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One-step production of phenol by selective oxidation of benzene in a biphasic system

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Abstract

Phenol production through the direct hydroxylation of benzene with hydrogen peroxide using a catalytic membrane reactor has been studied. The reaction was carried out in a biphasic system separated by a membrane. This new system showed a high selectivity to phenol, minimizing its over-oxidation in over-oxygenated by-products. The effect of various reaction parameters such as the addition of hydrogen peroxide mode, amount of hydrogen peroxide, type of membrane, type of catalyst and organic acid was investigated. The results showed that iron(II) sulphate as the catalyst, 18 mmol of hydrogen peroxide pumped for 4 h in the aqueous phase as oxidant feeding, acetic acid and polypropylene hydrophobic porous support gave the best system performance in terms of produced phenol (17.42 mmol), selectivity to phenol (99.94%), benzene conversion to phenol (1.20%), and hydrogen peroxide conversion to phenol (96.78%).

Keywords: Phenol production; Selective oxidation of benzene; Biphasic system; Membrane reactors; One-step phenol production

1. Introduction

Phenol is one of the most important chemical intermediates in many industrial fields [1,2]. More than 90% of the industrial production of phenol is done using the cumene process, which consists of three steps and produces acetone as a by-product. The concomitant dependence of the by-product, acetone, on the chemical market is a drawback in this process [3].

The one-step production of phenol by direct hydroxylation of benzene represents an attractive and challenging method not only for its economic advantage but also from a chemical transformation point of view, because the direct hydroxylation of the energetically stable benzene to produce phenol is one of the most difficult oxidation reactions. Indeed, its selectivity is usually rather poor since phenol is more reactive towards oxidation than benzene, and substantial formation of by-products such as biphenyl and further oxidation compounds is found. Biphenyl is formed by coupling hydroxycyclohexadienyl radicals and subsequent dehydration, while catechols, hydroquinones and benzoquinones are formed by further oxidation of phenol [4].

New approaches to produce phenol by a one-step process without by-products and with high selectivity have been explored. The gas phase oxidation of benzene to phenol by using nitrous oxide as oxidant have been studied by using H-Ga-ZSM-5 zeolite [5], HZSM-5 [6] and Fe/MFI catalysts [7]. Tani et al. performed hydroxylation of benzene to phenol under air and carbon monoxide catalyzed by molybdovanadophosphoric acid [8]. Itoh et al. [9] reported hydroxylation of benzene to phenol with oxygen and hydrogen using a catalytic palladium membrane. Remias et al. [10] studied the catalytic hydroxylation of benzene and cyclohexane using in situ generated hydrogen peroxide in comparison with the direct addition of hydrogen peroxide. Masumoto et al. [3] reported the liquid-phase oxidation of benzene to phenol by a vanadium catalyst in aqueous solvent with high acetic acid concentration. Park and Choi investigated the hydroxylation in photo catalytic systems by using TiO_2 as heterogeneous photocatalyst and polyoxometalate as a homogeneous photocatalyst [11]. The liquid phase direct hydroxylation of benzene was reported by Smith and Norman [4] using ferrous sulphate–H_2O_2 system (Fenton Reagent). Bianchi et al. [12,13] developed a system where over-oxidation problems were efficiently solved, because in their system the catalyst and the products were segregated into different environments. In particular, they mimic the biological systems where the active sites of several oxygenases are deeply buried in hydrophobic

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pockets where lipophilic substrates are readily oxidized, while the more hydrophilic reaction products are promptly released into the surrounding aqueous environment. The most interesting result of their work is the intuition that a biphasic system could be very promising for realizing the one-step process for phenol production.

In this work the liquid-phase catalytic benzene oxidation to phenol is studied by using a new biphasic system where a membrane is employed in order to avoid phase mixing during the oxidation reaction. Being a pioneering study, only some main operating parameters have been investigated for a reaction time of 4 h without analyzing the system lifetime in long time runs. Hydrogen peroxide as the oxidant, various metal salts as the catalysts, various organic acids to promote phenol extraction in the organic phase, and different kinds of membranes as the permselective barrier for separating the two phases were tested by determining specifically the selectivity and conversion of benzene to phenol.

2. Experimental

2.1. Chemicals

Benzene C_6H_6 (MW = 78.11 g mol^{-1}, purity 99.8%) from Carlo Erba Reagenti was used both as reagent and as solvent. Phenol C_6H_5OH (MW = 94.11 g mol^{-1}, purity 99.99%) and biphenyl $C_{12}H_{10}$ (MW = 154.21 g mol^{-1}, purity 99.99%) from Sigma–Aldrich were used for analytical calibrations.

Iron(II) sulphate $FeSO_4{\cdot}7H_2O$ (MW = 278.02 g mol^{-1}, purity = 99%), iron(II) oxalate dihydrate $FeC_2O_4{\cdot}2H_2O$ (MW = 179.9 g mol^{-1}, purity = 99%), iron(II) chloride tetrahydrate $FeCl_2{\cdot}4H_2O$ (MW = 198.81 g mol^{-1}, purity = 99%) and copper(I) chloride CuCl (MW = 98.99 g mol^{-1}, purity 99%) from Sigma–Aldrich were employed as catalysts.

Hydrogen peroxide H_2O_2 (30 wt.% solution in water) from Sigma–Aldrich was the oxidant.

Acetic acid (MW = 60.05 g mol^{-1}, purity 99.9%) from Carlo Erba Reagenti, ascorbic acid (MW = 176.13 g mol^{-1}, purity > 99%) from Fluka, and trifluoroacetic acid (MW = 114.02 g mol^{-1}, purity 99%) from Sigma–Aldrich were the organic acids tested to achieve acidic pH in the aqueous phase.

2.2. Analysis

Phenol and oxidation by-products in the organic phase were detected by high performance liquid chromatography (HPLC, Agilent 1100 Series instrument) using an Agilent ZORBAX Eclipse XDB-C8 (4.5 mm × 150 mm, 5 μm) column. The mobile phase consisted of an acetonitrile/water solution 80/20 (v/v) fed to a flow-rate of 1.0 mL min^{-1}. The column pressure was 49 bar and the injection volume was 20 μL.

Ultrapure water used throughout the work was obtained from Milli-Q equipment by Millipore.

A pH meter (WTW Inolab Terminal Level 3) with a glass pH-electrode SenTix 81 (WTW), was used for pH measurements.

2.3. Apparatus

Experimental tests in this exploratory phase of the work were conducted in a very simple reactor made with a two compartment cell to separate the organic and the aqueous phases (Fig. 1). The system was composed of:

- Aqueous phase: 130 mL of ultrapure water containing 0.41 mmol of catalyst, hydrogen peroxide as the oxidant, and 4 mmol of organic acid.
- Organic phase: 130 mL of benzene corresponding to 1453.82 mmol.
- Membrane placed between the compartments to separate the two phases.

The phases were stirred by two motors and thermostated by a water bath at 35 °C. The following membranes, in flat sheet configuration, were used in the experiments: hydrophobic polypropylene porous support (Accurel, Membrana, thickness 142 μm; pore size 0.2 μm; porosity 70%); hydrophilic polyacrylonitrile porous membrane (PAN 30 kDa, GKSS); hydrophobic polytetrafluoroethylene porous support (PTFE, Cole Parmer, pore size 0.2 μm).

Samples were withdrawn from the organic phase and analysed.

Obtained results are reported as selectivity to phenol, benzene conversion to phenol, and hydrogen peroxide conversion to phenol at a reaction time of 4 h.

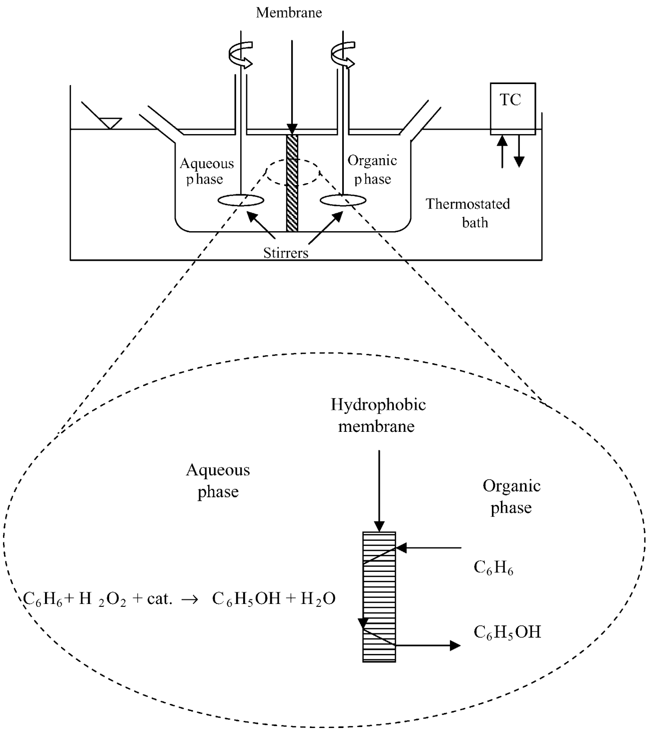


Fig. 1. Schematization of the used membrane reactor (V_{Cell} = 130 mL, T = 35 °C).

3. Results and discussion

The one-step benzene oxidation to phenol happens by the following reaction:

$$C_6H_6 + H_2O_2 \xrightarrow{cat} C_6H_5OH + H_2O \quad (1)$$

so it is necessary to place in contact benzene, hydrogen peroxide and the catalyst. The addition of hydrogen peroxide mode was the first parameter investigated. In particular, a constant amount of hydrogen peroxide of 18 mmol was added, testing three different ways: (i) one-step mode, meaning that all H_2O_2 was added at the start of the experimental run; (ii) pump top mode, by adding the H_2O_2 slowly for 4 h by means of an Ismatec peristaltic pump with a flow-rate of 4.2 mL/h with the drops injected on the water surface; (iii) pump bulk mode, similar to the previous one but with the difference that the oxidant injection was done in the bulk of the aqueous phase of Fig. 1. The initial pH of the aqueous solution containing the catalyst and acetic acid changed from 3.3 to 2.8–2.9 by adding H_2O_2 (18 or 36 mmol) in only one step and this pH was constant during the reaction course as can be also observed from the cycling mechanism of the Fenton reaction below.

The results, reported in Table 1, show that one-step addition of the oxidant at the start of the reaction gave a low conversion based on hydrogen peroxide (39.25%) and a low phenol concentration in the organic phase (5.14 g L^{-1}). Specifically, the reaction proceeded for 120 min with a similar trend with respect to the other addition mode of hydrogen peroxide (Fig. 2). Then, from 120 to 240 min, no phenol production was observed. Adding the hydrogen peroxide slowly (for 4 h) by means of a pump feeding to the bulk of the aqueous phase, a higher conversion based on hydrogen peroxide (96.78%) and a higher phenol production (13.29 g L^{-1}) were achieved. This difference can be explained with the high reactivity of phenol in the aqueous phase: indeed, when the oxidant was added slowly, the interfacial reaction at the aqueous phase-membrane side (see Fig. 1) is the limiting step, so the phenol can permeate through the membrane without over-oxidation caused by other attacks from the hydroxyl radical. Instead, when hydrogen peroxide was fed by the one-step mode, the permeation of produced phenol across the membrane become the limiting step, so a certain amount of phenol was subject to over-oxidation. In this case a greater by-product formation was observed, resulting in lower phenol production and uncontrolled oxidant consumption.

Table 1
Selectivity, benzene and hydrogen peroxide conversion by changing the hydrogen peroxide addition mode ($H_2O_{2(IN)}$ = 18 mmol, PP membrane, acetic acid, $FeSO_4$ as catalyst)

Mode of hydrogen peroxide feeding	Selectivity to phenol (%)[a]	Benzene conversion to phenol (%)[b]	Hydrogen peroxide conversion to phenol (%)[c]
One step	99.29	0.49	39.25
Pump top	99.91	0.81	65.06
Pump bulk	99.94	1.20	96.78

[a] Selectivity to phenol = [mmol phenol/(mmol phenol + mmol biphenyl)] × 100.

[b] Benzene conversion to phenol = (mmol phenol/mmol benzene initial) × 100.

[c] Hydrogen peroxide conversion to phenol = (mmol phenol/mmol hydrogen peroxide initial) × 100.

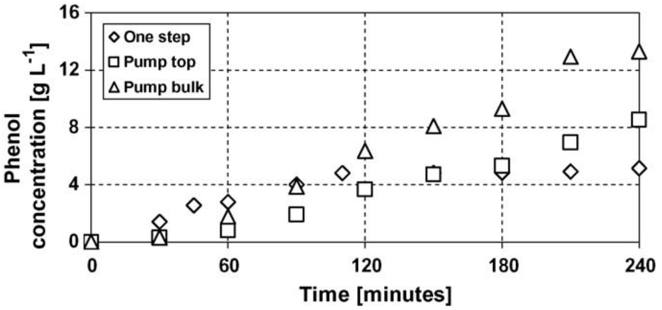


Fig. 2. Phenol concentration in the organic phase vs. time by changing the hydrogen peroxide addition mode.

The high value of selectivity to phenol reported in Table 1 was obtained thanks to its extraction from the membrane–aqueous phase interface to the organic phase so reducing the further contact between the phenol and the catalyst which was soluble in the aqueous phase. Indeed, the acidic pH of the aqueous phase promotes phenol extraction in the organic phase across the membrane that confirms also an insignificant back-diffusion of phenol from the organic to the aqueous phase. It is also noteworthy that in the organic phase only biphenyl was detected among the secondary products with very low concentration values.

Regarding the amount of hydrogen peroxide added in the aqueous phase, the results, reported in Table 2 and in Fig. 3, evidenced an optimal amount of 18 mmol. Indeed, an increase from 9 to 18 mmol increased the benzene and hydrogen peroxide conversion to phenol and the concentration of phenol in the organic phase. A further increase to 36 mmol caused: (i) decrease of benzene conversion to phenol (1.12 versus 1.20) promoting over-oxidation of part of phenol; (ii) decrease of hydrogen peroxide conversion to phenol that was half of the value measured with 18 mmol (45.17 versus 96.78); (iii) a slight decrease in phenol production (11.83 g L^{-1} versus 13.29 g L^{-1}). This behaviour can be explained considering that too much oxidant concentration in the aqueous phase causes an increase of oxidant capacity of the system. Thus, the fraction of produced phenol that did not permeate in the organic phase through the membrane is converted to over-oxidation products, which remain in the aqueous phase being more soluble in this one. This result means that the oxidant has to be present in the solution at appropriate concentration over the reaction time.

Table 2
Selectivity, benzene and hydrogen peroxide conversion vs. hydrogen peroxide amount (H_2O_2 added by pump bulk mode in 4 h, PP membrane, acetic acid, $FeSO_4$ as catalyst)

Amount of hydrogen peroxide (mmol)	Selectivity to phenol (%)	Benzene conversion to phenol (%)	Hydrogen peroxide conversion to phenol (%)
9	99.72	0.25	40.87
18	99.94	1.20	96.78
36	99.94	1.12	45.17

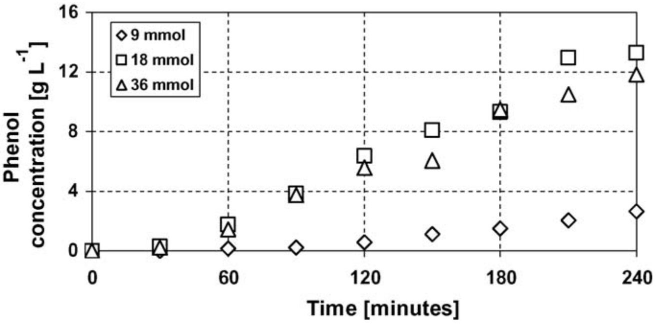


Fig. 3. Phenol concentration in the organic phase vs. time by changing the hydrogen peroxide amount.

Other tests were addressed to investigate the influence of the type of hydroxylation catalyst on the reaction. In particular, iron(II) and copper(I) catalysts were compared in terms of system performance, and different iron(II) salts were studied, to determine the influence of the anion type. The results, reported in Table 3 and Fig. 4, show that the best metal salt in terms of phenol production, and of conversion to phenol based on benzene and hydrogen peroxide, is iron(II) sulphate.

Very poor system performance was observed by using the copper(I) catalyst. This can be explained by the low rate of catalyst regeneration by the following mechanism. The two used Fenton catalytic systems work by means of the following reactions:

- Hydroxyl radical production

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + OH^\bullet + H_2O$$

$$Cu^+ + H_2O_2 + H^+ \rightarrow Cu^{2+} + OH^\bullet + H_2O$$

Table 3
Selectivity, benzene and hydrogen peroxide conversion by changing the type of metal and the type of anion of the salt used as the catalyst ($H_2O_{2(IN)}$ = 18 mmol by pump in 4 h, PP membrane, acetic acid)

Metal salt	Selectivity to phenol (%)	Benzene conversion to phenol (%)	Hydrogen peroxide conversion to phenol (%)
$FeSO_4$	99.94	1.20	96.78
$FeCl_2$	99.82	0.31	50.05
FeC_2O_4	99.95	0.58	47.04
CuCl	99.58	0.12	10.02

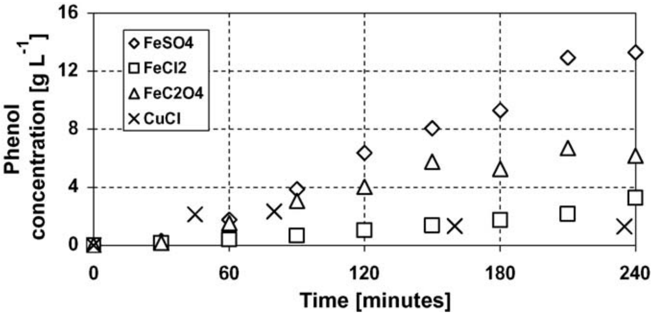
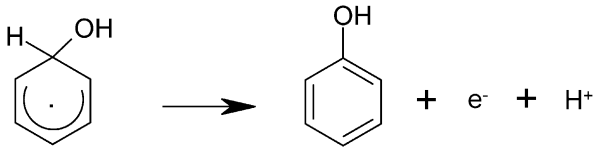


Fig. 4. Phenol concentration in the organic phase vs. time by changing the catalyst type.

The produced hydroxyl radical attacks benzene ring to form hydroxycyclohexadienyl radical. Then this radical is oxidized by Fe^{3+} (or Cu^{2+}) to form phenol and Fe^{2+} (or Cu^+), by the following semi-reaction:

- Oxidation:



- Reduction: catalyst regeneration

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (E^0 = 0.77\,V)$$

$$Cu^{2+} + e^- \rightarrow Cu^+ \quad (E^0 = 0.153\,V)$$

Since E^0 is proportional to ΔG^0 iron catalyst regeneration is thermodynamically more favoured than copper ion as evidenced from the E^0 values.

To confirm the hypothesis of copper deactivation, some tests were carried out by adding an equal amount of copper catalyst when the phenol concentration in the organic phase reached a constant value. A new increase of phenol concentration was observed. The deactivation of the Cu catalyst during the liquid-phase oxidation of benzene is also reported by Takata et al. [14], indeed this showed the irreversible formation of Cu precipitate with no regeneration of the active Cu^{2+} species which is responsible for the phenol formation.

Another important factor studied was the type of organic acid utilized for the aqueous phase acidification. Acidic pH is necessary to promote phenol extraction in the organic phase and also to give optimal pH for the Fenton catalytic system. Specifically, acetic acid ($pK_a = 4.76$), ascorbic acid ($pK_a = 4.2$) and trifluoroacetic acid ($pK_a = -0.6$) were considered to investigate the influence of the acidic strength on phenol production. Indeed, the Fenton reaction is influenced by pH for both iron solubility and iron redox cycling between the +2 and +3 oxidation state [15]. The results show that the best system performance was obtained by using acetic acid (see Table 4 and Fig. 5). The pH of the aqueous phase obtained by using acetic acid was 2.8 and this value is in agreement with the pH values found by Kavitha and Palanivelu [16] in order to promote the Fenton reaction and then the phenol production. The pH values obtained by using ascorbic and trifluoroacetic acids were 2.1 and 1.5, respectively.

Table 4
Selectivity, benzene and hydrogen peroxide conversion by changing the type of organic acid ($H_2O_{2(IN)}$ = 18 mmol by pump in 4 h, PP membrane, $FeSO_4$ as catalyst)

Acid type	Selectivity to phenol (%)	Benzene conversion to phenol (%)	Hydrogen peroxide conversion to phenol (%)
Acetic	99.94	1.20	96.78
Ascorbic	99.47	0.30	49.06
Trifluoroacetic	99.52	0.22	17.82

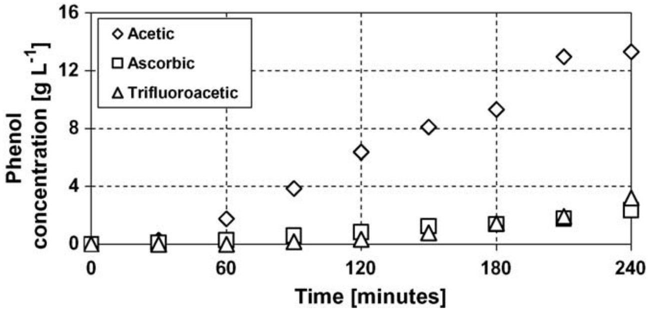


Fig. 5. Phenol concentration in the organic phase vs. time by changing the type of organic acid.

Table 5
Selectivity, benzene and hydrogen peroxide conversion vs. membrane type ($H_2O_{2(IN)}$ = 18 mmol by pump in 4 h, $FeSO_4$ as catalyst)

Membrane material	Selectivity to phenol (%)	Benzene conversion to phenol (%)	Hydrogen peroxide conversion to phenol (%)
PP	99.94	1.20	96.78
PTFE	99.90	0.84	67.46
PAN	99.74	0.22	36.21

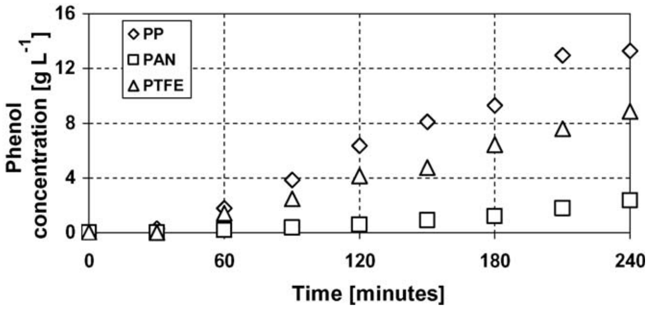


Fig. 6. Phenol concentration in the organic phase vs. time by changing membrane typology.

Membrane typology was also studied. In particular, the influence of the hydrophobic/hydrophilic character of the porous membrane material (PP, PTFE, hydrophobic; PAN, hydrophilic) was investigated. The aim of those tests was to compare the system performance by changing the membrane interface where the oxidation reaction takes place. Using the hydrophobic membrane (see Fig. 1) three steps happens: (i) benzene permeation across the membrane from the organic phase to the membrane interface aqueous side; (ii) interfacial oxidation reaction (1); (iii) phenol permeation across the membrane to the organic phase where it takes shelter from over-oxidation.

When a hydrophilic membrane is used, the catalyst and the oxidant should permeate across the membrane, the oxidation reaction (1) happens at the membrane interface organic side. Thus, phenol should take shelter from over oxidation because it is produced at the membrane-organic phase interface and it is suddenly extracted in the organic phase. The obtained results (Table 5 and Fig. 6) show that the hydrophobic polypropylene (PP) porous support was the best. Indeed, the contact angle of PP (120°) was higher than that of PTFE (110°). Moreover, the hydrophilic support showed the worst results.

4. Conclusions

The reported results show that iron(II) sulphate as catalyst, 18 mmol of hydrogen peroxide pumped for 4 h in the bulk of the aqueous phase as oxidant, acetic acid and polypropylene hydrophobic porous support as separation barrier, gave the best system performance in terms of phenol productivity (38.20 mmol g_{cat}^{-1} h^{-1}), selectivity to phenol (99.94%), benzene conversion to phenol (1.20%), and hydrogen peroxide conversion to phenol (96.78%). The results of this explorative study are encouraging and further research is in progress to improve the system performance.

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