CATALYTIC OXIDATION OF SUBSTITUTED PHENOLS IN A TRICKLE BED REACTOR

Vratislav TUKAC[1] and Jiri HANIKA[2]

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

Received January 24, 1997
Accepted February 26, 1997

The catalytic wet oxidation was studied of phenol, 2-aminophenol, salicylic acid and 5-sulfosalicylic acid performed in a laboratory trickle bed reactor. A three-phase high-pressure catalytic reactor with an inside diameter of 18 mm and length of catalytic bed of 200 mm was operated at temperatures 90–180 °C, pressures 2–7 MPa and liquid space velocity 1–10 h^{-1}. Simultaneously, the catalytic activity and the stability of extruded active carbon black Chezacarb® and active carbon Chemviron® were tested. At a comparable activity, the active carbon Chemviron® exhibited a greater mechanical strength and stability. The influence of phenol substituents on the oxidation conversion corresponded to their inductive effect: The electropositive amino group supported the oxidation, on the contrary, the presence of carboxy and sulfo groups on aromatic ring led to only low conversion. The complications on evaluating the experimental data are caused by the non-isothermal temperature profile along the catalyst bed, the non-ideal oxygen dissolution in aqueous solutions and especially the hydrodynamic effect of flow rate on the degree of catalyst wetting and thus on the entire effectiveness of the oxidation process.

Key words: Catalytic wet oxidation; Substituted phenols; Trickle bed reactor.

The disposal of toxic or bactericidal organic impurities in diluted aqueous solutions can be carried out to advantage by a so-called wet oxidation. This oxidation with air or oxygen is applied especially with waste waters from pharmaceutical and dye plants[1]. The products of this process at temperatures 125–320 °C and pressures 0.5–20 MPa are biologically degradable substances, mostly lower organic acids or even CO_2 and H_2O. The advantage of the process consists in the fact that dioxins are not formed from the phenolic substances as in incineration or a so-called supercritical oxidation[2], its disadvantages are, however, the energy demands and corrosive medium.

By modifying the procedure on using the homogeneous or heterogeneous catalysis[3,4] and the combination of oxygen and chemical oxidizing agents, *e.g.*, the Fenton agent[5] (H_2O_2/Fe), it is possible to reach a moderation of reaction conditions; further requirement of increasing the process capacity can be met by applying a continuous reactor. For the oxidation of polutant solutions whose rate is often limited by the oxygen dissolution and its transport to the catalyst surface, a trickle bed reactor[3] is suitable with regard to the large interfacial surface of catalyst bed.

To determine the overall efficiency and selectivity of the process of wet oxidation in a trickle bed reactor, it is necessary to study the mutual interactions between the catalytic effect on the mechanism and the rate of oxidation, mass and heat transfer and hydrodynamics in the three-phase reaction system.

The most active catalysts of wet oxidation contain copper[4] as the active component, however, they are not stable enough owing to its dissolution in the corrosive reaction mixture. An alternative is the use of different types of active carbons[6] which have weaker catalytic effects but have not disadvantages of metallic catalysts. A significant factor for the operation of trickle bed reactor is besides the stability of catalytic activity also the catalyst mechanical stability. The disintegration of particles of the reactor bed leads to the loss of catalyst amount and a hazard of the growth of its hydrodynamic resistance up to the limit of impenetrability.

Oxygen unlike other gases exhibits an anomaly of dissolution on temperature – a minimum in the vicinity of normal boiling point of water[7]. Thereof follows even different extent of the dependence of reaction rate on the oxygen partial pressure according to the level of total pressure in the reactor. Further significant factor is the dependence of heat transfer on the flow rate of the gas and especially liquid phase. Higher flow rate improves the heat transfer from the reactor wall and its conduction in the catalytic bed. The oxidation reactions themselves are exothermic[4], and the reaction mixture is heated spontaneously with the reaction heat liberated.

With regard to the liquid feed in the bed axis, small height of catalyst bed and low value of volumetric feed rate, it is possible to assume that in this case, the effect of the wall flow of liquid on the process does not apply. However, the velocity of the liquid phase flow determines also the efficiency of wetting[8] of the surface of catalytic bed, and its low value for small volumetric flow rates can fully compensate the corresponding long residence time of reaction mixture in the bed. The liquid flow rate may be, moreover, considerably decreased by evaporating the liquid phase into the gas stream.

The aim of this work has been to determine the effect of amino, sulfo, and carboxy groups on the wet oxidation of substituted phenols. Further, the possibility was tested of employing the extrudates of active carbon black and active carbon as a catalytic bed of trickle reactor for which the dissolution of active components, mostly heavy metals, does not take place in the reaction mixture. Simultaneously, the interaction was observed between the kinetics of oxidation and the hydrodynamically dependent wetting efficiency in the catalyst bed of continuous trickle bed reactor.

EXPERIMENTAL

All the chemicals were of a.r. grade purity: Phenol (Reactivul, Bucharest), 2-aminophenol (Merck, AG.), salicylic acid and 5-sulfosalicylic acid (Lachema, Brno), methanol (Penta, Prague), distilled water (Prague Institute of Chemical Technology), oxygen (Linde–Technoplyn, Prague). As catalysts, active carbon black[9] Chezacarb FD (Chemopetrol Group, Litvinov), extrudates 3 × 6 mm, of surface area 700 m^2/g and active carbon Chemviron Carbon WS4 AWD (Germany), extrudates 3.6 × 7.6 mm, of surface area 1 049 m^2/g were used.

The process was investigated in a laboratory trickle bed reactor which was formed by a stainless steel tube of inside diameter of 18 mm and length of 540 mm equipped with an axially located thermocouple well and heated with an electrical furnace. The height of catalyst bed amounted to 200 mm, above and below the bed, a layer of glass beads of diameter of 3 mm was filled. Oxygen was mixed with the fed liquid at the preheater inlet and behind the reactor, was separated in a pressure phase separator, and the liquid was released periodically. The experimental conditions were within the range of temperatures 90–180 °C, liquid feed 25–400 ml/h, at total pressures 2–7 MPa and constant exit gas 400 ml/min. The concentration of substrates used in the aqueous feed amounted to 0.1–0.5%.

The reaction mixture was analyzed by the HPLC chromatography with the UV detector at 254 nm, with the flow rate of 0.6 ml/min of the methanol–water mobile phase (2 : 3) and the Tessek (150 + 30) × 3 mm, Separon SGX C 18 of graning 7 μm stationary phase. An example of the reaction mixture chromatogram on the phenol oxidation, given in Fig. 1, illustrates the taking place consecutive oxidation reactions by showing the presence of the oxidation intermediates: hydroquinone, benzoquinone, and maleic and oxalic acids.

RESULTS AND DISCUSSION

The monitored key factors significant for evaluating the experimental data of the trickle bed reactor and their generalization are as follows: stability of activity and mechanical strength of the catalyst, quantification of the effect of mass and heat transfer on the overall reaction rate, and determination of the catalyst wetting efficiency. The existing non-isothermal character of temperature profile in bed, non-ideality of phase equilibria on dissolving oxygen and evaporation of a portion of reaction mixture into the gas stream are further factors which should be taken into account.

Two extruded catalysts of similar dimensions, *viz.* the active carbon black Chezacarb FD and the classical active carbon Chemviron were tested. Although the catalytic activity

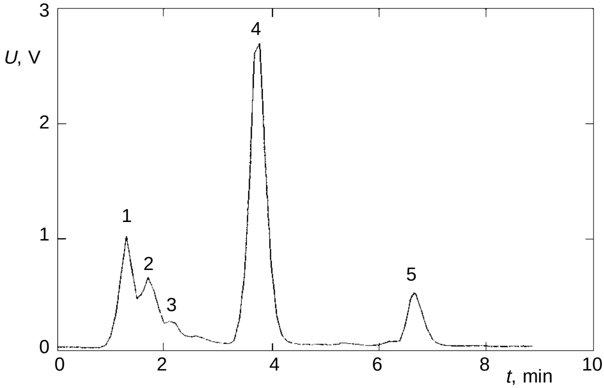

FIG. 1
HPLC chromatogram of reaction mixture of phenol oxidation, Chemviron catalyst; 140 °C, 5 MPa, volumetric feed rate 180 ml/h. 1 Maleic acid, 2 oxalic acid, 3 hydroquinone, 4 benzoquinone, 5 phenol

of both the sorbents was comparable, after about 50 h of operation, the crumbling of extrudates of Chezacarb (see Fig. 2) took place, and the bed volume was contracted by 16%. Under the same reaction conditions, the Chemviron extrudates kept compact, and therefore further experiments were carried out only with this active carbon. Advantages of the active carbon extrudates as the catalyst bed filling of the oxidation trickle bed reactor consist in a sufficient geometrical hydrophilic surface for interfacial mass transfer, large internal active surface and sorption capacity, and elimination of problems of activity and dissolution of the catalytically active components of classical supported catalysts.

The wet oxidation of an aqueous solution of organic polutant comprises two consecutive steps, *viz.* the oxygen transfer from the gas to the liquid phase, its dissolution and

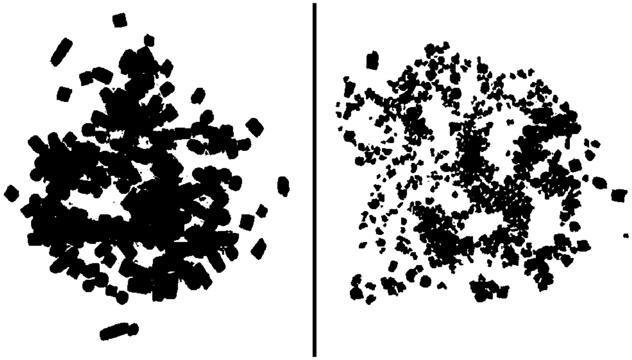

FIG. 2
Comparison of original (left side) and crumbled catalyst Chezacarb FD (right side) after 50 h operation time; bed contraction 16%

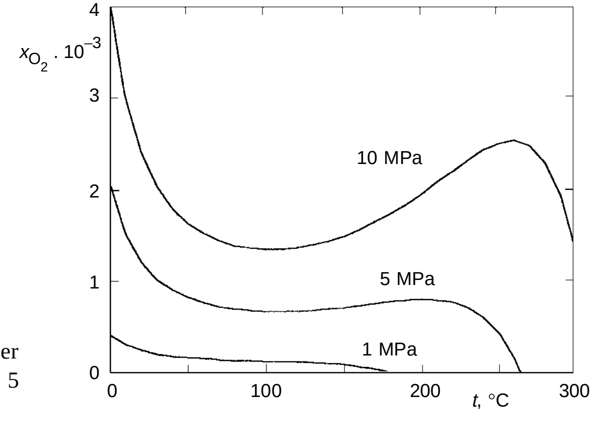

FIG. 3
Concentration of oxygen in water (x_{O_2}) at different total pressures (1, 5 and 10 MPa)

transfer to the catalyst surface and subsequently the chemical reaction between the dissolved oxygen and the organic substance. The oxygen concentration in the liquid is given by transport phenomena across the phase boundary influenced by the wetting efficiency of the bed and simultaneously by the temperature dependent gas solubility in water. In Fig. 3 plotted on the basis of published data[7], the strongly non-linear temperature dependences are evident of the oxygen mole fraction in water for the total pressure of 1, 5 and 10 MPa, which water saturated vapour pressure takes part in, too. At the total pressure about 5 MPa, the oxygen concentration is nearly constant within the range of temperatures of 100–200 °C so that the effect of temperature changes on the concentration of dissolved oxygen may be neglected in this range. This conclusion makes it possible to neglect the effect of temperature profile in the bed of trickle reactor on the oxygen concentration in the reaction mixture and considerably simplifies the data evaluation. The concentration of dissolved oxygen is, however, strongly dependent on its partial pressure, and the above-mentioned conclusion holds only for an isobaric reactor and a total pressure range of 4–5 MPa over considerably diluted aqueous solutions.

The dependence of the mean reaction rate of the phenol oxidation on the oxygen partial pressure is not too pronounced as it can be seen in logarithmic coordinates of Fig. 4. The very low reaction order of oxidation related to the oxygen partial pressure, equal to 0.06 as determined for volumetric feed rate of 70 ml/h, may be caused by a great sorption capacity of the active carbon bed with a slight oxygen consumption in

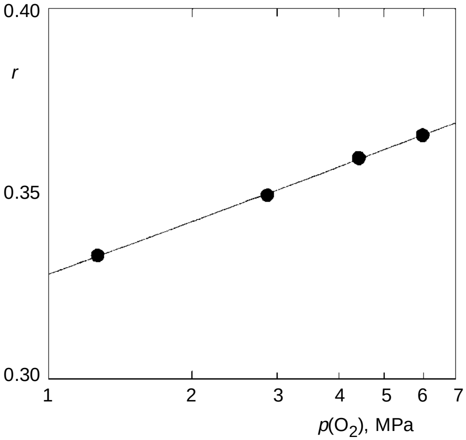

FIG. 4
Dependence of reaction rate of phenol oxidation r (mol/min g_{cat}) on oxygen partial pressure $p(O_2)$ (logarithmic scale); Chezacarb FD, 145 °C, volumetric feed rate 70 ml/h

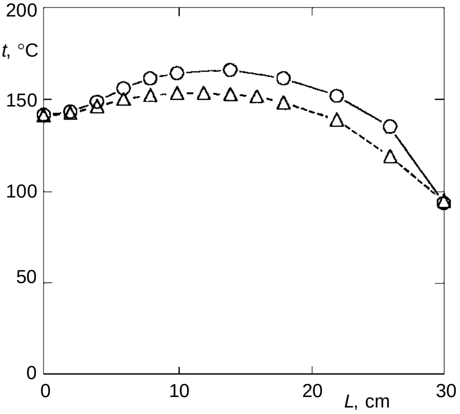

FIG. 5
Axial temperature profile (t, °C) along catalytic bed (bed depth L in cm) with and without reaction. ○ 0.5% phenol solution, Δ distilled water; Chemviron catalyst, volumetric feed rate 230 ml/h

the reaction. This "buffering" effect is given by a large value of the ratio of catalyst amount to a small value of the liquid feed of low concentration of substrate into the trickle bed reactor.

The comparison of longitudinal temperature profiles in the bed of trickle reactor for distilled water alone and the phenol solution under the same flow rates of phases and input power of heatings is depicted in Fig. 5. The curvature of both the temperature profiles is caused by the non-uniform reactor heating, moreover, the heat transfer from the reactor wall to the bed depends on the flow velocity. The catalytic layer begins 20 mm from the bed beginning. The overrun of temperature profile by about 10 °C with the phenol solution is caused by the reaction heat released. The wet oxidation is an exothermic reaction and the temperature adiabatic growth for the used phenol solution of concentration 0.054 mol/l on its full oxidation to water and carbon dioxide represents about 40 °C. In case that the overall conversion reaches about 25%, the adiabatic heating represents about 10 °C, which is in good agreement with the differences in the longitudinal temperature profiles depicted in Fig. 5.

The comparison of dependences of the oxidation conversions of single substituted phenols on the residence time modified by the catalyst amount in the reactor is shown in Fig. 6. The process conditions were suitable for a high conversion of phenol and aminophenol, on the contrary, with the salicylic and sulfosalicylic acids, the conversions reached only about 40%. For all four substances, however, the same main oxidation intermediates were identified, which indicates analogous mechanism of oxidation. The phenol substituents influence the oxidation according to their inductive effect, *i.e.*, the amino group with positive effect promotes oxidation, on the contrary, the electronegative carboxylic group decreases the oxidation rate. The additional negative effect of sulfo group on oxidation was not found but the sulfuric acid originating from the oxidation considerably decreased pH of the reaction mixture down to the value of 2.5. The

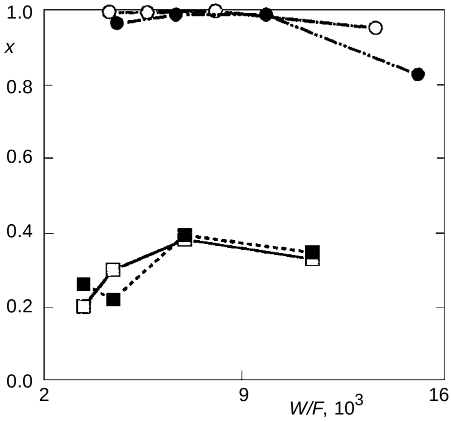

FIG. 6

Dependence of substrate conversion x on modified residence time W/F (min g_{cat}/l) in reactor; 140 °C, 5 MPa, Chemviron catalyst; ● phenol, ❍ 2-aminophenol, ■ salicylic acid, ❐ 5-sulfosalicylic acid high values of the parameter representing the kinetic coordinate – the residence time modified by the catalyst amount, are given by higher order of magnitude of catalyst amount compared to usually used in batch reactors.

The maximum of conversion reproduced for two different initial phenol concentrations is emphasized in Fig. 7 in the dependence of conversion on the flow rate, which is inversely proportional to the residence time, of liquid reaction mixture in the trickle bed reactor. A poor surface coverage of catalytic bed with liquid is responsible for this local maximum the former being defined by a so-called bed wetting efficiency which is significantly manifests itself at low bed load of trickle reactor when liquid passes through the bed in the form of fluctuating rivulets, the state designated also as channeling.

A simplified qualitative explanation of the origin of local extremes on the conversion dependence is to be formulated as follows: The phenol conversion x depends on the catalyst wetting efficiency η_c, the temperature dependent rate constant k and the ratio of catalyst mass W to volumetric feed F according to Eq. (*1*):

$$x = 1 - \exp\left(-\eta_c kW/F\right) . \qquad (1)$$

The solution is presented for illustration in Fig. 8 of the simple first-order kinetic equation towards substrate (Eq. (*1*)) for the ideal plug flow and for the case influenced by the wetting efficiency of bed. Simultaneously, the dependence of wetting efficiency on the flow rate[8] is plotted here, too. The convex beginning of the dependence corresponds to the transfer from isolated drop flow and semistagnant liquid hold-ups to the continuous flow of rivulets. The middle part corresponds to a gradual propagation of rivulets in the catalytic bed up to the concave curvature representing the consecutive

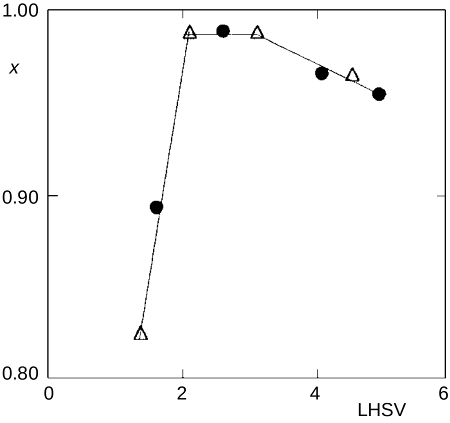

FIG. 7
Dependence of phenol conversion x influenced by catalyst wetting on liquid hourly space velocity parameter; feed concentration of phenol: Δ 2.5 g/l, ● 5 g/l

homogeneous surface coverage of catalytic bed with liquid. On the realistic conversion profile, it is possible to distinguish two local extremes, the local minimum where the imperfect wetting of catalyst compensates the long residence time of liquid in bed and subsequent local maximum corresponding to the dependences in Fig. 7, where the degree of wetting reaches a sufficient level, and the effect of shortening the residence time begins to prevail. The presented illustration represents only qualitative interpretation of the shape of the dependences. A precise quantitative description requires the experimental determination of hydrodynamic dependence of wetting efficiency and the detailed knowledge of kinetics in the test reactor.

CONCLUSION

The functional groups of substituted phenols manifest themselves in wet oxidation according to their induction effects, *i.e.*, the groups with positive induction effect (amino and hydroxy) influence the oxidation positively, the negative effect of (sulfo and carboxy) groups has a dominant effect on the slowing down the oxidation. On using the extruded active carbon as a filling of trickle bed reactor, it is possible to reach a high conversion of phenol oxidation, however, the Chezacarb FD extrudates have not a sufficient mechanical strength. The concentration of dissolved oxygen is nearly constant in the tested temperature range at the total pressure of 5 MPa, which makes it possible to neglect the effect of non-isothermal temperature profile in the bed on the oxygen concentration. The very low reaction order of oxidation towards oxygen can be caused by a great sorption capacity of the active carbon bed at a slight oxygen consumption in the reaction.

The hydrodynamically dependent degree of catalyst wetting may compensate the positive effect of residence time on the conversion of reaction. For a better exploitation of the catalyst filling and attaining the maximum conversions, it is suitable to perform

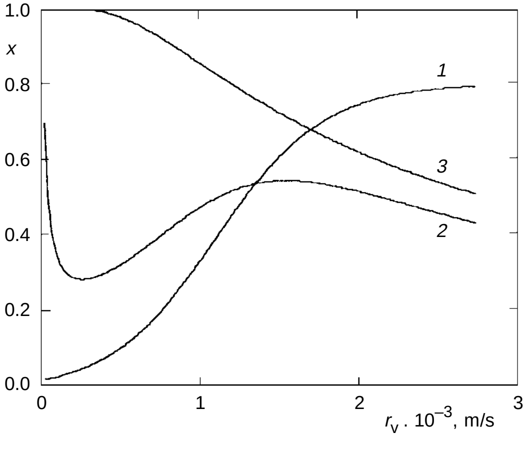

FIG. 8
Influence of wetting efficiency (superficial liquid velocity r_v (m/s)) on phenol conversion x in trickle bed reactor. *1* Wetting efficiency, *2* real conversion profile influenced by wetting efficiency, *3* ideal conversion profile without influence of poor catalyst wetting

the oxidation in a trickle bed reactor with feeds representing at least triple volume of catalytic bed per hour.

SYMBOLS

F	volumetric feed rate of liquid, ml/h
k	rate constant, mol/g s
LHSV	liquid hourly space velocity, h^{-1}
$p(O_2)$	oxygen partial pressure, MPa
r_v	superficial liquid velocity, m/s
W	catalyst mass, g
x	conversion, mole fraction
x_{O_2}	oxygen mole fraction
η_c	wetting efficiency

The authors thank the Grant Agency of the Czech Republic for the support in the frame of grant No. 104/96/0456.

REFERENCES

1. Mishra V. S., Mahajani V. V., Joshi J. B.: Ind. Eng. Chem. Res. *34*, 2 (1995).
2. Krajnc M., Levec J.: AIChE J. *42*, 1977 (1996).
3. Pintar A., Levec J.: Ind. Eng. Chem. Res. *33*, 3070 (1994).
4. Tukac V., Hanika J.: Collect. Czech. Chem. Commun. *60*, 482 (1995).
5. Debellefontaine H.: Environ. Pollution *92*, 155 (1996).
6. Tukac V., Hanika J.: Collect. Czech. Chem. Commun. *61*, 1010 (1996).
7. Cramer S. D.: Ind. Eng. Chem., Process Des. Dev. *19*, 300 (1980).
8. Tukac V., Hanika J.: Int. Chem. Eng. *29*, 177 (1989).
9. Lederer J., Necesany F., Lamac M.: *Proc. Aprochem '95, Kouty nad Desnou, Czech Republic, September 20–22, 1995*, p. 225. CSCHI, Prague 1995.