PREDICTION OF H$_2$S AND HCL FORMATION DURING RDF AND CO-GASIFICATION IN FLUIDIZED BED

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ABSTRACT: Most solid fuels contain S and Cl and during their gasification, the formation of pollutants such as H_2S and HCl becomes inevitable, however, a better understanding of the mechanism involved in their formation and subsequent destruction during the process could help to define operating conditions and to achieve synergy during co-gasification to minimize their emissions. The formation of these pollutants along with the partitioning of S and Cl in the gas and solid phases can be predicted using theoretical models in software packages like FactSage. If the tendency of H_2S and HCl emissions predicted by the model corresponds to what has been observed, then an overall mechanism could be derived at using the thermochemical stability data. In this paper a comparison between numerical and experimental results is presented. The results obtained seem to suggest a relationship between the levels of sulphur in the fuels and the concentration of H_2S in the gas phase, although the presence of K, Na and Ca may minimize the release of H_2S. The formation of HCl seemed to be greatly affected by the inorganic matter of the fuels.
Keywords: co-gasification, refuse derived fuel (RDF), emission reduction

1 INTRODUCTION

The formation of pollutants such as H_2S and HCl is inevitable, during the gasification process, and is related, to a large extent, to the presence of S and Cl in the solid fuels used. However, the presence of these pollutants in the gas produced is undesirable and limits end use applications.

According to some authors [1] the presence of H_2S in the gas, in subsequent combustion, may lead to the formation of sulphur oxides, while Kuramochi et al. [2] suggested that the H_2S, even in low concentration in the gasification gas, has a deleterious effect when it is used in fuel cells causing poisoning and equipment corrosion.

Due to its high reactivity and corrosive nature, HCl can lead to corrosion and degradation of equipment, as well as to the reduction of the efficiency in the removal of sulphur [3]. For applications in fuel cells, the concentration of HCl must be lower than 1ppmv, otherwise it can react with the electrolyte originating halides [3].

The formation of H_2S and the conversion rates of fuel-S into H_2S depend on a large number of factors, besides the type of fuel used. In fact, there are two groups of variables that influence the distribution of sulphur during pyrolysis and gasification: 1) those that are function of the initial condition of the fuel, such as volatiles content, ash and its composition and sulphur amount and 2) those that depend on the conditions used, such as reaction time and temperature [4].

The process atmosphere plays an important role in the formation of H_2S. The presence of greater amounts of oxygen in the system may lead to the formation of oxidized sulphur species, thus reducing the amounts of sulphur existing as H_2S. Several authors [5], [6], have reported that the increase of equivalence ratio (ER), in the absence of steam, produced larger decrease of H_2S and CS_2 in the obtained gasification gas and hence resulting in more COS and SO_2. On the other hand, the presence of steam may reduce the levels of these species in the syngas, including H_2S, because the presence of steam, especially at low gasification temperatures, may reduce the extent of pyrolysis reactions which could limit S release. However steam could also act as a hydrogen donor promoting the formation of H_2S [7].

As far as chlorine is concerned, independently of its amount in the solid fuels used, the dominant form of chlorine in the syngas is HCl, followed by KCl and NaCl [3]. It has been suggested that chlorine is not readily released into the gas phase, but is retained in the solid phase, and only 20-30% of chlorine in the char is released [8]. According to van Der Drift et al.[9] during biomass gasification only 15% of the chlorine is released into the gas phase.

The volatility of chlorine is not dependent on the atmosphere (oxidizing or reducing), although the presence of hydrogen donors, such as steam, may favour the formation of HCl. On the other hand, temperature seems to play an important role in the formation of HCl [8], [10].

Once low temperatures are associated with breaking of aliphatic C-Cl bonds, higher temperatures, that favour the breakage of aromatic and aliphatic bonds, lead to an increase in the HCl concentration in the gas phase.

It is clear that the operational parameters play an important role on the formation of H_2S and HCl, however the inorganic matter of the solid fuels may have a great influence on the concentration of these pollutants in the gas phase, once the metals present in the fuels may react with sulphur and chlorine preventing the emission of H_2S and HCl. Elements such as Ni, Si, Al, Fe, Na, K, Mg and Ca, among others, present in the fuels, may represent an available and inexpensive source of catalysts [11].

It has been observed that minerals could act as sorbents for the H_2S and it has been reported a high retention of S and Cl due to the presence of high levels of Ca, K and Na in the biomass [12], [13].

The work of Attar [4] referred to reactions involving iron, magnesium and calcium oxides and carbonates, resulting in the retention of sulphur in the solids, through reactions given below:
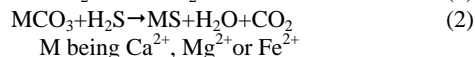
$$MO+H_2S \rightarrow MS+H_2O \qquad (1)$$
$$MCO_3+H_2S \rightarrow MS+H_2O+CO_2 \qquad (2)$$
$$M \text{ being } Ca^{2+}, Mg^{2+} \text{ or } Fe^{2+}$$

The utilization of coal with S, but having other mineral matter removed, produced greater concentrations of H_2S in the gas, in comparison to untreated coals, suggesting that the ash could act as sorbent for the H_2S through the formation of alkali and earth alkali sulphides[12].

The emission of chlorine is very dependent on the presence/concentration of alkali metals in the gasification

system [14]. The interactions between chlorine and alkali metals are so important that it was suggested that the volatilization of these metals may be more dependent on the concentration of Cl rather than on the concentration of the metals [15]. It was suggested by Kuramochi et al. [2] that although the amount of Cl in the fuel and the concentration of HCl formed could be correlated, this relation is not a linear one, because, metals can also produce stable compounds with chlorine.

It could be concluded that the development of synergies between properties of fuels with different compositions and levels of S, Cl, and metals, may have a strong impact on the minimization of the formation of H_2S and HCl.

With these work it is intended to:
• Study the effect of the fuel nature on the formation of H_2S and HCl;
• To make a comparison between the experimental results and the modelling using FactSage;
• To predict the formation of H_2S and HCl and the influence of the inorganic matter on the concentration of these pollutants using FactSage.

2 EXPERIMENTAL PART

The gasification tests were carried out in a bubbling fluidized bed gasifier at atmospheric pressure as previously described [16]. By means of a water cooled screw feeder the fuel was introduced into the bed.

A constant flow of nitrogen was used helping the feeding process and preventing pyrolysis during feeding.

The gas produced left the reactor and passed through a cyclone and quenching system, for tar and particle removal, then gas samples were collected for its characterization, including the quantification of H_2S and HCl.

Two different fuels were used in this work. Coal from Puertollano mines in Spain with a high level of ash and pelletized RDF produced from MSW (Municipal Solid Wastes) containing 50% wood, 15% plastics (no PVC), 35% paper and cardboard. In Table I, the results from the elemental and proximate analyses are shown, as well as the mineral composition of the ashes of RDF and coal.

Table I: Feedstock composition

	RDF	Coal
HHV (MJ/kg daf)	23.9	29.8
Fixed carbon (% w/w)	14.2	29.9
Volatiles (%w/w)	74.6	20.8
Ash (% w/w)	4.5	43.6
Moisture (%w/w)	6.7	5.7
C (%daf w/w)	53.4	73.1
H (%daf w/w)	7.8	6.5
S (%daf w/w)	0.07	1.9
N (%daf w/w)	0.4	1.7
Cl (%daf w/w)	0.06	0.07
O (%daf w/w)	38.3	16.7
Fe (%w/w)	0.1	1.6
Al (% w/w)	0.3	6.7
Ca (%w/w)	1.3	0.3
K (% w/w)	0.09	0.8
Na (%w/w)	0.07	0.06
Mg (%w/w)	0.1	0.3

The sulphur released in the form of H_2S was sampled using method 11 of EPA. Sulphide was retained in an absorbing solution of $CdSO_4$ and then analyzed by iodometry. The chlorine released as HCl was sampled using a methodology based on method 26 of EPA.

Chlorine was retained in deionised water, and the analysis was carried out using capillary ion electrophoresis. Chlorine captured in the condensation system was also analyzed using the same technique. Sulphur held in the condensation system was analyzed as SO_4^{2-} simultaneously with chlorine using capillary ion electrophoresis.

The amounts of S retained in the solids (char and ash from cyclone) were quantified by LECO SC 144-DR and LECO CHN-2000, while the Cl was quantified using capillary ion electrophoresis after leaching with water.

The simulation work was carried out using FactSage 5.4 software package and the Fact 5.3 database. The experimental work was simulated using the same experimental conditions. In all scenarios tested using FactSage a total of 694 output chemical species were produced.

3 RESULTS AND DISCUSSION

3.1 Fuel mixture effect-H_2S

Because the levels of sulphur were higher in the coal used compared with RDF, the increase of coal in the fuel mixture gave rise to a greater emission of H_2S into the gas phase, ranging from 320ppmv to 2681ppmv. However the relationship between the formation of H_2S and the levels of sulphur in the fuels did not seem to be a linear one. It was also observed (Figure 1) that as the amount of coal supplied in the mixture increased there was a reduction in the conversion of fuel-S into H_2S which may suggest that RDF had higher amounts of volatile sulphur.
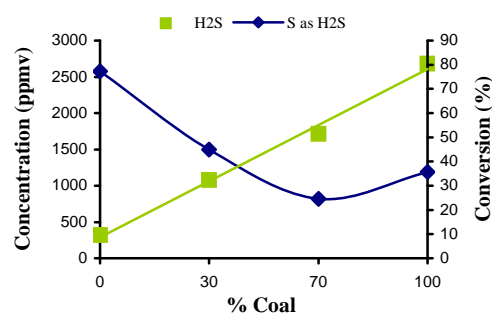

Figure 1: Effect of coal addition on the formation of H_2S (850ºC, Equivalence Ratio=0.2)

There could be several explanations for the lack of linear correlation. One could be, the nature of S in different fuels significantly varies, thus producing other sulphur compounds. It was determined that the majority of sulphur in the RDF was of organic origin in contrast with the sulphur in coal which was mostly in the pyrite form.

Khan [17] developed a relationship correlating the pyritic sulphur with the retention (of sulphur) in the solids, the formation of H_2S with the organic sulphur and the sulphur retained in the liquid phase with the total sulphur.

On the other hand, it was observed that the retention in the solid phase was greater as the amount of coal was larger (Figure 2). The retention of sulphur in the solid phase could be related with the presence of minerals in the coal ash that may have acted as sorbents and/or sites for adsorption by the porous char, and this agrees with the results of Khan [17].
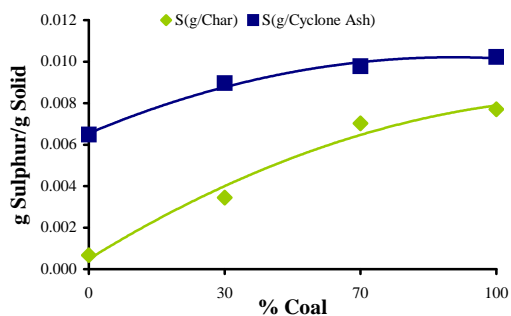

Figure 2: Effect of coal addition on the retention of S (850ºC, Equivalence Ratio=0.2)

In Figure (1) it is shown a decrease in the conversion of fuel-S into H_2S as the coal supply increased.

This fact can be associated with the higher sulphur retention in the solid phase but also suggests that the formation of other sulphur species were favoured by greater coal amount in the mixture.

A good agreement between experimental results and simulation work was observed (Figure 3). This enabled the use of simulation code to provide mechanistic explanation for experimental results. In Figure (4), it is shown that the increase of coal may not only have led to an increase of sulphur species but also to higher levels of these species in the gas stream.
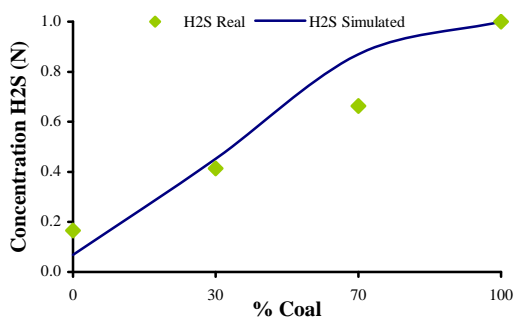

Figure 3: Comparison between experimental and simulation results for the effect of coal addition on the formation of H_2S (850ºC, Equivalence Ratio=0.2)

The suggestion of retention of sulphur in the solid phase by its reaction with metals in the solid phase does not seem to be confirmed by the results from FactSage (Figure 4), because no evidence was found regarding the formation of sulphur metallic species (except $FeS_{(s3)}$), and therefore the retention in the porous structure of the char appeared to be more consistent with the results obtained.
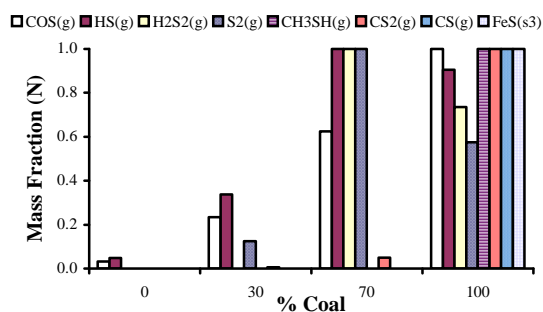

Figure 4: Formation of other sulphur species than H_2S-effect of coal addition

Although not shown in any figure, the results suggested that independently of the amount of coal used, the majority of the sulphur was not held in the quenching system, meaning that the cooling of the gas may not be sufficient to remove sulphur from the gas produced.

3.2 Fuel mixture effect-HCl

The concentration of HCl in the gas phase did not show a significant variation, as the amount of coal was increased in the fuel blend, as can be seen in the Figure (5). This was somehow expected once the Cl levels in both fuels are about the same. However the concentration of HCl showed a slight decrease, as the amount of coal was increased in the fuel blend, from 75ppmv to 48ppmv.

This may result from higher retention of Cl in the solids, due to the reaction of Cl and mineral elements in the fuel ash; however, as will be discussed later, the explanation may be a little more complex than that.
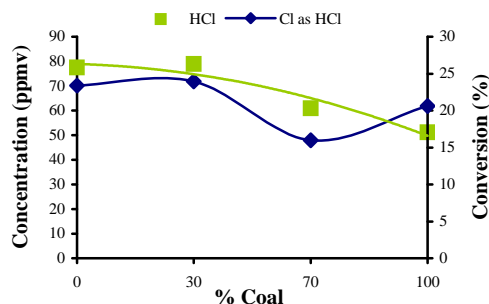

Figure 5: Effect of coal addition on the formation of HCl (850ºC, Equivalence Ratio=0.2)

In Figure (6), it can be observed that greater amount of coal led to a decrease in the retention of Cl in the cyclone ashes, (the retention in the char is negligible). According to Takeda et al. [8], the chlorine is not readily released, but it is firstly retained in the solid fraction (either by physical or chemical retention) and only then it is released to the gas phase. As the concentration of chlorine was greater in the cyclone ash, and based on the observations by Takeda et al. [8] it could be suggested that chlorine could volatilise and react with the inorganic matter, forming metallic chlorides that would condensate over the ashes in the cyclone (350ºC).
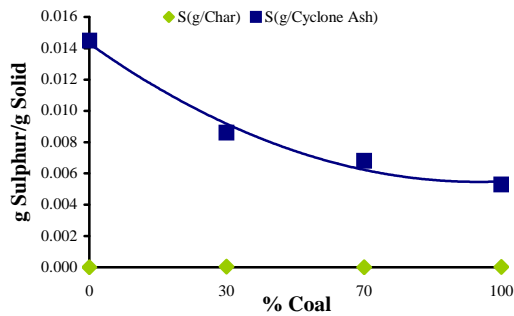
Figure 6: Effect of coal addition on the retention of Cl (850ºC, Equivalence Ratio=0.2)

Although the formation and subsequent condensation of metallic chlorides could be a strong possible route, it does not completely explain, at a first glance the results obtained and presented in Figure (5) and Figure (6), and some other parameters may have been involved. In spite of the results obtained with FactSage not being in a perfect agreement with those obtained experimentally (Figure 7), because FactSage is an application for calculation of phase equilibrium in multiphase systems, they tend to follow the same general trend, thus validating the experimental observations.
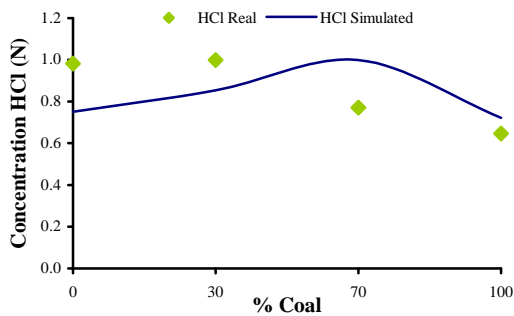

Figure 7: Comparison between experimental and simulation results for the effect of coal addition on the formation of HCl (850ºC, Equivalence Ratio=0.2)

As far as the formation of other chlorine species is concerned the results (Figure 8) show great variations.

However the amounts of $FeCl_{2(g)}$ and $ZnCl_{2(g)}$ appear to be higher as the amount of coal was increased, suggesting a direct link between the formation of these species and the levels of iron and zinc in the solid fuels, that were greater in coal.
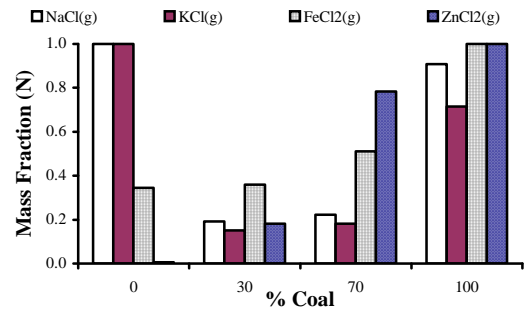

Figure 8: Formation of other sulphur species than HCl - effect of coal addition

A comparison between the results for HCl in the gas phase could suggest that the decrease of its concentration could be associated with the increase of $FeCl_{2(g)}$ and $ZnCl_{2(g)}$ concentration, and even with the increase of NaCl(g) and KCl(g). This explanation becomes more credible because most of these species were in the solid phase at the gas exit temperature of the cyclone (350ºC).

Although this explanation agrees well with the results observed for HCl levels, they did not appear to agree with the fact that Cl concentration decreased in the cyclone ashes.

Experimentally it was observed a significant increase in the gas velocity once the gas flow rate increased form 5.2 NL/min when only RDF was used to 10.2NL/min when 100% of coal was fed, which probably led to the entrainment of solid particles from the cyclone, leading to an underestimation of total Cl levels.

Hence was the case for sulphur it is very probable that the increase of coal has led to the formation of other chlorine species besides HCl, especially metallic chlorides that condensed in the cyclone over the ashes, leading to a reduction of HCl concentration in the gas phase and to an increase of chlorine in the solid phase which, however, was not confirmed experimentally.

3.3 Inorganic matter effect-H_2S

The results obtained experimentally seem to suggest a strong relationship between the emission of H_2S and the levels of inorganic matter in the solid fuels. On the other hand the simulation results, using FactSage, are in good agreement with experimental values, thus enabling the use of this programme to carry out further work to verify the influence of the metals on H_2S levels.

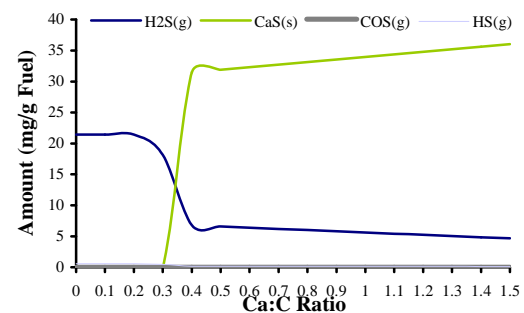In Figure (9) it is shown the effect of Ca increase on the concentration of H_2S.

Figure 9: Effect of Ca:C ratio on the formation of H_2S

The greater amounts of Ca was observed to produce lower H_2S in the gas phase accompaiend by more $CaS_{(s)}$ suggesting that calcium may play an important role in the removal of H_2S from the produced gas, confirming the results obtained by Attar [4]. The effect that Ca seems to have on H_2S is similar to its effect on the COS and HS levels, whose concentrations in the gas are reduced as the Ca:C ratio is increased.

The effect of potassium in the concentration of H_2S is presented in Figure (10).
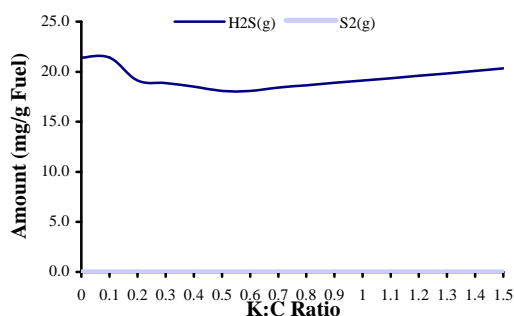

Figure 10: Effect of K:C ratio on the formation of H_2S

The increase of the potassium levels seem to have a small impact on the concentration of H_2S as well as on the levels of $S_{2(g)}$, which was the second most important sulphur species in the system. The increase of the K:C ratio up to 0.6 led to a reduction of 16% in the levels of H_2S, and an increase of 10.3% as the ratio was increase from 0.6 to 1.5.

The results presented in Figure (11) seem to indicate that the concentration of H_2S is not affected by the amount of Na in the system, except when the levels of Na are very high. In fact, only for Na:C ratios greater than 1.4 it was observed a reduction in the H_2S levels in the syngas, which can be related to the formation of $Na_2S_{(g)}$.
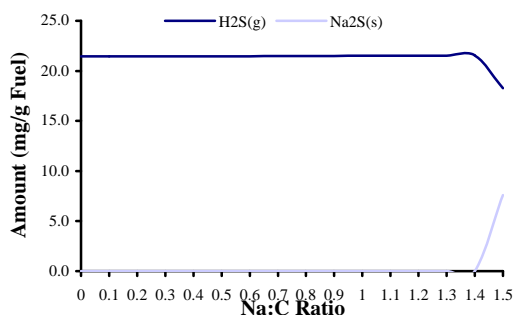

Figure 11: Effect of Na:C ratio on the formation of H_2S

Although not shown in Figure (11) the increase of sodium has led, preferentially, to an increase of NaOH, Na_2CO_3, $(Na_2O)(SiO_2)_{(s)}$.

3.4 Inorganic matter effect-HCl

The results obtained for the effect of Ca in the concentration of HCl, presented in Figure (12), seem to be in agreement with those obtained by Wei et al. [14], which suggest a strong relation between the levels of alkali and earth-alkali metals and the concentration of HCl. In fact, it was observed that the rise in the Ca:C ratio lowered HCl levels by about 99.8%.
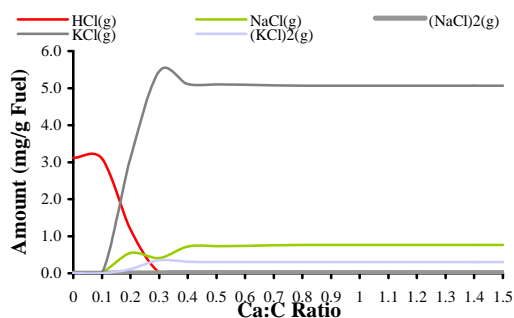

Figure 11: Effect of Ca:C ratio on the formation of HCl

However, the reduction in HCl does not seem to be related with the formation of calcium chlorides, as could be expected. In fact, with greater Ca:C ratios it was observed that higher amounts of sodium and potassium chlorides were released, suggesting that Ca plays an indirect role on the fate of Cl. An explanation for this behaviour lays with the fact that Ca may enable the release of sodium and potassium, through mechanisms involving silicates, resulting in more available Na and K, because it was observed that as the Ca:C ratio was increased the concentration of species such as $Ca_3MgAl_4O_{10(s)}$ became greater and the concentration of $NaAlSi_3O_{8(s)}$ and $KAlSi_2O_{6(s)}$ were reduced.

The increase of K:C ratio resulted in a reduction of the HCl levels and in an increase of the concentration of $KCl(g)$ and $(KCl)_2(g)$, (Figure 12).
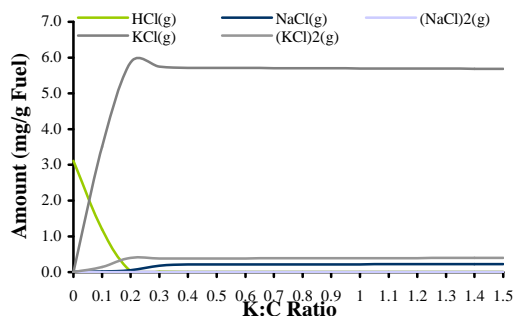

Figure 12: Effect of K:C ratio on the formation of HCl

The results shown in Figure (12) seem to agree with those from different authors [15], [14] that point out the important role of K regarding the fate of Cl, since by reacting with Cl, K leads to Cl becoming less available for the other reactions.

As the Na:C ratio was increased the levels of HCl were reduced by 99.6% (Figure 13). The results obtained seem to agree with those from Verdone et al. and Wei et al. ([18], [14]), that suggest that most of Na is in the form of NaCl and NaOH.
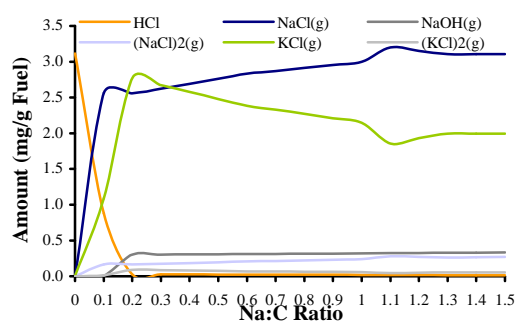
Figure 13: Effect of Na:C ratio on the formation of HCl

In fact, the reduction of HCl concentration seems to be related with the rise of NaCl. The results show that the sodium has both a direct and indirect effect on HCl. On one hand the increase of Na led to greater amounts of NaCl, as mentioned previously, and on the other hand has produced more KCl for a Na:C ratio of 0.2. For higher ratios, the concentration of KCl was also reduced.

4   CONCLUSIONS

The use of coal led to higher H_2S levels in the gas as expected, as the amount of sulphur in coal was greater than in RDF, however the relationship between the amounts of sulphur and the formation of H_2S seemed to be non linear, due to the retention of sulphur in the solid phase and the formation of other sulphur species.

The increase of the amounts of coal supplied to the gasifier resulted in a reduction of HCl concentration in the gas phase, which is probably related with the fact that Cl could have reacted with inorganic matter, hence forming metallic chlorides that condensed in the cyclone.

The use of a cooling system proved to be effective in the removal of Cl from the gas stream, but it seemed to be ineffective for the removal of S.

The predictions obtained using FactSage showed, in general, a good agreement with the experimental results, hence enabling the use of the model to explain experimental observations.

Based on the predictions it is believed that Ca may play an important role in the reduction of H_2S levels in the produced gas by its reaction with sulphur originating CaS(s), the sodium which may have a similar effect but only when present in high levels, on the other hand potassium did not prove to have a significant effect on the H_2S concentration.

The HCl seemed to be more sensitive to the presence of metals, since its concentration was reduced when the levels of Ca, Na and K were increased, Na and K seemed to have a direct effect on HCl concentration. Lower levels of HCl appeared to be correlated with the increase of the potassium and sodium chlorides, while Ca seemed to have an indirect effect since resulted in less HCl through the formation of sodium and, mostly, potassium chlorides.

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