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# Modeling the liquid phase autoxidation of cyclohexylbenzene to hydroperoxide



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#### ABSTRACT

The liquid phase autoxidation of cyclohexylbenzene (CHB) to CHB hydroperoxide (CHBHP) is the key step of green production of phenol. The CHB oxidation kinetics was originally investigated by semibatch experiments under various oxygen partial pressures. Kinetic models to deal with oxygen-rich and oxygen-poor conditions were developed on the basis of free radical chain mechanism. It was found that the activation energy of the rupture of the bond O—O of molecule CHBHP was close to that of cumene hydroperoxide, while the activation energy of hydrogen abstraction from the tert-butyl carbon of CHB was reasonably larger than that of cumene due to the steric effect. The kinetic model involving the oxygen addition to R• (Model II) can be used to deal with various oxygen partial pressure conditions. Based on the developed kinetic model, the simulation of well-mixed reactor operated under continuous conditions was performed, and the results were in good agreement with continuous experiments.

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#### 1. Introduction

The liquid phase oxidation of hydrocarbons into oxygenated chemicals is of vital importance to modern industrial economy due to its efficient conversion from cheap petroleum feed stocks to value-added organic chemicals important in petrochemical and polymer industries (Suresh, 2000). Some notable examples include the oxidation of *p*-xylene (PX) to terephthalic acid (Cao et al., 1994; Shang et al., 2015; Wang et al., 2007), that of cyclohexane to cyclohexanone and cyclohexanol (Suresh et al., 1988a,b,c), that of cumene to hydroperoxide (Andrigo et al., 1992; Bhattacharya, 2008), and so on. The cumene oxidation to hydroperoxide followed by acid decomposition to produce phenol (also called Hock process) is one of the most well known commercial processes. However, currently the Hock process is not economically favorable due to market saturation of the co-product, acetone, and utilization of the valuable resource propylene as starting material. One promising alternative route to produce phenol is through the liquid phase oxidation of cyclohexylbenzene (CHB), the production process is shown in Scheme 1 (Arends et al., 2002). For this route the only starting hydrocarbon raw material is benzene, which is cheap and easily obtained by economic entities like China whose coal resources are abundant. The exclusive formation of the final product, phenol, makes this route more competitive. In Scheme 1, the selective aerobic oxidation of CHB to CHB hydroperoxide (CHBHP) is the key step, since the oxidation process is slow and produces by-products. Although a few reports can be found for the liquid phase oxidation of CHB (Aoki et al., 2005; Arends et al., 2002; Bond et al., 1999), there is far fewer publications focusing on the oxidation kinetics and modeling, which is fundamental for the design and optimization of industrial reactor and insightful understandings of reaction mechanism.

The liquid phase autoxidation of hydrocarbons proceeds via a free radical chain mechanism (Emanuel et al., 1984). It is called autoxida-

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Scheme 1 - Phenol production through the route of cyclohexylbenzene autoxidation.

tion due to its characteristics of spontaneous occurrence even at low temperatures (Partenheimer, 1995). The hydrocarbon oxidation mechanism can be very complicated due to the branched radical chain and side reactions according to the previous work on cumene autoxidation (Andrigo et al., 1992; Bhattacharya, 2008; Krongauz et al., 2014). In the modeling of hydrocarbon autoxidation the number of rate constants to be determined will be large if all of the elementary reaction steps are considered. Furthermore, usually there are limited number of molecular products that can be measured due to the high activity and transient nature of free radicals. Some rate constants of elementary steps involving free radical chain can be determined by quantum chemical calculations, but it is time-consuming and far from accurate because of solvent effects (Reichardt and Welton, 2011).

Suitable simplifications for oxidation mechanism and pathways are necessary to handle the modeling of hydrocarbon oxidation. Using a substantial number of simplifying assumptions, the number of model parameters of cumene oxidation has been reduced from 14 to 3 (Andrigo et al., 1992). By using published frequency factors and suitable model assumptions, the model parameters of cumene oxidation were also remarkably reduced by Bhattacharya (2008). Based on the free radical chain mechanism, Sun et al. developed a simplified kinetic model of the PX oxidation, in which assumptions of equivalent reactivity for various free radicals were used (Sun et al., 2008). Through such model simplifications the number of model parameters was reduced dramatically (from 30 to 6), but the kinetic model demonstrated satisfactory fit to experimental data and predictive ability. Furthermore, the obtained rate constants concerning the hydrogen atom abstraction from methyl group and that from aldehyde group have remarkable agreements with the famous Hammett structure-reactivity relationship (Shang et al., 2015; Sun and Zhao, 2011). Similar simplification strategies to develop kinetic model have proven feasible in the liquid phase oxidation of MX (Sun et al., 2015).

In this present work, the autoxidation kinetics of CHB to CHBHP in the absence of catalyst was investigated by semibatch experiments under oxygen-rich and oxygen-poor conditions respectively. The kinetic models of CHB autoxidation taking into account key elementary steps were developed on the basis of the free radical chain mechanism, and further simplified using appropriate assumptions. The proposed kinetic models and related oxidation mechanism were verified by experiments carried out in a reactor with continuous air purge and continuous cyclohexylbenzene feed.

#### 2. Experimental

The experimental setup for liquid phase autoxidation of CHB is shown in Fig. 1. The reactor made of glass and equipped with four baffles has a volume of 300 ml and is oil-bathed. A condenser is equipped which serves as a cooler to condense the evaporated components to reduce the lost of reactants. During each experiment air from a gas cylinder is bubbled through the solution under vigorous agitation. The pressure inside reactor is adjusted by a backpressure valve and indicated by a sensor, and the temperature is monitored by a thermocouple and controlled by a computer. During each experiment, the fluctuation of temperature is less than 0.5 K, and that of pressure is less than 0.05 bar. The combustion side reactions are usually evaluated by measuring CO<sub>2</sub>/CO generated dur-

ing oxidation reactions using infrared sensor. In this work two sets of infrared gas analyzers (GXH-510) were used to monitor  $CO_2/CO$  concentration in tail gas and the results indicate the loss of reactants by combustion is small and can be neglected.

The oxidation kinetics of CHB was investigated under semibatch conditions, in which the liquid reactants were put into reactor at beginning while the gas oxidant air was introduced continuously. The continuous experiments were carried out to verify the modeling of the continuous process of CHB oxidation, in which both the liquid reactant and oxidant air were introduced into reactor continuously. The brief descriptions of the semibatch experiment, as well as the continuous one are given below.

#### 2.1. Semibatch experiments

In a typical semibatch experiment, about 300 g of reactant mixture, including reactant CHB and initiator CHBHP (e.g. 1.5 wt%) were put into the reactor. The chromatography-grade  $N_2$  is introduced into the reactor to replace air for 10 min, and the stirring with the agitation rate of 700 rpm and heating were started simultaneously. When the temperature and pressure (e.g. 0.20 MPa) inside the reactor reached the setting values and became stable, air was then introduced into the reactor to start the reaction. Samples were taken every 90 min.

#### 2.2. Continuous flow experiments

Before each continuous experiment, a semibatch experiment was firstly carried out. At some point of time, the reactant CHB is continuously fed into and the reaction solution is discharged out of the reactor. The conditions for continuous process such as pressure and agitation rate are same to those under semibatch condition. When new conditions such as temperature and  $\tau$  were changed, samples were taken after the reaction time outreached six times of the residence time  $\tau$ . For each experimental run, at least three samples were taken and then analyzed using the analytical method introduced below, and the average results were adopted to eliminate the experimental error.

The residence time  $\tau$  is calculated by the following equation:

$$\tau = (m/\rho)/q_{\rm v} \tag{i}$$

where *m* and  $\rho$  stand for the mass and the density of the reaction mixture inside reactor, and  $q_v$  represents the volume flow rate of the inlet reactants. The concentration changes of reactants in continuous flow experiments are much smaller than those in the semibatch experiments due to the limited reaction time, so the average density of reaction mixture is approximately equal to that of cyclohexylbenzene. As for the  $q_v$ , it is measured by the metering pump shown in Fig. 1. To measure the mass of reaction mixture inside the reactor, i.e.

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