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An MINLP Model that Includes the Effect of Temperature and Composition on Property Balances for Mass Integration Networks

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Abstract: The synthesis of water networks based on properties has commonly ignored the effect of temperature on the property balances that are part of the formulation. When wide differences of temperatures are observed within the process, such an effect might yield significant errors in the application of conventional property balances. In this work, a framework for the development of water networks that include temperature effects on property balances is presented. The approach is based on the inclusion of constants in the property operators that are commonly used to carry out the property balances. An additional term to take care of composition effects is also included. The resulting approach is embedded into a formulation based on a mixed-integer nonlinear programming model for the design of water networks. A case study is presented that shows that the proposed approach yields an improvement in the prediction of the resulting properties for the integrated network, thus affecting the optimal solution.

Keywords: mass integration; property integration; water networks; mixed-integer nonlinear programming

1. Introduction

Mass integration techniques have found special applications in the development of water networks that minimize the consumption of both fresh water requirements and wastewater sent to the environment. The initial studies were based on extensions of the pinch concept for energy integration [1–3]. The first reported mass integration strategy considered a set of process streams that served as removers of contaminants contained in other streams [4]. Another structure was then considered in the form of a direct recycle network, in which process streams could serve as sources to be allocated into process units that could serve as sinks. From this approach, a mass pinch point was detected that guided the design of a mass integration network with minimum consumption of fresh sources. Additional studies were developed following these concepts and objectives [5–9]. A review on the works for mass integration based on pinch methods is available in Foo [10]. Alternative approaches to the mass pinch approach were developed to formulate network synthesis methods based on mathematical programming techniques [11–17]. These works typically considered the concentration of contaminants as the task to be treated for the design of the network.

It was later recognized that integration tasks are not only affected by the concentration of pollutants within water and process streams, but also by their properties such as pH, COD, color and odor, among others. A novel framework for water networks based on properties was proposed by Shelley and El-Halwagi [18]. Applications of this concept and further developments were reported in several works from El-Halwagi's research group [19–23]. To trace properties within the network, the use of property balances was needed, for which property operators were used to allow linear mixing rules. The first mathematical programming optimization model for the synthesis of mass integration networks based on properties was reported by Ponce-Ortega *et al.* [24]. A mixed-integer nonlinear programming (MINLP) formulation was used to find the structure of the network with a minimum cost. Other network structures and optimization formulations were then developed [25–28]. A good description on the development of mass integration concepts and applications can be found in the books by El-Halwagi [29–31].

The works developed for mass and property integration networks have commonly neglected the effect of temperature on properties. Given the various levels of temperature observed in process units and resulting process streams, it becomes important to account for that factor. In this work, a framework for the inclusion of temperature effects on stream properties is proposed. The approach is based on the modification of the property operators that are used to carry out the property balances, which can also be used to include the effect of additional variables such as composition.

2. Problem Statement

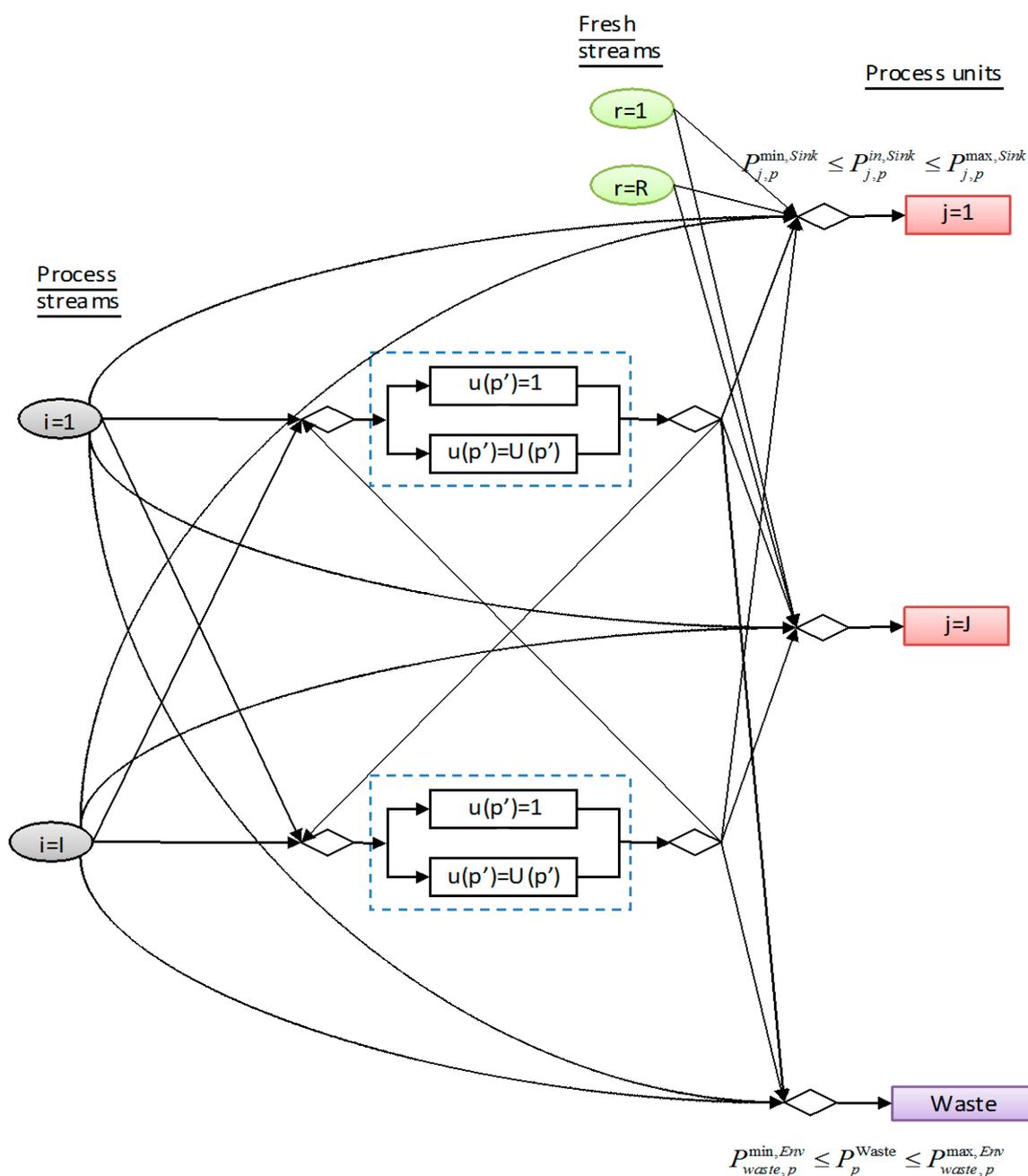
Given is a set of process units that can be used as sinks $\{j = 1, 2, \dots, J\}$. Each sink can process a given feed rate G_j , and its contents have some property values $P_{j,p}^{InSink}$ that are constrained between minimum and maximum values. In addition, given is a set of process streams $\{i = 1, 2, \dots, I\}$ with a flowrate W_i that can be recycled and/or reused in process sinks. There is set of fresh sources $\{r = 1, 2, \dots, R\}$ with costs $Cost_r^{Fresh}$ (\$/kg) and properties $P_{p,r}^{InFresh}$. There is a set of property interceptors $\{m = 1, 2, \dots, M\}$. Each property can be modified with the set of treatment units $\{u = 1, 2, \dots, U_p\}$, with cost $Cost_{u,m}^{Int}$, and given separation efficiencies $\alpha_{u,m}$. The waste stream must meet environmental

constraints. The objective is synthesizing an optimal water network such that the total annual cost is minimized.

3. Model Formulation

The model is based on a recycle/reuse structure, as in Ponce-Ortega *et al.* [25] (see Figure 1). It includes mass, energy and property balances, and disjunctive programming is used for the selection of property interceptors. A formulation that takes into account temperature and composition functionalities for property operators is included.

Figure 1. A recycle/reuse integration network with in-plant property interceptors.



Each process stream from the system in Figure 1 is split into unknown flows, to be allocated in process sinks, property interceptors and/or a waste stream. Fresh sources can only be sent to process sinks. The feed to process interceptors consists of process streams and/or streams exiting from other interceptors. The outlet of process interceptors can be sent to process sinks and/or waste stream.

3.1. Splitting of Process Streams

Each process stream i is split into J , M and waste fractions, with flows $w_{i,j}^{Sink}$, $w_{i,m}^{Int}$ and w_i^{Waste} sent to process sinks, property interceptors and waste stream,

$$W_i = \sum_{m \in M} w_{i,m}^{Int} + \sum_{j \in J} w_{i,j}^{Sink} + w_i^{Waste} \quad i \in I \quad (1)$$

3.2. Splitting of Fresh Streams

Similarly, each fresh source is split into J fractions with flows $f_{r,j}$ that can be sent to different process sinks,

$$F_r = \sum_{j \in J} f_{r,j} \quad r \in R \quad (2)$$

3.3. Mass Balance at Inlet of Process Interceptors

The flow to property interceptor m , d_m , that treats property p' is the summation of the flows from process streams $w_{i,m}^{Int}$, and the flow from other interceptors $q_{m,m'}$,

$$d_m = \sum_{i \in I} w_{i,m}^{Int} + \sum_{\substack{m' \in M \\ m' \neq m}} q_{m,m'} \quad m \in M \quad (3)$$

3.4. Property Balance at Inlet of Property Interceptors

Property balances are needed to calculate the property values at the inlet of property interceptors, and are carried out using property operators. Interceptor m treats property p , with property operators $\psi(p_i^{InSource})$ and $\psi(p_m^{OutInt})$ for process stream i and the outlet from other interceptors m' , respectively.

The resulting property for stream d_m is calculated through the following balance,

$$d_m \psi(p_m^{InInt}) = \sum_{i \in I} w_i^{Int} \psi(p_i^{inSource}) + \sum_{\substack{m' \in M \\ m' \neq m}} q_{m,m'} \psi(p_m^{OutInt}) \quad m \in M, \quad p \in P \quad (4)$$

Some property operators are shown in Table 1. It must be stressed that the effect of temperature is originally not included in such operators.

Table 1. Some 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	$\psi_\rho(\rho) = 1/\rho$
Viscosity	$\psi_\mu(\mu) = \log(\mu)$

3.5. Energy Balances at the Inlet of Property Interceptors

The energy balance for each interceptor m is given by,

$$d_m C_p^{InInt} (T_m^{InInt} - T_0) = \sum_{i \in I} w_{i,m}^{Int} C_{p_i}^{InSource} (T_i^{InSource} - T_0) + \sum_{m' \in M} q_{m,m'} C_{p_{m'}}^{OutInt} (T_{m'}^{OutInt} - T_0) \quad m \in M \tag{5}$$

where T_0 is a reference temperature, $T_i^{InSource}$ is the temperature of process stream i , $T_{m'}^{OutInt}$ is the outlet temperature from other interceptors m' , T_m^{InInt} is the inlet temperature to property interceptor d_m , and C_p s are heat capacities.

Property interceptors are assumed to operate at constant temperature,

$$T_m^{OutInt} = T_m^{InInt} \tag{6}$$

3.6. Property Interceptors

For property treatment, there is a set of property interceptors, $u(p')$, for which efficiency separation factors and operating costs are given. It is assumed that only one property is treated with the use of each interceptor.

For the selection of interceptors to treat property p' , the following disjunction is used,

$$\forall_{u \in U_p} \left[\begin{array}{l} Y_{u,m} \\ \psi(p_m^{OutInt}) = \psi(p_m^{InInt})(1 - \alpha_{u,m}) \\ Cost_m^{Int} = Cost_{u,m}^{Unit} \cdot d_m \end{array} \right] \quad \forall m$$

where $Y_{u,m}$ is a Boolean variable, which when true implies the selection of the intercepting unit m with total cost $Cost_m^{Int}$ operating with an efficiency separation factor $\alpha_{u,m}$; $\psi(p_m^{InInt})$ refers to the inlet value of property p , and $\psi(p_m^{OutInt})$ is the property value at the exit of the unit.

The disjunction is reformulated with the Convex Hull technique. Boolean variables are substituted by integer 0–1 variables, such that when the binary variable $y_{u,m}$ is equal to one, the unit m is used; otherwise, it is equal to zero. Since at most one type of interceptor is selected for the treatment of each property, the summation of the integer variables is bounded to one,

$$\sum_{u \in U_p} y_{u,m} \leq 1 \quad \forall m \quad (7)$$

Variables are disaggregated for the Convex Hull reformulation,

$$\psi(p_m^{OutInt}) = \sum_{u \in U_p} \psi_u(p_m^{OutInt}) \quad \forall m \quad (8)$$

$$\psi(p_m^{InInt}) = \sum_{u \in U_p} \psi_u(p_m^{InInt}) \quad \forall m \quad (9)$$

$$d_m = \sum_{u \in U_p} d_{u,m} \quad \forall m \quad (10)$$

$$Cost_m^{Int} = \sum_{u \in U_p} Cost_{u,m}^{Int} \quad \forall m \quad (11)$$

Constraints are written in terms of the disaggregated variables,

$$\psi_u(p_m^{OutInt}) = \psi_u(p_m^{InInt})(1 - \alpha_{u,m}) \quad \forall u, \forall m \quad (12)$$

$$Cost_{u,m}^{Int} = Cost_{u,m}^{Unit} \cdot d_{u,m} \quad \forall u, \forall m \quad (13)$$

To complete the reformulation, bounds are used for the disaggregated variables,

$$\psi_u(p_m^{OutInt}) \leq U^{\psi^{out}} \cdot y_{u,m} \quad \forall u, \forall m \quad (14)$$

$$\psi_u(p_m^{InInt}) \leq U^{\psi^{in}} \cdot y_{u,m} \quad \forall u, \forall m \quad (15)$$

$$d_{u,m} \leq U^d \cdot y_{u,m} \quad \forall u, \forall m \quad (16)$$

$$Cost_{u,m}^{Int} \leq U^{Cost} \cdot y_{u,m} \quad \forall u, \forall m \quad (17)$$

3.7. Stream Splitting at the Outlet of Each Property Interceptor

Each stream at the outlet of each interceptor m is split into flows $g_{m,j}^{Sink}$, $q_{m,m'}$ and g_m^{Waste} that go to process sinks, other property interceptors, and waste,

$$d_m = \sum_{j \in J} g_{m,j}^{Sink} + g_m^{Waste} + \sum_{\substack{m' \in M \\ m' \neq m}} q_{m,m'} \quad m \in M \quad (18)$$

3.8. Mass Balance for Process Sinks

The flow into process sink j , G_j , is the summation of flows from process streams, $w_{i,j}^{Sink}$, from property interceptors, $g_{m,j}^{Sink}$, and from fresh streams, $f_{r,j}$,

$$G_j = \sum_{r \in R} f_{r,j} + \sum_{m \in M} g_{m,j}^{Sink} + \sum_{i \in I} w_{i,j}^{Sink} \quad j \in J \quad (19)$$

3.9. Property Balance for Process Sinks

To implement property balances in the process sinks, property operators are used,

$$G_j \psi(p_j^{InSink}) = \sum_{r \in R} f_{r,j} \psi(p_r^{InFresh}) + \sum_{m \in M} g_{m,j}^{Sink} \psi(p_m^{OutInt}) + \sum_{i \in I} w_{i,j}^{Sink} \psi(p_i^{InSource}) \quad \forall j, \forall p \quad (20)$$

where $\psi(p_i^{InSource})$, $\psi(p_m^{OutInt})$ and $\psi(p_r^{InFresh})$ are the property operators for process stream i , outlet of property interceptors m , and fresh sources, respectively.

3.10. Energy Balance for Process Sinks

Energy balances for process sinks are written as,

$$G_j C p_j^{InSink} (T_j^{InSink} - T_0) = \sum_{r \in R} f_{r,j} C p_r^{InFresh} (T_r^{InFresh} - T_0) + \sum_{m \in M} g_{m,j}^{Sink} C p_m^{OutSink} (T_m^{OutSink} - T_0) + \sum_{i \in I} w_{i,j}^{Sink} C p_i^{InSource} (T_i^{InSource} - T_0) \quad j \in J \quad (21)$$

where $T_i^{InSource}$ is the temperature of process stream i , T_m^{OutInt} is the outlet temperature from interceptor m , $T_r^{InFresh}$ is the temperature of fresh source r , and Cps are heat capacities.

3.11. Mass Balance for Waste Stream

The waste stream flow is the summation of flows from process streams w_i^{Waste} and from the process interceptors g_m^{Waste} ,

$$Waste = \sum_{m \in M} g_m^{Waste} + \sum_{i \in I} w_i^{Waste} \quad (22)$$

3.12. Property Balance in Waste Stream

In terms of property operators, the property balance in the waste stream is written as,

$$Waste \psi(p^{Waste}) (T^{Waste} - T_0) = \sum_{m \in M} g_m^{Waste} \psi(p_m^{Waste}) + \sum_{i \in I} w_i^{Waste} \psi(p_i^{InSource}) \quad \forall p \quad (23)$$

It should be noticed that temperature adjustments are carried out with standard heaters or coolers, which are not considered as property interceptors.

3.13. Energy Balance in Waste Stream

Since temperature effects are included in the formulation, the energy balance for the waste stream is needed,

$$Waste C p^{Waste} (T^{Waste} - T_0) = \sum_{m \in M} g_m^{Waste} C p_m^{OutInt} (T_m^{OutInt} - T_0) + \sum_{i \in I} w_i^{Waste} C p_i^{InSource} (T_i^{InSource} - T_0) \quad (24)$$

Heat capacities in the energy balances are taken as a function of temperature. For instance, for each component i of the waste stream,

$$Cp_i^{Waste} = A_i + B_i T^{Waste} + C_i (T^{Waste})^2 \quad (25)$$

So the heat capacity of the stream would be,

$$Cp^{Waste} = \sum_i x_{Waste,i} Cp_i^{Waste} \quad (26)$$

3.14. Constraints

For process sinks, lower and upper limits on properties are given,

$$\psi(p_j^{\min, Sink}) \leq \psi(p_j^{In, Sink}) \leq \psi(p_j^{\max, Sink}) \quad \forall j \quad (27)$$

Likewise, for waste streams limits are established by environmental constraints,

$$\psi(p_{waste}^{\min, Env}) \leq \psi(p_{waste}) \leq \psi(p_{waste}^{\max, Env}) \quad (28)$$

The objective function is the minimization of the total annual cost, which consists of the cost of fresh streams, $Cost_r^{Fresh}$, and the yearly cost of property interceptors, $Cost_m^{Int}$,

$$\min TAC = H_v \sum_{r \in R} Cost_r^{Fresh} F_r + H_v \sum_{m \in M} Cost_m^{Int} \quad (29)$$

where H_v is an annualization factor.

3.15. Modification of Properties

Temperature and composition are two variables that affect properties, and they are considered in this work via the following framework.

3.16. Properties as a Function of Temperature

Previous works have ignored the effect of temperature on properties. However, given a set of properties p , there would be at least a subset that depends on temperature, $p(T)$. Each process stream has known properties $p_{T,i}^{InSource}$, or in terms of property operators $\psi(p_{T,i}^{InSource})$. Property balances are used when different streams are mixed, e.g., for the inlet of property interceptors, process sinks and waste, $\psi(p_{T,m}^{InInt})$, $\psi(p_j^{InSink})$ and $\psi(p^{Waste})$, respectively.

In this work we establish a framework for including temperature effects on properties through the use of property operators, which is a convenient approach given its applications for property balances.

In general, for any property operator we can write,

$$\psi(p_T^C) = C_{1,p(T)} + C_{2,p(T)} F_{p(T)}(T_X^C) + C_{3,p(T)} \psi_Z(p_{Z,X}) + C_{4,p(T)} \psi(p_{T,X}^{Unc}) \quad (30)$$

where for stream m, j , or waste, $\psi(p_T^C)$ is the corrected property operator $F_{p(T)}(T_X^C)$ is the temperature functionality, $\psi_Z(p_{Z,X})$ is the operator for concentration, $\psi(p_{T,X}^{Unc})$ is the uncorrected value of the operator for property $p(T)$.

For instance, for property interceptors,

$$\psi(p_T^{OutInt}) = C_{1,p(T)} + C_{2,p(T)}F_{p(T)}(T_X^{OutInt}) + C_{3,p(T)}\psi_Z(p_{Z,m}^{OutInt}) + C_{4,p(T)}\psi(p_{T,X}^{InInt,UnC}) \quad (31)$$

4. Methodology for Estimation of Parameters

The estimation of the parameters $C_{1,p(T)}$, $C_{2,p(T)}$, $C_{3,p(T)}$, $C_{4,p(T)}$ is carried out ahead of design. For instance, for the case when composition and temperature data are known, the following steps can be used to estimate such values.

For different process streams, values of properties of interest (viscosity, density, *etc.*) are calculated at different temperatures (from process simulators or from experimental data), and the functionality with temperature, $F_{p(T)}(T_X^C)$, is developed.

- (1) From the set of data, Equation (31) is used to obtain the parameter values. Temperature, $F_{p(T)}(T_X^C)$, concentration $\psi_Z(P_X)$ and the uncorrected property operator $\psi(p_{T,X}^{UnC})$ are independent variables.
- (2) To estimate the parameters, $\psi(p_{T,X}^{UnC})$ takes the value for the property operator $p(T)$ for the original process streams.
- (3) With the calculated parameters, the equation is implemented into the MINLP model.

We take two properties, viscosity and density, to illustrate this procedure.

4.1. Viscosity

Viscosity depends on composition and temperature. For pure substances, Duhne [32] proposed the following logarithmic relationship for the estimation of viscosities for liquids,

$$\ln \mu = A + \left(\frac{B}{T} \right) \quad (32)$$

where A and B are constants. Based on this relationship, the functionality for viscosity is taken as inversely proportional to temperature, so that the constraints for the optimization model can be written as,

$$\psi_{\mu(T)}(P_{\mu(T),X}^C) = C_{1,\mu(T)} + C_{2,\mu(T)}F_{\mu(T)}(T_X^C) + C_{3,\mu(T)}\psi_Z(P_{Z,X}) + C_{4,\mu(T)}\psi_{\mu(T)}(P_{\mu(T),X}^{UnC}) \quad (33)$$

$$F_{\mu(T)}(T_X^C) = \frac{1}{T_X^C} \quad (34)$$

4.2. Density

Variations in density are directly related to temperature. Therefore, constraints can be written as,

$$\psi_{\rho(T)}(P_{\rho(T),X}^C) = C_{1,\rho(T)} + C_{2,\rho(T)}F_{\rho(T)}(T_X^C) + C_{3,\rho(T)}\psi_Z(P_{Z,X}) + C_{4,\rho(T)}\psi_{\rho(T)}(P_{\rho(T),X}^{UnC}) \quad (35)$$

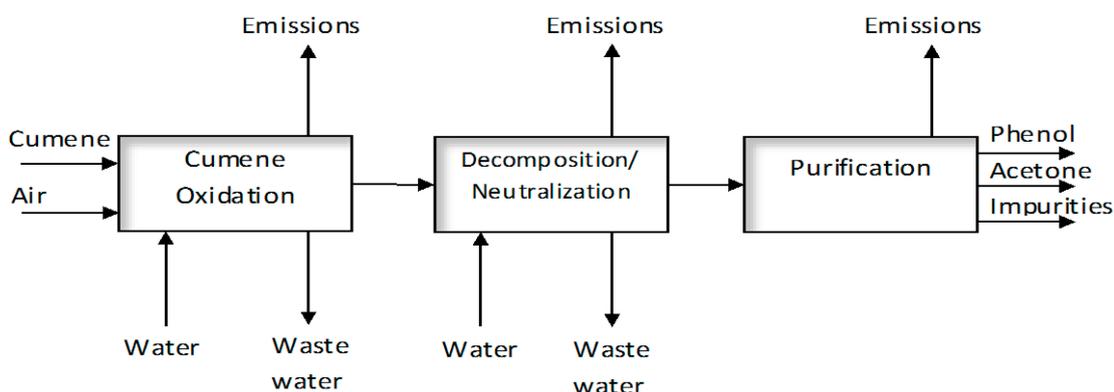
$$F_{\rho(T)}(T_X^C) = T_X^C \quad (36)$$

5. Case Study

To illustrate the proposed approach, the process for the production of phenol from cumene hydroperoxide is taken as a case study [25,33]. Phenol is subject to environmental regulations because of its toxic nature.

The process involves three stages. In the first one, the production of cumene hydroperoxide via air oxidation of cumene is carried out. The reaction takes place at temperatures between 90 and 120 °C, with pressures between 0.5 and 0.7 MPa. In the second stage, sulfuric acid is used to break the hydroperoxide molecule to produce phenol, with acetone as byproduct. Sulfuric acid is then neutralized with sodium hydroxide, forming organic and aqueous phases; the aqueous phase is sent to treatment of waste water, and the organic phase is sent to a final distillation system to purify the products (Figure 2).

Figure 2. Main steps for the production of phenol.



There are three aqueous streams that can be reused via process integration. Two fresh sources are also available. Data on stream flowrates, composition, toxicity, chemical oxygen demand and pH were taken from Ponce-Ortega *et al.* [25], while temperature data were taken from Kheireddine *et al.* [33]. There are two fresh sources, one consisting of high-quality water and another one of slightly contaminated water. From the several streams from the process, only wastewater streams are considered as process sources, one from the cumene peroxidation unit, another one from the cleavage section and the last one from the output from a final washer that uses fresh water. Three equipment units serve as process sinks, one washer after the peroxidation and separation units, a neutralizer that uses NaOH in the separation stage, and a final unit consisting of a washer to purify the product. Table 2 shows the relevant data for each stream. Values for heat capacity, density and temperature were calculated from the given conditions for each process stream.

The constraints for the three process units that serve as process sinks are given in Table 3 and Table 4. Temperature constraints are given in Table 5. For the waste stream, the operating cost due to cooling in order to meet environmental constraints was calculated from,

$$Cost_T^{Waste} = Cost_T^{Util} Waste C_p^{Waste} (T^{Waste} - T_{waste}^{Max, Env}) \quad (37)$$

where $Cost_T^{Util}$ is the utility cost, taken as 0.06688 \$/MMkJ. Data on cost and efficiency factors for property interceptors are reported in Table 6. Table 7 gives the constants for the calculation of heat capacities, while the parameters for density and viscosity corrections are reported in Table 8.

Table 2. Data for case study.

Stream	Flow (kg/h)	Z	Tox (%)	COD (mgO ₂ /L)	pH	ρ^* (kg/m ³)	μ^* (cP)	T (K)	Cp^{**} (kJ/kg K)
R1	-	0	0	0	7.0	994.0	0.913	298.15	4.1845
R2	-	0.010	0.1	0.010	7.1	986.1	0.743	308.15	4.1575
W1	3666	0.016	0.3	0.187	5.4	947.1	0.382	348.15	4.1601
W2	1769	0.024	0.5	48.450	5.1	958.8	0.442	338.15	4.1363
W3	1487	0.220	1.5	92.100	4.8	1022.1	0.745	313.15	3.7280

* Values obtained from simulations with Aspen Plus; ** Values obtained from reported sources.

Table 3. Upper limits for process sinks and waste stream.

Stream	Flow (kg/h)	Z^{max}	Tox^{max} (%)	COD^{max} (mgO ₂ /L)	pH^{max}	ρ^{max} (kg/m ³)	μ^{max} (cP)
G1	2721	0.013	2	100	8.0	1270	1.202
G2	1995	0.011	2	100	7.8	1113	2.230
G3	1129	0.100	2	100	8.2	1315	1.260
Waste	-	0.005	0.001	75	9.0	-	-

Table 4. Lower limits for process sinks and waste streams.

Sink/Waste	Flow (kg/h)	pH^{min}	ρ^{min} (kg/m ³)	μ^{min} (cP)
G1	2721	5.3	816	0.2
G2	1995	5.4	771	0.2
G3	1129	5.2	839	0.2
Waste	-	5.5	-	-

Table 5. Constraints for temperature in process sinks and waste stream.

Sink/Waste	T^{min} (K)	T^{max} (K)
G1	333.15	353.15
G2	303.15	348.15
G3	298.15	338.15
Waste	290.15	308.15

The model was implemented into the GAMS software, and solved using DICOPT. In order to observe the effect due to the corrections of properties with temperature, two solutions were obtained. The first solution was obtained using the model with the proposed estimations. The second one considered only the effect of mixing on the calculations of viscosity and density.

Table 6. Data for cost and efficiency for property interceptors.

Property	$\alpha_{u,m}$	$Cost_{u,m}^{Unit}$ (\$/kg)
$u(z_1)$	0.98	0.0143
$u(z_2)$	0.85	0.0073
$u(Tox_1)$	1.00	0.0216
$u(Tox_2)$	0.90	0.0165
$u(COD_1)$	0.80	0.0143
$u(COD_2)$	0.55	0.0071
$u(pH_1)$	0.50	0.1389
$u(pH_2)$	0.30	0.0397
$u(pH_3)$	-0.50	0.1433
$u(pH_4)$	-0.30	0.0419

Table 7. Constants for heat capacity estimations.

Compound	A_c	B_c	C_c
Water	5.8221	-0.01033	0.0000162
Phenol	1.0809	0.003375	0

Table 8. Parameters for temperature dependence.

$p(T)$	$C_{1,p(T)}$	$C_{2,p(T)}$	$C_{3,p(T)}$	$C_{4,p(T)}$
Viscosity	-2.6816	786.50	0.18400	-2.0699×10^{-5}
Density	6.8632×10^{-4}	1.0715×10^{-6}	-1.9655×10^{-4}	-3.9471×10^{-4}

When both temperature and composition effects on properties were included, the solution reported in Figure 3 was obtained. Values for properties at the process sinks and waste stream are given in Table 9. Three property interceptors are used as part of the network, one to treat phenol concentration $u(z_1)$, another one for toxicity treatment, $u(Tox_1)$, and the third one for pH adjustment, $u(pH_1)$. In this case, some direct use of split process streams into process sinks are observed, with the use of fresh sources in the second sink for adjustment. Cooling of the waste stream in order to meet environmental constraints is also observed. The total annual cost for this case was $\$7.8686 \times 10^5/\text{year}$.

To establish a comparison basis, the model was also solved without including the effect of temperature on properties. Figure 4 shows the solution obtained for such a case. Three property interceptors are again observed, along with the use of one fresh source and temperature treatment for the waste stream. The total annual cost of the network amounts to $\$7.5557 \times 10^5/\text{year}$. One can observe that the network structure for the two solutions is similar, but with differences in the flows for the streams. The difference in TCA is 4.14%, which is related to an improvement in the estimation of properties with the functionality implemented for temperature dependence.

Figure 3. Optimal structure when effects of temperature and composition were considered.

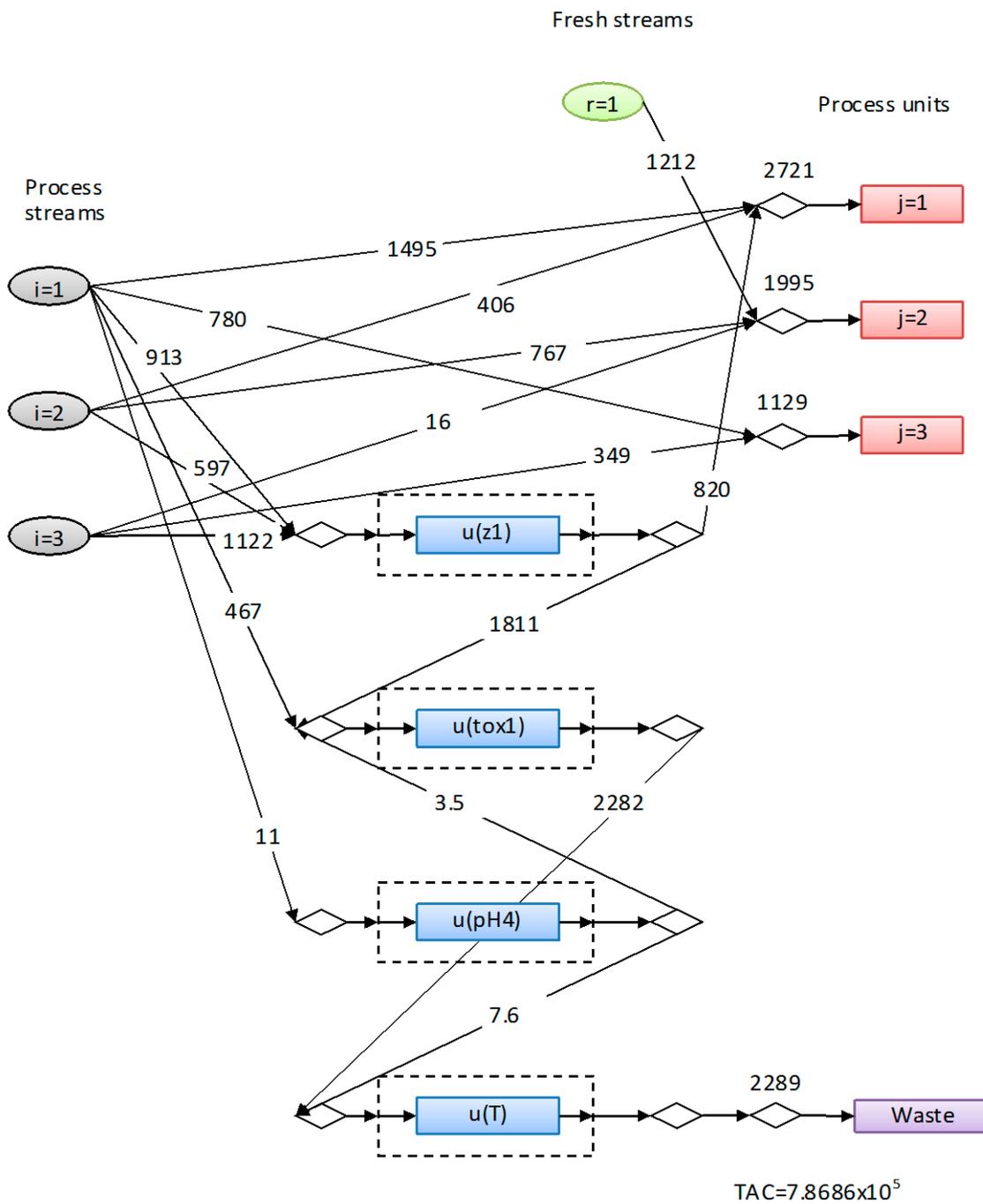
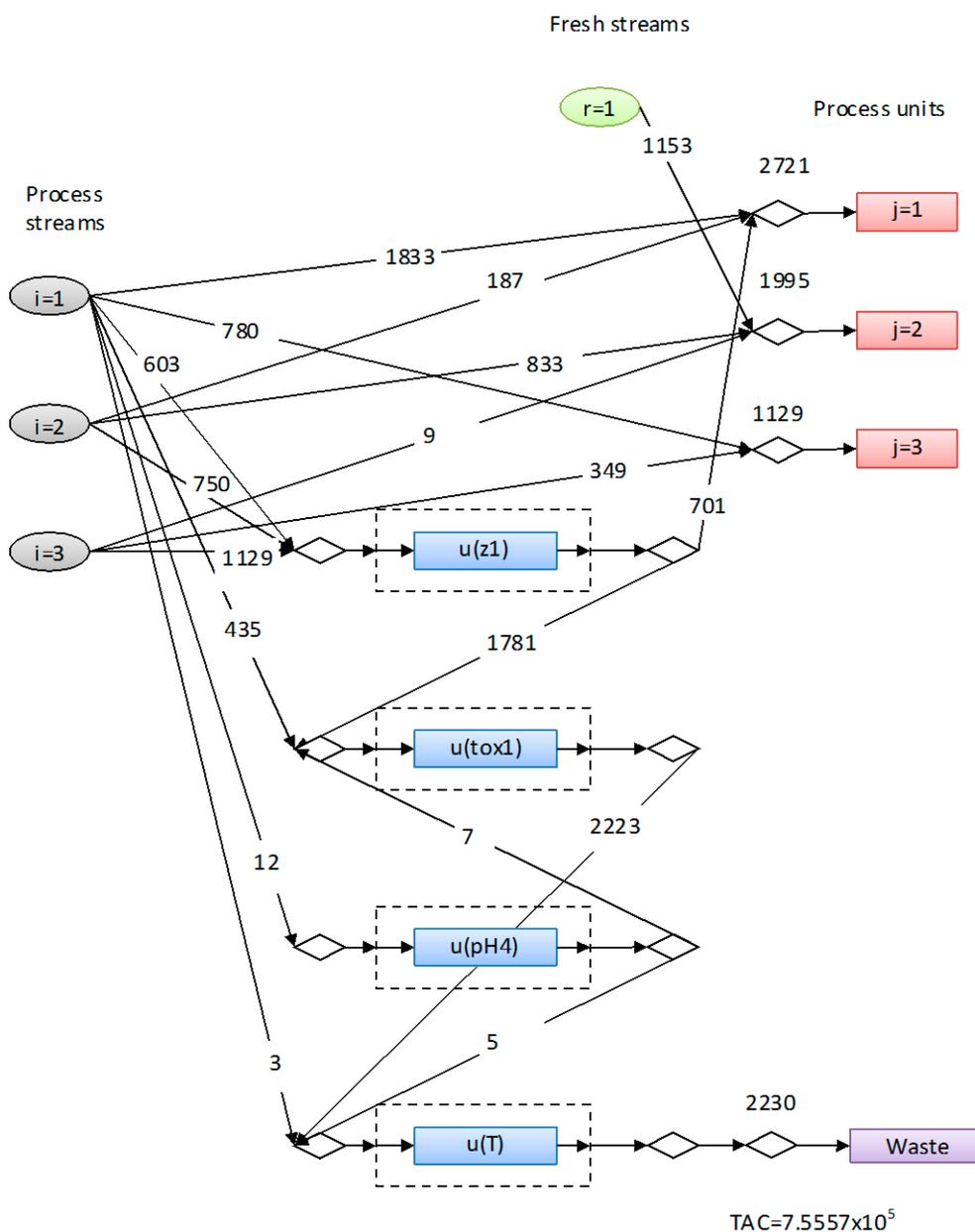


Table 9. Property values for sinks and waste stream.

$P_{p,j}^{InSink}$	Z	Tox (%)	COD (mgO ₂ /L)	pH	ρ (kg/m ³)	μ (cP)	T (K)
G1	0.013	0.4978	22.549	5.30	953.3	0.4220	341.28
G2	0.011	0.2043	19.515	6.79	980.7	0.6740	313.57
G3	0.079	0.6707	28.577	5.29	968.3	0.4558	338.15
Waste	0.005	0.0010	39.828	5.50	985.1	0.7441	308.15

Figure 4. Optimal structure when no effect of temperature and property composition was considered.



To observe how density and viscosity estimations were affected by including the dependence with temperature and composition, such values were also obtained from the Aspen Plus process simulator in order to validate the predictions. Values for density and viscosity obtained from the proposed optimization model (*i.e.*, model with $p(z,T)$, along with the values obtained without such modification were used for comparison.

Table 10 shows the results for density. It can be observed that the model that includes $p(T)$ provides lower errors for the streams of sinks G1 and G2 and for the waste stream. From the viscosity results of Table 11, one can see that for all streams the error is lower with the model that includes $p(T)$; the most notable difference is observed for the waste stream, which can be attributed to the cooling treatment from process streams at 348.15 K, 338.15 K, and 313.15 K, to a waste stream temperature of 308.15 K.

Table 10. Deviations in density estimations in process and waste streams.

Source	G1	G2	G3	Waste
Aspen	953.64	981.01	968.81	985.20
Model with $p(z,T)$	953.29	980.68	968.34	985.12
Error, %	0.04	0.033	0.049	0.01
Model, no $p(z,T)$	958.72	980.36	969.10	956.22
Error, %	0.53	0.07	0.03	2.94

Table 11. Deviations in viscosity estimations in process and waste streams.

Source	G1	G2	G3	Waste
Aspen	0.4208	0.6686	0.4506	0.7414
Model with $p(T)$	0.4220	0.6740	0.4558	0.7441
Error, %	0.29	0.80	1.17	0.37
Model, no $p(T)$	0.4297	0.6898	0.4694	0.4526
Error, %	2.12	3.17	4.18	38.95

6. Conclusions

An optimization model for the design of water networks that includes effects of temperature and composition on property operators has been presented. Property operators have been used as a convenient tool to carry out property balances for the design of the network. Typical formulations based on optimization techniques have included mass and property balances. In this work, a formulation that includes mass, property and energy balances has been used, along with a methodology to include the effect of variables such as temperature and composition on properties into the MINLP formulation. The results from the case study show that an improvement in the solution for the optimal network is obtained with the proposed approach.

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Author Contributions

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Nomenclature

A, B, C	empirical parameters
COD	chemical oxygen demand
$Cost^{Fresh}$	cost of fresh sources
$Cost^{Int}$	cost of property interceptor
C_p	heat capacity

d	stream flowrate
F, f	flowrate of fresh sources
G, g	flowrate of process sinks
H_V	operating hours per year
p, p'	any property
q	flowrate from interceptors
R, r	Flowrate of fresh sources
$sink$	process sink
$source$	fresh or stream source
T	temperature
TAC	total annual cost
Tox	toxicity
x	mole fraction
W, w	flowrate of process streams
$waste$	waste discharged to the environment
Y	Boolean variable
y	binary variable
z	pollutant concentration

Sets

I	process streams
J	sinks
M	properties to be treated
R	fresh sources
U_p	treatment units for each property

Subindices

i	process stream
j	sink
r	fresh source

Superscripts

C	corrected
In	inlet
Int	interceptor
max	maximum
min	minimum
Out	outlet
UnC	uncorrected

Greek symbols

α	separation efficiency of property interceptor
Ψ	property operator
ρ	density
μ	viscosity

Conflicts of Interest

The authors declare no conflict of interest.

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