다변량 통계 공정 모델을 이용한 PTA 공정에서 품질 제어

한인수, 김민진, 한종훈
포항공과대학교 화학공학과

Product Quality Control in a PTA Process using Multivariate Statistical Process Models

In-Su Han, Minjin Kim, Chonghun Han
Department of Chemical Engineering, Pohang University of Science and Technology

Introduction

Terephthalic acid is a monomer used to manufacture PET (polyethylene terephthalate), which then is formed into films, textiles, bottles, and plastic molds. Since the demand for terephthalic acid has been growing steadily and the market is large, the manufacturing processes are receiving increased attention. Several commercial processes each licensed by Amoco, Estman-Kodak, or Mitsubishi are being operated to manufacture terephthalic acid in the world. In all these commercial processes, *p*-xylene is partially oxidized with air to form terephthalic acid, and 4-CBA (4-carboxybenzaldehyde) is inevitably formed as an undesirable impurity during the oxidation. The amount of 4-CBA contained in the product determines the quality of terephthalic acid because the 4-CBA prevents the terephthalic acid from being polymerized stably in the PET manufacturing processes. Thus, the amount of 4-CBA should be minimized as possible as the process can achieve, and the variations in the 4-CBA content should be minimized as well so that the quality variations in the polymer product from terephthalic acid can be decreased. Therefore, the industry has been striving to minimize the 4-CBA content and its variability in the final product, through various manners such as modeling, optimizations, controls, and statistical analyses [Jaisinghani et al., 1997; Cincotti et al., 1999].

Multivariate statistical projection methods, such as PCA (principal component analysis), PCR (principal component regression), or PLS (partial least squares) methods, are widely used as powerful tools to identify sources of quality deviations and process faults and to model processes and product qualities in various industries. Eriksson et al. [1995] performed multivariate analyses of aquatic toxicity data using PLS method and compared its performance with a MLR (multiple linear regression) method. MacGregor and Kourti [1995] gave an overview of these methods and applied PCA and PLS methods to an industrial polymerization process for online monitoring and fault diagnosis.

In this study, we will present an application of multivariate statistical projection methods to an industrial terephthalic acid manufacturing process in order to identify and eliminate the major sources of the variations in the 4-CBA content in the terephthalic acid product. Process and quality measurement data are modeled and analyzed using partial least squares methods to find the major sources of the quality variability and then to examine the effects of eliminating these sources on the variability in the product quality. In addition, we will propose the control schemes to eliminate these sources through designing a control system and to set up a new operating condition through PLS modeling.

Process Description

A commercial process capable of processing *p*-xylene of about 430,000 tons per year is being currently operated in Korea to manufacture terephthalic acid. Figure 1 shows a simplified process flow diagram of this process consisting of major six unit processes: the oxidation, the centrifuging, the digestion, the filtering and drying, the catalyst purification, and the solvent separation process. In the oxidation process, pressurized-air directly oxidizes *p*-xylene with a combination of cobalt, manganese, and bromine as catalyst and with acetic acid as solvent. Crude terephthalic acid containing a large amount of 4-CBA is produced from the oxidation. During the oxidation reaction, terephthalic acid comes inevitably with 4-CBA that is an undesirable impurity and its concentration in the crude terephthalic acid is typically ranging from 3000 and 8000 ppm. After the oxidation, a portion of the crude terephthalic acid produced from the oxidation process is sold as a product after being filtered and dried in the filtering and drying process, and the rest in slurry is sent to the centrifuging process. In the centrifuging process, catalyst liquid is separated from the slurry and then is recycled to the catalyst purification process. After centrifuging, the crude terephthalic acid along with a small amount of catalyst is further oxidized to reduce the 4-CBA, thus converting into purified terephthalic acid. Small amount of pressurized air is supplied for oxidation and the concentration of 4-CBA is greatly lowered below 150 ppm in the digestion process. The filtering and drying process is responsible for filtering solid-type impurities and for drying wet terephthalic acid to make the final product as a form of dried-powder. The solvent separation process consisting of several distillation columns serves to separate the water generated by the oxidations from acid-water mixture, and the concentrated acetic acid is then recycled to various unit processes. Since heavy organic compounds, which are generated during the oxidations, contaminate the catalyst in liquid solvent, the catalyst purification process purifies the catalyst by separating the organic compounds from the catalyst solvent using several distillation columns.

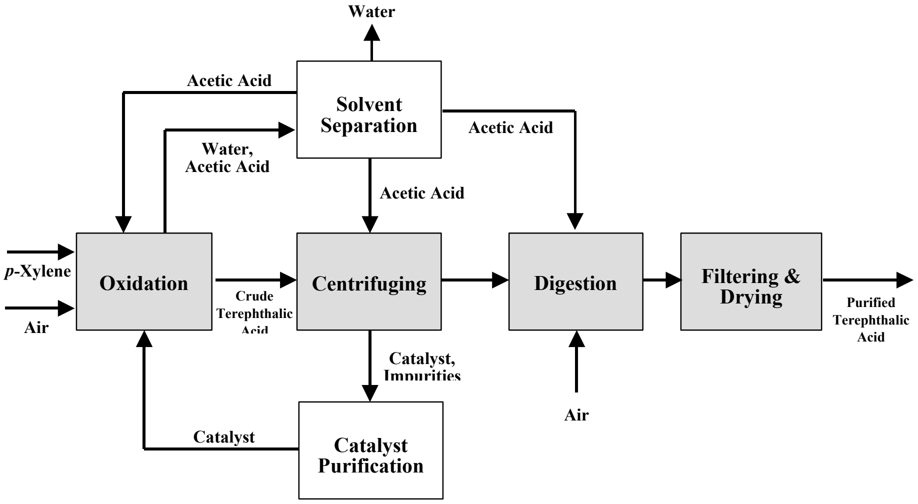

Figure 1. Simplified process flow diagram of a terephthalic acid manufacturing process.

Process Modeling and Analysis

The concentration of 4-CBA in purified terephthalic acid (final product) is the major quality variable in terephthalic acid manufacturing processes. Hence, the key process variables affecting the oxidations of *p*-xylene and 4-CBA should be identified first to control the 4-CBA within a desired degree. In the industrial process shown in Fig. 1, the average concentration of 4-CBA over a certain period is quite low enough to satisfy the PET manufacturers for which the purified terephthalic acid is supplied. However, there are large fluctuations in the concentration of 4-CBA, which causes the quality control to be difficult in the PET manufacturing processes. Not knowing exact sources of the quality fluctuations, they have had trouble controlling and reducing the variability in the product quality. In this section, first, the major sources of 4-CBA fluctuations are found out and then the effects of eliminating these sources on the variability in the 4-CBA content are examined through PLS modeling. PLS models for the oxidation and digestion processes are built from the data sets to identify the correlations between the 4-CBA concentration and the measurements for the process variables and catalyst concentrations. After performing the cross-validation of the unfolded data set, the final PLS model for the oxidation process has seven latent variables and explains 62.2% of the variance in the 4-CBA concentrations.

Results and Discussion

Figure 2 compares the observed and predicted values of the 4-CBA concentrations in the crude terephthalic acid from the oxidation process. As shown in the figure, the predicted values agree with the observed values in trend and most of the deviations from the average value can be predicted using the PLS model. Figure 3a shows the regression coefficients of the PLS model for the oxidation process. The higher a bar in the figure is, the more effect on the quality variable the corresponding variable has. And the sign of a regression coefficient denotes the direction of the effect on the quality variable. As shown in the figure, the concentrations of the catalysts (Mn and Br) into the oxidation process are strongly correlated to the 4-CBA concentrations in the crude terephthalic acid. It means that small fluctuations in the catalyst concentrations lead to large variations in the concentration of the 4-CBA. The process variables (V3, V4, V8 and V10) concerned with the process throughput also highly affect the variability in the concentration of the 4-CBA. Therefore, it can be concluded that the variations in the catalyst concentration and the changes in the process throughput are the main causes of the variability in the concentration of the 4-CBA in crude terephthalic acid. Figure 3b draws the regression coefficients of the PLS model for the digestion process. As can be seen in the figure, the 4-CBA in the crude terephthalic acid is strongly correlated with the concentration of the 4-CBA in the purified terephthalic acid. It means that most of the variations in the final quality is propagated from the oxidation process and thus that the stabilization of the oxidation process is very important to reduce the variability in the concentration of the 4-CBA in the final product.

Conclusions

Multivariate statistical projection methods were applied to an industrial chemical process, in order to reduce the variations in the product quality in a terephthalic acid manufacturing. Process and quality measurement data were modeled and analyzed using partial least squares methods to find out the sources of quality variability and to simulate the effects of these sources on the product quality. The results show that the major sources that cause the final product quality to vary highly are the variability in catalyst concentration and the changes in process throughput, and reveal that the standard deviation of the product quality after eliminating both two sources can be reduced by about 37 percent compared to the present value. To eliminate the major sources found from the analyses, it was proposed that the catalyst concentration in the acid solvent flowing into the oxidation reactors should be always maintained at a certain level over a long period of operating time by employing an online measurement and control system. In addition, a new operating condition was obtained from partial least squares modeling to cope with the frequent changes in process throughput so that the quality variations can be minimized.

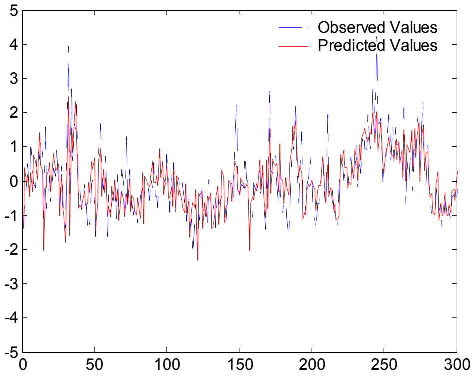

Figure 2. Comparison between the observed and the predicted values of the 4-CBA concentrations.

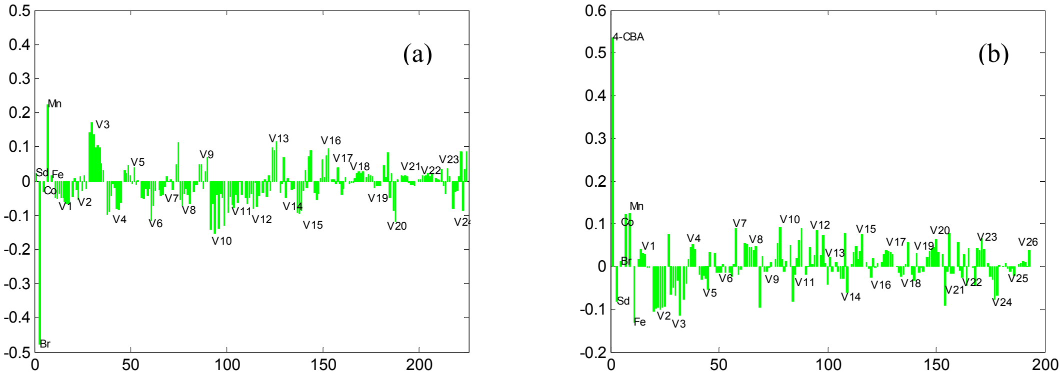

Figure 3. PLS regression coefficients for (a) the oxidation model and (b) the digestion model.

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