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Control structure design of an industrial crude terephthalic acid hydropurification process with catalyst deactivation

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ABSTRACT

Purified terephthalic acid (PTA) is a fundamental raw material for polyester and textile industry. The *p*-xylene oxidation process and crude terephthalic acid (CTA) hydropurification process are the two main sections of industrial PTA production. 4-Carboxybenzaldehyde is a byproduct of the first section that can lower the polymerization rate and the average molecular weight of the polymer. In this work, an improved complete plant dynamic model of the second section, CTA hydropurification with catalyst deactivation, was developed based on Aspen Dynamics. The present contribution considered the performance of the proposed catalyst deactivation model (Azarpour and Zahedi, 2012). Moreover, we designed a control structure for this process with catalyst deactivation, and the performance of the resulting control structure was analyzed using several criteria. Results showed that the proposed system provides a better control system and higher profit for the process.

1. Introduction

Purified terephthalic acid (PTA) is an essential link of the petrochemical industry. The raw material of PTA production, *p*-xylene (PX), comes from the catalytic reforming of upstream naphtha, and downstream PTA produces polyethylene glycol terephthalate, which is a key material for polyester and textile industries. With the worldwide development of these industries, global PTA markets exhibited strong growth at rates of around 6–8%/year until 2008 (Qian et al., 2012).

Industrial PTA production consists of two sections. The first section is an oxidation process, in which PX is oxidized to terephthalic acid (TA) in the temperature range of 190–200 °C with acetic acid as solvent, cobalt acetate and manganese acetate as catalyst, bromide as promoter, and air as oxygen source (Burri et al., 2002; Cincotti et al., 1997). During the oxidation process, a byproduct called 4-carboxy-benzaldehyde (4-CBA) has a mass fraction of around 3000 parts per million (ppm) in TA product. As 4-CBA is chemically and physically similar to TA, it is one of the most difficult contaminants to remove using separation processes and will lower the polymerization rate and the average molecular weight of the polymer (Pellegrini et al., 2011). The product of PX oxidation reaction process with high impurity content of 4-CBA is called crude terephthalic acid (CTA). Therefore, the second section of industrial PTA production, a hydropurification process, is carried out to decrease the 4-CBA content in CTA product. In this process, 4-CBA in CTA slurry is purified by hydrogen in water at 270–290 °C under 7.9 MPa pressure over 0.5 wt.% carbon-coated palladium (Pd/C) catalyst in a fixed-bed reactor. Thus, the major impurity, 4-CBA, is converted to *p*-toluic acid, which is relatively easy to separate from TA by crystallization and centrifugation (James, 1988). The final product (PTA) contains less than 25 and 150 ppm of 4-CBA and *p*-toluic acid, respectively. Worldwide consumption of this Pd/C catalyst has exceeded 1000 tons per year in the year 2000, with a corresponding total business of ca. 30 million USD/year (Pernicone et al., 1998). Catalyst loss is mainly cause by deactivation, and metal sintering is one of the most frequent causes of deactivation of industrial supported metal catalyst.

Although the hydropurification process is very important both on product quality and economy, most studies concentrate on the study of PX oxidation (Dong and Yan, 2013; Huang et al., 2007; Qian et al., 2012; Raghavendrachar and Ramachandran, 1992). Only a few articles about this process are available, and they mainly focused on catalyst deactivation. Zhang reported that the main causes of deactivation in industrial plant are loss in Pd and decrease in Pd surface area, and metallic terephthalate deposits were also found on the surface of exhausted catalyst (Xiong and Zang, 1994; Zhang, 1989). Nicola et al. used several physical techniques (i.e., SEM-EDS, CO chemisorption, and XRD) and found that Pd sinters

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Nomenclature

k_0	frequency factor of reaction (kmol kg_c^{-1} s^{-1})
n	order of reaction
E	activation energy (see Table 1, kJ/mol)
C	concentration (kmol m^{-3})
R	universal gas constant (J mol^{-1} K)
T	Temperature (K)
a	the metallic sintering dispersion parameter
m	sintering order
k_d	sintering rate constant (day^{-1})
S	surface of the catalyst (m^2 m^{-3})
S_0	initial active surface of the catalyst (m^2 m^{-3})
r_d	rate of deactivation (day^{-1})
t	time (h)
${}_{Int}F_{H_2}$	original SP of hydrogen flow (kg/h)
α	parameter used in module
P	gross profit (CNY/ton)
P_{PTA}	price of final production (CNY/ton)
P_{H_2}	price of hydrogen (CNY/kg)
P_{cata}	price of catalyst (CNY/ton)
K_c	gain (%/%)
τ_I	integral time (min)
ppm	percent per million

very easily; moreover, a rough proportionality exists between catalytic activity and Pd surface area, and Pd sintering was shown to be an important cause of deactivation for PTA catalysts (Pernicone et al., 1998). Zhang et al. studied mass transfer characteristics of the fixed-bed reactor for hydro-refining of TA. They developed a steady-state heterogeneous 1D model of the reactor that considers transport phenomenon by plug flow in the axial direction (Zhang et al., 2008). Zhong et al. simulated the CTA hydro-treating reaction and proposed a dynamic model of PTA hydrogenation reaction based on Aspen Plus and Aspen Dynamics (Weimin et al., 2012; Xing et al., 2010). Pellegrini et al. studied several spent Pd/C catalysts. Spent catalysts characterized by different lifetimes, positions in the catalytic bed, sintering degrees, and types of contaminant (mainly S, Pb, and Mo) have been investigated by TEM coupled with EDS detection, XRPD, EXAFS spectroscopy, and CO chemisorption. The catalyst lifetime can exceed two years under normal operating conditions, and catalyst deactivation occurs because of Pd sintering, with loss of available Pd surface atoms (Pellegrini et al., 2011). Azarpour et al. invented a fully dynamic fixed-bed reactor model and a Pd/C catalyst deactivation model for the industrial TBR of PTA production plant. This model can predict the concentration profiles of the reaction components and the trend of Pd/C catalyst deactivation. Additionally, it can be applied for catalyst deactivation and operational condition analysis (Azarpour and Zahedi, 2012). Nevertheless, whole plant simulation and analyses of this hydropurification process are lacking.

From an industrial control and economic perspective, dynamic modeling and control research is of great importance. It is an active research area. Over the years, numerous methods have been proposed for plantwide control (PWC) (Jagtap et al., 2013; Lin et al., 2006; Luyben, 2011; Robinson and Luyben, 2011a; Skogestad, 2004). Luyben et al. published several articles about plantwide system; they studied snowball effect (Luyben, 1994), inventory management (Belanger and Luyben, 1997), and PI controller tuning method (Luyben, 1989), proposed essential regulatory control issues, and suggested practical control system structuring guidelines (Luyben et al., 1997). Based on these studies, a heuristic nine-step PWC design procedure has been developed and widely applied in designing effective plantwide regulatory control systems (Luyben et al., 1997; Luyben, 2010, 2012; Robinson and Luyben, 2011b). However, heuristic-based methods always require substantial experience, and they do not use advantages of rigorous process simulators when designing a control structure. Another PWC method is the integrated framework of simulation and heuristics (IFSH) methodology proposed by Konda et al. (Murthy Konda et al., 2005; Vasudevan et al., 2009; Vasudevan and Rangaiah, 2010), which makes effective use of rigorous process simulators. The IFSH methodology has been applied to several chemical processes, such as ammonia process (Zhang et al., 2010), alkylation process (Tripathi et al., 2013), and biodiesel production process (Patle et al., 2014).

In the present research, based on the characteristics of industrial hydropurification with catalyst deactivation, an exact dynamic model is improved using Aspen Dynamics and validated using real plant data. Although the process has no recycle streams and little energy integration, the PWC control structure design method can still work in this process. Thus, a complete plant control structure for the catalyst deactivation phenomena is proposed based on the IFSH methodology. This paper is organized as follows. In Section 2, the chemical mechanisms of 4-CBA hydropurification are briefly described. In Section 3, the step-by-step IFSH method is applied for CTA hydropurification with catalyst deactivation. Moreover, the design and selection of control systems are also proposed. Several performance indexes are then introduced to assess the proposed control system in Section 4. In Section 5, dynamic responses of some disturbances are discussed, and the profits of the process are also calculated. Finally, conclusions are drawn in Section 6.

2. Overviews and simulation of industrial CTA hydropurification process

2.1. Process description

The CTA hydropurification process is extremely important for product quality. Impure TA with 4-CBA comes from the PX oxidation product silos. In the feed preparation unit, CTA powder is first mixed with deionized water using a feed drum. The slurry then enters into a series of successive pre-heaters to heat the reaction mixture to the desired reaction temperature. Some pumps are applied to increase the reactant pressure to 7.4 MP. Specifically, the hot steams of the first three pre heaters come from the third, second, and first crystallizers, respectively. The last two heat exchangers use hot oil coming from the recycle heat transfer oil furnace to maintain the temperature at which CTA is all dissolved in deionized water. Subsequently, the mixed slurry is injected to the top of the hydropurification reactor. Meanwhile, a highly pressurized hydrogen is also injected to the reactor. The mixture and hydrogen then react through the fixed catalyst bed. The outlet of the reactor is sent to a series of crystallizers. The steams of different temperature and pressure produced by the first three crystallizers are applied to the first three heat exchangers. The rest steams are sent to the utility system of different pressure ranks. The products from the crystallizer are centrifuged to separate TA cake from the solvent. This process is followed by vacuum and dryer. Finally, the product powder is transferred to the PTA silos after quality assurance. Fig. 1 shows the flow sheet of an actual CTA hydropurification plant.

2.2. Reaction kinetics

4-CBA hydropurification is a complicated process. The chemistry in the catalyst bed is shown in Eqs. (1) and (2). Reactions 1 and 2 are the main hydrogenation reactions. The intermediate product is 4-hydroxymethylbenzoic acid, and the final product is *p*-toluic acid.