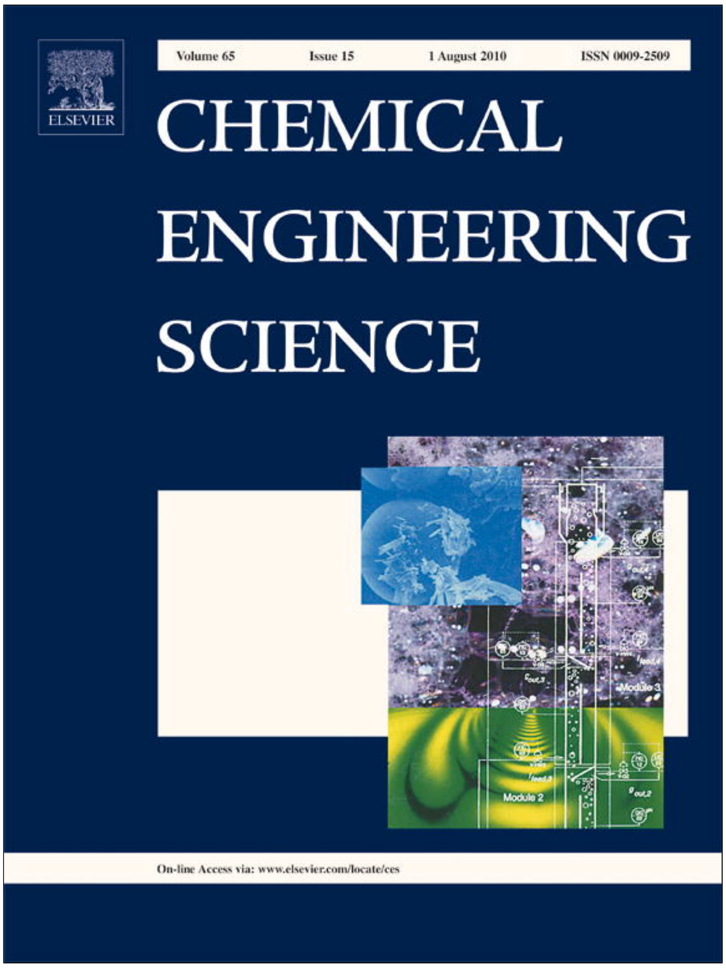
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Global optimization of mass and property integration networks with in-plant property interceptors

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A B S T R A C T

This paper presents a mathematical programming model for the optimal design of mass and property integration networks that include property interceptors within the structure of the network, as opposed to the end-of-pipe use of such interceptors. The model is based on a recycle and reuse scheme that simultaneously satisfies process and environmental constraints. The properties considered in this work are composition, toxicity, theoretical oxygen demand, pH, density and viscosity. The property mixing rules included in the model give rise to bilinear terms for the property operators, and a global optimization algorithm is used for the solution of the model. The model minimizes the total annual cost of the network, which includes the fresh sources cost and the annualized property treatment system and the piping costs. Three examples are included to show the applicability and advantages of the proposed model.

1. Introduction

During the last three decades, the exponential growth in population and industrialization has affected the massive use of natural resources to the point where their availability and their cost have become major challenges for sustainability. It is thus important to develop strategies to optimize the industrial use of natural resources. Also, environmental constraints have become tighter, which should affect the design of new processes or the modification of existing ones.

In this context, mass integration strategies have been effectively utilized to face both economic and environmental problems. Usually, mass integration strategies aim to optimize the allocation, transformation, and separation of species and streams. An important class of mass integration problems deals with the synthesis of networks that allow the recycle and reuse of process sources to minimize the consumption of fresh sources and waste discharges. The mass integration techniques for recycle/reuse can be classified into two categories (e.g., Pillai and Bandyopahyay, 2007; El-Halwagi, 2006), methodologies that use the principles of pinch analysis and methods based on mathematical programming techniques. For a recent survey on pinch analysis techniques see the review paper by Foo (2009).

Works based on mathematical programming techniques include the one by Takama et al. (1980), who addressed the water allocation problem in a petroleum refinery. This model considered all possible configurations between wastewater-treating units and water-using units in order to minimize both fresh water consumption and waste generation. The problem was treated with a two-level formulation in which only the upper level or allocation problem was solved. Quesada and Grossmann (1995) showed a model to obtain mass exchange networks when mass balances give rise to bilinear terms. To deal with the bilinear terms, they used a linear reformulation in order to obtain a valid lower bound to the optimal solution, and then applied a spatial branch and bound search to obtain the global optimum structure. Galan and Grossmann (1998) extended the model to include the selection of water treatment technologies. Lee and Grossmann (2003) developed a generalized disjunctive programming problem based on the model by Quesada and Grossmann (1995), taking as discrete choices the existence or not existence of process units. Karuppiah and Grossmann (2006) proposed a modification to the global optimization method by Quesada and Grossmann (1995) in order to improve the lower bounding step. They applied this new procedure for the synthesis of integrated water networks. Alva-Argaez et al. (1998) tackled the problem of waste

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water minimization by developing a superstructure that contained all the possibilities for water recycle, reuse and regeneration. The resulting model was a mixed integer nonlinear programming problem (MINLP) with bilinear terms. To avoid the complexities associated to the solution of the nonconvex MINLP, they decomposed it into a sequence of MILP problems to provide a near optimal solution. Huang et al. (1999) developed a superstructure for the water allocation problem, which was based on the one presented by Takama et al. (1980) but it contained new features such as the possibility to handle multiple sources and sinks. Additionally, it included the design of the treatment system so that the optimization process could not only minimize the amount of used water, but also the waste treatment capacity. Gabriel and El-Halwagi (2005) addressed the problem of the synthesis of mass exchange networks using a source-interception-sink representation with a simplified linear programming model. Ng et al. (2007a, 2007b) addressed the problem of maximum water recovery using a recycle/reuse scheme. Once the maximum water recovery policy has been accomplished, a regeneration system is used to meet environmental regulations over the load of contaminant. Lancu et al. (2009) tackled the problem of wastewater minimization for the multi-contaminant case through the regeneration of streams. They proposed the use of in-plant regeneration systems to reduce the amount of water sent to disposal. Hul et al. (2007), Tan et al. (2008), and Chakroborty (2009) have recently reported other works in this field.

It should be noted that many of the reported methods on the synthesis of recycle/reuse networks have ignored the fact that environmental and process constraints do not depend only on compositions and flows of the streams, but also on properties such as pH, density, viscosity, toxicity, color, and theoretical

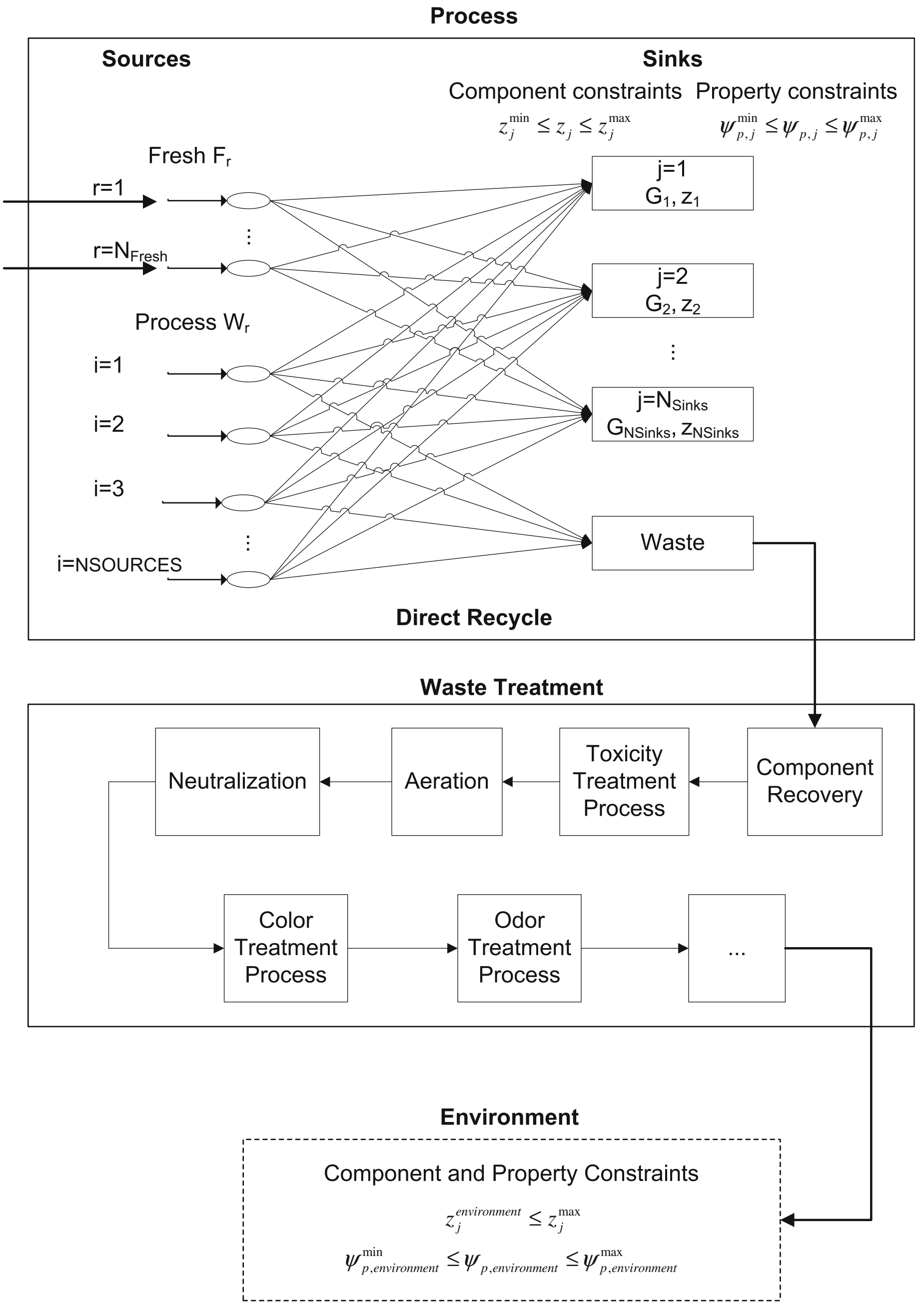

Fig. 1. Source–sink representation for mass and property integration including waste treatment.

oxygen demand. Shelley and El-Halwagi (2000) introduced the notion of clusters and used it as a basis for a component-less design method based on tracking functionalities and properties, rather than tracking their individual components. They also showed the possibility to apply this new concept in a way analogous to mass integration problems, as part of a framework that El-Halwagi et al. (2004) called property integration defined as a functionality-based holistic approach to the allocation and manipulation of streams and processing units, which is based on the tracking, adjustment, assignment, and matching of functionalities throughout the process. Property integration methodologies can be classified into graphical, algebraic, and optimization techniques. Graphical techniques are suitable when up to three properties are considered. Works showing such techniques have been developed by Shelley and El-Halwagi (2000), Eden et al. (2002), El-Halwagi et al. (2004), El-Halwagi and Kazantzi (2005), Kazantzi et al. (2007), and Eljack et al. (2008). When more than three properties are considered, algebraic and optimization-based tools are required (see for example the works by Qin et al., 2004; Grooms et al., 2005; Foo et al., 2006; Ng et al., 2008, 2009; Ponce-Ortega et al., 2009, 2010).

As a consequence of not including environmental constraints into the model formulation, the network that minimizes fresh water consumption or waste discharge minimization may be considered as an incomplete solution to the overall problem. It is possible that the additional waste treatment system needed to meet the environmental constraints can affect significantly the total cost of the complete network and yield a suboptimal solution. Ponce-Ortega et al. (2009) found that for a direct recycle scheme such as the one shown in Fig. 1, the simultaneous consideration of process and environmental constraints reduces the total annual cost of the network compared to a solution given by a sequential approach (i.e. the optimization of the mass exchange network followed by the final treatment of waste streams). Although the strategy proposed by Ponce-Ortega et al. (2009) considers a simultaneous approach, it assumes a centralized waste treatment plant, which implies that all the waste sources are collected and treated in a common facility. Galan and Grossmann (1998) found that the use of a distributed waste treatment system or recycle reuse network scheme (see Fig. 2) can reduce the flow rate to be processed in each treatment unit, therefore reducing the treatment unit cost. Ponce-Ortega et al. (2010) have recently proposed a simplified formulation for the recycle and reuse scheme; a conceptual model was used to avoid the mixing of streams, thus preventing the existence of bilinear products in the property balances around the mixing points. Their superstructure formulation can be seen in Fig. 3.

In this paper, a rigorous mathematical programming model is presented for the mass and property integration problem under a recycle and reuse configuration. Fig. 4 shows the model structure. The model includes an in-plant property treatment system as opposed to an end-of-pipe treatment facility, so that the waste is treated as part of the mass integration network. Both process and environmental constraints for properties such as toxicity, THOD, pH, viscosity and density are considered; mass and composition constraints are also included. The process sources can be segregated and sent to any treatment unit. It is assumed that only one property can be treated within each unit, and the outlet flow of each treatment unit can be sent either to the process units, waste or to treat a different property; the formulation prevents that a stream returns to the same unit or to a unit in which it has already been treated. The possibility to mix streams with unknown flows and properties gives rise to bilinear terms in the property balances as part of the MINLP problem.

2. Outline of the proposed model

The problem addressed in this paper consists of finding the optimal mass and property integration network under a recycle–reuse scheme that minimizes the total annual cost of the overall process while satisfying simultaneously process and environmental constraints. Such constraints are known prior to the optimization process. Also known are the process and fresh sources available, with given flow rates, compositions and properties. Additionally, the costs of piping and fresh sources, and the cost and efficiency of each available interceptor to treat the stream properties are known.

The sets used in the model formulation are defined as follows. *NSINKS* contains the sinks for the streams within the process, while *NSOURCES* and *FRESH* contain the process and fresh sources, and *NPROP* contains the properties constrained by process sinks or

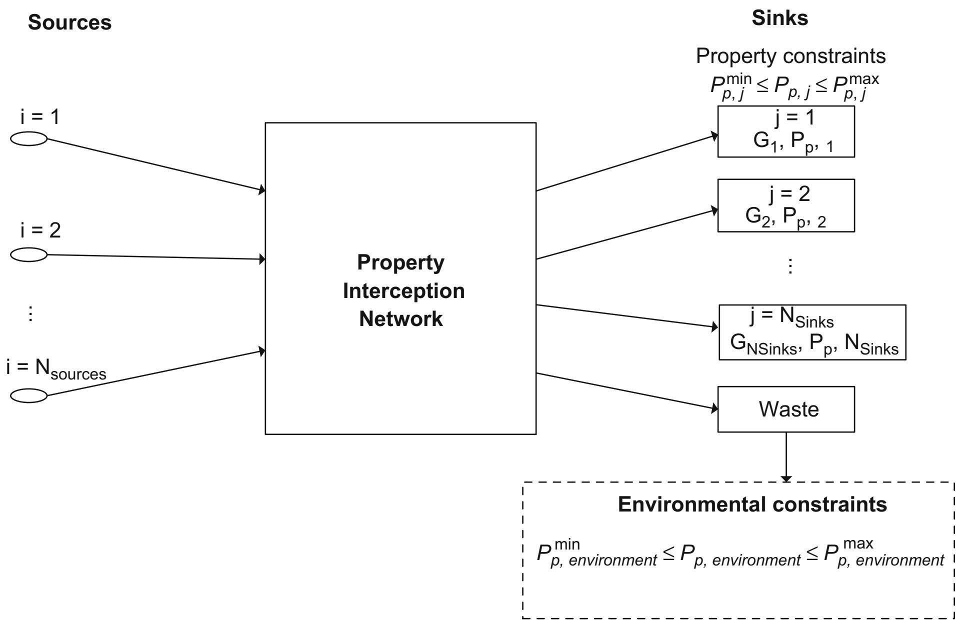

Fig. 2. Recycle and reuse network scheme.

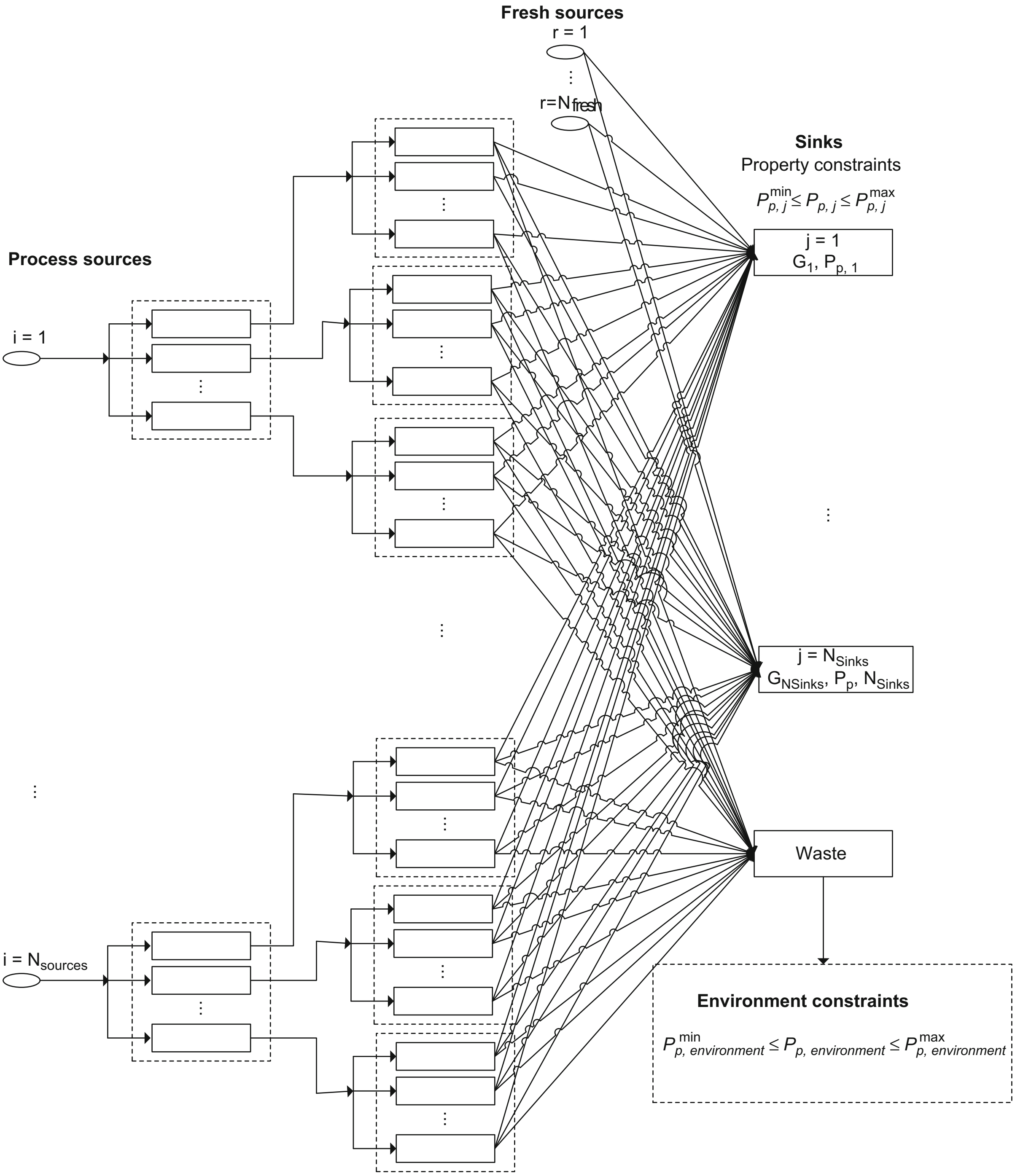

Fig. 3. Simplified formulation for the recycle and reuse mass and property integration.

by environmental regulations. *NUNINTS* accounts for all of the treatment units and *NINT* contains the available units to treat each property. The variables F_r, $f_{r,j}$, W_i, $w_{i,u}$, $d^1_{u,u}$, m_u, G_j and $g_{u,j}$ refer to the flow rates across the network (see Fig. 4). Property operators $\psi_p(P)$ are used; these operators are based on proper mixing rules for each property, as reported in Table 1. The properties considered in this paper are composition, toxicity, THOD, pH, density and viscosity. Properties are identified as follows. $P^{InSource}_{p,i}$ is the value for property p in source i, $P^{InUnit}_{p,u}$ and $P^{OutUnit}_{p,u}$ are the values at the inlet and at the outlet of treatment unit u, $P^{InFresh}_{p,r}$ is the value in fresh source r, and $P^{InSink}_{p,j}$ is the value for entering sink j. H_y is the operation time per year (taken here as 8000 h/yr), $Cost^{Fresh}_r$ is the cost per pound of fresh source r that is used. $Cost^{Unit}_u$ is the cost per pound treated in unit u. For piping costs, $pip^{In}_{i,u}$ is the cost from source i to unit u, pip^{Int}_{u,u^1} from unit u to unit u^1, $pip^{Exit}_{u,j}$ from unit u to sink j, and $pip^{InFresh}_{r,j}$ from fresh source r to sink j ($j \neq waste$). *TAC* is the total annual cost of the network.

3. Model formulation

The model is based on the configuration shown in Fig. 4, and consists of mass balances at mixing and splitting points of the

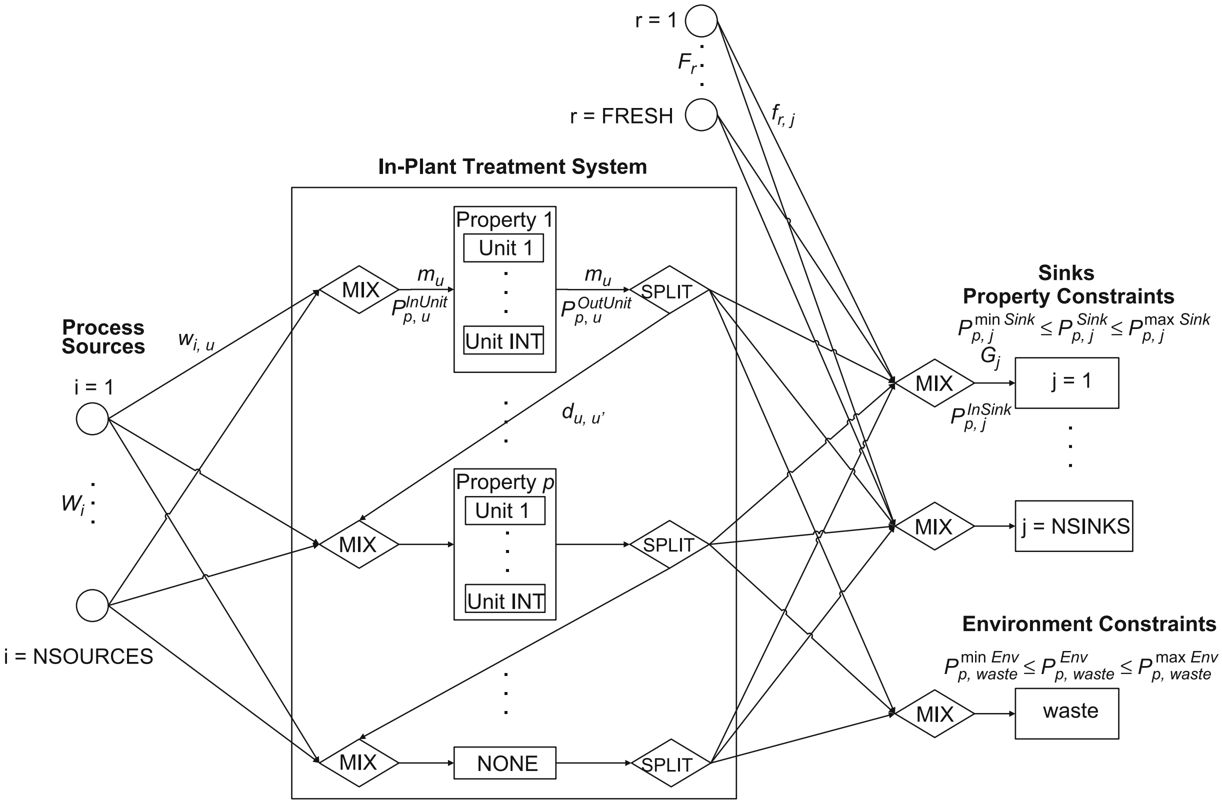

Fig. 4. Rigorous mass and property integration network: recycle and reuse scheme.

Table 1
Some mixing property operators.

Property	Operator
Composition	$\psi_z(z) = z$
Toxicity	$\psi_{Tox}(Tox) = Tox$
Chemical oxygen demand	$\psi_{COD}(COD) = COD$
pH	$\psi_{pH}(pH) = 10^{pH}$
Density	$\psi_\rho(\rho) = \frac{1}{\rho}$
Viscosity	$\psi_\mu(\mu) = \log(\mu)$
Reid vapor pressure	$\psi_{RVP}(RVP) = RVP^{1.44}$
Electric resistivity	$\psi_R(R) = \frac{1}{R}$
Paper reflectivity	$\psi_{R_\infty}(R_\infty) = R_\infty^{5.92}$
Color	$\psi_{Color}(Color) = Color$
Odor	$\psi_{Odor}(Odor) = Odor$

process, property balances in each mixing point, process and environmental constraints, and logic disjunctions to choose which interceptor should be used for each property adjustment that is needed. The disjunctions are reformulated using the convex hull formulation. The objective function is set as the minimization of the total annual cost of the network.

Splitting of fresh sources: Fresh sources can be sent to any sink to complement, if needed, the treatment capabilities of process sources to meet process constraints:

$$F_r = \sum_{\substack{j \in NSINKS \\ j \ne waste}} f_{r,j}, \quad r \in FRESH \tag{1}$$

Notice that the fresh sources cannot be sent to the waste.

Splitting of process sources: Process sources are segregated and sent to any of the treatment units to treat one property at a time:

$$W_i = \sum_{u \in NUNINTS} w_{i,u}, \quad i \in NSOURCES \tag{2}$$

Mass balance at the inlet of the property interceptors: A recycle and reuse strategy is used; hence, a mass balance in the mixing point prior to any interceptor indicates that the inlet flow should be equal to the flow sent from the process sources plus the flow coming from any other interceptor:

$$\sum_{i \in NSOURCE} w_{i,u} + \sum_{\substack{u^1 \in NUNITS \\ u^1 \ne u}} d_{u^1,u} = m_u, \quad u \in NUNITS \tag{3}$$

This scheme allows the treatment of more than one property for the process sources. The model has an additional restriction that avoids the possibility of a redundant recirculation, which means that a source cannot return to a treatment unit in which it has already been used.

Property tracking at the inlet of the property interceptors: To determine the properties at the inlet of any interceptor, the following property mixing rule is used:

$$\sum_{i \in NSOURCE} \left[w_{i,u} \psi_p \left(P_{p,i}^{InSource} \right) \right] + \sum_{\substack{u^1 \in NUNITS \\ u^1 \ne u}} \left[d_{u^1,u} \psi_p \left(P_{p,u^1}^{OutUnit} \right) \right]$$
$$= m_u \psi_p \left(P_{p,u}^{In\ Unit} \right), \quad u \in NUNITS, \ p \in NPROP \tag{4}$$

One must take into account that each property has a different mixing operator ψ_p. Table 1 presents a list of mixing property operators for some common properties. As can be seen in Eq. (4), the recycle and reuse configuration gives rise to bilinear terms, since both the mass recirculated and its properties are unknown. Also unknown are the total flow entering the interceptors and its property values.

Mass balances in the splitting point at the exit of the interceptors: The flow rate at the exit of any treatment unit is equal to the flow rate sent to the process sinks plus the flow rate sent to any other interceptor:

$$m_u = \sum_{j \in SINKS} g_{u,j} + \sum_{\substack{u^1 \in NUNITS \\ u^1 \neq u}} d_{u,u^1}, \quad u \in NUNITS \tag{5}$$

Mass balances at the mixing point before the sinks: The flow entering a process sink is equal to the sum of the flows coming from the interceptors plus the flow rate from fresh sources:

$$G_j = \sum_{r \in FRESH} f_{r,j} + \sum_{u \in NUNITS} g_{u,j}, \quad j \in NSINKS \tag{6}$$

Property tracking at the mixing point before the sinks: A property mixing rule is needed in tracking properties to determine the properties at the entrance of the process sinks. Notice that this balance also contains bilinear terms, given by the product of the flow coming from the treatment units and its property operator, and the product of the waste flow and its property operator:

$$G_j \psi_p \left(P_{p,j}^{InSink}\right) = \sum_{r \in FRESH} \left[\psi_p \left(P_{p,r}^{InFresh}\right) f_{r,j}\right] + \sum_{u \in NUNITS} \left[g_{u,j} \psi_p \left(P_{p,u}^{OutUnit}\right)\right],$$
$$j \in NSINKS, \; p \in NPROP \tag{7}$$

Constraints: A set of constraints for the process sinks and one for the waste discharged to the environment are needed; these constraints include maximum and minimum properties allowed because of process limits or environmental regulations.

For the process sinks:

$$P_{p,j}^{\min Sink} \le P_{p,j}^{inSink} \le P_{p,j}^{\max Sink}, \quad j \in NSINK, \; j \neq waste, \; P \in NPROP \tag{8}$$

For the waste discharged to the environment:

$$P_{p,j}^{\min Env} \le P_{p,waste} \le P_{p,j}^{\max Env}, \quad j = waste, \; P \in NPROP \tag{9}$$

Logic disjunctions: To treat each property, a set of interceptors with given efficiencies and unit costs is available. Each interceptor is associated with a certain extent of changing the value of the property. Therefore, as part of the optimization strategy, selection has to be made between a high efficiency—high cost unit, or a lower efficiency—lower cost unit; the best choice can vary for each problem. To model this decision, we use the following disjunction:

$$\underset{I(U) \in NINT}{\forall} \begin{bmatrix} Y_{I(U)}^{U(p)} \\ \psi_p \left(P_{p,U(p)}^{OutUnit}\right) = \psi_P \left(P_{p,U(p)}^{InUnit}\right)\left(1-\alpha_{I(U)}^{U(p)}\right) \\ Cost_{p,U(p)}^{unit} = Cost_{I(U)}^{U(p)} m_{U(p)} \end{bmatrix}$$

where $Y_{I(U)}^{U(p')}$ are logical variables, used to denote that the outlet property and the treatment cost depend on the unit selected; the property treated and the unit used for treatment are denoted as p' and $u(p')$, respectively, and the set of interceptors available to treat this property is given by $I(U)$. This disjunction implies that when the Boolean variable $Y_{I(U)}^{U(p')}$ is true (i.e., the associated binary variable $y_{I(U)}^{U(p')}$ is equal to 1) the unit with cost $Cost_{I(U)}^{U(p')}$ and efficiency $\alpha_{I(U)}^{U(p')}$ will be selected; notice that only one unit can be selected for each property, depending on the process requirements. If the unit is not selected, the Boolean variable $Y_{I(U)}^{U(p')}$ is false (i.e., the associated binary variable $y_{I(U)}^{U(p')}$ is equal to 0), in which case the property does not change and therefore no additional cost is included.

It should be stressed that only one property can be treated by each interceptor. Then, the property balance in each unit for the properties not treated is simply given by

$$\psi_{p'}\left(P_{p',U(p')}^{OutUnit}\right) = \psi_{p'}\left(P_{p',U(p')}^{InUnit}\right), \quad U(p') \in NUNITS, \; \forall p \neq p' \tag{10}$$

The disjunction is applied to all properties treated in the property interception network, and the number of interceptors to treat each property is known before the optimization process. All the terms in the disjunction are linear since the efficiency, $\alpha_{I(U)}^{U(p')}$, and unit cost, $Cost_{I(U)}^{U(p')}$, for the interceptors are given. The convex hull formulation (Raman and Grossmann, 1994) is used to model the disjunction as follows.

To select the unit to treat the property, the following equation is used:

$$\sum_{I(U)} y_{I(U)}^{U(p')} = 1, \quad U(p') \in NUNITS \tag{11}$$

Then, the optimization variables involved in the disjunction are disaggregated as follows:

$$\psi_{p'}\left(P_{p',U(p')}^{OutUnit}\right) = \sum_{I(U)} \psi_{p'}\left(p_{p',U(p')}^{OutUnit,I(U)}\right), \quad U(p') \in NUNITS \tag{12}$$

$$\psi_{p'}\left(P_{p',U(p')}^{InUnit}\right) = \sum_{I(U)} \psi_{p'}\left(p_{p',U(p')}^{InUnit,I(U)}\right), \quad U(p') \in NUNITS \tag{13}$$

$$m_{U(p')} = \sum_{I(U)} m_{U(p')}^{I(U)}, \quad U(p') \in NUNITS \tag{14}$$

$$Cost_{U(p')}^{unit} = \sum_{I(U)} Cost_{U(p')}^{unit,I(U)}, \quad U(p') \in NUNITS \tag{15}$$

The equations in the disjunction are rewritten in terms of the disaggregated variables:

$$\psi_{p'}\left(p_{p',U(p')}^{OutUnit,I(U)}\right) = \psi_{p'}\left(p_{p',U(p')}^{InUnit,I(U)}\right)\left(1-\alpha_{p',I(U)}^{U(p')}\right),$$
$$U(p') \in NUNITS, \; I(U) \in NINT \tag{16}$$

$$Cost_{U(p')}^{unit,I(U)} = Cost_{I(U)}^{U(p')} m_{U(p')}^{I(U)}, \quad U(p') \in NUNITS, \; I(U) \in NINT \tag{17}$$

Finally, upper limits for the disaggregated variables are needed:

$$\psi_{p'}\left(p_{p',U(p')}^{OutUnit,I(U)}\right) \le M^{\psi_{p'}} y_{I(U)}^{U(p')}, \quad U(p') \in NUNITS, \; I(U) \in NINT \tag{18}$$

$$\psi_{p'}\left(p_{p',U(p')}^{InUnit,I(U)}\right) \le M^{\psi_{p'}} y_{I(U)}^{U(p')}, \quad U(p') \in NUNITS, \; I(U) \in NINT \tag{19}$$

$$m_{U(p')}^{I(U)} \le M^m y_{I(U)}^{U(p')}, \quad U(p') \in NUNITS, \; I(U) \in NINT \tag{20}$$

$$Cost_{U(p')}^{Unit,I(U)} \le M^{Cost} y_{I(U)}^{U(p')}, \quad U(p') \in NUNITS, \; I(U) \in NINT \tag{21}$$

Table 2
Efficiency and unit cost per pound of total flow treated for each treatment unit.

Property	Interceptor	Efficiency, α	Unit cost (\$/lb)
Component	REC^1	0.98	0.0065
	REC^2	0.85	0.0033
Toxicity	TOX^1	1.00	0.0098
	TOX^2	0.90	0.0075
THOD	AER^1	0.80	0.0065
	AER^2	0.55	0.0032
pH	PH^1	0.99	0.0063
	PH^2	0.9	0.0032
	POH^1	−99	0.0065
	POH^2	−9	0.0034
None	NONE	0	0

These limits can be set from physical restrictions or from available process data.

It is important to stress that an additional unit with efficiency and cost equal to zero has been included. This fictitious unit is used for modeling purposes (represented as unit NONE in Fig. 4), and its only task is the mixing of streams.

The assumption that only one property can be treated within each unit implies that the rest of the properties in that unit

Table 3
Process (W) and fresh (F) sources characteristics for each example.

Stream	Flow rate (lb/h)	Composition (ppm)	Toxicity (%)	THOD (mg O_2/l)	*pH*	Density (lb/l)	Viscosity (cP)
Example 1							
W1	2900	0.033	0.8	75	5.3	2.000	1.256
W2	2450	0.022	0.5	88	5.1	2.208	1.220
F1	–	0	0	0	7.0	2.204	1.002
Example 2							
W1	8083	0.016	0.3	0.187	6.4	2.000	1.256
W2	3900	0.024	0.5	48.85	5.1	2.208	1.220
W3	3279	0.22	1.5	92.10	4.8	2.305	1.261
F1	–	0	0	0	7.0	2.204	1.002
F2	–	0.01	0.1	0.01	6.8	2.209	0.992
Example 3							
W1	3100	0.16	0.4	95	4.4	2.100	1.236
W2	1800	0.1	0.7	85	3.9	2.208	1.220
W3	1750	0.11	1.3	90	4.7	2.305	1.241
W4	2000	0.12	0.8	100	4.7	2.105	1.256
W5	1300	0.09	0.4	100	3.8	2.305	1.260
W6	1400	0.2	1.5	100	5.7	2.102	1.259
F1	–	0	0	0	7.0	2.204	1.002
F2	–	0.01	0.1	0.00	6.8	2.209	0.992
F3	–	0.09	0.5	0.00	7.1	2.215	0.988

Table 4
Process and environmental constraints for each example.

Sink	Flow rate (lb/h)	Composition (ppm)	Toxicity (%)	THOD (mg O2/l)	*pH*	Density (lb/l)	Viscosity (cP)
Example 1							
Maximum							
1	3000	0.013	2	75	8.0	2.8	1.202
2	1900	0.011	2	75	7.9	2.5	1.430
Waste	–	0.005	0	75	9.0	3.0	2.000
Minimum							
1	3000	0	0	0	5.9	1.8	0.871
2	1900	0	0	0	5.7	1.7	0.782
Waste	–	0	0	0	5.8	1.0	1.000
Example 2							
Maximum							
1	6000	0.013	2	75	8.0	2.8	1.202
2	2490	0.011	2	100	7.8	2.5	1.430
3	3287	0.1	2	100	8.2	2.9	1.260
Waste	–	0.005	0	75	9.0	3	2
Minimum							
1	6000	0	0	0	5.3	1.8	0.871
2	2490	0	0	0	5.4	1.7	0.782
3	3287	0	0	0	5.2	1.85	0.775
Waste	–	0	0	0	5.5	1.0	1.000
Example 3							
Maximum							
1	1900	0.1	2	100	8.0	2.8	1.292
2	1600	0.01	2	100	7.9	2.5	1.280
3	2800	0.04	2	100	8.1	2.9	1.270
4	2000	0.02	2	100	8.0	2.8	1.291
5	1800	0.01	2	100	8.0	2.7	1.281
6	1000	0.01	2	100	8.0	2.7	1.281
Waste	–	0.005	0	50	8.0	2.7	1.290
Minimum							
1	1900	0	0	0	5.8	1.8	0.871
2	1600	0	0	0	5.5	1.7	0.782
3	2800	0	0	0	5.4	1.85	0.775
4	2000	0	0	0	5.5	1.75	0.84
5	1800	0	0	0	5.5	1.85	0.85
6	1000	0	0	0	5.5	1.85	0.85
Waste	–	0	0	0	5.4	1.00	1.00

remain unchanged, as shown in Eq. (10). Nevertheless, the model could be easily adapted to consider treatment units capable of treating more than one property at a time; in that case, the efficiency parameter for each property would be known prior to the optimization process. If more than one property could be treated in the same unit, the disjunction here developed and its reformulation would still be valid, such that p would be the set of properties that change and p' the set of properties that would not change within the unit. This type of information would have to come from experimental data, and would be part of the design data prior to the model development.

Objective function: The objective function consists of the minimization of the total annual cost, which includes the cost for the fresh sources, the cost for the interceptors to treat the process sources, and piping costs:

$$\begin{aligned}\text{Min}\, TAC = {} & H_Y \sum_{r \in FRESH} Cost_r^{Fresh} F_r + H_Y \sum_{u \in NUNITS} Cost_u^{Unit} \\ & + H_Y \sum_{u \in NUNITS} \sum_{i \in NSOURCES} (pip_{i,u}^{In} w_{i,u}) \\ & + H_Y \sum_{u \in NUNITS} \sum_{u^1 \in NUNITS} \left(pip_{u,u^1}^{Int} d_{u,u^1}\right) \\ & + H_Y \sum_{u \in NUNITS} \sum_{j \in NSINKS} \left(pip_{u,j}^{Exit} g_{u,j}\right) \\ & + H_Y \sum_{r \in NFRESH} \sum_{j \in NSINKS} \left(pip_{r,j}^{InFresh} f_{r,j}\right) \end{aligned} \tag{22}$$

Reformulation and linearization (*Relaxed Model*): The existence of bilinear terms makes this model a nonconvex MINLP problem; to find the best possible solution, we use a deterministic global optimization technique similar to the one proposed by Quesada and Grossmann (1995) and improved by Karuppiah and Grossmann (2006).

First, a linear programming relaxation of the nonlinear model is constructed by replacing every nonconvex term (bilinear term) by a new variable; in this case

$$x_p^i = F^i \psi_p^i \tag{23}$$

where the bilinear term is the product of the flow rate F^i and the property operator ψ_p^i. Then, bounds are established over the variables of the bilinear terms:

$$F_L^i \le F^i \le F_U^i \tag{24}$$

$$\psi_{p,L}^i \le \psi_p^i \le \psi_{p,U}^i \tag{25}$$

Using these limits, one can write the following linear constraints:

$$x_p^i \ge F_L^i \psi_p^i + \psi_{p,L}^i F^i - F_L^i \psi_{p,L}^i \tag{26}$$

$$x_p^i \ge F_U^i \psi_p^i + \psi_{p,U}^i F^i - F_U^i \psi_{p,U}^i \tag{27}$$

$$x_p^i \le F_L^i \psi_p^i + \psi_{p,U}^i F^i - F_L^i \psi_{p,U}^i \tag{28}$$

$$x_p^i \le F_U^i \psi_p^i + \psi_{p,L}^i F^i - F_U^i \psi_{p,L}^i \tag{29}$$

Eqs. (26)–(29) correspond to the convex and concave envelopes of the bilinear terms over the given bounds (Sherali and Alameddine, 1992). In order to tighten the bounds from the LP relaxation, and thus reduce the number of iterations of the branch and bound procedure, one can partition the original domain $D_i = [F_L^i, F_U^i]$ of each flow F^i into an arbitrary number of intervals $(D_1^i, D_2^i, \ldots, D_N^i)$ using the points $F_L^i = F_1^i, F_2^i, \ldots, F_{N+1}^i = F_U^i$ with piecewise linear under estimators for the bilinear terms over each partition. The partition of the domain and the construction

Table 5
Flow rates obtained in the root node of the optimization algorithm.

Variable	Rigorous model flow (lb/h)	Relaxed model flow (lb/h)	Difference
F_1	358.7	0	358.7
$f_{1.1}$	358.7	0	358.7
$w_{1.COMP}$	2648.6	2000	648.6
$w_{1.TOX}$	112.7	0	112.7
$w_{1.THOD}$	138.6	0	138.6
$w_{1.PH}$	0	358.8	358.8
$w_{1.NONE}$	0	541.17	541.17
$w_{2.THOD}$	70.997	871.3	800.3
$w_{2.PH}$	0	119.86	119.86
$W_{2.NONE}$	2379	1458.8	920.17
$d_{COMP.TOX}$	727.64	0	727.64
$d_{TOX.POH}$	49.306	0	49.306
m_{COMP}	2648.60	2000	648.60
m_{TOX}	840.4	0	840.4
m_{THOD}	209.6	871.307	661.7
m_{PH}	0	478.6	478.6
m_{POH}	49.306	0	49.306
m_{NONE}	2379	2000	379
$g_{COMP.1}$	895.33	1000	104.66
$g_{COMP.2}$	1025.6	1000	25.62
$g_{TOX\cdot 3}$	791.12	0	791.12
$g_{THOD.1}$	0	694.08	694.08
$g_{THOD.2}$	209.60	0.753	208.84
$g_{THOD.3}$	0	176.47	176.47
$g_{PH\cdot 1}$	0	305.91	305.91
$g_{PH\cdot 2}$	0	172.77	172.77
$g_{POH.2}$	31.641	0	31.641
$g_{POH.3}$	17.665	0	17.665
$g_{NONE.1}$	1745.86	1000	745.86
$g_{NONE.2}$	633.13	726.47	93.33
$g_{NONE.3}$	0	273.52	273.52
$G_{S.1}$	3000	3000	0
$G_{S.2}$	1900	1900	0
G_{waste}	808.79	450	358.79

Table 6
Flows for Example 1.

Stream	Flow (lb/h)
F_1	513.5
$f_{1.1}$	377.6
$f_{1.2}$	135.8
$w_{1.COMP}$	2900
$w_{2.COMP}$	189.1
$w_{2.TOX}$	8.485
$w_{2.NONE}$	2252.3
$d_{COMP.TOX}$	955.0
$d_{COMP.NONE}$	126.6
$d_{TOX.THOD}$	20.85
$d_{TOX.POH}$	1.001
$d_{THOD.POH}$	20.85
m_{COMP}	3089.1
M_{TOX}	963.5
m_{THOD}	20.85
m_{POH}	21.85
m_{NONE}	2379
$g_{COMP.1}$	1003.6
$g_{COMP.2}$	1003.8
$g_{TOX.3}$	941.6
$g_{POH.3}$	21.85
$g_{NONE.1}$	1618.7
$g_{NONE.2}$	760.3
G_{S1}	3000
G_{S2}	1900
G_{waste}	963.51

of the piecewise estimators can be set using the following disjunctions:

$$\bigvee_{n=1\ldots N}\left[\begin{array}{c}\lambda_n^i\\ x_p^i \ge F^i\psi_{p,L}^i + F_n^i\psi_p^i - F_n^i\psi_{p,L}^i\\ x_p^i \ge F^i\psi_{p,U}^i + F_{n+1}^i\psi_p^i - F_{n+1}^i\psi_{p,U}^i\\ x_p^i \le F^i\psi_{p,L}^i + F_{n+1}^i\psi_p^i - F_{n+1}^i\psi_{p,L}^i\\ x_p^i \le F^i\psi_{p,U}^i + F_n^i\psi_p^i - F_n^i\psi_{p,U}^i\\ F_n^i \le F^i \le F_{n+1}^i\\ \psi_{p,L}^i \le \psi_p^i \le \psi_{p,U}^i\end{array}\right]$$

where λ_n^i is a logical variable; when it is true the constraints in the nth disjunction are enforced, and the rest of the constraints are neglected. The convex hull reformulation for this set of disjunctions is as follows (Karuppiah and Grossmann, 2006):

$$\sum_n \lambda_n^i = 1 \tag{30}$$

$$F^i = \sum_n \pi_n^i \tag{31}$$

$$\psi_p^i = \sum_n \chi_{p,n}^i \tag{32}$$

$$x_p^i \ge \sum_n \left(\pi_n^i\psi_{p,L}^i + F_n^i\chi_{p,n}^i - F_n^i\psi_{p,L}^i\lambda_n^i\right) \tag{33}$$

$$x_p^i \ge \sum_n \left(\pi_n^i\psi_{p,U}^i + F_{n+1}^i\chi_{p,n}^i - F_{n+1}^i\psi_{p,U}^i\lambda_n^i\right) \tag{34}$$

$$x_p^i \le \sum_n \left(\pi_n^i\psi_{p,L}^i + F_{n+1}^i\chi_{p,n}^i - F_{n+1}^i\psi_{p,L}^i\lambda_n^i\right) \tag{35}$$

$$x_p^i \le \sum_n \left(\pi_n^i\psi_{p,U}^i + F_n^i\chi_{p,n}^i - F_n^i\psi_{p,U}^i\lambda_n^i\right) \tag{36}$$

$$F_n^i\lambda_n^i \le \pi_n^i \le F_{n+1}^i\lambda_n^i \tag{37}$$

$$\psi_{p,L}^i\lambda_n^i \le \chi_{p,n}^i \le \psi_{p,U}^i\lambda_n^i \tag{38}$$

The partition is done only on the flow rates and not on the properties, in order to avoid a significant increase in the number of variables (both continuous and binary.) This is a key advantage that enables the computational algorithm to be efficient regardless of the number of targeted properties. As noticed by Karuppiah and Grossmann (2006), when the number of partitions increases, there is a trade-off between the computational effort and the relaxation tightness. The resulting model, which involves Eqs. (1)–(38), is a relaxed mixed integer linear programming (MILP) problem.

Global optimization algorithm: The steps of the global optimization algorithm are as follows (Quesada and Grossmann, 1995; Karuppiah and Grossmann, 2006):

- *Step* 1. *Preprocessing*: Determine the bounds for the variables by physical inspection or data given by the problem. Solve the original non-convex MINLP to obtain an initial overall upper bound (OUB) on the objective function. Any feasible solution (e.g., a local minimum solution obtained via a local optimization solver) provides a valid upper bound.
- *Step* 2. *Lower bounding*: Solve the relaxed MILP over a given subregion (the initial subregion is the entire feasible region) to obtain a valid lower bound. If the relaxed problem is infeasible or greater than the current OUB, discard that region.
- *Step* 3. Compare the upper and lower bounds. If tolerance is not achieved, select a branching variable. In this case, use only flow rates as branching variables. Although the bound contraction can be performed on the property operators, such strategy it is not implemented because of the large number of operators

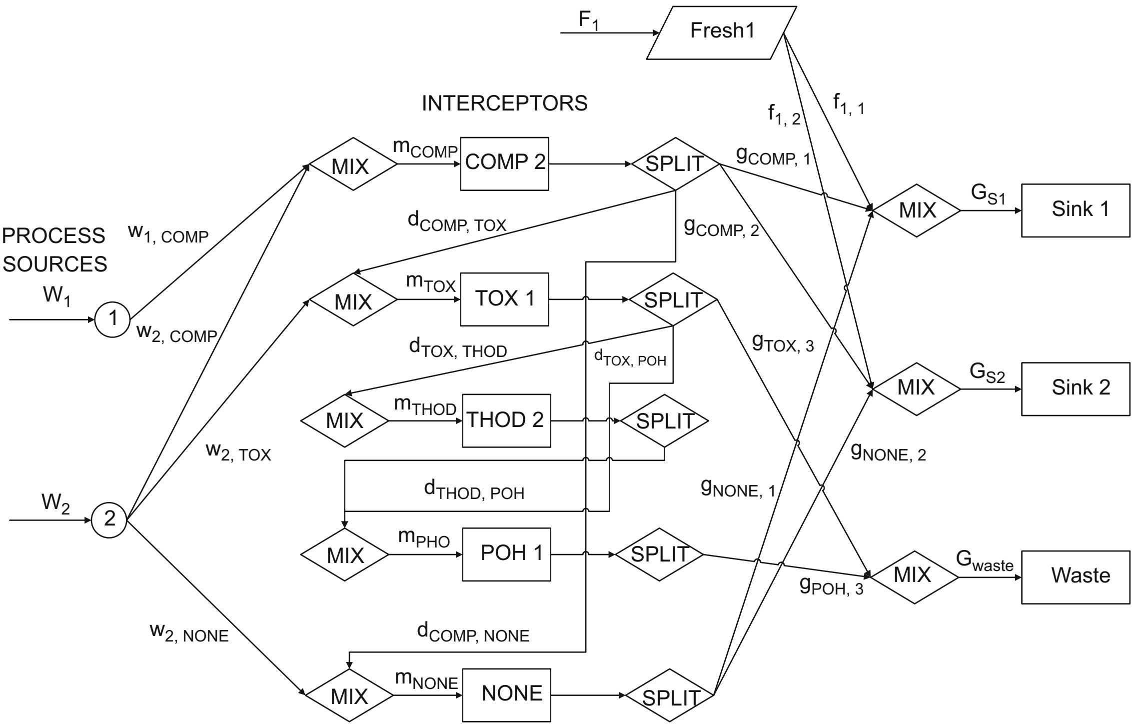

Fig. 5. Optimal solution for Example 1.

Table 7
Properties of the streams entering the sinks for the solutions to the examples.

Sink	Comp. (ppm)	Toxicity (%)	THOD (mg O_2/l)	*pH*	Density (lb/l)	Viscosity (cP)
Example 1						
1	0.013	0.539	72.489	6.144	2.132	1.202
2	0.011	0.619	75	5.939	2.095	1.221
Waste	0.005	0	75	5.8	2.013	1.253
Example 2						
1	0.013	0.479	23.286	6.359	2.114	1.202
2	0.011	0.689	39.377	6.065	2.135	1.247
3	0.018	0.34	9.879	6.309	2.038	1.249
Waste	0.005	0	63.529	5.677	2.22	1.247
Example 3						
1	0.097	0.644	86.683	5.8	2.252	1.224
2	0.01	0.837	94.417	5.5	2.143	1.241
3	0.04	0.773	93.013	5.4	2.18	1.239
4	0.02	0.815	93.791	5.5	2.155	1.24
5	0.01	0.837	94.417	5.5	2.143	1.241
6	0.01	0.837	94.417	5.5	2.143	1.241
Waste	0.005	0	50	5.4	2.136	1.245

involved with each stream, which would significantly increase the computational time to solve the problem.

- *Step* 4. Solve the MINLP, and update OUB if there is an improvement.
- *Step* 5. Repeat steps 2–4 for any active subregion until the upper and lower bounds are less or equal to a given tolerance. If the tolerance is reached or there are no subregions left, the global solution corresponds to the best upper bound.

It is also important to state that the branching variable (flow rate) is selected according to the following rules:

(1) Choose the flow rate that produces the highest difference between the MINLP and MILP problems.
(2) If no further improvement is achieved with the previous rule, or if the same variable occurs, select the flow rate that produces the second highest difference, and so on.

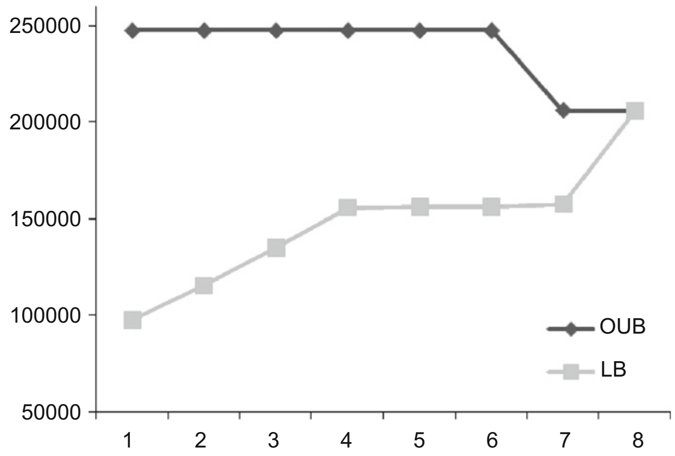

Fig. 6. Evolution of the global optimization algorithm for Example 1.

4. Case studies

Three examples were solved to show the application of the proposed methodology. An operation time of 8000 h/yr was considered for all of the examples. The properties assumed to be treated were composition, toxicity, THOD, and *pH*; the efficiency and cost of each available treatment units are given in Table 2.

Example 1. A motivational example is first considered with two process sources, two process sinks and one fresh source. Table 3 presents the characteristics of the process and fresh sources, and Table 4 gives the process and environmental constraints for this problem. The fresh source cost is $0.009/lb.

The solution in the root node for the MINLP yields an objective function value of $247,524/yr, which corresponds to the overall upper bound (OUB). The solution for the relaxed model gives an objective function of $97,489/yr. The objective now is to reduce the gap between both solutions by decreasing the objective function value of the MINLP problem and by increasing the objective function value of the relaxed (MILP) problem. To accomplish this task, different branching variables can be selected; as mentioned above, only flow rates are used here as branching variables because of the large number of partitions that property operators would require. From the results of the root node, the first branching variable was taken as the flow rate from the process source w_2 to the NONE (or fictitious) unit because this variable gave the highest difference in flow rate values from all the streams in the network (see Table 5). The domain is partitioned into two subregions, the first one corresponding to the interval $0 \leq w_{W2,NONE} \leq 2379.003$ lb/h, and the second one to the remaining interval of $2379.003 \leq w_{W2,NONE} \leq 2450$ lb/h. For the first subregion the total annual cost for the MINLP turned out to be $247,524/yr, whereas for the MILP problem the value was $97,321/yr. For the second subregion both problems are infeasible. As can be seen no improvement in the solution could be achieved by using $w_{W2,NONE}$ as branching variable, so the total flow rate entering the toxicity treatment unit (m_{TOX}) was selected as the new branching variable because it yields the second highest difference in flow rate values (see Table 5). For this new branching variable it was found that the solutions for the subregion $840.435 \leq m_{TOX} \leq 5450$ lb/h yielded total annual costs of $276,461/yr and $115,510/yr for the rigorous and relaxed model, respectively, while the analysis for the complementary subregion $0 \leq m_{TOX} \leq 840.435$ lb/h did not provide any improvement of the solutions. From this procedure, the OUB is kept as $247,524/yr because it is the best value up to this point, and the lower bound is updated to the best relaxed solution, which is $115,510/yr.

These steps were repeated until the best possible solution for the MINLP was detected, which had an objective function value of $205,908/yr, while that for the MILP was $205,884/yr; the gap between these solutions is 0.012%, and the optimal network is shown in Fig. 5; the flows for the optimal solution are given in

Table 8
Comparison between simultaneous, sequential, direct recycle and simplified recycle/reuse approaches for Example 1.

Concept	Optimal solution (simultaneous approach)	Sequential approach	Direct recycle	Simplified recycle/reuse
F_1 (lb/h)	513.5	515.3	2,268	268.16
Waste (lb/h)	963.5	965.3	2,718	718.16
Fresh sources cost ($/yr)	36,973	37,108	163,309	19,308
Treatment units cost ($/yr)	158,764	72,611	–	150,180
Piping cost ($/yr)	10,170	9,939	7,517	24,652
Network cost ($/yr)	205,908	119,660	170,826	194,140
Waste treatment system ($/yr)	–	152,146	358,800	–
Total annual cost ($/yr)	205,908	271,806	529,626	194,140

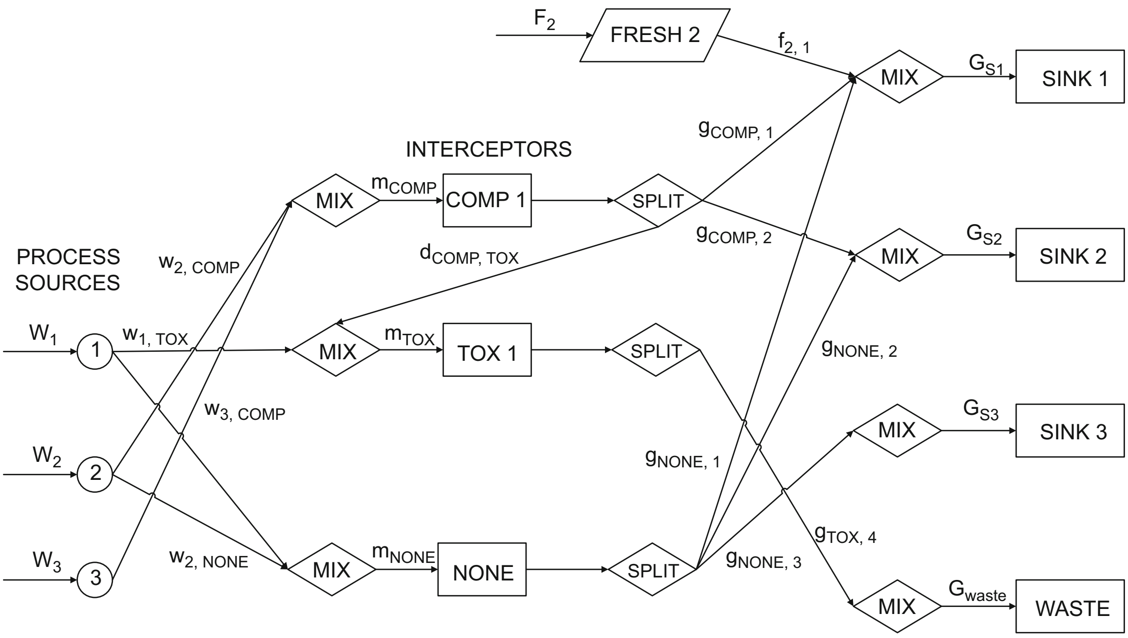

Fig. 7. Optimal solution for Example 2.

Table 9
Flows for Example 2.

Stream	Flow (lb/h)
F_2	977.5
$f_{2.1}$	977.5
$w_{1.TOX}$	536.04
$w_{1.NONE}$	7546.9
$w_{2.COMP}$	2023.0
$w_{2.NONE}$	1876.9
$w_{3.COMP}$	3279
$d_{COMP.TOX}$	2813.5
m_{COMP}	5302.0
m_{TOX}	3349.5
m_{NONE}	9,423.8
$g_{COMP.1}$	1370.8
$g_{COMP.2}$	1117.6
$g_{TOX.4}$	3349.5
$g_{NONE.1}$	3651.5
$g_{NONE.2}$	1372.3
$g_{NONE.3}$	4400
G_{S1}	6000
G_{S2}	2490
G_{S3}	4400
G_{waste}	3349.5

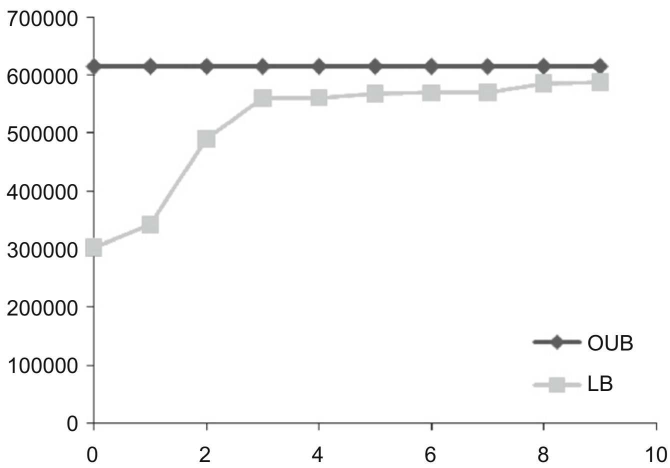

Fig. 8. Evolution of the global optimization algorithm for Example 2.

Table 6. As can be seen in Table 7, the sets of process and environmental constraints are both satisfied; notice that environmental restrictions are near their upper or lower bounds. Fig. 6 shows the evolution of the global optimization algorithm. We found that six intervals or partitions of the original flows domain (given by the difference between their original upper and lower bounds) yielded good results. In this example all of the treatment units were used. To treat composition and THOD the cheapest and least efficient units were selected, but for

toxicity and acidity the most efficient units were needed in order to satisfy the environmental constraints. The same problem was solved in a sequential manner, running first the model without environmental constraints, and then using property treatment systems as needed to meet such constraints. The total annual cost of the process network optimized under the first part of this sequential solution was \$119,660/yr; the waste obtained under this scenario did not satisfy the environmental constraints for the following properties: composition (0.013 ppm), toxicity (0.671%), THOD (80.578 mg O_2/lt), and *pH* (5.225). The cost to treat these properties to meet the environmental constraints turned out to be \$152,147/yr, which yielded a total annual cost of \$271,807/yr. This value is 32% higher than that obtained using the simultaneous approach proposed in this work.

Table 10
Comparison between simultaneous and sequential approaches for Example 2.

Concept	Optimal solution (simultaneous approach)	Sequential approach
F_2 (lb/h)	977.5	879.8
Waste (lb/h)	3349.5	3251.8
Fresh sources cost (\$/yr)	46,924	42,232
Treatment units cost (\$/yr)	538,316	155,504
Piping cost (\$/yr)	29,297	28482
Network cost (\$/yr)	614,538	226,219
Waste treatment system (\$/yr)	–	424,039
Total annual cost (\$/yr)	614,538	65,258

This problem was also solved using the methodologies proposed by Ponce-Ortega et al. (2009, 2010) in order to compare the results with a direct recycle approach and a simplified recycle/reuse approach. The solutions here presented illustrate the expected trends due to the typical behavior of each model. The direct recycle strategy had to be adjusted to obtain a comparable result, with the main modification consisting in the addition of restrictions over the properties in the process sinks since Ponce-Ortega et al. (2009) only considered constraints over the properties in the waste discharged to the environment. This modification yielded a solution with significantly higher fresh water consumption needed to satisfy process constraints, in addition to the increase in the cost of the treatment units because of the amount of waste generated. The total annual cost for the direct recycle strategy was \$529,626/yr, with a fresh water consumption of 2268 lb/h. This solution uses 342% more fresh water than the proposed methodology because the direct recycle strategy does not consider the regeneration of process streams. The simplified recycle and reuse strategy reported by Ponce-Ortega et al. (2010) yields a total annual cost by \$194,140/yr. However, it should be noted that this conceptual approach requires six treatment units, as compared to four for the solution obtained here. The reason is that in Ponce-Ortega et al. (2010) the structure of the property interceptor network is such that streams from process sources are segregated and each branch is treated for one property without recycle, such that each output goes to the process sinks or to the waste stream. As a consequence a high number of units will be promoted as part of the network structure in exchange for a more manageable model that avoids most of the bilinear terms of the one presented in this work. Table 8 lists the relevant results from these methodologies.

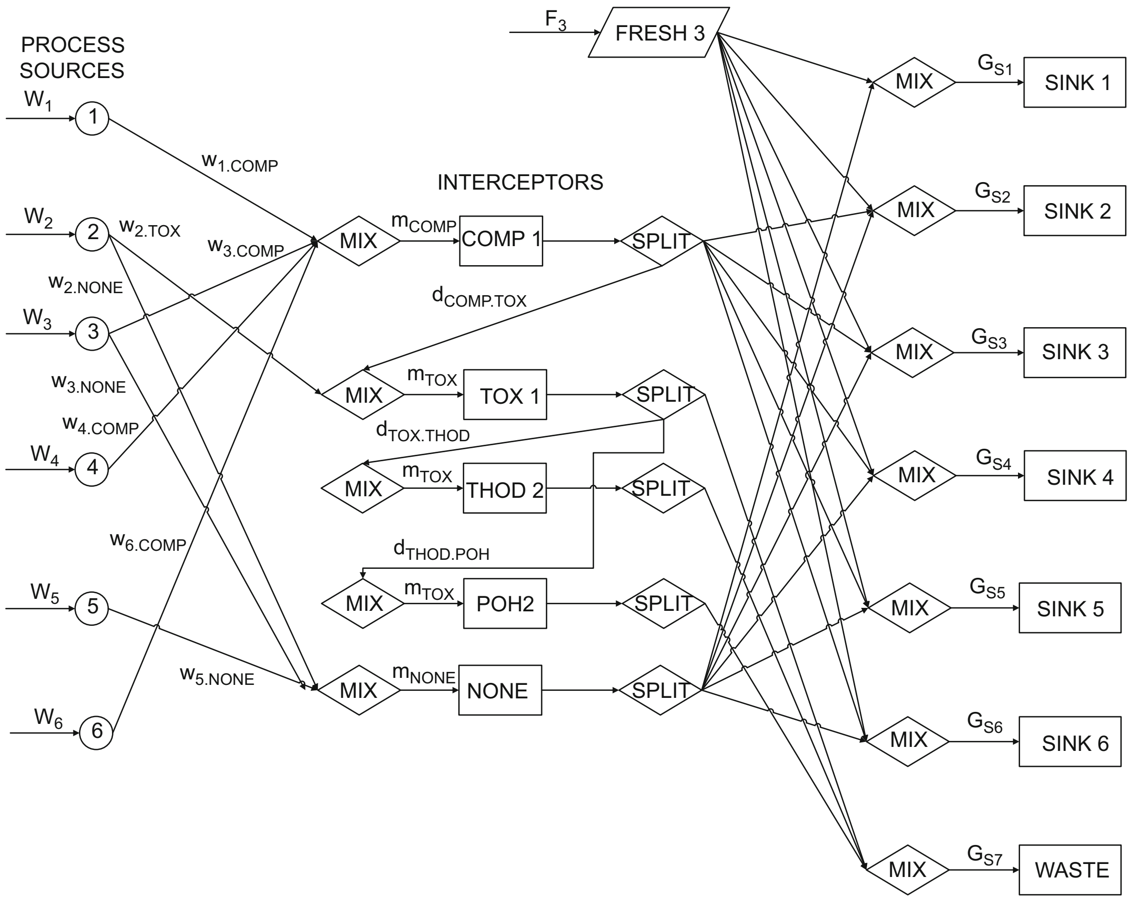

Fig. 9. Optimal solution for Example 3.

Example 2. In this example we consider the integration problem with three process sources and three process units; two fresh sources are available with unit costs of \$0.009/lb and \$0.006/lb. Table 3 presents the characteristics for the process and fresh sources, whereas Table 4 gives the process and environmental constraints that must be satisfied.

After exhausting every open node, the optimal solution was found with a minimum gap between MINLP and relaxed solutions of 4.4%. The total annual cost of the best network was \$614,539/yr, with the configuration shown in Fig. 7 and the flow structure given in Table 9. Table 7 reports the sink and waste properties obtained for this solution. In this case, only two treatment units, one for component recovery and the other one for toxicity, were needed to meet the environmental constraints; both units were the ones with maximum efficiency. Process sources 2 and 3 are mixed to be treated for composition. Process source 1 is split, a fraction of this source is treated for toxicity and the rest is mixed with a fraction of process source 2. The mixture of process sources 1 and 2 is sent directly to the process sinks without being treated by the property interceptors. As far as the fresh sources, only source 2 (the cheapest choice) was used. The evolution of the objective function values for the MINLP and the relaxed models for each of the 10 iterations needed to solve this problem can be observed in Fig. 8. In this example, 12 partitions of the domain were used. Table 10 compares the result from the solution obtained with the proposed method to the solution obtained with a sequential approach similar to the one used in Example 1. It can be seen how in this case the sequential solution yields a final network with a total annual cost 5.8% higher than the simultaneous solution.

Example 3. This example contains six process sources, six sinks and three fresh sources. Process and fresh sources data are given in Table 3. Table 4 presents the sinks and waste constraints. The cost of the fresh sources 1, 2 and 3 are \$0.008/lb, \$0.006/lb and \$0.003/lb, respectively.

The initial solution for the root node was obtained, and after visiting each open node it was found that no improvement to the initial solution could be detected. The optimal solution therefore corresponds to one of the root node, with a total annual cost of \$487,746/yr and a minimum gap between MINLP and relaxed solutions of 6.52%. The optimal network is shown in Fig. 9, and the flow rate distribution for the integrated process is given in Table 11. All the constraints are satisfied (see Table 7), and as in the previous examples the properties were near their maximum or minimum values. The network structure shows a noticeable use of the property interceptors. Process sources 1, 3, 4 and 6 are treated for composition; 477 lb/h of the output from the composition interceptor (equivalent to 6% of the total output) is mixed with 10 lb/h of process source 2 and treated for toxicity; from the output of the toxicity interceptor, 425 lb/h are sent for THOD treatment, and 61 lb/h for POH treatment. The total amount of process source 5 (1300 lb/h) together with some splits of process sources 2 and 3 bypass the use of the property interceptors and go directly to the process sinks. A sequential solution was also implemented for this case, and, as indicated in Table 12, the solution using the sequential approach gave an initial network with an annual cost 29% lower than the simultaneous approach, but when the final treatment system was added to the sequential solution for a complete network that meets the environmental constraints, the network cost increased to \$751,147/yr, or 54% higher than the simultaneous approach. For the sequential approach it can also be seen that the fresh water consumption was higher than in the network obtained with the simultaneous model. For the solution with

Table 11
Flows for Example 3.

Stream	Flow (lb/h)
F_3	237.79
$f_{3.1}$	93.52
$f_{3.2}$	25.95
$f_{3.3}$	38.62
$f_{3.4}$	34.27
$f_{3.5}$	29.19
$f_{3.6}$	16.22
$w_{1.COMP}$	3100
$w_{2.TOX}$	10.234
$w_{2.NONE}$	1789.7
$w_{3.COMP}$	1378.1
$w_{3.NONE}$	371.88
$w_{4.COMP}$	2000
$w_{5.NONE}$	1300
$w_{6.COMP}$	1400
$d_{COMP.TOX}$	477.55
$d_{TOX.THOD}$	425.19
$d_{TOX.POH}$	61.09
m_{COMP}	7878.1
m_{TOX}	487.79
m_{THOD}	425.19
m_{POH}	61.09
m_{NONE}	3461.64
$g_{COMP.2}$	1478.67
$g_{COMP.3}$	1697.9
$g_{COMP.4}$	1636.2
$g_{COMP.5}$	1663.5
$g_{COMP.6}$	924.17
$g_{TOX.7}$	62.59
$g_{THOD.7}$	364.09
$g_{POH.7}$	61.098
$g_{NONE.1}$	1806.4
$g_{NONE.2}$	95.36
$g_{NONE.3}$	1063.4
$g_{NONE.4}$	329.48
$g_{NONE.5}$	107.28
$g_{NONE.6}$	59.60
G_{S1}	1900
G_{S2}	1600
G_{S3}	2800
G_{S4}	2000
G_{S5}	1800
G_{S6}	1000
G_{waste}	487.7

Table 12
Comparison between simultaneous and sequential approach for Example 3.

Concept	Optimal solution (simultaneous approach)	Sequential approach
F_1 (lb/h)	–	1800.2
F_3 (lb/h)	237.79	166.09
Waste (lb/h)	487.7	2216.3
Fresh sources cost (\$/yr)	5707	119,200
Treatment units cost (\$/yr)	460,451	205,123
Piping cost (\$/yr)	21,587	20,792
Network cost (\$/yr)	487,746	345,116
Waste treatment system (\$/yr)	–	406,030
Total annual cost (\$/yr)	487,746	751,146

Table 13
Computational effort for the case studies.

Example	Number of process sources	Number of process sinks	Number of partitions	Time (s)
1	2	2	6	131.29
2	3	3	12	908.62
3	6	6	33	4505.17

Table 14
Computer benchmark using Linpack® java version.

	Benchmark
Millions of floating point operations per second	331.57 Mflops/s
Time	0.25 s
Norm res	5.68
Precision	2.2204×10^{-16}

the simultaneous approach, the selected units for component and toxicity treatment were the ones with maximum efficiency, but treatment for THOD and *pH* was satisfactorily met using the units with the lowest efficiency. For this example 32 intervals were used as partitions of the original flows domain.

Computational effort: The time needed to solve each of the examples in a computer with an Intel® Core™2 CPU T5200 at 1.6 GHz and 2.00 GB RAM is reported in Table 13. This computer was benchmarked using the java version of the linpack software (available at http://www.netlib.org/benchmark/linpackjava/), and the results are summarized in Table 14. It can be seen how the computational effort depends directly on the size of the problem, and more noticeably on the number of partitions of the original flows domain.

5. Conclusions

This paper has presented a mathematical representation of a mass and property integration using a recycle–reuse scheme for a network that includes process interceptors inside of the process. The formulation has considered simultaneously both process and environmental constrains for properties such as composition, toxicity, THOD, *pH*, density and viscosity. A set of disjunctions were formulated for the use of in-plant property interceptors. The resulting MINLP model for the mass integration network contains several bilinear terms, and it was solved using a global optimization strategy, which involves the solution of an MINLP model and a relaxed MILP model to provide under- and over-estimations of the objective function. A branch and bound strategy was used until the estimators approached each other within a minimum gap. Several partitions of the flows domain were implemented as part of the solution procedure. The solution to three examples has shown the application of the proposed methodology, and its advantage over a typical sequential approach of integrating a process network first and then adding the property treatment systems to meet the environmental constraints. A comparison has also been presented with previous works in which a centralized treatment system (direct recycle strategy), and a simplified recycle and reuse formulation have been used. It is also shown how the computational effort depends directly on the size of the problem and on the number of partitions chosen to strengthen the bounds of the relaxation procedure. Further work should aim towards the improvement of the property operators to make better predictions of the properties in the mixing points of the network. Also a more detailed design model for the property interceptors should be developed instead of using a constant value for the unit efficiency.

Notation

$Cost_r^{Fresh}$	unit cost for fresh utility r
$Cost_u^{Unit}$	unit cost for treatment unit u
$Cost_{U(p')}^{unit,I(U)}$	disaggregated variable for $Cost_u^{Unit}$
$d_{u^1,u}$	flow rate from treatment unit u^1 to treatment unit u
$f_{r,j}$	segregated flow rate from fresh source r to sink j
F_r	total flow rate for fresh source r
$g_{u,j}$	segregated flow rate from treatment unit u to process sink j
G_j	total flow rate for process sink j
H_Y	plant operating time, hours per year
m_u	total flow rate entering unit u
$m_{U(p')}^{I(U)}$	disaggregated variable for m_u
M^{Cost}	upper bound used in the convex hull formulation for the cost of the treatment unit
M^m	upper bound used in the convex hull formulation for the flow rate entering the treatment units
M^{ψ_p}	upper bound used in the convex hull formulation for the property operator
N_{Fresh}	total number of fresh sources
N_{int}	total number of units available to treat each property
$N_{properties}$	total number or properties
N_{Sinks}	total number of sinks
$N_{Sources}$	total number of process sources
N_{Units}	total number of treatment units
pH	potential of hydrogen
$pip_{u,j}^{Exit}$	piping cost to send segregated flow rate from treatment unit u to process sink j
$pip_{i,u}^{in}$	piping cost to send process source i to treatment unit u
$pip_{r,j}^{inFresh}$	piping cost to send fresh source r to treatment process sink j
$pip_{u^1,u}^{\mathrm{int}}$	piping cost to send segregated flow rate from treatment unit u^1 to treatment unit u
TAC	total annual cost
$THOD$	theoretical oxygen demand
Tox	toxicity
$w_{i,u}$	segregated flow rate from process source i to treatment unit u
$waste$	total flow rate for the waste stream discharged to the environment
W_i	total flow rate for process source i
x_p^i	variable that substitutes the product flow rate i times the property operator of the property p
$y_{I(U)}^{U(p')}$	binary variable used to select the appropriate treatment unit for each property
z	composition

Sets

FRESH	set for fresh sources, $\{r \mid r = 1, \ldots, N_{Fresh}\}$
NPROP	set for the properties, $\{p \mid p = 1,\ldots,N_{properties}\}$
NINT	set for the available units for each property, $\{I \mid I = 1, \ldots, N_{\mathrm{int}}\}$
NSINKS	set for sinks, $\{j \mid j = 1, \ldots, N_{Sinks}\}$
NSOURCES	set for process sources, $\{i \mid i = 1, \ldots, N_{Sources}\}$
NUNITS	set for the treatment units, $\{u \mid u = 1, \ldots, N_{Units}\}$

Greek letters

$\alpha_{I(U)}^{U(p')}$	efficiency of property interceptor for property p
λ_n^i	binary variable used to select the active region in the domain partition
μ	viscosity
π_n^i	disaggregated variable for the flow rate i used in the domain partition
ρ	density
$\chi_{p,n}^i$	disaggregated variable for the property operator p used in the domain partition
ψ_p	property operator for the mixing rule for property p

Indices

i	process source
In	inlet
j	sink
max	maximum
min	minimum
n	interval
Out	out
p	property
r	fresh source
Sink	sink
Source	source
u	unit
waste	waste discharged to the environment

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