

MASS TRANSFER LIMITED WET OXIDATION IN TRICKLE-BED REACTOR

Vratislav TUKAC¹, Jiri VOKAL and Jiri HANIKA²

Department of Organic Technology, Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic; e-mail: ¹ vratislav.tukac@vscht.cz, ² jiri.hanika@vscht.cz

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Catalytic activity of CuO-supported catalyst in phenol oxidation, and the influence of reaction conditions, *viz.* temperature (125–170 °C), oxygen partial pressure (1–7 MPa) and liquid feed (30–760 ml h⁻¹), in the continuous operation using 17.9 mm i.d. trickle-bed reactor is presented. The hydrodynamic impact on the three-phase trickle-bed reactor performance in an environmental application of catalytic wet oxidation was also investigated. The results of trickle-bed operation were strongly influenced by wetting efficiency. An insufficient catalyst wetting can be compensated by filling the catalyst bed voids by fine glass spheres. In the case of the gas transfer limited reaction, a better wetting of the catalyst can lead to worse reactor performance due to lower reaction rates.

Key words: Mass transfer; Wet oxidation; Trickle-bed reactor; Phenol; Catalysis; CuO.

Processes of wet oxidation of toxic contaminants or compounds degradable with difficulties in waste waters play an alternative role in decontamination of some industrial waste waters as well as waste waters from pharmaceutical and food industries. The main advantage of catalytic oxidation consists in reduced process and investment costs due to milder process conditions (see *e.g.*, Mishra *et al.*¹). Catalytic liquid-phase phenol oxidation proceeds by a combined redox and free-radical mechanism². A heterogeneous–homogeneous free-radical mechanism coupled with catalyst–surface redox cycle also was proposed for liquid-phase oxidation of other organic compounds. According to several papers (*e.g.*, Pintar and Levec³, Tukac and Hanika⁴), the reaction system is described by a large set of parallel–consecutive reactions producing a great number of intermediates. Also the overall oxidation rate slows down substantially in the stage of formation of relatively stable carboxylic acids, such as maleic, acetic and oxalic acids. The problems arising in scaling-up experimental data from laboratory autoclave measurements to the trickle-bed operation, as mentioned by Levec⁵, lead to the kinetic experiments using the trickle-bed reactor. In contrast to a usual slurry operation, the trickle-bed reactor has an advantage, a catalyst separation is not required, and a high catalyst–liquid ratio and also a high gas–liquid interfacial area are convenient. Due to the low oxygen solubility in the liquid reaction mixture, a high gas–liquid–solid interfacial area is more important than the catalyst activity. On the other hand, hydrody-

namic impact (wetting efficiency) having a controlling role at low liquid velocities typical of the waste water treatment processes, on the three-phase trickle-bed reactor performance was confirmed by many authors (*e.g.*, by El-Hisnawi *et al.*⁶, Tukac and Hanika⁷). However, if the reaction is gas limited, the gaseous reactant can easily access catalyst pores from the dry areas and, consequently, a higher reaction rate is observed with a decreased external catalyst wetting⁸. The above analysis is based on the assumption that particles in trickle beds are always internally wetted. An alternative for scale-up studies is the use of trickle-bed reactors diluted with fines (inert particles, by an order of magnitude smaller than the catalyst pellets). The absence of liquid spreading due to the use of low liquid velocities in laboratory reactors is compensated by fines which provide additional contact points for solids over which liquid films flow. This improves liquid spreading and helps to achieve the same liquid–solid contacting in laboratory reactors as obtained in industrial units at higher superficial liquid velocities. Fines decouple the hydrodynamics and kinetics and provide an estimate of the true catalyst performance in industrial reactor by improving wetting and catalyst utilization in a laboratory-scale unit at space velocities identical to those in industrial reactors.

EXPERIMENTAL

The trickle-bed operations were carried out⁹ in a stainless-steel tube of 17.9 mm i.d. equipped with an axial 4.4 mm o.d. thermowell allowing to measure temperature profile, under following conditions: liquid feed (F , $l\ h^{-1}$) ranged from 0.03 to $0.76\ l\ h^{-1}$, vent gas flow rate $3\text{--}108\ l\ h^{-1}$, overall pressure $1\text{--}7\ MPa$, temperature $125\text{--}170\ ^\circ C$ and the initial phenol concentration in water $5\ g\ l^{-1}$. The catalyst bed was packed with 4.7 mm equilateral cylinders of Cherox 46-00 (Chemopetrol Group Co., Czech Republic; 33% CuO on silicate carrier of porosity 0.45 and surface area $200\ m^2\ g^{-1}$). Catalyst weight (W , g) was 11.7 g. Two arrangements of catalytic bed were compared: (i) random-packed catalyst bed and (ii) catalyst bed voids filled with fine (1 mm) glass spheres. The latter arrangement exhibits a more efficient catalyst wetting as was also observed in the study of Al-Dahhan and Dudukovic¹⁰.

HPLC analysis of the reaction mixture was made using a $3 \times 300\ mm$ column, filled with Tessek $7\ \mu m$ Separon SGX C18, a UV detector operated at 254 nm and the eluent flow rate (40% aqueous methanol) $0.6\ ml\ min^{-1}$.

RESULTS AND DISCUSSION

A comparison of the phenol oxidation reaction occurring in random-filled bed of pelleted catalyst and the reaction in diluted bed with voids filled by fine glass spheres is presented.

The catalytic wet oxidation process involves three main individual steps: (i) transfer of oxygen from the gas to the liquid phase, (ii) adsorption of the reaction components on the catalyst surface, and (iii) the surface chemical reaction between organic substrate and oxygen. The reaction rate (r , $mol\ g^{-1}\ h^{-1}$) can be expressed by the Eq. (1), in which different reaction orders with respect to both the reaction components are assumed:

$$r = -\frac{dC_{\text{Ph}}}{d(W/F)} = \eta_c k C_{\text{Ph}} P_{\text{O}_2}^n \quad (1)$$

(C_{Ph} phenol concentration, mol l⁻¹; k rate constant, molⁿ⁻¹ l¹⁺ⁿ g⁻¹ h⁻¹; P_{O_2} oxygen partial pressure, MPa; η_c wetting efficiency; n reaction order).

The high catalyst–substrate ratio used in the trickle bed oxidation experiments causes the absence of an induction period observed in slurry systems for short reaction times and the reaction system follows the pseudo-first order of reaction kinetics with respect to phenol. However, the wetting efficiency (η_c) must be introduced into the modified pseudo-first-order kinetic equation (1) describing the trickle-bed data.

As can be seen from Fig. 1, there was found a slightly lower (0.5) oxygen reaction order (n) in diluted bed with voids filled by glass fines than was the reaction order in random-packed bed (0.7). A high excess of adsorbed oxygen has a “buffering” influence on the apparent reaction order with respect to oxygen and its value shifts from 0.5 observed for complete wetting in bed diluted by fines to 0.7 for the standard-random packed bed operation (Fig. 1). The oxygen reaction order was evaluated from Eq. (2), which describes the mean phenol conversion (x) in the bed:

$$\ln\left(\frac{1}{1-x}\right) = k \frac{W}{F} P_{\text{O}_2}^n \quad (2)$$

The reason for the increase of oxidation order is the existence of the unwetted catalyst surface area, which allows direct oxygen transfer into the poorly wetted standard random-packed bed.

A dominant impact of low oxygen concentration in the liquid reaction mixture on the rate of oxidation can be overcome only at high pressures, usually above 10 MPa. There-

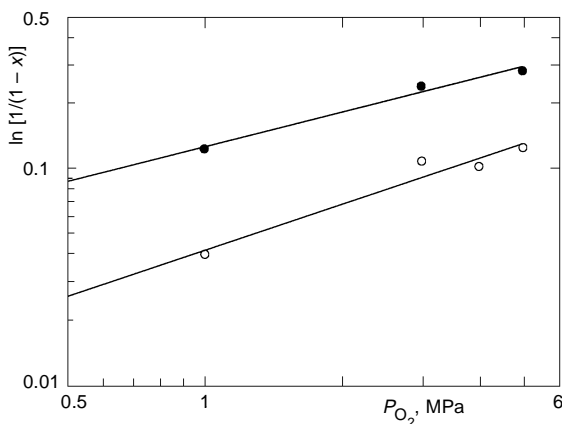


FIG. 1

Mean phenol conversion *versus* partial pressure of oxygen for standard random-packed bed and for the catalyst bed diluted with fines. Liquid feed 250 ml h⁻¹; temperature 150 °C; ○ random-packed bed; ● bed diluted with fines

fore, a low oxygen solubility in the reaction mixture and thus a low oxygen partial pressure appear to be the rate-limiting factor in the wet oxidation process. In the range of experimental conditions used in this study, an almost constant value of the oxidation rate independent of temperature has been observed. The opposite effects of temperature on the apparent kinetic constant and the oxygen solubility in the reaction mixture are probably the main reason for this fact.

In contrast to the common belief, the dilution of catalyst bed by fines causes a substantial decrease in the reaction rate in comparison with the standard random-packed bed of catalyst. This effect is probably associated with the existence of stable liquid lenses among fine particles of the diluted bed, due to water, a solvent with a high value of surface tension (Fig. 2).

At 167 °C, the mean oxidation rate in the bed filled with fines is independent in broad range of liquid flow rate. In contrast, in the random catalyst bed with a higher void fraction, the mean reaction rate is strongly dependent on the liquid velocity. On the other hand, at 129 °C, no perceptible differences between the reaction rates in random and diluted catalyst beds were found. Surprisingly, the lower reaction rate was found in completely wetted bed of catalyst diluted with fines, the better wetting occurred. This could be explained by different intrinsic residence times of the reaction mixture in the catalyst bed and also by a substantial decrease in the gas-liquid interfacial area discussed above. The bed filled with a mixture of catalyst pellets and inert glass fines is completely wetted and may be also "flooded" due to the low void fraction ($\epsilon = 0.1$) and high surface tension of the liquid. On the other hand, using a bed of extrudates with a void fraction of 0.4, the worse wetting results in the maximum value of phenol conversion on the mentioned dependence.

The oxygen concentration on the active catalyst surface is a result of the interaction of chemical reaction and transfer phenomena at the interfacial area. The latter is strongly influenced by the wetting efficiency, liquid maldistribution and/or tempera-

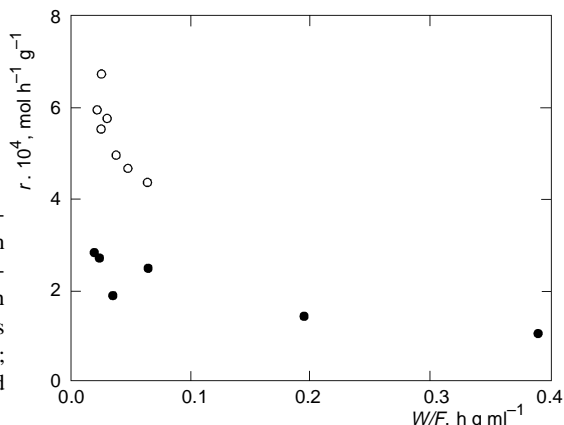


FIG. 2

Sensitivity of mean rate of phenol oxidation *versus* kinetic coordinate in trickle-bed reactor with the random-packed catalyst bed and bed filled with glass fines. Temperature 168 °C; gas flow rate 38 l h⁻¹; total pressure 5 MPa; ○ random-packed bed; ● bed diluted with fines

ture-dependent phase equilibria, *viz.* oxygen solubility in phenol solution, adsorption of reaction components on active sites of the catalyst, and the available interfacial area between gas and liquid. A comparison of experimental results obtained with and without insufficient catalyst wetting, at two different temperatures, is presented in Fig. 3.

The effect of bed dilution at 129 °C is not distinct, but at 168 °C the difference in phenol conversion is of the same magnitude as that caused by the temperature shift. The low wetting efficiency for low liquid flow rates compensates the effect of a long residence time on overall substrate conversion.

The gas flowing through porous bed of the catalyst (i) supplies the gaseous reactant to the surface reaction, (ii) enhances mass transfer, (iii) enhances liquid wetting of the catalyst surface, (iv) decreases the residence time in the bed by increasing the liquid velocity, and (v) by evaporating liquid phase. Both the positive and negative factors result in a conversion maximum, which appears in Fig. 4. In this case bed filled with fines is more sensitive to the gas flow rate due to a very low void fraction (0.1).

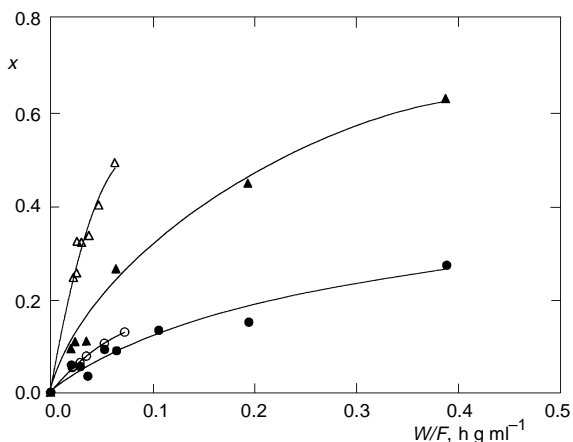


FIG. 3

Phenol conversion x versus kinetic coordinate W/F dependences at different temperatures using bed of pellets and the same amount of catalyst diluted with fines. Gas flow rate 38 l h^{-1} ; total pressure 5 MPa ; \circ $129 \text{ }^\circ\text{C}$, Δ $169 \text{ }^\circ\text{C}$ – random-packed bed; \bullet $129 \text{ }^\circ\text{C}$, \blacktriangle $167 \text{ }^\circ\text{C}$ – bed diluted with fines

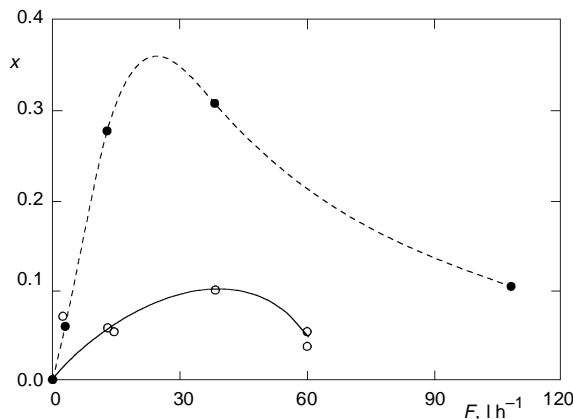


FIG. 4

Influence of oxygen flow on phenol conversion. Liquid feed F 400 ml h^{-1} ; mean temperature $140 \text{ }^\circ\text{C}$; total pressure 5 MPa ; \circ random-packed bed; \bullet bed diluted with fines

The course of conversion measured for the undiluted bed of extrudates exhibits a maximum on the dependence conversion *versus* gas flow rate. The decrease in phenol conversion for higher residence times of the reaction mixture in the catalyst bed is caused by a decrease in catalyst wetting owing to the formation of liquid rivulets and pockets inside the bed of catalyst fluctuating in time.

A longitudinal increase in temperature of the reaction mixture is presented in Fig. 5. A better utilization of the wetted catalyst at the beginning of the filled bed implies a higher temperature increase. Further courses for both catalyst beds resemble each other; the temperature decrease may be caused by different reaction steps occurring along the bed.

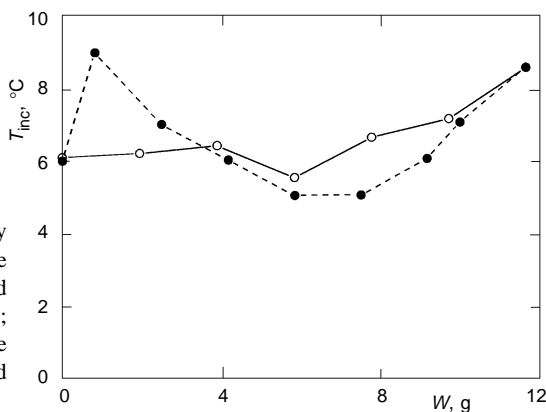


FIG. 5

Temperature increase (T_{inc}) caused by the reaction heat along (W , weight) the catalyst bed in beds with different void fraction. Liquid feed F 300 ml h⁻¹; mean temperature 140 °C; total pressure 5 MPa; ○ random-packed bed; ● bed diluted with fines

CONCLUSIONS

The results presented in this study document successful application of a supported copper catalyst in the trickle-bed reactor for transformation of concentrated aqueous phenol solution to biologically harmless carboxylic acids. The main problem of the use of trickle-beds reactors for this process is a low wetting efficiency of the catalyst bed and a low catalyst effectiveness factor. Dilution of the catalyst bed with fines causes a substantial decrease in the reaction rate in comparison with a standard random-packed catalyst. The reason is the high surface tension of aqueous phenol. The bed void fraction filled with liquid lenses offers only a small interfacial area for effective oxygen mass transfer. The intrinsic residence time in the bed and the wetted catalyst surface available for mass transfer are determined by the liquid and gas feed rates.

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