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# **Novel Batch Distillation Processes for the Separation of Systems with and without Chemical Reaction**

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# Nomenclature

$a, b, c, d$	Components ordered in increasing boiling point temperature
$B$	Bottom's fraction, mol
$\dot{B}$	Bottom's flow rate, mol/s
B1, B2, B3	Vessels
$D$	Distillate fraction, mol
$\dot{D}$	Distillate flow rate, mol/s
$F$	Amount of charge, mol
$\dot{F}$	Feed flow rate, mol/s
FC	Flow controller
$h$	Molar enthalpy, J/mol
$HU$	Liquid molar holdup, mol
$k$	Reaction rate constant, s <sup>-1</sup>
$K$	Vapour-liquid equilibrium constant
$K_{eq}$	Chemical equilibrium constant
$\dot{L}$	Molar liquid flow rate, mol/s
LC	Level controller
$\dot{L}/\dot{V}$	Internal reflux ratio
$M$	Middle vessel fraction, mol
$N$	Number of moles, mol
$n_{th}$	Equilibrium stages
$p$	Pressure, Pa
P	Pump
$p_i^0$	Saturated vapour pressure of component $i$ , Pa
$Q$	Energy demand, J
$\dot{Q}$	Energy stream, J/s
$r$	Latent heat of vaporisation, J/mol
$r$	Reaction rate, s <sup>-1</sup>
$R_B$	Reboil ratio
$R_L$	Reflux ratio
$S$	Selectivity
S1, S2, S3	Column sections
$t$	Time, s
$T$	Temperature, K
TC	Temperature controller
T1, ..., T12	Temperature profile along column from top to bottom, °C

$\dot{V}$	Vapour flow rate , mol/s
V1, V2, V3	Valves
$\dot{W}$	Flow rate of withdrawal stream, mol/s
W1, W2, W3	Heat exchangers
$x$	Molar fraction in the liquid phase, mol/mol
$X$	Conversion
$\bar{x}$	Average molar fraction in the liquid phase, mol/mol
$y$	Molar fraction in the vapour phase, mol/mol
$Y$	Yield
$z$	Molar fraction in the feed stream, mol/mol
$\alpha_{ij}$	Relative volatility between components $i, j$
$\gamma$	Activity coefficient
$\Delta D$	Infinitesimal change due to distillation
$\Delta N_R$	Infinitesimal change of the number of moles due to the reaction, mol
$\Delta R$	Infinitesimal change due to reaction
$\Delta t$	Infinitesimal time interval, s
$\theta^\circ$	Boiling point temperature, °C
$\nu$	Stoichiometric coefficient
$\pi_R$	Reaction pole
$\sigma$	Recovery
$\tau$	Relative time

## Subscripts

$a, b, c, d$	Components ordered in increasing boiling point temperature
$B$	Bottom vessel
$D$	Distillate vessel
$f$	Forward reaction
$i$	General component
$k$	Reaction counter
$L$	Lower column section
$M$	Middle vessel
$max$	Maximum
$min$	Minimum
$n$	Equilibrium stage counter, numbered from top to bottom
$p$	Reaction products
$off$	Off-cut
$r$	Reactants
$r$	Reverse reaction
$tot$	total
$U$	Upper column section
$\alpha$	Beginning of the process

$\omega$  End of the process

## Superscripts

$F$	Feed stream
$N$	Number of components
$L$	Liquid phase
$SP$	Setpoint
$V$	Vapour phase
$W$	Withdrawal stream

# 1. Introduction

Speciality chemicals and pharmaceutical agents are produced in small amounts that are usually required in very high purities. These chemicals have high market prices, and either short life cycles, or a fluctuating demand. They are therefore produced in multi-purpose discontinuous processes. These processes usually consist of one or more reaction steps, followed by separation processes. Here, the desired products are purified from solvents, by-products, and unreacted educts. Due to the short life cycles of the products, both the reaction as well as the separation processes should be capable to process a variety of mixtures, and to deliver a variety of product purities.

In batch synthesis, the reaction and separation tasks are in general sequentially ordered [Ahmad and Barton 1995]. The reactors and separators are therefore considered as independent unit operations, between which, the process fluids are transferred in batches. In this case, the nature of the mixture leaving the reactor usually determines the separation process, and therefore the separation has no influence on the reaction. If, on the other hand, the reaction and separation are integrated in one unit operation, the two phenomena reciprocally influence each other. In this way, the yield, selectivity, and conversion of the reaction can be improved, and the separation processes can be simplified.

Batch distillation is a classical unit operation for the separation of small amounts of liquid mixtures. It is very simple and flexible, and furthermore it can deliver very high product purities. Due to its importance on the industrial level, batch distillation has been extensively studied, and several modifications of the process have been developed. The operation of a batch distillation column has also been comprehensively investigated, with several operation policies being developed and applied on the industrial scale. The aim of most of the academic studies was to optimise the operation, to postulate alternative processes, to develop novel separation methods for azeotropic mixtures, and to increase the flexibility of the unit operation. In this optic, a novel batch distillation process, for the purification of a middle-boiling component from heavy and light-boiling impurities, is described and analysed in the first part of this work. The operation policy of this process is explained with the aid of simulation and experimental results. Furthermore, the advantages and disadvantages of the novel distillation process are shown.

In the pharmaceutical industry, it is common practice to couple a batch reactor with a rectifying column. In this way, the light-boiling reaction products can be removed from the reaction system upon their formation. However, only few research groups studied the integration of reaction with batch distillation, and in most cases, the numerous modifications of the batch distillation process have not been considered.



The main focus of this work is the synthesis of novel batch reactive distillation processes. Several novel processes are developed and analysed for a variety of reaction systems. For each case, the operation and basic control of the process is discussed, and the effect of the most important parameters is studied. Furthermore, the advantages of competing processes are outlined. In this way, new understanding of a bright spectrum of processes is gained, providing the process engineer with a large palette of alternative processes. The tools and criteria to select the best processes are also illustrated.

## 2. Literature review

The synthesis of pharmaceutical active agents and of speciality chemicals is usually carried out in multi-purpose plants that are operated discontinuously. Usually, a single synthesis is characterised by several reaction and separation steps which are sequentially ordered. Due to its flexibility, simple operation, and low capital costs, batch distillation has established itself as a standard unit operation for the separation of small amounts of liquid mixtures. This unit operation has therefore been extensively studied. In Section 2.1, the operation of the conventional batch distillation column is described, and its disadvantages are outlined. Hence, some alternative operation modes and some novel processes are introduced. In the second part, Section 2.2, the published research concerning the integration of batch reaction with distillation is reviewed.

### 2.1. Batch distillation processes

Batch distillation is a well-established process for the separation of small quantities of liquid mixtures required to be in high purity. The most common process for batch distillation is shown in Figure 2.1. Here, a charge is loaded into the still placed at the bottom of a rectifying column. The products are obtained in order of

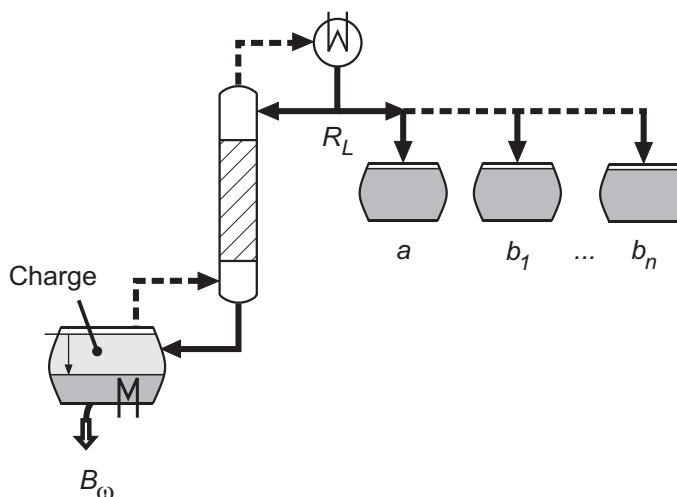


Figure 2.1.: Schematic representation of the regular batch distillation process.

increasing boiling point from the top of the column. During the separation process, the heavy boiler is enriched in the column's sump, from which a heavy-boiling fraction is recovered at the end of the process. The key success of batch distillation has been shown to be due to its simplicity and its flexibility. In fact, several mixtures can be processed in different batches in one single separation unit. Nevertheless, batch distillation presents some very important disadvantages that limit its applicability. The energy demand of batch distillation is generally much higher than that of the continuous process, and the control and operation are usually very complex due to the continuously changing concentrations in the column. The residence time of the mixture in the column's sump is very long. In the sump there is also the highest temperature, which, due to the enrichment in the heavy-boiling components, increase with time. Furthermore, the most volatile components come into contact with hot surfaces of the reboiler [Nitsche 1982]. These factors constitute a major disadvantage for temperature sensitive mixtures, which might degrade under these conditions.

For the reasons mentioned above, and with the help of the new computer based solving routines developed in the second half of the 1980's, alternative processes to the regular batch distillation have been extensively investigated. Two of these processes are illustrated in Figure 2.2.

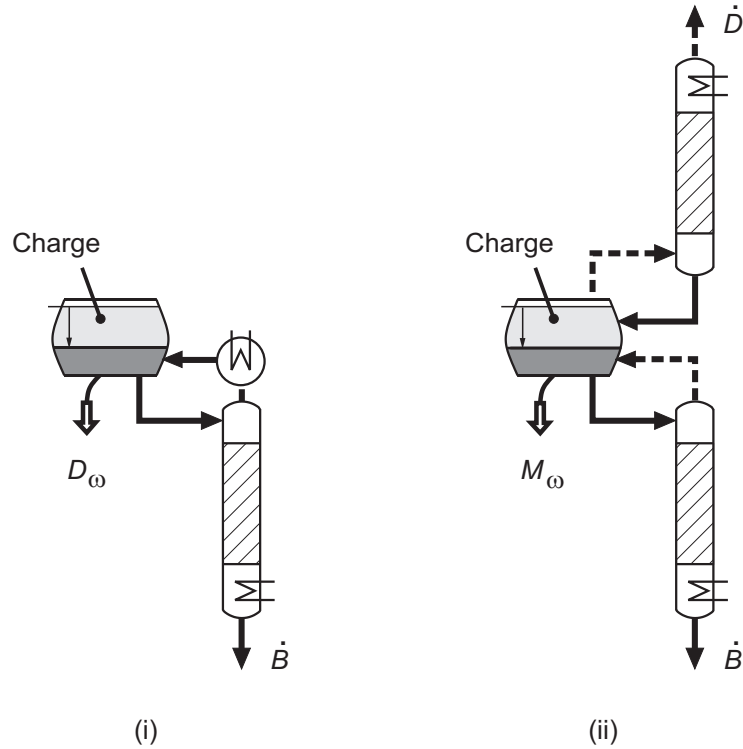


Figure 2.2.: Batch distillation: (i) inverted, and (ii) middle-vessel column configurations.

In the inverted batch distillation, the charge is loaded into a vessel placed at the head of the column, as shown in Figure 2.2 (i). The products are obtained in order of decreasing boiling point from the column's bottom, and a light-boiling fraction can be obtained at the end of the process from the feed vessel. In this case, the mixture in the feed vessel is subject to the lowest temperatures in the column, and this temperature decreases with time. Furthermore, Sørensen and Skogestad [1996] prove that if the mixture is rich in the heavy-boiling component, then the inverted column delivers time and energy savings with respect to the regular column.

In the middle vessel column, shown in Figure 2.2 (ii), the charge is loaded into the still placed in the middle of the column, between a stripping and a rectifying column section. The light and heavy-boiling products are simultaneously obtained from the column's head and sump, respectively. As discussed by Warter [2001], Warter et al. [2004] and other authors, this can have several advantages. The temperature in the middle vessel can be kept low throughout the process, reducing the thermal exposure of the components in the charge. Furthermore, the time required by the process can be reduced with respect to the regular column, and, in some cases, the separation procedure can be simplified. Warter and Stichlmair [2000], Skouras and Skogestad [2004a] and Rodriguez-Donis et al. [2001] show that the middle vessel column can be used for the separation of azeotropic mixtures, which would otherwise be impossible or very complex to perform in a regular batch distillation column.

### Operation modes for batch distillation processes

The three processes described in the previous section are characterised by an open operating procedure, where the initial mixture is loaded into a charge vessel, and the products are withdrawn from the column's head and sump. The reflux and/or reboil ratios can either be kept constant, or be used to regulate the composition of the product [Stichlmair and Fair 1998]. Alternatively, they can be used to optimise the process [Mujtaba and Macchietto 1992].

Batch distillation processes can be operated in a closed mode. In this case, there is no net product withdrawal from the system [Skogestad et al. 1997, Warter and Stichlmair 2002, Warter et al. 2004, Skouras and Skogestad 2004b]. The closed operation of a middle vessel column is shown in Figure 2.3. The charge is initially distributed between the middle, top and bottom vessels, which are connected to the column. During the closed operation, the temperatures in the rectifying and in the stripping column sections are controlled by setting the reflux rates from the top and the middle vessels, respectively. At the end of the process, the concentrations in the vessels reach steady state, therefore the temperature profile stabilises, and the column is operated under total reflux conditions. Warter and Stichlmair [2002] and Warter et al. [2004] experimentally validate the closed operation of a middle vessel column under level control in the top and middle vessels. Here, the distillation column is operated under total reflux, and therefore the best conditions for separations exist. Furthermore, the operation and control of this process are very simple; nevertheless,

the composition of the charge has to be accurately known at the beginning of the process. This might constitute a major disadvantage for the complex mixtures usually processed in batch distillation units, since the exact composition of the charge might fluctuate and be difficult to obtain.

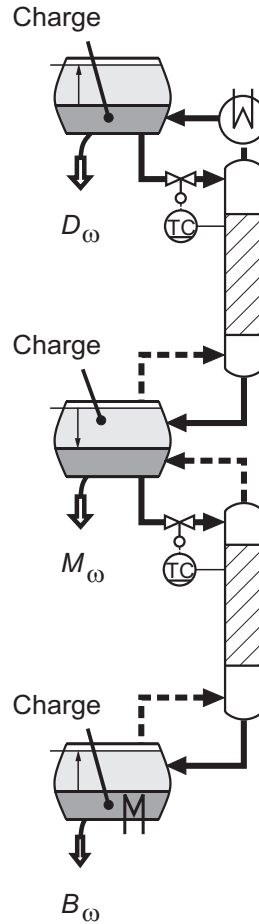


Figure 2.3.: Closed operation of a batch distillation in middle-vessel column under temperature control.

### Minimum energy demand

Distillation is an energy-intensive separation process, since heat has to be supplied to the system in order to create the second phase required for separation. Both during the design and operation phases, the energy required by the process plays a fundamental role. The minimum energy required for a given separation task is that needed by a distillation column having an infinite number of stages. This is therefore a theoretical minimum, which can be used during the design phase as a pre-selection tool to restrict the choice among the available batch distillation processes.

On the other hand, during operation, the minimum energy demand can be used as a measure of how far the process is from its thermodynamics optimal, and how wide the optimisation margins of the process are.

The most popular method for the calculation of the minimum energy demand is the one published by Underwood [1948]. This is an iterative method, which, under the assumption of constant molar overflow, allows the calculation of the minimum reflux ratio for ideal mixtures. Offers et al. [1995] describe a direct method to calculate the minimum reflux ratio for a given separation both for ideal and real systems. This method is applicable to multi-component batch distillation operated with constant product composition. The calculation of the minimum reflux and reboil ratios is repeated for every concentration in the still. The still's concentration can be determined via Rayleigh's equation, as described in Stichlmair and Fair [1998]. This calculation requires only the knowledge of the relative volatilities of the mixture in the still.

## 2.2. Integration of batch reaction with batch distillation

In batch synthesis, the products leaving a reactor are usually mixed to other products, to reactants and to solvents. These mixtures need to be separated into the single components, which are generally required in high purities. It is common industrial practice to carry out the reaction and separation processes sequentially in separate unit operations. In case of equilibrium limited reactions, this practice requires recycles of the reactants to the reactor. On the other hand, in case of sequential or parallel reactions, undesired side products might be formed at the expense of the main reaction products. Integrating reaction with separation in a single unit operation would remove the reaction products from the reaction region upon their formation, hence shifting the chemical equilibrium to the products' side, suppressing undesired side reactions and overcoming distillation barriers.

The integration of a reactor with a distillation unit is commonly called either reactive or catalytic distillation. In the case of batch processes, such integrated processes might be classified in two families. On the one hand, a batch or a semi-batch reactor can be coupled with a distillation column. Here, the reaction and separation processes are only coupled in time, but they are spatially separated, the reaction being limited to the reactor. On the other hand, the reaction can be carried out within the distillation column. Here, the reaction and separation are integrated both in time and space. In this case, one speaks of batch reactive distillation. In the following paragraphs, a literature review of the two processes is given.

### 2.2.1. Coupling of batch reactor with a distillation unit

When exothermic reactions are carried out in the liquid phase in stirred tank reactors, the temperature control of the system could be simplified by allowing the reaction mixture to react at its boiling point temperature. A total reflux condenser is placed on top of the reactor, so that setting the operating pressure of the condenser determines the operating temperature in the reactor. Another common practice in the pharmaceutical industry is to couple batch reactors with rectifying columns. In this case, the light-boiling reaction products are immediately removed from the reaction mixture. For equilibrium limited reactions, this shifts the conversion to the products' side, and improves the selectivity of the desired products by suppressing side reactions. Notwithstanding its popularity on industrial level and its early appearance in the literature [Ruby et al. 1978], this process has received limited attention by the academic world.

Ruby et al. [1978] were the first authors to consider a batch reactor coupled with a rectifying column. Here, a non-specified esterification reaction, with the formation of light-boiling products, is considered. However, the main focus of this publication is the solution of the mathematical problem. This was a main issue, since stable solvers for Differential Algebraic Equations (DAE) were developed only in later years as for example by Cuille and Reklaitis [1986]. In a second publication, Egly and Ruby [1980] compare experimental and simulated results of the optimised process. Furthermore, they experimentally show that the conventional control system for batch distillation is able to reject disturbances to the combined process.

Mayer and Wörz [1980] compare continuous reactive distillation, a batch reactor coupled with a rectification column, and a continuous stirred tank reactor (CSTR) coupled with a rectifying column. A fast equilibrium reaction is here taken into consideration. The boiling points of the reactants lie between those of the reaction products, which are therefore obtained as top and bottom fractions. The three configurations are studied for varying values of the reaction equilibrium constant, and for different volatilities of the components. The authors compare the conversion of one of the reactants for a given energy input to the process. For most cases, the continuous reactive distillation process shows the best results. However, for high values of the chemical equilibrium constant, and for increasing volatility of the heavy boiler, the difference between the continuous and the batch process are considerably reduced. This later result is however of minor importance, since in the continuous reactive distillation the reactive part of the column was limited to the stages below the feed point. The CSTR coupled with a rectifying column always shows the worst performance.

Reuter et al. [1989] treat in more detail the dynamic simulation of the batch distillation column. An equilibrium limited transesterification reaction, with the formation of light-boiling products, takes place in the column's sump. The simulated and experimental distillate concentrations are compared for an optimised process. The results show good agreement.

### Control of a batch reactor coupled with a rectifying column

The control issues are more extensively treated in Sørensen and Skogestad [1994]. The authors show that the open-loop reflux policies, i.e. constant reflux, or constant distillate flow rate policies, should not be applied to the batch reactor coupled with a distillation column. Furthermore, the authors compare three alternative control strategies for this process:

a) One-point bottom control, with direct control of the temperature in the reactor. Effective control is only obtained if the set-point temperature is set below to a maximum value, which is difficult to estimate a priori. The set-point temperature is, therefore, usually chosen to be too low, slowing down the process.

b) Two-point control, where both the distillate composition and the reactor temperature are controlled. This results in two control loops, which show strong interactions.

c) One-point column control. The temperature on a tray in the column is controlled by changes to the distillate stream. This is the usual control strategy adopted in batch distillation. The heat duty to the reboiler is either set to a constant value, or used to control the pressure drop in the column. In the latter case, the control loop is slow, and it is used to maximise the throughput of the column. The authors state that this control strategy is the simplest to implement and it delivers good control, provided that the temperature measurement point is properly selected. This control strategy is subsequently applied to an optimised process [Sørensen et al. 1996].

### Coupling a batch reactor with different column configurations

Li et al. [1998a] couple a semi-batch reactor with a rectifying column for a transesterification reaction in which a light-boiling alcohol, and a heavy-boiling ester are formed. The reactants are both charged to the reactor at the beginning of the process. However, in order to boost the reaction rate, excess reactant alcohol is continuously fed to the reactor. This maintains a relatively high alcohol concentration in the reactor, therefore improving the reaction rate. The product ester is then purified from the excess alcohol in a second distillation step. The authors solve a time optimisation problem, obtaining optimised profiles both for the feed flow rate, and the reflux ratio policy.

Mujtaba and Macchietto [1992] were the first to consider the combination of a batch reactor with an inverted and with a middle vessel column. Several chemical equilibrium limited reactions are taken into consideration, and the suitable column configurations for each reaction are identified. Furthermore, the authors state that in the case that the boiling point of the reaction products lies between that of the reactants, none of the discussed column configurations would be suitable. Nevertheless, the authors neither take into consideration semi-batch processes, nor reactive columns. In a later publication [Mujtaba and Macchietto 1994], the authors compare three column configurations for a given reactive mixture, where light and heavy-boiling components are formed.



### Overcoming distillation boundaries

Guo et al. [2003] address the feasibility of the combined batch reaction-distillation processes for ternary azeotropic mixtures. They develop simple criteria to graphically determine the feasible products. These require only the knowledge of the residue curve maps and the chemical equilibrium. In their work, semi-batch processes and reactive columns are however not considered. The authors show that distillation boundary lines could be crossed, and pure products could be obtained, depending on the position of the chemical equilibrium line and the column configuration. The results of the graphical analysis and the feasibility criteria are proved solving simplified, pseudo-steady-state material balances developed by Venimadhavan et al. [1999].

Espinosa [2002] presents a novel process, in which a batch reactor is coupled with a batch extractive distillation in a middle vessel column. This process is illustrated for the esterification of ethanol and acetic acid. This mixture presents a highly non-ideal vapour-liquid equilibrium, since three minimum binary azeotropes and a ternary azeotrope are formed. In this process, acetic acid is continuously fed to the upper part of the extractive column section, thus functioning both as an extractive solvent (in extractive distillation) and as reactant (in the middle vessel). An operating procedure is postulated, and the influence of the operating and geometrical parameters of the column are analysed.

### Suppressing side reactions

Gadewar et al. [2000] illustrate the application of a batch reactor coupled with a rectifying column for consecutive reactions, where the desired product is produced by the first reaction, and consumed in the second. Furthermore, this is the light-boiling component. They compare the selectivity and yield of the combined process with that of a plug flow reactor (PFR) as a function of the Damköhler numbers of the two reactions. The Damköhler number is a dimensionless number expressing the ratio of the characteristic liquid residence time to the characteristic reaction time. They show that the combined process always outperforms the PFR over the whole range of the Damköhler numbers. The study is repeated for a parallel reaction in which the desired product reacts with one of the reactants. Since, the desired product is the heavy-boiling component of the system, they suggest coupling the batch reactor with a stripping column. This is also compared to a PFR. Even though the two process alternatives show similar behaviour for various Damköhler numbers, the batch reactor coupled with the batch stripper shows the best yield and selectivity to the desired product. The simplified model developed by Venimadhavan et al. [1999] is applied also in this study.

### 2.2.2. Batch reactive distillation

The spatial integration of reaction with distillation requires special hardware, which enables the contact of the reactants to the catalysts and provides the necessary volume for the reaction, without diminishing the interfacial area between the liquid and the vapour phases [Krishna 2003]. Such hardware makes batch reactive distillation a very specific process, increases the investment costs, and reduces the flexibility of the batch unit. Furthermore, the chemical reaction has an important effect on the vapour-liquid equilibrium [Barbosa and Doherty 1988a;b], so that the so-called reactive distillation lines result [Frey and Stichlmair 1999]. These might give rise to reactive azeotropes, which are otherwise not present in the non-reactive case, hence creating new barriers to the separation process. For these reasons, batch reactive distillation has met little interest in the literature. Furthermore, only one real industrial application of the process has been published [Osorio et al. 2005], namely wine distillation for the production of Pisco.

Cuille and Reklaitis [1986] and Albet et al. [1994] address the problems associated with the simulation of a dynamic reactive distillation column. Albet et al. [1994] pay particular attention to the start-up procedure and to the initialisation of the model of the batch reactive distillation column. Wajge and Reklaitis [1999] introduce a simulation and optimisation framework for batch distillation with and without chemical reaction. Xu and Dudukovic [1999] present a model for the photo-catalysed chlorination of toluene. The reaction takes place both in the liquid and in the vapour phases. All the above-mentioned models are based on the assumption that vapour-liquid and reaction equilibria are reached on each tray. A detailed non-equilibrium stage model including the mass transfer between the phases for a heterogeneously catalysed batch reactive distillation column is solved in Schneider et al. [2001].

The esterification of methanol and acetic acid in a semi-batch reactive distillation column is studied by Fernholz et al. [2000] and Schneider et al. [2001]. The light-boiling reactant, methanol, is charged to the sump, and the heavy-boiling reactant, acetic acid, is continuously fed at the top of the reactive column section. Hence, the two reactants are subject to a counter current flow in the catalytic section. Methyl acetate, the light-boiling reaction product is therefore recovered as distillate fraction.

The control of batch and semi-batch reactive distillation columns has been discussed in Monroy-Loperena and Alvarez-Ramirez [2000], Balasubramhanya and Doyle [2000] and Engell and Fernholz [2003].

## 2.3. Modelling and simulation

Several authors have published the modelling of batch distillation processes. This is based on dynamic mass and energy balances, on vapour-liquid and chemical equilibrium relationships, and on the hydrodynamics of the column. The models presented in the literature differ on the grade of detail considered. The highest degree of detail is provided by the so-called non-equilibrium or rate-based models. Here, the mass transfer between the phases is described in detail, this requires empiric mass transfer correlations. In the greatest number of publications, the batch distillation processes, both non-reactive as well as reactive, are described by equilibrium stage models. It is assumed that vapour-liquid equilibrium is reached on every stage. Even though such relationships are simpler than those required for the rate-based models, several authors, as for example Warter et al. [2004] and Wittgens and Skogestad [2000], have shown that the simulated and experimental results are in sufficiently good agreement. Furthermore, in most models, it is assumed that the hydrodynamics of the column, i.e. pressure drop and holdup, have a negligible effect on the vapour-liquid equilibrium, and are therefore not included in the model.

The mathematical description of a batch distillation process results in a system of Differential-Algebraic-Equations (DAE). The current solvers are able to solve problems that have an index of 1. These are DAE systems which can be transformed in Ordinary-Differential-Equations (ODE) merely with algebraic manipulations [Pantelides et al. 1988]. However, if the hydrodynamics of the column, and in particular the pressure drop in the column, were not included in the modelling, a DAE system of index 2 would be required to describe the process. This means that it is not possible to convert the DAE into an ODE system with algebraic manipulation of the equations. Pantelides et al. [1988] suggest two ways to circumvent this problem. A simplified pressure drop relationship, relating the pressure drop on every equilibrium stage to the square of the vapour flow rate, can be included in the model description. The second possibility is to assume that the dynamics of the enthalpy changes on the stages are very slow compared to those of mass transfer between the phases. A pseudo-steady state energy balance can therefore be written.

The various batch distillation processes treated in this thesis have been described with the equilibrium stage model. The mathematical models involved and the simulation software used in this work are illustrated in Chapter 4.

### 3. Aim and outlook of the thesis

As has been outlined in the literature review, numerous authors studied different aspects of batch distillation and proved the flexibility of this well established unit operation. However, only few works treated the integration of batch reaction with batch distillation, and to date, there is no work that extensively treats the synthesis of integrated batch processes. The aim of this work is to provide the process engineer with novel tools for the design of batch distillation processes with particular attention paid to batch reactive distillation processes. This is achieved by describing the operation of novel processes, underlining their advantages, and marking their application fields.

A novel process for the purification of a middle-boiling component from light and heavy-boiling impurities is introduced in Chapter 5. An operation procedure and a basic control structure are postulated. These are subsequently verified by process simulations. The most important process parameters are identified, and a parametric study is performed. The novel process is compared to the batch distillation in a middle vessel column. This comparison illustrates the importance of the novel batch distillation process and marks its application field. Finally, the feasibility and the practical implementation of the process are demonstrated via experiments in a pilot-plant.

In each of the three following chapters, various batch reactive distillation processes are investigated and compared for a given reaction class. In Chapter 6, different processes for the treatment of equilibrium limited reactions are introduced for two different reaction structures. In Section 6.1, the operation procedure and basic control of several process alternatives are illustrated for a decomposition reaction where heavy and light-boiling products are formed. The combination of batch reactors with a distillation column, as well as batch reactive distillation columns are taken into consideration. In Section 6.2, an addition reaction with the formation of a middle-boiling component is considered. For this reaction type, several semi-batch processes are postulated and analysed. The reaction is carried out either in a semi-batch reactor coupled with a batch distillation column, or in the liquid phase of a batch reactive distillation column. These processes are compared at the end of the section.

Integrated processes for kinetically controlled reactions are discussed in Chapter 7. Only reactions with the formation of either light or heavy-boiling products are considered. Due to the long residence times required by the reaction, only reactors coupled with distillation columns play an important role in process synthesis for this class of reactions. Several operating procedures are postulated and verified by simulations. The simulation results are then used to compare these processes.

Finally, the importance of batch reactive distillation processes for the suppression of side reactions is illustrated in Chapter 8. The volatility of the main product and that of the key educt play an extremely important role in process synthesis. This is illustrated for two systems with parallel reactions. In both cases, the main product, formed in the first reaction, is a middle boiler. This then reacts with one of the educts, forming an undesired product. In one case, the key educt is a light-boiling component, and in the other, it is a heavy boiler. The reaction is carried out in integrated semi-batch processes. Both the combination of a semi-batch reactor with a batch distillation process, as well as batch reactive distillation processes are synthesised and compared.

## 4. Modelling and simulation

Batch processes, as opposed to continuous operation, are characterised by a non-steady state behaviour. Their mathematical description is therefore based on time dependent mass and energy balances, resulting in systems of equations which include both differential and algebraic equations. In the past decades, several solvers able to solve such complex systems have been developed and made commercially available. Furthermore, in recent years, tools for the optimisation of time dependent processes have also appeared, and the first works treating the optimisation of batch distillation processes have been published. However, this remains a young field requiring further research.

This chapter provides an overview of the basics of the thermodynamic principles and of the mathematical models necessary to describe the batch distillation processes developed in the course of the thesis.

### 4.1. Simulation software

The batch distillation processes investigated in this thesis are modelled using the software package "general PROcess Modelling System" (gPROMS) developed by Process Systems Enterprise Ltd., London. gPROMS is a powerful general purpose modelling and optimisation environment, used to enhance the design and operation of continuous and dynamic processes [gPROMS 2003]. It is an equation-based simulation environment, where the user can write his own mathematical models to express the physical and chemical relationships, as well as the operational task sequences describing the processes and their operation. gPROMS analyses the relationships governing the process and performs dynamic or steady-state simulation, optimisation, or parameter estimation.

In this modelling environment, it is possible to divide the complex process into sub-models that describe basic units. These sub-models can be called by higher hierarchy models, with which they exchange information. A gPROMS model consists of a system of models each with a different hierarchy. The models are connected together via data and material streams. The use of such a hierarchical modelling approach allows a complex process to be reduced to its component parts. This simplifies the model writing process, reduces model complexity, improves model readability, and facilitates debugging. It is also possible to use a model that has been written for a particular unit operation in other processes or even repeatedly in the same process.

The thermodynamic properties of the liquid and vapour phases are written in those

models having the lowest hierarchy. These models are then used in the next level, where the single process units (such as vessels, equilibrium stages, and heat exchangers) are described. The single process units are then connected together via material streams in the model having the highest hierarchy. This model represents the flow-sheet of the process. Moreover, the values of the constants are assigned in this model. These are then automatically passed to the models having lower hierarchy.

In the "PROCESS" section, the boundary conditions of the differential variables are assigned. The detailed operation of the process is also described in this section. gPROMS is able to treat discontinuities, thereby allowing for the simulation of complex operating procedures consisting of several phases.

## 4.2. Modelling of batch distillation column

A complex batch distillation column is modelled. This column is used as a super-structure for modelling the various processes described later in the thesis. However, in order to reduce the computational time and improve the stability of the mathematical model, the redundant parts of the complex column are removed.

The general complex column is illustrated in Figure 4.1 (i). The dotted lines represent the balance volumes. These are described with mass and energy balances as well as with equilibrium relationships. The equilibrium stage model is used for the description of the column. This is based on the assumption of perfect mass and energy transfer between the phases. Furthermore, the streams leaving an equilibrium stage are assumed to be in thermodynamic and mechanical equilibrium. An equilibrium stage, represented in Figure 4.1 (ii), is therefore described by the so-called MESH equations, which, for the time dependent case, are written as described below.

The component mass balance results from the principle of conservation of mass. This principle states that for every component, the number of moles accumulated in the control volume is equal to the difference between the number of moles entering and that leaving the control volume, added to the moles generated by the chemical reaction.

$$\begin{aligned} \frac{d(HU_n \cdot x_{n,i})}{dt} = & \dot{L}_{n-1} \cdot x_{n-1,i} + \dot{V}_{n+1} \cdot y_{n+1,i} - \dot{V}_n \cdot y_{n,i} - \dot{L}_n \cdot x_{n,i} + \\ & + \dot{F}_n \cdot z_{n,i} - \dot{W}_n \cdot x_{n,i} + \sum_k \{r_{n,k} \cdot \nu_{k,i}\} \cdot HU_n \cdot x_{n,i} \end{aligned} \quad (4.1)$$

The vapour-liquid equilibrium relates the molar fraction of each component in the vapour phase to that of the same component in the liquid phase. Under the assumption of an ideal gas phase, this is expressed by:

$$y_{n,i} \cdot p_n = \gamma_{n,i} \cdot p_{n,i}^0 \cdot x_{n,i} \quad (4.2)$$

In Chapter 5 a real mixture is modelled. The saturated vapour pressures ( $p^0$ ) and the activity coefficients ( $\gamma$ ) are therefore calculated using empirical models. In the

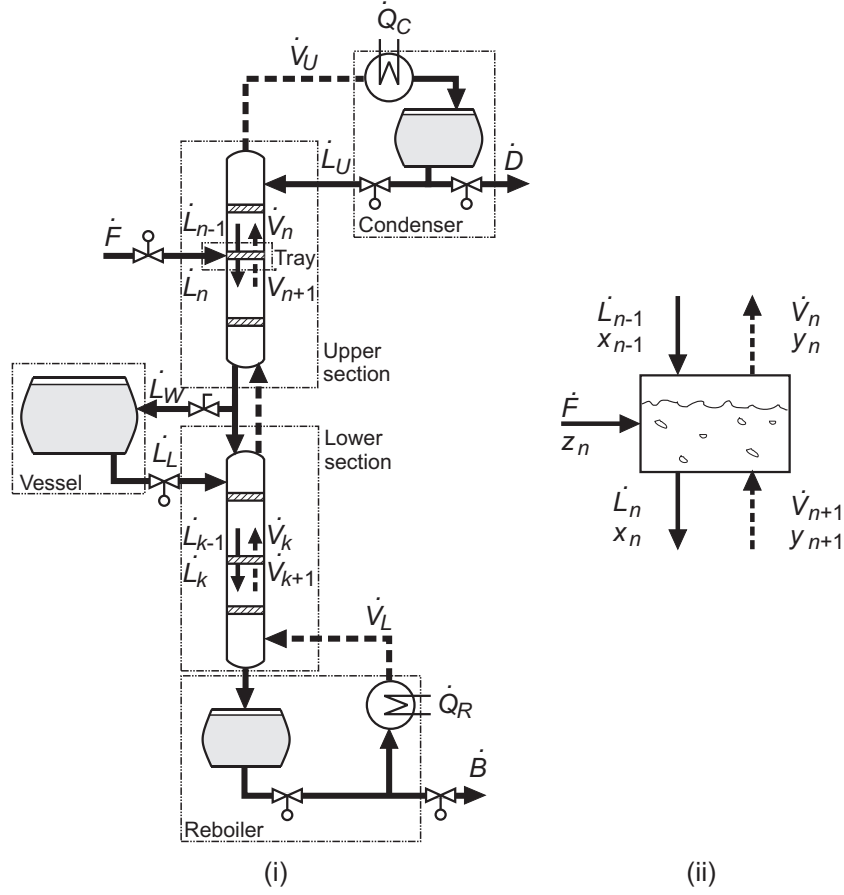


Figure 4.1.: (i) Flowsheet of the model of a complex batch distillation column, and (ii) scheme of an equilibrium stage.

rest of the work, the liquid is assumed to behave ideally, i.e.  $\gamma_i = 1$ ; and the relative volatilities ( $\alpha_{i,j}$ ) of the components are assumed to be independent of the temperature. The vapour-liquid equilibrium is therefore expressed in terms of the saturated vapour pressure of the heaviest boiling component and the relative volatilities with respect to this component:

$$y_{n,i} \cdot p_n = \alpha_{i,d} \cdot p_{n,d}^0 \cdot x_{n,i} \quad (4.3)$$

From the definition of mole fraction the following summations result:

$$\sum_{i=1}^C x_{n,i} = \sum_{i=1}^C y_{n,i} = 1 \quad (4.4)$$

Furthermore, the principle of conservation of energy gives the following energy



balance:

$$\begin{aligned} \frac{d(HU_n \cdot h_n^L)}{dt} = & \dot{L}_{n-1} \cdot h_{n-1}^L + \dot{V}_{n+1} \cdot h_{n+1}^V - \dot{V}_n \cdot h_n^V - \dot{L}_n \cdot h_n^L + \\ & + \dot{F}_n \cdot h_n^F - \dot{W}_n \cdot h_n^W + \dot{Q}_n \end{aligned} \quad (4.5)$$

As already discussed in the literature review in Section 2.3, if the hydrodynamics of the column are ignored, the resulting systems of equations cannot be solved by the current solvers. In order to isolate the thermodynamic behaviour of the system from its hydrodynamics, the models used do not take into consideration the hydrodynamics of the column. However, it is necessary to reduce the index of the system to 1. This is achieved by assuming that the dynamics of energy transfer are much slower than the mass transfer dynamics. This assumption translates to writing the energy balance as a steady state balance:

$$\begin{aligned} 0 = & \dot{L}_{n-1} \cdot h_{n-1}^L + \dot{V}_{n+1} \cdot h_{n+1}^V - \dot{V}_n \cdot h_n^V - \dot{L}_n \cdot h_n^L + \\ & + \dot{F}_n \cdot h_n^F - \dot{W}_n \cdot h_n^W \end{aligned} \quad (4.6)$$

In order to prove the validity of this later model, three models have been written: one including the detailed description of the fluid dynamics of a batch distillation column; one relating the pressure drop to the square of the vapour flow rate through the column; and the third one with a pseudo steady-state energy balance given by Equation 4.6. Under the assumption of no heat generation and no heat transfer on the stages, the three models deliver similar concentration and temperature profiles. It was therefore concluded that, as long as no heat is generated, and there is no external heat transfer on the stages, the simplified models have the advantage of requiring less geometric data of the distillation equipment, without reducing the quality of the thermodynamic results.

## 5. Separation of Zeotropic Ternary Mixtures via Batch Distillation in a Column with Side Withdrawal

As already pointed out in the literature review, several batch distillation processes are available for the separation of zeotropic mixtures. In this chapter, a novel process will be introduced. This is shown in Figure 5.1. It consists of a distillation column equipped with sump and distillate vessels, into which the charge is loaded at the beginning of the process. The main characteristic of this process is the withdrawal stream placed in the middle of the separation column. Here, a middle-boiling mixture having the required concentration can be continuously withdrawn during the process. The light-boiling fraction would, therefore, be recovered at the end of the process in the top vessel ( $D_\omega$ ); the middle-boiling fraction at the side withdrawal stream ( $\dot{W}$ ); and the heavy-boiling fraction in the reboiler vessel ( $B_\omega$ ).

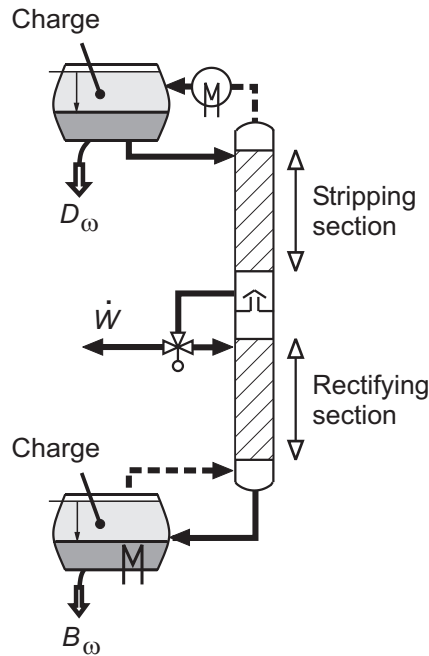


Figure 5.1.: Batch distillation column with side withdrawal.

## 5.1. Feasibility

To analyse the feasibility of the process, it is useful to conceptually divide the distillation column into two separate sections placed on top of each other, as shown in Figure 5.1. The lower column section can then be seen as a rectifying column, and the upper column section as a stripping column. The vapour leaving the rectifying section is directly fed to the bottom of the stripping section. Analogously, the liquid leaving the bottom of the stripping section provides both the reflux to the rectifying section and the product stream ( $W$ ).

This conceptual decomposition of the column allows for the application of feasibility studies developed for stripping and rectifying columns, provided that the concentration profiles of the two columns meet at the withdrawal stage. Therefore, it is possible to obtain a pure intermediate-boiling product from a column with an infinite number of stages operated with total reflux ratios, only if the top and bottom vessels do not contain the heavy and the light-boiling components, respectively.

Figure 5.2 shows the simulated concentration path of the liquid phase in the top vessel ( $x_D$ ), on the withdrawal tray ( $x_W$ ), and in the bottom vessel ( $x_B$ ) of a column having a very high number of stages and being operated at close to total reflux conditions. Here, the separation of an equimolar mixture of ethanol, 1-propanol and 1-butanol is depicted.

It is clearly visible that, as long as the top and bottom vessels contain heavy and light boiler respectively, the concentration of the intermediate boiler on the withdrawal tray is smaller than one. It follows that, to obtain a high purity intermediate-boiling component on the withdrawal stage, a two-step operating procedure is required. In the first operation step, the light boiler should be transferred from the bottom to the top vessel. Simultaneously, the heavy boiler is transferred from the top to the bottom vessel. During this process step, the concentration of the intermediate boiler in the column will be lower than the required purity. No product is therefore withdrawn from the column. This step is termed closed operation, and is equivalent to the process introduced by Sørensen and Prenzler [1997]. When the concentration of the intermediate boiler on the withdrawal stage has reached the required value, an intermediate-boiling fraction can be continuously withdrawn at the withdrawal stream. The procedure will be discussed in detail in the next section.

## 5.2. Description of the process

The process will be illustrated for the purification of 1-propanol ( $\theta_b^o(1\text{ bar}) = 97.8^\circ\text{C}$ ) from a mixture containing 0.1 mol/mol ethanol ( $\theta_a^o(1\text{ bar}) = 78.4^\circ\text{C}$ ) and 0.1 mol/mol 1-butanol ( $\theta_c^o(1\text{ bar}) = 117^\circ\text{C}$ ). The relative volatilities of the components do not vary much over the temperature range of the column, and their average values are:  $\alpha_{ab} = 2.0$  and  $\alpha_{bc} = 2.2$ . The total number of equilibrium stages in the column is  $n_{th} = 21$ , and the withdrawal stage is placed in the middle of the column. Further

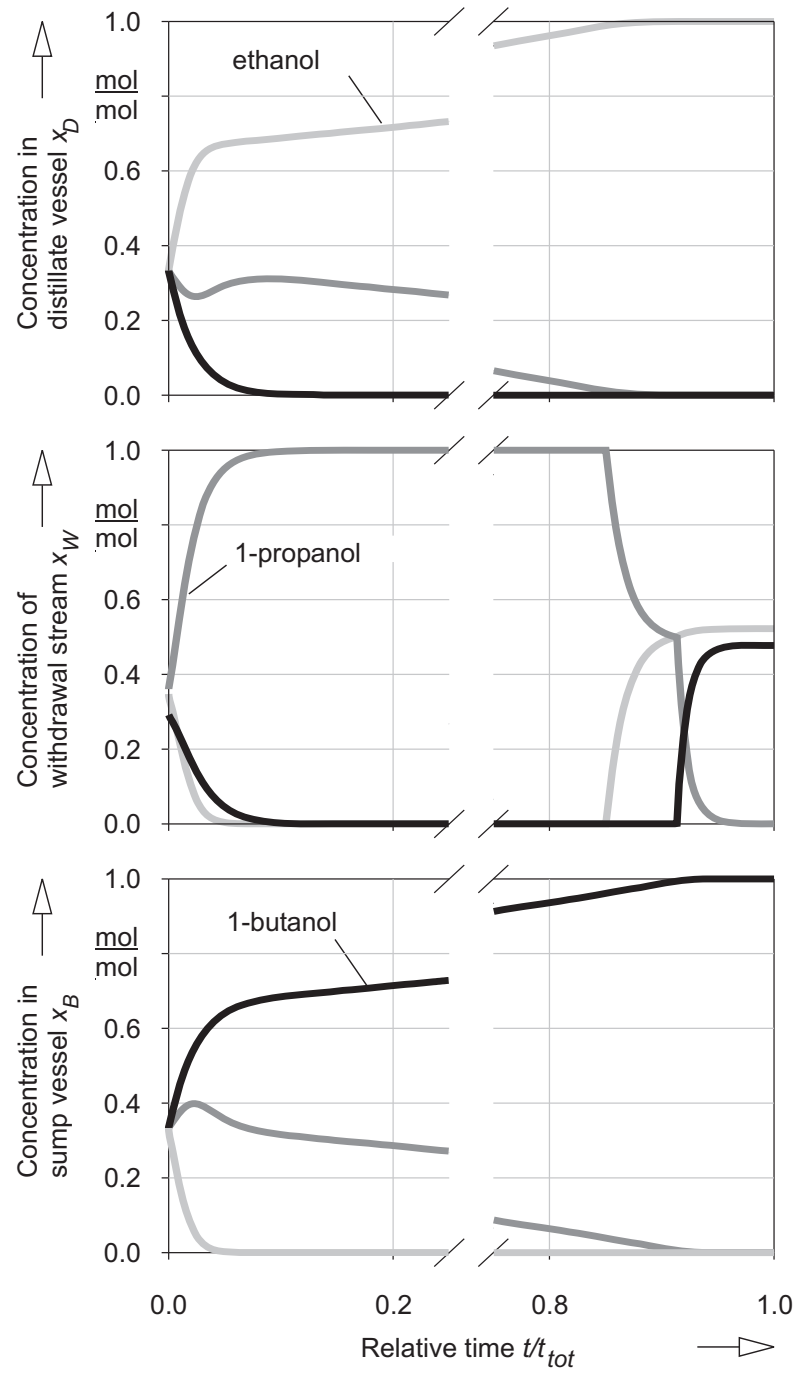


Figure 5.2.: Concentration path in distillate vessel, on the withdrawal stage and in the sump vessel at very high number of stages and close to total reflux conditions.

## 5.2. Description of the process

constants assigned in the simulation are summarised in Table 5.1.

Table 5.1.: Simulation parameters for the process described in Section 5.2.

Molar fractions in the charge	$(x_a, x_b, x_c)$	(0.1, 0.8, 0.1)
Number of equilibrium stages	$n_{th}$	21
Position of withdrawal stream	$n_W$	10
Position of upper TC	$n_U^{TC}$	8
Position of lower TC	$n_L^{TC}$	12
Setpoint to upper TC	$T_U^{SP}$	370.8 K
Setpoint to lower TC	$T_L^{SP}$	372.4 K
Final concentration of the side product	$x_{Wb}$	0.965 mol/mol

The charge to the process is divided in two equal fractions. A fraction is loaded into the reboiler vessel and the other into the vessel connected to the head of the column, as shown in Figure 5.3 (i). A constant heat duty is supplied to the reboiler, bringing the liquid to its boiling point. The vapour thus produced rises in the column and is condensed in the condenser at the column's head. The condensate flows to the top

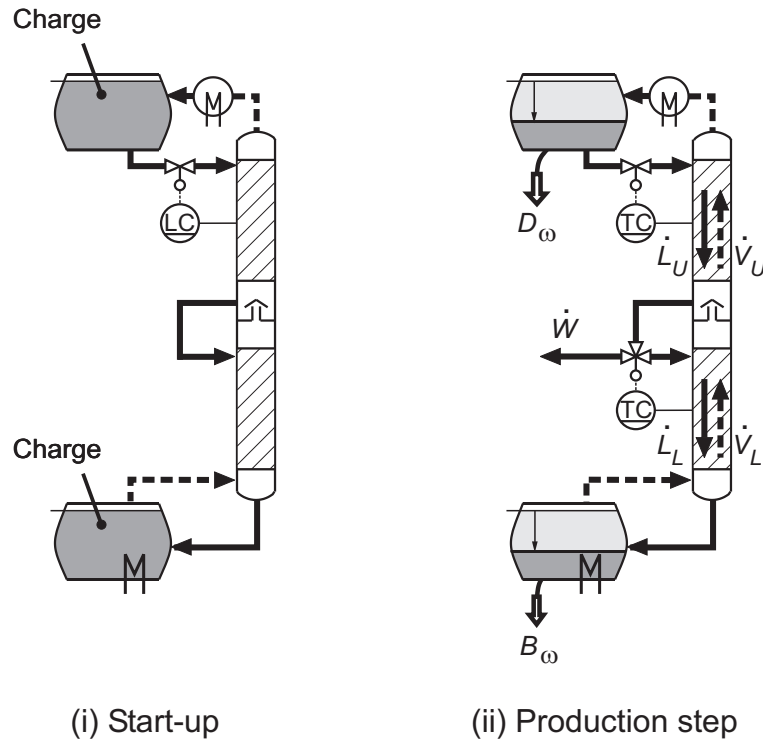


Figure 5.3.: Process steps: (i) start-up (close), and (ii) production (open).

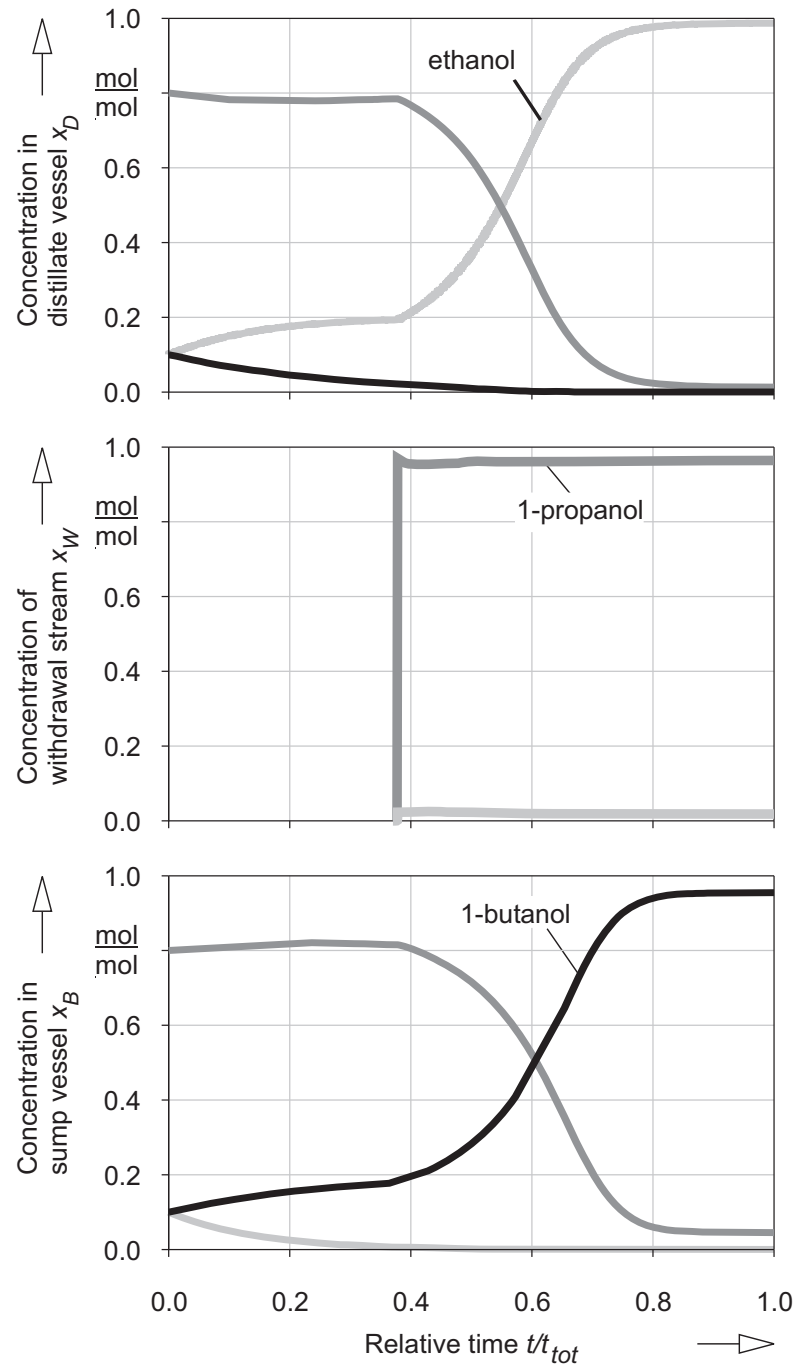


Figure 5.4.: Concentration path in the distillate vessel, the withdrawal stream, and in the sump vessel.

vessel, where it is mixed with the charge. The liquid outlet of this vessel thus provides the reflux to the column. During the start-up (close) phase, no product is withdrawn from the column; hence the level in the two vessels is kept constant. During the closed operation phase, the light-boiling component depletes from the lower vessel, while the heavy-boiling component depletes from the upper vessel. At the end of this process step, the concentration of the light boiler in the reboiler vessel and that of the heavy boiler in the top vessel reach very low values. This can be seen in Figure 5.4, which shows the concentration path in the top and bottom vessels, and on the withdrawal stage.

At this point, somewhere in the column, the concentration of the middle-boiling component reaches a maximum, which is close to one. In order to obtain the maximum possible concentration of the intermediate boiler, the withdrawal stream ( $\dot{W}$ ) is placed close to this stage. During this operation step, which is also referred to as production or open phase, the liquid flow rates to the two column sections are used to control the temperatures in the respective sections, Figure 5.3 (ii), hence determining the concentration of the liquid in the withdrawal stream. Furthermore, the concentrations of the light and heavy-boiling components increase in the top and bottom vessels, respectively.

The concentration profile in the liquid phase at two different times are shown in Figure 5.5. The equilibrium stages are here numbered from bottom to top. It can be seen that ethanol (light-boiling component) is only present on the upper stages of the column. Analogously, 1-butanol is only present in the lower column section. On the other hand, the concentration of 1-propanol is high throughout the column, showing

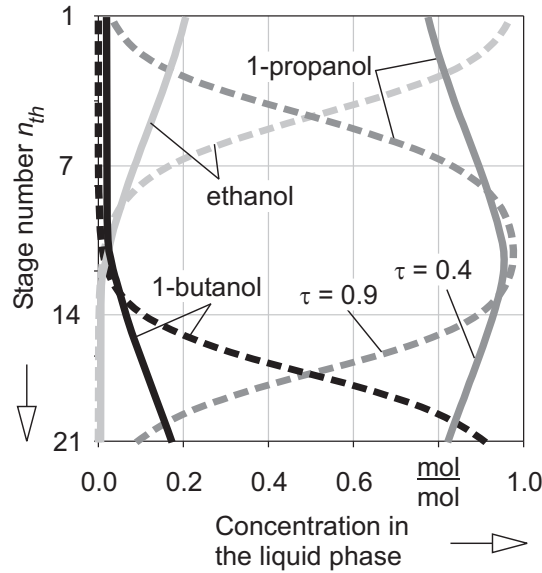


Figure 5.5.: Liquid concentration profile along the column at  $\tau = 0.4$  (full lines) and  $\tau = 0.9$  (dashed lines). The stages are numbered from top to bottom.

a flattened maximum in the middle of the column. The upper (stripping) column section is therefore needed to purify the intermediate-boiling component from the light boiler; and the separation between the intermediate and the heavy boiler occurs in the lower (rectifying) column section. Hence, manipulating the flow rates of the reflux streams to the upper and lower column sections controls the temperature profile in the corresponding sections, and therefore the purity of the withdrawal stream. In other words, the internal reflux ratio of the upper column section  $(\dot{L}/\dot{V})_U$  determines the concentration of light boiler in the product stream; and the internal reflux ratio of the lower section  $(\dot{L}/\dot{V})_L$  determines the concentration of the heavy boiler in the product stream. The internal reflux ratios are related to the flow rate of the product stream  $(\dot{W})$  through the mass balance around the withdrawal stage:

$$\begin{aligned}\dot{W} &= \dot{L}_U - \dot{L}_L \\ &= \dot{V} \cdot \left( \left( \frac{\dot{L}}{\dot{V}} \right)_U - \left( \frac{\dot{L}}{\dot{V}} \right)_L \right)\end{aligned}\quad (5.1)$$

The internal reflux ratios necessary to provide the required purity of the side product are shown in Figure 5.6. During the closed operation phase, when no product is withdrawn from the column (*rel. time*  $\leq 0.38$ ), the column is operated under total reflux conditions:  $(\dot{L}/\dot{V})_L = (\dot{L}/\dot{V})_U = 1$ . During the production phase, the internal reflux ratios are manipulated in the control loops of the two column sections. The flow rate of the product stream is initially ( $0.38 \leq \text{rel. time} \leq 0.60$ ) very high. This is due to the high concentrations of the intermediate boiler in the two vessels. As

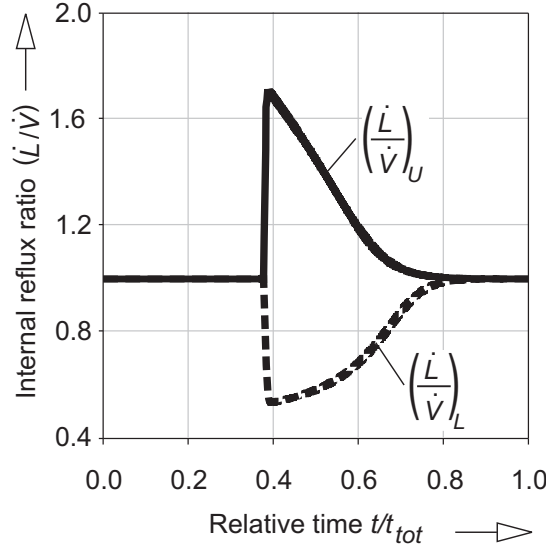


Figure 5.6.: Internal reflux ratios for the upper  $(\dot{L}/\dot{V})_U$  and lower  $(\dot{L}/\dot{V})_L$  column sections.



these concentrations decrease, the separations in both column sections become more difficult, and therefore the internal reflux ratios approach one. Hence, the flow rate of the product stream decreases. Towards the end of the process, the concentrations of 1-propanol in the upper and lower parts of the column are very small. The difference between the internal reflux ratios decreases, drastically reducing the flow rate of the product stream. At the end of the process, the reflux ratios tend towards one and the flow rate of the product stream towards zero:

$$\lim_{\tau \rightarrow 1} (\dot{L}/\dot{V})_L = \lim_{\tau \rightarrow 1} (\dot{L}/\dot{V})_U = 1 \Rightarrow \lim_{\tau \rightarrow 1} \dot{W} = 0 \quad (5.2)$$

A further purification of the light and heavy fractions can be achieved by taking an off-cut. This could be added to the charge of the following batch.

### 5.3. Parametric studies

The analysis of the process parameters is performed by systematically varying one parameter at a time, and studying the changes on the process outputs. The results of this analysis are presented and discussed in the following paragraphs. These are obtained under the assumption that the liquid phase behaves ideally, and that the relative volatilities are constant over the temperature range of the column. The physical properties of the ideal liquid phase are chosen to represent average values for the alcoholic mixture analysed in the previous section. The most important constant parameters applied in the simulation are summarised in Table 5.2.

Table 5.2.: Simulation parameters for the process described in Section 5.3.

Molar fractions in the charge	$(x_a, x_b, x_c)$	(0.1, 0.8, 0.1)
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	2.0
Number of equilibrium stages	$n_{th}$	15
Position of withdrawal stream	$n_W$	8
Position of upper TC	$n_U^{TC}$	6
Position of lower TC	$n_L^{TC}$	10
Setpoint to upper TC	$T_U^{SP}$	374 K
Setpoint to lower TC	$T_L^{SP}$	379 K

### 5.3.1. Geometric parameters

The geometric parameters influencing the separation capability of the process are the number of equilibrium stages and the position of the withdrawal stage. These are usually chosen during the design stage of the column, and the operator does not have the possibility to change them during operation. Other geometric parameters, such as column internals and diameter, are not considered here, since these have no influence on the thermodynamic study based on the equilibrium stage model.

#### Number of equilibrium stages

In this investigation, the total number of stages of the column is varied, while the other parameters are kept constant. The withdrawal stage is placed in the middle of the column so that the two column sections have the same number of equilibrium stages. Furthermore, the column is operated in closed loop and the relative position of the controlled temperatures with respect to the withdrawal stage is maintained unvaried. The set-points to the controllers are also kept constant. In this way, the concentration profile around the withdrawal stage is maintained constant throughout the investigation, and the composition of the withdrawal stream is independent of the total number of stages.

With increasing number of equilibrium stages, lower reflux ratios are required to achieve the required purity of the intermediate-boiling component. Hence, with increasing number of stages, the flow rate of the withdrawal stream increases, and in turn, the batch time decreases. Similarly to conventional batch distillation, the required concentration of the intermediate boiler can be reached only if the number of stages per column section is higher than the minimum number of stages. This, in turn, depends on the concentrations of the intermediate boiler in the top and bottom vessels. Therefore, the concentrations of the intermediate boiler in the top and bottom vessels at which the process becomes infeasible, decrease with increasing number of stages. The recovery of the intermediate boiler and the purities of the light and heavy-boiling components both increase with increasing number of stages.

#### Position of withdrawal stage

The position of the withdrawal stage determines the relative size of the two column sections. Hence, the optimal position of the withdrawal tray depends on the relative volatility of the components being separated in the corresponding column section. This means that the size of the upper column section is determined by the relative volatility between the light and the intermediate-boiling components ( $\alpha_{ab}$ ), and similarly, the size of the lower column section is determined by that between the intermediate and heavy boilers ( $\alpha_{bc}$ ). If, for instance, the separation of the intermediate boiler from the low boiler is more difficult than that from the high boiler, then a longer upper column section would be required and the position of the withdrawal

tray would shift downwards. In the case that the two separations are similar, then the best position for the withdrawal point would be the middle of the column.

### 5.3.2. Operational parameters

The column presents several operational parameters. Usually, the operator has access to some or all of these parameters during the operation of the process. Therefore, the operational parameters can be varied to reach the required separation. Among them, we find the composition of the charge, the reflux ratios, and the termination of the closed operation step.

#### Composition of the charge

To study the effect of the composition of the charge, equal amounts of feeds of different compositions are processed in the same column operated in closed loop. The separation task, i.e. the required composition of the intermediate-boiling fraction, is also unchanged throughout the investigation. The effect of the composition of the intermediate-boiling component on the duration of the process, and therefore on the energy demand, is shown in Figure 5.7. The duration of the process goes through a maximum. On the left-hand side of this maximum, the recovery of the intermediate boiler in the side product is very low. This is due to the fact that, for the given number of stages, the separation becomes infeasible at lower product recoveries. Therefore, the shorter duration of the process is not representative of reality.

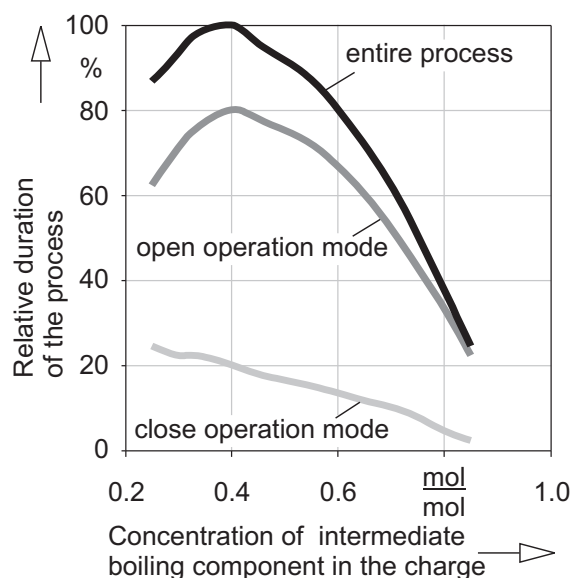


Figure 5.7.: Relative duration of the process versus the concentration of the intermediate boiler in the charge.

On the right-hand side of the maximum, the duration of the process decreases with increasing concentration of the intermediate-boiling component in the feed. This can be explained with the aid of Figure 5.8, which is a plot of the internal reflux ratios against the relative process time, with the concentration of the intermediate boiler in the charge ( $x_{b,\alpha}$ ) as parameter. For high concentrations of the intermediate boiler in the charge, the internal reflux ratios differ largely from one. This corresponds to a high production rate of the intermediate-boiling fraction. Therefore, at high concentrations of intermediate-boiling component, it is possible to withdraw a larger amount of product at higher flow rates. In their comparison of the inverted and regular batch distillation columns, Sørensen and Skogestad [1996] find similar results. They demonstrate that when the mixture to be separated is richer in the light-boiling component, a regular batch distillation column is time-saving when compared to an inverted batch distillation column.

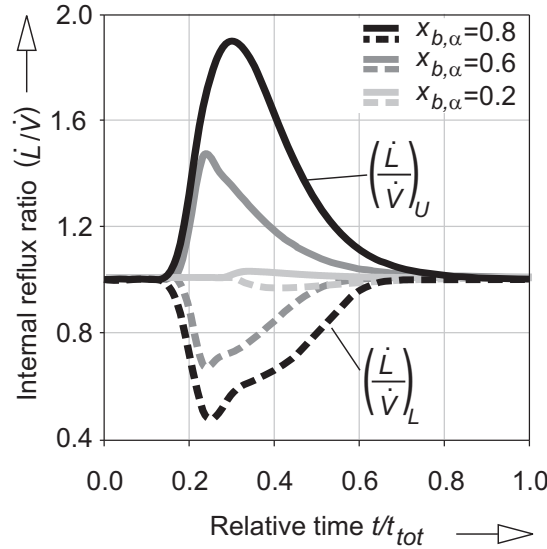


Figure 5.8.: Effect of the composition of the intermediate-boiling component in the charge ( $x_{b,\alpha}$ ) on the internal reflux ratios in the upper and lower column sections.

It can be further observed that the duration of the initial separation step also decreases with increasing concentration of intermediate boiler in the charge. During this phase the column is operated at total reflux. The duration of this step is therefore determined only by the amount of components that has to be transferred between the two vessels, and by the termination criterion.

### Termination criteria for the first process step

Increasing the duration of the first process step reduces the concentration of the light-boiling component in the sump, and that of the heavy boiler in the top vessel. Hence,

with increasing duration of this process step, the concentration of the intermediate-boiling component at the withdrawal point increases. This leads to: lower internal reflux ratios at the beginning of the second process step, higher feasible concentration of the intermediate-boiling fraction, and higher recoveries of the light and heavy-boiling fractions. Nevertheless, long times are required to obtain a pure intermediate-boiling component on the withdrawal stage. Therefore, the best termination criterion should be determined by process optimisation.

Our subsequent investigations are limited to the case that the feed is much richer in the intermediate boiler than in light and heavy boilers. In such cases, the relative content of the extreme boilers plays a minor role and influences mainly the duration of the start-up of the process i.e. the closed operation mode.

### Effect of the internal reflux ratios

In the first process step, the light and heavy-boiling components are separated under total reflux conditions. The analysis of the effect of different reflux ratios can therefore be limited to the second process step. During this study, it is assumed that the initial concentration of the light boiler in the sump, and that of the heavy boiler in the distillate vessel are both zero. The study is limited to the second process step. During this phase, the internal reflux ratios are set to constant values. The simulation is interrupted when one of the vessels is empty.

In Figure 5.9, the concentration of the intermediate boiler in the withdrawal stream ( $x_{Wb}$ ) and its molar recovery ( $\sigma_b$ ) are plotted against the relative distillation time for

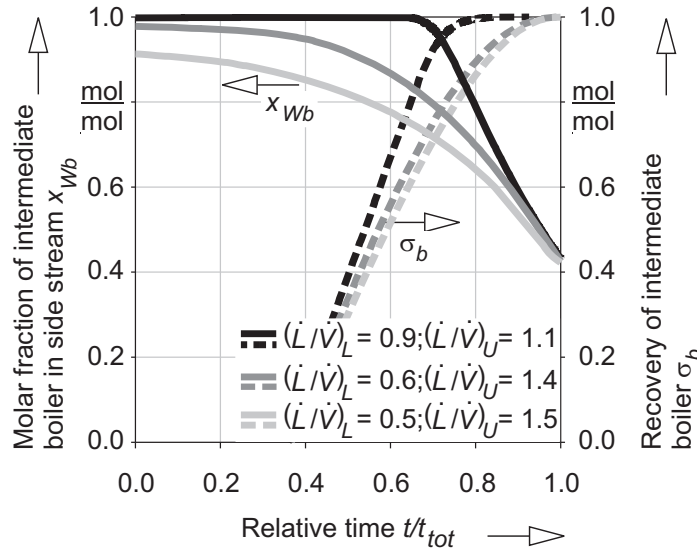


Figure 5.9.: Concentration of the side product (full lines) and molar recovery (dashed lines) plotted versus the relative distillation time, for different internal reflux ratios.

different values of internal reflux ratios. This plot shows that to achieve high recovery and high purity in the intermediate product, high reflux ratios are required. On the other hand, increasing the reflux ratios increases the duration of the process. However, at the end of the process, the applied constant internal reflux ratios are not able to maintain the purity of the product.

Additionally, to study the interactions between the two column sections, the internal reflux ratio of the upper column section  $(\dot{L}/\dot{V})_U$  is varied while the internal reflux ratio in the lower section  $(\dot{L}/\dot{V})_L$  is kept constant. It is observed that the concentration of high-boiling impurity in the side product increases as the internal reflux ratio in the upper column section  $(\dot{L}/\dot{V})_U$  decreases. The concentration of the low boiler in the withdrawal stream changes very slightly. Furthermore, the concentration of the heavy boiler in the upper column section considerably increases with decreasing  $(\dot{L}/\dot{V})_U$ , indicating a strong interaction between the upper and lower column sections.

## 5.4. Comparison with the middle vessel batch distillation column

Among others, Warter et al. [2002] and Skouras and Skogestad [2004b], analysed the batch distillation column with a middle vessel for the separation of zeotropic ternary mixtures. They state that, in some cases, the middle vessel batch distillation column might present important advantages over the regular batch distillation column. An extremely important advantage of this column is that the components in the feed are subject to a lower thermal stress. This is due to the possibility of keeping the charge cooled in the middle vessel, hence allowing separations that would otherwise be impossible to carry out in a conventional batch distillation column. Further advantages are the simpler process control and handling of liquid fractions; higher flexibility; and lower energy demand [Warter 2001].

Here, the batch distillation column with side withdrawal is compared with the middle vessel batch distillation column. The middle vessel batch distillation column, shown in Figure 5.10, consists of two column sections connected by the middle vessel. The upper column section functions as a regular batch column, while the lower column section resembles an inverted column. The low-boiling component is separated from the intermediate boiler in a rectifying section (upper section). The heavy-boiling component is simultaneously separated from the intermediate boiler in the inverted column (lower section). On the other hand, in Figure 5.1 it has been shown that the batch distillation column with side withdrawal can be visualised as an inverted batch distillation column placed on top of a regular batch distillation column. Here, the separation between the intermediate and the light-boiling components is carried out in an inverted column. The separation between the intermediate and the heavy-boiling components is simultaneously carried out in a regular column. This structural difference between the two columns is the base for their different behaviour.

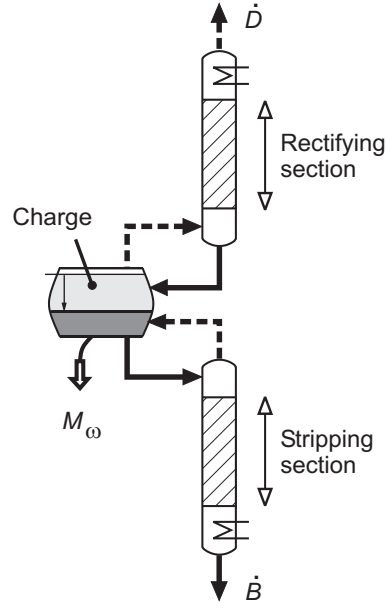


Figure 5.10.: Batch distillation column with a middle vessel.

The duration of the separation task carried out in the two columns is plotted in Figure 5.11 as a function of the concentration of the intermediate boiler in the charge and of the relative volatilities  $\alpha_{ab}$  and  $\alpha_{bc}$ , under the condition that these are equal ( $\alpha_{ab} = \alpha_{bc}$ ). The total number of stages, the final purity of the intermediate-boiling fraction, and the recovery of the middle-boiling component are the same in both processes. Both processes are operated with a constant heat duty. Furthermore, both the middle vessel and the side withdrawal stream are placed in the middle of the column. The simulation data is summarized in Table 5.3.

Table 5.3.: Simulation parameters for Section 5.4.

Number of equilibrium stages	$n_{th}$	28
Position of withdrawal stream	$n_W$	14
Position of middle vessel	$n_M$	14
Concentration of middle boiler in product:		
$\alpha_{ab} = \alpha_{bc} = 1.50$	$x_{Wb\omega}$	0.96
	$x_{Mb\omega}$	0.96
$\alpha_{ab} = \alpha_{bc} = 2.0$	$x_{Wb\omega}$	0.98
	$x_{Mb\omega}$	0.98
$\alpha_{ab} = \alpha_{bc} = 2.5$	$x_{Wb\omega}$	0.98
	$x_{Mb\omega}$	0.98

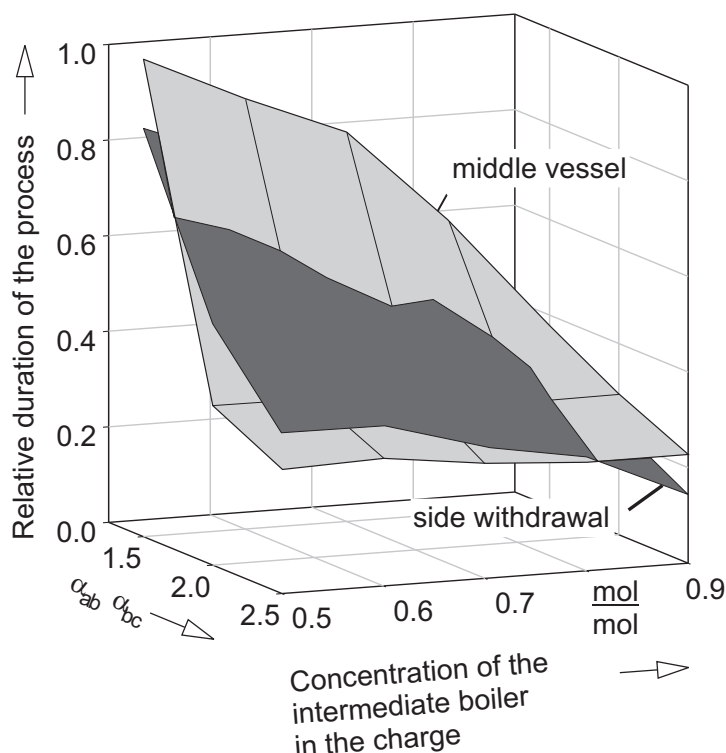


Figure 5.11.: Comparison of the relative duration of a batch distillation process in a middle vessel with that in a column with a side withdrawal.

For very difficult separations (low relative volatilities), the process with the side withdrawal requires shorter time, and therefore it has a lower energy demand, than that in the middle vessel column. On the other hand, for higher values of the relative volatilities, this is true only for mixtures that are very rich in the intermediate-boiling component.

Furthermore, in the middle vessel column, the two column sections are separated from each other by a huge holdup, and therefore the two sections are dynamically decoupled [Farschman and Diwekar 1998]. Unfortunately, this is not the case for the column with side withdrawal. The vapour passes directly from the lower to the upper column section, and the liquid phase flows directly from the upper to the lower column section. This introduces strong interactions between the two column sections. The design of the two control loops therefore has a higher degree of complexity. Nevertheless, if the required high purity product is the intermediate boiler, the column with side withdrawal allows for direct control of its purity, whereas in the middle vessel column, it is only possible to control the purity of the light and heavy components (impurities). The purity of the intermediate-boiling fraction therefore results from the extent of the distillation.



## 5.5. Experimental validation of the process

The batch distillation process with a side withdrawal was experimentally investigated in collaboration with Degussa AG. The aim of the experiments was to validate the operating procedure described in Section 5.2.

### 5.5.1. Apparatus

A simplified flow sheet of the experimental apparatus is shown in Figure 5.12. This is a packed distillation column having an internal diameter of 50 mm. The column is divided into three packed sections (S1, S2 and S3), each with a height of 1 m. It is possible to feed and withdraw a liquid stream above each column section. The vapour stream cannot leave the column, it therefore flows directly from each section to the one placed directly above. The lowest column section (S3) is placed above the reboiler (B3). This is a 20 l vessel provided with a spiral heat exchanger (W3), heated via a 3 kW thermostat. The uppermost section is connected to a vertical spiral condenser (W1). By operating valve V1, the condensate can either be fed back to the column, or be withdrawn to the stirred tank (B1) placed close to the head of the column. Liquid can be pumped (P1) back from this vessel to the column's head. This liquid stream passes through a heat exchanger (W2), where it is pre-heated before being fed back to the column. This avoids wild condensation of the rising vapour.

The temperature is measured at eleven points (TR2-TR12) along the column, at the condenser (TR1), in the reboiler (TR13), and in the liquid streams leaving and entering the column. The flow rate of the liquid stream leaving vessel B1 and the mass of liquid accumulated in the vessels B1 and B2 are also measured. Liquid samples are taken from the liquid streams entering and leaving the column, and from the reboiler vessel.

The individual column sections, the flanges connecting the various column parts and the reboiler are all insulated against thermal losses. Furthermore, the column can be ventilated with an inert gas, such as nitrogen. This gas leaves the top of the column via a vacuum pump (not shown in the flow sheet), which allows for the regulation of the operating pressure at the condenser.

### 5.5.2. Experimental procedure

The total charge has a mass of 10.4 kg, and a composition of 0.101 mol/mol ethanol, 0.798 mol/mol 1-propanol, and 0.101 mol/mol 1-butanol. The charge is divided in two equal parts. One part is charged to the reboiler (B3), and the second one is loaded into the distillate vessel (B1) connected to the head of the column. The liquid in the reboiler is heated with a constant heating load of approximately 2.7 kW. When the mixture in the reboiler reaches its boiling point, vapour starts to rise along the column. The temperatures in the column therefore rise from the bottom upwards. The rising vapour finally reaches the condenser (W1), where it is condensed. The condensate

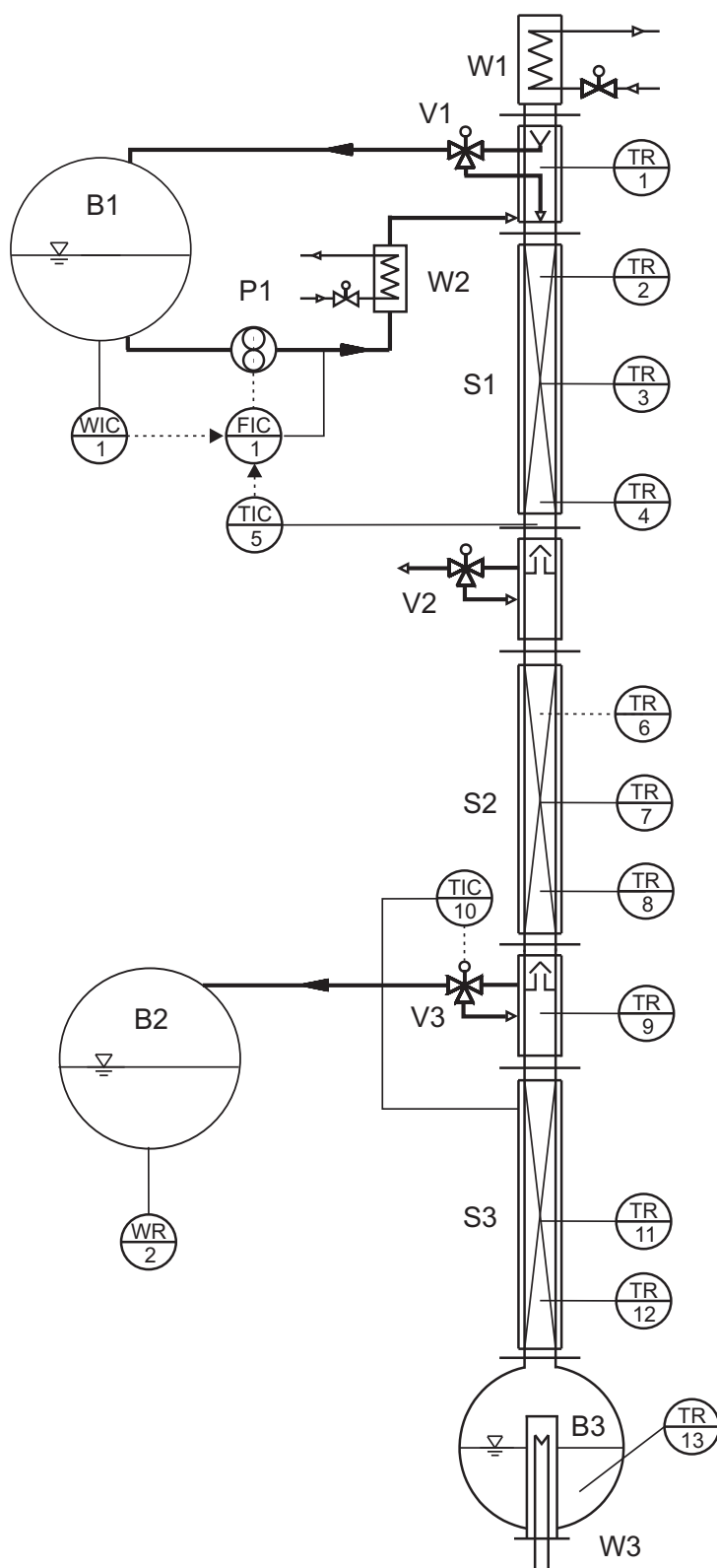


Figure 5.12.: Simplified flow sheet of the experimental apparatus.

is sent to the top vessel (B1). At this point, liquid is fed back from this vessel to the column, keeping the mass of liquid in the vessel constant (WIC1). This feed is pre-heated in W2 before entering the column. The liquid flowing down the column is passed from each section to its underlying one, without any being withdrawn. Enough time is allowed for the temperature profile along the column to reach steady state conditions. An offline analysis of the liquid in the top vessel and in the reboiler shows that the light boiler has depleted from the reboiler, and the heavy boiler is no longer present in the top vessel.

At this point, the control loop of the upper column section is changed to temperature control mode, i.e. WIC1 is deactivated, and TIC5 is activated. Simultaneously, the temperature control loop of the lower column section (TIC10) is closed. The upper control loop regulates the temperature in the upper column section by manipulating the flow rate of the liquid fed from the top vessel to the column. On the other hand, the lower temperature control loop manipulates the reflux ratio in the lower column section. This is achieved by operating valve V3, placed between the column sections S2 and S3.

### 5.5.3. Temperature and concentration profiles

A better understanding of the process and the operating procedure can be achieved by following the temperature and the concentration profiles shown in Figure 5.13 and Figure 5.14, respectively. The profiles are plotted starting from the point when the first vapour reached the condenser.

During the initial phase of the process, the total reflux operation, the temperatures in the reboiler vessel (T13) and in the lower column section (T10-T12) rise slightly, to reach steady state conditions. As the concentration profile clearly shows, during this

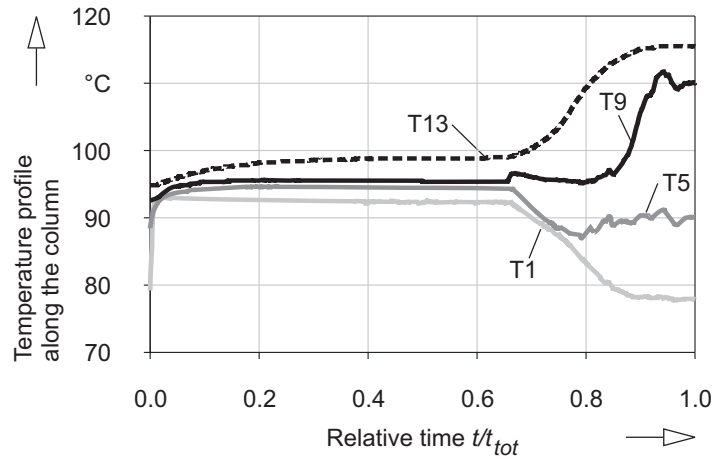


Figure 5.13.: Experimental temperature profile along the distillation column with a side withdrawal.

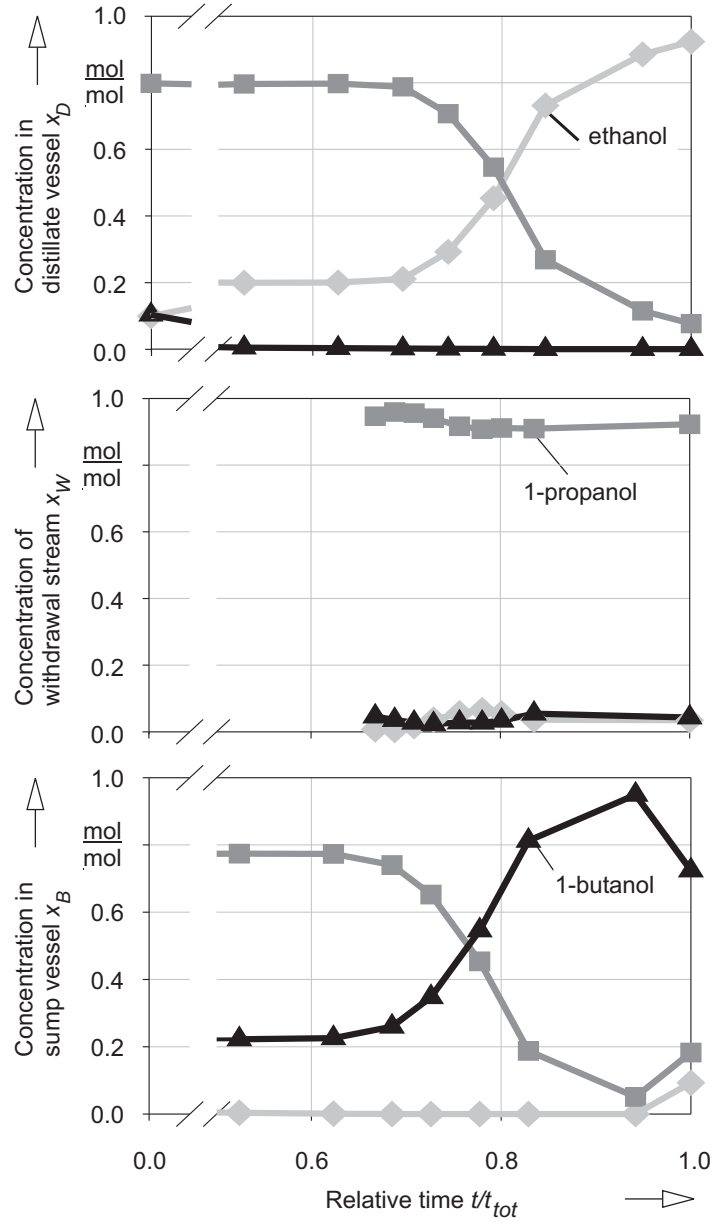


Figure 5.14.: Experimental concentration path in the distillate vessel (top), of the withdrawal stream (middle) and in the sump (bottom) for the distillation column with a side withdrawal.

process phase, the light boiler is transferred from the sump to the top vessel, and the heavy boiler follows the opposite path from the top to the sump vessel. By the end of this process phase ( $\tau = 0.66$ ), the temperature profile reaches steady state conditions, and the concentration of the light boiler in the sump and that of the heavy boiler in the top vessel reach very low values. This time is located via a real time analysis of the liquid phase in the reboiler and of that in the top vessel. The concentration of the intermediate boiler at the withdrawal point has, by this time, reached the required value. The control loop in the upper column section is therefore turned from mass to temperature control, and the temperature control loop of the lower column section is simultaneously closed. The reference temperatures of the two column sections are directed by the controller towards their set points. The liquid holdup in the top vessel and in the sump start decreasing, and the product is collected in the side vessel (B2). The concentration of the intermediate boiler is successfully maintained to the desired value. The concentration of the light boiler in the top vessel gradually increases as that of the intermediate boiler decreases. Analogously, the concentration of the heavy boiler in the sump increases. This is accompanied by a decrease in the temperature at the column's head, and by a temperature increase in the sump. Towards the end of the process, the temperature profile in the column stabilises once more ( $\tau = 0.90$ ), and the flow rate of the withdrawal stream ( $\dot{W}$ ) tends to zero.

The final concentrations and recoveries are given in Table 5.4. At the end of the process, the intermediate boiler has been recovered with the desired concentration ( $x_{B2\omega} = 0.92$  mol/mol) and with a high recovery ( $\sigma_b = 0.98$ ). Nevertheless, the concentration and recovery of the light and heavy-boiling fractions are low.

Table 5.4.: Summary of experimental results.

	Molar fraction of main product	Recovery of main product
Top Vessel (B1)	0.92	0.57
Side Vessel (B2)	0.92	0.98
Sump (B3)	0.72	0.62

#### 5.5.4. Conclusion

The simulated and experimental concentration paths of the withdrawal stream as well as those in the top and bottom vessels are in qualitative agreement. Therefore, the experimental investigation confirms the feasibility of process, and furthermore, the practical realisation of the batch distillation process with side withdrawal is demonstrated. Moreover, both the theoretical and the experimental investigations show that this batch distillation process is adequate for the purification of an intermediate boiler from light and heavy-boiling contaminants.

## 6. Integration of batch reaction with batch distillation - Equilibrium limited reactions

In recent years, there has been extensive research on process integration. Most of this research has focussed on attempts to integrate reaction with separation steps for complex continuous processes. In such cases, it might be possible to reduce very complex flowsheets to a couple of units where reaction and separation occur simultaneously. As has already been pointed out in the literature review, process integration for batch distillation has not received the same attention paid to continuous processes. This might be due to the fact that batch processes are usually applied in multipurpose plants where the same reactor is used for the production of various chemicals. For instance, in the pharmaceutical industry, flexibility of the batch units, hygiene and sterilisation are of primary importance. Nevertheless, batch reactors are very often directly coupled with a condenser or with a batch distillation column, as shown in Figure 6.1.

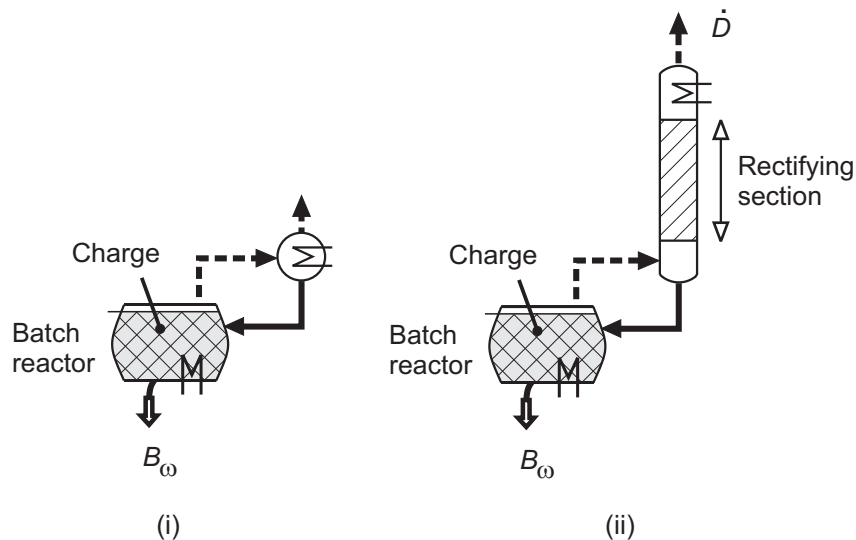


Figure 6.1.: Combination of a batch reactor with (i) a condenser, and (ii) a rectifying column.

To this date, little attention has been paid by the academic literature to the conceptual design of processes where a batch reactor is coupled with a batch distillation column. In order to fill this gap, in the following sections, some of the alternative processes in which a batch reactor is combined with a distillation unit are analysed via computer aided simulations. A few illustrative reaction families are considered. The various process alternatives are discussed for each family, and, where possible, the processes are compared in order to give to the process designer tools to select the appropriate process.

Every chemical reaction can be considered as an equilibrium reaction, where the concentrations of the reactants and the products are in equilibrium. If enough time is allowed for the reaction to reach equilibrium, the final concentration in the reactor is limited by the value of the equilibrium constant ( $K_{eq}$ ) which relates the concentrations of the products ( $x_p$ ) to that of the reactants ( $x_r$ ):

$$K_{eq} = \frac{\prod_p x_p^{\nu_p}}{\prod_r x_r^{\nu_r}} \quad (6.1)$$

where  $\nu_i$  indicates the stoichiometric coefficient of component  $i$ . In some cases, the equilibrium constant might be big enough for the reaction to reach almost complete conversion. On the other hand, for moderate values of the equilibrium constant, the conversion is limited by the equilibrium curve, so that non-reacted educts are still present in the reaction mixture even after infinite time. In this case, a separation step is required to recover the reactants; these are usually allowed to react once more. Le Chatelier's principle tells us that if one of the products is removed from the reaction environment, the reaction system shifts to re-establish equilibrium conditions, i.e. it tends to produce more of the removed product. Therefore, integrating reaction with separation yields higher conversions than those allowed by the equilibrium relationship.

## 6.1. Decomposition reaction

From the point of view of a distillation process, the boiling point order of the components present in the reaction mixture is of primary importance. As a first example, the case where an intermediate-boiling component ( $b$ ) decomposes into a light boiler ( $a$ ) and into a heavy boiler ( $c$ ) is considered.



For this reaction type, there are many process alternatives which the designer should consider. Since both products are extreme boilers, any one can be removed by a distillation process, and therefore the chemical equilibrium is shifted to the product's

side. The batch reactor can be alternatively coupled with a rectifying, a stripping, or a middle vessel column, as shown in Figure 6.2. In the first case, the light-boiling product ( $a$ ) is recovered at the head of the column, and as the reaction proceeds, the heavy boiler is enriched in the reactor placed at the sump. For the combination of a batch reactor with a stripping column, the heavy-boiling product ( $c$ ) is recovered from the sump. As the reaction proceeds, the light boiler is enriched in the reactor placed at the column's head. In a middle vessel column, the reactor takes the place of the middle vessel. The two products are simultaneously recovered from the top and bottom of the column. The concentration path in the middle vessel is bound by the equilibrium curve, and depends on the flow rates of the two product streams.

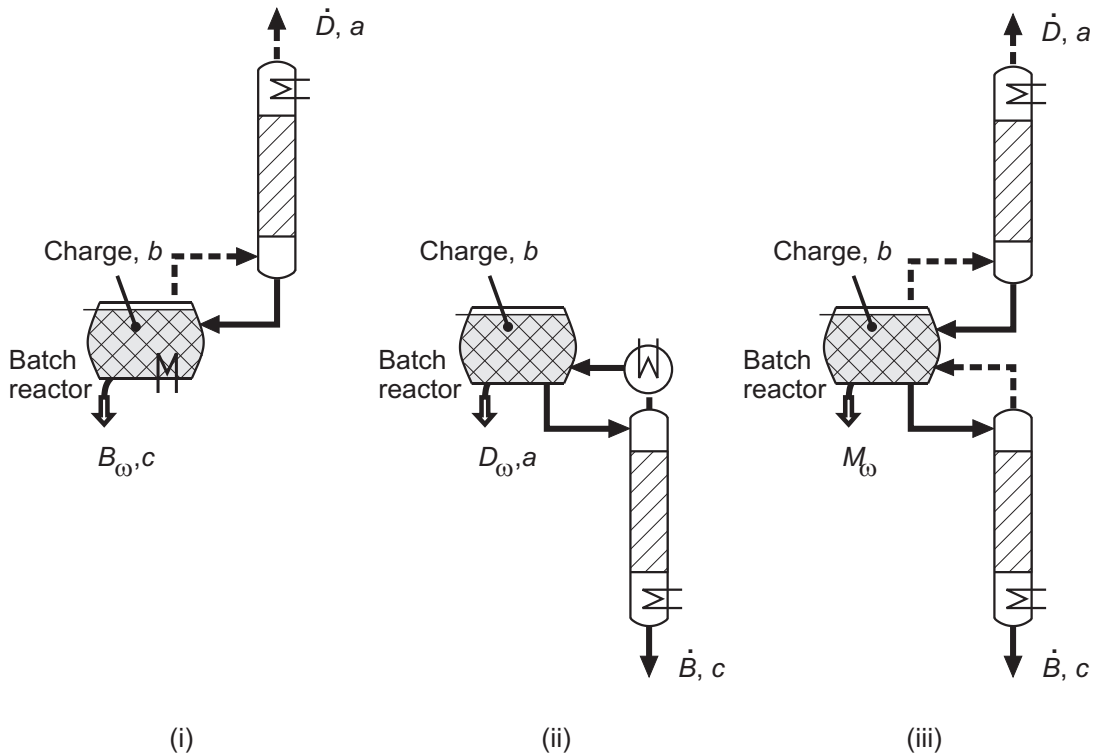


Figure 6.2.: Combination of a batch reactor with (i) a rectifying, (ii) a stripping, and (iii) a middle vessel column.

### 6.1.1. Minimum energy demand

One tool available to the process designer to perform a pre-selection among the three processes introduced in the previous paragraph, is the minimum energy demand of the process. The calculation of the minimum energy demand requires knowledge of the concentration in the still. For fast equilibrium reactions, the concentration in the reactor always lies on the chemical equilibrium curve. To facilitate the calculation, the



concentration change in the reactor can be constructed as a series of infinitesimally small distillation and reaction steps. This graphical construction is here explained with the aid of Figure 6.3 for the reaction



carried out in a batch reactor coupled with a rectification column having an infinite number of stages. An infinitesimal distillate withdrawal, with the light-boiling component ( $a$ ) having a concentration  $x_{Da} = 1$ , shifts the concentration in the reboiler from  $x_B$  along a straight line joining  $x_D$  and  $x_B$ . This is depicted in Figure 6.3 with  $(\Delta D)$ . The new concentration lies away from the chemical equilibrium. The infinitesimal reaction step  $(\Delta R)$  brings it back to the chemical equilibrium curve, moving along a stoichiometric line. Therefore, the concentration in the reboiler moves along the chemical equilibrium curve away from the concentration of the distillate product, and towards the heavy boiler ( $c$ ) which is obtained at the end of the process in pure form in the reactor vessel. The concentration path in a reactor coupled either with a stripping column, or with a middle vessel column, is constructed in a similar way.

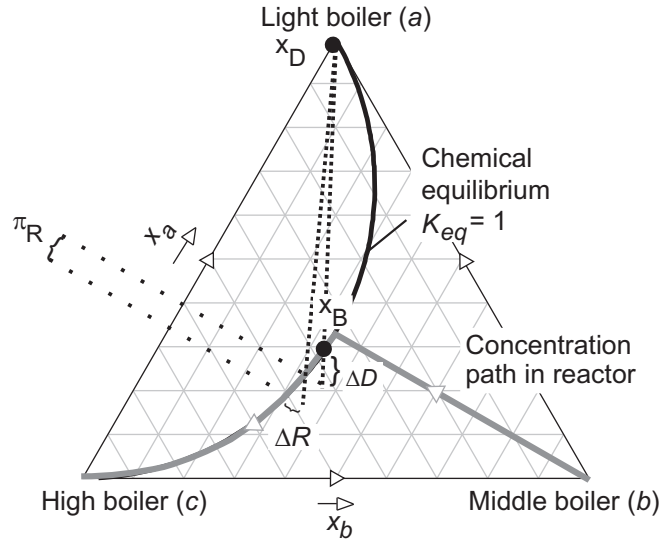


Figure 6.3.: Infinitesimal construction of the concentration path in the batch reactor coupled with a rectifying column for the Reaction (6.3).

The dimensionless minimum energy demand for a batch reactor coupled with a rectifying, a middle vessel and to a stripping batch distillation column, is shown in Figure 6.4 for various values of the relative volatilities. In the three cases, the chemical equilibrium constant has a value of  $K_{eq} = 1.0$ . The dimensionless minimum energy demand is expressed as:

$$Q_{min}/(r \cdot F) \quad (6.4)$$

with  $Q_{min}$  being the minimum energy demand of the process,  $r$  the latent heat of vaporisation of the charge, and  $F$  the amount of charge.

The process where a reactor is coupled with a middle vessel column has the lowest minimum energy demand for the whole conversion range, if the relative volatility of the light boiler ( $a$ ) to the intermediate boiler ( $b$ ) is equal to that of the intermediate boiler to the heavy boiler ( $\alpha_{ab} = \alpha_{bc}$ ), Figure 6.4 (ii). The combination of a batch reactor with a rectifying column requires the lowest minimum energy demand over a wide range of conversions if the relative volatility  $\alpha_{ab}$  is bigger than  $\alpha_{bc}$ , Figure 6.4 (i). Finally, the combination of a batch reactor with a stripping column could be advantageous if the separation of the heavy boiler from the intermediate boiler is easier than that between light and intermediate boiler ( $\alpha_{ab} < \alpha_{bc}$ ).

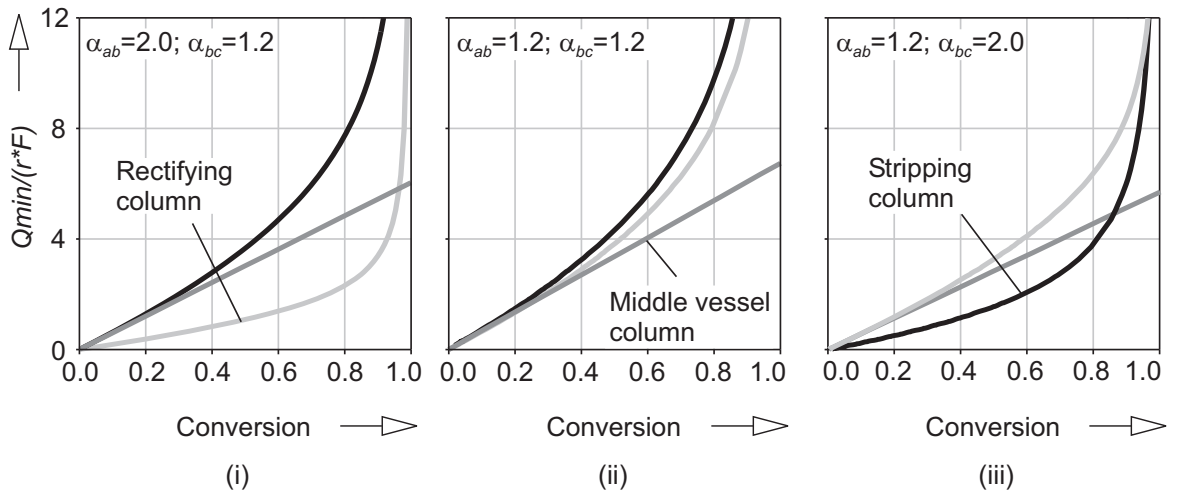


Figure 6.4.: Minimum energy demand for the combination of a batch reactor with a rectifying, a middle vessel and a stripping column, for the Reaction (6.3), with  $K_{eq} = 1$  and (i)  $\alpha_{ab} = 2.0$ ,  $\alpha_{bc} = 1.2$ , (ii)  $\alpha_{ab} = \alpha_{bc} = 1.2$ , and (iii)  $\alpha_{ab} = 1.2$ ,  $\alpha_{bc} = 2.0$ .

The stoichiometry of the reaction also influences the energy demand of the three processes. This is illustrated in Figure 6.5. Here, three equimolar reactions are taken into consideration. The minimum energy demand of a batch reactor coupled with a rectifying column decreases with increasing stoichiometric coefficient of the light-boiling component,  $\nu_a$ . This appears to be in contradiction with the fact that by increasing the stoichiometric coefficient of the light boiler, the amount of distillate to be recovered increases. On the other hand, the higher concentration of the light-boiler in the reactor allows for lower reflux ratios to be applied, therefore decreasing the energy demand. In the case that the stoichiometric coefficient of the light boiler is bigger than that of the heavy boiler ( $\nu_a > \nu_c$ ), this process presents a lower minimum energy demand than the combination of a batch reactor with a middle vessel column, also for very high conversions, as shown in Figure 6.5 (i). Analogously, the minimum

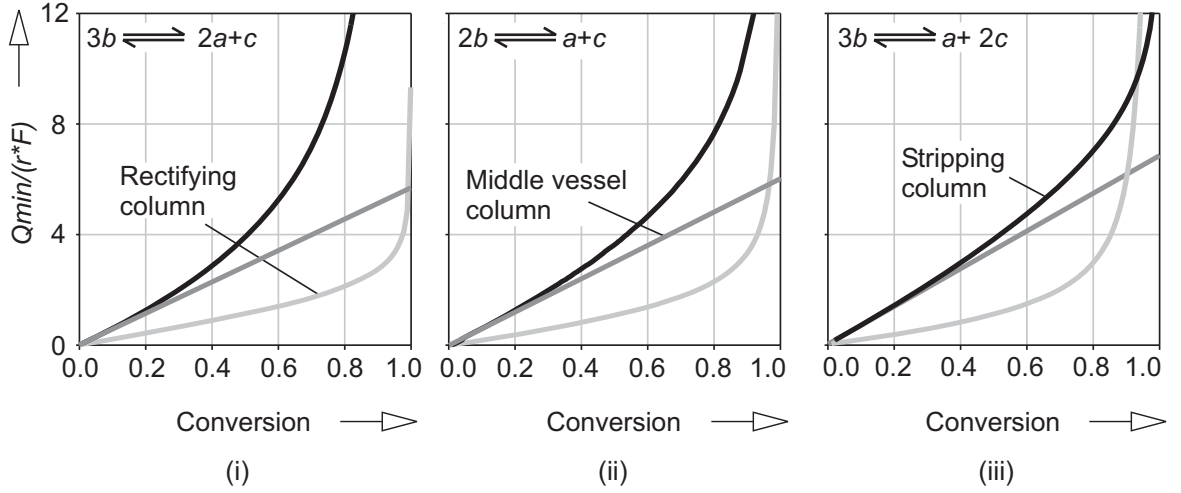


Figure 6.5.: Minimum energy demand for the combination of a batch reactor with a rectifying, a middle vessel and a stripping column, for the reactions (i)  $3b \rightleftharpoons 2a+c$ , (ii)  $2b \rightleftharpoons a+c$ , and (iii)  $3b \rightleftharpoons a+2c$ , with  $K_{eq} = 1$ ,  $\alpha_{ab} = 2.0$ , and  $\alpha_{bc} = 1.2$ .

energy demand of a batch reactor coupled with a stripping column decreases with increasing stoichiometric coefficient of the heavy boiler.

### 6.1.2. Combining a reactor with a rectifying batch distillation column

In this section a reactor is coupled with a rectifying batch distillation column as shown in Figure 6.6 (i). The decomposition Reaction (6.3):



takes place in the liquid phase within the reactor. The rectifying column has 30 equilibrium stages, and the concentration of the distillate product is maintained constant at  $x_{Da} = 0.98$ . The relative volatilities are  $\alpha_{ab} = 2.0$  and  $\alpha_{bc} = 1.5$ . The concentration profile in the reactor is shown in Figure 6.6 (ii). This has been obtained via rigorous simulation of the process, and compares very well with the concentration path shown in Figure 6.3 obtained via a geometrical construction. Every symbol in Figure 6.6 (ii) represents a time unit. At the beginning of the process, the fast decomposition reaction moves the concentration in the reactor from its initial point  $x_{B\alpha}$  along a stoichiometric line to the equilibrium curve. Since the light boiler is removed as distillate product, the concentration in the reactor moves along the chemical equilibrium curve away from the light-boiling component, and towards the heavy boiler (c). At the end of the process, the reactor contains the heavy-boiling product at

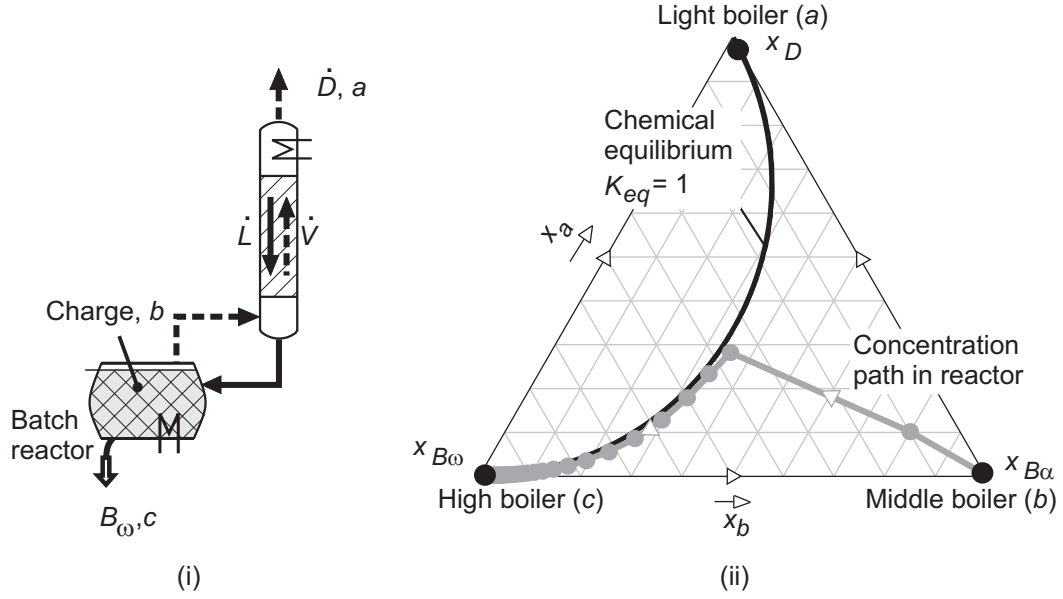


Figure 6.6.: Batch reactor coupled with a rectifying column (i) process scheme, and (ii) concentration path in the reactor for the Reaction (6.5).

the required purity. The reflux ratio ( $R_L$ ), Equation (6.6a), necessary to maintain the required distillate purity, and the recoveries of the two reaction products ( $\sigma_{Da}$  and  $\sigma_{Bc}$ ), defined in Equations (6.6b) and (6.6c), are plotted as a function of the relative distillation time in Figure 6.7 (i). It is evident that the last 10% recovery of the products consumes 80% of the total distillation time, and therefore of the total energy demand. This is clearly due to the very high reflux ratios required at the low concentrations of light boiler in the sump of the column during most of the process time.

$$R_L = \frac{\dot{L}}{\dot{D}} \quad (6.6a)$$

$$\sigma_{Da} = \frac{\nu_b \cdot D_a}{\nu_a \cdot B_{b,\alpha}} \quad (6.6b)$$

$$\sigma_{Bc} = \frac{\nu_b \cdot B_c}{\nu_c \cdot B_{b,\alpha}} \quad (6.6c)$$

It is therefore attempted to improve the process by imposing a maximum limit on the reflux ratio. When the reflux ratio reaches its maximum value ( $R_{L,max} = 50$ ), a low purity off-cut is taken at a lower reflux ratio ( $R_{L,off} = 10$ ). The off-cut is necessary to purify the heavy-boiling product from the non-reacted educt still present in the sump. With two such simple moves, the process time is reduced by 56%, but the recovery of the heavy-boiling product also decreases to  $\sigma_{Bc} = 85\%$ , since some unreacted educt is lost with the off-cut. As shown in Figure 6.7 (ii), during

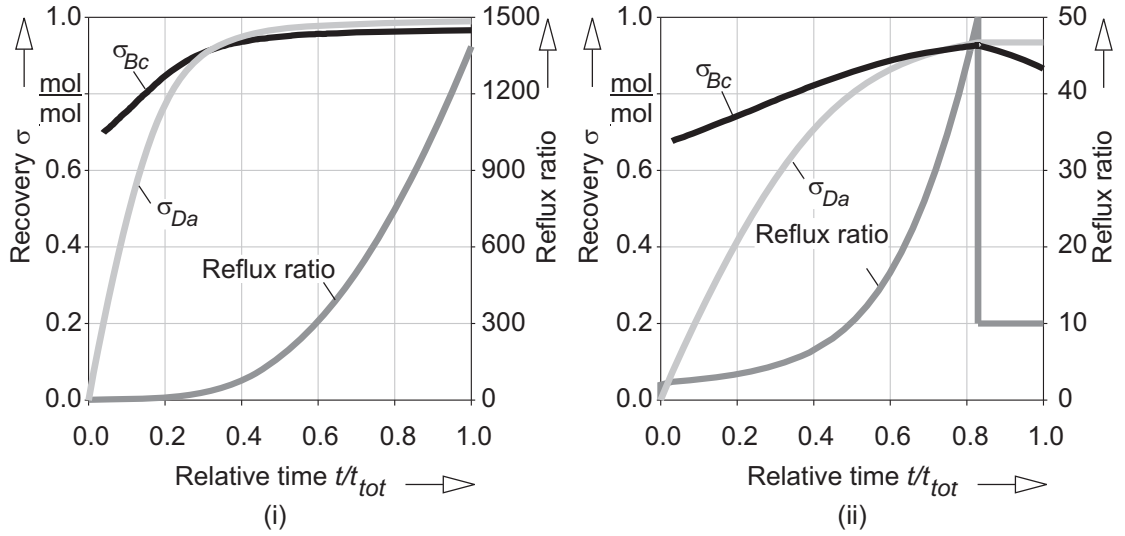


Figure 6.7.: Recovery of the light and heavy boilers, and reflux ratio for the Reaction (6.5) carried out in a batch reactor coupled with a rectifying column: (i) for the process without off-cut, and (ii) with off-cut.

the withdrawal of the off-cut, there is a decrease in the recovery of the heavy-boiling component, because some is lost with the off-cut. This phase is nevertheless necessary to reach the required high concentration of the sump product.

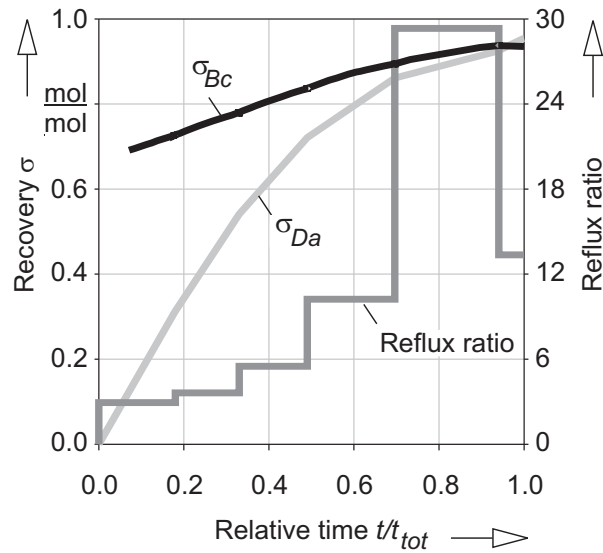


Figure 6.8.: Recovery of the light and heavy boilers, and reflux ratio for the Reaction (6.5) carried out in a batch reactor coupled with a rectifying column: optimised process.

In the two operating procedures described in the previous paragraphs, it is necessary to continuously adjust the reflux ratio in order to maintain the necessary distillate composition. Alternatively, the reflux ratio can be forced to follow a stepwise profile, i.e. it is maintained constant for given time intervals. An example of this reflux policy can be found in Li et al. [1998b]. They state that such a stepwise reflux profile is in practice easier to implement than a continuously changing reflux. Figure 6.8 shows the recoveries of the two reaction products for the modified process where a stepwise reflux ratio policy is used. The duration of the process is minimised under the conditions that the final purity of the distillate product is bigger than  $x_{Da, \omega} \geq 0.97$  mol/mol, and its recovery higher than  $\sigma_{Da} \geq 95$  %. Furthermore, the reflux ratio is not allowed to change before a minimum time interval of 240 s has elapsed. Here, the gOPT tool of gPROMS [gPROMS 2003] is used.

The most relevant simulation data for the three processes presented in this section is summarised in Table 6.1.

Table 6.1.: Simulation data for the processes presented in Section 6.1.2.

Molar fractions in the charge	$x_{Bb, \alpha}$	1.0 mol/mol
Number of equilibrium stages	$n_{th}$	30
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	1.5
Process with off-cut		
Maximum reflux ratio	$R_{L, max}$	50
Reflux ratio during off-cut	$R_{L, off}$	10
Optimised process		
Minimum final purity of distillate product	$x_{Da, \omega}$	$\geq 0.97$ mol/mol
Minimum recovery of light boiler	$\sigma_{Da, min}$	95 %
Minimum interval at constant reflux		240 s
Optimisation objective	$Q_{min}$	

## Comparison

The simulation results for the three processes are summarised in Table 6.2. The process without off-cut, where the reflux ratio is allowed to increase to arbitrary values requires the longest time, and therefore has the highest energy demand. The duration of the process with the off-cut and that of the optimised process are much shorter. These two processes have a time and energy saving of 57% and 64% with respect to the first process, respectively. However, the major time savings of these processes are paid for by a slight decrease in either the purity or the recovery of one of the components. In the optimised process, the recovery of the heavy boiler is increased at the expense of its purity. This is due to the fact that some non-reacted

educt is still present in the sump of the column at the end of the process. Nevertheless, the optimised process is easier to implement in the practical case due to the simpler stepwise profile of the reflux ratio.

Table 6.2.: Comparison of the three processes.

	Process without off-cut	Process with off-cut	Optimised process
$\tau$	1.00	0.43	0.36
$\sigma_{Da}$	0.99	0.98	0.95
$\sigma_{Bc}$	0.97	0.86	0.94
$x_{Da,\omega}$	0.98	0.98	0.98
$x_{Bc,\omega}$	0.98	0.95	0.90

### 6.1.3. Combining a reactor with a batch distillation in a middle vessel column

The two products of the decomposition Reaction (6.3):



are the light and heavy boilers in the mixture. This reaction can be carried out in a batch reactor coupled with a middle vessel column as shown in Figure 6.9 (i). The reaction educt ( $b$ ) is loaded into the reactor at the beginning of the process. The light and heavy-boiling reaction products are simultaneously recovered as overhead and bottom's products, respectively. The concentration path in the reactor is shown together with the concentration of the product streams and the equilibrium curve in Figure 6.9 (ii). The relative volatilities of the components in the mixture are  $\alpha_{ab} = \alpha_{bc} = 1.5$ . The reactor is therefore placed in the middle of the column. In this case, the concentration in the reactor vessel does not vary much during the whole duration of the process. Thereby the temperature and concentration profiles are almost stationary, thus considerably simplifying the design of the temperature control. The reflux ( $R_L = \dot{L}_U/\dot{D}$ ) and reboil ( $R_B = \dot{V}_L/\dot{B}$ ) ratios, and the recoveries of the two products ( $\sigma_{Da}$  and  $\sigma_{Bc}$ ) are plotted against the relative distillation time in Figure 6.10. The recoveries reach very high values at the end of the process, and they move along two paths lying very close to each other. This is due to the fact that the flow rates of the two product streams ( $\dot{D}$  and  $\dot{B}$ ) are similar. Furthermore, the reflux and reboil ratios are predominantly constant, and also take on similar values throughout the process, confirming the near to steady state character of this batch process.

The most relevant simulation data for the batch reactor coupled with a middle vessel column is summarised in Table 6.3.

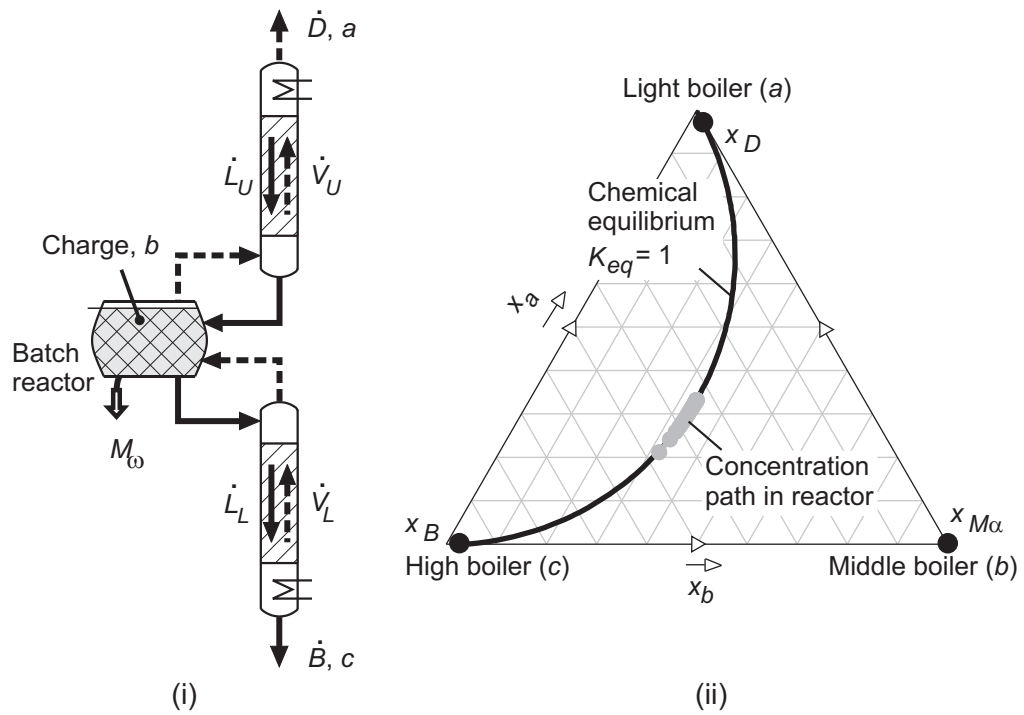


Figure 6.9.: Batch reactor coupled with a middle vessel column (i) process scheme, and (ii) concentration path in the reactor for the Reaction (6.7).

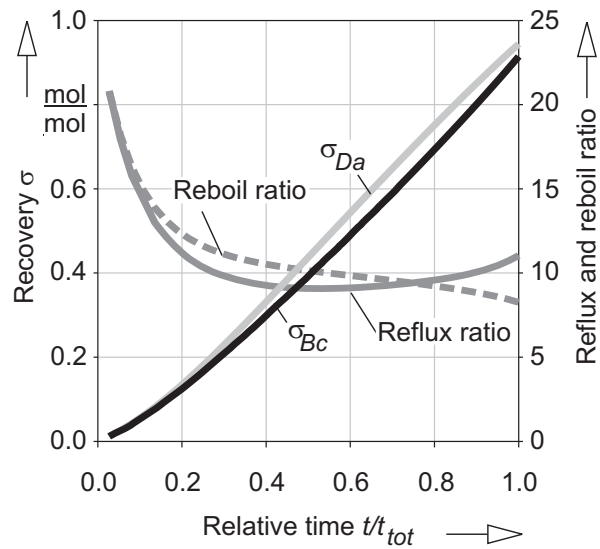


Figure 6.10.: Recovery of the light and heavy boilers; reflux and reboil ratios for the Reaction (6.7) carried out in a batch reactor coupled with a middle vessel column.



Table 6.3.: Simulation data for the processes presented in Section 6.1.2.

Molar fractions in the charge	$x_{Mb,\alpha}$	1.0 mol/mol
Number of equilibrium stages	$n_{th}$	30
Number of stages in upper column section	$n_{th,U}$	15
Relative volatilities	$\alpha_{ab}$	1.5
	$\alpha_{bc}$	1.5
Average concentration of distillate product	$\bar{x}_{Da}$	0.99 mol/mol
Average concentration of bottom product	$\bar{x}_{Bc}$	0.99 mol/mol

#### 6.1.4. Closed processes

In a closed process, the reaction/distillation system can be considered to be a closed system since no product stream leaves the process. Two such processes are described in this section. In the first process, two batch reactors are placed at the top and the bottom of a distillation column. This is shown in Figure 6.11 (i). In the second process, a batch reactor replaces the middle vessel of a middle vessel column operated in a closed mode. This process is shown in Figure 6.13 (i).

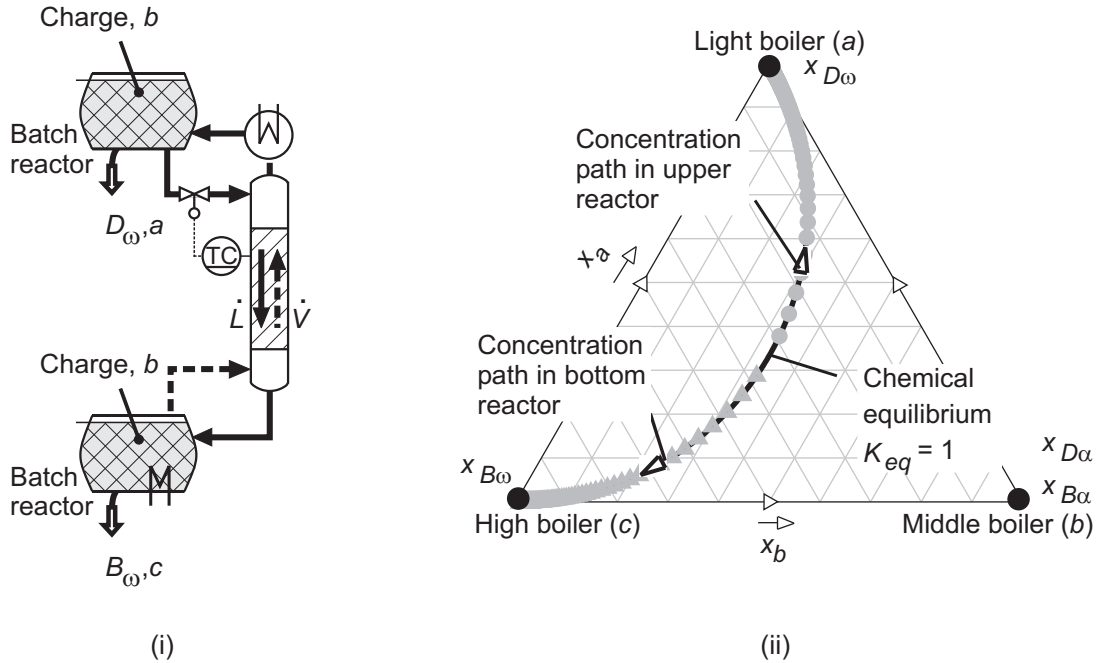


Figure 6.11.: Closed operation of a multi-vessel batch distillation column with two reactors: (i) process scheme, and (ii) concentration path in both reactors.

### Closed operation of a batch distillation column coupled with two reactors

In the process shown in Figure 6.11 (i) two reactors are coupled with a batch distillation column operated in closed mode. One is placed at the top and the other at the bottom of the distillation column. The educt ( $b$ ) is charged into both reactors, where it is decomposed to the light ( $a$ ) and heavy boiler ( $c$ ). Component  $a$  leaves the lowest reactor as it is formed, and accumulates in the top reactor. Analogously, component  $c$  is enriched in the lowest reactor. In both reactors, the concentration path follows the chemical equilibrium line. However, as shown in Figure 6.11 (ii), the concentration in the top reactor moves towards the pure light boiler, and simultaneously, that in the lower reactor migrates towards the pure heavy boiler.

The flow rate of the reflux stream from the top reactor ( $\dot{L}$ ) is used to control the temperature in the distillation column. The stoichiometric coefficients determine the shape of the equilibrium curve, and therefore the concentration path in the two reactors. The value of the internal reflux ratio of the column, defined as  $\dot{L}/\dot{V}$ , therefore depends both on the relative volatilities of the components in the mixture, as well as on the stoichiometric coefficients of the reaction. The reflux ratios for three different stoichiometries are plotted in Figure 6.12 (i) as a function of the conversion of the reaction educt. The relative volatilities of the components, the total number of stages, and the separation task are constant for the three cases. The charge is equally divided between the two reactors.

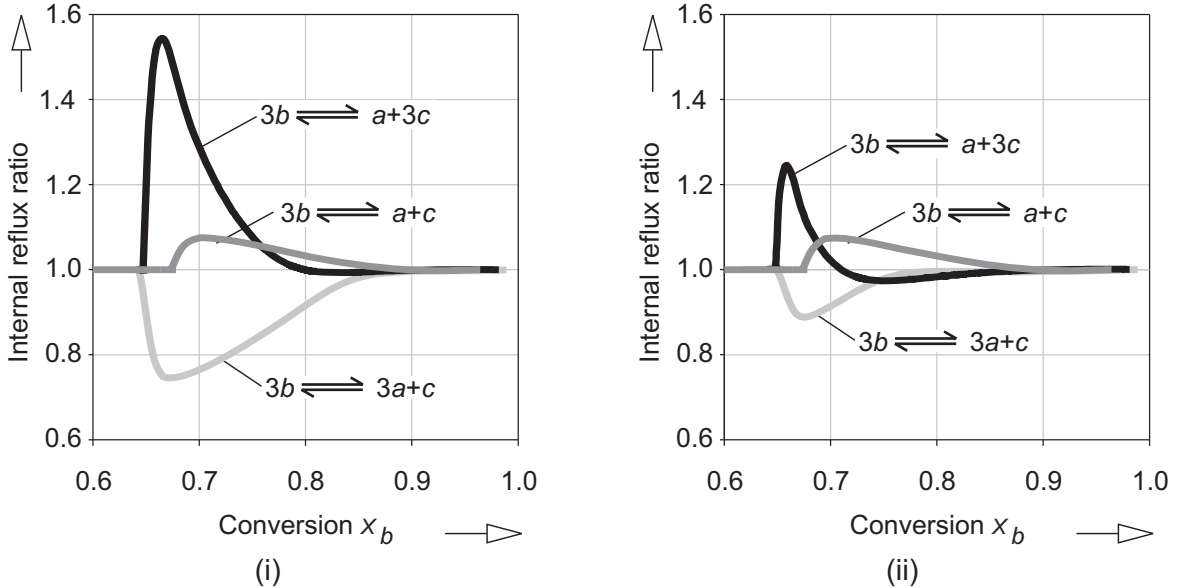


Figure 6.12.: Internal reflux ratios required by closed operation of multi-vessel batch distillation column with two reactors for three different stoichiometries when the charge is (i) equally distributed between the reactors, and (ii) distributed according to Equation (6.8).

### 6.1. Decomposition reaction

If the stoichiometric coefficients of the light and heavy-boiling reaction products are equal,  $\nu_c = \nu_a$ , then both are produced in the same amount in the two reactors. The vapour and liquid streams in the column are therefore approximately equal, i.e. the column operates close to total reflux conditions. In this case, operation of the column is very simple, and the maximum separation capability of the column is used. However, the situation changes with varying stoichiometry. If for instance the stoichiometric coefficient of the heavy boiler is bigger than that of the light boiler ( $\nu_c > \nu_a$ ), then in both reactors less light boiler is formed than heavy-boiling component. The column's task is mainly to transfer the heavy boiler to the bottom reactor, and it therefore assumes the character of a stripping column. Hence, the internal reflux ratio is initially larger than one, i.e.  $\dot{L} > \dot{V}$ . For higher conversions, the concentration of the light boiler in the bottom reactor and that of the heavy boiler in the top reactor become similar, so that the internal reflux ratio tends towards one. If, on the other hand, the stoichiometric coefficient of the light boiler is bigger than that of the heavy boiler ( $\nu_c < \nu_a$ ), then the internal reflux ratio is initially smaller than one, i.e.  $\dot{L} < \dot{V}$ .

By distributing the charge to the two reactors according to the ratio of the stoichiometric coefficients of the light and heavy-boiling products, as given by Equation (6.8), the internal reflux ratio takes values which are very close to unity, as shown in Figure 6.12 (ii). This is of great advantage because the flow rate of the reflux stream is almost constant, significantly simplifying the control of the process, and, furthermore,

Table 6.4.: Simulation data for the processes shown in Figure 6.11 (i).

Number of equilibrium stages	$n_{th}$	15
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	1.5
$2 b \rightleftharpoons a + c$		
Final concentration of distillate product	$x_{Da,\omega}$	0.98 mol/mol
Final concentration of bottom product	$x_{Bc,\omega}$	0.98 mol/mol
$3 b \rightleftharpoons a + 3 c$		
Final concentration of distillate product	$x_{Da,\omega}$	0.98 mol/mol
Final concentration of bottom product	$x_{Bc,\omega}$	0.98 mol/mol
$3 b \rightleftharpoons 3 a + c$		
Final concentration of distillate product	$x_{Da,\omega}$	0.99 mol/mol
Final concentration of bottom product	$x_{Bc,\omega}$	0.99 mol/mol
$3 b \rightleftharpoons a + c$		
Final concentration of distillate product	$x_{Da,\omega}$	0.96 mol/mol
Final concentration of bottom product	$x_{Bc,\omega}$	0.94 mol/mol

the maximum separation capability of the distillation column is used.

$$\frac{D_\alpha}{B_\alpha} = \frac{\nu_a}{\nu_c} \quad (6.8)$$

For an equimolar reaction (i.e. if the sum of the stoichiometric coefficients of the reactants is equal to that of the products) and an appropriate charge distribution, the process can be operated with total internal reflux ratio. Nevertheless, both purities and recoveries are high. These depend only on the duration of the separation process.

The main constants and the separation tasks for the process shown in Figure 6.11 (i) are reported in Table 6.4.

### Closed operation of a batch reactor coupled with a middle vessel column

The process shown in Figure 6.13 (i), consists of a reactor placed between a rectifying and a stripping column section, replacing the middle vessel of a middle vessel column. The intermediate boiling educt (*b*) is charged into the reactor at the beginning of the process. The reaction products leave the reactor, accumulate and enrich in the top vessel and in the column's sump. The internal reflux ratio of the rectifying section  $(\dot{L}/\dot{V})_U$  determines the purity of the light-boiling product, and similarly the internal reflux ratio of the stripping section  $(\dot{L}/\dot{V})_L$  determines the purity of the heavy-boiling product in the sump. The concentration in the reactor is determined by the chemical equilibrium curve, by the rate of removal of the two reaction products from the reactor, and by the position of the reaction pole  $\pi_R$ . If the internal reflux ratios of the two sections (hence the rates of removal of the reaction products from the reactor) are adjusted according to Equation (6.9), then the concentration in the reactor vessel would be constant and it would lie at the intersection of the chemical equilibrium curve with the straight line joining the vertex *b* of the triangular diagram and the reaction pole  $\pi_R$ . Equation (6.9) is derived in Appendix A.

$$\frac{\nu_a}{\nu_a + \nu_c} \cdot \left( \frac{\dot{L}}{\dot{V}} \right)_L + \frac{\nu_c}{\nu_a + \nu_c} \cdot \left( \frac{\dot{L}}{\dot{V}} \right)_U = 1 \quad (6.9)$$

This is shown in Figure 6.13 (ii) for the decomposition Reaction (6.3). Here, the concentration of the three components in the reactor, and the recoveries of the two products are plotted as a function of the relative distillation time. The initial charge to the reactor is pure educt. A minimum amount of charge consisting of pure products is loaded into the top and bottom vessels. The process is operated with constant internal reflux ratios, related by Equation (6.9). During most of the duration of the process, the concentration in the reactor is constant. Only at the end of the process, when the holdup in the reactor is very small, and most of the products have been recovered, does the concentration deviate from its initial value. However, this has no influence on the concentrations of the top and bottom products, which are very high throughout

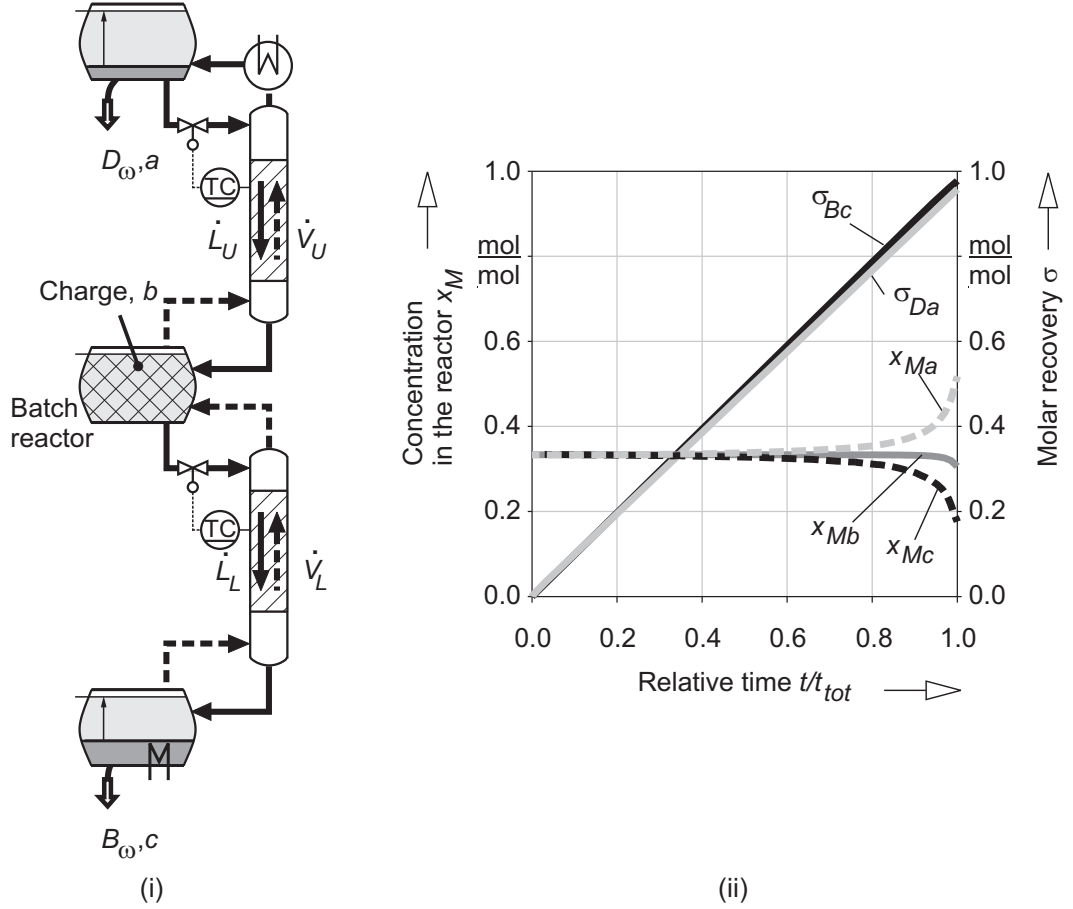


Figure 6.13.: Closed operation of a batch reactor coupled with a middle vessel column: (i) process scheme, and (ii) concentration path in the reactor, together with the recoveries of the light and heavy-boiling products.

the process:  $x_{Da, \omega} \geq 0.99$  and  $x_{Bc, \omega} \geq 0.99$ . Similarly to the corresponding open process, the concentration and temperature profiles in the column have steady state behaviour, significantly simplifying the design of the control system. The dynamic behaviour of the column is limited to the changing holdups in the reactor and in the two vessels. The simulation parameters are summarised in Table 6.5.

### 6.1.5. Conclusion

In this section, several combinations of a reactor with batch distillation processes have been illustrated for an equilibrium limited reaction where a light and a heavy boiler are formed by chemical reaction. For this class of reactions, the minimum energy demand of the processes, which can be calculated with short cut methods, depends both on the volatilities of the components in the mixture, as well as on the

Table 6.5.: Simulation data for the processes shown in Figure 6.13.

Number of equilibrium stages	$n_{th}$	30
Number of equilibrium stages in upper column section	$n_{th,U}$	15
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	1.5
Internal reflux ratio of the upper column section	$(\dot{L}/\dot{V})_U$	0.9
Internal reflux ratio of the lower column section	$(\dot{L}/\dot{V})_L$	1.1
Final concentration of distillate product	$x_{Da,\omega}$	0.99 mol/mol
Final concentration of bottom product	$x_{Bc,\omega}$	0.99 mol/mol

stoichiometric coefficients.

The concentration in a reactor coupled with a rectifying batch distillation column varies during the duration of the process. The reflux ratio necessary to maintain a constant distillate composition follows an exponentially increasing profile. Therefore, the control of the process is very complex. Two modified reflux policies have been illustrated. In both cases, the simplified operation of the process leads to a slight loss in product quality. The combination of a reactor with a stripping batch distillation column is expected to show a similar behaviour.

The closed operation of a batch distillation column with two reactors allows for a simplification of the operation of the process. However, the charge has to be appropriately distributed between the two reactors. If the reactants have different relative volatilities, they would be separated from each other. Therefore, this process is suitable for decomposition reactions, and for close boiling reactants.

The concentration in a reactor combined with a batch distillation column with a middle vessel can be maintained constant. In this case, the reflux and reboil ratios necessary to maintain constant distillate and bottom's concentrations do not change much during the process. Therefore, the control and operation are considerably simplified. Moreover, the open and closed operation modes of this process show little differences. These processes are, in general, suitable for reactions where the products are the light and heavy boilers of the system.

## 6.2. Production of a middle-boiling component

The processes discussed in the previous section are applicable in the case that one of the reaction products is the extreme boiler of the reaction mixture. In the case of an association reaction, where the product is a middle-boiling component:



a new class of processes should be taken into consideration. These processes are characterised by the continuous feed of one of the reactants. The second reactant is, once again, charged into the reactor or to the charge vessel of the column. These semi-batch processes are divided in two categories. In the first case, the reaction is carried out in a semi-batch reactor that is coupled with a distillation column; in the second group, the reaction is carried out in a reactive distillation column.

### 6.2.1. Semi-batch reactor coupled with a distillation column

The addition Reaction (6.11) is taken into consideration.



A semi-batch reactor is coupled with a rectifying column, as illustrated in Figure 6.14 (i). In this process, the heavy boiler ( $c$ ) is charged into the reactor, while the light-boiling reactant ( $a$ ) is continuously fed into the reactor. These react to form the middle boiler ( $b$ ), which, under appropriate conditions, is recovered as distillate product from the top of the column.

The presence of the feed stream to the reactor introduces further degrees of freedom to the process. The effect of the dimensionless flow rate of the feed stream ( $\dot{F} \cdot r / \dot{Q}$ ) on the concentration of the distillate is shown in figure 6.14 (ii), where the distillate concentration ( $x_D$ ) and the concentration in the sump ( $x_B$ ) are plotted for various flow rates of the feed stream. The flow rate of the distillate stream ( $\dot{D}$ ) is maintained constant. On the one hand, if the feed rate were too big, there would be non-reacted light boiling educt in the sump of the column, which would be preferentially removed as distillate product. On the other hand, if  $\dot{F}$  were too small, there would be too little intermediate-boiling product formed, therefore its concentration in the sump would be very small. The recovery of the intermediate boiler would be more difficult, and the distillate product would be contaminated with the heavy-boiling reactant.

The ratio  $\dot{F} / \dot{D}$  has an optimal value. This can be found by considering the process as a sequence of three infinitesimal steps:

- a) infinitesimal feeding of the light-boiling component to the reactor;
- b) reaction to re-establish chemical equilibrium conditions;
- c) distillation of the middle-boiling component.

In the following, the mass balances for the three infinitesimal steps are written for the addition Reaction (6.10), with  $\nu_a = 1$ . The initial charge to the reactor consists

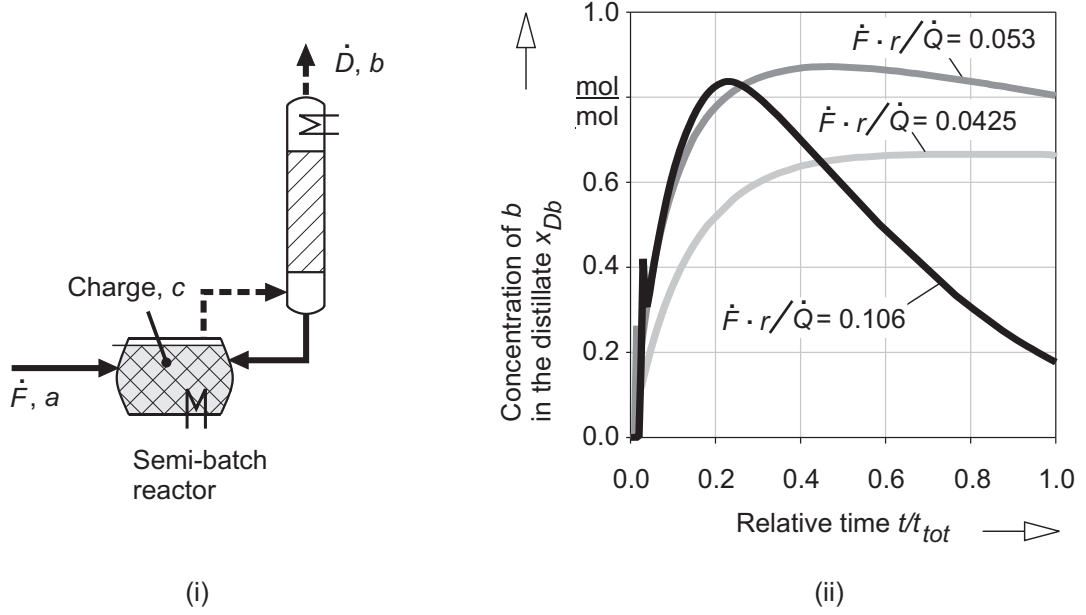


Figure 6.14.: Semi-batch reactor coupled with a distillation column: (i) process scheme; (ii) Effect of the flow rate of the feed on the concentration of the reaction product  $b$  for the process operated under a constant distillate flow rate  $\dot{D} \cdot r / \dot{Q} = 0.096$ .

of almost pure heavy-boiling educt  $c$ , i.e.  $N_a \ll N_b \rightarrow 0$ . Furthermore, the mixture in the reactor is initially in chemical equilibrium. The initial amounts of the three components  $N_a; N_b; N_c$  are therefore related by the equilibrium relationship:

$$K_{eq} = \frac{N_b^{\nu_b}}{N_a^1 \cdot N_c^{\nu_c}} \quad (6.12)$$

a) The infinitesimal feed of the light boiler shifts the system away from chemical equilibrium. Due to the feed, the new amounts of the three components may be written as:  $N_a + \dot{F} \cdot \Delta t$ ;  $N_b$ ; and  $N_c$ .

b) Equilibrium is re-established in a reaction step, hence the amounts of the three components may be written as:  $N_a + \dot{F} \cdot \Delta t - \Delta N_R$ ;  $N_b + \nu_b \cdot \Delta N_R$ ; and  $N_c - \nu_c \cdot \Delta N_R$ . Here,  $\Delta N_R$  is the change of number of moles of component  $a$  due to the chemical reaction.

Hence,

$$K_{eq} = \frac{(N_b + \nu_b \cdot \Delta N_R)^{\nu_b}}{(N_a + \dot{F} \cdot \Delta t - \Delta N_R) \cdot (N_c - \nu_c \cdot \Delta N_R)^{\nu_c}} \quad (6.13)$$

for  $N_a \rightarrow 0$ ; and ignoring the second power of infinitesimal differences:



$$\begin{aligned}
 K_{eq} &= \frac{N_b^{\nu_b} + \nu_b^2 \cdot N_b^{\nu_b-1} \cdot \Delta N_R}{(\dot{F} \cdot \Delta t - \Delta N_R) \cdot (N_c^{\nu_c} - \nu_c \cdot N_c^{\nu_c-1} \cdot \Delta N_R)} \\
 &= \frac{N_b^{\nu_b} + \nu_b^2 \cdot N_b^{\nu_b-1} \cdot \Delta N_R}{\dot{F} \cdot \Delta t \cdot N_c^{\nu_c} - N_c^{\nu_c} \cdot \Delta N_R}
 \end{aligned} \tag{6.14}$$

re-arranging:

$$\begin{aligned}
 \Delta N_R &= \frac{N_c^{\nu_c} \cdot K_{eq} \cdot \dot{F} \cdot \Delta t - N_b^{\nu_b}}{N_c^{\nu_c} \cdot K_{eq} + \nu_b^2 \cdot N_b^{\nu_b-1}} \\
 &= \frac{\dot{F} \cdot \Delta t \cdot N_b^{\nu_b} - N_b^{\nu_b} \cdot N_a}{\nu_b^2 \cdot N_b^{\nu_b-1} \cdot N_a + N_b^{\nu_b}} \\
 &= \frac{\dot{F} \cdot \Delta t - N_a}{1 + \nu_b^2 \cdot N_a / N_b} \\
 &\approx \dot{F} \cdot \Delta t
 \end{aligned} \tag{6.15}$$

c) The reaction step is followed by an infinitesimal distillation step, where the pure reaction product is obtained at the distillate. The amounts of the three components can therefore be written as:  $N_a$ ;  $N_b + \nu_b \cdot \Delta N_R - \dot{D} \cdot \Delta t = N_b + \nu_b \cdot \dot{F} \cdot \Delta t - \dot{D} \cdot \Delta t$ ; and  $N_c - \dot{F} \cdot \Delta t$ . Since the amount of the reaction product in the reactor ( $N_b$ ) is very small, the amount of distillate product should be smaller or equal to the amount of reaction product, otherwise the heavy-boiling educt would pollute the distillate product:

$$\dot{D} \leq \frac{\Delta N_R}{\Delta t} \cdot \frac{\nu_b}{\nu_a} = \dot{F} \cdot \frac{\nu_b}{\nu_a} \tag{6.16}$$

On the other hand, if too little distillate product were withdrawn, the amount of reaction product in the reactor would tend to increase. This favours the reverse reaction, leaving non-reacted light-boiling educt in the reactor, which preferentially ends at the top of the column, polluting the distillate.

Hence, the optimal value of the ratio between the feed and the distillate stream is equal to the ratio of the stoichiometric coefficient of the light-boiling educt ( $\nu_a$ ), to that of the reaction product ( $\nu_b$ ):

$$\frac{\dot{F}}{\dot{D}} = \frac{\nu_a}{\nu_b} \tag{6.17}$$

Figure 6.15 further illustrates the importance of the ratio between the flow rates of the feed and distillate streams  $\dot{F}/\dot{D}$ . The flow rate of the distillate stream is kept constant and that of the feed stream is varied stepwise around a fixed value given by Equation (6.17). When  $\dot{F}/\dot{D}$  drops below  $\nu_a/\nu_b = 0.5$ , the heavy-boiling reactant ( $c$ ) pollutes the distillate product. On the other hand, when  $\dot{F}/\dot{D}$  becomes bigger than  $\nu_a/\nu_b = 0.5$ , the non-reacted educt  $a$  pollutes the distillate product.

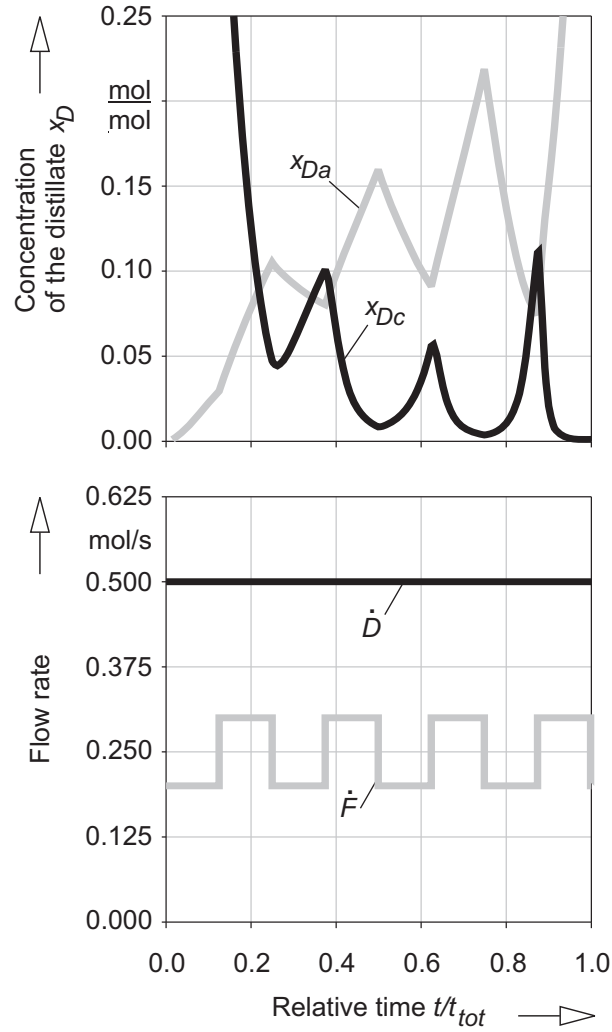


Figure 6.15.: Effect of the ratio  $\dot{F}/\dot{D}$  on the concentration of the light and heavy-boiling educts in the distillate stream.

Table 6.6.: Simulation data for the processes shown in Figure 6.16.

Number of equilibrium stages	$n_{th}$	30
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	1.5
Chemical equilibrium constant	$K_{eq}$	10
Final concentration of distillate product	$x_{Db,\omega}$	0.98 mol/mol
Recovery of intermediate boiler	$\sigma_{Db}$	0.95

Figure 6.16 (i) shows an improved process control scheme. The setpoint to the feed of the light-boiling reactant is determined in a cascade by the distillate's flow rate, which is manipulated to control the temperature at the column's head. In this way, the ratio of the two flow rates is kept constant. The concentration profiles in the reactor vessel and at the column's head are shown in Figure 6.16 (ii). In this case, the concentrations of the light boiler in the sump and at the column's head are very small. On the other hand, both the distillate concentration of the middle-boiling reaction product and its recovery are very high:  $x_{Db} = 0.98$  and  $\sigma_{Db} = 0.95$ , respectively. The simulation data is summarised in Table 6.6.

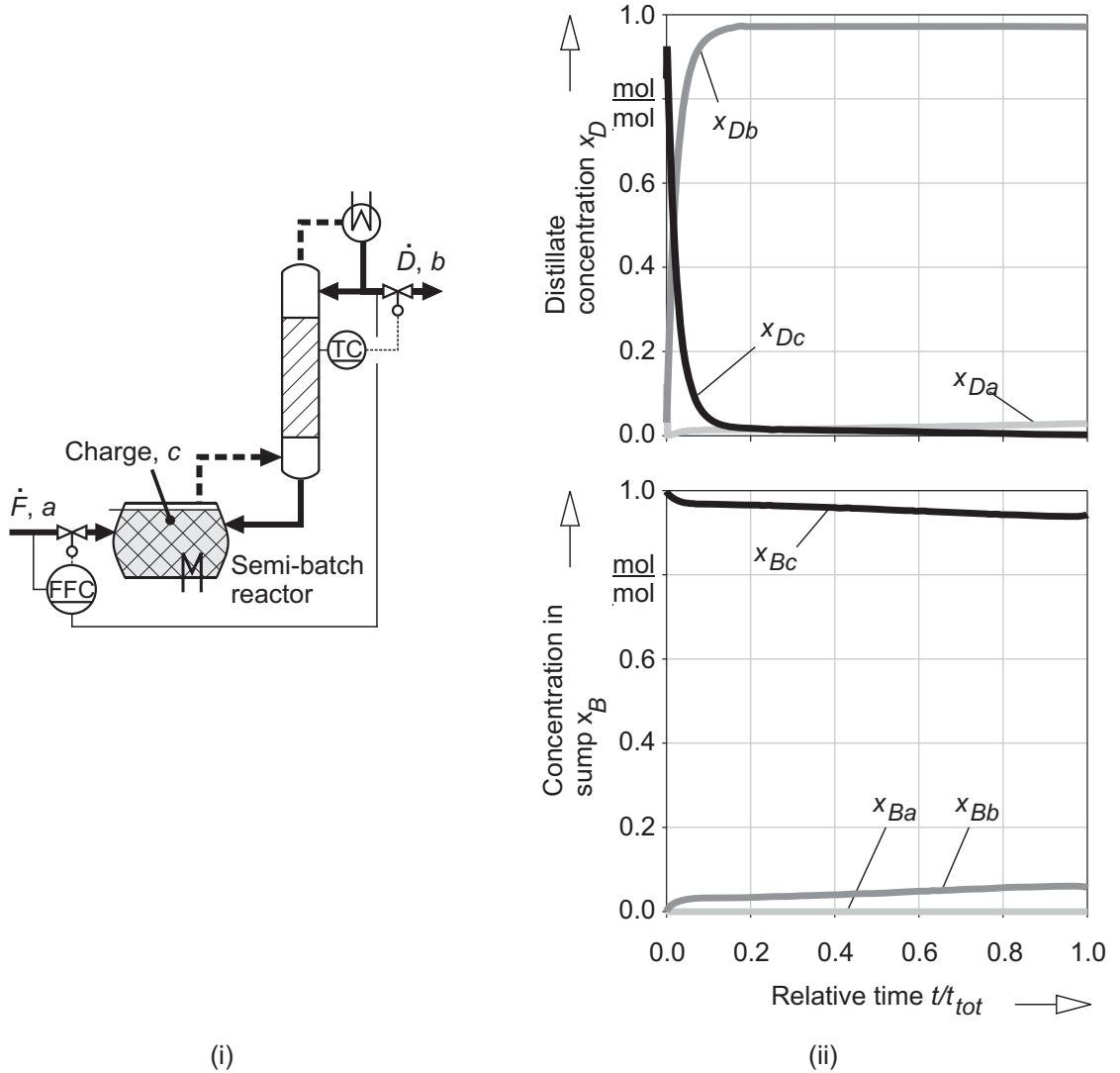


Figure 6.16.: Combination of a semi-batch reactor with a distillation column: (i) process; and (ii) distillate and bottom's concentrations.

### 6.2.2. Semi-batch reactive distillation

A semi-batch reactive distillation column is depicted in Figure 6.17 (i). This consists of a reactive column section (shown in grey) placed between the reboiler and a rectifying column section. The light-boiling reaction educt ( $a$ ) is charged into the column's sump, and the heavy-boiling educt ( $c$ ) is continuously fed into the top of a reactive column section. Due to their relative volatility, the two components tend to flow in opposite directions along the reactive column section, where the middle boiler ( $b$ ) is formed according to Reaction (6.11):

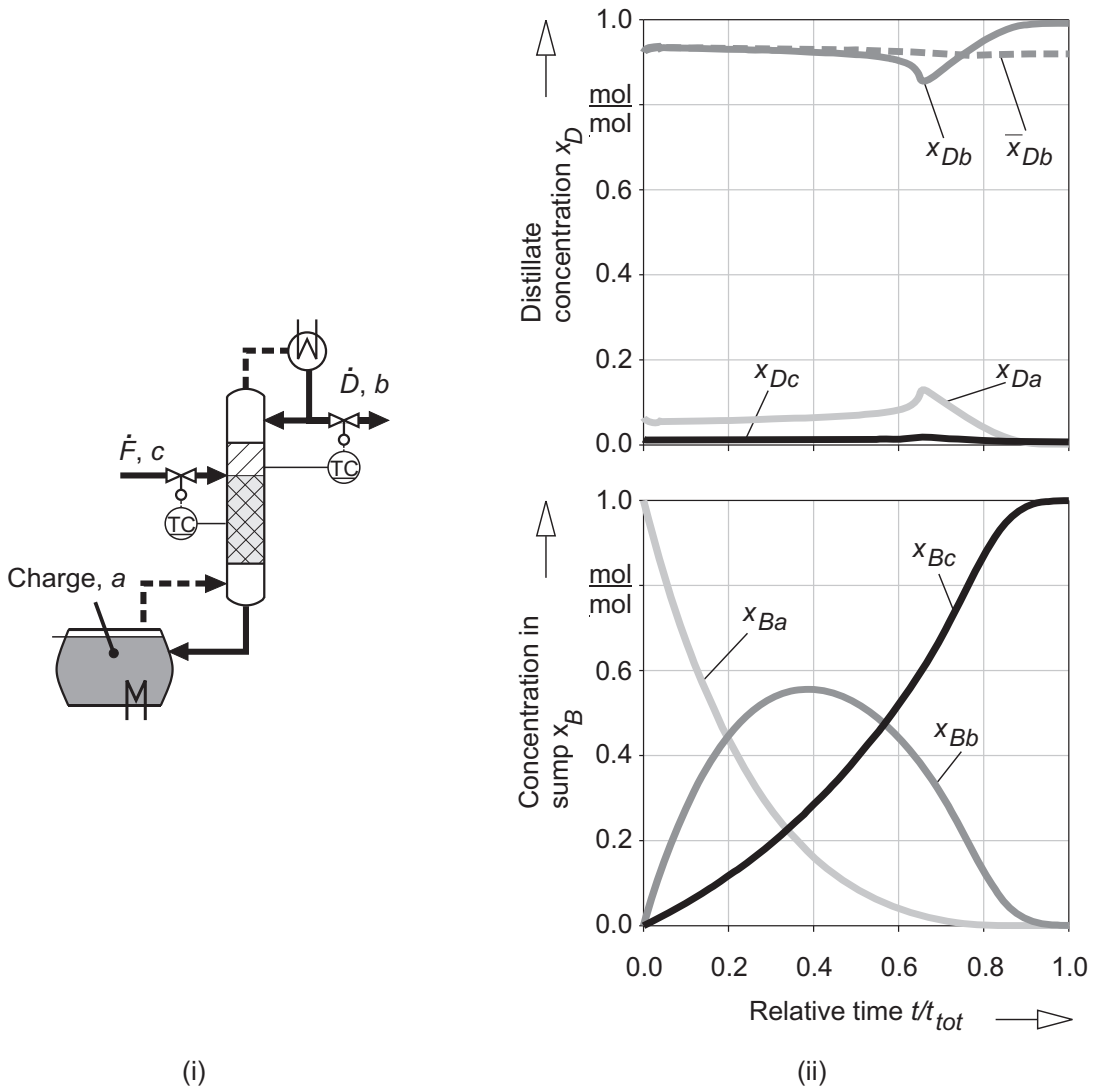
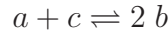


Figure 6.17.: Semi-batch reactive distillation column: (i) process scheme and, (ii) concentration path of the distillate and in the column's sump.

In the upper part of the column, above the reactive section, the reaction product is purified from the heavy-boiling educt, and is recovered as distillate product. To reduce the amount of non-reacted light boiler leaving the distillation column with the distillate, an excess of the heavy boiler is continuously fed into the column. This accumulates in the bottom vessel. When the light-boiling educt is entirely consumed, and its concentration in the column's sump reaches zero, the feed of the heavy boiler is interrupted. The distillation process is continued in order to recover the reaction product, and to purify the heavy-boiling educt for further use. During this process step, depending on the value of the reaction equilibrium constant, a considerable amount of the product might decompose forming the light-boiling educt, which would pollute the distillate product.

Figure 6.17 (ii) shows a plot of the concentration path in the reboiler ( $x_B$ ) and that of the distillate ( $x_D$ ) stream, for the process operated under temperature control. The average distillate composition ( $\bar{x}_{D,b}$ ) is plotted as a dotted line. In the column's sump, the concentration of the reaction educt  $a$  steadily decreases. However, its concentration in the distillate  $x_{D,a}$  is very low, meaning that it is consumed in the reactive column section, where the reaction product  $b$  is formed. The intermediate-boiling component is obtained in high purity as distillate product. Its concentration in the column's sump initially increases, to reach a maximum. It then gradually decreases to reach very low values at the end of the process. At a relative distillation time of  $\tau = 0.65$ , the concentration of educt  $a$  in the sump reaches very low values, indicating that it has been almost completely consumed by the reaction. Nevertheless, at this time, there is a large amount of reaction product left in the sump. This is recovered as distillate product in a subsequent distillation step, during which the feed of educt  $c$  is interrupted. At the end of the process, the excess non-reacted educt  $c$  is recovered in pure form in the sump of the column.

In Figure 6.18, the concentration profile in the column is plotted in a triangular diagram for a relative distillation time of  $\tau = 0.25$ . The concentration path of the liquid phase in the sump moves along the dotted line, from the pure light boiler to the pure heavy boiler. The concentration profile in the reactive column section (dark grey circles), follows the chemical equilibrium curve starting from the concentration in the reboiler and moving towards the heavy boiler. Above the feed stage, no reaction occurs in the liquid phase. Therefore, the profile in the rectifying section (light grey triangles), leaves the chemical equilibrium curve, and moves close to the  $b - c$  binary edge. The concentration of the intermediate boiler at the top of this section is very high.

From the above considerations, it follows that the reflux ratio of the rectifying column section, as well as the number of stages of this section determine the concentration of component  $c$  in the distillate. On the other hand, the concentration of component  $a$  in the distillate product is determined by both the number of stages in the reactive column section and the flow rate of the feed  $\dot{F}$  of the heavy-boiling reactant.

In Figure 6.19 the molar holdup ( $B$ ) in the sump is plotted for each component as

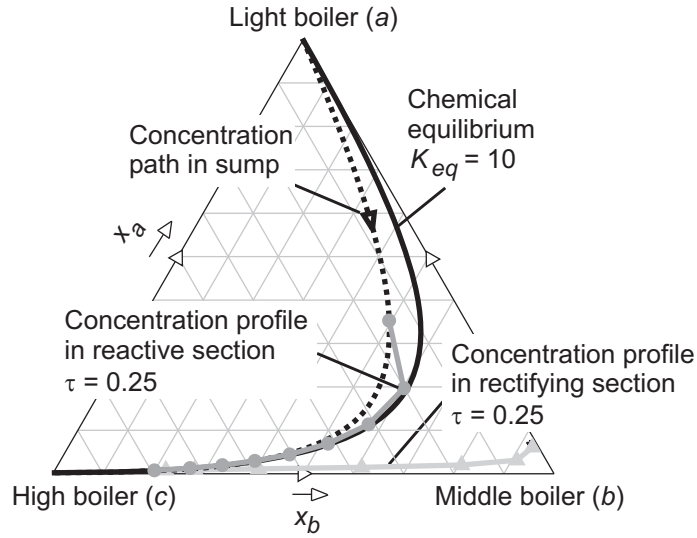


Figure 6.18.: Semi-batch reactive distillation column: concentration path in column for  $\tau = 0.25$ .

a function of the relative distillation time. The total molar holdup in the reboiler, and the total amount of heavy boiling educt fed into the sump are also plotted in this figure. The process requires a considerable excess of the reaction educt  $c$ . This accumulates in the reboiler, and it can be recovered only at the end of the process. Therefore, the temperature in the reboiler considerably increases. Since the maximum

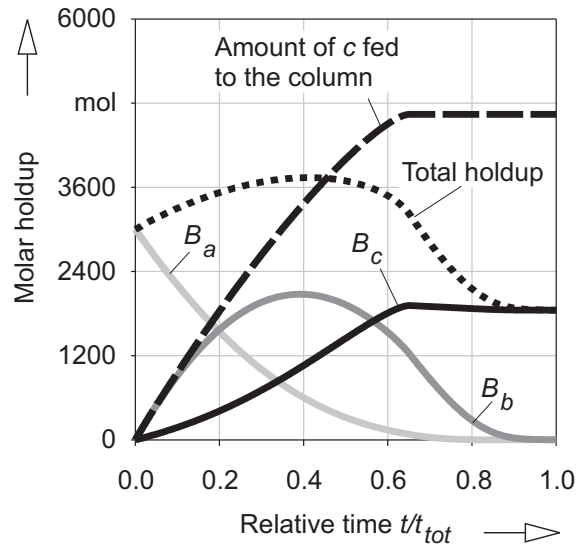


Figure 6.19.: Semi-batch reactive distillation column: molar holdups in the column's sump, and total amount of heavy-boiling educt  $c$  fed into the column.

Table 6.7.: Simulation data for the processes shown in Figure 6.17 (i).

Number of equilibrium stages	$n_{th}$	14
Position of feed stage	$n_{th, F}$	7
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	5.0
Chemical equilibrium constant	$K_{eq}$	10
Final concentration of distillate product	$x_{Db, \omega}$	0.92 mol/mol
Final concentration in sump	$x_{Bc, \omega}$	0.99 mol/mol

holdup in the sump is 1.5 times larger than the initial charge, it is necessary to over-dimension the sump. The simulation data for the process is summarised in Table 6.7.

### 6.2.3. Semi-batch reactive distillation in a column with a middle vessel

A semi-batch reactive distillation in the middle vessel column is shown in Figure 6.20 (i). The charge vessel, into which the light-boiling educt  $a$  is charged, is placed between the stripping column section and the reactive column section. Similarly to the process introduced in the previous section, the heavy-boiling educt  $c$  is continuously fed at the top of the reactive column section, above which there is a rectifying section. The concentration profile in the column is shown in Figure 6.20 (ii). In the rectifying column section (light grey triangles), the intermediate boiler  $b$  is purified from the heavy-boiling educt  $c$ , and is consequently obtained in high purity as distillate product. In the reactive column section, the light-boiling reactant  $a$ , which tends to climb up the column, reacts with the down-flowing educt  $c$  according to Reaction (6.11):



The concentration profile in the reactive column section (dark grey circles) is therefore anchored to the chemical equilibrium curve. In the stripping column section no reaction occurs, the concentration profile (black squares) leaves the chemical equilibrium curve, and moves from the middle vessel's concentration to the heavy-boiling component. The heavy boiler is obtained in pure form at the bottom of the column.

Analogously to the process introduced in the previous section, the concentration of component  $c$  in the distillate is determined by the reflux ratio of the rectifying column section, as well as by the number of stages of this section. On the other hand, the concentration of component  $a$  in the distillate product is determined by the number of stages in the reactive column section, and by the flow rate of the feed  $\dot{F}$  of the heavy-boiling reactant. The reboil ratio of the stripping column section determines the concentration of the bottom product.

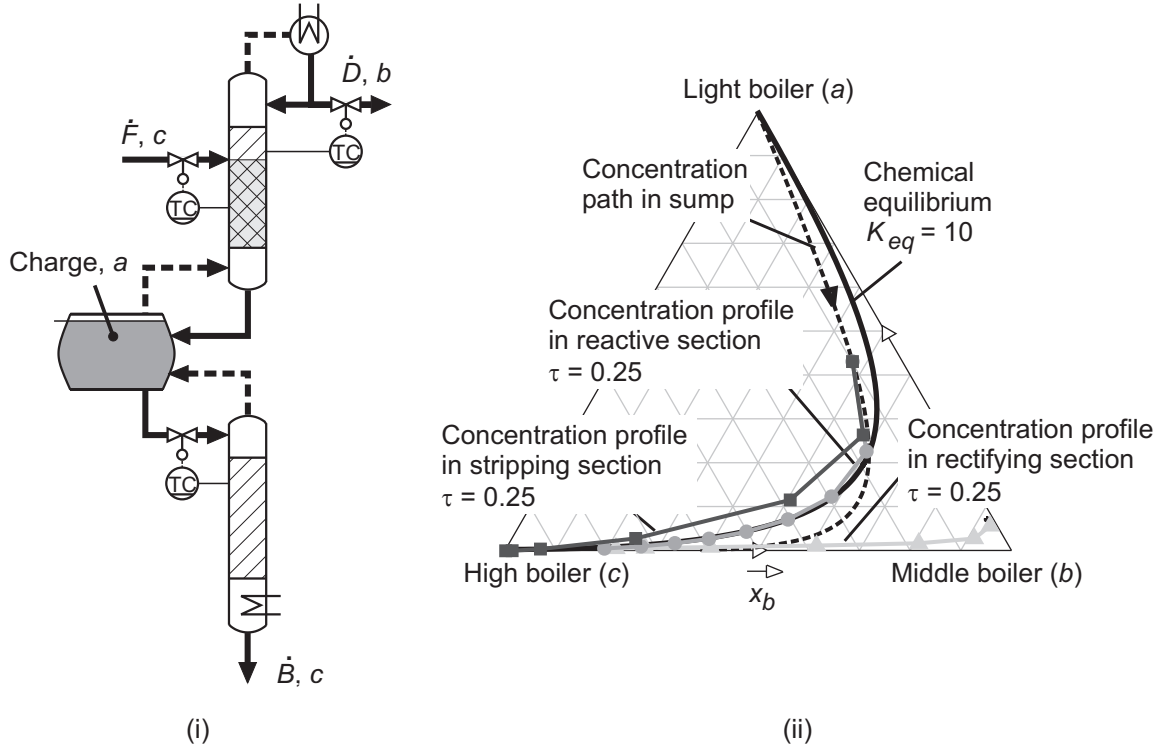


Figure 6.20.: Semi-batch reactive distillation in a column with a middle vessel: (i) process scheme, and (ii) concentration path in column for  $\tau = 0.25$ .

The molar holdups in the middle vessel ( $M$ ) and the flow rates of the feed stream ( $\dot{F}$ ) and that of the bottom product ( $\dot{B}$ ) are shown in Figure 6.21. The distillate consists mostly of the intermediate boiler, which is recovered with a purity of  $x_{Db} = 0.92$  and a recovery of  $\sigma_{Db} = 0.87$ . The amount of educt  $a$  in the middle vessel decreases steadily with time. This is mostly consumed by the chemical reaction. At the same time, the molar holdup of the intermediate boiler in the middle vessel initially increases to reach a maximum; it then decreases to zero at the end of the process. The excess heavy-boiling educt  $c$  is separated from the other components in the stripping column section, and it is recovered as a bottom product. Therefore, the amount of heavy-boiling educt accumulated in the middle vessel is very low. The amount of this component required by the process is plotted in Figure 6.21 as a dotted line. An excess of 20% of educt  $c$  is required. This excess is mostly recovered in the final phase of the process. During the initial phase, the flow rate of the feed stream ( $\dot{F}$ ) is much larger than that of the bottom product ( $\dot{B}$ ). As the concentration of  $a$  in the middle vessel decreases, and that of  $b$  increases, the required feed rate of the heavy boiler decreases, and at the same time  $\dot{B}$  increases. Therefore, some of the non-reacted educt  $c$  is recovered during the process and is fed back to the top of the reactive section. This reduces the total amount of  $c$  necessary for the process. After



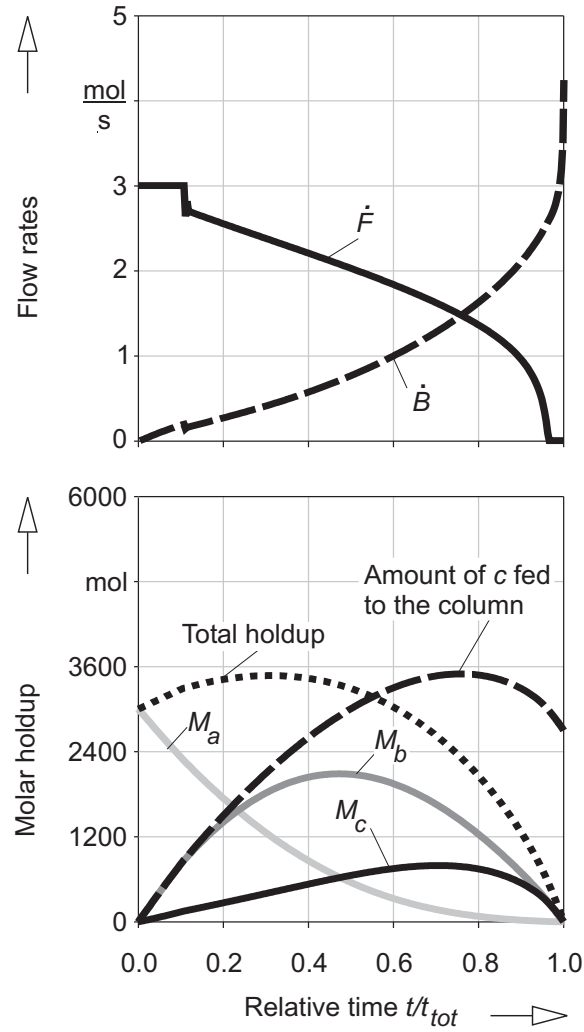


Figure 6.21.: Semi-batch reactive distillation in a column with a middle vessel: flow rates of feed stream  $\dot{F}$  and of bottoms stream  $\dot{B}$  (top); and molar holdups in middle vessel (bottom).

a relative time of  $\tau \approx 0.75$ , the flow rate of the bottom product becomes bigger than the feed rate, resulting in a net recovery of educt  $c$ .

The simulation data for the batch reactive distillation column with a middle vessel is presented in Table 6.8.

Table 6.8.: Simulation data for the processes shown in Figure 6.20.

Number of equilibrium stages	$n_{th}$	20
Position of feed stage	$n_{th, F}$	7
Position of middle vessel	$n_{th, M}$	15
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	5.0
Chemical equilibrium constant	$K_{eq}$	10
Final concentration of distillate product	$x_{Db, \omega}$	0.92 mol/mol
Concentration in sump	$x_{Bc}$	0.98 mol/mol

#### 6.2.4. Comparison

In this section, the three processes discussed in Sections 6.2.1, 6.2.2, and 6.2.3 are compared. For the aim of this comparison, the total number of stages of the various distillation columns, the relative volatility of the components, and the chemical equilibrium constant are assigned equal values for each process. The termination criteria for the two reactive distillation processes discussed in Sections 6.2.2 and 6.2.3 are also the same. The simulation is interrupted when the molar holdup of  $b$  in the feed vessel has dropped to zero. This is not possible for the process discussed in Section 6.2.1.

Table 6.9.: Simulation data for the comparison of the processes presented in Section 6.2.

Number of equilibrium stages	$n_{th}$	19
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	5.0
Final concentration of distillate product	$x_{Db, \omega}$	0.95 mol/mol
Final concentration in sump	$x_{Bc}$	0.98 mol/mol
Chemical equilibrium constant	$K_{eq}$	10
Semi-batch reactor coupled with a rectifying column		
Termination criterion	$R_{L, max}$	60
Batch reactive distillation in a regular column		
Position of feed stage	$n_{th, F}$	9
Termination criterion	$B_{b, \omega}$	1.0 mol
Batch reactive distillation in a column with a middle vessel		
Position of feed stage	$n_{th, F}$	9
Position of middle vessel	$n_{th, M}$	14
Termination criterion	$M_{b, \omega}$	1.0 mol

Here, the process is interrupted when the reflux ratio ( $R_L$ ) reaches a given maximum value, indicating that steady state conditions have been reached. Both termination criteria give, however, the maximum attainable recovery of the reaction product  $b$ . The final average distillate concentrations are also similar for the three processes. The main data is summarised in Table 6.9.

The conversions of the two reactants are plotted for the three processes in Figure 6.22. The conversion of reactant  $i$  is defined as the ratio of the number of moles of component  $b$  collected at the distillate to the number of moles of reactant  $i$  consumed in the process.

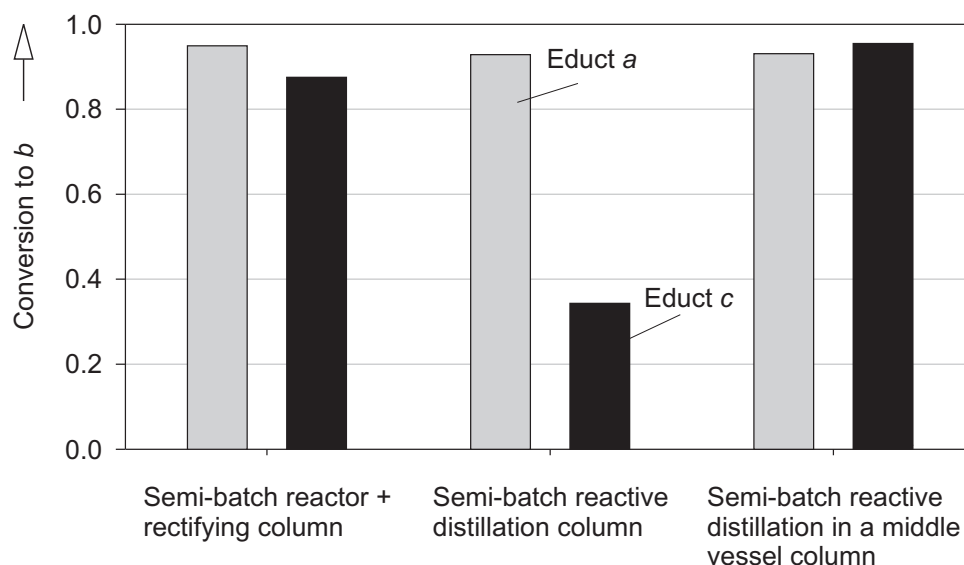


Figure 6.22.: Comparison of semi-batch modes for Reaction (6.11): conversion to the intermediate-boiling reaction product ( $b$ ).

The three processes show a high conversion of the light-boiling educt. Component  $a$  can only leave the system with the distillate. However, for the three processes, it is possible to keep the distillate concentration of the most volatile educt ( $x_{Da}$ ) at low values. The conversion of the heavy-boiling educt is different for the three processes. This is extremely low for the semi-batch reactive distillation. Here, a large excess of component  $c$  is required to keep a low concentration of  $a$  at the top of the reactive column section. However, this excess is recovered only at the end of the process. The maximum conversion of  $c$  is obtained for the semi-batch reactive distillation in a middle vessel column. Even though an excess of reactant  $c$  is required, it is mostly recovered as bottom product during the process, and is recycled to the top of the reactive column section. This reduces the actual amount of educt required at the beginning of the process.

The relative duration of the three processes, which is equivalent to the energy demand, is plotted in Figure 6.23. The duration of the semi-batch reactor combined

with a rectifying column is taken as reference. This process has the longest duration. The duration of the batch reactive distillation column is approximately 50% shorter than that of the reference process. The batch reactive distillation column with a middle vessel requires the shortest time. This process provides time savings of up to 60% for the studied system.

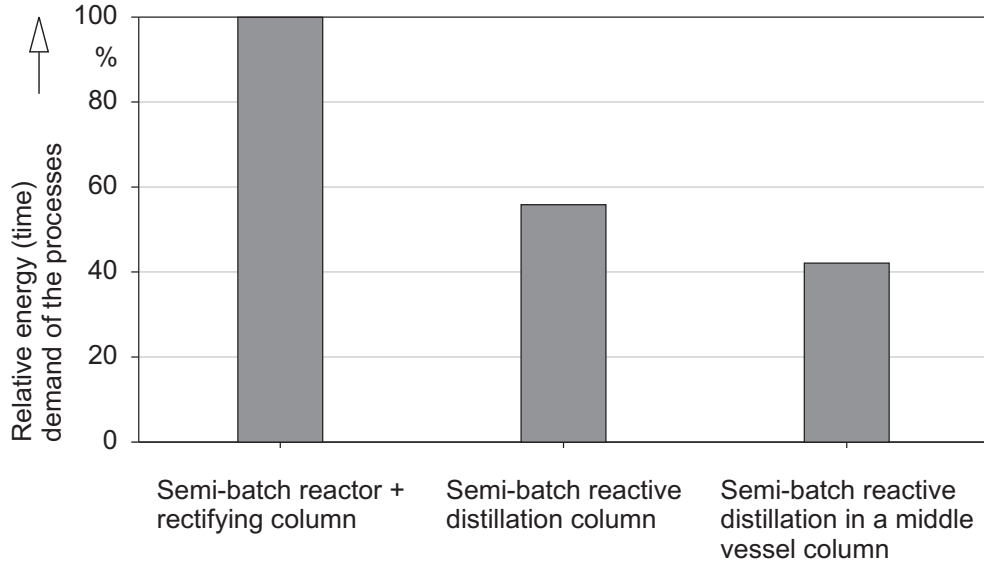


Figure 6.23.: Comparison of semi-batch modes for the Reaction (6.11): energy demand of the processes.

## 7. Integration of batch reaction with batch distillation - Kinetically controlled reactions

Kinetically controlled reactions are defined as those reactions which require a relatively long time to reach equilibrium conditions. In this case, the residence time of the reactants in the reactor is of primary importance. In this chapter, only combinations of batch reactors with distillation columns are taken into consideration. Various process alternatives, which have already been introduced in the previous chapter, are discussed for the decomposition of an intermediate-boiling component (*b*) to a light boiler (*a*) and a heavy boiler (*c*):



where  $k_f$  and  $k_r$  express the rate constants for the forward and reverse reactions, respectively. Furthermore, under the assumption of a molecular reaction, the reaction rate ( $r$ ) can be written as:

$$r = k_f \cdot x_b^2 - k_r \cdot x_a \cdot x_c \quad (7.2)$$

At chemical equilibrium, the reaction rate is zero, and therefore by combining Equation (7.1) with Equation (6.1), a relationship between the chemical equilibrium constant ( $K_{eq}$ ) and the rate constants ( $k_f$  and  $k_r$ ) is obtained:

$$K_{eq} = \frac{k_f}{k_r} \quad (7.3)$$

Figure 7.1 shows the concentration profile in a batch reactor for different values of the reaction rate constants and with  $K_{eq} = 1$ . The reactive system reaches chemical equilibrium after different residence times in the reactor, depending on the value of the rate constants. The light grey curve shows the concentration profile for a fast reaction ( $k_f = k_r = 1\text{ s}^{-1}$ ), in which case chemical equilibrium is reached instantaneously. For slow reactions, ( $k_f = 10^{-4}\text{ s}^{-1}$ ), chemical equilibrium is reached after much longer times.

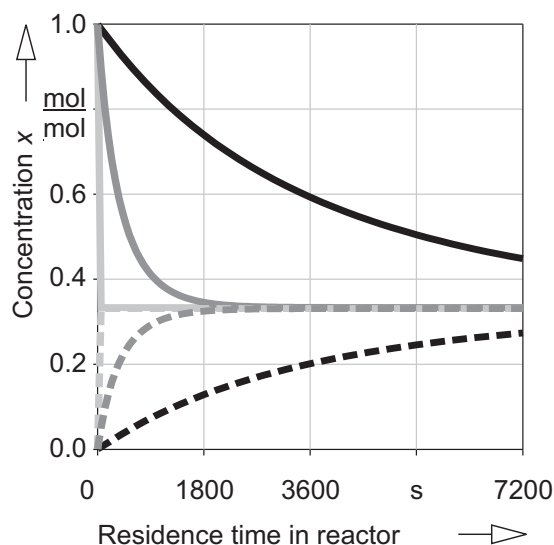


Figure 7.1.: Effect of reaction kinetics on the concentration path in a batch reactor for Reaction (7.1).

## 7.1. Combining a reactor with a regular batch distillation column

The combination of a batch reactor with a rectifying column has already been discussed in Section 6.1.2 for a fast reaction. For a slow reaction, the rate of formation of the reaction products is much slower; hence, for the same heat duty, an extremely high reflux ratio is required to obtain similar concentrations of the distillate product. This is shown in Figure 7.2 (i). Here, the reflux ratios required to maintain a distillate concentration of  $x_{Da} = 0.98 \text{ mol/mol}$ , for a fast reaction ( $k_f = 1 \text{ s}^{-1}$ ) and for two slow reactions ( $k_f = 10^{-3} \text{ s}^{-1}$  and  $k_f = 10^{-4} \text{ s}^{-1}$ ), are plotted with respect to the recovery of the light-boiling product ( $\sigma_{Da}$ ). The heat duty to the reboiler is the same for the three compared cases, and is constant for the whole duration of the process. The main simulation data for this comparison is reported in Table 7.1. It can be seen that the slower reactions require very high reflux ratios for the whole duration

Table 7.1.: Simulation data for the processes discussed in Section 7.1.

Molar fractions in the charge	$x_{Bb, \alpha}$	1.0 mol/mol
Number of equilibrium stages	$n_{th}$	30
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	1.5

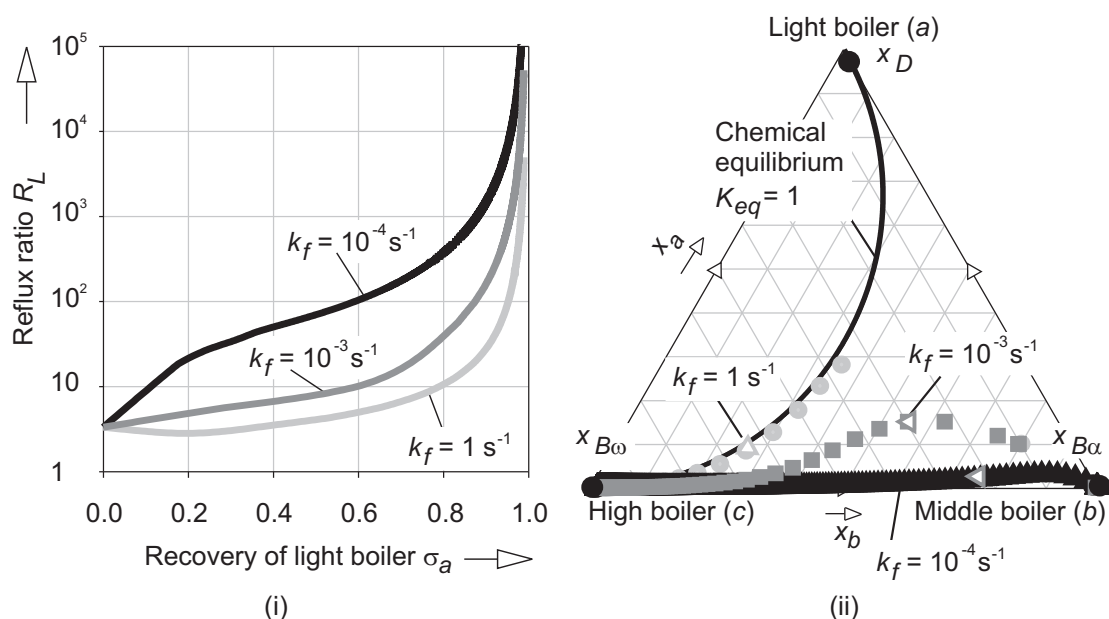


Figure 7.2.: Combination of a batch reactor with a rectifying column: effect of reaction kinetics (i) on the required reflux ratio ( $R_L$ ) of the distillation column; and (ii) on the concentration path in the reactor

of the process. This has a negative effect on the duration and, in turn, on the energy demand of the process. Furthermore, the concentrations in the reactor vessel, shown in Figure 7.2 (ii), do not approach the chemical equilibrium curve, and, as in the case of the slowest reaction kinetics, the concentration of the light-boiling component is very low. This indicates that, notwithstanding the very high reflux ratio, the light-boiling component is removed from the vessel upon its formation. Hence, the reaction kinetics dominate the dynamics of the process.

The extremely high reflux ratios needed for this process are difficult to implement in practice. As an alternative, a cyclic reflux procedure is studied. In this case, phases of total reflux and finite reflux operation cyclically follow each other. During the total reflux phases, no distillate is withdrawn. Time is allowed for the formation of the light-boiling product. Its concentration in the column and in the reactor therefore increase. This is followed by a finite reflux phase, during which the reaction product is withdrawn from the distillate with the required purity. After reaching a switching criterion, the distillate withdrawal is interrupted and the column is again operated with total reflux.

The selection of the switching criteria between the two phases of each cycle is of primary importance. The switching from the finite reflux to the total reflux operation should be effected when the concentration of the distillate drops under a given value. This could be inferred from an increase in temperature in the upper part of

the column. On the other hand, the switching from the total reflux to the finite reflux phases should be effected when a sufficient amount of light-boiling product is accumulated in the reactor. The implementation of this criterion might require a direct measurement of the concentration in the reactor, since a temperature measurement does not provide the required information.

The reflux ratio and the recovery of the two products ( $\sigma_{Da}$ ,  $\sigma_{Bc}$ ) are plotted in Figure 7.3 (i) for a very slow decomposition reaction with  $k_f = 10^{-4} \text{ s}^{-1}$ . The reflux ratio is initially increased to maintain a constant distillate concentration. When the reflux ratio reaches a predefined value, in this example  $R_L = 50$ , the operation is turned to total reflux (i.e.  $\dot{D} = 0$ ), and the cyclic operation starts. As time passes, the concentration of the reactant in the still ( $x_{Bb}$ ) decreases and that of the heavy-boiling product ( $x_{Bc}$ ) increases. According to Equation (7.2), the reaction rate decreases, and therefore the time required by the total reflux phase increases. However, for this case study, the recoveries of both products reach 80% just after two cycles. The concentration of the heavy boiler in the sump is, nevertheless, lower than 70%, hence the process should either be carried on as in Figure 7.3 (i), or a distillate off-cut should be taken at a low reflux ratio. In this way, the residue in the reactor vessel is purified.

During the total reflux phase, the column functions as a condenser with a large holdup, in which the light-boiling component is enriched. For extremely slow reactions, the total reflux phases might be very long, and it might be energetically

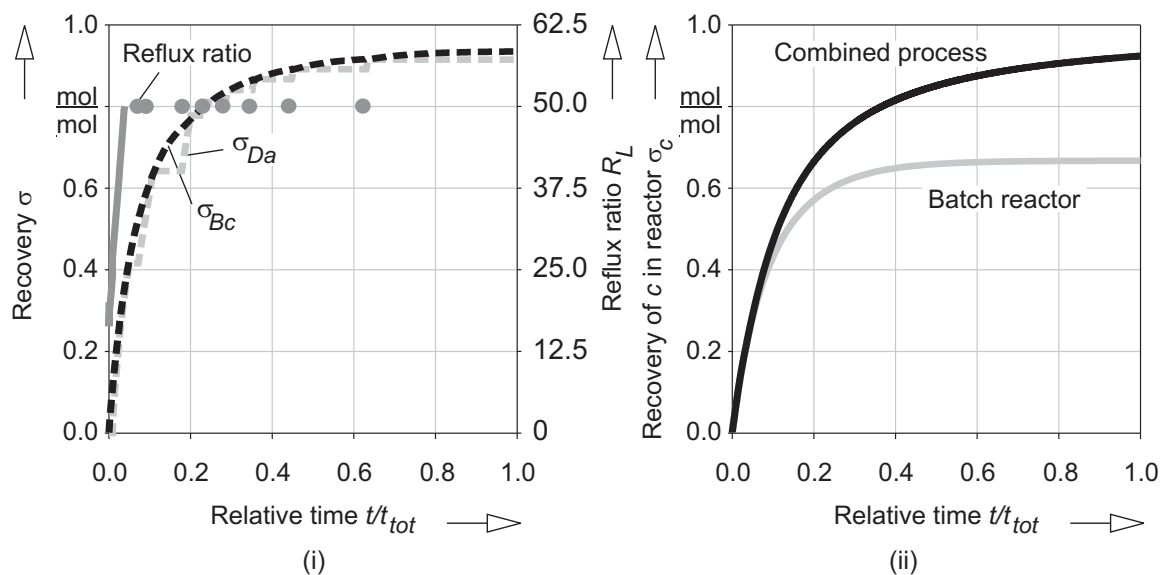


Figure 7.3.: (i) Cyclic reflux operation of a batch reactor coupled with a rectifying column. Reflux ratio, recovery, and purity of the reaction products. (ii) Recovery of the heavy-boiling reaction product for a batch reactor and for the combined process.



convenient to carry out the reaction at lower heat loads. The heat duty can be increased before the end of the total reflux phase, this provides the necessary vapour and liquid loads to the column.

The main advantage of this process is that for slow reactions it avoids the high reflux ratios required by the process discussed previously. This is achieved without any negative effect on the duration of the process, on the recovery and on the concentration of the products. Due to the continuous removal of one of the reaction products, the concentration of the reactant in the still of the combined process is higher than in a batch reactor. The rate of the forward reaction is also larger. Therefore, the combined process is faster than a batch reactor. The recovery of the heavy-boiling component for the reaction carried out in a batch reactor is plotted in Figure 7.3 (ii). The recovery of this component is limited by the chemical equilibrium. The recovery of the heavy boiler for the reactor combined with a batch rectifying column is also plotted in this figure. In this case, the light boiler is removed from the reactor. Therefore, the recovery is not limited by the chemical equilibrium, so that a much higher recovery is obtained.

## 7.2. Combining a batch reactor with a middle vessel column

The combination of a batch reactor with a middle vessel column is illustrated in Section 6.1.3 for a fast reaction. The process scheme is shown in Figure 6.2 (iii). For

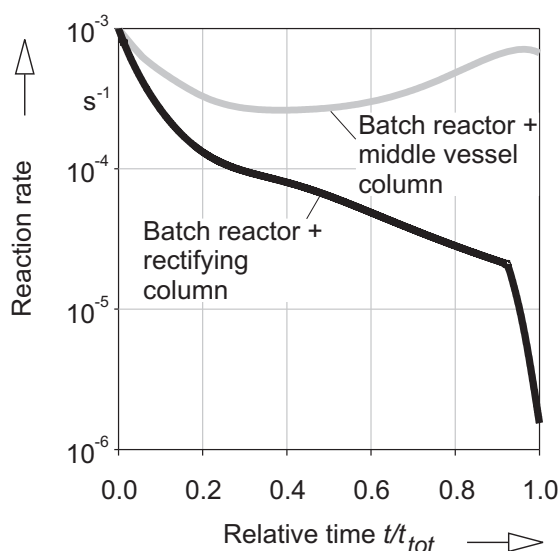


Figure 7.4.: Reaction rate for the decomposition Reaction (7.1) with  $k_f = k_r = 10^{-3} \text{ s}^{-1}$  carried out in a batch reactor coupled with a rectifying and with a middle vessel column.

slow reaction kinetics, in order to provide the required residence time in the reactor, very high reflux and reboil ratios are required. However, in this case, both light and heavy-boiling reaction products are removed from the reaction mixture. Thus the concentration of the educt in the reactor is higher than that in a reactor combined with a rectifying column. Figure 7.4 shows a comparison of the reaction rate in a batch reactor coupled with a rectifying and with a middle vessel column. The reaction rate constants are  $k_f = k_r = 10^{-3} \text{ s}^{-1}$ , and the two columns have the same number of equilibrium stages. The reaction rate for the process in the middle vessel is much higher, and therefore the duration of the process is shorter. For this case study, the duration of the process in the middle vessel is 64% shorter than that in a batch reactor coupled with a rectifying column.

The most relevant simulation data for the batch reactor coupled with a middle vessel column is summarised in Table 7.2.

Table 7.2.: Simulation data for the batch reactor coupled with a middle vessel column illustrated in Section 7.2.

Molar fractions in the charge	$x_{Mb,\alpha}$	1.0 mol/mol
Number of equilibrium stages	$n_{th}$	30
Number of stages in upper column section	$n_{th,U}$	15
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	1.5
Average concentration of distillate product	$\bar{x}_{Da}$	0.95 mol/mol
Average concentration of bottom product	$\bar{x}_{Bc}$	0.95 mol/mol

## 7.3. Closed Processes

Both processes described in Sections 7.1 and 7.2 require either high reflux ratios, or a complex operating procedure with a cyclic reflux policy. Hence, a simplification of the process is required. Closed processes, which are illustrated in Section 6.1.4 for a fast equilibrium limited reaction, significantly simplify the operation of the process, since no product is withdrawn from the system. The two available processes are described in Section 6.1.4.

### Closed operation of a batch distillation column coupled with two reactors

The process shown in Figure 7.5 (i) consists of two reactors placed at the bottom and at the head of a distillation column. The charge is initially loaded into both reactors so that the initial molar holdups are given by the ratios of the stoichiometric

coefficients of the two products, as given by Equation 6.8:

$$\frac{D_\alpha}{B_\alpha} = \frac{\nu_a}{\nu_c} \quad (7.4)$$

The distillation column is therefore operated at close to total reflux conditions. This has the double advantage of using the maximum separation capability of the distillation column, and more importantly, of drastically simplifying the operating procedure. Similarly to the case of fast reactions, a total reflux operation delivers high purities and high recoveries in both reactors only in the case of equimolar reactions.

The concentration path in the two reactors for Reaction (7.1)

$$2b \xrightleftharpoons[k_r]{k_f} a + c \quad (7.5)$$

and for two values of the reaction rate constants ( $k_f$  and  $k_r$ ) are plotted in a triangular diagram in Figure 7.5 (ii). Since the case studied is an equimolar reaction, the charge has been equally distributed between the reactors, and the column has been operated under total reflux.

Both profiles start from the reactant vertex. The concentration path in the upper reactor migrates from here towards the light boiler vertex. That in the bottom reactor simultaneously migrates towards the heavy-boiling component. The path followed

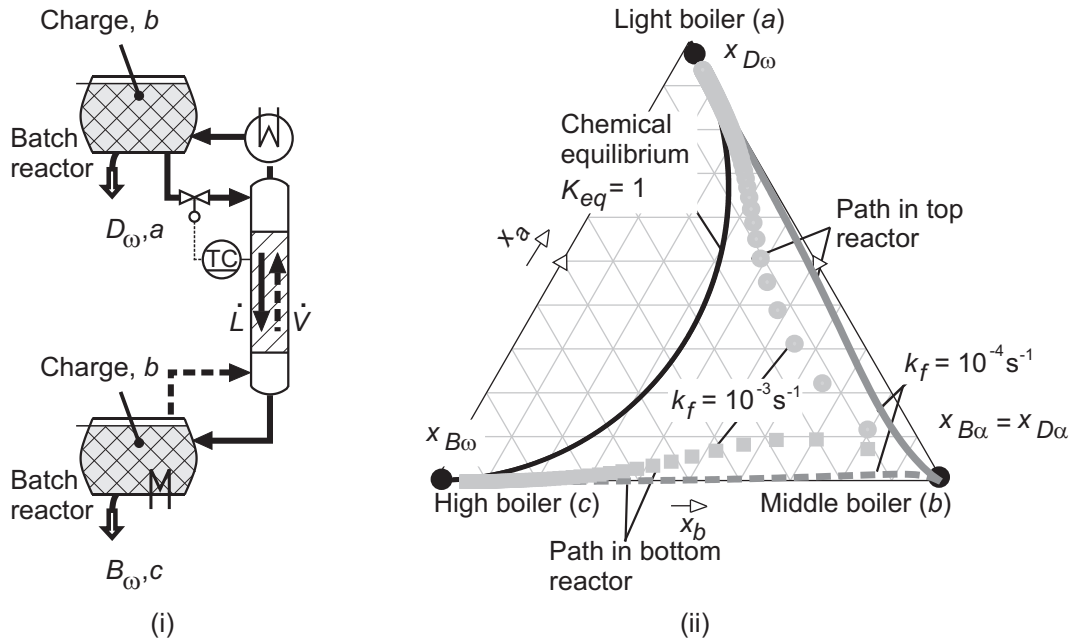


Figure 7.5.: Closed operation of a multi-vessel batch distillation column with two reactors: (i) process scheme, and (ii) concentration path in both reactors, for two different reaction rate constants.

depends on the reaction rate constant. For fast reactions the concentration profile jumps to the equilibrium curve and follows it, as shown in Figure 6.11 (ii). For very slow reactions, the concentration path in the upper reactor moves along the binary edge joining the intermediate to the light boiler. Similarly, the path in the lower reactor moves along the binary edge joining the intermediate to the heavy boiler. This is due to the fact that the reaction is much slower than the separation, and therefore the light and heavy-boiling products are respectively removed from the lower and upper reactors upon their formation.

The concentration paths in the reactors for a moderately slow reaction ( $k_f = k_r = 10^{-3} \text{ s}^{-1}$ ) are also plotted in Figure 7.5 (ii). In this case, the concentration paths lie between the binary edges and the chemical equilibrium curve. Here, the reaction and the separation processes have similar kinetics. Hence, the two processes strongly interact, and the dynamic behaviour of one influences the performance of the other.

The simulation data for the closed operation of a batch distillation column coupled with two reactors is summarised in Table 7.3.

Table 7.3.: Simulation data for the closed operation of a batch distillation column coupled with two reactors.

Molar fractions in the charge	$x_{Db, \alpha}$	1.0 mol/mol
	$x_{Bb, \alpha}$	1.0 mol/mol
Number of equilibrium stages	$n_{th}$	30
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	1.5
Final concentration of distillate product	$x_{Da, \omega}$	0.95 mol/mol
Final concentration of bottom product	$x_{Bc, \omega}$	0.95 mol/mol

### Closed operation of a reactor coupled with a middle vessel batch distillation column

The process shown in Figure 7.6 (i) consists of a reactor coupled with a closed middle vessel column. This process is illustrated for an equilibrium limited decomposition reaction in detail in Section 6.1.4. Reaction (7.6)



takes place only in the liquid phase in the middle vessel. The middle-boiling reaction educt is charged to this vessel, where it undergoes the decomposition reaction. The light and heavy-boiling products thus formed tend to move towards the upper and lower parts of the distillation column respectively. The reflux ratios of the two column

sections determine the purity of the two fractions collected in the top and bottom vessels. The concentration paths for two different values of the reaction rate constants are plotted in a triangular diagram in Figure 7.6 (ii). The concentration path in the reactor vessel is determined by the relative speeds of the reaction and separation processes. For very slow reactions, the two products are removed immediately upon formation, and the reactor contains almost exclusively the reaction educt  $b$ . On the other hand, for moderately slow reactions, where the reaction rate is comparable to the dynamics of the distillation column, the distillation process does not manage to remove the two reaction products upon their formation. The concentration in the reactor moves away from the educt vertex towards the chemical equilibrium curve. The path followed depends on the position of the reaction pole ( $\pi_R$ ), and on the reflux ratios of the two column sections. If the ratio of the rates at which the two reaction products are removed from the reactor vessel were equal to the ratio of the

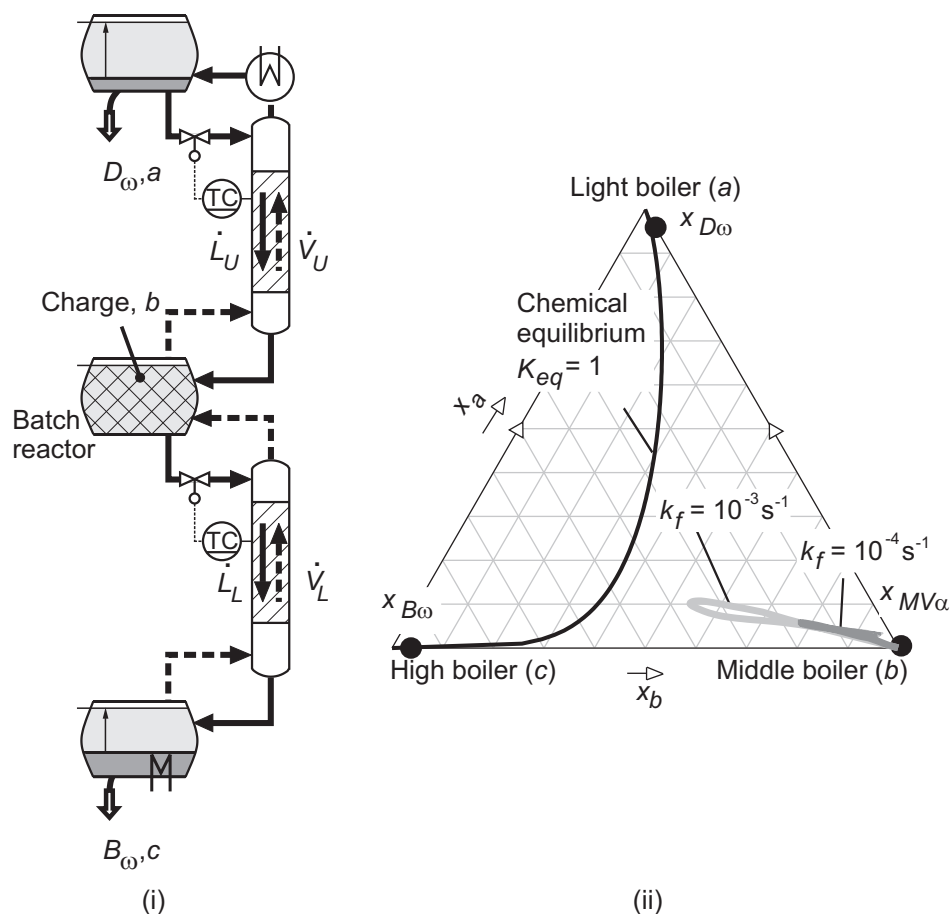


Figure 7.6.: Closed operation of a reactor coupled with a middle vessel batch distillation column for Reaction (7.6): (i) process scheme, and (ii) concentration path in the reactors, for two different reaction rate constants.

stoichiometric coefficients, then the concentration in the reactor vessel would move along the straight line joining the vertex  $b$  of the triangular diagram, to the reaction pole  $\pi_R$ . This condition is satisfied when the internal reflux ratios of the two column sections,  $(\dot{L}/\dot{V})_U$  and  $(\dot{L}/\dot{V})_L$ , are related via Equation (6.9):

$$\frac{\nu_a}{\nu_a + \nu_c} \cdot \left( \frac{\dot{L}}{\dot{V}} \right)_L + \frac{\nu_c}{\nu_a + \nu_c} \cdot \left( \frac{\dot{L}}{\dot{V}} \right)_U = 1 \quad (7.7)$$

Furthermore, if the rate of removal of the reaction products were much slower than the reaction rate, for instance under total reflux operation, the concentration in the vessel would reach the chemical equilibrium line.

In this process, the flow rate of the reflux stream from the top vessel and that from the reactor are used to control the concentrations at the top and bottom of the column, respectively. The internal reflux ratios,  $(\dot{L}/\dot{V})_U$  and  $(\dot{L}/\dot{V})_L$ , relate very closely to Equation (7.7). This is shown in Figure 7.7, where the left hand side of Equation (7.7) is plotted as a function of the relative distillation time. The value of this function oscillates around one.

$$f\left(\left(\frac{\dot{L}}{\dot{V}}\right)_L, \left(\frac{\dot{L}}{\dot{V}}\right)_U, \nu_a, \nu_c\right) = \frac{\nu_a}{\nu_a + \nu_c} \cdot \left( \frac{\dot{L}}{\dot{V}} \right)_L + \frac{\nu_c}{\nu_a + \nu_c} \cdot \left( \frac{\dot{L}}{\dot{V}} \right)_U \quad (7.8)$$

The simulation data for the closed operation of a reactor coupled with a middle vessel batch distillation column is summarised in Table 7.4.

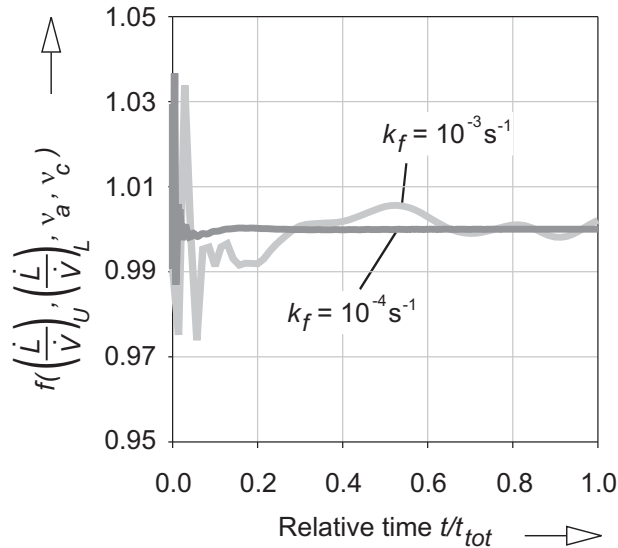


Figure 7.7.: Closed operation of a reactor coupled with a middle vessel batch distillation column for Reaction (7.6): plot of the function given in Equation (7.8).

Table 7.4.: Simulation data for the closed operation of a reactor coupled with a middle vessel batch distillation column.

Molar fractions in the charge	$x_{Mb,\alpha}$	1.0 mol/mol
Number of equilibrium stages	$n_{th}$	30
Number of stages in upper column section	$n_{th,U}$	15
Relative volatilities	$\alpha_{ab}$	1.5
	$\alpha_{bc}$	1.5
Average concentration of distillate product	$\bar{x}_{Da}$	0.95 mol/mol
Average concentration of bottom product	$\bar{x}_{Bc}$	0.95 mol/mol

## 7.4. Comparison

For kinetically controlled reactions, the open processes might require very high reflux and reboil ratios to keep a constant product concentration. Therefore, closed processes are very advantageous for this type of reactions. Two closed processes were illustrated in Section 7.3. The operation of both processes is greatly simplified with respect to the open processes. The concentration path in the reactors of the two closed processes greatly differ. On the one hand, in the closed operation of a batch distillation column coupled with two reactors, the concentration of the reaction educt in both reactors decreases during the process. Therefore, the rate of the chemical reaction decreases. On the other hand, in the closed operation of a reactor coupled with a middle vessel batch distillation column, the concentration of the educt remains high throughout the process. Hence, the reaction rate varies in a narrower range. For the case studied, the duration of this process is 70% shorter than that of the closed operation of a batch distillation column coupled with two reactors.

## 8. Integration of batch reaction with batch distillation - Sequential reactions

Side reactions, where the desired products further react to form undesired side products, are very common in reactive systems. Such reactions have the double drawback of decreasing the yield of the desired product, and at the same time, due to the formation of undesired components, increasing the complexity of the downstream separation process. In fact, both the reactants, as well as the desired products should be separated from the side products. Suppressing the side reactions is therefore an important task for the reaction engineer. It is common industrial practice to resort to selective catalysts, which do not allow the products to further react. As an alternative, the reaction products can be removed from the reaction zone upon their formation. In the latter case, a reactor could be coupled with a distillation process. The reaction products are therefore removed from the reactive mixture and are obtained either as overhead or bottoms of the distillation process.

As already pointed out in the literature review, only one publication [Gadewar et al. 2000] considered the combination of a batch reactor with a distillation process applied to the case of a sequential reaction. In this chapter, several sequential reactions are considered, and some combined processes are analysed.

### 8.1. Batch reactor

In the sequential reaction



the reactant  $c$  decomposes into the main product  $a$  which further reacts to the side product  $b$ . The yield and selectivity are usually used to characterise these reactive systems. The yield of the main product ( $Y_a$ ) is defined as the ratio of the number of moles of product formed to the maximum amount that could be formed by the reaction. For Reaction (8.1) this may be written as:

$$Y_a = \frac{\nu_c}{\nu_a} \cdot \frac{M_a}{M_{c,\alpha}} \quad (8.2)$$

The selectivity ( $S$ ) is defined as the ratio of the number of moles of the product formed to the number of moles of reactant consumed. This ratio is normalised with



the ratio of the stoichiometric coefficients:

$$S_a = \frac{\nu_c}{\nu_a} \cdot \frac{M_a}{M_{c,\alpha} - M_c} \quad (8.3)$$

The yield and selectivity of the main product are plotted in Figure 8.1 as a function of the conversion of the reactant ( $X_c = (M_{c,\alpha} - M_c)/M_{c,\alpha}$ ), for the reaction carried out in a batch reactor. If the rate constants of the two reactions are equal ( $k_1 = k_2$ ), the yield of the main product goes through a maximum. By the time that all the reactant  $c$  has been converted, the desired product  $a$  has completely reacted to the side product  $b$ , so that its yield and selectivity drop to zero. The situation becomes more drastic if the rate constant of the side reaction is larger than that of the main reaction ( $k_2 > k_1$ ). This is also shown in Figure 8.1 for the case that  $k_1/k_2 = 0.1$ . Here, the yield of the desired product also goes through a maximum, however, this is much smaller than for the previous case. On the other hand, if the rate constant of the first reaction is much larger than that of the second reaction ( $k_1/k_2 = 10$ ) both the yield and the selectivity of the desired product are high. This phenomenon is usually used in reaction engineering for the design of selective catalysts.

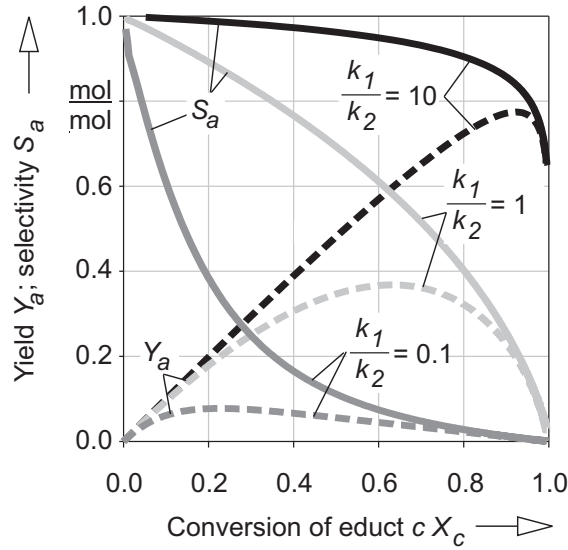


Figure 8.1.: Selectivity (full lines) and yield (dotted lines) of the main component  $a$  for the sequential Reaction (8.1) carried out in a batch reactor as a function of the conversion  $X_c$  of the educt, for three values of the ratio between the rate constant of the first to that of the second reaction ( $k_1/k_2$ ).

A further class of reactions is given by the parallel Reactions (8.4), where one of the reaction educts ( $a$ ), also referred to as key educt, reacts with one of the desired products ( $b$ ) produced by the first Reaction (8.4a) to form an undesired product ( $d$ ):



The yield and selectivity of the main product are referred to the key educt, since this is the limiting reagent. The definitions are given by Equation (8.5):

$$Y_b = \frac{\nu_a}{\nu_b} \cdot \frac{M_b}{M_{a,\alpha}} \quad (8.5a)$$

$$S_b = \frac{\nu_a}{\nu_b} \cdot \frac{M_b}{M_{a,\alpha} - M_a} \quad (8.5b)$$

The selectivity and the yield of the desired products are limited by the rate of the parallel Reaction (8.4b). In a batch reactor, the rate of the second reaction can be reduced by allowing a large excess of the educt which does not further react (*c*). This is achieved in a semi-batch reactor, where the key educt (*a*) is continuously fed to the reactor, maintaining a low concentration of this reactant. However, the speed of the second reaction increases with the consumption of educt *c* and with the formation of the product *b*. This product further reacts to the undesired product *d*, so that, depending on the reaction rate constants, for a complete conversion of educt *c*, the main product *b* might have been completely converted to the by-product. The situation worsens as the side reaction becomes faster and if the first reaction were equilibrium limited. In this case, the concentration of the main product in the batch reactor might be very small throughout the process.

## 8.2. Combination of batch reactor with distillation processes

The combined batch processes discussed in the previous chapters may also be applied to reactive systems with sequential reactions. The selection of the appropriate process depends on the volatilities of reactants and products, as well as on the type of reactive system. The key product, i.e. the reaction product which participates in the second reaction, should be removed from the reactor. The relative volatility of this component is therefore of primary importance. To further suppress the secondary reaction, the key reactant is continuously fed into the reactor, keeping its concentration very low. The reactor is, in this case, operated in a semi-batch mode. To illustrate the importance of the order of the relative volatilities of reactants and products, two cases are studied in the following sections. In both cases, the main product is produced by the first reaction. Furthermore, its boiling point lies between that of the two educts. This product then reacts with one of the two educts. The case where the key educt is the light boiler is considered in Section 8.2.1. In Section 8.2.2, the heavy boiler is the key educt.

### 8.2.1. Light-boiling key educt

In this section, the parallel Reaction (8.6) is studied.



The main product is a middle-boiling component ( $b$ ). However, this reacts in a second Reaction (8.6b) with the light-boiling educt ( $a$ ) to form an undesired heavy-boiling product ( $d$ ). The main reaction is similar to the case studied in Section 6.2. Analogously to that case, two process alternatives are studied. In the first process, a semi-batch reactor is coupled with a rectifying column. The process scheme is shown in Figure 8.2. In the second process discussed in this section, the same reaction is carried out in a batch reactive distillation column with a middle vessel, as shown in Figure 8.6.

#### Coupling of a semi-batch reactor with a rectifying column

the process scheme of a semi-batch reactor coupled to a rectifying column is shown in Figure 8.2. The key educt  $a$  is continuously fed to the reactor, so that its concentration is maintained very low. In this way, the middle-boiling reaction product is removed from the reactor and is obtained as overhead product. The concentrations of both components taking part in the second Reaction (8.6b) are very low, the rate of this reaction is therefore small. Hence, the by-product is formed only in small amounts. However, it should be noted that having an extremely low concentration of the intermediate boiler in the reactor has a negative effect on the duration of the separation process. This is due to the fact that a higher reflux ratio has to be applied in this case.

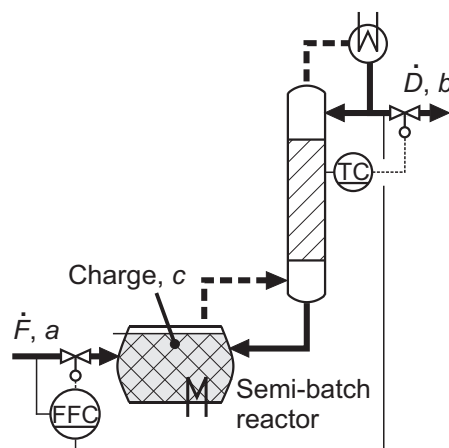


Figure 8.2.: Semi-batch reactor coupled with a rectifying column.

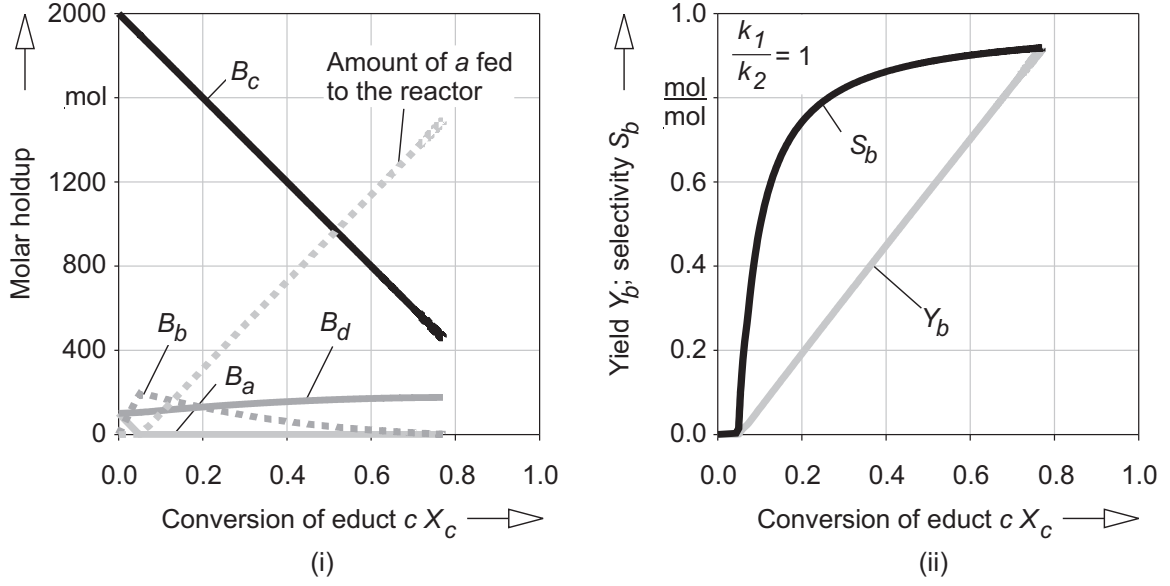


Figure 8.3.: Reaction (8.6) carried out in a semi-batch reactor coupled with a rectifying column: (i) molar holdups in the reactor ( $B$ ) and total amount of educt a fed to the reactor; and (ii) Yield and selectivity of the main product b with respect to the fed educt a, plotted against the conversion of educt c.

The component molar holdups in the reboiler ( $B$ ) together with the total amount of the light-boiling educt fed to the reactor are shown in Figure 8.3 (i). The simulation was carried out with a constant molar fraction of b in the distillate ( $x_{Db} = 0.98$ ). Furthermore, the flow rate of the feed  $\dot{F}$  to the semi-batch reactor was adjusted to the distillate flow rate  $\dot{D}$  according to Equation (6.17):

$$\frac{\dot{F}}{\dot{D}} = \frac{\nu_a}{\nu_b} \quad (8.7)$$

The process was terminated when the reflux ratio reached 1000. The maximum conversion of component c is  $X_c = 0.77$ . In this case, the yield and selectivity of the main product are defined in Equations (8.8a) and (8.8b), respectively:

$$Y_b = \frac{\nu_a}{\nu_b} \cdot \frac{M_{Db}}{M_{Ba,\alpha} + \int_0^1 \dot{F}(\tau) d\tau} \quad (8.8a)$$

$$S_b = \frac{\nu_a}{\nu_b} \cdot \frac{M_{Db}}{M_{Ba,\alpha} + \int_0^\tau \dot{F}(\tau) d\tau} \quad (8.8b)$$

Notwithstanding the low conversion of the heavy boiling educt, the yield and selectivity of the main product with respect to the limiting educt a, shown in Figure 8.3 (ii), are very high  $Y_b = S_b > 0.918$ . Furthermore, the reflux ratio necessary to maintain

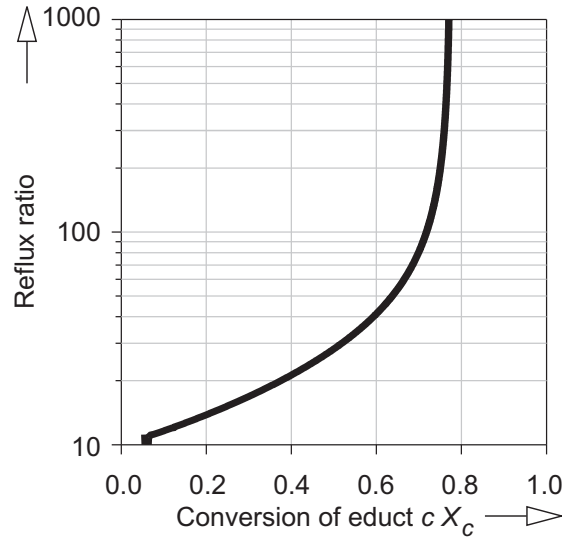


Figure 8.4.: Reflux ratio required by the semi-batch reactor coupled with a rectifying column for the case of the parallel Reaction (8.6).

the distillate concentration increases exponentially with time, as shown in Figure 8.4. Towards the end of the process, the reflux ratio increases asymptotically, and therefore the separation process becomes infeasible, so that the maximum conversion of the heavy-boiling educt is reached.

The effect of the feed ratio is shown in Figure 8.5. The process is operated with constant distillate concentration. The ratio between the feed rate of the light-boiling educt to the distillate flow rate ( $\dot{D}/\dot{F}$ ) is varied. Decreasing the ratio increases the instantaneous amount of the reaction product formed in the reboiler, so that the conversion of the high-boiling educt increases. On the one hand, this allows a lower reflux ratio to be applied to the process. Therefore, the average productivity of the process increases. On the other hand, the rate of the side Reaction (8.6b) increases, hence a larger amount of undesired by-product is formed and the selectivity of the process decreases. Furthermore, when the value of the ratio ( $\dot{D}/\dot{F}$ ) is increased above that given by Equation (8.7), the amount of product formed results to be smaller than the amount removed at the distillate. Therefore, the reflux ratio necessary to maintain the required purity increases faster and the process becomes infeasible at smaller conversions of the heavy-boiling educt.

Table 8.1 summarises the main data used for the simulation of the semi-batch reactor coupled with a rectifying column.

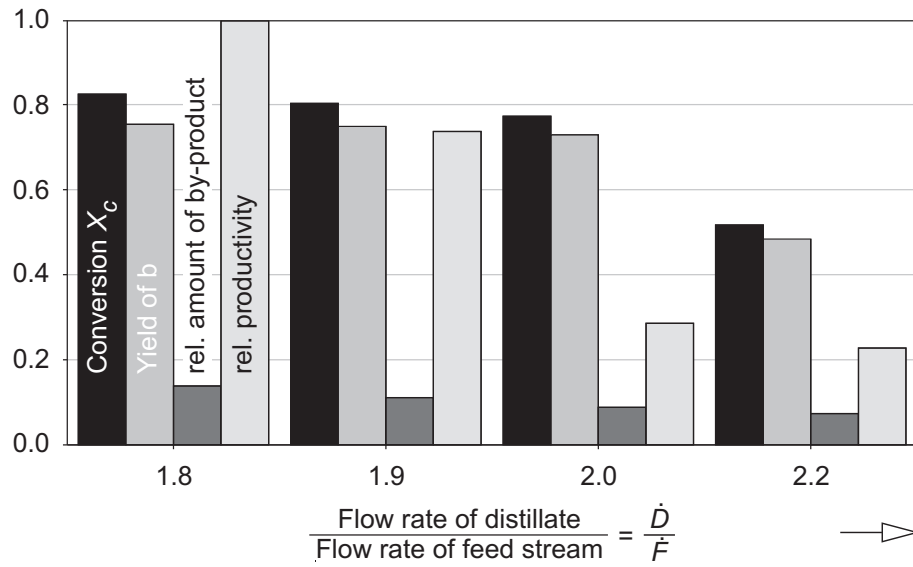


Figure 8.5.: Effect of the distillate to feed ratio  $\dot{D}/\dot{F}$  on the semi-batch reactor coupled with a rectifying column for the case of the parallel Reaction (8.6).

Table 8.1.: Simulation data.

Number of equilibrium stages	$n_{th}$	30
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	2.0
	$\alpha_{cd}$	2.0
	$\alpha_{ad}$	2.0
Reaction rate constants	$k_1$	$1 \text{ s}^{-1}$
	$k_2$	$1 \text{ s}^{-1}$
Concentration of distillate product	$x_{Db}$	0.98 mol/mol
Distillate to feed ratio	$\dot{D}/\dot{F}$	$\nu_b/\nu_a$

### Batch reactive distillation column with a middle vessel

The Reaction (8.6):



is carried out in a batch reactive distillation column with a middle vessel. The process scheme is shown in Figure 8.6. The light-boiling educt is initially charged to the middle vessel, and the heavy-boiling educt is continuously fed close to the top of the upper column. The reaction is carried out exclusively in the reactive section

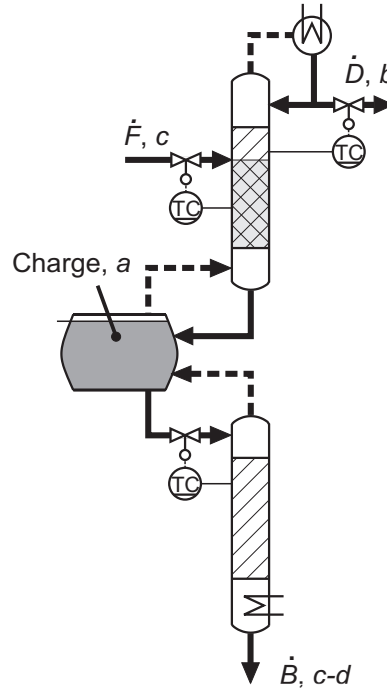


Figure 8.6.: Batch reactive distillation column with a middle vessel.

of the column. This section is included between the feed and the middle vessel. The equilibrium stages above the feed are necessary to purify the top product from the heavy-boiling educt. A heavy-boiling fraction is obtained as bottom's product. The process is operated in closed loop with three temperature controls, as depicted in Figure 8.6. The upper temperature control loop maintains a constant molar fraction of the main product in the distillate  $x_{Db} = 0.93$ . The molar holdups of the distillate and bottom's products, and in the middle vessel are plotted versus the relative distillation time in Figure 8.7. At the end of the process, the light-boiling product has been completely converted to the main and side-products. However, the molar holdup of the main product  $b$ , which is recovered exclusively with the distillate, is much lower than its theoretical maximum. The yield of this product is about 30%. The heavy-boiling side product is completely collected in the bottom's product together with the excess educt fed to the column. The yield of this product is approximately 70%. This means that the process does not suppress the side reaction. This is due to the relatively high concentrations of the key educt  $a$  and of the main product  $b$  in the lower part of the reactive column section. In this part of the column, the reaction rates of the main ( $r_1$ ) and of the side ( $r_2$ ) reactions, shown in Figure 8.8, are both very high. Furthermore, the reaction rate of the side reaction has values which are very close to that of the main reaction. This means that a considerable fraction of the main product reacts further in the second reaction.

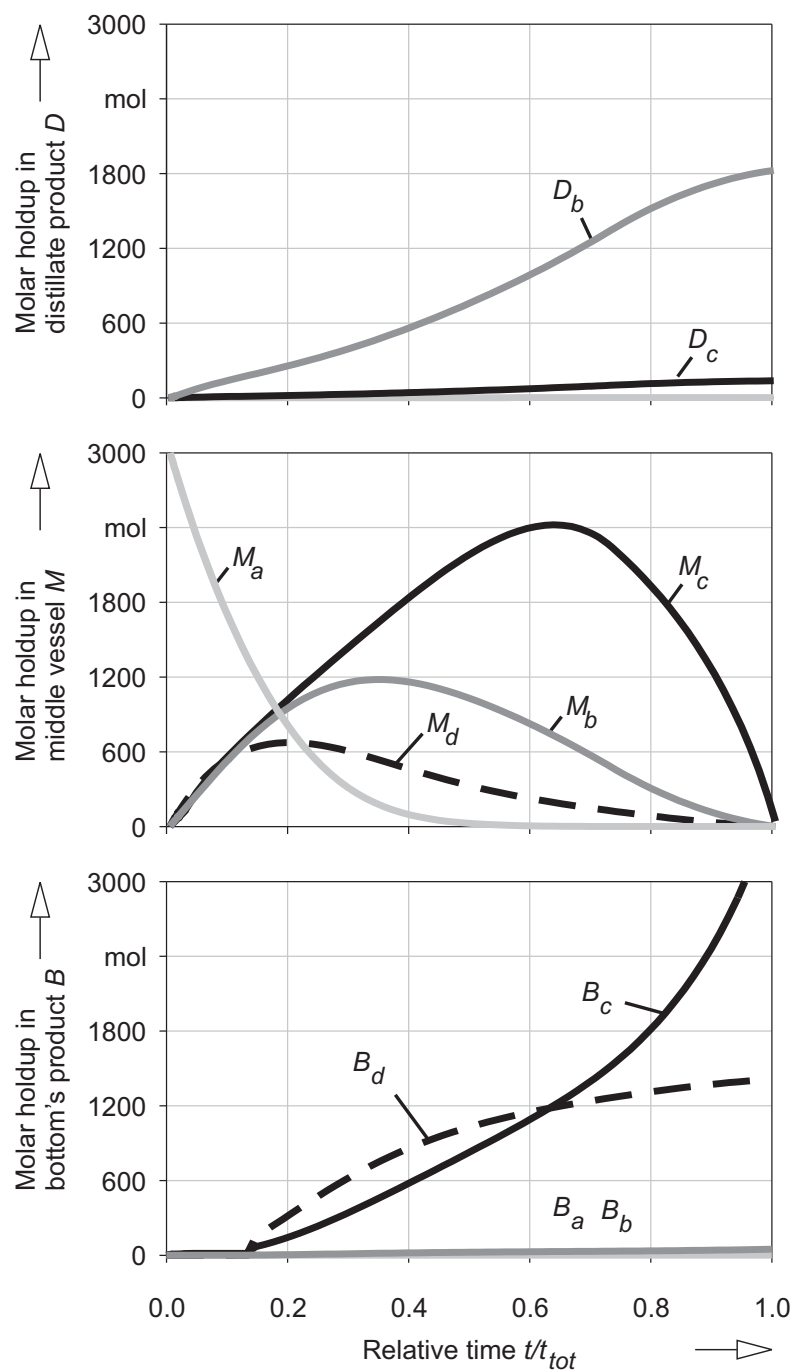


Figure 8.7.: Molar holdup of the distillate and bottoms products and in the middle vessel, for Reaction (8.9) carried-out in a batch reactive distillation column in a middle vessel.



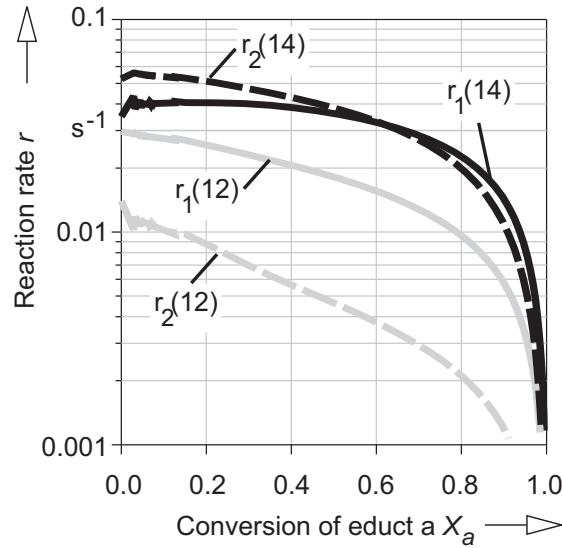


Figure 8.8.: Reaction rates of the main ( $r_1$ ) and of the side ( $r_2$ ) reactions in the reactive column section one ( $n_{th} = 14$ ) and two ( $n_{th} = 12$ ) equilibrium stages above the middle vessel.

Increasing the number of stages in the rectifying section allows lower reflux ratios to be used. Hence, the residence time of the main product in the reactive zone of the column is reduced, and the yield of this product is increased. Nevertheless, the concentration profile in the reactive zone changes only slightly. That is, the concentration of the light-boiling educt and that of the main product remain high in the lower part of the reactive section. The selectivity to the main product therefore increases only very slightly.

The data used for the simulation of the batch reactive distillation column with a middle vessel is reported in Table 8.2.

Table 8.2.: Simulation data: batch reactive distillation column with a middle vessel.

Total Number of equilibrium stages			19
Number of equilibrium stages above feed			9
Number of equilibrium stages in the reactive column section			5
Relative volatilities	$\alpha_{ab}$	2.0	
	$\alpha_{bc}$	2.0	
	$\alpha_{cd}$	2.0	
Reaction rate constants	$k_1$	$1 \text{ s}^{-1}$	
	$k_2$	$1 \text{ s}^{-1}$	
Concentration of distillate product	$x_{Db}$	0.93 mol/mol	

### 8.2.2. Heavy-boiling key educt

A very different situation results if the key educt is the heavy boiler, as represented by Reaction (8.10).



The first reaction producing the main product  $b$  remains unchanged. However, this time, the heavy-boiling educt takes part in both reaction steps. If this reaction were carried out in a semi-batch reactor coupled with a rectifying column, as in the previous case, there would be an excess of the heavy-boiling educt in the reactor. The product  $b$  would react with the excess educt  $d$ , according to Reaction (8.10b). This would consume the desired product. This reaction should therefore be carried out in a semi-batch reactor under an excess of the light-boiling educt ( $a$ ) and a continuous feed of  $d$ . The middle-boiling product ( $b$ ) thus formed is separated from the reaction mixture by coupling the reactor with a stripping column, as shown in Figure 8.9 (i). This column configuration is discussed in the next paragraph. Furthermore, a batch reactive distillation column, similar to the one shown in Figure 6.17 (i) has been studied.

#### Coupling of a semi-batch reactor with a stripping column

The process scheme of a semi-batch reactor coupled with an inverted column is shown in Figure 8.9 (i). The light-boiling educt is charged into the reactor at the beginning of the process. The heavy-boiling educt is continuously fed into the semi-batch reactor. The ratio between the flow rates of the feed stream ( $\dot{F}$ ) and of the bottom product stream ( $\dot{B}$ ) is related to the stoichiometric coefficient of the heavy-boiling educt ( $\nu_d$ ) and that of the main product ( $\nu_b$ ), according to Equation (8.11):

$$\frac{\dot{F}}{\dot{B}} = \frac{\nu_d}{\nu_b} \quad (8.11)$$

In this way, the same amount of main product produced by the reaction is removed from the reactor via distillation. Hence, the main product does not accumulate in the reactor, and therefore the side reaction is largely suppressed.

The concentration path in the reactor ( $x_D$ ) and the average bottom's concentration ( $\bar{x}_B$ ) are shown in Figure 8.9 (ii). In this case, the stripping column, having 15 equilibrium stages, is operated with a constant reboil ratio ( $R_B = 33$ ) until the light-boiling educt depletes from the reactor. The initial charge to the reactor contains some heavy-boiling educt, which immediately reacted to form the desired product. In this way, the initial concentration of the main product in the reactor is  $x_{D,b,\alpha} = 0.1$ . However, some of the product reacts with the heavy-boiling educt in the second Reaction (8.10b). The side product  $c$  thus formed contaminates the bottom product.

Due to the chosen feed policy, the molar fraction of  $b$  in the reactor remains constant throughout the process. In this case, the light-boiling educt is completely converted to the products. The selectivity to the desired component is approximately 86%.

The main constant parameters used to simulate this process are summarised in Table 8.3

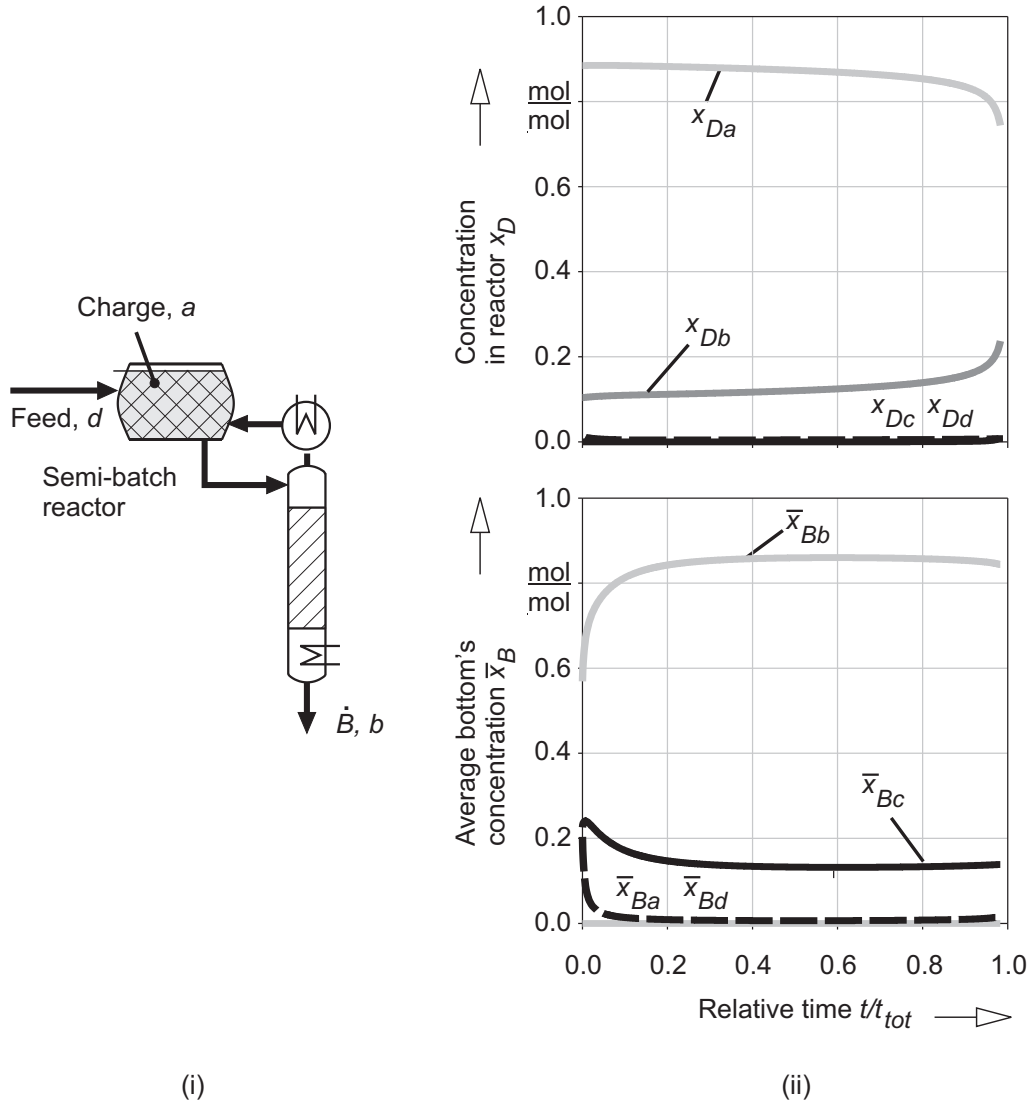


Figure 8.9.: Semi-batch reactor coupled with a stripping column for the production of a middle-boiling product according to the Reaction (8.10): (i) process scheme; and (ii) concentration path in the reactor, and average bottom's concentration.

Table 8.3.: Simulation data of a semi-batch reactor coupled with a stripping column

Number of equilibrium stages	$n_{th}$	15
Relative volatilities	$\alpha_{ab}$	2.0
	$\alpha_{bc}$	2.0
	$\alpha_{cd}$	2.0
Reaction rate constants	$k_1$	$1 \text{ s}^{-1}$
	$k_2$	$1 \text{ s}^{-1}$
Reboil ratio	$R_B$	33
Distillate to feed ratio	$\dot{D}/\dot{F}$	$\nu_b/\nu_a$

### Batch reactive distillation column

In Reaction (8.10), the educts have the highest and lowest volatilities. Furthermore, the volatility of the main product is higher than that of the undesired by-product. The process could therefore be carried out in the batch reactive distillation column shown in Figure 8.2. The light-boiling educt is charged to the reactor, while the heavy boiler is continuously fed to the top of the reactive column section. The two components tend to flow in opposite directions along the reactive section, they therefore react, forming component  $b$ . This rises along the column. However, the concentration of the heavy-boiling educt  $d$  on the upper stages of the reactive section is very high, so that most of component  $b$  further reacts to form the undesired side product  $c$ . The yield and selectivity of the main product are very low. This process is therefore not suitable for the Reaction (8.10).

## 9. Summary

The aim of this work is to provide the process engineer with criteria for the synthesis of batch distillation processes with particular attention paid to batch reactive distillation processes. To achieve this a novel batch distillation process together with several batch reactive distillation processes are developed and analysed. These processes are investigated, their advantages are outlined, and their fields of application are marked.

A novel batch distillation process for the purification of an intermediate boiler from light and heavy-boiling impurities is illustrated in Chapter 5. Based on feasibility studies, an operation procedure is postulated and is validated via simulations of the process. The effect of the most important design parameters is studied. This shows that the duration of the process decreases as the concentration of the intermediate boiler in the charge increases. The process is finally compared with the batch distillation in a middle vessel column. It is demonstrated that the duration of the novel process is shorter than that of the middle vessel column for charges rich in the intermediate boiler, and for difficult separations. However, the two column sections of the novel batch distillation process strongly interact, and therefore the control of this column configuration is more difficult than that of a middle vessel column. Moreover, an experimental investigation of the process is described. The simulated and experimental concentration and temperature profiles qualitatively agree. The feasibility of the novel process is demonstrated, and its practical implementation is explained.

The integration of batch reaction with batch distillation processes is discussed in the second part of this thesis. The investigation treats equilibrium limited reactions, kinetically controlled reactions, and sequential reactions. Several processes are developed and analysed for each reaction group. It is shown that the combination of a batch reactor with a batch distillation column is a very versatile process alternative, in which several reactions can be carried out.

Equilibrium limited reactions, where extreme boiling products are formed, can be carried out in a variety of integrated batch processes. Only the coupling of batch reactors with distillation columns is investigated. Both open and closed operation modes of these processes are analysed. In each case, complete conversion of the educt as well as very high product purities are obtained. This constitutes a very important advantage over the conventional sequential process. In this way, the handling of the liquid fractions between the reaction and separation is eliminated, the separation is simplified, and no recycles are necessary. Furthermore, if the separation is carried out in open processes, the minimum energy demand can be determined via short-cut methods. This reflects the minimum duration of the integrated batch processes. It is shown that the minimum energy demand greatly depends on the volatilities of

the components as well as on the stoichiometry of the reaction. This is therefore an important tool for an initial screening of process alternatives.

If the reaction products are intermediate boilers, integrated semi-batch processes are used. Two groups of processes have been identified. In one case, a semi-batch reactor is coupled with a rectifying column. The heavy-boiling educt is charged into the reactor at the beginning of the process. The light-boiling educt is continuously fed into the reactor, so that its concentration is maintained low throughout the process. In this way, the reaction product with the lowest boiling point is withdrawn as distillate product. In the second group of processes, reactive distillation columns are used. Here, the heavy boiling educt is continuously fed at the top of the reactive column section. It has been shown that the reactive batch distillation in a column with a middle vessel requires a much shorter time than the semi-batch reactor combined with a rectifying column. In the case studied, the duration of the process was reduced by about 60%.

The kinetics of the reaction have a very important influence on the separation process. For slow reaction kinetics, at a constant heat load (i.e. at a constant gas load), the reflux ratio required for the process drastically increases. For very slow reactions, the range of reflux ratios required cannot be applied in practice. In this case, a cyclic reflux policy can be applied. However, this complicates the operation of the process. Closed processes are therefore used. Here, no products are withdrawn from the column, thus allowing high reflux and reboil ratios to be easily applied. Two such processes have been analysed. On the one hand, a batch distillation column coupled with two reactors can be operated close to total reflux conditions, thus using the maximum separation capability of the column, and simplifying the control of the process. However, this process can only be applied when a decomposition reaction takes place in the liquid phase. On the other hand, a batch reactor can be coupled with a middle vessel batch distillation column operated in closed mode. In this case, both reaction products are simultaneously removed from the reactor, thus the concentration of the reactants is maintained high throughout the process. The rate of the chemical reaction is therefore maximised, and therefore the duration of the process is reduced. In the case studied, time savings of up to 70% are obtained.

In Chapter 8, sequential reactions are investigated. If the desired product has the possibility to react further, its yield in a batch reactor might be very low. This complicates the separation process, and the required amount of educts is increased. Therefore, suppressing the side reactions is a very important task in reaction engineering. Combining a batch (or a semi-batch) reactor with a batch distillation process allows for the removal of the desired product from the reaction environment. The volatilities of the components in the mixture play a very important role in process synthesis. It is shown that if the desired product is an intermediate boiler, the combination of a semi-batch reactor with a batch distillation column delivers high yield and selectivity. On the contrary, batch reactive distillation columns are not able to suppress the secondary reactions, since the educts and the products are in contact within the reactive column section.

This thesis has shown that the integration of reaction with batch distillation is very advantageous for the separation of zeotropic mixtures. However, several technical mixtures exhibit a non-ideal behaviour, with the formation of separation barriers. The separation of azeotropic mixtures via batch distillation requires the design of complex separation processes. When reaction is combined with batch distillation, the concentration path in the reactor is determined by both phenomena, and therefore distillation boundaries might be overcome. Hence, further investigation on process synthesis and analysis of reaction integrated with batch distillation for azeotropic mixtures is required.

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## A. Batch reactor coupled with a middle vessel column

The closed operation of a reactor coupled with a middle vessel batch distillation column is discussed in Section 6.1.4, and is shown Figure 6.13 (i). In this process the concentration in the middle vessel ( $x_M$ ) can be maintained constant if the internal reflux ratio of the column and the stoichiometric coefficients are related according to Equation (6.9). The relationship between the reflux ratios can be derived by mass balances around the distillate, middle, and bottom vessels.

Mass balance around the distillate vessel:

$$\frac{dD}{dt} = \dot{V}_U - \dot{L}_U = \dot{V}_U \cdot \left( 1 - \left( \frac{\dot{L}}{\dot{V}} \right)_U \right) \quad (\text{A.1})$$

Mass balance around the bottom vessel:

$$\frac{dB}{dt} = \dot{L}_L - \dot{V}_L = \dot{V}_L \cdot \left( \left( \frac{\dot{L}}{\dot{V}} \right)_L - 1 \right) \quad (\text{A.2})$$

Component balances around the middle vessel:

$$x_M \cdot \frac{dM}{dt} = -\frac{d(D \cdot x_D)}{dt} - \frac{d(B \cdot x_B)}{dt} + \nu \cdot r \cdot M \quad (\text{A.3})$$

Under the condition that the concentrations in the distillate and bottom vessels are constant, i.e.  $dx_D/dt = 0$  and  $dx_B/dt = 0$ , Equation (A.3) can be re-written as:

$$x_M \cdot \frac{dM}{dt} = -x_D \cdot \frac{dD}{dt} - x_B \cdot \frac{dB}{dt} + \nu \cdot r \cdot M \quad (\text{A.4})$$

With  $x_{Dc} = x_{Ba} = 0$ :

$$x_{Ma} \cdot \frac{dM}{dt} = -x_{Da} \cdot \frac{dD}{dt} + \nu_a \cdot r \cdot M \quad (\text{A.5})$$

$$x_{Mc} \cdot \frac{dM}{dt} = -x_{Bc} \cdot \frac{dB}{dt} + \nu_c \cdot r \cdot M \quad (\text{A.6})$$

And dividing Equation (A.5) by Equation (A.6)

$$\frac{x_{Ma}}{x_{Mc}} = \frac{\nu_a}{\nu_c} = \frac{-x_{Da} \cdot dD/dt + \nu_a \cdot r \cdot M}{-x_{Bc} \cdot dB/dt + \nu_c \cdot r \cdot M} \quad (\text{A.7})$$

$$\nu_a \cdot \left( -x_{Bc} \cdot \frac{dB}{dt} + \nu_c \cdot r \cdot M \right) = \nu_c \cdot \left( -x_{Da} \cdot \frac{dD}{dt} + \nu_a \cdot r \cdot M \right) \quad (\text{A.8})$$

In combination with Equations (A.1) and (A.2), and under the assumptions that  $x_{Da} = x_{Bc}$ , and  $V_U = V_L$ :

$$\nu_a \cdot \left( \left( \frac{\dot{L}}{\dot{V}} \right)_L - 1 \right) = \nu_c \cdot \left( 1 - \left( \frac{\dot{L}}{\dot{V}} \right)_U \right) \quad (\text{A.9})$$

$$\nu_a \cdot \left( \frac{\dot{L}}{\dot{V}} \right)_L + \nu_c \cdot \left( \frac{\dot{L}}{\dot{V}} \right)_U = \nu_a + \nu_c \quad (\text{A.10})$$

Therefore Equation (6.9) results:

$$\frac{\nu_a}{\nu_a + \nu_c} \cdot \left( \frac{\dot{L}}{\dot{V}} \right)_L + \frac{\nu_c}{\nu_a + \nu_c} \cdot \left( \frac{\dot{L}}{\dot{V}} \right)_U = 1 \quad (\text{A.11})$$