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Integrated Approach for Simultaneous Mass and Property Integration for Resource Conservation

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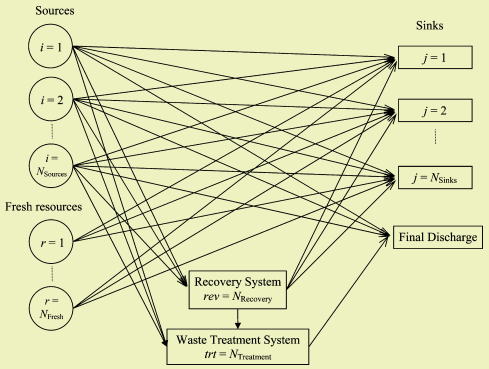
ABSTRACT: The objective of this work is to develop an integrated, systematic, and cost-effective design technique to synthesize a resource conservation network. On the basis of different characteristics for the process constraint and environmental discharge limit, mass and property integration techniques are adapted in this proposed approach. A conceptual framework is first developed to serve as the basis of the mathematical optimization model. A mixed-integer nonlinear programming (MINLP) formulation is developed to synthesize a resource conservation network with minimum total annualized cost. A case study on the production of phenol from cumene hydroperoxide is presented to illustrate the proposed approach.



KEYWORDS: *Material recovery, Process integration, Mass integration, Property integration, Optimization*

INTRODUCTION

Tons of pollutants are being disposed into the environment every day. It has caused accelerated and irreversible damage to the environmental surroundings and affected human health. Therefore, environmental protection has become a priority concern for the world. To control and diminish emissions, stringent environmental regulations were enforced. Process industries have been seriously affected by these restrictions, and this has stimulated them to search for competitive alternatives to reduce waste generation.

Through process integration, various optimization techniques were developed to systematically address the conservation of material and energy resources. One of the active areas for resource conservation activities is in-plant material recovery. The earliest attempt in developing systematic process integration tools for this area was initialized by El-Halwagi and Manousiousthakis,[1] who made use of the graphical targeting tool to establish the minimum consumption of external mass separating agent prior to the synthesis of a mass-exchange network. Thereafter, various comprehensive approaches on *mass integration* for environmental protection were proposed.[2−7]

For the special cases of mass integration, i.e., resource conservation network (RCN) such as water and hydrogen networks, various insight-based and mathematical optimization techniques were proposed to determine the minimum fresh material usage (e.g., water, hydrogen, etc.) and/or minimum cost solutions. This includes the insight-based pinch analysis techniques via graphical[8−16] and algebraic[17−24] approaches for RCNs with reuse/recycle,[8−12,15−20] regeneration,[13,23,24] and treatment.[14,21,22] In addition, mathematical optimization approaches[25−35] and a combination of insight-based and optimization approaches[36−38] were also presented for synthesis of RCNs. Takama and co-workers[25,26] first introduced the mathematical optimization approaches for RCN (i.e., water network) synthesis. This is then followed by other mathematical optimization approaches reported for reuse/recycle,[28,31,36,37] regeneration, and treatment,[32,33] as well as total RCN synthesis.[37,38] It is worth noting that the common feature of all mass-integration works is that all the previous works[8−38] are restricted to chemocentric for tracking individual chemical species.

However, many industrial applications are not directly governed by the chemical constituent of the stream but instead by the stream properties or functionalities. For example, the selection of solvent relies on their characteristics such as equilibrium distribution coefficients, viscosity, and volatility. Besides, it is also common to find environment regulations that set discharge limits based on certain properties (e.g., pH, color, toxicity, TOC, ozone-depleting ability, etc.).[3] Shelley and El-

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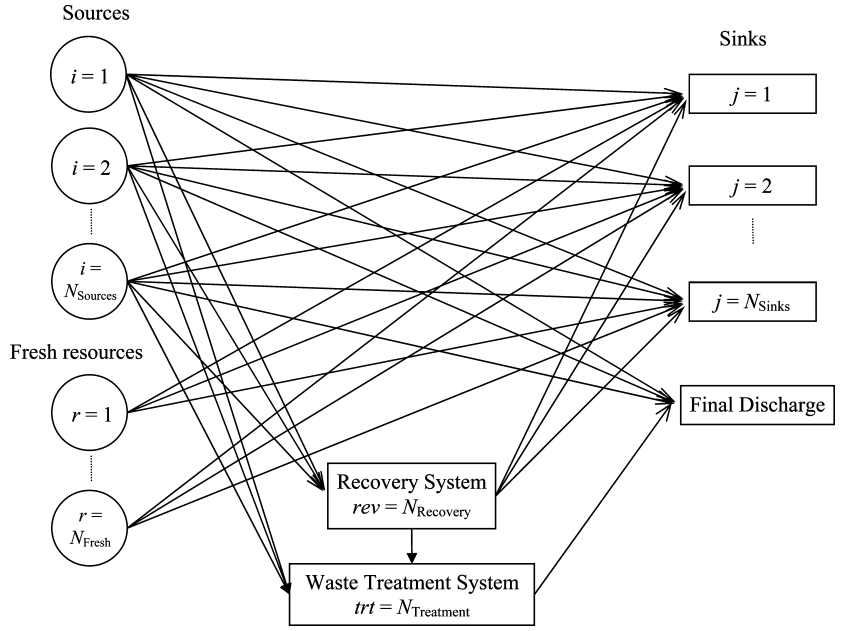

Figure 1. Source−sink representation that considers environmental constraints.

Halwagi[39] first developed the concept of property-based clusters to enable the conserved tracking of properties. Later works by El-Halwagi and co-workers[40] extended the concept into the paradigm of *property integration*, which may be defined as *a functionality-based holistic approach for the allocation and manipulation of streams and processing units, which is based on functionality tracking, adjustment, and assignment throughout the process*. Note that material properties can be broadly divided into two categories. The first category consists of the properties that are measured based on weighted averages of concentrations of multiple chemical species, e.g., theoretical oxygen demand (ThOD), chemical oxygen demand (COD), total suspended solid (TSS), etc., as found in the mass-integration problem. On the other hand, properties that cannot be measured based on weighted average (e.g., density, vapor pressure, viscosity, etc.) are addressed via linearized property operator.[39] In other words, various mass integration problems such as water and hydrogen network syntheses may be treated as special cases of property integration.[41] Various graphical,[40,42] algebraic,[43,44] and optimization techniques[41,45−49] have been developed for property-based material reuse/recycle problems, ranging from continuous[40−45,48,49] to batch processes.[46,47]

To date, most of the proposed techniques have focused on either process or environmental constraints, but not simultaneously. As such, there is a possibility that, after process optimization is performed, the quantity of the resulting waste streams may decrease but the treatment cost and environmental impact may increase. To address this issue, Ponce-Ortega et al.[48,49] presented several mathematical programming approaches for optimizing a material reuse/recycle network with simultaneous consideration of process and environmental constraints. A disjunctive programming formulation was presented by Ponce-Ortega et al.[48] to synthesize the reuse/recycle network and its wastewater treatment system that fulfill the environmental legislation. Besides, Ponce-Ortega et al.[49] presented a linearized model that addresses property-based reuse/recycle network with inception process and treatment system. In this work, an alternative mathematical optimization model is presented to simultaneously address process and environmental constraints for a RCN. Both component- and property-based constraints are incorporated in the synthesis of a RCN. In this work, a mixed-integer nonlinear programming (MINLP) formulation is presented to synthesize the RCN that complies with environmental legislation with minimum total annualized cost. A simulated industrial case study of phenol production is used to illustrate the proposed approach.

PROBLEM STATEMENT

Given is a process with the following.

- A set of *sources*: SOURCES = $\{i|i = 1, ..., N_{\text{Sources}}\}$. Each source, i, has a flow rate (w_i) and uth component concentration ($y_{i,u}$). Besides, source i is characterized by a set of properties: PROPERTIES = $\{q|q = 1, ..., N_{\text{Properties}}\}$, denoted as $p_{i,q}$.
- A set of *sinks*: SINKS = $\{j|j = 1, ..., N_{\text{Sinks}}\}$. Sinks are process units that can accept the sources. Each sink, j, requires a flow rate, g_j, and is constrained by the component concentration ($y_{j,u}$) and properties ($p_{j,q}$) of its feed, i.e.,

$$y_{j,u}^{\min} \le y_{j,u} \le y_{j,u}^{\max} \quad \forall\, j \text{ and } \forall\, u \tag{1}$$

$$p_{j,q}^{\min} \le p_{j,q} \le p_{j,q}^{\max} \quad \forall\, j \text{ and } \forall\, q \tag{2}$$

where $y_{j,u}^{\min}$ and $y_{j,u}^{\max}$ are the lower and upper concentration limits of component u acceptable by sink j, respectively. Meanwhile, $p_{j,q}^{\min}$ and $p_{j,q}^{\max}$ refer to the given lower and upper bounds, respectively, on acceptable property q.

External fresh resources, with different component concentrations and properties, are available, FRESH = $\{r|r = 1, ..., N_{\text{Fresh}}\}$, to supplement the use of process sources in the sinks, with the unit costs of rth fresh resource referred to as $\text{Cost}_r^{\text{Fresh}}$ ($/kg of the fresh resource).

Besides, material recovery from the waste streams through interception techniques (e.g., extraction, absorption, stripping, etc.) will first be considered before the waste is sent to the final treatment system (for environmental discharge). A set of recovery systems, RECOVERY = $\{\text{rev}|\text{rev} = 1, ..., N_{\text{Recovery}}\}$, is

available, with the unit costs of $\text{Cost}_{\text{rev},u}^{\text{Recovery}}$ to recover component u.

In addition, the environment legislation restricts certain qualities of waste to be discharged from the industries. In most cases, the discharge of waste is mainly dependent on various properties such as pH, conductivity, turbidity, toxicity, ThOD, etc. Thus, it is useful to define the environmental discharge constraints as follow:

$$p_q^{\text{min env}} \le p_q^{\text{discharge}} \le p_q^{\text{max env}} \quad \forall\ q \tag{3}$$

where $p_q^{\text{discharge}}$ is the value of property q in waste discharge; $p_q^{\text{min env}}$ and $p_q^{\text{max env}}$ are the lower and upper limits of environmental discharge of property q, respectively. To comply with the environment legislation, a set of treatment systems, TREATMENT = {trt|trt = 1, ..., $N_{\text{Treatment}}$}, is needed to remove the pollutants in the waste streams and/or to adjust its properties (i.e., pH) prior to its discharge to the environment. The unit cost of treating qth property in waste treatment unit trt is given as $\text{Cost}_{\text{trt},q}^{\text{Treatment}}$.

Note that the recovery system is used to recover valuable materials as byproducts, while the treatment system is used to treat the wastewater to comply with environmental regulations. Therefore, in this case study, the recovery system is utilized before considering the treatment system. In this work, the optimization objective is to synthesize a cost-effective RCN with consideration of mass and property integrations simultaneously.

SOLUTION APPROACH

Figure 1 shows the superstructure for the allocation of material sources to the process sinks, material-recovery and waste-treatment systems. The main objective of this work is to present a systematic procedure that optimizes the total annualized cost (TAC) that includes the cost of fresh resource consumption (C^{Fresh}), material recovery (C^{Recovery}), waste treatment ($C^{\text{Treatment}}$), discharge ($C^{\text{Discharge}}$), and annualized piping cost (C^{Piping}) for a RCN, given as follows:

$$\text{TAC} = (C^{\text{Fresh}} + C^{\text{Recovery}} + C^{\text{Treatment}} + C^{\text{Discharge}})\text{AT} + C^{\text{Piping}} \tag{4}$$

where AT is given as annual working hours (8000 h).

The operating cost of the fresh resource (C^{Fresh}) is given by eq 5.

$$C^{\text{Fresh}} = \sum_{r=1}^{N_{\text{Fresh}}} \left(\sum_{j=1}^{N_{\text{Sinks}}} h_{r,j} \right) \times \text{Cost}_r^{\text{Fresh}} \tag{5}$$

where $h_{r,j}$ refers the flow rate of fresh r that is allocated to sink j.

Besides, the overall cost of material recovery (C^{Recovery}) is given by the summation of the recovery for each component, as shown in eq 6:

$$C^{\text{Recovery}} = \sum_{\text{rev}=1}^{N_{\text{Recovery}}} \sum_{u=1}^{N_{\text{components}}} (\text{COST}_{\text{rev},u}^{\text{Recovery}} \times [\sum_{i=1}^{N_{\text{Sources}}} (u_{i,\text{rev}}^{\text{in}} \times y_{i,u}^{\text{in}}) - (u_{\text{rev}}^{\text{out}} \times y_{\text{rev},u}^{\text{out}})] \times I_u^{\text{Recovery}}) \tag{6}$$

where $u_{i,\text{rev}}^{\text{in}}$ is the inlet flow rate to recovery system rev from source i and $u_{\text{rev}}^{\text{out}}$ is the outlet flow rate of recovery system rev, with inlet and outlet concentrations of $y_{i,u}^{\text{in}}$ and $y_{\text{rev},u}^{\text{out}}$, respectively. I_u^{Recovery} is the binary term that represents the absence ($I_u^{\text{Recovery}} = 0$) or presence ($I_u^{\text{Recovery}} = 1$) for a given recovery system for component u.

In the case where the concentration of component u is too low for recovery, then it is not worth investing in additional equipment for the recovery system. Therefore, the minimum concentration of component u that is worth recovering ($y_{\text{rev},u}^{\text{min}}$) is included in the optimization model, as shown in eq 7. Equation 8 describes the mean inlet concentration to the recovery system ($y_{\text{rev},u}^{\text{in}}$).

$$\begin{aligned} &(y_u^{\text{L}} - y_{\text{rev},u}^{\text{min}}) \times (1 - I_u^{\text{Recovery}}) \\ &\le (y_{\text{rev},u}^{\text{in}} - y_{\text{rev},u}^{\text{min}}) \\ &\le (y_u^{\text{U}} - y_{\text{rev},u}^{\text{min}}) \times (I_u^{\text{Recovery}}) \end{aligned} \tag{7}$$

$$y_{\text{rev},u}^{\text{in}} = \frac{\sum_{i=1}^{N_{\text{Sources}}} (u_{i,\text{rev}}^{\text{in}} \times y_{i,u}^{\text{in}})}{\sum_{i=1}^{N_{\text{Sources}}} u_{i,\text{rev}}^{\text{in}}} \quad \forall\ \text{rev and } \forall\ u \tag{8}$$

where y_u^{L} and y_u^{U} are the lower and upper bounds for $y_{\text{rev},u}^{\text{in}}$, respectively. For cases where the value of ($y_{\text{rev},u}^{\text{in}} - y_{\text{rev},u}^{\text{min}}$) becomes positive, the constraint forces I_u^{Recovery} to take the value of 1. Otherwise, I_u^{Recovery} is forced to take the value of 0.

In addition, the waste treatment cost ($C^{\text{Treatment}}$) is a function of the flow rate ($F_{\text{T,trt}}^{\text{Waste}}$) and properties ($\overline{p}_q^{\text{Waste}}$) of the inlet wastewater to the treatment system trt, as well as the environmental discharge limits of the qth property ($p_q^{\text{min env}}$, $p_q^{\text{max env}}$). Besides, the unit cost of treatment ($\text{Cost}_{\text{trt},q}^{\text{Treatment}}$) is dependent on the treatment unit employed, as different types of treatment systems involve different capital and operating costs. In addition, it is assumed that the distance between treatment processes is fixed; hence, size and cost of piping within treatment processes is directly proportional with $F_{\text{T,trt}}^{\text{Waste}}$. In this work, it is assumed that the piping and capital costs for treatment system trt is incorporated in $C^{\text{Treatment}}$.

$$C^{\text{Treatment}} = f(F_{\text{T,trt}}^{\text{Waste}},\ \overline{p}_q^{\text{Waste}},\ p_q^{\text{min env}},\ p_q^{\text{max env}},\ \text{Cost}_{\text{trt},q}^{\text{Treatment}},\ I_{\text{trt},q}^{\text{Treatment}}) \tag{9}$$

where $I_{\text{trt},q}^{\text{Treatment}}$ is the binary term that represents the absence or presence for treatment system trt for property q. Equations 7 and 8 can be adapted in this task, where $y_{\text{rev},u}^{\text{min}}$ is revised based on the limits of environmental discharge of property q.

It is noted that both recovery and treatment systems can be generalized as separation systems. However, both systems serve for different objectives. The recovery system is used to recover valuable product, while the treatment system is used to treat wastewater to fulfill the environmental limits. To achieve maximum resource conservation, the recovery system should be employed prior to the treatment for discharge.

In general, the annualized piping cost (C^{Piping}) is proportional to the flow rate that passes through the pipe, with the piping cost coefficient shown in eq 10:

$$C^{\text{Piping}} = [\sum_{i=1}^{N_{\text{Sources}}} \sum_{j=1}^{N_{\text{Sinks}}} (v_{i,j} \times \text{COST}_{i,j}^{\text{Piping}}) + \sum_{r=1}^{N_{\text{Fresh}}} \sum_{j=1}^{N_{\text{Sinks}}} (h_{r,j} \times \text{COST}_{r,j}^{\text{Piping}}) +] \times \text{AF} \tag{10}$$

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where $\mathrm{COST}_{i,j}^{\mathrm{Piping}}$ and $\mathrm{COST}_{r,j}^{\mathrm{Piping}}$ are cost coefficients for piping for allocating source i and fresh r to sink j, respectively. Note that the cost coefficients of piping include the material of construction, diameter of the pipe, and Manhattan distance for source i or fresh r to sink j. In addition, v_{ij} is the flow rate of source i that is reused/recycled to sink j. Because the piping cost of waste treatment systems is often significantly lower than that of material reuse/recycle, it is ignored in this model. To annualize the piping cost, annualizing factor (AF) is included in eq 10 and can be defined as below,

$$\mathrm{AF} = \frac{m(1+m)^{\mathrm{yr}}}{(1+m)^{\mathrm{yr}} - 1} \tag{11}$$

where m = fractional interest rate per year and yr = number of years.

A mixing rule is needed to define all possible mixing patterns among these individual properties. One such form of mixing rule takes the following expression[39]:

$$\psi(\bar{p}_q) = \sum_i x_i \psi(p_{i,q}) \tag{12}$$

where $\psi(p_{i,q})$ and $\psi(\bar{p}_q)$ are operators on property $p_{i,q}$ and mixture property $\bar{p}_q$, respectively; x_i is the fractional contribution of source i in the total mixture flow rate.

The objective function (eq 4) is minimized subjected to the following constraints:

Splitting constraint for sources:

$$w_i = \sum_{j=1}^{N_{\mathrm{Sinks}}} v_{i,j} + \sum_{\mathrm{rev}=1}^{N_{\mathrm{Recovery}}} u_{i,\mathrm{rev}}^{\mathrm{in}} + z_i^{\mathrm{waste}} \quad \forall\ i \tag{13}$$

Overall material balance around the mixing point of the feed to the jth sink:

$$g_j = \sum_{i=1}^{N_{\mathrm{Sources}}} v_{i,j} + \sum_{r=1}^{N_{\mathrm{Fresh}}} h_{r,j} \quad \forall\ j \tag{14}$$

Material component constraints around the mixing point of feed to the sink j:

$$g_j \times y_{j,u} = \sum_{r=1}^{N_{\mathrm{Fresh}}} h_{r,j} \times y_{r,u} + \sum_{i=1}^{N_{\mathrm{Sources}}} v_{i,j} \times y_{i,u} \quad \forall\ j \text{ and } \forall\ u \tag{15}$$

Material property operator constraints around the mixing point of feed to the sink j:

$$g_j \times \psi(p_{j,q}) = \sum_{r=1}^{N_{\mathrm{Fresh}}} h_{r,j} \times \psi(p_{r,q}) + \sum_{i=1}^{N_{\mathrm{Sources}}} v_{i,j} \times \psi(p_{i,q}) \quad \forall\ j \text{ and } \forall\ q \tag{16}$$

Sink constraints:

$$y_{j,u}^{\min} \le y_{j,u} \le y_{j,u}^{\max} \quad \forall\ j \text{ and } \forall\ u \tag{17}$$

$$\psi(p_{j,q}^{\min}) \le \psi(p_{j,q}) \le \psi(p_{j,q}^{\max}) \quad \forall\ j \text{ and } \forall\ q \tag{18}$$

where $\psi(p_{j,q}^{\min})$ and $\psi(p_{j,q}^{\max})$ are the minimum and maximum allowable of qth property operators, respectively. Note that eq 18 is essentially an alternative version of eq 2.

The combined flow rate of the mixed sources entering the recovery system, $F_{\mathrm{rev}}^{\mathrm{Recovery}}$, is given by

$$F_{\mathrm{rev}}^{\mathrm{Recovery}} = \sum_{i=1}^{N_{\mathrm{Sources}}} u_{i,\mathrm{rev}}^{\mathrm{in}} \quad \forall\ \mathrm{rev} \tag{19}$$

Assuming no material losses and generation in the recovery system, the flow rate balance for the recovery system is shown as follows:

$$\sum_{i=1}^{N_{\mathrm{Sources}}} u_{i,\mathrm{rev}}^{\mathrm{in}} = u_{\mathrm{rev}}^{\mathrm{out}} \quad \forall\ \mathrm{rev} \tag{20}$$

The mixing rule of component u for the recovery system is as follows:

$$\sum_{i=1}^{N_{\mathrm{Sources}}} u_{i,\mathrm{rev}}^{\mathrm{in}} \times y_{\mathrm{rev},u}^{\mathrm{in}} = \frac{(100 - \mathrm{RE})}{100} u_{\mathrm{rev}}^{\mathrm{out}} \times y_{\mathrm{rev},u}^{\mathrm{in}} \times I_u^{\mathrm{Recovery}} + u_{\mathrm{rev}}^{\mathrm{out}} \times y_{\mathrm{rev},u}^{\mathrm{in}} \times (1 - I_u^{\mathrm{Recovery}}) \quad \forall\ u \text{ and } \forall\ \mathrm{rev} \tag{21}$$

where RE is the recovery efficiency (%).

All unused sources are fed to the waste treatment system before being discharged to the environment:

$$F^{\mathrm{Waste}} = \sum_{i=1}^{N_{\mathrm{Sources}}} z_i^{\mathrm{waste}} + \sum_{\mathrm{rev}=1}^{N_{\mathrm{Recovery}}} u_{\mathrm{rev}}^{\mathrm{out}} \tag{22}$$

The property operators mixing equation for the treatment system is as follows:

$$F^{\mathrm{Waste}} \times \psi(\bar{p}_q^{\mathrm{Waste}}) = \sum_{i=1}^{N_{\mathrm{Sources}}} z_i^{\mathrm{waste}} \times \psi(p_{i,q}) + \sum_{\mathrm{rev}=1}^{N_{\mathrm{Recovery}}} u_{\mathrm{rev}}^{\mathrm{out}} \times \psi(p_{\mathrm{rev},q}) \quad \forall\ q \tag{23}$$

For a decentralized treatment system trt, the waste flow rate is segregated into treatment ($F_{\mathrm{T,trt}}^{\mathrm{Waste}}$) and bypass flow rates ($F_{\mathrm{B,trt}}^{\mathrm{Waste}}$):

$$F^{\mathrm{Waste}} = \sum_{\mathrm{trt}=1}^{N_{\mathrm{Treatment}}} (F_{\mathrm{T,trt}}^{\mathrm{Waste}} + F_{\mathrm{B,trt}}^{\mathrm{Waste}}) \tag{24}$$

The waste discharge is constrained by the environmental discharge limit, given by

$$\sum_{\mathrm{trt}=1}^{N_{\mathrm{Treatment}}} [F_{\mathrm{T,trt}}^{\mathrm{Waste}} \times \psi(p_{\mathrm{T},q}^{\mathrm{Waste}}) + F_{\mathrm{B,trt}}^{\mathrm{Waste}} \times \psi(\bar{p}_q^{\mathrm{Waste}})] \le F^{\mathrm{Waste}} \times \psi(p_q^{\mathrm{env}}) \quad \forall\ q \tag{25}$$

where $p_{\mathrm{T},q}^{\mathrm{Waste}}$ is the qth property of treated waste from the waste-treatment system trt.

On the basis of the above formulation, a mixed-integer nonlinear programming (MINLP) model results. This formulation is solved to determine the minimum TAC for the RCN that fulfills the environmental constraints. Besides, the minimum use of fresh resource, the waste discharge, and the cost of material recovery and waste treatment are also determined. In this work, the global solver in the commercial optimization software Extended LINGO version 10.0 is used to obtain the global optimum solution. The solver uses a branch-and-bound (B&B) algorithm combined with linearization to find globally optimal solutions for NLP and MINLP problems.[50]

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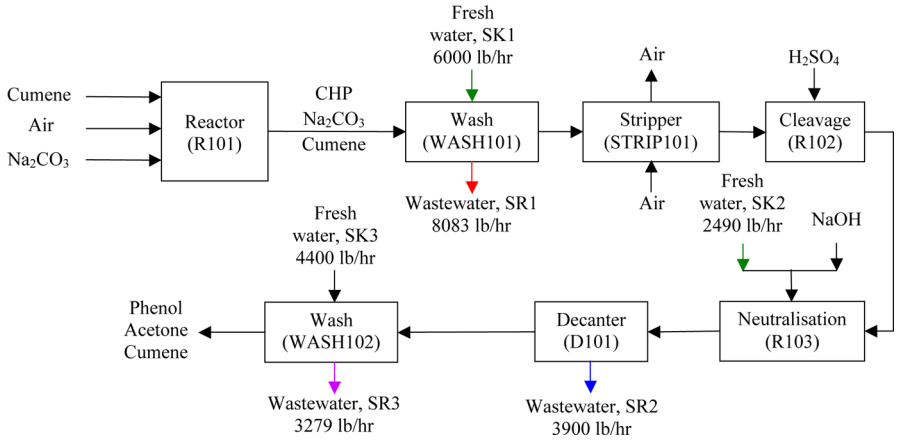

Figure 2. Schematic process flow sheet for phenol production case study.

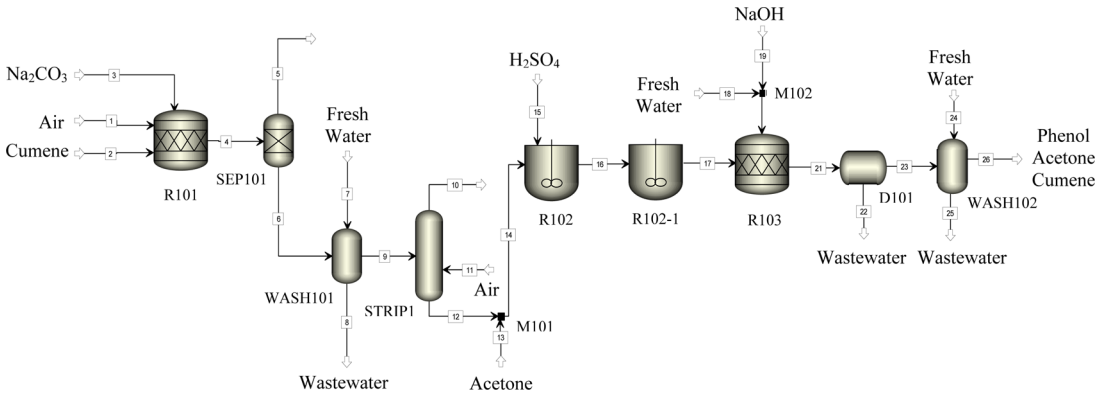

Figure 3. Simulated flow sheet for cumene peroxidation.

CASE STUDY

A case study on phenol production from cumene hydroperoxyde is used to illustrate the proposed approach with the objective to minimize its TAC, given as in eq 4. In this case study, the AT is assumed as 8000 h. Figure 2 shows a schematic process flow sheet for the production of phenol from cumene hydroperoxide (CHP). The process is modeled in Aspen Plus to obtain its streamflow rate, concentration, and property values (see simulation flow sheet in Figure 3).

In phenol production, cumene (C_9H_{12}) is fed to the reactor (R101) with air, along with the sodium carbonate (Na_2CO_3) that serves as a buffer solution. Cumene is oxidized into cumene hydroperoxide (CHP) in the reactor. The reactor effluent, which is a mixture of CHP and unconverted cumene (in Na_2CO_3 solution), is then sent to a wash operation (WASH101) for the removal of the excess buffer solution and water-soluble materials. Effluent from the washer is next sent to an air stripper, where the CHP concentration is increased to 80 wt %. The concentrated CHP stream is fed to the Cleavage unit (R102), where the CHP is decomposed to form phenol and acetone when sulphuric acid (H_2SO_4) is added. The resulting cleavage stream is then neutralized with diluted sodium hydroxide (NaOH) in the Neutralization tank (R103). The effluent stream is then separated into organic and water phases in the Decanter (D101). The water phase is sent to wastewater treatment, while the organic phase (mixture of phenol, acetone, and cumene) is washed with fresh water to remove the excess NaOH in a wash operation (WASH102). Finally, the organic phase is sent to distillation columns, where it is fractioned into the pure products of phenol and acetone (not shown in Figures 2 and 3).

From Figure 2, three wastewater sources are observed in the process, i.e., effluent from WASH101 (SR1), D101 (SR2), and WASH102 (SR3). Besides, three process sinks that may accept these water sources are also identified, i.e., WASH101 (SK1), R103 (SK2), and WASH102 (SK3). In this case study, phenol concentration is the primary constraint when the water reuse/recycle scheme is considered for the processes. The process constraints of sinks are shown in Table 1. In this case study, two fresh water sources (FW1 and FW2) are available for use. FW1 is a pure fresh feed, whereas FW2 has a phenol concentration of 100 ppm. The costs for FW1 and FW2 are assumed as \$0.044/lb and \$0.029/lb, respectively.

Table 1. Process Constraints of Sinks

sinks j	flow rate g_j (lb/h)	maximum inlet phenol concentration, $y_{j,u}^{max}$ (ppm)
SK1	6 000	15 000
SK2	2 490	100 000
SK3	4 400	15 000

From the simulation study via ASPEN Plus (Figure 3), properties of the process sources are obtained and are summarized in Table 2. Note that five properties are identified, i.e., concentrations of phenol and acetone, toxicity, ThOD (excluding contributions of phenol), and pH. In this case study, the ThOD value of the waste stream is calculated based on the theoretical oxygen demands of all organic components other

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Table 2. Properties for the Process Sources

sources i	flow rate, w_i (lb/h)	phenol concentration (ppm)	acetone concentration (ppm)	toxicity mortality (%)	ThOD (mg O_2 /l)	pH
SR1	8 083	16 000	0	89.6	190	6.68
SR2	3 900	24 000	10 000	100	48 850	6.46
SR3	3 279	220 000	28 000	100	92 100	5.69
fresh resource r		flow rate (lb/h)	phenol concentration (ppm)			
FW1		To be determined	0			
FW2		To be determined	100			

that phenol, as phenol is considered a toxic material where more stringent environmental legislation is enforced. In addition, the cost coefficients for piping from source i and fresh r to sink j are shown in Table 3. In this case study, m and yr in eq 11 are assumed as 10% and 5 years, respectively. On the basis of eqs 10 and 11, the annualized capital cost of piping can be determined.

Table 3. Cost Coefficients for Piping of Source i and Fresh r to Sink j ($/lb/h)

sources sinks	SR1	SR2	SR3	FW1	FW2
SK1	5	2	3	4.5	2.5
SK2	3.5	1	5	3	1
SK3	2	4	2	3.5	1.5

As shown in Table 2, significant amounts of acetone and phenol are found in the wastewater stream (especially SR2 and SR3). Because both chemicals are the main products of the process, their recoveries are first considered before the wastewater is treated for discharge. Note that regeneration reuse/recycle is not considered in this case study, as in the waste streams exist other trace metals (not shown in Table 2) that may accumulate in the system. In other words, even if the regeneration scheme is employed to lower the concentrations of acetone and phenol for further reuse/recycle of the wastewater streams, the limit for other trace metals will be exceeded. In addition, the cost for regenerating sources for further reuse/recycle is higher than the recovery systems.

Apart from increasing revenue for the company, phenol-recovery possesses an additional advantage in reducing the toxicity level of wastewater discharge. Note that the recovery system is used to recover valuable materials as byproducts, whereas the treatment system is used to treat the wastewater to comply with environmental regulations. Therefore, in this case study, the recovery system is utilized before considering the treatment system.

To recover phenol from wastewater, a solvent-extraction technique is selected in this case study because it is able to separate phenol from the wastewater stream with high purity as compared with other separation technologies. In this case study, the minimum concentration of phenol that is worth recovery is set as 500 ppm; y_u^L and y_u^U in eq 7 are assumed as any value that is lower than and greater than 500, respectively. It is further assumed that solvent extraction has a recovery efficiency of 93%, with the treatment cost summarized in Table 4.[51] As shown, the operational and fixed costs are given as $0.186/lb of phenol recovered and $0.015/lb of phenol recovered, respectively. Meanwhile, the recovered phenol can be sold as a byproduct at the price of $0.136/lb of phenol. Therefore, the total cost of phenol recovery is determined as $0.065/lb of recovered phenol. On the other hand, another type of separation technology (air stripping) is used to recover acetone

Table 4. Solvent Extraction Treatment Cost[51]

description	cost ($/lb of phenol recovered)
operational cost	0.186
fixed cost	0.015
subtotal	0.201
economic return (recovered phenol sales)	−0.136
total cost	0.065

from the wastewater. The removal efficiency for acetone in the air stripping units is assumed as 98%, with the estimated treatment cost of $0.033/lb of recovered acetone (cost breakdown is shown in Table 5).

Table 5. Air Stripping Treatment Cost

description	acetone recovery ($/lb of acetone recovered)
operational cost	0.125
fixed cost	0.0215
subtotal	0.1462
economic return (recovered acet. sales)	−0.113
total cost	0.033

Other than concentrations of acetone and phenol, three main properties are taken into consideration, i.e., toxicity, ThOD, and pH. To measure the toxicity of material, probit correlation (Y) and mortality response (P) in eqs 26 and 27 are used.[52,53]

$$Y = -0.22 + 5.27 \log(y^{\text{Toxic}}) \tag{26}$$

where y^{Toxic} (ppm) is the concentration of toxic material.

$$P(\%\text{mortality}) = 50\left[1 + \frac{Y-5}{|Y-5|}\,\text{erf}\left(\frac{|Y-5|}{\sqrt{2}}\right)\right] \tag{27}$$

where erf is Gauss error function, which can be solved by eq 28.[54]

$$\text{erf}\left(\frac{|Y-5|}{\sqrt{2}}\right) \approx \sqrt{1 - \exp\left(-\left(\frac{|Y-5|}{\sqrt{2}}\right)^2 \frac{\frac{4}{\pi} + 0.140012\left(\frac{|Y-5|}{\sqrt{2}}\right)^2}{1 + 0.140012\left(\frac{|Y-5|}{\sqrt{2}}\right)^2}\right)} \tag{28}$$

In this case study, phenol is recognized as the major contribution of toxicity as it has low acute and chronic toxicities, which are required to be well treated prior to environmental discharge.[54] Meanwhile, other organic components such as acetone do not impose any threat to the environment and human life; thus, acetone is not bounded with a discharge limit of toxicity.

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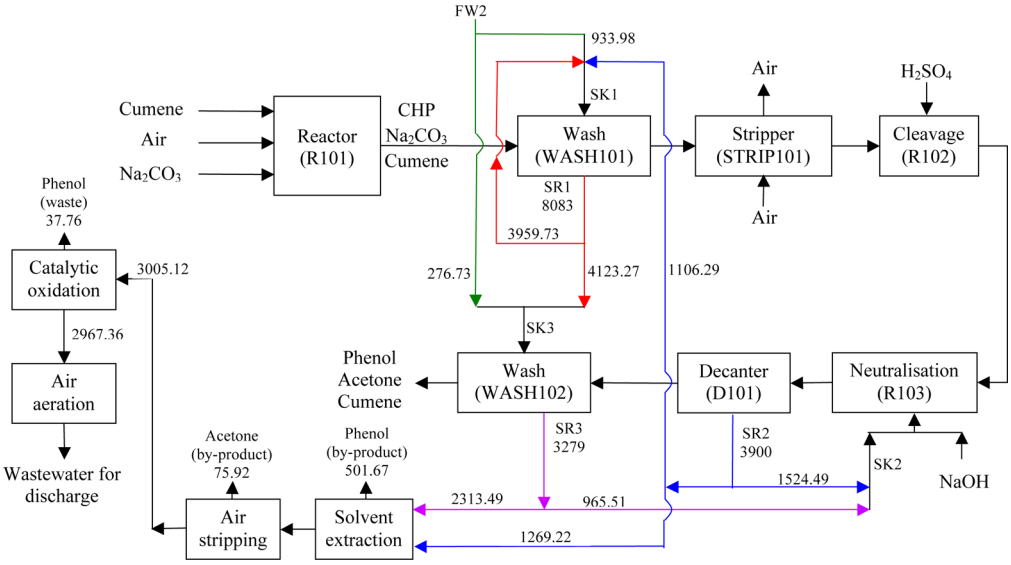

Figure 4. Network design for case study (flow rate in lb/h).

On the other hand, another important wastewater discharge limit for chemical components is chemical oxygen demand (COD). In practice, the COD is measured experimentally as the exact chemical composition of a stream is an unknown. During the preliminary design stage, it is difficult to predict the COD of a wastewater stream. Therefore, theoretical oxygen demand (ThOD), which refers to the theoretical amount of oxygen, O_2, that is required for oxidizing an organic component into its final oxidation form (carbon dioxide and water), is used in the synthesis of RCN for consideration of environmental legislation. The discharge limit of ThOD is strictly restricted because high values of ThOD in the effluents would reduce the oxygen available in the water and cause adverse effects on aquatic life. In this work, the ThOD of each organic component is determined by the following equation,

$$a\text{Organic Component} + bO_2 \rightarrow cCO_2 + dH_2O \tag{29}$$

where a, b, c, and d are stoichiometric coefficients of organic component, O_2, CO_2, and H_2O, respectively.

According to Nemerow,[55] the discharge limit of wastewater is given as follows:

$$\text{Toxicity}^{\text{env}} = 0\%\ \text{mortality} \tag{30}$$

$$F^{\text{Waste}} y_{\text{Phenol}}^{\text{env}} \leq 0.054\ \text{lb/h} \tag{31}$$

$$\text{ThOD}^{\text{env}} \leq 75\ \text{mg}\ O_2/\text{L} \tag{32}$$

$$5.5 \leq \text{pH}^{\text{env}} \leq 9.0 \tag{33}$$

where $\text{Toxicity}^{\text{env}}$, ThOD^{env}, and pH^{env} refer to environmental discharge limits of toxicity, ThOD, and pH, respectively. Meanwhile, $y_{\text{Phenol}}^{\text{env}}$ refers to the environmental limit of phenol concentration.

As mentioned previously, the toxicity in wastewater is mainly contributed by phenol; thus, to simplify the optimization model, toxicity calculation (eqs 26−28) can be solved independently based on phenol concentration. Toxicity of 0% mortality yields the phenol concentration of 1.1 ppm; thus, eq 30 is modified as below:

$$y_{\text{Phenol}}^{\text{env}} \leq 1.1\ \text{ppm} \tag{34}$$

It is noted that two environmental constraints (eqs 31 and 34) contain the phenol concentration. Therefore, treatment of phenol before discharge is crucial. In addition, the maximum discharge limit of ThOD is given as 75 mg O_2/L (eq 32). Meanwhile, the pH of the discharge stream is given in a range between 5.5 and 9.0 (eq 33).

To ensure the discharge wastewater fulfills the environmental legislation, a waste-treatment network is needed. In this work, it is assumed that the catalytic oxidation process is used as a toxicity-treatment process for phenol with estimated treatment cost (which includes fixed and operating costs) of \$0.164/lb of phenol removed. Besides, in order to reduce the high concentration of ThOD in the wastewater, aeration treatment is chosen, in which air is pumped into the wastewater to oxidize the organic components (to degrade into carbon dioxide and water). The treatment cost was contributed mainly by the cost of air handling ($\text{Cost}_{\text{Air}}^{\text{Treatment}}$), which is given as \$0.06/lb of air. To determine the amount of air (F^{Air}) needed for oxidation and cost of treatment for ThOD ($C^{\text{Treatment}}$), eqs 35 and 36 are included in the model.

$$F^{\text{Air}} = \left(\sum_{i=1}^{N_{\text{Sources}}} x_i \text{ThOD}_i - \text{ThOD}^{\text{env}}\right) \sum_{\text{trt}=1}^{N_{\text{Treatment}}} F_{\text{T,trt}}^{\text{Waste}} \tag{35}$$

$$C^{\text{Treatment}} = \text{Cost}_{\text{Air}}^{\text{Treatment}} F^{\text{Air}} \tag{36}$$

To adjust the pH of the wastewater, neutralization units may employ 0.5 M sulphuric acid (H_2SO_4) or 0.5 M sodium hydroxide (NaOH). The cost of chemicals (H_2SO_4 and NaOH), which are estimated based on United States vendors, are given as \$46/L and \$31/L, respectively.

In this case study, the general mixing rule of eq 12 is modified for ThOD as follows:

$$\overline{\text{ThOD}}(\text{mg of}\ O_2/\text{L of waste}) = \sum_{i=1}^{N_{\text{Sources}}} x_i \text{ThOD}_i \tag{37}$$

In addition, various mixing rules of pH are also given as equations below.

For acid mixing ($0 \leq \text{pH} \leq 7$):

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$$10^{-\overline{\mathrm{pH}}} = \sum_{i=1}^{N_{\mathrm{Sources}}} x_i 10^{-\mathrm{pH}_i} \tag{38}$$

For base mixing ($7 \le \mathrm{pH} \le 14$):

$$10^{\overline{\mathrm{pH}}-14} = \sum_{i=1}^{N_{\mathrm{Sources}}} x_i 10^{\mathrm{pH}_i-14} \tag{39}$$

For neutralization where acid and base streams are mixed, eq 40 is used.

$$10^{-\overline{\mathrm{pH}}} = \sum_{\mathrm{acid}=1}^{N_{\mathrm{Acid}}} x_{\mathrm{acid}} 10^{-\mathrm{pH}_{\mathrm{acid}}} - \sum_{\mathrm{base}=1}^{N_{\mathrm{Base}}} x_{\mathrm{base}} 10^{\mathrm{pH}_{\mathrm{base}}-14} \tag{40}$$

The model (eqs 5−8, 10, 11, 13−25, and 31−40) is solved by minimizing total annualized cost (eq 4). Extended LINGO version 10.0 with a global solver is utilized in this work to solve the proposed MINLP model. The global solution is obtained in 4 s on a Pentium (R) Dual CPU T2370, with 1.73 GHz CPU and 2 GB RAM, with the resulting water network as shown in Figure 4.

As shown in Figure 4, SR1 and SR2 are reused/recycled to SK1 (WASH 101), which is supplemented by FW2. Besides, no fresh water is used in SK2 (R103), which reuses the water from SR2 and SR3. Meanwhile, SR1 is also reused in SK3 (WASH102), which is also supplemented by FW2. Two wastewater streams generated from SR2 (1269.22 lb/h) and SR3 (2313.49 lb/h) are sent for byproduct recovery and wastewater treatment. As shown in Figure 4, phenol and acetone are recovered in their respective recovery systems (solvent extraction and air stripping). Next, the wastewater is treated with catalytic oxidation to reduce the toxicity level in the wastewater. Finally, air aeration is used to reduce the ThOD in the wastewater prior to its discharge to the environment. It is noted that a pH adjustment unit is not included in the treatment network as the discharge wastewater fulfills the environmental legislation.

Following the result from the optimization, the total annualized cost of the system is determined as $1,078,691/year with the freshwater flow rate of 1210.71 lb/h (FW2) and wastewater discharge flow rate of 2967.36 lb/h. Note that numerous network designs may achieve the minimum total annualized cost, with Figure 4 being one of the alternatives.

CONCLUSION

A new approach has been developed to simultaneously address component-based material recovery as well as property-based discharge constraints. The proposed optimization model determines the minimum total cost that includes the operational cost for fresh resources, material recovery and waste treatment, and the annualized piping and capital cost. A phenol production case study was solved to illustrate the developed approach. In future works, the model may be extended to consider detailed modeling of interception units, which explores trade-off for the design of those units.

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Notes

The authors declare no competing financial interest.

NOTATION

Sets

COMPONENTS, set of components
FRESH, set of fresh resources
PROPERTIES, set of properties
RECOVERY, set of recovery systems
SINKS, set of water sinks
SOURCES, set of water sources

Indices

i, index of sources
j, index of sinks
q, index of properties
r, index of fresh resources
rev, index of recovery systems
trt, index of waste treatment systems
u, index of component concentrations

Variables

C^{Fresh}, cost of fresh resource consumption
C^{Recovery}, cost of material recovery
$C^{\mathrm{Treatment}}$, cost of waste treatment
C^{Piping}, annualized piping cost
F^{Air}, flow rate of air
$F_{\mathrm{rev}}^{\mathrm{Recovery}}$, total flow rate of sources entering recovery system of rev
F^{Waste}, total wastewater flow rate
$F_{\mathrm{B,trt}}^{\mathrm{Waste}}$, flow rate of wastewater that bypass treatment system trt
$F_{\mathrm{T,trt}}^{\mathrm{Waste}}$, flow rate of wastewater to the treatment system trt
g_j, flow rate of sink j
$h_{r,j}$, flow rate of fresh r to sink j
I_u^{Recovery}, binary variable that represents the absence or presence for a given recovery system for component u
P, mortality response
pH_i, pH of stream i
$p_{i,q}$, qth property in source i
$p_{j,q}$, qth property entering to sink j
$p_{\mathrm{rev},q}$, qth property exit from recovery system rev
$\overline{p}_q$, mixture of property q
p_q^{Waste}, property q of wastewater
$p_q^{\mathrm{discharge}}$, discharge of property q in waste
$\overline{p}_{\mathrm{T},q}^{\mathrm{Waste}}$, property q of treated waste from waste treatment system
TAC, total annualized cost
$\overline{\mathrm{ThOD}}$, mean of theoretical oxygen demand
ThOD_i, theoretical oxygen demand of stream i
$u_{i,\mathrm{rev}}^{\mathrm{in}}$, inlet flow rate of stream i to rev-th recovery systems
$u_{\mathrm{rev}}^{\mathrm{out}}$, outlet flow rate of rev-th recovery systems
$v_{i,j}$, flow rate of source i to sink j
w_i, flow rate of source i
x_i, fractional contribution of source i of total mixture flow rate
x_{acid}, fractional contribution of acid stream
x_{base}, fractional contribution of base stream
$y_{i,u}$, uth component concentration in source i
$y_{j,u}$, uth component concentration entering sink j
$y_{r,u}$, uth component concentration of fresh r
$y_{\mathrm{Phenol}}^{\mathrm{discharge}}$, discharge concentration of phenol
$y_{i,u}^{\mathrm{in}}$, inlet concentration of stream i to rev-th recovery systems
$y_{\mathrm{rev},u}^{\mathrm{in}}$, inlet concentration of rev-th recovery systems
$y_{\mathrm{rev},u}^{\mathrm{out}}$, outlet concentration of rev-th recovery systems
y^{Toxic}, concentration of toxic material
Y, probit correlation

z_i^{waste}, flow rate of source i to waste
ψ, property operator

Parameters

a, stoichiometry coefficient
AT, annual working hours
b, stoichiometry coefficient
c, stoichiometry coefficient
$Cost_r^{Fresh}$, unit cost of rth fresh resources
$COST_{i,j}^{Piping}$, cost coefficient for piping between source i and sink j
$COST_{r,j}^{Piping}$, cost coefficient for piping between fresh r and sink j
$Cost_{rev}^{Recovery}$, unit cost of rev-th recovery systems
$Cost_{rev,u}^{Recovery}$, cost of recovery associated with the technology to recover component u
$Cost_{trt,q}^{Treatment}$, unit cost of waste treatment to treat qth property
$Cost_{Air}^{Treatment}$, unit cost of air aeration
d, stoichiometry coefficient
m, fractional interest rate per year
N_{Acid}, total number of acid streams
N_{Base}, total number of base streams
$N_{Components}$, total number of components
N_{Fresh}, total number of fresh resources
$N_{Properties}$, total number of properties
$N_{Recovery}$, total number of recovery systems
$N_{Sources}$, total number of sources
$p_{j,q}^{min}$, lower bound on acceptable property q by sink j
$p_{j,q}^{max}$, upper bound on acceptable property q by sink j
$p_q^{max\ env}$, upper limit of environmental discharge of property q
$p_q^{min\ env}$, lower limit of environmental discharge of property q
pH^{env}, environmental discharge limit of pH
RE, recovery efficiency
$ThOD^{env}$, environmental discharge limit of theoretical oxygen demand
$Toxicity^{env}$, environmental discharge limit of toxicity
yr, number of years
y_{Phenol}^{env}, environmental discharge limit of phenol
y_u^L, lower bound for inlet concentration of rev-th recovery systems
y_u^U, upper bound for inlet concentration of rev-th recovery systems
$y_{j,u}^{min}$, lower concentration limit of component u acceptable by sink j
$y_{j,u}^{max}$, upper concentration limit of component u acceptable by sink j
$y_{rev,u}^{min}$, minimum concentration of component u that is worth recovery

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