Analysis and Modeling of Industrial Purified Terephthalic Acid Oxidation Process

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Abstract: A mathematic model to predict the concentration of 4-carboxy-benzaldhyde (4-CBA) for an industrial Purified Terephthalic Acid (PTA) oxidation unit is built in this paper. The model is based on a mechanism model from the results of bench-scale laboratory experiment and chemical reaction principle, which is structured into two series ideal CSTR models. Six plant factors are designed to correct the deviation between the laboratory model and the industrial practice. For the existing of substantial time delays between process variables and quality variable, the weighted moving average method is applied to make each variable be in same time slice. The analysis of process data by projection on latent variables of Partial Least Square (PLS) and analysis of Hotelling's T-squared statistic value of Principal Component Analysis (PCA) are gave to discriminate the operating data into normal operating part and load down and load up operating part. At the each operating part, the typical data are selected to regress the plant factors. The proposed model predictive result follows the tracks of the observed value quite well. Compared with the empirical Amoco model, the proposed model is regarded as to be more suitable to be applied to industrial online soft sensor.

Key Words: Purified Terephthalic acid (PTA) process, mechanism model, plant factor, Partial Least Square (PLS), Principal Component Analysis (PCA), time delay

1. INTRODUCTION

In this Purified Terephthalic acid (PTA) oxidation reaction, a proprietary process of Amoco Chemical Company is employed for the catalytic liquid phase air oxidation of paraxilene. More than 30 patents about PTA oxidation process and the design of its oxidation reactor have been proposed in the past decade (Li, et al., 2001). The research works about oxidation mechanism with high temperature and normal pressure also have obtained many progresses (Lindahl, et al., 1989, Ge, 1993, Wang, 2001). Lindahl, et al. (1989) gave a set of empirical mathematical relationships between the oxygen uptake in the first crystallizer, the CO2 in the vent gas from the reactor stage and 4-carboxy-benzaldhyde (4-CBA) content levels. But the empirical model needs a bulk of data to regress model parameters and often suitable to a limited operating region. Ge (1993) provided the experiment results of catalytic oxidation kinetics of acetic acid-p-xylene system in liquid phase qualitatively. Wang (2001) proposed a first principle model based on bench-scale laboratory results. It simulated the effect of reactive temperature, catalyst ingredient and concentration, residence time, vent oxygen concentration to the concentration of the

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reactants. But the experimental model was only verified by few industrial data, and many of industrial application problems were not settled.

The paper proposes a practical mathematic model to predict the concentration of 4-carboxy -benzaldhyde (4-CBA) for an industrial purified terephthalic acid (PTA) oxidation unit. The first principle model based on laboratory experiments is applied and modified according to the analysis of the process. The main works comprise: 1. obtaining 133 sets of process variables and corresponding quality variables by considering the time delay between them with weighted moving average method; 2. distinguishing the operating into normal operating and load down and load up operating by projection on latent variables of Partial Least Square (PLS) and analysis of Hotelling's T-squared statistic value of Principal Component Analysis (PCA); 3. configuring and regressing six plant factors to correct the deviation between the laboratory experiment and the industrial process. The model is composed of two series CSTR ideal models. The plant factors are regressed by several sets of typical industrial data. The predictive accuracy of the process model could satisfy the accuracy requirement of online soft sensor.

2. PTA OXIDATION PROCESS

Fig. 1 presents the oxidation reaction mechanism commonly used (Wang, 2001). The oxidation reaction sequence of PX generates three kinds of intermediates, p-tolualdehyde (TALD), p-toluic acid (P-T) and 4-carboxybenza-ldehyde (4-CBA).

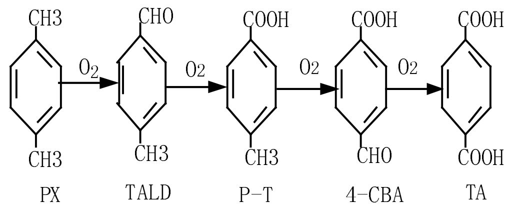

Fig. 1. The oxidation reaction process mechanism of PX

The industrial PTA oxidation process flowsheet is shown in Fig. 2. Paraxylene (PX), acetic acid solvent, promoter, and catalyst are continuously metered into feed mixing tank. The residence time is approximately 25 minutes. The mixed stream pumps the reactor, and the air are fed to the reactor through fourinlets. The oxidation reaction is conduced in two stages, first stage being the agitated oxidation reactor, while the second stage is the agitated first crystallizer. Exothermic heat of reaction is removed by condensing the boiling reaction solvent. A portion of this condensate is withdrawn to control the water concentration in the reactor, and the remainder is refluxed to the reactor.

Reactor effluent is depressurized and cooled to filtering conditions in a series of three crystallizing vessels (first crystallizer, second crystallizer and third crystallizer) for the secondary reaction and crystallization step. Air is fed to the first crystallizer for additional reaction, which used to do polishing oxidation of unreacted paraxylene from the reactor. Precipitated terephthalic acid (TA) is recovered by filtering and drying. The crude TA solids are conveyed to the purification section feed silos

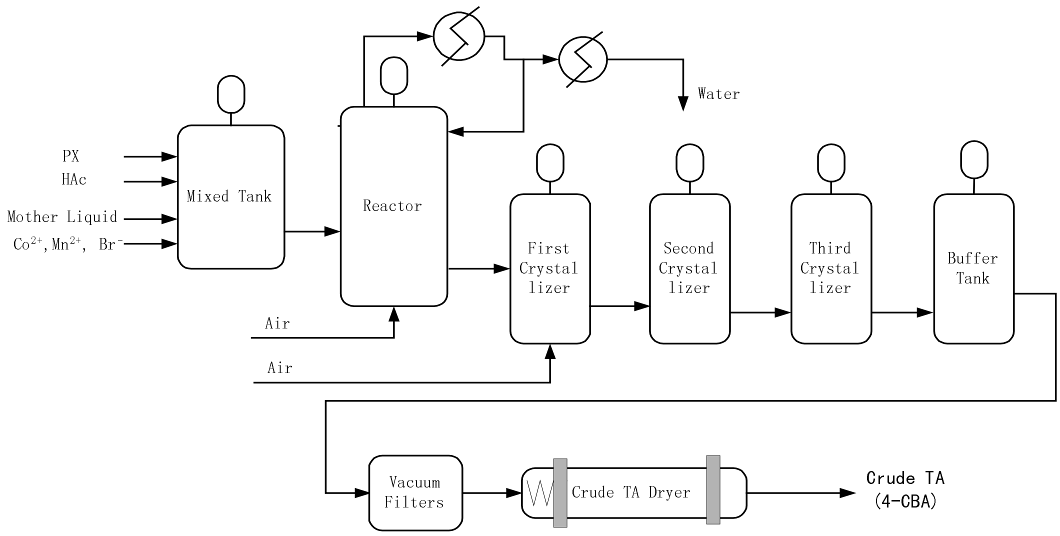

Fig. 2. Schematic layout of PTA Oxidation process

for additional processing as shown in Fig. 2.

Autoxidation of PX in acetic acid solvent with cobalt acetate, manganese acetate, and hydrobromic acid as catalysis proceeds by the following overall reaction to afford terephthalic acid in 95-96% molar yield. The combined yield of the intermediates (4-carboxybenzaldehyde, p-toluic acid and p-tolualdehyde) is about 3%. The detailed discussion about the oxidation mechanism of para-xylene can be found in Lindahl, et al. (1989), Ge (1993) and Wang (2001).

In the oxidation process, the concentration of 4-CBA is regarded as observer of the oxidation reactive progress. The 4-CBA content should be controlled in an interval. Excessive content level may lead to over-oxidation and loss more acetic acid, whereas low level represents under-oxidation and insufficient for PX convert to TA.

The concentration of 4-CBA is related with oxidation process. Therefore, the variables affect the oxidation process as well as the concentration of 4-CBA. In the oxidation reactor, the affect variables of the reactive system mostly are the residence time of reaction, the ratio of PX to acetic acid, the ingredient and the concentration of catalyst, reaction temperature and pressure, the partial pressure of oxygen and water content in the reactor. After the comparison of these variables and process variables, 10 process variables are selected as input variables of the model, which shown in Table 1.

The schematic layout of PTA oxidation process in Fig. 2 shows that there are exist substantial time delay between the different process variables and the quality variable. Every tank has residence time from 15 minutes to 71 minutes. The total time delay of the process is about 200 minutes. The sample frequency of 4-CBA from the crude TA dryer is 3 times a day by laboratory. While the process data pick periodic is 30 seconds by DCS.

The preliminary work of process modeling is to collect the process data and corresponding quality data as many as possible. Here the 'corresponding' mean both the time delay and sample frequency of the two kinds of data are considered.

Table 1. The all variables of the process model.

No.	Variable	Time delay(min)	Sample frequency
	Inputs		
1	Paraxylene to feed mixing tank	205	30 s
2	Feed to reactor	180	30 s
3	Catalyst concentration	185	30 s
4	Reactor temperature	110	30 s
5	Level of reactor	110	30 s
6	Reactor condenser to water withdraw	95	30 s
7	Vent O2 concentration from the reactor	95	30 s
8	Total water withdrawal	90	30 s
9	First crystallizer temperature	75	30 s
10	Vent O2 concentration from the first crystallizer	70	30 s
	Output		
11	4-CBA concentration in the crude TA	0	8 hours

3. ANALYSIS AND MODELING OF INDUSTRIAL PTA OXIDATION PROCXESS

According to the industrial process, the model is composed of two series CSTR ideal models. The two ideal CSTR models denote the oxidation reactor and the first crystallizer, respectively. Each of them follows with the mechanism model developed by Wang (Wang, 2001). The feed component of the first crystallizer is the effluent of the oxidation reactor.

Due to many factors, the plant data contain much gross error and not corresponded to each other well. Some for the measure instruments are often not well calibrated, for the process is not stable enough or the inaccuracy of quality data caused by artificial sample and analysis. In order to utilize plant data to build the industrial process model, it is necessary to screen the data using statistical methods. By these techniques some of the inherent characteristics of the data can be incorporated into the model thereby, increasing the model accuracy.

3.1 Preprocessing industrial data

For the oxidation process comprises nearly 10 tanks shown at Fig. 2, the residence time of the all tanks is about 200 minutes. Therefore it is reasonable to expect that not the current values of these variables, but more so the historical values of the variables over the last 200 minutes are likely to have a profound effect on the output variables at the present time. To take care of the historical effect of these variables a weighted moving average method is used to define the model input variables (Radhakrishnan, et al. 2000)

$$\begin{aligned} X(t) = {} & 0.05x(t-2t_d) + 0.1x(t-1.5t_d) + \\ & 0.2x(t-1.2t_d) + 0.4x(t-t_d) + \\ & 0.2x(t-0.5t_d) + 0.05x(t-0.2t_d) \end{aligned} \quad (1)$$

where $X(t)$ is the value at time t, $x(t-i)$ is the value at time $t-i$ of each input variables and t_d is time delay value of the variable, which is given in Table 1.

That is, the process variables at time t are the combination values of their historical data at time point $0.2t_d$, $0.5t_d$, t_d, $1.2t_d$, $1.5t_d$ and $2t_d$ before current. All of the process variables were defined in this manner as the input of the model. The weights values were decided on the basis of a residence time distribution study from the investigation on the operators and engineers and the analysis of process history data.

3.2 Analyzing the oxidation process

PLS and PCA are used to extract the information in the data by projecting them onto low dimensional spaces defined by the latent variables or principal components. For they are capable of tracking the progress of process and detecting the occurrence of observable upsets, PLS and PCA are widely applied in process analysis, monitor, fault diagnosis and statistical process control (Kourti, et al., 1995, MacGregor, et al. 1995).

The projection of the first two latent variables of PLS and Hotelling's T-squared statistic value of PCA to analysis historical data are illustrated in Fig. 3 and Fig. 4 from 133 sets of data of industrial PTA oxidation process.

It is obviously that there are two operating regions of the industrial data involved. Region I has the most number of points and the highest density, which belong to normal operating region and identified by the factory. Region II is a little away from region I and includes 6 points. This region is characterized as periodically load down and load up process for purging the dryer operation and adjusting the buffer tank, which the operating region is widely compared with region I.

The two operating regions have significant differences intrinsically. Thus, it is reasonable to divide the process model into two parts: normal operating part and load down and load up operating part, and be treated in different plant factors.

3.3 Setting the plant factors

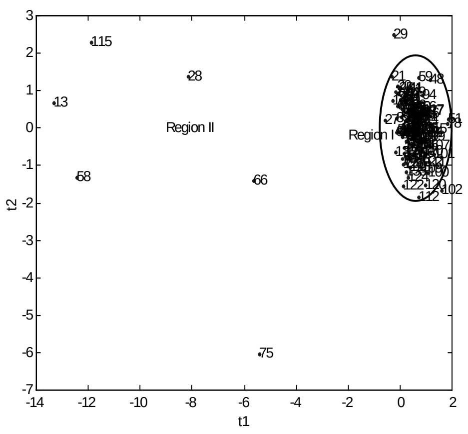

Fig. 3. Projection on latent variables determined by PLS of PTA oxidation process data

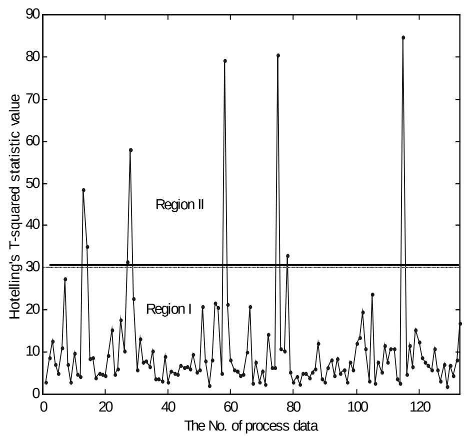

Fig. 4. Hotelling's T^2 statistic value determined by PCA of PTA oxidation process data

In the PTA oxidation process, many other factors are also effect the reaction but be hard to described in the mathematical model. For instance, the design of feed inlet of air flow, the existing of foam in the vapor phase, the effect of crystallized product to main oxidation reaction, the occurrence of subsidiary reaction and its product, the effects of other process parameters from the second crystallizer to the dryer sampling valve, etc.

To correct the deviation between the laboratory condition and industrial condition, six plant factors are set in the principle model. They correct the oxidation reactor's reactive kinetics parameters, k, the residence time, r, the feed concentration of PX, and the first crystallizer's reactive kinetics parameters, k, the residence time, r and the final discharge concentration of 4-CBA, respectively.

3.4 Regressing the plant factors

In this section, 6 sets of normal operating data from 127 total and 3 sets of load down and load up operating data from 6 total are selected as standard industrial process data to regress the two sets of plant factors, respectively. The regression algorithm is the modified Levenberg -Marquardt algorithm (Gao, 1995). It uses differential approximate the Jacobian matrix and the initial damped factor set to 40000, the adjust coefficient set to 2. To control the rate of convergence not less than a certain value, the damped factor should be larger than a threshold value. The enlarging damped factor procedure is limited to run 2 times continuously at one time and the initial value is set to initial damped factor at every time the procedure be called.

The result of plant factor regression is given in the table 2. After obtained the plant factors, the model is determined and able to predict the concentration of 4-CBA in the crude TA as a kernel part of on-line soft sensor.

Table 2. The two sets of plant factors regress results from each operating data.

	F1	F2	F3	F4	F5	F6
Normal operating	1.5911	0.8701	0.9838	0.1215	1.2705	0.3529
Load down and load up operating	1.1807	0.7677	0.5197	0.6395	1.0532	0.8768

4. RESULTS & DISCUSSION

The comparison of predictive results of the proposed model, Amoco empirical model (Lindahl, et al., 1989) and observed concentration of 4-CBA is given in Fig. 5. It is obviously illustrate that the predictive result of the proposed model follows to the tracks of the observed value quite well, especially at the normal operating part, whereas the predictive result of Amoco model only lie near the mean value of observed in normal operating region and can't well follow the observed change trend. This feature is important in applying to industrial online soft sensor, which the qualitative tendency is the preference. Though the predictive mean error of our model is $\pm 1.54\%$ and the maximum error is $\pm 6.03\%$, which are both a little worse than those of the Amoco model, $\pm 1.49\%$ and $\pm 4.67\%$.
At the points 7, 88 and 105, the observed quality value is badly higher than its neighbors. But its associated process variables have not marked changes compared with others. Similarly, the observed values at points 25, 26, 54 and 65 are less than the corresponding points of the model predict values extraordinary. Thus, these points can be regarded as outliers that their process data are anomalous. The predict result of load down and load up operating part are not very well as that of the normal operating part, which contributes to most predictive error for the whole MSE, because it is not operated at steady state that both the process variables and their residence time are under largely dynamic change. But the predictive trend of load down and load up operating is quite well, which was also confirmed by the engineers.

On the whole, the proposed model predictive accuracy is satisfied with the requirement of online soft sensor.

5. CONCLUSION

This paper proposed a practical mathematic model to predict the concentration of 4-CBA in PTA oxidation process. The model is based on a first principle model and modified according to the industrial practice. Several technologies are

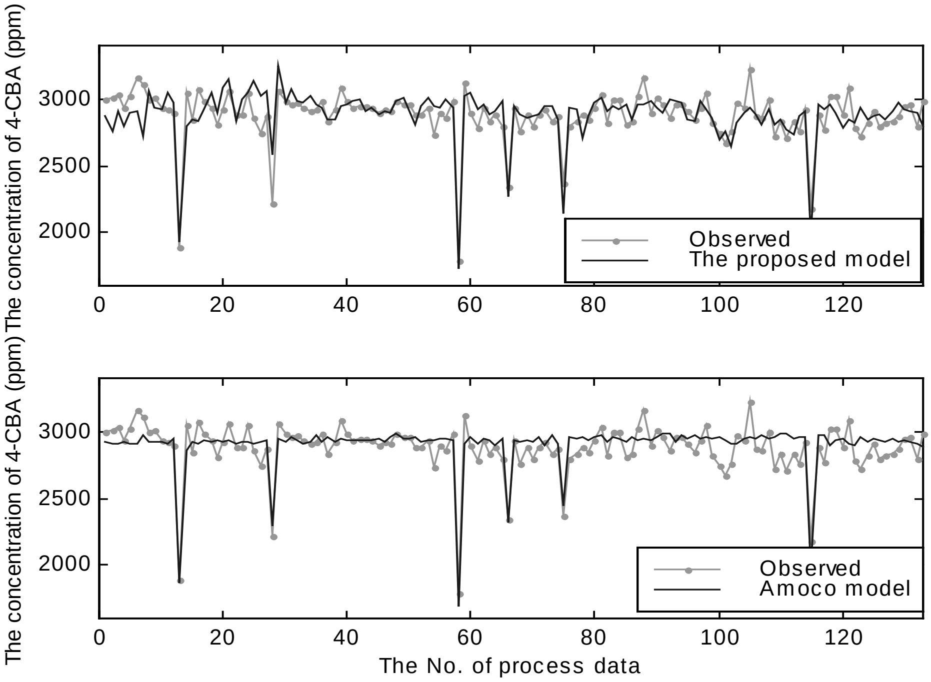

Fig. 5. The results comparison among the proposed model, Amoco empirical model and the observed values.

applied to cope with the problems in process data. Firstly, considering the exact estimation of the time delay between variables and quality variable is difficult, a weighted moving average method is used to combine 6 values at different time point from the 0.2 times estimated time delay to double time delay in the past as the model input variables. Then the projection on latent variables and Hotelling's T-squared statistic are made to identify two operating regions, which are also confirmed by the engineers. For many of factors in the industrial process are hard to considered in the mathematics model, six plant factors are used to correct the deviation between the laboratory model and the industrial process model. Robust nonlinear least square method, modified Levenberg-Marquardt method is applied to regress the six plant factors. Finally, the satisfactory predict results prove that the proposed model is inspiring in applying to industrial online soft sensor.

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