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# Non-catalytic liquid phase air oxidation of ethylbenzene to 1-phenyl ethyl hydroperoxide in low oxygen volume fraction

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#### Abstract

The catalyst and solvent free liquid phase air oxidation reaction of ethylbenzene (EB) to 1-phenyl ethyl hydroperoxide (PEHP) was investigated at scheduled temperature and pressure with a separate de-acidifying zone. The oxidation reaction was done in the titanium fabricated reactor at an oxygen volume fraction in the outlet gas less than 0.3%. The effects of several reaction parameters were studied in detail. In the optimal reaction conditions and instructions given in this work, the high selectivity to PEHP (above 95%) was achieved with EB conversion around 13%, and a clean feed (water and acid-free) was provided for propene epoxidation reaction.

## Keywords

Ethylbenzene air oxidation, Liquid-phase, 1-Phenyl ethyl hydroperoxide, Non-catalytic

## Introduction

The selective liquid phase air oxidation (autoxidation) of alkylbenzenes to valuable oxygenated products (ketones, aldehydes, and carboxylic acids) through their hydroperoxide intermediates is a chemical reaction of great industrial importance.<sup>1–3</sup> The organic hydroperoxides (ROOHs) are interesting products of hydrocarbon autoxidation which are used as oxidizing agents for olefins.<sup>4</sup> The important examples include cumene hydroperoxide production (more than  $5 \times 10^6$  annual tons) from the oxidation of the cumene (Hock process; for phenol and acetone production),<sup>5</sup> and the synthesis of terephthalic acid from Para-xylene oxidation,<sup>6</sup> or from methane,<sup>7</sup> ( $50 \times 10^6$  annual tons) for the polyester industry.

Liquid phase ethylbenzene (EB) autoxidation to 1-phenyl ethyl hydroperoxide (PEHP) with worldwide production greater than  $5 \times 10^6$  annual tons is another interesting hydrocarbon autoxidation process and improving the efficiency and selectivity toward the PEHP is the first objective for this reaction. PEHP is not the target, but an intermediate product used as an oxygen carrier in propene epoxidation reaction. As shown in Scheme 1, the PEHP production is a key step in the simultaneous production of styrene monomer (SM) and propene oxide (PO) through the well-known SMPO process.<sup>8</sup>



Scheme 1: SMPO Process

At present, the EB oxidation reaction is carried out industrially under conditions that are free of catalyst and solvent at temperatures between 141 and 148 °C and a pressure of three atmospheres.<sup>9,10</sup> Generally, during the oxidation reaction, EB conversion is maintained at about 12 wt.%. Nevertheless, for commercial applications, PEHP selectivity should be more than 95%. The main by-products are acetophenone (ACP) and 1-phenylethanol (1-PE). The ACP is converted to 1-PE by the hydrogenation process and 1-PE is converted into the styrene by the dehydration process.<sup>11</sup> Particular amounts of carboxylic acids and water are produced during the reaction, which is traditionally removed by alkali treatments. The oxidation reaction mixture is concentrated by vacuum distillation up to 20 wt.% with respect to PEHP, which is utilized as a feed (oxygen carrier) for the catalytic reaction of propene epoxidation.<sup>8</sup>

The oxidation reaction of EB in the presence of homogeneous or heterogeneous metal catalysts using oxidants such as  $H_2O_2$ , tert-butyl hydroperoxide (TBHP), and  $O_2$  has been studied by others.<sup>12–15</sup> However, when metal-containing compounds are used in the alkylaromatics oxidation processes, the ROOHs selectivity is low, and the products are mainly ketones and alcohols.<sup>16,17</sup> Therefore, in order to achieve high selectivity of ROOHs, it is necessary to use metal-free systems. In addition, since the epoxidation process is strongly hindered by the presence of metallic catalysts and it is very difficult to remove them by distillation,<sup>17</sup> it was decided that the oxidation reaction of EB was carried out without any catalyst, that provided the very best performance in PEHP production.

The oxidation of EB in the presence of metal-free organic catalysts such as N-Hydroxyphthalimids (NHPI) has also been studied by others.<sup>18–22</sup> In these processes, NHPI in combination with some metal salts or aldehydes acts as a precursor to phthalimide-N-Oxyl (PINO) radicals. The PINO radicals are able to abstract hydrogen atoms from organic substrates. The use of NHPI in the oxidation processes of alkylaromatics has many advantages, including higher conversion, greater hydroperoxide selectivity, and milder reaction conditions, compared to non-catalytic processes. However, there are serious drawbacks with the use of NHPI, for example, product separation is difficult, and the NHPI catalyst is not easily recovered and reused, leads to low synthetic efficiency. In recent years, the heterogenization of homogeneous catalysts, such as immobilization of homogeneous catalysts on solid supports, has been an important field of research because it allows researchers to design and prepare more effective catalysts.<sup>23–25</sup> However, immobilized NHPI is rarely reported.<sup>26–28</sup> Besides, due to the low solubility of NHPI in hydrocarbons, the use of a polar solvent is necessary.<sup>29</sup> Additionally, solvents such as acetonitrile or acetic acid are hydrogen-bond acceptors and form complexes with NHPI, which reduces catalytic activity.<sup>30,31</sup>Also, due to the polarity of PEHP, the solubility of NHPI increases in higher concentrations of PEHP and its recovery by cooling the reaction mixture is more difficult. These problems limit the use of NHPI in industrial applications.

Although the oxidation of EB to PEHP is important from an industrial point of view, the works published in the literature for non-catalytic EB air oxidation to PEHP are extremely scant.<sup>32–34</sup> It has been substantially studied kinetically.<sup>35–37</sup> However, in existing industrial process for EB oxidation, relatively large amounts of ACP and 1-PE are produced as side products and the processes necessary to convert these products to styrene is tedious. Although this oxidation process has been invented as early as 1969,<sup>32</sup> it is still necessary to be considered from the scientific and industrial community. Among them, a few kinds of literature are concentrated on the parameters of the oxidation reaction of EB, which are essential for reaction optimization.

In this present work, we reported investigations on the liquid phase autoxidation reaction of EB without the need for any metal or organic catalysts and with a particular attention to PEHP synthesis. This study led to a better selectivity for PEHP and lower production of secondary products (ACP and 1-PE). Also, a feed free of metal, water, and acid was prepared for propene epoxidation reaction, which can improve the life of the epoxidation catalyst. Since the distribution of the reaction products depends strongly on the reaction conditions, the effect of several important reaction parameters was studied in detail.

## Experimental

Ethylbenzene was oxidized in a stirred reactor of titanium with air as oxidant at the boiling point of water at the selected pressure and without using any catalysts. The pressure was adjusted so that the reaction mixture remained in the liquid phase while the water and light acids produced during the reaction evaporated along with some EB and entered the vapor phase. The evaporated mixture, then condensed and de-acidified in a separate zone by an alkaline solution. In this separate zone, organic and aqueous phases were easily separated from each other and a two-phase system was formed. The upper organic phase was pure and de-acidified EB, which was continuously returned to the oxidation reactor to continue the oxidation reaction.

#### Chemicals and reagents

EB was provided by the Pars Petrochemical Company in Iran, which contained 0.35% by weight of PEHP and was employed without further purification. Synthetic zeroes air (21%  $O_2$  with 79%  $N_2$ , dry and free of  $CO_2$ ) and nitrogen (99.999% of purity) were supplied by Roham Gas Company in Iran. ACP and 1-PE were purchased from Aldrich and used without further purification. Potassium Iodide, glacial acetic acid, sodium thiosulphate and isopropyl alcohol all with an analytical grade were purchased from the Merck Company.

Triphenylphosphine (TPP) purchased from Fluka was crystallized by n-hexane and dried in a nitrogen atmosphere. Its purity was checked by its melting point at 80 °C and also by thin layer chromatography.

#### Reaction equipment and setup

The semi-continuous laboratory reactor utilized in this work for the oxidation of EB is shown in Fig. 1. EB containing a small amount of PEHP is introduced as a feed into the reactor, and the air diluted with nitrogen is continuously introduced into the reactor.



Figure 1: Ethylbenzene oxidation reactor

The reaction vessel was a 1.2 liter double jacket continuous stirred-tank reactor (CSTR) connected to a titanium turbine type impeller powered by a variable speed (0-3000 rpm) engine, a dual jacket reflux condenser, a thermometer, a pressure sensor, two gas inlet systems with porous titanium disk mounted on the bottom; one for air and the other for  $N_2$ . For optimum performance, the baffles were installed inside the reactor. The gas and vapor mixtures that passed through the reactor were transferred through a reflux condenser at a temperature of 80 to 120 °C and then cooled down through a condenser at -5 °C. In the condenser, the vapors turned into liquid, and the remaining gas was heated to room temperature and then transferred to an oxygen-analyzer (Servomex 2223 oxygen analyzer) to measure the Oxygen Volume Fraction (OVF) in the exhaust gas. The OVF in the exhaust gas was adjusted by changing the flux of the inlet air. The condensed vapors containing EB, water, and light acids were transferred to a neutralization/separation vessel containing 5 wt.% sodium hydroxide aqueous solution. In this separate vessel, the neutralization of acids occurred and the neutralized EB (upper phase) was continuously directed to the oxidation reactor.

Since hydroperoxides are relatively stable against titanium, the reactors, vessels, fittings,

condensers, thermocouples, pressure sensors, impeller and sampling facilities were all selected from titanium to prevent the unwanted hydroperoxide decomposition. The reactor vessel was purchased from Buchiglasuster Company/Switzerland/(www.buchiglas.ch).

Using USH400 Lauda heating circulator, both the reactor vessel and the reflux condenser were heated. The task of this circulator was to heat the reaction mixture at the beginning of the oxidation reaction, as well as cool the reaction mixture after the reaction was sufficiently progressed. The synthetic zeroes-air (dry and free of  $CO_2$ ) and nitrogen gas, through two separate pressure cylinders and after passing through the mass flow controllers, Brooks model 5850TR, were introduced into the oxidation reactor.

#### Ethylbenzene autoxidation: general procedure

The oxidation experiments of EB were carried out in batch and semi-continuous mode with gas injection continuously. In a typical experiment, 900 mL (780.30 g) of EB containing approximately 0.35% by weight of PEHP was charged to the reactor. The reactor was flushed with  $N_2$  gas to replace existing air and was pressurized to around three atmospheres. Then the reactor content was heated to 155 °C and stirred vigorously at 1400 rpm. As soon as the temperature reached a stable state, a mixture of air and  $N_2$  was sent to the reactor at a rate of 200-1700 mL/min and the reaction began. In order to prevent the explosion, it is necessary to control the OVF in the reactor outlet gas in less than 5%. This can be accomplished by adjusting the flow of air into the reactor.

In the next step, the temperature program started, so that it remained at  $155 \,^{\circ}$ C for 30 minutes and then dropped to  $140 \,^{\circ}$ C for 240 minutes. By decreasing the reactor pressure, water and light acids along with a small amount of EB were continuously released from the reaction mixture. The pressure program was adjusted so that the reaction mixture remained at three atmospheres for 30 minutes and then dropped to 1.2 atmospheres for two hours and remained at this pressure before the end of the reaction. The reflux condenser temperature was set at  $80 - 120 \,^{\circ}$ C so that almost all reaction products, including PEHP, ACP, 1-PE,

and more than 75% by weight of EB, were condensed into the reactor.

By choosing suitable temperatures for the reactor and the reflux condenser, as well as the reactor pressure and the flow rate of the outlet gas, a mixture of gas and vapor containing  $N_2$ ,  $O_2$ , EB, water, and light acids were passed through the reflux condenser and were transferred to a cold condenser. In this cold condenser with a temperature of -5 °C, the vapors condensed into a separate zone of neutralization/phase separation. To eliminate remaining vapor that can be condensed, the exhaust gas was then passed through an additional cold trap with a temperature of -20 °C, was warmed to room temperature and then directed to an oxygen analyzer to measure the OVF.

The condensed liquid part was consisted mainly of EB and small quantities of water and light acids produced during the oxidation reaction, which after neutralization, by contacting with 5 wt.% NaOH aqueous solution, and the phase separation, the organic phase, which was pure and de-acidified EB, was continuously transferred to the oxidation reactor using a pump or gravity.

According to the data reported by Alcantara *et al.*,<sup>17</sup> we selected 1400 rpm as a suitable stirring speed. For the experiment at 1400 rpm, a sharp decrease in PEHP selectivity was observed when the EB conversion reached 13.45%. That's why in all experiments EB conversion was kept at less than 11%.

#### Safety

Autoxidation reactions of hydrocarbons are usually exothermic and proceed through a free radical chain mechanism and the reaction heat from non-isothermal conditions in the reactor decreases the selectivity of the reaction.<sup>38</sup> For safety reasons, the concentration of PEHP should be less than 20% by weight relative to the total weight of the reaction mixture. According to the results of the experiments performed in this work, in the selected temperature range from 140 to 155 °C, the PEHP was slowly decomposed and there was always a competition between the rate of production and the rate of PEHP decomposition.

During the oxidation reaction, the PEHP decomposition rate was increased with increasing concentrations. However, after reaching a concentration of 11%, the decomposition rate was much higher than that of PEHP production. Generally, the best way to avoid the thermal decomposition of PEHP is to scrupulously adhere to the recommended temperature, time, and concentrations proposed in this work.

In order to have a reaction mixture in the liquid phase, it is necessary to perform the reaction under pressure. The nature of the corrosion of the reaction mixture at high temperatures forces the usage of equipment made of titanium. The reactor surface effect is especially big for a small reactor in which the volume-to-wall surface ratio is low. The temperature of the outlet gas from the reactor is usually as high as the reactor temperature. To avoid the risk of explosion, usually after cooling to ambient temperature, the OVF in the outlet gas is kept at less than 5%. Fortunately, since in this work the condenser temperature was less than  $-5^{\circ}$ C, without the risk of explosion, the outlet gas from the reactor can have up to 21% oxygen.

#### Sampling and analytical methods

The sampling of the reaction mixture was performed at the specified time intervals. The samples were cooled down before the gas chromatography (GC) analysis to avoid evaporation of the hydrocarbons in the samples and the loss of the materials.

Quantitative measurement of PEHP was done by iodometric titration, utilized by Alcantara *et al.*<sup>17</sup> method or by a modified method, which has been described in the next section. The quantitative measurements of EB, ACP, and 1-PE were performed by GC analysis. After measuring the amount of PEHP and before GC analysis, toluene was added to the cooled samples as an internal standard. The identification of oxidation products was performed by comparing retention times for pure 1-PE and ACP in the chromatograph. In addition, the PEHP in the chromatograph did not completely decompose into the 1-PE and ACP.

On the other hand, PEHP is easily and quantitatively reduced by Triphenylphosphine

(TPP) to yield 1-PE,<sup>39</sup> (Eq. 1). This reaction previously used by Toribio *et al.*<sup>18</sup> for GC analysis of EB oxidation reaction mixtures.

$$PEHP + TPP \longrightarrow 1 - PE + TPPO \tag{1}$$

Indeed, if the chromatographic analysis of the sample is performed without hydroperoxide reduction with TPP, the actual concentrations of the components of the sample are not obtained correctly because only a small amount of hydroperoxide can provide a separate peak on the chromatogram. Also, a small amount of hydroperoxide in the chromatogram is decomposed into various derivatives, which did not actually exist in the prototype. In addition, at high temperatures of the gas chromatography system, the reaction between PEHP and EB can be continued and lead to the production of products that were not actually in the reaction mixture. Therefore, PEHP cannot be analyzed by GC. So, before analyzing the samples, it is necessary to reduce the PEHP with TPP to 1-PE.

The EB oxidation products, except PEHP, were analyzed periodically after adding a stoichiometric amount of solid TPP and also adding a certain amount of toluene as the internal standard. They were analyzed on an Agilent Technologies 6890N gas chromatography equipped with Cp-Wax 52CB capillary column (30 m length, 0.32 mm internal diameter and 0.5  $\mu m$  film thickness) and flame ionization detector (FID), 240 °C, He as a carrier gas and injection temperature 210 °C. The oven temperature was adjusted at 100 °C for just one minute and was increased by 13 °C/min up to 230 °C, where it was kept for just two minutes. This GC was calibrated for EB, ACP, and 1-PE.

If 15 to 30 minutes before the GC analysis, the stoichiometric amount of solid TPP is added to each sample and the resulting chromatogram differs significantly from the chromatogram of the sample without the addition of TPP, then it can be concluded that there was PEHP in the list of oxidation products. Actually, after reduction with TPP, the 1-PE peak raised markedly whilst the ACP peak decreased. Usually, the sum of 1-PE and ACP concentrations in the reduced sample was *not equal* to the sum of 1-PE and ACP concentra-

tions in the perfect sample that is untreated with TPP. This indicates that the sample has PEHP as the main component that is not decomposed completely during the GC analysis.

In summary, to determine the actual values of the components of the EB oxidation mixture, the samples were cooled at first, and the PEHP value was determined using an iodometric method. Then, the stoichiometric amount of TPP was added to reduce the PEHP to the 1-PE, and after 15 to 30 minutes, a certain amount of toluene was added to the samples as the internal standard. The actual concentrations of EB, ACP, and 1-PE, were quantified by integrating the corresponding chromatogram peaks and simultaneously solving equations; (2), (3), and (4).

$$[EB]_{real} = [EB]_{TPP} \tag{2}$$

$$[ACP]_{real} = [ACP]_{TPP}$$
(3)

$$[1-PE]_{TPP} = [1-PE]_{real} + [1-PE]_{PEHP}$$

$$\tag{4}$$

where,  $[EB]_{real}$ ,  $[ACP]_{real}$ , and  $[1-PE]_{real}$  are the actual concentrations of EB, ACP, and 1-PE contained in the reaction mixture at the certain moment, respectively. The  $[EB]_{TPP}$ ,  $[ACP]_{TPP}$ , and  $[1-PE]_{TPP}$  are the observed concentrations of EB, ACP, and 1-PE determined by integration of the GC peak related to EB, ACP, and 1-PE after treating the reaction mixture with TPP, respectively. The  $[1-PE]_{PEHP}$  is the stoichiometric quantity of 1-PE that is produced from the reaction of PEHP with TPP (Eq. 1).

It should be noted that the ACP concentration obtained from the chromatogram before reduction with TPP (direct injection of reaction mixture) is not actually the  $[ACP]_{real}$ ; because PEHP is decomposed to ACP and 1-PE in the GC injector. Subsequently, after determining the actual concentrations of the components of the EB oxidation reaction mixture, the EB conversion (%) and the PEHP selectivity (%) were calculated using the most common calculation procedure,<sup>4</sup> often defined as follows:

$$Con_{EB} = \frac{[PEHP] + [ACP] + [PE] + [Other]}{[EB]_0} \times 100$$
(5)

$$Sel_{PEHP} = \frac{[PEHP]}{[PEHP] + [ACP] + [PE] + [Other]} \times 100$$
(6)

where, [PEHP], [ACP] and [PE] are the weight percent concentrations of 1-phenyl ethyl hydroperoxide, acetophenone and 1-phenylethanol, respectively, in the sample and  $[EB]_0$  is the initial weight percent of EB.

#### Hydroperoxide determination

The standard iodometric titration for the determination of hydroperoxides has been used for many years. According to our knowledge, only procedure in which the focus had been on the determination of PEHP has been introduced by Alcantara *et al.*<sup>17</sup> The Alcantara method was modified in the present study, using absolute ethanol (Abs.EtOH) and solid potassium iodide (KI) instead of 99% isopropyl alcohol (IPA) and a saturated solution of KI in IPA. The procedure was as follows.

Sufficient Abs.EtOH (usually 20-25 mL) was added to the 0.5 g of KI in 100 mL volumetric flask, followed by 0.5 mL of acetic acid-sodium acetate buffer. The mixture was heated almost to boiling point (65 - 70 °C), kept at this temperature range for three to five minutes with slow magnetic stirring. Then, without cooling, 0.1-0.3 g of hydroperoxide containing sample was added and the solution was heated for further five to ten minutes. Depending on the amount of hydroperoxide present in the sample, the reaction mixture turns yellow to red. The liberated iodine was titrated with 0.1 N sodium thiosulfate solution until the yellow color of the iodine disappeared. A parallel analysis was done for the blank. All results indicated an average of at least three determinations. Because of the non-aqueous solution, starch is not a satisfactory indicator in this solvent system. The PEHP concentration (wt.%) in the samples was calculated according to Alcantara method.<sup>17</sup> For the same sample, both

the Alcantara method and the modified method, presented in this work, provided almost identical results which were confirmed by <sup>1</sup>HNMR analysis.

Actually, the selected sample for confirmation of the amount of PEHP was the crude product obtained from the oxidation reaction of EB with 10% by weight PEHP content, calculated by Alcantara method.<sup>17</sup> <sup>1</sup>HNMR spectrum was obtained in deuterochloroform (CDCl<sub>3</sub>) with a 250 MHz Bruker instrument. Tetramethylsilane (TMS) was used as an internal standard and chemical shift of the proton that is presented as  $\delta$ (TMS=0). A typical <sup>1</sup>HNMR spectrum is given in Fig. 2.



Figure 2: <sup>1</sup>HNMR spectra in CDCl<sub>3</sub> of the crude product obtained upon oxidation of EB

The hydroperoxy proton appeared as a broad singlet downfield from the TMS. The chemical shift was concentration dependent, as Fujiwara *et al.* showed;<sup>40</sup> at approximately 1M in  $CDCl_3$  the hydroperoxy proton gives a signal at about 8 ppm downfield. Interpretation and assignment of these peaks are summarized in Table 1.

Although aromatic protons appear in the same downfield region as ROOHs do, there is no problem in identifying the O–O–H signal as the hydroperoxy proton readily undergoes deuterium exchange. Methyl protons,  $\beta$  to the hydroperoxy, are unaffected by it and show a typical sharp singlet at nearly the same position as that of the non-peroxidic analog. The O–O–H signal was shifted up-field from 8.15 at 1.0 M to 7.75 ppm at 0.01 M; at infinite dilution, the signal is at 7.3-7.5 ppm (extrapolation from 0.01 M). It is presumed that the concentration dependence results from a decrease in intermolecular hydrogen bonding

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Chemical shift (ppm)	Peak kind	Iintegration	Assignments
$1.2 \sim 1.6$	Triplet	4.35	$CH_3$ protons of EB
$1.6 \sim 1.8$	Doublet	2.18	$CH_3$ protons of 1-PE
$2.6 \sim 2.8$	Singlet	1.00	$CH_3$ protons of ACP
$2.8 \sim 3.0$	Tetralet	3.03	$\alpha$ -H on EB
$5.0 \sim 5.1$	Tetralet	0.05	$\alpha$ -H on 1-PE
$5.2 \sim 5.4$	Tetralet	0.32	$\alpha$ -H on PEHP
$7.3 \sim 7.7$	Multiplet	10.42	aromatic $\operatorname{protons}^a$
01 00	D. 11.4	0.00	

Table 1: Assignments of peaks of <sup>1</sup>HNMR spectra of the crude EB oxidation products

 $\frac{8.1 \sim 8.2}{a \text{ This peak is covvered by } O-H \text{ proton of } 1-PE. b \text{ This peak is covered by } O-O-H \text{ proton of PEHP}.}$ 

due to dilution.<sup>41,42</sup> Compared with the hydroxyl proton of alcohols, the large downfield shift of the signal of the hydroperoxy proton cannot, therefore, be attributed to an unusual hydrogen bonding effect but is a reflection of the large de-shielding effect of the peroxy group. As can be seen in table 2, for the same sample, the results of <sup>1</sup>HNMR and those of the standard iodometric method of Alcantara,<sup>17</sup> as well as our modified method for the PEHP determination, were in good agreement.

Method	Concentration (wt.%)				
	PEHP	ACP	1-PE	EB	
Alcantara <sup>17</sup>	10.00	11.20	25.20	47.20	
Modified	10.20	11.53	24.80	53.47	
$^{1}\mathrm{HNMR}^{a}$	10.57	11.88	25.89	51.66	
1					

Table 2: Comparision of three methods for hydroperoxide determination

<sup>a 1</sup>HNMR spectra was obtained in CDCl<sub>3</sub>

## **Results and Discussion**

The non-catalytic reaction of EB autoxidation was carried out in a liquid phase at a temperature range of 140 to 155 °C and a pressure range of 1 to 3 atm. The three main products, including PEHP, ACP, and 1-PE were produced in this reaction (Scheme 2). Phenol, benzaldehyde, benzoic acid, and water were also obtained in small quantities.



Scheme 2 Ethylbenzene oxidation main products

In fact, the autoxidation of EB at a temperature of more than  $130 \,^{\circ}\text{C}$  is exactly an example of an auto-catalytic free radical chain reaction that prevents selectivity control. The mechanism of this reaction has been extensively studied by others,  $^{12,36,37}$  which the most accepted one is shown in Scheme 3;

Initiation by heat or light:

$$ROOH \longrightarrow RO' + HO' \tag{7}$$

$$RO' + RH \longrightarrow ROH + R'$$
 (8)

$$HO' + RH \longrightarrow H_2O + R'$$
(9)

Propagation:

$$R' + O_2 \longrightarrow ROO'$$
 (10)

$$ROO' + RH \longrightarrow ROOH + R'$$
(11)

*Termination:* 

$$ROO' + ROO' \longrightarrow ROH + Q = O + O_2$$
(12)

Scheme 3 Classical free radical chain reaction mechanism of hydrocarbon autoxidation.

Q=O denotes the respective carbonyl compounds.<sup>18</sup>

Since oxygen is too inactive for hydrogen absorption, the autoxidation of a hydrocarbon bond (C-H) to the hydroperoxide (C-O-O-H) group with oxygen is very slow. But when a small amount of free radicals is created by some of the initiation processes, it reacts with oxygen and produces peroxy radicals (ROO<sup>•</sup>). These peroxy radicals attract hydrogen from a hydrocarbon and promote the radical chain reaction. Although the oxidation of EB is favorable thermodynamically, it is kinetically hindered; so it is often necessary to carry out oxidation at fairly high temperatures. Therefore, the temperatures of 140 to  $155 \,^{\circ}$ C) are not unusual for the autoxidation of EB. In this temperature range, the decomposition of PEHP in order to produce free radicals (reaction 7) is a key step in the oxidation reaction. For this reason, before starting the oxidation reaction in the liquid phase, a small amount of hydroperoxide is added as a radical initiator to the hydrocarbon feed.<sup>37</sup> That is why in all experiments a small amount of PEHP (0.35 wt.%) was added to the reaction mixture.

The rate of such reactions is greatly increased by adding small amounts of transition metal ions, which catalyze the formation of radicals upon homolytic bond cleavage of the hydroperoxide.<sup>43,44</sup> Nevertheless, in the absence of active metal ions, a thermal oxidation reaction occurs. Although it was often assumed that radicals are generated upon O-O scission in hydroperoxide (reaction 7), Turra *et al.*<sup>45</sup> believed that unimolecular cleavage is too slow and inefficient to play an important role. Alternatively, they assumed a bimolecular initiation reaction in which the hydroxyl radical produced from the peroxide homolytic thermal decomposition, abstracts a hydrogen atom from an assisting molecule, leading to the formation of water (reaction 13). They also emphasized that the water acts as a 'spin-insulator' between the two radical products, hindering the immediate recombination to ROR. The  $\alpha$ -hydrogen in EB molecule, making reaction (13) energetically more favorable.

$$ROOH + R - H \longrightarrow RO' + H_2O + R'$$
(13)

The RO<sup>•</sup> and R<sup>•</sup> radicals will subsequently react with the substrate or with  $O_2$ , respectively, producing peroxy radical (reactions 10). The peroxy radicals (ROO<sup>•</sup>) can propagate the radical chain (reaction 11), or react together and lead to the radical termination (reaction 12). As mentioned by Herman *et al.*<sup>45</sup> the lifetime of the peroxy radicals ROO<sup>•</sup> ( $\approx$  1-10 s) is significantly shorter than the changing time of peroxy radicals to other radicals ( $\approx$  1-30 min.). Therefore, a quasi-steady state of peroxy radical concentration will be established. By increasing the PEHP concentration during the oxidation reaction, its thermal decomposition is increased by reaction (7) and according to the reaction (10), the concentrations of peroxy radicals, increases and the possibility of a termination reaction (12) increases. For this reason, the concentrations of the side products, ACP and 1-PE will increase over time. In order to prevent this behavior, the temperature program was selected from 155 to 140 °C, and the PEHP concentration was kept below 10% by weight.

In a stationary state, the initiation rate (of the R<sup>•</sup> radicals) must be equal to the termination rate (of the ROO<sup>•</sup> radicals):

$$r_7 = k_{12} [ROO^{\cdot}]^2 \tag{14}$$

The reaction rate:  $(Rate = -d[O_2]/dt = -d[RH]/dt = k_{10}[R^{\cdot}][O_2] = k_{11}[ROO^{\cdot}][RH])$ is:

$$Rate = \frac{k_{11} \cdot [RH] \sqrt{r_7}}{\sqrt{k_{12}}}$$
(15)

The hydroperoxide might be decomposed according to a first or even a second order reaction. Since there are different radicals (RO' and HO'), the reaction rate constant for the initiation is  $k_8 + k_9$ . However, the overall equation of the initiation velocity can be written as:

$$r_7 = k_7 [ROOH] \tag{16}$$

The equation for the reaction rate is:

$$Rate = \frac{k_{11}.\sqrt{k_7}.[RH].\sqrt{[ROOH]}}{\sqrt{k_{12}}}$$
(17)

The addition reaction of alkyl free radical ( $\mathbb{R}^{\cdot}$ ) to oxygen results in the synthesis of peroxy free radical ROO<sup>•</sup> (reaction 10). Based on the previous similar work,<sup>46</sup> it is believed that this reaction step is instantaneous because the conditions for high Oxygen Partial Pressure (OPP) are achieved. Anyway, in the present work, as previously assumed by Shang *et al.*,<sup>47</sup> this step of the reaction was recognized as the rate-determining step.

As concluded by Gutmann and co-workers,<sup>16</sup> the aerobic oxidation of EB to produce ACP through the intermediate of PEHP is generally accomplished by the decomposition of PEHP into 1-PE as an intermediate. The 1-PE is subsequently oxidized to ACP, and then the ACP is gradually more oxidized and converted to benzoic acid. This pathway is verified by Romeo and co-workers,<sup>44</sup> using hydrogen peroxide as an initiator for air oxidation of 1-PE to ACP with good yield. In order to avoid the subsequent oxidation of the target hydroperoxide products, the oxidation of hydrocarbons is usually carried out in less than 10% conversion. In any case, at high OPP for the oxidation reaction of EB, the subsequent oxidation of the ACP to benzaldehyde and then to benzoic acid is performed.

The concentration of hydroperoxides is also affected by the presence of acids and water. Indeed, the decomposition of hydroperoxides in the presence of acids is accelerated, for example, the decomposition of cumyl hydroperoxide with sulfuric acid in phenol production process,<sup>5</sup> can be expressed. Water has a negative effect on PEHP selectivity and product quality. The reaction rates of EB oxidation to 1-PE, as well as the oxidation of 1-PE to ACP, is the same and are faster compared to the subsequent oxidation of the ACP to benzoic acid. As a result, the amount of benzoic acid produced during the EB oxidation reaction was relatively small. In order to optimize the reaction parameters, the reaction conditions including reaction temperature and pressure, gas flow rate, reaction time, and OVF in outlet gas were investigated on the reaction performance.

#### Reaction time effect

In EB autoxidation reaction, a brief induction time was observed. Usually, if a small amount of PEHP (0.25 to 1% by weight) is added from the beginning to the reaction mixture, this step can be bypassed.<sup>37</sup> In this induction time, the original radicals are formed by thermal decomposition of the PEHP present in the reaction feed.

The effect of the reaction time on the conversion of EB at various temperatures is shown in Fig. 3. As can be seen in the figure, the EB conversion increased over time. The experiments showed that the initial reaction rate at temperatures below 140 °C was much slower than the other ones, for which an induction time of about 30 minutes was observed. After 30 minutes, the EB conversion rapidly increased over time. At the temperature of 155 °C, the induction time of the oxidation reaction was not apparent.



Figure 3: EB conversion at various temperatures for EB autoxidation reaction. OVF in outlet gas= 0.1%, gas flow rate= 1700 mL/min, pressure=1.2 atm., Temperature= $148 \degree \text{C}$ .

In optimum reaction conditions, the effect of reaction time on products selectivity is shown in Fig. 4. As seen in the figure, after four hours from the induction time, the selectivity of PEHP decreased while selectivity for ACP, 1-PE, and other side products increased. However, with the accumulation of PEHP, its decomposition accelerated and reduced the selectivity of PEHP. These results indicated that four hours was a good time to achieve the 91% selectivity of PEHP. At higher temperatures, the PEHP accumulation took place relatively less, because the thermal decomposition of PEHP was dominant and more side products were produced.

Fig. 5 shows the variations in PEHP concentration (wt.%) relative to the reaction time (hr.) at different temperatures. It can be seen that, after five to six hours, the concentration of PEHP begins to decrease at 148 °C and 155 °C, while at 120 °C and 140 °C, the concentration of PEHP increases linearly for 10 hours.



Figure 4: Selectivity of EB autoxidation products at 148 °C. OVF in outlet gas = 0.1%, gas flow rate = 1700 mL/min, pressure = 1.2 atm.



Figure 5: PEHP concentration at various temperatures for EB autoxidation reaction. OVF in outlet gas= 0.1%, gas flow rate= 1700 mL/min.

As illustrated in Fig. 6, there is a relationship between the conversion of EB and the selectivity of PEHP. In fact, when the EB conversion increased by about 12%, the selectivity of PEHP was dramatically reduced while selectivity for ACP, 1-PE and other by-products increased. So we kept the concentration of PEHP below 12% by weight. It can be concluded that by increasing the conversion of EB, the selectivity of PEHP increases. However, prolonging the reaction time up to 10 hours led to a substantial decline in the selectivity of PEHP and an increase in the selectivity of other by-products. It means that the reaction products are formed as a result of a competition between PEHP production and decomposition.

Indeed, over time, the concentration of PEHP increased from 0.35% to about 10% by



Figure 6: Product selectivity versus conversion for EB autoxidation reaction at 148 °C. OVF in outlet gas=0.1%, gas flow rate= 1700 mL/min.

weight, and after about 5 hours, the thermal decomposition of PEHP increased faster than its production rate, and the concentration of PEHP began to decrease. Under optimal reaction conditions, EB conversion was 11.1% and selectivity of PEHP was 95.02%. In the industrial unit, the EB conversion is controlled in less than 13% to ensure that the PEHP selectivity is greater than 90%.<sup>4</sup>

#### **Temperature effect**

In order to evaluate the effect of temperature on EB conversion and selectivity to PEHP for EB autoxidation reaction, four temperatures of 120, 140, 148, and 155 °C were selected. The results are shown in Figures 3, 5 and 7. The pressure was adjusted so that, at the selected temperature, the water and light acids produced during the reaction entered the vapor phase and evolved from the reaction medium through the gas stream.

By increasing the reaction temperature from 120 to 155 °C, the EB conversion was increased significantly (Fig. 3) and the selectivity of PEHP was decreased (Fig. 7). Based on the data presented in Fig. 5, due to the higher value of the rate constant at higher temperatures, although the concentration of dissolved oxygen was reduced, when the temperature was increased, the formation rate of hydroperoxide was high. The PEHP selectivity did not improve with increasing temperature (Fig. 7) because the PEHP decomposition was accel-



Figure 7: PEHP selectivity (%) versus time for EB autoxidation reaction at various temperatures. OVF in outlet gas = 0.1%, gas flow rate = 1700 mL/min.

erated at higher temperatures. However, this behavior for other side products (ACP, 1-PE, and acids) was inverted, and as the temperature rises, the selectivity for ACP and 1-PE were increased. Further increase in temperature facilitates the synthesis of other oxidation products (benzaldehyde, benzoic acid, and phenol). Although the stationary concentration for PEHP is generally higher at lower temperatures, the reaction rate for industrial applications is too low.

When the concentration of PEHP was more than 10 wt.%, it was observed that the PEHP selectivity was decreased and the selectivity of the ACP and 1-PE was increased, which can be due to the increase in decomposition rate relative to the rate of production of PEHP. Thus, the reaction temperature is an essential factor in maintaining high selectivity for PEHP and having the highest EB conversion, as well as minimal selectivity for ACP and 1-PE.

Based on the results of the experiments, the temperature range from 155 to 140 °C was determined as the temperature range for the experiments. Temperatures below 140 °C reduced EB conversion, while temperatures above 155 °C caused further oxidation to benzoic acid. After extensive experiments, the most effective temperature program for the EB autoxidation reaction was 30 minutes at 155 °C and then reduced to 140 °C for 240 minutes and kept at this temperature until the end of the reaction time. The reflux condenser temperature was so adjusted that the water and light acids produced during the oxidation reaction could be steadily released from the reactor, as soon as they were produced. This temperature range was from 80 to 120 °C.

#### Pressure effect

Almost all previous authors believe that the pressure applied to the EB autoxidation reaction is to maintain a reaction in the liquid phase. In any case, we found that the pressure should be so adjusted that at the selected reaction temperature, the water and light acids produced during the reaction can evaporate and leave the reaction mixture together with the gas stream.

Korthals *et al.* believed that water and ACP are essentially produced by PEHP decomposition under reaction conditions.<sup>36</sup> Water and acids restrict the oxidation reaction and reduce the PEHP production rate and product quality. Therefore, in the present work, the water generated was condensed in a cold trap and acids produced from the ACP oxidation reaction was controlled by controlling the OVF in the outlet gas. These acids were neutralized in a separate zone containing dilute sodium hydroxide solution. At high temperatures, the concentration of dissolved oxygen decreases and therefore, a higher pressure is required to have at least the oxygen concentration in the reaction mixture. At a higher temperature than the boiling point of EB and below the boiling point of water, at a selective pressure, water and light acids, along with a small amount of EB, entered the gas phase and left the reactor.

The vapors and gases released from the reactor were cooled down in a condenser at a temperature of -5 °C and were treated with an alkaline solution and de-acidified. After separating the phases, the neutralized EB was transferred to the reactor to continue the oxidation reaction. By examining the results of the experiments, we found that, according to the temperature schedule, the pressure should be reduced from 3.0 to 1.2 atmospheres. The selected pressure program, used in this work, included 30 minutes at 3 atm. and then

reduced to 1.2 atm. for 2 hours and then remained at this pressure until the end of the reaction.

#### Oxidant concentration and gas flow rate

Five semi-continuous experiments were carried out to investigate the effect of OVF in the exhaust gas on the conversion of EB and selectivity of hydroperoxide. By changing the ratio of air to nitrogen, the percentage of OVF in the outlet gas was adjusted for five different OVF of (0.1, 0.3, 0.5, 3.0, and 5.0)%. The results are listed in Table 3.

OVF	Conversion	Selectivity (%)			
	(%)	PEHP	ACP	PE	Others*
0.1	11.05	95.02	02.90	01.36	0.72
0.3	13.85	80.29	12.64	06.28	0.79
0.5	17.85	66.39	19.61	09.52	4.48
3.0	20.25	65.28	19.75	09.88	5.09
5.0	22.20	63.42	20.27	10.36	5.95

Table 3: The effect of OVF in the exhaust gas on EB autoxidation reaction<sup>a</sup>

<sup>a</sup>Reaction conditions: Temperature=148°C, Pressure=3 atm., Time=5 hours, gas flow rate=1700 mL/min, stirrer speed=1400 rpm. \*Others=mainly benzoic acid.

According to Table 3, EB conversion increased with increasing the OVF in the outlet gas while the PEHP selectivity was reduced. However, the selectivity of ACP, 1-PE, and other acidic side products have increased with the increase of EB conversion. This might be due to the thermal decomposition of PEHP to water and ACP, and to the oxidation of the ACP to benzaldehyde and then to benzoic acid. By increasing the gas flow rate of oxygen, the EB conversion slightly increased, which was neglected for the desired reaction. Also, the light acids and water produced during the reaction were removed from the oxidation reactor by increasing the gas flow.

In most of the previous work, a simplified kinetics for the oxidation of EB in the liquid phase was predicted based on the free radical mechanism,<sup>11,47,48</sup> in which all the elementary reaction steps were assumed to be of the first-order with respect to liquid reactants and zeroorder relative to gaseous reactants i.e. oxygen. In none of this kinetics explicitly have referred to the effect of the gaseous reactant. In fact, just as it was tested in the laboratory, only experiments performed at low oxygen concentrations showed such a relationship. However, as some previous authors have pointed out,<sup>49,50</sup> the effect of oxygen on the autoxidation of hydrocarbons in the liquid phase can only be ruled out if the oxygen partial pressure (OPP) is greater than a minimum value. This minimum value is between 0.066 and 0.132 atm.<sup>51</sup> Our experimental observations confirmed that the oxidation reaction rate of EB was clearly reduced when the OVF in the outlet gas was less than 0.30%. This suggested that, when the OVF was reduced from a certain value, the oxidation of EB was no longer zero-order with respect to a gaseous reactant (oxygen).

In this work, in agreement with Sun and co-workers,<sup>47</sup> for p-Xylene oxidation, we found that there is a threshold for the OVF in the exhaust gas, which is between 0.10 and 0.30%. When the OVF was less than 0.30%, it had a substantial effect on the oxidation kinetics of EB. As long as the OVF was greater than 0.30%, the oxidation kinetics of EB was almost independent of the OVF. Under the operating conditions of the industrial process of oxidation of EB, the OVF in the reactor falls within this range. Therefore, the amount of EB converted is equal to the amount of oxygen absorbed and only at very low OPP the oxidation rate decreased. On the other hand, additional oxygen resulted in the formation of more acidic by-products. For this reason, under optimized reaction conditions, the OVF in the outlet gases was set to less than 0.3%. The air used as a feed gas was diluted with pure  $N_2$  and gas from the oxygen analyzer to provide the required oxygen content in the feed.

The EB vapors, after neutralization in a separate zone, were condensed and returned to the oxidation reactor;. The selectivity of PEHP was reduced by increasing the OVF, which could be due to the formation of more by-products resulted from further oxidation of EB with additional oxygen. Excellent selectivity for PEHP (95%) along with moderate EB conversion (11%) was observed with OVF less than 0.1% in the outlet reactor gas. Increasing the OVF means increasing the concentration of oxygen in the gas feed and also increasing the PEHP yield. At high concentrations, and particularly for oxidation with OVF=5.0%, PEHP tended to decompose. In fact, the reduction of PEHP yield at higher concentrations has previously described.<sup>52</sup>

Increasing the concentration of oxygen in the gaseous feed was accompanied by an increase in the conversion of EB, which was higher in high concentrations of oxygen. In parallel with EB conversion, the formation of side products (ACP, 1-PE, and acids) was also observed. ACP was the second major product with a higher concentration than the 1-PE. ACP is formed directly from the termination reaction step,<sup>18</sup> or from the oxidation of 1-PE, or through the PEHP decomposition.<sup>36</sup> Apparently, the selectivity toward PEHP was lowest for the highest concentration of oxygen at the end of the test (5 hours).

Figs. 8, 9 and 10 show the effect of the flow rate of the exhaust gas on the EB conversion and the selectivity of PEHP, ACP, 1-PE, and other by-products.



Figure 8: The effect of gas flow rate on EB conversion (%) at 148 °C, during 5 hours, and OVF in outlet gas=0.1%.

As the gas flow rate rises from 200 to 1700 mL/min, the EB conversion increased slightly (Fig. 8), while PEHP selectivity (Fig. 9) and the selectivity of ACP and 1-PE (Fig. 10) remain at approximately the same level. Also, as shown in Fig. 10, by increasing the gas flow rate, the selectivity for other acidic products is reduced. However, a further increase in gas flow rate led to a nearly identical PEHP selectivity. Hence, the gas flow rate of 1700 mL/min was selected.



Figure 9: The effect of gas flow rate on PEHP selectivity (%) at 148 °C, during 5 hours, and OVF in outlet gas=0.1%.



Figure 10: The effect of gas flow rate on ACP, 1-PE, and other by-products selectivity (%) at 148°C, during 5 hours, and OVF in outlet gas=0.1%, others=mainly benzoic acid.

When air and nitrogen were fed into the reactor in such a way that the OVF was 0.1%, the PEHP selectivity was 95%, and when the OVF in outlet gas was 5.0%, the PEHP selectivity decreased to 63%. Nevertheless, careful scrutiny of the PEHP selectivity versus EB conversion revealed that, by increasing the EB conversion, the PEHP selectivity was decreased and at the same time selectivity to ACP, 1-PE, and other by-products were increased. The differences observed in the five concentrations of oxygen studied were the result of differences in differences of EB conversions. This kind of behavior is inherent in the autoxidation mechanism of hydrocarbons in liquid phase.<sup>53</sup>

## Conclusions

In the present work, the aerobic oxidation of EB to PEHP was explored in a liquid phase in a reactor of titanium an in semi-continuous mode. This industrially important oxidation reaction was carried out at a temperature and a pressure programmed with controlling the OVF in the reactor outlet gas to less than 0.3%. The water and light acids generated during the reaction were continuously abandoned by controlling the reflux condenser temperature and adjusting the flow rate of the reactor outlet gas. The reactor outlet gas was condensed in a separate container in which the distilled product was de-acidified by dilute alkali solution. After separating the organic and aqueous phases, the organic phase, which was EB, was returned to the oxidation reactor. The reaction mixture was distilled in a vacuum up to 20% by weight of PEHP, which can be used directly as a feed for the epoxidation reaction.

A technique was developed for preparing water and acid-free feed for propene epoxidation in the presence of a  $\text{Ti}/\text{SiO}_2$  heterogeneous catalyst in the well-known SMPO process. With this feed, catalyst life can be improved. Under optimized reaction conditions, when the EB conversion was about 11%, the PEHP selectivity was more than 95%.

The experiments showed that the OVF in the exhaust gas of the reactor has an important effect on the selectivity of PEHP and the reduction of the concentration of secondary products. That is, in identical conversions for EB with an OVF in the outlet gas of less than 0.3%, the increase in oxygen concentration in the gas feed increases the conversion of EB, but the high selectivity of PEHP and the selectivity of ACP and 1-PE are maintained at a low level.

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