Optimal Solvent Design for Batch Separation Based on Economic Performance

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A mixed-integer dynamic optimization (MIDO) framework for solvent design in batch processes is presented. Performance measures reflecting process economics and computed on the basis of process dynamics are used to validate candidate solvent structures built from the UNIFAC molecular groups. These define the discrete space in the overall material formulation and are combined according to molecular design feasibility rules to guarantee realistic molecular representations. The algorithm is based on the decomposition of the MIDO primal subproblem into several steps that are solved successively. This allows unsuitable solvents to be detected and discarded quickly and without significant computational cost. Emphasis is placed on problem formulation in order to match accuracy of process model and physical property predictions. The algorithm is applied successfully to an industrial case study dealing with a three-phase dehydration column and a decantation unit for solvent recovery. The proposed algorithm can be regarded as a promising initial step toward an integrated and simultaneous methodology for material process design in batch separation systems.

Introduction

Solvent design has attracted significant interest over the last two decades, not only because of the important role of solvents in process operations, but also because of the need to find substitutes for previously used solvents due to environmental, safety, and health regulations. New solvent selection criteria have been introduced, and more systematic and automated approaches to the problem have been or are being developed (Achenie et al., 2003). Thanks to technological advances in computer systems and to extensive research on molecular structure-based physical property estimation methods (such as group contribution methods), it is now possible to design simple molecules and computer-aided molecular design techniques (CAMD) are being used by some industrial practitioners. These molecular design methods are based on the fact that from a small set of structural groups a large number of molecules can be generated and evaluated with respect to a certain performance index.

Two types of performance indices can be identified. The first focuses on *solvent performance*, either by considering physical property targets as defined by Maranas (1996), or by considering solvent-performance measures that are process-dependent, such as selectivity or capacity (Odele and Macchietto, 1993). Most of the work on solvent design to date falls in this category. The second type of index that can be considered is a measure of *process performance*. In this approach priority is given to the overall solvent effect on the operation of the process, which allows task-level details and characteristics to be accounted for during the solvent selection procedure. It therefore leads to a tighter integration of process

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operation and solvent design and provides a more rational basis for making solvent choices. Buxton et al. (1999), Hostrup et al. (1999), Marcoulaki and Kokossis (2000b), and Buxton (2002) have studied such problems for the case of steady-state processes.

Computer-aided molecular design techniques can be further classified in terms of their solution algorithm into “generate and test” and optimization-based methods. Generate and test approaches (Gani and Brignole, 1983; Brignole et al., 1986; Joback and Stephanopoulos, 1989; Porter et al., 1991; Gani et al., 1991; Constantinou and Gani, 1994; Pretel et al., 1994; Constantinou et al., 1996; Modi et al., 1996; Harper et al., 1999; Hostrup et al., 1999; Harper and Gani, 2000) are based on the formation of all possible molecular structures from a specified set of building groups (generation step) and the screening of the generated molecules according to molecular design feasibility rules and preselected target physical property values (test step). In optimization methods (Macchietto, et al., 1990; Odele and Macchietto, 1993; Venkatasubramanian et al., 1994; Vaidyanathan and El-Halwagi, 1996; Maranas, 1996, 1997; Duvedi and Achenie, 1996; Churi and Achenie, 1996, 1997; Ismail et al., 1997; Pistikopoulos and Stefanis, 1998; Buxton et al., 1999; Vaidyaraman and Maranas, 1999; Marcoulaki and Kokossis, 2000a, 2000b; Barlatier, 2000; Buxton, 2002), optimal molecular structures are determined by formulating and solving an optimization problem of the form

$$\begin{aligned} \min_{n,x} / \max_{n,x} \quad & p(n,x) \\ \text{s.t.} \quad & h(n,x) = 0 \\ & g(n,x) \le 0 \\ & x \in \Re^N \\ & n \in \mathfrak{N}^r \end{aligned} \tag{1}$$

where p is the objective function expressing the performance index; h is a set of equality constraints, including molecular design feasibility rules, process model equations, and structure–property relationships (such as group contribution methods); g is a set of inequality constraints representing physical property, design, and process operation specifications; x is an N-dimensional vector of continuous variables (temperature, compositions, flow rates, etc.); and n is an r-dimensional vector of integer variables representing the number of each structural group in the designed molecule. One of the features of optimization is that it relies on an implicit search through all possible molecular structures. This is especially important when the performance criterion requires expensive calculations such as dynamic simulations or optimizations. On the other hand, due to the highly nonlinear nature of the problem, global solutions cannot be guaranteed unless global optimization algorithms are used (Sinha et al., 1999).

In this article, we propose a solvent selection methodology for batch processes that employs a *process performance* index computed on the basis of process dynamics. Our study is based on the work of Buxton et al. (1999), who developed such a methodology for steady-state processes in the context of the methodology for environmental impact minimization (MEIM) proposed by Pistikopoulos and Stefanis (1998). This approach allowed the optimization of the choice of solvent blends at the plantwide level. In particular, they formulated the problem as a mixed-integer nonlinear program (MINLP), with process performance being measured in terms of overall environmental metrics and proposed a stepwise decomposition-based solution algorithm. In this work, we focus entirely on monetary process performance indices. However, it is possible to consider other criteria—involving, for instance, environmental or safety aspects—by incorporating the proposed approach within a multiobjective framework (Stefanis et al., 1996).

A general mixed-integer dynamic optimization (MIDO) framework, suitable for solvent selection in batch separation applications is presented in the next section. The article continues with the proposed solution strategy, which is based on decomposition principles to reduce the complexity of the problem. In the last section the algorithm is demonstrated with a case study considering the selection of a solvent for a three-phase batch-dehydration column and decantation system.

Problem Statement

Problem description

The optimal solvent design problem for batch processes can be defined as follows:

Given

(1) A batch process requiring a solvent,
(2) A set of structural molecular groups, and
(3) A process performance index,

Find

(1) the solvent (combination of structural groups), and
(2) the operating policy

that achieve optimal process performance.

Since it is desirable to select candidate solvent molecules based on process performance indices to better integrate solvent design and process operation, the need for a sufficiently detailed process model, which enables the performance index to be calculated, is a key issue. In order to formulate the problem, the following additional information is thus required:

- A dynamic model of the batch process under consideration;
- Group-contribution methods for the prediction of the thermophysical properties appearing in the model; and
- A set of molecular feasibility rules to discard physically meaningless combinations of the groups.

Problem formulation

The optimal solvent design problem for batch processes, as described earlier, can be classified as a MIDO program. The differential equations appear due to the batch process model, and the integer variables represent the type and number of structural groups occurring in the optimal solvent molecule. Based on the general formulation for MIDO problems (Schweiger and Floudas, 1997; Bansal et al., 2000, 2002), the following general mathematical model is proposed for the solvent design case

$$
\begin{aligned}
\min_{u(t),d,n,y} \quad & J\left(\dot{x}_d(t_f), x_d(t_f), x_a(t_f), u(t_f), d, n, y, t_f\right) \\
\text{s.t.} \quad & h_d\left(\dot{x}_d(t), x_d(t), x_a(t), u(t), d, n, y, t\right) = 0, \\
& \hfill \forall t \in \left[t_0, t_f\right] \\
& h_a\left(x_d(t), x_a(t), u(t), d, n, y, t\right) = 0, \\
& \hfill \forall t \in \left[t_0, t_f\right] \\
& h_0\left(\dot{x}_d(t_0), x_d(t_0), x_a(t_0), u(t_0), d, n, y, t_0\right) = 0 \\
& h_p\left(\dot{x}_d(t_i), x_d(t_i), x_a(t_i), u(t_i), d, n, y, t_i\right) = 0, \\
& \hfill t_i \in \left[t_0, t_f\right], \quad i = 1, \ldots, N \\
& g_p\left(\dot{x}_d(t_i), x_d(t_i), x_a(t_i), u(t_i), d, n, y, t_i\right) \le 0, \\
& \hfill t_i \in \left[t_0, t_f\right], \quad i = 1, \ldots, N \\
& h_q(d, n, y) = 0 \\
& g_q(d, n, y) \le 0 \\
& x_d, x_a, u, d, n \in \Re^l \\
& y \in \{0,1\}^q
\end{aligned}
\tag{2}
$$

where $h_d = 0$ are differential equations arising from the process model; $h_a = 0$ are algebraic equations arising from the process and physical property model equations that must hold at all times (path constraints); $h_0 = 0$ is the set of initial conditions; $h_p = 0$ and $g_p \le 0$ represent the set of process specifications that must be satisfied at specific time instances, in the form of point equalities and inequalities, respectively; $h_q = 0$ are time-invariant equalities that include part of the physical property model and some molecular design feasibility rules; $g_q \le 0$ are time-invariant inequality constraints that include part of the process specifications and the remaining molecular design feasibility rules; $x_d(t)$ is the vector of state variables; $x_a(t)$ is the vector of algebraic variables; $u(t)$ is the vector of time-varying control variables; d is the vector of time-invariant continuous-search variables (that may include the final time t_f); n is the vector of time-invariant variables representing the number of each group in the solvent molecule; and finally, y is a set of binary variables used to constrain the n variables to integer values.

The development of MIDO algorithms is an active research area with a wide range of applications, including optimal design of robust dynamic systems (Samsatli et al., 1998), reduction of kinetic mechanisms (Androulakis, 2000), synthesis of reaction-separation systems (Balakrishma and Biegler, 1993), optimization of hybrid systems (Avraam et al. 1998, 1999), analysis of dynamic systems under uncertainty (Dimitriadis and Pistikopoulos, 1995), simultaneous design and control (Mohideen et al., 1996; Schweiger and Floudas, 1997; Kookos and Perkins, 2001; Bansal et al., 2002), control structure selection (Naraway, 1992), design of multicomponent batch distillation columns (Sharif et al., 1998), and design and operation of batch processes (Allgor and Barton, 1999; Allgor et al., 1999).

Issues in Problem Formulation. The validity of the optimal solvent identified depends on the accuracy and mathematical complexity of the different elements in the overall model. The accuracy of the model and the tightness of the constraints determine whether the set of top molecules identified through optimization contains or does not contain the true optimal solvent(s). The complexity of the mathematical formulation may require the development of tailored solution strategies and approximations in the solution.

Choice of Atom Groups. The set of structural atom groups should be chosen in view of the trade-off between computational complexity and solvent diversity. Use of molecular design feasibility rules can reduce the combinatorics of the problem without affecting the active search area. The limitations of the group-contribution methods used should be taken into consideration. For instance, when first-order methods are used, the search should be restricted to simple molecules, consisting of no more than 10 to 12 groups and with at most two functional groups. When, on the other hand, the formulation is capable of handling higher-order group-contribution methods (Constantinou and Gani, 1994; Marrero and Gani, 2001), then the search area can be expanded to cover more complex and larger molecules.

Choice of Dynamic Process Model. A dynamic process model must be used to model batch processes. There is a trade-off to be made between the detail in the dynamic process model, the accuracy in the physical property predictions, and the efficiency and robustness of the solution of the optimization problem. A more detailed process model requires additional property-based equations and possibly new properties, which may increase the complexity of the mathematical problem without significantly improving the results. If first-order group-contribution methods are used, the results may lack in accuracy and reliability. If, on the other hand, higher-order methods are used, the accuracy and reliability may improve, but problems related to the formulation and solution of the optimization problem arise due to an increased number of binary variables and equations (Churi and Achenie, 1996; Raman and Maranas, 1998; Apostolakou and Adjiman, 2003). The use of valid assumptions to simplify the model with a minimum loss of information is thus desirable.

Choice of Performance Index. The performance index (objective function) should be selected according to the specifications of the process and may be either single-objective or multiobjective. Proper selection of the weighting factors in multiobjective problems is of great importance in order to obtain meaningful results.

Solution Strategy

The overall solution strategy that we propose here for the optimal selection of solvents in batch processes is developed based on the work of Bansal et al. (2000) on MIDO algorithms and that of Buxton et al. (1999) on solvent design for steady-state operations.

According to Bansal et al. (2000) the overall problem can be decomposed into a primal, dynamic optimization, and a master mixed-integer linear subproblem, as shown in Figure 1. In the primal problem the solvent structure, represented by binary variables, is fixed and process operation is optimized. New solvent structures are obtained by solving the master problem. Following the principles of generalized Benders decomposition (Geoffrion, 1972), the two problems are solved iteratively, generating upper and lower bounds, re-

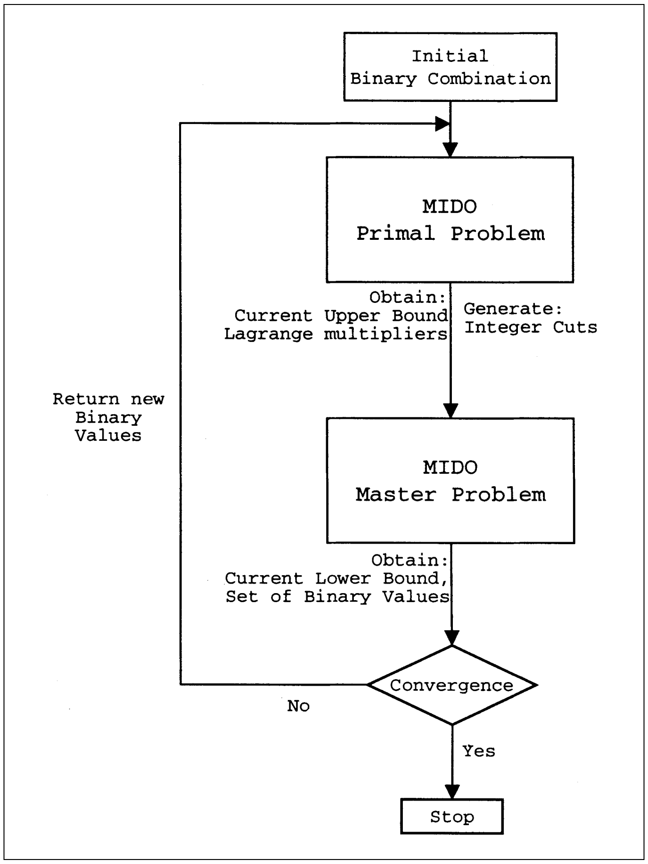

Figure 1. MIDO algorithm proposed by Bansal et al. (2002).

spectively, on the solution of the overall problem until convergence is achieved.

Experience has shown (Buxton et al., 1999; Buxton, 2002) that when detailed process models are included in the formulation of a solvent design application, the primal problem becomes very complex and expensive to solve. One major difficulty stems from the fact that the solvent structure changes from iteration to iteration, thus affecting greatly the phase behavior of the process mixture. In a separation process, for instance, it is possible for some candidate solvents to form one liquid phase with the process mixture only, while other candidate solvents may form two liquid phases. Furthermore, it should be noted that many candidate solvents are likely to violate the process requirements so that a large number of MIDO primal problems are infeasible. This results in a substantial computational effort, since each infeasible primal problem requires the solution of a large dynamic infeasibility minimization problem, as detailed in Bansal et al. (2002).

In order to avoid this time-consuming procedure, a decomposition-based algorithm is used. This algorithm is an extension to MIDO problems of the approach proposed by Buxton et al. (1999) for MINLPs arising in solvent design. Its main feature is the decomposition of the primal problem into several steps that are solved in series so as to initialize the overall primal problem. The order in which these steps are executed is such that inappropriate solvent molecules ("infeasible solvents") can be detected quickly and without significant computational effort and time. The overall solution strategy is presented in Figure 2. The main steps are described in the remainder of this section.

Integer initialization

The first step of the algorithm requires as an initial guess an integer combination $y^{(1)}$ that meets the molecular feasibility constraints. In the case of a solvent replacement problem, the solvent used on the process can be taken as an initial guess.

The kth iteration of the algorithm is now considered, and the relevant combination of the integer variables is denoted by $y^{(k)}$.

Step 1 of the primal problem

In the first step of the primal problem, several physical property tests are performed. These problem-dependent tests account for requirements, assumptions, or simplifications made in the development of the dynamic process model. Their role is to increase the efficiency of the algorithm by detecting infeasible primal problems without expensive calculations. The solvent structures that fail are physically inappropriate for the process under consideration.

If the candidate solvent fails one of the tests, it is deemed unsuitable for the process and the overall primal problem is classified as infeasible. Because it would be very expensive to solve a large dynamic infeasibility minimization problem (Bansal et al., 2002), a property test failure causes the algorithm to move directly to a reduced MILP master problem, which produces a new set of integer variables $y^{(k+1)}$. This reduced MILP can be solved readily. The integer combination $y^{(k)}$ that failed the physical property tests is added as an integer cut in both the reduced and the MIDO master problem. It is worth noting that the algorithm can function without these property tests, but with the possible additional cost of solving infeasible primal problems.

If the solvent candidate passes the tests, the first step is also used to calculate the primary properties of the solvent. Primary properties are those that depend only on molecular structure information (Constantinou and Gani, 1994). Critical properties, normal boiling point, and acentric factor are examples of such properties. They can then be fixed for the rest of the primal problem, thus simplifying the dynamic problem formulation.

Step 2 of the primal problem

The molecular structures that successfully complete all the physical-property tests proceed to step 2 of the primal problem. In this step three components of the process model are initialized successively: first the physical property models, then the phase equilibrium calculations (if necessary), and finally the material and energy balances. This is the most time-consuming step of the algorithm, since the solvent structure changes from iteration to iteration, leaving limited space for automation or reutilization of information from previous iterations. In this step, dynamic simulations of the model are performed by varying the values of the decision variables ($u(t)$

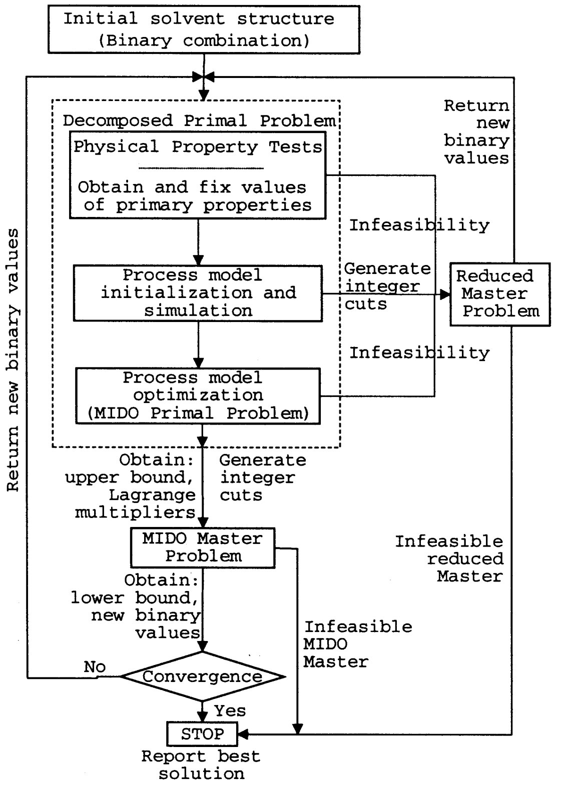

Figure 2. Stepwise Decomposition-based optimal solvent selection algorithm for batch processes.

and d) in order to obtain good initial guesses and bounds for the optimization that will follow. If an initialization or simulation failure occurs, the algorithm moves directly to the reduced master problem, which produces a new set of integer variables $y^{(k+1)}$. The molecular structure $y^{(k)}$ is added as an integer cut in both the reduced and the MIDO master problem.

Step 3 of the primal problem

In this step, the primal problem of the MIDO algorithm is solved according to the procedure proposed by Bansal et al. (2000) as follows:

Step 3.1. Fix the binary variables $y = y^{(k)}$ and the primary properties calculated in step 2. Solve problem (2) consisting of the dynamic process model, the physical-property estimation equations for secondary properties, the process specification constraints, and the equations relating $n^{(k)}$ to the binary variables, y. Since molecular design feasibility rules are pure integer/binary constraints (including only n and y), they are included in the master problem and are thus satisfied by definition. They can therefore be excluded from the primal problem. An upper bound, $J^{(k)}$, on the solution to the overall problem is obtained from the minimum of all the primal solutions obtained so far.

Step 3.2. Re-solve the primal problem starting from the optimal solution with additional constraints of the form $y^{(k)} - \bar{y}^{(k)} = 0$, where $y^{(k)}$ has now become a set of continuous search variables and $\bar{y}^{(k)}$ is the set of binary variables, which are fixed at the current solvent structure. Convergence to the same solution as in step 3.1 is achieved in one iteration, and the Lagrange multipliers $w^{(k)}$ corresponding to the new additional constraints $(y^{(k)} - \bar{y}^{(k)} = 0)$ are obtained. We should note here that by reformulating the problem in such a way the original binary variables, $y^{(k)}$, are relaxed, but are still forced to take integral values by the addition of the time-invariant constraints $y^{(k)} - \bar{y}^{(k)} = 0$. Multipliers are needed only for these constraints, and thus no intermediate adjoint problem needs to be solved.

If the dynamic optimization problem is infeasible, the algorithm moves directly to the reduced master problem, which reinitializes the y variables. The offending molecular structure is added as an integer cut in both the reduced and the MIDO master problem.

Master problems

Two mixed-integer linear-programming (MILP) master problems are included in the algorithm: the conventional MIDO master problem and the reduced master problem for the reinitialization of the y variables in the case of an infeasible primal problem.

The MIDO Master Problem. The kth MIDO master problem is constructed from the kth primal solution, $J^{(k)}$, the Lagrange multipliers, $w^{(k)}$, and the molecular design feasibility rules. Integer cuts are added to prevent previous integer solutions from being generated. The MIDO master problem is used only after a feasible primal problem. New molecular structures and lower bounds are generated from its solution. It is of the following form

$$\begin{aligned} \min_{n,\bar{y}} \quad & r(n, \bar{y}) \\ \text{s.t.} \quad & h_q(n, \bar{y}) = 0 \\ & g_q(n, \bar{y}) \le 0 \\ & n \in \Re^l \\ & \bar{y} \in \{0, 1\}^q \end{aligned} \tag{3}$$

The Reduced Master Problem. The reduced master problem is called whenever an infeasibility is found in any of the steps of the primal-problem solution. The reduced master problem is constructed from the molecular design feasibility rules and a simple objective function, $r(n, \bar{y})$, usually formulated on the basis of physical knowledge of the problem to guide the search toward suitable molecular structures. No primal-problem information is included in the reduced master problem. Finally, integer cuts are added to prevent previous integer solutions from recurring.

Instead of using a reduced master problem, integer cuts could be added to the MIDO master problem for every unsuitable solvent structure, despite the fact that no dual information is obtained from infeasible primal problems. In this work, only the use of the reduced master problem is considered.

Convergence

A conventional convergence criterion is employed (Buxton et al., 1999). The upper bound is updated only if the MIDO primal problem reaches an optimal solution, and the lower bound is updated only if the MIDO master problem reaches an optimal solution. Convergence is checked after every iteration that generates new bounds. If it is not achieved or if the reduced master is used, the decomposed primal problem is solved using the new molecular structure generated from the solution of one of the master problems. Finally, if any of the master problems becomes integer infeasible, the algorithm automatically stops reporting the minimum upper bound found.

In the next section, a case study is used to demonstrate the application of the framework discussed so far. Emphasis is placed on the formulation of the problem and the construction of the overall algorithm.

Case Study

Process description

The case study to be presented here is based on a separation system from an existing batch process. It consists of a batch-distillation (dehydration) column followed by a decantation unit. The feed to the separation system is a reaction product stream consisting of two main components: 17.45 kmol of water and 39.90 kmol of dimethyl acetamide (DMAC). Other components in the feed can be ignored due to their relatively low concentrations and the fact that they do not influence the water/DMAC phase equilibria much. Since water hydrolizes DMAC and DMAC is used as a solvent in a subsequent reaction step, the goal of the separation unit is to remove most of the water from the mixture. An important process constraint arises from the knowledge that the hydrolysis of DMAC is strongly activated at temperatures exceeding 390 K. This is a limiting factor for the effective operation of the atmospheric distillation column: the normal boiling points of water (373 K) and DMAC (439 K) and the mixture composition at the beginning of the batch distillation (30.4% mol of water) do not allow the removal of much of the water at temperatures lower than 390 K, while at higher temperatures the reaction starts to take place at very high rates, resulting in unnecessary losses of DMAC.

The introduction of an additional component, which will be referred to as "the solvent", can be proposed to enhance the operation of the distillation column. More specifically, the solvent should allow the efficient separation of water and DMAC at temperatures below 390 K and with minimum DMAC losses. Efficiency is of particular importance in this case, since the separation unit under consideration is the bottleneck in the overall batch process. Since water is more volatile than DMAC, it will leave the column from the top along with the solvent. A decanter that operates at 298 K is available for the recovery of the solvent. This enforces the additional requirement that water and solvent should form two almost pure liquid phases inside the decanter. DMAC and the rest of the solvent will remain in the reboiler at the end of the batch. In order to facilitate further processing, no more than 20 kmol of solvent and 9 kmol of water should be left in the reboiler. The state task network of the separation section is shown in Figure 3.

Since the separation section is a bottleneck in the overall process, a solvent that achieves the above specifications in the minimum possible batch time is sought. In order to formulate this problem, the process must first be described in more detail.

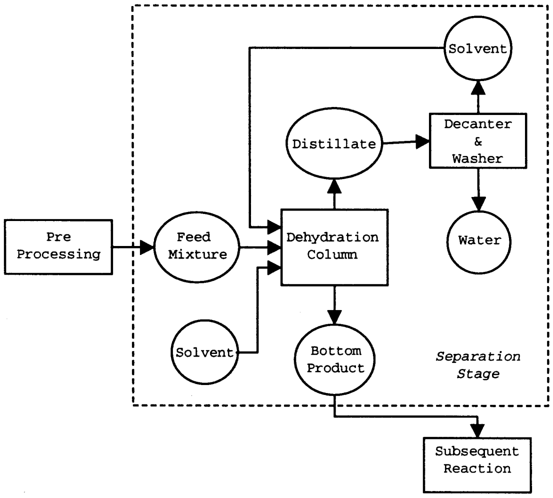

Figure 3. State task network of the dehydration–decantation separation unit for the removal of water from the feed mixture.

The solvent and feedstream are charged in the reboiler (still pot) of the dehydration column. The mixture is heated to its boiling point, and vapor consisting of water, solvent, and small amounts of DMAC makes its way up the column. At the top of the distillation column the vapor stream enters a total condenser. Part of the distillate is pumped back to the column as liquid reflux, while the rest goes to the decanter, where the solvent is recovered. Some key points on the operation of the separation section are noted below:

- There is no reflux at the beginning of the startup phase, and thus the column operates like a simple still pot, giving rather poor separation. Most of the DMAC losses take place during that period.
- During normal operation of the dehydration column, two liquid phases should coexist in the column trays, since the solvent has to be partially miscible with water in order for separation between water and solvent to be achieved effectively inside the decanter.
- The smaller the mutual solubilities of water and solvent are, the shorter the duration of the decantation.
- The decanter is configured such that the solvent is recovered as the top product. As a result, its density should be lower than the density of water.
- The partial miscibility of water and the solvent is also important for the solvent washing step, which follows the decantation step.
- The reboiler heating duty is provided by steam at 420 K. Availability of steam is not a limiting factor in the operation of the column.

The process specifications are summarized in Table 1. The separation batch time consists of the batch distillation time and the decantation and washing times. The batch distillation time depends mainly on the solvent and its initial composition in the reboiler and on the heating policy in the reboiler, while the decantation and washing times depend mostly on the degree of partial miscibility between the solvent and water.

Problem formulation

The optimal solvent selection problem for this case study is formulated as a MIDO of form (2) and in accordance with the requirements of the solution strategy proposed in the previous section. The overall formulation consists of:

(1) The dynamic process model;

(2) Structure–property relationships (group contribution methods);

(3) Molecular design feasibility rules;

(4) Process specifications;

(5) Physical property tests, and

(6) A process performance measure to be optimized (objective function).

During the detailed development of the model that follows, emphasis is placed on the assumptions made and their impact on the results. The batch distillation is the only part of the process that is modeled dynamically, as it has the largest impact on time.

Dynamic Process Model. The column is modeled as a plate column and consists of five equilibrium stages, a reboiler (still pot), and a condenser.

General assumptions. The following assumptions are made:

- Both thermal and phase equilibria hold on each plate. The vapor phase is assumed to be ideal, while the nonidealities in the two liquid phases are treated through component liquid activity coefficients calculated with the UNIFAC model (Fredenslund et al., 1975).
- The reaction between DMAC and water is neglected during the dehydration step, as the operating temperature remains below 390 K everywhere.
- Constant pressure and negligible vapor holdup on all trays are assumed. According to Wittgens (1999), these are common assumptions in distillation column modeling.
- The energy balance is neglected and a constant vapor flow of 3 kmol/h is assumed.
- The condenser is modeled together with the reflux drum as an equilibrium tray (Sørensen, 1994). Total condensation with no subcooling and perfect control of the reflux drum level are assumed.

Column Operation. The operation of the column is considered in two distinct phases, "startup" and "normal operation".

Startup Phase. Since the startup of the batch column leads to the largest DMAC losses, and its duration is not negligible, it is included in the overall model. At the beginning of the batch, all trays, the condenser and the reflux drum are empty. Vapor leaves the reboiler and makes its way up the column until it reaches the condenser. The column trays are then filled with liquid from the top to the bottom, and phase equilibrium starts to hold on each tray from the time it is filled (Sørensen, 1994). The column is not run at total reflux during the initial period of operation, as a significant amount of water can be removed during that time. However, the DMAC losses are constrained by specifying a limit of 0.3 kmol DMAC in the overall batch distillate. This dictates the minimum value of the reflux ratio. The modeling of the startup period causes discontinuities in the expressions for the liquid flows and vapor compositions. Smooth approximations based on hyperbolic tangent functions, proposed by Samsatli et al. (1998), are used to overcome this problem.

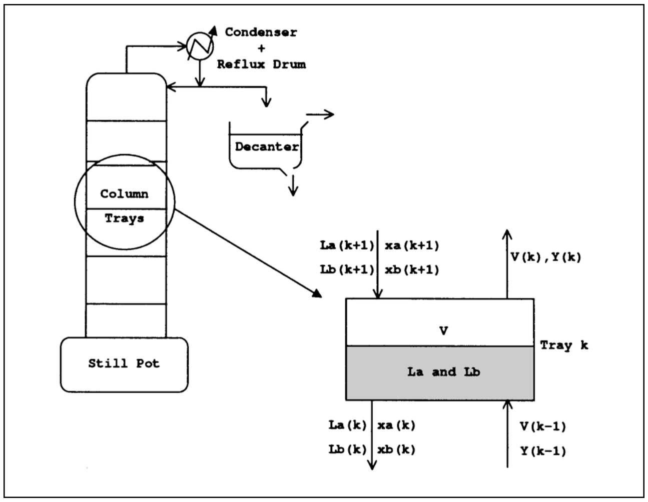

Figure 4. Column tray with two liquid phases *a* and *b*.

Normal Operation Phase. Phase equilibrium starts to hold on each tray after it is filled, and liquid holdups are assumed to be constant during normal operation of the column. In this case, it can be assumed that coexistence of two perfectly mixed liquid phases holds for each stage. The presence of two phases is expected, since the solvent has to be partially miscible with water for separation via decantation to be possible, and these two compounds are dominant in the column tray section. In the still pot, however, only one liquid phase exists and is modeled.

Process Model. The mathematical model of the batch distillation column is based on the preceding assumptions and the work of a number of authors (Sørensen, 1994; Wittgens, 1999; Pantelides, 2000). The notation is listed at the end of this article. A column tray is shown in Figure 4.

Reboiler:

Mass balance for component $i = 1, \ldots, NC$

$$\frac{d}{dt}(M_{reb,i}) = L_1^a x_{1,i}^a + L_1^b x_{1,i}^b - V_{reb} y_{reb,i} \tag{4}$$

Component holdup for $i = 1, \ldots, NC$

$$M_{reb,i} = x_{reb,i} M_{reb} \tag{5}$$

Total holdup

$$\sum_{i=1}^{NC} M_{reb,i} = M_{reb} \tag{6}$$

Trays $k = 1, \ldots, NT$ from bottom and up:

Mass balance for component $i = 1, \ldots, NC$

$$\frac{d}{dt}(M_{k,i}) = V_{k-1} y_{k-1,i} + L_{k+1}^a x_{k+1,i}^a + L_{k+1}^b x_{k+1,i}^b - V_k y_{k,i} - L_k^a x_{k,i}^a - L_k^b x_{k,i}^b \tag{7}$$

Component holdup for $i = 1, \ldots, NC$

$$M_{k,i} = x^a_{k,i} M^a_k + x^b_{k,i} M^b_k \tag{8}$$

Total holdup

$$M^a_k + M^b_k = M_k \tag{9}$$

Total condenser and reflux drum:

Mass balance for component $i = 1, \ldots, NC$

$$\frac{d}{dt}(M_{d,i}) = V_{NT} \cdot y_{NT,i} - L^a_d x^a_{d,i} - L^b_d x^b_{d,i} - D^a x^a_{d,i} - D^b x^b_{d,i} \tag{10}$$

Component holdup for $i = 1, \ldots, NC$

$$M_{d,i} = x^a_{d,i} M^a_d + x^b_{d,i} M^b_d \tag{11}$$

Total holdup

$$M^a_d + M^b_d = M_d \tag{12}$$

Vapor flows for $k = 1, \ldots, NT$ (constant)

$$V_k = V_{reb} \tag{13}$$

$$V_{reb} = C_1 \tag{14}$$

Liquid flow for $k = 1, \ldots, NT, d$; startup phase is considered

$$L_k = L^a_k + L^b_k \tag{15}$$

$$L_k = V_k \cdot Rfx \cdot \left[1 + \tanh\left(C_2\left(M_k - M_{\mathrm{spec},\boldsymbol{k}}\right)\right)\right] \tag{16}$$

$$\frac{L^a_k}{L_k} = \frac{M^a_k}{M_k} \tag{17}$$

Distillate flow; startup phase is considered

$$D = D^a + D^b \tag{18}$$

$$D = V_{NT} \cdot (1 - Rfx) \cdot \left[1 + \tanh\left(C_2\left(M_d - M_{\mathrm{spec},\boldsymbol{d}}\right)\right)\right] \tag{19}$$

$$\frac{D^a}{D} = \frac{M^a_d}{M_d} \tag{20}$$

Vapor composition for $k = 1, \ldots, NT, d$ and $i = 1, \ldots, NC$; initial phase is considered

$$y_{k,i} = y_{reb,i} \cdot \left[1 - \left(1 + \tanh\left(C_2\left(M_k - M_{\mathrm{spec},\boldsymbol{k}}\right)\right)\right)\right] + y^{eq}_{k,i}\left[1 + \tanh\left(C_2\left(M_k - M_{\mathrm{spec},\boldsymbol{k}}\right)\right)\right] \tag{21}$$

Phase equilibrium equations:

Reboiler (one liquid phase)

$$y_{reb,i} P_{reb} = x_{reb,i} P^{\mathrm{sat}}_{reb,i} \gamma_{reb,i}, \qquad \forall\, i = 1, \ldots, NC \tag{22}$$

$$\sum_{i=1}^{NC} y_{reb,i} = 1 \tag{23}$$

Trays and condenser with reflux drum $k = 1, \ldots, NT, d$ (two liquid phases: phase a is rich in solvent and phase b is rich in water)

$$y^{eq}_{k,i} P_k = x^a_{k,i} P^{\mathrm{sat}}_{k,i} \gamma^a_{k,i}, \qquad \forall\, i = 1, \ldots, NC \tag{24}$$

$$y^{eq}_{k,i} P_k = x^b_{k,i} P^{\mathrm{sat}}_{k,i} \gamma^b_{k,i}, \qquad \forall\, i = 1, \ldots, NC \tag{25}$$

$$x^a_{k,s} \geq C_{\mathrm{low}} \tag{26}$$

$$x^b_{k,s} \leq C_{\mathrm{up}} \tag{27}$$

$$\sum_{i=1}^{NC} y^{eq}_{k,i} = \sum_{i=1}^{NC} x^a_{k,i} = \sum_{i=1}^{NC} x^b_{k,i} = 1 \tag{28}$$

Equations 26 and 27 are used to differentiate the two liquid phases, and more importantly, to prevent convergence to physically unstable or metastable phase compositions. The numerical values for the constants C_{low} and C_{up} are chosen during step 2 of the primal problem, when the phase-equilibrium model is initialized.

Physical Property Models. The physical property models used are well-known group contribution methods.

Pure Component Properties. The pure component properties can be divided into primary and secondary properties:

Primary properties:

Critical temperature (Constantinou and Gani, 1994)

$$\exp\left(T_c / t_{c0}\right) = \sum_{j=1}^{NG} n_j \cdot t_{c1,j} \tag{29}$$

Critical pressure (Constantinou and Gani, 1994)

$$\left(P_c - p_{c1}\right)^{-0.5} - p_{c2} = \sum_{j=1}^{NG} n_j \cdot p_{c3,j} \tag{30}$$

Critical volume (Constantinou and Gani, 1994)

$$V_c - v_{c0} = \sum_{j=1}^{NG} n_j \cdot v_{c1,j} \tag{31}$$

Normal boiling point (Constantinou and Gani, 1994)

$$\exp\left(T_b / t_{b0}\right) = \sum_{j=1}^{NG} n_j \cdot t_{b1,j} \tag{32}$$

Secondary properties:

Acentric factor (from Reid et al., 1987)

$$\omega = \frac{\alpha}{\beta} \tag{33}$$

$$\alpha = -\ln(P_c) - 5.97214 - \frac{6.09648}{T_{br}} - 1.28862 \ln T_{br} + 0.169347 T_{br}^6 \tag{34}$$

$$\beta = 15.2518 - \frac{15.6875}{T_{br}} - 13.4721 \ln T_{br} + 0.43577 T_{br}^6 \tag{35}$$

$$T_{br} = \frac{T_b}{T_c} \tag{36}$$

Vapor pressure (Lee Kesler equation, from Reid et al., 1987)

$$\log\left(P_i^{\text{sat}}/P_c\right) = f_0 + \omega f_1 \tag{37}$$

$$f_0 = 5.97214 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 T_r^6 \tag{38}$$

$$f_1 = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln T_r + 0.43577 T_r^6 \tag{39}$$

$$T_r = \frac{T}{T_c} \tag{40}$$

Molar density (HBT technique, from Reid et al., 1987)

$$V_s = V_c \cdot V_0 (1 - \omega V_1) \tag{41}$$

$$V_0 = 1 - 1.528168(1 - T_r)^{1/3} + 1.43907(1 - T_r)^{2/3} - 0.81446(1 - T_r) + 0.190454(1 - T_r)^{4/3} \tag{42}$$

$$V_1 = \frac{-0.296123 + 0.386914 T_r - 0.0427258 T_r^2 - 0.0480643 T_r^3}{T_r - 1} \tag{43}$$

Mixture Properties: Phase Equilibria Calculations. The UNIFAC model of Fredenslund et al. (1975) as reformulated by Buxton et al. (1999) is used to compute activity coefficients. The activity coefficient for component $i = 1, \ldots, NC$ is given by

$$\ln(\gamma_i) = \ln\left(\gamma_i^C\right) + \ln\left(\gamma_i^R\right) \tag{44}$$

Table 1. Process Specifications

Process Variable	Value
Column temperature	390 K maximum
Initial charge of water in the reboiler	17.45 kmol
Initial charge of DMAC in the reboiler	39.90 kmol
Overall DMAC mole fraction in distillate	0.3 %mol maximum
Amount of solvent in bottom product	20 kmol maximum
Amount of water in column at end of batch	9 kmol maximum

Combinatorial part

$$\ln\left(\gamma_i^C\right) = \ln(R_i) - \ln\left(\sum_{ii} x_{ii} R_{ii}\right) - 5Q_i \ln(R_i) - 5Q_i \ln\left(\sum_{ii} x_{ii} Q_{ii}\right) + 5Q_i \ln(Q_i) + 5Q_i \ln\left(\sum_{ii} x_{ii} R_{ii}\right) - 5Q_i + 1 + C_i \tag{45}$$

$$C_i = \left(5 \sum_{ii} x_{ii} Q_{ii} - 1\right) \frac{R_i}{\sum_{ii} x_{ii} R_{ii}} \tag{46}$$

Residual part

$$\ln\left(\gamma_i^R\right) = R1_i - R2_i \tag{47}$$

$$R1_i = Q_i - \sum_j n_{i,j} q_j \ln(R3_j) + Q_i \ln\left(\sum_{ii} x_{ii} Q_{ii}\right) - \sum_j \frac{R4_{i,j}}{R3_j} \tag{48}$$

$$R2_i = Q_i \ln(Q_i) - \sum_j n_{i,j} q_j \ln\left(\sum_{mj} q_{mj} n_{i,mj} \psi_{mj,j}\right) \tag{49}$$

$$R3_j = \sum_{mj} q_{mj} \sum_{ii} n_{ii,mj} x_{ii} \psi_{mj,j} \tag{50}$$

$$R4_{i,j} = \sum_{mj} n_{i,mj} q_{mj} q_j \sum_{ii} n_{ii,j} x_{ii} \psi_{mj,j} \tag{51}$$

Volume R_i and area Q_i parameters for component $i = 1, \ldots, NC$

$$R_i = \sum_j n_{i,j} r_j \tag{52}$$

$$Q_i = \sum_j n_{i,j} q_j \tag{53}$$

Interaction parameters between group mj and group j

$$\psi_{mj,j} = \exp\left(-a_{mj,j}/T\right) \tag{54}$$

Molecular Design Feasibility Rules. The number of occurrences of group $j = 1, \ldots, NG$ in the solvent molecule $n_{s,j}$ is defined in terms of binary variables

$$n_{s,j} = \sum_{l=1}^{l_{\max}} 2^{l-1} z_{l,j} \tag{55}$$

and constrained further as described below.

Only three types of molecules are allowed: acyclic ($m = 1$), cyclic ($m = 0$), and bicyclic ($m = -1$). This is expressed as

$$z1 + z2 + z3 = 1 \tag{56}$$

$$z1 - z3 = m \tag{57}$$

The octet rule is enforced (Macchietto et al., 1990)

$$\sum_{j=1}^{NG} (2 - u_j) n_{s,j} = 2 \cdot m \tag{58}$$

Two adjacent groups in a molecule cannot be linked by more than one bond. This is the bonding rule (as modified by Buxton et al., 1999)

$$\sum_{j=1}^{NG} n_{s,j} \geq n_{s,j}(u_j - 1) + 2m, \qquad \forall j = 1, \ldots, NG \tag{59}$$

Bounds on the total number of groups and the composition of each group in the solvent molecule are imposed

$$n_{\min} \leq \sum_{j=1}^{NG} n_{s,j} \leq n_{\max} \tag{60}$$

$$n_{j,\min} \leq n_{s,j} \leq n_{j,\max} \tag{61}$$

No more than one functional group in acyclic molecules is allowed

$$\sum_{j=1}^{NGF} n_{s,j} \leq z1 \tag{62}$$

Aromatic molecules have an aromatic ring

$$\sum_{j=1}^{NGA} n_{s,j} = 6 \cdot z2 \tag{63}$$

Other limitations on group numbers and combinations of groups can be taken into account in a similar manner.

Process Specifications. According to Table 1:

- The temperature in the reboiler should not exceed 390 K

$$T_{reb} \leq 390 \tag{64}$$

- The total amount of water in the reboiler and the column trays at the end of the batch should be at most 9 kmol

$$M_{reb,w} + \sum_{k=1}^{NT} M_{k,w} \leq 9 \tag{65}$$

- The total amount of solvent in the reboiler at the end of the batch should be at most 20 kmol

$$M_{reb,s} \leq 20 \tag{66}$$

- The DMAC composition in the batch distillate (DMAC losses) should not exceed 0.3% (mol)

$$\frac{\int_0^{t_f} M_{d,DMAC}}{\int_0^{t_f} \Sigma M_{d,i}} \leq 0.003 \tag{67}$$

Physical Property Tests. Three physical property tests are used in this case study: the boiling point test, the partial miscibility (or phase split) test, and the density test. The boiling-point test guarantees appropriate solvent molecules for the dehydration column, while the partial miscibility and density tests account for the decanter and washing unit, which are not included in the process model.

Boiling Point Test. The boiling point of the optimal solvent should be close to that of water

$$355 \leq T_{b,s} \leq 395 \tag{68}$$

Partial Miscibility or Phase Split Test. The test consists of an LLE calculation for the solvent–water mixture at the decantation temperature (298 K) with additional constraints on the mole fraction of each component in each phase

$$x_i^a \gamma_i^a = x_i^b \gamma_i^b, \qquad i = s, w \tag{69}$$

$$\sum_i x_i^a = 1, \qquad i = s, w \tag{70}$$

$$\sum_i x_i^b = 1, \qquad i = s, w \tag{71}$$

$$x_w^a \leq 0.05 \tag{72}$$

$$x_s^b \leq 0.05 \tag{73}$$

In setting these bounds, as well as the bounds on the boiling point, the uncertainty in the predictions of the calculated properties has been taken into account. Thus, we have chosen to enlarge the set of allowed solvents to avoid eliminating promising alternative solvents.

Density Test. The density of the solvent should be lower than the water density to allow the decanter configuration to be used

$$V_{s,s} \cdot M.W._s \leq V_{s,w} \cdot M.W._w \tag{74}$$

Objective Functions. According to the solution strategy proposed, two objective functions have to be formulated: one for the primal problem and one for the reduced master.

Primal Problem. As was mentioned before, the main bottleneck of the overall process is its duration. This can be estimated as the sum of the distillation batch time plus the decantation and washing times. An estimate for the distillation batch time can be obtained directly from its dynamic process model. However, this is not true for the decantation and washing steps, since their models have not been considered explicitly inside the formulation. However, their duration can be assumed negligible compared to that of the distillation batch time. So, the primal problem objective function contains only one term that is the distillation batch time. Decantation and washing times are considered indirectly by constraining the amount of solvent remaining in the reboiler at the end of the batch distillation, and by guaranteeing low mutual solubilities and density difference between the solvent and water through physical property tests. Restricting the amount of solvent remaining in the reboiler is expected to reduce the time needed for subsequent process steps, while the partial miscibility and density tests guarantee more efficient decantation and washing operations

$$OBJ_{\text{primal}} = t_f \tag{75}$$

Reduced Master Problem. The reduced master problem is used whenever an infeasible primal problem occurs and its main objective is to provide a new integer combination (molecular structure). The objective used here was simply to maximize the number of groups appearing in the solvent molecule

$$OBJ_{\text{rmaster}} = \sum_{j=1}^{NG} n_{s,j} \tag{76}$$

Capabilities of the Formulation. The proposed formulation is able to take into consideration:

(1) The duration of the dehydration in the batch column through a direct simulation;

(2) Part of the distillation column operating policy (startup and reflux ratio);

(3) Phase equilibrium issues related to solvent selection;

(4) Solvent and DMAC losses;

(5) Solvent capacity (through the amount of solvent needed to remove the water); and

(6) The feasibility of the solvent recovery in the decanter (partial miscibility and density tests).

On the other hand, the formulation cannot:

(1) Distinguish between isomers;

(2) Predict with great accuracy physical property values;

(3) Account explicitly for reactivity issues;

(4) Take into consideration the reboiler heating policy;

(5) Handle phase transitions inside the distillation column; and

(6) Be used for control studies.

Solution procedure and results

The solution algorithm for this case study is presented in Figure 5.

The three physical property tests expressed in Eq. 68 to Eq. 74 are solved together with Eq. 29 to Eq. 54. UNIFAC binary interaction parameters for the LLE calculations in the partial miscibility test are obtained from Magnussen et al. (1981). Initialization of the primal problem is performed in three successive stages: First, the UNIFAC model is initialized. Then VLLE calculations for the column trays and VLE calculations for the reboiler are performed. This ensures that the candidate solvent is consistent with the assumptions made in the modeling of the normal operation of the column. Finally, the material balances of the dynamic process model are initialized. UNIFAC binary interaction parameters for the VLE calculations are obtained from Gani (2001). In our experience, the most difficult and time-consuming stage is the initialization of the VLLE calculations. It is achieved by breaking the overall calculation into two separate VLE ones and solving them by putting bounds on the mole fraction of the solvent in the liquid phase. In this way, it is possible to distinguish between the two liquid phases: L_a and L_b. The solutions of the two VLE calculations are then used as initial guesses for the overall VLLE calculation. Another source of numerical difficulties is the hyperbolic tangent functions used for modeling the startup of the column. The steepness in the gradients deteriorates and significantly delays the performance of the integrator at the switching point between the startup period and normal operation. The overall model, which consists of the process model equations (Eq. 4 to Eq. 28), the appropriate physical property models (Eq. 29 to Eq. 54) and the process specifications (Eq. 64 to Eq. 67), is solved in step 3 of the primal problem, minimizing the distillation batch time (Eq. 75).

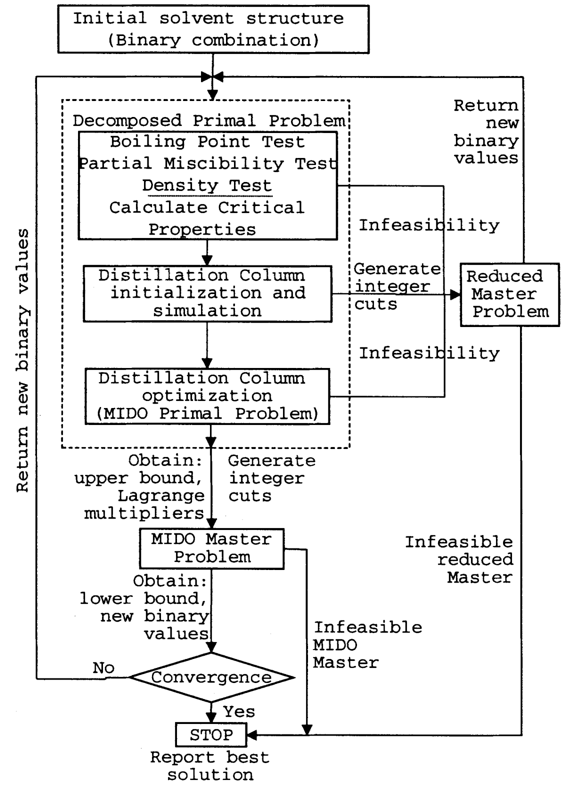

Figure 5. Optimal solvent selection algorithm for the case study.

The MIDO master problem is of the form shown in Eq. 3 where the equality and inequality constraints are the molecular-design feasibility rules (Eq. 55 to Eq. 63) together with the integer cuts generated from the primal problem. In the reduced master, Eq. 76 is maximized subject to the molecular design feasibility rules and integer cuts. Since the boiling point test can be formulated linearly by substituting Eq. 32 into Eq. 68, it was also included in the master problems, thus prohibiting inappropriate solvent molecules from occurring and re-

Table 2. Nine Groups Used in the Optimization Classified According to Their Chemical Type

Type	Groups
Main	CH_3, CH_2
Aromatic	ACH, $ACCH_3$
Functional	CH_3O, CH_2Cl, CH_3CO, CH_3N
Molecule	H_2O

ducing significantly the total computational time. In this case, the boiling-point test has to be performed for the initial solvent only, which is not generated from a master problem.

All physical property tests were performed in GAMS using CONOPT (Brooke et al., 1997), dynamic simulations and optimizations (steps 2 and 3 of the primal problem) were performed using gPROMS/gOPT (Process Systems Enterprise Ltd., 2000), and finally the two MILP master problems were solved using GMAS/CPLEX (Brooke et al., 1997).

The solvent structure search area was defined by all combinations between the nine UNIFAC groups appearing in Table 2. The set of functional groups was chosen with the aim of generating solvents that are partially miscible with water and nonreactive with the feed mixture. In addition, and in order to avoid the occurrence of complex molecules (since first-order group-contribution methods were used), no groups with valency greater than 2 were chosen. Finally, H_2O, CH_3CO, and CH_3N were used for the representation of water and DMAC to be possible.

Pentane was chosen as a first arbitrary guess. The algorithm converged in four iterations. All the steps are shown in Table 3. The optimal solvent was found to be toluene, with an objective value of 15.3 h. The performance of the optimal and some feasible solvent structures are presented analytically in Table 4. From this table, the estimated values for three primary properties (normal boiling point, critical temperature, and pressure) can be compared with those obtained from the literature (Reid et al., 1987), which proves to be of acceptable accuracy and within the reliability of the selected group contribution method (Constantinou and Gani, 1994). This is quite important, considering that the solvent's normal boiling point is itself one of the physical property tests and its reliability is crucial for the subsequent steps of the primal problem. Inaccurate predictions could result in misleading structures and therefore additional computational time.

The advantages of the decomposition of the primal subproblem and the utilization of a reduced master can be seen through an analysis of the progress of the algorithm (Table 3). A promising solvent structure, heptane (CH_3: 1, CH_2: 4), was easily determined after a rather bad initial guess, pentane (CH_3: 2, CH_2: 3), which failed the boiling point test. This yielded an upper bound (18.3) and a lower bound (16.2) at iteration 2. In the next iteration an undesirable structure, pentyl-methyl-ether (CH_3: 1, CH_2: 4, CH_3O: 1), was discarded quickly and without significant computational cost after violating the partial miscibility test. At the fourth iteration, toluene was shown to have a lower batch time (15.3 h), satisfying the convergence test and allowing the algorithm to terminate. The optimal solution was reached by solving only two full primal problems (dynamic optimizations). No attempt was made to solve the full primal problem for pentane and pentyl-methyl-ether, which are easily shown not to permit acceptable operation of the process. It is worth noting here that the discrete feasible region of both master problems was quite limited for this case study, since only nine groups were considered and since the boiling point test participated in the formulation. There were twelve feasible structures, and four of those could pass the physical property tests. However, even for this limited solution space the optimization algorithm investigated only half the structures in order to reach the solution.

The search was guided through the formulation of a meaningful primal problem objective function directly related to process economic performance. The overall framework proved to be flexible to accommodate and exploit effectively prior physical knowledge without loss of generality in terms of the solution. The inclusion of the linear boiling point test in the formulation of the two master problems illustrates exactly this feature. This guarantees the feasibility of each generated solvent with respect to its boiling point, and thus several infeasible primal problems are avoided.

Conclusions

In this article, we have presented a stepwise decomposition-based MIDO algorithm for solving solvent design problems for batch processes. Monetary process performance measures were studied, providing a strong basis for solvent selection. Furthermore, the methodology can be extended to handle more sophisticated indices dealing, for example, with

Table 3. Algorithm Steps for the Solution of the Case Study

		Primal Problem			Master Problem		Reduced Master	
Iteration	Solvent Structure	Prop. Tests	Initialization	Obj. Value	Structure	Obj. Value	Structure	Convergence
1	CH_3:2, CH_2:3	Fail	—	—	—	—	CH_3 : 2, CH_2 : 5	No
2	CH_3 : 2, CH_2 : 5	Pass	Pass	18.3	CH_3 : 1, CH_2 : 4, CH_3O: 1	— 16.2	—	No
3	CH_3 : 1, CH_2 : 4, CH_3O: 1	Fail	—	—	—	—	ACH: 5, $ACCH_3$: 1	No
4	ACH: 5, $ACCH_3$: 1	Pass	Pass	15.3	—	—	—	Yes

Table 4. Performance of the Optimal and Feasible Solvent Structures

	Toluene	Heptane
Molecular Structure	ACH: 5 $ACCH_3$: 1	CH_3 : 2 CH_2 : 5
Objective value	15.3	18.3
Batch duration (h)	15.3	18.3
Solvent feed (kmol)	27.8	32.9
Solvent consumption (kmol)	7.8	12.9
Solvent in bottom product (kmol)	20.0	20.0
Water in bottom product (kmol)	9.0	9.0
DMAC losses (% mol distillate)	0.3	0.2
Reflux ratio L/V	0.7	0.65
Maximum temperature in the reboiler (K)	391	370.5
Estimated density (kg/m^3 at 298 K)	879	700
Solubility at 298 K: solvent in water (% mol)	0.010	0.002
Solubility at 298 K: water in solvent (% mol)	0.200	0.080
Estimated normal boiling point (K)	386	379
Normal boiling point (K)	384	372
Estimated critical temperature (K)	597	550
Critical temperature (K)	592	540
Estimated critical pressure (Pa)	42×10^5	28×10^5
Critical pressure (Pa)	41×10^5	27×10^5

environmental (Buxton, 2002) or safety issues. Through consideration of model accuracy and computational cost management in the overall formulation and solution procedure, the algorithm can be applied successfully to an industrial case study, suggesting not only the best solvent structure but also the optimal operating policy when such a solvent is used.

Fixed process design was assumed all through this work, setting the proposed algorithm as a first successful step toward the development of integrated methodologies for the process/material design problem. As an intermediate step, design issues such as column diameter or number of trays can be incorporated in the optimization framework. In a more amibitious approach, decisions regarding process routes can be considered by defining alternatives according to physical property test results. In this way, the flexibility in resource utilization that batch processes offer can be effectively exploited. Of course, further developments of this methodology require the availability of more robust and efficient MIDO algorithms, since the complexity and the combinatorics of the problem will increase dramatically. The present work is a promising application of MIDO algorithms, and highlights both the versatility of MIDO formulations and the need for the development of new theories and algorithms for MIDO problems.

Notation

$a_{mj,j}$ = UNIFAC interaction parameter between group mj and j
C_2 = hyperbolic tangent coefficient (1,000 was used for the case study)
D = distillate flow rate, kmol/h
$l\max$ = determines the maximum composition of each group
L = liquid flow rate, kmol/h
m = chemical type (1 = acyclic; 0 = aromatic; −1 = bicyclic)
M = molar holdup, kmol
M.W. = molecular weight
$n_{i,j}$ = number of groups j in component i
NG = number of groups
NGA = number of aromatic groups
NGF = number of functional groups
NT = number of trays
$n_{i,j}$ = number of groups j in component i
OBJ = objective value
p_{c1} = universal constant used for GC calculations
p_{c2} = universal constant used for GC calculations
$p_{c3,j}$ = critical pressure of group j, Pa
P = pressure, Pa
P^{sat} = vapor pressure, Pa
P_c = critical pressure, Pa
q_j = Van der Waals area of group j
Q_i = Van der Waals area of component i
r_j = Van der Waals area of group j
R_i = Van der Waals volume of component i
Rfx = reflux ratio
$R1_i$ = modified residual activity coefficient of component i in the mixture
$R2_i$ = modified residual activity coefficient of component i in a reference solution containing only molecules of component i
t = time, h
t_{b0} = universal constant used for GC calculations
$t_{b1,j}$ = normal boiling point of group j, K
t_{c0} = universal constant used for GC calculations
$t_{c1,j}$ = critical temperature of group j, K
T = temperature, K
T_c = critical temperature, K
T_b = normal boiling point, K
T_{br} = normal boiling-point reduced temperature, K
T_r = reduced temperature
u_j = valency of group j
v_{c0} = universal constant used for GC calculations
$v_{c1,j}$ = critical molar volume of group j, m^3/kmol
V = vapor flow rate, kmol/h
V_c = critical volume, m^3/kmol
V_s = molar volume, m^3/kmol
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase
$z_{l,j}$ = binary variables
$z1$, $z2$, $z3$ = binary variables that determine the type of solvent molecule m

Greek letters

γ_i = activity coefficient of component i
γ_i^C = combinatorial part for the activity coefficient of component i
γ_i^R = residual part for the activity coefficient of component i
ω = acentric factor
$\psi_{mj,j}$ = UNIFAC interaction between groups mj and j

Subscripts

a = defines liquid phase a
b = defines liquid phase b
d = distillate
$DMAC$ = dimethyl acetamide
i,ii = index that denotes a component ($i \in \{s, w, DMAC\}$)
j = index that denotes a group
k = index that denotes a tray
l = index used to express the composition of each group with binary variables
mj = index that denotes a group
reb = reboiler
s = solvent
$spec$ = denotes a specified quantity
w = water

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Manuscript received Aug. 26, 2002, and revision received Apr. 8, 2003.