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A Unified Model of Property Integration for Batch and Continuous Processes

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This article aims to present a general model for synthesis of property-based resource conservation networks. The proposed model is applicable to batch and continuous processes. Therein, the process systems are characterized by properties instead of composition that is found in most published works to date in the area of resource conservation. By treating continuous process as a special case of batch processes, both kinds of operations can be optimized with a unified model that is developed on the basis of a superstructure. The overall framework of property network is adopted, where material reuse/recycle, interception, and waste treatment are all taken into consideration. Apart from direct reuse/recycle, interception devices are employed to improve stream properties for further recovery, whereas effluent treatment is needed for compliance with environmental discharge limits. In addition, storage vessels are employed in batch processes to override intrinsic time constraint. Four case studies are solved to illustrate the proposed approach. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 1845–1858, 2010

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Introduction

Business growth of the process industries is highly dictated by the enormous consumption of resources. Such consumption poses many economical, social, and ecological problems. Therefore, the efficient use of resources is recognized as a key challenge to business competitiveness and sustainability. The increase of public awareness toward resource conservation and shortage of natural resources has urged the process industry to move from traditional downstream pollution control activities to more aggressive pollution prevention incentives. One of the promising means to the latter is material recovery, with process integration techniques being recognized as systematic design tools in reducing the consumption of raw materials and generation of industrial wastes. Over the past two decades, significant progress has been made in the development of systematic process integration methodologies for resource conservation. In particular, mass integration has emerged as an effective technique to identify performance targets for the maximum extent of material recovery within individual processes.[1–4] As special cases of mass integration, water and hydrogen network syntheses are observed to be active research areas. Various works have been reported to minimize the requirement of material utilities (e.g., water, hydrogen, etc.) or associated network cost (e.g., capital and operating expenditures), for both continuous[5–18] and batch processes.[19–27]

It is worth noting that the foregoing research efforts have been restricted to ‘‘chemo-centric’’ or composition-based

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systems, where the characterization of the process streams and constraints on the process units are described in terms of the composition of pollutants. Notwithstanding the importance of pollutant composition in the characterization and design of chemical processes, many design problems are governed by properties or functionalities instead of chemical constituents. For instance, the selection of solvents typically relies on properties such as equilibrium distribution coefficients, viscosity, and volatility. Besides, the performance of a papermaking machine and, consequently, the quality of the produced papers primarily depend on objectionable material, reflectivity, and absorption coefficient. Similar examples are also found for various process units, e.g., vapor pressure in condensers, specific gravity in decantation, relative volatility in distillation, Henry's coefficient in absorption, etc. Furthermore, tracking individual components is prohibitively difficult in some cases, especially the one of bulk mixtures with numerous (almost infinite) components, e.g., complex hydrocarbons and lignocellulosic materials. However, the difficulty in enumerating the multitudinous constituents can be averted if one tracks such mixtures on the basis of their properties.

In response to the needs of tracking stream properties, the framework of *property integration* was proposed by El-Halwagi and coworkers.[28–33] It is defined as "*a functionality-based holistic approach to the allocation and manipulation of streams and processing units, which is based on functionality tracking, adjustment, and assignment throughout the process.*" It is worth emphasizing some differences that exist between property-based and the conventional composition-based problems. For example, mixing rules for most properties are nonlinear, whereas the mixing of composition is always linear. Besides, in the case of composition-based problems, external resources are mostly having lower impurity. For property-based problems, however, the property of external resources could take a superior or inferior value.

Shelley and El-Halwagi[28] first introduced the concept of clustering to enable the conservative tracking of stream properties for the recovery and allocation of volatile organic compounds (VOCs). Later, El-Halwagi et al.[29] addressed a more general problem of property integration that handles three properties. When more than three properties are considered, the algebraic tool developed by Qin et al.[30] is used. On the other hand, Kazantzi and El-Halwagi[31] and Foo et al.[32] incorporated property integration concept into pinch analysis techniques to locate rigorous targets for material reuse/recycle and process modification. Eljack et al.[33] reformulated a conventional forward problem into two reverse ones to reduce the model complexity. This is based on decoupling the constitutive equations from the balance and constraint equations. More recently, the property-based pinch targeting techniques were automated by Ng et al.[34–36] to locate the minimum flow rate/cost targets for various problems that could not be addressed via conventional pinch analysis. Such targeting approaches incorporate the concept of pinch analysis into mathematical optimization programs, which allows the flexibility in optimizing different objective functions. Additionally, the property integration framework has been extended for simultaneous process and molecular design.[37–39]

It is worthy of note that the aforementioned works are limited to property integration for steady-state continuous processes. However, relatively few works have been done for batch processes within the property integration framework. Grooms et al.[40] introduced the problem of synthesizing a property-interception and allocation network with the incorporation of steady-state and dynamic interception units. Most recently, Ng et al.[41] presented a mathematical model for the synthesis of property-based batch water networks with interception placement, where tank pairs are used for storage and dispatch of water sources to avoid their dynamic behavior. Nevertheless, the drawback of this approach is that, a larger number of tanks are possibly required. Although an inspection step was performed to remove the unnecessary tanks and to simplify the network after solving the optimization problem, such inspection can be inconvenient when handling complex problems with numerous process streams and units. On the other hand, the sequential approach of inspection after optimization may lead to suboptimum result.

Note that, none of the two works mentioned earlier has considered waste treatment for final discharge. This is the subject of the present work, with the aim to introduce a generic mathematical model for the synthesis of property-based resource conservation networks (PRCNs). The model is applicable to batch and continuous processes, where the synthesis task involves the allocation and interception of process streams to satisfy the input requirement of process units and to comply with environmental regulations. In addition, time dimension is taken into consideration when PRCNs are synthesized. A superstructure is constructed to incorporate all feasible network configurations and to facilitate the problem formulation. Four case studies are used to illustrate the proposed approach.

Problem Statement

The problem to be addressed in this work is stated as follows:

Given is a batch or continuous process with a set of process sources $i \in \mathcal{I}$ and a set of process sinks $j \in \mathcal{J}$. The sources are output streams from process units, which may be considered for reuse/recycle to replace the use of fresh resources, or discarded as effluent. Each source is characterized by its flow rate and a set of properties $p \in \mathcal{P}$. On the other hand, the sinks are process units with input requirements that need to be satisfied when material recovery is considered. Each sink has a specific flow rate requirement and a given range of acceptable property values. Available for service are a set of fresh (external) resources $r \in \mathcal{R}$ with specific property values, which may be purchased at different unit costs to satisfy the process sinks. In addition, a set of interception devices $k \in \mathcal{K}$ can be employed to intercept (regenerate) the process sources for further recovery or for discharge to the environment $e \in \mathcal{E}$. If the given process operates in batch mode, a set of storage vessels $s \in \mathcal{S}$ will be employed to override the inherent time constraint and to facilitate the allocation of process sources.

The objective is to synthesize a PRCN that achieves the optimum performance (e.g., minimum fresh resource usage, annual operating cost, and total annualized cost) for the given process, while satisfying all process and environmental constraints.

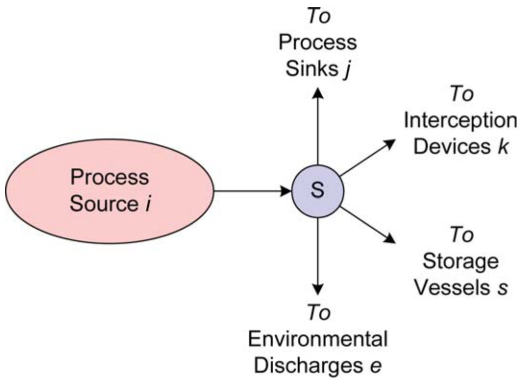

Figure 1. Schematic representation for a process source.

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

Mixing Rule and Property Operator

When several streams are mixed, a general mixing rule is needed to define all possible mixing patterns among these individual properties. This is given by:

$$\bar{f}\psi(\bar{p}) = \sum_{\ell} f_{\ell}\psi(p_{\ell}) \tag{1}$$

where $\psi(\bar{p})$ and $\psi(p_{\ell})$ are operators on mixture property $\bar{p}$ and stream property p_{ℓ}, respectively, while $\bar{f}$ is the total flow rate of the mixture, i.e.

$$\bar{f} = \sum_{\ell} f_{\ell} \tag{2}$$

The property operators can be evaluated from first principles or estimated through empirical or semi-empirical methods.[31,40] It is worthy of mention that, the correctness of mixing rules is important in property integration for setting performance targets and synthesizing an optimal network. Inaccurate mixing rules will lead to greater resource consumption, higher cost, or even an unachievable target.

Superstructure and Model Formulation

The mathematical model for a PRCN is formulated on the basis of a superstructure that includes all possible network connections. The superstructure consists of a series of schematic representations for process sources, process sinks, interception devices, storage vessels, and environmental discharge points (shown in Figures 1–5). To handle the time dimension of the batch processes, a set of time intervals $n \in \mathcal{N}$ are defined according to the start and end times of the process sources and sinks. In this case, the index n is used throughout the formulation to denote the time intervals. Although the use of time indices renders the formulation to be a model for batch processes, this model can be readily applied to continuous processes. The main reason is that, the continuous process is essentially a special case of batch processes in which all process sources and sinks exist simultaneously over the time horizon. Therefore, with the development of a unified model, property integration can be performed for both batch and continuous processes whenever it is needed. The formulation will be presented in the following paragraphs, where the indices, sets, parameters, and variables used are annotated in the Notation.

Material balances for process sources

Figure 1 shows the schematic representation for a process source i. The source may be sent to process sinks j, interception devices k, storage vessels s, and/or discharged to the environment e. According to this, Eq. 3 describes the flow rate balance on the splitting of source i in time interval n.

$$f_{in} = \sum_{j\in\mathcal{J}} f_{ijn} + \sum_{k\in\mathcal{K}} f_{ikn} + \sum_{s\in\mathcal{S}} f_{isn} + \sum_{e\in\mathcal{E}} f_{ien} \quad \forall i \in \mathcal{I}, n \in \mathcal{N} \tag{3}$$

Equation 4 states that the flow rate of each process source is given. Note that Y_{in} is a binary parameter to indicate the existence ($Y_{in} = 1$) of source i within time interval n. Since the values of properties of each source are given, the values of corresponding property operators are also known, as stated in Eq. 5.

$$f_{in} = F_i Y_{in} \qquad \forall i \in \mathcal{I}, n \in \mathcal{N} \tag{4}$$

$$\psi_{ip} = \Psi_{ip} \qquad \forall i \in \mathcal{I}, p \in \mathcal{P} \tag{5}$$

Material balances for process sinks

Figure 2 shows the schematic representation for a process sink j. The feed streams to the sink may come from process sources i, interception devices k, storage vessels s, and/or fresh resources r. Equation 6 describes the flow rate balance on the mixing of the streams to sink j in time interval n.

$$f_{jn} = \sum_{i\in\mathcal{I}} f_{ijn} + \sum_{k\in\mathcal{K}} f_{kjn} + \sum_{s\in\mathcal{S}} f_{sjn} + \sum_{r\in\mathcal{R}} f_{rjn} \quad \forall j \in \mathcal{J}, n \in \mathcal{N} \tag{6}$$

Equation 7 states that the flow rate of each process sink is given. Note that Y_{jn} is a binary parameter to indicate the existence ($Y_{jn} = 1$) of sink j within time interval n.

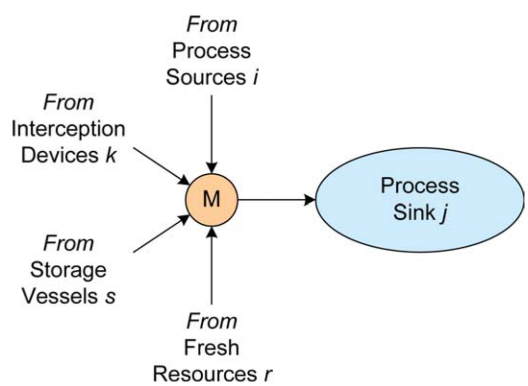

Figure 2. Schematic representation for a process sink.

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

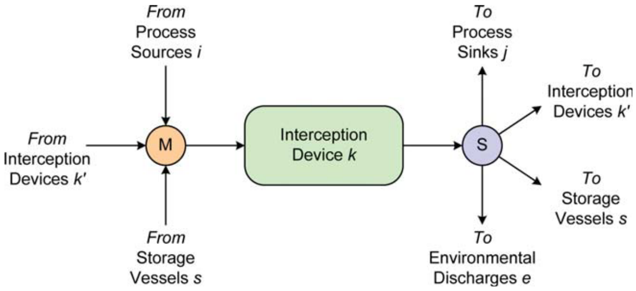

Figure 3. Schematic representation for an interception device.

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

$$f_{jn} = F_j Y_{jn} \qquad \forall j \in \mathcal{J}, n \in \mathcal{N} \tag{7}$$

Apart from the flow rate balances, property operator balances have to be considered for the sinks. Equation 8 depicts the property operator balance on the mixing of the streams to sink j in time interval n. Besides, property constraints are imposed by Eq. 9 to ensure that the feed to each sink is acceptable.

$$f_{jn}\psi_{jpn} = \sum_{i\in\mathcal{I}} f_{ijn}\psi_{ip} + \sum_{k\in\mathcal{K}} f_{kjn}\psi^{\text{out}}_{kpn} + \sum_{s\in\mathcal{S}} f_{sjn}\psi^{\text{out}}_{spn} + \sum_{r\in\mathcal{R}} f_{rjn}\Psi_{rp} \qquad \forall j \in \mathcal{J}, n \in \mathcal{N}, p \in \mathcal{P} \tag{8}$$

$$\Psi^{\min}_{jp} \leq \psi_{jpn} \leq \Psi^{\max}_{jp} \qquad \forall j \in \mathcal{J}, n \in \mathcal{N}, p \in \mathcal{P} \tag{9}$$

Material balances for interception devices

Figure 3 shows the schematic representation for an interception device k. The input streams may come from process sources i, other interception devices k', and/or storage vessels s, whereas the output streams may be assigned to process sinks j, other interception devices k', storage vessels s, and/or discharged to the environment e. Equations 10 and 11 describe the flow rate balances around the mixing and splitting points of device k in time interval n, respectively.

$$f^{\text{in}}_{kn} = \sum_{i\in\mathcal{I}} f_{ikn} + \sum_{k'\in\mathcal{K}} f_{k'kn} + \sum_{s\in\mathcal{S}} f_{skn} \qquad \forall k \in \mathcal{K}, n \in \mathcal{N} \tag{10}$$

$$f^{\text{out}}_{kn} = \sum_{j\in\mathcal{J}} f_{kjn} + \sum_{k'\in\mathcal{K}} f_{kk'n} + \sum_{s\in\mathcal{S}} f_{ksn} + \sum_{e\in\mathcal{E}} f_{ken} \quad \forall k \in \mathcal{K}, n \in \mathcal{N} \tag{11}$$

Equation 12 states that, the inlet flow rate of each interception device is limited to its treatment capacity. On the other hand, Eq. 13 states that the outlet flow rate of each device is a function of its inlet flow rate. This equation is essentially an overall flow rate balance for device k in time interval n, where a specific expression of G_k can be derived from the characteristic of device k.

$$f^{\text{in}}_{kn} \leq \hat{f}_k \qquad \forall k \in \mathcal{K}, n \in \mathcal{N} \tag{12}$$

$$f^{\text{out}}_{kn} = G_k\left(f^{\text{in}}_{kn}\right) \qquad \forall k \in \mathcal{K}, n \in \mathcal{N} \tag{13}$$

In addition, property operator balances are also needed for the devices. Equation 14 depicts the property operator balance around the mixing point of device k in time interval n. Besides, property constraints are imposed by Eq. 15 to control the quality of the input to each device, if necessary. Equation 16 states that the outlet property operator value of each device may depend on its inlet flow rate and property, where H_k represents the performance of device k.

$$f^{\text{in}}_{kn}\psi^{\text{in}}_{kpn} = \sum_{i\in\mathcal{I}} f_{ikn}\psi_{ip} + \sum_{k'\in\mathcal{K}} f_{k'kn}\psi^{\text{out}}_{k'pn} + \sum_{s\in\mathcal{S}} f_{skn}\psi^{\text{out}}_{spn} \qquad \forall k \in \mathcal{K}, n \in \mathcal{N}, p \in \mathcal{P} \tag{14}$$

$$\Psi^{\text{in,min}}_{kp} \leq \psi^{\text{in}}_{kpn} \leq \Psi^{\text{in,max}}_{kp} \qquad \forall k \in \mathcal{K}, n \in \mathcal{N}, p \in \mathcal{P} \tag{15}$$

$$\psi^{\text{out}}_{kpn} = H_k\left(f^{\text{in}}_{kn}, \psi^{\text{in}}_{kpn}\right) \qquad \forall k \in \mathcal{K}, n \in \mathcal{N}, p \in \mathcal{P} \tag{16}$$

Material balances for storage vessels

As mentioned earlier, storage vessels are needed for batch processes. Figure 4 shows the schematic representation for a storage vessel s. The input streams may come from process sources i, and/or interception devices k, whereas the output streams may be assigned to process sinks j, interception devices k, and/or discharged to the environment e. Equations 17 and 18 describe the flow rate balances around the mixing and splitting points of vessel s in time interval n, respectively.

$$f^{\text{in}}_{sn} = \sum_{i\in\mathcal{I}} f_{isn} + \sum_{k\in\mathcal{K}} f_{ksn} \qquad \forall n \in \mathcal{N}, s \in \mathcal{S} \tag{17}$$

$$f^{\text{out}}_{sn} = \sum_{j\in\mathcal{J}} f_{sjn} + \sum_{k\in\mathcal{K}} f_{skn} + \sum_{e\in\mathcal{E}} f_{sen} \qquad \forall n \in \mathcal{N}, s \in \mathcal{S} \tag{18}$$

Equation 19 is the overall flow balance for vessel s, which depicts that the amount of cumulative mass in the vessel at the end of a time interval n, is equal to the amount of mass cumulated from the previous time interval $n-1$ plus the difference between the inlet and outlet flows during time interval n. Note that Z^{cyc} is a binary parameter to indicate the operating pattern of a batch process, where $Z^{\text{cyc}} = 0$ means "single operation" that all production tasks take place within a non-repeated time horizon with no initial storage, while $Z^{\text{cyc}} = 1$ means "cyclic operation" that a number of repeating and identical production cycles are carried out. For the latter, the cumulative mass in a vessel at the end of the previous cycle is taken as the initial storage for the current one.

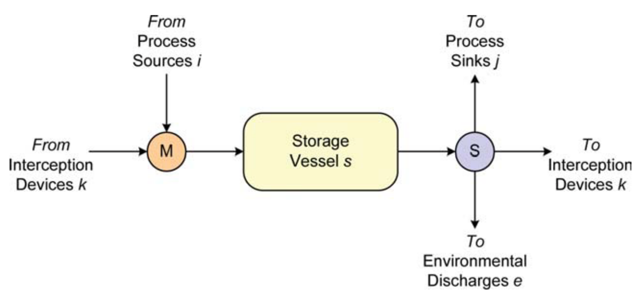

Figure 4. Schematic representation for a storage vessel.

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

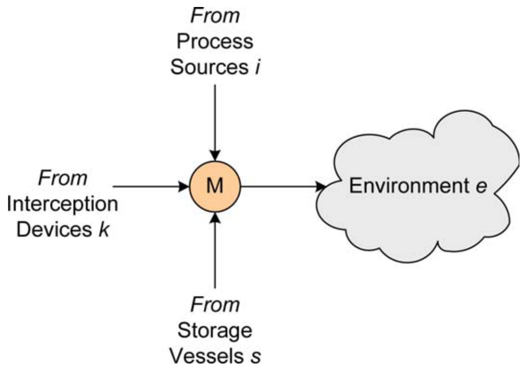

Figure 5. Schematic representation for environmental discharge.

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

$$q_{sn} = Z^{\text{cyc}} q_{s,N}\Big|_{n=1} + q_{s,n-1}\Big|_{n>1} + \left(f_{sn}^{\text{in}} - f_{sn}^{\text{out}}\right)\Delta_n \qquad \forall n \in \mathcal{N}, s \in \mathcal{S} \tag{19}$$

To provide sufficient time for the mixing of the input and content of a storage vessel (so that the mixture properties achieve constant/mean values before leaving the vessel), Eqs. 20 and 21 are included to forbid the inlet and outlet flows of each vessel from occurring in the same time interval.

$$F_s^{\min} z_{sn}^{\text{in}} \le f_{sn}^{\text{in}} \le F_s^{\max} z_{sn}^{\text{in}} \qquad \forall n \in \mathcal{N}, s \in \mathcal{S} \tag{20}$$

$$f_{sn}^{\text{out}} \le F_s^{\max}(1 - z_{sn}^{\text{in}}) \qquad \forall n \in \mathcal{N}, s \in \mathcal{S} \tag{21}$$

where z_{sn}^{in} is a binary variable to indicate the occurrence ($z_{sn}^{\text{in}} = 1$) of the inlet flow to vessel s in time interval n. Equation 22 is included to ensure that the amount of cumulative mass in each vessel do not exceed its storage capacity.

$$q_{sn} \le \hat{q}_s \qquad \forall n \in \mathcal{N}, s \in \mathcal{S} \tag{22}$$

In addition, property operator balances for the vessels are also needed. Equation 23 describes the property operator balance around the mixing point of vessel s in time interval n. Besides, property constraints are imposed by Eq. 24 to control the type of the input to each vessel, if necessary.

$$f_{sn}^{\text{in}} \psi_{spn}^{\text{in}} = \sum_{i \in \mathcal{I}} f_{isn} \psi_{ip} + \sum_{k \in \mathcal{K}} f_{ksn} \psi_{kpn}^{\text{out}} \quad \forall n \in \mathcal{N}, p \in \mathcal{P}, s \in \mathcal{S} \tag{23}$$

$$\Psi_{sp}^{\text{in,min}} \le \psi_{spn}^{\text{in}} \le \Psi_{sp}^{\text{in,max}} \qquad \forall n \in \mathcal{N}, p \in \mathcal{P}, s \in \mathcal{S} \tag{24}$$

Equation 25 is the overall property operator balance for vessel s in time interval n.

$$q_{sn} \psi_{spn}^{\text{out}} = Z^{\text{cyc}} q_{s,N} \psi_{sp,N}^{\text{out}}\Big|_{n=1} + q_{s,n-1} \psi_{sp,n-1}^{\text{out}}\Big|_{n>1} + \left(f_{sn}^{\text{in}} \psi_{spn}^{\text{in}} - f_{sn}^{\text{out}} \psi_{spn}^{\text{out}}\right)\Delta_n \quad \forall n \in \mathcal{N}, p \in \mathcal{P}, s \in \mathcal{S} \tag{25}$$

Material balances for environmental discharge

Figure 5 shows the schematic representation for environmental discharge. The effluent is made up of the streams from process sources i, interception devices k, and/or storage vessels s. Equations 26 and 27 describe the flow rate and property operator balances on the mixing of the streams to environment e in time interval n, respectively. Besides, property constraints are imposed by Eq. 28 to ensure that the effluent is in compliance with the environmental discharge limits.

$$f_{en} = \sum_{i \in \mathcal{I}} f_{ien} + \sum_{k \in \mathcal{K}} f_{ken} + \sum_{s \in \mathcal{S}} f_{sen} \qquad \forall e \in \mathcal{E}, n \in \mathcal{N} \tag{26}$$

$$f_{en} \psi_{epn} = \sum_{i \in \mathcal{I}} f_{ien} \psi_{ip} + \sum_{k \in \mathcal{K}} f_{ken} \psi_{kpn}^{\text{out}} + \sum_{s \in \mathcal{S}} f_{sen} \psi_{spn}^{\text{out}} \qquad \forall e \in \mathcal{E}, n \in \mathcal{N}, p \in \mathcal{P} \tag{27}$$

$$\Psi_{ep}^{\min} \le \psi_{epn} \le \Psi_{ep}^{\max} \qquad \forall e \in \mathcal{E}, n \in \mathcal{N}, p \in \mathcal{P} \tag{28}$$

Objective functions

The flexibility and adaptability of the performance index (i.e., objective function) is one of the advantages of mathematical approaches. In this work, the objective function of the PRCN synthesis problem includes the minimization of fresh resource usage, as well as for minimum cost (e.g., annual operating cost, total annualized cost, etc.), which will be shown in the following case studies.

Case Studies

Four case studies are solved to illustrate the proposed approach. The optimization platform employed is General Algebraic Modeling System (GAMS)[42] on a Core 2, 2.00 GHz processor. The solvers used are CPLEX for linear program (LP) and BARON for nonlinear program (NLP) and mixed-integer nonlinear program (MINLP).[43]

Case 1: Metal degreasing process

The first case is adapted from Shelley and El-Halwagi[28] and Qin et al.[30] where solvent recovery for a continuous metal degreasing process is considered. Figure 6 shows a schematic flow diagram for the process. A fresh organic solvent that contains numerous components is used in the

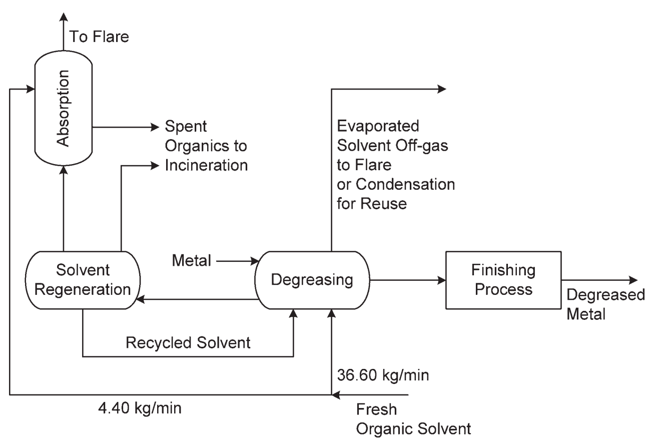

Figure 6. Schematic flow diagram for the metal degreasing process.

Table 1. Property Bounds and Required Flow Rate for the Degreaser

Property	Lower Bound	Upper Bound
Sulfur (wt %)	0	1
Density (kg/m^3)	555	615
RVP (atm)	2.1	4.0
Viscosity (cP)	0.171	0.202
Flow rate (kg/min)	36.6	

absorption column to capture light gases which escape from the solvent regeneration unit. Besides, the organic solvent is also used in the degreaser to degrease the metal parts. In the current practice, the off-gas VOCs that evaporate from the degreasing process are flared, which leads to economic loss and environmental pollution. Thus, it is desired to explore the potential for VOC recovery and reuse by condensing the off-gas and to optimize the use of fresh solvent.

Four properties [sulfur content, density, Reid vapor pressure (RVP), and viscosity] are examined to determine the suitability of a solvent for usage in the degreaser. On the other hand, the absorption column is neglected because it is not feasible for that to recycle the off-gas condensate at any temperature level.[30] Hence, the only one process sink left for the problem is the degreaser. Table 1 shows the range of acceptable properties for the degreaser and its required inlet flow rate. The mixing rules for the four targeted properties as well as their operator expressions are given in Table 2.[28,30]

Two scenarios are analyzed for this case study. In Scenario 1, two condensers with fixed condensation temperatures (240 and 250 K, respectively) are available to condense the off-gas, and each condensate is made into a process source. Table 3 shows the property of these sources, along with that of the fresh solvent. It can be observed from the experimental data reported by Shelley and El-Halwagi[28] that, the condensate flow rate is 30 kg/min when the off-gas is entirely condensed at 240 K and it is 28 kg/min for 250 K. Since the off-gas may be condensed to produce two different qualities of condensates, an additional variable y_i^{cond} is needed to denote the fraction of the off-gas that passed through the condenser, with the constraint in Eq. 29.

$$\sum_{i\in\mathcal{I}} y_i^{\text{cond}} \leq 1 \tag{29}$$

Then Eq. 4 is rewritten to Eq. 30 to express source flow rates.

$$f_{in} = \begin{cases} 30y_i^{\text{cond}}Y_{in} & \forall i = 240\text{ K condensate}, n\in\mathcal{N} \\ 28y_i^{\text{cond}}Y_{in} & \forall i = 250\text{ K condensate}, n\in\mathcal{N} \end{cases} \tag{30}$$

Table 2. Mixing Rules and Operator Expressions

Property	Mixing Rule	Operator
Sulfur (S)	$\bar{f}\bar{S} = \sum_\ell f_\ell S_\ell$	$\psi(S_\ell) = S_\ell$
Density (ρ)	$\bar{f}\frac{1}{\bar{\rho}} = \sum_\ell f_\ell \frac{1}{\rho_\ell}$	$\psi(\rho_\ell) = \dfrac{1}{\rho_\ell}$
RVP (RVP)	$\bar{f}\overline{RVP}^{1.44} = \sum_\ell f_\ell RVP_\ell^{1.44}$	$\psi(RVP_\ell) = RVP_\ell^{1.44}$
Viscosity (μ)	$\bar{f}\log(\bar{\mu}) = \sum_\ell f_\ell \log(\mu_\ell)$	$\psi(\mu_\ell) = \log(\mu_\ell)$

Table 3. Properties of the Fresh Solvent and Condensates

Property	Fresh Solvent	240 K Condensate	250 K Condensate
Sulfur (wt %)	0.1	0.7	1.5
Density (kg/m^3)	610	580	650
RVP (atm)	2.1	5.2	2.5
Viscosity (cP)	0.178	0.256	0.22

It is assumed that the amount of off-gas sent for condensation depends on the required condensate flow rates, and the excess off-gas is sent for flaring. In this instance, all condensates will be recycled to the process without discharge, as stated in Eq. 31.

$$f_{ien} = 0 \qquad \forall e\in\mathcal{E}, i\in\mathcal{I}, n\in\mathcal{N} \tag{31}$$

The objective of Scenario 1 is to minimize the fresh resource usage, i.e.

$$\min_{x_{11}\in\Omega_{11}} \sum_{r\in\mathcal{R}}\sum_{j\in\mathcal{J}}\sum_{n\in\mathcal{N}} f_{rjn}\Delta_n \tag{32}$$

where $\boldsymbol{x}_{11}$ is a vector of variables and Ω_{11} is a feasible searching space defined by the constraints. For this case, all variables and constraints related to the interception device and storage vessel are left out from the formulation because these facilities are not employed. Furthermore, the environmental constraints in Eqs. 26–28 are also omitted. As mentioned earlier, a continuous process is essentially a special batch process with simultaneous sources and sinks. Therefore, the process can be described by a single time interval where all sources and sinks have the same start and end times. In this scenario, the duration of the time interval is set to 1 min (unit time) to represent a moment within the operating period.

$$\boldsymbol{x}_{11} \equiv \left\{ \begin{matrix} f_{ien}, f_{ijn}, f_{rjn}, f_{in}, f_{jn}, \psi_{ip}, \psi_{jpn}, y_i^{\text{cond}} \\ \forall e\in\mathcal{E}, i\in\mathcal{I}, j\in\mathcal{J}, n\in\mathcal{N}, p\in\mathcal{P}, r\in\mathcal{R} \end{matrix} \right\} \tag{33}$$

$$\Omega_{11} = \{\boldsymbol{x}_{11} | \text{Eqs. 3, 5–9, and 29–31}\} \tag{34}$$

Note that the formulation takes on the form of an NLP because of the bilinear terms in Eq. 8. However, this

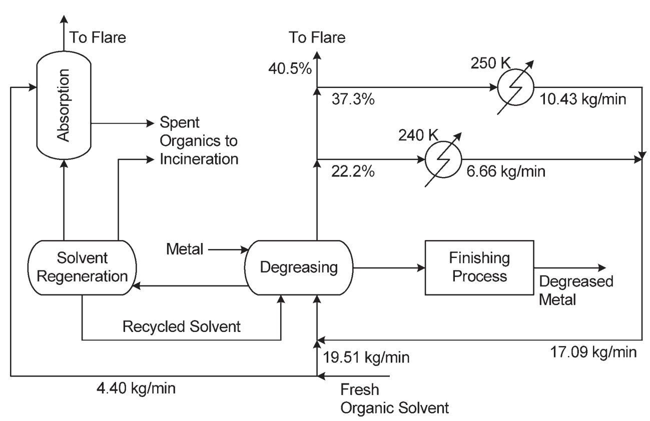

Figure 7. Optimal solvent recovery scheme for Scenario 1.

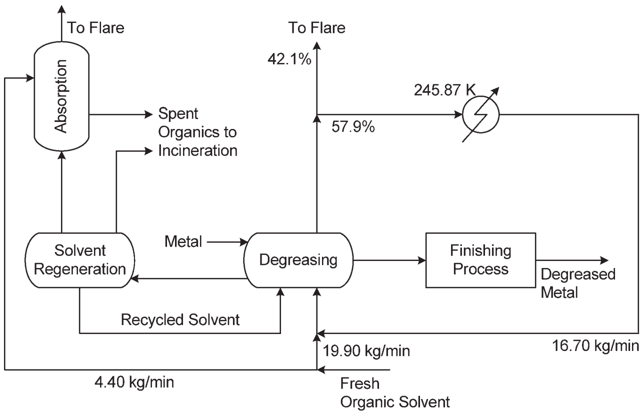

Figure 8. Optimal solvent recovery scheme for Scenario 2.

bilinearity can be readily linearized as given in Eq. 35 by substituting Eq. 5 into Eq. 8 and then combining Eqs. 8 and 9.

$$f_{jn}\Psi_{jp}^{\min} \leq \sum_{i\in\mathcal{I}} f_{ijn}\Psi_{ip} + \sum_{r\in\mathcal{R}} f_{rjn}\Psi_{rp} \leq f_{jn}\Psi_{jp}^{\max} \qquad \forall j\in\mathcal{J}, n\in\mathcal{N}, p\in\mathcal{P} \tag{35}$$

The consequent LP formulation (the same objective function subject to the constraints in Eqs. 3, 6, 7, 29–31, and 35) involves 22 constraints and eight continuous variables. The model is solved in 0.09 CPU seconds and the fresh solvent requirement is determined as 19.51 kg/min. Figure 7 shows the optimal solvent recovery scheme for Scenario 1. Note that 22.2 and 37.3% of the off-gas are condensed through the 240 and 250 K condensers, respectively, while the remaining (40.5%) is sent to flare.

In Scenario 2, a single condenser with variable condensation temperature is available. The allowable temperature range is set between 240 and 250 K, as stated in Eq. 36.

$$240 \leq t_i^{\text{cond}} \leq 250 \qquad \forall i\in\mathcal{I} \tag{36}$$

Note that the flow rate and properties of the condensate vary as the condensation temperature is varied. For simplicity, it is assumed that the variation of the flow rate and properties within the small temperature range is linear. In this instance, the functional relationship between condensation temperature and condensate flow rate and property can be derived from the condensate data in Table 3. Then Eqs. 4 and 5 are rewritten to Eqs. 37 and 38, respectively, to express the source flow rate and property.

$$f_{in} = (-0.2t_i^{\text{cond}} + 78)y_i^{\text{cond}}Y_{in} \qquad \forall i\in\mathcal{I}, n\in\mathcal{N} \tag{37}$$

$$\psi_{ip} = \begin{cases} 0.08t_i^{\text{cond}} - 18.5 & \forall i\in\mathcal{I}, p=\text{sulfur content} \\ 1/(7t_i^{\text{cond}} - 1100) & \forall i\in\mathcal{I}, p=\text{density} \\ (-0.27t_i^{\text{cond}} + 70)^{1.44} & \forall i\in\mathcal{I}, p=\text{RVP} \\ \log(-0.0036t_i^{\text{cond}} + 1.12) & \forall i\in\mathcal{I}, p=\text{viscosity} \end{cases} \tag{38}$$

The objective of Scenario 2 is to minimize the total annualized cost associated with fresh resource usage and condensation, i.e.

$$\min_{\mathbf{x}_{12}\in\Omega_{12}} \sum_{r\in\mathcal{R}}\sum_{j\in\mathcal{J}}\sum_{n\in\mathcal{N}} C_r f_{rjn}\Delta_n + 27000 + 1070\sum_{i\in\mathcal{I}}(273 - t_i^{\text{cond}})^{1.8} \tag{39}$$

where C_r is the unit cost for fresh resource r, and the annualized cost of the condenser is estimated as a function of its condensation temperature.[28] In this scenario, the pricing of the fresh solvent is given as \$0.08/kg. Besides, the duration of the time interval is set to the annual operating hours of 8760 h (525,600 min).

$$\mathbf{x}_{12} \equiv \left\{ \begin{matrix} f_{ien}, f_{ijn}, f_{rjn}, f_{in}, f_{jn}, \psi_{ip}, \psi_{jpn}, t_i^{\text{cond}}, y_i^{\text{cond}} \\ \forall e\in\mathcal{E}, i\in\mathcal{I}, j\in\mathcal{J}, n\in\mathcal{N}, p\in\mathcal{P}, r\in\mathcal{R} \end{matrix} \right\} \tag{40}$$

$$\Omega_{12} = \{\mathbf{x}_{12} | \text{Eqs. 3, 6–9, 29, 31, and 36–38}\} \tag{41}$$

The NLP formulation (for that the condensation temperature is treated as a variable) involves 24 constraints and 11 continuous variables. The model is solved in 0.27 CPU seconds with an objective value of \$1271000/year. Figure 8 shows the optimal solvent recovery scheme for Scenario 2. Note that 57.9% of the off-gas is condensed at 245.87 K, while the remaining (42.1%) is sent to flare.

Prior to the exploration of solvent recovery opportunities, the fresh solvent requirement for the base case shown in Figure 6 was 36.6 kg/min with an annual cost of \$1539000 (0.08 × 36.6 × 525600). By contrast, the results for Scenarios 1 and 2 correspond to 46.69 and 17.41% reductions in fresh solvent usage and total annualized cost, respectively. The result obtained in Scenario 1 is consistent with that of Qin et al.[30] (46% reduction in fresh solvent). However, the result in Scenario 2 was not compared with that of Shelley and El-Halwagi[28] since only three properties (sulfur content, density, and RVP) are examined in their original case study.

Case 2: Palm oil milling process

Resource recovery in a palm oil milling process is next considered. This case is adapted from Ng et al.[34] where the

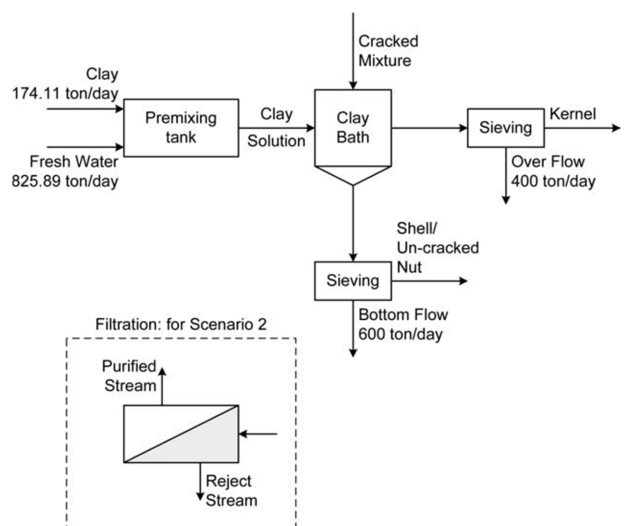

Figure 9. Schematic flow diagram for the clay bath system.

Table 4. Limiting Data for the Clay Bath System

	Flow Rate (ton/day)	Density (kg/m^3)	TSS (wt %)
Process sink			
Clay solution	1000	1120	≤10
Process source			
Over flow	380	1018	6.25
Bottom flow	570	1200	20
Fresh resource			
Fresh water	To be optimized	1000	0
Clay	To be optimized	2600	0.5

exploitation of material reuse/recycle opportunities is aimed at the clay bath system. Figure 9 shows a schematic flow diagram for this system. A clay bath is used to separate the cracked mixture that consists of kernels, shells, and some uncracked nuts based on the flotation principle. Because of their different densities, the clay bath that is prepared to an appropriate suspension density allows the kernels to float while the shells and uncracked nuts sink to the bottom. The clay bath consists of slurry water whose proportions are chosen to achieve the desired density. However, the quality of the slurry degrades during the operation through inadvertent separation of clay particles from water. Besides, some impurities of the cracked mixture also affect the density in the clay bath. Therefore, makeup water and clay are required to compensate for fluctuations and to maintain the operation efficiency. As shown in Figure 9, fresh water and clay are mixed in the premixing tank, and the clay solution is then fed to the clay bath where the cracked mixture is separated. Upon the separation, the lighter kernels leave the bath with the over stream, whereas the heavier shells and uncracked nuts leave with the bottom stream. Sieving is carried out for both streams to separate the solids (kernels and shells/uncracked nuts) from the liquid parts. The recovery of the waste liquids (i.e., over and bottom flows) is proposed of environmental concern.

Two properties, density and total suspended solid (TSS) content, are examined to determine the feasibility of material reuse/recycle. To prevent the accumulation of impurities in the clay bath, 5% of the liquid is purged from both the over and bottom flows. Note that the purge portion is excluded from the available flow rate. Table 4 shows the limiting data that include the required flow rate and acceptable properties for the clay solution, available flow rates and property values of the over and bottom flows, and property values of fresh water and clay. The mixing rules for the two targeted properties are given in Eqs. 42 and 43, respectively. Two scenarios are analyzed for this case study.

$$\bar{f}\frac{1}{\bar{\rho}} = \sum_{\ell} f_\ell \frac{1}{\rho_\ell} \tag{42}$$

$$\bar{f}\,\overline{TSS} = \sum_{\ell} f_\ell \, TSS_\ell \tag{43}$$

In Scenario 1, recycling the over and bottom flows is considered to prepare the clay solution. The objective is to minimize the fresh resource usage, i.e.

$$\min_{\boldsymbol{x}_{21}\in\Omega_{21}} \sum_{r\in\mathcal{R}} \sum_{j\in\mathcal{J}} \sum_{n\in\mathcal{N}} f_{rjn}\Delta_n \tag{44}$$

Here, the duration of the time interval is set to 1 day (unit time).

$$\boldsymbol{x}_{21} \equiv \left\{ \begin{matrix} f_{ien}, f_{ijn}, f_{rjn}, f_{in}, f_{jn} \\ \forall e\in\mathcal{E}, i\in\mathcal{I}, j\in\mathcal{J}, n\in\mathcal{N}, r\in\mathcal{R} \end{matrix} \right\} \tag{45}$$

$$\Omega_{21} = \{\boldsymbol{x}_{21} | \text{Eqs. 3, 4, 6, 7, and 35}\} \tag{46}$$

The LP formulation entails 16 constraints and seven continuous variables. Solving the model takes 0.09 CPU seconds and yields an objective value of 240.26 ton/day. This corresponds to fresh water and clay requirements of 179.92 and 60.34 ton/day, respectively. Figure 10 shows the optimal design of the clay bath system for Scenario 1. Note that all of the available over flow and 379.74 ton/day of the bottom flow are recycled into the premixing tank.

In Scenario 2, a filtration unit with constant fluid recovery factor (FR) and removal ratio (RR) is employed as the interception device to remove suspended solids. The filtration unit can be used to purify the over and bottom flows for further recovery of water and clay. As shown in Figure 9, the filtration unit has an input stream and two output streams of different TSS content, i.e., a lower impurity purified stream and a higher impurity reject stream. Since it is undesired to remix the output streams that are just separated by the filter, only one of them can be considered for reuse/recycle. In this instance, the purified stream whose quality is higher as compared with the reject stream will certainly be the choice. Such interception device is termed as a partitioning regeneration system[44] which may be modeled as follows.

Assuming no material loss and generation during the filtration, the overall flow rate and property operator balances for the filtration unit are described by Eqs. 47 and 48, respectively. Note that the purified stream is taken as the main output stream of the filtration unit. It is further assumed that the densities of the output (purified) and reject streams are fixed at 1100 and 1600 kg/m^3, respectively, i.e., $\psi^{out}_{kpn} = 1/1100$ and $\psi^{rej}_{kpn} = 1/1600$, $\forall k$ = filtration unit, $n\in\mathcal{N}$, p = density.

$$f^{in}_{kn} = f^{out}_{kn} + f^{rej}_{kn} \qquad \forall k = \text{filtration unit}, n\in\mathcal{N} \tag{47}$$

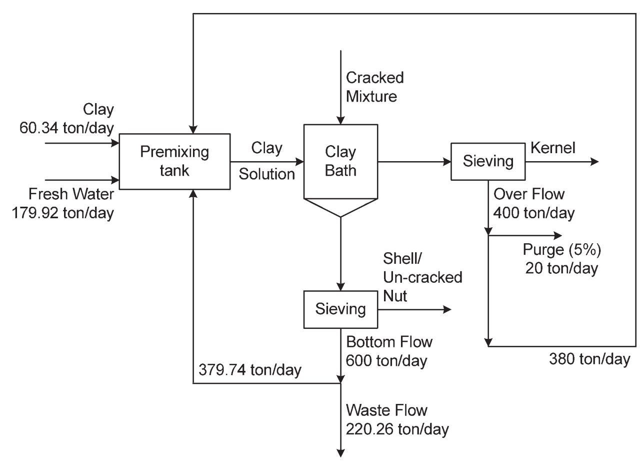

Figure 10. Optimal design of the clay bath system for Scenario 1.

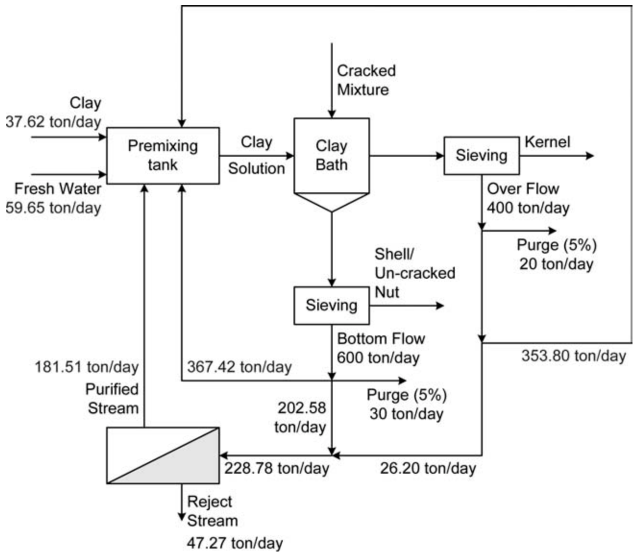

Figure 11. Optimal design of the clay bath system for Scenario 2.

$$f_{kn}^{\text{in}}\psi_{kpn}^{\text{in}} = f_{kn}^{\text{out}}\psi_{kpn}^{\text{out}} + f_{kn}^{\text{rej}}\psi_{kpn}^{\text{rej}} \qquad \forall k = \text{filtration unit}, \; n \in \mathcal{N}, p \in \mathcal{P} \tag{48}$$

The FR of the filtration unit is defined in Eq. 49 as the recovery fraction of fluid in the input stream that passed through the unit in the output stream,

$$FR = \frac{f_{kn}^{\text{out}}(\Phi - \psi_{kpn}^{\text{out}})}{f_{kn}^{\text{in}}(\Phi - \psi_{kpn}^{\text{in}})} \qquad \forall k = \text{filtration unit}, \; n \in \mathcal{N}, p = \text{TSS content} \tag{49}$$

where the impurity term Φ may be changed accordingly to the unit used, e.g., 1000000 for ppm, 100 for weight percent, and 1 for mass fraction. Besides, the RR of the filtration unit is defined in Eq. 50 as the ratio of the difference between the inlet and outlet impurity loads to the impurity load of the input stream.

$$RR = \frac{f_{kn}^{\text{in}}\psi_{kpn}^{\text{in}} - f_{kn}^{\text{out}}\psi_{kpn}^{\text{out}}}{f_{kn}^{\text{in}}\psi_{kpn}^{\text{in}}} \qquad \forall k = \text{filtration unit}, n \in \mathcal{N}, p = \text{TSS content} \tag{50}$$

For this case, the FR and RR are given as 0.95 and 0.9, respectively.

Then Eqs. 47–50 have replaced Eqs. 13 and 16 to constitute a complete model for the filtration unit with Eqs. 10–12, 14, and 15. The objective of Scenario 2 is to minimize the annual operating cost associated with fresh resource usage and interception, i.e.

$$\min_{\boldsymbol{x}_{22}\in\Omega_{22}} \sum_{r\in\mathcal{R}}\sum_{j\in\mathcal{J}}\sum_{n\in\mathcal{N}} C_r f_{rjn}\Delta_n + \sum_{k\in\mathcal{K}}\sum_{n\in\mathcal{N}} C_k^{\text{op}} f_{kn}^{\text{in}}\Delta_n \tag{51}$$

where the operating cost of interception is proportional to the inlet flow rate of the interception device, and C_k^{op} is the operating cost coefficient for interception device k. Since the investment cost of the filtration unit is not taken into account, its treatment capacity in Eq. 12 can be directly set to a reasonable upper bound for its inlet flow rate instead of being treated as a variable. In this scenario, the pricing of fresh water, clay, and filtration are given as \$1/ton, \$2/ton, and \$0.05/ton, respectively. Besides, the duration of the time interval is set to the annual operating hours of 7920 h (330 days).

$$\boldsymbol{x}_{22} \equiv \left\{ \begin{array}{c} f_{ien}, f_{ijn}, f_{ikn}, f_{ken}, f_{kjn}, f_{kk'n}, f_{rjn}, f_{in} \\ f_{jn}, f_{kn}^{\text{in}}, f_{kn}^{\text{out}}, f_{kn}^{\text{rej}}, \psi_{ip}, \psi_{jpn}, \psi_{kpn}^{\text{in}}, \psi_{kpn}^{\text{out}}, \psi_{kpn}^{\text{rej}} \\ \forall e\in\mathcal{E}, i\in\mathcal{I}, j\in\mathcal{J}, k,k'\in\mathcal{K}, n\in\mathcal{N}, p\in\mathcal{P}, r\in\mathcal{R} \end{array} \right\} \tag{52}$$

$$\Omega_{22} = \{\boldsymbol{x}_{22} | \text{Eqs. 3–12, 14, 15, and 47–50}\} \tag{53}$$

The NLP formulation entails 38 constraints and 20 continuous variables. Solving the model leads to an objective value of \$48288/year in 0.31 CPU seconds. Figure 11 shows the optimal design of the clay bath system for Scenario 2. Note that 353.8 and 367.42 ton/day of the over and bottom flows are directly recycled into the premixing tank. Besides, 26.2 and 202.58 ton/day of the over and bottom flows are filtered through the filtration unit and the purified stream is fully reused to prepare the clay solution.

When ignoring any possibility of resource recovery, the fresh water and clay requirements for the base case shown in Figure 9 were 825.89 and 174.11 ton/day, respectively, with an annual cost of \$387456 (825.89 × 1 × 330 + 174.11 × 2 × 330). By contrast, the result for Scenario 1 corresponds to 78.22 and 65.34% reductions in fresh water and clay usage, respectively. On the other hand, the result for Scenario 2 shows an 87.54% reduction in annual operating cost. The results presented in this case study were not compared with those of Ng et al.[34] because of the differences in

Table 5. Properties and Flow Rates of the Process Sources

Process Source	Flow Rate (kg/s)	Sulfur (ppm)	pH	Time (h) Start	End
Source 1	6	$20t + 10$	$2t + 8$	0	1
Source 2	2	30	7.7	3	4

t, time (h).

Table 6. Property Bounds and Required Flow Rates for the Process Sinks

Process Sink	Flow Rate (kg/s)	Sulfur (ppm)		pH		Time (h)	
		LB	UB	LB	UB	Start	End
Sink 1	8	0	17	6	7.2	5	6
Sink 2	3	0	20	7.35	7.5	7	8

LB, lower bound; UB, upper bound.

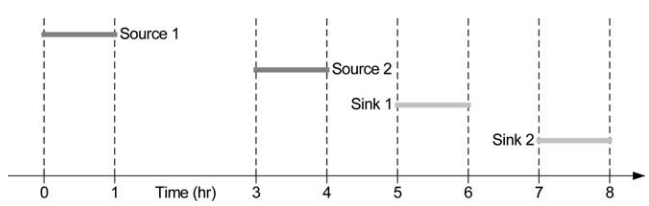

Figure 12. Gantt chart for the batch chemical process in Case 3.

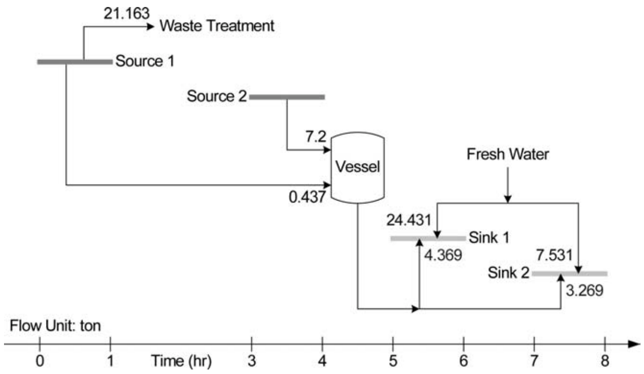

Figure 13. Optimal network configuration of the batch chemical process for Case 3.

targeted property and recovery scheme. In their original case study, density is solely considered as the most critical property for material reuse/recycle. Moreover, only the over flow is recycled in their first scenario and only the bottom flow is purified in the second one.

Case 3: Batch chemical process I

A case study taken from Ng et al.[41] is presented to demonstrate the application of the proposed model to a batch process. In this case, a chemical process which operates cyclically with an 8-h cycle time is considered. The process produces two water sources and has two water sinks. The first water source comes from a dynamic unit and, therefore, its properties are variable with time. On the other hand, the second source of constant property comes from a steady-state unit. The feed to water sinks must satisfy the required flow rate and property constraints on sulfur content and pH. Tables 5 and 6 show the relevant data for the water sources and sinks, respectively, while the corresponding Gantt chart is shown in Figure 12. The mixing rules for the two properties (sulfur content and pH) are given in Eqs. 54 and 55, respectively.

$$\bar{f}\,\overline{S} = \sum_{\ell} f_\ell S_\ell \quad (54)$$

$$\bar{f}10^{-\overline{pH}} = \sum_{\ell} f_\ell \left(10^{-pH_\ell}\big|_{pH_\ell<7} - 10^{pH_\ell-14}\big|_{pH_\ell>7}\right) \quad (55)$$

To break the dynamic behavior of Source 1, Ng et al.[41] proposed the use of tank pairs for alternate storage and dispatch. For the same purpose, here, the source is stored before reuse and/or interception. In this instance, any flow rates from Source 1 to water sinks and interception devices are forbidden, as stated in Eqs. 56 and 57.

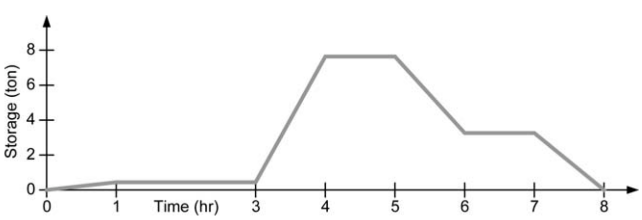

Figure 14. Storage profile of the storage vessel.

Table 7. Properties and Flow Rates of the Process Sources

Process Source	Flow Rate (ton/h)	Sulfur (ppm)	pH	Time (h) Start	End
Source 1	20	20	5	0	5
Source 2	30	30	9	3	7

$$f_{ijn} = 0 \qquad \forall i = \text{Source } 1, j \in \mathcal{J}, n \in \mathcal{N} \quad (56)$$

$$f_{ikn} = 0 \qquad \forall i = \text{Source } 1, k \in \mathcal{K}, n \in \mathcal{N} \quad (57)$$

Using Eq. 58, the averaged sulfur content and pH of Source 1 over its duration are determined as 20 ppm and 9, respectively.

$$\overline{P}_{ip} = \frac{\int_0^1 F_i(t)P_{ip}(t)dt}{\int_0^1 F_i(t)dt} \qquad \forall i = \text{Source } 1, p \in \{\text{sulfur content, pH}\} \quad (58)$$

where 0 and 1 are the start and end times of Source 1, respectively.

To remove sulfur pollutants, an activated carbon adsorption (ACA) column may be employed as the interception device. The ACA column is modeled as a single pass regeneration system[44] with constant removal efficiency of 90%. With the assumption of no water loss and generation during the adsorption, Eqs. 13 and 16 are expanded to Eq. 59 and Eqs. 60 and 61, respectively.

$$f_{kn}^{\text{out}} = f_{kn}^{\text{in}} \qquad \forall k = \text{ACA column}, n \in \mathcal{N} \quad (59)$$

$$\psi_{kpn}^{\text{out}} = \psi_{kpn}^{\text{in}}(1-0.9) \qquad \forall k = \text{ ACA column}, n \in \mathcal{N}, p = \text{ sulfur content} \quad (60)$$

$$\psi_{kpn}^{\text{out}} = \psi_{kpn}^{\text{in}} \quad \forall k = \text{ ACA column}, n \in \mathcal{N}, p = \text{pH} \quad (61)$$

On the other hand, acid (free of sulfur, pH 5) and alkali solutions (free of sulfur, pH 11) are readily available for pH adjustment. Besides, fresh water (free of sulfur, pH 7) may be used as needed.

The objective of this case study is to minimize the total annualized cost associated with fresh resource usage, interception, and storage, i.e.

$$\min_{x_3 \in \Omega_3} N^{\text{cyc}} \sum_{r\in\mathcal{R}} \sum_{j\in\mathcal{J}} \sum_{n\in\mathcal{N}} C_r f_{rjn}\Delta_n + N^{\text{cyc}} \sum_{k\in\mathcal{K}} \sum_{n\in\mathcal{N}} C_k^{\text{op}} f_{kn}^{\text{in}}\Delta_n + \sum_{s\in\mathcal{S}} C_s z_s \quad (62)$$

where N^{cyc} is the number of production cycles per year; C_s is the cost coefficient for storage vessel *s*. To take storage cost

Table 8. Property Bounds and Required Flow Rates for the Process Sinks

Process Sink	Flow Rate (ton/hr)	Sulfur (ppm) LB	UB	pH LB	UB	Time (h) Start	End
Sink 1	25	0	20	6	7	2	6
Sink 2	40	0	5	7	8	5	8

LB, lower bound; UB, upper bound.

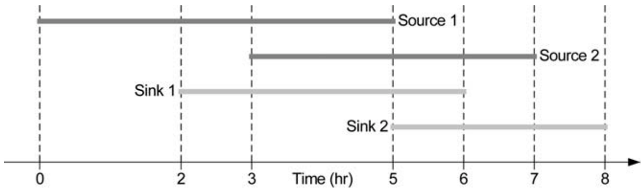

Figure 15. Gantt chart for the batch chemical process in Case 4.

into account, a binary variable z_s is needed to identify the presence of storage vessels. Equation 63 is introduced to correlate the binary variable with the cumulative mass in storage.

$$q_{sn} \le Q_s^{\max} z_s \qquad \forall n \in \mathcal{N}, s \in \mathcal{S} \tag{63}$$

Since the storage vessels employed in this case are assumed to have a standardized capacity, Eq. 22 can be replaced by Eq. 63. Furthermore, the treatment capacity of the ACA column is set to a constant of 10 kg/s. The cost data are given as follows: fresh water, \$0.01/kg; acid solution, \$0.2/kg; alkali solution, \$0.1/kg; the operating cost coefficient for the ACA column is \$0.05/kg intercepted water; the annualized cost of a storage vessel (including pumping and piping) is \$15000. The process operates for 365 days (1095 production cycles) a year.

$$\boldsymbol{x}_3 \equiv \left\{ \begin{array}{c} f_{ien}, f_{ijn}, f_{ikn}, f_{isn}, f_{ken}, f_{kjn}, f_{kk'n}, f_{ksn}, f_{rjn}, f_{sen}, f_{sjn}, f_{skn}, f_{in} \\ f_{jn}, f_{kn}^{\mathrm{in}}, f_{kn}^{\mathrm{out}}, f_{sn}^{\mathrm{in}}, f_{sn}^{\mathrm{out}}, q_{sn}, \psi_{ip}, \psi_{jpn}, \psi_{kpn}^{\mathrm{in}}, \psi_{kpn}^{\mathrm{out}}, \psi_{spn}^{\mathrm{in}}, \psi_{spn}^{\mathrm{out}}, z_s, z_{sn}^{\mathrm{in}} \\ \forall e \in \mathcal{E}, i \in \mathcal{I}, j \in \mathcal{J}, k, k' \in \mathcal{K}, n \in \mathcal{N}, p \in \mathcal{P}, r \in \mathcal{R}, s \in \mathcal{S} \end{array} \right\} \tag{64}$$

$$\Omega_3 = \{\boldsymbol{x}_3 | \text{Eqs. } 3\text{–}12, 14, 15, 17\text{–}21, 23\text{–}25, 56, 57, 59\text{–}61, \text{and } 63\} \tag{65}$$

Note that the formulation is an MINLP because of the introduction of binary variables along with the bilinear terms in property operator balances. The model involves 610 constraints, 316 continuous and 16 binary variables when the maximum number of storage vessels is set to two. The objective value of \$364994/year is obtained in 6.45 CPU seconds. Figure 13 shows the optimal network configuration of the batch chemical process for Case 3. Note that 31.96 ton/cycle of fresh water is required, while 21.16 ton/cycle of Source 1 is sent to waste treatment before discharge. Besides, one storage vessel is employed and its storage profile is shown in Figure 14.

The base case of this case study is a network design without water reuse features and storage vessels. The requirements of fresh water and alkali solution for that are 39.598 and 0.002 ton/cycle, respectively, with an annual cost of \$433858. By contrast, the result for Case 3 corresponds to a 15.87% reduction in total annualized cost. The resultant cost of \$364994/yearr is much higher as compared with that reported by Ng et al.[41] (\$167456/year) because of the difference in property mixing rule. In their original work, the mixing rule for pH is as follows:

$$\bar{f} 10^{-\overline{pH}} = \sum_{\ell} f_\ell 10^{-pH_\ell} \tag{66}$$

where only the concentration of hydrogen ions is taken into account. Therefore, this mixing rule can only be applied to the case of mixing acid streams. Applying it to the mixing of alkaline streams or neutralization process (mixing of acid and alkaline streams) will lead to incorrect calculations.

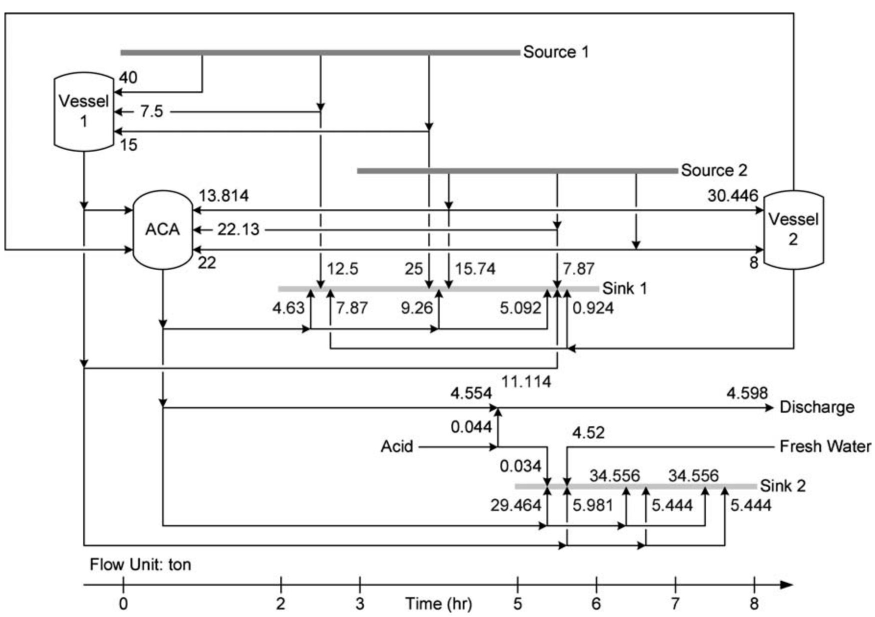

Figure 16. Optimal network configuration of the batch chemical process for Case 4.

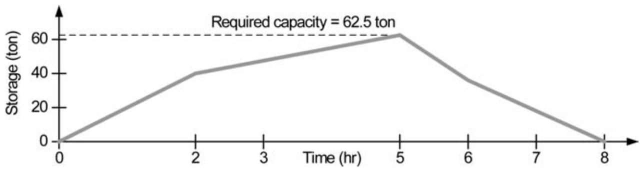

Figure 17. Storage profile of Vessel 1.

Case 4: Batch chemical process II

To demonstrate the applicability of the proposed model to a more complex problem, a modified case study from Case 3 is presented. Consider a chemical process which operates cyclically with an 8-h cycle time. The process produces two water sources and has two water sinks. Tables 7 and 8 show the relevant data for the water sources and sinks, respectively, while the corresponding Gantt chart is shown in Figure 15. It is assumed that all possibilities of process modification and rescheduling have already been explored and no further changes are needed. The mixing rules for sulfur content and pH are given in Eqs. 54 and 55, respectively. Similar to Case 3, an ACA column may be employed to remove sulfur pollutants (removal efficiency = 90%). Additionally, acid (sulfur-free, pH 3) and alkali solutions (sulfur-free, pH 11) are available for pH adjustment. Fresh water (sulfur-free, pH 7) is also available for usage. The environmental discharge limits for the two properties are as follows: sulfur content ≤ 10 ppm; 6.5 ≤ pH ≤ 7.5.

The objective of this case study is to minimize the total annualized cost associated with fresh resource usage, interception, storage, and piping, i.e.

$$
\begin{aligned}
\min_{\boldsymbol{x}_4 \in \Omega_4} & N^{\text{cyc}} \sum_{r\in\mathcal{R}} \sum_{j\in\mathcal{J}} \sum_{n\in\mathcal{N}} C_r f_{rjn} \Delta_n \\
& + N^{\text{cyc}} \sum_{k\in\mathcal{K}} \sum_{n\in\mathcal{N}} C_k^{\text{op}} f_{kn}^{\text{in}} \Delta_n + A \sum_{k\in\mathcal{K}} C_k^{\text{inv}} \hat{f}_k^{B_k} \\
& + A \sum_{s\in\mathcal{S}} \left(C_s^{\text{fix}} z_s + C_s^{\text{var}} \hat{q}_s \right) \\
& + A \sum \left(C_{\dagger\ddagger}^{\text{fix}} z_{\dagger\ddagger} + C_{\dagger\ddagger}^{\text{var}} \hat{f}_{\dagger\ddagger} \right) \\
& \dagger\ddagger \in \{ie, ij, ik, is, ke, kj, kk', ks, rj, se, sj, sk\}
\end{aligned}
\tag{67}
$$

where A is the annualization factor; C_k^{inv} and B_k are the investment cost coefficient and exponent for interception device k, respectively; C_s^{fix} and C_s^{var} are the fixed and variable cost coefficients for storage vessel s, respectively; $C_{\dagger\ddagger}^{\text{fix}}$ and $C_{\dagger\ddagger}^{\text{var}}$ are the fixed and variable cost coefficients for the pipe between † and ‡, respectively. To take storage and piping costs into account, two binary variables z_s and $z_{\dagger\ddagger}$ are needed to identify the presence of storage vessels and pipes, respectively. Equations 68 and 69 are introduced to correlate the binary variables with the storage capacity and piping flow rate, respectively, where $\hat{f}_{\dagger\ddagger}$ denotes the maximum flow rate in the pipe between † and ‡ which determines the required pipe size. Equation 70 can be used to eliminate some uneconomically small flow rates, if necessary.

$$Q_s^{\min} z_s \le \hat{q}_s \le Q_s^{\max} z_s \qquad \forall s \in \mathcal{S} \tag{68}$$

$$f_{\dagger\ddagger n} \le \hat{f}_{\dagger\ddagger} \le F_{\dagger\ddagger}^{\max} z_{\dagger\ddagger} \qquad \forall n \in \mathcal{N} \tag{69}$$

$$f_{\dagger\ddagger n}\left(f_{\dagger\ddagger n} - F_{\dagger\ddagger}^{\min}\right) \ge 0 \qquad \forall n \in \mathcal{N} \tag{70}$$

$$\dagger\ddagger \in \{ie, ij, ik, is, ke, kj, kk', ks, rj, se, sj, sk\}$$

The cost data are given as follows: fresh water, \$1/ton; acid solution, \$20/ton; alkali solution, \$10/ton; the operating cost coefficient, investment cost coefficient, and exponent for the ACA column are \$0.05/ton intercepted water, \$15000, and 1, respectively; the fixed and variable cost coefficients for a storage vessel are \$10000 and \$120/ton required capacity, respectively. For simplicity, all piping distances are assumed to be equal and, consequently, the fixed and variable cost coefficients for a pipe are \$2500 and \$20 h/ton, respectively. The process operates for 350 days (1050 production cycles) annually with an annualization factor of 0.1.

$$
\boldsymbol{x}_4 \equiv \left\{
\begin{array}{c}
f_{ien}, f_{ijn}, f_{ikn}, f_{isn}, f_{ken}, f_{kjn}, f_{kk'n}, f_{ksn}, f_{rjn}, f_{sen}, f_{sjn}, f_{skn} \\
f_{en}, f_{in}, f_{jn}, f_{kn}^{\text{in}}, f_{kn}^{\text{out}}, f_{sn}^{\text{in}}, f_{sn}^{\text{out}}, q_{sn}, \hat{f}_{ie}, \hat{f}_{ij}, \hat{f}_{ik}, \hat{f}_{is}, \hat{f}_{ke}, \hat{f}_{kj} \\
\hat{f}_{kk'}, \hat{f}_{ks}, \hat{f}_{rj}, \hat{f}_{se}, \hat{f}_{sj}, \hat{f}_{sk}, \hat{f}_k, \hat{q}_s, \psi_{epn}, \psi_{ip}, \psi_{jpn}, \psi_{kpn}^{\text{in}}, \psi_{kpn}^{\text{out}}, \psi_{spn}^{\text{in}} \\
\psi_{spn}^{\text{out}}, z_{ie}, z_{ij}, z_{ik}, z_{is}, z_{ke}, z_{kj}, z_{kk'}, z_{ks}, z_{rj}, z_{se}, z_{sj}, z_{sk}, z_s, z_{sn}^{\text{in}} \\
\forall e \in \mathcal{E}, i \in \mathcal{I}, j \in \mathcal{J}, k, k' \in \mathcal{K}, n \in \mathcal{N}, p \in \mathcal{P}, r \in \mathcal{R}, s \in \mathcal{S}
\end{array}
\right\}
\tag{71}
$$

$$\Omega_4 = \{\boldsymbol{x}_4 | \text{Eqs. 3–12, 14, 15, 17–28, 59–61, and 68–70}\} \tag{72}$$

The MINLP formulation entails 619 constraints, 335 continuous and 39 binary variables. The objective value of \$71671/year is obtained in 236.48 CPU seconds. Figure 16 shows the optimal network configuration of the batch chemical process for Case 4. Note that 4.52 ton/cycle of fresh water and 0.08 ton/cycle of acid solution are required, while 4.6 ton/cycle of treated water is discharged to the environment. Two storage vessels are employed and their storage profiles are shown in Figures 17 and 18, respectively. Besides, Figure 19 shows the input profile of the ACA column. A network design without water reuse and storage vessels is taken as the base case, for which the annual cost is found to be \$306468 (the requirements of fresh water, acid, and alkali solutions are 220, 0.75, and 0.58 ton/cycle, respectively, and a 29.6 ton/h treatment capacity is required for the ACA column; costs related to the pipe work are also included). By contrast, the result for Case 4 corresponds to a 76.61% reduction in total annualized cost.

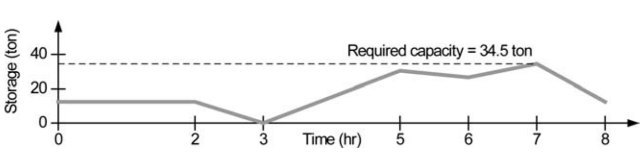

Figure 18. Storage profile of Vessel 2.

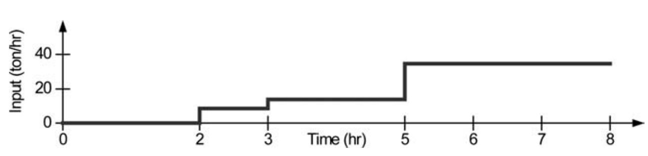

Figure 19. Input profile of the ACA column.

Conclusion

A generic mathematical model is presented for the synthesis of PRCNs. The time index was embedded in the formulation to reflect the time dimension of batch processes (if present). A superstructure was constructed to incorporate all possible interconnections for an optimal network. Four case studies have been solved to demonstrate the effectiveness of the newly proposed formulation. For a continuous process, all sources and sinks were treated as to exist simultaneously in a single time interval. Moreover, the duration of the time interval can be arbitrarily set to represent a moment or a certain operating period. On the other hand, the time horizon was divided into time intervals for a batch process according to the start and end times of the sources and sinks. The developed model follows the approach that all process sources and sinks are treated independently of each other. This assumption may fail when some process units whose outlet (source) flow rates and properties are dependent on their inlet (sink) conditions. Such aspect will be addressed in future works.

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Notation

Indices and sets

$e \in \mathcal{E}$ = environmental discharge points
$i \in \mathcal{I}$ = process sources
$j \in \mathcal{J}$ = process sinks
$k \in \mathcal{K}$ = interception devices
$n \in \mathcal{N}$ = time intervals
$p \in \mathcal{P}$ = properties
$r \in \mathcal{R}$ = fresh resources
$s \in \mathcal{S}$ = storage vessels

Parameters

A = annualization factor
B_k = investment cost exponent for interception device k
C_r = unit cost for fresh resource r
C_k^{inv} = investment cost coefficient for interception device k
C_k^{op} = operating cost coefficient for interception device k
$C_{\dagger\ddagger}^{\text{fix}}$ = fixed cost coefficient for the pipe between † and ‡, †‡ ∈ {*ie*, *ij*, *ik*, *is*, *ke*, *kj*, *kk′*, *ks*, *rj*, *se*, *sj*, *sk*}
$C_{\dagger\ddagger}^{\text{var}}$ = variable cost coefficient for the pipe between † and ‡, †‡ ∈ {*ie*, *ij*, *ik*, *is*, *ke*, *kj*, *kk′*, *ks*, *rj*, *se*, *sj*, *sk*}
C_s = cost coefficient for storage vessel s
C_s^{fix} = fixed cost coefficient for storage vessel s
C_s^{var} = variable cost coefficient for storage vessel s
Δ_n = duration of time interval n
F_i = given flow rate of process source i
F_j = required flow rate for process sink j
$F_{\dagger\ddagger}^{\max}$ = upper bound on flow rate in the pipe between † and ‡, †‡ ∈{*ie*, *ij*, *ik*, *is*, *ke*, *kj*, *kk′*, *ks*, *rj*, *se*, *sj*, *sk*}
$F_{\dagger\ddagger}^{\min}$ = lower bound on flow rate in the pipe between † and ‡, †‡ ∈ {*ie*, *ij*, *ik*, *is*, *ke*, *kj*, *kk′*, *ks*, *rj*, *se*, *sj*, *sk*}
$F_s^{\max}$ = upper bound on flow rate for storage vessel s
$F_s^{\min}$ = lower bound on flow rate for storage vessel s
N^{cyc} = number of production cycles per year
$\Psi_{ep}^{\max}$ = upper bound on operator value of property p to environment e
$\Psi_{ep}^{\min}$ = lower bound on operator value of property p to environment e
Ψ_{ip} = operator value of property p of process source i
$\Psi_{jp}^{\max}$ = upper bound on operator value of property p to process sink j
$\Psi_{jp}^{\min}$ = lower bound on operator value of property p to process sink j
$\Psi_{kp}^{\text{in,max}}$ = upper bound on operator value of property p to interception device k
$\Psi_{kp}^{\text{in,min}}$ = lower bound on operator value of property p to interception device k
Ψ_{rp} = operator value of property p of fresh resource r
$\Psi_{sp}^{\text{in,max}}$ = upper bound on operator value of property p to storage vessel s
$\Psi_{sp}^{\text{in,min}}$ = lower bound on operator value of property p to storage vessel s
$Q_s^{\max}$ = upper bound on storage capacity of storage vessel s
$Q_s^{\min}$ = lower bound on storage capacity of storage vessel s
Y_{in} = ∈{0,1}, for the existence of process source i in time interval n
Y_{jn} = ∈{0,1}, for the existence of process sink j in time interval n
Z^{cyc} = ∈{0,1}, 0 for single operation; 1 for cyclic operation

Variables

f_{en} = flow rate to environment e in time interval n
$\hat{f}_{\dagger\ddagger}$ = maximum flow rate in the pipe between † and ‡, †‡ ∈{*ie*, *ij*, *ik*, *is*, *ke*, *kj*, *kk′*, *ks*, *rj*, *se*, *sj*, *sk*}
$f_{\dagger\ddagger n}$ = flow rate from † to ‡ in time interval n, †‡ ∈ {*ie*, *ij*, *ik*, *is*, *ke*, *kj*, *kk′*, *ks*, *rj*, *se*, *sj*, *sk*}
f_{in} = flow rate from process source i in time interval n
f_{jn} = flow rate to process sink j in time interval n
$\hat{f}_k$ = treatment capacity of interception device k
f_{kn}^{in} = inlet flow rate to interception device k in time interval n
f_{kn}^{out} = outlet flow rate from interception device k in time interval n
f_{sn}^{in} = inlet flow rate to storage vessel s in time interval n
f_{sn}^{out} = outlet flow rate from storage vessel s in time interval n
ψ_{epn} = operator value of property p to environment e in time interval n
ψ_{ip} = operator value of property p of process source i
ψ_{jpn} = operator value of property p to process sink j in time interval n
ψ_{kpn}^{in} = inlet operator value of property p to device k in time interval n
ψ_{kpn}^{out} = outlet operator value of property p of device k in time interval n
ψ_{spn}^{in} = inlet operator value of property p to vessel s in time interval n
ψ_{spn}^{out} = outlet operator value of property p of vessel s in time interval n
$\hat{q}_s$ = storage capacity of storage vessel s
q_{sn} = cumulative mass in storage vessel s at the end of time interval n
$z_{\dagger\ddagger}$ = ∈{0,1}, for the presence of the pipe between † and ‡, †‡ ∈{*ie*, *ij*, *ik*, *is*, *ke*, *kj*, *kk′*, *ks*, *rj*, *se*, *sj*, *sk*}
z_s = ∈{0,1}, for the presence of storage vessel s
z_{sn}^{in} = ∈{0,1}, for the occurrence of the inlet flow to storage vessel s in time interval n

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