OXIDATION OF ETHENE IN A WALL-COOLED PACKED-BED REACTOR

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(Received May 1994; accepted for publication 30 September 1994)

Abstract—The selective oxidation of ethene over a silver on α -alumina catalyst was studied in a pilot plant with a wall-cooled tubular packed bed reactor. Gas and solid temperatures in the catalyst bed were measured at different axial and radial positions as well as concentrations at different axial position. Total pressure, inlet mole fraction ethene, mass flow rate and wall temperature were varied. The experiments are compared with model calculations. A pseudo-homogeneous model and a heterogeneous two-dimensional model were used for the calculations. Kinetics and heat transport parameters in the model have been determined independently in separate studies. The work is distinctive in the accuracy paid to a large number of experimental details. The models correspond reasonably well with the experiments at all operating conditions. The main problem in the description of the reactor is the inability of the kinetic expressions to predict the reaction rates over the entire range of partial pressures. As a result some systematic deviations are found, in particular in the predicted temperature profiles. The heterogeneous model gives better agreement with the experiments although systematically larger temperature differences are calculated on the basis of available correlations in literature than has been measured. On the basis of this work it is difficult to determine directly whether an influence of chemical reaction is present on the values of the heat transport parameters.

INTRODUCTION

In our laboratories the selective oxidation of ethene to ethene oxide is used as a model reaction for experimental and theoretical investigations of cooled tubular reactors. The reaction scheme for this oxidation is shown in Fig. 1.

For this highly exothermic reaction system, control of the temperature level is necessary to maintain high reaction rates and high selectivities, to avoid catalyst deactivation and to prevent safety problems. In view of the large cooling area per unit reactor volume, a cooled tubular reactor is the appropriate reactor choice for this purpose.

For reactor development purposes it is desirable to design such a reactor solely on the basis of kinetic data and heat transport data at relevant conditions. However, quite often, a large and expensive pilot plant programme has to be executed with tubes of an industrial size, to establish a proper reactor design. This is caused by unreliable results obtained from mathematical modelling of the reactor using literature relations for heat and mass transport. Reasons for this could be inconsistencies, inaccuracies in the interpretation of experimental data, which are used to derive these relations, and inadequacy of mathematical models [see Foyo de Azevedo *et al.* (1990); Borman and

Westerterp (1992); Borkink and Westerterp (1992a,b); Borman *et al.* (1992); Freiwald and Paterson (1992); Borkink *et al.* (1993)]. Some of these aspects will be commented on in the description of the experimental set-up and in the discussion of the theoretical backgrounds. To find causes of such inconsistencies the present authors set up a thorough experimental and theoretical programme. Accurate and well defined experiments have been performed in which kinetic parameters [see Borman and Westerterp (1994) and Schouten *et al.* (1994)] and heat transport parameters [see Borkink and Westerterp (1992b) and Borman *et al.* (1992)] are determined separately. In this publication the separately determined parameters are used for the modelling of the reactor. Experiments performed in a pilot plant with one, single reactor tube are critically compared with the results of model calculations so that the reliability of different models can be evaluated.

An industrial silver on α -alumina, Raschig ring is used as catalyst for the ethene oxidation. The reactions are carried out with ethene in an excess of air without addition of a chlorine modifier to the feed. In modern industrial processes an excess of ethene is selectively oxidized with pure oxygen and some chlorine containing compound is added to the reaction mixture to improve the selectivity [see Satterfield (1991)]. The influence of chlorine on the behaviour of the catalyst in the reactor will be reported in a future article.

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Fig. 1. Reaction scheme for the oxidation of ethene.

THEORETICAL BACKGROUNDS

Packed beds are almost exclusively described by models in which conductivities are described by a deterministic Fickian type of dispersion, superimposed on a plug flow. Coupled differential equations for momentum, heat and mass transport, with *effective* radial and axial transport parameters describe the system as a continuum. For beds with a smaller number of particles on a diameter, say, below 12, the discrete nature of the packing becomes increasingly important [see e.g. Vortmeyer and Winter (1984) and Dixon and Yoo (1991)]. At such small tube-to-particle diameter ratios the dimensions of the particle are not negligible in comparison with that of the tube diameter so the applicability of continuum models becomes quite doubtful. Also a wall effect is present due to the structured arrangement of the particles near the wall, leading to an increased porosity near the wall and to wall channelling [see Vortmeyer and Haidegger (1991), Daszkowski and Eigenberger (1992) and Borkink and Westerterp (1994)]. Because particles are ordered only within the first layers from the wall, the effect is more pronounced for fewer particles on a diameter. This effect is strongly dependent on the shape of the particles, e.g. Drahós *et al.* (1982) report only small radial variations in porosity for a packing consisting of Raschig rings, while the wall effect for a packing of spheres is thought to be more important. In cooled tubular reactors the tube-to-particle diameter-ratio for very exothermic reactions normally will be lower than 12 and can be even as low as three or four. Regrettably, there are no practical alternative models available; so even at such small tube-to-particle diameter ratios, continuum models are used. Some of the problems in the use of continuum models and effective parameters are discussed by Wijngaarden and Westerterp (1989). Fundamental deviations, conflicts with physical reality or apparent dependencies can be expected. They also derive a criterion that indicates whether a pseudo-homogeneous model can be used or that a

heterogeneous model must be taken. Because of the neglect of the discrete nature of the packing and the wall effect, several phenomena are lumped in the effective parameters. This leads to violation of the physical background of the parameters and can lead to relations between parameters representing independent physical phenomena. It is found sometimes that the relevant process parameters may combine differently under different conditions; for example, Dixon and Cresswell (1986) and Feyo de Azevedo *et al.* (1990) question the use of parameters obtained under stationary conditions for application to dynamic situations. It also remains to be seen whether it is possible to apply parameter values as obtained from pseudo-homogeneous models to heterogeneous models [see e.g. Vortmeyer (1982), Ramkrishna and Arce (1989) and Schwedock *et al.* (1989)]. Chandrasekharan and Calderbank (1979), Hofmann (1979), Löwe (1984) and Schwedock *et al.* (1989) observed that heat transport parameters depend on chemical reaction and they state that models generally predict too high hot-spot temperatures for exothermic reactions if the heat transport relations used are determined under non-reaction conditions. They conclude that heat transport and its parameters, $\lambda_{\text{eff},r}$ and α_w , should be increased under reaction conditions, whereas this increase depends on the extent of reaction.

Whether these dependencies result from inadequacies in the mathematical model or can be attributed to deficiencies in the interpretation of experimental data is not clear. They probably are an important reason why scale-up of cooled tubular reactors is so unreliable up to now.

In this study $d_i/d_p \approx 8$ so that it can be expected that the discrete character of the packing is important.

Model equations

Several assumptions have been made in deriving models: physical properties and heat transport parameters are considered to be constant and are

evaluated at inlet conditions. The gas is in plug flow so no radial velocity variation is incorporated in the model; axial dispersion of both mass and heat is neglected. This is allowed according to Borkink and Westerterp (1992a). Also, pressure drop over the reactor, local changes in porosity, free convection and heat transport by radiation are neglected. With the criteria of Mears (1971) it was verified that intraparticle resistances for heat and mass transport are not important. To simplify the calculations it is further assumed that radial concentration profiles are flat. According to calculations of Khanna and Seinfeld (1987) and Westerink *et al.* (1990) this is an acceptable simplification under non-run-away conditions. Although concentrations are almost uniform over the radius, this does not apply to the reaction rates R_i because of the radial temperature profile. The influence of temperature on the reaction rates is very large for the observed radial temperature differences up to 40 K. The average reaction rates $\bar{R}_i$ over a cylindrical slice can be calculated according to:

$$\bar{R}_i \equiv \frac{2\pi}{A_r} \int_{r=0}^{R_i} r R_i[T(r)] dr \quad (1)$$

Because radial dispersion is assumed to be infinitely large, eq. (1) can be used to eliminate radial terms in the mass balances. The mass balances for ethene and carbon dioxide over a volume element $A_r dz$ become:

$$\frac{\partial(v_s C_E)}{\partial z} = -\rho_b \left(\bar{R}_1 + \frac{1}{2} \bar{R}_2 \right) \quad (2)$$

$$\frac{\partial(v_s C_C)}{\partial z} = \rho_b \bar{R}_2 \quad (3)$$

The mole fraction of the other components can be calculated simply on the basis of the stoichiometry. A heat balance over a volume element $A_r dz$ yields:

$$\begin{aligned} (\rho C_p)_g v_s \frac{\partial T}{\partial z} &= \lambda_{\text{eff},r} \frac{1}{r} \frac{\partial}{\partial r} \left(r \left(\frac{\partial T}{\partial r} \right) \right) \\ &- \rho_b R_1 \Delta H_1 - \rho_b \frac{1}{2} R_2 \Delta H_2 \end{aligned} \quad (4)$$

A heterogeneous model taking into account the temperature differences between catalyst and gas gives, for the heat balances for the gas and the solid phase respectively:

$$\begin{aligned} (\rho C_p)_g v_s \frac{\partial T_g}{\partial z} &= \lambda_{\text{eff},r} \frac{1}{r} \frac{\partial}{\partial r} \left(r \left(\frac{\partial T_g}{\partial r} \right) \right) \\ &+ \alpha_p a_p (T_s - T_g) \end{aligned} \quad (5)$$

$$\rho_b \left[R_1(T_s) \Delta H_1 + \frac{1}{2} R_2(T_s) \Delta H_2 \right] = \alpha_p a_p (T_s - T_g) \quad (6)$$

On the basis of the Chilton–Colburn analogy mass transport limitations should also be present. For gases with a Lewis number $\lambda_g/(\rho c_p)_g D$ close to one, the following equality holds [see Wijngaarden and Westerterp (1989)]:

$$\frac{C_g - C_s}{C_g} = \frac{T_s - T_g}{\Delta T_{\text{ad}}} \quad (7)$$

Because in our system the adiabatic temperature rise is large, the temperature difference can be significant while a concentration gradient is hardly present, so usually mass transfer limitations can be neglected. In that case the mass balances of the heterogeneous model simplify to those of the pseudo-homogeneous model [see eqs (2) and (3)].

The value of the Nusselt number of the particle determines the importance of the heterogeneity [see Wijngaarden and Westerterp (1993)]. We have used the relation of Gnielinski (1982) [see eq. (8)] which applies to a fixed bed packed with Raschig rings:

$$\text{Nu}_p = 2.1 \left(2 + \sqrt{(0.664 \text{Pr}^{0.33} \text{Re}_p^{0.5})^2 + \left(\frac{0.037 \text{Re}_p^{0.8} \text{Pr}}{1 + 2.443 \text{Re}_p^{-0.1} (\text{Pr}^{0.66} - 1)} \right)^2} \right) \quad (8)$$

The shape factor 2.1, as suggested by Gnielinski for bed porosities between 0.50 and 0.79, accounts for the enhancement of the heat transfer due to the higher turbulence in a packed bed compared to that for a single particle.

Introducing dimensionless variables the equations can be rewritten as follows (see also the notation):

$$\begin{aligned} \frac{\partial \theta}{\partial \omega} &= \frac{4\Lambda}{\text{Bo}_r N} \frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \left(\frac{\partial \theta}{\partial \rho} \right) \right) \\ &+ \text{Da} \Theta_{\text{ad}} \left(R_1^* + \frac{1}{2} H R_2^* \right) \end{aligned} \quad (9)$$

$$\frac{\partial \zeta_E}{\partial \omega} = -\text{Da} \left(\bar{R}_1^* + \frac{1}{2} \bar{R}_2^* \right) \quad (10)$$

$$\frac{\partial \zeta_C}{\partial \omega} = \text{Da} \bar{R}_2^* \quad (11)$$

To solve the equations we use the following boundary conditions:

$$\rho = 0: \quad \frac{\partial \theta}{\partial \rho} = 0 \quad (12a)$$

$$\rho = 1: \quad \frac{\partial \theta}{\partial \rho} = \text{Bi}(\theta - 1) \quad (12b)$$

$$\omega = 0: \quad \theta(\rho) = 1 \wedge \zeta_i = 0 \quad (12c)$$

Equation (12c) applies because it has been ensured experimentally that the inlet temperature is constant over the inlet plane and equal to the wall temperature.

The energy balances of the heterogeneous model in dimensionless form are:

$$\frac{\partial \theta_g}{\partial \omega} = \frac{4\Lambda}{Bo_r N} \frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \left(\frac{\partial \theta_g}{\partial \rho} \right) \right) + St(\theta_s - \theta_g) \quad (13)$$

$$Da\Theta_{ad} \left(R_1^*[s] + \frac{1}{2} HR_2^*[s] \right) = St(\theta_s - \theta_g) \quad (14)$$

The equations are solved using a five-point collocation method in radial direction and a fourth-order Runge Kutta method in axial direction. The heterogeneous model requires an iteration technique for the determination of the catalyst temperature. To this end Brent's method is used [see Press *et al.* (1986)].

Heat transport and kinetic parameters

In the literature many correlations are available for heat transport coefficients and for the kinetics of the ethene oxidation. We have chosen to determine those parameters ourselves because of uncertainty in the values of the parameters in literature. In many investigations of cooled tubular reactors parameters are determined by fitting all model parameters simultaneously to experiments performed in a down-scaled replica of the reactor. This procedure generally will not lead to useful results. This is caused by the complex interaction between the different processes and the lumped nature of the models [see Froment and Hofmann (1987)], usually leading to strong cross-correlations of parameters estimated. In principle it is better to determine the model parameters separately and use experiments from a cooled tubular reactor only for comparison and not for fitting purposes.

From stationary heat transport experiments the following relations for $\lambda_{eff,r}$ and Nu_w were obtained [see Borman *et al.* (1992)]:

$$\lambda_{eff,r} = 0.37 + 2.54 \cdot 10^{-3} \cdot Re_p \quad (15)$$

$$Nu_w = 2.229 \cdot Re_p^{0.41} \quad (16)$$

A two-dimensional pseudo-homogeneous model was used to derive these heat transport correlations. Axial dispersion of heat was found to be of no significance provided correct boundary conditions were chosen [see Borkink and Westerterp (1992a)].

A separate study of the kinetics of the epoxidation gave the following kinetic relation for the epoxidation and the total combustion reaction:

$$r_i = \frac{k_i^* K_E^i P_E^i K_O^i P_O^i}{(1 + K_E^i P_E + K_O^i P_O + K_C^i P_C + K_W^i P_W + K_{EO}^i P_{EO})^2} \quad (17)$$

Table 1. Parameter values of eq. (17) for the kinetics of the ethene epoxidation

	r_1	r_2
k_r^*	$3.65 \cdot 10^5$	$3.16 \cdot 10^9$
T_{act}	8,790	12,800
K_E^*	0.022	0.0065
$T_{ads,E}$	3,000	3,600
K_O	1.5	2.95
K_{EO}	100	250
K_C	60	130
K_W	40	55

The parameter values can be found in Table 1.

The combustion of ethene oxide, reaction 3, was found to be negligible under our operating conditions. To determine the kinetics, data from an internal recycle reactor have been used completed with data at low product concentrations from a cooled tubular reactor using a differential interpretation method [see Schouten *et al.* (1994)].

The heat transport relations and the kinetics have been incorporated in the two dimensional pseudo-homogeneous (=PH-T) and heterogeneous model (=H-T). The results of the model calculations are compared to steady-state experiments in the pilot plant. This comparison should show whether it is possible to determine heat transport and kinetics separately and use the results in the modelling of our reactor. It also should show whether heat transport parameters, determined under non-reaction conditions, are applicable under reaction conditions. Model calculations with the heterogeneous model should show the applicability of heat transport parameters obtained from a pseudo-homogeneous model to a heterogeneous model.

EXPERIMENTAL SET-UP

In the pilot plant, steady-state temperature and concentration profiles are measured at different operating conditions in the range 435–495 K for wall temperature, 0.2–1.0 MPa for the pressure, 0.2–2.6 kg/m²s for the mass flow rates and feed mole fractions of ethene of 0.1–2.0 mol%.

The pilot plant can be divided in the gas supply section, the reactor section, the measurement and control section, and the cooling section.

Gas supply section

In this section, purified air, ethene and optionally, a third gas, are mixed, preheated and fed to the reactor, see Fig. 2. Air is compressed to 1.1 MPa, purified and dried in the filter system consisting of two oil filters, a two-column regenerative adsorption dryer, a dust filter and an active coal filter. After passing the filter system the air stream is free

Fig. 2. Schematic representation of the gas supply section. (A) compressor; (B) filter system; (C) buffer vessel; (D) flow control; (E) flow measurement; (F) electrical heater; (G) electrical tracing; (H) pressure safety valve.

Fig. 3. The reactor section: (A) catalyst bed; (B) inert layer; (C) sieve tray; (D) jacket; (E) sample tubes; (F) product cooler; (G) frame for temperature measurement.

of water, carbon dioxide, oil or other contaminants. A 60 l buffer vessel is installed to damp the fluctuations in the flow caused by the constant switching between the adsorption columns. The air flow is controlled by two mass flow controllers in parallel and can reach a maximum value of $6.8 \text{ kg/m}^2 \text{ s}$ in the reactor tube. Ethene with a purity of 99.9% is mixed into the air stream; optionally, carbon dioxide, water, ethene oxide or 1,2-dichloro-ethane may be added also. The flow of the mixture is measured by a Höntsch propeller measuring probe. An electrical oven with a capacity of 5 kW is installed to preheat the reaction mixture whereas the temperature is fine-tuned by controlling the electrical power supply to the electrical tracing of the feed pipe. The maximum power to the tracing is 1 kW. It is ensured the inlet radial temperature profile is flat and equal to the wall temperature by using a very large heating surface for the feed stream. The inlet temperature was measured at 1.5, 10.5, 18.5 and 26.5 mm distance from the wall. Usually these temperatures deviate less than 0.3 K from the wall temperature.

Reactor section

A vertical RVS-316 tube with an inner diameter of 53.1 mm, a wall thickness of 3.6 mm and a length of 1.625 m is used as the catalyst containing,

wall-cooled reactor tube, see Fig. 3. The sieve tray at the inlet contains 1.5 mm holes and has a total open area of 20%. To avoid entrance effects in the velocity and temperature profiles, inert material having a total height of 0.059 m, is first placed on this plate. The inert material consists of sintered α -alumina spheres with a diameter of $\pm 8 \text{ mm}$. Above this zone follows the catalyst layer with a height of 0.506 m. The reactor has been filled with catalyst by dropping the individual particles from the top at different angular positions so a random loose packing has been obtained. According to Reyes and Iglesia (1991) with such a type of packing wall effects are minimized. A total of 1.01 kg of catalyst has been used, resulting in a porosity of 0.504. The equivalent spherical particle diameter of the catalyst particles is 6.12 mm and the bed density equals 910 kg/m^3 . To avoid outlet effects, an inert layer having a height of 0.114 m, has been put on top of the catalyst. The exit gas is cooled and reduced in pressure via an electronic back-pressure controller and vented to a flare. Flare temperatures were kept above 900 K by burning additional gas.

Measurement and control section

A total of 32 gas and catalyst temperatures are measured simultaneously at different axial and

Fig. 4. Positions of gas (●) and catalyst (○) temperature measurements in the reactor. Also the sample locations are given (→).

radial positions in the tube. To this purpose a frame has been placed inside the reactor. This ladder type frame keeps the thermocouples well fixed at the desired positions. The ladder consists of two hollow, 1.5 mm outside diameter rods and a length of 1.25 m. In between the two rods eight rungs are tightened at different axial positions. In the rungs 0.55 mm holes have been drilled. The tip of a thermocouple, which all are of the K-type, is introduced from above through such a hole. The thermocouples have been led out of the reactor at the top via four special pressure seals. The thermocouples were purchased from one and the same batch and were aged deliberately [see Banis *et al.* (1994)]. To measure the catalyst temperature a thermocouple has been inserted into a hole of 0.55 mm, drilled in the catalyst particle. Catalyst temperatures were measured only in the centre of the tube at approximately 8 mm above the gas temperature locations. For the positions of all thermocouples, see Fig. 4.

Temperature sensors disturb the system due to changes in the packing arrangement, disturbances of the flow and heat conduction through thermocouples and the frame [see Khanna and Seinfeld (1987), Freiwald and Paterson (1992) and Mongkhonsi *et al.* (1992)]. For a discussion of existing methods to measure temperatures in a packed bed,

see Borman and Westerterp (1992). To minimize such effects, the frame has been kept small at only 0.45% of the reactor volume, the vertical rods have been put as close to the wall as possible and thin thermocouples of 0.5 mm have been selected. The thermocouples have been tied in bundles to the rods. To avoid heat conduction through the rungs poly-ether-ether-ketone, PEEK, a high temperature resistant polymer with a conductivity of 0.4 W/m K, has been used as the construction material. Thermocouples located at 1.5 mm from the wall exhibit deviations from the real local temperature due to heat losses to the wall [see Borkink and Westerterp (1992a)]. Although this will lead to lower temperatures in the hot-spot plane near the wall, the axial location of this plane will not deviate from that in a case where there were no thermocouples present, as shown by Mongkhonsi *et al.* (1992) for a similar situation. In two independent measurements it was found that the porosity in the bed increased from 0.47 to 0.50 due to the presence of the frame in the bed.

Concentrations are measured at different axial positions in the tube. To this end, sample points are located in the wall so disturbance of the flow is minimal. The flow velocity in the sample tubes should be equal, lower than the interstitial velocity in the bed itself. The internal diameter of the sample tubes is 1 mm; the gas flows through it to a multi-path, dead-end stream selector. Also feed and exit gases are led to the stream selector, through which the gas samples flow to a gas chromatograph fitted with a Chrompack PoraPlot Q fused silica column and a thermal conductivity detector. With the gas chromatograph the concentration of ethene and carbon dioxide in the gas was determined. The concentration of carbon dioxide in the reactor effluent is also measured on line with an infrared spectrometer.

In view of the danger of explosions [at ethene concentrations over 3%, see Siccama and Westerterp (1993)] the production of the toxic ethene oxide – with a maximum allowable concentration of 1 ppm – and the relatively large scale of the pilot plant, the installation has been automated and placed in a concrete bunker with walls of a thickness of 0.50 m: all events and data are registered, controlled and stored via a combination of a Hewlett Packard Data Acquisition and Control Unit and a Hewlett Packard RS/25C Vectra process computer. All electronic equipment has been placed in a movable cupboard. In case of an emergency all important equipment will be switched off, the ethene supply stopped and nitrogen introduced to cool the reacting system either automatically by the control system or by pressing an emergency button.

Cooling section

The cooling section has to ensure a constant wall temperature along the entire reactor length. To this

Fig. 5. Schematic representation of the cooling section. (A) circulation pump; (B) supply pump; (C) supply vessel; (D) jacket; (E) electrical oven; (F) buffer vessel; (G) condenser; (H) collection vessel; (I) pressure control system.

end, the reactor wall is surrounded by boiling water, circulated by a centrifugal pump (Fig. 5). The steam produced and the high flows create high heat-transfer coefficients along the wall, consequently the wall temperatures remain constant over the entire tube length.

The jacket around the tube, which has a diameter of 89 mm, is filled with demineralized water. A 37 l insulated buffer vessel is connected to the top of the jacket. This vessel is connected at the bottom with the centrifugal pump which returns the water to the bottom of the jacket. The vessel is positioned 3 m above the pump so that the hydrostatic pressure prevents cavitation. Vapour is conducted to a condenser and condensate returned via a collection vessel. To compensate for external heat

losses the jacket is surrounded over a length of 0.975 m by a 6 kW electrical heater. The pressure of the cooling system is controlled by a combination of a back-pressure controller and a nitrogen supply at the desired pressure. Gas is vented or supplied to the cooling section resulting in a constant pressure. By varying the pressure between 0.1 and 4 MPa, it is possible to set wall temperatures between 373 and 522 K. For safety reasons the cooling section is provided with a pressure safety valve. The level in the buffer vessel is measured and if necessary a water supply pump will pump fresh water into the cooling section.

The wall temperature is measured by four thermocouples located at different axial and angular positions in the outer side of the wall. Thermo-

couples, placed in 1 mm tubes, have been pressed into grooves along the tube wall. The temperature of the wall differed less than 0.5 K over the length of the catalyst bed.

RESULTS

The catalyst in the reactor achieved a stable and reproducible activity after about 200 h of use under standard conditions at $P = 0.5$ MPa, $T_w = 465$ K, $x_E = 0.8$ mol% and $\phi = 0.81$ kg/m² s. More information on the activation procedure is given in Schouten *et al.* (1994). Borman and Westerterp (1992) checked for a uniform activity of the catalyst over the length of the tube by repacking the catalyst bed. No deviations in temperature profile, overall conversion and selectivity were found.

The measured temperatures at equal radial, but different axial positions have been interpolated by means of a spline technique [see e.g. Fig. 6(a)]. These lines should not be confused with model lines. The experimentally observed dependencies on pressure, ethene partial pressure, mass flow and wall temperature respectively are discussed below. Also model calculations will be compared to the experimental results. Comparisons are made on the basis of bed conversion, selectivity and the axial temperature profile of the catalyst at the centre of the tube. At this position deviations in radial position have only a small effect because radial gradients are nearly flat in the centre of the tube. In addition temperatures in the centre are largest so discrimination between models is easier.

Experimental temperature and concentration profiles

In Figs 6(a) and 6(b) typical axial and radial temperature profiles in the reactor tube are shown. The highest temperatures are found in the centre of the tube. The radial temperature profiles are parabolically shaped. The location of the hot-spot at different radial positions is the same except for the position 1.5 mm from the wall. At this radial position the location of the hot-spot systematically is found further downstream in the tube. This shift cannot be explained by deviations in measured temperatures due to heat losses to the wall. The cause for this shift may be the wall effect: because of the increased porosity near the wall less catalyst is present. This leads to a decreased reactant consumption and thus the hot-spot shifts to somewhat further downstream in the reactor. Although the deviations in hot-spot location are small, neglect of the wall effect certainly will have an influence on the prediction of the reactor performance.

In Fig. 6(c) a typical concentration profile is shown. The consumption of ethene and the production of carbon dioxide are largest in the first part of the catalyst bed. Although still reactant is present at the end of the bed, almost no conversion takes place in this part of the reactor. The heat production by reaction and heat removal by radial conduction and convection, respectively HPR, HWR and HCR, over the length of the reactor tube have been determined from the experimental temperature and concentration profiles. The results are

Fig. 6(a). Axial profiles of gas and catalyst temperatures at different radial locations; $P = 0.50$ MPa, $T_w = 466.2$ K, $\phi_m = 0.82$ kg/m² s, $x_E = 0.715$ mol%.

Fig. 6(b). Radial profile of gas and catalyst temperatures at different radial locations. For conditions, see Fig. 6(a).

Fig. 6(c). Axial concentration profile for ethene and CO₂. For conditions, see Fig. 6(a).

Fig. 7. Experimentally determined heat production and heat removal rates over the length of the reactor; $T_w = 465 \text{ K}$, $P = 0.5 \text{ MPa}$, $x_E = 0.5 \text{ mol\%}$, $\phi_m = 0.82 \text{ kg/m}^2 \text{ s}$ (a) or $2.51 \text{ kg/m}^2 \text{ s}$ (b); HPR = heat production rate, HWR = heat removal rate by radial dispersion, HCR = heat removal rate by convection. Temperature profiles of the two experiments are shown in Fig. 11.

shown for two different mass flow rates, see Figs 7(a) and 7(b). The convective contribution becomes zero at the hot spot location because there $dT/dz = 0$. The heat production rate drops much more rapidly for lower mass flow rates than for higher ones. This can be explained by larger concentrations of reactant and smaller concentra-

tions of products at the end of the catalyst bed for higher mass flow rates, resulting in higher reaction rates.

Heterogeneous character of the bed

In Figs 8(a) and 8(b) the temperature difference between catalyst and gas in the centre of the bed is

Fig. 8. Axial profiles of temperature differences between catalyst and gas at varying ethene partial pressure (a) and varying wall temperature (b); $P = 0.5$ MPa, $T_w = 465$ K, $\phi_m = 0.82$ kg/m² s, $x_E = 0.5$ mol%. Calculations in Fig. 8(a) have been done with calculated Nu_p ($=30.5$) and with $2 \cdot Nu_p$.

shown for different partial pressures of ethene in the feed and different wall temperatures. In Fig. 8(a) experimental values are compared with model calculations while in Fig. 8(b) the experimental temperature differences are connected with lines drawn with the spline technique.

Interpolated catalyst temperatures have been obtained with the spline technique mentioned above. As expected the solid temperature is always higher than the gas temperature. Especially before the hot-spot the temperature differences can be considerable. The temperature difference is a measure of the rate of reaction, which is highest before the hot-spot. A maximum is found in temperature difference $T_s - T_g$ because of the combined effect of decreasing reactant concentrations and increasing reaction temperatures.

The correlation of Gnielinski (1982) [see eq. (8)] predicts larger differences between catalyst and gas temperatures than measured experimentally, although trends are the same. Larger values for the Nusselt number of the particle would give a better agreement. In Fig. 8(a) the temperature differences are calculated on the basis of the relation of Gnielinski and also for 2 times higher α_p values. Correspondence between calculated and measured values is much better in the latter case.

Scatter in the temperatures measured

In Fig. 6(b) at $z = 50$ and $r = 16$ mm and in Fig. 8(a) and (b) at $z = 150$ mm and $r = 0$ mm there is a small dip in the experimental temperature profiles. Also in other profiles deviations could be observed at the same spots. For a given packing these deviations are consistent. It has been checked that this was not caused by the thermocouples themselves by leading nitrogen instead of reaction mixture over the catalyst bed. All thermocouples gave equal temperatures within 0.2 K. The differences are due to the random nature of the packing. Temperatures are measured only at one angular location [see Borman and Westerterp (1992) and Dixon (1993)]. Although the effect is qualitatively comparable to the experiments of Borman, the deviations are much smaller. This is probably caused by the high accuracy of our temperature measurements and could also be explained by our efforts to obtain a truly random packing arrangement. The effect of temperatures varying at the several angular positions surely will play a role in practice whenever more crude packing methods are employed.

Influence of the total pressure

Experimentally almost no influence is observed of the total reactor pressure at equal mass flow rates. Both the conversion and the axial temperature profiles are almost identical for different pressures [see Figs 9(a) and (b)]. At higher pressures slightly higher hot-spot temperatures are found. The results indicate a surface coverage of

the catalytically active material near to one for both reactions. Also the model calculations show a limited dependence on pressure. However, some systematic deviations are found between calculated and experimental temperature profiles; the discussion is referred to. The heterogeneous model (HT) gives a better agreement with the experimental results than the pseudo-homogeneous model (PHT).

Influence of the ethene partial pressure in the feed

In Fig. 10(b) it is shown that the conversion over the catalyst bed remains the same for different ethene partial pressure in the feed and at constant total pressure. This means the order in ethene is about one. Only at high ethene partial pressures the conversion increases which can be attributed to the fact the temperatures in the bed are so high the reactor is close to a "runaway" [see Fig. 10(a)]. In this range also the selectivity drops, indicating the total combustion reaction is mainly responsible for the "runaway".

The models predict too high reaction rates especially towards the end of the tube, see Figs 10(c) and (d), and therefore temperatures towards the end of the tube decrease more slowly than the experimental ones. For the experiment performed at 0.906 mol% ethene the heterogeneous model predicts a "runaway". In a future article runaway in our system will be discussed in more detail.

Influence of the mass flow

Higher mass flow rates lead to a reduction of the residence time in the reactor and therefore the conversion drops [see Fig. 11(a)]. Lower mass flow rates do move the hot-spot closer to the entrance of the catalyst bed [see Figs 11(b) and (c)]. Because a smaller amount of wall area is available for heat removal in that case and because the radial heat transport coefficients are smaller at lower mass flow rates, the temperatures in the hot-spot increase.

This is confirmed in the model calculations: higher hot-spot temperatures are found in the first part of the bed and the hot-spot temperatures become less distinctive at higher flow rates.

Influence of the wall temperature

In the experiments with a different wall temperature, the inlet temperature was also changed so that wall and inlet temperature are always equal. At higher wall temperatures the conversion increases and the selectivity drops [see Figs 12(a), 12(b) and 12(c)]. Both reaction rates increase at higher temperature. The selectivity drop indicates a higher activation energy for the total combustion reaction.

The influence of wall temperature on the conversion and selectivity is predicted very well by the models at all three ethene concentrations. The correspondence between calculated and experimental axial temperature profiles is less satisfactory. The pseudo-homogeneous model gives too

Fig. 9. Axial centre line temperature profile of the catalyst (a) and conversion and selectivity (b) as a function of total pressure: $T_w = 465$ K, $\phi_m = 0.82$ kg/m² s, $x_E = 0.5$ mol%; PHT = pseudo-homogeneous two-dimensional model, HT = heterogeneous two-dimensional model.

Fig. 10. Axial temperature profile of the catalyst (a) conversion and selectivity (b) and axial concentration profiles of ethene (c) and carbon dioxide (d) as a function of ethene partial pressure in the inlet; $T_w = 465$ K, $P = 0.5$ MPa, $\phi_m = 0.82$ kg/m² s.

(c)

(d)

Fig. 10—Continued.

Fig. 11. Axial temperature profile of the catalyst (a) and conversion and selectivity (b) as a function of mass flow rate; $T_w = 465$ K, $P = 0.5$ MPa, $x_E = 0.5$ mol%. Calculations done with heterogeneous model [11(b)] and pseudo-homogeneous model [11(c)].

(c)

Fig. 11—Continued.

(a)

Fig. 12. Conversion and selectivity as a function of wall temperature at $x_E = 0.3\%$ (a), $x_E = 0.5\%$ (b) and $x_E = 0.9\%$ (c). For conditions see Fig. 13.

Fig. 12—Continued.

(a)

(b)

Fig. 13. Axial temperature profile of the catalyst at varying wall temperatures; $P = 0.5$ MPa, $\phi_m = 0.82$ kg/m² s, $x_E = 0.5$ mol%. Calculations done with pseudo-homogeneous model [13(a)] and heterogeneous model [13(b)].

Fig. 14. Axial centre line temperature profiles of the catalyst with and without incorporation of the effect of products on the kinetics of the reactions; $P = 0.5$ MPa, $\phi_m = 0.82$ kg/m² s, $x_E = 0.5$ mol% and $T_w = 465.4$ K; see also Table 2.

low hot-spot temperatures [see Fig. 13(a)]. The heterogeneous model also gives too low hot-spot temperatures at the low wall temperatures [see Fig. 13(b)]. At higher wall temperatures a better agreement with experiments is observed, but the location of the hot-spot is shifted somewhat towards the entrance of the tube compared to the experiments. The difference between the predictions of the pseudo-homogeneous and heterogeneous models respectively are large as could be expected on the basis of the already mentioned temperature differences between catalyst and gas [see Fig. 8(b)].

DISCUSSION AND CONCLUSIONS

With the experimental apparatus it was possible to obtain very accurate measurements of the temperatures in the reactor. The models are able to predict the behaviour of the reactor qualitatively very well, in particular the conversion and selectivity. Quantitatively the agreement between experimental and theoretical temperature profiles is less satisfactory: the model calculations give higher reaction rates in the second part of the reactor tube. As a result the temperatures predicted are too high in the last part of the catalyst bed. It is also observed models predict too low hot-spot temperatures. To some degree these deficiencies may be attributed to the inaccuracy of the kinetic expressions. Scouten *et al.* (1994) found that the experimentally obtained kinetic expressions were not able to fit the entire range of conversions; they found too low reaction rates at low product concen-

trations and too high rates at high product concentrations.

The heterogeneous model gives better results than the pseudo-homogeneous model. This should not be surprising in view of the differences in temperature between catalyst and gas which are really significant in some cases. The temperature differences predicted by the available relations in literature are systematically higher than are found experimentally.

The influence of products on the reaction rates is found to be very significant [see Scouten *et al.* (1994)]. Calculations have been made neglecting the inhibition of reaction rates by products. This results in strong differences between calculated and actual conversions, selectivities and temperature profiles, see Table 2 and Fig. 14. So the influence of the reaction products must be taken into account correctly. In these experiments the hot-spot location near the wall is found further downstream than

Table 2. Conversion and selectivities with and without incorporation of the effect of products on the kinetics of the reactions. For conditions see Fig. 14

Case	Model	Product inhibition	ξ	σ
exp.	—	—	0.474	0.596
1	PH-T	yes	0.481	0.572
2	H-	yes	0.517	0.552
3	PH-T	no	0.889	0.486
4	H-T	no	"runaway"	

at radial positions closer to the centre of the tube. Therefore it can be concluded probably a wall effect may be present. Although the differences are small under our operating conditions with Raschig rings at a tube-to-particle diameter-ratio of eight, a larger influence of the wall may be expected at lower d_t/d_p values – with a relatively larger wall zone – and/or with different particle shapes with more pronounced radial porosity distributions.

The total picture is disturbed by the inaccuracy of the kinetic equations and the inadequacy of the relation of Gnielinski in predicting the measured temperature differences, so it is difficult to conclude directly on the basis of our experimental and theoretical work whether heat and mass transport parameters can be determined independently and used for reactor modelling. To check this, the kinetics of the reaction should be known more accurately. A *different* reaction system could be chosen with better known kinetics, e.g. the hydrogenation of ethyne and ethene [see Bos *et al.* (1993)], the total combustion of propene [see Daszkowski and Eigenberger (1992)] or the combustion of carbon monoxide. In a future article the authors will demonstrate whether changing the heat transport parameters results in better agreement between experiments and calculations. Also heat transfer parameters will be measured separately.

This study emphasizes again the importance of complete and accurate chemical kinetics in the modelling of fixed-bed catalytic processes [see Froment and Hofmann (1987)].

Acknowledgements—The authors wish to thank the Royal Dutch Shell group for supplying the catalyst, P. J. Kerkhoven, G. J. M. Heesink and W. F. R. Groenen for their experimental work and O. D. Veehof and A. H. Pleiter for technical support.

NOTATION

H	ratio of reaction heats ($=\Delta H_2/\Delta H_1$)
A	area, m^2
C	concentration, mol/m^3
C_p	heat capacity, $\text{J}/\text{kg K}$
d	diameter, m
D	diffusion coefficient, m^2/s
H	ratio of reaction heats ($=\Delta H_2/\Delta H_1$)
k_r	reaction rate constant, $\text{mol}/(\text{s kg})$
K	adsorption constant, $1/\text{bar}$
L	bed length, m
N	number of particles on a tube diameter ($=d_t/d_p$)
p	pressure, Pa
P	pressure, bar
r	radial coordinate, m
r	reaction rate, $\text{mol}/(\text{s kg})$
R	radius, m
R	gas constant, $\text{J}/(\text{mol K})$ ($=8.134$)
R	production rate, $\text{mol}/(\text{s kg})$
R^*	dimensionless production rate ($=R/R^0$)
T	temperature, K
T_{act}	activation temperature ($=E/R$)

T_{ads}	adsorption temperature ($=\Delta H_{\text{ads}}/R$)
v	interstitial gas velocity, m/s
V	volume, m^3
x	mole fraction
z	axial coordinate, m

Greek letters

α	heat transfer coefficient, $\text{W}/\text{m}^2 \text{K}$
ΔH	reaction enthalpy, kJ/mol
ε	porosity
ζ	conversion
η	dynamic viscosity, Pa s
θ	dimensionless temperature ($=T/T_w$)
Θ_{ad}	dimensionless adiabatic temperature rise ($=\Delta H_1 C^0/(\rho C_p)_g T^0$)
λ	thermal conductivity, W/mK
Λ	tube slenderness ($=L/d_t$)
ρ	density, kg/m^3
ρ	dimensionless radial coordinate ($=r/R_t$)
σ	selectivity towards ethene oxide
ϕ	mass flow rate, $\text{kg}/\text{m}^2 \text{s}$
ω	dimensionless axial coordinate ($=z/L$)

Subscripts and superscripts

b	bed
C	carbon dioxide
E	ethene
eff	effective
EO	ethene oxide
g	gas
i	of reaction i
O	oxygen
p	particle
r	radial
s	solid
s	superficial
t	tube
w	wall
W	water
0	inlet conditions
1	of reaction 1: the epoxidation
2	of reaction 2: the total combustion of ethene
∞	pre-exponential
$-$	radial averaged

Dimensionless quantities

Bi	Biot number ($=\alpha_w R_t/\lambda_{\text{eff},r}$)
Bo_r	radial Bodenstein number ($=(\rho C_p)_g v_s d_p/\lambda_{\text{eff},r}$)
Da	Damköhler number ($=\rho_b R^0 L/s_2 C^0$)
Le	Lewis number ($=\lambda_g/(\rho C_p)_g D_g$)
Nu	Nusselt number ($=\alpha d_p/\lambda_g$)
Pr	Prandtl number ($=\eta C_p/\lambda_g$)
Re	Reynolds number ($=\rho_g v d_p/\eta$)
St	Stanton number ($=\alpha_p a_p L/(\rho C_p)_g v_s$)

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