

Oxygen-Oxidation of Ethylene Glycol in NaOH Solutions at Elevated Temperatures

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Poly(ethylene terephthalate) (PET) is converted to terephthalic acid (TPA) and ethylene glycol (EG) by hydrolysis in NaOH solution. Then, EG can be oxidized by oxygen to oxalic acid (OxA), more expensive chemical than EG. The second stage was investigated to improve the OxA yield. The yield of OxA was 80.0 C% under the conditions : 250 °C, 1 h, 1000 rpm, EG concentration 0.177 M, NaOH concentration 27.5 mol NaOH / kg-H₂O and P_{O₂} 7 MPa. Effect of reaction conditions on the OxA yield was measured in detail.

Introduction

Recently, the amount of production of PET resin has increased remarkably. The effort recycling waste PET has been made aiming at effective utilization of resources. "The law for promotion of sorted collection and recycling of containers and packaging" was enacted since April 1997, and the rate of collection of waste PET was reached 15.3 % in 1998 (the amount of production : 314,000 t) in Japan. Recycling of waste PET has been performed only by material recycling in Japan, whereas waste PET is suitable for chemical recycling since it has low additives and high purity.

A new chemical recycling process of waste PET has been proposed ; PET is converted to TPA and EG by hydrolysis. Then, only EG is oxidized by oxygen to OxA, more expensive than EG [1]. In this process, OxA yield was about 70 % or lower due to the formation of CO₂ from EG and glycolaldehyde (GA), which are intermediates of the oxidation of EG to OxA [2].

In this work, EG was oxidized by oxygen in NaOH solutions to investigate oxidation conditions to improve the OxA yield for chemical recycling of waste PET.

Materials and Methods

A mixture of 50 ml of 0.177 M EG solution and prescribed amount of NaOH was placed in a PTFE beaker (wall thickness 2.5 mm, O.D. 48.5 mm and depth 143 mm) in a SUS 316 stainless steel autoclave of 300 cm³ fitted with a magnet driving stirrer under N₂ and heated to 250 °C at 3 °C/min. in an electric furnace. After reaching 250 °C, the oxidation was started stirring rate at 1000 rpm by pressurizing oxygen at 5 MPa. After 1 h, the reaction product in the beaker was washed out with water and diluted to 500 cm³ to prepare a product solution. After removal of the sodium ions from the product solution using a cation-exchange column,

oxalate ion, EG and total organic carbon (TOC) content were determined by ion chromatography, high-performance liquid chromatography and TOC analyzer, respectively. The amount of CO_2 was calculated by the difference between initial EG concentration and TOC concentration in product solution. Intermediates of EG oxidation, which were actually consist of GA, glyoxal (Gox), glycolic acid (GcA) and glyoxylic acid (GoA), were defined as organic carbonaceous compounds except EG and OxA.

Results and Discussions

Experimental Conditions and Reaction Scheme

Effect of (a) initial EG concentration, (b) NaOH concentration and (c) oxygen partial pressure on the yields of products is shown in Figure 1 (a)~(c). EG was completely oxidized leaving a small amount of intermediates under each experimental condition. (a) The yields of OxA and CO_2 were almost constant at each initial EG concentration, and were ca. 75 % and 20 %, respectively. (b) The OxA yield was increased remarkably with increasing in NaOH concentration, whereas the CO_2 yield was decreased. (c) The OxA yield was increased a little with increasing in oxygen partial pressure to reach ca. 80 % at 7 MPa.

EG is oxidized to OxA through GA, Gox, GcA and GoA, as shown in Scheme 1. Since Gox, GcA and GoA were converted to OxA quantitatively [2], EG oxidation seems to be simplified as a parallel reaction, as shown in Scheme 2. One is a pathway affording OxA (1), and another one giving CO_2 (2).

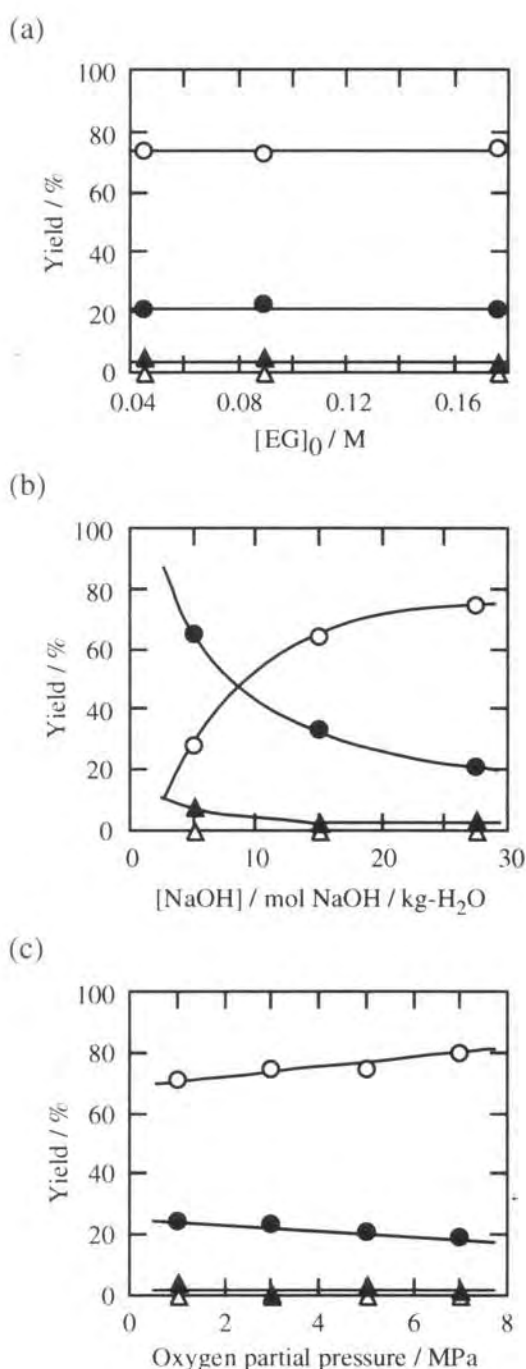


Figure 1 Effect of (a) initial EG concentration, (b) NaOH concentration and (c) oxygen partial pressure on the yields of products

250 °C, $[\text{EG}]_0=0.176 \text{ M}$, $[\text{NaOH}]=27.5 \text{ mol -NaOH} / \text{kg-H}_2\text{O}$, $P_{\text{O}_2}=5 \text{ MPa}$, 1 h, 1000 rpm

○:OxA, △:EG, ●:CO₂, ▲:Int.

Their reaction rates are denoted as v_1 and v_2 . The ratio v_1/v_2 means the selectivity of OxA formation to CO_2 , and this is independent on initial EG concentration, as shown in Figure 1 (a). On the other hand, the fact that v_1/v_2 was increased with increasing in NaOH concentration indicates that only v_1 depends on NaOH concentration. Further, the selectivity increased gradually with increasing oxygen partial pressure.

Any reactions giving OxA from organic compounds are expected to be base-catalyzed mechanism [3] and its rate equation is expressed as v_1 :

$$v_1 : d[\text{OxA}] / dt = k_1 [\text{EG}] [\text{OH}^-] P_{\text{O}_2} \quad (1)$$

Thus, the rate equation giving CO_2 may be written as Eq. (2) :

$$v_2 : d[\text{CO}_2] / dt = k_2 [\text{EG}]^l [\text{OH}^-]^m P_{\text{O}_2}^n \quad (2)$$

The rate constants, k_1 and k_2 are represented as follows :

$$k_1 = k_1^0 \exp(-E_1 / RT) \quad (3)$$

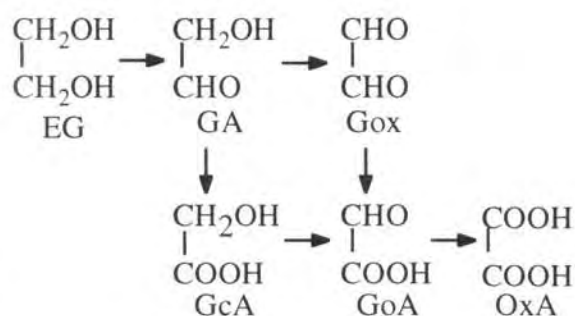
$$k_2 = k_2^0 \exp(-E_2 / RT) \quad (4)$$

Consequently, the differential selectivity can be written as follows :

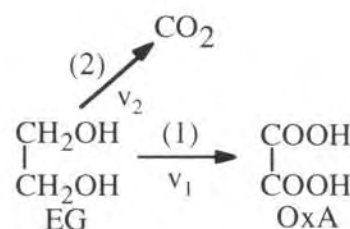
$$v_1 / v_2 = k_1^0 / k_2^0 \exp\{-(E_1 - E_2) / RT\} [\text{EG}]^{1-l} [\text{OH}^-]^{1-m} P_{\text{O}_2}^{1-n} \quad (5)$$

The calculation by the least-squares method was carried out for Eq. (5) to determine the relative reaction orders using the data in Figure 1 (a)~(c). The relative reaction orders with respect to EG concentration, NaOH concentration and oxygen partial pressure were 0.01, 1.3 and 0.18, respectively. Therefore, Eq. (2) can be written approximately as follows :

$$d[\text{CO}_2] / dt = k_2 [\text{EG}] P_{\text{O}_2} \quad (6)$$



Scheme 1 Oxidation scheme of EG



Scheme 2 Simplified oxidation scheme of EG

This is a typical form of the rate equation under wet oxidation of organic substrates [4]. The reason why the reaction orders calculated in this work did not agree with Eq. (6) is supposed that the intermediates are neglected in scheme 2.

The yields of OxA and CO_2 were 75.0 C% and 21.3 C% at 250 °C, 1 h, 1000 rpm, EG concentration 0.177 M, NaOH concentration 27.5 mol NaOH / kg- H_2O and P_{O_2} 5 MPa, whereas they were 28.9 C% and 13.7 C% at 200 °C. These facts suggest that the activation energy of OxA formation (E_1) is greater than that of CO_2 (E_2).

Recycling Process of Waste PET

A flowsheet of two stage process in which TPA and OxA are produced from waste PET is shown in Figure 2. The material balance was calculated using the present results. Waste PET is hydrolyzed quantitatively to sodium terephthalate (TPA-Na) and EG in 50 % NaOH solution. TPA is regenerated by addition of sulfuric acid to TPA-Na. EG is oxidized to sodium oxalate (OxA-Na) at 250 °C and oxygen partial pressure of 7 MPa. Though OxA and sodium sulfate are formed by addition of sulfuric acid to OxA-Na, they are able to be separated by cooling and crystallization. In this process, the amounts of TPA and OxA produced from 1,000 kg of waste PET are 865 kg and 375 kg (80.0 % yield). This process needs a large amount of NaOH and sulfuric acid, but we expect the cost-effectiveness of this process by the production of TPA and OxA which are more expensive chemicals than the raw material.

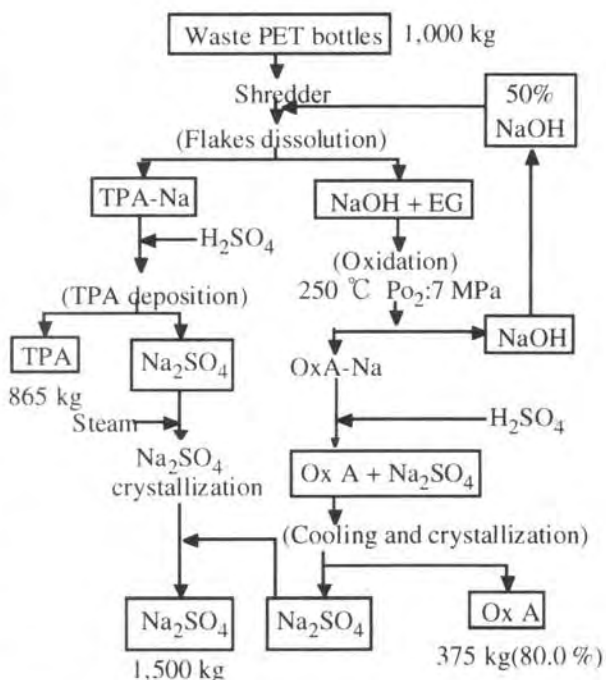


Figure 2 Flow sheet of alkaline hydrolysis-oxidation process of waste PET bottles

References

1. T.Yoshioka, Y.Kamiya, T.Sato and A.Okuwaki, *Proc. 1st Intl. Conf. Solvo-Thermal React.*, 1994, p.76
2. T.Yoshioka, M. Saito and A.Okuwaki, *74th National Meeting of the Chemical Society of Japan*, 1998, p.1148
3. T.Matsuura, "Sanzo Sanka Hannou", Maruzen, Tokyo (1977), p.165
4. Rajesh V. Shende and Vijaykumar V. Mahajani, *Ind. Eng. Chem. Res.*, **36** (11), 4809-4814 (1997)