

A Study on Treatment of Waste Fire Retardant Plastics using Wet Oxidation Method

M. Wakakura*¹, F. Adachi¹, T. Uchida¹
Y. Oka², A. Miyake², T. Ogawa²

¹Research and Industrial Institute of Kanagawa
705-1 Shimoimaizumi Ebina-city Japan

²Yokohama National University

E-mail: waka@kanagawa-iri.go.jp Fax: +81-46-236-1526

In order to develop the wasted treatment of flame resisting plastics, wet oxidation method was studied focusing on the oxidation products and behavior of fire retardant, antimony trioxide. ABS (acrylonitrile butadiene styrene resin) and Polypropylene were employed as a basic polymer. Aromatic bromine and antimony oxide were mixed into the basic polymer with several fraction as fire retardant.

Stainless steel autoclave was used as a reactor. CO, CO₂ and trace amounts of volatile organic compounds in discharged gases were measured. Organic acid, halogen ion and total amount of organic carbon in the autoclave were also measured.

Oxygen concentration of the air blown into the autoclave, catalysts, pH and temperature of reaction were employed as main factors affected to the decomposition and material recycle efficiency.

It became clearly from experiments as follows;

- 1) The use of special air over 50% oxygen concentration is favorable for decomposing the flame resisting plastics
- 2) Bromine compound and antimony oxide did not interrupt the wet oxidation of plastics differ from the behavior during incineration.
- 3) Organic acids were produced from wet oxidation of the plastics, and the yield could be mainly controlled by pH (NaOH amount) and reaction temperature.
- 4) Possibility of the recovery of bromine fire retardant and antimony oxide was shown.

Introduction

Recently flame resisting plastics are used as important materials in various field such as electrical household appliances and electrical equipment. As those plastics contain some fire retardant such as aromatic bromine compounds or antimony oxide, burnout those plastics is not easy using general incinerators.

We developed multi-stage incineration system (gasification of plastic and gas phase combustion and catalytic oxidation after incineration) to burnout incombustible plastics or those which produce harmful chemicals from general incinerator during waste treatment [1]. But even if used the improved incineration flame resisting plastics could not burn up to a satisfactory settlement.

Wet oxidation is the aqueous phase oxidation of materials which dissolved or suspended in water [2]. In general the temperature range of reaction set in 150 to 325°C with high pressure (1-10MPa) oxidative condition. This process using air or oxygen enriched air developed in mid-1940s as a method to recover vanillin from spent pulping liquor. Since early 1980s this process has been applied to defuse several hazardous chemical waste. Recently, some trials of wet oxidation of waste plastics such as polystyrene (PS), polypropylene (PP) or polyvinylchloride (PVC) were reported [3,4,5].

Materials and Methods

Table 1 shows the component of the flame resisting plastics. Tetrabromobisphenol A (TBBA) or dicabromodiphenyl oxide (DBDPO) and antimony trioxide were mixed into PP and ABS resin as fire retardant. To measure the catalytic activity about 30 of metal or metal oxide powder (NiO, CuO, Cu₂O, Co-Al₂O₃, Pt-Al₂O₃ etc) were prepared by ME Chemcat Ltd. Figure 1 shows the wet oxidation equipment made of SUS 316. Reactor was 1 litter voluminal autoclave fitted with an oxygen inlet pipe, liquid sampling pipe, magnetic blade-agitator, gas outlet pipe with the reflux condenser. Reaction temperature was controlled by electric band-heater and pressure was kept constantly by a self-relief valve.

The reactor was loaded with 750ml of distilled water, 5-10g of plastic pellet (approximately 2.5mmΦ, 5mmH), occasionally 0.5-3g of catalyst and alkalis or salts (NaOH or KOH, NaNO₃ etc). Reactor was heated under N₂ pressure condition, after reached to the desired temperature pre-heated oxygen flew into the reactor, and agitation of 1000rpm was started.

Vaporized water was cooled down in the condenser and returned into the reactor. Concentration of CO, CO₂, O₂, NO_x in the exhaust gas was measured continuously by gas monitors. Other oxidation products in the liquid and gas phase were sampled by the definite period and analyzed using ion-chromatography, gas-chromatography, GC-MC, TOC (total organic carbon) analyzer.

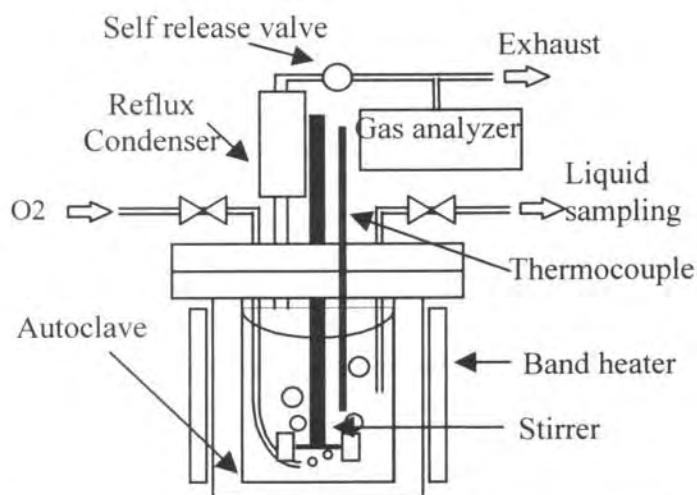


Fig.1 Schematic diagram of wet oxidation apparatus

Table 1 Composition of model flame resisting plastics

| Sample name | Base plastic (wt.%) | Flame retardant (wt.%) | Additional agent of flame inhibitor (wt.%) |
|-------------|---------------------|------------------------|--|
| ABS-1 | ABS resin (100) | — | — |
| ABS-2 | ABS resin (83.0) | TBBA (12.0) | Sb ₂ O ₃ (5.0) |
| ABS-3 | ABS resin (91.5) | TBBA (6.0) | Sb ₂ O ₃ (2.5) |
| ABS-4 | ABS resin (83.0) | DBDPO (12.0) | Sb ₂ O ₃ (5.0) |
| ABS-5 | ABS resin (91.5) | DBDPO (6.0) | Sb ₂ O ₃ (2.5) |
| PP-1 | PP (100) | — | — |
| PP-2 | PP (60.0) | TBBA (26.7) | Sb ₂ O ₃ (13.3) |
| PP-3 | PP (80.0) | TBBA (13.3) | Sb ₂ O ₃ (6.7) |
| PP-4 | PP (60.0) | DBDPO (26.7) | Sb ₂ O ₃ (13.3) |
| PP-5 | PP (80.0) | DBDPO (13.3) | Sb ₂ O ₃ (6.7) |

Result and Discussion

Figure 2 shows the influence of oxygen concentration of air on the oxidation rate defined by CO₂ conversion. Oxidation rate increased according to increase of oxygen concentration, but no concentration dependence was observed over 50% of oxygen.

As in Figure 3 oxidation rate of the fire resisting plastic was about equal to the rate of base plastic, it is said that fire retardant agents of this study (TBBA, DBDPO, Sb₂O₃) did not act as inhibitor of the wet oxidation differ from the behavior during incineration.

After 60 minutes sample compounds was going oxidized to organic acid (Acetic acid, Formic acid, Benzoic acid), CO, CO₂ etc.

TBBA was relatively easily decomposed to Br-ion, but decomposition yield of DBDPO was not so high contained in PP. The oxidative stability seemed to come on the molecular structure. TBBA has hydrogen atom in the molecular, and is extracted by activated Oxygen easily. DBDPO has not such hydrogen atom in the molecular. But as in Figure 4 DBDPO of ABS4 sample is decomposed. When changed the pH value at the wet oxidation of PP4 (PP with DBDPO) decomposition yield of DBDPO increased according to the increase of NaOH added in the reactor. It is estimated that decomposition of DBDPO depend on the existence of alkali and NH₃ from ABS seemed to promote the decomposition of DBDPO. Antimony trioxide was remained in the reactor oxidized to pentad oxide.

In case of incineration of the fire resisting plastic the generation of harmful bromine compounds such as brominated dioxine was not negligible. Antimony trioxide was vaporized producing bromine antimony oxides and discharged. Those antimony compounds is known as the biotoxic chemical.

Figure 5 is the conversion of nitrogen in the ABS sample to NH₃. 80-90% of nitrogen was changed to NH₃ not to NO_x differ from incineration. HCN was not directed. HCN is very toxic gas but repress the generation is not easy during the incineration of plastics which have CN band such as ABS, polyurethane etc.

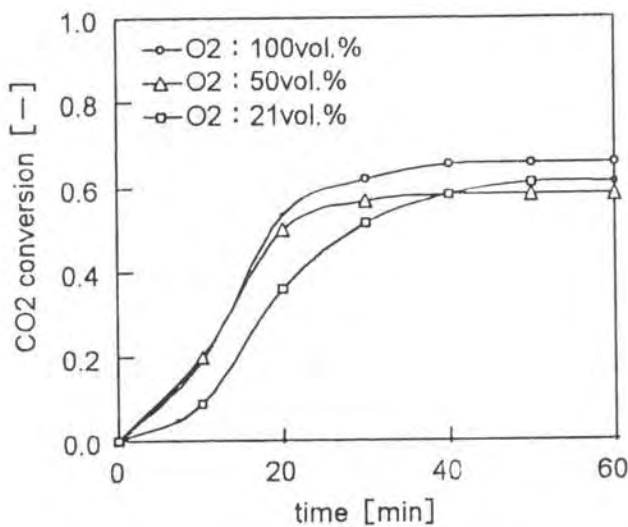


Fig.2 Influence of O₂ concentration of air
With time

240°C, Air flow rate: 2l/min, PP2:5g

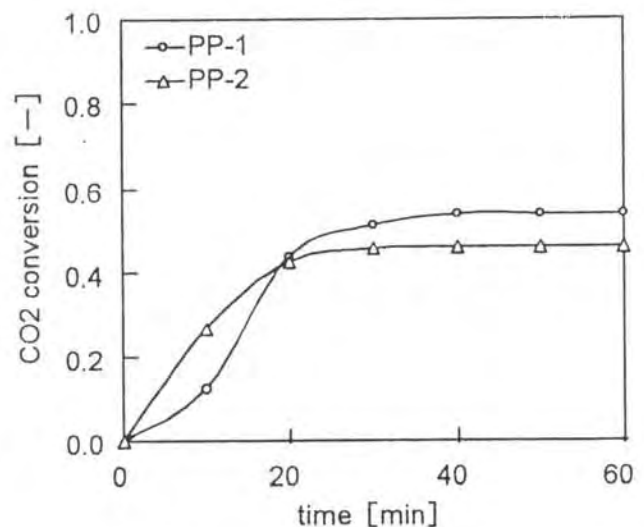


Fig.3. Influence of flame retardant

240°C, O₂ flow rate: 2l/min, Sample5g

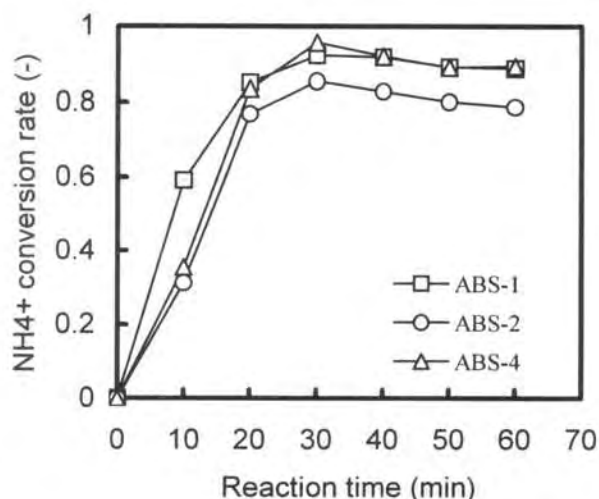
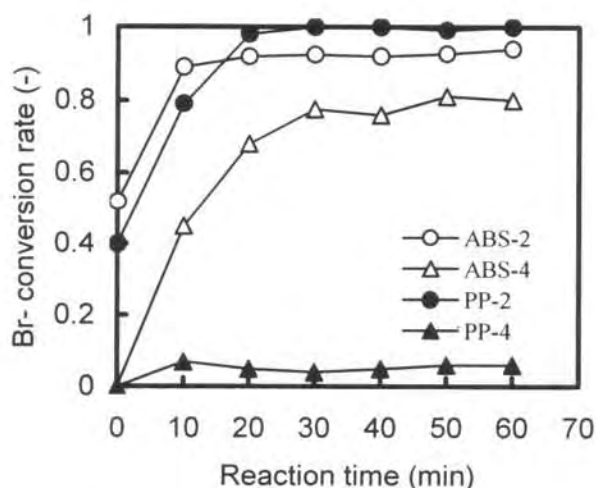


Fig.4. Variation of Br-conversion rate against time Fig.5 Variation of NH₄⁺ conversion rate against time

240°C, O₂ flow rate: 2l/min, Sample5g

240°C, O₂ flow rate: 2l/min, Sample5g

Conclusion

In case of ABS and PP based samples of this experiment, oxidation in high temperature water with oxygen enriched air seemed to proceed in two step. At first solid samples rapidly changed to water soluble materials, then oxidized to organic acid or CO, CO₂ etc.

Bromine fire retardant did not act as interfering substance of wet oxidation, and unheralded yield of organic acids was recovered from the waste plastic. The possibility of recovery of some bromine compound was estimated controlling the reaction condition such as pH, temperature.

Further experiments have to be made to alternate the yield of the specific oxidation product such as acetic acid for the purpose of material recovery of waste plastics.

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