

Equations (6) and (7) are combined to give the concentration of the solid component in the bulk liquid phase as follows

$$B_i = \frac{\left(\frac{m}{a}\right) B_s}{\frac{1}{\sinh m(\delta - \lambda)} + \left(\frac{m}{a}\right)} \quad (9)$$

The rate of gas absorption into the slurry is then calculated by eqn (9) and either eqn (4) or (5)

When the solid concentration is high or the interfacial area in the absorber is small, the second term in the denominator of eqn (9) becomes dominant over the first one and  $B_i$  approaches  $B_s$ . If the concentration of the absorbed gas at the liquid-gas interface is high, the position of the reaction plane,  $\lambda$ , approaches  $\delta$  and the first term in the denominator becomes much larger than the second one. Then, the value of  $B_i$  approaches zero.

To see the effect of the changes in  $m$  and  $A^*$  on the bulk concentration of the dissolved solid component, a numerical example is solved by the model of Uchida *et al* (eqn 5) and the results are shown in Fig. 1. The values used in the calculation are given in the same figure. This figure supports the above discussion. The similar results are also obtained by Ramachandran and Sharma's model.

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#### NOTATION

$A$  gas being absorbed or concentration of species A, moles/cm<sup>3</sup>  
 $a$  interfacial area, cm<sup>2</sup>/cm<sup>3</sup>

$A^*$  interfacial concentration of A, moles/cm<sup>3</sup>  
 $A_p$  surface area of solid particles, cm<sup>2</sup>/cm<sup>3</sup> slurry  
 $B$  concentration of dissolved solid component, moles/cm<sup>3</sup>  
 $B_i$  concentration of dissolved solid component in the bulk liquid phase, moles/cm<sup>3</sup>  
 $B_s$  saturation solubility of solid, moles/cm<sup>3</sup>  
 $D_A$  diffusivity of A in liquid phase, cm<sup>2</sup>/sec  
 $D_B$  diffusivity of B in liquid phase, cm<sup>2</sup>/sec  
 $k_L$  liquid film mass transfer coefficient in the absence of chemical reaction, cm/sec  
 $k_s$  mass transfer coefficient for solid dissolution in the absence of chemical reaction, cm/sec  
 $m$   $\sqrt{(k_s A_p / D_B)}$   
 $R$  rate of absorption of A into solid suspending solution, moles/cm<sup>2</sup> sec  
 $R_d$  rate of solid dissolution, moles/cm<sup>2</sup> sec  
 $R_B$  rate of diffusion of solid component from the bulk liquid phase to the liquid film, moles/cm<sup>2</sup> sec  
 $x$  distance into the liquid film, cm  
 $z$  number of moles of solid dissolved reacting with each mole of a

#### Greek symbols

$\delta$  liquid film thickness, cm  
 $\lambda$  reaction plane, cm

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## Ignition and extinction of autothermal reactors at periodic operation

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The influence of enforced concentration variations on autothermal operation was studied experimentally. The oxidation of propylene at a platinum gauze was chosen as example. At periodic processing the reactor could be operated within the temperature hysteresis.

In autothermal reactors the enthalpy of exothermic reactions can cause temperature instabilities at the catalyst, steep radial and axial temperature profiles and can lead to problems with the used materials. Considering consecutive reactions the preferred intermediate products are often difficult to isolate because of the fast rate of complete oxidation at high temperatures. To obtain the intermediate products tube bundle reactors with large cooling areas operating at high gas velocities become necessary.

Periodic operation may solve the mentioned problems in a simple way. Besides the feed concentration temperature, pressure or residence time may be varied periodically. Moreover, the reactor can be overloaded for short times—like in a combustion engine—and thus its performance can be remarkably improved.

Similar aspects of instationary processing in chemical reaction engineering have already been discussed theoretically, e.g. by Horn and Bailey [1-4] and experimentally [5, 6].

Considering a first order catalytic oxidation of a hydrocarbon in a CSTR at steady state the heat production by reaction must be equal to the heat transfer rate

$$-\Delta H_R K_{\text{eff}} C_{\text{hydro}} = \alpha(T_c - T_0) \quad (1)$$

It follows eqn (2), a straight line

$$k_{\text{eff}} = \frac{\alpha}{-\Delta H_R C_{\text{hydro}}} (T_c - T_0) = f_1(T_c) \quad (2)$$

The effective rate constant as a function of temperature can be described by eqn (3) [7, 8]

$$k_{\text{eff}} = \frac{k_{\text{max}} e^{-E_c/RT_c} \beta_{\text{max}} e^{-E_m/RT_c}}{k_{\text{max}} e^{-E_c/RT_c} + \beta_{\text{max}} e^{-E_m/RT_c}} = f_2(T_c) \quad (3)$$

In Fig. 1 function  $f_2(T_c)$  and  $f_1(T_c)$  for two inlet temperatures  $T_0$  are presented schematically. The dashed lines show the borders of the region for the catalyst temperatures and the effective reaction rate constants not obtainable at steady state processing.

The variation of the inlet hydrocarbon concentration in the shape of a square wave function can be used to operate in the hysteresis region. Variations of the inlet concentration (referring to the mean value)  $C^*$  between 0 and 2 result in a variation of the gradient  $f_1$  as shown in the inequation (4)

$$\infty > f_1 > \frac{1}{2} \frac{\alpha}{-\Delta H_R C_{\text{hydro}}} \quad (4)$$

To operate a reactor within a hysteresis in the mentioned way a distinct range of the frequency and of the inlet temperature must be observed.

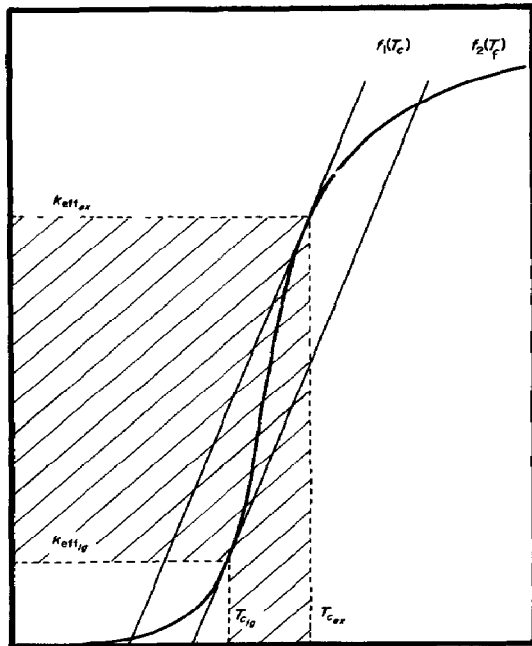


Fig 1 Ordinate  $k_{eff}$  (cm/sec) (reaction rate constant) abszisse  $T_c$  ( $^{\circ}\text{C}$ ) (temperature of catalyst) Schematic diagram of eqn (3) ( $k_{eff} = f_2(T_c)$ ) and eqn (2) ( $k_{eff} = f_1(T_c)$ ) Subscripts *ig*, ignition, *ex*, extinction

#### APPARATUS

A vertical glass tube with an inner diameter of 28 mm was chosen as reactor (Fig 2) An autothermal behaviour was approximated by a vacuum jacket and a heated air bath A platinum gauze was horizontally tightened in the tube (diameter of wires 0.06 mm, 1024 mesh/cm<sup>2</sup>, transparency 0.65, weight 0.377 g, heat capacity (300 $^{\circ}\text{C}$ ) 0.033 cal/g  $^{\circ}\text{C}$ , total surface 7.5 cm<sup>2</sup>) The advantages of this construction were simple geometry of the equipment, small pressure drop, no influence of pore diffusion on the reaction rate and small heat capacity The dosing equipment

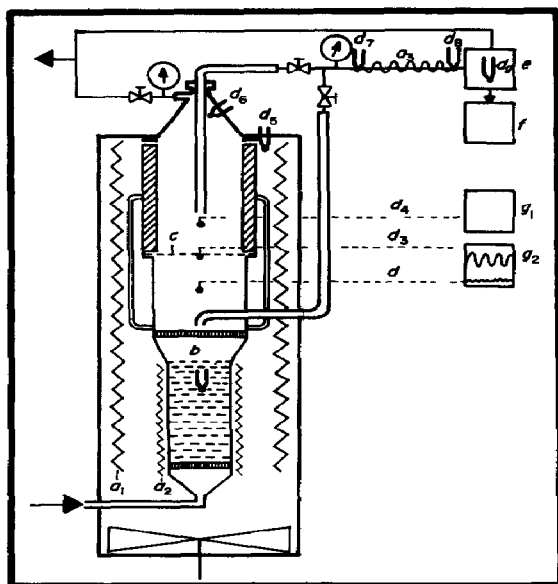


Fig 2 Experimental Setup (a) filament winding, (b) fluidized bed, (c) platinum gauze, (d) thermocouple, (e) automatic gas sampler, (f) gas chromatograph, (g) recorder

allowed a separate dosage of hydrocarbon, oxygen and helium Full details of the reactor are given in [9]

Concentration variations formed like a square wave function could be generated by magnetic valves In a period the reactants were completely replaced by helium during half the time of the period This arrangement made it possible to switch between reactants and helium at constant volumetric flow without any pressure fluctuations The reaction could be followed analytically and thermally For this purpose the inlet and outlet temperature were measured by thermocouples A tiny thermocouple welded on the platinum gauze was used to measure the temperature of the catalyst The gas was analysed gaschromatographically before and behind the catalytic gauze As the concentrations of the reactants as a function of time were detected discontinuously the singular analyses were carried out at different times after the beginning of a period The results taken from 25 different periods were combined This sampling technique was possible due to the high reproducibility of the concentration variations controlled by exact electronic clocks

#### EXPERIMENTAL CONDITIONS AND RESULTS

The ignition and extinction hysteresis for different inlet concentrations was experimentally determined at stationary operation Table 1 summarizes the experimental conditions

The temperatures given indicate the situation immediately after ignition The mean residence time is calculated from the molar flow ( $n$ ) by means of the catalyst and reactor data using an average gas temperature The heat produced is calculated from the conversion  $U$  and the reaction enthalpy  $\Delta H_R$  for complete combustion The heat produced by reaction is not only transferred by the reaction gas passing through the reactor A great deal of the developed heat leaves the reactor by radiation and by heat transfer to the reactor walls Figure 3 shows the temperature of the catalyst as function of the inlet temperature for the experimental conditions given in Table 1

The measured temperatures of the catalyst shortly before and after ignition as well as before extinction of the reaction, the inlet

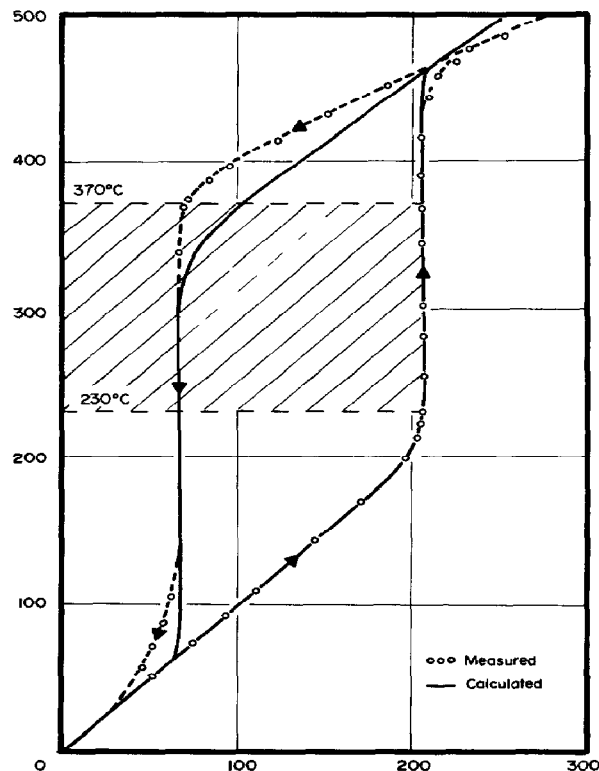


Fig 3 Ordinate  $T_c$  ( $^{\circ}\text{C}$ ) (temperature of catalyst) abszisse  $T_0$  ( $^{\circ}\text{C}$ ) (inlet temperature) Temperature hysteresis for an inlet concentration of propylene of 1.8 vol%

Table 1 Experimental conditions for a typical run (stationary operation)

Inlet concentrations		$p$ [atm]	
C <sub>3</sub> H <sub>6</sub>	[vol%] 1.8	$n$ [mmole/sec]	0.496
O <sub>2</sub>	[vol%] 8.1	$\tau$ [msec]	~1
He	[vol%] 90.1	$U$ [-]	0.90
Temperatures		$\Delta H_r$	[kcal/mole]
$T_0$	[°C] 205	heat produced	3.68
$T_c$	[°C] 468	$C_{p, gas}$	5.2
$T_e$	[°C] 273	heat transferred to gas	0.175

temperature at ignition and extinction and the concentration of the hydrocarbon in the fluid (at 4 different inlet concentrations of propylene 1.0, 1.2, 1.4 and 1.8 vol%) were taken to determine the kinetic parameters of eqn (3). The parameters obtained by nonlinear regression analysis are

$$\begin{aligned} E_{ch} &= 30.0 \text{ (kcal/mole)} \\ E_m &= 1.0 \text{ (kcal/mole)} \\ k_{max} &= 1.9 \times 10^{12} \text{ (cm/sec)} \\ \beta_{max} &= 7.74 \text{ (cm/sec)} \end{aligned}$$

Using these parameters the temperature hysteresis could be calculated. The result can be seen in comparison to the measured values in Fig 3.

In order to get some information of the system's dynamic properties the concentration of the intermediate product (CO) and of the final product (CO<sub>2</sub>) as well as the temperature of the catalyst were measured during a starting up procedure. The results are shown in Fig 4. The inlet concentrations of the reactants were twice as high as given in Table 1 in order to simulate the first half-period of a symmetric square wave inlet function of very low frequency. Thus (taken into account that in the second half of the period there are no reactants) the average inlet concentrations will be the same as given in Table 1. By means of the preheater the starting temperature of the catalyst was set to 505°C so that there was an immediate ignition when the reactants reached the catalyst. It can be seen by the late maximum of the temperature of the catalyst that the system is ruled by the heat capacity. Due to the storage capacity for mass of the system there is an overshooting of the carbon dioxide concentration during the starting up procedure so that for a short time a formal yield of more than 100% results. Moreover it can be seen that the storage capacity for carbon monoxide (due to the better adsorption at the catalyst) is greater than for carbon dioxide. The character of carbon monoxide as intermediate product can be recognized from the fact that after some seconds the yield of carbon dioxide increases at the expense of carbon monoxide. From the starting up procedure shown in Fig 4 a suitable length for the first half-period of a symmetrical square

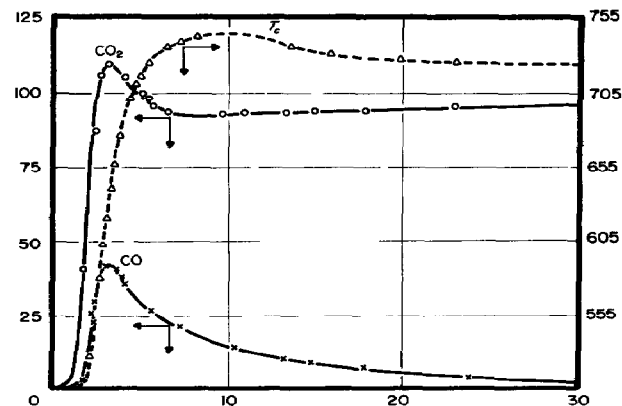


Fig 4 Ordinate (left)  $\eta$  (%) (yield) Ordinate (right)  $T_c$  (°C) (temperature of catalyst) Abscisse  $t$  (sec) (time) Oxidation of propylene at a platinum gauze-starting up procedure

wave inlet function can be estimated between 2 and 10 sec so that the most interesting range for the length of period should be between 4 and 20 sec.

By means of periodic operation it was now tried to keep the reaction in the hysteresis range not obtainable at steady state. Considering Fig 1 it can be understood that for this purpose the inlet temperature should be near the value needed for ignition at steady state. Figure 3 shows that with an inlet concentration of propylene of 1.8 vol% the range of the temperature of the catalyst not obtainable at steady state is between 230 and 370°C. The results shown in Fig 5 were obtained at an inlet temperature of 200°C. The time is to be read from the right side to the left because the figure is a copy of the original registration diagram.

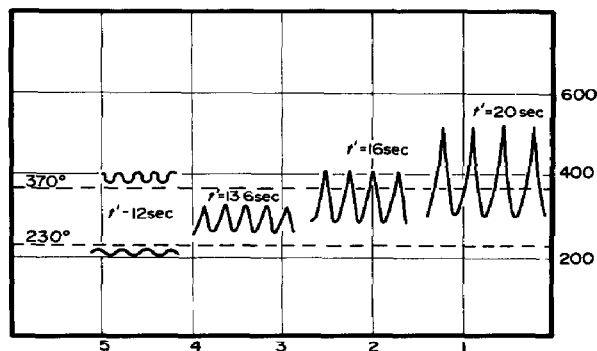


Fig 5 Ordinate  $T_c$  (°C) (temperature of catalyst) Abscisse  $t$  (sec) (time) Measured oscillations of the temperature of the catalyst in the hysteresis region for different lengths of period ( $C_{h_2} = 1.8$  vol%)

Periodic operation allows to keep the mean temperature of the catalyst as well as the upper and lower temperature of a period in the range not obtainable at stationary processing. Shape and amplitude of the oscillation are dependent on the length of the period as well as on the heat capacity of the system. It is interesting to compare the results for lengths of periods of 12, 13.6 sec. At the shorter periods the effective changes of the temperature at the catalyst are so small that the reactor nearly works like a stationary one. The reaction is either ignited or extinguished. The temperature of the catalyst oscillates near the upper or the lower stable operating point. With the apparatus shown in Fig 2 the minimum length of period to keep the temperature oscillation within the range of hysteresis is about 13.6 sec. With increasing length of period oscillations are generated with sharp temperature maxima. They are caused by retarded ignition and a quick conversion of the reactants afterwards.

The possibility of working in the hysteresis region is not restricted to thermal instabilities. With kinetic instabilities similar operation is possible. This is experimentally shown in [10].

#### DISCUSSION

By measurements of the temperature and conversion hysteresis the range of the temperature of the catalyst not obtainable at steady-state could be determined. The suitable length of period for periodic operation could be estimated by

measurements of a starting up procedure Using these results it could be shown experimentally that it is possible to operate a reactor by means of periodic processing within a temperature and conversion hysteresis At high frequencies the system cannot follow the enforced variations and works like a stationary reactor in one of the stable points of operation with suppressed amplitudes With decreasing frequencies the amplitudes of the cycles increase more and more The average temperature still remains within the temperature hysteresis, but the temperature maximum becomes so high that it might not be useful to decrease the frequency furthermore due to the temperature resistance of the apparatus or the selectivity of the intermediate product

This behaviour can be understood by the well-known equations for the mass and heat balances[7] The enforced concentration variations are damped by the mass-capacity of the system[4] With increasing mass-capacity the concentration amplitudes are lowered Caused by the high enthalpy of the considered reaction the concentration variations lead to additional temperature cycles The amplitudes of these cycles are mainly determined by the heat capacity of the system, e.g. the catalytic gauze, the holder of the gauze and the reactor wall The late maximum of the temperature during the starting up procedure and the concentration and temperature fluctuations at periodic operation show that the dynamic behaviour of the system is mainly ruled by its heat capacity The mass capacity at the catalytic gauze is very small

The advantages of periodic operation for exothermal reactions are not restricted to reaction models as investigated here Recently with the example of the production of ethylene oxide in a fixed-bed reactor it could be shown that the "hot spot" could be avoided without expensive cooling equipment using periodic operation[11]

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#### NOTATION

$A$	surface area, (cm <sup>2</sup> )
$C$	concentration, (mole/cm <sup>3</sup> )
$C^*$	concentration (referred to the average value during a period)
$C_p$	molar heat (at constant pressure), (cal/mole grd)
$E_{ch}$	activation energy of chemical reaction, (kcal/mole)
$E_m$	activation energy of mass transfer, (kcal/mole)

$F_0$	volumetric flow, (cm <sup>3</sup> /mole)
$\Delta H_r$	heat of reaction, (kcal/mole)
$k$	reaction rate constant, (cm/sec)
$n$	mole number, (mmole)
$\dot{n}$	molar flow, (mmole/sec)
$t$	time, (sec)
$t'$	length of period, (sec)
$T$	temperature, (°C or °K)
$U$	conversion

#### Greek symbols

$\alpha$	heat transfer coefficient, (cal/cm <sup>2</sup> sec grd)
$\beta$	mass transfer coefficient, (cm/sec)
$\eta$	yield, (%)
$\tau$	residence time, (ms)

#### Subscripts

$c$	values at the catalyst
$e$	outlet conditions
$eff$	effective values
$ex$	values for extinction
$gas$	values in the gas phase
$hy$	values of hydrocarbons
$ig$	values for ignition
$max$	maximum values
$0$	feed conditions

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### Effect of axial fluid thermal dispersion coefficient on Nusselt numbers of dispersion-concentric model of packed beds at low flow rates

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In deriving fundamental equations for packed bed reactor design the Dispersion-Concentric Model (original D-C Model) based on the following assumptions has widely been employed

(i) Dispersed plug flow with the dispersion coefficient

$$\alpha_{ax} = (0.7 \pm 0.1)\alpha_f + \alpha_{ax, turb} \quad (1)$$

for

$$Re < 2, \quad \alpha_{ax, turb} = 0$$

(ii) Concentric temperature (concentration) profiles in particles

The coefficient value 0.6-0.8 of eqn (1) comes from the diffusion experiments of many investigators (for example, see [1])

This paper is an extension of Wakao's work[1], criticizing the original D-C Model Several models[2,3] have been proposed to interpret anomalous decrease in Nusselt number at low Reynolds numbers In this paper it is shown that analysis based on the original D-C Model is also responsible for the anomaly

In fact, if temperatures were of center-symmetry, there would be no heat flow through the particles Therefore, assumption (ii) does not seem to depict the real heat transfer mechanism

In frequency response experiments at low Reynolds numbers, Littman, Barile and Pulsifer[4] pointed out the significance of