Dechlorination of fuels in pyrolysis of PVC containing plastic wastes

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ABSTRACT

The objective of this work is the study of several dechlorination methods devoted to reduce the chlorine content of the liquids obtained in pyrolysis of PVC containing plastic wastes. A mixture of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) has been pyrolysed in a 3.5 dm^3 semi-batch reactor at 500 °C for 30 min. Stepwise pyrolysis carried out at several temperature and time conditions, the addition of CaCO$_3$ for chlorine capture and a combination of both methods have been studied. Additionally, some thermogravimetric analyses have been carried out in order to establish the best conditions for PVC dehydrochlorination in the presence of other plastics. It has been proved that the application of dehydrochlorination methods plays a significant role in the characteristics of pyrolysis liquids. Stepwise pyrolysis is an effective method for reduction of the chlorine content of pyrolysis liquids; additionally, heavier hydrocarbons and lower quantity of aromatics in the liquids than in conventional pyrolysis are obtained. The addition of CaCO$_3$ leads to the retention of a significant amount of chlorine in the solid, but more chlorine than in a conventional run is found in the liquids, which contains a higher amount of aromatics.

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1. Introduction

Plastics consumption has drastically increased in the last few decades. Annual consumption of plastics in Occidental Europe is about 60 million tons, yielding almost 23 million tons of plastic wastes per year [1]. At present, in Europe, about 50% of the annually generated plastic wastes are valorized, 60% by incineration with energy recovery and about 40% by recycling. Most of the recycled plastics are mechanically recycled, while less than 1% is chemically recycled [1]. Pyrolysis may be an alternative for increasing the chemical recycling percentage and an opportunity to obtain valuable liquid fuels from plastic wastes.

The presence of some PVC in real streams of municipal plastic wastes is still very common. Due to the low consumption of PVC in commodity applications, it is a minority product which is not recovered in the industrial separation and classification plants and therefore usually forms part of the rejected streams of such plants [2,3]. These rejected streams, composed by very different and intermingled plastics, cannot be mechanically recycled. In the pyrolysis process (heating in an oxygen free atmosphere), the organic components of the material are decomposed generating liquid and gaseous products, which can be useful as fuels and/or sources of chemicals. The inorganic ingredients (fillers, metals, etc.) remain practically unaltered and free of the binding organic matter, and therefore metals could be separated and the remaining solid may be reused (additive, fillers, pigment, etc) or as a last resort, it would be a minimum waste to be landfilled. Pyrolysis is an especially appropriate recycling technique for waste streams containing different plastics for which mechanical recycling is not feasible. The study of the fate of chlorine in pyrolysis of PVC containing plastic wastes is of a great interest since chlorinated compounds can be formed in the pyrolysis liquids and this is very detrimental either in order to supply such liquids to an oil refinery or to use them directly as fuels.

The objectives of this paper are on the one hand to study and compare several dechlorination methods in the pyrolysis of PVC containing plastic wastes, and on the other hand to analyse the influence of these methods not only on the chlorine content of the pyrolysis products but also on the characteristics of such products. There are many references in the literature about the thermal decomposition of PVC since it is a polymer which produces hydrogen chloride (HCl) when it is moderately heated, creating toxic and corrosive conditions. Consequently its sustainability has been under discussion for many years [4] and for this reason the thermal behaviour and pyrolysis kinetics of both virgin and waste PVC, either alone or mixed with other plastics, have been widely studied and discussed by many authors [5–12].

The dechlorination attempts proposed until now can be divided in three groups: stepwise pyrolysis, catalytic pyrolysis and pyrolysis with adsorbents added to the sample. In stepwise pyrolysis, a previous low temperature step is carried out in order to remove the chlorine of

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the original sample as HCl, which evolves as a gas; then the sample is pyrolysed in a conventional run [13,14]. In catalytic pyrolysis, some metal containing catalysts have been studied in order to prove their potential dual use, as pyrolysis catalysts and as HCl formation inhibitors. Blazsó et al. [15] studied the inhibition of HCl formation by using several metal containing catalysts in liquid phase contact (LPC). Recently some research on catalytic dechlorination in vapour phase contact (VPC) has also been done [16]. Finally, the addition of adsorbents to the sample reduces the HCl emission since the evolved HCl is trapped by means of physical and/or chemical adsorption and retained in the solid fraction. Several materials as biomass constituents [17,18], petrochemical residues [19] and alkaline adsorbents ($CaCO_3$, CaO, $Ca(OH)_2$, Na_2CO_3, $NaHCO_3$) [20] have been used as HCl adsorbents.

However, most of these studies have been done pyrolysing PVC alone or simple polymer mixtures; only a few authors have applied dehydrochlorination methods to mixtures as complex as that used in this paper [21,22]. Additionally most of the studies focus only on the chlorine content of the pyrolysis products and no information is given about the influence of the dechlorination methods on the complete properties and characteristics of the liquid fuels obtained. In this paper two of the dechlorination methods (stepwise and addition of adsorbents) have been studied, applying them to a PVC containing plastic mixture which simulates the composition of complex real plastic waste streams. The distribution of chlorine among the products is presented and also a detailed characterization of such products. Additionally, the thermal behaviour of PVC has been studied by means of thermogravimetric analyses in order to determine the best conditions for the dehydrochlorination of the PVC containing plastic mixture.

2. Materials and methods

2.1. Materials

The following materials were used to prepare the plastic mixture for the experiments: virgin PS, PE and PP provided by Spanish chemical companies, a type of PVC typically used for rigid transparent applications provided by a PVC products manufacturing Spanish company and waste PET coming a Spanish plastic recycling company. All the plastic materials were used in pellet size (≈ 3 mm) for the pyrolysis experiments; additionally finely ground samples (≤ 1 mm) were prepared both for the thermogravimetric studies and for characterization purposes. Commercial $CaCO_3$ powder with a purity grade >98.5% was used as adsorbent.

The proportions used in the plastic mixture can be seen in Table 1. This composition was established characterizing real samples rejected from an industrial plant located in Amorebieta, in the north of Spain [2,3], and based on the composition proposed by other authors as representative of municipal plastic wastes in Europe [23–25]. The characterization results of both PVC alone and the plastic mixture are presented in Table 2. The chlorine content of the PVC sample is 36.3 wt.%, which is somewhat lower than the theoretical expected value according to the PVC chemical formula (56.8 wt.%); this is most probably due to the fact that the PVC sample is not a PVC pure resin

Table 1
Composition of the plastic mixture pyrolysed.

Material	wt.%
PE	40
PP	35
PS	18
PET	4
PVC	3

Table 2
Moisture, ash and elemental composition (wt.%) and GCV (MJ kg^{-1}) of PVC and the plastic mixture pyrolysed.

Sample	PVC	Plastic mixture
Moisture	0.2	0.1
Ash	0.0	0.0
C	44.4	84.7
H	5.7	12.5
N	0.2	<0.1
Cl	36.3	1.1
Others[a]	13.2	1.5
H/C ratio	1.5	1.8
GCV	26.0	43.9

[a] By difference.

but a PVC product which contains several additives apart from the PVC polymer.

2.2. Experimental

The thermal behaviour of PVC alone was studied using a Mettler Toledo TGA/SDTA851 analyser. The analyses were conducted with 7.5 mg samples, which were heated under nitrogen flow (50 mL min^{-1}) to 600 °C at a rate of 20 °C min^{-1}. The temperatures of the maximum degradation rates ($Tmax_1$ and $Tmax_2$) were determined from the derivative thermogravimetric (DTG) plot. The thermal behaviour of PVC in the mixture (in presence of all the other plastics) was studied with a LECO TGA-500 analyzer since larger samples were necessary for chlorine determination after the dehydrochlorination step. In this case, a total sample mass of 0.5 g was heated at a rate of 20 °C min^{-1} to the dehydrochlorination temperature and nitrogen was passed through at a rate of 50 mL min^{-1} during the analysis.

The pyrolysis experiments were carried out at 500 °C in nitrogen atmosphere, using an unstirred stainless steel 3.5 dm^3 reactor. Previous studies carried out by the authors [26,27] with other polymeric wastes (scrap tyres, automobile shredder residues, etc.) indicated that in the mentioned installation, 500 °C was the optimum temperature for treating such type of wastes by pyrolysis, since at lower temperatures complete decomposition of the organic matter was not achieved, and at higher temperatures the slight increase in gas yield was indeed counterbalanced by a detrimental effect on the liquid yield, so that 500 °C was chosen as the process optimal temperature for the samples under investigation.

Three types of experiments have been carried out. 1) A conventional experiment in which 100 g of the sample were placed into the reactor, which was then sealed. Nitrogen was passed through at a rate of 1 dm^3 min^{-1} and the system was heated at a rate of 20 °C min^{-1} to 500 °C, and maintained there for 30 min. It has been proved by the authors that in the mentioned installation at 500 °C after 30 min no more pyrolysis products evolve from the reactor [28–30]. During each run the vapours leaving the reactor flowed to a series of running water cooled gas–liquid separators where the condensed liquids were collected. The uncondensed products were passed through an activated carbon column and collected as a whole in Tedlar plastic bags, to be afterwards tested by gas chromatography. The experimental set-up can be seen in Fig. 1. 2) Stepwise pyrolysis, in which a previous dehydrochlorination step was carried out at 275 °C or at 300 °C during 30, 60 and 120 min and then the temperature was raised at 20 °C min^{-1} to 500 °C to complete the pyrolysis process. 3) Adsorption experiments in which 4.65 g $CaCO_3$ were added to the sample and then a conventional run was carried out. The reason why $CaCO_3$ was chosen as adsorbent was that it is a cheap product which could be appropriate to be used in an industrial scale. The amount of $CaCO_3$ used corresponds to an stoichiometric relation Ca:Cl of 3:1, which has been proposed by other authors [20,31] as enough to achieve an efficient HCl capture.