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# Use of Alkali Carbonate Sorbents for Capturing Chlorine-Bearing Gases from Corn Straw Torrefaction

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**ABSTRACT:** Combustion of torrefied biomass for power generation has many advantages over combustion of raw biomass, one of which is lower emissions of chlorine-bearing gases. This is because partial evolution of these gases takes place during the torrefaction process; hence, the resulting torrefied biomass has a lower chlorine mass fraction than its raw biomass precursor. Research showed that, during torrefaction of corn straw, the predominant chlorinated species in the evolving gas ("torgas") are $CH_3Cl$ and HCl. The former is more prevalent when torrefaction takes place at temperatures under 350 °C, whereas the latter is more abundant at higher temperatures. In this work, corn straw was torrefied at a furnace temperature of 300 °C for 20 min under atmospheric pressure in an inert nitrogen flow. Under this condition, corn straw lost nearly 40% of its original mass, along with 73% of its chlorine mass to the gas phase. To control the emissions of the chlorinated species, the torrefaction gas was heterogeneously reacted with beds of alkali carbonate sorbents kept at temperatures in the range of 25−500 °C. It was determined that the sorbents captured HCl more effectively than $CH_3Cl$, with amounts varying with both the type of sorbent and the sorbent/gas reaction temperature. HCl removal effectiveness varied in the range of 26−80%, whereas $CH_3Cl$ removal effectiveness varied in the range of 15−22% at the conditions implemented herein. Potassium carbonate ($K_2CO_3$) was found to be slightly more effective than sodium carbonate ($Na_2CO_3$) and significantly more effective than calcium carbonate ($CaCO_3$), particularly at low reaction temperatures.

## INTRODUCTION

Renewable biomass is of technological interest because it is considered as a fuel that will help to address climate change, because its combustion is considered nearly carbon neutral.[1,2] However, there are issues with the use of raw biomass as a fuel.[3] Its high moisture content and hydrophilicilty result in low specific internal energy (heating value) and high biodegradability. Its fibrous and tenacious nature results in poor grindability. Its high particle aspect ratios impair fluidization.[4] Its high chlorine and sulfur contents cause slagging, fouling, and corrosion,[5−7] particularly in high-temperature pulverized fuel boilers, which are lined with metallic water tube heat exchangers.

The aforementioned issues can be partially alleviated by thermal pretreatment of biomass in moderate temperatures and in the absence (or near absence) of oxygen; this pyrolytic process has been termed torrefaction. Typically, torrefaction takes place in nitrogen at temperatures at or lower than 300 °C for less than 1 h. It is a mild pyrolysis process, and the resulting residue is somewhat "coal-like".[3] It has less moisture and lower light-volatile hydrocarbon mass fractions than its raw biomass precursor. It has improved biodegradability and, hence, a longer storage life, better grindability, lower particle aspect ratios,[8] and higher heating value.

Torrefied biomass has lower sulfur and chlorine mass fractions than raw biomass;[9−14] thus, it is less problematic to burn alone or blended with coal in pulverized fuel boilers, where combustion temperatures are high and metallic surfaces abound. The lower emissions of the acid gases $SO_2$ and HCl[9−14] render their capture more manageable by the emission control equipment of power plants, and consequently, the lower amounts released to the atmosphere are more environmentally acceptable.[15]

Partial release of chlorine and sulfur to the gas phase during the torrefaction process is likely to be less problematic than during a subsequent combustion process. This is because the torrefaction furnaces can be refractory; thus, they should be relatively unaffected by corrosion or deposition. The predominant chlorine-bearing gases evolving during torrefaction have been identified to be $CH_3Cl$ and HCl.[16−18] Recent work by Ren et al.[18] torrefied corn straw and determined that $CH_3Cl$ was more prevalent when torrefaction took place at temperatures under 350 °C, whereas HCl was more abundant at higher temperatures. For example, at the torrefaction temperature of 275 °C, $CH_3Cl$ accounted for 22.7% and HCl accounted for 23.1% of the mass of chlorine in the raw biomass. Another 41.1% remained in the ash, and 13.1% was unaccounted for;[18] hence, the amounts of $CH_3Cl$ and HCl in the torgas were similar and together amounted to nearly 46% of the chlorine mass in the raw biomass.

Because nearly half of the chlorine mass of raw corm straw was released to the atmosphere during torrefaction, under such conditions, its control is of technological interest for maintaining a safe environment. Therefore, this work focuses

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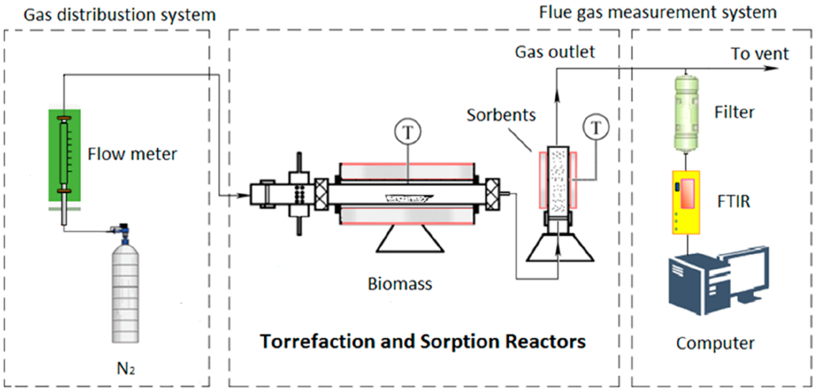


**Figure 1.** Schematic of the laboratory setup for torrefaction of corn straw in a horizontal fixed bed reactor and placement of sorbents in a separate vertical reactor.

on the control of chlorine-bearing gases by heterogeneously reacting them with alkali carbonate sorbents. On the basis of recent experiences[15] on controlling HCl emissions from combustion of corn straw and corn-based distillers dried grains with solubles (DDGS) using fixed beds of readily available alkali sorbents, this technique was also implemented herein to curtail chlorine-bearing gas concentrations in the torgas. Because torgas contains significant amounts of $CH_3Cl$, in addition to HCl, the sorption efficiencies of the alkali carbonate sorbents for both species were examined. Moreover, because torrefaction is a moderate temperature process, it is sensible that the sorbent bed also be kept at moderate temperatures for practical purposes. Hence, the following low-to-moderate sorbent bed temperatures were explored herein: 25, 300, and 500 °C, of which the first two are deemed as the most practical for torrefaction processing plants.

## BIOMASS PREPRATION AND CHARACTERIZATION: SORBENT SELECTION

Corn straw, a biomass with a high chlorine content (0.63%), was grown and harvested at the Harbin Province of China. Torrefaction of raw corn straw was carried out in a horizontal electrically heated muffle furnace, depicted in Figure 1, in the absence of oxygen for 20 min at 300 °C. Batches of 0.5 g of pulverized (75−150 $\mu$m) raw biomass was inserted in this furnace, preheated, and purged with nitrogen, where they experienced a heating rate of ∼60 °C/s.

The proximate and ultimate analyses of the torrefied biomass are shown in Table 1. During torrefaction at this temperature, corn straw lost 39.6% of its mass by devolatilization. After torrefaction, corn straw was ground in a household blender and sieved to the size cut of 75−150 $\mu$m. The proximate and ultimate analyses of the raw corn straw are given in Table 1. Proximate analysis was performed on the basis of the GB/T 212-2008 Chinese standard[19] in an electric oven (5E-DHG) and muffle furnace (5E-MF6000) both manufactured by Changsha Kaiyuan Instruments Co., Ltd. Ultimate analysis for carbon, hydrogen, and nitrogen was carried out by an elemental analyzer (CHN2200, manufactured by Elementar, Ltd.) according to the GB/T 30733-2014 Chinese standard,[20] whereas sulfur analysis was carried out in a Coulomb fixed sulfur analyzer ($5 \times 10^{-8}$ S manufactured by Changsha Kaiyuan Instruments Co., Ltd.) based on the GB/T 214-2007 Chinese standard.[21] The heating value of the biomass fuels was measured with a calorimeter (5E-AC/PL, manufactured by Changsha Kaiyuan Instruments Co., Ltd.) according to the GB/T 213-2008 Chinese standard.[22]

The sorbents used in this work were (i) calcium carbonate ($CaCO_3$) reagent obtained from J.T. Baker, Inc., (ii) sodium carbonate ($Na_2CO_3$) obtained from EM Science, and (iii) potassium carbonate anhydrous ($K_2CO_3$) obtained from Fisher Scientific. All sorbents were used in powder form, as shown in Figure 2.

**Table 1. Proximate and Ultimate Analyses (wt %) and Energy Contents (MJ/kg) of Raw Corn Straw**

| fuel type | corn straw raw | corn straw torrefied at 300 °C for 20 min |
|---|---|---|
| Proximate Analysis (Air-Dried Basis) | | |
| moisture (%) | 6.18 | 2.31 |
| volatile matter (%) | 71.21 | 50.34 |
| fixed carbon (%) | 16.12 | 38.83 |
| ash (%) | 6.49 | 8.52 |
| Ultimate Analysis (Air-Dried Basis) | | |
| carbon (%) | 45.84 | 53.19 |
| hydrogen (%) | 5.11 | 4.98 |
| oxygen (%) | 34.89 | 28.89 |
| nitrogen (%) | 1.28 | 1.94 |
| sulfur (%) | 0.21 | 0.17 |
| calcium (%) | 0.48 | 0.58 |
| sodium (%) | 0.01 | 0.02 |
| potassium (%) | 0.64 | 1.25 |
| magnesium (%) | 0.25 | 0.31 |
| chlorine (%) | 0.63 | 0.28 |
| K/Cl (molar ratio) | 0.92 | 4.06 |
| $Ca/Cl_2$ (molar ratio) | 1.35 | 2.42 |
| heating value (MJ/kg) | 16.8 | 19.4 |

The particle size distributions of the sorbent powders were obtained using a laser particle analyzer (Mastersizer 3000 by Malvern Panalytical), and results are included in Table 2. Results show that most sorbent particles were between 1 and 50 $\mu$m in diameter.

The specific surface area of the sorbents, in their as-received states, was measured according to the Brunauer−Emmett−Teller (BET) method using an Autosorb-iQ Quantachrome instrument in nitrogen. The surface area of $CaCO_3$ was measured to be 2.18 $m^2/g$ with a calculated corresponding average pore diameter of 19.1 nm. The surface area of $Na_2CO_3$ was lower at 0.12 $m^2/g$, whereas that of $K_2CO_3$ was yet lower, in fact, below the resolution of the instrument.

## EXPERIMENTAL APPARATUS AND PROCEDURE

Torrefaction of batches of pulverized corn straw was performed in an electrically heated horizontal fixed bed furnace at 300 °C for 20 min in an inert nitrogen flow. Sorption was performed subsequently in a vertically placed electrically heated furnace. Both furnaces, depicted in Figure 1, were fitted with Pyrex glass tubes. The tube in the first furnace was 10 cm in diameter and 150 cm in length, whereas the second furnace was 3 cm in diameter and 30 cm in length. In these fixed fuel bed experiments, the torrefaction of biomass happened first and then the effluent torgas passed through powders of sorbents placed in the second furnace. The temperature of the secondary

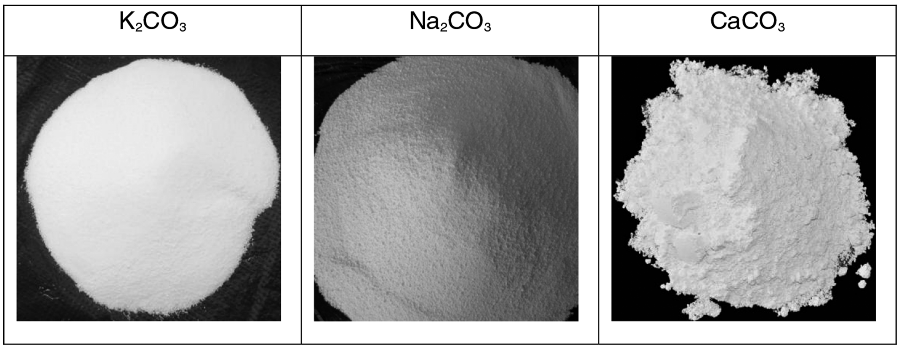
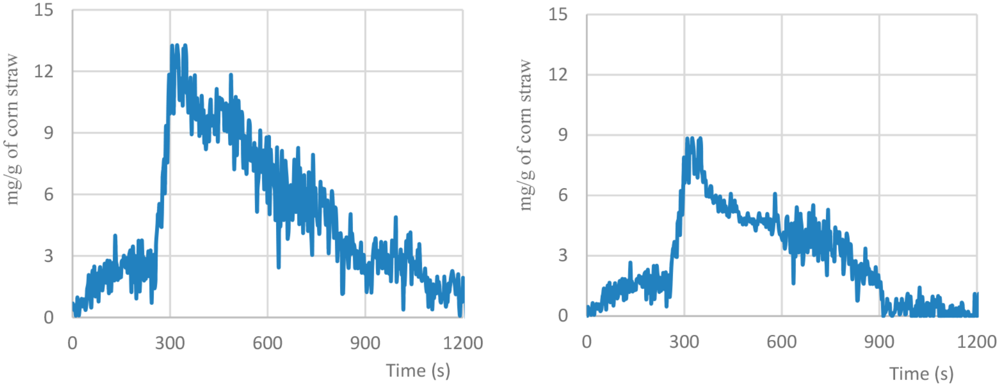


**Figure 2.** Fine powders of particles of the alkali carbonate sorbents.

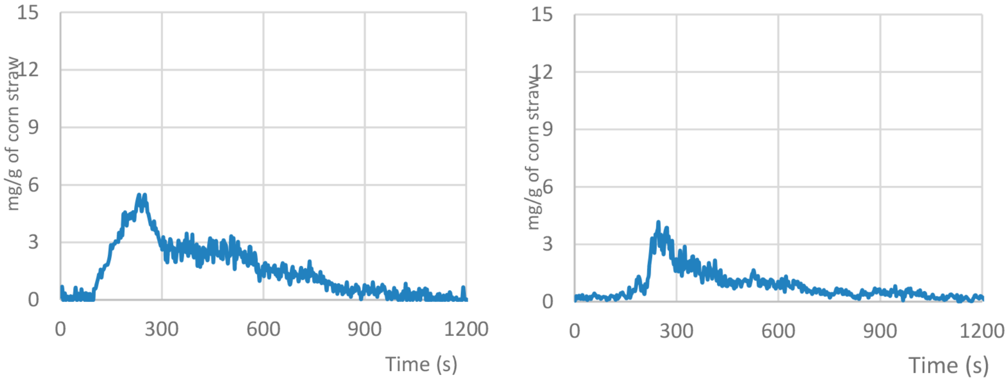
### Table 2. Alkali Carbonate Sorbent Particle Size Distributions

| | $CaCO_3$ | $K_2CO_3$ | $Na_2CO_3$ |
|---|---|---|---|
| $D_{10}$, particles with diameters smaller than the shown values account for 10% of the total number of particles ($\mu$m) | 2.3 | 1.4 | 5.1 |
| $D_{50}$, particles with diameters larger and smaller than the shown values account for 50% of the total number of particles ($\mu$m) | 17.1 | 10.8 | 25.2 |
| $D_{90}$, particles with diameters larger than the shown values account for 10% of the total number of particles ($\mu$m) | 46.6 | 41.9 | 52.4 |

furnace was maintained at 25, 300, or 500 °C. The Pyrex glass tube of the secondary furnace was fitted with fritted glass discs at its entrance and exit. A small amount of alkali carbonate sorbents (0.5 g) was placed therein and filled only a small fraction of the length of the tube. The nitrogen flow rate was kept at 3 L/min, which gently fluidized the sorbent powders in this vertically placed tube. The value of the weight hourly space velocity (WHSV), defined as the weight of the torrefaction effluent (nitrogen plus the volatiles) flowing per unit weight of the sorbent per hour, was calculated to be in the order of 200 $h^{-1}$. The effluent of this apparatus was heated to 180 °C to avoid condensation of $H_2O$, which can absorb HCl and, perhaps, $CH_3Cl$. It then passed through a fiber filter to collect any condensed matter. Thereafter, to monitor the HCl emissions, Fourier transform infrared (FTIR) spectroscopy (with a GASMET DX4000 instrument) was


(a) HCl release without sorbents

(b) HCl release upon $CaCO_3$ sorption at 25 °C


(c) HCl release upon $CaCO_3$ sorption at 300 °C

(d) HCl release upon $CaCO_3$ sorption at 500 °C

**Figure 3.** Evolution of specific mass emissions of HCl in the torrefaction effluents (a) in the absence of sorbents and (b−d) in the presence of calcium carbonate sorbent beds kept at different temperatures.

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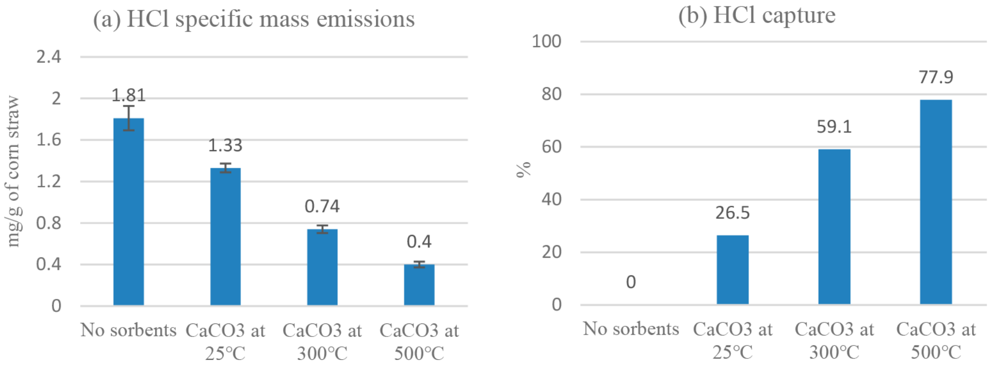

**Figure 4.** (a) Integrated mass emissions of HCl (mg/g of dry fuel) in the absence or presence of a $CaCO_3$ bed heated at different temperatures and (b) HCl emission reduction by passing the torrefaction effluent through $CaCO_3$ sorbent beds.

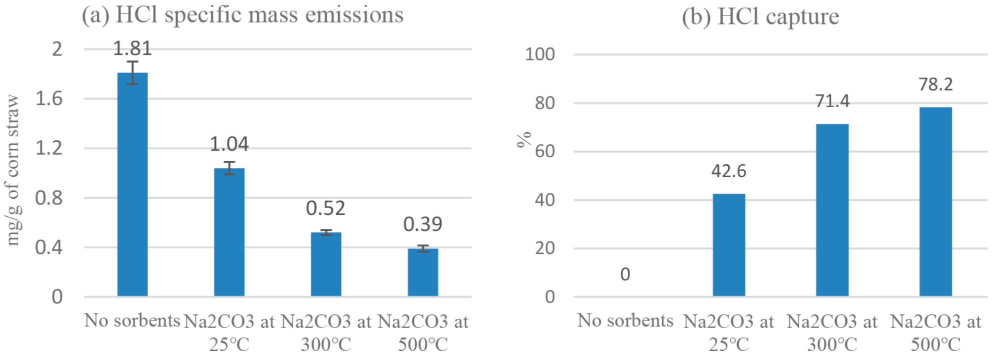

**Figure 5.** (a) Integrated mass emissions of HCl (mg/g of dry fuel) in the absence or presence of a $Na_2CO_3$ bed heated at different temperatures and (b) HCl emission reduction by passing the torrefaction effluent through $Na_2CO_3$ sorbent beds.

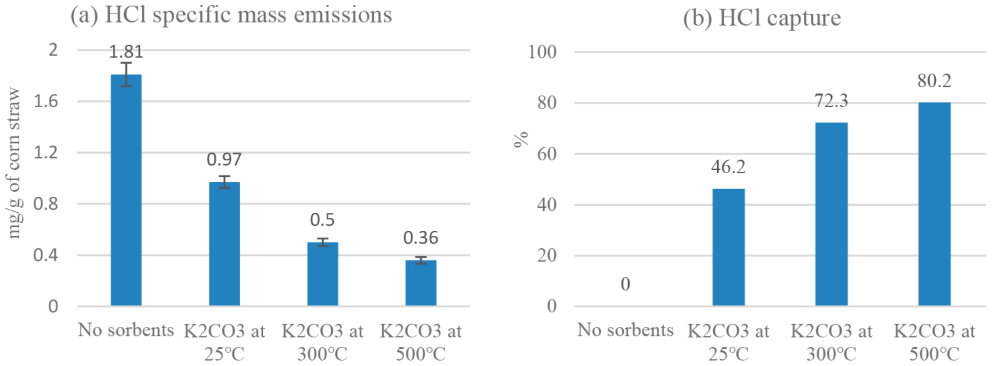

**Figure 6.** (a) Integrated mass emissions of HCl (mg/g of dry fuel) in the absence or presence of a $K_2CO_3$ bed heated at different temperatures and (b) HCl emission reduction by passing the torrefaction effluent through $K_2CO_3$ sorbent beds.

used. The effluent of the furnace first passed through a glass condenser, which was placed in an ice bath, and was subsequently channeled to the FTIR analyzer. All experiments were repeated 3 times, and mean values and standard deviations were calculated.

## ■ RESULTS AND DISCUSSION

**HCl Emissions of Biomass in the Absence and Presence of Alkali Carbonate Sorbents.** Typical time-resolved profiles of HCl emissions from 300 °C torrefaction of biomass in the horizontal furnace, as monitored by FTIR, are shown in Figure 3. The first profile, shown in Figure 3a, corresponds to raw effluent in the absence of sorbents, whereas the ensuing three profiles, panels b, c, and d of Figure 3, were recorded upon passing the effluent through calcium carbonate sorbent beds heated at the temperatures of 25, 300, and 500 °C, respectively. These experimentally measured mass emissions were first integrated with time, and upon subsequent normalization by the initial mass of biomass in each case, they are shown in Figure 4a.

During torrefaction, in the absence of sorbents, nearly 28% of the chlorine mass in the raw biomass was released as HCl. In the presence of sorbents, a great deal of HCl emissions was captured, and results are displayed in Figures 4, 5, and 6, for calcium carbonate, sodium carbonate, and potassium carbonate, respectively. As shown in Figure 4, the $CaCO_3$ sorbent captured 26.5, 59.1, and 77.9% of generated HCl at the 25, 300, and 500 °C sorbent bed temperatures, respectively. Correspondingly, as shown in Figure 5, the $Na_2CO_3$ sorbent captured 42.6, 71.4, and 78.2% of generated HCl at 25, 300, and 500 °C respectively. Finally, as shown in Figure 6, the $K_2CO_3$ sorbent captured 46.2, 72.3, and 80.2% of generated HCl at 25, 300, and 500 °C, respectively. It is notable that

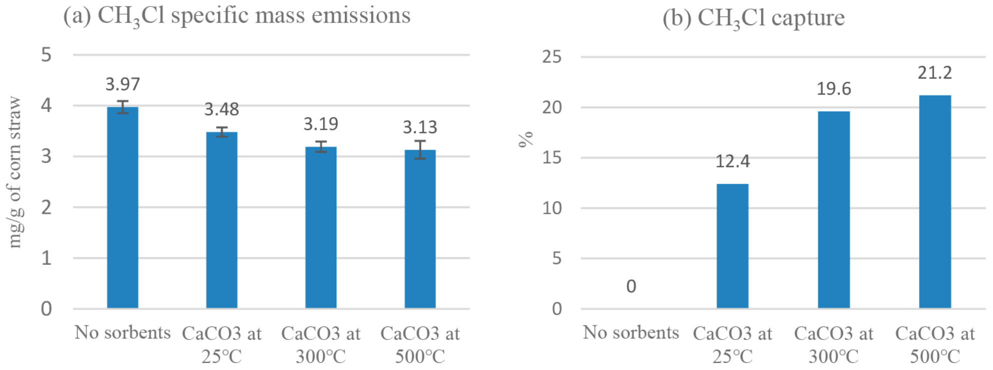

**Figure 7.** (a) Integrated mass emissions of $CH_3Cl$ (mg/g of dry fuel) in the absence or presence of a $CaCO_3$ bed heated at different temperatures and (b) $CH_3Cl$ emission reduction by passing the torrefaction effluent through $CaCO_3$ sorbent beds.

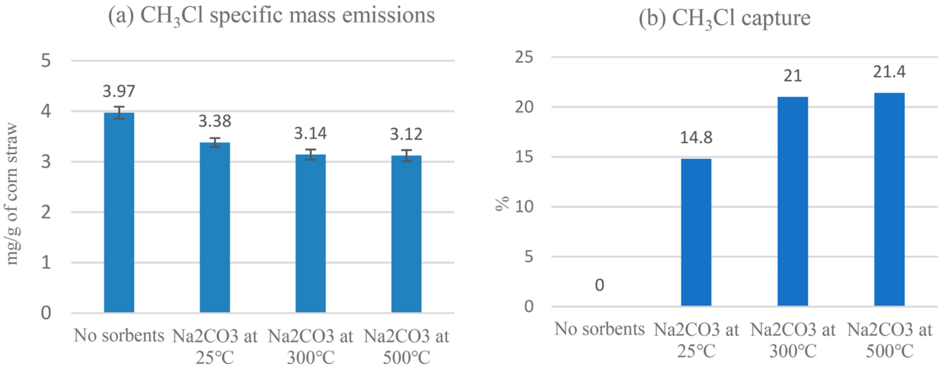

**Figure 8.** (a) Integrated mass emissions of $CH_3Cl$ (mg/g of dry fuel) in the absence or presence of a $Na_2CO_3$ bed heated at different temperatures and (b) $CH_3Cl$ emission reduction by passing the torrefaction effluent through $Na_2CO_3$ sorbent beds.

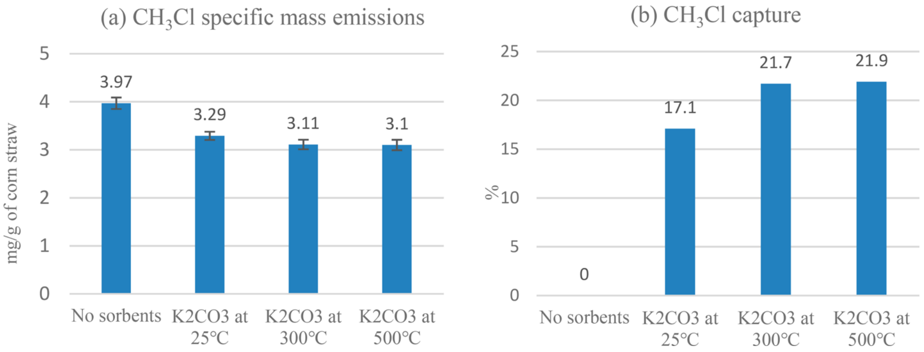

**Figure 9.** (a) Integrated mass emissions of $CH_3Cl$ (mg/g of dry fuel) in the absence or presence of a $K_2CO_3$ bed heated at different temperatures and (b) $CH_3Cl$ emission reduction by passing the torrefaction effluent through $K_2CO_3$ sorbent beds.

increasing the sorbent bed temperature from 25 to 300 °C increased the sorption capacity of the sorbents more than by increasing the temperature further from 300 to 500 °C. This may be attributed to the fact that such sorption reactions are thermodynamically favorable at low temperatures, but at increasing temperatures, they become asymptotically less favorable, as illustrated in an ensuing section of this paper as well as in Figure 5 in ref 15. Hence, the increase in sorbent sorption effectiveness may not justify the expense for heating the sorbent to a temperature higher than the torrefaction temperature itself, particularly so if, in practical systems, the torrefaction and sorbent beds share the same furnace.

Overall, these experiments showed that HCl capture can be realized by direct chlorination of the carbonate sorbents, in line with the findings of Snow et al.,[23] who reported that the direct sulfation of calcium carbonate (limestone) is not only possible but can also proceed to higher conversion than the sulfation of precalcined limestone. Thus, by analogy to the aforesaid direct sulfation reaction, the direct chlorination reaction of limestone, as expressed below, appears to also proceed to substantial conversion, as proposed by Shemwell et al.[24]

$$2HCl(g) + CaCO_3(s) \rightarrow CaCl_2(s) + CO_2(g) + H_2O(g)$$

Under the conditions of these experiments, the potassium carbonate sorbent proved to be the most effective (slightly better than $Na_2CO_3$) and the calcium-sorbent sorbent was the least effective for HCl capture. This is supported by chemical equilibrium calculations, which show that the chlorination reaction of potassium carbonate is more favorable than that of sodium carbonate, which, in turn, is more favorable than that of calcium carbonate, as illustrated in an ensuing section of this paper and also in Figure 5 in ref 15.

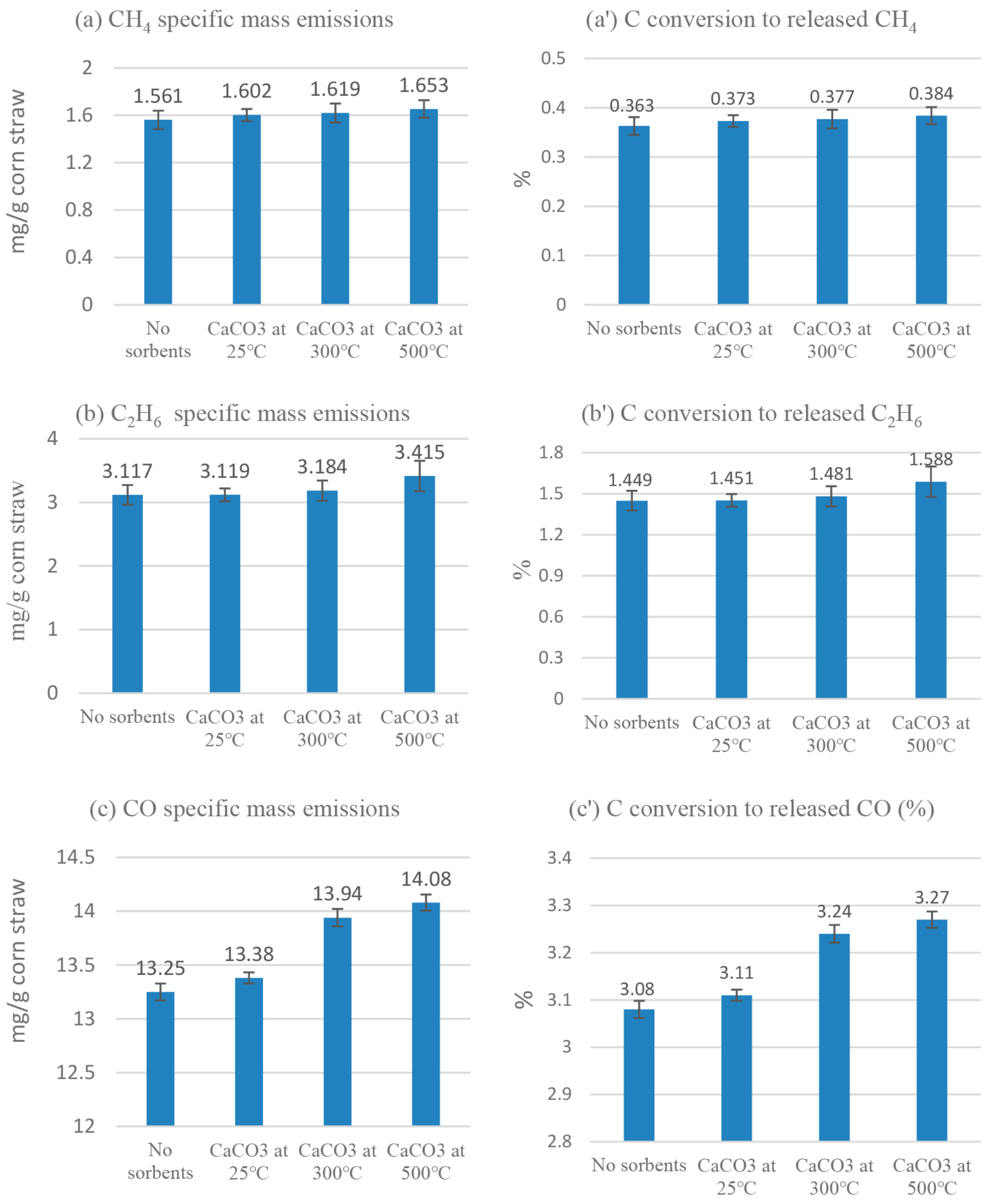

**Figure 10.** (a, b, and c) Integrated experimentally determined mass emissions of $CH_4$, $C_2H_6$, and CO (mg/g of dry fuel) in the absence or presence of a $CaCO_3$ bed heated at different temperatures and (a′, b′, and c′) percent of biomass carbon converted to $CH_4$, $C_2H_6$, and CO.

Previous research[25−30] has also evaluated the reaction of potassium-, sodium-, and calcium-based sorbents with HCl gas and reported significant capture, depending upon the amounts of the sorbents, the flue gas temperature, the sorbent−gas contact time, the sorbent porosity, the sorbent particle size, etc. Potassium carbonate and sodium carbonate have been identified to be the most effective sorbents for HCl, while calcium carbonate has been reported to have lower effectiveness,[25,31,32] which is in line with the results reported herein.

**$CH_3Cl$ Emissions of Biomass in the Absence and Presence of Alkali Carbonate Sorbents.** In these torrefaction experiments, nearly 40% of the biomass chlorine mass was released as $CH_3Cl$. In the presence of sorbents, a fraction of these emissions was captured, as illustrated in Figures 7−9.

As shown in Figure 7, using beds of a $CaCO_3$ sorbent heated to 25, 300, and 500 °C, as much as 12.4, 19.6, and 21.2% of generated $CH_3Cl$ were captured, respectively. While, as shown in Figure 8, using beds of a $Na_2CO_3$ sorbent heated to 25, 300, and 500 °C, as much as 14.8, 21, and 21.4% of generated $CH_3Cl$ were captured, respectively. Finally, as shown in Figure 9, using beds of a $K_2CO_3$ sorbent heated to 25, 300, and 500 °C, as much as 17.1, 21.7, and 21.9% of generated $CH_3Cl$ were captured, respectively. By comparison of the $CH_3Cl$ sorption capacities at the temperatures of 300 and 500 °C, it can be seen that they are nearly the same. Therefore, as in the case of HCl, it is notable that increasing the sorbent bed temperature from 300 to 500 °C only mildly increased the sorption capacity of the sorbents for $CH_3Cl$; therefore, again, the expense for heating the sorbent bed at the higher temperature may not be justified.

A comparison of the effectiveness of the three alkali carbonate sorbents for capturing $CH_3Cl$ reveals that the potassium carbonate sorbent was the most effective. The gap in performance among the three sorbents was most pronounced

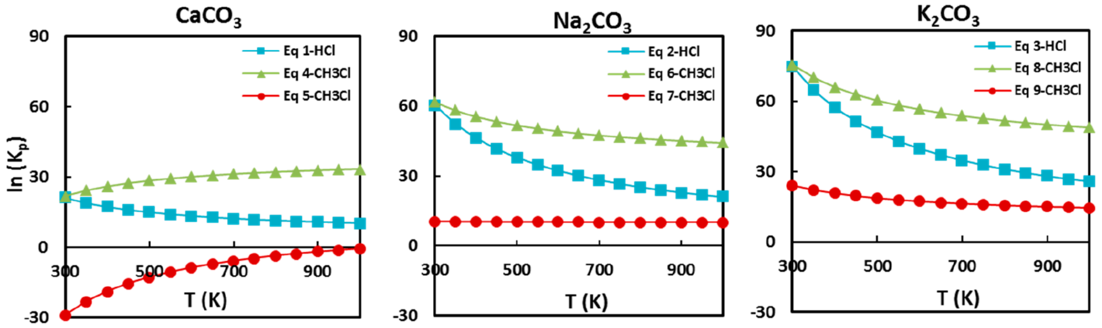

**Figure 11.** Equilibrium constant of reactions 1−9.

at the lowest temperature examined herein (25 °C), whereas as the temperature increases to 300 °C and, particularly, to 500 °C, the performance of the sorbents converges to a similar value. This behavior is supported by thermodynamic calculations, which are outlined in an ensuing section of this paper.

The aforementioned results show that all three alkali carbonates are more effective in capturing HCl than $CH_3Cl$. The reasons for this behavior may be based on chemical reaction thermodynamics or kinetics and are discussed further in the following section.

**Chemical Equilibrium Considerations for Possible HCl and $CH_3Cl$ Reactions.** The overall heterogeneous reactions of HCl gas with the three alkali carbonate sorbents are shown below, as outlined in past literature.[15,24]

$$2HCl(g) + CaCO_3(s) \leftrightarrow CaCl_2(s) + CO_2(g) + H_2O(g) \tag{1}$$

$$2HCl(g) + Na_2CO_3(s) \leftrightarrow 2NaCl(s) + CO_2(g) + H_2O(g) \tag{2}$$

$$2HCl(g) + K_2CO_3(s) \leftrightarrow 2KCl(s) + CO_2(g) + H_2O(g) \tag{3}$$

However, to the knowledge of the authors, there is paucity in the literature regarding the reactions of $CH_3Cl$ with the alkali carbonate sorbents. Prior work on the thermal decomposition of $CH_3Cl$ in the moderate temperature range of this investigation conducted by Won[33] showed that the thermal stability of $CH_3Cl$ is good in this temperature range. Non-chlorinated decomposition products may include $CH_4$ and $C_2H_6$. Smaller amounts of $C_2H_4$ were also detected but mostly at higher temperatures ($T > 850$ °C). Koper and Klabunde[34] examined the destructive adsorption of chlorinated hydrocarbons on calcium oxide at temperatures in the range of 300−500 °C and detected carbon monoxide in the products. On the basis of those results, possible overall reactions of $CH_3Cl$ gas with $CaCO_3$ that produce $CH_4$, CO, and $C_2H_6$ may be the following two:

$$2CH_3Cl(g) + CaCO_3(s) \leftrightarrow CaCl_2(s) + 2CO(g) + CH_4(g) + H_2O(g) \tag{4}$$

$$2CH_3Cl(g) + CaCO_3(s) \leftrightarrow CaCl_2(s) + CO_2(g) + C_2H_6(g) + 0.5O_2(g) \tag{5}$$

Similarly, possible overall sorption reactions of $CH_3Cl$ with $Na_2CO_3$ sorbents are

$$2CH_3Cl(g) + Na_2CO_3(s) \leftrightarrow 2NaCl(s) + 2CO(g) + CH_4(g) + H_2O(g) \tag{6}$$

$$2CH_3Cl(g) + Na_2CO_3(s) \leftrightarrow 2NaCl(s) + CO_2(g) + C_2H_6(g) + 0.5O_2(g) \tag{7}$$

Similarly, the overall sorption reactions of $CH_3Cl$ with $K_2CO_3$ sorbents are

$$2CH_3Cl(g) + K_2CO_3(s) \leftrightarrow 2KCl(s) + 2CO(g) + CH_4(g) + H_2O(g) \tag{8}$$

$$2CH_3Cl(g) + K_2CO_3(s) \leftrightarrow 2KCl(s) + CO_2(g) + C_2H_6(g) + 0.5O_2(g) \tag{9}$$

To evaluate the possibility that reactions 4−9 take place during these experiments, the evolution of $CH_4$, CO, and $C_2H_6$ was monitored in the torrefaction effluents in both the absence and the presence of one of the sorbents, $CaCO_3$. Experimentally measured specific mass emissions are shown in Figure 10, where it can be observed that the concentrations of these products increased consistently in the presence of the sorbents, because decomposition of $CH_3Cl$ takes place in this temperature range. The specific emissions of $CH_4$, $C_2H_6$, and CO increased mildly with an increasing temperature, as the amounts of $CH_3Cl$ decreased through the sorbent bed, as shown in Figures 7−9. This supports the proposed chemical mechanism and is in line with the observations of Koper and Klabunde[34] regarding the CO generation from destructive adsorption of chlorinated hydrocarbons on calcium oxide.

Thermodynamic chemical equilibrium constants, $K_p$, for reactions 1−9 are calculated on the basis of the free energy change as follows:

$$\ln K_p = \frac{-\Delta G_T^\circ}{RT} \tag{10}$$

where the Gibbs free energy could be calculated as follows:

$$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ \tag{11}$$

where $\Delta H_T^\circ$, $\Delta S_T^\circ$, and $T$ are the respective standard enthalpy change, standard molar entropy change, and reaction temperature.

Generally, when the value of $K_p$ is greater than 1000 [$\ln(K_p) > 6.9$], the reaction can be considered to proceed to completion.[35] Therefore, on the basis of the calculated thermodynamic equilibrium constants, shown in Figure 11,

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all reactions, with the exception of reaction 5, have $\ln(K_p) > 6.9$; therefore, they are favorable in this temperature range.

Potassium carbonate was shown to be the most effective sorbent, followed by sodium and then calcium, for capturing HCl and $CH_3Cl$ gases. This trend was observed both experimentally and theoretically by the aforesaid chemical equilibrium calculations. The fact that the experimentally measured values for the reduction of HCl were higher than the corresponding reduction values of $CH_3Cl$, contrary to the thermodynamic predictions based on chemical equilibrium, may be attributed to kinetic limitations for reactions 4−9, because the residence times of the torrefaction effluent gas ("torgas") through the sorbent bed were very brief. To the contrary, reaction kinetics for HCl sorption by alkali sorbents have been shown to be very fast (see refs 24, 36, and 37). Hence, because there is a scarcity of kinetic studies for $CH_3Cl$ by alkali sorbents, this may be a suggested topic of future research.

## ■ CONCLUSION

Because nearly half of the chlorine mass of raw corm straw is released to the atmosphere during torrefaction, control of emitted chlorinated gases is important. To achieve this goal, this study reacted the torrefaction gas heterogeneously with beds of powdered alkali carbonate sorbents ($CaCO_3$, $Na_2CO_3$, and $K_2CO_3$) kept at three different bed temperatures: 25, 300, or 500 °C. The results are summarized as follows:

Concentrations of $CH_3Cl$ in the torgas were found to be higher than those of HCl at the torrefaction temperature of 300 °C.

The removal efficiencies of HCl by the sorbents were found to be higher than the removal efficiencies of $CH_3Cl$ at all sorbent bed temperatures tested.

The removal efficiencies of both HCl and $CH_3Cl$ by the sorbents increased with increasing bed temperature. The increase was steep when the bed temperature was raised from 25 to 300 °C, whereas it was milder when the temperature was further raised from 300 to 500 °C. Therefore, it may be economically sensible to choose the sorbent utilization temperature to be in the former range, i.e., analogous to the operating temperature of the torrefaction process.

The type of alkali carbonate sorbent had a small influence in this temperature range, particularly so at the higher temperatures, although comparatively the potassium-based sorbent was the most effective and the calcium-based sorbent was the least effective at the lower temperatures.

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### Notes

The authors declare no competing financial interest.

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