

Modeling and Simulation of a Chemical Reactor for the Production of Acetic Acid – III. Dynamic Phase Transitions.

R. Waschler*, A. Kienle, S. Sviatnyi, E.D. Gilles
Max-Planck-Institut für Dynamik komplexer technischer Systeme
Leipziger Str. 44, 39120 Magdeburg, Germany

A. Anoprienko, T. Osipova
Donetsk State Technical University,
Artemstr. 58, 340000 Donetsk, Ukraine

Abstract

A special modeling and simulation approach is required to account for potential discrete events during the simulation of chemical plants. In the case of a reactor for the production of acetic acid discrete events may be caused by phase transitions or due to the extinction of the zero order reaction. It is shown how to handle such system discontinuities using an appropriate model formulation and exploiting the numerical methods of the simulation environment DIVA. Simulation results illustrate the effects of discrete events in the reactor model.

1 Introduction

In a previous study [3] a detailed two-phase model describing the reaction system of a chemical plant for the production of acetic acid ([1, 2, 4]) was developed. This model, consisting of submodels for the reactor itself interconnected with a condenser and a downstream separator, yielded significant improvements to a one-phase model of the reactor [7]. In particular, the stationary solutions obtained were in good agreement with measured data from the real plant.

However, the two-phase model did not take into account that situations may occur in which the assumption of a vapour-liquid equilibrium inside the reactor is no longer justified. Note that assuming a physical scenario of two coexisting phases corresponds to the idea that boiling conditions are prevailing. Yet, as soon as the reaction mixture becomes subcooled, for example during the dynamic transient caused by a disturbance to the plant, turning to a one-phase model description becomes necessary. Therefore, the

* Author to whom all correspondence should be addressed. Phone: ++49 391 6117-564. Fax: ++49 391 6117-545. Email: waschler@mpi-magdeburg.mpg.de

two-phase model has to be modified in order to enable the handling of these types of discontinuities in the physical structure of the investigated system.

In this contribution an appropriate hybrid model of the chemical reactor is presented, alongside a brief description of the numerical method to deal with discrete events. Simulation results show the capability of the new model formulation in coping with large disturbances to the plant.

Note that for further particulars - in terms of notation, basic model assumptions, physical property data and as far as questions of the reaction mechanism and other technical details like plant architecture are concerned - it is referred to [3].

2 The hybrid reactor model

In contrast to [3], where focus was on the stationary behaviour of the overall reaction system, consisting of the reactor, a condenser and a flashdrum, attention is now confined to the reactor itself. Obviously, the recycle streams from the condenser (specified by $K[\frac{kmol}{s}], x_{i,K}[\frac{kmol_i}{kmol_{ges}}], T_K[K]$) and the flashdrum ($L[\frac{kmol}{s}], x_{i,f}[\frac{kmol_i}{kmol_{ges}}], T_f[K]$) have to be taken into account and are assumed to be additional fixed feeds to the reactor, their values being those obtained by a stationary solution of the overall reaction system. Then, the system considered in this contribution is the one depicted in Figure 1. The

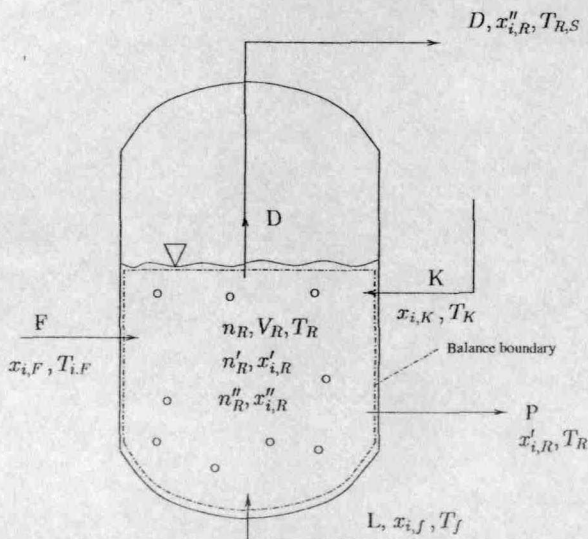


Figure 1: The reactor and variables necessary for its mathematical model

balance space under consideration is the vapour-liquid mixture inside the reactor and it is assumed that the dynamics of the pure vapour phase positioned above this mixture can be neglected, i.e., the vapour leaving the mixture ($D[\frac{kmol}{s}], x''_{i,R}[\frac{kmol_i}{kmol_{ges}}], T_{R,S}[K]$)

leaves the reactor immediately and unchanged. Besides the assumption of a constant overall molar holdup $n_R = \text{const.}$, further quasi-steady-state assumptions used during the modeling procedure concern the molar holdups of the liquid and the vapour phase as well as the concentrations of the vapour phase,

$$\frac{dn'_R}{dt} = 0, \quad \frac{dn''_R}{dt} = 0, \quad \frac{dx''_{i,R}}{dt} = 0. \quad (1)$$

Then, introducing the vapour fraction ψ_R and a fictitious vapour fraction ψ_R^* as auxiliary model variables, the required hybrid model description becomes feasible. Let ψ_R be defined as the ratio of the molar holdup in the vapour phase to the overall molar holdup, $\psi_R := \frac{n''_R}{n'_R + n''_R}$. Then it holds that the overall molar enthalpy h_R within the balance space is given by

$$h_R = (1 - \psi_R)h'_R(T_R) + \psi_R h''_R(T_R), \quad (2)$$

where the molar enthalpy h_R itself is determined from the energy balance

$$n_R \frac{dh_R}{dt} = Fh_F + Kh_K + Lh_L - Ph'_R(T_R) - Dh''_R(T_R). \quad (3)$$

Thus, equation (2) constitutes an implicit formulation for the computation of the vapour fraction. Yet, the energy content of the reactor may drop as boiling conditions are no longer valid. This results in negative values of the vapour fraction, corresponding to a negative molar holdup of the vapour phase, which, of course, is physically nonsensical. Therefore, equation (2) is modified to

$$h_R = (1 - \psi_R^*)h'_R(T_{R,S}) + \psi_R^* h''_R(T_{R,S}), \quad (4)$$

offering a possibility to calculate a – potentially *fictitious* – vapour fraction ψ_R^* at – potentially fictitious – boiling point conditions. Then the *real* vapour fraction ψ_R (taking values $\psi_R \in [0 \dots 1]$) is obviously given by

$$0 = \begin{cases} \psi_R & \text{if } \psi_R^* < 0 \\ \psi_R - \psi_R^* & \text{if } 0 \leq \psi_R^* \leq 1 \\ \psi_R - 1 & \text{if } \psi_R^* > 1 \end{cases}. \quad (5)$$

Here it should be noted that the case of a purely gaseous, super-heated reaction mixture corresponding to $\psi_R^* > 1$ is merely included for the sake of completeness and is of no practical interest.

As usual, component material balances and a summation condition

$$n'_R \frac{dx'_{i,R}}{dt} = Fx_{i,F} + Kx_{i,k} + Lx_{i,L} - Px'_{i,R} - Dx''_{i,R} + \sum_{i=1}^{NC} \nu_i r_0 V' \quad , \quad i=1, \dots, NC \quad (6)$$

$$0 = 1 - \left(\sum_{i=1}^{NC} x'_{i,R} + x'_{Rb} \right) \quad (7)$$

are used to compute the mole fractions of all components¹ in the liquid mixture. Vapour mole fractions follow from vapour-liquid-equilibrium calculations

$$0 = x''_{i,R} p \varphi_i(T_{R,S}) - x'_{i,R} \gamma_i(T_{R,S}) p_{i,S}(T_{R,S}) \varphi_{0,i,S}(T_{R,S}) \quad , \quad i=1, \dots, NC, \quad (8)$$

¹Contrary to [3], in this contribution we regard the Rhodium catalyst in the liquid phase x'_{Rh} as a fixed parameter and the number of components NC also includes CO .

where the $\gamma_i, \varphi_i, \varphi_{0,i,S}$ are obtained from physical property data calculations and set equal to 1 for *CO*. Note that these calculations are dispensable in the case of a purely liquid model where the $x''_{i,R}$ are simply fictitious variables.

The boiling point temperature $T_{R,S}$ follows from the summation condition of the mole fractions in the vapour phase

$$0 = 1 - \sum_{i=1}^{NC} x''_{i,R}, \quad (9)$$

and in the two-phase model the actual system temperature T_R is equal to $T_{R,S}$. However, as boiling conditions become invalid this approach can no longer hold. Therefore, a discontinuous structure for the temperature governing equation has to be established:

$$0 = \begin{cases} h_R - h'_R(T_R) & \text{if } \psi_R^* < 0 \\ T_R - T_{R,S} & \text{if } 0 \leq \psi_R^* \leq 1 \\ h_R - h''_R(T_R) & \text{if } \psi_R^* > 1 \end{cases} \quad (10)$$

Obviously, as long as the mixture inside the reactor is boiling, the system temperature T_R is still equal to the boiling point temperature $T_{R,S}$. Only when this two-phase scenario no longer prevails, T_R has to be calculated implicitly from enthalpy correlations.

Finally, the vapour and liquid streams leaving the reactor have to be calculated. In this context, one further assumption is necessary: we assume that the ratio of the molar flows leaving the system is equal to the ratio of the corresponding molar holdups, i.e.,

$$\psi_R = \frac{D}{D+P}. \quad (11)$$

Then, the overall material balance, using the assumption $n_R = \text{const}$, reads

$$\frac{dn_R}{dt} = 0 = F + K + L - P - D + \sum_{i=1}^{NC} \nu_i r_0 V'_R, \quad (12)$$

or, using (11),

$$0 = P - (F + K + L + \sum_{i=1}^{NC} \nu_i r_0 V'_R)(1 - \psi_R), \quad (13)$$

$$0 = D - (F + K + L + \sum_{i=1}^{NC} \nu_i r_0 V'_R)\psi_R. \quad (14)$$

Summarizing, the $2NC + 7$ unknown variables $x'_{i,R}, x''_{i,R}, h_R, \psi_R^*, \psi_R, T_S, T, P, D$ can be calculated from equations (6) and (7), (8), (3), (4), (5), (9), (10), (13), and (14), respectively.

3 Numerical method and simulation results

In the previous section a hybrid model formulation allowing the treatment of discrete events has been presented. In this section a brief description of the way the simulation environment DIVA [5, 6] treats events is given, the application to the reactor model is illustrated and simulation results are shown.

3.1 Numerical aspects

Discrete events occur at special points in time and are either caused by physical effects or prespecified in the context of a process control scheme.

In the latter case, denoted as an *explicit* event, the time of the event t_{ev} is well defined and known prior to the start of the simulation. Once the simulation time t reaches $t = t_{ev}$, the simulation is halted and the necessary change in the model equations is performed. This change corresponds to a switching between different sections of a discontinuous function.

In the other case a so-called *implicit* event occurs due to a specific physical phenomenon and the time of the event t_{ev} is not known prior to the simulation. Thus, a first task of the simulation environment is to detect the actual occurrence of the event. To achieve this, a so-called φ -function has to be defined and as soon as φ crosses zero (from $\varphi(t_{k-1})$ at time t_{k-1} to $\varphi(t_k)$ at time t_k in Figure 2) the implicit event is detected. Then, the simulation is halted and an iteration algorithm is started which solves for the time of the event t_{ev} as long as values of φ lie outside a user-defined boundary ϵ_φ . Once φ has entered the ϵ_φ -strip, t_{ev}^* is taken as the value of the time of the implicit event, model equations are switched to suit the new physical scenario, consistent initial conditions are computed and integration is resumed. A graphical illustration of this procedure is depicted in Figure 2.

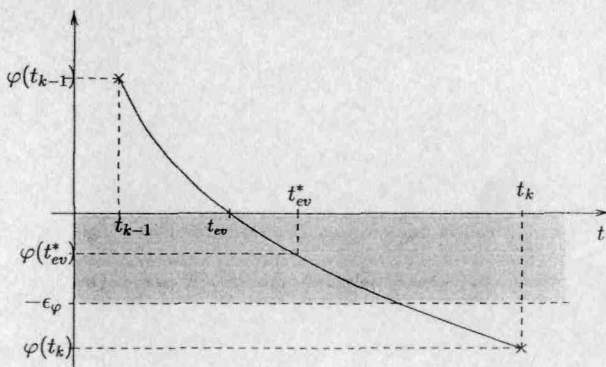


Figure 2: Illustration of the iteration for the time of the implicit event t_{ev} .

From the above it is clear that a suitable φ -function has to be defined also in the case of the reactor modeled in the previous section. Here, the physical scenario causing an implicit event is the vanishing of the vapour phase as boiling conditions are no longer valid. This effect is exactly related to the value of the (fictitious) vapour fraction ψ^* : as soon as ψ^* becomes zero, the vapour phase no longer exists and it becomes necessary to switch to the one-phase-model formulation. Thus, the obvious choice in our case is $\varphi = \psi^*$.

Note that the reactor model comprises two more implicit events: As the reaction is of order zero in the educts CH_3OH and CO , it has to be ensured that no reaction takes place when at least one of the educts is no longer available. However, this event causes

no further problems as it does not imply the need to change the structure of the model equations. Instead, only the reaction rate has to be set to zero.

3.2 Simulation results

In the sequel we present simulation results obtained with the model described above. As mentioned before, we assume all inputs to the reactor to take on fixed stationary values except for the molar feed flow of methanol which is increased by 10% at time $t = 0$. The impact of this feed disturbance can be seen in Figures 3 and 4.

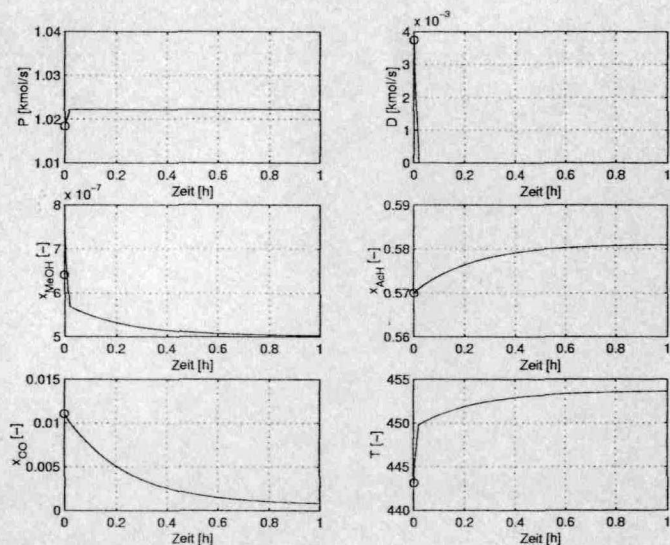


Figure 3: Dynamic transient to a new steady state after a feed disturbance in form of a 10% increase of molar methanol flow (the circles \circ indicate the initial conditions)

As a consequence of the disturbance, a new steady state is approached, characterized by a higher yield corresponding to more product acetic acid and less educts CO and methanol at a higher temperature (see Figure 3).

However, in the context of this contribution it is of interest to investigate what exactly happens during the transient from the first to the second steady state. As the methanol feed flow is increased, the methanol mole fraction initially increases and the mole fractions of the other components have to slightly decrease. In particular, the mole fraction of CO - the educt usually available in excess - will go down and cause the temperature to increase. This is due to the fact that in the two-phase regime the boiling point temperature and thus also the system temperature follow from the vapour summation condition and as the vapour-liquid equilibrium is extremely sensitive to changes in the light boiling component

CO (see also results in [3]), the scenario just described will result in a rise in temperature. This rise in temperature will increase the reaction rate and thus more educts CO and CH₃OH will be consumed and more product acetic acid will be obtained.

Moreover, an even more interesting effect in the context of this contribution can be observed looking at Figure 4. Although the temperature inside the reactor increases, the

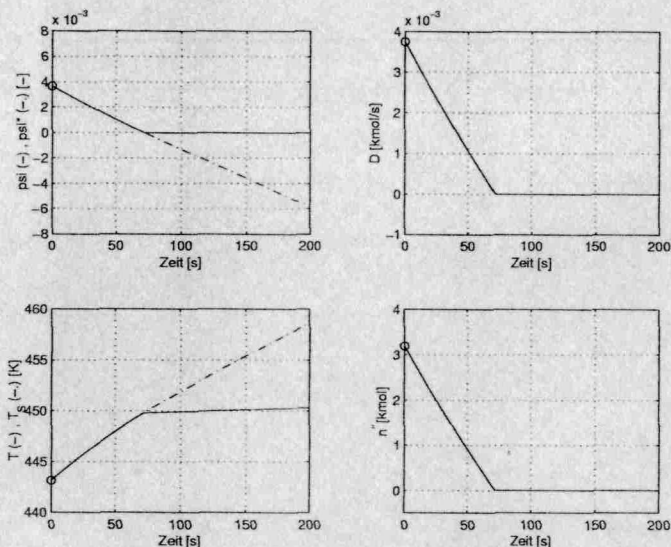


Figure 4: Behaviour of selected variables closely associated with the occurrence of a discrete event during the initial moments of a dynamic transient

vapour flow leaving the reactor decreases. This can be explained as a consequence of the fact that the rising temperature increases the molar enthalpies of the components in the reactor and thus with the flows leaving the system more energy will be removed, leading to a lower molar enthalpy h_R of the reactor contents. Bearing in mind that the vapour fraction ψ_R^* follows from energetic considerations (eq. (4)), it is obvious that ψ_R^* will decrease and this again will cause D to decrease (eq. (14)). All of this will happen as long as $\psi_R^* > 0$. Once ψ_R^* reaches zero, the discrete event associated with it is detected and the simulator switches to the one-phase model description. It is especially apparent that ψ_R and T_R become decoupled from their - now fictitious - counterparts ψ_R^* and $T_{R,S}$ (subfigures on the left) and that the vapour holdup n_R^* as well as the vapour flow D have vanished. So it can be stated that the phase transition has been detected and the necessary switching of the model structure has been successfully performed.

4 Conclusions and perspectives

In this paper it has been shown why it is necessary to enhance a former two-phase model for the reactor ([3]) to make the treatment of potential discrete events in the form of phase transitions possible. A modified model has been presented, a brief description of the underlying numerical method was given and simulation results proved the feasibility of the approach.

It has to be noted that investigations within this contribution were restricted to the open-loop behaviour of the reactor on its own. In a next step models of the condenser and the flashdrum will be added to the enhanced hybrid reactor model, thus completing the modeling of the reaction system. Then, concentration should be turned to the task of modeling the downstream separation system. Finally, all recycle loops connecting units of the separation system with the upstream reactor have to be closed and thus a model of the entire plant for the production of acetic acid will be developed.

Such a complete model promises to exhibit extremely interesting characteristics, both in its nonlinear steady state behaviour and in its dynamic features. It will be a highly challenging task trying to come up with strategies aiming at a plantwide control structure for this very complex dynamical system.

Moreover, the model should form the basis for a training simulation system supporting the teaching of personell and allowing safe investigation of potentially dangerous situations in case of control equipment failures.

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