KINETICS OF THERMAL DE-CHLORINATION OF PVC UNDER PYROLYTIC CONDITIONS

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Abstract

Although PVC-containing wastes are an important potential source of energy they are frequently disposed in landfill. In thermal treatment processes such as pyrolysis and gasification, the presence of poly(vinyl chloride) (PVC), a compound with 56.7% of chlorine, may cause problems concerned with environmental protection, as consequence of the formation of hydrochloric acid, chlorine gas and dioxins, as well as corrosion phenomena of the reactor/equipment materials. Thus, a possible solution may involve a previous removal of the chlorine from PVC containing waste through a pyrolysis process at low temperatures before the material being submitted to a subsequent thermal treatment, for energetic valorization. In this work, a kinetic model for the thermal decomposition of PVC has been developed, in view of its de-chlorination. DTA/TGA testing at different temperatures indicated a first order reaction and an activation energy of 133800 J/mol. An almost completed de-chlorination reaction was obtained at 340ºC under an inert atmosphere. The resulted material is a C_nH_n type polymer with potential to be used in an energy recovery process. Validation test performed at laboratory scale indicate that the temperature of 340ºC enables the removal of ~99.9 % of the chlorine present in PVC. The chloride can be fixed in the form of an aqueous solution of HCl or calcium chloride, driving to an alternative full process with environmental benefits and reduction of the costs associated to the PCV – containing materials/wastes management.

Keywords

De-chlorination, PVC, pyrolysis, Kinetics

5. Conclusions

The kinetics of the reaction of thermal decomposition of PVC was studied, leading to the development of a kinetic model, with the expression ln r = 31.3 - 16100/T + 1.020 ln C (HCl). This model was obtained for the decomposition temperatures lower than 340ºC, in which almost all chlorine is removed from the pure PVC through the chemical reaction described, with an activation energy of 133800 J/mol.

The kinetic model was verified at a laboratory scale, at a temperature up to 340ºC, and a reduction of 99.88% of the chlorine contained in the PVC sample has been observed. The final carbonaceous residue formed after the pyrolysis at 340ºC seems appropriate to be submitted to a subsequent energetic valorization process in order to produce a synthesis gas with high energetic potential.

The results obtained in the present work, were the basis for an ongoing project called “PVC4GAS-Material and energy valorization of PVC containing wastes”, that aims the validation at a pilot plant and the practical implementation of a developed technology based in the two stages above mentioned for the treatment of PVC-containing wastes from textile industry and polymeric sectors. The implementation of the described process for the treatment/valorization of the PVC-containing wastes has many advantages since it promotes the generation of three products with added value, namely concentrated hydrochloric acid, carbon-rich residue (carbonaceous residue - char) used as feedstock for production of heat and a synthesis gas that can be used in turbines or gas engines instead of natural gas.

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