PHENOMENON DRIVEN PROCESS DESIGN
Focus on multicomponent reactive and ordinary distillation

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Abstract

This thesis describes part of the work that has been done in the Chemical Process Engineering Laboratory of the University of Oulu to systematize conceptual process design. The aim has been to develop a design methodology, i.e. how process design is done, based on a carefully elaborated concept analysis. The starting point has been that all the knowledge related to process design, i.e. not only the procedural knowledge related to the design activity itself, but also the declarative knowledge related to the design target (process) and the environment (project) in which the design is done, should be systematized. The process design methodology can be represented within a single formalism by treating the activity, target and resources as structural parts of the project object. In that case, each design decision becomes properly constrained by the goal and the resources available, and is also stored together with the domain knowledge on which the decision was based. This holistic approach was adopted when the phenomenon driven process design methodology was built to systematize chemical process development while simultaneously supporting creativity.

This thesis concentrates on knowledge generation activity as part of the phenomenon driven process design methodology. A brief description of the generic chemical process object model is presented, after which the focus is on the design activity and the strategy of design. The phenomenon driven process design of an MTBE production process is described as an illustration of the methodology. It is shown how combinations of reaction and separation, such as reactive distillation, evolve naturally during a design project.

For the evaluation of attainable state distributions, which is an important design task implied by the methodology, a robust method was developed to solve the modified MESH equations of reactive distillation. The method was also applied when developing a rigorous calculation method for the determination of minimum energy demand of multicomponent distillation.

Keywords: design methodology, homotopy continuation, minimum reflux
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**List of publications**

This thesis includes the following original publications (Appendices I-VI):


Nomenclature

\[ a \] Interfacial area per unit volume of dispersion, m\(^2\)/m\(^3\)
\[ A \] Column cross-sectional area or active bubbling area, m\(^2\)
\[ C \] Number of components
\[ h \] Molar enthalpy of liquid, J/mol
\[ H \] Molar enthalpy of vapor, J/mol
\[ \mathcal{H} \] Homotopy
\[ j \] Molar diffusion flux vector, mol/m\(^2\)s
\[ K \] Reaction equilibrium constant
\[ l \] Vertical coordinate of column section, m
\[ L \] Liquid flow rate, mol/s
\[ LF \] Flow rate of liquid feed, mol/s
\[ n \] Vector of molar fluxes, mol/m\(^2\)s
\[ nr \] Number of reactions
\[ ns \] Number of equilibrium stages
\[ n_t \] Total molar flux, mol/m\(^2\)s
\[ P \] Pressure, Pa
\[ r \] Reflux ratio
\[ s \] Reboil ratio
\[ SL \] Liquid side stream flow rate, mol/s
\[ SV \] Vapor side stream flow rate, mol/s
\[ t \] Homotopy parameter
\[ T \] Temperature, K
\[ V \] Vapor flow rate, mol/s
\[ VF \] Flow rate of vapor feed, mol/s
\[ x \] Mole fraction in liquid phase
\[ x \] Vector of liquid mole fractions
\[ X \] Vector of variables of reactive distillation model
\[ xf \] Mole fraction in liquid feed
\[ y \] Mole fraction in vapor phase
\[ y \] Vector of vapor mole fractions
\[ yf \] Mole fraction in vapor feed
\( z \)  
Vector of variables

**Greek Letters**

\( \alpha \)  
Stoichiometric coefficient

\( \alpha \)  
Stoichiometric matrix (nr \( \times \) C)

\( \varepsilon \)  
Extent of reaction

\( \varepsilon \)  
Vector of extents of reactions

\( \nu \)  
Activity coefficient

**Subscripts**

\( B \)  
Bottom product

\( D \)  
Distillate

\( F \)  
Feed

\( i \)  
Component \( i \)

\( j \)  
Equilibrium stage \( j \)

\( r \)  
Reaction \( r \)

**Superscripts**

\( I \)  
Phase equilibrium

\( R \)  
Reaction
## Contents

Abstract  
Acknowledgments  
List of publications  
Nomenclature  
1 Introduction............................................................................................................. 9  
  2 Creativity and process design.................................................................................. 13  
    2.1 Unit operations................................................................................................. 13  
    2.2 Creative design................................................................................................. 15  
    2.3 Preconditions for systematizing process design................................................. 16  
3 Phenomenon driven process design......................................................................... 17  
  3.1 Ontological commitments.................................................................................... 17  
  3.2 Generic chemical process.................................................................................... 18  
    3.2.1 Explication of chemical process............................................................... 18  
    3.2.2 Purpose.................................................................................................... 18  
    3.2.3 Structure.................................................................................................. 19  
      3.2.3.1 Interior......................................................................................... 19  
      3.2.3.2 Boundary..................................................................................... 21  
      3.2.3.3 Interaction.................................................................................... 21  
      3.2.3.4 Exterior........................................................................................ 21  
    3.2.4 State......................................................................................................... 21  
    3.2.5 Performance............................................................................................. 22  
  3.3 Implications for design...................................................................................... 22  
  3.4 Generic process design activity......................................................................... 23  
    3.4.1 Structure of activity.................................................................................. 23  
    3.4.2 Design cycle and performance driven strategy.......................................... 24  
    3.4.3 Phenomenon driven ordering.................................................................... 25  
  3.5 Example........................................................................................................... 26  
    3.5.1 Specification of process purpose............................................................... 26  
    3.5.2 Properties of material and necessary phenomena...................................... 27  
    3.5.3 Creation of ‘primitive flowsheet’............................................................... 27
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5.4</td>
<td>Disaggregated two-boundary process</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>Reactive distillation</td>
<td>32</td>
</tr>
<tr>
<td>4.1</td>
<td>About state modeling</td>
<td>32</td>
</tr>
<tr>
<td>4.2</td>
<td>Motivation</td>
<td>34</td>
</tr>
<tr>
<td>4.3</td>
<td>Homotopy continuation</td>
<td>35</td>
</tr>
<tr>
<td>4.4</td>
<td>Tailored homotopy</td>
<td>36</td>
</tr>
<tr>
<td>4.5</td>
<td>Step size control</td>
<td>39</td>
</tr>
<tr>
<td>4.6</td>
<td>Implementation and performance</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>Minimum internal recycle in homogeneous distillation</td>
<td>42</td>
</tr>
<tr>
<td>5.1</td>
<td>Problem definition</td>
<td>42</td>
</tr>
<tr>
<td>5.2</td>
<td>Search strategy</td>
<td>45</td>
</tr>
<tr>
<td>5.3</td>
<td>Performance</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>Conclusions</td>
<td>51</td>
</tr>
<tr>
<td>7</td>
<td>References</td>
<td>54</td>
</tr>
</tbody>
</table>
1 Introduction

“Business as usual’ cannot continue if long term economic and commercial viability is sought.” R.V. Porcelli (1993)

The chemical and petroleum industries are experiencing fundamental changes. Rapid globalization of the industries, economic and political changes in the world order, environmentally driven governmental regulations and social pressures (e.g., decrease of consumption, increase of reuse and recycling), declining reserves of some raw materials, and increasing competition and overcapacity are the circumstances in which companies are fighting for their future existence.

As a response, the chemical and petroleum industries are slowly realizing the significance of new technologies - compared to incremental improvements in the existing processes - as a means of producing products more competitively while simultaneously protecting the environment. The need for more efficient and environmentally ‘cleaner’ processes has led to a growing interest in novel processes and hybrid process systems which combine conventional and non-conventional processes. Even though a notable risk has to be taken, the availability of modern, low-cost and continually more efficient computers together with the progress made in computational methods, modeling, process simulation, process control and experimental work facilitate investments in such technologies. The future trends and pressures faced by corporate managements will increasingly often lead to considerations other than short-term risks and costs. Clearly, therefore, an increased emphasis has to be put on innovative research and process design activities.

A methodology is an attempt to systematize an activity. The need to systematize can be questioned in arts, which is a field for talented creative individuals to express themselves. We need brilliant individuals in science as well, but in design science the need to systematize the design activity can no longer be questioned. This is especially true of process design, which is a cooperative activity involving extensive and ever-expanding use of computers. The need to systematize process design derives from the necessity to have several individuals with different backgrounds act together and communicate with each other and with computers. While nobody questions the importance of the systematization of process design in itself, the misconception that
systematization kills creativity still seems to persist. Such a fear is partly justified from the point of view of how we systematize. Obviously, a process design methodology in the form of a prefixed sequence of tasks with an associated set of heuristics to support decision making may not be precisely what we need. A good process design methodology, on the other hand, should not only make scope for but also lead the way to creative solutions. The other features of a good process design methodology include the following two: (1) It should integrate the design activities, such as process engineering, control engineering, and safety engineering, instead of supporting the old inefficient diversified pattern. (2) It should permit a natural way of incorporating the use of computers in decision making and knowledge storage and retrieval.

The development of a methodology for conceptual process design has been the main focus in the Laboratory of Chemical Process Engineering of the University of Oulu for several years. A careful concept analysis has already been accomplished and, as a result, a highly unified representation of all knowledge from molecular characterization of matter up to managing a design project has been formulated (Pohjola 1997). The accomplished concept analysis has been the backbone of the methodology development work done in the laboratory, and the systematization of process design based on this knowledge representation has solidified into a novel methodology called the ‘Phenomenon Driven Process Design’ methodology (PDPD methodology).

This doctoral thesis is an integral of the work dating back to the year 1993, when the design and synthesis of combined reaction and separation processes was introduced as the topic of a cooperative research project between the University of Oulu and the University of Trondheim (Norwegian University of Science and Technology). The topic together with the systematization done in the Oulu University led to the launching of a phenomenon oriented design approach. The approach suggests ‘phenomenon’ and ‘material’ as the new building blocks of process design that replace the traditional unit operations. The price that inevitably has to be paid in the form of more complex models and algorithms in process state evaluation results in a more versatile search space for process structure and possibilities for beneficial coupling of phenomena and thus opens up a systematic approach towards novel process concepts. One such concept is ‘reactive distillation’, which may, for instance, cut down the total annual production costs by an order of magnitude. Later, when the approach was formalized into the PDPD methodology, an example of reactive distillation was taken as a case study to illustrate the new, more creative design perspective offered by the methodology. This work allowed further refinement of a procedural model inherent to the PDPD methodology called ‘phenomenon driven ordering’. At that time, it became clear that few design and synthesis tools presented in the literature were insufficient for satisfactorily dealing with the design issues of reactive distillation; successful control of coupled phenomena requires detailed knowledge of their individual mechanisms and understanding, on that basis, of how their rates and extents interfere. Thus, the determination of a feasible state distribution based on a structural description of the phenomena involved emerged as a logical design step in the search for process design solutions. The work was first directed towards rate based modeling of the reactive distillation section, and the effect of the heat of reaction was analyzed as a separate contribution. Later, the familiar equilibrium stage models were adopted and a robust method for the calculation of
attainable state distributions in reactive distillation columns was developed based on the block oriented modeling approach. This tradeoff, which cost the lower flexibility concerning the possible specifications, was considered necessary here; the block oriented way of modeling made it possible to develop a practicable global solution algorithm for early design purposes. The feasible state distributions can be evaluated by the model in reactive distillation columns as a subactivity implied by the PDPD methodology.

During the course of developing the methodology to be reported in this thesis, it has been regarded as important to remain free from the implementation constraints posed by any individual object-oriented computer environment. Instead, implementation of the methodology is a focus of parallel and future work; there are two larger projects under way at the Laboratory of Chemical Process Engineering, which have a significant emphasis on the implementation aspects. One is the MECANOX project of the national Nanotechnology Program financed by TEKES, and the other is an EU project called POEM. The POEM project, which was launched in December 1998, builds upon the PDPD methodology and aims to develop a computer environment that could be used as a design partner by human designers in a project of conceptual process design. Thus, when experiences accumulate from various applications in the near future, the performance of the methodology can be further assessed against such criteria as the creativity of design solutions, the responsibility of decision making, the effectiveness of activity management and the capability of integrating knowledge from different disciplines.

This doctoral thesis includes the six original publications in the appendices I-VI. In paper I (Appendix I), the basis underlying the PDPD methodology is presented. The paper suggests the need to move from unit operation based to phenomena based creative design. The inadequacy of unit operation based design approaches is made clear by presenting some known applications of combined reaction and separation processes, where the decomposition into traditional unit operations does not apply. Furthermore, the three key concepts of process (Pohjola et al. 1994) - phenomenon, control and purpose - are briefly explicated and the design principles based on these explications are presented. In paper II (Appendix II), the above ideas are formalized into an early version of the phenomenon driven ordering of design activities inherent to the PDPD methodology. The procedural model is illustrated by a short example of MTBE production process design. This example has been extended in chapter 3.5 of this summary paper to illustrate phenomenon driven ordering by explaining how the disaggregation of a process arises from the characterization of the phenomena involved (knowledge generation) and how a new milestone for the design has to evolve dynamically during a process design project.

Paper III (Appendix III), where the PDPD methodology is formally presented, reviews the whole process of methodology research done so far. The paper gives a holistic view of chemical process design and bridges the cultural gaps between the seemingly separate modeling domains. Conceptual design, as an activity of an organization, is represented as communication between the process modeling and process metamodeling activities, the former referring to activities on process specifications and the latter to management activities. Process analysis as an activity differentiating process behavior from causalities, which is the best known process
modeling subactivity for chemical engineers, is linked to process synthesis and evaluation and put into the perspective of design management. The paper emphasizes the interpretation that chemical process simulation is a subactivity of process design necessary to specify the process state distributions serving process performance evaluation at the end of each design cycle.

The theme of this thesis, phenomenon driven process design, can be viewed as an activity to find feasible means to make given phenomena advance as desired in order to achieve material state distributions satisfying locally and temporally the given product specifications. Thus, an assessment of feasible state distributions is a crucial part of design when process solutions are sought. When the phenomenon to be controlled is a complex aggregate of subphenomena - as in the reactive distillation example in chapter 3.5 - the search for achievable state distributions can be tedious. For that purpose, a new method has been presented in paper V for solving the equilibrium stage models of ordinary and reactive distillation. The method retains the accuracy of the MESH equations and simultaneously has the robustness required of short-cut design methods. ‘Robustness’ here means that the solution of the NAEs is found without any need for manual iteration and an initial guess given by the user. This and similar methods together with the continually increasing computer capacity may provide the missing link to the new generation short-cut design methods, which do not rely on the success of analytical or numerical solutions of oversimplified systems.

The robustness of the method is particularly convincing in solving highly nonideal distillation problems. This has been the stimulus for developing an exact calculation method for solving the minimum energy limit of multicomponent distillation, which problem has persisted - in spite of the valuable attempts to solve it. In paper VI, a fully automated solving procedure for the rigorous calculation of the minimum energy requirement of homogeneous multicomponent distillation has been presented. Examples of several multicomponent mixtures with highly nonideal thermodynamics have been given in paper VI. Furthermore, paper VI discusses some pitfalls in the minimum energy calculation, which make part of the recent achievements questionable in view of their usefulness for nonideal mixtures. Chapter 5 in this summary paper focuses on this problem.

In paper IV, a rate based modeling approach based on the Maxwell-Stefan equations is applied to a catalytic distillation section. The specific aim of the paper was to examine the effect of the heat of reaction on the vertical vapor composition profiles, i.e. how highly nonequimolar mass transfer affects the profiles. It was shown in the paper that a favorable cancellation takes place in the equations and, as a result, suppresses nearly totally the influence of nonequimolar effects in most practical cases. Because paper IV makes merely a small contribution to the main theme of the work, only a short review has been presented in chapter 4.1 of this summary paper. At any rate, its message as such is valuable, because it may lead to major simplifications without a loss of realism when rate based models and respective solution algorithms are written for reactive distillation columns.
2 Creativity and process design

“We should not consider that the list of devices from which we select the equipment for designing our processes - columns, mixers, exchangers, extractors, reactors, filters, etc. - is frozen for ever. New principles stemming from basic research open the way to innovative designs and it is the duty of chemical engineering researchers to involve themselves in such applications.”  J. Villermaux (1993)

Design can be categorized into routine, innovative and creative design. While the innovative and creative aspects of process design are becoming increasingly important for chemical and petroleum companies, process design is still suffering from the conservative notion that process design is a routine activity accomplished by (1) ‘piecing together the unit operations’, whereas (2) “the creation of new unit operations and the development of novel types of equipment are not part of the design of process” (Sargent 1989). At its extreme, this conservatism has led to the conclusion that (3) ‘process design is a combinatorial problem’ emerging from existing solutions of process units and from the possible ways to interconnect them. In the following few chapters, the above three statements will be re-evaluated.

2.1 Unit operations

The concept of unit operation was introduced at the early stages of the chemical engineering discipline. It was recognized that the processes employed in chemical industry involved a relative small number of elementary operations. The systematic study of these individual unit operations led to the development of respective mathematical models and methods to compute their behavior in standard equipment. Thus, one-to-one correspondence between unit operation and equipment was assumed to exist, and a natural framework for process design by piecing together the appropriate unit operations was established.
Over the years, **creative** engineers have devised new unit operations. Although the chemical reactions were included, the earlier description became insufficient, and a parallel concept of more elementary unit operation was later introduced. Several unit operations were seen to take place in a single piece of equipment, and, as a consequence, the one-to-one correspondence was obviously no more valid. For example, an object-oriented view, where reactive distillation was defined as a unit operation composed of unit operations, was proposed. Thus, the concept of unit operation was expanded and, supposedly, unit operation based design was thought to be retained. It was still possible to define a process as a collection of ‘unit operations’ - though more elementary ones.

What has been the inheritance from this very first paradigm based on the concept of unit operation? Certainly, it made it possible to act routinely in conceptual process design. Mathematical models were - and still are - built for the unit equipment, thus supporting the traditional one-to-one correspondence. The fixed model structures together with the domain knowledge of the respective process units have allowed the development of fast and efficient solving procedures. Steady-state flowsheeting with modular (unit) process simulators, such as ASPEN PLUS, became a routine employed by chemical engineers, and some analysis of a large number of process alternatives based on the unit models became possible during conceptual design. The way of thinking in terms of unit operations still predominates in chemical engineering.

It is not surprising that the first attempts to systematize process design were made in terms of the unit operation driven methodology. The Douglas methodology (Douglas 1988) is unit operation driven. The prevalent one-to-one correspondence leads to its basic weakness: the process is disaggregated structurally in a predefined way (which is arbitrary or weakly justified by: 'this is the way it has been done in the past'). The decisions made at the early stages of design, when the process structure is synthesized, are usually the most crucial, as they largely determine the performance of the process. When the process is decomposed in a predefined way into separate, traditional unit operations, implicit decisions on process structure have already been made and potential new solutions may have been lost. The innovative aspect of design remains in the linking of these predefined building blocks. If a new unit operation is invented, it is certainly not done within the methodology, because it does not support that kind of creativity. In such a situation, the Douglas methodology has to be restructured to include the new unit operation, as it has been done in the case of reactive distillation (Douglas & Stephanopoulos 1995).

Still, disaggregation into the traditional unit operations may already lead to a huge number of alternatives. According to Douglas (1988), the search space for a flowsheet may involve $10^4$ to $10^9$ alternatives. Disaggregation into even more elementary unit operations will further increase the possibilities. Even though many of the alternatives can be eliminated on the basis of experience, economic objective functions together with the limited accuracy of the applicable short-cut and unit process models and cost data will lead to a flat optimum with a high uncertainty. In other words, with the level of knowledge they represent, the synthesis problem is not solvable. Thus, one may question whether process design is a combinatorial problem, even though it can be represented as a finite amount of building blocks and their possible interconnections.
2.2 Creative design

While the first statement, that process design consist of piecing together unit operations, has some truth value due to the redefinition of the building blocks, the second statement (i.e. that the creation of new unit operations and the development of novel types of equipment are not part of process design) can be disproved. Frequently, chemical companies have reported successful, strictly scheduled projects, where novel and efficient designs have been carried out (e.g. Smith 1984, Agreda et al. 1990, Kitchen & Mansfield 1992). Remarkable competitive benefits compared to traditional processes, i.e. processes based on well-known unit operations, have been gained by these novel solutions. For instance, the development of Eastman Kodak’s commercial process for the production of methyl acetate was such a successful design project. Based on the articles of Agreda et al. (1990) and Siirola (1995), a brief characterization of the design is given below.

- The operating and capital costs of the final design were one-fifth of the conventionally generated and optimized unit operation design.
- The entire conceptual design was completed in less than a year.
- The careful knowledge acquisition led to the invention of the process. Literature and patent reviews were made and many ideas were considered. Hand and computer calculations were used to test the ideas.
- The available unit model libraries were insufficient for simulation purposes. The necessary process state models and simulation capabilities were created during the design.
- Deep knowledge was exploited early. The most relevant features of the process were sought. Some detailed considerations, such as the internal geometry, the process control structure and corrosion tests, were considered crucial at an early phase of the design already.
- The missing knowledge was generated. Extensive laboratory work was carried out at different levels of detail and in different scales.
- The final process was the culmination of collaboration between many scientists and engineers.

This single example shows that creative process design, in its proper meaning, is something else than “piecing together unit operations”, and also that the design is driven by knowledge acquisition, i.e. knowledge is needed to determine most crucial process aspects, to understand whether new process ideas are feasible, and, of course, to solve the existing problems and to identify new ones. Systematic study of the relevant features has produced natural rather than artificial, constraints to the design and to creativity. The process structure can been seen to evolve naturally. Even though process design has a hierarchic structure, the knowledge needed can be deep, problem specific or qualitative, and does not need to conform strictly to any general predefined hierarchy levels of process design. The state models have been developed and modified purposefully to acquire knowledge of the target - which is the process to be designed.
2.3 Preconditions for systematizing process design

When generic computer-based design procedures are suggested, the importance of problem specific deep knowledge should not be overlooked. The academic desire to find general ‘subroutine-like’ design approaches has led to continually diverging paths between the design theory and practice. According to Perris (1994), process synthesis, knowledge based systems (KBS) and process control are examples of points where the gap between the academia and the industry has been widening.

When a process design task is expressed in a tractable mathematical form suitable to be processed by a computer, abstractions have been made. These abstractions are based on assumptions, simplifications and necessary data. Thus, the resulting solution has only limited significance. These abstractions are crucial in process design, because we are designing something that does not exist. Deep knowledge and experience will help the process designer to approximate the credibility of the mathematical tools relative to the specific problem at hand as well as to select other appropriate tools for generating the knowledge needed for reliable decision making. The attempts to see process design as a kind of general routine activity suitable to be fully computerized have failed, and it can be argued that these attempts will continue to fail. Fortunately, the recent chemical engineering literature has placed the human designer in a central role in process design and, as a consequence, a more realistic view concerning process design and AI has arisen (Ballinger et al. 1994, Han et al. 1995, Alha & Pohjola 1994).

The importance of human beings has been considered crucial in the development of the process design methodology developed at the Laboratory of Chemical Process Engineering of the University of Oulu: the chemical process has been viewed as an artifact which is the result of human interference with the nature by taking purposefully spontaneous phenomena under control. Thus, process design can be characterized as follows:

- Process design is a creative activity. This presumably puts limits on how process design is systematized and how ‘detailed’ a level is attainable. It does not follow that the design activity for building methodologies did not contain a good amount of generic features.
- Process design is decision making. The properties of a chemical process are directly related to the human decision making which makes it an artifact. Every artifact can be said to have a purpose given to it by its designer or user and, consequently, a performance, i.e. a goodness with respect to that purpose. While the behavior is ultimately dictated by the fundamental laws of natural phenomena, the other features of the process are largely a direct result of human decision making.
- Process design is human, target-oriented activity. How the target is described dictates largely what the model of the activity will be like. Thus the methodology of process design will crucially depend on the generic model of the chemical process adopted.
3 Phenomenon driven process design

“In chemical process engineering we see an evolution in modeling from the language of “unit operations” to the language of “elementary physical and chemical phenomena”. This is due to the inadequacy of unit operations to formalize a large and growing number of specialized process units.” G. Stephanopoulos et al. (1990)

Process design methodology is a model of how process design is done. It should formalize all the knowledge related to process design, i.e. not only the procedural knowledge related to the design activity itself, but also the declarative knowledge related to the design target (process) and to the environment (project) in which the design is done. Indeed, it is hard to accept any attempt to model a purposeful activity without considering what is being acted upon, and with what goal and with what resources this is being done. The process design methodology can be represented within a single formalism by treating the activity, target and resources as structural parts of the project object. Then, besides each design decision being properly constrained by the goal and the resources available, it will be stored together with the domain knowledge which the decision was based on.

This thesis concentrates on the knowledge generation activity as part of the phenomenon driven process design methodology. First, to clarify the process concepts, a brief description of the generic chemical process object model will be presented. Then, the focus will shift to the design activity and the strategy of the design. Finally, the phenomenon driven process design of an MTBE production process will be described as an illustration of the methodology.

3.1 Ontological commitments

An ontological commitment is a metalevel decision on how the world is viewed. The development of the concepts of the phenomenon driven process design methodology is based on the following ontological commitments.
• The world is made of real things and abstract things. The real things are things that we can build conceptual models for. The abstract things make up our symbol systems and appear as atomic elements in conceptual models. All the real things can be viewed as descendants of the generic real thing.
• The generic real thing can be modeled as an object having four attributes: Purpose, Structure, State and Performance. These constitute a necessary and sufficient set of attributes to describe all the properties of any real thing.
• The structure of a real thing has two dimensions: topological structure and unit structure. The topology of a real thing can be modeled as a set of objects (nodes) belonging to the same class as the original object and a set of relationships (links) between the nodes. The unit structure of a real thing can be modeled as a set of objects (parts) belonging to classes other than the original object class and a set of relationships (links) between the parts.

3.2 Generic chemical process

3.2.1 Explication of chemical process

The definition of a generic chemical process is based on the following verbal explication of the concept of chemical process (Pohjola et al. 1994):

(Chemical) process is control of (physico-chemical) phenomena for a purpose

The explication raises three further concepts - control, phenomenon, and purpose - into a central role. The definition implies the idea that a phenomenon which is originally a nonartifact, advancing spontaneously according to the laws of nature, may be turned into an artifact by successful human intervention. The term “purpose” in the definition refers to the purpose of the process and implies that there should be a justification for the intervention. The term “control” refers to the degrees of freedom of the process designer in the attempts to make the phenomenon advance as desired to fulfill the purpose of the process (Fig. 1.).

3.2.2 Purpose

The purpose of a chemical process makes explicit the constraints posed on the functionality of the process and on its performance, thus indicating the good that the process does and including the list of criteria to be used to evaluate how well it manages to do so. The formal part usually includes the product specification as a constraint for either the composition or the functionality of the product. The performance constraints are the measures of goodness dictated by external forces or included for ethical reasons.
3.2.3 Structure

The unit structural parts of any process are instances of four object classes: Boundary, Interior, Interaction, and Exterior. The list of these classes appended with a relation class for specifying the links between the parts, constitutes the value type of Structure in the unit-structural dimension. The distinctive features of the generic chemical process class arise from the identification of the associated subclasses (Fig. 2.).

In the topological dimension, a process may disaggregate into a set of subprocesses interlinked in various ways (Fig 3.). Typically, the links are specified as identity relations for unit structural parts of pairs of subprocesses.

3.2.3.1 Interior

Process interior is the body of material in which the phenomena to be taken under control take place. Phenomena advance spontaneously driven by the energy according to the causal laws of nature and can be controlled only indirectly by controlling the state of material. Process interior has structural parts of three types: Material, Phenomenon, and Energy.
The term “material” has been reserved to denote macroscopic matter in the methodology. Accordingly, material is assumed to remain as a continuum no matter how far its spatial disaggregation is continued. Material can be disaggregated to submaterials representing either phases or components. The topological links of a composite material...
consist of the laws which describe the mixture properties in terms of the node properties. Molecule and Atom are the value types in the unit-structural dimension of Material.

The phenomenon to be taken under control is typically a composite phenomenon. Complete control of a composite phenomenon implies a need to make all subphenomena advance as desired. The cause, the effect and the preconditions are the unit-structural parts of the phenomenon. The topological links include the temporal relationships between the subphenomena. The state of a phenomenon is characterized by its rate and extent.

3.2.3.2 Boundary

Process boundary is what surrounds the interior material and restricts it spatially, giving the process interior an identity with respect to the process exterior. The structure of the process boundary is specified in terms of pieces and interfaces and their interlinks. The specification fixes the geometry of the closed surface and the distribution of the permeability characteristics along the surface. Accepting a fluid-fluid interface as a piece of the process boundary makes it possible to view the process as an aggregate of two subprocesses sharing the selectively permeable fluid-fluid interface as a common piece of interface.

3.2.3.3 Interaction

Process interaction is an object with the value type of its structure attribute being a list of three classes: MaterialFlow, EnergyFlow, and InformationFlow. Some material flows are usually given constraints under the purpose specification of a process.

3.2.3.4 Exterior

Exterior is included among the unit-structural parts of process together with the Interior, Boundary, and Interaction. As the process environment is the most relevant aspect for the process performance evaluation, the specification of the process exterior is an important step of process design.

3.2.4 State

State is an attribute which links an object to time. The state of a composite process is an aggregate of the states of its structural nodes. Aggregation takes place via the links (e.g.
identity relations) specified in the topological dimensions. The state of a single process (node) is obtained by aggregating the states of its boundary, interior, interaction and exterior by applying the material and energy balances. The states of these objects are again aggregates of the states of their structural nodes or parts. Especially, the state of a process interior is an aggregate of the states of the interior phenomenon and the interior material. The aggregation is via phenomenal laws, such as rate and equilibrium equations.

### 3.2.5 Performance

Performance is an assessment of the goodness of a process using explicit criteria. The value may be verbal or numerical, depending on the criterion and the evaluation method used. The value should have the credibility implied.

### 3.3 Implications for design

Chemical process has been viewed as a hierarchy of objects, each of which is a descendant of the generic real thing. They hence have the same list of attributes: Purpose, Structure, State, and Performance. As a result, a highly unified representation of declarative knowledge is obtained. Furthermore, the concept analysis implies the following:

- The degrees of freedom in boundary design together with those of interaction in the form of material, energy and information flows across the boundary provide the principal means of control for a process designer. Process design thus mostly consists of making decisions on boundary and interaction.
- To control a phenomenon, one has to control its rate and extent. The rate and extent of a phenomenon depend on the thermodynamic state of the material. This implies that domain knowledge in the form of rate and extent relations is needed. On the basis of this knowledge, decisions on boundary and interaction are made, by which the thermodynamic state of the material becomes, if possible, such that the rate and extent variables of the phenomenon become favorable.
- Degrees of freedom are obtained by isolating the material to be processed into several interiors, that is, by disaggregating the process into several subprocesses. Each subprocess has its own boundaries and interactions and thus an individual thermodynamic state.
- Boundary should not be understood only as a vessel wall, but as any real phase boundary, such as a gas-liquid interface or a membrane. Boundary can be understood to also include what is normally referred to as the vessel internals, e.g. the plates and the packing of a column or even the solid catalyst of a fixed bed reactor.
There are several degrees of freedom available for the designer, which are not systematically exploited in the conventional process design. For instance, process interior can be made to include auxiliary material needed to induce auxiliary phenomena that can be used to control the necessary (desired and undesired) phenomena. Process boundary can be chosen to have different permeability characteristics to increase the degrees of freedom of interaction (selective output), or to have different geometries or to be movable for achieving different interior distributions, or to be made of material having catalytic effects.

3.4 Generic process design activity

3.4.1 Structure of activity

The unified attribute list (Purpose, Structure, State, Performance) also applies to the activity object - because activity itself is an artifact. Activity disaggregates into four subactivities according to the attribute list of the target of activity. The order is the same as the order of the four attributes in the list. The performance of the target results from what is specified under the Structure and State attributes. Based on the performance, the Structure and State attributes are refined. Thus, the refinement forms a nested loop, where structure optimization takes place in the outer loop and state optimization in the inner loop.

Fig. 4. Familiar task structure in process design.
The Purpose attribute reflects the importance of metamodeling. It can be argued that every time we have a model, we also have a metamodel describing the model in its current state and expressing our expectations or requirements about the future state of the model. Thus, the designer has to specify at least some requirements for the purpose and some constraints for the structure of the process model to be built.

The four subactivities are closely related to the generalized four-step design paradigm (Siirola 1995): formulation, synthesis, analysis, and evaluation (see Fig. 4.). At the formulation step, the process specifications and performance criteria are named. This is followed by an iteration of three steps: generation of an alternative (synthesis), determination of the behavior of the alternative generated (analysis), and comparison of the performance of the proposed alternative against the goals and specifications presented at the formulation step (evaluation).

### 3.4.2 Design cycle and performance driven strategy

The design activity can be disaggregated into a management activity object and a modeling activity object. The management activity communicates mainly at the metalevel (Pohjola 1998), and the knowledge generation (modeling) activity communicates mainly with the process model. Together with the process object and the messages passing between the objects result in what is called “design cycle” (Fig. 5.).

**Fig. 5.** Object-oriented representation of the generic process design cycle.
The communications takes place cyclically and can be visualized to advance spirally upwards as the objects are updated and the design progresses. The management’s decision to establish new subgoals (and resources) keeps the cycle going.

The value of the conceptual model of a chemical process derives from the prospects of commercialization of the process, i.e. from its feasibility and from the credibility of the feasibility assessment. The performance driven strategy (Pohjola & Alha 1994) guides a project management to set subgoals in a manner which simultaneously aims to maximize the credibility of the feasibility assessment and to minimize the consumption of resources, i.e. in order of relevance in view of the process performance.

The management should have knowledge of the order of relevance. There can be no knowledge in the form of a predefined generic list of subgoals, and thus the idea of what is the next relevant feature to be specified has to evolve dynamically. This argument is in good agreement with the modern principles of research and design management (Roussel et al. 1991).

In the present methodology, the feasibility assessment is given under the Performance attribute of a process object. The value of process Performance is updated in each design cycle and passed to the management. The management should be able to make decisions about continuing or interrupting the project based on that value.

The credibility of a feasibility assessment of a chemical process is difficult to quantify because of the subjective elements it involves. If the definition of a generic process is adopted, a feasibility assessment is made on the basis of how the three aspect categories of the definition have been covered in the process model version:

- What are the performance criteria applied.
- What is the relevance of the structural and behavioral features for the performance evaluation.
- What is the credibility of the knowledge underlying these specifications.
- What is the credibility of the performance evaluation method itself.

### 3.4.3 Phenomenon driven ordering

In any process design project, the first subgoal includes a prescriptive metamodel of the phenomenon to be taken under control. The metamodel specifies the proper level of detail of the structural and behavioral descriptions of the phenomenon and expresses the expectations about the credibility of the knowledge behind these values.

The first step towards a credible description is to properly identify the interior phenomenon. Some of the necessary subphenomena can be picked up from the functional specification of the process. Still, there are other subphenomena to identify, which either have been ignored or have not been named explicitly. The reasoning about the possibility for a phenomenon to occur implies a proper identification of the interior material. Thus, domain knowledge is generated and applied to identify and describe the process interior. Again, some of the necessary submaterials can be picked up from the process purpose specification.
The first feasibility assessment of the chemical process under design is made on the basis of the inherent controllability of the process interior, keeping the control specifications at minimum. If an interior can be predicted to achieve a state which results in a material output satisfying the product specifications, the interior can be characterized as inherently controllable.

If a single-node process, which is the default starting structure, was assumed during the first design cycle and the result was a credible assessment that simultaneous control of the identified subphenomena is not feasible in that structure, then a more appropriate process topology should be included in the next goal (disaggregation of the process). Then, a specific purpose is assigned by the designer for each new subprocess of the resulting composite process. Also, the rest of the design activity disaggregates into parallel subactivities, each including the identification of each interior and the specification of their states. The feasibility assessment of the total process is made on the basis of an aggregate of the state relation models.

Thus, when the design progresses, the structural evolution of the process takes place via decisions on the process topology and unit structure. In other words, decisions are made on (a) interior unit structure: material structure, phenomenon structure (necessary/undesired, auxiliary), (b) interior state: material state, material state distribution, phenomenon state (rate and extent relations), (c) boundary properties to support interior state and interaction: rigidity, permeability, geometry, and (d) interaction properties to support the interior state. If there are no means (auxiliary phenomena, boundary, interaction) to guarantee the controllability of phenomena, the interior is disaggregated into subinteriors to permit generation of discontinuities into material state distributions and to give a chance to control the phenomena in each subinterior separately.

### 3.5 Example

#### 3.5.1 Specification of process purpose

This example illustrates phenomenon driven ordering by applying it to a conceptual design of a MTBE (methyl tert-butyl ether) production unit. The focus is on reactive distillation. A design case is considered where an MTBE unit is added between an existing FCC unit which outputs a butane-butene (BB) fraction and an existing sulfuric acid alkylation unit. By processing the FCC-BB fraction in an MTBE unit, improved feed quality and a reduced load of the alkylation unit are achieved together with an improved gasoline pool quality. The functional specification of the MTBE unit can be stated: Convert isobutene from the fluid catalytic cracking butane-butene fraction and purchased methanol to MTBE and separate it from the remaining C4 fraction.

Acid consumption is a primary concern of a sulfuric acid alkylation unit. Oxygenate contaminants from the MTBE unit (methanol, MTBE) increase acid consumption. Residual isobutene in the butane-butene output from the MTBE unit decreases the octane level achieved in alkylation and may increase the consumption of acid. The
demands concerning the gasoline pool and the composition and production rate of FCC-BB pose limits for the MTBE purity and isobutene conversion. In this example, 99 mol-% purity of MTBE is required. The MTBE unit performance constraints (not detailed here) would include an upper cost limit and safety and operability constraints.

### 3.5.2 Properties of material and necessary phenomena

The material to be processed consists of at least n-butane, isobutane, 1-butene, isobutene, cis- and trans-2-butene (FCC-BB), methanol and MTBE. The mole fraction of isobutene in the FCC-BB flow is 0.15. The phenomenon necessary for fulfilling the functional specification is the chemical reaction:

$$\text{CH}_3\text{OH} + \text{iso-C}_4\text{H}_8 \leftrightarrow \text{C}_5\text{H}_{12}\text{O} \text{ (MTBE)}$$

The reaction is exothermic and equilibrium limited. A catalyst is needed. In this example, it is assumed that the liquid phase reaction is catalyzed by an ion exchange resin (solid). The only known side reactions are isobutene hydration to tertiary butyl alcohol, isobutene dimerization to di-isobutene and methanol dehydration to dimethyl ether and water. Isobutene selectivity up to almost unity has been achieved in typical MTBE reactors by keeping the methanol-to-isobutene ratio in the reacting mixture at unity or higher and the water level low.

### 3.5.3 Creation of 'primitive flowsheet'

A boundary is introduced to restrict material. The functional specification names the necessary material input and output flows (necessary material interaction). Because we are concerned with bulk production and the output from the FCC unit and the feed into the alkylation unit are continuous (existing processes), it is postulated that the material state distribution should be steady, i.e. the process is continuous. The 'primitive flowsheet' has been sketched in Fig. 6.

How to output MTBE and the remaining C4 separately from the same interior with a single liquid phase? Can selective outputs be achieved by introducing a suitable state distribution? What should that distribution be? How can we achieve and maintain it? By the knowledge available (designers), the functional specification cannot be fulfilled and thus the interior of the primitive flowsheet does not have sufficient inherent controllability. It is hence necessary to disaggregate the interior.

By disaggregating the interior to a two-boundary interior, two different output material flows can be created. The chemical reaction can be characterized by an unfavorable reaction equilibrium, a high heat of reaction and a significant rate of reaction at the distillation temperatures at moderate pressures. Thus, an attempt is made to disaggregate the process with a selective permeable vapor/liquid phase boundary.
Knowledge is needed concerning the change of phase phenomenon (e.g. boiling points of pure components, possible azeotropes, stability of the liquid phase, VLE behavior).

3.5.4 Disaggregated two-boundary process

The primitive flowsheet is disaggregated into the two-boundary process shown in Fig. 6. Can we control such a process within the performance constraints defined for the purpose? The purpose has specified the constraints for the quality of the output flows. Based on the constraints and the knowledge of the rates and extent relations of the phenomena (chemical reaction and change of phase), it is clear that the process does not have the controllability to fulfill the purpose, if the state distributions are spatially even. Plugflow type distributions are attained when the rigid boundary is made tubular and equipped with flow regulators, such as a distillation column (counter-current flows). The distribution in a distillation column cannot be arbitrary, as the properties of the phenomena and the means to control impose limits on the attainable distributions.

In order to sketch a two-dimensional residue curve map for a preliminary analysis of the rates and extents of the phenomena C4 hydrocarbons are lumped together (because of their similar physical properties). The mixture has two minimum boiling binary azeotropes, one between methanol and MTBE and one between methanol and the lumped C4 hydrocarbons. The azeotropes divide the composition triangle into two distillation regions. The reaction rate is dependent on temperature, and thus a lower limit for temperature can be estimated. This gives the minimum pressure in the column. The reaction equilibrium is dependent on temperature. Only one 'boiling point reaction equilibrium' trajectory exists with a fixed pressure in the composition triangle. This limits the feasible area of operation where the reaction goes forward to MTBE, and gives a maximum attainable MTBE composition (which is lower than the requisite purity). From that knowledge, it can be concluded that MTBE should be purified by mere distillation (no reaction) to the final purity in the lower part of the column, and that the MTBE composition should be as high as possible in the lower part of the reactive section, but still in the feasible area of operation. The top of the column should be capable of purifying the remaining C4 fraction. Because the system has the minimum boiling azeotrope between methanol and the lumped C4 fraction, the following possibilities seem to be available: to control the state distribution by means of reacting methanol and isobutene to a sufficiently low level (decreasing the mole fraction of isobutene in the azeotrope and the total amount of methanol) or to introduce auxiliary phenomena to assist the purification. The necessary task of auxiliary phenomena, without disaggregating the two boundary process, could be to remove methanol from the top part of the column (making it ‘heavier’) or reacting it into another component suitable to the gasoline pool or suitable to be reversed it back to methanol.

The most relevant feature of the two-boundary process is believed to be the purification of the C4 fractions of methanol, i.e. the question of whether a feasible state distribution can be attained in top part of the column. The credible assessment of feasible state distributions in reactive distillation processes can be a tedious task.
Successful control of coupled phenomena requires detailed knowledge of their individual mechanisms and consequent understanding of how their rates and extents interfere. Different levels of detail are abstracted for the mathematical state models, depending on their purposes. Furthermore, experimental knowledge generation and verification of the simulation results are often necessary for a credible feasibility assessment of the processes.

**Fig. 6. Boundary disaggregation and feasible distributions.**

The following preliminary evaluation of the achievable state distributions is based on the modified MESH equations. For the moment, side reactions are ignored and the C4 fractions, except isobutene, are lumped to n-butane. The column is assumed to have 30 stages (guessed), the column pressure is 0.5 MPa, and the stages from 1 (total condenser) to 21 are reactive. The vapor feed of n-butane (85 mol-%) and isobutene (15 mol-%) enters the 20th stage from the top, and the pure liquid methanol is fed to the
15th stage to increase the amount of reactants in the liquid phase. Isobutene and methanol enter at the stoichiometric ratio, i.e. at equal molar flow rates. The data and specifications are given in paper V. In Fig. 7., the simulated liquid composition profiles of the column are given. A 99 mol-% purity of MTBE is obtained and the distillate contains 99.85 mol-% n-butane (lumped C4) and 0.05 mol-% methanol. The profiles show that methanol reacts almost instantaneously after entering the column.

Fig. 7. Liquid mole fraction profiles for quaternary MTBE reactive distillation.

A two-boundary process may be technically feasible. The above analysis, which was based on equilibrium relations, shows that a feasible state distribution can be achieved to satisfy the product specifications. In order to make the result more credible, rate considerations of the phenomena (including side reactions) cannot be avoided. Thus, a state model with a more detailed description of phenomena would be needed. These models together with the experimental work and the experience and creativity of the designers would help to find the next relevant feature of the two-boundary process. The next relevant feature could be, for instance, to attain a favorable reaction rate, to control undesired reactions, to avoid corrosion caused by the solid acid catalyst, to solve the catalyst loading policy, to maintain reasonable catalyst life, to obtain a reasonable vapor/liquid interfacial area in the catalytic section, to avoid an excessive pressure drop, etc.

If the two-boundary process is believed to be technically feasible (credibly) at the cost of the complicated interactions and geometry of the boundary, should the design be rejected for economic or safety reasons? Should the process be disaggregated further to get the undesired phenomena under better control? These considerations might lead to disaggregation by a rigid boundary, as is shown in Fig. 6. After that, further disaggregation might be necessary for economical purification of the remaining C4 from methanol.

As a summary, phenomenon driven ordering was applied at a principal level to the design of a MTBE production process. The intention was to show that the controlled
disaggregation would release the degrees of freedom, and that the degrees of freedom which are available for the respective disaggregation level should be used systematically to get the phenomena (desired/undesired) under control. At each level of disaggregation, abstractions of the process are made concerning the phenomena involved, and relevant features of the process are sought. It is believed that in real problems, the combinatorial explosion of solutions is avoided by knowledge generation of the target (i.e. the process to be designed). Because creativity in process design can be oriented by knowledge, the philosophy of ‘the more you know, the less you can do’ would apply in chemical process design.
4 Reactive distillation

“Last but not least we acknowledge the appeal of working on new, alternative and surprising concepts, yet want to stress that for many years much more of our effort in science must still be directed to a better and more profound understanding, and further development, of existing methods and technologies.”  K.R. Westerterp (1992)

4.1 About state modeling

During the past decade, reactive distillation has incurred increasing attention. If the reaction takes place simultaneously with distillation, total annualized costs an order of magnitude lower compared to the conventional arrangements may result due to the reduced amount of process recycle streams and the simplified process schemes. It is not surprising, therefore, that the major chemical and petroleum companies are actively interested in this topic. The interest has also been wide among academics and software vendors.

Reactive distillation design touches upon several branches of the chemical engineering discipline, such as reaction engineering, catalysis and multicomponent distillation. The different phenomena involved make the design different compared to that of ordinary distillation columns (Ciric & Gu 1994). Thus, contemporary design relies on complex computer calculations, where the necessary data are extracted from the laboratory scale and sophisticated state models are used to study process behavior.

Over generations, the concept of equilibrium stage has been the basis of modeling distillation columns. Also, most of the modeling of reactive distillation employs the concept of equilibrium stage. Simply, the terms and relationships are added to the traditional MESH equations to describe the consumption or production of components involved in vapor or liquid phase chemical reactions. Unfortunately, there are no equilibrium stages in reality, as perspicaciously pointed out by Wesselingh (1997). After Sawistowski & Pilavakis (1979) presented a nonequilibrium stage model for reactive distillation and Krishnamurthy & Taylor (1985) presented the second generation nonequilibrium model for multicomponent separation processes, several rate based
models able to take a chemical reaction into account have emerged. Reactions have usually been modeled as pseudohomogeneous, but efforts have been made to account for the solid catalyst more explicitly (Zheng & Xu 1992, Sundmacher & Hoffmann 1996). A nonequilibrium model has also been developed for homogeneous reactive distillation, where the direct interaction between mass transfer and reaction in the liquid film is included (Higler et al. 1998).

A rate based modeled catalytic distillation section was considered in paper IV. The term ‘catalytic distillation’ was used to restrict the reaction to a reaction zone of a reactive distillation column at the surface of a solid catalyst which is in contact with the liquid but not with the vapor. The linearized theory of multicomponent mass transfer based on the Maxwell Stefan equations was applied to the vapor film, and the effect of total molar flux on the vapor bulk composition profiles was investigated.

In rate based modeling, material and energy balances are written separately for the vapor and liquid phases. The phases are coupled by the interface mass and energy balances. Phase equilibrium is assumed to hold at the interface. In practice, the coupling variables consist of the component molar fluxes through the interface. When a plug flow of vapor is assumed, the following component and total molar balances are obtained for a differential slice of vapor:

\[ dV = n_t aA dl \]  \hspace{1cm} (2)

\[ d(yV) = naA dl \]  \hspace{1cm} (3)

Substituting equation

\[ n = j + n_t y \]  \hspace{1cm} (4)

and equation (2) into equation (3), the terms explicitly including \( n_t \) cancel out, leaving simply:

\[ Vdy = jaA dl \]  \hspace{1cm} (5)

where \( n \) is the component flux vector, \( j \) is the diffusional flux vector, \( n_t \) is the total molar flux and \( y \) is the vector of molar fractions on the vapor side. In this case, the coupling variables consist of the diffusion fluxes.

This cancellation eliminates part of the effect of \( n_t \) on the component balance. In fact, equation (5) is structurally identical to the component balance to be obtained for truly equimolar countertransfer. A contribution of \( n_t \) still remains on both sides. It was proved in paper IV that \( n_t \) makes both sides of equation (5) increase or decrease, respectively, and a further cancellation can be expected. It was also shown that the further cancellation is strong enough, with \( n_t \) values arising from typical reactive distillation situations, to suppress any practical effect on the composition profiles compared to a case, where equimolar countertransfer is valid. The result holds when plug flow of vapor is assumed, when there is no reaction in the film and the interface equilibrium compositions do not depend on the section height considered. In these
conditions major simplifications without a loss of realism can be expected when rate based models and respective solution algorithms are written for reactive distillation columns.

4.2 Motivation

Nonequilibrium stage models require not only data on physical properties and chemical kinetics, but also hydrodynamic information for the calculation of mass transfer and reaction rates, i.e. values for the interfacial area, film thickness, holdup and mass and heat transfer coefficients. As these values are functions of the flows, compositions, temperatures and column internals, and are not - despite the recent advances - easily available, reliable use of nonequilibrium models in conceptual process design is still somehow limited. Contrary to this, a minimum amount of data is needed for equilibrium stage models, which makes their use attractive for early design considerations. Any further simplification would be doubtful in view of the complexity of the reactive distillation columns involving multicomponent mixtures and highly nonideal thermodynamics.

There are no generally accepted shortcut design methods for reactive distillation (Perez-Cisneros et al. 1996). Despite the progress in utilizing the graphical methods, useful shortcut methods are often not available in the design of distillation columns for highly nonideal multicomponent mixtures.

As the equilibrium stage models should give qualitatively correct state distributions with a moderate amount of physical data, it would be attractive to employ them at the early design phase as new-generation shortcut design models. This is my aim from the methodological point of view, i.e. it is intended to predict achievable state distributions in conventional and reactive distillation columns as functions of the means (boundary and interaction) to control the process interior (material and phenomena). Thus, at this level of abstraction, a credible assessment of feasible state distributions reflects the performance of a process to fulfill its purpose, and thus facilitates decision-making at the early phase of a conceptual design project.

While a decade ago it was not realistic to suggest a model based on MESH equations as a ‘sledge hammer’ for synthesis and design purposes, the situation is different today. Increasingly efficient and inexpensive computers allow us to develop fast enough global NAE solving algorithms for cases where convergence problems are encountered with the traditional local methods. If a fast and globally convergent algorithm for solving the MESH equations of ordinary and reactive distillation could be developed, the model would be able to work independently in the core of computer programs, and an analysis-driven synthesis, which is characteristic of processes involving highly nonideal mixtures, would be accomplished by the designer based on the reliable knowledge about process state without the dimensionality restrictions implicit in graphical methods.
4.3 Homotopy continuation

Due to the lack of global convergence properties in the Newton or quasi-Newton methods, the first homotopy continuation methods (continuation, embedding or homotopy methods) were introduced in the late 70’s and early 80’s for solving chemical engineering problems. The methods have been known to mathematicians for more than a hundred years, but only two decades ago, with much slower computers and more expensive computation time than today, they were still mostly too expensive to be used in chemical engineering problems. Recently, the chemical engineering community has begun to show increasing interest in the homotopy continuation methods. Even though this interest has mainly been academic, the fundamental changes taking place in the chemical process industries (as discussed in Introduction) serve as a stimulus toward designing and understanding novel processes, which, in turn, is likely to lead to new requirements for both the state models and the solvers. The traditional solving approaches have often proved to be excessively laborious, or even unsuccessful - thus making the homotopy continuation methods more attractive.

A homotopy \( H(z, t) \) is a continuous blending of two functions: \( f(z) \) of the actual problem \( f(z)=0 \), and \( g(z) \) of a problem \( g(z)=0 \), whose solution is known or easily determined. The blending is made by means of the homotopy parameter \( t \). The linear convex homotopies can be given in the form

\[
H(z, t) = tf(z) - t g(z) = 0
\]  

(6)

The equation shows that at \( t=0 \) the homotopy \( H(z, t) \) reduces to the easy problem \( g(z)=0 \) and at \( t=1 \) to the actual problem \( f(z)=0 \). Different choices for \( g(z) \) lead to different homotopies, such as Newton, fixed point and affine homotopies:

\[
H(z, t) = tf(z) - t g(z) = 0
\]  

(7) (Newton)

\[
H(z, t) = tf(z) - t (z - z_0) = 0
\]  

(8) (Fixed point)

\[
H(z, t) = tf(z) - t A(z - z_0) = 0
\]  

(9) (Affine)

In equation (9), \( A \) denotes a proper weighting matrix to avoid scaling problems. The weighting matrix \( A \) is typically chosen as \( f'(z_0) \), where \( z_0 \) are the (guessed) values of the variables \( z \) at the beginning of a homotopy calculation.

The homotopy path from zero to one can be followed by taking sequential steps in \( t \) and by applying Newton’s method in each step to track the curve. The parametrized \( t \) may lead to poor performance and, if turning points are encountered, to a failure in the solution procedures. Arclength is a more natural parameter. Equation (6) can be converted to an initial value problem (IVP) of a system of ordinary differential equations by differentiation with respect to arclength, as shown, for example, in Seader (1985). The movement along the path can be accomplished by a predictor-corrector continuation procedure. For numerical purposes, pseudo-arclength methods or dynamic reparametrization methods (parameter switching) can be used to approximate the idea.
An extensive introduction to the topic and illustrations of various implementations, as well as references to relevant earlier work, are given in Allgower & Georg (1990) and Wayburn & Seader (1987).

The above traditional homotopies cannot guarantee a bounded path in the prescribed domain of chemical engineering problems. Mapping methods (Seader et al. 1990), the use of complex arithmetic (Taylor et al. 1996), and bounded homotopies based on the traditional ones (Paloschi 1995 and Paloschi 1997) have been suggested to overcome the problem.

In addition to the above causes of failure, other problems encountered with homotopies, such as non-uniqueness and isolas, are discussed by Wayburn & Seader (1987) and Christiansen (1997).

The Newton homotopy is mostly used in distillation problems. It was first introduced for solving homogeneous distillation problems by Salgovic et al. (1981), heterogeneous distillation by Kovach & Seider (1987), and reactive distillation by Chang & Seader (1988).

Another class of homotopies consists of the problem dependent homotopies, where an artificial or physical homotopy parameter is chosen in such a way that the homotopy has a physical interpretation along the solution curve, i.e. along the homotopy path. Byrne & Baird (1985) reported a problem dependent homotopy for solving homogeneous distillation problems. Because the methods used by them are proprietary, the homotopy was not explained in detail. Vickery & Taylor (1986) developed the thermodynamic homotopy for homogeneous distillation, where nonlinearities of the K-values and enthalpies were introduced gradually with the help of the homotopy parameter. Later, Vickery et al. (1988) used stage efficiency as a homotopy parameter for solving homogeneous distillation problems.

For reactive distillation, as for many other engineering problems, it is possible to find a homotopy that takes advantage of the special features of the problem. In this work, a robust method based on a problem dependent homotopy for predicting state distributions in ordinary and reactive distillation columns was developed.

### 4.4 Tailored homotopy

A state model of reactive equilibrium stage is composed of heat and material balances and phase and chemical equilibrium relationships, i.e. of modified MESH equations. Below these equations have been reformulated to describe a problem dependent homotopy for a homogeneous reactive equilibrium stage \( j \). A schematic representation of the structure and the associated state variables of an equilibrium stage are given in Fig. 8.

- The overall material balance:

\[
L_{j,1} - L_j + LF_j - SL_j + V_{j,1} - V_j + VF_j - SV_j + \sum_r \alpha_{r,j} e_{r,j} = 0
\]  

(10)
• The component material balances \((i = 1...C-1)\):

\[
x_{ij}L_{j-1} - x_{ij} \left( L_j + SL_j \right) + x_{ij}LF_j + y_{ij}VF_j + y_{f,i}VF_j + \sum_r \alpha_{ij} e_{r,ij} = 0
\]

(11)

• The phase equilibrium relationships \((i = 1...C-1)\):

\[
y_{ij} - ty_{ij}^t - (1-t) \frac{y_{ij}V_{j+1} + y_{f,i}VF_j}{V_{j+1} + VF_j} = 0
\]

(12)

where \(t\) is the homotopy parameter and \(y_{ij}^t\) is the vapor mole fraction for component \(i\) in phase equilibrium with \(x_{ij}\). When \(t=0\), the equation (12) uncouples the vapor and liquid phases, and the vapor mole fractions in the exit streams are simply those obtained by vapor material balances from the input vapor flows.

![Fig. 8. Adiabatic reactive equilibrium stage.](image)

• The summation equations for the mole fractions:

\[
\sum_{i=1}^C x_{ij} - 1 = 0
\]

(13)

\[
\sum_{i=1}^C y_{ij} - 1 = 0
\]

(14)
The heat (enthalpy) balance:

\[
(1-t) \left( L_{j-1} - L_j + LF_j - SL_j + V_{j-1} - V_j + VF_j - SV_j + \sum_i \sum_j \alpha_{ij} x_{ij} \right) + \\
\left[ L_{j-1} h_{j-1} - \left( L_j + SL_j \right) h_j + LF_j h_{Fj} + V_{j-1} H_{j-1} - \left( V_j + SV_j \right) H_j + VF_j H_{Fj} \right] = 0
\]

(15)

where \( h(T, P, X) \) is the liquid molar enthalpy and \( H(T, P, Y) \) is the vapor molar enthalpy based on the elemental reference state. When \( t \) approaches zero, the enthalpy balance equation (15) approaches the total mass balance equation (10). The way, in which the enthalpy balance is embedded in the homotopy leads to a faster and more robust solution algorithm than that obtained by introducing a proper homotopy, where the constant molar overflow solution is mixed with the enthalpy balance.

The equilibrium relations for the liquid phase chemical reactions (\( r=1: nr \)):

\[
K_r^R - \prod \left( v_{ij} x_{ij} \right)^{\alpha_{ij}} = 0
\]

(16)

which can be given with the homotopy parameter \( t \) as:

\[
tK_r^R + (1-t) \prod \left( v_{ij} x_{ij}^{t} \right)^{\alpha_{ij}} - \prod \left( v_{ij} x_{ij} \right)^{\alpha_{ij}} = 0
\]

(17)

where

\[
x_{ij}^{t} = \frac{x_{ij} L_{j-1} + xf_{ij} LF_j}{L_{j-1} + LF_j}
\]

(18)

When the stage is nonreactive, the chemical equilibrium relations are replaced by the trivial equations \( \varepsilon_j = 0 \).

When \( t=0 \), equation (17) introduces a ‘false equilibrium constant’ to analogously remove the equilibrium relations - in this case the reaction equilibrium relations - from the equation set. Thus, the liquid mole fractions in the exit streams similarly result in those obtained by liquid material balances from the input liquid flows to the stage.

The following specifications are always made: column pressure, number of equilibrium stages, feed specifications (compositions, locations, total flow rates, temperatures and pressures) and specifications for sidestreams (locations and total flow rates).

The partial/total condenser and the reboiler can be assumed to be reactive. The energy balance equations associated with them are replaced by the column specification equations. These two specifications have to be chosen in such a way that there is a solution for the equations along the homotopy path. The following list fulfills the requirements: distillate rate, bottom rate, reflux ratio, reboil ratio, reflux liquid rate and
boilup vapor rate. These are the typical design mode specifications, which lead to direct control of the internal recycle of a column, and thus to the achievable state distributions.

The solution of appropriate linear equations, where no separation takes place on the stages and where the constant molar overflow is valid, can be given as an initial guess with a small value of $t$ for solving the nonlinear equations. Thus, $2C+2+nR$ variables per stage, $y_j, x_j, V_j, L_j$, and the extents of reactions $\epsilon_j$ are solved from the above equations by following the homotopy path from $t>0$ to $t=1$. The equilibrium compositions $y_j'$, and the stage temperatures $T_j$ are solved as functions of $x_{i,j}$ and $P$ in a nested iteration loop.

Alternatively, equation (16) can be used directly without using (17) and (18) in the homotopy model. In that case, the initial guess is solved iteratively from a reduced equation set, using, for example, a traditional Newton-Raphson method.

4.5 Step size control

The above problem dependent homotopy for homogeneous ordinary and reactive distillation together with the explained specifications and the starting guesses make it possible to inspect the homotopy path from a physical point of view. It can be concluded that the model for a whole column has a physically interpreted solution along the homotopy path from $t>0$ to $t=1$, i.e. a continuous solution curve exists in the domain of interest. Furthermore, turning points are avoided along the homotopy curve within $0<t\leq 1$. Mixing of the feed streams with column internal flows is done in the initial guess, and there are no other sources in the model equations that could cause discontinuity in the variables when $t$ is continually increased towards unity (see Fig. 9.). Thus, arclength or dynamic reparametrization methods are not necessary for solving the problem.

![Homotopy paths exhibiting a 'turning point' and 'stiffness'.](image-url)
Even though turning points are avoided, the path may still be ‘stiff’. By ‘stiffness’ it is meant in this context that a small step in $t$ leads to a dramatic change in some of the variables (see Fig. 9.). This makes it impractical to use the classical homotopy continuation method, where the earlier, corrected solution is given as an initial guess in the next step of $t$.

Fortunately, a fast and reliable method can be constructed through a simple predictor-corrector procedure: A sufficiently small positive value of $t$ is assigned, so that the first corrector step is successful. The tangent vector $dX/dt$ to the curve is calculated:

$$\mathcal{H}_X \frac{dX}{dt} = \frac{d\mathcal{H}}{dt}$$

(19)

where $\mathcal{H}_X$ is the Jacobian of $\mathcal{H}$

The vector $dX/dt$ serves as a linear estimator for the solution curve as a function of $t$. The discrepancies of the (well-scaled) equations are calculated with selected values of $t$ and with respective estimations of the vector of variables $X$. Then the step in $t$ is predicted by a polynomial interpolation based on the sum of squares of the discrepancies and the prespecified tolerance for that. At each predicted value of $t$, the corrector step to the homotopy curve is accomplished by a tailored Newton-based method. Naturally, the initial guess is obtained from the tangent estimation. If an estimated value for a variable is not in the domain, a value near the boundary of the domain is selected. If the correction step is successful, a new step is estimated. The same procedure is repeated until $t=1$ is encountered.

The corrector step may naturally fail with long steps. On the other hand, too small steps make the method unnecessarily slow. Thus, heuristics for increasing or decreasing step size has been included by adjusting the tolerance of the error for the step size estimation based on the difficulty of the corrector step.

### 4.6 Implementation and performance

The homotopy continuation method has been implemented in the MATLAB programming language. The iterative parts are speeded up by generating the MATLAB MEX files (C-binary files). The derivatives of Jacobian, concerning the physical and chemical properties, are currently calculated numerically. Thus, no restrictions are made for the determination of enthalpies or phase and chemical equilibrium ratios. The simple extension of the Thomas algorithm is applied to the block tridiagonal Jacobian matrix.

The method has been tested extensively for homogeneous multicomponent distillation. The solution of the MESH equations is found without any need for manual iteration, and no initial guess needs to be given by the user. All the performed test cases for reactive distillation also show global convergence characteristics, i.e. the probability of success approaches unity.
For highly nonideal distillation problems with two to four components and 50 to 100 equilibrium stages, the method usually takes about three to eight continuation steps with less than forty Newton steps altogether. For reactive distillation problems, extra steps and iterations are needed. Even though the code is not optimized concerning the speed, the execution time is more likely to be seconds than minutes with the current PC technology.

There are many possibilities to further speed up the process. For instance, analytical derivatives could possibly be supplied for the Jacobian, temperature could be included as a variable in the MESH equations (if the robustness of the method can be retained), and the homotopy could be transformed into ordinary differential equations (IVP).

Direct use of equation (16) in reactive distillation seems to result in a shorter execution time, even though the initial guess must be solved iteratively. In the examples studied, it has often led to less ‘stiff’ problems and thus to easier corrector steps and, as a consequence, longer successful steps in $t$. At any rate, the solution is found with both initializations.

The equilibrium chemical reactions are assumed to take place in the liquid phase, but the method is also able to accommodate vapor phase equilibrium reactions or to include reaction kinetics through holdup or residence time. Another possibility to approach cases where the reaction is not fast enough to reach near equilibrium is to use the homotopy parameter $t$ in equation (17) to indicate the extent of reaction, i.e. to introduce an equilibrium constant which is a linear combination with the ‘false equilibrium constant’ and the actual constant. Thus, at each stage, the reaction advances into the right direction to the extent defined by the value of the parameter.
5 Minimum internal recycle in homogeneous distillation

“In spite of numerous valuable attempts, a universal procedure, which supplies the minimum energy requirement for nonideal, multicomponent distillation at the touch of a button, has not yet been found.” J. Koehler et al. (1995)

5.1 Problem definition

The minimum energy requirement of a distillation column is an increasingly important piece of information due to the growing interest in saving energy. As the column dimensions (diameter, heat transfer area) are dependent on the energy input, the minimum energy requirement may also indicate investment costs. A search of the minimum internal flows in a column may thus serve as an early assessment of the structural alternatives at the process synthesis step of conceptual design. While modern process control methods and high-efficiency packings and trays make it possible to operate closer to the minimum energy limit, the prediction of the limit itself, especially in multicomponent nonideal distillation, has persisted as a fundamental problem not yet completely solved.

An extensive review of the current minimum energy calculations is given by Koehler et al. (1995). Among the papers published after the review, the work of Bausa et al. (1996) is the only remarkable step forward in developing approximative calculation methods for nonideal multicomponent mixtures. The method of Bausa et al. (1996) is based on the material and energy balance equations for both column sections separately. The total energy balance of the column is used for the determination of a feasible reboiler duty, when first the condenser duty and the product flow rate have been fixed. All the pinch points are calculated for both sections from prespecified product compositions by using a continuation method and bifurcation analysis. Then the pinch points in each section and the corresponding product compositions are linearly connected, leading to two simplexes. The smallest value of reflux that connects the simplexes is the minimum one. As the authors have pointed out, their linear approximation of the column profiles between the pinch points is not exact. For highly
nonideal mixtures or when a higher accuracy is needed, some other criteria should be used. However, when a proper connection between the profiles was made (even a linear approximation), the authors were capable of finding out whether the separation is feasible at the minimum reflux.

Simple distillation columns with single feed, single distillate and single bottom product are most often used to separate two chemical species in a multicomponent feed. While it is generally accepted that minimum flows are specified with the key components (e.g. King, 1980, Henley & Seader 1981, Nandakumar & Andres 1981), there is an implicit suggestion in the current literature that full product specifications could be made in the calculation of minimum flows. The reason is obvious. All the approximation methods assume that physically correct column products can be given as an input specification. The same assumption is also made in many of the rigorous methods. Generally, this is only possible in binary distillation; feasible product compositions are not known for multicomponent nonideal distillation - particularly in azeotropic systems. Furthermore, the product composition areas of ternary distillation, in which infinitely many stages are specified for the stripping and rectifying sections, are not the same as ‘the feasible separation regions’ (given in Fidkowski et al. 1993 and in Wahnschafft et al. 1992). The desire to specify the product compositions has led to several consequences:

- The method of Koehler et al. (1991) uses the concept of reversible distillation column to calculate the pinch point curves for the column products. The pinch point pair which controls at the minimum reflux is chosen from the curves according to an angle criterion. Because the column sections are not properly connected, the criterion is not sufficient for multicomponent mixtures to guarantee that the column profiles would ever meet, even though the total energy and mass balance are used for fixing the product compositions. Thus, the method of Koehler is generally only applicable to binary distillation.
- The composition profiles of the stripping and rectifying section may meet each other with a minimum value for reflux before the pinches occur in the column sections. This is a clear indication that unfeasible product compositions have been specified for the minimum energy calculations. A misleading example is given in Koehler et al. (1995, Fig. 18.).
- A certain number of stages in one section (or even both) is needed for attaining the prespecified product compositions. A small change in product compositions, which would possibly fulfill the process constraints, might give a notably smaller energy input. The situation is complicated further when a large finite number of stages is assumed (either explicitly or implicitly) and product compositions are needed as an input.
- A lower minimum energy throughput may lead to a better sharpness of separation.

To sum up, the entire peculiar behavior of multicomponent ‘minimum reflux’ columns is a direct consequence of the unfeasible specifications for minimum energy calculations. If, theoretically, a certain separation is possible in a binary simple distillation column having a finite number of equilibrium stages, it is also possible in a
column having an infinite number of equilibrium stages in both sections. This is not true of multicomponent distillation, and thus the minimum energy calculation methods, which require full product specifications, are, in principle, iterative. Methods which do not connect column sections are not generally applicable to nonideal multicomponent distillation.

The following definition has been accepted in this work: Minimum reflux and reboil ratios (i.e. minimum energy requirement) are based on the specifications for the degree of separation between two key components. The minimum reflux and reboil ratios are finite, and product withdrawals are permitted. The ratios are theoretical and purely thermodynamically fixed values. They are the minimum amounts of reflux and reboil required to achieve given product specifications (key components) in a column with an infinite number of equilibrium stages.

A feasible exact method for nonideal mixtures, which would be applicable to all splits and all possible column profiles in minimum energy conditions, has been lacking. Some tailored calculation algorithms which use the pinch condition have been proposed, as reviewed in Koehler et al. (1995). Because reliable exact methods are still lacking, conventional simulation programs are used extensively in the industrial practice for the determination of the minimum energy requirement. This is often a time-consuming process with many manual iterations.

In paper VI, a new exact method based on rigorous column simulation with a large number of equilibrium stages was developed to solve the minimum energy requirement of nonideal multicomponent distillations. The problem dependent homotopy continuation method of ordinary distillation presented above operates independently in the core of the computer program, and there is no need for manual iteration.

The structure of the single-feed, two-product distillation column (simple distillation column) to be studied is depicted in Fig. 10. In addition to the process boundary (column wall) and the material and energy interactions with the exterior, the gravity-driven vapor and liquid flows of the interior material are shown with the internal recycle separated from the net flows up and down.

Internal recycle is the designer’s central degree of freedom. It can be varied over a wide range independent of the net flows. In the internal recycle loop the total molar flow up is always equal to the total molar flow down at any given height. In constant molar overflow (CMO) distillation the recirculating total molar flow is invariant with height in the whole column. Reflux ratio and reboil ratio are the two variables by which the net total molar flows up and down are related to the internal recycle. It is by the internal recycle that a composition distribution in the vertical direction is generated, enabling the desired separation.

The aim of the work reported in paper VI was to simulate the column in the structure shown in Fig. 10 by applying the robust method developed for predicting the vertical composition profiles in the two phases, starting from a given feed specification and minimizing the internal recycle at a large number of equilibrium stages.

As the method serves to predict the achievable vertical state distributions of a column, rather than only the minimum energy consumption, feasible product compositions are not needed as input data. Instead, the separation is specified directly by key components - as it should be.
5.2 Search strategy

The occurrence of distillation boundaries is characteristic of azeotropic mixtures. In ternary systems these boundaries are approximated by residue curves and distillation lines. Distillation boundaries divide the composition space into separate distillation regions. In each region pure components or azeotropes define the highest and lowest boiling compositions, which can be taken (in desired purity) as a bottom product or a distillate in a simple distillation column, respectively. The region where the distillation would take place is usually determined by the feed composition. Under special circumstances the distillation boundaries can be crossed. Thus, it is well known that the continuous distillation boundaries are not properly represented by the residue curves or distillation lines.

Consider ternary distillation of acetone, chloroform and benzene. The mixture has a binary maximum boiling azeotrope between acetone and chloroform, and thus a single distillation boundary is established. Assume a simple distillation column with 150 equilibrium stages and a partial condenser. Let the mole fractions of acetone and chloroform in the feed be 0.3 and let the feed enter, at the saturation temperature and column pressure (1atm), the 75th stage from the top.

Figure 11 shows several liquid mole fraction profiles of direct splits for the above case. For each specified value of reboil ratio \(1 < s < 19\), the reflux ratio \(r\) which produces the distillate in the purity of 99 mol-% of acetone was searched. The uppermost profile in which the saddle pinches approach the azeotrope was obtained with \(s = 19\) and \(r = 61.89\). When the saddle pinches merge at the azeotrope, the distillation line boundary is actually part of the profile. It is shown in the figure that this boundary (or residue curve boundary) is crossed with smaller values of \(s\) and \(r\). Increasing values
of $s$ enhance separation, until the continuous distillation boundary is reached. This limiting profile, which leads to the maximum reboil ratio (reflux ratio) in minimum recycle conditions, is between the fourth and fifth profiles from the bottom.

The different separations (1) towards the lightest compositions (as in Fig. 11.) and (2) towards the heaviest compositions and (3) the preferred separation establish the three different classes of separation in multicomponent distillation. The aim of a simple distillation column is primarily to separate two key components. If feasible amount of keys cannot be given, or a preferred separation along the transition line is not desired, it is always possible to select the locally heaviest or lightest component for one key (or, in the case of azeotrope, one component which is forming the azeotrope). If these components (compositions) are not known, the distillation line which goes through the feed point, can be generated. This line gives not only information about the stable (heaviest) and unstable (lightest) nodes of the region, but also about the minimum number of equilibrium stages for each section necessary for approaching the nodes from the feed point within a specified accuracy. For fixing the number of stages for the determination of the minimum internal recycle, a suitable multiplier is about four.

The other key can be more difficult to specify for azeotropic mixtures. The parametric study (see Fig. 11.) can be accomplished, if necessary, for tracking the continuous distillation boundary.

![Fig. 11. Several direct splits with varying reflux and reboil ratios ($x_{D,acetone}=0.99$).](image-url)
Another problem for the calculation of the minimum internal recycle is due to an input multiplicity. If the composition profiles are calculated for a column with a large enough number of stages in each section, every given pair of reflux and reboil ratios produces a certain separation, and the column has principally been described in the minimum recycle conditions. In other words, if the solution of the distillation equations $f(X)=0$ is unique in the domain, the reboil and reflux ratios are the minimum ones for the attained separation. Unfortunately, an ‘apparent input multiplicity’ is inherently present when the reflux ratio and the reboil ratio (or other similar variables which fix the column operation) are used as independent variables. An arbitrary selection of ratios may not lead to the minimum recycle for the attained separation within the numerical solving accuracy. This numerically ‘apparent input multiplicity’ is not a multiplicity in a strict mathematical sense. It can be viewed as a set of indistinguishable approximations for distinct solutions. Examples of apparent input multiplicities are given in paper VI.

As it has been pointed out by Skogestad (1997), the pinch adjacent to the feed stage will effectively stop composition changes to spread between the top and bottom part of the column, and will therefore lead to a decoupling of the two column ends. Despite the number of components present, small values of $r$ and $s$ will always lead to a double feed pinch (preferred separation) and to perfect decoupling when enough stages have been specified for the sections. In the area of a single feed pinch, one section ‘dominates’ the behavior of the simple distillation column (see paper VI). Frequently, the type of split exposes the dominant section. When the recycle ratio of that section ($r$ or $s$) has been specified, the other ratio can often be searched without having any influence on the product composition of the dominant section as long as the single feed pinch is present.

When the feed is specified and the feasible product compositions of the keys are fixed, an efficient search algorithm for minimum $r$ and $s$ determination can be presented as follows:

1. Assign a small value to the reflux ratio (or reboil ratio) to decouple the column sections and to exclude apparent input multiplicity. If possible, select the ratio of the non-dominant section.
2. Find the reboil ratio (reflux ratio) which yields the bottom product (distillate) in the desired purity of the key.
3. Find the reflux ratio (reboil ratio) which gives the distillate (bottom product) in the desired purity of the key.
4. If the purity of the bottom product (distillate) changes, return to 2.

If a single or double feed pinch actually occurs in the minimum recycle conditions, only one search for $r$ and $s$ is commonly needed to obtain the right amount of keys. If the dominant section is not known, one extra search for $s$ or $r$ is needed. When feed pinches are not present in the minimum recycle conditions, a few more cycles (2 to 4) are necessary.
5.3 Performance

The problem of minimum internal recycle has been decomposed into two one-dimensional search problems. In the current implementation the golden section search method has been applied. At each search point, the solving of MESH equations is first attempted by a tailored Newton-based method. If the solution is not found, the homotopy continuation method is employed.

The method has been successfully applied to highly nonideal ternary and quaternary mixtures. In table 1 the minimum internal recycle conditions are given for various acetone-chloroform-benzene distillations and in table 2 for acetone-chloroform-benzene-toluene distillations. The residue curve maps for the mixtures contain inflection points, tangent pinches and curved distillation boundaries. More examples are given in paper VI.

In Fig. 12. the liquid mole fraction profiles for the examples of table 1 are depicted. Note that the profiles are highly curved, and the approximation methods could thus be inaccurate for these examples. The three upper profiles are within the composition region where the residue curves are inflectional.

<table>
<thead>
<tr>
<th>Feed composition</th>
<th>Number of stages</th>
<th>Keys: distillate bottom</th>
<th>Product compositions: distillate bottom</th>
<th>$r_{\text{min}}$</th>
<th>$x_{\text{min}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0.1200/0.0500/0.8300 (l)</td>
<td>100</td>
<td>$x_D,1 = 0.999$</td>
<td>$0.9999/0.0002/0.0008$</td>
<td>4.93</td>
<td>0.79</td>
</tr>
<tr>
<td>2 0.1200/0.0500/0.8300 (l)</td>
<td>100</td>
<td>$x_D,1 = 0.700$</td>
<td>$0.7001/0.2426/0.0573$</td>
<td>8.03</td>
<td>1.84</td>
</tr>
<tr>
<td>3 0.3000/0.3000/0.4000 (l)</td>
<td>120</td>
<td>$x_B,1 = 0.990$</td>
<td>$0.0000/0.0102/0.9898$</td>
<td>5.64</td>
<td>1.89</td>
</tr>
<tr>
<td>4 0.1500/0.7000/0.1500 (l)</td>
<td>100</td>
<td>$x_B,3 = 0.010$</td>
<td>$0.1801/0.8099/0.0100$</td>
<td>2.04</td>
<td>13.66</td>
</tr>
<tr>
<td>5 0.0500/0.4500/0.5000 (l)</td>
<td>100</td>
<td>$x_B,3 = 0.010$</td>
<td>$0.0501/0.9499/0.0000$</td>
<td>14.31</td>
<td>2.98</td>
</tr>
<tr>
<td>6 0.0500/0.4500/0.5000 (l)</td>
<td>100</td>
<td>$x_B,3 = 0.350$</td>
<td>$0.0500/0.3501/0.5999$</td>
<td>14.31</td>
<td>2.98</td>
</tr>
</tbody>
</table>

Pressure: 101.3 kPa; boiling liquid feed; partial condenser

The minimum values are naturally for the specified number of stages. A sufficient number of stages can usually be given based on the distillation lines. If a high accuracy is needed and large tangent pinches are present, a too few stages may be applied. At any rate, a large number of stages - well above that needed in process design - can be specified to approach the ratios of infinitely high columns. Numerical error and thermodynamic inaccuracies will, at any rate, impair the results in nonideal mixtures.
Fig. 12. Liquid mole fraction profiles for several acetone/chloroform/benzene distillations with minimum internal recycle.

Table 2. Minimum r and s for various acetone/chloroform/benzene/toluene distillations.

<table>
<thead>
<tr>
<th>Feed composition</th>
<th>Keys: distillate bottom</th>
<th>Product compositions: distillate bottom</th>
<th>r_{min}</th>
<th>s_{min}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.500/0.200/0.150/0.150</td>
<td>100 x_{D,1} = 0.990</td>
<td>0.9901/0.0000/0.0099/0.0000</td>
<td>2.25</td>
</tr>
<tr>
<td>2</td>
<td>0.500/0.200/0.150/0.150</td>
<td>100 x_{D,1} = 0.010</td>
<td>0.9990/0.0000/0.0010/0.0000</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>0.500/0.200/0.150/0.150</td>
<td>100 x_{D,1} = 0.999</td>
<td>0.9399/0.0000/0.0099/0.0000</td>
<td>2.63</td>
</tr>
<tr>
<td>4</td>
<td>0.300/0.300/0.200/0.200</td>
<td>110 x_{D,4} = 0.010</td>
<td>0.0970/0.3333/0.1390/0.0000</td>
<td>0.39</td>
</tr>
<tr>
<td>5</td>
<td>0.300/0.300/0.200/0.200</td>
<td>110 x_{D,4} = 0.010</td>
<td>0.3713/0.3713/0.2437/0.0100</td>
<td>0.40</td>
</tr>
<tr>
<td>6</td>
<td>0.300/0.300/0.200/0.200</td>
<td>110 x_{D,4} = 0.010</td>
<td>0.5804/0.4096/0.0101/0.0000</td>
<td>3.20</td>
</tr>
<tr>
<td>7</td>
<td>0.100/0.700/0.100/0.100</td>
<td>90 x_{D,2} = 0.990</td>
<td>0.0102/0.9898/0.0000/0.0000</td>
<td>3.12</td>
</tr>
<tr>
<td>8</td>
<td>0.100/0.700/0.100/0.100</td>
<td>90 x_{D,2} = 0.010</td>
<td>0.1465/0.5500/0.0180/0.0158</td>
<td>1.64</td>
</tr>
<tr>
<td>9</td>
<td>0.100/0.700/0.100/0.100</td>
<td>90 x_{D,2} = 0.001</td>
<td>0.1117/0.7816/0.1088/0.0000</td>
<td>0.33</td>
</tr>
<tr>
<td>10</td>
<td>0.400/0.100/0.100/0.400</td>
<td>100 x_{D,4} = 0.999</td>
<td>0.9990/0.0000/0.0001/0.0000</td>
<td>2.12</td>
</tr>
</tbody>
</table>

Pressure: 101.3 kPa; boiling liquid feed; total condenser
The method has yielded the minimum reflux and reboil ratios for all the examples without any manual iteration. Because feasible product compositions are not needed, the method proposed in this paper is applicable to nonideal multicomponent distillation.

The code has not been optimized for the speed, and further work is needed. For instance, analytical derivatives could be supplied for the Jacobian, the homotopy could be transformed into ordinary differential equations (IVP), and a more efficient search algorithm could be used instead of the golden section method. Even though the MESH equations are solved 40 - 60 times during the minimum recycle calculation, 233 MHz Pentium II machines reduce the execution time - with the current implementation - down to less than 10 minutes for most of the examples in tables 1 and 2.

In all the examples, a simple distillation column (one-feed two-product) was assumed. Because the method is iterative and based on rigorous solving of the MESH equations it should be extendible to multiple feeds and sidestream columns.
6 Conclusions

Even though the first paradigm of the chemical engineering discipline, i.e. thinking in terms of unit operations, yielded a unifying concept for systematizing the process design activities, conceptual design can still be said to be non-methodological - partly because the iterative combination of the existing elements has not been an adequate approach. Over the years, novel and competitive process solutions have been created using other approaches than searching from the possible conventional process arrangements. Today, more than ever, environmental and safety regulations, the growing demands for product quality as well as the increasingly competitive markets necessitate continuous improvement of the existing chemical processes and development of new ones. Creative and innovative aspects of design are becoming an essential part of the methodology of process R&D.

Creativity in process design is associated with certain individuals, and the view that process design is an art, that cannot be systematized due to its creative aspects is currently prevalent. In this thesis, it is claimed that the activity of conceptual design can be modeled (as a methodology) and creativity can be simultaneously supported.

Conceptual design involves human input and is thus fundamentally different from the main interest in the discipline, i.e. state modeling. Despite the importance of state model building and solving in process design, conceptual design cannot be equated to it. The purpose, the structure, or the performance of a chemical process cannot be predicted from causal laws, as can the behavior of a process. The human input makes design both creative and unpredictable, and a description of a detailed, predefined task sequence supported by heuristics would not be accepted as the model of conceptual process design.

Unit operations alone are not a sufficient set of building blocks for creative process design. By accepting that the conceptual design of a chemical process consists of deciding upon the control of phenomena to fulfill a purpose, the structural building blocks of the process follow from that very definition, i.e. the things to be controlled are phenomenon and material, and the means of control are boundary and interaction. When an object-oriented model of process is adopted based on the ontological commitments inherent in the methodology implying that an attribute value can be an object, it follows that objects can be repeatedly subdivided into subobjects. This makes the search base endless and allows any level of abstraction in two mutually orthogonal
structural coordinates: topology and unit structure. Thus, (1) the artificial constraints in process description, which may limit the search space, are removed, (2) the building blocks can be chosen from any level of abstraction instead of the single level represented by unit operation, and (3) the explication of the process raises three further central concepts: control, phenomenon and purpose.

The performance driven strategy of process design aims to guarantee reasonable consumption of resources by suggesting that the design decisions are made in an order of relevance with respect to the process performance measured by various criteria, such as controllability, profitability and safety. The strategy itself does not indicate how to apply this principle and guidance is needed for how to find out the most relevant feature of the target, the next most relevant feature, etc. This practical guide is the principle of phenomenon driven ordering. The designer needs to decide on how detailed the structural description of the phenomenon should be and to name the next relevant feature at the respective level of process abstraction based on the knowledge about the rate and extent of the phenomenon. The most relevant structural process features are detailed first. When phenomenon driven ordering is applied, the subgoals evolve dynamically.

The behavior of the process at each level of abstraction is determined by the behavior of each node (subprocess) and by the links resulting from the structural arrangements of the nodes. The state of a single node is obtained by aggregating the states of its boundary, interior, interaction and exterior by applying material and energy balances. The state of the interior is an aggregate of the states of the interior phenomenon and material via phenomenal laws, such as rate and equilibrium relations. Thus, in principle, an object-oriented process model, such as above, makes it possible to develop process state models at different levels of detail based on the structural specifications of the process model. Work on such an object-oriented state modeling tool is under way (Marquardt 1994). At any rate, it appears that the development of state models will continue to be limited to a small group of experts - at least in the near future.

During the course of the state modeling on reactive distillation done in this work, it became obvious that block oriented modeling gives some benefits even though the flexibility of equation oriented modeling is lost. When a block model is made, declarative and procedural knowledge can be effectively exploited and lead to more robust solution algorithms compared to a situation where the different knowledge types are kept apart. In spite of the many drawbacks, block oriented state modeling has proven to be a powerful and easily accessible tool for many engineers.

In this thesis, a robust method was developed for solving state models of homogeneous conventional and reactive distillation. The modified MESH equations for reactive distillation were formulated as a problem-dependent homotopy in such a way that the homotopy path to a solution was continuous in the domain of interest, and that the path did not have turning points. This allowed the development of a fast (in view of the homotopy methods) and robust solving method. ‘Robust’ here means that the solution is found without any need for manual iteration and any initial guess given by the user.

The purpose of the method is to credibly approximate the state distributions which can be attained in ordinary and reactive distillation columns. Because the method serves
early design purposes, it was considered important that the user is freed from the model solving procedure and the traditional MESH equations could be exploited in place of the shortcut design methods. This is because (1) shortcut design methods for reactive distillation are lacking, and (2) nonidealities are usually encountered in real problems.

The homotopy continuation method for solving the MESH equations was in a key position when a new rigorous method was developed for the calculation of a minimum internal recycle of nonideal homogeneous distillations. The homotopy method provides the necessary robustness when the implemented local method causes convergence problems. In this work, the calculation of a minimum internal recycle relies on simulation with a large number of equilibrium stages to mimic a column with an infinite number of stages. Only a feasible amount of key(s) are needed. For all examples, the developed method has indicated the minimum reflux and reboil ratios with the ‘touch of a button’.

The process synthesis utilizes abductive logic while the process analysis is deductive by nature. This is illustrated (Fig. 4.) by the formation of a feedback from the process evaluation activity to the process synthesis activity, i.e. alternating steps of process synthesis, analysis and evaluation are needed for a decision on process structure. The global algorithms may free the human from interfering with the state model solving, thus making it possible to automate the full synthesis, analysis and evaluation loop in certain ‘simple’ design tasks. In that case, the computer could suggest a solution to the designer by ‘deciding’ upon the structure of a process. If the solving procedure is fast enough, the result would seem to approach deductive logic, i.e. as the structure of a process could be deduced from the input specifications. Certain well defined MINLP problems or distillation sequencing problems, when the mixtures are highly nonideal, could be examples with the aid of continually more efficient computers.
References


