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Recovery of copper from PVC multiwire cable waste by steam gasification

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ABSTRACT

Screened multiwire, PVC insulated tinned copper cable was gasified with steam at high temperature (HTSG) under atmospheric pressure for recovery of copper. Gases from the process were additionally equilibrated at 850 °C on the bed of calcined clay granules and more than 98% of C + H content in the cable was transformed to non-condensing species. Granules prepared from local clay were generally resistant for chlorination, there was also almost no deposition of metals, Cu and Sn, on the catalytic bed. It was found that 28% of chlorine reacted to form CaCl₂, 71% was retained in aqueous condensate and only 0.6% was absorbed in alkaline scrubber. More than 99% of calcium existed in the process solid residue as a mixture of calcium chloride and calcium oxide/hydroxide. PVC and other hydrocarbon constituents were completely removed from the cable sample. Copper was preserved in original form and volatilization of copper species appeared insignificant. Tin was alloying with copper and its volatilization was less than 1%. Fractionation and speciation of metals, chlorine and calcium were discussed on the basis of equilibrium model calculated with HSC Chemistry software. High temperature steam gasification prevents direct use of the air and steam/water is in the process simultaneously gaseous carrier and reagent, which may be recycled together with hydrocarbon condensates.

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1. Introduction

Processing of electrical cable wastes is usually set to recovery of metals, in the first place of copper, although recycling of polymers is also being developed (Boss, 2014; de Araújo et al., 2008). The process consists of numerous mechanical operations, such as grinding, size classification and separation according to physical properties. It is worth noting that an unconventional operation like ultrasonic cavitation in aqueous phase was also investigated (Yang et al., 2011). Recovered metal (copper) is recycled as a copper scrap. Cables are part of electronic waste, processed mainly due to precious metals content. This processing is carried out in the reactor with molten metal bath in the Noranda process, in the Kaldor furnace (Boliden) or Isasmelt furnace (Umicore) Cui and Zhang, 2008, with firing of plastics in oxygen enriched atmospheres. Generally, the presence of halides is avoided in pyrometallurgy. However, the volatilization of metal chlorides as a method of metal recovery was also reported in the literature (Kameda et al., 2013). Therefore, a high temperature chemical processing of multiwire, layered, flexible cables with polyvinyl chloride shielding,

frequently integrated with other electronic elements, seems to be a problem worth of more careful analysis. Gasification with steam enables almost complete elimination of char from metals/inorganic structure and decrease (possibly by catalytic conversion) of oils and tars content in the product gas. Such gasification is discussed in this paper for the cable with a high content of chlorine.

Considering high temperature (800–1000 °C) equilibria in the C/H/O system, it is clear that gaseous H₂O is an oxidizing agent for hydrocarbons, which enables elimination of O₂/N₂ combination (the air) and enrichment the product gas in H₂. Such a process, in the laboratory scale, was described in the literature (Kantarelis et al., 2009) for plastics derived from waste cables. Experiments were performed with plastics of general CH_{1.68}O_{0.24} formula but after removal of copper and PVC below 1 wt.%. Two kinds of experiments were carried out: high temperature pyrolysis (HTP) and high temperature steam gasification (HTSG) with maximum conversion of plastics of 89 wt.% and 92 wt.%, respectively. The final concentration of H₂ was equal to 40 vol.% in both cases. A significant decrease of tar concentration in the product gas was observed for HTSG (140 mg/Nm³) in comparison with HTP (500 mg/Nm³) performed at 1050 °C.

Steam gasification of PVC was suggested as an alternative processing of waste PVC (Slapak et al., 2000). The process carried

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out at 980 °C should give a syngas with the heating value of 8.6 MJ/Nm³ and the composition (on the dry and HCl free basis) of 63 vol.% of H₂, 20 vol.% of CO, 15 vol.% of CO₂ and 3 vol.% of CH₄. Approximately a half of chlorine from PVC waste could be regained as pure HCl gas (for scrubbing) and a half should be converted to CaCl₂ due to the reaction with lime (filler). On the other hand, PCV gasification, especially in the presence of metals, is accompanied by higher emission of pollutants. A comparison of decomposition process of two commercial cables, with PVC and halogen free, at 700 °C under atmosphere with deficit of oxygen, showed that in the presence of metal, the production of PAHs decreases, while chlorinated species increases. The co-presence of PVC and metal resulted in higher emission of furans than dioxins and with rather high chlorination degree equal to 2 or 3 chlorine atoms in the molecule (Conesa et al., 2013).

The use of catalyst for high gas efficiency in the process of gasification with steam is obvious. For example, pyrolysis followed by steam catalytic (Ni–Mg–Al catalyst) gasification at 800 °C of light fraction of municipal plastic waste, mainly PE and PET, without catalyst led to 49 and 40 wt.% of original material transformation into gas and oil, respectively, whereas volatiles were completely transformed into the gas with catalyst presence (Wu and Williams, 2010).

Processing of the electrical and electronic waste, including recycling of plastics (Wang and Xu, 2014) and pyrolysis (de Marco et al., 2008) should optimize recovery of materials and minimize final waste volume and process emissions. Flexible cables are significant part of the electrical and electronic waste and due to PCV content appear an inconvenient component. Therefore, its transformation into metallic and inorganic solid residue and non-condensing, H₂-rich gas seems to be possible with allothermal steam gasification. There are following key features of such process: (1) there is no gaseous substrate (including the air or N₂/O₂ mixture), (2) steam is a gaseous carrier as well as reactant, (3) condensation of steam enables removal of non-volatile oils, tars as well as inorganics (e.g. HCl), (4) condensate and non-volatile organics may be recycled to gasifier and solid residue from gasifier plus non-condensing gases are the only products of the process. An experiment discussed in this paper was conceived as an attempt of such a transformation of an inconvenient part of electrical and electronic waste, i.e. multilayer PCV/copper cable. The process involves equilibration of metallic copper with molten chlorides and gaseous products of steam gasification of PCV, in the first place HCl at high partial pressure. A problem of possible copper fractionation is important for electronic waste transformation by allothermal steam gasification (Mońka et al., 2011; Zielińska et al., 2014).

The intention of the experiment was the transformation of plastic/polymer elements of the cable sample into gaseous species and the separation of metallic elements preserved in the original form. The catalyst is necessary for high level transformation of oils and tars into non-condensing volatiles, e.g. (Wu and Williams, 2010). Because gasses passing to catalytic section were rich in HCl, only the use of inert materials should be considered. We had found that catalytic granules prepared from clay have efficiently supported hydrocarbons conversion in experiments with steam gasification of oat (by 86% in comparison with bed of fused silica pellets) (Zabłocka-Malicka et al., 2015). We supposed that this material would combine at least moderate catalytic properties and necessary chemical inertness. Generally, granules were designed as a support for catalytically active substances for further experiments.

2. Materials and methods

2.1. Cable

Screened multiwire, PVC insulated tinned copper cable used in the experiment was a commercial product. It is consisted of two

copper cords (PVC shielded) in polyester foil and tinned copper braid in the center of the cable. The next three PVC shielded copper cords were coupled with central structure with two thin cotton cords and surrounded by polyester foil. The final shielding was the combination of tinned copper braid and polyvinyl chloride protection cover. PVC insulation was a typical plasticized polyvinyl chloride. Mass of the cable sample was equal to 63.544 g.

The composition of the cable components is presented in Table 1. It was based on weights of separated cable parts and chemical analysis: tin, carbon and hydrogen in non-metallic insulations (41.2 wt.% of C and 4.9 wt.% of H) as well as chlorine and calcium content in gasification products. The material balance presented in Table 1 was calculated taking into account the stoichiometry of PVC (C₂H₃Cl), phthalate plasticizer (DEHP, C₂₄H₃₈O₄), polyester (C₁₀H₈O₄) and cotton (C₆H₁₀O₅). It was applied in equilibrium calculations of gasification process. Moreover, LHV (low heating value) of the cable was determined by bomb calorimetry and was found equal to 8.8 MJ/kg (15.9 MJ/kg for separated non-metallic insulations).

2.2. Catalyst

Catalyst granules were prepared from local clay (deposit of Dzierżoniów county), which was dried at ambient temperature and pulverized below 0.25 mm. This powder was blended with polyethylene glycol (Carl Roth GmbH, ROTH 600, molar mass: 57–630 g/mol) and distilled water in wt. proportions of 50/25/7, then homogenized. Granules with diameter of 5–8 mm were formed from this soft and plastic blend and dried for 24 h at 105 °C, then heated to 875 °C for 9 h, calcined for 3 h and cooled down gradually to ambient temperature. Weight losses during drying and calcination were equal to ~15% and ~40%, respectively. Preparation procedure was based on the one given in the literature (Miao et al., 2010). The catalyst had good mechanical strength, small S_{BET} area, characteristic of macroporous solids and high proportion of mesopores. Mass of the catalytic bed applied in experiment was equal to 50.04 g. Elemental composition and basic properties of catalyst used in the experiment are given in Table 2.

2.3. Gasifying reactor

The experiment of gasification was performed under atmospheric pressure in a simple quartz reactor, consisted of three tubes of 22, 30 and 38 mm diameter and length of 500, 750 and 1000 mm, respectively – Fig. 1. Tops of inner tubes were covered by: perforated lower plate as a sample of the gasified cable support and perforated upper plate as a catalyst support. The reactor was sealed with temperature resistant siloxane layer (Sodual Ltd.) put on the mineral wool at the top, and with the water seal at the bottom. Temperatures of the sample (lower and upper parts) as well as catalytic bed were controlled by three K-type thermocouples placed in a thin quartz tube inside the reactor, and registered by digital recorder APAR AR 206/8 (Poland). Process gases flew out from the reactor to the Liebig condenser by glass connector.

The steam was generated at the bottom part of the reactor in a quartz tube of 17 mm diameter by vaporization of distilled water supplied by stepper motor driven peristaltic pump (201.SMA.150.050, Williamson Manufacturing Company Ltd.) at 0.542 cm³/min. The reactor was heated by three tube furnaces separately powered by electronic controllers RE31 or RE15 with SSR units (LUMEL S.A., Poland) supported with K-type thermocouples. The excess of the steam condensing in the Liebig condenser was collected in a glass container whereas non-condensed gases were washed in the scrubber with NaOH solution (10 g of NaOH in 50 cm³). The scrubber was also the closing of the gasifier gas line. Finally, gasses were combusted in a micro-flare.

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