

# The directional regulation process of p-xylene oxidation to p-toluic acid based on the kinetics modeling

Yudong Li<sup>1</sup>, Weizhong Zheng<sup>1</sup>, Weizhen Sun<sup>1\*</sup>, Ling Zhao<sup>1</sup>

*1 State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China*

*\*Corresponding author: sunwz@ecust.edu.cn*

## Highlights

- The reaction kinetics model of PX to p-TA is developed.
- The directed regulation process of PX to p-TA based on the kinetics model is established.
- The proposed kinetics model has high accuracy (error<5%).

## 1. Introduction

The p-toluic acid (p-TA), derived from the petroleum-based compound p-xylene (PX) is widely used in medical and material fields. One of the most common applications of p-TA is to synthesize monomer terephthalic acid (TA), a precursor to polyethylene terephthalate (PET) used in bottles and fabrics<sup>1</sup>. However, the traditional industrial process of TA preparation usually has a large operation cost due to rigorous conditions (180 °C to 200 °C)<sup>2</sup> which easily results in the burning of acetic acid in the reaction process. Moreover, excessive acetic acid burning leads to a serious environmental problem because great greenhouse gas is discharged into the environment. From a cost and environmental perspective, the concept for TA production has been a noticeable shift in current. The bulk oxidation of PX to p-TA, then to TA can effectively avoid the combustion of acetic acid and the introduction of impurities, simultaneously achieving lower cost and better environmental benefits. It is a fact that the reaction kinetic is an essential aspect of industrial processes. The systemic reaction kinetic modeling can help to understand the reaction mechanism and locate the parameters that affect the oxidation reaction process. Therefore, in this work, the lumped reaction kinetic model of bulk PX to p-TA is proposed to predict their reaction behaviors.

## 2. Methods

The liquid phase oxidation of PX in the presence of a metal-based/bromine catalyst (Co/Mn/Br) belongs to a classical free-radical-chain reaction. The free-radical-chain reaction mechanism was applied to this system. In the bulk oxidation of PX catalyzed by cobalt iso-octoate, all the elementary reactions involve PX, intermediates, and free radicals concurrently, which causes a more complex reaction process. The kinetic model based on this mechanism which involves abundant parameters can lead to model overfitting, as the measurable components are limited. We assumed that the different free radicals present the same reactivity for abstracting  $\alpha$ -H atom. Thus, it was estimated that all substrates have equivalent initiation rate constants, and the difference in termination rate constants of various peroxy-radicals is the same and can be neglected. Thus, according to the typical reaction mechanism of hydrocarbon oxidation, a simplified oxidation reaction mechanism was applied in the PX to p-TA process. The semicontinuous experiments were conducted in a 1L batch reactor with a strong stirring of 800 rpm. The product components were analyzed by High-Performance Liquid Chromatography (HPLC) to help the reaction kinetics model established.

## 3. Results and discussion

The reaction conditions of temperatures, catalyst concentrations, airflow, etc., play a large effect on the reaction behaviors. The yield of target product p-TA was first increased and then decreased with temperature and catalyst concentration increased. The reaction behavior of PX to p-TA was well-correlated by the kinetics model. The built kinetic model can well predict the component's concentration change with temperature and catalyst concentrations change. The error of the kinetic model is less than 5%. The directed regulation strategy can be achieved based on this complex kinetic model. The component PX is performed to form the aldehydes or monocarboxylic acids with a low reaction temperature or residence time. In contrast, it performed to the dicarboxylic acid in a high temperature

or residence time. Thus, it is possible to achieve the directed regulation of the production of different products in the bulk PX oxidation process.

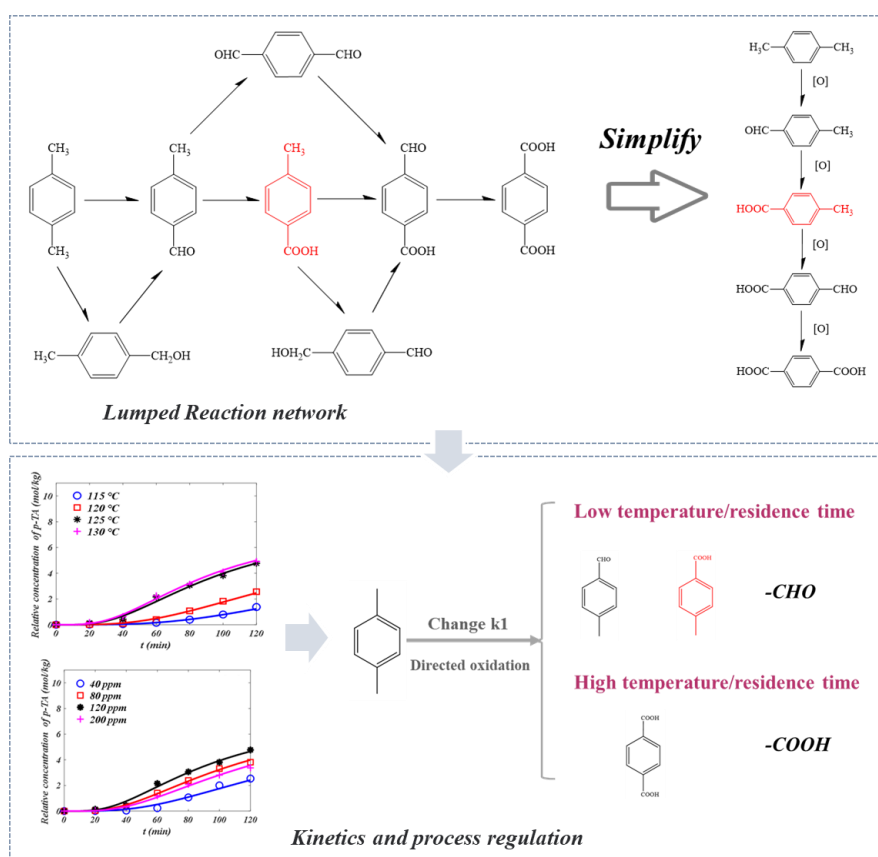


Figure 1. Kinetics modeling and directed regulation of PX to p-TA.

#### 4. Conclusions

The kinetic modeling of the bulk PX to p-TA plays an excellent predictive ability. The directed regulation process based on the complex kinetic model realizes the product selectivity, reaction rate, and reaction path regulation which improves reaction efficiency, selectivity, and product quality.

#### References

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#### Keywords

Bulk PX oxidation; Kinetic modeling; Directed regulation.