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Synthesis of C-H-O Symbiosis Networks

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The concept of synthesizing carbon, hydrogen, and oxygen (C-H-O) SYmbiosis Networks (CHOSYNs) for the design of eco-industrial parks is introduced. Within a CHOSYN, compounds containing C-H-O are exchanged, converted, separated, mixed, and allocated. The use of C-H-O as the basis for integration creates numerous opportunities for synergism because C, H, and O are the primary building blocks for many industrial compounds that can be exchanged and integrated. A particularly attractive feature of the CHOSYN framework is its ability to use atomic-based targets to establish benchmarks for the design of macroscopic systems involving multiple processes. Several structural representations, benchmarking, and optimization formulations are developed to embed potential CHOSYN configurations of interest and to synthesize cost-effective networks. A case study with several scenarios is solved to demonstrate the new concept and tools. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 1242–1262, 2015

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Introduction

The increasing world population, dwindling natural resources, and escalating environmental concerns continue to highlight the need for sustainable designs of industrial processes. Primary objectives of sustainable design include profitability and capital-productivity enhancement, resource (mass and energy) conservation, pollution prevention, and process-safety improvement. These objectives can be methodically achieved and reconciled using process integration which is a "holistic approach to process design and operation which emphasizes the unity of the process."[1] Systematic process integration methodologies and tools have been developed for the optimal synthesis and design of industrial processes. Recent reviews of the topic can be found in literature.[1–9]

A key branch of process integration is mass integration which is a systematic methodology that provides fundamental understanding and global insights for identifying performance targets and optimizing the generation, routing, and allocation of species and streams.[1] The first contribution in mass integration was made by El-Halwagi and Manousiouthakis,[10] who introduced the concept of synthesizing mass-exchange networks that can preferentially transfer a set of targeted species from a process rich stream to process and external lean streams. Later, the broader concept of mass integration was introduced to deal with optimal generation, routing, and allocation of species and streams throughout the process.[11]

Important classes of mass integration deal with resource conservation via recycle from sources to sinks with focus on specific species such as water and hydrogen. Wang and Smith,[12] developed the water-pinch analysis to identify targets for minimum fresh-water usage and wastewater discharge. Gabriel and El-Halwagi[13] developed the material recovery pinch diagram to minimize the usage of fresh resources and waste discharge through direct recycle strategies. Mathematical programming optimization approaches have also been developed for the targeting and synthesis of water recycle and management networks.[13–16] Also, combined water, heat-recovery, and property integration networks have been synthesized using optimization approaches.[17,18]

Alves and Towler[19] developed an integrated approach for the synthesis of hydrogen networks. Hallale and Liu[20] extended this concept by including pressure constraints and the addition of separation units. Graphical and algebraic techniques were also developed to identify the hydrogen requirement targets.[21,22] Jia and Zhang[23] considered the presence of light hydrocarbons and separation from hydrogen-rich streams. Liu et al.[24] investigated the use of graphical techniques for identifying the pinch location in hydrogen networks including the use of purification devices. Hasan et al.[25] presented an approach to the optimal design of a fuel gas network (FGN). Jagannath et al.[26] extended this approach to minimize flaring through integration with FGNs.

The aforementioned mass-integration approaches for the optimal generation and allocation of specific species have provided substantial insights and savings to individual processes. Additional benefits can accrue when mass integration is applied to multiple processes that form a cluster. In this context, the concept of eco-industrial parks (EIPs) is attractive. Lowe defines an EIP as "a community of manufacturing and service businesses located together on a common property. Members seek enhanced environmental, economic, and social performance through collaboration in managing environmental and resource issues."[27] An EIP is an enabling tool in industrial ecology which seeks to take advantage of the synergy between different systems.[28]

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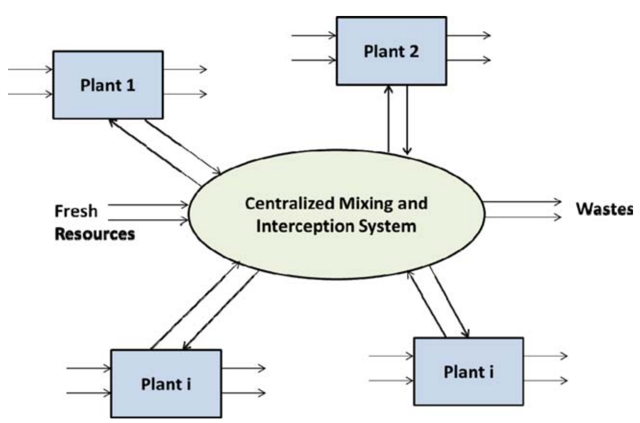

Figure 1. A mass-integration representation of EIPs.[31]

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Although the definition is continuing to evolve, the concept of industrial symbioses is used to describe industrial systems in close proximity which share resources and infrastructure in an attempt to mimic environmental ecology.[29] One of the earliest examples of an EIP is in Kalundborg, Denmark,[30] where an industrial symbiosis network has evolved over time to exchange and share material and energy resources among various production facilities (e.g., gypsum, cement, steel, power, pharmaceuticals, and wallboard). An EIP offers a significant opportunity to advance sustainable design by enhancing material and energy conservation and reducing the environmental footprint.

Spriggs et al. proposed a mass-integration representation of the EIP problem (Figure 1) and extended the use of the material recovery pinch diagram for the exchange of materials (e.g., by-products, waste streams, and material utilities) among multiple processing plants through the utilization of a centralized facility that allows segregation, mixing, separation, and treatment of the exchanged streams.[31] Chew et al. developed a mathematical program formulation for the synthesis of direct and indirect interplant water networks.[32] Lovelady and El-Halwagi developed an optimization approach for the implementation of the mass-integration approach to the design of EIPs for managing water resources.[33] Roddy proposed the building of syngas networks as a mean of reducing industrial carbon footprint.[34] Several additional approaches have been proposed for the design of EIPs while accounting for natural resources (mass and energy) and various characteristics and objectives such as mass, heat, and properties.[35–43]

With the substantial discoveries of shale gas reserves, the renewed interest in effective utilization of crude oil and coal resources, and the growing need to utilize renewable biomass resources, there are significant opportunities for value-added processing pathways.[44–48]

Given the anticipated growth in the aforementioned processing pathways as well as the tremendous size of existing industrial infrastructure, there are unique opportunities for the development of multi-plant coordination networks through EIPs in which compounds containing carbon, hydrogen, and oxygen (C-H-O) are exchanged, converted, split, mixed, and allocated. These possible C-H-O compounds are numerous and their synergistic usage among multiple plants can lead to various benefits including conservation of material and energy resources, reduction of environmental emissions, improvement in capital productivity, increase in material utilization, and enhancement in natural-resource monetization.

This article introduces the concept of synthesizing C-H-O SYmbiosis Networks (CHOSYNs). A CHOSYN is defined as a cluster of multiple plants with shared centralized facilities that are designed to enable the exchange, conversion, separation, treatment, splitting, mixing, and allocation of streams containing C-H-O compounds. It is worth noting that the focus of CHOSYN is the integration emanating from the atomic level (C, H, and O). As such, it encompasses earlier work that was based on specific species (e.g., water and hydrogen) and provides more insights and options than the approaches that use the specific species. Additionally, the use of C-H-O as the basis for integration creates numerous opportunities for synergism because C, H, and O are the primary building blocks for many industrial compounds that can be exchanged and integrated. Furthermore, there are various technologies that share the use of C-H-O compounds.

First, the problem statement is introduced along with the design challenges. Next, a structural representation is developed to embed potential CHOSYN configurations of interest. Atomic-based targeting is used to benchmark the performance of the network. Then, an optimization formulation is devised to synthesize cost-effective networks for the general cases. A case study with different scenarios is solved to illustrate the applicability of the concept and associated tools.

Problem Statement

The problem of synthesizing a CHOSYN may be stated as follows:

Given is a set PROCESSES = $(p|p = 1, 2, \ldots, N_{\text{Process}})$ of industrial processes that exist in the same industrial zone. Each process receives a set FEEDS$_p$ = $(f_p|f_p = 1, 2, \ldots, N_p^{\text{Feed}})$ of feedstocks. The processes produce a number of sources and include a number of sinks that are defined through the following sets:

The set SOURCES = $[i|i = 1, 2, \ldots, N_{\text{Sources}}]$ represents streams that are to be integrated within the CHOSYN. This set is composed of two subsets: external and internal. The subset EXTERNAL_SOURCES = $[i|i = 1, 2, \ldots, N_{\text{External Sources}}]$ includes all the fresh streams that are to be purchased for use in the CHOSYN. Conversely, the subset INTERNAL_SOURCES = $[i|i = N_{\text{External\_Sources}} + 1, N_{\text{External\_Sources}} + 2, \ldots, N_{\text{Sources}}]$ is composed of output streams from the industrial processes that are to be integrated with the rest of the CHOSYN. Each source i has a flow rate G_i (unknown for external sources and known for the base-case of internal sources), pressure P_i^{Source} and temperature T_i^{Source}. The sources contain a set COMPONENTS = $[c|c = 1, 2, \ldots, N_c]$ of C-H-O species. The cth species is given by the following chemical formula $C_{\alpha_c}H_{\beta_c}O_{\gamma_c}$ where α_c, β_c, and γ_c are the atomic coefficients for carbon, hydrogen, and oxygen, respectively, in species c. The composition of species c in source i is designated by $x_{c,i}$.

The set SINKS = $[j|j = 1, 2, \ldots, N_{\text{Sinks}}]$ represents units or systems in the existing industrial processes that can accept the internal and external sources. Each sink has a set of Sink_Inlet$_j$ = $[v_j^{\text{in}}|v_j^{\text{in}} = 1, 2, \ldots, N_j^{\text{Inlet\_Sink}}]$ of inlet ports each requiring a certain flow rate $H_{v_j^{\text{in}}}^{\text{In}}$, pressure $P_{v_j^{\text{in}}}^{\text{In}}$, and

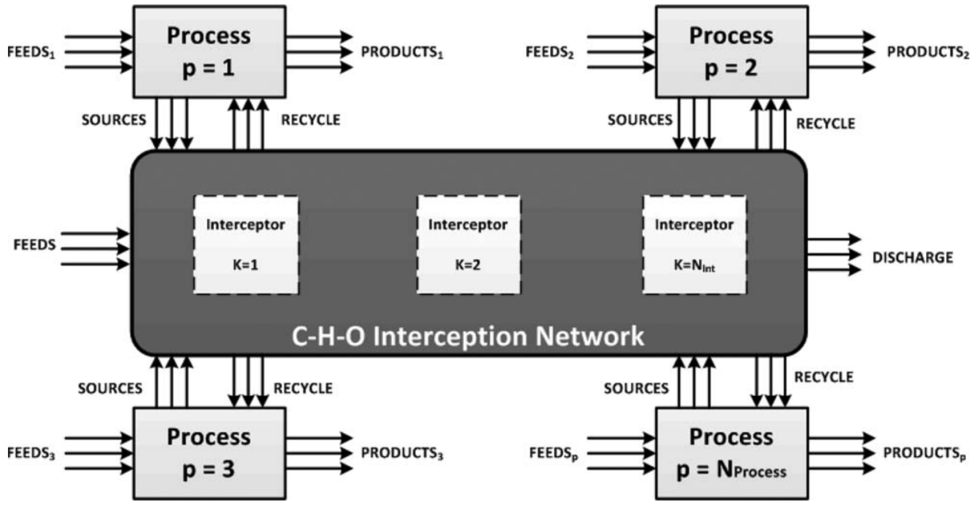

Figure 2. Schematic representation of CHOSYN Synthesis.

temperature $T^{\text{In}}_{v_j^{\text{in}}}$. The following are constraints on the flow rate, pressure, and temperature for the feed to each inlet port of a sink

$$H^{\text{In,min}}_{v_j^{\text{in}}} \leq H^{\text{In}}_{v_j^{\text{in}}} \leq H^{\text{In,max}}_{v_j^{\text{in}}} \quad \forall v_j^{\text{in}} \tag{1}$$

$$P^{\text{In,min}}_{v_j^{\text{in}}} \leq P^{\text{In}}_{v_j^{\text{in}}} \leq P^{\text{In,max}}_{v_j^{\text{in}}} \quad \forall v_j^{\text{in}} \tag{2}$$

$$T^{\text{In,min}}_{v_j^{\text{in}}} \leq T^{\text{In}}_{v_j^{\text{in}}} \leq T^{\text{In,max}}_{v_j^{\text{in}}} \quad \forall v_j^{\text{in}} \tag{3}$$

The composition of the feed to each inlet port of a sink is governed by the following constraints

$$z^{\text{In,min}}_{c,v_j^{\text{in}}} \leq z^{\text{In}}_{c,v_j^{\text{in}}} \leq z^{\text{In,max}}_{c,v_j^{\text{in}}} \quad \forall v_j^{\text{in}}, c \tag{4}$$

There are also constraints on the desired ratios of compositions, that is

$$r^{\text{min}}_{c,c',v_j^{\text{in}}} \leq \frac{z^{\text{In}}_{c,v_j^{\text{in}}}}{z^{\text{In}}_{c',v_j^{\text{in}}}} \leq r^{\text{max}}_{c,c',v_j^{\text{in}}} \quad \forall v_j^{\text{in}}, \forall c, c' \text{ where } c, c' \in \text{COMPONENTS and } c \neq c' \tag{5}$$

Available for service as needed is a set of interceptor units: INTERCEPTORS = (k/k = 1, 2, …, N_{Int}). These are new units that may be added to segregate, mix, chemically convert, separate, heat, cool, pressurize, and depressurize the various sources and allocate them to the different process sinks.

The aim is to synthesize a CHOSYN capable of managing the production, transformation, separation, and distribution of the sources containing the C-H-O compounds to achieve a desired objective or a combination of objectives (e.g., maximum profit, minimum cost, minimum consumption of fresh materials, and minimum environmental discharge). Figure 2 is a schematic representation of the CHOSYN synthesis problem which illustrates the interaction between the individual processes or plants with the CHOSYN.

Synthesis Approach

The problem is represented using the source-interception-sink representation[11] as shown by Figure 3. This structural representation is rich enough to embed potential configurations of interest. Each source is split into a number of fractions that are assigned to the inlet ports of the interceptors. The splits from all the sources are mixed at the inlet ports of the interceptors. An interceptor can have multiple ports to facilitate multiple inputs. These interceptors operate on the sources to induce chemical and/or physical changes. The streams leaving the outlet ports of the interceptors are split and fed to the inlet ports of the sinks where the mixed feeds must satisfy the constraints given by Eqs. 1–5.

The streams exiting from the outlet ports of the sinks may constitute terminal output streams (e.g., final products and by-products or discharged wastes) or may be recycled to form internal sources that are to be further intercepted. A sink may produce an output stream which is recycled such as sink $j = 1$ in Figure 3. A portion of a particular output stream can be recycled such as sink $j = 2$ in Figure 3, and finally an entire output of a sink may be recycled back such as sink $j = \text{N}_j$ in Figure 3. The recycled streams generate the internal sources which may enter the interceptor network. The existence or absence of these configurations are all embedded by the superstructure and are to be determined through optimization as will be described later.

Optimization formulation

The following constrains are used for the mixing and splitting of streams to and from the interceptors:

Source Splitting Mass Balance. Each interceptor, k, has a number of inlet and outlet ports that are described by the indices u_k^{in} and u_k^{out}, respectively. Each source, i, is split into fractions that are assigned to the inlet ports of the interceptors. The flow rate of each fraction connecting source i with inlet port u_k^{in} is termed $G_{i,u_k^{\text{in}}}$. Therefore, the mass balance for splitting each source is given by

$$G_i = \sum_k \sum_{u_k^{\text{in}}} G_{i,u_k^{\text{in}}} \quad i \in \text{SOURCES} \tag{6}$$

Interceptor Inlet Ports Mass Balances. The following are the overall and component mass balances at the inlet ports of the interceptors

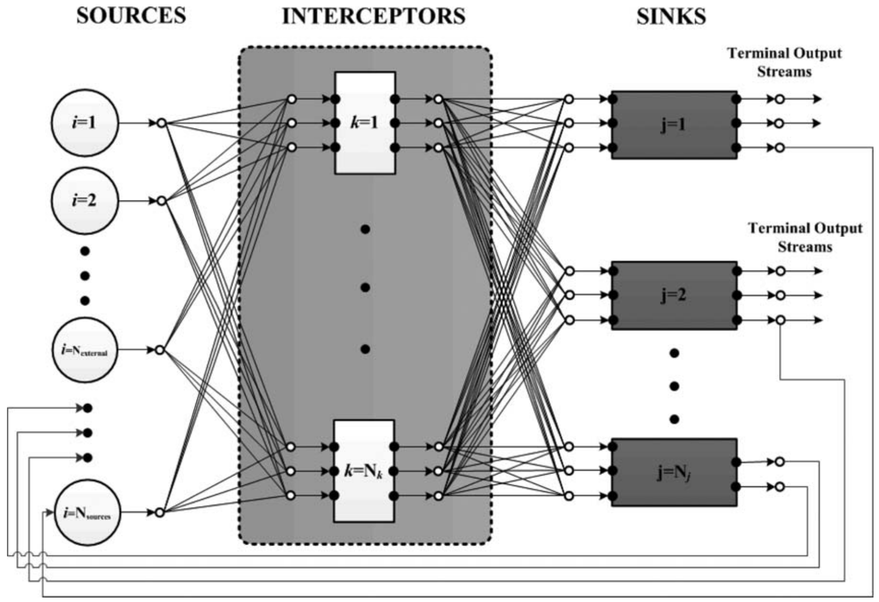

Figure 3. Source-interceptor-sink structural representation of CHOSYN.

$$W^{\mathrm{In}}_{u_k^{\mathrm{in}}} = \sum_{i=1}^{N_{\mathrm{Sources}}} G_{i,u_k^{\mathrm{in}}} \quad \forall u_k^{\mathrm{in}}, \quad k \in \mathrm{INTERCEPTORS} \tag{7}$$

$$W^{\mathrm{In}}_{u_k^{\mathrm{in}}} y^{\mathrm{In}}_{c,u_k^{\mathrm{in}}} = \sum_{i=1}^{N_{\mathrm{Sources}}} G_{i,u_k^{\mathrm{in}}} x_{c,i} \quad \forall u_k^{\mathrm{in}}, \quad k \in \mathrm{INTERCEPTORS}, \quad c \in \mathrm{COMPONENTS} \tag{8}$$

where $W^{\mathrm{In}}_{u_k^{\mathrm{in}}}$ and $y^{\mathrm{In}}_{c,u_k^{\mathrm{in}}}$ are, respectively, the inlet flow rate and the cth component composition for the stream fed to port u_k^{in}.

Interceptor Unit Modeling Equations and Constraints. The modeling equations for the kth interceptor are given by

$$\Phi_k(W^{\mathrm{Out}}_{u_k^{\mathrm{out}}}, y^{\mathrm{Out}}_{c,u_k^{\mathrm{out}}}, W^{\mathrm{In}}_{u_k^{\mathrm{in}}}, y^{\mathrm{In}}_{c,u_k^{\mathrm{in}}}, G_{i,u_k^{\mathrm{in}}}, x_{c,i}, D_k^{\mathrm{Int}}, O_k^{\mathrm{Int}}, S_k^{\mathrm{Int}} \quad \forall u_k^{\mathrm{in}}, u_k^{\mathrm{out}}, c, i) = 0 \quad k \in \mathrm{INTERCEPTORS} \tag{9}$$

where $W^{\mathrm{Out}}_{u_k^{\mathrm{out}}}$ and $y^{\mathrm{Out}}_{c,u_k^{\mathrm{out}}}$ are, respectively, the outlet flow rate and the cth component composition for the stream leaving port u_k^{out}. The terms $D_k^{\mathrm{Int}}, O_k^{\mathrm{Int}}$, and S_k^{Int} represent the design, operating, and state variables of the kth interceptor. The term Φ_k represents the vector of unit performance functions for interceptor k. Similarly the vector Ξ_k represents the vector of constraints for the kth interceptor

$$\Xi_k(W^{\mathrm{Out}}_{u_k^{\mathrm{out}}}, y^{\mathrm{Out}}_{c,u_k^{\mathrm{out}}}, W^{\mathrm{In}}_{u_k^{\mathrm{in}}}, y^{\mathrm{In}}_{c,u_k^{\mathrm{in}}}, D_k^{\mathrm{Int}}, O_k^{\mathrm{Int}}, S_k^{\mathrm{Int}} \quad \forall u_k^{\mathrm{in}}, u_k^{\mathrm{out}}, c) \geq 0 \quad k \in \mathrm{INTERCEPTORS} \tag{10}$$

It is worth noting that the unit performance equations and constraints for the interceptors are provided for actual units with the right level of details. For instance, if an interceptor is a given chemical conversion unit (or cluster of units), the main and side reactions along with the conversion and yield of different species are reported as a function of the inlet streams and design and operating variables that are allowed to be optimized. These performance equations may be based on first principles, semiempirical representations, or empirical formulas based on regression of actual process or experimental data. This modeling approach leads to high-fidelity results that are practically implementable while using the sufficient level of details.

Mass Balance for Splitting the Outlet Streams from the Interceptors. The flow rate of each fraction connecting the outlet port of an interceptor, u_k^{out} with inlet port v_j^{in} of a sink is termed $H_{u_k^{\mathrm{out}},v_j^{\mathrm{in}}}$. Therefore, the mass balance for splitting each stream leaving an outlet port of the interceptor is given by

$$W^{\mathrm{Out}}_{u_k^{\mathrm{out}}} = \sum_{j=1}^{N_{\mathrm{Sinks}}} \sum_{v_j^{\mathrm{in}}} H_{u_k^{\mathrm{out}},v_j^{\mathrm{in}}} \quad \forall u_k^{\mathrm{out}}, \quad k \in \mathrm{INTERCEPTORS} \tag{11}$$

Sink Inlet Ports Mass Balances. The following are the overall and component mass balances at the inlet ports of the sinks

$$H^{\mathrm{In}}_{v_j^{\mathrm{in}}} = \sum_{k=1}^{N_{\mathrm{Intereptors}}} \sum_{u_k^{\mathrm{out}}} H_{u_k^{\mathrm{out}},v_j^{\mathrm{in}}} \quad \forall v_j^{\mathrm{in}}, \quad j \in \mathrm{SINKS} \tag{12}$$

$$H^{\mathrm{In}}_{v_j^{\mathrm{in}}} z^{\mathrm{In}}_{c,v_j^{\mathrm{in}}} = \sum_{k=1}^{N_{\mathrm{Intereptors}}} \sum_{u_k^{\mathrm{out}}} H_{u_k^{\mathrm{out}},v_j^{\mathrm{in}}} y^{\mathrm{Out}}_{c,u_k^{\mathrm{out}}} \quad \forall v_j^{\mathrm{in}}, \quad ,j \in \mathrm{SINKS}, \quad c \in \mathrm{COMPONENTS} \tag{13}$$

Sink Unit Modeling Equations and Constraints. The modeling equations for the jth interceptor are given by

$$\Psi_j(H^{\mathrm{Out}}_{v_j^{\mathrm{out}}}, z^{\mathrm{Out}}_{c,v_j^{\mathrm{out}}}, H^{\mathrm{In}}_{v_j^{\mathrm{in}}}, z^{\mathrm{In}}_{c,v_j^{\mathrm{in}}}, D_j^{\mathrm{Sink}}, O_j^{\mathrm{Sink}}, S_j^{\mathrm{Sink}} \quad \forall v_j^{\mathrm{in}}, v_j^{\mathrm{out}}, c) = 0 \quad j \in \mathrm{SINKS} \tag{14}$$

where $H^{\mathrm{Out}}_{v_j^{\mathrm{out}}}$ and $z^{\mathrm{Out}}_{c,v_j^{\mathrm{out}}}$ are, respectively, the outlet flow rate and the cth component composition for the stream leaving port v_j^{out}. The terms $D_j^{\mathrm{Sink}}, O_j^{\mathrm{Sink}}$, and S_j^{Sink} represent the design, operating, and state variables of the jth sink. The term Ψ_j represents the vector of unit performance functions for sink j. Each sink inlet port is subject to the previously described constraints

$$H_{v_j^{\text{in}}}^{\text{In,min}} \le H_{v_j^{\text{in}}}^{\text{In}} \le H_{v_j^{\text{in}}}^{\text{In,max}} \quad \forall v_j^{\text{in}} \tag{1}$$

$$P_{v_j^{\text{in}}}^{\text{In,min}} \le P_{v_j^{\text{in}}}^{\text{In}} \le P_{v_j^{\text{in}}}^{\text{In,max}} \quad \forall v_j^{\text{in}} \tag{2}$$

$$T_{v_j^{\text{in}}}^{\text{In,min}} \le T_{v_j^{\text{in}}}^{\text{In}} \le T_{v_j^{\text{in}}}^{\text{In,max}} \quad \forall v_j^{\text{in}} \tag{3}$$

$$z_{c,v_j^{\text{in}}}^{\text{In,min}} \le z_{c,v_j^{\text{in}}}^{\text{In}} \le z_{c,v_j^{\text{in}}}^{\text{In,max}} \quad \forall v_j^{\text{in}}, c \tag{4}$$

$$r_{c,c',v_j^{\text{in}}}^{\text{min}} \le \frac{z_{c,v_j^{\text{in}}}^{\text{In}}}{z_{c',v_j^{\text{in}}}^{\text{In}}} \le r_{c,c',v_j^{\text{in}}}^{\text{max}} \quad \forall v_j^{\text{in}}, \\ \forall c, c', \text{where } c, c' \in \text{COMPONENTS} \quad \text{and } c \neq c' \tag{5}$$

The objective function of this optimization formulation may be in the form of one or more metrics such as minimum total annualized cost (TAC), maximum profit, maximum net present value, minimum usage of fresh, minimum environmental discharge, and so forth. The solution to this optimization formulation gives enough information on the structure of the CHOSYN, the assignment of the streams, the addition of new interceptors, and the chemical and physical transformations of the C-H-O compounds.

Preliminary Screening Using Two Targets

The development of the modeling and cost equations for the interception technologies with appropriate level of details and accuracy can be a laborious task especially for emerging technologies. Furthermore, depending on the nature of the modeling and cost equations, the global solution of the foregoing optimization formulation may be challenging. Therefore, it is useful to first use targeting approaches using molecular insights and simple cost data to shed some light on the system and to provide preliminary screening prior to developing and solving the detailed optimization formulation. In this context, two targeting approaches are proposed: maximum atomic integration of internal resources and raw-material cost targeting.

Atomic targeting using maximum mass integration

This case deals with the scenario of interest in maximizing the integration of process (internal) sources toward meeting the demands of the sinks. As mentioned in the problem statement, the internal sources contain a set COMPONENTS = $[c|c = 1, 2, \ldots, N_c]$ of C-H-O species. The cth species is given by the following chemical formula $C_{\alpha_c}H_{\beta_c}O_{\gamma_c}$ where α_c, β_c, and γ_c are the atomic coefficients for carbon, hydrogen, and oxygen, respectively, in species c. The molar flow rate of the ith source is G_i and the mole fraction of species c in source i is $x_{c,i}$. The atomic balances for carbon, hydrogen, and oxygen over all the internal streams can be carried out using the following expression

$$\begin{bmatrix} A_{\text{C}}^{\text{Internal\_Sources}} \\ A_{\text{H}}^{\text{Internal\_Sources}} \\ A_{\text{O}}^{\text{Internal\_Sources}} \end{bmatrix} = \begin{bmatrix} \alpha_1 & \beta_1 & \gamma_1 \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \alpha_c & \beta_c & \gamma_c \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \alpha_{N_c} & \beta_{N_c} & \gamma_{N_c} \end{bmatrix} \begin{bmatrix} x_{1,N_{\text{External\_Sources}+1}} & \cdots & x_{1,i} & \cdots & x_{1,N_{\text{Sources}}} \\ & & \cdot & & \\ & & \cdot & & \\ & & \cdot & & \\ x_{c,N_{\text{External\_Sources}+1}} & \cdots & x_{c,i} & \cdots & x_{N_c,N_{\text{Sources}}} \\ & & \cdot & & \\ & & \cdot & & \\ & & \cdot & & \\ x_{N_c,N_{\text{External\_Sources}+1}} & \cdots & x_{N_c,i} & \cdots & x_{N_c,N_{\text{Sources}}} \end{bmatrix} \begin{bmatrix} G_{N_{\text{External\_Sources}+1}} \\ \cdot \\ \cdot \\ \cdot \\ G_i \\ \cdot \\ \cdot \\ \cdot \\ G_{N_{\text{Sources}}} \end{bmatrix} \tag{15}$$

On the right-hand side, the atomic coefficients of carbon, hydrogen, and oxygen in each component is multiplied by the mole fraction of each component. This product is subsequently multiplied by the flow rate of the corresponding stream to get the atomic flow rate in each stream. The result on the left-hand side is the "atomic flow rates" of carbon, hydrogen, and oxygen in the internal sources (designated by $A_{\text{C}}^{\text{Internal\_Sources}}, A_{\text{H}}^{\text{Internal\_Sources}}$, and $A_{\text{O}}^{\text{Internal\_Sources}}$, respectively).

To find the minimum requirement for the atomic flow rates of carbon, hydrogen, and oxygen needed by the sinks (referred to as: $A_{\text{C}}^{\text{Sinks}}, A_{\text{H}}^{\text{Sinks}}$, and$A_{\text{O}}^{\text{Sinks}}$, respectively), the following optimization formulation is developed:

For carbon

$$\text{Minimize} \quad A_c^{\text{Sinks}} = \sum_j \sum_{v_j^{\text{in}}} H_{v_j^{\text{in}}}^{\text{In,min}} \sum_c z_{c,v_j^{\text{in}}}^{\text{In}} \alpha_c \tag{16}$$

This objective function seeks to determine the minimum requirement of carbon-atom flow rate needed by all the sinks. The innermost summation calculates the mole fractions of component c each multiplied times the number of carbon atoms in that component. When this summation is multiplied times the molar flow rate entering the sink inlet port, v_j^{in}, the product is the carbon-atom flow rate entering the inlet port sink, v_j^{in}. The outside double summation adds up the carbon-atom flow rates over all inlet ports of the sinks. The objective function is subject to the following constraints

$$z_{c,v_j^{\text{in}}}^{\text{In,min}} \le z_{c,v_j^{\text{in}}}^{\text{In}} \le z_{c,v_j^{\text{in}}}^{\text{In,max}} \quad \forall v_j^{\text{in}}, c \tag{4}$$

$$r_{c,c',v_j^{\text{in}}}^{\text{min}} z_{c',v_j^{\text{in}}}^{\text{In}} \le z_{c,v_j^{\text{in}}}^{\text{In}} \le r_{c,c',v_j^{\text{in}}}^{\text{max}} z_{c',v_j^{\text{in}}}^{\text{In}} \quad \forall v_j^{\text{in}}, \\ \forall c, c' \text{ where } c, c' \in \text{COMPONENTS and } c \neq c' \tag{17}$$

Constraint (17) is a rearranged form of constraint (5) dealing with the required ratios of mole fraction but written in a form that highlights its linearity.

The following constraint is added to ensure that the mole fractions of the formed species entering each inlet port of a sink add up to one

$$\sum_{c} z^{\mathrm{In}}_{c,v_j^{\mathrm{in}}} = 1 \quad \forall v_j^{\mathrm{in}}, j \in \mathrm{SINKS} \tag{18}$$

Similarly for hydrogen and oxygen, respectively, the objective functions are written as

$$\text{Minimize} \quad A_{\mathrm{H}}^{\mathrm{Sinks}} = \sum_{j} \sum_{v_j^{\mathrm{in}}} H^{\mathrm{In,min}}_{v_j^{\mathrm{in}}} \sum_{c} z^{\mathrm{In}}_{c,v_j^{\mathrm{in}}} \beta_c \tag{19a}$$

and

$$\text{Minimize} \quad A_{\mathrm{O}}^{\mathrm{Sinks}} = \sum_{j} \sum_{v_j^{\mathrm{in}}} H^{\mathrm{In,min}}_{v_j^{\mathrm{in}}} \sum_{c} z^{\mathrm{In}}_{c,v_j^{\mathrm{in}}} \gamma_c \tag{19b}$$

Subject to Eqs. 4 and 17.

The identified minimum requirements for the atomic flow rates of carbon, hydrogen, and oxygen ($A_{\mathrm{C}}^{\mathrm{Sinks}}$, $A_{\mathrm{H}}^{\mathrm{Sinks}}$, and $A_{\mathrm{O}}^{\mathrm{Sinks}}$) are compared with the atomic flow rates for carbon, hydrogen, and oxygen available in the internal sources to determine the targets as the net differences as follows

$$\text{Net difference for carbon}-\text{atom flow rate } A_{\mathrm{C}}^{\mathrm{External\_Sources}} = A_{\mathrm{C}}^{\mathrm{Internal\_Sources}} - A_{\mathrm{C}}^{\mathrm{Sinks,min}} \tag{20a}$$

$$\text{Net difference for hydrogen}-\text{atom flow rate} A_{\mathrm{H}}^{\mathrm{External\_Sources}} = A_{\mathrm{H}}^{\mathrm{Internal\_Sources}} - A_{\mathrm{H}}^{\mathrm{Sinks,min}} \tag{20b}$$

$$\text{Net difference for oxygen}-\text{atom flow rate} A_{\mathrm{O}}^{\mathrm{External\_Sources}} = A_{\mathrm{O}}^{\mathrm{Internal\_Sources}} - A_{\mathrm{O}}^{\mathrm{Sinks,min}} \tag{20c}$$

A positive net difference for Eqs. 20a–c indicates a surplus that corresponds to a target for external sources being zero. If any of Eqs. 20a–c yields a negative net difference, external sources are needed to at least compensate for these deficiencies. This provides an opportunity to gauge if internal resources may be sufficient from a particular atomic flow and aids in identifying minimum targets for the external resources that are needed to supplement these internal sources. Therefore, the targets for minimum external supply of C, H, and O are given by

$$A_{\mathrm{C}}^{\mathrm{Externalmin}} = \arg\max \{A_{\mathrm{C}}^{\mathrm{Sinks,min}} - A_{\mathrm{C}}^{\mathrm{Internal\_Sources}}, 0\} \tag{21a}$$

$$A_{\mathrm{H}}^{\mathrm{Externalmin}} = \arg\max \{A_{\mathrm{H}}^{\mathrm{Sinks,min}} - A_{\mathrm{H}}^{\mathrm{Internal\_Sources}}, 0\} \tag{21b}$$

$$A_{\mathrm{O}}^{\mathrm{Externalmin}} = \arg\max \{A_{\mathrm{O}}^{\mathrm{Sinks,min}} - A_{\mathrm{O}}^{\mathrm{Internal\_Sources}}, 0\} \tag{21c}$$

Figure 4a shows the superstructure for the targeting approach and Figure 4b summarizes the steps used in this targeting algorithm. The streams leaving the process sinks are fed to a block that extracts the internal sources and calculates the atomic flow rates ($A_{\mathrm{C}}^{\mathrm{Internal\_Sources}}$, $A_{\mathrm{H}}^{\mathrm{Internal\_Sources}}$, and $A_{\mathrm{O}}^{\mathrm{Internal\_Sources}}$) according to Eq. 15. Next, the optimization programs given by Eqs. 4, 16−19 are solved to determine minimum sink requirements of C, H, and O ($A_{\mathrm{C}}^{\mathrm{Sinks,min}}$, $A_{\mathrm{H}}^{\mathrm{Sinks,min}}$, and $A_{\mathrm{O}}^{\mathrm{Sinks,min}}$). Next, the minimum external targets of C, H, and O are determined from Eqs. 21a–c. The interception network combines the needed internal and external sources, reacts them to produce the desired species that are separated and rendered at the right conditions to meet the constraints for each inlet port of a sink (v_j^{in}).

In the interest of this level of targeting, the interception network is treated as a gray box that ensures atomic balance but does not details the specific technologies that are required to carry out the interception tasks (unlike Figure 3 of the general approach which defines each interception technology and determines its optimal performance, size, type, and cost). This distinction is consistent with the notion of top-level targeting that focuses on benchmarking using a big-picture approach to support the detailed approach given by the general formulation described by Eqs. 1–14 and Figure 3. Because the gray box of interceptors does not include detailed characterization of conversion and yield, it produces optimistic results based on stoichiometric targeting. If the targets are not attractive enough, there is no need to solve the more complex general formulation. Conversely, if the targets are promising, they pose lower bounds on the consumption of the external resources when the general formulation is solved with detailed modeling and cost equations. This approach provides valuable insights and bounds and offers a hierarchical procedure in which relevant details are invoked and used when sufficient promising indicators are identified.

Raw-material cost targeting

Even when the target for external sources is zero, some of these fresh resources may be purchased because of economic reasons. A useful preliminary targeting approach is to check the cost of the external sources compared to the cost of the other external sources that are currently being used as well as the internal sources they are intended to replace. One possible objective is to minimize the cost of the external sources

$$\text{Minimize} \sum_{i \in \mathrm{EXTERNAL\_SOURCES}} \mathrm{Cost}_i^{\mathrm{Source}} G_i^{\mathrm{Used}} \tag{22}$$

Another possible objective function is to minimize the cost of all process sources and waste treatment for the whole CHOSYN

$$\begin{aligned} \text{Minimize} & \sum_{i \in \mathrm{SOURCES}} \mathrm{Cost}_i^{\mathrm{Source}} G_i^{\mathrm{Used}} \\ + & \sum_{i \in I\mathrm{NTERNAL\_SOURCES}} \mathrm{Cost}_i^{\mathrm{Waste}} G_i^{\mathrm{Waste}} \end{aligned} \tag{23}$$

where $\mathrm{Cost}_i^{\mathrm{Source}}$ is the cost of the ith source ($/kmol), G_i^{Used} is the flow rate used of source i (kmol/s), $\mathrm{Cost}_i^{\mathrm{Waste}}$ is the cost of treatment ($/kmol), and G_i^{Waste} is the flow rate of the ith internal source not used in the CHOSYN (kmol/s) and discharged as waste. The objective function is subject to the following constraints:

Carbon, hydrogen, and oxygen atomic flow rates in all sources

$$\mathrm{A}_{\mathrm{C}}^{\mathrm{Sources}} = \sum_{i} G_i^{\mathrm{Used}} \sum_{c} x_{c,i} \alpha_c \tag{24a}$$

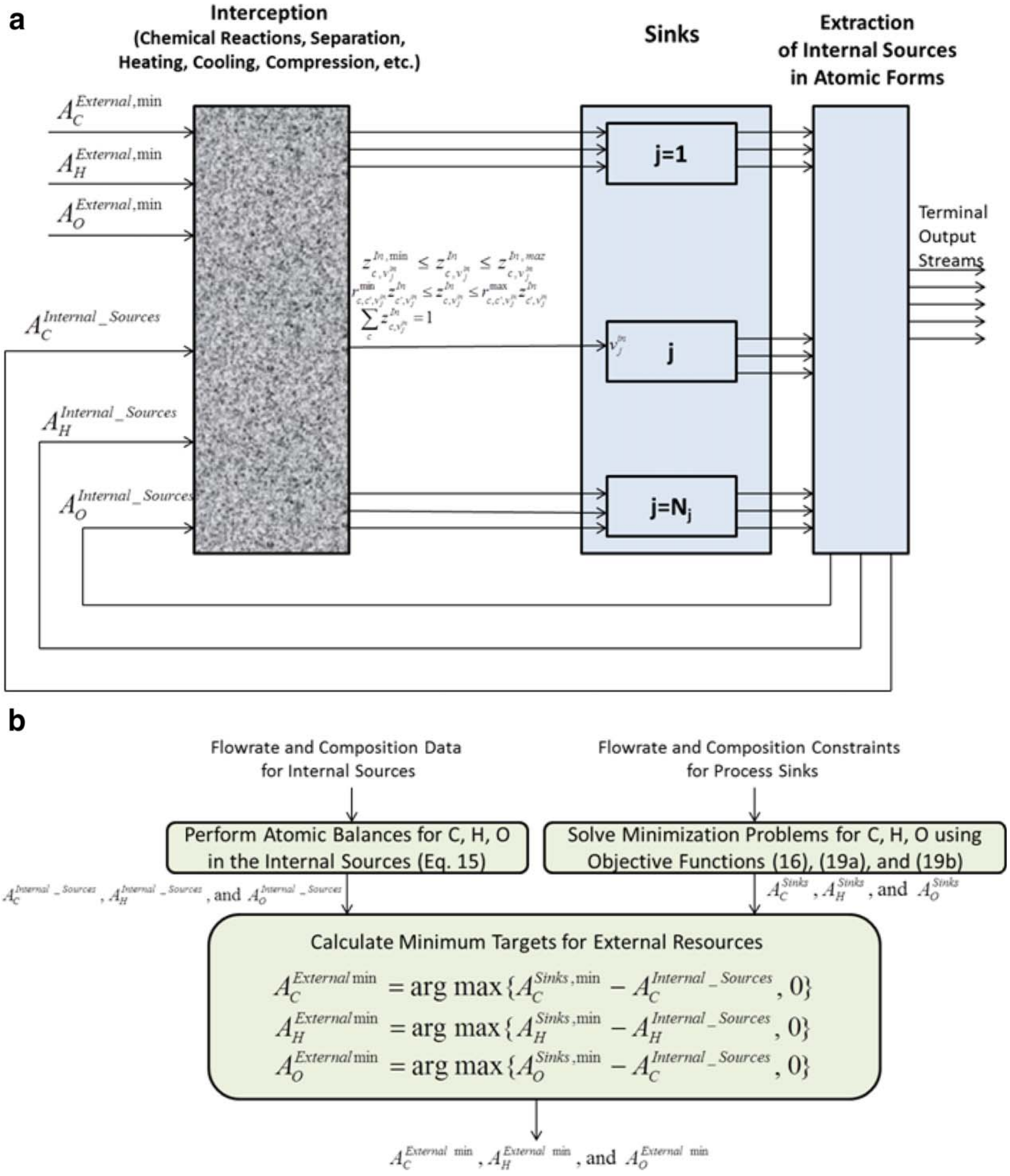

Figure 4. (a) Representation of the external-resource targeting framework. (b) A flowchart for the targeting approach.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$A_{\mathrm{H}}^{\mathrm{Sources}} = \sum_i G_i^{\mathrm{Used}} \sum_c x_{c,i}\beta_c \tag{24b}$$

$$A_{\mathrm{O}}^{\mathrm{Sources}} = \sum_i G_i^{\mathrm{Used}} \sum_c x_{c,i}\gamma_c \tag{24c}$$

where G_i^{Used} is the flow rate of the *i*th source that will be used in the CHOSYN. It is bounded by the following constraints

$$G_i^{\mathrm{Used}} \le G_i^{\mathrm{Available}} \quad i \in \mathrm{EXTERNAL\_SOURCES} \tag{25}$$

where $G_i^{\mathrm{Available}}$ is the maximum available flow rate of the *i*th external source. For internal sources, the following constraint applies

$$G_i^{\mathrm{Used}} \le G_i \quad i \in \mathrm{INTERNAL\_SOURCES} \tag{26}$$

which limits the used flow rate of an internal source to the available flow rate from the producing process. The unused flow rate must leave the CHOSYN and is designated as waste

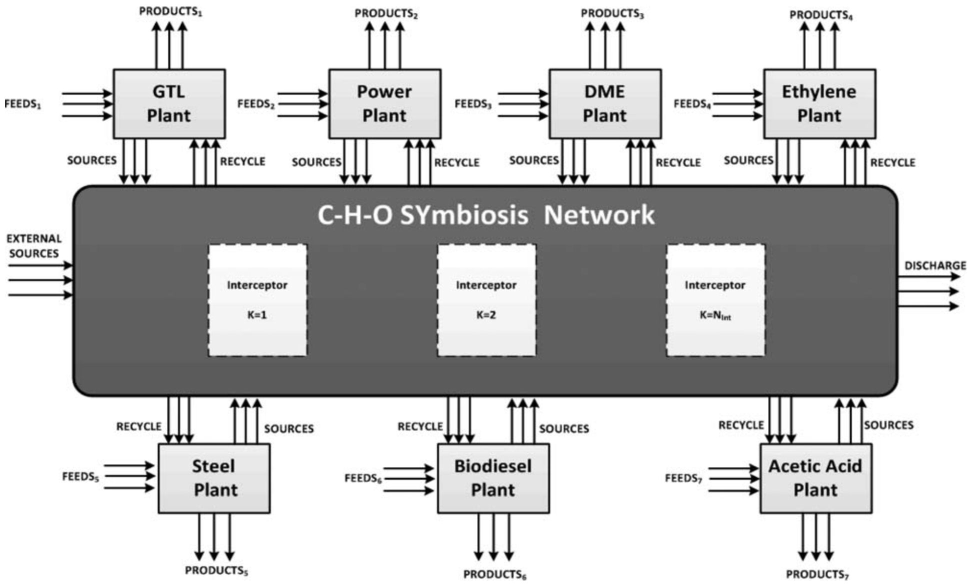

Figure 5. Case study schematic representation.

$$G_i^{\text{Waste}} = G_i - G_i^{\text{Used}} \quad i \in \text{INTERNAL\_SOURCES} \tag{27}$$

Furthermore, the carbon, hydrogen, and oxygen atomic needs are described by the previously mentioned Eqs. 16–18 coupled with constraints (4) and (17)

$$A_c^{\text{Sinks}} = \sum_j \sum_{v_j^{\text{in}}} H_{v_j^{\text{in}}}^{\text{In,min}} \sum_c z_{c,v_j^{\text{in}}}^{\text{In}} \alpha_c \tag{28}$$

$$A_{\text{H}}^{\text{Sinks}} = \sum_j \sum_{v_j^{\text{in}}} H_{v_j^{\text{in}}}^{\text{In,min}} \sum_c z_{c,v_j^{\text{in}}}^{\text{In}} \beta_c \tag{29}$$

$$A_{\text{O}}^{\text{Sinks}} = \sum_j \sum_{v_j^{\text{in}}} H_{v_j^{\text{in}}}^{\text{In,min}} \sum_c z_{c,v_j^{\text{in}}}^{\text{In}} \gamma_c \tag{30}$$

$$z_{c,v_j^{\text{in}}}^{\text{In,min}} \le z_{c,v_j^{\text{in}}}^{\text{In}} \le z_{c,v_j^{\text{in}}}^{\text{In,max}} \quad \forall v_j^{\text{in}}, c \tag{4}$$

$$\begin{gathered} r_{c,c',v_j^{\text{in}}}^{\min} z_{c',v_j^{\text{in}}}^{\text{In}} \le z_{c,v_j^{\text{in}}}^{\text{In}} \le r_{c,c',v_j^{\text{in}}}^{\max} z_{c',v_j^{\text{in}}}^{\text{In}} \quad \forall v_j^{\text{in}}, \\ \forall c, c' \text{ where } c, c' \in \text{COMPONENTS and } c \ne c' \end{gathered} \tag{17}$$

A primary benefit of this targeting approach is its ability to determine potential economic benefit of integrating the multiple processes with internal and external sources. It uses readily available operating-cost data of raw materials and waste treatment. If the targeted CHOSYN does not make a profit based on operating-cost data, there is no need to solve the general formulation which includes unit modeling and fixed costs. This target also sets a lower bound on the operating cost of the CHOSYN.

Table 1. Description and Capacity of Industrial Plants Included in the Industrial Complex

Industrial Plant	Basis	Capacity
GTL plant	FT liquid	25,000 bbl/day
Power plants	Power generation	Two plants (600 MW each)
DME plant	DME product	600,000 tons/year
Ethylene plant	Ethyelene product	200,000 tons/year
Steel plant	Steel production	2,000,000 tons/year
Biodiesel plant	Biodiesel product	50,000,000 gallons/year
Acetic acid plant	Acetic acid product	800,000 tons/year

Case Study

A case study is presented to illustrate the applicability of the developed approach and targeting methods. The objective is to design a CHOSYN to integrate several plants in order to benefit from potential C-H-O synergistic opportunities, reduce the cost of external resources and waste generation, and enhance the use of internal sources. Consider an industrial cluster made up of seven plants shown in Figure 5. The EIP includes typical sized processing facilities: gas-to-liquid (GTL) plant, power plant, dimethyl ether (DME) plant, ethylene plant, steel production plant, biodiesel plant, and acetic acid plant. The plants are located in the same vicinity and, therefore, transportation cost of the integrated streams is negligible compared to the other costs. An input–output process model is developed for each of the various plants using available literature data.

The first task in synthesizing CHOSYNs is to identify the role of each plant in the EIP. This includes identifying the plants that are willing to provide sinks (receive resources from other plants) within the plant and sources (provide resources to other plants). In addition, a plant can serve as a sink while also providing sources to other plants. In this case study, there are six internal C-H-O sources and five sinks along with external sources.

Plant description

The following section provides a brief plant description along with the assumed product capacities, feedstock, and by-products. Table 1 summarizes the industrial plants involved in the industrial cluster and the plant capacities. The plants are diverse in the: types of products (liquid fuels, chemicals, specialty chemicals, and power), feedstock state (solid, liquid, and gaseous), plant size, and environmental impact.

GTL Plant. GTL technology involves the conversion of natural or shale gas into liquid transportation fuels.[49] Although the term liquid transportation fuels can be used to describe a variety of products including: methanol, ethanol, DME, it is mostly used to describe the use of Fischer–

Tropsch (FT) technology to produce longer chain hydrocarbon liquid fuels.[50] As described by Gabriel et al., the GTL process consists of three main sections: synthesis gas production and conditioning, FT Synthesis, and FT product upgrading and separation.[51] In this study, the GTL liquids capacity is 25,000 bbl/day and the performance models and data are taken from literature.[51,52]

Power Plant. With growing stringency of CO_2 emission standards, extensive effort has been invested in identifying opportunities to reduce, sequester, or utilize CO_2 from power plants. As part of this case study, the power plant participates by providing captured CO_2 for utilization by the other industrial plants. The power plant is fueled by natural gas and produces approximately 3.49 g mol CO_2 per MJ.[53] In this case study, two typical size power plants each with a capacity of approximately 600 MW make available equal amounts of captured CO_2 for integration.

DME Plant. DME is produced using a direct or indirect reaction pathway.[54] The direct synthesis involves the conversion of synthesis gas (syngas) to DME. The indirect synthesis involves the conversion of synthesis gas to methanol followed by methanol conversion to DME (reactions below). In this study, the DME plant uses the indirect synthesis route

$$CO+2H_2 \rightarrow CH_3OH \tag{31}$$

$$2CH_3OH \rightarrow CH_3OCH_3+H_2O \tag{32}$$

Ethylene Plant. Ethylene, an important petrochemical intermediate, is produced from a variety of feedstock materials including ethane, naphtha, and LPG. In recent years, a global shift has taken place driven by the increased ethane-based capacity in the United States. This shift is largely due to the substantial increase in shale gas production which typically has a larger fraction of natural gas liquids (NGLs) compared to conventional gas reserves. In this case study, the capacity of the ethylene plant is 200,000 tons/year and is an ethane-based plant.

Steel Plant. The steel-making process produces different types of by-product gases including: blast furnace gas which is produced during hot metal production using coke as a reducing agent or coke oven gas (COG).[55] These gases are typically recycled within the steel plant and used as a fuel for power generation.[56] The plant capacity is 2,000,000 tons/year and the COG reformate is made available as a source for integration in the CHOSYN.

Biodiesel Plant. A variety of renewable sources can be used to produce biodiesel, a promising biofuel currently used as a fuel additive. Transesterification is the method most commonly used to convert oils and fats in biomass to biodiesel. This transesterification reaction involves the reaction of triglyceride and methanol to produce the biodiesel along with glycerol as a by-product.[57] Glycerol can be sold but due to current market saturation this is becoming more difficult. As part of the assessment, the biodiesel plant converts 150,000 tons/year of biomass (soybean oil) into 50 million gallons per year of biodiesel with 700,000 kg/year glycerol by-product.

Acetic Acid Plant. Acetic acid can be produced from various starting materials including: methanol, acetaldehyde, ethylene, and glucose fermentation. Most worldwide production of acetic acid involves the reaction of carbon monoxide and methanol in the presence of a metal carbonyl catalyst in what is termed methanol carbonylation. In this case study, methanol carbonylation is used for the acetic acid plant basis. The plant capacity is 800,000 tons/year of acetic acid.

Sinks description

Sinks are processing units within a plant willing to receive sources from the same plant and from other plants that are part of the industrial cluster. Not every plant in the eco-industrial park is necessarily a sink. This may be due to strict composition requirements, safety concerns, or reliability. In this study, the five sinks are: FT synthesis reactor, ethane steam cracker, methanol dehydration reactor, biodiesel transesterification, and methanol carbonylation reactor. The power plant and the steel plant provide sources to the other plants but do not make any sinks available to receive internal sources. Each sink has specific input requirements and constraints including: flow rate, acceptable impurities, and composition constraints. This includes maximum impurity concentration, minimum species concentration, and composition ratio between species. The following sections summarize the key information and constraints.

FT Synthesis (GTL Plant). The FT synthesis reactor is a sink within the GTL plant which converts the synthesis gas into a distribution of varying length hydrocarbons and steam. An Anderson–Schulz–Flory distribution can be used to model the FT synthesis product distribution. This distribution can be manipulated by changing operating conditions but also by the choice of catalyst. In general, two types of catalysts are used in FT synthesis, cobalt and iron, with particular syngas input constraints. The syngas composition for the different synthesis (Methanol, DME, and FT synthesis) is governed by a stoichiometric constraint (M).[58] For FT synthesis, M depends on whether the FT synthesis is considered high-temperature (HT) or low-temperature (LT). For high-temperature FT

$$M=\frac{H_2-CO_2}{CO+CO_2}=2 \tag{33a}$$

Conversely, for low-temperature Fischer-Tropsch (LTFT)

$$M=\frac{H_2}{CO}\cong 2 \tag{33b}$$

The LTFT is chosen as the FT technology with the allowable impurities being CO_2 and CH_4. The maximum allowable impurities concentration is 5 mol %. In addition, a range is allowed for M

$$(1.9 \leq H_2 : CO \text{ molar ratio } \leq 2.1) \tag{34}$$

Ethane Steam Cracker (Ethylene Plant). Sweet ethane gas is required for the steam crackers which typically operate at 1700 F.[59] Some allowable impurities include H_2, CH_4, C_3H_8, and C_2H_4 and these impurities are usually part of the cracker output recycle. The maximum allowable impurities composition is 10 mol %. In the steam cracker, ethane is converted to ethylene along with a variety of by-products. The overall ethane to ethylene molar conversion is approximately 70%, with the main by-product being a hydrogen-rich off-gas which is described in Table 2.

Methanol Dehydration Reactor (DME Plant). Methanol dehydration is another sink requiring a relatively pure methanol input. Steam represents the only allowable impurity with a maximum allowable composition of 1 mol %. The presence of steam shifts the equilibrium in reverse reducing DME yield. The methanol molar conversion is

Table 2. Internal Sources Available in the Eco-Industrial Park

Internal Sources	1	2	3	4	5	6
Plant	GTL plant	Ethylene plant	DME plant	Biodiesel plant	Steel plant	Power plant
Description	FT tail gas	Ethane cracker off-gas	Methanol by-product	Glycerol by-product	COG reformate	Captured CO_2
Flow (kmol/h)	1500	1000	650	25	2500	10000
Composition (mol %)						
H_2	40	70	–	–	68	–
CO	25	–	–	–	17	–
CO_2	18	–	–	–	2	100
H_2O	2	–	–	–	11	–
CH_4	15	20	–	–	2	–
C_2H_4	–	10	–	–	–	–
CH_3OH	–	–	100	–	–	–
$C_3H_8O_3$	–	–	–	100	–	–

approximately 80% with the unreacted methanol being separated in a subsequent column. This unreacted methanol can be recycled back to the dehydration reactor to reduce the fresh methanol requirement; however, in this case study it is made available for integration as part of the EIP.

Biodiesel Transesterification (Biodiesel Plant). The transesterification involves the reaction of the biomass (soybean oil) and methanol to produce biodiesel and glycerol as the by-product. The optimal methanol to biomass molar ratio is 6:1.[57] Overall, the biodiesel plant requires 50,000 tons/year of methanol for the transesterification. Water represents the only allowable impurity along with the methanol stream with a maximum allowable composition of 1 mol %.

Methanol Carbonylation Reactor (Acetic Acid Plant). Methanol carbonylation involves the reaction of methanol and carbon monoxide to produce acetic acid

$$CO + CH_3OH \rightarrow CH_3COOH \tag{35}$$

Although the reaction involves one mole of carbon monoxide and one mole of methanol, in practice the CO:CH_3OH molar ratio is between 1.4 and 1.6. In this case study, the molar composition of methanol must be greater than 40% while the allowable impurities (H_2O, H_2, CH_4, and CO_2) must not constitute more than 3 mol %.

Internal sources description

The internal sources represent streams which each plant makes available for integration. In reality, not every by-product or waste stream would be made available for integration. Whether due to process safety concerns or to avoid potential processing disruptions, an industrial plant may choose to not make any stream available for integration. In addition, internal sources can also be portions of a stream excess to the plant needs. Each internal source has a given flow rate and composition. These sources range from waste streams with little or no selling value (captured CO_2) to high value streams such as methanol from the DME plant. By making the sources available, the plant may avoid waste disposal charges, increase the value of a by-product stream, or convert a waste stream into a valuable product.

In this case study, the six internal sources (Table 2) include: FT tail gas,[51] ethane steam cracking offgas,[59] DME by-product methanol,[54] biodiesel by-product,[57] COG reformate,[55] and captured CO_2.[60] The GTL plant produces a 15,000 kmol/h tail gas stream. In a GTL plant, the utilization of the FT synthesis tail gas is an important process decision variable.[51] The tail gas can be recycled to the reformer or the FT reactor feed to increase the overall conversion. The remaining tail gas is burned for heat generation. In practice, the GTL plant has excess energy which in most cases is used to produce power and subsequently exported to the grid. In this case study, 90% of the tail gas is recycled while the remaining tail gas which would otherwise be burned is made available for integration.

During the steam ethane cracking to produce ethylene, a hydrogen-rich offgas is produced.[59] The unutilized portion of this stream is made available as internal source 2 for utilization in the EIP. The unreacted methanol in the DME plant which can be recycled directly in the process is made available as internal source 3. Internal source 4 glycerol, a major by-product of biodiesel production[57] is currently a low-value by-product given the market saturation. COG a major by-product of the steel making industry is source 5. This gas can be reformed to produce a hydrogen-rich syngas,[55] while captured CO_2 from the power plant is source 6. The flow rate and composition of each internal source is detailed in Table 2.

External sources description

As unintegrated plants, each satisfies its input requirements using existing external sources. Not all external sources can be easily substituted by an internal source or an alternative external source. For example, if a plant is currently purchasing coal that is gasified to produce syngas; this represents a major hurdle in replacing the coal and the subsequent infrastructure. These types of scenarios require that consideration is made for the cost savings associated with replacement; but also the capital investment associated with the internal source adjustment and the capital invested in building an infrastructure reliant on the existing external sources (e.g., coal). A variety of additional external sources are also available for utilization. These may be utilized along with the internal sources in the existing infrastructure or may require new infrastructure. Table 3 provides the cost data for the external sources and Table 4 shows the composition of these streams.

Solution approach

The information and data provided in the previous sections are used to synthesize the CHOSYN via the aforementioned optimization and targeting approaches. First, the atomic targeting approach is formulated to identify base case atomic deficiencies (needs of external resources) and maximum atomic utilization for C, H, and O. This is followed by the raw-material cost targeting, used to target for the best

Table 3. External Sources Purchase Price

External Source	Cost Basis	Cost
Shale gas	\$/MMBTU	3.00
Ethane	\$/kg	0.220
Methanol	\$/kg	0.565
Hydrogen	\$/kg	2.000
Carbon monoxide	\$/kg	0.075
1:1 Syngas	\$/kg	0.200
2:1 Syngas	\$/kg	0.320
3:1 Syngas	\$/kg	0.410
Steam	\$/kg	0.006
Oxygen	\$/kg	0.110

combination of internal and external sources to minimize the cost of external sources. For the atomic and economic potential targeting, the interception network is considered a black box capable of converting the selected sources to the required species for the sinks while meeting the sink constraints (Figure 6).

These targets do not identify the specific interceptors required to achieve these targets or the capital investment associated with the interceptor network. These are determined through the general optimization formulation of the superstructure shown by Figure 3.

Interceptor network

The final step is to use the information from the targeting to help in synthesizing the CHOSYN. This is crucial in making a final determination if such a CHOSYN can provide actual savings compared to an unintegrated industrial cluster. The general modeling equations for the *j*th interceptor as described by Eq. 14 are included for specific interceptor models such as methanol synthesis, water-gas shift (WGS) reactor, and reformer models. As described, these models are a function of operating conditions along with inlet composition and flow rate. Each interceptor also has a particular input–output process model. The interceptor models also prevent certain sources from entering specific interceptors. For example, the gas plant may only receive natural gas or shale gas resources.

Interceptor network unit models

The process models consist of a mix of gray-box and black-box models. The black-box models are input–output models which include mass and energy balances along with unit size. The gray-box process models include variable inputs, outputs, and unit performance. The models are described in terms of molar flows, component molar flow, and temperature of the various streams.

Gas Plant. A typical gas plant is used for acid gas removal, dehydration, nitrogen removal, and fractionation. The gas plant may only exist if shale gas is chosen as an external source. The plant includes a demethanizer and de-ethanizer capable of producing pipeline quality natural gas and a 90% ethane stream, respectively. In addition, the de-ethanizer produces a propane rich stream (75% propane). This propane rich stream can be sold or mixed with the pipeline quality natural gas. An additional constraint is placed on the pipeline C2+ concentration to ensure that it does not exceed 5 mol %. The gas plant power requirement and energy requirement are 970 kWh/day and 30 MMBTU/h, respectively, per MMscfd of feed.[61] In the formulation, two distinct gas plants are modeled. The first type of gas plant includes a de-ethanizer to produce an ethane stream appropriate for ethylene production. The second type of gas plant does not include a fractionation section. In this case, the demethanizer produces a NGLs stream which can be sold as a by-product or sent to a reformer subject to the pipeline constraint.

Syngas Generation Unit. The syngas generation unit (SGU) consists of the necessary reforming system along with the necessary utility system and H_2O removal. The reforming system can accept any of the available resources. The type of reformer depends on the oxidant chosen such as: H_2O (steam reforming), CO_2 (dry reforming), O_2 (partial oxidation), and multiple oxidants indicate combined reforming. The total Gibbs free energy minimization method is used to model the reforming used for syngas generation.[45] The following species were chosen to accurately represent the reforming outputs: $CH_{4(g)}$, $CO_{2(g)}$, $CO_{(g)}$, $H_2O_{(g)}$, $H_{2(g)}$ and solid carbon modeled as graphite $C_{(s)}$. The method of Lagrange's undetermined multipliers is used to find the set of n_c that minimizes the total Gibbs free energy for a given temperature and pressure. This can be expressed as

$$\sum_{c=1}^{N-1} n_c\left(\Delta G^0_{f_c} + RT\ln\frac{y_c\phi_c P}{P^0} + \sum_e \lambda_e a_{ce}\right) + \left(n_{C(s)}\Delta G^0_{f_{c(s)}}\right) = 0 \tag{36}$$

where $\Delta G^0_{f_c}$ is the standard Gibbs of formation of species c, R the molar gas constant, T temperature (K), $\hat{\phi}_c$ is the fugacity coefficient of species c, a_{ce} is the number of atoms of the eth element and A_e is the total mass of the eth element, and λ_e the Lagrange multiplier for element e, subject to the mass balance constraints

Table 4. External Sources Composition

External Resources	1	2	3	4	5	6	7	8	9	10
Description	Shale gas	Ethane	Methanol	CO	1:1 Syngas	2:1 Syngas	3:1 Syngas	H_2	H_2O	O_2
Composition (mol %)										
CH_4	85	–	–	–	–	–	–	–	–	–
C_2H_6	11	100	–	–	–	–	–	–	–	–
C_3H_8	3	–	–	–	–	–	–	–	–	–
CO_2	1	–	–	–	–	–	–	–	–	–
CH_3OH	–	–	100	–	–	–	–	–	–	–
H_2	–	–	–	–	50	67	75	100	–	–
CO	–	–	–	100	50	33	25	–	–	–
H_2O	–	–	–	–	–	–	–	–	100	–
O_2	–	–	–	–	–	–	–	–	–	100

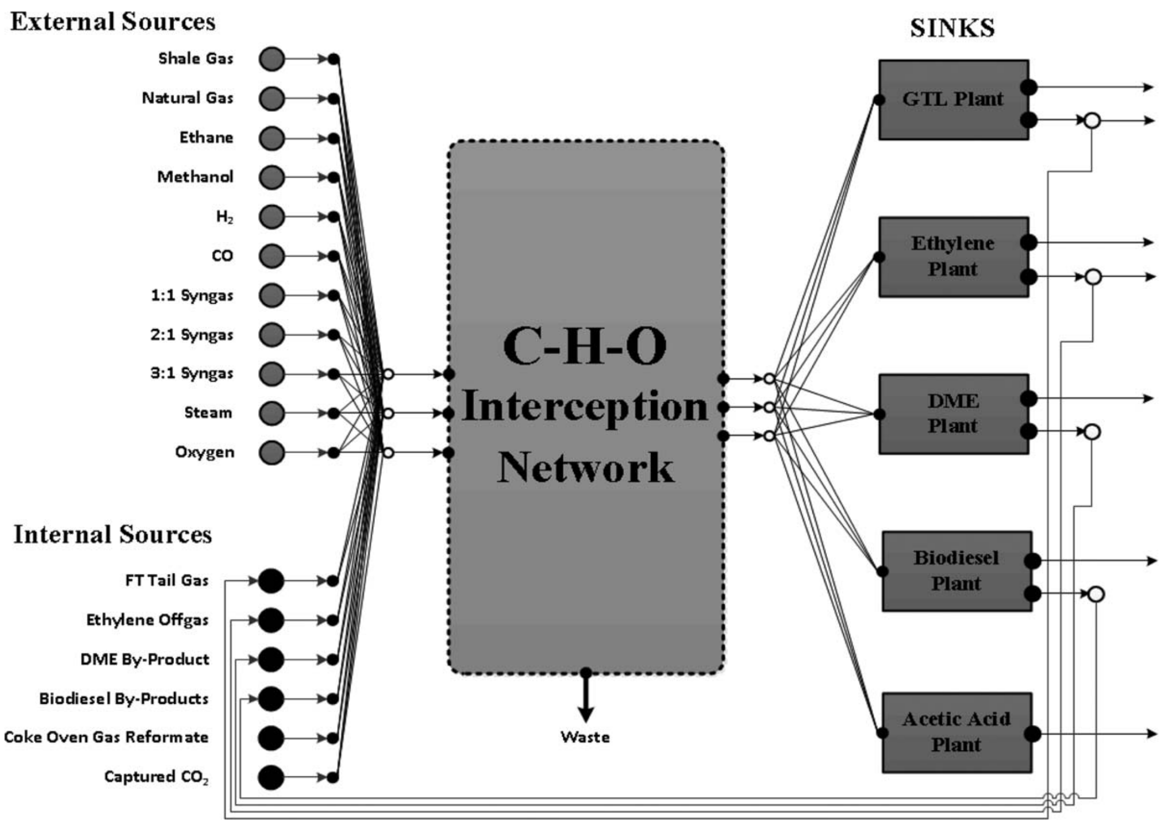

Figure 6. CHOSYN case study representation.

$$\sum\nolimits_c n_c a_{ce} = A_e \tag{37}$$

In this approach, the choice of reactions does not enter directly into the formulation and thus the input–output model allows any CHO inputs subject to the atomic mass balance constraints. The reformer pressure is set at 20 bar[62] while the temperature is allowed to vary between 1000 and 1500 K. The different oxidants (H_2O, CO_2, and O_2) are allowed to vary with the maximum 4:1 allowable steam to carbon (S:C) ratio. As described in Noureldin et al., a systematic approach is ensured through the utilization of correlations for $\Delta G^0_{f_c}$ and ΔH^0_f and the dependence on temperature. The corresponding energy balance is also calculated. In this formulation, glycerol reforming is carried out in an independent reforming system which is modeled in a similar manner. The raw syngas exiting the reformer section is sent to a cooler followed by a flash column to remove any water. The syngas composition from each reforming technology can be quite different. This impacts the downstream syngas conditioning including the need for CO_2 removal and H_2: CO ratio adjustment.

Syngas Conditioning (Shift Reactor). Depending on the reformer technology chosen, different syngas conditioning technologies may be necessary. Following reforming, a WGS or reverse-water-gas shift reactor may be needed to adjust the H_2:CO ratio. The WGS reactor is modeled as an equilibrium reactor along with an energy balance. The model is based on the following reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{38}$$

CO_2 Separator. To meet the sink constraints, the syngas can be sent to a CO_2 separator to reduce CO_2 content of the syngas. Typically, industrial scale CO_2 removal units involve the selective absorption of CO_2 using monoethanolamine (MEA) or diethanolamine. Typically, CO_2 capture efficiencies range between 85 and 95% and a purity of 99.5%.[63] The modeled CO_2 separator is capable of removing up to

Table 5. Fixed Capital Investment Data

Unit	Capcaity Basis	Base Case Capacity	Base Case Cost ($MM)	*b*	*n*	Reference
Gas plant &NGL fractation	MMscf/day	600	900.0	19.39	0.60	61
Satd. gas plant	MMscf/day	13	33.0	5.50	0.70	61
Reforming	MMBTU/h	159	35.6	1.03	0.70	67
Glycerol reforming	MMBTU/h	159	35.6	1.03	0.70	67
Methanol synthesis plant[a]	TPD	5000	780.0	4.71	0.60	44
CO_2 separator	ton CO_2/h	28	25	2.1	0.75	68
LT shift reactor	ton/h	161	3.4	0.20	0.56	67
HT shift reactor	ton/h	161	2.3	0.13	0.56	67
CO separation	lb/h	14,260	45.0	0.14	0.60	67

[a] Excluding reforming (40% of TFC for methanol plant).

Table 6. Operating Cost Data

Utilities Cost	Basis	Cost
Heating	\$/MMBTU	4
Cooling	\$/MMBTU	2
Power	\$/kWh	0.06
Labor cost	\$/h	30

90 mol % of CO_2 with a purity of 99.5%.[64] In this study, the CO_2 separator is assumed to be an MEA system with the total cost of CO_2 removal assumed to be \$30 per ton.[63] This includes an operating cost of approximately \$15 per ton.

CO Separation. The separation of carbon monoxide from a syngas mixture is important where pure CO is required such as the production of acetic acid, polyurethane, formic acid, and phosgene. Although pressure swing adsorption produces a CO-rich by-product stream, this does not yield a CO stream with a sufficient purity for use in the previously mentioned processes. The CO separation can be through the cryogenic separation, the COSORB® process or the methanation of H_2 product. These methods are able to produce a 99+ mol % CO stream but vary in cost and CO recovery. These methods also require varying degree of H_2O and CO_2 prior to CO removal. The CO separation is modeled as a typical COSORB® process which produces a 99.5 CO mol % stream with a 98% CO recovery.[65] The absorption–desorption reaction is represented by the following equation

$$CuAlCl_4C_7H_8+CO \leftrightarrow CuAlCl_4CO+C_7H_8 \qquad (39)$$

During the absorption, the reaction proceeds to the right while during regeneration the complex is heated and the reaction proceeds to the left. The utility consumption for the CO separation is as follows:

Electrical power: 12 kW/kmol CO recovered
Stripper Reboiler Duty: 25 MJ/kmol CO recovered
Cooling Water: 140 MJ/kmol CO recovered

Methanol Synthesis Plant. The methanol synthesis reactor converts CO and H_2 into methanol and water. This conversion is favored by low temperature and high pressure. The methanol synthesis section is modeled based on the information provided in Ehlinger et al.[44] The molar hydrogen conversion to methanol is approximately 36%. The major operating cost for methanol production is the feedstock cost and oxidation (steam or oxygen) involved in the syngas generation section (≈ 90%).[44] These costs are included as part of the previously mentioned reforming model. In addition, heating and cooling utilities along with power consumption for the methanol synthesis portion of the plant are as follows:

Heating: 1 MMBTU/ton methanol produced
Cooling: 7.5 MMBTU/ton methanol produced
Power Consumption: 80 kW/ton methanol produced

Table 7. Atomic Targeting for the Case Study

Description	Carbon	Hydrogen	Oxygen
Source atomic flow (kmol/h)	12,520	11,710	22,470
Minimum sink atomic requirement (kmol/h)	20,798	69,754	17,995
Atomic balance (kmol/h)	−8,278	−58,044	4475
Atomic deficiency (%)	40	83	–
Atomic surplus (%)	–	–	25

Economics

The capital and operating cost for the interceptor network are calculated using various literature sources. The fixed capital investment (FCI) is annualized over a period of 10 years to convert to annualized fixed capital (AFC). The plants are assumed to operate 8000 h/year.

Capital Investment. The FCI for the interceptors is calculated using estimates from various literature sources. A Lang factor of 5 is used to convert the purchased equipment cost (PC) to the FCI.[66] The FCI for each interceptor is summarized in Table 5 for 2014. The correlations summarized in Table 5 are of the form

$$\mathrm{FCI}=b\mathrm{Capacity}^n \qquad (40)$$

where b is the cost constant, Capacity is the capacity of the equipment or plant, and n is the scaling factor for the equipment.

Operating Cost. The major components of the operating cost for the CHOSYN are external sources (raw materials), utilities cost, labor cost, and maintenance cost (Table 6). The annual operating cost (AOC*)* is calculated as follows

$$\mathrm{AOC}=C_{\mathrm{RM}}+C_{\mathrm{OL}}+C_{\mathrm{UT}}+0.06\,C_{\mathrm{MT}} \qquad (41)$$

where C_{RM}, C_{OL}, C_{UT}, and C_{MT} represent the operating costs associated with raw materials, labor, utilities, and maintenance, respectively.[69]

The operating labor cost can be estimated using the correlation by Alkhayat and Gerrard.[69] This is given by

$$N_{\mathrm{OL}}=(6.29+31.7P^2+0.23N_{\mathrm{np}})^{0.5} \qquad (42)$$

where N_{OL} is the number of operators in each shift, P is the number of processing steps which handle particulate solids, N_{np} is the number of process steps that handle nonparticulate solids. In this study, P is zero due to the lack of solids handling processing steps. This reduces Eq. 42 to

$$N_{\mathrm{OL}}=(6.29+0.23N_{\mathrm{np}})^{0.5} \qquad (43)$$

Assuming that a single operator works on average 49 weeks per year and five 8-h shifts per week leads to a total of 245 shifts per operator per year. For a plant operating 365 days/year, 24 h/day, and 3 shifts/day a total of 1095 shifts required per year. This means that approximately 4.5 operators are required for each operator needed in the plant at any specific time. In this case study, it is assumed that the cost of system operators is \$30 per h which is comparable for Gulf Coast region.[69]

The maintenance cost is calculated through the following expression

$$C_{\mathrm{MT}}=0.06\mathrm{FCI} \qquad (44)$$

Results and Discussion

Atomic targeting using maximum mass integration

As described earlier, the atomic target for a CHOSYN is an important first step in identifying which atoms are in excess or deficiencies with respect to the internal sources (Table 7). The minimum atomic flows $A_{\mathrm{c}}^{\mathrm{Sinks}}$, $A_{\mathrm{H}}^{\mathrm{Sinks}}$, and $A_{\mathrm{O}}^{\mathrm{Sinks}}$ are then determined for the sinks subject to the restrictions previously described by constraints (4), (17), and (18). This target is for the maximum utilization of internal sources to achieve the sink demands. The results shown by Table 7

Table 8. Existing External Sources Flowrate and Cost

Industrial Plants	Flow (kmol/h)	External Sources Cost ($MM/year)	Total Site External Source Cost Breakdown (%)
GTL plant	29,500	802	46
Ethylene plant	1250	66	4
DME plant	4500	554	31
Biodiesel plant	225	32	2
Acetic acid plant	4360	295	17
Total	39,835	1750	100

were obtained by solving a linear program (LP) using the software LINGO. The LP has 373 variables and 240 constraints. The solution time was 1 s using an Intel i5–2500 CPU @3.3 GHz.

The atomic deficiency indicates that even if all the internal sources are used towards meeting the minimum sink atomic requirements and constraints on ratios and compositions, it would not be enough to meet the carbon and hydrogen demand. The hydrogen deficiency indicates that the internal source are only able to provide a small fraction of the hydrogen requirement and that the majority of that demand must be met using external sources. This indicates that the focus of external source addition will be to provide the necessary carbon and meet the minimum sink hydrogen requirement as that is the highest atomic deficiency.

The results also show that the bulk of the oxygen required by the sinks can be provided by upgrading the internal sources. The surplus of oxygen also indicates that complete utilization of the internal sources is not possible as this would exceed the sink requirements. This provides a lower bound on the internal source utilization and potential waste generation. Of the internal sources, CO_2 is the largest source (10,000 kmol/h) and this provides 20,000 kmol/h of oxygen. Given that this CO_2 accounts for approximately 90% of the oxygen provided by the internal sources and is more than required by the sinks, the expectation for the subsequent targets and CHOSYN implementation is that a portion of the CO_2 available will not be utilized. This is an important insight from a design perspective in which the maximum CO_2 utilization can be determined. This also shows that CO_2 utilization is not only reduced by energy constraints, economic constraints but also by simple atomic constraints.

Raw-material cost targeting

Once the overall atomic targets are established, it is important to identify the best utilization of available internal and external sources. As previously discussed, the raw material cost targeting provides a target based on the cost of the various internal and external sources to satisfy the sink requirements. This can be a variety of targets including minimum fresh cost or minimum waste. For this target, the internal and external sources enter the CHOSYN, the species are broken down into CHO atoms and all the species required to achieve the particular objective are built subject to the sink constraints. At this level of targeting, there is no need to specify the individual interceptors, interceptor configuration, or the interceptor network. The approach assumes that the technology exists to convert the chosen sources into the necessary combination of required species. Later, in the implementation stage, the type, performance, configuration, and cost of the interceptors will be determined.

Table 8 summarizes the type and cost of the external sources used in the unintegrated plants. Based on 8000 h of operation, this is equivalent to $1.84 billion in total external source cost. Depending on the EIP ownership model, the sources made available can range from waste streams to final products. If the EIP has a single owner, plants would not be directly compensated for sources they make available to other plants. Of the available internal sources, the by-product methanol streams can be internally recycled reducing the external source purchase cost to $1.75 billion. The GTL plant is the largest single user of external sources and accounts for approximately 46% of the total raw material cost for the industrial cluster.

Minimum Fresh Cost (Total Site Objective). If the entire site has a single owner, then the internal sources are exchanged for no cost to potential users on-site. Using the raw materials cost targeting approach, the minimum external sources cost is calculated to be $232 million. This target represents a potential 87% reduction in external source cost compared to the total cost for the individual unintegrated plants. In this case, the external sources utilized are exclusively shale gas (11,349 kmol/h) and steam (4803 kmol/h). The remaining sink requirements are met by utilizing the available internal sources. The results show that not all the available internal sources are to be utilized. This is attributed to the constraints on composition and ratios of components.

Approximately 30% of the available captured CO_2 stream (2955 kmol/h) is sent to waste. It is important to recognize that from this target, the existing external sources have been replaced by internal and external sources which would require additional capital investment. This means that even though the internal sources can potentially provide the entire sink oxygen requirement and in fact is in excess, the actual utilization is lower due to economic objectives. Once detailed capital and operating costs of the CHOSYN are considered, the actual CO_2 utilization should be even lower as it becomes not economical to convert into other species.

When compared to the maximum atomic utilization target, the minimum fresh target leads to the same maximum atomic utilization target for hydrogen (58,044 kmol/h). The lack of hydrogen and the fact that hydrogen deficiency was by far the highest, leads to an optimal solution that aims to meet the minimum sink hydrogen requirement. This is also related to the abundance of a cheap source of carbon and oxygen in the form of CO_2. Thus, there is a strong link between maximizing a particular atomic utilization and minimum fresh cost target, with the target matching closely the minimum deficiency for one of the atoms.

Minimum External Source Cost (Single Plant Objective). If the objective is to first minimize the external source purchase cost for an individual plant, then the maximum internal source routing to that site would take place with any remaining sources available from the other plants. This may be the case if the intention is to begin integration with one plant and subsequently increase the site integration or if an individual plant commands much greater decision control compared to the rest. For example, if the GTL plant is taken as the basis, the external sources cost for the FT synthesis reactor as part of the unintegrated site is approximately $800 million per year.

By making all the internal sources available for the GTL plant, the external source cost can be reduced to $93 million

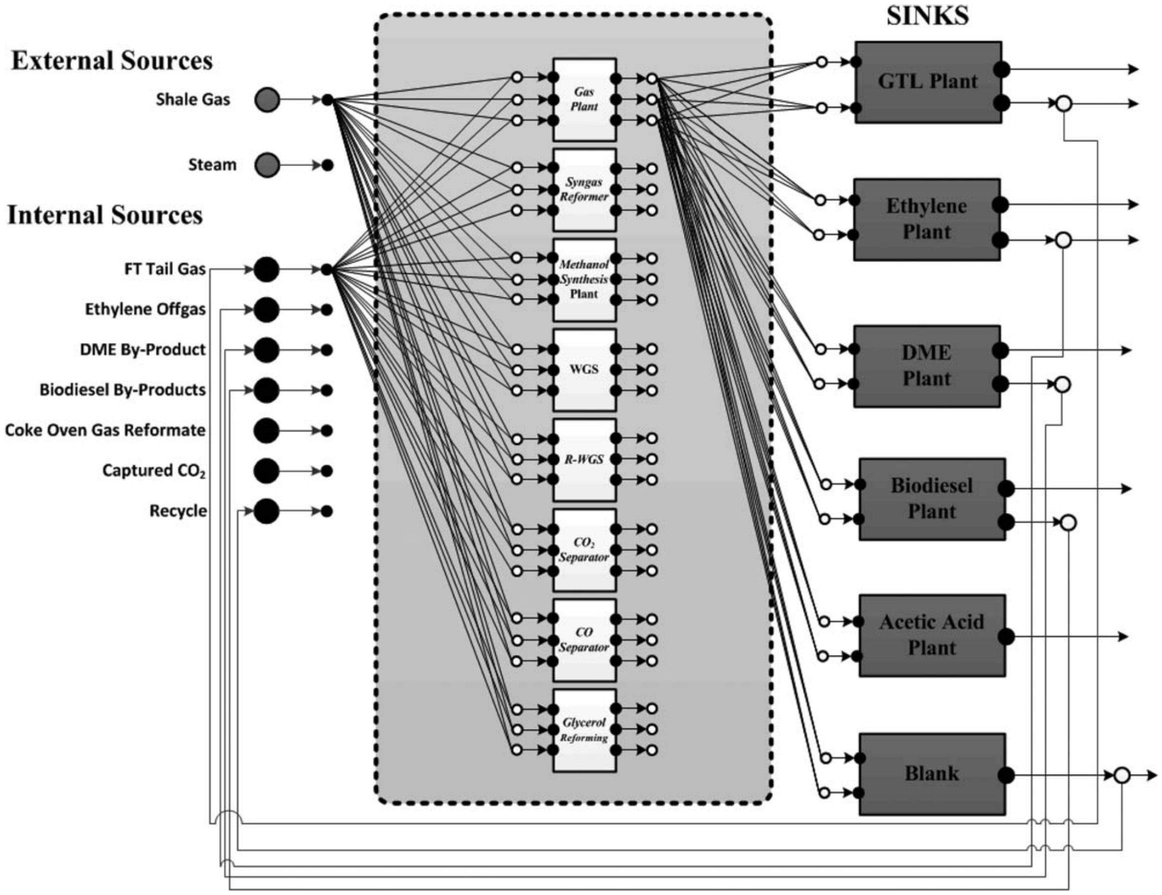

Figure 7. CHOSYN implementation for case study.

per year, a potential savings of 89%. Once again, the selected external sources are shale gas (4473 kmol/h) and steam (2960 kmol/h). The GTL plant uses all of the available internal sources with the exception of the captured CO_2 source where only 4500 kmol/h are utilized. This leaves 3500 kmol/h of the captured CO_2 available for utilization by the remaining sinks along with the necessary external sources. The external source cost for the remaining sinks is approximately $140 million.

CHOSYN design

The aforementioned targets identify benchmarks and the appropriate external resources to maximize economic potential if internal sources are used. The final step is to use these targets to aid in the synthesis of an interceptor network capable of converting the various internal and external sources into the necessary species. The interceptor network must also take into account both capital and operating costs. As part of the formulation the following questions are answered

Does an implementation exist capable of achieving these targets?

Does the implementation utilize the same external sources?

Given the capital and operating cost associated with the implementation is this an improvement over the unintegrated industrial complex?

If a single plant within the industrial complex proposes utilization of the internal sources does this represent an economic benefit for the plant and/or the industrial complex?

CHOSYN interceptor network formulation

Figure 7 is the superstructure for the CHOSYN of the case study. It is used to allocate all the sources (internal and external) to each of the individual interceptors as previously discussed. There are multiple input and output nodes from each interceptor and sink. In addition, sources may be directed to a blank sink which then recycles these sources to enter the CHOSYN. Finally, sources to be discarded are directed to a waste sink.

The optimization program described by Eqs. 1–14 was developed for the case study using the previously described data, constraints, and cost functions. The software LINGO was used with the Global Solver to solve the resulting mixed integer nonlinear program (MINLP). The MINLP has 635 variables and 360 constraints. The solution time was 180 s using an Intel i5–2500 CPU @3.3 GHz. The solution is shown by Figure 8 which represents the CHOSYN implementation for the optimal interceptor network. The amount of external source utilization is slightly greater than indicated by the targets and subsequently the internal source utilization is lower. Therefore, once the total cost (operating and capital) associated with internal source conditioning is considered, the decision can be to discharge or sell these internal sources rather than upgrade them. Similar to the initial targets, shale gas and steam are the chosen external sources. Again, this indicates that current feedstock prices favor the

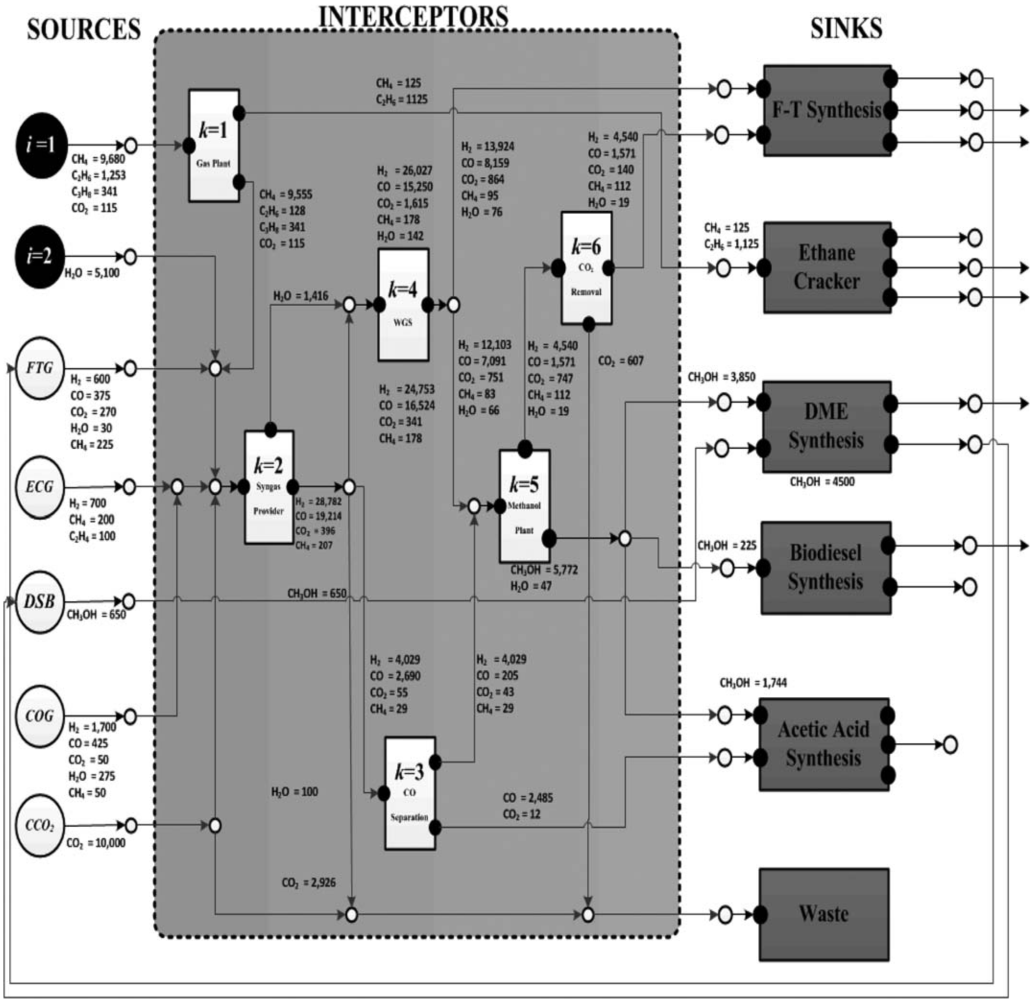

Figure 8. CHOSYN implementation for case study (entire site objective—all flows in kmol/h).

investment to convert these resources into the higher value products over direct purchase of these products.

Unlike the maximum-utilization target, not all of the internal sources are used in the network. In the implementation, the glycerol by-product of biodiesel production is sold. The capital investment required for glycerol reforming along with the energy requirement to produce syngas is much greater than the value of this syngas and thus it is better to sell the glycerol as a by-product. Assuming that the glycerol is sold for \$0.2/kg, approximately \$4 million can be generated annually from the sale.

The amount of CO_2 sent to waste (3533 kmol/h) is approximately 10% greater than the amount in the raw material target (2955 kmol/h). This decrease in CO_2 utilization is related to the cost-benefit of upgrading the CO_2 into useful products. In the targeting, the assumption is that the sources can all be completely converted to the target species. In reality, at the maximum allowable reformer temperature (1500 K) approximately 98% of the hydrocarbons (CH_4, C_2H_6, C_3H_8, and C_2H_4) are converted into the target species. The lower hydrocarbon conversion impacts hydrogen yield more than carbon monoxide leading to a lower H_2:CO ratio. These lower ratios would not meet the sink constraints. This explains the shift in CO_2 utilization to greater steam utilization to increase the hydrogen yield to achieve the H_2:CO ratios required by the sinks and other interceptor units.

The shale gas enters a gas plant which fractionates the shale gas to produce an ethane-rich stream, natural gas stream, and propane-rich by-product stream. The 240 MMSCFD gas plant has an energy requirement of 7200 MMBTU/h and a power requirement of 233,000 kWh/day. The produced ethane stream is 90 mol % ethane and 10 mol % methane. This stream is sent to the ethane cracker for ethylene production. The pipeline quality natural gas stream and the propane-rich by-product stream are both sent to the SGU along with the COG, ethylene offgas, and the FT Tail gas streams. These streams are reformed in a combined reformer in the presence of steam and the captured carbon dioxide. The syngas provider produces a syngas with a H_2:CO ratio of 1.5:1. In addition, the syngas provider removes the water from the syngas and makes it available for further utilization. The energy requirement of the syngas provider is approximately 4350 MMBTU/h.

The produced syngas is split into two streams. One stream makes up 14 mol % of the total syngas produced and is sent to the CO separation unit. The CO separator produces a carbon monoxide stream which is 99.5 mol % CO. The CO separator recovers 2485 kmol/h with a total energy requirement of 59 MMBTU/h and a power requirement 716,000 kWh/day. This CO stream is subsequently sent to the acetic acid sink. The second syngas split is sent to a WGS reactor where carbon monoxide and steam are converted to hydrogen and

Table 9. Capital Investment for CHOSYN Implementation (Entire Site Objective)

Unit	Cost Basis	Capacity	FCI 2014 ($MM)	AFC ($MM/year)
Gas plant &NGL fractation	MMscf/day	240	520	52
Reforming	MMBTU/h	4350	354	35
CO separation	ton/h	69.4	185	19
LT shift reactor	ton/h	555	7	1
Methanol synthesis plant	ton/h	188	733	73
CO_2 removal unit	ton CO_2/h	27	25	2
Total			1824	182

carbon monoxide. The WGS is necessary to increase the H_2:CO ratio to achieve the ratio required by the sinks and other interceptors. The WGS utilizes approximately 93 mol % of the water generated by the syngas provider. The use of a LT WGS at 285°C results in 90% water conversion and increases the H_2:CO ratio from 1.5 to 1.7. The WGS heating requirement is approximately 170 MMBTU/h.

The syngas from the WGS reactor is split into a stream to the methanol synthesis plant (47 mol %) and one that is directly fed to the FT synthesis sink (53 mol %). The syngas stream sent to the methanol plant is combined with the CO separator by-product stream which is a hydrogen-rich stream. The combination of these streams leads to a methanol synthesis feed with a syngas ratio of H_2:CO close to 2.2 which satisfy the interceptor constraints. As previously indicated, the methanol synthesis plant includes the necessary compression and product separation. In the methanol plant, the hydrogen conversion is 72 mol % and produces a methanol product stream which is 99% methanol and 1% water. The methanol plant is designed to produce 1.5 million tons per year of methanol. This results in a heating requirement of 186 MMBTU/h and cooling requirement of 1400 MMBTU/h. In addition, the power consumption is 357,600 kWh/day. The produced methanol product is sent to the following sinks: DME synthesis, biodiesel tran-esterification, and acetic acid synthesis.

The methanol synthesis off-gas stream is sent to a CO_2 removal unit which ensures that the FT synthesis feed impurities are less than 5 mol % as indicated in the sink constraint description. The methanol synthesis off-gas is hydrogen-rich and thus is sent to the FT synthesis reactor to combine with the aforementioned WGS output stream to satisfy the FT synthesis sink constraints. It is important to realize that the methanol produced as by-product from DME synthesis which was made available as an internal source for integration with any of the sinks is recycled directly to the DME synthesis and does not enter any interceptors.

The results show that some internal sources are recycled within the plant where they originate (DME synthesis by-product methanol) while others may be utilized by other plants (e.g., ethane cracker off-gas). If the plants are considered simultaneously, this removes the constraints placed by individual plants on specific resource utilization which can potentially lead to a better economic solution. The interceptors vary in complexity and in implementation the interceptors consist of individual process units (e.g., CO_2 removal), major processing sections (e.g., SGU), and entire plants (e.g., gas plant).

Table 9 summarizes the FCI for the interceptor network and the annualized fixed capital (AFC) using a 10-year linear depreciation with no salvage value. The methanol plant is the largest single capital investment accounting for approximately 40% of the FCI.

Assuming the working capital investment is 10% of the total capital investment (TCI), this would result in TCI being approximately $2 billion. The results show that the external source cost is dominated by the cost of the shale gas. The steam represents a cheap hydrogen-rich source and is utilized globally for the steam reforming of methane for hydrogen production. In addition to the external sources cost (Table 10), the utilities and labor cost were also calculated for the various interceptor units. The gas plant and NGL fractionation are the largest utility users with approximately $180 MM/year for heating and cooling. The gas plant and SGU account for roughly 84% of the total utility cost. In particular, the heating requirement constitutes the bulk of the utility cost.

The operating cost was also calculated for the interceptor network (Table 11). The AOC is calculated using Eq. 41.

Table 10. External Sources Cost for CHOSYN Implementation (Entire Site Objective)

External Sources	Cost Basis	Price ($)	C_{RM} ($MM/year)
Shale gas	$/MMBTU	3	228
Steam	$/1000 kg	6	4
Total			232

Table 11. Operating Cost ($MM/year) for CHOSYN Implementation (Entire Site Objective)

	Cost ($MM/year)
C_{RM}	232
C_{UT}	434
C_{OL}	10
C_{MT}	109
AOC	785

Table 12. Utilities and Labor Cost for CHOSYN Implementation (Entire Site Objective)

Interceptor	Cost Basis	C_{UT} ($MM/yr)	C_{OL} ($MM/year)
Gas plant & NGL fractionation	MMscf/day	235	2.2
Syngas generation unit	MMBTU/h	139	1.7
CO separation	kmol CO recovered	16	1.3
Water-gas shift reactor	H_2O conversion	5	1.2
Methanol synthesis plant	ton methanol	36	1.9
CO_2 removal unit	ton CO_2/h	3	1.2
Total		434	10

Table 13. Economic Summary for CHOSYN Implementation (Entire Site Objective)

Economic Summary	Value
Eco-Industrial Park Integration Cost	
Additional AFC ($MM/year)	182
Additional AOC ($MM/year)	785
Additional TAC ($MM/year)	967
Overall CHOSYN Economic Outcome	
Unintegrated external sources cost ($MM/year)	1840
Savings due to integration ($MM/year)	873
CHOSYN savings (% of unintegrated complex)	47%
Payback period (years)	1.7

Table 14. Sensitivity of CHO Interceptor Network Savings to Change in Shale Gas Price

Shale Gas Price ($/MMBTU)	TAC ($MM/year)	Annual Savings (%)	Payback Period (years)
3	967	47	1.7
5	1375	25	2.8
7	1781	3	7.6

Based on the results given by Tables 9 and 12, the TAC for the CHOSYN is $967 MM/year which represents a $660 MM of annual savings compared to the unintegrated industrial cluster. Table 13 summarizes the key economic findings for the implementation of the optimal CHOSYN.

In the case study, the shale gas price was assumed to be $3/MMBTU. Assuming an additional 25% cost margin between shale gas and natural gas, this price corresponds to a natural gas cost of $3.75/MMBTU. With the increasing demands for shale gas utilization, the base-case design should be examined for a possible increase in shale gas price. Table 14 shows the impact of an escalation in shale gas price to 5 and 7 ($/MMBTU) on the annual savings and payback period of the CHOSYN.

Single plant objective CHOSYN implementation

A situation may exist where only one member of the industrial cluster is willing to make a capital investment to utilize the available internal sources from the other plants. A difference between the entire site integration and only one plant is that resources of importance to the individual plants may not be now made available for integration. For example, the methanol by-product from DME synthesis would not be made available for integration as this would naturally be recycled in the DME plant to reduce fresh consumption. Figure 9 represents the implementation for a single plant (GTL plant) utilization of the internal sources made available.

The raw material target indicated the use of shale gas (4958 kmol/h) and steam (3325 kmol/h). All the internal sources are utilized with the exception being the DME process by-product methanol which is not made available for integration. The CO_2 utilization is approximately 3670 kmol/h. In the CHOSYN implementation, the shale gas utilization is similar to the value predicted by the raw material target while the steam consumption increases (4300 kmol/h) and CO_2 utilization decreases (3251 kmol/h). In addition, the glycerol generated in the biodiesel production is sold and not utilized in the CHOSYN. The implementation helps to explain the 30% increase in steam utilization. If the steam

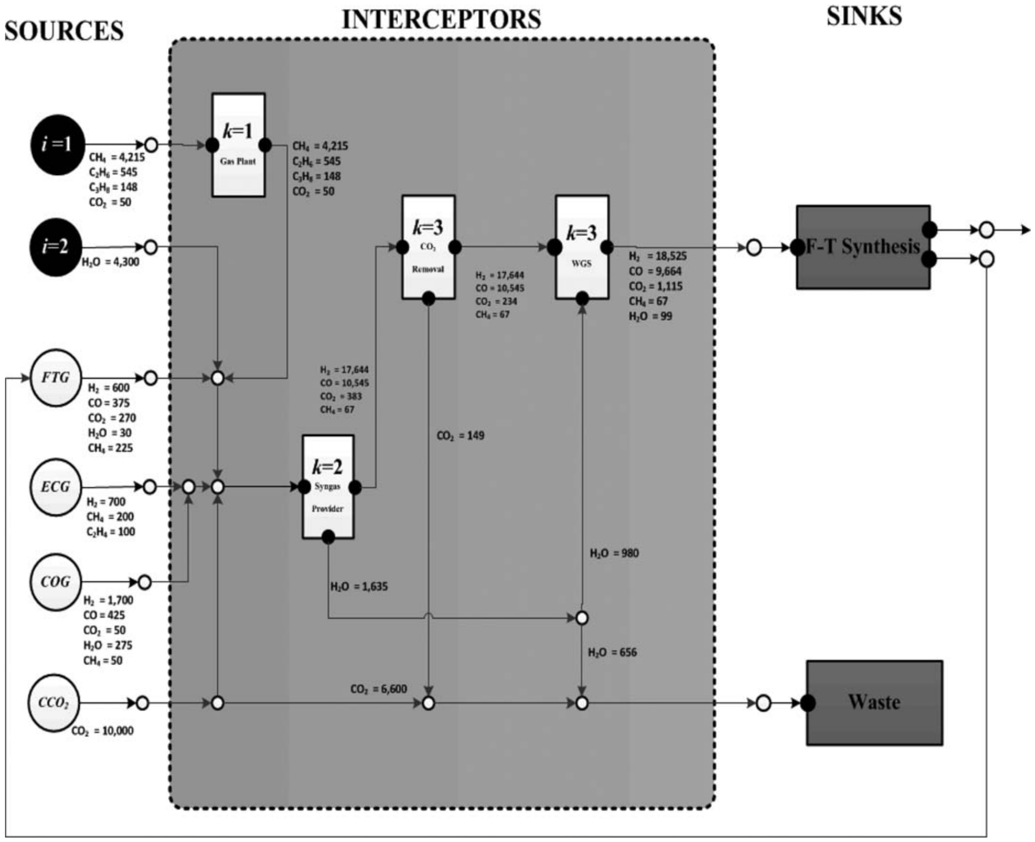

Figure 9. CHOSYN implementation (single plant objective—all flows in kmol/h).

Table 15. Capital Investment for CHOSYN Implementation (Single Plant Objective)

Unit	Cost Basis	Capacity	FCI 2014 ($MM)	AFC ($MM/year)
Gas plant	MMscf/day	100	136	13.6
Syngas generation unit	MMBTU/h	2550	243	24.3
CO_2 removal unit	ton CO_2/h	7	9	0.9
LT shift reactor	ton/h	360	6	0.6
Total			394	39.4

utilization remains as indicated by the target, the SGU produces a syngas with a low H_2:CO ratio (close to 1.2:1). This requires extensive syngas conditioning which drastically increases the size and cost of the subsequent WGSR and CO_2 removal units. By increasing the steam input and reducing the CO_2 input, the H_2:CO ratio of the syngas is closer to 1.7:1 which reduces the duty and the size of the subsequent syngas conditioning units.

Similar to the implementation for the entire site integration, shale gas enters a gas plant sized to process 100 MMSCFD. This gas plant is approximately 40% of the size of the gas plant required for the complete site integration. The gas plant does not include NGLs fractionation as it is not needed. The gas plant power requirement and energy requirement are 9700 kWh/day and 3000 MMBTU/h, respectively. The output stream along with steam, captured CO_2, and the remaining internal sources are sent to the SGU which requires 2713 MMBTU/h. The SGU produces a syngas with a H_2:CO ratio that is close to 1.7:1.

The syngas is subsequently sent to a CO_2 removal unit which removes 39 mol % of the CO_2 in the syngas generation output. The syngas stream is sent to a WGS reactor where approximately 8 mol % of the CO reacts with steam to increase the H_2:CO to 1.9:1. The WGS reactor operates at 345°C and the heating requirement is approximately 307 MMBTU/h. Once again the results show that the optimal implementation solution relates to minimizing the amount of hydrogen generated by satisfying the lower bound on hydrogen requirement for the FT synthesis.

Table 15 summarizes the FCI for the interceptor network and the AFC. The FCI for the CHOSYN is approximately $394 MM. This represents only 22% of the CHOSYN FCI for the entire site integration while the GTL plant makes up 45% of the external source cost. The SGU is the single most expensive item and makes up 62% of the FCI.

The annual external sources (raw material) cost, utility cost, and labor cost were all calculated for the interceptor network. The total utility cost is approximately $189 MM while the labor cost is close to $6 MM. The total annualized operating cost is $322 MM. The utilities cost accounts for 59% of the TAC compared to 45% for the total site integration.

Conclusions

The new problem of synthesizing a CHOSYN has been introduced. Focus is given to integrating multiple facilities through a common interception system while tracking individual carbon, hydrogen, and oxygen atoms and using atomic-based targeting to synthesize a macroscopic system. A systematic approach for the design and integration of CHOSYNs has been presented. First, two atomic-based targets are identified to determine maximum utilization and minimum cost of raw materials. Next, an optimization formulation was devised to synthesize a CHOSYN that include distribution, allocation, physical, and chemical conversions of internal and external streams as well as usage in existing and added infrastructure. The atomic utilization and raw material targets are not only important in benchmarking the potential for a CHOSYN and determining the potential feedstock which make the most economic sense but also for gaining a deeper understanding of the system from a process design perspective.

The unique feature of the C-H-O basis is the ability to identify the potential synergy among all the various species involved in the system. Whether the raw materials (e.g., shale gas, biomass, and coal), intermediates (e.g., H_2, CO, CO_2, MeOH, and C_2H_6), or products (e.g., chemicals, petrochemicals, and fuels), they all share fundamental atomic relationships. The key becomes how to manipulate the available species to produce the system which maximizes economic benefit, raw material utilization, capital utilization, and minimizes waste generation. A case study was solved and analyzed for various objectives. The resulting savings and the attractive payback periods indicate that the implementation of CHOSYNs may yield significant economic benefit. This includes the reduction in external sources, reduction in waste disposal, and the upgrading of by-product streams to higher value products.

Notation

A = atomic flow rate
AOC = annual operating cost
b = coefficient for fixed capital (Eq. 40)
c = index for components
C_{MT} = operating cost associated with maintenance
C_{OL} = operating cost associated with labor
C_{UT} = operating cost associated with utilities
C_{RM} = operating cost associated with raw materials
Capacity = capacity/throughput of a unit or a plant
Cost = cost of purchasing a source or treating/discharging a waste
D = design variables
FCI = fixed capital investment
G = source flow rate
H = sink flow rate
i = index for sources
j = index for sinks
k = index for interceptors
M = stoichiometric constraint (such as Eqs. 33a, b)
N_c = number of chemical components
$N_{\mathrm{External\ Sources}}$ = number of external sources
$N^{\mathrm{Inlet\_Sink}}$ = number of inlets to a sink
N_{Int} = number of interceptors
N_{Sinks} = number of sinks
N_{Sources} = number of sources
O = operating variables
P = pressure
r = ratio of compositions entering the sink
R = universal gas constant
S = state variables
T = temperature
u = index for inlets and outlets of sinks
v = index for sink inlet

W = flow rate for an interceptor
x = composition of source
y = composition of feed to interceptor
z = composition of feed to sink

Subscripts

c = species
C = carbon
e = element
f = feed
H = hydrogen
i = sources
j = sinks
k = interceptor
MT = maintenance
np = nonparticulate solids processing steps
p = process
O = oxygen
OL = operating labor
RM = raw materials
v = sink inlet and outlet ports
u = interceptor inlet and outlet ports
UT = utilities

Superscripts

Available = amount available from process or external sources
In = entering a sink
Internal_Sources = internal sources
max = maximum
min = minimum
n = scaling factor for fixed capital (Eq. 40)
Sinks = associated with a sink
Sources = associated with a source
Used = utilized through recycle
Waste = discharged waste

Greek letters

α = atomic coefficient for carbon
β = atomic coefficient for hydrogen
γ = atomic coefficient for oxygen
λ = Lagrange multiplier
Φ_k = vector of unit performance functions for interceptor k
Ξ_k = vector of constraints for interceptor k
Ψ_j = vector of unit performance functions for sink j

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