

KINETIC STUDY OF THERMAL DE-CHLORINATION OF PVC-CONTAINING WASTE

A. Castro^{1,2,a}, C. Carneiro¹, C. Vilarinho², D. Soares², C. Mações³, C. Sousa³ and F. Castro²

¹ CVR - Centre for Waste Valorization, Guimarães, Portugal

² CT2M - Centre for Mechanical and Materials Technologies, Mechanical Engineering Department, University of Minho, Guimarães, Portugal

³ Endutex - textile coatings, SA

^a acaastro@cvresiduos.pt

ABSTRACT

With the increasing of plastics content in solid waste, both municipal and industrial, also increases the interest in its use as an energy source.

Some of these wastes are an important potential source of energy and might be valorized using the pyrolysis or gasification processes. However, the presence of high chlorine contents in its composition prevents its management by a thermal process, as consequence of toxic compounds production and their release to the atmosphere.

The present work asses a possible process for treating PVC-containing wastes in an environmentally friendly way. It is based on the effective de-chlorination of PVC-containing wastes through a pyrolysis process at low temperature before the carbonaceous residue from PVC-containing wastes being subject to a subsequent thermal treatment for energetic valorization.

Keywords: Pyrolysis, thermal degradation, PVC-containing waste, energy valorization;

INTRODUCTION

The presence of organic compounds on wastes, especially plastics, is considered an important source of energy. However, most of these plastics contain polyvinyl chloride (PVC), causing recycling problems when it is considered a thermal valorization process for its treatment [1], preventing the use of those residues on these processes, which main goal is the energy recovery [2,3]. A possible solution is to remove the chlorine from PVC-containing waste through a pyrolysis process before being subjected to a thermal treatment, for energetic valorization.

Pyrolysis is one of the applied techniques for energetic valorization and is defined as a process of irreversible chemical modification of compounds under the action of heat and in the absence of oxygen, causing thermal degradation [1]. The reaction involved in this process is endothermic and the characteristics of the obtained products are function of the waste composition and of several operating factors, such as the temperature, pressure and residence time in the pyrolysis reactor.

The pyrolysis process is considered by several authors [2 - 8] as a possible technique for the energy recovery from PVC-containing wastes, through the thermal degradation of the chlorine

molecule. PVC pyrolysis involves significant cross-linked reactions with the formation of polyaromatic structures (possibly chlorinated) and a carbonaceous residue (char) [9]. Thus, it is possible to break down this molecule, allowing the chlorine recovery as hydrochloric acid or chloride [10], with potential economic gains.

However, the presence of poly(vinyl chloride) in wastes composition confines their management by thermal valorization processes as consequence of environmental problems and corrosion of the equipment. In fact, high levels of chlorine in wastes composition are responsible for the formation of hydrochloric acid, chlorine gas and dioxins [11]. Therefore, a preview thermal treatment by a pyrolysis process to remove the chlorine from PVC-containing wastes will be a suitable step if done prior to an energy recovery process to produce a synthesis gas.

Considering thermogravimetric analysis, it is assumed that the degradation of PVC occurs between 200 and 400 °C [2, 12]. At 250 °C, the decomposition of PVC has already been initiated, reaching a maximum at approximately 300 °C. At 350 °C the amount of chlorine present in PVC waste is less than 0.1%, which means that at this temperature, 99.5% of the whole chlorine has already been released [2]. At the end of the process of chlorine removal, a residual amount of chlorine remains on the waste [9].

The C-Cl bonds in the structure of PVC have a relatively lower binding energy than the C-C and C-H bonds, which justifies that the bonds of chlorine are the first to be broken, thus starting the thermal degradation of PVC. The de-chlorination of PVC is a free radicals chain reaction therefore requiring low activation energy to start, occurring at low temperatures [4, 7].

De-chlorination of PVC wastes is a mandatory step for any treatment process, able to recover energy from these wastes. In fact, from the decomposition of PVC, one polymeric fraction can be obtained with high energetic value:



As a matter of fact, products from the decomposition will be of the type C_nH_n .

This work aims the contemplation of new valorization processes and use of PVC-containing wastes. For the PVC molecule de-chlorination, tests were performed at low temperature pyrolysis and subsequent gasification of the remaining fraction in order to produce a synthesis gas with high energetic potential.

EXPERIMENTAL WORK

In this work, the kinetics of thermal de-chlorination has been studied, by simultaneous DTA/TGA determinations, under inert atmosphere. With all the experimental data obtained a multivariate regression of $\ln(r)$ has been performed in function of $1/T$ and $\ln([\text{HCl}])$. The kinetic model has been calculated just for points where temperature was lower than 340 °C, and the obtained model is:

$$\ln r = 31,3 - \frac{16100}{T} + 1,020 \ln[\text{HCl}] \quad \text{with } r^2 = 0,9912$$

This allows considering that reaction as a first order one with activation energy of $133800 \text{ J/mol} \pm 760 \text{ J/mol}$.

For the kinetic study, a DTA/TGA (SDT 2960 from TA Instruments) testing at different temperatures has been carried out in order to determine the relationship between the rate of PVC de-chlorination and the temperature of the thermal treatment, under an inert atmosphere. It was used a commercial pure PVC powder with the chemical formula $\text{C}_2\text{H}_3\text{Cl}$, in which 56,7% is chlorine. The reference is VICIR S 950 and it is a vinyl chloride homopolymer produced by a suspension polymerization process.

Experiments have conducted up to 5 different maximum temperatures: 250, 275, 300, 325 and 400 °C, with a heating rate of 10 °C per minute until the desired temperature is reached. After reaching this temperature, a stage has been done during 360 minutes. Heat flux (weight corrected heat flow in W/g) and weight of sample, has been continuously recorded.

DTA/TGA testing performed indicates that the temperature of 340 °C enables the removal of 88 % of the chlorine present in the PVC material. The resulting de-chlorinated fraction, carbonaceous residue, has also been characterized and it is mainly constituted by carbon. This carbonaceous residue was testing up to 500°C in DTA/DTA and was verified that the combustion reaction of the carbonaceous material is complete at 493°C demonstrating potential as a fuel source to a following gasification in order to produce a synthesis gas with high energetic potential.

To characterize the sample of PVC used and the carbonaceous residue formed, it has been used an TruSpec Elemental Determinator, model TruSpec CHN, of Leco with a burn time of 452 seconds and an Philips Analytical sequential X-ray fluorescence (XRF) Spectrometer model X'Unique II.

Table 1. Comparison between the chemical composition (in wt%) of PVC sample used and the carbonaceous residue obtained from pyrolysis at 340 °C.

	PVC (initial sample)	PVC (Carbonaceous residue)
Carbon	38,4	89
Hydrogen	4,9	7
Chlorine	56,7	0,07

Through table 1, we are able to conclude that the de-chlorinated fraction obtained at 340°C is mainly constituted by carbon presenting residual chlorine content, 0,07 %.

Tests were performed in the laboratory and pilot scale, where the variables temperature, pressure and residence time inside the reactor were studied, as well as its influence on the reaction products obtained.

The pilot plant consists in a reactor where the pyrolysis occurs, with a stainless steel body heated by electrical resistance and a column of water where the gas is bubbled, as exemplified in figure 1. Measuring instruments such as thermocouples and pressure gauges are used to control the conditions (temperature and pressure) inside the reactor.

The fixation of the released chlorine is obtained by water absorption, forming HCl (hydrochloric acid), CaCl₂ (calcium chloride) and also NaCl (sodium chloride), when the aqueous solution, containing CaO (calcium oxide) or NaOH (sodium hydroxide), respectively.

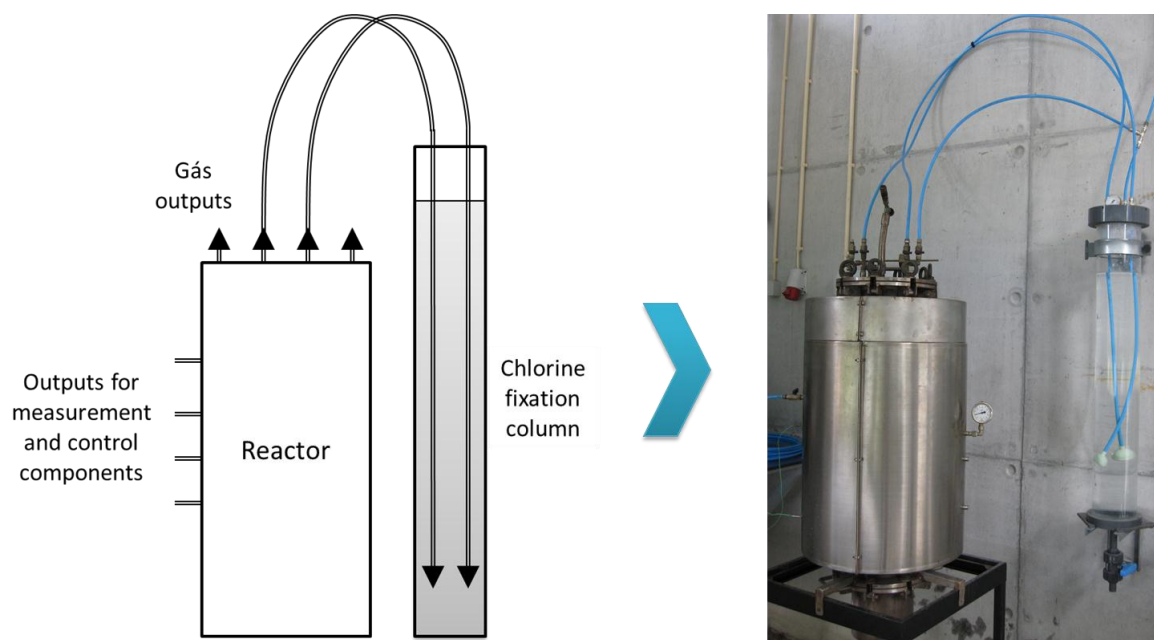


Figure 1: Scheme of pilot scale used for the tests.

Initially, a slight vacuum is created to remove the oxygen inside the reactor, then the test is initiated and divided into two stages. The first stage is a low-temperature pyrolysis or carbonization, where the de-chlorination of the PVC-containing waste reaction occurs, the released chlorine is recovered in the column in the form of hydrochloric acid, sodium chloride or calcium chloride. After the first stage is completed, second stage, takes place, then the carbonaceous residue (without chlorine) resulting from the first stage, is energetically valorized, at temperatures above 550 ° C.

The residence time in the reactor was tested by the pressure differences, viewed through the pressure gauge in the reactor. Thus, the reaction starts in vacuum and is assumed as completed when the pressure reaches zero, i.e. atmospheric pressure. During the reaction, when the pressure is 0,5 bar above atmospheric pressure, it is enough for the syngas formed inside the reactor can bubble in column. After all the gas is released, then the pressure drops to zero on the gauge, i.e., atmospheric pressure, thus giving the information that the reaction is complete.

All materials used in building a pilot plant must be well chosen, because of corrosion of materials and isolation. The absence of leakage or entry of gases must also be controlled, since the produced gases are toxic and cannot leak to the atmosphere, and also because as pyrolysis is a process that must take place in anoxic environment, thus it should be affected by any entry of oxidizing agents.

The main reaction product is a synthesis gas for burning to produce heat.

CONCLUSIONS

In this work, the kinetics of the reaction of thermal decomposition of PVC were studied, leading to the development of a kinetic model, with the expression $\ln r = 31,3 - 16100/T + 1,020 \ln C (\text{HCl})$. This model was obtained for the decomposition temperatures lower than 340 °C, in which almost all chlorine is removed from the pure PVC through the chemical reaction described, with an activation energy of 133800 J/mol, value very close to the one obtained by others researchers [4].

The kinetic model was verified in laboratorial trials, and it was observed a reduction of 88 % of the chlorine contained in PVC, making it suitable to be used in a recovery process to obtain a synthesis gas.

During the pyrolysis treatment, released chlorine can be fixed in the form of aqueous solution of hydrochloric acid, calcium chloride or sodium chloride. This process shall constitute an attractive route, envisaging environmental benefits, thereby avoiding deleterious effects of toxic gas emissions.

In this study, we propose a methodology to remove chlorine from PVC-containing wastes allowing the valorization of the chlorine-free remaining fraction. A double benefit can thus be achieved as it not only saves the cost of landfilling but also produces an value added syngas.

It is concluded that for PVC-containing waste, the solution can pass through a full treatment consisting of two phases. Where the first is to remove the chlorine from the PVC molecule and the second is to valorize the remaining fraction.

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