

## How to Start Up Reactive Distillation Towers

F. Reepmeyer, J.-U. Repke, F. Forner\*, G. Wozny

Department of Process Dynamics and Operation, Technical University Berlin, Germany

\* to whom correspondence should be addressed: TU Berlin, Str. d. 17. Juni 135 / KWT-9, 10623 Berlin. Phone: +49 30 314 26905 Fax: +49 30 314 26915 email: florian.forner@tu-berlin.de

### Abstract

In this contribution, a rigorous process model to simulate the start up of reactive distillation (RD) columns from the cold and empty state is developed and experimentally validated with a transesterification process. Strategies for time optimal start up of an RD column are presented. The total reflux strategy, which is mostly used for conventional distillation is only recommendable with limitations for RD. New, alternative strategies for the minimization of the necessary start up time like the recycling of off-spec bottom and top product or the initial charging with product are presented. Suitable strategies can save up to 85% of the needed time for column start up. A rule of thumb to find the optimal start up strategy for a given reactive distillation process is presented.

**Keywords:** Reactive Distillation, Start Up, Dynamic Simulation, Transesterification

### 1 Introduction

Reactive distillation (RD) can be defined as the integration of chemical reaction and thermal separation in one process step. Significant savings of investment and capital costs can be realized by reactive distillation. Further advantages like overcoming equilibrium limitations, achieving higher selectivity, easier separation of azeotropic mixtures or use of reaction heat for the distillation call attention for RD as an interesting process alternative for the chemical industry. Industrial applications are for example esterifications, like the production of ethyl acetate or etherifications like the MTBE process. For an extensive overview on industrial applications of RD please refer to chapter one of (*Sundmacher and Kienle, 2003*). The integration of reaction and separation increases the complexity of the process. This requires a better knowledge of the process and the kinetic activities. Various published papers on design studies and steady state simulation of RD processes can be found. A comprehensive overview is given by (*Doherty and Buzad, 1992*) and (*Taylor and Krishna, 2000*). On dynamic simulation of RD processes, which gained attention just recently, sources are sparse. Information can be found in (*Alejski and Duprat, 1996*) or (*Scenna et al., 1998*) for the production of acetates with different alcohols. Fuel additives like MTBE and TAME have been analyzed by (*Abufares and Douglas, 1995*) or (*Sundmacher, 1995*). But these papers all focus on the dynamic behaviour near a known operating point based on a known steady state.

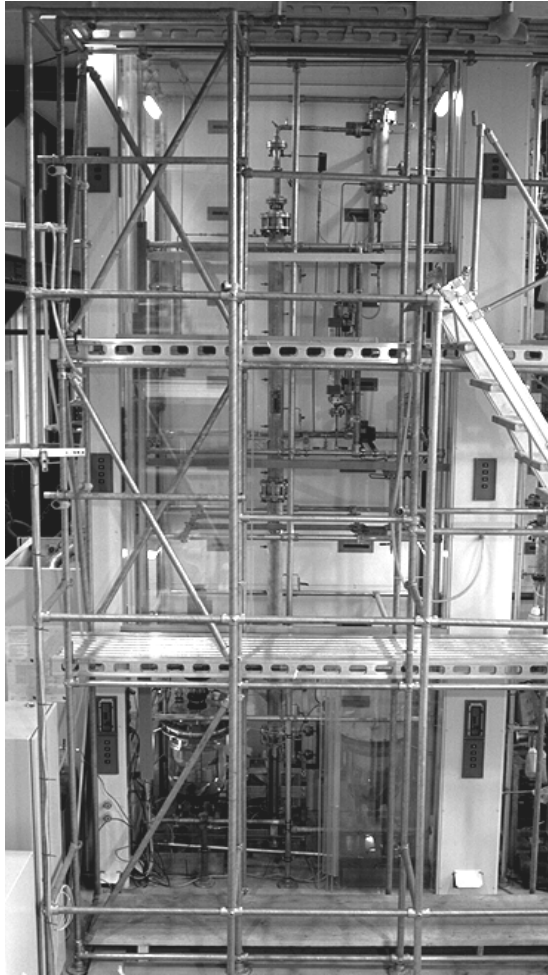
The start up of each distillation column and especially an RD column is a very complex process which is difficult to control. In contrast to distillation without reaction, the off-spec product produced during start up is often difficult to recycle. Also control of a start up

process is very challenging. Almost all process variables change rapidly in value, control variables like heating power, reflux ratio or feed flow have to be switched at least once, but mostly several times to reach the correct steady state. Different start up strategies can yield different, undesired steady states as (*Blagov et al., 2000*) and (*Güttinger, 1998*) show. (*Scenna and Benz, 2003*) describe multiple steady states for different initial conditions as starting point. In these publications, the column does not start from a cold and empty state, but from a defined state, with trays filled, warm and in phase equilibrium. But in order to have consistent and physically sound starting values for a process, it is necessary to simulate the complete start up process. Also, to have a precise prediction of start up time and cost of the start up process, it is crucial to have a model for the complete process. This model needs to be tested experimentally. In this paper at first the pilot plant is presented, where experiments for an RD process have been conducted. Then the developed rigorous model to simulate the start up process of an RD column from the cold and empty state is explained and validated. Different possible start up procedures are presented and applied to five typical RD processes using the rigorous model. The results are compared to derive general statements for an optimal start up strategy.

## 2 Pilot RD Column for Transesterification

For a profound understanding of the dynamic process behaviour during start up as well as for the validation of the model, it is crucial to carry out experiments. Here experimental data has been collected for a transesterification process operated in a pilot plant at the Technical University Berlin (**Fig. 1**). The temperature in the column is measured via PT100 sensors on every second tray, the pressure at top and bottom is documented. The plant also has six liquid sampling stations over the column height. The two feeds can be preheated separately to a defined temperature. The column is completely automated with a Freelance 2000 process control station. All other details are listed in **Tab. 1**. For more construction details please refer to (*Bock, 1998*).

The sample reaction is a transesterification of a fatty methyl ester with isopropanol to isopropylester and methanol. For this transesterification process the differences in boiling points are very high. The considered conditions of this process are as follows: The reaction is homogeneously catalyzed with sulphuric acid, which leaves the column with the bottom product. The catalyst behaves like an inert and is therefore not included in the balances as a separate component. The column has two feed streams, one at the top of the column and one at the bottom. The ester is premixed with catalyst so that it yields 1 mass % of acid in the ester feed. The mixture of acid and ester is then preheated to 80°C and fed to the top tray. The alcohol is prevaporized and then inserted at the bottom tray. This will yield a counter current flow of the educts in the column. With a hold-up of 0.33 l per tray, the residence time of the ester is about 1.8h.



**Fig. 1:** Rd Column at TU Berlin

**Tab. 1:** Pilot plant data

Parameter	Value
Number of Trays	28
Column length [mm]	400
Tray Diameter [mm]	107
Tray Height [mm]	180
Weir Height [mm]	31
Weir Length [mm]	10
Heat Duty [kW]	max. 6
Holdup in Reboiler [l]	5.7
Upper Feed Tray	4
Upper Feed Stream [l/h]	max. 6
Upper Feed Composition	Educt Ester with Catalyst
Lower Feed Tray	27
Lower Feed Stream [l/h]	max. 4
Lower Feed Composition	Educt Alcohol

### 3 Rigorous Start Up Model

For developing suitable guidelines for starting up reactive distillation columns, a rigorous model to simulate the complete start up process from cold and empty state is needed, because it is too cost intensive to conduct several pilot plant experiments before actually starting a reactive distillation column. Therefore a model has been developed and validated for a RD process, which can simulate the complete start up process of reactive distillation columns from the cold and empty state.

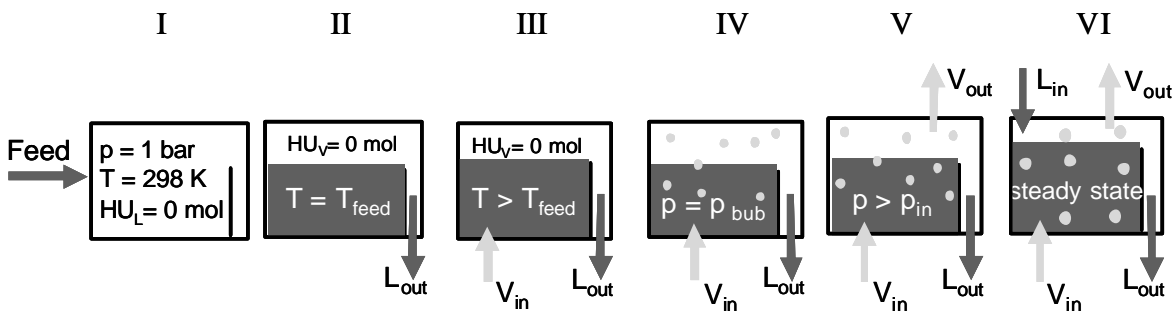
#### 3.1 Model Description

The dynamic behaviour of the trays is described with a rigorous model with the following assumptions:

- ▶ each tray can be modelled as a theoretical stage
- ▶ reaction only in the liquid phase
- ▶ kinetic description of reaction via  $r_A = -k_{forward} \cdot c_A \cdot c_B + k_{back} \cdot c_C \cdot c_D$
- ▶ vapour phase behaves ideal
- ▶ vapour and liquid phase are in thermodynamic equilibrium, when both phases exist
- ▶ column at start up is cold (298 K) and empty (very small liquid hold-up, for computational reason)

To describe the dynamics of the column from a cold and empty state three conditions for switching of equations are considered. These conditions for a change in the equation system are:

- ▶ liquid leaves the tray, if level is higher then weir height (Francis formula). It is assumed that there is no weeping through the tray holes because the holes in the special bubble cap trays are very small, stage II in **Fig. 2**.
- ▶ vapour leaves the tray if pressure on tray is higher than the liquid inlet pressure (tray pressure plus pressure drop through liquid hold-up) on tray above, stage V in **Fig. 2**.
- ▶ phase equilibrium is assumed, if the bubble conditions of the liquid on the tray are reached. Before that, there is no vapour phase present, stage IV in **Fig. 2**.



**Fig. 2:** Different stages during start up of a tray

**Fig. 2** illustrates the different stages of an arbitrary feed tray during the start up process. In stage I, the tray is empty at 1 bar (or any other arbitrary pressure), feed is entering the tray. In stage II, the tray is filled with liquid, temperature is the same as feed temperature (assuming no heat loss), a liquid stream is leaving the tray. If the reboiler is turned on, vapour starts to ascend in the column until in stage III, the vapour from the stage below enters the tray. With this stream the tray is heated up until bubble conditions are reached in stage IV. In this stage, the phase equilibrium equation is activated. Now there is vapour accumulating on the tray until the pressure is higher than on the tray above and a vapour stream is leaving as shown in stage V. If the reflux is entering the column, the trays above the feed tray are filled and in stage VI all entering and leaving streams are greater zero.

In these modelling assumptions, the pressure on the tray, as well as vapour and liquid hold up are integration variables and not fixed to a certain value. The pressure at the column top is fixed at 1 bar for the presented examples, but can also be fixed at any arbitrary value or controlled.

The describing equations besides the energy, mass and component balances are the Francis weir equation for the leaving liquid stream (equation 1) and a pressure drop relation for the leaving vapour stream as in equation 2.

*IF level*  $\geq$  *weirheight* *THEN*

$$F_{out,liq} = length \cdot \left( \frac{(level - weirheight)^{1.5}}{c_{fw}} \right) \mathbf{r}^l \quad (1)$$

*ELSE*

$$F_{out,liq} = 0$$

*IF*  $p_{tray} \geq p_{in}$  *THEN*

$$F_{out,vap} = f(p_{tray} - p_{in}) \quad (2)$$

*ELSE*

$$F_{out,vap} = 0$$

Also the phase equilibrium equations are switched. Equation 3 shows the used replacements for the fill up process.

*IF*  $p_{bub} \geq p_{tray}$  *THEN*

$$y_i \cdot p_{tray} = x_i \cdot g_i \cdot p_i^{vap}$$

$$p_{tray} = p_{bub} = \sum_i x_i \cdot g_i \cdot p_i^{vap}$$

$$V_{tray} = M_{Tot,vap} \cdot v^v + M_{Tot,liq} \cdot v^l \quad (3)$$

*ELSE*

$$y_i = x_i$$

$$p_{tray} = 1 \text{ bar}$$

$$M_{Tot,vap} = 0$$

For a detailed description of the whole model, please consult (Reepmeyer et al., 2003). With the mentioned switches in the describing equations, the DAE system is not smooth, but shows discontinuities that introduce problems with the numerical solution. The integrator step size decreases drastically before an equation switch. Also the variable bounds have to be chosen carefully, as well as the initial conditions. These are for all trays as follows:

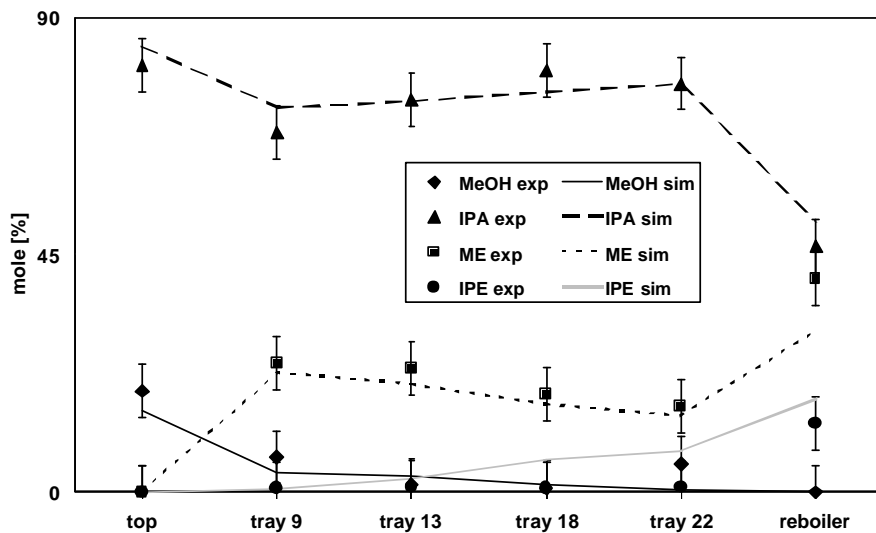
$$\begin{aligned}
 M_{Tot,liq} &= 0.001 \text{ mol} \\
 x_i &= x_{feed} \\
 T &= 298 \text{ K} \\
 p &= 1 \text{ bar}
 \end{aligned}
 \tag{4}$$

The liquid hold up is very small (0.0003% of steady state value, only unequal to zero because of computational reasons) and the initial liquid composition has feed composition, but this is an arbitrary choice. The pressure on all trays is ambient pressure. All calculations have been conducted with the commercial simulation tool gPROMS<sup>®</sup> from PSEnterprise.

### 3.2 Model validation

For the validation of the model, it has been applied to the previously presented transesterification process carried out in the pilot plant. During the start up, the temperature profile has been continuously recorded. Liquid samples have been withdrawn from 4 trays over the column height as well as from top product and reboiler approx. every 40 minutes for dynamic validation. The samples have been analyzed with a gas chromatograph.

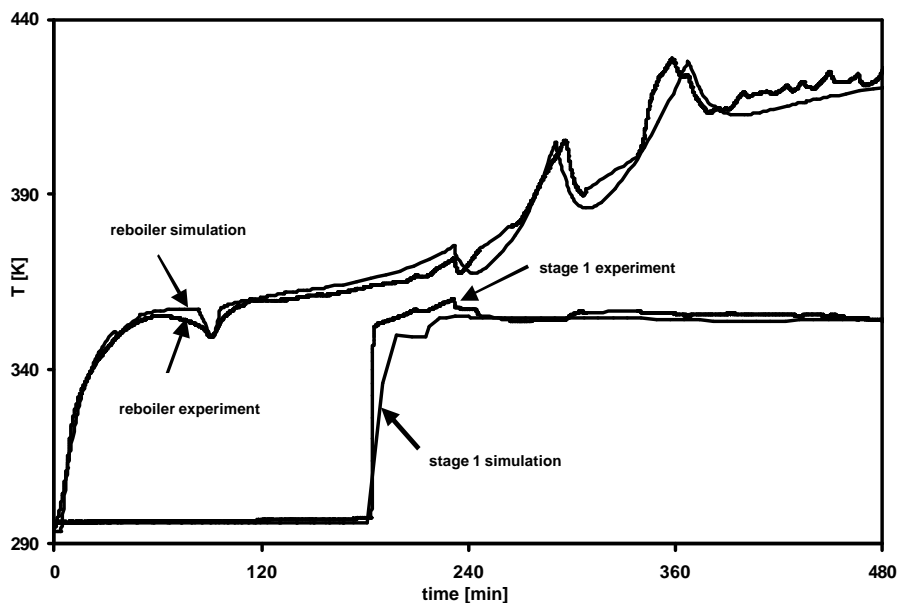
The results of the simulation are then being compared to the measured data from the pilot plant for the final steady state point as well as the dynamic start up profile. At first **Fig. 3** shows the comparison of experimental steady state composition profile and simulated results.



**Fig. 3:** Steady State Model Validation – liquid mol fraction [%] (*Reepmeyer et al., 2004*)

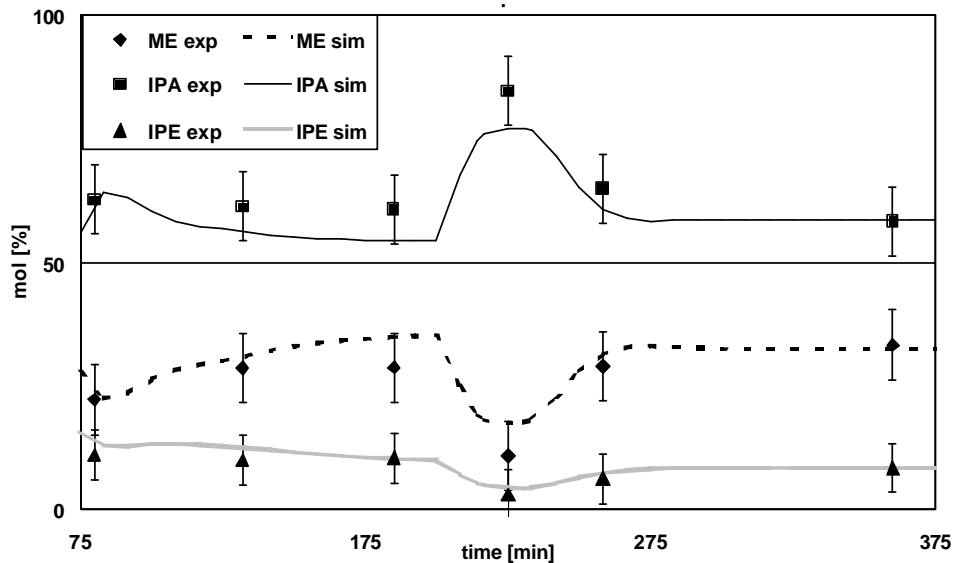
The simulation matches the experiments pretty well in the steady state mode; the highest deviation is about 8 mol% for the reboiler methyl ester concentration. All other values are within 5% precision. For the simulation of the start up process, the exact description of the dynamic behaviour of the RD column is important. **Fig. 4** gives a dynamic temperature profile for experiment and simulation both starting from cold and empty state at

time zero. Due to the manual control of the reboiler heat duty (no PI controller implemented) the experimental curve shows some peaks in the reboiler temperature. In the model this has been taken into account by directly giving the heat duty to the reboiler. The comparison with the simulation results shows that the dynamics and the time constant for vapour flow and reboiler temperature are very well predicted. The first drop in the reboiler temperature profile is the time, where reflux reaches the bottom. The time, where the vapour reaches the condenser is also very well predicted.



**Fig. 4:** Dynamic model validation – temperature start up profile  
(Reepmeyer et al., 2004)

To trust the prediction of a dynamic model, more than else for reactive distillation, it is not just important to match the temperature profile but also the composition profile. **Fig. 5** shows the dynamic experimental data in dots and the simulation data as lines. In this case the manipulated variable has been the reboiler duty. The error bars indicate a 5% error. Here as well a good prediction precision can be stated.



**Fig. 5:** Dynamic Model Validation – Bottom concentration (*Reepmeyer et al., 2004*)

## 4 Column Start Up

In this section, at first start up strategies known from conventional distillation are presented. As will be shown later, these procedures do not show satisfactory results when applied to reactive distillation so that alternative strategies need to be developed.

### 4.1 Conventional Strategies

The start up procedure for distillation columns without reaction has already been examined. (*Kister, 1979*) describes problems with column start ups. (*Doherty and Buzad, 1992*) developed a procedure for generating start up sequences utilizing process knowledge for heat integrated columns. (*Löwe and Wozny, 2001*) developed an optimized strategy for the start up of an energy integrated column system and validated the results. The strategy that is recommended for most of the column start up processes is the total reflux operation (*Kister, 1992*). (*Ruiz et al., 1988*) and (*Fang, 2004*) published various papers on dynamic simulation of distillation columns with this strategy. For the start up process from cold and empty state for reactive distillation, no guidelines or “good practice” advice can be found in the open literature. From distillation without reaction, several strategies are known. The three most common strategies for conventional distillations are:

- ▶ conventional: set all control variables to steady state values and wait
- ▶ total reflux: column is run in loop operation, no distillate removal
- ▶ total distillate removal: exact opposite to before mentioned strategy, column is run without reflux

For an extensive description of the start up strategies for distillation without reaction, please refer to (*Flender, 1999*). The measure for reaching steady state is the so called MX-function in equation 5 developed by (*Yasuoka and Nakanishi, 1982*).



$$MX_{top} = \sum_i (x_{i,actual} - x_{i,steadystate}) \quad (5)$$

The function is the sum of differences between the actual composition in the top product and the steady state composition over all components. If the MX function is permanently below 0.001, the desired steady state is defined to be reached.

## 4.2 Alternative Start Up Strategies

For reactive distillation, new innovative start up strategies have been developed and tested with the validated rigorous model. These are for example:

### Product recycle

During the start up phase, bottom and top product are off specification, they can only be discarded or have to be separated in a further separation step. Therefore it would be helpful to recycle the stream to the column, if the starting up period is not significantly prolonged. For simulation, the bottom product stream is split, and then a part of the stream is mixed with the feed stream and fed to the column. Different schemes have been analyzed:

- ▶ No recycle is the base case with conventional settings of all control variables
- ▶ Split factor = recycle stream / product stream = 1 means, that as much product is recycled as is withdrawn from the column (this is done for a duration of 5000 sec and 10000 sec)

The recycle times are chosen, because it is two times / four times the residence time in the column.

### Initial Charge of Product

As a second alternative, initial charges of product or educt in excess have been tested. Five schemes have been implemented to the rigorous model:

- ▶ Initial charge with feed
- ▶ Initial charge with high boiling liquid feed component in excess
- ▶ Initial charge with low boiling liquid feed component in excess
- ▶ Initial charge with liquid resembling the steady state bottom product and
- ▶ Initial charge with liquid resembling the steady state top product

Initial charge here means liquid hold up up to weir height (no liquid flow leaving the tray) on all trays at 1 bar and ambient temperature of 298K.

## 5 Application to example systems

The different strategies for the start up of reactive distillation columns have been applied to the presented transesterification process (“IPE”) as well as to the following typical RD processes from the literature. For descriptions of the configurations, please refer to the cited papers.

- ▶ “EtAc”: esterification of ethanol and acetic acid to ethyl acetate and water (*Lee and Dudukovic, 1998*)
- ▶ “MTBE”: etherification of methanol and isobutene to MTBE (*Nijhuis et al., 1993*)
- ▶ “EG”: hydration of ethylene oxide and water to ethylene glycol with the side reaction ethylene glycol and ethylene oxide to diethylene glycol (*Ciric and Gu, 1994*)
- ▶ “DMC”: transesterification of ethylene carbonate and methanol to dimethyl carbonate and ethylene glycol (*Fang, 2004*)

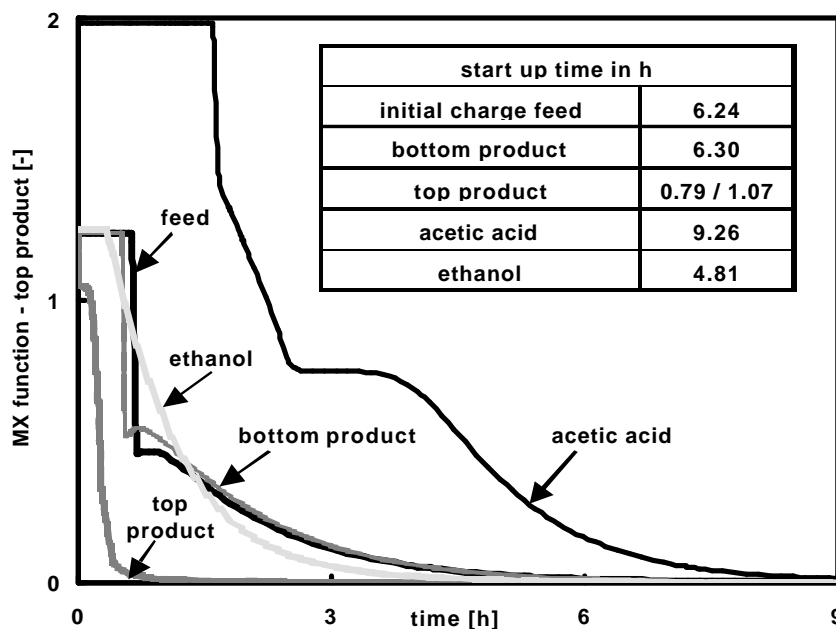
For all the systems the steady state concentration profile from our own simulation with the presented model has first been compared to data in the literature, except for the dimethyl carbonate process for which no appropriate data could be found. Very good agreement could always be stated (for EtAc, please refer to *Reepmeyer et al., 2004*). In the next step, the start up time with the conventional and alternative strategies has been computed with the dynamic model. As an example the results for the ethyl acetate process are presented in **Tab. 2**:

**Tab. 2:** Calculated start up time for ethyl acetate process

strategy	start up time in min	strategy	start up time in min
conventional (base case)	426	initial charge feed	375
total reflux	406	initial charge bottom product	378
total distillate removal	446	initial charge top product	65
recycle bottom product SF=1	447	initial charge acetic acid	556
recycle top product SF=1	547	initial charge ethanol	289

As can be seen, there are no significant savings in start up time, if only the reflux ratio is manipulated. Recycle of a product stream even prolongs the start up time, but it has to be taken into account that in this case, the off-spec product does not have to be

discarded. The best results are achieved with initial charging of product. For these strategies, the dynamic characteristics of the MX-function of the top product are presented in **Fig. 6** (for more detailed results of the product recycle, refer to (Reepmeyer et al., 2004)).



**Fig. 6:** MX function for initial charging – ethyl acetate process (Reepmeyer et al., 2004)

As can be seen from **Fig. 6** the longest start up time is needed if acetic acid (high boiler) is initially charged. Heating up the high boiler takes the longest time because the only heat flow into the column is to the reboiler, so the ascending vapour stream heats the above trays. More energy is lost while vaporizing the high boiler acetic acid. The more low boiler is on the tray (ethanol and top product) the faster the steady state is reached. For initial charge of top product to the column, the start up time can be reduced by 85% from 7.1h to 1.07h (the first number in the table in **Fig. 6** gives the duration for  $MX_{Top}$  being steady state, the second for  $MX_{bottom}$ ). For the ethyl acetate it is therefore useful to keep top product from the last charge to prefeed the column before the next start up.

For all the considered processes, the start up time for the base case (conventional strategy) and the optimal strategy are given in **Tab. 3**. The savings in start up time are highest for the EtAc process; important savings are also achieved for the EG, the MTBE and the DMC process, whereas for the transesterification IPE no significant savings are reached. In the case of the first four systems, initially charging the column with a product or educt leads to the best results. To derivate a general rule for choosing an appropriate start up procedure, the example systems have been classified with two dimensionless numbers, the Damköhler number  $Da$  and the relative volatility of the product component  $\alpha$  given by equation 6.

$$Da = \frac{M_{tot,liq}}{L} k_{ref} \quad (6)$$

$$a_{product} = \frac{p_{product}^{vap}}{p_{lightkey}^{vap}}$$

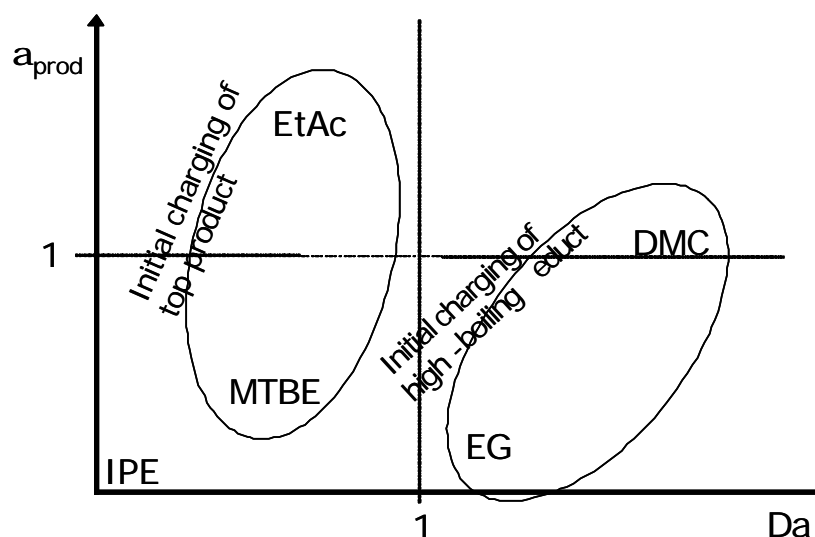
The values are given in **Tab. 3** and are presented as well in **Fig. 7**. Except for the isopropyl ester process, a relation between the Damköhler number and the optimal start up strategy can be found; the relative volatility does not show any influence. This result leads to the following rule of thumb for the start up strategy of reactive distillation processes:

$Da > 1$  – Initial charging of high-boiling educt

$Da < 1$  – Initial charging of top product

**Tab. 3:** Start up times and classifications of the example processes (ini.ch. = initial charging, rec. = recycle)

	EtAc	MTBE	EG	DMC	IPE
start up time base case [min]	426	87	968	151	310
optimized start up time [min]	65	73	599	95	301
savings	85%	16%	38%	37%	3%
optimal strategy	ini. ch. of top product	ini. ch. of top product	ini. ch. of high boiling educt	ini. ch. of high boiling educt	rec. of top product
$a_{Pr\ oduct}$	1.63	0.105	0.004	1	7e-6
Da	0.0367	0.0271	1.2186	1949.3	0.0199



**Fig. 7:** Rough classification of the example systems

## 6 Conclusion

In this paper, a rigorous model to simulate the start up process of a reactive distillation column from the cold and empty state has been presented. The model has been validated using steady state data from the literature as well as own dynamic experimental data from a transesterification process in a 10cm pilot plant column with 28 trays. The steady state as well as the dynamic behaviour of an RD column can be captured very well by the developed model. With this model, different start up strategies have been tested. It has been found that the strategy of total reflux, recommended for conventional distillation without reaction, is not suitable for reactive distillation. New alternative strategies have been developed and applied to five different example systems which are typical for reactive distillation applications (two transesterifications “IPE” and “DMC”, an esterification “EtAc”, an etherification “MTBE” and a hydration “EG”).

With initial charging of light boiling component in the column, the start up time can be reduced significantly. For the ethyl acetate case, initial charging with ethanol in excess gives 32% savings in time and initial charging with top product (ethyl acetate - ethanol mixture) will decrease the start up time by 85%. By classifying the systems and comparing the results computed with the rigorous model, a general rule of thumb for the time optimal start up strategy of a reactive distillation process could be developed, which relates the optimal strategy to the dimensionless Damköhler number.

The presented results were developed for homogeneously catalysed RD in tray columns. For the application of the results to catalytic packing, more investigations focused on packed columns are needed.

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## Nomenclature

$c_A, c_B, c_C, c_D$	concentration of components [mol/m <sup>3</sup> ]
$cfw$	resistance coefficient in Francis formula
$Da$	Damköhler number [-]
$F_{out, liq}, F_{out, vap}$	leaving liquid/vapor stream [mole/sec]
$k_{forward}, k_{back}$	forward and backward frequency factor [m <sup>3</sup> /mol s]
$k_{ref}$	reaction constant forward reaction at 298 K [1/s]
$L$	molar liquid flow from the tray [mol/s]
$M_{tot, liq}, M_{tot, vap}$	complete liquid / vapor hold up on tray [mol]
$MX_{Top}$	MX function for top product stream [-]

$p_i^{vap}, p_{bub}$	vapor pressure for component I / bubble pressure on tray [bar]
$p_{lightkey}^{vap}$	vapor pressure of component with second lowest boiling point [bar]
$\Delta p$	pressure drop between two trays [bar]
$r_A$	reaction rate of A [mol/s]
$T, p_{tray}$	temperature [K] and pressure [bar] on tray
$v^l, v^v$	liquid/vapor volume [m <sup>3</sup> /mol]
$V_{tray}$	complete tray volume [m <sup>3</sup> ]
$x_i, y_i, x_{feed}$	liquid/vapor mole fraction of component I, feed [mol/mol]
$g_i$	activity coefficient for component I [-]
$\rho^l$	liquid density [kg/m <sup>3</sup> ]

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