EXPERIENCE IN REACTIVE DISTILLATION

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ABSTRACT

Reactive and catalytic distillation has attracted growing interest, both in industry and in scientific research. This contribution gives an overview over the simulation tools that are available today and the design methods for reactive distillation that have now been introduced into the industrial practice in a large chemical company. A process synthesis gives good qualitative reference points. Process simulation tools have been developed which are mainly equilibrium-based. However they must be significantly improved in order to apply them for industrial plants. The scale-up from the miniplant used for the development of a new process is well known for conventional distillation, but complicated by several factors for reactive distillation especially in the case of heterogeneous catalysis. For that case the scale-up procedure remains still not solved. To overcome these problems reference plant experience on an industrial scale is necessary. . Other options both for homogeneous and heterogeneous catalysis are possible and will be discussed in the contribution. Attention is drawn to the fact that reaction and distillation does not necessarily have to be performed in a one single column. For slower reactions a broad range of equipment not necessarily containing columns can be used.

INTRODUCTION

Reactive distillation is a key opportunity for improving the structure of a process [1][2]. But the combination of distillation and reactions is possible of course only if the operating windows of both unit operations overlap in a sufficient broad region. That means that the reactions have to allow for reasonable conversion at pressure and temperature lying in the operating window od distillation. In addition the type of the catalysis is important. Homogeneous catalysis is possible in most cases but needs a separation step to purify and recycle the catalyst. This can be avoided in

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heterogeneous catalysis, but here special constructions are necessary to fix the catalyst in the reaction zone. If everything harmonizes, considerable advantages arise as can be seen with reference to Eastman-Kodak Chemicals. For the production of methyl acetate via reactive distillation only one column is needed instead of nine and a reactor, as can be seen in figure 1.

Is this an exception or does it stand for a type of process with a comparable potential for improvement?
The question is

- how processes can be identified that exhibit potential for reactive distillation?
- how such a process can be developed?
- how the equipment can be designed?

Some answers to this question will be offered from the viewpoint of an industrial user. The first question refers to the phase of process synthesis, the second to process development by simulation and experimental validation, and the third to the choice and design of suitable equipment.

The results presented here are not only internal research results but also from joint research in Europe:

In view of the fact that, unlike conventional distillation, there is no integrated development strategy for progressing from the idea to a working process for reactive distillation, several European companies and universities joined forces in 1996 to work on a development strategy for reactive distillation processes under the umbrella of a Brite-Euram project [3]. This first Brite-Euram Project had a duration of 3 years and a budget of about 3,8 million dollars. The key subject areas for this project were process synthesis, process design and experiments using industrially relevant reaction systems and catalyst systems. In the areas of process synthesis and design, computational tools were developed in accordance with the CAPE programming guidelines.

Now a second European project has started [http://www.cpi.umist.ac.uk/intint/]. It is called “Intelligent Column Internals for Reactive Separations” (INTINT) and deals specifically with the design of suitable column internals adopted to the requirements of reaction and distillation. Again, experimental results and simulation tools are the key subjects. The project duration is also 3 years, till 2003, and the budget is comparable to that of the first EU project. Fig. 2. Shows the partners involved in the projects. In both projects the main task of the Universities was to develop methods and software; the task of the industial partners was to run the experiments [4].

In addition, results of internal research at BASF will be reported in terms of the suitable equipment selection.

Process Synthesis

In reactive distillation, the reaction is superimposed by distillative separation. On the one hand, this results in synergistic effects, e.g. in a shift of the chemical equilibrium because of the product removal from the reaction zone On the other hand, exactly these synergies make reactive distillation so extraordinarily complex. It should be borne in mind that today's Eastman-Kodak process was not patented until 60 years after the first MeAc patent [5].

A vital aim of process synthesis is therefore to reduce the complexity of R&D in order to enable simple solutions to be recognized in a short time horizon. In order to analyse systematically processes involving reversible reactions, a comprehensive process synthesis strategy has been developed. One element of this strategy is the analysis of reactive distillation lines. Reactive distillation lines enable the feasibility of reactive distillation processes to be examined simply. The simplification is based on the fact that, according to the Gibbs phase rule (see figure 3), the number of degrees of freedom of a system in physical and chemical equilibrium is reduced by the number of independent equilibrium reactions. Thus, in the case of a liquid-boiling system composed of the three components A, B, C which react according to A + B <=> C, only one concentration has to be defined in order to fix the composition, unlike the case of a system without a reaction where two concentrations have to be defined.

In order to be able to handle these concentration constrains appropriately, various authors have developed transformation methods [6]. These transformation methods enable reactive distillation to be described by a system of equations which is known from conventional distillation. The transformation converts the concentration parameters x and y for the liquid- and gas-phase concentrations into the concentration parameters X and Y, see figure 4.

At the same time, the transformation eliminates the reaction term in the balance equation. The operating line for the rectifying section of a reaction column is formally identical to the operating line of a non-reactive column. An infinite reflux ratio gives an expression which is formally identical to that for calculating conventional distillation lines [7]. Accordingly, we will refer to lines which have been calculated by this procedure as reactive distillation lines. These analogies are found for all the relationships which are important in distillation [8][9].

These analogies become particularly clear if we look at the synthesis of methyl acetate (MeAc) from methanol (MeOH) and acetic acid (HAC) as an example. Essentially, we see diagrams which are similar to the distillation line diagrams of non-reactive systems. As a result of the transformation, the four pure substances lie at the corners of a square and the non-reactive binary systems lie along the edges. The highest boiling point in the system is that of acetic acid, while the lowest boiling point is displayed by the MeOH/MeAc azeotrope (figure 5). The reactive distillation line diagram makes it possible to determine the product regions of a reactive distillation for infinite reflux. Analogously to conventional distillation, the top and bottom products have to lie on a reactive distillation line and on the balance line. It can be seen that the desired products, namely MeAc and water, do not lie in the product region.

But by analogy with extractive distillation, it can be expected that a second feed point would drastically widen the product region at a finite reflux ratio and thus also increase the conversion. Between the two feed points, the column profile is perpendicular to the distillation lines (figure 6). Since this effect results from the finite reflux ratio, we can expect the product purity and conversion to increase with an increase of the reflux ratio and then slowly to decrease again. The limiting value which is established for an infinite reflux ratio is determined by the azeotrope concentration in the methyl acetate/methanol system.

Our calculations using an equilibrium stage model agreed well with the experiments based on separation performance measurements using catalytic rings as internals (figure 7). On the basis of these results, we have to contradict various publications which attribute the decrease the reaction-kinetic effects. The primary effect is the saddle-point character of the products and the related choice of a second feed point. The options for calculation and especially interpretation of reactive distillation lines which have merely been outlined here are implemented in the program SYNTHESISER, a software product from the first EU-project.

Process design and optimization

While process synthesis gives good qualitative reference points, for industrial implementation we need quantitative results which are as exact as possible. The development of a program called DESIGNER [10] to simulate reactive rectification was therefore a further major focus of the first EU project.

Ar first, process synthesis is used to determine whether a reactive distillation is feasible and, if so, the configuration required (second feed point, combination of reactive and nonreactive zones) is found. This provides first initial guesses and thus a good starting point for deriving a first approximation of process design using the stage model. The results from the stage model in turn give good initial values for subsequent refinement using the mass transfer model.

After the introductory estimate, a first profile can be determined by the relaxation method which gives initial values sufficiently good for the subsequent use of a rigorous method of solution (figure 8). Figure 9 shows an example of process simulation using the mass transfer model and kinetic data for the reaction. The simulation and experiment results are shown for the synthesis of MTBE from isobutene and methanol. This is an example of a reaction in which the number of moles of products is different from the number of moles of reactants. The heat of reaction is of the same order of magnitude as the molar heat of vaporization of the participating components. It can be seen that computational results and the experimental points fit well.

This process simulator is a result of the first European project and has not (yet) been commercialised. However there are simulation programs on the market that do the same job at least to some extent with a comparable accuracy. Some of the major companies have developed their own tools suitable for reactive distillation simulation. It is an open question if a rate-based approach as Designer is really necessary. In some cases reactive distillation can be simulated sufficiently accurate using an equilibrium stage model.

Limitations of the methods for synthesis and design, THE SCALE-UP PROBLEM

Up to now, it has been shown what can be achieved using the tools and methods developed in the last few years and especially in the first EU project. A question which is at least as interesting is what are the challanges. In this context, attention should be focused on the reactive distillation with main and secondary reactions e.g a simple esterification, see figure 10. For such a reaction system, it is frequently the case, for time and cost reasons, that a complete kinetic model cannot be developed.

It may have practically no consequences if the process development chemist or engineer lacks an understanding of the secondary reactions on the basis of standard kinetic studies, since they frequently play hardly any role, as long as the distillation does not continuously shift the equilibrium. However, the careful process engineer will carry out experiments in a reaction column to verify the achievable purities and yields. And in that moment he can discover the inefficiency of (not) scale-up procedures. The reason is that in all experiments, reaction and mass transfer interact with one another. This interaction can be explained with reference to the main reaction, see figure 11. If a separation process is superimposed on this reaction, the products water and ester (as an example, not valid for every ester) are separated off as low and high boilers respectively. However, the removal of the product accelerates the forward reaction changing conversion and possibly selectivity. We would like to refer to the separartion efficiency in a reaction column using the term separation performance and the efficiency to convert the educts using the term reactor performance.

If a development engineer has to design an industrial column only on the basis of miniplant experiments, he has to maintain not only the separation performance but also the ratio of separation performance/reactor performance so that main and secondary reactions proceed to a comparable extent in the industrial-scale reaction column. One way in which this can be achieved is in terms of construction by separating reaction and product separation from one another both in miniplant tests and on an industrial scale. This is possible, for example, when the reaction is carried out in the presence of a heterogeneous catalyst in the downcomer or with side reactors at the column. An alternative is to use a structured packing with well defined paths for the liquid flow. Here the problem has not yet beed solved, the main reason being the lack of reference columns on an industrial scale.

The way we see is either

- to develop scale-up methods or
- to carry out reactive distillation experiments on an industrial scale.

The latter possibility, which represents a step back into the process engineering stone age in the design of columns, will in many cases mean the end of the line for reactive distillation, since a company will only seldom be prepared, for time and cost reasons, to build integrated experimental plants on an industrial or semi-industrial scale. So developing an appropriate scale-up procedure for reactive column internals is a key task. The second European project („INTINT“) will hopefully provide some contributions.

Choice of equipment

Up to now it was assumed that reaction and distillation can favourably be combined in a column; in a normal distillation column in the case of homogeneous catalysis and in a column with special internals or an additional exterior volume in the case of heterogeneous catalysis. This was discussed in the previous chapter under the aspect of scale-up in connection with separation and reaction perfomance. However columns are an appropriate solution only for reactions that are so fast as to achieve considerable conversions in the residence time range of such columns. The question is whether the full potential for combining reaction and distillation can be found and industrially implemented using columns only.

At BASF, there has been some research on this point in the last couple of years, and the results will be included in the following chapters [11]. For reasons of simplicity the focus will be on equilibrium reactions where the advantages of combining reactions and distillation are obvious. The aspects influencing the choice of the equipment will become particularly clear.

In simple equilibrium reactions, the reaction equation can be described like this:

$$A_1 + A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_3 + A_4 \tag{1}$$

The rate constants for the forward and the reverse reaction may be different. The equilibrium state (when the reaction velocity goes to zero) is described by the law of mass action:

$$\frac{c_3^* \; c_4^*}{c_1^* \; c_2^*} = \frac{k_1}{k_{-1}} = K_c \tag{2}$$

The conversion of the stoichiometrically limiting reactant, for example component 1, in the equlibrium state is:

$$U_1^* = 1 - \frac{\dot{V} \; c_3^* \, c_4^*}{\dot{V}_0 \, c_1^* \, c_2^* \, K_c} \tag{3}$$

The indices o indicate the initial state, the indices * the final state, i.e. the equilibrium state. This last equation was developed using some additional simple balance equations.

The equation shows, that the most efficient way of enhancing the conversion is to reduce the concentration of one of the reaction products. That is the principle of superimposing a distillation on a reaction - the theme of this contribution. In the equation the volume effect of a superimposed distillation has been taken into account.
Fig. 12 (equilibrium lines) is a graphical representation of the equation above that shows more clearly the possibilities of such a combination: The fractional conversion of component 1 approaches 1 only if the concentration of one reaction product is significantly reduced. This holds true even for extremely unfavourable equilibrium constants. If, for example, the equilibrium constant is 0.01, at the equilibrium state only 1 % of component 1 has been converted. However if component 3 is removed to x = 0.0001 mole/mole, conversion of more than 90 % is possible for component 1.

The real conversion may be defined in analogy to an equilibrium conversion but without the equilibrium values:

$$U_1 = \frac{n_1^0 - n_1}{n_1^0} \tag{4}$$

The reaction velocity of reactant 1 can, in most cases, be described by the simple equation

$$\tau = k_1 c_1 c_2 - k_{-1} c_3 c_4 \tag{5}$$

Assuming stoichiometric input, with the volume correction term taking into account the distillation and with some simple balance equations, the equations above can be rearranged in the following way

$$U_1 = \tau \frac{k_1 c_1 c_2 - k_{-1} c_3 c_4}{c_1^0} \tag{6}$$

Hence the real conversion is increased if the reverse reaction is suppressed by removing one of the reaction products, for example by decreasing the concentration of component 3. The real conversion is also influenced by the residence time τ or by the product τk . This can be seen in figure 12, kinetic line. It is obvious that the suppression of the reverse reaction influences conversion only up to a certain limit. A further drop in the concentration of the reaction product does not increase the conversion. The contribution of the reverse reaction has become so low that the conversion depends on the forward reaction rate only which is a function of the residence time τ and of the reaction constant k.

Thus two operating conditions can be distinguished:

- The range in which the conversion is influenced mainly by the concentration of the component to be separated; this range is called "controlled by distillation".
- The range in which the conversion is influenced mainly by the residence time and the reaction constant; this range is called "controlled by kinetics"

Industrial process design should aim at operating conditions within these two ranges: just the sufficient residence time and only the necessary expenditure for the distillation.

So we have a second scale-up problem: What is the suitable equipment for complying with these demands? That means more precisely: How can the reactor performance be reached over a broad range of reaction velocities? As preparation for discussion on this question, an alternative configuration is considered (figure 13): A reaction can be run within a column – that normally is understood as reactive distillation – but can also be run in an outside reactor with a pump recycle. Such a sequential arrangement exhibits the same conversion as the simultaneity of reaction and separation as can be seen from figure 14, where a reactor with pump recycle system and a reactive distillation configuration are compared.

So different equipment may be chosen to combine reaction and distillation within the limiting conditions of reaction velocity, relative volatility and catalytic mechanism as is indicated in figure 15.

Equipment in question are

- stirred vessels,
- cascades of stirred vessels, both with or without columns,
- reaction columns.

Additional volume can be provided for all of them, examples are listed in figure 16.

The next considerations concentrate on homogeneous catalysis. Similar considerations apply to heterogeneous catalysis, and this will be commented on later.
At first, a slow reaction is considered. "Slow" means, that the reaction time is slow, compared with the residence times typical for separation equipment such as distillation trays. For residence time reasons a stirred vessel or, better, a cascade of stirred vessels is needed. Each vessel is supplied with energy to evaporate the component to be separated. If the relative volatility of this component is very high, a one stage evaporation is sufficient. At a lower relative volatility the separation requires more stages, i.e. a column has to be put on top of the vessel. If the separation is even more difficult, a stripping section must be added to the column and a reboiler is necessary. In the limiting case of a very low relative volatility, each stage of the cascade can be operated as a countercurrent stage. The first stage is additionally provided with a fractionating column to enrich the component to be separated. Such a setup is equivalent to a reaction column with a large holdup on each reaction stage.

Fast reactions do not demand long residence times, „fast“ meaning that the reaction reaches equilibrium in the residence time range that is typical for column internals. The equipment therefore may be selected under the aspect of separation efficiency . If the relative volatility of the component to be removed is low, a considerable number of stages is necessary. The only appropriate equipment is a column. Depending on the required residence time it may be a packed or a tray column. A relative volatility in the medium range allows the number of stages to be reduced, though the total hold up has to be kept constant. A tray column, perhaps with special bubble cap trays is possible. At a certain (low) relative volatility the number of stages necessary to influence the reaction in a desired way becomes so small and consequently the volume per stage becomes so large that a small reactor with a superimposed column or even a reactor with an evaporator can be used.
In the range of medium reaction velocities, mixed constructions are the ideal solution, for example special column trays with large holdup or reactor cascades with a column on the first stage only.
The resulting principles for the choice of equipment for homogeneous catalysis are presented in figure 17.

As mentioned earlier, heterogeneous catalysis can be treated in a similar manner: Additional, separate reaction volumes are necessary to retain the catalyst. These volumes can be arranged either within the equipment or in a side position [12], coupled by recycle systems. Figure 18 lists the equipment alternatives for heterogeneous catalysis [13]. As in the case of homogeneous catalysis, principles for the choice of equipment may be formulated. Some, not all of the possibilities are shown in fig. 19 [14]-17].

After the choice of the equipment, which is in principle determined by the reaction velocity and the relative volatility the next step follows: the proper design of the chosen equipment under the special conditions of the process. Only if this step is done with care will the advantage of the proper choice of equipment - the optimum in energy consumption - be realized.

SOME REMARKS ON THE ROLE OF CATALYSIS

Catalysis can be autocatalytic, homogeneous or heterogeneous. This is of course also true for reactive distillation.

In the case of autocatalytic reactions the reaction velocity can only be influenced by the reaction temperature, in other words for reactive distillation by the pressure of the equipment.

Homogeneous catalysis allows the reaction velocity to be influenced by changing the catalyst concentration. Thus the reaction velocity can be adapted over a wide range to the needs of the distillation equipment.

Heterogeneous catalysis requires a construction to fix the catalytic particles in the reaction zone. This may cause construction and operation problems and is in addition a limiting factor to the catalyst concentration that can be achieved. The reaction velocity can be enhanced only to the limit set by the attainable concentration range. Furthermore the possibility of enhancing the reaction velocity by a higher temperature or pressure of the equipment is limited, because in general the catalyst consists of ion exchanger particles, whose temperature range is limited.

So, homogeneous catalysis is much more flexible but has its price in an additional separation step necessary for the catalyst recycle and by demands for expensive materials in the case of mineral acids. Heterogeneous catalysis is simpler in principle, but technical problems have to be solved. In general the equipment will need more volume, for example the columns must have a bigger diameter. It should be clear from these considerations that a single case decision is needed for every individual design.

CONCLUSIONS

In the case of conventional distillation, a sufficient knowledge has, thanks to intensive development, been gathered to enable the efficient process synthesis, design and scale-up to be solved quickly in many cases [18]. For reactive distillation, the methods of design and synthesis have been developed to a considerable extent, partly with the aid of the many analogies to distillation. A major focus of research and development in future years should be the scale-up of reaction columns. This is where great deficiencies still lie, see figure 20. In addition the methodology to choose the best equipment will have to be improved. In the expert community, only columns are often seen as a possible choice. Work will have to be done to ensure that the benefit of combining reaction and distillation can be enjoyed to the full by employing the most suitable equipment.

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Symbols Used

A_i		component i
c_i	kmole/m^3	component concentration
k_1	m^3/kmole h	rate constant of the forward reaction
k_{-1}	m^3/kmole h	rate constant of the reverse reaction
K_c		equilibrium constant
U_i		fractional conversion of component i
V	m^3	volume
$\dot{V}$	m^3/h	volumetric flow rate
ν_i		stoichiometric factor
τ	h	residence time

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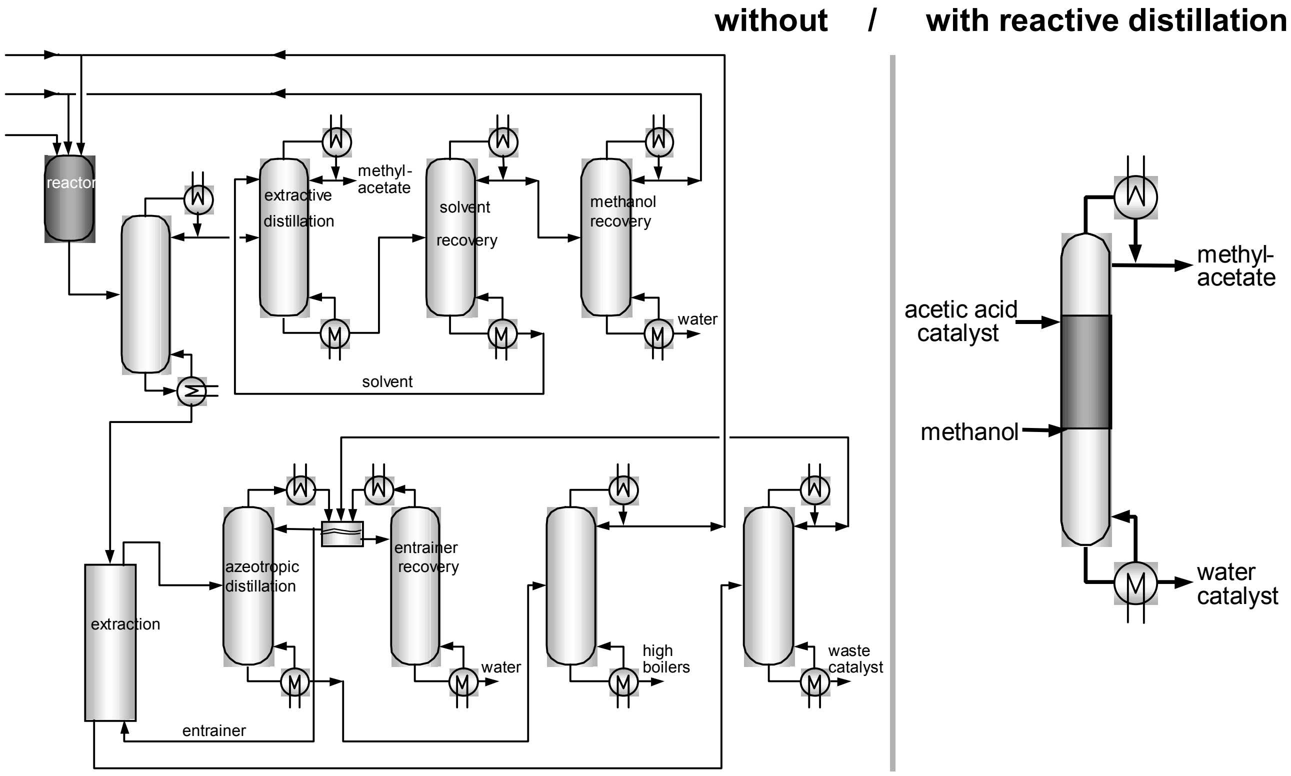


Fig. 1 Eastman Kodak process for methyl acetate

Universities and research institutes
Bath (UK), Clausthal (D), Dortmund (D), Delft (NL), ICSO (PL), IIC (PL), Helsinki (FIN), Lappeenranta (FIN), Moscow (RU), Plock (PL), Stuttgart (D), UMIST(UK)
Industry
AEA (UK), Axiva (D), BASF AG (D), BP Chemicals (UK), DSM (NL), Julius Montz (D), Neste Oy (FIN), PETROM (RO), Snamprogetti (I), Sulzer AG (CH)

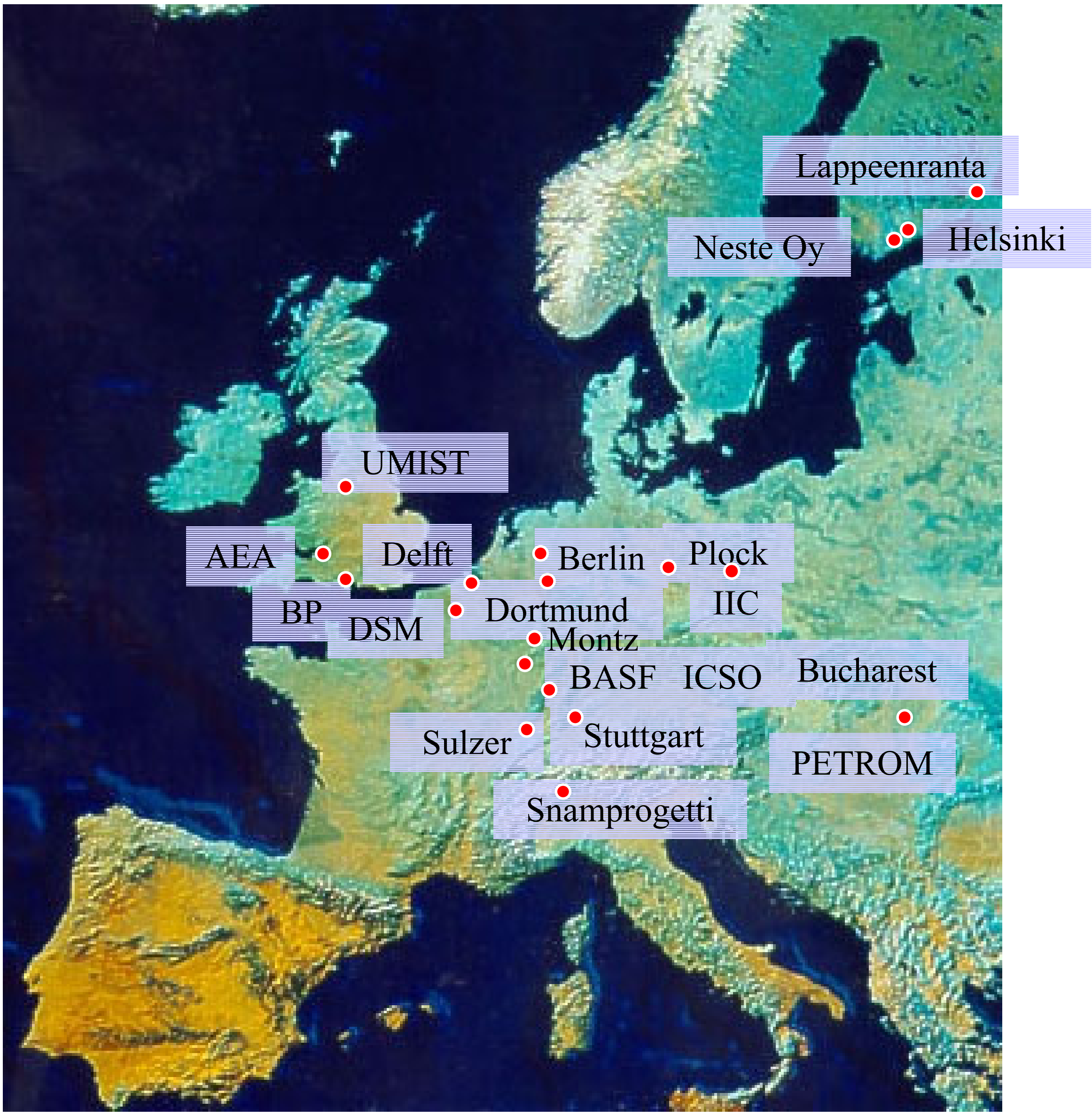
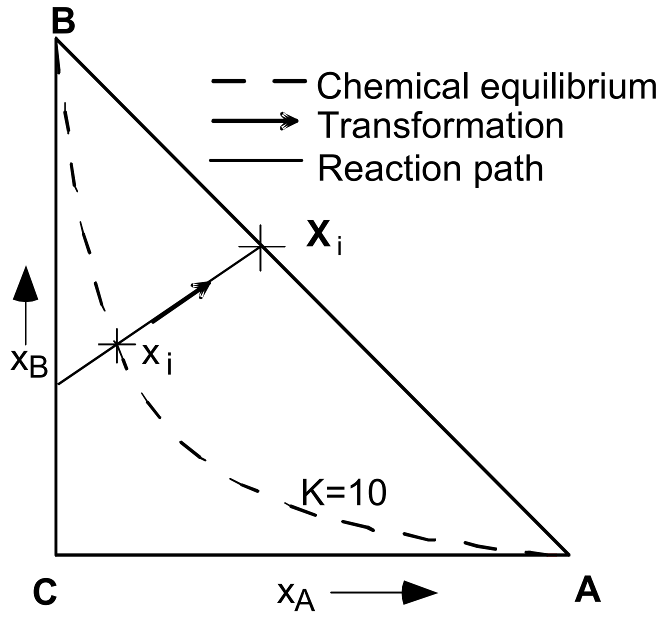


Fig.2 cooperation partners in the European research projects on reactive distillation

transformation of variables for the system A + B ↔ C

- **Gibbs phase rule: F = C – Ph – R + 2**



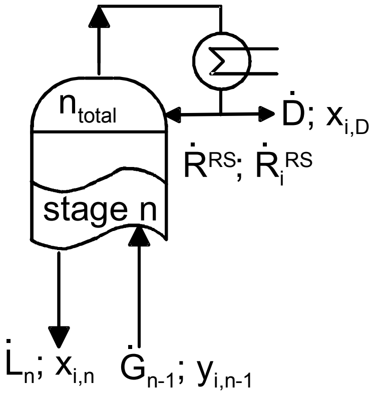
$$\sum_{i=1}^{nc} \nu_i A_i = 0$$

$$X_i = \frac{x_i - \frac{\nu_i x_P}{\nu_P}}{1 - \frac{\nu_T x_P}{\nu_P}}$$

$$Y_i = \frac{y_i - \frac{\nu_i y_P}{\nu_P}}{1 - \frac{\nu_T y_P}{\nu_P}}$$

Fig. 3 applying Gibbs rule

Balance: Rectifying operating line of a RD column



$$\dot G_{n-1} = \dot D + \dot L_n - \dot R^{RS}$$

$$\dot G_{n-1} y_{i,n-1} = \dot D x_{i,D} + \dot L_n x_{i,n} - \dot R_i^{RS}$$

$$\overline{G_{n-1}} = \overline{L_n} + \overline{D}$$

$$\overline{G_{n-1}} Y_{i,n-1} = \overline{L}_n X_{i,n} + \overline{D} X_{i,D}$$

$$Y_{i,n-1} = \frac{v_n}{v_n + 1} X_{i,n} + \frac{1}{v_n + 1} X_{i,D}$$

$$v \rightarrow \infty \quad ; Y_{i,n-1} = X_{i,n}$$

Fig.4 transformed variables

Reactive distillation lines: HAC + MeOH ↔ MeAc + H2O

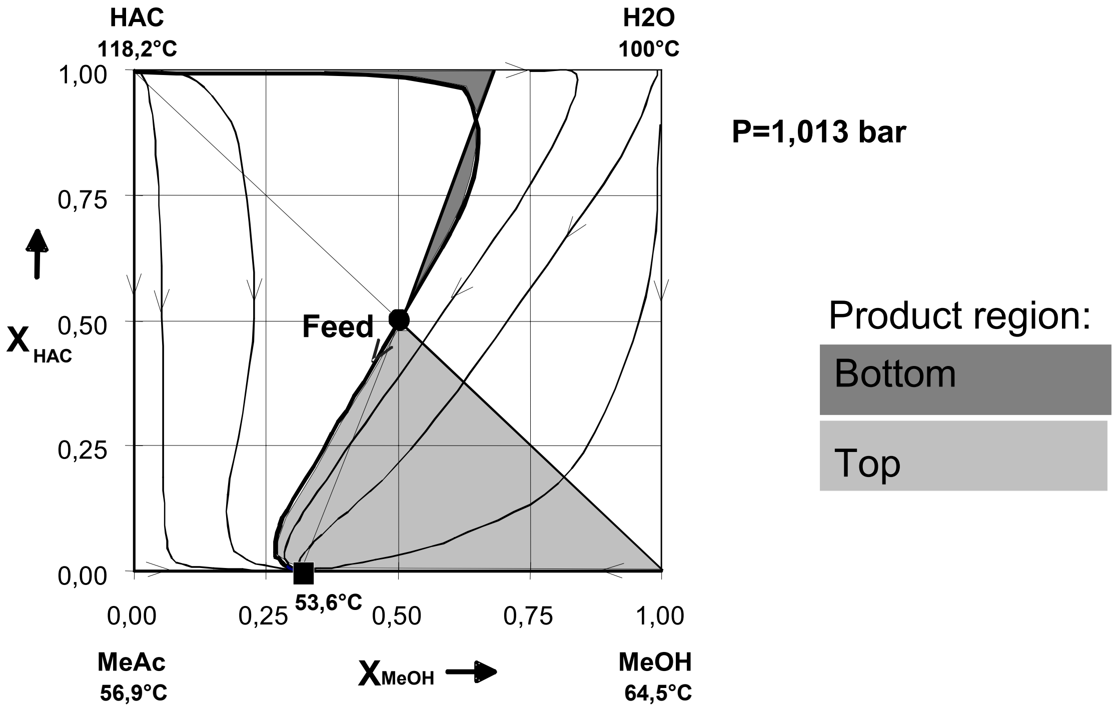


Fig. 5 reactive distillation lines, one feed

Production of methyl acetate with catalytic distillation

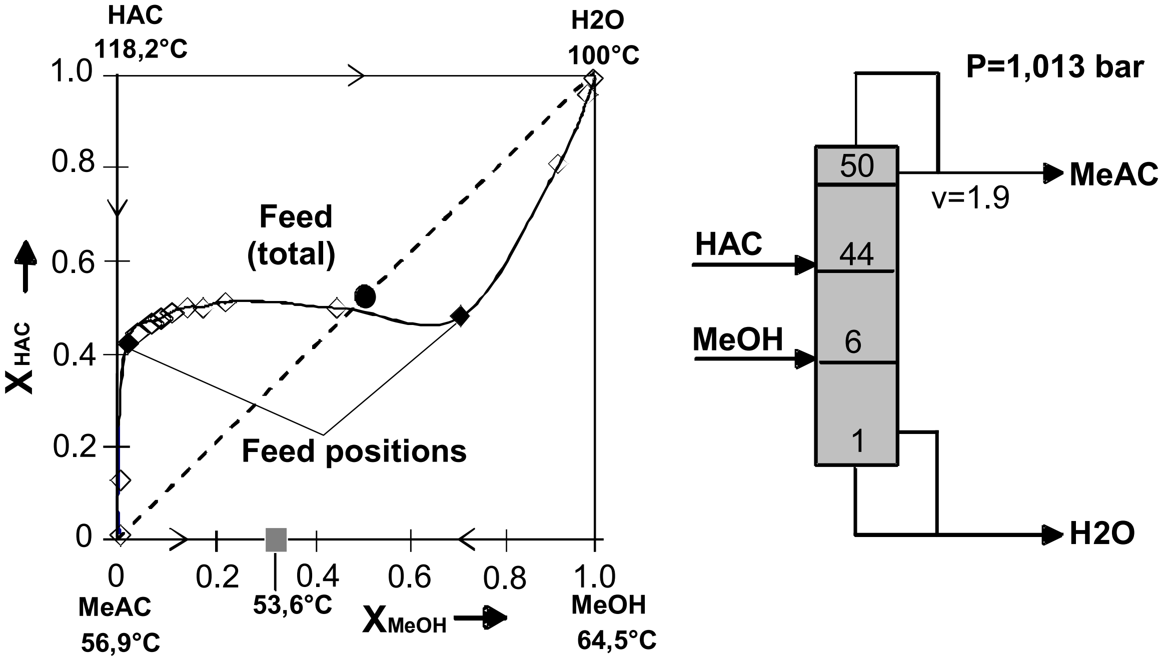


Fig. 6 reactive distillation lines, two feeds

Comparison: Simulation / Experiment

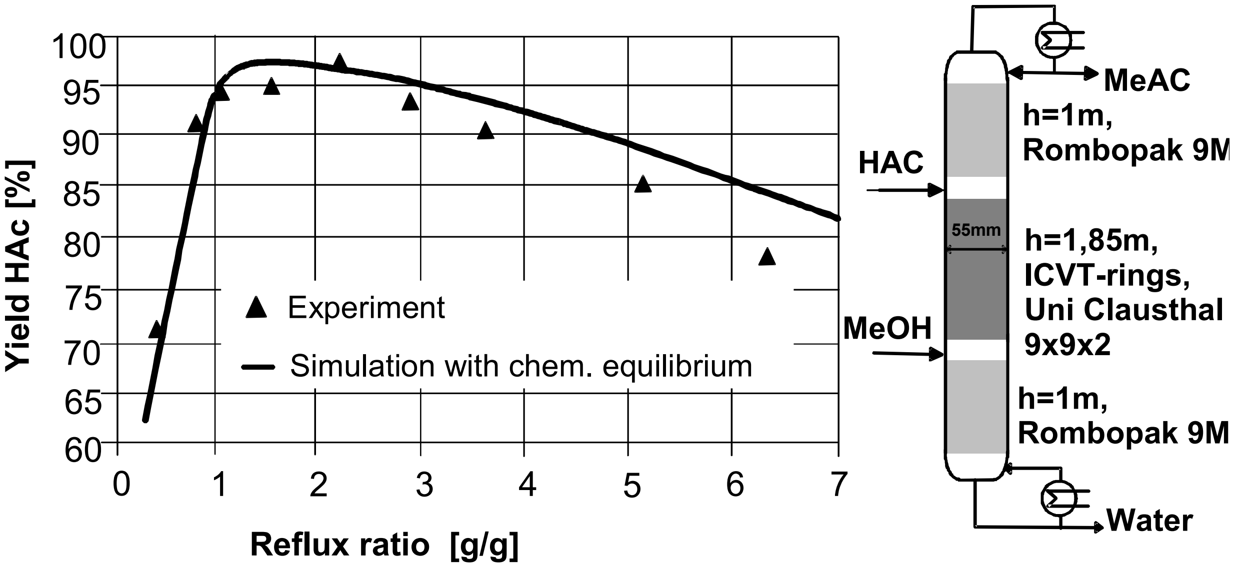


Fig. 7 comparison simulation – experiment for an equilibrium stage model

convergence with DESIGNER

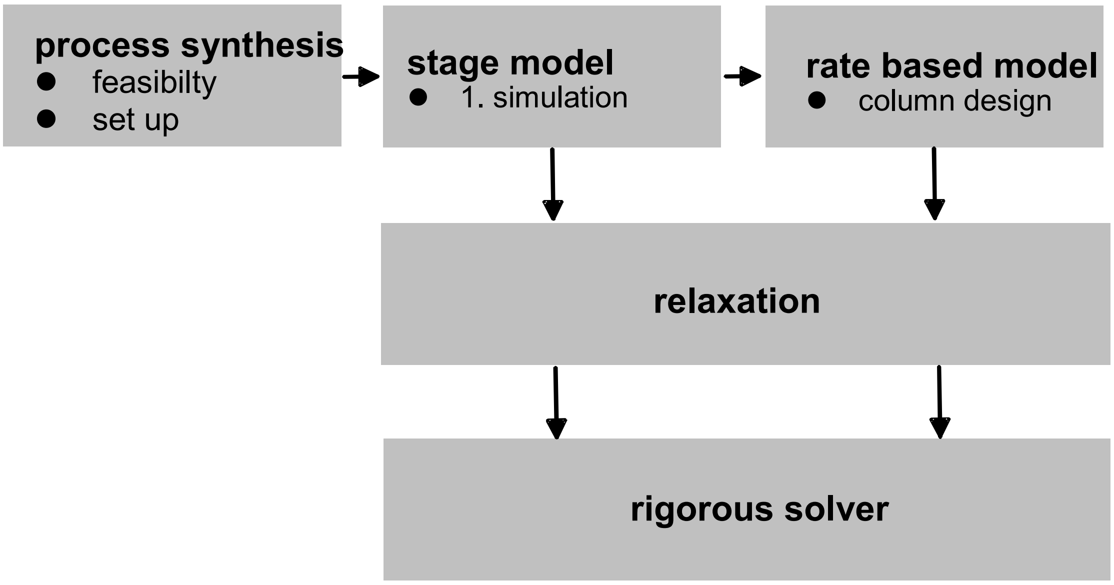
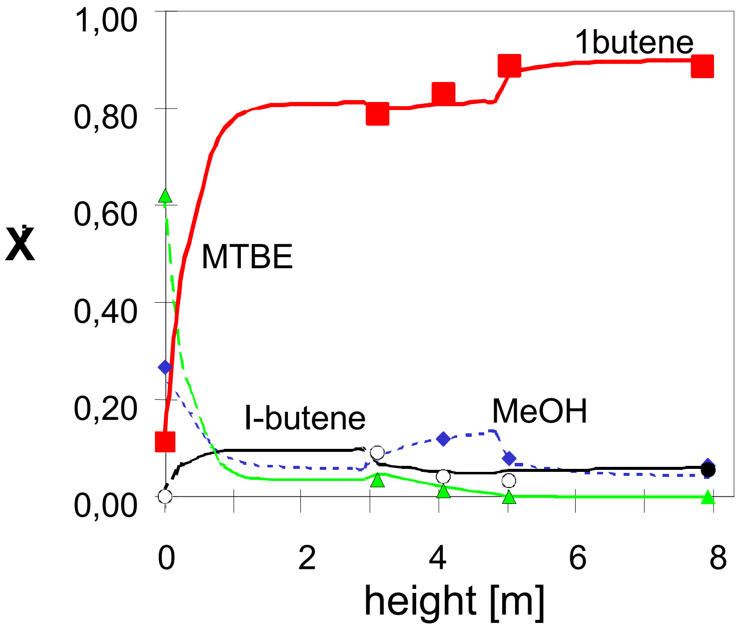


Fig. 8 methods of convergence

DESIGNER: comparison experiment/simulation

- simulation of the University Helsinki/[9]
- experiments with cat. rings of the University Clausthal



IB+MeOH⇆MTBE
Δh_R=-35kJ/mol

Fig 9 comparison experiment/simulation

1. alkohole + acid ⇄ ester + water
2. 2 alkohols ⇄ ether + water
3. alkohole ⇄ alkene + water
4. ester ⇄ acid + alkene
5. ....
6. ....

Fig. 10 esterification, main and side reactions

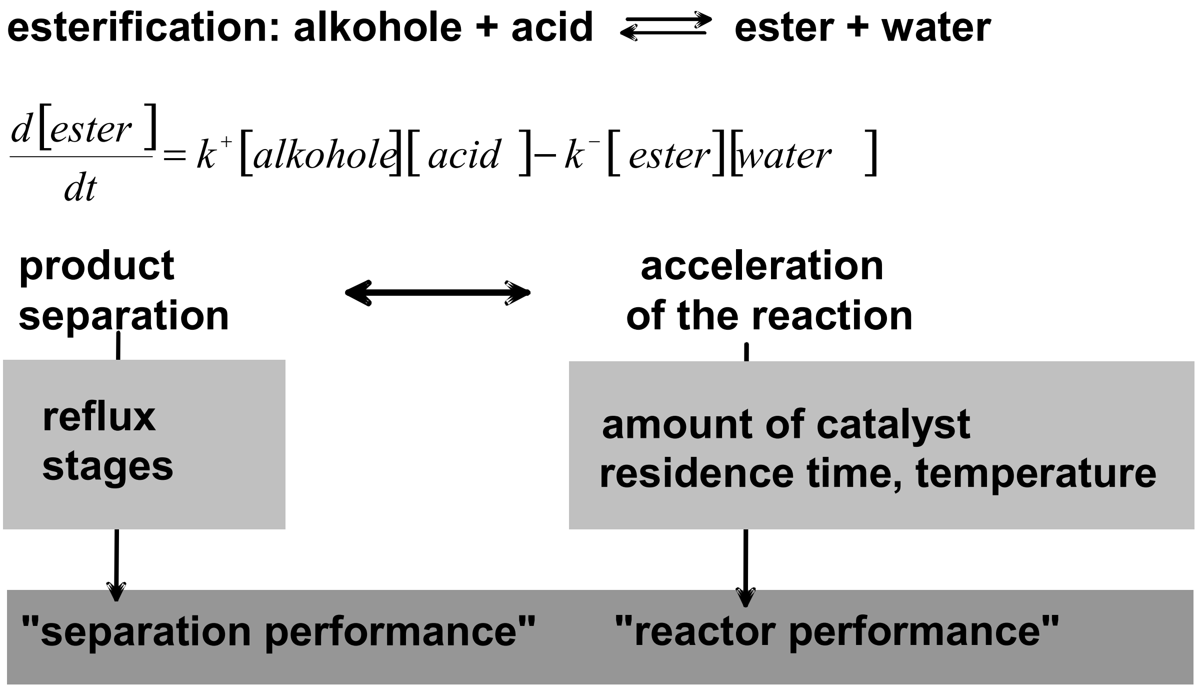


Fig. 11 interaction between reaction and separation

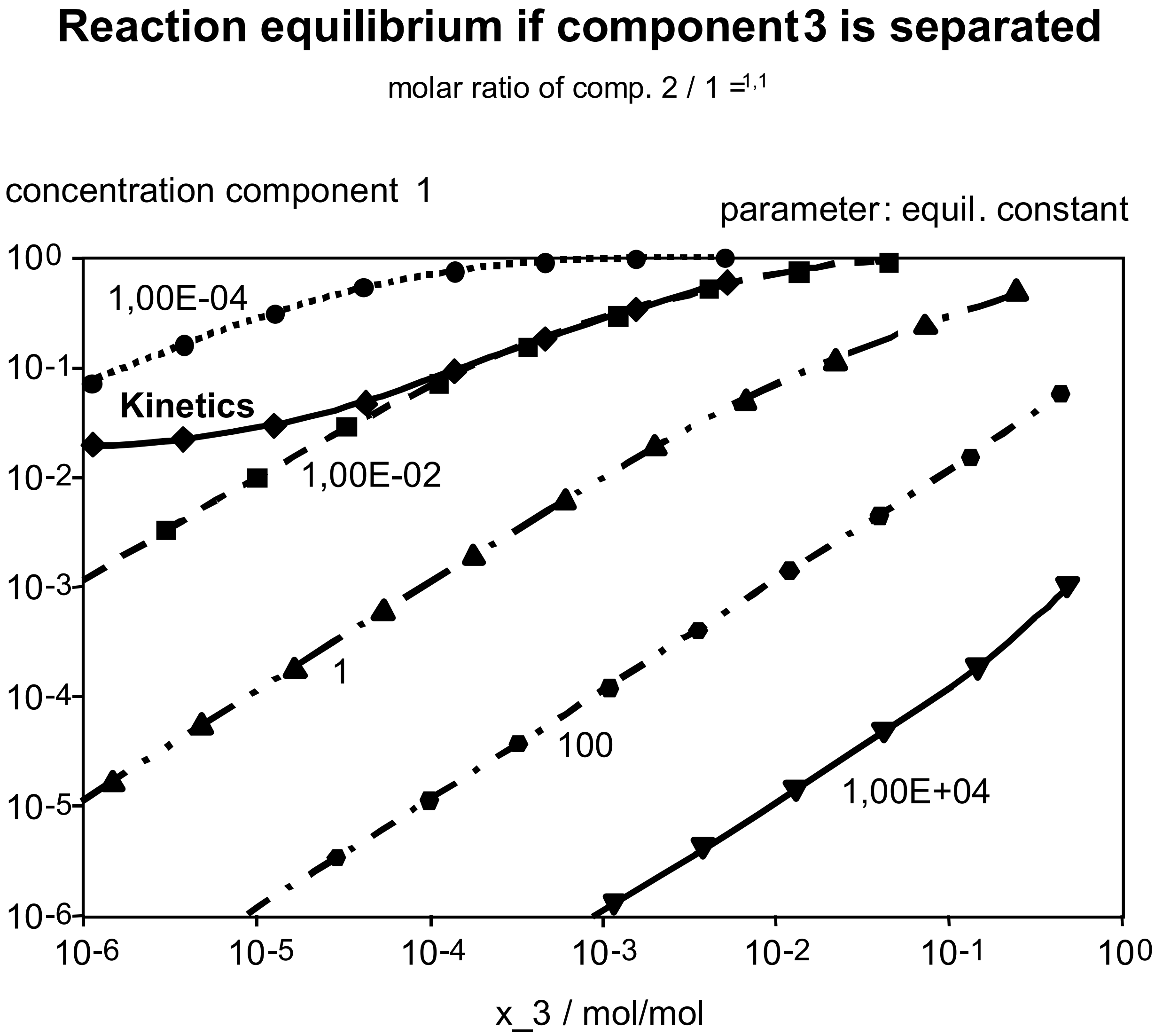
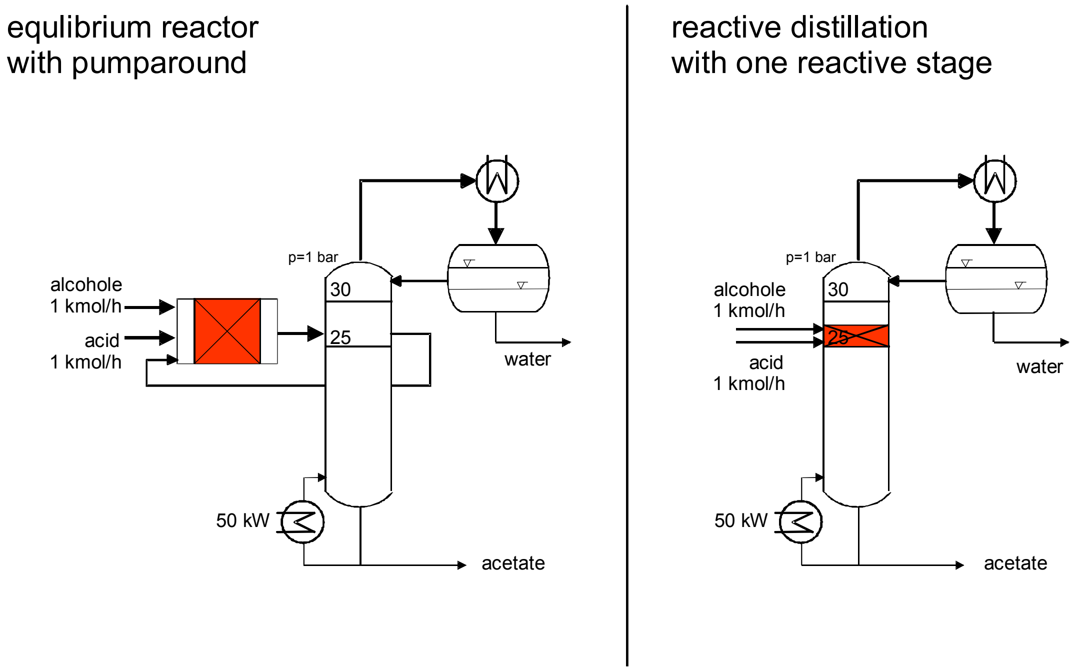


Fig. 12 equilibrium lines and kinetic line

reactive distillation (esterification)


equlibrium reactor
with pumparound

reactive distillation
with one reactive stage

Fig. 13 alternative configurations: reactive internals or side reactor

Reactive distillation for acetate synthesis:

reactor with pumparound vs. reactive distillation

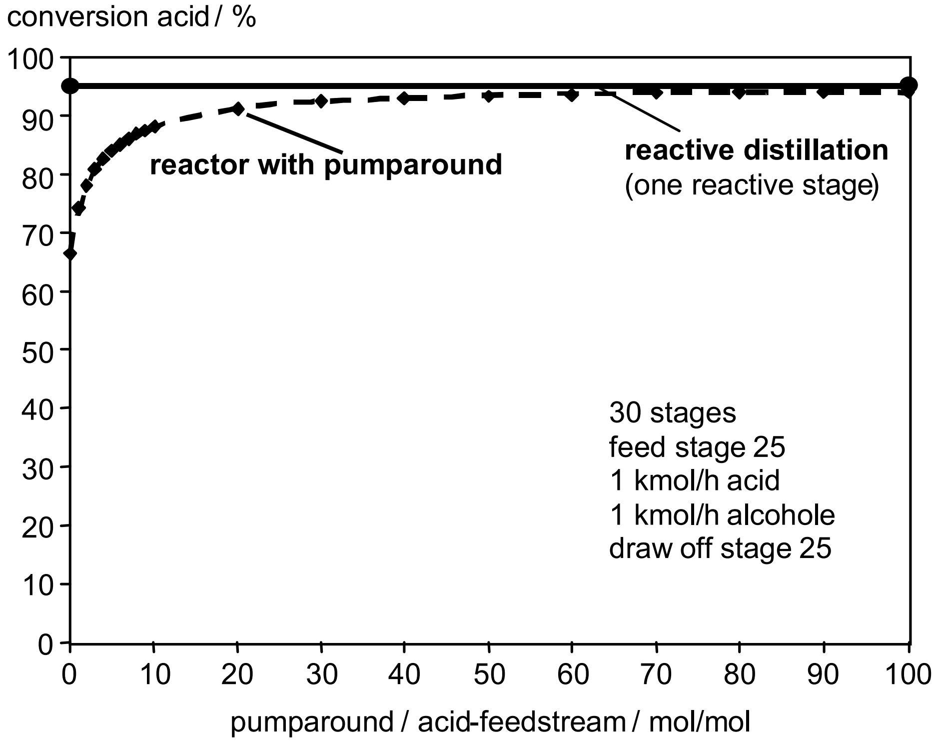


Fig. 14 comparison reactor with pumparound /reactive distillation

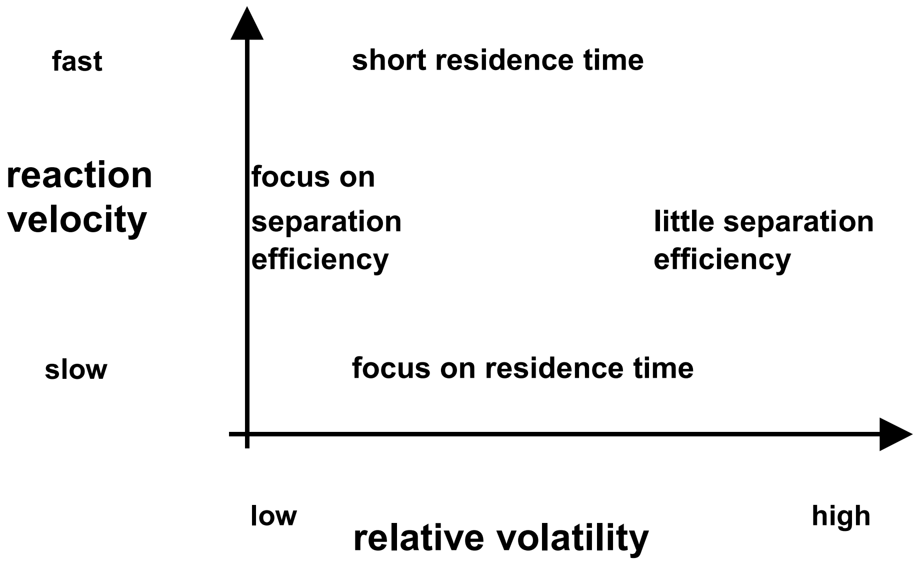


Fig. 15 design with respect to residence time and relative volatility

homogeneous catalysis

- rectification column
- column with larger volume in the bottom
- stirred vessel with rectifying column
- strirred vessel with full column
- vessel cascade with column
- strirred vessel with evaporator
- evaporator
- ....

Fig. 16 equipment suitable for combining reaction and distillation (homogeneous catalysis)

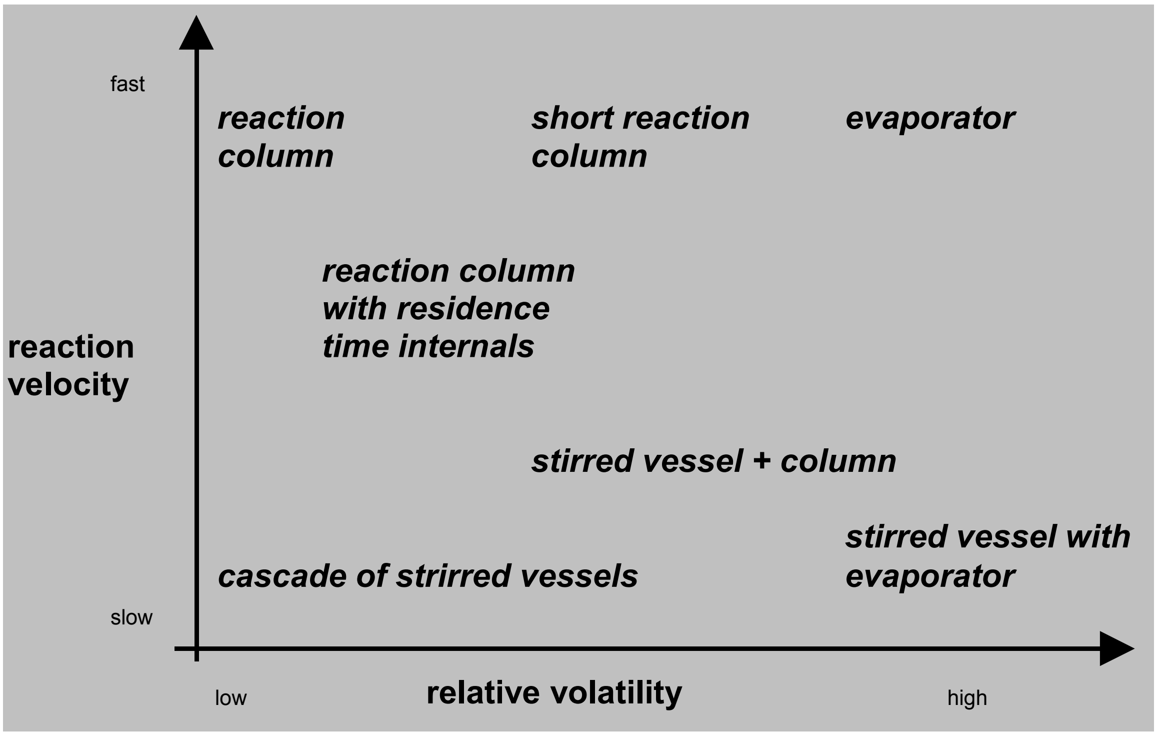


Fig. 17 principles of the selection of equipment (homogeneous catalysis)

heterogeneous catalysis

- rectification column with catalytic packings
- rectification column with catalytic internals in the downcomers
- rectification column with side stream reactors
- column and reactor with pumparound
- evaporator and reactor with pumparound
- ......

Fig. 18 equipment suitable for combining reaction and distillation (heterogeneous catalysis)

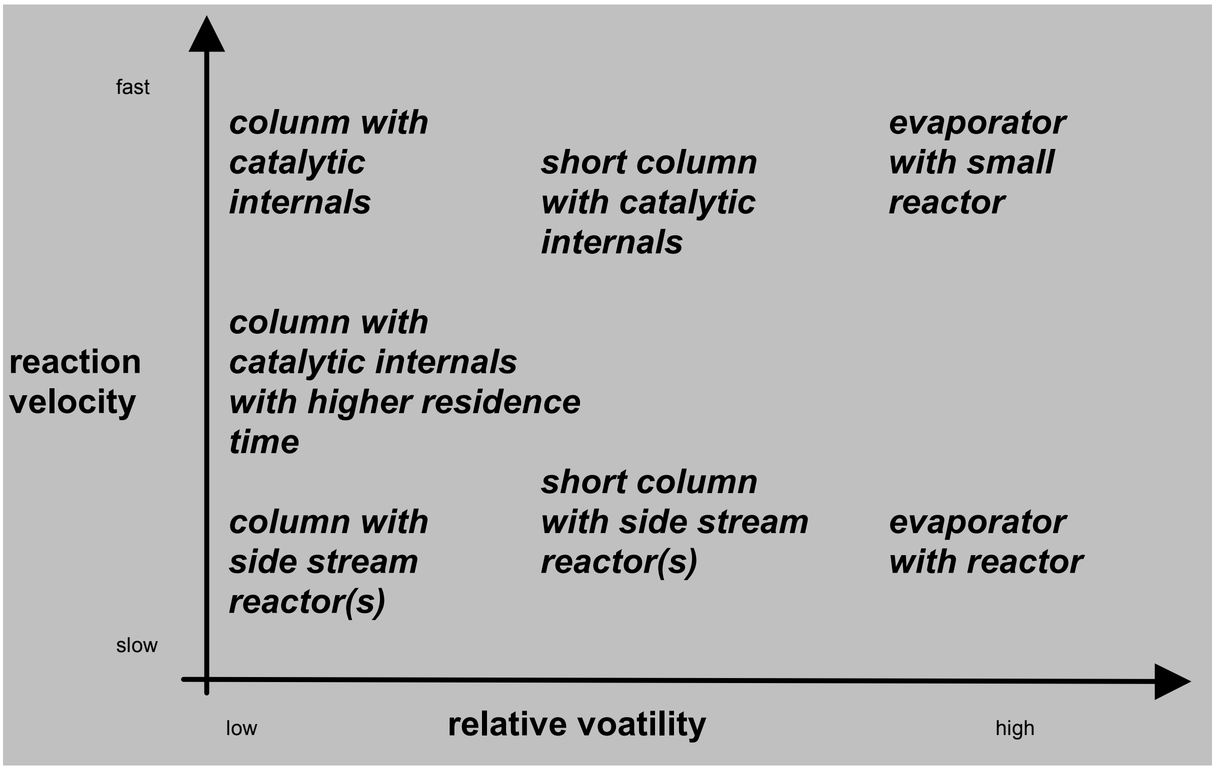


Fig. 19 principles of the selection of equipment (heterogeneous catalysis)

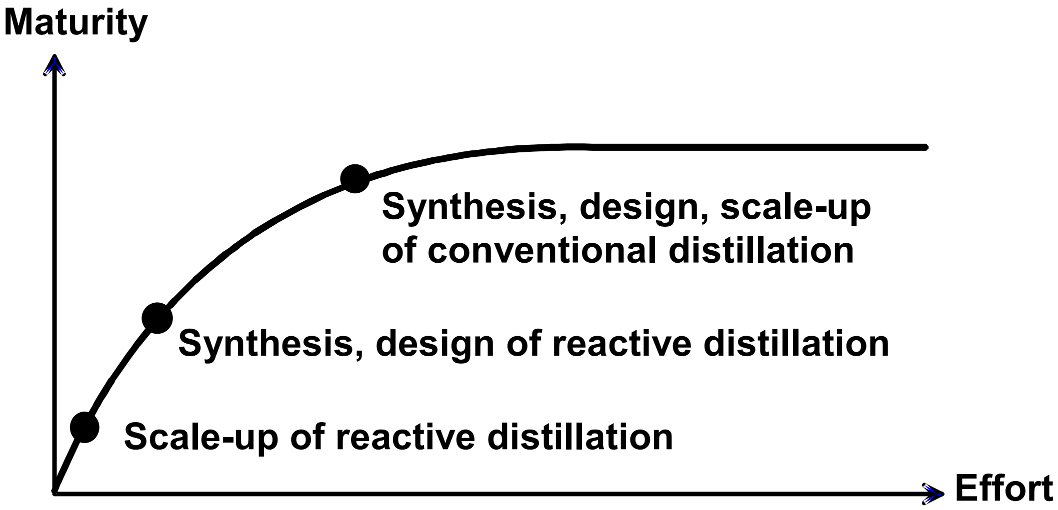


Fig. 20 state of the art