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Effect of PET on Pyrolysis of Brominated High Impact Polystyrene (HIPS-Br) and PVC/PE/PP/PS Mixed Plastics

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INTRODUCTION

The decomposition of waste plastics into fuel represents a sustainable way for the recovery of the organic content of the polymeric waste and preserves valuable petroleum resources in addition to protecting the environment. The plastic waste from electric and electronic equipment consists of high impact polystyrene (HIPS), acrylonitrile-butadiene-styrene copolymer (ABS) as a major part and these plastics contains various additives, e.g., flame retardants. More than half of the computer housings analyzed was made of HIPS with the next biggest fraction being ABS. The presence of PET during the feedstock recycling of municipal waste plastics has affected the formation of decomposition products and dehalogenation efficiency of the catalyst/sorbents [1, 2]. In the present investigation, we report the pyrolysis of PET with HIPS/Br alone and PP/PE/PS/PVC/HIPS-Br mixed plastics. The dehalogenation (Br, Cl) of liquid products with calcium carbonate carbon composite (Ca-C) were performed.

EXPERIMENTAL

Commercially available high impact polystyrene (HIPS) containing brominated (Br: 10.8 wt%) flame retardant was used in the present investigation. The synergist Sb_2O_3 was 5 wt%, the flame retardant was decabromo diphenyl oxide (DDO). Poly(ethylene terephthalate) (PET), High density polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(vinyl chloride) (PVC) were commercially available samples. The mixture of PP, PE, PS was abbreviated as 3P in the manuscript.

The plastic samples of 3P/PVC/HIPS-Br mixed with PET were subjected to thermal decomposition. Another series of pyrolysis experiments were carried out in the presence of Ca-C catalyst applying vapor phase contact. The pyrolysis of plastic mixtures was performed in a Pyrex glass reactor (length: 35 cm; i.d: 3 cm) under atmospheric pressure by batch operation under the similar experimental conditions and temperature program using setup shown in Fig 1.

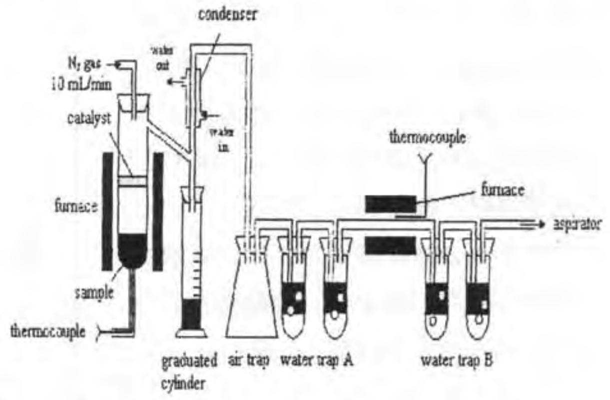

Figure 1. Schematic experimental setup

Approximately, 10 g of plastics were loaded into the reactor for the thermal decomposition and for the catalytic experiments. The solid catalyst (1 mm av. dia.) was loaded into the reactor 10 cm above the plastic bed whereas the plastic sample was kept at the bottom of the reactor. Gas chromatograph equipped with FID, AED, and MSD were used for the qualitative and quantitative analysis of liquid products. Ion-chromatograph and combustion flask were used for the quantitative halogen content analysis in residue and water traps.

RESULTS AND DISCUSSION

The effect of PET on the pyrolysis of brominated flame retardant containing high impact polystyrene (HIPS-Br) and mixed with PE/PP/PS/PVC was performed at 430°C under atmospheric pressure using a batch operation method. The cumulative volume of liquid products from the thermal degradation of HIPS-Br started to accumulate earlier than that of HIPS-Br/PET degradation. The addition of PET to

HIPS-Br affected significantly the formation of decomposition products and the degradation behavior of HIPS-Br. We have found the following observations on the addition of PET during the pyrolysis of HIPS-Br alone are (i) the rate of formation and the yield of liquid products decreased, (ii) the residue and gaseous products formation increased, (iii) the average carbon number (Cnp) of liquid products reduced from 12.5 to 9.1, (iv) the yield of high molecular weight hydrocarbons (C_{16}-C_{20}) decreased and the amount of hydrocarbons from C_6 to C_{10} doubled, (v) heavy waxy compounds were formed on the top of the glass reactor wall in addition to the solid residue on the bottom of the reactor, (vi) antimony compounds were observed in the solid residue, as opposed to the formation of antimony tribromide ($SbBr_3$) detected in the liquid products of HIPS-Br in the absence of PET. The effect of PET on the pyrolysis of 3P/PVC/HIPS-Br was performed in the absence and presence of catalysts/sorbents for the dehalogenation of halogenated hydrocarbons.

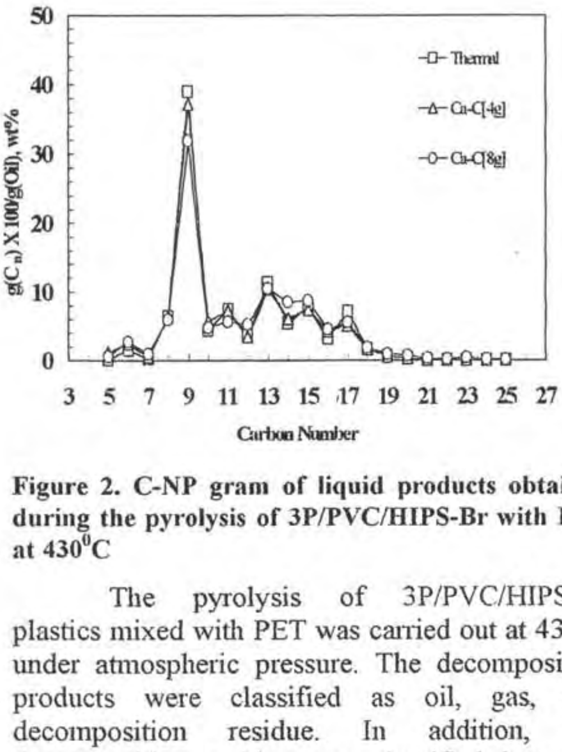

Figure 2. C-NP gram of liquid products obtained during the pyrolysis of 3P/PVC/HIPS-Br with PET at 430^{0}C

The pyrolysis of 3P/PVC/HIPS-Br plastics mixed with PET was carried out at 430^{0}C under atmospheric pressure. The decomposition products were classified as oil, gas, and decomposition residue. In addition, the decomposition residue was classified into two parts, the carbon residue including the char and the tar remained at the bottom of the reactor and the wax, which is coated on the top portion of the wall of the pyrex glass reactor. The results showed that the thermal decomposition of 3P/PVC/HIPS-Br produced higher liquid yield than the thermal and catalytic decomposition of 3P/PVC/HIPS-Br/PET. The presence of PET in the plastic mixture has decreased the formation of gaseous products (17 to 13 wt%) and increased the carbon residue (12 to 25 wt%). However, the addition of PET to 3P/PVC/HIPS-Br reduced the dehalogenation efficiency of the catalyst (Fig 3).

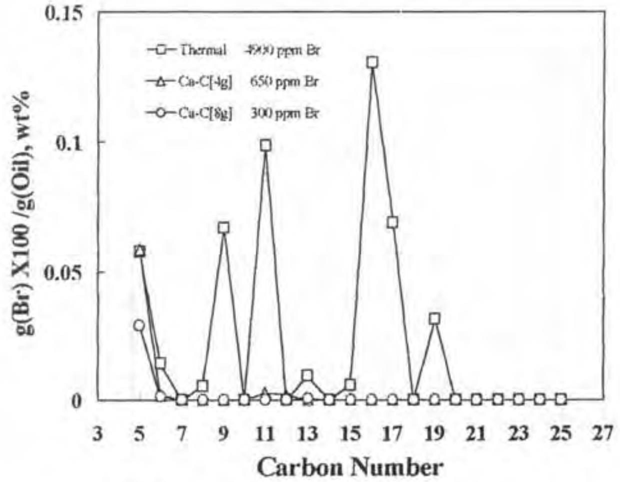

Figure 3. Cl-NP gram of liquid products obtained during the pyrolysis of 3P/PVC/HIPS-Br with PET at 430^{0}C

In the case of 8 g Ca-C used for the dehalogenation, the liquid products still contained 300 ppm of bromine and 20 ppm of chlorine.

CONCLUSIONS

In the presence of PET, additional brominated and chlorinated hydrocarbons were produced. Furthermore, vinyl bromide and ethyl bromide were evolved, which appear to be formed from the ethylene segments of PET via bromination reactions. The formation of $SbBr_3$ was hindered and the yield of liquid products was decreased from 3P/PVC/HIPS-Br.The use of Ca-C removed more than 94% of the bromine and more than 99% of the chlorine content of the liquid during the pyrolysis of 3P/PVC/HIPS-Br mixed with PET. The complete removal of halogenated hydrocarbons is possible with the calcium and iron based catalysts/sorbent. Detailed investigations will be discussed during the presentation.

REFERENCES

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