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A review on superstructure optimization approaches in process system engineering

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A B S T R A C T

In this paper, we survey the main superstructure-based approaches in process system engineering, with a particular emphasis on the existing literature for automated superstructure generation. We examine both classical and more recent representations in terms of generality, ease of use, and tractability. We also discuss the implications that different representations may have on strategies for algebraic modeling and optimization. We then review the state-of-the-art in software implementations to support synthesis. Finally, we examine the use of evolutionary—recently referred to as superstructure-free—approaches, in which algorithmic procedures dynamically generate and evaluate candidate process structures.

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1. Introduction

Conceptual process design is a central pillar of chemical engineering, concerning the definition, simulation, optimization, and control of chemical processes. This design task involves the synthesis of complex chemical processes through the integration of simpler unit blocks characterized by physical and chemical properties. Methodological developments in process synthesis has been addressed by the Process Systems Engineering (PSE) community (Klatt and Marquardt, 2009; Cremaschi, 2015; Grossmann and Harjunkoski, 2019), which has developed powerful mathematical optimization and simulation tools to address chemical process design and control problems. In particular, Mixed-Integer Nonlinear Programming (MINLP) and Generalized Disjunctive Programming (GDP) techniques are well-suited to problems involving selection among discrete process alternatives with nonlinear process phenomena (Grossmann, 1989; Grossmann et al., 2000; Grossmann, 2002; Trespacios and Grossmann, 2014; Chen and Grossmann, 2019).

Two main approaches exist for conceptual process design: hierarchical decomposition (Douglas, 1985; Sirola and Rudd, 1971) and superstructure synthesis (Umeda et al., 1972; Chen and Grossmann, 2017), with superstructure synthesis preferred for its systematic evaluation of a large space of structural alternatives

(Saif et al., 2009; Barnicki and Sirola, 2004; Westerberg, 2004). Hierarchical decomposition involves a sequential procedure in which the process design is progressively defined in stages (or levels). At each level, specific decisions are made based on engineering judgement and rules-of-thumb, starting with broader decisions of the greatest consequence. For detailed reviews on hierarchical decomposition approaches see the works of Dimian (2003) and Goh and Ng (2015). However, interactions between decisions at different detail levels (e.g. separation design and heat integration) are difficult to capture with hierarchical decomposition (Duran and Grossmann, 1986b; Lang et al., 1988). In contrast, superstructure synthesis attempts to solve the simultaneous design problem as a mathematical programming problem. Hybrid approaches combining ideas from both hierarchical decomposition and mathematical programming have also been studied by Daichendt and Grossmann (1997) and more recently by Zhang et al. (2016). Targeting techniques are also available, which identify *a priori* characteristics of advantageous structures by analyzing physical properties of the chemical system; these have been applied to great effect in heat exchanger networks (Linnhoff and Hindmarsh, 1983; Hohman, 1971), and in heat and water integration (Klemeš and Kravanja, 2013). The composite curves diagram in pinch analysis (Linnhoff and Hindmarsh, 1983) and the attainable region-based methods, introduced by Horn (1964) and popularized by Glasser et al. (1987), are among the most notable targeting techniques, used in the design of heat exchanger networks and reaction-separation systems. More recent contributions by Feinberg and Ellison (2001) and Frumkin and Doherty (2018) extend ideas of the latter beyond their geometric origins.

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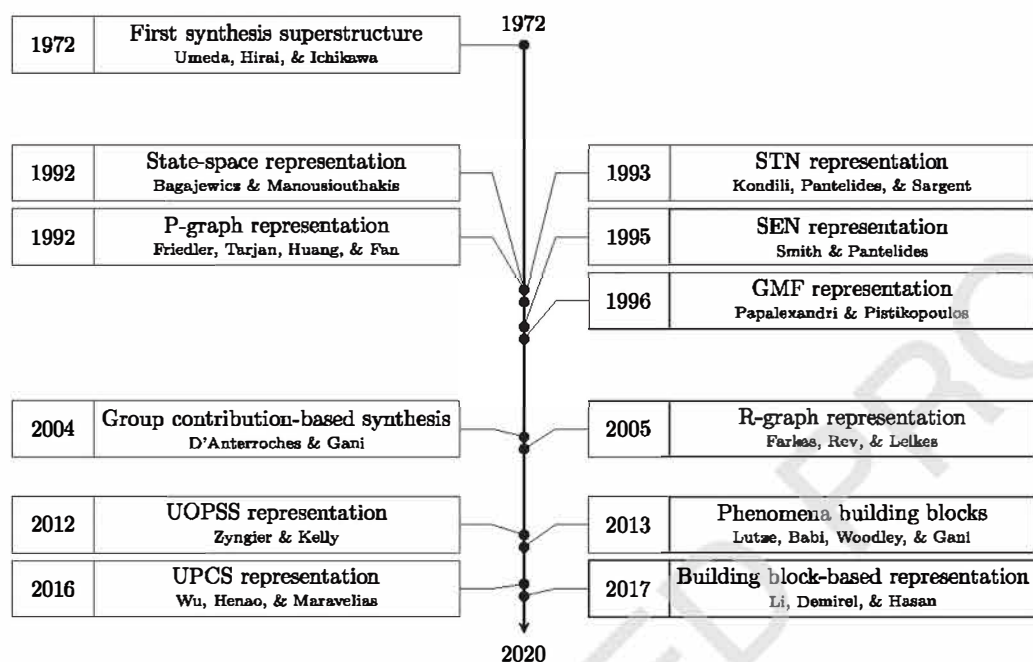


Fig. 1. Abbreviated timeline of superstructure synthesis representations.

Superstructure-based process synthesis, introduced in Umeda et al. (1972), involves three main sequential steps: (i) the postulation of a superstructure, which encapsulates the set of all feasible alternative process structures; (ii) the translation of the superstructure into a mathematical programming model; and (iii) the computation of an optimal structure by solving the mathematical optimization model. The approach gained traction first in subsystems (Sargent and Gaminibandara, 1976; Grossmann and Sargent, 1976), then in general flowsheet design (Kocis and Grossmann, 1989). Early reviews in the area can be found by Nishida et al. (1981), Westerberg (1991), and Bagajewicz and Manousiouthakis (1992).

An inherent limitation of superstructure-based approaches is the need to define an initial superstructure to capture all the desired alternatives. A poorly-constructed superstructure may omit several feasible or optimal process flowsheets. Moreover, the choice of representation may impact tractability of the resulting optimization formulation (Yeomans and Grossmann, 1999). In response, the community has developed two main approaches: (a) automated superstructure generation methods, and (b) evolutionary “superstructure-free” approaches. In automated superstructure generation, the superstructure is constructed from a set of alternatives via deterministic algorithmic procedures; on the contrary, in the superstructure-free approach, candidate structures are dynamically generated during the search process.

In this paper, we provide a critical review of the state-of-the-art in superstructure based synthesis, with a focus on the methods and tools available to generate appropriate superstructure representations. We then compare these approaches to superstructure-free design strategies. The rest of the paper is organized as follows. In Section 2, we survey the representations and algorithmic procedures proposed in the literature to automate the generation of the superstructure of a given process. We also describe algorithmic post-processing procedures proposed to reduce the complexity or the redundancy of superstructure representations, and to translate the superstructure into a mathematical programming formulation. In Section 3, we discuss implications of the superstructure representation on modeling and solution strategies. In Section 4, we review current software implementations for process synthesis.

Then, in Section 5, we briefly summarize superstructure-free approaches. Methodological conclusions and final remarks follow in Section 6.

2. Superstructure representations

In this section we present the different techniques proposed in the literature to generate and optimize the superstructure of a given chemical process. Selection of the appropriate superstructure representation is a necessary prerequisite in automated superstructure generation. Over the years, several representations and generation approaches have been proposed in literature (see Fig. 1); these can be divided into two classes: the traditional approaches proposed in the 1990s, and newer representations developed after the turn of the millennium. The traditional approaches involve network or graph representations in which the chemical process is divided into stages (or states) and tasks. These interlinked states and tasks describe the progressive transformation of the inputs (or raw materials) into the desired outputs (or final products) by means of sequential operations (or functions). Computer-aided generation of alternatives in these approaches can be done with means-ends analysis (Siirola et al., 1971).

In recent years, new challenges and opportunities—detailed in the following review papers—have spurred renewed interest in process design, leading to the development of several new superstructure representations. There have been efforts to design more sustainable processes (Martín and Adams II, 2019) for the circular economy (Avraamidou et al., 2020). Interest in process intensification renewed interest in representations able to capture selection and integration of physical and chemical phenomena, in contrast to traditional equipment-oriented superstructures (Sitter et al., 2019; Tula et al., 2019a; Tian et al., 2018a). At the same time, equipment size reductions from process intensification have led to interest in modular process units (Baldea et al., 2017), with applications in the oil and gas industry (Tsay et al., 2018). New superstructures that aim to simplify solution strategies and software platforms to support the use of these new representations have also arisen (Mitsos et al., 2018; Tula et al., 2019b). Finally, Ryu et al. (2020) explicitly examines the interactions needed to synthesize a process em-

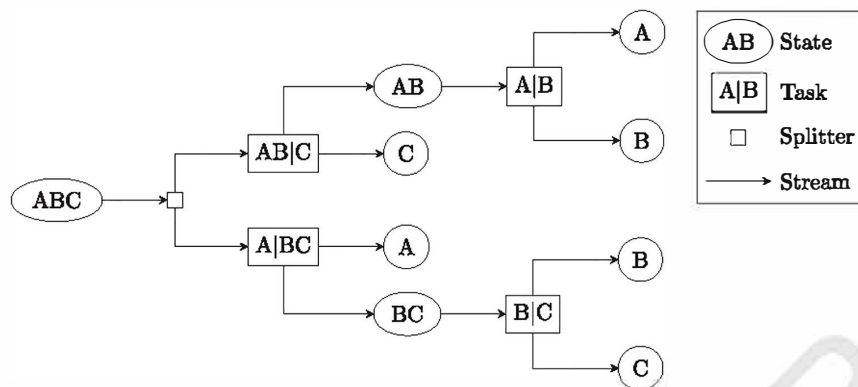


Fig. 2. State-Task Network (STN) superstructure for a 3 component sharp split distillation sequence.

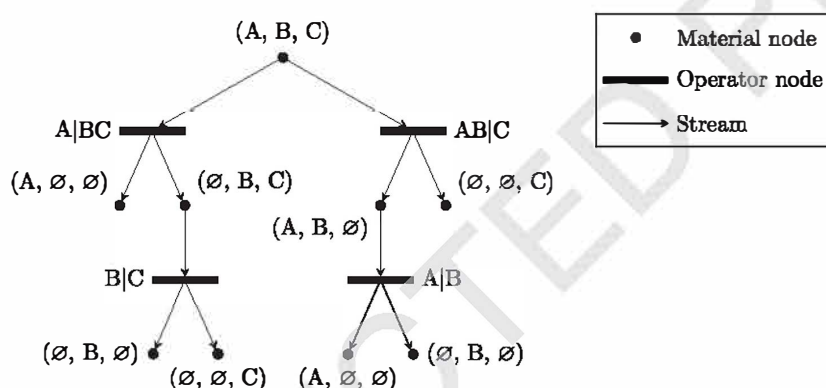


Fig. 3. P-graph network superstructure (PNS) for a 3 component sharp split distillation sequence.

129 bedding multiple different representations. In the following sections, we elaborate on both traditional and new representations
 130 that build on its ideas. As previously introduced, the STN can be
 131 constructed by taking into account all of the tasks needed to convert a process through means-ends analysis (Sirola et al., 1971),
 132 and connecting them via associated intermediate states.
 133

134 2.1. State-task network representation

135 The state-task network (STN) representation (see Fig. 2) was
 136 first introduced in Kondili et al. (1993) for multi-product/multi-
 137 purpose scheduling problems, and extended to process flowsheet
 138 design by Yeomans and Grossmann (1999), in which the repre-
 139 sentation is applied to the synthesis of distillation sequences with
 140 and without heat integration. The STN representation consists of
 141 a directed graph with two main classes of nodes: states and tasks.
 142 States, as their name implies, represent a physical or compositional
 143 state of the feeds, intermediates, or products. The transition be-
 144 tween these states is accomplished through processing tasks. A su-
 145 perstructure task can be conditional or common to all the alterna-
 146 tive structures; this distinction is only made when the superstruc-
 147 ture is translated into a mathematical programming formulation.

148 For conceptual design, the processing tasks also need to be as-
 149 sociated with equipment selection. Due to its origins as a multi-
 150 product scheduling representation, the STN supports variable task-
 151 equipment (VTE) assignment, in addition to the more traditional
 152 one task-one equipment (OTOE) assignment. In VTE, a single piece
 153 of equipment may perform multiple different processing tasks (e.g.
 154 batch reactors that perform both reaction and mixing tasks), and
 155 the final equipment-task assignment is given by the optimization
 156 result. However, OTOE is far more common in overall flowsheet de-
 157 sign, with each task associated *a priori* to a piece of equipment. In
 158 that way, the superstructure more closely resembles a process flow
 159 diagram with conditional flow paths. The STN-OTOE representation

is still commonly used today, and has inspired new representations
 that build on its ideas. As previously introduced, the STN can be
 constructed by taking into account all of the tasks needed to convert a process through means-ends analysis (Sirola et al., 1971),
 and connecting them via associated intermediate states.

165 2.2. P-Graph representation

166 The process graph (P-graph) concept first appeared in
 167 Friedler et al. (1992a). As such, it is a contemporary to the
 168 STN, with many similarities between the two representations. The
 169 P-graph is a bipartite graph (see Fig. 3), whose vertices consist of
 170 material (M-type) and operating unit (O-type) nodes. An operating
 171 unit accepts one or multiple input materials, and produces one
 172 or more outputs. P-graph material nodes correspond to STN state
 173 nodes; P-graph operating units, to STN tasks.

174 Drawing upon ideas from graph theory,
 175 Friedler et al. (1992b) show that combinatorially feasible pro-
 176 cess structures are subgraphs of the P-graph that satisfy the
 177 following system of axioms.

Axiom S1. Every final product of the process is represented by a
 178 M-type vertex in the graph.
 179

Axiom S2. A M-type vertex represents a raw material, if and only
 180 if it has no incoming incident arcs.
 181

Axiom S3. Every operating unit defined in the synthesis problem
 182 corresponds to an O-type vertex in the graph.
 183

Axiom S4. There exists at least one path from each operation unit
 184 node to a node representing a final product.
 185

Axiom S5. Every material node should represent an input or an
 186 output to/from at least one operating unit node.
 187

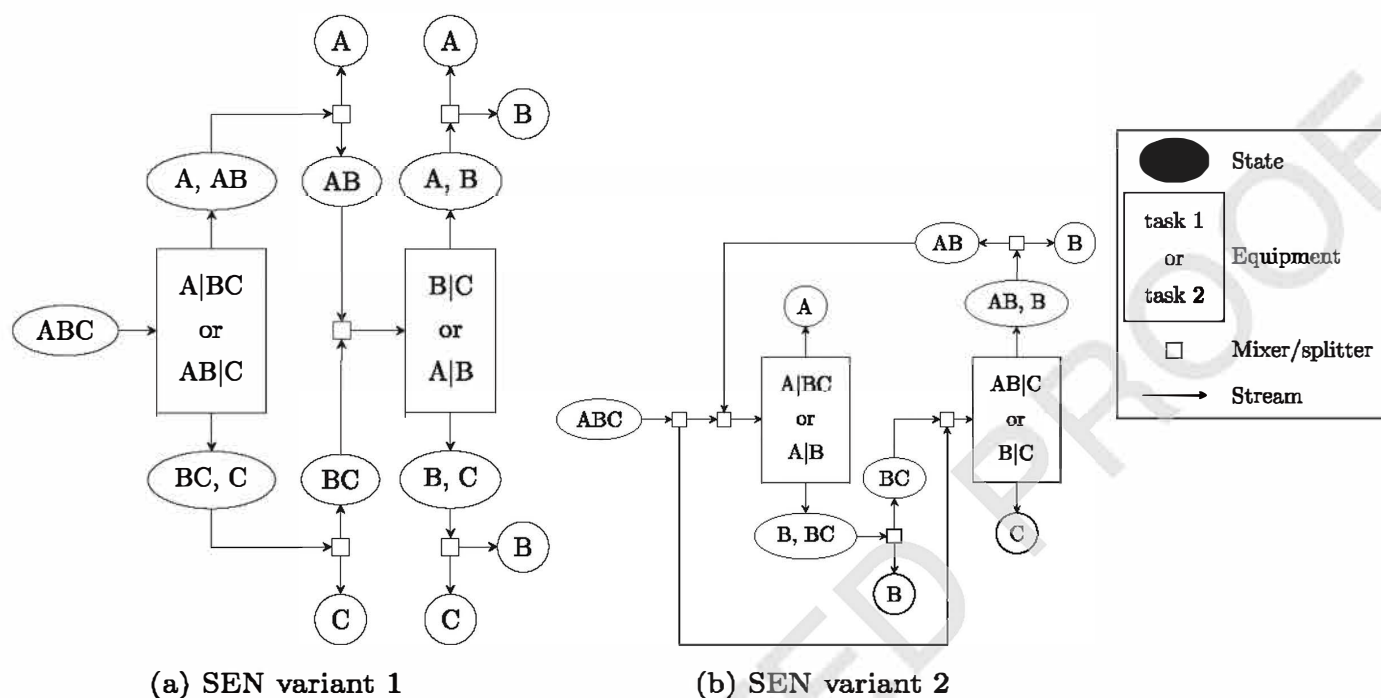


Fig. 4. State-Equipment Network (SEN) superstructure for a 3 component sharp split distillation sequence.

188 **Axiom S1** ensures that all desired products appear in the super-
 189 structure, while **Axiom S2** defines which nodes are the raw materi-
 190 al input nodes. **Axiom S3** ensures that all considered operating
 191 units appear in the graph. **Axiom S4** requires that each operating
 192 unit be connected to at least one final product, i.e. there are no
 193 irrelevant operations. Finally, **Axiom S5** enforces that every materi-
 194 al node is connected to at least one operating unit node, i.e. there
 195 are no irrelevant materials. The set of structures described by these
 196 axioms is closed under union, and the superstructure corresponds to
 197 the union of all the structures.

198 The P-graph methodology distinguishes itself among early super-
 199 structure representations by providing a systematic algorithm
 200 for generating the P-graph (Friedler et al., 1993). The computa-
 201 tional complexity of this algorithm is polynomial in the number
 202 of the materials and in the maximal degree of its vertices
 203 (Friedler et al., 1993). An accelerated branch-and-bound (ABB)
 204 strategy was also developed to exploit the P-graph representa-
 205 tion by restricting the search to combinatorially feasible structures
 206 and solving the relaxations at branched nodes in reduced space
 207 (Friedler et al., 1996). It is noteworthy that contemporary to this,
 208 the same motivations guided development of the logic-based outer
 209 approximation algorithm for Generalized Disjunctive Programming
 210 (Türkay and Grossmann, 1996) (see also Section 3.3). Connections
 211 between the P-graph representation and GDP formulations were
 212 subsequently explored in Brendel et al. (2000).

213 The mathematical rigor unpinning the P-graph methodology is
 214 a key advantage of the approach; however, its closed implementa-
 215 tion and complex notation limit its accessibility to a chemical en-
 216 gineering audience. For more detail, recent reviews on the P-graph
 217 approach may be found by Lam (2013) and Friedler et al. (2019).

218 2.3. State-equipment network representation

219 In the state-equipment network (SEN) representation (see
 220 Fig. 4), introduced by Smith and Pantelides (1995), the superstruc-
 221 ture nodes are states and equipment, with task assignment to the
 222 equipment determined as an optimization result. For some prob-
 223 lem classes, e.g. distillation sequence design, SEN requires fewer

operator (equipment/task) nodes than the equivalent STN repre-
 224 sentation. For a three-component system with sharp separations, 225
 226 the SEN requires two equipment nodes versus four task nodes for
 227 the STN; for a four-component system, the ratio is four to 10 for
 228 the SEN and STN, respectively. However, with the SEN, the combi-
 229 natorial complexity is found in the equipment interconnections,
 230 so it is more effective when the equipment selection is known *a*
 231 *priori* (Yeomans and Grossmann, 1999), as in distillation sequences
 232 and reactor selection (Ramapriya et al., 2018).

233 Note that multiple logically-equivalent SEN variants may be
 234 possible with differing assignment of potential tasks to the equip-
 235 ment, as seen in Section 2.3 for a distillation sequence superstruc-
 236 ture. Variant 1 (Fig. 4a) has a more intuitive flow pattern, with the
 237 first separation taking place in the first column, and the second
 238 separation taking place in the second column. Variant 2 (Fig. 4b)
 239 groups the tasks by the split taking place, with the A|B separation
 240 in the first column, and the B|C separation in the second column.
 241 As a result, variant 2 potentially has less physical property vari-
 242 ation between discrete task selections at either the condenser or
 243 reboiler end of the column, with a high concentration of the same
 244 pure component. This could improve computational performance
 245 in optimization algorithms. The relative merits of these two vari-
 246 ants remains an open question.

247 Related to both the STN and SEN is the Resource-Task Network
 248 (RTN) representation, introduced by Pantelides (1994), in which
 249 the resource nodes can refer to material states (as in the STN)
 250 and/or equipment (as in the SEN). The RTN is more common in
 251 process scheduling applications, but can be useful in simultane-
 252 ous scheduling and design problems. We omit a detailed discussion
 253 here and refer the interested reader to recent reviews on schedul-
 254 ing formulations (Harjunkoski et al., 2014; Brunaud et al., 2020).

255 The recent Processing Step-Interval Network, proposed by
 256 Bertran et al. (2016), can also be seen as an extension of the
 257 STN/SEN, with influence from early heat exchanger network mod-
 258 els (Yee and Grossmann, 1990). The representation adds structure
 259 and nuance to the states through the use of processing intervals.
 260 An example of its use can be found in Garg et al. (2019) for the
 261 production bio-succinic acid.

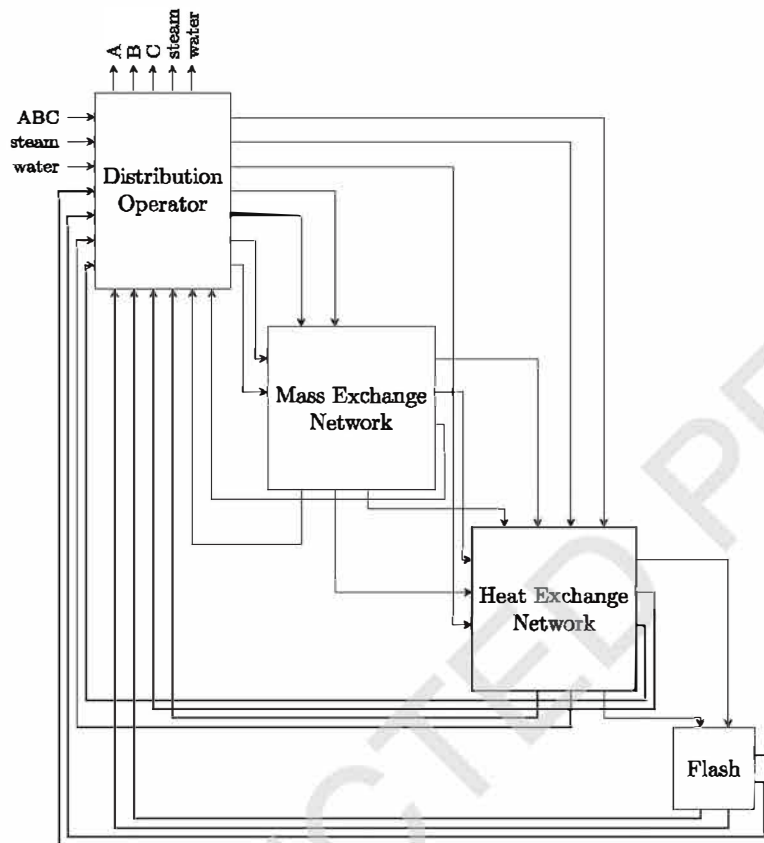


Fig. 5. State-Space Representation (SSR) superstructure for a 3 component sharp split distillation sequence. Boxes represent state-space operators. Arrows represent state variables that are inputs to or outputs from their respective operators.

2.4. State-space representation

The state-space representation (SSR) was adapted from the concept of “state space” in system theory (Zadeh and Desoer, 1979). In the state-space approach, the design problem is posed as identification of the properties of the input-state-output relations between input and output variables (Bagajewicz and Manousiouthakis, 1992). The input/output variables are defined by the process engineer, while the input-state-output relations between variables yield a given structure. For process synthesis, the structure involves sequential applications of two classes of functions, namely (a) mixing and splitting of streams in the distribution network, and (b) unit operations which determine the process operator.

The SSR was motivated by the ability to easily generate complex distillation configurations such as Petlyuk columns. In Bagajewicz and Manousiouthakis (1992), the SSR for a distillation network is introduced as the integration of heat- and mass-exchanger operations. The state space approach was further extended by Wilson and Manousiouthakis (2000), which explores the limits of discretization of the design space. Another similarly-motivated extension was recently developed by Liesche et al. (2019).

The SSR is characterized by matrix operations involving the state variables. The numerical structure of these matrix operators ultimately translates to a physical process structure. Visualization of the SSR (see Fig. 5) involves abstract boxes representing the operators, interconnected by the state variables serving as inputs to or outputs from these operators. The mathematical convenience of the matrix-operator interpretation has gained the SSR significant popularity in process integration (mass/heat/work exchange) appli-

cations (see Table A.2). In Saif et al. (2009), a comprehensive survey on the applications of the SSR methodology to optimization of membrane and hybrid membrane process systems for wastewater treatment is presented.

The SSR is a very general representation, but given its abstractness and lack of supporting software tools, it has seen limited uptake outside of its proven area of process integration (Fig. 6).

2.5. R-graph representation

Farkas et al. (2005b,c) adapt the SEN-OTOE to create the R-graph representation, in which nodes correspond to the inlet and outlet ports of each candidate process unit. The inlet ports function as multi-stream mixers, while the outlet ports correspond to splitters. Directed edges between the ports represent process streams, which always originate from an outlet port and end at an inlet port. The R-graph representation also features source and sink units, corresponding to raw materials and products, respectively. The source unit only has an outlet port, while the sink unit only has an inlet port. By definition, all R-graph nodes must be connected to another node in the graph.

The R-graph is motivated by modeling concerns that may arise in the traditional STN or SEN approach. First is the problem of multiplicity and redundancy, whereby a superstructure encodes multiple equivalent solutions, needlessly increasing the computational cost of the search algorithm. These redundant structures are easily created when unit bypasses are possible. In addition, no unique algebraic description is generally available for a given superstructure. Simple algebraic transformations can give rise to an infinite number of mathematical programming formulations that all yield the same engineering solution.

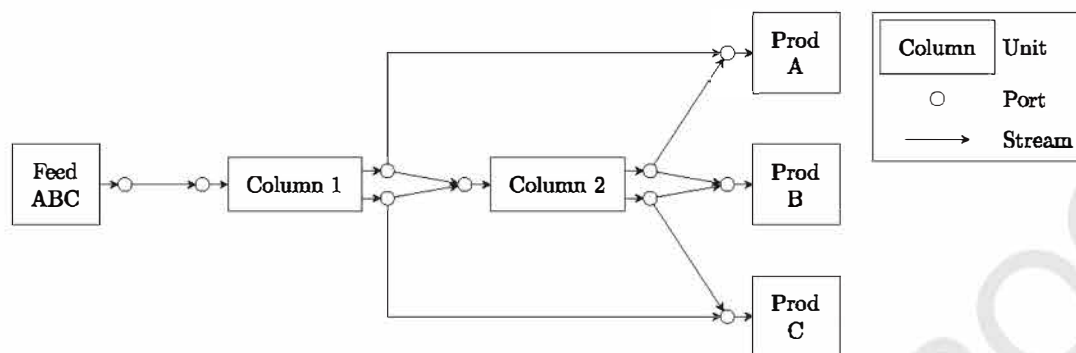


Fig. 6. R-graph superstructure for a 3 component sharp split distillation sequence.

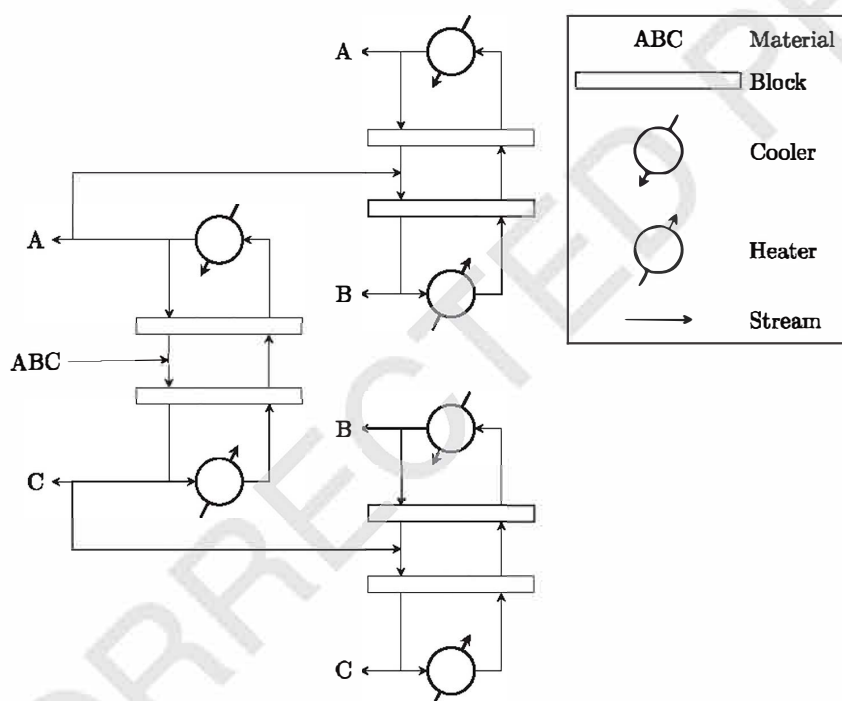


Fig. 7. GMF superstructure for a 3 component sharp split distillation sequence.

321 Farkas et al. (2005b) address superstructure multiplicity by
 322 proposing techniques to consider only R-graphs that are non-
 323 isomorphic. They then introduce the “basic” GDP (BGDP) model
 324 in the spirit of the GDP formulation in Yeomans and Gross-
 325 mann (1999), but exploiting the R-graph to avoid introduc-
 326 ing additional logical relations that would be required to de-
 327 fine certain substructures. Kocis and Grossmann (1988) and
 328 Sztikai et al. (2002) perform a computational analysis on litera-
 329 ture synthesis problems, demonstrating the procedures to build
 330 the BGDP and various mathematical representations (Farkas et al.,
 331 2005c). The methodology is then applied to distillation column de-
 332 sign and optimization by Farkas et al. (2005a).

333 As with the P-graph approach, the R-graph exploits mathemat-
 334 ical properties of graphs to improve solution strategy performance.
 335 Here, the R-graph also takes advantage of logical representability
 336 benefits conferred by GDP modeling. However, no software tools
 337 exist to support the R-graph approach, and the modern-day bene-
 338 fits of BGDP over a traditional GDP are an open question given the
 339 prevalence of linear preprocessing for logical relations (Fig. 8).

340 2.6. Generalized modular framework representation

341 The generalized modular framework (GMF) representation was
 342 introduced by Papalexandri and Pistikopoulos (1996) to simplify

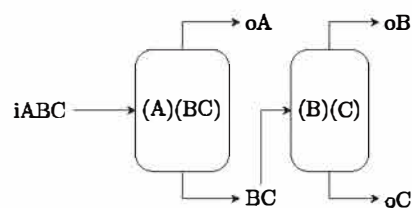


Fig. 8. Group contribution based flowsheet for 3 component sharp split distillation sequence.

343 superstructure generation with an aim to identify advantageous 343
 344 structural alternatives without needing to explicitly pre-postulate 344
 345 them, much like the state-space representation. GMF was also first 345
 346 developed with a focus on mass and heat exchange networks, with 346
 347 a later distillation sequencing example by Proios et al. (2005) (see 347
 348 Fig. 7). GMF is one of the first major representations to explicitly 348
 349 facilitate design of reactive separation systems (Papalexandri and 349
 350 Pistikopoulos, 1996). The reaction-separation superstructure intro- 350
 351 duced by Linke and Kokossis (2003) can be seen as an extension 351
 352 based around similar ideas. More recently, GMF has also been ex- 352
 353 tended to explore operability issues of design (Tian et al., 2018b). 353

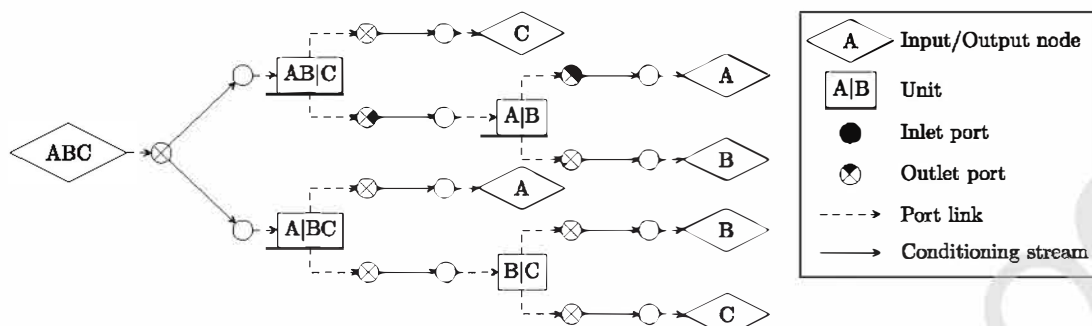


Fig. 9. UPCS representation for a 3 component sharp split distillation sequence.

354 2.7. Group contribution based methodology

355 The group contribution based process flowsheet synthesis
 356 approach is detailed by d'Anterrosches and Gani (2004,
 357 2005), drawing inspiration from group contribution methods
 358 in thermodynamic property prediction for molecular design
 359 (Fredenslund, 2012). In property prediction, a function is developed
 360 relating the contribution of different molecular groups (atoms with
 361 different bonding relationships) to the value of a physical property
 362 of interest. For molecular design, this prediction function is used to
 363 determine the optimal molecular groups that constitute a potentially
 364 novel molecule. Applied to flowsheet synthesis, a group can
 365 be represented by a process unit or a set of units, with the goal to
 366 determine which collection of process units contribute to give the
 367 best flowsheet performance. The approach, computer-aided flowsheet
 368 design (CAFD), is illustrated for the design of a distillation
 369 column by d'Anterrosches and Gani (2005).

370 As with molecular design, a difficulty of this method is obtaining
 371 parameters for the prediction function that determines the
 372 contribution of various potential process groups to an overall design
 373 objective, and their ability to satisfy process specifications.
 374 However, if parameters are found that give accurate predictions,
 375 evaluation of different process alternatives is generally computationally
 376 inexpensive. Tula et al. (2014, 2015) present a recent
 377 overview of the CAFD framework (Fig. 9).

378 2.8. Phenomena-building block approach

379 In the early 2010s, renewed interest in process integration
 380 and nontraditional process units led to the development of the
 381 phenomena-building block (PBB) approach by Lutze et al. (2013),
 382 extending phenomena-centric ideas promoted by Hauan and
 383 Lien (1998). As with earlier strategies like the state-space and GMF
 384 representations, PBB allows for a broader design space that can
 385 automatically generate processes with novel combinations of chemical
 386 and physical phenomena taking place within process units. A
 387 major challenge with approaches that attempt to propose novel
 388 equipment is the selection of an appropriate optimization objective
 389 function. As a proxy, many methods use thermodynamic insights,
 390 seeking to minimize either energy or exergy use in the process.
 391 Kuhlmann and Skiborowski (2016) propose use of development
 392 of an PBB equipment database as one solution to this challenge.
 393 Other strategies avoid this problem entirely by proposing screening
 394 rules that leave a tractable set of promising candidate flowsheets
 395 to evaluate (Holtbruegge et al., 2014). However, these screening
 396 rules may require simplifying assumptions about the process
 397 to be made, and may prematurely exclude advantageous process
 398 structures.

2.9. Unit, port, conditioning stream representation

399

The unit, port, conditioning stream (UPCS) representation was
 introduced by Wu et al. (2016), consisting of three elements: (a)
 units, which can be general process units, source units, or sink
 units; (b) ports, which correspond to unit inlets and outlets, and
 serve as multi-stream mixers and splitters; and (c) conditioning
 streams, which link outlet and inlet ports, while also handling temperature
 and pressure change operations.

The UPCS representation is heavily influenced by ideas in the
 STN, the P-graph, the R-graph, and the more recent unit operation-
 port-state (UOPSS) superstructure (Zyngier and Kelly, 2012). The
 UPCS thus continues the tradition of drawing inspiration from the
 process scheduling literature (Kelly, 2004; 2005).

As in the P-graph method, Wu et al. (2016) describe an algorithm
 to generate a UPCS superstructure. First, the set of considered process
 units are selected based on knowledge of the applicable reaction and
 separation tasks. Next, inlet and outlet ports are defined for each
 unit, and streams are created to connect each outlet port to all inlet
 ports. From this fully-connected starting point, the authors describe
 four rules to prune invalid and unnecessary connections, based on the
 set of "minimal" and "feasible" components for each port. Minimal
 components are those that must be present at an inlet or outlet port.
 For example, a reactor $A + B \rightarrow C$ would be ineffective without
 components A or B, so those would be considered minimal components
 for the reactor inlet port. Feasible components are those that may
 be present at a given port. All minimal components are also feasible,
 but a reactor inert I may be considered feasible but not minimal.

Rule 1. All minimal components for outlet ports should be feasible
 for connected inlet ports.

Rule 2. All minimal components for inlet ports should be feasible
 in at least one connected outlet port.

Rule 3. All outlet ports connected to a reactor inlet port must contain
 at least one feasible component that is minimal for the reactor inlet.

Rule 4. All minimal components for a separator inlet port must be
 feasible in connected outlet ports.

Rule 1 ensures that inlet ports do not receive infeasible components
 from connections to outlet ports. Rule 2 ensures that each inlet port
 receives its necessary components. Rule 3 reduces the number of
 streams connected to a reactor inlet. It is worth noting that in some
 systems, inerts may be important to the reaction controllability, so
 care should be given to which components are deemed feasible versus
 minimal. Rule 4 avoids unnecessary mixing and separation by
 preventing, among other possibilities, a pure component at a
 separator outlet from being immediately remixed into the separator
 inlet.

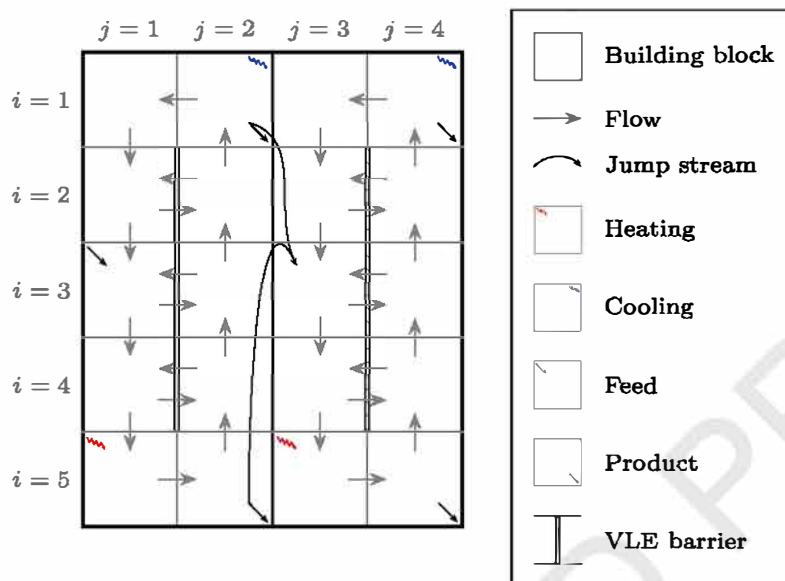


Fig. 10. Building block-based superstructure for a 3 component sharp split distillation sequence.

446 By shifting temperature and pressure change complexity to the
 447 streams, UPCS generates visually simpler superstructures than the
 448 STN-OTOE. Use of ports also reduces bypass redundancy, as with
 449 the R-graph representation. However, even after screening with the
 450 described connectivity rules, automated superstructure generation
 451 techniques often produce many more interconnections than are ac-
 452 tive in the final solution. As a result, the authors also introduce
 453 simplification strategies that reduce the number of conditioning
 454 streams that must be considered. These simplifications are made
 455 based on engineering judgement and restrict the generality of the
 456 strategy. However, they reflect real optimization tradeoffs between
 457 the generality of a superstructure representation, the fidelity of
 458 the physical property calculations, and the computational tractabil-
 459 ity of its solution. By distinguishing between minimal and feasible
 460 components, the UPCS provides more chemical engineering nuance
 461 than the P-graph, while also providing a general algorithm for gen-
 462 erating its representation.

463 2.10. Building block-based superstructure

464 The building block-based superstructure (BBS) (Demirel et al.,
 465 2017) is the most recent contribution that attempts to provide
 466 a very general representation, capable of capturing aspects of
 467 novel equipment design. The representation consists of a two-
 468 dimensional grid of blocks, pictured in Fig. 10. Each block rep-
 469 resents a control volume, capable of admitting flow across its
 470 boundaries to/from its adjacent blocks. Flow across these bound-
 471 aries can be fully restricted, semi-restricted (to represent mem-
 472 brane/separation systems), or fully open. Each block admits raw
 473 material feed into and product withdrawal from the control vol-
 474 ume, as well as chemical reactions. Each block also admits tem-
 475 perature and pressure change operations. The control volume of
 476 each block is assumed to be well-mixed, with uniform composi-
 477 tion, temperature, and pressure in its exit streams.

478 Unlike the graph-based representations, the BBS approach
 479 prioritizes generality and graphical accessibility over solution
 480 tractability. By allowing a broad range of operations in each grid
 481 cell, the BBS permits the representation of diverse equipment de-
 482 signs without the need to explicitly postulate alternatives, includ-
 483 ing novel combinations of phenomena that may lead to new equip-
 484 ment designs. Moreover, the two-dimensional grid layout facili-
 485 tates an elegant visualization of the optimal structure. Discretiza-

tion in the spatial domain for plug flow reactors and membranes
 can also be represented as a series of linked grid blocks. However,
 the structure of the BBS creates a difficult mathematical program-
 ming problem.

The BBS therefore challenges the state-of-the-art in modeling
 and solution techniques. To tackle tractability considerations, two
 main avenues of investigation have arisen: new solution techni-
 ques tailored to the block-grid structure and the careful appli-
 cation of problem-specific engineering expertise. Symmetry is a
 prominent feature of the BBS, due to the versatility of its blocks.
 Each block in the BBS is identical, except the boundary blocks,
 which have fewer interconnections. Li et al. (2018) therefore pro-
 pose symmetry-breaking constraints to reduce the resulting combi-
 natorial redundancy. Iterative strategies that explore partitions of
 the feasible region in a “frame-by-frame” manner have also been
 proposed (Li et al., 2018). However, as with most problems, spe-
 cialized process knowledge can be a much more powerful tool.
 By carefully applying domain restrictions, e.g. pre-specifying flow
 directions, block boundaries, raw material/product block identi-
 ties, reaction blocks, etc., the problem can be made much more
 tractable. To aid in this, Li et al. (2018) proposes the use of “jump
 streams” to connect arbitrary blocks with each other, avoiding the
 need for specifying empty blocks to accomplish the desired connec-
 tivity. An example of their use can be seen in Fig. 10, where the
 distillate and bottoms of the first column are connected to the feed
 of the second column. Engineering knowledge also plays a role in
 superstructure generation. In general, it is an open question how
 many rows and columns should be postulated in the initial su-
 perstructure. For the special case of distillation sequence design,
 the number of BBS rows should correspond to the number of col-
 umn trays to be considered. In this example, the BBS representa-
 tion, pre-specified for the three component sharp split distillation
 sequence design, resembles the SEN variant 1 (see Fig. 4a). How-
 ever, successive restrictions of the design space based on engineer-
 ing knowledge can compromise solution novelty—a central feature
 of the BBS representation—and so these restrictions should be ap-
 proached carefully. Ultimately, the BBS provides an initial start-
 ing point for approaching the central tradeoff in superstructure-
 based synthesis (between generality, model fidelity, and tractabil-
 ity) that emphasizes the former two factors, and the solution strat-
 egy should be tailored accordingly.

527 3. Modeling and solution strategies

528 This paper is focused primarily on discussing different super-
529 structures, but we will briefly touch on the modeling and solution
530 strategies here, because they can often be a factor in selection of
531 the representation. The classic approach involves posing a math-
532 ematical programming formulation as a large-scale mixed-integer
533 nonlinear programming (MINLP) problem (Grossmann et al., 2000).
534 Discrete decision variables capture structural alternatives; continu-
535 ous variables, the process conditions (e.g. temperatures, flowrates,
536 pressures, and equipment sizes). This formulation, expressed
537 within an algebraic modeling platform, would then be sent to a
538 numerical solver to obtain optimal values of the decision variables.

539 In general, process design is a computationally difficult prob-
540 lem, with nonconvex functions involved describing the process
541 units and their interconnections. These complications can lead to
542 intractable formulations, which modelers often address by impos-
543 ing simplifying assumptions (e.g. ideal thermodynamics and linear
544 approximations) or tailored restrictions of the search space.
545 Grossmann and Santibanez (1980) address the use of linear ap-
546 proximations in superstructure optimization problems. In addition,
547 more general advanced strategies have been developed to effect-
548 ively model and solve this difficult class of problems. In the fol-
549 lowing subsections, we present several themes common among
550 these strategies: logic-based modeling, surrogate models, and de-
551 composition algorithms.

552 3.1. Logic-based modeling

553 Process design problems offer significant mathematical struc-
554 ture in the discrete domain, a feature exploited by the graph-based
555 superstructures (P-graph, R-graph, UPCS). Likewise, the struc-
556 tural relationships described by a superstructure can be encoded
557 through logic-based modeling. Generalized Disjunctive Program-
558 ming (GDP) (Raman and Grossmann, 1994) offers an intuitive way
559 to express the logical-OR (disjunctive) relationship between differ-
560 ent process alternatives, while also capturing the connection be-
561 tween these logical clauses and the algebraic relations that de-
562 scribe each respective alternative (Chen and Grossmann, 2019).
563 GDP also allows imposition of logical statements; for example, that
564 selection of a cheaper reactor necessitates feed pretreatment.

565 GDP is an extension of disjunctive programming from the op-
566 erations research community (Balas, 2018) to allow for nonlinear
567 algebraic relationships. Therefore, it unlocks a suite of solution
568 strategies that may be applied to the synthesis problem, including
569 systematic reformulations to different MINLP representations that
570 may yield improved computational performance (Trespalcios and
571 Grossmann, 2014). GDP modeling also preserves logical structure
572 for tailored decomposition algorithms (see Section 3.3).

573 3.2. Surrogate models

574 In process design, many process unit alternatives may fea-
575 ture complex first-principle models describing transport, thermo-
576 dynamic, and/or kinetic relationships that are relevant to the prob-
577 lem, but too computationally expensive to include directly in the
578 optimization formulation. In this case, surrogate models (or meta-
579 models) pay a key role—replacing these expensive models with a
580 more tractable approximation that is trained with simulated data
581 from the model, or with experimental measurements (Cozad et al.,
582 2014). Standard optimization algorithms can then be applied us-
583 ing the surrogate models, as in Mencarelli et al. (2019), or trust
584 region-based methods can be used (Eason and Biegler, 2016). If the
585 surrogate does not provide derivative information, then derivative-
586 free “black box” algorithms may be necessary (Rios and Sahinidis,
587 2013).

Different classes of surrogates can be used, ranging from lin- 588
ear surrogates to Gaussian processes to artificial neural networks 589
(ANNs). In Super-O, piecewise linear representations of different 590
process segments can be used as the building blocks of a super- 591
structure optimization (Bertran et al., 2016). Henao and Maravelias 592
(2010, 2011) introduce a surrogate-based superstructure framework 593
based on the STN-OTOE approach. Fahmi and Cremaschi (2012) in- 594
tegrate GDP and ANNs—the trained ANN surrogates are substituted 595
in place of the first-principle models in a GDP formulation. Kriging 596
interpolators have also been used (Davis and Ierapetritou, 2015; 597
Caballero and Grossmann, 2008). Recently, Schweidtmann and Mit- 598
sos (2019) introduced a framework for global optimization of su- 599
perstructure synthesis problems with ANNs. 600

Note that in this work, we do not touch on training and par- 601
ameter estimation concerns associated with using surrogate mod- 602
els. Instead, we refer the reader to a recent review paper in the 603
area of surrogate modeling for process design (McBride and Sund- 604
macher, 2019). 605

606 3.3. Decomposition algorithms

Decomposition algorithms that partition a problem into multi- 607
ple tractable subproblems are commonly used to tackle large-scale 608
optimization challenges. Classic examples of this include the Outer 609
Approximation (OA) (Duran and Grossmann, 1986a) and General- 610
ized Benders Decomposition (GBD) (Geoffrion, 1972) algorithms, 611
which separate the design problem into a master problem that 612
solves a linear approximation of the full space problem and a sub- 613
problem that evaluates a fixed flowsheet configuration taking into 614
account the nonlinear relationships. At each iteration, the solution 615
of the master problem proposes a new realization of the discrete 616
variables for the subproblem, and the nonlinear subproblem so- 617
lution, if feasible, gives new candidate solution points. The sub- 618
problem solution also gives new variable values at which to add 619
linearizations to augment the master problem; OA and GBD differ 620
in the generation of these linearizations. Termination occurs when 621
the solution of the master problem converges with the solution of 622
the subproblem. 623

This two-level decomposition between discrete flowsheet se- 624
lection and detailed evaluation remains the most common theme 625
among decomposition strategies for process design. Kocis and 626
Grossmann (1989) present a specialized MINLP decomposition ap- 627
proach for synthesis based on Lagrangean decomposition. The dis- 628
crete elements of an MINLP for process synthesis usually de- 629
scribe logical relationships between superstructure alternatives. 630
With GDP, decomposition may be applied directly on this logi- 631
cal layer. The logic-based outer approximation (LOA) algorithm 632
(Türkay and Grossmann, 1996) exploits this structure to solve 633
the nonlinear subproblems in reduced space, avoiding zero-flow 634
numerical challenges present in MINLP formulations. Logic-based 635
branch and bound (LBB) (Lee and Grossmann, 2000) does the same 636
to solve node relaxations in reduced space, as with the ABB strat- 637
egy for P-graph (Friedler et al., 1996). 638

Note that strategies presented in this section differ from hi- 639
erarchical decomposition (Douglas, 1985) in that the decomposi- 640
tion takes place within an computational solution framework with 641
mathematical guarantees on convergence to optimality. In particu- 642
lar, LBB and a global optimization extension to LOA, GLOA (Lee and 643
Grossmann, 2001), offer convergence guarantees to within an ϵ tol- 644
erance. The other discussed decomposition strategies assume con- 645
vexity, yielding a numerical heuristic for nonconvex chemical pro- 646
cess flowsheet problems. Hybrid strategies have also been pro- 647
posed in which physical insights are used as rules of thumb to 648
screen the solution space before applying a mathematical program- 649
ming algorithm (Bommareddy et al., 2011). 650

651 4. Software implementations

652 Well-established commercial software tools exist for process
653 simulation, but not yet for process synthesis (Tula et al., 2018).
654 As a result, standard industrial practice for synthesis remains ei-
655 ther trial-and-error using simulators, guided by engineering intu-
656 ition or an expert system package, or the development of special
657 purpose implementations in algebraic modeling systems. However,
658 to provide general capabilities for systematic superstructure syn-
659 thesis, new tool sets are needed.

660 To be successful, our community needs software tools to ac-
661 commodate two classes of users: general users who wish to tackle
662 an understood problem, and advanced users whose design chal-
663 lenges lead them to push the state-of-the-art. The former desire a
664 tool with an accessible interface that will consistently deliver re-
665 liable answers for their analyses. The latter, frequently academics
666 or researchers at national labs and major corporations, demand all
667 of the above in addition to the ability to adapt or extend the tool
668 for unknown or unforeseen challenges. The needs of general users
669 limits technology transfer from academia into industry. Academic
670 software rarely benefits from the funding required to create an e-
671legant user interface. Moreover, the finesse required to reproduce
672 academic results often necessitates hiring a student from the rel-
673 evant research group. On the other hand, without investing in ad-
674 vanced functionality and flexibility for advanced users, innovation
675 in the tool will eventually stagnate, and these users may opt to
676 develop a more capable alternative. Developers must balance these
677 issues among other considerations when choosing where to devote
678 limited resources.

679 Actively developed synthesis software packages include Pro-
680 CAFD (Tula et al., 2017), P-Graph Studio (Friedler et al., 2019),
681 MIPSYN (Kravanja and Grossmann, 1990), SYNOPSIS (Tian et al.,
682 2018b), and Pyosyn (Chen et al., 2019), all of which find their roots
683 in academia. ProCAFD is the most sophisticated of these tools in
684 its support of general users, with a graphical user interface and
685 the ability to automatically generate process alternatives from a
686 set of raw materials, products, and reactions. It builds upon pre-
687 existing work in the ICAS (Gani et al., 1997) tool set. P-Graph Stu-
688 dio also features a graphical interface; however, it is less adapted
689 to chemical engineering use, requiring more user input to set up
690 the problem. MIPSYN, on the other hand, has a simple graphical
691 interface, but includes a notion of chemical engineering unit mod-
692 els to aid the user. MIPSYN poses synthesis problems as MINLP
693 or reformulations of GDP models (Ropotar and Kravanja, 2009),
694 which are solved via an integration with the GAMS algebraic mod-
695 eling platform (Brook et al., 1988). SYNOPSIS and Pyosyn are both
696 newer synthesis frameworks, created as part of two Department
697 of Energy projects: RAPID (Bielenberg and Palou-Rivera, 2019) and
698 IDAES (Miller et al., 2018), respectively. SYNOPSIS is built upon the
699 GMF superstructure representation, though the tool itself has not
700 yet been publicly released. As with MIPSYN, an integration with
701 GAMS allows solution of the resulting MINLP models. Pyosyn, on
702 the other hand, does not prescribe a choice of superstructure, in-
703 stead focusing on support for high level modeling representations
704 and solution strategies. Pyosyn supports GDP modeling with the
705 open-source Pyomo.GDP (Chen et al., 2018) library, which also en-
706 ables a suite of solution schemes (Chen and Grossmann, 2019).
707 Specialized chemical engineering support is provided by the IDAES
708 unit model library (Lee et al., 2018), with network representation
709 capabilities using Pyomo.Network.

710 Most of the described tools have a closed-source code base,
711 with some providing free academic licenses upon request. This has
712 the advantage of protecting intellectual property and generating a
713 revenue stream to fund continued research, general user-oriented
714 features such as improved graphical interfaces, and customer sup-
715 port. However, the community must also support open platforms

716 that allow for prototyping of new innovations and integration of
717 these tools with existing capabilities; otherwise, it risks stagnation
718 as in the process simulation domain.

719 5. Superstructure-free approaches

720 Given the challenges of properly generating and solving the su-
721 perstructure synthesis problem, evolutionary "superstructure-free"
722 approaches have been a longstanding fixture of chemical engineer-
723 ing practice (Nishida et al., 1981). Boonstra et al. (2016) discuss
724 the distinction between superstructure-based and superstructure-free
725 approaches. Superstructure-free approaches also tend to adopt a
726 two-level decomposition approach, separating the discrete topolog-
727 ical decision and the detailed flowsheet evaluation, as detailed in
728 Section 3.3. However, instead of a mathematical programming ap-
729 proach to propose flowsheets from the combinatorial search space,
730 an evolutionary algorithm dynamically generates alternative struc-
731 tures, which are then evaluated by an optimization algorithm. Preuss et al. (2014) compare use of an evolutionary algorithm for the upper level and a purely MILP-based approach.

732 Voll et al. (2012) describe a two-phase hybrid proce-
733 dure, combining an evolutionary algorithm and a determinis-
734 tic optimization phase for the energy supply system problem. Neveux (2018) present a similar approach: a structure is generated according to the following mutation rules: (i) block addition between two existing blocks, (ii) block removal, and (iii) permutation of two streams. An NLP is then solved to evaluate the performance of the structure generated. Machine learning has also been proposed as a flowsheet identification technique (Zhang et al., 2019).

743 Superstructure-free approaches avoid the need for integer vari-
744 ables to model the on/off state of a unit. This often expedites the
745 rate at which new candidate flowsheets are generated. However,
746 rigorous lower-bounding guarantees to assert mathematical opti-
747 mality without exhaustive enumeration are lost. In applications for
748 which these mathematical lower bounds are unimportant or out-
749 weighed by other considerations, superstructure-free approaches
750 can be a valuable search heuristic.

751 6. Conclusions

752 Process design is a central challenge of chemical engineering,
753 for which superstructure optimization is a powerful analysis tool.
754 When selecting the correct superstructure representation for a
755 given design problem, the relevant factors are generality, ease of
756 use, and tractability. The representation must capture the relevant
757 choices in processing unit or phenomenological alternatives, clearly
758 represent the space of options, and support formulation of a math-
759 ematical programming problem that is amenable to available opti-
760 mization strategies. In this review, we present the main contribu-
761 tions that led to development of the existing representations, and
762 offer the reader our perspective on their relative strengths with re-
763 spect to different criteria. We discuss algorithms that exist for au-
764 tomated generation of both the process alternatives as well as their
765 superstructure representation. We also discuss implications that a
766 choice of representation can have on the modeling and solution
767 phases of superstructure-based synthesis.

768 Finally, we highlight the central tradeoff that exists in tack-
769 ling superstructure optimization problems: between the generality
770 of the representation, the fidelity of the process unit/phenomena
771 models, and the tractability of solution strategies. The systematic
772 and integrated analysis of alternative structures is the key advan-
773 tage of the superstructure-based approaches; however, they often
774 yield large-scale non-convex mathematical programming formula-
775 tions, which are difficult to solve. We highlight various model-
776 ing and optimization strategies that aim to overcome this chal-
777 lenge. In some cases, authors have chosen to pursue evolution-

Table 1
Acronyms.

Acronyms (alphabetical order)	
ANN	Artificial neural network
BGDP	Basic generalized disjunctive problem
CAFD	Computer aided flowsheet design
CAMD	Computer aided molecular design
GDP	Generalized disjunctive programming
GMF	Generalized modular framework
MINLP	Mixed integer nonlinear programming
NLP	Nonlinear problem
OTOE	One task-one equipment
PBB	Phenomena building blocks
PSE	Process system engineering
SEN	State equipment network
SSR	State-space representation
STN	State-task network
UOPSS	Unit-operation-port-state superstructure
UOSS	Unit-operation-stock superstructure
UPCS	Unit, port, conditioning stream
VTE	Variable task-equipment

778 ary “superstructure-free” approaches in which alternative process
779 structures are dynamically generated and evaluated from a base
780 case flowsheet. This may lead to faster search speeds in the dis-
781 crete design space, at the expense of losing finite time mathemat-
782 ical convergence guarantees.

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792 Declaration of Competing Interest

793 The authors declare that they have no known competing finan-
794 cial interests or personal relationships that could have appeared to
795 influence the work reported in this paper.

796 Appendix A. Superstructure synthesis case studies

797 **Table A.2** summarizes literature case studies that have been ex-
798 amined with each representation. We denote with “*” those exam-
799 ples involving solution of an MINLP or nonlinear GDP, “•” those in-
800 volving solution of an MILP (including linear approximation of an
801 MINLP), and “–” where the problem was solved by other means.

Table A.2

Superstructure design examples and case studies.

- [Pierce and Realf \(1996\)](#): multi-chip module scheduling and design
- * [Caballero and Grossmann \(2001\)](#): 5 hydrocarbon distillation sequence
- [Tao et al. \(2003\)](#): azeotropic separation design
- * [Ahadi-Oskui et al. \(2006\)](#): cogeneration power plant, 32 alternatives
- [Montolio-Rodríguez et al. \(2007\)](#): acetic acid production

(continued on next page)

Table A.2 (continued)

STN	<ul style="list-style-type: none"> • Karuppiah et al. (2008): corn-based ethanol plant synthesis • Drobež et al. (2009): biogas process design * Heno and Maravelias (2011): plant subsystems using surrogate models (amine scrubbing, malic anhydride) • Martín and Grossmann (2013): biorefinery optimization • Wang et al. (2014): thermal power plant design – Halim and Srinivasan (2006): waste minimization • Liu et al. (2006): process retrofit downstream bioprocessing • Voll et al. (2013): distributed energy system design (linearized MINLP) • Vance et al. (2013): sustainable energy supply chain, 21 structures • Heckl et al. (2015): multi-period design for corn processing • Ong et al. (2017): biorefinery design (linearized MINLP) • Edeleva and Stennikov (2018): energy systems optimization • How et al. (2018): biomass supply chain network design
P-Graph	<ul style="list-style-type: none"> • Aviso and Tan (2018): polygeneration • Éles et al. (2018): plant energy supply • Chin et al. (2019): heat-integrated water network (linearized NLP) • Bartos and Bertok (2019): production line balancing – Xu et al. (2015): downstream bioprocess design • Several other examples exist with a similar modeling and solution approach: automotive ammonia production, biomass networks, benzaldehyde production, carbon capture storage, reaction pathway identification, enterprise wide supply, steam supply, and heat integration. We refer interested readers to the recent review paper of Friedler et al. (2019). * Smith and Pantelides (1995): ethylbenzene production – Dünnebiel and Pantelides (1999): thermally linked distillation columns – Linke and Kokossis (2007): extension for Denbigh reaction systems
SEN	<ul style="list-style-type: none"> * Nie et al. (2012): scheduling and dynamic optimization of batch processes * Moreno-Benito et al. (2016): batch process development with dynamics * Cui et al. (2017): coal-based methanol distillation sequence • Madenoor Ramapriya et al. (2018): biorefinery design • Bagajewicz et al. (2002): water treatment network, 8 process units * Dong et al. (2008): integrated heat and water network design, 3 process units * Liao et al. (2010): hydrogen distribution network retrofit, moderate size * Zhou et al. (2012b): water allocation with heat integration
State-Space	<ul style="list-style-type: none"> * Zhou et al. (2012a): hydrogen distribution network design for hydrotreating * Saif and Elkamel (2013): membrane network design * Hong et al. (2016): heat-integrated water network, 15 process units – Pichardo and Manousiouthakis (2017): hydrogen production from natural gas • Böcking et al. (2019): membrane network design with experimental validation
R-graph	<ul style="list-style-type: none"> • Emhamed et al. (2007): desalination facility location • Proios et al. (2005): 4 component heat-integrated distillation sequence design • Algusane et al. (2006): reactive adsorption column design
GMF	<ul style="list-style-type: none"> • Damartzis et al. (2016): amine-based CO₂ capture process design • Tian et al. (2018c): heat exchanger network synthesis with safety and operability * Tian et al. (2020): methyl tert-butyl ether (MTBE) reactive distillation

(continued on next page)

Table A.2 (continued)

Process Group	<ul style="list-style-type: none"> – Tula et al. (2015): hydrodealkylation of toluene – Lucay et al. (2015): mineral concentration * Kuhlmann and Skiborowski (2017): ethanol dehydration – Kuhlmann et al. (2018): transesterification of propylene carbonate
PBB	<ul style="list-style-type: none"> – Garg et al. (2019): bio-succinic acid production * Kuhlmann et al. (2019): ethyl tert-butyl ether (ETBE) production * Wu et al. (2017): bio-process design (25 binaries) * Fasahati et al. (2019): cyanobacteria biorefinery
UPCS	<ul style="list-style-type: none"> * Peng et al. (2019): concentrated solar power plant design * Ng et al. (2019): lignocellulosic biorefinery design • Matsunami et al. (2020): solid drug manufacturing * Li et al. (2018): process integration
Building Block	<ul style="list-style-type: none"> • Li et al. (2018): fuel gas network synthesis—4 headers, 5 sinks

802 The references in the table below are curated from the list of arti-
803 cles citing each representation's source publication, as identified by
804 their respective publishers. See Table 1 for definition of acronyms.

805 Supplementary material

806 Supplementary material associated with this article can be
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