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Proceedings Paper:

Advances in Process Synthesis: New Robust Formulations

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ABSTRACT

We present new modifications to superstructure optimization paradigms to i) enable their robust solution and ii) extend their applicability. Superstructure optimization of chemical process flowsheets on the basis of rigorous and detailed models of the various unit operations, such as in the state operator network (SON) paradigm, is prone to non-convergence. A key challenge in this optimization-based approach is that when process units are deselected from a superstructure flowsheet, the constraints that represent the deselected process unit can be numerically singular (e.g., divide by zero, logarithm of zero and rank-deficient Jacobian). In this paper, we build upon the recently-proposed modified state operator network (MSON) that systematically eliminates singularities due to unit deselection and is equally applicable to the context of both simulation-based and equation-oriented optimization. A key drawback of the MSON is that it is only applicable to the design of isobaric flowsheets at a pressure fixed *a priori*. In this paper, as a first step towards the synthesis of general flowsheets with variable pressures, we extend the MSON to the synthesis of a gas-liquid absorption column at variable pressure (i.e., the pressure is a degree of freedom that may be optimized). We illustrate the use of the extended MSON on a carbon-capture process. The extended MSON is robust and enables the design of the column on the basis of detailed thermodynamic models and simulation-based optimization.

Keywords: Absorption, Algorithms, Carbon Dioxide Capture, Optimization, Process Synthesis

INTRODUCTION

Process synthesis is central to the conceptualization of new chemical processes that can meet the manifold constraints of a circular economy. Process synthesis is the activity of identifying an optimal flowsheet which entails choosing a) process units (e.g., unit operations) from a set of alternatives, b) the connectivity of selected process units, and c) the degrees of freedom of selected units such that a design objective is optimized and all process constraints are satisfied.

Superstructure optimization is a mathematical programming approach to process synthesis. While there are several representations of a process superstructure [1], here, we focus our attention on the State Operator Network (SON) representation [2] of the process superstructure. A key feature of the SON is that each allowed process unit is described by its rigorous model which includes MESH equations and equipment sizing and costing correlations. The SON relies on a network of conceptual mixers and splitters that enable up to full connectivity between the set of selected process units. A mixer and a splitter are located at each inlet and outlet, respectively, of each process unit.

The optimization of the SON is a challenging mixed-integer nonlinear programming problem (MINLP). A particular issue in the optimization of the SON, which is the subject of this paper, is the fate of a process unit that is deselected, that is, excluded from the flowsheet. Naturally, when a process unit is deselected, mass flowrates at each inlet of the unit must be set to zero. However, the models of many process units are well defined only at strictly positive mass flows. At zero-valued inlet flows, several numerical singularities (including undefined behaviour) in the constraint functions that describe the unit and/or in their derivatives can occur. For example, consider an isobaric-isenthalpic flash unit. At zero-valued flows, a two-phase solution to the phase-equilibrium problem does not exist. Further, the Jacobian of the mass-balance constraints of the unit is rank-deficient [3]

and costing and sizing correlations that depend on the flowrates may become numerically singular. As a result, the optimization of the SON may fail to converge.

To overcome this challenge, one may reformulate the SON MINLP using Generalized Disjunctive Programming (GDP) [4]. However, the application of GDP to simulation-based superstructure optimization is limited and computationally expensive [5]. Specifically, the initialization of the master problem in Logic-based Outer Approximation is computationally expensive when applied to simulation-based superstructure optimization [6]. Other reformulations include the Big-M reformulation of all the constraints that describe each unit, or multiplication of the constraints of each unit by the corresponding binary variable [7]. Not only do these modifications not fully eliminate singularities due to zero flows [6], but these also require modifications to the high-dimensional number of constraints that describe each process unit.

In this paper, we build upon the recently developed Modified State Operator Network (MSON) [6]. The MSON modifies mixers by introducing fictitious inlet streams that become active when a unit is deselected and take on strictly positive flowrates as well as intensive property values chosen to guarantee successful evaluation of the model of the corresponding process unit. The MSON modifies splitters to reject any flows at the outlets of the deselected process unit that arise due to these fictitious inlet flows. Further any quantities computed in the deselected unit that result in non-zero contributions to the flowsheet objective, design constraints and so on are also modified to take a zero value when the unit is deselected, thus resulting in an exact reformulation.

The SON and MSON are only applicable to the synthesis of isobaric flowsheets. The MSON is further limited as the pressure needs to be fixed *a priori*. In this paper, we present advances to the MSON towards the synthesis of general flowsheets in which: i) the pressure of any unit operation does not have to be fixed *a priori* and ii) unit operations can operate at different pressures. We address the first stipulation in the context of the synthesis of a counter-current separation column. We note that Smith (1996) [8] briefly outlined the use of pressure-driven flows between process units via a network of compressors and expanders to address the second stipulation.

A particular arena of superstructure optimization that has received much attention in the literature [9-10], including the pioneering work of Sargent and Gaminibandara (1976) [11], is the synthesis of separation columns (that is, the optimal design of number of stages and column degrees of freedom), especially distillation columns. The problem is of renewed importance today as separations are highly energy and capital intensive and improved designs are crucial to the success of emerging areas such as carbon capture and biomanufacturing [12].

The consideration of varying pressures is particularly important in this context, e.g., it can facilitate the design of separation solvents for carbon capture as the optimal choices of solvent, pressure and column configuration are intrinsically linked [13]. While we do not model any pressure drop in the column, the column pressure is a degree of freedom that we optimize, unlike our previous work [6]. The proposed extensions of the MSON are general and can be applied to any process unit in which the pressure is a degree of freedom. Additionally, the formulations presented here are amenable to both simulation-based optimization and equation-oriented optimization.

In the next section we present three different counter-current column synthesis formulations: (i) a counter-current column SON based on the R-graph decomposition of columns previously given by Farkas et al. (2008) [14] where we show how the standard formulation of the SON can suffer from numerical singularities, (ii) an exact MSON formulation of the same column that relies on a simple modification to the mixers and splitters to eliminate singularities due to deselection of stages, (iii) an extended MSON formulation so that the column pressure may be treated as a degree of freedom. We then present details of the implementation of the extended MSON and the application of the extended MSON to the design of carbon capture column. Lastly, we present results and conclusions.

COLUMN SYNTHESIS FORMULATIONS

Consider a counter-current separation column such as a gas-liquid absorption column, liquid-liquid extraction column or the rectifying section of a distillation column. The column separation is driven by the contacting of two phases, labelled vapour and liquid here for convenience.

The column synthesis problem may be formulated as follows: Given a multi-component vapour feed to be separated, a solvent that is the mass separation agent and a maximum of N^U theoretical (equilibrium) stages, find the optimal number of stages and values of the column degrees of freedom such that the design objective is minimized and constraints on product purity and recovery are satisfied. The MSON formulation for column synthesis has previously been derived formally in full detail [5]. Here, we present the details of the SON and MSON in the context of column synthesis for completeness.

SON

We decompose a column of N^U stages into equivalent conditional subsections [14]. Each subsection i has 2^{i-1} identical equilibrium stages and an associated binary variable z_i that takes the value 1 when the subsection is selected, where $i \in \mathcal{R}$, where $\mathcal{R}$ is the set of conditional subsections. For example, a column with a maximum of 15 stages is decomposed into four subsections of 1, 2, 4

and 8 stages, respectively as shown in Figure 1. As an alternative example, a column of 31 stages is decomposed into five subsections of 1, 2, 4, 8 and 15 stages, respectively. The number of subsections $|\mathcal{R}|$ is equal to the minimum number of bits required to express integer N^U in binary notation. Each subsection has a vapour outlet, a vapour inlet, a liquid outlet and a liquid inlet as shown in Figure 1. We further include the following permanent units in the column superstructure: a vapour source, a liquid source, a vapour sink and liquid sink as shown in Figure 1. Each sink and source have one inlet and outlet each. The vapour feed to be separated and the fresh solvent enter the column via the vapour and liquid sources, respectively. The product and the spent solvent leave the column via the vapour and liquid sinks, respectively. We assume that all unit operations operate at pressure P.

Mixer-splitter network

For each phase (vapour or liquid), we use a network of mixers and splitters to enable flows between the column subsections, and the corresponding source and sink. A mixer is placed at each of the inlets of the column subsections and at the inlet of the sink. A splitter is placed at each of the outlets of the column subsections and at the outlet of the corresponding source. The vapour mixer at inlet $i \in \mathcal{I}^V$, where $\mathcal{I}^V$ is the set of vapour inlets, allows the mixing of vapour streams that leave from splitters at the outlets of the subsections $i+1, \dots, \mathcal{R}$ and the vapour source. Similarly, the liquid mixer at inlet $i \in \mathcal{I}^L$, where $\mathcal{I}^L$ is the set of liquid inlets, allows the mixing of liquid streams that leave splitters at the outlets of subsections $1, \dots, i-1$ and the liquid source. An example column subsection with its mixers and splitters and their connections in detail is shown in Figure 2. Splitters and mixers are assumed to be isenthalpic and ideal. We consider a multi-component mixture with K components. $f_i^{in,V}$, $\boldsymbol{q}_i^{in,V}$ and $T_i^{in,V}$ represent the flowrate, composition and temperature of the vapour stream at inlet i. $f_o^{out,V}$, $\boldsymbol{q}_o^{out,V}$ and $T_o^{out,V}$ represent the flowrate, composition and temperature of the vapour stream at outlet o. $f_{o,i}^V$, $\boldsymbol{q}_{o,i}^V$ and $T_{o,i}^V$ represent the mass flowrate, composition and temperature, respectively of the vapour stream that flows from splitter o to mixer i. All streams are assumed to be at constant pressure P. The following balances hold for vapour mixers:

$$f_i^{in,V} = \sum_{o \in \mathcal{M}_i^V} f_{o,i}^V \tag{1}$$

$$f_i^{in,V} q_{i,c}^{in,V} = \sum_{o \in \mathcal{M}_i^V} f_{o,i}^V q_{o,i,c}^V \quad \forall c \in \{1, \dots, K\} \tag{2}$$

$$f_i^{in,V} h_{en}^V\left(T_i^{in,V}, P, \boldsymbol{q}_i^{in,V}\right) = \sum_{o \in \mathcal{M}_i^V} f_{o,i}^V h_{en}^V\left(T_{o,i}^V, P, \boldsymbol{q}_{o,i}^V\right) \tag{3}$$

where $\mathcal{M}_i^V$ denotes all the vapour splitters that a vapour mixer i may be connected to, and for vapour splitters:

$$f_o^{out,V} = \sum_{i \in \mathcal{S}_o^V} f_{o,i} \tag{4}$$

$$T_o^{out,V} = T_{o,i}^V \quad \forall i \in \mathcal{S}_o^V \tag{5}$$

$$\boldsymbol{q}_o^{out,V} = \boldsymbol{q}_{o,i}^V \quad \forall i \in \mathcal{S}_o^V \tag{6}$$

where $\mathcal{S}_o^V$ denotes all the mixers that splitter o may be connected to. Analogous relationships may be written for the liquid mixers and splitters.

Note that the mixers and splitter alone cannot guarantee flow in the desired direction between two units at different pressures, and thus, limit the SON to the synthesis of isobaric flowsheets.

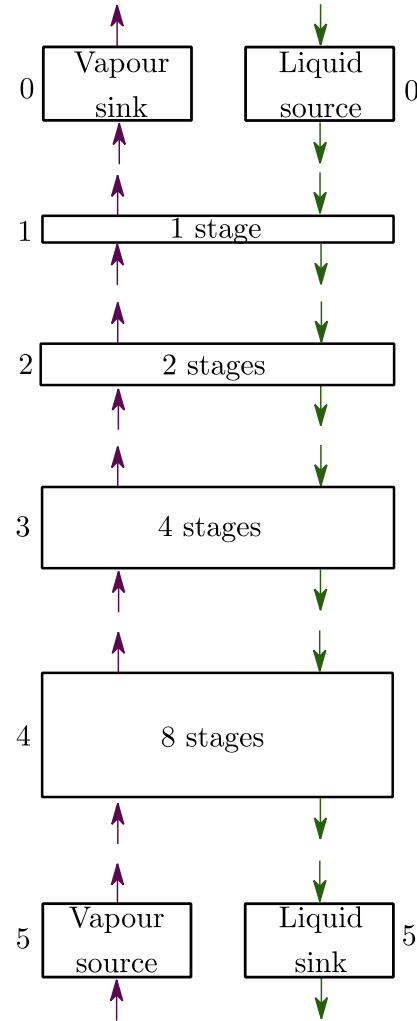**Figure 1**: Schematic of the vapour source, liquid source, vapour sink, liquid sink, and the 4 columns subsections with 1, 2, 4 and 8 stages in a column superstructure with at most 15 stages. The vapour and liquid sources and sinks have one inlet and outlet each. Each column subsection has one vapour inlet, one liquid inlet, one vapour outlet and one liquid outlet. Process units in the superstructure are labelled by numbers.
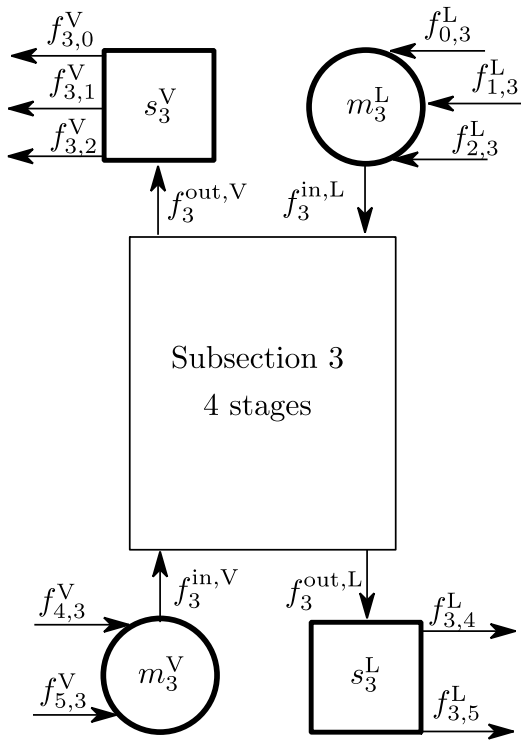
Figure 2: Detailed schematic of subsection 3 with 4 stages from Figure 1. The vapour mixer m_3^V allows the mixing of vapour streams that flow from subsection 4 and the vapour source. The liquid mixer m_3^L allows the mixing of vapour streams that flow from the liquid source, subsection 1 and subsection 2. The vapour splitter s_3^V allows the vapour that leaves subsection 3 to go to mixers at the inlets of subsections 1 and 2 and the vapour sink. The liquid splitter s_3^L allows the liquid that leaves subsection 3 to go to mixers at the inlets of subsection 4 and the liquid sink.

Flow-validity constraints

Flow validity constraints ensure that the flows to a column subsection that is deselected, $z_i = 0$, are zero. Further constraints, given in [6], ensure that the flows do not bypass selected subsection.

Process unit-level constraints

Each process unit (the sources, the sinks and the conditional subsections) is represented in the column superstructure via its rigorous model, which is referred to as process unit-level constraints here. Each source and sink may be represented by simple constraints that equate the state at the inlet to that at the outlet. Each column subsection is represented by a rigorous model for each of the equilibrium stages in the subsection. This includes the MESH equations. As the pressure drop is assumed to be zero, the pressure at the vapour and liquid outlets of each stage (and subsection i where $i \in \mathcal{R}$) is set equal to the pressure at the inlet. Thus,

$$P_i^{\text{out,V}} = P_i^{\text{out,L}} \tag{7}$$

$$P_i^{\text{out,V}} = P_i^{\text{in,V}} \tag{8}$$

$$P_i^{\text{in,V}} = P \tag{9}$$

For each subsection, we compute variables $\widehat{\rho_i^L}$, $\widehat{\rho_i^V}$ and $\widehat{v_i^V}$:

$$\widehat{\rho_i^L} = \sum_{j \in 2^{i-1}} \rho_j^L \tag{10}$$

$$\widehat{\rho_i^V} = \sum_{j \in 2^{i-1}} \rho_j^V \tag{11}$$

$$\widehat{v_i^V} = \sum_{j \in 2^{i-1}} v_j^V \tag{12}$$

Where ρ_j^L, ρ_j^V and v_j^V are the mass density of the liquid stream that exits stage j, the mass density of the vapour stream that exits stage j and volumetric flowrate of the vapour stream that exits stage j, respectively.

Column-level constraints

We use column-level equations (also known as flowsheet-level equations in [6]) to compute the total dimensions and cost of the column. Some of these flowsheet-level constraints may depend on a few "output variables" whose values are obtained by solving the process unit-level constraints. D, the diameter of the column and H, its height, are computed using [15]:

$$N = \sum_{i \in \mathcal{R}} 2^{i-1} z_i \tag{13}$$

$$\overline{\rho^L} = \frac{\sum_{i \in \mathcal{R}} \widehat{\rho_i^L}}{N} \tag{14}$$

$$\overline{\rho^V} = \frac{\sum_{i \in \mathcal{R}} \widehat{\rho_i^V}}{N} \tag{15}$$

$$\overline{v^V} = \frac{\sum_{i \in \mathcal{R}} \widehat{v_i^V}}{N} \tag{16}$$

$$u^{\text{flood}} = (-0.171 lt^2 + 0.27 lt - 0.047)\sqrt{\frac{\overline{\rho^L} - \overline{\rho^V}}{\overline{\rho^V}}} \tag{17}$$

$$D = \sqrt{\frac{4\overline{v^V}}{\pi u^{\text{flood}}}} \tag{18}$$

$$H = 1.15 \frac{lt}{E} N \tag{19}$$

where lt and E are the tray spacing and stage efficiency, respectively. We also introduce flowsheet-level constraints to compute the total capital investment (TCI), the annual operating expenses ($OPEX$) and the total annualized cost (TAC) using costing correlations [6,16]. We also impose constraints on the minimum purity and flowrate of the vapour stream that exits the flowsheet.

Numerical singularities

When a column subsection is deselected, all flows into the unit are driven to zero by the flow-validity constraints. Due to this, within each column subsection, a solution to the phase equilibrium equations at each stage does not exist. The mass-balance equations are also

rank-deficient. Sizing, costing or even mass transfer correlation that depends on the flowrates associated with a deselected stage can become singular (that is, the function or derivative may be numerically undefined).

MSON

To overcome numerical singularities for any deselected process unit, we have developed the MSON formulation [6], which relies on the modification of mixers and splitters associated with the conditional subsections. The mixers and splitters associated with the sources and sinks remain unchanged and the pressure of all column subsections is a constant and fixed *a priori*.

Modified mixer

We introduce a fictitious stream into each modified vapour mixer i (associated with column subsection $i \in \mathcal{R}$) with mass flowrate $f_i^{M,V}$, composition $\boldsymbol{q}_i^{A,V}$ and temperature $T_i^{A,V}$, as shown in Figure 3. Due to Equations (20) – (22), the flowrate, composition and temperature at the inlet of subsection i are $f_i^{M,V}$, $\boldsymbol{q}_i^{A,V}$ and $T_i^{A,V}$, respectively, when subsection i is deselected and all other flows into the mixer are zero. Further, due to Equation (23), $f_i^{M,V}$ takes the constant value $f_i^{A,V}$ when the conditional subsection is deselected and takes the value zero otherwise. Due to this, when the subsection is selected, the modified mixer equations are fully equivalent to a standard mixer. Analogous relationships are written for the modified liquid mixers.

$$f_i^{in,V} = \sum_{o \in \mathcal{M}_i^V} f_{o,i}^V + f_i^{M,V} \tag{20}$$

$$f_i^{in,V} q_{i,c}^{in,V} = \sum_{o \in \mathcal{M}_i^V} f_{o,i}^V q_{o,i,c}^V + f_i^{M,V} q_{i,c}^A \forall c \in \{1, \dots, K\} \tag{21}$$

$$f_i^{in,V} h_{en}^V \left(T_i^{in,V}, P, \boldsymbol{q}_i^{in,V}\right) = \sum_{o \in \mathcal{M}_i^V} f_{o,i}^V h_{en}^V \left(T_{o,i}^V, P, \boldsymbol{q}_{o,i}^V\right) + f_i^{M,V} h_{en}^V \left(T_i^{A,V}, P, \boldsymbol{q}_i^{A,V}\right) \tag{22}$$

$$f_i^{M,V} = f_i^{A,V} (1 - z_i) \tag{23}$$

$f_i^{A,V}$, $\boldsymbol{q}_i^{A,V}$ and $T_i^{A,V}$ and the corresponding constants for the modified liquid mixer are chosen such that the two fictitious streams are in vapour-liquid equilibrium at pressure P. When a column subsection is not selected, thanks to the fictitious streams that enter via the modified vapour and liquid mixers, a two-phase solution exists in each stage. Thus, no singularities are encountered in the MESH equations and sizing correlations that describe the subsection.

Modified splitter

We modify the splitters associated with the conditional column subsections as shown in Figure 4. With the modified splitters we can correct for the fictitious non-

zero flows at the outlets of deselected process units caused due to fictitious mixer streams. We describe each modified vapour splitter o, (associated with column subsection $o \in \mathcal{R}$) using Equations (5) and (6) and,

$$f_o^{out,V} = \sum_{i \in \mathcal{S}_o^V} f_{o,i} + f_o^{S,V} \tag{24}$$

$$0 \le f_o^{out,V} - f_o^{S,V} \le f^U z_o \tag{25}$$

$$0 \le f_o^{S,V} \le f^U (1 - z_o) \tag{26}$$

where f^U is an upper bound on the flowrates.

Equations (24)-(26), ensure that when the subsection is deselected, any vapour that leaves the subsection (due to the fictitious flows in the modified mixers) leaves the splitter o via a fictitious stream with flowrate $f_o^{S,V}$, composition $\boldsymbol{q}_o^{out,V}$ and temperature $T_o^{out,V}$ and is not propagated to the rest of the flowsheet. On the other hand, when the subsection is selected, the fictitious stream is constrained to have a zero flowrate, and hence has no effect on the rest of the flowsheet. As before, the composition and temperature of the streams that leave the splitters are set equal to that at the inlet of the splitter. A vapour splitter and a modified vapour splitter are shown in Figure 4. The modified liquid splitter is analogous.
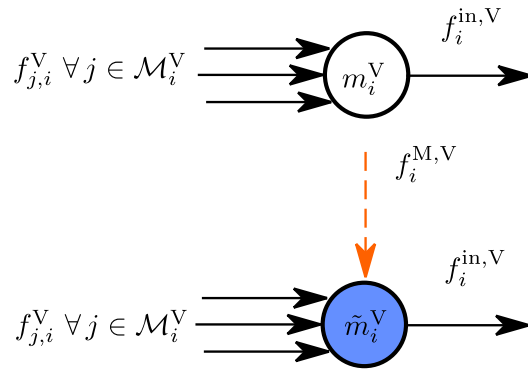

Figure 3: A vapour mixer (denoted by an open circle) at inlet i and a modified vapour mixer (denoted by a shaded circle) at inlet i.

Modified output variables

As a result of the fictitious flows into a deselected unit, several of the variables associated with the unit may take a spurious non-zero value. However, only a small subset of these variables, the output variables, is used in column-level computations. We introduce a "corrected output variable" x_j^S for any output variable x_j and enforce the following Big-M constraints:

$$-M(1 - z_i) \le x_j - x_j^S \le M(1 - z_i) \tag{27}$$

$$-M z_i \le x_j^S \le M z_i. \tag{28}$$

We further modify the column-level constraints that

depend on an output variable x_j to depend on the corrected output variable x_j^{S}. In the case of column synthesis, we reformulate constraints (10)-(12) in terms of these corrected output variables to obtain:

$$\overline{\rho^{\mathsf{L}}} = \frac{\sum_{i \in \mathcal{R}} \widehat{\rho_i^{\mathsf{L}^{\mathsf{S}}}}}{N} \tag{29}$$

$$\overline{\rho^{\mathsf{V}}} = \frac{\sum_{i \in \mathcal{R}} \widehat{\rho_i^{\mathsf{V}^{\mathsf{S}}}}}{N} \tag{30}$$

$$\overline{\upsilon^{\mathsf{V}}} = \frac{\sum_{i \in \mathcal{R}} \widehat{\upsilon_i^{\mathsf{V}^{\mathsf{S}}}}}{N} \tag{31}$$

Process unit-level constraints

The process unit-level constraints and all column-level constraints that do not depend on any of the output variables are unchanged. Numerical singularities by the use of the MSON are entirely averted as shown in [6].
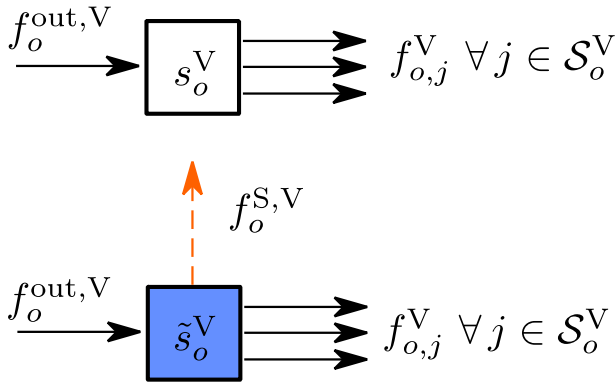

Figure 4: A vapour splitter (denoted by an open square) at outlet o and a modified vapour splitter (denoted by a shaded square) at outlet o. A ficitious stream (denoted by the dashed arrow) with flowrate $f_o^{\mathsf{S,V}}$ leaves the modified splitter.

EXTENDED MSON (E-MSON)

In the derivation of the SON and MSON we assume that the pressure at the inlet of any unit (that is, the outlet of any mixer) is fixed at P. The operating pressure of any column subsection is also fixed at P, thanks to Equations (7)-(9). Further, we introduce fictitious streams in the modified mixers with states such so that when the unit is deselected, a two-phase solution is guaranteed for a column subsection at pressure P. However, if the deselected subsection is at any other pressure, the states of the fictitious stream may not necessarily result in a two-phase solution. Indeed, for any general process unit, the state of the fictitious stream in the mixer may not lead to the successful solution of the unit constraints when the operating pressure varies.

To overcome this limitation we first add the following constraint to each vapour splitter as well as each modified vapour splitter o in the superstructure:

$$P_{o,i}^{\mathsf{V}} = P_o^{\mathrm{out,V}} \quad \forall i \in \mathcal{S}_o^{\mathsf{V}} \tag{32}$$

where $P_{o,i}^{\mathsf{V}}$ is the pressure of a vapour stream that flows from splitter o to mixer i. Analogous constraints are added to the liquid splitters.

We also modify the mixers in the flowsheet. The "mixing" of two streams that arise from two process units at unequal pressures may physically result in unintended flows, e.g., mass flows from the high-pressure unit into the low-pressure unit. Thus, in the extended MSON, only the mixing of streams that are at equal pressures is allowed. We note that this mixing rule is trivially satisfied for the column synthesis problem studied here (as all streams are at P). The following pressure-mixing equation is introduced into the model of each vapour mixer i to describe the pressure at each vapour inlet:

$$f_i^{\mathrm{in,V}} P_i^{\mathrm{in,V}} = \sum_{o \in \mathcal{M}_i^{\mathsf{V}}} f_{o,i}^{\mathsf{V}} P_{o,i}^{\mathsf{V}} \tag{33}$$

Due to the pressure-mixing constraint, the pressure at the inlet i is equal to that of stream(s) with strictly positive mass flowrates into unit i. The enthalpy balance for each mixer is modified to incorporate the pressure of each stream, yielding:

$$f_i^{\mathrm{in,V}} h_{en}^{\mathsf{V}} \left(T_i^{\mathrm{in,V}}, P_i^{\mathrm{in,V}}, \boldsymbol{q}_i^{\mathrm{in,V}} \right) = \sum_{o \in \mathcal{M}_i^{\mathsf{V}}} f_{o,i}^{\mathsf{V}} h_{en}^{\mathsf{V}} \left(T_{o,i}^{\mathsf{V}}, P_{o,i}^{\mathsf{V}}, \boldsymbol{q}_{o,i}^{\mathsf{V}} \right) \tag{34}$$

A similar pressure-mixing equation is introduced into the modified vapour and liquid mixers. The pressure of the fictitious vapour and liquid streams in the modified mixer i is denoted by P_i^{A}.

$$f_i^{\mathrm{in,V}} P_i^{\mathrm{in,V}} = \sum_{o \in \mathcal{M}_i^{\mathsf{V}}} f_{o,i}^{\mathsf{V}} P_{o,i}^{\mathsf{V}} + f_i^{\mathsf{M,V}} P_i^{\mathsf{A}} \tag{35}$$

Due to Equation (35), the pressure at the inlet i is equal to that of stream(s) with strictly positive mass flows into unit i. When the unit i is deselected, the pressure at the inlet takes the value P_i^{A} that leads to successful evaluation of the process unit-level constraints that describe i. The enthalpy balance in modified mixers is also adapted, in an analogous matter to Equation (34).

The E-MSON only requires the modification to mixers and splitters. All process unit-level constraints and column-level constraints are the same as the MSON. The E-MSON can be used to model a process unit with variable pressure and ensures successful solution when the unit is deselected, irrespective of its operating pressure. Further, the extended mixers and splitters are also necessary to allow the E-MSON to be applied to the synthesis of flowsheets in which the unit operations are at different pressures. However, to fully address the latter case for a general flowsheet, additional logical constraints as well as compressors and expanders are needed and we leave this for future work.

IMPLEMENTATION

The E-MSON problem formulation is a mixed-integer nonlinear programming problem (MINLP) that is solved using the outer approximation equality relaxation augmented penalty (OA-ER-AP) algorithm [17] that we have implemented in C++ [6]. All constraints of the primal problem are implemented and solved in gPROMS Model-Builder 7.0.7 [18]. Each stage in the column is modelled as an equilibrium stage and all thermodynamic properties are computed using the SAFT-γ Mie equation of state [19,20]. The master problem is solved using Gurobi 10.0.2 [21] via its C++ application programming interface (API).

CASE STUDY DESCRIPTION

We consider the synthesis of a gas-liquid absorption column with at most 15 theoretical stages. The column must recover methane from a carbon dioxide and methane stream, by physical absorption at high pressure. Given a feed of carbon dioxide and methane at flowrate 1 kmol s⁻¹, 298 K and pressure P with 20% CO_2 and tetra(oxymethylene)dimethylether ($CH_3O(CH_2O)_4CH_3$) as a solvent at 298 K and pressure P, find the optimal theoretical number of stages N, flowrate of fresh solvent F as well as column pressure P such that the treated gas has a flowrate of at least 0.66 kmol s⁻¹ and is at least 97% methane and the total annualized cost TAC is minimized. The TAC depends on the total capital investment TCI and the annual operating expenses $OPEX$. We assume E is 0.8, lt is 0.6m, the cost of capital is 15%, the column lifetime is 10 years and that 2 MPa $\leq P \leq$ 7.5 MPa. Details of the model can be found in [6, 16].

RESULTS

The superstructure for the column to be designed has 4 conditional subsections with 1, 2, 4 and 8 equilibrium stages, respectively. The results of the case study are summarised in Table 1. The optimal column has 4 theoretical stages, obtained by selecting only subsection 3. The OA-ER-AP algorithm converges to a solution in 8 major iterations, 5 of which are found to be feasible. With the E-MSON, the primal problems are solved robustly, no singularities are detected, and a solution is obtained for the equations of the deselected subsections, despite the variation of the column pressure in the course of optimization. The primal problem in the E-MSON has 910 equality constraints (excluding the equations corresponding to SAFT-γ Mie), 87 inequality constraints and 49 degrees of freedom to be optimized (including fictitious flowrates in the modified mixers and splitters). The runtime (wall clock time) of the primal problem solution is 65 s on average with the standard deviation of 22 s. Across the five feasible iterations, the primal problems take 72.2 s to converge to a solution, with the standard deviation of 14.5 s.

Table 1: Results of the E-MSON for the synthesis of a counter-current carbon-capture column. The first row shows the results for the variable-pressure case with the use of the E-MSON. The second row shows the results of the same case study in the fixed-pressure case with the use of the MSON where all streams and the column are at an *a priori* fixed pressure of 7.5 MPa. F is in kmol/s, P is in MPa and TAC, TCI and $OPEX$ are in Million USD.

Case	P	F	N	TAC	TCI	$OPEX$
E-MSON	2.6	1.9	4	0.37	0.58	0.26
MSON	7.5	0.6	6	0.59	1.37	0.32

We compare the results of the E-MSON with that of the MSON in which the column pressure and that of the feed and pure solvent are arbitrarily fixed at 7.5 MPa. The *a priori* fixed-pressure column has a minimum TAC that is 59% higher than the column in which pressure has been optimized, a TCI that is 136% higher and 2 more equilibrium stages. In the fixed pressure case, a column with 4 stages was found to be infeasible. The 6-stage column at 7.5 MPa has a 34% higher TAC than a 6-stage column at the optimal pressure of 2.6 MPa. The pressure heavily impacts the relative solubilities of CO_2 and CH_4, product recovery, product quality and the capital cost of the absorber. The comparison across the two cases highlights the importance of making the pressure an additional degree of freedom in separation column synthesis both for the study of specific separation solvents as well as for solvent design. As we only use local optimization algorithms, the inferior performance of the fixed-pressure column could also be due to convergence of the MSON to low-quality local minima. However, to assuage discrepancies across formulations, we used the same initial guesses, solvers and solver parameters in both cases.

In our future work we shall extend the design envelope to also consider i) the compression/expansion of the feed, ii) the solvent regeneration and recycle and iii) the cost of make-up solvent.

CONCLUSION

In this paper, we extended the state operator network paradigm of superstructure optimization that was previously implicitly limited to the synthesis of isobaric flowsheets. We built upon the recently-developed MSON that guarantees convergence of deselected units, thus, making the MSON robust and amenable to high-fidelity simulation-based optimization. We developed E-MSON, the extended MSON which retains the robustness of the MSON while making it applicable to the synthesis of columns as well as isobaric flowsheets in which the operating pressure is a variable.

By introducing pressure as an additional degree of freedom in absorption column synthesis, we found in our case study that overall costs decreased by 37%. The extended-MSON is a first step towards fully general superstructure optimization within the SON paradigm in which all unit operations are at variable pressures. The results of the paper indicate that modelling the effects of pressure rigorously can lead to superior designs. Furthermore this work expands the applicability of the state operator network to superstructure optimization problems with rigorous process models.

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