

OPTIMIZATION OF REACTIVE DISTILLATION COLUMN
USING GENETIC ALGORITHM

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
in
Chemical Engineering

By
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Department of Chemical Engineering
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Rourkela



CERTIFICATE

This is to certify that the thesis entitled, “OPTIMIZATION OF REACTIVE DISTILLATION COLUMN” submitted by Ketan Gulati and Varun Bharti in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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Abstract

The reactive distillation combines both chemical reaction and multi component separation into a single unit. It is a unit operation in which chemical reaction and distillative separation are carried out simultaneously within a fractional distillation apparatus. Reactive distillation (RD), the combination of chemical reaction and distillation in a single unit operation, has proven to be advantageous over conventional process systems consisting of separate reactor and distillation units. A simulation model based on an extension of conventional distillation is proposed for the simulation step of the optimization problem. A reactive distillation column has been synthesized for the production of ethylene glycol for the given number of trays, feed distribution, liquid hold up in each plate, boil up fraction assuming ideal vapor liquid equilibrium relation. The objective function is the minimization of the total annualized cost and to evaluate the objective function, the operating conditions determined by the column simulation for each decision vector have to be calculated. The optimization of the objective function has been done by using genetic algorithm, and the results obtained are similar to those previously reported.

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Chapter 1

INTRODUCTION

Reactive Distillation

Reactive Distillation column
For production of ethylene
glycol

1.1.1 REACTIVE DISTILLATION

The reactive distillation combines both chemical reaction and multi component separation into a single unit. It is a unit operation in which chemical reaction and distillative separation are carried out simultaneously within a fractional distillation apparatus. Reactive distillation (RD), the combination of chemical reaction and distillation in a single unit operation, has proven to be advantageous over conventional process systems consisting of separate reactor and distillation units. Reactive distillation may be advantageous for liquid-phase reaction systems when the reaction must be carried out with a large excess of one or more of the reactants, when a reaction can be driven to completion by removal of one or more of the products as they are formed, or when the product recovery or by-product recycle scheme is complicated or made infeasible by azeotrope formation. For consecutive reactions in which the desired product is formed in an intermediate step, excess reactants can be used to suppress additional series reactions by keeping the intermediate species low. A reactive distillation can achieve the same end by removing the desired intermediate from the reaction zone as it is formed. Similarly, if the equilibrium constant of a reversible reaction is small, high conversions can be achieved by use of a large excess is small. Alternatively, by Le Chatelier's principle, the reaction can be driving to completion by removal of one or more of the products as they formed. Typically, reactants can be kept much closer to stoichiometric proportions in a reactive distillation. When a reaction mixture exhibits azeotropism, the recovery of products and recycle of excess reagents can be quite complicated and expensive. Reactive distillation can provide a means of breaking azeotropes by altering or eliminating the condition for azeotrope formation in the reaction zone through the combined effects of vaporization -condensation and consumption production of the species in the mixture. Alternatively, a reaction may be used to convert the species into components that are more easily distilled. In each of these situations the conversion and selectivity often can be improved markedly, with much lower reactant inventories and recycle rates, and much simple recovery schemes. The capital savings can be quite dramatic. Although reactive distillation has many potential applications, it is not appropriate for all situations. Since it is in essence a distillation process, it has the same range of applicability as other distillation operations. Distillation based equipment is not designed to effectively handle

solids, superficial components (where no separate vapor and liquid phase exist) , gas phase reactions, or high temperature or high pressure reactions such as hydrogenation , the steam reforming, gasification and hydro-dealkylation. Reactive distillation columns can be attractive whenever conversions are limited by unfavorable reaction equilibrium and when selectivity can be increased by allowing simultaneous reaction and separation in the same processing unit. It offers significant economic advantages in some systems, particularly when reactions are reversible or when the presence of azeotropes makes conventional separation systems complex and expensive.

1.1.2 ADVANTAGES

These advantages include:

- capital cost savings from the elimination of unit operations;
- improved selectivity and conversion;
- potential to overcome chemical equilibrium limitations;
- ability to react away azeotropes;
- And use of heat of reaction to reduce energy consumption through energy integration.

1.1.3 DISADVANTAGES

However, there are drawbacks to reactive distillation which include:

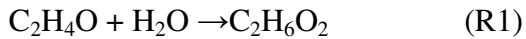
- incompatibility of process conditions for reaction and separation,
- residence time requirements,
- volatility constraints for the reagents and products in the reaction zone of the distillation column and
- most importantly, the lack of well established design methods.

There are many documented success stories involving the industrial implementation of reactive distillation. The applications of reactive distillation in the chemical and petroleum industries have increased rapidly in the past decade (Taylor and Krishna, 2000; Doherty and Malone, 2001). One such example is the manufacturing of methyl acetate by the Eastman Chemical Company. In this case a single reactive distillation column

replaced the traditional flow sheet consisting of eleven major unit operations along with an assortment of heat exchangers, pumps and controllers. The result was a five-fold reduction in capital investment and energy consumption over the conventional design for methyl acetate production (Siirola, 1996; Doherty & Malone, 2001).

1.2 REACTIVE DISTILLATION COLUMN FOR THE PRODUCTION OF ETHYLENE GLYCOL

The optimization of a reactive distillation column for the production of ethylene glycol from ethylene oxide and water is studied. Ethylene glycol (C₂H₆O₂) is produced from the reaction of ethylene oxide (C₂H₄O) and water:



However, the ethylene glycol produced can further react with ethylene oxide to produce the unwanted byproduct diethylene glycol (C₄H₁₀O₃):



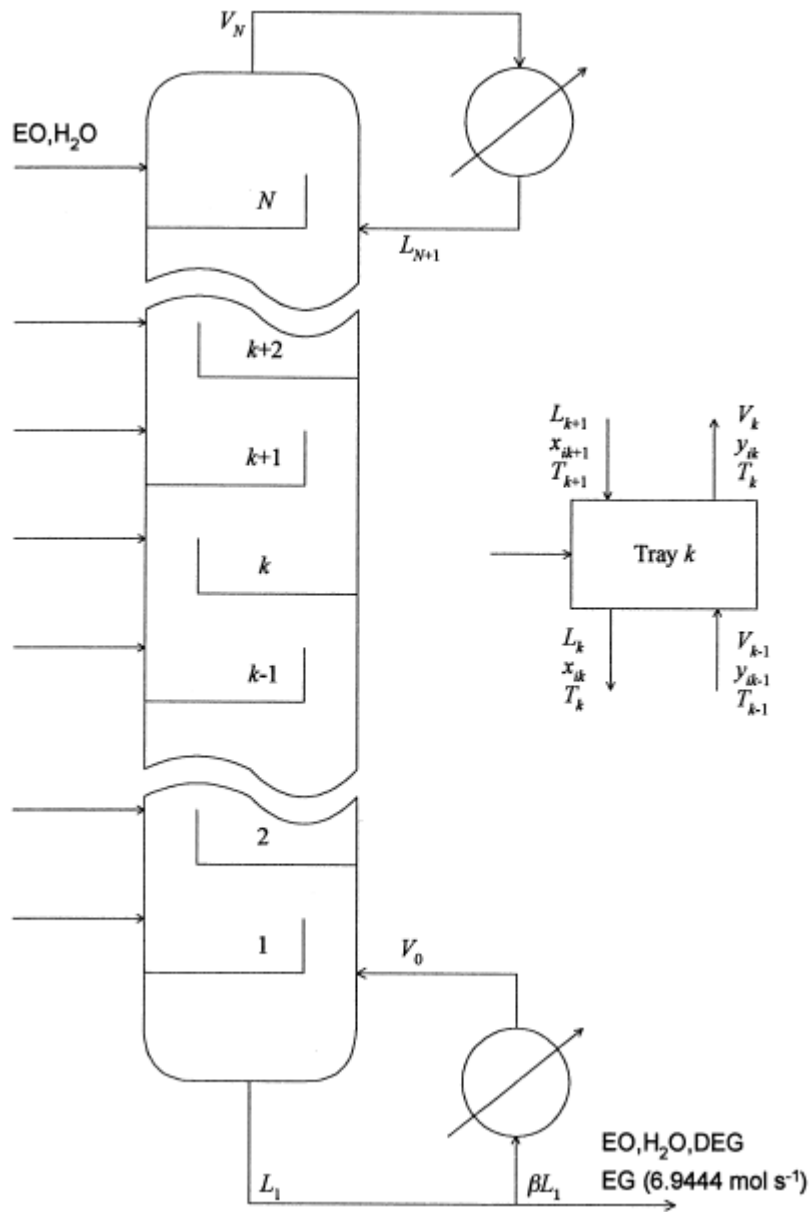


Fig 1.1: Reactive distillation column for the production of ethylene glycol

Both reactions are highly exothermic and occur at moderate temperatures, allowing production via a reactive distillation column. Both reactions are exothermic and occur at temperatures that make feasible the production and separation of ethylene glycol in the same unit. Higher extensions of the first reaction over the second reaction are obtained using a low molar fraction of ethylene oxide in the liquid phase and a high value of the molar fraction of water in the liquid phase. The separation of ethylene glycol from the reactants is favored by the difference in volatility between the product and the reactants, whereby the product moves towards the bottom of the column, and the reactants (more volatile) towards the top, giving rise to two different sections: a reaction zone and a stripping zone. For this reactive distillation column, the flow rate of distillate is set to zero, contributing to a high molar fraction of water at the top of the column.

Chapter 2

LITERATURE REVIEW

The study of RD dates back as far as the early 1920s (Backhaus, 1921), but the idea did not draw significant interest until the advent of effective algorithms for the simulation and design of reactive distillation systems. There is a large number of examples of RD simulation found in the literature (Chang & Seader, 1988; Venkataraman, Chan, & Boston, 1990; Nijhuis, Kerkhof, & Mak, 1993; Abufares & Douglas, 1995; Jimoh, Arellano-Garcia, Bock, & Wozny, 1999; Chen, Huss, Malone, & Doherty, 2000; Yang, Yang, & Wang, 2001; Chen, Huss, Malone, & Doherty, 2002; Smejkal & Soos, 2002; Baur, Taylor, & Krishna, 2003). There have been a number of different approaches to reactive distillation design. Barbosa and Doherty (1988a,b) adapted the residue curve maps of conventional distillation columns to RD systems near chemical equilibrium. Buzad and Doherty (1994, 1995) extended the theory of Barbosa and Doherty and proposed the fixed point method.

A number of papers and patents have explored the RD systems. The literature up to 1992 was reviewed by Doherty and Buzad (1992). Most of the papers were discussed by steady-state design and optimization problems. Only a few papers studied the dynamic of reactive distillation or the interaction between design and control. Recent books by Doherty and Malone (2001) and Sundmacher and Kienle (2003) present detailed discussions of technology and its current status. The literatures state that the most common applications of reactive distillation are etherification and esterification reactions. Most of these papers focus on real chemical systems, and each system has its own set of complexities in vapor–liquid equilibrium non ideality (azeotropes), reaction kinetics, physical properties, etc. The discrete nature of chemical species and specific complexities in the VLE seems to cloud the picture in understanding reactive distillation systems. On the other hand, the ideal reactive distillation of Luyben (2000) and Al-Arfaj and Luyben (2000) seems to offer a continuous spectrum in studying the process behavior by stripping away all the non-ideal VLE and specific reaction rates. Only a limited number of papers study the ideal reactive distillation systems. Al-Arfaj and Luyben (2000) studied the control of an ideal two-product reactive distillation system. Simple ideal physical properties and kinetics are assumed so that the control issue can be explored

without being clouded by complexities of a specific chemical system. Sundmacher and Qi (2003) also compare the conceptual design of reactive distillation process configurations for ideal binary mixtures, and comparisons are made to the conventional process. A recent paper by Kaymak and Luyben (2004) also makes quantitative comparisons of simple reactive distillation for different chemical equilibrium constants and relative volatilities (Kaymak et al., 2004).

Most of the studies in reactive distillation are simulation studies, viz. the resulting composition profiles are determined after specification of feed composition and quality, column pressure, reflux or reboiler ratio, total number of stages, feed plate location and liquid-phase volumes on each stage. The optimizations were also performed with non-ideal vapor liquid equilibrium, considering either distributed feed and reaction trays or single feed and reaction tray. The results show that the optimized objective function values are very similar, and mostly independent of the number of trays and of the reaction distribution. The reactive distillation differs from the conventional distillation in that a tubular type of reactor, the reactive flash cascades to be specific (Doherty and Malone, 2001), is cascaded with separation units. From this perspective, the composition profile inside the reactive zone becomes important for an effective operation of the reactive flash cascades. Moreover, typical distillation columns follow certain temperature profile. That is, the temperature increases as one step down the column. The composition as well as the temperature effects should play some role for the performance of a reactive distillation column. The reactant feed location is an obvious design degree of freedom to locate optimal composition and temperatures profiles inside the column. It then becomes obvious that the feed tray location should be included as a design variable.

Pekkanen (1995) presents a design algorithm for a local optimization' approach for reactive distillation. This approach is characterized as stage by stage specification', where the design procedure starts from both column ends and design specifications are made at each stage as the calculation progresses. The column is thus not optimized as a whole since not all the parameters are simultaneously varied. Okasinski and Doherty (1998) have extended the fixed point design method for systems with isomolar or non isomolar liquid-phase reaction, non-ideal vapor liquid equilibrium and allowing for a distribution of liquid holdups on the reactive stages. Huss et al. (1999) give emphasis to conceptual

column design through geometric methods, and have shown that equilibrium reactive designs can be the starting point for rate-based designs.

There are several simulation algorithms available (Buzad & Doherty, 1995), some implemented in commercial simulators, such as AspenPlus (Venkataraman, Chan & Boston, 1990). Abufares and Douglas (1995) developed a dynamic mathematical model for a methyl tertiary butyl ether (MTBE) catalytic distillation process, which was implemented in the dynamic simulator SpeedUp. Recently, Huss, Chen, Malone and Doherty (1999) proposed a general framework based on conceptual design for solving both equilibrium and rate-based reactive distillation processes. Schenk, Gani, Bogle and Pistikopoulos (1999) have defined a general modeling framework that allows both rate-based and equilibrium-based models, steady state or dynamic, to be formulated and solved. Jimoh, Arellano-Garcia, Bock and Wozny (1999) have experimentally validated their steady-state and dynamic model for reactive distillation using a pilot-scale column and investigated the trans-esterification of methyl myristate with isopropanol to methanol and isopropyl myristate. The optimizations were also performed with non-ideal vapor liquid equilibrium, considering either distributed feed and reaction trays or single feed and reaction tray. The results show that the optimized objective function values are very similar, and mostly independent of the number of trays and of the reaction distribution.

R.M. Lima, R.L. Salcedo, D. Barbosa presented a methodology to improve the efficiency of stochastic methods applied to the optimization of chemical processes with a large number of equality constraints. The methodology is based on two steps:

- (a) the optimization of the simulation step, which involves the optimum choice of design variables and subsystems to be simultaneously solved;
- (b) the optimization of the nonlinear programming (NLP) problem using stochastic methods.

For the first step a flexible tool (SIMOP) is used, whereby different numerical procedures can be easily obtained, taking into account the problem formulation and

specific characteristics, the need for specific initialization schemes and the efficient solution of systems of nonlinear equations.

The global optimization of chemical processes using stochastic methods is becoming a common practice in process optimization. In recent years, examples of application of stochastic methods to the solution of nonlinear programming (NLP) problems, mixed-integer nonlinear programming (MINLP) problems and NLP problems subject to differential-algebraic equations, arising from process design, synthesis and optimal control problems, have been reported. Examples include the design of heat exchange networks (HEN) (Athier et al., 1998; Yu et al., 2000), synthesis of residence time distribution (RTD) models (Laquerbe et al., 2001), design of distillation processes (Cardoso et al., 2000; Hanke and Li, 2000; Ramanathan et al.,2001), dynamic optimization of batch reactors (Carrasco and Banga, 1997; Lima et al., 2004; Zhang and Smith, 2004), dynamic optimization of crystallization processes (Choong and Smith, 2004a,b,c) and dynamic optimization of bioprocesses (Banga et al., 1997). This has been mainly driven by the need to achieve better solutions, escaping from sub-optimal solutions associated with the development of new and more robust optimization algorithms.

Stochastic methods are an attractive option for global optimization due to:

- (a) the capacity to escape local optima and find solutions in the vicinity of the global optimum;
- (b) the easiness of implementation;
- (c) the ability to deal with “black box” simulation approaches, without requiring derivatives or any knowledge about the simulation structure.

The main drawbacks of these methods are that:

- (a) They do not guarantee global optimality, nevertheless, several studies demonstrated their ability to reach the best known solutions;
- (b) They may require a large number of function evaluations.

However, the availability of computing power at a low cost has enabled the application of stochastic algorithms to even larger problems. Stochastic methods present a considerable flexibility over deterministic methods for process engineering, being able to be linked with user developed simulations, independently of the model type, viz. first principle models, data-driven models or hybrid models; or with process simulators like SPEEDUP, as done by [Li et al. \(2000\)](#), or high-level modeling systems such as ASCEND ([Locke and Westerberg, 1983](#); [Piela et al., 1991](#); [Silva and Salcedo, 2005](#)).

These modeling systems have the main advantage of disposing of advanced modeling or process languages that help to:

- (a) Write consistent models ([Piela et al., 1991](#));
- (b) Facilitate the reuse of existing models ([Marquardt, 1996](#));
- (c) Decrease the time required to build, manage and debug large scale models.

However, the heavy structure of these modeling systems and the high number of simulation evaluations required, may introduce a significant computer burden for any large-scale optimization problem. Generally, stochastic methods only need to evaluate the objective function values in order to update the vector of design variables. This evaluation is made in a “black-box” approach, which means that, whenever an equation-oriented model is used, it is not enough to write down the equations that describe the process, but it is also necessary to implement a strategy to solve the simulation step. [Banga and Casares \(1987\)](#) have developed ICRS, a random search algorithm integrating two algorithms of [Book and Ramirez \(1976, 1984\)](#) to choose sets of design variables and assignment of output variables to equations, able to handle nonlinear equality constraints. Although [Casares and Rodriguez \(1989\)](#) explain how ICRS can be applied to deal with simulations involving irreducible subsystems, the examples reported ([Banga and Casares, 1987](#); [Casares and Rodriguez, 1989](#)) have only included simulation models with sequential solutions. [Choi et al. \(1999\)](#) have proposed a feasible point strategy with the aim of finding feasible points, and to avoid to deal with a large number of equality constraints (typical in chemical process optimization problems) with stochastic optimization algorithms. Their strategy was based on the combination of a generalized

reduced gradient (GRG) algorithm and a stochastic algorithm, where the equality constraints were dealt by the GRG algorithm. In this work, a methodology was build, within an integrated framework, equation-oriented models for stochastic optimizers.

The main features of this methodology, named SIMOP, for Simulation for Optimization, are:

- (a) an equation oriented model interpreter, providing an easy way to write down the process model;
- (b) Application of the strategy developed by [Salcedo and Lima \(1999\)](#) to choose optimum sets of design variables and output sets, in order to efficiently solves nonlinear systems of algebraic equations;
- (c) Integration of specific numerical solvers used to solve parts of the numerical procedure;
- (d) Automatic generation of numerical procedures based on FORTRAN code;
- (e) Link with specific stochastic solvers.

Thus, SIMOP uses decomposition strategies applied in equation-oriented simulation approaches, associated with the optimum choice of design variables, in order to obtain numerical procedures to be used in process optimization using stochastic algorithms. The aim of this methodology is to improve the efficiency of the simulation process, oriented to the improvement of the performance of stochastic optimizers.

The simulation and optimization of the reactive distillation problem proposed by [Ciric and Gu \(1994\)](#) was used in M. F. Cardoso, R. L. Salcedo*, S. Feyo de Azevedo, D. Barbosa work as a case study to evaluate the capabilities of the methodology to simulate and optimize problems, involving complex recycle structures and with a high degree of nonlinearity. Different numerical procedures were studied in order to evaluate the convergence and efficiency of the simulations. These studies were based on the

performance of the solver applied to the solution of the systems of nonlinear equations, and based on the evaluation of condition number estimators of the Jacobian matrix of these systems.

According to Ciric and Gu (1994) there are two reasons for producing ethylene glycol via reactive distillation. Firstly, the large difference in volatilities between ethylene oxide and ethylene glycol will lead to a rapid separation of these two components in the column, improving the overall selectivity. Secondly, part of the heat required for the separation is obtained from the heat of reaction, which allows the reduction of energy costs. This problem has been proposed and solved by Ciric and Gu (1994), using a MINLP model and a generalized Benders decomposition (GBD) algorithm. The model is based on a rigorous tray-to-tray model, including material and energy balances for each tray, vapor-liquid equilibrium (VLE) relationships, stoichiometric equations, kinetic relationships and logical relationships between process variables and the number of trays of the column.

This process has been analyzed by several researchers, concerning the occurrence of multiple steady states (Baur et al., 2000; Ciric and Miao, 1994), different kinetic and VLE models (Cardoso et al., 2000; Okasinski and Doherty, 1998), different operating conditions (Al-Arfaj and Luyben, 2002; Cardoso et al., 2000; Okasinski and Doherty, 1998), the dynamic behavior and control strategies (Al-Arfaj and Luyben, 2002; Kumar and Daoutidis, 1999; Monroy-Loperena et al., 2000) and the use of non-equilibrium models considering mass transfer rates across the vapor-liquid interface (Baur et al., 2000). Additionally, optimization-based techniques have been also used to obtain optimum steady state designs for the reactive distillation column. Jackson and Grossmann (2001) have applied a general disjunctive programming approach to obtain optimal designs. The optimum design presented by these authors corresponds to a reactive distillation column with a higher number of theoretical trays when compared with the optimal design of Ciric and Gu (1994). Cardoso et al. (2000) have used two stochastic based optimizers, MSIMPSA and MSGA, to obtain optimal designs, using an equation-oriented numerical procedure.

These authors achieved similar results to those previously reported (Ciric and Gu, 1994), and have concluded that for the ethylene glycol reactive distillation column the number of theoretical stages is not an important design variable, such that near optimum column designs could be obtained by fixing the number of stages and simply solving the corresponding NLP subproblem. This is because the dominant cost is due to the reactants cost, and not to the column itself.

The simulation of reactive distillation processes involves the simultaneous solution of material and energy balances and stoichiometric relationships, and this corresponds to the solution of a considerable large set of non-linear equations. The calculation procedures reported for solving sets of non-linear equations can be divided broadly into four categories (Chang & Seader, 1988; Venkataraman et al., 1990; Biegler, Grossmann & Westerberg, 1997; Lee & Dudukovic, 1998):

- (i) Methods using equation decomposition (or tearing/ partitioning);
- (ii) Relaxation techniques;
- (iii) Methods incorporating Newton or quasi-Newton algorithms;
- (iv) homotopy-continuation method.

Decomposition methods allow the identification of blocks which need the simultaneous solution and blocks which can be solved sequentially. For example, Ledet and Himmelbleau (1970) propose a method that identifies a minimum set of recycle variables, which may then be used with direct substitution. These methods are fast and efficient in what concerns the use of computer storage space. However, when differences in boiling point values between components are large, when kinetics are complex, or when liquid solutions are highly non-ideal, these direct methods suffer from poor convergence characteristics. With relaxation techniques, the liquid-phase compositions are computed based on non-steady-state material balances (Bastos, 1987), which in subsequent iterations proceed towards the steady-state solution. Relaxation techniques are reliable

but can be slow specially as the solution is approached (Bastos, 1987; Chang & Seader, 1988; Venkataraman et al., 1990). Newton or quasi-Newton methods converge quickly from suitable starting guesses (Murthy, 1984; Chang & Seader, 1988). When the starting point is far from the solution, these methods can converge to impossible physical conditions or may not converge at all. Bastos (1987) has developed an algorithm for the simulation of conventional distillation columns that makes use of a modified Newton Raphson method. As a first step the algorithm applies a relaxation technique to improve the starting guess for the composition profile and flow rates in the column, which are needed by the Newton-Raphson method. Homotopy-continuation methods have the advantage of forcing the desired solution by tracking a homotopy curve regardless of the choice of the initial estimates. Lee and Dudukovic 1998 have found these to be superior to Newton-based methods for solving the non-linear system of equations arising in reactive distillation, despite a longer computational burden.

The objective of the optimization problem defined by Ciric and Gu (1994) is the minimization of the performance index defined by the annual cost of operation of the column and the annualized investment for the production of 25 kmol h⁻¹ of ethylene glycol, subject to the constraints defined by the mathematical model of the column (see Appendix A). The annual cost of operation takes in consideration the consumption of raw materials, steam and cooling water. The annualized investment is determined by the costs of the column, the reboiler and the condenser.

For the reactive distillation column specified as above, M. F. Cardoso, R. L. Salcedo*, S. Feyo de Azevedo, D. Barbosa proposed a simulation model based on the following steps:

- (i) An initial estimate of the molar feed flow rate not specified by the decision vector, viz. a torn (recycle) variable, is specified. We have chosen F 21 as the torn variable, although other recycle variables may equally work. This torn variable was found to be appropriate from an information flow point of view, and need not be a true recycle variable (from a material flow point of view).
- (ii) An initial estimate of the composition profile in the column was next obtained.

- (iii) This estimate is improved by a relaxation method.
- (iv) The material balance equations were then solved with the Newton Raphson method, and a new composition profile was computed.
- (v) The torn variable was re-evaluated and the equations describing the reactive distillation process were again solved (Fig. 2).
- (vi) The algorithm ended when the global material balance to the column is verified (after convergence on the torn variable) or when a non-plausible column was obtained. The simulation was aborted when convergence on the torn variable was obtained but not on the global material balance, or when the Newton Raphson method exceeded a pre-specified maximum number of iterations.

M. F. Cardoso, R. L. Salcedo*, S. Feyo de Azevedo, D. Barbosa calculated and plotted water composition and ethylene glycol profiles for the best solution obtained by Ciric and Gu (1994), Temperature profile for the best solution obtained by Ciric and Gu (1994), Water and ethylene glycol composition profiles for a solution obtained with active constraints on the maximum molar flow rates(FIG2), Temperature profile for a solution obtained with active constraints on the maximum molar flow rates(FIG3), Water and ethylene glycol composition profiles for a solution obtained without constraints on the maximum molar flow rates(FIG4), Temperature profile for a solution obtained without constraints on the maximum molar flow rates(FIG5), Water and ethylene glycol composition profiles for the best solution obtained with active constraints on the maximum molar flow rates(FIG6), Temperature profile for the best solution obtained with active constraints on the maximum molar flow rates(FIG7).

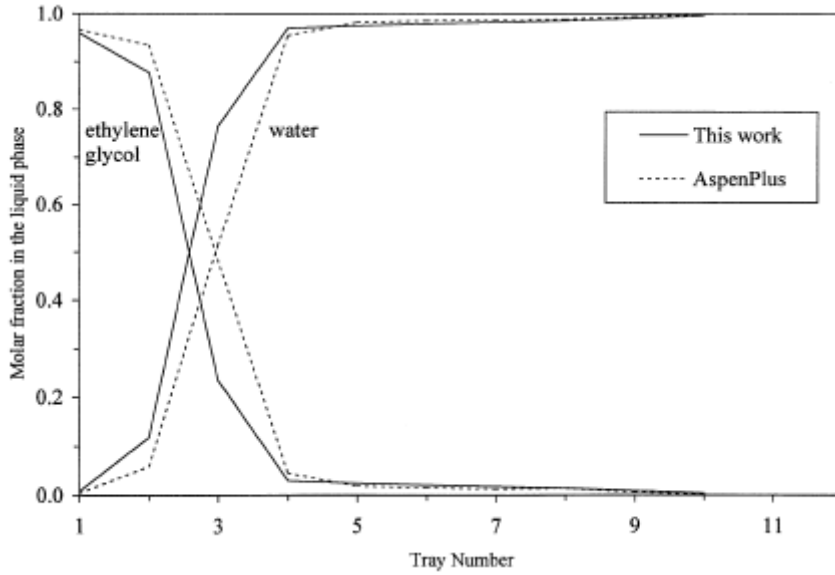


Fig 2.1 . Water and ethylene glycol composition profiles for a solution obtained with active constraints on the maximum molar flow rates.

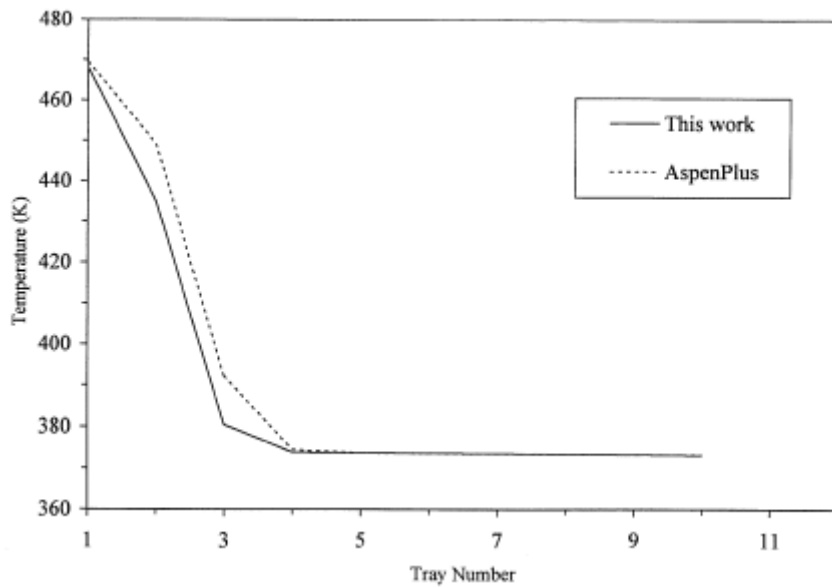


Fig 2.2. Temperature profile for a solution obtained with active constraints on the maximum molar flow rates.

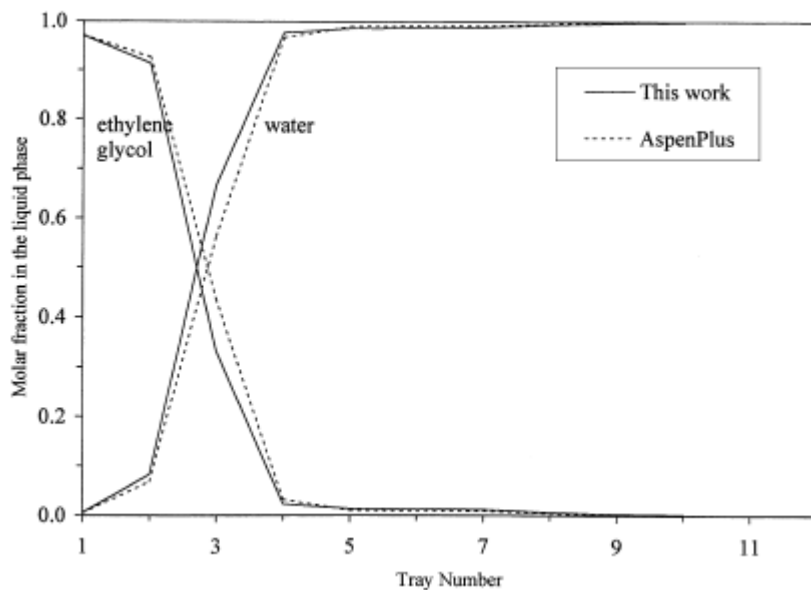


Fig 2.3. Water and ethylene glycol composition profiles for a solution obtained without constraints on the maximum molar flow rates.

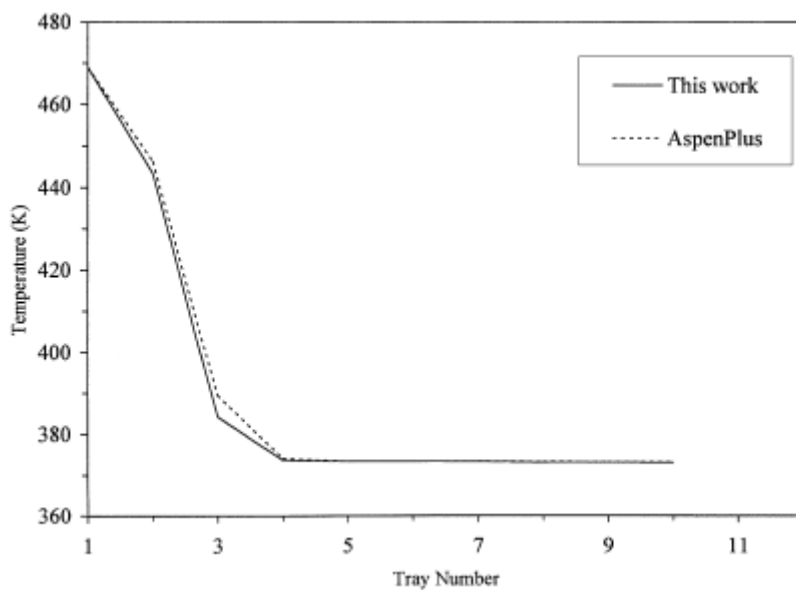


Fig. 2.4. Temperature profile for a solution obtained without constraints on the maximum molar flow rates.

Chapter 3

Genetic Algorithm

Genetic algorithm

Using genetic algorithm

Using genetic algorithm tool

3.1 GENETIC ALGORITHM

The genetic algorithm is a method for solving both constrained and unconstrained optimization problems that is based on natural selection, the process that drives biological evolution. The genetic algorithm repeatedly modifies a population of individual solutions. At each step, the genetic algorithm selects individuals at random from the current population to be parents and uses them to produce the children for the next generation. Over successive generations, the population "evolves" toward an optimal solution. Genetic algorithm can be applied to solve a variety of optimization problems that are not well suited for standard optimization algorithms, including problems in which the objective function is discontinuous, nondifferentiable, stochastic, or highly nonlinear.

The genetic algorithm uses three main types of rules at each step to create the next generation from the current population:

- *Selection rules* select the individuals, called *parents*, that contribute to the population at the next generation.
- *Crossover rules* combine two parents to form children for the next generation.
- *Mutation rules* apply random changes to individual parents to form children.

The genetic algorithm differs from a classical, derivative-based, optimization algorithm in two main ways, as summarized in the following table.

Table – 3.1

Classical Algorithm	Genetic Algorithm
Generates a single point at each iteration. The sequence of points approaches an optimal solution.	Generates a population of points at each iteration. The best point in the population approaches an optimal solution.
Selects the next point in sequence by deterministic computation .	Selects the next population by computation which uses random number generations.

Fitness Values and Best Fitness Values

The *fitness value* of an individual is the value of the fitness function for that individual. Because the toolbox finds the minimum of the fitness function, the *best* fitness value for a population is the smallest fitness value for any individual in the population.

Parents and Children

To create the next generation, the genetic algorithm selects certain individuals in the current population, called *parents*, and uses them to create individuals in the next generation, called *children*. Typically, the algorithm is more likely to select parents that have better fitness values.

Outline of the Algorithm

The following outline summarizes how the genetic algorithm works:

- 1** The algorithm begins by creating a random initial population.
- 2** The algorithm then creates a sequence of new populations. At each step, the algorithm uses the individuals in the current generation to create the next population. To create the new population, the algorithm performs the following steps:
 - a** Scores each member of the current population by computing its fitness value.
 - b** Scales the raw fitness scores to convert them into a more usable range of values.
 - c** Selects members, called parents, based on their fitness.
 - d** Some of the individuals in the current population that have lower fitness are chosen as *elite*. These elite individuals are passed to the next population.
 - e** Produces children from the parents. Children are produced either by making random changes to a single parent — *mutation* — or by combining the vector entries of a pair of parents — *crossover*.
 - f** Replaces the current population with the children to form the next generation.
 - g** The algorithm stops when one of the stopping criteria is met.

Creating the Next Generation

At each step, the genetic algorithm uses the current population to create the children that make up the next generation. The algorithm selects a group of individuals in the current population, called *parents*, who contribute their *genes*— the entries of their vectors— to

their children. The algorithm usually selects individuals that have better fitness values as parents. A function can be specified that the algorithm uses to select the parents in the **Selection function** field in the **Selection** options.

The genetic algorithm creates three types of children for the next generation:

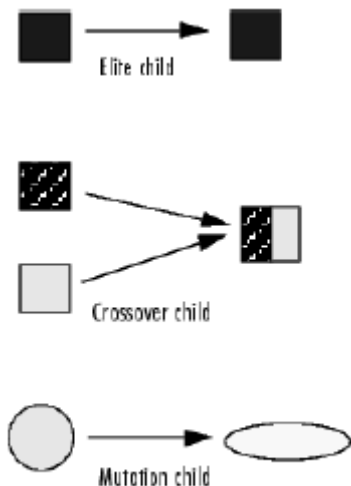
- *Elite children* are the individuals in the current generation with the best fitness values. These individuals automatically survive to the next generation.
- *Crossover children* are created by combining the vectors of a pair of parents.
- *Mutation children* are created by introducing random changes, or mutations, to a single parent.

Crossover Children

The algorithm creates crossover children by combining pairs of parents in the current population. At each coordinate of the child vector, the default crossover function randomly selects an entry, or *gene*, at the same coordinate from one of the two parents and assigns it to the child.

Mutation Children

The algorithm creates mutation children by randomly changing the genes of individual parents. By default, the algorithm adds a random vector from a Gaussian distribution to the parent. The following schematic diagram illustrates the three types of children.



3.2 Using the Genetic Algorithm

There are two ways in which genetic algorithm can be used with the toolbox:

- Calling the genetic algorithm function `ga` at the command line.
- Using the Genetic Algorithm Tool, a graphical interface to the genetic algorithm.

Calling the Function `ga` at the Command Line

To use the genetic algorithm at the command line, call the genetic algorithm function `ga` with the syntax `[x fval] = ga(@fitnessfun, nvars, options)`

where

- `@fitnessfun` is a handle to the fitness function.
- `nvars` is the number of independent variables for the fitness function.
- `options` is a structure containing options for the genetic algorithm. If you do not pass in this argument, `ga` uses its default options.

The results are given by

- `x` — Point at which the final value is attained
- `fval` — Final value of the fitness function

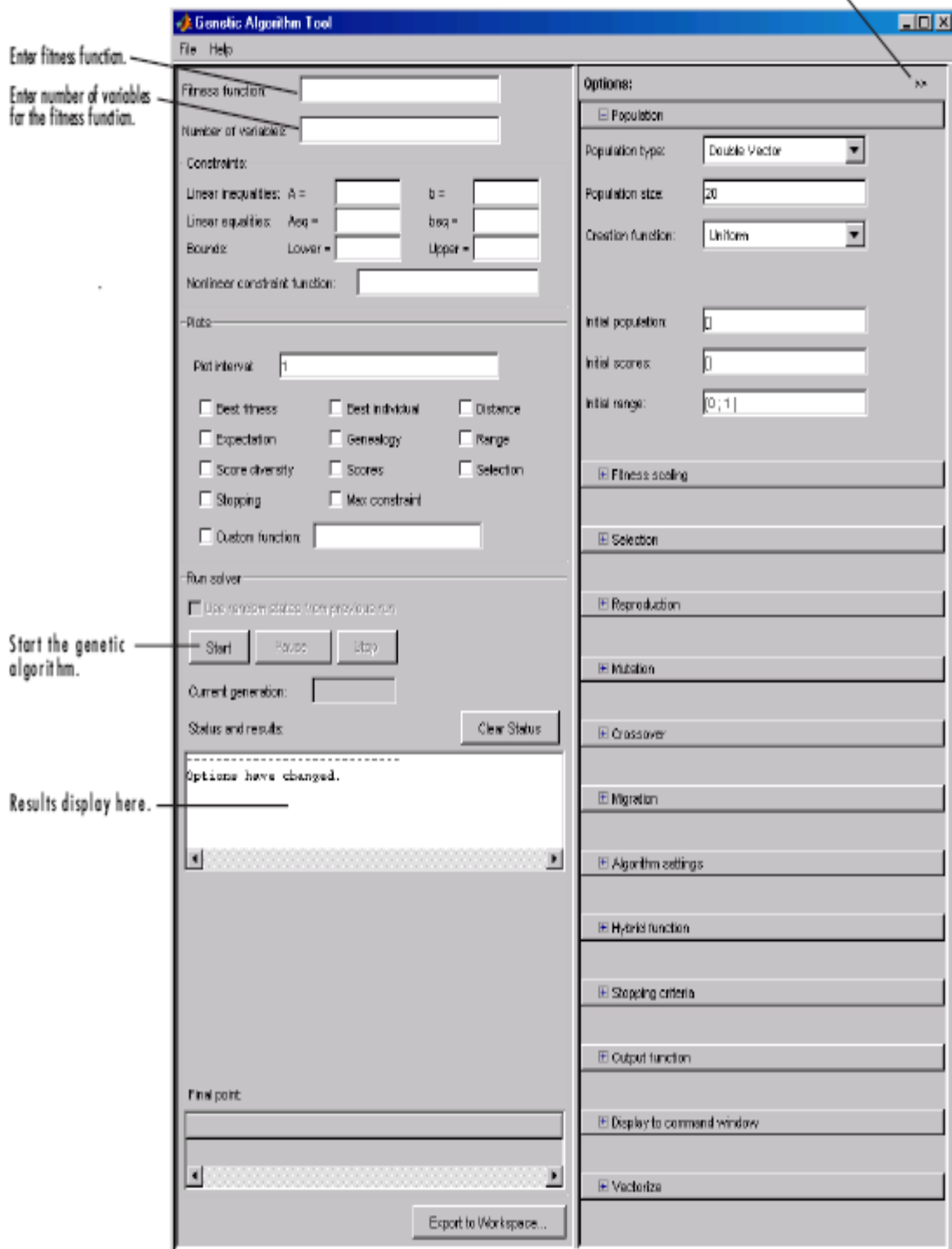
Using the function `ga` is convenient if you want to

- Return results directly to the MATLAB workspace
- Run the genetic algorithm multiple times with different options, by calling `ga` from a M-file.

3.3 Using the Genetic Algorithm Tool

The Genetic Algorithm Tool is a graphical user interface that enables you to use the genetic algorithm without working at the command line. To open the Genetic Algorithm Tool, enter `gatool` at the MATLAB command prompt.

This opens the tool as shown in the following figure.



To use the Genetic Algorithm Tool, the following information must be first entered:

- **Fitness function** — The objective function to be minimized. Enter the fitness function in the form @fitnessfun, where fitnessfun.m is an M-file that computes the fitness function. The @ sign creates a function handle to fitnessfun.

- **Number of variables** — The length of the input vector to the fitness function. You can enter constraints or a nonlinear constraint function for the problem in the **Constraints** pane. If the problem is unconstrained, these fields are left blank. To run the genetic algorithm, click the **Start** button. The tool displays the results of the optimization in the **Status and results** pane. The options for genetic algorithm can be changed in the options pane.

Chapter 4

Theory

Simulation problem

Initialization

Assumptions

4.1 General structure of the simulation problem

For the reactive distillation column specified as above, we propose a simulation model based on the following steps:

- (i) An initial estimate of the molar feed flow rate not specified by the decision vector, viz. a torn (recycle) variable, is specified.
- (ii) An initial estimate of the composition profile in the column is next obtained.
- (iii) This estimate is improved by a relaxation method.
- (iv) The material balance equations are then solved with the Newton}Raphson method, and a new composition profile is computed.
- (v) The torn variable is re-evaluated and the equations describing the reactive distillation process are again solved .
- (vi) The algorithm ends up when the global material balance to the column is verified (after convergence on the torn variable) or when a non-plausible column is obtained.

Table-4.1

Variables calculated and specified - simulation algorithm

Variable	Number	Specified	Calculated
Number of trays		1	1
Compositions			
Liquid	C(N+1)		C(N+1)
Distillate	C		C
Flow Rates			
Liquid	N+1		N+1
Vapor	N+1		N+1
Distillate		1	1
Bottom components	C		1 C-1
Feeds	NNf	NNf-1	1
Column temperatures	N		N
Boil up fraction		1	1
liquid hold up	N	N	
Duties			
Condenser		1	1
Reboiler		1	1
Extent of reactions	NR		NR
vapor-liquid equilibrium constants	NC		NC
Column dimensions			
Height		1	1
Diameter		1	1
Total	$N(Nf+2C+R+4)+3C+9$	$N(Nf+1)+3$	$N(2C+R+3)+3C+6$

4.2.1 Details on initialization

The starting guess of the torn variable should be large enough to accommodate the desired production rate, considering that conversion is not complete. When the simulation starts, this variable is estimated such that the sum of all the feed flow rates of this component is at least 50% larger than the specified production flow rate of ethylene glycol. This value was set by taking into account several items: the stoichiometry of the ethylene glycol production reaction (reaction (R1)), the existence of a secondary reaction that produces diethylene glycol from ethylene glycol (reaction (R2)); and that not all the water fed to the column reacts, some exiting the column with the products. For the subsequent step of the simulation of a reactive or non-reactive distillation column, a starting guess for the composition profile is also necessary.

The initial composition profile is estimated based on the following assumptions:

- (i) The extent of reactions (R1) and (R2) is the same in all trays with liquid holdup, and null in all the other trays.
- (ii) The starting guess for the composition of the liquid phase on the last tray, N, is 95% of component 2 and 5% of component 3.
- (iii) The composition of component 1 on tray N is reevaluated if liquid holdup for reaction exists. This composition value must be correctly estimated because if it is null, then the reaction term is also null giving rise to infeasible columns. The correction of this composition is performed taking into account the extension value for reaction (R1):

$$\xi_{1N} = W_N k_{r1N} x_{1N} x_{2N}$$

Where ,

W_N is the liquid holdup,

K_{r1N} is the reaction constant,

and x_{1N} and x_{2N} are the composition of components 1 and 2, in tray N. The composition values for all components are then normalized such that the stoichiometric equation for tray N is obeyed.

- (iv) For each one of the other trays, with the estimated compositions of the top and

bottom trays, the compositions of components 2-4 are computed using linear interpolation, and the composition of component 1 is set null for all trays. If on tray k there is liquid holdup for reaction, the composition of component 1 is recalculated using the procedure for tray N .

4.2.2 Temperature profile

The temperature on each tray is computed with the corresponding stoichiometric vapor phase (Eq. (A.4)). The solution of this equation is obtained with the Newton Raphson method.

4.2.3 Liquid and vapor molar flow rates

The liquid molar flow rate of the first tray is computed with the reboiler material balance for the species corresponding to the specified product. The vapor flow rate into the first tray V_0 , is the y_{L1} fraction vaporized in the reboiler. Knowing V_0 , the vapor flow rates of all the trays of the column are recursively computed from stage 1 to stage N , using the energy balance over each tray (Eq. (A.5)). The liquid molar flow rates of each tray of the column are recursively computed from stage N to stage 2, using the global material balance over each tray (Eqs. (A.1) and (A.2)).

4.2.4 The Newton Raphson method

The Newton Raphson algorithm is used to compute the composition profile by solving the material balance. The application of this method was based on the algorithm proposed by Bastos (1987), but considering that the chemical reaction may be distributed over several column trays.

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4.3 Assumptions

The simulation model was developed assuming that:

- (a) Vapor and liquid phases are in equilibrium on each tray;
- (b) No reaction occurs in the vapor phase;
- (c) The liquid phase is always homogeneous;
- (d) The enthalpy of liquid streams is negligible;

(e) The heat of vaporization is constant;

(f) The dependence of the reaction rates can be expressed in an Arrhenius form.

Chapter 5

Results and Discussion

The feed distribution in the reactive distillation column is shown in table-2. We have taken water feed rate to be concentrated on the topmost tray, and ethylene oxide to be distributed over the plates 5-10. The assumed value of Liquid hold up was 0.958 and the liquid hold up in each plate is given.

Table-5.1

Column specifications

Tray	Feed		liquid hold up	Molar flow rate	
	Ethylene Oxide	Water		Vapor	Liquid
1	0	0	0	172.3	179.2
2	0	0	0	172.3	179.2
3	0	0	0	172.3	179.2
4	0	0	0	172.3	179.2
5	1.36	0	0.55	174.7	179.2
6	1.32	0	0.48	176.9	181.6
7	1.3	0	0.45	179.2	184.3
8	1.38	0	0.37	181.5	186.8
9	0.56	0	1.47	183.9	189.1
10	2.24	7.31	0.01	186.1	192.5

$\beta = 0.958$, Column diameter = 1.27 m , Column height = 11.72 m, $Q_B = 6.6$ MW, $Q_C = 7.7$ MW

The molar flow rate of vapor and liquid at each tray was tabulated, and composition profiles (fig 9) of ethylene glycol and water was plotted against trays. The plot of temperature profile was shown in fig 8. The plots obtained are similar to the plots obtained by Ciric and Gu.

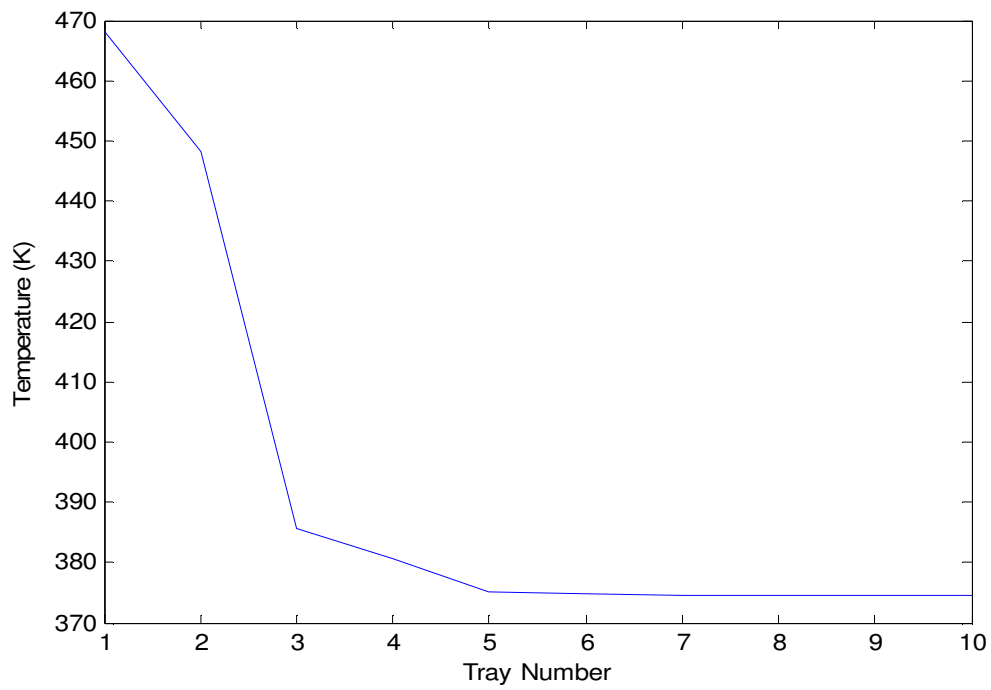


Fig. 5.1. Temperature profile

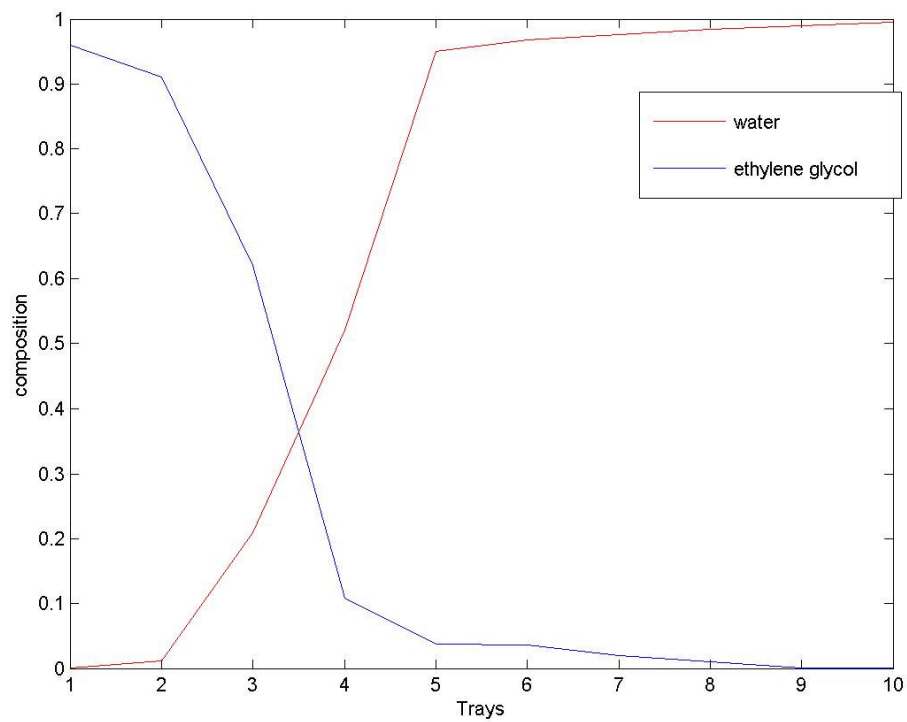


Fig 5.2: Composition Profile

The optimization of cost function was solved by *genetic algorithm* , the algorithm written in matlab is given below. The default options were used with lower bound for column diameter to be 1 m.

```

F11=0.00;
F12=0.00;
F13=0.00;
F14=0.00;
F15=1.36;
F16=1.32;
F17=1.30;
F18=1.38;
F19=0.56;
F110=2.24;
F21=0.00;
F22=0.00;
F23=0.00;
F24=0.00;
F25=0.00;
F26=0.00;
F27=0.00;
F28=0.00;
F29=0.00;
F210=7.31;
C0=10000;
CC=24.5E-3;
CR=146.8E-3;
CT=15.7;
CS=222;
C1=21.9E-3;
C2=43.7E-3;
H0=3;
QB=6.6E6;
QC=7.7E6;
X= [0.00 0.00 0.00 0.00 0.55 0.48 0.45 0.37 1.47 0.01]

```

```

F=F11+F12+F13+F14+F15+F16+F17+F18+F19+F110+F21+F22+F23+F24+F25+F26+F27...
+F28+F29+F210;

```

```

W1=0.61+(1.27*sum(x)/D^2);

```

```

Y =
C0+((C1+C2)*F)+CR*QB+CC*QC+(CT*(D)^1.55)*W1+((CS*D)*(H0+((W1)^0.802)));

```

The plot of fitness function with the number of iterations were generated showing the best fitness and mean fitness.

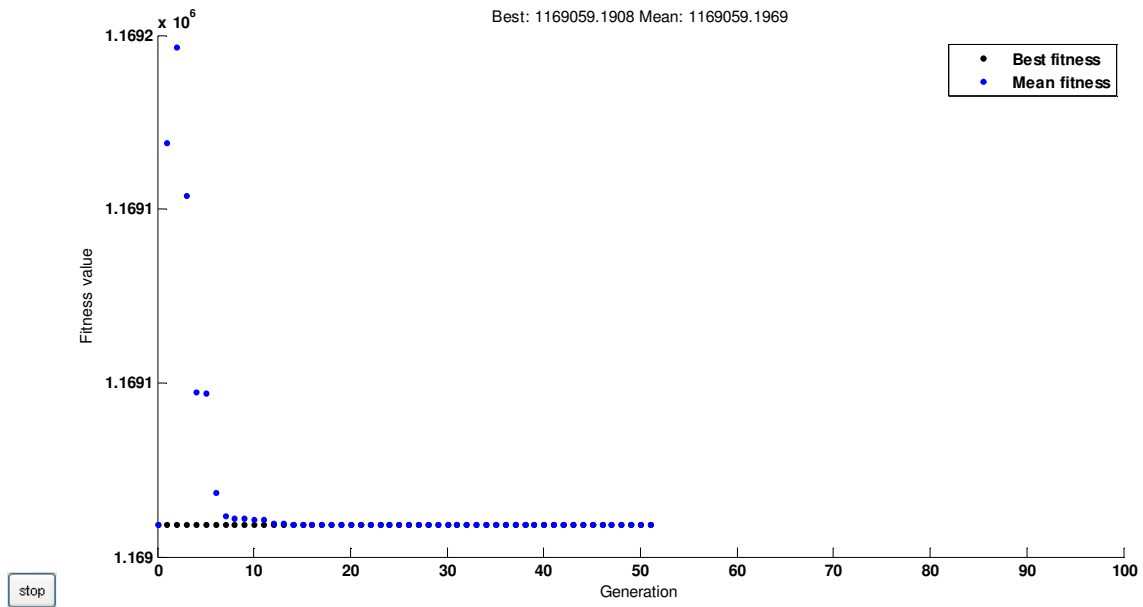


Fig 5.3: Fitness function versus number of iterations.

The optimum cost obtained is Rs 1,169,059.19 US\$ per year at column diameter = 1.27 m and column height = 11.72 m.

Chapter 6

Conclusion

Conclusion

Ciric and Gu (1994) proposed an interesting technique for the synthesis of reactive distillation columns, which can be applied to generic situations where there is more than one chemical reaction, or when reaction equilibrium or constant molar flows cannot be assumed. With this column model they have built an MINLP problem. The solution of this problem yields the optimum number of trays, the optimal feed tray locations and the composition profiles. In this work, we propose a new simulation /optimization model for the formulation of reactive distillation columns as per Ciric and Gu (1994), where the simulation algorithm is based on conventional distillation (Bastos, 1987) and the optimization is performed by genetic algorithm. The simulation starts with an initial estimate of one molar feed flow rate not specified by the decision vector, viz. a torn variable. An estimate of the initial composition profile in the column is next obtained, which is further improved by a relaxation method. The material balance equations are then solved with the Newton Raphson method, and a new composition profile is computed. The torn variable is re-evaluated and the equations describing the reactive distillation process are again solved. The algorithm ends up when the global material balance to the column is obeyed, after convergence on the torn variable, or when a non-plausible column is obtained. The results show that the proposed simulation /optimization algorithms are capable of providing solutions which are very close to the global optimum, and thus constitute viable methods for the design of reactive distillation columns.

APPENDIX (A)

Table – 3
Reaction Data

Reaction	Rate (mol m ⁻³ s ⁻¹)	ΔH (J mol ⁻¹)
(R1)	$3.15 \times 10^{15} \exp(-9547/T)x_1 x_2$	-80.0×10^3
(R2)	$6.3 \times 10^{15} \exp(-9547/T)x_1 x_3$	-13.1×10^3

Table – 4
Vapor liquid equilibrium constant , K, at 1 atm

Component	K (dimensionless)
Ethylene oxide	$71.9 \exp\{5.720[(T - 469)/(T - 35.9)]\}$
Water	$221.2 \exp\{6.310[(T - 647)/(T - 52.9)]\}$
Ethylene glycol	$77.0 \exp\{9.940[(T - 645)/(T - 71.4)]\}$
Diethylene glycol	$47.0 \exp\{10.42[(T - 681)/(T - 80.6)]\}$

Table – 5
Cost data

Ethylene oxide cost	43.7×10^{-3} US\$ mol ⁻¹
Water cost	21.9×10^{-3} US\$ mol ⁻¹
c_{SH}	222 US\$ yr ⁻¹
c_T	15.7 US\$ yr ⁻¹
c_R	146.8×10^{-3} US\$ W ⁻¹ yr ⁻¹
c_C	24.5×10^{-3} US\$ W ⁻¹ yr ⁻¹
c_O	10,000 US\$ yr ⁻¹

Material, energy and stoichiometric balances

Material balance over the bottom tray:

$$F_{i1} - L_1 x_{i1}(1 - \beta) + L_2 x_{i2} - V_1 K_{i1} x_{i1} + \sum v_{ij} \xi_{j1} = 0 \quad i = 1, \dots, C. \quad (A.1)$$

Material balance over tray k:

$$F_{ik} + V_{k-1}K_{ik-1}X_{ik-1} + L_{k+1}X_{ik+1} - L_kX_{ik} - V_kK_{ik}X_{ik} + \sum v_{ij}\xi_{jk} = 0, k = 2, \dots, N, i = 1, \dots, C \quad (A.2)$$

Stoichiometric equations:

$$\sum x_{ik} - 1 = 0, k = 1, \dots, N, \quad (A.3)$$

$$\sum K_{ik}X_{ik} - 1 = 0, k = 1, \dots, N. \quad (A.4)$$

Energy Balance over Tray k:

$$\lambda V_{k-1} - \lambda V_k - \sum \Delta H_j \xi_{jk} = 0, k = 1, \dots, N. \quad (A.5)$$

Material balance over the reboiler:

$$B_i = (1 - \beta)L_1x_{i1}, \quad i = 1, \dots, C.$$

Overall balance of component i:

$$xd_i D_{ist} + B_i = P_i, \quad i = 1, \dots, C.$$

where,

N_c is the number of components,

F_{ik} is the molar flow rate of component i fed to tray k,

Q_B is the reboiler duty,

Q_C is the condenser duty,

D is the diameter of the column,

W_K is the liquid holdup of tray k,

H_0 is the extra column height,

H_{min} is the minimum space between trays,

L_k and V_k are the liquid and vapor flow rates for tray k, respectively,

X_{ik} is the molar fraction of component i in the liquid phase for tray k,

K_{ik} is the vapor-liquid equilibrium constant of component i for tray k,

v_{ij} is the stoichiometric coefficient of component i in reaction j,

ξ_{jk} the extent of the reaction j on tray k,

K_{jk} is the kinetic constant of reaction j on tray k,

T_k is the temperature of tray k,

H_j is the enthalpy of reaction j, is the heat of vaporization,

B_i is the bottom flow rate of component i,

P_i is the production rate of component I, is fraction of L1 vaporized in the reboiler,

x_{di} is the molar fraction of the component i in the distillate,

D_{ist} is the distillate molar flow and

F_{max} is the maximum molar flow rate.

The optimization problem is defined as:

$$FOB_j = \min \{ \sum c_i \sum F_{ik} + c_H Q_B + c_W Q_C + A_F (C_{cs} + C_{ci} + C_r + C_c) \}. \quad (A.6)$$

Here,

c_i is the cost of raw material i,

F_{ik} is the feed rate of material i to tray k,

c_H is the cost of steam,

c_W is the cost of cooling water, and

Q_B and Q_C correspond to reboiler and condenser duties.

A_F is an annualizing factor;

C_{cs} , C_{ci} , C_r and C_c are the installed costs of the column shell, trays, reboiler, and condenser. The column investment costs is calculated by (Douglas, 1988)

$$C_{cs} = 0.3639(M\&S)D^{1.066}H^{0.802}(2.18 + F_c), \quad (A.7)$$

$$C_{ci} = \sum 0.0168(M\&S)D^{1.55}H_k F_c^1. \quad (A.8)$$

Here, M&S is the Marshall and Swift Index published Periodically by the Chemical Engineering Journal,

D is the column diameter,

H is the height of the column,

F_c and F_c^1 are construction factors and H_k is the height of tray k.

Eq. (B.2) is simplified by assuming $D^{1.066} = D$ (Ciric & Gu, 1994). The reboiler and condenser investment costs are evaluated by

$$C_r = cr_1 + cr_2 Q_B. \quad (A.9)$$

$$C_c = cc_1 + cc_2 Q_c. \quad (A.10)$$

The height of tower is evaluated by

$$H = H_0 + \sum H_k, \quad (A.11)$$

Where

H_0 is a fixed extra column height corresponding to the free space below the bottom tray

and above the top tray. The heights H_k are evaluated by adding the minimum tray

spacing, H_{\min} to the height of liquid in tray k , corresponding to volume W_K :

$$H_k = H_{\min} + 1.27W_k/D^2. \quad (A.12)$$

Ciric and Gu (1994) set H_0 and H_{\min} respectively to 3.0 and 0.61 m. Substitution of these

expressions into Eq.(B.1), after some algebraic simplification, provides

$$FOB_j = \min\{c_o + \sum c_i \sum F_{ik} + c_f Q_B + c_c Q_c + c_T D^{1.55} * \sum(0.61 + 1.27W_k/D^2) + c_{SH} D (H_0 + \sum(0.61 + 1.27W_k/D^2))^{.802}\} \quad (A.13)$$

where c_o , c_c , c_i , c_T and c_{SH} correspond to cost parameters.

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