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Release of Chlorine during Mallee Bark Pyrolysis

Muhammad Usman Rahim,[†] Xiangpeng Gao,[†] Manuel Garcia-Perez,[‡] Yi Li,[†] and Hongwei Wu^{*,†}

[†]Department of Chemical Engineering and Fuels and Energy Technology Institute, Curtin University, GPO Box U1987, Perth, Western Australia 6845, Australia

[‡]Biological Systems Engineering, Washington State University, L. J. Smith 205, Post Office Box 64120, Pullman, Washington 99164-6120, United States

ABSTRACT: Mallee bark (75–150 μm) was pyrolyzed at 400–900 $^{\circ}\text{C}$ under various conditions to investigate chlorine (Cl) release and distribution among char, tar, and gas. All Cl species in the bark are in form of water-soluble chlorides. In a fixed-bed pyrolysis reactor, the release of Cl is insensitive to pyrolysis temperature between 400 and 900 $^{\circ}\text{C}$, with Cl completely released with volatiles ($\sim 77\%$ in tar and $\sim 23\%$ in gas). In a drop-tube/fixed-bed reactor, under continuous feeding, the amount of Cl released at 400 $^{\circ}\text{C}$ is similar to that in the fixed-bed reactor. However, Cl retention in char increases with temperature, reaching a maximum at 600 $^{\circ}\text{C}$ ($\sim 42\%$), and then decreases with further temperature increases (e.g., only $\sim 6\%$ at 900 $^{\circ}\text{C}$). In the same drop-tube/fixed-bed reactor under pulsed feeding conditions, Cl release and distribution follow similar trends but to a lesser extent. The results confirm that volatile–char interactions also play important roles in Cl release and distribution among products during biomass pyrolysis and that Cl in char is thermally unstable at elevated temperatures. Calculations by difference further suggest that substantial Cl (47–84%) is present in tars. Quantification of Cl in tar was then carried out experimentally via *in situ* combustion of biomass volatiles produced using a two-column pyrolysis/combustion reactor. The results confirm the presence of substantial organically bounded Cl in tar. The mass balances of Cl in char, tar, and gas achieve $\sim 100\%$ closure during biomass pyrolysis in the fixed-bed reactor between 400 and 900 $^{\circ}\text{C}$, as well as that during biomass pyrolysis in the drop-tube/fixed-bed reactor below 600 $^{\circ}\text{C}$. However, at temperatures >600 $^{\circ}\text{C}$, 100% Cl mass balance cannot be achieved during *in situ* combustion of volatiles and the data suggest that some Cl react with inorganic species (e.g., Na and K) in the gaseous phase to form alkali chlorides, which are deposited on the reactor wall.

1. INTRODUCTION

Mallee biomass, as a byproduct of managing dryland salinity that seriously threatens the premium agricultural lands in Western Australia, is considered to be a key second-generation lignocellulosic feedstock projected for future bioenergy supply in the state.^{1–4} One important feature of mallee is the presence of abundant chlorine (Cl) and other inorganic species (such as alkali and alkaline earth metallic (AAEM) species, mainly Na, K, Mg, and Ca) concentrated mainly in bark and leaf.⁵ The released Cl is known to be responsible for various ash-related issues^{6–9} during combustion or gasification. In the application of biomass pyrolysis for bio-oil and biochar production, these species are important considerations as well. For instance, the presence of Cl and other inorganic species is an important parameter in the specifications of using these high-energy-density fuels for subsequent energy applications.^{10–14} On the other hand, if retained in biochar, Cl (a plant micronutrient) and other nutrient species may be recycled for plant growth when biochar is returned to the field for soil amendment and carbon sequestration.⁵ Therefore, a thorough understanding on the release of Cl during pyrolysis is essential to developing technologies for biomass use.

During biomass pyrolysis under slow heating rate, the release of Cl was reported to be temperature-dependent, with a significant amount of Cl released between 200 and 500 $^{\circ}\text{C}$,^{5,15,16} and the remaining Cl released around 800 $^{\circ}\text{C}$.^{17–20} Chlorine release also largely depends upon its mode of occurrence in biomass during pyrolysis. Accordingly, it was proposed that organic Cl transfers to tar first and then possibly releases to the

gaseous phase as $\text{HCl}(\text{g})$.^{15,16,18} Inorganic Cl was speculated to release as $\text{HCl}(\text{g})$ below 500 $^{\circ}\text{C}$ through either ion-exchange reactions between solid potassium chloride $\text{KCl}(\text{s})$ and proton-donating sites (e.g., carboxylic groups)^{15,16,18} or direct transfer of Cl to a liquid tar phase,²⁰ depending upon assumptions for the type of inorganic Cl after biomass drying. Also notably, previous studies^{21,22} on brown coal pyrolysis suggested that the prolonged volatile–char interactions play important roles in the release of Cl and AAEM species during the pyrolysis of Loy Yang brown coal in a fluidized-bed/fixed-bed reactor. However, the release of Cl in those previous studies was mainly based on the quantification of Cl retentions in chars. Little work has been performed on direct quantification of Cl in volatiles (including Cl in gas and Cl in tar). Also, the *in situ* experimental quantification of Cl in tars has received little attention. Clearly, experimental data and knowledge on these aspects are critical toward not only understanding Cl release mechanisms during biomass pyrolysis but also for biomass to energy conversion applications.

Therefore, the primary objective of this study is to carry out a systematic investigation on the release of Cl during the pyrolysis of mallee bark under a wide range of temperatures and reactor configurations. Three types of reactor configurations are considered, including a fixed-bed reactor and a drop-tube/fixed-bed reactor (with either continuous or pulsed feeding).

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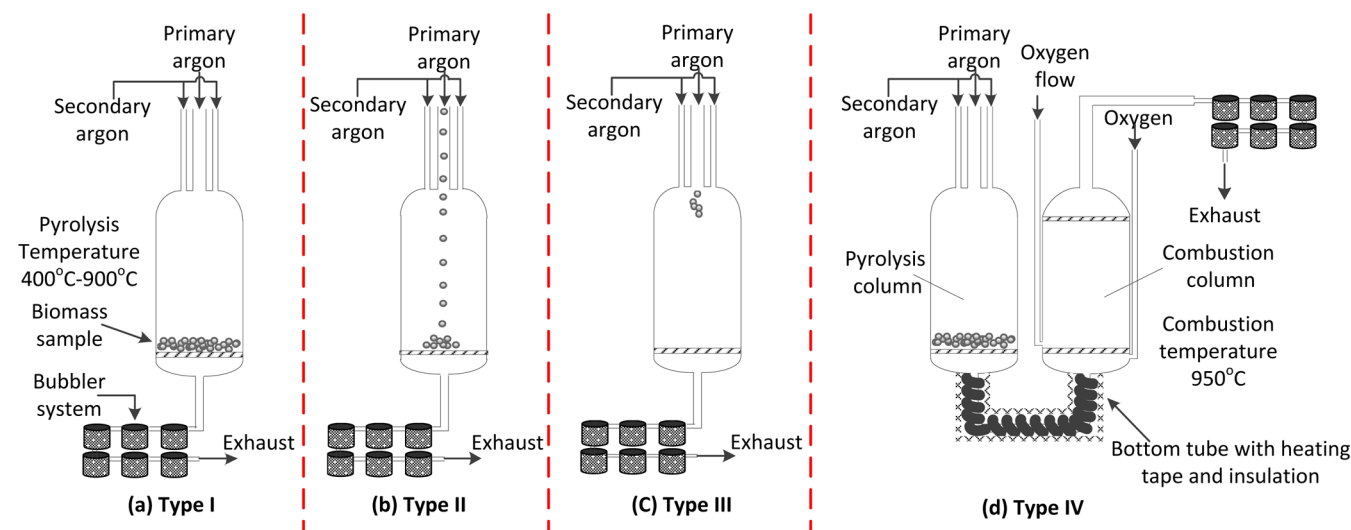


Figure 1. Schematic diagrams of four types of experiments carried out in this study: (a) type I, pyrolysis in a fixed-bed reactor; (b) type II, pyrolysis in a drop-tube/fixed-bed reactor with continuous feeding; (c) type III, pyrolysis in a drop-tube/fixed-bed reactor with pulsed feeding; and (d) type IV, pyrolysis followed by *in situ* combustion of volatiles in a two-column pyrolysis/combustion reactor.

Distributions of Cl among various biomass pyrolysis products are reported. Cl in gas phase and Cl in tar are successfully quantified using a two-column pyrolysis/combustion reactor.

2. EXPERIMENTAL SECTION

2.1. Biomass Samples. The bark component was separated from a batch of green mallee trees (*Eucalyptus polybractea*) harvested from Narrogin, Western Australia, Australia. The bark sample was then further processed by cutting and sieving to prepare a size fraction of 75–150 μm after drying at 40 $^{\circ}\text{C}$ for 24 h. The resulting sample is hereafter referred to as “raw biomass”.

2.2. Pyrolysis Experiments. Three types (I, II, and III) of pyrolysis experiments were carried out in this study, using argon [ultrahigh purity (UHP)] as carrier gas. Type I experiments were conducted in a fixed-bed pyrolysis reactor system (see Figure 1a). Briefly, the reactor was preloaded with ~ 1.0 g of raw biomass sample. The reactor was then heated to a desired pyrolysis temperature at ~ 10 K min^{-1} , with a further holding of 10 min. The reactor temperature was controlled via a controller with an accuracy of well below 0.5% of the setting temperature. Type II experiments used a drop-tube/fixed-bed reactor (estimated heating rate of ~ 1000 K s^{-1}) equipped with a continuous feeder (see Figure 1b). A total of ~ 1.0 g of raw biomass sample was continuously fed into the reactor at a feeding rate of ~ 100 mg min^{-1} . Once the biomass particles were injected into the hot reactor, rapid pyrolysis took place, producing char particles that remained on the reactor frit, while the volatiles were swept through the char bed. A unique feature of this continuous feeding drop-tube/fixed-bed reactor is that volatiles continuously contact with nascent char particles, resulting in extensive so-called “volatile–char interactions”.²² Type III experiments used the same drop-tube/fixed-bed reactor system but equipped with a pulsed feeder (see Figure 1c). Briefly, ~ 0.1 g of raw biomass sample was fed into the reactor in one shot. In both type II and III experiments, the reactor was further held for 10 min in the furnace after the feeding was completed.

All pyrolysis experiments were carried out between 400 and 900 $^{\circ}\text{C}$, and the gas residence time was kept as ~ 1.5 s via adjusting the flow rate of carrier gas from 1.5 to 2.6 L min^{-1} . Once a pyrolysis experiment was completed, the reactor was lifted out of the furnace and cooled naturally with argon continuously passing through the reactor. Hereafter in this paper, these types of experiments are referred to as “fixed-bed (FB) configuration”, “continuous feeding drop-tube/fixed-bed (CFDT/FB) configuration”, and “pulsed feeding drop-tube/fixed-bed (PFDT/FB) configuration”, respectively. Subsequently, char samples produced from the three types of configurations at 400–

900 $^{\circ}\text{C}$ are denoted as “FB-char-XXX”, “CFDT/FB-char-XXX”, and “PFDT/FB-char-XXX”, where “XXX” stands for the pyrolysis temperature. In each pyrolysis experiment, the Cl-containing volatiles (including tar and noncondensable gas) were passed through six bubblers with each containing ~ 150 g of 0.1 M sodium hydroxide (NaOH) solution to ensure complete capture of Cl in the gas phase. The bubblers were immersed in an ice bath to facilitate the absorption of Cl by the 0.1 M NaOH solution. Typically, tars in the pyrolysis gas were also condensed in the bubblers. Therefore, Cl captured in the solutions is in ionic form, i.e., water-soluble chloride (Cl^{-}). After each experiment, Cl^{-} contained in the solutions was quantified.

2.3. *In Situ* Combustion of Volatiles Generated from Biomass Pyrolysis. Besides water-soluble Cl (i.e., Cl^{-} or gas Cl), there may also be water-insoluble Cl (i.e., tar Cl) present in the volatiles collected at the exits of the reactor systems after pyrolysis. To quantify the total Cl in the volatiles, another type of experiment (type IV) was also carried out using a two-column pyrolysis/combustion reactor system (see Figure 1d). Fundamentally, the two-column reactor system consists of a pyrolysis reactor and a combustion reactor in two stages. The pyrolysis reactor can be operated in each of the three types described in the previous section (type I, fixed-bed reactor; type II, drop-tube/fixed-bed reactor with continuous feeding; or type III, drop-tube/fixed-bed reactor with pulsed feeding). In the pyrolysis reactor, biomass pyrolysis took place, generating volatiles that were then combusted *in situ* in the combustion reactor. The *in situ* combustion converts all Cl in the volatiles into ionic form, which can be captured by 0.1 M NaOH solution, enabling the quantification of total Cl in the volatiles. In this study, the pyrolysis reactor was operated at different temperatures (400–900 $^{\circ}\text{C}$) for type I and II experiments (see section 2.2). The combustion reactor was operated at 950 $^{\circ}\text{C}$. Two streams of oxygen was supplied to the combustion reactor, including primary oxygen (0.4 L min^{-1}) introduced below the bottom quartz frit and a stream of secondary oxygen (0.4 L min^{-1}) above the frit to achieve complete combustion. The flue gas after combustion was then introduced into the bubblers, which were loaded with 0.1 M NaOH solution, for Cl collection and quantification.

2.4. Characterization and Analysis of Samples. The biomass and char samples collected were subject to proximate and ultimate analyses. analysis was determined with a Mettler thermogravimetric analyzer (TGA) according to ASTM E870–82. The ultimate analysis was performed via a series of analytical techniques. Total carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) contents were determined using a Perkin-Elmer 2400 series II CHNS/O elemental analyzer according to AS1038.6.4. Cl in the biomass or biochar sample was determined using an approach that is a combination of the Eschka²³

and combustion methods. The oxygen (O) content was determined by difference on a dry and ash-free (daf) basis.

To quantify the water-soluble Cl content in a biomass or char sample, continuous leaching of the sample using deionized water was carried out using a semi-continuous leaching apparatus. Briefly, 100 mg of raw biomass was leached in the leaching apparatus for 4 h by a continuous flow of deionized water at 100 mL/min, delivered by a high-performance liquid chromatography (HPLC) pump. The leachate was swept out of the reactor, and the biomass sample remained on the frit. Cl in the leachates was quantified using ion chromatography (IC; model Dionex ICS-1100) with an IonPac AS22 fast analytical column (4×150 mm) and 2.25 mM $\text{NaCO}_3/0.7$ mM NaHCO_3 solution as an eluent. Cl absorbed in the 0.1 M NaOH solution from each pyrolysis experiment was also quantified using the same method. For quantification of AAEM species in raw biomass and char samples, the sample was ashed using a heating program up to 600 °C, acid-digested, and quantified using IC (model Dionex ICS-3000) with a CS12A column and 20 mM methanesulfonic acid (MSA) solution as an eluent, following a procedure detailed elsewhere.²⁴ The raw biomass and selected chars were also characterized using scanning electron microscopy (model: Zeiss EVO 40XVP) equipped with an energy-dispersive X-ray spectrometer (SEM-EDS).

3. RESULTS AND DISCUSSION

3.1. Mode of Occurrence of Cl in Biomass. Inorganic elements (e.g., Cl and AAEM species) in solid fuels may exist as free ions in aqueous solution in pores, distribute as discrete salt/mineral particles, and/or bond organically to carbonaceous material in the fuel.^{15,16,25} To understand the mode of occurrence of these inorganic species, the raw biomass sample was first subject to water leaching to quantify water-soluble species, the result of which is presented in Figure 2. The initial

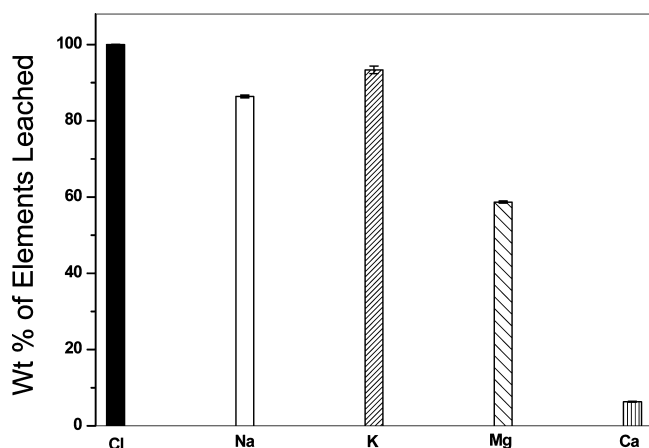


Figure 2. Mass percentage of water-soluble elements leached from the raw biomass via water leaching.

concentrations of Cl and other inorganic species in the biomass are presented in Table 1. It should be noted that, in this study, the water leaching was carried out using a semi-continuous leaching apparatus that rapidly swept the leachate out of the reactor, with the biomass particles remaining on the frit inside the reactor. Such leaching has a unique feature of minimizing the contact between the leachate and the biomass particles being leached, offering significant advantage over the conventional batch leaching process commonly used in such applications. The leachate from batch leaching of biomass with water contains acidic organic matter that may, in turn, interact with the biomass matrix to leach out part of organically bound inorganic species. As shown in Figure 2, 100% of Cl,

88% of Na, 95% of K, and 55% of Mg in biomass are water-soluble but only ~5.5% of Ca in biomass can be leached by water. The results suggest that all Cl species in raw biomass exist as either free ions in aqueous solution and/or deposit as discrete water-soluble salt particles, such as alkali chlorides.

3.2. Char Yield and Properties of Char from Mallee Bark Pyrolysis. Figure 3 presents the char yields from the pyrolysis of raw biomass in various reactor systems as a function of temperature. Below 600 °C, char yields are strongly dependent upon the pyrolysis temperature. Increasing the pyrolysis temperature from 400 to 600 °C leads to a considerable reduction in char yields from ~36.5 to ~25.9, from ~31.3 to ~20.8, and from ~27.9 to ~17.9 wt % db for biomass pyrolysis in the fixed-bed, continuous feeding drop-tube/fixed-bed, and pulsed feeding drop-tube/fixed-bed reactors, respectively. A further increase in pyrolysis temperature over 600 °C leads to little change in the char yield. However, a significant decrease (~7.8% db) in the char yield is evident for biomass pyrolysis in type II experiments (i.e., pyrolysis in the drop-tube/fixed-bed configuration with continuous feeding) between 800 and 900 °C. This can be attributed to the continuous volatile–char interactions, leading to the so-called “self-gasification”^{26,27} between reactive agents, such as CO_2 and H_2O (generated from the inherent moisture in biomass and/or produced from pyrolysis), in volatiles and the nascent char on quartz frit. Indeed, the SEM images for the char-produced from type II experiments at 600 and 900 °C clearly demonstrate that significant gasification reactions have taken place on the surface of char produced at 900 °C, as evidenced by the eroded surface texture with small cavities and/or grooves (see Figure 4). It should be noted that such reactions would be negligible in type I experiments, because the volatiles (hence, the reactive agents within) produced under fixed-bed slow-heating conditions would have been swept out of the reactor below 600 °C. Similarly, such self-gasification reactions would proceed to a much less extent in type III experiments, where with pulsed feeding, the lengthy period for interactions between the nascent chars on the frit with volatiles generated from the pyrolysis of the next batch of biomass particles is absent.

As expected, Figure 3 shows that, at a given temperature, biomass pyrolysis in type I experiments (slow-heating pyrolysis in a fixed-bed reactor) has a higher char yield than those in type II and III experiments. At pyrolysis temperatures lower than 800 °C, at which self-gasification reactions are expected to be insignificant, char yields from biomass pyrolysis in type III experiments (fast-heating pyrolysis in the drop-tube/fixed-bed reactor with pulsed feeding) are lower than those in type II experiments (fast-heating pyrolysis in the drop-tube/fixed-bed reactor with continuous feeding). The data suggest that the lengthy and continuous volatile–char interactions in type II experiments also have produced coke, which deposits on the nascent char, leading to an increase in the char yield. Similar phenomena on coke formation were also reported previously during coal gasification²⁸ and biomass thermochemical conversions.^{29,30} Clearly, the results also, in turn, suggest that, upon volatile–char interactions, there are competitions between coke formation and nascent char “self-gasification”, which becomes important at 800 °C or above.

The properties of chars produced from biomass pyrolysis under various conditions using different reactor systems are presented in Table 1, along with those of the raw biomass. As expected, the contents of ash and fixed carbon increased with the pyrolysis temperature, accompanied with a decrease in the

Table 1. Proximate and Ultimate Analyses of Raw Biomass and Its Derived Chars Prepared under Various Conditions^a

samples	moisture (wt %, ad)	proximate analysis (wt %, db)			ultimate analysis (wt %, daf)						contents of AAEM species (wt %, db)			
		VM ^b	ash	FC ^c	C	H	N	S	Cl	O ^d	Na	K	Mg	Ca
raw biomass	5.7	77.3	4.7	18.0	48.92	4.97	0.23	0.03	0.41	45.44	0.1364	0.2589	0.2062	1.3677
FB-char-400	6.0	36.0	10.8	53.2	73.71	2.94	0.62	0.02	0.01	22.69	0.3833	0.7055	0.5711	3.7948
FB-char-500	4.4	26.1	13.6	60.3	73.33	2.81	0.55	0.02	0.01	23.28	0.4628	0.8704	0.7096	4.6583
FB-char-600	3.8	21.7	13.4	64.9	87.83	1.86	0.59	0.01	0.01	9.70	0.4947	0.9543	0.7762	5.0640
FB-char-700	3.9	18.7	14.5	66.8	92.37	0.99	0.58	0.01	0.01	6.03	0.4786	0.9903	0.8177	5.0935
FB-char-800	3.8	17.0	14.5	68.5	93.54	1.07	0.78	0.01	0.01	4.60	0.4551	1.0176	0.8328	5.0616
FB-char-900	3.4	15.6	15.1	69.3	94.32	0.69	0.64	0.01	0.01	4.34	0.4274	0.9454	0.7687	4.9628
CFDT/FB-char-400	6.0	43.3	11.1	45.6	69.31	3.74	0.55	0.02	0.01	26.37	0.4302	0.6907	0.6463	4.1725
CFDT/FB-char-500	6.3	32.4	17.9	49.7	75.83	2.35	0.57	0.04	0.56	20.65	0.5788	0.9432	0.8646	5.5712
CFDT/FB-char-600	3.2	21.9	18.0	60.1	82.67	1.73	0.50	0.07	1.01	14.02	0.6313	1.0433	0.9763	6.3093
CFDT/FB-char-700	2.2	18.6	21.2	60.2	81.39	1.32	0.35	0.06	1.02	15.86	0.5567	1.0325	0.9838	6.4913
CFDT/FB-char-800	3.0	19.6	20.3	60.1	89.82	0.89	0.43	0.07	0.67	8.13	0.3957	0.9703	0.9856	6.4693
CFDT/FB-char-900	2.6	16.5	29.5	54.0	93.54	1.77	0.63	0.07	0.30	3.48	0.2848	0.8891	1.4732	9.9793
PFDT/FB-char-400	6.4	35.8	15.6	48.6	72.80	3.10	0.64	0.10	0.03	23.34	0.4353	0.8142	0.6918	4.5158
PFDT/FB-char-500	5.1	29.2	18.4	52.4	75.76	2.61	0.62	0.07	0.10	20.84	0.5893	1.1145	0.9792	6.8765
PFDT/FB-char-600	4.1	23.5	24.2	52.3	89.69	2.10	0.69	0.08	0.31	7.14	0.6805	1.1451	1.1388	7.1341
PFDT/FB-char-700	3.6	20.5	23.1	56.4	88.55	1.02	0.56	0.10	0.40	9.37	0.5986	1.1216	1.0803	7.4232
PFDT/FB-char-800	3.2	18.6	23.7	57.7	92.30	0.53	0.45	0.11	0.27	6.34	0.4493	1.0948	0.9964	6.7806
PFDT/FB-char-900	3.7	19.5	26.6	53.9	95.58	0.79	0.63	0.17	0.20	2.62	0.3737	1.0382	1.1053	7.9897

^aFB-char-XXX, char prepared under a fixed-bed reactor configuration at XXX °C; CFDT/FB-char-XXX, char prepared under a continuous feeding drop-tube/fixed-bed configuration at XXX °C; and PFDT/FB-char-XXX, char prepared under a pulsed feeding drop-tube/fixed-bed configuration at XXX °C. ^bVolatile matter. ^cFixed carbon. ^dBy difference.

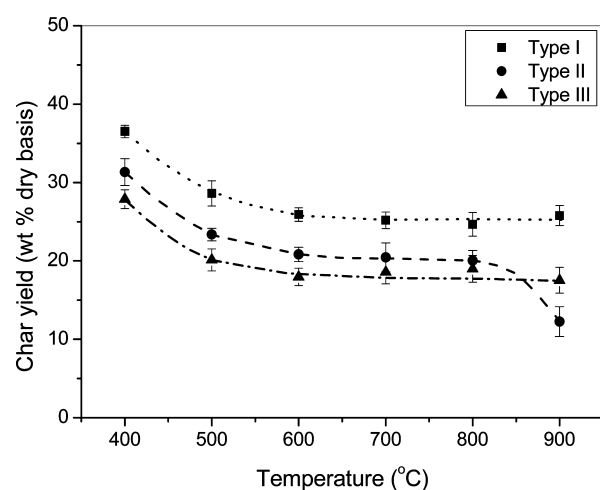


Figure 3. Char yields as a function of the temperature in three types of experiments: i.e., type I, pyrolysis in a fixed-bed reactor; type II, pyrolysis in a drop-tube/fixed-bed reactor with continuous feeding; and type III, pyrolysis in a drop-tube/fixed-bed reactor with pulsed feeding.

content of volatile matter. Accordingly, the carbon content increased, while the contents of hydrogen and oxygen decreased with an increasing pyrolysis temperature. Table 1 clearly shows a significant discrepancy in the Cl content in chars produced under different conditions, indicating that Cl release is strongly dependent upon biomass pyrolysis conditions (to be discussed in the next section).

3.3. Release of Cl during Biomass Pyrolysis under Various Conditions. Figure 5 presents the data on the distribution of Cl in pyrolysis products (char, gas, and tar; see panels a, b, and c, respectively), along with Cl mass balance (see panels d–f) as a function of the pyrolysis temperature using

different reactor systems. It should be noted that gas Cl is the water-soluble Cl (in ionic form, most likely as $\text{HCl}^{15,16,31}$) directly captured by the bubbler system, while tar Cl is calculated by difference. Therefore, tar Cl is mostly in the form of organically bound Cl in tar, which is water-insoluble.

In a fixed-bed reactor under slow-heating conditions (type I; see Figure 5a), little Cl is retained in char even at 400 °C. In other words, nearly all Cl species are released as part of volatiles (~23% as gas Cl and ~77% as tar Cl). Such a significant Cl release during pyrolysis at a temperature below 500 °C was also observed in previous studies for both other biomass fuels^{5,15,16} and low-rank coal.²¹ Further increasing the pyrolysis temperature up to 900 °C results in little change in Cl distribution (see Figure 5d) because of the “progressive nature” of slow pyrolysis; i.e., pyrolysis at 900 °C first experiences 400 °C, at which Cl would have been released. Conversely, Cl release follows a completely different trend in type II (i.e., pyrolysis in the drop-tube/fixed-bed reactor with continuous feeding) experiments, as shown in panels a–c and e of Figure 5. A considerably higher amount of Cl is retained in the char. Char Cl increases substantially with the temperature, from ~0.8% at 400 °C to ~44.1% at 600 °C, coinciding with reductions in both tar Cl and gas Cl. This can be attributed to the recombination of Cl in volatiles into the char (with either an organic char matrix²¹ or, more importantly, inherent metals,³² such as AAEM species in char) as a result of the lengthy and continuous volatile–char interactions; such reactions appear to intensify as the temperature increases. Indeed, the data in Figure 6 show that, even at 600 °C, almost all of AAEM species in biomass are retained in the nascent char, providing an abundant source of such metals for Cl recombination. Furthermore, results from water leaching of the char produced at 600 °C also suggest ~90.2% of Cl in char being water-soluble as ionic chloride. A further increase in the pyrolysis temperature

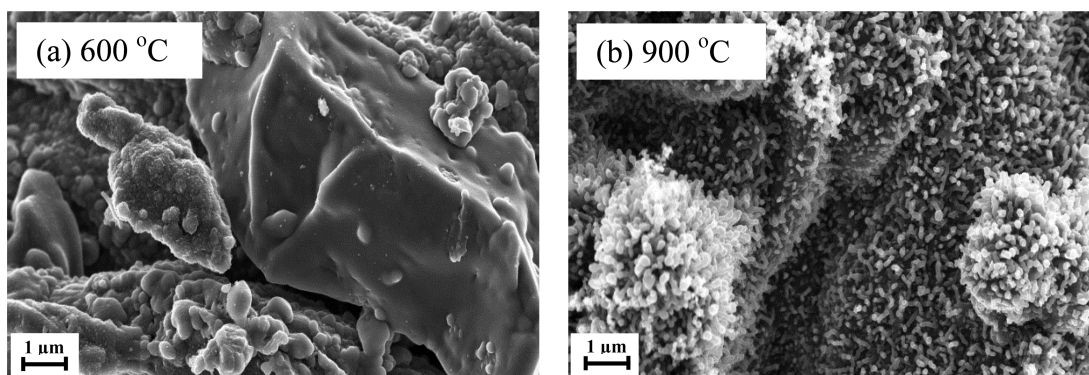


Figure 4. SEM images of char samples produced from pyrolysis in a drop-tube/fixed-bed reactor with continuous feeding at (a) 600 °C and (b) 900 °C.

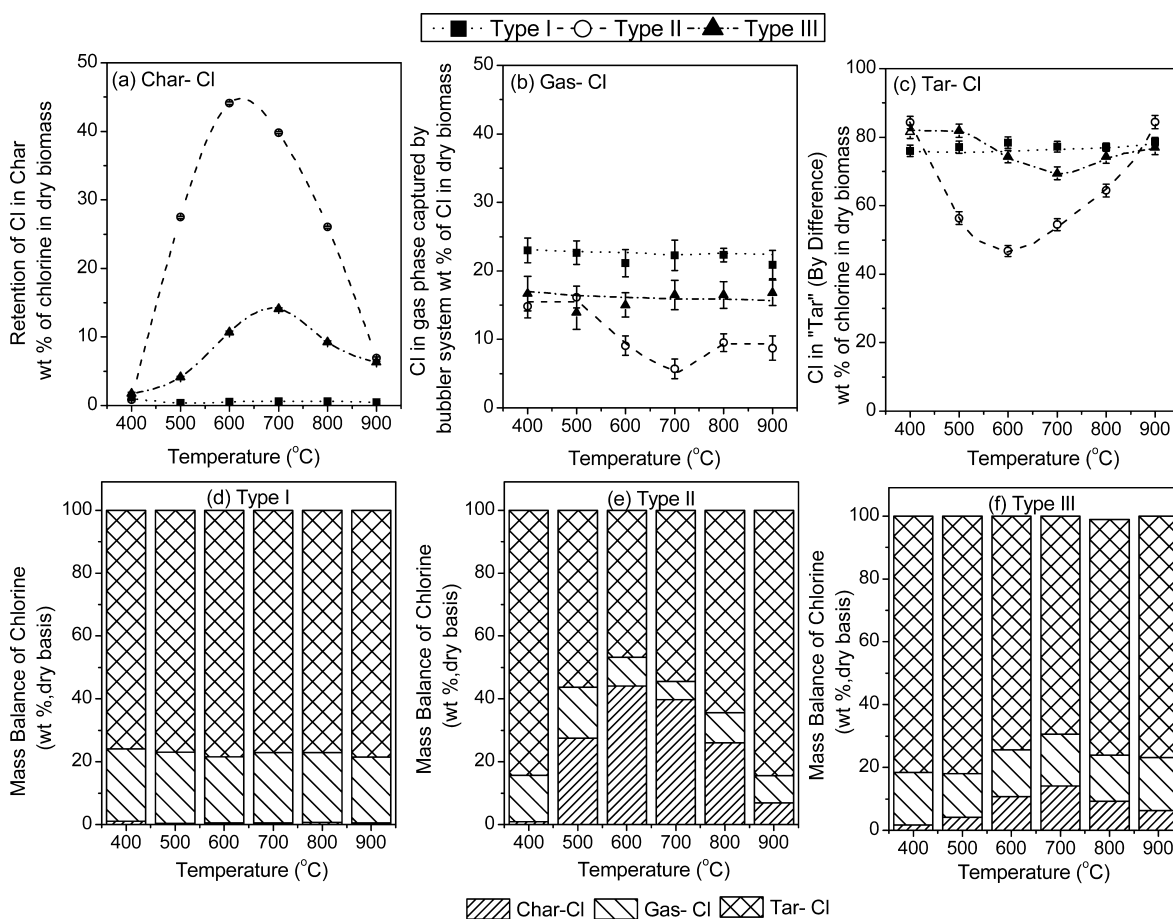


Figure 5. Distribution of chlorine among (a) char, (b) gas, and (c) tar and mass balance of chlorine during three types of pyrolysis experiments, including (d) type I (using a fixed-bed reactor), (e) type II (using a drop-tube/fixed-bed reactor with continuous feeding), and (f) type III (using a drop-tube/fixed-bed reactor with pulsed feeding). The mass balance of chlorine is presented as the weight percent of total chlorine in dry biomass. Chlorine in tar is calculated by difference from chlorine in char and gas.

leads to a substantial reduction in char Cl, e.g., to 26% at 800 °C and 6% at 900 °C, clearly indicating that less thermally stable bonds between Cl in volatiles and nascent char can be formed as the temperature increases, leading to increases in tar Cl and gas Cl. These results are in agreement with the previous observations in brown coal pyrolysis in a fluidized-bed/fixed-bed reactor.²¹ Likewise, volatile–char interactions also proceed but at a much less extent in type III experiments (i.e., fast pyrolysis in the drop-tube/fixed-bed reactor with pulsed feeding). Indeed, char Cl follows a similar trend with much

lower Cl retentions (see Figure 5a). It is also interesting to note that, at 400 °C, while no obvious differences are observed in char Cl (see Figure 5a), for all three types of pyrolysis, gas Cl (see Figure 5b) in type I experiments in a fixed-bed reactor is considerably higher than those in type II and III experiments under fast-pyrolysis conditions. This indicates that, under fast-heating conditions, the released gas Cl also appears to react with tar in volatiles, leading to a noticeable increase in tar Cl. It is surprising to note that, for type II experiments, a further increase in the temperature to 900 °C leads to a drastic increase

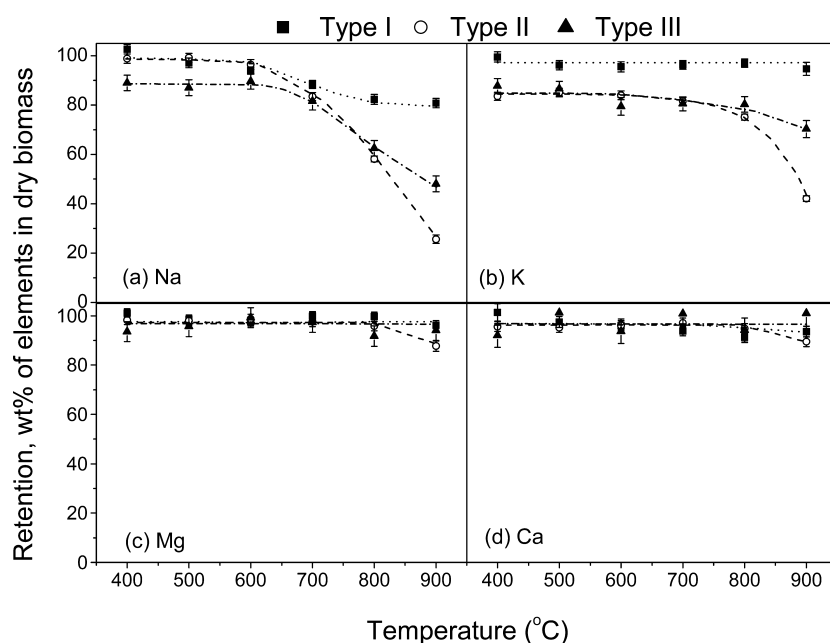


Figure 6. Retention of AAEM species in char produced from various types of biomass pyrolysis experiments, including type I (using a fixed-bed reactor), type II (using a drop-tube/fixed-bed reactor with continuous feeding), and type III (using a drop-tube/fixed-bed reactor with pulsed feeding).

of tar Cl, accompanied by the sharp decrease in char Cl, while no obvious changes were observed for gas Cl (see panels b and c of Figure 5). This is possibly due to the formation of alkali chloride salts in the gas phase and their subsequent reaction and/or deposition in the reaction system, thereby contributing to tar Cl. This will be discussed in section 3.4. Nevertheless, calculations based on the Cl balance in Figure 5 (see panel d–f) clearly suggest that substantial amounts (47–84%; see Figure 5c) of Cl can be present as tar Cl during biomass pyrolysis in the three types of experiments under various conditions.

As shown in Figure 6, the release of AAEM species follows trends that are completely different to Cl release, which was also reported previously²¹ for the pyrolysis of other low-rank fuels. The release of Na and K commences from 700 °C and becomes significant at 800 and 900 °C. This can be attributed to the intensified interactions between volatiles and nascent char²² as well as the increasing volatility of these species as the temperature increases. While following a similar trend, the release of K appears to be more difficult than Na, possibly because of the nature of K^{15,16} being more electropositive than Na and, hence, capable of forming intercalation compounds with carbons (hence, retained) in char.³³ Mg and Ca are divalent species and known to be difficult to release during pyrolysis because these species are heavier and of divalent bond with the char matrix, as suggested previously in a study on brown coal pyrolysis.³⁴ However, there is a small but appreciable increase in Mg and Ca release from 800 to 900 °C during pyrolysis in type II experiments. This can be attributed to the lengthy and continuous volatile–char interactions under such conditions.

3.4. Direct Determination of Cl in Tar under Various Conditions. As described in section 3.3, substantial amounts (47–84 wt %; see Figure 5c) of Cl may be present as tar Cl during biomass pyrolysis, depending upon the pyrolysis conditions. Direct combustion of Cl-containing volatiles (type IV experiment; see section 2.3) produced from slow pyrolysis in the fixed-bed reactor and the fast pyrolysis with continuous

feeding was conducted to quantify the total Cl present in tar. Such results are presented in Figure 7, along with the calculated

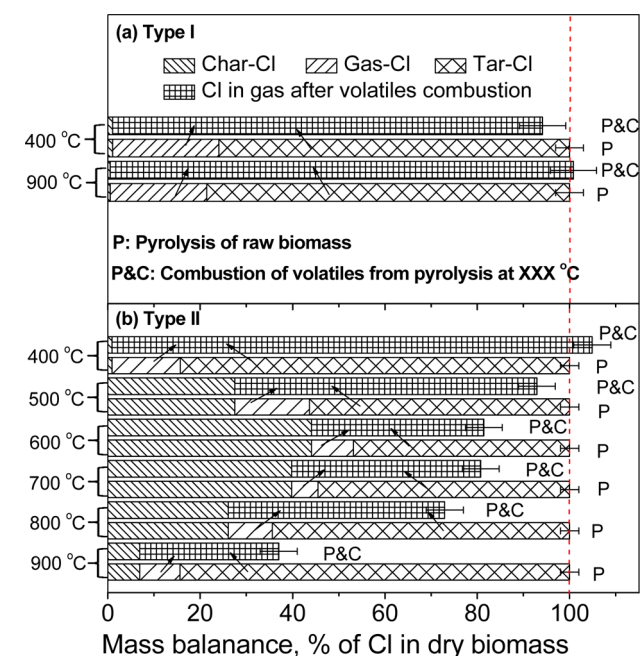


Figure 7. Mass balance of chlorine from pyrolysis and combustion of volatiles produced *in situ* from raw biomass during different types of pyrolysis experiments, including type I (using a fixed-bed reactor) and type II (using a drop-tube/fixed-bed reactor with continuous feeding).

data based on differences (from Figure 5) for benchmarking. As expected, for biomass pyrolysis in the fixed-bed reactor (at 400 and 900 °C), the combustion of Cl-containing volatiles achieves close to 100% Cl mass balance (see Figure 7a). This clearly demonstrates that, under the pyrolysis conditions, the majority of Cl is indeed organically bound in tar (i.e., tar Cl)

and can be recovered after combustion. Similarly, close to 100% mass balance of Cl has also been achieved after the *in situ* combustion of volatiles produced from type II experiments under fast pyrolysis in the drop-tube/fixed-bed reactor with continuous feeding at 400 and 500 °C (see Figure 7b). However, as the pyrolysis temperature further increases, there is an enhanced reduction in the mass balance of Cl after volatile combustion. The results suggest that the *in situ* combustion of volatiles generated at higher temperatures cannot recover all Cl in the volatiles after combustion. In other words, part of Cl seems to be lost during the *in situ* combustion of volatiles.

The significant discrepancies observed in the Cl mass balance as presented in Figure 7b at high temperatures (>500 °C) appear to be related to the release behavior of AAEM species (particularly Na and K) during pyrolysis. Under the pyrolysis conditions (type II experiments using a drop-tube/fixed-bed reactor with continuous feeding), the data in Figure 6 show that the release of Na starts from 600 °C and increases substantially with a further increase in the pyrolysis temperature. While it is small (~10%) at low temperatures, the release of K starts to increase from 700 °C and accelerates with a further increase in the pyrolysis temperature. At 900 °C, the release of both Na and K are substantial, while the release of Mg and Ca are minimal. It should be noted that the *in situ* combustion of volatiles (generated from biomass pyrolysis in the drop-tube/fixed-bed reactor with continuous feeding) takes place at 950 °C. Therefore, the AAEM species (dominantly Na and K) would likely combine with the released Cl to form alkali chlorides via a series of gas-phase reactions during *in situ* volatile combustion. The formed alkali chlorides may react with the quartz reactor and/or deposit on the reactor surface, leading to substantial reduction in the Cl mass balance after volatile combustion. This is supported by the evidence (results not shown here) that the combustion column became opaque after *in situ* combustion of volatiles and the observation of alkali and chlorine in the EDS spectrum from the analysis of the internal surface of the broken piece of the reactor. Indeed, as shown in Figure 8, the molar ratio of (Na + K)/Cl in the volatiles increases substantially as the pyrolysis temperatures increases above 600 °C, indicating that more Na and K are available to react with Cl in the volatiles released during *in situ*

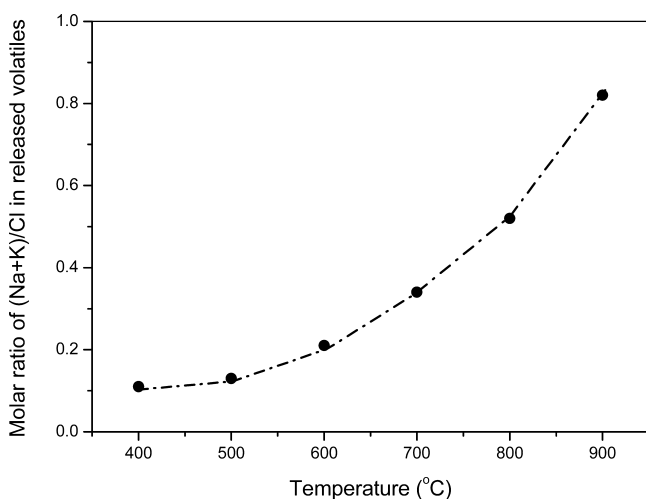


Figure 8. Molar ratio of (Na + K)/Cl in released volatiles during biomass pyrolysis in a drop-tube/fixed-bed reactor with continuous feeding.

combustion. It should also be noted that, when the pyrolysis was carried out under slow-heating conditions (the pyrolysis column is operated as a fixed-bed reactor), almost all Cl species (see Figure 5) were released at 400 °C, while nearly all AAEM species were retained in char (see Figure 6). Under such conditions, the opportunity for AAEM and Cl combination in volatiles during *in situ* combustion in the combustion column was limited, resulting in almost complete recovery of Cl present in tar after *in situ* combustion of volatiles.

4. CONCLUSION

This paper reports new data on the release of Cl and its distribution among char, tar, and gas during biomass pyrolysis under various conditions. All Cl in the raw biomass can be dissolved in water as ionic chloride. Little Cl was retained in char at a temperature as low as 400 °C under all reaction conditions. In a fixed-bed reactor, Cl release during biomass pyrolysis is insensitive to pyrolysis temperatures between 400 and 900 °C. In a drop-tube/fixed-bed reactor under continuous feeding, Cl retention in char increases as the pyrolysis temperature increases to 600 °C, at which Cl retention in char reaches a maximum of ~42% and then decreases to ~6% as the pyrolysis temperature further increases to 900 °C. Under pulsed feeding condition, similar trends (but to a much lesser extent) are observed for Cl release and distribution during biomass pyrolysis due to reduced volatile–char interactions and subsequent “self-gasification” between char and reactive gasification agents in volatiles at 900 °C. Calculations based on difference suggest that ~47–84 wt % of Cl is present in tars, depending upon pyrolysis conditions. Such findings were further confirmed experimentally via the quantification of Cl in tar using a two-column pyrolysis/combustion reactor, which burns the volatiles produced *in situ* from biomass pyrolysis and converts all Cl in volatiles into ionic forms, which are water-soluble for quantification. Furthermore, ~100% mass balance of Cl in char, tar, and gas can be achieved during biomass pyrolysis in a fixed-bed reactor at 400–900 °C or in the drop-tube/fixed-bed reactor below 600 °C. For volatiles produced from biomass pyrolysis in the drop-tube/fixed-bed reactor with continuous feeding at temperatures >600 °C, 100% Cl mass balance closure is not achievable because the volatiles contain abundant released inorganic species (Na and K), which appear to capture some Cl during *in situ* volatile combustion to form alkali chlorides deposited on the reactor wall.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone: +61-8-92667592. Fax: +61-8-92662681. E-mail: h.wu@curtin.edu.au.

Notes

The authors declare no competing financial interest.

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