아임계수 조건에서 **p-xylene** 의 테레프탈산으로의 무촉매 부분 산화 반응

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Uncatalyzed Partial Oxidation of p-Xylene to Terephthalic Acid in Sub-critical Water

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1. Introduction

Terephthalic acid (TPA) has recently become an important, fast-growing chemical as a raw material for polyethylene terephthalate (PET) or polyester fiber. In 1999, ca. 26 million tons of PET was manufactured worldwide, and its growth is estimated at a minimum of 5% annually to the year 2002. Nowadays, most of TPA used worldwide is obtained by selective oxidation, is commercially manufactured by the dioxygen oxidation of *p*-xylene using a catalyst combination of cobalt and manganese salts and a bromide ion promoter in acetic acid medium at 443–483 K. The commercial process has been optimized to the point where typical crude TPA purities of 98–99.5% are produced in yields of 96–97 mol% based on *p*-xylene feed at an oxidizer contact time of 45–90 min [1-5].

However, Chavan et al. [4] pointed out that the following three improvements are desirable in the existing process: (i) reduction or elimination of the significant acetic acid oxidation to CO and CO_2 (5–10 wt.% of TPA, (ii) alternatives to the highly corrosive acetic acid and bromide ion promoters, and (iii) reduction or elimination of the 4-carboxybenzaldehyde and other impurities from crude TPA to eliminate the purification required for the polyester industry.

Kim et al. [1-3] attempted to eliminate corrosion of reactor materials using partial oxidation of *p*-xylene in sub- and supercritical water without a catalyst. H_2O_2 was used for an oxidant and a reaction promoter. They obtained the less product yields compared with former catalytic reactions. In particular, TPA yield was less than 30%. However, they presented economical, environmentally friendly possibility that we may not use catalyst and hazardous solvent for organic synthesis.

Holiday et al. [6] presented that sub-critical water can be used as a synthetic medium for reactions for alkyl aromatic compounds. They obtained a 64% yield of TPA from *p*-xylene with $MnBr_2$ as the catalyst at rising temperature and pressure conditions with time. Dunn et al. [7,8] also reported TPA synthesis in sub- and supercritical water with various catalysts. The highest yield of TPA obtained was 57±15 % in supercritical water and 49±8 % in sub-critical water, respectively. These yields were obtained after the levels of $MnBr_2$ as a catalyst and hydrogen peroxide as an oxidant reached 0.1 and 8.

In this study, partial oxidation of *p*-xylene to TPA was performed in the Hastelloy-C batch reactor without a catalyst in sub- or near-critical water. Sub-critical water was used as a solvent or reaction medium, since the previous research [1-3] showed that toluene yield was unwillingly increased in supercritical water. Hydrogen peroxide was used as oxidant for partial oxidation of *p*-xylene. We added successively hydrogen peroxide to the reactor as the oxidation proceeds. The distribution of reaction products was obtained with time. We inspected the reaction pathway presented by previous researcher through HPLC analysis.

2. Experiments

2.1 Apparatus
We used the batch type reactor. The internal volume of the reactor is 1379 cm^3; its material is used

with a Hastelloy-C autoclave of cylindrical vessel type equipped with a magnet drive agitator having variable-speed arrangements. To be heated and kept at fixed temperature, the reactor was equipped with an electric heater. Reaction temperature was controlled using a temperature controller of an accuracy of 1°C. The pressure gauge was compensated for because a deadweight tester (Superb Instrument Ltd.), release valve, and safety rupture were placed on top of the reactor vessel. A thermocouple was well immersed in the reaction mixture. Water and hydrogen peroxide as an oxidant was fed by high-pressure mini-pumps (Milton Roy Co. model NSI-33R). The feeds were preheated to about 20°C above the reaction temperature and mixed at the T-joint near the reactor. The effluent mixture was depressurized to atmospheric pressure as it passed through a sample loop that consisted of high-pressure valves (HiP Equipment Co.) and a tube (1/4 in. SUS 316).

2.2 Procedure

The autoclave was charged with a known concentration of hydrogen peroxide and water. The injected water was used to remove dissolved air from the distilled water. The reaction mixture was heated to the desired temperature with constant stirring (300 rpm). In this work, temperature was varied from 270 to 380 °C. The amount of water supplied to the reactor with increasing temperature was varied from about 1100 to 250 cm^3. Once the temperature was attained, *p*-xylene was fed to the reactor at a desired experimental amount. To quantify the effect of oxidant in the present work, hydrogen peroxide was first loaded with the stoichiometric requirements for TPA (six molar equivalents) and added successively to the reactor as the oxidation proceeds. In addition, the added amount of water was then fed in the reactor to set the predetermined pressure at reaction temperatures. The samples were cooled instantly at conditions near the ambient pressure in the sample loop. They were finally collected in the sampling vessel for analysis. After sampling, the water pressure was maintained by adding a little water to keep the reaction condition at constant pressure.

2.3 Analysis

Liquid products were analyzed by using a high performance liquid chromatography (HPLC) system that consisted of an isocratic pump (Younglin model M930) with a Waters column of symmetry C-18 (Part No. WAT046980). We did not use gradient elution method and modified the analytical method developed by Viola and Cao [9]. The mobile phase components were 80 vol.% water (HPLC-grade, J. T. Baker), 20 vol.% acetonitrile (HPLC-grade, J. T. Baker) with 1 mL of 85 wt.% phosphoric acid (Aldrich). The injection volume was 20 μL. A constant flow rate of 1.0mL/min was maintained.

3. Results and Discussion

We used hydrogen peroxide as an oxidant or a promoter of oxidation of *p*-xylene. From the proposed reaction pathway, the stoichiometric requirements for partial oxidation to TPA are six molar equivalents of *p*-xylene. Considering purity and molecular weight of chemicals, stoichiometric requirements of hydrogen peroxide solution was 5.5 g per 1 g of *p*-xylene loading. To accelerate and complete the oxidation of *p*-xylene, loading amount of oxidant was, however, used two or three times more than calculated.

3.1 Organic Compounds from Partial Oxidation

In this work, various organic compounds were produced by the partial oxidation of *p*-xylene to TPA. Main products were *p*-tolualdehyde, *p*-toluic acid, terephthal-aldehyde, 4-carboxybenzaldehyde, terephthalic acid, benzaldehyde and benzoic acid. Also, there were small amounts of products such as 4-carboxy-benzyl alcohol, 4-hydroxy benzoic acid, 4-hydroxy-methylbenzaldehyde, 4-hydroxy benzaldehyde, *p*-toluic alcohol. 1,4-Benzenedimethanol was not detected. However, this intermediate must be produced referring to the main reaction pathway.

3.2 Possible Reaction Pathways

Cao et al. [10] proposed reaction pathway for the liquid-phase oxidation *p*-xylene catalyzed by cobalt naphthenate. Kim et al. [2] proposed new reaction pathway through toluene occurred by breaking C-C bond into a benzyl group (-ArCH$_3$) and a methyl group (-CH$_3$). They predicted methyl
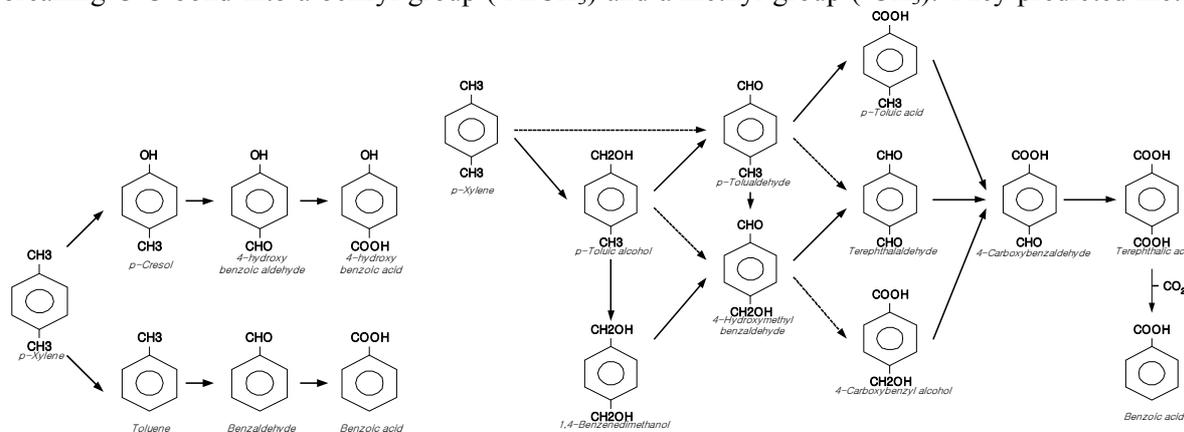
Figure 1. Proposed sub reaction pathway.   **Figure 2. Proposed main reaction pathway.**

group to form methyl alcohol with the excess water. As reaction temperature rises, the decomposition of *p*-xylene to toluene becomes more active, e.g., benzaldehyde and benzoic acid are more produced in supercritical water than sub-critical water. We proposed sub reaction pathway as shown in figure 1. This reaction pathway includes minor products detected by HPLC and produced by oxidation of *p*-cresol as well as toluene. Reaction pathway in figure 1 was only observed in uncatalyzed system [1-3]. We expected that this were due to difficulty in generating methylbenzyl radical (CH$_3$ArCH$_2^{\bullet}$). Higher reaction temperature is indispensable to dissolve *p*-xylene in water. In addition, excessive oxidant is necessary for the oxidation. Hence thermal decomposition of *p*-xylene and substitution with hydroxyl group occurred.

Figure 2 showed the main reaction pathway proposed by this work. This reaction pathway is not much distinct from Cao et al. [10] for catalyzed system and Kim et al. [2] for uncatalyzed system. Recently, Partenheimer [11] reproduced reaction network during the autoxidation of *p*-xylene with a Co/Mn/Br catalyst. He presented relative reactivities for some main products. Generally known, reactivity of *p*-toluic acid is 10 times less than *p*-xylene. Alcohols, such as *p*-toluic alcohol and 4-carboxybenzyl alcohol, have a higher reactivity than aldehydes or *p*-xylene. In figure 3, solid line represents more probable reaction path than dashed line. We expect that the oxidation to aldehydes take place through the hydroxylation of methyl group. However, alcohols were not detected or negligible in our HPLC analysis. This is due to high reactivity of alcohols and the time interval between loading of hydrogen peroxide and first sampling after loading.

3.3 Product Distribution with Time

Figure 3 and 4 presented the concentration distributions of main products by partial oxidation from *p*-xylene to TPA at 350 $^{\circ}$C and 300 $^{\circ}$C with time. Hydrogen peroxide was added to the reactor successively. *p*-Tolualdehyde was first produced and oxidized to *p*-toluic acid, terephthalaldehyde, 4-carboxybenzaldehyde. It is no wonder that final products are carbon dioxide and water. However, we did not analyze gaseous products. TPA and benzoic acid were considered as the final product of partial oxidation of *p*-xylene. As shown in figure 5, there were large amounts of benzoic acid and benzaldehyde instead of TPA, *p*-toluic acid and 4-carboxybenzaldehyde. This is due to thermal decomposition and decarboxylation of TPA. Benzaldeyde concentration increased as thermal decomposition was activated. In addition, as shown in figure 6, decarboxylation of TPA launched as soon as TPA was produced from 4-carboxybenzaldehyde. Therefore, concentration of benzoic acid increased without oxidation of benzaldehyde at 300 $^{\circ}$C.

4. Conclusion

Partial oxidation of *p*-xylene was performed without a catalyst. As temperature rises, thermal
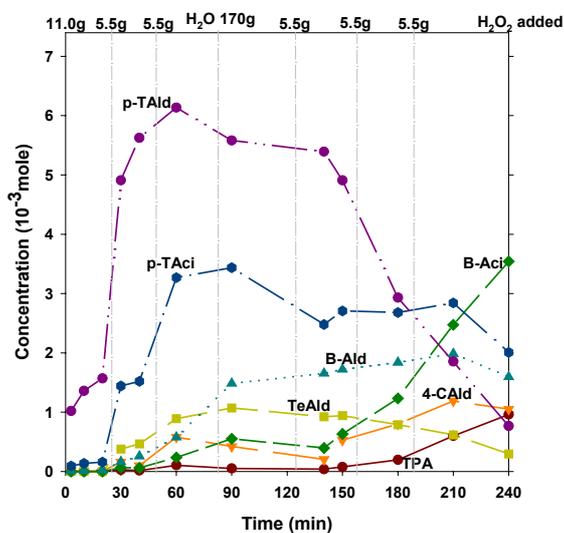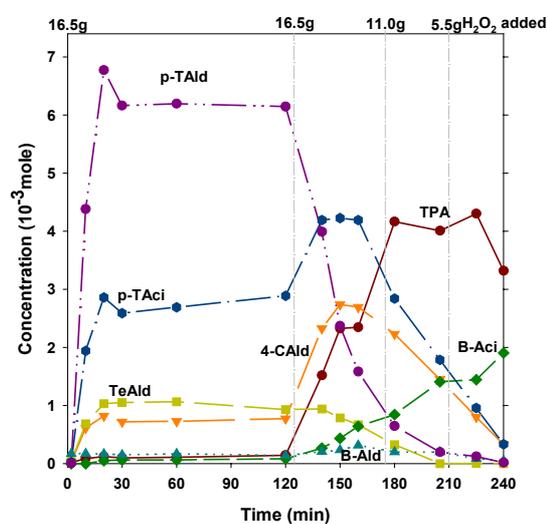

Figure 3. Main products at 350 °C, 230bar.   Figure 4. Main products at 300 °C, 220bar.

decomposition of *p*-xylene launches. Therefore, reaction pathway through toluene becomes important and production of benzoic acid increases. Hydrogen peroxide was used as an oxidant for a partial oxidation. Loading amount of hydrogen peroxide controls the reaction step and production of organic compounds. As soon as TPA is produced from 4-carboxybenzaldehyde, TPA simultaneously begins to decarboxylate into benzoic acid. Furthermore, these carboxylic acids are finally converted into carbon dioxide and water if proper temperature and sufficient oxidant are supported.

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