Chemical Recycling of Polycarbonate to Raw Materials by Thermal Decomposition with Calcium Hydroxide/Steam

Toshiaki Yoshioka,* Katsuya Sugawara, Tadaaki Mizoguchi, and Akitsugu Okuwaki[†]
Environmental Conservation Research Institute, Tohoku University, Aramaki Aza Aoba 6-6-07, Aoba-ku, Sendai 980-8579
[†]*Graduate School of Environment Studies, Tohoku University, Aramaki Aza Aoba 6-6-07, Aoba-ku, Sendai 980-8579*

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We investigated the influence of the decomposition conditions (temperature: 500, 700, 900 °C, steam concentration: 0, 35, 86 vol %, $Ca(OH)_2/PC$ molar ratio: 0 or 5) on polycarbonate (PC). Without steam and $Ca(OH)_2$ the liquefaction yield was 57 wt % (low and high boiling products 14, 43 wt %, respectively), the gasification yield 12 wt %, and the carbonization yield 31 wt % at 500 °C. At a steam concentration of 86 vol %, 84 wt % liquids (low and high boiling products 17, 67 wt %, respectively), 1 wt % gases and 15 wt % residues were observed. The amount of low boiling products increased from 17 to 31 wt %, and the amount of high boiling products decreased from 67 to 49 wt % when $Ca(OH)_2$ was added at a steam concentration 86 vol %. At this time, the yield of phenol in the low boiling fraction increased from 15 to 74 mol % (20 wt % of all products).

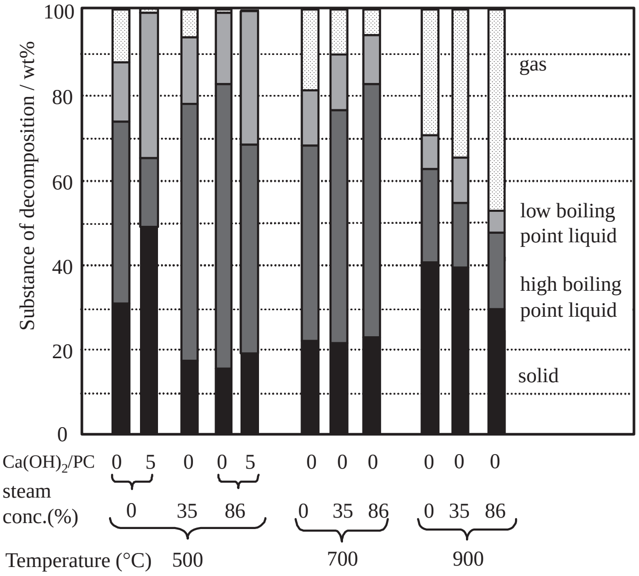


Figure 1. Influence of the decomposition temperature, steam concentration, and $Ca(OH)_2$ on the yields of products.

Various methods for plastic recycling technology are now developed. One of the proposed technologies is the conversion to oil, performed by three large plants in Japan. Polyolefines, such as polyethylene, polypropylene, and polystyrene, can be converted into oil via thermal decomposition.

PC is a plastic used in various applications, and in order to use valuable resources effectively, it is necessary to recycle them. Today physical recycling of PC is carried out. In chemical recycling of PC, solvolysis is well known.[1–3] In this process the heat transfer between organic solvent and PC is very excellent. Further it is possible to supply hydrogen required for the radical stabilization during the degradation of the PC. It suppresses the generation of residual substance.[4] Hu et al. reported that 96 mol % of bisphenol A (BPA) was obtained using a MeOH/toluene system.[1] 95 mol % of BPA was obtained by aminolysis.[2] However in order to extend the object of recycling to composite materials containing PC, development of a new technology for getting monomers and fuels is desired. Yoshioka et al. reported that the addition of $Ca(OH)_2$ to PET affects a high selectivity of benzene without producing sublimation substances during the thermal decomposition.[5] In order to apply this result also to PC, we performed thermal decomposition of PC by the addition of $Ca(OH)_2$ and considered the influence of the reaction temperature, steam concentration and $Ca(OH)_2$ addition on the decomposition of PC.

0.60 g of PC pellets ($\phi 2 \times 3$ mm) or a mixture of PC pellets and 0.87 g of $Ca(OH)_2$ powder (molar ratio ($Ca(OH)_2$/unit structure of PC):5) was used as a sample. After checking for reaching predetermined temperature and having become a stationary state, the sample was slowly dropped into a reactor made of quartz for 20 min.[5] The moment of having supplied a sample to a reactor was considered as the reaction start. The sample was decomposed on quartz wool of the middle of the reactor with filter plate at temperatures between 500, 700, 900 °C with a helium flow-rate of 50 mL/min or with steam/helium (steam concentration: 0, 35, 86 vol %). In case of steam addition, water was vaporized at 450 °C in a second reactor, and led into the decomposition reactor. Liquid products were collected in cooling traps cooled with iced water and liquid nitrogen. Gases were gathered in a gas pack. Quantitative analysis was conducted using GC–MS, GC–FID, and GC–TCD.

The influence of the decomposition temperature, steam concentration, and $Ca(OH)_2$ on the yields of gases, liquids, and solids is shown in Figure 1. Liquid is classified into the low boiling fraction (<280 °C) and the high boiling fraction (>280 °C). The yield of liquids was decreased with increasing temperature. On the other hand, the yield of gases was increased. The yields of liquids increased with increasing the steam concentration at 500 and 700 °C. The yield of liquids was 84 wt % at 500 °C and 71 wt % at 700 °C in steam concentration 86 vol %. When $Ca(OH)_2$ was added to PC at 500 °C, the yield of the low boiling fraction increased irrespective of the existence of steam, and reached 17 wt % at a steam concentration of 86 vol % and the high boiling fraction was 67 wt % in case of the molar ratio ($Ca(OH)_2/PC$) of 0. On the other hands, in case of the molar ratio ($Ca(OH)_2/PC$) of 5, the yield of the low boiling fraction was 31 wt %, and the yield of the high boiling fraction was 49 wt %, respectively.

Figure 2 shows the composition of low boiling fraction at

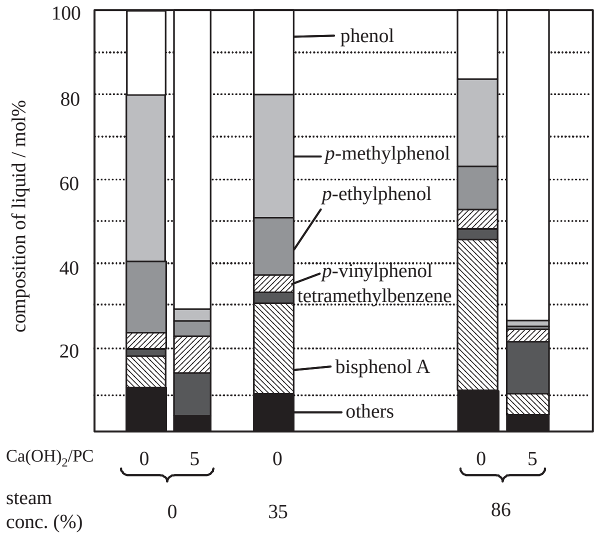
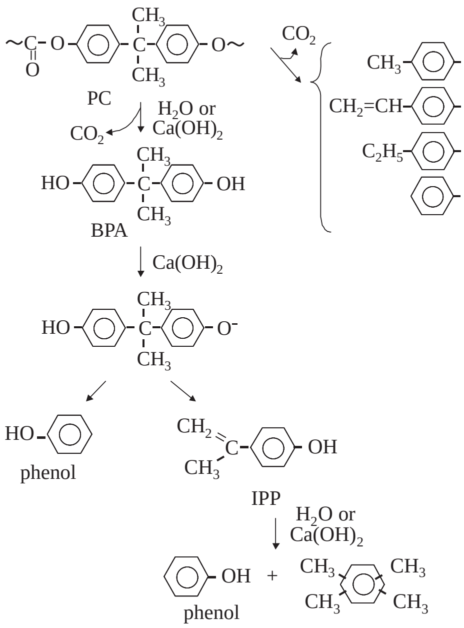


Figure 2. Composition of low boiling fractions at 500 °C.

500 °C. Main products of phenols were phenol, *p*-methylphenol, *p*-ethylphenol, and *p*-vinylphenol, tetramethylbenzene, and BPA. The total molar yield of main phenols in the low boiling fraction was almost constant at about 80 mol %, when steam concentration was changed from 0 to 86 vol %. The yield of *p*-methylphenol, however, fell from 40 to 20 mol %, and the yield of BPA increased from 8 to 36 mol % with increasing steam concentration. This result shows that the hydrolysis of the carbonate group is preferred rather than cleavage of C–C bonds in a steam atmosphere. Others consist of benzene, *p*-isopropylphenol, biphenyl, 2-vinyl-2,3-dihydronaphtofuran, 4-(dimethylphenylmethyl)phenol, 5-*tert*-butylbiphenyl-2-ol, 1,2-bis(4-hydroxyphenyl)ethane, and 1,3-dimetyl-2(2,4,6-trimetylphenyl)-1,3-cyclopentadiene. The product composition at 700 °C was almost the same as at 500 °C. However, the yields of gases such as H_2, CO, CO_2, and CH_4 of a low molecular weight increased to 30–48 wt % at 900 °C, and the yields of liquids decreased to less than 30 wt %. Carbonization has taken place since there is much solid. It will be for the radical reaction by heat to occur more quickly than hydrolysis. In addition, decomposition was not observed at 400 °C, but only melting of PC irrespective of the existence of steam. Remained PC was 97.3 wt % with steam concentration 0 vol % and 99.8 wt % with steam concentration 86 vol %.

The total molar yield of main phenols increased to 90 mol % with decreasing the others yield by the addition of $Ca(OH)_2$. Moreover, the addition of $Ca(OH)_2$ led to a high selectivity for phenol (70 mol %) irrespective of steam concentration. In any steam concentration, the yields of gases became less than 1 wt % when $Ca(OH)_2$ was added. CO_2 the most part of gases was fixed as $CaCO_3$, because the investigation of the solid reactor residue by XRD showed a mixture of $Ca(OH)_2$ and $CaCO_3$.



We suppose the reaction mechanism of PC decomposition with steam and/or $Ca(OH)_2$. When NaOH is used as an additive for decomposition of PC, Na_2CO_3, and BPA are generated (decomposition with organic solvent, 60 °C).[1] Therefore, the same degradation mechanism occurs using $Ca(OH)_2$ as an additive. It is well known that PC is decomposed into alkylphenols.[6] PC hydrolyzed into BPA preferentially in existing steam or $Ca(OH)_2$. This indicates that high selectivity of BPA by the addition of steam. Since $Ca(OH)_2$ is a strong base, the hydroxy group acts as an anion and cleavage of BPA proceeds. After that *p*-isopropenykphenol (IPP) and phenol are generated.[7] IPP is mainly decomposed into phenol and tetramethlbenzene.

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