

Novel Reaction Scheme for the Selective Oxidation of o-Xylene to Phthalic Anhydride

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The oxidation of o-xylene to phthalic anhydride is one of the important industrial processes based on selective oxidation reactions. For the last 50 years vanadia - titania catalysts have been used in this process. The reaction parameters like temperature range of operation, reactor inlet pressure, contact time, etc. slightly changed during this continuous process optimization. However, the fundamental understanding of the by-product formation is still an open task. By using a sample port pilot plant, a detailed investigation was conducted for the first time of the by-product formation at different operation conditions. Several hitherto unknown intermediates could unambiguously be identified. The combination of process conditions and by-product formation enables the discussion of a new improved reaction scheme for the catalytic oxidation of o-xylene.

1. Introduction

Phthalic anhydride (PA) is produced commercially by passing a mixed gas containing o-xylene (OX) and oxygen (air) at elevated temperatures through a reactor packed with a catalyst enabling the catalytic oxidation of the o-xylene. Mixtures of o-xylene and naphthalene are known too as feedstock. (Tadanori, 1988; Suter, 1972; Towae et al., 1992). In order to achieve high selectivities to PA and to avoid catalyst destruction by temperature run-away, multi-layer catalyst systems are used nowadays. A specific catalyst layer management was developed by Süd-Chemie AG during the last 6 years that renders possible optimized hot spot control. The different layers of the catalyst show significant differences in catalytic activity and selectivity due to the gas phase changing along the reactor (Vejux et al., 1978).

Historically, catalyst development and process optimization went in parallel. Supported by kinetic and surface science investigations a number of assumptions were made on the reaction mechanism. The formation of under- and over-oxidation products was in the focus to enhance the efficiency of the commercial process. The collection of experimental data and theoretical calculations resulted in the following reaction scheme (Fig. 1). However, most of the published results are based on tests using laboratory or bench scale reactors. In these studies, almost no data are reported from pilot plants or

even commercial plants. Therefore, only a limited view was possible on realistic conditions during the o-xylene conversion mechanisms. This study utilizes for the first time a commercial-scale pilot plant charged with a commercial multilayer catalyst and equipped with axial sample ports for the on-line investigation of the oxidation process. Thus, for the first time, a detailed reaction scheme could be developed under industrial process conditions generating a deeper understanding of the by-product formation as function of the reaction propagation as well as the process conditions.

1.1 Catalyst

Initially, the catalyst for this process was based on pure vanadia. The material was loaded into the reactor in form of extrudates, which resulted in poor conversion rates, low selectivities and short life times. Soon the system was changed to vanadia diluted by titania, mainly anatase. The next step in catalyst development history was the change to coated shell catalysts. In relation to the parallel process optimization different layers of sphere or ring type catalysts were used. At the moment a four layer system of coated rings containing vanadia / titania is the leading commercial catalyst.

1.2 Kinetics

The reaction path from OX to PA is commonly described by a rake mechanism consisting of a number of parallel and serial reactions. Tolualdehyde and phthalide are seen as the main intermediates. The most important by-products are maleic anhydride (MA), CO and CO₂. The reaction paths towards the other by-products are widely unknown. MA is described to be formed either by direct oxidation of OX or by over-oxidation of PA. CO and CO₂ are described as combustion products that can form from any of the mentioned components.

Reference	Reaction path according to Figure 1											
	1	2	3	4	5	6	7	8	9	10	11	12
Herten, Froment, 1968	x	x	x		x	x	x				x	x
Calderbank et al., 1980	x	x	x		x	x		x				
Yabrov, Ivanov, 1980	x	x	x		x	x	x	x		x	x	x
Skrzypek et al., 1986	x	x	x		x	x		x	x	x		
Papageorgiou et al., 1994	x	x	x			x				x		
Dias et al., 1995	x	x	x		x	x					x	x
Anastasov et al., 2003	x	x	x		x	x		x				
Gimeno et al., 2008	x	x	x		x	x		x				
Wachs et al., 1987	x	x	x	x		x				x		

Table 1: Reaction paths considered in kinetic modelling

Most previous kinetic schemes reveal a reduced number of reaction paths to the main intermediates as shown in Fig 1. Moreover, some components that appear in the course of the reaction are not taken into account for kinetic modelling. Tab. 1 gives an overview of the reaction paths considered in literature on kinetic modelling.

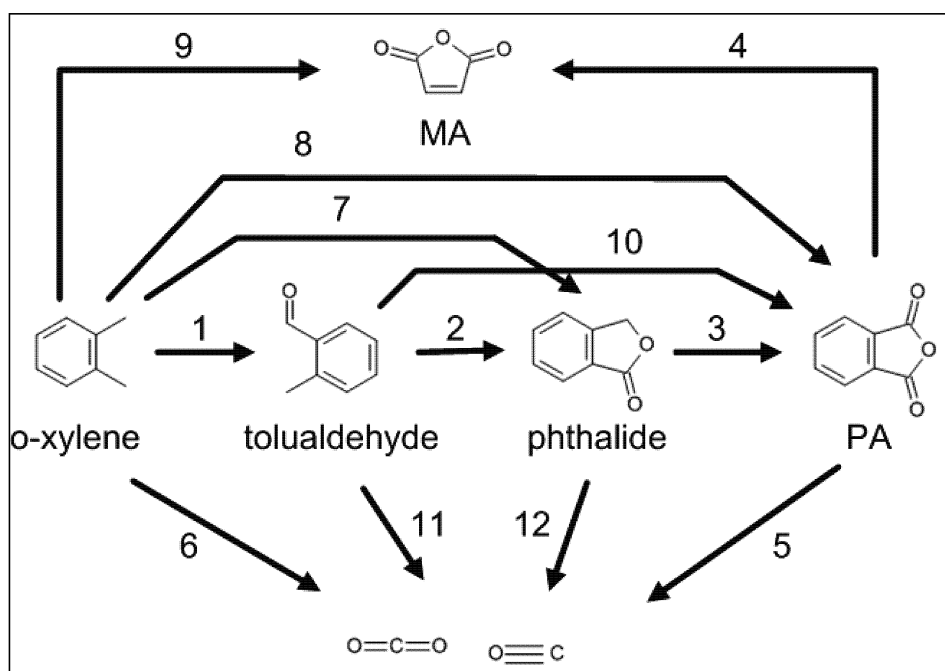


Figure 1: Reaction scheme for the oxidation of OX to PA as reported in the literature

Different from the rake mechanism described by several researchers, Ivanovskaya et al. (1991) suggested that the main route of PA formation is via phthalane (di-hydro-benzofuran) and iso-coumarone (3,4-benzofuran). Recently, Ballarini et al (2009) reported of an additional selective oxidation path from tolualdehyde via phthalaldehyde to phthalic anhydride.

2. Experimental

The commercial catalyst by Süd-Chemie AG (PHTHALIMAX[®]) was used for the investigation. The catalyst is a vanadia-titania mixture based shell catalyst coated on an inert steatite ring support (8 x 6 x 5 mm dimension).

A thermocouple can be directed in a centered thermocouple well (o.d. 3 mm) to any axial position within the reactor (i.d. 25 mm) in order to record temperature profiles. OX is evaporated and mixed with air prior to entering the reactor. The flow rate of liquid OX is controlled by a coriolis-type mass flow controller, the air flow rate is controlled by a thermal mass flow controller.

Fully automated, computer-controlled on-line gas phase analysis can be conducted at reactor entrance and exit as well as twelve other, equally distributed sampling points (6 mm pipes) along the reactor. The total reactor length is 4.5 m.

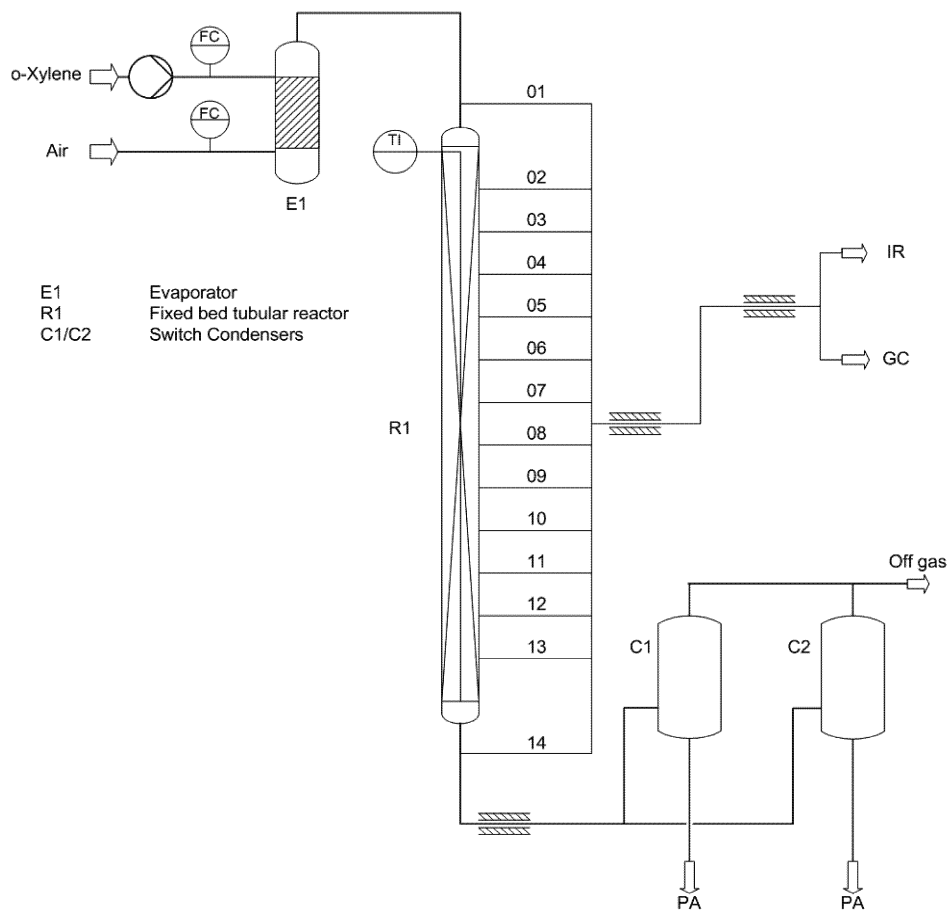


Figure 2: Process flow sheet of the oxidation reactor

The first sampling point is located 150 mm from the entrance of the reactor pipe to the salt bath. Following sampling points have a distance of 250 mm. All sampling lines are connected by a series of multiport valves, which direct the gas stream to the GC and IR analyser. Concentrations of organic compounds are analyzed by means of a standard Agilent 6820N gas chromatograph using a 60m Zebron ZB-5 capillary column. After the sampling loop for the GC, the gas stream is passed through a series of condensers in order to clean the gas stream from any organic, high boiling point compounds and the to further analyze the gas stream for CO, CO₂ and oxygen concentrations by means a NIR analyzer (Emerson NGA 2000) with a paramagnetic channel for the oxygen analysis. The fully automated on-line gas phase analysis method consists of 20 minutes purging the lines with process gas before starting the GC method. The IR analysis is conducted with the start of the GC method for 30 seconds, after which both the IR and the GC lines from the reactor are purged by nitrogen.

At the reactor outlet, crude PA is condensed by water cooled switch condensers. The remaining off gas is totally oxidized in a catalytic exhaust converter.

The industrial reaction conditions for the selective oxidation of OX range between an OX load per tube of 40 g/Nm³h to 100 g/Nm³h. After loading, the catalyst first is calcined in air and subsequently activated in the reaction mixture at temperatures above 370 °C.

3. Results

The reaction conditions applied with an OX load of 80 g/Nm³h at an air flow rate of 4 Nm³/h and a salt bath temperature of 350 °C are not severe and create a steady hotspot. Several gas phase components, such as toluquinone and 2,3-dimethyl-p-benzoquinone not reported yet in the current literature, were observed for the first time in this study. Most of these previously unknown components are reaction intermediates. Figure 3 shows the concentration profiles of some of these components: dimethyl maleic anhydride, 2,3-dimethyl-p-benzoquinone, toluquinone, p-benzoquinone and phthalaldehyde.

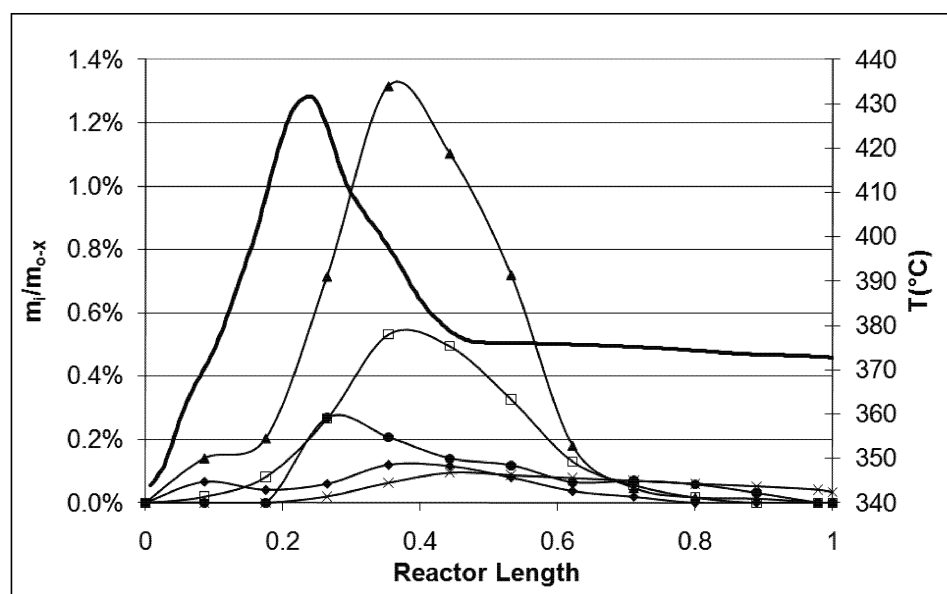


Figure 3: Yield of a selection of by-products in *o*-xylene oxidation, some of which were previously unknown in literature, over the reactor length in wt% based on the *o*-xylene input where \blacklozenge is 2,3 dimethyl-*p*-benzoquinone, \times dimethyl maleic anhydride, \square toluquinone, \blacktriangle phthalaldehyde, \blacksquare *p*-benzoquinone

These intermediates are especially of interest in investigating the formation of the main side-products CO, CO₂ and MA, which account for the largest part of the loss in PA selectivity. Both CO and CO₂ are produced mainly around the hotspot. Also, the concentration of MA rises shortly after the hotspot and remains nearly constant, with a slight rise in the second layer, where the PA concentrations are still relatively low. Consequently, MA is probably produced by a reaction path that is independent of the PA formation, although the over-oxidation of PA cannot be unambiguously ruled out.

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