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The Effect on Conversion of Flow Rate Variations in a Heterogeneous Catalytic Reactor

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The unsteady state behavior of a tubular heterogeneous catalytic reactor, in which significant adsorption effects occur, has been investigated theoretically and experimentally. Transient responses of conversion to step increases and decreases of flow rate as well as to periodic variations in flow rate are considered. A simplified procedure for anticipating gross effects in cyclic processes is suggested.

A mathematical model has been developed by Lehr, Yurchak, and Kabel (*1*) to predict the product distribution of a heterogeneous catalytic tubular reactor as a function of time following a step increase in flow rate. The model comprises component material balances which take the form of simultaneous partial differential equations. The rate of reaction on the catalyst surface is accounted for by extending typical Langmuir-Hinshelwood kinetics to the unsteady state. The Langmuir (monolayer) theory of activated adsorption is used to describe the adsorption rate processes and equilibria. Mass transfer effects are known to be negligible at steady state conditions (*6*) and are taken to be so in the unsteady state also (*1*). To evaluate the model, Lehr (*2*) and Kabel (*3*) performed experiments on the vapor-phase dehydration of ethanol to diethyl ether as catalyzed by ion exchange resin in the acid form:

$$2\,C_2H_5OH = (C_2H_5)_2O + H_2O \qquad (1)$$

The model was found to be in qualitative agreement with all experimental observations and in quantitative agreement with many of them. The objects of the research reported in this paper are to add rigor to the model used by Lehr et al., to consider theoretically and experimentally the response of the reactor to a step decrease in flow rate, and to examine the effect of periodic variations in flow rate on production rate (or conversion) of the reactor.

The development and rationale of the model are given in complete detail elsewhere (*1*, *2*, *4*). Some modifications to the model of Lehr et al. have been made. In the original paper (*1*), it was assumed that the superficial velocity through the reactor could be taken as constant during the transient period. The model used in this work eliminates this assumption. The present model also achieves greater flexibility by employing a numerical integration technique along the time characteristic as well as the velocity characteristic. Other very minor changes are described, and the effects of all modifications are considered in detail by Denis (*4*). The above modifications provide the model with additional rigor which is necessary for the accurate description of the transient behaviors in this paper. However the modifications lead to no significant changes in the results of Lehr, Yurchak, and Kabel.

NONISOTHERMAL EFFECTS

In all experiments an attempt was made to keep the reactor isothermal. For steady state conditions, the catalyst bed temperature was maintained within 0.1°C. of the temperature of the surrounding thermostatic bath. However, in this reaction system, substantial amounts of ethanol and water are adsorbed. Heat release on the order of 15,000 cal./g. mole accompanies the adsorption of these materials (3). Because of the thermal resistance of the bed and the significant changes in the degree of component adsorption which occur during the transient period, the temperature within the bed departs from its steady state value. For a step increase in feed rate at 109.5°C., a maximum temperature drop of 1.6°C. was indicated by a thermocouple centrally located in the bed. For a step decrease in feed rate at the same temperature, a maximum temperature rise of 0.4°C. was observed. This drop (rise) is attributed primarily to the strong desorption (adsorption) of water overshadowing the partially compensating adsorption (desorption) of alcohol. Other factors affecting the reactor temperature such as the increased (decreased) rate of the exothermic surface reaction at the higher (lower) flow rate and the effect of the higher (lower) flow rate on heat dissipation are small by comparison.

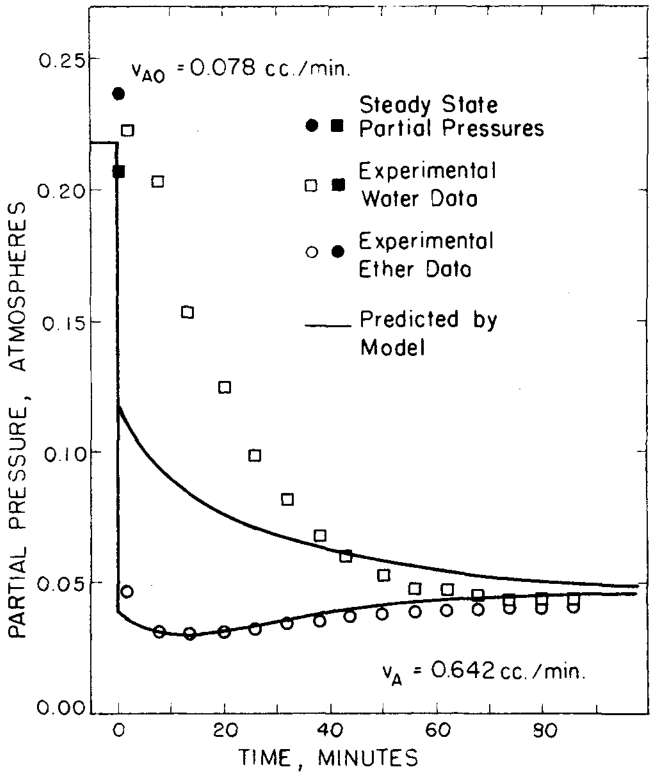

Fig. 1. Response of system to step increase in flow rate at 109.5°C. and 0.964 atm. total pressure.

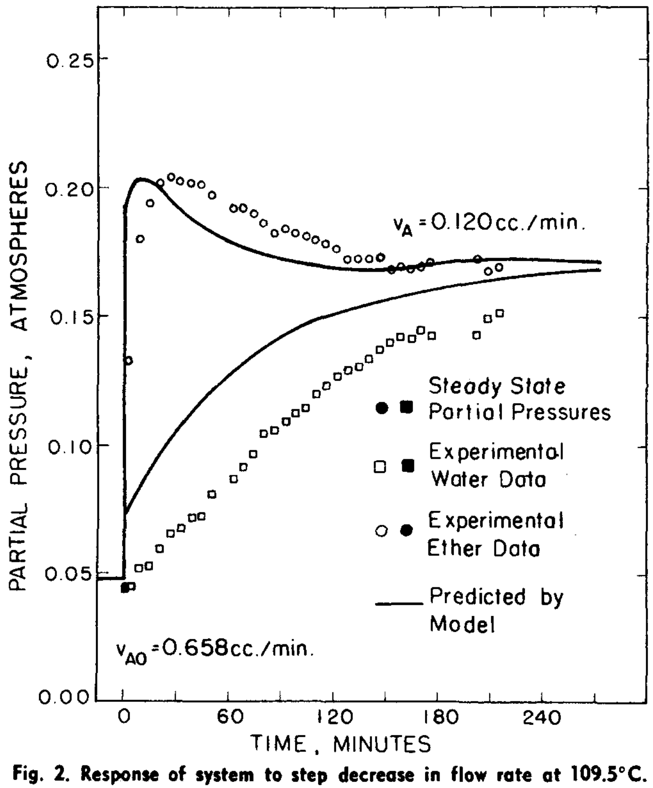

Fig. 2. Response of system to step decrease in flow rate at 109.5°C. and 0.964 atm. total pressure.

Because the departure from isothermal operation was small, no attempt was made to predict the thermal variations theoretically, although it can be done (5). Instead, a mean bed temperature as a function of time was calculated from the experimentally observed temperatures and was incorporated into the computations directly. The necessary rate and equilibrium constants at the different temperatures were calculated from Arrhenius relationships. The coefficients in the various Arrhenius equations were determined from the available (1) rate and equilibrium constants at 105.8° and 120°C.

Step Increase in Flow Rate

The effect of the variation in temperature on the predicted behavior is seen by consideration of Figure 1, which shows the experimental and predicted transient curves for a step increase in flow rate. The partial pressures of ether and water at the initial and final steady states are identical, within the experimental error of the gas chromatographic analysis. This is consistent with the stoichiometry of reaction 1 for pure ethanol as feed. At the initial steady state, more water and less ethanol are adsorbed on the catalyst than will be the case at the final steady state. Immediately after the imposition of the higher flow rate, the reaction rate will be low corresponding to the catalyst conditions of the initial steady state, and the residence time will be low as in the final steady state. Thus the rate of reaction will actually be lower than its final steady state value. The effect of the minimum rate on the water curve is masked by the large amounts of water which are desorbed from the catalyst during the transient period. The minimum in reaction rate is better reflected in the ether curve, since ether is only slightly adsorbed.

The predicted minimum in ether concentration for a constant temperature solution of the model (not shown on the figure) occurs at 8 min. When temperature variation is considered, the predicted minimum on Figure 1 occurs at 11 min., which is closer to the experimentally observed minimum of 14 min. Since the measured temperature would not fully reflect the thermal variations on the catalyst surface, this allowance for nonisothermal operation still falls short. The time of occurrence of the ether minimum is therefore a function of the temperature drop in the reactor. The reasonableness of this is seen from the following argument. If ethyl ether is not adsorbed, its only mode of production is through the chemical reaction. As the reactor temperature falls and then rises again with time, the rate of reaction and hence the ether partial pressure must also decrease and then rise again. Of course even at constant temperature, the rate falls below that at the final steady state as explained earlier. Superimposed on these effects is the small but significant desorption of ethyl ether which tends to mask the effects of the minimal reaction rate early in the transient period. In the previous paper (*1*), isothermal computed solutions were compared with experimental results at 105° and 120°C. It is shown (*4*) that theoretically accounting for nonisothermal effects would substantially improve agreement with the 105°C. experiment but would have little effect on the excellent agreement already achieved at 120°C.

STEP DECREASE IN FLOW RATE

The equipment, method of operation, and analysis techniques for all experimental work reported in this paper were identical to those described by Lehr (2) for the step increase in flow rate at 120°C.* The experimental data obtained for a step decrease in liquid alcohol feed rate from 0.658 to 0.120 cc./min. are shown on Figure 2. Actually, the flow rate was stepped down to 0.138 cc./min., but it drifted downward reaching 0.120 cc./min. at the termination of the run. This may have been caused by a continuously increasing pressure drop resulting from slight swelling of the catalyst upon the adsorption of water.

Separation of the ether and water curves occurs during the transient period as in Figure 1, but in this case the ether concentration passes through a maximum rather than a minimum. The curve for water partial pressure increases gradually until it begins to converge with the ether curve near the final steady state. The qualitative explanation of this behavior is analogous to that for the step increase in flow rate. Since the concentration of water on the catalyst is proportional to its concentration in the vapor P_W, and since P_W is smaller at the initial steady state than at the final steady state, there is less water on the catalyst initially than finally. Thus much of the water produced by the reaction remains adsorbed during the transient period. The final steady state water partial pressure can be attained only after the excess sites for water adsorption have been occupied.

Ether, which is only slightly adsorbed, climbs rapidly to a maximum since the rate of reaction is greatest near the beginning of the transient period when the catalyst is largely occupied by ethanol and relatively free of water. The maximum is not instantaneous because of the slight adsorption of ether and because the observed temporary increase in temperature (0.4°C.) gives rise to a higher reaction rate sometime after the flow rate is decreased.

The Behavior of Alcohol

The experimental results for alcohol behavior following a step increase and a step decrease in flow rate at 109.5°C. are shown in Figure 3. During the first residence time (typically less than 1 min.), the partial pressure of alcohol P_A changes sharply for both cases and thereafter continues more gradually in the same direction until the final steady state is reached. The adsorbing capability of the catalyst for alcohol is not great or rapid enough to dampen the sudden surge (step increase) or sudden depletion (step decrease) of alcohol at zero time. After about one residence time, however, adsorption processes become effective, and a more smoothly curving line is produced. This initial abrupt rise or fall also occurs for the other components. The extent of the change is very great for ether which is only slightly adsorbed and almost nonexistent for water which is strongly adsorbed.

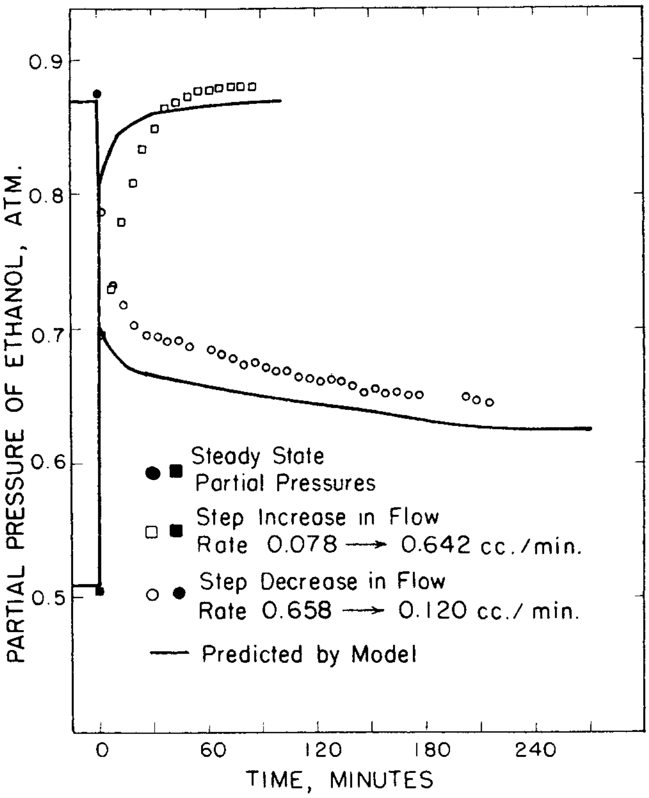

Fig. 3. Response of ethanol concentration to step changes in flow rate at 109.5°C. and 0.964 atm. total pressure.

For the step increase in flow rate the slow approach of P_A toward its relatively high value at the final steady state results mainly from the fact that alcohol is removed from the vapor by adsorption as well as via the surface reaction. However the large amount of water being desorbed also contributes in causing P_A to increase gradually rather than quickly. This effect is most clearly seen in the linear portion (between 0 and 30 min.) of the experimental data for the step increase in flow rate on Figure 3. The large amount of water being added to the vapor stream increases the mole fraction of water there, thus depressing the mole fraction of alcohol by mere dilution. Since the total pressure is constant, the partial pressure of the alcohol is also reduced. Generally, such a dilution effect by any component can affect the curves of the other components. The reverse of this reasoning would apply to the step decrease case.

In the two runs shown in Figure 3, the temperatures were the same with the greater range of flow rates for the step increase case. Yet the step decrease case required two to three times as long to achieve its new steady state. This is believed to occur because of the greater final space velocity in the step increase case. That is, the more reactor volumes of feed that can be passed through the reactor per unit time, the more rapid will be the achievement of a new steady state.

Comparison of Predicted and Experimental Behaviors

The comparison of predicted to experimental results for the two transient runs at 109.5°C. illustrates the capabilities and shortcomings of the model. The average of the absolute values of the percentage deviations of predicted steady state product compositions from those determined experimentally was 7.6%. This is well within the accuracy

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* All parameters used with the model in the computations reported in this paper are given in Table 1 of reference (*1*) or derived therefrom with the following exceptions: $L = 20$, $W_c = 24.091$, $\rho_c = 0.238$, and $\rho_{v_A} = 0.784$.

of the steady state correlation for this reaction by Kabel and Johanson (*6*).

The predicted ether curve of Figure 1 matches the experimental data very closely. The predicted values of ether partial pressure at the maximum and minimum points on Figures 1 and 2 are almost identical to the experimental values. The predicted times for the maximum and minimum ether concentrations fall short of the experimental times as explained earlier. It should also be noted that values for the adsorption rate and equilibrium constants of ethyl ether were estimated as discussed by Lehr et al. (*1*).

The model's most significant limitation is its failure to match the experimental water curves, although the model successfully accounts for the strong direct effect of water on the rate of reaction. This weakness occurs because the model inherently accounts for monolayer adsorption only by virtue of its use of the Langmuir isotherm. In fact, water can be adsorbed in multilayers. Thus, water which would not be expected to participate directly in the reaction and which is not accounted for by the model will still be manifest moving between the vapor and adsorbed phases in the experimental case. Despite the likelihood that these molecules do not participate directly in the reaction, their adsorption or desorption during the unsteady state, if accounted for by the model, would affect the partial pressures of all components and hence in a minor way the predicted rate of reaction.

This lack of accounting of multilayer adsorption of water is also responsible for the inability of the model to predict the partial pressure of alcohol quantitatively during the early part of the transient period. For the step increase in flow rate, the predicted P_A curve is too high near the beginning because insufficient water is being desorbed, according to the model, to adequately predict the actual extent of dilution of the alcohol in the vapor stream. Similarly, for the step decrease, the model does not allow for sufficient water to be removed by adsorption to sufficiently concentrate the vapor stream with alcohol and thus to achieve agreement with the experimental curve. This dilution-concentration effect is also at least partially responsible for the experimental ether partial pressures falling above the predicted values on Figure 2. The same effect is present in the opposite direction in the ether curve of Figure 1, but it is less noticeable because of the low ether concentration in that case.

The predicted ether curve of Figure 2 displays a local maximum at about 220 min. This is the result of the increasing conversion which results from the previously mentioned continuous decrease in flow rate. This effect is obscured until about 140 min. by the pronounced rate maximum discussed earlier for this case. The model was programmed to take into consideration the actual flow rate up to the time of experimental run termination, 215 min. From that time on to the final steady state, the flow rate was taken to be constant at 0.120 cc./min., yielding the expected decrease in ether concentration.

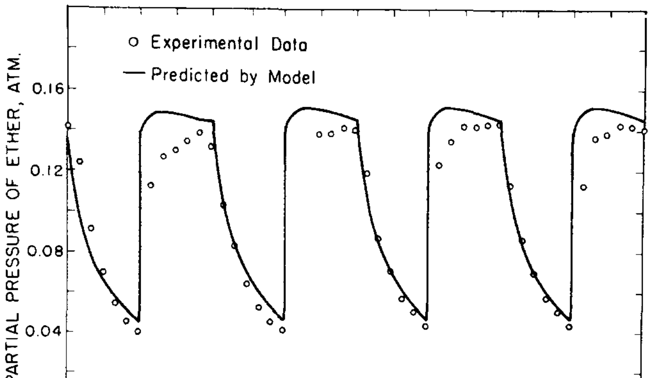

Fig. 4. Response of ethyl ether concentration to sawtooth cycled flow rate.

PERIODIC VARIATION OF FEED RATE

Because of the effects on the rate of reaction of transient operation following step changes in flow rate, one wonders if operation in a regime of periodic variation of feed rate might not allow reactor performance to be improved beyond that obtained in normal steady state operation. Douglas (*7*) analyzed theoretically the effect of periodic variations of feed composition and flow rate to a continuous flow stirred tank reactor. His conclusion was that "sometimes it is better to design control systems which amplify the effects of disturbances, than to force the system to operate close to the optimum steady-state conditions." By using the methods discussed earlier, the effect on overall conversion (or production rate) of periodic unsteady state operation of a tubular heterogeneous catalytic reactor is considered here. The criterion of performance is to be the overall production rate of product for transient and steady state operation at identical time average flow rates. The production rate is the total molar flow rate multiplied by the mole fraction of a component in the effluent.

Experimental Study

Reaction 1 was selected for study because of the investigators' experience with this reaction system and knowledge of the relevant parameters for it. The purpose of the experiment is to show that a real reaction system behaves consistently with predictions from theory, and hence that a model such as is used here can point the way to improved reactor performance by dynamic operation.

The flow rate was varied according to a forcing function, hereafter called a *sawtooth,* which consisted of the flow rate increasing linearly with time over the first half of the cycle followed by a step decrease in flow rate with operation continuing at the low flow rate for the second half of the cycle period. It was hoped that the severity of the ether minimum concentration, and hence reaction rate, induced by a step increase in flow rate could be reduced by the gradual feed rate increase, and, conversely, that full advantage could be taken of the maximum rate occurring upon a step decrease by stepping down sharply and operating at the low flow rate for a period of time.

A 72 min. period was chosen to allow a sufficient number of samples, one every 6 min., for subsequent graphical integration to determine time-average production rates. Initially, a steady state was established at 109°C. with a liquid alcohol flow rate of 0.167 cc./min. Beginning at zero time, the flow rate was increased manually by equal increments every minute until a flow rate of 0.56 cc./min. was reached at the end of 36 min. The flow rate was then reduced instantly to 0.167 cc./min. and allowed to remain there for another 36 min. The cycle was repeated eight times to ensure that a quasi steady state (the state where conditions are the same at each point in the reactor at all corresponding times of two consecutive cycles) had been reached. Figure 4 shows the ether response for the first four cycles. The data for the third and fourth cycles are the same within experimental error. Thus, the quasi steady state was reached by the fourth cycle. Possible effects of imperfect experimental step and ramp forcing functions in producing discrepancies between predicted and observed results have been con-

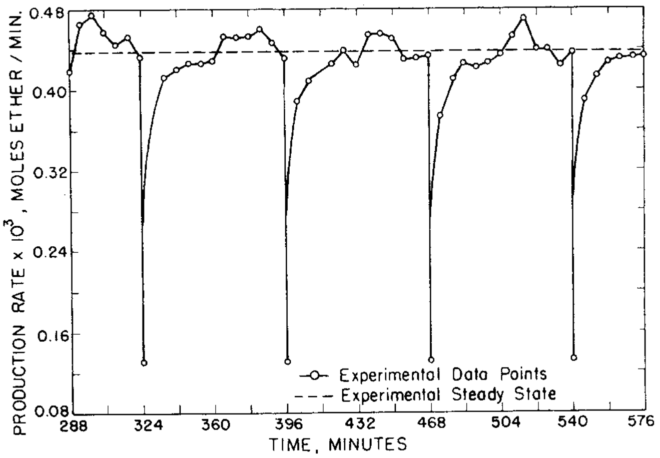

Fig. 5. Instantaneous ether production rate in response to sawtooth cycled flow rate.

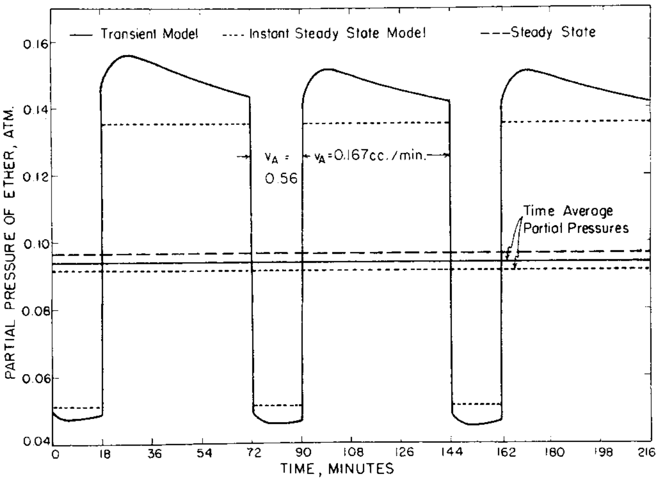

Fig. 6. Predicted responses of ethyl ether concentration to square wave cycled flow rate.

sidered and ruled out. The response of flow rate to a valve adjustment was precise and practically instantaneous compared with the measured process responses.

Liquid product, collected over the entire last (eighth) cycle, was weighed and analyzed. The time-average feed rate determined directly from the weight of the liquid sample was 0.2645 cc./min. The time-average feed rate calculated by integration from the minimum feed rate and feed rates along the linear ramp from the minimum to the maximum feed rate was 0.2655 cc./min. This very close check indicates that a negligible amount of product was lost while the liquid sample was collected. The pressure and the average temperature over the last cycle of the transient run were 0.958 atm. and 109.4°C.

Instantaneous molar production rates for ethyl ether and water were calculated independently from the composition of each sample and the flow rate at the time of the sampling. Figure 5 shows the resulting data for ether. The solid lines on this figure indicate the graphical integration which was done over each of the cycles 5, 6, 7, and 8 to determine the time-average molar production rates of ether shown in Table 1. Water data were handled similarly. The overall production rates for ether and water at quasi steady state should be the same, although instantaneous values need not be. An independent value of each production rate was determined for the last cycle by using the liquid sample analysis.

From the experimental results of Table 1, it is seen that the independently determined ether and water data confirm one another within experimental error. Also, the results of the liquid and gas sample calculations are in essential agreement. The ether results are believed to be the more reliable. A comparison of the steady state production rates with those from transient operation show that for this reaction system the transient operation actually proved to be disadvantageous.*

Theoretical Considerations

For theoretical analysis of this reaction system two flow rate forcing functions were used: the sawtooth function and a square wave function. The square wave variation of flow rate is particularly amenable to interpretation since it is merely a combination of the previously discussed step functions. So that the square wave can alternate between the same values of flow rate as the sawtooth and achieve the same time-average flow rate, its high and low flow rate periods must be 18 and 54 min., respectively.

Figure 4 illustrates the application of the model to the experimental case of the sawtooth variation of flow rate. The cycles were repeated until quasi steady state was reached within a specified tolerance. Production rate for each cycle was calculated by a cumulative numerical integration as the run progressed.*

Instant Steady State Model Although it is evident that a substantial time is required for the reaction system to achieve a new steady state following a perturbation, it has proved quite helpful to employ the concept of an instantaneous establishment of the new steady state. The value of such a concept lies in the fact that a transient process can be approximated by a sequence of steady state processes. Since steady state data and descriptions of steady state processes are much more readily available and more easily understood, an instant steady state model allows a quick determination of the direction of the gross effects of a transient process without elaborate experimentation and/or analysis. The instant steady state model also assists in physical visualization of the process.

Figure 6 illustrates several interpretations of the response of ether partial pressure during the first three predicted cycles of the square wave variation of flow rate. The solid lines show that the expected minima and maxima in ether concentration occur after step changes to high and low flow rates, respectively. From the dotted lines which show the steady state concentrations at high

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* It must be pointed out that the product analyses from a steady state run, performed a day later at the time-average flow rate and temperature of the cycled run, gave values of 3.78×10^{-4} and 4.14×10^{-4} g. moles/min. for water and ether production rates, respectively, in contrast to the values of 4.82×10^{-4} and 4.37×10^{-4} shown in Table 1. These values would actually indicate an improvement in performance due to transient operation. There is little doubt, however, that the values actually obtained in the run are in error. A comparison of product composition vs. flow rate data for this particular run and similar data for many other similar runs performed in the course of this research shows this run to be well out of line. Thus, the steady state values shown in Table 1 and on Figure 5 represent best estimates of results for the conditions of this run based upon data from a large number of similar runs.

* This integration is similar to that used for the experimental study, except that the flow rate of the effluent was used rather than that at the inlet. This procedure is more rigorous because production rate is dependent on instantaneous outlet flow rates which differ from inlet flow rates during the transient period because of adsorption and desorption. Inlet flow rate had to be used for the experimental run because accurate measurement of the instantaneous effluent flow rate is very difficult and therefore was not attempted.

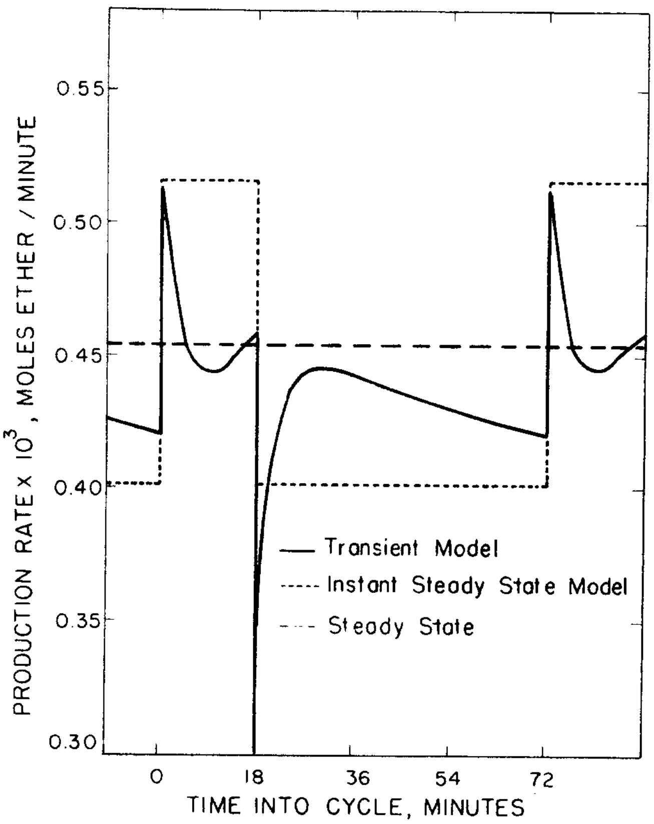

Fig. 7. Predicted production rate for square wave cycled flow rate.

and low flow rates, it is seen that the transient processes do not achieve steady state before the next adjustment of flow rate. Figure 7 shows the variation of ether production rate over the period of one square wave cycle. By comparison of areas under curves of interest, the time-average production rate predicted by the transient model is seen to be greater than that of the instant steady state model, and the true steady state production rate is greater than either of the time-average values.*

Thus, both models predict that it is disadvantageous to operate in the transient rather than the steady state regime. The reason for this is made clear by considering the instant steady state model. According to the model, the reactor is operating part time at one steady state and part time at another; that is, over a complete cycle the reactor experiences two different residence times. This is similar to the case of a tubular reactor in laminar flow in which a variety of residence times exist under steady state conditions. It is well known that the existence of different residence times in the same reactor gives a lower conversion than a constant residence time at the same bulk average flow rate when reaction rate decreases with progress of the reaction. The reason for this is that time spent in the reactor by a reacting mixture at low flow rate beyond the mean residence time for a complete cycle does not fully compensate for the decrement in residence time below the mean residence time suffered by the reacting mixture at high flow rate. For reaction 1, where rate does decrease with increasing conversion, this is because the unrealized potential for production by the high flow rate (and thus high reaction rate) fluid relative to the mean is greater than the production accomplished by the low flow rate (and thus low reaction rate) fluid in the time beyond the mean.

Interpretation of Theory and Experiment

The transient and instant steady state models have also been applied to the experimental case of the sawtooth cycled flow rate. A comparison of the transient model and experimental data is given on Figure 4. Both experiment and model display the nonlinear decrease of ether concentration with linearly increasing feed rate. In fact, the instant steady state model predicts this behavior as well. The maximum in ether concentration following the step decrease in flow rate is quite evident on the predicted curve and appears right at the end of the cycle in the experimental data. Both model and experiment predict the establishment of the quasi steady state by the fourth cycle.

The ether production rate behaviors predicted by both models are shown on Figure 8. Again, the transient model predicts a higher time-average production rate than the instant steady state model, and both models show cycled operation to be inferior to true steady state. The shapes of the transient curves are explained as follows. The initial gradual increase in flow rate at the previously existing high conversion level gives an increased production rate which then falls off as conversion drops. However, the continually increasing flow rate overcomes this ultimately giving a steady rise in production rate. Next, the sudden decrease in flow rate coupled with the low conversion conditions of the previous high flow rate gives a sharp drop in production rate. This is followed by a rise through a maximum and a gradual decrease toward steady state, following the conversion behavior shown in Figure 2 at constant flow rate. It is easier to see these effects in computed rather than in experimental results. Nevertheless, they are also to be seen in the experimental data of Figure 5 within the limitations of data scatter and cycle timing. Similar rea-

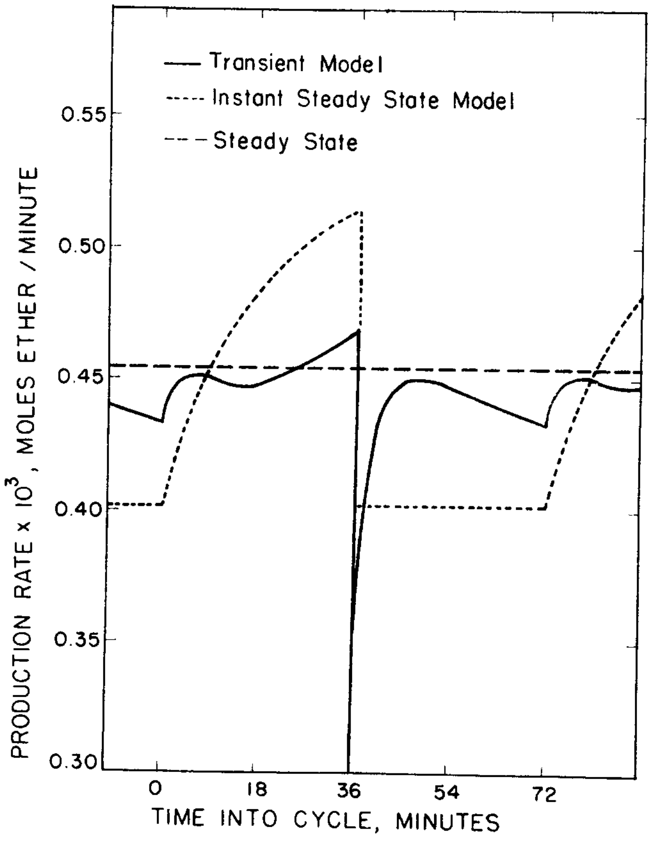

Fig. 8. Predicted production rate for sawtooth cycled flow rate.

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* A similar conclusion can be reached by comparing areas under curves on Figure 6 and weighting them properly by flow rates. The time-average partial pressure lines are obtained from $\int F\, P_E\, dt / \int F\, dt$.

soning may be used to interpret the less complex curves of Figure 7.

The numerical and experimental results are summarized in Table 1, where they are seen to be consistent within experimental error. These data show only a slight improvement of the sawtooth over the square wave type of flow variation. The reason for this does not lie in the ability of the sawtooth function to take advantage of one transient effect while suppressing another, as was put forth in the experimental section. Application of the instant steady state analysis shows that the farther the flow rate is removed from the mean the greater will be the inherent disadvantage of cycling relative to true steady state operation. Although the sawtooth and square wave functions have the same extreme and mean values, the sawtooth function also contains flow rates closer to the mean than its extreme values. This makes it a slightly less severe disturbance than the square wave function and accounts for the 4.389 to 4.306 advantage enjoyed by the instant steady state model sawtooth variation in Table 1. It should also be noted that the advantage of the sawtooth over the square wave variation has been reduced considerably when the transient model is employed. This is because the square wave function displays more pronounced transient effects because of the greater severity in its perturbations.

The overall conversion resulting from cycling flow rates relative to that in true steady state operation also will be affected by the concentration dependence of the rate of reaction. For the case considered here, the reaction is slightly less than second order. Thus, in this system the observed effects are somewhat more pronounced than they would be if the reaction were of lower order.

The data of Table 1 also show that the phenomena which occur in the unsteady state period do provide some improvement in system performance above that which would be obtained if new steady states were established rapidly following a perturbation. However, this improvement is inadequate to overcome the inherent disadvantage in performance relative to a true steady state which occurs because of flow rate variation. The circumstances illustrated in the present study are those which will most commonly occur. That is, the rate of reaction in most systems does decrease with increasing conversion. However, cycling of flow rate could be expected to provide improved performance in reaction systems having rates which increase with increasing extent of reactions. Examples of such behavior can be found in autocatalytic reactions and in intermediate reactions occurring in a sequence of reactions in a series.

CONCLUSIONS

A mathematical model is available for the prediction of the transient responses to variations in flow rate for a tubular heterogeneous catalytic reactor in which significant adsorption effects occur. The model has been tested by comparison with experimental data for the cases of step increase, step decrease, and sawtooth cycling of flow rate. It was found to be qualitatively correct in all aspects and to provide accuracy within experimental error in many aspects.

The complete transient model is quite complex and requires a large amount of data. For estimation of gross effects, it is suggested that the dynamic operations often can be approximated by assuming that a new steady state is reached quickly following each perturbation to the system. This approach can result in an adequate understanding of a complex physical system and a large saving of time and effort. However, the user is cautioned that effects which occur during the actual unsteady state period can be accounted for only by a complete transient analysis.

Table 1. Production Rate Data for Steady State and Cycled Operation

Experimental results

Cycle number	Production rate $\times 10^4$ moles water/min.	Production rate $\times 10^4$ moles ether/min.
5 (gas sampling)	4.09	4.23
6 (gas sampling)	4.15	4.27
7 (gas sampling)	4.16	4.21
8 (gas sampling)	4.28	4.27
8 (liquid sampling)	4.27	4.16
Steady state	4.82	4.37

Numerical results

Type of flow variation	Production rate $\times 10^4$, moles of ether or water/min.
Sawtooth	
Transient model	4.42
Instant steady state model	4.389
Square wave	
Transient model	4.40
Instant steady state model	4.306
Steady state	4.53

This work indicates that for most reacting systems, periodic variation of the flow rate will result in a decrement in performance. However, there are systems where the reverse will be true. It is expected that the greatest promise in improving production rate by dynamic operation lies in the cycling of such parameters as feed concentration and temperature rather than flow rate. Such dynamic operations are also expected to be effective in improving product distribution in systems involving simultaneous reactions.

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NOTATION

F = total molar flow rate, moles/min.
P_A, P_W, P_E = partial pressure of ethanol, water, and ether, respectively, atm.
t = time, min.
v_A = liquid ethanol flow rate, cc./min.
v_{A0} = initial liquid ethanol flow rate, cc./min.

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