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Infinite DimEnsionAl State-space: A Systematic Process Intensification Tool With Application to Hydrogen Production

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**Publication Date** 2016

Peer reviewed|Thesis/dissertation

University of California

Los Angeles

Infinite DimEnsionAl State-space:

A Systematic Process Intensification Tool

With Application to Hydrogen Production

A thesis submitted in partial satisfaction of the requirements for the degree Master of Science in

**Chemical Engineering** 

by

Patricia Aida Pichardo

2016

#### ABSTRACT OF THESIS

Infinite DimEnsionAl State-space: A Systematic Process Intensification Tool With Application to Hydrogen Production By: Patricia Aida Pichardo

Master of Science in Chemical Engineering University of California, Los Angeles, 2016 Professor Vasilios Manousiouthakis, Chair

In this work, process intensification is identified as a process synthesis activity aiming at significant improvements over traditional process designs. The infinite-dimensional state-space conceptual framework is proposed as a systematic process intensification tool, as it can identify intensified process designs, and can assess fundamental limitations to the attainable performance of networks of technologies under consideration. The synthesis of intensified flowsheets, in an energy efficiency sense, is pursued through simultaneous synthesis of the flowsheet and its heat exchange network, and atomic balance, Gibbs free energy minimization based equilibrium reactor models that are employed for the first time. The employed approach enables a broad state-space search, for process intensification opportunities, even by low dimensional IDEAS linear programming approximations that are always feasible. Application of the proposed method to natural gas reforming based hydrogen production, identifies intensified process designs featuring hot utility costs that can be lower by over an order of magnitude to those of traditional designs.

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# **COMMITTEE PAGE:**

The thesis of Patricia Aida Pichardo is approved.

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2016

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## **ACKNOWLEDGEMENTS:**

I would like to thank Professor Vasilios Manousiouthakis for helping me throughout the entirety of this project as my research advisor. Financial support through DOE grant DE-EE0005763 "Industrial Scale Demonstration of Smart Manufacturing Achieving Transformational Energy Productivity Gains" is acknowledged. Discussions with Omar Sheikh, and Jeremy Conner, and free access to the UNISIM software by Honeywell Inc., are also acknowledged.

### **1. INTRODUCTION:**

The academic development of the Chemical Engineering profession was first focused on Process Analysis. For decades, researchers developed first principle based models aiming to capture the behavior of chemical processes<sup>1-2</sup>. The continuous improvement of computer technology, combined with advances in model simulation methods, has enabled the repeated adhoc use of these process analysis methods in chemical process design. Process Synthesis methods have also slowly begun to appear, though few and far in between: Solvay cluster synthesis<sup>3-5</sup>, heat integration<sup>6-9</sup>, mass integration<sup>10</sup>, and reaction attainable region based synthesis<sup>11-17</sup>. Optimization formulations, such as nonlinear programs (NLP's), or mixed integer nonlinear programs (MINLP's), have also been used for flowsheet synthesis<sup>18,19</sup>. Unfortunately, these formulations tend to be non-convex, and thus their instances with a significant number of variables cannot be solved globally within realistic time frames.

Process intensification is a strategy for making dramatic reductions (order 100 or more) in the size of a chemical plant that attains given production objectives<sup>20</sup>. These reductions can come from reducing the number of units employed in the chemical plant as well as decreasing the size of individual units. Expanding the scope of process intensification beyond size has led to its characterization as "any chemical engineering development that leads to substantially smaller, cleaner, and more energy efficient technology"<sup>21</sup>. Stankiewicz<sup>22</sup> refers to the methyl acetate process by Eastman Chemical<sup>23</sup> as a widely regarded textbook example of process intensification. This patented process<sup>24</sup> employs only three major pieces of equipment, as opposed to the traditional manufacturing process, which employs twenty-eight major pieces of equipment. This kind of reactor and separation unit replacement by highly integrated reactive

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distillation column equipment<sup>22</sup> has been pursued using such process synthesis tools as residue curve maps<sup>25, 26</sup>.

In Moulijn's and Stankiewicz's book on process intensification<sup>27</sup> process synthesis is considered to be a process intensification method worthy of a chapter (11), which "focuses on the application of *process synthesis* principles to the optimal design of integrated chemical processing plants". In the first chapter of that same book, Stankiewicz and Drinkenburg<sup>28</sup> identify process synthesis as a software method that is a part of the process intensification toolbox, and state that "Process synthesis is in some sense a sister discipline of process intensification". More recently, Moulijn et al<sup>29</sup> do not identify process intensification (PI) as a process synthesis activity. Rather they state "This paper aims to ... explore and activate the interface between process systems engineering (PSE) and PI." Further, comparing the statements of Stankiewicz<sup>22</sup> on the methyl acetate process, and Siirola<sup>24</sup> "process synthesis is the invention of flowsheet alternatives at conceptual design stage of the innovation process", leads one to conclude that process intensification is a process synthesis activity. This realization, combined with the lack of methods for process intensification, and reinforced by the suggestion of Moulijn et al<sup>29</sup>, that "a distinction needs to be made between PI as an *objective* for process development and design and PI as a scientific *skill* area.", leads us to pursue the development of systematic process intensification tools within the process synthesis toolbox. In particular, the dramatic improvements in process performance metrics sought by process intensification (being treated as an objective), make sine qua non the development of tools that have the ability to identify in a quantitative manner, performance limitations by any particular technology under consideration.

The Infinite DimEnsionAl State-space (IDEAS) framework is a process synthesis methodology that can serve as a systematic process intensification tool. Indeed, IDEAS can

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identify fundamental limitations to the level of performance attainable by any particular technology or combination of technologies, without any a priori commitment to any particular design. If these performance limits are close to the performance of existing known designs, then process intensification is not feasible based on the technology (technologies) under consideration, and additional/alternative technologies must be considered. If, on the other hand, the performance limits indicate potential significant improvements over the limits of known designs, then IDEAS identifies process intensifying designs that realize this superior performance.

The remaining article is structured as follows: The IDEAS formulation to process flowsheeting is presented, including a property that enables the applicability of IDEAS to the employed reactor models. Next, an illustrative case is presented, in which the IDEAS conceptual framework is employed as a tool in identifying intensified process flowsheets for natural gas reforming based hydrogen production. Finally, the obtained results are discussed, and conclusions are drawn.

#### 2. IDEAS MATHEMATICAL FORMULATION OF PROCESS FLOWSHEETING:

The IDEAS framework decomposes a process network into an operator network (OP), where the unit operations (reactors, separators, heat exchangers, etc.) occur, and a distribution network (DN), where the flow operations (mixing, splitting, recycling, and bypass) occur. IDEAS represents a paradigm shift which establishes that chemical process nonlinearities need not be manifested during flowsheet optimization, but rather can be fully accounted for prior to optimization. Within the IDEAS framework, the optimal process network synthesis problem is formulated as an infinite linear program (ILP), whose solution is approximated by finite-dimensional linear programs of ever-increasing size. It should be noted that the IDEAS infinite dimensional linear programming (ILP) formulation identifies the synthesis problem's global optimum, while the IDEAS finite dimensional linear programs represent approximations of the global optimum that can identify intensified process designs.

IDEAS has been successfully applied to numerous globally optimal process network synthesis problems, such as mass-exchange network synthesis,<sup>30</sup> complex distillation network synthesis,<sup>31-33</sup> power cycle synthesis,<sup>34</sup> reactor network synthesis,<sup>35,36</sup> reactive distillation network synthesis,<sup>37</sup> separation network synthesis,<sup>38</sup> attainable region construction,<sup>39–42</sup> and batch attainable region construction<sup>43</sup>. More recently, the IDEAS framework has been used to incorporate efficiency considerations, which constitute one of the criteria employed in the expanded definition of process intensification<sup>44</sup>, in reactor network synthesis, by minimizing the network's entropy generation. In particular, it has been shown that the entropy generation and energy consumption of isothermal, isobaric reactor networks only depend on the network's inlet and outlet stream compositions and flow rates, and are independent of the network structure, as long as the universe of realizable reactor/mixer units consists of either only endothermic units,

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interacting with a single hot reservoir, or only exothermic units interacting with a single cold reservoir, respectively<sup>45</sup>. It has also been shown that when the universe of realizable reactor/mixer units consists of both endothermic and exothermic units, the network's entropy generation and energy consumption depend on the network structure<sup>45</sup>. These results have provided the inspiration for the work presented in this manuscript. Indeed, close examination of the reactions taking place in a reformer reveals that the universe of realizable reformer units consists of both endothermic units. In turn, this realization suggests that the energy consumption characteristics of an overall hydrogen production network (flowsheet) depend on the network structure, and can be dramatically altered, through the possible use of endothermic and/or exothermic reformer units, thus opening up dramatic opportunities for process intensification according to the latter's expanded definition<sup>21</sup>.

In this work, the IDEAS framework is employed for process flowsheet intensification. Process flowsheets are networks that employ a variety of process units, including reactors, separators, pumps, compressors, turbines, valves, heat exchangers, and many others. As stated earlier, one way to intensify a process is to increase the efficiency of its energy use. Thus, the process intensification goal that we aim to improve in this work will be the cost of the hot and cold utilities consumed by the process, which we will minimize. Hot and cold utilities at multiple temperature levels will be considered, reflecting the availability of both renewable and nonrenewable energy resources. Possible opportunities for heat integration will also be explored by incorporating heat exchanger network (HEN) synthesis in the overall process network (PN) synthesis task, and carrying out simultaneously HEN and PN synthesis. Models for all the processes employed in this work are presented next, and the applicability of IDEAS to each such

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process model is ascertained. First however, a proposition is proved, which is subsequently used to establish the applicability of IDEAS to the reactor model employed in this work.

#### **Proposition 1**

Consider the following two optimization problems:

$$\begin{cases} \nu(a) = f(\hat{n}) \triangleq \min_{n \in \mathbb{R}^{k}} f(n) \\ s.t. \ An = a \\ n \ge 0 \end{cases} \text{ and } \begin{cases} \nu(\lambda a) = f(\hat{n}_{\lambda}) \triangleq \min_{n_{\lambda} \in \mathbb{R}^{k}} f(n_{\lambda}) \\ s.t. \ An_{\lambda} = \lambda a \\ n_{\lambda} \ge 0 \end{cases}$$

where  $\lambda > 0, A \in \mathbb{R}^{l \times k}, a \in \mathbb{R}^{l}$  and  $f(\cdot)$  is a homogeneous function of degree one, i.e.

$$f: \mathbb{R}^k \to \mathbb{R}, f: n \to f(n), f: \lambda n \to f(\lambda n) = \lambda f(n) \quad \forall \lambda > 0 \quad \forall n \in \mathbb{R}^k.$$

Then,

a. 
$$v(\lambda a) = f(\hat{n}_{\lambda}) = f(\lambda \hat{n}) = \lambda f(\hat{n}) = \lambda v(a).$$

b. If the optimization problem v(a) has a unique global optimum  $\forall a \in \mathbb{R}^l$ , then

$$\hat{n}_{\lambda} = \lambda \hat{n} \ \forall \lambda > 0.$$

## **Proof:**

a. Based on the proposition statement,  $\hat{n}$  and  $\hat{n}_{\lambda}$  are the global minima of  $\nu(a)$  and  $\nu(\lambda a)$  respectively.

Since 
$$\begin{cases} A\hat{n} = a \\ \hat{n} \ge 0 \end{cases} \stackrel{\lambda > 0}{\Leftrightarrow} \begin{cases} A\lambda\hat{n} = \lambda a \\ \lambda\hat{n} \ge 0 \end{cases}$$
, then  $\lambda\hat{n}$  is a feasible point of  $\nu(\lambda a)$ .

This means that  $f(\lambda \hat{n}) \ge f(\hat{n}_{\lambda}) = v(\lambda a)$ .

Define  $\overline{n}_{\lambda} \triangleq \frac{1}{\lambda} \hat{n}_{\lambda}$ .

Since 
$$\begin{cases} A\hat{n}_{\lambda} = \lambda a \\ \hat{n}_{\lambda} \ge 0 \end{cases} \stackrel{\lambda > 0}{\Leftrightarrow} \begin{cases} \frac{1}{\lambda} A\hat{n}_{\lambda} = \frac{1}{\lambda} \lambda a \\ \frac{1}{\lambda} \hat{n}_{\lambda} \ge 0 \end{cases} \stackrel{\overline{n}_{\lambda} = \frac{1}{\lambda} \hat{n}_{\lambda}}{\Leftrightarrow} \begin{cases} A\overline{n}_{\lambda} = a \\ \overline{n}_{\lambda} \ge 0 \end{cases}$$
, then,  $\overline{n}_{\lambda}$  is a feasible point for  $\nu(a)$ .

This means that  $f(\overline{n}_{\lambda}) \ge f(\hat{n}) = v(a)$ .

In addition, since  $f(\cdot)$  is a homogeneous function, it holds  $f\left(\frac{1}{\lambda}\hat{n}_{\lambda}\right) = \frac{1}{\lambda}f(\hat{n}_{\lambda})$ .

It then holds,

$$v(a) = f(\hat{n}) \le f(\bar{n}_{\lambda}) = f\left(\frac{1}{\lambda}\hat{n}_{\lambda}\right) = \frac{1}{\lambda}f(\hat{n}_{\lambda}) = \frac{1}{\lambda}v(\lambda a) \le \frac{1}{\lambda}f(\lambda \hat{n}) = \frac{1}{\lambda}\lambda f(\hat{n}) = v(a). \text{ O.E.}\Delta a$$

b. Consider, in addition that the optimization problem  $\nu(a)$  has a unique global optimum  $\forall a \in \mathbb{R}^{l}$ .

Let the global optimum of  $v(\lambda a)$ ,  $\hat{n}_{\lambda}$ , be such that  $\hat{n}_{\lambda} \neq \lambda \hat{n}$ . It holds however that  $\lambda \hat{n}$  is a feasible point of  $v(\lambda a)$ . Then  $f(\hat{n}_{\lambda}) < f(\lambda \hat{n})$ , which in turn implies  $v(\lambda a) = f(\hat{n}_{\lambda}) < f(\lambda \hat{n}) = \lambda f(\hat{n}) = \lambda v(a)$ . This is in contradiction with  $v(\lambda a) = \lambda v(a)$ which was established in part a. above. Thus,  $\hat{n}_{\lambda} = \lambda \hat{n}$ . O.E.A.

Having established Proposition 1, we next outline the concept of a process information map and discuss how establishing a number of properties that process information maps naturally possess, enables the development of the IDEAS conceptual framework. Historically, in the modular approach to process simulation (see for example review<sup>46</sup>) "each chemical processing step is represented as a separate mathematical model called a unit module ... the process flow sheet is translated into an information flow sheet ... process topology may be expressed directly on the FORTRAN level by use of stream (information) vectors." However, although information vectors were used to express process topology, information maps (and their properties) were not explicitly focused on. Process information maps taking inlet stream information (such as flows, component concentration, enthalpies, and so on) and transforming it to similar outlet stream information, give rise to process operators that are nonlinear, and result in nonconvex optimal network synthesis formulations. IDEAS provides a radical departure from this approach. It considers that the process operator OP takes extensive inlet stream information (e.g. flow), available at appropriately defined conditions (e.g. temperature, concentration, residence time, etc.) and transforms it to extensive outlet stream information (e.g. flow) available at corresponding conditions. The resulting IDEAS process operator is linear for any chemical process, as a result of the property of chemical processes, that when their inlet flow rates increase proportionally (without altering their associated conditions), their outlet flow rates also increase by the same proportion, while their associated conditions remain unaltered.

Thus, having established the linearity of the IDEAS process operator OP, we are now in a position to justify the claim that the IDEAS representation gives rise to linear problem formulations. The constraints in the DN arise due to mixing and splitting operations, and are linear in the extensive (flow) variables. This fact, combined with the OP linearity, results in a linear feasible region that captures all possible process networks, by considering that the OP network inlets correspond to all possible associated conditions, and by allowing the DN network to consider all possible interconnections between external outlets (inlets)/OP inlets (outlets). The models of the various flowsheet processes are first presented, and then the applicability of

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IDEAS is established. The latter is accomplished by establishing that each process information map satisfies the following properties:

Consider the information map  $\Psi: D_1 \times D_2 \subset \mathbb{R}^{n_1} \times \mathbb{R}^{n_2} \to \mathbb{R}^p$ ,

$$\Psi: u = \begin{bmatrix} u_1^T & | & u_2^T \end{bmatrix}^T \rightarrow \Psi(u) = \Psi(u_1, u_2)$$

that helps define the set *D* as follows:  $D = \{ u \in D_1 \times D_2 \subset \mathbb{R}^{n_1} \times \mathbb{R}^{n_2} : \Psi(u_1, u_2) = 0 \}$ 

Let the considered process model have information map  $\Phi: D \subset \mathbb{R}^{n_1} \times \mathbb{R}^{n_2} \to \mathbb{R}^{m_1} \times \mathbb{R}^{m_2}$ ,

$$\Phi: u = \begin{bmatrix} u_1^T & | & u_2^T \end{bmatrix}^T \to y = \Phi(u) = \begin{bmatrix} y_1^T & | & y_2^T \end{bmatrix}^T = \begin{bmatrix} \Phi_1(u_1, u_2) \end{bmatrix}^T & | & \begin{bmatrix} \Phi_2(u_1, u_2) \end{bmatrix}^T \end{bmatrix}^T.$$

Having defined the maps  $\Phi$ ,  $\Psi$ , we can now state the properties that must hold to ensure IDEAS applicability.

#### Property 1:

$$\exists \Psi_1 : \mathbb{R}^{n_1} \to \mathbb{R}^{p \times n_2}, \Psi_1 : u_1 \to \Psi_1(u_1) \text{ such that}$$
$$\Psi(u_1, u_2) = \Psi_1(u_1)u_2 \quad \forall u = (u_1, u_2) \in D_1 \times D_2 \subset \mathbb{R}^{n_1} \times \mathbb{R}^{n_2}$$

Property 1 is best understood as follows: First, there exists a (possibly nonlinear) map  $(\Psi_1)$  that maps the unit sub-vector  $u_1$  to a linear operator (matrix)  $\Psi_1(u_1)$  that belongs to the space of matrices  $\mathbb{R}^{p \times n_2}$ . Then, the image of the vector  $(u_1, u_2)$  through the map  $\Psi$  is the composition of the linear operator  $\Psi_1(u_1)$  with the sub-vector  $u_2$ .

Property 2:

 $\exists \Phi_3 : \mathbb{R}^{n_1} \to \mathbb{R}^{m_1}, \Phi_3 : u_1 \to \Phi_3(u_1)$  such that

$$y_1 = \Phi_1(u_1, u_2) = \Phi_3(u_1) \quad \forall u = (u_1, u_2) \in D \subset \mathbb{R}^{n_1} \times \mathbb{R}^{n_2}$$

Property 2 implies that  $y_1 = \Phi_1(u_1, u_2)$  can be evaluated based only on knowledge of  $u_1$ , without requiring any knowledge of  $u_2$ .

Property 3:

 $\exists \Phi_4 : \mathbb{R}^{n_1} \to \mathbb{R}^{m_2 \times n_2}, \Phi_4 : u_1 \to \Phi_4(u_1) \text{ such that}$  $\Phi_2(u_1, u_2) = \Phi_4(u_1)u_2 \quad \forall u = (u_1, u_2) \in D \subset \mathbb{R}^{n_1} \times \mathbb{R}^{n_2}$ 

Property 3 is best understood as follows: First, there exists a (possibly nonlinear) map  $(\Phi_4)$  that maps the unit sub-vector  $u_1$  to a linear operator (matrix)  $\Phi_4(u_1)$  that belongs to the space of matrices  $\mathbb{R}^{m_2 \times n_2}$ . Then, the image of the vector  $(u_1, u_2)$  through the map  $\Phi$  is the composition of the linear operator  $\Phi_4(u_1)$  with the sub-vector  $u_2$ .

Once these properties have been established, an infinite sequence  $\{u_1(i)\}_{i=1}^{\infty}$  that consists of all possible values of  $u_1$  such that the union of  $u_1$  values considered is dense in the set where  $u_1$ can vary, is considered. The sequences  $\{\Psi_1(u_1(i))\}_{i=1}^{\infty}, \{\Phi_4(u_1(i))\}_{i=1}^{\infty}, \{\Phi_3(u_1(i))\}_{i=1}^{\infty}$  of linear maps and vectors belonging to  $\mathbb{R}^{p \times n_2}, \mathbb{R}^{m_2 \times n_2}, \mathbb{R}^{m_1}$  respectively can then be created using the maps  $\Psi_1, \Phi_4, \Phi_3$  respectively. These sequences can then be used to evaluate the infinite sequence of domains for  $\{u_2(i)\}_{i=1}^{\infty}$ , the infinite sequence  $\{y_2(i)\}_{i=1}^{\infty} = \{\Phi_4(u_1(i)), u_2(i)\}_{i=1}^{\infty}$  and the infinite sequence  $\{y_1(i)\}_{i=1}^{\infty} = \{\Phi_3(u_1(i))\}_{i=1}^{\infty}$ . Next, the applicability of IDEAS is established for all unit operations considered in this work.

#### Reactors

Since the study's main focus is energy efficiency, equilibrium reactor models will be considered in order to reduce the four-dimensional-space of species mole fractions to the twodimensional space of atomic fractions. In particular, a Gibbs free energy minimization problem will be solved to identify the reactor's exit species concentrations using only temperature, pressure, and inlet atomic ratio specifications. First, the following Gibbs free energy minimization problem is considered.

$$\begin{cases} \pi\left(T, P, \left\{\alpha_{i}\right\}_{i=1}^{m}\right) \triangleq \min_{\left\{n_{j}^{(k)}\right\}_{(j,k)=(1,1)}^{(N,N,P)}} G\left(T, P, \left\{n_{p}^{(k)}\right\}_{(p,k)=(1,1)}^{(n,N,P)}\right) \\ s.t. \quad \alpha_{i} - \sum_{k}^{NP} \sum_{j}^{n} M_{i} v_{ij} n_{j}^{(k)} = 0 \quad \forall i = 1, NE \\ n_{j}^{(k)} \ge 0 \quad \forall j = 1, NC; \quad \forall k = 1, NP \end{cases}, \text{ where}$$

$$G\left(T, P, \left\{n_p^{(k)}\right\}_{(p,k)=(1,1)}^{(n,NP)}\right) = \sum_{k=1}^{NP} \sum_{j=1}^n n_j^{(k)} \mu_j^{(k)} \left\{T, P, \left\{\frac{n_j^{(k)}}{\sum_l^n n_l^{(k)}}\right\}_{j=1}^n\right\}, \text{ and } \alpha_i \text{ is the mass flowrate of the ith}$$

element. Application of the aforementioned proposition 1 to this optimization problem necessitates that the objective function be first order homogeneous. In general,

$$G\left(T, P, \left\{n_p^{(k)}\right\}_{(p,k)=(1,1)}^{(n,NP)}\right)$$
 is a function of  $n \times NP + 2$  variables, and when treated as such it is not

homogeneous. However, when T, P are fixed at  $T = \overline{T}$ ,  $P = \overline{P}$ , then the restriction of G at

$$T = \overline{T}, P = \overline{P}, G\left(\overline{T}, \overline{P}, \left\{n_p^{(k)}\right\}_{(p,k)=(1,1)}^{(n,NP)}\right)$$
, is a first order homogenous function.

Indeed, let  $\lambda > 0$ . Then

$$G\left(\overline{T},\overline{P},\left\{\lambda n_{p}^{(k)}\right\}_{(p,k)=(1,1)}^{(n,\text{NP})}\right) = \sum_{k=1}^{NP} \sum_{j=1}^{n} \lambda n_{j}^{(k)} \mu_{j}^{(k)} \left\{T,P,\left\{\frac{\lambda n_{j}^{(k)}}{\sum_{l}^{n} \lambda n_{l}^{(k)}}\right\}_{j=1}^{n}\right\} \Leftrightarrow$$

$$G\left(\overline{T},\overline{P},\left\{\lambda n_{p}^{(k)}\right\}_{(p,k)=(1,1)}^{(n,\text{NP})}\right) = \lambda \left\{\sum_{k=1}^{NP} \sum_{j=1}^{n} n_{j}^{(k)} \mu_{j}^{(k)} \left\{T,P,\left\{\frac{n_{j}^{(k)}}{\sum_{l}^{n} n_{l}^{(k)}}\right\}_{j=1}^{n}\right\}\right\} \Leftrightarrow$$

$$G\left(\overline{T},\overline{P},\left\{\lambda n_{p}^{(k)}\right\}_{(p,k)=(1,1)}^{(n,\text{NP})}\right) = \lambda G\left(\overline{T},\overline{P},\left\{n_{p}^{(k)}\right\}_{(p,k)=(1,1)}^{(n,\text{NP})}\right)$$

 $G\left(\overline{T}, \overline{P}, \left\{\lambda n_{p}^{(k)}\right\}_{(p,k)=(1,1)}^{(n,NP)}\right) = \lambda G\left(\overline{T}, \overline{P}, \left\{n_{p}^{(k)}\right\}_{(p,k)=(1,1)}^{(n,NP)}\right)$ Since  $G\left(\overline{T}, \overline{P}, \left\{n_{p}^{(k)}\right\}_{(p,k)=(1,1)}^{(n,NP)}\right)$  is a first order homogenous function, the problem constraints are

linear, and the problem variables are nonnegative, and proposition 1 can be applied. Selecting

$$\lambda \triangleq 1 / \sum_{i=1}^{m} \alpha_i > 0$$
, then yields:

$$\begin{cases} \pi \left(T, P, \left\{\frac{\alpha_{i}}{\sum\limits_{i}^{m} \alpha_{i}}\right\}_{i=1}^{m}\right) \triangleq \min_{\left\{\frac{n_{j}^{(k)}}{\sum\limits_{i}^{m} \alpha_{i}}\right\}_{(j,k)=(1,1)}^{(n,NP)}} G\left(T, P, \left\{\frac{n_{p}^{(k)}}{\sum\limits_{i}^{n} \alpha_{i}}\right\}_{(p,k)=(1,1)}^{(n,NP)}\right) \\ s.t. \quad \frac{\alpha_{i}}{\sum\limits_{i}^{m} \alpha_{i}} - \sum\limits_{k}^{NP} \sum\limits_{j}^{n} M_{i} V_{ij} \frac{n_{j}^{(k)}}{\sum\limits_{i}^{NE} \alpha_{i}} = 0 \quad \forall i = 1, m \\ \frac{n_{j}^{(k)}}{\sum\limits_{i}^{m} \alpha_{i}} \ge 0 \qquad \forall j = 1, n; \quad \forall k = 1, NP \end{cases}$$

where  $\frac{\alpha_i}{\sum_{i=1}^{m} \alpha_i}$  is the mass fraction of the ith element.

It is this optimization that will be solved to model the reactor units in this work.

The IDEAS information maps for reactors are then defined as follows:

$$u = \begin{bmatrix} u_1^T & | & u_2^T \end{bmatrix}^T = \begin{bmatrix} T^V & P^V & \left\{ \frac{\alpha_i^W}{\sum_{i=1}^m \alpha_i^W} \right\}_{i=1}^m & | & F^W & f_1^W & \cdots & f_n^W & \dot{Q} \end{bmatrix}^T$$

$$y = \left[ y_1^T \mid y_2^T \right]^T = \left[ T^V P^V \left\{ \frac{\alpha_i^W}{\sum_{i=1}^m \alpha_i^W} \right\}_{i=1}^m P^W \left\{ x_k^V \right\}_{k=1}^n h^V \mid F^W \dot{Q} f_1^W \dots f_2^W F^V H^W \right]$$

$$\text{where } u_{1} \in D_{1} \triangleq \begin{cases} u_{1} = \left[ T^{V} \quad P^{V} \quad \left\{ \frac{\alpha_{i}^{W}}{\sum_{i}^{m} \alpha_{i}^{W}} \right\}_{i=1}^{m} \right]^{T} \in \mathbb{R}^{m+2} : \\ T^{V} \ge 0, \ P^{V} \ge 0, \ \sum_{i=1}^{m} \frac{\alpha_{i}^{W}}{\sum_{i}^{m} \alpha_{i}^{W}} = 1, \ \frac{\alpha_{i}^{W}}{\sum_{i}^{m} \alpha_{i}^{W}} \ge 0 \ \forall i = 1, m \end{cases} \\ u_{2} \in D_{2} \triangleq \begin{cases} u_{2} = \left[ F^{W} \quad f_{1}^{W} \quad \cdots \quad f_{n}^{W} \quad \dot{\mathcal{Q}} \right]^{T} \in \mathbb{R}^{n+2} : F^{W} \ge 0, \ f_{k}^{W} \ge 0 \ \forall k = 1, n \end{cases} \\ \left\{ \dot{\mathcal{Q}} \ge 0 \text{ if reactor is heated} \\ \dot{\mathcal{Q}} \le 0 \text{ if reactor is cooled} \right\} \end{cases}$$

The map  $\Psi_1 : \mathbb{R}^{m+2} \supset D_1 \rightarrow \mathbb{R}^{1 \times 2}$  for the considered reactor model is defined as follows:

$$\Psi_{1}: u_{1} \to \Psi_{1}(u_{1}) \triangleq \begin{bmatrix} T^{V} & P^{V} & \left\{ \frac{\alpha_{i}^{W}}{\sum_{i}^{m} \alpha_{i}^{W}} \right\}_{i=1}^{m} \end{bmatrix} \in \mathbb{R}^{m \times (n+1)}, \text{ and}$$
$$\Psi_{1}(u_{1}) u_{2} = \begin{bmatrix} a_{1}^{W} & -R_{1,1}^{W} & \cdots & -R_{1,n}^{W} & 0\\ \vdots & \vdots & \ddots & \vdots & \vdots\\ a_{m}^{W} & -R_{m,1}^{W} & \cdots & -R_{m,n}^{W} & 0 \end{bmatrix}^{T} \begin{bmatrix} F_{1}^{W} \\ f_{1}^{W} \\ \vdots\\ f_{n}^{W} \\ \dot{Q} \end{bmatrix} = 0$$

Where  $R_{i,k}^V = (ANM^{-1})_{i,k}$ , i = 1, m; k = 1, n, where *A* is the diagonal matrix, whose entries are the molar masses of each atom or each inert molecule, *N* is the matrix of stoichiometric coefficients,  $v_{i,k}$  that quantify the number of ith atoms in the kth species, and *M* is the diagonal matrix, whose entries are the molar masses of each species,.

The maps  $\Phi_3 : \mathbb{R}^{m+2} \supset D_1 \rightarrow \mathbb{R}^{m+n+4}$  and  $\Phi_4 : \mathbb{R}^{m+2} \supset D_1 \rightarrow \mathbb{R}^{(n+4) \times (n+2)}$  are defined as follows:

$$\Phi_{3}: u_{1} \rightarrow y_{1} = \Phi_{3}(u_{1}) \triangleq \begin{bmatrix} T^{V} \\ P^{V} \\ \left\{ \frac{\alpha_{i}^{W}}{\sum_{i}^{m} \alpha_{i}^{W}} \right\}_{i=1}^{m} \\ P^{V} \\ \left\{ M_{k} \cdot \arg \min \pi \left( T^{V}, P^{V}, \left\{ \frac{\alpha_{i}^{W}}{\sum_{i}^{m} \alpha_{i}^{W}} \right\}_{i=1}^{m} \right) \right\}_{k=1}^{n} \\ h_{PR} \left( T^{V}, P^{V}, \left\{ M_{k} \cdot \arg \min \pi \left( T^{V}, P^{V}, \left\{ \frac{\alpha_{i}^{W}}{\sum_{i}^{m} \alpha_{i}^{W}} \right\}_{i=1}^{m} \right) \right\}_{k=1}^{n} \\ \end{bmatrix}$$

$$\Phi_{4}: u_{1} \to \Phi_{4}(u_{1}) \triangleq \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & \ddots & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ h^{V} & 0 & 0 & 0 & 1 \end{bmatrix} \in \mathbb{R}^{(n+4) \times (n+2)}, \text{ and}$$

$$\begin{bmatrix} F^{W} \end{bmatrix} \qquad \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$y_{2} = \begin{bmatrix} I & 0 & 0 & 0 & 0 \\ \dot{Q} \\ f_{1}^{W} \\ \vdots \\ f_{n}^{W} \\ F^{V} \\ H^{W} \end{bmatrix} = \Phi_{4}(u_{1})u_{2} = \begin{bmatrix} I & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ h^{V} & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} F^{W} \\ f_{1}^{W} \\ \vdots \\ f_{n}^{W} \\ \dot{Q} \end{bmatrix}$$

## Separators

The considered separator model is assumed to have no heat inlet ports, a single heat outlet port at a temperature Tabove the environmental temperature  $T_{\sigma}$ , and inlet and outlet streams with potential and kinetic energy terms that can be neglected. A Carnot engine is coupled to separator units, so as to calculate the ideal work of separation, which is later used in the IDEAS formulation for the separator units. Consider also that the separator is coupled to a power engine operating between T and  $T_{\sigma}$ . Then, the following proposition holds:

#### **Proposition 2**

Consider a separator operating at steady-state, having a single outlet heat port at  $T \ge T_{\sigma}$ , and inlet and outlet streams with potential, and kinetic energy terms that can be neglected. Then the ideal work of separation, and the associated ideal separator cold utility load are:

$$\dot{W}_{ldeal} = \dot{W} - \dot{W}_{\sigma} = \sum_{i \in S_{\sigma}} F_i \left( H_i - T_{\sigma} S_i \right) - \sum_{i \in S_l} F_i \left( H_i - T_{\sigma} S_i \right)$$

$$\dot{Q}_{\sigma} = \sum_{i \in S_I} F_i T_{\sigma} S_i - \sum_{i \in S_O} F_i T_{\sigma} S_i$$

**Proof:** 

$$\begin{cases} 0 = \sum_{i \in S_{I}} F_{i}H_{i} - \sum_{i \in S_{O}} F_{i}H_{i} - \dot{Q} + \dot{W} \\ 0 = \sum_{i \in S_{I}} F_{i}S_{i} - \sum_{i \in S_{O}} F_{i}S_{i} - \frac{\dot{Q}}{T} + \dot{S}_{G} \wedge \dot{S}_{G} \ge 0 \\ 0 = \dot{Q} - \dot{Q}_{\sigma} - \dot{W}_{\sigma} \\ 0 = \frac{\dot{Q}}{T} - \frac{\dot{Q}_{\sigma}}{T_{\sigma}} + \dot{S}_{G,\sigma} \wedge \dot{S}_{G,\sigma} \ge 0 \end{cases} \\ \Leftrightarrow \begin{cases} \dot{W} = -\sum_{i \in S_{I}} F_{i}H_{i} + \sum_{i \in S_{O}} F_{i}H_{i} + \dot{Q} \\ \dot{Q} = T\sum_{i \in S_{I}} F_{i}S_{i} - T\sum_{i \in S_{O}} F_{i}S_{i} + T\dot{S}_{G} \wedge \dot{S}_{G} \ge 0 \\ \dot{W}_{\sigma} = \left(1 - \frac{T_{\sigma}}{T}\right)\dot{Q} - T_{\sigma}\dot{S}_{G,\sigma} \\ \dot{Q}_{\sigma} = \frac{T_{\sigma}}{T}\dot{Q} + T_{\sigma}\dot{S}_{G,\sigma} \wedge \dot{S}_{G,\sigma} \ge 0 \end{cases} \\ \Leftrightarrow$$

$$\begin{cases} \dot{W} = \sum_{i \in S_o} F_i \left( H_i - TS_i \right) - \sum_{i \in S_I} F_i \left( H_i - TS_i \right) + T\dot{S}_G \\ \dot{Q} = T \sum_{i \in S_I} F_i S_i - T \sum_{i \in S_o} F_i S_i + T\dot{S}_G \land \dot{S}_G \ge 0 \\ \dot{W}_{\sigma} = \left( T - T_{\sigma} \right) \left( \sum_{i \in S_I} F_i S_i - \sum_{i \in S_o} F_i S_i + \dot{S}_G \right) - T_{\sigma} \dot{S}_{G,\sigma} \\ \dot{Q}_{\sigma} = T_{\sigma} \left( \sum_{i \in S_I} F_i S_i - \sum_{i \in S_o} F_i S_i + \dot{S}_G \right) + T_{\sigma} \dot{S}_{G,\sigma} \land \dot{S}_{G,\sigma} \ge 0 \end{cases}$$

$$\begin{cases} \dot{W} = \sum_{i \in S_o} F_i \left( H_i - TS_i \right) - \sum_{i \in S_I} F_i \left( H_i - TS_i \right) + T\dot{S}_G \\ \dot{Q} = T \sum_{i \in S_I} F_i S_i - T \sum_{i \in S_o} F_i S_i + T\dot{S}_G \land \dot{S}_G \ge 0 \\ \dot{W}_{\sigma} = \left( T - T_{\sigma} \right) \left( \sum_{i \in S_I} F_i S_i - \sum_{i \in S_o} F_i S_i + \dot{S}_G \right) - T_{\sigma} \dot{S}_{G,\sigma} \\ \dot{Q}_{\sigma} = \sum_{i \in S_I} F_i T_{\sigma} S_i - \sum_{i \in S_o} F_i T_{\sigma} S_i + T_{\sigma} \left( \dot{S}_G + \dot{S}_{G,\sigma} \right) \land \dot{S}_{G,\sigma} \ge 0 \land \dot{S}_G \ge 0 \\ \dot{W} - \dot{W}_{\sigma} = \sum_{i \in S_o} F_i \left( H_i - T_{\sigma} S_i \right) - \sum_{i \in S_I} F_i \left( H_i - T_{\sigma} S_i \right) + T_{\sigma} \left( \dot{S}_G + \dot{S}_{G,\sigma} \right) \end{cases}$$

The ideal work of separation is obtained by considering that the separator, and the coupled power engine are both reversible (their rates of entropy generation are both zero), i.e.  $\dot{S}_G = 0 \land \dot{S}_{G,\sigma} = 0$ . Then the ideal work of separation, and the associated ideal separator cold utility load are:

$$\dot{W}_{Ideal} = \dot{W} - \dot{W}_{\sigma} = \sum_{i \in S_{O}} F_{i} \left( H_{i} - T_{\sigma} S_{i} \right) - \sum_{i \in S_{I}} F_{i} \left( H_{i} - T_{\sigma} S_{i} \right)$$

$$\dot{Q}_{\sigma} = \sum_{i \in S_I} F_i T_{\sigma} S_i - \sum_{i \in S_O} F_i T_{\sigma} S_i \cdot \text{O.E.}\Delta.$$

The IDEAS information maps for separators, where the first exit stream is the pure species separated, are then defined as follows:

$$u = \begin{bmatrix} u_1^T & | & u_2^T \end{bmatrix}^T = \begin{bmatrix} T_1^V & P_1^V & \{x_{1,k}^V\}_{k=1}^n & \{x_{2,k}^V\}_{k=1}^n & | & F_1^V & F_2^V & H^W & S^W \end{bmatrix}^T$$

$$y = \begin{bmatrix} y_1^T & | & y_2^T \end{bmatrix}^T;$$

$$y_1 = \begin{bmatrix} T_1^V & P_1^V & \{x_{1,k}^V\}_{k=1}^n & \{x_{2,k}^V\}_{k=1}^n & T_2^V & T^W & P_2^V & P^W & h_1^V & h_2^V & s_1^V & s_2^V \end{bmatrix}^T$$

$$y_2 = \begin{bmatrix} F_1^V & F_2^V & f_1^W & \dots & f_n^W & H^W & S^W & F^W & \dot{Q} & \dot{W}_{Ideal} \end{bmatrix}^T$$

where 
$$u_{1} \in D_{1} = \begin{cases} u_{1} = \begin{bmatrix} T_{1}^{V} & P_{1}^{V} & \{x_{1,k}^{V}\}_{k=1}^{n} & \{x_{2,k}^{V}\}_{k=1}^{n} \end{bmatrix}^{T} \in \mathbb{R}^{2n+2} : \\ T_{1}^{V} \ge 0, \ P_{1}^{V} \ge 0, \ \sum_{k=1}^{n} x_{1,k}^{V} = 1, \ x_{1,k}^{V} \ge 0 \ \forall k = 1, n \\ \\ \sum_{k=1}^{n} x_{2,k}^{V} = 1, \ x_{2,k}^{V} \ge 0 \end{cases} \end{cases}$$

$$u_2 \in D_2 \triangleq \left\{ u_2 = \begin{bmatrix} F_1^V & F_2^V & H^W & S^W \end{bmatrix}^T \in \mathbb{R}^{n+4} : F_1^V \ge 0, \ F_2^V \ge 0 \right\}$$

No map  $\Psi_{\scriptscriptstyle 1}$  need be defined for the considered separator model.

The maps  $\Phi_3 : \mathbb{R}^{2n+2} \supset D_1 \rightarrow \mathbb{R}^{2n+10}$  and  $\Phi_4 : \mathbb{R}^{2n+2} \supset D_1 \rightarrow \mathbb{R}^{(n+7)\times 4}$  are defined as follows:

$$\Phi_{3}: u_{1} \rightarrow y_{1} = \Phi_{3}(u_{1}) \triangleq \begin{bmatrix} T_{1}^{V} & & \\ P_{1}^{V} & \\ \left\{ x_{1,k}^{V} \right\}_{k=1}^{n} & \\ \left\{ x_{2,k}^{V} \right\}_{k=1}^{n} & \\ T_{1}^{V} & & \\ T_{1}^{V} & & \\ P_{1}^{V} & & \\ P_{1}^{V} & & \\ h_{PR} \left( T_{1}^{V}, P_{1}^{V}, \left\{ x_{1,k}^{V} \right\}_{k=1}^{n} \right) \\ h_{PR} \left( T_{1}^{V}, P_{1}^{V}, \left\{ x_{2,k}^{V} \right\}_{k=1}^{n} \right) \\ s_{PR} \left( T_{1}^{V}, P_{1}^{V}, \left\{ x_{2,k}^{V} \right\}_{k=1}^{n} \right) \\ s_{PR} \left( T_{1}^{V}, P_{1}^{V}, \left\{ x_{2,k}^{V} \right\}_{k=1}^{n} \right) \\ \end{bmatrix},$$

$$\begin{split} \Phi_{4} : u_{1} \rightarrow \Phi_{4}(u_{1}) &\triangleq \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ x_{1,1}^{V} & x_{2,1}^{V} & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ x_{1,n}^{V} & x_{2,n}^{V} & 0 & 0 \\ 1 & 1 & 0 & 0 \\ -T_{\sigma}s_{1}^{V} & -T_{\sigma}s_{2}^{V} & 0 & T_{\sigma} \\ h_{1}^{V} - T_{\sigma}s_{1}^{V} & h_{2}^{V} - T_{\sigma}s_{2}^{V} & -1 & T_{\sigma} \end{bmatrix} \in \mathbb{R}^{(n+7)\times4}, \text{ and} \\ \end{split}$$

## **Pressure Changing Devices**

The IDEAS information maps for pressure changing devices are then defined as follows:

$$u = \begin{bmatrix} u_1^T & | & u_2^T \end{bmatrix}^T = \begin{bmatrix} T^W & P^W & P^V & \{x_k^W\}_{k=1}^n & \zeta & | & F^W \end{bmatrix}^T$$
$$y = \begin{bmatrix} y_1^T & | & y_2^T \end{bmatrix}^T = \begin{bmatrix} T^W & P^W & P^V & \{x_k^W\}_{k=1}^n & \zeta & \{x_k^V\}_{k=1}^n & h^W & s^W & T_{isentropic}^V & T^V & h^V & | & F^W & F^V & f_1^W & \dots & f_n^W & H^W & W \end{bmatrix}^T$$

where,  $\zeta = \begin{cases} 1/\eta & compressors / pumps \\ \eta & turbines \\ 0 & valves \end{cases}$ 

$$u_{1} \in D_{1} = \begin{cases} u_{1} = \begin{bmatrix} T^{W} & P^{W} & P^{V} & \left\{ x_{k}^{W} \right\}_{k=1}^{n} & \zeta \end{bmatrix}^{T} \in \mathbb{R}^{n+4} : \\ T^{W} \ge 0, \ P^{W} \ge 0, \ \sum_{k=1}^{n} x_{k}^{W} = 1, \ x_{k}^{W} \ge 0 \ \forall k = 1, n; \ 0 \le \zeta \le 1 \end{cases} \end{cases},$$

 $u_2 \in D_2 \triangleq \left\{ u_2 = \left[ F^w \right]^T \in \mathbb{R} : F^w \ge 0 \right\}$ 

No map  $\Psi_1$  need be defined for the considered pressure changing device model.

The maps  $\Phi_3 : \mathbb{R}^{n+4} \supset D_1 \rightarrow \mathbb{R}^{2n+9}$  and  $\Phi_4 : \mathbb{R}^{n+4} \supset D_1 \rightarrow \mathbb{R}^{(n+4)\times 1}$  are defined as follows:

$$\begin{split} \Phi_{3} : u_{1} \rightarrow y_{1} = \Phi_{3}(u_{1}) & T^{W} \\ P^{W} \\ P^{V} \\ \left\{ x_{k}^{W} \right\}_{k=1}^{n} \\ \zeta \\ \left\{ x_{k}^{W} \right\}_{k=1}^{n} \\ h_{PR} \left( T^{W}, P^{W}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right) \\ P_{PR} \left( s_{PR} \left( T^{W}, P^{W}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right), P^{V}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right) \\ T_{PR} \left( \left[ \zeta h_{PR} \left( T_{PR} \left( s_{PR} \left( T^{W}, P^{W}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right), P^{V}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right) \right) \\ H_{PR} \left( \left[ \zeta h_{PR} \left( T_{PR} \left( s_{PR} \left( T^{W}, P^{W}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right), P^{V}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right), P^{V}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right) \right] \\ \left[ \left[ \zeta h_{PR} \left( T^{W}, P^{W}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right) (1 - \zeta) \\ \left[ \left[ \zeta h_{PR} \left( T^{W}, P^{W}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right) (1 - \zeta) \right] \right] \right] \\ \end{split} \right] \end{split}$$

$$\Phi_{4}: u_{1} \to \Phi_{4}(u_{1})$$

$$\begin{bmatrix} 1 \\ 1 \\ x_{1}^{W} \\ \vdots \\ h^{W} \\ \end{bmatrix} \left[ \zeta \left( \begin{array}{c} h_{PR} \left( T_{PR} \left( s_{PR} \left( T^{W}, P^{W}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right), P^{V}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right), P^{V}, \left\{ x_{k}^{W} \right\}_{k=1}^{n} \right) - \right] \right] \in \mathbb{R}^{(n+4) \times 1}$$

$$y_{2} = \begin{bmatrix} F^{W} \\ F^{V} \\ f_{1}^{W} \\ \vdots \\ f_{n}^{W} \\ H^{W} \\ W \end{bmatrix} = \Phi_{4}(u_{1})u_{2} = \begin{bmatrix} 1 \\ 1 \\ x_{1}^{W} \\ \vdots \\ h^{W} \\ H^{W} \\ H^{W} \\ W \end{bmatrix} = \left[ \begin{bmatrix} f^{W} \\ f_{n}^{W} \\ f_{n}^{W} \\ H^{W} \\$$

#### **Heat Exchange Network**

In this work, the heat exchanger network shown in Figure 1 is considered. It contains three categories of heat exchangers: hot stream - cold stream heat exchangers; stream - point load heat exchangers, where a stream is cooled (heated) by a cold (hot) point load; and point load point load heat exchangers where hot (cold) point loads and cold (hot) point loads are matched. External utilities as well as unit loads are typically considered as either hot or cold point loads. Streams are created by comparing each state with every other state, for equality of the two states'



**Figure 2** Representation of heat exchange network structure pressure and composition components. Once all streams have been created, all

feasible/desirable/non-forbidden stream-stream heat exchangers, stream-point load heat exchangers, and point load-point load heat exchangers are generated. Thermodynamic feasibility of each exchanger is verified throughout its length. The objective function to be minimized in this work is the overall utility cost, for all external hot utilities.

The IDEAS information maps for stream-stream heat exchangers, whose first stream is considered to be hot, are then defined as follows:

$$u = \begin{bmatrix} u_1^T & | & u_2^T \end{bmatrix}^T = \begin{bmatrix} T_1^V & T_2^V & T_1^W & T_2^W & P_1^V & P_2^V & \left\{ x_{1,k}^V \right\}_{k=1}^n & \left\{ x_{2,k}^V \right\}_{k=1}^n & | & F_1^W & F_2^W \end{bmatrix}^T \\ \begin{cases} y = \begin{bmatrix} y_1^T & | & y_2^T \end{bmatrix}^T = \\ \begin{bmatrix} T_1^V & T_2^V & T_1^W & T_2^W & P_1^V & P_2^V & \left\{ x_{1,k}^V \right\}_{k=1}^n & P_1^W & P_2^W & \left\{ x_{1,k}^W \right\}_{k=1}^n & \left\{ x_{2,k}^W \right\}_{k=1}^n & h_1^W & h_2^W & h_1^V & h_2^V & | & F_1^W & F_2^W & F_1^V & F_2^V & \dot{Q} \end{bmatrix}^T \end{cases}$$

where 
$$u_{1} \in D_{1} = \begin{cases} u_{1} = \begin{bmatrix} T_{1}^{V} & T_{2}^{V} & T_{1}^{W} & T_{2}^{W} & P_{1}^{V} & P_{2}^{V} & \left\{ x_{1,k}^{V} \right\}_{k=1}^{n} & \left\{ x_{2,k}^{V} \right\}_{k=1}^{n} \end{bmatrix}^{T} \in \mathbb{R}^{2n+6} :$$
  

$$\begin{cases} T_{1}^{V} \ge 0, \ T_{2}^{V} \ge 0, \ T_{1}^{V} \ge 0, \ T_{2}^{V} \ge 0, \ T_{2}^{W} \ge 0, \ P_{1}^{V} \ge 0, \ P_{2}^{V} \ge 0, \\ \sum_{k=1}^{n} x_{1,k}^{V} = 1, \ x_{1,k}^{V} \ge 0 \ \forall k = 1, n; \ \sum_{k=1}^{n} x_{2,k}^{V} = 1, \ x_{2,k}^{V} \ge 0 \ \forall k = 1, n \end{cases}$$

 $u_2 \in D_2 \triangleq \left\{ u_2 = \begin{bmatrix} F_1^W & F_2^W \end{bmatrix}^T \in \mathbb{R}^2 : F_1^W \ge 0, \ F_2^W \ge 0 \right\}$ 

The map  $\Psi_1 : \mathbb{R}^{2n+6} \supset D_1 \rightarrow \mathbb{R}^{1\times 2}$  for the considered stream-stream heat exchanger model is defined as follows:

$$\Psi_{1}: u_{1} \to \Psi_{1}(u_{1}) \triangleq \begin{bmatrix} h_{1}^{W} - h_{1}^{V} & h_{2}^{W} - h_{2}^{V} \end{bmatrix} \in \mathbb{R}^{1\times 2}, \text{ and } \Psi_{1}(u_{1})u_{2} = \begin{bmatrix} h_{1}^{W} - h_{1}^{V} & h_{2}^{W} - h_{2}^{V} \end{bmatrix} \begin{bmatrix} F_{1}^{V} \\ F_{2}^{V} \end{bmatrix} = 0$$

The maps  $\Phi_3 : \mathbb{R}^{2n+6} \supset D_1 \to \mathbb{R}^{4n+12}$  and  $\Phi_4 : \mathbb{R}^{2n+6} \supset D_1 \to \mathbb{R}^{5\times 2}$  are defined as follows:

$$\begin{split} \Phi_{3} : u_{1} \rightarrow y_{1} = \Phi_{3}(u_{1}) &\triangleq \begin{bmatrix} 1 & 0 \\ 0 & 1 \\ 1 & 0 \\ 0 & 1 \\ h_{l}^{W} - h_{l}^{V} & 0 \end{bmatrix}, \\ \Phi_{4} : u_{1} \rightarrow \Phi_{4}(u_{1}) &\triangleq \begin{bmatrix} 1 & 0 \\ 0 & 1 \\ h_{l}^{W} - h_{l}^{V} & 0 \end{bmatrix} \in \mathbb{R}^{5 \cdot 2}, \text{ and } y_{2} = \begin{bmatrix} F_{1}^{W} \\ F_{2}^{W} \\ F_{2}^{W} \\ F_{2}^{W} \\ F_{2}^{W} \\ F_{2}^{W} \\ F_{2}^{V} \\$$

The IDEAS information maps for stream-point load heat exchangers, where the stream is always designated as first, are then defined as follows:

$$u = \begin{bmatrix} u_1^T & | & u_2^T \end{bmatrix}^T = \begin{bmatrix} T_1^V & T_1^W & T_2 & P_1^V & \left\{ x_{1,k}^V \right\}_{k=1}^n & | & F_1^W \end{bmatrix}^T$$
$$y = \begin{bmatrix} y_1^T & | & y_2^T \end{bmatrix}^T = \begin{bmatrix} T_1^V & T_1^W & T_2 & P_1^V & \left\{ x_{1,k}^V \right\}_{k=1}^n & P_1^W & \left\{ x_{1,k}^W \right\}_{k=1}^n & h_1^W & h_1^V & | & F_1^W & F_1^V & \dot{Q} \end{bmatrix}^T$$

where 
$$u_1 \in D_1 = \begin{cases} u_1 = \begin{bmatrix} T_1^V & T_1^W & T_2 & P_1^V & \{x_{1,k}^V\}_{k=1}^n \end{bmatrix}^T \in \mathbb{R}^{n+4} : \\ T_1^V \ge 0, \ T_1^W \ge 0, \ T_2 \ge 0, \ P^V \ge 0, \ \sum_{k=1}^n x_k^V = 1, \ x_k^V \ge 0 \ \forall k = 1, n \end{cases}$$
$$u_2 \in D_2 \triangleq \left\{ u_2 = \begin{bmatrix} F_1^W \end{bmatrix}^T \in \mathbb{R} : F_1^W \ge 0 \right\}$$

No map  $\Psi_1$  need be defined for the considered stream-point load heat exchanger model.

The maps  $\Phi_3 : \mathbb{R}^{n+4} \supset D_1 \rightarrow \mathbb{R}^{2n+7}$  and  $\Phi_4 : \mathbb{R}^{n+4} \supset D_1 \rightarrow \mathbb{R}^{3\times 1}$  are defined as follows:

$$\Phi_{3}: u_{1} \rightarrow y_{1} = \Phi_{3}(u_{1}) \triangleq \begin{bmatrix} T_{1}^{V} \\ T_{2} \\ P_{1}^{V} \\ \left\{ x_{1,k}^{V} \right\}_{k=1}^{n} \\ P_{1}^{V} \\ \left\{ x_{1,k}^{V} \right\}_{k=1}^{n} \\ h_{PR} \left( T_{1}^{W}, P_{1}^{V}, \left\{ x_{1,k}^{V} \right\}_{k=1}^{n} \right) \\ h_{PR} \left( T_{1}^{V}, P_{1}^{V}, \left\{ x_{1,k}^{V} \right\}_{k=1}^{n} \right) \end{bmatrix}$$

$$\Phi_4: u_1 \to \Phi_4(u_1) \triangleq \begin{bmatrix} 1\\1\\h_1^W - h_1^V \end{bmatrix} \in \mathbb{R}^{3\times 1}, \text{ and } y_2 = \begin{bmatrix} F_1^W\\F_1^V\\\dot{Q} \end{bmatrix} = \Phi_4(u_1)u_2 = \begin{bmatrix} 1\\1\\h_1^W - h_1^V \end{bmatrix} \begin{bmatrix} F_1^W\\F_1^V \end{bmatrix}$$

The IDEAS information maps, for point load-point load heat exchangers with the cold point load designated with a superscript C and the hot point load with a superscript H, are then defined as follows:

$$u = \begin{bmatrix} u_1^T & \mid & u_2^T \end{bmatrix}^T = \begin{bmatrix} T^C & T^H & \mid & \dot{Q} \end{bmatrix}^T$$
  

$$y = \begin{bmatrix} y_1^T & \mid & y_2^T \end{bmatrix}^T = \begin{bmatrix} T^C & T^H & \mid & \dot{Q} \end{bmatrix}^T$$
  
where  $u_1 \in D_1 \triangleq \left\{ u_1 = \begin{bmatrix} T^C & T^H \end{bmatrix}^T \in \mathbb{R}^2 : T^C \ge 0, \ T^H \ge 0 \right\}, \ u_2 \in D_2 \triangleq \left\{ u_2 = \begin{bmatrix} \dot{Q} \end{bmatrix}^T \in \mathbb{R} : \dot{Q} \ge 0 \right\}.$ 

No maps  $\Psi_1, \Phi_3$ , or  $\Phi_4$  need be defined for the considered reactor model.

Having established the applicability of IDEAS to all considered unit operation models, the structure of the process network is discussed next. The process network is decomposed into several subnetworks as shown below in Figure 3. First, a



distribution network (DN) **Figure 3** IDEAS representation of a process flowsheet where stream splitting and mixing occurs. Then, a heat exchange network (HEN) is considered as outlined in the heat exchanger section above. All unit operations (aside from heat exchangers) are included in an operator network (OP). Finally, a mixing network (MIX) is employed to account for the mixing of process unit outlet streams with identical states, as there is no benefit in allowing streams with the same state to enter the DN at different locations.

A linear objective is considered in the proposed IDEAS formulation, which can be generally presented as  $\sum_{i=1}^{N_{HU}} C_i \dot{Q}_{HU_i}$ . This objective function can be used to quantify the varying costs of the hot utilities necessary for the synthesized network through a change in the cost coefficients *C*.

### **IDEAS Mathematical Formulation**

The above presented mathematical models of all considered processes (reactors, separators, etc.) are combined to yield the following IDEAS mathematical formulation:

$$\nu \triangleq \inf \sum_{i=1}^{N_{HU}} C_i Q_{HU_i}$$

Subject to

$$F_{i}^{U} = \sum_{p=1}^{N_{DN_{o}}} \lambda_{p,i}^{YU} F_{p,i}^{YU} + \sum_{l=1}^{N_{oP_{i}}} \lambda_{l,i}^{WU} F_{l,i}^{WU} + \sum_{l=1}^{N_{HEN_{i}}} \lambda_{l,i}^{HU} F_{l,i}^{HU} \quad \forall i = 1, N_{DN_{i}}$$
(1)

$$F_{i}^{X} = \sum_{s=1}^{N_{MIX_{i}}} \lambda_{i,s}^{XV} F_{s}^{V} = \sum_{p=1}^{N_{DNO}} \lambda_{p,i}^{YX} F_{p,i}^{YX} + \sum_{l=1}^{N_{OP_{i}}} \lambda_{l,i}^{WX} F_{l,i}^{WX} + \sum_{l=1}^{N_{HEN_{i}}} \lambda_{l,i}^{HX} F_{l,i}^{HX} \quad \forall i = 1, N_{MIX_{O}}$$

$$(2)$$

$$F_{p}^{Y,l} \leq \sum_{i=1}^{N_{DN_{i}}} \lambda_{p,i}^{YU} F_{p,i}^{YX} + \sum_{i=1}^{N_{MIX_{o}}} \lambda_{p,i}^{YX} F_{p,i}^{YX} \leq F_{p}^{Y,u} \quad \forall p = 1, N_{DN_{o}}$$
(3)

$$\begin{bmatrix} \sum_{i=1}^{N_{DN_{i}}} \lambda_{p,i}^{YU} F_{p,i}^{YU} + \\ \sum_{i=1}^{N_{MX_{o}}} \lambda_{p,i}^{YX} F_{p,i}^{YX} \end{bmatrix} x_{p,k}^{Y,l} \leq \begin{bmatrix} \sum_{i=1}^{N_{DN_{i}}} \lambda_{p,i}^{YU} F_{p,i}^{YU} x_{i,k}^{U} + \\ \sum_{i=1}^{N_{MX_{o}}} \lambda_{p,i}^{YX} F_{p,i}^{YX} \end{bmatrix} \leq \begin{bmatrix} \sum_{i=1}^{N_{DN_{i}}} \lambda_{p,i}^{YU} F_{p,i}^{YU} + \\ \sum_{i=1}^{N_{MX_{o}}} \lambda_{p,i}^{YU} F_{p,i}^{YU} + \\ \sum_{i=1}^{N_{MX_{o}}} \lambda_{p,i}^{YX} F_{p,i}^{YX} \end{bmatrix} \\ \leq \begin{bmatrix} \sum_{i=1}^{N_{DN_{i}}} \lambda_{p,i}^{YU} F_{p,i}^{YU} + \\ \sum_{i=1}^{N_{MX_{o}}} \lambda_{p,i}^{YX} F_{p,i}^{YX} \end{bmatrix} x_{i,k}^{Y,u} \quad \forall k = 1, n \; \forall p = 1, N_{DN_{o}}$$

$$\begin{bmatrix} \sum_{i=1}^{N_{DN_{i}}} \lambda_{p,i}^{YU} F_{p,i}^{YU} + \\ \sum_{i=1}^{N_{MXO}} \lambda_{p,i}^{YX} F_{p,i}^{YX} \end{bmatrix} h_{p}^{Y,l} \leq \begin{bmatrix} \sum_{i=1}^{N_{DN_{i}}} \lambda_{p,i}^{YU} F_{p,i}^{YU} h_{i}^{U} + \\ \sum_{i=1}^{N_{MXO}} \lambda_{p,i}^{YX} F_{p,i}^{YX} \end{bmatrix} \leq \begin{bmatrix} \sum_{i=1}^{N_{DN_{i}}} \lambda_{p,i}^{YU} F_{p,i}^{YU} + \\ \sum_{i=1}^{N_{MXO}} \lambda_{p,i}^{YX} F_{p,i}^{YX} \end{bmatrix} h_{p}^{Y,u} \forall p = 1, N_{DN_{O}}$$

$$(5)$$

$$f_{l,k}^{W} = \sum_{i=1}^{N_{DN_{i}}} \lambda_{l,i}^{WU} F_{l,i}^{WU} x_{i,k}^{U} + \sum_{i=1}^{N_{MIX_{O}}} \lambda_{l,i}^{WX} F_{l,i}^{WX} x_{l,k}^{X} \quad \forall k = 1, n \quad \forall l = 1, N_{OP_{i}}$$
(6)

$$H_{l}^{W} = \sum_{i=1}^{N_{DN_{i}}} \lambda_{l,i}^{WU} F_{l,i}^{WU} h_{i}^{U} + \sum_{i=1}^{N_{MXO}} \lambda_{l,i}^{WX} F_{l,i}^{WX} h_{i}^{X} \quad \forall l = 1, N_{OP_{i}}$$

$$(7)$$

$$S_{l}^{W} = \sum_{i=1}^{N_{DN_{i}}} \lambda_{l,i}^{WU} F_{l,i}^{WU} s_{i}^{U} + \sum_{i=1}^{N_{MIX_{o}}} \lambda_{l,i}^{WX} F_{l,i}^{WX} s_{i}^{X} \quad \forall l = N_{R} + 1, N_{S}$$
(8)

$$F^{U} \ge 0, \ F^{YU} \ge 0, \ F^{WU} \ge 0, \ F^{HU} \ge 0, \ F^{X} \ge 0, \ F^{YX} \ge 0, \ F^{WX} \ge 0, \ F^{HX} \ge 0$$
 (9)

Where:

$$\begin{split} \lambda_{p,i}^{YU} &= \begin{cases} 1 \text{ if } P_p^Y = P_i^U \\ 0 \text{ otherwise} \end{cases}, \lambda_{l,i}^{WU} = \begin{cases} 1 \text{ if } P_l^W = P_i^U \\ 0 \text{ otherwise} \end{cases}, \lambda_{p,i}^{YX} = \begin{cases} 1 \text{ if } P_p^Y = P_i^X \\ 0 \text{ otherwise} \end{cases}, \lambda_{l,i}^{WX} = \begin{cases} 1 \text{ if } P_l^W = P_i^X \\ 0 \text{ otherwise} \end{cases} \end{cases}$$

$$\lambda_{i,s}^{XV} = \begin{cases} 1 \text{ if } P_s^V = P_i^X, \{x_{s,k}^V\} = \{x_{i,k}^X\}, h_s^V = h_i^X \\ 0 \text{ otherwise} \end{cases}$$

Next, the proposed IDEAS framework is illustrated on a process intensification case study for natural gas reforming based hydrogen production.

# 3. CASE STUDY: PROCESS INTENSIFICATION OF NATURAL GAS REFORMING BASED HYDROGEN PRODUCTION

Steam reforming of natural gas (and other light hydrocarbons) is currently the most economical process for hydrogen production<sup>47</sup>. The commonly accepted reactions for steam reforming of methane are as follows:

 $CH_4 + H_2O = CO + 3H_2$  (r1)  $\Delta H_1 = 206.1kJ / mol$  (endothermic)  $CO + H_2O = CO_2 + H_2$  (r2)  $\Delta H_2 = -41.15kJ / mol$  (exothermic)  $CH_4 + 2H_2O = CO_2 + 4H_2$  (r3)  $\Delta H_3 = 164.9kJ / mol$  (endothermic)

Hydrogen is used in refineries as raw material for the hydrocracking of oil aiming at gasoline production. In addition, hydrogen is envisioned to be an energy carrier for vehicular transportation through its use in hydrogen fuel-cell-powered cars. The steam reforming process is typically carried out industrially at around 1100K and is highly endothermic. This large endothermic heat load is provided through the burning of natural gas and other available fuel resources in large furnaces operating at temperatures well above 1200K. Steam reforming has been the subject of process integration studies<sup>48</sup>. As process integration evolves into process intensification<sup>49</sup>, steam reforming is increasingly the focus of process intensification efforts (see <sup>50</sup> and references therein) aiming to improve the economics of this capital and operating cost intensive process. In this case study, the IDEAS framework is applied to the process intensification of a natural gas reforming based flowsheet for hydrogen production.

A baseline flowsheet is first created on the UniSim (Honeywell Inc. trademark) software, that captures a traditional design of this process. The Peng Robinson equation of state is used to capture the thermodynamic properties of the gas mixture. Natural gas (1 kmol/hr) and water (2 kmol/hr) enter the flowsheet at 298K. Subsequently, both are compressed to 5 bar through the

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use of a compressor and a pump. Prior to entering a reformer with outlet temperature 1100K, the water and carbon dioxide undergo heating. The reformer outlet is subsequently fed into a sequence of high temperature shift (650K outlet temperature), low temperature shift (475K outlet temperature) reactors with cooling in between. The resultant stream is then cooled before undergoing water, carbon dioxide and hydrogen separation all at 313K. The water, unreacted methane, and carbon monoxide are recycled to the reformer, while hydrogen (4 kmol/hr) and carbon dioxide (1 kmol/hr) are the flowsheet products.



**Figure 4** Flowsheet depiction of a traditional natural gas based hydrogen production process. External hot utility loads of 216.8 kJ/mol of CH<sub>4</sub> fed, 21.78 kJ/mol of CH<sub>4</sub> fed, and 11.84 kJ/mol CH<sub>4</sub> fed are needed at 1200K, 770K and 420K respectively.

The IDEAS methodology is employed to synthesize alternative flowsheet designs to this traditional flowsheet. Given the aforementioned efficiency in searching the design space, afforded by the employed Gibbs free energy minimization based reactor modeling, low dimensional IDEAS LP approximations are employed which identify intensifying designs in the order of a few minutes. The overall stoichiometry of the traditional flowsheet (1 kmol/hr of CH<sub>4</sub>

in, 2 kmol/hr H<sub>2</sub>O in, 4 H2 kmol/hr out, 1 CO<sub>2</sub> kmol/hr out) is imposed on all of these IDEAS designs. Multiple optimization instances are carried out for varying cost coefficient ratios of the three hot utilities. In particular, cost coefficient ratios of 24:2:1 ( $Q_{HU_1} : Q_{HU_2} : Q_{HU_3}$ ), 4:2:1, 3:2:1, and 2.5:2:1 are considered. When the cost coefficient of the 1200K (HU1) utility is double the cost coefficient of the 770K utility (HU2), the IDEAS flowsheet uses no 1200K utility. Table 1 below summarizes the amount of utility consumed in these flowsheets.

**Table 1.** Utility consumption with cost coefficient ratio of 4:2:1

	HU1(1200K)	HU2(770K)	HU3(420K)
Cost Coefficient (\$/(kJ/s))	0.017	0.0085	0.00425
Baseline Utility Consumption (kJ/s)	60.5	6.26	3.11
IDEAS (4:2:1) Utility Consumption (kJ/s)	0	68.97	8.9

In the IDEAS flowsheet, the reformer has a load of -5kJ/mol of CH<sub>4</sub> fed. In addition, external hot utility loads of 248 kJ/mol of CH<sub>4</sub> and 32.01 kJ/mol of CH<sub>4</sub> are needed at 770K and 420K respectively. The flowsheet produces pure CO<sub>2</sub> as process by-product as well as 4 moles of pure H2 per mol of CH<sub>4</sub> fed. Removing the need for a 1200K external hot utility, allows the flowsheet's energy needs to be potentially met through use of renewable energy sources, such as solar concentrated power. As the cost coefficient ratio between the 1200K and 770K utility varies from 2.5:2 to 24:2, the amount of 1200K utility used by the IDEAS flowsheet will decrease from 26.26 kJ/s (for 2.5:2 ratio) to 0 kJ/s (for 4:2 ratios and above). These results are summarized in Table 2 below. Ignoring small flows, Figure 5 depicts the resulting IDEAS flowsheet structure with cost coefficient ratio of 2.5:2:1. As seen in the Figure below, a reversegas-shift (RGS) reactor is implemented into the traditional flowsheet along with steam-methane reformers, and high-temperature (HTS) and low-temperature shift (LTS) reactors. Natural gas (1 kmol/hr) and water (2 kmol/hr) enter the flowsheet at 298K. Subsequently, both are compressed to 5 bar through the use of a compressor and a pump. Prior to entering the reformer operating at 1100K, the water and carbon dioxide undergo heating. The reformer outlet is subsequently fed into a sequence of high temperature (650K), low temperature (475K) gas shift reactors with cooling in between. The resultant stream is then cooled before undergoing water, carbon dioxide and hydrogen separation all at 313K. The water, unreacted methane, and carbon monoxide are recycled to the reformer, while hydrogen (4 kmol/hr) and carbon dioxide (1 kmol/hr) are the flowsheet products. Table 3 includes the exit temperature information of all process units considered in the IDEAS flowsheet depicted below.

Metric	Baseline	IDEAS 24:2:1	IDEAS 4:2:1	IDEAS 3:2:1	IDEAS 2.5:2:1
Total Hot Utility Cost (24:2:1)	6.22	0.62			
Total Hot Utility Cost (4:2:1)	1.10		0.62		
Total Hot Utility Cost (3:2:1)	0.83			0.64	
Total Hot Utility Cost (2.5:2:1)	0.71				0.69
HU at 1200K, (kJ/s)	60.3	0	0	3.37	26.26
HU at 770K, (kJ/s)	6.06	68.97	68.97	66.6	46.73
HU at 420K, (kJ/s)	3.29	8.9	8.9	7.64	5.14

Table 2. Summary Table of Natural Gas Based Hydrogen Production Case Study



Figure 5 Flowsheet depiction of an IDEAS generated natural gas based hydrogen production process.

The use of equilibrium reactors, modeled through the presented Gibbs free energy minimization approach, leaves each reactor's feed completely undefined in terms of species molar composition, imposing only a two dimensional restriction on the feed's atom molar ratios (H/C, O/C). In turn this allows the employed finite dimensional IDEAS representation (with limited number of states), to consider large portions of the species' state space and to identify CO-rich reformer feeds that make the reformer exothermic, and can be constructed from the streams being made available from the reactor/separator universe (H2O separators, H2 separators, CO2 separators, high/low temperature shift reactors, and reverse gas shift reactors) considered in the employed finite dimensional IDEAS representation. Figures 6, and 7 illustrate the dependence of the total utility cost, and the utility consumption respectively on the 1200K utility to 770K utility cost coefficient ratio, for the traditional and the IDEAS designs. At small

coefficient ratios, IDEAS generates flowsheets that use a combination of 1200K and 770K utilities to reduce the total external hot utility cost.

Temperature (K)									
Reformer 1	Reformer 2	Reformer 3	H <sub>2</sub>	CO <sub>2</sub>	Flash	RGS	HTS	LTS	
			Separator	Separator					
1145	1145	1100	313	313	313	750	650	475	

**Table 3** Process unit outlet temperatures

At coefficient ratios of 4:2 and above, no 1200K utilities are employed in the IDEAS flowsheets. The impact on the utility cost is significant. At coefficient ratio 4:2, the IDEAS utility cost is \$0.62, while the baseline design is \$1.10. At coefficient ratio 24:2 the total utility cost discrepancy between the two designs is so pronounced (\$6.22 to \$0.62) that it justifies the characterization of IDEAS as a systematic process intensification tool.

#### 4. DISCUSSION-CONCLUSIONS

The IDEAS conceptual framework has been put forward as a systematic tool to carry out process intensification studies for total process flowsheets. Efficient use of hot utility resources has been the driving force in this study. This has allowed the use of process models (e.g. equilibrium reactor models) that enable the systematic search of the large space of alternative process designs. The power of the IDEAS methodology as a process intensification tool is demonstrated on a case study of natural gas reforming based hydrogen production. Minimization of the total external hot utility consumption is pursued for various cost coefficient ratios of the hot utilities considered. For large cost coefficient ratios of the hottest (1200K) available utility to the second hottest (770K) available utility, IDEAS is able to identify optimal flowsheets that do not require a heat source at 1200K, but rather only at 770K. This comes at the expense of increased separation costs, which however are not a focus of this study, since the flowsheet synthesis method is carried out without commitment to any particular separation technology. The reduction (and often the elimination) of the 1200K utility heat load, while keeping true to the energy conservation laws of thermodynamics, necessitates that utility loads at lower temperatures be increased. Since no other material resources are allowed to enter the flowsheet, to ensure a fair comparison to the baseline case, this energy redirection is accomplished by increasing the flowrates through the flowsheet separators. Reducing (or even removing) the 1200K utility load, reduces (or removes) the need for burning natural gas or other fossil fuels to power the reformer, and introduces the possibility of using renewable energy sources, while the natural gas is only used as raw material, and not as an energy source. The HHV of natural gas is 52.2MJ/kg, and with a density of 22kg/Mcf, the HHV of natural gas is 1148.4MJ/Mcf<sup>51</sup>. According to the U.S. Energy Information Administration<sup>52</sup>, the average price of natural gas for

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2015 was \$12.23/Mcf. Thus, the cost coefficient of natural gas used as an energy source (hot utility) is \$1.064\*10-5/kJ (\$0.038/kWh). A potential renewable (and free on an energy input basis) energy resource that can be brought to bear as a hot utility for the above described natural gas reforming process is concentrated solar power (CSP)<sup>53</sup>. Solar concentration takes place typically in solar trough and solar tower configurations. A variety of working fluids can be used, including molten salts and synthetic oils. According to the National Renewable Energy Laboratory<sup>54</sup>, solar towers can currently deliver temperatures of 835K, and are expected to reach 920K by 2020. This is also confirmed by Poullikkas<sup>53</sup>, who states that CSP tower plants using molten salts can deliver temperatures around 820K. Similarly, solar troughs can currently deliver 720K, and are expected to reach 773K by 2020<sup>54</sup>.

Our future research will focus on the optimization of alternative objective functions. Among them are total hot/cold/electric utility cost (to account for separator operating costs), and such capital cost measures as heat exchange network total heat transfer area, and reactor capital costs expressed in terms of reactor volume and catalyst weight. More realistic separator technologies will also be considered.



Figure 7 Total Hot Utility Cost versus the ratio of 1200K:770K utility





Figure 6 Cost Coefficient Ratio versus the varying external hot and cold utilities

#### **NOTATION:**

 $A = \begin{bmatrix} A_1 & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & A_m \end{bmatrix}$  diagonal matrix, whose entries are the molar masses of each atom or each

inert molecule(kg/mol)

- $C_i$  Cost coefficient of ith external hot utility (k/kJ/s)
- $F_i^U$ ,  $i = 1, N_{DN_i}$ , mass flow rate of ith DN network inlet (kg/s)

 $F_{s}^{V}$ ,  $s = 1, N_{OP_{o}} + N_{HEN_{o}}$ , mass flow rate of the sth OP and HEN unit outlet (kg/s)

 $F_l^W$ ,  $l = 1, N_{OP_i} + N_{HEN_i}$ , mass flow rate of the lth OP and HEN inlet (kg/s)

 $f_{l,k}^{W}$ ,  $l = 1, N_{OP_{i}}$ , k = 1, n, mass flow rate of the lth OP inlet's kth species (kg/s)

 $F_i^X$ ,  $i = 1, N_{MIX_o}$ , mass flow rate of the ith MIX outlet (kg/s)

 $F_p^Y$ ,  $p = 1, N_{DN_o}$ , mass flow rate of the pth DN outlet (kg/s)

 $F_p^{Y,l}$ ,  $p = 1, N_{DN_o}$ , lower limit of the mass flow rate of the pth DN outlet (kg/s)

 $F_p^{Y,u}$ ,  $p = 1, N_{DN_o}$ , upper limit of the mass flow rate of the pth DN outlet (kg/s)

 $F_{l,i}^{WU}$ ,  $l = 1, N_{OP_i} + N_{HEN_i}$ ,  $i = 1, N_{DN_i}$ , mass flow rate from the ith DN inlet to the lth OP and HEN inlet (kg/s)

 $F_{l,i}^{WX}$ ,  $l = 1, N_{OP_i} + N_{HEN_i}$ ,  $i = 1, N_{MIX_o}$ , mass flow rate from the ith MIX outlet to the lth OP and HEN inlet (kg/s)

 $F_{p,i}^{YU}$ ,  $p = 1, N_{DN_o}$ ,  $i = 1, N_{DN_i}$ , mass flow rate from the ith DN inlet to the pth DN outlet (kg/s)

 $F_{p,i}^{YX}$ ,  $p = 1, N_{DN_o}$ ,  $i = 1, N_{MIX_o}$ , mass flow rate of the ith MIX outlet to the pth DN outlet (kg/s)

G Gibbs free energy (J)

H, specific enthalpy (J/kg)

 $H^{W}$ , total enthalpy flow of the process unit inlet (J/s)

 $h_i^U$ ,  $i = 1, N_{DN_i}$ , total specific enthalpy of the ith DN inlet (J/kg)

 $h^{V}$ , total specific enthalpy of the process unit outlet (J/kg)

 $h^{W}$ , total specific enthalpy of the process unit inlet (J/kg)

 $h_i^X$ ,  $i = 1, N_{MIX_0}$ , total specific enthalpy of the ith MIX outlet (J/kg)

 $h_p^Y$ ,  $p = 1, N_{DN_o}$ , total specific enthalpy of the pth DN outlet(J/kg)

 $h_{p}^{Y,l}$ ,  $p = 1, N_{DN_{o}}$ , lower limit of total specific enthalpy of the pth DN outlet(J/kg)

 $h_{p}^{Y,u}$ ,  $p = 1, N_{DN_{0}}$ , upper limit of total specific enthalpy of the pth DN outlet(J/kg)

 $M = \begin{bmatrix} M_1 & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & M_n \end{bmatrix}$ : diagonal matrix, whose entries are molar masses of each species (kg/mol)

 $n_i^{(k)}$ : Molar flow rate of the jth species present in the kth phase at equilibrium (moles j/s)

 $N_{DN}$  Number of inlet streams in the DN

 $N_{DN_0}$  Number of outlet streams in the DN  $N_{OP}$  Number of inlet streams in the OP  $N_{OP_0}$  Number of outlet streams in the OP  $N_{\rm HEN.}$  Number of inlet streams in the HEN  $N_{HEN_0}$  Number of outlet streams in the HEN  $N_{MIX}$  Number of inlet streams in the MIX  $N_{MIX_0}$  Number of outlet streams in the MIX  $N_R$  Number of reactors  $N_s$  Number of separators  $N_{C/P}$  Number of compressors/pumps  $N_{HEX}$  Number of heat exchangers  $P_i^U$ ,  $i = 1, N_{DN_i}$ , pressure of the ith DN inlet (J/kg)  $P^V$ , pressure of the process unit outlet (bar)  $P^{W}$ , pressure of the process unit inlet (bar)  $P_i^X$ ,  $i = 1, N_{MIX_o}$ , pressure of the ith MIX outlet (bar)

 $P_p^Y$ ,  $p = 1, N_{DN_o}$ , pressure of the pth DN outlet (bar)

 $\dot{Q}$  heat load (J/s)

 $Q_{HU_i}$  external ith hot utility load (J/s)

 $R = ANM^{-1}$  Matrix that converts mass fractions of elements to mass fractions of species

S, specific entropy (J/kg)

 $S^W$ , total entropy flow for the process unit inlet (J/kg)

 $s^{V}$ , total specific entropy for the process unit outlet (J/kg)

 $S_o$  exiting streams in considered mass/energy/entropy balance

 $S_{I}$  entering streams in considered mass/energy/entropy balance

 $T^{V}$ , temperature of process unit outlet (K)

 $T^{W}$ , temperature of process unit inlet (K)

 $x_{i,k}^{U}$ ,  $i = 1, N_{DN_i}$ , k = 1, n, mass fraction of the ith DN inlet's kth species.

 $x_k^V$ , k = 1, n, mass fraction of the process unit's outlet kth species

 $x_k^W$ , k = 1, n, mass fraction of the lth process unit's inlet kth species

 $x_{i,k}^{X}$ ,  $i = 1, N_{MIX_{o}}$ , k = 1, n, mass fraction of the ith MIX outlet's kth species

 $x_{p,k}^{Y}$ ,  $p = 1, N_{DN_{o}}$ , k = 1, n, mass fraction of the pth DN outlet's kth species

 $x_{p,k}^{Y,l}$ ,  $p = 1, N_{DN_o}$ , k = 1, n, lower limit of the mass fraction of the pth DN outlet's kth species

 $x_{p,k}^{Y,u}$ ,  $p = 1, N_{DN_o}$ , k = 1, n, upper limit of the mass fraction of the pth DN outlet's kth species.

 $\alpha_k$  Molar flow rate of kth atom at the inlet of the reactor process unit (mol/s)

 $\lambda_{p,i}^{WU}$  Flag that denotes the existence of flow from the ith DN inlet to the pth DN outlet  $\lambda_{l,i}^{WU}$  Flag that denotes the existence of flor from the ith DN inlet to the lth OP inlet  $\lambda_{p,i}^{WX}$  Flag that denotes the existence of flor from the ith MIX outlet to the pth DN outlet  $\lambda_{l,i}^{WX}$  Flag that denotes the existence of flor from the ith MIX outlet to the lth OP inlet  $\lambda_{l,i}^{WX}$  Flag that denotes the existence of flor from the ith DN inlet to the lth OP inlet  $\lambda_{l,i}^{HU}$  Flag that denotes the existence of flor from the ith DN inlet to the lth HEX inlet  $\lambda_{l,i}^{HX}$  Flag that denotes the existence of flor from the ith MIX outlet to the lth HEX inlet  $\lambda_{l,i}^{XV}$  Flag that denotes the existence of flor from the ith MIX outlet to the lth HEX inlet  $\lambda_{l,i}^{XV}$  Flag that denotes the existence of flor from the sth process unit outlet to the ith MIX inlet  $\mu_{i}$  chemical potential of the jth species (J/mol)

 $N = \begin{bmatrix} v_{1,1} & \dots & v_{1,n} \\ \vdots & \ddots & \vdots \\ v_{m,1} & \dots & v_{m,n} \end{bmatrix}$ : matrix of stoichiometric coefficients  $v_{l,k}$ , that quantify the number of ith

type atoms in the kth species'molecule

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