Periodic Operation of a Trickle-Bed Reactor

The influence of periodic water flow on SO_2 oxidation in a trickle bed of activated carbon catalyst was investigated, whereby gaseous reactants were introduced into the trickle-bed reactor continuously, but water was turned on and off. Mean liquid superficial velocities of 0.86 and 1.65 mm/s were used. At the latter, an increase in the oxidation rate of about 30 to 45% was found within a range of cycle periods from 2 to 80 min. A temperature change of up to 7°C was observed in the bed during periodic operation. An explanation of the improved average oxidation rate under periodic operation is developed in terms of the steady-state rates with and without water flow for symmetrical and asymmetrical cycles.

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Introduction

Trickle-bed reactors (TBR) are a widely used class of three-phase chemical reactors. They find application in solid-catalyzed reaction systems in which one reactant is a gas and the other is a liquid. They may also be used for highly exothermic reactions between gaseous reactants, such as the Fischer-Tropsch synthesis, in which the liquid phase acts as a heat sink. Alternatively, the liquid phase in the TBR serves to remove reaction products in, for example, some oxidation processes.

A common feature of reactions carried out in a TBR is that gaseous reactants must dissolve into and then pass through the liquid phase to reach the catalyst surface. In some cases, the transport resistance provided by the liquid lowers the rate of reaction thereby decreasing conversion. However, the liquid phase is essential to the system and cannot be eliminated. There is a trade-off, therefore, between flushing the catalyst with liquid to remove heat or reaction product and the transport resistance provided by the presence of a liquid.

Is it possible to improve the performance of a TBR by reducing the mass transfer resistance and still achieve adequate flushing of the catalyst? Some researchers have suggested that this can be accomplished using ordered rather than random packing to create separated flows. In this configuration, liquid would flow on one side of the catalytically active packing and gas on the other (Yang and Cussler, 1987). Another possibility would be to flush the bed with liquid periodically instead of continuously. When liquid flow is cut off or drastically reduced, the bed partially drains. This thins out or even removes the liquid film surrounding the packing particles, with a consequent decrease in the transport resistance for the gaseous reactants. Periodic operation can thus be viewed as a means of segregating, at least partially, liquid and gaseous reactants.

The objective of the present study was to examine the effect of periodic flow, as described above, on the rate of reaction in a TBR. The reaction considered is the catalytic oxidation of sulfur dioxide on activated carbon in the presence of water. The SO_3 product formed on the carbon catalyst dissolves to form aqueous H_2SO_4. Without removal by water, SO_3 accumulates on the carbon surface, eventually inhibiting further oxidation. Thus, the water flow continuously regenerates the carbon and maintains its activity. Water also removes the heat of reaction.

The relevance of this contribution is that periodic operation may prove to be a method of improving the performance of trickle beds in cases where mass transfer between the gas phase and the catalyst surface significantly affects the overall rate of reaction. Some important industrial reactions such as hydrodesulfurization of certain petroleum stocks fall into this group of trickle-bed reactions. Periodic operation of the SO_2 oxidation system also suggests a method of flue gas desulfurization to produce a relatively concentrated sulfuric acid solution as a by-product. Considerably more research and development will be needed to achieve such a process, however.

Although flow pulsing of a trickle bed does not seem to have been considered in the published literature prior to this contribution, there are related studies. Hatziantoniou and Andersson (1984) used a ceramic honeycomb monolith impregnated with Pd to study the hydrogenation of nitrobenzoic acid in an aqueous solution. The liquid phase and hydrogen were in concurrent downflow in the parallel channels of the monolith, but the liquid flow was pulsed so that gas and liquid formed slugs of roughly equal residence time in the monolith. According to a Swedish patent (Berglin and Herrmann, 1988) slug flow results if the liquid phase is added continuously. Unfortunately, the perfor-

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mance of the pulsed reactor was not compared with that of a continuously operating TBR, even though Hatziantoniou and Andersson (1984) show that higher effectiveness factors should result with their pulsed monolith reactor. The same authors (Hatziantoniou and Andersson, 1982) earlier demonstrated enhanced liquid-wall surface mass transfer with pulsed liquid flow. The performance of the pulsed monolithic three-phase reactor with a complex hydrogenation section was also studied by the Chalmers Technical University team (Hatziantoniou et al., 1986), but comparison with a TBR was not made. Soni and Crynes (1981) used monolithic catalysts for hydrodesulfurization of high-boiling unsaturates but the pulsing conditions are not discussed. An industrial-scale version of a three-phase monolithic reactor is mentioned by Irandoust and Andersson (1988).

Workers at Chalmers have, in separate studies, examined segregated flow using crossflow monolithic catalyst in which the liquid phase flows downward in parallel channels, while the gas phase moves across in a separate set of channels (De Vos et al., 1982, 1986). Although comparisons with a TBR were not made directly, De Vos et al. (1982) estimated that effectiveness factors would be higher for flow segregation. Plate-type, three-phase reactors employing segregation of liquid and gas phases are also discussed in the literature (Hatziantoniou et al., 1986; Carlsson et al., 1983).

As will be demonstrated in this contribution, periodic operation of a TBR can substantially improve rates of reaction and conversions of a limiting reactant. Improvement requires operation in a flow rate range where a minimum occurs in the reaction rate vs. liquid flow rate curve. Under these conditions, wetting plays an important role in the behavior of the reactor, and the influence of cycling results then from the interplay of mass transfer and local heat removal with reaction rate in the trickle bed.

Experimental Details

The equipment used for this study has been described previously (Berruti et al., 1984). The major modification was that a plexiglas column of 4.0 cm ID served as the reactor. As in Berruti's work, the liquid phase was fed into the trickle bed through a distributor containing 27 tubes, and was further spread over the cross-section by an inert prepacking supported by the carbon. Some details of the packing were modified. Glass helices were used in an effort to improve liquid distribution over the carbon and thereby improve the contact between phases. Furthermore, the prepacking contributed to establishing absorption equilibrium between the gas and liquid phases at the entrance to the catalytic bed.

The gas phase was introduced cocurrently with water at the

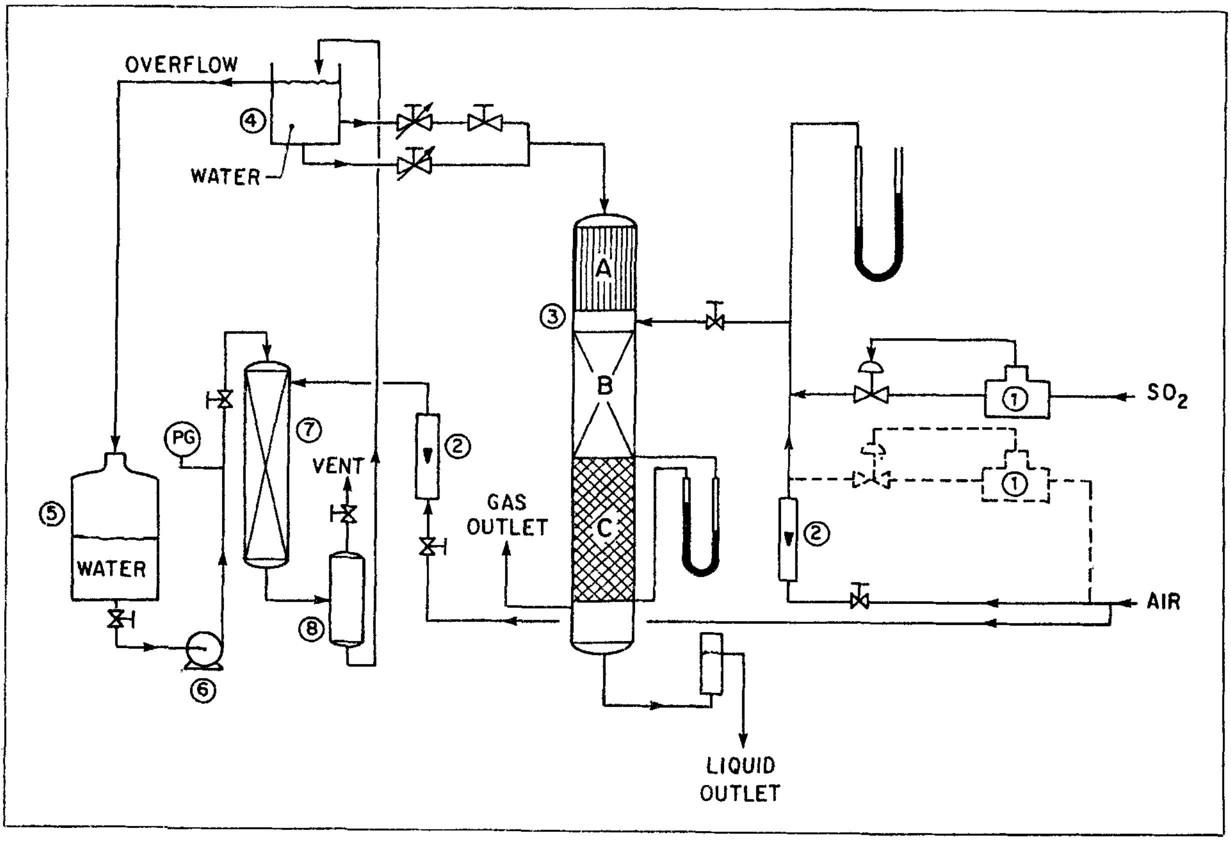

Figure 1. Experimental system.

A = tube distributor
B = prepacking
C = activated carbon packed bed
1 = mass flow indicators/controllers
2 = gas or liquid rotameters
3 = reactor (point of introduction of gaseous reactants)
4 = overflow tank for constant flow rate
5 = water hold-up tank
6 = absorber pump
7 = absorption column
8 = gas-liquid disengager

top of the reactor. Its composition was 1.3% SO_2 (anhydrous) and 98.7% air. A schematic diagram of the conditions most often used are given in Figure 1. A constant gas flow of 25.4 mL (STP)/s was used. The trickle bed was packed with activated carbon (Calgon Corp., type BPL), whose properties are given in Table 1. The reactor-to-particle diameter ratio of 46 was thought sufficient to prevent wall effects. Characteristics of the bed are also given in Table 1. Ambient pressures and temperatures were employed.

During cycling experiments a "mixing-cup" sample was collected over an entire period, and the sulfuric acid content of the liquid effluent was analyzed by the wet chemistry method described by Hartman and Coughlin (1972), in which sulfuric acid concentrations were obtained from total acidity and sulfurous acid determinations. The sulfuric acid concentration is a measure of the oxidation rate. Concentrations of the liquid samples were recorded once the reactor was at the cycle-invariant state; this was assumed to occur when acid concentrations in successive cycles differed by less than 5%.

Usually, the term reaction rate implies a measurement at a single composition. However, in this study, the rate was taken as the average of the rate of sulfur dioxide oxidation over a considerable change in the sulfur dioxide concentration (30–50% conversion). The rates reported are therefore "mean rates" for the average sulfur dioxide and oxygen composition in the gas phase. Mata and Smith (1981), who also investigated the catalytic oxidation over activated carbon, used this approach to analyze their data.

Results

Steady-state experiments

A steady-state study of the influence of constant liquid flowrates was carried out to provide a basis of comparison for the flow-cycling study. Steady-state measurements were carried out using the same apparatus, as well as procedures similar to those employed with flow cycling, except, of course, that the liquid flowrate was held constant.

Data collection under steady-state operation began two hours after start-up with drainage from the bed diverted to a collection vial to give a 200-mL sample. Samples of this size were taken periodically to monitor the onset of steady-state as well as to measure reproducibility at steady state. The absence of any trend in the data with time was considered to be steady-state.

Steady-state data are shown in Figure 2 as the average rate of sulfuric acid production per kg of catalyst vs. the superficial liquid velocity. The rate goes through a minimum between 2 and 5 mm/s. A similar result was obtained by Mata and Smith (1981) using the same catalyst. The curve shown in the figure is a quadratic fit of the data using a nonlinear least squares procedure (standard SAS package). The vertical lines show the 95% confidence limits of the mean for several liquid flow rates where replication was undertaken. The standard deviation for the set was 5 μmol/kg · s. This estimate of error suggests that the minimum in the production rate curve cannot be explained by uncertainty in the experimental data. The curve is used further on to normalize the cycling rate data.

Table 1. Calgon BPL-Activated Carbon as Catalyst and Trickle-Bed Parameters

Carbon Source	Bituminous Coal
Activation Method	High-Temperature Steam
Particle Size	14–30 mesh (0.55–1.19 mm)
Mean Diameter	0.87 mm
Particle Porosity	0.6
BET Surface Area	1,100 m^2/g
Mean Pore Radius	1.3 nm
Bed Dimensions	40 mm ID × 160 mm
Dry Catalyst Mass	98 g
Dry Catalyst Vol.	115 mL
Bed Porosity	0.43
Type of Prepacking	Glass Beads
Depth of Prepacking	60 mm

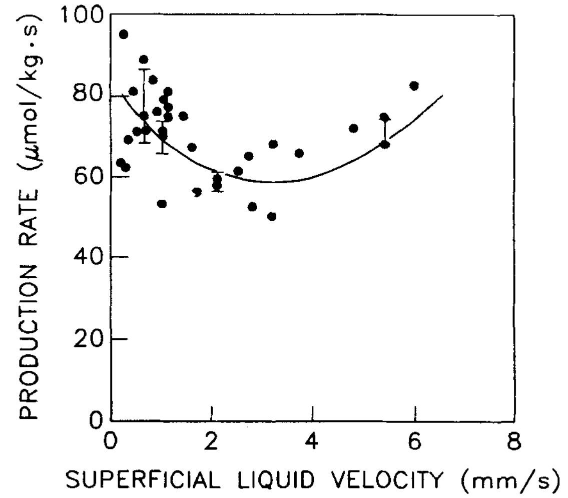

Figure 2. Steady-state rate of SO_2 oxidation in trickle bed of BPL activated carbon vs. superficial liquid velocity.

Flow cycling experiments

Only the liquid flowrate was cycled in the experiments described here. In most cases an on–off mode was used. Several seconds are required for drainage of the aqueous phase from the bed. Nevertheless, the shortest cycle period used lasted two minutes. Consequently, the on–off operation can be described as square-wave cycling. A constant flow of gas containing the SO_2 and O_2 reactants passed through the reactor during the entire on–off cycle.

At a given liquid flowrate, experiments were arranged randomly, by alternating cycling runs having short and long periods with steady-state runs.

Symmetrical cycling (split = 0.5) with zero liquid flow in one half-cycle increases the rate of acid production in comparison with steady-state operation at the mean liquid flow rate. This is shown in Figure 3, in which measured time-average rates under cycling have been normalized with respect to the corresponding steady-state rate at the mean superficial velocity, as given by the curve in Figure 2. These normalized rates are plotted against the cycle period in the figure. If periodic operation did not affect trickle-bed performance, the normalized rate would be unity. Individual points exhibit scatter, but they are adequately correlated by the solid line obtained by a nonlinear least-squares fit of these data. At most periods, the increase of the oxidation rate approaches 40% for an average superficial liquid velocity of 1.65 mm/s. There is little change in the rate improvement attained through liquid-flow cycling over the range of periods studied.

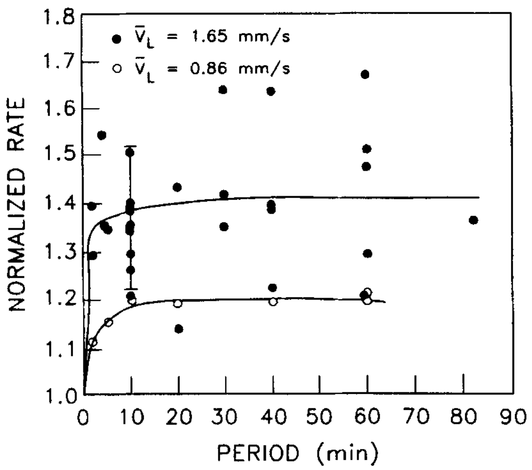

Figure 3. Time-average rate of SO_2 oxidation vs. cycle period for mean liquid superficial velocities.

Steady-state rate of oxidation was normalized. Cycles are symmetrical with a split of 0.5. ± one standard deviation is shown for $\bar{V}_L$ = 1.65 mm/s.

Data for the two mean liquid superficial velocities, $\bar{V}_L$, tested, 1.65 and 0.86 mm/s, are shown. Only the magnitude of the improvement changed; the length of the cycle period at an average superficial velocity of 0.86 mm/s had, again, little influence on the rate improvement for the operating conditions investigated.

Cycling of the liquid flowrate between two finite values was also investigated. Specifically, the influence of the cycle period at a split of 0.5 was studied. Gas superficial velocity was held constant at 20 mm/s, and its composition was 98.7% air and 1.3% sulfur dioxide, respectively. The liquid superficial velocity was varied between 1.2 and 4.0 mm/s. A mixing-cup sample was collected over an entire period and its sulfuric acid content analyzed as described before. Figure 4 presents the SO_2 oxidation rates obtained during this cycling operation as well as the corresponding steady-state rate for the average liquid flowrate as a function of the cycle period. About 12% improvement results from cycling.

Discussion

In previous studies of periodic operation (Silveston and Hudgins, 1987) the time-average reaction rate was usually found to be sensitive to the length of the period of cycling. This is not the case in these experiments. The explanation is that during the zero-flow half-cycle, sulfur trioxide forms on the activated carbon catalyst and is absorbed by the liquid trapped within porous carbon particles. During the liquid-flow half-cycle, the accumulated acid was flushed from the reactor and was captured at the outlet along with the acid formed in the half-cycle. The quantity of trapped liquid was determined by holdup measurements. These were performed using the "weighing method" described by Goto and Smith (1975). To simulate cycling conditions, only the liquid phase was halted and the gas flow continued to pass through the column. The static holdup was determined once draining of the bed was complete. It was constant at about 20% of the total bed volume. The dynamic holdup at 1.65 mm/s was about 20%.

If this explanation is correct, the acid concentration should be high in the first drops of water leaving the bed after liquid flow has been switched on and it should then fall until it reaches a steady-state value which measures the acid formed during steady-state operation at the liquid flow rate. This explanation was tested by monitoring the acid concentration leaving the bed during the liquid flow half-cycle, once the cycle-invariant state had been reached. Measurements are shown in Figure 5. Different periods were studied at an average superficial liquid velocity of 1.65 mm/s. The figure shows the expected fall in sulfuric acid concentration during the first few minutes after liquid begins to flow through the bed. As anticipated, the H_2SO_4 concentration eventually falls to its corresponding steady-state level. (Note that the corresponding steady-state rate of SO_2 oxidation occurs at a superficial liquid velocity of 3.30 mm/s. This is because this velocity must be averaged over the two half-cycles, one with flow and the other without flow, to give a mean velocity of 1.65 mm/s.) The three horizontal lines shown give the mean and 95% confidence levels of the steady-state H_2SO_4 concentration at a mean velocity of 1.65 mm/s. The confidence limits are based on the estimated standard deviation of the steady-state rate data.

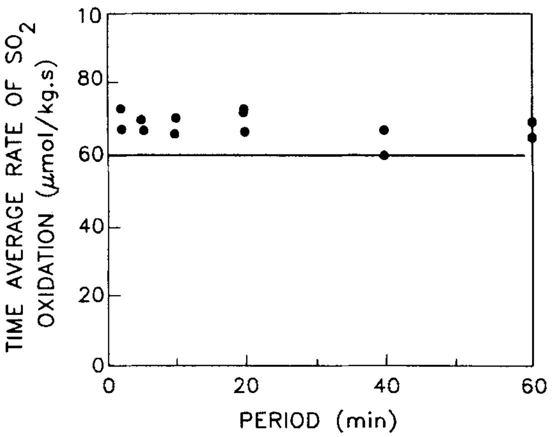

Figure 4. Time-average SO_2 oxidation rate vs. period for symmetrical cycling between liquid superficial velocities of 1.2 and 4.0 mm/s.

Split = 0.5; solid line = corresponding steady-state rate of reaction.

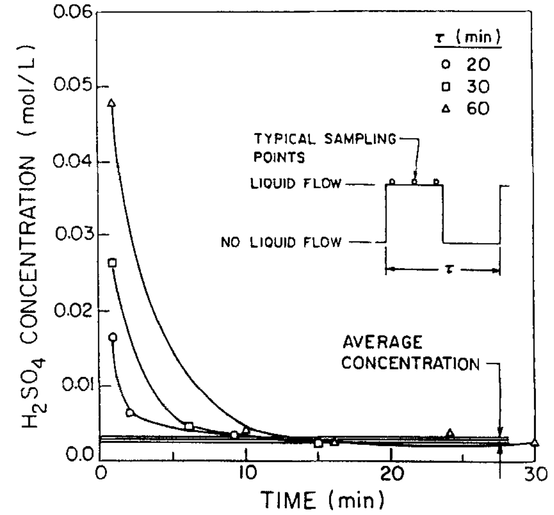

Figure 5. Instantaneous concentration of H_2SO_4 leaving TBR during liquid-flow half-cycle.

The dramatic fall in sulfuric acid concentration leaving the bed during the first minutes of liquid flow can be exploited to increase the H_2SO_4 concentrations produced in the TBR by means of asymmetrical cycling, i.e., use of cycle splits less than 0.5. Cycle split is defined as the fraction of cycle period during which water passes through the bed. In practice, this means that water is used just intermittently to flush away the product. This mode of cycling with water flow through the bed for just one quarter of the cycle (split = 0.25) and one tenth of the cycle (split = 0.10) is compared with symmetrical cycling (split = 0.5) in Figure 6. The concentration of the sulfuric acid leaving the reactor is plotted in this figure as a function of the cycle period and split. It can be seen that the period has just a small effect on concentration, compared with the large influence of cycle split. An asymmetric cycle with a split of 0.1 increases the concentration by at least fivefold over the acid concentration observed for symmetric cycles.

Smaller splits can be used to raise the concentration even further. The minimum split at any period, however, would arise from the time needed to flush product out of the porous carbon particles. This minimum limit was explored in a further experiment. Figure 7 shows the sulfuric acid concentrations obtained during cycling at a split of 0.01. The superficial liquid velocity was 0.033 mm/s and the period was 90 min, which means that the reactor was exposed to the gaseous reactant mixture for 89 min and then the product was flushed out of the bed by water at 3.0 mm/s for 1 min (SO_2 and air continued to be fed during flushing). The experiment was carried out continuously over eight days. The acid concentration leaving the reactor decays slowly with time from 0.180 mol/L to 0.130 mol/L, which is still almost eight times the comparable steady-state concentration of 0.023 mol/L at a mean superficial velocity of 0.033 mm/s. The small decrease in acid concentration over the eight days indicates a reduced catalyst activity, since the inputs were held constant. The decline appears to be related to SO_3 adsorption, since the catalyst activity was fully restored by washing the catalyst with deionized water.

It seems likely from these experiments that asymmetrical cycling can be used together with acid recycle to substantially increase the concentration of the sulfuric acid provided. From a process viewpoint, it may be possible to obtain concentrated acid in this way, despite the low SO_2 concentration in the feed gas.

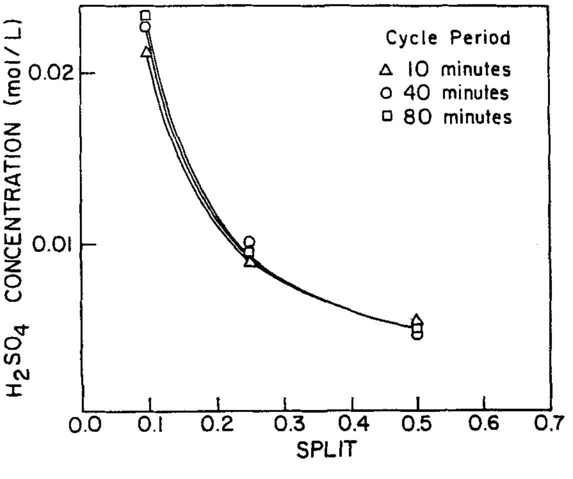

Figure 6. Time-average concentration of H_2SO_4 leaving trickle bed vs. cycle split at different periods.

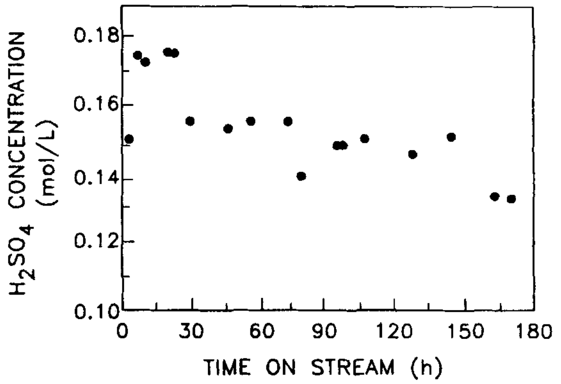

Figure 7. Time-average concentration of H_2SO_4 leaving trickle bed during asymmetrical cycling.
Split = 0.01 vs. time on stream; period = 90 min.

As was mentioned earlier, the steady-state reaction rate passes through a minimum as a function of the liquid flow. Figure 2, though a steady-state result, is the key to interpreting what is happening during cycling. The explanation of the minimum reaction rate given by Mata and Smith is that at high liquid flow rates, turbulence increases the rate of mass transfer so that the reaction rate increases with the flow rate, whereas at low liquid flow rates, where wetting influences the SO_2 oxidation rate, the oxidation rate increases as the flow rate decreases. Low liquid flow rates result in a nonuniform distribution of liquid and thus in liquid-poor regions in the bed. In these regions, the external surfaces of catalyst particles are exposed to the gas reactant mixture, offering an alternative to mass transfer through the liquid film. This decreases the mass-transfer resistance and increases the reaction rate. This effect is observed only when the limiting reactant is present in the gas phase, as is the case in the SO_2–O_2 system. A relationship between wetting efficiency and the rate of reaction in trickle beds has been developed by Herskowitz and Smith (1983). It has been demonstrated experimentally for the hydrogenation of crotonaldehyde on Pd (Sedricks and Kenney, 1983) and for the hydrogenation of α-methylstyrene on Pd/Al_2O_3 (Morita and Smith, 1978; Herskowitz et al., 1979).

This explanation can be checked by calculations, using the data of Komiyama and Smith (1975) and the correlations developed by Goto and Smith (1975). In Figure 8, we compare experimental rate data for the system taken for feed water flow that is not saturated in oxygen. The curve above the data is the one given in Figure 2, and represents the experimental results under the normal conditions used in this study. It can be seen that saturating the inlet water with air increases the rate of acid production substantially; nonetheless, if the water stream is not saturated, a minimum in the curve of rate vs. superficial velocity is still observed. The upper horizontal line shows the rate of production that would result if only diffusion and reaction inside the carbon particle controlled. This assumes, therefore, that the water surrounding the particle is saturated in air. The upper line results from an interpolation of the measurements of Komiyama and Smith for the particle size used in this study. We follow Mata and Smith (1975) in assuming that the units for the intrinsic rate of reaction are based upon a unit volume of carbon particles, although this was not indicated by the original investigators. Since the predicted rate is almost an order of magnitude

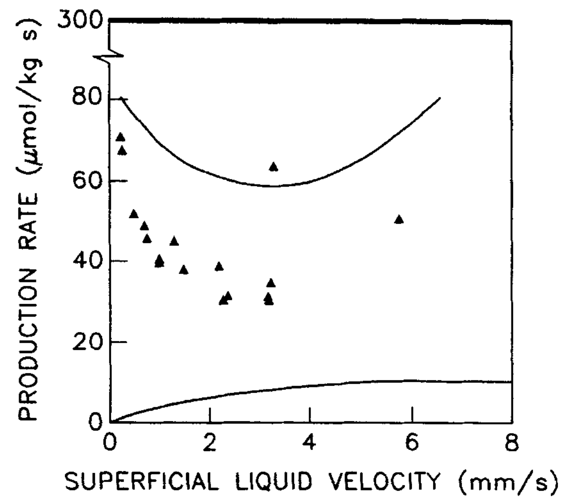

Figure 8. H_2SO_4 production rate at steady state vs. liquid superficial velocity with predicted rates of production.

Assuming control by either gas-liquid mass transfer or internal diffusion and surface reaction. Liquid feed to reactor was not saturated with air.

greater than the measured values, internal diffusion and reaction cannot be controlling in our experiments.

The lower curve in the figure assumes that only transport of oxygen from the gas phase to the flowing water controls. For this prediction of rate, the Goto and Smith (1975) correlation was used. This lies well below the data given in the figure, but nonetheless indicates that gas-liquid mass transfer dominates the kinetics for this system. The difference between this curve and the data points at superficial liquid velocities exceeding 2 or 3 mm/s can be explained by incomplete wetting of the carbon particles even at these relatively high liquid velocities. This is discussed further by Haure et al. (1989). The difference is also accounted for by residual oxygen in the water fed to the carbon bed. The presence of a distributor above the bed makes it impossible to use a fully deaerated liquid stream while still ensuring good distribution of flow across the bed. If we now consider data below a superficial velocity of 2 mm/s, it is clear that such high rates can result only from direct contact between the gas phase and the surface of the catalyst. In this situation, oxygen entering with the water phase decreases, and the liquid flow rate drops, whereas the rates of acid production increase. The lower curve must give the maximum rate of oxygen transport from the gas phase to the catalyst surface through the liquid phase.

All the steady-state reaction rate data can be modeled under the assumption that the wetting efficiency is a unique function of the liquid flow rate using the model proposed by Mata and Smith (1981). A good fit of the data shown in Figure 2 was obtained (Haure et al., 1989) by calculating the wetting efficiency variation with the liquid flow rate from the correlation given by Herkowitz and Smith (1983) and rate data for the BPL activated carbon obtained by Komiyama and Smith (1975).

Figure 2 appears to predict that at zero liquid flow rate, the rate of sulfuric acid production reaches its highest value. However, this cannot be possible. Given enough time without liquid flow, the catalyst must be poisoned by the build-up of adsorbed sulfur trioxide so that the rate of oxidation must fall to zero. Under dynamic conditions, however, the oxidation rate at zero or very low flow rates can be very high.

For experiments in which the liquid flow rate is cycled, the time taken to poison the catalyst must be an important variable which limits cycle length. An experiment was done in order to determine the time of poisoning of the catalyst. The bed was flooded and the gas mixture was then introduced for a fixed time. After this, the bed was flushed with water, during the first minute of which, a liquid sample was collected and the sulfuric acid concentration measured. The resulting graph of acid concentration vs. time of zero liquid flow is shown in Figure 9. After 22 hours of "dry" operation, the concentration of sulfuric acid resulting from flushing is 1.21 M. This indicates that sulfur dioxide oxidation is still taking place on the activated carbon even after 22 h. Siedlewski (1965) reported reaction times up to 20 hours without deactivation, even though this figure should be taken as approximate for the measurements considered in this work, since the systems differed substantially. The explanation for the continued activity of the catalyst is that it is fully wetted by water and dilute acid so that the water held in the interior acts as a sink for SO_3, thereby preventing poisoning. As long as the period is well below the time of poisoning, the cycle period should have little effect on the time-average rate of acid production. Since in Figure 3, periods were always less than 1.5 h and the poisoning time more than 20 h, the period should have just a minor effect on the oxidation rate. This is exactly what is observed in the figure. The small increase in oxidation rate with period in this figure is explained by the results shown in Figure 5.

From the explanation presented above, it should be possible to predict the increase under cycling. In Figure 10, the data from Figure 2 have been replaced by smooth curves to demonstrate this.

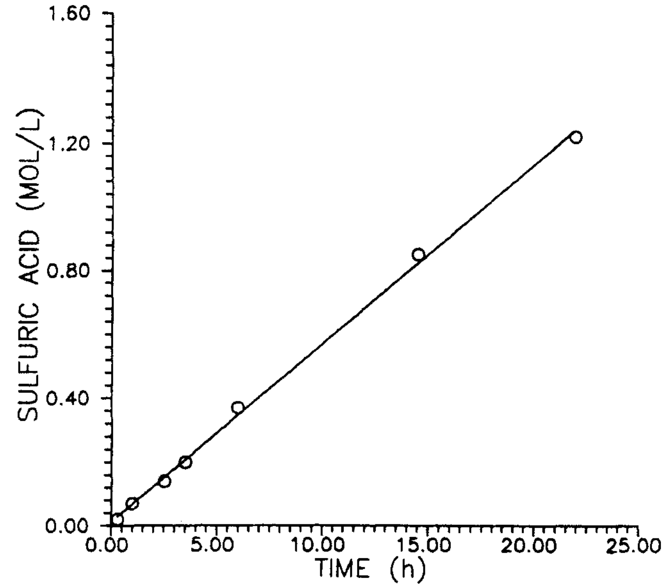

Figure 9. Mean sulfuric acid concentration during first minute of liquid flow vs. duration of zero liquid flow (Vg = 20 mm/s).

At a high liquid superficial velocity, V_{L1}, the steady-state rate of H_2SO_4 formation is located at SS_1, whereas at zero liquid

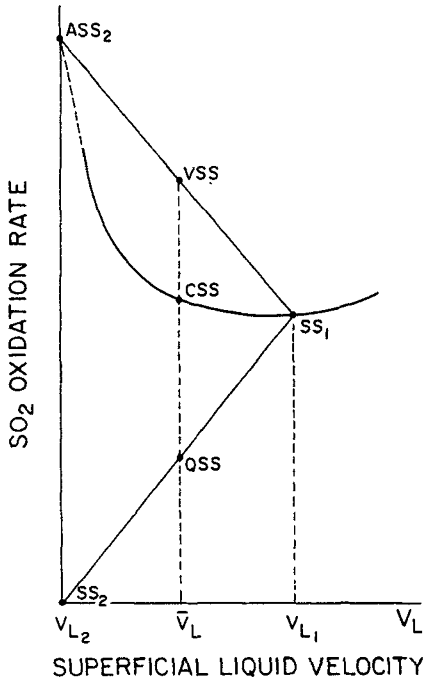

Figure 10. Steady-state rate of SO_2 oxidation vs. liquid superficial velocity showing construction lines for predicting QSS rate and VSS rate.

flow, $V_{L2} = 0$, the ultimate steady-state rate is zero and is given by SS_2. The mean rate corresponding to extremely slow cyclic operation, referred to as the quasisteady-state (QSS), using equal periods of flow and zero flow, is found by joining SS_1 and SS_2 with a straight line to give QSS at a mean liquid superficial velocity of $(V_{L1} + V_{L2})/2 = \bar{V}_L$. The QSS rate is lower than the corresponding steady-state rate located at CSS at the mean superficial velocity, as Figure 10 shows. Under this condition, steady operation would be superior to cycling operation.

However, if cycling is somewhat more rapid, the catalyst is not poisoned by SO_3 build-up. Thus, high rates of SO_2 oxidation are possible. If periods of the order of several hours are used, the rate at $V_{L2} = 0$ will be the apparent steady state (ASS_2) rather than SS_2. By joining ASS_2 to SS_1 and taking the mean rate for symmetrical cycles at the average superficial velocity, $\bar{V}_L$, we obtain a virtual steady-state rate located at VSS in Figure 10 that is higher than the corresponding steady state (CSS). Predicted values are given in Table 2 for various cycling operations. When the experimental values for SO_2 oxidation are examined, however, they fall a little above the predicted ones. This difference appears to be due to mean bed temperatures in cycling being a few degrees higher than bed temperatures at steady state. The cause is not hard to discern. In steady operation, the flow of water removes the heat of reaction from the bed. However, in cycling operation during the dry part of the cycle, there is no water flow to remove the heat of reaction. The mass flow of gas is relatively unimportant as a heat transfer medium. Consequently, on average, the bed operates at a higher temperature and the reaction rate is thus measurably higher than in steady state.

Table 2. Average Trickle-Bed Temperature under Steady-State Operation

Superf. Liquid Vel., mm/s	Avg. Trickle Bed Temp., °C
0.2	29.6
1.0	28.9
4.6	27.1

Table 3. Predicted* vs. Experimental SO_2 Oxidation Rates**

Cycle Split	Mean Superf. Liquid, mm/s	CSS	Time Avg. VSS	Periodic Rate Exp.	% Diff.†
0.5	1.7	67	82	88.7	8
0.5	0.8	80	85	90.8	7
0.25	0.8	80	88	94	7
0.1	0.33	97	97	97.7	1

*VSS predicted from steady-state rates in Figure 2; construction shown in Figure 9

**Oxidation rates: μmol/kg · s

†(Experimental − predicted)/predicted as %

Temperature was observed to increase en route to the steady state at low flows (Haure et al., 1989). Only mean steady-state temperatures are shown in Table 3. However, it can be seen that, at a liquid velocity of 0.2 mm/s, the bed temperature increases by 2.5° over the temperature measured at 4.6 mm/s. As discussed previously, this appears to be the result of inadequate heat removal at the lower velocity. Using a literature value of the activation energy of 49 kJ/mol for SO_2 oxidation over carbon (Brodzinsky et al., 1980), this temperature difference would predict a rate increase of 19% if the reaction were kinetically controlled. However, since we demonstrate in Figure 9 that mass transfer limits the reaction rate in this system, the temperature rise is a result of the rate increase rather than a cause. A comparison between temperatures measured during steady state and cycling operation is shown in Figure 11. The two curves indicate that the bed operates at a mean temperature several degrees higher in cycling operation than in steady operation. Comparison between experimental and predicted rates at a

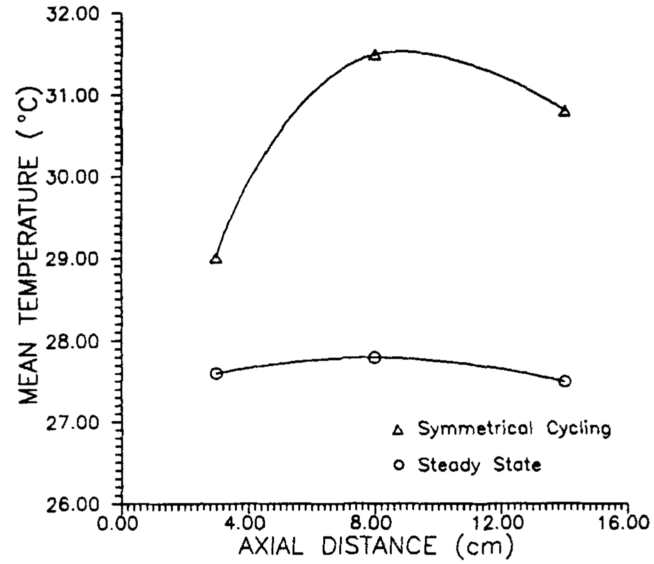

Figure 11. Mean temperature along axial dimension of TBR (V_L = 1 mm/s).

mean superficial liquid velocity of 1.65 mm/s is made in Table 3. Evidently, the differences in reaction rate of about 7 to 8% in the table, result from the temperature difference shown in the figure. Based on the activation energy of 49 kJ/mol, the observed difference of 4° results in a rate increase of 30%. However, if mass transfer controls, the activation energy will be of the order of 10 kJ/mol, resulting in an increase of about 6%. This compares well with the observed increase of 7 to 8% shown in Table 3.

The results obtained for the 0.86 mm/s liquid velocity data can be predicted using the construction shown in Figure 10. Cycling between two finite liquid flow rates can also be predicted using this simple method. By weighing the reaction rates in proportion to the respective partial cycles used with the two liquid flows, the time-average reaction rate for asymmetrical cycles can also be estimated. Thus, graphical calculation can be used to explain all the cycling results, provided that allowances are made for small increases in the mean bed temperature during cycling. Because the steady-state data are adequately predicted by the model due to Mata and Smith, Figure 10 can be used to predict to a first approximation the time-average SO_2 oxidation rate under periodic operation of a trickle bed.

The significance of this work is not confined to the catalysis of SO_2 oxidation by carbon. Morita and Smith (1978), Herskowitz et al. (1979), and Sedricks and Kenney (1983) show that reaction rates go through minima when the liquid flow rate is varied for other TBR systems. Consequently, the reaction rate improvement resulting from cycling, shown in Figures 3 and 4, should be achievable in other trickle-bed systems, as in the hydrogenation of organic liquids for example. An estimate of the magnitude of improvement can be made if suitable steady-state data are available by using the procedure described in this section.

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