# Development of Thermodynamic Properties Package Libraries for Using in GAMS through Extrinsic Functions

*Juan I. Manassaldi [a], Miguel C. Mussati [a,b], Nicolás J. Scenna [a], Sergio F. Mussati [a,b]*

[a] CAIMI Centro de Aplicaciones Informáticas y Modelado en Ingeniería (UTN-FRRo), Zeballos 1341, S2000BQA, Rosario, Argentina
jmanassaldi@frro.utn.edu.ar, nscenna@santafe-conicet.gov.ar
[b] INGAR Instituto de Desarrollo y Diseño (CONICET-UTN), Avellaneda 3657, S3002GJC, Santa Fe, Argentina
mmussati@santafe-conicet.gov.ar, mussati@santafe-conicet.gov.ar

## Abstract

This article shows the development of optimization models using extrinsic functions for GAMS. Precisely, different dynamic link libraries have been implemented for the calculation of thermodynamic properties in GAMS environment. A simple case study taken from Perry's Chemical Engineers' Handbook, Sec. 13 Pg. 34 corresponding to the Example 3 is used to illustrate the model implementation and to discuss the obtained results. It consists of a multicomponent distillation column butane-pentane splitter.

The obtained results showed that the usage of the proposed extrinsic functions allow to significantly reduce the model size (number of variables and constraints) as well as CPU times required by the optimization algorithms.

## 1. Mathematical model

The simplest design problem of a tray distillation column considers that the number of trays is fixed, and the goal is to select the optimal feed location. Figure 1 shows a simple "superstructure" proposed by Sargent and Gaminibandara (1976) in order to consider the feed location as an optimization variable. As shown in Fig. 1, the feed *LF* is split in several streams which are connected with the candidate trays. In the most general case, the number of splits is the same to the number of trays, excluding the condenser and reboiler (Grossmann et al., 2005).

The steady-state mathematical model is based on mass and energy balances around each one of the stage. Precisely, the resulting model involves the following constraints:
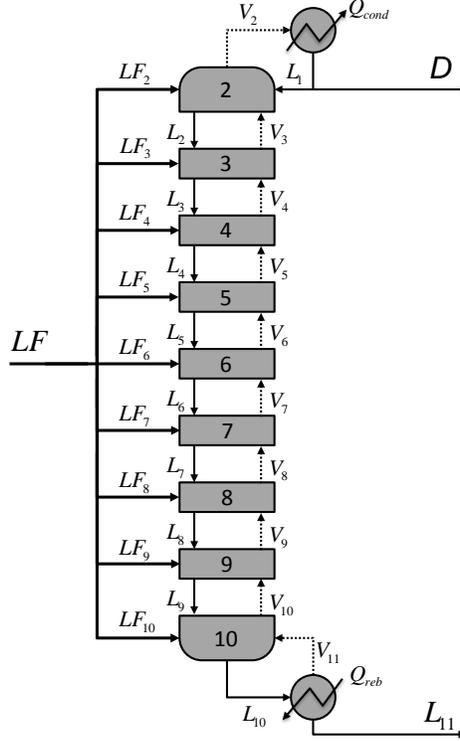
**Figure 1**. Schematic of the Distillation Column Superstructure.

## 1.1. Mass and energy balance in the Condenser

Eq. (1) corresponds to the components mass balance in the condenser (stage 1). *L*, *V* and *D* represent, respectively, the molar flow rate of liquid, vapor and distillate. *x* and *y* refer to the molar fractions in the liquid and vapor phases, respectively. The subindex *s* represents the stages of the column (*s* = 1 to 11) and the subindex *i* refers to the components.

$$V_{s+1}y_{s+1,i} = \left(L_s + D\right)x_{s,i} \quad \forall i; \forall s / s = 1 \tag{1}$$

The energy balance is given in Eq. (2). *Q*$_{cond}$ refers to the heat duty in the condenser and *Hl* and *Hv* represent the values of enthalpies in the liquid and vapor phases, respectively.

$$V_{s+1}Hv_{s+1} = Q_{cond} + \left(L_s + D\right)Hl_s \quad \forall s / s = 1 \tag{2}$$

## 1.2. Mass and energy balance in the Reboiler

Equations (3) and (4) express the mass and energy balances in the reboiler (stage 11). *Q*$_{reb}$ refers to the heat duty required by the reboiler.

$$L_{s-1}x_{s-1,i} = V_s y_{s,i} + L_s x_{s,i} \quad \forall i; \forall s / s = 11 \tag{3}$$

$$L_{s-1}Hl_{s-1} + Q_{reb} = V_s Hv_s + L_s Hl_s \quad \forall s / s = 11 \tag{4}$$

## 1.3. Mass and energy balance in the intermediated trays

In each intermediate stage, the possibility of the input of the feeding stream ($LF_s$) is considered. Thus, the corresponding mass and energy balances of the intermediate stages are expressed by Eqs. (5) and (6).

$$LF_s xf_i + L_{s-1} x_{s-1,i} + V_{s+1} y_{s+1,i} = V_s y_{s,i} + L_s x_{s,i} \quad \forall i; \qquad \forall s / 2 \leq s \leq 10 \tag{5}$$

$$LF_s Hlf + L_{s-1} Hl_{s-1} + V_{s+1} Hv_{s+1} = V_s Hv_s + L_s Hl_s \qquad \forall s / 2 \leq s \leq 10 \tag{6}$$

$xf_i$ and $Hlf$ are model parameters and they refer, respectively, to the molar fraction of the compound $i$ in the feed and the enthalpy of the feed stream.

The mass balance in the splitter is given by Eq. (7).

$$LF = \sum_{\forall s / 2 \leq s \leq 10} LF_s \tag{7}$$

Here, it is important to mention, that no integer variables are involved to select the feed tray. It is appropriate to mention this because integer variables (binary variables) are usually included to model discrete decisions related with the selection of the optimal number of trays and/or tray feed, among others, leading to MINLP models which are more difficult to solve than NLP models. Thus, for the sake of simplicity, a NLP model instead of a MINLP is here considered.

To complete all the mass balances, the sum of molar fractions in each one of the phases (liquid and vapor) must be equal to one, which are imposed by Eqs. (8) and (9):

$$\sum_i x_{s,i} = 1 \quad \forall s \tag{8}$$

$$\sum_i y_{s,i} = 1 \quad \forall s \tag{9}$$

## 1.4. Liquid-Vapor Equilibrium

In each stage ($s$), the liquid and vapor phases are in equilibrium. Therefore, the fugacity of component $i$ in the liquid phase $l$ ($fugl_{s,i}$) must be equal to the fugacity of the same component in the vapor phase $v$ ($fugv_{s,i}$) which is imposed as follows.

$$fugl_{s,i} = fugv_{s,i} \quad \forall s; \forall i \tag{10}$$

## 1.5. Physicochemical properties of the mixture

The physicochemical properties involved in mass and energy balances and equilibrium equations are calculated in Eqs. (11-14). All functions indicated in the right hand sides of Eqs. (11-14) correspond to extrinsic functions and depend on the selected library (*raultlaw.dll* or *pengrobinson.dll*, as will be described later).

$$fugl_{s,i} = f_i^l \left( T_s, P_s, x_{s,C3}, x_{s,iC4}, x_{s,nC4}, x_{s,iC5}, x_{s,nC5} \right) \quad \forall s ; \forall i \tag{11}$$

$$fugv_{s,i} = f_i^v \left( T_s, P_s, y_{s,C3}, y_{s,iC4}, y_{s,nC4}, y_{s,iC5}, y_{s,nC5} \right) \quad \forall s \; ; \; \forall i \tag{12}$$

$$Hl_s = h_i^l \left( T_s, P_s, x_{s,C3}, x_{s,iC4}, x_{s,nC4}, x_{s,iC5}, x_{s,nC5} \right) \quad \forall s \tag{13}$$

$$Hv_s = h_i^v \left( T_s, P_s, y_{s,C3}, y_{s,iC4}, y_{s,nC4}, y_{s,iC5}, y_{s,nC5} \right) \quad \forall s \tag{14}$$

## 1.6. Objective function

Finally, a simple objective function taken from Caballero and Grossmann (2010) is used as objective function. As it can be seen in Eq. (15), it depends in the heat loads in the condenser and the reboiler.

$$z = 0.2 \, Q_{cond} + Q_{reb} \tag{15}$$

## 2. Model implementation aspect

Different dynamic link libraries have been developed to estimate physicochemical properties according to different packages.

Some features of the libraries:

- Contain a database of 430 pure compounds.
- In a txt file, the IDs of the intervening compounds and their interaction parameters (if necessary) should be defined.
- The input arguments of the function vary with the number of compounds involved.
- They support up to 18 compounds. Temperature + Pressure + 18 compounds = 20 argument (maximum arguments of extrinsic function for GAMS).
- All the functions have as input arguments the Temperature, Pressure and molar fraction of each component of the mixture. For example, for a binary mixture, the functions will have 4 input arguments.
- All the extrinsic functions have an analytic implementation of their gradient vector and Hessian matrix.
- Functions implemented in each library:
  - Liquid and vapor phase density.
  - Liquid and vapor phase enthalpy.
  - Liquid and vapor phase entropy.
  - Fugacity of each component in each phase.
- The database for pure compounds corresponds has been taken from:

  ChemSep v7.15 pure component data - Copyright (c) Harry Kooijman and Ross Taylor (2016) - http://www.perlfoundation.org/artistic_license_2_0

- The libraries were developed with Dev C ++ using tdm-gcc as a compiler.
- More information about the library can be found in the compilation section of the *lst* file.

## 3. Discussion of results

### 3.1. Case Study 1. Model verification (simulation mode)

In order to verify the accuracy of the proposed model, the predicted results have been compared to those obtained using a simulator process (COCO simulator). Only for a valid comparison, the proposed model was used here as a "simulator", that is, the mathematical model was solved with zero degrees of freedom.

The model was implemented in the *PRexample.gms* file. Table 1 shows the parameters of the model taking from Perry's Chemical Engineers' Handbook (2007). The column feed stream (LF) is at its bubble point and its corresponding temperature (TF) is obtained in the file *bubble.gms*.

**Table 1.** Parameters of the model

| Parameter | Value |
|---|---|
| $LF$ (gmol s$^{-1}$) | 12.6 |
| $TF$ (K) | 354.0428 |
| $PF$ (bar) | 8.27 |
| $xf_{C3}$ | 0.05 |
| $xf_{iC4}$ | 0.15 |
| $xf_{nC4}$ | 0.25 |
| $xf_{iC5}$ | 0.2 |
| $xf_{nC5}$ | 0.35 |
| $P_s$ (bar) | 8.27 |

As is known, the degrees of freedom of a traditional distillation column with the fixed feed location are two. For the purpose of reproducing the case study presented in Perry's Chemical Engineers' Handbook (2007), it is assumed that the feed is located in the stage 6 ($LF_6=LF=$ 12.6 gmol/s and $LF_{s\neq6} = 0$). The degrees of freedom of the equations system are "closed" by fixing the total flow-rate of the liquid stream leaving the reboiler $L_{11}$ and the total flow-rate of the reflux $L_1$ (liquid that return from condenser to column), according to the values listed in Table 2. The value of $L_1$ corresponds to the reflux ratio proposed in the original example ($RR = L_1/D=$ 2.58).

**Table 2.** Fixed variables to close the degrees of freedom

| Variable | Fixed Value |
|---|---|
| $L_{11}$ | 6.4387 |
| $L_1$ | 15.8962 |

As it can be seen in Table 3, the total number of variables and equations are the same (276) indicating that the degrees of freedom of the equation system are closed.

Therefore, for the data input listed in Table 2, the mathematical model runs in the simulation mode instead of the optimization mode.

**Table 3.** Model size under simulation mode.

| Model statistics | Value |
|---|---|
| Single equations | 276 |
| Single variables | 276 |

## 3.2. Solution strategy

The proposed solution strategy is shown in Fig. 2. First, a mathematical model (Model 1) which consists of the mass and energy balances combined with an ideal physicochemical model (Raoult's Law) is solved and the obtained optimal solution is used as initialization to solve a second optimization model (Model 2) obtaining the desired solutions of the proposed example. Model 2 corresponds to the rigorous model using Peng Robinson as a thermodynamic package instead of the ideal physicochemical model (Raoult's Law). So, two mathematical models are included in the *PRexample.gms* file:
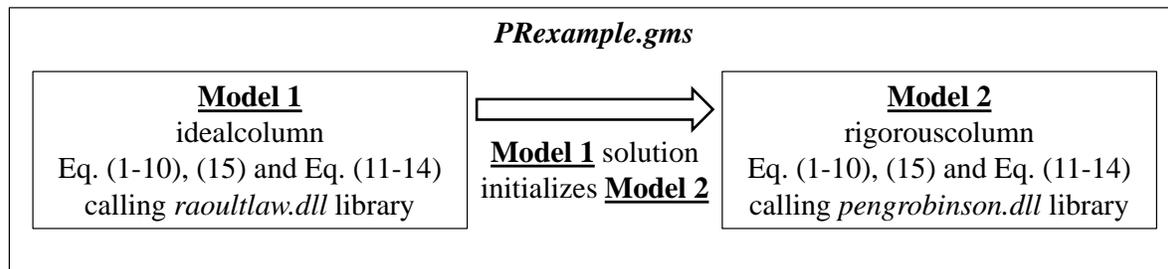


**Figure 2.** Solution strategy.

The comparison of the main variables between the process simulator and the optimization model is illustrated in Table 4, observing a good agreement between them.

Similarly, in Table 5 can be see that the internal profiles of temperature and flow-rates inside the distillation column that were obtained with the mathematical model (GAMS) are similar to those of the process simulator.

**Table 4.** Numerical values of the main variables obtained by GAMS model and process simulator

| Variable | | GAMS | COCO |
|---|---|---|---|
| Feed stream flow rate -stage 6- (gmol s$^{-1}$) | $LF$ | 12.6 | 12.6 |
| Distillate flow rate (gmol s$^{-1}$) | $D$ | 6.1613 | 6.1613 |
| Bottom product flow rate (gmol s$^{-1}$) | $L_{11}$ | 6.4387 | 6.4387 |
| Reflux Ratio | $L_1/D$ | 2.58 | 2.58 |
| Heat duty of condenser (kW) | $Q_{cond}$ | 419.65 | 419.669 |
| Heat duty of reboiler (kW) | $Q_{reb}$ | 429.553 | 429.573 |
| Mole fraction of light key in bottom (LKB) | $x_{11,nC4}$ | 0.0663 | 0.0663 |

| Mole fraction of heavy key in distillate (HKD) | $x_{1,iC5}$ | 0.0944 | 0.0944 |
|---|---|---|---|
| $z$ -objective function- | | 513.4830 | 513.5068 |

**Table 5.** Profiles of temperature and flow-rates obtained by GAMS model and COCO simulator

| | Temperature [K] | | Liquid molar flow [gmol s$^{-1}$] | | Vapor molar flow [gmol s$^{-1}$] | |
|---|---|---|---|---|---|---|
| | COCO Simulator | GAMS model | COCO Simulator | GAMS model | COCO Simulator | GAMS model |
| Stage 1 | 336.61 | 336.6008 | 15.8962 | 15.8962 | - | - |
| Stage 2 | 346.06 | 346.0529 | 15.5876 | 15.5876 | 22.0574 | 22.0575 |
| Stage 3 | 352.27 | 352.2595 | 15.3945 | 15.3945 | 21.7489 | 21.7489 |
| Stage 4 | 356.44 | 356.4358 | 15.2721 | 15.2721 | 21.5558 | 21.5558 |
| Stage 5 | 359.28 | 359.2746 | 15.189 | 15.189 | 21.4334 | 21.4334 |
| Stage 6 | 361.23 | 361.2261 | 27.9526 | 27.9526 | 21.3503 | 21.3503 |
| Stage 7 | 364.75 | 364.7396 | 28.0494 | 28.0495 | 21.5139 | 21.5139 |
| Stage 8 | 367.8 | 367.7986 | 28.1101 | 28.1101 | 21.6107 | 21.6108 |
| Stage 9 | 370.58 | 370.5716 | 28.1443 | 28.1444 | 21.6714 | 21.6714 |
| Stage 10 | 373.17 | 373.1632 | 28.1357 | 28.1357 | 21.7056 | 21.7057 |
| Stage 11 | 375.73 | 375.723 | 6.4387 | 6.4387 | 21.6969 | 21.697 |
| RMSD | 0.00728 | | 0.0000426 | | 0.0000603 | |

### 3.3. Case Study 2. Optimization problem statement

The proposed model is used here to determine simultaneously the optimal feed location and the optimal operating conditions that minimize the objective function while satisfying desired targets of separation. In order to compare the results, the separation values obtained in the previous example $x_{1,iC5}$ =0.0944 and $x_{11,nC4}$ = 0.0663 are now considered as upper bounds. Formally, the proposed optimization problem can be mathematically expressed as follows:

*Min.* $z = 0.2\ Q_{cond} + Q_{reb}$

s.t.

$$\begin{cases} Eq.\ (1-14) \\ x_{1,iC5} \leq 0.0994 \\ x_{11,nC4} \leq 0.063 \end{cases}$$

As a result, the optimization problem provides:

- Minimal Objective function value.
- Optimal values of temperature, composition and molar flow rate of all internal streams,
- Optimal location of the feed stream.

**Table 6.** Optimization model size.

| Model statistics | Value |
|---|---|
| Single equations | 277 |
| Single variables | 287 |

According to the Table 6, ten (10) are the degrees of freedom for the optimization problem.

The optimization values obtained with the GAMS model which are marked with * in Table 7 were used to fix the corresponding variables in the process simulator. Therefore, the results of COCO simulator correspond to a simulation of the column but using the optimal values obtained with the GAMS model. In other words, a simulation run performed in COCO that corresponds to the optimal solution obtained with GAMS. This is has been done as another "verification" of the implemented model to compare the differences between the two solutions. Precisely, Tables 7 and 8 list the optimization results obtained from GAMS and COCO.

**Table 7.** Numerical values of the main variables obtained by GAMS model and process simulator.

| Variable | | GAMS | COCO |
|---|---|---|---|
| Feed stream flow rate -stage 5- (gmol s$^{-1}$) | $LF_5$ | 12.6 | 12.6 [a] |
| Distillate flow rate (gmol s$^{-1}$) | $D$ | 6.2435 | 6.2435 |
| Bottom product flow rate (gmol s$^{-1}$) | $L_{11}$ | 6.3565 | 6.3565 [a] |
| Reflux Ratio | $L_1/D$ | 2.3709 | 2.3709 [a] |
| Heat duty of condenser (kW) | $Q_{cond}$ | 401.3904 | 401.408 |
| Heat duty of reboiler (kW) | $Q_{reb}$ | 411.1469 | 411.166 |
| Mole fraction of light key in bottom (LKB) | $x_{11,nC4}$ | 0.0663 [b] | 0.0663 |
| Mole fraction of heavy key in distillate (HKD) | $x_{1,iC5}$ | 0.0944 [b] | 0.0944 |
| z (objective function) | | 491.4250 | 491.4476 |

(*a*) Specifications imposed in the simulator
(*b*) values that reached the upper bounds

**Table 8.** Profiles of temperature and flow-rates obtained by GAMS model and process simulator.

| | Temperature [K] | | Liquid molar flow [gmol/s] | | Vapor molar flow [gmol/s] | |
|---|---|---|---|---|---|---|
| | COCO Simulator | GAMS model | COCO Simulator | GAMS model | COCO Simulator | GAMS model |
| Stage 1 | 336.93 | 336.9253 | 14.8025 | 14.8025 | - | - |
| Stage 2 | 346.55 | 346.5431 | 14.5108 | 14.5108 | 21.0459 | 21.046 |
| Stage 3 | 352.71 | 352.7057 | 14.3315 | 14.3315 | 20.7542 | 20.7543 |
| Stage 4 | 356.77 | 356.7618 | 14.2142 | 14.2142 | 20.575 | 20.575 |
| Stage 5 | 359.49 | 359.4847 | 26.9712 | 26.9712 | 20.4576 | 20.4577 |
| Stage 6 | 362.75 | 362.7414 | 27.0481 | 27.0481 | 20.6147 | 20.6147 |

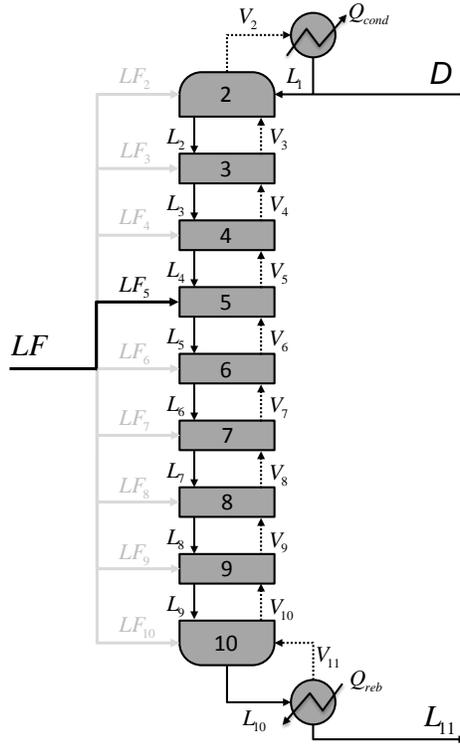| | | | | | |
|---------|---------|-----------|---------|---------|---------|---------|
| Stage 7 | 365.65 | 365.647 | 27.094 | 27.0941 | 20.6915 | 20.6916 |
| Stage 8 | 368.36 | 368.3533 | 27.1298 | 27.1299 | 20.7375 | 20.7376 |
| Stage 9 | 370.91 | 370.9052 | 27.152 | 27.152 | 20.7733 | 20.7733 |
| Stage 10 | 373.36 | 373.349 | 27.1384 | 27.1384 | 20.7954 | 20.7955 |
| Stage 11 | 375.81 | 375.8069 | 6.35653 | 6.3565 | 20.7818 | 20.7819 |
| RMSD | 0.006501 | | 0.00004359 | | 0.00007977 | |



**Figure 3.** Optimal feed location.

## 4. Analysis of modeling including and excluding the developed library

To evaluate the performance of the developed library, the previous problem was implemented in a traditional way in GAMS. That is, all the equations corresponding to Peng Robinson were included in the model (written in the *gms* file). Table 9 presents a comparison of both implementations.

**Table 9.** Model size and performance including and excluding the proposed library

| Model statistics | Including the library | Excluding the library |
|------------------|----------------------|----------------------|
| Objective function | 491.4250 | 491.4250 |
| Resource usage | 0.0347 | 0.518 |
| Iteration count | 20 | 21 |
| Single equations | 277 | 2169 |
| Single variables | 287 | 2135 |
| Non zero elements | 1710 | 10422 |
| Code length | 2418 | 26860 |

Both models were solved from the same starting point and as shown in table 9 both obtained the same solution (491.4250). It is important to note that the computation time is low for both models but the difference between them is significant (0.0347 sec. vs. 0.518 sec.).

Table 9 shows a large difference between the sizes of the models. The total number of equations when including Peng Robinson in the formulation (without extrinsic function) increases by approximately 783% (277 vs 2169). Also a similar increase (743%) is observed for the total number of variables (287 vs 2135). The increase of the size model is mainly due to the large number of variables and equations necessary only for the calculation of physical properties (Peng Robinson).

## 5. Conclusion

Different dynamic link libraries with extrinsic functions for GAMS have been implemented. The developed libraries correspond to the calculation of thermodynamic properties according to different theoretical approaches.

The results showed a decrease in the size of the model and in the calculation times. Another important advantage is that the number of equations that must be typed in the *gms* file is decreased, thus reducing the possible sources of error.

The precision of the results obtained from GAMS is equivalent to that obtained from process simulators but with the main advantages that GAMS allows to solve large optimization problems. Physical-chemical packages can be easily included in the mass and energy balances corresponding to the different process-units. Due to the generality of the developed libraries, they can be considered in any type of chemical processes simulation and/or optimization purposes.

The following are libraries that are already finished:

- Raoult's Law (ideal liquid + ideal gas)
- Peng Robinson equation of state (both phases)
- NRTL (liquid phase) + Ideal gas (vapor phase)
- The International Association for the Properties of Water and Steam (both phases).

Currently, the following are libraries that are under development:

- NRTL (liquid phase) + Peng Robinson (vapor phase)
- UNIQUAC (liquid phase) + Ideal gas (vapor phase)
- UNIQUAC (liquid phase) + Peng Robinson (vapor phase)
- MBWR (both phases)

## References

Caballero, J.A., and Grossmann, I.E. (2010). Hybrid Simulation-Optimization Algorithms for Distillation Design. In Computer Aided Chemical Engineering, S.P. and G.B. Ferraris, ed. (Elsevier), pp. 637–642.

Green, D.W., and Perry, R.H. (2007). Perry's Chemical Engineers' Handbook, Eighth Edition (New York: McGraw-Hill Education).

Grossmann, I.E., Aguirre, P.A., and Barttfeld, M. (2005). Optimal synthesis of complex distillation columns using rigorous models. Comput. Chem. Eng. *29*, 1203–1215.

Sargent, R.W.H., and Gaminibandara, K. (1976). Optimum design of plate distillation columns. Optim. Action 267–314.