

Chemical Engineering Report Series

Kemian laitetekniikan raporttisarja

Espoo 2005

No. 47

MODELLING AND SIMULATION OF PROCESS CONFIGURATIONS COMBINING DISTILLATION AND REACTION

Kaj Jakobsson



TEKNILLINEN KORKEAKOULU
TEKNISKA HÖGSKOLAN
HELSINKI UNIVERSITY OF TECHNOLOGY
TECHNISCHE UNIVERSITÄT HELSINKI
UNIVERSITE DE TECHNOLOGIE D'HELSINKI

Chemical Engineering Report Series

Kemian laitetekniikan raporttisarja

No. 47

Espoo 2005

MODELLING AND SIMULATION OF PROCESS CONFIGURATIONS COMBINING DISTILLATION AND REACTION

Kaj Jakobsson

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission for public examination and debate in Auditorium Ke 2 at Helsinki University of Technology (Espoo, Finland) on the 21th of January, 2005, at 12 o'clock.

Helsinki University of Technology
Department of Chemical Technology
Laboratory of Chemical Engineering and Plant Design

Teknillinen korkeakoulu
Kemian tekniikan osasto
Kemian laitetekniikan ja tehdassuunnittelun laboratorio

Distribution:

Helsinki University of Technology

Laboratory of Chemical Engineering and Plant Design

P. O. Box 6100

FIN-02015 HUT

Tel. + 358-9-4511

Fax. +358-9-451 2694

E-mail: Kaj.Jakobsson@hut.fi

© Kaj Jakobsson

ISBN 951-22-7459-0

ISSN 1236-875X

Otamedia Oy

Espoo 2005

ABSTRACT

Process intensification refers to technologies and strategies that enable simpler and more efficient processes compared to conventional processes. Some features of such intensified processes are less recycle streams, reduced need for waste handling and lower investment and operating costs compared to conventional processes. One way of doing this is by making two or more process steps simultaneously and not one after another as it is traditionally done. In this work two such approaches, reactive distillation (RD) and the side reactor configuration (SRC), are studied. RD combines chemical reaction and distillation into a single process unit. In SRC a liquid stream rich in reagents is withdrawn from the distillation and fed into a side reactor. The reactor effluent is returned back into the same column. The final product is then obtained from the distillation column just as in RD processes.

Two models for simulation and design of processes combining reaction and distillation were developed. The first model is for the reactive distillation process. The modelling approach is based on a direct account of the diffusion with multi-component interaction effects, reaction kinetics, and heat transport. The model includes mass transfer in the film region, a catalyst efficiency determination based on the mass transfer inside the catalyst, and hydrodynamic models for reactive trays. This model was successfully tested against experiments from a pilot scale unit.

A new reactive distillation process for producing 2-methoxy-2,4,4-trimethyl pentane is discussed.

The other model is for the Side Reactor Concept (SRC). The model of the distillation column is derived from the mass and energy balances, equilibrium, and summation relations of a stage in a reactive distillation column. Rigorously calculated Murphree multi-component efficiencies are included to account for non-ideality of the stages. This model also includes a series of continuously stirred tank reactors (CSTR) representing the side reactor stage. Co-current flow and gas and liquid phases and heterogeneous catalyst are allowed in the reactor.

The use of SRC and RD is discussed in two case studies, in the production of TAME and isooctene. The study showed that SRC is a potential process option, especially because the reactor conditions can be optimised to improve the performance of the process.

PREFACE

The research described in this thesis was done in the Laboratory of Chemical Engineering and Plant Design in Helsinki University of Technology during 1996-2004. The main part of the work was accomplished within the frame of BRITE-EURAM Project Reactive Distillation (CEC Project No. BE95-1335).

I am very grateful to my supervisor Juhani Aittamaa for his guidance and encouragement during this work. I thank professor Andrzej Gorak for guidance and encouragement during the EU project. I thank all partners of the Reactive Distillation project for giving me the important opportunity to work in the project.

I thank my co-authors Tuomas Ouni, Antti Hasanen, Sini Pakkanen, Kari Keskinen, Liisa Struckmann, and Satu Hyvärinen. I warmly thank my colleagues and friends Antti Pyhälähti, Kimmo Klemola, Eugeny Kenig, and Peter Banik for co-operation and advices. I also thank the staff of the Laboratory of Chemical Engineering and Plant Design for creating a good working atmosphere.

The support by the European Commission in the frame of the BRITE-EURAM program (CEC Project No. BE95-1335) is greatly acknowledged.

The financial support of the PROTEK programme of the Academy of Finland is greatly acknowledged.

The financial support of TEKES (National Technology Agency of Finland) is greatly acknowledged.

Konrad-Zuse-Zentrum in Berlin is acknowledged for the DAE-solver LIMEX used in DESIGNER.

Finally, my warmest thanks to my wife Hanni and to my children Kim, Outi and Eva for giving me a wonderful life, which is much richer than I ever expected.

Espoo May 2004

Kaj Jakobsson

LIST OF PUBLICATIONS

This thesis is based on the following publications (Appendices I-VII), which are referred to in the text by their roman numerals:

- I Kenig, E.Y., Pyh alahti, A., Jakobsson, K., G orak, A, Aittamaa, J., Sundmacher, K., Advanced Rate-based Simulation Tool for Reactive Distillation, *AIChE J.* **50** (2004) 322-342.
- II Kenig, E., Jakobsson, K., Banik, P., Aittamaa, J., Gorak, A., Koskinen, M., Wettmann, P., An integrated tool for synthesis and design of reactive distillation, *Chem. Eng. Sci.* **54** (1999) 1347-1352.
- III Jakobsson, K., Pyh alahti, A., Pakkanen, S., Keskinen, K., Aittamaa, J., Modelling of a Side Reactor Configuration Combining Reaction and Distillation, *Chem. Eng. Sci.* **57** (2002) 1521-1524.
- IV Pyh alahti A., and Jakobsson, K., The Ratebased Mixed Pool Model of a reactive distillation column, *Ind. Eng. Chem. Res.* **42** (2003) 6188 – 6195.
- V Ouni, T., Jakobsson, K., Pyh alahti, A., Aittamaa, J., Enhancing Productivity of Side Reactor Configuration through Optimising the Reaction Conditions, *Chem. Eng. Res. Des.* **82**(A2) (2004) 167-174.
- VI Rihko-Struckmann, L.K., Karinen R.K., Krause, A.O.I., Jakobsson, K., Aittamaa J.R. Process Configurations for the Production of the 2-methoxy-2,4,4-trimethylpentane - a Novel Gasoline Oxygenate, *Chem. Eng. Process.* **43** (2004) 57-65.
- VII Jakobsson, K., Hasanen, A., Aittamaa, J., Modelling of a Countercurrent Hydrogenation Process, *Chem. Eng. Res. Des.* **82**(A2) (2004) 203-207.

Kaj Jakobsson's contribution to the appended publications

- I, II, IV The papers are related to the BRITE-EURAM Project Reactive Distillation. The author participated in model development, validation, simulation, and experimental planning of the project. The author was the co-ordinator of the computer implementation of the models. The author did most of the model implementation, testing, and validation. The author participated in the definition of research plan and writing of the manuscript together with the co-authors.
- III The author participated in the model development, validation, and implementation. The author participated in the definition of research plan and wrote the manuscript together with the co-authors.
- V The author participated in the model development. The author participated in the definition of research plan and wrote the manuscript together with the co-authors.
- VI The author participated in the model development and simulation. The author participated in the definition of research plan and wrote the manuscript together with the co-authors, this concerning only the process design part of the paper.
- VII The author participated in the definition of research plan and wrote the manuscript together with the co-authors. The author participated in model development, validation, simulation, and implementation.

MODELLING AND SIMULATION OF PROCESS CONFIGURATIONS COMBINING DISTILLATION AND REACTION

ABSTRACT

PREFACE

LIST OF PUBLICATIONS

1	INTRODUCTION	7
2	MODELING ASPECTS OF REACTIVE DISTILLATION	9
2.1	Independent equations and variables of the rate-based stage	10
2.2	Reboiler and condenser model	12
2.3	Solution method	13
2.3.1	Newton's method	14
2.3.2	Jacobian matrix	14
2.3.3	Thomas algorithm	15
2.3.4	Determination of the step length S	16
2.3.5	Initialisation of the variables	16
2.3.6	Relaxation method	17
2.3.7	Hybrid method	18
2.4	Mass transfer model	19
2.5	Reaction modelling	20
2.6	Modelling of hydrodynamics	21
2.6.1	Rate-based mixed pool model	21
2.6.2	Model equations for the mixed pool model	22
2.6.3	Solver	24
2.7	Implementation of DESIGNER	24
2.7.1	Self-standing DESIGNER	24
2.7.2	DESIGNER in flowsheeting program FLOWBAT	25
3	VALIDATION OF THE REACTIVE DISTILLATION MODEL	26
3.1	Distillation without reaction	26
3.2	Comparison with experimental results from RD	28
3.3	Simulations with the mixed pool model	31
4	APPLICATION OF THE REACTIVE DISTILLATION MODEL TO SIMULATION OF COUNTER-CURRENT REACTORS	35
4.1	Modelling	35
4.2	Simulations	35
4.3	Discussion and conclusions counter-current reactor modelling	38
5	REACTIVE DISTILLATION PROCESS FOR GASOLINE OXYGENATE	39
5.1	Process design	39
5.2	Conclusions RD for gasoline oxygenate	42
6	MODELLING A SIDE REACTOR CONFIGURATION COMBINING REACTION AND DISTILLATION	43
6.1	Modelling	44
6.2	Method of solution	45
6.3	Model testing	46
6.4	Conclusions SRC modelling	48
7	SIDE REACTOR CONFIGURATION VS. REACTIVE DISTILLATION - SOME CASE STUDIES	49

7.1 TAME production	49
7.2 Isobutylene dimerisation	51
7.3 Conclusions SRC vs. RD	54
8 CONCLUSIONS AND DISCUSSION	55
8.1 Modelling	55
8.2 Processes	58
REFERENCES	60
NOTATION	64

1 INTRODUCTION

Process intensification (PI) is one of the challenges of process design today. PI refers to technologies and strategies that enable simpler and more efficient processes compared to conventional processes. Some features of such intensified processes are less recycle streams, reduced need for waste handling, and lower investment and operating costs compared to conventional processes. One way of doing this is to perform two or more process steps simultaneously and not one after another as it is traditionally done. An example of this is reactive distillation (RD). RD combines chemical reaction and distillation into a single process unit. In some applications, when reaction equilibrium prevents high conversions, the coupling of a reactor with distillation to remove the reaction products from the reaction zone can improve the overall conversion and selectivity significantly. In other applications, reactions are used to overcome the separation problems caused by azeotropes.

Applicability of RD is highly dependent on the chemical system at hand. Optimal or nearly optimal process conditions must be found both for the separation and reaction. The reaction rate at distillation conditions must be high enough without harmful side reactions.

Pyh lahti (1996) and later Taylor and Krishna (2000) and Sundmacher and Kienle (2003) have discussed in their reviews of RD also various hardware structures for reactive distillation. If the catalyst used in the process is homogeneous, the conventional distillation trays can be used. However, some consideration must be given in arranging adequate liquid hold-up and operation regime on the tray. When a solid catalyst is applied, additional things must be considered. The catalyst must usually be stationary in the column. Mass transfer must be efficient at the catalyst liquid interface as well as at the vapour liquid interface. No excessive pressure drop should be developed. Swelling of the catalyst must be taken into account. Changing catalyst should be easy and the internals should be cheap and durable. There are several strategies to place the heterogeneous catalyst in the column. It can be placed in containers on or between the distillation trays, the catalyst might be in the form of rings or pellets used as random packing, or the catalyst might be put in pockets in structures like structured distillation packing. Fulfilling all requirements of the column internals is difficult and the hardware aspects are often the main obstacles to using RD.

If a slow liquid phase reaction is considered, there is a contradiction between the requirements of having a large catalyst hold-up for reaction and to have an adequately void catalyst for vapour passage. The traditional ways to compensate for the catalyst deactivation, that is, adding excess catalyst or increasing the reaction temperature, are seldom feasible in RD applications. To overcome these problems and to maintain the benefits of the combined process, the side reactor concept (SRC) can be used instead. In SRC a liquid stream rich in reagents is withdrawn from the distillation column and fed into a side reactor. The reactor effluent is returned back to the same column. The final product is then obtained from the distillation column just as in RD processes. In SRC technology the hardware can be built from technically proven distillation and reactor components. In RD applications, new proprietary or untested catalyst/separation systems must be used.

RD process design requires detailed modelling of the process. The accurate modelling of the RD process is a considerable effort and requires detailed knowledge of reaction kinetics, vapour liquid equilibrium, mass transfer, and hydrodynamics. The available design tools use much too idealised models and contain only idealised distillation and reaction models, and lack adequate models to describe mass transport and reactions simultaneously. The models for hydrodynamic phenomena are generally not adequate.

The main target of this thesis is to present a process simulator (called DESIGNER) to model, design, and study the complex behaviour of the RD column for industrial process design.

The simulation of SRC is also challenging. Especially the coupled behaviour of the reactor and separator tends to make the simulators using unit modular approach to fail when calculating industrial scale SRC processes. Thus a new software tool to simulate and optimise processes that combine distillation column with a reactor sequence was also developed. This kind of combination is particularly interesting when new intensified and integrated processes are developed.

2 MODELING ASPECTS OF REACTIVE DISTILLATION

One way of modelling reactive distillation is to use the equilibrium stage model combined with the equations for chemical reaction. It is well known that real distillation plates deviate significantly from ideal plates and this non-ideality must be included in the models of distillation columns. The ideal stage concept is too restricted and therefore mass transfer effects in the reaction zone are considered when the new model DESIGNER was developed. This approach is based on a direct account of the multi-component diffusion, reaction kinetics, and heat transport. The particular interest in the DESIGNER development was the mass transfer model including fast reaction in the film region, mass transfer inside the catalyst affecting the catalyst efficiency, and hydrodynamic models for catalyst supports [1].

In this work the reactive distillation column is modelled as a sequence of rate-based segments, see Figure 1. This modelling concept was first introduced by a series of papers by Taylor and Krishnamurthy (1985a, b, c, d and 1986). The model was further developed to a second-generation model by Taylor *et al.* (1994). The adaptation of this concept for reactive distillation has been done among others by Zheng and Xu (1992) and Sundmacher and Hoffmann (1996).

The rate-based segments are connected counter-currently and can be identified with real trays or segments of a packed column. The stages are interrelated via mass and energy balance equations.

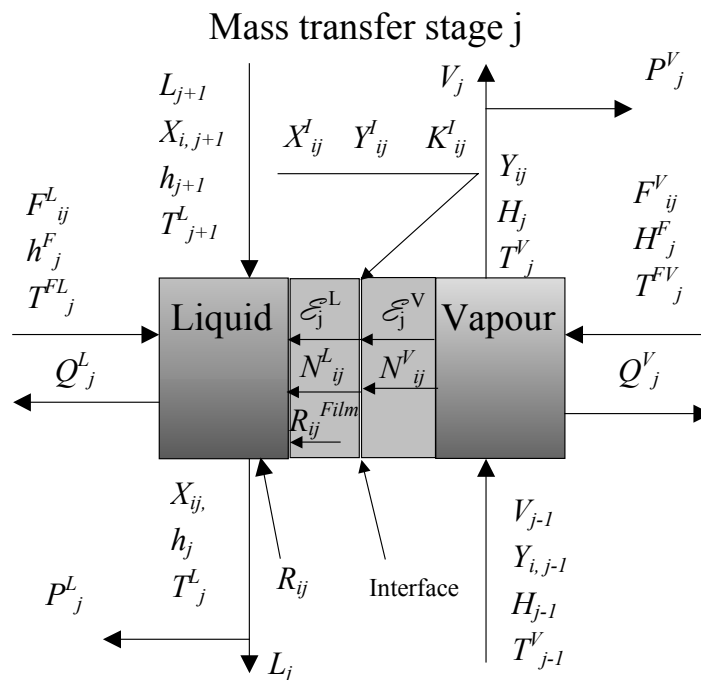


Figure 1. Schematic figure of a rate-based stage.

2.1 Independent equations and variables of the rate-based stage

The independent variables and equations used in the stage model are presented in this section. The detailed derivation of these equations is found in Taylor and Krishna (1993). In this formulation the mass and energy balances are written around balance boundaries that are formed of a slice of column section consisting of the vapour and liquid phase. The mass transfer between the phases is assumed to take place according to the two-film theory. At the phase interface equilibrium is assumed. The reaction on the stages is modelled in one of the following ways.

- 1) The reaction is modelled as homogeneous reaction in the liquid bulk.
- 2) For heterogeneous catalytic liquid phase reactions the effect of the mass transfer resistances in the catalyst pellets based on the theory by Sundmacher and Hoffmann (1996) is implemented.
- 3) The reaction is modelled as homogeneous reaction in the liquid film based on the theory presented by Kenig and Gorak (1996). In this model the calculation of reaction rate is incorporated in the liquid side mass transfer model. This model is used for fast homogeneous reactions.

The original set of equations and variables presented by Taylor and Krishna (1993) are modified here to include the source term of the reactions in the mass balances and to account for the reaction in the liquid film.

The heat of the reaction is not treated in our set of equations as a variable since we start our enthalpy calculation from the heat of formation of a compound. Thus the reaction enthalpies are included in the energy balances implicitly.

The equations for the rate-based stage

Total mass balance, vapour:

$$M_{totj}^V \equiv P_j^V + V_j - V_{j+1} - F_{totj}^V + N_{totj} = 0 \quad (1)$$

Component mass balance, vapour:

$$M_{ij}^V \equiv (P_j^V + V_j) Y_{ij} - V_{j+1} Y_{i,j+1} - F_{ij}^V + N_{ij} = 0, \quad i=1..NC \quad (2)$$

Total mass balance, liquid:

$$M_{ij}^L \equiv P_j^L + L_j - L_{j+1} - F_{totj}^L - N_{totj} - R_{totj}^L - R_{totj}^{film} = 0 \quad (3)$$

Component mass balance, liquid:

$$M_{ij}^L \equiv (P_j^L + L_j) X_{ij} - L_{j+1} X_{i,j+1} - F_{ij}^L - N_{ij} - R_{ij}^L - R_{ij}^{film} = 0, \quad i=1..NC \quad (4)$$

Mass transfer relations, vapour:

$$R_{ij}^V \equiv N_{ij} - N_{ij}^V = 0, \quad i=1..NC-1 \quad (5)$$

Mass transfer relations, liquid:

$$R_{ij}^L \equiv N_{ij} - N_{ij}^L + R_{ij}^{film} = 0, \quad i=1..NC-1 \quad (6)$$

Energy balance, vapour:

$$E_j^V \equiv (P_j^V + V_j) H_j - V_{j-1} H_{j-1} - F_{tot j}^V H_j^F + Q_j^V + \mathcal{E}_j^V = 0 \quad (7)$$

Energy balance, liquid:

$$E_j^L \equiv (P_j^L + L_j) h_j - L_{j+1} h_{j+1} - F_j^L h_j^F + Q_j^L - \mathcal{E}_j^L = 0 \quad (8)$$

Energy balance, interface:

$$E_j^I \equiv \mathcal{E}_j^V - \mathcal{E}_j^L = 0 \quad (9)$$

Equilibrium relation at interface:

$$Q_{ij}^I \equiv K_{ij} X_{ij}^I - Y_{ij}^I = 0, \quad i=1..NC \quad (10)$$

Summation at interface, vapour:

$$S_j^V \equiv \sum_{I=1}^{NC} Y_{ij}^I - 1 = 0 \quad (11)$$

Summation at interface, liquid:

$$S_j^L \equiv \sum_{I=1}^{NC} X_{ij}^I - 1 = 0 \quad (12)$$

Pressure drop, stage N-1:

$$PB_{N-1} \equiv PRES_{N-1} - PRES_{spec} \quad (13)$$

Pressure drop stages < N-1:

$$PB_j \equiv PRES_j - PRES_{j+1} - \Delta P_{j+1} \quad (14)$$

The total number of independent equations on one rate-based stage is as follows:

M_{ij}^V	total mass balance around the vapour phase	1
M_{ij}^V	component material balances around the vapour phase	NC
E_j^V	energy balance around the vapour phase	1
R_{ij}^V	mass transfer relations for vapour	$NC-1$
S_j^V	summation vapour	1
Q_j^I	equilibrium relations at interface	NC
E_j^I	enthalpy balance over the interface	1
M_{ij}^L	total mass balance around the liquid phase	1
M_{ij}^L	component mass balances around the liquid phase	NC
E_j^L	enthalpy balance around liquid phase	1
R_{ij}^L	mass transfer relations, liquid	$NC-1$
S_j^L	summation liquid	1
PB_j	hydraulic equation (pressure drop)	1

		$5 NC + 6$

The independent variables used are:

V_j	vapour flow bulk	1
Y_{ij}	concentration, vapour	NC
T_{ij}^V	bulk temperature, vapour	1

Y_{ij}^I	interface concentration vapour	NC
X_{ij}^I	interface concentration liquid	NC
T_{ij}^I	interface temperature	1
L_j	liquid flow, bulk	1
T_{ij}^L	bulk temperature, liquid	1
X_{ij}	concentration, liquid	NC
N_{ij}	mass transfer rate	NC
$PRES_j$	pressure	1

		5 NC + 6

The variables are ordered into vector (\mathbf{x}_j) as follows:

$$(\mathbf{x}_j)^T \equiv (V_j, L_j, Y_{1j} \dots Y_{NC,j}, X_{1j} \dots X_{NC,j}, T_j^V, T_j^L, Y_{1j}^I \dots Y_{NC,j}^I, X_{1j}^I \dots X_{NC,j}^I, T_j^I, N_{1j} \dots N_{NC,j}, PRES_j) \quad (15)$$

The corresponding equations per stage are ordered into vector (\mathbf{F}_j) as follows:

$$(\mathbf{F}_j)^T \equiv (M_{ij}^V, M_{1j}^V \dots M_{NC,j}^V, E_j^V, R_{1,j}^V \dots R_{NC-1,j}^V, S_j^V, Q_{1,j}^I \dots Q_{NC,j}^I, E_j^I, M_{1,j}^L \dots M_{NC,j}^L, E_j^L, R_{1,j}^L \dots R_{NC-1,j}^L, PB_j) \quad (16)$$

2.2 Reboiler and condenser model

The reboiler and the (total) condenser stages $j=1, j=N$ are modelled as equilibrium stages with the well-known MESH equations.

Boiler, condenser-independent equations:

M_{ij}	Total mass balance	1
M_{ij}	Component mass balance	NC
Q_{ij}	Equilibrium relation	NC
S_j	Summation	1
SP_j	Spec: $B-L_1 = 0$, reboiler	1
	(Spec: $L_N - rf \cdot V_N = 0$, condenser)	(1)
PB_j	Hydraulic	1

		2 NC+4

Variables:

V_j	molar flow vapour	1
$Y_{i,j}$	molar fraction vapour	NC
T_j	Temperature	1
$X_{i,j}$	molar fraction liquid	NC
L_j	molar flow liquid	1
$PRES_j$	Pressure	1

		2 NC+4

The variables are ordered into vector (\mathbf{x}_j) (boiler) as follows:

$$(\mathbf{x}_1)^T \equiv (V_1, L_1, Y_{1,1} \dots Y_{NC,1}, X_{1,1} \dots X_{NC,1}, T_j, PRES_j) \quad (17)$$

The variables are ordered into vector (\mathbf{x}_N) (condenser) as follows:

$$(\mathbf{x}_N)^T \equiv (V_N, L_N, X_{1,N} \dots X_{NC,N}, Y_{1,1} \dots Y_{NC,1}, T_j, PRES_j) \quad (18)$$

The corresponding equations on stage 1 (boiler) are ordered into vector (\mathbf{F}_1) as follows:

$$(\mathbf{F}_1)^T \equiv (M_{1,1} \dots M_{NC,1}, Q_{1,1} \dots Q_{NC,1}, M_H, S_1, SP_1, PB_1) \quad (19)$$

The corresponding equations on stage N (boiler) are ordered into vector (\mathbf{F}_1) as follows:

$$(\mathbf{F}_N)^T \equiv (M_{1N}, M_{1,N} \dots M_{NC,N}, Q_{1,N} \dots Q_{NC,N}, S_N, SP_N, PB_N) \quad (20)$$

2.3 Solution method

According to Chang and Seader (1988), the calculation procedures suitable for solving mass and energy balances and equilibrium relations in multi-component reactive distillation have been reported since 1970. Recent papers focusing on the numerical solution of RD model equations, Alejski *et al.* (1988), Venkataram *et al.* (1990), Simandl and Svrcek (1991), Yuxiang and Xien (1992), Zhu and Shen (1995), and Sundmacher and Hoffman (1996), show that strategies used for solving the independent equations and variables for a reactive or rate-based distillation problem Taylor and Krishna (1993), Powers *et al.* (1988) can be divided basically into three categories of solving non-linear algebraic model equations:

1. Simultaneous correction methods (Newton-Raphson or similar)
2. Continuation-homotopy methods
3. Relaxation methods

The simultaneous correction methods are fast and robust, if a good initial point can be provided. Continuation-homotopy methods and relaxation methods have a larger domain of convergence, but they require longer computing times.

In this work the first attempt to solve the highly non-linear set of the governing equations was done using the Newton's method.

To overcome the initialisation problem, a hybrid method combining the relaxation and Newton's method was developed. In the relaxation method the steady state solution is found through the change of the column state with time.

The dimension of the blocks A_j , B_j and C_j is the same as the dimension of the corresponding stage (model equations x variables). The dimensions of the blocks are listed in Table 3.

Table 3. The dimensions of the Jacobian blocks

Block	Dimension	Corresponding stages
B_1	$(2 \times NC + 4) \times (2 \times NC + 4)$	Reboiler x Reboiler
C_1	$(2 \times NC + 4) \times (5 \times NC + 6)$	Reboiler x Normal stage
A_2	$(5 \times NC + 6) \times (2 \times NC + 4)$	Normal x Reboiler
A_j, B_j, C_j	$(5 \times NC + 6) \times (5 \times NC + 6)$	Normal x Normal
C_{N-1}	$(5 \times NC + 6) \times (2 \times NC + 4)$	Normal x Condenser
A_N	$(2 \times NC + 4) \times (5 \times NC + 6)$	Condenser x Normal
B_N	$(2 \times NC + 4) \times (2 \times NC + 4)$	Condenser x Condenser

The Jacobian block matrices A , B and C are quite sparse. Especially the blocks A and C have only a small number of non-zero terms. These blocks are computed analytically. The computation of the B blocks of the Jacobian is done numerically.

2.3.3 Thomas algorithm

The linearised subset of the equations is solved with the Thomas algorithm; see for example King (1980). The smaller sizes of the condenser and the reboiler blocks require modifications to the Thomas algorithm. This leads to a slightly modified Thomas algorithm where stages 1, 2, N-1 and N have to be treated separately.

$$\begin{aligned}
 \mathbf{w}_1 &= \mathbf{B}_1 & j=1 \\
 \mathbf{u}_1 &= (\mathbf{w}_1)^{-1} \mathbf{C}_1 & j=1 \\
 \mathbf{w}_2 &= \mathbf{B}_2 - \mathbf{A}_2 \mathbf{u}_1 & j=2 \\
 \mathbf{u}_j &= (\mathbf{w}_j)^{-1} \mathbf{C}_j & 2 \leq j \leq N-1 \\
 \mathbf{w}_j &= \mathbf{B}_j - \mathbf{A}_j \mathbf{u}_{j-1} & 3 \leq j \leq N-1
 \end{aligned}$$

$$\begin{aligned}
 \mathbf{g}_1 &= (\mathbf{w}_1)^{-1} \mathbf{F}_1 & j=1 \\
 \mathbf{g}_2 &= (\mathbf{w}_2)^{-1} (\mathbf{F}_2 - \mathbf{A}_2 \mathbf{g}_1) & j=2 \\
 \mathbf{g}_j &= (\mathbf{w}_j)^{-1} (\mathbf{F}_j - \mathbf{A}_j \mathbf{g}_{j-1}) & 3 \leq j \leq N-1 \\
 \mathbf{g}_N &= (\mathbf{w}_N)^{-1} (\mathbf{F}_N - \mathbf{A}_N \mathbf{g}_{N-1}) & j=N
 \end{aligned}$$

Back substitution

$$\begin{aligned}
 \Delta \mathbf{x}_N &= \mathbf{g}_N & j=N \\
 \Delta \mathbf{x}_{N-1} &= \mathbf{g}_{N-1} - \mathbf{u}_{N-1} \Delta \mathbf{x}_N & j=N-1 \\
 \Delta \mathbf{x}_j &= \mathbf{g}_j - \mathbf{u}_j \Delta \mathbf{x}_{j+1} & 2 \leq j \leq N-2 \\
 \Delta \mathbf{x}_1 &= \mathbf{g}_1 - \mathbf{u}_1 \Delta \mathbf{x}_2 & j=1
 \end{aligned}$$

The Thomas algorithm is robust and effective. The algorithm is bound to the strictly tridiagonal structure which means that each stage in the column can only interact with variables of plates above and below. For example, adding an equation for an internal stream from stage $j+7$ to stage j as a specification to the column would cause an off-diagonal term in the Jacobian. This means that a considerable change has to be done in the algorithm. However, adding specifications that preserve the tridiagonal structure of the Jacobian is straightforward.

2.3.4 Determination of the step length S

The user has three options for determining the step length S (see eq. 21) in the algorithm.

The three options for determining the step length S are as follows:

1. Quadratic optimisation combined with control of the step length that allows the Newton step be taken only if the calculated residual is improved. The algorithm reduces the step length S until the residual is smaller than the residual in the previous iteration.
2. Newton step limited only by the improvement of the residual functions. As in method 2, the algorithm reduces the step length S until the residual is smaller than the residual in the previous iteration.
3. S limited only by the allowed maximum changes of the variables

In all methods, the iteration is terminated, if the step length becomes smaller than a predefined value.

Method 1 is the default method and it usually works fast and robust. In some special cases, when particularly nursing the solution is necessary, methods 2 and 3 are useful.

Common for all three methods is that the maximum change of one variable is limited by maximum and minimum values and by the fraction of the change of the variable towards the limit.

2.3.5 Initialisation of the variables

A known property of the Newton's method is that a good initial estimate of the column state is needed to reach the convergence. Therefore, the variables of the real stage are initialised by solving an equilibrium stage distillation model before attempting to solve the rate-based model. If a previously solved case is available, this can also be used to initialise the variables. This is useful in solving complicated flowsheets.

The Murphree's efficiency is incorporated into the equilibrium model. The user can vary the efficiency to make the separation of the equilibrium stage model more consistent with the rate-based model.

and \mathbf{X}_{ij}^I are interfacial vapour and liquid composition vectors, T_j^I is the interfacial temperature, and \mathbf{N}_{ij} is the vector of mass transfer rates. Further variables in Eq. (31) denote the following equation groups: M_{ij}^V and M_{ij}^L total material balances for the vapour and liquid phases, \mathbf{M}_{ij}^V and \mathbf{M}_{ij}^L component material balances for the vapour and liquid phases, E_j^V , E_j^L and E_j^I energy balances for the vapour and liquid phases and around the interface, \mathbf{R}_{ij}^V and \mathbf{R}_{ij}^L mass transfer rates in the vapour and liquid phases, S_j^V and S_j^L are summation equations for the vapour and liquid phases, and \mathbf{Q}_{ij}^I is equilibrium equations at the interface.

Vectors \mathbf{Y}_{ij} , \mathbf{X}_{ij} , \mathbf{X}_{ij}^I , \mathbf{M}_{ij}^V , \mathbf{M}_{ij}^L and \mathbf{Q}_{ij}^I are of dimension n and vectors \mathbf{Y}_{ij}^I , \mathbf{R}_{ij}^V , \mathbf{N}_{ij} , and \mathbf{R}_{ij}^L are of dimension $NC-1$. The vapour and liquid inertia terms U_j^V and U_j^L are taken to be constant.

The algorithm starts by the initialisation of the DAE system. The requirement is that the algebraic part of the equation system is satisfied. This can be achieved by initialising the bulk liquid compositions X_{ij} and interfacial compositions X_{ij}^I by the average feed liquid compositions, setting the vapour compositions Y_{ij} , Y_{ij}^I and the temperatures T^L , T^I , T^V to the bubble point conditions. The mass transfer rates are set to zero and the reaction rates are computed at this condition. Finally, the total mass and energy balances for each stage of the column are solved to yield the liquid and vapour flow rates.

The DAE system is solved with the LIMEX code available from the Konrad-Zuse-Zentrum (Berlin, Germany).

Important parameters for the performance of the algorithm are the inertia terms U^L and U^V , the integration time Δt , and the maximum value for the loop counter. It is fairly easy to find suitable values for the parameters by trial and error.

Sometimes this initialisation procedure fails and the flow values become negative. For such cases, the user can specify the stage liquid compositions directly. In this case, the reaction rates are first set to zero and calculated using the following relations:

$$R_{ij}^{film} = (1.0 - e^{(-kt)})R_{ij}^{film} \quad (32)$$

$$R_{ij} = (1.0 - e^{(-kt)})R_{ij} \quad (33)$$

2.3.7 Hybrid method

To overcome the initialisation problem of Newton and to shorten the long computation time of the relaxation method, a hybrid method was developed. This method combines both the relaxation method and the Newton's method. The flow chart of the hybrid method is presented in Figure 2.

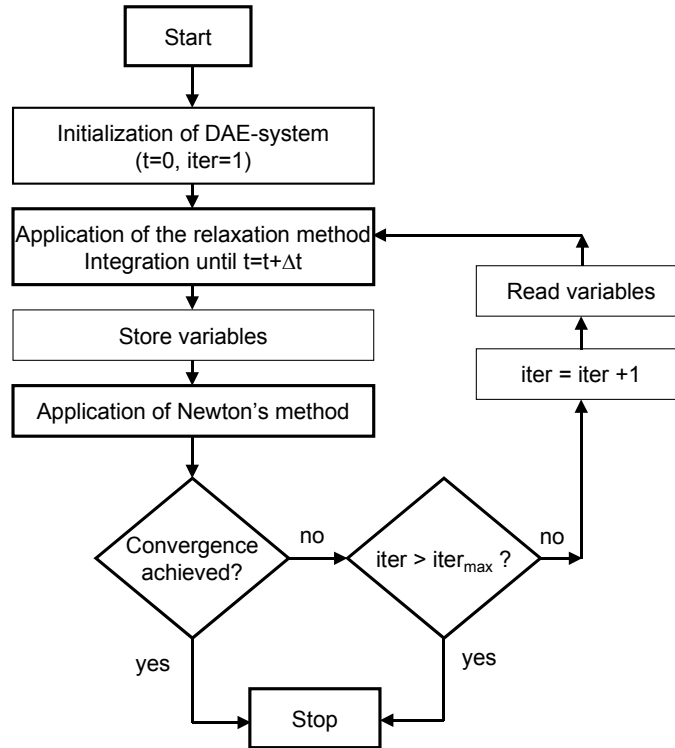


Figure 2. The flow chart of the hybrid algorithm.

Starting from the point found as described in the previous section, the problem is integrated to the pre-set time t and switched to the Newton solver. If the Newton solver fails, the program returns to the integrator and continues the calculation. A loop counter controls whether a pre-set maximum number of the relaxation/Newton iterations is reached.

When applying the hybrid method, it is especially important to set limitations for the variables during the Newton iteration to keep the variables in physically meaningful region. If the variables are not kept in this region, the physical property routines might fail and abort the program.

2.4 Mass transfer model

Mass transfer in the stage is described by the two-film model, which assumes that for each phase, all of the transport resistance is concentrated in a thin film adjacent to the phase interface. In the bulk fluid outside this film, complete mixing is presumed with no composition gradient at all. In both films, one-dimensional diffusion transport normal to the interface takes place.

Multi-component diffusion in the films is described by the Maxwell-Stefan equations taken in a generalised form, which corresponds to real gases and liquids (see Taylor and Krishna, 1993). In this stage model, the equilibrium state exists only at the interface.

The liquid mass transfer rate is calculated from equation (34)

$$(N_i) = (N_i^L) = C_t [R_i^L]^{-1} a [\Gamma_i^L] \left[(X_i^I) - (X_i^L) \right] + N_{t,i} (X_i^L), \quad i = 1..(NC - 1) \quad (34)$$

The vapour mass transfer rate is calculated from equation (35)

$$(N_i) = (N_i^V) = C_t [R_i^V]^{-1} a \left[(Y_i^V) - (Y_i^I) \right] + N_{t,i} (Y_i^V), \quad i = 1..(NC - 1) \quad (35)$$

where in equation (34)

$$R_{ii} = \frac{X_i}{k_{inc}} + \sum_{m=1, m \neq i}^{nc} \frac{X_m}{k_{im}} \quad \text{and} \quad R_{ij} = -X_i \left(\frac{1}{k_{ij}} \right) - \left(\frac{1}{k_{inc}} \right) \quad i \neq j \quad (36)$$

The vapour phase is treated similarly.

The enthalpy transfer from the vapour phase and to the liquid phase is computed with equations (37) and (38), respectively.

$$\mathcal{E}^V = h^V a (T^V - T^I) + \sum_{i=1}^{nc} N_i \overline{H}_i^V \quad (37)$$

$$\mathcal{E}^L = h^L a (T^I - T^L) + \sum_{i=1}^{nc} N_i \overline{h}_i^L \quad (38)$$

2.5 Reaction modelling

There are two basic methods to compute the reaction rates. In the first one the description of the kinetic mechanisms is introduced as a source term in the balance equations. This is suitable when reaction rate is slow compared to mass transfer. This approach is also usual when the *quasi-homogeneous approach* with effective kinetic expressions is used for the description of heterogeneously catalysed RD, as can be found in several commercial simulators.

The second method is necessary when the reaction velocity is comparable with that of mass transport. In this case, the reaction influences the concentration and temperature profiles in the film region, thus changing the whole process behaviour. If the reaction is considered in the liquid film, the governing equation includes a matrix diffusion term (described by the Maxwell-Stefan equations) and a reaction term (Kenig and Górak, 1995). In DESIGNER, it is also possible to use a detailed model for the heterogeneous catalyst mass transfer efficiency, which is based on the work of Sundmacher and Hoffmann (1996).

The implementation of the two latter methods in the set of independent equations and variables of the stage model is straightforward. The film reaction model requires adjusting the form of the balance equations in the liquid bulk and in mass transfer equations slightly. The method of Sundmacher and Hoffmann (1996) requires no changes in the independent equations.

2.6 Modelling of hydrodynamics

The hydrodynamic models for the column segments implemented into DESIGNER are as follows [I]:

- *completely mixed liquid - completely mixed vapour*
- *completely mixed liquid - vapour plug flow*
- *mixed pool model*, in which the liquid on the plate is assumed to be flowing through a series of completely mixed pools [IV]
- *eddy diffusion model*, based on analytical solution of the linearised eddy diffusion equation group, and an eddy diffusion model based on rigorous numerical solution of the eddy diffusion equation group.

The first two models represent the straightforward applications of known theories (see Taylor and Krishna (1993), the second model is a modification of the model of Hung (1991) which permits reaction to be allowed for). The first two models also use the solver that was presented above in this thesis.

The rate-based mixed pool model and the eddy diffusion models for reactive distillation are new developments in this project. In this thesis, the rate-based mixed pool model is presented in more detail.

Recently, hydrodynamic aspects of cross-flow operation of distillation columns have been studied in the papers of Kooijman and Taylor (1995), Muller and Segura (2000), and Higler *et al.* (1999).

2.6.1 Rate-based mixed pool model

The liquid flow pattern on the tray influences the mass transfer and reaction rates on a distillation tray. Traditionally, this phenomenon has been lumped together with many other factors affecting performance of the tray to a quantity called stage efficiency.

The situation is more complicated, if a reaction takes place on the tray. Reaction rates depend on concentrations and temperatures and thus a rigorous model should consider their possible variations.

The idea of the mixed pool model is that the liquid on the tray is assumed to flow through a series of internally completely mixed cells. This kind of system can describe approximately the solution of the eddy diffusion model. Its advantage is that the second order differential equation group involved in the eddy diffusion model is replaced with a group of algebraic equations. Thus the effort of solving the eddy diffusion problem rigorously in a non-ideal, reactive multi-component system is avoided [IV].

Figure 3 presents the division of the tray into mixed cells. In this case vapour is assumed to flow unmixed from each cell to the corresponding cell on the upper tray and liquid is flowing to opposite directions on the adjacent trays so that the liquid entering the tray contacts first with vapour from the outlet side cell of the tray below. This is the normal flow pattern with cross-flow trays. With some tray constructions it is also possible to change the liquid flow pattern so that the liquid entering a tray

encounters first the vapour leaving the liquid inlet side of the tray below. The third flow pattern considered is such that all vapour leaving a tray is assumed to undergo complete mixing between the trays. Lewis (1936) has treated the theoretical efficiencies in these cases.

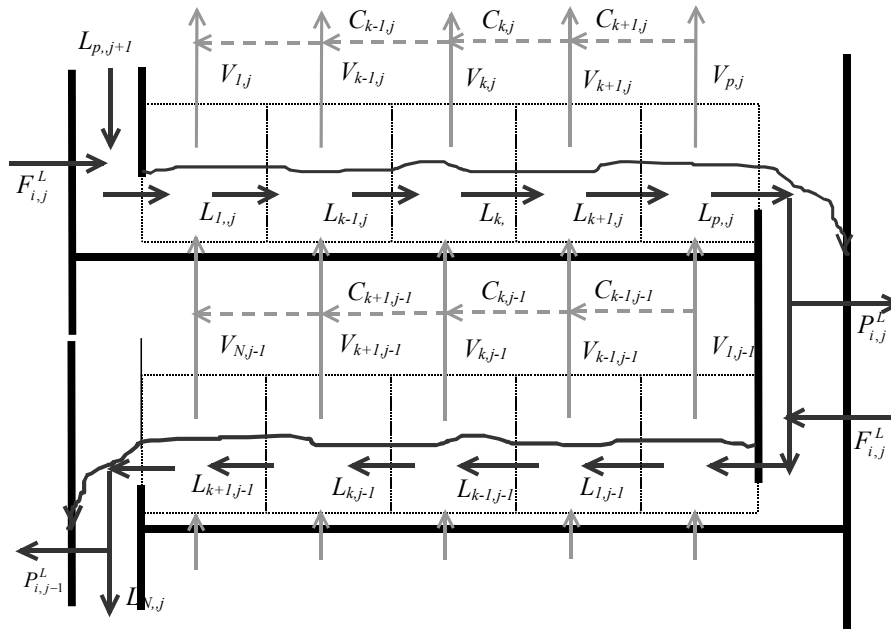


Figure 3. The mixed pools of a distillation tray when vapour is unmixed and liquid flows to contrary direction on adjacent trays (L liquid flow, V vapour flow, C vapour flow correction factor, F liquid feed, P liquid product flow).

The basis of the current model is the model presented earlier in this thesis (sections 2.1-2.5). Thus the model uses the Maxwell-Stefan multi-component mass transfer equations, which take into account the mass transfer resistances of each phase and also the interactions of the transferring components. An alternative vapour-liquid mass transfer model available is the modification of the previous one as presented by Hung (1991) and Taylor et al. (1994). In that model, the mass transfer resistances of individual phases are combined to an overall mass transfer resistance. The main benefit of this model is that it enables convenient handling of vapour plug flow.

The liquid film reaction – mass transfer model of Kenig and Górak (1995) is available, if a fast reaction takes place in liquid film. The model for reaction and mass transfer in macroporous catalyst by Sundmacher and Hoffman (1996) is implemented as well.

2.6.2 Model equations for the mixed pool model

The mixed pool model is somewhat simpler than the similar approach by Higler et al. (1999). The most significant difference is that the stages are not divided into cells in vertical direction. There are also some differences in the models implemented and in the overall structure of the equation group, resulting in a smaller number of independent equations and variables [IV].

Each pool has virtually the same variables and equations as the whole tray in the traditional rate-based model. The only deviation is that the pressure is assumed to be constant throughout the plate. Thus, if the number of mixed pools is u and the number of components is n then there are $5un+5u+1$ variables on a tray instead of the $5n+6$ variables of the traditional rate-based stage. The appropriate number of pools can be determined using the correlations of Ashley and Haselden (1970) and Alejski (1991). The liquid is assumed to be completely mixed in the direction perpendicular to the flow direction.

The independent variables for each tray are:

- u liquid flow rates
- $u \times n$ liquid mole fractions
- $u \times n$ liquid mole fractions at the interface
- u liquid temperatures
- u interfacial temperatures
- $u \times n$ mass transfer fluxes
- pressure
- u vapour temperatures
- $u \times n$ vapour mole fractions at the interface
- $u \times n$ vapour mole fractions and
- u vapour flow rates.

The corresponding equations to be solved are:

- u liquid-side total mass balances
- $u \times n$ liquid-side component mass balances
- $u \times (n-1)$ liquid-side mass transfer equations
- u liquid-side interface concentration summation equations
- u liquid-side energy balances
- u interfacial energy balances for each pool
- $u \times n$ interfacial equilibrium equations
- 1 pressure drop condition
- u vapour-side energy balances
- u vapour-side interfacial concentration summation equations
- $u \times (n-1)$ vapour-side mass transfer equations
- $u \times n$ vapour-side component mass balances and
- u vapour-side total mass balances.

The reboiler and condenser of the column are modelled as an equilibrium stage.

To model the mass transfer in each pool, it is possible to use either the mixed liquid - mixed vapour or the mixed liquid - plug flow vapour model. The former model is based on the model presented by Taylor and Krishna (1993), whereas the latter model has its origin in Taylor et al. (1994). Both models have been modified by adding the reaction terms to the material balances. In addition, there are two modifications of the latter model, one of them based on the leaving vapour composition and the other based on the entering composition.

In order to simplify the calculation, constant pressure drop was given as a specification.

2.6.3 Solver

The model is solved using the Newton's method. Thomas algorithm for a block tridiagonal matrix with numerically calculated derivatives is used to solve the linearised subset of the model equations. The implementation of the solver to this problem posed no special problems, but it was noticed that heavy damping of the correction steps was necessary in order to keep the solution on the convergence path.

Initialisation of the variables is of great importance for finding the solution. One way to provide good initial values is to use the solution of one mixed cell per tray as the basis of the solution. The problem is solved first with a rate-based model with each tray as a single mixed cell and the resulting concentrations, temperatures, and so on are used as the initial values for the multiple-cell mixed pool model. This method gave satisfactory results so that convergence was achieved. The rate-based distillation model is a rather heavy initialisation procedure. This problem is not prohibitive, because mixed pool model is not required for every routine simulation. More likely it will be used for checking the design of some critical devices and in such a case a tedious initialisation process is tolerable.

2.7 Implementation of DESIGNER

2.7.1 Self-standing DESIGNER

DESIGNER was first implemented as a self-standing program [II]. The implementation was made in FORTRAN. DESIGNER contains a model library of thermodynamics, physical properties, and hydrodynamic correlations for the mass transfer coefficients, interfacial area, pressure drop, hold-up, weeping and entrainment which cover a number of different column internals and flow conditions.

This version of DESIGNER was made compatible with SYNTHESIZER. This tool was designed to support the decision process as to whether RD is beneficial for a given chemical reaction system as compared to conventional sequential reaction and distillation processes. Furthermore, SYNTHESIZER gives first rough information about attainable separating cuts and the column design. This tool is able to handle multi-reaction systems. It is based on the knowledge obtained from industry and from the open literature.

As SYNTHESIZER is designed to be used in the very first evaluation phase of the process development, only limited information about the reaction system is needed: the stoichiometry of each reaction, the type of reactions, some qualitative information about the reactions and VLE.

DESIGNER and SYNTHESIZER together form an integrated tool for synthesis and design of reactive distillation. SYNTHESIZER and DESIGNER have been linked together under a common user interface. The interface modifies the results obtained from SYNTHESIZER into the input needed for DESIGNER, and proposed designs can be simulated.

2.7.2 DESIGNER in flowsheeting program FLOWBAT

DESIGNER was implemented as a unit into FLOWBAT which is a unit modular flowsheet simulator (Keskinen and Aittamaa, 2004).

FLOWBAT is designed for the simulation of chemical processes in steady state. It can be used in different phases of process design: preliminary studies for reaction equilibrium, material and energy balances using simple models, solving material and energy balances using rigorous models, solving recycle systems, optimisation of flowsheets, providing thermodynamic data from databases, simulation of single equipment, and so on.

FLOWBAT has a large data bank for the basic thermodynamic properties of pure compounds. It also has the capability to estimate various properties of pure compounds when the available data is not complete. It has an extensive collection of methods to calculate and estimate thermodynamic properties of mixtures. There are many options to calculate the vapour-liquid equilibrium of a complex mixture. DESIGNER retrieves these values and methods for its use.

One of the important features of FLOWBAT is its capability to carry out performance calculations even with constraints set to the flowsheet. This means that the user can define the objective to be minimized/maximized. Normally, this includes the selection of variables to be optimised (FLOWBAT finds the best values for them), writing constraints for the variables to be optimised, writing constraints for dependent variables (FLOWBAT calculates them on the basis of values determined for the variables to be optimised), and calculation of the objective function value. FLOWBAT does not have general built-in cost estimation methods for equipment investment and operating costs; these are part of the input the user must write.

Once the flowsheet is solved, there is normally a need to have tables of the thermodynamic and transport properties of the process flows. This data is needed in the detailed design of single equipment. FLOWBAT has the capability to output these tables.

3 VALIDATION OF THE REACTIVE DISTILLATION MODEL

DESIGNER has been tested against known distillation data without reaction as well as with reactive distillation data gathered in the project. The power of the new hybrid solver is also demonstrated.

Numerical examples were used to study the solution strategy. Two interesting chemical systems were considered: the production of MTBE (etherification) and the production of MeOAC (esterification), both being examples of existing reactive distillation processes. According to the experience of the author, it is not easy to reach convergence in these types of problems with commercial software. The examples showed that the solution strategy, that is, applying the hybrid solver made the solution possible without tedious nursing of the problem [I].

3.1 Distillation without reaction

The distillation experiments were carried out at Helsinki University of Technology in a sieve plate column and are described elsewhere in detail (Halmu and Multala, 1978). The column had 12 plates, a reboiler, and total condenser. The feed was introduced into plate 3 of the column when the first plate is the one just above the reboiler. Altogether four runs were carried out with composition measurement on every plate. The compositions of the feed, distillate, and bottoms were measured as well. The chemical system used in the experiments was water, ethanol, and n-butanol. The main specifications of the sieve plate are found in Table 1.

Table 1. Main specifications of the sieve trays.

Diameter	0.25 m
Active area	0.0449 m ²
Height of weir	0.04 m
Width of flow path	0.233 m
Distance of weirs	0.17 m

The four available experiments were simulated using the model presented in section 2. It can be seen in Figure 4, where simulated liquid compositions are plotted against the experimental values, that the agreement with the simulations and the experiments is good. The typical deviation of the simulated liquid compositions (molar fractions) using the model was typically less than 1 %.

It is interesting to note that here the Murphree plate efficiencies were back-calculated for the simulated plates and the values of these were typically around 50 %. Thus the deviation from ideal plates was significant (Jakobsson and Aittamaa, 2001).

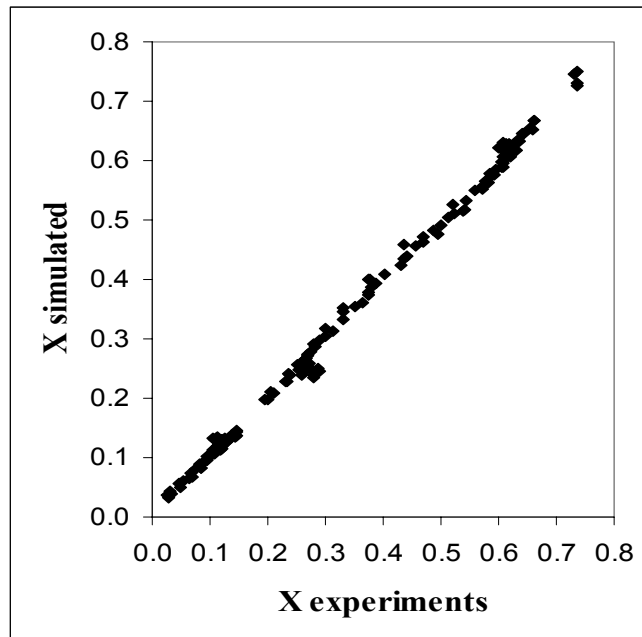


Figure 4. Simulated against experimental liquid compositions with the rate-based model of all test runs with water, ethanol, and n-butanol.

Reference calculations with a rigorous multi-component Murphree vapour phase efficiency model (Ilme, 1997) based on Maxwell-Stefan equations shows that the two methods for computing the real plate behaviour, the rate-based approach and the rigorous efficiency calculation, seem to produce equally good results when compared with experimental results of a pilot scale sieve plate column. The agreement between the simulated and the measured compositions is good; in both cases deviation is typically less than 1 %. Figure 5 shows the simulated against experimental liquid compositions for these runs.

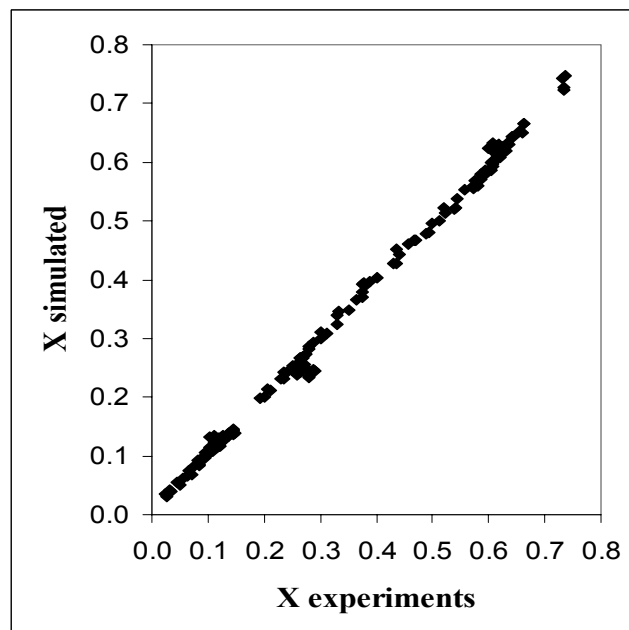


Figure 5. Simulated against experimental liquid compositions with an efficiency model of all test runs with water, ethanol and n-butanol.

3.2 Comparison with experimental results from RD

DESIGNER has been tested against experimental results gathered from the test runs of the pilot scale RD column [I]. The first column used as an example here had a catalytic section in the middle part of the column. The total height of the column is 12 m and the diameter of the column is 0.16 m. This catalytic section consists either of a packed bed of catalytically active rings (see Sundmacher and Hoffmann (1996)) or of new structured catalytic packing supplied by Monz (Górak et al., 1998). The rectifying and stripping parts consist of two separately supported packing sections and are filled with Intalox Metal Tower Packing. The methanol feed was introduced just above and the hydrocarbon feed just below the catalyst section.

In Figure 6, the results of a simulation of an experiment with the catalytic rings are presented. In the simulations 4 components (methanol, i-butene, MTBE, and 1-butene) were chosen to describe the system under consideration. The simulated results agree well with the experimental values.

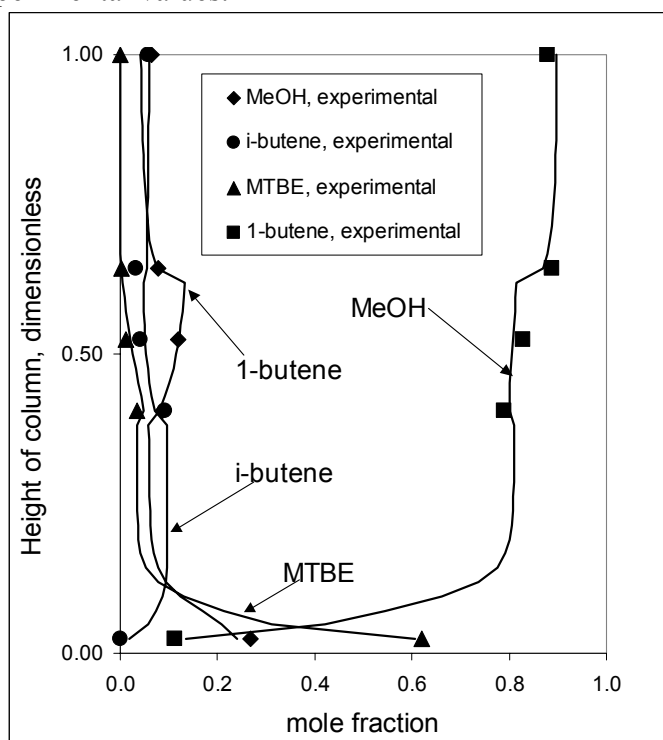


Figure 6. Calculated and experimental liquid phase concentrations for the column with the reactive section filled with catalytically active rings.

A further case study concerns the column with the structured catalytic packing Montz Multipak. The column structure is similar to that described above, except that the catalyst section is equipped with catalytic structured packing. The chemical system used involves 11 components (methanol, i-butene, i-butane, n-butane, propane, 1-butene, tr-2-butene, cis-2-butene, isopentane, n-pentane, and MTBE). The catalyst section in the column contained totally 3.6 - 4.0 kg of dry Amberlyst 15 ion-exchange resin. Altogether 11 test runs are performed. The pressure of the column varied between 800 and 1000 kPa, the reflux ratio between 2 and 3. The molar ratio methanol/isobutene varied between 1.27 and 1.41.

It can be seen Figure 7 that the condenser compositions agree well, and this can be attributed to the well-predicted azeotropic behaviour of methanol and hydrocarbons. The agreement between the simulated and the measured values is also good for the catalytical section of the column.

Figure 8 shows the simulated and experimental liquid bottoms product compositions of MTBE for all 11 test runs. The reaction rates seem to be slightly underestimated Figure 9. This leads to deviations between the simulated and experimental values.

Generally, a good agreement between the simulated and experimental conversion of isobutene could be established, with an average deviation less than 5 %.

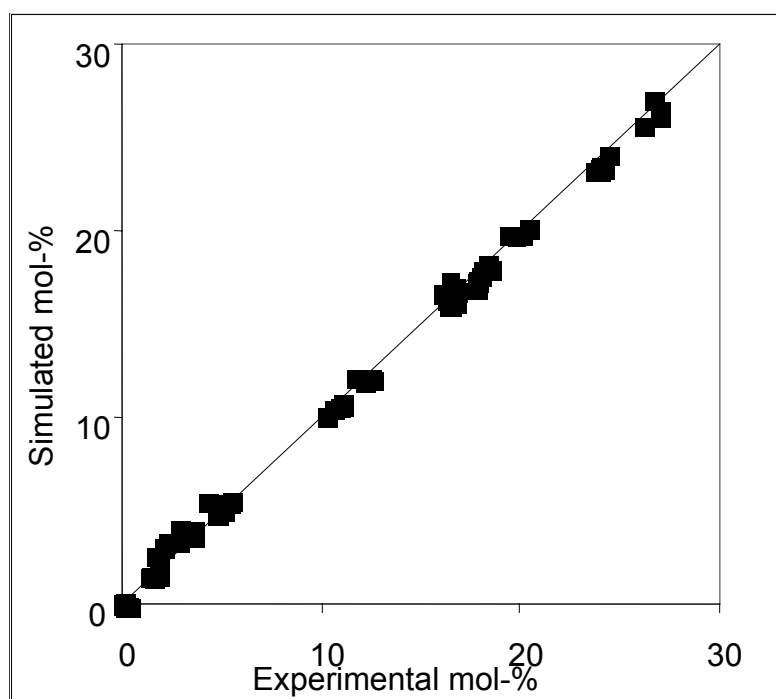


Figure 7. Experimental and simulated liquid compositions of distillate for all components in 11 test runs with the reactive section of column filled with catalytic structured packing Montz Multipak.

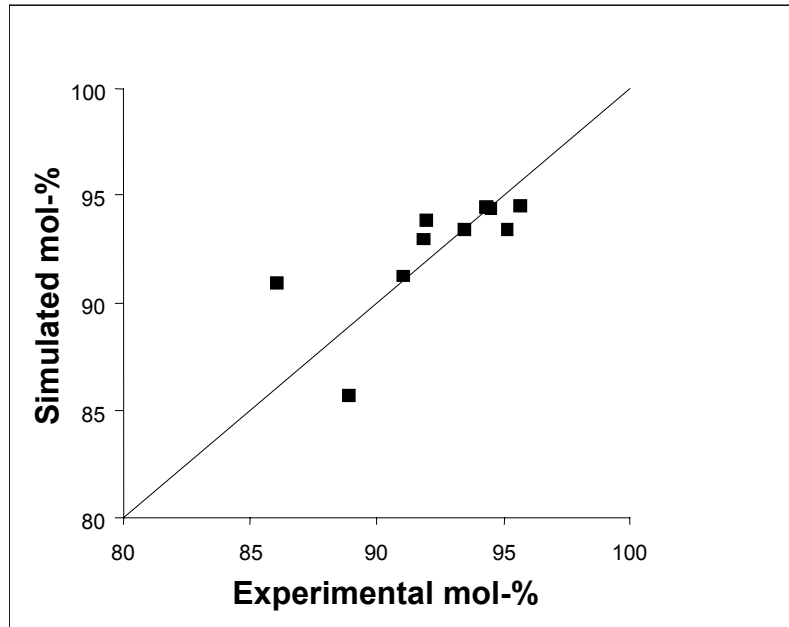


Figure 8. Experimental and simulated liquid compositions of MTBE in bottoms product of all 11 test runs with the reactive section of column filled with catalytic structured packing Montz Multipak.

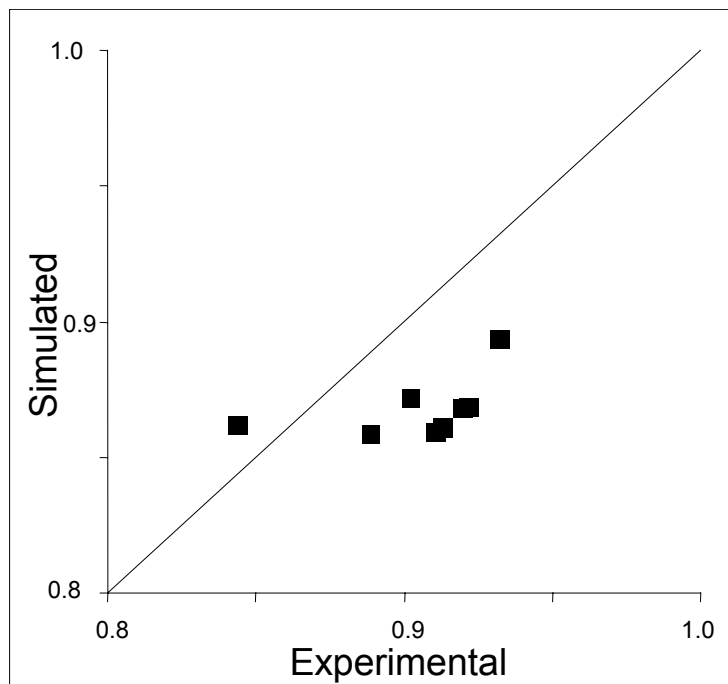


Figure 9. Experimental and simulated conversion of isobutene of all 11 test runs with the reactive section of column filled with catalytic structured packing Montz Multipak.

These case studies were solved with the Newton's method. Although convergence was good, the computations with the rate-based model usually took 50 to 60 times longer than with the ideal stage model used as a reference. This is explained both by a larger set of independent variables and equations and by the need of using more stages in the rate-based model. The calculation time was typically several minutes.

3.3 Simulations with the mixed pool model

The model behaviour was studied with two fictive test cases [IV]. The first test case was a small-scale reactive distillation column involving MTBE reaction. The simulated column has 20 trays (reboiler tray 1, condenser tray 20). Reactions took place in the reactive section in the middle of the column (trays 8-13). The upper and lower ends of the column consist of inert trays. The simulation involves four components, methanol, isobutene, methyl-tert-butyl-ether (MTBE) and isobutane. Isobutane is an inert component. The reactive trays are treated as cross-flow trays with catalyst placed as an even layer on the trays. The goal was to test the significance of this flow pattern to the composition profiles and, consequently, the effect on the reaction rates on the trays, for example to find out if developing such devices would be worthwhile.

This test case was simulated using several flow models:

- Case 1 was a mixed liquid-mixed vapour model without division to cells.
- Case 2 was a mixed liquid-vapour plug flow model without division into cells.
- Case 3 was a mixed pool model otherwise exactly identical with case 1 but with 4 cells per stage and with complete vapour mixing between the trays (Lewis case 1), see Figure 10. Case 4 was otherwise identical to the case 2 but with each tray divided to 4 cells and with complete vapour mixing between the trays.
- The cases 5, 6, and 7 were mixed pool models with 5 cells per tray and with vapour flow patterns corresponding to the Lewis cases 1, 2, and 3 respectively. See Figure 10.

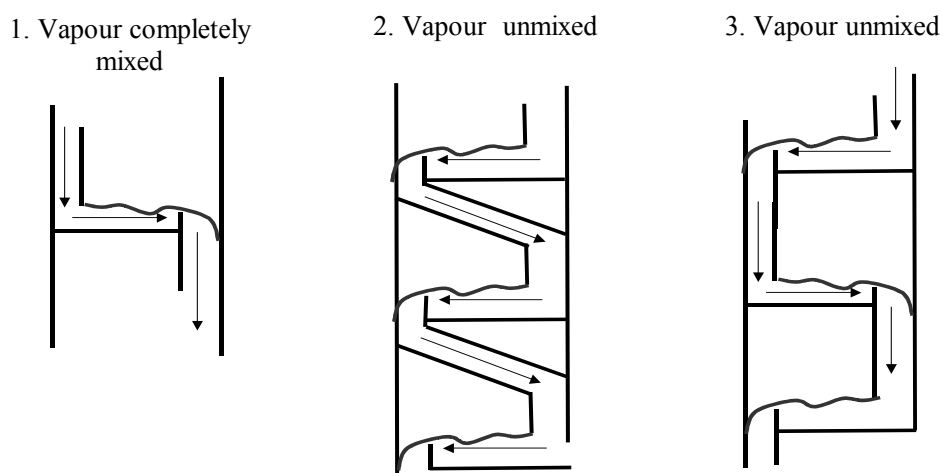


Figure 10. Liquid and vapour flow pattern in three different Lewis cases.

In Figure 11 the calculated molar fractions of isobutene on the reactive trays 8-13 with the case 3 (mixed vapour-mixed liquid, 4 cells per tray) are presented. The figure shows that there is a significant composition gradient of the reactive component along the flow path of the tray.

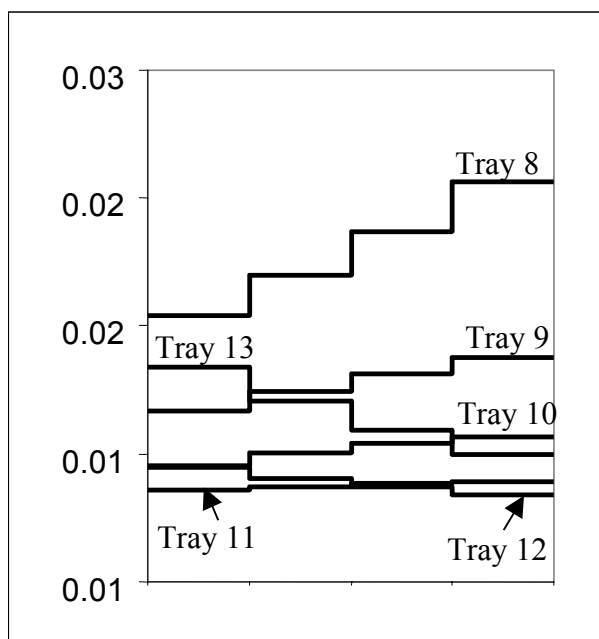


Figure 11. Mole fractions of isobutene along the flow path of the reactive trays in the first test example, case 3.

Figure 12 presents the formation rate of MTBE on these trays in case 3. It can be observed how the reaction rate is changing along the liquid flow path on the tray. On tray 8 the reaction rate is both the fastest and the slowest in the column.

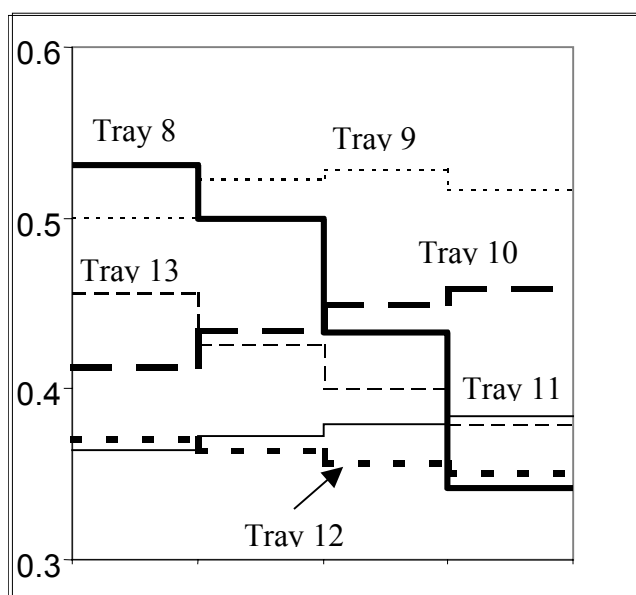


Figure 12. Production rates (mmol/s) of MTBE along the flow path of the reactive trays 8-13

The effect of tray scale concentration gradients was small between the models applied in the first test example (Cases 1-7). Both the product compositions and the average compositions on the trays are almost similar in all the calculated cases, that is the simulation with the rate-based model without any division into mixed pools produced the same results.

One would expect a significant effect at least if the number of trays is small and heat effects are large so that the lateral variations of the flow rates and concentrations on the individual trays cannot cancel out each other. To test this hypothesis, another test case was set up. The column should be short, thus a column with six stages was selected: reboiler, lower feed stage, two reactive stages, upper feed stage, and condenser. Heat of reaction should be high, thus the MTBE system of the first test case was modified so that the reaction enthalpy was increased by 150 kJ/mol. Thus the reaction system was changed from reasonably exothermal to highly exothermal. The isobutene-isobutane mixture enters from lower feed tray and methanol from upper feed tray and feed mixture contains 50 % of isobutene.

The results achieved using the mixed liquid-mixed vapour model with 5 mixed cells per stage and with complete vapour mixing between the stages are presented in Table 2. The reference case, otherwise identical, but without division into mixed cells is presented in Table 3. As can be seen, the effect of tray scale phenomena is very significant. The reaction rate achieved with the reference model in this case is approximately 1.3 mol/s, whereas according to the mixed pool model the reaction rate is only 0.7 mol/s. In addition, the distribution of the components between the bottom product and distillate is clearly different.

Table 2. Feeds and products of the second simulation example case 1, mixed pool model with 5 cells per stage and mixed liquid-mixed vapour model, assuming complete vapour mixing between the stages.

	isobutene mol/s	methanol mol/s	MTBE mol/s	Isobutene mol/s
Feed	6.000	5.000	0.000	5.000
Distillate	1.438	3.957	0.288	4.616
Bottom	3.862	0.343	0.411	0.384
Reaction	-0.700	-0.700	0.700	0.000

Table 3. Feeds and products of the second simulation example case 2, mixed liquid-mixed vapour model, without division to cells, mol/s.

	isobutene mol/s	methanol mol/s	MTBE mol/s	isobutane mol/s
Feed	6.000	5.000	0.000	5.000
Distillate	2.049	2.808	0.702	4.096
Bottom	2.606	0.848	0.643	0.904
Reaction	-1.345	-1.345	1.345	0.000

The liquid flow leaving the stage is presented in Figure 13 for the both calculated cases. The difference between the flows in the two cases is remarkable and would have an effect on the design of the trays.

The example could be relevant to industrial practice for short columns involving high thermal effects (for example, a reactive absorber). They are often used for highly exothermal systems and have frequently rather a small number of stages.

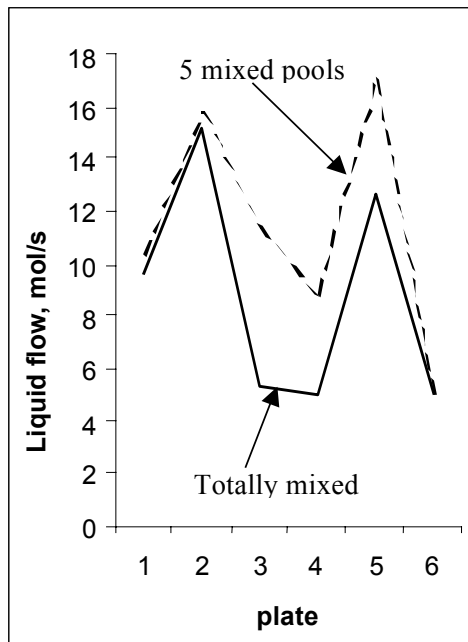


Figure 13. Liquid streams leaving the stages in the second example.

These two numerical studies done with the mixed pool model indicates that the flow pattern might have an important effect on a real RD plate and process. However, the overall performance of the whole process is also affected strongly by the interaction of the adjacent plates. It must be noted that the simulation results and conclusions presented above are based solely on theoretical considerations.

4 APPLICATION OF THE REACTIVE DISTILLATION MODEL TO SIMULATION OF COUNTER-CURRENT REACTORS

Mathematical models of counter-current reactor configurations like counter-current trickle-bed reactors are in principle close to reactive distillation: counter-current gas/liquid contact and a liquid phase reaction taking place in a heterogeneous catalyst.

In this section, the application of the RD model developed in section 2 is used to study counter-current hydrogenation operation [VII].

4.1 Modelling

In the implementation, it is possible to specify independently the model for mass/heat transfer, mass/heat transfer coefficient, interfacial area, pressure drop, VLE model, and reaction-kinetic model for each section. Thus the calculation segments can be used flexibly for modelling different parts of a reactor. Each segment can represent an adiabatic/non-adiabatic reactor segment, it can be used to model only separation, feed (quench) or product stage, or heat exchanger.

4.2 Simulations

In the simulation examples, the features of the model are demonstrated and a comparison with the co-current process option is shown. It is implicitly assumed that the counter-current process would use catalytic packing of the random packing type (used in reactive absorption and distillation). The mass transfer coefficients were calculated with correlations borrowed from distillation design for random packed beds (Onda *et al.*, 1968). The specific area and diameter of 1" Raschig rings were used in the simulations. Heat transfer coefficients were calculated by Chilton-Colburn analogy.

The first example is to consider a hypothetical counter-current hydrogenation step of an i-octane process. The process is developed by Neste Engineering to convert existing MTBE plants for i-octane production because of the MTBE ban in California 2004 (Sloan *et al.*, 2000).

In the hydrogenation step the i-octene is transformed into i-octane. A counter-current adiabatic reactor with bed height of 6 m was simulated. The reactor height was divided into thirty 20.0 cm high calculation segments. The liquid feed was mainly iso-octene in 4:1 ratio of 2,4,4-Trimethyl-1-pentene (TMP-1)/2,4,4-Trimethyl-2-pentene (TMP-2). Some 3-methylpentane, and trimers and tetramers of i-butene were present as impurities. The catalyst amount was adequate to reach 25 % conversion of TMP-1. The liquid feed was of 80 °C and H₂ 30 °C. The pressure of the column was 30 bar.

Figure 14 shows how the model predicts the temperatures of the gas and liquid phases. The plotted values represent the properties of the gas leaving a particular reactor segment. The difference of the temperatures is at its maximum at the end of the reactor. The temperature of the cold gas feed raises rapidly to the level of the

liquid. In the middle the differences even out due to good heat transfer. In the upper part the gas temperature remains slightly above the liquid temperature due to heat transfer resistance. The raise of the temperature due to exothermic reaction is clearly shown.

Another interesting phenomenon that the model shows/predicts can be seen in Figure 15, where at the lower part of the reactor the hydrocarbons are vaporising due to the elevated temperature. It is obvious that the model also predicts better solubility of hydrogen into the liquid phase in this section of the reactor.

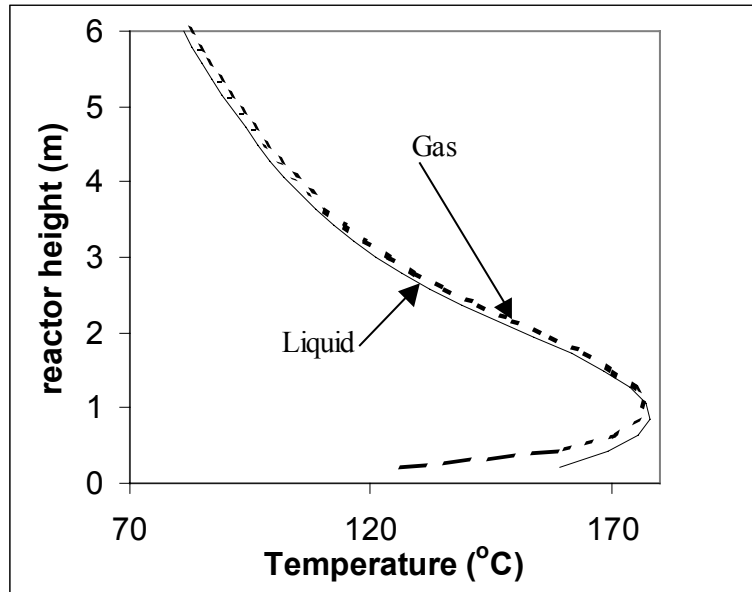


Figure 14. Temperature profile of liquid and gas along the height of the counter-current *i*-octane hydrogenation reactor.

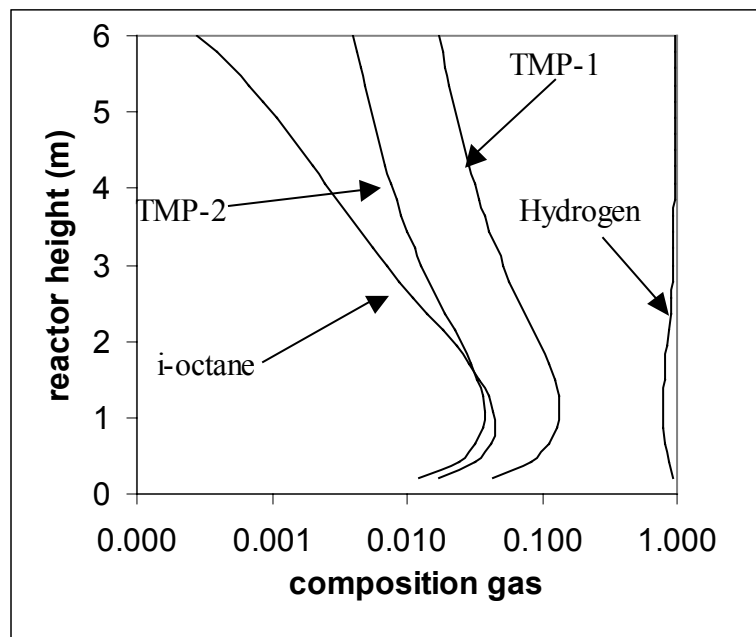


Figure 15. Composition profiles along the height of the counter-current *i*-octane hydrogenation reactor (note logarithmic scale!).

As another example, a counter-current operation to separate the hydrogen sulphide from a hydrodesulphurisation process is considered. Hydrodesulphurization is removal of sulphur with hydrogen. As the H_2S acts as a catalyst poison, the counter-current operation has been proposed to protect high performance catalysts. Stripping H_2S from the liquid phase by operating the reactor counter-currently does this. The chemical system consisted of dibenzothiophene, diphenyl, cyclohexylbenzene, 4,6-dimethyldibenzothiophene, 3-(3-Methylphenyl)-1-methylbenzene, 3-methylcyclohexyltoluene, hydrogen, hydrogen sulphide and n-eicosane. In the mixture, dibenzothiophene and 4,6-dimethyldibenzothiophene represent sulphuric compounds of a refinery mixture, and other four aromatic compounds are the products of the hydrodesulphurisation. The liquid feed consisted of the both sulphuric compounds each 1 w-%, the rest being n-eicosane. The gas feed was pure hydrogen and the reactor was operated at 8 MPa pressure, 99.9 % conversion of the dibenzothiophene was desired. The gas composition profile of H_2S in Figure 16 shows how H_2S is stripped from the liquid phase to the gas phase and the H_2S is accumulating in the gas phase towards the end of the reactor.

The co-current operation of the hydrodesulphurisation reactor was modelled for comparison purposes. The reactor model is described by Toppinen *et al.* (1996). The correlation used for liquid-side mass transfer coefficient was by Turek & Lange (1981). Other mass transfer resistances, pressure drop, and liquid maldistribution were assumed to be negligible. H_2S composition in co-current reactor is shown in Figure 17. Accumulation of H_2S in both phases is taking place simultaneously. In the bottom of the reactor, H_2S -composition in the liquid phase is significantly larger than in the gas phase.

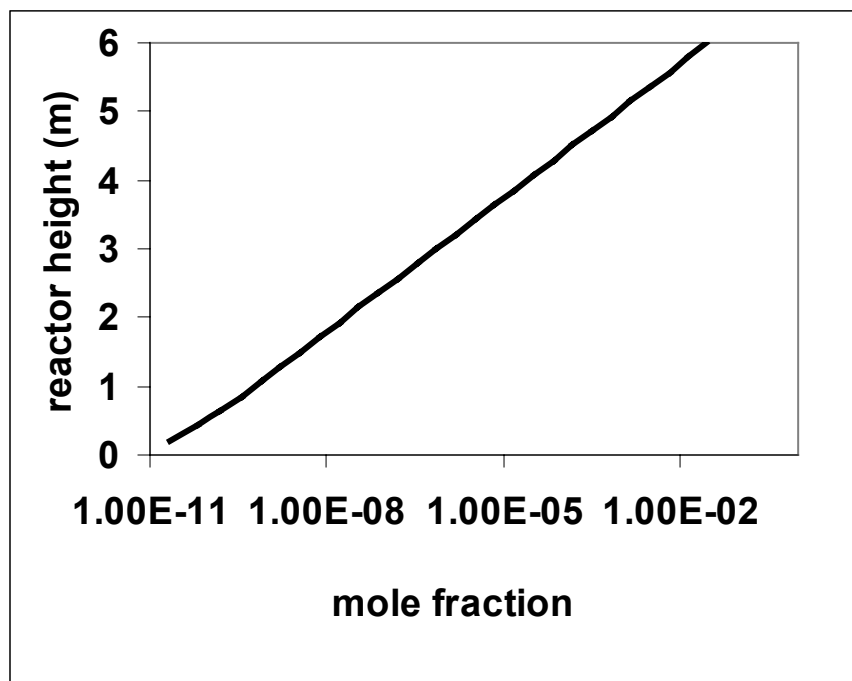


Figure 16. Composition profile of H_2S in gas phase along the height of the countercurrent hydrodesulphurisation reactor.

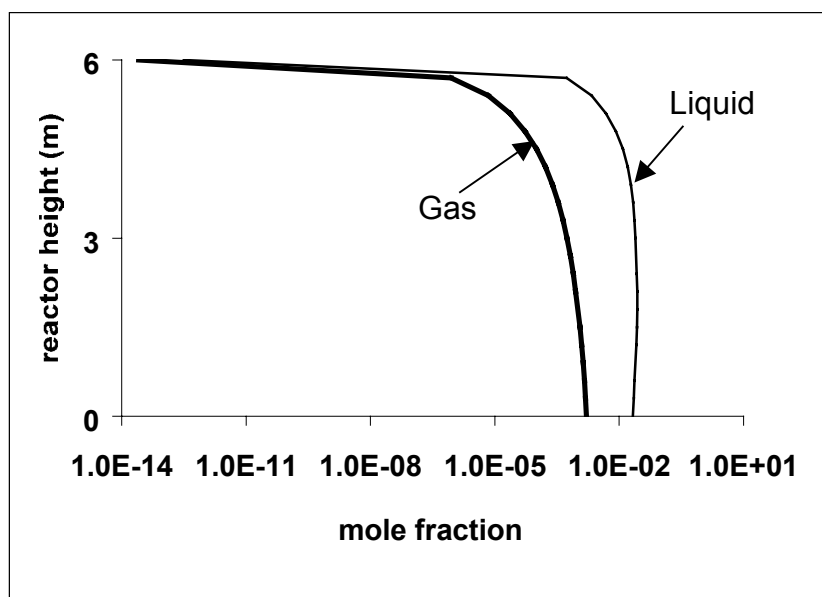


Figure 17. Composition profile of H_2S in gas and liquid phase in co-current trickle-bed hydrodesulphurisation reactor.

4.3 Discussion and conclusions counter-current reactor modelling

Above was shown that the so-called rate-based approach can be used as a useful tool for modelling countercurrent hydrogenation processes. The countercurrent calculation segments can be used flexibly for modelling different functional sections of the reactor.

The calculation examples showed that the rate-based stage model used here for reactor modelling can handle as a concept various real phenomena in a hydrogenation reactor. In the first example a hypothetical countercurrent hydrogenation step of an i-octane process was shown. The simulation in adiabatic mode with cold H_2 feed showed temperature difference between gas and liquid phases especially in the end of the reactor. The adiabatic operation lead to a sharp temperature rise in the reactor since the reaction is exothermic. This in turn vaporised a fraction of the liquid phase. These are not desired phenomena in a real process but they show how the model can handle these phenomena. In the second example the countercurrent operation was used to separate the hydrogen sulfide from a hydrodesulfurisation process. The model showed how H_2S was stripped from the liquid phase to the gas phase and the accumulating in the gas phase towards the end of the reactor.

It is obvious that the quality of the simulations in real cases would be highly dependable on the sub-models for reaction kinetics, mass and heat transfer coefficients, interfacial area, pressure drop etc.

5 REACTIVE DISTILLATION PROCESS FOR GASOLINE OXYGENATE

Tertiary ethers have had a major role in gasoline development during the last two decades. The ethers 2-ethoxy-2-methylpropane (ETBE), 2-methoxy-2-methyl-butane (TAME), and especially 2-methoxy-2-methylpropane (MTBE) were the most economical solutions to increase the octane level of gasoline, to promote cleaner burning of gasoline, and thus decrease tail pipe emissions. The removal of the smog in Los Angeles was attributed to be the consequence of introducing MTBE to gasoline. Later, however, because of leakage of gasoline storage tanks, MTBE was detected in ground water. This led to the ban of MTBE from gasoline pool by the end of year 2003 in California. [VI]

Refineries in the USA and Canada are interested in new alternatives for the existing MTBE plants and isobutene (2-methylpropene) feed stocks. Some companies have announced new process configurations to produce high-octane gasoline components from the isobutene, for example Sloan et al. (2000). In this process isobutene is first dimerised to isooctenes (mainly 2,4,4-trimethyl-1-pentene (TMP-1) and 2,4,4-trimethyl-2-pentene (TMP-2)), which can thereafter be hydrogenated to isooctane (2,2,4-trimethylpentane).

The isooctene process neglects the oxygenate raw material methanol that would be available in large scale particularly if MTBE production is reduced. The alkenes TMP-1 and TMP-2 have a double bond attached in a tertiary carbon and are reactive in etherification. The reaction schema is illustrated in Figure 18. The resulting ether, 2-methoxy-2,4,4-trimethyl pentane (C8ME), has high octane ratings. So, the etherification of alkenes can increase the octane value, which would also improve the quality of the product.

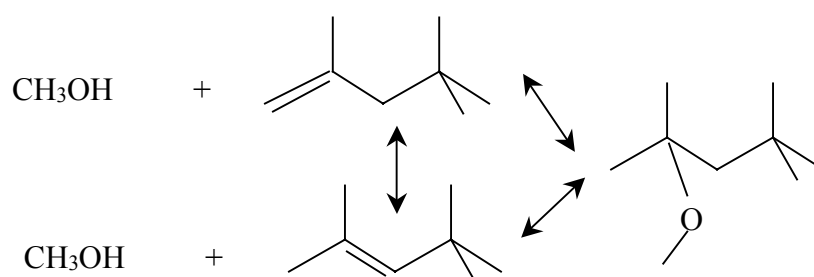


Figure 18. Reaction schema for etherification of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene with methanol

5.1 Process design

Process configurations based on the new kinetic model [VI] were calculated for hydrocarbon feed presented in Table 4. The isobutene feed was assumed to be 100 000 tons per year. The feed to the etherification unit contained small amount of isooctane. The ratio of TMP-1 and TMP-2 was assumed to be in the thermodynamic equilibrium. The equilibrium conversions of TMP-1 and TMP-2 with methanol are relatively low.

Table 4. The composition of the hydrocarbon feed

Compound	feed rate (kmol h ⁻¹)	Concentration (mol dm ⁻³)	Mole fraction
TMP-1	82	5.8	0.76
TMP-2	24	1.7	0.22
IOCT	2	0.5	0.02
Total	108	-	1.00

The rate of etherification is slowing down as the hydrocarbon chain is growing. Based on calculations, it is obvious that economical process for the production of 2-methoxy-2,4,4-trimethyl pentane (C8ME) cannot be based on a once-through type reactor system, but a recycled reactor separation system is required [VI].

The applicability of RD configurations for the etherification of TMP-1 and TMP-2 was studied. Figure 19 illustrates one configuration. The effect of the amount of the catalyst on one plate was studied by trial and error. The simulations were calculated with catalyst amount of 2000 kg dry catalyst on each plate, corresponding to 4.5 m³ volume of wet catalyst on a plate. The total amount of dry catalyst in the column was the same as in the simulation of tubular reactors.

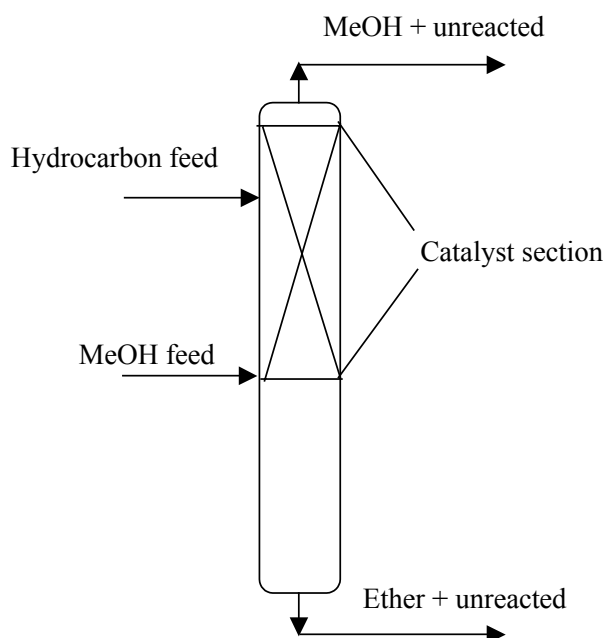


Figure 19. The configuration of the RD column. Total amount of 30 plates. The hydrocarbon feed on plate 19, MeOH feed on plate 10. Pressure 0.1 Mpa. Catalyst placed on plates six to 28.

The heaviest component of the reaction mixture is the ether product C8ME that is removed from the reaction mixture by distillation and this stream was optimised to include less than 0.4 wt% methanol. It is important to mix the product free from methanol into gasoline pool without further purification or methanol recovery steps. Unreacted TMPs and methanol are taken from the top of the column. The distillate contains most of the fed inert isooctane as well as all the unreacted methanol and even one third of the unreacted alkenes, which makes the distillate stream large.

A conversion of 35.3 % was obtained with this configuration. This is an improvement of the conversion compared with the tube reactor cases where only 17-19 %

conversions were obtained. However, this configuration with a large distillate stream and relatively low conversion is probably not an economical configuration.

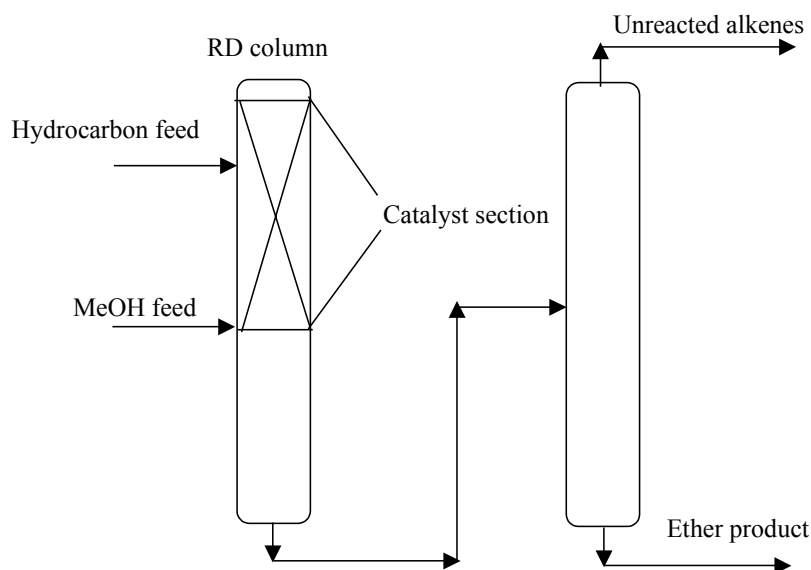


Figure 20. Process configuration with RD column and ether fractionator.

Two other RD schemes shown in Figure 20 were studied. The simulated process consisted of two columns. The first column was an RD column from which only a negligible distillate (2.6 % of the bottom flow) was taken at the top of the column, that is, the column was operated practically at total reflux. Reducing the amount of the distillation flow made it possible to increase the methanol conversion significantly. In fact, if the distillation flow was depressed to be very small, nearly complete conversion of methanol could be achieved. In consequence, the only product stream was taken from the bottom, which included the ether product. The second column was used to separate the ether formed in the RD column from the mixture of the unreacted feed.

This rather unusual operation mode for the RD column was chosen in order to force the entire methanol to react in the RD column and to get a methanol-free product. The process was simulated varying the amount of the methanol feed into the column (MeOH/trimethylpentene feed ratio 0.38 in run 1 and 0.47 in run 2, respectively). The bottom product flow was fixed to the amount to the hydrocarbon feed.

The results of the two cases, run 1 and run 2, are presented. Run 1 represents a case with a lower methanol feed. The total conversion of the reactive hydrocarbons in this process was 35.9 % and a conversion of 95 % was obtained for methanol. Obviously the conversion of the process could be increased by feeding more methanol into the column. This could be seen in the results of run 2. In this case, the conversion of the hydrocarbons reached 44.5 % and the one for methanol 94.3 %, but the penalty is paid by the increased amount of energy used in the column. The methanol feed, the total product amount, and the condenser and reboiler duties are shown for the two runs in Table 5. The increase in the reaction rate was due to a more favourable methanol profile in the column, that is, larger methanol composition in the lower part of the column.

Table 5. Methanol feed and total product amount and reboiler and condenser duties for RD simulations.

	Run 1	Run 2
MeOH feed (kmol h ⁻¹)	40.1	50.1
Total product (kmol h ⁻¹)	108.2	108.2
Reboiler duty (kW)	6649	12 440
Condenser duty (kW)	-6225	-12 040

The ether C8ME and the non-converted TMP-1 and TMP-2 mixture are very interesting gasoline components because of their high octane value. The specifications of maximum alkenic concentration in gasoline would, however, prevent the extensive usage of alkenic trimethylpentenes. Therefore, it will be necessary to separate the ether C8ME from the non-converted hydrocarbons, which can be done easily by distillation. The non-converted TMP-1 and TMP-2 have to be hydrogenated. This process schema is economically interesting in cases where only part of the alkenic trimethylpentenes, say less than 35 %, needs to be converted to ethers. In cases where high C8ME conversion is desired, the distillate containing the unreacted alkenes needs to be recycled back to the etherification reactor. In this case the hydrogenation step is not required.

5.2 Conclusions RD for gasoline oxygenate

The rate of etherification reaction of methanol with 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene was found to be significantly slower compared with the formation rates of lighter ethers, which are used in gasoline. The reaction was strongly equilibrium limited. Therefore, in an adiabatic tubular reactor only low conversion was possible to obtain in simulations. According to simulation results, the conversion of the alkenes could be increased considerably by RD.

6 MODELLING A SIDE REACTOR CONFIGURATION COMBINING REACTION AND DISTILLATION

Reactive distillation has undisputed benefits in certain applications like in the methyl acetate process. However, several aspects limit the applicability of RD. Distillation and reaction must take place at the same temperature and it is known that reaction rates are very sensitive to temperature. Thus RD has a narrow available temperature range.

If high pressures are applied, separation of phases becomes difficult because the volatility of components goes towards unity. In low pressures, the vapour density is small resulting in large gas volumes and large vacuum equipments.

High temperatures (above 150 °C) have the disadvantage that in distillation we must use hot oil systems, furnaces, or electric heating. Low temperatures (below 20 °C) in turn lead to the use of a refrigeration system.

If we consider the RD column as a reactor, we need large liquid/catalyst hold-up. From the reaction point of view, free space is a disadvantage in the reactor. Distillation in turn needs free space for vapour flow and a large mass transfer area. Hold-up is not an advantage for distillation.

Finally, the catalyst deactivation, which is normally compensated with excess of catalyst or by increasing the reaction temperature or in-situ regeneration is impossible in RD columns. This demand of special needs leads to tailor-made solutions in RD column technology and potentially to high costs.

Some of the disadvantages of RD can be relieved and the benefits of a combined process can still be preserved by considering a Side Reactor Configuration (SRC). See Figure 21 for a schematic process flowsheet of the side reactor process. A liquid-side draw from the column is taken and fed into the reactor. The reactor effluent is then returned back into the distillation column. The reactor can be in one phase or a traditional fixed-bed catalyst reactor can be used. The adequate catalyst amount is easily arranged in SRC where traditional reactor types and catalyst structures can be used. In addition, the reaction conditions in SRC are less limited by the distillation requirements, particularly the reaction profile can be optimised.

Design and understanding of this new combined process is more demanding than the design of the traditional sequential processes. According to the experience of the author, the simulation of the side reactor concept and particularly the optimisation of them are quite tedious tasks with commercial simulators.

A new software tool to simulate and optimise processes that combine distillation column with a reactor sequence has been developed. This kind of combination is particularly interesting when new intensified and integrated processes are developed. The unit block contains both the distillation column model and the models for the coupled reactors [III]. The model is implemented in FLOWBAT (Keskinen and Aittamaa, 2004).

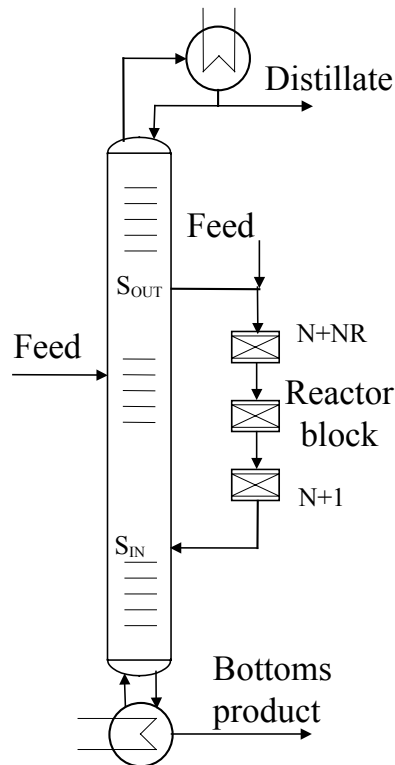


Figure 21. Schematic figure of a side reactor process.

6.1 Modelling

The target was to develop a model for simulation, design and optimisation. An adequate set of specifications of the process is also needed for the process design.

The model of the distillation column is derived from the mass and energy balances, equilibrium, and summation relations of a stage in a reactive distillation column. Murphree efficiency is included to account for non-ideality of the stages. This allows the possibility to the efficiency calculations of various complexities ending up in methods based on multi-component Maxwell-Stefan diffusion equations. In addition to this equation group, a set of specification equations is included. This allows the user to specify for example product purity, temperature, liquid, and vapour flows, and so on.

A series of continuously stirred tank reactors (CSTR) represents the side reactor stage. Co-current flow and two phases are allowed in the reactor. As in the distillation model, a set of specification equations is available.

The combined reactor and distillation column model can be used for the simulation of a single distillation column and one sequence of interlinked reactors. The basic reactor stage can work as a continuous stirred tank reactor (isothermal or adiabatic). A series of reactor stages can be used to model a fixed-bed or tubular reactor. The heat flows and the pressure can be specified on each reactor segment. A reactor stage can also be specified to work as a heater or a cooler of a stream.

6.2 Method of solution

Since the new SRC model should also be for plant optimisation studies, the Newton's solution method was chosen. In solving the linearised subsystem of the model equations, new elimination and back substitution method was developed. The method takes into account the structure of the Jacobian **Error! Reference source not found.** The Jacobian structure of the combined model contains two non-zero off-diagonal blocks and the one "missing" block of the tridiagonal structure in the reactor part of the model [III] for details see Pakkanen (2000).

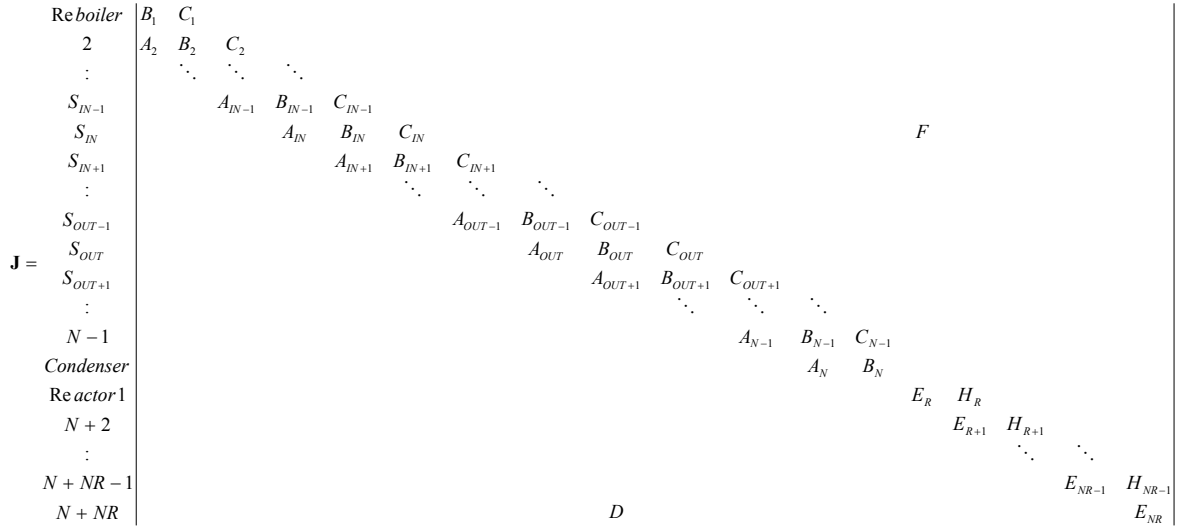


Figure 22. Schematic Structure of the Jacobian matrix of SRC model. A , B , C are normal jacobian blocks appearing in distillation. E block is due to equations and variables of the reactor. H describes the connections of the reactor block to adjacent reactor block. F describes the connection of the reactor to the stage S_{IN} and D describes the effect of stage S_{OUT} to the first reactor block. S_{IN} is the stage where the reactor effluent is returned to the column, S_{OUT} is the outdraw stage, the reboiler is stage 1, condenser is stage N , NR number of reactor blocks see Figure 21.

The elimination and back substitution method to obtain the Newton's step $\Delta \mathbf{x}$ (see equation 21) is described in the following. The notation follows that of Figure 22.

Stage 1:

$$\begin{aligned} B_1 &\leftarrow B_1^{-1} \\ C_1 &\leftarrow B_1 \cdot C_1 \\ G_1 &\leftarrow B_1 \cdot G_1 \end{aligned}$$

Stage 2: when $j=1, N+NR-1$

$$\begin{aligned} B_j &\leftarrow (B_j - A_j \cdot C_{j-1})^{-1} \\ C_j &\leftarrow B_j \cdot C_j \\ G_j &\leftarrow B_j \cdot (G_j - A_j \cdot G_{j-1}) \end{aligned}$$

Stage 3:

$$F_{IN} \leftarrow B_{IN} \cdot F_{IN}$$

Stage 4: when $j=IN+1,N$

$$F_j \leftarrow -B_j \cdot A_j \cdot F_{j-1}$$

Stage 5: when $j=OUT+1,N$

$$D_j \leftarrow -D_j - D_{j-1} \cdot C_{j-1}$$

when $j=OUT,N-1$

$$D_{N+1} \leftarrow D_{N+1} - D_j \cdot F_j$$

when $j=N+1,N+NR-1$

$$D_j \leftarrow -D_j - D_{j-1} \cdot C_{j-1}$$

$$E_{N+NR} \leftarrow (E_{N+NR} - D_{N+NR,N+NR-1} \cdot H_{N+NR-1})^{-1}$$

when $j=OUT,N+NR-1$

$$G_{N+NR} \leftarrow G_{N+NR} - D_j \cdot G_j$$

$$G_{N+NR} \leftarrow E_{N+NR} \cdot G_{N+NR}$$

Backsubstitution

Stage 1:

$$\Delta x_{N+NR} \leftarrow G_{N+NR}$$

Stage 2: when $j=N+NR-1,N$

$$\Delta x_j \leftarrow G_j - C_j \cdot \Delta x_{j+1}$$

Stage 3: when $j=N-1,IN$

$$\Delta x_j \leftarrow G_j - C_j \cdot \Delta x_{j+1} - F_j \cdot \Delta x_{N+1}$$

Stage 4: when $j=IN-1,1$

$$\Delta x_j \leftarrow G_j - C_j \cdot \Delta x_{j+1}$$

6.3 Model testing

MTBE Production

To test the performance of the model, the production of MTBE with SRC concept was simulated. The chemical system of these test examples included isobutane, isobutene, MeOH, MeOMe, MTBE, Water, DIB, and TBA as components. Simulated isobutene conversions varied from 94 to 98 %. The model could find the solution typically in less than 10 Jacobian evaluations.

Isobutene dimerisation

As another example, simulation of the dimerisation of isobutene is presented. The flowsheet of the process and some process conditions are depicted in Figure 22. The flow rates and compositions of the main components and streams of the process are

presented in Table 6. The conversion of isobutene in the simulated case was 83 %. The model performed well also in this case.

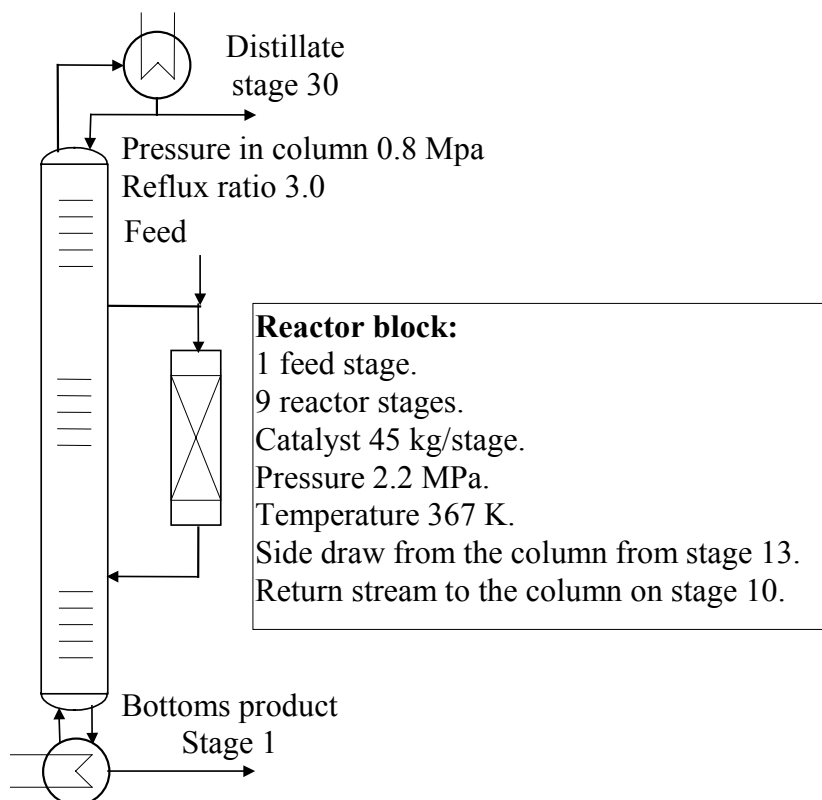


Figure 22. The flowsheet of the dimerisation process and some process conditions.

Table 6. The main compositions and flows of the isobutene dimerisation. F_L feed to the reactor. $S_{L,OUT}$ side draw from column into the reactor. $RET_{L,IN}$ effluent of the reactor. BOT_L bottoms product flow. $DIST_L$ distillate.

	Component	F_L	$S_{L,OUT}$	$RET_{L,IN}$	BOT_L	$DIST_L$
Molar fraction	Isobutane	0.594	0.847	0.752	0.000	0.898
	Isobutene	0.396	0.132	0.093	0.000	0.100
	Diisobutylene	0.000	0.001	0.128	0.865	0.000
	Trimer	0.000	0.000	0.013	0.086	0.000
	Tetramer	0.000	0.000	0.000	0.000	0.000
	Isooctane	0.008	0.000	0.007	0.047	0.000
Total flow (kmol/h)		100	30.0	113.0	16.7	66.1

The new model has also been tested for cases where heat exchangers are coupled with adiabatic reactors. The use of the specification equations that are implemented in the model enabled this.

6.4 Conclusions SRC modelling

The side reactor concept (SRC) that combines reactors with a distillation column to one interlinked process has shown great potential as a process option when new processes are developed or old processes are further intensified.

When new processes are developed and designed they must be optimised and their feasibility studied. Traditionally the flowsheet is solved iteratively by the sequential modular approach. This procedure can be tedious because of the coupling of the reactor and separation makes the convergence of the whole process difficult.

A new unit model was developed to design and optimise SRC processes. It was implemented into a flowsheet simulator to enable study of large-scale processes. As the method of solution the Newton's method was chosen. All the model equations were solved simultaneously and the method included a new elimination and back substitution method developed for this type of combination of reactors and a distillation column.

7 SIDE REACTOR CONFIGURATION VS. REACTIVE DISTILLATION - SOME CASE STUDIES

Reactive distillation (RD) and side-reactor concept (SRC) were compared by using some industrial examples. These were chosen to present equilibrium-limited (*tert*-amyl methyl ether (TAME) production) and selectivity-limited (2-methylbutene dimerization) reactions [V].

7.1 TAME production

TAME reaction is an equilibrium-limited reaction where high conversion can be achieved only by combining multiple-stage reactors with a separation system. The reaction rate increases with temperature, whereas at lower temperatures the reaction equilibrium is shifted towards the products. A combined reaction and separation allows sufficiently high reaction temperatures, since the product is being constantly removed and adjusting the temperature for more favourable equilibrium becomes less significant.

When applying reactive distillation to TAME production, these benefits can be exploited to a certain extent. However, there is a number of relatively heavy components at the reaction mixture that force the distillation temperature to be fairly high. This leads to either a need for large catalyst amounts or, alternatively, to long residence times in the reactive stages of the column. The contradiction between the requirements of reaction and separation is quite evident. If either high catalyst amounts or large inner flows due to the demand for high residence times are applied to achieve feasible conversion, the reactive distillation column becomes very large. Applying the side-reactor concept in production of TAME does not necessarily remove the need for large catalyst amounts, but the catalyst can be better exploited when the single phase operating conditions are more freely adjustable.

TAME process was simulated with both RD and SRC [V]. In RD the column had a total of 30 ideal stages, of which 13 were reactive (stages 11-23, reboiler stage 1). The amount of catalyst at one stage was set to be 800 kg, adding up to a total of 10 400 kg dry catalyst in the entire column. Feed was introduced below the reactive zone, in order to prevent the light precursors from leaving the column with top product without meeting the catalyst first. The column operated at a pressure of 5 bar, which set the reaction temperature to a feasible level (to around 343 K).

When SRC was applied, an amount of catalyst identical to the RD case (10 400 kg) was divided between 3 reactors in series. The first reactor contained 1 160 kg, the second 3 490 kg, and the third 5 750 kg of catalyst. The diameter of the column was 3.3 m for each of the reactors and lengths of the 1st, 2nd, and 3rd reactor were 1 m, 2 m, and 6 m, respectively. The reactors operated at pressure of 15 bar, and without any external heating or cooling. The inlet temperatures were regulated in the case of optimised SRC. A distillation column with 30 ideal stages was used here as well. The feed from the 3rd reactor was introduced at stage 10, and the recycle stream back to the reactors was taken from stage 20. The column operated at pressure of 5 bar.

In Figure 23, the conversions of a reactive distillation system and two side-reactor configurations are plotted against reflux ratio of the system. In each configuration, the catalyst amount and feed composition are the same. The feed consisted of equimolar amounts of methanol and 2-methyl butene. It can be seen that the conversion in the reactive distillation column reaches its maximum value at relatively low reflux ratios.

Conversion in the adiabatic SRC (no heating or cooling between the reactors) rises steadily with the reflux ratio, reaching and surpassing the conversion of RD at high reflux ratios. The conversion of an adiabatic SRC stays below the one of RD's at lower reflux ratios, because part of the reflux flow is not going to the reactors, but is needed for the separation. In addition, the gas phase never meets the catalyst.

When the inlet temperatures of the reactors are optimised, the results show a remarkable improvement in the conversion. Even with very low reflux ratios the conversion in the SRC exceeds the maximum obtainable conversion for RD. In case of TAME reaction, the reason for increased conversion is clear. Since high temperatures favour high reaction rates, high conversion can be achieved in the first reactor with high inlet temperature and low catalyst amounts. Low temperatures and high residence times can then be applied to the latter reactors, yielding a conversion higher than is possible to achieve with an adiabatic reactor train.

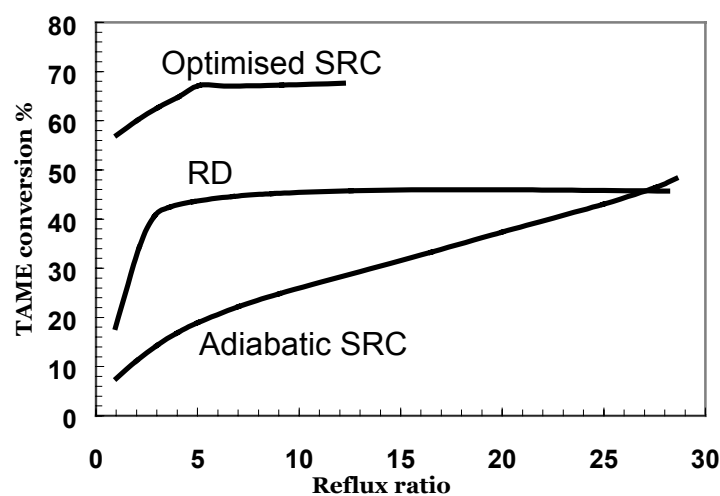


Figure 23. Comparison between conversions of reactive distillation, adiabatic side reactor concept and reactor train -optimised side reactor concept. TAME conversion is plotted against reflux ratio. For SRC the reflux flow rate is combined recycle and reflux flow rate

The feed is introduced into the reactor series when SRC is applied. Due to this, the conversion in SRC is at least the once-through conversion of the reactor series. In an optimised case, the conversion of SRC at its minimum corresponds to the optimised once-through conversion of three tubular reactors in series. In adiabatic SRC, the once-through conversion is not so high, since all the potential of the reactor series has not been used.

If TAME processes applying RD use a pre-reactor with a conversion of 65-70 %, RD column feed then has a precursor/product ratio of around 1/3 in weight fractions. At these high conversion levels, the superiority of SRC cannot be demonstrated as clearly as it is done at lower conversion levels. A number of simulations with a pre-reactor were performed in order to find optimal process conversions for SRC and RD. Both process alternatives could be optimised to give a conversion above 90 %.

At higher conversions, when a pre-reactor is applied, SRC loses part of its advantage. Since the output of the pre-reactor, which is the feed to the SRC, already has high conversion, it is not useful to introduce it to the reactor train. Hence the feed is introduced in the distillation column, and only the recycle stream from the column is led through the reactor train. However, more flexible reactor and catalyst options together with less restricted hardware design makes SRC an attractive process alternative.

7.2 Isobutylene dimerisation

In this process 2-methylbutene (isobutylene) is dimerised into 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene (isooctene). This reaction is not limited by reaction equilibrium, but prevention of oligomerisation is desirable to maintain the quality of the product. Oligomerisation takes place if the temperature of the reaction mixture is too high, whereas at lower temperatures the conversion of isobutylene remains unfeasibly low. The reaction is a catalytic liquid-phase reaction, which sets requirements for the reactor pressure. Therefore the operating window for the reaction is fairly limited, which is known to be problematic from the reactive distillation point of view. When SRC is applied, the possibility of manipulating both the reaction and separation conditions is again better.

The reaction is highly exothermic, so it could still be an interesting candidate for reactive distillation. In the study, the ideal stage reactive distillation model was used. UNIFAC was used as the activity coefficient model. Some interesting designs are represented in Table 7. These designs have 78 ideal stages. The feed is introduced on stage 7 (stage 1 is the reboiler). The combined dimer and the isooctane composition was kept under 0.7 mol-%. Some of the designs included an external reactor.

Table 7. Column details, conversions and selectivities for 4 optimised reactive distillation columns for isobutylene dimerisation.

Design	A	B	C	D
Pressure in column [MPa]	1.58	1.51	1.4	1.58
Reflux ratio	4.8	30.0	4.8	4.8
Reboiler duty [MW]	14.8	97.3	14.8	9.4
Catalytic stages in column	12-71	12-56	12-71	12-71
Dry catalyst on stage [kg]	300	300	1600	300
Dry catalyst in the column [kg]	18000	13500	96000	18000
Dry catalyst in the whole system [kg]	21475	16975	99475	18000
Conversion of isobutene in the column	91.2	95.3	95.3	93.0
Conversion of isobutene in the whole process	93.4	96.5	96.4	93.0
Dimer selectivity in column	88.2	94.2	86.0	89.3
Dimer selectivity in the whole process	90.9	95.3	89.2	89.3

Designs A, B and D seem to be reasonable in respect that it might be possible to implement 300 kg of dry catalyst per ideal stage in an RD column. However, the conversion of the isobutylene is not high enough in designs A and D. Design B demonstrates the trend how the conversion can be increased by a higher reflux ratio, in this case 30.0. This value is obviously unrealistic, which can be seen from the reboiler duty 97.3 MW. A comparison of designs A and C shows how increasing the total amount of catalyst in the column affects the conversion. The conversion is significantly higher, but the amount of catalyst reaches a value of 1600 kg dry catalyst per ideal stage, this being an unrealistic amount.

A recent application to produce diisobutylene with a side reactor process is proposed by Sloan *et al.* (2000). The isooctene product is taken from the bottom of the distillation column and the unreacted C4 stream is recycled into the reactor section. A schematic block diagram of the process is presented in Figure 24. The side reactor concept allows using a larger amount of catalyst in the system as reactive distillation does. Optimising the inlet temperatures in the reactor train and using one external reactor to push the overall conversion towards 100 % gives promising results even without any external heating or cooling. As Table 8 shows, optimising the feed temperatures of the reactors allows the overall conversion reach as high a figure as over 99 %, keeping the selectivity at the same time over 95 %. The advantage of optimised SRC shows that the selectivity can be increased at the cost of conversion, still keeping the overall yield at a higher level than is possible to reach with RD.

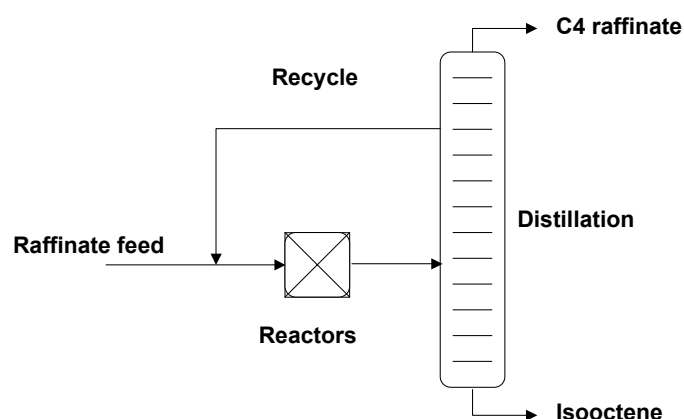


Figure 24. Schematic block diagram of the SRC process for dimerising isobutylene.

Design A from was picked as a reference process in comparing the performance of SRC in isobutylene dimerisation. The results of the comparison are presented in Figure 25, where the overall yield of diisobutylene is plotted against the reflux ratio of the distillation column. The catalyst amount was 18 000 kg dry catalyst in total in all simulations for RD and SRC. In case of adiabatic SRC, the inlet stream to reactor train was at the same temperature as the column side-draw plate. In optimised SRC the temperatures of the reactors were optimised.

Table 8. Process details, conversions and selectivities for 4 optimised side reactor configurations for isobutylene dimerisation.

Design	A	B	C	D
Pressure in column [MPa]	1.0	1.0	1.0	1.0
Reflux ratio	2,3	2,7	3,6	3,5
Reboiler duty [MW]	22,2	22,1	21,8	22,7
Dry catalyst in the system [kg]	57148	57148	57148	57148
Conversion of isobutene in the whole process	98,1	97,8	97,5	99,3
Dimer selectivity in the whole process	95,8	96,5	97,3	95,5

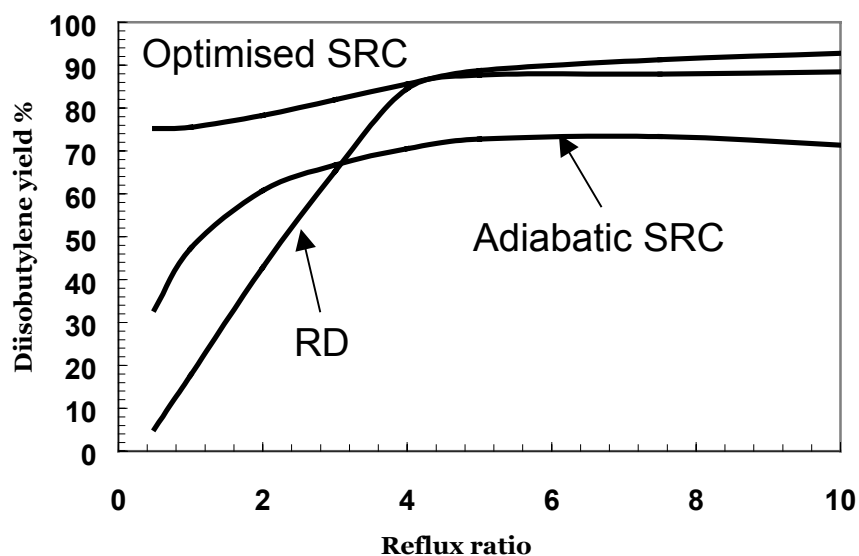


Figure 25. Comparison between conversions of reactive distillation, adiabatic side reactor concept, and reactor train -optimised side reactor concept. Diisobutylene yield is plotted against reflux ratio. For SRC the reflux flow rate is combined recycle and reflux flow rate.

The results are not as spectacular as in TAME production, but it must be kept in mind that even though the optimisation was heuristic, it was holistic for the reactive distillation column, including feed compositions, number of ideal plates, pressure, and so on. Still the performance of the optimised SRC excels the one of RD at every reflux ratio. The performance curves of RD and optimised SRC overlap only at the vicinity of the optimal reflux ratio of RD, 4.8.

Adiabatic SRC does not in this case reach the performance of RD at high reflux ratio, but the quality of the product actually starts to decline at high reflux ratios. This is most probably due to the high flow rate through the reactors, which reduces the temperature reducing the reaction rates.

7.3 Conclusions SRC vs. RD

The main reactions of both processes presented above, TAME and dimerisation, shows characteristics that make the process configuration combining reaction and distillation attractive. At low internal and recycle flow rates, traditional SRC with adiabatic reactor train fails to reach similar conversions and selectivities as RD. However, optimising the conditions in the side reactor concept improves the performance of the process remarkably, making it an interesting process alternative to reactive distillation.

8 CONCLUSIONS AND DISCUSSION

8.1 Modelling

Two new modelling tools for simulation and design of processes combining reaction and distillation have been created. The first tool is for the reactive distillation process where the reaction takes place inside the distillation column. The other tool models the Side Reactor Concept (SRC), where a liquid side draw from the column is taken and fed into the reactor and the reactor effluent is then returned back into the distillation column.

The traditional way to model a distillation column is to use the so-called equilibrium stage model. In actual operation, the distillation plates rarely behave as an equilibrium stage. It has been found experimentally that plate efficiencies often vary in various column sections and in multi-component systems even each component has individual plate efficiencies that deviate from component to component.

Two main approaches are available to calculate the real separation of a distillation column. In the first procedure binary NTUs (number of transfer units) are first estimated for all components. Then Murphree point efficiencies are calculated from these NTUs using the two-film theory and the Maxwell-Stefan equations. For large plates, mixing models for liquid and vapour flows on the plate are used to obtain the plate efficiencies (see Ilme, 1997). These methods can be used for calculating reactive distillation problems (Kettunen, 1988). This model is also implemented in the distillation stage model of the SRC model presented in this thesis.

Another approach is the rate-based approach (see Taylor and Krishnamurthy, 1985a, Taylor et al., 1994) in which the heat and mass transfer including multi-component interactions between the components are directly calculated using heat and mass transfer coefficients on the plate. In this approach, the film theory and the Maxwell-Stefan equations for diffusion are applied, too. In small columns, the rate-based model and the multi-component efficiency model predict similar results as shown above in section 3.1.

The RD tool presented here is based on the rate-based approach, a large spectrum of reactions (homogeneous and heterogeneous; slow, average and fast; equilibrium and kinetically controlled) is considered, reaction is accounted for in both bulk and film phases, various hydrodynamic models and a large choice of hydrodynamic and mass transfer correlations for various types of column internals (trays, random and structured packing, catalytic packing) are implemented in the code.

In the development of the tools (RD, SRC), the method of solution was under special attention. For the RD model, a hybrid method was developed, in which the robustness of the relaxation method and the speed of the Newton's method were combined. The relaxation method is used in the beginning of the computation to find a good starting point for the Newton's method. The final solution is found by the Newton's method. It was shown that the new hybrid algorithm broadens the domain of convergence remarkably compared to the use of the Newton's method alone. This is an important result. According to the experience of the author, the convergence properties of the commercial simulators tend to be poor in reactive distillation cases. Poor convergence

usually leads to tedious nursing of the solution by techniques such as “homotopy by hand” where the solution is found by small consecutive changes of the specifications or by manipulating for example thermodynamic parameters. These means are familiar for chemical engineers applying intensive simulation in their work.

The relaxation method is relatively slow but it is quite robust. The long calculation time of the relaxation method is compensated by the fact that it is often enough to find one good solution near the desired specifications. Using this as the starting point, the Newton’s method usually converges rapidly to the desired solution.

The SRC model was implemented as a unit in a unit modular flowsheet simulator. The equations were solved simultaneously with the Newton’s method. A new elimination and back-substitution algorithm was developed for the equation group evolving from the SRC process.

The developed software tools are flexible and open, allowing easy adaptation to various process configurations and process conditions. The implementation of both models was done into the flowsheeting software FLOWBAT.

The validation of the RD model was done against experimental measurements of both reactive distillation in packed columns and normal distillation problems in a tray column. The simulations in the tray column agree excellently with measurements. Also the reactive distillation simulations were encouraging. The test system presented in this thesis was the production of MTBE. This system is a proven and well-known reactive distillation example, but for model validation it provides a good benchmark system. The first tests and simulations were done with a column setup where the reactive zone consisted of reactive Raschig rings. The simulated and experimental values agreed well. The other set of simulations were done in a column where the reactive zone was filled with catalytic structured packing. The simulation agreed well with the experimental results also in this case.

Simulation results obtained by the RD model DESIGNER have been published also for ethyl acetate synthesis by reactive distillation by Kenig et al. (2001).

It was shown that the developed RD model could be used as a useful tool for modelling of counter-current reactor in case of hydrogenation processes. The calculation segments could be used flexibly for modelling different functional sections of the reactor. Each calculation segment represents an adiabatic/non-adiabatic reactor (CSTR) stage. The stage can be used to model a separation section of the reactor, a feed (quench) or product stage or a heat transfer section.

In its basic implementation (presented above in sections 2.1 – 2.5), the rate-based approach does not take into account the composition gradients evolving on large distillation trays. To take this into account, a mixed pool and an eddy diffusion model was developed.

When considering simulations with the mixed pool model, it was shown with a MTBE production example that the change of concentrations over a tray is significant in comparison to the difference between adjacent trays. However, in a reacting system the final difference between the mixed pool model and otherwise identical rate-based

model but without division into cells, was small. The probable reason is that in a relatively tall distillation column there is rarely such huge concentration difference over a single tray that the effect of its concentration profile on the overall performance of the column would be significant. MTBE formation is a reaction where conversion is limited by equilibrium and tends to compensate the changes as well.

In the same way, the results involving the vapour plug flow model are rather near to each other, but both differ somewhat more from the results achieved with the mixed vapour model. Thus it seems that in this case the method used for calculating the local mass transfer rate is more important than the tray scale hydrodynamic model. In addition, when the effect of the vapour flow pattern from plate to plate was tested, the results differed very little from the mixed vapour case.

In a short column with high heat of reaction the situation is different. In this case, the ratio of the rate of reaction with mixed pool model over the complete liquid mixing was about 0.5. The calculations showed large variation of the internal liquid streams of the column due to the heat of reaction. The example could be relevant to industrial practice for short columns involving high thermal effects. This kind of equipment could be, for example, a reactive absorber. They are often used for highly exothermal systems and moreover, they have frequently rather small number of stages.

These numerical examples show that there are still interesting aspects to study in the operation and design of an RD column. If a cross-flow operation is considered, the composition gradients and the behaviour of the reaction are also dependent of the reaction type. An equilibrium reaction such as the MTBE reaction and an irreversible consecutive reaction (Higler et al. 1999b) have different demands on the structures and flows of the tray.

In a broader scope the reactive distillation model and the side reactor model presented in this thesis belongs to the unit operations approach of modelling. The use of software tools similar to the current process flowsheeting programs (among others Aspen Plus[®], PRO/II, CHEMCAD, HYSYS) was established as a common practice in chemical and petrochemical industries during 1980's. This thesis shows that unit models can still be improved in many aspects. Previously ignored important real phenomena can be included in the models or new multifunctional units can be included in the model libraries of such software.

Typically unit models do not include calculation of local conditions of the real process unit. Ideal mixing or plug flow is a common assumption. A current trend in modelling is to introduce flow fields in the models. One approach is to use modelling blocks including modelling of mass transfer, VLE and reaction kinetics interconnected with fixed flow fields. This idea was used here in the development of the mixed pool model for reactive distillation on large plates. Other approaches to combine mass transfer and reaction with flow fields are also under study for example Alopaeus et al. (2002), Moilanen et al. (2004) and Laakkonen et al. (2004) have used population balances together with flow fields to model local conditions in two phase stirred tank reactors.

The future modelling target is to use CFD in (reactive) distillation modelling. Recent studies are concentrated in characterising flows on (reactive) sieve trays or in

(catalytic) packed beds (see for example van Baten and Krishna 2002, van Baten and Krishna 2001, van Baten et al. 2001abc, Krishna et al. 1999, Mohamed Ali 2002a,b) At the moment the most feasible way to use CFD is to study the hydrodynamic properties of equipment designs. The combination of rigorous phase equilibria, interfacial mass transfer models and kinetic models with CFD calculations for distillation columns is at the moment hampered by huge calculation times.

8.2 Processes

The applicability of a few process configurations for the production of new gasoline oxygenate, 2-methoxy-2,4,4-trimethyl pentane were studied.

Reactive distillation is an interesting process option when the reaction is strongly equilibrium-limited. Thus the once-through conversion is not usually high enough and a reactor separator system must be considered.

Two RD configurations were tested. The other represents an unusual configuration where practically no distillate is taken from the column. According to the simulation results, RD could increase the conversion of the alkenes considerably.

The contradiction between the large catalyst hold-up and high residence times required by the reaction and the large vapour space required by the distillation diminishes the applicability of RD. There are additionally well-known limitations of RD, such as the narrow operating window and difficulties with the catalyst inside the column.

A comparison between reactive distillation and both adiabatic and temperature-controlled side reactor configuration was done with two industrial examples. The examples present different types of reactions, equilibrium-limited reaction of TAME production and selectivity-limited reaction of isobutylene dimerisation.

The main reactions of both processes, TAME and dimerisation, show characteristics that make the process configuration combining closely distillation and reaction attractive. In both cases, the side reactor configuration shows good techno-economical properties. The main advantage of SRC over RD is the capability of having the full potential of both reactor and distillation units in use. This feature is highlighted at low conversion levels, as was shown in the TAME example.

These results are in line with the pioneering experimental work with SRC presented by Schoenmakers and Buehler (1982) where they concluded that heterogeneous catalysis in external reactors using ion-exchange resins as catalysts is equivalent to homogeneous catalysis in an RD column with respect to conversion and energy consumption. Furthermore, Schoenmakers and Bessling (2003) draw the attention to the fact that a combination of reaction and distillation does not necessarily have to be operated in a column. For slower reactions a broad range of equipment not necessarily containing columns can be used.

The results in this thesis show that the side-reactor concept gives more freedom of choice in process design and this in turn leads to efficiency and better economics of the process.

REFERENCES

- Alejski, K., Computation of the Reacting Distillation Column Using a Liquid Mixing Model on the Plates, *Comput. Chem. Eng.* **15** (1991) 313.
- Alejski, K., Szymanowski, J., Bogacki, M., The application of a minimization method for solving reacting-distillation problems, *Comput. Chem. Eng.* **12** (1988) 833-839.
- Alopaeus, V., Koskinen, J., Keskinen, K.I., Majander, J. Simulation of the population balances for liquid-liquid systems in a nonideal stirred tank. Part 2 - parameter fitting and the use of the multiblock model for dense dispersions, *Chem. Eng. Sci.* **57** (2002) 1815-1825.
- Ashley, M.J. and G. G. Haselden, The calculation of plate efficiency under conditions of finite mixing in both phases in multiplate columns, and the potential advantage of parallel flow, *Chem. Eng. Sci.* **25** (1970) 1665-.
- Ball, W.E., 44th National meeting of A.I.Ch.E., New Orleans 1961.
- van Baten, J.M., and Krishna, R., Gas and liquid phase mass transfer within KATAPAK-S® structures studied using CFD simulations, *Chem. Eng. Sci.* **57** (2002) 1531 – 1536.
- van Baten, J.M., Ellenberger, J. and Krishna, R., Radial and axial dispersion of the liquid phase in a KATAPAK-S structure: Experiments vs CFD simulations, *Chem. Eng. Sci.* **56** (2001a) 813 – 821.
- van Baten, J.M., Ellenberger, J. and Krishna, R., Hydrodynamics of reactive distillation tray column with catalyst containing envelopes: Experiments vs. CFD simulations, *Catalysis Today* **66** (2001b) 233 – 240.
- van Baten, J.M. and Krishna, R., Liquid phase mass transfer within KATAPAK-S structures studied using CFD simulations, *Catalysis Today* **69** (2001) 371-377.
- van Baten, J.M., Ellenberger, J. and Krishna, R., Hydrodynamics of distillation tray column with structured catalyst containing envelopes: Experiments vs. CFD simulations, *Chemical Engineering & Technology* **24** (2001c) 1077-1081.
- Chang, Y.A., Seader, J.D., Simulation of continuous reactive distillation by a homotopy-continuation method, *Comput. Chem. Eng.* **12** (1988) 1243-1255.
- Gani, R., Cameron, I.T., Extension of dynamic models of distillation columns to steady-state simulation, *Comp. Chem. Eng.* **13** (1989) 271-280.
- Gorak, A, Kreul, L.U, Skowronski, M., Patent Pending DE 197 01 045 A1 (1998).
- Halmu, A., Multala, R., Raportti monikomponenttisislauprojektin No 1. koetislauksista, Tislauksen prosessidynamiikkaa, report 25, Helsinki University of Technology, the laboratory of chemical engineering (1978) (in finnish).
- Higler, A., Krishna, R., Taylor, R., Nonequilibrium cell model for multicomponent (reactive) separation processes, *AIChE J.* **45** (1999a) 2357-2370.
- Higler, A. P.; Taylor, R.; Krishna, R., The influence of mass transfer and mixing on the performance of a tray column for reactive distillation, *Chem. Eng. Sci.* **54**(1999b), 2873-2881.
- Hung, J-S. A second generation nonequilibrium model for computer simulation of multicomponent separation processes. 1991, Ph.D.Thesis, Clarkson Univ.
- Ilme, J., Estimating plate efficiencies in simulation of industrial scale distillation columns, *Lappeenranta University of Technology, Research papers* 57, Ph.D. Dissertation (1997).
- Ishikawa, T., Hirata, M., Extractive distillation calculations by modified relaxation method, *J. Chem. Eng. Jpn.* **5** (1972) 125-131.

- Jakobsson, K., and Aittamaa, J., Comparison of plate efficiency estimation models to experimental results of pilot scale: a case study, Proceedings of Separations Technology Topical Conference 2001 Vol 1., AIChE Annual meeting, November 4-9, 2001, Reno, NV
- Jelínek, J., Hlaváček, V., Steady state countercurrent equilibrium stage separation with chemical reaction by relaxation method, *Chem. Eng. Commun.* **2** (1976) 79-83.
- Jelínek, J., Hlaváček, V., & Kubíek, M., Calculation of multistage countercurrent separation Processes –II; Multicomponent multistage separation by relaxation method, *Chem. Eng. Sci.* **28** (1973a) 1825-1832.
- Jelínek, J., Hlaváček, V., & Kubíek, M., Calculation of multistage countercurrent separation Processes –III; Computation of interlinked columns, *Chem. Eng. Sci.* **28** (1973b) 1833-1838.
- Kenig, E. Y. and Górák, A. A film model based approach for simulation of multicomponent reactive separation, *Chem. Eng. Process.* **34** (1995) 97-103.
- Kenig, E. Y., H. Bäder, A. Gorak, B. Bessling, T. Adrian, and H. Schoenmakers, Investigation of Ethyl Acetate Reactive Distillation Process, *Chem. Eng. Sci.* **56** (2001) 6185.
- Keskinen, K.I., Aittamaa, J., eds., FLOWBAT, User's Instruction manual, Helsinki University of Technology, Laboratory of Chemical Engineering and Plant Design, Espoo, 2004.
- Ketchum, R.G., A combined relaxation-Newton method as a new global approach to the computation of thermal separation processes, *Chem. Eng. Sci.* **34** (1979) 387-395.
- Kettunen, M., Tislauksen mallitus, kun reaktio tapahtuu kolonnissa, Ms. S. Thesis, (1988) Helsinki University of Technology, Laboratory of Chemical Engineering and Plant Design, Espoo, Finland. (in finnish).
- King, C.J., Separation processes 2nd edition, McGraw-Hill, New York 1980.
- Kooijman, H.A., Taylor, R., A nonequilibrium model for dynamic simulation of tray distillation columns, *AIChE J.* **41** (1995) 1852-1863.
- Krishna, R., Van Baten, J.M., Ellenberger, J., Higler, A.P. and Taylor, R., CFD simulations of sieve tray hydrodynamics, *Chem. Eng. Research & Design, Trans.I.Chem.E.* **77** (1999) 639 – 646.
- Krishna, R., and Standart, G. L., Mass and Energy Transfer in Multicomponent systems, *Chem. Eng. Commun.* **3**, 201 (1979).
- Krishnamurthy, R., Taylor, R., A nonequilibrium stage model of multicomponent separation processes. Part I: model description and method of solution, *AIChE J.* **31** (1985a) 449-445.
- Krishnamurthy, R., and Taylor, R., A nonequilibrium stage model of multicomponent separation processes. Part II: comparison with experiments, *AIChE J.* **31** (1985b) 456-465.
- Krishnamurthy, R., Taylor, R., A nonequilibrium stage model of multicomponent separation processes. Part III: the influence of unequal component efficiencies in process design problems, *AIChE J.* **31** (1985c) 1973-1985.
- Krishnamurthy, R., Taylor, R., Simulation of packed distillation and absorption column, *Ind. Eng. Chem. Proc. Des. Dev.* **24** (1985d) 513.
- Krishnamurthy, R., Taylor, R., Absorber simulation and design using a nonequilibrium stage model, *Can. J. Chem. Eng.*, **64** (1986) 1976-.
- Laakkonen, M., Alopaeus, V., Aittamaa, J., Validation of bubble breakage, coalescence and mass transfer models for gas-liquid dispersion in agitated

- vessel, 2nd International Conference on Population Balance Modelling, May 5-7, 2004, Valencia, Spain.
- Lewis, W. K., Rectification of binary mixtures, *Ind. Eng. Chem.* **28** (1936) p. 399.
- Mohamed Ali, A., P. J. Jansens, Z. Olujic. CFD simulation software – A Design Tool for Packed Column Internals. Proceedings of the Topical Conference Distillation Tools for the Practicing Engineer. AIChE Spring Meeting, New Orleans, LA, USA, 2002a.
- Mohamed Ali, P. J. Jansens, Z. Olujic. Experimental Characterisation and CFD Simulation of Gas Distribution Performance of Liquid (Re)Distributors and Collectors in Packed Columns. Proceedings of the International Conference on Distillation & Absorption 2002, Baden-Baden, Germany, 30 September - 2 October, 2002b.
- Moilanen, P., Laakkonen, M., Aittamaa, J., CFD modelling of local bubble size distributions in agitated gas-liquid vessels - verification against experiments, ESCAPE-14, May 16-19, 2004, Lisbon, Portugal.
- Muller, N.P., Segura, H., An overall rate-based stage model for cross flow distillation columns, *Chem. Eng. Sci.* **55** (2000) 2515.
- Onda, K., Takeuchi, H., Okumoto, Y., 1968, Mass transfer coefficients between gases and liquid in packed columns, *J. Chem. Eng. Jpn.* **1** 56-62.
- Powers, M.F., Vickery, D.J., Arehole, A., Taylor, R., A nonequilibrium stage model of multicomponent separation process -V. computational methods for solving the model equation, *Comp. Chem. Eng* **12** (1988) 1229-1241.
- Pakkanen, S., Prosessilaskennan ratkaisumenetelmien kehittäminen, M.Sc. Thesis, Helsinki University of Technology, Espoo, 2000.
- Pyhalahti A., Reactive Distillation in Literature, *Plant Design Report Series*, Report No. 42, Helsinki University of Technology, Espoo 1996, p. 108.
- Rose, A., Sweeney, R.F., Schrodt, V.N., Continuous distillation calculations by relaxation method, *Ind. Eng. Chem.* **50** (1958) 737-742.
- Schoenmakers, H.G., Bessling, B., Reactive and catalytic distillation from an industrial perspective, *Chem. Eng. Process.* **42** (2003), 145-155.
- Schoenmakers, H.G., & Buehler, W.K., Distillation Column with External Reactors – an Alternative to the Reaction Column, *Ger. Chem. Eng.* **5** (1982), 292-296.
- Seader, J.D., The rate-based approach for modeling staged separations. *Chem. Engng Progr.* **85** (1989) 41-49.
- Simandl, J., Svrcek, Y., Extension of the simultaneous-solution and inside-outside algorithms to distillation with chemical reactions, *Comput. Chem. Eng.* **15** (1991) 337-348.
- Sloan, H.D., Birkhoff, R., Gilbert, M.F., Pyhalahti, A., Nurminen, M., NPRA 2000 Annual meeting, AM-00-34.
- Sundmacher, K., Hoffmann, U., Development of a new catalytic distillation process for fuel ethers via a detailed nonequilibrium model, *Chem. Eng. Sci.* **51** (1996) 2359-2368.
- Sundmacher, K., Kienle, A. (eds.), *Reactive Distillation Status and Future Directions*, WILEY-VCH, Weinheim 2003.
- Taylor, R., Krishna, R., *Multicomponent mass transfer*, John Wiley, New York 1993.
- Taylor, R., Krishna, R., Modelling reactive distillation, *Chem. Eng. Sci.* **55** (2000) 5183-5229.
- Taylor, R.; Kooijman, H. A.; Hung, J. S. A second generation nonequilibrium model for computer simulation of multicomponent separation processes, *Comp. Chem. Eng.* **18** (1994) 205-217.

- Toppinen, S., Aittamaa, J., Salmi, T., Interfacial mass transfer in trickle-bed reactor modelling, *Chem. Eng. Sci.* **51** (1996) 4335-4345.
- Turek, F., Lange, R., Mass transfer in trickle-bed reactors at low Reynolds number, *Chem. Eng. Sci.* **36** (1981) 569-579.
- Venkataram, S., Chan, W.K., Boston, J.F., Reactive distillation using ASPEN PLUS, *Chem. Eng. Prog.* **86**(8) (1990) 45-54.
- Yuxiang, Z., Xien X., Study on catalytic distillation processes, Part II. Simulation of Catalytic Distillation Processes - Quasi-Homogeneous and Rate-Based Model, *Trans IchemE.* **70** (1992) 465-470.
- Zheng, Y., Xu, X., Study on catalytic distillation process Part II. Simulation of catalytic distillation process, *Trans.Inst.Chem.Eng.* **70** 9A (1992) 465-470.
- Zhu, J., Shen, F., The modeling and simulation of reactive distillation processes, *Foundations of Computer-Aided Process Design*, Biegler, L.T, Doherty, M.F., Eds., 1995.

NOTATION

A	Jacobian block
<i>a</i>	Interfacial area, m ²
B	Jacobian block
C	Jacobian block
<i>C_i</i>	molar concentration, mol/m ³
\mathcal{E}	Energy transfer rate, W
<i>F</i>	Feed, mol/s
F	Vector of residual functions
g	Vector, Thomas algorithm
\overline{H}	Molar enthalpy vapour, J/mol
\overline{H}_i^V	Partial molar enthalpy vapour, J/mol
\overline{h}	Molar enthalpy liquid, J/mol
\overline{h}_i^L	Partial molar enthalpy liquid, J/mol
<i>h</i>	Heat transfer coefficient eqs. (37) and (38), W/(m ² K)
<i>i</i>	Component
J	Jacobian matrix
K	K-value
<i>k</i>	Mass transfer coefficient, m/s
<i>k</i>	Tuning factor of the effect of reaction eqs. (32) and (33)
<i>L</i>	Liquid flow rate, mol/s
<i>N</i>	Mass transfer flux, mol/s
<i>N</i>	Number of stages
<i>NC</i>	Number of components
ΔP	Pressure drop, MPa
<i>P</i>	Product flow, mol/s
<i>PRES</i>	Pressure, MPa
<i>Q</i>	Energy flow to stage, W
<i>R</i>	Reaction rate, mol/s
[<i>R</i>]	Matrix of mass transfer resistances
<i>t</i>	Time, s
<i>T</i>	Temperature, K
u	Vector, Thomas algorithm
<i>V</i>	Total vapour flow, mol/s
w	Matrix, Thomas algorithm
<i>X</i>	Liquid bulk compositions
x	Vector of variables
<i>Y</i>	Vapour phase compositions

Greek letters

[β_L]	Bootstrap matrix for the liquid phase
[β_V]	Bootstrap matrix for the vapour phase
[Γ_i^L]	Thermodynamical correction factor liquid phase

Subscripts

i	Component
j	Stage
spec	Specified
t	Total
tot	Total

Superscripts

F	Feed
film	Film
I	Interface
L	Liquid bulk
V	Vapour bulk