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Slurry loop tubular membrane reactor for the catalysed aerobic oxidation of τ benzyl alcohol^{Ch up}

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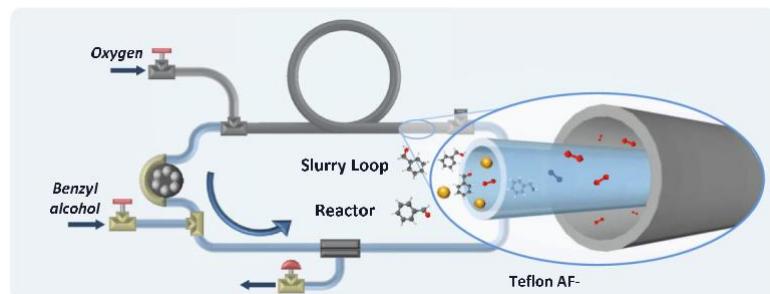
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HIGHLIGHTS

- A slurry loop reactor was designed for the aerobic oxidation of benzyl alcohol.
- A tubular membrane was incorporated for safe and controlled oxygen delivery.
- Similar oxidation rate was achieved to that of a conventional autoclave reactor.
- The addition of a crossflow filter in-side the loop allowed for continuous operation.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel reactor that combines a catalyst slurry flowing inside a loop configuration, incorporating a tubular membrane (Teflon AF-2400) for controlled oxygen delivery was designed and employed for the aerobic oxidation of benzyl alcohol using a 1 wt% Au-Pd/TiO₂ powdered catalyst. This reactor keeps the liquid phase saturated with oxygen, while avoiding the creation of bubbles in it, thus enhancing operation safety. Experimental results in batch mode compared with those of a conventional autoclave demonstrated that the slurry loop membrane reactor reached a similar oxidation turnover frequency (20,000–25,000 h⁻¹) with comparable values of benzaldehyde selectivity (~70%). Continuous operation was achieved by using a crossflow filter connected to the loop to keep the catalyst from exiting the reactor. Using a 60 cm long tubular membrane, with the slurry flow circulating at 10 mL/min, continuous reaction was performed at 100–120 °C, 0–5 bar oxygen pressure and 1.2–5.0 g/L catalyst loading. Selectivity to benzaldehyde increased by either decreasing the reaction temperature or increasing the external oxygen pressure. The oxygen consumption rate decreased linearly with the catalyst loading, suggesting negligible gas-liquid mass transfer resistance. This was further evidenced by doubling the length of the tubular membrane, which had no effect on the oxidation turnover frequency. The slurry loop membrane reactor showed significantly better performance than packed-bed membrane micro-channel reactors, and similar performance as that of a trickle-bed capillary reactor. This reactor can be implemented for a wide range of applications, which rely on the use of powder catalyst, are limited by gaseous reactant availability and require safe operation.

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1. Introduction

The selective oxidation of alcohols is of great interest in the chemical industry [1–4], as aldehydes and ketones are valuable molecular platforms in organic synthesis, manufacture of fragrances and preparation of drug candidates [1,5]. From a green chemistry perspective, the utilization of pure oxygen and environmentally friendly heterogeneous catalysts has attracted much attention [6–12]. In this regard, continuous flow oxidations can offer advantages, allowing for improved control over the operating parameters and safety of hazardous reactions [7,13].

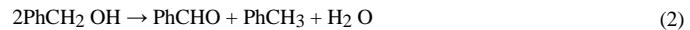
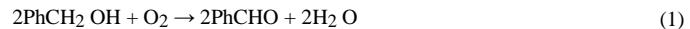
For flow synthesis, it is common to find heterogeneous catalytic processes that involve the use of packed-bed reactors [14–17]. However, the use of a suspension of fine catalyst particles in a liquid medium offers better temperature control, the possibility of reducing mass transfer resistances and improving catalyst performance [18,19]. Continuous slurry reactors for bulk and fine chemical production are well-established [19–22], while for pharmaceuticals are rather less common. Buisson et al. [23] performed a gas-liquid-solid slurry hydrogenation of a pharmaceutical molecule in flow using a Corning Advanced Flow reactor, achieving similar performance to batch. In that work the catalyst entered and exited the reactor with the fluid. Catalyst use can be reduced by retaining a fixed amount of catalyst inside the reactor undergoing intense mixing. Such configuration is found in the industrially-established loop reactors, such as the Buss reactor (Buss ChemTech AG) [24], which has found applications both in fine chemistry and pharma industry [20,22,25].

Aerobic oxidation of alcohols can pose safety risks due to flammability [12,13,26,27]. In this regard, various research groups have tried to address this issue by using either diluted oxygen [28,29], or micro-channel reactors which have been shown to be safe to operate [9,15,30–32]. Keeping the gaseous phase oxidant separate from the organic substrate by using membrane contactors represents an alternative solution [7,13,33,34]. A membrane that has been used for this purpose is the Teflon AF-2400, first introduced by Ley and co-workers

[35] for continuous dissolution of CO₂ to synthesise carboxylic acids. This membrane has recently attracted much attention for its chemical inertness and high permeability to light gases [36–38].

We have previously employed Teflon AF-2400 membranes for the aerobic oxidation of benzyl alcohol [34,39]. In these works, 1 wt% Au-Pd/TiO₂ catalyst was packed in a tubular Teflon AF-2400 membrane, with an inner (ID) and outer diameter (OD) of 0.8 and 1.0 mm respectively, and inside a rectangular microchannel with a 0.07 mm thick flat membrane on one side of the channel. Results indicated the presence of mass transfer resistances and limited supply of oxygen for the very active catalyst utilised. In order to address these issues, a novel reactor that benefits from having a Au-Pd/TiO₂ catalyst in a slurry form, flowing inside a loop configuration that contains a tubular membrane (Teflon AF-2400) was developed in this work. A crossflow filter inside the loop was employed to ensure the catalyst remained within the loop, allowing for the continuous withdrawal of the reaction mixture.

Under aerobic conditions various reactions can take place on the catalyst surface and extensive work on the reaction mechanism of benzyl alcohol aerobic oxidation on supported gold and palladium catalysts exists in the literature [40–45]. The reactions responsible for the formation of benzaldehyde are the dehydrogenation of benzyl alcohol, along with the hydrogenolysis and disproportionation reactions both responsible for the production of benzaldehyde and toluene which is the main by-product [42,45]. Secondary by-products formed during the oxidation of benzyl alcohol are benzoic acid, dibenzyl ether and benzyl benzoate [44–46]. All the elementary reactions can be condensed to two macroscopic reactions: the oxidation and the dis-proportionation of benzyl alcohol as described in Eqs. (1) and (2) respectively [43].



2. Materials and methods

2.1. Catalyst preparation and characterisation

The catalyst employed in this study was a nominal 1 wt% bimetallic Au-Pd/TiO₂ with a 1:19 Au:Pd weight ratio, and has been used in previous studies [39]. Gold precursor (HAuCl₄·3H₂O, Johnson Matthey) and palladium precursor (PdCl₂, Johnson Matthey) were mixed with titania (TiO₂, Evonik P25) to form a slurry mixture. This was then spray-dried at a nozzle temperature of 220 °C and calcined in static air at 400 °C for 3 h. Characterisation with laser diffraction particle size analysis (Beckman Coulter, LS 13 320) showed a bimodal particle size distribution with two peaks at 8.1 μm and 27.4 μm; the overall mean particle size was 9.3 μm with a covariance of 89.8%. These relatively large sizes are due to agglomeration, as the size of the primary TiO₂ particles is in the nanometre scale. Analysis using inductively coupled plasma atomic emission spectroscopy revealed a content of gold and palladium of 0.05 wt% and 0.85 wt% respectively, which is slightly different from the expected 1:19 Au-to-Pd ratio, due to experimental error during the catalyst preparation. Transmission electron microscopy indicated that the metal particle size was in the range of 1–2 nm [39].

2.2. Reactor design and operation

2.2.1. Slurry loop tubular membrane reactor

The slurry loop tubular membrane (SLTM) reactor consisted of a tube-in-tube reactor made of a stainless steel tube (Swagelok, OD: 1/8", tube wall: 0.035") that contained the Teflon AF-2400 tubular gas-permeable membrane (Biogeneral, ID: 0.8 mm, OD: 1.0 mm, length: 60 cm). The tubular membrane was connected to a polytetrafluoroethylene (PTFE) loop (ID: 1.0 mm, OD: 1.6 mm, Kinesis). A liquid-solid slurry mixture of the catalyst, benzyl alcohol and its oxidation products, was continuously pumped within the loop at a flowrate of 10 mL/min by means of a recirculation pump. Pure oxygen (BOC, N5.5 grade) was pressurised outside the polymeric membrane; it permeated through the membrane and reacted with the flowing liquid at the catalyst particles. The set-up could be operated either in a batch or a continuous mode, and the use of a stainless steel crossflow filter (Mott, 0.1 μm 316L) allowed for the continuous separation of the liquid from the slurry mixture. Further details on the crossflow filtration system are provided in the [Supplementary Information](#). A schematic of the set-up for the continuous operation is shown in Fig. 1. The filter was connected to the loop and to a T-junction, where neat benzyl alcohol (Sigma Aldrich, 99.0%) was delivered by means of a high pressure liquid chromatography pump (Knauer P2.1S). The outlet of the loop reactor assembly, which was on the back of the crossflow filter, was connected to an adjustable back pressure regulator (Zaiput, BPR-01) which maintained the liquid pressure inside the loop at a constant value. This was kept 0.5 bar higher than the oxygen pressure outside the membrane in both batch and continuous operations, in order to avoid oxygen breakthrough into the liquid. The whole set-up was immersed in a stirred temperature bath (Diameter: 230 mm, Boro 3.3, VWR International), containing heat transfer fluid (Paratherm NF), which was placed on a hotplate (Stuart US152). The temperature was monitored by a thermocouple immersed in the bath and connected to the hotplate, while another thermocouple measured the temperature at the inlet of the tubular membrane.

Since the pumping section was placed outside the temperature bath, complete isothermal condition in the liquid circulating inside the loop was not possible. Simulations were performed using COMSOL Multiphysics® 5.3a, showing that despite the fact that the desired temperature was reached at the inlet of the tubular membrane at

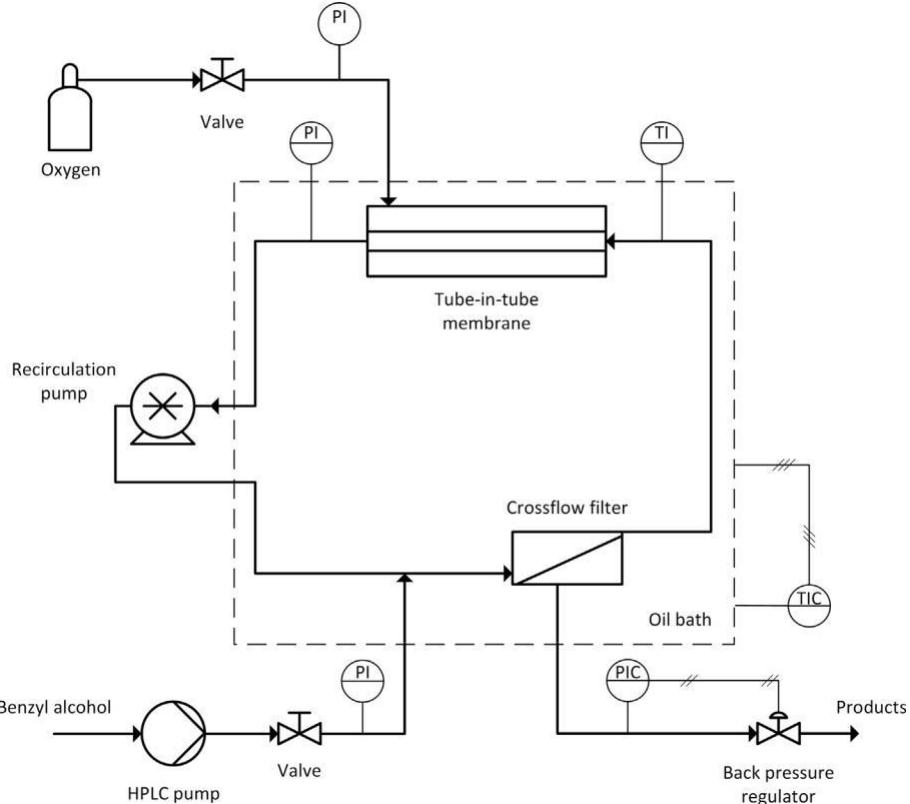


Fig. 1. Schematic of the experimental set-up of the slurry tubular membrane reactor for the continuous catalytic aerobic oxidation of benzyl alcohol. PI, pressure indicator; PIC, pressure indicator and controller (back pressure regulator); TI, temperature indicator; TIC, temperature indicator and controller.

steady-state conditions, the average liquid temperature in the loop was lower than the desired value (see *Supplementary Information*). Note that for experiments with the SLTM reactor, the reported temperature value is the one recorded by the thermocouple at the inlet of the tube-in-tube contactor.

Batch experiments performed with the SLTM reactor were carried out without the use of the crossflow filter. Once the reaction was finished, the slurry catalyst was removed from the loop by disconnecting the outlet of the recirculation pump and the slurry mixture was filtered by means of glass microfibre filter (Whatman, Grade GF/B). After each experiment thorough cleaning of the reactor was performed, which involved flowing acetone, water and small amounts of aqua regia through the loop in order to remove residual catalyst particles.

Residence time distribution (RTD) analyses were carried out on the loop reactor in order to characterise its macromixing behaviour. Ultraviolet–Visible (UV–Vis) spectroscopy (Ocean Optics DH-2000-BAL + UV-VIS-ES) was utilized to detect the tracer concentration (Basic Blue 3, Sigma-Aldrich) both inside the loop and at the inlet section of the reactor (see *Supplementary Information*). The recirculation pump was set to a flowrate of 10 mL/min and an inlet flowrate of 0.025 mL/min was used, resulting to a ratio (recycle ratio) between the recycle and the inlet flowrate of around 400. This value was the same as the one used for the reaction experiments.

2.2.2. Batch autoclave reactor

For comparative purposes, the performance of the Au-Pd/TiO₂ catalyst was also studied in a conventional batch reactor. The batch reactions were carried out in a stainless steel Parr autoclave reactor (Parr 5500 Series compact reactor, 50 mL) with external heating and a gas pressure line. The vessel was charged with 10 mL benzyl alcohol (Sigma Aldrich, 99.0%) and the desired amount of catalyst, purged five times with oxygen at 5 bar and the stirring rate slowly increased up to 1800 rpm. The oxygen pressure was adjusted at the desired value and

the heating rate was automatically controlled in order to reach 120 °C inside the stirred liquid. The reaction start was set to the time when the thermocouple inside the batch measured the value of 120 °C. After waiting for the desired reaction time, the stirring was stopped, the re-actor cooled down inside an ice bath and samples were withdrawn.

2.2.3. Continuous trickle-bed capillary reactor

The Au-Pd/TiO₂ catalyst was pelletized, sieved to a size of 90–125 µm, packed in a 60 cm PTFE long capillary (ID: 1.0 mm, OD: 1.6 mm, Kinesis) and tested in a trickle-bed reactor configuration. Details about the set-up are provided in the *Supplementary Information*. The capillary reactor was immersed in a heat transfer fluid (Paratherm NF) inside a stirred temperature bath (Diameter: 230 mm, Boro 3.3, VWR International) at 120 °C placed on top of a hotplate (Stuart US152). Pure benzyl alcohol (Sigma Aldrich, 99.0%) was delivered at 0.025 mL/min using a 8 mL stainless steel syringe (Harvard Apparatus) driven by a syringe pump (Harvard Apparatus, PHD ULTRA), while the oxygen (BOC, N5.5 grade) flowed at 2.5 NmL/min by means of a mass flow controller (Brooks SLA5850S). These flows were combined in a T-mixer (PEEK, OD: 3.2 mm, hole diameter: 1.3 mm, Upchurch) and the resulting reaction mixture (Taylor flow) entered the packed catalyst at 120 °C and 5 bar. The reaction start was set to the time when the thermocouple inside the bath measured 120 °C and samples were withdrawn after 1 h from the start of the reaction.

For all the three reactors, the samples were analysed by a gas chromatograph (Agilent Technologies, 7820A) using a flame ionisation detector (FID), a HP-INNOWAX (19091-133) capillary column and an auto-liquid sampler [47]. Benzyl alcohol conversion, X, was calculated using Eq. (3), where C_{BzOH,in} and C_{BzOH,out} are the concentrations of benzyl alcohol at the inlet and the outlet of the reactor respectively, or at the beginning and the end of reaction for the batch experiments. Concerning selectivity of the two main products, namely benzaldehyde, S_B, and toluene, S_T, their definition is given in Eqs. (4) and (5), where

Table 1

Effect of oxygen pressure on benzyl alcohol conversion and selectivity to ben-zaldehyde, toluene, benzoic acid and benzyl benzoate in an autoclave reactor. Temperature, 120 °C; benzyl alcohol volume, 10 mL; catalyst mass, 50 mg; re-action time, 58 min; CCT_b, 17 gcat·s/galcohol.

| Oxygen pressure, bar | Conversion, % | Selectivity, % | | |
|----------------------|---------------|----------------|---------|--------------|
| | | Benzaldehyde | Toluene | Benzoic acid |
| 1 | 23 | 61 | 35 | 0.47 |
| 2 | 45 | 62 | 36 | 0.47 |
| 3 | 82 | 65 | 30 | 1.4 |
| 4 | 95 | 71 | 21 | 3.7 |
| 5 | 96 | 70 | 17 | 7.5 |

C_{BzAl,out} and C_{Tol,out} are the concentrations of benzaldehyde and toluene at the outlet of the reactor or at the end of the reaction time.

$$X = \frac{C_{BzOH,in} - C_{BzOH,out}}{C_{BzOH,in}} \quad (3)$$

$$SB = \frac{C_{BzAl,out}}{C_{BzOH,in} - C_{BzOH,out}} \quad (4)$$

$$ST = \frac{C_{Tol,out}}{C_{BzOH,in} - C_{BzOH,out}} \quad (5)$$

The carbon balance for all the experiments was calculated based on the concentration of the detected compounds at the outlet relative to the concentration of neat benzyl alcohol at the inlet (9.7 M), and it was found to be between 96-104%. Furthermore, experimental reproducibility was checked and a variation of around ± 3% (absolute) for benzyl alcohol conversion and product selectivity was found for the experiments that were repeated. In order to characterise the time that the reactant spent in contact with the catalyst, the catalyst contact time, CCT_c, is used and reported in Eq. (6) where m_{cat} is the catalyst mass, ρ_{BzOH} the density and v_{BzOH,in} the inlet flowrate of benzyl alcohol. The typical catalyst contact time was around 17 gcat·s/galcohol, corresponding to a flowrate of 0.025 mL/min and 7 mg catalyst.

$$C = \frac{C_{BzOH,in} - C_{BzOH,out}}{m_{cat}} \quad (6)$$

For the experiments conducted in batch, the catalyst contact time was determined according to Eq. (7), where V_{BzOH} is the volume of benzyl alcohol loaded at the beginning of the reaction and τ is the re-action time.

$$CCT_c = \frac{m_{cat}}{\rho_{BzOH} V_{BzOH,in} \tau} \quad (7)$$

To quantify the catalyst activity for the continuous operation, the average total turnover frequency, TOF_{T,c}, was calculated according to Eq. (8). In order to distinguish between the two different contributions to the overall turnover frequency, the extent of the oxidation, TOF_{O,c}, and disproportionation average turnover frequency, TOF_{D,c}, was de-termined according to Eqs. (9) and (10) respectively, where F_{BzOH,in} is the inlet molar flowrate of benzyl alcohol and n_{metal} the number of Au-Pd moles in the catalyst.

$$TOF_{T,c} = \frac{\rho_{BzOH} v_{BzOH,in} m_{cat} \tau}{\rho_{BzOH} V_{BzOH,in} X F_{BzOH,in}} \quad (8)$$

For the batch experiments, the average turnover frequencies were calculated according to Eqs. (11), (12) and (13) where n_{BzOH} is the

$$TOF_{O,c} = \frac{n_{BzOH} (S_B - S_T)}{n_{metal} \tau} \quad (11)$$

$$TOF_{D,c} = \frac{2 X F_{BzOH,in} S_T}{n_{metal} \tau} \quad (12)$$

$$TOFD,c = \frac{2 X F_{BzOH,in} S_T}{n_{metal} \tau} \quad (13)$$

initial molar amount of benzyl alcohol in the reactor.

$$TOFT,b = \frac{X n_{BzOH}}{n_{metal} \tau} \quad (14)$$

$$TOFO,b = \frac{X n_{BzOH} (S_B - S_T)}{n_{metal} \tau} \quad (15)$$

$$TOFD,b = \frac{2 X n_{BzOH} S_T}{n_{metal} \tau} \quad (16)$$

Directly related to the oxidation turnover frequency of the catalyst is the oxygen consumption rate, OCR, at standard temperature and pressure conditions (STP, 0 °C and 1 atm), which was quantified for the continuous operation, using Eq. (14)

$$OCR = \frac{1}{2} F_{BzOH,in} X (S_B - S_T) \tilde{V}_{O2} \quad (17)$$

where \tilde{V}_{O2} is the molar volume of oxygen under STP conditions (22.414 L/mol).

3. Results and discussion

3.1. Batch slurry loop tubular membrane reactor performance and comparison with autoclave reactor

(5)

To establish a benchmark for the SLTM reactor, the oxidation of benzyl alcohol over the Au-Pd/TiO₂ catalyst was carried out under various conditions in a batch autoclave reactor. First, the effect of oxygen pressure on conversion and reaction selectivity was investigated. A series of experiments were conducted under different oxygen pressures (1–5 bar) at 120 °C. Each experiment was performed using the same catalyst concentration (5.0 g/L) and was run for 58 min. The results are reported in Table 1. Conversion increased rapidly when the oxygen pressure was raised from 1 to 3 bar, while with further increase in pressure, the reaction almost reached completion. Concerning product selectivity at an oxygen pressure of 4 bar, the benzaldehyde selectivity reached a maximum of 71% and toluene selectivity 21%. A similar trend was found in the work of Dimitratos et al. [48], where a 1 wt% Au-Pd/TiO₂ catalyst was tested at 120 °C in a 100 mL autoclave. For oxygen pressures higher than 3.4 bar, at constant conversion (10%) an increasing benzaldehyde selectivity was obtained, indicating that the oxygen quickly reacted with the adsorbed species and its availability was only dependent on the stirring rate.

In the oxidation of benzyl alcohol, other by-products such as benzoic acid and benzyl benzoate are also produced. As illustrated in Table 1, increasing the oxygen pressure enhanced the production of the sequential oxidation products; benzoic acid and benzyl benzoate, the selectivity of which, reached a maximum of approximately 7.5% and 4.8% respectively, at 5 bar oxygen pressure. This trend was also observed by Cao et al. [32], who tested a similar catalyst in a micro trickle-bed reactor at 120 °C, where increasing oxygen pressure led to an increased selectivity to benzyl benzoate and benzoic acid, reaching maxima of 2% and 3% respectively, at 5 bar.

Following this, the effect of the catalyst loading on conversion and selectivity at 120 °C and 5 bar oxygen was assessed and the results are shown in Fig. 2. Halving the catalyst amount from 5.0 g/L to 2.5 g/L brought benzaldehyde selectivity up to 76%, while conversion was reduced to 82%. Using one quarter of the original 5.0 g/L catalyst concentration, benzaldehyde selectivity increased to 84% at the expense of toluene, and the conversion dropped to 27%. Moreover, these experiments showed that the selectivities to benzyl benzoate and benzoic acid were not strongly dependent on the catalyst loading (see Supplementary Information). A similar trend was observed in the work of Dimitratos et al. [48], where using a catalyst concentration below

(6)

Table 1, increasing the oxygen pressure enhanced the production of the sequential oxidation products; benzoic acid and benzyl benzoate, the selectivity of which, reached a maximum of approximately 7.5% and 4.8% respectively, at 5 bar oxygen pressure. This trend was also observed by Cao et al. [32], who tested a similar catalyst in a micro trickle-bed reactor at 120 °C, where increasing oxygen pressure led to an increased selectivity to benzyl benzoate and benzoic acid, reaching maxima of 2% and 3% respectively, at 5 bar.

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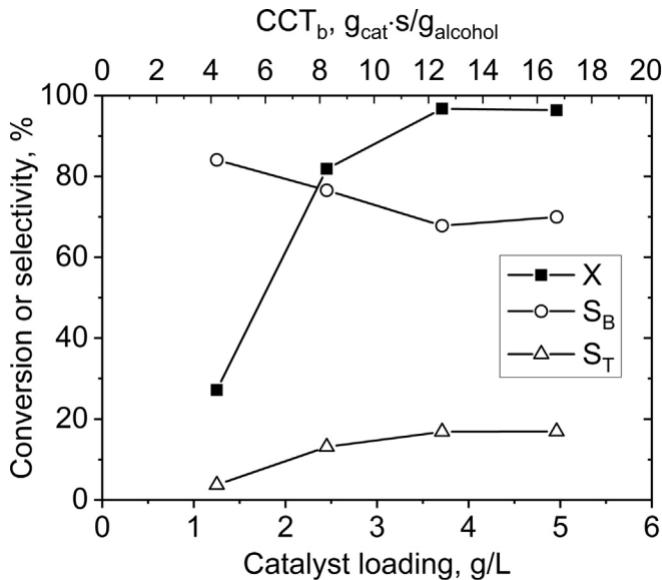


Fig. 2. Effect of catalyst loading on benzyl alcohol conversion, X, benzaldehyde selectivity, S_B, and toluene selectivity, S_T, in an autoclave reactor. Temperature, 120 °C; oxygen pressure, 5 bar; benzyl alcohol volume, 10 mL; reaction time, 58 min.

concentration from 1.3 g/L to 3.7 g/L resulted in a decrease in benzaldehyde selectivity and an increase in toluene selectivity, and this was attributed to mass transfer limitations. However, in our batch experiments at 5.0 g/L catalyst loading similar values of product selectivity were found compared to 3.7 g/L. This can be ascribed to the fact that the reaction already reached completion using 3.7 g/L catalyst loading.

To compare the performance of the autoclave with the SLTM reactor, a series of experiments were performed in the SLTM reactor operated in a batch configuration, without the use of the crossflow filter. For these experiments, a 200 cm long tubular membrane was employed and the slurry catalyst was recirculated through the reactor at a flowrate of 10 mL/min; a reaction temperature of 120 °C was used and an oxygen pressure of 5 bar was applied. The results from these experiments are shown in Fig. 3 and the catalyst contact time is used as means of comparison between the two reactor configurations. With the SLTM reactor, conversion increased rapidly up to approximately 69% in 1 h, equivalent to 17 g_{cat}·s/g_{alcohol} catalyst contact time. In the autoclave however, almost complete conversion was obtained when the same catalyst contact time was used. Benzaldehyde selectivity was 71% and toluene selectivity 24%, values that are comparable with the case of the autoclave and that were almost constant regardless of the catalyst contact time. In the SLTM reactor however, the selectivity to other by-products, such as benzoic acid and benzyl benzoate did not exceed 3%.

It is noteworthy to compare the performance for the two reactors at different catalyst contact times using turnover frequencies, TOF_b. Fig. 4a illustrates how the catalyst loading influenced the turnover frequency for the oxidation reaction in both reactor configurations. At low catalyst contact time (2–6 g_{cat}·s/g_{alcohol}) both reactors exhibited a similar TOF_{O,b} in the range of 20,000–25,000 h⁻¹. However, at catalyst contact times larger than 8 g_{cat}·s/g_{alcohol} (where high conversions were achieved) the TOF_{O,b} decreased in both reactor configurations, before reaching a value of approximately 15,700 h⁻¹ for the autoclave and 7300 h⁻¹ for the SLTM reactor. The turnover frequency for the disproportionation reaction in both reactors is displayed in Fig. 4b. At high catalyst contact times, the rate of disproportionation was in the same order of magnitude for both the autoclave and the SLTM reactor, however at lower values of the catalyst contact time, CCT_b, the TOF_{D,b} in the case of the SLTM reactor reached ~30,000 h⁻¹, while in the autoclave, the disproportionation appeared to be suppressed. This

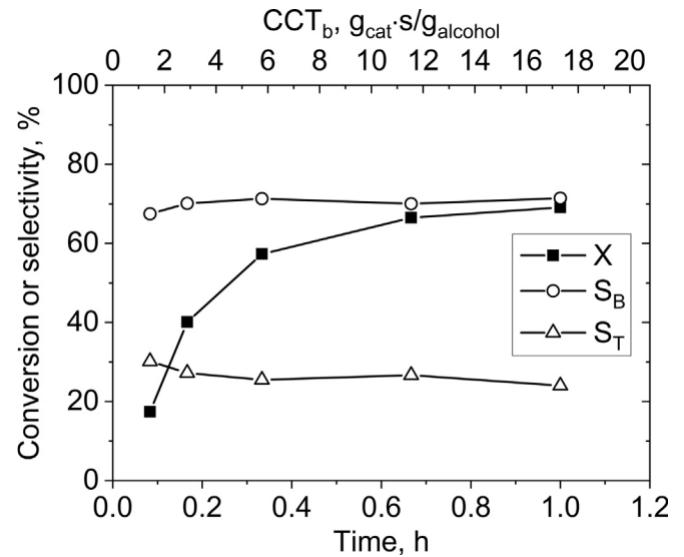


Fig. 3. Benzyl alcohol conversion, X, benzaldehyde selectivity, S_B, and toluene selectivity, S_T, as a function of reaction time in the SLTM reactor operating in a batch configuration. Temperature, 120 °C; oxygen pressure, 5 bar; membrane length, 200 cm; catalyst loading, 5.0 g/L; reactor volume, 2.08 mL.

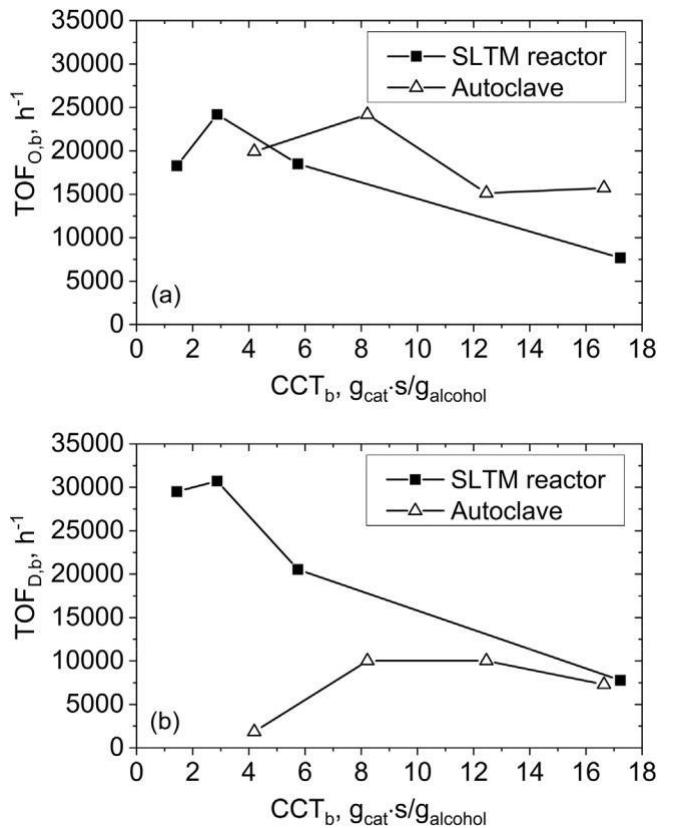


Fig. 4. Turnover frequencies of the oxidation reaction, TOF_{O,b}, (a) and the disproportionation reaction, TOF_{D,b}, (b) as a function of the catalyst contact time, CCT_b, in the batch SLTM and autoclave reactors. Temperature, 120 °C; oxygen pressure, 5 bar. SLTM reactor: catalyst loading, 5.0 g/L; membrane length, 200 cm; reactor volume, 2.08 mL. Autoclave: benzyl alcohol volume, 10 mL; reaction time, 58 min.

shows that toluene selectivity in the autoclave decreased when reducing catalyst contact time, unlike in the SLTM reactor. It is possible that this is evidence of poorer catalyst suspension at high catalyst loading or of mass transfer resistances being present. It is also important to note

that CCT_b was increased in different ways in the two reactors: in the autoclave by increasing catalyst loading at constant reaction time, in the SLTM by increasing reaction time at constant catalyst loading. Nevertheless, comparable TOF_{O,c} and benzaldehyde selectivity were observed in both reactors, indicative of a similar performance for the oxidation of benzyl alcohol. It is not possible to exclude the presence of bottlenecks in the transfer of oxygen through the liquid to the catalyst surface in the SLTM reactor, which can be responsible for its worse performance compared to the autoclave at higher CCT_b values. In addition, while in the SLTM reactor no other by-products except toluene were produced, in the autoclave the selectivity to benzoic acid and benzyl benzoate reached around 12%, even for the experiment performed at a low catalyst concentration (1.3 g/L). This may be due to higher degree of contact surface area between the stirred liquid with the oxygen bubbles inside the autoclave, leading to further oxidation of the product and suppression of reactions that occur in the absence of oxygen. On the other hand, the SLTM reactor, having a fixed gas-to-liquid surface, provided a better control of oxygen delivery, causing the formation of no other products, but benzaldehyde and toluene.

3.2. Residence time distribution of slurry loop tubular membrane reactor

The use of a crossflow filter allowed for continuous operation of the SLTM reactor and the operating parameters were varied to observe their effect on conversion and product selectivity in the aerobic oxidation of benzyl alcohol in flow. The macro-mixing characterisation of the reactor was carried out by evaluating the residence time distribution (RTD) by performing a step-input injection of a tracer (see *Supplementary Information*). Eq. (15) shows the RTD of the ideal CSTR, ECSTR, as function of the mean residence time, τ , while Eq. (16) ex-

presses the normalised tracer concentration in the loop outlet, $C_{out,48}$ as the convolution integral of the RTD of an ideal CSTR with the nor-

minalised inlet tracer concentration in the loop inlet, C_{in} . The convolution

between the experimental C_{out}

and the RTD of a CSTR was accomplished

iteratively in order to fit the experimental function in Python [49] and further details are reported in the *Supplementary Information*.

$$ECSTR(t) = \frac{1}{\tau} e^{-\frac{t}{\tau}} \quad (15)$$

$$C_{out}(t) = \int_0^t C_{in}(t-t') ECSTR(t') dt \quad (16)$$

The fitting revealed that the macro-mixing behaviour of the SLTM reactor is equivalent to that of an ideal CSTR with a residence time of 60 min, which is close to the expected value of 58 min. As shown in the RTDs of loop reactors by Melo et al. [50] for relatively high recycle ratios, the tracer output signal from a pulse experiment has a distinct exponential trend, which is in agreement with the RTD of an ideal CSTR.

3.3. Catalyst stability test

The stability of the Au-Pd/TiO₂ catalyst was assessed in the SLTM reactor under continuous operation conditions. For these experiments, the oxygen pressure outside the membrane was 4 bar and the reactor temperature was maintained at 120 °C. Benzyl alcohol was continuously introduced into the system at a flowrate of 0.025 mL/min and 7 mg of catalyst was used. The catalyst contact time was 17 gcat·s/galcohol, equivalent to having a slurry catalyst loading of 5.0 g/L in the loop. Fig. 5 shows the result from a 4.5 h continuous reaction experiment.

At these conditions, ~45% of benzyl alcohol was converted. The main products were benzaldehyde and toluene, the reaction selectivity of which was ~66% and 30% respectively. Other by-products were also formed and these were benzoic acid (1.4%) and benzyl benzoate

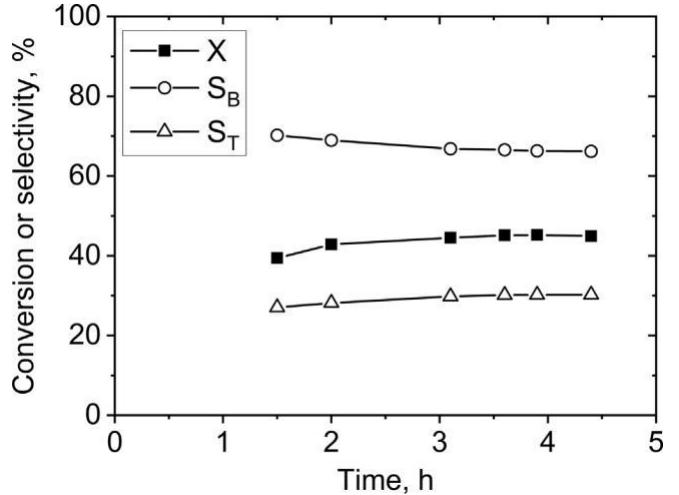


Fig. 5. Benzyl alcohol conversion, X, benzaldehyde selectivity, S_B, and toluene selectivity, S_T, as function of reaction time in the continuous SLTM reactor. Temperature, 120 °C; oxygen pressure, 4 bar; benzyl alcohol flowrate, 0.025 mL/min; catalyst concentration, 5.0 g/L; reactor volume, 1.46 mL; CCT_c, 17 gcat·s/galcohol.

(1.2%). The overall selectivity of these minor by-products was typically < 3% in all the flow experiments. The reaction lasted 4.5 h and as illustrated in Fig. 5, the catalyst performance was constant enough to enable a consistent catalyst testing under different operating conditions. For each of the following reaction tests performed in the SLTM reactor, the samples were collected after 2.5 h operation.

3.4. Effect of temperature on continuous slurry loop tubular membrane reactor performance

Previous reports have highlighted how benzaldehyde selectivity is sensitive to reaction temperature, particularly in reactions over a Au-Pd/TiO₂ catalyst. Typically, reaction selectivity to benzaldehyde drops at high temperatures, despite the exponential increase in the average total turnover frequency [32,51,52]. To explore how temperature affected the performance of the catalyst in the SLTM reactor, a series of experiments were conducted at 100–120 °C. The reactor was pressurised to 5 bar of oxygen and 17 gcat·s/galcohol catalyst contact time was used, corresponding to 5.0 g/L catalyst concentration. The temperature at the inlet of the membrane was recorded at steady-state conditions. Simulations were performed with COMSOL Multiphysics® 5.3a for all the oil bath temperatures, showing that the same temperature was reached along the slurry loop membrane reactor, apart from the sections of the loop placed outside the thermal bath. The latter experienced lower temperatures, bringing the liquid average temperature inside the loop to around 3 °C less than the temperature measured at the inlet of the tubular membrane (see *Supplementary Information*). The results of these experiments are reported in Fig. 6 and show benzaldehyde selectivity decreasing from 75% to 67% in the range from 100 °C to 120 °C and a corresponding rise of toluene selectivity in the same temperature range.

Galvanin et al. [42] proposed a microkinetic model for the aerobic oxidation of benzyl alcohol over a Au-Pd/TiO₂ catalyst, which discussed this selectivity trend. In particular, the reaction mechanism behind the production of toluene at higher temperatures was ascribed to a hydrogenolysis reaction, whereas at lower temperatures, disproportionation was shown to be the dominant pathway. However, by increasing the temperature both pathways are promoted, leading to a higher selectivity to toluene and a corresponding lower benzaldehyde production.

Given the complexity of the reaction network, the TOF_{O,c} and TOF_{D,c} were assessed individually (Fig. 7). The TOF_{T,c} increased with

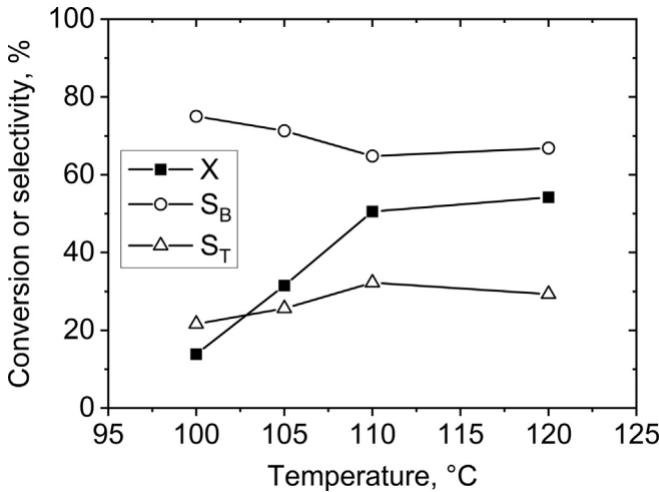


Fig. 6. Benzyl alcohol conversion, X, benzaldehyde selectivity, S_B, and toluene selectivity, S_T, as a function of reaction temperature in the continuous SLTM reactor. Oxygen pressure, 5 bar; benzyl alcohol flowrate, 0.025 mL/min; cata-lyst concentration, 5.0 g/L; reactor volume, 1.46 mL; CCT_c, 17 gcat·s/galcohol.

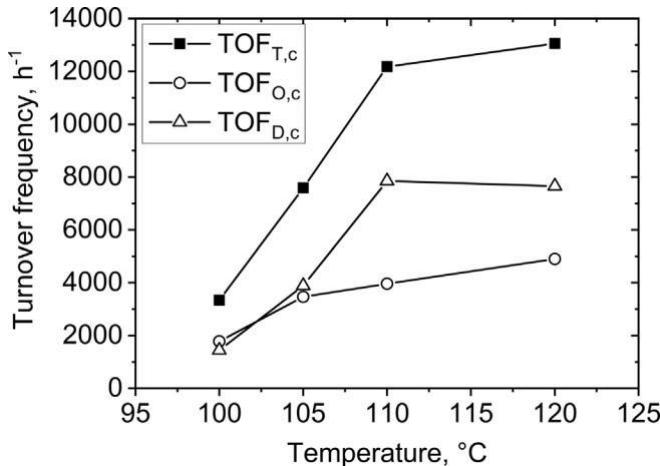


Fig. 7. Turnover frequency of the overall, TOF_{T,c}, oxidation, TOF_{O,c} and disproportionation, TOF_{D,c}, reaction as a function of the reaction temperature in the continuous SLTM reactor. Oxygen pressure, 5 bar; benzyl alcohol flowrate, 0.025 mL/min; catalyst concentration, 5.0 g/L; volume of the reactor, 1.46 mL; CCT_c, 17 gcat·s/galcohol.

temperature from 3342 h⁻¹ at 100 °C to 13,057 h⁻¹ at 120 °C. At higher reaction temperatures, it is evident that the disproportionation reaction becomes more dominant than the oxidation pathway. Cao et al. [47] observed a similar trend. The two reactions had comparable turnover numbers at 100 °C when the performance of a 1 wt% Au-Pd/TiO₂ cat-alyst was assessed in a micro packed-bed reactor with premixed oxygen/benzyl alcohol. However, at 120 °C the turnover number of the disproportionation reaction was in the order of 6000, corresponding to a TOF_{D,c} of 4300 h⁻¹. This was approximately three times higher than the oxidation turnover number (TOF_{O,c} = 1400 h⁻¹), unlike in the continuous SLTM reactor (Fig. 7) in which the TOF_{D,c} was around 1.5 times the TOF_{O,c}.

3.5. Effect of oxygen pressure on continuous slurry loop tubular membrane reactor performance

To investigate the effect of oxygen pressure on conversion and product selectivity, the pressure of oxygen outside the membrane was varied from 0 to 5 bar and the results are displayed in Fig. 8. Under anaerobic conditions, achieved by pressurising with 3 bar of nitrogen

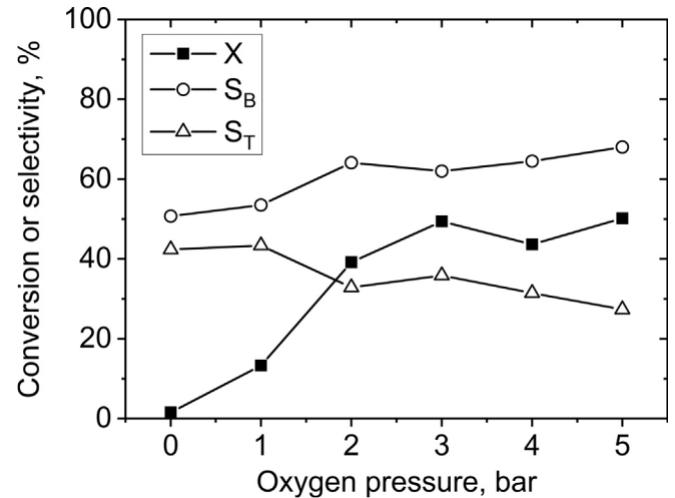


Fig. 8. Effect of oxygen pressure on benzyl alcohol conversion, X, benzaldehyde selectivity, S_B, and toluene selectivity, S_T, in the continuous SLTM reactor. Temperature, 120 °C; benzyl alcohol flowrate, 0.025 mL/min; catalyst con-centration, 5.0 g/L; reactor volume, 1.46 mL; CCT_c, 17 gcat·s/galcohol.

outside the membrane, the benzyl alcohol conversion was 2% and si-milar selectivities to benzaldehyde and toluene were observed; 51% and 42% respectively. Given that only the disproportionation and hy-drogenolysis reactions take place in the absence of oxygen, one would anticipate that equimolar amounts of benzaldehyde and toluene would be produced [47]. The slightly higher benzaldehyde selectivity was likely due to presence of residual air in the gas line.

Increasing the oxygen pressure in the SLTM reactor led to an in-crease in both conversion of benzyl alcohol and selectivity to benzal-dehyde. With respect to 0 bar oxygen pressure, benzaldehyde selectivity increased by 22% at 3 bar reaching a value of 62%, with a corre-sponding suppression of toluene selectivity and an increase in conver-sion to around 50%. Interestingly, the increase of benzyl alcohol con-version/benzaldehyde selectivity with oxygen pressure was observed up to 3 bar, after which only marginal increases in both were noticed. At 5 bar, maximum benzaldehyde selectivity and benzyl alcohol con-version were observed: 68% and 50% respectively.

These results are in agreement with the findings of Dimitratos et al. [48] who observed that for oxygen pressures in excess of 50 psi (3.4 bar), the TOF_{T,b} remained constant, while selectivity to benzalde-hyde increased marginally from 65% at 50 psi to around 70% at 100 psi. Cao et al. [47] also observed that TOF_{T,c} of a 1 wt% Au-Pd/TiO₂ catalyst was constant at oxygen pressures of 4 and 5 bar using a micro packed-bed reactor operated at 120 °C with premixed oxygen/benzyl alcohol.

3.6. Effect of membrane length and catalyst mass on continuous slurry loop tubular membrane reactor performance

To understand the role of oxygen availability on the reactor per-formance, a second SLTM reactor was designed and built consisting of a longer membrane (120 cm) and an overall reactor volume of 1.84 mL. For consistency, all the reactions were conducted under the same conditions; a reaction temperature of 120 °C, 5 bar oxygen pressure and 17 gcat·s/galcohol catalyst contact time were utilized. With a longer membrane the TOF_{O,c} remained almost unchanged, suggesting that there was no limitation in the oxygen supply (see Table 2).

In order to establish whether in the SLTM reactor gas-liquid mass transfer resistances were present, the catalyst loading inside the loop was decreased, whilst maintaining the same inlet flowrate of 0.025 mL/ min. These experiments were also performed using an oxygen pressure of 5 bar and reaction temperature of 120 °C. Fig. 9 shows that reducing

Table 2

Benzyl alcohol conversion, X, benzaldehyde selectivity, S_B, and toluene selectivity, S_T, along with turnover frequencies of the overall, TOF_{T,c}, oxidation, TOF_{O,c}, and disproportionation, TOF_{D,c}, reactions for two membrane lengths in the continuous SLTM reactor. Temperature, 120 °C; oxygen pressure, 5 bar; benzyl alcohol flowrate, 0.025 mL/min; catalyst concentration, 5.0 g/L; CCT_c, 17 gcat·s/galcohol.

| Membrane length, cm | Reactor volume, mL | X, % | S _B , % | S _T , % | TOF _{T,c} , h ⁻¹ | TOF _{O,c} , h ⁻¹ | TOF _{D,c} , h ⁻¹ |
|---------------------|--------------------|------|--------------------|--------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| 60 | 1.46 | 50 | 68 | 27 | 12,092 | 4921 | 6612 |
| 120 | 1.84 | 44 | 70 | 27 | 10,504 | 4449 | 5732 |

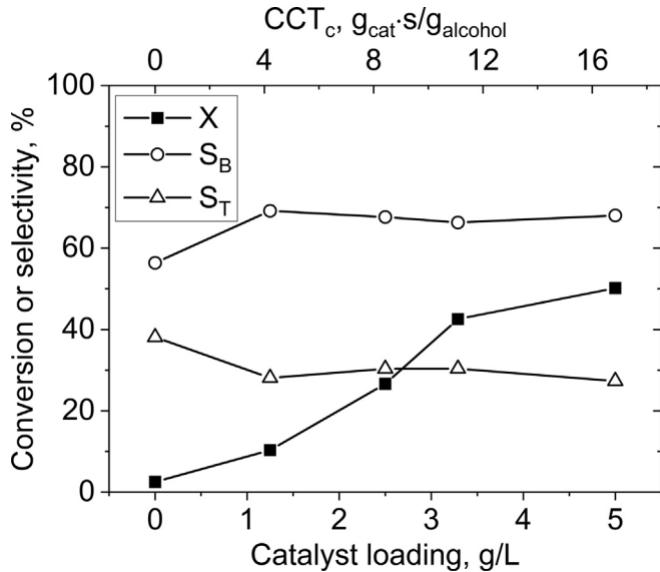


Fig. 9. Effect of catalyst loading on benzyl alcohol conversion, X, benzaldehyde selectivity, S_B, and toluene selectivity, S_T, in the continuous SLTM reactor. Temperature, 120 °C; oxygen pressure, 5 bar; benzyl alcohol flowrate, 0.025 mL/min; reactor volume, 1.46 mL.

the catalyst loading from 5.0 g/L to 1.3 g/L, reduced benzyl alcohol conversion from 50% to 10%. A blank reaction was also conducted and in the absence of any catalyst only 3% benzyl alcohol conversion was observed at the same benzyl alcohol flowrate.

Concerning the product selectivity, it is noteworthy mentioning the important role of the Au-Pd catalyst, which was able to bring benzaldehyde selectivity from 56% in the case of the blank test to 69% using 1.3 g/L catalyst loading in the reactor, while a further increase in the catalyst loading did not appear to have a significant effect. The opposite effect on toluene selectivity was observed upon addition of the catalyst.

The oxygen consumption rate was determined using Eq. (14) and is presented in Fig. 10, as function of the catalyst concentration inside the loop reactor. The maximum oxygen consumption rate observed was calculated to be approximately 0.55 mL/min, which was achieved with 5.0 g/L catalyst concentration and dropped to 0.27 mL/min when the catalyst concentration was halved. As demonstrated in Fig. 10, the rate at which oxygen is consumed is directly proportional to the catalyst concentration and this linearity indicates absence of gas-liquid mass transfer resistance under these operating conditions. However, the presence of liquid-solid resistance to mass transport cannot be excluded.

The inverse of the oxygen consumption rate (with the exception of the blank test) was plotted against the reciprocal of the catalyst loading (see Supplementary Information). A linear fitting and a quadratic fitting of these data were performed and a 95% χ^2 test resulted in the rejection of the linear fitting and acceptance of the nonlinear fitting. This indicates that the reaction does not follow first order kinetics [53], as also demonstrated by Galvanin et al. [42]. Furthermore, the small value of the intercept for the quadratic fitting confirmed negligible gas-liquid mass transfer resistance, as previously discussed.

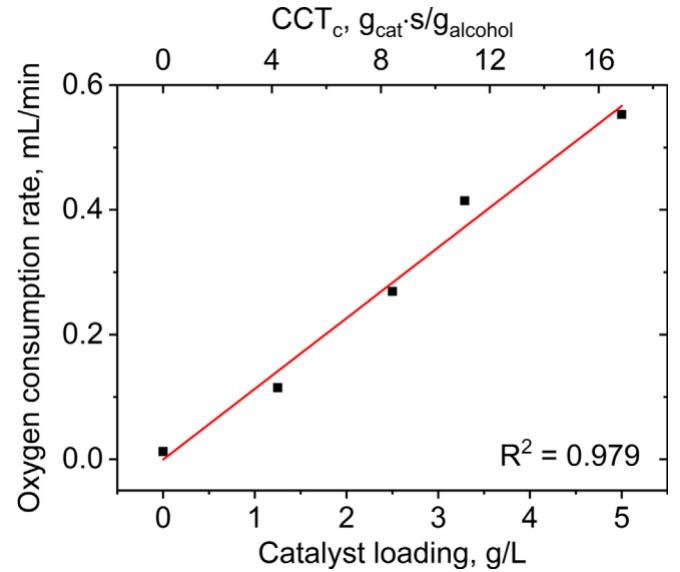


Fig. 10. Oxygen consumption rate (standard temperature and pressure) as a function of catalyst loading in the continuous SLTM reactor. Temperature, 120 °C; oxygen pressure, 5 bar; benzyl alcohol flowrate, 0.025 mL/min; reactor volume, 1.46 mL.

3.7. Slurry loop tubular membrane reactor performance comparison with other reactor configurations

In order to compare the catalyst performance in the SLTM reactor and in packed-bed configurations, experiments were carried out in a trickle-bed capillary reactor. Moreover, results from our previous work on a flat membrane packed-bed reactor and a micro trickle-bed reactor operated at a high volumetric gas-to-liquid ratio (G/L, standard temperature and pressure) are also used for the comparative study [39,54]. To ensure an accurate comparison with the SLTM reactor, 7 mg of catalyst was used, which corresponded to a catalyst contact time of 17 gcat·s/galcohol in the trickle-bed capillary reactor. In our previous work [39], the same catalyst was employed in the same particle size fraction and packed inside a rectangular microchannel (length: 75 mm; width: 3 mm; depth: 1 mm), having a flat Teflon AF-2400 membrane (length: 85 mm; width: 30 mm; thickness: 0.07 mm) to provide oxygen from one side of the channel. Given the large amount of catalyst employed (0.1 g) and the relatively low benzyl alcohol flowrate (0.010 mL/min) in the above flat membrane reactor, the catalyst contact time was significantly larger than in the case of the SLTM reactor and the trickle-bed capillary reactor. The comparison of the performance of these reactor configurations is reported in Table 3, where information regarding the catalyst contact time and the specific surface area of the membrane per catalyst mass, A_s, is included.

Despite the higher oxygen pressure of 6.3 bar and substantially higher catalyst contact time employed in the flat membrane packed-bed reactor, benzyl alcohol conversion (43%) and benzaldehyde selectivity (62%) did not exceed those observed in the SLTM reactor, which used a smaller catalyst amount relative to the membrane surface area. The presence of mass transfer resistances in the oxygen transverse transport in the liquid bulk through the flat membrane packed-bed reactor led to

Table 3

Benzyl alcohol conversion, X, benzaldehyde selectivity, SB, and toluene selectivity, ST, along with turnover frequencies of the oxidation, TOFO_c, and dis-proportionation, TOFD_c, reactions for different reactor configurations. Temperature, 120 °C. SLTM reactor: oxygen pressure, 5 bar; membrane inner surface area, 15 cm²; benzyl alcohol flowrate, 0.025 mL/min. Flat membrane packed-bed reactor [39]: oxygen pressure, 6.3 bar; membrane surface area, 2.25 cm²; catalyst particle size, 90–125 µm; catalyst mass, 0.1 g. Trickle-bed capillary reactor: oxygen pressure, 5 bar; oxygen flowrate, 2.5 NmL/min; catalyst particle size, 90–125 µm; benzyl alcohol flowrate, 0.025 mL/min. Micro trickle-bed reactor [54]: oxygen pressure, 2 bar; oxygen flowrate, 4 NmL/min; catalyst particle size, 63–75 µm; benzyl alcohol flowrate, 0.75 µL/min. Autoclave: oxygen pressure, 5 bar; catalyst loading, 5 g/L. G/L is volumetric gas-to-liquid ratio at standard temperature and pressure conditions.

| Reactor | X, % | SB, % | ST, % | TOFO _c , h ⁻¹ | TOFD _c , h ⁻¹ | CCT _c , g _{cat} ^s /g _{alcohol} | A _s , cm ² /g _{cat} |
|---|------|-------|-------|-------------------------------------|-------------------------------------|--|--|
| SLTM (continuous) | 50 | 68 | 27 | 4921 | 6612 | 17 | 2094 |
| Flat membrane packed-bed (6.3 bar) [39] | 43 | 62 | 37 | 76 | 209 | 577 | 22.5 |
| Trickle-bed capillary (G/L = 100) | 68 | 62 | 30 | 5388 | 9749 | 17 | — |
| Micro trickle-bed (G/L = 3577) [54] | 97 | 82 | 13 | 3221 | 1213 | 76 | — |
| Autoclave | 96 | 70 | 17 | 11,674 | 7457 | 17 | — |

low reaction rate (TOFO_c < 143 h⁻¹). Furthermore, the highest benzaldehyde selectivity recorded was 70%, obtained at even higher oxygen pressure (8.4 bar) and increased catalyst contact time (1150 g_{cat}^s/galcohol) [39].

Because of PFR-like conditions and of the direct contact of the oxygen bubbles with the substrate, reaction in the trickle-bed capillary reactor at a volumetric G/L of 100 achieved a higher conversion (68%) compared to the SLTM reactor. However, a lower benzaldehyde selectivity (62%) was obtained and the oxidation turnover frequency was in the same order of magnitude as in the SLTM reactor (4900–5400 h⁻¹). Moreover, unlike in the flat membrane packed-bed and the SLTM reactor where only benzaldehyde and toluene were detected, in the trickle-bed capillary reactor, benzyl benzoate was also produced, with reaction selectivity of 4.6% (see Supplementary Information), suggesting that the sequential oxidation of benzaldehyde occurred.

The lower conversion of the SLTM reactor with respect to the trickle-bed capillary reactor might also be due to some catalyst particles being trapped inside the crossflow filter, thereby reducing the concentration of catalyst immersed in the slurry inside the loop, or the fact that the SLTM reactor was operating at a slightly lower average volumetric temperature than the trickle-bed reactor, causing an overall consistent decrease in conversion. This suggests that the use of a smaller crossflow filter area which would decrease the amount of deposited catalyst on the filter and a better thermal insulation of the parts of the loop assembly outside the oil bath, could improve the performance of the continuous SLTM reactor.

In our previous work, the aerobic oxidation of benzyl alcohol was carried out in a silicon-glass microreactor operated under trickle-bed conditions at much higher gas-to-liquid ratios than in the trickle-bed capillary reactor [54]. Different hydrodynamic regimes resulting from various gas-to-liquid ratios were mapped and it was suggested that the thinning of the contacting liquid film over the catalyst particle's surface with increasing superficial gas velocity was beneficial for achieving a higher gas-liquid mass transfer.

As the hydrodynamics changed from a liquid-dominated slug regime to a gas-continuous segregated flow, conversion and product selectivity improved until a maximum was reached. Table 3 shows the results for the gas-dominated regime with sufficiently wetted catalyst, which led to 97% conversion with 82% benzaldehyde selectivity in the micro trickle-bed reactor. Benzaldehyde selectivity was higher than the selectivity achieved in the autoclave (70%), despite the much lower operating oxygen pressure (2 bar). However, the two reactors showed similar benzyl alcohol conversion (96–97%) and toluene selectivity (13–17%). This suggests that despite having a fully oxygenated environment, the liquid film shear and liquid/oxygen and oxygen/solid contact seemed to play an important role in improving conversion and selectivity.

4. Conclusions

A slurry loop tubular membrane (SLTM) reactor was designed and demonstrated to be an effective and safe reactor for the catalytic aerobic oxidation of benzyl alcohol. The reactor is flexible, as any powdered catalyst can be used in batch or continuous operation. The comparison between the SLTM reactor operated in batch mode and the conventional autoclave (Parr reactor) showed comparable turnover frequencies at long catalyst contact times, demonstrating the capability of the SLTM reactor to provide an intense oxygenation degree for the reaction. The addition of a crossflow filter to the reactor loop allowed to keep the catalyst confined inside the loop, avoiding the need for continuous catalyst feed when operating in a continuous mode. RTD analysis showed a macro-mixing behaviour similar to that of a CSTR. High selectivity to benzaldehyde was observed when increasing oxygen pressure and decreasing reaction temperature, highlighting the importance of these operating parameters in tuning product selectivity. The oxygen supply was found to be sufficient and not limited by the gas-liquid mass transfer resistance. In fact, by doubling the length of the tubular membrane the average turnover frequency for the oxidation reaction was constant and the oxygen consumption rate linearly decreased as the catalyst loading was decreased. Due to its effective oxygen delivery and use of a catalyst powder in a slurry form, the SLTM reactor showed superior performance in terms of benzaldehyde selectivity and reaction rate compared to a flat membrane packed-bed reactor. When the SLTM was compared to a trickle-bed capillary reactor with premixed oxygen and substrate, a similar performance was obtained. Other reactions can be performed in the SLTM reactor involving a wider spectrum of catalysts, including those that are difficult to pelletize, with the additional benefits of having small mass transport resistances and the possibility of operating safely if a gaseous oxidant is to be employed.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2019.122250>.

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