A NOVEL APPROACH TO PROCESS DEBOTTLENECKING AND INTENSIFICATION: INTEGRATED TECHNIQUES FOR TARGETING AND DESIGN

A Dissertation

by

MUSAED MUHAMMAD M. AL THUBAITI

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2007

Major Subject: Chemical Engineering

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ABSTRACT

A Novel Approach to Process Debottlenecking and Intensification: Integrated
Techniques for Targeting and Design. (December 2007)

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Continuous process improvement is a critical element in maintaining competitiveness of the process industries. An important category of process improvement is process debottlenecking which is associated with plants that have sold-out products while making a profit. In such cases, market conditions and the prospects for enhancing revenues and profits drive the process to increase production.

To overcome the limitation of conventional sequential unit-by-unit debottlenecking approach, this work introduces a new approach. This new approach is simultaneous in nature and is based on posing the debottlenecking task as a process integration task which links all the design and operating degrees of freedom and exploits synergies among the units and streams to attain maximum debottlenecking. Additionally, this new approach considers heat integration of the process while simultaneously performing the debottlenecking. Because of the general nonconvexity of the process model, a rigorous interval-based bounding technique is used to determine the target for maximum extent of debottlenecking aside from the problem nonconvexity. Inclusion isotonicity using interval arithmetic is used to determine a global bound for the maximum extent of process debottlenecking. Focus is given to no/low cost debottlenecking such as modest changes in design and operating degrees of freedom. Two case studies are solved to illustrate the applicability of the new approach and its superior results compared to the conventional sequential approach.

Intensification, to debottleneck a process and to improve process safety is also addressed in this work. A new definition and classification of intensification is introduced. This classification distinguishes between two types of intensification: single unit and whole process. Process integration and optimization techniques are used to develop a systematic procedure for process intensification. Focus is given to the interaction among the process units while enhancing the intensification of the process. A case study is solved to illustrate the usefulness of the developed approach.

DEDICATION

To the memory of my oldest brother, Khalid. It has been many years since you were chosen by Allah, and yet there is not a day that goes by that I don't think of you. This work is for you, beloved brother.

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First, I would like to highly praise and relate my deeply felt thankfulness to Almighty Allah for His limitless mercy and blessings; not only in giving me the strength to complete this dissertation, but also for facilitating my educational career, from childhood to this current project.

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My parents have been a constant source of encouragement, perspective and love and they have prayed to Allah for my success throughout the entirety of my life and continue to do so. Their desire to see that I succeed is surpassed only by their limitless love and generosity through every means. For that, I am eternally gratefully. Thank you, Mom and Dad.

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To my sons, Khalid, Abdulaziz, and Muhammad, thank you for your understanding when I was not home. You have been and will continue to be the light of my life. Khalid, from today forward we will have more time to play basketball; Abdulaziz, we will have more time to draw and paint; Muhammad we will wrestle more. I promise!

Finally, I would like to express my utmost appreciation for the generous support of the Saudi Arabian Oil Company (Saudi Aramco) for sponsoring me in the PhD program.

TABLE OF CONTENTS

Page

LIST OF FIGURES

FIGURE Page

LIST OF TABLES

TABLE Page

CHAPTER I

INTRODUCTION

The chemical process industries may be classified into business sectors based on their products that include: petrochemicals, polymers, specialty products, biotech products, and pharmaceuticals. These sectors differ in terms of their production quantities and/or profit margins. For instance, the petrochemicals sector is geared towards manufacturing bulk products that typically garner low profit margins. On the other hand, the pharmaceuticals sector produces smaller quantities that generate considerable profits. Though each of these industries face their own unique challenges in manufacture of their respective products, the chemical industry, in particular, is facing a number of important challenges that affect them exclusively and in a variety of different ways. These challenges include:

1. Competition: Due to globalization (e.g., easier movement of capital, information technology, new production technologies, new markets), the chemical industry is taking advantage of larger markets and is optimizing its resources within a larger sphere of opportunities. At the same time, however, globalization is also imposing enormous competitive pressures on companies. Older chemical plants that were built in an era when profit margins were greater, face increasing pressure today to redesign and modernize while simultaneously improving their cost efficiency and production capacity of existing facilities.

This dissertation follows the style and format of *Journal of Environmental Engineering*.

2. Environmental Concerns and Regulations: Increasing public awareness through the coordinated efforts of local communities, regulatory agencies and non-governmental agencies has exerted considerable influence on the chemical industry toward preserving the environment. Additionally, governmental regulations, particularly in the areas of the environment and process safety, are also impacting the business performance of chemical companies. As a result, the chemical industry has had to change its understanding of process design and operations, while constantly undertaking efforts to increase its resource efficiency from a raw material and energy point of view (Van der Helm and High 1996).
3. Others: Additional factors or challenges facing the chemical industry include increases in the cost of raw material and energy, the availability of more cost efficient technologies, etc.

As a result of abovementioned challenges, most, if not all, existing chemical processes must be continually retrofitted during their lifetime (Diwekar 2003; Fisher et al. 1987; Rapoport et al. 1994; Turton et al. 2003; Uerdingen et al. 2003) There are several different retrofitting approaches that demand varying levels of effort and expertise. Retrofitting problems can be one or more of the following types of modifications (Fisher et al. 1987):

1. The operating conditions of the plant are altered: No process equipment changes are needed and thus, almost no investment costs are associated with this type of modification.

2. The piping which connects an equipment is altered: The equipment might be used for a new purpose. Repiping generally involves low investment costs.
3. The flowsheet topology is unchanged but equipment is refitted: Some equipment can be altered without having to replace it altogether. An example of this is the retrofitting of a distillation column with new column internals. This type of modification incurs moderate investment costs.
4. New equipment is added and old equipment decommissioned: This type of modification can change the process flowsheet topology at a considerable investment expense. This kind of retrofit includes, for example, the integration of new technologies into an existing process.

Importance of retrofitting in the chemical industry

Since the so-called energy crisis in the 1970s, research on retrofit design has accelerated. Earlier work concentrated on applications of heat integration methods to increase the energy efficiency of process plants. In addition to energy conservation, retrofit projects now address mass conservation, environmental and safety concerns, etc.

The Chemical Manufacturers Association reported (1999) that the total capital expenditures of the U.S. chemical industry for 1999 were distributed over five categories:

1. Plants and equipment
2. Research and development
3. Health and safety

4. Environmental protection
5. Hazardous waste site clean-up and remediation

These expenditures amounted to about 53.9% for plants and equipment, 27.5% for research and development, 7.8% for health and safety, 6.6% for environmental protection, and 4.2% for hazardous waste site clean-up and remediation.

Moreover, the survey also identified the capital expenditure distribution by different project types in the plants and equipment category:

- Capacity expansions (of existing production plants)
- Plant maintenance (replacement of worn-out equipment)
- Improvement of production cost efficiency (raw material and energy efficiency)
- New production plants
- Environmental protection
- Health and safety
- Other projects

Amazingly, only 14.7% of the capital expenditures in the plant and equipment category accounted for the construction of new production plants – the only non-retrofit category. Higher capital investments were spent on retrofitting projects (capacity expansions, plant maintenance, and improvements of production cost efficiency.) Additionally, it has been estimated that 70-80% of all process design projects between 1984 and 1989 have dealt with retrofit designs (Grossmann et al. 1987).

Differences between grassroot and retrofitting designs

In many cases, retrofitting problems are analyzed and evaluated with tools that were specifically developed for grassroot design. However, there are fundamental differences between the two design approaches. These differences include:

- Retrofitting is highly plant-specific: Solutions to a retrofit problem are most often pre-determined to a certain degree by the historical evolution of the structure of the process plant. As a result, a solution has to be individually “tailored” to the process plant investigated.
- Retrofitting is driven by constraints: In conjunction with the previous point, a number of important constraints (e.g., limited space availability, availability of different types of utilities) limit the search space for solutions.
- Retrofit implementation is a challenge: The implementation of a solution to a retrofit problem has to be coordinated in a manner that minimizes the impact on plant operations (Cabano 1987). Different implementation strategies are listed in order of preference:
    1. Implementation in the plant without impact on production capacity and minor impact on plant operations: This can be done, for example, by installing and testing of new equipment in the plant while the plant is operating; then by connecting the new equipment to the plant in a minimum of timeframe when the plant is not required to be operating at maximum production capacity; and then by compensating the resulting production losses afterwards.

2. Implementation during the routine maintenance shut-down: This may lead to a longer process downtime and possibly incur production losses.
3. Implementation during a non-routine shut-down: By consequence, there is a fair chance that the yearly production capacity might not be met since production losses result from this strategy.

Furthermore, data on the changes in operating conditions after retrofitting might have to be gathered and extrapolated from tests runs in the plant, prior to the planned plant modifications.

- The combinatorial size of the evaluation problem: The solution of a retrofit problem requires the evaluation of a larger number of alternatives as compared to grassroot problems. For instance, Grossmann et al (1987) show that for retrofit of a distillation sequence separating a mixture of N components, the number of tasks considered is $N - 1$ times that for the grassroots design. This is due to the fact that not only do process retrofit alternatives have to be evaluated, but also that the reuse of existing equipment has to be considered since economics dictate the reuse of existing equipment as much as possible. Existing equipment might, however, be required to operate far from its design conditions. Therefore, both the evaluation of process retrofit alternatives and the rating of existing equipment under different operating conditions need to be undertaken in search of a solution to the retrofit problem. It is difficult to treat both tasks independently from each other as can be easily done in grassroot design.

- Retrofitting requires different mathematical tools: Different mathematical tools are needed to rate existing equipment as compared to grassroot design. The presence of existing equipment requires different and often more complex simulation models for evaluating retrofit designs. In particular, shortcut design methods, which are used successfully to screen alternatives for new designs, are often not appropriate or inadequate for retrofits. Consequently, the evaluation of design alternatives with rigorous models for existing equipment is a more complex task.
- Experience in plant operations is available: The experience in operating the investigated plant is a source of important information for retrofit design. These insights can be used to reduce considerably the combinatorial size of the retrofit problem. Experience can be transformed into specific heuristic rules and can help to quickly rate process retrofit alternatives.

Different retrofitting methods

Different retrofitting methods were proposed to solve different retrofitting problems. In some cases, one method can be used for more than one problem. Below is a list of the most commonly used methods for plant retrofitting:

- Methods to improve economics through increased energy efficiency or conversion of raw material: Proposed retrofitting methods that target energy saving through Heat Exchange Network (HEN) retrofitting are either based on the concept of pinch technology, mathematical programming techniques, or both.

The pinch technology was first introduced by Linnhoff and Flower (1978) to design optimal heat exchanger networks and was later extended by Linnhoff et al. (1982) for the minimization of energy-use in the design of entire processes (including the HEN). Tjoe and Linnhoff (1986) then presented a method that adapts the latter method to the specific context of retrofit design.

Important contributions to develop the mathematical programming techniques were made by Jones et al. (1986), Saboo et al. (1986), and Ciric and Floudas (1989.)

Each of above mentioned approaches have its advantages and limitations. To combined the advantages of both types of approaches, Zhu and Asante (1999) developed an approach that uses the pinch technology in order to generate promising HEN designs and then finding the best solution through mathematical programming techniques. A similar approach was adopted by Kovac and Glavic (1995) and Kovac-Kralj et al. (2000) but extended to the retrofitting of entire processes (not only the HEN) with respect to energy consumption (Wang et al. 2003.)

Zheng and Cao (2007) introduced a new graphic method for process energy analysis and integration, involving an energy Flow Framework Diagram (EFD), which consists of a series node and node partners between utility buses and energy loss buses, thermodynamic principles of energy analysis and energy integration by the EFD, and a series of restrictive criterions and revelatory criterions to use the EFD. Some measures were demonstrated by application of the EFD method for a synthetic gas-based 56 kt a^{-1} one-step dimethyl ether production process.

Energy efficiency can be improved through retrofitting units or systems other than HEN. For example, a leading Asian chemical company was conducting a retrofit within a large aromatics plant. As part of this process, an energy improvement study was performed that considered the energy needs of the aromatic complex as a whole, and not just the individual units. This study showed that by incorporating process design changes to the separation system, significant operating cost benefit could be achieved. The result was 20 percent reduction in the overall energy required by the plant complex (Evans 2003). Additionally, Energy requirements can be reduced by the use of a more reactive solvent (Oyenekan and Rochelle 2006).

Al-Otaibi and El-Halwagi (2006) developed a procedure for plant retrofitting to maximize the process yield, and hence reduce the consumption of raw material. This procedure consists of the following key steps:

1. Maximize routing of targeted raw material to the reaction system
2. Maximize reactor yield
3. Reroute desired product from undesirable outlets to the desirable outlet, and
4. Minimize the fresh consumption of the targeted raw material through recovery and recycle

- Methods for improving the overall cost efficiency: An important approach to improving the overall cost efficiency was proposed by Fisher et al. (1987). It combines sensitivity analysis with elements of the hierarchically structured and heuristically-driven method for grassroot design introduced by Douglas (1985). This work was partially automated and further extended by Nelson and Douglas (1990). Uerdingen et al. (2003 and 2005), introduced a new methodology for identifying and screening the retrofit potential of a chemical process. The method is organized in five steps: (1) base case analysis, (2) generation of retrofit options, (3) rough economic evaluation of the retrofit options, (4) process optimization with regard to retrofit options that do not require investment, and (5) feasibility study as well as the economic profitability of the retrofit options that require investment. Jackson and Grossmann (2002) addressed the retrofit problem using a hierarchical approach and mathematical programming tools. Unlike the hierarchy of five decision levels proposed by Douglas for process synthesis, this method uses two levels: a high level for simultaneously analyzing the entire network, and a low level for analyzing a specific process flowsheet in detail.
- Methods for waste minimization: Due to increased environmental awareness and regulations, more attention was given to the waste reduction and the reuse of waste instead of end-of-pipe methods. A number of retrofit design methods that tackle the problem of waste minimization in existing processes have been reported in literature. Douglas (1992) modified his hierarchically-structured and

heuristic-driven approach for the design of new processes to include the objective of waste minimization. Later, two different approaches to perform retrofit design for waste minimization were proposed by Van der Helm and High (1996) and Dantus and High (1996). Both approaches are structured in a procedure that includes three main steps: base case modeling of the existing process in a flowsheet simulator, identification of process retrofit alternatives on the basis of a case specific study of the process (not generalizable), and optimization with regard to economic performance while minimizing waste by source reduction. Another retrofit design method for waste minimization has been introduced by Halim and Srinivasan ((2002a,b.)

El-Halwagi and Manousiouthakis (1989) introduced the problem of synthesizing mass-exchange networks (MENs), which seeks to transfer certain species from a set of rich streams (typically terminal streams) to a set of lean streams (such as solvents, adsorbents, etc.) They proposed systematic composite representations to identify targets for the maximum extent of mass exchange among process streams and minimum usage of external lean streams. The synthesis of MENs has also been successfully used in waste recovery/separation applications. Dhole et al. (1996) and El-Halwagi and Spriggs (1998) addressed the recycling/reuse problem through a source–sink representation. Polley and Polley (2000) proposed a set of rules for sequencing mixing and recycling options. In addition to recycle/reuse, stream interception has been used as an effective strategy for material recovery and waste reduction. Interception refers to the use of a separation device or network to remove targeted species from in-plant streams. El-Halwagi et al. (1996) developed an integrated approach to the synthesis of waste interception networks using mass-separating agents. Gabriel and El-Halwagi (2005) introduced a systematic procedure for material recovery and pollution prevention through simultaneous recycling/reuse and interception.

- Methods to improve other objectives such as flexibility: Continuous processes are constantly influenced by varying input parameters and external disturbances (e.g. varying feed-rates from other plants, extreme variations of the outside temperature). Most of these uncertainties are handled by the process control system. However, variations in operating conditions cannot be completely prevented. Therefore, processes have to exhibit a certain degree of operational flexibility to encompass sudden changes in operating conditions. A retrofit design method that focuses on improving the flexibility in plant operations was presented by Pistikopoulos and Grossmann (1988, 1989). This method makes use of a flexibility index that defines the maximum allowable variation range of uncertain parameters in order to maintain operations (Grossmann and Floudas 1987; Swaney and Grossmann 1985). Given a pre-defined index value of flexibility, this method minimizes the capital costs related to process modifications in order to achieve the desired value.

Papalexandri and Pistikopoulos (1993) presented a mixed integer nonlinear programming (MINLP) model for the retrofit of HENs in order to improve their flexibility. As stream flowrates and inlet temperatures and/or heat transfer coefficients are allowed to vary within either specified ranges or discrete sets, a multiperiod hyperstructure network representation is developed based on critical operating conditions (i.e. periods of operation) that limit the network's flexibility. This multiperiod hyperstructure includes all possible network configurations. Structural modifications, such as new stream matches, exchanger reassignments, splitting and mixing of streams are explicitly modeled either considering one-to-one or one-to-many assignment of heat exchangers to stream matches. Energy recovery and utility consumption are not predetermined but are optimized as part of a total annualized cost along with the structural modification cost in the objective function.

- Methods for increasing the throughput of a current process by debottlenecking it: Although capacity expansion was identified as the most important retrofit incentive in terms of capital expenditure, very few retrofit design methods that approach this aspect of retrofit design are reported in literature. Rapoport et al., (1994) presented a method that mainly aims at expanding the production capacity of a plant, but also targets retrofit incentives to use new raw materials. The method consists of an interactive algorithm that is based on heuristics rules and is organized in a hierarchical procedure. Moreover, tools for the design of equipment and for the calculation of capital costs are used to evaluate the generated process retrofit alternatives. Later, Ben-Guang et al. (2000) proposed another systematic procedure to deal with increasing production capacity in continuous processes. However, the procedure is only intended as a conceptual guide to efficient project management with regard to retrofitting for capacity expansion since at each step of the method the applied strategies are formulated in a rather general context. This type of process retrofitting, which is also called process debottlenecking, will be discussed in more detail in next chapter.

Process retrofitting through process intensification

Process intensification is gaining much attention as one of the key objectives in designing new plants and retrofitting existing units. Several drivers have contributed to this increasing attention. For instance, enhanced process safety and homeland security are tied to process intensification. As the inventory and flows of hazardous substances are lowered, the process risk is typically reduced. Additionally, conservation of natural resources (including better utilization of mass and energy) may be linked to process intensification.

The term “Process Intensification” has different definitions. The most general definition of Process Intensification as, “Any chemical engineering development that leads to a substantially smaller, cleaner and more energy efficient technology” was proposed by Stankiewicz and Moulijn (2000). Based on this definition, Process Intensification is categorized into two classes: Equipment and Methods. This definition and classification of process intensification are discussed in detail in Chapter V.

While cost reduction was the main motivation for process intensification, it quickly became apparent that there are other important potential benefits, particularly in respect of improved intrinsic safety. It is obvious that smaller is safer. Huge inventories of hazardous materials were the main causes of the more severe chemical disasters of the past century (e.g., Oppau/Ludwigshafen Flixborough in 1974, San Juan, Mexico City in 1984, and Bhopal in 1984). Process Intensification can dramatically reduce inventory through smaller equipment, improve reactor/yield, minimizing feedstock, etc. Furthermore, process intensification enhances safety through the development of products that cannot be safely or successfully produced because of high reaction rates, dangerously exothermic reactions, or reactants are too hazardous.

Other important benefits of process intensification are improving process chemistry, reducing environmental impact and energy consumption, enhancing corporate image through being innovative and environmentally friendly, and finally, value customers through "just in-time" manufacturing or philosophy.

Process Intensification is used in different retrofitting problems. For example, a process can be retrofitted by using intensified equipments to minimize waste, increase process yield, improve safety, reduce operating, and reduce energy consumption(Harmsen and Hinderink 1999; Meili 1997; Phillips et al. 1997; Rijkens 2000; Xu 2001)

Main objectives of this work

This work addresses the problem of plant retrofitting associated with plants that have sold-out and profitable products. In such cases, market conditions and the prospects for enhancing the company's revenues and profits drive the process to increase production. When the process reaches maximum production rate without satisfying the market demand, it is referred to as being “bottlenecked.” The process units restricting the production are designated by “bottlenecks.” The task of eliminating these bottlenecks is called “debottlenecking.” This work discusses the first two types of process retrofitting to debottleneck a plant. Theses two types of plant retrofitting (manipulation of operating conditions and simple piping) will be referred to as no/low cost debottlenecking approach throughout this work. A separate Chapter in this dissertation has been designated to discuss the current understanding of process intensification and the use of process intensification in the debottlenecking process. The dissertation introduces several novel techniques for retrofitting and intensification. These techniques are systematic and generally applicable. Principles of process integration and systems optimization are used in developing these techniques. The usefulness of these techniques is illustrated by addressing several case studies of industrial relevance.

CHAPTER II

PROBLEM STATEMENT

The overall problem to be addressed in this dissertation deals with the development of design tools for enhancing the productivity of processing facilities. In particular, two process objectives are considered: debottlenecking and intensification. Debottlenecking is aimed at increasing production by eliminating processing hurdles (bottlenecks) that limit the product throughput. Intensification is geared towards issues such as increasing the throughput through the same processing equipment of decreasing the process physical size or the utilities for a given production rate. The problem may be formally stated as follows:

Given a process with certain feedstock of raw material(s) and existing process units, which are referred to as sinks. The set of sinks is SINKS= {u:u= 1, N_{sinks}} and each sink has a set of input streams ($INPUT_u$) and a set of output streams ($OUTPUT_u$). The input stream, i_u, has a flowrate G_{i_u} at temperature T_{i_u}. Each stream has a set K of desired components. The k^th component has a composition referred to as $x_{i_u,k}$. Each stream is either a hot stream with T^{Supply} to be cooled to T^{Target} or a cooled stream with t^{Supply} to be heated to t^{Target}. Each sink has a range of acceptable flowrate and composition of species; and any stream must satisfy that range before being fed to that sink, i.e.

$$G_{i_u}^{min} \le G_{i_u} \le G_{i_u}^{max} \qquad i_u \in INPUT_u, \quad u \in SINKS \qquad (2.1)$$

$$x_{i_u,k}^{min} \le x_{i_u,k} \le x_{i_u,k}^{max} \qquad i_u \in INPUT_u, \quad u \in SINKS, \quad k \in K \qquad (2.2)$$

$$T_{i_u}^{\min} \le T_{i_u} \le T_{i_u}^{\max} \tag{2.3}$$

For each sink, there are vectors of design and operating degrees of freedom abbreviated as (d_u and o_u), respectively. These vectors are subjected to manipulation and optimization. They correspond to no/low cost modifications such as the changes in design and operating conditions. D_u and O_u designate the intervals of permissible values of design and operating degrees of freedom for sink *u*, respectively. Hence, $d_u \in D_u$ and $o_u \in O_u$.

The aim of this dissertation is to develop systematic techniques that enable answering the following questions:

1. What is the true potential or the maximum production from the process (Targeting)?
2. How this maximum production can be achieved at the most cost effective manner?
3. What are the minimum utility requirements to achieve the maximum production flowrate?
4. What is the maximum achievable production flowrate using existing equipments and without the addition of new pieces of equipments?
5. How Process Intensification can be utilized for process production maximization, process safety, yield enhancement, etc.

These five questions will be addressed throughout the dissertation. Chapter III will address the first two questions, Chapter IV will address questions three and four, and Chapter V will address the last question.

CHAPTER III

NO/LOW-COST SIMULTANEOUS PROCESS DEBOTTLENECKING

Introduction

Continuous process improvement is a critical element in maintaining competitiveness of the process industries. There are various forms of process improvement such as yield enhancement, quality improvement, material and energy conservation, waste minimization, and safety enhancement (e.g., El-Halwagi, 2006). In particular, there is an important category of process improvement which is associated with plants that have sold-out and profitable products. In such cases, market conditions and the prospects for enhancing the company's revenues and profits drive the process to increase production. When the process reaches maximum production rate without satisfying the market demand, it is referred to as being "bottlenecked." The process units restricting the production are designated by "bottlenecks." The task of eliminating these bottlenecks is called "debottlenecking."

Debottlenecking of individual units (in contrast to the more complex scope of overall plant debottlenecking) has received considerable attention in literature. For example, individual distillation columns have been debottlenecked through internal modifications (Fair and Seibert, 1996; Shakur et al., 2000; Summer et al., 1995), hydraulic analysis (Bellner and Kister, 2004), changing the reflux ratio, and the feed tray modification (Modashia et al., 2000). Stripping columns have been debottlenecked through solvent replacement (Saremi et al., 2000).

The area of developing systematic techniques for debottlenecking a total site has received much less attention than the debottlenecking of individual units. The conventional approach in total-site debottlenecking has been sequential in nature where bottlenecks are identified and removed one at a time. The active bottleneck is first identified then relaxed or removed through capacity expansion of the unit, changes in design and operating variables, unit replacement or addition, and stream rerouting. As a result of debottlenecking the unit, a new bottleneck is formed somewhere else in the process. The same approach is repeated for removing the new bottleneck. This sequential debottlenecking approach involves two activities: identification of active bottlenecks and removal of bottlenecks. Bottleneck identification may be achieved through various means. Actual process performance may be analyzed to detect the active bottleneck. Process experience may be used to point to likely bottlenecks.

Process simulation may be used to recognize active bottlenecks by increasing production and detecting the first unit to reach its maximum capacity. Litzen and Bravo (1999) used simulation software to relate the flowrate of the finished product into feed rates of various equipment and then summarized the bottlenecks on a "stair-stepped" chart by arranging them from lowest to highest. In the next stage, equipment bottlenecks were sequentially removed by taking advantage of extra equipment capacities elsewhere. In addition to the limitation of being sequential, this approach does not provide a methodical way of relating the flowrate of the finished product to the feed rate of the equipment, particularly for highly interacting systems.

Hierarchical and heuristic techniques have been used for debottlenecking. The hierarchical approach relies on intuition, engineering knowledge, and physical principles to decompose the problem into sequential stages. A hierarchical approach was introduced by Fisher et al. (1985) who proposed a method for screening alternatives and modifying equipment sizes, replacing units, and adding new equipment. Rapoport et al. (1994) developed a heuristic approach that includes procedure for equipments deign, for capital costs, and for economic evaluation. This approach was applied to add a new unit into an aromatic plant. While heuristic approaches utilize engineering insights, they are not guaranteed to identify optimum solutions for general cases.

Optimization techniques may be used to solve a production maximization problem and identify the bottleneck as the unit for which at least one of its constraints becomes active (Ben-Guang et al., 2000). Once a bottleneck is identified, a combination of process analysis and process synthesis techniques can be used to screen debottlenecking alternatives and select a solution. Zhang et al., (2001) proposed a two-stage debottlenecking approach for refinery operations. In the first stage, a linear programming model is used to identify major bottlenecks by locating the equipment that required extra capacity. It is also worth mentioning that only throughput to the reactors and columns are constrained instead of modeling all equipment in the refinery. In the second stage, bottlenecks are relaxed or removed. This method first deals with high-level bottlenecks that may be removed by modifying the hydrogen and energy network structures without involving the process details. For other types of bottlenecks (referred to as low-level bottlenecks), the method uses detailed process models to search for debottlenecking options. Although this method employs a simultaneous approach for identifying bottlenecks, only capacity constraints were considered. Process operational constraints (temperature, pressure, etc.) were assumed unlikely to be overcome and were not included in the bottlenecks identification model. This assumption excludes the option of using different/new technologies and equipments. Additionally, the option of adding new equipment during the bottleneck-identification stage was not considered (assuming a fixed configuration). Consequently, stream rerouting was not an option in the debottlenecking stage and the target for debottlenecking is not identified. Finally, in the debottlenecking stage, high-level bottlenecks are removed first, then a detailed process model is used to remove the low-level bottlenecks. Hence, this debottlenecking procedure is sequential and may lead to sub-optimal solutions.

Harsh et al., (1989) developed an algorithmic approach and applied it to the retrofitting of an ammonia process. After identifying the process bottlenecks, mixed integer nonlinear programming (MINLP) was applied to relax binding constraints through addition or modification of process equipment. Because of the nonconvexity of most process debottlenecking problems, it is a challenge to develop general-purpose algorithmic approaches that guarantee efficient convergence (and in some cases even convergence) to a global optimum (Mizsey and Fonyo, 1990).

A combination of more than one approach can also be used. Kovac and Glavic (1995) introduced a combined approach based on thermodynamic principles and algorithmic method. Mizsey and Fonyo (1990) used a combination of the hierarchical and algorithmic methods. They used the hierarchical approach in the preliminary screening to generate good initial estimates followed by the use of an algorithmic approach to synthesize the final flowsheet.

As mentioned earlier, the most commonly-used debottlenecking approach is the sequential method. In spite of its extensive usage, it is important to examine the ability of a sequential approach in attaining the true potential of the process and in achieving maximum debottlenecking. In particular, the following questions are important:

- Does the sequence of debottlenecking the units (e.g., the active bottlenecks) affect the ultimate extent of debottlenecking the whole process? If so, what is the optimal sequence of debottlenecking?
- In tackling an active bottleneck, should it be debottlenecked to the maximum extent? If not, then to what extent?
- If no new units are added to the process, is it possible to identify a target for maximum extent of debottlenecking ahead of detailed debottlenecking and without commitment to the debottlenecking strategies?

In order to answer these questions, the following motivating example is analyzed.

Motivating example

Consider the hydrocarbon processing facility shown by Fig. 3-1. Two feeds (mass flowrates are F_1 and F_2) are mixed in 2:1 ratio. The product (F_4) is cooled, compressed, and fed to the first separator. The bottom of the first separator is cooled and fed to the first reactive separator while the top product is fed to the second separator. The top product of the first reactive separator and the bottom product of the second separator are fed to the second reactive separation system along with an additional stream (F_{13}). The top cut of the second reactive separation system is the main product of the process. It is a sold-out product and there is a need to increase production by debottlenecking the process by manipulating design and operating variables of existing units without investing in new units. The volumetric flowrate to the compressor should not exceed a maximum value V_5^{max}. At present, the values of Q_4, Q_7, and Q_9 are $2x10^6$, $1x10^5$, and $3x10^5$ kJ/hr, respectively and the flow rate of F_{14} is 29,421 kg/hr.

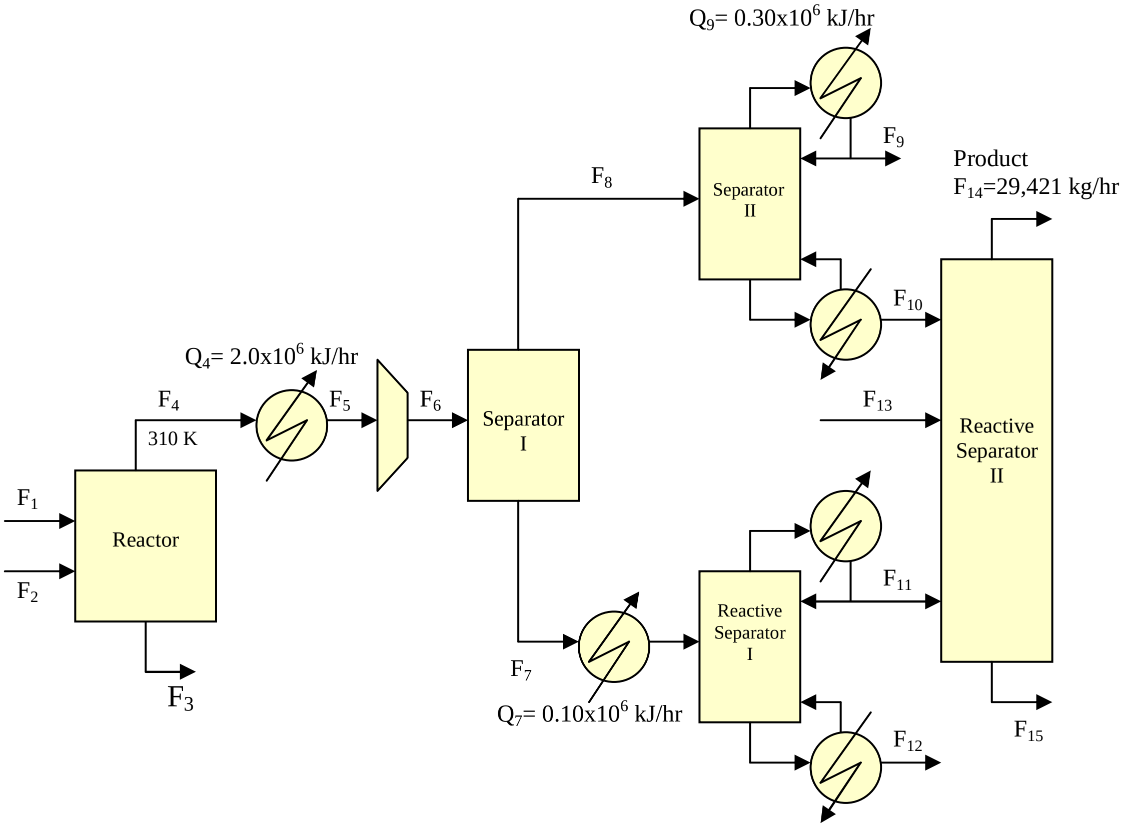

Fig. 3-1. Flowsheet of motivating example (base case)

The objective of this case study is to identify maximum extent of debottlenecking needed to maximize production (F_{14}). In this case, we limit the study to the situation when debottlenecking is achieved without investing in new capital. As such, the no/low cost modifications of design and operating variables are considered. Let us also consider the case when a total cooling duty of up to 5×10^6 kJ/hr is the only available debottlenecking tool.

Sequential Approach: As mentioned earlier, this approach relies on two steps: identification of the currently active bottleneck and maximum relaxation of this bottleneck. These two steps result in the creation of a new active bottleneck and the procedure is repeated. To increase mass flowrate, the temperature of the compressor feed can be decreased. The reactor constraints must also be considered to insure that the maximum capacity of the reactor will not be violated. By reducing the temperature of the compressor feed from 310 K to the minimum value of 288 K (which corresponds to a cooling duty $Q_4 = 4.18*10^6$ kJ/hr), maximum debottlenecking of the compressor is 95,000 kg/hr. The corresponding flow of F_7 is calculated to be 44,122 kg/hr which exceeds the current capacity of the second separation column (41,000 kg/hr). Consequently, the first reactive separation column is now the bottleneck. It can be debottlenecked to a maximum capacity of 45,200 kg/hr when the cooling duty Q_7 is increased to $0.52*10^6$ kJ/hr. Finally, the remaining cooling capacity is used to increase Q_9 to consume the remaining cooling utility in the plant ($Q9 = 0.30*10^6$ kJ/hr) in order to increase the production flowrate, F_{14}. The result is that the flowrate of F_{14} is 31,113 kg/hr (an increase of about 6%). This is the maximum product flowrate achievable using the sequential debottlenecking approach (Fig. 3-2).

Suppose that an alternate solution is selected. For instance, let us choose some arbitrary (but feasible) values of cooling duties. Instead of the values determined from the sequential approach (Q_4, Q_7, and Q_9 = $4.18*10^6$, $0.52*10^6$, and $0.30*10^6$ kJ/hr, respectively), let us choose the following arbitrary values: Q_4, Q_7, and Q_9 = $3.00*10^6$, $0.10*10^6$, and $1.90*10^6$ kJ/hr, respectively. For these cooling duties, the value of product flowrate, F_{14}, is 48,460 kg/hr which is superior to the result obtained through the sequential approach. There are important observations from this example:

- Conventional engineering approach of sequential debottlenecking can lead to sub-optimal results,
- A new perspective is needed in debottlenecking: a holistic approach is needed to treat the process as a whole and to integrate the various units, streams, design and operating variables, simultaneously. In this context, process integration can provide a uniquely useful framework for this new design paradigm, and
- Because of the non-linearity and non-convexity of most process models, a global bounding approach is needed to yield meaningful results.

Objective

The objective of this work is to introduce a new approach to no/low-cost debottlenecking by focusing on the integrated nature of the process. As will be shown, this approach is superior to the conventional sequential approach. Specifically, this work will contribute the following:

1. A systematic procedure for the simultaneous debottlenecking will be developed,
2. A targeting approach will be developed. Because of the non-linearity and non-convexity of most process models, a global bounding technique will be employed to determine rigorous targets for debottlenecking, and
3. An optimization formulation will be developed and solved to identify process modifications needed to attain the desired target for debottlenecking.

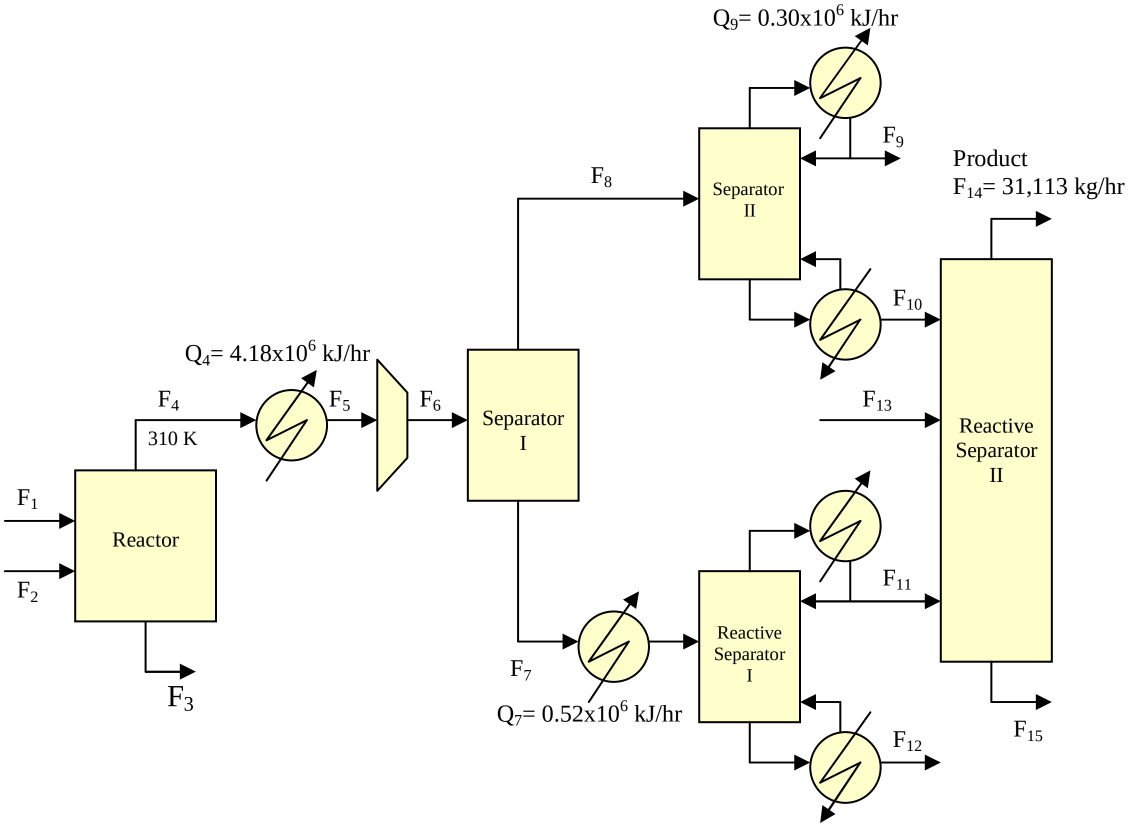

Fig. 3-2. Flowsheet of motivating example (sequential debottlenecking)

Problem statement

Given a process with certain feedstock of raw material(s) and existing units of the process, which are referred to as sinks. The set of sinks is SINKS= {u:u= 1, N_{sinks}} and each sink has a set of input streams ($INPUT_u$) and a set of output streams ($OUTPUT_u$). The input stream, i_u, has a flowrate G_{i_u}. Each stream has a set K of desired components. The k^{th} component has a composition referred to as $x_{i_u,k}$. Each sink has a range of acceptable flowrate and composition of species; and any stream must satisfy that range before being fed to that sink, i.e.

$$G_{i_u}^{min} \le G_{i_u} \le G_{i_u}^{max} \qquad i_u \in INPUT_u, \quad u \in SINKS \qquad (3\text{-}1)$$

$$x_{i_u,k}^{min} \le x_{i_u,k} \le x_{i_u,k}^{max} \qquad i_u \in INPUT_u, \quad u \in SINKS, \quad k \in K \qquad (3\text{-}2)$$

For each sink, there are vectors of design and operating degrees of freedom abbreviated as (d_u and p_u), respectively. These vectors are subjected to manipulation and optimization. They correspond to no/low cost modifications such as the changes in design and operating conditions. D_u and P_u designate the intervals of permissible values of design and operating degrees of freedom for sink *u*, respectively. Hence, $d_u \in D_u$ and $p_u \in P_u$. Examples of d_u include structural decisions such as increasing surface area, adding or replacing internals such as packing, trays and baffles, etc. Examples of p_u include operating conditions that can be altered for existing equipment such as temperature, pressure, etc.

The objective is to maximize no/low-cost debottlenecking to maximize production of a desired product and to identify the most cost-effective strategies to attain this maximum production. No/low-cost debottlenecking is limited to manipulating design and operating variables of existing units.

Solution approach

The solution approach is based on the following key steps:

1. Formulation of the production maximization problem as an optimization problem at no/low cost modification options. In this step, an optimization program is formulated to simultaneously link all the design and operating degrees of freedom. It also exploits synergies among the units and streams in order to attain maximum production flowrate.
2. Utilization of interval arithmetic for bounding. Because of the non-linearity and non-convexity of most chemical process models, it is essential to identify bounds within the range of the function that will yield the most meaningful results. Interval arithmetic is used to identify the upper bound of production flowrate. It is important to mention that interval arithmetic does not necessarily guarantee the feasibility of the upper bound. Instead, it guarantees that the maximum achievable value of the function (production flowrate in our case) will not exceed this upper bound. The identification of the upper bound in this step serves as the target for the next step.
3. The identification of a feasible maximum production flowrate. In this step, production is maximized subject to the developed model and the identified target, which is equal to the upper bound as determined in the previous step. If a feasible

solution is found, we move to the next step. Otherwise, the current upper bound is reduced by a certain value (ε). This process continues until a feasible solution is reached. If the feasible solution is much less than targeted, select tighter interval-bounding technique and go back to step II.

4. Determination of the most cost-effective implementation to achieve maximum production flowrate. As there are often several paths to reaching maximum production flowrate, the most cost-effective one must be identified. In this step, the cost is minimized subject to the cost model and the maximum production value (identified in the previous step).

This approach simultaneously links all the design and operating degrees of freedom for the entire process and identifies the maximum achievable production flowrate. It also guarantees a global bound for targeting the maximum attainable debottlenecking through the implementation of the interval arithmetic technique. Finally, this approach identifies the most cost-effective approach to attaining maximum production flowrate. Fig. 3-3 shows a flowchart that outlines the solution approach.

Model development for no/low cost debottlenecking option

The objective function here is to maximize the production $\left(G_p\right)$. In order to develop the constraints, the process model should be described in terms of the decision variables and the optimization degrees of freedom for the various units. An effective way of describing the process model in terms of the manipulated design and operating variables is based on the concept of path equations (Noureldin and El-Halwagi, 1999). The flowsheet is described as a number of sources (process streams) and sinks (process units). Consider a process unit, u, with a set of input streams INPUT$_u$ = $\{i_u \mid i_u = 1,2...,N_u^{in}\}$ and a set of output streams OUTPUT$_u$ = $\{j_u \mid j_u = 1,2...,N_u^{out}\}$. The input stream, i_u, has a flowrate G_{i_u}. Each stream has a set K of targeted components. The kth component has a composition referred to as $x_{i_u,k}$. Similarly the output streams have flowrates and compositions referred to as W_{j_u} and $y_{j_u,k}$, respectively.

The decision variables for unit u can be classified into design and operating variables, designated as d_u and p_u, respectively. Hence, the performance model for unit u can be expressed as a set of equations represented by:

$$\begin{aligned}(W_{j_u}, y_{j_u,k} : j_u = 1,2,..., N_u^{out} \text{and } k \in K) = \\ f_u(G_{i_u}, x_{i_u,k} : i_u = 1,2,..., N_u^{in} \text{and } k \in K, d_u, p_u)\end{aligned} \tag{3-3}$$

For each unit, there are bounds on the admissible ranges for the design and operating variables, i.e.

$$d_u^{\min} \le d_u \le d_u^{\max} \tag{3-4}$$

and

$$p_u^{\min} \le p_u \le p_u^{\max} \tag{3-5}$$

Additionally, the overall and component material balances for unit u can be written as:

$$\sum_{j_u=1}^{N_u^{out}} W_{j_u} = \sum_{i_u=1}^{N_u^{in}} G_{i_u} \tag{3-6}$$

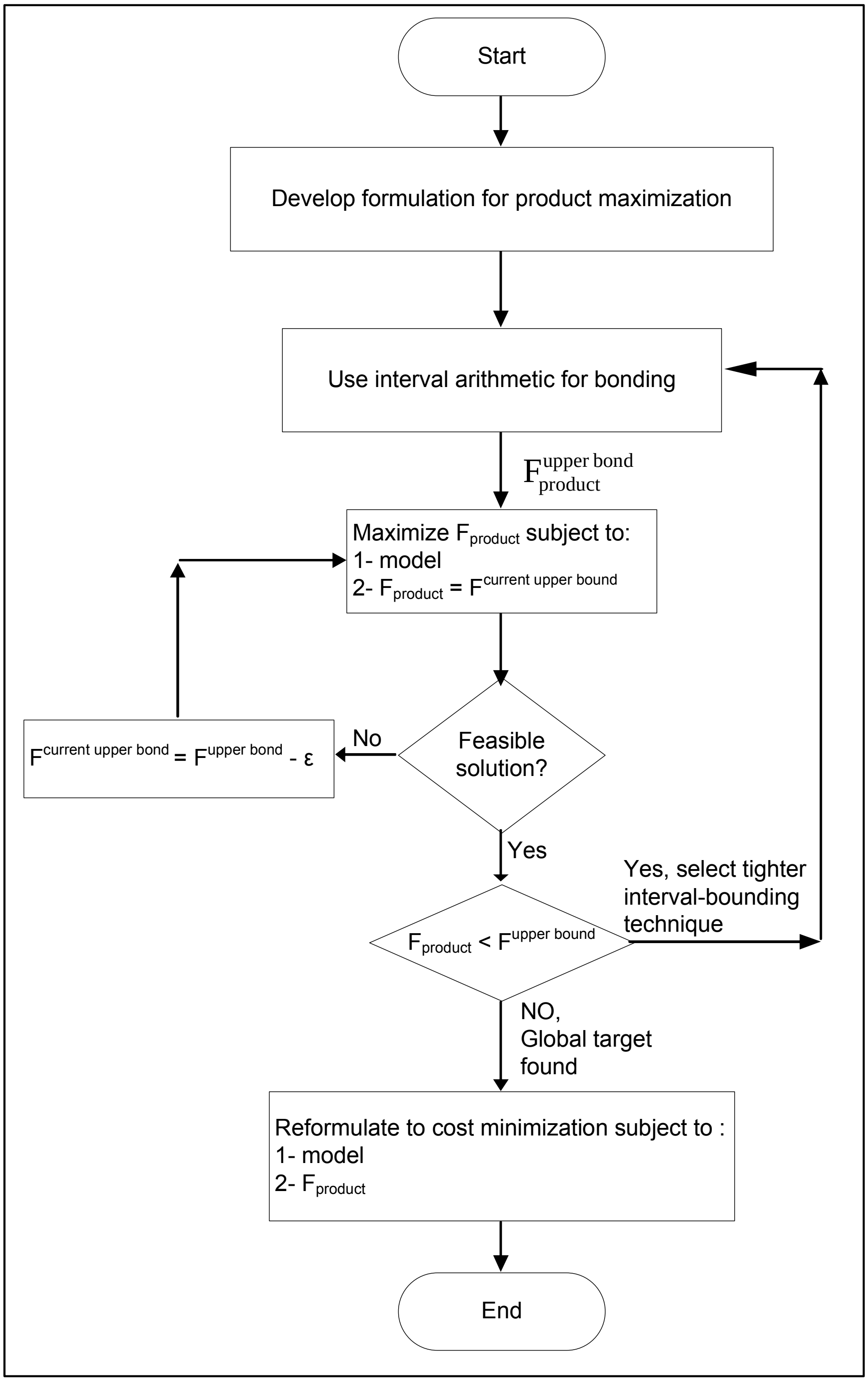

Fig. 3-3. Flowchart of the debottlenecking approach

and

$$\sum_{j_u=1}^{N_u^{out}} W_{j_u} * y_{j_u,k} = \sum_{i_u=1}^{N_u^{in}} G_{i_u} * x_{i_u,k} + \text{Net\_Gen}_{u,k} \qquad k \in K \qquad (3\text{-}7)$$

where Net_Gen$_{u,k}$ is the net rate of generation of component k in unit u.

Other important constraints include feed-flowrate limitations to each unit:

$$G_u^{\min} \le \sum_{i_u=1}^{N_u^{in}} G_{i_u} \le G_u^{\max} \qquad (3\text{-}8)$$

Composition limitations:

$$x_{i_u,k}^{\min} \le x_{i_u,k} \le x_{i_u,k}^{\max} \qquad (3\text{-}9)$$

It is also necessary to account for the competing demands for utilities. The process has several utilities (e.g., heating, cooling, steam, etc.). Let us use the index q to designated the type of utility and $Q_{q,u}$ as the rate of consuming the qth utility at the uth unit. Suppose that the maximum plant capacity of the qth utility is $Q_q^{\max}$. Therefore, the following utility-capacity constraint should be used:

$$\sum_{u=1}^{N_{Sinks}} Q_{q,u} \le Q_q^{\max} \qquad (3\text{-}10)$$

The foregoing formulation is a non-linear program (NLP) whose solution provides the maximum extent of debottlenecking and the optimal values of the design and operating variables. Because of the general nature of the process model (path equations), the formulated NLPs are likely to be non-convex thereby rendering the identification of a global solution a challenging task. Therefore, it is necessary to determine rigorous targets on maximum extent of debottlenecking prior to solution. In this regard, interval analysis can provide a very effective tool for bounding the solution.

Interval analysis

Interval analysis is a useful concept that can be used for inclusion of functional ranges. Interval arithmetic was first introduced by Moore (1966) for rounding floating-point computing errors. The most significant characteristic of interval arithmetic is that resulting intervals are guaranteed to contain the set of all possible results from any interval computation. Methods and applications of interval analysis have been addressed by many authors (Hua et al., 1999; Moore, 1979; Noureldin and El-Halwagi, 1999; Ratschek and Rokne, 1984; Schnepper and Stadtherr, 1996; Sinha et al., 2003; Vaidyanathan and El-Halwagi, 1994).

Interval operations enable the processing of ranges. Consider a real variable x, bounded by the ranges, $x^l \leq x \leq x^u$. The interval X can be defined such as $x \in X$ where $X = [x^l, x^u]$. In the same manner, an interval Y can be defined for a real variable y such that $y \in Y$. In order to deal with processing the intervals that bound real numbers, interval arithmetic could be utilized. Let us designate * as an interval arithmetic operation (e.g. addition, subtraction, multiplication, division) such that:

$$X * Y = \{x * y : x \in X, y \in Y\} \qquad (3\text{-}11)$$

Constructive rules for interval operations include the following:

$$X+Y = [\, x^l , x^u] + [\, y^l , y^u] = [\, x^l + y^l, x^u + y^u] \qquad (3\text{-}12)$$

$$X-Y = [\, x^l , x^u] - [\, y^l , y^u] = [\, x^l - y^u, x^u - y^l] \qquad (3\text{-}13)$$

$X\,Y = [\,x^l , x^u][\,y^l , y^u] = [\min(\,x^l y^l, x^u y^u, x^l y^u, x^u y^l), \max(\,x^l y^l, x^u y^u, x^l y^u, x^u y^l)]$ (3-14)

$X / Y = [\,x^l , x^u]/[\,y^l , y^u] = [\,x^l , x^u][1/y^u , 1/y^l]$ when $0 \notin [\,y^l , y^u]$ (3-15)

Another useful property is the inclusion isotonicity of interval operations

If $X \subset W$ and $Y \subset Z$ then $X{*}Y \subset W{*}Z$ (3-16)

Interval arithmetic can be used to identify bounds on the range of the function. Consider a function f(x) whose range over interval X is defined as $\square f(X)$, i.e. $\square f(X) = \{f(x){:}x \in X\}$ where x is an n-dimensional vector and $x \in X$. An inclusion function F is called an inclusion function for f over interval X if

$\square f(X) \subseteq F(X)$ (3-17)

This inclusion is generally applicable regardless of the non-linearity and non-convexity of the function.

Motivating example revisited

To demonstrate the applicability of the simultaneous debottlenecking approach and to compare it to the conventional sequential approach, the motivational example of the hydrocarbon processing facility is revisited. As before, this example is limited to the situation where debottlenecking is achieved without an investment of new capital.

A model was formulated to maximize the value of the product flowrate, F_{14}, through simultaneous debottlenecking of units. By using the proposed interval inclusion technique, a target for the product flowrate (F_{14}) was found to be 93,416 kg/hr. Next, a product maximization nonlinear programming problem was formulated. The interval-based target was included as a constraint. The optimization software LINGO was used to solve the problem. The identified value of the maximum product flowrate was found to match the target (93,416 kg/hr). Therefore, a global solution has been identified (Fig. 3-4). Clearly, the identified solution is superior to the result obtained through the sequential approach (31,113 kg/hr) and that obtained at arbitrary cooling duties (48,460 kg/hr). The large difference in solutions obtained by the sequential and the simultaneous approaches underscores the significance of developing the simultaneous approach. In the case of the sequential approach, the obtained solution suggested maximum debottlenecking of the compressor followed by maximum debottlenecking of recative separator I. On the other hand, the newly-developed simultaneous approach suggested partial debottlenecking of the compressor and maximum debottlenecking of separator II with no debottlenecking of reactive separator I. The latter suggestion is indeed sensible given that separator II has a strong effect on the flow rate of F_{14}.

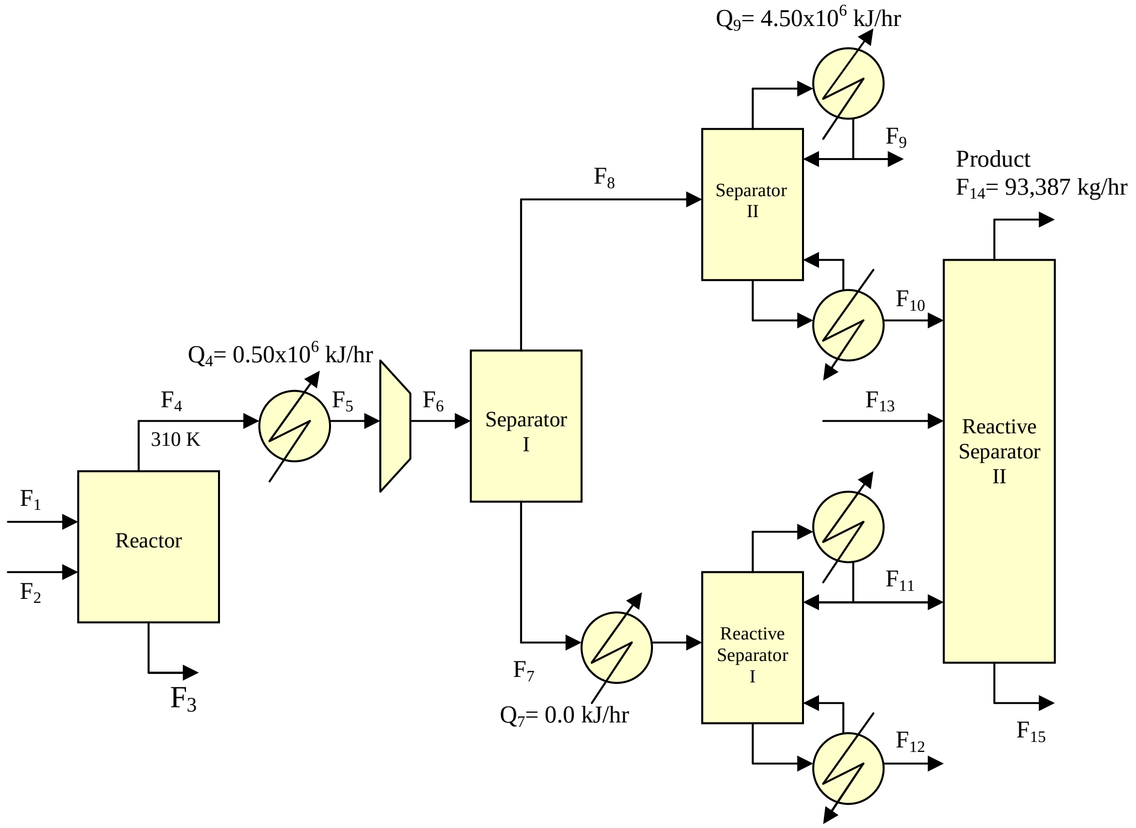

Fig. 3-4. Flowsheet of motivating example (simultaneous debottlenecking)

Second case study: styrene production

A petrochemical complex (Fig. 3-5) produces a number of products and byproducts including hydrogen and a stream containing phenyl acetylene. Both streams are fed to a styrene plant where the following main reaction takes place to produce styrene:

$$C_6H_5C \equiv CH + H_2 \xrightarrow{r_1} C_6H_5CH = H_2$$

Phenyl Acetylene Styrene

This reaction is carried out in a bubble column slurry reactor (BCSR) where hydrogen is bubbled in a slurry containing the phenyl acetylene stream and the catalyst.

The reaction takes place in the slurry phase. A consecutive reaction also takes place in the BCSR and results in the undesirable conversion of styrene to ethyl benzene as follows:

$$\underset{\text{Styrene}}{C_6H_5CH = H_2} + H_2 \xrightarrow{r_2} \underset{\text{Ethyl Benzene}}{C_6H_5CH_2CH_3}$$

Mochizuki and Matsui (1976) studied the kinetics of these two reactions and proposed the following rate expressions at the reaction temperature of 322 K:

$$r_1 = \frac{53.0C_A C_B}{(1 + 7.3C_A + 9.8C_B^{0.5} + 0.29C_C)^3} \tag{3-18}$$

and

$$r_2 = \frac{0.43C_B C_C}{(1 + 7.3C_A + 9.8C_B^{0.5} + 0.29C_C)^3} \tag{3-19}$$

At present, the plant has a maximum production of the phenyl acetylene stream (flowrate: 21.7 kmol/hr and concentration of 0.2 kmol/m^3) is fed to the BCSR. Additionally, the maximum flowrate of hydrogen allotted to the styrene plant is also fed to the BCSR (flowrate: 141.9 kmol/hr of pure hydrogen). The hydrogen is fed to the reactor via a pressure regulator at a maximum pressure of 1,200 kPa. The current production of styrene is 13.3 kmol/hr. It is desired to enhance the production of styrene by deobttlenecking the BCSR without spending capital investment. Because of the competing nature of the two reaction, the BCSR may be optimized by adjusting its flowrate and pressure of the hydrogen, the interphase mass transfer, the reaction kinetics, and the composition profiles. The BCSR model is given in Appendix II.

By using the proposed interval inclusion technique, a target for the styrene production rate was found to be 14.2 kmol/hr. Next, a product maximization nonlinear programming problem was formulated. The interval-based target of styrene production was listed as a constraint. The optimization software LINGO was used to solve the problem. The identified value of the maximum product flowrate was found to match the target (14.2 kmol/hr). Consequently, the global solution has been determined. The optimum values for the hydrogen flowrate and pressure were found to be 90.1 kmol/hr and 1,182 kPa, respectively. Therefore, as a result of the proposed approach, the flowrate of hydrogen has been decreased by 36.5%, the pressure has been reduced by 1.5%, and the styrene production has been increased by 6.8%.

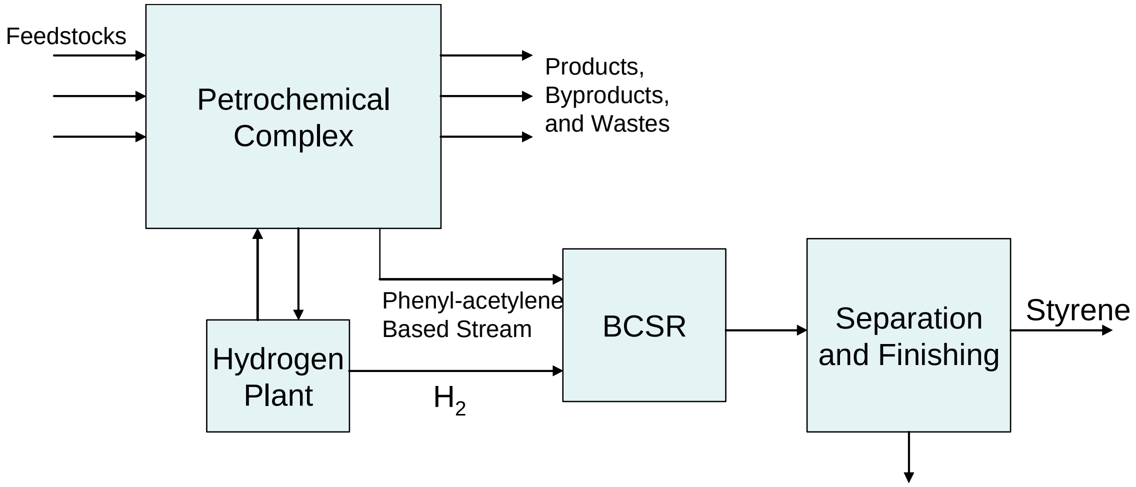

Fig. 3-5. Flowsheet for the styrene case study

Conclusions

A novel methodology for debottlenecking a chemical process for production maximization has been introduced. This new approach is simultaneous in nature and is based upon posing the debottlenecking task as a process integration task which links all the design and operative degrees of freedom; and exploits synergies among the units and streams to attain maximum debottlenecking. A mathematical representation was formulated to characterize the various interactions among the operating variables and how they affect the extent of debottlenecking. Because of the non-linearity and non-convexity of most process models, a global bounding technique was employed to determine rigorous targets for debottlenecking. An optimization formulation was developed and solved to identify process modifications needed to attain the desired target for debottlenecking. Finally, two case study were solved to illustrate the applicability and merits of the new approach.

CHAPTER IV

SIMULTANEOUS PROCESS DEBOTTLENECKING AND HEAT INTEGRATION

Introduction

Proper heat integration in a chemical plant is essential for an efficient operation and can lead to considerable cost savings. Over the past 30 years, significant research contributions have been made in developing design techniques for the synthesis of heat exchange networks. Much of this work has focused on heat integration as the overarching goals with objectives such as minimizing heating and cooling utilities and total annualized cost of the network. On the other hand, much less work has been done in the area of reconciling heat integration with other process objectives.

One of the key process objectives is debottlenecking. For profitable processes with sold-out products, there is an incentive to increase the product throughout. As production is increased, a processing unit or a process resource reach their maximum capacity and form a bottleneck. In such cases, it is necessary to “debottleneck” the process to increase the production. An important class of debottlenecking is the no/low cost approach in which no new equipment are added. It involves modification of design and operating conditions and rerouting of streams. Such modifications may lead to changes in heat duties. Since the focus here is on no/low cost strategies, no new heat exchangers, furnace, boilers, or cooling/refrigeration systems are to be added. This issue poses two challenges. First, maximum use should be made of current utilities to avoid the installation of new boilers, furnaces, or cooling/refrigeration systems. Second, effective utilization of existing heat exchangers should be made so as to mitigate the need for adding new heat exchangers. In order to address the foregoing challenges, we propose to include a combination of heat integration and retrofitting of heat exchange networks (HENs) into the overall design procedure for process debottlenecking. Such retrofitting must take into consideration the existing equipment and layout and account for the trade-offs among energy savings, modification costs, and debottlenecking benefits.

Retrofitting is complicated, as a chemical plant is primarily comprised of the process equipment, the utility system, and a heat exchange network. These components are interconnected and a change in any one of them will have an affect on the other systems. Retrofitting of heat exchange network may be considered in an effort to reduce utility costs or as a result of changes in streams or other operating conditions within the plant (e.g. as a result of debottlenecking.)

In a typical chemical plant, heat integration is a critical element in the debottlenecking process. The difficulty of incorporating heat integration into a debottlenecking design method lies in the strong interaction between the two objectives. One way to resolve the conflict is to adopt a decomposition approach, where a certain extent of debottlenecking is related to a certain set of heating and cooling requirements. With the heating and cooling requirements temporarily fixed; and with all flow-rates and temperatures of hot and cold streams known; the minimum heating and cooling duties may be calculated (Douglas 1985; Linnhoff and Hindmarsh 1983; Saboo et al. 1985). The procedure is then repeated and a tradeoff is established between the debottlenecking and heat integration. While this approach may be readily implemented and automated, it may be limited because it is sequential and it may fail to properly consider the strong interaction between the process and potential heat integration. In general, this sequential approach leads to suboptimal solutions.

Papoulias and Grossmann (1983) developed a strategy for simultaneous optimization of the process and heat integration based on mixed integer linear programming (MILP). However, while the flow rates of the streams can be treated as continuous variables, the temperatures can only be assumed as discrete values. Duran and Grossmann (1986) developed a model that overcomes this limitation. They proposed a set of inequalities that rely on a pinch location model and predict the minimum utility requirements for variable flows and temperatures for the process streams and fixed minimum temperature approach. A smooth approximation is used to handle the structural non-differentiabilities that arise in the formulation. This formulation is very effective in handling a wide variety of heat integration problems. However, care must be given to cases when the approximation at some points becomes ill-conditioned and for cases involving errors associated with the heat loads of isothermal streams and intermediate utilities. Yee and Grossmann (1990) introduced a superstructure representation which includes many possible flowsheet alternatives. However, the number of variables and constraints that are needed to produce the required mathematical representations may be large (Bagajewicz et al. 1998). Thus, simplifying assumptions are required.

Grossmann et. al. (1998) developed another method for the simultaneous optimization of flowsheet and heat integration. It is based on introducing integer variables that give a general formulation for heat loads and the composite curves. This method overcomes the limitations of smooth approximation method.

In chapter III a new approach for simultaneous no/low cost debottlenecking of chemical plant was introduced. Heat integration was not considered in this approach. In this chapter, we will introduce a simultaneous approach to the debottlenecking and heat integration. This approach will consider the retrofitting of plant's heat exchange network at no/low cost strategy. A case study will be presented to show the applicability of this approach.

Problem statement

Given a process with certain feedstock of raw material(s) and existing units of the process, which are referred to as sinks. The set of sinks is SINKS= $\{u:u= 1, N_{sinks}\}$ and each sink has a set of input streams ($INPUT_u$) and a set of output streams ($OUTPUT_u$).

The input stream, i_u, has a flowrate G_{i_u} at temperature T_{i_u}. Each stream has a set K of desired components. The k^th^ component has a composition referred to as $x_{i_u,k}$. Each sink has a range of acceptable flowrate and composition of species; and any stream must satisfy that range before being fed to that sink, i.e.

$$G_{i_u}^{min} \le G_{i_u} \le G_{i_u}^{max} \qquad i_u \in INPUT_u, \quad u \in SINKS \qquad (4\text{-}1)$$

$$x_{\mathrm{i_u},k}^{\min} \le x_{\mathrm{i_u},\mathrm{k}} \le x_{\mathrm{i_u},k}^{\max} \qquad \mathrm{i_u} \in \mathrm{INPUT_u}, \quad \mathrm{u} \in \mathrm{SINKS}, \quad \mathrm{k} \in \mathrm{K} \tag{4-2}$$

$$\mathrm{T_{i_u}^{min}} \le \mathrm{T_{i_u}} \le \mathrm{T_{i_u}^{max}} \tag{4-3}$$

For each sink, there are vectors of design and operating degrees of freedom abbreviated as ($\mathrm{d_u}$ and $\mathrm{o_u}$), respectively. These vectors are subjected to manipulation and optimization. They correspond to no/low cost modifications such as the changes in design and operating conditions. $\mathrm{D_u}$ and $\mathrm{O_u}$ designate the intervals of permissible values of design and operating degrees of freedom for sink *u*, respectively. Hence, $\mathrm{d_u} \in \mathrm{D_u}$ and $\mathrm{o_u} \in \mathrm{O_u}$. Examples of $\mathrm{d_u}$ include structural decisions such as increasing surface area, adding or replacing internals such as packing, trays and baffles, etc. Examples of $\mathrm{o_u}$ include operating conditions that can be altered for existing equipment such as temperature, pressure, etc.

There are two sets of streams; a set of hot streams and a set of cold steams. The set of hot streams that are to be cooled, $H = \left\{ i \middle| i = 1, N_{HP} + N_{HU} \right\}$, consist of a subset of process hot streams, $HP = \left\{ i \middle| i = 1, N_{HP} \right\}$, and a subset of utility hot streams $HU = \left\{ i \middle| i = 1, N_{HU} \right\}$. On the other hand the set of cold streams that are to be heated, $C = \left\{ i \middle| i = 1, N_{CP} + N_{CU} \right\}$, consists of a subset of process cold streams, $CP = \left\{ i \middle| i = 1, N_{CP} \right\}$, and a subset of utility cold streams, $CU = \left\{ i \middle| i = 1, N_{CU} \right\}$. The process has a fixed value of ΔT_m. Streams flowrates, and inlet and outlet temperatures are unknown and should be determined optimally in the feasible space for the process optimization and heat integration.

The objective is to maximize production of a desired product by using no/low cost strategies such as modification of design and operating conditions, minor structural modifications, heat integration, and retrofitting of heat exchangers.

Solution approach

The solution approach is based on the following key steps:

1. Targeting: in this step, the maximum achievable value of production flowrate is determined. The interval arithmetic is used for targeting proposes (upper bound.) This step is essential to identify bounds within the range of the function that will yield the most meaningful results. It is important to mention that interval arithmetic does not necessarily guarantee the feasibility of the upper bound. However, it guarantees that the maximum achievable value of the function (production flowrate in our case) will not exceed this upper bound.
2. Simultaneous production maximization and utility optimization: in this step, the maximum production flowrate and minimum heating and cooling duties are simultaneously optimized. The process debottlenecking model, introduced in chapter III, is expanded to include the process heat integration. This model is explained in detail later in this chapter.
3. Minimum heat transfer area calculation: in this step, the minimum required heat surface area for heat transfer among hot streams, cold streams, and utilities in the HEN is calculated. The area is calculated assuming overall countercurrent heat exchange which manifests itself as horizontal heat transfer on the composite

curves. This is the minimum area only when the heat transfer coefficients for all streams and utilities are equal. This step is essential since our approach is based on no/low-cost debottlenecking and the need to examine the possibility of current heat exchange network (available heat exchangers) handling required heat exchange.

To determine the minimum heat transfer area, utility streams must be included with the process streams in the composite curves to obtain the balanced composite curves (Smith 2005). The minimum area of heat transfer, $A_{\min}$, can be calculated from:

$$A_{\min} = \sum_{i=1}^{Interval} \left(\frac{1}{F \Delta T_{LM}} \right)_i \sum_{j=1}^{Streams} \left(\frac{q_j}{h_j} \right)_i \quad (4\text{-}4)$$

where q_j is heat exchange by stream *j* in interval *i*

h_j is heat transfer coefficient of stream *j* in interval *i*

F is the correction fact accounting for non-countercurrent flow

ΔT_{LM} is log mean temperature difference in interval *i*

If the calculated heat transfer area is equal to or less than available heat transfer area, we go to step VI. Otherwise, we go to nest step.

4. If excess utilities are available in the process, the minimum utility consumption is increased by an increment (ω) and the procedure returns to step II. This should continue until calculated heat transfer area becomes equal to or less than available heat transfer area and we go to step VI; or until there is not more utility and we go to step V.

5. If all excess utilities are consumed and the calculated heat transfer area is still higher than available heat transfer area, a new target for production flowrate is determined and we go back to step II. The new target is equal to the optimum production flowrate (determined previously in step II) minus a small value ε.
6. Once we reach a calculated heat transfer area that is equal to or less than available heat transfer area, the heat exchange network is retrofitted. It is important to mention that when calculated heat transfer area is equal to or less than the available heat transfer area, it does not imply that the current heat exchange network can be retrofitted, at no/low cost retrofitting, to accommodate changes in process's flowrates and temperatures.

   The task in this step is to match the hot and cold process streams with each other or with external utilities with the current process network of heat exchangers to satisfy the minimum utility that was calculated in step II. If HEN can be retrofitted we stop; otherwise we go back to step IV.

   Fig. 4-1 shows a flowchart that outlines this solution approach.

Simultaneous production maximization and utility optimization

As mentioned previously in this work the maximum production flowrate and minimum heating and cooling duties are simultaneously optimize. It is based on interacting two formulations. First, a sub-model is developed and solved maximizing the production flowrate . It is similar to the model developed in Chapter III. The second one is for heat integration and utility optimization. In this model, streams flowrates and temperatures are considered as optimization variables and these two sub-models communicate simultaneously.

Grossmann et. al. (1998) developed a method for the simultaneous synthesis of the heat exchange network and the process. This method is slightly modified and used in this chapter to determine minimum utility consumption while dealing with streams flowrates and temperatures as optimization variables. The method is based on the HEN pinch concept. To better understand this method the solution will first be presented graphically. By plotting the composite hot and cold streams, we can see how these individual streams merge into one composite stream through linear superposition (Fig. 4-2). As both composite streams move until they touch at the pinch point, we can observe the following properties:

1. The only potential pinch point candidates (Fig. 4-2) are the corner points on the composite streams, as these correspond to the inlets of any hot or cold streams. The set of pinch point candidates are represented by P.

   The total heat lost by the hot streams in the network must equal the total heat gained by the cold streams; resulting in a total balance of energy in the system. In order to achieve a minimum utility consumption, no heat may be transferred across the pinch. Hence, we can break the problem down into two separate portions – above the pinch and below the pinch (Fig. 4-3). If the heat lost by the hot stream equals the cold stream's heat gain, then the energy is balanced for each part.

2. The heat exchange becomes thermodynamically feasible when the cold composite stream lies above the hot composite stream at each level. This reveals the true pinch points.
3. Should the composite streams touch at any pinch point candidate, other than at the true pinch point (Fig. 4-4), the hot composite stream must be slid vertically until it touches the cold composite stream at that pinch point candidate. In contrast to statement 3 (above), we can readily anticipate that an exchange situation such as this (4) is thermodynamically infeasible, as both streams must touch only at the true pinch point.

Therefore, the following expressions hold true:

$$\begin{array}{l}\text{Heat lost by the hot}\\ \text{streams above the}\\ \text{pinch point candidate}\end{array} - \begin{array}{l}\text{heat gained by the cold}\\ \text{stream above the pinch}\\ \text{point candidate}\end{array} = \alpha \quad , \quad \alpha \geq 0 \tag{4-5}$$

and

$$\begin{array}{l}\text{Heat lost by the hot}\\ \text{streams below the}\\ \text{pinch point candidate}\end{array} - \begin{array}{l}\text{heat gained by the cold}\\ \text{stream below the pinch}\\ \text{point candidate}\end{array} = \alpha \quad , \quad \alpha \leq 0 \tag{4-6}$$

while α vanishing only at the true pinch point. In other words,

$$\begin{array}{l}\text{Heat lost by the hot}\\ \text{streams above the}\\ \text{pinch point candidate}\end{array} - \begin{array}{l}\text{heat gained by the cold}\\ \text{stream above the pinch}\\ \text{point candidate}\end{array} \geq 0 \qquad p \in P \tag{4-7}$$

and

$$\begin{array}{l}\text{Heat lost by the hot}\\ \text{streams below the}\\ \text{pinch point candidate}\end{array} - \begin{array}{l}\text{heat gained by the cold}\\ \text{stream below the pinch}\\ \text{point candidate}\end{array} \leq 0 \qquad p \in P \tag{4-8}$$

As the equality applies in equations 4-7 and 4-8 only when the pinch point candidate is true. Equations 4-7 and 4-8 characterize the two pinch points and meet the criteria needed to promote the feasibility of the thermodynamic exchange. This is in contrast to the infeasibility of the heat exchange, should the two composite streams touch at any pinch point candidate other than at the pinch point that is true. We can thus, eliminate either equation 4-7 or 4-8 as being feasible, since the network's total energy must always be balanced. Equation 4-8 and the energy balance equation will therefore be used in this work to identify the true pinch point and ensure thermodynamic feasibility.

To minimize the utility we need to evaluate the optimum flow rates of all the hot and cold streams, and the location of pinch points within the HEN. As previously discussed, since the problem of locating the pinch and insuring thermodynamic feasibility entails incorporating energy balance constraints below each pinch point candidate, one ought to have explicit expressions for the exchange loads of the hot and the cold below each potential pinch point. It is, therefore, convenient to introduce the following binary integer variables:

$$\lambda_{i,p}^{t} = \begin{cases} 1 \text{ if } T_i^t < T^p & i \in H \\ 0 \text{ if } T_i^t \geq T^p & p \in P \end{cases} \tag{4-9}$$

$$\lambda_{i,p}^{s} = \begin{cases} 1 \text{ if } T_i^s < T^p & i \in H \\ 0 \text{ if } T_i^s \geq T^p & p \in P \end{cases} \tag{4-10}$$

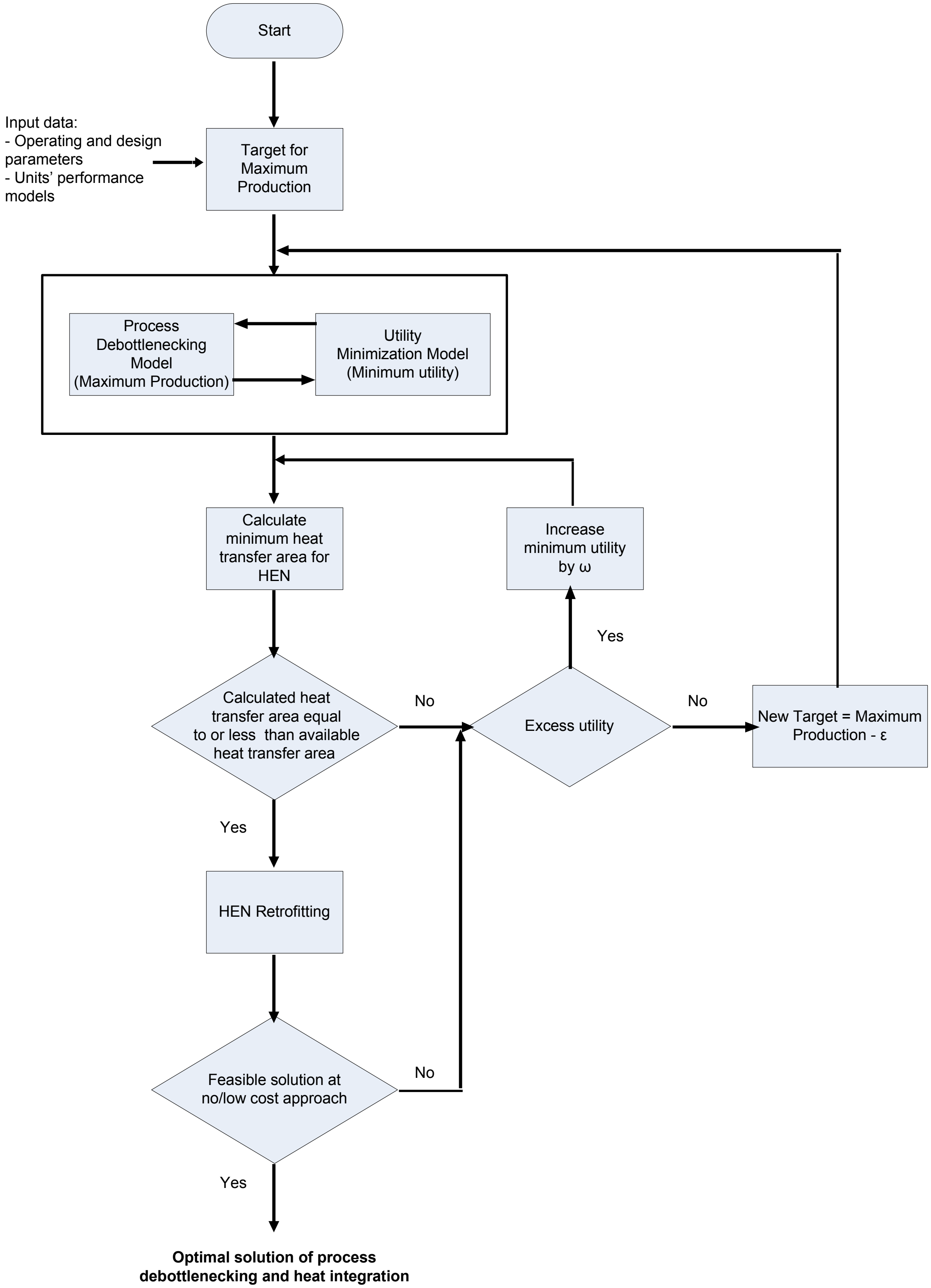

Fig. 4-1. Flowchart of the simultaneous debottlenecking and heat integration approach

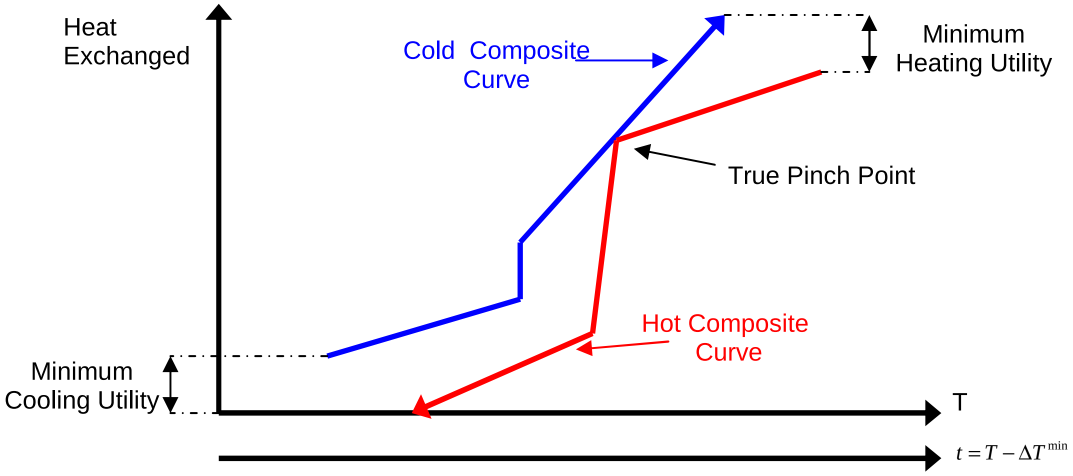

Fig. 4-2. Pinch diagram when composite curves touch at the true pinch point.

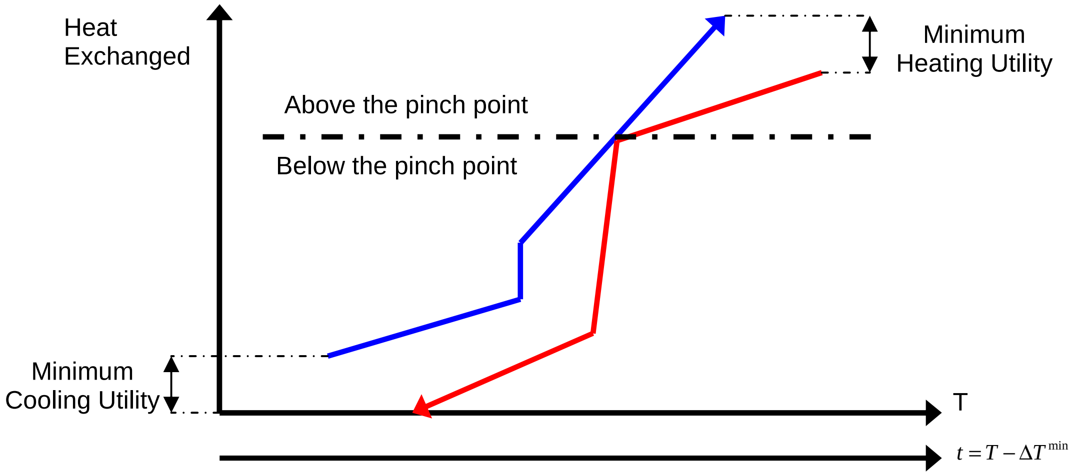

Fig. 4-3. Breaking the pinch diagram to two parts: above the pinch point and below the pinch point.

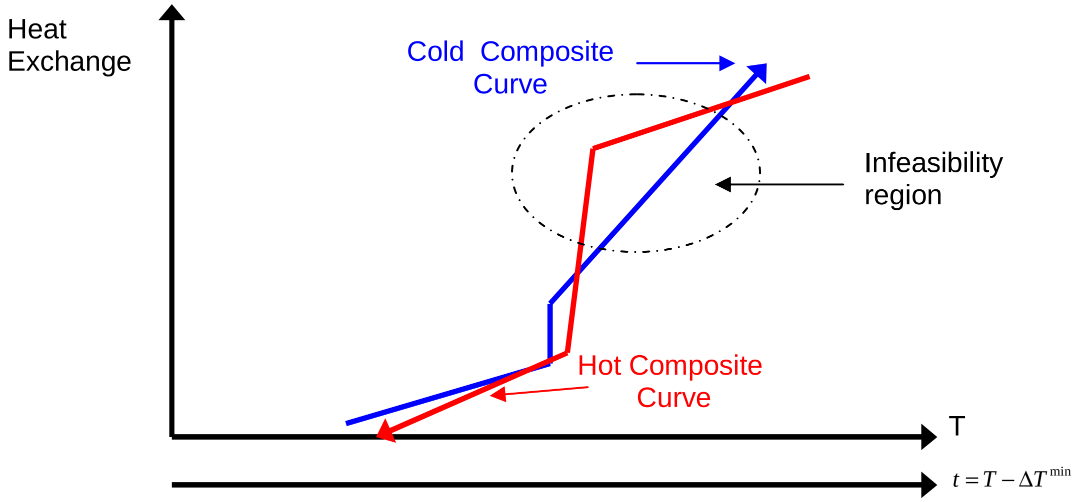

Fig. 4-4. Composite curves touch at a point other than the true pinch point.

$$\eta^{t}_{j,p} = \begin{cases} 1 \text{ if } t^{t}_{j} < t^{p} \\ 0 \text{ if } t^{t}_{j} \geq t^{p} \end{cases} \qquad \begin{matrix} j \in C \\ p \in P \end{matrix} \tag{4-11}$$

$$\eta^{s}_{j,p} = \begin{cases} 1 \text{ if } t^{s}_{j} < t^{p} \\ 0 \text{ if } t^{s}_{j} \geq t^{p} \end{cases} \qquad \begin{matrix} j \in C \\ p \in P \end{matrix} \tag{4-12}$$

where T^{p} and t^{p} are the equivalent temperature of the i^{th} hot stream and the j^{th} cold stream at the pinch point candidate $p \in P$ in the heat exchange network. Therefore, we have the following expressions:

$$\begin{matrix} \text{Heat lost be hot stream} \\ i \text{ below a potential pinch} \\ \text{point in the HEN} \end{matrix} = F_i\, Cp_i \left\{ \lambda^{t}_{i,p} \left(T^{p} - T^{t}_{i} \right) - \lambda^{s}_{i,p} \left(T^{p} - T^{s}_{i} \right) \right\} \qquad \begin{matrix} i \in H \\ p \in P \end{matrix} \tag{4-13}$$

and

Heat gained be cold stream

j below a potential pinch $= f_j\, Cp_j \left\{ \eta^s_{j,p}\left(t^p - t^s_j\right) - \eta^t_{j,p}\left(t^p - t^t_j\right) \right\}$ $\quad j \in C,\ p \in P \quad$ (4-14)

point in the HEN

The above expressions parameterize the exchange load below the pinch point candidates. To examine the validity of above expressions, let consider all the possible locations of hot stream *i* with respect to the pinch:

1. when hot stream *i* lies completely above a potential pinch point p, according to equations 4-9 and 4-10 we have $\lambda^t_{i,p} = \lambda^s_{i,p} = 0$ and the i^{th} hot stream load below the potential pinch point is zero, as expected.
2. when the hot stream *i* lies completely below the potential pinch point, then the value of each $\lambda^t_{i,p}$ and $\lambda^s_{i,p}$ is unity and the i^{th} hot load below the potential pinch point is

$$F_i\, Cp_i \left\{ \left(T^p - T^t_i\right) - \left(T^p - T^s_i\right) \right\} = F_i\, Cp_i \left(T^s_i - T^t_i\right)$$

which is the proper expression.

3. when the i^{th} hot stream straddles the potential pinch point ($T^s_i > T^p$ and $T^t_i < T^p$), then $\lambda^s_{i,p} = 0$ and $\lambda^t_{i,p} = 1$. Thus, the hot i^{th} stream load below the potential pinch point is

$$F_i\, Cp_i \left\{ \left(T^p - T^t_i\right) - 0 \right\} = F_i\, Cp_i \left(T^p - T^t_i\right)$$

which represent the correct expression.

Having established that, we are in the position to present the mathematical formulation of simultaneous production maximization and utility optimization as follows:

Simultaneous production maximization and utility optimization mathematical formulation

Objective function: Max G_p

where G_p is the production of desired component

subject to

units' performance models

$$
\begin{aligned}
&(W_{j_u}, y_{j_u,k}, T_{j_u}^{out} : j_u = 1,2,...,N_u^{out} \text{ and } k \in K) = \\
&\qquad f_u(G_{i_u}, x_{i_u,k}, T_{j_u}^{in} : i_u = 1,2,...,N_u^{in} \text{ and } k \in K, d_u, p_u)
\end{aligned}
\tag{4-15}
$$

bounds on the admissible ranges for the design and operating variables of each unit

$$d_u^{min} \leq d_u \leq d_u^{max} \tag{4-16}$$

and

$$o_u^{min} \leq o_u \leq o_u^{max} \tag{4-17}$$

overall material, energy and component balances for units u's

$$\sum_{j_u=1}^{N_u^{out}} W_{j_u} = \sum_{i_u=1}^{N_u^{in}} G_{i_u} \tag{4-18}$$

$$\sum_{j_u=1}^{N_u^{out}} W_{j_u} * h_{j_u} = \sum_{i_u=1}^{N_u^{in}} G_{i_u} * h_{i_u} \tag{4-19}$$

and

$$\sum_{j_u=1}^{N_u^{out}} W_{j_u} * y_{j_u,k} = \sum_{i_u=1}^{N_u^{in}} G_{i_u} * x_{i_u,k} + \mathrm{Net\_Gen}_{u,k} \qquad k \in K \qquad (4\text{-}20)$$

where Net_Gen$_{u,k}$ is the net rate of generation of component k in unit u.

Feed-flowrate limitations to each unit:

$$G_u^{\min} \le \sum_{i_u=1}^{N_u^{in}} G_{i_u} \le G_u^{\max} \qquad (4\text{-}21)$$

Composition limitations:

$$x_{i_u,k}^{\min} \le x_{i_u,k} \le x_{i_u,k}^{\max} \qquad (4\text{-}22)$$

Temperature limitations:

$$T_{i_u}^{\min} \le T_{i_u} \le T_{i_u}^{\max} \qquad (4\text{-}23)$$

Utility-capacity constraint

$$\sum_{u=1}^{N_{Sinks}} Q_{q,u} \le Q_q^{\max} \qquad (4\text{-}24)$$

where q designated the type of utility

$Q_{q,u}$ rate of consuming the q^{th} utility at the u^{th}

$Q_q^{\max}$ maximum plant capacity of the q^{th} utility

Overall energy balance

$$\sum_{i \in H} F_i Cp_i \left(T_i^s - T_i^t\right) - \sum_{j \in C} f_j Cp_j \left(t_j^t - t_j^s\right) = 0 \qquad (4\text{-}25)$$

where F_i is flowrate of hot stream *i*

f_i is flowrate of cold stream *j*

Cp is specific heat capacity

T^s and t^s are supply temperatures for hot and cold streams, respectively

T^t and t^t are target temperatures for hot and cold streams, respectively

Heat exchange between hot and cold streams below the pinch pint

$$\sum_{i\in H} F_i Cp_i \left\{ \lambda^t_{i,p}\left(T^p - T^t_i\right) - \lambda^s_{i,p}\left(T^p - T^s_i\right) \right\} - \sum_{j\in C} f_j Cp_j \left\{ \eta^s_{j,p}\left(t^p - t^s_j\right) - \eta^t_{j,p}\left(t^p - t^t_j\right) \right\} \le 0 \tag{4-26}$$

$$F^l_i \le F_i \le F^u_i \qquad i \in H \tag{4-27}$$

$$f^l_j \le f_j \le f^u_j \qquad j \in C \tag{4-28}$$

$$T^{s,\min}_i \le T^s_i \le T^{s,\max}_i \qquad i \in H \tag{4-29}$$

$$T^{t,\min}_i \le T^t_i \le T^{t,\max}_i \qquad i \in H \tag{4-30}$$

$$t^{s,\min}_j \le t^s_j \le t^{s,\max}_j \qquad j \in C \tag{4-31}$$

$$t^{t,\min}_j \le t^t_j \le t^{t,\max}_j \qquad j \in C \tag{4-32}$$

$$\left(L - T^p\right)\lambda^t_{i,p} < T^t_{i,p} - T^p \le \left(U - T^p\right)\left(1 - \lambda^t_{i,p}\right) \qquad i \in H, p \in P \tag{4-33}$$

$$\left(L - T^p\right)\lambda^s_{i,p} < T^s_{i,p} - T^p \le \left(U - T^p\right)\left(1 - \lambda^s_{i,p}\right) \qquad i \in H, p \in P \tag{4-34}$$

$$\left(L - t^p_j\right)\eta^t_{j,p} < t^t_{j,p} - t^p_j \le \left(U - t^p_j\right)\left(1 - \eta^t_{j,p}\right) \qquad j \in C, p \in P \tag{4-35}$$

$$\left(L - t^p_j\right)\eta^s_{j,p} < t^s_{j,p} - t^p_j \le \left(U - t^p_j\right)\left(1 - \eta^s_{j,p}\right) \qquad j \in C, p \in P \tag{4-36}$$

$$\lambda^t_{i,p} = 0,1 \qquad i \in H \tag{4-37}$$

$$\lambda^s_{i,p} = 0,1 \qquad i \in H \tag{4-38}$$

$$\eta^t_{j,p} = 0,1 \qquad j \in C \tag{4-39}$$

$$\eta^{s}_{j,p} = 0,1 \qquad j \in C \tag{4-40}$$

Case study

To demonstrate the applicability of our proposed approach for simultaneous debottlenecking and heat integration, the motivating example of the hydrocarbon processing facility, introduced in Chapter III, is revisited (Fig. 4-5.) As before, this example is limited to the situation where debottlenecking is achieved without an investment of new capital. Table 4-1 shows the operating conditions of the process (base case.) Heat exchangers, their duties, and heat transfer areas are presented in Table 4-2. By using the proposed interval inclusion technique, a target for the product flowrate (F_{14}) was found to be 93,417 kg/hr. Next, a simultaneous product maximization and heat integration nonlinear programming problem was formulated. The interval-based target was included as a constraint. The optimization software, LINGO 10.0, was used to solve the problem. The identified value of the maximum product flowrate was found to match the target (93,417 kg/hr), heating duty of 4.96×10^6 kJ/hr and cooling duty of 5.10×10^6 kJ/hr. The calculated heat transfer area was 2254 m^2 which is much higher than the available heat transfer area (935 m^2.) Since there were no excess heating and cooling duties, a new target was determined (new target = current maximum production – ε.) This procedure continued until a feasible solution was reached. The solution shows that the maximum production from the process at no/low-cost debottlenecking approach is 38,337 kg/hr. The heating and cooling duties at this production level were 1.49×10^6 and

1.54 x 10^6 kJ/hr, respectively. The heat transfer area was 600 m^2. Table 4-3 shows the heat exchanger network retrofitting results.

Conclusions

A novel methodology for simultaneous process debottlenecking and heat integration has been introduced. This approach simultaneously identifies the maximum achievable production flowrate at no/low cost strategy while considering heat integration of the process. Furthermore, the approach considers the retrofitting of the process heat exchange network using no/low cost strategies. Finally, a case study was solved to illustrate the applicability and merits of the new approach.

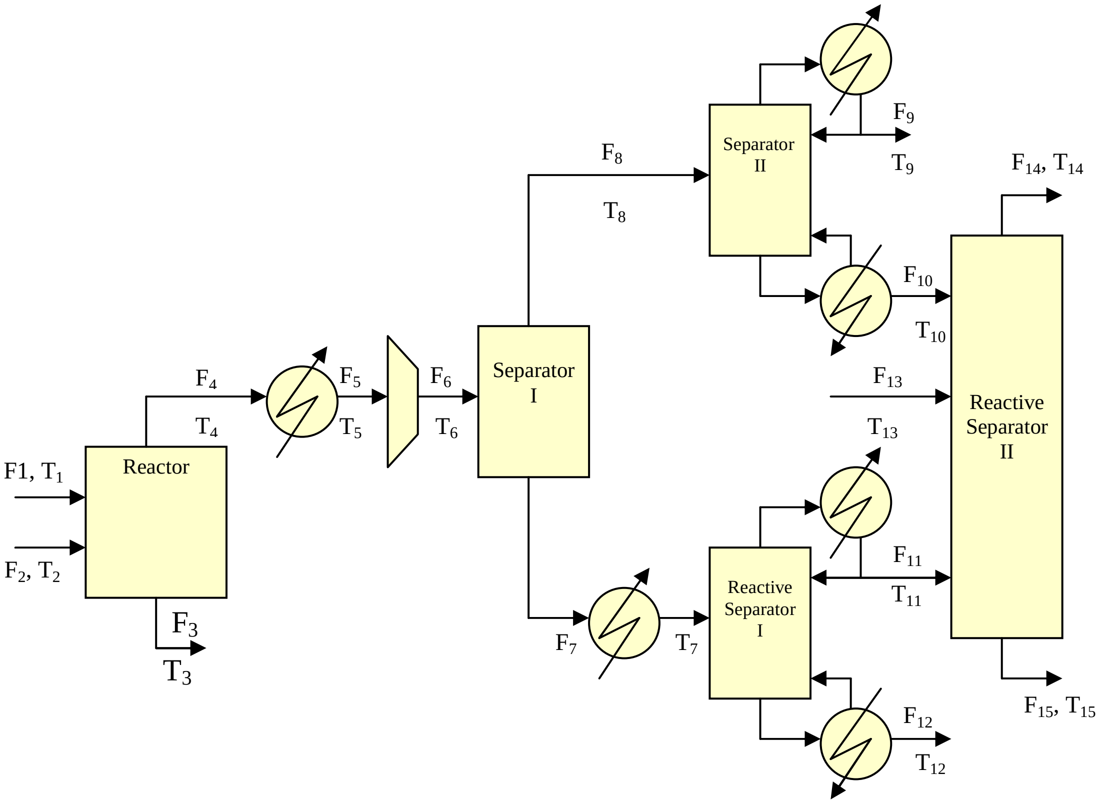

Fig. 4-5. Flowsheet of case study (base case)

Table 4-1. Case study operating conditions (base case)

Stream	Flowrate (kg/hr)	Temperature (K)
F1	65620.38	305
F2	32810.19	305
F3	4921.53	310
F4	93509.04	310
F5	93509.04	299
F6	93509.04	307
F7	20779.79	304.8
F8	72729.25	307
F9	68801.83	300
F10	3927.426	362
F11	2493.57	330
F12	18286.21	350
F13	23000	320
F14	29421	335

Table 4-2. Case study heat exchangers duties and areas (base case)

Heat Exchanger	Duty (kJ/hr) x10^5	Required Heat Transfer Area (m^2)	Available Heat Transfer Area (m^2)
HE-4	20	390.0	409.0
HE-7	1	15.5	16.3
HE-9	3	83.0	91.3
HE-10	2.67	67.0	70.4
HE-11	3.01	68.5	71.9
HE-12	23.2	197.2	276.1

Table 4-3. Case study heat exchanger network retrofitting

Heat Exchanger	Assignment	Duty (kJ/hr) x10^5	Required Heat Transfer Area (m^2)
HE-4	F9 - CU	9.51	264.0
HE-7	F7 - CU	0.23	3.5
HE-9	F4 - CU	4.94	47.9
HE-10	HU - F12	4.86	41.3
HE-11	F11 - F12	0.72	26.2
HE-12	HU - F10	9.28	233.0

CHAPTER V

PROCESS INTENSIFICATION: NEW UNDERSTANDING AND SYSTEMATIC APPROACH

Introduction

The introduction of reactive distillation was among the first high-impact process-intensification activities used in the chemical industry. The term “Process Intensification” was not highly publicized until the 1970s when ICI invented the HiGee rapidly rotating mass transfer device. Until the early 1990s, process intensification focused on primarily four areas; the use of centrifugal forces, compact heat transfer, intensive mixing, and combined technologies. Since 2000s the growth of process intensification has been accelerating as many research centers in different countries had entered the field, international conferences and smaller symposia on process intensification have been organized.

Process intensification is gaining much attention as one of the key objectives in designing new plants and retrofitting existing units. Several drivers have contributed to this increasing attention. For instance, enhanced process safety and homeland security are tied to process intensification. As the inventory and flows of hazardous substances are lowered, the process risk is typically reduced. Additionally, conservation of natural resources (including better utilization of mass and energy) may be linked to process intensification. Given the complexity of a typical process and the various objectives, it is important to develop an effective framework for generating and pursuing valid opportunities for process intensification.

While cost reduction was the main motivation for process intensification, it quickly became apparent that there are other important potential benefits, particularly with respect to improving inherent safety. This is particularly important when dealing with hazardous materials. In such case, smaller inventory is typically safer. Huge inventories of hazardous materials were the main causes of the more severe chemical disasters of the past century (e.g., Oppau/Ludwigshafen in 1921 (600 dead & 1500 injured), Flixborough in 1974 (600 dead & 1500 injured), San Juan, Mexico City in 1984 (500 dead & 7000 injured), and Bhopal in 1984 (3,800 dead, 2,720 permanently disabled)). Process Intensification can dramatically reduce inventory through smaller equipment, improved reactor/yield, minimizing feedstock, etc. Furthermore, process intensification enhances safety through the development of products that cannot be safely or successfully produced in conventional ways because of high reaction rates, dangerously exothermic reactions, or reactants are too hazardous.

Other potential benefits of process intensification are improving process chemistry, reducing environmental impact and energy consumption, enhancing corporate image through being innovative and environmentally friendly, and finally, value customers through “just in-time” manufacturing or philosophy (Stankiewicz and Moulijn 2004a; Tsouris and Porcelli 2003).

Literature is rife with case studies on process intensification in the chemical process industries. However, while many of these papers discuss the application of novel equipment or new technologies (e.g., multi-functional equipment); the term “Process Intensification” is defined differently. A common definition of process intensification was given by Stankiewicz and Moulijn (2000) as: “Any chemical engineering development that leads to a substantially smaller, cleaner and more energy efficient technology.” Based on this definition, Stankiewicz and Moulijn (2000) categorized process intensification into two classes: Equipment and Methods (Fig. 5.1.) The Equipment Class includes reactors and equipment for non-reactive operations. On the other hand, the Methods Class includes multi-functional reactors, hybrid separators, alternative energy resources and a category for any other methods used.

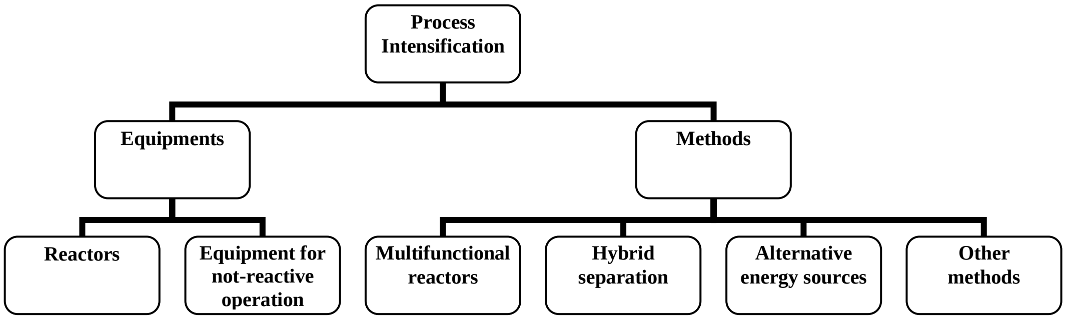

Fig. 5.1. Process intensification classification by Stankiewics and Drinkenburg (2000).

Motivations and objectives

Notwithstanding the usefulness of earlier process intensification activities, they have been mostly limited to intensifying individual units. While intensifying individual units may lead to intensifying the whole process, it is important to distinguish unit intensification from process intensification. According to such distinction, process intensification focuses directly on the whole process. Therefore, there is a great need to develop systematic methods for process intensification with focus on the holistic nature of the process. Because the focus of earlier work was on single-unit intensification (reactors, hybrid separators, etc.) which did not fully account for the strong interactions among all units within the process, the effect of intensifying a single unit on the rest of the process was not considered. For example, distillation columns were intensified in order to improve unit performance and reduce capital costs (Fair and Seibert 1996; Meili 1997; Olujic et al. 2003; Shakur et al. 2000; Summer et al. 1995). Other separation systems (e.g., strippers, deaerators) were also intensified (Bisschops et al. 1997; Eimer 2003; Saremi et al. 2000; Willink 2000; Zheng et al. 1997). Additionally, the reactors were intensified in order to improve safety by reducing their size or improving their performance through internal modifications (Kooijman 2000; Liu et al. 2005). Multi-functioning equipment, such as the reactive separators and static mixer reactors, were used for intensification (Cummings et al. 1999; Dautzenberg and Mukherjee 2001; Guilleminot et al. 1993; Harmsen and Hinderink 1999; Phillips et al. 1997; Stankiewicz 2003; Trent et al. 1999; Turunen 1997; Xu 2001). Furthermore, intensification of the membrane systems, in order to improve unit performance or minimize fresh water consumption, has been reported (Belyaev et al. 2003; Falk-Pedersen et al. 2003; Rijkens 2000; Van der Bruggen et al. 2004a; Van der Bruggen et al. 2004b).

Secondly, there were limitations in the lack of systematic methods used to achieve intensification. Most of the reported case studies were based on individual experiences with specific process or equipment. Additionally, some of the reported intensification techniques do not fit under any other common classification of process intensification alternatives (Belyaev et al. 2003; Eimer 2003; Guilleminot et al. 1993; Schneider 1999).

The main objective of this chapter is to overcome these limitations by defining broader categories for "Intensification" while using process integration as a holistic and systematic framework for intensification. We first introduce a new definition and classification for intensification. The new classification divides intensification into two main classes: Single-Unit Intensification and Process Intensification. Single-Unit Intensification is aimed at intensifying a pre-specified unit in isolation to the rest of the process in order to minimize the unit size at the given throughput; maximize the unit throughput at a given size; minimize the unit hold-up or maximize the unit performance at a given unit size and throughput. On the other hand, Process Intensification is aimed at minimizing the process inventory of materials, maximizing the process throughput, or minimizing the process consumption of utility materials and feedstock. In the case of Process Intensification, units that need to be intensified are not pre-specified. Furthermore, more than one unit can be intensified simultaneously. General mathematical formulations for different classes of intensification are proposed to assist engineers and designers in performing intensification. Finally, to show the applicability of this work, a case study is presented.

New definition of intensification

In this work we define Intensification as any activity which is characterized by one or more of the following:

1. Smaller equipment for given throughput. An activity is process intensification if result in producing the same throughout using smaller equipment (or less volume) that compared to those commonly used today.
2. Higher throughput for given equipment size or given process. An activity is process intensification if result in producing higher throughput using the same equipment or process.
3. Less holdup for equipment or less inventory for process of certain material for the same throughput. Any activity that results in reducing holdup or inventory of certain material for the same production is process intensification. Reducing equipment holdup and process inventory of hazardous material has been discussed in the literature. Reported case studies focus on reducing equipment holdup or process inventory through reducing equipment size. However, methods that can be used to reduce holdup and/or inventory and not related to equipment size (e.g., reduce inventory through change in mode of the process (continuous vs. batch), or change reaction pathways), have not been discussed. This category includes activities that can be used to reduce holdup and/or inventory and are not related to equipment size.
4. Less usage of utility materials, and feedstock for a given throughput and given equipment size. Any activity that result in less usage of material utilities (heating or cooling utilities, solvents, etc.) and/or feedstock is process intensification. As the case with previous category, literature discussed this category only through reducing the equipment size. This category includes activities that reduce utility

usage or feedstock and are not related to equipment size (e.g., solvent usage can be reduced by optimizing circulation rate and/or optimum operating of regeneration system.)

5. Higher performance for given unit size. Any activity that result in improving unit performance (heat duty of heat exchanger, yield of reactor) for given unit size and throughput is a process intensification.

The key building blocks of this classification is shown by Fig. 5.2.

Problem statement

The problem of process intensification can be stated as follow: Given a process with units that are referred to as sinks. The set of sinks is SINKS= $\{\bar{J} \mid \bar{J} = 1,2..., \mathrm{N}_{\text{existing sinks}} \text{ and } 1,2..., \mathrm{N}_{\text{new sinks}}\}$ and each sink has a set of input streams ($INPUT_{\bar{J}}$) and a set of output streams ($OUTPUT_{\bar{J}}$). The input stream, $i_{\bar{J}}$, has a flowrate $G^{in}_{i_{\bar{J}},\bar{J}}$ and properties $P^{in}_{i_{\bar{J}},\bar{J},p}$ (e.g. composition, density, temperature, and vapor pressure.)

Each sink has a range of acceptable flowrate and properties; and any stream must satisfy that range before being fed to that sink, i.e.

$$G^{in\ \min}_{i_{\bar{J}},\bar{J}} \leq G^{in}_{i_{\bar{J}},\bar{J}} \leq G^{in\ \max}_{i_{\bar{J}},\bar{J}} \qquad i_{\bar{J}} \in INPUT_{\bar{J}},\ \bar{J} \in SINKS \tag{5.1}$$

$$P^{in\ \min}_{i_{\bar{J}},\bar{J},p} \leq P^{in}_{i_{\bar{J}},\bar{J},p} \leq P^{in\ \max}_{i_{\bar{J}},\bar{J},p} \qquad p \in P \tag{5.2}$$

For each sink, there are vectors of design and operating degrees of freedom abbreviated as $d_{\bar{J}}$ and $o_{\bar{J}}$, respectively. These vectors are subjected to manipulation and optimization. $D_{\bar{J}}$ and $O_{\bar{J}}$ designate the intervals of permissible values of design and operating degrees of freedom for sink $\bar{J}$, respectively. Hence, $d_{\bar{J}} \in D_{\bar{J}}$ and $o_{\bar{J}} \in O_{\bar{J}}$.

Examples of $d_{\bar{J}}$ include structural decisions such as increasing surface area, adding or replacing internals such as packing, trays and baffles, etc.

Examples of $o_{\bar{J}}$ include operating conditions that can be altered for existing equipment such as temperature, pressure, etc.

The objective is to:

1. Intensify a given unit to minimize its size for a given throughput, maximize its throughput for a given unit size, minimize its holdup for a given size and throughput, or maximize its performance for a given size and throughput.
2. Simultaneously intensify the whole process to maximize process throughput, minimize process inventory, or minimize process utility materials and feedstock.

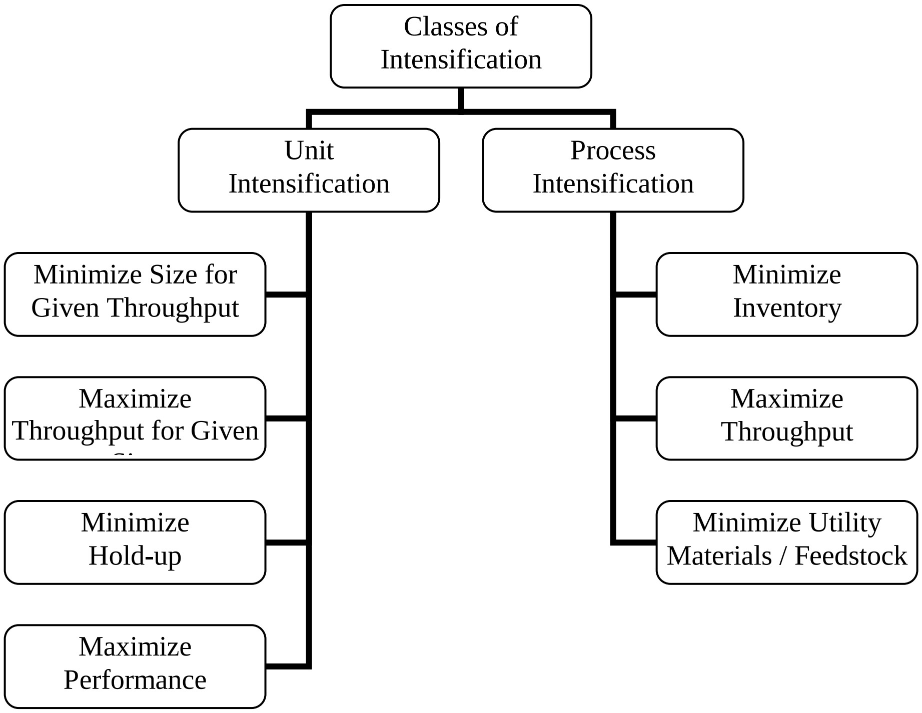

Fig. 5.2. New classification of process intensification

Unit intensification

Unit $\bar{J}$ is intensified to achieve one of the following objectives:

1. Minimize unit size for a given unit throughput

Subject to

$$Size_{\bar{J}} = f_{\bar{J}}(G^{out}_{k_{\bar{J}},\bar{J}}, p^{out}_{k_{\bar{J}},\bar{J},p}, G^{in}_{i_{\bar{J}},\bar{J}}, p^{in}_{i_{\bar{J}},\bar{J},p}, d_{\bar{J}}, \text{and } o_{\bar{J}}) \tag{5.3}$$

In case of new unit intensification $G^{out}_{k_{\bar{J}},\bar{J}}$, $p^{out}_{k_{\bar{J}},\bar{J},p}$, $G^{in}_{i_{\bar{J}},\bar{J}}$, and $p^{in}_{i_{\bar{J}},\bar{J},p}$ are constants and

$d_{\bar{J}}$, and $o_{\bar{J}}$ are vectors that are subjected to manipulation and optimization.

2. Maximize throughput for a given unit size

   Subject to

   $$G^{out}_{k_{\bar{J}},\bar{J}} = \varsigma_{\bar{J}}(Size_{\bar{J}}, p^{out}_{k_{\bar{J}},\bar{J},p}, G^{in}_{i_{\bar{J}},\bar{J}}, p^{in}_{i_{\bar{J}},\bar{J},p}, d_{\bar{J}}, \text{and } o_{\bar{J}}) \qquad (5.4)$$

   In case of new unit intensification $p^{out}_{k_{\bar{J}},\bar{J},p}, G^{in}_{i_{\bar{J}},\bar{J}}$, and $p^{in}_{i_{\bar{J}},\bar{J},p}$ are constants and $Size_{\bar{J}}, d_{\bar{J}}$, and $o_{\bar{J}}$ are subjected to manipulation and optimization. On the other hand, in case of an existing unit intensification $Size_{\bar{J}}, p^{out}_{k_{\bar{J}},\bar{J},p}, G^{in}_{i_{\bar{J}},\bar{J}}, p^{in}_{i_{\bar{J}},\bar{J},p}$ and $d_{\bar{J}}$, and $o_{\bar{J}}$ are subjected to manipulation and optimization.

3. Minimize unit holdup for given throughput and size

   Subject to

   $$holdup = f_{\bar{J}}(Size_{\bar{J}}, G^{out}_{k_{\bar{J}},\bar{J}}, p^{out}_{k_{\bar{J}},\bar{J},p}, G^{in}_{i_{\bar{J}},\bar{J}}, p^{in}_{i_{\bar{J}},\bar{J},p}, d_{\bar{J}}, \text{and } o_{\bar{J}}) \qquad (5.5)$$

   In case of new unit intensification $G^{out}_{k_{\bar{J}},\bar{J}}, p^{out}_{k_{\bar{J}},\bar{J},p}, G^{in}_{i_{\bar{J}},\bar{J}}$, and $p^{in}_{i_{\bar{J}},\bar{J},p}$ are constants and $Size_{\bar{J}}, d_{\bar{J}}$, and $o_{\bar{J}}$ are subjected to manipulation and optimization. On the other hand, in case of an existing unit intensification $Size_{\bar{J}}, G^{out}_{k_{\bar{J}},\bar{J}}, p^{out}_{k_{\bar{J}},\bar{J},p}, G^{in}_{i_{\bar{J}},\bar{J}}$, and $p^{in}_{i_{\bar{J}},\bar{J},p}$ are constant, and $d_{\bar{J}}$, and $o_{\bar{J}}$ are subjected to manipulation and optimization.

4. Maximize performance (e.g., unit's product purity in a separator, reactor yield in a reactor, heat duty in heat exchanger.)

Subject to

$$performance = \theta_{\bar{J}}(Size_{\bar{J}}, G^{out}_{k_{\bar{J}},\bar{J}}, p^{out}_{k_{\bar{J}},\bar{J},p}, G^{in}_{i_{\bar{J}},\bar{J}}, p^{in}_{i_{\bar{J}},\bar{J},p}, d_{\bar{J}}, \text{and } \mathrm{o}_{\bar{J}}) \tag{5.6}$$

In case of new unit intensification $G^{out}_{k_{\bar{J}},\bar{J}}, p^{out}_{k_{\bar{J}},\bar{J},p}, G^{in}_{i_{\bar{J}},\bar{J}}$, and $p^{in}_{i_{\bar{J}},\bar{J},p}$ are constants and $Size_{\bar{J}}, d_{\bar{J}}$, and $\mathrm{o}_{\bar{J}}$ are subjected to manipulation and optimization. While in case of an exiting unit intensification $Size_{\bar{J}}, G^{out}_{k_{\bar{J}},\bar{J}}, p^{out}_{k_{\bar{J}},\bar{J},p}, G^{in}_{i_{\bar{J}},\bar{J}}$, and $p^{in}_{i_{\bar{J}},\bar{J},p}$ are constant, and $d_{\bar{J}}$, and $\mathrm{o}_{\bar{J}}$ are subjected to manipulation and optimization.

Process intensification

Since there are strong interactions among all units within the process, any change in one part of the process will have an affect on the entire process. Thus, a simultaneous approach must be used. The first step in intensifying the whole process is to develop a process model that is described in terms of the decision variables and the optimization degrees of freedom for the various units. An effective way of describing the process model in terms of the manipulated design and operating variables is based on the concept of path equations (Noureldin and El-Halwagi 1999). The flowsheet is described as a number of sources (streams) and sinks (units). Consider a process unit, $\bar{J}$, with a set of input streams $INPUT_{\bar{J}} = \{i_{\bar{J}} \mid i_{\bar{J}} = 1,2...,\mathrm{N}^{\mathrm{in}}_{\bar{\mathrm{J}}}\}$ and a set of output streams $OUTPUT_{\bar{J}} = \{k_{\bar{J}} \mid k_{\bar{J}} = 1,2...,\mathrm{N}^{\mathrm{out}}_{\bar{\mathrm{J}}}\}$. Each input stream has a flowrate $G^{in}_{i_{\bar{J}},\bar{J}}$ and properties $p^{in}_{i_{\bar{J}},\bar{J},p}$, and is fed with j^{th} = $\{j \mid j = \text{a stream which is destined to } i_{\bar{J}} = 1,2,\ldots,N_{existing}, 1, 2, \ldots, N_{new}\}$ number of streams that have a flowrate $g^{in}_{j,i_{\bar{J}},\bar{J}}$ and properties $p^{in}_{j,i_{\bar{J}},p}$. Where N_{new} are existing sources and N_{new} are external source that can be added to the process or replace an existing source. Similarly, each output stream has a flowrate $G^{out}_{k_{\bar{J}},\bar{J}}$ and properties $p^{out}_{k_{\bar{J}},\bar{J},p}$ and is split into j^{th} streams that have flowrate $g^{out}_{k_{\bar{J}},j,\bar{J}}$ and properties $p^{out}_{k_{\bar{J}},j,p}$.

The decision variables for unit $\bar{J}$ can be classified into design and operating variables, designated as $d_{\bar{J}}$ and $o_{\bar{J}}$, respectively. Hence, the performance model for unit $\bar{J}$ can be expressed as:

$$\begin{aligned}&(G^{out}{}_{k_{\bar{J}},\bar{J}},\ p^{out}_{k_{\bar{J}},\bar{J},p} : k_{\bar{J}} \mid k_{\bar{J}} = 1,2\ldots,\mathrm{N}^{\mathrm{out}}_{\bar{\mathrm{J}}} \text{ and } \mathrm{p} \in \mathrm{P}) = \\ &\qquad \delta_{\bar{J}}(Size_{\bar{J}}, G^{in}_{i_{\bar{J}},\bar{J}},\ p^{in}_{i_{\bar{J}},\bar{J},p} : i_{\bar{J}} \mid i_{\bar{J}} = 1,2\ldots,\mathrm{N}^{\mathrm{in}}_{\bar{\mathrm{J}}}, \text{and } \mathrm{p} \in \mathrm{P}, \text{ and } d_{\bar{J}}, \mathrm{o}_{\bar{J}})\end{aligned} \tag{5.7}$$

A performance model for each unit in the process needs to be developed. However, details of these performance models are different. For instance, if the process that to be intensified has a reactor that can not be modified, minimum details are needed in this reactor's performance model. On the other hand, however, if the reactor is subject for intensification, detailed performance model must be developed.

Parameters in performance models can be constant or optimization variables. For instance, in case of intensifying a new unit, unit size is an optimization variable, while it is constant in case of existing unit intensification.

For each unit, $\bar{J}$, there are bounds on the admissible ranges for the operating and design variables, i.e.

$$o_{\bar{J}}^{\min} \le o_{\bar{J}} \le o_{\bar{J}}^{\max} \tag{5.8}$$

$$d_{\bar{J}}^{\min} \le d_{\bar{J}} \le d_{\bar{J}}^{\max} \tag{5.9}$$

Additionally, overall material and energy for the unit $\bar{J}$ can be written as:

$$\sum_{i_{\bar{J}}=1}^{N_{\bar{J}}^{in}} G^{in}_{i_{\bar{J}},\bar{J}} = \sum_{k_{\bar{k}}}^{N_{\bar{J}}^{out}} G^{out}_{k_{\bar{J}},\bar{J}} \tag{5.10}$$

$$\sum_{i_{\bar{J}}=1}^{N_{\bar{J}}^{in}} G^{in}_{i_{\bar{J}},\bar{J}} * h^{in}_{i_{\bar{J}},\bar{J}} = \sum_{k_{\bar{k}}}^{N_{\bar{J}}^{out}} G^{out}_{k_{\bar{J}},\bar{J}} * h^{out}_{k_{\bar{J}},\bar{J}} \tag{5.11}$$

where

$$G^{in}_{i_{\bar{J}},\bar{J}} = \sum_{j=1}^{N_j} g^{in}_{j,i_{\bar{J}},\bar{J}} \qquad i_{\bar{J}} = 1,2,...,N \tag{5.12}$$

and

$$G^{out}_{k_{\bar{J}},\bar{J}} = \sum_{j=1}^{N_j} g^{out}_{k_{\bar{J}},j,\bar{J}} \qquad k_{\bar{J}} = 1,2,...,N \tag{5.13}$$

If properties are involved, then property-mixing expressions (e.g., El-Halwagi et al, 2004) are added:

$$\sum_{i_{\bar{J}}=1}^{N_{\bar{J}}^{in}} G^{in}_{i_{\bar{J}},\bar{J}} * \psi(p^{in}_{i_{\bar{J}},\bar{J}}) = \sum_{k_{\bar{k}}}^{N_{\bar{J}}^{out}} G^{out}_{k_{\bar{J}},\bar{J}} * \psi(p^{out}_{k_{\bar{J}},\bar{J}}) \tag{5.14}$$

where ψ is the property mixing operator.

Since flowrates can not be negative, non-negativity constraints are added of each source:

$$g^{in}_{j,i_{\bar{J}},\bar{J}} \geq 0 \qquad (5.15)$$

$$g^{out}_{k_{\bar{J}},j,\bar{J}} \geq 0 \qquad (5.16)$$

Other important constraints include flowrate limitations to each unit:

$$G^{in\ \min}_{i_{\bar{J}},\bar{J}} \leq G^{in}_{i_{\bar{J}},\bar{J}} \leq G^{in\ \max}_{i_{\bar{J}},\bar{J}} \qquad (5.17)$$

and properties limitations:

$$P^{in\ \min}_{i_{\bar{J}},\bar{J},p} \leq P^{in}_{i_{\bar{J}},\bar{J},p} \leq P^{in\ \max}_{i_{\bar{J}},\bar{J},p} \qquad (5.18)$$

Having established that, we are in a position to use the above general mathematical formulation for different process intensification objectives as follows:

Maximize throughput for a given process (Max $G^{process}$)

The objective here is maximizing the process throughput. Performance model for process units need to be developed as was shown earlier in this chapter (Equation 5.7.) It is important to mention that the equipments size in units performance models are fixed as the investing in adding new equipments are not considered. Additionally equations 5.10 to 5.18 are used to count for material and energy balances, design and operating limitations, and logical constraints.

It is also necessary to account for the competing demands for utilities. The process has several utilities (e.g., heating, cooling, steam, etc.). Let us use the index q to designate the type of utility and $Q_{q,\bar{J}}$ as the rate of consuming the qth utility at the $\bar{J}\,th$ unit. Suppose that the maximum plant capacity of the qth utility is $Q_q^{\max}$. Therefore, the following utility-capacity constraint should be used:

$$\sum_{j=1}^{N_j} Q_{q,\bar{J}} \le Q_q^{\max} \tag{5.19}$$

Minimize process inventory at given throughput

Minimize inventory, practically of hazardous material, is generally aimed to improve process safety. The question is “what is the safe inventory?” The minimum inventory based on safety considerations was defined as “the minimum quantity that is consistent with safe and stable operation”. This is normally the lowest inventory with witch the process could operate without increasing safety concerns (Wade 1987). Thus, reducing material inventory is an operating decision and can come only from changes in the process or in the way it is operated.

There are two different kinds of inventory that are considered in this work; feedstock inventory and intermediate material inventory. Another kind of inventory, which is utility material inventory, is not included under this class of process intensification since it is covered under minimizing utility materials.

Feedstock Inventory

Every process needs a certain inventory of feedstock if there is not continuous supply of feedstock through piping. The amount of feedstock inventory depends on the type of process and location. Feedstock inventory is related to process throughput of desire product and process yield as follow:

$$\left(\text{Feedstock inventory} = \frac{\text{process throughput}}{\text{process yield}} * \text{inventory period}\right) \tag{5.20}$$

At constant process throughput and fixed inventory period feedstock inventory is at minimum when the process yield is at maximum value. Thus, above equation can be rewritten as:

$$\left(\text{Minimum feedstock inventory} = \frac{\text{process throughput}}{\text{maximum process yield}} * \text{inventory period}\right) \tag{5.21}$$

A procedure has been developed by Al-Otaibi and El-Halwagi (2006) to maximize the process yield and hence minimizing the feedstock inventory without the addition of new equipments. Since in this type of process intensification the addition of new equipments is considered, Al-Otaibi and El-Halwagi’s method was modified.

This procedure consists of the following key steps:

1. Maximize routing of targeted raw material to the reaction system
2. Maximize reactor yield
3. Reroute desired product from undesirable outlets to the desirable outlet, and
4. Minimize the fresh consumption of the targeted raw material through recovery and recycle

The following is a brief description of these steps.

Step 1: Maximizing routing of raw material to reactor: The first step in this procedure is aimed at the maximization of reactor feed. Let us consider Fig. 5.3: In this process, A is the total fresh feed of the targeted raw material. As a result of losses prior to the reactor, a fraction (α) of the fresh feed reaches the reaction system leading to a load (a = α A) of the targeted reactant fed to the reactor. The reaction system consists of current reactors and new candidates of intensified reactors. Based on the path equations for all the units leading to the reactor, we can express the fraction α as a function of the design and operating variables of the units preceding the reaction system, i.e.

$$\alpha = \psi(\mathrm{d}_{\bar{\mathrm{J}}}, \mathrm{o}_{\bar{\mathrm{J}}} \; \forall \bar{J} \text{ preceding the reaction system}) \tag{5.22}$$

One can determine the value of fresh feed reaches the reactor as:

$$a = \alpha * A \tag{5.23}$$

Step 2: Maximizing reactor yield: The actual yield of the reactor can be written as follow:

$$\text{Actual yield of a reactor } \left(\text{Yield}_{\text{reactor}}\right) = \frac{\text{Amount of desired product generated in the reactor}}{\text{Amount of limiting reactant fed to the reactor}} \tag{5.24}$$

Let $\text{Yield}_{\text{reactor}}$ be given by this expression:

$$\text{Yield}_{\text{reactor}} = \omega \begin{bmatrix} (\text{Feed}_{\text{existing reactor}}, \text{d}_{\text{existing reactor}}, \text{o}_{\text{existing reactor}}) * I \\ + (\text{Feed}_{\text{new reactor}}, \text{d}_{\text{new reactor}}, \text{o}_{\text{new reactor}}) * II \end{bmatrix} \tag{5.25}$$

where

I and II are binary variable and $I + II = 1$

$Feed_{existing\ reactor}$, $d_{exisiting\ reactor}$, $o_{existing\ reactor}$ are the vectors of feed conditions, design variables, and operating variables of existing reactor, respectively.

$Feed_{new\ reactor}$, $d_{new\ reactor}$, $o_{new\ reactor}$ are the vectors of feed conditions, design variables, and operating variables of new reactor, respectively.

One can determine the value of product leaving the reaction system (Fig. 5.4) as:

$$b = \omega * a \tag{5.26}$$

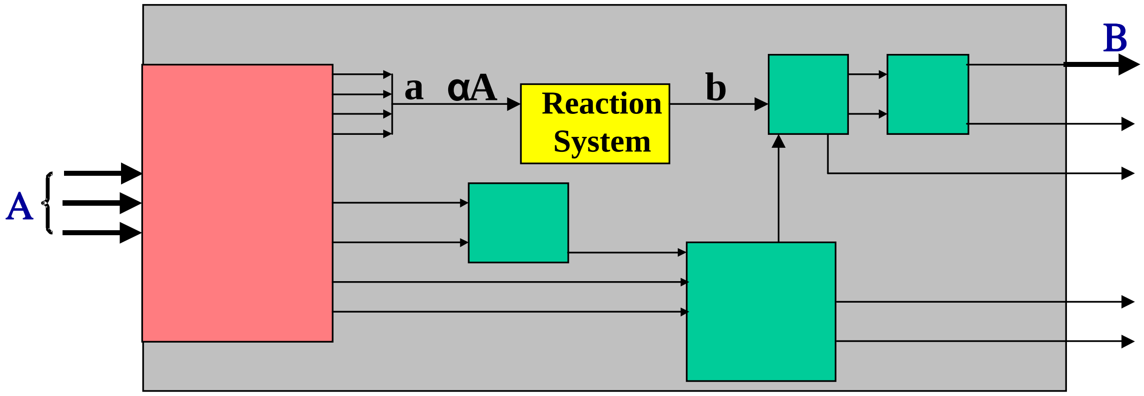

Fig. 5.3. Evaluating feed to reactor

Step 3: Rerouting the product from undesirable outlets to desirable outlets: After the reaction system, the generated product along with byproducts, wastes, and unreacted raw materials are processed through separation and finishing units. As a result, a certain amount, *l*, of product is lost with terminal streams leaving in undesirable outlets (i.e., streams other than the main product stream going to sales.)

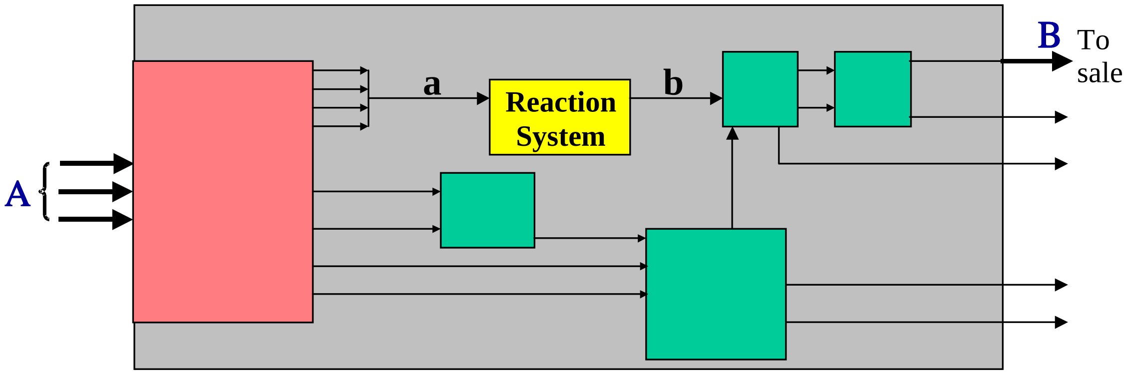

Fig. 5.4. Maximization of the reaction yield

Thus, our objective is to minimize the losses and reroute them to the desirable outlet (main product stream). This objective is achieved through manipulation of the current separation and finishing units' design and operations condition and/or through the addition of new equipments. The product losses can be expressed through the path equations for the separation and finishing units as a function of the design and operating variables of these units, i.e.,

$$l = \phi(\mathrm{d}_{\bar{J}}, \mathrm{o}_{\bar{J}} \forall \bar{J} \text{ following the reaction system}) \tag{5.27}$$

Step 4: Minimizing fresh feed Usage through Recycle: In this step, the unreacted raw material is recycled. The existing and new recovery devices can recover an amount, *r*, which can be expressed through the path equations for the recovery units as a function of the design and operating variables of these units, i.e.,

$$r = \xi(\mathrm{d}_{\bar{J}}, \mathrm{o}_{\bar{J}} \forall \bar{J} \in \text{Recovery Units}) \tag{5.28}$$

In recycle, it is necessary to consider the supply and demand of raw materials. Clearly, one cannot recycle more than the available recyclable raw materials. Additionally, each unit has a maximum capacity that should not be exceeded. Hence, the maximum recyclable raw materials are the lower of two loads: the maximum recoverable load and the fresh feed requirement of the reactor (Noureldin and El-Halwagi 1999). Therefore,

$$\begin{gathered}\text{Maximum recyclable load of raw material} = \\ \operatorname{argmin}\left\{r^{\max} = \text{Fresh feed requirement of the process}\right\}\end{gathered} \tag{5.29}$$

Intermediate Material Inventory

Unlike feedstock inventory, in most cases intermediate material inventory is convenient, but not essential. It is stored either because unreliability of intermediate material producing unit or when the producing unit is at different site. One of the worst disasters in the history of the chemical industry occurred in Bhopal, India in 1984 was a result of a leak of intermediate material (methyl isocyanate). After this accident many companies announced that intermediate material (keeping in mined those intermediate are usually reactive chemicals and therefore are likely to be hazardous) would not be stored but would be used as soon as they are produced (Kletz 1991). Many process safety experts suggest a target of zero inventory of intermediate material. This can be achieved through producing intermediate materials on site in reliable producing unit so that they will be used as soon as they are produced.

Hendershot reported that in 1980s many plants significantly reduced the quantity of toxic intermediates stored in existing plants (prompted by the Bhopal tragedy) by focusing on the reliable operation of the plants, so that it was not necessary to maintain a large inventory to keep other parts of a plant running when an unreliable plant unit shut down (Hendershot 2006).

A study done at AIChE showed that methyl isocyanate could be generated and immediately converted to final product in continuous reactors that contained a total inventory of less than 10 kg of methyl isocyanate (Stankiewicz and Moulijn 2004b). Thus, minimizing the intermediate material inventory can be achieved though single unit intensification as explained earlier in this chapter.

Minimizing utilities and feedstock

A process may be intensified to minimize utilities and feedstock using energy integration and mass integration (El-Halwagi 2006; Kemp 2007; Shenoy 1995; Smith 2005). Additionally a recent review for process integration techniques that are used to minimize utilities and feedstock was published by Dunn and El-Halwagi (2003).

Case study: process intensification of acetaldehyde production through ethanol oxidation

The approach developed to reduce process inventory will be applied in this case study based on the process described by Al-Otaibi and El-Halwagi (2006).

Consider the process of producing acetaldehyde via ethanol oxidation. A schematic process flowsheet is shown in Fig. 5.5. Ethanol feedstock (50% ethanol, the rest being mostly water and some organic impurities (Miller 1968), is partially vaporized in a flash drum, mixed with preheated air, and fed to a catalytic reactor. Ethanol reacts with oxygen to form acetaldehyde and water according to the following equation:

$$CH_3CH_2OH + \frac{1}{2} O_2 \rightarrow CH_3CHO + H_2O \tag{5.30}$$

The reactor yield (designated by $Y_{reactor}$ and defined as the ratio of mass of acetaldehyde formed in the reactor to mass of ethanol fed to the reactor) is given by (McCabe and Mitchell 1983):

$$Y_{reactor} = 0.33 - 4.2 \times 10^{-6} \times (T_{rxn} - 580)^2 \tag{5.31}$$

where T_{rxn} is the reactor temperature (K). At present the reactor is operated at 600 K and the current reactor yield is 0.328 kg acetaldehyde formed in the reactor per kg ethanol fed to the reactor.

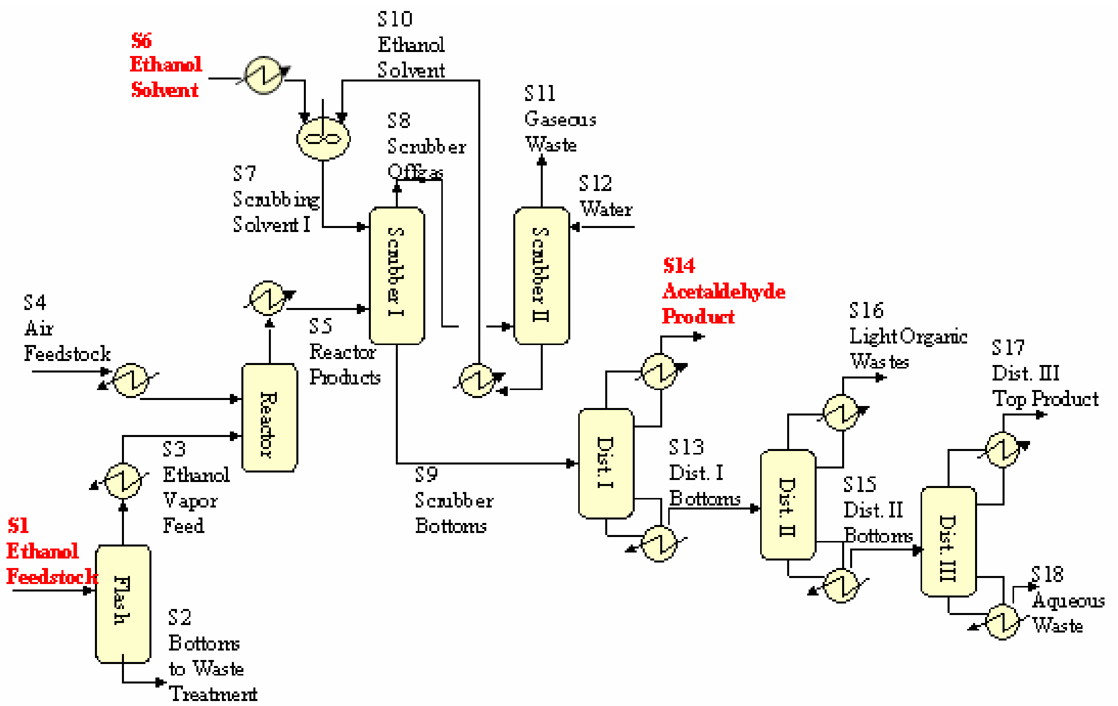

Fig. 5.5. Schematic representation of acetaldehyde process

The reactor product is scrubbed first with cold dilute solvent to cool the reactor offgas and to scrub several species (primarily ethanol and water). The gases leaving the top of the scrubber are scrubbed again with water to remove additional alcohol and acetaldehyde (Faith et al. 1965). The off-gas leaving the second scrubber, mostly nitrogen and trace amounts of oxygen, acetaldehyde, ethanol and water is released to atmosphere (McKetta 1999). The liquid from the second scrubber is recycled as scrubbing agent for the first scrubber with fresh alcohol as make up for the purge and the losses. The liquid from the first scrubber is distilled and acetaldehyde is recovered as the overhead product of the first distillation column. The bottoms of this column are fed to a second distillation column where light organic wastes (including some acetaldehyde) are collected from the top and passed to waste treatment. The bottoms of the second distillation column are fed to a third distillation column where ethanol (with some water) is separated as the overhead product and is subsequently fed to a boiler to utilize its heating value. The bottoms of the ethanol recovery column is mostly water and is fed to the biotreatment facility.

The plant receives ethanol from remote supplier and hence keeps an inventory of the for two weeks. Based on the base case about 11,240 tons of ethanol is stored. Ethanol is a hazardous material and highly flammable liquid. When ethanol mixes with air, explosive mixtures are produced that can be ignited by electrostatic charges. Ethanol is very irritating when it contacts the eye and skin. Its inhalation with height concentration and for long time may result in deadly consequences. Due to its dangerous nature, ethanol needs special storing and fire-fighting which makes storing it in copious quantities highly discouraged. And hence, it was decided to minimize the inventory of ethanol while holding the same throughput of the process (162,000 t/y acetaldehyde) and without investing in adding new process equipments. As per our new definition of process intensification, existing process intensification procedure will be followed.

Solution Approach

Ethanol is used in the process as a fresh feedstock to the process (E1, in stream S1) and solvent in scrubber I (E6, in stream S6). Flowrate of E1 can be related to the flowrate of acetaldehyde as showing below

$$\text{Process yield} = \frac{\text{Acetaldehyde in final product stream}}{\text{Fresh ethanol fed to process as feedstock}} \qquad (5.32)$$

or

$$\text{Process yield} = \frac{A14}{E1} \Rightarrow E1 = \frac{A14}{\text{process yield}} \qquad (5.33)$$

where A14 is the mass flowrate of acetaldehyde in the final acetaldehyde product (in stream S14).

The flowrate of ethanol makeup (E6) is a function of ethanol temperature as shown below:

$$E6 = 400 * \frac{TE}{298} \qquad (5.34)$$

where *TE* is the temperature of ethanol makeup. Therefore, ethanol consumption in ton per year can be written as follow:

$$Ethanol\ consumption = E1 + E6 = \frac{A14}{process\ yield} + 400 * \frac{TE}{298} \tag{5.35}$$

and ethanol inventory (for two weeks) can be written as follow:

$$Ethanol\ inventory = \frac{E1 + E6}{24} = \frac{A14}{process\ yield * 24} + 400 * \frac{TE}{298 * 24} \tag{5.36}$$

Thus, for minimum ethanol inventory process yield needs to be at maximum and *TE* at minimum.

To maximize the process yield a procedure developed by Al-Otaibi and El-Halwagi (2006) for maximizing process yield will be used in this work.

The following flows may be assumed to hold throughout the case study (even after process changes):

- No ethanol in S4, S12, S14, or S16.
- No acetaldehyde in S1, S2, S4, S6, S12, or S15.

The following are additional constraints and path equations to track ethanol and acetaldehyde in terms of the optimization variables.

Reactor

The reaction temperature affects the reactor yield as given by Equation 5.31. The feasibility range for the reaction temperature is given by:

$300 \leq T_{rxn}\ (K) \leq 860$ (5.37)

The reactor yield can also be written in terms of the amounts of generated acetaldehyde and consumed ethanol in the reactor, i.e.

$$Y_{reactor} = \frac{AR}{E_{feed}} \tag{5.38}$$

where E_{feed} is the ethanol fed to the reactor and AR is the generated acetaldehyde in the reactor. The ethanol consumed in the reactor (ER) is related to AR through stoichiometry and molecular weights. Therefore,

$$ER = (46/44) * AR \tag{5.38}$$

Flash Column

The ethanol losses in the bottoms stream of the flash drum may be reduced by manipulating the flash temperature according to the following relationship:

$$E2 = \alpha * E1 \tag{5.39}$$

where

$$\alpha = 10.5122 - 0.0274 * T_{flash} \tag{5.40}$$

where T_{flash} is the temperature of the flash drum in K and is bounded by the following constraint:

The range for the flash temperature is:

$$380 \le T_{flash}\ (K) \le 384 \tag{5.41}$$

At present, the flash temperature is 380 K.

Ethanol Makeup

$$E6 = 400 * \frac{TE}{298} \qquad (5.42)$$

The range for the makeup temperature is:

$$285 \leq TE\ (K) \leq 300 \qquad (5.43)$$

First Distillation Column

The acetaldehyde recovered in the first distillation column is a function of reboiler heat duty of that column. The relationship is given by:

$$A14 = \beta * A9 \qquad (5.44)$$

where

$$\beta = 0.14 * Q_R + 0.89 \qquad (5.45)$$

where Q_R is the reboiler heat duty (heat flow rate) in MW. The range of the reboiler duty is:

$$0.55 \leq Q_R\ (MW) \leq 0.76 \qquad (5.46)$$

For the base case, the reboiler duty (heat flow rate) is 0.62 MW.

Third Distillation Column

To reduce ethanol losses (with the aqueous waste going to biotreatment), the reflux ratio of the third distillation column may be manipulated. The following relations may be used:

$$E17 = \gamma * E15 \tag{5.47}$$

where

$$\gamma = 0.653 * e^{(0.085*RR)} \tag{5.48}$$

where RR is the reflux ratio in the third distillation column. Currently, the reflux ratio for the column is 3.5 and the working range for the reflux ratio is:

$$2.5 \leq RR \leq 5.0 \tag{5.49}$$

Direct recycle is allowed only from the top of the third distillation column to the flash column.

In addition to the given path equations and constraints, one can also write the material balance equations for acetaldehyde and ethanol throughout the process. The plant is to produce 162,000 t/y of acetaldehyde (i.e., A14 = 162,000 t/y). The present (base case) value of the overall process yield is 0.601.

Results

A nonlinear programming formulation has been developed to minimize the ethanol inventory subject to the aforementioned process model. The program has 33 constraints and 35 variables. The optimization software LINGO was solved using the generalized reduced gradient (GRG) method to simultaneously solve the program and yield an optimum solution for the minimum ethanol inventory for two weeks to be 7, 098 tons at process yield of 0.953 and TE at 298 K. This is approximately 37% less the amount of ethanol that is stored for the base case (11,239 tons). The optimal values of some of the optimization values are listed in Table 5.1.

Conclusions

Limitations of previous work in intensification were overcome through defining broader categories for "Intensification" while using process integration as a holistic and systematic framework for intensification. Intensification was classified into two classes: Unit Intensification and Process Intensification. A mathematical formulation for each intensification was proposed. In the case of process intensification, units that need to be intensified are not pre-specified and more than one unit can be intensified simultaneously. A case study showed the applicability of the new classification and proposed mathematical formulation.

Table 5.1. Optimum values of key variables

Optimization Variable	**Optimum Value**
Reaction temperature	580.0 K
Flash temperature	383.7 K
Ethanol makeup temperature	298 K
Reboiler heat duty (heat flow rate) for the first distillation column	0.76 MW
Reflux ratio for third distillation column	5.0
Ethanol recycled from the top of third distillation column to the flash column:	322,709 t/y

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

A novel methodology for debottlenecking a chemical process for production maximization has been introduced. This new approach is simultaneous in nature and is based upon posing the debottlenecking task as a process integration task which links all the design and operative degrees of freedom. It exploits synergies among the units and streams to attain maximum debottlenecking. This approach is capable of identifying the true potential or maximum production of the process ahead of time (targeting step.) Two case studies were used to illustrate the applicability of the new approach in debottlenecking the whole process, identifying the right extent of debottlenecking each unit and achieving superior results compared to the conventional sequential debottlenecking approach.

The work has also introduced a simultaneous approach to process debottlenecking and heat integration. This approach simultaneously identifies the maximum achievable production flowrate at no/low cost strategy while considering heat integration of the process. Furthermore, the approach considers the retrofitting of the process heat exchange network using no/low cost strategies.

Finally, the current limitations of process intensification (limited to single-unit intensification and lack of a systematic approach) were overcome through defining broader categories for intensification while using process integration as a holistic and systematic framework for process intensification. First, a new definition and classification for "Intensification" were introduced. The new classification divides intensification into two main classes:

1. Single Unit Intensification: that is aimed at intensifying a pre-specified unit in isolation to the rest of the process in order to:
    - Minimize the unit size at the given throughput
    - Maximize the unit throughput at a given size
    - Minimize the unit hold-up
    - Maximize the unit performance at a given unit size and throughput
2. Process Intensification: in this type of intensification units that need to be intensified are not pre-specified and more than one unit can be intensified simultaneously to:
    - Minimizing the process inventory of materials
    - Maximizing the process throughput
    - Minimizing the process consumption of utility materials and feedstock

Mathematical formulations for different classes of intensification were proposed to assist engineers and designers in performing intensification.

Recommendations for future work

The research conducted in this dissertation can be extended to address even broader areas. These include:

- Process debottlenecking with utility optimization and heat exchange network retrofitting.

- Simultaneous process debottlenecking with optimization of combined heat and power.
- Expansion of proposed approaches to include process debottlenecking with investment in new equipment.
- Incorporation of time based operation into debottlenecking strategies.
- Development of metrics to reconcile safety and economic objectives for the process and guide process intensification strategies.

REFERENCES

Al-Otaibi, M., and El-Halwagi, M. (2006). "Targeting techniques for enhancing process yield." *Chemical Engineering Research & Design*, 84(A10), 943-951.

Bagajewicz, M. J., Pham, R., and Manousiouthakis, V. (1998). "On the state space approach to mass/heat exchanger network design." *Chemical Engineering Science*, 53(14), 2595-2621.

Bellner, S. P., and Kister, H. Z. (2004). "Hydraulic analysis is key to effective low-cost demethanizer debottleneck." *AIChE Spring National Meeting*, 825-835, New Orleans, LA, USA.

Belyaev, A. A., Yampolskii, Y. P., Starannikova, L. E., Polyakov, A. M., Clarizi, G., Drioli, E., Marigliano, G., and Barbieri, G. (2003). "Membrane air separation for intensification of coal gasification process." *Fuel Processing Technology*, 80 119-141.

Ben-Guang, R., Fang-Yu, H., Kraslawski, A., and Nyström, L. (2000). "Study on the methodology for retrofitting chemical processes." *Chemical Engineering Technology*, 23(6), 479-484.

Bisschops, M. A. T., Van Der Wielen, L. A. M., and Van Der Wielen, K. C. A. M. (1997). "Centrifugal adsorption to remove volatile organic compounds from water." *2nd International Conference on Process Intensification in Practice*, Antwerp, Belgium.

Cabano, L. J. (1987). "Retrofit projects – the ultimate management challenge." *Chemical Engineering Progress*, 83 (4), 27-31.

Chemical Manufactures Association (1999). *The CMA economic survey. Outlook for 2000 and beyond*, Arlington, VA.

Ciric, A. R., and Floudas, C. A. (1989). "A retrofit approach for heat-exchanger networks." *Computer and Chemical Engineering*, 13 (6), 703-715.

Cummings, C. J., Quarderer, G., and Tirtowidjojo, D. (1999). "Polymer devo & pelletization in rotating packed bed." *3rd International Conference on Process Intensification for the Chemical Industry*, Antwerp, Belgium.

Dantus M.M. and High K.A. (1996). “Economic evaluation for the retrofit of chemical processes through waste minimization and process integration.” *Industrial and Engineering Chemistry Research*, 35 (12), 4566-4578.

Dautzenberg, F. M., and Mukherjee, M. (2001). "Process intensification using multifunctional reactors." *Chemical Engineering Science*, 56 (2), 251-267.

Dhole, V. R., Ramchandani, N., Tainsh, R. A., and Wasilewski, M. (1996). "Make your process water pay for itself." *Chemical Engineering*, 103, 100-103.

Diwekar, U. M. (2003). "Greener by design." *Environmental Science and Technology*, 37, 5432-5444.

Douglas, J. M. (1992). "Process synthesis for waste minimization." *Industrial and Engineering Chemistry Research*, 31(1), 238-243.

Douglas, J. M. (1985). "A Hierarchical design procedure for process synthesis." *AIChE Journal*, 31(3), 353-362.

Dunn, R. F., and El-Halwagi, M. M. (2003). "Process integration technology review: background and applications in the chemical process industry." *Journal of Chemical Technology and Biotechnology*, 78 (9), 1011-1021.

Duran, M. A., and Grossmann, I. E. (1986). "Simultaneous optimization and heat integration of chemical processes." *AIChE Journal*, 32(1), 123-138.

Eimer, D. (2003). "PI thinking applied to natural gas treating." *Better Processes for Bigger Profits; 5th International Conference on Process Intensification for Chemical Industry,* Maastricht, The Netherlands.

El-Halwagi, M. M. (2006). *Process integration*, Academic Press/Elsevier, New York.

El-Halwagi, M. M. (1990). "Optimization of bubble column slurry reactors via delayed feed addition." *Chemical Engineering Communication*, 92, 103-119.

El-Halwagi, M. M., Glasgow, I. M., Qin, X. Y., and Eden, M. R. (2004). "Property integration: Componentless design techniques and visualization tools." *AICHE Journal*, 50 (8), 1854-1869.

El-Halwagi, M. M., Hamad, A. A., and Garrison, G. W. (1996). "Synthesis of Waste Interception and Allocation Networks." *AIChE Journal*, 42(11), 3087-3101

El-Halwagi, M. M., and Manousiouthakis, V. (1989). "Synthesis of mass exchange networks." *AIChE Journal*, 35, 1233-1244.

El-Halwagi, M. M., and Spriggs, H. D. (1998). "Solve design puzzles with mass integration." *Chemical Engineering Progress*, 94, 25-44.

Evans, L. B. (2003). "Saving energy in manufacturing with smart technology." *World Energy*, 6 (2), 112-118.

Fair, J. R., and Seibert, A. F. (1996). "Understand distillation-column debottlenecking options." *Chemical Engineering Progress*, 96, 42-48.

Faith, W. L., Keyes, D. B., and Clark, R. L. (1965). *Industrial chemicals*, 3rd Ed., John Wiley, New York.

Falk-Pedersen, O., Gronvold, M. S., and Nokleby, P. (2003). "Membrane gas/liquid contactors." *5th International Conference on Process Intensification for Chemical Industry,* Maastricht, The Netherlands.

Fisher, W. R., Doherty, M. F., and Douglas, J. M. (1987). " Screening of process retrofit alternatives." *Industrial and Engineering Chemistry Research*, 26(11), 2195-2204.

Fisher, W. R., Doherty, M. F., and Douglas, J. M. (1985). "Evaluating significant economic trade-offs for process design and steady-state control optimization problems." *AIChE Journal*, 31, 1538-1547.

Gabriel, F.B., and El-Halwagi, M.M. (2005). “Simultaneous synthesis of waste interception and material reuse network: Problem reformulation for global optimization.” *Environmental Progress*, 24 (2), 171-180.

Gestrich, W.,Eisenwein, H., and Krauss, W. (1978). "Liquid site mass transfer in bubble layers." *International Chemical Engineering*, 18 (1), 28-38.

Grossmann, I. E., and Floudas, C. A. (1987). "Active constraint strategy for flexibility analysis in chemical processes." *Computer and Chemical Engineering*, 11 (6), 675-693.

Grossmann, I. E., Hector, Y., and Kravanja, Z. (1998). "A Rigorous disjunctive optimization model for simultaneous flowsheet optimization and heat integration." *Computers and Chemical Engineering*, 22, S157-S164.

Grossmann, I. E., Westerberg, A. W., and Biegler, L. T. (1987). "Retrofit design of processes." *1st International Conference on Foundations of Computer Aided Operations*, Elsevier, Park City, UT, 403-442

Guilleminot, J. J., Choisier, A., Chalfen, J. B., Nicolas, S., and Reymoney, J. L. (1993). "Heat transfer intensification in fixed bed adsorber." *Heat Recovery System and CHP*, 13(4), 297-300.

Halim, I., and Srinivasan, R. (2002a). "Systematic waste minimization in chemical processes. 1. Methodology." *Industrial and Engineering Chemistry Research,* 41(2), 196-207.

Halim, I., and Srinivasan, R. (2002b). "Systematic waste minimization in chemical processes. 2. Intelligent decision support system." *Industrial and Engineering Chemistry Research,* 41(2), 208-219.

Harmsen, G. J., and Hinderink, A. P. (1999). " We want less: Intensification by process synthesis methods." *3rd International Conference on Process Intensification for the Chemical Industry,* Antwerp, Belgium.

Harsh, M. G., Saderne, P., and Biegler, L. T. (1989). "A mixed integer flowsheet optimization strategy for process retrofits - the debottlenecking problem." *Computer and Chemical Engineering,* 13, 947-957.

Hendershot, D. (2006). "Chemical plants - inherent safety." *Process Safety Progress* 25(4), 265-265

Hikita, H., Asai, S., Tanigawa, K., Segawa, K., and Kitao, M. (1980). "Gas holdup in bubble columns." *Chemical Engineering Journal,* 20, 59-67.

Hua, J. Z., Maier, R. W., Tessier, S. R., Brennecke, J. F., and Stadtherr, M. A. (1999). "Interval analysis for thermodynamic calculation in process design: A novel and completely reliable approach." *Fluid Phase Equilibria,* 158-160, 607-615.

Jackson, J. R., and Grossmann, I. E. (2002). "High-level optimization model for the retrofit planning of process networks." *Industrial & Engineering Chemistry Research,* 41(16), 3762-3770.

Jones, D. A., Yilmaz, A. N., and Tilton, B. E. (1986). "Synthesis techniques for retrofitting heat recovery systems." *Chemical Engineering Progress,* 82(7), 28-33.

Kemp, I. C. (2007). *Pinch analysis and process integration,* Butterworth-Heinemann, New York.

Kletz, T. (1991). *Plant design for safety: A user-friendly approach,* Taylor & Francis, London, UK.

Kooijman, C. (2000). "Liquid phase hydrogenation: An energy saving alternative." *2nd Dutch Process Intensification Symposium: A Challenge for the Process Industry,* Rotterdam, The Netherlands.

Kovac, A., and Glavic, C. (1995). "Retrofit of complex and energy intensive processes – I." *Computer and Chemical Engineering,* 19(12), 1255-1270.

Kovac-Kralj, A., Glavic, C., and Kravanja, Z. (2000). "Retrofit of complex and energy intensive processes II: Stepwise simultaneous superstructural approach." *Computer and Chemical Engineering,* 24 (1), 125-138.

Linnhoff, B., and Flower, J. R. (1978). "Synthesis of heat-exchanger networks. 1. Systematic generation of energy-optimal networks." *AIChE Journal*, 24 (4), 633-642.

Linnhoff, B., and Hindmarsh, E. (1983). "The pinch design method for heat-exchanger networks." *Chemical Engineering Science*, 38(5), 745-763.

Linnhoff, B., Townsend, D. W., Boland, D., Hewitt, G. F., Thomas, B. E. A., Guy, A. R., and Marsland, R. H. (1982). *User guide on process integration for the efficient use of energy institution of chemical engineers,* Institution of Chemical Engineers, Rugby, Warwickshire, UK.

Litzen, D. B., and Bravo, J. L. (1999). "Uncover low-cost debottlenecking opportunities." *Chemical Engineering Progress,* 95 (3), 25-32.

Liu, T., Gepert, V., and Veser, G. (2005). "Process intensification through heat-integrated reactors for high-temperature millisecond contact-time catalysis." *Chemical Engineering Research and Design*, 83(A6), 611-618.

McCabe, R. W., and Mitchell, P. J. (1983). "Oxidation of ethanol and acetaldehyde over alumina-supported catalysts." *Industrial and Engineering Chemistry Product Research and Development*, 22(2), 212-217.

McKetta, J. J., ed. (1999). *Encyclopedia of chemical processing and design,* Marcel Dekker,Inc., New York, NY.

Meili, A. (1997). "Practical process intensification shown with the example of a hydrogen peroxide distillation system." *2nd International Conference on Process Intensification in Practice,* Antwerp, Belgium.

Miller, S. A. (1968). "Acetaldehyde manufacture." *Chemical and Process Engineering,* 49 (3), 75-82.

Mizsey, P., and Fonyo, Z. (1990). "Toward a more realistic overall process synthesis - the combined approach." *Computers and Chemical Engineering,* 14, 1213-1236.

Mochizuki, S. and T. Matsui (1976). "Selective hydrogenation and mass transfer in a fixed bed catalytic reactor with gas liquid concurrent up flow." *AIChE Journal*, 22(5), 904-909.

Modashia, A. D., Karvekar, N. P., and Shah, K. P. (2000). "Debottlenecking of methanol-water distillation column in ammonia plant." *Fertilizer News*, 45, 71-75.

Moore, R. E. (1979). *Methods and applications of interval analysis*, SIAM, Philadelphia, PA.

Moore, R. E. (1966). *Interval analysis*, Prentice Hall, Englewood Cliffs, NJ.

Nelson, D.A. and Douglas, J.M. (1990). “A systematic procedure for retrofitting chemical plants to operate utilizing different reaction paths.” *Industrial and Engineering Chemistry Research,* 29 (5), 819-829.

Noureldin, M. B., and El-Halwagi, M. M. (1999). "Interval-based targeting for pollution prevention via mass integration " *Computers and Chemical Engineering,* 23 (10), 1527-1543

Olujic, Z., Kaibel, B., Jansen, H., Rietfort, T., Zich, E., and Frey, G. (2003). "Distillation column internals/configurations for process intensification." *Chemical and Biochemical Engineering,* 17 (4), 301-309.

Oyenekan, B., and Rochelle, G. (2006). "Energy performance of stripper configurations for CO2 capture by aqueous amines." *Industrial and Engineering Chemistry Research,* 45 (8), 2457-2464.

Papalexandri, K. P., and Pistikopoulos, E. N. (1993). "An MINLP retrofit approach for improving the flexibility of heat exchanger networks." *Annals of Operations Research*, 42(1), 119-168.

Papoulias, S. A., and Grossmann, I. E. (1983). "A structural optimization approach in process synthesis .2. Heat-recovery networks." *Computers and Chemical Engineering,* 7(6), 707-721.

Phillips, C. H., Lauschke, G., and Peerhossaini, H. (1997). "Intensification of batch chemical processes by using integrated chemical reactor-heat exchangers." *Applied Thermal Engineering,* 17, 809-824.

Pistikopoulos E.N. and Grossmann I.E. (1989). "Optimal retrofit design for improving process flexibility.2. Optimal level of flexibility.” *Computer and Chemical Engineering*, 13 (10), 1087-1096.

Pistikopoulos E.N. and Grossmann I.E. (1988). “Stochastic optimization of flexibility in retrofit design of linear-systems.” *Computer and Chemical Engineering*, 12 (12), 1215-1227.

Polley G.T. and Polley H.L. (2000). “Design better water networks.” *Chemical Engineering Progress*, 96 (2), 47-52.

Rapoport, H., Lavie, R., and Kehat, E. (1994). "Retrofit design of new units into an existing plant: Cast study: Adding new units to an aromatics plant." *Computer and Chemical Engineering*, 18(8), 743-753.

Ratschek, H., and Rokne, J. (1984). *Computer methods for the range of functions*, Halsted Press, New York, NY.

Rijkens, H. C. (2000). "Membrane developments for natural gas conditioning." *2nd Dutch Process Intensification Symposium*, Rotterdam, The Netherlands.

Saboo, A. K., Morari, M., and Colberg, R. D. (1986). "RESHEX – An interactive package for the synthesis and analysis of resilient heat exchange networks. I: Program description and application." *Computer Chemical Engineering*, 10, 577-589.

Saboo, A. K., Morari, M., and Woodcock, D. C. (1985). "Design of resilient processing plants .8. A resilience index for heat-exchanger networks." *Chemical Engineering Science*, 40(8), 1553-1565.

Saremi, H. S., Abdi, N., and Kashani, M. A. (2000). "Blending amines debottlenecks Iranian gas plant." *Oil and Gas Journal*, 98, 60-61.

Schneider, G. (1999). "Flow conditioners and static mixers iramprove the efficiency of nitric acid plants." *3rd International Conference on Process Intensification for the Chemical Industry*, Antwerp, Belgium.

Schnepper, C. A., and Stadtherr, M. A. (1996). "Robust process simulation using interval methods." *Computers and Chemical Engineering*, 20, 187-199.

Shakur, M. S., Brauer, J. R., Leyen, I. E., Gueguen, C., and Guilloit, P. (2000). "The debottlenecking of a packed deethanizer with high capacity trays." *Petrole et Techniques*, 427, 66-75.

Shenoy, U. V. (1995). *Heat exchanger network synthesis*, Gulf Publishing Company, Houston, TX.

Sinha, M., Achenie, L. E. K., and Gani, R. (2003). "Blanket wash solvent blend design using interval analysis." *Industrial Engineering Chemical Research*, 42, 516-527.

Smith, R. (2005). *Chemical process design and integration*, 2nd Ed., John Wiley & Sons, Ltd, West Sussex, England.

Stankiewicz, A. (2003). "Reactive separation for process intensification: An industrial prospective." *Chemical Engineering and Processing*, 42, 137-144.

Stankiewicz, A., and Moulijn, J., eds. (2004a). *Process intensification: History, philosophy, principles,* Marcel Dekker, Inc., New York.

Stankiewicz, A., and Moulijn, J. A., eds. (2004b). *Re-engineering the chemical processing plant – process intensification,* Marcel Dekker, Inc., New York.

Stankiewicz, A., and Moulijn, J. A. (2000). "Process intensification: Transforming chemical engineering." *Chemical Engineering Progress*, 96, 22-34.

Summer, D. R., McGuire, P. J., Resetarits, M. R., Graves, E. C., Harper, S. E., and Angelino, S. J. (1995). "High-capacity trays debottleneck Texas C3 splitter." *Oil and Gas Journal,* 93, 45-50.

Swaney, R. E., and Grossmann, I. E. (1985). "An index for operational flexibility in chemical process design." *AIChE Journal*, 31 (4), 621-630.

Tjoe, T. N., and Linnhoff, B. (1986). "Using pinch technology for process retrofit." *Chemical Engineering,* 93 (8), 47-60.

Trent, D., Tirtowidjojo, D., and Quaderer, G. (1999). "Reactive stripping in a reacting packed bed for the production of hypochlorous acid." *3rd International Conference on Process Intensification for the Chemical Industry*, Antwerp, Belgium.

Tsouris, C., and Porcelli, J. (2003). "Process intensification – Has its time finally come?" *Chemical Engineering Progress,* 99(10), 50-55.

Turton, R., Bailie, R. C., Whiting, W. B., and Shaeiwitz, J. A. (2003). *Analysis, synthesis, and design of chemical processes*, 2nd Ed., Prentice Hall, Upper Saddle River, NJ,.

Turunen, I. (1997). "Intensification of the anthraquinone process for production of hydrogen peroxide." *2nd International Conference on Process Intensification in Practice,* Antwerp, Belgium.

Uerdingen, E., Fischer, U., Gani, R., and Hungerbuhler, K. (2005). "A new retrofit design methodology for identifying, developing, and evaluating retrofit projects for cost-efficiency improvements in continuous chemical processes." *Industrial and Engineering Chemistry Research,* 44(6), 1842-1853.

Uerdingen, E., Fischer, U., Hungerbuhler, K., and Gani, R. (2003). "Screening for profitable retrofit options of chemical processes: A new method." *AIChE Journal*, 49 (9), 2400-2418.

Vaidyanathan, R., and El-Halwagi, M. M. (1994). "Global optimization of non-convex nonlinear programs via interval analysis." *Computers and Chemical Engineering*, 18, 889-897.

Van der Bruggen, B., Curcio, E., and Drioli, E. (2004a). "Process intensification in the textile industry: The role of membrane technology." *Journal of Environmental Management*, 73, 267-274.

Van der Bruggen B, Verberk, J., and Verhack, J. (2004b). “Comparison of pressure-driven membrane processes and traditional processes for drinking water production in Europe based on specific impact criteria.” *Water SA*, 30 (3), 413-419.

Van der Helm, D. U., and High, K. A. (1996). "Waste minimization by process modifications." *Environmental Progress*, 15(1), 56-61.

Wade, D. E. (1987). "Reduction of risks by reduction of toxic material inventories." *International Symposium on Preventing Major Chemical Accidents*, New York.

Wang, Y., Du, J., Wu, J., He, G., Kuang, G., Fan, X., Yao, P., Lu, S., Li, P., Tao, J., Wan, Y., Kuang, Z., and Tian, Y. (2003). "Application of total process energy-integration in retrofitting an ammonia plant." *Applied Energy*, 76 (4), 467-480.

Willink, K. T. (2000). "Twister supersonic gas conditioning process." *2nd Dutch Process Intensification Symposium: A Challenge for the Process Industry*, Rotterdam, The Netherlands.

Xu, Z. (2001). "Converting batch processes into continuous processes, development of the helix reactor." *4th International Conference on Process Intensification for Chemical Industry*, Brugge, Belgium.

Yee, T. F., and Grossmann, I. E. (1990). "Simultaneous optimization models for heat integration - II: Heach exchanger network synthesis." *Computers and Chemical Engineering*, 14(10), 1165-1184.

Zheng, C., Guo, K., Song, Y., Zhou, X., and Ai, D. (1997). "Industrial practice of HYGRAVITEC in water deaeration." *2nd International Conference on Process Intensification*, Antwerp, Belgium.

Zheng, D., and Cao, W. (2007). "Retrofitting for DME process by energy-flow framework diagram." *Chemical Engineering and Processing*, 46 (1), 2-9.

Zhang, J., Zhu, X. X., and Towler, G. P. (2001). "A level-by-level debottlenecking approach in refinery operation." *Industrial Engineering Chemical Research*, 40, 1528-1540.

Zhu, X. X., and Asante, N. D. K. (1999). "Diagnosis and optimization approach for heat exchanger network retrofit." *AIChE Journal*, 45 (7), 1488-1503.

APPENDIX I

PROCESS MODEL FOR THE MOTIVATING EXAMPLE

The following equations provide the appropriate level of details for modeling the various units of motivating example:

Reactor

$$F_1 = 2*F_2 \tag{I-1}$$

$$F_1 + F_2 \leq 100{,}000 \text{ kg/hr} \tag{I-2}$$

$$F_4 = 0.95*(F_1 + F_2) \tag{I-3}$$

Cooler and Compressor

$$F_4 = F_5 = F_6 \tag{I-4}$$

The volumetric flowrate to the compressor should not exceed a maximum value $V_5^{\max}$. At present, the compressor is running at its maximum volumetric flowrate capacity and is, therefore, the process bottleneck. More mass flowrate can be passed through the compressor by further cooling the gas passing through the compressor. The gas leaves the reactor at 310 K. The stream can be further cooled be increasing cooling duty (Q_4) provided that the temperature of the gas does not go below 288 K, otherwise undesirable condensation occurs. The following expressions model the cooler and compressor:

Cooling Duty of the Cooler

$Q_4 = F_4 * C_P * (T_4 - T_5)$ (I-5)

where

$C_P = 2.0 \ \frac{kJ}{kg.K}$ (I-6)

and

$T_4 = 310$ K (I-7)

Relating mass flowrate to volumetric flowrate fed to the compressor (assuming ideal gas law), we get

$F_5 = \frac{M * P * V_5}{R * T_5}$ (I-8)

where

M = 30 kg/kg-mole (I-9)

R = 0.082 m^3.atm/kg-mole.K (I-10)

P = 15 atm (I-11)

$V_5 \le V_5^{\max}$ (I-12)

$V_5^{\max}$ = 5,100 m^3/hr (I-13)

$T_5 \ge T_5^{\min}$ (I-14)

$T_5 \le T_4$ (I-15)

$T_5^{\min} = 288$ K (I-16)

First Separator

The bottom-to-feed ratio in the first separator is related to the cooling duty Q_4 (in kJ/hr) as follows:

$$F_7 = \frac{Q_4 * F_6}{9*10^6} \tag{I-17}$$

Material balance around the first separator gives:

$$F_8 = F_6 - F_7 \tag{I-18}$$

First Reactive Separator

The maximum capacity of the second separator (F_7 in kg/hr) is dependent on the extent of cooling before the separator (Q_7) as follows:

$$F_7 \le F_7^{\max} \tag{I-19}$$

$$F_7^{\max} = 40{,}000 + 0.01 * Q_7 \tag{I-20}$$

The ratio of the top product to the feed is given by:

$$F_{11} = 0.12*F_7 \tag{I-21}$$

Second Separator

The bottom product (F_{10} in kg/hr)is related to the feed and the cooling duty of the overhead condenser (Q_9 in kJ/hr) as follows:

$$F_{10} = \frac{0.9*Q_9 * F_8}{5*10^6} \tag{I-22}$$

Second Reactive Separator

Overall material balance:

$$F_{14} = F_{13} + F_{11} + F_{10} \quad \text{(I-23)}$$

$$F_{13} = 23{,}000 \text{ kg/hr} \quad \text{(I-24)}$$

Cooling Utility Capacity

The cooling utilities used to provide Q_4, Q_7, and Q_9 come from the same refrigeration system whose capacity cannot exceed a maximum limit Q^{max}, i.e.

$$Q_4 + Q_7 + Q_9 \leq Q^{max} \quad \text{(I-25)}$$

$$Q^{max} = 5*10^6 \text{ kJ/hr} \quad \text{(I-26)}$$

APPENDIX II

PROCESS MODEL FOR THE SECOND CASE STUDY

(STYRENE PRODUCTION)

In this case study, the styrene production process is to be debottlenecked by debottlenecking the BCSR. Modeling of the BCSR is based on a two-phase multi-stage model (El-Halwagi, 1990). Fig. II-1 is a schematic representation of this model. The reactor is divided into a number of cells: a set of slurry cells and a set of bubble cells. Interphase mass transfer of hydrogen takes place from the bubble phase to the slurry phase. The gas-to-liquid mass transfer coefficient is described by Gestrich et al. (1978):

$$k_l a = 0.0424(\frac{H}{D_R})^{-0.561}(\frac{\rho_l S_t^3}{g\mu_l^4})^{0.116}\varepsilon_g U_g^{0.21} \tag{II-1}$$

where $k_l a$ is the interphase mass transfer coefficient, H is the reactor height, D_R is the reactor diameter, ρ_l is the liquid density, S_t is the surface tension of the liquid, g is the gravitational acceleration, μ_l is the liquid density, U_g is the superficial velocity of the gas, and ε_g is the fractional volume of the bed occupied by the bubbles and is given by Hikita and Kikukawa (1974) as follows:

$$\varepsilon_g = 0.061 S_t^{-0.67}\mu_l^{-0.05}U_g^{0.47} \tag{II-2}$$

Let components A, B, C, and D be phenyl acetylene, hydrogen, styrene, and ethyl benzene, respectively. The main modeling equations for the nth stage may be written as follows:

Material balance on component A around the nth slurry stage:

$$U_l C_{A,n} - U_l C_{A,n-1} + r_{1,n} \Delta Z_n (1 - \varepsilon_{g,n}) = 0 \tag{II-3}$$

Where U_l is the superficial velocity of the liquid and is assumed to remain constant throughout the reactor height. The terms $C_{A,n}$ and $C_{A,n-1}$ are the compositions of A leaving and entering the nth slurry stage, $r_{1,n}$ is the rate of depletion (kmol/m^3.s) of A in the nth stage.

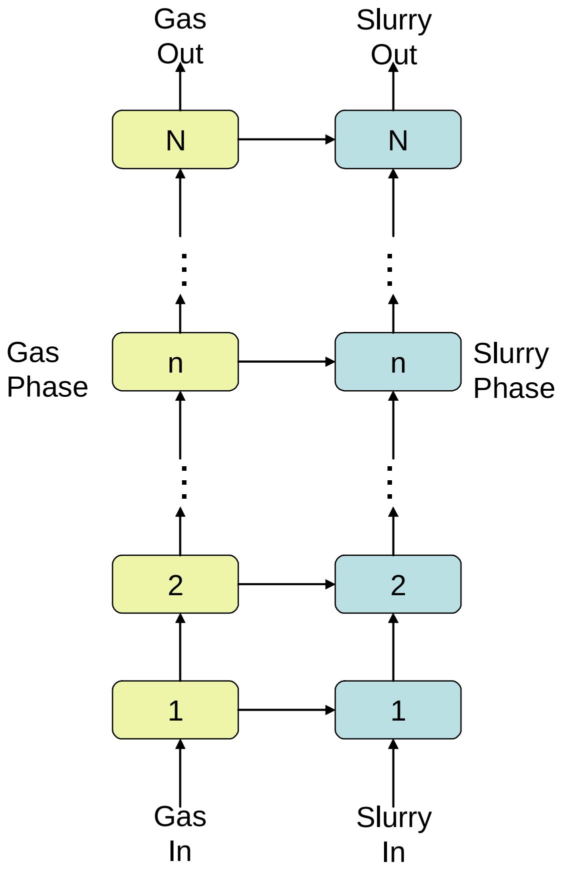

Fig. II-1. The two-phase multi-stage BCSR representation

For simplicity, the nth-stage slurry concentration of each component in the rate expression is taken as the arithmetic average of the inlet and outlet compositions of the component for that stage. For example,

$$r_{1,n} = \frac{53.0\,\overline{C}_{A,n}\,\overline{C}_{B,n}^{\,0.5}}{(1+7.3\overline{C}_{A,n}+9.8\overline{C}_{B,n}+0.29\,\overline{C}_{C,n})^{3}} \qquad \text{(II-4)}$$

Where $\overline{C}_{A,n}$, $\overline{C}_{B,n}$, and $\overline{C}_{C,n}$ are the arithmetic average compositions in the nth slurry stage of components A, B, and C, respectively. For instance, the expression for component A is given by:

$$\overline{C}_{A,n} = \frac{C_{A,n-1}+C_{A,n}}{2} \qquad \text{(II-5)}$$

The term ΔZ_n is the height of the nth cell and is taken in this case study equal to the reactor diameter (D_R). The fractional volume of the gas phase in the nth stage is calculated using the superficial gas velocity entering the stage, i.e.,

$$\varepsilon_{g,n} = 0.061 S_t^{-0.67} \mu_l^{-0.05} U_{g,n-1}^{0.47} \qquad \text{(II-6)}$$

The material balance for component B around the nth slurry stage is given by:

$$U_l C_{B,n} - U_l C_{B,n-1} - (k_l a)_n (C_{B,n}^{*} - C_{B,n})\Delta Z_n + r_{1,n}\Delta Z_n (1-\varepsilon_{g,n}) = 0 \qquad \text{(II-7)}$$

where $C_{B,n}^{*}$ is the slurry phase composition of component B in equilibrium with the gas-phase composition of component B in stage n. It is given by:

$$C_{B,n}^{g} = m C_{B,n}^{*} \qquad \text{(II-8)}$$

where m is Henry's coefficient whose value in this case study is

$$1.25\frac{kmol\ \ B/m^3 of\ \ gas}{kmol\ \ B/m^3\ of\, slurry} \tag{II-9}$$

The gas-phase composition of B in the nth stage is calculated through the ideal gas law:

$$C_{B,n}^{g} = \frac{y_{B,n}P_{n}^{g}}{RT} \tag{II-10}$$

In this case study, hydrogen in the gas phase is taken as pure (i.e., mole fraction $y_{B,n}$ = 1) and the gas-phase pressure drop is assumed to be negligible (i.e., the gas phase pressure P_n^g is constant throughout the reactor).

The material balance for component B around the nth gas stage is given by:

$$U_{g,n}C_{B,n}^{g} - U_{g,n-1}C_{B,n-1}^{g} + (k_l a)_n (C_{B,n}^{*} - C_{B,n})\Delta Z_n = 0 \tag{II-11}$$

In order to insure proper suspension of the catalyst and the slurry, the superficial velocity of the gas in any stage should not drop below a minimum required gas velocity, i.e.

$$U_{g,n} \geq U_{g}^{\min} \tag{II-12}$$

For the BCSR of this case study, the value of $U_g^{\min}$ is 0.056 m/s.

The material balance for component C around the nth slurry stage is given by:

$$U_l C_{C,n} - U_l C_{C,n-1} + (r_{2,n} - r_{1,n})\Delta Z_n (1 - \varepsilon_{g,n}) = 0 \tag{II-13}$$

The following data are used in this case study: H = 2.4 m, D_R = 0.8 m, inlet composition of phenyl acetylene to the slurry phase: $C_{A,0}$ = 0.2 kmol/m^3, μ_l =5.7x10^{-4} kg m^{-1} s^{-1}, U_l = 0.06 m/s, ρ_l =870 kg/m^3, and S_t= 0.029 N/m.

VITA

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