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Minimum Entropy Generation for Isothermal Endothermic/Exothermic Reactor Networks

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It was shown in an earlier work by us that entropy generation and energy (hot utility or cold utility) consumption of isothermal, isobaric reactor networks depend only on the network's inlet and outlet stream compositions and flow rates and are not dependent on the reactor network structure, as long as the universe of realizable reactor units and network outlet mixing units are either all endothermic interacting with a single hot reservoir, or all exothermic interacting with a single cold reservoir, respectively. It is shown that when the universe of realizable reactor/mixer units, of isothermal, isobaric, continuous stirred tank reactor networks, consists of both endothermic units interacting with a single hot reservoir and exothermic units interacting with a single cold reservoir, the network's net (hot minus cold) utility consumption depends only on the network's inlet and outlet stream compositions and flow rates (and does not depend on the network's structure). In contrast, the network's entropy generation depends on the network's inlet and outlet stream compositions and flow rates, and the network's hot utility (or cold utility) consumption. The latter, in general, depends on the network structure, thus making entropy generation also, in general, depend on network structure. Thus, the synthesis of isothermal, isobaric reactor networks, with fixed inlet and outlet stream specifications, is equivalent to the synthesis of minimum hot (or cold) utility consuming such networks. The Infinite DimEnsionAl State-space conceptual framework is used for the problem's mathematical formulation, which is then used to rigorously establish the above equivalence. A case study involving Trambouze kinetics demonstrates the findings. *AIChE J*, 61: 103–117, 2015
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Introduction

This work is a continuation of a previously published contribution by the authors on the synthesis of reactor networks with known entropy generation.[1] In this earlier work, it was rigorously demonstrated, using the Infinite DimEnsionAl State-space (IDEAS) framework, that if the universe of reactors that could possibly help realize the reactor network consists of either only endothermic reactors or only exothermic reactors, then the quantification of entropy generation and utility consumption can be performed irrespective of the network's internal structure, and depends only on reactor network inlet and outlet compositions. In turn, this allows the creation of entropy and energy consumption isoclines within an attainable region diagram, allowing reactor network design to be pursued based on rigorous tradeoffs among entropy generation, energy consumption, and other reactor network performance specifications (such as conversion, yield, selectivity, etc.). This work relaxes the aforementioned assumption that the universe of feasible reactors consists of either only endothermic reactors or only exothermic reactors, and considers the existence of both exothermic and endothermic continuous stirred tank reactors in the reactor universe. It is shown that while net energy consumption remains a function of only network inlet/outlet compositions, entropy generation and hot utility (or cold utility) consumption, are also strong functions of the network's internal structure. Thus, it is desirable and meaningful to quantify minimum entropy generation over all reactor networks that meet predefined performance specifications. To this end, the IDEAS conceptual framework will be used.

The method of entropy generation minimization has been applied to several industrial reactions to determine the optimal reactor temperature profile[2–6] using optimal control theory. Unfortunately, this technique allows only the identification of a locally optimal solution rather than a globally optimal one. In addition, only single reactors are considered in those studies. Other authors have relied on MINLP formulations,[7] and references therein to energetically optimize networks of nonisothermal reactors, but with no entropy generation considerations.

This work uses the IDEAS framework for the quantification of both entropy generation and energy consumption for isothermal, isobaric reactor networks whose universe of feasible reactor units include units of both the exothermic and endothermic type. The IDEAS framework decomposes a reactor network into an operator, OP network, where the reactor unit operations occur, and a distribution, DN

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network, 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,[8] complex distillation network synthesis,[9–11] power cycle synthesis,[12] reactor network synthesis,[13,14] reactive distillation network synthesis,[15] separation network synthesis,[16] attainable region construction,[17–20] and batch attainable region construction.[21]

The rest of the article is structured as follows: CSTR models using a mass basis and a molar basis are presented, the applicability of IDEAS to the entropy generation and energy consumption quantification problem is demonstrated, and the resulting IDEAS mathematical formulation is presented. Next, properties of the entropy generation and net energy consumption functions are rigorously established in a theorem, which establishes the net energy consumption function's dependence on only network inlet and outlet information, and the entropy generation function's dependence on both network inlet and outlet information and network cold/hot utility consumption. A case study involving Trambouze kinetics is used to illustrate the proposed reactor network synthesis method, and conclusions are drawn.

Applicability of IDEAS to Isothermal Reactor Network Synthesis

For this work, the following assumptions are considered:

- Reactor network is isothermal, that is, all the reactors, streams are at the same temperature T.
- Reactor network is isobaric, that is, all the reactors, streams are at the same pressure P.
- No work is consumed or generated.
- Reactor network consists of only CSTR units.
- The universe of isothermal, isobaric reactors consists of reactors of both the exothermic and endothermic types.
- An infinite reservoir at constant temperature T_H $(T_H > T)$ is considered to provide heat to any endothermic reactor, and an infinite reservoir at constant temperature T_C $(T_C < T)$ is considered to provide heat to the exothermic reactor.

Reactor Model—Variable Density Model (Mass Basis)

$$F^{in}=F^{out}=F \tag{1a}$$

$$\left\{\begin{array}{c} z_k^{in}-z_k^{out}+\sigma M_k r_k\left(\left\{C_i\left(\left\{z_l^{out}\right\}_{l=1}^n,T,P\right)\right\}_{i=1}^n\right)=0 \quad \forall k=1,n \\ \sigma=\dfrac{V}{F} \end{array}\right\} \tag{2a}$$

$$C_i^{out}=C_i\left(\left\{z_j^{out}\right\}_{j=1}^n,T,P\right) \quad \forall i=1,n \tag{3a}$$

where

$$\sum_{j=1}^n z_j^{in}=1, z_j^{in}\geq 0 \quad \forall i=1,n; \ \sum_{j=1}^n z_j^{out}=1, z_j^{out}\geq 0 \quad \forall i=1,n \tag{3'a}$$

Equation 3a aims to capture the thermodynamic model of the underlying mixture. Several models can be brought into the form of 3a. For example, if a compressibility factor model (Z) is used, then

$$C_i^{out}=C_i\left(\left\{z_j^{out}\right\}_{j=1}^n,T,P\right)=x_i^{out}\left(\frac{P}{RT}\right)\left(\frac{1}{Z\left(\left\{x_j\right\}_{j=1}^n,T,P\right)}\right) \quad \forall i=1,n \tag{4a}$$

$$x_i^{out}=\frac{z_i^{out}}{M_i\sum_{k=1}^n\left(\frac{z_k^{out}}{M_k}\right)} \quad \forall i=1,n \tag{5a}$$

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

$$\sum_{j=1}^n x_j^{out}=1, x_j^{out}\geq 0 \quad \forall i=1,n \tag{5'a}$$

$$\left\{\begin{array}{l} h^{arr}-F\sum_{l=1}^n\left(z_l^{out}/M_l\right)H\left(T,P,\left\{C_i\left(\left\{z_j^{out}\right\}_{j=1}^{n-1},T,P\right)\right\}_{i=1}^n\right)+\dot{Q}^R=0 \\ \dot{Q}^R>0 \iff \lambda=1; \dot{Q}^R<0 \iff \lambda=0 \end{array}\right\} \tag{6a}$$

$$\left\{\begin{array}{l} s^{arr}-F\sum_{l=1}^n\left(z_l^{out}/M_l\right)S\left(T,P,\left\{C_i\left(\left\{z_j^{out}\right\}_{j=1}^{n-1},T,P\right)\right\}_{i=1}^n\right) \\ \quad +\dot{Q}^R\left(\dfrac{\lambda}{T_H}+\dfrac{(1-\lambda)}{T_C}\right)+\dot{S}_G^R=0 \\ \dot{Q}^R>0 \iff \lambda=1; \dot{Q}^R<0 \iff \lambda=0 \end{array}\right\} \tag{7a}$$

Reactor Model—Constant Density Model (Molar Basis)

$$q^{in}=q^{out}=q \tag{1b}$$

$$\left\{\begin{array}{c} C_k^{in}-C_k^{out}+R_k\left(\left\{C_k^{out}\right\}_{k=1}^n\right)\tau=0 \quad \forall k=1,n \\ \tau=\dfrac{V}{q} \end{array}\right\} \tag{2b}$$

$$\left\{\begin{array}{c} h^{arr}-q\left(\sum_{l=1}^n C_l^{out}\right)H\left(T,P,\left\{C_k^{out}\right\}_{k=1}^n\right)+\dot{Q}^R=0 \\ \lambda=H\left(\dot{Q}^R\right)=\left\{\begin{array}{ll} 1 & \text{if } \dot{Q}^R>0 \\ 0 & \text{if } \dot{Q}^R<0 \end{array}\right\} \end{array}\right\} \tag{6b}$$

$$\left\{\begin{array}{c} s^{arr}-q\left(\sum_{l=1}^n C_l^{out}\right)S\left(T,P,\left\{C_k^{out}\right\}_{k=1}^n\right)+\dot{Q}^R\left(\dfrac{\lambda}{T_H}+\dfrac{(1-\lambda)}{T_C}\right)+\dot{S}_G^R=0 \\ \lambda=H\left(\dot{Q}^R\right)=\left\{\begin{array}{ll} 1 & \text{if } \dot{Q}^R>0 \\ 0 & \text{if } \dot{Q}^R<0 \end{array}\right\} \end{array}\right\} \tag{7b}$$

Entropy/Enthalpy Relations for both VDF and CDF Models

$$S\left(T,P,\left\{C_k\right\}_{k=1}^n\right)=\sum_{k=1}^n\frac{C_k}{\sum_{l=1}^n C_l}S_k(T,P)+S^E\left(T,P,\left\{C_k\right\}_{k=1}^n\right) -R\sum_{k=1}^n\frac{C_k}{\sum_{l=1}^n C_l}\ln\left(\frac{C_k}{\sum_{l=1}^n C_l}\right) \tag{10}$$

$$H\left(T,P,\{C_k\}_{k=1}^n\right)=\sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} H_k(T,P)+H^{\mathrm{E}}\left(T,P,\{C_k\}_{k=1}^n\right) \tag{11}$$

$$H^{\mathrm{E}}\left(T,P,\{C_k\}_{k=1}^n\right)=-RT^2\sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \left.\frac{\partial\left[\ln\gamma_k\left(T,P,\{C_k\}_{k=1}^n\right)\right]}{\partial T}\right|_{P,C_k} \tag{12}$$

$$S^{\mathrm{E}}\left(T,P,\{C_k\}_{k=1}^n\right)=-RT\sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} \left.\frac{\partial \ln\gamma_k\left(T,P,\{C_k\}_{k=1}^n\right)}{\partial T}\right|_{P,C_k} -R\sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l}\ln\gamma_k\left(T,P,\{C_k\}_{k=1}^n\right) \tag{13}$$

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

Applicability of IDEAS to VDF Model

The aforementioned reactor model can be used to construct the following input–output information map
$\Phi : D \rightarrow R^{3n+2}\times R$, $\Phi : u \rightarrow y$ such that

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

$$u^T \hat{=} \left[u_1^T | u_2^T\right] \hat{=} \begin{bmatrix} T & P & z_1^{\mathrm{in}} & z_1^{\mathrm{out}} & \cdots & z_n^{\mathrm{out}} & \lambda & | & F & h^{\mathrm{arr}} & \dot{Q}^R & s^{\mathrm{arr}} & \dot{S}_G^R \end{bmatrix}$$

$$y^T \hat{=} \left[y_1^T | y_2^T\right] \hat{=} \Phi^T(u_1,u_2)$$

$$\hat{=} \begin{bmatrix} \sigma & z_2^{\mathrm{in}} & \cdots & z_n^{\mathrm{in}} & x_1^{\mathrm{out}} & \cdots & x_n^{\mathrm{out}} & & \\ & C_1^{\mathrm{out}} & \cdots & C_n^{\mathrm{out}} & H\left(T,P,\{C_i^{\mathrm{out}}\}_{i=1}^n\right) & S\left(T,P,\{C_i^{\mathrm{out}}\}_{i=1}^n\right) & | & F \end{bmatrix}$$

where

$$D \hat{=} \left\{ u \in R^{n+3}\times\{0,1\}\times R^5 : \Phi_3(u_1,u_2) =0 \wedge \sum_{i=1}^n z_i^{\mathrm{out}}-1=0 \wedge u_1 \geq 0 \wedge F \geq 0 \wedge \dot{S}_G^R \geq 0 \right\} \quad \text{and}$$

$$\Phi_3(u_1,u_2) \hat{=} \begin{bmatrix} h^{\mathrm{arr}}-F\sum_{l=1}^n \left(z_l^{\mathrm{out}}/M_l\right) H\left(T,P,\{C_i^{\mathrm{out}}\}_{i=1}^n\right)+\dot{Q}^R \\ s^{\mathrm{arr}}-F\sum_{l=1}^n \left(z_l^{\mathrm{out}}/M_l\right) S\left(T,P,\{C_i^{\mathrm{out}}\}_{i=1}^n\right)+\dot{Q}^R\left(\frac{\lambda}{T_H}+\frac{(1-\lambda)}{T_C}\right)+\dot{S}_G^R \end{bmatrix}$$

The evaluation of the images $\Phi^T(u_1,u_2)$, $\Phi_3(u_1,u_2)$ given u_1 and u_2, is illustrated next for the variable density reactor case.

Consider that u_1 is known. The residence time σ can first be evaluated by solving Eq. 2a for the first species $(k=1)$. From the solution of Eq. 2a for all other species k, $\forall k=2,n$, $\left\{z_k^{\mathrm{in}}\right\}_{k=2}^n$ can be evaluated. Knowledge of the network's temperature and pressure, and of the outlet species mass fractions, yields the outlet species mole fractions and concentrations, and the outlet molar enthalpy and molar entropy, from Eqs. 10, 13 and 11, 12, respectively. Knowledge of $\lambda \in \{0,1\}$ determines the sign of $\dot{Q}^R$, as according to Eqs. 6a and 7a, $\dot{Q}^R>0 \Longleftrightarrow \lambda=1$; $\dot{Q}^R<0 \Longleftrightarrow \lambda=0$

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 carried out, so that the following IDEAS properties can be shown to hold for the maps Φ_1, Φ_2 and for the domain defining map Φ_3.

IDEAS Property 1

$\exists\Phi_4 : \left\{R^{n+3}\times\{0,1\}\right\} \rightarrow R^{3n+2}$, such that $\Phi_1(u_1,u_2) =\Phi_4(u_1)$ $\forall(u_1,u_2)\in D$. This implies that $\Phi_1(u_1,u_2)$ can be evaluated based on knowledge of u_1 alone, and independently of u_2.

IDEAS Property 2

$\exists\Phi_5 : \left\{R^{n+3}\times\{0,1\}\right\} \rightarrow R^{1\times 5}$, such that $\Phi_2(u_1,u_2)= \Phi_5(u_1)\cdot u_2$ $\forall(u_1,u_2)\in D$. This map is $\Phi_5 : u_1 \hat{=} [T \;\; P \;\; z_1^{\mathrm{in}}\, z_1^{\mathrm{out}} \cdots z_n^{\mathrm{out}} \lambda]^T \rightarrow \Phi_5(u_1) \hat{=} [1 \;\; 0 \;\; 0 \;\; 0 \;\; 0]$. It can be readily verified that: $y_2 \hat{=} [F] = [1 \;\; 0 \;\; 0 \;\; 0 \;\; 0][F \;\; h^{\mathrm{arr}} \;\; \dot{Q}^R \;\; s^{\mathrm{arr}} \;\; \dot{S}_G^R]^T=\Phi_5(u_1)\cdot u_2$.

IDEAS Property 3

$\exists\Phi_6 : \left\{R^{n+3}\times\{0,1\}\right\} \rightarrow R^{2\times 5}$, such that $\Phi_3(u_1,u_2)=\Phi_6(u_1)\cdot u_2$ $\quad\forall(u_1,u_2)\in R^{n+3}\times\{0,1\}\times R^5 : \sum_{i=1}^n z_i^{\mathrm{out}}-1=0 \wedge u_1 \geq 0 \wedge F \geq 0 \wedge \dot{S}_G^R \geq 0$.

This map is

$$\Phi_6 : u_1 \hat{=} \begin{bmatrix} T & P & z_1^{\mathrm{in}} & z_1^{\mathrm{out}} & \cdots & z_n^{\mathrm{out}} & \lambda \end{bmatrix}^T \rightarrow \Phi_6(u_1) \hat{=}$$

$$\begin{bmatrix} -\sum_{l=1}^n \left(z_l^{\mathrm{out}}/M_l\right) H\left(T,P,\{C_i^{\mathrm{out}}\}_{i=1}^n\right) & 1 & 1 & 0 & 0 \\ -\sum_{l=1}^n \left(z_l^{\mathrm{out}}/M_l\right) S\left(T,P,\{C_i^{\mathrm{out}}\}_{i=1}^n\right) & 0 & \left(\frac{\lambda}{T_{\mathrm{H}}}+\frac{(1-\lambda)}{T_{\mathrm{C}}}\right) & 1 & 1 \end{bmatrix}$$

It can be readily verified that

$$\Phi_3(u_1,u_2) \hat{=} \begin{bmatrix} -\sum_{l=1}^n \left(z_l^{\mathrm{out}}/M_l\right) H\left(T,P,\{C_i^{\mathrm{out}}\}_{i=1}^n\right) & 1 & 1 & 0 & 0 \\ -\sum_{l=1}^n \left(z_l^{\mathrm{out}}/M_l\right) S\left(T,P,\{C_i^{\mathrm{out}}\}_{i=1}^n\right) & 0 & \left(\frac{\lambda}{T_H}+\frac{(1-\lambda)}{T_C}\right) & 1 & 1 \end{bmatrix} \begin{bmatrix} F \\ h^{\mathrm{arr}} \\ \dot{Q}^R \\ s^{\mathrm{arr}} \\ \dot{S}_G^R \end{bmatrix} = \Phi_6(u_1)\cdot u_2$$

The above imply that for fixed u_1, $\Phi_5(u_1)$, and $\Phi_6(u_1)$ are linear operators. In turn this implies that $y_2 \hat{=} \Phi_2(u_1,u_2)=\Phi_5(u_1)\cdot u_2$ is linear in u_2 and the domain defining constraint $\Phi_3(u_1,u_2)=\Phi_6(u_1)\cdot u_2=0$ is also linear in u_2. Therefore, for a fixed u_1, the used reactor model is defined by a linear input–output map $\Phi_5(u_1)$ with domain defined also through the linear map $\Phi_6(u_1)$.

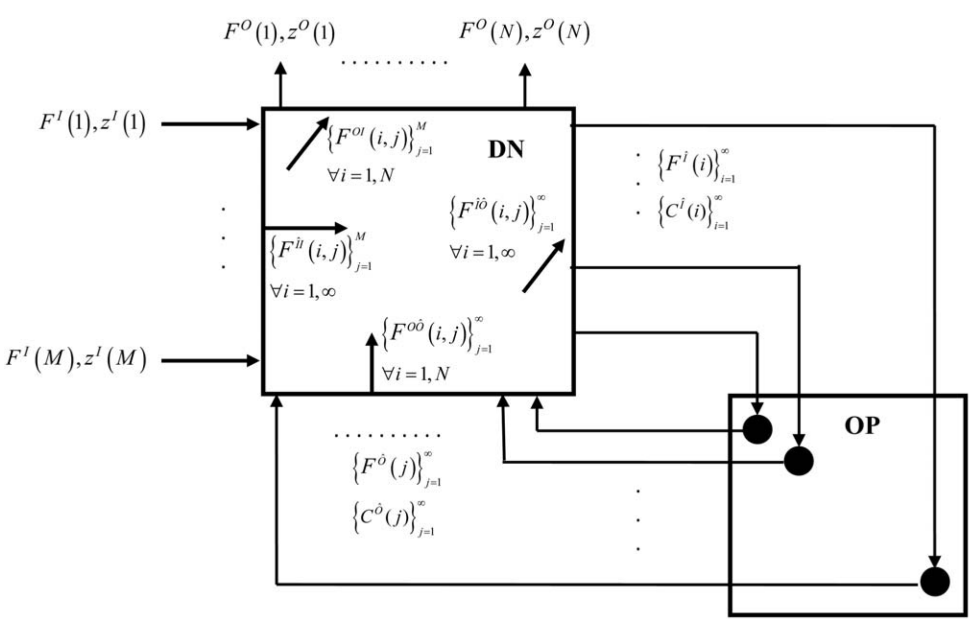

Figure 1. IDEAS representation for isothermal variable density reactor network.

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_5 is then used to create the sequence $\{\Phi_5(u_1(i))\}_{i=1}^{\infty}$ of linear maps from R^5 to R, each of which has its domain defined as a subset of the null space of a corresponding linear map from R^5 to R, the collection of which forms the sequence $\{\Phi_6(u_1(i))\}_{i=1}^{\infty}$. 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 1 for a variable density reactor network with n components, M network inlet streams, and N network outlet streams.

IDEAS Mathematical Formulation (Variable Density Reactor Network)

Under the previously mentioned assumptions that the network is homogeneous, isothermal, and isobaric, and assuming that all reactors and mixers are perfectly mixed, the resulting IDEAS feasible region is defined by the total mass, component mass, energy, and entropy balance constraints given below. Let S_1^R and S_2^R denote the index sets corresponding to all realizable exothermic and endothermic reactors, respectively. Let also S_1^O and S_2^O denote the index sets corresponding to all realizable exothermic and endothermic overall network outlet mixers, respectively. Then, $S_1^R \cup S_2^R=\{1,\ldots,\infty\}$, $S_1^O \cup S_2^O=\{1,\ldots,N\}$ and the aforementioned constraints can be written as

$$F^I(i)=\sum_{j=1}^{N}F^{OI}(j,i)+\sum_{j\in S_1^R}F^{\hat{I}I}(j,i)+\sum_{j\in S_2^R}F^{\hat{I}I}(j,i) \quad \forall i=1,M \tag{14}$$

$$F^O(i)=\sum_{j=1}^{M}F^{OI}(i,j)+\sum_{j\in S_1^R}F^{O\hat{O}}(i,j)+\sum_{j\in S_2^R}F^{O\hat{O}}(i,j) \quad \forall i=1,N \tag{15}$$

$$F^{\hat{I}}(i)=\sum_{j=1}^{M}F^{\hat{I}I}(i,j)+\sum_{j\in S_1^R}F^{\hat{I}\hat{O}}(i,j)+\sum_{j\in S_2^R}F^{\hat{I}\hat{O}}(i,j) \quad \forall i\in S_1^R \tag{16}$$

$$F^{\hat{I}}(i)=\sum_{j=1}^{M}F^{\hat{I}I}(i,j)+\sum_{j\in S_1^R}F^{\hat{I}\hat{O}}(i,j)+\sum_{j\in S_2^R}F^{\hat{I}\hat{O}}(i,j) \quad \forall i\in S_2^R \tag{17}$$

$$F^{\hat{O}}(j)=\sum_{i=1}^{N}F^{O\hat{O}}(i,j)+\sum_{i\in S_1^R}F^{\hat{I}\hat{O}}(i,j)+\sum_{i\in S_2^R}F^{\hat{I}\hat{O}}(i,j) \quad \forall j\in S_1^R \tag{18}$$

$$F^{\hat{O}}(j)=\sum_{i=1}^{N}F^{O\hat{O}}(i,j)+\sum_{i\in S_1^R}F^{\hat{I}\hat{O}}(i,j)+\sum_{i\in S_2^R}F^{\hat{I}\hat{O}}(i,j) \quad \forall j\in S_2^R \tag{19}$$

$$F^{\hat{O}}(i)=F^{\hat{I}}(i) \quad \forall i\in S_1^R\cup S_2^R \tag{20}$$

$$\begin{aligned} z_k^{\hat{I}}(i)F^{\hat{I}}(i)=&\sum_{j=1}^{M}z_k^I(j)F^{\hat{I}I}(i,j)+\sum_{j\in S_1^R}z_k^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)\\ &+\sum_{j\in S_2^R}z_k^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j) \quad \forall i\in S_1^R;\ \forall k=1,n \end{aligned} \tag{21}$$

$$\begin{aligned} z_k^{\hat{I}}(i)F^{\hat{I}}(i)=&\sum_{j=1}^{M}z_k^I(j)F^{\hat{I}I}(i,j)+\sum_{j\in S_1^R}z_k^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)\\ &+\sum_{j\in S_2^R}z_k^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j) \quad \forall i\in S_2^R;\ \forall k=1,n \end{aligned} \tag{22}$$

$$\begin{aligned} z_k^{O}(i)F^{O}(i)=&\sum_{j=1}^{M}z_k^I(j)F^{OI}(i,j)+\sum_{j\in S_1^R}z_k^{\hat{O}}(j)F^{O\hat{O}}(i,j)\\ &+\sum_{j\in S_2^R}z_k^{\hat{O}}(j)F^{O\hat{O}}(i,j) \quad \forall i=1,N;\ \forall k=1,n \end{aligned} \tag{23}$$

$$\dot{Q}^R(i)=\sum_{l=1}^{n}\left(z_l(i)\big/M_l\right)H^{\hat{O}}(i)F^{\hat{O}}(i)-h^{\mathrm{arr}}(i) \quad \forall i=1,\infty \tag{24}$$

$$h^{\text{arr}}(i)=\left[\begin{array}{c}\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{I}(j)F^{\hat{I}I}(i,j)+\sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)+\\ \sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)\end{array}\right]\quad\forall i\in S_1^R\cup S_2^R \tag{24$'$}$$

$$\dot{Q}^{O}(i)=\sum_{l=1}^{n}\left(z_l(i)/M_l\right)H^{O}(i)F^{O}(i)-\left[\begin{array}{c}\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{I}(j)F^{OI}(i,j)+\sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)F^{O\hat{O}}(i,j)+\\ \sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)F^{O\hat{O}}(i,j)\end{array}\right]\quad\forall i=1,N \tag{25}$$

$$\dot{S}_G^R(i)=\sum_{l=1}^{n}\left(z_l(i)/M_l\right)S^{\hat{O}}(i)F^{\hat{O}}(i)-s^{\text{arr}}(i)-\frac{\dot{Q}^{R}(i)}{T_{\text{C}}}\quad\forall i\in S_1^R \tag{26}$$

$$\dot{S}_G^R(i)=\sum_{l=1}^{n}\left(z_l(i)/M_l\right)S^{\hat{O}}(i)F^{\hat{O}}(i)-s^{\text{arr}}(i)-\frac{\dot{Q}^{R}(i)}{T_{\text{H}}}\quad\forall i\in S_2^R \tag{27}$$

$$s^{\text{arr}}(i)=\left[\begin{array}{c}\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{I}(j)F^{\hat{I}I}(i,j)+\sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)+\\ \sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)\end{array}\right]\quad\forall i\in S_1^R\cup S_2^R \tag{27$'$}$$

$$\dot{S}_G^O(i)=\sum_{l=1}^{n}\left(z_l(i)/M_l\right)S^{O}(i)F^{O}(i)-\left[\begin{array}{c}\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{I}(j)F^{OI}(i,j)+\sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{O\hat{O}}(i,j)+\\ +\sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{O\hat{O}}(i,j)\end{array}\right]-\frac{\dot{Q}^{O}(i)}{T_{\text{C}}}\quad\forall i\in S_1^O \tag{28}$$

$$\dot{S}_G^O(i)=\sum_{l=1}^{n}\left(z_l(i)/M_l\right)S^{O}(i)F^{O}(i)-\left[\begin{array}{c}\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{I}(j)F^{OI}(i,j)+\sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{O\hat{O}}(i,j)+\\ +\sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{O\hat{O}}(i,j)\end{array}\right]-\frac{\dot{Q}^{O}(i)}{T_{\text{H}}}\quad\forall i\in S_2^O \tag{29}$$

$$F^{I}\geq 0;F^{O}\geq 0;F^{\hat{I}}\geq 0;F^{\hat{O}}\geq 0;F^{OI}\geq 0;F^{\hat{I}I}\geq 0;F^{O\hat{O}}\geq 0;F^{\hat{I}\hat{O}}\geq 0 \tag{30}$$

$$\dot{Q}^{R}(i)\leq 0\quad\forall i\in S_1^R;\dot{Q}^{R}(i)\geq 0\quad\forall i\in S_2^R;\dot{Q}^{O}(i)\leq 0\quad\forall i\in S_1^O;\dot{Q}^{O}(i)\geq 0\quad\forall i\in S_2^O \tag{31}$$

Equations 14–19 correspond to mixing and splitting total mass balances in the DN. Equations 20–22 represent the action of the OP unit. Equation 23 represents a component mass balance at the DN outlet combined with stream composition-related specifications on the network outlets. Equations 24 and 25 are based on energy balances at each reactor inlet and at each network outlet, respectively. Equation 24′ describes the enthalpy arriving at the ith reactor and Eq. 27′ describes the entropy arriving at the ith reactor. Equations. 26 and 27 are based on reactor entropy generation balances of exothermic and endothermic reactors. Equations 28 and 29 are exothermic and endothermic network outlet entropy generation balances, respectively. Finally, Eqs. 30 and 31 are inequalities which denote the physical properties of mass flows and the direction of heat transfer (exothermic and endothermic).

Then, the reactor network's cold utility consumption, hot utility consumption, and total entropy generation can be written as

$$\dot{Q}^{\text{CU}}\triangleq-\left(\sum_{i\in S_1^R}\dot{Q}^{R}(i)+\sum_{i\in S_1^O}\dot{Q}^{O}(i)\right)\geq 0 \tag{32}$$

$$\dot{Q}^{\text{HU}}\triangleq\sum_{i\in S_2^R}\dot{Q}^{R}(i)+\sum_{i\in S_2^O}\dot{Q}^{O}(i)\geq 0 \tag{33}$$

$$\dot{S}_G^T=\sum_{i\in S_1^R}\dot{S}_G^R(i)+\sum_{i\in S_1^O}\dot{S}_G^O(i)+\sum_{i\in S_2^R}\dot{S}_G^R(i)+\sum_{i\in S_2^O}\dot{S}_G^O(i)\geq 0 \tag{34}$$

Objective Function Formulation: Reactor Network Entropy Generation

The entropy generation rate/utility consumption rate of the network is equal to the sum of entropy generation rates/utility consumption rates at every reactor and every overall network outlet mixing junction. The theoretical development below will demonstrate that the above derived formulas can be simplified to the point where utility consumption depends only on the reactor network's inlet and outlet compositions, while entropy generation depends on the network's internal structure through the network's endothermic reactors absorbing heat from a reservoir at T_H, and exothermic reactors rejecting heat to a reservoir T_C. First however, a key mathematical result is presented, as it is needed in the proof of the theorem that follows.

Definition. *Let* $f : \mathrm{N}\times\mathrm{N} \to \mathrm{R}$ *be a function. The series* $\sum_{(n,m)\in\mathrm{N}\times\mathrm{N}} f(n,m)$ *is absolutely convergent if and only if for some bijection* $g : \mathrm{N} \to \mathrm{N}\times\mathrm{N}$, *the series* $\sum_{n=0}^{\infty} f(g(n))$ *is absolutely convergent. Then*

$$\sum_{(n,m)\in\mathrm{N}\times\mathrm{N}} f(n,m) = \sum_{n=0}^{\infty} f(g(n)).$$

Fubini's Theorem for Infinite Sums

Let $f : \mathrm{N}\times\mathrm{N} \to \mathrm{R}$ be a function such that $\sum_{(n,m)\in\mathrm{N}\times\mathrm{N}} f(n,m)$ is absolutely convergent.[22]

Then, we have

$$\sum_{n=0}^{\infty}\left(\sum_{m=0}^{\infty} f(n,m)\right) = \sum_{(n,m)\in\mathrm{N}\times\mathrm{N}} f(n,m)$$
$$= \sum_{(m,n)\in\mathrm{N}\times\mathrm{N}} f(n,m) = \sum_{m=0}^{\infty}\left(\sum_{n=0}^{\infty} f(n,m)\right)$$

Proof Sketch. The proof is given only for nonnegative $f(n,m)$, as a general $f(n,m)$ can be decomposed into nonnegative and nonpositive parts.[22]

Since $f(n,m)$ is nonnegative, and $\sum_{(n,m)\in\mathrm{N}\times\mathrm{N}} f(n,m)$ is absolutely convergent, it then holds $\sum_{(n,m)\in\mathrm{N}\times\mathrm{N}} f(n,m) = \sum_{n=0}^{\infty} f(g(n)) \hat{=} L$. Again, the nonnegativity of $f(n,m)$implies $\sum_{n=0}^{N}\left(\sum_{m=0}^{M} f(n,m)\right) \leq \sum_{(n,m)\in\mathrm{N}\times\mathrm{N}} f(n,m) = L\ \forall N \in \mathrm{N},\ \forall M \in \mathrm{N}$. Taking the supremum (limit) as $M \to \infty$, then implies $\sum_{n=0}^{N}\left(\sum_{m=0}^{\infty} f(n,m)\right) \leq L\ \forall N \in \mathrm{N}$. The nondecreasing nature of $\sum_{n=0}^{N}\left(\sum_{m=0}^{\infty} f(n,m)\right)$ with respect to N and its boundedness established above, then establish convergence of this sequence of N, existence of $\sum_{n=0}^{\infty}\left(\sum_{m=0}^{\infty} f(n,m)\right)$, and the inequality $\sum_{n=0}^{\infty}\left(\sum_{m=0}^{\infty} f(n,m)\right) \leq L$.

Next, we show $\sum_{n=0}^{\infty}\left(\sum_{m=0}^{\infty} f(n,m)\right) \geq L - \varepsilon\ \forall \varepsilon > 0$. From the definition of L it holds $\forall \varepsilon > 0\ \exists \bar{N}(\varepsilon)$: $\sum_{n=0}^{\bar{N}(\varepsilon)} f(g(n)) \geq L - \varepsilon$.

Since $\bar{N}(\varepsilon)$ is finite, there exist finite $N'(\varepsilon), M'(\varepsilon)$ such that

$$\left\{(n,m) \in \mathrm{N}\times\mathrm{N} : 0 \leq n \leq N'(\varepsilon), 0 \leq m \leq M'(\varepsilon)\right\} \supset$$
$$\left\{(n,m) \in \mathrm{N}\times\mathrm{N} : (n,m) = g(\bar{n}), \bar{n} \in \mathrm{N}, 0 \leq \bar{n} \leq \bar{N}(\varepsilon)\right\}$$

In turn, this implies

$$\forall \varepsilon > 0 \sum_{n=0}^{\infty}\left(\sum_{m=0}^{\infty} f(n,m)\right) \geq \sum_{n=0}^{N'(\varepsilon)}\left(\sum_{m=0}^{M'(\varepsilon)} f(n,m)\right)$$
$$\geq \sum_{n=0}^{\bar{N}(\varepsilon)} f(g(n)) \geq L - \varepsilon.\ \ \mathrm{O.}E.\Delta.$$

To appreciate the importance of this theorem, consider the following example.

Let $f : \mathrm{N}\times\mathrm{N} \to \mathrm{R}, f : (n,m)$

$$\to f(n,m) \hat{=} \left\{\begin{array}{c} 1\ \forall (n,n) = (0,0), (1,1), \ldots, (\infty,\infty) \\ -1\ \forall (n,n-1) = (1,0), (2,1), \ldots, (\infty,\infty) \\ 0 \quad \text{otherwise} \end{array}\right\}$$

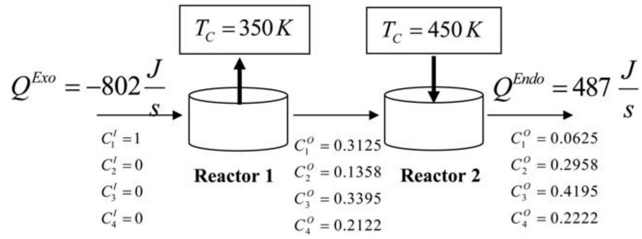

Figure 2. Baseline reactor network design.

Then

$$1 = \sum_{n=0}^{\infty}\left(\sum_{m=0}^{\infty} f(n,m)\right) \neq \sum_{m=0}^{\infty}\left(\sum_{n=0}^{\infty} f(n,m)\right) = 0.$$

Thus, for this example, the order of summation is not interchangeable. It is easy to verify that the assumption of absolute convergence is not satisfied.

Having established Fubini's Theorem for the interchange of double infinite sums, we now proceed to present this work's main theorem. ■

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 all feasible reactors and network outlet mixing junctions exhibit heat generation and consumption, that all network concentrations are bounded, that the mass enthalpy and entropy functions are bounded over their domain in temperature–pressure–composition space, and that the total mass flow in the network is finite, the network's utility consumption, and entropy generation satisfy the following*

$$\begin{aligned}\dot{Q}^{\mathrm{HU}} - \dot{Q}^{\mathrm{CU}} &= \sum_{j=1}^{N}\sum_{l=1}^{n}\left(z_l(j)\big/M_l\right) H^O(j) F^O(j) \\ &- \sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)\big/M_l\right) H^I(j) F^I(j)\end{aligned} \tag{35}$$

$$\dot{S}_G^T = \left[\begin{array}{c} \sum_{i=1}^{N}\sum_{l=1}^{n}\left(z_l(i)\big/M_l\right)\left(S^O(i) - \frac{H^O(i)}{T_{\mathrm{H}}}\right) F^O(i) - \\ \sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)\big/M_l\right)\left(S^I(j) - \frac{H^I(j)}{T_{\mathrm{H}}}\right) F^I(j) + \\ \dot{Q}^{\mathrm{CU}}\left(\frac{1}{T_{\mathrm{C}}} - \frac{1}{T_{\mathrm{H}}}\right)\end{array}\right] \tag{36}$$

Proof. From the following equations

$$\dot{Q}^{\mathrm{CU}} = -\left[\sum_{i\in S_1^R} \dot{Q}^R(i) + \sum_{i\in S_1^O} \dot{Q}^O(i)\right] \tag{32}$$

$$\dot{Q}^{\mathrm{HU}} = \sum_{i\in S_2^R} \dot{Q}^R(i) + \sum_{i\in S_2^O} \dot{Q}^O(i) \tag{33}$$

$$\dot{S}_G^T = \sum_{i\in S_1^R} \dot{S}_G^R(i) + \sum_{i\in S_1^O} \dot{S}_G^O(i) + \sum_{i\in S_2^R} \dot{S}_G^R(i) + \sum_{i\in S_2^O} \dot{S}_G^O(i) \tag{34}$$

$$(24)\wedge(24') \Rightarrow$$

$$\dot{Q}^{R}(i)=\sum_{l=1}^{n}\left(z_l(i)/M_l\right)H^{\hat{O}}(i)F^{\hat{O}}(i)-\left[\begin{array}{c}\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{I}(j)F^{\hat{I}I}(i,j)+\sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)+\\ \sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)\end{array}\right]\forall i=1,\infty \quad (24'')$$

$$\dot{Q}^{O}(i)=\sum_{l=1}^{n}\left(z_l(i)/M_l\right)H^{O}(i)F^{O}(i)-\left[\begin{array}{c}\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{I}(j)F^{OI}(i,j)+\sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)F^{O\hat{O}}(i,j)+\\ \sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)F^{O\hat{O}}(i,j)\end{array}\right]\forall i=1,N \quad (25)$$

Using the above equations, it holds that

$$\dot{Q}^{\mathrm{HU}}-\dot{Q}^{\mathrm{CU}}=\sum_{i\in S_2^R}\dot{Q}^{R}(i)+\sum_{i\in S_2^O}\dot{Q}^{O}(i)+\sum_{i\in S_1^R}\dot{Q}^{R}(i)+\sum_{i\in S_1^O}\dot{Q}^{O}(i)=\sum_{i=1}^{\infty}\dot{Q}^{R}(i)+\sum_{i=1}^{N}\dot{Q}^{O}(i)$$

$$=\sum_{i=1}^{\infty}\left(\begin{array}{c}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)H^{\hat{O}}(i)F^{\hat{O}}(i)-\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{I}(j)F^{\hat{I}I}(i,j)-\\ \sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)-\sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)\end{array}\right)$$

$$+\sum_{i=1}^{N}\left(\begin{array}{c}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)H^{O}(i)F^{O}(i)-\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{I}(j)F^{OI}(i,j)-\\ \sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)H^{\hat{O}}(j)F^{O\hat{O}}(i,j)-\sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)H^{\hat{O}}(j)F^{O\hat{O}}(i,j)\end{array}\right)$$

It is easy to verify that the above series are all absolutely convergent if the total mass flow in the network is finite. Thus, Fubini's theorem for infinite sums[22] is applicable, and the above is equivalent to

$$=\sum_{i=1}^{\infty}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)H^{\hat{O}}(i)F^{\hat{O}}(i)-\sum_{i=1}^{\infty}\left(\begin{array}{c}\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{I}(j)F^{\hat{I}I}(i,j)+\\ +\sum_{j=1}^{\infty}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)\end{array}\right)$$

$$+\sum_{i=1}^{N}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)H^{O}(i)F^{O}(i)-\sum_{i=1}^{N}\left(\begin{array}{c}\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{I}(j)F^{OI}(i,j)+\\ \sum_{j=1}^{\infty}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)\left(H^{\hat{O}}(j)F^{O\hat{O}}(i,j)\right)\end{array}\right)$$

$$=\sum_{i=1}^{\infty}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)H^{\hat{O}}(i)F^{\hat{O}}(i)-\left(\begin{array}{c}\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{I}(j)\sum_{i=1}^{\infty}F^{\hat{I}I}(i,j)+\\ \sum_{j=1}^{\infty}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)\sum_{i=1}^{\infty}F^{\hat{I}\hat{O}}(i,j)\end{array}\right)$$

$$+\sum_{i=1}^{N}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)H^{O}(i)F^{O}(i)-\left(\begin{array}{c}\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{I}(j)\sum_{i=1}^{N}F^{OI}(i,j)\\ +\sum_{j=1}^{\infty}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)\sum_{i=1}^{N}F^{O\hat{O}}(i,j)\end{array}\right)$$

$$=\sum_{j=1}^{\infty}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{\hat{O}}(j)\left(F^{\hat{O}}(j)-\sum_{i=1}^{\infty}F^{\hat{I}\hat{O}}(i,j)-\sum_{i=1}^{N}F^{O\hat{O}}(i,j)\right)+$$

$$+\sum_{i=1}^{N}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)H^{O}(i)F^{O}(i)-\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{I}(j)\left(\sum_{i=1}^{N}F^{OI}(i,j)+\sum_{i=1}^{\infty}F^{\hat{I}I}(i,j)\right)$$

$$=\sum_{j=1}^{N}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{O}(j)F^{O}(j)-\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)H^{I}(j)F^{I}(j)\quad \text{O.E.}\Delta$$

From the above, Eq. 35 is satisfied.

Similarly, network total entropy generation can be evaluated from Eq. 34 as

$$\dot{S}_G^T=\sum_{i\in S_1^R}\dot{S}_G^R(i)+\sum_{i\in S_1^O}\dot{S}_G^O(i)+\sum_{i\in S_2^R}\dot{S}_G^R(i)+\sum_{i\in S_2^O}\dot{S}_G^O(i)$$

$$=\sum_{i\in S_1^R}\left(\begin{array}{c}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)S^{\hat{O}}(i)F^{\hat{O}}(i)-\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{I}(j)F^{\hat{I}I}(i,j)+\\ -\sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)-\sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)-\dfrac{\dot{Q}^R(i)}{T_C}\end{array}\right)$$

$$+\sum_{i\in S_1^O}\left(\begin{array}{c}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)S^{O}(i)F^{O}(i)-\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{I}(j)F^{OI}(i,j)-\\ \sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{O\hat{O}}(i,j)-\sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{O\hat{O}}(i,j)-\dfrac{\dot{Q}^O(i)}{T_C}\end{array}\right)$$

$$+\sum_{i\in S_2^R}\left(\begin{array}{c}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)S^{\hat{O}}(i)F^{\hat{O}}(i)-\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{I}(j)F^{\hat{I}I}(i,j)-\\ \sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)-\sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)-\dfrac{\dot{Q}^R(i)}{T_H}\end{array}\right)$$

$$+\sum_{i\in S_2^O}\left(\begin{array}{c}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)S^{O}(i)F^{O}(i)-\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{I}(j)F^{OI}(i,j)-\\ \sum_{j\in S_1^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{O\hat{O}}(i,j)-\sum_{j\in S_2^R}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{O\hat{O}}(i,j)-\dfrac{\dot{Q}^O(i)}{T_H}\end{array}\right)$$

The above series are again all absolutely convergent, as the total mass flow in the network is finite. Thus, Fubini's theorem for infinite sums[22] is again applicable, and the above is equivalent to

$$=\sum_{i=1}^{N}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)S^{O}(i)F^{O}(i)+\sum_{i=1}^{\infty}\sum_{l=1}^{n}\left(z_l(i)/M_l\right)S^{\hat{O}}(i)F^{\hat{O}}(i)$$

$$-\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{I}(j)\left(\sum_{i=1}^{N}F^{OI}(i,j)+\sum_{i=1}^{\infty}F^{\hat{I}I}(i,j)\right)$$

$$-\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{\hat{I}\hat{O}}(i,j)-\sum_{i=1}^{N}\sum_{j=1}^{\infty}\sum_{l=1}^{n}\left(z_l(j)/M_l\right)S^{\hat{O}}(j)F^{O\hat{O}}(i,j)$$

$$-\left[\frac{\left(\sum_{i\in S_1^R}\dot{Q}^R(i)+\sum_{i\in S_1^O}\dot{Q}^O(i)\right)}{T_C}+\frac{\left(\sum_{i\in S_2^R}\dot{Q}^R(i)+\sum_{i\in S_2^O}\dot{Q}^O(i)\right)}{T_H}\right]$$

$$=\sum_{i=1}^{N}\sum_{l=1}^{n}\left(z_l(i)\Big/M_l\right)S^O(i)F^O(i)-\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)\Big/M_l\right)S^I(j)F^I(j)$$

$$+\frac{\dot{Q}^{\mathrm{CU}}}{T_{\mathrm{C}}}+\frac{-\dot{Q}^{\mathrm{HU}}}{T_{\mathrm{H}}}$$

$$=\sum_{i=1}^{N}\sum_{l=1}^{n}\left(z_l(i)\Big/M_l\right)\left(S^O(i)-\frac{H^O(i)}{T_{\mathrm{H}}}\right)F^O(i)$$

$$-\sum_{j=1}^{M}\sum_{l=1}^{n}\left(z_l(j)\Big/M_l\right)\left(S^I(j)-\frac{H^I(j)}{T_{\mathrm{H}}}\right)F^I(j)$$

$$+\dot{Q}^{\mathrm{CU}}\left(\frac{1}{T_{\mathrm{C}}}-\frac{1}{T_{\mathrm{H}}}\right)$$

From the above, Eq. 36 is satisfied. O.E.Δ.

The above theorem establishes several important facts regarding isothermal, isobaric reactor networks that use both endothermic and exothermic reactor/network outlet mixing units. First, the network's net (hot minus cold) utility consumption depends only on the network's inlet and outlet stream compositions and flow rates, and does not depend on the network's structure. Therefore, if one is to pursue the synthesis of such reactor networks (isothermal, isobaric, and consisting of reactor/mixer units belonging to a universe that contains both endothermic and exothermic units), using only inlet/outlet stream, and network net utility consumption specifications, then an attainable region-based synthesis approach, combined with net utility consumption isoclines in the spirit of our earlier work,[1] is feasible to pursue. Indeed, at every point of concentration space that belongs to the attainable region, a unique net utility consumption value can be assigned, as the structure of the networks that deliver this composition outlet (and there can be many such networks) does not affect the value of the net utility consumption at that point in concentration space. Thus, rigorous tradeoffs between reactor network outlet performance and net utility consumption specifications can be readily carried out without a network having to be designed.

The second important fact established in the above theorem is that the network's entropy generation depends on the network's inlet and outlet stream compositions and flow rates, and on the network's hot utility (or cold utility) consumption. In turn, this implies that the minimum entropy generation and minimum hot (or cold) utility cost reactor network synthesis problems are equivalent, over the class of isothermal, isobaric, reactor networks consisting of reactor/mixer units belonging to a universe that contains both endothermic and exothermic units, and satisfying fixed inlet and outlet stream specifications. In addition, if one is to pursue the synthesis of isothermal, isobaric, reactor networks consisting of reactor/mixer units belonging to a universe that contains both endothermic and exothermic units, using inlet/outlet stream, and network entropy generation, hot utility consumption, and/or cold utility consumption specifications, then an attainable region-based synthesis approach is, in general, not feasible to pursue. As can be seen from Eqs. 24″, 25, 32, and 33, the hot and cold utility consumptions depend, in general, on the network structure, as they consist of all mixer and reactor heat loads exchanged with the two reservoirs. Thus, at every point of concentration space that belongs to the attainable region, no unique entropy generation, hot utility consumption, and/or cold utility consumption value can be assigned, as the structure of the networks that deliver this composition outlet (and there can be many such networks) affects the values of these quantities at that point in concentration space. Thus, the globally optimal synthesis of such reactor networks can be pursued only through solution of the linear programming formulations arising from the IDEAS conceptual framework. A case study involving Trambouze kinetics is used to demonstrate these findings. ■

Case Study

Consider the following Trambouze reaction scheme, taking place at $T=400\,\mathrm{K}$ and $P=10^5\,\mathrm{Pa}$, in a homogeneous, isothermal, isobaric, constant density, and single inlet/outlet continuous stirred tank reactor network, with a feed concentration of $1\,\mathrm{mol/m^3}$ of pure reactant A and volumetric feed flow rate of $1\,\mathrm{m^3/s}$. The reaction scheme is as follows

$$A(1)\overset{k_1=0.025\frac{\mathrm{mol}}{\mathrm{m^3\cdot s}}}{\rightarrow}B(2)$$

$$A(1)\overset{k_2=0.2\mathrm{s}^{-1}}{\rightarrow}C(3)$$

$$A(1)\overset{k_3=0.4\frac{\mathrm{m^3}}{\mathrm{mol\cdot s}}}{\rightarrow}D(4)$$

Reaction rates for all species are as follows

$$R_1\left(\frac{\mathrm{mol}}{\mathrm{m^3\cdot s}}\right)=-k_1-k_2C_1^{\mathrm{out}}-k_3\left(C_1^{\mathrm{out}}\right)^2$$

$$R_2\left(\frac{\mathrm{mol}}{\mathrm{m^3\cdot s}}\right)=k_1$$

$$R_3\left(\frac{\mathrm{mol}}{\mathrm{m^3\cdot s}}\right)=k_2C_1^{\mathrm{out}}$$

$$R_4\left(\frac{\mathrm{mol}}{\mathrm{m^3\cdot s}}\right)=k_3\left(C_1^{\mathrm{out}}\right)^2$$

The reactor network's inlet and outlet are considered to be at the reactor network's operating temperature and pressure $T=400\,\mathrm{K}$ and $P=10^5\,\mathrm{Pa}$, and the reacting mixture is considered to be ideal, that is, mixing effects are neglected and excess entropy/enthalpy terms are set to zero. The four pure species' molar entropy, S_k and molar enthalpy, H_k at $T=400$ K and $P=10^5\,\mathrm{Pa}$ are shown in Table 1. These values suggest that some reactors in the reactor network require cooling, which is provided by a single infinite reservoir at $T_{\mathrm{C}}=350\,\mathrm{K}$, while other reactors in the reactor network require heating, which is provided by a single infinite reservoir at $T_{\mathrm{H}}=450\,\mathrm{K}$.

Close examination of the above reaction scheme reveals that

$$R_1+R_2+R_3+R_4=0$$

Thus, application of the dimensionality reduction principle for single inlet and single outlet reactor networks[19] yields that for any reactor network stream it holds that

$$C_1^I=C_1+C_2+C_3+C_4\Rightarrow 1\ \mathrm{mol/m^3}=C_1+C_2+C_3+C_4$$

The desired network outlet concentration vector is chosen as $\left[C_A^O\quad C_B^O\quad C_C^O\quad C_D^O\right]=\left[0.0625\quad 0.2958\quad 0.4195\quad 0.2222\right]$, which satisfies the above condition.

In addition, as will be subsequently demonstrated, as the reaction rates of components 3 and 4 depend only on C_1^{out}, the change in the concentrations of components 2, 3, and 4

Table 1. Pure Species Molar Entropy and Enthalpy at $T = 400$ K and $P = 10^5$ Pa

k	$A(1)$	$B(2)$	$C(3)$	$D(4)$
S_k(J/(mol · K))	−451	−445	−439	−440
H_k(J/mol)	−24000	−16000	−35000	−15300

across each reactor can be determined as only a function of the residence time τ, and possibly C_1^{out}.

Under the aforementioned mixture properties, Eqs. 10–14 can be simplified into Eqs. 10′–14′ as follows

$$S\left(T,P,\{C_k\}_{k=1}^n\right)=\sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} S_k(T,P) \tag{10′}$$

$$H\left(T,P,\{C_k\}_{k=1}^n\right)=\sum_{k=1}^n \frac{C_k}{\sum_{l=1}^n C_l} H_k(T,P) \tag{11′}$$

$$H^{\text{E}}\left(T,P,\{C_k\}_{k=1}^n\right)=0 \tag{12′}$$

$$S^{\text{E}}\left(T,P,\{C_k\}_{k=1}^n\right)=0 \tag{13′}$$

In turn, the vectors u and y, which describe the information map under consideration, can be defined from above as

$$\Phi : \boldsymbol{u}=\begin{bmatrix}\boldsymbol{u}_1\\ \boldsymbol{u}_2\end{bmatrix} \rightarrow \boldsymbol{y}=\begin{bmatrix}\boldsymbol{y}_1\\ \boldsymbol{y}_2\end{bmatrix}=\Phi(\boldsymbol{u}_1,\boldsymbol{u}_2)=\begin{bmatrix}\Phi_1(\boldsymbol{u}_1,\boldsymbol{u}_2)\\ \Phi_2(\boldsymbol{u}_1,\boldsymbol{u}_2)\end{bmatrix}$$

$$\boldsymbol{u}^T \hat{=} \left[\boldsymbol{u}_1^T | \boldsymbol{u}_2^T\right] \hat{=} \left[T \quad P \quad C_1^{\text{in}} \quad C_1^{\text{out}} \quad \lambda \quad | \quad q \quad \dot{Q}^R \quad \dot{S}_G^R\right],$$

$$\boldsymbol{y}^T \hat{=} \left[\boldsymbol{y}_1^T | \boldsymbol{y}_2^T\right] \hat{=} \Phi^T(\boldsymbol{u}_1,\boldsymbol{u}_2) \hat{=}$$

$$\left[\tau \quad \left(C_2^{\text{out}}-C_2^{\text{in}}\right) \quad \left(C_3^{\text{out}}-C_3^{\text{in}}\right) \quad \left(C_4^{\text{out}}-C_4^{\text{in}}\right) \quad | \quad q\right]$$

Where

$D \hat{=} \{\boldsymbol{u} \in R^4 \times \{0,1\} \times R^3 : \Phi_3(\boldsymbol{u}_1,\boldsymbol{u}_2)=0 \wedge \sum_{i=1}^n C_i^{\text{out}} - C_1^I = 0 \wedge \boldsymbol{u}_1 \geq 0 \wedge F \geq 0 \wedge \dot{S}_G^R \geq 0\}$, and $\Phi_3(\boldsymbol{u}_1,\boldsymbol{u}_2) \hat{=} \begin{bmatrix} -q\sum_{l=1}^n \left(C_1^{\text{out}}-C_1^{\text{in}}\right)H_l(T,P)+\dot{Q}^R \\ -q\sum_{l=1}^n \left(C_1^{\text{out}}-C_1^{\text{in}}\right)S_l(T,P)+\dot{Q}^R\left(\frac{\lambda}{T_{\text{H}}}+\frac{(1-\lambda)}{T_{\text{C}}}\right)+\dot{S}_G^R \end{bmatrix}$ for which all the properties described above hold true.

Knowing $\boldsymbol{u}_1$, the reactor model then allows us to first determine the residence time τ as follows

$$C_1^{\text{out}}-C_1^{\text{in}}=\tau\left(-k_1-k_2C_1^{\text{out}}-k_3\left(C_1^{\text{out}}\right)^2\right)$$

$$\Rightarrow \tau=\left(\frac{C_1^{\text{out}}-C_1^{\text{in}}}{-k_1-k_2C_1^{\text{out}}-k_3\left(C_1^{\text{out}}\right)^2}\right) \tag{37}$$

The change in concentrations for species 2, 3, and 4 can then be determined from the following equations

$$C_2^{\text{out}}-C_2^{\text{in}}=\Delta C_2=\tau k_1 \tag{38}$$

$$C_3^{\text{out}}-C_3^{\text{in}}=\Delta C_3=\tau k_2 C_1^{\text{out}} \tag{39}$$

$$C_4^{\text{out}}-C_4^{\text{in}}=\Delta C_4=\tau k_3\left(C_1^{\text{out}}\right)^2 \tag{40}$$

The corresponding finite linear programming formulation of the reactor network synthesis consisting of a single inlet and single outlet and featuring minimum entropy generation for an ever increasing sequence of L reactors is given below. Let S_1^L and S_2^L denote the index sets corresponding to all realizable exothermic and endothermic reactors, respectively, within the considered set of L reactors. Then, $S_1^L \cup S_2^L = \{1,\ldots,L\}$, and the LP can be written as follows

Table 2. Exothermic and Endothermic Heat Loads for IDEAS and Baseline Designs

Heat Transferred	$\sum_{i_1} \dot{Q}(i_1)$ (Exothermic)	$\sum_{i_2} \dot{Q}(i_2)$ (Endothermic)
Baseline Network	−802.082	486.999
IDEAS Network (1/16 discretization)	−436.633	121.75
IDEAS Network (1/32 discretization)	−391.570	76.963
IDEAS Network (1/50 discretization)	−378.54	63.94

$$\inf \dot{S}_G^T$$

s.t.

$$1=q^{OI}(1,1)+\sum_{i=1}^L q^{\hat{I}I}(i,1) \tag{41}$$

$$1=q^{OI}(1,1)+\sum_{j=1}^L q^{O\hat{O}}(1,j) \tag{42}$$

$$q^{\hat{I}}(i)=q^{\hat{I}I}(i,1)+\sum_{j=1}^L q^{\hat{I}\hat{O}}(i,j) \quad \forall i=1,L \tag{43}$$

$$q^{\hat{O}}(j)=q^{O\hat{O}}(1,j)+\sum_{i=1}^L q^{\hat{I}\hat{O}}(i,j) \quad \forall j=1,L \tag{44}$$

$$q^{\hat{O}}(i)=q^{\hat{I}}(i)\forall i=1,L \tag{45}$$

$$C_1^{\hat{I}}(i)q^{\hat{I}}(i)=C_1^I q^{\hat{I}I}(i,1)+\sum_{j=1}^L C_1^{\hat{O}}(j)q^{\hat{I}\hat{O}}(i,j) \quad \forall i=1,L \tag{46}$$

$$C_1^I q^{OI}(1,1)+\sum_{j=1}^L C_1^{\hat{O}}(j)q^{O\hat{O}}(1,j)=C_1^O \tag{47}$$

$$\left[\sum_{j=1}^L \Delta C_k(j)q^{\hat{I}}(j)\right]=C_k^O \quad \forall k=2,4 \tag{48}$$

$$\dot{Q}^R(i)=q^{\hat{I}}(i)\sum_{l=1}^n \left(C_1^{\text{out}}(i)-C_1^{\text{in}}(i)\right)H_l(T,P) \quad \forall i=1,L \tag{49}$$

Table 3. Flow Rates, and from-to Nodes for IDEAS Optimal Network (1/32 Discretization)

From	To	Flow	From	To	Flow
Inlet	1	0.00188	2	1	0.05076
Inlet	2	0.00362	4	2	0.04713
Inlet	3	0.00631	1	3	0.05264
Inlet	4	0.00841	5	4	0.03871
Inlet	5	0.0870	6	5	0.4145
Inlet	6	0.0740	11	5	0.5371
Inlet	7	0.0153	7	6	0.2451
Inlet	8	0.05895	8	6	0.0987
Inlet	9	0.04308	9	7	0.2297
Inlet	10	0.09335	3	8	0.05895
Inlet	11	0.5179	10	9	0.1867
Inlet	12	0.0900	12	10	0.09335
5	13	1	8	11	0.01918
13	14	1	6	12	0.00333
14	Outlet	1	–	–	–

Table 4. Species Concentrations across each Reactor of IDEAS Optimal Network (1/32 Discretization)

Reactor	C_A^{in}	C_A^{out}	ΔC_B	ΔC_C	ΔC_D	$\dot{Q}$(J/s)
1	0.15625	0.125	0.01388	0.01388	0.00347	−0.603
2	0.1875	0.125	0.02777	0.02777	0.00694	−1.163
3	0.21875	0.125	0.04166	0.04166	0.01041	−2.026
4	0.28125	0.125	0.06944	0.06944	0.01736	−2.700
5	0.34375	0.125	0.09722	0.09722	0.02430	−83.315
6	0.5	0.125	0.1666	0.1666	0.04166	−57.459
7	0.53125	0.5	0.003472	0.01388	0.01388	−1.021
8	0.5625	0.125	0.1944	0.1944	0.04861	−18.915
9	0.59375	0.5	0.01041	0.04166	0.04166	−2.872
10	0.75	0.5	0.02777	0.1111	0.1111	−6.223
11	0.96875	0.40625	0.08163	0.2653	0.2151	−209.439
12	0.96875	0.5	0.05208	0.20833	0.20833	−5.834
13	0.125	0.09375	0.01652	0.01239	0.00232	16.089
14	0.09375	0.0625	0.02000	0.01000	0.00125	60.874

$$\dot{S}_G^R(i)=q^{\hat{I}}(i)\sum_{l=1}^{n}\left(C_1^{\text{out}}(i)-C_1^{\text{in}}(i)\right)S_l(T,P)-\frac{\dot{Q}^R(i)}{T_{\text{C}}}\quad \forall i\in S_1^L \tag{50}$$

$$\dot{S}_G^R(i)=q^{\hat{I}}(i)\sum_{l=1}^{n}\left(C_1^{\text{out}}(i)-C_1^{\text{in}}(i)\right)S_l(T,P)-\frac{\dot{Q}^R(i)}{T_{\text{H}}}\quad \forall i\in S_2^R \tag{51}$$

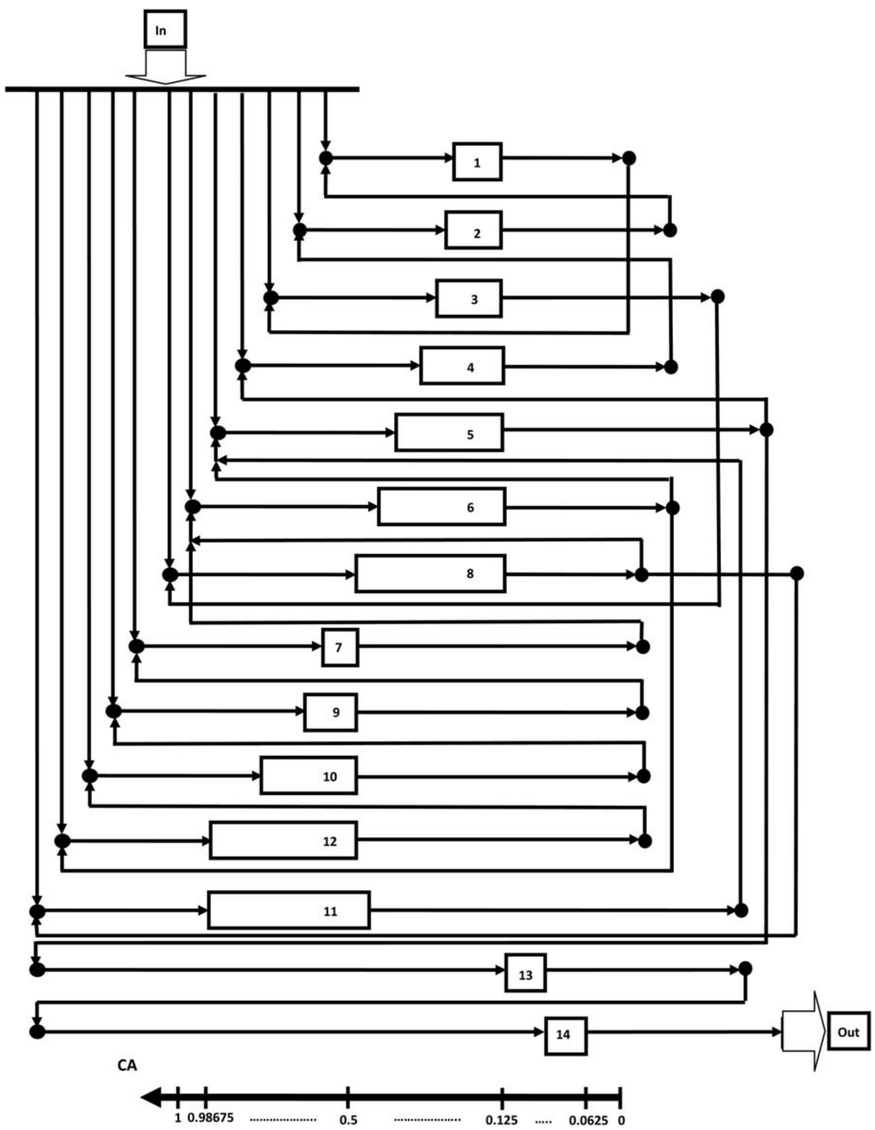

Figure 3. IDEAS-generated minimum entropy generation network (1/32 discretization).

Table 5. Flow Rates, and from-to Nodes for IDEAS Optimal Network (1/16 Discretization)

From	To	Flow	From	To	Flow
Inlet	3	0.1127	2	3	0.6759
Inlet	5	0.1159	6	4	0.4053
Inlet	7	0.1163	4	5	0.4053
Inlet	8	0.0528	10	5	0.1546
Inlet	9	0.4863	7	6	0.4053
Inlet	10	0.116	9	7	0.814
3	1	0.7885	9	8	0.1585
8	1	0.2114	7	9	0.4863
5	2	0.6759	7	10	0.03866
1	Outlet	–	–	–	–

$$\dot{S}_G^T=\left[\sum_{l=1}^{n}\left(C_l^O-C_l^I\right)\left(S_l(T,P)-\frac{H_l(T,P)}{T_\mathrm{H}}\right)-\sum_{i\in S_1^R}\dot{Q}^R(i)\left(\frac{1}{T_\mathrm{C}}-\frac{1}{T_\mathrm{H}}\right)\right] \tag{52}$$

$$q^I\geq 0; q^O\geq 0; q^{OI}\geq 0; q^{\hat{I}}\geq 0; q^{\hat{O}}\geq 0; q^{\hat{I}I}\geq 0; q^{O\hat{O}}\geq 0; q^{\hat{I}\hat{O}}\geq 0; \dot{Q}^R(i)\leq 0 \ \ \forall i\in S_1^L; \dot{Q}^R(i)\geq 0 \ \forall i\in S_2^L; \dot{Q}^R(i)\geq 0 \ \forall i\in S_2^L$$

A reactor network that delivers the specified outlet concentration vector $\left[C_A^O \quad C_B^O \quad C_C^O \quad C_D^O\right]=[0.0625 \quad 0.2958 \quad 0.4195 \quad 0.2222]$ is considered as the baseline design. It consists of two CSTRs in series with residence times $\tau_1=5.432$s and $\tau_2=6.4$s, respectively; it generates 1.20944 J/(K s) of entropy; and it has exothermic and endothermic heat loads equal to −802 and 487 J/s, respectively. The IDEAS method is carried out for the following levels of discretization: 1/2, 1/4, 1/8, 1/16, 1/32, and 1/50.

The results are as follows:

In the optimum IDEAS design at the 1/16 discretization level, the entropy generated [0.9777 J/(K s)] is 19.2% lower than the entropy generated [1.20944 J/(K s)] in the original two CSTR baseline design.

In the optimum IDEAS design at the 1/32 discretization level, the entropy generated [0.9477 J/(K s)] is 3% lower than the entropy generated [0.9777 J/(K s)] in the optimum design at the 1/16 discretization level, and 21.6% lower than the entropy generated [1.20944 J/(K s)]in the original two CSTR baseline design.

In the optimum design at the 1/50 discretization level, the entropy generated [0.9405 J/(K s)] is 0.8% lower than the entropy generated [0.9477 J/(K s)] at the 1/32 discretization level, and 22.2% lower than the entropy generated [1.20944 J/(K s)] in the original two CSTR baseline design.

At the 1/2, 1/4, and 1/8 discretization levels, there are no feasible designs, due to the stringent outlet concentration specifications on all species involved, and particularly the 0.0625 specification on the outlet concentration of species A.

In addition, the number of reactors in the network generated by the IDEAS at the 1/16 discretization level is around 2/3 the number of reactors in the network generated by IDEAS at the 1/32 discretization level (10 reactors vs. 14 reactors).

If the temperatures of the reservoirs (hot and cold) were infinitesimally away from the temperature of the reactor network, then entropy generation would become independent of the network structure. In this case, a reversible entropy generation lower bound can be quantified through an entropy balance around the network. If only the heat effect contribution to entropy generation is considered, to maintain consistency with the irreversible case discussed above, we would generate only 0.7875 J/(K s) through reversible heat transfer between the reactor network and its isothermal surroundings. Given that the outlet concentration specifications are the same, and based on the presented theorem, minimization of entropy generation is equivalent to hot (or cold) utility minimization. If one were to compare the difference in exothermic and endothermic heat loads between the baseline and IDEAS designs, then the IDEAS-generated network (for 1/32 discretization level) is seen to generate 51% less exothermic heat load and to require 84% less endothermic heat load. The heat loads for all designs are shown in Table 2 below.

In the tables and figures below, detailed information is provided about the optimal IDEAS designs obtained for the 1/32, and 1/16 discretizations. Tables 3 and 4 and Figure 3 show information on the IDEAS optimal design for the 1/32 discretization, whereas Tables 5 and 6 and Figure 4 show information on the IDEAS optimal design for the 1/16 discretization.

We next discuss the IDEAS-generated reactor network based on the 1/32 discretization. As compared to the baseline case, this network exhibits several characteristics not known in advance, and worthy of elaboration. The most striking of these characteristics is the splitting of the network feed, in varying quantities, so it can help form the feed to each and every exothermic reactor in the IDEAS network (Reactors 1–12). Conversely, the network feed does not contribute to the feed of any endothermic reactor in the IDEAS network. Another network characteristic is that it uses two clusters of exothermic reactors; one cluster with $C_A^{\mathrm{out}}=0.5$ (Reactors 7, 9, 10, and 12), and another cluster with $C_A^{\mathrm{out}}=0.125$ (Reactors 1–6 and 8). The feed to each one of the reactors in those two clusters is generated by mixing part of the network feed with an outlet from some other exothermic reactor. In contrast, the endothermic reactors (Reactor 13 and 14) form a sequence whose outlet is the outlet of the network.

Table 6. Species Concentrations across each Reactor of IDEAS Optimal Network (1/16 Discretization)

Reactor	C_A^{in}	C_A^{out}	ΔC_B	ΔC_C	ΔC_D	$\dot{Q}$(J/s)
1	0.125	0.0625	0.04	0.02	0.0025	121.7499
2	0.1875	0.0625	0.08	0.04	0.005	−22.9166
3	0.25	0.125	0.055556	0.055556	0.013889	−45.8332
4	0.25	0.1875	0.020408	0.030612	0.01148	−73.5969
5	0.3125	0.1875	0.040816	0.061224	0.022959	−147.194
6	0.5	0.25	0.0625	0.125	0.0625	−331.25
7	0.5625	0.5	0.006944	0.027778	0.027778	−8.33324
8	0.625	0.125	0.222222	0.222222	0.055556	−183.333
9	0.75	0.5	0.027778	0.111111	0.111111	−33.333
10	0.875	0.125	0.333333	0.333333	0.083333	−275.001

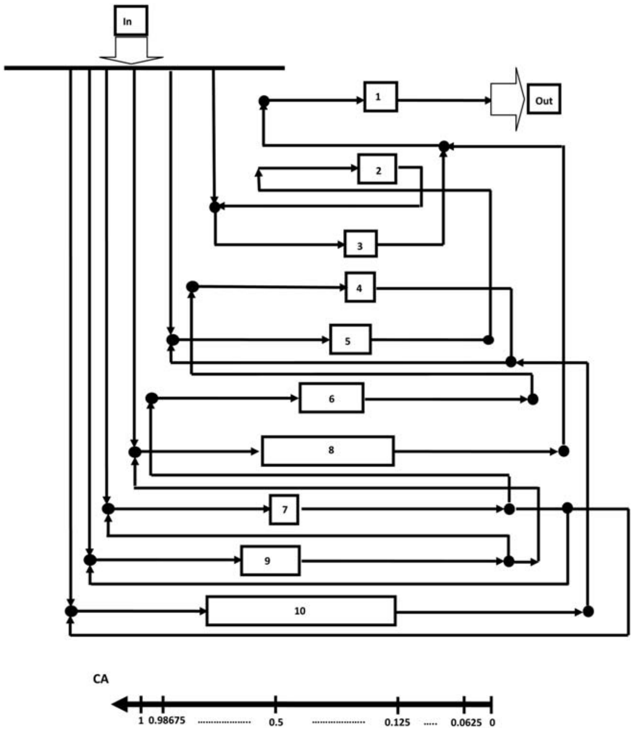

Figure 4. IDEAS-generated minimum entropy generation network (1/16 discretization).

The IDEAS optimal network obtained for the 1/16 discretization, features some similar characteristics to the optimal design obtained for the 1/32 discretization. For example, the network feed is again split into many streams (six in number) which contribute to the formation of the feed of exothermic reactors, while it does not contribute to the feed of the single endothermic reactor in the IDEAS network. Another feature similar to the 1/32 optimal design is that the network outlet is the outlet of the network's single endothermic reactor.

Discussion—Conclusions

This work demonstrated the importance of the internal structure of an isothermal, continuous stirred tank reactor network featuring both endothermic and exothermic reactors, in determining the entropy generated by the network. This stands contrary to the case where the feasible reactor universe consists of either only endothermic or only exothermic reactors, where entropy generation is uniquely determined by the network's inlet and outlet specifications and is independent of the network structure. A theorem is rigorously established suggesting that the synthesis of isothermal reactor networks featuring minimum entropy generation and having known and fixed inlet and outlet specifications, is equivalent to the synthesis of isothermal reactor networks featuring minimum hot (or cold) utility consumption and having known and fixed inlet and outlet specifications. A case study is used to illustrate the proposed IDEAS-based network synthesis methodology. The networks generated by IDEAS demonstrate several unique characteristics. The network feed contributes to the formation of the feed of many if not all exothermic reactor units of the network. The network outlet is the outlet of an endothermic reactor. The entropy generation of the IDEAS design at the highest level of discretization, is shown to be around 22.2% lower than the entropy generated in the original two CSTR baseline design.

Notation

C_i = ith component molar concentration, mol/m^3

C_i^{in} = ith component reactor inlet molar concentration, mol/m^3

C_i^{out} = ith component reactor outlet molar concentration, mol/m^3

F = mass flow rate, kg/s

F^{in} = inlet mass flow rate, kg/s

F^{out} = outlet mass flow rate, kg/s

$G^E\left(T,P,\{C_k\}_{k=1}^n\right)$ = excess Gibbs free energy associated with a general stream of temperature, pressure, and composition T, P, and $\{C_k\}_{k=1}^n$, respectively, J/kg

h^{arr} = enthalpy arriving at reactor inlet J/s. This is different than the reactor's inlet enthalpy, as it does not account for stream mixing heat effects which are directly incorporated into the reactor's overall heating/cooling need

$H\left(T,P,\{C_k\}_{k=1}^n\right)$ = molar enthalpy associated with a stream of temperature, pressure, and composition T, P, and$\{C_k\}_{k=1}^n$, J/mol

$H^{\mathrm{id}}\left(T,P,\{C_k\}_{k=1}^n\right)$ = ideal molar enthalpy associated with a temperature, pressure, and composition T, P, and$\{C_k\}_{k=1}^n$, J/mol

$H^{\mathrm{E}}\left(T,P,\{C_k\}_{k=1}^n\right)$ = excess molar enthalpy associated with a general stream of temperature, pressure, and composition T, P, and $\{C_k\}_{k=1}^n$, J/mol

$H_k(T,P)$ = pure component ideal molar enthalpy associated with a constant density stream of temperature and pressure T, P, respectively, J/mol

$k_1 : 0.025\,\frac{\mathrm{mol}}{\mathrm{m^3 \cdot s}}$ = zeroth-order Trambouze kinetics constant

$k_2 : 0.2\mathrm{s}^{-1}$ = first-order Trambouze kinetics constant

$k_3 : 0.4\,\frac{\mathrm{m^3}}{\mathrm{mol \cdot s}}$ = second-order Trambouze kinetics constant

M_k = kth species molecular weight, g/mol

P = pressure, Pa

$\dot{Q}^T$ = total network energy consumption rate, J/s

$\dot{Q}^{\mathrm{HU}}$ = hot utility consumption rate, J/s

$\dot{Q}^{\mathrm{CU}}$ = cold utility consumption rate, J/s

q = volumetric flow rate, m^3/s

q^{in} = inlet volumetric flow rate, m^3/s

q^{out} = outlet volumetric flow rate, m^3/s

R = universal gas constant, J/(K mol)

R_k = kth component generation rate, molar model, mol/(m^3 s)

r_k = kth component generation rate, mass model, mol/(m^3 s)

s^{arr} = entropy arriving at reactor inlet, J/(K s). This is different than the reactor's inlet entropy, as it does not account for stream mixing heat effects which are directly incorporated into the reactor's overall heating/cooling need, and entropy generation

$S\left(T,P,\{C_k\}_{k=1}^n\right)$ = molar entropy associated with a stream of temperature, pressure, and composition T,P, and$\{C_k\}_{k=1}^n$, J/(mol K)

$S^{\mathrm{id}}\left(T,P,\{C_k\}_{k=1}^n\right)$ = ideal molar entropy associated with a general stream of temperature, pressure, and composition T,P, and $\{C_k\}_{k=1}^n$, J/(mol K)

$S^{\mathrm{E}}\left(T,P,\{C_k\}_{k=1}^n\right)$ = excess molar entropy associated with a general stream of temperature, pressure, and composition T, P, and $\{C_k\}_{k=1}^n$, J/(mol K.)

$S_k(T,P)$ = pure component ideal molar entropy associated with a general stream of temperature and pressure T, P, respectively, J/(mol K)

S_1^R, S_1^L = entropy generation in exothermic reactor, J/(s K)

S_2^R, S_2^L = entropy generation in endothermic reactor, J/(s K)

S_1^O = entropy generation in exothermic network mixing outlet, J/(s K)

S_2^O = entropy generation in endothermic network mixing outlet, J/(s K)

$\dot{S}_G^T$ = total network entropy generation rate, J/(s K)

$\dot{S}_G^R$ = reactor entropy generation rate, J/(s K)

T = temperature, K

T_C = temperature of cold infinite capacity reservoir, K
T_H = temperature of hot infinite capacity reservoir, K
u = input vector of an information map
V = reactor volume, m^3
x_i = ith component mole fraction
y = output vector of an information map
z_k = kth component mass fraction
z_i^{in} = ith component reactor inlet mass fraction
z_i^{out} = ith component reactor outlet mass fraction
$\gamma_k(T, P, \{C_k\}_{k=1}^n)$ = liquid-phase activity coefficient function associated with a liquid stream of temperature, pressure, and composition T, P, and $\{C_k\}_{k=1}^n$, respectively, J/kg
$\lambda = H(\dot{Q}^R) = \left\{\begin{matrix} 1 \text{ if } \dot{Q}^R > 0 \\ 0 \text{ if } \dot{Q}^R < 0 \end{matrix}\right\}$ = exothermic reactor flag identifier defined as a Heaviside function of $\dot{Q}^R$.
ρ = density, kg/m^3
σ = volume to mass flow rate ratio for variable density fluid reactor, (m^3 s)/kg
τ = residence time for constant density fluid reactor, s
Φ = input–output information map for process model
$\wedge$ = logical symbol indicating "and"

IDEAS variables

M = number of IDEAS network inlets
N = number of IDEAS network outlets
$C_k^I(j)$ = kth component concentration in the jth network inlet $\forall k=1,n; \forall j=1,M$, mol/m^3
$C_k^O(i)$ = kth component concentration in the ith network outlet $\forall k=1,n; \forall i=1,N$, mol/m^3
$C_k^{\hat{I}}(i)$ = kth component concentration in the ith OP inlet $\forall k=1,n; \forall i=1,\infty$, mol/m^3
$C_k^{\hat{O}}(i)$ = kth component mass fraction in the ith OP outlet $\forall k=1,n; \forall i=1,\infty$, mol/m^3
$F^I(j)$ = jth network inlet mass flow rate $\forall j=1,M$, kg/s
$F^O(i)$ = ith network outlet mass flow rate $\forall i=1,N$, kg/s
$F^{\hat{I}}(j)$ = jth OP inlet mass flow rate $\forall j=1,\infty$, kg/s
$F^{\hat{O}}(i)$ = ith OP outlet mass flow rate $\forall i=1,\infty$, kg/s
$F^{OI}(i,j)$ = jth network inlet mass flow rate to the ith network outlet $\forall j=1,M; \forall i=1,N$, kg/s
$F^{\hat{I}I}(i,j)$ = jth network outlet mass flow rate to the ith OP inlet $\forall j=1,M; \forall i=1,\infty$, kg/s
$F^{O\hat{O}}(i,j)$ = jth OP outlet mass flow rate to the ith network outlet $\forall j=1,\infty; \forall i=1,N$, kg/s
$F^{\hat{I}\hat{O}}(i,j)$ = jth OP outlet mass flow rate to the ith OP network outlet $\forall j=1,\infty; \forall i=1,\infty$, kg/s
$H^I(j)$ = enthalpy associated with jth network inlet stream $\forall j=1,M$, J/mol
$H^O(i)$ = enthalpy associated with ith network outlet stream $\forall i=1,N$, J/mol
$H^{\hat{I}}(j)$ = enthalpy associated with jth OP inlet stream $\forall j=1,\infty$, J/mol
$H^{\hat{O}}(i)$ = enthalpy associated with ith OP outlet stream $\forall i=1,\infty$, J/mol
$\dot{Q}^R(i)$ = heat rate for ith reactor in IDEAS reactor network $\forall i=1,\infty$, J/s
$\dot{Q}^O(i)$ = heat of mixing rate at ith DN network outlet $\forall i=1,N$, J/s
$q^I(j)$ = jth network inlet volumetric flow rate $\forall j=1,M$, m^3/s
$q^O(i)$ = ith network outlet volumetric flow rate $\forall i=1,N$, m^3/s
$q^{\hat{I}}(j)$ = jth OP inlet volumetric flow rate $\forall j=1,\infty$, m^3/s
$q^{\hat{O}}(i)$ = ith OP outlet volumetric flow rate $\forall i=1,\infty$, m^3/s
$q^{OI}(i,j)$ = jth network inlet volumetric flow rate to the ith network outlet $\forall j=1,M; \forall i=1,N$, m^3/s
$q^{\hat{I}I}(i,j)$ = jth network outlet volumetric flow rate to the ith OP inlet $\forall j=1,M; \forall i=1,\infty$, m^3/s
$q^{O\hat{O}}(i,j)$ = jth OP outlet volumetric flow rate to the ith network outlet $\forall j=1,\infty; \forall i=1,N$, m^3/s
$q^{\hat{I}\hat{O}}(i,j)$ = jth OP outlet volumetric flow rate to the ith OP network outlet $\forall j=1,\infty; \forall i=1,\infty$, m^3/s
$S^I(j)$ = entropy associated with jth network inlet stream $\forall j=1,M$, J/(mol K)
$S^O(i)$ = entropy associated with ith network outlet stream $\forall i=1,N$, J/(mol K)
$S^{\hat{I}}(j)$ = entropy associated with jth OP inlet stream $\forall j=1,\infty$, J/(mol K)
$S^{\hat{O}}(i)$ = entropy associated with ith OP outlet stream $\forall i=1,\infty$, J/(mol K)
$u(i)$ = input of the ith OP unit information map $\forall i=1,\infty$
$y(i)$ = output of the ith OP unit information map $\forall i=1,\infty$
$z_k^I(j)$ = kth component mass fraction in the jth network inlet $\forall k=1,n; \forall j=1,M$
$z_k^O(i)$ = kth component mass fraction in the ith network outlet $\forall k=1,n; \forall i=1,N$
$z_k^{\hat{I}}(i)$ = kth component mass fraction in the ith OP inlet $\forall k=1,n; \forall i=1,\infty$
$z_k^{\hat{O}}(i)$ = kth component mass fraction in the ith OP outlet $\forall k=1,n; \forall i=1,\infty$
$\lambda(i) = H(Q(i)) = \left\{\begin{matrix} 1 & \text{if } Q(i) > 0 \\ 0 & \text{if } Q(i) < 0 \end{matrix}\right\}$ = exothermic reactor flag identifier defined as a Heaviside function of $Q(i)$.
$\tau(i)$ = residence time of the ith OP unit $\forall i=1,\infty$, s

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