Fairly Linear Mixed Integer Nonlinear Programming Model for the Synthesis of Mass Exchange Networks

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A fairly linear optimization model for the synthesis of mass exchange networks has been developed. Superstructure, detailed modeling equations, and solutions of example problems are presented. The predominantly linear character of the model can be kept as long as single-component mass exchange network synthesis problems and packed columns as mass exchangers are considered. At the cost of introducing nonlinear constraints, the optimization model can be extended to handle multicomponent problems and staged columns as well. The new model applies the key ideas of the simultaneous heat exchanger network synthesis model of Yee and Grossmann [*Comput. Chem. Eng.* **1990**, *14* (10), 1165−1184].

Introduction

Mass exchange networks (MENs) are systems of interconnected direct-contact mass-transfer units that use process lean streams or external mass separating agents (MSAs) to selectively remove certain components (often pollutants) from rich process streams. In the context of the overall process, the MEN is usually a part of the separation network. The main function of the MENs is to fully exploit the on-site cleaning capacities of the chemical facility; hence, MENs achieve environmental protection goals through process integration. A compendium of mass exchange networks and their applications can be found in ref 2.

The first, pinch-based solution methodology of El-Halwagi and Manousiouthakis[3] was extended by Hallale and Fraser.[4,5] Using the advanced targeting methods of Hallale and Fraser, both the capital cost and the total annual cost (TAC) of the network can be predicted ahead of any design. Still, pinch technology for mass exchange network synthesis (MENS) does not provide a systematic way for deriving the optimal network structure. The network design includes trial and error elements, especially when large or multiple component problems are considered.

Sequential mathematical programming approaches, that are mainly automated versions of the pinch design technique, were developed to facilitate the targeting step in the case of large problems, where the graphical approach of the pinch method is not convenient to use.[2,6] The attribute "sequential" denotes that the synthesis is still decomposed into targeting and design steps. As a consequence, the trade-off between investment and operating costs is not taken into account rigorously.

Design methods based on simultaneous optimization offer the possibility of designing the MEN in a single automated step. The whole MENS problem is formulated as a mathematical optimization problem that is to be solved for a global optimum. Most conveniently, binary variables are used to represent the network structure; hence, the optimization problem to be solved is usually a mixed integer nonlinear programming (MINLP) problem. The first simultaneous MINLP model for MENS was presented by Papalexandri et al.[7] Comeaux[8] aimed at simplifying the model formulation and adopted pinch principles to be able to formulate the MENS problem as a moderate size nonlinear programming (NLP) problem.

A good summary of the systematic (mathematical programming-based) approach to process synthesis can be found in ref 9. A review of mathematical programming-based methods for MENS can be found in ref 6.

Motivation and Aim of the Work

Szitkai et al.[10] compared the advanced pinch and the simultaneous mathematical programmig methods and concluded that, by using the MINLP model of Papalexandri et al.,[7] most of the advanced pinch-based designs of Hallale and Fraser can be reproduced or improved. The solutions of example problems proved that Papalexandri's model is superior to the insight-based NLP method of Comeaux.[8] Still, as was shown, Papalexandri's MINLP method in some cases delivers worse solutions than the advanced pinch design method of Hallale and Fraser. The most probable reason for this is that Papalexandri's MINLP model cannot be solved for global optimality using the commercially available algorithms because her model contains plenty of bilinear mass balances, which set up a nonconvex search space.

The aim of this work has been to develop a robust MINLP model for MENS. Regarding the assumptions and the modeling principles of the simultaneous optimization model of Yee and Grossmann,[1] that was originally developed for heat exchanger network synthesis (HENS), it was expected that a similar modeling technique would be applicable to MENS as well, resulting in a fairly linear and, hence, more easily solvable MINLP model.

Comparison of MENS and HENS

Adopting the modeling principles of a well functioning MINLP model for HENS in an optimization model for MENS

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Table 1. Analogy between MENS and HENS

	MENS	HENS
transported quantity	mass	heat
driving force	conc difference	temp difference
source	rich process streams	hot process streams
sink	lean process streams	cold process streams

is possible since the single component MENS problem can be regarded as an analogue of the HENS problem. The main points of the analogy are outlined in Table 1. As Table 1 shows, both kinds of networks transport a certain quantity among sources and sinks due to the existence of driving forces.

HENS is not dealt with in this article, a recent review of the area can be found in ref 11.

Although the existence of an analogy between HENS and MENS is apparent, there are a few fundamental differences between the two synthesis problems that have to be considered when constructing a superstructure and a mathematical programming model for the synthesis of MENs. These differences are the following: (1) In the case of MENS, equilibrium relations between the rich and the lean streams have to be taken into account when calculating the driving forces of the mass transfer or when sizing the mass exchangers. (2) Analogies between HENS and MENS can be drawn only in the case of single component MENS problems. The heat analogue of multiple components does not exist. (3) The problem statement of MENS[2] includes the determination of the process lean stream flow rates, while, in the case of the HENS problem, the cold stream flow rates are given a priori. (4) In the case of MENS problems, it makes no sense to define external rich streams. Resulting from point 1, phase equilibrium calculation is to be added to the mathematical programming model. Point 2 requires the addition of nonlinear component mass balances or necessitates the application of a modeling technique that can account for multiple components. Because of point number 3, the lean stream balances (flow rates multiplied by concentrations) become nonlinear. The analogous constraints, representing cold stream balances in the HENS model of Yee and Grossmann,[1] are linear. Allowing for point 4 results in a slightly different superstructure compared to that of Yee and Grossmann.[1]

Superstructure

The new MEN superstructure keeps most of the properties of the original HEN superstructure of Yee and Grossmann.[1] It consists of several serially connected identical stages (k) where lean and rich streams are driven in a counter-current way. The number of the superstructure stages can be set arbitrarily, but it has to be large enough so that the superstructure could embed the optimal structure. According to our experience, for problems with moderate numbers of streams, the sum of the number of the lean and the rich streams is usually a good choice for the maximum number of stages. Any of the rich (R) and lean (L) streams can be matched once in each of the stages. As Figure 1 shows, stream matchings in the stages are formed in a way in which streams are split toward the possible mass exchangers as they enter the stages. After leaving the exchangers, the streams are mixed again.

The main characteristics of the model is that in the superstructure only mixing of streams with equal concentrations is allowed. This allows streams to only be characterized by concentrations at the stage borders (concentration locations). No separate in- and outlet concentrations for the exchangers are introduced. The amounts of transferred masses in the exchangers are model variables to be optimized. There are no individual stream flow rate variables; flow rates of the mass exchangers can be back-calculated after obtaining the solution. Mass balances are set up only for the stages and not for the mass exchangers. This allows an almost linear formulation, as will be shown in the next section.

Similar to the original model for HENS,[1] our new model for MENS does not rely on the concept of the pinch point.[2] At the same time, engineering knowledge can be built into the model, if necessary, by forbidding matches or restricting the values of the model variables.

In Figure 1, the superstructure is shown for two rich streams, two lean streams, and two stages; y and x denote rich and lean mole fractions, while the indices S and T stand for source and target concentrations.

It can be seen that no distinction is made between process and external lean streams; both kinds are equally represented in each of the superstructure stages. This is because the external lean streams of MENs are not analogous to the cold utility streams of HENs. While the cold utility is usually the coldest stream in ordinary HENS problems, external lean streams of MENS problems are not always the leanest; hence, they cannot be used exclusively at the clean end of the rich streams. The superstructure contains rich−lean matches only; no exchangers are considered outside the superstructure stages. At this point, the new MEN superstructure differs from the original HEN superstructure.

The superstructure of the new model allows somewhat less complex network structures compared to that of Papalexandri et al.,[7] but at the same time, it is ensured that the solution is industrially feasible. Without the introduction of piping costs, the model of Papalexandri et al.[7] often results in technically infeasible "spaghetti" networks and enables the design of recycle loops. Resulting from its stagewise layout, applying the proposed new superstructure results in moderately complex recycle free MENs.

Single Component MINLP Model

In eqs 1−23, the model is derived for single component MENS problems. The notation of the mathematical programming problem follows the notation of the superstructure shown in Figure 1. Index i represents rich process streams given in set R and index j denotes lean process streams given in set L, while index k is used to denote the superstructure stages given in set ST. Exchangers in the stagewise superstructure are indexed using three indices: i, j, and k. In each stage (k) of the superstructure, matching of a rich stream i and a lean stream j is allowed only once (see Figure 1). The model consits of the following group of equations and inequalities.

Mass Balances for the Rich Streams in Each Stage. The variables R and L stand for total rates of the rich and the lean streams, y stands for the concentrations, and me stands for the rates of the exchanged masses of the mass exchange units. Note that the total rates are usually either mass rates (kg/s) or amount rates (mol/s); corresponding concentrations are then either mass fractions or amount fractions, and the corresponding rates of exchanged masses are either mass rates or amount rates.

$$R_i(y_{i,k} - y_{i,k+1}) = \sum_{j \in L} me_{i,j,k} \qquad i \in R,\ k \in \mathrm{ST}\backslash\mathrm{last} \tag{1}$$

Overall Mass Balances for the Rich Streams.

$$R_i(y_{i,\mathrm{S}} - y_{i,\mathrm{last}}) = \sum_{j \in L} \sum_{k \in \mathrm{ST}} me_{i,j,k} \qquad i \in R \tag{2}$$

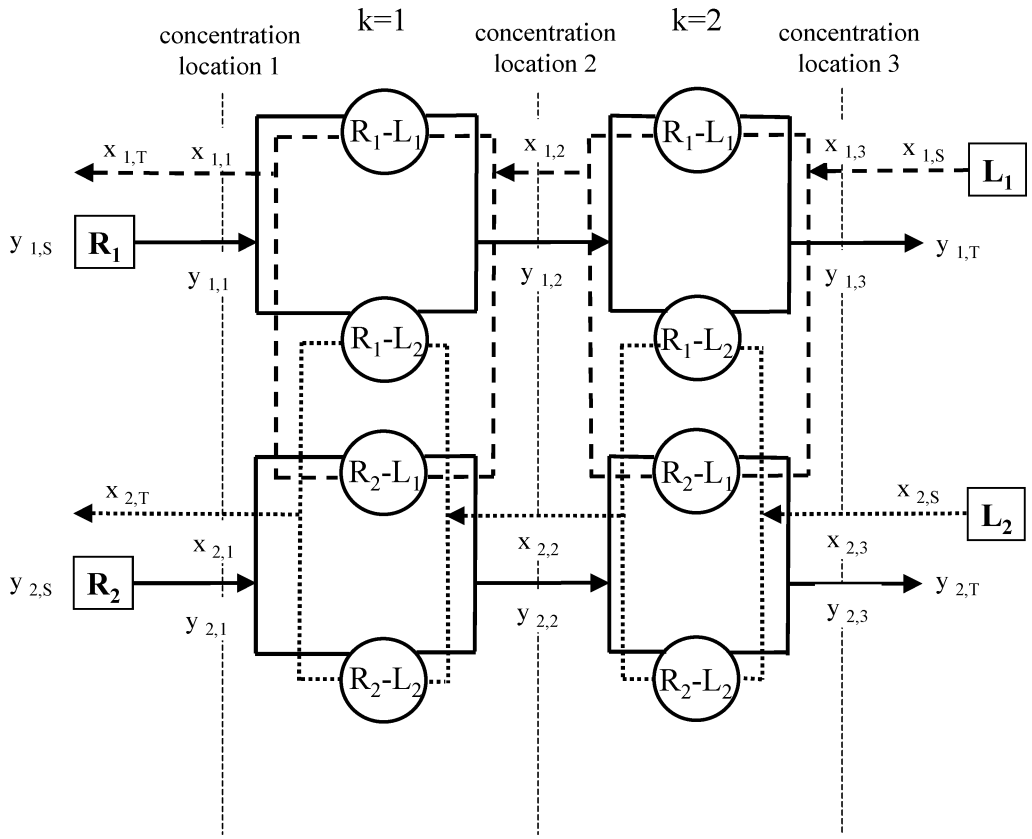

Figure 1. New superstructure for MENS. Two rich streams, two lean streams, and two stages are shown.

Mass Balances for the Lean Streams in Each Stage.

$$L_j(x_{j,k} - x_{j,k+1}) = \sum_{i \in R} me_{i,j,k} \qquad j \in L,\ k \in \mathrm{ST}\backslash\mathrm{last} \tag{3}$$

Overall Mass Balances for the Lean Streams.

$$L_j(x_{j,\mathrm{first}} - x_{j,\mathrm{S}}) = \sum_{i \in R} \sum_{k \in \mathrm{ST}} me_{i,j,k} \quad j \in L \tag{4}$$

Inequalities That Ensure the Monotonity of the Rich and Lean Stream Concentrations along the Stages. They represent the fact that the rich streams become cleaner and cleaner, while the lean streams can only take up the pollutants.

$$y_{i,k} \geq y_{i,k+1} \qquad i \in R,\ k \in \mathrm{ST}\backslash\mathrm{last} \tag{5}$$

$$x_{j,k} \geq x_{j,k+1} \qquad j \in L,\ k \in \mathrm{ST}\backslash\mathrm{last} \tag{6}$$

Target and Source Concentrations. The following inequalities and equations represent constraints on the target concentrations and define the source concentrations of both the rich and the lean streams.

$$y_{i,\mathrm{last}} \leq y_{i,\mathrm{T}} \qquad i \in R \tag{7}$$

$$x_{j,\mathrm{first}} \leq x_{j,\mathrm{T}} \qquad j \in L \tag{8}$$

$$y_{i,\mathrm{first}} = y_{i,\mathrm{S}} \qquad i \in R \tag{9}$$

$$x_{j,\mathrm{last}} = x_{j,\mathrm{S}} \qquad j \in L \tag{10}$$

Logical Constraints. Big-M constraints (eq 11) set the exchanged mass of an exchanger ($me_{i,j,k}$) to zero when the binary variable denoting the existence of the match ($bz_{i,j,k}$) equals zero. As will be outlined later, the numerical stability of the solution can be improved when using relaxed binary variables ($z_{i,j,k}$) in the equations and a penalty term in the objective function ensuring that in the solution the relaxed variables take the values of the binary variables.

$$me_{i,j,k} - \Omega^{\mathrm{UP}}_{i,j} z_{i,j,k} \leq 0 \qquad i \in R,\ j \in L,\ k \in \mathrm{ST} \tag{11}$$

The scalars $\Omega^{\mathrm{UP}}_{i,j}$ are upper bounds on the exchanged masses and can be calculated using the source and target concentrations and the maximum flow rates of the rich and the lean streams, as is shown in eq 12. If the flow rate and concentration units are properly chosen, then the calculated $\Omega^{\mathrm{UP}}_{i,j}$ constants do not turn out to be "big" numbers; therefore, eq 11 will not cause numerical problems during the solution procedure.

$$\Omega^{\mathrm{UP}}_{i,j} = \min\{L_j^{\max}(x_{j,\mathrm{T}} - x_{j,\mathrm{S}});\ R_i(y_{i,\mathrm{S}} - y_{i,\mathrm{T}})\} \tag{12}$$

On the other hand, constraints are used to provide reasonable lower bounds $\Omega^{\mathrm{LOW}}_{i,j}$ for the exchanged masses. Equation 13 prevents getting negligible amounts of mass transfer, i.e., getting negligibly sized exchangers in the solution. The scalars $\Omega^{\mathrm{LOW}}_{i,j}$ are to be given problem specifically.

$$me_{i,j,k} - \Omega^{\mathrm{LOW}}_{i,j} z_{i,j,k} \geq 0 \qquad i \in R,\ j \in L,\ k \in \mathrm{ST} \tag{13}$$

The following constraints allow the calculation of the driving forces at both ends of the mass exchangers ($dy_{i,j,k}$ and $dy_{i,j,k+1}$). Phase equilibrium is given in a simplified linear form; $b_{i,j}$ and $m_{i,j}$ denote the intercepts and the slopes of the equilibrium lines. $\Gamma_{i,j,k}$ variables represent the upper bounds of the driving forces and can be calculated based on the rich and lean stream data. Equations 14−17 allow the calculation of the driving forces when the particular matches do exist (the corresponding binary variables $bz_{i,j,k}$ equal 1); otherwise, the driving force variables

can take arbitrary values. Matches that do not exist exchange no mass (see eq 11); hence, their corresponding cost will equal zero, independent of the value of their driving force variables (see eq 22).

$$dy_{i,j,k} \le y_{i,k} - m_{i,j}x_{j,k} - b_{i,j} + \Gamma_{i,j,k}(1 - z_{i,j,k}) \qquad i \in R, j \in L, k \in \mathrm{ST} \quad (14)$$

$$dy_{i,j,k} \ge y_{i,k} - m_{i,j}x_{j,k} - b_{i,j} - \Gamma_{i,j,k}(1 - z_{i,j,k}) \qquad i \in R, j \in L, k \in \mathrm{ST} \quad (15)$$

$$dy_{i,j,k+1} \le y_{i,k+1} - m_{i,j}x_{j,k+1} - b_{i,j} + \Gamma_{i,j,k}(1 - z_{i,j,k}) \qquad i \in R, j \in L, k \in \mathrm{ST\backslash last} \quad (16)$$

$$dy_{i,j,k+1} \ge y_{i,k+1} - m_{i,j}x_{j,k+1} - b_{i,j} - \Gamma_{i,j,k}(1 - z_{i,j,k}) \qquad i \in R, j \in L, k \in \mathrm{ST\backslash last} \quad (17)$$

When it is not acceptable to express a phase equilibrium relation in a simple linear form, we suggest piecewise linearizing the equilibrium curve.

The next two inequalities (eqs 18 and 19) control the minimum and the maximum number of mass exchange units ($U^{\min}$ and $U^{\max}$) of the solution. For example, one can prescribe that the solution must contain at least three exchangers but not more than six. These constraints also ease the solution procedure.

$$\sum_{i\in R}\sum_{j\in L}\sum_{k\in \mathrm{ST}} z_{i,j,k} \le U^{\max} \quad (18)$$

$$U^{\min} \le \sum_{i\in R}\sum_{j\in L}\sum_{k\in \mathrm{ST}} z_{i,j,k} \quad (19)$$

Equation 20 contributes to the numerical stability of the solution procedure to a great extent. As can be seen, eqs 11−19 contain only the relaxed version ($z_{i,j,k}$) of the binary variables ($bz_{i,j,k}$), denoting the existence of the matches. By eq 20, the integer-infeasible path MINLP (IIP-MINLP) model formulation by Soršak and Kravanja[12] is introduced. The equation states that the relaxed version of the binary variable ($z_{i,j,k}$) must be equal to the real binary variable ($bz_{i,j,k}$) within a positive ($pz_{i,j,k}$) and a negative tolerance ($sz_{i,j,k}$). At the same time, a penalty term in the objective function (eq 23) ensures that in the solution $z_{i,j,k}$ must equal $bz_{i,j,k}$, i.e., both $pz_{i,j,k}$ and $sz_{i,j,k}$ are zero. The main idea of this formulation is that using relaxed binary variables in the equations enables the solver to search for feasible solutions through infeasible solutions, too. The formulation is useful when the master problem predicts topology solutions that are actually infeasible. It significantly speeds up the search.

$$z_{i,j,k} = bz_{i,j,k} + pz_{i,j,k} - sz_{i,j,k} \qquad i \in R, j \in L, k \in \mathrm{ST} \quad (20)$$

Logarithmic Mean Concentration Differences. The following equations are Chen's approximations[13] for the logarithmic mean concentration differences (lmcd), that are needed for sizing the mass exchangers.

$$lmcd_{i,j,k} = (dy_{i,j,k}dy_{i,j,k+1}(dy_{i,j,k} + dy_{i,j,k+1})/2)^{1/3} \qquad i \in R, j \in L, k \in \mathrm{ST\backslash last} \quad (21)$$

Capital Costs. For a precise estimation of the capital costs of the packed columns, the exchanger mass-based costing equation of Hallale[14] is applied. It is important to note that the variable $mass_{i,j,k}$ in eq 22 denotes the estimated mass of the equipment in kilograms, while $me_{i,j,k}$ still represents the amount of pollutants that are transferred from the rich stream into the lean stream in the particular exchanger. K_W is a problem specific coefficient and can be calculated according to ref 14.

$$mass_{i,j,k}K_W lmcd_{i,j,k} = me_{i,j,k} \qquad i \in R, j \in L, k \in \mathrm{ST} \quad (22)$$

Objective Function. Finally, the objective function, the total annual cost (TAC) of the network, is defined. In the simplest case, it consists of the annualized investment cost, that is a function of the exchanger masses $f(mass_{i,j,k})$, and of the variable cost that depends on the lean stream flow rates. The parameter c_j is the cost coefficient of the lean streams. The minimum TAC is to be found. The last term of the objective function is the penalty term belonging to eq 20; the w weighting factor is an arbitrary large number.

$$\mathrm{TAC} = \sum_{i\in R}\sum_{j\in L}\sum_{k\in \mathrm{ST}} f(mass_{i,j,k}) + \sum_{j\in L} c_j L_j + w\sum_{i\in R}\sum_{j\in L}\sum_{k\in \mathrm{ST}} (pz_{i,j,k} + sz_{i,j,k}) \quad (23)$$

The model outlined above is a MINLP problem because binary variables ($bz_{i,j,k}$) are used to denote the existence of the matches and because the lean stream mass balances (eqs 3 and 4), the sizing and costing equations (eqs 21 and 22), and the objective function (eq 23) are nonlinear. The costing equations can be included in the objective function. When doing so, the only nonlinear terms of the model remaining are the lean stream balances (eqs 3 and 4) and the objective function. So far, no such linear model for the synthesis of MENs has been presented.

The new formulation can keep its simplicity as long as the costing equations have the form as presented. This is the case when only packed columns are considered. When considering trayed columns and applying the Kremser equation and its extensions, several additional binary variables and nonlinear equality constraints must be included (see Szitkai et al.[15]). If it is acceptable, linear costing relations can be applied too; the model can be further simplified this way.

Resulting from its near linearity, the outlined MINLP model can be solved reliably using the commercially available MINLP algorithms. Initialization of the model variables becomes an important issue only in the case of large numbers of streams and superstructure stages.

Multiple Component MINLP Model

The proposed MINLP model for MENS can be extended to handle multiple component problems as well.

By introducing nonlinear component balances and flow rate variables for the mass exchangers, multiple component problems could be solved in a way similar to the case of the formulation of Papalexandri et al.[7] This way only the superstructure of the new model would remain intact; almost all the other equations have to be changed back to the usual bilinear mass balance formulation. It is necessary to note that if a bilinear mass balance formulation is applied to the mass exchangers then there is no need for assuming that only streams with equal concentrations are to be mixed. Resulting from this, application of the stagewise superstructure would not be reasonable any more.

Therefore, in the following, a method is presented that enables the solution of multiple component MENS problems, while keeping most of the original modeling principles. The basic idea is to apply a multiple model structure similar to the one of multiperiod optimization problems, now with an index of components, $c \in C$, instead of time periods. Equations are written as many times as the number of components, and they are solved for all of the components simultaneously, yielding the same structure of the two networks. This is achieved by

using (1) only one set of binary variables for all component subnetworks, (2) the same lean stream flow rates in all subnetworks, and (3) additional concentration constraints for the matches ensuring identical stream splits in the subnetworks.

The application of the first two points is straightforward. The derivation of the concentration constraints that ensure identical stream splits at the matches in both of the networks is shown next for two components. Both components, let us say A and B, are present in the rich and lean streams that are countercurrently matched. The rich and the lean stream flow rates and compositions of an exchanger are denoted by $r_{i,j,k}$ and $y_{i,k}$ and $l_{i,j,k}$ and $x_{j,k}$, respectively. The exchanged mass rates of A and B in a particular exchanger ($me^{A}_{i,j,k}$ and $me^{B}_{i,j,k}$) can be calculated as follows:

$$me^{A}_{i,j,k} = l_{i,j,k}(x^{A}_{j,k} - x^{A}_{j,k+1}) = r_{i,j,k}(y^{A}_{i,k+1} - y^{A}_{i,k}) \qquad i \in R, j \in L, k \in \mathrm{ST}\backslash\mathrm{last} \quad (24)$$

$$me^{B}_{i,j,k} = l_{i,j,k}(x^{B}_{j,k} - x^{B}_{j,k+1}) = r_{i,j,k}(y^{B}_{i,k+1} - y^{B}_{i,k}) \qquad i \in R, j \in L, k \in \mathrm{ST}\backslash\mathrm{last} \quad (25)$$

Expressing and eliminating the ratio $l_{i,j,k}/r_{i,j,k}$, eqs 24 and 25 can be reduced to the following concentration constraint:

$$(x^{A}_{j,k} - x^{A}_{j,k+1})(y^{B}_{i,k+1} - y^{B}_{i,k}) = (y^{A}_{i,k+1} - y^{A}_{i,k})(x^{B}_{j,k} - x^{B}_{j,k+1}) \qquad i \in R, j \in L, k \in \mathrm{ST}\backslash\mathrm{last} \quad (26)$$

The extension to multiple component problems is then straightforward:

$$(x_{j,c,k} - x_{j,c,k+1})(y_{i,c+1,k+1} - y_{i,c+1,k}) = (y_{i,c,k+1} - y_{i,c,k})(x_{j,c+1,k} - x_{j,c+1,k+1}) \qquad i \in R, j \in L, c \in C\backslash\mathrm{last}, k \in \mathrm{ST}\backslash\mathrm{last} \quad (27)$$

Altogether, this means that there are $ij(k-1)(c-1)$ number of concentration constraints. Equation 27 ensures identical stream splittings in the networks without having to calculate any of the flow rates of the mass exchangers. At the cost of these new nonconvex constraints, the original MINLP formulation can also be kept in the case of multiple component problems.

The complete multiple component model formulation is outlined in eqs 28−50.

$$R_i(y_{i,c,k} - y_{i,c,k+1}) = \sum_{j \in L} me_{i,j,c,k} \qquad i \in R, c \in C, k \in \mathrm{ST}\backslash\mathrm{last} \quad (28)$$

$$R_i(y_{i,c,\mathrm{S}} - y_{i,c,\mathrm{last}}) = \sum_{j \in L} \sum_{k \in \mathrm{ST}} me_{i,j,c,k} \qquad i \in R, c \in C \quad (29)$$

$$L_j(x_{j,c,k} - x_{j,c,k+1}) = \sum_{i \in R} me_{i,j,c,k} \qquad j \in L, c \in C, k \in \mathrm{ST}\backslash\mathrm{last} \quad (30)$$

$$L_j(x_{j,c,\mathrm{first}} - x_{j,c,\mathrm{S}}) = \sum_{i \in R} \sum_{k \in \mathrm{ST}} me_{i,j,c,k} \qquad j \in L, c \in C \quad (31)$$

$$(x_{j,c,k} - x_{j,c,k+1})(y_{i,c+1,k+1} - y_{i,c+1,k}) = (y_{i,c,k+1} - y_{i,c,k}) \times (x_{j,c+1,k} - x_{j,c+1,k+1}) \qquad i \in R, j \in L, c \in C\backslash\mathrm{last}, k \in \mathrm{ST}\backslash\mathrm{last} \quad (32)$$

$$y_{i,c,k} \geq y_{i,c,k+1} \qquad i \in R, c \in C, k \in \mathrm{ST}\backslash\mathrm{last} \quad (33)$$

$$x_{j,c,k} \geq x_{j,c,k+1} \qquad j \in L, c \in C, k \in \mathrm{ST}\backslash\mathrm{last} \quad (34)$$

$$y_{i,c,\mathrm{last}} \leq y_{i,c,\mathrm{T}} \qquad i \in R, c \in C \quad (35)$$

$$x_{j,c,\mathrm{first}} \leq x_{j,c,\mathrm{T}} \qquad j \in L, c \in C \quad (36)$$

$$y_{i,c,\mathrm{first}} = y_{i,c,\mathrm{S}} \qquad i \in R, c \in C \quad (37)$$

$$x_{j,c,\mathrm{last}} = x_{j,c,\mathrm{S}} \qquad j \in L, c \in C \quad (38)$$

$$me_{i,j,c,k} - \Omega^{\mathrm{UP}}_{i,j,c} z_{i,j,k} \leq 0 \qquad i \in R, j \in L, c \in C, k \in \mathrm{ST} \quad (39)$$

$$me_{i,j,c,k} - \Omega^{\mathrm{LOW}}_{i,j,c} z_{i,j,k} \geq 0 \qquad i \in R, j \in L, c \in C, k \in \mathrm{ST} \quad (40)$$

$$dy_{i,j,c,k} \leq y_{i,c,k} - m_{i,j,c} x_{j,c,k} - b_{i,j,c} + \Gamma_{i,j,c,k}(1 - z_{i,j,k}) \qquad i \in R, j \in L, c \in C, k \in \mathrm{ST} \quad (41)$$

$$dy_{i,j,c,k} \geq y_{i,c,k} - m_{i,j,c} x_{j,c,k} - b_{i,j,c} - \Gamma_{i,j,c,k}(1 - z_{i,j,k}) \qquad i \in R, j \in L, c \in C, k \in \mathrm{ST} \quad (42)$$

$$dy_{i,j,c,k+1} \leq y_{i,c,k+1} - m_{i,j,c} x_{j,c,k+1} - b_{i,j,c} + \Gamma_{i,j,c,k}(1 - z_{i,j,k}) \qquad i \in R, j \in L, c \in C, k \in \mathrm{ST}\backslash\mathrm{last} \quad (43)$$

$$dy_{i,j,c,k+1} \geq y_{i,c,k+1} - m_{i,j,c} x_{j,c,k+1} - b_{i,j,c} - \Gamma_{i,j,c,k}(1 - z_{i,j,k}) \qquad i \in R, j \in L, c \in C, k \in \mathrm{ST}\backslash\mathrm{last} \quad (44)$$

$$\sum_{i \in R} \sum_{j \in L} \sum_{k \in \mathrm{ST}} z_{i,j,k} \leq U^{\max} \quad (45)$$

$$U^{\min} \leq \sum_{i \in R} \sum_{j \in L} \sum_{k \in \mathrm{ST}} z_{i,j,k} \quad (46)$$

$$z_{i,j,k} = bz_{i,j,k} + pz_{i,j,k} - sz_{i,j,k} \qquad i \in R, j \in L, c \in C, k \in \mathrm{ST} \quad (47)$$

$$lmcd_{i,j,c,k} = (dy_{i,j,c,k} dy_{i,j,c,k+1}(dy_{i,j,c,k} + dy_{i,j,c,k+1})/2)^{1/3} \qquad i \in R, j \in L, c \in C, k \in \mathrm{ST}\backslash\mathrm{last} \quad (48)$$

$$mass_{i,j,k} K_{\mathrm{W},c} lmcd_{i,j,c,k} = me_{i,j,c,k} \qquad i \in R, j \in L, c \in C, k \in \mathrm{ST} \quad (49)$$

$$\mathrm{TAC} = \sum_{i \in R} \sum_{j \in L} \sum_{k \in \mathrm{ST}} f(mass_{i,j,k}) + \sum_{j \in L} c_j L_j + w \sum_{i \in R} \sum_{j \in L} \sum_{k \in \mathrm{ST}} (pz_{i,j,k} + sz_{i,j,k}) \quad (50)$$

As will be demonstrated by an example problem in the next section, the model works well for two component problems. In the case of more than two components, the assumption of only mixing streams with equal concentrations may become too strict. The problem may not have enough degrees of freedom and, hence, may not be solvable. In this case, one cannot avoid applying the usual bilinear mass balance formulation.

Examples

In this section, the solutions of three example problems are presented: two with a single component and one with two components. None of the examples consider reaction heat or regeneration of the MSAs. (1) The first example is a single component problem where only packed columns are used in the MEN. (2) The second example is also a single component problem. but now with staged columns. (3) The third example is a compatible two component problem with staged column mass exchangers.

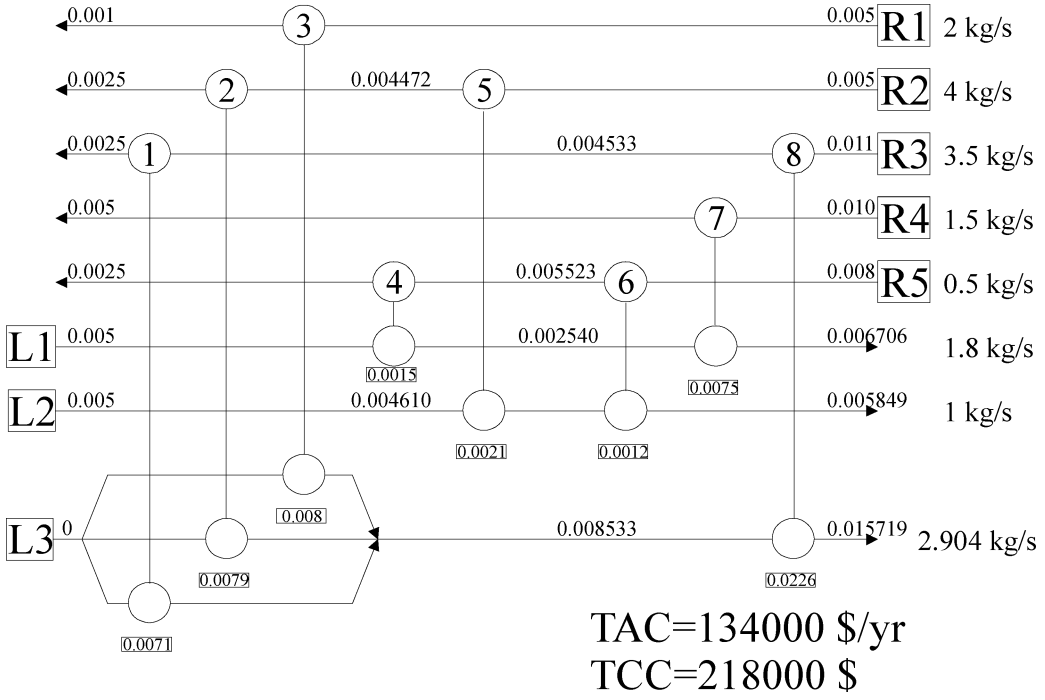

Figure 2. Solution of example problem 1.

Table 2. Stream Data for Example Problem 1

rich stream	R (kg/s)	y_S[a]	y_T[a]
R_1	2	0.005	0.0010
R_2	4	0.005	0.0025
R_3	3.5	0.011	0.0025
R_4	1.5	0.010	0.0050
R_5	0.5	0.008	0.0025

MSA	L^{max} (kg/s)	x_S[a]	x_T[a]	m	b
L_1	1.8	0.0017	0.0071	1.2	0
L_2	1	0.0025	0.0085	1	0
L_3	∞	0	0.017	0.5	0

[a] Mass fraction.

GAMS 2.25 for Windows/DICOPT++ was used to solve the MINLP problems. Details of the GAMS program package can be found in ref 16 and in the GAMS solver manuals.[17]

Example 1. Example problem 4.1 from the Ph.D. thesis of Hallale[14] is reconsidered. Ammonia is removed from five gaseous streams, which are composed mainly of air. Three water-based lean streams are available. These comprise two process MSAs, L_1 and L_2, and an external MSA, L_3. Stream data can be found in Table 2. Packed columns are specified as mass exchangers, and the exchanger mass-based costing method of Hallale is used with the following cost coefficient and costing equation:

$$K_W = 0.02 \text{ kg of } NH_3/(\text{s kg}) \tag{51}$$

$$\text{TCC} = 1.1N_{\text{units}} \times \$618\left(\frac{\sum_{i,j,k} mass_{i,j,k}}{N_{\text{units}}}\right)^{0.66} \tag{52}$$

The variable N_{units} represents the number of mass exchange units in the network. The capital cost of the MEN involves both the cost of the column shells and the cost of the packing. The problem has been solved in two different ways.

At first, the external lean stream flow rate L_3 was fixed to its pinch-targeted minimum[14] (L_3 = 2.48 kg/s). In this case, only the total capital cost of the network (TCC), i.e., the cost of the network structure, can be optimized. Hallale's solution featured a total capital cost of $298,000. Using the new MINLP model, including the method for improving the numerical stability of the solution procedure (see eqs 20 and 23), and fixing the external MSA (L_3) flow rate to 2.48 kg/s, our solution's optimal TCC was $307,000. Since the difference of the TCCs is less than 3%, we can state that the pinch solution could be reproduced.

Table 3. Cost Results of Example Problem 1

objective function	comment	TCC ($)	TAC ($/yr)
TCC	Hallale[4] minimal utility	298 000	
TCC	new MINLP model minimal utility	307 000	
TAC	new MINLP model		134 000

In the second case, the objective function was the TAC of the network; both the capital cost and the variable cost of the MEN were optimized. The annualization factor of the capital cost was taken to be 0.225; the cost of the external MSA was taken to be $0.001/kg, and 8150 working hours per year were assumed. Our solution features a TAC of $134,000.

The latter solution is shown in Figure 2 where plain numbers without dimensions represent mass fractions and numbers in boxes show the amounts of transferred mass in the exchangers in kilograms per second. Mass exchangers are numbered from 1 to 8. A summary of the solutions is shown in Table 3.

The example problem was solved using GAMS/DICOPT++ calling CPLEX for the MILP and CONOPT for the NLP subproblems. The solution took 13.52 s of CPU time on a PC/Athlon-64 machine. The optimal solution was obtained in the 18th main iteration cycle. The model consisted of 436 single equations and contained 517 single variables whereof 60 variables were binary.

As the results show, the new MINLP model is well applicable. A pinch solution of an example problem could be reproduced; the difference in the TCCs is just 3%. Using our MINLP model, simultaneous optimization of the variable and the investment costs can be carried out, without having to deal with the initial

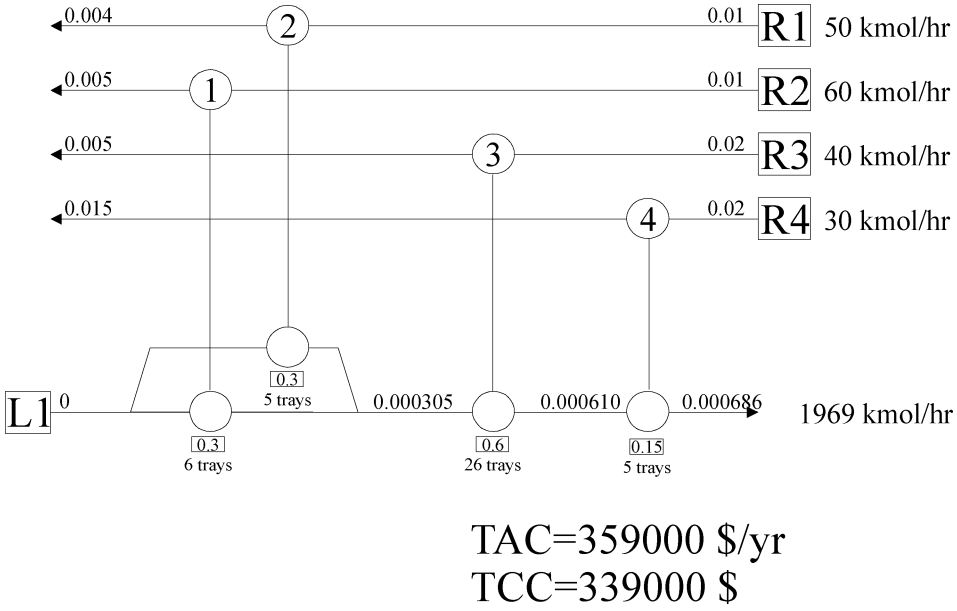

Figure 3. Optimal solution of example problem 2.

Table 4. Stream Data for Example Problem 2

rich stream	R (kmol/h)	$y_S{}^a$	$y_T{}^a$
R_1	50	0.01	0.004
R_2	60	0.01	0.005
R_3	40	0.02	0.005
R_4	30	0.02	0.015

MSA	L^{max} (kmol/h)	$x_S{}^a$	$x_T{}^a$	m	b
L_1	∞	0	/	26.1	−0.00326

[a] Amount fraction.

values of the model variables. At the same time, no heuristic or trial and error approach is to be applied when deriving the network structure.

Example 2. Equations that enable theoretical stage-based capital costing can also be included in the model. For the precise handling of the Kremser equation, the proposed method of Szitkai et al.[10,15] can be applied. It is important to notice that the Kremser equation-based capital costing procedure itself contains more nonlinear equations and binary variables than the whole new MINLP model; hence, application of the Kremser equation in our model is possible but not advisable. Alternatively, the new formulation for the Kremser equation of Shenoy and Fraser[18] can be applied.

An example considering tray columns is presented here.

In example 2, the purpose is to remove sulfur dioxide (SO_2) from four gaseous streams (example problem 3.1 from ref 14). Only one external MSA is available that is pure water (L_1). The stream data are given in Table 4. The tray columns are used as mass exchangers. The capital cost is based on the shell cost $\$12{,}800 H_t^{0.95} D^{0.6}$ and on the cost of the trays. The cost of a tray is $\$608 e^{0.8D}$, where D is the column diameter and H_t is the total column height. The overall efficiency of the trays is fixed at 20%. The inactive height is 3 m; the tray spacing is 0.5 m.

The number of theoretical stages is calculated using the highly nonconvex Kremser equation. It has been assumed that the absorption factor is greater than 1.

The problem has been solved using the new model, and the objective function to be minimized was the total annual cost. The annualization factor was taken to be 0.225; 8150 working hours per year were assumed, and the cost of the external MSA was \$0.003/kg (\$0.054/kmol). The optimal solution is shown in Figure 3. The solution of Hallale, with pinch technology, was TCC = \$860,000 (TAC = \$427,000/yr).

The example problem was solved using GAMS/DICOPT++ calling CPLEX for the MILP and CONOPT for the NLP subproblems. The solution took 2.08 s of CPU time on a PC/Athlon-64 machine. The optimal solution was obtained in the second main iteration cycle. The model consisted of 246 single equations and contained 215 single variables whereof 20 variables were binary.

One can conclude that good solutions can be found, even if including the Kremser equation in the MINLP model.

Example 3. The COG sweetening example of El-Halwagi and Monousiouthakis[3] is chosen to test the multiple component version of our MINLP model. This example problem is a compatible two-component problem, featuring two rich and two lean streams. The two components are H_2S and CO_2. The problem data are shown in Table 5. The concentrations are given in mass fractions; the intercepts of the equilibrium lines are zero. Sieve-tray columns are considered with an annualized capital cost of \$4552/yr per equilibrium stage.

Table 5. Stream Data for Example Problem 3

rich stream	R (kg/s)	$y_{S,H_2S}{}^a$	$y_{T,H_2S}{}^a$	$y_{S,CO_2}{}^a$	$y_{T,CO_2}{}^a$
R_1	0.9	0.07	0.0003	0.06	0.005
R_2	0.1	0.051	0.0001	0.115	0.01

MSA	L^{max} (kg/s)	$x_{S,H_2S}{}^a$	$x_{T,H_2S}{}^a$	$x_{S,CO_2}{}^a$	$x_{T,CO_2}{}^a$	m_{H_2S}	m_{CO_2}	cost (\$/yr)/(kg/s)
L_1	2.3	0.0006	0.031	0	0.171	1.45	0.35	117 360
L_2	∞	0.0002	0.0035	0	0.103	0.26	0.58	176 040

[a] Mass fraction.

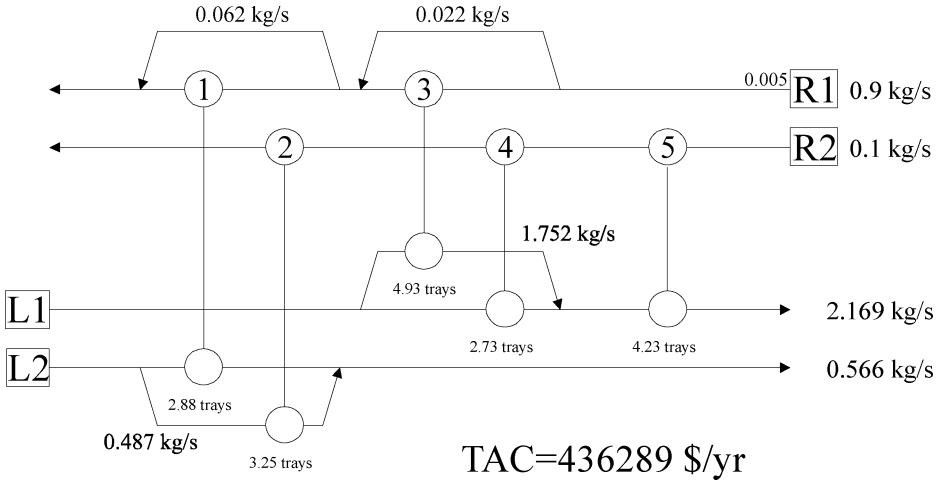

Figure 4. Solution of the COG sweetening problem obtained using the new MINLP model.

The solution obtained by the nonlinear, two-component version of the new MINLP model is presented in Figure 4.

The example problem was solved using GAMS/DICOPT++ calling CPLEX for the MILP and CONOPT for the NLP subproblems. The solution took 4.82 s of CPU time on a PC/Athlon-64 machine. The optimal solution was obtained in the second main iteration cycle. The model consisted of 496 single equations and contained 431 single variables whereof 20 variables were binary.

Since the COG sweetening example considers trayed-columns as mass exchangers, the Kremser equation had to be added to the new MINLP model. It was assumed that the absorption factor is greater than 1. Still, as Figure 4 shows, the new model gave a very good solution. The TAC of our solution is \$436,289/yr, which is just 1% more expensive compared to the pinch target (theoretical minimum of the TAC according to pinch theory) of Hallale,[14] \$431,600/yr.

Conclusions

A new, fairly linear MINLP model for the synthesis of MENs has been developed, based on the superstructure and optimization model developed by Yee and Grossmann[1] for designing HENs. Using the new model, one can obtain the proper trade-off between capital and external MSA costs by taking all the driving forces as optimization variables. The model's main advantage can be fully exploited in the case of single component problems with packed columns as mass exchangers. At the cost of introducing nonlinear constraints, the optimization model can be extended to handle multicomponent problems and staged columns as well. The model easily allows one to consider forbidden matches and to impose different restrictions on exchanging masses. The search for and stability of the numerical solution can be enhanced by using the integer-infeasible path MINLP (IIP-MINLP) model formulation.

Solutions of example problems justify the applicability of the model and predict that the new model could be applied to design the MEN part of more complex process synthesis problems.

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Nomenclature

Acronyms

HENS = heat exchanger network synthesis
MEN = mass exchange network
MENS = mass exchange network synthesis
MILP = mixed integer linear programming
MINLP = mixed integer nonlinear programming
MSA = mass separating agent
NLP = nonlinear programming
TAC = total annual cost
TCC = total capital cost

Sets

C = set of components
R = set of rich streams
L = set of lean streams
ST = set of superstructure stages

Indices

i = index of rich streams
j = index of lean streams
k = index of superstructure stages
c = index of components
first = the first superstructure stage
last = the last superstructure stage

Problem Specific Constants

$y_{i,S}$ = source concentration of rich stream i, mass or amount fraction, [-]
$x_{j,S}$ = source concentration of lean stream j, mass or amount fraction, [-]
$y_{i,T}$ = target concentration of rich stream i, mass or amount fraction, [-]
$x_{j,T}$ = target concentration of lean stream j, mass or amount fraction, [-]
L_j^{max} = upper bound on the flow rate of lean stream j, [kg/s] or [kmol/h]
$\Omega_{i,j}^{UP}$ = upper bound on the rate of the exchanged mass at match ijk, [kg/s] or [kmol/h]
$\Omega_{i,j}^{LOW}$ = lower bound on the rate of the exchanged mass at match ijk, [kg/s] or [kmol/h]
$m_{i,j}$ = slope of the equilibrium line, [-]
$b_{i,j}$ = intercept of the equilibrium line, mass or amount fraction, [-]

$\Gamma_{i,j,k}$ = upper bound on the driving force at match *ijk*, mass or amount fraction, [-]
U^{MAX} = maximum number of units in the MEN, [-]
U^{MIN} = minimum number of units in the MEN, [-]
K_W = sizing coefficient according to Hallale,[14] [1/s]
c_j = cost coefficient of lean stream *j*, [($ s)/(kg yr)] or [($ h)/(kmol yr)]
w = weighting coefficient, [-]

Binary Variables

$bz_{i,j,k}$ = binary variable denoting the existence of match *ijk*

Positive Variables

R_i = flow rate of rich stream *i*, [kg/s] or [kmol/h]
$y_{i,k}$ = concentration of rich stream *i* at concentration location *k*, mass fraction or amount fraction, [-]
$me_{i,j,k}$ = rate of exchanged mass at match *ijk*, [kg/s] or [kmol/h]
L_j = flow rate of lean stream *j*, [kg/s] or [kmol/h]
$x_{j,k}$ = concentration of lean stream *j* at concentration location *k*, mass fraction or amount fraction, [-]
$z_{i,j,k}$ = "relaxed" binary variable denoting the existence of match *ijk*
$dy_{i,j,k}$ = driving force, mass fraction or amount fraction, [-]
$lmcd_{i,j,k}$ = logarithmic mean concentration difference, mass fraction or amount fraction, [-]
$mass_{i,j,k}$ = mass of the exchanger unit at match *ijk*, [kg]
$pz_{i,j,k}$ = positive deviance, [-]
$sz_{i,j,k}$ = negative deviance, [-]
N_{units} = number of units, [-]
H_t = height of packed columns, [m]
D = diameter of packed columns, [m]

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