

# BEHAVIOUR OF CATALYTIC OXIDATION OF DILUTE COMBUSTIBLE GAS IN A JACKETED FIXED BED REACTOR UNDER FLOW REVERSAL PROCESS

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## ABSTRACT

*An experimental study of the catalytic oxidation of combustible gas in air has been made under flow reversal operation. The experiments were done using a three-zone reactor consisting of two beds packed with an inert having high heat capacity solid placed at both ends of a bed packed with catalyst. The catalyst bed was cooled by passing a fluid through a jacket surrounding the bed. The influence of the operating parameters upon the shape of temperature profiles, percent conversion and heat removal through the coolant were studied. The experiments showed that the maximum measured reactor temperature and heat removal were insensitive to changes in cycle duration and initial temperature but sensitive to feed flow rate and changes in reactant concentration.*

## INTRODUCTION

Periodic flow reversal was proposed by Russian researchers (Boreskov et al., 1977) as a means of operating a reactor without feed preheating or external heat exchange between the feed and flue gas.

Matros (1989) described various reactor-inert bed configurations related to the periodic flow reversal concept. The simplest one consists of beds filled with an inert packing placed at either end of a cylindrical reactor filled with catalyst. Once started operation of periodic flow reversal process can be commenced. Periodic flow reversal consists of preheating the feed gas to the reactor in the regenerator by cooling the bed of inert solids. Cooling sets up a rising temperature front that creeps towards the reactor inlet. Hot flue gas leaving the reactor is cooled by the regenerator at the outlet of the reactor. By a judicious choice of the cycle period, the rising temperature front can be kept according to the required one or the descending temperature front can be kept from reaching the end of the regenerator bed. Flow reversal inverts the role of the regenerator beds. The bed that cooled the product gases prior to the direction switch now becomes the inlet regenerator and heats the reactant gases, while the bed that heated the reactants now becomes the outlet regenerator that collects heat from the product gas leaving the reactor bed.

Matros (1989) observed that flow reversal was quite robust with respect to a temporary flow cut off or a decrease in reactant concentration. The autothermal character of periodic flow reversal means, however, that an increase in reactant concentration can sharply raise the reactor temperature as Eigenberger and Nieken (1988) have demonstrated. The high bed temperature that can arise has limited the application of flow

reversal to reactions of low exothermicity or to low concentrations for reactions with a high heat reaction. Matros (1989) had attacked this problem by withdrawing the reactants midway through the reactor and passing them through an external heat exchanger. This reduces the mean reactor temperature but it does not eliminate high temperature in the bed before the heat exchanger. Eigenberger and Nieken (1988) suggested control by by-passing the outlet regenerator with a portion of the product gas. Although this solves the high temperature problem for prolonged operation at a reactant concentration higher than the design value, it does not prevent an excessive temperature rise in the bed when a pulse of reactant at high concentration enters the reactor-regenerator system.

An alternate solution is to embed coolant tubes in the catalyst bed. Using boiling liquid in these tubes should permit good control of a sudden upset. High heat capacity coolant provides thermal ballast that will smooth out concentration, inlet temperature and flow rate variations. Cooling tubes offer a second advantage: the system creates a high temperature region at the inlet followed by falling temperature. This temperature profile is advantageous for equilibrium-limited, exothermic catalytic reactions. From a heat transfer and thermodynamic standpoint, a further advantage of embedded cooling tubes is that heat is withdrawn at the highest temperature in the reactor-regenerator system. The proposed design for the cooled bed appears in Figure 1.

The objective of this research program was to investigate experimentally the performance of this periodic flow reversal system which consists of a reactor and a heat reservoir / preheater. The packed beds on either end of the reactor serve as recuperators

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as has been described by Purwono (1997). The final goal was to develop sufficient understanding to design a full-scale system.

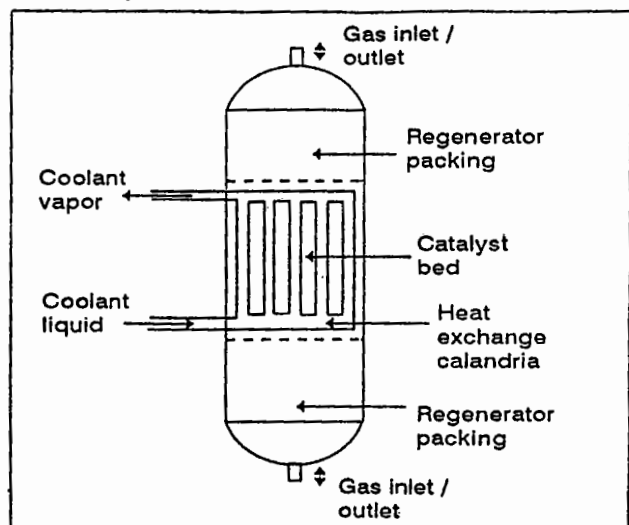


Figure 1. Schematic of a full-scale application of periodic flow reversal to a packed bed catalytic reactor with cooling of the catalyst bed.

## EXPERIMENTAL

An alternative to the coolant in tube design (Figure 1), where the catalyst was placed in the tube and coolant was circulated outside, a system was built in order to simulate the full scale reactor as it is shown in Purwono (1997).

The initial plan was to remove heat by generating steam. Unfortunately, despite the heavy insulation, a large heat loss took place so that a very small liquid flow rate was needed. Arranging for such flow rates and control of the steam draw-off proved impractical; instead, cooling was carried out by withdrawing sensible heat by water or air.

All experiments involved combustion. Performance was expressed in terms of the conversion of the gaseous fuel leaving the bed and the temperature profiles in the reactor and the regenerators. To characterize the profile, thermocouples were placed in all three sections of the system.

Most experiments were performed using a commercial shell-impregnated 0.1 % Pt on gamma-alumina catalyst (Girdler T-309) supplied as  $3.18 \times 10.3$  mm tablets. This catalyst was chosen because it was active at 200 °C. Regenerators were packed with 3.2 mm spheres of a chrome steel alloy that were non-catalytic, similar in diameter to the catalyst, and had a high heat capacity.

Propylene was used as a reactant so that the

behaviour of hydrocarbons could be examined. Its heat combustion is 2058 kJ/mol. Among the hydrocarbons, propylene has the advantage that catalytic oxidation can also be initiated at relatively low temperatures (Volts et al., 1973).

## RESULTS OF STATIONARY CYCLING STATE

### Preliminary experiment

This contribution deals only with the stationary cycling performance of this reverse flow reactor-heat exchanger design. For the design of reverse flow reactors, the following performance information is important: 1) temperature profile in the regenerator and in the catalyst bed, including the maximum temperature and its location and evolution with time, 2) heat removal in the reactor cooling system, 3) effect of reactant concentration and flow rate on the profile maximum temperature and heat removal, 4) influence of cycle period on the maximum temperature and heat removal, and 5) influence of the heat exchanger operation (counter-current vs co-current flow) and coolant heat capacity on maximum temperature and heat removal.

In the experiments, a partial, two-level, 4-factorial design was used. The "base case" of the design was feed concentration = 0.2 %, feed flow rate = 500 mL/min, initial temperature = 200 °C and cycle time = 30 min.

### Temperature profile and maximum temperature

Temperature profiles in the regenerator and the catalyst bed for the respective base cases is the same as for CO oxidation shown by Purwono (1997).

Inspection of the forward and reverse flow profiles shows that they are identical except for small variations of readings caused by small differences in the position of the tips of different thermocouples within the bed. This symmetry means that only one flow direction needs to be considered.

The temperature rises rapidly at the entrance to the catalytic bed leading to a maximum temperature within the first 5 cm of its entrance. Spacing of the thermocouples in the bed limited the resolution. The temperature drops rapidly after the peak as heat is carried in the flow direction from the combustion zone into the remainder of the catalyst bed and the second regenerator.

The evolution of the temperature profiles appears in Figure 2. The maximum measured temperature is always seen for the second thermocouple located 2.5 cm after the entrance. This suggests that the reactant

ignites within the first 1 to 2 cm of the bed. Also, the sharp temperature decrease beyond the second thermocouple suggests that combustion is complete within the first 4 cm of bed.

One minute after a flow switch, a second maximum is seen just before the end of the reactor. This second peak results from thermal inertia as it is located in the combustion zone of the previous half-cycle in which flow was in the reverse direction. Heat dissipation from convective flow and axial conduction as well as radial conduction to the cooling jacket results in cooling after the combustion zone. This produces a temperature minimum in the center of the bed. It also causes the second maximum temperature to disappear within 5 min of the switch in flow direction. After 5 min, convection from the combustion zone and radial heat loss affect the declining temperature profile seen in Figure 2.

Use of a coolant decreases the temperature in the final half of the catalyst bed. A decreasing profile is desirable in order to approximate the optimum temperature profile of an exothermic, equilibrium-limited reaction. Conversions for such reactions should be substantially higher than those attainable in an isothermal reactor of the same length.

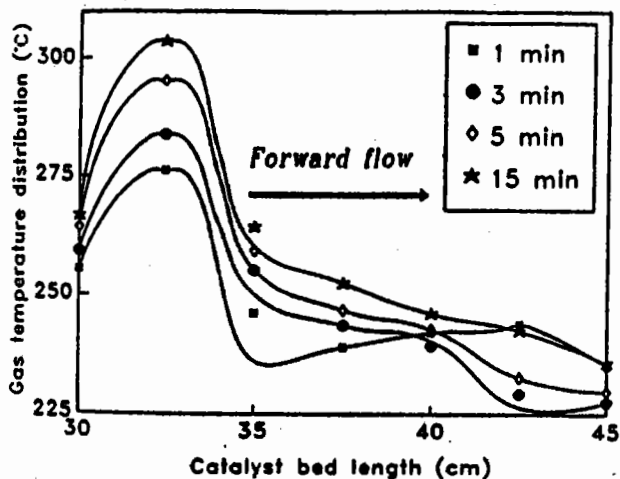


Figure 2. Evolution of temperature profiles within a half-cycle after a stationary periodic state has been reached (base-case condition).

Further measurements at times intermediate to those shown in Figure 2 show the evolution of the temperature profile. Figure 3 shows the evolution of the temperature profiles 2.5 cm downstream from the entrance, at the bed midpoint and 2.5 cm before the exit. In the combustion zone, temperature measurements just beyond the entrance in the hot spot

location increase rapidly in the first 5 min after a flow switch; thereafter, the change diminishes and becomes very small just before a switch in the feed direction. The rate of temperature change is sluggish at the midpoint of the bed. The temperature just before the reactor outlet decreases for the first 2 min and thereafter increases. This was the thermocouple that exhibited a second peak discussed in the paragraph above.

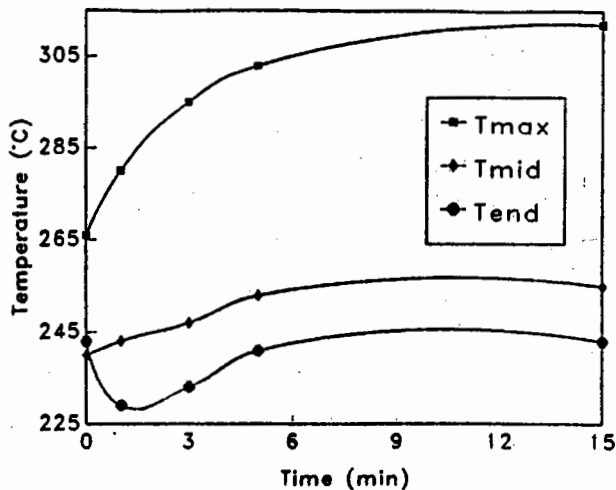


Figure 3. Evolution of temperature at three points in the catalytic bed during a half-cycle after a stationary cycling state has been attained.  $T_{max}$  is the measurement at the thermocouple located at 2.5 cm;  $T_{mid}$  is located at 7.5 cm, and  $T_{end}$  is located at 12.5 cm beyond the entrance.

#### Effect of operating variables

The effect of concentration was studied by increasing the propylene concentration from 0.2 % to 0.4 % while keeping the other variables at their base levels. Increasing combustant concentration raises temperatures throughout the catalyst and regenerator beds; however, the shape of the temperature profiles is unchanged from those in Figure 2. Figure 4 shows the effect of propylene concentrations on the maximum measured temperature and heat removal. As expected, the maximum measured temperature and heat removal increase with concentration as a result of the increased heat released. Indeed, the temperature rise at the entrance of the bed as measured by the maximum temperature should be proportional to the adiabatic temperature rise. Increasing the propylene from 0.2 to 0.4 % doubles the heat released. Accompanying these changes in feed concentration, the maximum temperature for propylene combustant increases by 95 °C, while the heat removal increases by 12.7 J/min. The

heat loss becomes more severe at the higher temperatures. The figure shows that maximum temperature and heat removal are not linear in concentration. Heat loss is one reason; another is that when combustion concentration increases, the inlet temperature and the width of the hot zone region also increase. It is heat removal and heat loss that influence the ratio of the maximum measured temperature to the adiabatic temperature rise for the system.

The temperature profile at the end of the catalyst bed is almost the same for a two-fold change in combustant concentration. This observation supports our earlier conclusion that combustion goes to completion in the first few centimeters of the bed. The higher temperatures at higher combustant concentrations augment heat removal as well as heat loss so that heat convected to the regenerator is similar for low and high propylene concentrations.

If combustant concentrations exceed a threshold, temperatures at the front of the bed rise rapidly and thermal runaway occurs. At the other extreme, the heat removal at low combustant concentration reduces bed temperatures and eventually extinguishes combustion. Although it is important to know these concentration constrains for design purposes in flow reversal, high heat losses in laboratory-scale equipment make assessment of these concentrations of doubtful value for large-scale reactors; thus, they were not considered in this study. Nevertheless, runaway was observed in several experiments.

Because complete combustion was observed in all experiments presented in this paper, the primary effect of feed flow is on the rate of heat release in the catalyst bed. In the runs of this effect, flow rate was increased from 500 to 1000 mL/min while the other variables were kept constant. The effect of feed flow rate on the maximum measured temperature and heat removal is similar to that shown in Figure 4. As flow rate doubles from 500 to 1000 mL/min, the maximum measured temperature increases by 107.1 °C for propylene oxidation. The heat removal also increases by 15.4 J/min. The maximum temperature rise is related to the ratio of the heat released to the axial heat convection which is known as the Damkohler number. According to Bathia (1991) and Gupta and Bathia (1991), in the mathematical analysis of the adiabatic flow reversal, the higher the Damkohler number, the higher the maximum bed temperature achieved. In addition, by doubling the flow rate, the heat release per unit catalyst volume about doubles and thus results in an increase of the maximum temperature. Therefore, the temperature profiles for doubling the flow rate should be the same

as those for doubling the combustant concentration. This was indeed observed.

The hot spot location is unaffected by flow rate in the range of 500 to 1000 mL/min, indicating that combustion is complete in the first few centimeters of the catalyst bed. The width of the hot region increases with flow rate as a result of convective and conductive heat flow. There is a possibility that the higher space velocity widens the combustion zone, which would also extend the hot region.

Calculation of the ratio of maximum measured temperature rise to the adiabatic temperature rise demonstrates that the ratio increases, as expected, as volumetric flow rates increase. This is caused by greater heat release at greater flow rates, whereas the adiabatic temperature rise depends only on concentration. The increase in the ratio is commensurate with flow rate eventhough the percentage of heat removed decreases as the flow rate increases. Heat losses, however, increase to balance the reduced heat removal in the coolant.

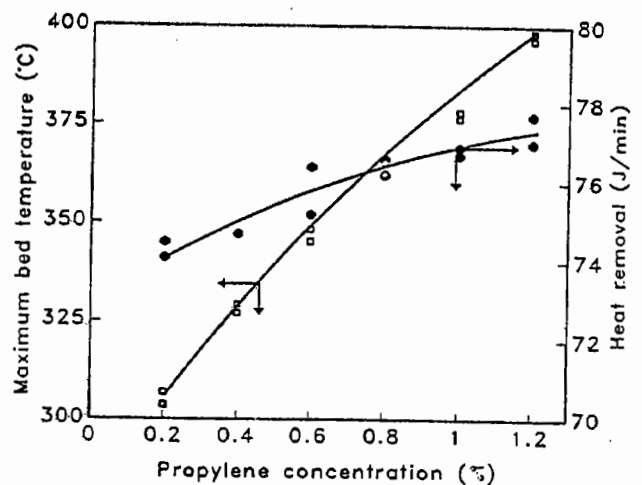


Figure 4. Effect of combustant concentration on maximum measured temperature in the catalyst bed.

Provided the cycle is not so long as to permit the cooling front in the upstream regenerator to penetrate the catalyst bed and thereby blow out combustion, the cycle period should have just a small effect on the temperature profile in the catalyst bed and on the heat removal through the coolant. Figure 5 is a plot of the maximum measured bed temperature and the heat removal by the coolant vs. cycle period. These results show that cycle period is not an important operating variable.

The slowly rising maximum bed temperature is readily explained by the development of the

temperature profile with time during a half-cycle. It can be seen in Figure 3 that the temperature peak just after the bed entrance develops very quickly and increases in magnitude appreciably during the first minute. Thereafter the maximum temperature increases more slowly with time.

Apart from the temperature profile, short cycles do not affect operability. Increasing cycle period beyond 1 to 2 hours, however, leads to blow-out as just mentioned. Blow-out due to cycle period was not observed experimentally. The maximum cycle period can be estimated from the velocity that the cold front moves through the upstream regenerator. The thermal front velocity is the distance in the regenerator bed that temperature travels in the time interval. Calculations were made for the base case experiments and are presented in Figure 6. The front velocity is a complex function of the gas velocity and temperature gradients at the point of measurement. The distinct increase of front velocity with bed temperature, shown in Figure 6, can be explained by the increasing local gas velocity as the temperature in the regenerator rises. The mass flow, of course, remains constant. The change in front velocity suggests that the dominant mechanism for heat transport in the bed is convective.

The reactor is constructed of three zones and the regenerator depth is 30 cm. Assuming the blow-out condition to be the time it takes for the cooling front to reach the entrance to the catalyst bed, and averaging the velocity in Figure 6 to be 0.05 mm/s, the maximum half-cycle duration is about 100 min. This is somewhat more than three times the maximum experimental duration. Consequently, the experimental unit could have operated with a cycle period of about 210 min without blow-out of the reaction.

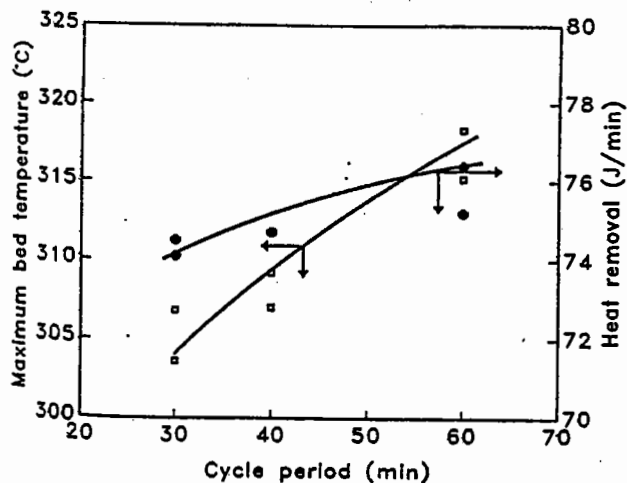


Figure 5. Effect of cycle period on the maximum temperature.

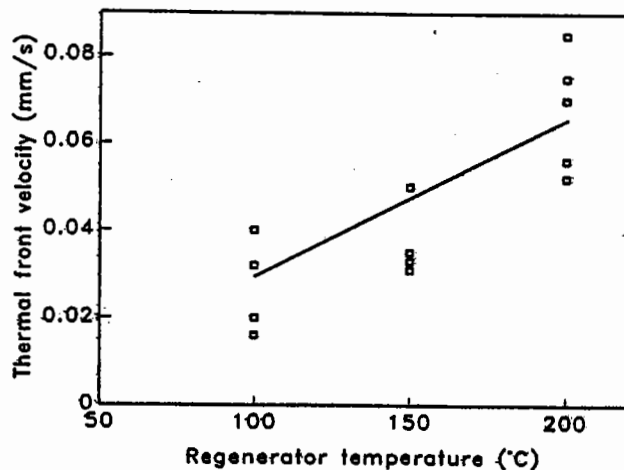


Figure 6. Thermal front velocity in the regenerator as a function of regenerator temperature.

## DISCUSSION

This paper has examined a modification of the flow reversal system developed by Matros and co-workers over the past two decades. The questions addressed in this section are 1) how the performance of the bed with heat exchange compares with the adiabatic operation used by Boreskov and Matros (1983) as well as many other publications of this research group (Matros, 1989) and 2) the potential applications of flow reversal with a cooled catalyst bed.

Adiabatic operation was approximated in this study by operating the flow reversal reactor without coolant flow. Temperature profiles in the regenerators without coolant are similar to those observed when an air coolant was used, but are 5 to 10 °C higher. However, in the catalyst bed, the temperature profile differs significantly. Comparison of successive axial profiles in the catalyst bed for operation under identical conditions but with an air coolant and with no coolant has been shown by Purwono et al. (1997). After 1 min, the maximum bed temperature is about 10 °C higher in the absence of coolant but increases to about 40 °C over the next 14 min. The bed mid-point temperature without coolant is about 25 °C higher at the end of half-cycle. The second temperature peak at the bed outlet, a souvenir of the previous cycle, persists for about 3-4 min after the change of flow direction, whereas with coolant, this souvenir vanishes within one to 2 minutes. A striking effect is the pronounced negative temperature gradient following the maximum when the coolant is used. The negative gradient for no coolant experiment after the maximum is due in part to heat loss and so would be less in a full-scale application.

Interposing an external heat exchanger between

halves of the catalyst bed as Matros (1989) proposed would reduce the maximum and mean bed temperatures. However, this mode would substitute a temperature discontinuity for part of the negative gradient. Because the peak temperature would be in the first section of the split bed, it would be less stable with respect to runaway for concentration or flow burst that might arise in an upstream process upset.

By reducing bed temperatures, the use of coolant in the catalytic bed extends the concentration and flow rate range in which periodic flow reversal can be used. Thus, the technique could be applicable for commercial, exothermic reactions such as partial oxidation or ammonia synthesis. For such reactions, it would offer the same advantages that flow reversal can be used for cold feed whereas a cold product gas is obtained. There appear to be several possible applications: 1) combustion of more concentrated waste gases that might normally be used to fire a waste heat boiler, and 2) equilibrium-limited exothermic reaction (e.g., methanol or ammonia synthesis) where the negative gradient following the sharp temperature peak at the entrance to the catalyst peak can be used to increase conversion per pass. Reactant flow rates, bed depth, coolant temperature and flow rates can be varied so that the temperature gradient matches that is needed to maintain maximum rates as conversion increases. From the discussion at the end of the previous section, it is clear that long cycle periods are preferred when the goal is to have a large negative temperature gradient to increase conversion.

Combustion of waste gases using flow reversal has the advantage that heat is discharge to the boiling fluid at a high temperature. This temperature could be controlled by a choice of flow rate and bed design. Raising temperature in a waste-heat boiler elevates steam pressure. In this application, a uniform temperature in the catalyst bed is desirable so direction switching at short intervals, e.g., 5 min, should be used.

## CONCLUSIONS

A laboratory scale non-adiabatic-flow reversal reactor with integral heat exchange was successfully operated on a dilute combustible gas stream. Integral heat exchange works well, 15 to 25 % of the heat of reaction was removed from the system. The maximum bed temperature was experimentally found to be sensitive to the changes of feed flow rates and reactant concentrations. Experimentally, it was not sensitive to the length of a cycle.

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