Analysis and Removal of Residual Acetic Acid in Terephthalic Acid

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Abstract: The residual acetic acid in TPA (terephthalic acid) produced by oxidation of p-xylene was analyzed with a method composed of successive neutralizations and enrichment, and the acetic acid with concentration of below 100 ppm could be determined precisely. The analysis of acetic acid in TPA has been regarded to be very hard due to specific physical properties of TPA. The removal of the acetic acid has been tried with drying or washing with water because the competitiveness of medium purity TPA (MTA or QTA in commercial term) can be increased very much if the residual acetic acid can be removed up to the level of concentration of high purity TPA (PTA in commercial term). It was confirmed that the concentration of acetic acid in medium purity TPA could not be reduced below about 400 ppm with drying at high temperature or washing with water. However, the concentration could be about 30 ppm if the medium purity TPA was maintained for 30 min when about 50% of TPA were dissolved in water. It seems that about half of acetic acid can be removed only after the dissolution of TPA even though half of acetic acid can be removed quite easily. The PTA, produced with hydrogenation in water, also seems to contain about 50 ppm of acetic acid, however, this should be confirmed with more detailed experiment.

Keywords: terephthalic acid, acetic acid, analysis, removal

1. Introduction

Terephthalic acid (TPA), which is mainly used for the production of polyester, is one of the most important chemicals with an annual production capacity of more than 2400000 ton in the year 2000. The production capacity of Korea is highest in the world with the capacity of 45400000 ton [1]. TPA is usually produced by a liquid phase oxidation of p-xylene in acetic acid and classified as high purity TPA (purified TPA or PTA in commercial term) and medium purity TPA (MTA, medium grade TPA or QTA, qualified TPA in commercial term) depending on the quality and purification process such as hydrogenation [2]. The scheme to describe the processes is represented in Figure 1.

![Figure 1. Scheme to produce PTA or MTA/QTA from p-xylene.](image)

The most important differences between PTA and MTA/QTA are the contents of 4-carboxybenzaldehyde (4-CBA) and p-toluic acid, intermediates from p-xylene to TPA, and acetic acid as shown in Table 1 [2]. It is generally accepted that the
quality of PTA is better than that of MTA/QTA because of the purification by hydrogenation in water at high temperature. The 4-CBA, acetic acid and coloring materials are decreased through this hydrogenation. However, the MTA/QTA is relatively inexpensive compared with PTA because of the simplified process.

The total contents of mono acids such as benzoic acid, p-toluic acid and 4-CBA that can be chain stoppers in the polymerization for polyester are not so much different for the case of MTA/QTA and PTA. However, the existence of acetic acid in MTA/QTA can be a serious problem because of corrosion and smell.

MTA/QTA producers may claim that the quality of MTA/QTA is similar to that of PTA if the acetic acid is removed to the level of PTA. In that case, the MTA/QTA can be very competitive because of the lower production cost. Therefore, the removal of acetic acid in TPA is very important considering of the production capacity of TPA. However, up to now no effort to remove the acetic acid has been reported [3].

On the other hand, considering the huge production capacity of TPA, any small improvements in the process are very important. The desirable improvements in the TPA production include [4]: i) decrease the destruction of raw materials and solvent; ii) increase the selectivity of the reaction to eliminate the purification step, hydrogenation in water solvent; iii) replace the corrosive acetic acid with water and HBr with a non-corrosive free radical carrier, respectively. For example, it has been attempted to replace the acetic acid solvent with water [5,6] and to eliminate corrosive bromine component [7,8] and to utilize carbon dioxide as a co-oxidant [9]. They have also been numerous efforts [10-12] to improve the Co/Mn/Br catalyst system including the incorporation of transition, lanthanide and alkali metals such as Zr, Ce, Hf, Mo, Na and K.

However, the attempts have not been so successful to be applied in a commercial operation. Because of the diminishing returns of research on TPA process [13] due to the long history of TPA production and research, the improvement of quality of MTA/QTA by removal of the residual acetic acid is very important.

The analysis of acetic acid in TPA has been regarded as a very difficult process because of the following reasons: i) The acidity of acetic acid (pKa=4.75) is very similar to that of TPA (pKa of 1st acid=3.51). ii) The solubility of TPA is extremely low. For example the solubility at 200°C in water and acetic acid is 1.7 g and 1.8 g/100 g-solvent, respectively [14]. iii) The TPA cannot be liquefied or gasified easily to have the sublimation temperature of 404°C. iv) The concentration of acetic acid in TPA is less than 1000 ppm even though the concentration of TPA is more than 99%.

The acetic acid in TPA can be analyzed with a few methods, but the detection limit is very high and the reproducibility is very low. The TPA, after esterification with excess alcohol such as methanol, can be analyzed with GC etc. The concentration of acetic acid that can be analyzed is very high due to the dilution with excess alcohol. The degree of esterification of TPA and acetic acid should be equal or checked. Moreover, the esters, formed from TPA and alcohol, such as dimethyl terephthalate (DMT) are not so easy because the boiling point is still high (284°C) and solubility is low (1.0 g of DMT dissolves in 100 g of methanol at 25°C).

The ion chromatography has been reported to be used for the analysis of acetic acid in TPA [15]. However, the detection limit in actual condition has been very high of about 500 ppm.

Any method to determine the residual aliphatic acid (with concentration below 100 ppm) such as acetic acid in aromatic acid (such as TPA, isophthalic acid (IPA), 2,6-naphthalenedicarboxylic acid (NDCA)) has not been reported yet [3], as far as the author knows, even though the concentration of aliphatic acid is very important to the end users and producers of TPA, IPA and NDCA etc.

In this paper, analysis method to determine trace amount of acetic acid and the study to remove the acetic acid are reported.

2. Experimental

2.1. Analysis of Acetic Acid

The residual acetic acid was concentrated via successive neutralizations after separation of TPA, and was analyzed with GC.

The analysis procedure involve following consecutive steps: weighing and dissolution, addition of an international standard, acidification, separation of TPA, salt formation of acetic acid and internal standard, concentration via evaporation of water, acidification (to re-form free acids) and analysis. The detailed procedure is described in Table 2.

The separated acetic acid with internal standard was analyzed using GC (HP 5890) with FID detector and the column was FFAP.

2.2. Removal of Acetic Acid

The acetic acid was removed with drying in a fluid bed dryer, in vacuum in a rotary evaporator or washing with water at high temperature. Nitrogen was utilized as sweeping gas for drying. A 1000 cc Autoclave was used to wash out the acetic acid in TPA at high temperature. The concentration of TPA in water slurry was 15-25 wt%.

The concentration of acetic acid after the removal with drying was checked with the method described above. The removed acetic acid to water solvent through washing with water was also determined periodically, after sampling of the liquid portion, by analysis of the water solution with GC. The solid after separation of water was also analyzed to confirm the analysis result of the liquid.
Table 2. Detailed Procedure to Analyze the Residual Acetic Acid in TPA

<table>
<thead>
<tr>
<th>Step</th>
<th>Procedure</th>
<th>Purpose or remark</th>
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<tbody>
<tr>
<td>1</td>
<td>Weighing of about 10 g of sample</td>
<td>0.06 M TPA or 0.12 M H⁺</td>
</tr>
<tr>
<td>2</td>
<td>Dissolution in 65 mL of 2 N KOH</td>
<td>0.13 M OH⁻</td>
</tr>
<tr>
<td>3</td>
<td>Addition of 2 g of international standard (usually 2000 ppm of n-proionic acid in water)</td>
<td>400 ppm to TPA</td>
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<tr>
<td>4</td>
<td>Addition of 40 mL of water</td>
<td>Dilution</td>
</tr>
<tr>
<td>5</td>
<td>Addition of 75 mL of 2 N HCl</td>
<td>1) Precipitation of TPA</td>
</tr>
<tr>
<td>6</td>
<td>Filter out the precipitated TPA</td>
<td>2) 0.15 M H⁺ (0.02 M excess)</td>
</tr>
<tr>
<td>7</td>
<td>Addition of 20 mL of 2 N KOH</td>
<td>0.04 M OH⁻ (0.02 M excess)</td>
</tr>
<tr>
<td>8</td>
<td>Evaporation of the solution</td>
<td>1) Concentration of the KOAc</td>
</tr>
<tr>
<td>9</td>
<td>Addition of 20 mL of 2 N HCl</td>
<td>2) Residue: KCl, KOAc, KOH, CH₃CH₂COOK</td>
</tr>
<tr>
<td>10</td>
<td>Analysis with GC</td>
<td>1) 0.04 M H⁺ (0.02 M excess)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2) The concentration of acetic acid and n-proionic acid is about 1/2 of the original sample</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FID detector, PFAP column</td>
</tr>
</tbody>
</table>

2.3. Reagent

All TPA samples were commercial products manufactured in plants of Korea. The TPA samples were used without any treatment.

All other chemicals such as acetic acid and n-proionic acid were guaranteed grade reagents supplied by Aldrich.

3. Results and Discussion

3.1. Analysis of Acetic Acid

The quantitative analysis of acetic acid in medium purity TPA has been regarded as very difficult because the concentration of acetic acid is just about several hundreds ppm in TPA (>96%) whose acidity is very similar to that of acetic acid. Moreover, the solubility of TPA is extremely low and the sublimation temperature is 404 °C.

However, the solubility difference between acetic acid and TPA is remarkable. In this study, therefore, the sample was dissolved in an alkaline solution as a salt and acidified subsequently to acetic acid and TPA to precipitate the TPA selectively. The acetic acid and internal standard can be concentrated, after removal of TPA, via salt formation with excess alkali and subsequent evaporation of water. The salts were acidified to re-form free acids for analysis with GC. The detailed procedure to analyze the concentration of acetic acid is described in Table 2.

The concentration of acetic acid and internal standard (before the analysis with GC) is about 1/2 to that of the original sample. Therefore, the detection limit can be very low of about dozens of ppm.

The GC chart of acetic acid (150 ppm) and internal standard, n-proionic acid (400 ppm) added to TPA is shown in Figure 2 and shows that the acetic acid can be analyzed quite precisely with the method.

The accuracy and reliability of the analysis method are represented in Figure 3. The GC peak area ratio of acetic acid and internal standard, proionic acid, depends linearly with the added acetic acid concentration. Therefore, the concentration of residual acetic acid in TPA can be analyzed reproducibly.

![Figure 2. Typical GC chart of acetic acid and n-proionic acid added to TPA.](image)

![Figure 3. The dependence of GC peak area ratio (acetic acid/n-proionic acid) on the concentration of added acetic acid.](image)
The concentration of acetic acid in PTA (high purity TPA) purified with hydrogenation in water was analyzed to be about 50 ppm even without the addition of extra acetic acid. It may be assumed that the acetic acid used as solvent in the oxidation of p-xylene can be removed even after the dissolution in water through the dehydration process for PTA. However, this residual acetic acid in PTA should be analyzed after removal in water to support this finding.

3.2. Removal of Acetic Acid

The competitiveness of MTA/QTA compared with PTA can be very high if the acetic acid in MTA/QTA can be removed up to the level of PTA with a simple or inexpensive process. Therefore, the removal of acetic acid was tried with drying or washing in water.

The acetic acid was very hard to be removed with simple drying at higher temperature (160~180 ℃) compared with the temperature (about 130~140 ℃) of a dryer used in a commercial plant as shown in Figure 4. The concentration of acetic acid was as high as 404 ppm after drying for 17 h at 180 ℃ and was 579 and 460 ppm after drying for 4 h at 160 and 180 ℃, respectively. Drying in a vacuum was not so efficient to remove the acetic acid either. The residual concentration of acetic acid after drying in vacuum at 90 ℃ was similar to that after drying in 180 ℃ with flowing nitrogen.

The activation energy for desorption of physisorbed species is known to be about 25 kJ/mol [16]. The desorption rate at 180 ℃ will be 1.36 times that at 160 ℃ if the activation energy for desorption is 25 kJ/mol. The ratios of desorption rate determined by this experiment were 1.34, 1.44, and 1.36 for 0.5, 1, and 4 h of drying, respectively. Therefore, it can be supposed that the drying at the temperature of 160~180 ℃ corresponds only to the desorption of physisorbed acetic acid. It can be understood that the chemisorbed acetic acid in TPA cannot be removed with drying at the temperature range. The chemisorbed acetic acid may be estimated to be about 400 ppm.

On the other hand, the drying of the GTA, produced in a pilot plant, with high content of acetic acid of 5% was very efficient. The concentration of acetic acid decreased from 5.0% to about 0.1% in 30 min at 180 ℃. The physisorbed acetic acid can be easily removed by a simple drying.

The TPA containing acetic acid was washed with water after partial dissolution of TPA to remove the acetic acid and the results are displayed in Figure 5. The solubility of TPA at 160, 200 and 240 ℃ in water is 0.8, 1.7 and 9 g/100 g, respectively, as shown in Table 3. The concentration of TPA in water slurry in this experiment was 15 or 25%. The portion of TPA, when the concentration of TPA is 25%, that dissolves is about 51 and 27.0% when the temperature is 200 and 240 ℃, respectively. The portion is 45.0% when the TPA concentration and temperature are 15% and 240 ℃, respectively. Therefore, the treatment with water at 200 or 160 ℃ can be regarded as pure washing.

The concentration of residual acetic acid after washing at 160 ~200 ℃ is quite high, just a bit lower than the concentration for the case with drying. However, the acetic acid could be removed up to 50 ppm in 45 min when the temperature was

![Figure 4. The concentration of residual acetic acid after drying in various conditions.](image1)

![Figure 5. The concentration of residual acetic acid after washing in water in various conditions (temperature and concentration of TPA).](image2)

<table>
<thead>
<tr>
<th>Temperature (℃)</th>
<th>In water</th>
<th>In acetic acid</th>
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<tbody>
<tr>
<td>25</td>
<td>1.9×10⁻²</td>
<td>3.5×10⁻²</td>
</tr>
<tr>
<td>120</td>
<td>8.0×10⁻²</td>
<td>0.3</td>
</tr>
<tr>
<td>160</td>
<td>0.38</td>
<td>0.75</td>
</tr>
<tr>
<td>200</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>240</td>
<td>9</td>
<td>4.5</td>
</tr>
</tbody>
</table>

240 ℃. At this temperature, 27% of TPA dissolves. If the content of TPA was decreased up to 15% (45% of TPA dissolves), the acetic acid can be removed more easily. The concentration of residual acetic acid was 28 ppm in 30 min. The acetic acid may be supposed to be removed only after dissolution of considerable amount of TPA. The chemisorbed acetic acid is imagined to be in the lattice of TPA which is described in a reference [17].

4. Summary and Conclusion

The residual acetic acid in TPA can be analyzed reproducibly via the enrichment of acetic acid through consecutive neutralizations and evaporation of water solvent. The acetic acid in TPA is quite hard to be removed with a simple process such as drying or washing in water. However, the acetic acid can be removed to less than 50 ppm only after dissolution of considerable amount of TPA in water. The PTA purified with hydrogenation in water solvent seems to contain about 50 ppm of acetic acid. However, this should be confirmed in more detail.

참 고 문 현

2. http://www.samnam.co.kr/english