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CHEMICAL RECYCLING OF PLASTICS FROM WASTE PRINTED CIRCUIT BOARD WITH RECOVERY OF HALOGEN AND METAL

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We already reported monomer recycling of thermosetting resins with high oil yield in the liquid-phase cracking using hydrogen donor solvent. Real waste printed circuit board, we used here, contained 5.2wt% of Br and 67.8wt% of inorganic material with thermosetting resins. Experiments were carried out in a 200-ml stainless steel magnedrive autoclave at 400-440 °C under 2.0 MPa of initial nitrogen pressure with tetralin, decalin or conventional petroleum derived solvent. Conversions to gas and liquid, after reaction, were very high of almost 100wt%/organic material, when we used tetralin and 80-90 wt% by the use of petroleum oil as solvent. Halogen content in the gaseous product was very low of less than 2ppm. Bromine content in the liquid product was 2,600 ppm from the thermal reaction and decreased to 102, 54 and less than 1ppm by the addition of $CaCO_3$, Na_2CO_3 and K_2CO_3 catalyst respectively. This indicates that the liquid product could be used for fuel or for chemical use. Bromine content in the solid product also decreased to 260 and 170ppm by washing solid product with water when we used Na_2CO_3 and K_2CO_3. This indicates that resins, halogen and metal can be separated clearly and reused respectively in our proposed process.

Key words: printed circuit board, thermosetting resin, liquid-phase cracking, hydrogen donor solvent, dehalogenation

1. INTRODUCTION

Recycling including collection and separation of the used electric appliances were performed actively in a big scale facility now. Separation by gravity, air and magnet was performed and valuable metal was recovered now. However, printed circuit board with plastic materials was treated to land filling or incineration as an industrial waste dust. In electronic appliances, many varieties of plastics including thermoplastics and thermosetting resins with brominated flame retardant materials, such as 4-bromo-bisphenol-A and decabromo- biphenyl-ether, were used with metal and glass cloth. We have already reported that the thermosetting resins, such as phenol resin, epoxy resin and the other plastics, can be converted to monomer compounds with high yield in the liquid-phase cracking using hydrogen donor solvent, such as tetralin [1]. Braun et al also reported hydrogenolytic degradation of thermosetting resins using tetralin [2]. Waste printed circuit board is a multi-compound material and contains several percentages of Br and Cl and more than 50wt% of inorganic material, such as metal and glass cloth. Therefore separation, fixation or removal of halogen atom from these wastes and recovery of organic and inorganic materials is urgent and important subject from the standpoint of environmental protection and effective reuse of material.

In this study, we applied liquid-phase cracking of printed circuit board at 400-440 °C under 2.0 MPa of initial nitrogen pressure in the presence of tetralin, decalin or conventional petroleum derived solvent. Degradation by liquid-phase cracking of plastics and resins to liquid product and separation, fixation and removal of halogen atom from gas and liquid products and to solid product were first conducted using alkali earth and alkali carbonate catalyst. Then effective removal of halogen atom from metal and glass cloth in the solid product was discussed by washing solid product with water.

2. EXPERIMENTAL

Printed circuit board which we used here was not special product and was usually assembled for the

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Table 1 Experimental results (Reaction Temperature : 440 °C , Reaction Time : 1 hr)

Sample waste	Printed Circuit Board							
Inorganics (wt%)	67.8							
Organics (wt%)	32.2							
Br (wt%)	5.20							
Cl (wt%)	0.028							
Solvent	Tetralin		Decalin		LCO*			
Additives	non	K_2CO_3	non	K_2CO_3	non	$CaCO_3$	Na_2CO_3	K_2CO_3
Conv. (wt%)	36.4	34.7	32.2	32.8	26.0	30.1	32.8	22.7
Gas (wt%)	6.6	2.8	0.0	0.2	10.6	10.2	0.3	3.6
Br (ppm)	2.70	0.38	2.70	0.38	2.70	0.38	0.38	0.38
Cl (ppm)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Liquid (wt%)	28.6	30.6	31.3	32.1	14.3	18.1	31.8	16.8
Br (ppm)***	53.0	2.0	15.0	<1	746.8	845.9	44.2	10.8
Cl (ppm)***	-	-	-	-	85.3	9.9	17.6	7.9
Water (wt%)	1.2	1.3	0.9	0.6	1.1	1.8	0.7	2.0
Solid (wt%)	63.6	65.3	67.8	67.2	74.0	69.9	67.2	77.3
Br (wt%)	2.60	2.40	2.80	1.50	3.5(2.4**)	2.4(1.4**)	0.6(0.026**)	2.6(0.017**)
Cl (ppm)	-	-	-	-	160	35	2	6

* LCO : Cl, Br <1ppm, ** After washing solid product by water, *** Halogen content in liquid product with solvent

electric-electronic product. This contained 5.20 and 0.028wt% of Br and Cl respectively and consisted of 32.2wt% of organics and 67.8wt% of inorganic material including metal and glass cloth. Flame retardant material contained in this material was 4-brommo-bisphenol-A. Semi-quantitative analysis of metal in the printed circuit board was conducted by ICP-AES. The waste materials were crushed to under 0.15mm. Experimental runs were carried out in a 200-ml stainless steel magnedrive autoclave at 400-440 °C under 2.0 MPa of initial nitrogen pressure in the presence of tetralin, decalin or conventional petroleum derived solvent. Tetralin and decalin were used as a model for a typical hydrogen-donor and non-donor solvent respectively. We also used LCO (light cycle oil) from FCC unit in the petroleum refinery process as an inexpensive and conventional solvent. In some experiments, alkali-earth and alkali carbonate catalyst: $CaCO_3$, Na_2CO_3 and K_2CO_3, was used for fixing halogen atom into the solid product and for decreasing halogen concentration in the gas and liquid product. Slurry products were separated into solid and liquid by filtration and liquid products were vacuum-distilled at 330 °C and 3 torr into the distillable oil and vacuum residue. The distillable oil product contains solvent and the product from solvent and resin. The yield of the liquid product from the waste was calculated by the following equation.

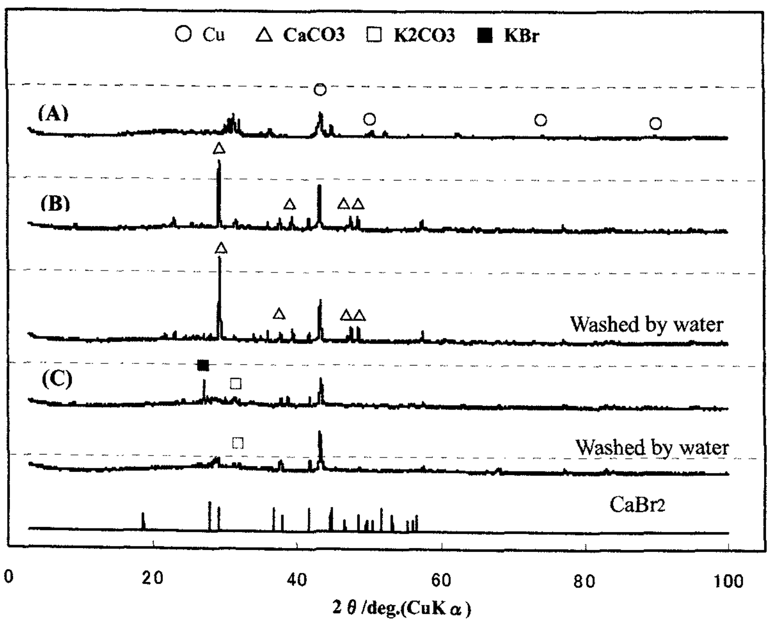

Fig. 1 XRD patterns (A) printed circuit board

(B) solid product using $CaCO_3$

(C) solid product using K_2CO_3

(Recycling with Solvent (LCO) at 440°C)

$$\frac{\text{Liquid product (g)} - \text{Charged solvent (g)}}{\text{Charged coal (g)}} \times 100(\text{wt.\%})$$

Gaseous products were subjected to gas chromatography for compositional analysis. The distillable oil was also analyzed by gas chromatography equipped with FID detector and an OV-1 glass capillary column (60m in length and 0.25mm in i.d.) and by mass spectrometry for identification purposes. The conversion was calculated from the solid product gravimetrically. The solid product, containing halogenated metallic-salt, metal, glass etc, was washed with distilled water to remove halogenated metallic-salt using ultrasonic extraction apparatus.
Characterization of metals, including halogenated alkali-earth and alkali compounds in the solid product were performed by means of X-ray powder diffraction (Rigaku R-300 CuK α).
Analyses of Cl and Br content in gas, liquid and solid products were conducted by conventional ion-chromatography with bomb combustion and water absorption methods respectively. Identification and analysis of metal compound were performed by ICP-AES and X-ray diffractometry.

3. RESULTS AND DISCUSSION

3.1 Liquid-phase cracking of printed circuit board

Conversion and the yield of gas, liquid and solid products from the experiments were shown in **Table 1** with Br and Cl contents in each product. The waste samples from printed circuit board showed almost 100wt% conversion of organic material with high recovery of liquid product when we use tetralin and decalin as model solvent in the liquid-phase cracking at 440 °C. The yield of gas was low less than 7wt%. The gaseous product consisted of mainly carbon dioxide, hydrogen, carbon monoxide and small amount of C1-C3 hydrocarbon gases.
The lower reaction temperature of 400 °C and the use of catalyst did not affect the conversion and product yield. However halogen content in the liquid product was higher at lower reaction temperature. Halogen content in the gaseous and liquid product decreased by the use of alkali-carbonate drastically and was lowest to less than 0.4 ppm(gas) and less than 2 ppm(liquid) respectively by K2CO3 addition as shown in **Table 1.** From the experimental results using LCO as practical and conventional solvent, the yield of gaseous product increased by increasing methane generation than that from model solvent use and the yield of liquid product decreased in some reaction conditions. Differences in conversion from between tetralin and LCO are due to the weak hydrogen donation of LCO for the degradation of thermosetting resins. Halogen content in the gaseous product was also very low of less than 3 ppm from the thermal reaction and less than 1 ppm from the catalytic reaction. Bromine content in the liquid product mixed with solvent was 750-850 ppm from the reaction without catalyst and by the use of CaCO3 catalyst. However this decreased to 44 and 11 ppm by the use of Na2CO3 and K2CO3 catalyst respectively. Bromine and chlorine balance between reactant printed circuit board and the products including washing solvent for solid product reached to 96.4 and 95.6wt% during the reaction using LCO at 440 °C. Liquid product from the waste printed circuit board contained 20-42wt% /organics of monomer compounds, such as phenol and isopropylphenol derived from phenol resin or epoxy resin in addition to toluene and ethylbenzene derived from polystyrene respectively. This indicates that the halogen atom was fixed in some portion by metal in the waste and was effectively fixed forming halogenated sodium or potassium-salt. In these cases, halogen content in the liquid product was enough low and therefore the liquid product can be used for fuel

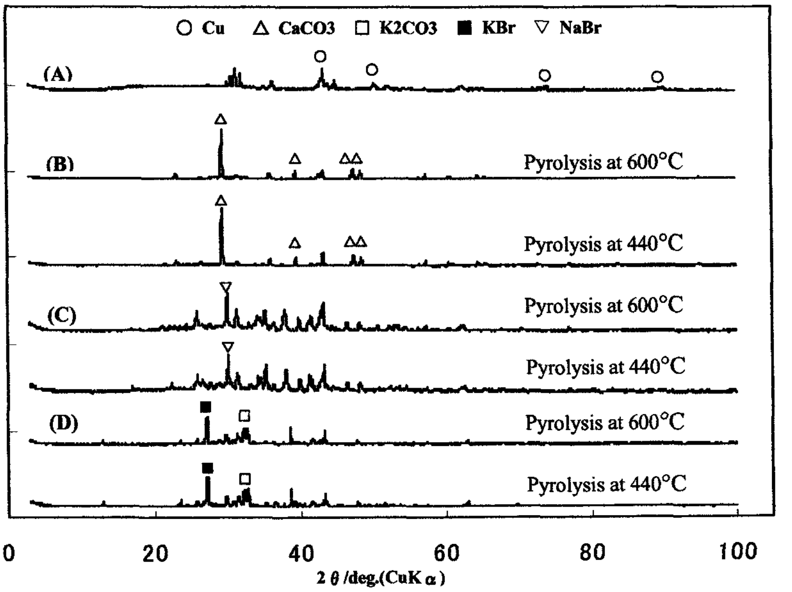

Fig. 2 XRD patterns (A) printed circuit board
(B) solid product from the pyrolysis with CaCO3
(C) solid product from the pyrolysis with Na2CO3
(D) solid product from the pyrolysis with K2CO3

or for chemical use. However in the case of CaCO3, fixation of brome was not proceeding effectively.

3.2 Characterization of the solid product

From the semi-quantitative analysis by ICP-AES, detected main composition of metals were Cu:32wt%, Si:19wt%, Ca:7wt% and Sn:6wt% with less than 1wt% of Pb, Fe, Na, Al, Zn, Mg, Ti, Ni, Pb. Copper metal was detected in the printed circuit board clearly by XRD analysis as shown in **Figure 1**. Bromine content in the solid product was 0.6-3.5wt% from the thermal and catalytic reaction. However only CaCO3 was found in the solid product and CaBr2 was not found before and after water washing (**Figure 1**), when we use CaCO3 as a catalyst. Bromine content in the solid product decreased little from 2.4 to 1.4wt% in this case, as shown in **Table 1**. In the thermal and catalytic reaction using CaCO3, Br was expected to produce several metallic bromide or condensed heavy organic compounds derived from 4-bromo-bisphenol-A. However CuBr and Cu2Br were not detected in XRD analysis. In the case of Na2CO3 and K2CO3 use, bromine was fixed as a NaBr and KBr as shown in **Figure 1**. As generally known, NaBr and KBr were enough soluble to water and KBr in the solid product diapered by water washing. Content of Br in the solid product decreased obviously to 260 and 170 ppm by washing solid product with water, when we used Na2CO3 and K2CO3 as catalyst. Similar behavior of bromine in the solid product from the pyrolysis without using any solvent at 440 and 600 °C was observed also as shown in **Figure 2**. It has been well known that calcium is effective to fix chlorine from PVC treatment. However calcium cannot use to fix bromine from organic bromine compounds in the electric-electronic products.

Our result indicates that organic bromine in the printed circuit board was effectively fixed by Na2CO3 and K2CO3 into the solid product and also separated from metal and glass cloth by conventional washing treatment by water.

4. Conclusion

Schematic flow for printed circuit board recycling using K2CO3 catalyst was shown in **Figure 3**. In our proposed process using catalyst, resins, halogen and metal can be separated clearly respectively and are possible to reuse again. As a result, we can propose new and effective recycling system to reuse resin, metal, glass cloth and also bromine from waste printed circuit board.

5. References

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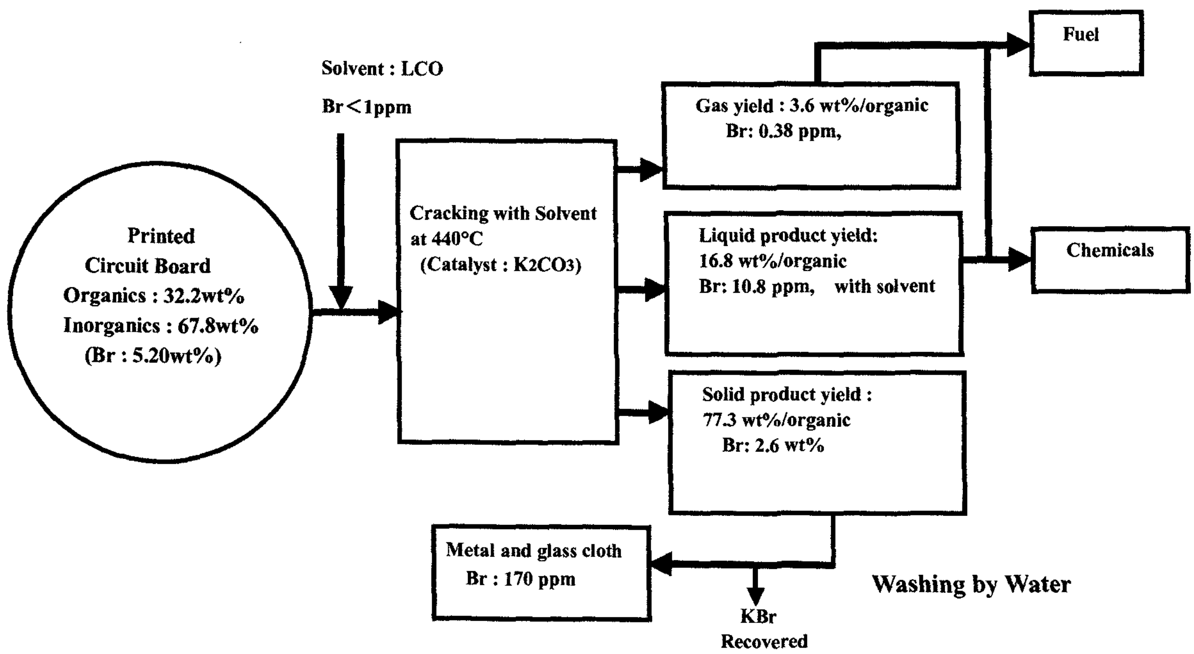

Fig. 3 Schematic Flow for Recycling of Printed Circuit Board
(K2CO3 use as catalyst)

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