On the dynamic behavior of the catalytic fixed-bed reactor in the region of multiple steady states—I. The influence of heat conduction in two phase models

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Abstract—Till now the use of two phase models for the catalytic fixed-bed reactor in the region of multiple steady states led to somewhat confusing results. A continuum of multiple steady state solutions has been obtained no matter whether the continuous two phase models proposed by Liu and Amundson and the cell models developed by Amundson and co-workers were used. It will be shown in this paper that the infinite multiplicity of steady states is reduced to a few solutions if one assumes heat conduction to take place in the catalyst phase.

Differences between former models and the proposed model are explained in the example of ignition and blow-out of reaction.

INTRODUCTION

A GREAT variety of assumptions concerning the development of models for the dynamic behavior of the catalytic fixed-bed reactor has been reported in recent years. There is the detailed consideration of the effects in a single catalyst pellet, there are the two phase models (either the cell models or the continuous two phase models) and there are the quasi-homogeneous models which treat the reactor like an empty tubular reactor.

In particular the behavior of the various models differs in those regions in which the reactor can operate in multiple steady states because of a strong exothermic reaction. In the work of Wicke and co-workers accurate experimental results showing the behavior of the reactor in this range have been published[1, 2]. It seems reasonable therefore to test the models against this experimental research.

Two different physical effects are responsible for the fact that multiple steady states can exist. The first is due to the component of heat conduction which is opposite in direction to fluid flow. It was van Heerden who showed[3] that multiple steady states can arise in reactors with steep temperature profiles due to this feedback effect. Instabilities of quasi-homogeneous models can be attributed only to this cause.

The second effect comes about from the fact that the reaction takes place on the surface or inside of the catalyst pellet. Under certain reaction conditions the temperature and concentration in the pellet can lie on two different levels, in spite of unchanging conditions in the surrounding gas phase. This phenomenon has first been used by Wagner[4] to account for instability in the two phase model.

Since in a catalytic fixed-bed reactor with strongly exothermic reaction both of these effects occur simultaneously, it seems reasonable to look for a model in which both effects are usefully coupled together. This idea has been proposed by Wicke several times[1, 5, 6].

Based on physical considerations a model will be described which essentially makes use of this assumption. This model in similar form has already been proposed by Gilles and co-workers [10] and turns out to be a modification of the well known two phase model of Liu and Amundson[7, 8]. The general behavior of the model will be discussed, and in part II of this paper it will be compared qualitatively with the experimental results of Padberg and Wicke[1].

TWO PHASE MODELS

In two phase models the complex behavior in

the reactor is concentrated in two homogeneous phases, in the flowing fluid and in the fixed catalyst. This assumption either leads to the cell models or to the homogeneous two phase models. In this paper two phase models with only axial dependency will be considered. Such models have been examined in detail by Amundson and co-workers, the continuous model in the fundamental work of Liu and Amundson[7, 8, 9], the cell models together with Vanderveen and Luss in [11]. It turned out that the two phase models in the region of multiple steady states not only have two, but in the continuous case an infinite number of stable steady state solutions. For the continuous model this fact can easily be explained with the well known graphical illustration of heat generation and heat rejection[5, 7]. As shown in Fig. 1 for the adiabatic case there is only one steady solution for the catalyst temperature (intersection of heat generation curve Q_{II} with heat rejection line Q_{II}) for fluid temperatures $T_f < T_{f1}$ and $T_f > T_{f3}$. For fluid temperatures $T_{f1} < T_f < T_{f3}$ there are three possible solutions, the upper and lower of which are stable. At fluid temperatures within the hatched region the catalyst temperature jumps from the lower to the upper steady state. At which value of fluid temperature this jump takes place depends on how the steady state has been reached. If
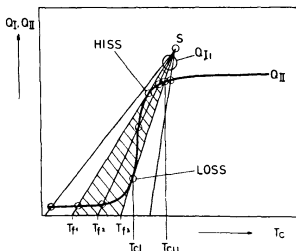
reaction has been ignited for instance by slowly raising the feed temperature, the "lowest steady state" (LOSS) will be established in the reactor. It is characterized by the fact that the catalyst temperature remains at the lower steady state until fluid temperature T_{f3} is reached. If T_{f3} is exceeded there is only one intersection left on the upper model the catalyst temperature jumps vertically from T_{CL} to T_{CU}. On the other hand if feed temperature is lowered slowly from very high temperatures, the "highest steady state" (HISS) will be established. It is characterized by the fact that the catalyst temperature then always takes on its highest possible value.

Depending on how the steady state has been reached the catalyst temperature can jump from the lower to the upper state at every value of fluid temperature within the range of ambiguity. Figure 2 shows the profiles of catalyst and fluid temperature for some of the possible stable steady states. The infinite multiplicity of solution-profiles is bounded by the highest and the lowest steady state. As Aris and Schruben[12] recently have shown with a simplified reactor model, catalyst temperature may jump even several times between the upper and the lower steady state. This multiplicity of steady state solutions

Fig. 1. Graphical illustration of possible steady state solutions for the simple adiabatic two-phase model[7].
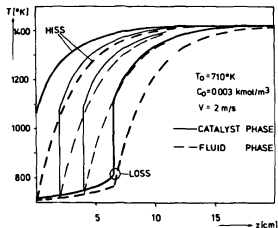

Fig. 2. Multiple steady states of the adiabatic two-phase model without heat conduction: possible stable state profiles between the highest (HISS) and the lowest steady state (LOSS).

leads to very perplexing results concerning the dynamic behavior[11, 12].

If one introduces an additional coupling effect for these models, e.g. in the homogeneous model by considering dispersion of matter and heat in the fluid[9], in the discrete models by looking for a coupled cell model[11], the region of multiplicity becomes smaller but the basic problem is not yet solved. As is shown in the cited papers, ignition still may take place at every point within the range of multiplicity between the lowest and the highest steady state.

INFLUENCE OF HEAT CONDUCTION

This infinite multiplicity of the steady state solution is in fact a confusing conception, not proved by experimental results. It claims that, of two adjacent catalyst pellets, one is in the upper—and the other in the lower steady state whereas the latter could exist in the upper steady state as well. But if one assumes heat conduction to take place not only in the fluid (as in [9]) but also in the catalyst phase, only a small heat conductivity is sufficient to transfer the adjacent pellets to the upper steady state. This statement may be proved simply:

We consider the lowest steady state (LOSS) in Fig. 2. For a small amount of time heat conduction should be allowed. Because $dT_c/dz = \infty$ in the ignition zone, during the first moment an infinitely large heat flow $\dot{Q} = -\lambda_{\text{eff}} \cdot dT_c/dz$ would flow towards the inlet of the reactor. By this means a part of the catalyst lying upstream is ignited. When switching off heat conduction, the ignition zone is located a little further to the left. This consideration may be repeated until the highest steady state (HISS) is reached.

So, due to the effect of heat conduction in the catalyst phase, at least the "highest steady state" (HISS) will be reached if somewhere in the reactor ignition has taken place.

The above considerations apply for any value of heat conductivity no matter how small. In fact the effective heat conductivity in the catalyst phase, i.e. between adjacent catalyst pellets, seems to be at least of the same order as the effective heat conductivity in the fluid phase. In

a rough scheme Fig. 3 shows three regions in which heat-exchange between adjacent catalyst pellets takes place.* In region I pure heat conduction takes place by direct contact and through the stationary fluid interstices. Range II marks the larger holes where vorticity is caused by the flowing fluid. In this region heat transport without doubt is brought about by convection. But it seems more reasonable to attribute this effect to the heat transport within the catalyst phase than to region III where heat exchange between adjacent catalyst pellets clearly takes place though the *flowing* fluid. (Region II seems essentially responsible for the increase of the effective heat conductivity with increasing fluid velocity).

Additionally at higher temperatures radiation between the pellets takes place. It may also be treated like heat conduction in the catalyst phase, while the pseudo-heat-conductivity due to radiation increases with the third power of temperature [13].
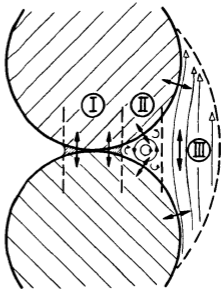

Fig. 3. Schematic illustration of heat exchange between adjacent catalyst pellets: I Exchange by pure conduction, II Exchange by fluid vortices in the larger interstices, III Exchange through the flowing fluid.

THE CONTINUOUS TWO PHASE MODEL WITH HEAT CONDUCTION IN THE CATALYST PHASE

As pointed out, an appreciable amount of effective heat conduction takes place in the catalyst phase. By this means the behavior of the two phase model in the region of multiple steady states is changed considerably. The resulting effects will be examined by numerical computations. The model chosen is the simple two phase model of Liu and Amundson[7, 8], extended by the effect of heat conduction in the catalyst phase. It corresponds to a model proposed by Gilles and co-workers[10]. The model equations are:

$$\frac{\partial C_f}{\partial t} + v\frac{\partial C_f}{\partial z} = A_1(C_c - C_f) \quad (1)$$

$$\frac{\partial T_f}{\partial t} + v\frac{\partial T_f}{\partial z} = A_2(T_c - T_f) + A_3(T_w - T_f) \quad (2)$$

$$\frac{\partial C_c}{\partial t} = A_4(C_f - C_c) + A_5 \cdot r_{(C_c,T_c)} \quad (3)$$

$$\frac{\partial T_c}{\partial t} = A_6(T_f - T_c) + A_7 \cdot r_{(C_c,T_c)} + A_8 \frac{\partial^2 T_c}{\partial z^2}. \quad (4)$$

For the constants A_i, the following relationships apply:

$$A_1 = \beta \cdot \frac{a_r}{\gamma} \qquad A_2 = \frac{\alpha_{FC}}{\rho c_{pf}} \cdot \frac{a_r}{\gamma}$$

$$A_3 = \frac{2\alpha_{wF}}{r_1 \cdot \rho c_{pf}} \qquad A_4 = \frac{3\beta}{s \cdot \gamma_i}$$

$$A_5 = -\frac{S_g \cdot \rho_c}{\gamma_i} \qquad A_6 = \frac{3\alpha_{FC}}{s \cdot \rho c_{pc}}$$

$$A_7 = \frac{S_g \cdot \rho_c}{\rho c_{pc}}(-\Delta H_R) \qquad A_8 = \frac{\lambda_{eff}}{\rho c_{pc}}$$

The reaction rate r is taken for a simple first-order reaction

$$r_{(C_c,T_c)} = k_0 \cdot C_c \cdot e^{-E/RT_c}.$$

The parameters are the same as used by Liu and

Amundson[7, 8]; they are presented in Table 1.

Computing the behavior of an industrial reactor the model equations might be extended in terms of dispersion of matter and heat in the fluid. But it turns out that the basic behavior of the model will not be changed.

Choosing boundary conditions for the temperature of the catalyst phase the usual assumption was made that no heat of exchange by radiation or conduction takes place over the frontal surface of the catalyst bed.

Then the boundary conditions are:

$$c_{f(z=0)} = C_0; \; T_{f(z=0)} = T_0;$$

$$\left(\frac{\partial T_c}{\partial z}\right)_{(z=0)} = \left(\frac{\partial T_c}{\partial z}\right)_{(z=L)} = 0. \quad (5)$$

As initial conditions for transient computations, the corresponding steady state profiles were chosen.

$$C_{f(z,t=0)} = C_{f(z)}; \; T_{f(z,t=0)} = T_{f(z)};$$

$$C_{c(z,t=0)} = C_{c(z)}; \; T_{c(z,t=0)} = T_{c(z)}. \quad (6)$$

Table 1. Reaction parameters of the numerical examples

Reaction:	frequency factor $k_0 = 0.079$ [m/sec]
	activation energy $E = 24200$ [kcal/kmol]
	heat of reaction $(-\Delta H_R) = 66600$ [kcal/kmol].
Catalyst:	specific inner surface S_g, $\rho_c = 2 \times 10^8$ [m²/m³]
	void fraction of particle $\gamma_i = 0.4$
	radius of particle $s = 0.00475$ [m]
	heat capacity ρ . $c_{pc} = 188.5$ [kcal/m³ grd]
	specific outer surface $a_v = 410$ [m²/m³].
Reactor:	length $L = 0.5$ [m]
	radius $r_1 = 0.021$ [m]
	void fraction $\gamma = 0.35$
	interstitial velocity $v = v_0 = 2.0$ [m/sec]
	wall temperature $T_w = 310$ [°K]
	heat capacity of fluid $\rho c_{pf} = 0.28$ [kcal/m³ grd]
	feed concentration $C_0 = 0.003$ [kmol/m³].
Transfer coefficients:	
	mass transfer coefficient
	fluid-catalyst $\beta = 0.0581$ [m/sec]
	heat transfer coefficient fluid-
	catalyst $\alpha_{FC} = \alpha_{FC0} = 97.7$ [kcal/m² hr grd]
	heat transfer coefficient
	fluid-wall $\alpha_{wF} = 30.5/0$. [kcal/m² hr grd]
	effective heat conductivity in the catalyst
	phase $\lambda_{eff} = \lambda_{eff0} = 0.001$ [kcal/m sec grd]
	radiation constant
	$C_r = 3 \times 10^{-8}$ [kcal/m² hr grd⁴]

The following examples show the differences between the models, with and without heat conduction in the catalyst phase.

Ignition and blow-out of reaction due to changes of the feed temperature will be considered.

Figures 4 and 5 show the ignition resulting from each model. The first important fact is that ignition takes place in both cases if the feed temperature is raised from $T_0 = 720 \rightarrow 725°K$. The ignition temperature turns out to be almost independent of heat conduction. But the following transient behavior is clearly different. In the first case without heat conduction (Fig. 4) a temperature maximum develops in the middle of the reactor. The stationary profiles show the "lowest steady state" (LOSS), as can be seen by solving the steady state equations. (The "highest steady state" (HISS) for $T_0 = 725°K$ is also shown in Fig. 4).

In the second case the temperature maximum moves to the front of the reactor, driven by the

Fig. 5. Transient profiles of the cooled reactor for ignition of reaction *with* heat conduction in the catalyst phase.

backward conduction of heat (Fig. 5). The stationary profiles show good agreement with the profiles of the highest steady state (HISS) without heat conduction.

The transient profiles of concentration are in complete accordance with the corresponding temperature-curves. As is well-known, the dynamic behavior of the fixed-bed reactor is determined by the change of catalyst temperature. Compared with it the other variables change so quickly that they can be treated as quasi-stationary. Therefore in the following examples only temperature profiles will be presented. Figures 6 and 7 show the blow-out of reaction, caused by a reduction of feed temperature. In the case of no heat conduction (Fig. 6) the computation starts with the highest steady state (HISS) which is possible for $T_0 = 705°K$. This initial state can be reached by slowly lowering the feed temperature from high values down to 705°K. A further decrease to $T_0 = 690°K$ causes a separation of the ignition zone from the front of
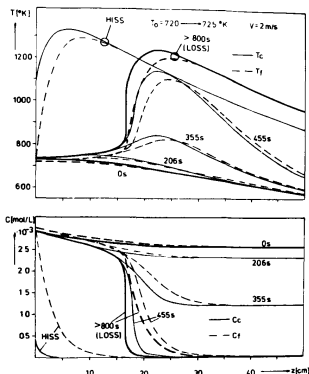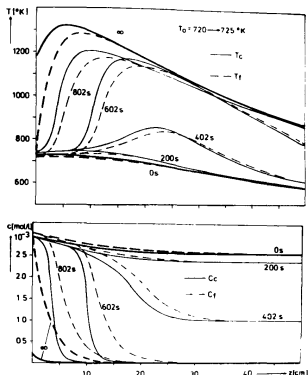

Fig. 4. Transient profiles of the cooled reactor for ignition of reaction *without* heat conduction in the catalyst phase.
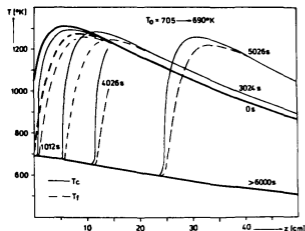
Fig. 6. Transient temperature profiles of blow-out of reaction *without* heat conduction in the catalyst phase.
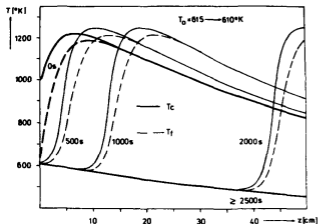

Fig. 7. Transient temperature profiles of blow-out of reaction *with* heat conduction in the catalyst phase.

the reactor. With slowly increasing velocity the ignition zone moves downstream and leaves the reactor.

Under the influence of backward conduction of heat the reaction remains ignited down to much lower temperatures. Only if the feed temperature is reduced from $T_0 = 615 \to 610°K$ the ignition zone separates from the front of the reactor. After separation the ignition zone moves noticeably more quickly out of the reactor.

As the maximum hysteresis of feed temperature between ignition and blow-out of reaction is only 20°K in the case without heat conduction, it

increases to 110°K when heat conduction is considered. Thereby it can be seen how the influences of the above mentioned effects for multiple steady states are summed up.

It seems noteworthy to observe that when considering heat conduction in the catalyst phase, the blow-out of reaction starts at the front of the reactor: if the reaction parameters (feed temperature or concentration, flow velocity) are reduced below distinct blow-out-values, the ignition zone separates from the front of the reactor and continuously moves out. The reason for this behavior will be examined in part II of the paper.

Considering heat conduction in the catalyst phase, the equivalence between heat and mass transport in the fixed-bed reactor is abandoned. Therefore graphical methods to get steady state solutions according to Fig. 1 are no longer valid. Nevertheless, they are not completely useless: in the lower steady state the temperature profiles are so flat that heat conduction has no considerable influence. Therefore the ignition-conditions may still be calculated from the steady state equations without heat conduction.

NUMERICAL TREATMENT

Equations (1)–(4) without the heat conduction term were calculated by use of the characteristic method as given by Liu and Amundson[7]. The initial and final steady state profiles were calculated directly from the steady state equations.

In the case of the complete system of Eqs. (1)–(6) with heat conduction, the steady state solutions are obtained by transient computation.

A finite difference method was used, based on a modification of the characteristic method. Computation time could be reduced to a tolerable level by automatic time-step control. With 200 equidistant space increments the computation time ratio (real time vs. computation time) on a CDC 6600 was 20 : 1, but for many runs 100 space increments were sufficient. Thereby the time ratio was improved to better than 100 : 1. Some control runs with a computer program of Luebeck[14] based on the solution of the integral form of the system equations lead to similar results.

Further details of the applied computation method will be given elsewhere.

NOTATION

(see also Table 1)

A_i system constants
C_c catalyst concentration
C_f fluid concentration
C_0 feed concentration
L reactor length
T_c catalyst temperature
T_f fluid temperature
T_0 feed temperature
T_w wall temperature
r reaction rate
s index for steady state
t time coordinate
v interstitial mean velocity
w moving velocity of creeping profiles
z space coordinate

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Résumé—Jusqu'à présent l'utilisation de modèles à deux phases pour les réacteurs catalytiques à lit fixe dans la région d'états stables multiples donnait des résultats assez confus. Un continuum de solutions multiples à l'état stable a été obtenu en utilisant ou bien les modèles continus à deux phases proposés par Liu et Amundson ou bien les modèles développés par Amundson et ses associés. L'auteur montre dans cette étude que la multiplicité infinie des états stables est réduite à quelques solutions, si l'on suppose que la conduction thermique se produit dans la phase catalytique. Des différences entre les modèles précédents et le modèle proposé sont illustrées par l'exemple du déclanchement et de la fin de la réaction.

Zusammenfassung—Die Benutzung des Zweiphasenmodells für den katalytischen Festbettreaktor führte im Bereich mehrfacher stationärer Zustände bisher stets zu Schwierigkeiten, da sich ein Kontinuum von mehrfachen stationären Lösungen ergab. Dabei war es gleichgültig, ob die von Liu und Amundson aufgestellten kontinuierlichen Zweiphasenmodelle oder die von Amundson und Mitarbeitern entwickelten Zellenmodelle zugrunde gelegt wurden. In der vorliegenden Arbeit wird gezeigt, daß sich die unendliche Mannigfaltigkeit stationärer Lösungen auf wenige Lösungen reduziert, wenn man annimmt, daß Wärmeleitung in der Katalysatorphase stattfindet.
Unterschiede zwischen den bisher benutzten Modellen und dem vorgeschlagenen Modell werden am Beispiel der Zündung und des Verlöschens der Reaktion dargelegt.