Mass-Transfer-Limited Wet Oxidation of Phenol

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The hydrodynamics and the mass-transfer impact of the three-phase trickle-bed reactor performance in an environmental application of phenol catalytic wet oxidation is described. The activities of both the CuO-supported catalyst and the extruded active carbon were compared. To avoid liquid maldistribution, also the bed of catalyst particles with void fraction diluted by fine glass spheres was used. Under the conditions of the gas component transfer limitation, a better wetting of the catalyst can lead to the worse reactor performance due to lower reaction rates.

Processes of wet oxidation of toxic contaminants or hardly biodegradable compounds play an alternative role in decontamination of some industrial wastewaters as well as wastewaters from pharmaceutical and food industries. The main advantage of catalytic oxidation consists in reduced process and investment costs due to milder process conditions [1, 2]. Therefore, the catalytic wet oxidation of bioresistant pollutants appears to be a promising pre-treatment process preceding the biological wastewater treatment. Copper oxide seems to be the best catalyst [3, 4] for wet oxidation of water pollutants in the slurry batch reactor. On the other hand, active carbon exhibits also catalytic activity in wet oxidation [5], in addition to the charcoal catalyst [6, 7] it gives the best results in three-phase fixed catalyst bed. Exploitation of active carbon-based catalysts has been yet very intensively studied [8, 9] due to catalyst cost and absence of negative environmental impacts. The extent of the continuous wet oxidation carried out in the trickle-bed reactor is not controlled [10, 11] only by reaction kinetics itself, but often is limited by both reactant's transport and effective catalyst external surface wetting. Mentioned phenomena, and also the mass transfer between all phases of the system and the catalyst bed wetting efficiency depend on fluid flow conditions, characterized mainly by liquid and gas flow-rate.

The problems arising in scaling-up experimental data from laboratory autoclave measurements to the trickle-bed operation, as mentioned by *Pintar et al.* [12], lead to the kinetic experiments using the trickle-bed reactor. In contrast to a usual slurry operation, the trickle-bed reactor has advantages, 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 thân the catalyst activity. On the other hand, hydrodynamic impact (wetting efficiency) having a controlling role at low liquid velocities typical of the wastewater treatment processes, on the three-phase trickle-bed reactor performance was confirmed by many authors (*e.g.* by *El-Hisnawi et al.* [13], *Tukač* and *Hanika* [14]). Based on reaction conditions used, namely temperature, the reaction between dissolved gaseous and liquid reactants can be limited by their mass transport. However, if the reaction is a gas-limited one, the gaseous reactant can easily access catalyst pores from the nonwetted dry areas in the bed and, consequently, a higher reaction rate is usually observed with a decreased external catalyst wetting [11]. The above analysis is based on an assumption that particles in trickle beds are always internally wetted. An alternative for scale-up studies is the use of trickle beds diluted with fines (inert particles, by an order of magnitude smaller than the catalyst pellets). The absence of liquid spreading due to the application 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 decoupage 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

Experiments were carried out in the laboratory

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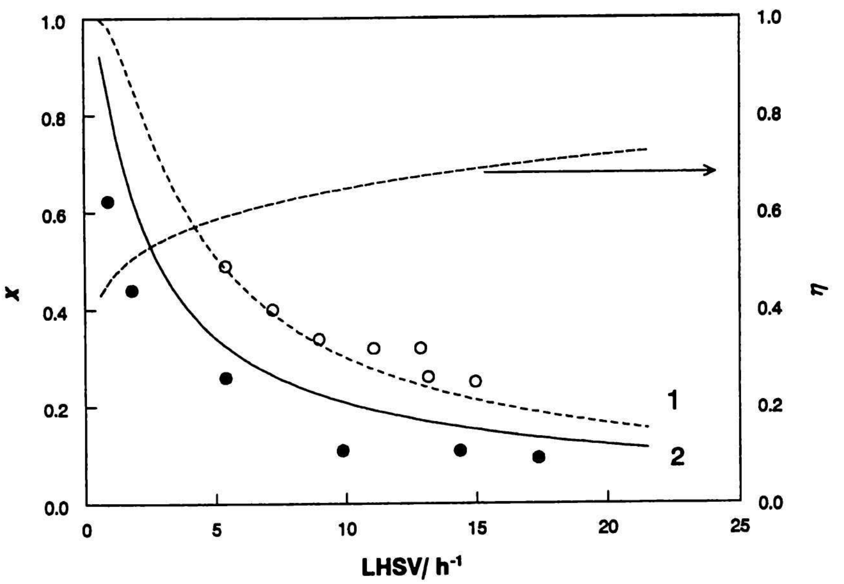

Fig. 2. Phenol conversion x and wetting efficiency (η) *vs.* liquid hourly space velocity (LHSV). Temperature 168 °C, gas flow-rate 38 dm^3 h^{-1}, and total pressure 5 MPa, ○ random-packed bed, ● bed diluted with fines of supported CuO. *1.* Completely wetted catalyst bed, *2.* η-dependent wetting.

uid hourly space velocity in Fig. 2. Though, both sets of experimental data qualitatively match the model quite well. This implies that the reaction conditions are under gas-limited circumstances and better wetting of catalyst bed gives worse reactor productivity.

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 are strongly influenced by the wetting efficiency, liquid maldistribution and/or temperature-dependent phase equilibrium, *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, and for two catalysts with different activity is presented in Fig. 3. The mean oxidation rate of less active copper catalyst in the bed filled with fines is independent of kinetic coordinate in a broad range of the liquid flow-rate. In contrast, in the random catalyst bed with a higher void fraction, the mean reaction rate is more strongly dependent on liquid hourly space velocity (LHSV) and thus on the liquid velocity. Surprisingly, the lower reaction rate was found in completely wetted bed of catalyst diluted with fines. 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 ($\varepsilon = 0.2$) 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 high value of phenol reaction rate on the mentioned dependence.

To distinguish between gas-limited and liquid-limited reaction conditions a comparison between the overall rate of oxidation and gas-liquid and liquid-solid mass transfer of oxygen has to be done.

To evaluate mass transfer coefficients under reaction conditions the frequently used correlations of *Goto* and *Smith* [16] were chosen.

Gas-liquid volumetric mass transfer coefficient was calculated with $\alpha_\mathrm{L} = 1.9\ \mathrm{cm}^{-1.59}$ by eqn (*2*)

$$\frac{k_\mathrm{L}a}{D} = \alpha_\mathrm{L}\left(\frac{G_\mathrm{L}}{\mu}\right)^{0.41}\left(\frac{\mu}{\rho D}\right)^{1/2} \tag{2}$$

Liquid-solid mass transfer coefficient was calculated with $\alpha_\mathrm{S} = 45\ \mathrm{cm}^{-1.44}$ by eqn (*3*)

$$\frac{k_\mathrm{S}a_\mathrm{S}}{D} = \alpha_\mathrm{S}\left(\frac{G_\mathrm{L}}{\mu}\right)^{0.56}\left(\frac{\mu}{\rho D}\right)^{1/3} \tag{3}$$

Comparison of experimental mean lumped reaction rates (r_o) reduced by equilibrium liquid oxygen concentration (c_o) with gas-liquid ($k_\mathrm{L}a$) and liquid-solid ($k_\mathrm{S}a_\mathrm{S}$) mass transfer coefficients is presented in Fig. 4. Mass transfer of oxygen from bulk liquid to active catalytic surface seems to be in an order magnitude higher than that through gas-liquid interphase. If the reduced reaction rate is lower than the gas-liquid mass transfer, the regime of oxidation is in kinetic region with respect to the external mass transfer. At higher temperature the reduced reaction rate is

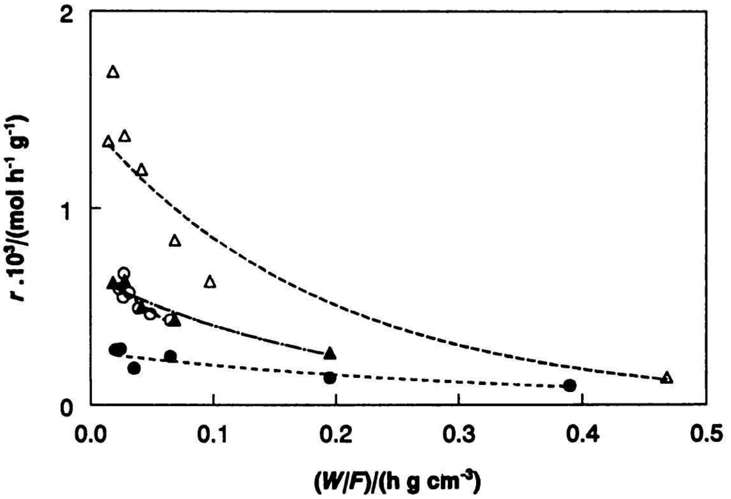

Fig. 3. Mean phenol oxidation rate *vs.* kinetic coordinate W/F. Temperature 168 °C, ○ random-packed bed, ● bed diluted with fines of supported CuO; △ random-packed bed, ▲ bed diluted with fines of active carbon catalyst, gas flow-rate 38 dm^3 h^{-1} and total pressure 5 MPa.

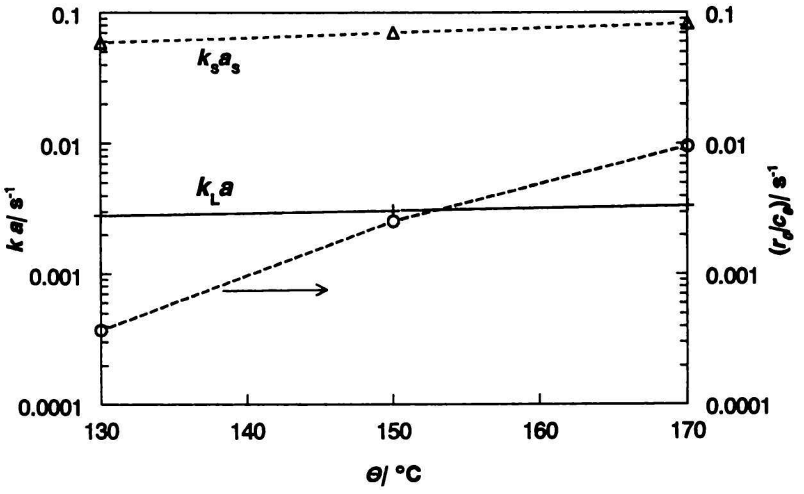

Fig. 4. Comparison of temperature dependences of oxygen mass transfer coefficients with reduced lumped oxidation rate. Liquid feed 200 cm^3 h^{-1}, random-filled CuO catalyst, + gas-liquid volumetric mass transfer coefficient, △ liquid-solid mass transfer coefficient, ○ reduced rate of oxidation.

higher than the gas-liquid mass transfer coefficient and thus the operation becomes to be gaseous reactant-limited. Apparent activation energy of the experimental lumped oxidation rate over the whole temperature range reaches 121 kJ mol^{-1}, *i.e.* mass transfer limitation does not prevail. On the other hand, uneven wetting of catalyst surface due to the liquid maldistribution can lead to the higher reaction rate owing to the direct oxygen mass transfer from the gas phase to the unwetted catalyst surface.

CONCLUSION

The main problem of successful application of trickle-bed reactor for catalytic wet oxidation process consists in interaction of effective wetting of the catalyst bed and mass transfer phenomena depending on both hydrodynamics and reaction conditions, *e.g.* temperature, pressure, catalyst activity, *etc.* Trickle-bed reactor can operate at liquid-phase-mass-transfer-limited conditions, when better wetting of catalyst bed improves reactor productivity. Another situation is characterized by the higher intrinsic reaction rate value (*i.e.* at higher temperature or using more active catalyst), when oxygen mass transfer from gas phase to catalyst surface limits the rate of oxidation and the complete wetted catalyst surface is undesirable. In such case dilution of the catalyst bed with fines causes a substantial decrease in the reaction rate in comparison with a standard random-packed catalyst. The bed void fraction filled with liquid lenses offers only a small interfacial area for effective oxygen mass transfer. The intrinsic residence time of the reaction mixture 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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SYMBOLS

a	effective interfacial area	m^{-1}
C_{Ph}	phenol concentration	$\mathrm{mol\ dm}^{-3}$
d	particle diameter	mm
D	oxygen diffusivity in water	$\mathrm{m}^2\ \mathrm{s}^{-1}$
F	liquid feed	$\mathrm{cm}^3\ \mathrm{h}^{-1}$
G_{L}	liquid superficial velocity	$\mathrm{kg\ m}^{-2}\ \mathrm{s}^{-1}$
k	reaction rate constant	$\mathrm{g}^{-1}\ \mathrm{h}^{-1}\ \mathrm{MPa}^{-n}$
k_{L}	gas-liquid mass transfer coefficients	$\mathrm{m\ s}^{-1}$
k_{S}	liquid-solid mass transfer coefficients	$\mathrm{m\ s}^{-1}$
l	length	mm
n	reaction order with respect to oxygen	
P_{O_2}	oxygen partial pressure	MPa
r	reaction rate	$\mathrm{mol\ g}^{-1}\ \mathrm{h}^{-1}$
W	mass of catalyst	g
x	reactant conversion	

Greek Letters

α	parameter of Goto and Smith correlations	$\mathrm{cm}^{\mathrm{power}-2}$
ε	bed void fraction	
ϕ	tube diameter	mm
η_{c}	wetting efficiency	
μ	liquid viscosity	Pa s
θ	temperature	°C
ρ	density of liquid	$\mathrm{kg\ m}^{-3}$

Subscripts

L	liquid
S	solid
G	gas
Ph	phenol

REFERENCES

1. Mishra, V. S., Mahajani, V. V., and Joshi, J. B., *Ind. Eng. Chem. Res. 34*, 2 (1995).
2. Levec, J., *Chem. Biochem. Eng. Quarterly 11*, 47 (1997).
3. Tukač, V. and Hanika, J., *Collect. Czech. Chem. Commun. 60*, 482 (1995).
4. Pintar, A. and Levec, J., *Ind. Eng. Chem. Res. 33*, 3070 (1994).
5. Tukač, V. and Hanika, J., *Collect. Czech. Chem. Commun. 61*, 1010 (1996).
6. Tukač, V. and Hanika, J., *Chem. Biochem. Eng. Quarterly 11*, 187 (1997).
7. Tukač, V. and Hanika, J., *Collect. Czech. Chem. Commun. 62*, 866 (1997).
8. Tukač, V. and Hanika, J., *J. Chem. Technol. Biotechnol. 71*, 262 (1998).
9. Fortuny, A., Font, J., and Fabregat, A., *Appl. Catal., B: Environ. 19*, 165 (1998).
10. Tukač, V., Vokál, J., and Hanika, J., *Collect. Czech. Chem. Commun. 63*, 1938 (1998).
11. Wu, Y. Khadilkar, M. R., Al-Dahhan, M. H., and Dudukovic, M. P., *Ind. Eng. Chem. Res. 35*, 397 (1996).
12. Pintar, A., Berčič, G., and Levec, J., *Chem. Eng. Sci. 52*, 4143 (1997).
13. El-Hisnawi, A. A., Dudukovic, M. P., and Mills, P. L., *ACS Symp. Ser. 196*, 431 (1982).
14. Tukač, V. and Hanika, J., *Int. Chem. Eng. 29*, 177 (1989).
15. Al-Dahhan, M. H. and Dudukovic, M. P., *AIChE J. 42*, 2594 (1996).
16. Goto, S. and Smith, J. M., *AIChE J. 21*, 706 (1975).