

Municipal waste pyrolysis:

Chlorine capture by addition of calcium and sodium-based sorbents.

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ABSTRACT

Now in the case of the municipal waste treatments, it is widely accepted that pyrolysis can be an attractive alternative to incineration, if the process is followed by an energy valorisation of the solid residue^{1,2}.

During pyrolysis of PVC containing waste, chlorine is evolved mostly in pyrolytic gases, mainly as HCl^{3,4}. When lignin is present in the waste, a large proportion of the chlorine is entrapped in the solid char, less HCl being emitted⁵. When basic sorbents are added during pyrolysis, it is possible to trap the chlorine under leachable form in the char. The purpose of this work is to analyse the extrapolation of laboratory scale experiments to pilot scale facilities and to evaluate efficiency of the chlorine trapping during the pyrolysis of wood-PVC mixtures in a rotating kiln. When the char during pyrolysis entraps the chlorine under leachable form, it can be eliminated before further use. It is important to guide the chlorine either in the gas or in the char outputs by selected additions, in order to fit with the requirements of the fuels end users.

KEYWORDS

Waste, pyrolysis, wood, PVC, chlorine, sludge, lime, limestone.

EXPERIMENTAL

Materials

PVC was obtained by Solvay Company from recycled water bottles (particles size in the range of 1-5 mm): it contains 53% Cl⁻, 0.07% H₂O, 0.1% ashes with traces of 230 ppm Ca, 190 ppm Zn, 150 ppm Al, 150 ppm Si, 120 ppm Mg, 110 ppm Na, 37 ppm Sn and other minor elements. Four different powdered sorbents were tested in mixtures with PVC and their characteristics are given in table 1. Fine granular quartz (diameter between 0.2 and 0.8 mm account for 60%) from Merck Company was added to the charge for weight compensation.

Wood chips of a few millimetres contain about 37% water.

Sewage sludge from a German municipal sewage sludge treatment plant, contains 122 kg/t of calcium and the water content is about 50%.

Laboratory scale experiments (ULB)

All experiments were performed in a fixed-bed reactor⁶ with the same amount of PVC (3g) and with additions of different alkaline sorbent, in order to obtain different Ca or Na/Cl

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atomic ratios. Inert silicon dioxide is added in order to reach a total amount of charge of 15g. The starting mixtures were heated at atmospheric pressure up to 500°C during 25 min (heating rate of 35°C/min).

The hot pyrolytic gases are carried out of the furnace by a nitrogen flow (0.4 dm³/min). Condensable matter is recovered in cold traps and weighted. The uncondensed gases are washed (in water for HCl trapping) and collected for analysis. The mass of solid, condensable gases and hydrochloric acid are measured. The quantity of uncondensable gases is determined by difference.

Pilot scale experiments (CUTEC)

CUTEC pilot plant in Clausthal consists of the following main components:

- a 10 to 50 kg/h indirectly heated rotary kiln of a length over all of 5.8 m and a diameter of 300 mm (40 kW heated length of 3.6 m length),
- the pyrolytic residue is discharged through an electrically heated delivery chamber,
- the pyrolytic gas is directed from the kiln's delivery connection piece into a three-staged washing column filled with Raschig rings;
- the purified pyrolytic gas arrives after post cooling in the succeeding combustion chamber where it is burnt, along with natural gas for supporting the flame,
- the flue gas at 1000°C is cooled down and cleaned with sodium hydrogen carbonate and activated coal,
- the flue dust is separated by means of a cloth filter.

The material to be treated is delivered from the feeding shaft flooded with inert gas nitrogen into the kiln via a conveyor worm.

At the hot gas output of the rotary kiln, a discontinuous gas sampling of the pyrolytic gas device is equipped with a so called-finger type cooler and behind it a spiral cooler.

Another discontinuous gas sampling of the purified uncondensable pyrolytic gas is placed after washing column.

Analysis

Leaching tests were performed on all residual solids: approximately 3 g of sample in 50 ml of water (10 g in 400 ml of water for pilot scale experiments) during 1 h at 50°C. Chloride anions were titrated in all the solutions with silver nitrate (potentiometric titration).

Minerals present in the char before and after washing were determined by X-ray powder diffraction (XRD) on a Philips PW 1729 equipment (Cu K α , 32 kV, 28 mA).

Ashes were analysed by a SEM Jeol JSM 820, coupled with an energy dispersion microanalysis device (EDAX 9100). The accelerating voltage was 20 kV.

Uncondensed gases were analysed on two Varian 3300 chromatographs (porapak Q and molecular sieve columns, catharometer detectors).

RESULTS AND DISCUSSION.

Laboratory scale experiments

Without any additive, there are no significant differences between the results obtained for PVC and PVC-quartz mixtures neither on phase's distribution, nor on hydrochloric acid production (table 1) because the quartz is completely inert in these conditions. More than 70% of chlorine is recovered as hydrochloric acid. The remaining chlorine is probably in the condensable gas phase as organic chlorinated compounds (only traces of chloromethane and chloroethylene are observed in the uncondensable gaseous phase).

Phases distribution

The mass of the pyrolytic solid, liquids, gases and HCl issued from the treatment of different PVC-additive mixtures are presented in table 1 for the liquids and the gases (excluding HCl). For all experiments, the char fraction is given after subtracting the inert quartz mass.

For each sorbent used during pyrolysis of PVC, when the mass of the sorbent in the raw mixture increases, the mass of the char increases proportionally. This is due to the formation of the reaction products (calcium or sodium chloride) and to an excess of unreacted additives. Simultaneously, the liquid production also increases. The decarbonisation is enhanced when the presence of sorbent increases in the raw mixture. For the uncondensable gases, the situation is quite different. NaHCO_3 and Na_2CO_3 produce a larger quantity of gases, because of the sorbent decomposition at a lower temperature than the other additives. With hydrated lime, a decrease of the gas production is observed, which is connected to the absence of CO_2 production and the formation of condensable water.

Chlorine capture

The chlorine is distributed between HCl in the pyrolytic gases, chlorine in the char under leachable form, and by difference (18-28%) as under non-leachable form in the char and as chlorinated compounds in the condensable gases. These results are presented in table 2.

For the different sorbents, the percentage of chlorine found as hydrochloric acid in the hot gases is calculated from the HCl measured in the washing solution of the gases. By comparison with the 72% of chlorine found as HCl during pure PVC pyrolysis, the percentage of HCl eliminated from the pyrolytic gases is calculated and presented in fig. 1 for different sorbent's additions. (various Ca/Cl or Na/Cl atomic ratios).

The leachable chlorine from the char is also included in table 2 and presented in fig. 2 in function of the quantity of sorbent.

With the use of sorbents, there is a significant decrease of the chlorine emitted as hydrochloric acid in the hot pyrolytic gases, the chlorine being found in a leachable form in the char. The quantity of chlorine bled from the char increases with the amount of sorbent added. The efficiency of the four sorbents added to PVC-quartz mixtures are discussed hereafter.

1. CaCO_3 : for the stoichiometry of the reaction ($\text{Ca/Cl} = 1/2$), 56% of chlorine is still present as HCl in the gas phase (only 22% of chlorine has been eliminated from the pyrolytic gases). It is necessary to reach a ratio about 3/1 (6 times the stoichiometry) to trap all the HCl. For this ratio, 75% of the chlorine input will be found in the washing solution of the char. By increasing the nitrogen flow rate through the furnace from 0.4 up to 5 dm^3/min (simulating a higher gas flow through the furnace which decreases the gases residence time), the chlorine capture decreases drastically from 82 to 57%. There is a decrease of the leachable part of the char from 60 to 53%. Pre-drying the charge could be useful to increase the efficiency of the sorbents.
2. Ca(OH)_2 : for the stoichiometry of the reaction ($\text{Ca/Cl} = 1/2$), 96% of HCl in the hot pyrolytic gases is trapped, and 66% of the chlorine input is leachable from the char. With the ratio 2/1 (four times the stoichiometry), 98% of the total chlorine input is trapped in the char in leachable form.
3. Na_2CO_3 : for the stoichiometry of the reaction ($\text{Na/Cl} = 1/1$), 78% of HCl in the hot pyrolytic gases is trapped, and 70% of the chlorine input is leachable from the char. It is necessary to add this sorbent in a ratio 3/2 to trap all the HCl and to reach 79% leachable chlorine in the char.

4. NaHCO_3 : for the stoichiometry of the reaction ($\text{Na}/\text{Cl} = 1/1$), 100% of HCl in the hot pyrolytic gases is trapped, and 79% of the chlorine input is leachable from the char.

Char characterisation

The observation of the chars by SEM confirmed that no more chlorine stays in the solid after the washing step. We can conclude that the 18 to 28% of the total chlorine input is present in the uncondensable gases, except for the $\text{Ca}(\text{OH})_2$ addition in the ratio 2/1 where 98% of the chlorine has been eliminated by char washing. High-temperature ashes were obtained by fixed-bed combustion at 500°C during 8h from the char produced by pyrolysis of PVC, quartz and $\text{Ca}(\text{OH})_2$ (Ca/Cl atomic ratio of 2/1). The analysis of this sample by XRD shows the presence of:

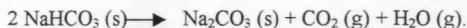
- quartz (SiO_2),
- hydrated lime ($\text{Ca}(\text{OH})_2$)
- calcite (CaCO_3)
- larnite ($2\text{CaO}\cdot\text{SiO}_2$)
- $\text{CaCl}_2\cdot\text{Ca}(\text{OH})_2\cdot\text{H}_2\text{O}$.

Interpretation of results

By addition of alkaline sorbents during pyrolysis, there is proof that the chlorine has moved from the gas phase to the char in the form of calcium or sodium chloride⁴.

Large differences are observed between the efficiency of the sorbents at stoichiometric (Ca or Na/Cl atomic ratios (table 2, figures 1 and 2). Among the calcium-based sorbents, hydrated lime reached the highest HCl trapping in hot pyrolytic gases (96%). Calcium carbonate clearly had the poorest behaviour (22%), which is probably due to low specific area and the formation of a calcium hydroxy-chloride layer. A large excess is needed to achieve the capture process (stoichiometry 6/1 to trap 100% HCl).

The efficiency of the sodium bicarbonate is close to that of the hydrated lime. This can be explained by the fact that NaHCO_3 when heated in the furnace decomposes according to the reaction:



The sodium carbonate becomes the reactant responsible for the HCl capture. As this sorbent shows an efficiency of about 20% less than with sodium hydrogenocarbonate (table 2), the results should be less good than obtained. However, PVC and NaHCO_3 are in good contact in the crucible and their decomposition starts in the same temperature range. Moreover, the release of water and carbon dioxide increases the porosity of the particles, so explaining the good results obtained with bicarbonate in our experimental conditions.

Nevertheless, the use of sodium bicarbonate is not recommended because the stoichiometry of the reaction uses respectively 2.2 and 1.7 times the quantity of this sorbent compared to calcium hydroxide or sodium carbonate. Moreover, very fine granulometry could provide the blowing out by the gas stream of fine particles before the starting of the reactions.

The best choice of chlorine sorbents would be between hydrated lime and cheap calcite. Beside the material costs, a decrease of the amount of calcite is expected in rotating kilns by the fact that the abrasion of calcite particles could reactivate the sorbent during the process.

There is a significant shift for the chlorine from paths a and c to path d⁴ (fig 3)

The results obtained at laboratory scale under static conditions are hereafter compared with pilot tests on a 20 kg/hr rotating kiln at 500°C.

Pilot scale experiments

The working program involves the comparison of the behaviour of chlorine issued from the pyrolysis of PVC with wood and with calcium carbonate or hydroxide. The results are focused on mass balance and on chlorine trapping by char washing.

Preliminary tests at laboratory scale

Pyrolysis of 110g of mixtures of wood chips / PVC (10/1) with and without limestone (Ca/Cl = 3:1) in a batch rotary kiln are carried out under a nitrogen flow (1.4 l/min) at 500°C during 1 hour. In both cases, only less than 0.5% of the chlorine input is present in the pyrolytic gases as HCl. It has been shown that in the presence of limestone, 24% of the chlorine is present as leachable calcium chloride in the char. In absence of limestone the chlorine is mainly entrapped in the char, with only 1.6% of leachable chlorine (path c).

Phases distribution and chlorine capture

As for lab-scale experiments, less than 0.5% of the chlorine input is present in the pyrolytic gases as HCl.

The pyrolysis of wood chips at 22 kg/hr during 7.3 hours (160 kg) generates 27 kg char, 20 kg gas and 113 kg of condensable gas (oil and water)

The pyrolysis of a mixture of wood chips and PVC (10:1) at 20 kg/hr during 4.6 hours (92 kg) gives about 16 kg char, 10 kg gas and 66 kg of condensable gas (oil and water). Char washing can only leach 2% of the chlorine input out. Thought, examination of the char after leaching by scanning electron microscope coupled with energy dispersion analysis confirms the presence of chlorine (in non-leachable form).

The pyrolysis of the same mixture wood-PVC with additions of limestone (10:1:4.7) (i.e Ca/Cl = 3:1) at 22.8 kg/hr during 6 hours (137 kg) gives about 61 kg char, 14 kg gas and 61 kg of condensable gas (oil and water). Examination of the char (SEM + EDAX) confirms the presence of chlorine associated with calcium before leaching. Char washing can leach out about 60% of the chlorine input.

The pyrolysis of the same mixture wood-PVC with additions of hydrated lime containing sludge (10:1:11) (i.e Ca/Cl = 2:1) at 22 kg/hr during 5.5 hours (121 kg) gives about 38 kg char, 13 kg gas and 71 kg of condensable gas (oil and water). Char washing can also leach about 60% of the chlorine input out. Calcium is also associated with chlorine in the char. By pre-heating the mixture in the feeding worm and increasing the furnace temperature up to 700°C, the leachable chlorine in the char reached 86%.

INTERPRETATION OF RESULTS

The interpretations of the results are based on the chlorine distribution illustrated in figure 3⁴.

The results obtained with the wood-PVC mixture are in accordance with the predictions made by the laboratory experiments on PVC-lignin and PVC-cellulose systems⁵ the chlorine is mainly adsorbed on the char (path c).

By limestone and sewage sludge additions to the wood-PVC mixture, the hydrogen chloride reacts preferentially with calcium to form calcium chloride (path d). At 500°C, the 60% leachable chlorine from the char obtained in both cases are slightly less than those at laboratory scale (see figure 2):

- By limestone, for Ca/Cl = 3:1 (i.e. stoichiometry 6:1): 60% compared to 75%

- By sewage sludge, for $\text{Ca/Cl} = 2:1$ (i.e. stoichiometry 4:1): 60% compared to 98%.
-

CONCLUSIONS

Depending on the waste nature (municipal or industrial waste, automobile shredder refuse, contaminated mud,...), we can conclude that the chlorine could be entrapped in the char in a non-leachable form by wood⁵. By selected additions into the waste input, such as calcium or sodium-based sorbents, the majority of the chlorine could be eliminated before the energetic valorisation of the char. Indeed, when chlorine is stabilised as calcium or sodium chloride, washing the char before the energy valorisation can easily leach it out. Cotreatment of waste with high chlorine content with sewage sludge containing calcium could be interesting. Further consideration should be given for this evaluation.

These basic additions could also stabilise the heavy metals as oxides in the char ashes instead as volatile chlorides.

The elimination of a large part of the chlorine during pyrolysis could lead to substantial economies on the flue gas cleaning system after combustion of the pyrolytic gases.

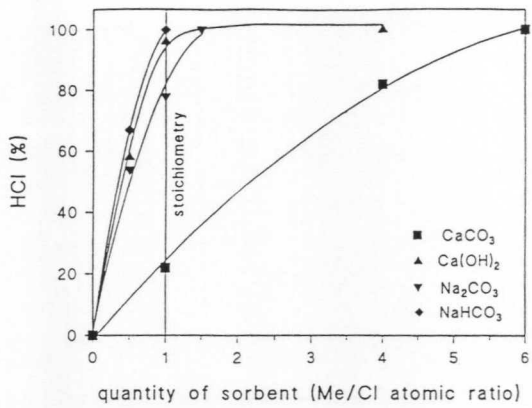


Figure 1: HCl eliminated from the pyrolytic gases for different sorbent's additions.

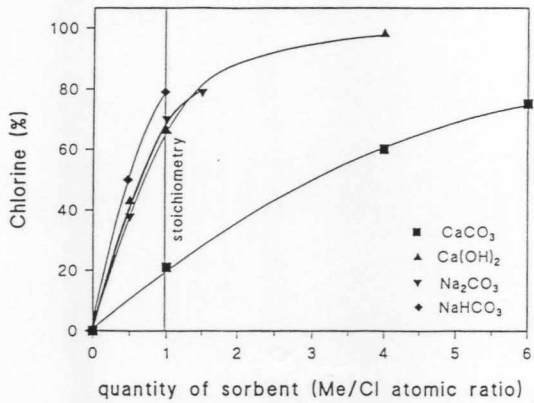


Figure 2: Leachable chlorine from char for different sorbent's additions (% of chlorine input).

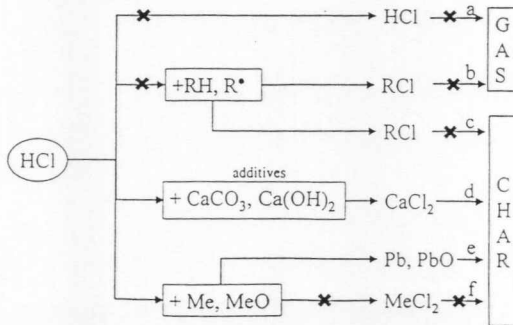


Figure 3: Paths for chlorine during pyrolysis⁴

Table 1

Mass balance of PVC pyrolysis in presence of calcium and sodium based sorbents.

Samples	PVC (g)	Sorbent (g)	Quartz (g)	Char** (g)	Liquids (g)	Gases (g)	HCl (g)
PVC-alone	3.02	0	0	0.45	0.98	0.42	1.17
PVC-Q	3.03	0	12.01	0.41	1.01	0.45	1.16
CaCO ₃ 1/2	3.06	2.27	9.73	2.95	1.01	0.46	0.91
CaCO ₃ 2/1	3.01	9.01	3.04	9.79	1.36	0.66	0.21
CaCO ₃ 3/1	3.00	13.51	0	14.36	1.35	0.80	0
CaCO ₃ 2/1*	3.00	9.08	3.05	9.79	0.61	1.17	0.51
Ca(OH) ₂ 1/4	3.00	0.83	11.17	1.62	1.47	0.26	0.48
Ca(OH) ₂ 1/2	3.00	1.68	10.43	2.64	1.85	0.14	0.05
Ca(OH) ₂ 2/1	3.01	5.41	6.65	6.35	1.95	0.12	0
Na ₂ CO ₃ 1/2	3.00	1.19	10.84	1.63	0.96	1.07	0.53
Na ₂ CO ₃ 1/1	3.00	2.38	9.62	2.63	1.41	1.08	0.26
Na ₂ CO ₃ 3/2	3.00	3.58	8.42	3.89	1.48	1.21	< 0.01
Na ₂ CO ₃ 2/1	3.00	4.76	7.24	4.89	1.53	1.34	0
NaHCO ₃ 1/8	3.00	0.47	11.53	0.71	1.09	0.63	1.04
NaHCO ₃ 1/4	3.00	0.95	11.05	1.05	1.39	0.73	0.78
NaHCO ₃ 1/2	3.00	1.90	10.10	1.72	1.62	1.17	0.39
NaHCO ₃ 1/1	3.00	3.78	8.22	2.96	1.58	2.24	< 0.01

* N₂ flow rate of 5 dm³/min

** Weight of solid residue after subtraction of the quartz charge

Table 2

Chlorine distribution between HCl in pyrolytic gases and in the washing solution of the char for different Ca/Cl or Na/Cl atomic ratios

Sorbent type	Ca/Cl or Na/Cl atomic ratio	Shift from stoichiometry	Cl as HCl in pyrolytic gases (% of Cl input)	Leachable Cl from char (% of Cl input)	HCl eliminated from pyrolytic gases (%)
PVC without sorbent	---	---	72	0	0
CaCO₃	1/2	St	56	21	22
CaCO ₃	2/1	4×St	13	60	82
CaCO ₃	3/1	6×St	0	75	100
CaCO ₃	2/1*	4×St	31*	53	57*
Ca(OH) ₂	1/4	St/2	30	43	58
Ca(OH)₂	1/2	St	3	66	96
Ca(OH) ₂	4/2	4×St	0	98	100
Na ₂ CO ₃	1/2	St/2	33	38	54
Na₂CO₃	1/1	St	16	70	78
Na ₂ CO ₃	3/2	1.5×St	0	79	100
NaHCO ₃	1/2	St/2	24	50	67
NaHCO₃	1/1	St	0	79	100

* nitrogen flow rate of 5 dm³/min

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