# SYNTHESIS OF OPTIMAL DISTILLATION SEQUENCES FOR THE SEPARATION OF ZEOTROPIC MIXTURES USING TRAY-BY-TRAY MODELS

Hector Yeomans and Ignacio E. Grossmann
Carnegie Mellon University
Pittsburgh, PA 15213

*Abstract*

This paper describes a Generalized Disjunctive Programming (GDP) model for the synthesis of distillation sequences using rigorous design equations. The model is obtained systematically from the State Equipment Network (SEN ) representation of superstructures, and results from the separation of three component mixtures illustrate its robustness and computational efficiency.

*Keywords*

Distillation sequences, tray-by-tray models, superstructure, MINLP, disjunctive program

## Introduction

The optimal synthesis of distillation continues to be a central problem in the design of chemical processes, due to the high investment and operating costs involved in these systems. The recent trends in this area have been to address models of increasing complexity through the use of mathematical programming. Examples of these models include the short-cut models by Novak et al. (1996) and Yeomans and Grossmann (1998b), and the rigorous tray-by-tray models by Bauer and Stichlmair (1998) and Smith and Pantelides (1995). The high degree of nonlinearity and the difficulty of solving the corresponding MINLP optimization models, however, have prevented these methods from becoming tools that can be readily used by industry. For instance, a common problem that is experienced with rigorous models is when the columns are "deleted", as then the equations describing the MESH equations become singular.

This goal of this paper is to present a Generalized Disjunctive Programming (GDP) model for the synthesis of rigorous distillation sequences, that can avoid the existing pitfalls of MINLP optimization models. The case of separation of zeotropic mixtures is addressed, and its potential use for azeotropic distillation will be discussed.

## Problem Definition

The objective of this paper is to generate an optimization model for the design of optimal distillation systems. Given is a feed stream with known composition required to be separated into essentially pure component product streams. The model has the following characteristics: (1) it is based on rigorous calculations, (2) ideal or non-ideal VLE equilibrium equations, (3) covers only simple column configurations.

## Synthesis Framework

The tray-by-tray optimization model was systematically derived by the application of the synthesis framework proposed by Yeomans and Grossmann (1998a). The framework consists of three steps: (1) Generation of a superstructure of all possible flowsheet alternatives based on the State Task Network (STN) or State Equipment Network (SEN) representations. (2) Modeling of the superstructure using Generalized Disjunctive Programming (GDP; Raman and Grossmann, 1994; Turkay and Grossmann, 1996). (3) Solve the GDP model with a modification of the Logic-Based Outer Approximation Algorithm (Turkay and Grossmann, 1996).

The first step of the synthesis framework requires the identification of three key elements of any synthesis problem: states, tasks and equipment. These elements are assembled in a flowsheet, and linked to one another depending on the choice of representation (SEN or STN). Each of these representations can be translated into a unique mathematical programming model in GDP form, which is then solved with special purpose algorithms. To tackle the problem of interest, the SEN superstructure representation was used.

## Superstructure Representation

Consider the separation of a three component mixture, where A,B and C represent the components ordered by decreasing relative volatility. There are four tasks that can be identified for this case: the separation of A from BC, of AB from C, of A from B and the separation of B from C. The minimum number of equipment units required to perform these separations is two, given that sharp splits are required and only one separation path is selected.

Considering a superstructure with the minimum number of equipment units, Figure 1 shows the SEN representation for the problem. Mixers and splitters are permanent equipment with permanent tasks, while the distillation columns represent permanent equipment with conditional tasks.

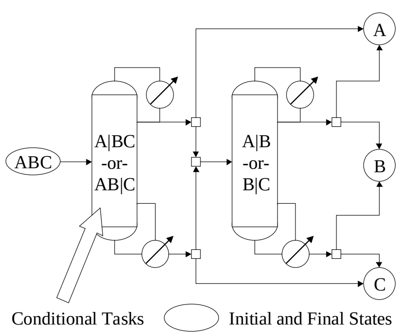



*Figure 1. Sample SEN Superstructure*

At this point the superstructure in Figure 1 is valid for aggregated, short-cut or rigorous models. If rigorous models are used, another discrete decision to make is the selection of the number trays in the column. This decision is not explicitly linked to the choice of a task, so it is possible to model a single column as a superstructure of smaller equipment units –the trays– that can be represented also as a SEN. For this case a tray can perform one of two tasks: VLE Mass exchange or no mass exchange as seen in Figure 2.

Because only simple column design is used, the feed tray, reboiler and condenser tray are considered equipment with one permanent task, but they can become conditional if complex columns configurations are included.

## GDP Model for SEN Representation

The second stage of the synthesis framework requires the modeling of the superstructure representation as a Generalized Disjunctive Programming (GDP) problem. In this model, each discrete choice of a task or equipment is represented as a disjunction. The equations and constraints that apply whenever the equipment or task exists, are grouped with brackets in each disjunction. The equations and constraints that apply when a task or equipment does not take place are also grouped in brackets in the same disjunction. The *OR* logic operator ($\vee$) denotes the discrete choice between equations, and a set of boolean variables ($Y$) indicates a choice and propagate its effect to the rest of the problem by means of Logic Relationships ($\Omega(Y)=True$).

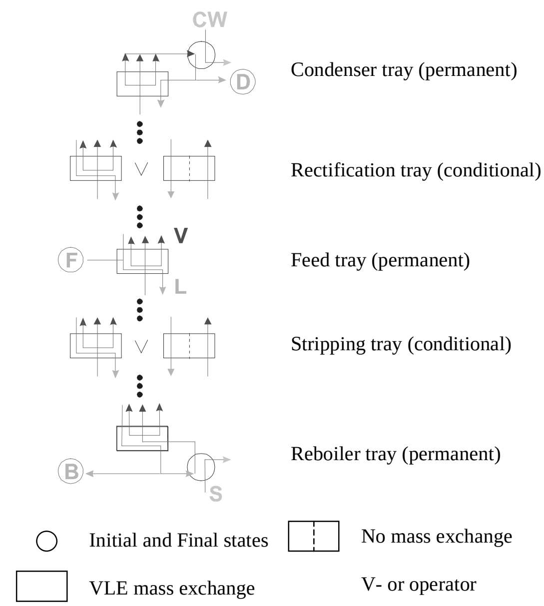



*Figure 2. Superstructure for rigorous column*

The following model is based on the superstructure shown in Figure 1, but it can easily be extended to superstructures with more columns and tasks. The variable definition for the model can be found at the end of this paper, and the following set definitions were used: C is the set of i components to be separated; COL is the set of available columns j; TS is the set of available trays n; TM is the set of conditional trays (TM$\subseteq$TS); NRT, NCT and NFT are the reboiler, condenser and feed trays, respectively. These are the permanent trays.

$$\min \sum_{j\in COL} \left\{ f(NT_j, Dc_j) + \alpha QR_j + \beta QC_j \right\} \qquad (1)$$

$$\text{s.t.} \quad F_2^i = D_1^i + B_1^i$$

$$NT_j = \sum_{n\in TM} STG_n + 3 \qquad (2)$$

$$DC_j = f(T_j^V, P_{n,j}, R_j, VAP_{n,j}) \quad n \in NCT$$

$$\left.\begin{array}{l} F_j^i + L_{n+1,j}^i + V_{n-1,j}^i - L_{n,j}^i - V_{n,j}^i = 0 \\ \sum_{i\in C}\begin{pmatrix} hF_j^i + hL_{n+1,j}^i + hV_{n-1,j}^i \\ - hL_{n,j}^i - hV_{n,j}^i \end{pmatrix} = 0 \\ F_j^i = FED_j x_{F,j}^i \\ hF_j^i = f(T^L{}_{n,j}) \end{array}\right\} n \in NFT \quad (3)$$

$$\left.\begin{array}{l} V_{n-1,j}^i - L_{n,j}^i - D_j^i = 0 \\ \sum_{i\in C}\left(hV_{n-1,j}^i - hL_{n,j}^i - hD_j^i\right) = QC_j \\ D_j^i = DIS_j x_{n,j}^i \\ D_j^i = R_j L_{n,j}^i \\ hD_j^i = f(T^L{}_{n,j}) \end{array}\right\} n \in NCT \quad (4)$$

$$\left.\begin{array}{l} L_{n+1,j}^i - B_j^i - V_{n,j}^i - = 0 \\ \sum_{i\in C}\left(hL_{n+1,j}^i - hV_{n,j}^i - hB_j^i\right) = QR_j \\ B_j^i = BOT_j x_{n,j}^i \\ hB_j^i = f(T^L{}_{n,j}) \end{array}\right\} n \in NRT \quad (5)$$

$$\left.\begin{array}{l} L_{n,j}^i = LIQ_j x_{n,j}^i \\ V_{n,j}^i = VAP_j y_{n,j}^i \\ \sum_{i\in C} x_{n,j}^i = 1 \\ \sum_{i\in C} y_{n,j}^i = 1 \\ f_i^L = f_i^V \\ hL_{n,j}^i = f(T_{n,j}^L) \\ hV_{n,j}^i = f(T_{n,j}^V) \end{array}\right\} n \in TS \quad (6)$$

$$\left.\begin{array}{l} L_{n+1,j}^i + V_{n-1,j}^i - L_{n,j}^i - V_{n,j}^i = 0 \\ \sum_{i\in C}\left(hL_{n+1,j}^i + hV_{n-1,j}^i - hL_{n,j}^i - hV_{n,j}^i\right) = 0 \end{array}\right\} n \in TM \quad (7)$$

$$\begin{bmatrix} \boldsymbol{Y_{n,j}} \\ f_i^L = f(T_{n,j}^L, P_{n,j}, x_{n,j}) \\ f_i^V = f(T_{n,j}^V, P_{n,j}, y_{n,j}) \\ T_{n,j}^L = T_{n,j}^V \\ STG_n = 1 \end{bmatrix} \vee \begin{bmatrix} \neg \boldsymbol{Y_{n,j}} \\ x_{n,j}^i = x_{n+1,j}^i \\ y_{n,j}^i = y_{n+1,j}^i \\ T_{n,j}^L = T_{n+1,j}^L \\ T_{n,j}^V = T_{n-1,j}^V \\ f_i^L = 0 \\ f_i^V = 0 \end{bmatrix} \quad n \in TM \quad (8)$$

$$\begin{array}{l} \begin{bmatrix} \boldsymbol{Y^1_{A|BC}} \\ x_{n,1}^A \ge \zeta \\ D_1^A \ge \mu F_1^A \end{bmatrix} \vee \begin{bmatrix} \boldsymbol{Y^1_{AB|C}} \\ x_{n,1}^B \ge \zeta \\ D_1^B \ge \mu F_1^B \end{bmatrix} \quad n \in NCT \\ \begin{bmatrix} \boldsymbol{Y^2_{A|B}} \\ x_{n,1}^A \ge \zeta \\ D_1^A \ge \mu F_1^A \end{bmatrix} \vee \begin{bmatrix} \boldsymbol{Y^2_{B|C}} \\ x_{n,1}^B \ge \zeta \\ D_1^B \ge \mu F_1^B \end{bmatrix} \quad n \in NCT \end{array} \quad (9)$$

$$\begin{array}{ll} Y_{A|BC}^1 \Leftrightarrow Y_{B|C}^2, & Y_{AB|C}^1 \Leftrightarrow Y_{A|B}^2 \\ Y_{n,j} \Rightarrow Y_{n-1,j}, & Y_{n-1,j} \Rightarrow Y_{n,j} \end{array} \quad (10)$$

$$\begin{array}{l} F, FED, D, DIS, B, BOT, L, LIQ, V, VAP \in R^+ \\ R, T, P, NT, QR, QC, x, y, f, STG \in R^+ \\ hD, hB, hF, hL, hV \in R \\ Y = \{True, False\} \end{array}$$

Equation (1) is the objective function, a nonlinear cost function in terms of the number of trays, column diameter and duties of reboiler and condenser. (2) defines the overall column interconnection, as well as the costing variables. Equations (3), (4) and (5) are the mass and energy balances for the permanent trays (feed, condenser and reboiler, respectively). The block in (6) represents all the equations that are valid for both permanent and conditional trays. (7) are the mass and energy balances for the conditional trays. The disjunction in (8) indicates the discrete choice for conditional trays: whenever VLE takes place, fugacities are defined and liquid and vapor temperatures are equal; if the choice is not VLE, then compositions and temperatures in the tray will depend on adjacent trays, while the fugacities of liquid and vapor are set to zero. The disjunctions in (9) enforce the discrete choice of task selection for each column, based on purity and recovery specifications for the key component recovered at the top of each column. Finally, (10) includes the logic relationships that hold in the superstructure.

## Numerical Examples

The model described above was solved with a modified Logic-Based Outer Approximation algorithm (Yeomans and Grossmann, 1998b). The algorithm was implemented with the GAMS modeling environment (Brooke et al., 1992), on a HP 9000 C-110 workstation.

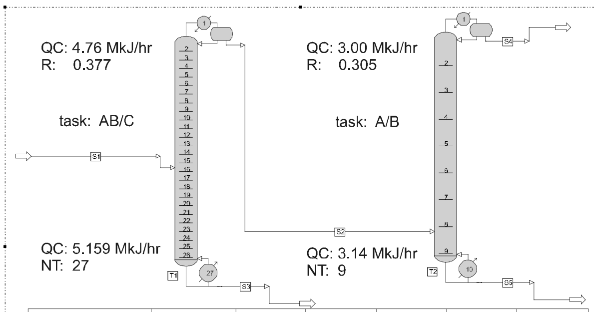
| Parameter | Value |
|---|---|
| Continuous Variables | 1962 |
| Discrete Variables | 56 |
| Constraints (NLP) | 2037 |
| Max Trays per column | 30 |
| Objective Value | M$ 2.694 |
| CPU Time | 42 min. 21 sec. |
| OA Iterations | 3 |

*Table 1. Results for the separation of C3,C4 ,C5.*

Two numerical examples were used to test the model. The first one requires the separation of a mixture of butane (C4), pentane (C5) and hexane (C6) into pure components. The second example is for the separation of a mixture of benzene, toluene and o-xylene into pure components. Both systems were modeled with ideal equilibrium, and reasonable bounds on the number of trays required for the separation. The objective function is the present cost of the equipment and utility costs.

Figure 3 shows the optimal configuration obtained, and Table 1 shows relevant computational information. The results from the model were confirmed with the commercial simulator PROII, with very good agreement.

It is worth noting that the optimal solution removes the most abundant component last, violating a well-known heuristic. 80% of the CPU time was for the master problem since it has more than 10,000 variables and more than 6,000 constraints. Because of the nature of disjunctive programs, the size of the NLP subproblems was considerably reduced, compared to MINLP models.




| Stream Name<br>Stream Description | | S1 | S2 | S3 | S4 | S5 |
|---|---|---|---|---|---|---|
| Phase | | Liquid | Liquid | Liquid | Liquid | Liquid |
| Temperature | K | 323.770 | 315.085 | 379.338 | 306.680 | 347.192 |
| Pressure | KPA | 307.015 | 307.015 | 307.015 | 307.015 | 307.015 |
| Flowrate | KG-MOL/HR | 200.000 | 149.790 | 50.210 | 103.799 | 45.991 |
| Composition | | | | | | |
| BUTANE | | 0.500 | 0.668 | 0.000 | 0.963 | 0.002 |
| PENTANE | | 0.250 | 0.317 | 0.050 | 0.037 | 0.948 |
| HEXANE | | 0.250 | 0.015 | 0.950 | 0.000 | 0.050 |

*Figure 3. Optimal Design for separation of ABC*

In the second example for the separation of benzene, toluene and o-xylene, the optimal solution separates the most abundant component first, the o-xylene, in a 36-tray column. The mixture of benzene and toluene is then separated in a 26-tray column. The optimal net present cost is M$1.30, and the solution was obtained in 5 OA iterations, with a total CPU time of 2.3 hrs. This high CPU time is due to the bound in the number of trays per column, which was set up to 50.

## Conclusions

A mathematical programming model for the design of distillation sequences with tray-by-tray models was presented. The model was derived systematically, according to the synthesis framework proposed by Yeomans and Grossmann (1998). Two examples that have been tested suggest that the proposed method is robust and efficient for modeling the separation of ideal and zeotropic mixtures. It is important to remark that even though this model has not been tested for the separation of azeotropic mixtures, it can potentially solve these problems, provided an appropriate superstructure is developed. The main significance of this work is that the numerical difficulties of MINLP models produced by disappearing column sections and flows can be overcome.

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## Notation

$B^i_j$ = Bottoms flow of species i in column j, kmol/hr
$BOT_j$ = Total bottoms flow in column j
$DC_j$ = Column diameter, ft.
$D^i_j$ = Distillate flow of species i in column j
$DIS_j$ = Total distillate flow in column j
$f_i$ = Fugacity of liquid or vapor of species i
$F^i_j$ = Feed flow of species i into column j
$FED_j$ = Total feed flow into column j
$hB^i_j$ = Liquid enthalpy of i in the bottoms, kJ/kmol
$hD^i_j$ = Liquid enthalpy of species i in the distillate
$hF^i_j$ = Liquid enthalpy of species i in feed of column j
$hL^i_{n,j}$ = Liquid enthalpy of species i in liquid stream
$hV^i_{n,j}$ = Vapor enthalpy of species i in vapor stream
$L^i_{n,j}$ = Liquid flow of species i out of tray n, in column j
$LIQ_{n,j}$ = Total liquid flow out of tray n in column j
$NT_j$ = Number of trays in column j
$QC_j$ = Condenser heat load of column j, kJ/hr
$QR_j$ = Reboiler heat load of column j
$R_j$ = Reflux ratio for column j
$STG_{n,j}$ = Binary variable indicating a stage uses VLE
$T_{n,j}$ = Temperature of liquid or vapor in tray n,K
$P$ = Pressure (stage or column), bar
$x^i_{n,j}$ = Mole fraction of species i in the liquid phase
$y^i_{n,j}$ = Mole fraction of species i in the vapor phase
$\mu$ = Recovery fraction with respect to feed
$\varsigma$ = Purity specification (fraction)
$\alpha,\beta$ = Utility cost coefficients