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Effect of the Reaction Bath Temperature in a Fixed-bed Reactor for Oxidation of *o*-Xylene over V_2O_5/TiO_2 Catalysts

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Abstract–The effects of the reaction variables in the operation of a fixed-bed reactor for oxidation of *o*-xylene over V_2O_5/TiO_2 catalysts were studied experimentally using a bench reactor. Reaction temperature, feed flow rate and feed concentration of *o*-xylene were found to have significant effects on the product distribution and the temperature profile in the reactor. Drastic enhancements of *o*-xylene oxidation reaction were observed at some conditions, which was ascribed to the effect of heat accumulated in the bed and indicated a possible way to increase the productivity in the industrial condition.

Key words: Fixed-bed Reactor, *o*-Xylene Oxidation, Reaction Variables, Heat Effect, Temperature Profile

INTRODUCTION

Oxidation of *o*-xylene is an important industrial process for producing phthalic anhydride which is raw material for plasticizers, dyes and insect repellents. The reactors used in this process are of non-adiabatic fixed-bed type and they have possibilities of runaway reaction and explosion. So understanding their behavior is very important for safe and economic operation in the plant.

Even though most work studied on this reaction is concentrated on finding the reaction kinetics [Calderbank, 1974; Pant and Chanda, 1976; Skrzypek and Grzesik, 1985], there are some reports related to the operation of the process. Nikolov and Anastasov [1992] examined the influence of the inlet temperature on the performance of the fixed-bed reactor and reported that the highest yield of phthalic anhydride was achieved at a low inlet gas temperature. The behavior of an industrial reactor was also studied experimentally with respect to the coolant temperature by the same authors [Nikolov and Anastasov, 1989]. Calderbank et al. [1997] pointed out an inefficiency of conventional fixed-bed reactors and suggested a "rich-feed diluted catalyst" strategy for an economic operation. In these reactors, the temperature in the beginning of the bed is too high and it drops sharply in the rest part, which leads to an unsatisfactory operation. Dual catalyst bed and dual salt bath were also suggested by Anastasov and Nicolov [1996] as an effort to enhance the effectiveness of the catalyst bed. Papageorgiou and Froment [1996] studied various reactor schemes including three-bed multi-tubular reactor, multi-tubular reactor, and multi-bed adiabatic reactor to increase the selectivity to phthalic anhydride from the process.

Some workers investigated the sensitivity of the maximum temperature (hot spot) of the fixed-bed reactor to the changes in the operating variable. The parametric sensitivity of the coolant temperature was studied by Lopez et al. [1981] and an a priori run away criterion for hot spot operation was established. Westerink et al. [1990] using one- and two-dimensional models have studied the influence of several variables on the hot spot temperature of the reactor. Borio et al. [1989] also analyzed the parametric sensitivity behavior of the reactors with various cooling-medium flow arrangements and suggested the co-current arrangement as the most desirable design. But the characteristics of the fixed-bed reactor in this process still are not well known so that the operation of the industrial process heavily depends on the past experience of the operators.

In this work, the effects of reaction variables on the product distribution, the temperature profile and the production rate of phthalic anhydride were investigated by experiments with a bench reactor. The variables considered include the bath temperature, the feed flow rate and the feed composition.

EXPERIMENTAL

A bench-scale fixed-bed reactor (Fig. 1) was built and it consisted of a feed preparation unit, a tubular reactor, a temperature controller and a gas analysis unit. *o*-Xylene was injected at a preset rate into the feed stream by a micro-metering pump and air flow from a compressor was controlled by a mass flow controller. *o*-Xylene and air were heated to the desired temperature in the oven before they were introduced to the reactor.

The fixed-bed reactor was made of a stainless steel tube (2.5 cm ID, 5 cm OD, 75 cm length), which was surrounded by a furnace heater (called "reaction bath" hereafter). The heater was divided into six blocks that could be controlled separately. A thermo-well was located in the center of the reactor so that a thermocouple lead could be moved inside to measures the axial distribution of the temperature in the reactor.

A part of the product stream passed through the sampling loop of a gas chromatography for analysis of the product composition. Organic products were separated by a capillary column (DB-5) and their composition was detected by FID. Major product ob-

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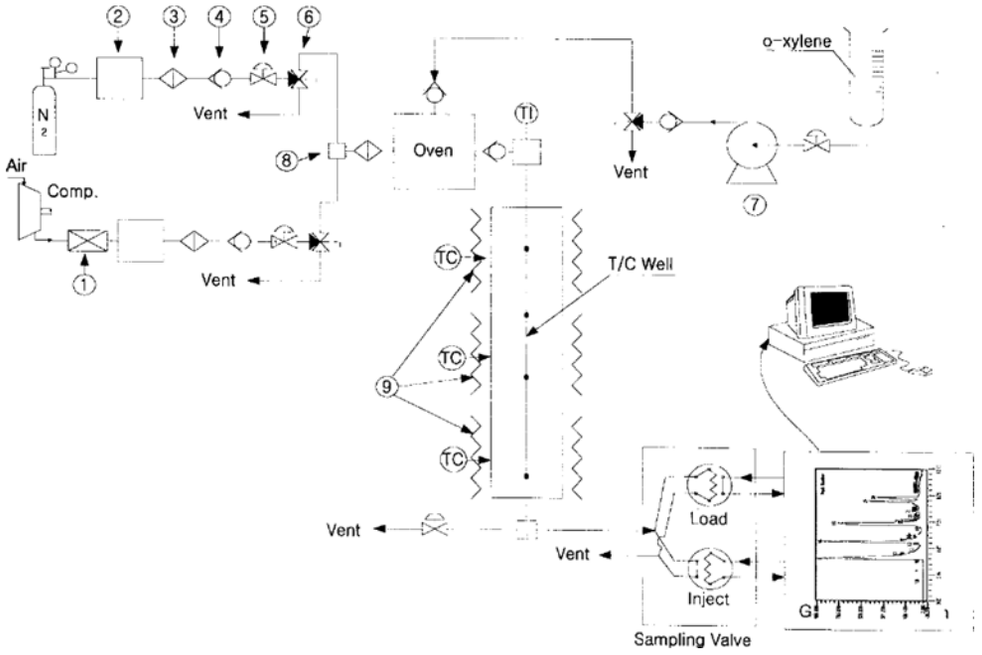

Fig. 1. Experimental apparatus.
1. Drying column 2. Mass flow controller 3. Line filter 4. Check valve 5. Needle valve
6. 3-way valve 7. Micro-metering pump 8. Cross 9. Furnace

tained from the reactor was phthalic anhydride (it will be called "PA" hereafter), but o-tolualdehyde (TA) and phthalide (PI) were obtained significantly when the conversion was not high. Maleic acid, benzoic acid, phthalic acid, benzene-acetaldehyde and capric acid were occasionally observed in small amounts so they were not considered in calculating the product selectivity. Carbon oxides were not analyzed by GC but their concentrations could be calculated from a carbon balance.

The catalysts used in the experiments are V_2O_5 over TiO_2, which were donated by a Korean chemical company. Catalyst pellets had a hollow cylinder shape whose surface was covered with the catalyst powder. Two kinds of catalysts (type A and type B), which have different activities, were used and they were packed into the reactor in the ratio of 1 : 1, 1 : 2, and 2 : 1.

Reaction was started by feeding *o*-xylene and air into the catalyst bed which had been heated to the desired temperature. Bed temperature reached a steady value in 30 minutes and the outlet stream from the reactor was analyzed. Reaction experiments were performed at the bath temperatures of 280 °C, 300 °C, and 325 °C with various air flow rates (2-8 L/min) and feed concentrations (1.0-4.0 mole% in *o*-xylene). The pressure in the reactor was 1 atm throughout the experiments.

RESULTS AND DISCUSSIONS

Since there are many factors influencing the reaction, experiments were performed initially to find the more important reaction variables. In most experiments, the dominant factor was the reaction bath temperature and the effects of the feed flow rate and the feed concentration were also significant, but the effect of different catalyst packing was not very significant in the reaction conditions employed in this study. The experimental results at various conditions showed a consistent trend regarding the effects of the reaction variables so some typical results are presented below to explain this trend.

Fig. 2a shows the effects of the changes in the bath temperature

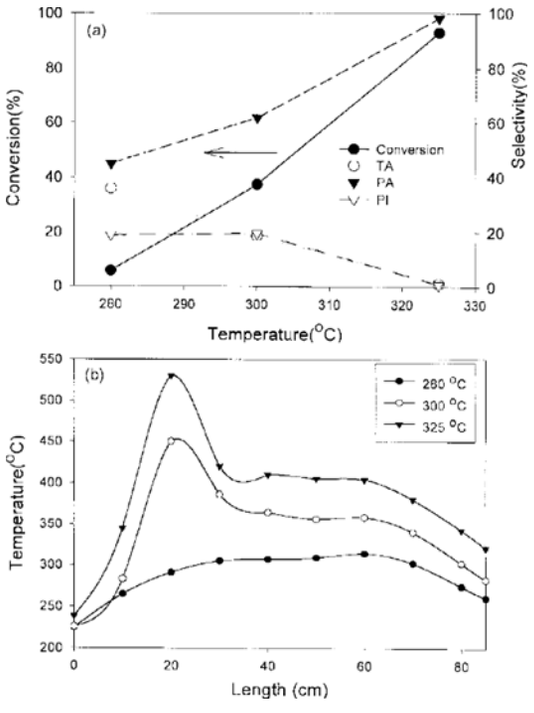

Fig. 2. (a) Effect of the bath temperature on the product selectivity (catalyst ratio 1 : 1, *o*-xylene concentration 2%, air 4 *l*/min; CO_2 excluded in selectivity calculation). (b) Effect of the bath temperature on the temperature profile (catalyst ratio 1 : 1, *o*-xylene concentration 2%, air 4 *l*/min).

on product selectivity and conversion. Reaction conversion was below 10% at 280 °C, but it increased rapidly to reach 90% at 325 °C. At lower temperatures, the intermediate products, *o*-tolualdehyde and phthalide, were produced significantly, but at 325 °C only phthalic anhydride was obtained without these intermediate compounds. Here the selectivity to carbon oxides was not shown in the figures for simplicity since it did not show significant changes (in the range of 15-20%) in the reaction conditions employed in this study.

The temperature profiles in Fig. 2b also show significant changes with the bath temperature. At 280 °C, the measured temperature at the center of the tubular reactor remained rather flat around 280 °C. But at 300 °C and 325 °C, maximum points (hot spot) were observed at the location of 20 cm from the entrance. The temperature at the hot spot became higher in the reaction at 325 °C.

These results show that bath temperature is an important factor which influences the operation of the reactor for oxidation of *o*-xylene. With an increase of the bath temperature by 20-25 °C, the reaction rate became higher, to result in a much higher conversion of *o*-xylene. The observations that the selectivity to phthalic anhydride increased with the change in the temperature while the amount of intermediate products decreased imply that phthalic anhydride is formed from *o*-xylene via phthalide and *o*-tolualdehyde, which agrees with the reaction mechanism suggested by previous workers [Dias et al., 1996; Papageorgiou et al., 1994; Skrzypek et al., 1985].

The temperature profiles observed show that the temperature of the catalyst bed could not be maintained at the bath temperature. The temperature of the reaction mixture reached to the bath temperature in the inlet region, after which the temperature became much higher than that. At higher temperatures of the bath, a hot spot appeared and the bed temperature remained at an even higher level. This is because the amount of heat generated from the oxidation reactions is large and the heat transfer to the outside is slow due to low thermal conductivity of the bed so that the heat of reaction is accumulated within the bed. Due to this heat in the bed, the reaction rate in the reactor became higher, which in turn resulted in generation of reaction heat in a larger amount to raise the reaction rate even further. It seems that the heat accumulated in the bed is the reason for the acceleration of the reaction rate at higher temperatures.

Next, the feed rates were changed while the bath temperature and the feed concentration of *o*-xylene were maintained. Fig. 3a and 3c show that the resulting effects became different depending on the bath temperature. When the bath temperature was 300 °C, the conversion of *o*-xylene and the fraction of phthalic anhydride in the product decreased along with the increase in the feed rates. But at 325 °C the conversion and the selectivity to phthalic anhydride remained constant at high values near 90% even when the feed rates were increased by four times.

The observed temperature profiles also show clear differences (Fig. 3b and 3d). At the bath temperature of 325 °C, a hot spot appeared along the length of the reactor while the temperature profile for reaction at 300 °C remained flat. It is notable that the maximum temperatures at the hot spot increased along with a movement of the location of the hot spot backward according to the change in the feed rates for the reaction at 325 °C.

In an isothermal reaction of a tubular reactor, the conversion

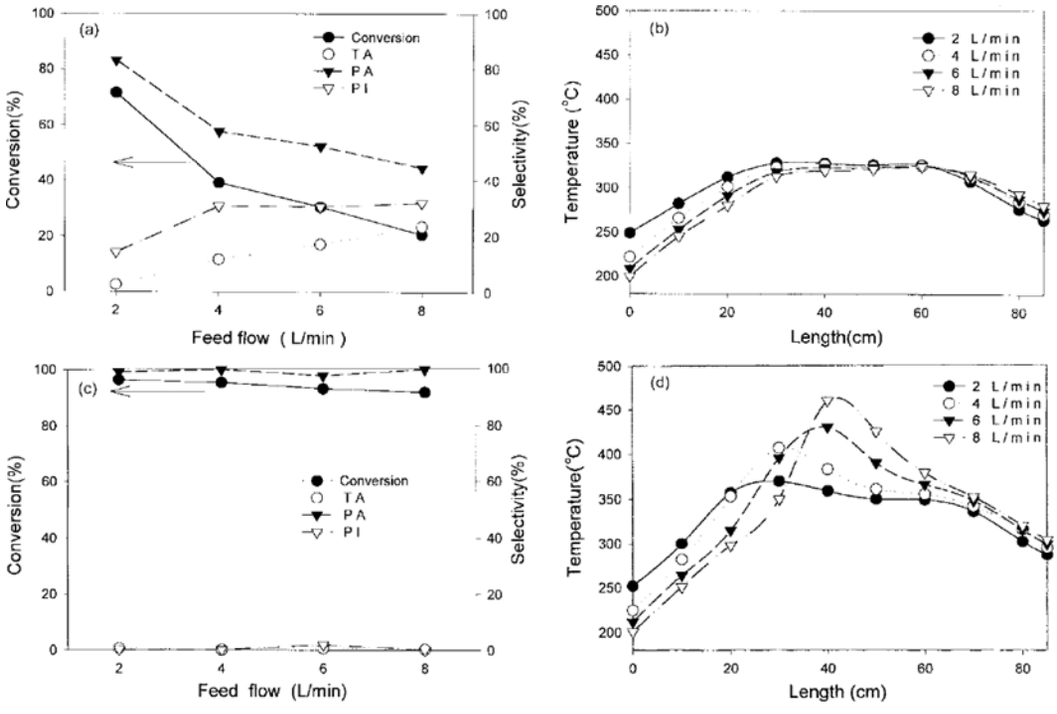

Fig. 3 (a) Effect of the feed rate on the product selectivity (catalyst ratio 1:2, *o*-xylene concentration 2%, bath temperature 300 °C; CO_2 excluded in selectivity calculation). (b) Effect of the feed rate on the temperature profile in the reactor (catalyst ratio 1:2, *o*-xylene concentration 2%, bath temperature 300 °C). (c) Effect of the feed rate on the product selectivity (catalyst ratio 1:2, *o*-xylene concentration 2%, bath temperature 325 °C; CO_2 excluded in selectivity calculation). (d) Effect of the feed rate on the temperature profile in the reactor (catalyst ratio 1:2, *o*-Xylene concentration 2%, bath temperature 325 °C).

usually decreases with an increase of the feed rate due to a reduction of the residence time in the reactor. This is the case with reaction at 300 °C, where no significant heat effects seem to appear. But in the reaction at 325 °C, where the heat effect became severer, the conversion of *o*-xylene stayed constant at the values over 90% even with the increase in the feed rate. The fact that a similar conversion was obtained even when the residence time became shorter means that the rate of reaction became higher with the increase in the feed rate. This phenomenon can only be explained by the effects from the heat generated during the oxidation reaction. At the bath temperature of 325 °C, the reaction rate was high enough to accumulate the heat of reaction in the bed, as seen in the above. With the increase in the feed rate, larger amount of reactants were injected into the reactor so that more heat could be generated to result in a higher temperature level in the bed. In this case, the reaction rate along the reactor became high enough to convert all the reactants introduced in spite of the shorter residence time. This explanation is consistent with the observation that higher values of the maximun temperatures were obtained with the increase in the feed rate.

Fig. 4a-4d show the changes in the conversion of *o*-xylene and the temperature profile when the concentration of *o*-xylene was increased from 1% to 3%. At the reaction temperature of 300 °C, the conversion of reactant decreased with the increase in the *o*-xylene concentration, and a temperature profile with mild hot spot was observed (Fig. 4a and 4b). But at 325 °C, the reactant conversion remained constant around 95% and a temperature profile with a sharp maximum point in the beginning part of the reactor was obtained (Fig. 4c and 4d). These trends were similar to those for the changes in the feed rates and could be explained similarly with the heat accumulated in the bed. But when the feed concentration was varied, the corresponding heat effects on the reaction seemed more significant. At 300 °C, conversion was reduced to a lesser extent with the increase in the *o*-xylene concentration and the temperature profiles had broad maximum points at higher concentration of *o*-xylene.

The changes in the location of the maximum point in the temperature profile were different depending on whether the feed rate or the feed composition was changed. When the feed rate was increased, the hot spot moved to the direction of reactor exit. On the other hand, the location of the hot spot did not change with the increase in the *o*-xylene fraction. It seems that a higher feed rate increased the linear velocity of the reactant flow in the reactor to push backwards the location of the hot spot. In the case of the change in the feed composition, the linear velocity of the reactant flow was almost same so that no change in the location of hot spot occurred.

The fact that high conversion around 90% was maintained even when the feed flow rate or the feed concentration was increased several times means that it may be possible to increase the production rate significantly by changing the feed conditions. Table 1 shows the changes in the rate of producing phthalic anhydride with a variation of reaction variables. The selectivities of converted *o*-xylene to CO_2 were between 15.3% and 19.3%, which was rather independent of the reaction condition. The yield of phthalic anhydride from *o*-xylene varied from 1.8% to 76.8% depending

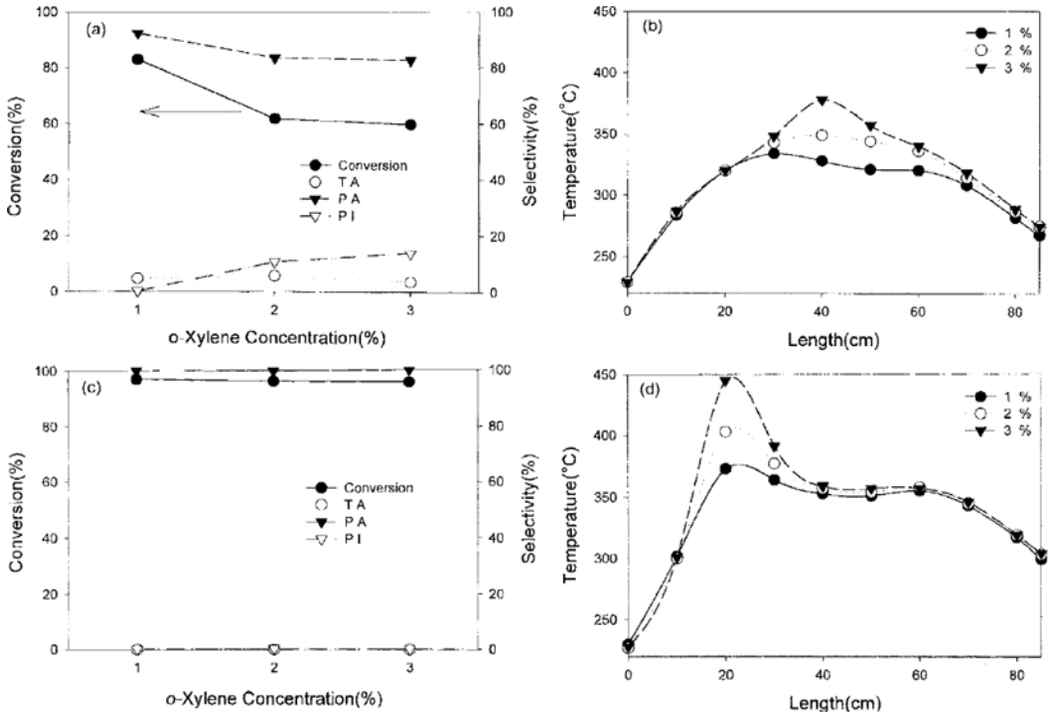

Fig. 4. (a) Effect of the *o*-xylene concentration on the product selectivity (catalyst ratio 2:1, air 2 *l*/min, bath temperature 300 °C; CO_2 excluded in selectivity calculation). (b) Effect of the *o*-Xylene concentration on the temperature profile in the reactor (catalyst ratio 2 : 1, air 2 *l*/min, bath temperature 300 °C). (c) Effect of the *o*-xylene concentration on the production selectivity (catalyst ratio 2 : 1, air 2 *l*/min, bath temperature 325 °C; CO_2 excluded in selectivity calculation). (d) Effect of the *o*-xylene concentration on the temperature profile in the reactor (catalyst ratio 2:1, air 2 *l*/min, bath temperature 325 °C).

Table 1. Production rates of phthalic anhydride at various reaction conditions

Reaction condition		CO_2 selectivity (%)	PA yield (%)	PA production rate (g/hr)
Bath temperature (°C)	280 °C	15.3	1.8	0.5
(2%, 4 L/min, cat 1:1)	300 °C	17.5	18.8	5.2
	325 °C	19.3	74.3	21.1
Feed flow rate	2 L/min	19.2	76.8	11.2
(2%, 325 °C, cat 1:2)	4 L/min	18.8	75.0	21.6
	6 L/min	18.2	70.8	29.5
	8 L/min	17.8	71.9	41.2
o-Xylene concentration	1%	19.3	76.6	5.7
(%)(325 °C, 2 L/min	2%	18.9	76.1	11.2
cat 2:1)	3%	18.0	76.0	16.7

on the conversion of *o*-xylene and the product selectivity. According to Table 1, the production rates for phthalic anhydride could be increased almost proportionally to the concentration of *o*-xylene in the feed or the flow rate of the feed at 325 °C. These results show that there is a big potential for an increase in the production rate in the industrial plant by increasing the feed rate or the feed concentration. But the conditions used in these experiments are much milder than those in industry so it is necessary to apply the industrial reaction conditions to reactor analysis through further experimental work. There are also possibilities of a run-away reaction in this oxidation reactor if the feed rate or the feed composition is increased too much. So the parametric sensitivity of the reaction condition needs to be analyzed via a pilot plant experiment or an accurate modeling work.

CONCLUSIONS

From the bench experiments of *o*-xylene oxidation over V_2O_5/TiO_2 catalysts the following conclusions were obtained.

1. Of the reaction variables investigated, the bath temperature was the most important factor, which affected the product distribution and the temperature profile in the reactor significantly.
2. The conversion of *o*-xylene and the selectivity to phthalic anhydride could be maintained at high values even when the feed flow rate or the feed concentration or *o*-xylene was increased several times.
3. The reaction heat accumulated in the catalyst bed is the main reason for the drastic enhancement of *o*-xylene reaction, which could be utilized in the industrial process to increase the production rate for phthalic anhydride with further experimental work at the plant conditions.

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