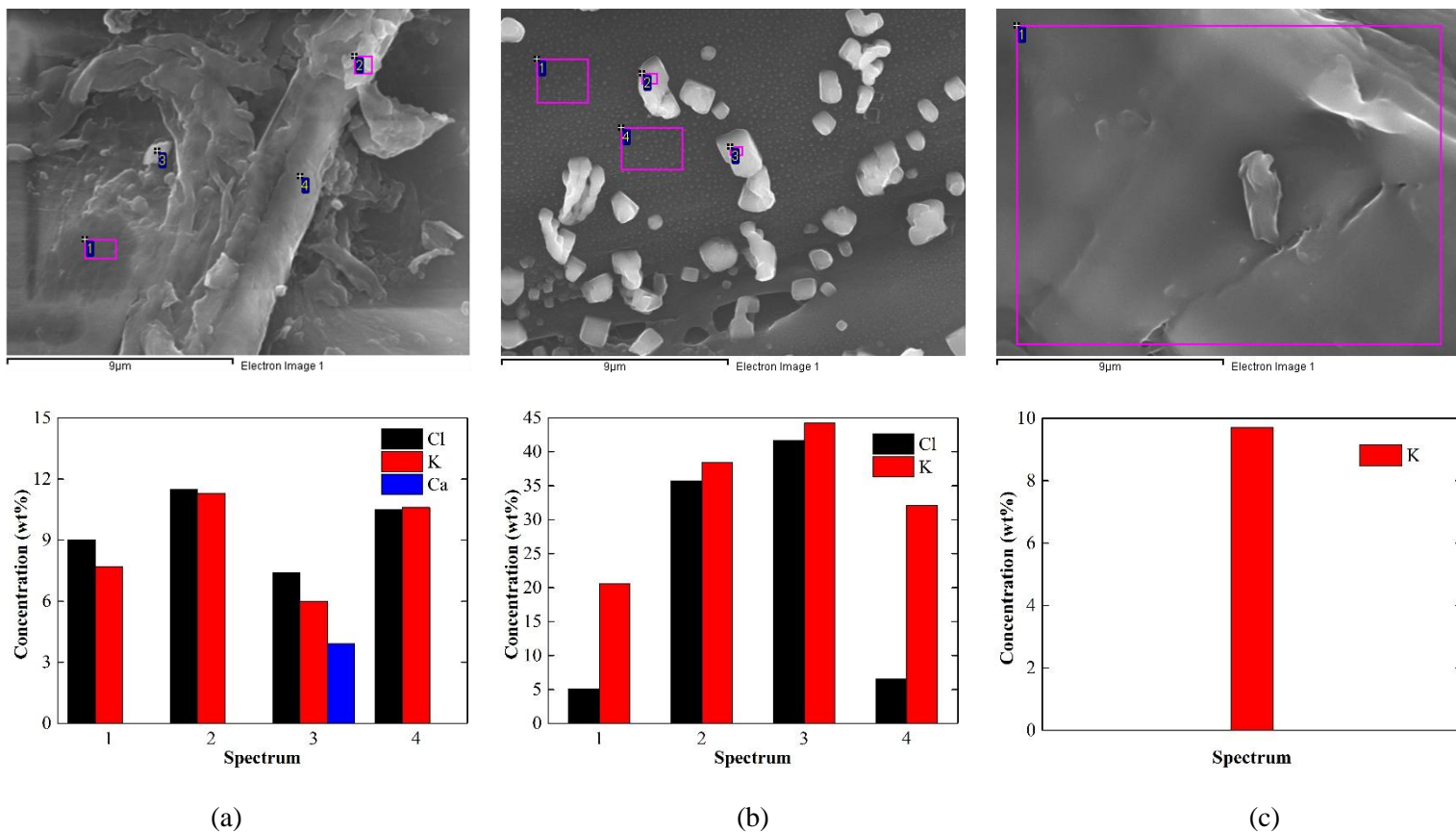


Figure 11 Morphology and composition of: 2% KCl doped wood (a); char of 2% KCl doped wood from pyrolysis at 500°C with the heating rate of 500°C/min (b); washed char of 2% KCl doped wood from pyrolysis at 500°C with the heating rate of 500°C/min (c). The remaining elements not shown in the figure are C and O.

Supplementary Material

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