

On the dynamic behavior of the catalytic fixed-bed reactor in the region of multiple steady states — II. The influence of the boundary conditions in the catalyst phase*

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Abstract—It has been shown in a preceding paper that a reasonable two-phase model for the catalytic fixed-bed reactor in the region of multiple steady states should take into account heat conduction in the catalyst phase. In this paper the study of the proposed model will be continued using the example of the adiabatic fixed-bed reactor. It turns out that the behavior in the region of multiple steady states is essentially affected by the boundary conditions of the catalyst phase. If one assumes that the catalyst phase is isolated adiabatically at the front of the reactor, threefold stable steady states in a wide range of hysteresis can be obtained. If heat exchange by radiation takes place in the frontal surface of the catalyst phase threefold stable steady states can also occur but the range of hysteresis is much narrower. Twofold stable steady states exist only if the fixed-bed is composed of three parts; the first and third parts consist of inert material and the second contains the active catalyst. The results of the computation of this example will be compared qualitatively with the experiments of Padberg and Wicke.

INTRODUCTION

THE DYNAMIC behavior of the model given in part I of the paper[1] will be examined in detail in the region of multiple steady states. Since the behavior of the model is to be tested against the experimental results of Padberg and Wicke[2] the study concerns only the adiabatic case. The mathematical model to be considered consists of Eqs. (1)–(4) with the initial conditions Eq. (6) and the parameter values from Table 1 given in part I of this paper. In the following examples the system parameters feed temperature T_0 and flow velocity v will be varied. A variation of the feed concentration leads to similar results.

An increase of flow velocity has a threefold effect upon the behavior of the reactor:

(1) Cooling by convection in the front part of the reactor will be increased because more feed must be heated up to reaction temperature. Thus the zone of main reaction moves deeper into the reactor.

(2) The heat transfer between fluid and catalyst

is increased, with the result that the excess temperatures of the catalyst phase are lowered and the zone of main reaction moves further back into the reactor. As to the mass transfer it will be assumed that the main resistance lies within the pores of the catalyst. Therefore a change of fluid velocity is almost insignificant to the mass transfer.

(3) The effective heat conductivity is increased. This effect acts against the preceding two but it cannot prevent the ignition zone from being blown out of the reactor with increasing flow velocity.

In the model equations the change of the heat transfer coefficient with fluid velocity is approached in the same way as in the papers of Wicke[4] and Amundson[5]:

$$\alpha_{FC(v)} = \alpha_{FC_0} \cdot \left(\frac{v}{v_0}\right)^{0.6} \quad (1)$$

The change of the effective heat conductivity

*For Notation see part I[1] of this paper.

is calculated according to Yagi and co-workers [6], using the following numerical values

$$\lambda_{\text{eff}(v)} = \lambda_{\text{eff}0} \left(0.15 + 0.85 \frac{v}{v_0} \right). \quad (2)$$

Values of the constants are given in [1, Table 1].

THE BEHAVIOR OF THE MODEL, USING ADIABATIC BOUNDARY CONDITIONS

At first we are going to examine in detail the behavior of the model with adiabatic boundary conditions of the catalyst phase [Eq. (5), part I]. Ignition and blow-out of reaction due to changes of feed temperature are shown in Figs. 1 and 2. Compared to the cooled reactor [1, Fig. 5]

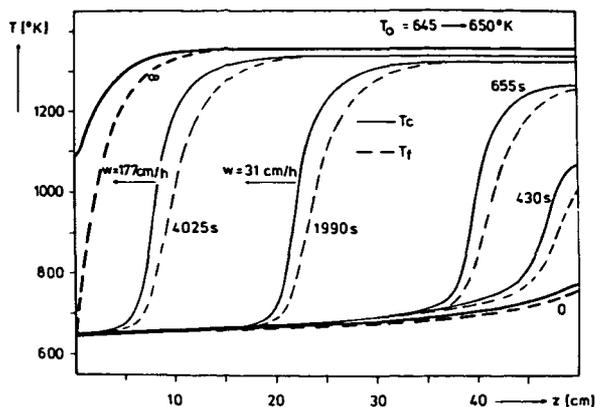


Fig. 1. Transient temperature profiles for ignition of reaction (adiabatic boundary conditions in the catalyst phase).

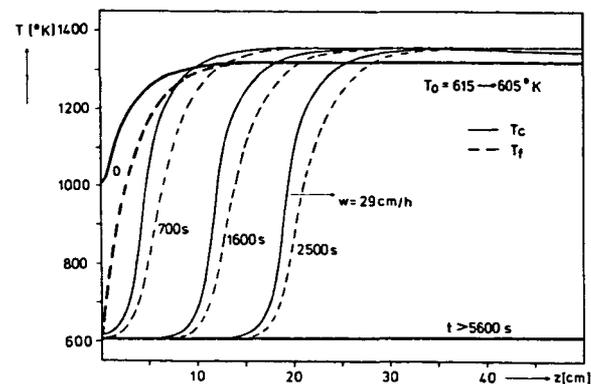


Fig. 2. Transient temperature profiles for blow-out of reaction (adiabatic boundary conditions).

ignition takes place at lower feed temperatures (Fig. 1). As usual in the adiabatic case ignition starts at the end of the reactor. (Without heat conduction ignition would take place at the same increase of feed temperature $T_0 = 645 \rightarrow 650^\circ\text{K}$). An ignition zone develops which moves to the front of the reactor. The moving velocity w of the zone decreases the closer the ignition zone approaches the beginning of the reactor.

The blow-out of reaction (Fig. 2) takes place at approximately the same value of feed temperature as in the cooled case [1, Fig. 7]. Decreasing the feed temperature below a certain blow-out value, the reaction zone separates from the front of the reactor and moves out with almost constant velocity w . The blow-out of reaction is obviously coupled with the appearance of so-called "creeping profiles" as investigated by Wicke and co-workers [2, 3].

Through variation of either feed conditions or flow velocity the creeping profiles may be stopped at any position in the reactor or changed in their moving direction. In Fig. 3 the position and creeping velocity w of the profiles dependent on the feed temperature is shown.

A question arises relating to the type of the shown middle profile ($T_0 = 630^\circ\text{K}$, $w = 0$). Padberg and Wicke [2] assumed that such a solution is neither stable or unstable but indifferent because in the experiment the temperature profile could be stabilized under almost the same conditions at any position in the middle of the

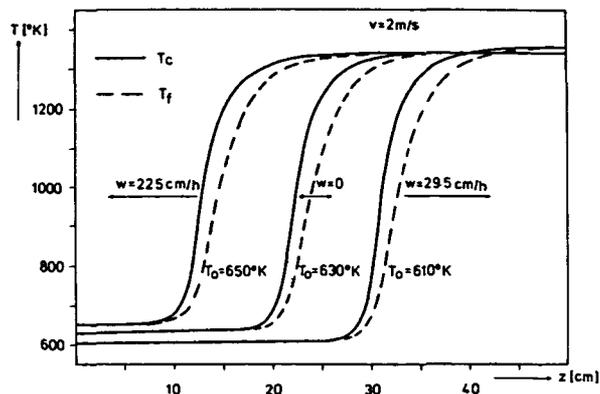


Fig. 3. Creeping profiles dependent on feed temperature (adiabatic boundary conditions).

reactor. For the bilateral infinitely long reactor this assumption will be correct but in the case of finite length, the computed solution turns out to be clearly stable (every stable solution becomes indifferent in the infinitely long reactor).

Twofold stable steady state solutions have already been recognized in the preceding examples: a lower solution with flat temperature profiles (almost no conversion) and an upper one with the ignition zone at the front of the reactor. The appearance of a stable solution with ignition zone in the the middle of the reactor means that, within a certain range of parameters, threefold stable states can exist. Obviously they are separated by two unstable solutions. For $T_0 = 630^\circ\text{K}$ the three stable steady states and the approximate position of the unstable profiles are shown in Fig. 4.

In the given example the range of feed temperature where the middle stable state (③ in Fig. 4) can exist is narrower than the hysteresis between ignition and blow-out of reaction. Figure 5 shows the positions of these middle stable profiles dependent on feed temperature. For feed temperatures above 642°K and below $623,5^\circ\text{K}$ the middle stable state vanishes together with the adjacent unstable solution. Therefore the computation with $T_0 = 644^\circ\text{K}$ and $T_0 = 623^\circ\text{K}$ lead only to twofold stable states. For $T_0 = 644^\circ\text{K}$ solutions according to the profiles ①, ④, ⑤ and for $T_0 = 623^\circ\text{K}$ solutions according

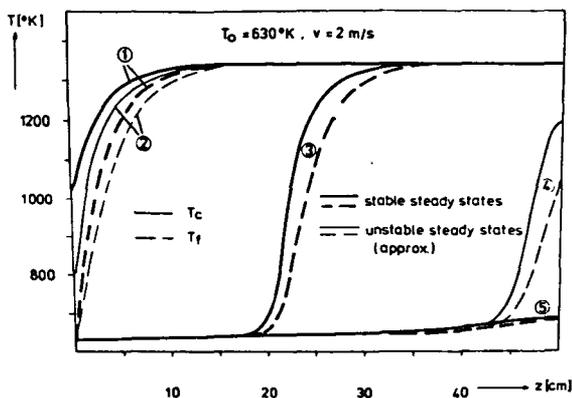


Fig. 4. Temperature profiles of a fivefold steady state (adiabatic boundary conditions). ①, ③, ⑤ stable steady states ②, ④ approximate position of the unstable steady states.

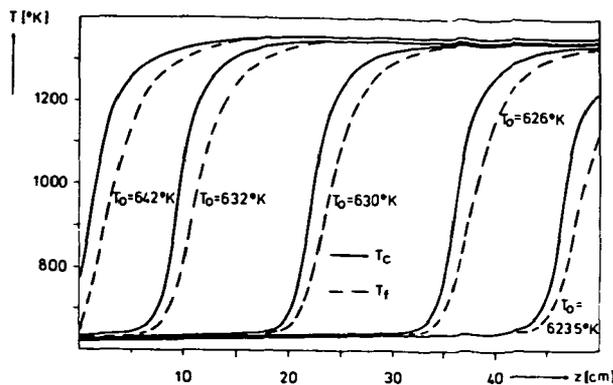


Fig. 5. The position of the middle stable state profile (No. ③) dependent on feed temperature (adiabatic boundary conditions).

to the profiles ①, ②, ⑤ in Fig. 4 were obtained. (In a longer reactor also operating conditions can exist where either only the first three steady states ①, ②, ③ or the last three steady states ③, ④, ⑤ are possible).

The existence of three stable steady states is somewhat striking since it has not yet been observed in experiments. According to the experimental results of Padberg and Wicke[2] only two stable steady state solutions are to be expected. A lower state with flat profiles and an upper steady state which acts like the computed middle steady state: by changing the feed parameters or the flow velocity, its ignition zone can be shifted over the whole length of the reactor.

The upper stable state in which the ignition zone is fixed at the beginning of the reactor down to rather low values of feed temperature (blow-out temperature) has never been realized in these experiments. Obviously its existence is due to the boundary condition at the reactor entrance. If the ignition zone is located in the middle of the reactor (Fig. 5) a considerable amount of heat flows backward towards the entrance of the reactor because of heat conduction in the catalyst phase. At the upper stable state the ignition zone is located at the beginning of the reactor. As the catalyst phase is terminated adiabatically at the front of the reactor, no backflow of heat due to conduction over the

front of the reactor is possible. An accumulation of heat results, causing high excess temperatures of the catalyst phase. Compared to the middle stable state (Fig. 5) where the catalyst temperature exceeds the fluid temperature by not more than 230°K in the ignition zone, the temperature excess in the upper stable state is about 400°K.

This increased temperature excess is the reason for the fact that the ignition zone is fixed at the entrance of the reactor down to blow-out conditions, no matter whether blow-out is provoked by lowering the feed temperature or the feed concentration, or by raising the fluid velocity.

THE INFLUENCE OF RADIATION LOSSES AT THE FRONT OF THE CATALYST PHASE

The presented results show that the assumption of an adiabatic termination of the front of the catalyst phase has to be revised in cases where a high temperature excess of the catalyst phase can occur at the beginning of the reactor. For if the catalyst temperature at the entrance exceeds the fluid temperature considerably, a certain amount of heat will leave the front of the catalyst phase by radiation.

A rough estimation of this effect will be obtained if one considers a reactor as shown in Fig. 6. To achieve a uniform distribution, the

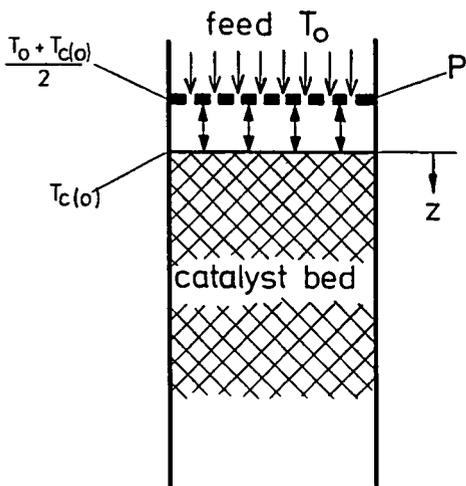


Fig. 6. Schematic picture of a reactor for approximate evaluation of radiation effects at the front of the catalyst phase.

feed (temperature T_0) will be led through a perforated plate P. Closely below the plate the active bed begins. The perforated plate will be heated up by radiation from the front of the catalyst and will be cooled by the flowing fluid. Thus some mean temperature T_p between the feed temperature T_0 and the temperature of the front of the catalyst $T_{c(0)}$ will be achieved on the plate P. In the case considered, arithmetic mean temperature is assumed. Thus

$$T_p = (T_0 + T_{c(0)})/2.$$

Then a heat flow Q_R due to radiation leaves the front of the catalyst:

$$Q_R = C_R \{ T_{c(z=0)}^4 - T_p^4 \}.$$

This heat must flow to the front of the catalyst phase by means of heat conduction. Therefore the boundary condition for the front of the catalyst phase is:

$$\lambda \frac{\partial T_c}{\partial z_{(z=0)}} = C_R \left\{ T_{c(z=0)}^4 - \left(\frac{T_{c(z=0)} + T_0}{2} \right)^4 \right\}. \quad (3)$$

As before, adiabatic termination is considered as boundary condition at the end of the reactor; (the radiation balance is almost equalized at the reactor exit).

$$\frac{\partial T_c}{\partial z_{(z=L)}} = 0. \quad (4)$$

The following example is computed with these changed boundary conditions (value of C_R see [1, Table 1]). The behavior in the range of multiple steady states will now be considered dependent on changes of the flow velocity. (Changes of feed temperature and concentration lead to similar results). The computations show that threefold stable states can still exist if one considers heat exchange by radiation at the front of the catalyst bed. But the range of existence is much narrower compared to the adiabatic termination of the reactor. Therefore it might be difficult to verify this case experimentally. An example for threefold stable states is given in

Fig. 7 for $T_0 = 650^\circ\text{K}$ and $v = 2.45 \text{ m/sec}$.† In this example threefold stable states exist only between $2.2 \text{ m/sec} < v < 2.45 \text{ m/sec}$. (In the case of adiabatic boundary conditions the range is $2.4 < v < 3.6 \text{ m/sec}$). With fluid velocities below $v = 2.2 \text{ m/sec}$ the ignition zone is fixed at the entrance of the reactor (then solutions according to the profiles ①, ④, ⑤ in Fig. 4 exist). If the fluid velocity is above $v = 2.45 \text{ m/sec}$ the ignition zone is located in the middle of the reactor, separated from the entrance (then solutions according to ③, ④, ⑤ Fig. 4 exist). If the ignition zone is separated from the reactor entrance ($v > 2.45 \text{ m/sec}$ in Fig. 7) the profiles of the upper steady state coincide with the middle stable profiles in the case of adiabatic boundary conditions. This fact seems reasonable since the change from one to the other of the considered boundary conditions can have no influence upon the behavior of the reactor as long as the fluid and catalyst temperatures at the front and the end of the reactor are almost the same.

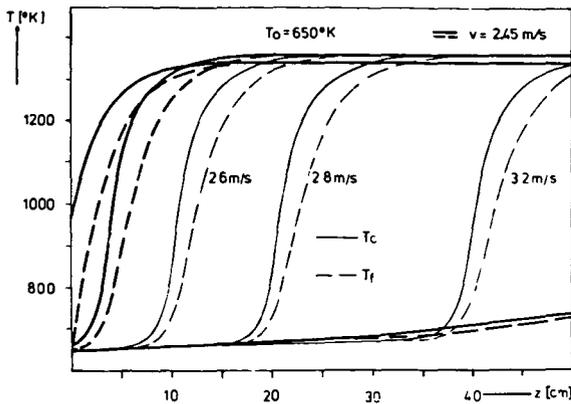


Fig. 7. Threefold stable state profiles (thick lines) and upper temperature profiles in the case of twofold stable states (thin lines) if radiation at the front of the catalyst phase is considered.

THE INFLUENCE OF INERT MATERIAL BEFORE AND BEHIND THE ACTIVE CATALYST BED

Indeed the experiments of Wicke and co-workers[2, 7] were not carried out in a reactor relating to Fig. 6 but in a reactor where the active

†In contrast to the other examples this example has been calculated with $\beta(v) = 0.0581 (v/v_0)^{0.6}$.

bed was surrounded by inert material. This construction of the bed is shown in Fig. 8. If both the inert parts of the bed are long enough, catalyst and fluid temperature will be equalized at the entrance and the end of the bed. As stated above it then does not matter which of the used boundary conditions will be considered. The following examples are computed with adiabatic boundary conditions. [1, Eq. (5)]. The only difference from the computations of the first passage arises from considering the frequency factor: during the computation of the inert parts of the bed it will be put to zero:

If z_s and z_E mark the beginning and the end of the active catalyst bed then $k_0 = 0$ if $0 < z < z_s$ and $z_E < z < L$. (In comparison to the preceding examples the following computations will be carried out with an active catalyst bed being 10 cm shorter).

The influence of feed temperature upon the temperature profiles of the upper steady state is shown in Fig. 9. (For the parameters of each

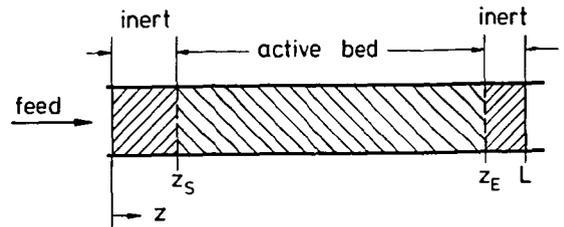


Fig. 8. Schematic picture of a reactor with a catalyst bed composed of active catalyst with two parts of inert material at both ends.

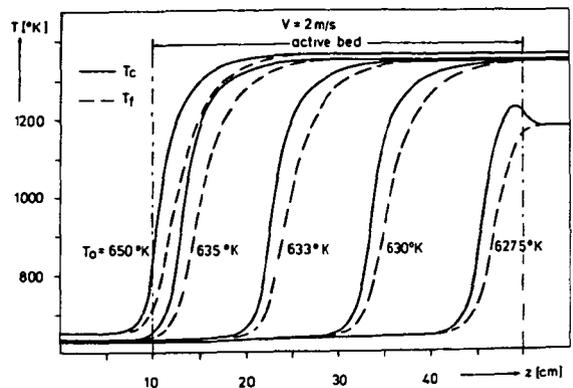


Fig. 9. Temperature profiles of the upper steady state in a reactor with end parts of inert material.

of the drawn profiles a lower steady state with flat profiles exists as well). It can be seen that no increased temperature excess appears at the beginning of the active bed even at high feed temperatures. Due to the backward conduction of heat into the inert front part of the bed, no accumulation of heat can take place and therefore the necessary conditions for a third stable state with ignition zone at the beginning of the active bed are not fulfilled.

The inert end part of the bed influences the reaction profiles if the ignition zone is located at the end of the active bed ($T_0 = 627.5^\circ\text{K}$ in Fig. 9). In this case, a heat flow due to conduction takes place from the end of the active catalyst bed to the inert material. Thus the catalyst temperatures are lowered, and blow-out takes place earlier compared to the case where the active bed is terminated adiabatically. In the example of Fig. 9 the reaction is blown-out for $T_0 < 627^\circ\text{K}$ in any case, whereas with the same parameters but adiabatic termination of the active bed the reaction can be ignited down to $T_0 = 626^\circ\text{K}$.

It has been shown that the reactor has only twofold stable steady states if the inert front part of the bed is long enough. These stable states are obviously separated by an unstable solution with an ignition zone at the end of the reactor (in close vicinity of the profiles $T_0 = 627.5^\circ\text{K}$ in Fig. 9). Therefore ignition and blow-out of reaction take place at the end of the reactor as in the empty tubular reactor if these unstable profiles are exceeded.

Figure 10 shows the ignition of reaction caused by the decrease of flow velocity $v = 1.9 \rightarrow 1.8$ m/sec. During the beginning of ignition the fluid temperature temporarily exceeds the catalyst temperature in the inert end part of the bed: heat conduction in the active catalyst is not sufficient to heat up this inert part so that a considerable amount of heat is transferred by convection from the fluid. Therefore ignition takes place later and develops slower as compared to the active catalyst bed with adiabatic termination.

Altogether the range of hysteresis between

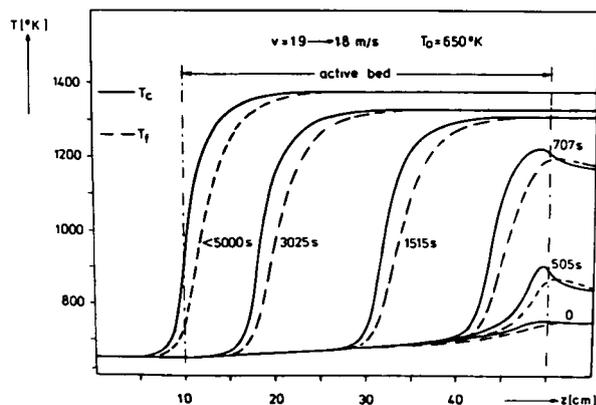


Fig. 10. Transient temperature profiles for ignition of reaction in a reactor with end parts of inert material.

ignition and blow-out of reaction will be lowered by the influence of an inert end part of the bed.

Figure 11 shows steady state profiles of the ignited and the blown-out reactor dependent on the values of fluid velocity. The range of multiple steady states between ignition and blow-out of reaction lies between $v = 1.9$ and $v = 2.5$ m/sec. This example shows qualitatively

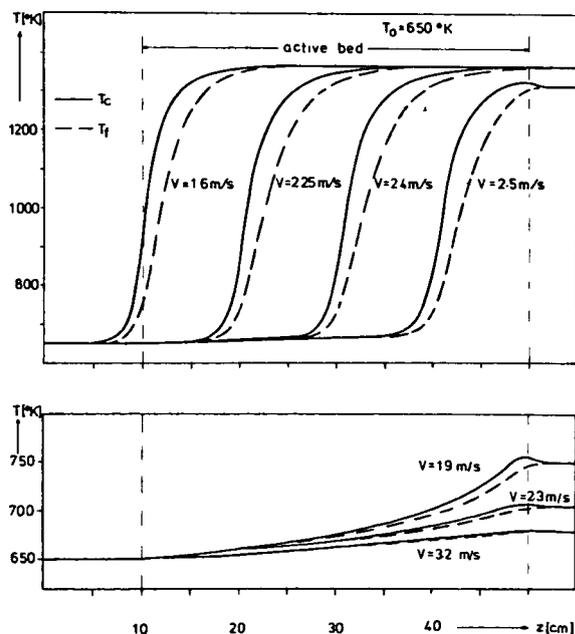


Fig. 11. Temperature profiles of the lower and upper steady state dependent on flow velocity (reactor with end parts of inert material).

good accordance with the experimental results of Padberg and Wicke[2]: with small flow velocities only one steady state exists with an ignition zone at the beginning of the active catalyst bed. The temperature profiles are S shaped; a distinct "tail" leads into the inactive front part of the bed. As the fluid velocity increases, the ignition zone is blown deeper into the reactor but the shape and the slope of the temperature profiles remain almost unchanged. At high fluid velocities and unchanged feed values only the blown-out steady state exists.

Recently published experimental results of Fieguth and Wicke[7] show that the range of multiple steady states becomes smaller with raising fluid velocity. At high fluid velocities only unique steady state solutions exist. This behavior will also be described by the applied model: due to the increased heat transfer between the fluid and catalyst phase (Eq. 1) the temperatures in both phases equalize with increasing fluid velocities. Thus one of the causes of multiple steady states, i.e. the lift of catalyst temperature above fluid temperature, disappears. The second cause of multiple steady states, the influence of backward conduction of heat, will be compensated by the increased cooling due to convection.

CREEPING PROFILES

As stated above, the considered boundary conditions have no influence upon the behavior of the reaction as long as the temperature of fluid and catalyst at the entrance and the end of the reactor are almost the same. Therefore the creeping profiles, as shown in Fig. 3 will also occur in a reactor with inert parts at the beginning and the end of the catalyst bed. The variation of the maximum temperature raise in the reactor, depending on the moving velocity w of the profiles, is clearly visible. The balance equations for this effect given by Wicke and Vortmeyer [3. Eq. (7)] are fulfilled.

The influence of the flow velocity v upon the moving velocity w of the profiles has been studied experimentally by Wicke and Vortmeyer [3]. An applicable interpretation of the depen-

dency based upon simple theoretical considerations was given[3.8]. Numerical inquiries by Jahnel and Vortmeyer[9], using a quasihomogeneous model, lead to similar results. Moreover, they showed that a change of activation energy and order of reaction has no influence upon this dependency[10]. Considering the moving velocity of creeping profiles dependent on the flow velocity, the kind of model used is obviously of little importance. It has only to be taken into account that complete conversion occurs within a short ignition zone and that out of this ignition zone backward conduction of heat takes place. This heat conduction has to depend on the fluid velocity according to the Yagi-Kunii relation[6].

CONCLUSIONS

1. The infinite multiplicity of steady state solutions of the simple two-phase model is reduced to a few solutions by the effect of heat conduction in the catalyst phase.

2. If adiabatic boundary conditions at the beginning of the active catalyst bed are considered, a maximum of threefold stable steady states has been observed. The stable states obviously are separated by two unstable solutions.

3. The first of the threefold stable states (with ignition zone at the beginning of the reactor) is due to an accumulation of heat at the front of the reactor caused by the adiabatic boundary condition.

4. Depending on the reactor parameters and the operating conditions in the region of multiple steady states, two-fold stable steady states may also occur if one of the stable states (and an adjacent unstable state) disappears.

5. Threefold stable states can also occur if heat exchange by radiation at the front of the catalyst bed is taken into account.

6. Because of the backward conduction of heat into the inert material, no accumulation of heat at the front of the active catalyst can take place if the fixed bed is composed of an inert part lying in front of the active catalyst. In this case only twofold stable states have been observed.

7. Compared to an adiabatic boundary condition at the end of the active bed the hysteresis between ignition and blow-out of reaction is smaller if the rear part of the fixed bed (behind the active catalyst) is inert material.

8. Within the region of multiple steady states similar effects (i.e. ignition and blow-out of reaction, shifting of ignition zones) can be caused by changes of feed temperature as well as by feed concentration or flow velocity (whereas

a larger decrease of feed concentration as well as a high raise of flow velocity lead from the region of multiple states to unique operating conditions).

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Résumé—Une étude précédente soulignait le fait qu'un modèle biphasé pour le réacteur catalytique à lit fixe dans la région d'états stables multiples devait tenir compte de la conduction thermique dans la phase catalytique. Dans l'étude présente, l'auteur continue d'analyser le modèle proposé en utilisant l'exemple du réacteur adiabatique à lit fixe. On trouve que le comportement du réacteur dans la région des états stables multiples est surtout affecté par les conditions limites de la phase catalytique. Si l'on admet que la phase catalytique est adiabatiquement isolée près de l'entrée du réacteur, on peut obtenir un triple état stable dans une gamme très large d'hystérésis. Si l'échange de chaleur par radiation se produit à la surface avant du catalyseur, on obtient également un triple état stable mais la gamme d'hystérésis est bien plus petite. Des états stables doubles existent seulement si le lit fixe est composé de trois parties: la première et la troisième étant constituées d'une matière inerte et la seconde contenant le catalyseur actif. Les résultats numériques de cet exemple sont comparés qualitativement aux expériences de Padberg et Wicke.

Zusammenfassung—In einer vorangegangenen Arbeit wurde gezeigt, daß ein sinnvolles Zweiphasenmodell für den katalytischen Festbettreaktor im Bereich mehrfacher stationärer Zustände Wärmeleitung in der Katalysatorphase mitberücksichtigen sollte. In der vorliegenden Arbeit wird die Untersuchung des vorgeschlagenen Reaktormodells am Beispiel des adiabaten Festbettreaktors fortgeführt. Dabei zeigt sich, daß das Verhalten im Bereich mehrfacher stationärer Zustände entscheidend von den Randbedingungen der Katalysatorphase beeinflußt wird. So existieren drei stabile stationäre Lösungen in einem weiten Hysteresebereich, wenn man annimmt, daß die Katalysatorphase adiabat abgeschlossen ist. Auch wenn man Strahlungsaustausch über die Stirnflächen der Katalysatorschüttung zuläßt, können drei stabile stationäre Lösungen existieren, allerdings nur in einem schmalen Bereich der Reaktionsparameter. Ist die aktive Katalysatorschüttung dagegen von einer genügend langen inerten Vor- und Nachschüttung eingeschlossen, so existieren nur zwei stabile stationäre Lösungen. Ergebnisse der Berechnung dieses Falles werden den experimentellen Untersuchungen von Padberg und Wicke gegenübergestellt.