Valorization of Waste-Derived Inorganic Sorbents for the Removal of HCl in Syngas

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Abstract

Syngas production via the pyro-gasification of waste biomass is a promising means of managing waste while producing renewable fuel. However, such waste may contain a significant level of impurities such as chlorine, which may result in hydrogen chloride (HCl) being formed in the syngas produced. The presence of HCl gas may increase the risk of corrosion and may be harmful to health and to the environment. Consequently, stricter limits on HCl concentration in syngas are being imposed by environmental regulations and syngas end-use specifications, which is driving the search and development of more efficient and cost-effective methods of eliminating HCl. One such method is dry adsorption using inorganic sorbents. In literature, the majority of sorbents studied are based on commercialised products, and thus, there lack studies on the use of waste-derived sorbents for treating HCl in syngas. Therefore, this paper presents an experimental study on the adsorption potential of the solid waste sorbent, CCW-S, which is compared to that of the commercial sorbent, Bicar. Various physico-chemical analyses were performed on the sorbents before and after the tests, including ICP, FTIR, XRD and TEM-EDX. The first set of adsorption tests were performed using a gas mixture of 500 ppm HCl in nitrogen (HCl/N₂) at ambient conditions (25 °C, 1 atm). The results revealed that Bicar was the better performing sorbent with an average breakthrough time of 66 h and a HCl adsorption capacity of 27 wt%, whereas the performance of CCW-S was lower (7.8 h and 4 wt%). Furthermore, TEM-EDX images of CCW-S particles show the participation of the impurities—Al, Fe, and Mg—in HCl capture. When the second set of adsorption tests were conducted with a simulated HCl/syngas atmosphere, a significant decrease in sorbent performance was observed, which showcases inhibitory interactions occurring between syngas and the sorbents, in relation to HCl adsorption. The results of this preliminary investigation reveal a promising opportunity to valorize industrial residues as cheap and efficient sorbents for the removal of HCl in syngas. This will enable a wider market penetrating of waste-derived syngas, while meeting the quality requirements of increasingly strict environmental regulations and end-use devices.

Keywords Syngas · Hydrogen chloride · Inorganic waste sorbents · Dry adsorption

Statement of Novelty

Our work demonstrates the potential to use industrial solid wastes containing calcium carbonate as cheap and effective sorbents for removing HCl in syngas, which is currently lacking in literature.

Introduction

Syngas produced from the pyro-gasification of waste biomass has many industrial applications including electricity and heat production, as well as the synthesis of transportation fuels, methanol and ammonia [1, 2]. Nonetheless, waste

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biomass may have significant concentrations of chlorine, which may lead to the formation of hydrogen chloride (HCl) in syngas produced by the pyro-gasification process. Several problems may occur due to the presence of HCl gas, including the corrosion of metal equipments, health problems and environmental issues [3, 4], which therefore necessitates the removal of HCl from syngas before use. The level of syngas cleaning required is governed by the quality requirements of the end-use applications and environmental emissions regulations [5]. As we can see in Table 1, the concentrations of HCl typically found in waste-derived syngas are significantly higher than those required by various syngas applications and the emission standards of areas like the European Union (EU) and Japan [4, 6, 7]. Thus, it is imperative to develop HCl removal methods that are cost-effective, efficient and environmentally friendly.

Dry adsorption is as a promising technique for eliminating HCl in syngas, which is based on chemical reactions involving HCl and metal-based solid particles (sorbents) [8–16]. A potential benefit of using this technique is that the sorbents can be regenerated using methods such as heating, which can be economically and environmentally interesting when compared to other methods, such as wet scrubbing, that produce wastewater which is costly to treat. Another advantage of the dry adsorption method is that it opens up opportunities to valorize metal-based solid wastes from industrial processes. In literature, various sorbents for HCl removal have been studied, and can be classified into three groups: alkali-based sorbents, alkaline-earth based sorbents and other metal based sorbents.

- Alkali-based sorbents studied by researchers are mostly sodium and potassium compounds due to their strong HCl binding capabilities [17–20]. For example, Krishnan et al. [21] have shown that Nahcolite (NaHCO_3) can remove HCl from a gas mixture to concentrations as low as 1 ppm in the temperature range of 525–650 °C.
- Although the performance of alkaline earth-based sorbents is lower than that of alkali-based sorbents, they are significantly cheaper, and thus have attracted the attention of many researchers [22–26]. Slaked lime (Ca(OH)_2), limestone (CaCO_3) and quicklime (CaO) are the most commonly studied, which have been shown to strongly bind to HCl in temperature range of 500–600 °C [27–30].

- Other metal based sorbents containing aluminium, iron, and zinc have also received considerable research interest [22, 31, 32]. As an example, studies by Ohtsuka et al. [33] have shown that the addition of Al_2O_3 to Na_2CO_3 can reduce HCl in syngas to less than 1 ppm at 400 °C.

Although many literature works exist on the removal of HCl from flue gas using commercial sorbents, there lack studies on the cleaning of waste-derived syngas derived from waste biomass using solid waste sorbents. Hence, this paper evaluates and compares the performance of the solid waste sorbent, CCW-S, to the performance of the commercial sorbent, Bicar. CCW-S is a calcium carbonate residue recovered from an industrial process for producing sodium carbonate, that has been carbonated naturally by atmospheric carbon dioxide for a long duration. Bicar, on the other hand, is a commercial sorbent used in industry for flue gas treatment of acid gases. The experiments conducted with these sorbents will involve the adsorption of HCl in nitrogen and synthetic syngas atmospheres at ambient conditions, in order to study the influence of gas matrix on the sorbent performance. Various physico-chemical characterisation methods will be conducted on the sorbents before and after the tests to enable a better understanding of the sorbent adsorption behaviour.

Experimental Methods

Sample Characterization

The physico-chemical properties of CCW-S and Bicar were analyzed before and after the tests using various techniques. Their mineral content was determined using an inductively coupled plasma with an atomic emissions spectra (ICP-AES, HORIBA Jobin-Yvon Ultima 2) and their molecular bonds were identified using fourier transform infrared spectrometry (FTIR, 8400S—Shimadzu). Furthermore BET analyses were performed to determine the specific surface area of the particles, using Micromeritics 3Flex analyzer. The crystalline structures were studied with X-ray diffraction (XRD, Philips Panalytical X'pert Pro MPD diffractometer) and environmental scanning electron microscopy (ESEM, XL30 ESEM apparatus—FEI Company) in order to obtain information related to the particles' morphology. A Transition electron microscope coupled to an energy dispersive

Table 1 Typical HCl concentrations in waste-derived syngas and target levels of associated syngas applications [4, 6, 7, 9]

Contaminant (mg/Nm ³)	Waste gasification	Gas engine	Gas turbine	Methanol synthesis	Fischer–Tropsch synthesis	EU/Japanese standards ^a
HCl	0–300	< 1	< 1	< 0.1	< 0.01	10/90

^aAt 11% O₂

X-ray (TEM-EDX) was employed to perform imaging and elemental mapping of chemical species in the samples.

Before characterization and tests, the two sorbents were sieved to obtain samples with particle sizes below 315 μm , and then dried at ambient temperature for 48 h. For analyses with FTIR, reference samples of calcium carbonate (CaCO_3 —calcite, from Fisher Scientific) and sodium bicarbonate (NaHCO_3 , from Acros Organics) were used, with each sample having more than 98% purity.

Experiments with HCl in Nitrogen

Gas Matrix and Reactor Operating Conditions

The first set of experiments were performed with a 500 ppmv mixture of hydrogen chloride in nitrogen (HCl/N_2) under ambient conditions (25 $^\circ\text{C}$, 1 atm). Figure 1 gives a schematic representation of the experimental setup for the tests. A glass fixed-bed reactor (height = 120 mm, internal diameter = 10 mm), was equipped with a porous glass disc to hold the sorbent particles and allow the passage of gas through the sorbent bed. The bed height was kept at 7.6 mm for all sorbents by adjusting the mass of sorbent used for the experiments (0.3–0.5 g) according to their bulk densities. After placing the sorbents in the reactor, glass beads (4.2 g, 1 mm size) were added as inert particles to maintain the bed height. The 500 ppmv HCl/N_2 gas passed through the

sorbent bed in a downward flow at a flowrate of 50 mL/min, which was controlled by a mass flow meter. Thus, the gas residence time in the sorbent bed was maintained at 0.714 s.

Gas Sampling and Analysis

Gas was sampled at the reactor outlet with a gas cell, and then analyzed for its HCl content using FTIR. The gas cell had internal dimensions of 29 mm $\times$ 135 mm and was equipped with windows made of calcium fluoride (CaF_2). Figure 2 gives an example of the infrared spectrum of HCl in 500 ppmv HCl/N_2 gas mixture, which appears as a series of regular peaks between 2650 and 3100 cm^{-1} . The residual HCl gas was scrubbed in an aqueous solution of KOH as shown in Fig. 1.

Experiments with HCl in Syngas

Gas Matrix and Reactor Operating Conditions

The second set of experiments involved the use of 200 ppmv HCl in a simulated syngas matrix (HCl/syngas) under ambient conditions (25 $^\circ\text{C}$, 1 atm), whose composition is shown in Table 2. These experiments were conducted with an online HCl analyzer named ProCeas, which will be described in the next section. In order to minimize the response time of this analyzer, a higher gas flowrate of 500

Fig. 1 Experimental setup

Fig. 2 Infrared spectrum of 500 ppmv HCl/N_2 (25 $^\circ\text{C}$, 1 atm)

Table 2 Composition of syngas mixture used in experiments

Components	Nominal value	Analytical value
Hydrogen chloride, HCl (ppmv)	200	232
Methane, CH_4 (vol%)	5	4.96
Carbon dioxide, CO_2 (vol%)	25	24.9
Hydrogen, H_2 (vol%)	30	30.6
Carbon monoxide, CO (vol%)	Balance	Balance

Fig. 3 Zoom of infrared spectrums of 500 ppmv HCl/N₂ and 200 ppmv HCl/syngas (25 °C, 1 atm)

mL/min was employed. Thus, to maintain the gas residence time in the sorbent bed at 0.714 s, a larger reactor (height = 168 mm, internal diameter = 14 mm) was used and a bed height of 39 mm was fixed. For these experiments, the sorbent mass of 4–5 g was in the range, depending on the sorbent bulk density.

Gas Sampling and Analysis

FTIR technique could not be used to analyze the concentration of HCl in the syngas matrix because the infrared spectrum of methane, CH₄, overlapped that of HCl as shown in Fig. 3. Hence, a new HCl analyzer called ProCeas was employed, which was manufactured by AP2E. ProCeas uses an enhanced IR laser technology called Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS), which enables simultaneous online analysis of HCl and CH₄. During the experiments, the analyzer was directly connected to the reactor outlet and the HCl gas concentration was recorded at 1-s intervals.

Results and Discussion

Characteristics of Sorbents Before Experiments

Table 3 displays the bulk density, surface area and particle diameter of the sorbents before the experiments were performed. We can observe that Bicar has about twice as much surface area as CCW-S, which is favorable for HCl adsorption.

The inorganic element composition of the sorbents before the tests are displayed in Table 4. We observe that CCW-S mainly contains Ca, whereas majority of Bicar is composed

Table 3 Physical characteristics of sorbents before tests

Sorbent	Bulk density (kg/m ³)	Surface area (m ² /g)	Particle diameter, d ₅₀ (μm)
CCW-S	840	5	113
Bicar	986	13	136

Table 4 ICP results of sorbent materials before tests

Sorbent	Ca (g/kg)	Na (g/kg)	Al (g/kg)	Fe (g/kg)	Mg (g/kg)
CCW-S	454.8	–	1.8	3.4	2.7
Bicar	1.6	192.9	0.2	0.1	0.1

Fig. 4 Infrared spectra of sorbents and reference compounds before tests

of Na. CCW-S also has a significant concentration of contaminants (Al, Fe and Mg) due to its waste origin.

Figure 4 shows the infrared spectra of CCW-S and Bicar as well as the reference spectra of pure CaCO₃ and NaHCO₃. Compared to pure CaCO₃, CCW-S shows similar peaks at 1404, 873 and 713 cm⁻¹, which correspond to C–O bonds [34]. This suggests that calcium carbonate (calcite) is a major compound in this industrial waste. Furthermore, the spectrum of Bicar is almost identical to that of pure NaHCO₃, with peaks appearing between 600 and 1926 cm⁻¹.

XRD analysis was performed in order to identify the crystalline structure of the inorganic compounds in the sorbents. The results are displayed in Table 5 and Fig. 5. For CCW-S, the XRD analysis shows that calcium carbonate is the main component of this material, which has a rhombohedral structure that is characteristic of calcite. In contrast, Bicar is observed to be composed of only NaHCO₃ with a monoclinic crystalline structure. These results are in agreement with the observations made using the FTIR technique. However,

Table 5 XDR results of sorbents before tests

Sorbent	Reference code	Compound name	Chemical formula	Crystal system
CCW-S	00-047-1743	Calcium carbonate	CaCO_3	Rhombohedral
Bicar	00-021-1119	Sodium hydrogen carbonate	NaHCO_3	Monoclinic

Fig. 5 XDR results of sorbents before tests. Filled triangle: calcium carbonate (CaCO_3)—rhombohedral, filled diamond: sodium hydrogen carbonate (NaHCO_3)—monoclinic. **a** CCW-S. **b** Bicar

despite the detection of impure elements in CCW-S by ICP (Al, Fe and Mg), their crystals have not been identified by XRD possibly because their concentrations are below the instrument's detection limit.

Adsorption of HCl in Nitrogen

Breakthrough Curves

Figure 6 displays the breakthrough curves obtained for the tests with 500 ppmv HCl/N_2 gas, which shows the evolution of the exit HCl concentration with time. Henceforth, we will define the breakthrough time t_b as the duration for which the exit HCl concentration is zero. The corresponding t_b value for each sorbent is displayed in Table 6. The tests, which were conducted at least three times for each sorbent, were repeatable with a deviation in t_b of 2.4 and 6.5% from the mean value for Bicar and CCW-S respectively.

It is obvious from Fig. 6 and Table 6 that Bicar has a long breakthrough time of 64 h and a high HCl adsorption capacity of 26.8 wt%, where the HCl adsorption capacity was calculated by dividing the mass of adsorbed HCl by the

initial sorbent mass. CCW-S, however, has a significantly lower performance. These results are coherent with those of several authors who have found calcium-based sorbents to be less reactive with HCl than sodium-based sorbents [18–21, 33, 35]. An explanation for the relatively slow reactions of CaCO_3 in CCW-S with HCl gas has been linked by Duo et al. [36] to the reaction's chemical free energy (ΔG_c). They show that for a reaction involving CaCO_3 and HCl in an atmosphere containing trace amounts (500 ppm) of H_2O and CO_2 , $-\Delta G_c$ is only 50 kJ/mol at 25 °C, which provides a very low driving force for the reaction to occur. However, $-\Delta G_c$ can increase to 80 kJ/mol if the temperature rises to 600 °C under the same atmosphere, thereby possibly leading to a significant increase in the adsorption rate of HCl by CCW-S. Another reason for the lower performance of CCW-S compared to Bicar might be its relatively small surface area (Table 3), which lowers the chances of collision with HCl molecules, and thus lowers the reaction rate. These proposed explanations suggest that the adsorption efficiency of CCW-S can be significantly improved by operating at higher temperatures and increasing the particle surface area by thermal activation to generate pores.

Fig. 6 Breakthrough curves for tests under HCl/N₂ gas conditions (25 °C, 1 atm). **a** CCW-S. **b** Bicar

Table 6 Break through times and HCl adsorption capacities of CCW-S and Bicar in HCl/N₂ atmosphere (25 °C, 1 atm)

Sorbent	t_b (h)	HCl capacity (wt %)
CCW-S	7.5–8.0	3.9
Bicar	64.7–66.3	26.8

In Fig. 6, a flat region can be observed on the graphs at an HCl outlet concentration of about 200 and 250 ppm for the adsorption tests with CCW-S and Bicar respectively. This may be due to the occurrence of monolayer adsorption on the particle surface, which deserves further investigation by performing adsorption isotherm experiments.

Effect of Sorbent Mineral Elements

TEM-EDX analysis was performed on CCW-S and Bicar particles to qualitatively investigate the effect of the major elements—Ca, C, O, Na—and inorganic elements—Ca, Na, Al, Fe and Mg—on the formation of new products at the sorbent surface. Figure 7 displays cartographic pictures that showcase the distribution of inorganic elements on the surface of a CCW-S particle after the test with HCl/N₂ gas. The particle in this figure clearly shows Cl (HCl) fixed on its surface. In addition, the cartographs of Ca and Cl are almost identical, which implies that a chlorinated product is formed on the particle. The elements, O and C, also have a similar distribution on the particle surface as Ca, indicating that not all of CaCO₃ in the particle is converted. Furthermore, the impurities—Al, Fe and Mg—appear to also adsorb HCl although in relatively small amounts because of their low content in the CCW-S sample.

Figure 8 displays the TEM-EDX cartograph of a Bicar particle. As seen by the brightness of the cartograph, Cl

(HCl) is strongly fixed onto a portion of the Bicar particle surface to form a chlorinated product. It is also obvious that not all of NaHCO₃ is converted because the elements, O and C, are present and have a similar distribution as Na on the particle. As a result of the high purity of Bicar (Table 4), a small scatter of Al, Fe and Mg can be seen on the particle surface, in the same region as Cl, which indicates that these impurities also adsorb HCl just as they do for CCW-S. The adsorption of HCl by Mg and Al has been well documented in literature [31, 37–39].

Effect on Sorbent Crystalline Structure

The crystalline structures of the sorbents after tests with HCl/N₂ gas are displayed in Table 7 and Fig. 9. The results show that CCW-S largely contains the same CaCO₃ crystal structures before and after the tests (Table 5), and therefore, the content of any chlorine-containing crystal in the sorbent is below the detection limit of the XRD analyzer. This is expected due to the low reactivity of CCW-S observed in Table 6, implying that the CCW-S particle analysed using the TEM-EDX technique was one of the few that actually adsorbed HCl to form chlorinated products via the following possible reactions.

For Bicar, NaCl crystals of cubic structure were detected alongside NaHCO₃. This indicates that Bicar adsorbed HCl via the chemical reaction:

Fig. 7 TEM-EDX cartographic photos of CCW-S particles after tests under HCl/N_2 gas conditions (25 °C, 1 atm). **a** Particle. **b** Chlorine, Cl. **c** Calcium, Ca. **d** Oxygen, O. **e** Carbon, C. **f** Aluminium, Al. **g** Iron, Fe. **h** Magnesium, Mg

Fig. 8 TEM-EDX cartographic photos of Bicar particles after tests under HCl/N_2 gas conditions (25 °C, 1 atm). **a** Particle. **b** Chlorine, Cl. **c** Sodium, Na. **d** Oxygen, O. **e** Carbon, C. **f** Aluminium, Al. **g** Iron, Fe. **h** Magnesium, Mg

Table 7 XRD results of crystalline structures present in sorbents after tests with HCl/N₂

Sorbent	Reference code	Compound name	Chemical formula	Crystal system
CCW-S	00-047-1743	Calcium carbonate	CaCO ₃	Rhombohedral
Bicar	00-021-1119	Sodium hydrogen carbonate	NaHCO ₃	Monoclinic
	96-900-8679	Halite	NaCl	Cubic

Fig. 9 XDR results of sorbents after tests under HCl/N₂ gas conditions (25 °C, 1 atm). Filled triangle: calcium carbonate (CaCO₃)—rhombohedral, filled diamond: sodium hydrogen carbonate (NaHCO₃)—monoclinic, filled inverted triangle: halite (NaCl)—cubic. **a** CCW-S. **b** Bicar

Effect on Sorbent Particle Surface Structure

ESEM analysis of the particle surfaces of the sorbents, before and after the tests, are shown in Fig. 10. There is an insignificant difference in the surface structure of CCW-S before and after the tests under HCl/N₂ atmosphere. This confirms the XRD results in Tables 5 and 7, showing that little change in the crystal system occurred.

Bicar particles, after HCl adsorption, are seen to have deposits of cubic crystals on their surface which are not present on the original particles. These cubic crystals correspond to the NaCl crystals detected using XRD (Table 7). These results as well as those of the XRD analysis, confirm the formation of a chlorinated-product layer on particles of Bicar as a result of chemisorption of HCl on the particles.

Adsorption of HCl in Syngas

For experiments using 200 ppmv HCl/Syngas mixture, the breakthrough curves and sorbent performance results are

shown in Fig. 11 and Table 8. We can see that the breakthrough times, t_b , for CCW-S and Bicar are 2.7 h and 48.2 h respectively, which in comparison to their corresponding values under the HCl/N₂ gas mixture (Table 6), is a significant decrease of 5.3 and 16.5 h respectively. Furthermore, the HCl adsorption capacities of the two sorbents dramatically decrease in the presence of syngas.

To verify that this decrease in performance of CCW-S and Bicar was not due to reactor scale-up and change of HCl analyzer, an adsorption test was repeated with CCW-S in the 'large' reactor configuration using 500 ppm HCl/N₂ gas. The results were then compared with those obtained with the 'small' reactor set-up under the same atmosphere. Figure 12 shows that, despite the difference in reactor scale and HCl analyzer, the value of t_b remained 8 h, and thus, the breakthrough time was unaffected by the reactor and HCl analyzer used. We can therefore attribute the reduced performance of CCW-S and Bicar to competitive interactions that occurred between HCl and the syngas components at the active sites of the sorbents.

Fig. 10 ESEM photos of sorbents before and after tests under HCl/N₂ gas conditions (25 °C, 1 atm). **a** CCW-S, before. **b** CCW-S, after. **c** Bicar, before. **d** Bicar, after

Fig. 11 Breakthrough curves for HCl/Syngas conditions (25 °C, 1 atm)

Fig. 12 Comparing breakthrough curves for adsorption tests with CCW-S in small and large reactor, under 500 ppmv HCl/N₂ conditions (25 °C, 1 atm)

Table 8 Breakthrough time and HCl adsorption capacities of CCW-S and Bicar in HCl/syngas atmosphere (25 °C, 1 atm)

Sorbent	t_b (h)	HCl capacity (wt %)
CCW-S	2.7	0.5
Bicar	48.2	6.7

In literature, several authors have studied the influence of gas atmosphere composition on HCl adsorption capacity of carbon-based and sodium-based sorbents [30, 40–42]. All of these authors agree that the presence of CO₂ and H₂O significantly lowers the performance of the sorbents. They attribute this to the shift in position of equilibrium to the left of the reversible reactions in Eqs. (1)–(3) due to the increase

in the partial pressures of CO₂ and/or H₂O. However, CO₂ has much more influence on this shift in position of equilibrium than H₂O, and hence, the mechanism is called sorbent recarbonation.

Conclusion

In this paper, the dry adsorption potential of a solid waste sorbent, CCW-S, is compared to that of a commercial sorbent, Bicar. Various physico-chemical analyses were performed on each sorbent before and after the tests, including ICP, FTIR, XRD and TEM-EDX. The analysis results revealed that CCW-S was largely composed of CaCO₃, and Bicar was purely NaHCO₃. The impurities—Al, Fe and Mg—were also detected in CCW-S.

The first set of adsorption tests were performed using a gas mixture of 500 ppm HCl in nitrogen (HCl/N₂) at ambient conditions (25 °C, 1 atm). The results revealed that Bicar was the better performing sorbent with an average breakthrough time and HCl adsorption capacity of 66 h and 26.8 wt%, whereas the performance of CCW-S was lower (7.8 h and 3.9 wt%). Furthermore, TEM-EDX images of CCW-S particles revealed the participation of the impurities—Al, Fe, and Mg—in HCl capture. In addition, XRD and ESEM analyses showed the formation of new crystals on the surface of Bicar particles, although no new crystals were observed on the particles of CCW-S.

The second set of adsorption experiments were conducted with CCW-S and Bicar sorbents, using a simulated HCl/Syngas atmosphere at ambient conditions. The breakthrough times and HCl adsorption capacities of the sorbents were, respectively, 48.2 h and 6.7 wt% for Bicar, and, 2.7 h and 0.5 wt% for CCW-S. This significant decrease in the sorbent performance in the presence of syngas highlights important interactions between HCl and syngas components, which deserves further investigation.

Future experiments on CCW-S will aim to improve its performance by determining the optimum adsorption temperature, and performing thermal activation and regeneration tests. Furthermore, an investigation of the effect of different partial pressures of CO₂ (in syngas) on the performance of CCW-S will be performed.

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