

A CONCEPTUAL DESIGN OF NOVEL REACTOR FOR LIQUID-PHASE OXIDATION OF P-XYLENE

Weizhen Sun, Ling Zhao*

State-Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

Summary

Though the production of terephthalic acid (TPA) from p-xylene (PX) is of vital importance in chemical industry, reactor pattern for this process keeps unchanged in past decades. A novel reactor with high efficiency for PX oxidation is conceptually designed in this work. On the basis of reaction mechanism and kinetic experiments, autocatalysis of p-xylene (PX) oxidation to terephthalic acid (TPA) is firstly elucidated. Then, a simulation is made by establishing the adiabatic model of novel reactor, which is combination of well-mixed flow reactor (MFR) and plug flow reactor (PFR). The results show that the performance of new reactor is excellent when the volume fraction of PFR keeps within 10-20%.

Keywords

Conceptual design; Autocatalysis; Reactor simulation.

Introduction

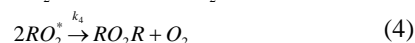
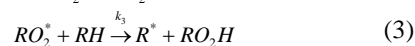
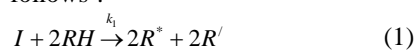
As raw material to produce polyethylene terephthalate (PET), terephthalic acid (TPA) is mainly manufactured by the liquid-phase catalytic oxidation of p-xylene (PX). Although various commercial technologies have been developed to produce TPA, the reactor pattern nearly keeps unchanged till now, either bubbling-type with low aspect ratio or stirring-type. In both types of reactors, liquid phase can be roughly looked on as ideal mixed flow (IMF) as a result of rigorous air bubbling or and mechanical agitating. The most important advantage of IMF for the oxidation of PX is to meet with the need of heat transfer owing to its strong heat liberation. However, the high conversion and yield of this process, usually above 99%, 95% respectively, lead to a huge reactor volume. Also, due to the superiority of large scale, the single reactor for the commercial production of TPA has been becoming bigger and bigger. Moreover, such an IMF results in a higher concentration of undesired intermediate products.

In this work, the autocatalytic characteristic of PX oxidation was elucidated on the basis of reaction mechanism and kinetic experiments. Accordingly, an optimized flow pattern combination for liquid phase in PX oxidation was proposed and reactor simulation concerning material and heat balance was performed.

Autocatalysis of PX

The oxidation of PX catalyzed by Co/Mn/Br (Amoco/MC

system) is a typical free radical chain reaction, which mechanism has been extensively studied, e.g. by Jones¹ and by Partenheimer². Massimo summarized the typical radical chain mechanism of organic substrate RH as follows³:



Generally, step (2) is much faster than step (3), so the concentration of R* is very low in comparison with RO₂*. Also, the chain initiation step (1) is usually the rate-determining one. Being a consecutive reaction involving various intermediates, e.g. p-tolualdehyde (TALD), p-toluic acid (p-TA) and 4-carboxybenzaldehyde (4-CBA), reaction pathway of PX oxidation is more complicated. Recently, we elucidated the reaction mechanism of PX oxidation and established its kinetic model⁴. From above mentioned reaction mechanism, it can be seen that the production of intermediate RO₂* can accelerate consumption of substrate RH by step (3). This is a typical characteristic of the autocatalytic reaction.

The occurrence of maximum reaction rate versus conversion is also an obvious characteristic of autocatalysis. The autocatalysis of PX oxidation was also verified experimentally⁵. In performed kinetic experiment of PX oxidation, it was found that maximum oxidation

* To whom all correspondence should be addressed: Pro. Ling Zhao, Email: zhaoling@ecust.edu.cn.

rate exists during the increasing of PX conversion, shown in Fig. 1.

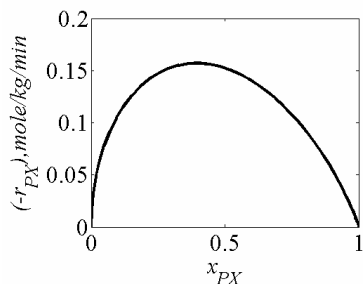


Fig. 1 Relationship between reaction rate and PX conversion

It's known that, neither plug flow nor mixed flow is most efficient for those autocatalytic reactions requiring a high conversion. In general, there are three schemes to optimize such process: (1) combination of reactor and separator; (2) using recycle reactor; (3) a mixed flow reactor (MSR) followed by a plug flow reactor (PFR)⁶. The first two schemes require recycling of reactant, which is energy-consuming. Here, we will discuss the scheme (3), i.e. a MSR followed by a PFR.

Reactor Simulation

Generally, for autocatalytic reactions, if maximization of reaction rate is what we only focused on, the volume partition between MSR and PFR can be calculated by minimizing the total volume. However, PX oxidation is such a reaction with strong heat liberation, which should be removed timely to avoid the hot spots in reactor. So, volume partition here should also involve the temperature distribution through the whole reactor.

In order to determine the suitable volume partition between MSR and PFR, a reactor model in adiabatic situation is established, which takes into consideration the complicated consecutive reaction of PX oxidation, evaporation of acetic acid and water, and reaction heat liberation⁵. In this model, total space-time was fixed at 30 minutes, compared with present industrial reactors' with about 60 minutes. Also, typical conditions for industrial reactors are set as input parameters of this model. The simulation results were plotted in Fig. 2.

It can be seen that, when the volume fraction of PFR is increased, the outlet composition of main intermediates, e.g. p-TA and 4-CBA will become lower, but temperature fluctuation bigger. Although the volume fraction of PFR is only 10%, outlet composition of the new reactor can compete with the one of present industrial reactor, that is, the new reactor volume is only one half of the industrial one. Moreover, temperature fluctuation is within an acceptable range. So, the performance of PX oxidation becomes better when volume fraction of PFR kept within 10~20%.

Its actual performance still needs to be verified, though the simulation results show that new reactor is excellent. Experiments related to the conceptual design of new

reactor are being carried out, and results will be reported in the near future.

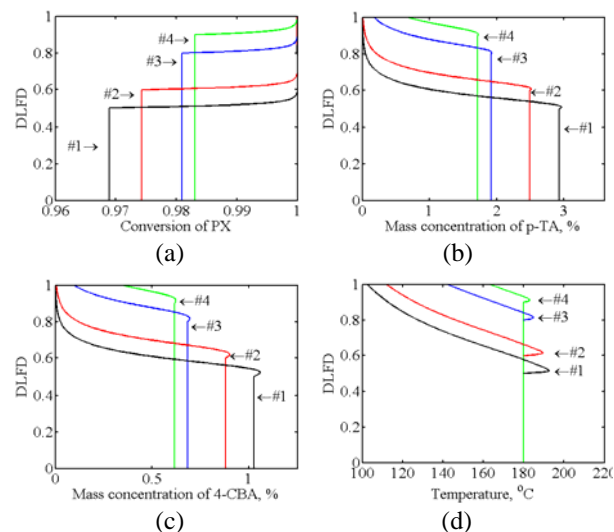


Fig. 2 Distribution profiles of key variables along flow direction.

DLFD: Dimensionless Length along Flow Direction. V_{MSR}/V_{PFR} : #1—5/5; #2—6/4; #3—8/2; #4—9/1.

Conclusions

The autocatalytic characteristic of PX oxidation was elucidated from reaction mechanism, and was also verified by kinetic experiments. The reactor model simulation for a MSR followed by a PFR was performed. The simulation results show that performance of PX oxidation will become better when the volume fraction of PFR keeps within 10~20%.

References

1. Jones, G. H., p-Xylene autoxidation studies. Oxidation of cobalt(II) and manganese(II) acetates by peracids. *Journal of the Chemical Society D: Chemical Communications* **1979**, 12, 536 - 537.
2. Partenheimer, W., A Chemical Model for the Amoco "MC" Oxygenation Process to Produce Terephthalic Acid, in: *Catalysis of Organic Reactions*, (Ed.: D. W. Blackburn). Marcel Dekker: New York, 1990.
3. Morbidelli, M.; Paludetto, R.; Carr, S., Gas-liquid autoxidation reactors. *Chemical Engineering Science* **1986**, 41, (9), 2299-2307.
4. Sun, W.; Pan, Y.; Zhao, L.; Zhou, X., Simplified Free-Radical Reaction Kinetics for p-Xylene Oxidation to Terephthalic Acid. *Chemical Engineering & Technology* **2008**, 31, (10), 1402-1409.
5. Sun, W. Process Analysis and Modeling of Liquid-Phase Oxidation of p-Xylene. PhD Thesis, East China Univ. of Sci. and Tech., Shanghai, 2009.
6. Levenspiel, O., *Chemical Reaction Engineering*. Third Edition ed.; John Wiley & Sons, Inc.: New York, 2002; p 668.