CHEMICAL ENGINEERING TRANSACTIONS

VOL. 32, 2013

Chief Editors: Sauro Pierucci, Jiří J. Klemeš
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ISBN 978-88-95608-23-5; **ISSN** 1974-9791

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1332114

A Continuous Membrane Reactor for Benzene Hydroxylation to Phenol

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Phenol production from direct hydroxylation of benzene with H_2O_2, for the first time carried out in a membrane reactor operating in a continuous mode, was studied. The performance was compared also with those of another membrane reactor operating in semi-batch configuration. In these systems the phenol produced was recovered by using water on the stripping side of the membrane reactor, where the membrane was always in contact with a "fresh" stripping stream, promoting a more efficient removal of the phenol present in the retentate side. The influence of the hydrophilic and hydrophobic character of the membrane material on the phenol recovery was investigated at different flow rates of the feed and the stripping phases. The results indicated that the better performance was achieved using a hydrophilic membrane, with a total feed flow rate of 2 mL min^{-1} and a stripping flow rate of 1 mL min^{-1}, in terms of phenol recovery (25 %) and selectivity (94 %). In addition the continuous removal of the phenol from the reaction side reduces the possible formation of by-products such as benzoquinone, avoiding completely biphenyl formation that was not detected in all the tests carried out in the continuous mode.

1. Introduction

Phenol is an important raw material for the synthesis of petrochemicals, agrochemicals, and plastics Today almost 95% of phenol is produced by the so called "cumene process" (Niwa et al., 2002). This process, although refined the cumene process has some disadvantages: poor ecology, an explosive intermediate (cumene hydroperoxide) and a multistep character and the production of a large amount of acetone as a by-product that makes difficult to achieve high phenol yields with respect to benzene. Indeed in this traditional process, the one-pass yield of phenol, based on the amount of benzene initially used, is less than 5%.

The search for new way for phenol production based on the direct benzene oxidation became more intensive in the last decade (Bianchi et al., 2000; Molinari et al. 2006; Al-Megren et al. 2013). Many studies report the innovative potentialities and the emerged role of the membrane reactors (MRs) (Armor, 1998; Coronas et al., 1999) for improving existing industrial processes and for introducing new production methodologies. Higher energy efficiency, modularity and easy scale-up are some other advantages of MRs with respect to conventional fixed bed reactors. In this work a continuous membrane reactor is and compared with a semi-batch configuration, to reduce the tar formation and to enhance the recovery of the phenol using the iron(II) as catalyst. The main advantage of operating in a continuous system is that the performance does not depend on time, as in the case of the semi-batch system. Therefore, for a defined set of operating conditions, the performance of the system was univocally defined. In both the configurations, semi-batch system and continuous membrane reactor, the membrane was always in contact with a "fresh" stripping stream; therefore, a more efficient removal of the phenol present in the retentate side could be obtained. Moreover, the use of water as a stripping stream is an attractive pathway for the direct synthesis of phenol via "green" process with the aim to develop more efficient and

Please cite this article as: Al-Megren H.A., Poerio T., Brunetti A., Barbieri G., Drioli E., Al-Hedaib B. S. A., Al-Hamdan A. S. N. , Al-Kinany M.C., 2013, A continuous membrane reactor for benzene hydroxylation to phenol , Chemical Engineering Transactions, 32, 679-684 DOI: 10.3303/CET1332114

environmentally benign processes. The influence of hydrophilic and hydrophobic character of the membrane material on the MR performance was also investigated at different flow rates of the feed and the stripping phases.

2. Experimental

2.1 Apparatus, materials, methods and operating conditions of catalytic tests

The experimental measurements were mainly carried out with different membrane unit configurations: semi-batch membrane system (Figure 1 a) and continuous stirred membrane reactor (Figure b).

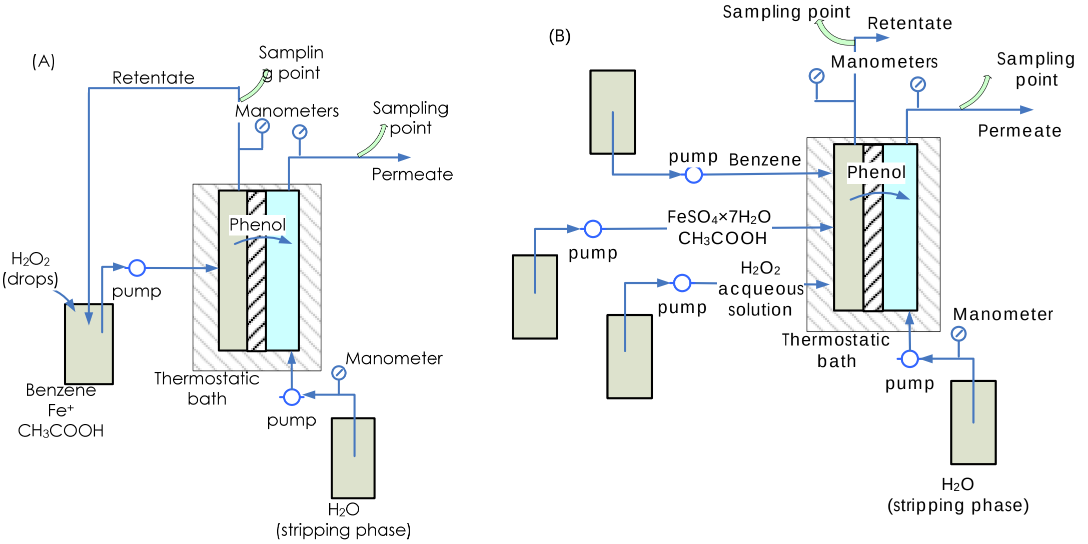

Figure 1: Scheme of semi-batch membrane (a) and continuous membrane systems (b) [Sep. Pur. Technol, 2013, http://dx.doi.org/10.1016/j.seppur.2013.01.019]

For both configurations, the core of the system was the flat sheet membrane hosted in a module. The flat sheet membranes of polypropylene (PP) and polyethersulfone (PES), pore size 0.2 µm, manufactured by Membrana, were used. The module was a stainless steel cell with two chambers, the feed/reaction and the stripping sides. The feed/reaction chamber had three lines, one for the feed, another for the retentate and a third one for loading or empty out the module during its assembling, start-up or cleaning phase. The stripping side was provided with three lines too, two of them for feeding the stripping liquid and for the permeate removal, the other for loading or emptying out. The membrane area available for permeation was 19.6 cm^2. In the semi-batch configuration the system operated as follows: The benzene was contained in a tank together with catalyst in homogeneous phase (solubilized in water and acetic acid). The hydrogen peroxide was added periodically (every ten minutes) into this tank, so that the reaction occurred. This solution, completely stirred, was pumped to the membrane module to favour the removal of phenol through the membrane itself. In this case, the membrane acted as a separation device, whereas the reaction mainly occurred in the tank. Once the phenol was produced and kept in contact with the membrane, it had to be passed selectively through the membrane by means of the stripping action of benzene. In the continuous membrane reactor (Figure 1 b), both reaction and stripping phases were fed continuously to the membrane module. The latter operated, in this case, not only as a separation device but as a reactor itself, since both the catalyst and the reactants were directly fed in it and the reaction occurred in the retentate side of the membrane module. The operating conditions of catalytic tests carried out in both configurations of membrane units schematized in Figures 1 are reported in Table 1.

The composition of the feed phase in the semi-batch unit was the following: 5.5 mol of distilled water, 2.9 mol of benzene, 1.8 mmol of $FeSO_4 \times 7H_2O$, 7.5 mmol of CH_3COOH and 1.2 mmol of H_2O_2 every 10 minutes. Each run lasted 180 minutes. During the catalytic tests, samples of the organic phase were withdrawn every 30 minutes and analysed. After sampling, the analysis of organic phase composition was performed analysing the solutions by gas chromatograph mass spectrometer (GC–MS QP2010S) from Shimadzu. A high performance liquid chromatography (HPLC, Agilent 1100 Series instrument) was used for measuring the concentrations of phenol and oxidation by-products (benzoquinone, hydroquinone, resorcinol (dihydroxybenzene)) in the aqueous and organic phases. The HPLC was provided of a Kinetex C18 (150 mm × 4.60 mm) column by UV readings at 265 nm wavelength and the mobile phase was made up of an aqueous solution of formic acid (0.1 % v/v) and an acetonitrile solution of formic acid (0.1 % v/v) fed at a flow-rate of 0.5 mL min^{-1}. The column pressure was 155 bars and an injection volume of 20 µL was used. The results of experimental tests were elaborated using the following parameters:

Table 1. Operating conditions of catalytic tests used in semi-batch and continuous membrane reactors.

	Continuous membrane reactor	**Semi batch configuration**
Temperature	35°C	35°C
Feed flow rates	Stream 1: 1.8 mL min^{-1} Stream 2: 0.1 mL min^{-1} Stream 3: 0.1 mL min^{-1}	Feed phase: 2 and 5 mL min^{-1} Stripping phase: 2 and 5 mL min^{-1}
Phase composition	Stream 1: benzene Stream 2: aqueous solution of $FeSO_4 \times 7H_2O$ (0.075 M) and of CH_3COOH (0.3 M); Stream 3: aqueous solution of H_2O_2 (0.75 M) Stripping phase: distilled water	Feed phase composition: H_2O: 5.5 mol; Benzene: 2.9 mol; H_2O_2: 1.2 mmol every 10 minutes; CH_3COOH: 7.5 mmol; $FeSO_4 \times 7H_2O$: 1.8 mmol. Stripping phase: distilled water
Stripping phase flow rate	1 and 2 mL min^{-1}	

Phenol concentration in the retentate and permeate, and amount of by-products (mg) detected in the both phases.

Phenol recovery, it compares the moles of phenol recovered in the permeate with the ones totally produced by the reaction and shared between the retentate and the permeate:

$$\text{Phenol recovery} = \frac{(\text{moles of Phenol})^{\text{Permeate}}}{(\text{moles of Phenol})^{\text{Permeate}} + (\text{moles of Phenol})^{\text{Retentate}}} \times 100$$

Phenol selectivity compares the moles of phenol with respect to the eventual presence of by-products recovered in the permeate and it gives an indication of the capability of the membrane system to separate the phenol selectively with respect to the other species present in the reaction phase.

$$\text{Phenol Selectivity} = \frac{(\text{moles of Phenol})^{\text{Permeate}}}{(\text{moles of all oxidized products})^{\text{Permeate}}} \times 100$$

Conversion of hydrogen peroxide to phenol:

$$\text{Conversion} = \frac{(\text{moles of phenol produced})}{(\text{moles of } H_2O_2 \text{ fed to the reactor})} \times 100$$

Phenol Overall Produced is the sum of the overall phenol amount presents both in retentate and permeate.

$$\text{Phenol Overall Produced} = (\text{mass of phenol})^{\text{Permeate}} + (\text{mass of phenol})^{\text{Retentate}}, \text{mg}$$

Phenol productivity

$$\text{Phenol productivity} = \frac{(\text{moles of Phenol})^{\text{Permeate + Retentate}}}{\text{Catalyst weight} \times \text{hours}}, \text{mol } g_{\text{Catalyst}}^{-1} \text{ h}^{-1}$$

3. Results and discussion

3.1 . Catalytic tests in semi-batch and continuous membrane systems.

The catalytic tests were carried out following the scheme reported in Figure 1. Both PES and PP membranes were used, in semi-batch mode as well as for the continuous systems, to evaluate which membrane type was most suitable for the application in the benzene oxidation to phenol. The results of catalytic tests are summarized in Tables 2 and 3 in terms of overall phenol produced and phenol recovered in the permeate at different stripping flow rate for both continuous membrane reactor and semi-batch system. With respect to the semi-batch system, the continuous system showed a much higher percentage of phenol recovered in the permeate. As can be seen, the PES membranes gave the best results in terms of phenol recovered for the continuous system at a flow rate of 2 mL min^{-1}. The PES membrane offered better performance than the PP membrane, mainly owing to its hydrophilic character, favoured a very good contact between the retentate and stripping side with an easier passage of the phenol produced through the membrane. As a consequence the amount of phenol removed from the reaction side and recovered was higher. The lower phenol recovery obtained in the semi-batch systems can be due to fouling formation on the membrane surface. Indeed the reaction takes places in the tank, where the consecutive catalytic reactions happen on the phenol produced with consequent by-products and tars formation and thus membrane fouling.

Table 2 Comparison of phenol produced and recovered at different flow rates of the stripping phase (permeate side) in a continuous and semi-batch systems using PES membranes

Membrane System/ Stripping flow rate (mL min^{-1})	Phenol produced (mg)	Phenol recovered (wt. %)
Semi-batch /2	554.1	0.17
Semi-batch/ 5	1670.9	0.51
Continuous/1	74.3	17.18
Continuous/2	106.3	27.29

Table 3 Comparison of phenol produced and recovered at different flow rates of the stripping phase (permeate side) in a continuous and semi-batch systems using PP membranes

Membrane System/ Stripping flow rate (mL min^{-1})	Phenol produced (mg)	Phenol recovered (wt. %)
Semi-batch /2	823.7	0.22
Semi-batch/ 5	1175.5	0.12
Continuous/1	58.32	13.01
Continuous/2	72.90	22.11

The selectivity at the beginning of the catalytic test carried out in the semi-batch system using PP membrane was very high (ca. 97 %) and gradually lowered down to ca. 80 % (Figure 3) while the reaction was running. Instead in a continuous membrane reactor the selectivity value was kept constant for all duration of the catalytic tests (Figure 4). The use of a continuous system avoided the formation of the biphenyl; a by-product always detected using the semi-batch system. In this last operational mode, in fact, the feed/retentate side operated as a “traditional batch” reactor where the conversion of the reactants evolved with time until reaching a plateau. Once the phenol was produced by reaction, part of it was continuously removed by the stripping phase; however, the phenol that was not removed remained in the reaction side and, in contact with the oxidant, leading to the formation of over-oxidation products whose concentration in the retentate side increased, thus, during time. Since the permeation through the membrane was based on a concentration gradient process, this higher concentration of by-products in the retentate side also favoured their passage in the permeate. As a consequence, the selectivity decreased.

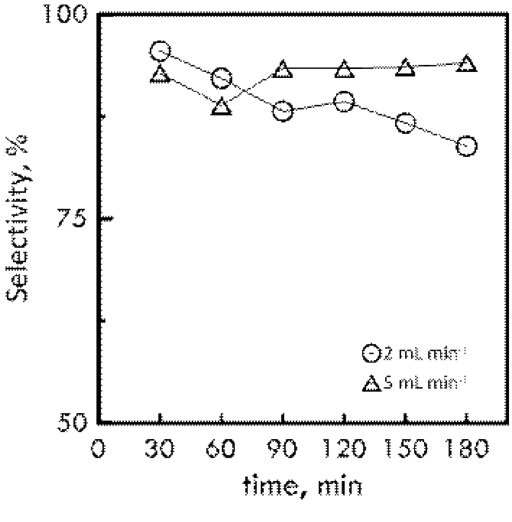

Figure 3: Selectivity permeate side using PP membranes at different flow rates in the semi-batch system

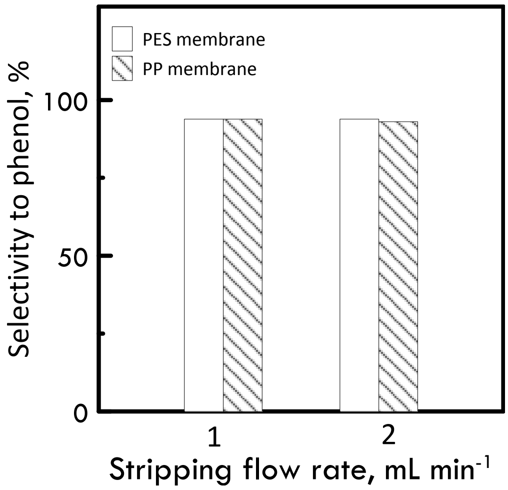

Figure 4: Selectivity permeate side using PES and PP membranes at different flow rates in the continuous membrane reactor

In Tables 4 and 5 the comparison of amount of the by-products detected in the retentate for PES and PP membranes at different flow rates of the stripping phase (permeate side) in a continuous and semi-batch membrane systems was reported. These results confirmed the formation of larger amount of by-products in the semi-batch system with respect to the continuous membrane reactor.

Table 4: Comparison of amount of by-products detected in the retentate for PES membranes at different flow rates of the stripping phase (permeate side) in a continuous and semi-batch membrane systems

Membrane System/ Stripping flow rate (mL min^{-1})	Benzoquinone (mg)	Hydroquinone (mg)	Biphenyl (mg)
Semi-batch /2	23.3	n.d.	13.7
Semi-batch/ 5	37.3	n.d.	17.0
Continuous/1	3.07	n.d.	n.d.
Continuous/2	6.86	n.d.	n.d.

Table 5: Comparison of amount of by-products detected in the retentate for PP membranes at different flow rates of the stripping phase (permeate side) in a continuous and semi-batch membrane systems.

Membrane System/ Stripping flow rate (mL min^{-1})	Benzoquinone (mg)	Hydroquinone (mg)	Biphenyl (mg)
Semi-batch/2	21.4	n.d.	14.8
Semi-batch/5	30.0	n.d	12.8
Continuous/1	4.45	n.d.	n.d.
Continuous/2	3.42	n.d.	n.d.

4. Conclusions

In this work the phenol production from direct hydroxylation of benzene was for the first time carried out in a membrane reactor operating in a continuous mode. The performance was compared also with that of another membrane system operating in semi-batch configuration. The experimental results indicated that these systems allowed phenol production to be obtained by direct oxidation. The selectivity was significantly high, exceeding 90 %, in some cases and ca. 0.557 mmol h^{-1} g^{-1}catalyst was the productivity.

The use of the hydrophilic membrane, in the continuous membrane reactor, assured a better contact between the reactants and stripping phases allowing the attainment of higher phenol recovery and higher selectivity when referred to the hydrophobic membrane.

The continuous removal of the phenol from the reaction side reduces the formation of by-products such benzoquinone, avoiding completely biphenyl formation that was not detected in all tests carried out in the continuous mode. In the continuous membrane reactor tars formation was avoided.

Comparing the two configurations, the continuous system resulted more promising than the semi-batch system, mainly regarding the total amount of phenol recovered in the permeate. The continuous system showed a better capability of stripping as well as a significantly higher selectivity. In particular, with the continuous membrane reactor more than 25 % of the phenol produced was recovered in the stripping phase with respect to less than 1 % achieved in the semi-batch membrane system.

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