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Process Intensification

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2.1

Introduction

Since its emergence in the early 1980s, process intensification (PI) has received significant attention from the chemical and process engineering research community. PI promises novel, more efficient technologies with the potential to revolutionize the process industries. The term process intensification is associated mainly with more efficient and compact processing equipment that can potentially replace large and inefficient units commonly used in chemical processing but also includes methodologies, such as process synthesis methods, that enable the systematic development of efficient processing units. To date, numerous technologies have emerged from PI research activities and a number of commercial-scale applications have successfully been implemented. In a recent survey of industrial and academic experts, PI has recently been highlighted as one of the key enabling technologies required for the sustainable development of the chemical industry (Tsoka et al. 2004).

One of the earliest and most prominent applications linked to process intensification has been the redesign of the Eastman Chemicals methyl acetate process (Siirola 1995). The original process was highly complex and consisted of more than twenty pieces of equipment. Through integration of reaction and separation processing tasks into multifunctional reaction/reactive separation equipment it was possible to devise an intensified process consisting of only three pieces of equipment. Since the success of the Eastman process, numerous other PI technologies have been developed and applied. Prominent examples (Stankiewicz and Drinkenburg 2004) include efficient reaction equipment such as spinning disk reactors and monolithic reactors, equipment for nonreactive operations such as compact heat exchangers, multifunctional reactor concepts such as reactive separations, hybrid separations such as membrane distillation, alternative energy sources such as ultrasound, and many other technologies.

The numerous technological breakthroughs have led to comprehensive PI dissemination efforts for academic research as well as commercial applications including

international conferences, symposia, and networks. Most recently, a textbook by leading academic and industrial PI scientists and engineers has been published to provide a good overview over the technology developments to date (Stankiewicz and Moulijn 2004). PI developments have their origins in commodity chemicals due to the strength of the industry sector in the 1980s as well as the large economic impact of even small efficiency gains. As a result of the evolution of the chemical industries, PI has found applications in other sectors including fine chemicals and bioprocessing. This has resulted in a new definition of PI, which is now widely understood as the development of novel equipment, processing techniques, and process development methods for chemical and biochemical systems (Stankiewicz and Drinkenburg 2004).

Process intensification plays an important role in the chemical industry's attempt to develop into a sustainable industry that is both economically and ecologically viable. The following benefits associated with process intensification are important factors for sustainable development (Siirola 1995):

- The development of more profitable processes, that are cheaper to run, require less energy, and produce less waste and by-products. Process intensification is linked to reduced costs for land, equipment, raw materials, utilities, and waste processing.
- The acceleration of the process development cycle. This is particularly important in industry sectors where time to market is a crucial factor, such as fine chemicals or pharmaceuticals.
- The development of greener and safer processes, which is closely linked with good company image. Such a positive image is crucial for enterprises in the chemical process industries in order to remain viable businesses.

Most of the reported developments have been realized on an ad hoc basis, drawing on design engineers' intuition and expertise. Only more recently, the fundamental principles underlying process intensification technologies have been called upon in the form of systematic design procedures. The development of reactive distillation processes, such as the Eastman process mentioned above, is a typical example of an area where initial success stories have resulted from intuition and systematic design methods have subsequently been developed that can guide the designer in the development of such a system (Ciric and Gu 1994; Cardoso, Salcedo, Foyo de Azevedo 2000; Hauan, Westerberg and Lien 2000; Hauan, Ciric and Westerberg 2000; Ismail, Pistikopoulos and Papalexandri 1999; Okasinski and Doherty 1998; Linke and Kokossis 2003a). Such methods are generally computer-aided design techniques that screen numerous novel and existing design options and assist the design engineer in the identification of promising process intensification routes. However, such methods are still emerging and very few tools are currently commercially available.

Computer-aided tools have great potential to accelerate process intensification technology development. They enable the systematic screening and scoping of large numbers of alternative processing options and can identify novel options of phenomena exploitation that may lead to higher efficiencies. Such tools provide the basis for systematic approaches to novelty in process intensification and have the potential to

identify processing options, which can easily be missed in design activities that rely on intuition and past experiences. The next section provides an overview over current process intensification technologies. In the remainder of this chapter we will present a number of recently developed systematic computer-aided process intensification methods.

2.2

Process Intensification Technologies

A large number of process intensification technologies have been developed. According to Stankiewicz and Drinkenburg (Stankiewicz and Drinkenburg 2004), the existing technologies can be broadly classified into process-intensifying equipment (hardware) and process-intensifying methods (software). PI applications often result from a combination of equipment and methods. For instance, the application of methods often leads to the development of novel equipment. In the same vane, novel apparatuses often make use of new processing methods.

The following sections will provide a brief overview of important process intensification methods and equipment and discuss industrial applications. A more detailed description of PI technologies can be found elsewhere (Stankiewicz and Moulijn 2004).

2.2.1

Process Intensification Equipment

Process intensifying equipment (hardware) can be broadly classified into equipment for reaction systems and equipment for nonreactive systems (Stankiewicz and Drinkenburg 2004). Examples of reaction equipment include spinning disk reactors, static mixer reactors, monolithic reactors, and microreactors. Static mixers, compact heat exchangers, rotating packed beds and centrifugal adsorbers are examples of equipment for nonreactive operations. Process intensifying equipment generally aims at improving crucial processing characteristics in terms of mixing, heat transfer, and mass transfer over those realizable in conventional equipment. Such equipment is generally smaller than their conventional counterparts, albeit offering improved processing performances. A number of PI equipment developments are illustrated below.

Spinning Disk Reactors

The fluid dynamics of multiphase contact are dominated by surface forces so that very small interfacial areas are developed. This results in a lack of countercurrent interfacial motion in conventional multiphase contacting equipment, which in turn causes a low intensity operation in terms of reaction, mass, and heat transfer. The processing characteristics can be significantly enhanced through the application of a high-acceleration field. In the spinning disc reactor (SDR) (Ramshaw 2004), such an

acceleration field is established within a rotor that receives and discharges the working fluid. In general, the spinning disk device achieves highly efficient gas-liquid contacting from which numerous applications benefit, such as evaporators, aerators/desorbers and reactors. The device is very compact and has been demonstrated to allow very good control over multiphase reactions, even in highly viscous systems.

Multifunctional Heat Exchangers

Multifunctional heat exchangers combine heat transfer phenomena with other phenomena such as reaction, separation, or mixing in a single piece of equipment. A combination of heat transfer with one or more of these phenomena allows one to achieve better process performances or control for many systems. A reactor heat exchanger is a typical example for such a multifunctional heat exchanger (Thonon and Tochon 2004). Integrating the reactor within the heat exchangers enables better heat management that can significantly improve process yields and selectivities as well as reduce process energy requirements.

Microreaction Technology

Microreaction technology (Ehrfeld 2004) achieves intense mixing and very high heat transfer rates by significantly decreasing the characteristic dimensions of a processing system to the scale of micrometers. The availability of high transfer rates for heat and mass in conjunction with very small material holdups allows good control over reaction systems, i.e., over reaction yields, selectivities and energy management. For instance, it is possible to operate highly exothermic reactions at isothermal conditions using microreactors. Apart from more intense processing, microreaction technology offers advantages in process control, because the starting and boundary conditions for reactors and unit operations can be adjusted precisely and are easily scaled-up using parallelization.

Structured Catalysts

Structured catalysts, such as monoliths, offer a number of advantages over nonstructured catalysts in terms of high rates, high selectivities, low energy consumption and easy scale-up (Moulijn, Kapteijn and Stankiewicz 2004). Monolithic catalysts are metallic or nonmetallic bodies that contain large numbers of channels of defined cross sectional shapes and sizes (Stankiewicz and Drinkenburg 2004). They cause very low pressure drops, offer high surface areas per reactor volume, allow the use of very small catalyst particles, such as zeolites, and exhibit very high catalytic activities due to short diffusion paths in the thin wash coat layer. The process-intensifying benefits from a structured reactor results mainly from the possibility to decouple reaction kinetics, transport phenomena and hydrodynamics so that each can be optimized independently in order to achieve very good reactor performances (Moulijn, Kapteijn and Stankiewicz 2004).

2.2.2

Process Intensification Methods

According to Stankiewicz and Drinkenburg (2004), process intensifying methods (software) include multifunctional reactors, hybrid separations, the use of alternative energy sources and other computer-aided methods. A number of multifunctional reactor concepts have been developed including reactive separations, heat integrated reactors and fuel cells. Hybrid separations generally combine two or more types of unit operations into a single system and include processes such as membrane distillation and membrane adsorption amongst others. Alternative energy sources are used in process intensification to allow a better exploitation of chemical and physical phenomena. Such methods include the application of centrifugal fields, ultrasound, microwaves and electric fields. Other process intensifying methods that do not fall into the above categories have been classed as “other methods” by Stankiewicz and Drinkenburg (2004). This class contains dynamic strategies for reactor operation, but also computer-aided design methods, such as process synthesis tools, that allow the systematic identification of promising design options that allow efficient processing. We explain a number of important process intensification methods below.

Reactive Separations

Reactive separations are classes of reactors that facilitate component separations in the reaction zones with the aim to improve reaction yields and selectivities or to facilitate difficult separations. Examples of reactive separation processes include reactive extraction where a solvent is used to transfer components in and out of the reaction zone, reactive distillation where vapor is used as the separating agent, and membrane reactors, where the permeability and selectivity of a membrane is exploited to selectively add and remove components from the reaction zone. The most prominent success of reactive separations is the Eastman methyl acetate reactive distillation process mentioned in the introduction.

Hybrid Separations

Hybrid separations are processing methods that exploit the synergies between different separation techniques in a single operation. Prominent examples of hybrid separations include extractive distillation, adsorptive distillation, membrane distillation, and membrane extraction. Hybrid separations are generally developed for systems where the performance of a unit operation is inefficient or problematic. For instance, distillation is an efficient process for the separation of close-boiling systems. The introduction of a suitable solvent into the column, i.e., extractive distillation, allows one to increase the driving forces in the column and thus improve the efficiency of the operation. The viability of a hybrid separation process depends strongly on the system under consideration. More information on the selection of hybrid separation processes can be found in Stankiewicz (2004).

Process Synthesis

Process synthesis refers to the systematic development of process flow sheets through “the automatic generation of design alternatives and the selection of the better ones based on incomplete information” (Westerberg 1989). Process synthesis methods support the engineer in finding novel, improved solutions to process design problems. The synthesis objectives aim at finding those processing options that enable the production of desired chemicals in the most cost effective and environmentally benign manner possible. A number of process synthesis tools have been developed that can systematically determine the most promising process designs for a number of systems including reaction systems, reactive separations, hybrid separations, as well as water and energy management. Such methods will be described in detail later.

2.2.3

Process Intensification in Industrial Practice

There are a number of incentives for enterprises in the chemical industries to adopt process intensification technologies. Through the intensification of processes, step-by-step improvements can be realized that offer a strong possibility to fulfill current business requirements that are becoming more demanding in the current economic climate (Bakker 2004). A strong driver for the introduction of process intensification technologies is the need to remain competitive in expanding markets by achieving and maintaining the best low-cost position. Other strong drivers include the need to meet tightening legislative and environmental requirements. Process intensification technologies can positively respond to these drivers (Bakker 2004) as they offer numerous related advantages such as energy savings, reductions in space requirements, reductions in the number of required processing steps, reduced emissions and waste, and more flexible feedstock specifications.

Bakker (2004) describes the possibilities for introducing process intensifying technologies into an industrial process taking into account six largely sequential process development phases:

- *New ideas for a process.* The development of a chemical path leading to a desired product defines the core of the process. There are typically a number of possible pathways that can be followed and it is important to consider PI technologies in order to determine the most intensified process option. This phase has great potential for introducing process intensification options because conceptual process changes are relatively cheap. At the end of this development phase, the chemical pathway is identified and a number of process parameters, such as concentrations and temperatures, have been roughly specified.
- *Determining the process chemistry.* This phase is concerned with identifying the optimal design and conditions for the reaction system so as to identify the intrinsically optimal route that produces the least by-products and waste. In this phase, the process design is also decided and care needs to be taken to ensure that the overall

process design achieves optimal performance and can easily be implemented. Generally, the consideration of process changes in this phase is still relatively cheap.

- *Pilot plant studies.* This phase is typically concerned with optimizing performances on an equipment level in order to overcome heat and mass transfer limitations, for instance, by making use of process intensification equipment. The testing of PI options is still relatively cheap in this phase.
- *Plant design.* At this point, the process design is fixed and it is difficult to introduce major changes as this would require revisiting of the previous phases. It is important that the benefits of process intensification technologies have been identified before this phase.
- *Start-up.* At start-up, the process system is fully specified and there is no more room to introduce process intensification options.
- *Debottlenecking and trouble-shooting.* Once the process is operating, it is difficult to make significant changes as this would incur downtimes and loss of production. This is only viable if step changes in efficiencies can be gained from a process change. The application of process intensification technologies may offer such savings and their economic benefits should be identified in order to decide on high-impact retrofit projects.

Clearly, the quick evaluation of various processing scenarios is very important in order to identify the most intensified process for a given product. Without systematic methods, such a screening is likely to be incomplete and promising process options are likely to be missed. Computer-aided methods offer great potential to realize quick and systematic process screening so as to minimize the risk of choosing underperforming processing options.

2.3

Computer-Aided Methods for Process Intensification

The ability to process large amounts of data in modern computers has opened up the possibility of developing practical and user-friendly software tools to assist process engineers and process designers in their decision-making tasks. In the past, the lack of powerful computers and other data processing tools resulted in design tools that would heavily draw on past design experiences. Experience from previously successful designs, encapsulated in heuristics, were the basis for new process developments. However, the application of heuristics very often created contradictions and confusion and good, novel design options were often missed. With today's vast computing power, it is possible to do away with heuristic rules and develop systematic methods that are not limited to the reproduction of past designs. For a widespread use of such computer-aided process intensification methods to be reached, the research community needs to deliver design methodologies that can be translated into usable software. In this section, we will describe a number of available methodologies and models that could become part of such a software toolbox.

Systematic computer-aided process intensification methods are required to generate a set of feasible process design alternatives and to select the most efficient configurations from the set. Ideally, such decision support tools should allow a systematic determination of the most promising process designs, which closely approach the performance limits of the system and meet the business constraints, out of the set of all feasible alternative structural and operational process design options.

Due to the complexity of the overall problem, applications of systematic decision-making technologies have addressed closely defined design subproblems, such as reaction, heat integration, and separation systems. These various subproblems exhibit a variety of challenging features. For instance, in reactor optimization these arise mainly from the highly complex chemical and physical models that need to be processed. In energy systems such as heat exchanger networks, on the other hand, the challenge is of combinatorial nature as vast numbers of different feasible design options exist. Separation system design presents examples of intermediate complexity in terms of model complexities. Despite the challenges in solving the individual design subproblems, the decomposition of the overall design problem into such subproblems makes numerous limiting assumptions that present opportunities for process choices.

The conventional approach to process design has similarities with a bow tie model: one starts broad and collects all available process information. A structure is used, e.g., a tree diagram, to create a format for the required information. In this stage, all relevant factors that are anticipated to have an influence on the process are collected. Boundaries of the process are generally set early to reduce rework later on. Clearly, such an approach limits the degree of design novelty that can be achieved. It must be recognized that the system boundary is mostly an arbitrary construct defined by the interest and the level of ability and/or authority of the participating actors. From the above discussion, it is clear that process alternatives are commonly generated based on intuition and case-based reasoning. This provides a strong chance that promising design candidates are not arrived at and that novelty is not automatically accounted for in the design process. This risk of selecting underperforming designs can be reduced through systematic approaches that allow one to capture all possible design alternatives in a process representation and screen for the design that delivers the best possible performance for the specified performance measure. The following sections describe such methodologies for reaction system design, integrated reaction-separation systems, separation systems, solvent-process systems, and integrated water and wastewater systems.

2.3.1

Reaction Systems

The reactor is the part of the process where value is added by converting raw materials into valuable products. The intensification of this unit is crucial for profitability. Reactor design is particularly difficult since reaction, heat, and mass transfer phenomena need to be exploited simultaneously. Reaction and mass transfer models

tend to be highly complex and difficult to process numerically. There are a number of decisions that have to be made in reactor design such as the selection of appropriate mixing and contacting patterns, the choice of optimal reaction volumes, decisions on temperature policies, and the identification of the best feeding, recycling and bypassing strategies. In order to identify the reactor design options that achieve the best possible performance for a given system, this information needs to be analyzed simultaneously as one decision tends to impact the others. Such an activity is generally beyond the capabilities of a design engineer without the assistance of systematic design methods. As a result, the designer commonly employs textbook knowledge, heuristics, empiricism, past experience and qualitative reasoning on the basis of analogies with similar systems and case studies, which tend to be insufficient to guide the development of high-performance reactor designs for systems of industrial complexity. This design practice results in a lack of innovation, quality and efficiency in many industrial designs.

The complexities of the reactor design task make the development of systematic computer-aided design methods a challenging task. From a practical viewpoint, such methods need to be applicable to general reaction systems and capable of supporting decision-making to enable the designer to quickly identify high-performance reactor designs. Over the past two decades, a number of such methods have evolved that can provide performance targets for the reaction system under consideration as well as guide design suggestions in terms of the best mixing, feeding, recycling, and operational policies at a conceptual level. In this section, we describe recent developments in reactor network synthesis that provide systematic decision support for various reactor design aspects such that the system's performance is maximized with respect to the design objectives employed. Initial efforts in reactor network synthesis have focused on the development of systematic design methods for single-phase systems. More recent efforts have addressed multiphase systems. We will review the single-phase developments first, in order to give an overview over the different approaches followed.

Approaches to conceptual reactor design can be broadly divided into optimization-based and graphical methods. Optimization-based approaches make use of superstructure formulations. Reactor network superstructures include different possible structural design options in a single model, which is then searched in order to determine the optimal candidates. Achenie and Biegler (1986; 1988; 1990) were the first to propose the optimization of comprehensive reactor network superstructures combining options arising from combinations of axial dispersion models and recycle-PFR representations. The structures were searched using deterministic optimization techniques in the form of nonlinear programming (NLP) methods to identify the most promising design candidates embedded in the superstructures. Later, Kokossis and Floudas (1990; 1994) introduced the idea of a reactor network superstructure modeled on a mixed integer nonlinear programming (MINLP) formulation. They proposed superstructures to account for all possible interconnections amongst the generic structural units of ideal CSTRs and PFRs (represented by CSTR cascades) with the aim to screen for design options and estimate the limiting performance of the reaction system. Schweiger and Floudas (1999) later replaced the PFR represen-

tation by rigorous DSR models in order to avoid the inaccuracies introduced by the use of CSTR cascades. The above methods all made use of deterministic optimization approaches to identify locally optimal designs. Marcoulaki and Kokossis (1999) have recently presented the application of a global search strategy in the form of simulated annealing. Their approach allows to establish solid performance limits for the reaction system and to systematically develop designs that can achieve the targets. We will explain this approach in detail later.

In a parallel effort to the development of optimization-based approaches, Glasser, Hildebrandt and Crowe (1987) presented a graphical procedure, the attainable region (AR) method, which has its roots in the insightful methods originally proposed by Horn (1964). This method allows one to identify the reactor network with maximum performance in terms of yield, selectivity or conversion, which can be located on the boundary of the AR in the form of DSR and CSTR cascades with bypasses. A number of extensions that generalize the AR method have been published (Hildebrandt, Glasser and Crowe 1990; Hildebrandt and Glasser 1990; Glasser, Hildebrandt and Glasser 1992; Glasser, Hildebrandt and Godorr 1994; Glasser and Hildebrandt 1997; Feinberg and Hildebrandt 1997). Though very useful for single-phase systems in lower dimensions, in higher dimensions the developments face both graphical and implementation problems and often lead to complex designs with multiple DSR and CSTR units and complex feeding and bypassing strategies. In an attempt to exploit insights gained from the AR concept to enhance superstructure optimization, Biegler and coworkers established rules for an efficient formulation and optimal search of superstructures. Balakrishna and Biegler (1992a,b) and Lakshmanan and Biegler (1996, 1997) presented NLP and MINLP formulations of this approach as well as a number of applications.

From a practical viewpoint, a useful approach for reactor network synthesis should be able to identify the performance limits for the reaction system and to identify designs that can approach these limits. Targets can guide design evaluation in light of the ultimate performance possible for a given system and are also very useful to identify retrofit projects as they provide the incentives associated with such a project. Optimization-based methods can fulfill both of these requirements, provided confidence can be established in the optimization results. If local search strategies are deployed, there is no reason to be confident that the obtained solution can not be substantially improved. It is therefore important that global search strategies are adopted as in the method proposed by Marcoulaki and Kokossis (1999). Their application of stochastic optimization enables confidence in the optimization results, can afford particularly nonlinear reactor models, and is restricted neither by the dimensionality nor the size of the problem. Marcoulaki and Kokossis (1999) optimize the rich and inclusive superstructures formulated by Kokossis and Floudas (1990, 1994) to identify performance targets and to extract numerous design candidates that approach the targets. A reactor network superstructure containing three reactor units, each of which allows choices between CSTRs and PFRs with side feeding, is shown in Fig. 2.1. The superstructures generally feature complete connectivities between the reactor units, the feed streams and the reactor units, and the reactor units and the product. Structural restrictions that may result from practical consider-

ations can be introduced as constraints for the optimal search. The stochastic search of the superstructures using the simulated annealing algorithm has been observed to systematically converge to the globally optimal domain, i.e., the performance targets of the system, and to produce numerous design alternatives with performances close to these targets for the numerous systems studied (Marcoulaki and Kokossis 1999).

The stochastic optimization-based reactor synthesis approach has been extended to multiphase systems to enhance its industrial relevance. Multiphase reactors are most frequently used in chemical processes besides fixed-bed reactors. A multiphase reactor network synthesis method needs to handle additional degrees of freedom that arise from the presence of multiple fluid phases in the system. When formulated as a superstructure optimization problem, the problem poses additional challenges to capture a significantly larger number of possible network configurations and to handle models for mass transfer and hydrodynamic effects. Mehta and Kokossis (1997) have proposed a compact representation of design options for multiphase reactors in the form of generic multiphase reactor units comprised by compartments and shadow compartments. A reactor module contains a single reactor compartment in each phase, which contains a single reactor unit, and can exist as either a CSTR or a PFR with side feeding. Each reactor compartment features diffusional mass transfer links with its shadow compartments in the different phases of the reactor unit. By combining different mixing and contacting patterns in compartments of different phases, a single multiphase reactor unit can represent all the conventional industrial reactors such as bubble columns, cocurrent and counter-current beds, and agitated reactors. By combining a number of such multiphase reactor units and their mixing and contacting options, it is possible to derive novel reactor configurations that can improve or enhance the performance of a multiphase reaction process. When embedded into a superstructure, a model can be formulated that contains all possible novel and conventional multiphase reactor design options from which the optimal candidates can be extracted using optimization techniques. Mehta and Kokossis (1997) adopted the stochastic optimization scheme proposed for single-phase systems (Marcoulaki and Kokossis 1999). The resulting methodology enables the development of performance targets and design options for multiphase systems.

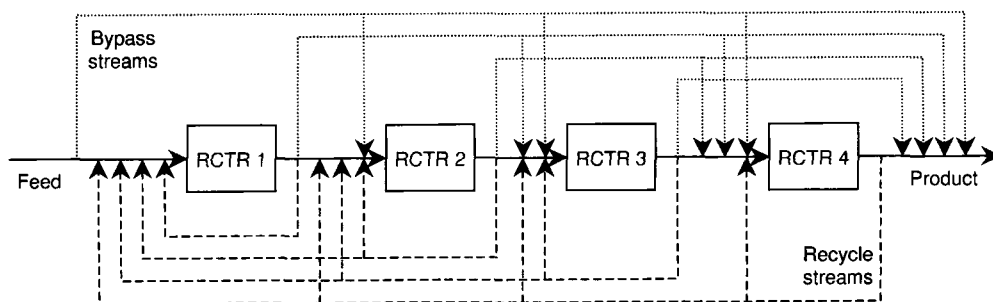


Figure 2.1 Single-phase reactor network superstructure representation.

Mehta and Kokosis (2000) have extended the approach to account for nonisothermal systems. Two approaches have been developed to handle temperature effects. Both approaches introduce elements associated with the manipulation of temperature changes. A conceptual approach (profile-based approach) imposes temperature profiles onto the reactor units, whereas a detailed approach (unit-based approach) introduces heaters and coolers into the reactor unit representations. The profile based approach allows one to determine the optimum temperature policies without considering the details of heat transfer mechanisms. As the profiles are imposed rather than simulated, the approach adds no further computational difficulties compared to the isothermal reactor network synthesis. The solutions obtained are easy to interpret and thus the approach helps in understanding of dominant tradeoffs in the problems. Results from the unit-based approach (UBS) provide the target that can be obtained from a network of adiabatic reactors with consideration of direct and indirect intermediate heat transfer options.

The multiphase reactor network synthesis approach has been successfully applied to a number of industrial problems (Mehta 1998). For illustration purposes, consider the chlorination of butanoic acid as an example of a gas-liquid system. The chlorination of butanoic acid (BA) to monochlorobutanoic acid (MBA) and dichlorobutanoic acid (DBA) involves two reactions in the liquid phase.



The reactions occur in the liquid phase and the gas phase contains chlorine feed and hydrogen chloride product. The modeling assumptions and problem data for this study are given in Mehta (1998).

The study aimed at identifying reactor designs that can achieve the highest possible yield of MBA. The best conventional reactor design was observed to achieve a maximum yield of 74.4% (mechanically agitated vessel). Reactor network optimization of a superstructure identified a maximum yield of 99.6%. A number of designs were obtained from the optimization of a superstructure of three generic multiphase reactor units that achieve performances close to the target value. Designs range from simple designs employing only one reactor unit to designs featuring three units. Two simple designs are illustrated in Fig. 2.2.

Despite their successes, current reactor network design methods still suffer from a number of shortcomings. As mentioned above, the attainable region is difficult to construct for problems containing a large number of reactions and components, local deterministic optimization-based techniques suffer from initialization and convergence problems, whereas stochastic optimization techniques such as the ones proposed by Marcoulaki and Kokosis (1999) and Mehta and Kokosis (1997) have proven to be fairly reliable but require long computational times to converge. Moreover, the optimization results are often incomprehensibly complex and impractical to implement, and the methods offer no insights into the key features that cause good performance in the designs identified. Research is in progress to address these issues. Most recently, a novel approach has been proposed that combines knowledge

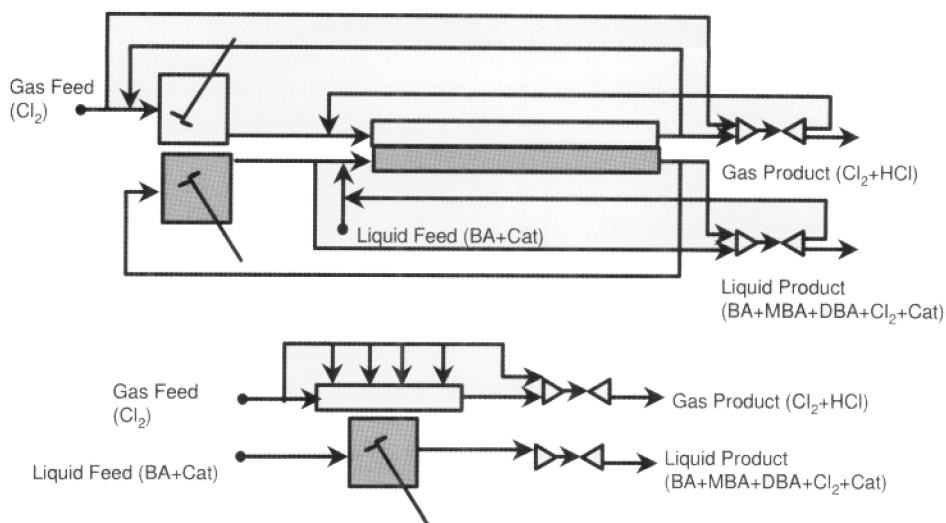


Figure 2.2 Reactor designs for the chlorination of butanoic acid (Mehta 1998).

acquisition tools with stochastic optimization methods to robustly and quickly address complex reactor design problems (Ashley and Linke 2004). The method uses knowledge derived from reaction pathway information to gain an understanding of the system and devise a set of rules that are used to guide the optimal search. The approach was observed to consistently outperform the stochastic optimization-based methods in terms of search speed. Moreover, the knowledge gained during the search can be processed to provide insights into important features that determine a design with performances close to the targets of the system.

2.3.2

Reactive and Reaction-Separation Systems

As indicated in Section 2.2, the combination of separation and reaction has given rise to a number of process intensification methods such as reactive distillation and reactive extraction. The appropriate integration of reaction and separation may lead to significant reductions in capital requirements, raw material waste and other operating costs. However, we would like to stress that the integration of these phenomena is by no means beneficial for all types of systems. There are strong and complex interactions between the various individual subsystems in a process flow sheet, in particular between the reaction and the separation systems that need to be considered in order to develop the most efficient processing options. The development of systematic synthesis tools for integrated reaction and separation systems is considerably more challenging than for the case where only one of these systems is considered as is the case in reactor network synthesis. As a result of these challenges, the

area has received considerably less attention and the developments have mainly been confined to subproblems of integrated reaction and separation problems, such as reactor-separator-recycle, and specific reactive separation systems, such as reactive distillation column design. No general method capable of determining the most appropriate way of integrating reaction and separation is available, be it in a reactive separation process or in a process with separate reaction and separation units. We will review the existing approaches below before we describe in detail a method for integrated reactive/reaction-separation systems design.

A first approach to reactor-separator-recycle process network synthesis was proposed by Kokossis and Floudas (1991), who extended their reactor superstructure formulations to account for the design of a separation train, in terms of determining separation task sequences, and the determination of recycle policies. Smith and Pantelides (1995) reformulated the problem to use more detailed separation process models in conjunction with process units that do not perform predefined tasks. An alternative approach was presented by Fraga (1996), who proposed a discretized reactor-separator synthesis problem that can be optimized using dynamic programming techniques. All presented approaches represent only systems with a single fluid phase, and can not account for reactive separation options.

For the synthesis of specific reactive separation systems, a number of graphical techniques have been presented. Such methods aim at producing feasible rather than optimal design candidates and are available for reactive distillation, reactive extraction and reactive crystallization problems (Hauan, Westerberg and Lien 2000; Hauan, Ciric and Westerberg 2000; Okasinski and Doherty 1998; Barbosa and Doherty 1988; Ng and Berry 1997; Ng and Samant 1998; Nisoli, Malone and Doherty 1997). Ciric and Gu (1994) were the first to propose an optimization-based approach for reactive distillation column design with the number of stages and the feed locations being the structural decision variables. The problem was formulated as a MINLP and solved using a local deterministic optimization algorithm. Cardoso et al. (2000) later proposed the optimization of the same representation using stochastic techniques in the form of simulated annealing.

A more general approach to reactive/reaction separation system synthesis has been presented by Papalexandri and Pistikopoulos (1994), who propose the optimization of superstructures of postulated units for reaction and separation using local deterministic optimization techniques. Additional applications in reactive and reactor/separation system synthesis using this method were reported in separate publications (Ismail, Papalexandri and Pistikopoulos 1999; Ismail, Papalexandri and Pistikopoulos 2001). The approach is limited by the multiphase reaction options it can handle and must cope with large MINLP formulations that include nonlinearities of the most general type.

A general framework for the synthesis and optimization of processes involving reaction and separation was presented by Linke and Kokossis (2003a). The scheme employs rich and inclusive superstructure formulations of two different types of synthesis units and stream networks that allow for a conceptual as well as a rigorous representation of the chemical and physical phenomena encountered in general reaction and separation systems. Stochastic search techniques in the form of simulated

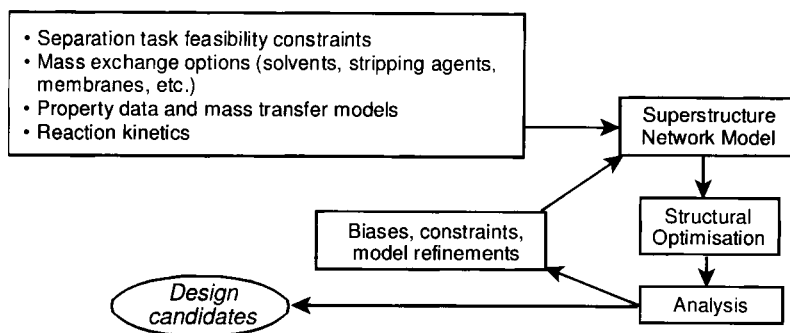


Figure 2.3 Strategy for reactive/reaction separation systems design (Linke 2001).

annealing and Tabu search can be applied to identify robust performance targets and a set of processing options from the superstructures that closely achieve the targets (Linke and Kokossis 2003b). The synthesis method is applied as part of an overall strategy (Linke 2001) as illustrated in Fig. 2.3. In the first instance, the available process design information for candidate reactive separation and mass exchange operations is incorporated into generic synthesis unit models. The proposed methodology utilizes two types of generic units, the reactor/mass exchanger (RMX) and the separation task (ST) unit, which are described below. Superstructures of these generic units are then formulated and the performance targets as well as a set of design candidates are obtained subsequently via robust stochastic optimization techniques. The overall synthesis strategy as well as the flexible process representation allows for iterations to incorporate the insight gained during the synthesis process.

The two different types of synthesis units employed in the superstructures allow one to handle detailed information on reaction, mass and heat exchange (RMX unit) as well as conceptual information in the form of separation tasks (ST units). The generic RMX unit is a flexible and compact representation of the possibilities for phenomena exploitation in processing equipment. The RMX unit follows the *shadow compartment* concept described in Section 2.3.1 and consists of compartments in each phase present in the system. The streams processed in the different compartments of the generic unit can exchange mass across a physical boundary, which can either be a phase boundary or a diffusion barrier. Each compartment features a set of mutually exclusive mixing patterns through which a compact representation of all possible contacting and mixing pattern combinations between streams of different phases can be realized. With different combinations of mixing patterns in the compartments, the existence of mass transfer links between compartments, and decisions on the presence of catalysts, a variety of processing alternatives can be represented by a single generic RMX unit. For a vapor-liquid-liquid system featuring reactions in one heterogeneously catalyzed liquid phase, the six design alternatives in terms of phase interactions can be represented including a homogeneous reactor, a vapor-liquid and a liquid-liquid mass exchanger, a rectifier, a stripper, and gas-liquid-

liquid reactors. Each of these instances represents a number of design alternatives resulting from different possible combinations of mixing patterns and flow directions in the compartments of the different phases.

In contrast to the rigorous representation of reaction and mass transfer phenomena by RMX units, the ST units represent venues for composition manipulations of streams without the need for detailed physical models. In accordance with the purpose of any separation system, the separation task units generate a number of outlet streams of different compositions by distributing the components present in the inlet stream amongst the outlet streams. The ST units can accommodate for the different synthesis aims in the screening and design stages outlined in the previous section by different levels of component distribution and separation task constraints. Nonsharp separations arising from operational constraints on the separation tasks can easily be accomplished. The ST units can perform a set of feasible separation tasks according to the separation order to define a set of outlet streams. Depending upon the order in which the tasks are performed, a variety of processing alternatives exist for a single ST unit such as different distillation sequences performing the same separation tasks.

The synthesis units are combined in network superstructures to provide for a framework that enables the simultaneous exploration of the functionalities of the different synthesis units along with all possible interactions amongst them. A number of synthesis units and a complete stream network are required to capture all different design options that exist for a process. Novelty is accounted for in the superstructures as the representations are not constrained to conventional process configurations but instead include all possible novel combinations of the synthesis units. The superstructure generation and the design instances that can be extracted from such superstructures are described in detail in Linke and Kokossis (2003a).

The synthesis method has been applied to a number of case studies including reactive/reaction-distillation systems, reactive/reaction-extraction systems and bioreaction-separation systems (Linke 2001). For illustration purposes, we will discuss below an application in reactive/reaction-distillation and an application in the development of optimal wastewater treatment processes.

The method was applied to synthesize process designs for ethylene glycol ($C_2H_6O_2$) production from ethylene oxide and water (Linke and Kokossis 2003a). The model consists of two reactions as follows:



The process goal is the production of 25 kmol/h of ethylene glycol with a minimum purity of 95 mol%. Ideal vapor and liquid phases are assumed (Ciric and Gu, 1994). The case study aimed at identifying the performance target and designs that minimize raw material and utility costs. Network superstructures of four multiphase RMX units were generated accounting for vapor and liquid phases. The stream network includes complete intraphase as well as inter-phase connectivity amongst all compartments of the generic units present. Network optimization reveals a perform-

ance target of around 2180k\$/yr for the system, an improvement of 7% over the optimal reactive distillation column reported earlier (Ciric and Gu 1994). A number of designs were identified that exhibit performances close to the target. Figure 2.4 shows two such design alternatives of similar performance.

In a different case study, the method was applied to design activated sludge processes (Rigopoulos and Linke 2002) using the comprehensive kinetic model available for activated sludge systems (Henze, Grady, Gujer et al. 1987). The study aimed at identifying optimal schemes for combined oxidation/denitrification of wastewater that minimize both, the effluent COD and total nitrogen content (N). Superstructures were generated using RMX units to represent the possible single-phase and gas-liquid reactors and ST units to facilitate sludge separation. The study identified

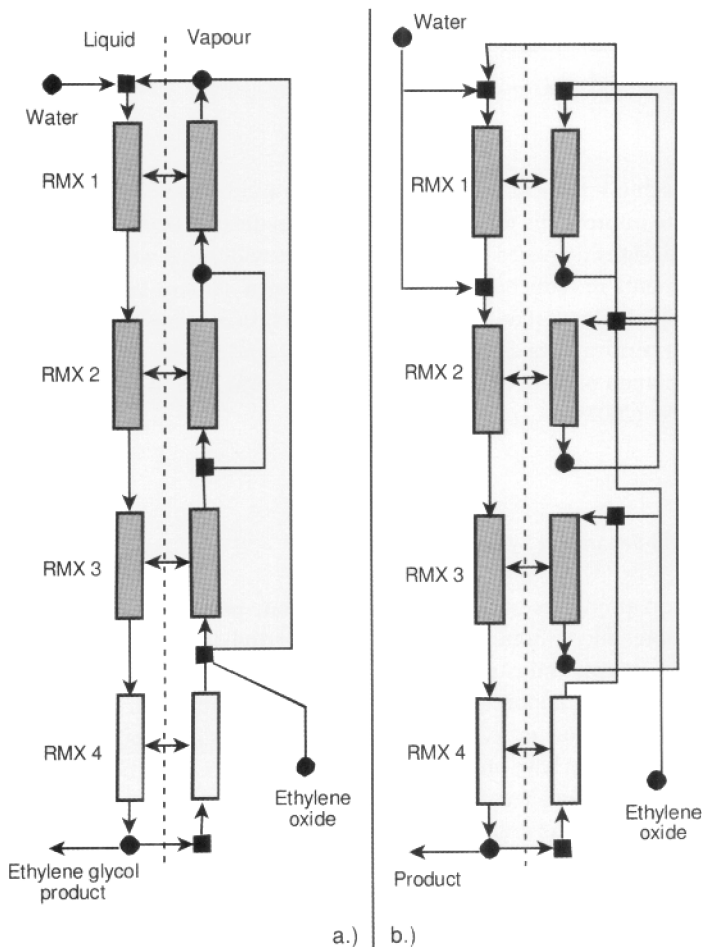


Figure 2.4 Strategy for reactive/reaction separation systems design (Linke 2001).

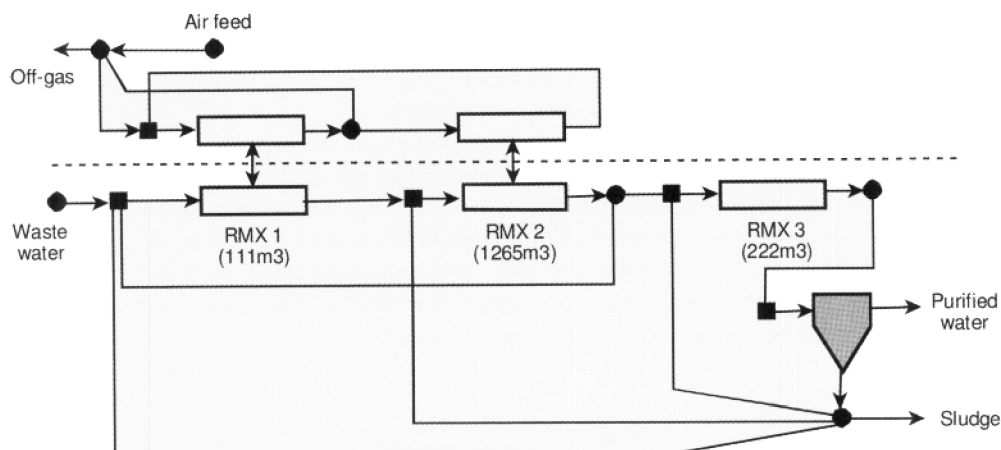


Figure 2.5 Activated sludge process design.

designs that would achieve reductions by 97.4% in COD and by 84.9% in N. There is significant scope to improve the total nitrogen content reduction performances by adopting the novel designs delivered by this study. The new designs were observed to achieve improvements in reduction rates of total nitrogen content between 33% (Bardenpho process) and 80% (Ludzack-Ettinger process) over their conventional counterparts. A high performance design identified in this study is shown in Fig. 2.5. Details on the exploitation of the chemical and physical design insights are given in Rigopoulos and Linke (2002).

2.3.3

Membrane and Hybrid-Separation Systems

Membrane separation processes such as gas permeation, pervaporation, reverse osmosis, ultrafiltration, microfiltration, dialysis, and electrodialysis are frequently used in the chemical process industry. In addition, various membrane hybrid processes are used that couple membrane separation processes with other separation processes including adsorption or evaporation. Systematic design procedures for membrane separation systems have only emerged recently and it is common practice to compare a few known design alternatives in simulation studies. A large amount of work has been published in this area, a few of which are listed here. Stern, Perrin and Naimon (1984) and Stookey, Graham and Pope (1984) have analyzed the performance of single stage membrane permeators with recycle options. Mazur and Chan (1982) have studied multistage systems for natural gas processing and Kao (1988) have investigated recycle strippers and enrichers. Rautenbach and Dahm (1987) and Bhide and Stern (1991a,b) have performed economic feasibility studies for various membrane network configurations with and without recycle streams. Agarwal and

Xu (1995, 1996) have provided broad guidelines based on process economics for two compressor cascades. Clearly, by their very nature, all of these approaches do not allow one to systematically identify the most efficient process option that may exist for a given membrane separation problem.

Few approaches have considered the use of optimization technology to guide membrane network design selection. Tessendorf, Gani and Michelsen (1998) have presented various aspects of modeling, simulation, design and optimization of membrane-based separation systems modeled using orthogonal collocation. The proposed model can handle multicomponent mixtures and considers the effects of pressure drop and energy balances. Qi and Henson (1997, 2000) proposed an optimization-based approach that makes use of local deterministic optimization techniques to solve NLP and MINLP formulations for the design of gas permeation membrane networks using spiral wound permeators. Most recently, Marriott and Sorenson (2003a, b) have developed a general approach to modeling membrane modules considering rigorous mass, momentum and energy balances. Their approach constitutes a feed side flow model coupled with a permeate side flow model and a local transport model for the membrane system. They employ the detailed models in superstructure formulations, which are optimized using genetic algorithms. Their application focuses on pervaporation systems and due to the complex models employed, the optimizations have proved to be extremely computationally demanding.

A further membrane network synthesis approach has been proposed recently (Uppaluri, Linke and Kokossis 2004) that capitalizes on the developments in integrated reaction and separation process synthesis presented in the previous section (Linke and Kokossis 2003a) to develop a comprehensive gas permeation membrane network representation in the form of superstructures that make use of variants of the RMX unit presented previously. The superstructures capture all possible conventional and novel combinations of cocurrent, counter-current and cross flow gas permeation membrane units. The networks can be optimized using robust stochastic optimization techniques in the form of Simulated Annealing to extract those designs that exhibit the best economic performances. It overcomes major limitations of existing approaches as it allows one to quickly screen amongst all possible structural and operational process alternatives that may exist for gas permeation networks, to identify the performance limits of the system, and can accommodate for user preferences and problem specific modeling aspects. The approach can also be extended to account for hybrid separations by incorporating additional RMX and ST units in the superstructure formulations. The approach has been applied in a number of case studies in gas permeation network design as well as membrane hybrid network design. We will present two such applications below.

In one case study, membrane networks are developed that exhibit minimum total cost for the recovery of hydrogen from synthesis gas using polysulfone membranes (Uppaluri, Linke and Kokossis 2004). High-purity hydrogen is required (99% H₂) at high recovery. A number of optimal designs obtained from superstructure optimization for RMX units with different flow patterns are shown in Fig. 2.6. The designs using countercurrent membrane units exhibit the lowest network cost compared to

networks with other flow patterns; however, the performance variations between various flow patterns is fairly small so that designs with cocurrent and cross flow patterns may be viable options if they are seen to offer operational advantages for this particular problem.

In another case study, the superstructure optimization approach was applied to synthesize optimal hybrid adsorption/membrane process configurations for the

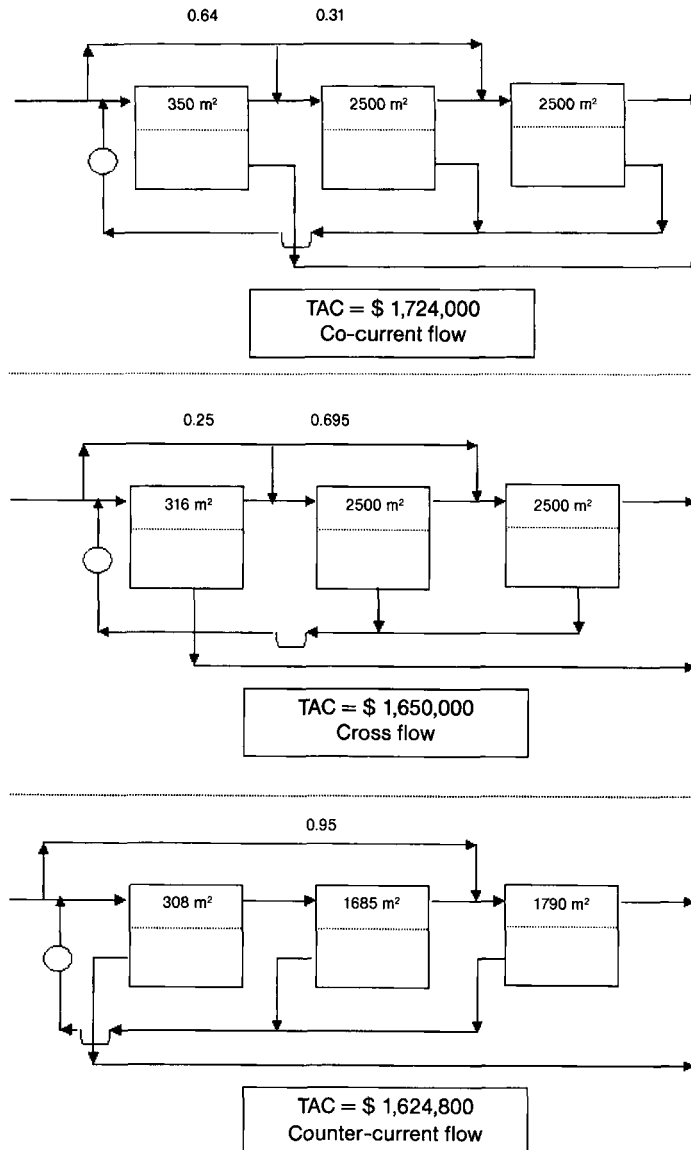


Figure 2.6 Membrane networks for hydrogen recovery from synthesis gas.

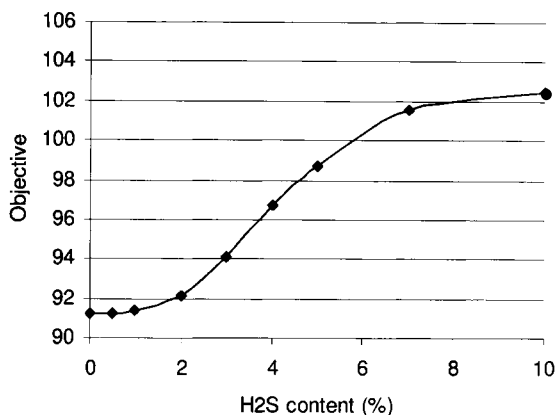


Figure 2.7 Effect of feed gas hydrogen sulfide content on optimal process cost.

sweetening of crude natural gas to meet pipeline specifications (Linke and Kokossis 2003a). Superstructures featuring three RMX units to represent the poly(ether-urethane-urea) membrane units and three ST units to represent the irreversible fixed-bed adsorption process are optimized. The study sought to identify the most economic designs in terms of the total annualized network cost as well as to establish the influence of the hydrogen sulfide content in the feed gas on the performance targets of the membrane-absorption hybrid processes. The network optimization revealed a number of different processing options for different hydrogen sulfide feed concentrations. The optimal designs for the cases of lower hydrogen sulfide feed concentrations feature only networks of membrane units, whereas adsorption-membrane hybrid systems were observed at higher concentrations. The dependence of the optimal total annualized process cost on the hydrogen sulfide feed concentrations is shown in Fig. 2.7. Details on the case study can be found in Linke and Kokossis (2003a).

2.3.4

Process-Solvent Systems

So far, we have presented a number of computer-aided methods for process intensification. These methods allow for the determination of the best processing schemes for a defined process system. Many processes make use of additional materials such as solvents to perform processing tasks. The process performance is strongly dependent on solvent properties and solvent selection is crucial to achieve optimal process intensification. Due to the strong interactions between the solvent and the process design, it is important to select the solvent and the process simultaneously. However, as process performance information is generally unavailable in the molecular design stage, available computer-aided solvent design methods (e.g., Marcoulaki and Kokossis 2000; Buxton, Livingston and Pistikopoulos 1999; Gani and Brignole 1983) design molecules for simultaneous optimality in a number of thermodynamic properties that are anticipated to have a significant effect on the process performance. A

processing scheme is then designed in a subsequent stage for the solvent identified in computer-aided molecular design. Clearly, the success of such a design philosophy is highly sensitive to the formulation of the objective function and thermodynamic property constraints employed in solvent design and selection. The appropriate levels of importance of the thermodynamic properties used to judge the molecular performance are easily misrepresented without process performance feedback. If any important thermodynamic property effects are accidentally excluded, overestimated, or underestimated, the resulting process designs will inevitably underperform. As this is the case most of the time, there is a high risk of failure to provide optimal solutions to the overall design problem with such a sequential design strategy.

Despite the potential for identification of improved designs, very few approaches have been reported that account for process performance feedback in molecular design. A possible design strategy has been proposed by Hostrup, Harper and Gani (1999). However, their method does not account for structural design interactions between computer-aided solvent and process design. This is a tribute to the combinatorial explosion problems faced when attempting to integrate process synthesis approaches with computer-aided solvent design approaches in a unified optimization model. A first approach to the simultaneous design process and solvent structures was proposed by Linke and Kokossis (2002). They developed a representation and optimization framework that exploits all possible molecular and process design options for solvent-processing reaction-separation systems. The proposed system representation takes the form of a process-molecule synthesis supermodel, which combines the superstructure based process design method (Linke and Kokossis 2003a) as presented in Section 2.3.2 to capture all possible processing options with a computer-aided design representation (Marcoulaki and Kokossis 2000) to capture all possible molecular structures of the solvent. The supermodels are then searched using simulated annealing to identify the optimal process-solvent system. Apart from the degrees of freedom associated with the process design options, the type and number of functional groups of the GC method that comprise the solvent molecules are treated as optimization variables during the search.

The method was applied to the synthesis of reaction-extraction bioprocesses together with the corresponding solvents for (reactive) liquid-liquid extraction. The case study aimed at identifying optimal processes and solvents for the production of ethanol by fermentation as described by Fournier (1986). The objective for the study involved the identification of processing options that achieve maximum ethanol yields and glucose conversion while minimizing solvent flow rates. The objective function and problem data are given in Linke and Kokossis (2002).

The classical fermentor design followed by a countercurrent liquid-liquid extractor using dodecanol as the solvent was taken as the reference design for the study. The performance target for this system was identified at an objective function value of 3.66 and the design achieved a glucose conversion into ethanol of 60.5%. By allowing process and solvent optimization, designs could be identified that achieved performance targets of 3135, a performance gain of three orders of magnitude. A number of process configurations together with different solvent molecules were revealed

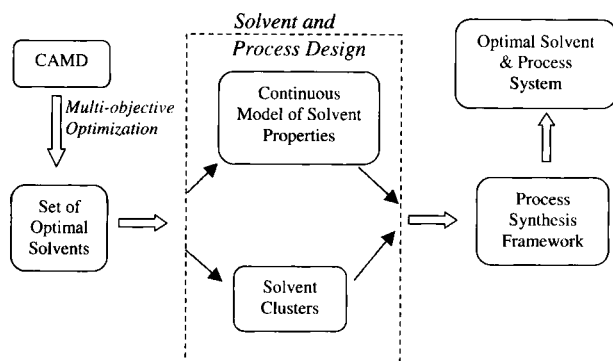


Figure 2.8 Synthesis strategy for process-solvent systems.

that allowed one to achieve near complete conversion of glucose ($X_{\text{Glu}} > 99\%$) into ethanol at moderately increased solvent flows. The optimal process design options feature combinations of fermentor, reactive fermentor and extractors with recycles in the solvent as well as aqueous phases. More detail on the results of this study can be found in Linke and Kokossis (2002). Even though the results were impressive, serious numerical problems during the optimization were reported. The possible performance gains have stimulated additional research into a more numerically friendly method for the integrated design of processes and solvent.

Such an approach was proposed recently by Papadopoulos and Linke (2004). They decomposed the design problem into a computer-aided solvent design and a process synthesis part. At the solvent design level, the design problem is reformulated as a multiobjective optimization problem in order to capture the relationships between physical properties and performance/environmental indices expected to impact on process performance and to extract solvent design candidates across the Pareto-optimal front without having to make limiting assumptions prior to process design. The identified set of Pareto-optimal solvents is then introduced in the process synthesis task. A number of process synthesis tools can be employed in this approach, including the generic reaction-separation process synthesis scheme described in Section 2.3.1. The decomposition-based approach is illustrated in Fig. 2.8. Overall, this approach has been observed to be robust and quick for all cases studied, including liquid-liquid extraction, extractive distillation and reactive/reaction-extraction systems.

2.3.5

Water and Wastewater Systems

The previous sections have presented a number of computer-aided methods for the identification of process intensification options in reaction systems, reactive and reaction-separation systems, hybrid separation systems, and solvent-based process systems. Another area where computer-aided methods are useful for the identification of optimal processing schemes, is the design of industrial water-using systems.

The design of such a system for the efficient use of the water resources is a complex problem involving a number of different tradeoffs. Apart from major process changes, e.g., replacing wet cooling towers by air-coolers, the efficiency of the water system can generally be significantly improved through a variety of practices that include water reuse, regeneration at different process stages, and recycling.

The distinctive features of the wastewater minimization problem dictate the need for a focused rather than general purpose approaches. A major feature of the water system design problem in a typical industrial site is that the largest water users, e.g., cooling towers and steam system, are generally not mass transfer operations. Another advantage is the possibility that a limiting water profile can be constructed (Wang and Smith 1994), which allows the analysis of all water-using operations of water system on a common basis. This allows the combination of such insights gained from a graphical analysis of the problem with powerful optimization-based methods to systematically generate highly efficient water networks. In this section, we describe such an approach, which combines graphical water-pinch concepts with mathematical programming techniques in the form of superstructure models formulated as an MINLP problem (Alva-Argaez 1999). The optimization strategy employs a decomposition scheme and associates binary variables with the existence of different connections. The use of binary variables enables the approach to address complexity issues of the water network as it allows one to incorporate many practical constraints into the analysis, such as geographical constraints, flow rate constraints, and forbidden/compulsory matches. The formulation extends the domain of water pinch analysis with elements of capital cost to study the tradeoffs between freshwater costs, mass exchanger costs, and the cost of the required pipework. Consequently, the optimization results in cost-efficient networks rather than networks featuring minimum freshwater consumption. Former limitations of the water pinch method (Wang and Smith 1994) to address multiple contaminants are thus overcome since there are, in principle, no limits on the number of components or the number of freshwater sources. The design problem for a water-using system involves water-related elements in the form of:

- a number of freshwater sources available to satisfy the demand
- water-using operations described by loads of contaminants and concentration levels.

The water system design problem with its sources and operations is sketched in Fig. 2.9. The design task is to find the network configuration to minimize the overall demand for freshwater (and consequently reduce wastewater volume) compatible with minimum total annual cost. The synthesis objective thus combines terms for low freshwater consumption, suitable network topology for water reuse, and low investment cost. The investment cost of the network includes piping costs and the approximate length of the pipe can be specified for each possible connection together with the materials of construction. The cost of mass exchange units assumes thermodynamic parameters and equilibrium relationships between the process streams and the water streams for the key contaminants, as well as the corresponding design equations and cost functions. The water-using system synthesis problem is initially

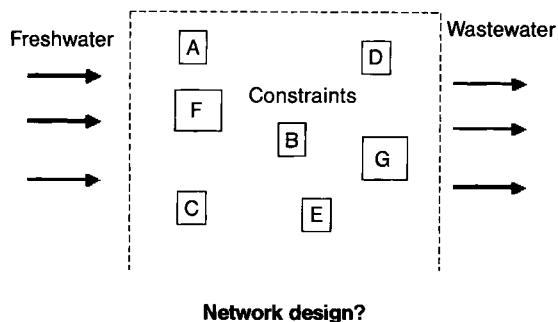


Figure 2.9 Water systems design problem.

presented based on the optimization of a superstructure representation. A natural decomposition of the problem is then developed based on the physical nature of the design problem as engineering insights gained through water pinch analysis. This allows the projection of the bilinear terms in the problem formulation following a recursive procedure which results in an efficient solution of the MINLP formulation.

The method relies on the optimization of a superstructure model that facilitates all possible connections between freshwater sources and operations and different water-using operations. The process streams in the mass exchange operations are considered implicitly in the superstructure model through the construction of the limiting water profiles. The number of units in the water network determines existing units and discrete options account for connections between sources and sinks of water. The superstructure is developed so that each freshwater stream entering the network is split amongst the water-using operations, each operation is preceded by a mixer fed by streams from the freshwater splitters and reuse streams emanating from the outlets of all other operations, and each operation is followed by a splitter that feeds the final mixer and the other operations in the system. The nonlinearities in the superstructure formulation are due to bilinear terms that appear in the mass balances (superstructure mixers and splitters), the nonlinear terms of the sizing equations, and the cost functions for the water-using operations. An example of a superstructure with a single freshwater source and two water-using operations is shown in Fig. 2.10. Unlike some of the previous Mass Exchanger Network (MEN) developments (Papalexandri, Pistikopoulos and Floudas 1994), the superstructure provides options for water streams to merge. The minimum allowable composition difference used by mass exchanger network synthesis developments (Papalexandri, Pistikopoulos and Floudas 1994; El-Halwagi and Manousiouthakis 1989, 1999a,b; Papalexandri and Pistikopoulos 1994) to avoid infinite sized mass exchangers is built into the limiting water profile data. In this approach, the given value is only a lower bound and it does not imply any preoptimized cost tradeoff between capital and operating costs.

A customized solution strategy for the superstructure optimization problem was developed by making use of insights gained from water pinch analysis. From water pinch analysis it is known that for all water-using operations, at least one of the contaminants will reach its maximum permissible value in the optimal solution. If this was not the case, the flow rate through a particular unit could be decreased further

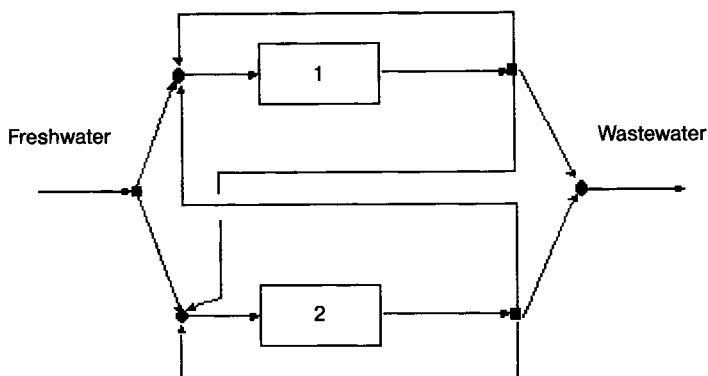


Figure 2.10 Water network superstructure.

to decrease the water consumption, and disprove optimality. Since the mass load of an operation is fixed, the outlet concentrations must be maximized to reduce the water flow. Motivated by this observation and provided all outlet concentrations are set to their maximum levels in the water-using operations, an upper bound can systematically be obtained for the performance of the system. The observation is further exploited with the development of a “natural” decomposition strategy that is explained next.

The original MINLP problem is decomposed into two related subproblems that are solved sequentially within an iterative procedure. A primal problem (P_1) is developed in a first instance by projecting the nonlinear constraints onto the concentration space according to the observations in the previous section. The projection is consistent with the objective of minimum freshwater demands. Given that the “limiting” contaminants define the water demand in the operations, the fact of having a set of nonlimiting contaminants far away from the initial assumption does not detract from the quality of the solution obtained. Experience with the procedure shows that in numerous multicontaminant problems the minimum freshwater demand is identified under these conditions and the calculation of the outlet concentrations of nonlimiting contaminants is not significant. However, the projection is likely to correspond to an infeasible solution as not all contaminants will be able to reach their maximum level for a given mass load and water flow rate. Thus, there are limiting contaminants which achieve their maximum level and determine the water demand for the operation and nonlimiting contaminants that exit the operation at a lower concentration and do not affect the water consumption in the particular operation.

The cost functions are linearized in problem (P_1), which then becomes a mixed-integer linear programming (MILP) problem that can be solved to global optimality using any reliable branch and bound algorithm. Once the flow pattern corresponding to the optimal solution of problem (P_1) is identified, a second problem (P_2) can be solved to find the set of concentrations corresponding to the design obtained. Problem (P_2) is formulated as an LP model that includes mass balance equations projected onto the flowrate space with respect to all flows in the network. The exit concentrations of all contaminants are the variables of the problem.

The overall procedure constitutes a robust methodology as will be illustrated below on the basis of an example in the design of a water system for an oil refinery. The mixed integer models allow one to consider the system-wide interactions between design decisions. In particular, the models can consider tradeoffs between various design alternatives, striking a balance between increased design expenditures and resulting improvements in the system's operation such as decreases in operating cost.

The petroleum and petrochemical industry are heavy users of water. Oil refineries not only face the challenge of reducing the amount of waste generated, but also a fierce competitive market with other water users. Water reuse and recycling are widely practiced in petroleum refining operations; however, typically no systematic methods for exploring new design alternatives to make the most of water reuse and recycling are used. The presented methodology was applied in an oil refinery case study that considered a number of water users, namely an atmospheric distillation unit (CDU), vacuum distillation operation (VDU), hydrotreating (HDS), crude desalting (desalter), cooling tower (c. tower), boiler house, delayed coker, and other operations grouped together (others). The study considered three contaminants: hydrocarbons (HC), hydrogen sulfide (H_2S) and salts (salts). The problem data, equipment cost correlations, and modeling assumptions are given elsewhere (Alva-Argaez 1999).

The total annual cost of the design proposed without applying optimization techniques is 4,430 k\$/yr. This base case already accounts for some water reuse as the effluent from the CDU steam stripping feeds the desalter. The design corresponding to the base case is illustrated in Fig. 2.11. The problem was solved using the presented methodology considering simultaneously the freshwater cost, the cost associ-

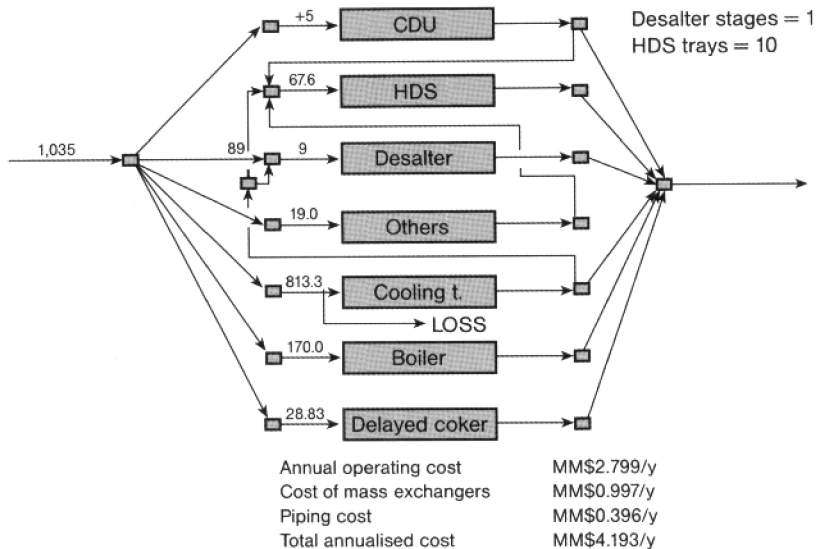


Figure 2.11 Base case water network design for an oil refinery.

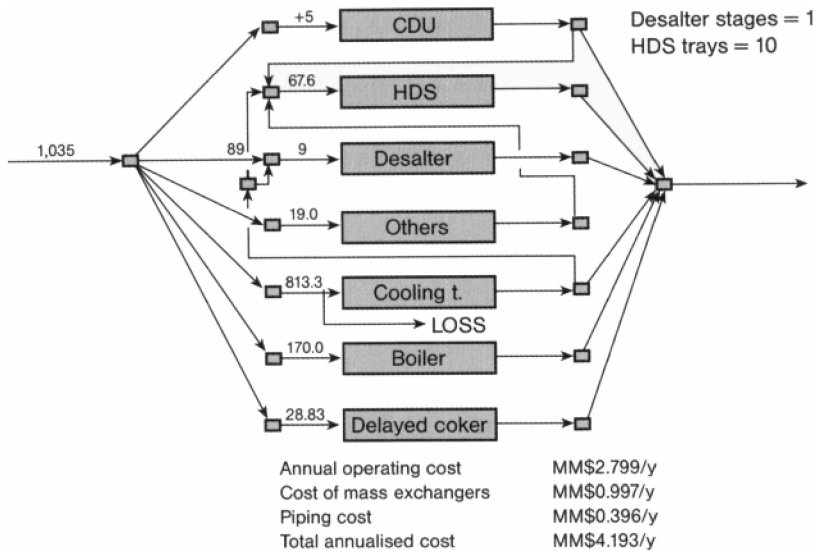


Figure 2.12 Optimal water network design for an oil refinery.

ated with the mass exchangers and the piping cost. The optimal design (Fig. 2.12) was found after about 30 s of CPU time on an antiquated Pentium III processor. The optimized design incurs a total annualized cost of 4,040 k\$/yr, corresponding to cost savings of about 10% as compared to the base case.

2.4

Concluding Remarks

There is constant pressure on the chemical process industry to improve processes and to create new process routes in order to remain competitive in a global market place and to comply with environmental regulations. This translates into a constant need to develop new, more efficient process technologies. Process intensification technologies have proven their value in improving process efficiencies. Most process intensification technologies, in terms of equipment and process concepts, have been invented through the ingenuity of a small number of individuals. Systematic computer-aided approaches have the capability of enhancing the innovation process significantly by offering valuable decision-support to the process designer. This chapter has presented important process intensification technologies as well as a number of the available computer-based methods that allow the systematic generation of intensified processes for reaction systems, reactive/reaction-separation systems, membrane (hybrid) separation systems, process-solvent systems and water and wastewater systems. A major advantage of all the presented methods is their ability to determine robust performance targets and to identify a variety of design

options with similar close-to-target performances. By providing this information, the design tools offer invaluable decision support to the design engineer as it will allow the inspection of similarities and differences between high-performance candidates in order to select the most practical and novel process designs. Most of these methods have only recently been developed in academia and a close collaboration between academia and industry is essential to mature the technologies so that they can be used routinely by design engineers throughout the world.

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