PRODUCTIVITY ENHANCEMENT THROUGH PROCESS INTEGRATION

A Dissertation

by

METEAB AUJIAN ALOTAIBI

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

August 2005

Major Subject: Chemical Engineering

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Approved by:

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ABSTRACT

Productivity Enhancement Through Process Integration (August 2005)

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Chair of Advisory Committee: Dr. Mahmoud M. El-Halwagi

A hierarchical procedure is developed to determine maximum overall yield of a process and optimize process changes to achieve such a yield. First, a targeting procedure is developed to identify an upper bound of the overall yield ahead of detailed design. Several mass integration strategies are proposed to attain maximum yield. These strategies include rerouting of raw materials, optimization of reaction yield, rerouting of product from undesirable outlets to desirable outlets, and recycling of unreacted raw materials. Path equations are tailored to provide the appropriate level of detail for modeling process performance as a function of the optimization variables pertaining to design and operating variables. Interval analysis is used as an inclusion technique that provides rigorous bounds regardless of the process nonlinearities and without enumeration. Then, a new approach for identification of cost-effective implementation of maximum attainable targets for yield is presented. In this approach, a mathematical program was developed to identify the maximum feasible yield using a combination of iterative additions of constraints and problem reformulation. Next, cost objectives were employed to identify a cost-effective solution with the details of design and operating variables. Constraint convexification was used to improve the quality of the solution

towards globability. A trade-off procedure between the saving and expenses for yield maximization problem is presented. The proposed procedure is systematic, rigorous, and computationally efficient. A case study was solved to demonstrate the applicability and usefulness of the developed procedure.

DEDICATION

To my late father

To my mother

To my wife

To my son, Nawaf and daughter, Sadeem

and

To my brothers and sisters

ACKNOWLEDGMENTS

I wish to express my deep thanks and gratitude to my advisor, Dr. Mahmoud El-Halwagi, for providing me guidance and encouragement during my study. He set a great example for me as a knowledgeable and dedicated person. It was a pleasure working and dealing closely with him. Thank you is not enough.

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Finally, my deep thanks and appreciation go to my family here and abroad for their sincere prayers, continuous support and encouragement.

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CHAPTER I

INTRODUCTION

Processing facilities are facing an increasingly competitive market. Globalization is resulting in the growing integration of technologies, resources, and economies around the world. It makes chemical manufacturers struggle to ensure sales, protect market share, and remain competitive in a global marketplace. In order to face competition, manufacturers have to make high quality products with competitive prices and be quickly responsive to changing market conditions. Additionally, production constraints are continually evolving to address such important issues as resource conservation, sustainability, quality, health, safety and environment. As a result, the processing facilities must strive to improve their economic performance. One of the key strategies for improving process economics is the increase of capital productivity. Towards this objective, enhancing process yield is an instrumental strategy in increasing capital productivity.

Yield is one of the most important characteristics impacting overall process economics. As such, it is necessary to develop cost-effective ways of enhancing yield. In this context, one should distinguish between the process yield and the reactor yield.

This dissertation follows the style and format of *Trans IChemE, Part A, Chemical Engineering Research and Design*.

The theoretical yield of a reactor is the maximum stoichiometric amount of the desired product obtained from the limiting reactant. The actual yield of a reactor is the amount of the desired product actually obtained from the limiting reactant, i.e.

$$\text{Actual yield of a reactor} = \frac{\text{Amount of desired product generated in the reactor}}{\text{Amount of limiting reactant fed to the reactor}} \qquad (1.1a)$$

For instance, consider a reaction which produces an amount "b" of the desired product from a certain amount "a" of the limiting reactant. In this case, we have:

$$\text{Actual yield of a reactor "Yield}_{\text{reactor}}\text{"} = \frac{b}{a} \qquad (1.1b)$$

The actual yield may not reach the theoretical yield because of several limitations including the side reactions consuming the limiting reactant, reverse reactions, and design and operating conditions.

On the other hand, the overall process yield is the amount of desired product going to sales obtained from a limiting fresh feed entering the process, i.e.

$$\text{Process yield} = \frac{\text{Amount of desired product leaving the process to sales}}{\text{Amount of limiting fresh raw material entering the process}} \qquad (1.2a)$$

For instance, consider a process which produces an amount "B" of the desired product that is to be sold. The amount of a limiting fresh raw material purchased and fed to the process is "A". In this case, we have:

$$\text{Process yiled} = \frac{B}{A} \qquad (1.2b)$$

Figure 1.1 illustrates a generic process with the quantities involved in defining the reactor and process yields.

Although the reactor yield has a considerable effect on the overall process yield and plant economics, the overall process yield directly and considerably affects the process economics and capital productivity. Additionally, enhancing the process yield is closely tied to the conservation of raw materials and the minimization of waste discharge.

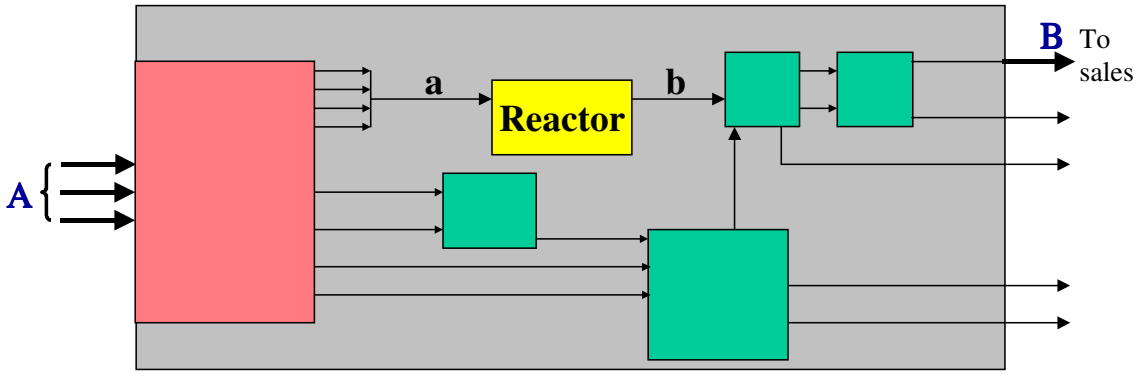


Figure 1.1. General process scheme to differentiate between reactor yield and process yield.

For example, isopropanol is produced by reaction of propylene with water. The reported process yield is 0.9 Ib of isopropanol / Ib of propylene (Elkin et al., 1979). For plant capacity of 600 MMIb/year and propylene price ranges between \$0.30-0.40/ Ib, increasing the process yield to 0.92 could make annual revenue in the range of $\$4.35\times10^6$ - 5.8×10^6. Such revenue represents saving the consumption of raw material for fixed production capacity. This show the importance of process yield increase even it is slight increase.

1.1 Objective

The objective of this work is to develop a systematic procedure for the enhancing overall process yield. Various techniques will be devised to identify maximum achievable process yield and to determine cost-effective process changes to reach the true potential of the process. Chapter II will present a review of the concepts and literature related to the process integration and optimization is presented. This is because the tools utilized in this work fall under these two areas. Then, the problem that addressed in this work is formally stated in Chapter III. In Chapter IV, a hierarchical approach is proposed to optimize several process modifications (e.g., stream rerouting) and process performance (e.g., separation, reaction) by manipulation of operating conditions (e.g. temperature, pressure, residence time). Inclusion techniques are used to identify bounds on performance without enumeration and regardless of the nonlinearity characteristics of process models. In chapter V, an optimization formulation is developed to identify cost-effective implementation of this target. This mathematical optimization problem is

expected to be NLP/MINLP (Non-Linear Programming/Mixed Integer Non-Linear Programming). A mathematical optimization technique is proposed to improve the quality of the NLP/MINLP solution. A case study is presented in Chapters IV and V to illustrate the applicability of the developed procedure. Conclusions and recommendations for further work are presented in chapter VI.

CHAPTER II

LITERATURE REVIEW

In this chapter, a thorough review for the literature related to the tools that have been utilized in this research is presented. These tools fall under the two main areas of process integration and mathematical programming. From process integration tools, targeting and path equations are used in this research. Here, a review of process integration concept and applications is presented. Review of the concepts and applications of targeting and path equations are presented in Chapter IV. In mathematical programming, global optimization and the available techniques to find the global solution are covered in this review. Review for the reformulation and linearization techniques that are used in this work is addressed in Chapter V.

2.1 Process Integration

As a result of the environmental and energy challenges facing the process industries, researchers over the past two decades have focused their attention on reducing environmental impact and energy usage and conserving material. To achieve these objectives, the focus has moved from unit-based approach to wide system-based approach. In other words, one can say: work on the whole picture first, details later.

These recent research efforts have led to the development of integrated methodologies/procedures for process design that seek to conserve energy and reduce

waste materials from a wide systems point of view. Towards these objectives, understanding the integrated nature of the process is very crucial when working on the individual units of that process. Altering operation of a stream or units can affect the whole process and has impact on the process operations and economics. The integrated approach should cover different process objectives whether they are technical or economical. Technical objective can be in the form of productivity enhancement, eliminating/reducing environmental impact, or resolving safety concerns. These challenges can be tackled via recently-developed tools and techniques that combined under a general theme called process integration.

Process integration is a framework of design methodologies which emphasize the unity of the process. The main categories of process integration are mass integration and energy integration. Mass integration is a holistic approach to the generation, separation, and routing of species and streams throughout the process. In other words, it is a systematic methodology that involves first, a comprehensive understanding of the global nature of mass flow within the process and second, utilizes this understanding to identify performance targets and optimum allocation, separation, and generation of streams and species (El-Halwagi and Spriggs, 1998). In the past, the concept of end-of-the-pipe treatment was the most dominant concept when dealing with waste and their environmental impact. The goal here was to come up with a recovery system that results in effective recycle and reuse of such wastes. Generally, there will be alternatives of process schemes and conditions to achieve this goal. These alternatives will be subjected to screening based on their economics. Currently, the development of process integration

methodologies has enabled the engineer to apply cost-effective approach that can identify a system to reduce the waste to the acceptable figures. The following sections provide review for the concepts and applications of process integration tools.

2.1.1 Energy Conservation Systems

Energy integration is a similar approach that globally addresses allocation, generation, and exchange of energy throughout the process. More demand for expensive utilities have resulted in the development of energy integration techniques. The word of energy here covers all forms of energy whether it is heating, cooling, power generation/consumption, or compression/expansion. Energy integration task is accomplished through optimal allocation of Heat Exchanger Networks (HENs). HEN is network of one or more heat exchangers for recovering process heat. The role of energy integration is to synthesize cost-effective HEN. A representation of this task is shown in Figure 2.1.

The synthesis of HENs for a certain process carries out several tasks such as (Dunn and El-Halwagi, 2003):

- Type and level of heating/cooling utilities to be used.
- Determining the optimal heating/cooling load to be removed/added by each utility.
- Identifying the optimal configuration of matching the hot and cold streams (i.e., stream pairings) including stream splitting/mixing.

Review of energy integration methods can be found elsewhere (Linnhoff, 1993; Shenoy, 1995; Douglas, 1988; Gundersen and Naess, 1988).

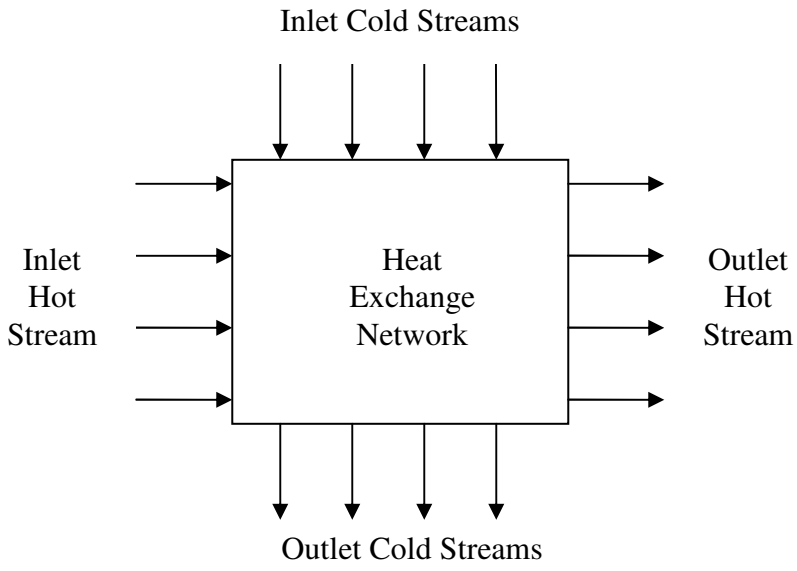


Figure 2.1. Graphical representation of the HEN synthesis task.

2.1.2 Wastewater and Water Systems

One of the active research areas in process integration is water conservation and its waste reduction. The pressure from the environmental regulators and the concerns about water availability drive the efforts in this area. Again, the objective is to identify cost-effective design that reduces wastewater and/or conserves fresh water. The design methodology may involve direct recycle and reuse options for water. The techniques reported recently in the literature include:

- Water pinch analysis (Wang and Smith, 1994; Hallale, 2000; Bagajewicz, 2000).
- Mathematical programming approaches (Alva-Argaez', et al., 2000; Keckler and Allen, 1999; Parthasarathy et al., 2001b).
- The source-sink graphical methodology (El-Halwagi, 1997; Dunn and Dobson, 1999; Dunn and Wenzel, 2001).

Some of the tasks carried out in the synthesis of waste water reduction and water conservation networks (Dunn and El-Halwagi, 2003):

- Identifying the recycled/reused streams among wastewater streams.
- Identifying the optimal recycled or reused load of each wastewater stream.
- Developing the optimal allocation and configuration of wastewater streams including stream splitting and mixing.

2.1.3 End-of-the-Pipe Waste Minimization Systems

Other area in process integration which drives more attention is separation and recycling waste minimization systems. The aim is to identify end-of-the-pipe cost-effective waste separation system among many process options. In other word, it is to synthesize mass-exchange network, MEN (El-Halwagi and Manousiouthakis, 1990a, b). MEN is a network of one or more mass exchangers that carry out the task of waste recovery. In each mass exchanger, mass-separating agent is employed to enhance the pollutant transfer from its waste stream to the MSA-carrying stream. The units of absorption,

extraction, stripping, and ion exchange are among the examples of mass exchangers. MEN design task involves identifying cost-effective network of mass exchangers that optimally transfer certain undesirable species from a group of rich (waste) streams to a group of lean (MSA) streams. Figure 2.2 shows graphical representation for a single mass exchanger while the whole network (MEN) synthesis task is graphically outlined in Figure 2.3. The tasks that carried out here may include (Dunn and El-Halwagi, 2003):

- Identifying type and quantity of mass separating agents to be used.
- Identifying the optimal mass load of each MSA to be removed/added by each MSA.
- Identifying the optimal configuration of matching the waste and MSA streams (i.e., stream pairings) including stream splitting and mixing.

Following are areas that employ MEN synthesis task:

- MENs for multiple component systems (El-Halwagi and Manousiouthakis, 1989b; Gupta and Manousiouthakis, 1994).
- MENs involving regeneration systems (El-Halwagi and Manousiouthakis, 1990b; Garrison et al., 1995).
- MENs involving chemical reactions (El-Halwagi and Srinivas, 1992; Srinivas and El-Halwagi, 1994a; Dunn and El-Halwagi, 1993; Warren et al., 1995).
- MENs combined with heat integration (Srinivas and El-Halwagi, 1994b).

- MENs with flexibility (Zhu and El-Halwagi, 1995; Papalexandari et al., 1994; Papalexandari and Pistikopoulos, 1994).
- MENs for wastewater reduction systems (Wang and Smith, 1994; Dunn and El-Halwagi, 1996).
- MENs for fixed load removal (Kiperstock and Sharratt, 1995)
- MENs with controllability (Huang and Edgar, 1995a, 1995b).

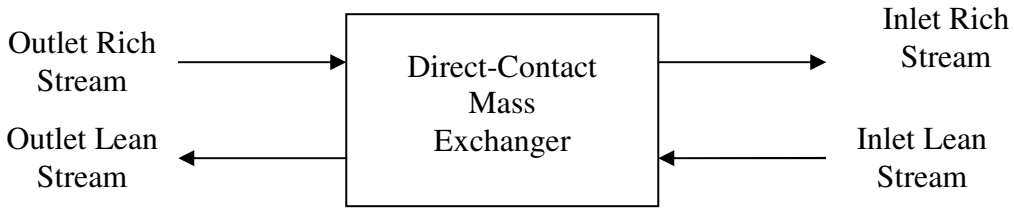


Figure 2.2. Graphical representation of single mass exchanger (Dunn and El-Halwagi, 2003).

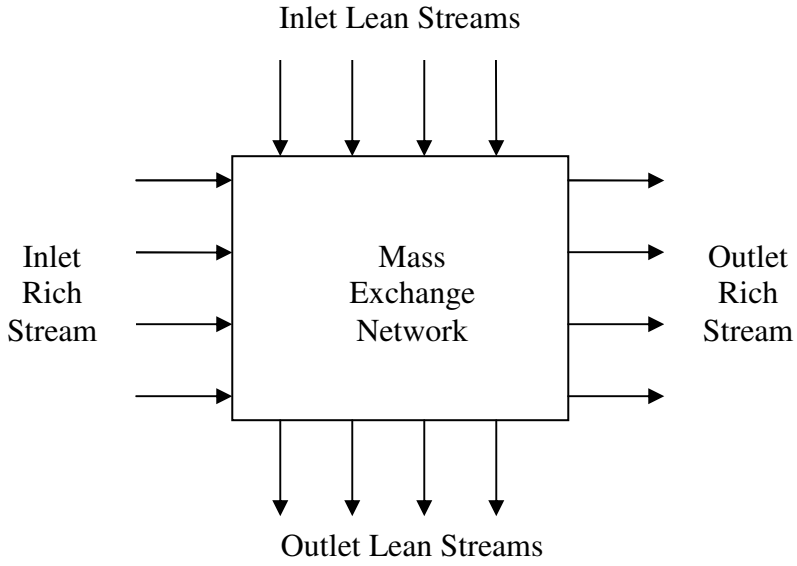


Figure 2.3. Mass Exchange Network (MEN) Synthesis (El-Halwagi and Manousiouthakis, 1989a).

Another class of separations that involves the use of energy-separating agents (ESA) is the heat-induced Separation networks (HISEN). Condensation, crystallization, evaporation, and drying are among the examples of HISEN. Here, ESA is employed to separate species via phase change. Figure 2.4 shows schematic representation of a single heat-induced separation unit. The process integration task in HISEN is to identify a cost-effective system to reduce waste to specified level through stream heating/cooling. The HISEN system has heat-induced separators and heat exchangers (Dunn and El-Halwagi, 1994a, 1994b; Dye et al., 1995; El-Halwagi et al., 1995). That task is graphically outlined in Figure 2.5.

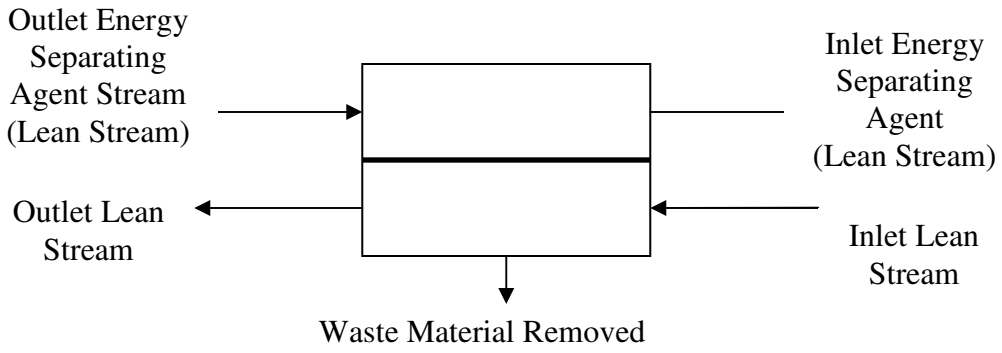


Figure 2.4. Schematic representation of a single heat-induced separation unit (Dunn and El-Halwagi, 2003).

Pressurization/depressurization units are included Within the HISEN synthesis task to tackle emission of gases that have volatile organic compounds (VOCs). This inclusion yields a recovery system named as energy-induced separation network (EISEN) (Dunn et al., 1995).

Following are some of the tasks handled when synthesizing HISENs/EISENs (Dunn and El-Halwagi, 2003):

- Identifying type of energy separating agents to be used.
- Decision on whether stream pressurization/depressurization is to be employed and the level of employed pressurization/depressurization if any.
- Identifying the optimal mass and heat load to be removed/added by each ESA.
- Identifying the optimal configuration of matching the waste and ESA streams (i.e., stream pairings) including arranging separators, heat exchangers and compressors/turbines and stream splitting and mixing.

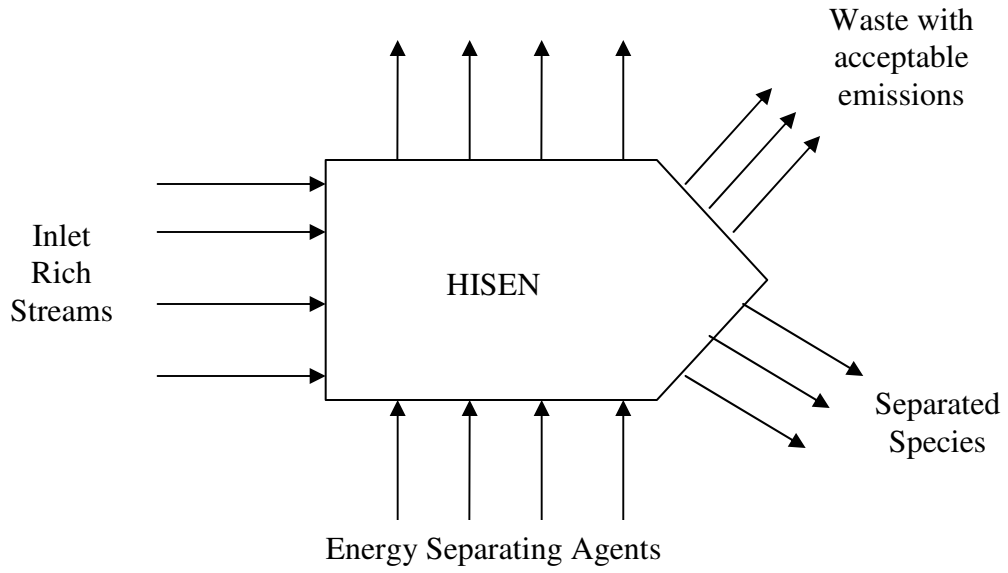


Figure 2.5. Representation of Heat-Induced Separation Network Synthesis (Srinivas and El-Halwagi, 1994a, Parthasarathy et al., 2001a).

HISEN and EISEN synthesis task is utilized in the following areas:

- HISENs for VOC condensation systems with single component (Dunn and El-Halwagi, 1994b).
- Graphical approach for HISENs for VOC condensation systems with single component (Richburg and El-Halwagi, 1995).
- HISENs for VOC condensation systems with multiple components (Dunn and El-Halwagi, 1994a).
- HISENs for fixed load removal (El-Halwagi et al., 1995).
- Combined HISEN and membrane systems (Crabtree et al., 1998).
- A spreadsheet-based approach for HISENs and EISENs applied for condensation-hybrid processes (Dunn and Dobson, 1998; Dobson, 1998).
- HISENs for crystallization systems (Parthasarathy et al., 2001b).
- HISENs for component-less VOC condensation systems using clusters (Shelley and El-Halwagi, 2000).

Pressure-based membrane system is another system in which systematic design methodologies have been developed for end-of-the-pipe treatment (El-Halwagi, 1992; Srinivas and El-Halwagi, 1993). Also, another application that involves membrane systems is the application of MEN and EISEN along with membrane systems in designing VOC recovery systems (Dunn and El-Halwagi, 1996).

2.1.4 In-plant Waste Minimization Systems

In contrary to end-of-the-pipe recycle/reuse approach for waste minimization, in plant separation approach has been developed due to its economical viability. It is obvious that dealing with pollution at its source can be proved to be more economical than the conventional end-of-the-pipe approach. This approach has been addressed via the four main strategies (Dunn and El-Halwagi, 2003):

1. Reaction path strategy: it is applicable if the undesirable species are generated in the process via reaction. The strategy calls for finding an alternative reaction path that eliminate or minimize the use of raw materials or the production of by-products that has environmental impact (Crabtree and El-Halwagi, 1995).
2. Substitution strategy: it is applicable for species fed/used in the processes (not generated via reaction). It calls for substituting undesirable species with more environmentally benign material (Hamad and El-Halwagi, 1998; Dunn et al., 1997; Joback, 1994; Constantinou et al., 1995).
3. Heat-integration-based strategy: it is applicable for emissions from or associated with in-plant utility systems such as blowdowns. It calls for the implementation of in-plant modifications based on heat integration. The aim here is to minimize such emissions from thermal pollution or associated with utility systems (Linnhoff, 1994; Linnhoff, 1995; Dhole, 1995).
4. Recycling strategy: it is applicable for undesirable species that are not generated in the process and cannot be replaced. It calls for implementing in-plant modifications for

recycling streams that carry the undesirable species. The design of wastewater minimization systems, waste interception and allocation networks (WINs), heat-induced waste minimization networks (HIWAMINs) and energy-induced waste minimization networks (EIWAMINs) were the outcome of this strategy (Wang and Smith, 1994; Dunn and Dobson, 1999; El-Halwagi, et al., 1996; Dunn and Srinivas, 1997).

There are several waste reduction methodologies that have been developed recently based on in-plant modifications. They include:

1. Synthesis of waste interception and allocation networks "WINs" (Figure 2.6), (El-Halwagi et al., 1996; El-Halwagi, 1997).
2. Synthesis of heat-induced waste minimization networks "HIWAMINs" (Dunn and Srinivas, 1997).
3. Synthesis of energy-induced waste minimization networks "EIWAMINs" (Dunn et al., 1999).

Graphical representation of the HIWAMIN and EIWAMIN design methodologies is shown in Figure 2.7.

Recently, other methodologies have been developed to address pollution prevention based on material substitution and chemistry changes (El-Halwagi, 1997; Anastas and Williamson, 1996; Anastas and Farris, 1994; Chase, 1995).

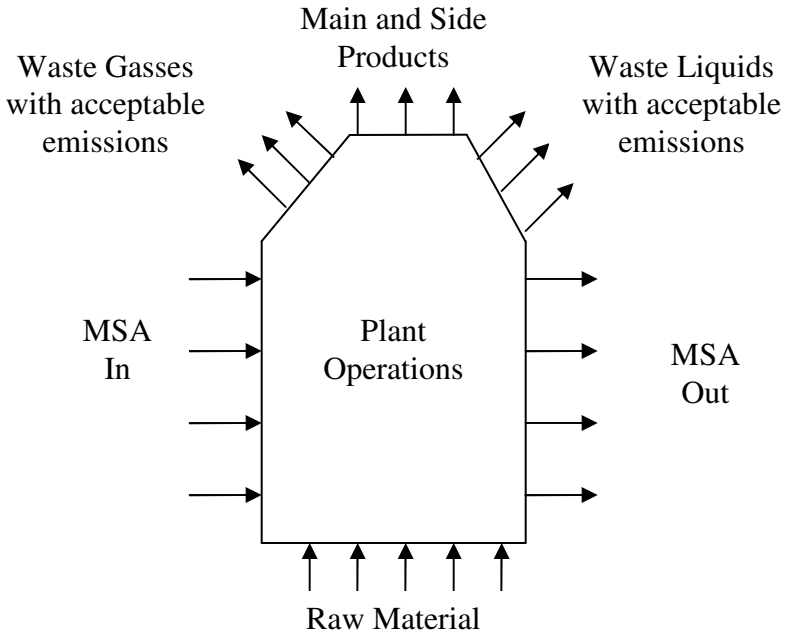


Figure 2.6. Graphical representation of WIN synthesis (Dunn and El-Halwagi, 2003).

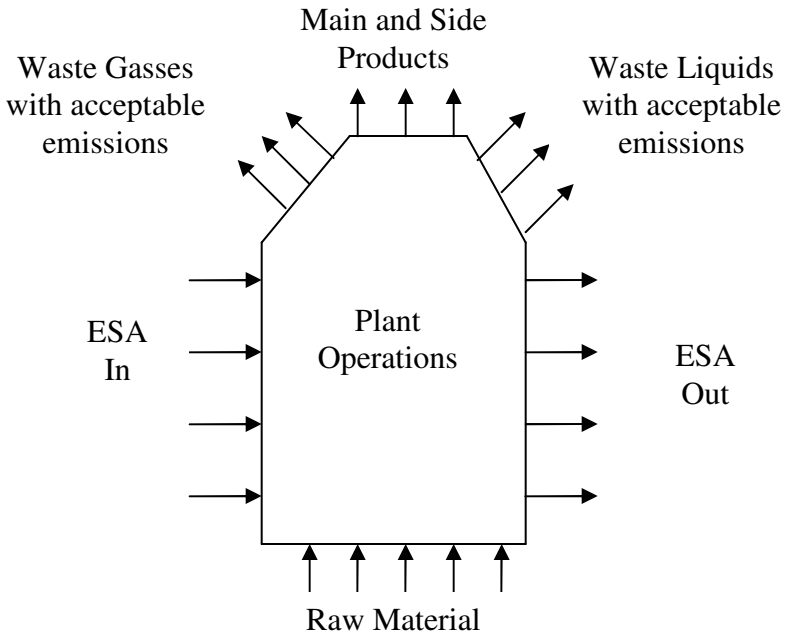


Figure 2.7. Graphical representation of HIWAMIN and EIWAMIN synthesis (Dunn and El-Halwagi, 2003).

2.2 Mathematical Programming

Our objective here is to provide a general review on optimization and in particular the techniques that have been applied or studied for nonlinear programming (NLP) and mixed integer nonlinear programming (MINLP). Optimization plays major role in process systems engineering. This is due to the fact that many problems in this area can be formulated as mathematical programming models. Considerable progress has been made in these areas for the last five decades. There have been a number of algorithms developed for determining the optimum solution for mathematical programming problems. However, since the nonlinear models involve nonconvex functions the solution that conventional techniques yield is local solution. In general, no algorithm can determine smooth global optimum solution for nonconvex NLP problems with certainty in a finite number of steps. The exception here is that if pre-specification for tolerance of the global solution is applied.

Optimization can be classified according to type of variables and type of solution. In terms of variables, there are continuous and discrete variable optimization. For the solution-based classification, there are local and global optimization. Linear (LP) and nonlinear programming (NLP) are among problems in continuous optimization. Within LP, there is linear complementary programming (LCP). NLP can be quadratic programming (QP), semidefinite programming (SP) and others. Any SP problem can be convex or nonconvex. The discrete variable optimization can be mixed-integer linear

programming (MILP) and mixed-integer nonlinear programming (MINLP). If all variables are integer, the problem called integer programming (IP).

The methods that solve global optimization problems can be classified as stochastic and deterministic methods. The stochastic methods depend on analogies to physical conditions by generating points similar to the equilibrium conditions. These methods include simulated annealing (Kirkpatrick et al., 1983), genetic algorithms (Holland, 1975), and Tabu search (Glover, 1990). A brief review for each of these methods is presented later in this section. Deterministic methods for NLP and MINLP include:

1. Lipschitzian methods (Hansen et al., 1992a; Hansen et al., 1992b).
2. Branch and bound methods (Al-Khayyal, 1992; Al-Khayyal and Falk, 1983; Horst and Tuy, 1987).
3. Cutting plane methods (Tuy et al., 1985).
4. Difference of convex (DC) and reverse convex methods (Tuy, 1987).
5. Outer-approximation (OA) methods (Horst et al., 1992).
6. Primal-dual methods (Floudas and Visweswaran, 1990; Shor, 1990).
7. Reformulation–linearization methods (Sherali and Alameddine, 1992; Sherali and Tuncbilek, 1992).
8. Interval methods (Vaidyanthan and El-Halwagi, 1994; Hansen, 1980).

In process systems engineering, there are many applications of optimization which falls under one of the above mentioned classes. Most of process design problems come as NLP

or MINLP problems. On the other hand, problems related to scheduling and planning tend to be LP or MILP problems.

2.2.1 Continuous Variable Optimization

As mentioned above, NLP, LP and QP are among the continuous variable problems. General formulation for NLP can take the following format:

$$\begin{aligned} &\text{Min } f(x) \\ &\text{s.t.} \\ &h(x) = 0 \\ &g(x) \le 0 \\ &x \in X \end{aligned} \qquad (2.1)$$

Where f(x) is the objective function, h(x) =0 are equality constraints that describe the system performance and $g(x) \le 0$ are inequality constraints that specify or restrict the feasible plans/schedules. The variables x are assumed to be continuous variables. In order for the above problem to be convex, objective function must be convex and there should be a convex feasible region. For the last condition about convexity of feasible region to hold, g(x) and h(x) have to be convex and linear, respectively. In fact, problem (2.1) can be nonconvex, convex, or strictly convex. In general, any local solution for the convex problem is a global solution while strictly convex problem has only unique global solution.

Problem (2.1) can be linear (LP) when the objective function and the constraints are linear. One main feature of LP is its ability to converge in finite number of steps. Simplex method is the standard method for solving LP (Dantziq, 1963; Wright, 1996).

In order for problem (2.1) to be of QP type, there should be at least one quadratic term. Positive semidefinite QP implies its convexity. A convex QP can be solved in finite number of steps. Range space methods, Schur complement methods and null space algorithms (Gill et al., 1981) are among the famous methods of solving QP.

2.2.1.1 NLP Solution Techniques

1. Successive quadratic programming (SQP)

It finds the solutions by developing search directions at each iteration. SQP can be classified according to the following:

a. Active set versus barrier methods: It generates search directions by using bounds and inequality constraints. This is accomplished by reformulating/linearizing the complementarity conditions of Karush-Kuhn Tucker conditions (KKT) (Fletcher, 1987; Nocedal and Wright, 1999). Active set methods are preferred for QP problems with few inequality constraints or good starting guess while barrier methods are favorable with many inequality constraints problems (Biegler and Grossmann, 2004).

Examples for applications of these two methods in process systems engineering include linear model predictive control (MPC) problems (Rao et al., 1998) and nonlinear MPC problems (Albuquerque et al., 1997).

b. Providing second-order information: It uses the second derivatives for objective or constraint functions to develop the Hessian matrix for the QP problems. Positive definite quasi-Newton approximations to the reduced Hessian are developed for functions without second derivatives (Fletcher, 1987).
c. Line search versus barrier methods: both methods are used to improve the convergence for the problems with poor starting guess. Trust region methods are efficient with ill-conditioned NLPs while line search methods are efficient for problems with good starting points and well-conditioned QP (Byrd et al., 1997).

2. Gradient-based NLP solvers

a. LANCELOT (Conn et al., 2000): it develops an augmented lagrangian for NLP in order to find the solution of bound constrained subproblems. Then, it updates the penalty parameter and multipliers continuously until satisfaction of KKT conditions is achieved. It is efficient for problems with exact second derivatives (Biegler and Grossmann, 2004).

b. MINOS (Murtagh and Saunders, 1987): it chooses active set at each iteration and implements reduced space decomposition to the augmented lagrangian NLP. It is efficient for problems with reasonable numbers of nonlinear constraints. It has interfaces with GAMS (Brooke et al., 1998) and AMPL (Fourer et al., 1992).

c. Generalized reduced gradient (GRG) methods: After selecting the active set and applying reduced space decomposition, GRG methods apply unconstrained quasi-Newton method to the variables remaining after eliminating the dependent and bounded variables. The GRG-based solvers include SOLVER code which is available with MS Excel and CONOPT which has interfaces with GAMS and AMPL.

3. Methods for Derivative Free Optimization (DFO)

They are the methods that do not require information on function derivatives. They include:

a. Classical direct search methods: these methods were the most dominant methods in chemical engineering two decades ago. Values for objective function of unconstrained minimization are required with these methods. Methods of this type include conjugate direction method (Powell, 1964), Simplex and complex searches (Nelder and Mead, 1965), the adaptive

random search methods (Luus and Jaakola, 1973; Goulcher and Cesares Long, 1978).

b. Simulated Annealing (SA): It relates multivariate/combinatorial optimization to statistical mechanics by making analogy between current state of thermodynamic system and current solution to the combinatorial problem. The energy equation for the thermodynamic system is analogous to the objective function, and ground state is analogous to the global minimum (Kirkpatrick et al., 1983). In other words, it makes analogy to the motion of molecules in the cooling and solidification (Laarhoven and Aarts, 1987). At each iteration, the method changes values of variables and objective function. If the change improves the solution, the change is accepted. If the solution is not improving, the change is accepted with certain probability. Based on the later result, variables are changed in the other direction. The method will continue until no further improvement is achieved.

c. Genetic Algorithms (GA), (Holland, 1975): these algorithms use another analogy for improving the solution by modifying its gene pool. Two types of this modification may used in these algorithm. They are crossover and mutation. In crossover modification, vector elements with highest objective function values or other criteria are randomly swapped. On the other hand, mutation adds random variable to these elements. Applications of these algorithms in process engineering include synthesis of mass exchange network (Garrard and Fraga, 1998), batch process scheduling

(Jung et al., 1998) and (Loehl et al., 1998), and sensor network design (Sen et al., 1998).

d. Tabu search: its concept as described by Glover (1986) is "a meta-heuristic superimposed on another heuristic". In this method, moves that take the solution are forbidden or penalized in order to avoid cycling. It doesn't accept a new solution unless it is to avoid a path already investigated. It begins by searching to a local optimal solution. The method records recent moves to avoid retracing the steps used. At the beginning, such recording represents a coarse examination of the solution space. This process called 'diversification'. The search will have more chance to generate local optimal solutions when candidate locations are identified in another process called 'intensification' (Perry et al., 1997).

e. Multidimensional search algorithm: it is developed based on the classical search approach that uses Nelder and Mead's simplex approach (Dennis and Torczon, 1991). It uses reflection, expansion, and contraction steps to treat the increase in the number of variables that terminates the Nelder-Mead algorithm. The approach generates local optimal solution for unconstrained problems (Torczon, 1991).

2.2.2 Discrete Variable Optimization

The importance of discrete variable in process systems engineering comes from the need to model selection decision. In this section, techniques developed for MILP and MINLP are reviewed.

2.2.2.1 Mixed-Integer Linear Programming

Methods for solving MILP depend heavily on branch and bound method (Nemhauser and Wolsey, 1988). In this later method, the integer space is branched into relaxed subproblems. In the first node, the integer variables are considered as continuous. This step generates lower bound for the optimal solution with noninteger values for some integer variables. The branching will continue and the solution at each node assumed as lower bound to the following nodes. An upper bound is found if a solution with integer values for the integer variables is reached. The procedure will continue until a certain tolerance is achieved between the two bounds.

In rare cases, most of the nodes are covered and the optimal solution is not reached. In these cases, the problem is assumed as NP-hard. Two techniques were suggested to handle this problem. They are the pre-processing and cutting planes techniques. In pre-processing techniques, one or more of the following actions may be taken: automatic elimination of variables and constraints, fixing the integer variables, reducing the bounds, reformulating the constraints. In the cutting techniques, part of the feasible region that

does not have the integer optimal solution may excluded from further enumeration. The outcome of such cutting is a tight lower bound for LP relaxation. MILP solvers include CPLEX, XPRESS, and OSL. Recent review on MILP can be found elsewhere (Johnson et al., 2000).

2.2.2.2 Mixed-Integer Nonlinear Programming

In contrast to MILP, chemical engineers have been involved heavily in developing techniques to solve MINLP. MINLP can be assumed in the following form:

$$\begin{aligned} &\text{Min } f(x, y) \\ &\text{s.t.} \\ &g(x, y) \leq 0 \\ &h(x, y) = 0 \\ &x \in X \\ &y \in Y \end{aligned} \tag{2.2}$$

Where f, g, and h are convex and differentiable functions, and x and y are the continuous and discrete variables, respectively.

Following are the most popular methods that solve MINLP:

1. Branch and Bound (BB): it is similar to the one for MILP. However, NLP subproblems are solved at each node instead of solving LP subproblems in MILP case (Borchers and Mitchell, 1994; Gupta and Ravindran, 1985; Leyffer, 2001;

Stubbs and Mehrotra, 1999). The search is stopped when all discrete variables take integer values.

In extension to this method, the solution of the MILP master problem at each major iteration by can be avoided by initially solving linearized NLP subproblem. Then, an LP-based branch and bound method is applied to solve NLP subproblems until feasible integer solution is found (Quesada and Grossmann, 1992). A significant reduction in the number of covered nodes is achieved with this extension. Such technique is suitable for problems that have difficulty in solving MILP master problem (Biegler and Grossmann, 2004).

2. Outer-Approximation (OA): it performs iterative calculations for the continuous feasible region to generate an upper bound. It alternates between nonlinear subproblems and linearized and relaxed MILP. The calculations are stopped when a specified tolerance between the two bounds is revealed (Duran and Grossmann, 1986; Fletcher and Leyffer, 1994; Quesada and Grossmann, 1992).
3. Generalized benders decomposition (GBD): it differs from OA in the definition of MILP master problem in a way that only active inequalities are considered in this method (Benders, 1962; Geoffrion, 1972). This method's lower bounds are Generally weaker than OA's bounds. It is because only one new cut is introduced at each iteration. There are two approaches to strength these bounds:

    a. Addition of user-supplied constraints to the master problem.
    b. Generation of multiple cuts from the solution of the NLP subproblem (Magnanti and Wong, 1981).

4. Extended Cutting Plane method (ECP): it requires only the solution of a single MILP solution, obtained at the previous iteration due to the presence of an additional linear constraint (westerlund and Pettersson, 1995). The method linearizes the most violated constraint at the predicted variables. The solution is reached when a specified tolerance is achieved for maximum constraint violation.

Quadratic approximations of the Hessian of the lagrangian for the NLP subproblem are suggested in case that MINLP (equation 2.2) is not linear in y (Fletcher and Leyffer, 1994). The advantages of such approximations are the following:

1. Reduction in the number of major iterations due to the improved representation of the continuous space (Biegler and Grossmann, 2004).
2. Generation of rigorous solution with convex objective and constraints functions (Biegler and Grossmann, 2004).
3. Substantial reduction in the number of iterations with OA algorithm when the objective function is not linear in the integer variable y (Fletcher and Leyffer, 1994).

The main disadvantage of these approximations is the need to solve mixed-integer quadratic programming (MIQP) instead of MILP.

In case of nonlinear equality constraints (h(x, y) in equation (2.2)), two problems arises here (Biegler and Grossmann, 2004):

1. The impossibility to enforce such equality when linearized.
2. Such nonlinearities may cause nonconvexities.

An equality relaxation is suggested through replacing such nonlinear equality by linearized inequality (Kocis and Grossmann, 1987). The sign of the multiplier associated to the nonlinear equation h(x, y) is utilized with this relaxation. this relaxation is valid with OA algorithm as GBD algorithm includes such equations in the lagrangian cuts. The relaxation will make the OA procedure a rigorous one provided that these relaxed equations will relax as convex inequalities.

The following two problems arise with nonconvex objective and inequality functions and/or nonlinear equalities:

1. More than one local optimum solution may present for the NLP subproblem.
2. Global optimum solution may be cut off due to invalid bounding representation for the master problem.

To handle these problems, some approaches are proposed:

1. Introduction of exponential transformations: to handle the nonconvexities in the geometric constraints.
2. Development of rigorous global optimization algorithm that Treats specific forms of the nonlinearities such as bilinear, linear fractional, trilinear, trilinear fractional, and concave separable. Floudas and Visweswaren (1990) proposed a global optimization approach for several classes of nonconvex nonlinear problems. If the nonconvexity in the problem are due to the presence of bilinear terms, they suggested partitioning the variable set into a new subset in such a way that the partition ensures that both objective function and constraints are convex. On the other hand, for nonconvex quadratic or polynomial terms, they introduced transformation variables so as to reformulate the problem in such a way that the nonconvexities are due to bilinear terms in the objective function and/or constraint set. The resulting variable set can then be partitioned so as to satisfy convexity conditions.
3. Reducing the effects of nonconvexities through applying heuristic strategy. For example, the effect of nonconvexities in the MILP is reduced by adding slacks that will reduce cutting-off a feasible solution (Viswanathan and Grossmann, 1990).
4. Testing the global convexity followed by checking the linearizations' validety such as testing all linearizations with respect to the current solution (Grossmann and Kravanja, 1997).

The available computer codes for solving MINLP include the following:

1. DICOPT (Viswanathan and Grossmann, 1990): it solves master problem and NLP subproblems. The code relaxes the NLP problem to produce a linearization for the master problem. It is associated with GAMS.
2. MINLP_BB: it uses branch-and-bound method and based on SQP algorithm (Leyffer, 2001). This code is available in AMPL.
3. BARON (Sahinidis, 1996): it uses branch-and-bound method.
4. SBB: it also uses branch-and-bound method and available in GAMS.
5. α-ECP: it is based on the extended cutting plane method (Westerlund and Petersson, 1995; Pörn and Westerlund, 2000).
6. MINOPT (Schweiger and Floudas, 1998): It uses OA and GBD methods and applicable mainly to dynamic optimization problems.

2.2.3 Global Optimization Techniques for NLP and MINLP

Special structures can be assumed for the continuous terms (bilinear, linear fractional, trilinear) to address nonconvexities in NLP and MINLP problems within a rigorous global optimization approaches. Uderestimators can be used as lower-bounds for these terms to convexify MINLP problems. Then, this convex formulation can be solved using global optimization techniques for continuous variables. The most popular techniques in this regard is based on the spatial branch and bound methods. Such methods divide the feasible region of continuous variables. A comparison is carried out between the two subregions in order to eliminate the subregions that have no optimal solution. A spatial

branch and bound algorithm have been proposed for nonconvex NLP problems with concave separable, linear fractional and bilinear programs (Quesada and Grossmann, 1995). In this algorithm, linear and nonlinear underestimators have been used.

Methods for nonconvex MINLP based on the spatial branch and bound procedure include:

1. Branch and bound method (Ryoo and Sahinidis, 1995; Tawarmalani and Sahinidis, 2000): it divides on the continuous and discrete variables and use underestimators along with bounds reduction. it is available in BARON. Another Branch and bound Method has recently developed (Adjiman and Floudas, 1996) that make the same branching task according to certain decisions.
2. SMIN-BB and GMIN-BB algorithms (Adjiman et al., 1997; Adjiman et al., 2000): it is applicable for twice-differentiable nonconvex MINLP problems and uses convex underestimators for general and special functions.
3. Spatial branch and bound algorithm with reformulation (Smith and Pantelides, 1999): it is applicable for nonconvex MINLP problems. It is available in gPROMS (Barton and Pantelides, 1994).
4. The branch-and-contract method (Zamora and Grossmann, 1998b; Zamora and Grossmann, 1999): it is applicable for process models with bilinear, linear fractional, and concave separable functions. It contracts the bounds and makes the spatial search at each node of the tree using the outer-approximation algorithm.

5. Generalized branch-and-cut (GBC) algorithm (Kesavan and Barton, 2000b): it is generalization of an earlier decomposition algorithm by the same authors (Kesavan and Barton, 2000a) that involves set of heuristics.
6. Two-level-branch and-bound-method (Lee and Grossmann, 2001): it is applicable for nonconvex disjunctive programming problems.

The difference between these methods is in the way they branch on the discrete and continuous variables. These branching techniques can be classified according to the following (Grossmann and Biegler, 2004):

1. Applying spatial branch and bound on both variables of the bounding problem.
2. Applying spatial branch and bound on the continuous variables and solving the corresponding MINLP problem at each node.
3. Branching on the discrete variables and apply spatial branch and bound on nodes to find a feasible value for the discrete variables.

These techniques make tightening for the lower and upper bounds of the variables to improve the quality of the underestimators. Such techniques can find a rigorous global optimum. However, the computation of these methods can be expensive because of the infinite numbers of tree searches (Grossmann and Biegler, 2004).

Literature on the underestimators for some major nonconvex functions is reviewed below. The details of these underestimators are presented in Chapter V.

1. Minimization of concave functions

These functions receive a lot of treatment among other classes of global optimization problems. Algorithms developed by Tuy and Horst (1988) and Benson and Horst (1991) are among the algorithms developed to solve these functions over a convex feasible region. Underestimator for univariate concave separable function can be developed by a straight line matching concave function at the upper and lower bound (Falk and Soland, 1969).

2. Bilinear and fractional terms

Bilinear and linear fractional terms are available in many optimization problems such as engineering design problems. Underestimators for the bilinear and linear fractional terms are derived using the general approach proposed by McCormick (1976). After developing the appropriate underestimators, they can be included in global optimization algorithms. Linear estimators for the bilinear terms have been proposed in algorithm developed by Al-Khayyal and Falk (1983). For a solution at nonextreme point, asymptotic behavior can happen in this type of algorithm (Swaney, 1993). Another algorithm for bilinear models has been developed based on linearization-reformulation technique (Sherali and Alameddine, 1992). This algorithm can produce stronger bounds for the global solution but the problem size increases exponentially with the number of original constraints (Grossmann and Biegler, 2004).

Another algorithm has been developed for solving problems with sum of linear fractional terms and linear constraints (Falk and Palocsay, 1992). Bounds on the feasible subsets are added and tightened iteratively for a sequence of linear problems. Additionally, convergence properties for this algorithm are developed by the same authors. Parametric linear programming algorithms have been developed for the minimization of the sum of two linear fractional functions over a polytope (Konno et al., 1991). This approach has been generalized to the linear fractional terms (Falk and Palocsay, 1992).

Another algorithm to solve bilinear and/or fractional problems has been proposed depending on Benders decomposition (Floudas and Visweswaran, 1990). It solves a sequence of subproblems and relaxed dual subproblems which can grow exponentially with the number of decomposed variables (Grossmann and Biegler, 2004).

3. General functions

A general approach to underestimate continuous and differentiable nonlinear functions is to add a sufficiently large quadratic term (Maranas and Floudas, 1994a;b). This underestimation along with other understimation have been included within a spatial branch and bound method (Adjiman et al., 2000).

4. Reduction of variable bounds

Underestimators provide lower bounds to the global solution and the quality of these underestimators is strongly dependant upon the bounds on the variables. Reducing the size of the range ($x^L \le x \le x^U$) can improve the quality of the convex relaxation at the corresponding node. A contraction subproblem for the variables x_i has been suggested with the assumption that the original optimization problem has linear or convex separable discrete variables y (Maranas and Floudas, 1997; Sourlas and Manousiouthakis, 1995; Zamora and Grossmann, 1998b). This contraction subproblem is assumed to be as follow:

$$\begin{aligned} &\min \textit{ or } \max \quad x \\ &\textit{s.t.} \qquad \bar{f}(x,y) \le CUB \\ &\qquad\quad \bar{g}_j(x,y) \le 0 \quad j \in J \\ &\qquad\quad x \in X, \qquad y \in Y \end{aligned} \tag{2.3}$$

Where the parameter CUB represents the current upper bound of the objective function. If bound x_i^L is selected to be contracted, the above optimization will be a minimization problem while selecting x_i^U direction will make the problem a maximization one.

Optimizing the variable bounds prior to performing the global optimization as proposed by Quesada and Grossmann (1993) can be expensive if many variables are exist and the above problem is nonlinear. To overcome this problem, two methods have been suggested:

a. Development of bound contraction strategy (Zamora and Grossmann, 1999): in this strategy, the variables with high potential to the greatest reduction are sequentially chosen.

b. Range reduction (Ryoo and Sahinidis, 1995; Ryoo and Sahinidis, 1996): in this strategy, bounding inequalities for the existing variables when solving the relaxed problem can be developed at each node. If $x_j^L - x_j \le 0, \quad j \in J$ is active at the solution, These inequalities will be in the following form:

$$x_j \le x_j^L + \frac{x_i^U - x_i^L}{\tilde{\lambda}_j} \tag{2.4}$$

And if $x_j - x_j^U \le 0, \quad j \in J$, is active:

$$x_j \le x_j^U + \frac{x_i^U - x_i^L}{\tilde{\lambda}_j} \tag{2.5}$$

Where $\tilde{\lambda}_j$ is the Lagrange multiplier.

CHAPTER III

PROBLEM STATEMENT

The overall aim of this dissertation is concerned with the determination of maximum process yield and optimizing the process changes to reach this target yield. This task can be decomposed into the following four hierarchical problems:

1. The problem of targeting overall yield of a process.
2. The problem of identifying the attainable process yield.
3. The problem of identifying cost-based strategies needed to implement the attainable yield.
4. The cost-benefit problem of developing a trade-off between the enhanced process yield and its corresponding cost.

Each of these problems is stated more formally below:

1. ***The problem of targeting overall yield of the process*** can be stated as follows:

Given a process with certain feed of raw material, it is desired to identify the target for maximum process yield. In this problem, we focus our attention to the case when yield is to be maximized using *existing equipment and without the addition of new pieces of equipment*. This case typically corresponds to the objective of maximizing capital productivity for the design and operating changes are carried out to maximize the productivity of the existing capital of the process.

The existing units of the process are referred to as sinks. The set of sinks is SINKS= {u:u= 1, N_{sinks}}. 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 targeted components. The k^{th} component has a composition referred to as $x_{i_u,k}$. Each sink has range of acceptable flowrate and composition of species under study:

$$G_{i_u}^{min} \le G_{i_u} \le G_{i_u}^{max} \qquad i_u \in INPUT_u, \quad u \in SINKS \tag{3.1}$$

$$x_{i_u,k}^{min} \le x_{i_u,k} \le x_{i_u,k}^{max} \qquad i_u \in INPUT_u, \quad u \in SINKS, \quad k \in K \tag{3.2}$$

Any stream must satisfy that range before being fed to that sink For each sink, there are vectors of design and operating degrees of freedom abbreviated as d_u and p_u, respectively. These vectors are subject to manipulation and optimization. D_u and P_u designates the intervals of permissible values of design and operating degrees of freedom for sink u, respectively. Hence,

$$d_u \in D_u \tag{3.3}$$

and

$$p_u \in P_u \tag{3.4}$$

2. ***The problem of identifying attainable yield of the process*** can be stated as follows:

Given the process described in the first part above and additionally has predetermined upper bound for its yield, it is desired to identify the achievable maximum process yield. The interval-based approach that is used in addressing the first problem gives upper bound value for process yield. In this problem, the attainable overall yield needs to be determined. In addition, the changes that are required to achieve this yield need to be determined. These changes must fall in the vectors of design and operating degrees of freedom. Again, our focus is to the case when yield is to be maximized using *existing equipment and without the addition of new pieces of equipment*.

3. ***The problem of identifying cost-effective strategies to implement the achievable process yield*** can be stated as follows:

Given the above-stated process with predetermined maximum attainable yield, it is desired to identify the cost-effective strategies to implement achievable maximum process yield. In addition to maximum achievable yield, solving the second problem has identified the design and operating changes need to be implemented in order to achieve this level of process yield. Implementing these changes is going to create additional operating/capital cost. In this regard, a cost minimization problem needs to be solved. Solving this problem will identify the minimum incremental cost for each of the process changes and the combined total minimum cost needed to obtain the maximum yield.

4. ***The cost-benefit problem of developing a trade-off between levels of enhanced process yield and their correspondent costs*** can be stated as follows:

Given a process with predetermined maximum achievable yield and its correspondent cost, it is required to develop a relationship between different levels for the improvement on that yield and the cost needed for each of these levels. The maximum achievable yield that is identified in the second problem is not necessarily feasible/economical for each operating facility. Such infeasibility may be in the form of technical/financial constraints such as limited supply of a specific operating utility or insufficient financial resource to implement the changes suggested by the solution of the third problem. Developing this trade-off will enable each operating facility to select the level of enhancement in the process yield depending on its available resources.

Chapter IV will address the first problem while Chapter V will address problems two through four.

CHAPTER IV

INTERVAL-BASED TARGETING OF PROCESS YIELD

A hierarchical procedure is developed to identify maximum targets for the overall yield of the process. First, we identify the key causes for loss in overall process yield. Then, several mass integration strategies are proposed to attain maximum yield. These include rerouting of raw materials, optimization of reaction yield, rerouting of product from undesirable outlets to desirable outlets, and recycle of unreacted raw materials. Path equations are tailored to provide the appropriate level of details for modeling the process performance as a function of the optimization variables pertaining to design and operating variables. Interval analysis is used as an inclusion technique that provides rigorous bounds regardless of the process nonlinearities. The proposed procedure is systematic, rigorous, and computationally efficient. A case study is used to illustrate the applicability of the proposed procedure.

4.1 Introduction

The processing facilities are facing an increasingly competitive market. Globalization is resulting in the growing integration of technologies, resources, and economies around the world. Additionally, production constraints are continually evolving to address such important issues as resource conservation, sustainability, quality, and safety. As a result, the processing facilities must strive to improve their economic performance. One of the key strategies for improving process economics is the increase of capital productivity.

Towards this objective, enhancing process yield is an instrumental strategy in increasing capital productivity. It is important to distinguish the process yield from the reactor yield.

The theoretical yield of a reactor is the maximum stoichiometric amount of the desired product obtained from the limiting reactant. The actual yield of a reactor is the amount of the desired product actually obtained from the limiting reactant, i.e.

$$\text{Actual yield of a reactor} = \frac{\text{Amount of desired product generated in the reactor}}{\text{Amount of limiting reactant fed to the reactor}} \qquad (1.1a)$$

For instance, consider a reaction which produces an amount “b” of the desired product from a certain amount “a” of the limiting reactant. In this case, we have:

$$\text{Actual yield of a reactor "Yield}_{\text{reactor}}\text{"} = \frac{b}{a} \qquad (1.1b)$$

The actual yield may not reach the theoretical yield because of several limitations including the side reactions consuming the limiting reactant, reverse reactions, and design and operating conditions.

On the other hand, the overall process yield is the amount of desired product going to sales obtained from a limiting fresh feed entering the process, i.e.

$$\text{Process yield} = \frac{\text{Amount of desired product leaving the process to sales}}{\text{Amount of limiting fresh raw material entering the process}} \qquad (1.2a)$$

For instance, consider a process which produces an amount "B" of the desired product that is to be sold. The amount of a limiting fresh raw material purchased and fed to the process is "A". In this case, we have:

$$\text{Process yiled} = \frac{B}{A} \qquad (1.2b)$$

Figure 4.1 illustrates a generic process with the quantities involved in defining the reactor and process yields.

Although the reactor yield has a considerable effect on the overall process yield and plant economics, the overall process yield directly and considerably affects the process economics and capital productivity. Additionally, enhancing the process yield is closely tied to the conservation of raw materials and the minimization of waste discharge.

It is important to identify bound on process performance before making extensive design and optimization computations. In this regard, targeting is an important concept. Targeting refers to the identification of bounds on the system performance *prior to* and without commitment to the final design configuration. Therefore, targeting enables the designer to identify benchmarks for improvement opportunities ahead of detailed design. Over the past two decades, several important contributions have been made in the area of

targeting the performance of complex systems. Examples include the targeting of heat-exchange networks (e.g., Linnhoff and Hindmarch, 1983), mass-exchange networks (e.g., El-Halwagi and Manousiouthakis, 1989), reactor networks (e.g., Hildebrandt and Bielger, 1995; Glasser et al., 1987), wastewater discharge (e.g., Wang and Smith, 1994), material recycle/reuse (El-Halwagi et al., 2003), and distillation networks (e.g., Doherty and Malone, 2001).

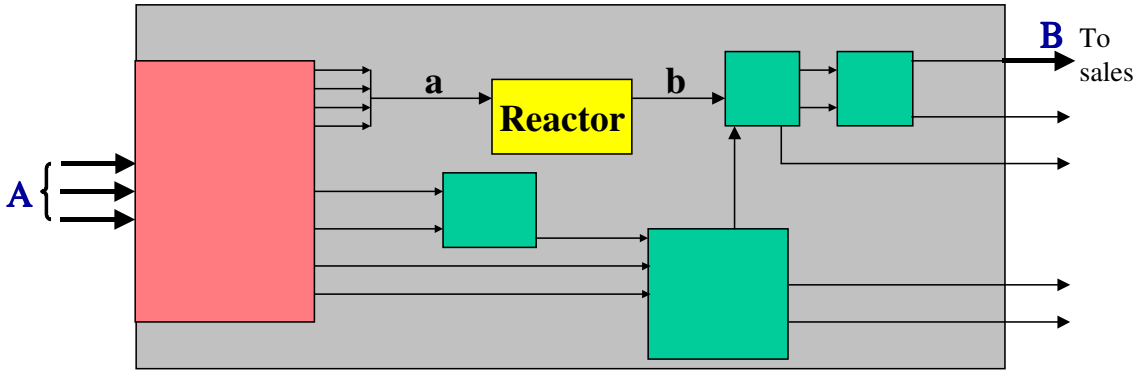


Figure 4.1. General process scheme to differentiate between reactor yield and process yield.

4.2 Objective

The purpose of this work is to develop a systematic procedure for the targeting of maximum process yield. First, we identify the key causes for loss in overall process yield. Then, we review the basic concepts of interval analysis which will be used as a key element in the targeting procedure. Next, a hierarchical approach is proposed to optimize several process modifications (e.g., stream rerouting) and process performance (e.g., separation, reaction) by manipulation of operating conditions (e.g. temperature, pressure,

residence time). Next, inclusion techniques are used to identify bounds on performance without enumeration and regardless of the nonlinearity characteristics of process models. A case study is used to illustrate the applicability of the developed procedure.

4.3 Problem Statement

The problem of targeting overall yield of the process can be stated as follows:

Given a process with certain feed of raw material, it is desired to identify the target for maximum process yield. In this research, we focus our attention to the case when yield is to be maximized using *existing equipment and without the addition of new pieces of equipment*. This case typically corresponds to the objective of maximizing capital productivity for the design and operating changes are carried out to maximize the productivity of the existing capital of the process.

The existing units of the process are referred to as sinks. The set of sinks is SINKS= {u:u= 1, N_{sinks}}. 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 targeted components. The k^{th} component has a composition referred to as $x_{i_u,k}$. Each sink has range of acceptable flowrate and composition of species under study:

$$G_{i_u}^{min} \le G_{i_u} \le G_{i_u}^{max} \qquad i_u \in INPUT_u, \quad u \in SINKS \tag{3.1}$$

$$x_{i_u,k}^{min} \le x_{i_u,k} \le x_{i_u,k}^{max} \qquad i_u \in INPUT_u, \quad u \in SINKS, \quad k \in K \tag{3.2}$$

Any stream must satisfy that range before being fed to that sink For each sink, there are vectors of design and operating degrees of freedom abbreviated as d_u and p_u, respectively. These vectors are subject to manipulation and optimization. D_u and P_u designates the intervals of permissible values of design and operating degrees of freedom for sink u, respectively. Hence,

$$d_u \in D_u \tag{3.3}$$

and

$$p_u \in P_u \tag{3.4}$$

4.4 Solution Strategy

While the above-stated problem can be formulated as a mixed-integer nonlinear program (MINLP), its global solution may be quite elusive because of the highly nonlinear and non-convex nature of most chemical processing models. Therefore, our strategy will depend on the following three elements:

1. Description of process model that are tailored at the right level of details to enable yield maximization
2. Inclusion techniques that provide rigorous bounds on process performance regardless of the nature of nonlinearity and non-convexity of process model.
3. Decomposition of the yield targeting procedure through a hierarchical approach.

Hence, we first develop the path equations to provide the right appropriate level of process-modeling details. Next, we use interval analysis as a powerful inclusion technique. Finally, we propose a hierarchical procedure that decomposes the problem into successive stages that are globally solvable then merges the solution fragments into an overall process target. In the following, we review the basic concepts and literature survey of path equations and interval analysis. Then, the targeting procedure will be described.

4.5 Path Equations

The appropriate level of the process model may be described using the concept of the path equations and its graphical analogue (the path diagram). It is analytical tool that tracks the flow and composition of the specific targeted species within the process through material balances and unit performance equations that are constructed based on the manipulated design and operating variables (e.g., El-Halwagi et. al., 1996; Noureldin and El-Halwagi, 1999). For instance, this concept can be used to describe interactions among sources (streams containing the targeted species) and sinks (process units that can process the sources).

Consider a 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 k^{th} component has a

composition referred to as $x_{i_u,k}$. Similarly the output streams have flowrates and compositions referred to as G_{j_u} and $x_{j_u,k}$, respectively. It is useful to limit the variables included in the model to the optimization (manipulated) variables that are allowed to be changed. For unit u, let the vectors representing design and operating manipulated variables be designated as d_u and p_u, respectively. Therefore, the process model for unit u can be expressed as:

$$\begin{aligned}&(G_{j_u}, x_{j_u,k} : j_u = 1,2,..., N_u^{out} \text{ and } k \in K) = \\ &f_u(G_{i_u}, x_{i_u,k} : i_u = 1,2,..., N_u^{in} \text{ and } k \in K, d_u, p_u)\end{aligned} \tag{4.1}$$

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

$$\sum_{j_u=1}^{N_u^{out}} G_{j_u} = \sum_{i_u=1}^{N_u^{in}} G_{i_u} \tag{4.2}$$

and

$$\sum_{j_u=1}^{N_u^{out}} G_{j_u} * x_{j_u,k} = \sum_{i_u=1}^{N_u^{in}} G_{i_u} * x_{i_u,k} + Net\_Gen_{u,k} \qquad k \in K \tag{4.3}$$

where $Net\_Gen_{u,k}$ is the net rate of generation of component k in unit u.

4.6 Interval Analysis

Interval analysis is a useful concept that has enabled the researchers to estimate and control floating-point computational errors. Interval arithmetic was first introduced by Moore (1966). Methods and applications of interval analysis have been addressed by many authors (e.g. Moore 1979; Ratscheck and Rokne, 1984; Hansen, 1992; Vaidyanathan and El-Halwagi, 1994).

There are some interval-based applications in chemical engineering that are reported in the literature. Schnepper and Stadtherr (1996) used interval analysis for solving a system of nonlinear equations in process simulation problem. Other applications of interval analysis include thermodynamic calculations (Hua et al., 1999; Gau et al., 2000), parameter estimation (Gau and Stadtherr, 2000; 2002) and optimal design of solvent blending (Sinha et al., 2003; Achenie and Sinha, 2003). Additionally, interval analysis can be used as an effective targeting framework. For instance, Noureldin and El-halwagi (1999) used the inclusion arithmetic of interval analysis to develop the targeting procedure for the pollution prevention. In the following, we quickly review the basics of interval analysis.

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:

$$X * Y = \{x * y : x \in X, y \in Y\} \tag{4.4}$$

Constructive rules for interval operations include the following:

$$X+Y = [\, x^l , x^u] + [\, y^l , y^u] = [\, x^l + y^l, x^u + y^u] \tag{4.5}$$

$$X-Y = [\, x^l , x^u] - [\, y^l , y^u] = [\, x^l - y^u, x^u - y^l] \tag{4.6}$$

$$X\,Y = [\, x^l , x^u][\, y^l , y^u] = [\min(\, x^l y^l, x^u y^u, x^l y^u, x^u y^l), \max(\, x^l y^l, x^u y^u, x^l y^u, x^u y^l)] \tag{4.7}$$

$$X / Y = [\, x^l , x^u]/[\, y^l , y^u] =[\, x^l , x^u][1/y^u , 1/y^l] \quad \text{when } 0 \notin [\, y^l , y^u] \tag{4.8}$$

Another useful property is the inclusion isotonicity of interval operations

$$\text{If } X \subset W \text{ and } Y \subset Z \text{ then } X*Y \subset W*Z \tag{4.9}$$

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 □f(X), i.e. □ f(X) = {f(x):x∈ X} where x is an n-dimensional vector and x∈ X. An inclusion function F is called an inclusion function for f over interval X if

$$\square\ f(X) \subseteq F(X) \tag{4.10}$$

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

4.7 Hierarchical Procedure

In order to develop the targeting procedure, it is first necessary to diagnose the causes of loss in overall process yield. The following are the principal causes:

- Inefficient allocation of raw materials to the reaction system
- Reaction yield not reaching its maximum
- Loss of product in terminal streams other than the desired outlet stream to sales (e.g., losses in byproduct streams, waste discharges)
- Inefficient recovery and recycle of unreacted raw materials

Consequently, the proposed hierarchical procedure consists of the following 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
4. Minimize the fresh consumption of the targeted raw material through recovery and recycle

The following is a description of these steps.

Step I: Maximizing routing of raw material to reactor:

The first step in this procedure is aimed at the maximization of reactor feed. Let us consider Figure 4.2a. 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 reactor leading to a load (a = α A) of the targeted reactant fed to the reactor. 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 reactor, i.e.

$$\alpha = \psi(d_u, p_u \forall u \text{ preceding the reactor}) \tag{4.11}$$

Since

$$d_u \in D_u \tag{4.12}$$

and

$$p_u \in P_u \tag{4.13}$$

Therefore, using interval inclusion, we get

$$[\alpha^{min} \quad \alpha^{max}] = \Psi(D_u, P_u \forall u \text{ preceding the reactor}) \tag{4.14}$$

where Ψ is the inclusion function of ψ. Therefore, the maximum value of the fraction α can be readily calculated as:

$$\alpha^{max} = \Psi^{max} \tag{4.15}$$

where Ψ^{max} is the upper bound of the inclusion domain of Ψ. Consequently,

$$a^{max} = \alpha^{max} A \tag{4.16}$$

This is a rigorous bound which is independent of the nature of nonlinearity and non-convexity of the function Ψ. Figure 4.2b is an illustration of the maximum rerouting to the reactor.

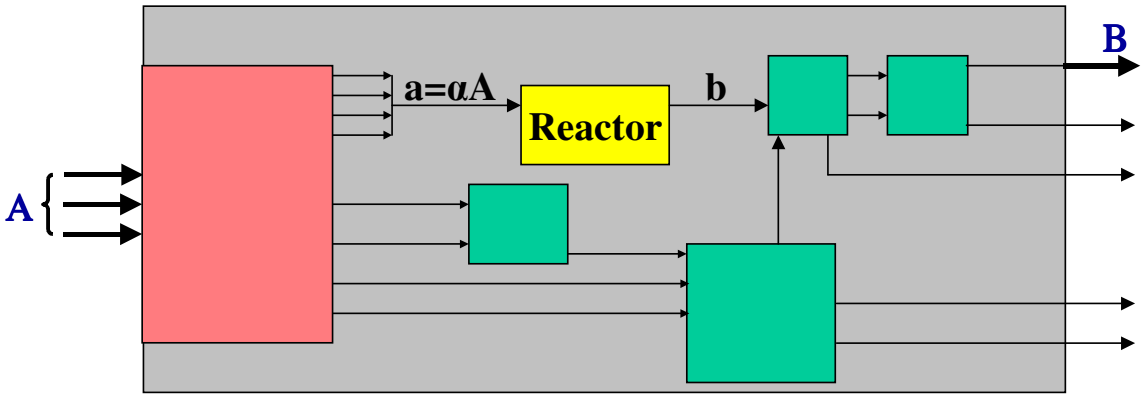


Figure 4.2a. Evaluating feed to reactor.

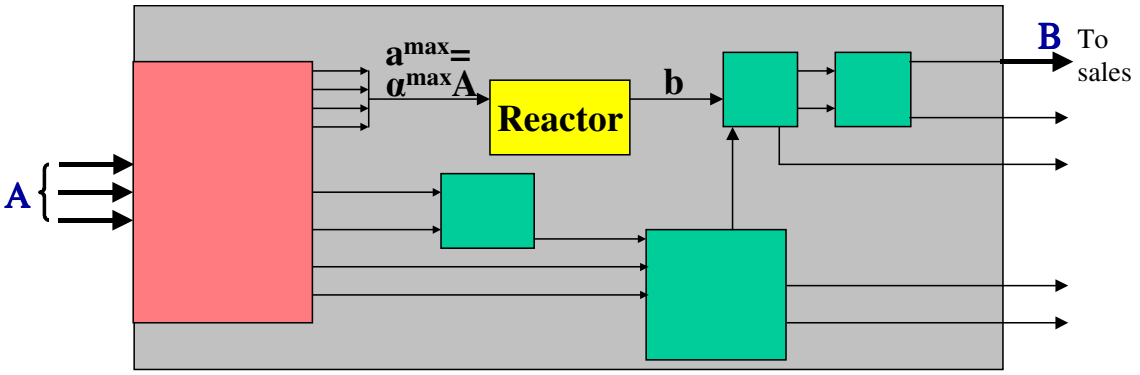


Figure 4.2b. Maximizing routing of raw material to reactor.

Step II: Maximizing reactor yield:

Let the actual yield of the reactor (defined by Eq. 1.1a) be given by this expression:

$$\text{Yield}_{\text{reactor}} = \omega(\text{Feed}_{\text{reactor}}, \text{d}_{\text{reactor}}, \text{p}_{\text{reactor}}) \tag{4.17}$$

where $\text{Feed}_{\text{reactor}}$, $\text{d}_{\text{reactor}}$, $\text{p}_{\text{reactor}}$ are the vectors of feed conditions, design variables, and operating variables, respectively. Their interval inclusions are referred to as $\text{FEED}_{\text{reactor}}$, $\text{D}_{\text{reactor}}$, $\text{P}_{\text{reactor}}$, respectively. Using interval analysis to evaluate the inclusion function for the yield, we get

$$\text{YIELD}_{\text{reactor}} = [\omega^{\min} \ \omega^{\max}] = \Omega(\text{FEED}_{\text{reactor}}, \text{D}_{\text{reactor}}, \text{P}_{\text{reactor}}) \tag{4.18}$$

Recalling the definition of the reactor yield (Eq. 1.1a), one can determine the maximum value of product leaving the reactor (Figure 4.3) as:

$$\text{b}^{\max} = \omega^{\max} \text{a}^{\max} \tag{4.19}$$

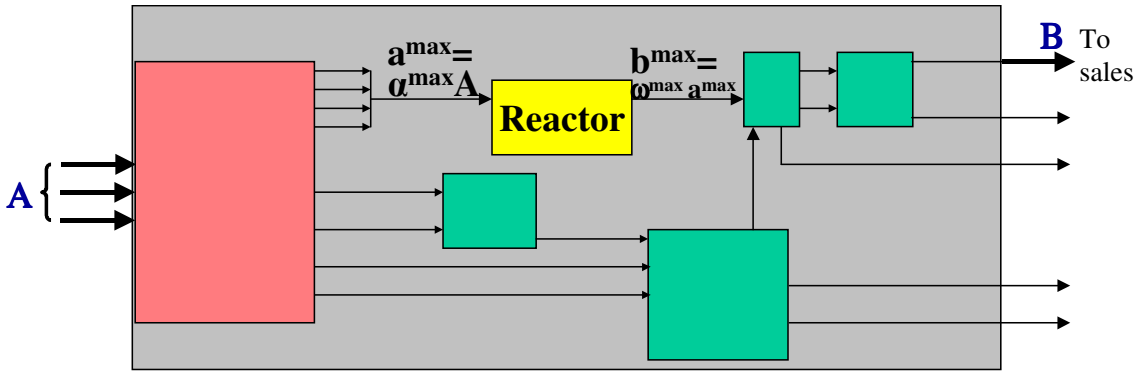


Figure 4.3. Maximization of the reactor yield.

Step III: Rerouting the product from undesirable outlets to desirable outlets:

After the reactor, 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). Hence, our objective is to manipulate the separation and finishing units so as to minimize the losses and reroute them to the desirable outlet (main product stream). Figure 4.4 illustrates this rerouting. 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.,

$$l = \phi(d_u, p_u \forall u \text{ following the reactor}) \tag{4.20}$$

Since

$$d_u \in D_u \tag{4.21}$$

and

$$p_u \in P_u \tag{4.22}$$

Therefore, using interval inclusion, we get

$$[l^{min} \quad l^{max}] = \Phi(D_u, P_u \forall u \text{ following the reactor}) \tag{4.23}$$

where Φ is the inclusion function of ϕ. Therefore, the minimum value of the product losses can be readily calculated as:

$$l^{min} = \Phi^{min} \tag{4.24}$$

where Φ^{min} is the lower bound of the inclusion domain of Φ based on the interval inclusion. With the losses minimized, the net effect is that the product will be rerouted from undesirable outlets to desirable outlets.

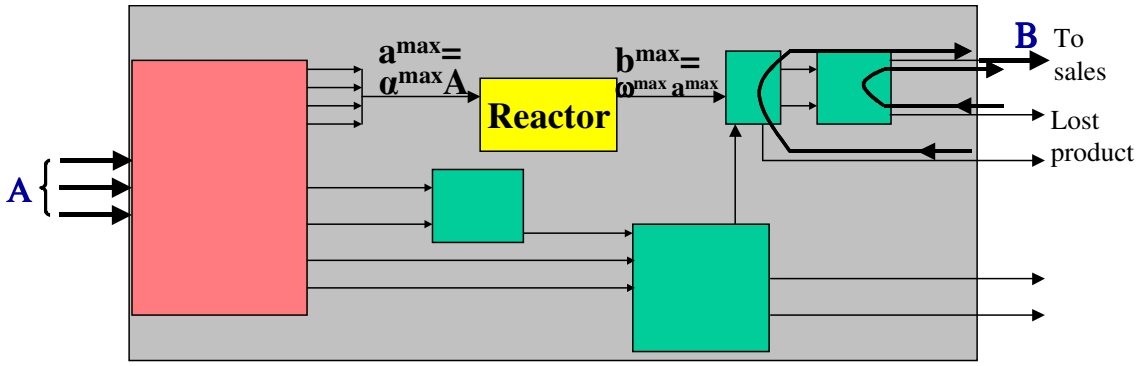


Figure 4.4. Routing product from undesirable outlets to desirable outlets.

Step IV: Minimizing fresh feed usage through recycle:

In this step, the unreacted raw material is recycled. The existing 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.,

$$r = \xi(d_u, p_u \forall u \in \text{Recovery Units}) \tag{4.25}$$

Substituting the intervals for the design and operating variables of the recovery units and performing interval inclusion calculations, we get

$$[r^{min} \quad r^{max}] = \Xi(D_u, P_u \forall u \text{ following the reactor}) \tag{4.26}$$

where Ξ is the inclusion function of ξ. Therefore, the maximum recoverable raw materials correspond to r^{max}.

It is worth noting that 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), i.e.

Maximum recyclable load of raw material = argmin {r^{max}, Fresh feed requirement of the reactor} (4.27)

Figure 4.5 is a schematic presentation of the flowchart for the targeting procedure. It illustrates the aforementioned hierachical steps.

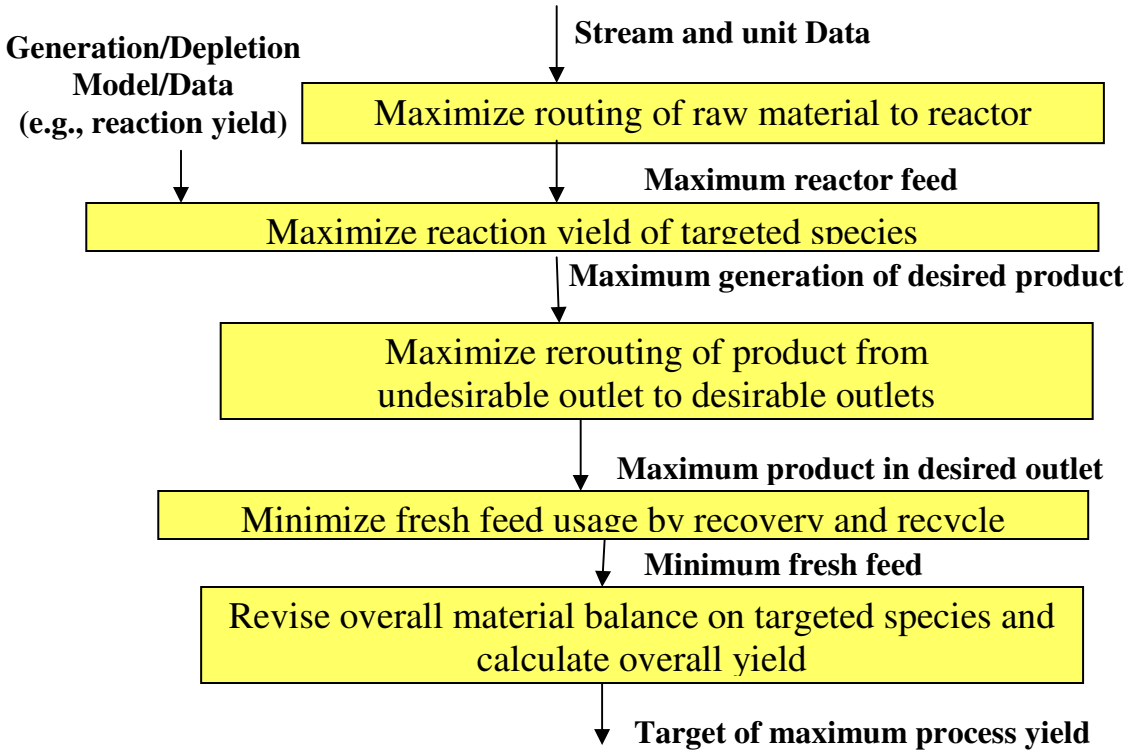


Figure 4.5. Flowchart for hierarchical yield-targeting procedure.

The computed target is a global upper bound on the process yield regardless of the nonlinearities involved in the process. bounding characterisitics and iclusion isotonicity of interval analysis are independent of nonlinearities and nonconvexities of the system. Additionally, the inclusion techniques are computationally efficient. To illustrate the applicabilty of the developed procedure, we solve the following case study on identifying the maximum yield for an ethanol oxidation process.

4.8 Case Study: Yield Targeting in Acetaldehyde Production through Ethanol Oxidation

Consider the process of producing acetaldehyde via ethanol oxidation. A schematic process flowsheet is shown in Figure 4.6. 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:

$$CH_3CH_2OH + ½\ O_2 \rightarrow CH_3CHO + H_2O$$

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, 1983):

$$Y_{reactor} = 0.33 - 4.2*10^{-6}*(T_{rxn} - 580)^2 \qquad (4.28)$$

where T_{rxn} is the reactor temperature (K). At present the reactor is operated at 500 K and the current reactor yield is 0.3 kg acetaldehyde formed in the reactor per kg ethanol fed to the reactor.

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 are released to atmosphere (Aguiló and Penrod, 1999). The liquid from the second scrubber is recycled as scrubbing agent for the first scrubber with 5% of 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 are mostly water and are fed to the biotreatment facility.

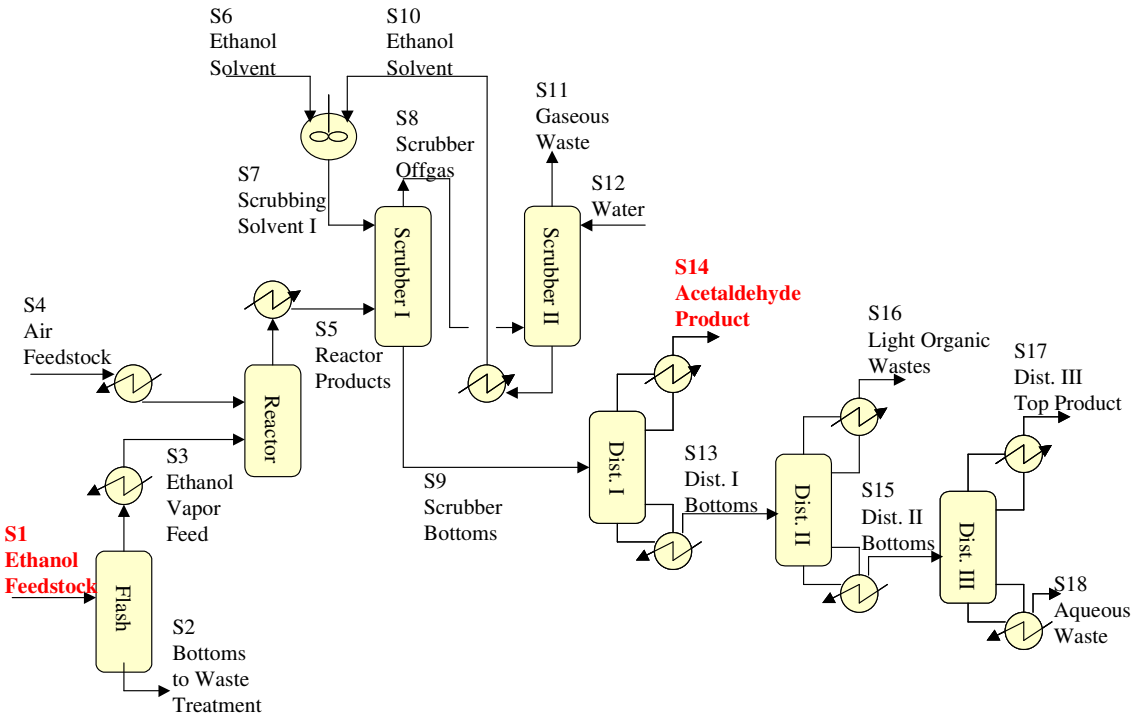


Figure 4.6. Schematic representation of acetaldehyde process.

The objective of this case study is to maximize the overall process yield without adding new process equipment. The overall process yield (Process yield) is defined as:

$$\text{Process yield} = \frac{\text{Acetaldehyde in final product stream}}{\text{Fresh ethanol fed to process as feedstock}} \tag{4.29a}$$

In the definition of the process yield the use of the phrase “ethanol fed to the process as a feedstock” excludes the use of ethanol for non-reactive purposes such as solvents (e.g., stream S6). Therefore, the process yield is given by:

$$\text{Process yield} = \frac{\text{A14}}{\text{E1}} \tag{4.29b}$$

where A14 is the mass flowrate of acetaldehyde in the final acetaldehyde product (in stream S14) and E1 is the mass flowrate of ethanol in the fresh feedstock to the process (in stream S1).

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

- No ethanol in S4, S12, S14, or S16.
- E6 = 400 ton ethanol/yr
- 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 Eq. (4.28). The feasibility range for the reaction temperature is given by:

$$300 \leq T_{rxn}\,(\text{K}) \leq 860 \tag{4.30}$$

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

$$Y_{reactor} = \frac{AR}{E_{feed}} \tag{4.31}$$

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 is related to AR through stoichiometry and molecular weights. Therefore,

$$ER = (46/44)*AR \tag{4.32}$$

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:

$$E2 = \alpha*E1 \tag{4.33}$$

Where

$$\alpha = 10.5122 - 0.0274*T_{flash} \tag{4.34}$$

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

$$380 \leq T_{flash}\ (K) \leq 384 \tag{4.35}$$

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:

$$A14 = \beta * A9 \quad (4.36)$$

Where

$$\beta = 0.14 * Q_R + 0.89 \quad (4.37)$$

where Q_R is the reboiler heat duty in MW. The range of the reboiler duty is:

$$0.55 \leq Q_R \text{ (MW)} \leq 0.76 \quad (4.38)$$

For the base case, the reboiler duty is 0.55 MW.

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

$$E17 = \gamma * E15 \quad (4.39)$$

where

$$\gamma = 0.653 * e^{(0.085*RR)} \quad (4.40)$$

where RR is the reflux ratio in the third distillation column. Currently, the reflux ratio for the column is 2.5 and the working range for the reflux ratio is:

$$2.5 \leq RR \leq 5.0 \quad (4.41)$$

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 100,000 ton/yr of acetaldehyde (i.e., A14 = 100,000 ton/yr). The present (base case) value of the overall process yield is 0.65. It is desired to explore the process potential using existing units and without adding new pieces of equipment. What is the target for maximum overall process yield?

4.8.1 Solution

Let us apply the hierarchical procedure to identify the target for maximum yield of the process. In maximizing the routing of raw materials to the reactor, we use the inclusion of Eqs. (4.33) and (4.34) over the interval given by Eq. (4.35). Then, we maximize the reactor yield by calculating the inclusion of Eq. (4.28) over the interval given by Eq. (4.30). Routing of the desired product from undesirable outlets to the desirable outlet involves calculating the inclusion of Eqs. (4.36) and (4.37) over interval (4.38). Finally, the recyclable ethanol stream (overhead of the third distillation column) can be maximized by calculating the inclusion of Eqs. (4.39) and (4.40) over interval (4.41). The maximum recoverable ethanol from the top of the third distillation column is recycled to the flash column to minimize the usage of fresh ethanol. The procedure is followed and the material balance equations along with the given path equations are used to evaluate the revised flows of ethanol and acetaldehyde. The result is that the target for maximum process yield is 0.955. This is approximately four times the overall process yield at the base case. With such a promising result, the detailed design of the process should be considered. In this context, mass integration strategies (e.g., Dunn and El-Halwagi, 2003) can be instrumental in detailing the design.

4.9 Special Cases of Overall Process Yield Targeting and Maximization

There are some cases where the maximum achievable yield can be identified by observation and/or minimal calculations and without detailed enumeration like the one

technique discussed in our work. It is the objective of this work to predict overall yield for any process without the need to go through the process insights. This study will cover some process categories which differ from each other in the number of reactions that take place in each reactor and the assumption of losses of fresh feed and desired product within the process. Here, two process categories are addressed as follow:

4.9.1 Process with One Reaction and No Losses

For this category, the following assumptions are considered:

1) Only one reaction is taking place in the reactor.
2) No losses of desired product. In another word, all reactor effluents of desired product are going with the product stream.
3) No losses of process feed. All process feed is going to the reactor.

Figure 4.7 shows typical process of this category where the reaction is assumed to take place in the reactor:

$$A \rightarrow B$$

This reactor yield (Y_R) can be predicated from the stoichiometic data as follow:

$$Y_R = \frac{\text{amount of B produced in reactor}}{\text{amount of A in reactor feed}} \tag{4.42}$$

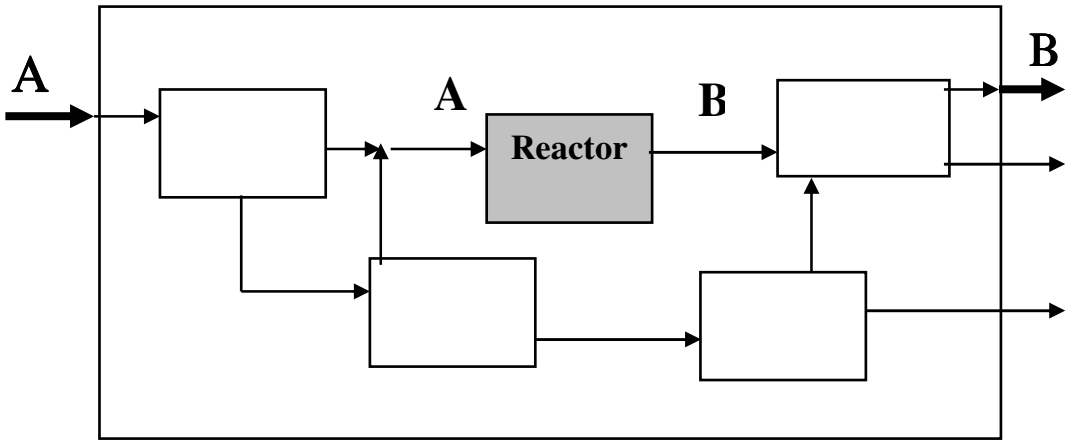


Figure 4.7. Typical process with one reaction and no losses.

In other words, it represents the stoichiometic ratio of reaction product to reactant.

The process yield (Y_P) is defined as:

$$Y_P = \frac{\text{amount of B in process desired product stream}}{\text{amount of A in process fresh feed}} \tag{4.43}$$

Since there are no losses of reactant A ahead of reactor then amount of A in the process feed is equal to the amount of A in reactor feed. The same applies for the product (B) i.e. amount of B in the process desired product stream is equal to the amount of B in reactor effluent. Based on this, the process yield will be equal to the reactor yield. Hence, the only way to maximize the process yield with such conditions is to maximize the reactor yield. When applying the targeting procedure presented in this work, the only applicable strategy (step) is step II (i.e. maximizing the reactor yield).

4.9.2 Process with More Than One Reaction and No Losses

The following assumptions will hold for this category:

1) Two or more reactions taking place in the reactor
2) No losses of feed or product within the process or with byproduct/waste streams.

For example, Figure 4.8 shows certain process where the following reactions are assumed to take place in the reactor:

$$A \rightarrow B$$

$$A \rightarrow C$$

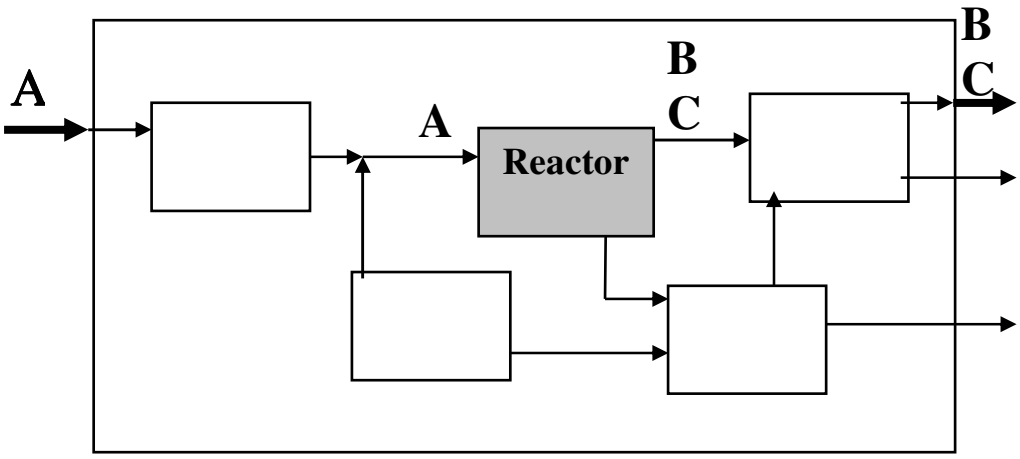


Figure 4.8. Typical process with two reactions and no losses.

Additionally, it has been assumed that the first reaction ($A \rightarrow B$) is the main reaction (i.e. B represents the desired product) while the second reaction ($B \rightarrow C$) is assumed to be the

side reaction (i.e. C is the side product). In addition to the definitions of reactor and process yields above, reactor selectivity (S) and conversion (X) is defined as:

$$S = \frac{\text{amount of B produced in reactor}}{\text{amount of A consumed in reactor}} \tag{4.44}$$

$$X = \frac{\text{amount of A consumed in reactor}}{\text{amount of A fed to reactor}} \tag{4.45}$$

The amount of reactant A consumed in the reactor is subset of the amount of A fed to the reactor. When tracking A in the reactor, it has three possibilities:

- It reacts to form the desired product B;
- It reacts to form the undesired product C;
- It doesn't react and leaves the reactor as effluent.

The selectivity represented here by the first possibility above. The only way to maximize yield for this category of processes is increase the selectivity.

Additionally, if we assume that there is no desired product fed to the process or produced in the process except the amount produced in the reactor, the reactor yield is equal to the product of multiplying selectivity by conversion i.e.:

$$Y_R = S*X \tag{4.46}$$

When applying the assumption of no losses of feed and desired product as in category I, it is concluded that process yield is equivalent to reactor yield, i.e.:

$$Y_P = S*X \qquad (4.47)$$

The only way to enhance the yield of this category is to increase the reactor yield which in turn can be increased by improving the selectivity and/or conversion.

The case where there could be one or more reactions and losses of feed and/or desired product within the process represents the general case. It is the case for which the procedure in this research has been developed.

4.10 Conclusions

A targeting procedure was developed to identify an upper bound on the overall yield of the process. This target is identified ahead of detailed design. A hierarchical approach was devised to optimize several process modifications (e.g., stream rerouting) and process performance (e.g., separation, yield, recovery) by manipulation of operating conditions (e.g. temperature, pressure, residence time). Next, inclusion techniques were used to identify bounds on performance without enumeration and regardless of the nonlinearity characteristics of process models. Tailored process models were developed using the concept of path equations to provide the appropriate level of details and degrees

of freedom for yield maximization. A case study was solved to demonstrate the usefulness of the developed procedure.

Having the identification of process yield target, a detailed design of the process is to be considered. In this regard, an optimization formulation is to be developed to identify cost-effective implementation of this target. This task is addressed in the next chapter.

CHAPTER V

MATHEMATICAL PROGRAMMING APPROACH FOR YIELD MAXIMIZATION AND COST MINIMIZATION

5.1 Introduction

The methodology developed in Chapter IV generates a target (upper bound) for the process yield. Once a target is identified, it is important to devise cost-effective, implementable solution that attaints the target. In this chapter, an optimization procedure is developed to achieve this target and to identify cost-effective strategies to attain this yield target. The proposed approach is based on the following key steps:

- Formulation of the yield-maximization problem as an optimization problem
- Reformulation of optimization program to enhance solution quality
- Identification of a feasible target for yield
- Determination of cost-effective implementation of attainable target

Figure 5.1 shows a flowchart that outlines the proposed procedure. The procedure starts by developing a formulation for maximization of process yield. This objective function is subject to two main sets of constraints:

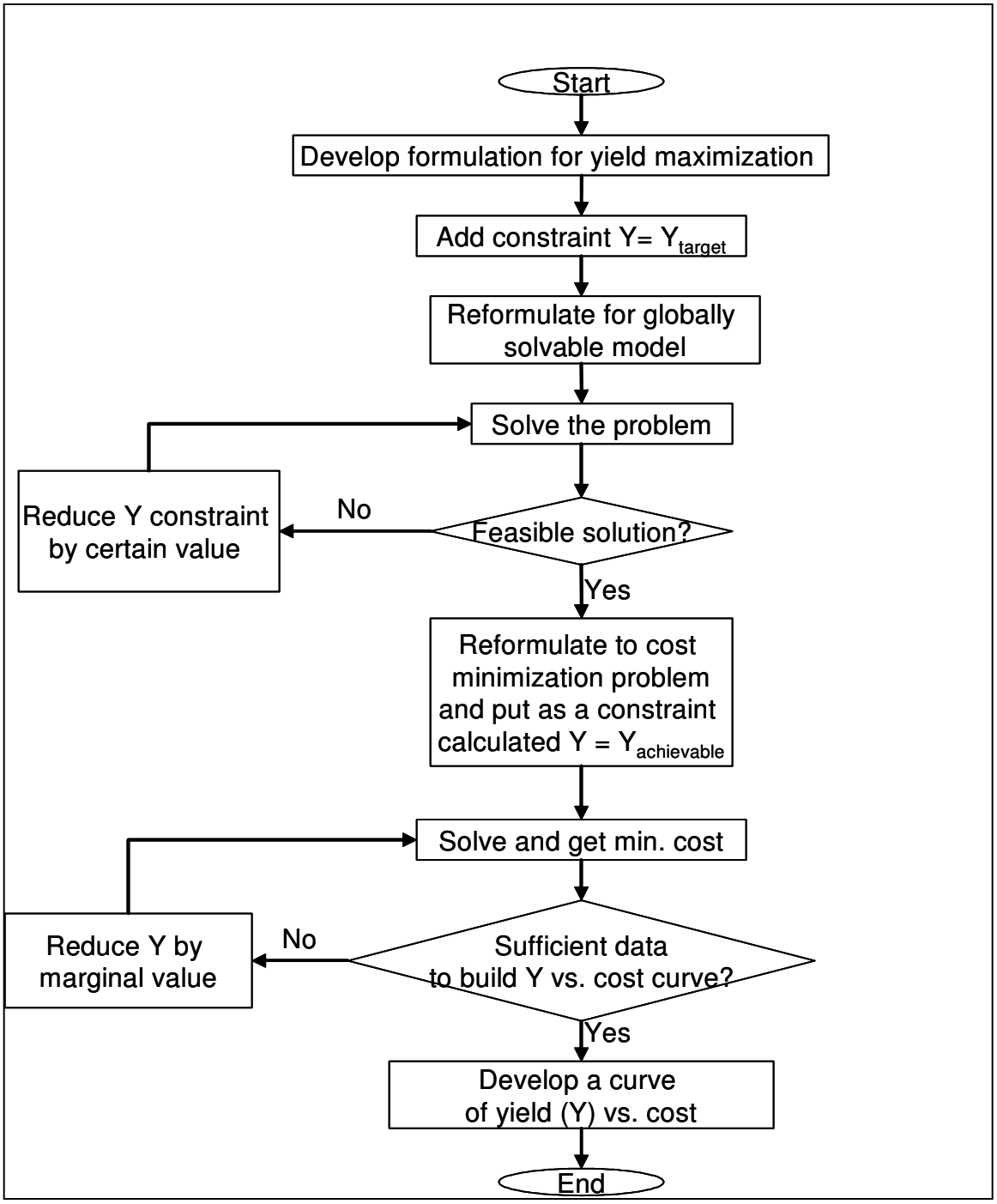


Figure 5.1. Flow chart of process yield implementation.

I. Material balance on desired product and fresh feed: Fresh feed and desired product for a certain process are targeted species to be evaluated for yield maximization problem. Based on that, material balance for both species is to be developed on overall process, part of the process ahead of reactor, part of the process after reactor and around reactor. These equations are part of the problem constraints. The development of these equations and their general format are shown later in the formulation section.

II. Unit performance equations: In Chapter IV, four strategies were developed. Each of these strategies is represented by unit performance equations and lower and upper bounds of manipulated variables. The performance equations are formulated as equality constraints while variable bounds are in the form of inequality constraints.

The developed formulation is generally a Mixed Integer Non-Linear Program (MINLP). Survey for the literature on this kind of problem is presented in chapter II. One of the available techniques that improve the solution quality is the problem reformulation and linearization of the nonlinear terms. This technique is suggested for the problem under study in order to generate global or close to global solution.

The procedure in Chapter IV identified an upper bound on the attainable target for yield. As such, it is important to determine the maximum attainable target. In this regard, an iterative procedure is proposed whereby one yield constraint is added to the optimization formulation. First, the upper bound constraint is added and the optimization program is solved with the objective of maximizing yield. If a feasible solution is found, then the

upper bound is attainable. Otherwise, a yield value that is slightly lower than the upper bound is added as a constraint and the program is resolved. If a feasible solution is found, then the maximum attainable target has been identified. Otherwise, the process is repeated until a feasible solution is found. Following the identification of maximum achievable yield, a cost minimization program is to be developed for this yield. This is to be done by replacing the objective function of yield maximization problem by cost minimization function. This latter function involves cost figures of manipulated parameters in unit performance equations. Multiple runs are conducted for different yields in order to generate yield versus cost curve (Figure 5.2).

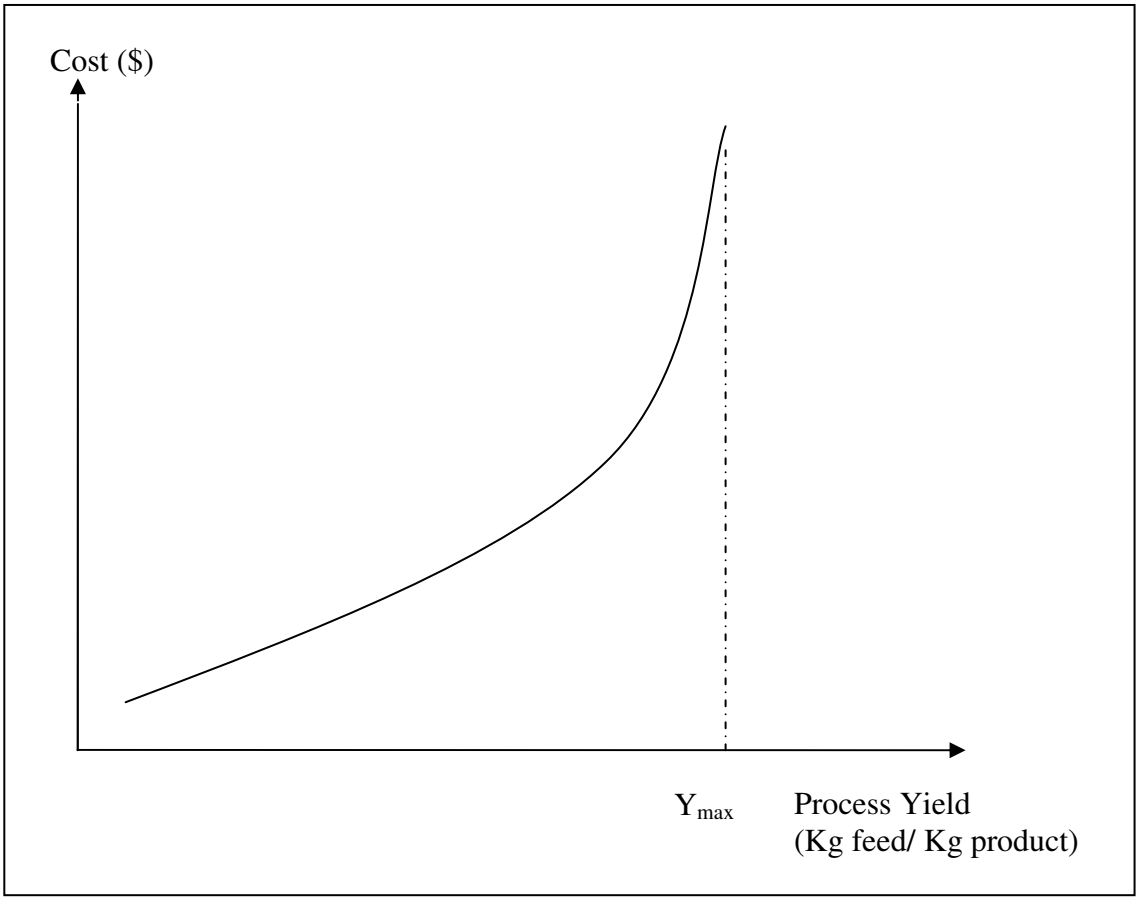


Figure 5.2. Typical process yield vs. cost curve.

5.2 Formulation of Process Yield Maximization

The objective function here is the process yield (Y) which generally defined by equation (1.2). In more specific, is defined as:

$$Y_p = \frac{G_p * x_{p,p}}{G_f * x_{f,f}} \tag{5.1}$$

Where G_p represents flow rate of desired product stream p while $x_{p,p}$ is composition of desired product p in that stream. G_f is the flow rate of fresh feed stream f and $x_{f\,f}$ is the composition of fresh feed f in that stream.

In order to develop the constraints, the material balance is first developed for the overall process for both fresh feed and desired product is developed. Figure 5.3 shows graphical representation of the process material balance (the dashed oval represents the boundary of this balance) for the feed. Similar representation applies for desired product. The developed equations will take the form:

For the desired product:

$$\sum_{j=1}^{N_{process}^{out}} G_j * x_{j,p} = \sum_{i=1}^{N_{process}^{in}} G_i * x_{i,p} + Net\_Gen_p \tag{5.2}$$

- set of process input streams (i): i = {i=1,2, …, $N_{process}^{in}$ }

- set of process output streams (j): j = {j=1,2, …, $N^{out}_{process}$ }

For the fresh feed:

$$\sum_{j=1}^{N^{out}_{process}} G_j * x_{j,f} = \sum_{i=1}^{N^{in}_{process}} G_i * x_{i,f} + Net\_Gen_f \qquad (5.3)$$

- set of process input streams (i): i = {i=1,2, …, $N^{in}_{process}$ }

- set of process output streams (j): j = {j=1,2, …, $N^{out}_{process}$ }

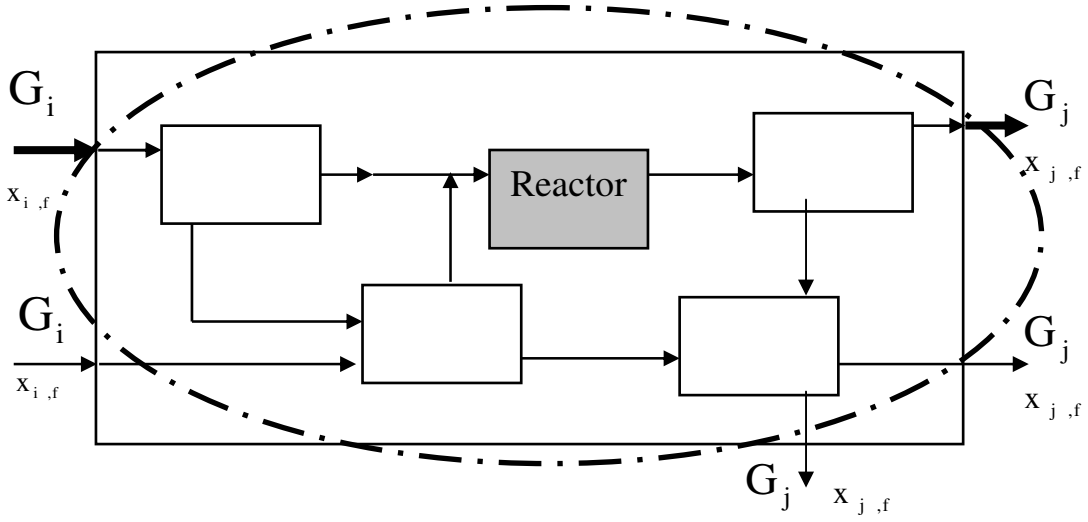


Figure 5.3. Graphical representation of process feed overall material balance.

Where G_j and G_i are the flow rates of process output stream j and process input stream i, respectively. $x_{j,p}$ and $x_{i,p}$ are compositions of process desired product (p) in each

stream, respectively and $x_{j,f}$ and $x_{i,f}$ are compositions of process fresh feed (f) in each of these streams, respectively. The set i is set of process input streams (i): i = {i=1,2, …, $N^{in}_{process}$ } and set j is set of process output streams (j): j = {j=1,2, …, $N^{out}_{process}$ }. Net_Gen_p and Net_Gen_f are the net depletion (or generation) of process desired product (p) and fresh feed (f), respectively.

In the same manner, similar equations are developed for the part of process ahead of reactor and the part after reactor. Figure 5.4 represents fresh feed balance for the part ahead of reactor.

For the fresh feed ahead of reactor:

$$\sum_{j=1}^{N^{out}_{ahead}} G_j * x_{j,f} = \sum_{i=1}^{N^{in}_{ahead}} G_i * x_{i,f} \qquad (5.4)$$

The set i here is set of input streams (i) for part of process ahead of reactor, i: i = {i=1,2, …, N^{in}_{ahead} } and set j is set of output streams (j) for part of process ahead of reactor, j: j = {j=1,2, …, N^{out}_{ahead} }.

Figure 5.5 shows desired product balance for the part after reactor. Here, two set of equations are developed, one for the fresh feed and one for the desired product.

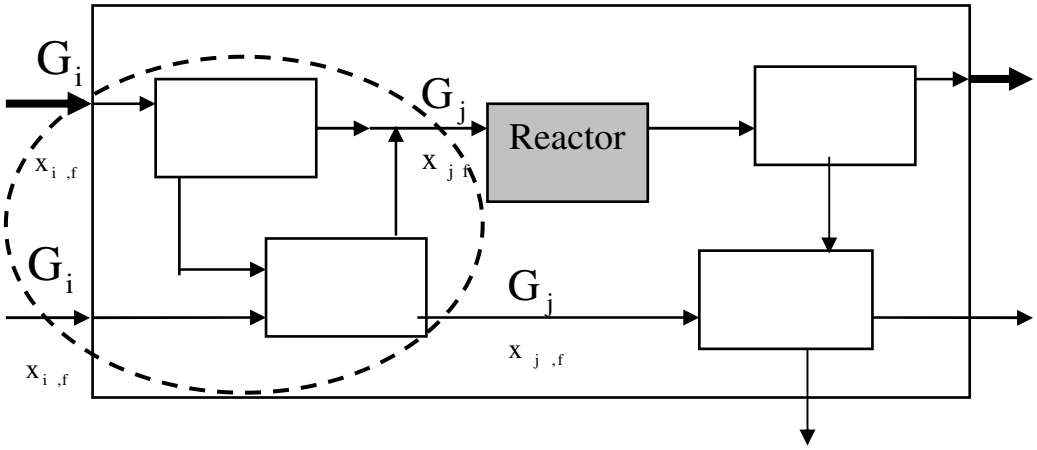
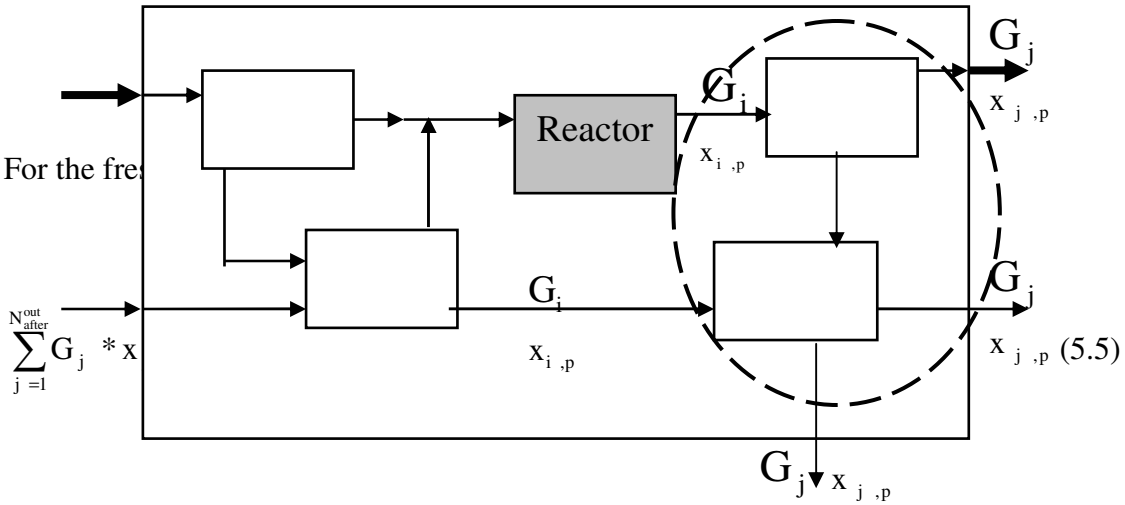


Figure 5.4. Fresh feed balance for the part ahead of reactor.



$$\sum_{j=1}^{N_{after}^{out}} G_j * x_{j,p} \quad (5.5)$$

Figure 5.5. Desired product balance for the part after reactor.

For the desired product after reactor:

$$\sum_{j=1}^{N_{after}^{out}} G_j * x_{j,p} = \sum_{i=1}^{N_{after}^{in}} G_i * x_{i,p} \quad (5.6)$$

Similarly, set i is set of input streams (i) for part of process after reactor, i: i = {i=1,2, …, N_{after}^{in} } and set j is set of output streams (j) for part of process after reactor, j: j = {j=1,2, …, N_{after}^{out} }.

Next, material balance around the reactor for both reactor's feed (i.e. reactant) and reactor's main product (reaction product) are constructed.

Reactant balance around reactor:

$$\sum_{j=1}^{N_R^{out}} G_j * x_{j,f} = \sum_{i=1}^{N_R^{in}} G_i * x_{i,f} + Net\_Gen_{R,f} \quad (5.7)$$

Desired product balance around reactor:

$$\sum_{j=1}^{N_R^{out}} G_j * x_{j,p} = \sum_{i=1}^{N_R^{in}} G_i * x_{i,p} + Net\_Gen_{R,p} \quad (5.8)$$

Where set i is set of input streams (i) to the reactor, i: i = {i=1,2, …, N_R^{in} } and set j is set of output streams (j) to the reactor, j: j = {j=1,2, …, N_R^{out} }. $Net\_Gen_{R,f}$ is net rate of generation of feed f from reactor R and $Net\_Gen_{R,p}$ is net rate of generation of desired product p from reactor R.

From the previous chapter, four strategies have been identified to maximize the process yield. These strategies are:

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
4. Minimize the fresh consumption of the targeted raw material through recovery and recycle

The equations which represent each of these strategies can be mathematically formulated. These equations are performance equations for units that handle targeted species in the above strategies and upper and lower bound of the manipulated variables. Performance equations will be listed as equality constraints and the upper and lower bound of each manipulated variable will be listed as inequality constraints.

1. Unit performance equation for maximizing reactor feed:

$$\alpha = \psi(d_u, p_u) \tag{5.9}$$

Where α as explained in chapter IV is fraction of the fresh feed reaches the reactor out of total fresh feed to the process. d_u and p_u are manipulated design and operating variables for sink u $\forall$ u preceding the reactor. The lower and upper bounds of these variables are to be listed as follow:

$$d_u^{min} \le d_u \le d_u^{max} \tag{5.10}$$

$$p_u^{min} \le p_u \le p_u^{max} \tag{5.11}$$

Another equation is to be included that relates fraction α with process fresh feed and reactor feed:

$$\sum_{i=1}^{N_{process}^{in}} G_i * x_{i,f} = \alpha * \sum_{i=1}^{N_R^{in}} G_i * x_{i,f} \tag{5.12}$$

2. Reactor performance equation for maximizing reactor yield: The reactor yield as defined by equation (1.1) is desired product that produced in the reactor divided by reactant fed to the reactor, i.e.:

$$Y_R = \frac{Net\_Gen_{R,p}}{\sum_{i=1}^{N_R^{in}} G_i * x_{i,f}} \tag{5.13}$$

Reactor performance is normally represented by reactor yield as function of reactor feed, design and operating properties as follow:

$$Y_R = \omega(Feed_R, d_R, p_R) \tag{5.14}$$

And the lower and upper bounds of each of these variables:

$$Feed_R^{min} \le Feed_R \le Feed_R^{max} \tag{5.15}$$

$$d_R^{min} \le d_R \le d_R^{max} \tag{5.16}$$

$$p_R^{min} \le p_R \le p_R^{max} \tag{5.17}$$

Following are reactor stiochiometric ratio:

$$\frac{Net\_Gen_{R,f}}{S_f * M_f} = \frac{Net\_Gen_{R,p}}{S_p * M_p} \tag{5.18}$$

For reactor balance equations above, $Net\_Gen_{R,f}$ and $Net\_Gen_{R,p}$ are the net depletion (or generation) of reactor feed (f) and desired product (p), respectively. set i is set of reactor input streams i: i = {i=1,2, …, N_R^{in}} and set j is set of reactor output streams j: j = {j=1,2, …, N_R^{out}}. S_f and S_p are the stiochiometric coefficients of reactant (f) and reaction product (p), respectively. M_f and M_p are their molecular weights.

The following logical constraint is added to make sure that there is no reactant (f) consumed in the reaction more than what is available of it in the reactor feed:

$$\sum_{i=1}^{N_R^{in}} G_i * x_{i,f} \ge Net\_Gen_{R,f} \tag{5.19}$$

3. Unit performance equation for maximizing desired product:

$$l = \phi(d_u, p_u) \tag{5.20}$$

Where l as previously explained is the amount of product that is lost with terminal streams leaving in undesirable outlets. d_u and p_u are manipulated design and operating variables for sink u $\forall u$ following the reactor. The lower and upper bounds of these variables are to be listed as follow:

$$d_u^{min} \le d_u \le d_u^{max} \tag{5.21}$$

$$p_u^{min} \le p_u \le p_u^{max} \tag{5.22}$$

The amount l represent the difference between the total amount of desired product leaving in all outlet streams and amount of that product in the desired outlet i.e.:

$$l = \sum_{j=1}^{N_{process}^{out}} G_j * x_{j,p} - G_p * x_{p,p} \tag{5.23}$$

4. Unit performance equation for minimizing fresh feed:

$$r = \xi(d_u, p_u) \tag{5.24}$$

Where *r* as previously explained is the amount of unreacted fresh feed that can be recovered through recovery devices. d_u and p_u are manipulated design and operating variables for sink u $\forall$ u recovery unit. The lower and upper bounds of these variables are as follow:

$$d_u^{min} \le d_u \le d_u^{max} \tag{5.25}$$

$$p_u^{min} \le p_u \le p_u^{max} \tag{5.26}$$

Since r is the recyclable amount, it is greater than or the equal the actual recycled (unreacted) feed:

$$r \ge \sum_{j=1}^{N_{recycle}^{out}} G_j * x_{j,f} \tag{5.27}$$

Where set j is set of output recycled feed streams (j), j = {j=1,2, …, $N_{recycle}^{in}$}. The set recycle is subset of unreacted fresh feed (set j in equation (5.3)). The rest of later set is assumed to be waste j, j = {j=1, 2, …, N_{waste}^{in}}.

$$\sum_{j=1}^{N_{process}^{out}} G_j * x_{j,f} = \sum_{j=1}^{N_{waste}^{out}} G_j * x_{j,f} + \sum_{j=1}^{N_{recycle}^{out}} G_j * x_{j,f} \tag{5.28}$$

The recycled and fresh feed balance in front of the process is:

$$\sum_{i=1}^{N_{ahead}^{in}} G_i * x_{i,f} = \sum_{i=1}^{N_{process}^{in}} G_i * x_{i,f} + \sum_{jr=1}^{N_{recycle}^{out}} G_j * x_{j,f} \quad (5.29)$$

The developed formulation for yield maximization problem can now be stated in the following general format:

Maximize Yp,

This objective function is subject to the following constraints:

$$Y_p = \frac{G_p * x_{p,p}}{G_f * x_{f,f}} \quad (5.1)$$

$$\sum_{j=1}^{N_{process}^{out}} G_j * x_{j,p} = \sum_{i=1}^{N_{process}^{in}} G_i * x_{i,p} + Net\_Gen_p \quad (5.2)$$

$$\sum_{j=1}^{N_{process}^{out}} G_j * x_{j,f} = \sum_{i=1}^{N_{process}^{in}} G_i * x_{i,f} + Net\_Gen_f \quad (5.3)$$

$$\sum_{j=1}^{N_{ahead}^{out}} G_j * x_{j,f} = \sum_{i=1}^{N_{ahead}^{in}} G_i * x_{i,f} \quad (5.4)$$

$$\sum_{j=1}^{N_{after}^{out}} G_j * x_{j,f} = \sum_{i=1}^{N_{after}^{in}} G_i * x_{i,f} \quad (5.5)$$

$$\sum_{j=1}^{N_{after}^{out}} G_j * x_{j,p} = \sum_{i=1}^{N_{after}^{in}} G_i * x_{i,p} \quad (5.6)$$

$$\sum_{j=1}^{N_R^{out}} G_j * x_{j,f} = \sum_{i=1}^{N_R^{in}} G_i * x_{i,f} + Net\_Gen_{R,f} \quad (5.7)$$

$$\sum_{j=1}^{N_R^{out}} G_j * x_{j,p} = \sum_{i=1}^{N_R^{in}} G_i * x_{i,p} + Net\_Gen_{R,p} \tag{5.8}$$

$$\alpha = \psi(d_u, p_u) \tag{5.9}$$

$$d_u^{min} \le d_u \le d_u^{max} \tag{5.10}$$

$$p_u^{min} \le p_u \le p_u^{max} \tag{5.11}$$

$$\sum_{i=1}^{N_{process}^{in}} G_i * x_{i,f} = \alpha * \sum_{i=1}^{N_R^{in}} G_i * x_{i,f} \tag{5.12}$$

$$Y_R = \frac{Net\_Gen_{R,p}}{\sum_{i=1}^{N_R^{in}} G_i * x_{i,f}} \tag{5.13}$$

$$Y_R = \omega(Feed_R, d_R, p_R) \tag{5.14}$$

$$Feed_R^{min} \le Feed_R \le Feed_R^{max} \tag{5.15}$$

$$d_R^{min} \le d_R \le d_R^{max} \tag{5.16}$$

$$p_R^{min} \le p_R \le p_R^{max} \tag{5.17}$$

$$\frac{Net\_Gen_{R,f}}{S_f * M_f} = \frac{Net\_Gen_{R,p}}{S_p * M_p} \tag{5.18}$$

$$\sum_{i=1}^{N_R^{in}} G_i * x_{i,f} \ge Net\_Gen_{R,f} \tag{5.19}$$

$$l = \phi(d_u, p_u) \tag{5.20}$$

$$d_u^{min} \le d_u \le d_u^{max} \tag{5.21}$$

$$p_u^{min} \le p_u \le p_u^{max} \tag{5.22}$$

$$l = \sum_{j=1}^{N_{process}^{out}} G_j * x_{j,p} - G_p * x_{p,p} \tag{5.23}$$

$$r = \xi(d_u, p_u) \tag{5.24}$$

$$d_u^{min} \le d_u \le d_u^{max} \tag{5.25}$$

$$p_u^{min} \le p_u \le p_u^{max} \tag{5.26}$$

$$r \ge \sum_{j=1}^{N_{recycle}^{out}} G_j * x_{j,f} \tag{5.27}$$

$$\sum_{j=1}^{N_{process}^{out}} G_j * x_{j,f} = \sum_{j=1}^{N_{waste}^{out}} G_j * x_{j,f} + \sum_{j=1}^{N_{recycle}^{out}} G_j * x_{j,f} \tag{5.28}$$

$$\sum_{i=1}^{N_{ahead}^{in}} G_i * x_{i,f} = \sum_{i=1}^{N_{process}^{in}} G_i * x_{i,f} + \sum_{jr=1}^{N_{recycle}^{out}} G_j * x_{j,f} \tag{5.29}$$

From the above formulation, equations (5.1)-(5.8), (5.12), (5.19), (5.23), (5.27)-(5.29) have bilinear terms while equations (5.1), (5.12) and (5.13) have trilinear terms. Equations (5.9), (5.14), (5.20) and (5.24) can be linear, bilinear or nonlinear. The rest of equations in the formulation are linear. In this analysis, equation (5.1) was assumed to take the form:

$$Y_p * G_f * x_{f,f} = G_p * y_{p,p}$$

With this nonlinearity in the above formulation, finding global and unique solution is not guaranteed using available optimization programs. In the next section, techniques are presented to tackle these nonlinearities.

5.3 Reformulation of Yield Maximization Model

Special structures have been identified in the formulation above such as bilinear and trilinear terms. This categorization enables the researcher to develop a suitable global optimization approach through addressing the nonconvexities in these terms. Most of the deterministic methods depend on the development of valid convex underestimators for the nonconvex functions. The generation of the global optimal solution of the original nonconvex problem can be accomplished through iterative improvements of the above-mentioned estimators and identifying the global solution of the convex problem (Adjiman et al., 1998). The generation of convex underestimators is based on reformulation of the problem in order to transforms complex nonconvex terms into simpler terms such as bilinear, univariate concave, convex, linear fractional and simple power terms. This is done by adding new variables and constraints to the original problem. The approach here is to use underestimators to formulate lower-bounding convex MINLP (see Figure 5.6), (Grossmann and Biegler, 2004). This underestimation is to be used with global optimization techniques and in particular spatial branch and bound methods. These later methods divide the feasible region and eliminate subregions that don't contain optimal solution.

General approach for deriving underestimators of bilinear models was presented by McCormick (1976). It involves the addition of one more variable to the problem and more inequality constraints. Al-Khayyal and Falk (1983) presented a branch and bound algorithm for problems with bilinear objective functions and linear constraints. In this

algorithm, linear estimators were used for the bilinear terms. Sherali and Alameddine (1992) developed a linearization reformulation technique (RLT). The method firsts reformulates the problem by constructing a set of nonnegative variable factors using the problem constraints. Then, this nonlinear program is linearized by defining a new set of variables, one for each nonlinear term. A linear programming problem whose optimal value provides a tight lower bound on the optimal value to the bilinear programming problem. This technique generates tight linear bounds. A review of models and application for bilinear programming can be found in Al-Khayyal (1992).

Consider the following programming problem:

$$\begin{aligned} \min \quad & Z = f(x, y) \\ s.t. \quad & g_j(x, y) \le 0 \quad j \in J \\ & x \in X, \quad y \in Y \end{aligned} \tag{5.30}$$

where $f(x, y)$ and $g(x, y)$ are generally nonconvex.

5.3.1 Bilinear Terms

Let us assume that the bilinear term xy has the domains $[x^L, x^U]$, $[y^L, y^U]$ for variable x and y, respectively. In accordance with Al-Khayyal and Falk (1983), new variable BT can be proposed as convex underestimators. This variable will replace the bilinear term of xy in the problem and satisfies the following relationship:

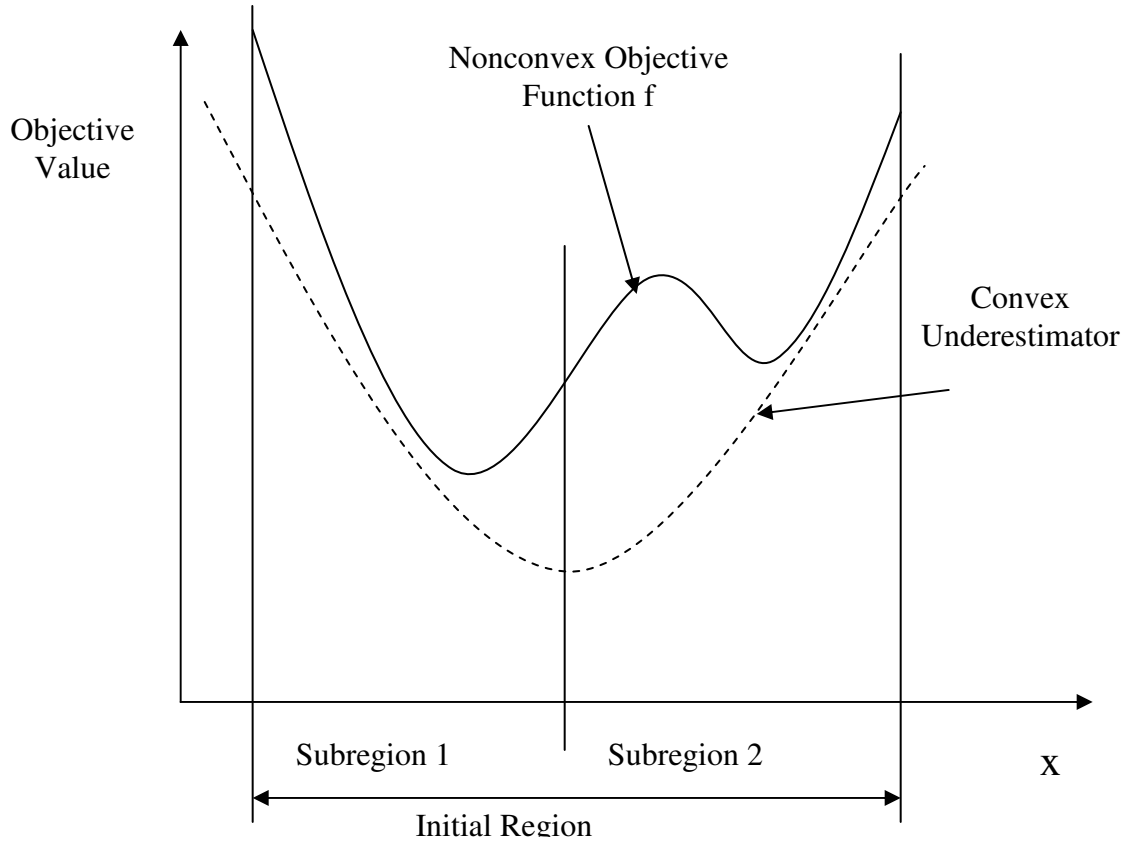


Figure 5.6. Convex underestimator for nonconvex function (Grossmann and Biegler, 2004).

$$BT = \max\{x^L y + y^L x - x^L y^L; \quad x^U y + y^U x - x^U y^U\} \tag{5.31}$$

The following two linear inequality constraints are added to the formulation to represent the lower bound of the underestimator:

$$BT \geq x^L y + y^L x - x^L y^L$$

$$BT \geq x^U y + y^U x - x^U y^U \tag{5.32}$$

And the following two linear inequality constraints represent the upper bound for BT:

$$BT \le x^U y + y^L x - x^U y^L$$
$$BT \le x^L y + y^U x - x^L y^U \tag{5.33}$$

5.3.2 Trilinear Terms

The products of N univariate functions can be developed by applying the convex lower bounding of products of two univariate functions (Maranas and Floudas, 1995). Based on this, new variable TT can be proposed as convex lower bounding function for trilinear terms xyz inside the region $[x^L, x^U]\times[y^L, y^U]\times[z^L, z^U]$:

$$\begin{aligned} TT \ge \max\{ & xy^L z^L + x^L yz^L + x^L y^L z - 2x^L y^L z^L, \\ & xy^U z^U + x^U yz^L + x^U y^L z - x^U y^L z^L - x^U y^U z^U, \\ & xy^L z^L + x^L yz^U + x^L y^U z - x^L y^U z^U - x^L y^L z^L, \\ & xy^U z^U + x^U yz^U + x^U y^U z - 2x^U y^U z^U \} \end{aligned} \tag{5.34}$$

$$\begin{aligned} TT \ge \max\{ & xy^L z^L + x^L yz^L + x^L y^L z - 2x^L y^L z^L, \\ & xy^U z^l + x^U yz^U + x^L y^U z - x^L y^U z^L - x^U y^U z^U, \\ & xy^L z^U + x^L yz^L + x^U y^L z - x^U y^L z^U - x^L y^L z^L, \\ & xy^U z^U + x^U yz^U + x^U y^U z - 2x^U y^U z^U \} \end{aligned} \tag{5.35}$$

$$\begin{aligned} TT \ge \max\{ & xy^L z^L + x^L yz^L + x^L y^L z - 2x^L y^L z^L, \\ & xy^L z^U + x^L yz^U + x^U y^U z - x^L y^L z^U - x^U y^U z^U, \\ & xy^U z^L + x^U yz^L + x^L y^L z - x^U y^U z^U - x^L y^L z^L, \\ & xy^U z^U + x^U yz^U + x^U y^U z - 2x^U y^U z^U \} \end{aligned} \tag{5.36}$$

These three convex lower bounding alternatives can be combined to produce the following eight linear inequality constraints which make tight convex underestimator for the term xyz:

$$\begin{aligned}
&TT \geq xy^L z^L + x^L yz^L + x^L y^L z - 2x^L y^L z^L, \\
&TT \geq xy^U z^U + x^U yz^L + x^U y^L z - x^U y^L z^L - x^U y^U z^U, \\
&TT \geq xy^L z^L + x^L yz^U + x^L y^U z - x^L y^U z^U - x^L y^L z^L, \\
&TT \geq xy^U z^L + x^U yz^U + x^L y^U z - x^L y^U z^L - x^U y^U z^U, \\
&TT \geq xy^L z^U + x^L yz^L + x^U y^L z - x^U y^L z^U - x^L y^L z^L, \\
&TT \geq xy^L z^U + x^L yz^U + x^U y^U z - x^L y^L z^U - x^U y^U z^U, \\
&TT \geq xy^U z^L + x^U yz^L + x^L y^L z - x^U y^U z^L - x^L y^L z^L, \\
&TT \geq xy^U z^U + x^U yz^U + x^U y^U z - 2x^U y^U z^U
\end{aligned} \tag{5.37}$$

5.3.3 Fractional Terms

For the linear fractional term x/y inside the region $[x^L, x^U] \times [y^L, y^U]$, the following convex lower bound is proposed (Maranas and Floudas, 1995):

$$\frac{x}{y} \geq \max\left\{\begin{bmatrix} \frac{x^L}{y} + \frac{x}{y^U} - \frac{x^L}{y^U} & if\ x^L \geq 0 \\ \frac{x}{y^U} - \frac{x^L y}{y^L y^U} + \frac{x^L}{y^L} & if\ x^L < 0 \end{bmatrix}, \begin{bmatrix} \frac{x^U}{y} + \frac{x}{y^L} - \frac{x^U}{y^L} & if\ x^U \geq 0 \\ \frac{x}{y^L} - \frac{x^U y}{y^L y^U} + \frac{x^U}{y^U} & if\ x^U < 0 \end{bmatrix}\right\} \tag{5.38}$$

For linear fractional terms with negative sign (i.e. –x/y):

$$-\frac{x}{y} \geq \max\left\{\begin{bmatrix} -\dfrac{x^L}{y} - \dfrac{x}{y^U} + \dfrac{x^L}{y^L} & if\ x^L \leq 0 \\ -\dfrac{x}{y^L} + \dfrac{x^L y}{y^L y^U} - \dfrac{x^L}{y^U} & if\ x^L > 0 \end{bmatrix}, \begin{bmatrix} -\dfrac{x^U}{y} - \dfrac{x}{y^U} + \dfrac{x^U}{y^U} & if\ x^U \leq 0 \\ -\dfrac{x}{y^U} + \dfrac{x^U y}{y^L y^U} - \dfrac{x^U}{y^L} & if\ x^U > 0 \end{bmatrix}\right\} \tag{5.39}$$

The underestimator (FT) can represent the fractional term x/y by adding the following constraints to the formulation:

$$FT \geq \begin{bmatrix} \dfrac{x^L}{y} + \dfrac{x}{y^U} - \dfrac{x^L}{y^U} & if\ x^L \geq 0 \\ \dfrac{x}{y^U} - \dfrac{x^L y}{y^L y^U} + \dfrac{x^L}{y^L} & if\ x^L < 0 \end{bmatrix} \tag{5.40}$$

$$FT \geq \begin{bmatrix} \dfrac{x^U}{y} + \dfrac{x}{y^L} - \dfrac{x^U}{y^L} & if\ x^U \geq 0 \\ \dfrac{x}{y^L} - \dfrac{x^U y}{y^L y^U} + \dfrac{x^U}{y^U} & if\ x^U < 0 \end{bmatrix} \tag{5.41}$$

Zamora and Grossmann (1998b) derived convex quadratic/linear underestimators for the heat transfer area of heat exchangers, which can be applied to any linear fractional term (Grossmann and Biegler, 2004):

$$\frac{x}{y} \geq \frac{1}{x}\left(\frac{x+\sqrt{x^L y^U}}{\sqrt{x^L}+\sqrt{x^U}}\right)^2 \tag{5.42}$$

Another convex underestimator developed by Tawarmalani and Sahinidis (2001) of *x/y* as long as $y = 0$:

$$\begin{aligned}
&z = \frac{x}{y} \\
&(z - z_p)(y - y_p)(x^U - x^L)^2 \geq x^U (x - x^L)^2 \\
&z_p \geq \frac{x^L (x^L y_p - x(y^L + y^U) + x^U (y^L - y_p + y^U))}{(x^U - x^L) y^L y^U} \\
&y^L (x^U - x) \leq y_p (x^U - x^L) \leq y^U (x^U - x) \\
&y^L (x - x^L) \leq (y - y_p)(x^U - x^L) \leq y^U (x - x^L) \\
&z - z_p, z_p, y_p \geq 0
\end{aligned} \tag{5.43}$$

The convex hull of x^L/y and x^U/y represents the convex envelope of the last underestimator which can be shown to be stronger than the first two underestimators for the fractional term (Grossmann and Biegler, 2004).

5.3.4 Fractional Trilinear Terms

Maranas and Floudas (1995) derived the following three convex lower bounding alternatives for the fractional trilinear term xy/z inside the region $[x^L, x^U] \times [y^L, y^U] \times [z^L, z^U]$ with $x^L, y^L, z^L \geq 0$:

$$
\begin{aligned}
\frac{xy}{z} \geq \max\{&\frac{xy^L}{z^U}+\frac{x^L y}{z^U}+\frac{x^L y^L}{z}-2\frac{x^L y^l}{z^U},\\
&\frac{xy^L}{z^U}+\frac{x^L y}{z^L}+\frac{x^L y^U}{z}-\frac{x^L y^U}{z^L}-\frac{x^L y^L}{z^U},\\
&\frac{xy^U}{z^L}+\frac{x^U y}{z^U}+\frac{x^U y^L}{z}-\frac{x^U y^L}{z^U}-\frac{x^U y^U}{z^L},\\
&\frac{xy^U}{z^L}+\frac{x^U y}{z^L}+\frac{x^U y^U}{z}-2\frac{x^U y^U}{z^L}\},\\
\frac{xy}{z} \geq \max\{&\frac{xy^L}{z^U}+\frac{x^L y}{z^U}+\frac{x^L y^L}{z}-2\frac{x^L y^l}{z^U},\\
&\frac{xy^U}{z^U}+\frac{x^U y}{z^L}+\frac{x^L y^U}{z}-\frac{x^L y^U}{z^U}-\frac{x^U y^U}{z^L},\\
&\frac{xy^L}{z^U}+\frac{x^L y}{z^L}+\frac{x^U y^L}{z}-\frac{x^U y^L}{z^L}-\frac{x^L y^L}{z^U},\\
&\frac{xy^U}{z^L}+\frac{x^U y}{z^L}+\frac{x^U y^U}{z}-2\frac{x^U y^U}{z^L}\},\\
\frac{xy}{z} \geq \max\{&\frac{xy^L}{z^U}+\frac{x^L y}{z^U}+\frac{x^L y^L}{z}-2\frac{x^L y^l}{z^U},\\
&\frac{xy^L}{z^L}+\frac{x^L y}{z^L}+\frac{x^U y^U}{z}-\frac{x^L y^L}{z^L}-\frac{x^U y^U}{z^L},\\
&\frac{xy^U}{z^U}+\frac{x^U y}{z^U}+\frac{x^L y^L}{z}-\frac{x^U y^U}{z^U}-\frac{x^L y^L}{z^U},\\
&\frac{xy^U}{z^L}+\frac{x^U y}{z^L}+\frac{x^U y^U}{z}-2\frac{x^U y^U}{z^L}\}
\end{aligned}
\tag{5.44}
$$

The following eight convex constraints are obtained by combining the above three alternatives:

$$\frac{xy}{z} \geq \frac{xy^{L}}{z^{U}} + \frac{x^{L}y}{z^{U}} + \frac{x^{L}y^{L}}{z} - 2\frac{x^{L}y^{l}}{z^{U}},$$
$$\frac{xy}{z} \geq \frac{xy^{L}}{z^{U}} + \frac{x^{L}y}{z^{L}} + \frac{x^{L}y^{U}}{z} - \frac{x^{L}y^{U}}{z^{L}} - \frac{x^{L}y^{L}}{z^{U}},$$
$$\frac{xy}{z} \geq \frac{xy^{U}}{z^{L}} + \frac{x^{U}y}{z^{U}} + \frac{x^{U}y^{L}}{z} - \frac{x^{U}y^{L}}{z^{U}} - \frac{x^{U}y^{U}}{z^{L}},$$
$$\frac{xy}{z} \geq \frac{xy^{U}}{z^{U}} + \frac{x^{U}y}{z^{L}} + \frac{x^{L}y^{U}}{z} - \frac{x^{L}y^{U}}{z^{U}} - \frac{x^{U}y^{U}}{z^{L}},$$
$$\frac{xy}{z} \geq \frac{xy^{L}}{z^{U}} + \frac{x^{L}y}{z^{L}} + \frac{x^{U}y^{L}}{z} - \frac{x^{U}y^{L}}{z^{L}} - \frac{x^{L}y^{L}}{z^{U}},$$
$$\frac{xy}{z} \geq \frac{xy^{U}}{z^{U}} + \frac{x^{U}y}{z^{L}} + \frac{x^{L}y^{U}}{z} - \frac{x^{L}y^{U}}{z^{U}} - \frac{x^{U}y^{U}}{z^{L}},$$
$$\frac{xy}{z} \geq \frac{xy^{L}}{z^{U}} + \frac{x^{L}y}{z^{L}} + \frac{x^{U}y^{L}}{z} - \frac{x^{U}y^{L}}{z^{L}} - \frac{x^{L}y^{L}}{z^{U}},$$
$$\frac{xy}{z} \geq \frac{xy^{U}}{z^{L}} + \frac{x^{U}y}{z^{L}} + \frac{x^{U}y^{U}}{z} - 2\frac{x^{U}y^{U}}{z^{L}} \qquad (5.45)$$

5.3.5 Univariate Concave Terms

Univariate concave functions can be underestimated by linearizing these functions at the lower bound of their variable range (Adjiman et al., 1998). The following linear function of x represents the convex envelope of the concave function ut(x) over the region $[x^{L}, x^{U}]$:

$$ut(x^{L}) + \frac{ut(x^{U}) - ut(x^{L})}{(x^{U} - x^{L})} + (x - x^{L}) \qquad (5.46)$$

5.3.6 General Functions

A convex lower bounding function L for a continuous and differentiable f(x) can be developed by adding a quadratic term (Maranas and Floudas, 1994):

$$L(x) = [f(x) + \alpha \sum_{i=1}^{n} (x^L - x)(x^U - x)] \tag{5.47}$$

α is a nonnegative parameter which must be greater than or equal to the negative one half of the minimum eigenvalue of f(x) over the region $[x^L, x^U]$:

$$\alpha \geq \max\{0, -\frac{1}{2}\lambda_{\min}) \tag{5.48}$$

Detailed discussion on the derivation of α can be found elsewhere (Adjiman et al., 1998; Maranas and Floudas, 1994).

The following example which has bilinear tem is considered for underestimators:

$$\begin{aligned} &Minimize \quad -x - y \\ &s.t. \\ &xy \leq 4 \\ &0 \leq x \leq 4 \\ &0 \leq y \leq 8 \end{aligned} \tag{5.49}$$

Underestimator (b) is developed for the bilinear term xy using equations (5.32) & (5.33). In addition to replacing xy in the above formulation, the following constraints of lower and upper bounds for b are included in the reformulated model:

$$\begin{aligned} & b \geq 0 \\ & b \geq 8x + 4y - 32 \\ & b \leq 4y \\ & b \leq 8x \end{aligned} \tag{5.50}$$

When solving the reformulated model above using Lingo program (Schrage, 2003), the global solution found to be -8.5 at x=0.5 and y-8. This result conforms with the one reported in the literature (Floudas and Visweswaren, 1990).

5.4 Case Study: Yield Maximization for Acetaldehyde Production Process

Here the case study in Chapter IV is revisited by developing a mathematical programming for the problem. Previously, linear and/or convex equations were assumed in the whole formulation. The linear equations could be developed for the fresh feed and desired product balance equations by using the species flowrate instead of the bilinear term in the species composition and stream total flowrate. In addition to the typical constraints listed in the general formulation of the previous section, additional constraint on the process yield to restrict its value to be less than or equal to the value predicted by interval analysis (Chapter IV). This is as explained before because chapter IV procedure gives upper bound for the process yield that can't be exceeded provided that only process

parameters are to be manipulated with the existing equipment. This means that there is no additional equipment to be added in order to enhance the process yield.

5.4.1 Problem Formulation

The developed formulation is shown below (refer to Figure 4.6 of process flow sheet):

The objective function that needs to be maximized is the process yield (YP):

$$YP=A14/E1 \tag{5.51}$$

The problem constraints are as follows:

1. Process overall material balance for the desired product (acetaldehyde):

$$A1 + A4 + A6 + A12 + AR = A11 + A18 + A14 + A2+A16 + AW \tag{5.52}$$

Where

Ai: acetaldehyde flowrate in metric ton per year (MT/yr) in stream i, i=1,2,…n.

AR: acetaldehyde produced in the reactor (MT/yr),

AW: portion of acetaldehyde from stream 17 subject to waste treatment (MT/yr).

2. Process overall material balance for the fresh feed (ethanol):

$$E1 + E4 + E6 + E12 = ER + E11 + E18 + E14 + E2 + E16 + EW \quad (5.53)$$

Where

Ei is ethanol flowrate in stream i (MT/yr), i=1,2,3,…..n.

ER: ethanol consumed in reactor (MT/yr),

EW: portion of ethanol from stream 17 subject to waste treatment (MT/yr),

3. For the fresh feed ahead of reactor:

$$EG = E2 + E3 \quad (5.54)$$

Where

EG: combined flowrate of ethanol fed to the process (consist of fresh feed and recycled feed) (MT/yr).

4. For the fresh feed after reactor:

$$E9 = E14 + E16 + E15 \quad (5.55)$$

$$E15 = E17 + E18 \quad (5.56)$$

5. For the desired product after reactor:

$$A5 + A6 + A12 = A11 + A18 + A16 + A14 + A17 \quad (5.57)$$

$$A9 = A5 + A6 + A12 - A11 \quad (5.58)$$

$$A9 = A14 + A15 + A16 \quad (5.59)$$

$$A15 = A17 + A18 \quad (5.60)$$

6. Reactant balance around reactor:

$$E5 = E3 - ER + E4 \quad (5.61)$$

7. Desired product balance around reactor:

$$AG + A4 + AR = A5 + A2 \quad (5.62)$$

8. Unit performance equation for maximizing reactor feed:

$$E2 = \alpha * EG \quad (5.63)$$

$$\alpha = -0.0274 * TF + 10.5122 \quad (5.64)$$

$$TF \geq 380 \quad (5.65)$$

$$TF \leq 384 \quad (5.66)$$

9. Reactor performance equation for maximizing reactor yield:

$$Y_R = 0.33 - 0.0000042*(T_R - 580)*(T_R - 580) \quad (5.67)$$

$$T_R \geq 300 \quad (5.68)$$

$$T_R \leq 860 \quad (5.69)$$

From reactor yield definition:

$$Y_R*E3 = AR \quad (5.70)$$

Reactor stiochiometric ratio:

$$ER = (46/44)*AR \quad (5.71)$$

Logical constraint:

$$ER \leq E3 \quad (5.72)$$

10. Unit performance equation for maximizing desired product:

$$\beta = 0.14*QR + 0.89 \quad (5.73)$$

$$A14 = \beta * A9 \quad (5.74)$$

$$QR \leq 0.76 \quad (5.75)$$

$$QR \geq 0.55 \quad (5.76)$$

11. Unit performance equation for minimizing fresh feed:

$$\gamma = 0.653*\exp(0.085*RR) \quad (5.77)$$

$$E17 = \gamma * E15 \quad (5.78)$$

$$RR \geq 2.5 \quad (5.79)$$

$$RR \leq 5 \quad (5.80)$$

Recyclable and waste unreacted feed balance:

$$E17 = EC + EW \quad (5.81)$$

Where

EC: flowrate of ethanol that is subject to recycling from stream 17 (MT/yr).

The recycled and fresh feed balance in front of the process is:

$$EG = EC + E1 \quad (5.82)$$

Other equality constraints stated in the problem statement in Chapter IV:

$$E4 = 0 \quad (5.83)$$

$$E6 = 400 \quad (5.84)$$

$$E14 = 0 \quad (5.85)$$

$$E16 = 0 \quad (5.86)$$

$$E12 = 0 \quad (5.87)$$

$$A1 = 0 \quad (5.88)$$

$$A2 = 0 \quad (5.89)$$

$$A4 = 0 \quad (5.90)$$

$$A6 = 0 \quad (5.91)$$

$$A12 = 0 \quad (5.92)$$

$$A15 = 0 \quad (5.93)$$

The plant capacity constraint:

$$A14 = 100000 \quad (5.94)$$

One last constraint is inequality constraint that assures the calculated process yield will not exceed the upper bound came out of interval analysis procedure:

$$YP \leq 0.955 \tag{5.95}$$

The above formulation was solved using Lingo software and the optimal solution for the yield found to be 0.955. The code for the problem and its solution by Lingo is shown in Appendix A. The optimal values for the manipulated variables are also listed in the solution which tell the designer/operator the changed that he/she need to implement to achieve the maximum process yield.

5.4.2 Problem Reformulation

It is known that mathematical programming software such as Lingo gives upper bound for minimization problem and lower bound for maximization problem. In this context, the maximum process yield predicted above is lower bound. Next, the reformulation for the problem to count for nonlinearity in the general problem is considered. The reformulation is accomplished through using the underestimators for nonlinear terms in the original formulation. Underestimation for nonlinear/nonconvex maximization problem gives upper bound. In the formulation above, there are two bilinear terms that are considered for underestimation in equations (5.51) and (5.70). Here we assumed that equation (5.51) is in the following form:

YP*E1=A14

In order to overcome the problem of nonconvexity in these bilinear terms, we are going to reformulate the problem using equations 5.32 and 5.33. The following ranges are assumed for the four parameters:

$$0 \le E3 \le 350{,}000 \tag{5.96}$$

$$0.3 \le YR \le 0.35 \tag{5.97}$$

$$0 \le E1 \le 250{,}000 \tag{5.98}$$

$$0 \le YP \le 0.955 \tag{5.99}$$

The following constrains which represent the underestimators for the two bilinear terms are added to the formulation in addition to replacing bilinear terms that appeared in equations 5.51 and 5.70 by BP1 and BR3:

$$YR \ge 0.3 \tag{5.100}$$

$$YR \le 0.35 \tag{5.101}$$

$$E3 \ge 0 \tag{5.102}$$

$$E3 \le 350000 \tag{5.103}$$

$$BR3 \ge 0.3*E3+350*YR \tag{5.104}$$

$$BR3 \ge 0.35*E3+350000*YR-122500 \tag{5.105}$$

$$BR3 \le 0.35*E3 \tag{5.106}$$

$$BR3 \leq 0.3*E3+350000*YR-105000 \quad (5.107)$$

$$YP \geq 0 \quad (5.108)$$

$$YP \leq 0.955 \quad (5.109)$$

$$E1 \geq 0 \quad (5.110)$$

$$E1 \leq 250000 \quad (5.111)$$

$$BP1 \geq 0 \quad (5.112)$$

$$BP1 \geq 0.955*E1+250000*YP-238750 \quad (5.113)$$

$$BP1 \leq 0.955*E1 \quad (5.114)$$

$$BP1 \leq 250000*YP \quad (5.115)$$

This reformulated model generates identical process yield as the one generated by the original model (Appendix A). Because of this match between the upper and lower bound of the yield, this solution represents a global solution for the problem. This indicates the successful usage of underestimators for the bilinear terms. The reformulated model along with its results is shown in Appendix B. This global solution is equivalent to the one predicted by interval-based procedure (chapter IV) for the same case study. This match tells us that the upper bound figure for the process yield is in fact achievable.

5.5 Yield-Cost Trade-Off

The next step in our methodology (Figure 5.1) of implementing the targeted process yield is making criteria based on the cost for the decision on the implementable process yield. The criteria will involve optimizing the cost of implementing the changes in the

manipulated variables at different levels of the process yield. The goal here is to develop relationship between that cost and its equivalent yield. We know from the beginning that this relationship is of exponential form. This is because the cost will increase with increasing the yield until it reaches the maximum yield calculated in the previous section (Figure 5.2).

This criteria is implemented through using the same formulation developed in the previous section with some changes. These changes include changing the objective function to be minimizing the cost of changing the manipulated variables to their optimum values. The original objective function (process yield) would go as inequality constraint equivalent to the maximum yield predicted in the preceding section. The cost function covers the partial ranges of manipulated parameters from the base case to the optimum. This new formulation is to be solved to predict the cost of implementing the highest achievable process yield.

In order to make it easy for the decision makers in increasing the process yield and because of some limitations, the next task is to develop multiple cost figures at different levels of process yield. The limitations here might be in the form of technical limitations such as utilities availability or financial one like budget limitations. This task is accomplished through changing the equality constraint on process yield in the cost minimization model. The outcome of these multiple model calculations is a relationship between the cost of manipulating the process parameters and their equivalent process yield (Figure 5.2).

Another helpful relationship can be developed to study the impact of enhancing the process yield on either the saving of fresh feed or increase in desired product flow rate. This is because the flowrate of either fresh feed or desired product is fixed.

5.6 Case Study (Revisited): Cost Minimization for Acetaldehyde Production Process

To demonstrate the yield-cost trade-off procedure, the case study of ethanol oxidation to produce acetaldehyde is revisited. The cost functions for the different process performance parameters (in $/year) are as follows:

1. Cost of manipulating reactor performance parameters for maximizing reactor yield:

$$C1 = 3570*(TR-500) \tag{5.116}$$

2. Cost of manipulating unit performance parameters for minimizing fresh feed:

$$C2 = 6400*(RR-2.5) \tag{5.117}$$

3. Cost of manipulating unit performance parameters for maximizing reactor feed:

$$C3 = 2100*(TF-380) \tag{5.118}$$

4. Cost of manipulating unit performance parameters for maximizing desired product:

$$C4=160*(QR-0.55) \quad (5.119)$$

The above four functions will form the objective function for the cost model. Another inequality constraint is added to formulation to make the yield is greater than or equal to the achievable value for process yield computed in the yield maximization case study (section 5.4).

The formulation in this format was solved using Lingo and the resultant annual cost was $23,700. This value represents the annual additional cost of implementing the optimum values for the manipulated variables in order to achieve the maximum process yield. This cost minimization model along with its results is shown in Appendix C.

The next step is to calculate the cost at multiple lower process yields. This is done through changing the value of yield constraint to be less than the maximum yield value. Multiple runs using Lingo software were made. Based on these results, the relationship between the process yield and cost of its implementation is represented in Figure 5.7.

Another graph can be developed to study the impact of enhancing the process yield on the fresh feed saving. The base case annual consumption of fresh ethanol feed is 185000 Metric ton. This relationship is presented in Figure 5.8 based on the ethanol price of $418/ metric ton.

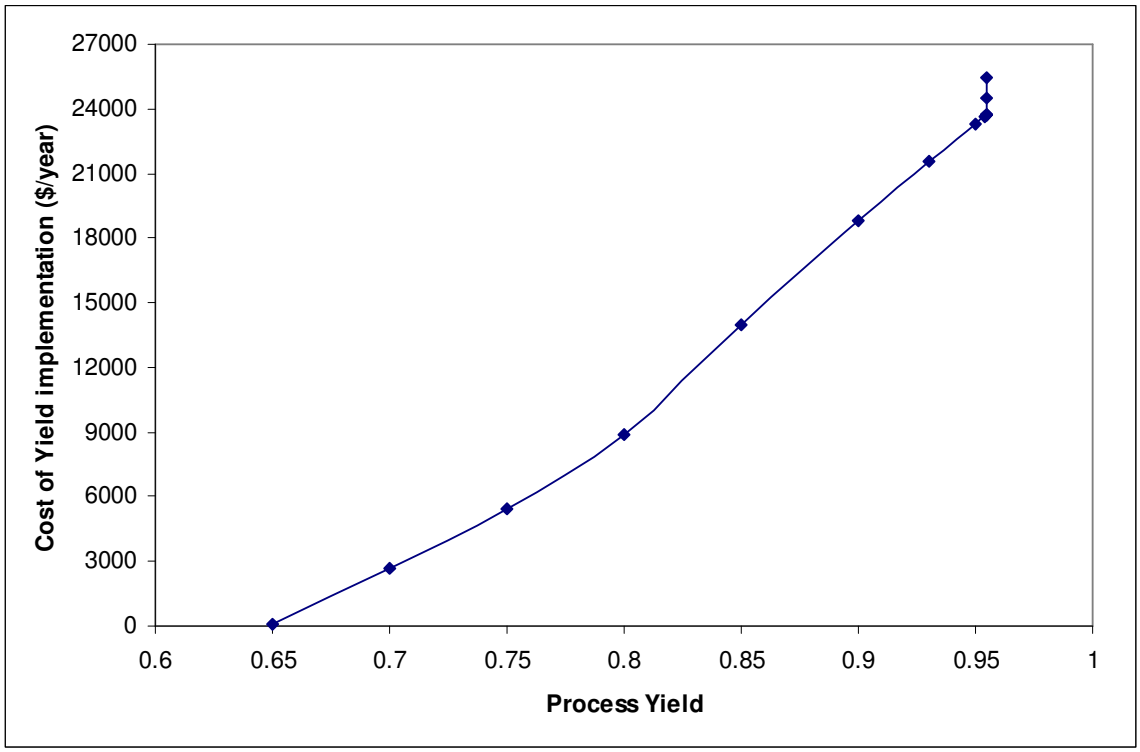


Figure 5.7. Trade-off relationship between process yield and its implementation cost.

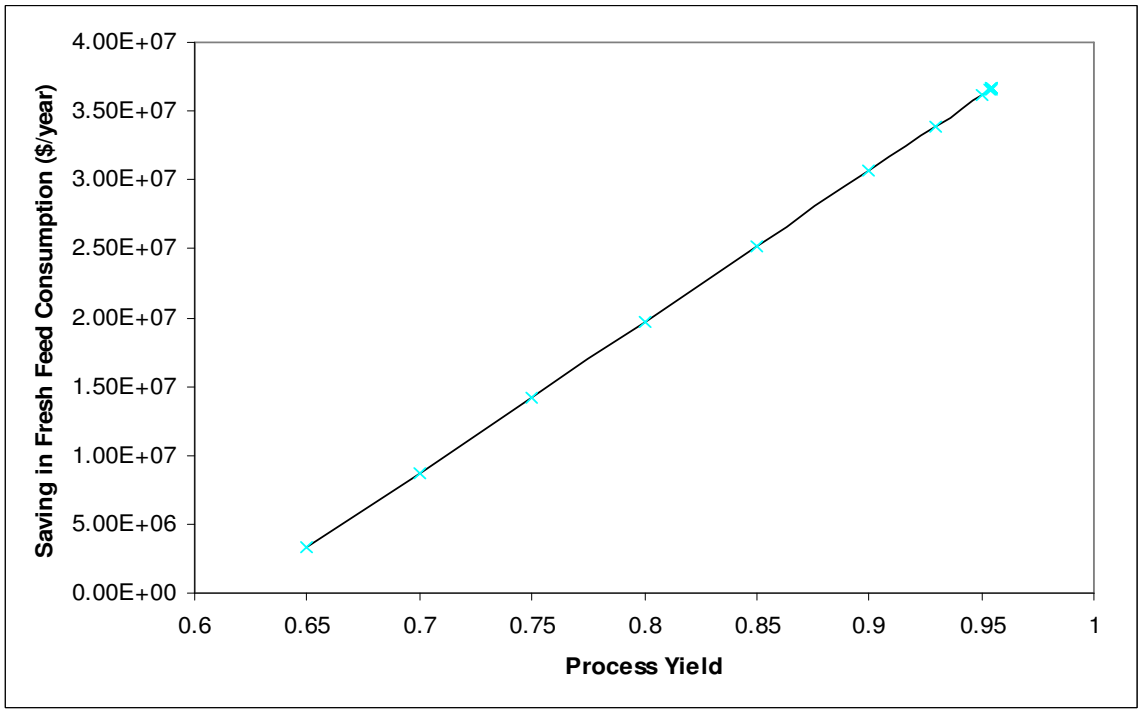


Figure 5.8. Effects of process yield improvements on fresh feed saved.

5.7 Conclusions

This chapter has presented a new approach to the identification of cost-effective implementation of maximum attainable targets for yield. First, a mathematical program was developed to identify the maximum feasible targets using a combination of iterative additions of constraints and problem reformulation. Next, cost objectives were employed to identify a cost-effectives solution with the details of design and operating variables. Constraint convexification was used to improve the quality of the solution towards globability. Various forms on non-convex terms were addressed using underestimation techniques. The case study presented in Chapter IV was revisited and a detailed solution was globally identified.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

A targeting procedure was developed to identify an upper bound on the overall yield of the process. This target is identified ahead of detailed design. A hierarchical approach was devised to optimize several process modifications (e.g., stream rerouting) and process performance (e.g., separation, yield, recovery) by manipulation of operating conditions (e.g. temperature, pressure, residence time). Tailored process models were developed using the concept of path equations to provide the appropriate level of details and degrees of freedom for yield maximization. Next, inclusion techniques were used to identify bounds on performance without enumeration and regardless of the nonlinearity characteristics of process models.

Since this inclusion-based approach generates upper bound on the process yield, a new approach to the identification of cost-effective implementation of maximum attainable targets for yield has presented. In this regard, a mathematical program was developed to identify the maximum feasible targets using a combination of iterative additions of constraints and problem reformulation. Next, cost objectives were employed to identify a cost-effectives solution with the details of design and operating variables. Constraint convexification was used to improve the quality of the solution towards globability. Various forms on non-convex terms were addressed using underestimation techniques. A

trade-off procedure between the saving and expenses for yield maximization problem is presented. This procedure will be a useful tool for the operating facilities to select the level of productivity enhancement to be implemented based on their constraints and available resources. A case study was solved to demonstrate the usefulness of the developed procedure. In this case study, a detailed solution was globally identified.

6.2 Recommendations for Future Work

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

- Extending the problem to cover multiple objectives such as mitigating environmental impact and eliminating/reducing safety issues in addition to the objective of maximizing the overall yield.
- Incorporating the energy integration tasks along with the objective of yield maximization.
- Incorporating the detailed modeling of the whole process and the modeling of the individual units such as reactor into the targeting procedure.
- Incorporating process dynamics and targeting maximum yield under time-based disturbances using an integrated approach to design and operation.

NOMENCLATURE

A	process targeted fresh feed
Ai	flow rate of acetaldehyde in stream i, ton/year
AR	flow rate of acetaldehyde produced in the reactor, ton/year
a	targeted reactant fed to the reactor
a^{max}	maximum possible amount of reactant fed to the reactor
argmin	refers to after recycling and generation minimization
B	process desired product
b	reactor product
b^{max}	maximum possible amount of reactor product
BP1	product of multiplying process yield (YP) by ethanol fresh feed (E1)
BR3	product of multiplying reactor yield (YR) by ethanol fed to the reactor(E3)
C	process undesired /byproduct
Ci	cost function for process manipulated parameter i
CUB	current upper bound of the objective function
$D_{reactor}$	interval inclusion of $d_{reactor}$
$d_{reactor}$	vector of reactor design variables
D_u	permissible values of design degrees of freedom for sink u
d_u	vector of design degrees of freedom for sink u
E_{feed}	Flow rate of ethanol fed to reactor, ton/year
Ei	flow rate of ethanol in stream i, ton/year
ER	flow rate of ethanol generated in the reactor, ton/year

$f(\boldsymbol{x})$	function of vector $\boldsymbol{x}$
$F(X)$	inclusion of function f over interval X
$FEED_{reactor}$	interval inclusion of $Feed_{reactor}$
$Feed_{reactor}$	vector of reactor feed conditions
g	inequality constraint
G_f	flowrate of fresh feed stream f
G_p	flowrate of desired product stream p
G_i	flowrate of the input stream i
G_{i_u}	flowrate of the ith sources entering sink u
$G_{i_u}^{max}$	maximum flowrate of the ith inlet to sink u
$G_{i_u}^{min}$	maximum flowrate of the ith inlet to sink u
G_j	flowrate of output stream j
h	equality constraint
i	index for entering source (input stream)
i_u	index for an entering source to sink u
J	set of real numbers
j	index for exiting source (output stream)
j_u	index for an exiting source from sink u
INPUT	set of input streams
$INPUT_u$	set of input streams to sink u
K	index for targeted components set K
l	amount of process product lost in terminal streams

l^{max}	maximum possible value of process product losses
l^{min}	minimum possible amount of process product losses
L(x)	lower bounding function of continuous and differentiable f(x)
M_f	molecular weight of reactant f
M_p	molecular weight of reaction product p
N^{in}_{after}	set of input streams to process after reactor
N^{in}_{ahead}	set of input streams to process ahead of reactor
$N^{in}_{process}$	set of input streams to the process
N^{in}_{R}	set of input streams to the reactor
N^{in}_{u}	set of input streams to sink u
N^{out}_{after}	set of output streams from process after reactor
N^{out}_{ahead}	set of output streams from process ahead reactor
$N^{out}_{process}$	set of output streams from the process
$N^{out}_{recycle}$	set of recyclable output streams
N^{out}_{waste}	set of waste output streams
N^{out}_{u}	set of output streams from sink u
N_{sinks}	total number of sinks
Net_Gen_f	net rate of generation of process fresh feed f
Net_Gen_p	net rate of generation of process desired product p
$Net\_Gen_{R,f}$	net rate of generation of feed f from reactor R

$Net\_Gen_{R,p}$	net rate of generation of desired product p from reactor R
$Net\_Gen_{u,k}$	net rate of generation of component k in sink u
OUTPUT	set of output streams
$OUTPUT_u$	set of output streams from sink u
$P_{reactor}$	interval inclusion of $p_{reactor}$
$p_{reactor}$	vector of reactor operating variables
p_u	vector of operating degrees of freedom for sink u
P_u	permissible values of operating degrees of freedom for sink u
Q_R	reboiler heat duty, MW
S	reactor selectivity
Si	stands for stream i
S_f	stiochiometric coefficient of reactant f
S_p	stiochiometric coefficient of reaction product p
SINKS	set of process unit processing the targeted species
r	amount of raw material that can be recovered and recycled
r^{max}	maximum recoverable amount of raw material
r^{min}	minimum recoverable amount of raw material
RR	reflux ratio
T_{flash}	temperature of the flash drum, K
T_R	reactor temperature, K
T_{rxr}	reactor temperature, K
U	index for a unit
Ut(x)	concave function

x	real variable, reactor conversion
x^l	lower bound on interval *X*
x^u	upper bound on interval X
$x_{f,f}$	composition of fresh feed f in process main feed stream f
$x_{i,f}$	composition of fresh feed f in input stream i
$x_{i,\,p}$	composition of desired product p in input stream i
$x_{j,f}$	composition of fresh feed f in output stream j
$x_{j,\,p}$	composition of desired product p in output stream j
$x_{p,p}$	composition of desired product p in process desired outlet stream p
X	interval
W	interval
y	real variable
y^l	lower bound on interval *Y*
y^u	upper bound on interval *Y*
$y_{j_u,k}$	Composition of the kth component in the jth outlet stream to sink u
Y	interval, process yield
$Y_{achievable}$	achievable process yield
$Y_{\max}$	maximum process yield
Y_p	overall process yield
Y_R	reactor yield
$Y_{reactor}$	reactor yield
Y_{target}	process yield target

$\text{Yield}_{\text{reactor}}$	reactor yield
$\text{YIELD}_{\text{reactor}}$	inclusion function of $\text{Yield}_{\text{reactor}}$
Z	interval, objective function
z	real variable

Greek

α	fraction of feed that reaches reactor, parameter, lagrange multiplier
$\alpha^{\max}$	upper bound of feed fraction that reaches reactor
$\alpha^{\min}$	lower bound of feed fraction that reaches reactor
β	fraction of recoverable desired product
γ	fraction of recoverable raw material
ξ	path operator for recoverable raw material as defined by Eq. (4.25)
Ξ	inclusion function of ξ
Φ	inclusion function of ϕ
$\Phi^{\min}$	upper bound of Φ
ϕ	path operator for product losses as defined by Eq. (4.20)
ψ	Path operator for reactor feed as defined by Eq. (4.11)
Ψ	inclusion function of ψ
$\Psi^{\max}$	upper bound of inclusion function Ψ
ω	path operator for reactor yield as defined by Eq. (4.17)
$\omega^{\max}$	upper bound of ω

ω^{min}	lower bound of ω
Ω	inclusion function of ω

Subscripts

f	index for feed
i	index for entering stream
j	index for exiting stream
k	index for component
p	index for product
R	index for reactor
u	index for sink

Superscripts

in	index for entering stream
l	lower bound of an interval
max	index for maximum
min	index for minimum
out	index for exiting stream
u	upper bound of an interval

Abbreviations

BB	branch and bound method
BT	product of bilinear term
DFO	derivative free optimization
FT	product of fractional term
ECP	extended cutting plane method
EISEN	energy-induced separation network
ESA	energy-separating agent
EIWAMIN	energy-induced waste minimization network
GA	genetic algorithm
GBC	generalized branch-and-cut method
GBD	generalized benders decomposition method
GRG	generalized reduced gradient method
HEN	heat exchanger network
HISEN	heat-induced separation network
HIWAMIN	heat-induced waste minimization network
IP	integer programming
KKT	karush-kuhn tucker conditions
LCP	linear complementary programming
LP	linear programming
MEN	mass exchanger network
MILP	mixed-integer linear programming

MINLP	mixed-integer nonlinear programming
MIQP	mixed-integer quadratic programming
MPC	model predictive control
NLP	nonlinear programming
OA	outer approximation method
QP	quadratic programming
SA	simulated annealing
SP	semidefinite programming
SQP	successive quadratic programming
WIN	waste interception and allocation network
TT	product of trilinear term

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APPENDIX A

LINGO PROGRAM FOR CHAPTER V CASE STUDY

(ORIGINAL FORMULATION OF YIELD MAXIMIZATION)

A.1 Lingo input code for maximization of acetaldehyde process yield (Original formulation)

```
max = YP;
YP<=0.955;
YP = A14/E1;
E1 + E4 + E6 + E12 = ER + E11 + E18+ E14 + E2+E16 + EW;
A1 + A4 + A6 + A12 + AR = A11 + A18 + A14 + A2+A16 + AW;
E15=E17+E18;
A15=A17+A18;
A14 = 100000;
E4 = 0;
E6 =400;
E14 =0;
E16=0;
E12 =0;
A1 = 0;
A2 = 0;
A4 = 0;
A6 = 0;
```

A12 = 0;

A15 = 0;

YR*E3 = AR;

YR = 0.33 - 0.0000042*(TR - 580)*(TR - 580);

TR >= 300;

TR <= 860;

ER = (46/44)*AR;

E5 = E3 - ER + E4;

ER <= E3;

EG = EC + E1;

EG = E2 + E3;

E9=E14 + E16 + E15;

E17 = EC + EW;

A17 = AC + AW;

AG + A4 + AR = A5 + A2;

A5 + A6 + A12 = A11 + A18+A16 + A14 + A17;

Gama = 0.653*@exp(0.085*RR);

E17= Gama*E15;

RR>=2.5;

RR<=5;

E2= Alfa*EG;

Alfa = -0.0274*TF + 10.5122;

TF>=380;

```
TF<=384;
Beta = 0.14*QR + 0.89;
A14= Beta*A9;
A9 = A5 + A6 + A12 - A11;
A9=A14+A15+A16;
QR<=0.76;
QR>=0.55;
```

A.2 Lingo output code for maximization of acetaldehyde process yield (Original formulation)

Local optimal solution found at iteration: 121

Objective value: 0.9545792

Variable	Value	Reduced Cost
YP	0.9545792	0.000000
A14	100000.0	0.000000
E1	104758.2	0.000000
E4	0.000000	0.000000
E6	400.0000	0.000000
E12	0.000000	0.000000
ER	104923.2	0.000000

E11	0.000000	0.9101481E-05
E18	235.0225	0.000000
E14	0.000000	0.000000
E2	0.000000	0.000000
E16	0.000000	0.000000
EW	0.000000	0.9112210E-05
A1	0.000000	0.000000
A4	0.000000	0.000000
A6	0.000000	0.000000
A12	0.000000	0.000000
AR	100361.3	0.000000
A11	0.000000	0.9547697E-05
A18	0.000000	0.9547697E-05
A2	0.000000	0.000000
A16	361.3007	0.000000
AW	0.000000	0.9547697E-05
E15	199602.0	0.000000
E17	199367.0	0.000000
A15	0.000000	0.000000
A17	0.000000	0.000000
YR	0.3300000	0.000000
E3	304125.2	0.000000
TR	579.9999	0.000000

E5	199202.0	0.000000
EG	304125.2	0.000000
EC	199367.0	0.000000
E9	199602.0	0.000000
AC	0.000000	0.000000
AG	0.000000	0.000000
A5	100361.3	0.000000
GAMA	0.9988225	0.000000
RR	5.000000	0.000000
ALFA	0.000000	2.771252
TF	383.6569	0.000000
BETA	0.9964000	0.000000
QR	0.7600000	0.000000
A9	100361.3	0.000000

Row	Slack or Surplus	Dual Price
1	0.9545792	1.000000
2	0.4207928E-03	0.000000
3	0.000000	1.000000
4	0.000000	-0.9101481E-05
5	0.000000	-0.9547697E-05
6	0.000000	0.9101481E-05
7	0.000000	0.000000

8	0.000000	-0.3640064E-07
9	0.000000	0.9101481E-05
10	0.000000	0.9101481E-05
11	0.000000	-0.9101481E-05
12	0.000000	-0.9101481E-05
13	0.000000	0.9101481E-05
14	0.000000	0.9547697E-05
15	0.000000	-0.9547697E-05
16	0.000000	0.9547697E-05
17	0.000000	0.9547697E-05
18	0.000000	0.9547697E-05
19	0.000000	0.9547698E-05
20	0.000000	-0.3251280E-07
21	0.000000	0.9887960E-02
22	279.9999	0.000000
23	280.0001	0.000000
24	0.000000	-0.9101481E-05
25	0.000000	0.000000
26	199202.0	0.000000
27	0.000000	0.1072922E-07
28	0.000000	-0.1072922E-07
29	0.000000	0.000000
30	0.000000	-0.1072922E-07

31	0.000000	0.000000
32	0.000000	0.000000
33	0.000000	0.000000
34	0.000000	1.818815
35	0.000000	0.9112210E-05
36	2.500000	0.000000
37	0.000000	0.1544173
38	0.000000	-0.9112210E-05
39	0.000000	0.000000
40	3.656934	0.000000
41	0.3430657	0.000000
42	0.000000	0.9616814
43	0.000000	0.9582193E-05
44	0.000000	0.000000
45	0.000000	0.9547697E-05
46	0.000000	0.1346354
47	0.2100000	0.000000

APPENDIX B

LINGO PROGRAM FOR CHAPTER V CASE STUDY

(CONVEXIFIED FORMULATION OF YIELD MAXIMIZATION)

B.1 Lingo input code for maximization of acetaldehyde process yield (convexified formulation case)

```
max = YP;
YP<=.955;
BP1 = A14;
E1 + E4 + E6 + E12 = ER + E11 + E18+ E14 + E2+E16 + EW;
A1 + A4 + A6 + A12 + AR = A11 + A18 + A14 + A2+A16 + AW;
E15=E17+E18;
A15=A17+A18;
A14 = 100000;
E4 = 0;
E6 =400;
E14 =0;
E16=0;
E12 =0;
A1 = 0;
A2 = 0;
A4 = 0;
```

```
A6 = 0;

A12 = 0;

A15 = 0;

BR3 = AR;

YR = 0.33 - 0.0000042*(TR - 580)*(TR - 580);

TR >= 300;

TR <= 860;

ER = (46/44)*AR;

E5 = E3 - ER + E4;

ER <= E3;

EG = EC + E1;

EG = E2 + E3;

E9=E14 + E16 + E15;

E17 = EC + EW;

A17 = AC + AW;

AG + A4 + AR = A5 + A2;

A5 + A6 + A12 = A11 + A18+A16 + A14 + A17;

Gama = 0.653*@exp(0.085*RR);

E17= Gama*E15;

RR>=2.5;

RR<=5;

E2= Alfa*EG;

Alfa = -0.0274*TF + 10.5122;
```

TF>=380;

TF<=384;

Beta = 0.14*QR + 0.89;

A14= Beta*A9;

A9 = A5 + A6 + A12 - A11;

A9=A14+A15+A16;

QR<=0.76;

QR>=0.55;

YR>=0.3;

YR<=.35;

E3>=0;

E3<=350000;

BR3>=0.3*E3+350*YR;

BR3>=0.35*E3+350000*YR-122500;

BR3<=.35*E3;

BR3<=0.3*E3+350000*YR-105000;

YP>=0;

YP<=0.955;

E1>=0;

E1<=250000;

BP1>=0;

BP1>=0.955*E1+250000*YP-238750;

BP1<=0.955*E1;

BP1<=250000*YP;

B.2 Lingo output code for maximization of acetaldehyde process yield (convexified formulation case)

Local optimal solution found at iteration: 18

Objective value: 0.9548443

Variable	Value	Reduced Cost
YP	0.9548443	0.000000
BP1	100000.0	0.000000
A14	100000.0	0.000000
E1	104752.8	0.000000
E4	0.000000	0.000000
E6	400.0000	0.000000
E12	0.000000	0.000000
ER	104923.2	0.000000
E11	0.000000	0.3815502E-05
E18	229.6210	0.000000
E14	0.000000	0.000000
E2	0.000000	0.000000
E16	0.000000	0.000000
EW	0.000000	0.3820000E-05
A1	0.000000	0.000000

A4	0.000000	0.000000
A6	0.000000	0.000000
A12	0.000000	0.000000
AR	100361.3	0.000000
A11	0.000000	0.4003927E-05
A18	0.000000	0.4003927E-05
A2	0.000000	0.000000
A16	361.3007	0.000000
AW	0.000000	0.4003927E-05
E15	195014.5	0.000000
E17	194784.9	0.000000
A15	0.000000	0.000000
A17	0.000000	0.000000
BR3	100361.3	0.000000
YR	0.3300000	0.000000
TR	579.9967	0.000000
E5	194614.5	0.000000
E3	299537.7	0.000000
EG	299537.7	0.000000
EC	194784.9	0.000000
E9	195014.5	0.000000
AC	0.000000	0.000000
AG	0.000000	0.000000

A5	100361.3	0.000000
GAMA	0.9988225	0.000000
RR	5.000000	0.000000
ALFA	0.000000	1.144234
TF	383.6569	0.000000
BETA	0.9964000	0.000000
QR	0.7600000	0.000000
A9	100361.3	0.000000

Row	Slack or Surplus	Dual Price
1	0.9548443	1.000000
2	0.1556920E-03	0.000000
3	0.000000	0.4000000E-05
4	0.000000	-0.3815502E-05
5	0.000000	-0.4003927E-05
6	0.000000	0.3815502E-05
7	0.000000	0.000000
8	0.000000	-0.8018393E-05
9	0.000000	0.3815502E-05
10	0.000000	0.3815502E-05
11	0.000000	-0.3815502E-05
12	0.000000	-0.3815502E-05
13	0.000000	0.3815502E-05

14	0.000000	0.4003927E-05
15	0.000000	-0.4003926E-05
16	0.000000	0.4003927E-05
17	0.000000	0.4003927E-05
18	0.000000	0.4003927E-05
19	0.000000	0.4003927E-05
20	0.000000	-0.1499294E-07
21	0.000000	0.5247528E-02
22	279.9967	0.000000
23	280.0033	0.000000
24	0.000000	-0.3815502E-05
25	0.000000	0.000000
26	194614.5	0.000000
27	0.000000	0.4497881E-08
28	0.000000	-0.4497881E-08
29	0.000000	0.000000
30	0.000000	-0.4497881E-08
31	0.000000	0.000000
32	0.000000	0.000000
33	0.000000	0.000000
34	0.000000	0.7449554
35	0.000000	0.3820000E-05
36	2.500000	0.000000

37	0.000000	0.6324665E-01
38	0.000000	-0.3820000E-05
39	0.000000	0.000000
40	3.656934	0.000000
41	0.3430657	0.000000
42	0.000000	0.4032912
43	0.000000	0.4018393E-05
44	0.000000	0.000000
45	0.000000	0.4003927E-05
46	0.000000	0.5646076E-01
47	0.2100000	0.000000
48	0.3000000E-01	0.000000
49	0.2000000E-01	0.000000
50	299537.7	0.000000
51	50462.33	0.000000
52	10384.50	0.000000
53	2523.117	0.000000
54	4476.883	0.000000
55	0.000000	0.1499294E-07
56	0.9548443	0.000000
57	0.1556920E-03	0.000000
58	104752.8	0.000000
59	145247.2	0.000000

60	100000.0	0.000000
61	0.000000	-0.4000000E-05
62	38.92301	0.000000
63	138711.1	0.000000

APPENDIX C

LINGO PROGRAM FOR CHAPTER V CASE STUDY

(COST MINIMIZATION)

C.1 Lingo input code for cost minimization of acetaldehyde process

```
min=C1+C2+C3+C4;
BP1 = A14;
YP>=0.9545;
E1 + E4 + E6 + E12 = ER + E11 + E18+ E14 + E2+E16 + EW;
A1 + A4 + A6 + A12 + AR = A11 + A18 + A14 + A2+A16 + AW;
E15=E17+E18;
A15=A17+A18;
A14 = 100000;
E4 = 0;
E6 =400;
E14 =0;
E16=0;
E12 =0;
A1 = 0;
A2 = 0;
A4 = 0;
A6 = 0;
A12 = 0;
```

A15 = 0;

BR3 = AR;

YR = 0.33 - 0.0000042*(TR - 580)*(TR - 580);

TR >=300;

TR <= 860;

ER = (46/44)*AR;

E5 = E3 - ER + E4;

ER <= E3;

EG = EC + E1;

EG = E2 + E3;

E9=E14 + E16 + E15;

E17 = EC + EW;

A17 = AC + AW;

AG + A4 + AR = A5 + A2;

A5 + A6 + A12 = A11 + A18+A16 + A14 + A17;

Gama = 0.653*@exp(0.085*RR);

E17= Gama*E15;

RR>=2.5;

RR<=5;

E2= Alfa*EG;

Alfa = -0.0274*TF + 10.5122;

TF>=380;

TF<=384;

Beta = 0.14*QR + 0.89;

A14= Beta*A9;

A9 = A5 + A6 + A12 - A11;

A9=A14+A15+A16;

QR<=0.76;

QR>=0.55;

C1=3570*(TR-500);

C2=6400*(RR-2.5);

C3=2100*(TF-380);

C4=160*(QR-0.55);

YR>=0.3;

YR<=.35;

E3>=0;

E3<=350000;

BR3>=0.3*E3;

BR3>=0.35*E3+350000*YR-122500;

BR3<=.35*E3;

BR3<=0.3*E3+350000*YR-105000;

YP>=0;

YP<=0.955;

E1>=0;

E1<=250000;

BP1>=0;

BP1>=0.955*E1+250000*YP-238750;

BP1<=0.955*E1;

BP1<=250000*YP;

C.2 Lingo output code for cost minimization of acetaldehyde process

Local optimal solution found at iteration: 57

Objective value: 23695.44

Variable	Value	Reduced Cost
C1	0.000000	0.9998967
C2	15982.28	0.000000
C3	7679.562	0.000000
C4	33.60000	0.000000
BP1	100000.0	0.000000
A14	100000.0	0.000000
YP	0.9545000	0.000000
E1	104842.9	0.000000
E4	0.000000	0.000000
E6	400.0000	0.000000
E12	0.000000	0.000000
ER	104923.2	0.000000

E11	0.000000	0.3326086
E18	319.7540	0.000000
E14	0.000000	0.000000
E2	0.000000	0.000000
E16	0.000000	0.000000
EW	0.000000	0.3330791
A1	0.000000	0.000000
A4	0.000000	0.000000
A6	0.000000	0.000000
A12	0.000000	0.000000
AR	100361.3	0.000000
A11	0.000000	0.3492955
A18	0.000000	0.3492955
A2	0.000000	0.000000
A16	361.3007	0.000000
AW	0.000000	0.3492955
E15	226374.5	0.000000
E17	226054.7	0.000000
A15	0.000000	0.000000
A17	0.000000	0.000000
BR3	100361.3	0.000000
YR	0.3031200	0.000000
TR	500.0000	0.000000

E5	225974.5	0.000000
E3	330897.7	0.000000
EG	330897.7	0.000000
EC	226054.7	0.000000
E9	226374.5	0.000000
AC	0.000000	0.000000
AG	0.000000	0.000000
A5	100361.3	0.000000
GAMA	0.9985874	0.000000
RR	4.997231	0.000000
ALFA	0.000000	33572.77
TF	383.6569	0.000000
BETA	0.9964000	0.000000
QR	0.7600000	0.000000
A9	100361.3	0.000000

Row	Slack or Surplus	Dual Price
1	23695.44	-1.000000
2	0.000000	0.3487739
3	0.000000	-87193.49
4	0.000000	-0.3326086
5	0.000000	-0.3492955
6	0.000000	0.3326086

7	0.000000	0.000000
8	0.000000	-0.1783528E-02
9	0.000000	0.3326086
10	0.000000	0.3326086
11	0.000000	-0.3326087
12	0.000000	-0.3326087
13	0.000000	0.3326086
14	0.000000	0.3492955
15	0.000000	-0.3492955
16	0.000000	0.3492955
17	0.000000	0.3492955
18	0.000000	0.3492955
19	0.000000	0.3492955
20	0.000000	-0.1568309E-02
21	0.000000	548.9081
22	200.0000	0.000000
23	360.0000	0.000000
24	0.000000	-0.3326086
25	0.000000	0.000000
26	225974.5	0.000000
27	0.000000	0.4704927E-03
28	0.000000	-0.4704927E-03
29	0.000000	0.000000

30	0.000000	-0.4704927E-03
31	0.000000	0.000000
32	0.000000	0.000000
33	0.000000	0.000000
34	-0.2764131E-07	75400.62
35	-0.1252547E-01	0.3330791
36	2.497231	0.000000
37	0.2769135E-02	0.000000
38	0.000000	-0.3330791
39	0.000000	-76642.34
40	3.656934	0.000000
41	0.3430657	0.000000
42	0.000000	35182.41
43	0.000000	0.3505575
44	0.000000	0.000000
45	0.000000	0.3492955
46	0.000000	4765.537
47	0.2100000	0.000000
48	0.000000	-0.1033237E-03
49	0.000000	-1.000000
50	0.000000	-1.000000
51	0.000000	-1.000000
52	0.3120000E-02	0.000000

53	0.4688000E-01	0.000000
54	330897.7	0.000000
55	19102.33	0.000000
56	1092.000	0.000000
57	955.1166	0.000000
58	15452.88	0.000000
59	0.000000	0.1568309E-02
60	0.9545000	0.000000
61	0.5000000E-03	0.000000
62	104842.9	0.000000
63	145157.1	0.000000
64	100000.0	0.000000
65	0.000000	-0.3487739
66	125.0000	0.000000
67	138625.0	0.000000

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