Chlorine Fixing Ability of Electric Arc Furnace Dust During the Thermal Degradation of Polyvinyl Chloride under Oxidative Conditions

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Abstract

Electric arc furnace dust (EAFD) and polyvinyl chloride (PVC) are two hazardous wastes that are accumulated world-wide at an alarming rate. Utilising these two wastes simultaneously towards a sustainable recycling loop can greatly mitigate their environmental impact. Herein, EAFD was studied as a potential emission fixator of evolved gaseous HCl generated from the thermal decomposition of PVC under different operational conditions: EAFD-PVC mass ratio, solid reactants geometry, O_2 partial pressure, holding temperature, holding time and heating rate. The highest chlorine fixation percentage was calculated to be 78.9% and was obtained at an EAFD-PVC mass ratio of 1:1 (thin disks geometry), while the rest escaped in the form of HCl/Cl_2. No significant variation was observed on the percentage of fixed chlorine when the thermal treatment was performed using different geometries: long cylinder, thin disks, and powder forms with a maximum difference in fixation of only 5.6% between extremities. Increasing O_2 partial pressure positively affected the chlorine fixation percentage increasing it from 39.9 to 48.4% at 0 and 21 kPa partial pressures, respectively. Increasing both the holding temperature and holding time under oxidative conditions negatively affected the percentage of fixed chlorine due to oxidation of formed $FeCl_2$ back to Fe_2O_3. The heating rate did not show any significant effect on the amount of fixed HCl, suggesting that the speed of chlorination reactions can be identical to or faster than the decomposition rate of PVC. Overall, EAFD is believed to be an excellent candidate for capturing HCl contained in PVC upon thermal degradation.

Paper type: Research paper

Keywords:EAFD, PVC, chlorine fixation, chlorine capturing, recycling.

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Introduction

Polyvinyl chloride (PVC) is one of the most widely used plastics in household items, piping, industrial applications and as a major component in thermoplastics. The extensive usage of PVC in all life segments is attributed to its good mechanical properties and its superior chemical stability (Masuda *et al*., 2006). In 2020, the plastic converters demand for PVC in Europe amounted to 4.7 million tons per year (Plastics-Europe, 2021). As a waste material, the disposal of PVC is considered challenging as it cannot be effectively treated without leaving any negative environmental footprint due to its high chlorine content. The latter participates in the formation of notorious polyaromatic chlorinated hydrocarbons. Landfilling and incineration of PVC are currently considered the main routes for its disposal. While landfilling does not greatly contribute to the emission of hazardous materials, the stable nature of the polymer body in landfill conditions (Mersiowsky *et al*., 1999) may eventually lead to the occupation of vast dumping areas. The indefinite accumulation of this waste material goes in parallel with the increased prices of landfills, thus deeming this approach obsolete and economically unjustified. Alternatively, PVC can be incinerated, and energy can be extracted in the process (i.e., the waste-to-energy approach) (Ahmed *et al*., 2018). However, during the incineration, PVC decomposes into hydrogen chloride (HCl) and chlorinated hydrocarbons such as poly-chlorinated dibenzo-p-dioxins and furan (PCDD/Fs) (Katami *et al*., 2002).

Many efforts were dedicated for the mitigation of these emissions by utilising metal oxides as a body for the fixation of these emissions (Altarawneh *et al*., 2021; Ballistreri *et al*., 1980; Masuda *et al*., 2006; Meng *et al*., 2021; Ye *et al*., 2021). Ballistreri *et al*. (Ballistreri *et al*., 1980), studied the effect of eight metal oxides including ZnO and Fe_2O_3 on the organic emissions from the decomposition of PVC. It was shown that ZnO and Fe_2O_3 both reduce the amounts of aromatics evolved from the degradation of PVC to levels significantly lower than those of pure PVC (Ballistreri *et al*., 1980). Masuda *et al*. (Masuda *et al*., 2006), studied the chlorine fixation capacity of eight metal oxides and their effect on the organic emissions including chlorobenzene which is one of the main precursors of PCDD/Fs. It was shown that ZnO and PbO both significantly reduce the amounts of emitted of HCl and chlorobenzene (Masuda *et al*., 2006). Ye *et al*. (Ye *et al*., 2021) studied the ability of Fe_3O_4, one of the major iron bearing compounds in EAFD in capturing emitted HCl from PVC degradation and the formed gaseous and solid products. Meng *et al*. (Meng *et al*., 2021) studied the effect of six different metal oxides on the onset de-hydrochlorination temperature, the thermodynamics, kinetics and the percentage of formed liquid and volatile matter. Finally, Altarawneh *et al*. (Altarawneh *et al*., 2022a; Altarawneh *et al*., 2022b, c) studied the kinetics of PVC thermal degradation in the presence of stoichiometric quantities of ZnO, $ZnFe_2O_4$, Fe_2O_3, and Fe_3O_4 along with the pyrolysis products at different holding temperatures.

From the summary above, it would be useful to consider how real metallurgical waste samples (EAFD) can interact with PVC for the co-remediation of hazardous materials generated from both plastic and metallurgy industries. Due to the small particle size of EAFD and its high content of metal oxides (Al-Harahsheh, 2017), studying its ability in fixing the chlorine present in PVC is important. Previously, the kinetics and thermodynamics of the reactions between HCl and the main components of EAFD were studied (Al-Harahsheh, 2017; Al-Harahsheh *et al*., 2015). The possibility of extracting zinc and lead from EAFD upon the thermal treatment with PVC has also been studied (Al-Harahsheh *et al*., 2022; Al-Harahsheh *et al*., 2021a; Al-Harahsheh *et al*., 2021b). Both the kinetics and thermodynamics suggest that EAFD can be considered an excellent candidate to inhibiting HCl evolution from the decomposition of PVC (Al-Harahsheh, 2017; Al-Harahsheh *et al*., 2015) in a process that convert its metal oxides into their corresponding metal chlorides. To the author's best knowledge, there has been no systematic study addressing the chlorine fixation capacity of EAFD during the thermal degradation of PVC. Herein, the chlorine fixing ability of EAFD will be presented when thermally treated with PVC at different O_2 partial pressures, heating rates, final holding temperatures, holding times, solid reactant geometries and EAFD-PVC mass ratios. Outcomes reported here shall find direct applications in the design of a continuous unit operation that effectively recycle both categories of pollutants.

1 Materials and Methods
1.1 Materials

Powdered PVC used in this work was purchased from Sigma-Aldrich with a K-value of 69–71, whereas EAFD was collected from a Jordanian smelter. EAFD used in this work was washed to dissolve inorganic chlorides, namely NaCl and KCl (Al-Harahsheh *et al*., 2018). The chemical composition of the washed EAFD used in this work is reported in **Table 1**.

Table 1 Chemical composition of washed EAFD used in this work.

Element	Zn	Fe	Ca	Na	Pb	Cu	Cr
%(w/w)	31.53±0.06	19.84±0.07	3.46±0.28	0.26±0.01	3.53±0.02	0.38±0.01	0.16±0.01
Element	K	Si	Mn	Mg	Ni	Cd	
%(w/w)	0.06±0.01	2.52±0.02	1.5±0.01	0.82±0.03	0.02±0.00	0.02±0.00	

All samples (including leaching and acidification solutions) were prepared using type I ultra-pure water. The chlorine content was determined using a potentiometric titration technique utilizing a solution of high-purity $AgNO_{3(s)}$ as a titrant, while the acidification of the leaching samples was performed using a trace analysis grade nitric acid (HNO_3).
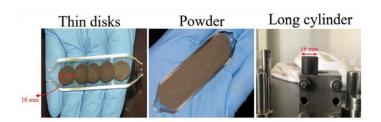
1.2 Experimental procedure and analytical techniques

Three solid mixtures of EAFD and PVC with different mass ratios were prepared (1:1, 1:2, and 1:3 EAFD:PVC). Mixing was performed by hand in a glass bottle (tumbling mill) containing ceramic balls for 15 minutes to produce mixtures of uniform particle size and high homogeneity. Powders were then pressed into pellets of different sizes or left as a powder for the purpose of obtaining different gas-solid surface areas during the thermal treatment (see **Figure 1**).

The pellets/powder were then heated up to the desired reaction temperature (250, 300, 350, or 400°C) in an electrically controlled furnace at a specified heating rate (5, 10, or 20°C/min). The reactor is a U-shaped Pyrex tube of 30 mm internal diameter (**Figure 2**) was connected from one end to a mass flow meter and from the other end to a capturing system (condenser and gas wash bottles).

The first gas wash bottle was fitted with a pH electrode connected to a readout to track the course of the reaction. The purpose of the condenser and the gas wash bottles is to capture and dissolve any emitted gaseous metal chlorides or excess unreacted HCl. A schematic illustration of the experimental setup is presented in Fig. 2.

A mass flow meter was used to control the environment of the reaction (either inert or oxidative) by adjusting the ratio between Air and N_2 which was necessary to obtain different O_2 partial pressures (0, 5, 10, 15, and 21kPa). Two reaction holding times were used: 30 and 60 minutes. After the thermal treatment, the system was cooled down under N_2 flow of 400mL/min for 10 minutes. The solid residue was then collected, weighed, and stored in a desiccator for further use. The reactor, crucible that is holding the pellet(s)/powder, and the condenser were then washed using hot ultra-pure type I water (60°C) to dissolved condensed chlorides on the internal surfaces of the glassware. The solution was then made up to 500 mL and stored in a centrifuge tube. Likewise, water in the gas wash bottle was made up to 500mL and stored for further use. Solid residues were then ground in a glove box under dry N_2. A mass of about 0.25g was taken from the ground

Fig. 1 Different geometries of the solid reactants (Thin disks, Powder, and Long cylinder) (Al-Harahsheh *et al.*, 2022).
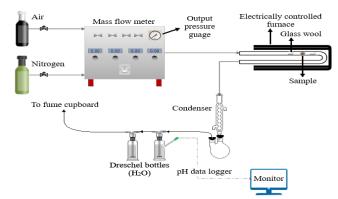

Fig. 2 Thermal treatment experimental setup (Al-Harahsheh *et al.*, 2022).

powders and was leached in a 75mL of ultra-pure type I water at 50°C for 60 minutes. The suspension was then filtered, and the filtrate was diluted 10 times using a solution of 1% HNO_3, while the filter cake was dried for 30 minutes at 105°C and stored in a desiccator. Solid samples were characterized using X-Ray diffraction (XRD) technique, while liquid samples were characterized using potentiometric titration technique. The solution used for the titration was a 0.02 M of $AgNO_3$. The amount of $AgNO_3$ solution consumed was then stoichiometrically balanced for the calculation of the concentration of chloride ions in the liquid samples. It was noted that the chloride ions in the two gas wash bottles (Fig. 2) came from the unreacted $HCl_{(g)}$ only. This means that all metallic chlorides have condensed on the internal walls of the reactor and inside the condenser and none has reached the gas wash bottles. This was confirmed by analyzing the water in the bottles for metallic content using Atomic Absorption Spectroscopy (AAS) technique. Hence, the percentage of fixed chlorine in this work is reported from the water used for solid leaching and will be referred to as "Solid residue" and from the water used for equipment washing and will be referred to as "Volatilized".

2 Results and Discussion
2.1 Chlorine fixation

The percentage of chlorine fixed was calculated according to the following equation:

$$\%\text{Fixated} = \frac{Mass\ Cl^-\ in\ leaching\ water\ +\ mass\ Cl^-\ in\ washing\ water}{Total\ Cl\ mass\ in\ the\ reactants} \tag{1}$$

The weight percentage of Cl in the PVC monomer amounts to 56.72%. This percentage along with the mass of PVC in the pellet were used to calculate the value of the denominator in Equation 1. The numerator, however, was calculated based on the concentrations of Cl^- obtained from the potentiometric titration tests.

2.2 Effect of EAFD:PVC ratio

Figure 3 shows the percentage of fixed chlorine by EAFD for different EAFD: PVC mass ratios. The "mass loss percent" appearing in Fig. 3 represents the percentage of total weight loss during the thermal treatment process and was calculated according to the following equation:

$$\text{Mass loss\%} = \frac{Mass\ reactants\ before\ thermal\ treatment - Mass\ reactants\ after\ thermal\ treatment}{Mass\ reactants\ before\ thermal\ treatment} \qquad (2)$$

As the percentage of PVC increases in the solid reactants, the overall mass loss increases as well. For 1:1, 1:2, and 1:3 EAFD: PVC ratios, the overall mass loss was 33.2, 34.6 and 40.1%, respectively. This increase in the loss can be attributed to the increase in the amount of excess unreacted HCl as the percentage of PVC increases (e.g., 1:3 ratio). This result can also be confirmed from the pH values of the water contained in the first gas wash bottle in which the pH was 1.88, 1.35, and 1.18 for ratios 1:1, 1:2, and 1:3, respectively; showing lower pH values as the PVC content increases. Mechanistically, a higher EAFD: PVC ratio entails that there are not enough de-chlorination sites (the Metal-O surface linkages) in EAFD to capture emitted HCl.
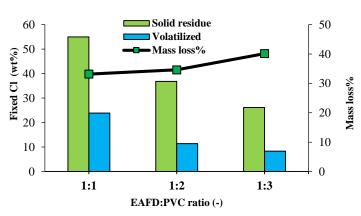
In terms of fixed chlorine, more is volatilized (in the form of metal chlorides) at lower PVC content (e.g., 1:1). The overall fixed chlorine is the sum of percentages from "solid residue" and "volatilized" (Fig. 3) giving values of

Fig. 3 Percentage of fixed Cl on EAFD for EAFD: PVC mass ratios of 1:1, 1:2, and 1:3 (10°C/min heating rate, 30 min holding time, 300°C holding temperature, 21kPa O_2 partial pressure and pellets in the form of thin disks).

78.9, 48.2, and 34.5% at 1:1, 1:2, and 1:3 ratios, respectively. The increase in metal chlorides volatilization at lower PVC percentages maybe assigned to the exothermic nature of the chlorination reactions. Thus, as the amount of EAFD increases, more metal oxides are available for chlorination, leading to higher heat generation causing more metal chlorides to volatilize. Based on the data appearing in Fig. 3, it can be concluded that for a complete chlorine fixation, higher EAFD ratios are required (i.e., higher than 1:1).

Evidence of chlorination can be provided by comparing the XRD patterns of washed EAFD with thermally treated EAFD-PVC mixture, and the leaching residue of the thermally treated EAFD-PVC mixture appearing in **Figure 4**.
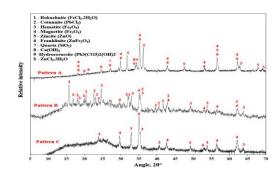

Fig. 4 X-Ray diffraction patterns of washed EAFD (Pattern A), the solid residue from the thermal treatment of EAFD and PVC (Pattern B) (heating rate of 20°C/min, holding temperature of 300°C, O_2 partial pressure of 21kPa, holding time of 30 minutes, long cylinder geometry and 1:2 EAFD: PVC ratio) and the powder produced from the leaching of the thermal treatment residue (Pattern C).

Pattern A in Fig. 4 represents the main phases present in a washed EAFD sample. The most important phases are ZnO, $ZnFe_2O_4$, Fe_3O_4, and $Pb_3(CO_3)_2(OH)_2$. After the thermal treatment with PVC, all zinc and lead-containing species and some of Fe_3O_4 were converted into metallic chlorides as can be seen in Pattern B where $PbCl_2$, $FeCl_2.2H_2O$, and $ZnCl_2.3H_2O$ can be seen. The presence of ZnO and $ZnFe_2O_4$ also

significantly alters the degradation mechanism of PVC lowering its onset degradation temperature by means of direct chlorine abstraction from the polymer chain (Altarawneh *et al.*, 2022b, c). All chloride peaks appearing in Pattern B disappeared when the solid residue was exposed to water leaching yielding Pattern C. The leaching residue (i.e., Pattern C) contained only Fe_2O_3 and Fe_3O_4, while zinc and lead species (oxides or chlorides) completely disappeared. This is also confirmed by the high (>95%) recovery values for zinc and lead reported elsewhere (Al-Harahsheh *et al.*, 2022; Al-Harahsheh *et al.*, 2021a).

2.3 Effect of solid reactant geometry

Figure 5 represents the percentage of fixed chlorine for the three different reactant geometries (long cylinder, thin disk, and powder forms).

The overall chlorine fixation for long cylinder, thin disks, and powder geometries are 48.4, 48.2, and 42.83%, respectively. The drop in fixed chlorine from 48.4% in the case of long cylinder to 42.83% in the case of powder can be assigned to the fact that HCl gas can escape more easily in the case of powder causing a higher overall mass loss (Fig. 5) and a drop in fixed chlorine. Moreover, the extensive oxidation of Fe_3O_4 (which can react with HCl) to stable Fe_2O_3 (which does not react with HCl) and the oxidation of any formed $FeCl_2$ back to Fe_2O_3 in the case of powder reactants also contributes greatly to the drop in fixed chlorine. In the powder form, the surface area between solid reactants and O_2 gas is much greater than in the case of pellets leading to more oxidation. The importance of this oxidation reaction (oxidation of $Fe_3O_4/FeCl_2$ to Fe_2O_3) can
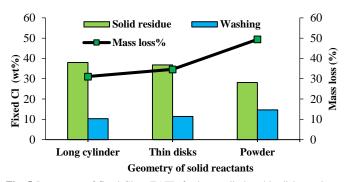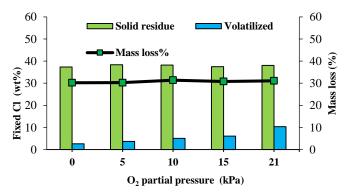

Fig. 5 Percentage of fixed Cl on EAFD for long cylinder, thin disks, and powder geometries (10°C/min heating rate, 30 min holding time, 300°C holding temperature, 21kPa O_2 partial pressure and EAFD:PVC ratio of 1:2).

only be realized if we refer to the thermodynamics paper published earlier to this work (Al-Harahsheh, 2017). In that study, it was confirmed that the chlorination of Fe_3O_4 is thermodynamically favorable, while the chlorination of Fe_2O_3 is not possible (Al-Harahsheh, 2017). This, in turn, can potentially result in less HCl fixation, and less iron recovery in the leaching solution (Al-Harahsheh *et al*., 2022; Al-Harahsheh *et al*., 2021a). The increase in the mass loss% in the case of powder (Fig. 5) is also an indicator of the extensive oxidation reactions taking place which result in more volatilization of formed metallic chlorides due to the exothermic nature of the oxidation.

2.4 Effect of the oxygen partial pressure

Figure 6 shows the percentages of fixed chlorine by EAFD at different oxygen partial pressures (0, 5, 10, 15, and 21kPa). Clearly, the overall mass loss remains almost the same (just above 30%) at all O_2 partial pressures.

The percentage of fixed chlorine, however, does show a trend with O_2 partial pressure; the overall captured percentage was 39.9, 42.1, 43.3, 43.6, and 48.4% at 0, 5, 10, 15, and 21kPa, respectively. Such a result agrees with the recovery percentages of zinc and lead metals reported in Al-Harahsheh *et al*. (Al-Harahsheh *et al*., 2021a); zinc and lead recoveries in that study increased from 88.3% and 57.7% at O_2 pressure of 0 kPa to 97% and 86.4% at O_2 pressure of 21kPa, respectively. The higher recoveries of zinc and lead means that more metallic chloride species were formed during the thermal treatment, leading to a higher chlorine fixation. It is worth mentioning that more volatilization can be seen at higher O_2 pressures which can be attributed to the exothermic nature of the oxidation reactions leading to metal chloride volatilization.

Fig. 6 Percentage of fixed Cl on EAFD for five different O_2 partial pressures (10°C/min, 30 min holding time, 300°C holding temperature, long cylinder geometry and EAFD:PVC ratio of 1:2).

2.5 Effect of the holding temperature

As mentioned previously in the experimental procedure, reaction mixtures were heated up to 300°C and held at it for either 30 or 60 minutes. **Figure 7** shows the chlorine fixing ability of EAFD for holding temperatures of 250, 300, 350, and 400°C at a holding time of 30 minutes. The overall mass loss increases greatly from 29.5 and 31.1% at 250 and 300 °C to 46.9 and 52.2% at 350 and 400°C, respectively. This is due to the significant increase in the vapor pressure of both $PbCl_2$ and $ZnCl_2$ going from 250 to 400°C. Besides the mass loss, the overall percentage of fixed chlorine showed a systematic drop changing from 52.26% at 250 °C to 48.4, 45.6, and 44.3% at 300, 350, and 400°C, respectively.

This drop in fixed chlorine is caused by the faster oxidation kinetics of formed $FeCl_2$ back to Fe_2O_3 at higher temperatures and due to a longer exposure to oxygen when higher temperatures were to be reached. This is confirmed from the thermodynamics data presented in **Figure 8** where the oxidation of $FeCl_2$ back to Fe_2O_3 with the release of chlorine in the form of Cl_2 gas is thermodynamically favorable. This result is also evident from a previous study (Al-Harahsheh *et al*., 2021a) where the iron recovery dropped from 31.7% at 250°C to 21.6, 14.4, and 12.5% at 300, 350, and 400°C, respectively (suggesting the conversion of $FeCl_2$ back to Fe_2O_3). Such a behavior is in good agreement with the chlorine fixation data reported here.

The change in the recovery of both zinc and lead was insignificant which further emphasizes the thermodynamics presented in Fig. 8. Further details on metal recoveries and thermodynamics of reactions are reported elsewhere (Al-Harahsheh *et al*., 2021a).

2.6 Effect of holding time

The effect of the holding time on the percentage of fixed chlorine is shown in **Figure 9**.
The overall fixed chlorine decreases with an increase in the holding time; percentage captured is 48.4 and 43.3% at holding times of 30 and 60 minutes. As the holding time increases, formed metallic chlorides are exposed to the oxidative environment for a longer period of time resulting in the oxidation of formed $FeCl_2$ back to Fe_2O_3 causing chlorine to escape as a Cl_2 gas. Such a result is also evident from the drop in the recovery of iron reported in a previous study (Al-Harahsheh *et al*., 2021a).

2.7 Effect of heating rate

Figure 10 shows the percentages of captured chlorine at heating rates of 5, 10, and 20°C/min. The overall fixation of chlorine does not vary greatly with the heating rate. The fixed percentages (from solid residue and volatilized) are 46.1, 48.4, and 49.0% at heating rates of 5, 10, and 20°C/min. This suggests that EAFD can capture an almost similar amount of HCl regardless of the heating rate. This means that the chlorination reactions are significantly faster than the decomposition of PVC. The most pronounced difference among the three heating rates is the overall mass loss%; in the case of 5°C/min, it has a value of 38.6% compared to 31.1 and 31.7% at 10 and 20°C/min, respectively. This can possibly be assigned to the exposure to oxidative conditions for a longer period of time causing more metal chlorides volatilization.
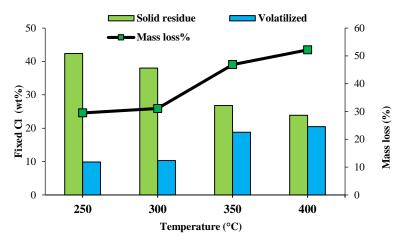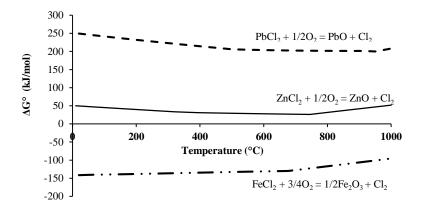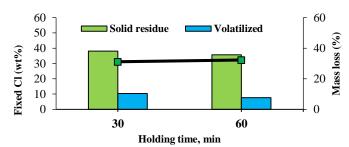
Fig. 7 Percentage of fixed Cl at holding temperatures of 250, 300, 350, and 400°C (10°C/min, 30 min holding time, O_2 partial pressure of 21kPa, long cylinder geometry and EAFD:PVC ratio of 1:2).

Fig. 8 Oxidation thermodynamics of $FeCl_2$, $PbCl_2$, and $ZnCl_2$ into Fe_2O_3, PbO, and ZnO calculated using Facility for the Analysis of Chemical Thermodynamics (FactSage) software.

Fig. 9 Percentage of fixed Cl at holding times of 30 and 60 min (heating rate of 10°C/min, holding temperature of 300°C, O_2 partial pressure of 21 kPa, long cylinder geometry and EAFD:PVC ratio of 1:2).

The data presented above suggest that metallurgical wastes (e.g., EAFD) which are rich in metal oxides can be considered as excellent candidates for the mitigation of gaseous emitted HCl from the thermal degradation of PVC. Among the many studied parameters, the most pronounced factors affecting the capturing capacity of EAFD are the O_2 partial pressure, solid reactants geometry, holding temperature and the mass ratio of EAFD to PVC.
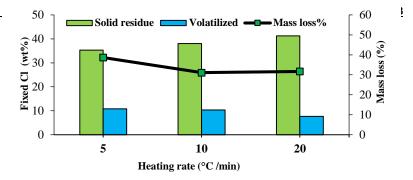

Fig. 10 Percentage of fixed Cl at heating rates of 5, 10, and 20°C/min (holding time of 30 minutes, holding temperature of 300°C, O_2 partial pressure of 21kPa, long cylinder geometry and EAFD:PVC ratio of 1:2).

Conclusions

The chlorine fixation ability of EAFD during the thermal degradation of PVC was studied experimentally under inert and oxidative conditions. EAFD was mixed with PVC at different ratios and was exposed to thermal treatment under different O_2 partial pressures, holding temperature, holding time, heating rates and reactants geometries. The following points are the main conclusions stemmed from this work:

- EAFD can be considered an excellent candidate for fixing HCl evolved from the decomposition of PVC. This result is confirmed using chloride content analysis of the leaching residues of the thermal treatment products under different conditions.
- Based on the EAFD: PVC ratios used in this work, it can be concluded that an EAFD percentage higher than 50 wt% should be used to capture more than 78.9% of the chlorine present in PVC (applies to EAFDs with similar chemistry to the one presented in this work).
- EAFD-PVC mixtures can be thermally treated in the form of powder or pellets with no significant change in the percentages of chlorine fixed; a result suggests that a significant portion of the reactions take place via a direct reaction between EAFD and the PVC monomer.
- The overall fixation of chlorine increased with the increase in the O_2 partial pressure. The maximum difference in fixation between extremities was 8.5% (inert and 21kPa).
- Both holding time and holding temperature affected the percentage fixed of chlorine in a negative manner; the higher the holding time and temperature, the less chlorine is captured. This can be assigned to the oxidation of formed iron chloride ($FeCl_2$) back to Fe_2O_3.
- The use of different heating rates (5, 10, and 20°C/min) did not have a significant impact on the amount of captured HCl. This suggests that the chlorination reactions are fast enough and are able to capture the similar percentage of chlorine even at an increased release rate of HCl at higher heating rates (e.g., 20°C/min).

Acknowledgment

Nomenclature

pH	=potential hydrogen	[-]
%Fixated	=percentage of fixed chlorine on EAFD	[%]
ΔG°	=change in standard Gibbs free energy	[kJ/mol]
Wt%	=weight percentage	[%]

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