



Performance of ceramic foams as gas–liquid contactors for phenol wet oxidation in the trickle regime



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ABSTRACT

The scope of this work was to study the performance of a foam packed bed reactor for homogeneous wet oxidation of phenol, a relevant gas–liquid reaction in industrial wastewater treatment. The use of open-cell foams, macroporous structures constituted by interconnected channels with high bed porosity and surface area, largely enhances interfacial mass transfer rates, without significantly increasing pressure drop.

Phenol (45 mol/m^3) was oxidized in the aqueous phase by oxygen dissolved from the gas (6 bar), using Cu(II) salt (0.44 mol/m^3) as homogeneous catalyst. Experiments were performed in a continuous reactor with partial liquid recycle. The fresh feed and total reactor flow rates have been adjusted to obtain different space times (395–1177 s) and liquid superficial velocities ($0.84\text{--}3.5 \times 10^{-3} \text{ m/s}$). Temperature has also been varied within the range 110–140 °C. Experimental phenol conversions are compared to that obtained from a simple perfect mixing model. Finally, the performance of the foam has been compared to that of a random packing bed made of spheres.

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1. Introduction

Open-cell foams are macroporous reticulated 3D structures constituted by interconnected channels. These structures are currently used in the process industry as filter media. In the last years, the interest of foams as structured beds for chemical reactors has raised. The high bed porosity of these structures results in very low pressure drop, compared to randomly packed beds, while the surface area and the potential for developing turbulent flow are kept high. For this reason, foams are potentially a good alternative to traditional packings (e.g. random packings) in reactions where an efficient phase contact is required, such gas–liquid and gas–liquid–solid reactions [1,2].

Foams have already been tested in various gas reactions catalysed by solids, such as exhaust gas purification [3–7], catalytic combustion [8–12], reforming [13,14] and Fischer–Tropsch synthesis [15]. Furthermore, their properties (especially the related to enhanced mass transfer) are potentially useful for the improvement of gas–liquid reactions, where mass transfer between phases plays a critical role. In spite of this, the applications of these solid foams as packings in multiphase reactors are rather scarce. Only

works limited to the study of hydrodynamics and mass transfer have been reported in the literature [16–21].

In the present work, a relevant reaction in wastewater treatment, the wet oxidation of phenol, has been considered. Phenol is a priority pollutant, very harmful even at low concentrations. Water effluents containing phenol in low concentration (COD 20–200 g/L) are produced in the chemical, petroleum or coke industries [2]. In these cases, the wet oxidation of phenol is the preferred treatment technique. This process uses oxygen and can be catalysed by homogenous (dissolved Cu, Fe, etc.) or heterogeneous (CuO, Fe, Pt, Ru, etc.) catalysts [2,22–28]. Copper is very active, particularly in the homogeneous form at pH 4, as studied in a previous work, where the kinetics of this reaction was studied and modelled [29]. The use of homogeneous Cu(II) requires a separation operation (e.g. ion exchange) downstream the process to recover the catalyst and fulfil with the environmental regulations.

The scope of the present work is to study the performance of ceramic foams as packing for gas–liquid reactions in fixed beds. The homogeneous process using Cu(II) as catalyst is considered. To accomplish this goal, a continuous reactor with partial liquid recycle is used. First, the reactor performance is studied in a preliminary test, and the reaction products are identified and quantified. Then, the influence of the main operating variables affecting reaction rate and oxygen mass transfer, namely liquid superficial velocity, copper concentration and temperature, is studied. Finally, the

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performance of the reactor is compared to that of a trickle bed packed with spheres.

2. Materials and methods

2.1. Experimental device

The experimental device consisted of a continuous fixed-bed bench-scale reactor. The reactor tube (stainless steel, 0.050 m internal diameter and 0.600 m length) housed the foam bed (0.200 m length), made of two cylindrical blocks (0.100 m length each). The foam blocks, supplied by Fraunhofer IKTS, are made of alumina with pore density 20 ppi (pores per inch) and 88% open porosity. The main geometrical properties of the foam have been measured experimentally using the photographs taken with a stereomicroscope (ZEISS), as reported elsewhere [30]: average pore size 1.38×10^{-3} m, strut diameter 0.46×10^{-3} m, and packing density 480 kg/m^3 . The external surface area of the foam was estimated as $2545 \text{ m}^2/\text{m}^3_{\text{bed}}$.

The reactor tube was externally heated by a PID-controlled electric oven, in order to keep isothermal conditions. Gas and liquid streams were heated and fed separately to the reactor tube, flowing in parallel downwards. The gas (oxygen 99.9%, Praxair) was fed from a cylinder using a BRONKHORST mass flow controller (1 NL/min). The liquid flow rate was set by a piston pump, connected to a filter and a pulse dumpener to reduce the characteristic pulsing of this type of pumps. The liquid was distributed uniformly over the cross-sectional area in the form of droplets using a stainless steel nozzle with 6 holes. A plastic transparent tube was used to check that the nozzle of the top of the bed was operating properly and that there was no stagnant liquid accumulated inside the reactor. The reactor effluent was cooled down and sent to a phase separator, where the gas stream was vented and the liquid stream was partly recycled to the reactor, and partly vented. The recycled liquid was mixed with the fresh feed delivered by a second pump.

The reactor was operated in continuous mode. The recycle ratio of the liquid (recycle to fresh feed flow rates) was maintained high through the experiments (6.5–60). After setting the operating variables, the reactor evolved to a steady state (constant concentrations upon time). At this point, liquid samples of the reactor effluent were collected.

The liquid feed was a buffered phenol and Cu(II) aqueous solution. Phenol solutions (45 mol/m^3) were prepared by mixing phenol (99%, Sigma–Aldrich) and distilled water in adequate proportions. Cu(II) was added by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ (Panreac) in the phenol solution (0.44 mol Cu/m^3). The pH of this solution was kept constant during the reaction using a pH 4 buffer solution (made of Na_2HPO_4 , NaH_2PO_4 and H_3PO_4 , Panreac). In a previous work, it has been observed that this pH leads to the highest phenol conversion [29].

Phenol and the reaction products in the liquid phase were analysed using High-Performance Liquid Chromatography (HPLC, Agilent 1200 series, Zorbax SB-Aq column and UV–vis) and a standard Chemical Oxygen Demand (COD) method [29].

2.2. Reactor modelling

As indicated previously, the foam fixed-bed reactor was operated at steady state with partial liquid recycle and high recycle ratio. This results in a very small conversion per pass, and hence, the recycle reactor can be described by the continuous perfectly mixed reactor model. This statement has been checked by solving both models plug flow with recycle and perfectly mixed reactor for the experimental conditions corresponding to the lowest recycle ratio (recycle to fresh feed flow rates = 6.5). At these conditions,

discrepancies in predicted phenol conversion was 1.7%, which is within the error of the experiments. Hence, the simplest model, the continuous perfectly mixed reactor model, has been used:

$$\tau = \frac{C_{B0} - C_B}{(-r_B)_{VL}} \quad (1)$$

The space time (τ = liquid volume in the reactor/fresh feed flow rate) can be calculated using:

$$\tau = \frac{V_{\text{bed}} \varepsilon_L}{q_{\text{fresh}}} \quad (2)$$

where V_{bed} is the bed volume ($3.04 \times 10^{-4} \text{ m}^3$), ε_L is the liquid hold-up ($\text{m}^3_{\text{liq}}/\text{m}^3_{\text{bed}}$), C_{B0} and C_B are phenol molar concentrations in the reactor inlet and outlet streams, and $(-r_B)_{VL}$ is phenol reaction rate per unit volume of liquid, that is calculated using the rate law developed in a previous work [29]:

$$(-r_B)_{VL} = k C_{\text{Cu}}^{1/2} C_A^{1/2} C_B \quad (3)$$

where C_i are molar concentrations (mol/m^3) in the bulk liquid (A = dissolved oxygen and B = phenol) and $k = 2.5 \times 10^6 \exp(-8997/T) \text{ m}^3_{\text{liq}}/\text{mol s}$ is the kinetic constant.

The liquid hold-up (ε_L) has been measured experimentally by the draining method, as part of a previous work [30], and correlated as a function of Reynolds number. This expression has been used to calculate the liquid hold-up at the operating conditions of the experiments of the present work.

The model has been solved considering that the oxygen mass transfer resistance in the gas phase is negligible (gas phase is pure oxygen). In addition, if the mass transfer resistance in the liquid phase was also negligible, the concentration of oxygen in the bulk liquid (C_A) would be equal to the interphase concentration (C_{Ai}), which is calculated using Henry's law. For a given set of operating conditions, Eqs. (1)–(3) can be solved for C_B and then phenol conversion calculated. The actual phenol conversions obtained experimentally would be equal, or lower, if the mass transfer resistance in the liquid phase is not negligible, than the conversions predicted by this model.

3. Results and discussion

3.1. Wet oxidation of phenol

The wet oxidation of phenol at pH 4 catalysed by aqueous Cu(II) has been selected as model reaction to study the performance of the fixed bed equipped with foam packing for gas–liquid reactions. The reactor was operated in parallel downflow, with partial recycle of the liquid feed, and flow rates corresponding to the trickle regime. Thus, the maximum liquid and gas superficial mass flow rates were $3.0 \text{ kg/m}^2 \text{ s}$ and $0.016 \text{ kg/m}^2 \text{ s}$, respectively. These values fall within the trickle regime region in the diagram proposed for the air–water system by Sie and Krishna [31]. According to this diagram, the transition to the bubbling regime would take place at low gas superficial mass flow rates for liquid superficial mass flow rates higher than $12 \text{ kg/m}^2 \text{ s}$, which is far from the maximum value considered in the experiments.

In a preliminary test, the reactor has been operated at 140°C with a continuous liquid fresh feed of $1.56 \times 10^{-7} \text{ m}^3/\text{s}$, containing 45 mol/m^3 of phenol and 0.44 mol/m^3 of Cu(II) and total reactor feed (fresh feed plus recycle) set to $4.82 \times 10^{-6} \text{ m}^3/\text{s}$ (recycle to fresh flow ratio = 30). Oxygen was fed continuously at 6 bar and a flow rate of $1.7 \times 10^{-5} \text{ Nm}^3/\text{s}$.

The steady state performance of the reactor at these conditions is summarized in Table 1. Reported concentrations were measured by HPLC, resulting in a 28% phenol conversion. The reactor effluent contains unreacted phenol, together with other aromatic oxygenates, such as catechol, hydroquinone and *p*-benzoquinone,

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