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Catalysis Today 79–80 (2003) 427–431

CATALYSIS TODAY

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Periodic state of wet oxidation in trickle-bed reactor

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Abstract

Catalytic wet oxidation of different organic pollutant in an industrial process water treatment increases its importance with respect to sustainable chemical technologies R&D. Trickle-bed reactor can enable capacity demands, high pressure and temperature operation conditions using sufficiently active catalyst with a long term stability. The paper deals with phenol removal by wet oxidation on an active carbon extruded catalyst using high-pressure laboratory trickle-bed reactor. To suppress external mass transfer resistance both a diluted catalytic bed by inert fines and liquid feed rate modulation were applied. The forced pulsing flow regime was created by ON–OFF liquid feed flow modulation. Feed period length and split can influence both reactor throughput and its hydrodynamics, e.g., liquid holdup, wetting efficiency and pressure drop. If the period length was comparable with an effective liquid residence time, mean dynamic liquid holdup at periodic operation mode was found to be lower than the steady state one and thus phenol conversion was found to be 10% higher than that measured at steady state conditions.

Keywords: Trickle-bed reactor; Wet oxidation; Active carbon catalyst; Periodic operation

1. Introduction

Phenolic compounds are bactericides and represent undesirable pollutants in many industrial wastewaters. Their decomposition by a high capacity continuous three-phase process carried out in the trickle-bed reactor [1] seems to be promising solution of the environmental problems. The objective of this work was to investigate the impact of dynamically changing extent of wetted catalyst external surface and intensify mass transfer of gaseous oxygen on catalytic wet oxidation rate of aqueous phenol under periodic modulated liquid feed.

Catalytic wet oxidation of phenolic compounds in trickle-bed reactor was carried out both in laboratory scale [2–4] and industry application [1]. Full-scale trickle-bed reactors for wastewater treatment usually operate in natural pulsing hydrodynamic regime, to minimise mass transfer resistance of reactants [1]. To achieve natural pulsing flow regime a high-defined gas–liquid feed rates are necessary [1], which result in relatively low value of residence time for slow wet oxidation reaction. An alternative is represented by periodical liquid feed modulation. Periodically renewal of the catalyst external surface due to implicit and/or forced pulsing liquid flow allows both direct oxygen mass transfer through unwetted catalyst surface and also the re-supply of the other reactant dissolved in the liquid phase. Depending on the conditions, either gas or liquid components could be the limiting reactant [5–7] controlling the overall rate of substrate oxidation. Liquid feed cycle period length and its split into liquid rich and dry parts determine overall reactor throughput under periodic operation of trickle-bed reactor [10,11].

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0920-5861/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0920-5861(03)00052-X

To avoid liquid maldistribution and reach complete catalyst wetting, diluted catalyst bed [8] with inert fine glass spheres was used as an alternative to pulsing flow. Continuous wet oxidation carried out in a trickle bed is rarely controlled only by reaction kinetics; usually the process is limited by transfer of both reactants and effective wetting of the catalyst external surface [6,7].

In comparison with other GLS processes, e.g., atmospheric pressure hydrogenation [9–11], only few papers deal with periodic operation of high-pressure trickle-bed reactor, e.g., hydrogenation of aqueous crotonaldehyde [12].

2. Experimental

Experiments were carried out in laboratory trickle-bed reactor consisting of a high-pressure stainless steel tube (length = 500 mm, ID = 18 mm), equipped with an axial 3.2 mm OD thermowell to allow measurement of the temperature profile. The reactor was filled with 11.7 g of catalyst (Chemviron Carbon^{TM} WS 4A), an active carbon extrudate (ID = 4 mm and mean length 5.3 mm) surface area 1300 $m^2\,g^{-1}$ and porosity of 0.55. To distinguish between wetting and mass transfer resistance, two different catalyst beds were used: (i) randomly packed bed of catalyst; (ii) catalyst bed with void fraction filled with fine [7,8] glass spheres (ID = 1 mm) to enhance the wetted surface and prevent liquid maldistribution with resulting wall flow. The latter arrangement provides more efficient catalyst wetting. The oxidation of 0.5% phenol aqueous solution by pure oxygen was investigated in the temperature range of 125–170 °C and at the total pressure of 1–7 MPa. Volumetric liquid hour space velocity ranged from 1 to 20 h^{-1}. Liquid and gas flow rates, temperature and pressure drop fluctuations in the experimental trickle-bed reactor were monitored and controlled by Bronkhorst Hi-Tech mass flow and back-pressure metres connected via an Advantech Adam 4000 RS 485 remote system with a PC data logger. The implicit pulsing flow appears at high liquid and gas flow rates and induced pulses were created by a periodically stopping of the liquid and/or gas flow.

HPLC analysis of the reaction mixture was carried out using a 3 mm × 300 mm column filled with Tessek 7 μm Separon SGX C18, an UV detector operated at 254 nm and the eluent flow rate (40% aqueous methanol) was 0.3 $cm^3\,min^{-1}$.

3. Results and discussion

To distinguish between oxygen and phenol considered to be a reaction limiting reactant a comparison of the reactor behaviour for the randomly catalyst packed bed (11.7 g) and the identical bed with the same amount of the catalyst diluted by fine glass spheres (4.5 g, diameter = 1 mm) was made. Above all, the effect of the two phase flow and the bed dilution on reactor behaviour is discussed from the point of view of pulsing flow regime in the catalyst bed. Intrinsic residence time of the liquid reaction mixture in the catalytic bed, the wetting efficiency of the catalyst surface, and the effectiveness of oxygen mass transfer were investigated in this paper.

In the steady state operation mode of trickle beds uneven wetting of catalyst and liquid maldistribution, existence of wall flow usually decrease reactor throughput. To avoid these phenomena the filling of bed void fraction by tiny inert particles was employed. An interesting comparison of phenol conversion vs. modified liquid residence time at steady state condition is shown in Fig. 1. There is possible to recognise apparent difference between conventional and diluted

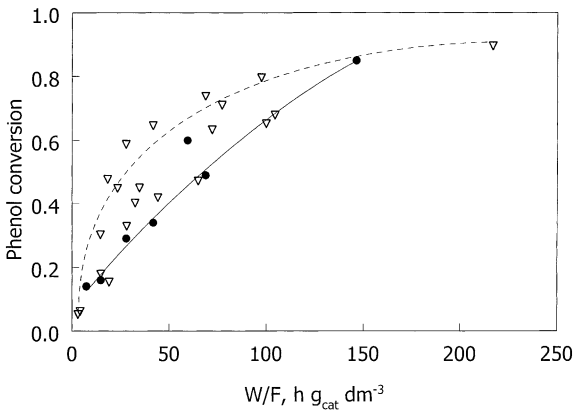

Fig. 1. Effect of catalyst bed dilution by inert fines on phenol conversion. Modified residence time (W/F) is weight of catalyst (W) divided by volumetric liquid feed (F). Steady state regime: oxygen feed rate Q_G 20 N $dm^3\,h^{-1}$, 165 °C and 5 MPa. (∇) Conventional packed bed; (●) diluted bed.

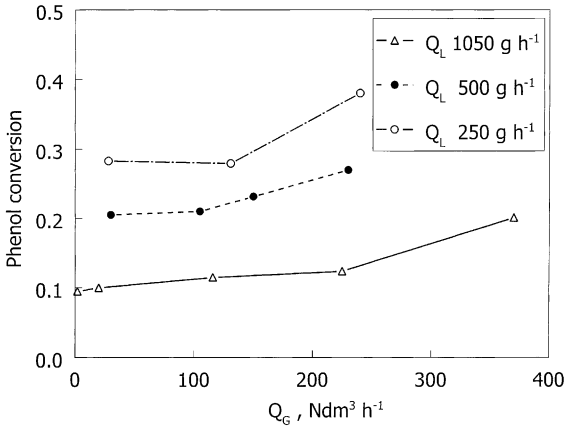

Fig. 2. Effect of gas flow rate (Q_G) on phenol conversion at different liquid feed rates (Q_L). Steady state conditions: conventional bed, 150 °C and 5 MPa.

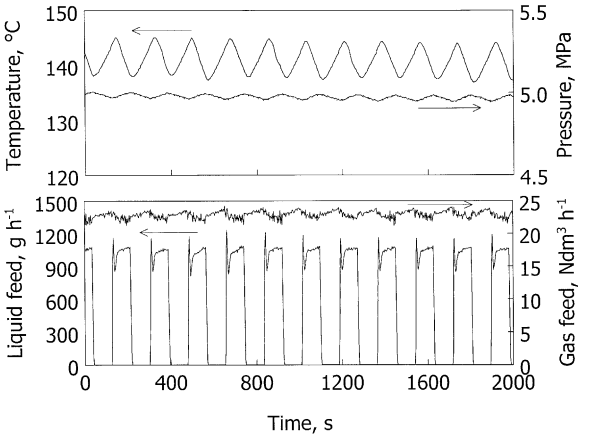

Fig. 3. Dynamics of a high-pressure trickle bed with forced periodic liquid pulses, mean liquid feed $Q_L = 500\,g\,h^{-1}$ and oxygen feed rate $Q_G = 23\,N\,dm^3\,h^{-1}$, period length 180 s, split 0.5.

catalyst bed in the range of low residence time values. The reason of the higher reactor throughput in case of undiluted catalyst bed follows from direct oxygen mass transfer from gas phase to catalyst surface on dry unwetted zones. It means that gaseous oxygen represents the rate limiting reactant. Furthermore, presumption of oxygen limited reaction is also supported by a positive effect of gas velocity on overall phenol conversion as can be seen in Fig. 2. It implies that mass transfer of oxygen from the gas phase limits rate of phenol oxidation. Improved wetting efficiency of catalyst and liquid distribution result in oxygen transfer through flowing film of liquid and thus can lead to worse reactor behaviour. The higher liquid holdup and thus lower gas–liquid mass transfer interfacial area suppress the direct oxygen transport from gas phase to catalyst surface. Main conclusions from the steady state measurements with and without dilution of catalyst bed are as follows: to increase reactor throughput when gas component is considered to be a rate limiting reactant, direct oxygen transfer across gas–solid interface area and supply of catalyst surface by liquid reactant have to be available.

Periodic liquid flow ON–OFF modulation meets both demands due to periodic renewal of liquid on catalyst surface and negligible liquid film resistance in "dry" part of liquid feed period.

An example of dynamic reactor behaviour is shown in Fig. 3. In the lower part of this figure instantaneous gas and liquid flow rates during periodic interruption of the liquid feed are shown. Transient waves of pressure and gas flow rate are shifted in time, due to equipment configuration with constant vent flow of the gas. The mean value of pressure fluctuation lies below 2% of pressure at continuous conditions, and it is possible to neglect it. The magnitude of a measured pressure drop was comparable with a noise of pressure transducers and therefore have to be neglected. Very interesting is also periodic change of temperature measured in axial position in the centre of catalyst bed. Temperature response to liquid pulses suggests intensive cooling of the bed by flowing liquid, but a velocity of a liquid slugs movement is probably responsible for a quarter period phase shift. Fast temperature increase, in the second part of period follows after the interruption of liquid feed. This fact can be explained by a sudden decrease of mass transfer resistance and possible direct gaseous oxygen supply to catalyst surface where it reacts with adsorbed phenol. Due to reaction heat and sorption capacity of the bed, temperature increase is observed, even if cool liquid feed is again pumped to the reactor.

Liquid feed cycle period has strong effect on hydrodynamics of the system. Effect of feed cycle period on dynamic liquid holdup is presented in Fig. 4, both for continuous and periodic regime measured as an amount of liquid drained from the catalyst bed after feed stop. The same mean value of feed rate

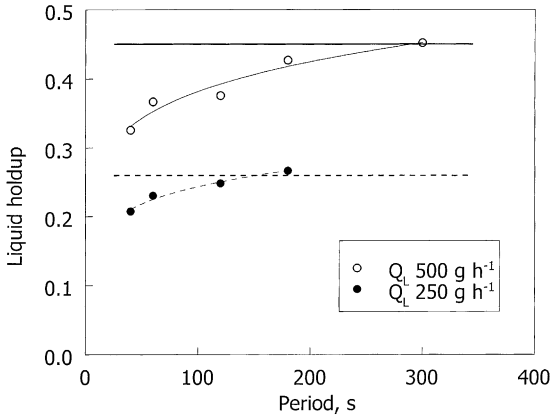

Fig. 4. Dynamic liquid holdup vs. liquid feed period. Gas continuous Q_G 20 N dm^3 h^{-1}, pressure 5 MPa, split of period 0.5.

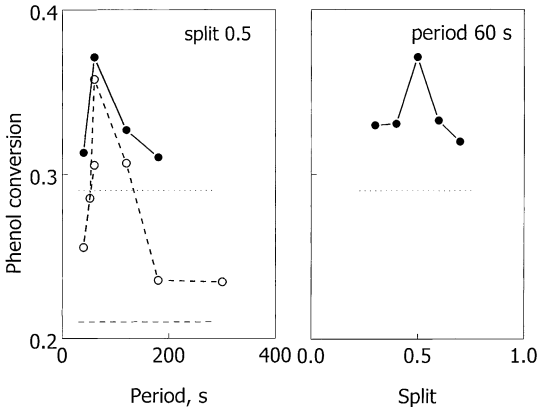

Fig. 5. Effect of liquid feed period and split on phenol conversion. Horizontal lines represent steady state conversion (---, ···) and dynamic points for Q_L 500 (○) and 250 g h^{-1} (●), respectively, Q_G 23 N dm^3 h^{-1}.

was used in experiment. For shorter time of period mean value of dynamic holdup in periodic operation is lower than that measured in the steady state operation with constant liquid feed rate. If the period length increases the liquid holdup rises and reaches holdup values for steady state conditions measured at constant feed of liquid. The higher is the mean liquid flow rate the higher difference between periodic and steady state holdups at the shortest tested period time was observed.

The main task of a forced liquid pulses investigation is to find an optimal feed cycle period length and its split value. The influence of liquid pulses period length with cycle split of 0.5 on phenol conversion was investigated. The results are shown in Fig. 5. A period of 60 s seems to be the optimal one for mean liquid flow rate of 500 and 250 g h^{-1}. Also for the last mentioned flow rate, i.e., superficial liquid velocity 0.28 mm s^{-1} and gas velocity 0.42 mm s^{-1}, split value 0.5 and period length 60 s gave the best results. The conversion measured under pulsing flow regime at the same mean feed rate is more than 10% higher than that value, attained in the steady state regime (see Fig. 5). The optimal period length and split are closely joined with character of movement of liquid slugs flowing downwards in the catalyst bed. Optimal results were obtained for period length which is comparable with the true liquid residence time, based on dynamic liquid holdup draining time (57 s) detected at outlet from bed of catalyst after liquid feed stop. This result was measured for relatively short catalyst bed (<0.2 m). Future experiments have to be planned in case of a longer bed depth where pulse attenuation can occur.

4. Conclusions

Periodic operation of trickle-bed reactors significantly increases phenol wet oxidation rate in comparison to reaction rate measured at the steady state operation mode. Temperature effects of an exothermic reaction, periodic wetting of external catalyst surface and improvement in oxygen mass transfer from gas phase to catalyst active sites are strongly influenced by operation parameters like gas and liquid flow rates, inlet temperature and pressure, and by feed modulation parameters, period length and split. Optimisation of parameters and a thorough sensitivity study should be the next step in future research on trickle-beds behaviour under periodic operation mode.

Acknowledgements

The financial support of this study by the Ministry of Education Czech Republic (grant no. CEZ: MSM-223100001) is acknowledged.

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