

# High Selective Conversion of Poly(ethylene terephthalate) into Oil Using $\text{Ca}(\text{OH})_2$

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(Received November 19, 2003; CL-031117)

It is a well known fact that sublimation substances, such as benzoic acid and terephthalic acid, are produced in the thermal decomposition of PET, and this causes problems in plastic recycling plants. However, it is clear that the addition of  $\text{Ca}(\text{OH})_2$  affects the high selectivity of benzene without producing sublimation substances. The yield of benzene was 35.85 wt % at 700 °C and a 10.0  $\text{Ca}(\text{OH})_2$ /PET molar ratio. This value means that the selectivity of benzene is 78.8% for liquid products, and 85.1 wt % for aromatic ring in input PET.

Various methods for plastic recycling technology are now being developed. One of the proposed technologies is conversion into oil, and is being investigated by three large plants in Japan. Polyolephine plastics, such as poly(ethylene), poly(propylene), and poly(styrene), can be converted into oil via thermal decomposition. However, thermal decomposition of poly(ethylene terephthalate) (PET) causes not only corrosion and blockade of piping but also a failure in efficiency by the generation of a sublimation substances, such as terephthalic acid and benzoic acid.

In chemical recycling of PET, solvolysis,<sup>1-7</sup> such as hydrolysis, methanolysis, and glycolysis, is well known and utilized by some commercial plants. These processes are applied mainly to PET bottle of high purity. However, it is important to extend these applications to various types of PET materials, such as film, tape, fiber, and card, and mixed waste plastics. Some studies were pushed forward to investigate liquefaction of PET. Masuda et al.<sup>8</sup> reported that 56 wt % oil was produced at 500 °C with a steam and geothite catalyst. The oil is consisted of 46 wt % acetophenone, 28 wt % benzene, and 14 wt % phenol. Obuchi et al.<sup>9</sup> reported that thermal decomposition of 15 wt % PET and 85 wt % PP mixture yielded a 70 wt % oil containing aromatic and aliphatic hydrocarbons. However, requirements for liquefaction of PET include the high selectivity of some useful products such as benzene, toluene, xylene, and the lowering of carbon residue. This paper remarks upon the high selectivity of benzene without the production of sublimation substances via the addition of  $\text{Ca}(\text{OH})_2$ .

A mixture of PET powder (60–100 mesh) of 1 g and  $\text{Ca}(\text{OH})_2$  powder was dropped into a reactor made of quartz and quartz wool over a course of 20 min. The sample was placed in the reactor, set at 700 °C with a helium flow-rate of 50 mL/min (see Figure 1). In case of steam addition, water was pumped into the second reactor set at 450 °C, thus producing steam. The reaction temperature was measured at the quartz wool contained in the reactor. The products were then trapped in the gas packs, using the empty traps containing liquid nitrogen. Quantitative analyses were conducted using GC–MS, FID and GC–TCD.

Products from the thermal decomposition of PET were clas-

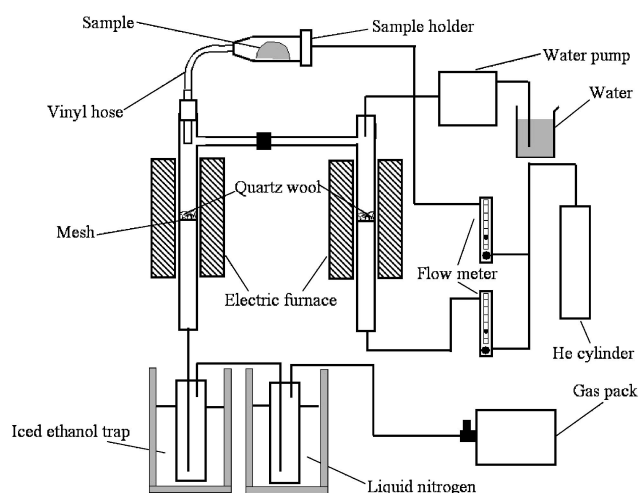
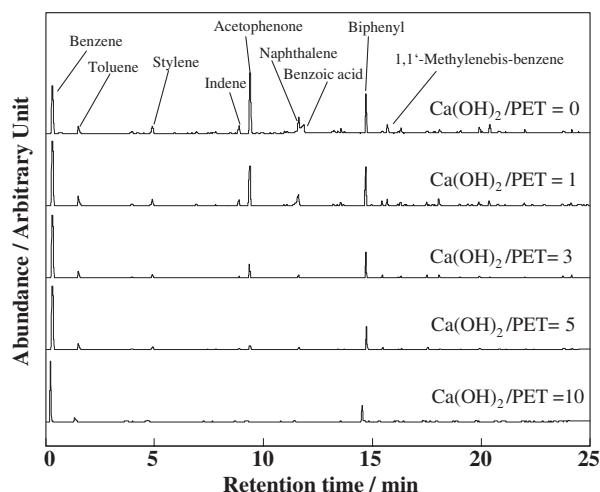


Figure 1. Experimental apparatus.

Table 1. Products of the thermal decomposition of PET and mixture of  $\text{Ca}(\text{OH})_2$  /PET

| Mixture ratio of $\text{Ca}(\text{OH})_2$ to PET | 0             | 1             | 3             | 5             | 10            |
|--------------------------------------------------|---------------|---------------|---------------|---------------|---------------|
| <b>Solid / wt %</b>                              | <b>29.73</b>  | <b>36.17</b>  | <b>26.29</b>  | <b>21.40</b>  | <b>21.94</b>  |
| Residue                                          | 29.46         | 36.10         | 26.29         | 21.40         | 21.94         |
| Terephthalic acid                                | 0.28          | 0.07          | 0.00          | 0.00          | 0.00          |
| <b>Liquid / wt %</b>                             | <b>34.99</b>  | <b>40.02</b>  | <b>43.70</b>  | <b>41.58</b>  | <b>45.51</b>  |
| Benzene                                          | 9.21          | 15.95         | 28.02         | 31.54         | 35.85         |
| Toluene                                          | 1.69          | 2.25          | 2.62          | 2.46          | 2.34          |
| Ethylbenzene                                     | 0.47          | 0.61          | 0.68          | 0.54          | 0.62          |
| Stylene                                          | 1.74          | 1.67          | 1.68          | 1.46          | 1.36          |
| Benzaldehyde                                     | 0.18          | 0.18          | 0.00          | 0.00          | 0.00          |
| p-Methylstyrene                                  | 0.23          | 0.27          | 0.22          | 0.00          | 0.00          |
| Indene                                           | 0.64          | 0.51          | 0.36          | 0.24          | 0.16          |
| Acetophenone                                     | 10.84         | 8.64          | 4.12          | 1.47          | 0.60          |
| Benzoic acid                                     | 4.16          | 1.25          | 0.00          | 0.00          | 0.00          |
| Naphthalene                                      | 0.94          | 1.29          | 0.47          | 0.34          | 0.30          |
| 5-Ethylindene                                    | 0.34          | 0.39          | 0.00          | 0.00          | 0.00          |
| 1,1'-Biphenyl                                    | 2.28          | 2.99          | 3.71          | 3.02          | 3.50          |
| 4-Methyl-1,1'-biphenyl                           | 0.28          | 0.32          | 0.33          | 0.24          | 0.25          |
| 1,1'-Methylenebisbenzene                         | 0.70          | 0.79          | 0.17          | 0.00          | 0.00          |
| Fluorene                                         | 0.00          | 0.35          | 0.39          | 0.27          | 0.52          |
| Diphenylmethanone                                | 0.00          | 1.28          | 0.66          | 0.00          | 0.00          |
| Phenanthrene                                     | 0.49          | 0.37          | 0.27          | 0.00          | 0.00          |
| 1-[1,1'-Biphenyl-4-yl]ethanone                   | 0.81          | 0.92          | 0.00          | 0.00          | 0.00          |
| <b>Gas / wt %</b>                                | <b>35.28</b>  | <b>23.81</b>  | <b>30.01</b>  | <b>37.02</b>  | <b>32.55</b>  |
| Hydrogen                                         | 0.17          | 0.53          | 1.42          | 1.48          | 1.79          |
| Carbon monoxide                                  | 15.37         | 14.14         | 14.57         | 8.78          | 7.16          |
| Methane                                          | 1.59          | 1.76          | 3.32          | 3.58          | 4.62          |
| Carbon dioxide                                   | 17.10         | 6.16          | 8.75          | 21.46         | 17.80         |
| Etylene                                          | 0.96          | 1.13          | 1.85          | 1.58          | 1.12          |
| Ethane                                           | 0.09          | 0.10          | 0.10          | 0.15          | 0.07          |
| <b>SUM</b>                                       | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> |



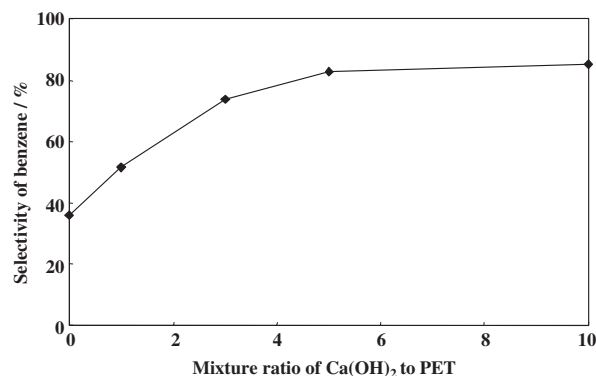
**Figure 2.** GC-MS total ion chromatogram for products of PET and  $\text{Ca}(\text{OH})_2/\text{PET}$ .

sified into three groups: solids, liquids, and gases, as shown in Table 1. The GC charts for liquid products are presented in Figure 2. The values were standardized on the basis of PET weight. The solids consist of carbon residue and were contained in terephthalic acid. The maximum yield of solids was 36.17 wt % in  $\text{Ca}(\text{OH})_2/\text{PET} = 1$ . The yield decreased with the addition of  $\text{Ca}(\text{OH})_2$ , moreover, formation of terephthalic acid was not recognized over  $\text{Ca}(\text{OH})_2/\text{PET} = 3$ . The yield of liquids (45.51 wt %) increased with the addition of  $\text{Ca}(\text{OH})_2$  for  $\text{Ca}(\text{OH})_2/\text{PET} = 10$ .

The main gas components are carbon monoxide, carbon dioxide, hydrogen, methane ethylene, and ethane. Total gas yields are between ca.23 and 37 wt % in each  $\text{Ca}(\text{OH})_2/\text{PET}$  ratio, and did not depend on the addition of  $\text{Ca}(\text{OH})_2$ . However, the yields of carbon dioxide and hydrogen increase with decreasing carbon monoxide. This behavior contributes to the proceeding production of calcium terephthalate. The yield of hydrogen also increases with the addition of  $\text{Ca}(\text{OH})_2$ , indicating that water-gas shift reaction utilizes the  $\text{H}_2\text{O}$  produced from the decomposition of  $\text{Ca}(\text{OH})_2$  and the ethylene glycol from the hydrolysis of PET. These reactions result in the decrease of residue. We have been able to conclude that from the addition of  $\text{Ca}(\text{OH})_2$  the yields of hydrogen and carbon dioxide have increased, while the residues and carbon monoxide have decreased, thus confirming the mechanism for the water-gas shift reaction.<sup>10</sup>

In the case of PET, many products, such as benzene, toluene, acetophenone, benzoic acid biphenyl etc., are produced. As the molar ratio of  $\text{Ca}(\text{OH})_2/\text{PET}$  is increased the production of all substances, except benzene, may be controlled; i.e. the selectivity of benzene is increased. The number of products was decreased with increasing molar ration of  $\text{Ca}(\text{OH})_2$ .

Figure 3 shows the effect of the molar ratio of  $\text{Ca}(\text{OH})_2/\text{PET}$  for the selectivity of benzene for aromatic ring in input PET. The selectivity was 38.5 wt % in case of PET, however, it reached 85.1 wt % for 10  $\text{Ca}(\text{OH})_2/\text{PET}$  molar ratio. This clearly indicates that the addition of  $\text{Ca}(\text{OH})_2$  affects the selectivity of benzene. This is caused by the formation of calcium ter-



**Figure 3.** Effect of mixture ratio of  $\text{Ca}(\text{OH})_2/\text{PET}$  on selective of benzene.

ephthalate. Therefore, produced  $\text{H}_2\text{O}$  from  $\text{Ca}(\text{OH})_2$  accelerates the hydrolysis of PET, and calcium terephthalate thus formed simultaneously. The calcium terephthalate is then decomposed to benzene and  $\text{CaCO}_3$ , and the later to  $\text{CaO}$  via decarboxylation. Generation of sublimation substances, such as benzoic acid and terephthalic acid, was not recognized over  $\text{Ca}(\text{OH})_2/\text{PET} = 3$ .

A molar ratio of 1 is ideal for the production of calcium terephthalate. However, the yield and selectivity of benzene depends on molar ratio of  $\text{Ca}(\text{OH})_2$ . This indicates that raising the contact efficiency between PET and  $\text{Ca}(\text{OH})_2$  is important.

The amount of benzene from recycled PET is not enough in comparison with petroleum industry. However, benzene is one of the raw chemicals and its application is very wide in many chemical industries. The selective production of benzene is able to increase efficiency in oil plant for plastic waste recycling. This means realization of material cycle by combination with petroleum industry.

We thank Ministry of the Environment and Ministry of Education, Culture, Sports, Science and Technology, Japan.

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