

EFFECT OF POLYOLEFINS ON THE PYROLYSIS OF BROMINE AND CHLORINE CONTAINING MIXED WASTE PLASTICS FOR PRODUCTION OF HALOGEN FREE LIQUID PRODUCTS

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Abstract: The pyrolysis of non-halogenated polyolefins for the production of chemical feedstock/fuels is well known process today. However, the pyrolysis of polyolefins mixed with the halogenated (chlorinated and brominated) plastics produces the various halogenated (organic and inorganic) hydrocarbons in pyrolysis products and removal of such halogen compounds is possible by use of suitable catalysts/sorbents. The pyrolysis of polyvinyl chloride and high impact polystyrene with brominated flame retardant mixed plastics were studied and we showed that the utilization of catalysts/sorbents can be minimized or avoided by selection of suitable process conditions and parameters.

1. Introduction

Plastics have characteristic properties such as durability, lightness, versatility for enormous number of valuable application in the modern society in domestic, industrial applications and have become indispensable in our daily lives. The enormous amount of mixed waste plastics is coming from various sectors including electrical and electronic appliances. Among the various available treatment methods for the treatment of mixed waste plastics, feedstock recycling has more advantageous. Feedstock recycling is a decomposition of plastics waste by means of physical-chemical treatment for obtaining the chemical feedstock. We have shown various catalysts/sorbents and reactions conditions for the production of chlorine free hydrocarbons from the PVC mixed waste plastics by

catalytic/sorptive and/or non-catalytic methods. In recent years, much attention has been paid to the possibility of recycling plastics by pyrolysis and the introduction of the Waste Electronic and Electrical Equipment (WEEE) Directive by the European Commission has inspired an increasing amount of research into using pyrolysis to recycle WEEE plastics. Unfortunately, WEEE plastics often contain toxic brominated flame retardants, which makes them particularly problematic to recycle. The waste plastics such as brominated high impact polystyrene (HIPS-Br) from the electric and electronic appliances along with the other polyolefins poses various problems than the chlorinated plastics due to the presence of inorganic compounds as synergist (Sb_2O_3 etc.) and brominated flame retardants. In the present investigation, we showed the non-catalytic two step pyrolysis process for the production of halogen free/less hydrocarbons as a major liquid product.

2. Experimental

High impact polystyrene (HIPS) with several types of flame retardant and synergist was chosen as it is one of the most commonly used plastics in electrical and electronic equipment. The polyvinyl chloride (PVC) has been chosen as the chlorinated plastics along with the other polyolefins such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and is usually flame retarded by aryl bromines with antimony trioxide as a synergist. The HIPS contained either decabromodiphenyl oxide or decabromodiphenyl ethane flame retardant and either 5% or 0% antimony trioxide. The schematic experimental setup for the pyrolysis of mixed plastics has been given in fig.1. Decabromo diphenyl ether with antimony trioxide shown as DDO-Sb(5) and Decabromo diphenyl ether without antimony trioxide shown as DDO-Sb(0). The detailed information on the samples and pyrolysis procedure has been given elsewhere [1-3].

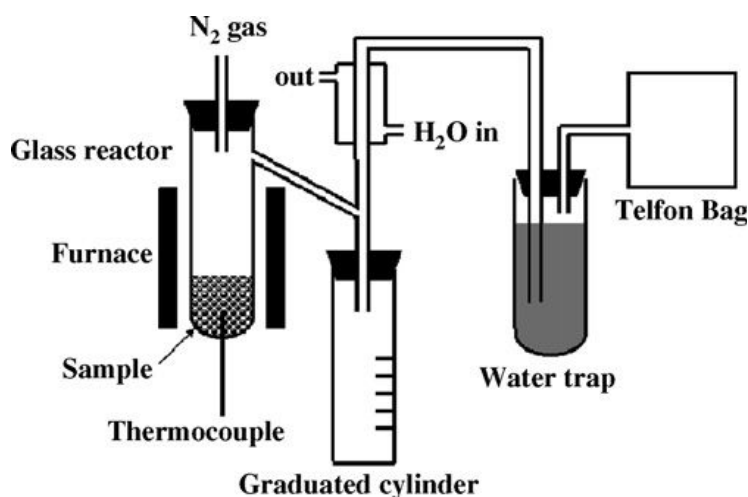


Fig. 1 Schematic experimental setup for the pyrolysis of mixed plastics

3. Results and Discussion

3.1 Pyrolysis of PVC/PVDC mixed plastics

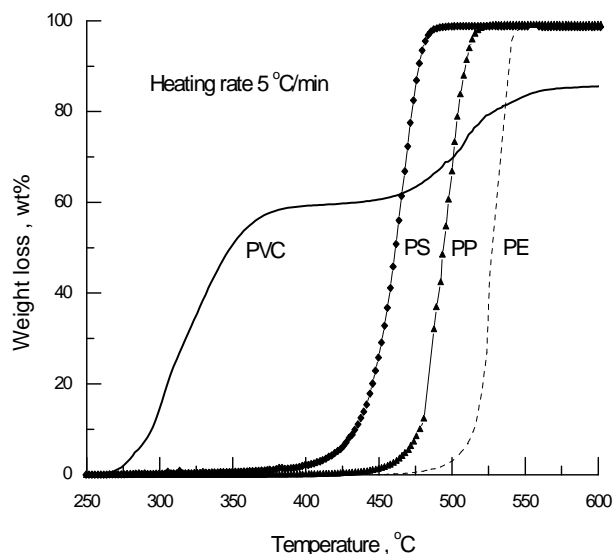


Fig.2 TGA Profiles of PVC, PP, PE, and PS

TGA studies showed (Fig. 2) the decomposition temperature of PVC and they are much lower than for PE, PP, and PS which are main components in municipal waste plastics. The first decomposition step is the loss of HCl from either PVC or PVDC. The formation of chlorinated hydrocarbons during PVC, PVDC mixed plastics pyrolysis can be followed from Scheme 1. The HCl evolved from the PVC or PVDC reacts with the olefinic hydrocarbons produced from the commingled plastics such as PE, PP and PS. Based on the decomposition behavior of PVC and PVDC samples, the temperature profiles were modified from mode 1 (single step) to controlled pyrolysis (two step) to remove the HCl evolved from the PVC or PVDC from the Pyrolysis of plastic wastes. For the pyrolysis of 3P/PVC (mode 1), the reactor temperature was increased from room temperature to the final temperature of 430⁰C and kept till the end of pyrolysis experiment (nitrogen 30 ml/min). For the pyrolysis of 3P/PVC (mode 2), the reactor temperature was increased from room temperature to 330⁰C (nitrogen flow 55 ml/min) and kept for 2 h at 330⁰C (nitrogen flow 55 ml /min) and then subsequently increased to a final temperature of 430⁰C and kept till the end of the pyrolysis experiment [3].

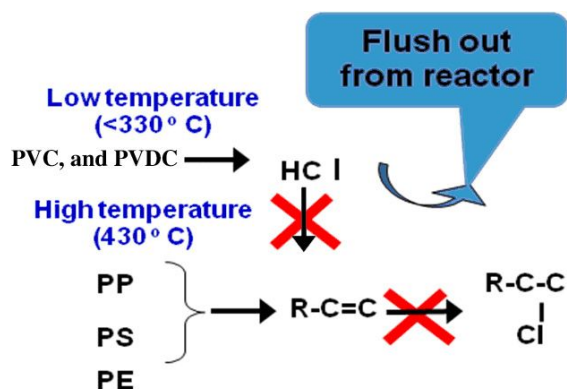


Fig.3 Plausible steps for the formation of chlorinated hydrocarbons during pyrolysis of PVC, PVDC mixed plastics.

3.2 Pyrolysis of BFR (Brominated Flame Retardant) containing mixed plastics

The waste plastics from electric and electronic equipment contains brominated flame retardants and also contain antimony trioxide, which is added to the polymers as a synergist to increase the flame retardant properties of the brominated additives. Antimony trioxide is used as a synergist in combination with polybromodiphenyl oxides (commonly referred to as polybrominated diphenyl ethers or PBDEs) and decabromodiphenyl ethane, both of which are used as fire retardants in polystyrene based polymers and co-polymers. Antimony trioxide acts as a synergist by promoting the release of bromine radicals during combustion via the formation of volatile antimony bromides, the bromine radicals then quench the combustion process by aggressively scavenging other radicals which are required for the propagation of a flame. Water is a secondary product of the conversion of antimony trioxide to antimony bromide and it is thought that the hydrogen necessary for this reaction is obtained from the polymer chains. Therefore, antimony trioxide is thought to have a significant impact on the pyrolysis of flame retarded polymers. Several investigations have been carried out into the effect that antimony trioxide has on both the pyrolysis products and the fate of the bromine content of plastics during pyrolysis. Similar to PVC/PVDC mixed plastics, the pyrolysis mixed plastics containing BFRs produce the bromine compounds in the pyrolysis products and needs suitable catalyst/sorbent for the removal of bromine compounds from the pyrolysis liquid products, in order to use them as fuel or chemical feedstock. Based on the thermogravimetric profiles (Fig. 3), we have showed the controlled pyrolysis method (Fig. 4) with the two steps to produce the bromine less pyrolysis liquids from the HIPS-Br plastic mixed with polyolefins.

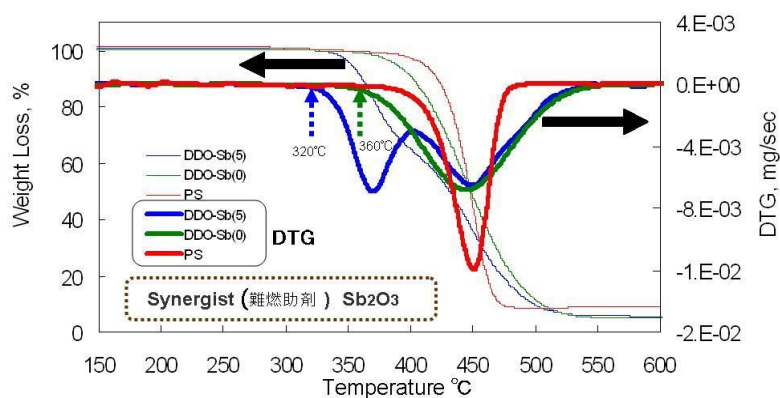


Fig.4 Thermogravimetric profiles of Brominated flame retardant containing various polystyrene samples

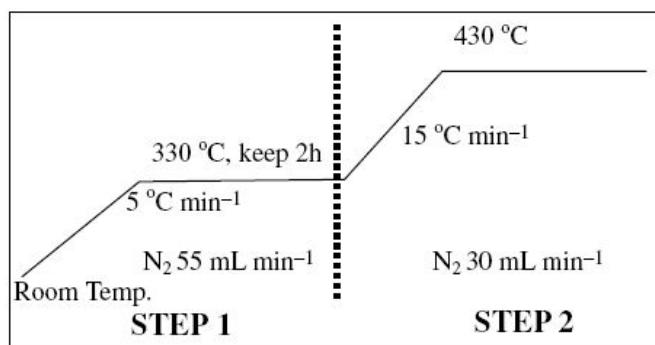


Fig.5 Temperature profile for the pyrolysis of Brominated flame retardant containing polystyrene with various polyolefins (HIPS-Br with PE/PP/PS)

4. Conclusions

We present the pyrolysis of PVC/PVDC or HIPS-Br containing mixed polyolefins liquid products with the very low halogen compounds without the use of any catalyst or sorbents. The optimization of process parameters is more effective in controlling the quantity and quality of pyrolysis products.

References

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