Modeling and Simulation of a Chemical Reactor for the Production of Acetic Acid – II. Two-Phase Model.

A. Kienle*, F. Pfisterer, R. Waschler, 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 two-phase model for the production of acetic acid is presented and simulation results are compared to results obtained for a one-phase model described in a previous study. It is shown that the new model yields significant improvements in describing both the nonlinear steady state and the dynamic transient behaviour as can be seen from comparisons with measured data from the real plant.

1 Introduction

Acetic acid is an important intermediate product in industrial organic chemistry. Currently, different processes are used for the production of acetic acid on an industrial scale [2, 1]. In this contribution, focus is on methanol carbonylation, where acetic acid is produced from methanol and carbon monoxide according to

$$CH_3OH + CO \longrightarrow CH_3COOH, \quad \Delta H_{R,0} = -138,6 \quad kJ/mol. \tag{1}$$

The reaction is markedly exothermic and is carried out in homogeneous liquid phase using rhodium carbonyl catalyst and iodide promoters according to the Monsanto process [2, 1].
A simplified flowsheet of a typical production plant to be considered in this contribution is shown in Fig. 1. The plant consists of a reaction and a separation system, which serves for the purification of produced acetic acid. As a first step towards the development of model based plantwide control strategies for this type of process a dynamic model of the reaction system has been developed. The reaction system consists of a stirred tank reactor where conversion takes place in the liquid phase according to Eq. (1). A part of the reaction mixture is vapourized through the heat generated by the reaction. The vapour is condensed and recycled into the reactor. In addition, a flash unit has to be taken into account, which is used for the separation and recycle of the rhodium catalyst.
In a previous study a very simple reactor model with a single homogeneous liquid phase has been developed [9]. It has been shown, that this model exhibits pronounced ignition/extinction

*Author to whom all correspondence should be addressed. Phone: ++49 391 6117-522. Fax: ++49 391 6117-501. Email: kienle@mpi-magdeburg.mpg.de

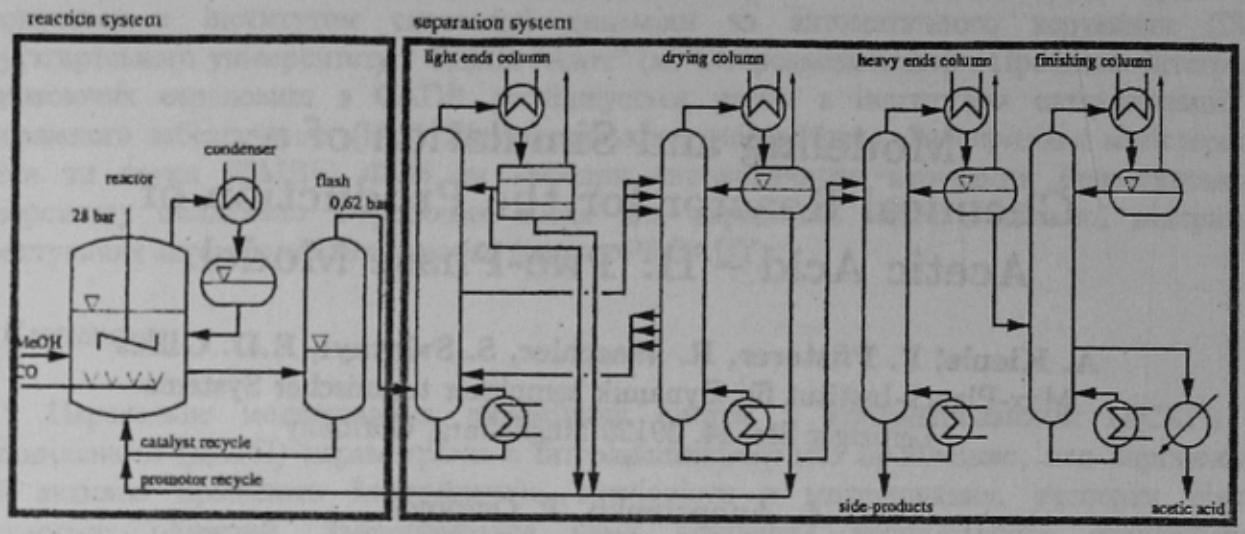

Figure 1: Production of acetic acid according to the Monsanto process.

phenomena, which are related to the existence of multiple steady states over a wide range of operating conditions. Instead, in this contribution a two phase model will be presented, which takes into account partial vapourization of the reaction mixture and finite solubility of gaseous carbon monoxide in the liquid phase. The nonlinear steady state and dynamic transient behaviour of the two phase model is analyzed and compared to the predictions of the model mentioned above. Finally, it is shown that the two phase model is in good agreement with measured data, which have been obtained from an industrial plant in Sewerodonetsk (Ukraine) with a capacity of 150 000 t/a of acetic acid.

2 The Two-Phase Model

The considered reaction system consists of the reactor itself, followed by a condenser, and a flashdrum, as indicated in Figure 2. The underlying modular modeling strategy is to first develop models for each basic unit (i.e., reactor, condenser, and flashdrum) and then to aggregate these basic models to obtain the overall model of the reaction system. This way of modeling is in accordance with the philosophy of the simulation environment DIVA [4].
For each of the basic units an equilibrium model is developed, i.e., liquid and vapour phase are assumed to be in thermodynamic equilibrium. Two slightly different versions of the model are considered.

1. Model 1 neglects the finite solubility of carbon monoxide in the reaction mixture, i.e., it is assumed that CO dissolves completely in the liquid mixture inside the reactor. It is assumed, in addition, that the catalyst cannot be vapourized, and hence equilibrium conditions are only formulated for the NC components water (index H_2O), methanol ($MeOH$), acetic acid (AcH), and methyl iodide (MeI), whereas the NI components CO and rhodium (Rh) do only occur in the liquid phase model equations.

2. Model 2 takes into account the finite solubility of CO which is described in form of ideal solubility by an application of Raoult's law. The problem with this approach is that it becomes necessary to compute the vapour pressure of CO in the super-critical region. To overcome this difficulty we follow a proposal by Prausnitz et al. [7] who suggest to apply extrapolation of the vapour pressure of CO on a linear plot of $\ln(p_{s,CO})$ versus

$\frac{1}{T}$ from physically meaningful data to the temperatures needed for the problem under consideration.

Note that for both models it is assumed that the remaining rest of CO in the product stream P is separated before this stream enters the flashdrum (see Figure 2). In addition, for Model 2 another CO-separator is inserted after the condenser (not shown in Fig. 2). This corresponds to the real situation observed at the industrial plant in Sewerodonetsk. In what follows, the

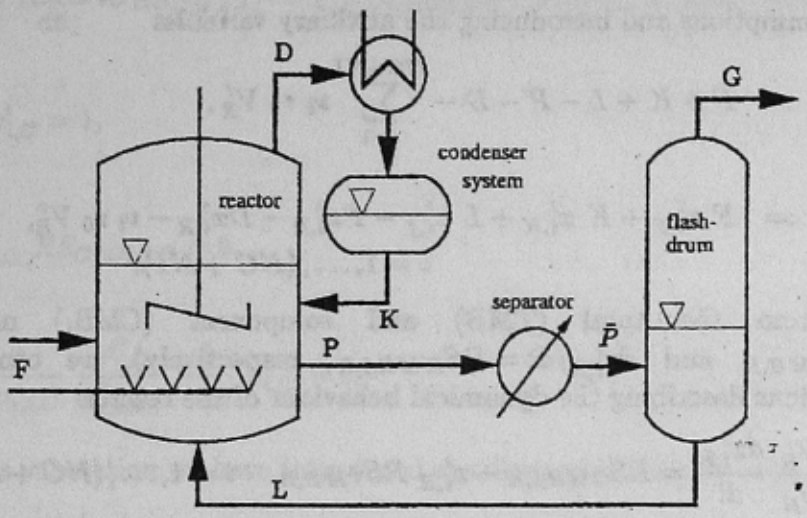

Figure 2: Configuration of Model 1

equations describing the modular systems of the overall Model 1 are presented. Where necessary, the modifications for Model 2 are added.

2.1 Model of the Reactor (Index 'R')

The assumptions made in order to obtain a mathematical model of the reactor are

1. Only the brutto reaction given by Eq. (1) is considered. Therefore, only the educts methanol and carbon monoxide, product acetic acid, rhodium catalyst, promoter methyl iodide, and the additional component water have to be taken into consideration. By-products are neglected.

2. The molar holdup of the vapour phase is assumed negligible compared to the liquid holdup ($n''_R = 0$).

3. The volume of the liquid reactor mixture is constant ($V'_R = const$). At the real plant this geometric constraint corresponds to an overflow with fixed weir height.

4. The reactor is assumed to be adiabate.

5. The pressure inside the reactor is constant ($p_R = const$), corresponding to ideal pressure control.

6. The kinetics of the brutto reaction can be described by [3]

$$r_0 = \delta \cdot 0.4986 \cdot e^n \cdot \left(\frac{x'_{MeI}}{v'_R}\right)^{1.05} \cdot \left(\frac{x'_{Rh}}{v'_R}\right)^{0.99} \left[\frac{kmol}{m^3\ s}\right], \text{ where} \qquad (2)$$

$$n = -7830\left(\frac{1}{T_R} - \frac{1}{443}\right) \text{ and } \delta = \begin{cases} 1 & \text{if } x_{MeOH} > 0 \text{ and } x_{CO} > 0 \\ 0 & \text{if } x_{MeOH} \le 0 \text{ or } x_{CO} \le 0 \end{cases} \quad (3)$$

Since the reaction is of order zero with respect to the educts $MeOH$ and CO, the Kronecker symbol δ is introduced to take into account that the reaction rate vanishes when one of the educts is totally consumed. Within the framework of the simulation environment DIVA this discontinuity problem is handled by the concept of event-functions [5].
Using these assumptions and introducing the auxiliary variables

$$RS_{TMB,R} := F + K + L - P - D - \sum_{i=1}^{NC+NI} \nu_i \, \tau_0 \, V'_R,$$

and

$$RS_{CMB,i,R} := F \, x'_{i,F} + K \, x'_{i,K} + L \, x'_{i,f} - P x'_{i,R} - D x''_{i,R} - \nu_i \, \tau_0 \, V'_R, \quad i = 1, \ldots, (NC + NI),$$

(originating from the total (TMB) and component (CMB_i) material balances $dn'_R/dt = RS_{GMB,R}$ and $dn'_{i,R}/dt = RS_{KMB,i,R}$, respectively), we come up with the following equations describing the dynamical behaviour of the reactor:

$$CMB_i: \quad \frac{V'_R}{v'_R} \frac{dx'_{i,R}}{dt} = RS_{CMB,i,R} - x'_{i,R} \, RS_{TMB,R}, \quad i = 1, \ldots, (NC + NI - 1), \quad (4)$$

$$\textit{summation condition liquid (SCL):} \quad \sum_{i=1}^{NC+NI} x'_{i,R} = 1, \quad (5)$$

$$\textit{constant volume (CV):} \quad \sum_{i=1}^{NC} v'_{i,R} \, RS_{CMB,i,R} = 0, \quad (6)$$

$$\textit{energy balance (EB):} \quad \frac{dH'_R}{dt} = F \, h'_F + K \, h'_K + L \, h'_L - P \, h'_R - D \, h''_R$$

$$\approx \sum_{i=1}^{NC} h'_{i,R} \, RS_{CMB,i,R} + h_{0,CO} \cdot RS_{CMB,CO,R} = 0, \quad (7)$$

$$\textit{vapour liquid equilibrium (VLE):} \quad x''_{i,R} \, p_R \, \varphi''_{i,R} = \gamma_{i,R} \, x'_{i,R} \, p_{s,i,R} \, \varphi''_{0,i,s,R}, \quad i = 1, \ldots, NC, \quad (8)$$

$$\textit{summation condition vapour (SCV):} \quad \sum_{i=1}^{NC} x''_{i,R} = 1. \quad (9)$$

In these equations the quantities $h'_{i,R}$ and $v'_{i,R}$ are the partial molar enthalpies and volumes of the different components. For simplicity, it is assumed that they are equal to the corresponding quantities of the pure components, i.e., excess enthalpy and excess volume are neglected in (7) and (6). As the necessary data to describe the molar enthalpy of CO are not available, the standard enthalpy of creation $h_{0,CO}$ is used. Further, quasi-steady-state behaviour is assumed for the temperature. Consequently, the corresponding contributions in the total differential of the enthalpy and the volume have been neglected in Eqs. (6) and (7). This is known to be a very useful model assumption for many reactive as well as nonreactive processes, as shown in [6]. Hence, Eqs. (6) and (7) are algebraic equations for the unknown vapour and liquid flow rates in the outlet.
For Model 2 we have to add the equation $x''_{CO,R} = (p_{S,CO,R}/p_R) \cdot x'_{CO,R}$, describing ideal solubility of CO, and the upper boundary of equation (9) has to be corrected to $NC + 1$.

2.2 Model of the Condenser (Index 'C')

The assumptions for the model of the condenser are similar to and follow from those stated in the previous subsection for the reactor. To be more precise, assumptions 2, 3, 4 and 5 are adjusted and applied to the condenser model. Moreover, it is assumed that the condensation is complete and instantaneous. Then the model equations describing the condenser are

$$CMB_i: \quad \frac{V'_C}{v'_C}\frac{dx'_{i,C}}{dt} = RS_{CMB,i,C} - x'_{i,C}\,RS_{GMB,C}\,, \quad i = 1,\ldots,(NC-1)\,, \tag{10}$$

$$SCL: \quad \sum_{i=1}^{NC} x'_{i,C} = 1, \tag{11}$$

$$CV: \quad \sum_{i=1}^{NC} v'_{i,C}\,RS_{CMB,i,C} = 0\,, \tag{12}$$

$$VLE: \quad \sum_{i=1}^{NC} \frac{p_C}{p_{s,i,C}}\frac{\varphi''_{i,C}}{\varphi''_{0,i,s,C}}\frac{1}{\gamma_{i,C}}\,x''_{i,C} = 1. \tag{13}$$

As in the previous subsection we have introduced auxiliary variables, namely

$$RS_{TMB,C} = D - K\,, \tag{14}$$

$$RS_{CMB,i,C} = D\,x''_{i,R} - K\,x'_{i,C}, \quad i = 1,\ldots,NC\,. \tag{15}$$

For Model 2 equations (11) and (13) have to be altered to $\sum_{i=1}^{NC+1} x'_{i,C} = 1$, and $\sum_{i=1}^{NC} \frac{p_C}{p_{s,i,C}}\frac{\varphi''_{i,C}}{\varphi''_{0,i,s,C}}\frac{1}{\gamma_{i,C}}\,x''_{i,C} + \frac{p_C}{p_{S,CO,C}}x''_{CO,C} = 1$, respectively. Moreover, the CMB_i of Eq. (10) have to be evaluated for $i = 1,\ldots,NC$.

2.3 Model of the Flashdrum (Index 'f')

As mentioned above (see also Fig. 2), it is asssumed that CO is filtered out by the separator and the modified product stream, designated by $(\bar{P}, x'_{i,\bar{R}},\, i = 1,\ldots,NC+NI-1)$, enters the flashdrum according to

$$\bar{P} = P\cdot(1 - x'_{CO,R}), \tag{16}$$

$$x'_{i,\bar{R}} = \frac{x'_{i,R}}{1 - x'_{CO,R}}, \quad i = 1,\ldots,NC+NI-1. \tag{17}$$

Further, it is assumed, similar to the reactor, that the molar holdup of the vapour phase is negligible ($n''_f = 0$), that the pressure within the flashdrum is constant ($p_f = const.$), and that the flashdrum is adiabate. However, contrary to the reactor and the condenser, it is assumed that the molar and not the volumetric holdup of the liquid in the flashdrum is constant. This approach facilitates the modeling process a great deal and leads to the following model equations for the flashdrum:

$$CMB_i: \quad \frac{dn'_{i,f}}{dt} = \frac{V'_f}{v'_f}\frac{dx'_{i,f}}{dt} = \bar{P}\,x'_{i,R} - G\,x''_{i,f} - L\,x'_{i,f}\,, \quad i = 1,\ldots,NC, \tag{18}$$

$$SCL: \quad \sum_{i=1}^{NC+NI-1} x'_{i,f} = 1, \tag{19}$$

$$VLE: \quad x''_{i,f}\, p_f\, \varphi''_{i,f} = \gamma_{i,f}\, x'_{i,f}\, p_{s,i,f}\, \varphi''_{0,i,s,f}, \quad i = 1, \ldots, NC, \tag{20}$$

In particular, three different scenarios can occur for the flashdrum, depending on the operating conditions:

1. the matter inside the flashdrum is subcooled liquid ($L = \bar{P}$, $G = 0$),
2. two phases do actually coexist inside the flashdrum ($L = (1 - \Psi)\bar{P}$, $G = \Psi\bar{P}$, where Ψ is defined as $\Psi := G/\bar{P}$),
3. the matter inside the flashdrum is overheated vapour ($G = \bar{P}$, $L = 0$).

The decision which of these situations has to be taken into consideration at each simulation step follows from an energy balance. Thus, it is possible to deal with transients between the different scenarios. Again, this problem is tackled by the model using event-functions [5].

2.4 Physical Properties

An important task in the modeling of a chemical plant deals with the specification of the physical properties of the components involved in the process. A detailed description of the methods used for our reaction system would be too comprehensive to be given here. Therefore we confine ourselves to stating that the Antoine equation is used to calculate vapour pressures, the Redlich-Kwong equation is applied in order to obtain fugacity coefficients and molar volumes of the vapour phase; for a description of activity coefficients the UNIQUAC-correlation is used; the Cavett equation leads to molar volumes of the liquid phase. For the enthalpies of the liquid phase we make use of Watson's equation and a polynomial approach yields the enthalpies of the vapour phase [8].
All data used for the models in this publication are taken from the Dortmund Physical Properties Data Bank (DDB).

3 Results

In this section some simulation results are presented. Two-phase Model 1 is used for comparisons of its nonlinear behaviour with results obtained for the one-phase model proposed in [9].
In a second step the two-phase Models 1 and 2 are compared with regard to agreement with measured data from the real plant.

3.1 Nonlinear analysis

For investigations of the nonlinear behaviour we restrict ourselves to the reactor-condenser system, i.e., we eliminate the flashdrum and hence the catalyst recycle from Model 1. This is done in order to allow a comparison with the results obtained for the simple one-phase model of the reactor without condenser as described in [9].
In particular, it has been shown ([9]) that the one-phase model exhibits strong ignition/extinction phenomena. This implies that during startup the reactor, depending on the initial conditions, can either tend towards an undesired low-production steady state as shown in Fig. 3 or to a desired high-production steady state.
Instead, the more detailed two-phase model predicts negligible hysteresis phenomena and the desired high-production steady state is rapidly approached as depicted in Fig. 4.

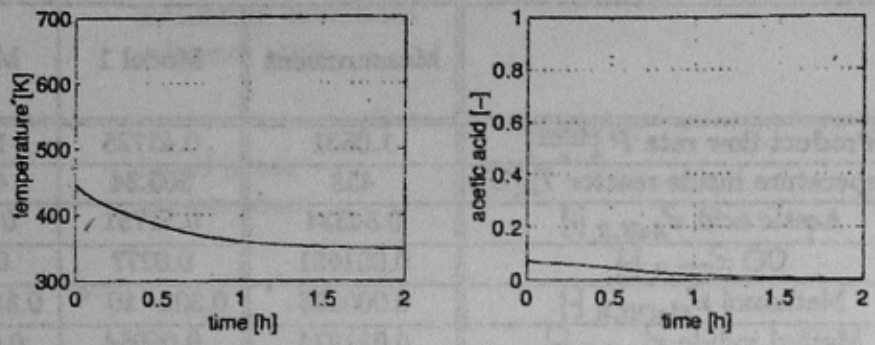

Figure 3: Predicted startup behaviour of the one-phase model for a given catalyst feed mole fraction $x'^{*}_{Rh,F}$, the reaction extinguishes.

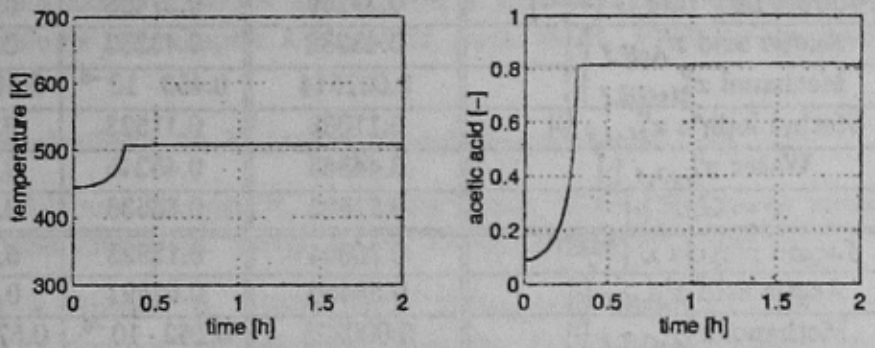

Figure 4: Predicted startup behaviour of the two-phase model for a given catalyst feed mole fraction $x'^{*}_{Rh,F}$, the reaction ignites.

3.2 Comparison with measured data

Table 1 presents results obtained with the two-phase models. Column 1 contains measured data from the plant, in column 2 results from a simulation of the two phase model with infinite CO-solubility (Model 1) are displayed and column 3 contains the corresponding simulation results originating from the model which assumes ideal solubility of CO in the reaction mixture (Model 2).
Obviously, Model 2 leads to much better results than Model 1, especially as far as reactor temperature and streams are concerned. Moreover, the fact is striking that both models yield good agreement of the simulated mole fractions with measured data.

4 Conclusions and Perspectives

A two-phase model for the production of acetic acid has been presented. It has been shown that this model is an obvious improvement to the one-phase model described in [9]. Moreover, it has been shown by comparisons with measured data that neglecting the finite solubility of CO in the liquid mixture inside the reactor leads to only modest results as far as reactor temperature and process streams are concerned whereas even a simple approach like ideal solubility yields considerable improvements.
Further investigations will have to tackle the problem of describing the finite solubility of CO also inside the flashdrum. Then investigations of the nonlinear steady state and the dynamic transient behaviour of the overall system including reactor, condenser and flashdrum should be taken into consideration. Interesting phenomena can be expected, especially due to the closed-loop character of the system with catalyst recycle.

	Measurement	Model 1	Model 2
Product flow rate P $[\frac{kmol}{s}]$	1.0531	0.42725	1.1418
Temperature inside reactor T_R[K]	458	505.34	436.54
Acetic acid $x'_{AcH,R}$ [-]	0.54334	0.51751	0.57702
CO $x'_{CO,R}$ [-]	0.001651	0.0277	0.0120
Methanol $x'_{MeOH,R}$ [-]	0.000623	$0.302 \cdot 10^{-6}$	$0.832 \cdot 10^{-6}$
Methyl iodide $x'_{MeI,R}$ [-]	0.031974	0.06054	0.033827
Rhodium catalyst $x'_{Rh,R}$ [-]	$1.319 \cdot 10^{-4}$	$2.268 \cdot 10^{-3}$	$0.195 \cdot 10^{-2}$
Water $x'_{H_2O,R}$ [-]	0.42230	0.39403	0.37517
Product flow rate G $[\frac{kmol}{s}]$	0.29169	0.27498	0.28579
Acetic acid $x''_{AcH,f}$ [-]	0.43982	0.43232	0.43231
Methanol $x''_{MeOH,f}$ [-]	0.001514	$0.453 \cdot 10^{-6}$	$0.162 \cdot 10^{-5}$
Methyl iodide $x''_{MeI,f}$ [-]	0.11035	0.11523	0.11522
Water $x''_{H_2O,f}$ [-]	0.44565	0.45245	0.45247
$\psi = G/P$ [-]	0.27525	0.66538	0.25334
Liquid recycle L $[\frac{kmol}{s}]$	0.76804	0.13828	0.84230
Acetic acid $x'_{AcH,f}$ [-]	0.58480	0.63691	0.63553
Methanol $x'_{MeOH,f}$ [-]	0.000278	$0.162 \cdot 10^{-6}$	$0.577 \cdot 10^{-6}$
Methyl iodide $x'_{MeI,f}$ [-]	0.001931	0.006775	0.00676
Rhodium catalyst $x'_{Rh,f}$ [-]	$1.811 \cdot 10^{-4}$	$5.085 \cdot 10^{-4}$	$2.646 \cdot 10^{-3}$
Water $x'_{H_2O,f}$ [-]	0.41281	0.35580	0.35506

Table 1: Comparison of the two two-phase models

Finally, modeling and simulation of the separation system shown in Fig. 1 will lead to a complete model of the Monsanto process. This complete model should also serve as a first step towards plantwide control strategies which will be the ultimate objective of further research.

5 Notation

$\Delta H_{R,0}$	molar enthalpy of reaction $[kJ/kmol]$
$F, D, K, P, \bar{P}, G, L$	total molar flow rates defined in Fig. 2 $[\frac{kmol}{s}]$
$x_{i,k}$	mole fraction of component i in subsystem $k \in \{R, C, f\}$ [–]
r_0	brutto reaction rate $[\frac{mol}{m^3 s}]$
ν_i	stochiometric coefficients [–]
V, v	volume $[m^3]$ and molar volume $[\frac{m^3}{kmol}]$, respectively
H, h	entahlpy $[kJ]$ and molar enthalpy $[\frac{kJ}{kmol}]$, respectively
T	temperature $[K]$
p	pressure $[Pa]$
φ	fugacity coefficient [–]
γ	activity coefficient [–]
t	time $[s]$

Subscripts

i	component $i \in \{H_2O, MeOH, AcH, MeI, CO, Rh\}$

S	saturation conditions
0	reference state

Superscripts

$(')$	liquid phase
$('')$	vapour phase

References

[1] Victor H. Agreda and Joseph R. Zoeller. *Acetic Acid and its Derivatives.* Marcel Dekker, New York, 1993.

[2] Adolfo Aguilo, Charles C. Hobbs, and Edward G. Zey. *Ullmanns Encyclopedia of Industrial Chemistry*, volume A 1, chapter Acetic Acid, pages 45–64. VCH Verlagsgesellschaft mbH, Weinheim, 1990.

[3] Azot. *Kurzbeschreibung des Essigsäure Produktionsverfahrens*, 1983.

[4] Peter Holl, Wolfgang Marquardt, and Ernst Dieter Gilles. DIVA - A powerful tool for dynamic process simulation. *Comp. Chem. Engng.*, 12:421–425, 1988.

[5] K. D. Mohl, A. Spieker, R. Köhler, E. D. Gilles, and M. Zeitz. DIVA - A simulation environment for chemical engineering applications. In *Informatics, Cybernetics and Computer Science (ICCS-97), Collected Volume of Scientific Papers*, pages 8–15. Donetsk State Technical University, Donetsk, Ukraine, 1997.

[6] K. Mornhinweg. Modellierung, Auslegung und dynamische Simulation einer Reaktivdestillationskolonne zur Herstellung von Ethylenglykol, 1997. Diplomarbeit, Universität Stuttgart.

[7] J. M. Prausnitz, Ruediger N. Lichtenthaler, and Edmundo Gomes de Azevedo. *Molecular Thermodynamics of Fluid-Phase Equilibria.* Prentice-Hall, Englewood Cliffs, 1986.

[8] Robert C. Reid, John M. Prausnitz, and Thomas K. Sherwood. *The Properties of Gases and Liquids.* McGraw-Hill, New York, 1977.

[9] S. Sviatnyi, A. Kienle, E.D. Gilles, A. Anoprienko, and T. Osipova. Modelling and simulation of a reactor for acetic acid synthesis using the simulation enviroment DIVA. In *Informatics, Cybernetics and Computer Science (ICCS-97)*, pages 16–21. Donetsk State Technical University, Donetsk, 1997. In russian.