MODEL-BASED DESIGN, CONTROL AND OPTIMISATION OF CATALYTIC DISTILLATION PROCESSES

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ABSTRACT

In this contribution, the benefits of using dynamic models of different complexity and size for process design, optimal operation and control of catalytic distillation processes are discussed for the case study of the heterogeneously catalysed reactive distillation of methyl acetate. Dynamic reactive distillation experiments at pilot plant scale were performed using the catalytic structured packing MULTIPAK. A dynamic rate-based model were developed which contains hydrodynamic effects as liquid holdup, liquid backmixing and pressure drop as well as reaction kinetics and which describes the process behaviour accurately. For offline and online optimisation and control, reduced order and simplified models were applied. A systematic control structure selection and controller design studies for the experimental column were conducted. The linear controller shows good performance over a wide range of operating conditions.

INTRODUCTION

Reactive distillation (RD), the combination of chemical reaction and distillation in a single column, is one of the most important industrial applications of the multifunctional reactor concept. Recently, it has drawn considerable attention because of its striking advantages, especially for equilibrium-limited reactions. Several reviews have been published in the last decade which give an excellent overview of RD processes [1-3]. Reactive distillation processes can be divided into homogeneous processes, either auto-catalysed or homogeneously catalysed, and heterogeneous processes, in which the reaction is catalysed by a solid catalyst. The latter, often referred to as catalytic distillation (CD), permits an optimum configuration of the reaction and separation zones in a RD column and the expensive recovery of liquid catalysts can be avoided.

The most promising column internals for CD are structured catalytic packings that combine favourable characteristics of traditional structured packings and heterogeneous catalysts. In these packings, like MULTIPAK [4] or KATAPAK-SP [5], catalytic beads are immobilised within gauze pockets. The alternation of two different layers (“catalytic pockets” and "open channels") results to a so-called hybrid sandwich structure which allows easy access of the liquid to the catalyst and free paths for the rising vapour to ensure counter-current operation in presence of small catalyst particles without flooding problems. In this way, structured catalytic packings permit excellent solid-liquid as well as liquid-vapour mass transfer.

In catalytic distillation, thermodynamic and diffusional couplings in the phases and at the interface which are of multicomponent character are accompanied by complex chemical reactions. As a consequence, special rate-based mathematical models which take the column hydrodynamics, mass transfer resistances, reaction kinetics and dynamic process behaviour into account are required to describe such processes adequately for process design and scale-up issues.

Steady state experiments for the synthesis of methyl acetate [6] and various ethers like MTBE and TAME [7] have already been published. However, experimental data for the analysis of the dynamic behaviour of RD columns with structured catalytic packings are rarely available.

The availability of a reliable dynamic model is the precondition for model-based process control and optimisation. On the one hand the integration of reaction and separation is advantageous from the design point of view as the same task is performed with less equipment and less energy, but on the other hand it creates a challenge to control. Compared to reaction and separation processes in series, the integration leads to a reduction of the number of manipulated variables,, measurements and also of operational degrees of freedom [8]. Therefore tight control is required as disturbances may lead to a significant loss of performance. For the design of an appropriate control structure and a controller, model-based approaches can be applied. Control structure selection for RD processes was carried out previously by open-loop and closed-loop simulations of different scenarios or by investigations of the non-linear steady state behaviour [9]. For a systematic control structure selection and also for the optimisation of batch trajectories simplified models have to be applied. These simplified models can be derived from complex models.

The aim of this paper is to give a comprehensive overview of the use of dynamic modelling for different tasks, e. g. dynamic simulation, scale-up, controller design and optimisation, in the synthesis of methyl acetate in a CD column. The derived models are validated with experimental data from a pilot plant. The rigorous model is used as a reference model for simulations of the closed-loop performance.

The paper is divided into four chapters: in the first one we discuss the rigorous model development, necessary model parameters as mass transfer coefficients, hydrodynamic quantities and reaction kinetics. Then the experimental set-up of the used RD pilot plant is presented. Different experimental runs are used for the model validation and shown in the third section. Afterwards, optimisation issues are discussed and a systematic control structure selection and controller design studies for the experimental column are presented.

RIGOROUS MODELLING

Extensive surveys on modelling approaches for catalytic distillation processes have been published in [2-3]. However, only a limited number of publications deal with the transient behaviour of CD columns equipped with catalytic structured packings. Most contributions are based on equilibrium models assuming thermodynamic and chemical equilibrium on each stage. However, equilibrium is rarely attained since mass and heat transfer as well as chemical reactions are rate driven by chemical potential and temperature.

Kreul published a dynamic rate-based model, modelling vapour and liquid phase separately, for packed RD columns [10]. The reaction kinetics were implemented by means of an overall kinetic approach lumping several effects as reaction kinetics, liquid backmixing and mass transfer resistances together. Further investigations have shown, that this approach yields good predictions in a certain operating range but leads to deviations if it is extrapolated to different process conditions. In this contribution, the approach has been extended by including the catalyst phase as well as considering the non-ideal flow behaviour in the liquid phase. This is essential to reflect the complex hydrodynamics occurring in structured catalytic packings.

Modelling approach

The rate-based-model (RBA) used in this paper is based on the two-film theory and comprises the material and energy balances of a differential element of the vapour and of the liquid phase (see Fig. 1). The dynamic component balances for the liquid and the vapour are:

$$\frac{\partial U_{Li}}{\partial t} = \frac{D_{ax,L}}{u_L}\frac{\partial^2}{\partial z^2}\left(Lx_i^B\right) - \frac{\partial}{\partial z}\left(Lx_i^B\right) + \left(N_{Li}a^i + N_{Si}a^{cat}\right)A_c \quad ; \qquad i=1,\dots,nc \qquad (1)$$

$$0 = \frac{\partial}{\partial z}\left(Vy_i^B\right) - N_{Li}a^iA_c . \qquad (2)$$

The dynamic energy balances are:

$$\frac{\partial E_L}{\partial t} = \frac{\alpha_{ax,L}}{u_L}\frac{\partial^2}{\partial z^2}\left(L\bar{h}_L\right) - \frac{\partial}{\partial z}\left(L\bar{h}_L\right) + \left(Q_La^i + Q_Sa^{cat}\right)A_c - Q_L^{HL} \quad ; i=1,\dots,nc \quad (3)$$

$$0 = \frac{\partial}{\partial z}\left(V\bar{h}_V\right) - Q_La^i A_c - Q_V^{HL} . \qquad (4)$$

Because the column is operated at atmospheric pressure the vapour holdup is negligible. Moreover, reaction rates are taken into account by considering the solid catalyst phase. Due to the rate limited kinetics, diffusion phenomena inside the catalyst are neglected.

Mass and heat transfer

Diffusional interaction phenomena like osmotic or reverse diffusion which may occur in multicomponent systems are taken into account via the Maxwell-Stefan equations for mass transfer (see e.g. [11,12]):

$$N_i = J_i + N_t \Delta\chi_i \; ; \quad i = 1,\dots,nc-1. \tag{5}$$

The diffusive fluxes in the regarding film are calculated by:

$$(J) = -c_t \left[R\right]^{-1} \left[\Gamma\right] (\Delta\chi). \tag{6}$$

The elements of matrix $[R]$ are defined as:

$$R_{ii} = \frac{\chi_i}{\beta_{inc}} + \sum_{\substack{k=1 \\ k \neq i}}^{nc} \frac{\chi_k}{\beta_{ik}} \tag{7}$$

$$R_{ij} = -\chi_i \left(\frac{1}{\beta_{ij}} - \frac{1}{\beta_{inc}} \right). \tag{8}$$

The binary mass transfer coefficient β_{ij} may be calculated using a Sherwood correlation for binary systems. It was published elsewhere for the catalytic structured packing MULTIPAK [6]. In this study mass transfer resistances between the liquid bulk phase and the catalyst pellets are taken into consideration according to Wakao and Kaguei [13]. The mass transfer in the non-catalytic section equipped with ROMBOPAK-6M was calculated using the correlations published by Pelkonen [14].

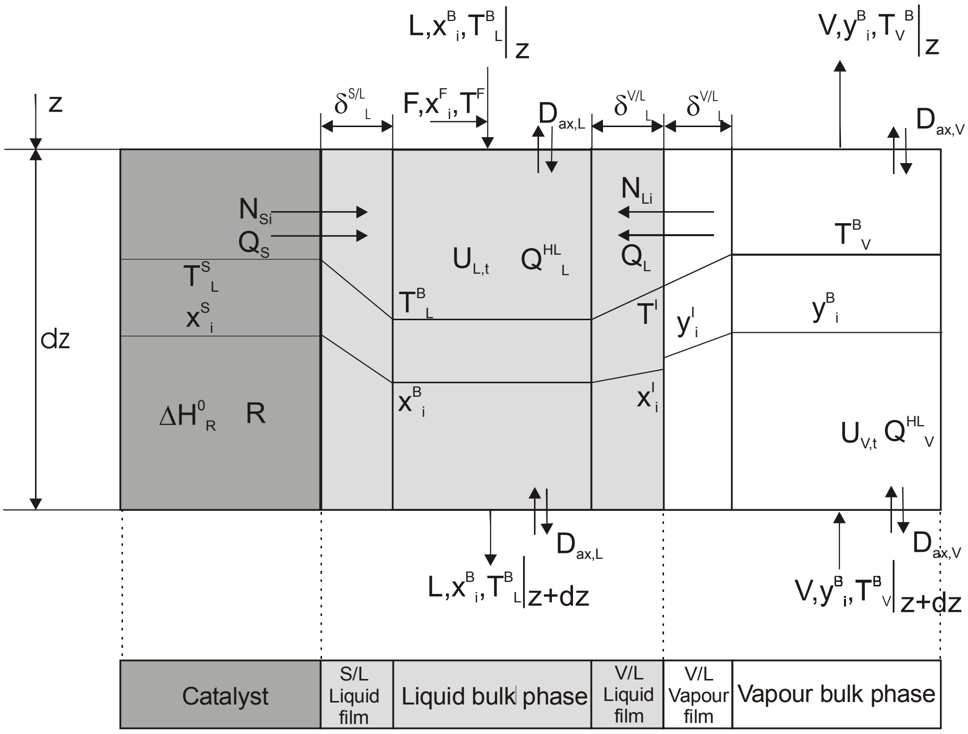


Figure 1: Three-phase rate based approach for catalytic distillation processes.

Hydrodynamics

Modelling approaches for the simulation of the transient behaviour of catalytic distillation columns require detailed information about the hydrodynamics of the columns internals as structured packings and liquid distributors as well as the column periphery such as the top and bottom section.

Liquid holdup and pressure drop correlations were derived for the catalytic packing MULTIPAK [10]. Liquid backmixing in MULTIPAK was extensively studied by Noeres et al. [15].

Correlations for the description of the liquid holdup and pressure drop in the non-catalytic packing ROMBOPAK-6M were published by Mackowiak [16]. The hydrodynamic characteristics of the column periphery were determined at pilot scale (see experimental set-up.

Chemical system and reaction kinetics

The synthesis of methyl acetate from methanol and acetic acid is a slightly exothermic equilibrium limited liquid phase reaction:

$$CH_3OH + (CH_3)COOH \leftrightarrow (CH_3)COO(CH_3) + H_2O \quad \Delta H_R^0 = -4.2\,kJ/mol \quad (9)$$

The low equilibrium constant and the strongly non-ideal behaviour which causes the forming of the binary azeotropes methyl acetate / methanol and methyl acetate / water make this reaction system interesting as a possible RD application [17]. Therefore, the methyl acetate synthesis was chosen as a test system. Since the process is carried out under atmospheric pressure the maximum process temperature is lower than 390 K and no side reactions in the liquid phase like the formation of diethyl ether occur [18].

Several authors published different approaches to describe the heterogeneously catalysed reaction for this chemical system. Kreul identified an overall kinetic by trickle-bed reactor experiments lumping intrinsic kinetics, mass transfer resistances as well sorption effects together [10]. Pöpken et al. carried out an extensive study on the methyl acetate synthesis using Amberlyst 15W [19]. Own laboratory experiments were conducted to investigate the reaction kinetics of the methyl acetate reaction catalysed by Lewatit K2621. A modified LHHW-model published by Poepken was refitted using our new reaction kinetics data as well as binary adsorption data:

$$r = \frac{1}{\nu_i}\frac{dn_i}{dt} = m_{cat}\left(\frac{k_1\, a'_{HAC}\, a'_{MEOH} - k_{-1}\, a'_{MEAC}\, a'_{H2O}}{(a'_{HAC} + a'_{MEOH} + a'_{MEAC} + a'_{H2O})^2}\right) \qquad (10)$$

$$a'_i = \frac{K_i\, a_i}{M_i}. \qquad (11)$$

The temperature dependence of the reaction rate constants are expressed by the Arrhenius equation. All reaction kinetic parameters are given by Tab. 1.

Thermodynamics and physical properties

The vapour-liquid equilibrium was calculated using the modified Wilson equation [10]. For the vapour phase, the dimerisation of acetic acid was taken into account using the chemical theory to correct vapour phase fugacity coefficients [20]. Binary diffusion coefficients for the vapour phase and for the liquid phase were estimated via the methods purposed by Fuller et al. and Tyn and Calus respectively (see [21]). Physical properties as densities, viscosities and thermal conductivities were calculated by the methods given in [21]. Heat losses through the column wall were measured at pilot scale.

Table 1: Parameter set for reaction kinetics model (Eqns. (10,11)).

	$E_{A,1}$	$E_{A,-1}$	k_1^0	k_{-1}^0	$\bar{\sigma}$
adsorption-based approach	[J/mol]	[J/mol]	[mol/(g s)]	[mol/(g s)]	[%]
	5.94 E+04	6.09 E+04	8.00 E+06	6.18 E+05	4.51
	K_{HAC}	K_{MEOH}	K_{MEAC}	K_{H2O}	m^S/m_{cat}
binary adsorption data	[-]	[-]	[-]	[-]	[-]
	0.24	1.57	0.125	1.60	0.56

Numerical solution

The rigorous model presented above yields to a system of partial differential and algebraic equations. A discretisation in axial direction (column height) results in a complex and highly non-linear differential-algebraic equation system (DAE), which can only be solved numerically. Therefore, all model equations have been implemented into the dynamic modelling environment gPROMS [22].

For the numerical solution, a careful analysis of the full system of equations and determination of appropriate initial conditions was necessary in order to prevent high index problems. As these problems often arise in process engineering applications due to simplifications that impose additional constraints on the differential variables, the complete dynamic behaviour of the system as well as changes of the total and specific component molar holdups in every segment are considered

EXPERIMENTAL SET-UP

All experiments were performed in the pilot plant shown in Fig.2. The glass column has a inner diameter of 100mm and an effective packing height of 3 m. The operating pressure lies between 10 and 1013 mbar and the operating temperature is up to 390 K. The column is equipped with catalytic (MULTIPAK-I) and non-catalytic (ROMBOPAK-6M) structured packings. A detailed description of the packings and of the column configuration is given in Tabs.2 and 3.

Feed and product streams, the heat duty and the column wall heating jackets are controlled by a process control system. All process data like temperatures, flow rates, liquid levels and system pressures are collected and monitored by a process control system. Liquid phase samples are withdrawn from the three liquid distributors (Q2, Q6, Q10) as well as from the reboiler (Q15). The samples are analysed by a gas chromatograph including a flame ionisation detector (FID) and a thermal conductivity detector (TCD). Moreover, the liquid phase composition in the reflux line (QI 501) and in the reboiler (QI 502) are determined by an online nearinfrared spectrometer (NIR).

The experimental design was supported by theoretical parameter studies to determine an appropriate operating range for the experimental test runs to investigate the dynamic process behaviour.

Table 2: Characteristic geometrical data of the catalytic and non- catalytic packings used in this work.

geometrical data		unit	MULTIPAK I (catalytic)	ROMBOPAK 6M (non-catalytic)
height of packing segment	H_P	[mm]	166	130
number of packing segments	n	[-]	6	8
catalyst volume faction	ψ_{Cat}	[-]	0.256	-
specific surface area	a	[m^2/m^3]	370	230
void fraction	ε	[-]	0.654	0.95
inclination angle	θ	[deg.]	60	-
effective catalyst beads size	d_p	[mm]	0.50 – 0.62	-
corrugation spacing	S	[mm]	7.5	-

EXPERIMENTAL MODEL VALIDATION

Figure 3 shows the simulated steady-state methyl acetate concentration profiles for different operating conditions. The distillate composition in the optimum operating range shows only a minor dependency upon the reflux ratio. For model validation it is necessary to measure the column profiles as well. Several test runs were conducted to investigate the transient process behaviour and to collect dynamic data for a sufficient model validation.

All test runs presented in this contribution were performed as follows: The column was heated up with the initial amount of methanol given in Tab. 3 under total reflux conditions without acetic acid feed. After steady state conditions were reached, the acetic acid was fed into the column ($t = 0s$). The complete schedule of the experimental runs is given in Tab. 3.

Figures 4 and 5 show the predicted and the measured liquid concentrations and temperatures at different heights along the column. At the beginning of run A the acetic acid feed is switched on and the methyl acetate concentration rises rapidly. At the end of period I the reflux ratio is changed and distillate – a mixture of methyl acetate and methanol near the binary azeotrope - is withdrawn at the top of the column. At the end of period II quasi-steady-state conditions are reached. The system is perturbed by a further change in the reflux ratio and moves to a different operating point.

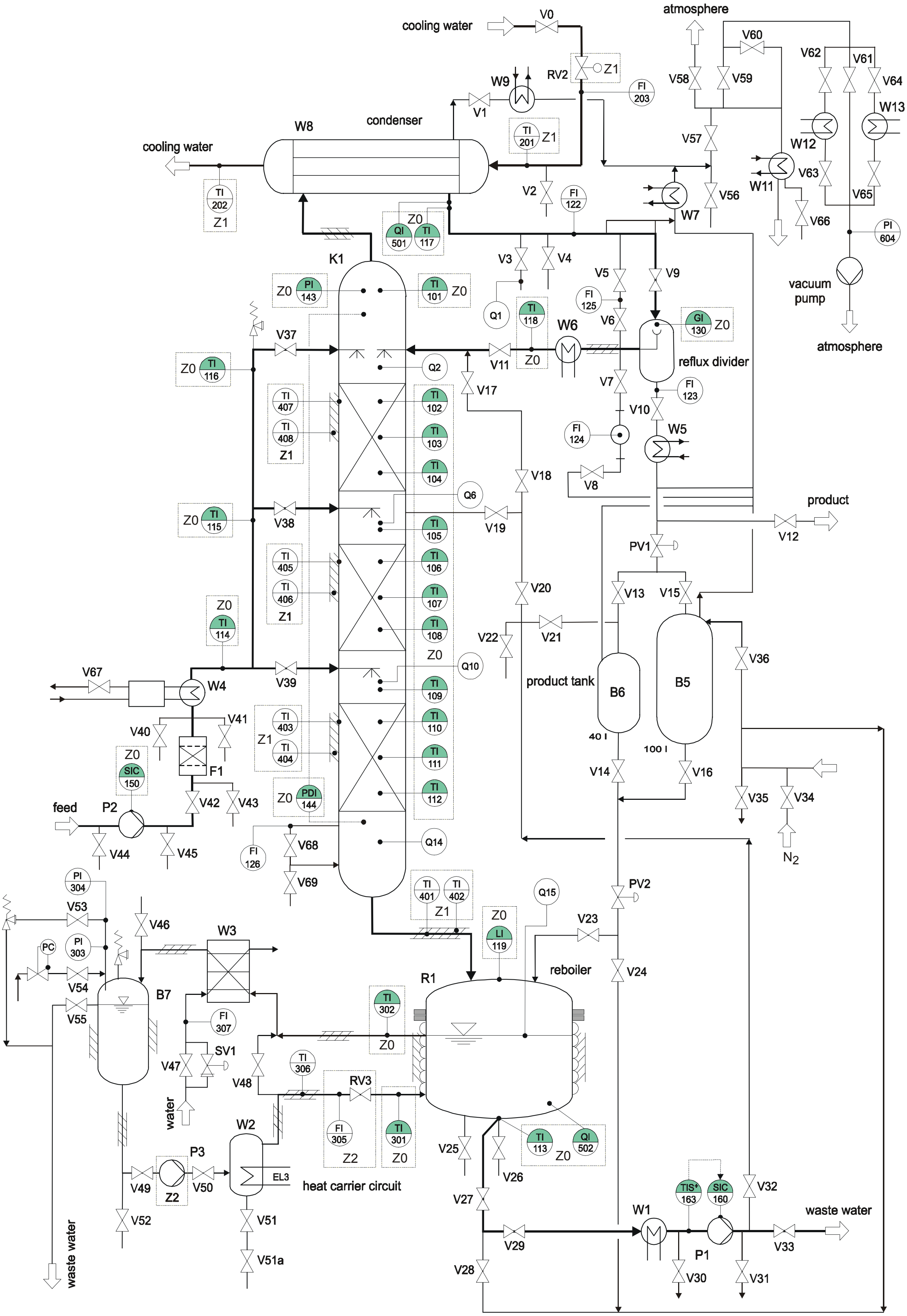
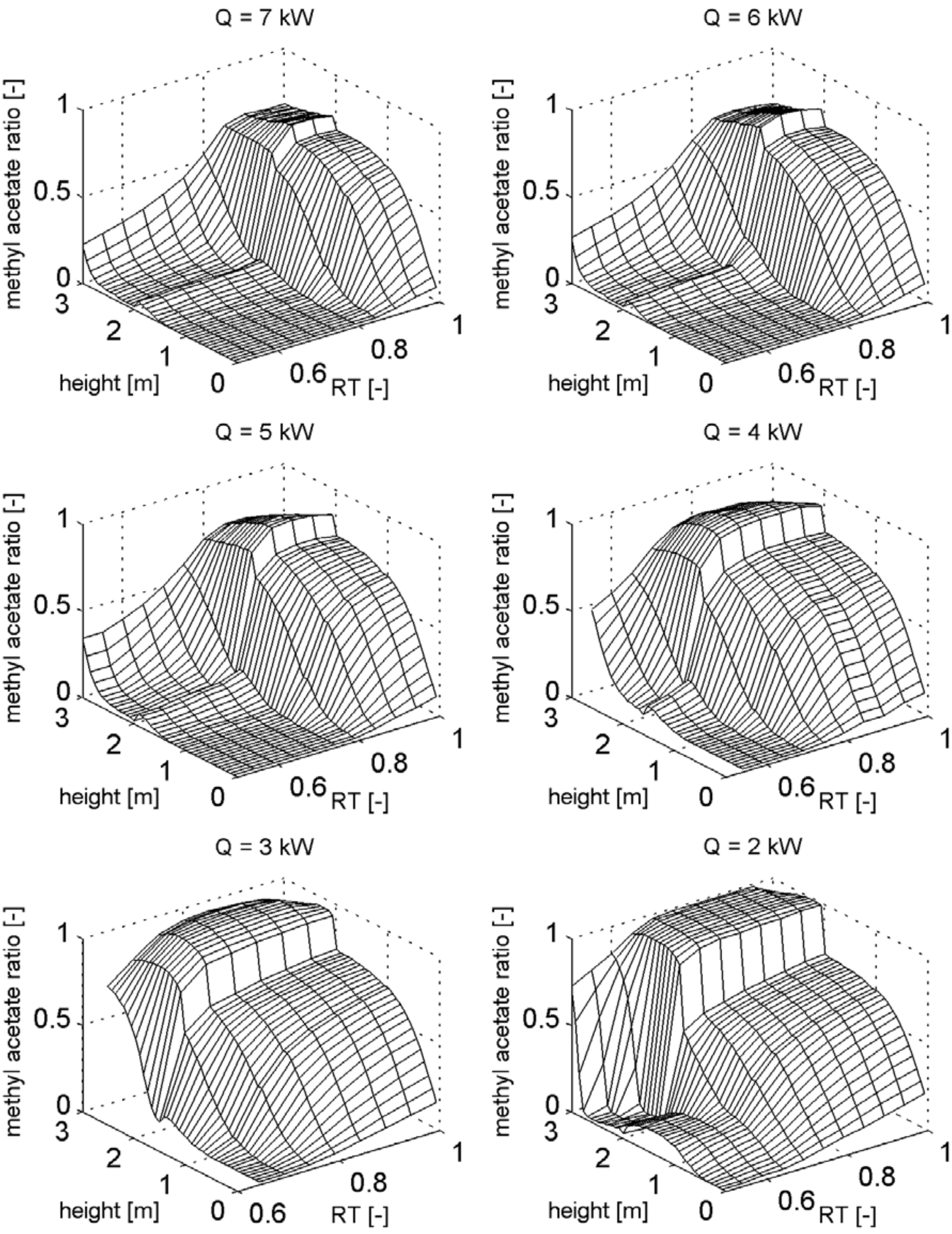


Figure 2: Flow sheet of RD pilot plant column.


Q = 7 kW

Q = 6 kW

Q = 5 kW

Q = 4 kW

Q = 3 kW

Q = 2 kW

Figure 3: Steady-state methyl acetate concentration profiles in dependence upon the modified reflux ratio RT as well as the heat duty Q.

The transient and the quasi-steady-state behaviour is predicted quite well by our rigorous model (see Figs. 4 and 5). However, after the second perturbation (period III) the deviations between experiment and simulation are getting larger. Possible explanations for this could be on the one hand the extreme operating conditions. Due to the low reflux ratio the liquid load drops from an average value of 5 $m^3/(m^2/h)$ to a value below 1.5 $m^3/(m^2/h)$. This liquid load is extensively below the load point [23] at the lower end of the loading range of the catalyst packing which results in decreased catalyst wetting and reduced reaction rate. As industrial RD processes should be operated at higher liquid loads which ensure a sufficient catalyst wetting the model is able to predict a broad range of reasonable process states with sufficient accuracy. On the other hand, the deviations between experiment and simulation at the end of the test run can be explained by the batch character of all runs – small deviations between experiment and model are integrated by the column reboiler over the process time.

To examine the extrapolation capability of the dynamic model, further experiments at different operating conditions were performed. Figures 6 and 7 show the transient liquid concentration and temperature profiles of run B. Deviations of the simulated liquid bulk temperature after the start-up are due to lower boiling trace components which are not considered in the column model. After the start-up phase the temperature along the catalytic section of the column shows a steep rise caused by the acetic acid feed. After a temperature maximum, the produced methyl acetate accumulates inside the column and therefore the liquid temperature falls. In period II, distillate is withdrawn and in the catalytic section the low boiling component methyl acetate impoverishs. The simulated temperature profiles are in good agreement with the experimental data.

The results presented here demonstrate clearly that our rigorous model predicts the dynamic and quasi-steady-state behaviour of this RD process well.

Table 3: Column configuration and initial process conditions.

run		A	B
column top pressure, p	[bar]	1,013	1,013
initial methanol holdup, U_{MEOH}	[mol]	1,248	1,140
feed position, h_{Feed}	[m]	2	2
column internals (2m – 3m)	[-]	ROMBOPAK 6M	ROMBOPAK 6M
column internals (1m – 2m)	[-]	MULTIPAK-I	MULTIPAK-I
column internals (0m - 1m)	[-]	MULTIPAK-I	MULTIPAK-I

Table 4: Experimental schedule of dynamic RD experiments.

run		A			B		
period number		I	II	III	I	II	III
duration t	[s]	4680	5580	10950	1800	7590	9600
heat duty, Q	[W]	6000	6000	6000	6000	6000	6000
reflux ratio, ν	[-]	∞	10	1	∞	3	4
feed rate, $F_{HAC,2m}$	[mol/s]	0.024	0.024	0.024	0.027	0.027	0.027

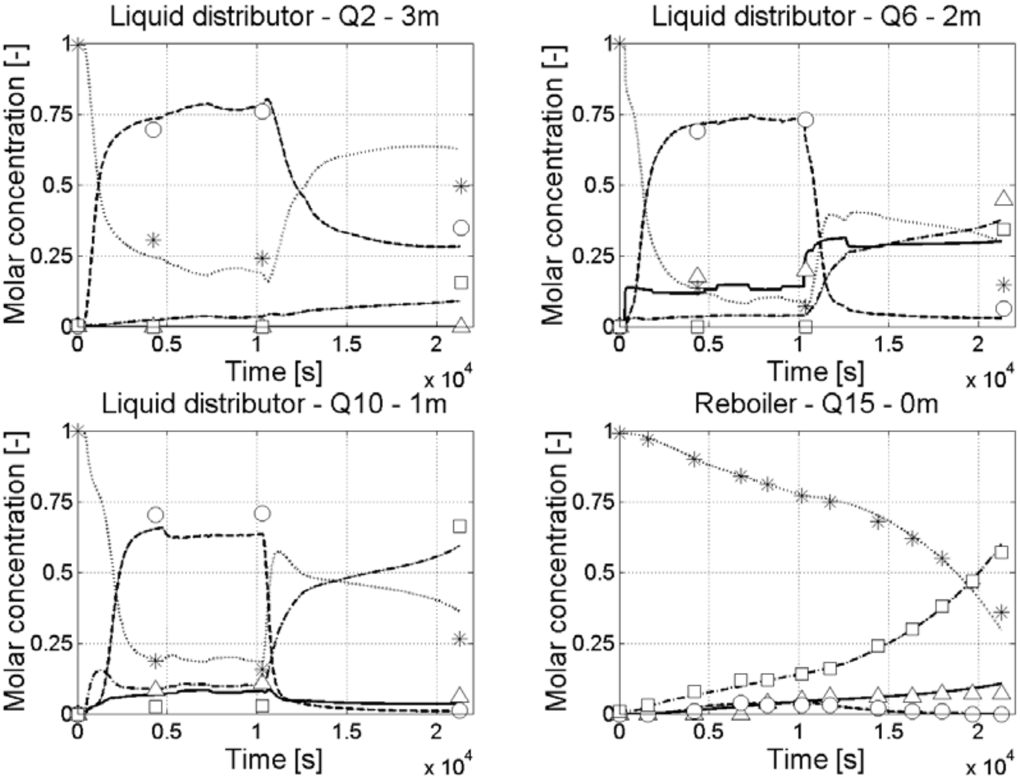


Figure 4: Dynamic liquid bulk concentrations of run A: experimental and simulation results (∆ - acetic acid, ∗ ···· methanol, ο - - methyl acetate, ☐ -·- water).

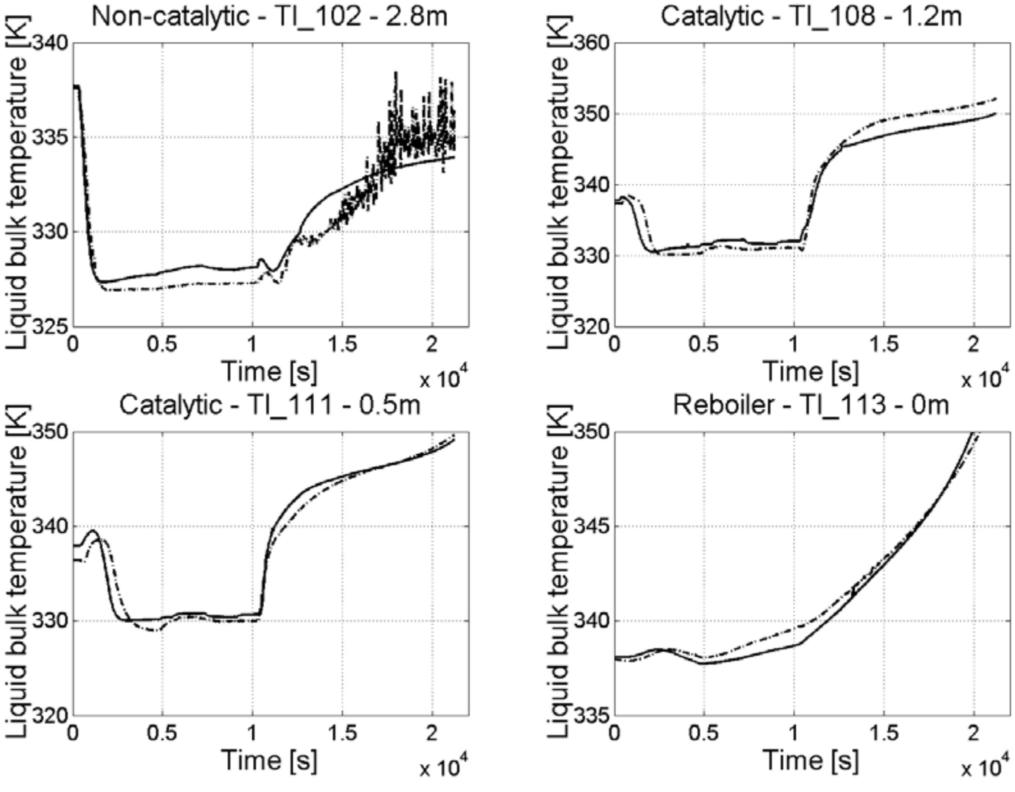


Figure 5: Dynamic liquid bulk temperatures of run A: experimental (- -) *and simulation results* (-).

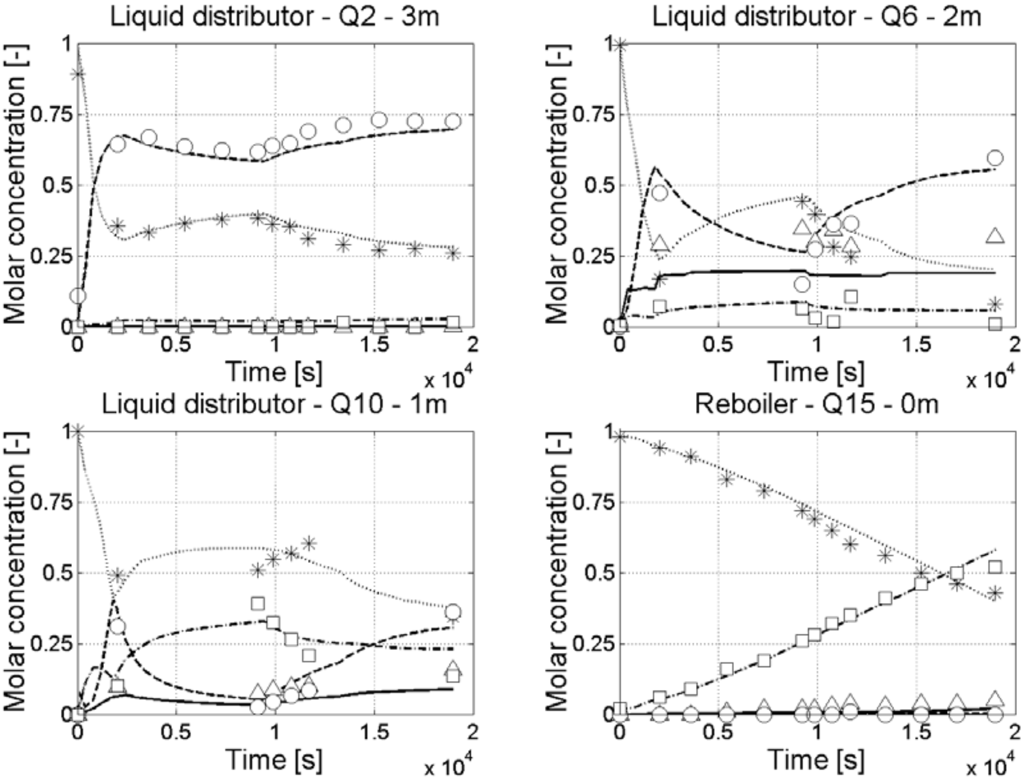


Figure 6: Dynamic liquid bulk concentrations of run B: experimental and simulation results (Δ - acetic acid, ∗ ···· methanol, ο - - methyl acetate, ☐ -·- water).

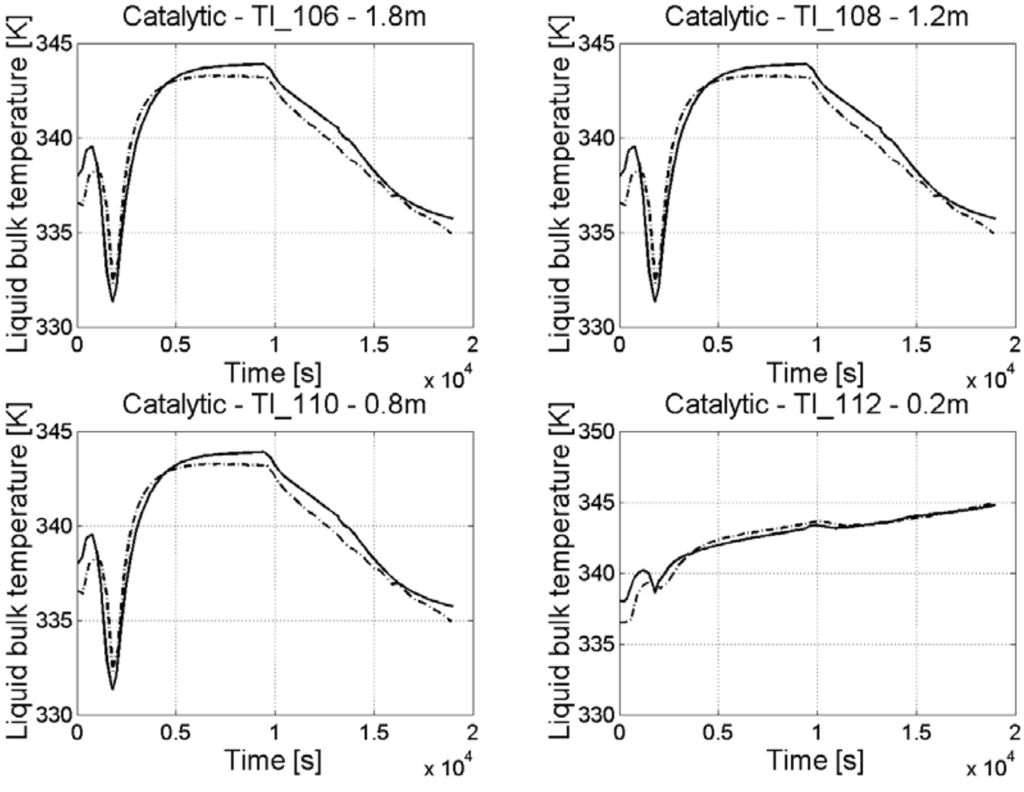


Figure 7: Dynamic liquid bulk temperatures of run B: experimental (- -) *and simulation results* (-).

CONTROL AND OPTIMISATION

Because of its complexity the rate based model is not suitable for controller design and optimisation of the RD process. Therefore an extended equilibrium stage model which includes a reaction kinetic is used for these tasks. Fig. 8 shows a comparison of simulation results of the RBA and the equilibrium stage model for a typical trajectory of input variables.

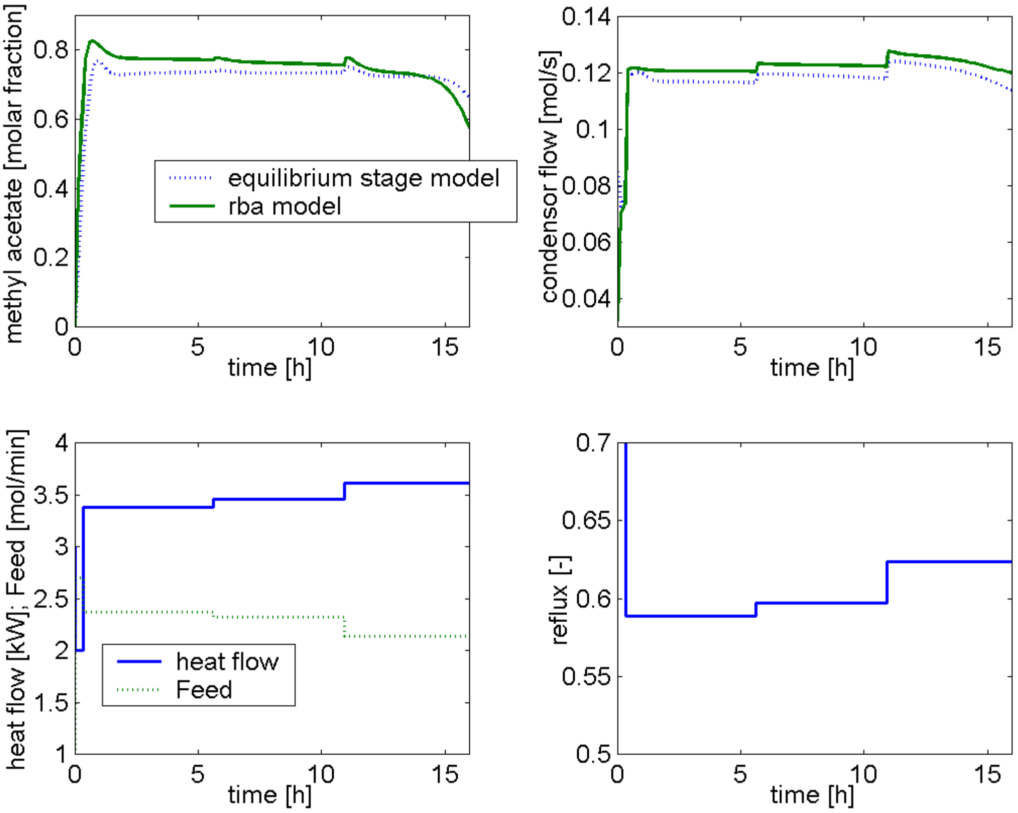


Figure 8: Comparison of the RBA and the equilibrium stage model.

The dynamic behaviour is covered well by the simplified model and the deviations between the absolute values are acceptable for control purposes. The computational time for the simulation of the equilibrium stage model compared to the RBA model is approximately 20 times smaller. This advantage motivates the use of the simplified model for control and optimisation purposes.

Linear controller design

The standard approach to control chemical processes is the use of linear multi input multi output (MIMO) controllers. Due to the instationary character of the semi-batch process at hand, the change in process dynamics has to be taken into account, i. e. a robust controller has to be developed. Distillation processes usually offer a large number of possible control variables, e. g. temperatures, concentrations. For the semi-batch RD, available manipulated variables are the feed rate of acetic acid (HAc), the heat duty in the reboiler and the reflux ratio. Potential control variables are the temperatures at different locations and the product concentrations in the reboiler and at the top of the column. Tab. 5 summarises the available measurements and their numbering.

Table 5: Available measurements and location in the column

number	measurement	part of column
1	mole fraction HAc	condenser/reflux line
2	mole fraction MeOH	condenser/reflux line
3	mole fraction MeAc	condenser/reflux line
4	mole fraction H_2O	condenser/reflux line
5	mole fraction HAc	reboiler
6	mole fraction MeOH	reboiler
7	mole fraction MeAc	reboiler
8	mole fraction H_2O	reboiler
9,...,12	temperature	separation packing
13,...,16	temperature	catalytic packing 1
17,...,20	temperature	catalytic packing 2
21	temperature	reboiler
22	molar flow rate	condenser

For the 22 measurements and 3 manipulated variables numerous control structures can be chosen. In [24] a systematic approach for control structure selection is proposed. The described integrated approach yields a promising control structure and a low order controller without a priori assumptions on the controller structure and without a need for many intuitive decisions by the designer. Starting from a linear model of the given system with all possible inputs and outputs, the procedure to determine the optimal control structure applied to the RD is as outlined below:
In order to develop the linear controller for the semi-batch process in a first step a nominal trajectory has to be determined. Based on the equilibrium stage model Fernholz et al. calculated an optimal trajectory for the manipulated variables by maximising the productivity of the process [25].
At a quasi stationary point in the middle of this batch, which is taken as the nominal operating point, a linear state space model is determined. The resulting linear system, which was determined by linearisation of the non-linear equilibrium stage model, has 85 states (the nominal values of the manipulated variables $RT_s = 0.597$, $Q_s = 3400\,W$, $F_s = 0.04\,mol/s$). Under these conditions a methyl acetate mole fraction of about 80% results. The dynamic behaviour of the heating system is approximated by a first order model.

For the systematic control structure selection it is assumed that the mole fraction of methyl acetate in the reflux is always chosen as control variable as it describes the product quality. Furthermore the ratio between the heat duty and the HAc-feed represents one degree of freedom. As consequence it is impossible to use both variables as independent control inputs. Therefore we investigate systems with 2 input and 2 output variables which yields in 42 potential control structures.

In a first selection step, the plant dynamics of all possible structures are checked for non-minimum phase elements as the attainable performance of linear control systems is limited by right-half-plane (rhp) zeros, time-delays and unstable poles

[26]. By considering the multivariable zeros and only the smallest delay, the attainable performance is over-estimated. For the closed loop a rise time of 500 seconds is assumed. As the bandwidth is limited by $0.3 \cdot \omega_N$ structures with rhp-zeros below 0.006 are excluded. The remaining structures are given in Tab. 6.

Table 6: Remaining control structures after analysis of rhp zeros.

manipulated variables: heat duty, reflux ratio		manipulated variables: HAc feed, reflux ratio	
structures	smallest rhp zero	structures	smallest rhp zero
3 21	-	3 13	37.7811
3 22	-	3 14	1.2408
3 9	0.1532	3 15	0.4353
3 10	0.0224	3 17	0.1340
3 11	0.0169	3 5	0.1257
3 8	0.0124	3 6	0.1165
3 6	0.0115	3 1	0.1029
		3 18	0.0964
		3 4	0.0930
		3 9	0.0920
		3 19	0.0701
		3 12	0.0444
		3 10	0.0403
		3 11	0.0334

For further reduction of the number of combinations, the directionality of the remaining control structures is regarded. The directionality of the plant can be measured by the minimised condition number γ^*. A large minimised condition number indicates that the plant gain varies strongly with the direction of the inputs, the gain matrix is then called ill-conditioned. The advantage of using the minimised condition number is its scaling independence. A large minimised condition number implies numerical problems in the controller design and robustness problems if decoupling is enforced. However, it is known that the condition number is only critical around the closed-loop bandwidth which is not known at this stage. So the condition numbers will only eliminate such structures which have a comparatively large condition number over a large frequency range. Only the structures {3 5}, {3 6} and {3 19} with the manipulated variables feed and reflux ratio have minimised condition numbers $\gamma^* > 10$. These structures are not considered in the further selection process.

The criteria discussed above give only qualitative indications whether a control structure is likely to lead to good controller performance or not. For a quantitative investigation, the promising candidate structures must be compared directly with respect to their attainable performance. A rigorous comparison is possible under mild assumptions on the problem setting using convex optimisation [27, 28]. The key idea is to use the Youla parameterisation of all closed-loop systems which is affine in a free transfer matrix, and to optimise the free parameter for convex performance criteria [29]. As described in [24] the minimisation of the integral squared error of the outputs for step changes of the setpoints can be formulated as a quadratic program. In this formulation input limitations and steady state accuracy are included as linear constraints. In Tab. 7 the main properties of the attainable performance are summarised for the remaining best structures.

Table 7: Attainable performance properties, t_A = rise time, O = overshoot.

manipulated variables	structure	output	t_A [h]	O [%]	comments
heat duty / reflux ratio	{3 22}	y_1	0.17	9	-
		y_2	0.02	3	-
heat duty / reflux ratio	{3 10}	y_1	0.23	2	-
		y_2	0.08	4	-
heat duty / reflux ratio	{3 11}	y_1	0.23	3	-
		y_2	0.05	2	coupled
HAc feed / reflux ratio	{3 13}	y_1	0.34	4	-
		y_2	0.16	1	-
HAc feed / reflux ratio	{3 14}	y_1	0.27	7	-
		y_2	0.31	1	-
HAc feed / reflux ratio	{3 4}	y_1	0.23	2	-
		y_2	0.16	2	-

From an engineering point of view it is not surprising that the structure {3 22} shows a good performance as the heat duty directly determines the vapour flow and therefore the molar flow rate of the product. This signifies that one degree of freedom is only substituted by another one. From this it follows that the resulting control structure may be considered as a single input single output structure. The second degree of freedom, e. g. the vapour flow, is not used. Regarding the location of the temperature measurements 13 and 14 it is also obvious that these temperatures can be controlled easily by the HAc-feed. For this reasons the structures {3 22}, {3 13} and {3 14} in Tab. 7 are omitted.

For the remaining structures, a linear controller design is carried out using multivariable frequency response approximation [30]. The nominal desired closed-loop systems are defined by the results of the computation of the attainable performance. The resulting linear MIMO controllers were applied to the non-linear RBA model. In Fig. 9, the disturbance rejection for the structure {3 11} is depicted for the disturbance scenario summarised in Tab. 8. It can be concluded that the developed controller is robust against the given uncertainties and shows good performance as predicted by the linear analysis. The rigorous RBA model used in the simulation differs from the model from which the linearisation was computed. So the given results also demonstrate the robustness of the controller.

Table 8: Disturbances to the process.

disturbance	nominal value	1st value	2nd value	time
heat duty [kW]	3.5	0	-1	3:10 h
modified reflux ratio [-]	0.6	0	-0.1	4:40 h
factor reaction rate [-]	1	1	0.5	6:10 h
heat loss per stage [W]	0	0	10	7:40 h
feed [mmol/s]	39	0	-10	9:10 h

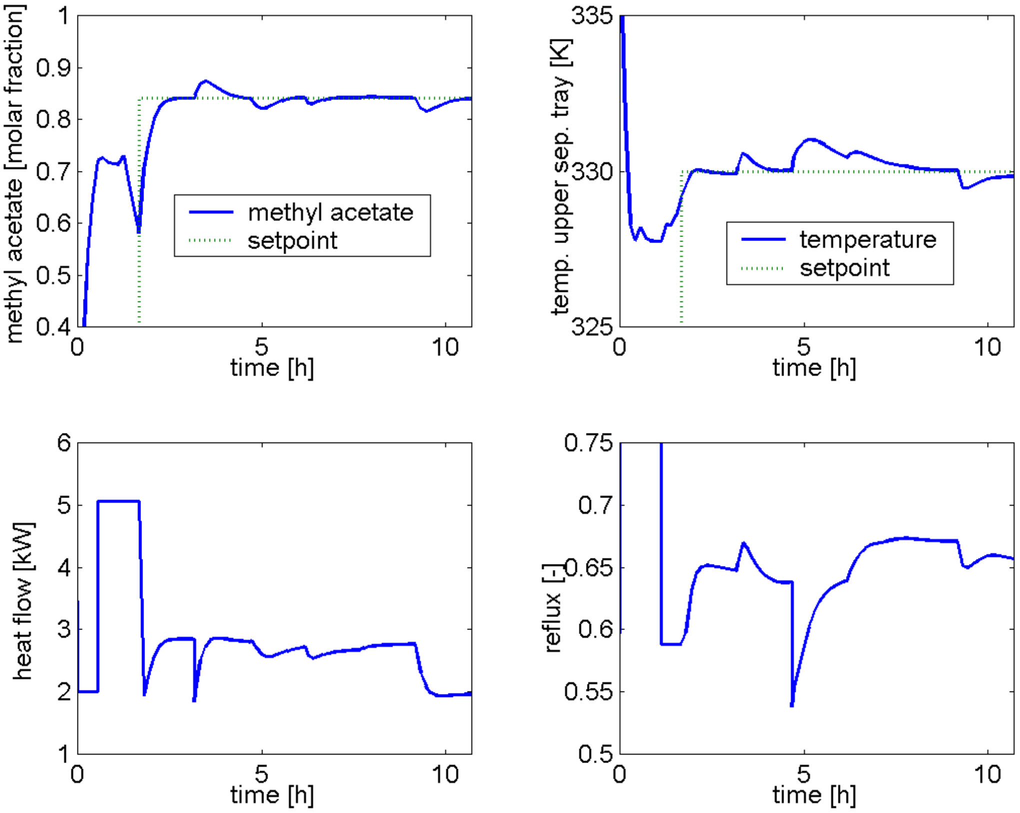


Figure 9: Performance of the controller for the structure {3 11} with the manipulated variables heat duty and modified reflux ratio.

Optimisation

The robust controller is used in the optimisation of the process in a closed loop fashion. In contrast to the open-loop optimisation which was investigated by Fernholz et al. [25], in the closed-loop approach the setpoints of the control variables are used as free parameters instead of the manipulated variables. By applying the open-loop optimisation process it is not assured that a linear controller is able to track the computed trajectory due to changes in the steady state gain of the process. If the controller action is considered in the optimisation, the controllability of the process with the controller is maintained. This is the steady state gain of the process may change its sign so that linear controllers fail. Setpoints which lead to this situation are therefore not optimal and are thus penalised.

In the literature different formulations of the optimisation problem for batch distillation columns can be found [31, 32, 33]. For the problem at hand the profit is maximised. The cost function f is defined as:

$$f = \frac{n_{MeAc}}{t_f + t_{startup} + t_{shutdown}}. \tag{12}$$

The decision variables are the setpoints of the methyl acetate fraction in the reflux and the molar product flow, the feed rate of acetic acid and the final time of the batch. To ensure that the column is operated within its limits upper and lower bounds to the manipulated variables are introduced. A lower bound of the mole fraction of methyl acetate in the distillate tank is prescribed as well as lower bounds for the conversion of methanol and acetic acid are defined. Thus the closed-loop optimisation problem is formulated as:

$$\max_{t_i, y_i^s, F_i} f \tag{13}$$

subject to the plant dynamics

$$F(\dot{x}(t), x(t), y(t), u(t)) = 0 \tag{14}$$

and the constraints

$$\begin{gathered}
Q_{i,min} \leq Q_i \leq Q_{i,max} \\
RT_{i,min} \leq RT_i \leq RT_{i,max} \\
F_{i,min} \leq F_i \leq F_{i,max} \\
x_{MeAc}^{distillate} \geq x_{MeAc}^{min} \\
C_{MeOH}(t_f) \geq C_{MeOH}^{min} \\
C_{HAc}(t_f) \geq C_{HAc}^{min} \\
\sum_{i=1}^{N} t_i = t_f
\end{gathered} \tag{15}$$

where y_i^s are the setpoints of the control variables. Due to the dynamic equality constraints, a dynamic non-linear optimisation problem results. It is solved by transformation to a non-linear program using control vector parameterisation [25]. The time horizon is divided into five intervals in which the free variables are parameterised functions of time, here piecewise constant values are taken. The length of the intervals are free variables. The optimisation is performed using the SQP-based algorithm provided by gOPT [22].

Fig. 10 shows a comparison between the two optimisation strategies. For the start up interval in both cases the open-loop approach was used as in that interval changes in the gain are inevitable and therefore a linear controller must fail.

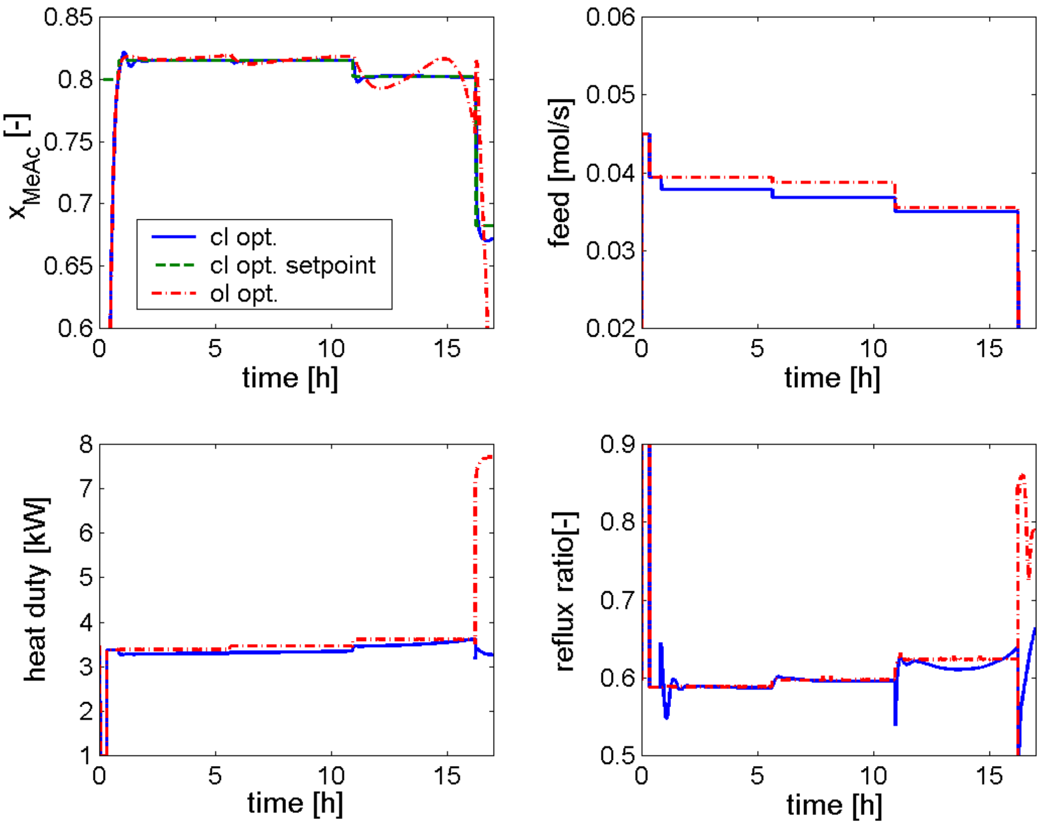


Figure 10: Comparison between open-loop and closed-loop optimisation.

From Fig. 10 it follows that the calculated trajectories of the manipulated variables are similar except for the last interval. In the closed-loop formulation constant values for the methyl acetate fraction are stipulated in the different time intervals. Regarding the trajectory of the heat duty, the drift of the process can be recognised.

CONCLUSIONS AND OUTLOOK

Model based design, control and optimisation issues of catalytic distillation processes were discussed in this contribution.

A rigorous rate-based approach has been developed which describes packing characteristics as liquid holdup, liquid backmixing and pressure drop as well as reaction kinetics. Extensive pilot plant experiments for methyl acetate synthesis have been performed and transient concentration and temperature profiles were used to validate the dynamic process model.

The results presented in this contribution demonstrate clearly that the suggested rigorous rate-based model reflects the dynamic and pseudo steady state behaviour of the regarding RD process. The posed model is applicable to process design and scale-up issues. Moreover, it was used as a reference for simplifications of the model.

These reduced models are necessary for control and optimisation purposes as the rigorous model is not suitable for these tasks due to its complexity. Based on a linearisation of a simplified equilibrium stage model including a reaction kinetics term a systematic control structure selection procedure was applied. The resulting controller was verified using the complex rate based model and shows good performance and robustness to model uncertainties and disturbances. Using the derived linear controller a closed-loop optimisation based on the equilibrium stage model was performed. This approach ensures the controllability of the process for the calculated trajectories. But as linear controllers are not able to drive the process in arbitrary regions of operation, non-linear model based controllers should be applied. For the necessary effective simulation of the process local linear models interpolated by radial basis functions will be used. The developed control strategies will be applied to the pilot plant in order to verify the developed concepts.

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NOTATION

A_c	column cross section, m^2
a’	modified activity coefficient
a^{cat}	specific gas-liquid interfacial area, m^2/m^3
a^i	specific gas-liquid interfacial area, m^2/m^3
c	molar concentration, mol/m^3
C	conversion
$D_{ax,L}$	axial dispersion coefficient, m/s^2
(J)	diffusion flux vector, $mol/(m^2s)$
[R]	inverse mass transfer coefficient matrix, s/m
E_A	activation energy, J/mol
E	specific energy holdup, J/m
ΔH_R^0	standard reaction enthalpy, kJ/mol
V	vapour molar flow rate, mol/s
h	molar enthalpy, J/mol
K	binary adsorption coefficient
k	reaction rate coefficient, mol/(gs)
L	liquid molar flow rate, mol/s
m_{cat}	catalyst amount, g
nc	number of components of mixture
n	molar amount, mol
N	molar flux, $mol/(m^2s)$
Q	heat flux, W/m^2
r_i	reaction rate, mol/s
RT	modified reflux ratio, $\nu/(\nu-1)$
t	time, s
T	temperature, K

u_L	liquid velocity, m/s
U	specific molar holdup, mol/m
x	liquid mole fraction, mol/mol
y	vapour mole fraction, mol/mol
z	axial co-ordinate, m

Greek letters

α_{AX}	thermal dispersion coefficient, m^2/s
χ	mole fraction
β	mass transfer coefficient, m/s
δ	Film thickness, m
γ^*	minimised condition number
$[\Gamma]$	Thermodynamic correction matrix
λ	Molecular thermal conductivity, W/m K
$\overline{\sigma}$	mean relative error
υ	stoichiometric coefficient
ω_N	band width of rhp-zero, rad/s

Subscripts

i,j,k	component indices
t	total

Superscripts

B	bulk phase

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