

Attainable Composition, Energy Consumption, and Entropy Generation Properties for Isothermal/Isobaric Reactor Networks

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ABSTRACT: A methodology for the quantification of entropy generation and energy consumption in isothermal, isobaric reactor networks is presented. The proposed methodology employs the Infinite Dimensional State-space (IDEAS) conceptual framework, which is shown to be applicable to the problem under consideration. The IDEAS framework considers all possible reactor units, and all possible mixing and splitting interconnections among them. It will be shown mathematically that, under certain conditions, entropy generation and energy consumption are functions of only the inlet and outlet stream compositions and flow rates and are not dependent on the reactor network structure, as long as there exists a network able to deliver the considered outlets from the known inlets. This theoretical result provides the foundation for a graphical method that can quantify entropy generation and energy consumption, by first identifying the reactor network's Attainable Region (AR) and then depicting the behavior of the entropy generation and energy consumption functions within the AR. The proposed methodology is demonstrated on a case study featuring reversible reactions both in series and in parallel. Finally, conclusions are drawn.

1. INTRODUCTION

Quantifying the entropy generation and energy consumption for a given process is the first step toward its energetic optimization. According to Bejan, entropy generation minimization (EGM) is the method of thermodynamic optimization of real systems that owe their thermodynamic imperfection to heat transfer, fluid flow, and mass-transfer irreversibility.¹ Identifying processes that feature minimum entropy generation is highly desirable, since such processes can be thought of as realizable approximations to ideal reversible processes, and can thus be expected to be highly efficient.

A multitude of approaches have been proposed for the study of EGM problems, depending on the type of “thermodynamic imperfection” under consideration. Minimizing the entropy generation in a reactor is analogous to maximizing the obtainable work associated with the driving force of the chemical reaction occurring in the process.² This is elaborated further in the next section.

Several authors^{3–7} have presented work on the minimization of the entropy generated in a reactor for a variety of industrially relevant reactions using optimal control theory. While interesting and insightful, the method of optimal control of a single reactor suffers from clear limitations. Most importantly, combinations of reactors and reactor networks are not explored as potentially better alternatives to single reactor systems, and the solutions are locally, rather than globally optimal. Similarly, several authors have discussed the topic of energetically optimizing a network of nonisothermal reactors through the use of locally optimizing mixed-integer nonlinear program (MINLP) formulations,^{8,9} and targeting strategies,¹⁰ although with no mention of entropy generation considerations.

This work employs the Infinite Dimensional State-space (IDEAS) framework for the quantification of both entropy generation and energy consumption for isothermal, isobaric reactor networks. The flow sheet is decomposed into two types of

operations: flow operations (mixing, splitting, recycling, and bypass) and unit operations (reactors, distillation columns, heat exchangers, etc.). The IDEAS framework decomposes a process network into an operator (OP) network, where the unit operations (reactors, distillation columns, heat exchangers, etc.) occur, and a distribution network (DN), where the flow operations (mixing, splitting, recycling, and bypass) occur. IDEAS has been successfully applied to numerous globally optimal process network synthesis problems, such as mass exchange network synthesis,¹¹ complex distillation network synthesis,^{12–14} power cycle synthesis,¹⁵ reactor network synthesis,^{16,17} reactive distillation network synthesis,¹⁸ separation network synthesis,¹⁹ attainable region (AR) construction,^{20–23} and batch attainable region construction.²⁴

The novelty of this work is 2-fold. First, it pursues, for the first time, the quantification of multiple parameters, namely entropy generation and energy consumption for networks of unit operations rather than individual units. Given that appropriately designed reactor networks can be superior (either in terms of network volume, attainable outlet concentrations, or other criteria) to optimally designed single reactor units, it is highly desirable for a method that systematically quantifies network entropy generation and energy consumption for reactor networks to be developed. To this end, the second item of novelty brought about by this work is the discovery of an important network property that allows for the systematic quantification of the network entropy generation and energy consumption to be based solely on network input and output information.

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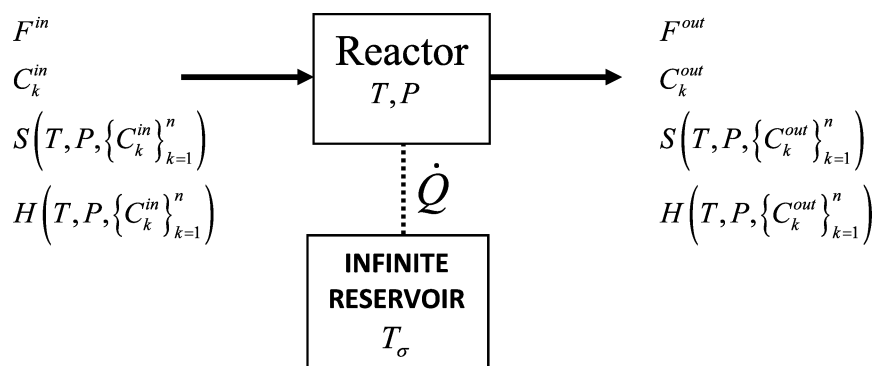


Figure 1. Reactor model (Molar Basis).

The rest of the paper is structured as follows. First, the motivation behind this work and its significance are presented, reactor models employing both mass and molar basis are developed, the network synthesis methodology is established, the applicability of IDEAS to the entropy generation and energy consumption quantification problem is demonstrated, and the resulting IDEAS mathematical formulation is presented. Next, the entropy generation and energy consumption functions are quantified and then simplified based on theorem 1, which establishes the functions' dependence only on network inlet and outlet information. Subsequently, the AR concept is used as a platform within which the property quantification problem is solved. Finally, a case study is used to illustrate the proposed global method, and conclusions are drawn.

2. MOTIVATION AND SIGNIFICANCE

Application of the first law of thermodynamics for an open, steady-state, isothermal, isobaric process with one input, one output, and no work production/consumption²⁵ yields

$$\dot{n}_{\text{out}}H(T, P, \{C_k^{\text{out}}\}_{k=1}^n) - \dot{n}_{\text{in}}H(T, P, \{C_k^{\text{in}}\}_{k=1}^n) = \dot{Q} \quad (1)$$

In the presence of heat-transfer irreversibility between the system (at T) and the surroundings (at T_σ), an entropy balance for the same process²⁵ yields

$$\dot{n}_{\text{out}}S(T, P, \{C_k^{\text{out}}\}_{k=1}^n) - \dot{n}_{\text{in}}S(T, P, \{C_k^{\text{in}}\}_{k=1}^n) - \frac{\dot{Q}}{T_\sigma} = \dot{S}_G \quad (2a)$$

where heat is exchanged with an infinite reservoir at temperature T_σ . Equation 2a denotes the general case of entropy generation for a process under the restrictions introduced at the beginning of this section. A model to which this equation corresponds is shown in Figure 1, with matching equations (eqs 10a and 10b, presented later in this work, indicating mass and molar entropy balances, respectively). All subsequent proofs and derivations included herein will also be based on this general representation.

For the special case of heat transfer reversibility between the system and the surroundings ($T_\sigma = T$), that same entropy balance (eq 2a) becomes

$$\dot{n}_{\text{out}}S(T, P, \{C_k^{\text{out}}\}_{k=1}^n) - \dot{n}_{\text{in}}S(T, P, \{C_k^{\text{in}}\}_{k=1}^n) - \frac{\dot{Q}}{T} = \dot{S}_G \quad (2b)$$

Since the Gibbs free energy can be defined in terms of entropy and energy as

$$\begin{aligned} \dot{n}_{\text{out}}G(T, P, \{C_k^{\text{out}}\}_{k=1}^n) - \dot{n}_{\text{in}}G(T, P, \{C_k^{\text{in}}\}_{k=1}^n) \\ = \dot{n}_{\text{out}}H(T, P, \{C_k^{\text{out}}\}_{k=1}^n) - \dot{n}_{\text{in}}H(T, P, \{C_k^{\text{in}}\}_{k=1}^n) \\ - T(\dot{n}_{\text{out}}S(T, P, \{C_k^{\text{out}}\}_{k=1}^n) - \dot{n}_{\text{in}}S(T, P, \{C_k^{\text{in}}\}_{k=1}^n)) \end{aligned} \quad (3)$$

for the reversible heat-transfer case, the following then holds:

$$\begin{aligned} \dot{S}_G \stackrel{(1)}{\underset{(2b)}{=}} \left\{ \dot{n}_{\text{in}}S(T, P, \{C_k^{\text{in}}\}_{k=1}^n) - \dot{n}_{\text{out}}S(T, P, \{C_k^{\text{out}}\}_{k=1}^n) \right. \\ \left. - \frac{\dot{n}_{\text{in}}H(T, P, \{C_k^{\text{in}}\}_{k=1}^n) - \dot{n}_{\text{out}}H(T, P, \{C_k^{\text{out}}\}_{k=1}^n)}{T} \right\} \stackrel{(3)}{\Rightarrow} \\ \dot{S}_G = \left\{ \frac{\dot{n}_{\text{in}}G(T, P, \{C_k^{\text{in}}\}_{k=1}^n) - \dot{n}_{\text{out}}G(T, P, \{C_k^{\text{out}}\}_{k=1}^n)}{T} \right\} \quad (4) \end{aligned}$$

From the above discussion, it is clear that entropy generation for an isothermal, isobaric reactor, with reversible heat transfer, is related to the change in Gibbs energy between the inlet and outlet composition. At the equilibrium state, the total Gibbs energy is at a minimum, with respect to all possible changes at the given temperature T and pressure P .²⁵ It then becomes clear that, for a fixed reactor inlet $\{C_k^{\text{in}}\}_{k=1}^n$, the entropy generated by the isothermal, isobaric reactor process, with reversible heat transfer, approaches its supremum value, when the reactor outlet $\{C_k^{\text{out}}\}_{k=1}^n$ approaches the equilibrium state that the underlying reaction scheme possesses at the reactor's operating temperature and pressure. Since it is approached for an infinite reactor size, one can loosely associate a general trend of increasing reactor network entropy generation with increasing reactor network volume, although this by no means implies that there is a unique correspondence between the two measures (i.e., there can exist multiple reactor networks with identical total network volume and different values of entropy generation, and vice versa, there can exist multiple reactor networks with identical entropy generation and different values of total network volume).

A more exact physical interpretation of entropy generation by a process is related to the thermodynamic efficiency of that process. Consider a complex manufacturing process that generates/consumes work and involves several subprocesses, including a reactor network subprocess. The efficiency of such a process can be assessed by quantifying, as lost work, the difference between real work generated/consumed when its subprocesses are irreversible and the ideal work generated/consumed

when its subprocesses are reversible. Summarizing the lost work for each of its subprocesses yields the lost work for the entire manufacturing process.²⁵ It becomes apparent from the above discussion that the synthesis of the most thermodynamically efficient overall process is equivalent to the minimization of the lost work summary for all subprocesses comprising the considered process. However, the lost work (W_{lost}) for a subprocess is equal to the product of the temperature of the surroundings (T_σ (K)) times the entropy generation of the subprocess (\dot{S}_G), i.e.,

$$\dot{W}_{\text{lost}} = T_\sigma \dot{S}_G \quad (5)$$

Thus, the synthesis of the most thermodynamically efficient overall process is equivalent to the minimization of the sum of the entropy generation terms for each subprocess comprising the considered process. The focus of this effort is on the quantification of entropy generation for an isothermal, isobaric reactor network as a first step toward the quantification of entropy generation for general complex manufacturing processes. Subsequent research efforts will also focus on other network types, such as nonisothermal, nonisobaric reactor networks, distillation networks, etc. Representing such networks as systems containing some subsystems that are isothermal, isobaric networks operating at different temperatures and pressures will allow the results obtained here to serve as building blocks for the quantification of these properties for general manufacturing processes. This will be the subject of future work.

Having provided physical interpretations of entropy generation for isothermal, isobaric reactor networks, it becomes apparent that it is advantageous to identify the energy consumption, and entropy generation for such a network at the early conceptual design stage, namely before a particular network structure is chosen. Given the wide array of choices for the reactor network selection, it is clear that no single value for the aforementioned two quantities can be identified. It would nevertheless be highly desirable to identify ranges of values for these quantities over all feasible reactor networks, and how other network design specifications may affect these ranges.

Commonly employed reactor network design specifications are related to the network's outlet concentrations. Examples include reactant conversion, alternative product selectivity, upper and/or lower bounds on outlet concentrations of particular species, etc. All these specifications can be readily represented in reactor network outlet concentration space. In that same space, the set of all attainable outlet concentration points, termed the Attainable Region (AR), can be readily quantified using a variety of techniques.^{20,21,26} A representation of all these attributes (attainable region, entropy generation, energy consumption, design specifications) on a common diagram would allow for a rigorous trade-off analysis among all these considerations while selecting an optimal reactor network structure.

It will be subsequently demonstrated in this paper how the IDEAS framework described above can be used to establish that the entropy generation and energy consumption of an isothermal, isobaric reactor network with irreversible heat transfer and known feed can be quantified as a function of only network outlet concentrations and independent of the network's internal structure (Theorem 1). This will allow for all the attributes discussed above to be represented on a single AR diagram, thus facilitating rigorous

trade-off analysis during reactor network design optimization. For energy-intensive processes, with high heating/cooling costs, it can be expected that minimization of lost work (which is equivalent to minimization of entropy generation) will lead to designs that are close to the economic optimum. This may not be the case for nonenergy intensive processes for which other objectives should be sought, such as maximizing profitability, including the installed equipment cost. Nevertheless, even in these latter cases, the simultaneous depiction of all these network properties on a single diagram can facilitate the design engineer in arriving at an economic optimum.

The strength of the new methodology is illustrated in the case study below.

3. APPLICABILITY OF IDEAS TO ISOTHERMAL REACTOR NETWORK SYNTHESIS

For this work, the following assumptions are considered:

- The reactor network is isothermal, i.e., all the reactors and streams are at the same temperature (T).
- The reactor network is isobaric, i.e., all the reactors and streams are at the same pressure (P).
- No work is consumed or generated.
- The reactor network consists of both CSTR and PFR reactor units.
- The universe of considered isothermal, isobaric reactors either consists only of units that accept heat or units that reject heat. This allows consideration of the reactors in which both endothermic and exothermic reactions occur, as long as the reactor's overall energy flow is in the same direction as the energy flow for every reactor in the network.
- An infinite reservoir at constant temperature T_σ is considered to provide heat to each reactor in the former case (net endothermic reaction, $T_\sigma > T$), or to remove heat from each reactor in the latter case (net exothermic reaction, $T_\sigma < T$).

It should be noted that isothermal reactor networks are not infrequent. Particularly, it is known that, for reactors in which multiple reactions are carried out, the operating temperature should be the highest allowable temperature, if the activation energies of the various reactions are such that the favorable product distribution is obtained at a high temperature.²⁷ Thus, these reactor networks should naturally be isothermal, with all reactors operating at the maximum allowable temperature.

The reactor model resulting from the aforementioned assumptions is illustrated in Figure 1, and the associated modeling equations for PFR ($\lambda = 0$) and CSTR ($\lambda = 1$) reactor units, are listed below. Equations 6a and 6b correspond to total mass balances, while eqs 7a and 7b correspond to component mass balances. Equation 8 clarifies the relationship between the i th species concentration (C_i) and the system's mass fractions $\{z_k\}_{k=1}^n$. Equations 9a (and 9b) and 10a (and 10b), shown later in this work, are the energy and entropy balances around the reactor, involving the mass (volumetric) heat generation and mass (volumetric) entropy generation functions, respectively. Equations 11a (and 11b) and 12a (and 12b), which are also shown later in this work, relate the heat generation and entropy generation rate functions to their mass (volumetric) counterparts, respectively. Equations 13 and 14 quantify molar entropy and molar enthalpy in terms of excess molar entropy

and enthalpy for any mixture, and will be applied to both the reactor unit's inlet and outlet streams.²⁵ Finally, eqs 15 and 16 quantify excess molar entropy and enthalpy in terms of liquid-phase activity coefficients, which are presumed available from some thermodynamic model, such as Wilson, NRTL, etc. The derivation of the excess molar enthalpy and entropy equations (eqs 15 and 16) can be found in Appendix A.

Reactor Model–Variable Density Model (Mass Basis):

$$\dot{m}^{\text{in}} = \dot{m}^{\text{out}} = \dot{m} \quad (6a)$$

$$\left\{ \begin{array}{l} \left\{ \frac{dz_k}{d\tau} = M_k R_k(\{C_i\}_{i=1}^n) \quad \forall k = 1, n \right\} \quad \lambda = 0 \\ \left\{ z_k|_{\tau=0} = z_k^{\text{in}}, \quad z_k|_{\tau=\sigma} = z_k^{\text{out}} \quad \forall k = 1, n \right\} \\ \left\{ z_k^{\text{in}} - z_k^{\text{out}} + \sigma M_k R_k(\{C_i^{\text{out}}\}_{i=1}^n) = 0 \quad \forall k = 1, n \right\} \quad \lambda = 1 \\ \sigma = \frac{V}{\dot{m}} \end{array} \right. \quad (7a)$$

$$C_i = C_i(\{z_j\}_{j=1}^{n-1}, T, P), \quad C_i^{\text{out}} = C_i(\{z_j^{\text{out}}\}_{j=1}^{n-1}, T, P)$$

$$\forall i = 1, n \quad (8a)$$

Equation 8a aims to capture the thermodynamic model of the underlying mixture. Several models can be brought into the form of eq 8a. For example, if a compressibility factor model (Z) is employed, then

$$C_i = x_i \left(\frac{P}{RT} \right) \left(\frac{1}{Z(\{x_j\}_{j=1}^{n-1}, T, P)} \right) \quad (8b)$$

$$x_i = \frac{z_i}{M_i \sum_{k=1}^n \left(\frac{z_k}{M_k} \right)} \quad \forall i = 1, n - 1 \quad (8c)$$

where R is the universal gas constant and x_i and z_i ($\forall i = 1, n$) designate the i th species mole fraction and mass fraction, respectively.

$$\begin{aligned} & \sum_{l=1}^n \left(\frac{z_l^{\text{in}}}{M_l} \right) H(T, P, \{C_i(\{z_j^{\text{in}}\}_{j=1}^{n-1}, T, P)\}_{i=1}^n) \\ & - \sum_{l=1}^n \left(\frac{z_l^{\text{out}}}{M_l} \right) H(T, P, \{C_i(\{z_j^{\text{out}}\}_{j=1}^{n-1}, T, P)\}_{i=1}^n) \\ & + Q_m = 0 \end{aligned} \quad (9a)$$

$$\begin{aligned} & \sum_{l=1}^n \left(\frac{z_l^{\text{in}}}{M_l} \right) S(T, P, \{C_i(\{z_j^{\text{in}}\}_{j=1}^{n-1}, T, P)\}_{i=1}^n) \\ & - \sum_{l=1}^n \left(\frac{z_l^{\text{out}}}{M_l} \right) S(T, P, \{C_i(\{z_j^{\text{out}}\}_{j=1}^{n-1}, T, P)\}_{i=1}^n) \\ & + \frac{Q_m}{T_\sigma} + S_G^m = 0 \end{aligned} \quad (10a)$$

$$\dot{Q} = Q_m \dot{m} \quad (11a)$$

$$\dot{S}_G = S_G^m \dot{m} \quad (12a)$$

Reactor Model–Constant Density Model (Molar Basis):

$$F^{\text{in}} = F^{\text{out}} = F \quad (6b)$$

$$\left\{ \begin{array}{l} \left\{ \frac{dC_k}{d\tau} = R_k(\{C_k\}_{k=1}^n) \quad \forall k = 1, n \right\} \quad \lambda = 0 \\ \left\{ C_k|_{\tau=0} = C_k^{\text{in}}, \quad C_k|_{\tau=\tau} = C_k^{\text{out}} \quad \forall k = 1, n \right\} \\ \left\{ C_k^{\text{in}} - C_k^{\text{out}} + R_k(\{C_k^{\text{out}}\}_{k=1}^n) \tau = 0 \quad \forall k = 1, n \right\} \quad \lambda = 1 \\ \tau = \frac{V}{F} \end{array} \right. \quad (7b)$$

$$\begin{aligned} & \left(\sum_{l=1}^n C_l^{\text{in}} \right) H(T, P, \{C_k^{\text{in}}\}_{k=1}^n) \\ & - \left(\sum_{l=1}^n C_l^{\text{out}} \right) H(T, P, \{C_k^{\text{out}}\}_{k=1}^n) + Q_F = 0 \end{aligned} \quad (9b)$$

$$\begin{aligned} & \left(\sum_{l=1}^n C_l^{\text{in}} \right) S(T, P, \{C_k^{\text{in}}\}_{k=1}^n) \\ & - \left(\sum_{l=1}^n C_l^{\text{out}} \right) S(T, P, \{C_k^{\text{out}}\}_{k=1}^n) + \frac{Q_F}{T_\sigma} + S_G^F = 0 \end{aligned} \quad (10b)$$

$$\dot{Q} = Q_F F \quad (11b)$$

$$\dot{S}_G = S_G^F F \quad (12b)$$

Entropy/Enthalpy Relations for Both VDF and CDF Models:

$$\begin{aligned} S(T, P, \{C_k\}_{k=1}^n) &= \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} S_k(T, P) \\ &+ S^E(T, P, \{C_k\}_{k=1}^n) \\ &- R \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \ln \left(\frac{C_k}{\sum_{l=1}^n C_l} \right) \end{aligned} \quad (13)$$

$$H(T, P, \{C_k\}_{k=1}^n) = \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} H_k(T, P) + H^E(T, P, \{C_k\}_{k=1}^n) \quad (14)$$

$$\begin{aligned} H^E(T, P, \{C_k\}_{k=1}^n) \\ = -RT^2 \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \frac{\partial [\ln \gamma_k(T, P, \{C_k\}_{k=1}^n)]}{\partial T} \Big|_{P, C_k} \end{aligned} \quad (15)$$

$$\begin{aligned} S^E(T, P, \{C_k\}_{k=1}^n) &= -RT \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \frac{\partial \ln \gamma_k(T, P, \{C_k\}_{k=1}^n)}{\partial T} \Big|_{P, C_k} \\ &- R \sum_{k=1}^n \left(\frac{C_k}{\sum_{l=1}^n C_l} \right) \ln \gamma_k(T, P, \{C_k\}_{k=1}^n) \end{aligned} \quad (16)$$

Having presented isothermal CSTR/PFR reactor models for the constant density (molar model) and variable density (mass model) cases, the applicability of IDEAS to the constant density reactor models is demonstrated next. In a similar manner, IDEAS can be readily shown to be applicable to the variable density reactor models as well, although this is not shown here in the interest of space.

The aforementioned reactor model can be employed to construct the following input–output information map:

$$\Phi: D \rightarrow R^{2n+7} \times R^3, \quad \Phi: u \rightarrow y$$

such that

$$\Phi: u = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \rightarrow y = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \Phi(u_1, u_2) = \begin{bmatrix} \Phi_1(u_1, u_2) \\ \Phi_2(u_1, u_2) \end{bmatrix}$$

where

$$\begin{aligned}
 D &\triangleq \{u \in R^{n+2} \times R: u_1 \geq 0 \wedge u_2 \geq 0\} \subset \{R^{n+2} \times R\} \\
 u^T &= [u_1^T \mid u_2^T] = [C_1^{\text{in}} \quad C_1^{\text{out}} \quad \dots \quad C_n^{\text{out}} \quad \lambda \mid F] \\
 y^T &= [y_1^T \mid y_2^T] = \Phi^T(u_1, u_2) \\
 &= [\tau \quad C_1^{\text{in}} \quad \dots \quad C_n^{\text{in}} \quad C_1^{\text{out}} \quad \dots \quad C_n^{\text{out}} \quad S^{\text{in}} \quad H^{\text{in}} \quad S^{\text{out}} \quad H^{\text{out}} \quad Q_F \quad S_G^F \mid F \quad \dot{Q} \quad \dot{S}_G]
 \end{aligned}$$

The evaluation of the image $\Phi^T(u_1, u_2)$, given u_1 and u_2 , is illustrated next for the constant density reactor case.

Consider that u_1 is known. For the CSTR model ($\lambda = 1$), τ can first be evaluated by solving eq 7b for the first species ($k = 1$). From the solution of eq 7b for all other species k ($\forall k = 2, n$), $\{C_k^{\text{in}}\}_{k=2}^n$ can be evaluated. For the PFR model ($\lambda = 0$), τ and $\{C_k^{\text{in}}\}_{k=2}^n$ can be evaluated through backward integration of eq 7b until C_1 is equal to C_1^{in} . With knowledge of the outlet/inlet species concentrations, since the network is isothermal and isobaric, the molar outlet/inlet entropy, and molar outlet/inlet enthalpy for each stream can be obtained from eqs 13 and 16, and eqs 14 and 15, respectively. Given the temperature of the environment (T_e), the volumetric utility consumption rate (Q_F) and volumetric entropy generation rate (S_G^F) can then be evaluated from eqs 9b and 10b, respectively. Evaluation of the reactor flow rate (F), heating/cooling rate (\dot{Q}), and entropy generation rate (\dot{S}_G) requires knowledge of both u_1 and u_2 and is performed using eqs 11b and 12b.

The above decompositions of the input vector u to u_1 and u_2 , of the output vector y to y_1 and y_2 , and of the map Φ to Φ_1 and Φ_2 are performed so that the following IDEAS properties can be shown to hold:

IDEAS Property 1:

$$\exists \Phi_3: R^{n+2} \rightarrow R^{2n+7}$$

such that

$$\Phi_1(u_1, u_2) = \Phi_3(u_1) \quad \forall (u_1, u_2) \in D$$

This implies that $y_1 \triangleq \Phi_1(u_1, u_2) = \Phi_3(u_1)$ can be evaluated based only on the knowledge of u_1 , independent of u_2 .

IDEAS Property 2:

$$\exists \Phi_4: R^{n+2} \rightarrow R^3$$

such that

$$\Phi_2(u_1, u_2) = \Phi_4(u_1) \cdot u_2 \quad \forall (u_1, u_2) \in D$$

This map is

$$\Phi_4: u_1 \triangleq \begin{bmatrix} C_1^{\text{in}} \\ C_1^{\text{out}} \\ \vdots \\ C_n^{\text{out}} \\ \lambda \end{bmatrix} \rightarrow \Phi_4(u_1) \triangleq [1 \quad Q_F \quad S_G^F]^T$$

Equations 10b and 11b can be used to readily verify that

$$y_2 \triangleq [F \quad \dot{Q} \quad \dot{S}_G]^T = [1 \quad \dot{Q} \quad S_G^F]^T \cdot F = \Phi_4(u_1) \cdot u_2$$

This implies that, for fixed u_1 , $\Phi_4(u_1)$ is a linear operator, and $y_2 \triangleq \Phi_2(u_1, u_2) = \Phi_4(u_1) \cdot u_2$ is linear in u_2 . Therefore, for a fixed u_1 , the employed reactor model is defined by a linear input–output map $\Phi_4(u_1)$. An infinite sequence $\{u_1(i)\}_{i=1}^\infty$, consisting of all possible values of u_1 , is then considered, such that the union of the considered u_1 values is dense in the set over which u_1 can vary. The map Φ_4 is then used to create the sequence $\{\Phi_4(u_1(i))\}_{i=1}^\infty$ of linear maps, each element of which is the image of an element of $\{u_1(i)\}_{i=1}^\infty$ under the map Φ_4 . These sequences are then used to define the domain and action of a linear operator (IDEAS OP) that quantifies the effect of all reactor units and has its domain and range be subsets of infinite dimensional spaces.

The IDEAS representation is illustrated in Figure 2 for a reactor network with n components, M network inlet streams, and N network outlet streams. Under the previously mentioned assumptions that the network is homogeneous, isothermal, and isobaric, the resulting IDEAS feasible region is defined by the total mass, component mass, energy, and entropy balance constraints given below:

$$F^I(j) = \sum_{i=1}^N F^{\text{OI}}(i, j) + \sum_{i=1}^\infty F^{\hat{\text{I}}}(i, j) \quad \forall j = 1, M \quad (17)$$

$$F^{\text{O}}(i) = \sum_{j=1}^M F^{\text{OI}}(i, j) + \sum_{j=1}^\infty F^{\hat{\text{O}}}(i, j) \quad \forall i = 1, N \quad (18)$$

$$F^{\hat{\text{I}}}(i) = \sum_{j=1}^M F^{\hat{\text{I}}}(i, j) + \sum_{j=1}^\infty F^{\hat{\text{I}}\hat{\text{O}}}(i, j) \quad \forall i = 1, \infty \quad (19)$$

$$F^{\hat{\text{O}}}(j) = \sum_{i=1}^N F^{\text{OI}}(i, j) + \sum_{i=1}^\infty F^{\hat{\text{I}}\hat{\text{O}}}(i, j) \quad \forall j = 1, \infty \quad (20)$$

$$F^{\hat{\text{O}}}(i) = F^{\hat{\text{I}}}(i) \quad \forall i = 1, \infty \quad (21)$$

$$\begin{aligned}
 C_k^{\hat{\text{I}}}(i) F^{\hat{\text{I}}}(i) &= \sum_{j=1}^M C_k^{\text{I}}(i) F^{\hat{\text{I}}}(i, j) + \sum_{j=1}^\infty C_k^{\hat{\text{O}}}(j) F^{\hat{\text{I}}\hat{\text{O}}}(i, j) \\
 &\quad \forall i = 1, \infty; \forall k = 1, n
 \end{aligned} \quad (22)$$

$$\begin{aligned}
 (C_k^{\hat{\text{O}}}(i))^L F^{\text{O}}(i) &\leq \left[\sum_{j=1}^M C_k^{\text{I}}(j) F^{\text{OI}}(i, j) + \sum_{j=1}^\infty C_k^{\hat{\text{O}}}(j) F^{\text{OI}\hat{\text{O}}}(i, j) \right] \\
 &\leq (C_k^{\hat{\text{O}}}(i))^U F^{\text{O}}(i) \quad \forall i = 1, N; \forall k = 1, n
 \end{aligned} \quad (23)$$

$$(F^{\text{O}}(i))^L \leq F^{\text{O}}(i) \leq (F^{\text{O}}(i))^U \quad \forall i = 1, N \quad (24)$$

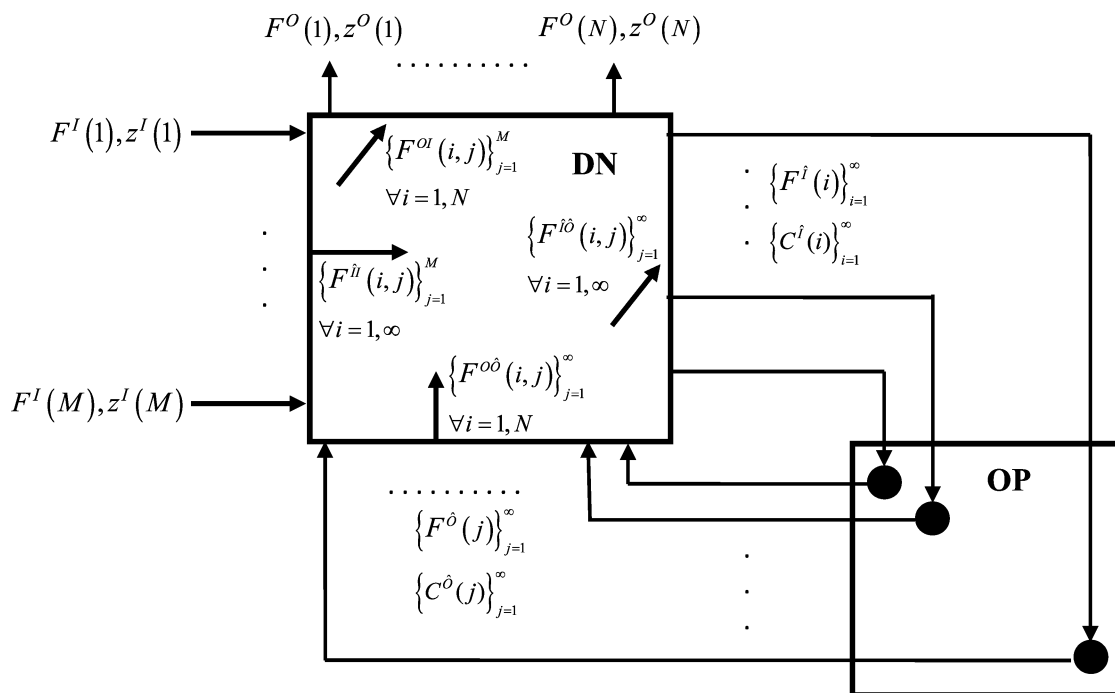


Figure 2. IDEAS representation for isothermal reactor network.

$$\begin{aligned} \dot{Q}^R(i) &= [H^{\hat{O}}(i) \left(\sum_{k=1}^n C_k^{\hat{O}}(i) \right) \left(\sum_{j=1}^N F^{OO}(j, i) \right) \\ &+ \sum_{j=1}^{\infty} F^{\hat{IO}}(j, i) - H^{\hat{I}}(i) \left(\sum_{k=1}^n C_k^{\hat{I}}(i) F^{\hat{I}}(i) \right)] \\ \forall i &= 1, \infty \end{aligned} \quad (25)$$

$$\begin{aligned} \dot{Q}^M(i) &= [H^{\hat{I}}(i) F^{\hat{I}}(i) - \sum_{j=1}^{\infty} (H^{\hat{O}}(j) \left(\sum_{k=1}^n C_k^{\hat{O}}(j) F^{\hat{IO}}(i, j) \right) \\ &- \sum_{j=1}^M (H^{\hat{I}}(j) \left(\sum_{k=1}^n C_k^{\hat{I}}(j) F^{\hat{II}}(i, j) \right))] \end{aligned} \quad (26)$$

$$\begin{aligned} \dot{Q}(i) &\triangleq \dot{Q}^R(i) + \dot{Q}^M(i) \Rightarrow \\ \dot{Q}(i) &= [H^{\hat{O}}(i) \left(\sum_{k=1}^n C_k^{\hat{O}}(i) \right) \left(\sum_{j=1}^N F^{OO}(j, i) \right) \\ &+ \sum_{j=1}^{\infty} F^{\hat{IO}}(j, i) - \sum_{j=1}^{\infty} (H^{\hat{O}}(j) \left(\sum_{k=1}^n C_k^{\hat{O}}(j) F^{\hat{IO}}(i, j) \right) \\ &- \sum_{j=1}^M (H^{\hat{I}}(j) \left(\sum_{k=1}^n C_k^{\hat{I}}(j) F^{\hat{II}}(i, j) \right))] \quad \forall i = 1, \infty \end{aligned} \quad (27)$$

$$\begin{aligned} \dot{Q}^O(j) &= [(H^{\hat{O}}(j) \left(\sum_{k=1}^n C_k^{\hat{O}}(j) F^{\hat{O}}(j) \right) \\ &- \sum_{i=1}^{\infty} (H^{\hat{O}}(i) \left(\sum_{k=1}^n C_k^{\hat{O}}(i) F^{OO}(j, i) \right) \\ &- \sum_{i=1}^M (H^{\hat{I}}(i) \left(\sum_{k=1}^n C_k^{\hat{I}}(i) F^{OI}(j, i) \right))] \quad \forall j = 1, N \end{aligned} \quad (28)$$

$$\begin{aligned} \dot{S}_G(i) &= \left[S^{\hat{O}}(i) \left(\sum_{k=1}^n C_k^{\hat{O}}(i) \right) \left(\sum_{j=1}^N F^{OO}(j, i) + \sum_{j=1}^{\infty} F^{\hat{IO}}(j, i) \right) \right. \\ &- \sum_{j=1}^{\infty} (S^{\hat{O}}(j) \left(\sum_{k=1}^n C_k^{\hat{O}}(j) F^{\hat{IO}}(i, j) \right) \\ &- \sum_{j=1}^M (S^{\hat{I}}(j) \left(\sum_{k=1}^n C_k^{\hat{I}}(j) F^{\hat{II}}(i, j) \right) - \frac{\dot{Q}(i)}{T_{\sigma}} \left. \right] \\ \forall i &= 1, \infty \end{aligned} \quad (29)$$

$$\begin{aligned} \dot{S}_G(j) &= \left[(S^{\hat{O}}(j) \left(\sum_{k=1}^n C_k^{\hat{O}}(j) F^{\hat{O}}(j) \right) \right. \\ &- \sum_{i=1}^{\infty} (S^{\hat{O}}(i) \left(\sum_{k=1}^n C_k^{\hat{O}}(i) F^{OO}(j, i) \right) \\ &- \sum_{i=1}^M (S^{\hat{I}}(i) \left(\sum_{k=1}^n C_k^{\hat{I}}(i) F^{OI}(j, i) \right) - \frac{\dot{Q}(j)}{T_{\sigma}} \left. \right] \\ \forall j &= 1, N \end{aligned} \quad (30)$$

$$\left\{ \begin{aligned} \frac{dC_k(i)}{d\tau} &= R_k(\{C_k(i)\}_{k=1}^n) \quad \forall k = 1, n \\ C_k(i)|_{\tau=0} &= C_k^{\hat{I}}(i) C_k(i)|_{\tau=\tau} = C_k^{\hat{O}}(i) \end{aligned} \right\} \quad \lambda(i) = 0, \forall i = 1, \infty \quad (31a)$$

$$\begin{aligned} C_k^{\hat{I}}(i) - C_k^{\hat{O}}(i) + R_k(\{C_k^{\hat{O}}(i)\}_{k=1}^n) \tau &= 0 \\ \lambda(i) &= 1, \forall i = 1, \infty \end{aligned} \quad (31b)$$

$$\begin{aligned} F^{\hat{I}} &\geq 0; \quad F^{\hat{O}} \geq 0; \quad F^{OI} \geq 0; \quad F^{\hat{I}} \geq 0; \quad F^{\hat{O}} \geq 0; \\ F^{\hat{II}} &\geq 0; \quad F^{OO} \geq 0; \quad F^{\hat{IO}} \geq 0 \end{aligned}$$

Equations 17–20 correspond to mixing and splitting total mass balances in the distribution network (DN). Equation 21 represents the action of the OP unit. Equation 22 represents a component mass balance at the OP inlet, while eq 23 represents a component mass balance at the DN outlet combined with stream composition related specifications on the network outlets. Equation 24 represents upper and lower bounds on each DN network outlet flow variable. Equations 25 and 26 are based on energy balances at each reactor inlet and at each reactor to help quantify the utility consumption around the i th reactor due to reaction, $\dot{Q}^R(i)$ ($\forall i = 1, \infty$), and the utility consumption due to the mixing of the DN streams that constitute the inlet stream of the i th reactor, $\dot{Q}^M(i)$ ($\forall i = 1, \infty$). These two utility consumptions are considered together to always have either a heating or cooling effect, releasing or absorbing heat to the infinite reservoir that interacts energetically with the reactor network. In this case, both utility consumptions can be combined into one term, quantifiable by eq 27, which yields the total utility consumption around the augmented i th reactor $\dot{Q}(i)$ ($\forall i = 1, \infty$). Equation 28 is based on an energy balance that helps quantify the utility consumption $\dot{Q}^O(j)$ ($\forall j = 1, N$), because of mixing at the j th outlet at the DN network outlet. Similarly, eqs 29 and 30 are based on entropy balances that help quantify the entropy generation around the augmented i th reactor, $\dot{S}_G(i)$ ($\forall i = 1, \infty$) and the entropy generation due to mixing at the j th outlet of the IDEAS DN network, $\dot{S}_G^O(j)$ ($\forall j = 1, N$), respectively. Finally, the inlet and outlet compositions ($C_k^I(i)$ and $C_k^O(i)$) of every OP unit must satisfy relation (31a) for PFR reactors and relation (31b) for CSTR reactors.

4. REACTOR NETWORK UTILITY CONSUMPTION AND ENTROPY GENERATION FORMULATIONS

The heat generation (or consumption) rate of the reactor network is equal to the sum of heat generation (or consumption) rate at every reactor, and every overall network outlet mixing junction. Similarly, the entropy generation rate of the network is equal to the sum of entropy generation rates at every reactor and every overall network outlet mixing junction. This yields the following mathematical expressions for these entities:

$$\dot{Q}^T = \sum_{i=1}^{\infty} \dot{Q}(i) + \sum_{j=1}^N \dot{Q}^O(j) \quad (32)$$

$$\dot{S}_G^T = \sum_{i=1}^{\infty} \dot{S}_G(i) + \sum_{j=1}^N \dot{S}_G^O(j) \quad (33)$$

The above equations can be used to define network utility consumption and entropy generation constraints in IDEAS formulations of the reactor network synthesis problem. However, the theoretical development below will demonstrate that, when all feasible reactors exhibit heat generation (or consumption), the above-derived formulas can be simplified to the point where both utility consumption and entropy generation are only related to the overall network's inlets and outlets.

Theorem 1: Consider the homogeneous, isothermal, isobaric reactor network illustrated in Figure 2, featuring n components, M network inlet streams, and N network outlet streams. Under the assumptions that (i) all feasible reactors and network outlet mixing junctions exhibit heat generation (or consumption), (ii) all network concentrations are bounded, (iii) the molar

enthalpy and entropy functions are bounded over their domain in temperature–pressure–composition space, and (iv) the total mass flow in the network is finite, the network's utility consumption and entropy generation satisfy the following:

$$\begin{aligned} \dot{Q}^T = & \left[\sum_{j=1}^N (H^O(j) (\sum_{k=1}^n C_k^O(j)) F^O(j)) \right. \\ & \left. - \sum_{i=1}^M (H^I(i) (\sum_{k=1}^n C_k^I(i)) F^I(i)) \right] \end{aligned} \quad (34)$$

$$\begin{aligned} \dot{S}_G^T = & \left[\sum_{j=1}^N \left(\left(S^O(j) - \frac{H^O(j)}{T_\sigma} \right) (\sum_{k=1}^n C_k^O(j)) F^O(j) \right) \right. \\ & \left. - \sum_{i=1}^M \left(\left(S^I(i) - \frac{H^I(i)}{T_\sigma} \right) (\sum_{k=1}^n C_k^I(i)) F^I(i) \right) \right] \end{aligned} \quad (35)$$

Proof: Equations 27, 28, and 32 imply the following:

$$\begin{aligned} \dot{Q}^T = & \left[\sum_{i=1}^{\infty} [H^{\hat{O}}(i) (\sum_{k=1}^n C_k^{\hat{O}}(i)) (\sum_{j=1}^N F^{O\hat{O}}(j, i)) \right. \\ & + \sum_{j=1}^{\infty} F^{\hat{I}\hat{O}}(j, i) - \sum_{j=1}^{\infty} (H^{\hat{O}}(j) (\sum_{k=1}^n C_k^{\hat{O}}(j)) F^{\hat{I}\hat{O}}(i, j)) \\ & - \sum_{j=1}^M (H^{\hat{I}}(j) (\sum_{k=1}^n C_k^{\hat{I}}(j)) F^{\hat{I}\hat{I}}(i, j))] \\ & + \sum_{j=1}^N [(H^O(j) (\sum_{k=1}^n C_k^O(j)) F^O(j)) \\ & - \sum_{i=1}^{\infty} (H^{\hat{O}}(i) (\sum_{k=1}^n C_k^{\hat{O}}(i)) F^{O\hat{O}}(j, i)) \\ & - \sum_{i=1}^M (H^{\hat{I}}(i) (\sum_{k=1}^n C_k^{\hat{I}}(i)) F^{O\hat{I}}(j, i))]] \Leftrightarrow \\ \dot{Q}^T = & \left[\sum_{i=1}^{\infty} \sum_{j=1}^N (H^{\hat{O}}(i) (\sum_{k=1}^n C_k^{\hat{O}}(i)) F^{O\hat{O}}(j, i)) \right. \\ & + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (H^{\hat{O}}(i) (\sum_{k=1}^n C_k^{\hat{O}}(i)) F^{\hat{I}\hat{O}}(j, i)) \\ & - \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (H^{\hat{O}}(j) (\sum_{k=1}^n C_k^{\hat{O}}(j)) F^{\hat{I}\hat{O}}(i, j)) \\ & - \sum_{i=1}^{\infty} \sum_{j=1}^M (H^{\hat{I}}(j) (\sum_{k=1}^n C_k^{\hat{I}}(j)) F^{\hat{I}\hat{I}}(i, j)) \\ & + \sum_{j=1}^N (H^O(j) (\sum_{k=1}^n C_k^O(j)) F^O(j)) \\ & - \sum_{j=1}^N \sum_{i=1}^{\infty} (H^{\hat{O}}(i) (\sum_{k=1}^n C_k^{\hat{O}}(i)) F^{O\hat{O}}(j, i)) \\ & \left. - \sum_{j=1}^N \sum_{i=1}^M (H^{\hat{I}}(i) (\sum_{k=1}^n C_k^{\hat{I}}(i)) F^{O\hat{I}}(j, i)) \right] \end{aligned}$$

Given the theorem's assumptions that (i) all network concentrations are bounded, (ii) the molar enthalpy and entropy

functions are bounded over their domain in temperature–pressure–composition space, and (iii) the total mass flow in the network is finite, all seven sums in the right-hand side of the above equation for \dot{Q}^T are absolutely summable. Then, all these sums are finite, and Fubini's theorem for infinite sums²⁸ suggests that the order of summation can be switched for each sum. It then becomes apparent that the first and second terms cancel with the sixth and third terms, respectively. Then,

$$\begin{aligned}\dot{Q}^T &= \left[-\sum_{i=1}^{\infty} \sum_{j=1}^M (H^I(j) \left(\sum_{k=1}^n C_k^I(j) \right) F^{\hat{I}}(i, j)) \right. \\ &\quad + \sum_{j=1}^N (H^O(j) \left(\sum_{k=1}^n C_k^O(j) \right) F^O(j)) \\ &\quad \left. - \sum_{j=1}^N \sum_{i=1}^M (H^I(i) \left(\sum_{k=1}^n C_k^I(i) \right) F^{OI}(j, i)) \right] \Leftrightarrow \\ \dot{Q}^T &= \left[\sum_{j=1}^N (H^O(j) \left(\sum_{k=1}^n C_k^O(j) \right) F^O(j)) \right. \\ &\quad \left. - \sum_{i=1}^M H^I(i) \left(\sum_{k=1}^n C_k^I(i) \right) \left(\sum_{j=1}^N F^{\hat{I}}(j, i) + \sum_{j=1}^N F^{OI}(j, i) \right) \right]\end{aligned}$$

The use of eq 17 then establishes the desired formula for \dot{Q}^T .

Next consider entropy generation. Equations 29, 30, and 33 imply the following:

$$\begin{aligned}\dot{S}_G^T &= \sum_{i=1}^{\infty} \left[S^{\hat{O}}(i) \left(\sum_{k=1}^n C_k^{\hat{O}}(i) \right) \left(\sum_{j=1}^N F^{O\hat{O}}(j, i) + \sum_{j=1}^N F^{\hat{I}\hat{O}}(j, i) \right) \right. \\ &\quad - \sum_{j=1}^{\infty} (S^{\hat{O}}(j) \left(\sum_{k=1}^n C_k^{\hat{O}}(j) \right) F^{\hat{I}\hat{O}}(i, j)) \\ &\quad \left. - \sum_{j=1}^M (S^I(j) \left(\sum_{k=1}^n C_k^I(j) \right) F^{\hat{I}}(i, j)) - \frac{\dot{Q}(i)}{T_\sigma} \right] \\ &\quad + \sum_{j=1}^N \left[(S^O(j) \left(\sum_{k=1}^n C_k^O(j) \right) F^O(j)) \right. \\ &\quad - \sum_{i=1}^{\infty} (S^{\hat{O}}(i) \left(\sum_{k=1}^n C_k^{\hat{O}}(i) \right) F^{O\hat{O}}(j, i)) \\ &\quad \left. - \sum_{i=1}^M (S^I(i) \left(\sum_{k=1}^n C_k^I(i) \right) F^{OI}(j, i)) - \frac{\dot{Q}^O(j)}{T_\sigma} \right] \Leftrightarrow \\ \dot{S}_G^T &= \sum_{i=1}^{\infty} \sum_{j=1}^N (S^{\hat{O}}(i) \left(\sum_{k=1}^n C_k^{\hat{O}}(i) \right) F^{O\hat{O}}(j, i)) \\ &\quad + \sum_{i=1}^{\infty} \sum_{j=1}^N (S^{\hat{O}}(i) \left(\sum_{k=1}^n C_k^{\hat{O}}(i) \right) F^{\hat{I}\hat{O}}(j, i)) \\ &\quad - \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (S^{\hat{O}}(j) \left(\sum_{k=1}^n C_k^{\hat{O}}(j) \right) F^{\hat{I}\hat{O}}(i, j)) \\ &\quad - \sum_{i=1}^{\infty} \sum_{j=1}^M (S^I(j) \left(\sum_{k=1}^n C_k^I(j) \right) F^{\hat{I}}(i, j)) - \frac{\sum_{i=1}^{\infty} \dot{Q}(i)}{T_\sigma} \\ &\quad + \sum_{j=1}^N (S^O(j) \left(\sum_{k=1}^n C_k^O(j) \right) F^O(j)) \\ &\quad - \sum_{j=1}^N \sum_{i=1}^{\infty} (S^{\hat{O}}(i) \left(\sum_{k=1}^n C_k^{\hat{O}}(i) \right) F^{O\hat{O}}(j, i)) \\ &\quad - \sum_{j=1}^N \sum_{i=1}^M (S^I(i) \left(\sum_{k=1}^n C_k^I(i) \right) F^{OI}(j, i)) - \frac{\sum_{j=1}^N \dot{Q}^O(j)}{T_\sigma}\end{aligned}$$

Employing again Fubini's theorem for infinite sums, and based on similar arguments to those provided above, allows us to cancel the first and second terms with the sixth and third terms, respectively, in the right-hand side of the above expression. Then, using eq 32, and the newly established eq 34, yields

$$\begin{aligned}\dot{S}_G^T &= -\sum_{i=1}^{\infty} \sum_{j=1}^M (S^I(j) \left(\sum_{k=1}^n C_k^I(j) \right) F^{\hat{I}}(i, j)) \\ &\quad + \sum_{j=1}^N (S^O(j) \left(\sum_{k=1}^n C_k^O(j) \right) F^O(j)) \\ &\quad - \sum_{j=1}^N \sum_{i=1}^M (S^I(i) \left(\sum_{k=1}^n C_k^I(i) \right) F^{OI}(j, i)) \\ &\quad - \frac{1}{T_\sigma} \left[\sum_{j=1}^N (H^O(j) \left(\sum_{k=1}^n C_k^O(j) \right) F^O(j)) \right. \\ &\quad \left. - \sum_{i=1}^M (H^I(i) \left(\sum_{k=1}^n C_k^I(i) \right) F^I(i)) \right] \Leftrightarrow \\ \dot{S}_G^T &= \sum_{j=1}^N (S^O(j) \left(\sum_{k=1}^n C_k^O(j) \right) F^O(j)) \\ &\quad - \sum_{j=1}^M (S^I(j) \left(\sum_{k=1}^n C_k^I(j) \right) \left(\sum_{i=1}^{\infty} F^{\hat{I}}(i, j) + \sum_{i=1}^N F^{OI}(i, j) \right)) \\ &\quad - \frac{1}{T_\sigma} \left[\sum_{j=1}^N (H^O(j) \left(\sum_{k=1}^n C_k^O(j) \right) F^O(j)) \right. \\ &\quad \left. - \sum_{i=1}^M (H^I(i) \left(\sum_{k=1}^n C_k^I(i) \right) F^I(i)) \right]\end{aligned}$$

The use of eq 17 then establishes the desired formula for \dot{S}_G^T .

The importance of the above theorem is best realized when considering a nonisothermal reactor network. In that case, entropy generation cannot be quantified solely based on the inlets and outlets of the reactor network; it also is dependent on the internal network structure. The reason is that some of the network's reactors may be exothermic, while others are endothermic; therefore, some of the reactors may be heat-integrated, exchanging heat with each other. In fact, as the theorem demonstrates, even for an isothermal reactor network, entropy generation cannot be quantified solely based on the inlets and outlets of the reactor network; it also is dependent on the internal network structure. Indeed, if some reactors are exothermic and others are endothermic, and/or if the mixing unit that yields the overall reactor network outlet is exothermic (endothermic) and the network reactors are endothermic (exothermic), then entropy generation is dependent on the network structure. The exothermic reactors would provide heat to a reservoir whose temperature T_C is below the network temperature T , while the endothermic would receive heat from a reservoir whose temperature T_H is above the network temperature T . Therefore, the resulting contributions to the overall network energy generation/consumption cannot be added, rendering the network structure, in this case, essential to the calculation. On the other hand, when all reactors are exothermic (endothermic) and the product mixer unit is also exothermic (endothermic), then the above theorem establishes that the network's total utility consumption \dot{Q}^T and entropy generation \dot{S}_G^T are dependent only on the network inlet and outlet information and are not dependent on the network structure. In turn, this implies that the synthesis of isothermal, isobaric reactor networks where entropy generation and utility

consumption levels are quantified can be pursued within the AR conceptual framework.²⁹ Even though the development leading to this result employed the constant density reactor model case, a similar result where the total network utility consumption and entropy generation are dependent only on the network inlet and outlet information and not on the network structure can be readily obtained using the variable density reactor model case. ■

5. ATTAINABLE REGION-BASED QUANTIFICATION OF ENTROPY GENERATION AND UTILITY CONSUMPTION FOR ISOTHERMAL REACTOR NETWORKS

It has been determined above that entropy generation and utility consumption network properties are dependent only on the reactor network's inlet and outlet compositions. Consider a single inlet–single outlet (SISO) reactor network with known inlet composition and known reaction kinetics. The collection of all feasible reactor network outlet concentration vectors then is a convex subset of concentration space called the Attainable Region (AR). Since any point of the AR represents a feasible reactor network's outlet composition vector, and given that the reactor network's inlet composition vector is known, the above theorem suggests that a value of entropy generation and a value of utility consumption can be associated with each AR point.

The AR can be quantified either by using a linear programming approach,²⁰ a bounding plane approach,²⁶ or the Shrink-Wrap algorithm.²¹ The latter procedure is cursively described as follows. Starting with an initial convex superset guaranteed to contain the AR, a finite collection of points approximating the set is considered. At each extreme point of this approximated set, backward PFR and CSTR trajectories are generated and their intersection with the approximated superset is examined. If such an intersection exists, the current extreme point is kept; otherwise, it is discarded, thus reducing the set. The procedure continues by identifying the list of extreme points for the reduced set, and repeating the extreme point elimination process. The procedure concludes if all extreme points satisfy the PFR/CSTR trajectory criterion or represent a feed point. The final list of extreme points constitutes an approximation of the true AR, which can be refined by considering a larger number of points to approximate the initial convex superset.

The dimension of the concentration space in which the AR is constructed can be reduced, if linear dependence relations are satisfied by the generation rates of the species involved in the reaction scheme.²² In particular, for a SISO reactor network, if relation (36) holds true, then relation (37) holds true as well for any stream in the reactor network.

$$\sum_{k=1}^n \eta_k R_k = 0 \quad (36)$$

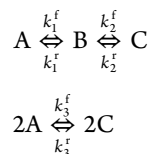
$$\sum_{k=1}^n \eta_k (C_k - C_k^I) = 0 \quad (37)$$

where η_k is a scalar, R_k is the generation rate of species k ($\forall k = 1, n$), C_k is the concentration of species k ($\forall k = 1, n$) in any stream, and C_k^I is the concentration of species k ($\forall k = 1, n$) in the network inlet stream.

The above results for AR construction and dimensionality reduction, coupled with the results of the theorem, will be next utilized in a case study that quantifies entropy generation and energy consumption for feasible reactor networks.

6. CASE STUDY

Consider the following reversible reaction scheme, taking place at $T = 400$ K and $P = 10^5$ Pa, in a homogeneous, isothermal, isobaric, constant-density, and SISO network, with a feed concentration of 1 mol/m^3 of pure reactant A and volumetric feed flow rate of $1 \text{ m}^3/\text{s}$. The reaction scheme is as follows:



All reactions obey simple elementary rate laws, such that the resulting species generation rates can be written as

$$R_A = -k_1^f \left(C_A - \frac{C_B}{K_1} \right) - k_3^f \left(C_A^2 - \frac{C_C^2}{K_1^2 K_2^2} \right)$$

$$R_B = k_1^f \left(C_A - \frac{C_B}{K_1} \right) - k_2^f \left(C_B - \frac{C_C}{K_2} \right)$$

$$R_C = k_2^f \left(C_B - \frac{C_C}{K_2} \right) + k_3^f \left(C_A^2 - \frac{C_C^2}{K_1^2 K_2^2} \right)$$

where

$$\begin{aligned} K_1 &= \frac{C_{Be}}{C_{Ae}} = \frac{k_1^f}{k_1^r}, & K_2 &= \frac{C_{Ce}}{C_{Be}} = \frac{k_2^f}{k_2^r}, \\ K_3 &= \frac{C_{Ce}^2}{C_{Ae}^2} = K_1^2 K_2^2 = \frac{k_3^f}{k_3^r} \end{aligned}$$

Close examination of the above reaction scheme reveals that

$$R_A + R_B + R_C = 0$$

Thus, application of the aforementioned dimensionality reduction principle, for SISO reactor networks, reveals that, for any reactor network stream, it holds:

$$C_A + C_B + C_C = C_A^0 + C_B^0 + C_C^0 = C_A^0 = 1 \text{ mol/m}^3$$

At equilibrium, it holds that $R_B = 0$, and $R_C = 0$. Therefore,

$$\begin{aligned} R_A + R_C = 0 &\Leftrightarrow k_1^f \left(C_{Ae} - \frac{C_{Be}}{K_1} \right) + k_2^f \left(C_{Be} - \frac{C_{Ce}}{K_2} \right) \\ &= 0 \xrightarrow{C_{Ce} = C_A^0 - C_{Ae} - C_{Be}} \\ &\quad \left(k_1^f - \frac{k_2^f}{K_2} \right) \\ C_{Be} &= \frac{\left(\frac{k_1^f}{K_1} + k_2^f + \frac{k_2^f}{K_2} \right) C_{Ae} + \frac{\frac{k_2^f}{K_2} C_A^0}{\left(\frac{k_1^f}{K_1} + k_2^f + \frac{k_2^f}{K_2} \right)} \end{aligned}$$

Using the new variables

$$\alpha \triangleq \frac{k_1^f - \frac{k_2^f}{K_2}}{\frac{k_1^f}{K_1} + k_2^f + \frac{k_2^f}{K_2}} \quad \text{and} \quad \beta \triangleq \frac{\frac{k_2^f}{K_2} C_A^0}{\frac{k_1^f}{K_1} + k_2^f + \frac{k_2^f}{K_2}}$$

then yields $C_{Be} = \alpha C_{Ae} + \beta$. Combining with $R_A = 0$ yields

$$k_3^f \left[\frac{(\alpha + 1)^2}{K_1^2 K_2^2} - 1 \right] C_{Ae}^2 - \left[k_1^f \left(1 - \frac{\alpha}{K_1} \right) + 2k_3^f \frac{(C_A^0 - \beta)(\alpha + 1)}{K_1^2 K_2^2} \right] C_{Ae} + \left[k_1^f \frac{\beta}{K_1} + k_3^f \frac{(C_A^0 - \beta)^2}{K_1^2 K_2^2} \right] = 0$$

For given kinetic and equilibrium constants and given network feed composition C_{Ae} , the above quadratic equation can determine the equilibrium concentration of species A. The equilibrium concentration of species B and C can then be trivially obtained.

The reactor network's inlet and outlet are considered to be at the reactor network's operating temperature ($T = 400$ K) and pressure ($P = 10^5$ Pa), and the reacting mixture is considered to be ideal, i.e., mixing effects are neglected and excess entropy/enthalpy terms are set to zero. The molar entropy (S_k) and the molar enthalpy (H_k) of the three pure species at $T = 400$ K and $P = 10^5$ Pa are shown in Table 1. These values suggest that each

Table 1. Molar Entropies and Enthalpies of Pure Species A, B, and C at $T = 400$ K and $P = 10^5$ Pa

	$k = A$	$k = B$	$k = C$
S_k (J/(mol K))	−451	−443	−435
H_k (J/mol)	−24 437	−25 429	−25 125
G_k^0 (J/mol)	155 963	151 771	148 875
α_k (J/(mol K))	−368.99	−357.66	−350.68

reactor in the reactor network requires cooling, which is provided by an infinite reservoir at $T_\sigma = 298$ K. For this reservoir temperature, the quantity α_k , which is defined as $\alpha_k(T, P) \triangleq S_k(T, P) - [(H_k(T, P))/T_\sigma]$, can be evaluated for each species. If one considers no pressure dependence of the enthalpy and entropy functions, this allows evaluation of the pure species

Gibbs free energy, at standard state (liquid at $P = 10^5$ Pa) and at the reactor network temperature $T = 400$ K, as

$$G_k^0(T = 400 \text{ K}, P = 10^5 \text{ Pa}) \equiv H_k(T = 400 \text{ K}, P = 10^5 \text{ Pa}) - 400 \cdot S_k(T = 400 \text{ K}, P = 10^5 \text{ Pa})$$

From the Gibbs free energy values of the pure species in Table 1, the reaction Gibbs free energies for reactions 1 and 2 are $\Delta G_{\text{React},1}^0 = G_B^0 - G_A^0 = -4192$ J/mol, and $\Delta G_{\text{React},2}^0 = G_C^0 - G_B^0 = -2897$ J/mol. In turn, the equilibrium constants for the three reactions can be evaluated as

$$K_1 \equiv \exp\left(\frac{-\Delta G_{\text{React},1}^0}{RT}\right) = \frac{k_1^f}{k_1^b} = 3.527$$

$$K_2 \equiv \exp\left(\frac{-\Delta G_{\text{React},2}^0}{RT}\right) = \frac{k_2^f}{k_2^b} = 2.389$$

and

$$K_3 \equiv \exp\left(\frac{-\Delta G_{\text{React},3}^0}{RT}\right) = K_1^2 K_2^2 = \frac{k_3^f}{k_3^b} = 70.99$$

Considering the forward kinetic constants of the three reactions to be $k_1^f = 1 \text{ s}^{-1}$, $k_2^f = 0.1 \text{ s}^{-1}$, $k_3^f = 2 \text{ (m}^3/\text{mol)}^2 \text{ s}^{-1}$ yields $k_1^f/K_1 = 0.2835 \text{ s}^{-1}$, $k_2^f/K_2 = 0.04185 \text{ s}^{-1}$, and $k_3^f/(K_1^2 K_2^2) = 0.0281 \text{ (m}^3/\text{mol)}^2 \text{ s}^{-1}$, and $\alpha = 2.252$ and $\beta = 0.0983$ for $C_A^0 = 1 \text{ mol/m}^3$. In turn, this yields the quadratic equation $-1.7C_{Ae}^2 - 0.52C_{Ae} + 0.05 = 0$, which has a single physically meaningful positive root: $C_{Ae} = 0.0768 \text{ mol/m}^3$. The corresponding equilibrium concentration of species B can then be evaluated as $C_{Be} = 0.2712 \text{ mol/m}^3$, which is consistent with the AR results shown in Figures 3 and 4, obtained using the Shrink-Wrap algorithm.²¹ (The C_1 and C_2 axes correspond to C_A and C_B , respectively, in Figure 3, whereas, in Figure 4, they correspond to C_C and C_B , respectively.)

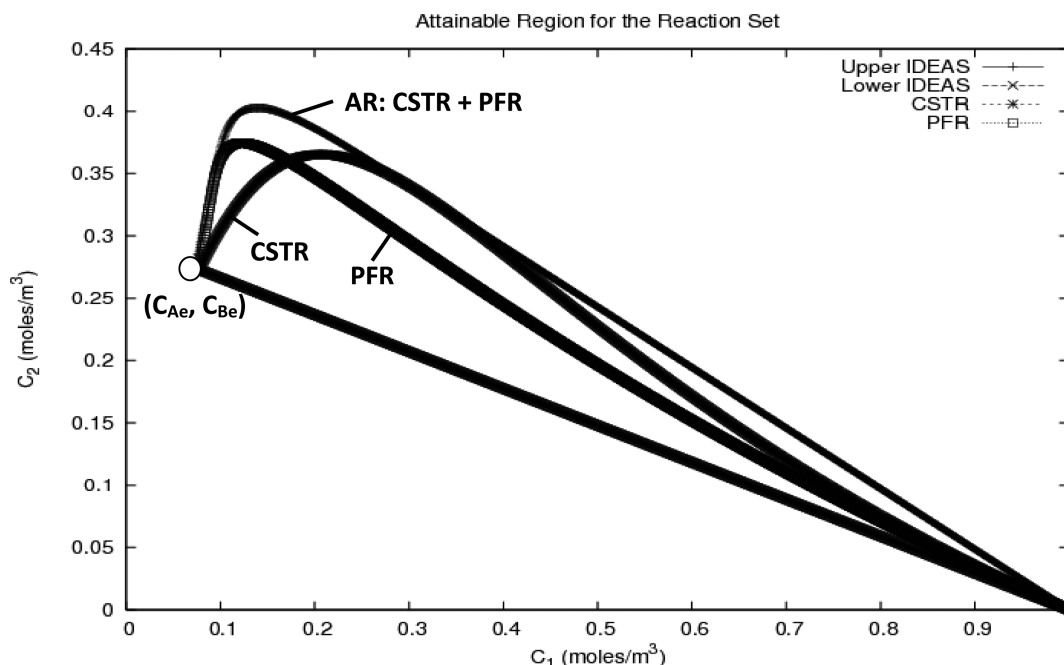


Figure 3. Attainable region (AR) and CSTR/PFR trajectories that determine the AR (discretization 3000×3000 ; C_1 and C_2 correspond to C_A and C_B , respectively).

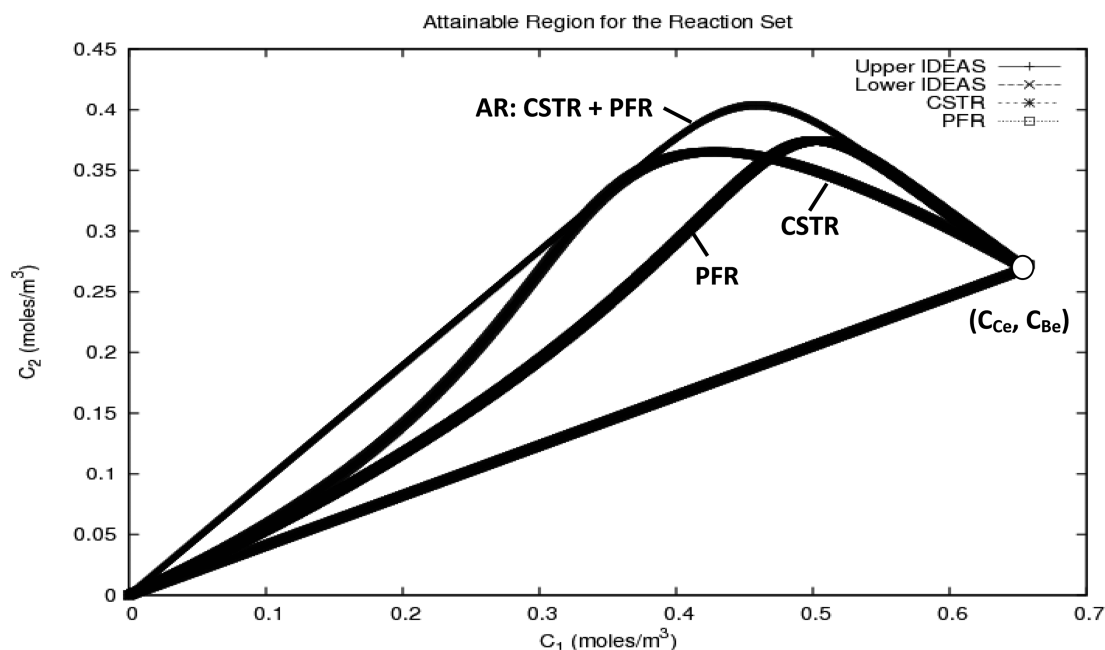


Figure 4. Attainable region (AR) and CSTR/PFR trajectories that determine the AR (discretization 3000×3000 ; C_1 and C_2 correspond to C_C and C_B , respectively).

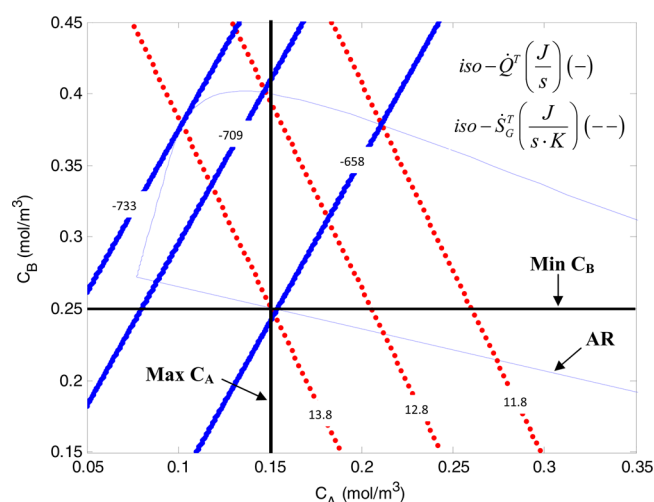


Figure 5. Entropy generation (\dot{S}_G^T) and utility consumption (\dot{Q}^T) isoclines on a C_B vs C_A AR diagram.

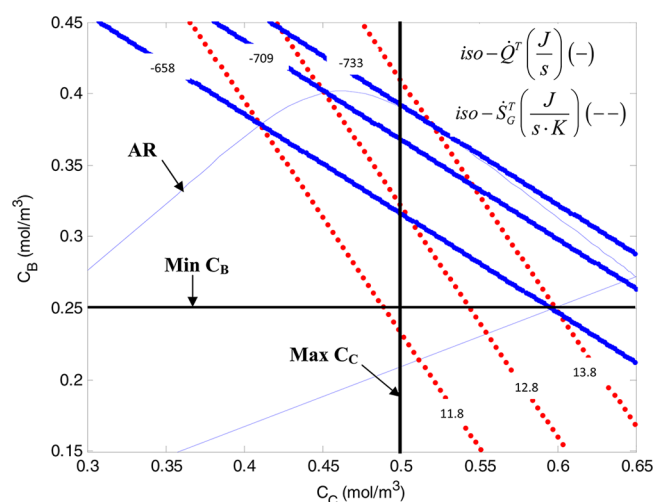


Figure 6. Entropy generation (\dot{S}_G^T) and utility consumption (\dot{Q}^T) isoclines on a C_B vs C_C AR diagram.

As can be seen in Figure 3 (Figure 4), the upper AR boundary can be formed by a CSTR followed by a PFR, for small concentrations of A (high concentrations of C), and by mixing of the feed with a CSTR outlet, for high concentrations of A (small concentrations of C).

Since the reactor network's inlet consists of pure A, it then holds that $S^I = -451 \text{ J/(mol K)}$ and $H^I = -24 437 \text{ J/mol}$. Since the reacting mixture is considered to be ideal, the network outlet stream's entropy and enthalpy are

$$S^O = \sum_{k \in \{A, B, C\}} \frac{C_k}{\sum_{l \in \{A, B, C\}} C_l} S_k(T, P)$$

and

$$H^O = \sum_{k \in \{A, B, C\}} \frac{C_k}{\sum_{l \in \{A, B, C\}} C_l} H_k(T, P)$$

Then, the network entropy generation and utility consumption can be evaluated as

$$\begin{aligned} \dot{S}_G^T \text{ (J/(s K))} &= (C_A^O + C_B^O + C_C^O) \cdot F \cdot \left[\left(S^O - \frac{H^O}{T_\sigma} \right) - \left(S^I - \frac{H^I}{T_\sigma} \right) \right] \Rightarrow \\ \dot{S}_G^T \text{ (J/(s K))} &= \sum_{k \in \{A, B, C\}} C_k \alpha_k(T, P) + 368.99 \end{aligned}$$

and

$$\begin{aligned} \dot{Q}^T \text{ (J/s)} &= (C_A^O + C_B^O + C_C^O) \cdot F \cdot [H^O - H^I] \Rightarrow \\ \dot{Q}^T \text{ (J/s)} &= \sum_{k \in \{A, B, C\}} C_k H_k(T, P) + 24 437 \end{aligned}$$

Therefore, the $iso-\dot{S}_G^T$ (J/(s K)) and $iso-\dot{Q}^T$ (J/s) lines are linear and can be drawn on an AR diagram, as shown in Figures 5 (C_B vs C_A) and 6 (C_B vs C_C). The AR diagrams equipped with $iso-\dot{S}_G^T$ (J/(s K)) and $iso-\dot{Q}^T$ (J/s) lines can be used to quantify the AR composition, entropy generation, and utility consumption properties simultaneously. As expected from the above discussion (see section 2), it can be verified that the entropy generation is zero for an outlet concentration of pure reactant A (no reaction) and increases as the outlet composition approaches the equilibrium value.

7. CONCLUSIONS

This work presents a method to quantify entropy generation, utility consumption, and composition (using attainable region (AR) information) for isothermal, isobaric reactor networks. The infinite dimensional state-space (IDEAS) framework is shown to apply to this synthesis problem. A theorem is proven which establishes that, under certain assumptions, the entropy generation and utility consumption properties of an isothermal, isobaric reactor network are dependent only on the composition of the network outlet streams, regardless of the network's internal structure. In turn, this implies that quantifying the entropy generation and the energy consumption can be achieved by simply quantifying the AR for the considered reaction kinetic scheme from a known network inlet. Although, for energy-intensive processes tradeoffs between entropy generation, energy consumption, and outlet composition will lead to a final design that is close to an entropy generation minimizing design, the final design may not possess minimal entropy generation characteristics for non-energy-intensive processes.

■ APPENDIX A

The molar free energy, enthalpy (H), and entropy (S) of a multicomponent liquid mixture are quantified from ref 25 (p 414) as

$$\begin{aligned} H(T, P, \{C_k\}_{k=1}^n) &= H^E(T, P, \{C_k\}_{k=1}^n) + H^{id}(T, P, \{C_k\}_{k=1}^n) \\ S(T, P, \{C_k\}_{k=1}^n) &= S^E(T, P, \{C_k\}_{k=1}^n) + S^{id}(T, P, \{C_k\}_{k=1}^n) \end{aligned}$$

The ideal mixture molar enthalpy and entropy (H^{id} and S^{id} , respectively) can be evaluated from ref 25 (p 412) as follows:

$$\begin{aligned} H^{id}(T, P, \{C_k\}_{k=1}^n) &= \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} H_k(T, P) \\ S^{id}(T, P, \{C_k\}_{k=1}^n) &= \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} S_k(T, P) - R \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \ln \left(\frac{C_k}{\sum_{l=1}^n C_l} \right) \end{aligned}$$

The excess molar entropy ($S^E(T, P, \{C_k\}_{k=1}^n)$) and excess molar enthalpy ($H^E(T, P, \{C_k\}_{k=1}^n)$) can be evaluated from the excess Gibbs free energy ($G^E(T, P, \{C_k\}_{k=1}^n)$), which, in turn, can be expressed in terms of liquid activity coefficients, as shown in ref 25 (pp 415, 418):

$$\frac{G^E(T, P, \{C_k\}_{k=1}^n)}{RT} = \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \ln \gamma_k(T, P, \{C_k\}_{k=1}^n)$$

$$\begin{aligned} H^E(T, P, z_k) &= -RT^2 \left. \frac{\partial \left[\frac{G^E(T, P, \{C_k\}_{k=1}^n)}{RT} \right]}{\partial T} \right|_{P, C_k} \\ &= -RT^2 \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \left. \frac{\partial [\ln \gamma_k(T, P, \{C_k\}_{k=1}^n)]}{\partial T} \right|_{P, C_k} \\ S^E(T, P, \{C_k\}_{k=1}^n) &= \frac{H^E(T, P, \{C_k\}_{k=1}^n) - G^E(T, P, \{C_k\}_{k=1}^n)}{T} \\ &= -RT \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \left. \frac{\partial \ln \gamma_k(T, P, \{C_k\}_{k=1}^n)}{\partial T} \right|_{P, C_k} \\ &\quad - R \sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \ln \gamma_k(T, P, \{C_k\}_{k=1}^n) \end{aligned}$$

Several temperature-dependent local composition models, such as Wilson, NRTL, UNIFAC, and UNIQUAC, etc., can be used to define the liquid-phase activity coefficient functions $\ln \gamma_k(T, P, \{C_k\}_{k=1}^n)$ ($\forall k = 1, n$).

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Notes

The authors declare no competing financial interest.

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■ NOMENCLATURE

T_σ = temperature of infinite heating/cooling reservoir (K)
 \dot{W}_{lost} = lost work due to process irreversibility (J/s)
 \dot{n}^{in} = inlet mixture molar flow rate (mol/s)
 \dot{n}^{out} = outlet mixture molar flow rate (mol/s)
 F = volumetric flow rate (m^3/s)
 F^{in} = inlet volumetric flow rate (m^3/s)
 F^{out} = outlet volumetric flow rate (m^3/s)
 M_k = k th species molecular mass (kg/mol)
 \dot{m} = mixture mass flow rate (kg/s)
 \dot{m}^{out} = outlet mixture mass flow rate (kg/s)
 \dot{m}^{in} = inlet mixture mass flow rate (kg/s)
 C_i = i th component molar concentration (mol/ m^3)
 C_i^{in} = i th component inlet molar concentration to the IDEAS unit model (mol/ m^3)
 C_i^{out} = i th component outlet molar concentration from the IDEAS unit model (mol/ m^3)
 z_k = k th species mass fraction
 z_i^{in} = i th component inlet mass fraction
 z_i^{out} = i th component outlet mass fraction
 x_i = i th component mole fraction
 R_k = molar rate of generation of the k th species per unit volume (mol/($m^3 s$))
 $\bar{\sigma}$ = design specification variable of mass model reactor (($m^3 s$)/kg)
 σ = design specification final value of mass model reactor (($m^3 s$)/kg)
 $\bar{\tau}$ = running residence time in the PFR model (s)
 τ = final residence time for the CSTR and PFR models (s)

V = reactor volume (m^3)
 T = temperature (K)
 P = pressure (Pa)
 ρ = density (kg/m^3)
 R = universal gas constant ($\text{cal}/(\text{K mol})$)
 Φ = input–output information map for the process model
 u = input vector of an information map
 y = output vector of an information map
 H^{in} = molar enthalpy inlet to the IDEAS unit model (J/mol)
 H^{out} = molar enthalpy outlet from the IDEAS unit model (J/mol)
 S^{in} = molar entropy inlet to the IDEAS unit model ($\text{J}/(\text{mol K})$)
 S^{out} = molar entropy outlet from the IDEAS unit model ($\text{J}/(\text{mol K})$)
 k = reaction rate constant (s^{-1})
 $H(T, P, \{C_i\}_{i=1}^n, \{z_j^{\text{in}}\}_{j=1}^{n-1}, T, P)_{i=1}^n$, $H(T, P, \{C_i\}_{i=1}^n, \{z_j^{\text{out}}\}_{j=1}^{n-1}, T, P)_{i=1}^n$, $H(T, P, \{C_i\}_{i=1}^n)$ = molar enthalpy of a stream with temperature T , pressure P , and composition $\{C_i\}_{i=1}^n$, where $\{C_i\}_{i=1}^n$ can be a function of mass fraction $\{z_j\}_{j=1}^n$ (J/mol)
 $S(T, P, \{C_i\}_{i=1}^n, \{z_j^{\text{in}}\}_{j=1}^{n-1}, T, P)_{i=1}^n$, $S(T, P, \{C_i\}_{i=1}^n, \{z_j^{\text{out}}\}_{j=1}^{n-1}, T, P)_{i=1}^n$, $S(T, P, \{C_i\}_{i=1}^n)$ = molar entropy of a stream with temperature T , pressure P , and composition $\{C_i\}_{i=1}^n$, where $\{C_i\}_{i=1}^n$ can be a function of mass fraction $\{z_j\}_{j=1}^n$ ($\text{J}/(\text{mol K})$)
 $H(T, P, \{C_k^{\text{out}}\}_{k=1}^n)$ = molar enthalpy associated with a general outlet stream of temperature T , pressure P , and composition $\{C_k^{\text{out}}\}_{k=1}^n$ (J/mol)
 $H(T, P, \{C_k^{\text{in}}\}_{k=1}^n)$ = molar enthalpy associated with a general inlet stream of temperature T , pressure P , and composition $\{C_k^{\text{in}}\}_{k=1}^n$ (J/mol)
 $S(T, P, \{C_k^{\text{out}}\}_{k=1}^n)$ = molar entropy associated with a general outlet stream of temperature T , pressure P , and composition $\{C_k^{\text{out}}\}_{k=1}^n$ ($\text{J}/(\text{mol K})$)
 $S(T, P, \{C_k^{\text{in}}\}_{k=1}^n)$ = molar entropy associated with a general inlet stream of temperature T , pressure P , and composition $\{C_k^{\text{in}}\}_{k=1}^n$ ($\text{J}/(\text{mol K})$)
 $G(T, P, \{C_k^{\text{out}}\}_{k=1}^n)$ = molar Gibbs free energy associated with a general outlet stream of temperature T , pressure P , and composition $\{C_k^{\text{out}}\}_{k=1}^n$ (J/mol)
 $G(T, P, \{C_k^{\text{in}}\}_{k=1}^n)$ = molar Gibbs free energy associated with a general inlet stream of temperature T , pressure P , and composition $\{C_k^{\text{in}}\}_{k=1}^n$ (J/mol)
 $H^{\text{id}}(T, P, \{C_k\}_{k=1}^n)$ = ideal molar enthalpy associated with a temperature T , pressure P , and composition $\{C_k\}_{k=1}^n$ (J/mol)
 $S^{\text{id}}(T, P, \{C_k\}_{k=1}^n)$ = ideal molar entropy associated with a general stream of temperature T , pressure P , and composition $\{C_k\}_{k=1}^n$ ($\text{J}/(\text{mol K})$)
 $H^{\text{E}}(T, P, \{C_k\}_{k=1}^n)$ = excess molar enthalpy associated with a general stream of temperature T , pressure P , and composition $\{C_k\}_{k=1}^n$ (J/mol)
 $S^{\text{E}}(T, P, \{C_k\}_{k=1}^n)$ = excess molar entropy associated with a general stream of temperature T , pressure P , and composition $\{C_k\}_{k=1}^n$ ($\text{J}/(\text{mol K})$)
 $H_k(T, P)$ = pure component molar enthalpy associated with a general stream of temperature T and pressure P (J/mol)
 $S_k(T, P)$ = pure component molar entropy associated with a general stream of temperature T and pressure P ($\text{J}/(\text{mol K})$)
 $G^{\text{E}}(T, P, \{C_k\}_{k=1}^n)$ = excess Gibbs molar free energy associated with a general stream of temperature T , pressure P , and composition $\{C_k\}_{k=1}^n$ (J/mol)
 $\gamma_k(T, P, \{C_k\}_{k=1}^n)$ = liquid-phase activity coefficient function associated with a liquid stream of temperature T , pressure P , and composition $\{C_k\}_{k=1}^n$ (J/mol)
 Q_{F} = reactor heat input on a per unit volume basis (J/m^3)

Q_{m} = reactor heat input on a per unit mass basis (J/kg)
 \dot{Q} = reactor heat rate input (J/s)
 S_{G}^{F} = reactor entropy generation per unit volume ($\text{J}/(\text{m}^3 \text{K})$)
 S_{G}^{m} = reactor entropy generation per unit mass ($\text{J}/(\text{kg K})$)
 \dot{S}_{G} = reactor entropy generation rate ($\text{J}/(\text{s K})$)
 \dot{Q}^{R} = heat generation/consumption rate for the i th reactor in the IDEAS reactor network $\forall i = 1, \infty$ (J/s)
 $\dot{Q}^{\text{M}}(i)$ = heat generation/consumption rate due to mixing of streams entering the i th reactor in the IDEAS reactor network $\forall i = 1, \infty$ (J/s)
 $(\dot{Q}(i))(\dot{Q}^{\text{R}}(i) + \dot{Q}^{\text{M}}(i))$ = heat generation/consumption rate for the augmented i th reactor in the IDEAS reactor network $\forall i = 1, \infty$ (J/s)
 $\dot{Q}^{\text{O}}(i)$ = heat of mixing rate at the i th DN network outlet $\forall i = 1, N$ (J/s)
 \dot{Q}^{T} = total network energy consumption rate (J/s)
 $\dot{S}_{\text{G}}(i)$ = entropy generation rate for the augmented i th reactor in the IDEAS reactor network $\forall i = 1, \infty$ ($\text{J}/(\text{s K})$)
 $\dot{S}_{\text{G}}^{\text{O}}(i)$ = entropy generation rate at the i th DN network outlet $\forall i = 1, N$ ($\text{J}/(\text{s K})$)
 $\dot{S}_{\text{G}}^{\text{T}}$ = total network entropy generation rate ($\text{J}/(\text{s K})$)

IDEAS Variables

M = number of IDEAS network inlets
 N = number of IDEAS network outlets
 $C_k^{\text{I}}(j)$ = k th component concentration in the j th network inlet $\forall k = 1, n; \forall j = 1, M$
 $C_k^{\text{O}}(i)$ = k th component concentration in the i th network outlet $\forall k = 1, n; \forall i = 1, N$
 $C_k^{\text{I}}(i)$ = k th component concentration in the i th OP inlet $\forall k = 1, n; \forall i = 1, \infty$
 $C_k^{\text{O}}(i)$ = k th component concentration in the i th OP outlet $\forall k = 1, n; \forall i = 1, \infty$
 $F^{\text{I}}(j)$ = j th network inlet flow rate $\forall j = 1, M$
 $S^{\text{I}}(j)$ = molar entropy associated with the j th network inlet stream $\forall j = 1, M$
 $H^{\text{I}}(j)$ = molar enthalpy associated with the j th network inlet stream $\forall j = 1, M$
 $F^{\text{O}}(i)$ = i th network outlet flow rate $\forall i = 1, N$
 $S^{\text{O}}(i)$ = molar entropy associated with the i th network outlet stream $\forall i = 1, N$
 $H^{\text{O}}(i)$ = molar enthalpy associated with the i th network outlet stream $\forall i = 1, N$
 $F^{\text{I}}(j)$ = j th OP inlet flow rate $\forall j = 1, \infty$
 $S^{\text{I}}(j)$ = molar entropy associated with the j th OP inlet stream $\forall j = 1, \infty$
 $H^{\text{I}}(j)$ = molar enthalpy associated with the j th OP inlet stream $\forall j = 1, \infty$
 $F^{\text{O}}(i)$ = i th OP outlet flow rate $\forall i = 1, \infty$
 $S^{\text{O}}(i)$ = molar entropy associated with the i th OP outlet stream $\forall i = 1, \infty$
 $H^{\text{O}}(i)$ = molar enthalpy associated with the i th OP outlet stream $\forall i = 1, \infty$
 $F^{\text{OI}}(ij)$ = j th network inlet flow rate to the i th network outlet $\forall j = 1, M; \forall i = 1, N$
 $F^{\text{II}}(i, j)$ = j th network outlet flow rate to the i th OP inlet $\forall j = 1, M; \forall i = 1, \infty$

$F^{\text{OO}}(i, j)$ = j th OP outlet flow rate to the i th network outlet
 $\forall j = 1, \infty; \forall i = 1, N$

$F^{\text{IO}}(i, j)$ = j th OP outlet flow rate to the i th OP network outlet
 $\forall j = 1, \infty; \forall i = 1, \infty$

$\tau(i)$ = residence time of the i th OP unit $\forall i = 1, \infty$

$\lambda(i)$ = technology flag of the i th OP unit (i.e., $\lambda(i) = 0$ for PFR and $\lambda(i) = 1$ for CSTR) $\forall i = 1, \infty$

$u(i)$ = input of the i th OP unit information map $\forall i = 1, \infty$

$y(i)$ = output of the i th OP unit information map $\forall i = 1, \infty$

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