

ENERGETIC VALORISATION OF PVC-CONTAINING WASTE

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

¹ CVR - Centre for Waste Valorisation, Guimarães, Portugal.

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

³ Endutex - textile coatings, SA

*Corresponding author: acastro@cvresiduos.pt, T: +351 253 510 025; F: +351 253 510 029.

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Abstract

Wastes are increasingly regarded as important sources of energy, particularly their polymeric component. It is known that most of these wastes contain polyvinyl chloride (PVC) in their composition, constraining therefore the use of a thermal valorisation process in their treatment [1].

This work aims the development of an integrated process for the material and energetic valorisation of the PVC-containing wastes. A two-step process was firstly defined and tested at a laboratory scale and subsequently its feasibility evaluated by a factorial plan of tests performed in a pilot plant, designed and built in the aim of the Project PVC4GAS.

The pilot plant consists of a reactor, with a stainless steel body heated by electrical resistances, a column to clean the produced gas and three sequential columns to fix the released chlorine before it burns.

Initially, a slight vacuum is created in the reactor to remove most of the oxygen trapped inside the reactor, and subsequently the test is performed in two stages. The first stage consists of a low-temperature pyrolysis (400±10 °C) or carbonization, for the de-chlorination of the PVC-containing waste. The resulting carbonaceous residue is energetically valorized at temperatures above 550°C, in a second stage of the process. The tests showed that the temperature of 800 °C leads to a gas with better powerful properties.

The main process product is a synthesis gas with fuel power, which might after treatment by low temperature pyrolysis, be used in different types of equipments as substitute of traditional fuels. Hydrochloric acid and a coke with carbon content higher than 37 % are also generated during the developed process.

1- INTRODUCTION

PVC (polyvinyl chloride) is commonly used in the plastic industrial activities, making it a constituent regularly present in several wastes. The presence of PVC in solid wastes composition jeopardizes its use in energetic valorisation processes as consequence of environmental problems and corrosion phenomena of the equipments [2, 3]. In fact, high levels of chlorine in wastes composition are responsible for the formation of hydrochloric acid, chlorine gas and dioxins [4]. Therefore, prior to an energy recovery process, a treatment to remove the chlorine from the PVC containing wastes should be provided and implemented. This procedure will deflects the landfilling of this typology of wastes providing instead the energetic valorisation of the de-chlorinated fraction.

After the chlorine removal, by a pyrolysis heat treatment, the residues might be safely used for energetic valorisation with fuels production [5].

The pyrolysis process is considered by several authors [2, 6 - 11] as the most promising technique for the energy recovery from PVC-containing wastes. It 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 of the chlorine molecule [1]. The reaction is endothermic and therefore requires an external source of heat for the reaction to be initiated. The PVC pyrolysis involves significant cross-linked reactions with the formation of polyaromatic structures (possibly chlorinated) and a carbonaceous residue (char) [12]. It is possible to break down the PVC molecule, allowing the chlorine recovery as hydrochloric acid or chloride [13], with potential economic gains.

The nature of the products obtained through the pyrolysis process is influenced by several factors, such as the composition of the waste, temperature, pressure and reaction / residence time in the pyrolysis reactor.

This work aims the valorisation of a PVC-containing waste, in a two phases process: low temperature pyrolysis, for the study of the thermal de-chlorination of PVC molecule and subsequent energetic valorisation of the remaining fraction in order to produce a synthesis gas with high energetic potential. This synthesis gas can be used to replace natural gas or other fossil fuels used in equipment's.

2- MATERIALS AND METHODS

The pilot plant includes a reactor heated by electrical resistances where the pyrolysis and the subsequent process for the energetic valorisation occur as well as four sequential columns, where the gas is bubbled in water, as shown in figure 1. The whole process control was guaranteed by temperature and pressure measurements inside the reactor and by the evaluation of the pH during the de-chlorination process. The released chlorine can be fixed in water, in a solution of CaO (calcium oxide) or of NaOH (sodium hydroxide), forming HCl (hydrochloric acid), CaCl₂ (calcium chloride) and NaCl (sodium chloride), respectively.

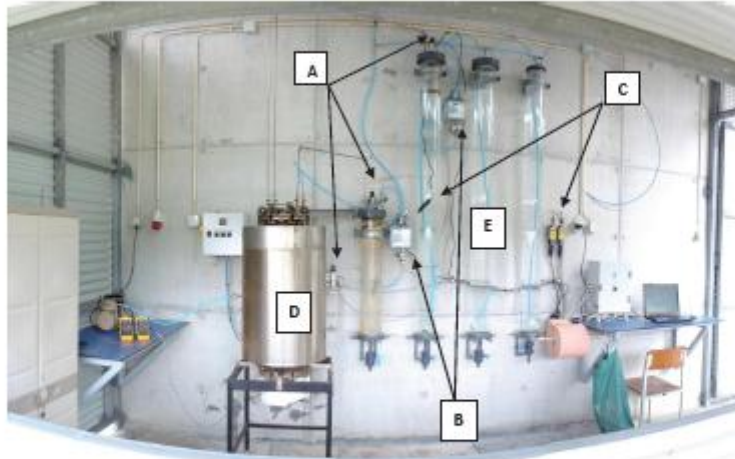


Figure 1: Pilot plant. A - pressure gauges, B - flowmeters; C - pH meters; D - reactor, E - water columns.

The absence of leakage or gases inlet have also been ensured, since the produced gases are toxic and cannot leak to the atmosphere, and the pyrolysis is a process that must take place in anoxic environment.

In the pilot plant two types of tests were carried out, namely low temperature pyrolysis and energetic valorisation of the chlorine-free fraction. For that purpose, a factorial plan of trials has been followed up in order to test all the operational parameters, such as the temperature and the residence time in the reactor, the amount of PVC-containing waste to be treated, which in turn, had a direct influence on the content of chlorine released and on the amount and composition of the produced gas.

The pyrolysis tests were performed at 400 °C, in order to remove all the chlorine present in the wastes that is not fixed in the form of titanium chloride and calcium chloride, which presence is consequence of the existence of calcium carbonate and titanium dioxide in the composition of the original waste. The PVC-containing waste is composed mostly by PVC (45 %), and the remaining is essentially composed by plasticizers, polyester and the already mentioned calcium carbonate and titanium dioxide [14]. At the beginning of the tests a vacuum atmospheres is generated to enable an anoxic atmosphere. The tests have been carried out during 1h20 and, at the end, a scan is performed with compressed air, to eliminate the potentially acidic atmosphere inside the reactor. During these trials, the chlorine released was fixed in aqueous solution, through its bubbling across the fixation columns and forming hydrochloric acid (HCl).

Tests of energetic valorisation of the de-chlorinated fraction were made in the temperature range 700 – 800 °C [15], and the best results concerning the chemical composition of the produced gas were obtained at 800 °C.

The total residence time of the residue in the reactor was approximately 160 minutes, being 80 minutes the time of each stage.

3- RESULTS AND DISCUSSION

The pyrolysis at low temperature enables the formation of hydrochloric acid and of a carbon-rich residue, with about 90 % of carbon [15] as reaction products. The energetic valorisation promotes the generation of a produced-gas with high calorific value. At the end of the two phases only about 20 % of the initial mass is present in the form of coke, with a carbon content of approximately 37 % [14].

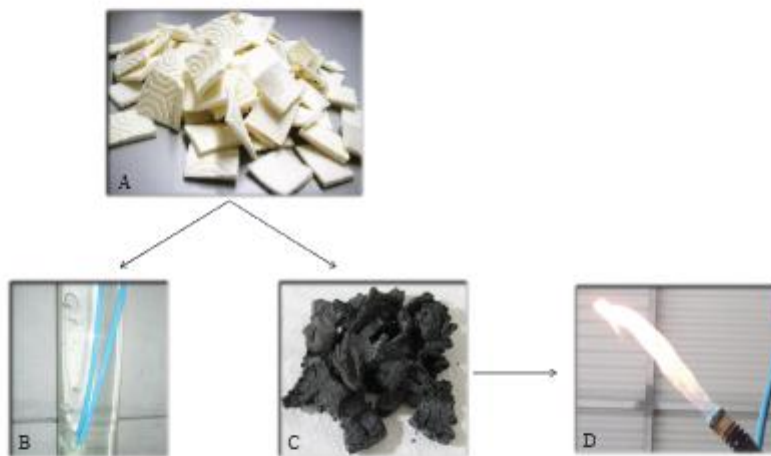


Figure 2: A. Raw material used in the tests performed in the pilot plant (industrial waste with PVC in its composition) and the reaction products obtained during the tests. B and C - hydrochloric acid and carbonaceous residue resulting from the pyrolysis treatment at low temperature and D - burning of the produced gas produced during the energetic valorisation of the carbonaceous residue resulting from the pyrolysis.

Mass losses and volume of gas released were recorded during the two phases of the process - pyrolysis and energetic valorisation. Experimental results are presented in tables 1 and 2.

Table 1: Mass loss and volume of produced gas in the pyrolysis test (phase 1).

Initial mass of waste for pyrolysis (g)	250,0
Final mass of waste after pyrolysis (g)	60,4
Weight loss (%)	75,8
Gas flow (l)	21,0

Table 2: Mass loss and volume of produced gas in energetic valorisation test (phase 2).

Initial mass of waste for valorisation (g)	60,4
Final mass of waste after valorisation (g)	54,4
Weight loss (%)	14,9
Gas flow (l)	29,0

The carbonaceous residue, resulting from the first stage, was energetically valorized by increasing the oven temperature to 800 °C. From phase 2 the main reaction product is a synthesis gas with fuel power, which may, after treatment, be used as substitute of natural gas or other fossil fuels. The produced gas is mostly composed by hydrogen, carbon monoxide and methane (table 3). For a complete test, a mass of 250 g of industrial PVC-containing waste, generates 50 L of gas, from which 29 L are gas with added value, containing 11.6 L of hydrogen, 4.9 L of carbon monoxide and 3.2 L of methane.

Table 3: Characterization of the gas produced during the phase of energetic valorisation at 800 °C, the remaining 20% corresponds to other hydrocarbons.

Compound	Content (%)
H ₂	40,0
CO	17,0
CO ₂	5,0
CH ₄	11,0
H ₂ O	11,8

4- CONCLUSIONS

From the experimental work, it can be concluded that the proposed technology in two steps for the treatment and energetic valorisation of PVC-containing wastes, is technically viable and its future implementation may represent an alternative management for these wastes.

The pyrolysis treatment at 400 °C promotes the de-chlorination of PVC-containing wastes, resulting therefore in a carbonaceous residue that can be energetically valorized in order to produce a synthesis gas with high energetic potential. The optimum temperature for the adapted process is 800 °C.

The chlorine released during the pyrolysis treatment at low temperature can be fixed in the form of an aqueous solution of hydrochloric acid, calcium chloride or sodium chloride making this route attractive due its economical and environmental benefits, avoiding the deleterious effect of toxic compounds emissions to the atmosphere.

The proposed process for the treatment and valorisation of PVC-containing wastes, shows great advantages since it promotes the generation of four reaction products with increased value: concentrated hydrochloric acid, a carbon-rich residue (carbonaceous residue) which can be used as raw material for the production of heat, a produced gas rich in hydrogen which

can substitute natural gas and other fuels, and finally, a coke with 37 % of carbon that can be introduced in the cement production processes.

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