LIQUEFACTION OF PRINTED CIRCUIT BOARD BY USING WASTE BIOMASS DERIVED TAR

Tohru Kamo*[1], Liu.Yufeng[2], Naoya Akaishi[2],
Mariko Adachi[2], Hajime Yasuda[1], Hideki Nakagome[2]

[1] *National Institute of Advanced Industrial Science and Technology (AIST),*
16-1 Onogawa, Tsukuba 305-8569, Japan
[2] *Chiba University, Faculty of Engineering, 1-33 Yayoi-cho, Inage-ku,*
Chiba-shi 263-8522, Japan
E-mail: tohru-kamo@aist.go.jp

Abstract: Recovery of the useful materials from end-of-life electronic equipments is very important not only for reduction of waste materials but also for effective use of limited natural resources. Recently, we showed that approximately 50 wt% of epoxy board was dissolved in tar derived from dry distillation of Japanese cedar at 220 °C under atmospheric pressure. However, solubilization rate of the waste printed board was insufficient for practical industrializing.In this work, more than 70 wt% of Japanese cedar converted into tar by heating it in some organic solvents at 300 °C. Epoxy printed circuit boards were solubilized almost completely in the tar at 250-300 °C. Moreover, urethane, FRP, PET, and polycarbonate were also solubilized. Character of the tar was very sensitive to the temperature of tar formation.

1. Introduction

End-of-life electric devices and automobiles contain a lot of useful materials such as gold, palladium, and rare metals. Recovering the useful materials from the scrapped industrial products is very important for reducing wastes and using limited resources effectively. We have been developing two technologies, gasification in molten carbonates or liquefaction in biomass derived tar, to recover metals in circuit boards.

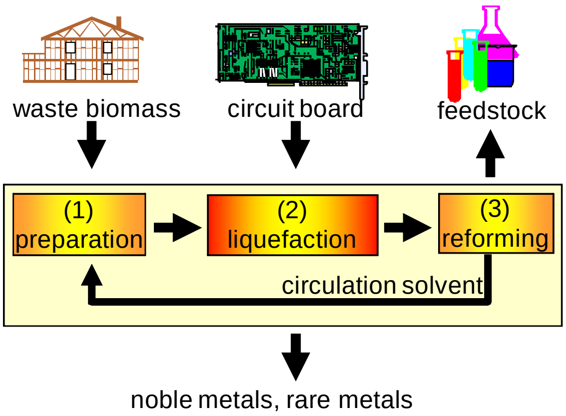

Fig.1 Outline of resources recovery process from the end-of-life electric devices

Thermosetting resins such as epoxy resin used in the electric circuit boards is not liquefied by conventional pyrolysis. Recently, we showed approximately 50 % of epoxy board was liquefied at 220 °C under atmospheric pressure in a tar which was produced from Japanese cedar by dry distillation [1]. In order to increase the solbilzation rate of the epoxy boards and to produce the tar from Japanese cedar efficiently, we are developing a new process in which a part of the liquefied product is used as a circulation solvent. This process consists of three steps as shown in Fig.1, (1) preparation of the tar from waste biomass in circulation solvent, (2) liquefaction of the circuit boards in the tar, and (3) reforming of the liquefied product into the circulation solvent.

In this work, liquefaction of some plastics was carried out in the tar derived from Japanese cedar, and benzyl alcohol was used as an alternative of the circulation solvent.

2. Experiment

Preparation of tar was carried out in an autoclave (200 ml) at 200- 350 ˚C for 120 minutes under an initial nitrogen pressure of 2.0 MPa. In the most of experiments, Japanese cedar powder (10 g, 100 mesh), benzyl alcohol (40 g), and sodium hydroxide (0.4 g) were charged into the autoclave. In some experiments, cresols or sulfuric acid was used as solvent or additives, respectively. The autoclave was heated up to the desired reaction temperature within 20 minutes and quenched by blowing air after completion of the reaction. Gaseous products were collected in a gas bag, and were analyzed with an automatic gas chromatograph (GL-Science, GC-312). Products were separated into liquid product and tar respectively by vacuum fractionation at 140˚C for 60 minutes. The liquid products were analyzed by gas chromatography (Shimadzu, GC17A) with a capillary column (HP-5, 0.32 mm, 30 m). Compounds in the liquid products were identified by GC-MS (Agilent Technology, HP-5973). The molecular weight of tar was measured by gel permutation chromatography (Tosoh, SC08020) with a gel column (TSK gel Super HM-M).

Liquefaction of the epoxy board was carried out in a glass flask (300 ml) connected to a water cooling reflux condenser at 200 – 350 ˚C for 120 minutes under atmospheric pressure. Epoxy sample pieces (5 mm square, 1 g) and the tar (10 g) were charged into the glass flask. Products were washed with tetrahydrofuran, filtrated by a stainless steel net, and dried at 110˚C for 12 hours under vacuum. Solubilization rate of the epoxy board was derived from an equation (1) shown below.

$$\text{Solubilization rate (\%)} = 100 - (c-b)/(a-b) \times 100 \quad (1)$$

a:weight of glass fiber composite epoxy board,

b:weight of glass fiber in the epoxy board

c:weight of solid residue

3. Results and discussion

Distributions of products derived from reaction of Japanese cedar powder (10 g) with sodium hydroxide (0.4 g) in benzyl alcohol (40 g) are shown in Fig. 2. The tar shown in the figure indicates unreacted Japan cedar or a heavy product which was not distilled under vacuum at 140 ˚C. On the reaction of Japanese cedar in benzyl alcohol at 250 ˚C, the Japanese cedar powder changed to dark-brown particles, and its weight decreased to 14.6% by decarbonation or dehydration. Benzyl alcohol was almost stable at 250 ˚C, because benzaldehyde was not detected in recovered solvent. Yield of the benzaldehyde increased with temperature at 250-325 ˚C, and benzyl alcohol converted into toluene and benzene dominantly at more than 350 ˚C. We estimated that Japanese cedar have some effects to accelerate decomposition of benzyl alcohol, because aromatic compounds, such as benzaldehyde or toluene shown in Fig.3, were not detected even if only benzyl alcohol was heated at 350˚C. Weight of the tar exceeded initial weight of the Japanese cedar powder at more than 300˚C. From this experimental result, we estimate that a part of the solvent was taken into tar at high temperature.

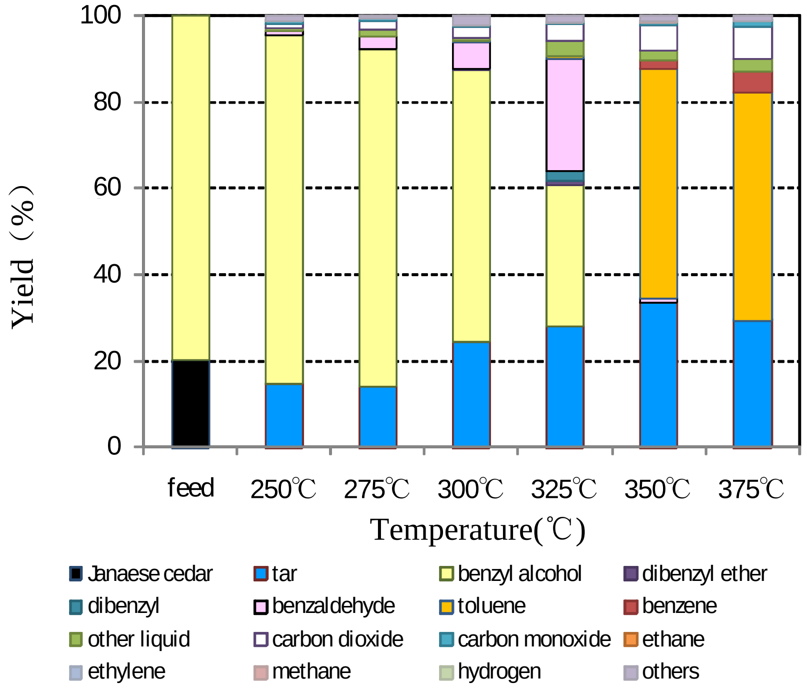

Fig.2 Distribution of products derived from reaction between Japanese cedar and benzyl alcohol.

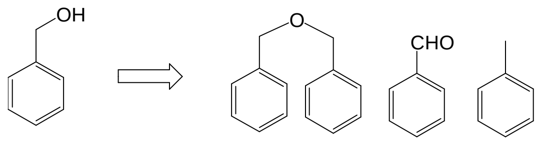

Fig.3 Main products derived from thermal decomposition of benzyl alcohol.

The elemental analyses data of the tar, Japanese cedar, and benzylalcohol are shown in Fig. 4. Two molar ratios of the tar, H/C and O/C, decreased with an increase in temperature of preparation, respectively. The solid lines are indicating theoretical elemental composition of the products which are formed from the Japanese cedar by dehydration, decarbonation, dehydrogenation, dealkalylation, and solvent addition. The elemental compositions of the tar derived from these reactions are expected to lie on the lines respectively. We estimate that two reactions, decarbonation and dehydration, occurred mainly in a reaction of the Japanese cedar and benzyl alcohol at 250˚C, because transfer of the solvent to the tar was not observed. On the other hand, we estimate not only decarbonation or dehydration, but also solvent addition occurred, because weight increase of the tar derived from the Japanese cedar reaction was observed at more than 250˚C.

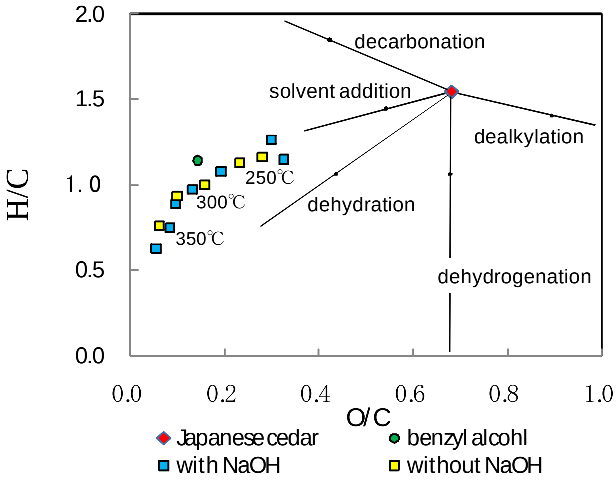

Fig. 4 Elemental analyses data of Japanese cedar, tar, and benzyl alcohol

Solvent extraction of the tar derived from Japanese cedar was carried out using methanol or tetrahydrofuran (THF). Fraction distributions of the tar prepared at various temperatures are shown in Fig. 5. The Japanese cedar powder was hardly extracted by methanol or THF. THF-insoluble fraction decreased and methanol-soluble fraction increased at high preparation temperature. The increase of THF-insoluble fraction at 375˚C implies that condensation reaction of the tar was promoted at high preparation temperature.

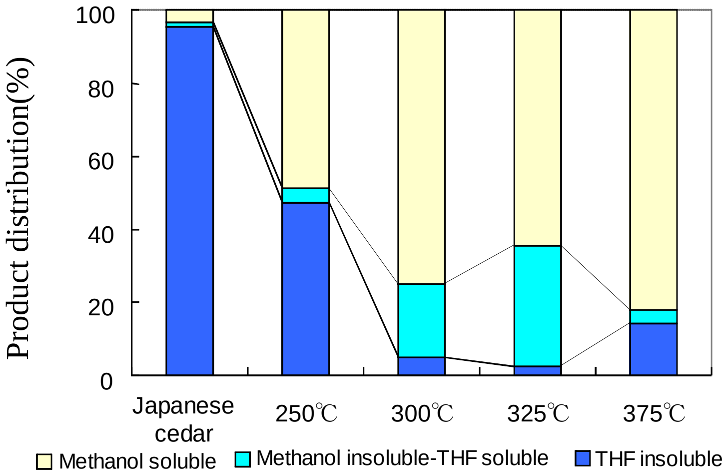

Fig.5 Fraction distributions of the tar prepared at various temperatures

Hydrogen contained in tar was classified as shown following by the chemical shift value that was measured by ^{1}H-NMR, α-hydrogen (2.0-4.2 ppm), β-hydrogen (2.0-1.0 ppm), γ-hydrogen (0.5-1.0 ppm), and aromatic hydrogen (6.5- ppm), (Fig.6). Comparatively much β-hydrogen and γ-hydrogen were contained in the tar prepared at 250 ˚C. However, at a high preparation temperature, the percentage of β-hydrogen or γ-hydrogen decreased and that of aromatic hydrogen increased. These analysis results suggest that comparatively much alkylchains exist in the tar prepared at low temperature, however, decomposition of alkylchain and condensation of aromatic compounds are accelerated at high temperature.

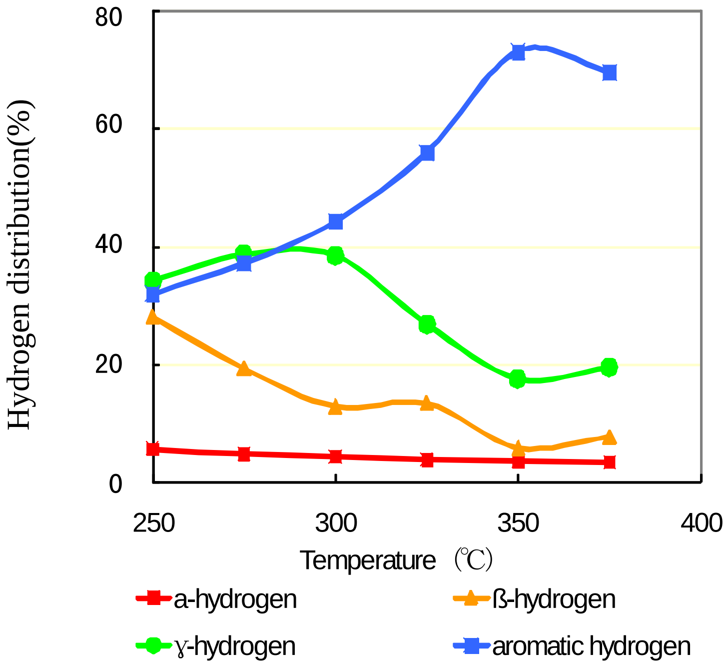

Fig.6 Distributions of hydrogen contained in tar classified by ^{1}H-NMR

Solubilization rates of the epoxy board which was liquefied at 300˚C for 120 minutes in the tar derived from Japanese cedar are shown in Fig.7. The epoxy board was liquefied nearly completely in the tar prepared at 300 ˚C (Fig. 8), but it was not liquefied in the tar prepared at 250˚C. At higher temperature, the solubilization rate of the epoxy board decreased with an increase in temperature drastically. These experimental results show that the liquefaction rate of an epoxy board is very sensitive to the preparation temperature of tar, and it is very important to investigate the relationship between the chemical structure of the tar and a liquefaction reaction mechanism.

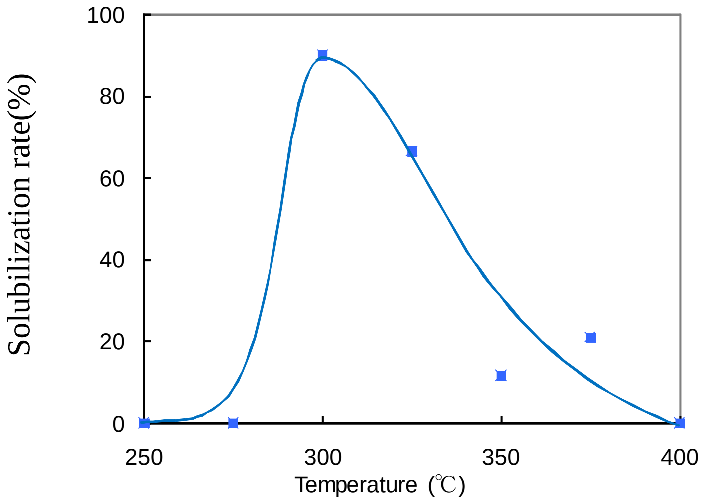

Fig. 7 Effect of tar preparation temperature for solubilization rate of epoxy board

Fig.8 Recovered glass fiber from epoxy board by using tar prepared at 300˚C

The solubilization rate of FRP (glass fiber reinforced unsaturated polyester), urethane resin, PET (polyethylene terephthalate), and polycarbonate were shown in Fig.9. These liquefactions were carried out at 250˚C or 300˚C for 120 minutes in the tar prepared at 300˚C. These plastics which have used widely in electric devices were liquefied almost completely at 250˚C or 300˚C in the tar derived from Japanese cedar. Our experimental results suggest that liquefaction of the plastics used in electric devices is an effective method to recover useful resources from end-of-life industrial products.

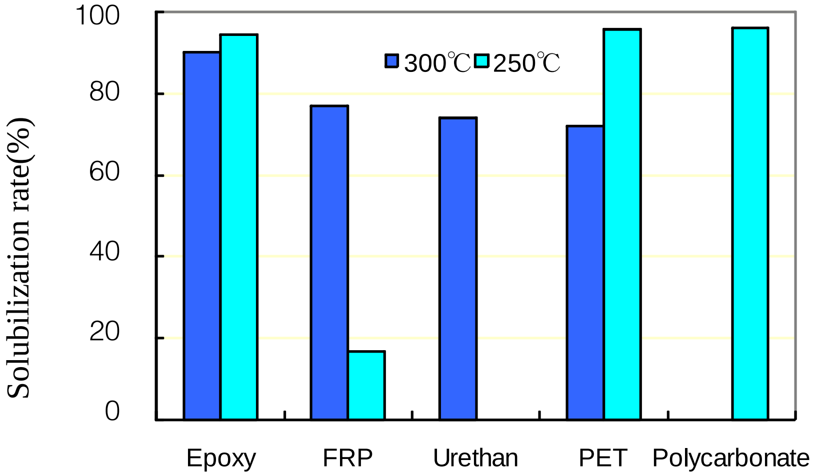

Fig. 9 Solbilization rate of various plastics on the liquefaction in the tar derived from Japanese cedar

4. Conclusion

Liquefaction of epoxy resin board was carried out to recover useful resources from end-of-life electric equipments. The epoxy board was liquefied almost completely at 250-300°C under atmospheric pressure in the tar derived from Japanese cedar. Yields of the tar, which was derived from a reaction of Japanese cedar and benzyl alcohol, were much larger than that of conventional dry distillation. Preparation temperature of the tar is very important to increase the solubilization rate of the epoxy board. By using the tar derived from a reaction of Japanese cedar and benzylalcohol, many kind of plastics, epoxy board, urethane, FRP, PET, and polycarbonate, were liquefied almost completely.

References

[1] T. Kamo, N. Akaishi, B. L. Wu, M. Adachi, H. Yasuda, H. Nakagome, *Proceeding of the 4th International Symposium on Feedstock Recycling of Plastics*. **2007**,159.