ACKNOWLEDGMENTS

ABSTRACT

The problem of heat transfer in a catalyst filled wall-cooled reactor tube where a strongly exothermic reaction takes place has been studied. The reaction was hydrogenation of carbon monoxide over a commercial cobalt supported on silica catalyst.

A highly instrumented pilot reactor with measuring and analytical systems for recording of axial and radial temperature profiles and axial concentration profiles was constructed. Furthermore, mathematical models were developed for prediction of the reactor performance under steady state conditions, and an experimental investigation was carried out to obtain data for model discrimination and parameter estimation. The models were discretized into a set of algebraic equations by the method of orthogonal collocation.

Experimentally determined temperature and concentration profiles were provided from measurements in the pilot reactor at steady state operating conditions. Due to a very narrow limit of possible operating conditions the possibilities of variations of experimental parameters were rather restricted. This was due to instability problems commonly encountered in highly exothermic fixed bed operations. The experiments were performed at temperatures around 500 K, partial pressure of synthesis gas in the range 0.18–0.3 MPa and a H_2:CO ratio of about 2.2 giving conversions in the range 25–50 %. The reaction mixture was diluted with N_2, keeping the total pressure constant at 1.0 MPa.

Rate expressions of the Langmuir-Hinshelwood type were used to describe the rate of CO consumption and the rate of CH_4 formation. Kinetic parameters were estimated using a plug-flow model with measured axial temperature profiles. The kinetic expressions gave an acceptable fit between simulated and experimental concentration profiles.

Different reactor models including both heat and mass transfer were investigated. The models were adapted to give a best fit to the experimental data by estimation of parameters related to the thermal conductivity of the bed. The fit of the different models was evaluated by comparison of calculated and measured data for the optimal parameters.

The traditional dispersion model with constant void fraction, velocity and radial thermal conductivity was compared with a physically more realistic model where these parameters were dependent on radial position. Different assumptions concerning the variations of the conductivity in the near-wall region were evaluated for the last model. The radial dependence of void fraction and velocity was estimated using expressions obtained from the literature.

The model with radial dependent parameters and velocity seemed to have the potential of giving a better description of the temperature profiles in the reactor than the traditional model. But the local velocity model was rather sensitive to assumptions made on the variations in radial conductivity in the near-wall region. To make further statements as to the influence of the wall effect on the conductivity, an accurate and detailed description of the flow profile in the near-wall region is necessary. This was, however, not obtainable in this study because the detailed void fraction profile for the reactor bed was not known.

The best fit between calculated and measured temperature profiles was obtained when the radial conductivity was assumed to be proportional to the local velocity. Using the traditional dispersion model the estimated radial thermal conductivity was about 70% higher than values predicted by available correlations and about twice the value estimated by the local velocity model for the core of the bed.

It is a common observation that effective radial conductivities estimated from measurements under reactive conditions are considerably higher than those obtained from correlations based on cold-flow measurements using the traditional dispersion model. This overestimation of the effective conductivity led to calculated temperature differences which were smaller than the observed ones. Using the local velocity model, more realistic values of the radial conductivity in the core of the bed may be obtained, giving a better description of the real temperature profiles in this region.

1. INTRODUCTION

The work leading to this thesis was carried out as a part of the Norwegian State R&D Program for Utilization of Natural Gas, the SPUNG program. The main object of this program, which started in 1987, is to obtain a better utilization of the huge amount of natural gas on the Norwegian continental shelf. The main areas of natural gas utilization covered by SPUNG are chemical conversion, gas energy utilization and liquefied natural gas.

The object of chemical conversion is the production of liquid fuels and other petrochemical products from methane. Production of methanol and liquid hydrocarbons is usually carried out via the synthesis gas route. Synthesis gas is produced from methane by steam reforming or partial oxidation. Liquid fuels can be obtained from direct conversion of synthesis gas by the Fischer–Tropsch reaction, or from methanol as intermediate by Mobils's MTG process.

The Fischer–Tropsch synthesis was used in Germany during the 2. World War, but later the process has only been utilized by South Africa in their Sasol plants. The reason for this is that the process has been economically unattractive, but recently new interest has been focused on the Fischer–Tropsch synthesis as a way of utilizing remote gas fields. This has led to the developement of Shell's SMDS process based on fixed bed technology (Sie et al., 1991) and Statoil's GMD process based on slurry technology (Roterud et al., 1989).

The fixed bed reactor project which is a part of the chemical conversion program, was aimed at the study of heat transfer in reactors under strongly exothermic reactive conditions. Such reactors are important in natural gas conversion, and the influence of reaction and heat transfer on conversion, selectivity and reactor stability is of prime concern both in design, operation and control of this type of reactors. The Fischer–Tropsch reaction meeting the requirements of high exothermicity and relevance in natural gas conversion was chosen as the model reaction for this study. This reaction has been and will be an object of research at the Laboratory of Industrial Chemistry in Trondheim.

1.1. FIXED BED REACTORS

The major part of industrial catalytic processes is carried out in fixed bed reactors. These reactors are mainly large capacity units for the production of bulk chemicals. The reactors are usually classified as adiabatic, multibeded adiabatic with interstage heat exchange, multitubular or tube–bundle reactors and fixed bed reactors with internal heat exchange depending on the mode of heat transfer between the reaction zone and the surroundings (Froment and Hofmann, 1987). The design of an adiabatic and a multitubular reactor is shown in Figure 1–1.

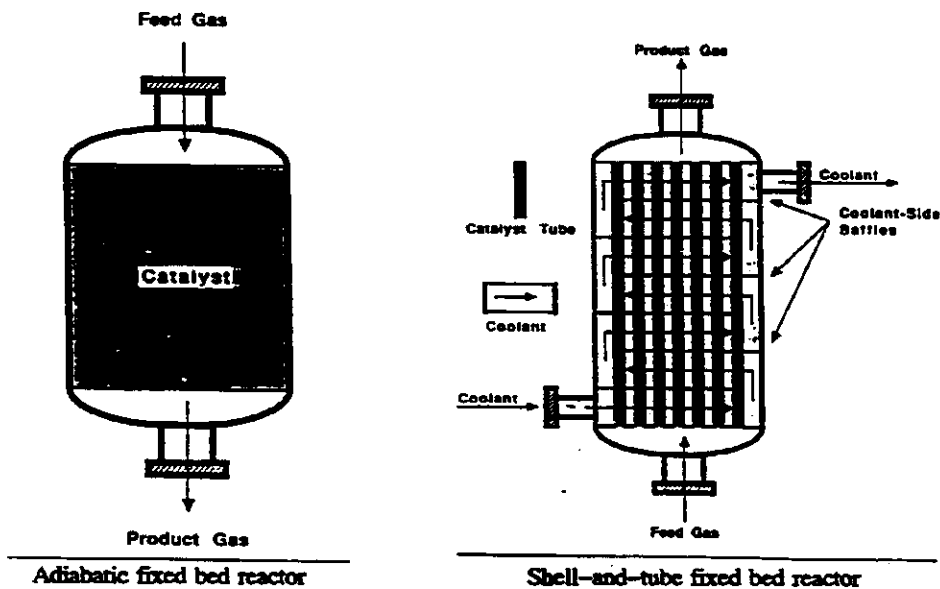| Adiabatic fixed bed reactor | Shell–and–tube fixed bed reactor |

Figure 1–1. Adiabatic and multitubular fixed bed reactors. From Cropley, 1990.

Adiabatic reactors are preferred because of simpler technology and ease of operation, but for highly exothermic reactions the temperature rise will be unacceptably high, and highly

endothermic reactions may be extinguished when carried out in a single adiabatic step. In these cases multibed adiabatic reactors with interstage heat exchange or reactors with continous heat exchange have to be used.

For strongly exothermic reactions the removal of heat from the reacting zone is a key issue in the design of reactors for such processes. It is usually desirable or necessary to operate these reactors within a narrow range of temperatures to optimize productivity and selectivity and to prevent excessive catalyst deactivation due to local overheating in the bed. Since highly exothermic processes often are operated near or in the instability region additional constraints are put on the temperature control of the reactor system to prevent thermal runaway and subsequent catalyst damage and safety hazards.

High conversion in exothermic equilibrium reactions is favored by low temperatures. Nonisothermal operation is preferred in this case and the optimum temperature profile decreases toward the exit. The optimum profile is better approximated in a multitubular reactor than in a multibed reactor (Froment and Hofmann, 1987).

The type of fixed bed reactor used for these reactions is almost exclusively the wall-cooled multitubular reactor comprising many thousands parallel reactor tubes within a reactor shell through which heat transfer oil, water or molten salts are circulated. The advantages of this reactor compared with the multibed adiabatic reactor with interstage cooling are better approximation of optimum temperature profile and better temperature control through precise control of the temperature and flow-pattern of the heat exchange medium. A multitubular reactor can be held stable at an operating point which is inherently unstable by keeping the coolant temperature within narrow limits (Eigenberger and Schuler, 1989).

Examples of exothermal reactions carried out in multitubular reactors are various oxidation reactions and synthesis gas conversion reactions. The heavy paraffin synthesis stage in the Shell Middle Distillate Synthesis Process (SMDS) is a Fischer-Tropsch synthesis over a supported cobalt catalyst; carried out in a multitubular fixed bed reactor with boiling water as the cooling medium (Sie et al., 1991).

1.2. SCOPE OF THE WORK

Design and operation of chemical reactors rely to a considerable extent on the use of reactor models to predict the performance. Models are used in determination of design parameters and process conditions to optimize performance and maintain safety, in scale–up of experimental data from laboratory and pilot reactors and for state estimation in model–based control systems.

The validity of the reactor models rely basically on the model structure and model parameters being able to describe the essential features of the reactor in a realistic way. This can only be confirmed by comparison of simulated data with measurements from real reactors.

The main objectes of this work were the design and construction of a fixed bed pilot reactor to obtain experimental data for such evaluations and the developement of mathematical models for simulation of the reactor behaviour. Comparison of experimental measurements with output from reactor models is used for model discrimination and verification and enables the estimation of unknown model parameters.

The transfer of heat from the catalyst bed to the cooling medium is of prime concern in the design and operation of wall cooled reactors for strongly exothermic reactions. The most important parameters, besides the kinetics, are the parameters controlling the radial transfer of heat in the catalyst bed and from the bed to the cooling medium. Due to the substantial discrepancies between heat transfer parameters measured under reactive and non–reactive conditions reported in the literature, the evaluation of the heat transfer characteristics of the bed under reactive conditions is of great importance in reactor modeling.

These discrepancies are seen when heat transfer parameters are estimated using traditional dispersion models. Such models use average values for the void fraction, fluid velocity and dispersion coefficients in the radial direction. These values are assumed to be constant and independent of radial position. Measurements show however, that the void fraction is radially dependent, increasing towards the wall. Measurements of radial velocity profiles are not easily obtained, but fluid mechanics theory give strong evidence that both velocity and dispersion

coefficients are dependent on local void fraction and wall effects. These subjects have received attention during the last years, and models based on radially varying parameters have been put forward. Comparison of calculated temperature and concentration profiles from these models with experimentally measured profiles both under reactive and non-reactive conditions is of great interest to reveal their potential.

In this work attention has been focused on comparison of experimental data from the pilot reactor with simulated data from the traditional dispersion model and from models with radially varying parameters in order to reveal the differences between the models. The experimental data were measured under reactive conditions, and the models were adapted to give a best fit to the data by estimation of some key parameters. These were parameters related to the catalyst activity and to the radial thermal conductivity of the bed.

2. LITERATURE REVIEW

2.1. DESIGN AND OPERATING PRINCIPLES FOR MULTITUBULAR FIXED BED REACTORS

This chapter is concerned with the design of the wall cooled multitubular reactor for exothermic reactions which is the basis of this work. In this type of reactor all the tubes should ideally behave equal. This implies that inlet conditions and wall temperature are equal and that concentration and temperature profiles within the tubes are equal. Consequently, for experimental and modeling studies only one tube has to be considered. This view was the basis for the construction of the pilot reactor which was intended to simulate one tube under conditions most similar to real industrial conditions as was practically possible. For obvious reasons the lenght of the reactor and the gas loading had to be lower than in an industrial reactor. Thus conversion was obtained with lower superficial velocity which makes the heat transfer characteristics of the pilot reactor different from an industrial reactor. This implies that some modeling and scale–up considerations were necessary.

The main concern in the design of multitubular reactors for highly exothermic reactions is the transfer of heat from the reacting zone inside the tubes to the cooling medium to obtain thermal stability. Thermal stability in multitube systems depends largly upon properly matching the maximum heat flux in the catalyst bed to the tube diameter. The catalyst characteristics strongly influence this relationship, and the key parameter is the apparent activation energy of the catalyst (Croply, 1990).

The tube length and mass velocities in industrial reactors show vide variations. The length may vary in the range from a few metres up to 15 m, and the mass velocity in the range 1–20 kg/m² s. The tube diameter for exothermic reactions, however, generally lies in the narrow range 2–5 cm, and the ratio of internal tube diameter to catalyst particle diameter is usually between 5 and 10 (Cresswell, 1986). Smaller particles tend to decrease the effective radial thermal conductivity of the bed and cause excessive pressure drop, while larger particles may

cause increased intraparticle mass transfer resistance as well as reduced heat removal from the pellet to the fluid, thereby increasing the risk of particle thermal instability.

The construction of the cooling system is also a primary concern in the design of multitubular reactors. For stable operation the heat generated by the reaction has to be balanced by heat removal through the cooling system. Figure 2-1 shows a typical reactor and cooling system including a control system for precise control of the coolant temperature at the desired operating point. Especially, when the desired operating point is unstable as shown in Figure 2-2, the coolant temperature has to be kept within narrow limits. For strongly exothermic reactions which are not equilibrium controlled great emphasis is laid upon keeping the temperature differences between the cooling medium inlet and outlet small, as heating of the cooling medium causes unwanted effects (Eigenberger and Ruppel, 1986).
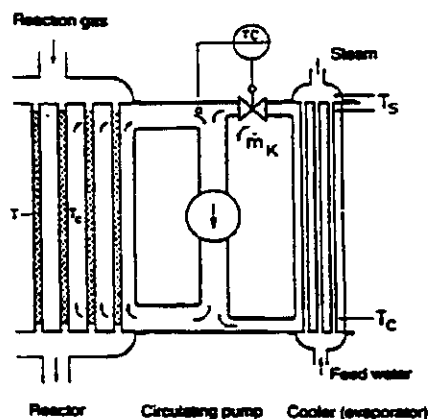

Figure 2-1. Cooled, tube-bundle reactor. From Eigenberger and Schuler, 1989.

Careful control of the inlet temperature may also be necessary if the system tends to be unstable. The inlet temperature is often kept at the coolant temperature to avoid wrong-way behaviour.
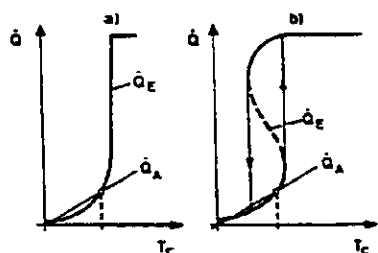
Figure 2-2. Heat generation, $\dot{Q}_E$, and removal, $\dot{Q}_A$, from cooled, tube-bundle reactor with an exothermic (consecutive) reaction: a) calculations based on an ideal tubular reactor; b) calculations based on an actual reactor with axial thermal feedback by conduction. From Eigenberger and Schuler, 1989.

The stabilty diagram shown in Figure 2-2a is typical for a reactor where axial feedback of heat is neglectible. This system causes no particular problems concerning control and safe operation. Reactors following the stability diagram of Figure 2-2b are, however, much more difficult to control. Here axial feedback of heat through conduction plays a significant role, and the system having multiple steady states is much more sensitive to variations in coolant temperature. But for industrial fixed bed reactors under typical operating conditions, axial feedback is relatively unimportant and not likely to cause severe stability problems (Froment, 1974).

An important element in the design of industrial reactors is the scale-up of pilot reactor data and data from different types of laboratory reactors. As an industrial reactor can not be expected to behave exactly like a smaller pilot reactor some element of modeling has to be done. Guidelines for design and scale-up are discussed by e.g. (Doraiswamy and Sharma, 1984; Froment and Hofmann, 1987; Froment and Bischoff, 1990).

2.2 REACTOR MODELING

2.2.1. Introduction

The state of a heterogeneous fixed bed catalytic reactor is governed by the chemical reaction taking place on the catalytic surface and the transportation of heat and mass in the catalyst pellets, between the surface of the pellets to the bulk fluid phase and transportation of heat, mass and momentum in the bulk fluid phase by convection and diffusion. In a wall cooled multitubular reactor with an exothermic reaction there is also a transport of heat from the bed through the reactor wall to the cooling medium.

Ideally, a model should describe all the transport processes taking place in the reactor. But because of the complexity of such an approach simplifications have to be made. The first simplification is the choice of model structure e. g. a continuum model for a randomly packed bed of solid catalyst particles with interstitial fluid flow. Values for all the parameters involved in the different processes are also hard to get either experimentally or theoretically. Lumping of mechanisms and determination of lumped parameter values either by fitting the model to experimental data or using correlations from the literature is therefore done.

The choice of model complexity is mainly governed by the different models ability to represent the chemical reactor system under the conditions of interest and by the reliability of the parameters involved. Reliable reactor design and simulations are based in the first place on accurate kinetic expressions and accurate kinetic parameters (Froment, 1984). It often turns out that the kinetic equations are simplified to such an extent that they do not reflect essential features of the reaction and are valid only for extremely narrow operating conditions. Under such circumstances no type of reactor models can be expected to give accurate results because kinetic parameters may play a major role on reactor behaviour (Feyo de Azevedo and Wardle, 1989).

The most common class of models is the dispersion models which are based on the approach of solid particles and fluid phase forming an anisotropic continuum where the conservation

equations for energy, mass and momentum can be represented by partial differential equations and appropriate initial– and boundary conditions. If concentration and temperature gradients between gas and particles are small, a homogeneous model may be used. But if gradients are significant a two phase heterogeneous model taking into account interphasial transport between the gas phase and the catalyst particles may be applied. Intraparticle concentration– and temperature gradients may also be of importance and equations describing transport and reaction inside the pellet may be incorporated in the model. One dimensional models may be used where radial gradients are small, otherwise a two dimensional model taking into account both radial and axial gradients must be used.

An overview of the different types of model equations and discussions of their development and limitations are given in several text books (Carberry, 1976; Froment & Bischoff, 1990; Hill, 1977; Doraiswamy & Sharma, 1984) and reviews (Froment, 1967; Froment, 1974; Hlavacek and Vortruba, 1977; Froment, 1984; Froment and Hofmann, 1987; Feyo de Azevedo et. al., 1990).

Chapter 2.2.2 gives an overview of the different classes of models used for fixed bed reactors. A comparison of the fluid phase dispersion model and cell model is done, and the need to use the heterogeneous approach with an additional model for the catalyst particle phase is discussed. In chapter 2.2.3 the homogeneous and heterogeneous dispersion models are discribed, and some correlations for the dispersion coefficients and heat transfer coefficients are revealed. In the following chapters some topics concerning the limitations of traditional dispersion models are discussed. These are the discrepancies found between the value of the radial thermal conductivity estimated under reactive and non reactive conditions, the possibility of radial nonuniformity in packed beds and the validity of using a heat transfer coefficient to describe heat transfer at the wall.

2.2.2. Model structures

2.2.2.1. Fluid phase model classes

The simplest model for heat and mass transport in a packed bed is the one dimensional plug flow model. This model predicts that a pulse input of tracer material moves undisturbed through the bed with a velocity equal to the interstitial velocity of the fluid under non reacting conditions. But experimental evidence shows that the pulse tends to broaden and flatten out as it moves down the bed, and furthermore, radial gradients are frequently encountered in fixed bed reactors. To account for this Fickian form axial and radial dispersion terms are added to the plug flow model to give the two-dimensional dipersion model.

The effect of axial dispersion at higher Reynolds numbers where molecular diffusion can be neglected, has been examined by Sundaresan et al. (Sundaresan et al., 1980), and it is shown that a travelling pulse is shaped into a curve of the form of a normal distribution. This implies some model predictions which are not consistent with experimental evidence. The extent of backmixing is on a larger scale than what is found experimentally by Hiby (Hiby, 1963) and predicted speed of signal propagation (in attenated form) is infinite. The Fickian type of dispersion models make the assumption that axial mixing is determined by concentration gradients. But Sundaresan et al. (Sundaresan et al., 1980) point out that axial mixing is not concerned with molecular diffusion, turbulent diffusion or Taylor dispersion, but rather with mechanical mixing caused by fluid flow.

The quasicontinuum dispersion model further assumes a continous distribution of mass and energy through the reactor, and this is obviously an approximation regarding the discrete nature of the packed bed. But for a comparatively long bed and a particle diameter being at least one order of magnitude smaller than the tube diameter, this approximation is acceptable (Langers and Machnig, 1974).

Other classes of models with different descriptions of the flow pattern in the reactor have been proposed. Some of the classes are shown in Fig. 2-3. These models represent the reactor

as a finite number of discrete reaction units with interconnections to account for axial flow and axial and radial mixing. The cell model (Deans and Lapidus, 1960) considers the packing as a two-dimensional network of mixing cells with radial and axial connections. One weakness of this model is the prediction of an infinite speed of wavefront propagation. Calderbank (Calderbank et. al., 1968) proposed a three-dimensional model where the bed is represented by a series of close-packed layers of spherical particles. The flow pattern inside each layer gives a good discription of radial mixing but any axial mixing is ignored.
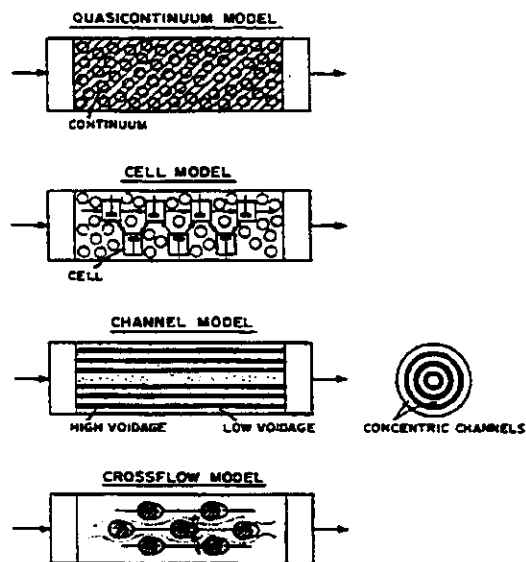
Figure 2-3. Some fixed bed reactor models. From Doraiswamy and Sharma, 1984.

The two types of models described here, i.e. the conventional dispersion models and the cell models, seem at first glance fundamentally different. The dispersion models are represented by partial differential equations of the parabolic type and have inherent in their solution the types of weaknesses described above while the different types of cell models are described by discrete difference equations.

Sundaresan et al. (Sundaresan et al., 1980) have compared the solution of the dispersion model with solutions for alternative formulations of the cell model and have found no major differences. The dispersion term, i.e. the mixing cells, in a cell model with infinite signal propagation between the cells introduces a Poisson distribution of a pulse input while the dispersion model gives a normal distribution. This implies that this cell model have no backmixing but have an infinite speed of signal propagation. If the cells are connected by ideal plug flow reactors with finite signal propagation the signal propagation in the reactor model becomes finite.

Sundaresan et al. concludes from their investigations that although the fine structures of the solutions differs substantially between the cell model and the dispersion model, the two types of models show no great difference in the overall results and that the dispersion model is satisfactory for present design purposes.

A comparison of the dispersion model and the cell model was also performed by Gunn and Pryce (Gunn and Pryce, 1969). They measured axial mixing by the method of frequency responce and estimated parameters of the dispersion model and the cell model at different Reynolds numbers. The variance obtained for the estimated normal distribution parameter of the dispersion model, the Peclet number $(d_p v_0/D_{az})$, was about the same as the variance for the Poisson distribution parameter of the cell model, the ratio of the mixing length to the particle diameter. The values of the Poisson parameter were so large that the Poisson distribution was well discribed by a normal distribution explaining the similarities between the two models.

Gunn and Pryce (Gunn and Pryce, 1969) conclude that the degree of mechanical mixing in the voids is small, and that axial dispersion is due to the random movement of fluid elements and therefore is a diffusion like process thus favouring the dispersion model.

An extension of the cell model proposed by Schmitzlein and Hofman (Schmitzlein and Hofmann, 1987) is shown in Fig. 2–4. This model treats the bed composed of particles of the same size and shape as a hexagonal packing of spheres. Radial symmetry leads to mixing cells in the shape of a torous (TOROUS–Model). These cells are connected with channels which is modeled as ideal plugflow reactors. This gives the repetive pattern of unit cells each

composed of 5 minireactors as shown in Fig. 2–4. It is claimed (Küfner and Hofmann, 1990) that a heterogeneous TOROUS model corrected for radial velocity and porosity variations gives a better description of the observed temperature profile in a fixed bed reactor than homogeneous and heterogeneous dispersion models.

Model of elementary unit
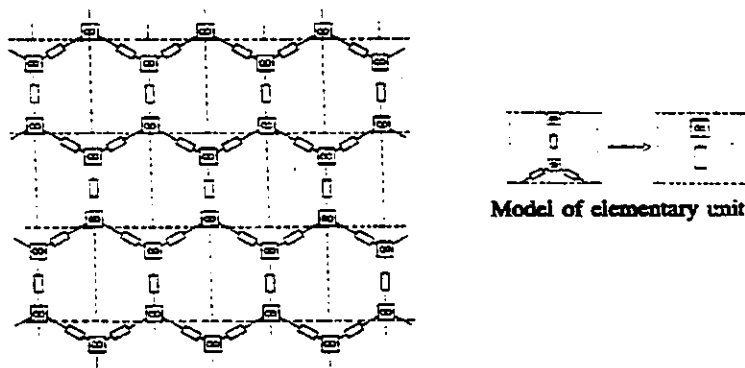
Model structure of the minireactor network

Figure 2–4. TOROUS model. From Schnitzlein and Hofmann, 1987.

2.2.2.2. Solid phase modeling

Homogeneous models which implicitely assume that concentrations and temperature are the same in the catalyst particles as in the gas phase surrounding the particles, are attractive for computational simplicity, and do not require knowledge of the parameters controlling internal pellet heat– and mass transport and interfacial transport between pellet and bulk gas phase. But when diffusional limitations in the pellets are significant or pellet temperature differs significant from fluid temperature, the homogeneous model fails.

In some cases the effect of these transport limitations can be approximated by the use of a

steady state effectiveness factor in the rate expression (Satterfield, 1970). If an effectiveness factor can be calculated on the basis of fluid phase temperature and concentrations, a homogenus model may be used to simulate the steady state behaviour.

Whether a homogeneous model can be used for dynamic simulations too, is not so clear. If concentration or temperature differences exist between fluid and solid phase due to transport limitations, a steady state effectiveness factor would have to be included in the kinetic term in the homogeneous model's mass and heat balances in order to calculate correct reaction rates.

Agreement in dynamic simulation results between a pseudo–homogeneous model with inclusion of a steady state effectiveness factor and a heterogeneous model, and in addition good fit to experimental temperature profiles, has been reported for methanol oxidation (Windes, 1986; Schwedock et al., 1989a; Schwedock et al., 1989b).

On the other hand Ramkrishna and Arce (Ramkrishna and Arce, 1989) concludes from a theoretical study of an isothermal first order reaction that the use of a steady state effectiveness factor can be made only when diffusion limitations in the particles are too strong to permit worthwhile conversion in the reactor. Thus the pseudo–homogeneous reactor model would be invalid for transient analysis, and a heterogeneous model must be used. This conclusion however regards transient mass transfer analysis which is not commonly encountered.

A prerequisite for the use of a pseudo–homogeneous model in transient analysis is that the dynamics is mainly controlled by one of the phases while the other is in a pseudo steady state. In view of this a distinction must be made between mass transfer and heat transfer. The dynamics of heat transfer is mainly controlled by the solid phase because it has a much higher heat capacity than the fluid phase. Typically more than 99 % of the heat capacity of the bed lies in the solid phase. Under such circumstances the fluid phase is in a pseudo thermal equilibrium. The dynamics of mass transfer is generally much faster than that of heat transfer and within the time scale of heat transfer dynamics mass transfer may be considered to be in a pseudo steady state. In industrial operation of fixed bed reactors with relatively slow

variations in control variables the time scale of heat transfer is of most interest, and a pseudohomogeneous dynamic model possibly including steady state effectiveness factors may give satisfactory results (Windes, 1986).

But in the region of severe operating conditions where instabilities and thermal runaway may occur, the use of a pseudohomogeneous model is more questionable. The influence of the dynamics of the fluid phase under such conditions is not well known.

Most dynamic simulations concern only solid phase heat transfer and assume the mass balances and fluid phase heat balance to be in a quasi steady state. This is partially due to mathematical problems of solving the coupled dynamic mass and heat transfer equations simultanously because of the different time scales and consequent stiffness of the system, and partially due to the difficulties of getting experimental data for mass dynamics because of its relatively fast transient responce.

2.2.3. Dispersion models

2.2.3.1. Transport processes in packed beds

The most general heterogeneous model considers the fluid and the catalyst particles as two separate phases. The reaction takes place on the catalytic surface inside the catalyst pores, and mass is transported in the pores and in the stagnant fluid layer surrounding the particles by diffusion and in the bulk fluid by convection and diffusion. For heat transport the picture is even more complex. The different mechanisms are shown in Figure 2–5 and summarized in Table 2–1 according to Kulkarni and Doraiswamy, and Lemcoff et al. (Kulkarni and Doraiswamy, 1980; Lemcoff et al., 1990).
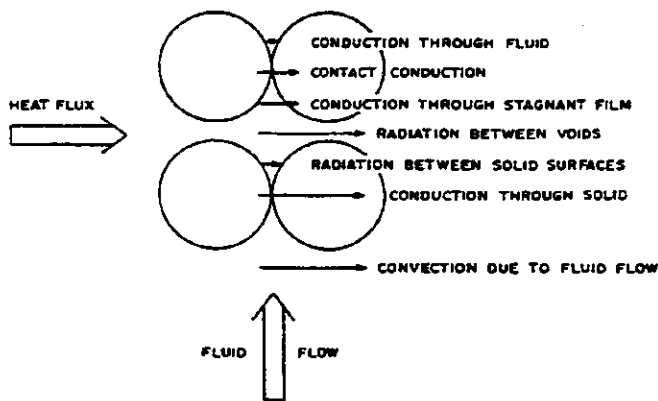
CONDUCTION THROUGH FLUID
CONTACT CONDUCTION
CONDUCTION THROUGH STAGNANT FILM
RADIATION BETWEEN VOIDS
RADIATION BETWEEN SOLID SURFACES
CONDUCTION THROUGH SOLID

HEAT FLUX

CONVECTION DUE TO FLUID FLOW

FLUID FLOW

Figure 2–5. Mechanisms for radial transport of heat in a packed bed. From Kulkarni and Doraiswamy, 1980.

No attempts have yet been done to model all the different heat transfer mechanisms in detail. Both the complexity and the number of unknown parameters of such a model would have been too extensive to handle. Instead, lumping of mechanisms into effective parameters is done, giving rise to simpler models where the effective parameters are determined from available correlations and tuning of the model to fit experimental data.

For modeling purposes the usual procedure is to lump the different elementary mechanisms into a contribution of effective conductivity under non-flow conditions, λ^0_{er} and a flow dependent or dynamic contribution, λ^d_{er} as shown in table 2–1. These mechanisms operate in parallel so that the effective conductivity of the bed under flow conditions is the sum of the two contributions. The stagnant conductivity is assumed to be isotropic, but the dynamic contribution is split into an axial and a radial contribution to account for the differences in effective conductivity in the two directions.

Table 2-1. Heat transfer mechanisms in polytropic packed bed reactors

	Heat transfer mechanisms	Parameter lumping
1	Conduction through the solid particles	λ_p, λ^0_s
2	Conduction through contact surface of adjacent particles	λ^0_s
3	Conduction through stagnant film between two particles	λ^0_s
4	Radiation between adjacent and distant particles	λ^0_s
5	Radiation between neighbouring gas pockets	λ^4_s
6	Solid–fluid transfer by conduction through stagnant film	h_s
7	Molecular conduction in the fluid phase	λ^0_s
8	Turbulent diffusion and mixing in the fluid phase	λ^4_s
9	Convection in the fluid phase	
10	Conduction between the particles and the wall	α_w
11	Radiation between the particles and the wall	α_w
12	Heat transfer between the fluid and the wall	α_w

The lumping of Table 2-1 refers to the so-called pseudo-heterogeneous model (Carberry and White, 1969). It restricts the solid phase energy balance to the dimension of one particle with an effective conductivity λ_p. The long range conductivity of the solid phase is lumped into λ^0_s, which in turn is lumped with λ^4_s to constitute the effective radial and axial conductivity of the fluid phase.

The most general form of the heterogeneous model uses a three dimensional approach for the solid phase where the conductivity inside each pellet and conductivity in the axial and radial reactor coordinate directions are included. These equations are rather complex and hardly used

without simplifications. De Wasch and Froment (De Wasch and Froment. 1971) distinguished between radial conduction in the solid and in the fluid phase but considered the pellets as point sources of energy. But the most common form of the heterogeneous approach is the pseudo–heterogeneous and often with additional simplifications as discussed in the next chapter.

The two–dimensional pseudo–homogeneous model basically also uses the parameters of Table 2-1, but no distinction is made between the solid and the fluid. This means that λ_p is only used in the estimation of λ^0_{er} and h_c is not used.

2.2.3.2. Model equations

Here the partial differential equations for the heterogeneous and homogeneous dispersion models are given, and ways of combining the two approaches are discussed. Such combinations are often desirable in order to reduce the complexity of the more general heterogeneous model. The notation used in the equations is defined in the symbol list and shown in Figure 2–6.
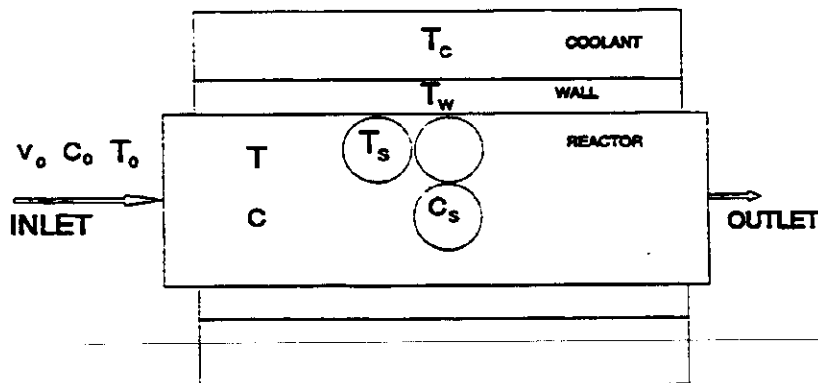

Figure 2–6. Schematic for the reactor models.

The pseudo-heterogeneous two-dimensional model equations are:

Fluid phase:
heat balance:

$$e_0 \rho_g C_{pg} \frac{\partial T}{\partial t} = -v_0 \rho_g C_{pg} \frac{\partial T}{\partial z} + \lambda_{ez} \frac{\partial^2 T}{\partial z^2} + \lambda_{er} \frac{1}{r} \frac{\partial}{\partial r} (r \frac{\partial T}{\partial r}) + a_s h_c (T_s^s - T) \qquad (2\text{-}1)$$

mass balance:

$$e_0 \frac{\partial C_i}{\partial t} = -v_0 \frac{\partial C_i}{\partial z} + D_{ez} \frac{\partial^2 C_i}{\partial z^2} + D_{er} \frac{1}{r} \frac{\partial}{\partial r} (r \frac{\partial C_i}{\partial r}) + a_s k_c (C_{s,i}^s - C_i) \qquad (2\text{-}2)$$

Solid phase:
heat balance:

$$\rho_p C_{ps} \frac{\partial T_s}{\partial t} = \lambda_p \frac{1}{x^2} \frac{\partial}{\partial x} (x^2 \frac{\partial T_s}{\partial x}) + \rho_p (-\Delta H) r_v \qquad (2\text{-}3)$$

mass balance:

$$\frac{\partial C_{s,i}}{\partial t} = D_p \frac{1}{x^2} \frac{\partial}{\partial x} (x^2 \frac{\partial C_{s,i}}{\partial x}) + \rho_p \bar{r}_{v,i} \qquad (2\text{-}4)$$

Initial conditions fluid phase:
at t = 0, all z and r
$$T(z,r) = T^0(z,r) \qquad (2\text{-}5a)$$
$$C_i(z,r) = C_i^0(z,r) \qquad (2\text{-}5b)$$

Initial conditions solid phase:
at t = 0, all z, r and x
$$T_s(z,r,x) = T_s^0(z,r,x) \qquad (2\text{-}6a)$$
$$C_{s,i}(z,r,x) = C_{s,i}^0(z,x,r) \qquad (2\text{-}6b)$$

Boundary conditions fluid phase:

at t > 0

$$\frac{\partial T}{\partial r} = \frac{\partial C_i}{\partial r} = 0 \qquad\qquad \text{at } r = 0, \quad \text{all } z \qquad\qquad (2\text{-}7a)$$

$$-\lambda_{er}\frac{\partial T}{\partial r} = \alpha_w(T - T_w) \qquad\qquad \text{at } r = R, \quad \text{all } z \qquad\qquad (2\text{-}7b)$$

$$\frac{\partial C_i}{\partial r} = 0 \qquad\qquad \text{at } r = R, \quad \text{all } z \qquad\qquad (2\text{-}7c)$$

$$\lambda_{ez}\frac{\partial T}{\partial z} = v_0\rho_g C_{pg}(T - T_0) \qquad\qquad \text{at } z = 0, \quad \text{all } r \qquad\qquad (2\text{-}7d)$$

$$D_{ez}\frac{\partial C_i}{\partial z} = v_0(C_i - C_{0,i}) \qquad\qquad \text{at } z = 0, \quad \text{all } r \qquad\qquad (2\text{-}7e)$$

$$\frac{\partial T}{\partial z} = \frac{\partial C_i}{\partial z} = 0 \qquad\qquad \text{at } z = L, \quad \text{all } r \qquad\qquad (2\text{-}7f)$$

Boundary conditions solid phase:

at t > 0

$$\frac{\partial T_s}{\partial x} = \frac{\partial C_{s,i}}{\partial x} = 0 \qquad\qquad \text{at } x = 0, \quad \text{all } z \text{ and } r \qquad\qquad (2\text{-}7g)$$

$$-\lambda_p\frac{\partial T_s}{\partial x} = h_c(T_s^s - T) \qquad\qquad \text{at } x = d_p/2, \quad \text{all } z \text{ and } r \qquad\qquad (2\text{-}7h)$$

$$-D_p\frac{\partial C_{s,i}}{\partial x} = k_c(C_{s,i}^s - C_i) \qquad\qquad \text{at } x = d_p/2, \quad \text{all } z \text{ and } r \qquad\qquad (2\text{-}7i)$$

The pseudo-homogeneous model generally assumes that the concentrations of species are the same in the fluid inside the particles as in the bulk fluid. Furthermore, it is assumed that the temperatures of the fluid phase and the solid phase are the same. These assumptions are justified if the rates of intra-particle and inter-particle mass and heat transfer are fast compared with the rate of chemical reaction.

One way of combining the heterogeneous and the homogeneous approach is by the introduction of an effectiveness factor in the rate expressions in the homogeneous equations (Satterfield, 1970), as shown in equation 2-8 and 2-9. A direct method to get an equation for the effectiveness factor would be to solve the pellet mass balance analytically. This is, however, possible only for a few simple cases. There are exact solutions for a first order reaction in a slab, sphere and infinite cylinder with or without external mass transfer limitations. More complicated solutions can also be obtained for first order and other shapes (Gunn, 1967). For more complicated kinetic expressions no exact solutions exist but, approximations can be used in some cases.

More general methods for estimating effectiveness factors including the effect of internal particle temperature gradients and external heat and mass transfer limitations are discussed in the book of Froment and Bischoff (Froment and Bischoff, 1979). Several criteria for estimating the importance of the different kinds of limitations on the observed reaction rate are described. These include the extended Weisz-Prater criterion for pore diffusion and calculation of the maximum temperature rise in the pellet. A criterion for the absence of combined intraparticle and interfacial gradients ($\eta = 1 \pm 0.05$) for a n'th order reaction based on observed rate and fluid concentration and temperature is proposed by Mears (Mears, 1971a; Mears, 1971b).

The use of an effectiveness factor and criteria based on approximate solutions of the pellet equations are in principle limited to a single reaction with a relatively simple kinetic expression under steady state conditions. For complex reactions the pellet equations have to be solved numerically. Windes (Windes, 1986) solved the pellet equations numerically for a wide range of fluid conditions and fitted the obtained effectiveness factors to a polynomal form. Thus empirical equations for the effectiveness factor were obtained. According to

Windes (Windes, 1984) simulations with a pseudo-homogeneous model using empirical correlations for the effectiveness factor gave good consistency between simulations and experimental data both under steady state and dynamic conditions for a polytropic fixed bed reactor. A general mathematical model for calculation of catalyst effectiveness factors with multiple reactions and complex kinetics has been developed by Christiansen and Jarvan (Christiansen and Jarvan, 1986). The set of coupled differential equations describing reaction and transport in the catalyst particle is solved numerically by the method of orthogonal collocation (Villadsen and Stewart, 1967; Villadsen, 1970; Villadsen and Michelsen, 1978).

It thus seems that the use of a pseudo-homogeneous model with the inclusion of expressions relating the effectiveness factors to fluid temperature and composition may be an alternative to a heterogeneous model where intraparticle mass transfer limitations are of importance.

The pseudo-homogeneous two-dimensional model equations are:

dynamic heat balance:

$$(1-\epsilon_0)\rho_s C_{ps}\frac{\partial T}{\partial t} = -v_0\rho_g C_{pg}\frac{\partial T}{\partial z} + \lambda_{az}\frac{\partial^2 T}{\partial z^2} + \lambda_{er}\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial T}{\partial r}) + \rho_b\eta(-\Delta H)r_v \qquad (2-8)$$

pseudo steady state mass balance:

$$0 = -v_0\frac{\partial C_i}{\partial z} + D_{az}\frac{\partial^2 C_i}{\partial z^2} + D_{er}\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial C_i}{\partial r}) + \rho_b\eta r_{v,i} \qquad (2-9)$$

Initial conditions:

at t = 0, all z and r

$$T(z,r) = T^0(z,r) \qquad (2-10)$$

Boundary conditions:

at t > 0

$$\frac{\partial T}{\partial r} = \frac{\partial C_i}{\partial r} = 0 \qquad \text{at } r = 0, \quad \text{all } z \qquad (2\text{-}11a)$$

$$-\lambda_{er}\frac{\partial T}{\partial r} = \alpha_w(T-T_v) \qquad \text{at } r = R, \quad \text{all } z \qquad (2\text{-}11b)$$

$$\frac{\partial C_i}{\partial r} = 0 \qquad \text{at } r = R, \quad \text{all } z \qquad (2\text{-}11c)$$

$$\lambda_{az}\frac{\partial T}{\partial z} = v_0\rho_g C_{pg}(T-T_0) \qquad \text{at } z = 0, \quad \text{all } r \qquad (2\text{-}11d)$$

$$D_{az}\frac{\partial C_i}{\partial z} = v_0(C_i-C_{0,i}) \qquad \text{at } z = 0, \quad \text{all } r \qquad (2\text{-}11e)$$

$$\frac{\partial T}{\partial z} = \frac{\partial C_i}{\partial z} = 0 \qquad \text{at } z = L, \quad \text{all } r \qquad (2\text{-}11f)$$

The formulation of the pseudo–homogeneous equations 2–8 and 2–9 reflects the assumptions made concerning their validity. That is neglectable heat capacity of the fluid phase compared with the solid phase and quasi steady state of the fluid phase in the time scale of temperature variations. The inclusion of an effectiveness factor in the rate term of equation 2–8 and 2–9 accounts for the possibilty of internal pellet mass transfer limitations, but fluid–solid heat transfer resistance is neglected.

Neglection of interparticle heat transfer resistance may be unacceptable even under normal steady state operating condition (Froment and Bischoff, 1979, p. 213) but each pellet may usually be viewed as internally isothermal. On the basis of this approach the following simplified steady state heterogeneous model is proposed:

heat balance:

$$0 = -v_0 \rho_g C_{pg} \frac{\partial T}{\partial z} + \lambda_{ez} \frac{\partial^2 T}{\partial z^2} + \lambda_{er} \frac{1}{r} \frac{\partial}{\partial r}(r \frac{\partial T}{\partial r}) + a_v h_c(T_s - T) \tag{2-12}$$

$$\rho_b \eta(T_s, C_i)(-\Delta H) r_v(T_s, C_i^s) = a_v h_c(T_s - T) \tag{2-13}$$

mass balance:

$$0 = -v_0 \frac{\partial C_i}{\partial z} + D_{ez} \frac{\partial^2 C_i}{\partial z^2} + D_{er} \frac{1}{r} \frac{\partial}{\partial r}(r \frac{\partial C_i}{\partial r}) + \rho_b \eta(T_s, C_i^s) r_v(T_s, C_i^s) \tag{2-14}$$

Boundary conditions are the same as for the pseudo–homogeneous model and are given by equations 2–11a to 2–11f.

The existance of intraparticle and interparticle mass and heat transfer resistance can only be verified by experimental techniques or simulations with heterogeneous models if the intrinsic kinetic and effective diffusivities are well known, but some general conclusions can be made regarding the importance of the different mechanisms (Froment and Bischoff, 1979, p. 213).