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KINETICS IN THE SPINNING-CATALYST-BASKET (S. C. B. R.)

CINÉTICA NO REACTOR CATALÍTICO DE LEITO ROTATIVO (S. C. B. R.)

An exothermic catalytic oxidation reaction is taken as a quantitative example of the considerations which apply in interpreting kinetics in the S. C. B. R. In particular, the effects of variations in rotational speed and gas flow rate to the reactor are examined in appraising the approach to isothermality of a catalyst pellet on which the catalytic air-oxidation of o-xylene occurs.

1. INTRODUCTION

The S. C. B. R. has been developed (1,2) to overcome the shortcoming of more conventional reactors, e. g. tubular reactors in the measurement of gas-solid (especially catalytic) reactor kinetics. Ideally, one requires for this measurement a well mixed reactor operating with uniform gas and catalyst conditions in the absence of concentration or temperature gradients between particles and gas. With reference to the first of these ideals, perfect mixing in the bulk gas is readily obtained at moderate rotating speeds in the S. C. B. R. Hence the rate of reaction is a function of the bulk gas conditions and the reactor truly simulates a C. S. T. R. The existence of negligible concentration and temperature gradients would signify that the observed rate of reaction in terms of the bulk gas concentration would represent the rate of chemical reaction on the catalyst surface. In such a situation, the particle temperature would approach that of the bulk and could be obtained from measurement of the bulk gas temperature.

Recent work (3,4) indicating variations in the rates of mass transfer to and from catalyst particles in the S. C. B. R. not only with rotating speed but also with radial position shows that the circulation rates past the particles necessary to reduce interfacial resistence and give such high rates of transfer are much higher than those which fulfil the perfect mixing criterion. The above raises the questions as to the extent to which temperature gradients exist between the catalyst particles and the enclosing bath, and as to whether there is the possibility of multiple steady state operating temperatures for these particles.

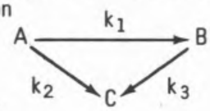
It is, therefore, convenient to consider the gas space of the stirred reactor as comprising two zones, viz. a boundary layer and the bulk gas, and to determine the extent to which the reactor approaches ideal conditions. The approach adopted here was to estimate an average heat generation rate per particle in the catalyst basket and by use of the heat transfer coefficients predicted analogously from the mass transfer coefficients (3,4) calculate the steady state operating temperature of the particles.

The assumptions in this approach are :

1. The heat of reaction is generated uniformly on the surface of the catalyst and that all heat transfer occurs by convection. The latter condition was latter modified when an approximation as to the average particle temperature in any one radial direction was made on the assumption that some limited conduction took place ;
2. Good gas to wall heat transfer gives virtually isothermal conditions. This is a good approximating above very moderate rotating speeds.

2. STUDY REACTION

The catalytic gas-solid reaction under study was the air oxidation of O-xylene to phthalic anhydride over a commercial vanadia catalyst. Calderbank (6) showed that this oxidation may be adequately represented by the following scheme of first order reactions where «A» is o-xylene, «B» is phthalic anhydride and «C» represents the products of combustion



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where

$$\frac{k_1}{k_1 + k_2} = 0.75 \tag{1}$$

$$k_1 + k_2 = \begin{cases} \exp\left(18.6 - \dfrac{27{,}120}{RT}\right) & T \leqslant 713°K \quad (2) \\ \exp\left(2.64 - \dfrac{4{,}476}{RT}\right) & T > 713°K \quad (3) \end{cases}$$

$$k_3 = \exp\left(15.4 - \frac{30{,}500}{RT}\right) \tag{4}$$

in the units (gmol/gr.hr.atm.).
These data were obtained in a S. C. B. R. with a very dilute o-xylene feed.

3. REACTOR

The S. C. B. R. in which the above exothermic reactions were taking place was similar to the cylindrical spinning catalyst basket reactor described by Brisk et al. (1), and its dimensions were :

Vessel volume – 60 cm^3
Basket volume – 22.9 cm^3

The basket was packed with 210, 0.5 cm diameter spherical catalyst particles weighting 32 gm, the calculated bed porosity being 0.4.

4. HEAT GENERATION RATE FOR A SINGLE PARTICLE

On the assumption that the bulk gas phase and the space between the particles was perfectly mixed and equal to the outlet gas concentration, the reactor was treated as a homogeneous C. S. T. R. as a mean of estimating the bulk gas concentration.
The overall differential rate equations for the amount of component present at any instant are:

$$\frac{dC_A}{dt} = (-K_1^* C_A - K_2^* C_A)\, N \tag{5}$$

$$\frac{dC_B}{dt} = (K_1^* C_A - K_3^* C_B)\, N \tag{6}$$

$$\frac{dC_C}{dt} = (K_2^* C_A - K_3^* C_B)\, N \tag{7}$$

where N is the number of particles in the spinning basket and the rate constants K_i^* $(i = 1, 2, 3)$ are expressed in terms of one particle.
An overall mass balance for each component gives

$$F\,(C_{A_i} - C_{A_0}) = (K_1^* + K_2^*)\, C_{A_0}\, N \tag{8}$$

$$F\,(C_{B_i} - C_{B_0}) = (-K_1^* C_{A_0} + K_3^* C_{B_0})\, N \tag{9}$$

$$F\,(C_{C_i} - C_{C_0}) = (-K_2^* C_{A_0} - K_3^* C_{B_0})\, N \tag{10}$$

being F the gas flow and the subscripts «i» and «o» referring respectively to the inlet and outlet compositions.

Since $C_{B_i} = C_{C_i} = 0$, these mass balances reduce to

$$C_{A_i} - C_{A_0} = (K_1^* + K_2^*)\, C_{A_0}\, N/F \tag{11}$$

$$C_{B_0} = (K_1^* C_{A_0} - K_3^* C_{B_0})\; N/F \tag{12}$$

$$C_{C_0} = (K_2^* C_{A_0} + K_3^* C_{B_0})\; N/F \tag{13}$$

The rate of heat generation per particle is

$$Q_p = -(C_{A_0} K_1^* \Delta H_1 + C_{A_0} K_2^* \Delta H_2 + C_{B_0} K_3^* \Delta H_3) \tag{14}$$

where ΔH_j $(j = 1, 2, 3)$ are the heats of reaction (7), (8).
Using the above equations (11), (12) and (13) to express Q_p in terms of C_{A_i} we obtain finally

$$Q_p = -\frac{(\Delta H_1 K_1^* + \Delta H_2 K_3^*)\, C_{A_i}}{1 + (K_1^* + K_2^*)\, Z} - \frac{(\Delta H_3 K_1^* K_3^* Z\, C_{A_i})}{(1 + K_3^* Z)\,[1 + (K_1^* + K_2^*)\, Z]} \tag{15}$$

where $Z = N/F$.

The first term in equation (15) represents the contribution to the heat generation from reactions involving the disappearance of o-xylene. The second term represents the heat generated by the combustion of P. A., – a significant factor at high temperatures and when the o-xylene has been exhausted.
The rate constants K_i^* are composed of the kinetic rate constants and the mass transfer rate combined by the established additivity of resistances rule. The kinetic rate constants are defined by equations (1) to (4) and the mass transfer rates being calculated from Pereira and Calderbank (3,4) mathematical model for gas flow in the S. C. B. R., the required working being covered as follows:

Basket porosity	0.4
Particle radial position	0.75 (0.5) 3.25 cms.
Basket rotating speed (rpm)	1000 (1000) 8000
Temperature	400 (25) 500°C

In order to reduce the complexity of the calculations, the following approximations were made:

1. Since the mass transfer coefficients for the three particles in any one radial direction deffered by <20 % at any one rotating speed, the mean of these values was taken;
2. These mean values were themselves averaged for several bath temperatures at any one r.p.m. The standard deviation was <5% in any case.

Such averaging is realistic because the contribution of the mass transfer resistance to the overall rate constant is negligible for rate constants K_2^*, K_3^*, at all temperatures, and is of sizable impact only in K_1 at relatively high temperatures.
The rate constants computed as above were used in equation (15) and rates of heat generation per particle were evaluated at various jacket temperatures (300-600 °C), gas flow rates (12-18 cm^3/sec) and basket rotating speed (1000-8000 r.p.m.) for two inlet o-xylene concentrations (1 - 2 10^{-4} gr mol/L). In figs. 1 and 2 are represented two typical heat generation curves which present the expected double sigmoid shape.

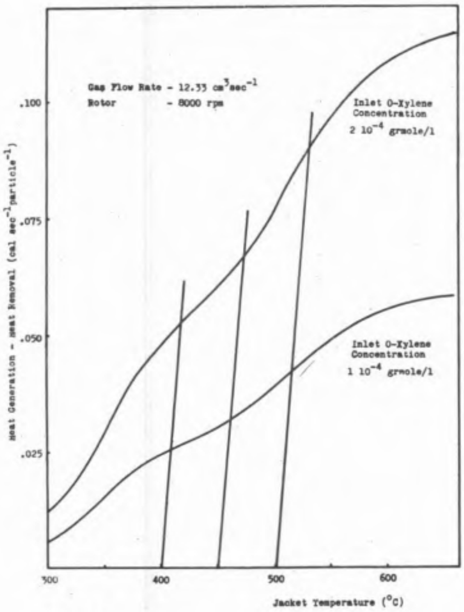

Fig. 1

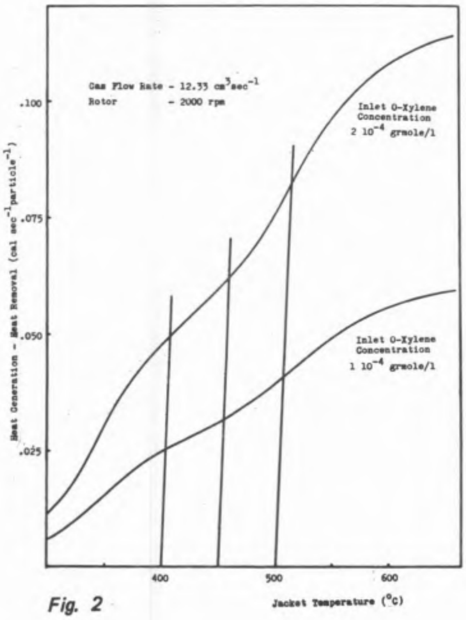

Fig. 2

Heat generation and heat removal rates for a single particle in the S.C.B.R. at various jacket temperatures two gas flow rates and two o-xylene inlet concentrations

5. HEAT REMOVAL RATE FROM A SINGLE PARTICLE

Assuming that the reactor is operating isothermally and that the jacket temperature represents the bulk gas temperature, the rate of heat exchange between the particle and the gas is

$$Q_p = h.a. \quad (T_c - T_j) \tag{16}$$

where h is the heat transfer coefficient, a the surface area of the spherical particle, T_c the particle temperature and T_j the jacket temperature. Values of h were computed from Pereira and Calderbank (3,4) gas flow model in the C. S. B. R. using the analogy between heat and mass transfer.

$$h = \frac{J_h C_p \rho U}{P_r . 67} \tag{17}$$

and (5)

$$J_h = 1.07 J_d \tag{18}$$

Heat removal lines are represented in figs. 1 and 2 at various jacket temperatures. In the above figures the heat generation and heat removal curves have been combined. Their relative position and interception precludes any possibility of multiple steady state operating temperature of the catalyst particles for jacket temperature between 400 and 500 °C, the operating limits of the reactor. This conclusion applies equally well at all inlet o-xylene concentrations and all gas flow rates.

6. TEMPERATURE DIFFERENCE BETWEEN PARTICLE AND JACKET

From the above figs. 1 and 2 it is apparent that significant temperature differences do exist between the particles and the bulk, as seen by the intersection of the heat generation and removal lines, which is an estimate of the steady state operating temperature of each particle.

In accordance with the fact that the mass transfer coefficient decreases towards the centre of the basket (3,4), the particle temperature also increased in that direction. Also, such predictions of the particle temperatures assume non-interacting particles whereas, in reality, the particles are in close point contact due to their uneven surfaces, and therefore interparticle heat transfer will take place by the following routes:

1. Pure conductive heat transfer through the areas of contact assuming a finite heat transfer rate;
2. Convective transfer to the gas between the particles and thereafter to adjacent particles in all directions;
3. A radiative component of heat transfer is also a possibility.

By these mechanisms, the extreme temperature gradients predicted for the central particles will, in fact, be over estimations. A more realistic estimate of the particle temperature is the mean of the three particles that the basket can accomodate in any one radial direction. In figs. 3 and 4 the temperature difference between particles and jacket calculated as above are represented for various rotating speeds of the basket, jacket temperatures and two flow rates. The results presented are for an inlet o-xylene concentration of 2 10^{-4} gmol/L as such represent the limiting case, i. e. the maximum temperature gradients.

The following trends are apparent:

1. As the volumetric flow rate increases, the temperature difference increases. This is a result of the lower residence time, lower conversion and therefore higher rate of heat generation;
2. As the rotating speed increases ΔT falls away and asymptotes at

rotating speeds greater than 6000 r.p.m. This profile matches the profile presented by Brisk (1) calculated from experimental mass transfer coefficients, and therefore supports Pereira and Calderbank model from which heat and mass transfer coefficients were derived;

3. Finally, the curves indicate that at rotating speeds less than about 2000 r.p.m. physical and thermal phenomena significantly affect the operation of the reactor.

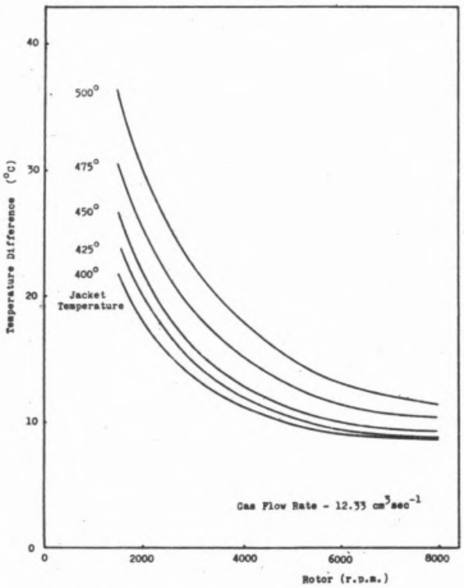

Fig. 3

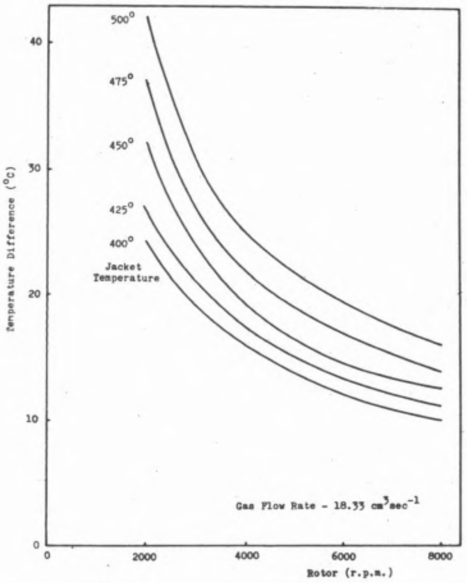

Fig. 4

Temperature difference between particle and jacket at various jacket temperatures and two gas flow rates

7. SELECTIVITY TO PHTHALIC ANHYDRIDE

Using the estimates of the actual particle temperature, graphs of selectivity (to P. A.) versus bath temperature were constructed for various rotating speeds to give a quantitative evaluation of the deviation from ideality experienced in the S. C. B. R. Ideality being considered as the case where the particle surface temperature is equal to the jacket (or bulk) temperature – in effect perfect mixing with no boundary layer.

The selectivity to phthalic anhydride $\phi_{P.A.}$ given by the above reaction scheme is given by

$$\phi_{P.A.} = \frac{K_1^*}{\dfrac{K_1^* + K_2^*}{1 + K_3^* \, N/F}} \qquad (19)$$

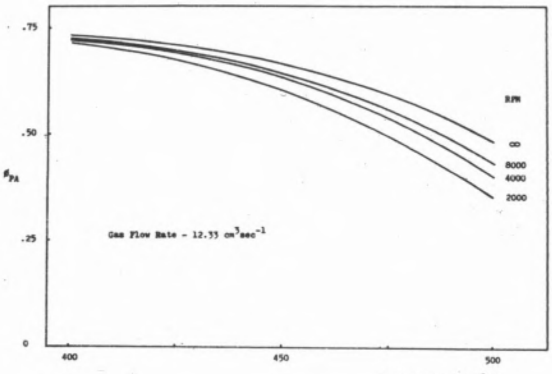

Fig. 5

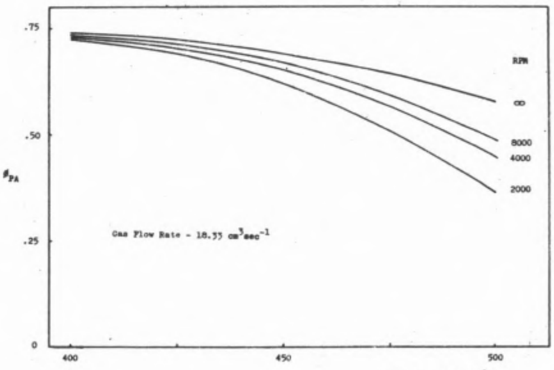

Fig. 6

Selectivities to phthalic anhydride with and without transport resistance compared at various jacket temperatures and rotational speeds for two gas flow rates

The effect of the rotating speed on the selectivity to P. A. is illustrated in figures 5, 6. The asymptotic behaviour of the temperature difference versus rotating speed curves (figures 3,4) is translated into a situation where the approach to ideal behaviour achieved in the 7000-8000 r.p.m. and represents the optimum performance of the S. C. B. R. in terms of rotating speed. Although the variation in selectivity between 4000 r.p.m. and 7-8000 r.p.m. is negligible, it is apparent that the rate of increase of the deviation from ideality is increasing rapidly as the rotating speed falls below 4000 r.p.m. This is evidenced by the large decrease shown for the 2000 r.p.m. curve. Comparison of figs. 5 and 6 shows the effect of the variation in flowrate. Although the selectivity at $RPM = \infty$ tends towards 0.75 as the flow rate increases, the rate at which the selectivity declines with reduction in rotating speed is significantly faster.

8. CONCLUSIONS

The non-isothermality of the S. C. B. R. in this example is very apparent and could lead a lack of appreciation of the proper selectivities achievable with the catalyst. It is apparent that the feed concentration of o-xylene would have to be largely reduced to obtain reliable kinetic data at the basket speeds conveniently obtained. A reduction in flow rate can also be advantageous in that the conversion is increased and the rate of reaction consequently reduced.

NOTATION

a	Spherical particle surface area (cm^2)
C_A, C_B, C_C	Concentration of A, B and C (gr. mole/cm^3)
C_D	Specific heat (cal/gr)
F	Gas flow rate (cm^3/sec)
h	Heat transfer coefficient (cal/cm^2 °C)
ΔH	Heat of reaction (cal/gr. mole)
J_d, J_h	Mass and heat transfer coefficients
k_1, k_2, k_3	Rate constants (gr mol/gr. hr. atm.)
K_1^*, K_2^*, K_3^*	Rate constants (cm^3/sec. particle)
N	Number of particles in the reactor
Pr	Prandtl number
Q_p	Rate of heat generation and heat removal (cal/sec particle)
R	Universal gas constant (cm^3 atm./gr. mol. °K)
T_c, T_j	Catalyst and jacket temperatures (°K)
T	Absolute temperature (°K)
U	Superficial gas velocity (cm/sec)
Z	Defined as N/F
ρ	Gas density (gr/cm^3)
$\phi_{P.A.}$	Selectivity to Phthalic Anhydride

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RESUMO

Tomou-se uma reacção de oxidação catalítica exotérmica como exemplo quantitativo das considerações que se aplicam à interpretação da cinética num S. C. B. R. São examinados em particular os efeitos de variações na velocidade de rotação e no caudal de alimentação do gás ao reactor, ao analisar-se a isotermicidade de uma esfera de catalisador sobre a qual se verificasse a oxidação catalítica pelo ar do orto-xileno.

DISCUSSION

H. SPATH : Do you have considered possible contribution from homogeneous oxidation to the overall conversion ?
Using rather low flow rates through the reactor you have a long residence time of the reacting gas in the dead volume of the reactor and therefore some homogeneous processes cannot be definitaly neglected.

J. PEREIRA : Yes. There was no homogeneous reaction when the reactants were fed in the absence of any catalyst, over the temperature range.