

THE EFFECTS OF SOLVENTS ON THE CHEMICAL DECOMPOSITION OF FOAMED PHENOL RESIN IN HIGH —TEMPERATURE FLUIDS

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Abstract

In this study waste plastics such as phenol resin foam powder were decomposed into their monomer and oligomer compounds in sub- and supercritical fluids. Solvents play important roles as stable physical medium at high temperature and reactive chemical reagents to accelerate decomposition reaction of the thermosetting resin. In the decomposition reaction at relatively high temperature, methylene bonds of plastics were cleaved selectively via the ionic reaction by solvents. The solvent participating mechanism of decomposition was confirmed to make clear the decomposition products of phenol resin foam. The methylated reaction also occurred in the reaction in methanol, and cresol and trimethylphenol were found as main products. Almost all foamed phenol resin was solubilized in the reaction in *m*-cresol and 1-heptanol suggesting new solubilization mechanism.

Keywords: High Temperature Water, High Temperature Methanol, Phenol Resin, Thermosetting Resin, Chemical Recycling

1. Introduction

The chemical recycling of waste plastics has been gaining greater attention in recent years as a means of obtaining valuable products from wastes. Thermal cracking of thermosetting resin is a well-known technique and fluidized-bed pyrolysis technology has been under development. It is well known that water under supercritical conditions is much less polar and can homogenize substantial amounts of non-polar organic compounds. Furthermore, it is pointed out that the supercritical water is emerging as a medium, which could provide the optimum conditions for a variety of chemical reactions, among them the destruction of hazardous waste. We have already confirmed that waste plastics such as phenol resin decompose into their monomeric compounds in sub- and supercritical water (Fig.1) [1], [2].

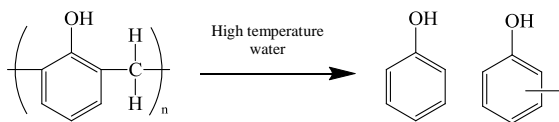


Fig.1. Decomposition reaction of foamed phenol resin.

2. Materials and Methods

Foamed phenol resin was reacted after pulverizing. A 10 mL tubing bomb autoclave and 2 L batch-type autoclave were used as the reactor. The typical reaction was carried out for 0.1 g of foamed phenol resin in 1.0 mL water with Na₂CO₃ or methanol. *m*-Cresol, toluene and 1-heptanol which were the new solvents were used with a 10 mL tubing bomb autoclave to decompose foamed

phenol resin effectively. After the reaction, products were extracted by ether and analyzed by GC and GC/MS (Fig.2). In the thermal analysis the temperature increasing rate was 10°C/min.

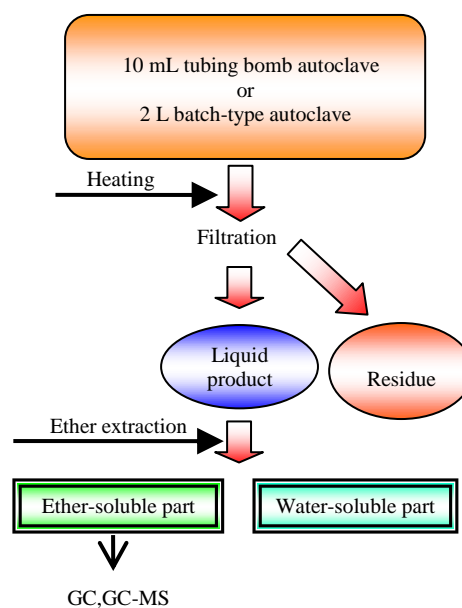


Fig.2. Experiment method.

3. Results and Discussion

3.1. Decomposition reaction in high temperature water

Foamed phenol resin was decomposed into their monomers by the reactions at 350°C under an Ar atmosphere in high temperature water with Na₂CO₃ for 2 h. According to GC/MS analysis, phenol and cresol

were found as main components in the liquid phase (Fig.3). The decomposition was accelerated by the quantity of Na_2CO_3 addition increasing. In addition, the yield of their monomers was higher at longer reaction time and higher temperature (Fig.4). Residue was produced about 40% in the severe conditions. However, carbonization reaction occurred at the high reaction temperature.

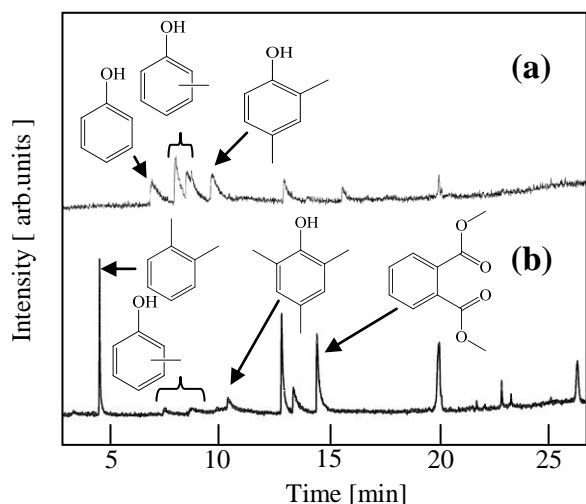


Fig.3. GC/MS chromatogram of the products in the reaction of foamed phenol resin by using 2 L batch-type autoclave (a) in water 400 mL with Na_2CO_3 at 350°C for 1 h and (b) in methanol 400 mL at 280°C for 1 h.

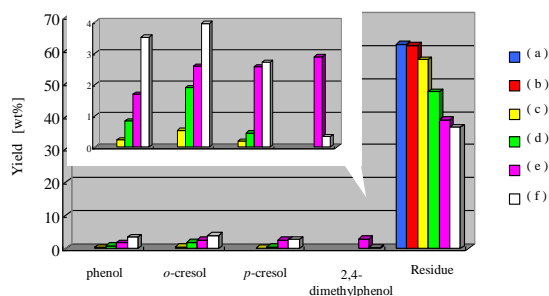


Fig.4. Decomposition reaction of foamed phenol resin in water 1.0 mL with Na_2CO_3 for 2 h by using 10 mL tubing bomb autoclave (a) at 280°C, (b) at 300°C, (c) at 320°C, (d) at 350°C, (e) at 400°C, (f) at 430°C.

3.2. Decomposition reaction in high temperature methanol

Foamed phenol resin was decomposed by reactions at 280°C in high temperature methanol without the addition of additive. However the decomposition ability of high temperature methanol was lower than that of high temperature water with Na_2CO_3 at 350°C. Foamed phenol resin decomposed mainly into 2,4,6-trimethylphenol and xylene in high temperature methanol as shown in Fig.3. It is considered that xylene was produced from the plasticizer.

3.3. Examination of the new solvents

m-Cresol and toluene which have similar structure of foamed phenol resin were used as the new solvent. Foamed phenol resin hardly was decomposed in toluene at 350°C, while foamed phenol resin was decomposed successfully and solubilized in *m*-cresol at 350°C (Fig.5). Therefore hydroxyl group play an important role for the decomposition reaction. The total yields of the monomers which were phenol, *o*-cresol, *p*-cresol and 2,4-dimethylphenol were about 30% on decomposition reaction in *m*-cresol at 350°C. It was about 10 times of the total yields of the monomers by decomposition reaction in water with Na_2CO_3 at 350°C.

1-Heptanol is a straight-chain compound and was used to compare with the reaction of *m*-cresol. Not only decomposition reaction in *m*-cresol, but also it in 1-heptanol was able to solubilize foamed phenol resin.

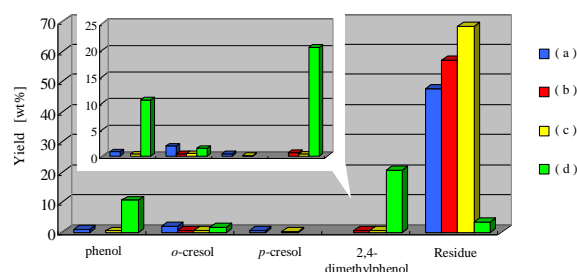


Fig.5. Decomposition reaction of foamed phenol resin at 350°C for 2 h by using 10 mL tubing bomb autoclave (a) in water 1.0 mL with Na_2CO_3 , (b) in methanol 1.0 mL, (c) in toluene 1.0 mL, (d) in *m*-cresol 1.0 mL.

4. Conclusions

Decomposition reaction of phenol resin foam could be carried out using methanol at around 300°C. Indicating that the decomposition reaction proceeded at lower temperature when methanol was used as the solvent. However, solid residue was produced either solvent above 35%. Meanwhile foamed phenol resin was decomposed successfully in *m*-cresol and 1-heptanol.

References

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- [2] T. Sugeno and H. Tagaya. Treatment of phenol resin foam powder and prepolymer in high-temperature fluids. *PACIFICHEM 2010*, Honolulu, (2011); Abstract 587.