

CATALYTIC COMBUSTION WITH PERIODIC FLOW REVERSAL

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ABSTRACT

Operation of fixed-bed reactors with periodic flow reversal as proposed and demonstrated by Matros and co-workers is a novel mode of operation for weakly exothermic or equilibrium limited reactions. In the present paper catalytic combustion in monolith type catalysts is considered. The influence of the operating parameters upon the shape of the temperature profiles in the stationary state as well as the stability of the ignited state are studied by model calculations. The advantages of inert front- and end sections and of hot gas withdrawal from the centre of the reactor are discussed. Experimental results for the catalytic combustion of traces of methane and propene in air show general agreement with the simulations.

KEYWORDS

Catalytic combustion; periodic flow reversal; periodic operation; Matros type operation; monolith catalyst; reactor stability.

INTRODUCTION

Operation of fixed bed reactors with periodic flow reversal has occasionally been proposed in the patent literature. Major industrial implementations of this technique however have not become known until the pioneering work of Matros, Boreskov and co-workers on SO_2 oxidation [1 - 3]. In fixed-bed reactor operation with periodic flow reversal the front and end parts of the catalyst bed act as regenerative heat exchangers for feed and effluent allowing weakly exothermic reactions to be operated autothermally at high reaction temperatures. Thus catalytic combustion of traces of undesired components in air should be well suited for this way of operation as was pointed out in a patent by Wojciechowski [4]. It is the aim of this contribution to discuss the influence of the various reaction and reactor parameters and to present experimental results of catalytic combustion in monolith catalysts with periodic flow reversal.

1. Start-up and stationary state

In fixed bed reactors the feed gas has to be heated up above ignition temperature in order to start the catalytic reaction. In case of the adiabatic catalytic combustion reaction in Fig. 1 the steady state temperature and conversion profiles labeled 1 are established if the feed temperature is 600°C . If the feed temperature is lowered to ambient a creeping reaction front (profiles 2, 3 ...) slowly moves out of the reactor until the reaction is completely extinguished. The phenomenon of creeping or wandering reaction front has obtained considerable attention in the chemical reaction engineering literature [e.g. 5 - 8] since it was first discussed by Wicke and co-workers [9, 10].

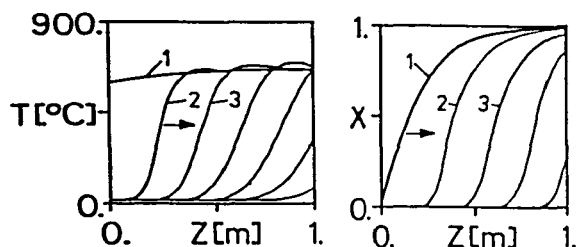


Fig. 1:
Moving temperature and conversion fronts
after step decrease of feed temperature.

1 steady state profiles;
2, 3 transient profiles every 200 sec.

If the flow direction is reversed periodically prior to extinction, the reaction zone may get trapped inside the catalyst bed (Fig. 2). It usually takes a large number of cycles until the final stationary solution is established. Figs. 2 b, c give the corresponding temperature and conversion profiles immediately prior to flow reversal. The final stationary solution (Fig. 2c) is no steady state in the usual sense but consists of profiles moving between the depicted extreme

positions where the movement is exactly repeated in each cycle. The figures show that autothermal operation with reaction temperatures of 800°C and ambient feed temperature is possible in spite of the fact that the adiabatic temperature rise in the example is only 50°C. This is due to the fact that the front and end sections of the catalyst bed act as regenerative heat exchangers.

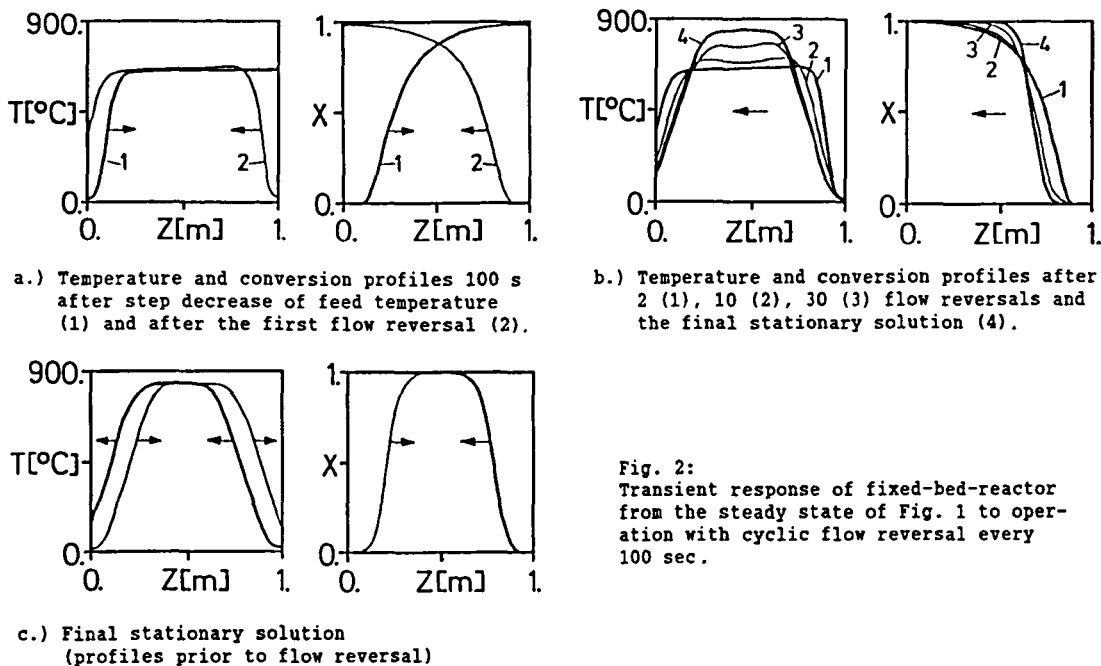


Fig. 2:
Transient response of fixed-bed-reactor from the steady state of Fig. 1 to operation with cyclic flow reversal every 100 sec.

2. Mathematical model and numerical method

It is well known that a quasihomogeneous spatially one dimensional axial dispersion model is able to represent the basic features of fixed bed reactor dynamics. Since in the following examples the gas residence time is in the order of 1 sec, the continuity equation and the mass balance can be considered in quasi steady state as compared to the energy balance. Two different model versions have been used in the simulations. The first version assumes a first order rate velocity, constant gas density ρ_G and constant flow velocity v which allows for the following dimensionless form of the model equations (dimensionless length ξ , conversion X , dimensionless temperature θ see Notation).

$$\text{Mass balance:} \quad 0 = \frac{1}{Pe_c} \frac{\partial^2 X}{\partial \xi^2} - \frac{\partial X}{\partial \xi} + k^* (1-X) e^{-\frac{E^*}{v + v^*}}$$

$$\text{Energy balance:} \quad \frac{\partial v}{\partial \tau} = \frac{1}{Pe_t} \frac{\partial^2 v}{\partial \xi^2} - \frac{\partial v}{\partial \xi} + k^* (1-X) e^{-\frac{E^*}{v + v^*}}$$

Boundary conditions:

$$\left. \frac{\partial X}{\partial \xi} \right|_{\xi=0} = Pe_c X \Big|_{\xi=0}, \quad \left. \frac{\partial X}{\partial \xi} \right|_{\xi=1} = 0, \quad \left. \frac{\partial v}{\partial \xi} \right|_{\xi=0} = Pe_t v \Big|_{\xi=0}, \quad \left. \frac{\partial v}{\partial \xi} \right|_{\xi=1} = 0$$

The model behaviour can therefore be characterized by the following operating parameters:

$$\text{dimensionless rate constant} \quad k^* = k \frac{I_1}{v}; \quad \text{dimensionless activation energy} \quad E^* = \frac{E/R}{\Delta T_{ad}};$$

$$\text{mass and heat Peclet numbers} \quad Pe_c = \frac{v L}{D}; \quad Pe_t = \frac{v \varepsilon \rho_G c_p G L}{\lambda};$$

$$\text{dimensionless cycle time} \quad \Delta \tau = \frac{\rho_G c_p G v \varepsilon}{\rho c_p L} \Delta t.$$

Their influence will be discussed in following subsections.

Table 1 gives the parameter values used in the simulations unless different values are stated in the figure captions. They refer to a combustion reaction for traces of organic compounds in air in a ceramic honeycomb catalyst.

For design calculations (Fig. 10 to 12) a model version accounting for axially varying flow velocity and density, different catalyst sections and heat transfer to the surroundings was used. Details of this model will be published in /12/.

In both cases the numerical technique applied was a modified Crank-Nicolson method with automatic space grid adjustment comparable to the one given in /11/. Usually between 100 to 200 grid points were used. Stationary states were approached by dynamic simulation until no further change in subsequent cycles was observed. This resulted in rather large computer time consumptions, for a stationary solution usually in the order of 1 CPU hr on a μ VAX II.

3. Influence of model parameters on the stationary state.

To examine the influence of the above defined operating parameters, simulations have been performed in which representative parameters are varied in a reasonable range. In the following figures only stationary solutions prior to flow reversal (similar to Fig. 2c) are shown. An arrow marks the current direction of flow.

Main points to be discussed are the shape and the height of the stationary temperature profile. Since the feed concentration was kept constant and total conversion was obtained throughout the cycle period, the heat generated (and removed) was the same in the following examples. The maximum temperature T_{max} in the catalyst thus depends only upon how much heat is accumulated under different operating conditions.

3.1 Rate constant

Fig. 3 shows the influence of the rate constant k . Surprisingly, neither the front nor the end parts of the temperature profiles are affected by the rate constant. The maximum temperature shows an apparent wrong way behaviour: the lower the rate constant the higher the maximum temperature. This can probably be understood best if it is realized that in periodic operation the front and end sections of the catalyst bed act as regenerative heat exchangers. The better the heat exchange, i.e. the longer these sections can act as regenerators and not as reactors, the more heat is accumulated and the higher is the reactor peak temperature. This condition is obviously better fulfilled with a lower reaction rate constant. With a very rapid reaction most of the heat of reaction is already liberated close to the ends of the catalyst bed from where it is transferred more easily out of the reactor. If the rate constant is reduced below a certain limit total conversion can not be sustained over the whole length of the cycle period and the maximum temperature drops again. As discussed in Section 4 this results in a complete extinction of the reaction.

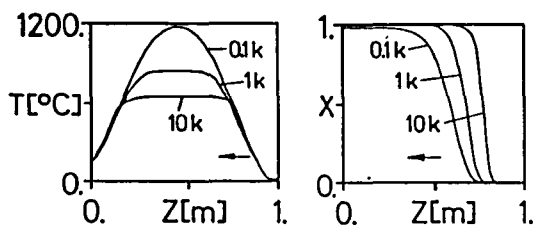


Fig. 3:
Influence of rate constant k on the stationary solution.

3.2 Activation energy

The influence of the activation energy can be seen in Fig. 4. Here the rate constants for the two activation energies have been adjusted so that at 500°C the reaction rates are equal. Again an apparently wrong way behaviour can be observed: with lower activation energy a higher maximum temperature is obtained. The explanation is similar to the one discussed above for the rate constant. As can be seen from the conversion profiles, with a large activation energy the heat is liberated in a narrow front closer to the right end of the catalyst bed.

The fact that neither the slopes of the temperature profiles nor the exit temperature are affected substantially by either the rate constant or the activation energy can be attributed to the fact that in all examples the same amount of heat generated has to be transferred out of the reactor by convection in the same time period.

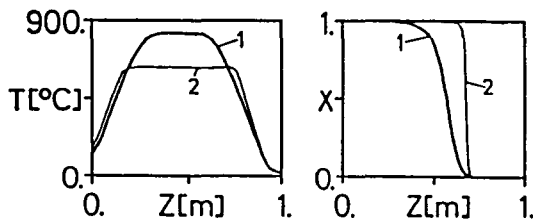


Fig. 4:
Influence of activation energy. The reaction rate at 500°C is the same in both cases.
Switching time: 100 sec
1 $E/R = 8000$ K
2 $E/R = 30000$ K.

3.3 Axial dispersion

It is well known in fixed bed reactor modelling that the influence of the axial dispersion of heat dominates over that of mass if a strongly exothermic reaction is considered. Therefore the axial dispersion of mass will not be discussed separately, the heat and mass Pe-numbers have been set equal in the following examples. This time the expected behaviour is observed (Fig. 5). The stronger the axial dispersion i.e. the lower the Pe-number, the more heat is conducted to the ends of the fixed bed. Consequently, less heat accumulation results in a lower maximum temperature and a smaller slope of the temperature profiles.

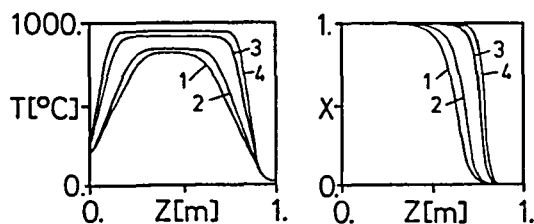
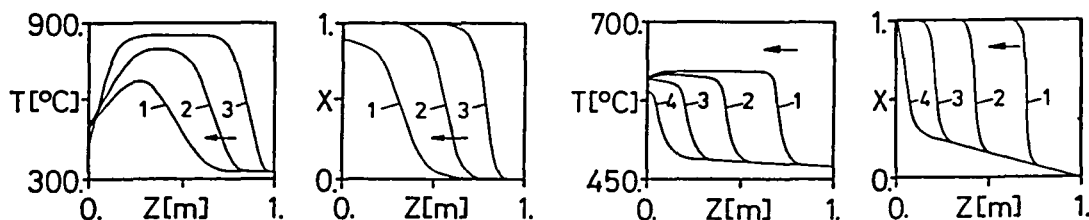


Fig. 5:
Influence of dispersion ($Pe=Pe_c=Pe_t$).
1 $Pe = 150$
2 $Pe = 200$
3 $Pe = 800$
4 $Pe = 1200$

3.4 Cycle period

The influence of the cycle period is again in accord with intuition. The longer the period, the more heat accumulated tends to be transferred over the end sections of the reactor. Hence the maximum temperature will decrease with increasing cycle period (Fig. 6). Above a certain maximum period the stationary temperature profile does not allow for total conversion over the whole length of the cycle (see profile 1 in Fig. 6a). If the cycle period is further increased, total extinction results. The maximum allowable cycle period (extinction limit) turns out to be larger with higher activation energy (Fig. 6, 7) but it always lies in the order of $\Delta\tau = 1$, the time span a heat wave needs to travel through the reactor packing.



a.) Inlet gas temperature: 330°C
E/R: 8000 K;
1 cycle period 500 sec,
2 300 sec, 3 100 sec.

b.) Inlet gas temperature: 480°C
E/R: 30000 K;
1 cycle period 400 sec,
2 800 sec, 3 1100 sec, 4 1300 sec.

Fig. 6:

Influence of cycle period. $\Delta t = 1100$ sec corresponds to $\Delta\tau = 1$.

4. Stability

It is obvious that the operation of a fixed bed reactor with cyclic flow reversal is closely connected with a stability problem. Two stable stationary solutions are possible: an extinguished one where no or only minor conversion takes place and the temperature is everywhere close to feed temperature, and the ignited state that has been discussed so far. Since both stationary solutions incorporate a complex dynamic behaviour no standard stability analysis is applicable. Only a few simulation results will be discussed instead. The most obvious parameter for a stability diagram is the cycle period. As shown in Fig. 7 the familiar hysteresis between ignition and extinction can be obtained if the cycle period is varied. The detection of the ignition and extinction limits requires rather time consuming calculations, examples of which are given in Figs. 8 and 9. Obviously a self-ignition is only possible if a noticeable reaction and hence heat evolution takes place at feed temperature (Fig. 9).

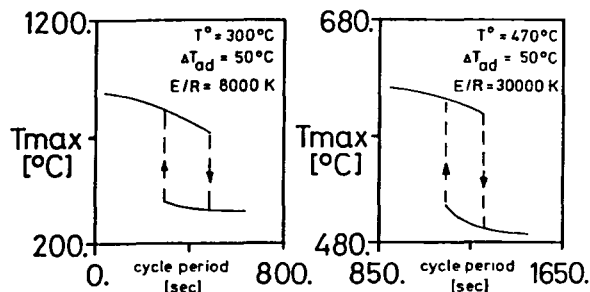


Fig. 7:
Ignition/extinction hysteresis (maximum temperature versus switching time) with different activation energy and feed temperature.

A different shape of the stability diagram is obtained if the rate constant k instead of the cycle period is changed. As was pointed out under 3.1 the maximum temperature *increases* with decreasing reaction rate up to a limit value which corresponds to the profile with $0.1 k$ in Fig. 3.

5. Operational considerations

In this section a few operational considerations will briefly be discussed using simulation results based upon the aforementioned second model version. Details of the model, its parameters and further results will be published in /12/.

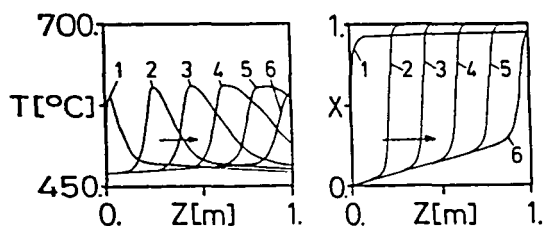


Fig. 8:
Profiles within one cycle period close to the extinction limit ($E/R = 30000$ K).
Plot after 1 sec (1) and every 260 sec (2)...(6).

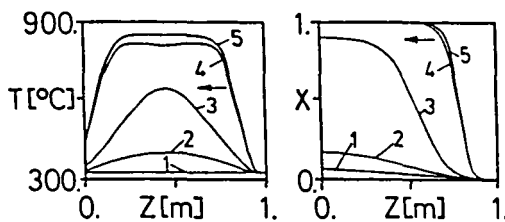


Fig. 9:
Ignition of reaction.
Flow reversal every 100 sec. Plot after 1 sec (1), 20000 sec (2), 30000 sec (3), 40000 sec (4) and 80000 sec (5).

5.1 Inert front and end sections

The above mentioned results make it obvious that high maximum temperatures can be obtained if the reaction in the front and end sections of the catalyst bed is inhibited i.e. if inert front and end sections will be used. This has already been proposed by Wojciechowski /4/. As can be seen in Fig. 10 the maximum temperature is the higher the smaller the active portion of the packed bed. A sudden extinction from a profile with the highest maximum temperature takes place if the active portion is reduced below a certain minimal value.

5.2 Maximum temperature control

In the catalytic combustion of traces of undesirable components in air the feed concentration may vary considerably with time. It is therefore necessary to prevent an extinction due to a low feed concentration as well as an overheating of the bed due to a rich fuel mixture. It is common practice to add additional fuel (e.g. propane, methane) if the gas is too lean. The case of a too rich gas mixture can pose more severe problems especially if monolith catalysts with a low heat capacity are used. In this case, the tolerable temperature limit may be exceeded within one cycle period if the feed concentration is too high; the only obvious counter-measure is the dilution of the feed with additional air.

If the rise in the feed concentration is not too strong, the prolongation of the cycle period is an obvious alternative (see Section 3.4). Another possibility would be a heat sink in the middle of the packed bed, e.g. a heat exchanger.

There is, however, a much simpler and equally effective method consisting of the withdrawal of a portion of hot gas from the centre of the catalyst bed. Fig. 11 gives some simulation results. As can be seen it is possible to obtain a flat temperature profile at a desirable temperature level. This technique allows utilization of heat at high temperatures from the combustion of a lean, not selfburning gas.

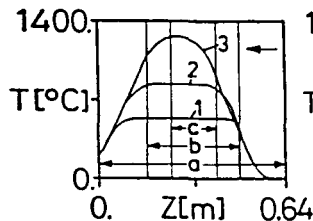


Fig. 10

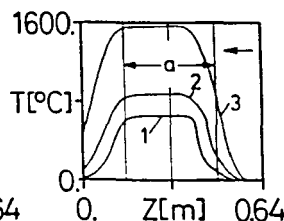


Fig. 11

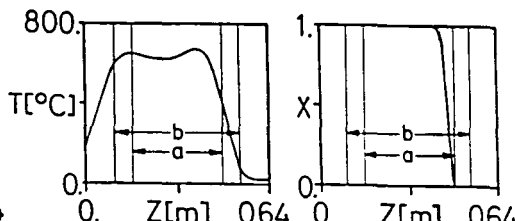


Fig. 12

Fig. 10:
Influence of inert front and end sections.
1 active catalyst in a, 2 active catalyst in b, 3 active catalyst in c.

Fig. 11:
Influence of gas withdrawal.
 $\Delta T_{ad} = 100$ K, $\Delta t = 60$ sec, active zone in a;
15% gas withdrawal (1), 10% (2), 0% (3).

Fig. 12:
Simulation results with radial heat losses and compensatory heating.
Active catalyst in a, electric heating in b.

5.3 Radial heat losses and compensatory heating

In an experimental set-up of laboratory scale radial heat losses will inevitably prevent a purely adiabatic operation. In order to design a set-up in which these effects are minimized via compensatory electrical heating a series of simulations have been undertaken. The aforementioned second version of the model with additional energy balance equations for wall and insulation was used. Fig. 12 shows one of the final results corresponding to the experimental set up given in Fig. 11. It can be seen that in spite of the compensatory heating a shallow dent in the middle of the temperature profile cannot be avoided. It results from the fact that the main reaction zones always remains close to the ends of the active section.

6. Experimental set-up and first experimental results

A sketch of the experimental set-up is given in Fig. 13. The reactor section consists of a tube of 50 mm inner diameter and a total length of 345 mm. Inert and active sections of the packing

were made out of commercial ceramic monoliths for automotive exhaust purification which were kindly provided by DEGUSSA. The square channels of the monolith are 1 mm wide with a wall thickness of 0.2 mm resulting in a void fraction of $\epsilon = 0.8$. The active portions contain a wash coat with precious metals as catalyst. 14 thermocouples are inserted in the channels of the monolith to measure the temperature profile at different positions. Temperatures are automatically recorded and displayed as temperature profiles over the reactor length. Heating wires for compensatory heating are placed around a first layer of insulating material of 20 mm thickness upon which a second layer of insulation was positioned. The compensatory heating is used for start-up purposes; in normal operation, its temperature is controlled to a value close to the one which is established in the centre of the reactor.

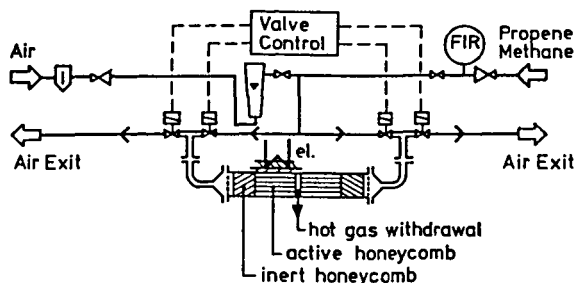


Fig. 13:
Experimental set-up

The experiments show the same qualitative behaviour as discussed in Section 3. Fig. 14a gives results for the oxidation of traces of methane and propene in air, the adiabatic temperature rise being equal in both runs. Since methane is much more "inert" than propene (lower rate constant) a higher reactor temperature results for the methane oxidation, which is in general accord with Section 3.1.

Fig. 14b shows the influence of the cycle period with propene as feed gas. The results agree with the findings in section 3.4.

Quantitative comparisons between experiments and simulations are impeded by the peculiarities of radial heat loss and compensatory heating in our experimental set-up. However satisfactory agreement can be obtained if the wall heat transfer coefficient is properly adjusted (Fig. 14c).

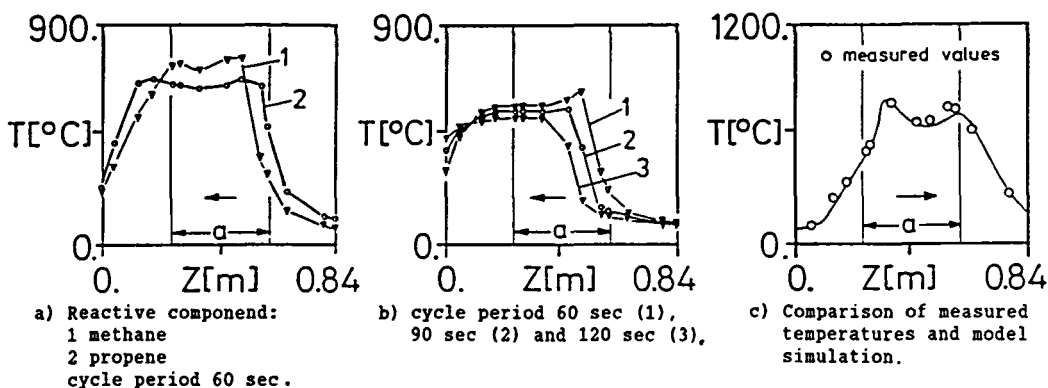


Fig. 14:
Experimental results obtained from the laboratory reactor.
 $\Delta T_{ad} = 100$ K, active catalyst in a.

ACKNOWLEDGEMENT

The provision of monolith oxidation catalysts through DEGUSSA AG, Hanau is gratefully acknowledged.

TABLE 1

inlet concentration of reactive species	c^*	$1.21\text{E-}04$ kmol/m^3
diffusivity constant	D	$5.\text{E-}03$ m^2/sec
activation temperature	E	8000. K
heat of reaction	$-\Delta H_r$	206000. kJ/kmol
rate constant of reaction	k	29732. sec^{-1}
reactor length	L	1. m

feed temperature	T^*	293. K
gas velocity	v	1. m/sec
heat capacity of gas	$\rho_G c_{pG}$	0.5 $\text{kJ/m}^3/\text{K}$
heat capacity of fixed bed	$\bar{\rho} \bar{c}_p$	400. kJ/m^3
effective axial heat conductivity	λ	$2.06\text{E-}03$ $\text{kJ/m}^3/\text{K}$
bed void fraction	ε	0.8
switching time (cycle period)	Δt	100 sec

NOTATION

c	concentration of reactive species, kmol/m^3
c_{pG}	specific heat capacity of gas, kJ/kg/K
D	diffusivity coefficient, m^2/sec
E	activation energy, kJ/kmol
E^*	dimensionless activation energy $E^* = E / (R \Delta T_{ad})$
$(-\Delta H_r)$	heat of combustion, kJ/kmol/K
k	rate konstant, sec^{-1}
k^*	dimensionless rate konstant $k^* = k L/v$
L	reactor length, m
Pe_c	Peclet number for mass transfer
Pe_t	Peclet number for energy transfer
R	universal gas constant, kJ/kmol/K
t	time, sec
Δt	switching time (cycle period), sec
T	Temperature, K
ΔT_{ad}	adiabatic temperature rise, K $\Delta T_{ad} = (-\Delta H_r) c^0 / (\rho_G c_{pG})$
v	gas velocity, m/sec

x	conversion of reactive species $x = 1 - c / c^0$
z	axial coordinate, m

Greek letters :

ξ	dimensionless axial coordinate $\xi = z / L$
ε	bed void fraction
ν	dimensionless temperature $\nu = T - T / \Delta T_{ad}$
λ	effective axial heat conductivity, $\text{kJ/m}^3/\text{K}$
ρ_G	gas density, kmol/m^3
$\bar{\rho} \bar{c}_p$	overall heat capacity of gas and monolith, $\text{kJ/m}^3/\text{K}$
τ	dimensionless time $\tau = (\rho_G c_{pG} v \varepsilon t) / (\bar{\rho} \bar{c}_p L)$
$\Delta \tau$	dimensionless cycle time
ν^*	$\nu^* = T / \Delta T_{ad}$

Superscript:
entrance condition

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