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CO_2 Mitigation in Chemical Processes: Role of Process Recycle Optimization

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ABSTRACT

In designing low-carbon processes, the unintended emission of CO_2 remains a significant concern due to its global environmental impact. This paper explores carbon management within chemical processes, specifically examining the correlation between the process material balance (PMB) and CO_2 emissions to understand and identify the potential for reducing these emissions. We interrogate the foundational issue of carbon discharge by analyzing the interplay among mass, energy, and entropy balances, which collectively influence the PMB. We introduce the concept of the Target Material Balance (TMB), which represents the material balance of a process corresponding to minimum CO_2 emissions within the given constraints. We could ask what decisions in the design and operation of processes result in higher CO_2 emissions than the TMB. We will focus on the interaction between reactions and recycles and how the arrangement of recycles in processes can inadvertently change the PMB, thereby increasing CO_2 emissions substantially above that of the TMB. We will demonstrate how recycle streams can be introduced to modify the PMB to approximate the TMB more closely. We will finally illustrate these concepts using simple examples, which demonstrate that a carbon-emitting process, such as reforming, can have the TMBs adjusted to create a design that not only reduces carbon emissions but eliminates them entirely.

Keywords: Carbon Dioxide, Process Synthesis, Energy, Optimization, Methane Reforming, Process Material Balance, Target Material Balance, Minimizing CO_2 Emissions, Work Analysis, Entropy Analysis

INTRODUCTION

Process Systems Engineering (PSE) is a connecting force in chemical engineering, providing both a scientific foundation and computational resources to tackle current and future challenges in areas like energy, environmental science, the 'industry of tomorrow,' and sustainability [1]. The methodologies developed within PSE can be classified into heuristic, insight-based, and mathematical optimization approaches [2]. Heuristic methods leverage the designer's experience and intuition, while insight-based approaches depend on deep understanding and analytical insights.

Heat exchanger network synthesis, commonly referred to as "pinch analysis," is a heuristic method developed by Linnhoff and team in the late 1970s [3][4]. The approach offers a systematic method for reducing energy consumption in industrial processes by optimizing heat recovery systems.

Mathematical optimization techniques systematically enumerate various potential unit operations, alternate system configurations, process integration structures, operating modes, and other crucial aspects within a superstructure representation. Sorin et al. [5] use a reducible superstructure to minimize a system's exergy. However, the effectiveness of a superstructure-based solution is contingent on the comprehensiveness and richness of the proposed superstructure and process units, with no assurance of identifying the global optimum of the system.

The second law of thermodynamics, or entropy, is seldom explicitly employed in process design [6]. Instead, entropy's application is primarily implicit, such as in determining phase and reaction equilibria, rather than being directly utilized in the process design or synthesis. Echoing this sentiment, Leites et al. (2003) [7] identify a "lack of understanding" of how second law methodologies can enhance process reversibility as a principal factor behind suboptimal designs, which in turn leads to elevated energy consumption. A review of the methodologies for conducting exergy and energy analyses of thermal power plants notes that most approaches either adopt a superstructure methodology or focus on the analysis and optimization of a specific proposed flowsheet [8]. This highlights a gap in leveraging thermodynamic principles, specifically entropy, more effectively and explicitly in pursuing energy-efficient process designs.

The second law of thermodynamics is implicitly used in process design, for example, by minimizing Gibbs Free Energy to predict chemical and phase equilibrium [9] [10], analyze the temperature dependence of reactions in novel chemistries [11], or predict the effect of feed composition on unwanted side reactions [12].

These methods fall short in offering guidance on the explicit application of second-law analysis for ascertaining the performance limits of a reversible process. The scope of the pinch approach has been extended to encompass targeting for both work and heat exchangers [13]. A superstructure methodology is utilized in order to identify the optimal network configuration.

Process Targeting refers to any methodical procedure for determining the fundamental performance limits of a proposed process pathway based on its inputs and outputs. It enables designers to compare process pathways purely based on thermodynamics, unconstrained by the specifics of design and equipment. This conceptual phase offers the broadest optimization space of any stage of design; the optimization spaces of all subsequent stages of design are just subsets of the optimization space defined during Process Targeting.

By omitting this phase of design, the chosen superstructure or flowsheet may operate within a constrained optimization space that may not contain the global optimal performance and, hence, may impose unnecessary performance limits. The majority of a process's economic and environmental impacts are determined during the conceptual stage of design [14], so it is crucial that the superstructure or flowsheet chosen contains sufficient richness and appropriate interconnections so that its performance is contained in full optimization space.

There is also an argument to be made for Process Targeting based on the scientific principle of Falsificationism – a hypothesis regarding process performance cannot be falsified by a plant design failing to meet the stipulations of the hypothesis because that failure could be attributable to specific design decisions or equipment limitations. Conversely, if the fundamental performance limits defined by Process Targeting do not meet the stipulations of a hypothesis, then that hypothesis is sufficiently falsified.

Hence, initiating the design procedure with Process Targeting is important for two main reasons – it is more compatible with the defined scientific method than other design approaches that start with equipment and/or a pre-defined flowsheet, and it allows for consideration of a broader optimization space for finding the best-performing processes.

This manuscript seeks to demonstrate this design approach by applying it to a straightforward chemical system in the earliest stages of design, by defining a Target Material Balance (TMB) which serves as a performance target against which subsequent Process Material Balances (PMBs) can be compared at each stage of design. At each stage of design, the available optimization space narrows down to a selected subset of the space defined by previous design decisions and, correspondingly, the limits of the PMB gradually become more constrained with each subsequent design decision.

The TMB serves as a goal, indicating an optimum point in terms of a selected objective function [15], and decisions made at each stage of design can be evaluated in terms of how the new constraints it imposes impacts the PMB, that is moves it further from the TMB.

This approach is intended to adhere to the knowledge-generation standards defined by the Falsificationist scientific method and to thereby circumvent design decisions that impose unnecessary constraints during the early design stages.

The proposed approach [15] [16] [17] uses the deceptively simple concepts of material, energy and entropy balances during the conceptual phase of design, as the first and second laws of thermodynamics dictates the outer limits of the optimization space and therefore, the bounds of the PMB.

Heuristics to improve the reversibility of a process have been suggested, including reducing driving forces and the design of the reactor among others [7]. However, the nuanced impact of choices related to recycles on the PMB tends to be overlooked in the initial design phases. These decisions may inadvertently set the bounds of process efficiency and CO_2 emissions, their impact being locked into subsequent design stages, ultimately influencing the profitability and performance of the operating plant. Recognizing this intricate interplay underscores the need for a more comprehensive integration of mass, energy and entropy/work considerations in the early design stages.

THEORY

A process can be defined by the set of material balances and associated extents [18]. Consider a set of N species, where a species j is denoted by A_j and $1 \leq j \leq N$. We specify that j must either be a feed to or a product (final or intermediate) of the process. We can represent the set of species as vector $\underline{\boldsymbol{A}}^T$= {$A_1$, A_2..., A_N} where $\underline{\boldsymbol{A}}^T$ represents the transpose of vector $\underline{\boldsymbol{A}}$. Let n_j be the number of moles of species A_j. We can represent the composition of a process stream as vector $\underline{\boldsymbol{n}}^T$ = {n_1, n_2, ..., n_N}.

We denote the number of independent material balances (IMBs) that describe the relationship between the elements of $\underline{\boldsymbol{A}}$ as S. IMBs have also been called independent chemical reactions, but in this paper, we will refer to IMBs, as the IMBs may not reflect or coincide to the actual individual reactions occurring in the process. Different procedures to determine the IMBs have been reported by Yin, (1989) [6].

The stoichiometric matrix $\boldsymbol{v}$, with elements v_{ij} where $1 \leq i \leq N$ and $1 \leq j \leq S$, is defined such that the S IMBs can be written as $\boldsymbol{v}\underline{\boldsymbol{A}} = \underline{\boldsymbol{0}}$. We define the extent vector $\underline{\boldsymbol{\varepsilon}}$ of the S IMBs as $\underline{\boldsymbol{\varepsilon}}^T$= {$\varepsilon_1$,$\varepsilon_2$, ...,$\varepsilon_S$}. The relationship between the molar composition of the reaction mixture $\underline{\boldsymbol{n}}_{\boldsymbol{out}}$, the initial or feed composition $\underline{\boldsymbol{n}}_{\boldsymbol{in}}$and the stoichiometric matrix $\boldsymbol{v}$ is given by:

$$\underline{\boldsymbol{n}}_{\boldsymbol{out}} = \underline{\boldsymbol{n}}_{\boldsymbol{in}} + \boldsymbol{v}^{\boldsymbol{T}}\underline{\boldsymbol{\varepsilon}} \qquad (1)$$

where the range of $\underline{\boldsymbol{\varepsilon}}$ is such that all $n_i \geq 0$

We begin by defining properties that will be used to analyze heat and work flows in a process. The molar enthalpy of component A_i in a mixture at temperature T and pressure P is denoted $\hat{H}_i(T,P)$. The molar enthalpies of formation of $\underline{\boldsymbol{A}}$ can be combined into vector $\underline{\widehat{\boldsymbol{H}}}(T,P)^T = \{\hat{H}_1(T,P), \hat{H}_2(T,P), \ldots.. \hat{H}_N(T,P)\}$. Similarly, the molar Gibbs Free energy of formation vector of $\underline{\boldsymbol{A}}$ in a mixture at T and P is defined as $\underline{\widehat{\boldsymbol{G}}}(T,P)^T = \{\hat{G}_1(T,P), \hat{G}_2(T,P), \ldots, \hat{G}_N(T,P)\}$, where $\hat{G}_i(T,P)$ is the molar Gibbs Free energy of formation component A_i at T and P.

The enthalpy of a stream of composition $\underline{\boldsymbol{n}}$ at temperature T and pressure P is defined by: $H(T,P) = \underline{n}^T \cdot \underline{\hat{H}}(T,P)$. The Gibbs Free Energy of a stream at temperature T and pressure P is similarly defined by: $G(T,P) = \underline{n}^T \cdot \underline{\hat{G}}(T,P)$. Consider a process, as shown in Fig. 1, where the inlet and outlet stream are at ambient temperature T^o and ambient pressure P^o, and where a quantity Q of heat at T^o and work W are added to the process, as shown in Fig. 1.

An energy balance across the process gives:

$$\Delta H = H_{out}(T^o,P^o) - H_{in}(T^o,P^0) = Q(T^o) + W \qquad (2)$$

Similarly, an entropy balance, combined with eq. (2), assuming reversibility gives, work or Gibbs Free Energy balance:

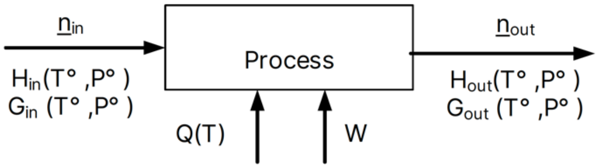

Figure 1. Schematic diagram of mass, heat, and work-flows in a generalized process. Note the process is not assumed to e either isothermal or isobaric

$$\Delta G = G_{out}(T^o,P^o) - G_{in}(T^o,P^0) = W_{rev} \qquad (3)$$

For irreversible processes, the actual work added to the process, W, is such that W > W_{rev} =ΔG. (When ΔG<0, $|W| < \Delta G$) Thus, more work than the reversible limit (target) is added to processes where ΔG<0, and less work is produced than the reversible limit when ΔG>0.

For the overall process, including utility streams, ΔG ≤ 0 and typically ΔH ≤ 0 in that the process must be designed so as to supply heat and work requirements. Thus, processes need to satisfy the following constraints.

$$\underline{\boldsymbol{\varepsilon}} = (v^T)^{-1}(\underline{\boldsymbol{n}}_{out} - \underline{\boldsymbol{n}}_{in}) \qquad (4)$$

$$\Delta H = \boldsymbol{v}^T\underline{\boldsymbol{\varepsilon}} \cdot \underline{\hat{H}}(T,P) \leq 0 \qquad (5)$$

$$\Delta G = \boldsymbol{v}^T\underline{\boldsymbol{\varepsilon}} \cdot \underline{\hat{G}}(T,P) \leq 0 \qquad (6)$$

The PMB is given by $\boldsymbol{v}\underline{\boldsymbol{A}} \cdot \underline{\boldsymbol{\varepsilon}} = 0$ and is thus set by the choice of extents of the IMBs. Furthermore, the PMB also sets ΔH and ΔG for the process and ensures that eq.(5) and (6) are satisfied. We define the TMB as $\boldsymbol{v}\underline{\boldsymbol{A}} \cdot \underline{\boldsymbol{\varepsilon}}^* = 0$, where the equality holds for either equation (5) and (6), ie ΔH=0 and ΔG<0 in a heat-limited process or ΔH<0 and ΔG=0 in a work-limited process. The TMB describes the limit or target for the PMB.

We will explore the relationship between the TMB, PMB and flowsheet by using the concept of the process target on a simple, well studied and industrially important process, namely production of methanol from natural gas

Example: Analyzing the overall process for conversion of methane to methanol

Consider reforming methane to produce 1mol/s of methanol. We define $\underline{\boldsymbol{A}}^T$= {$CH_4$, O_2, CH_3OH, H_20, CO_2}. There are only two IMBs in this case, and the set of independent equations will be defined as:

$$CH_4 + 1/2O_2 \rightarrow CH_3OH_{(l)} \qquad (I)$$

ΔH_I=-164.3 kJ/mol; ΔG_I=-115.6 kJ/mol

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(l)} \qquad (II)$$

ΔH_{II}=-890.3 kJ/mol; ΔG_{II}=-817.8 kJ/mol

Defining the extent of the reactions as ε_I and ε_{II}, respectively, we see that the requirement of a production rate of 1 mol/s of methanol, sets the value of ε_I=1. Thus, we require:

$$\text{From eq(4) : } \varepsilon_I \Delta H_I + \varepsilon_{II}\Delta H_{II} = -164.3 - 890.3*\varepsilon_{II} \leq 0$$

$$\text{From eq(5): } \varepsilon_I \Delta G_I + \varepsilon_{II}\Delta G_{II} = -115.6 - 817.8*\varepsilon_{II} \leq 0$$

We see that the above equations are satisfied for $\varepsilon_I=1$ and $\varepsilon_{II}=0$. As ΔH and ΔG are negative for IMB (I), the process would be exothermic and would be irreversible if work was not recovered from the process. Combusting more CH_4 via IMB (II) will make ΔH and ΔG even more negative, consequently increasing CO_2 emissions.

The PMB for $\varepsilon_I=1$ and $\varepsilon_{II}=0$ is:

$$CH_4 + 1/2O_2 \rightarrow CH_3OH_{(l)} \qquad \text{(PMB1)}$$

with ΔH=-164.3 kJ/mol and ΔG=-115.6 kJ/mol.

Thus, in principle, 1 mole of methane is converted to 1 mole of methanol and no CO_2 or water is produced as a waste product. The process will also reject heat, and if no work recovery is in place, it will lose 115.6 kJ/mol of work potential.

According to Monjur et al. (2021) [20], the PMB for a conventional natural gas to methanol process is:

$$1.069\ CH_4 + 0.638O_2 \rightarrow CH_3OH + 0.069\ CO_2 + 0.134\ H_2O \qquad \text{(PMB2)}$$

with ΔH=-225.7 kJ/mol and ΔG=-172.0 kJ/mol

PMB2 corresponds to extent $\varepsilon_I=1$ and $\varepsilon_{II}=0.069$. Notice that a conventional process produces both CO_2 and water as waste products and simultaneously rejects more heat and work than PMB1.

Monjur et al. optimizes the natural gas to methanol flow sheet and finds PMB3 with $\varepsilon_I=1$ and $\varepsilon_{II}=0.055$ giving:

$$1.055\ CH_4 + 0.610O_2 \rightarrow CH_3OH + 0.055\ CO_2 + 0.110\ H_2O \qquad \text{(PMB3)}$$

with ΔH=-213.2 kJ/mol and ΔG=-160.5 kJ/mol

We see that this improved design reduces the amount of CO_2 produced and that both ΔH and ΔG across the process are also less negative compared to PMB2. Thus, the improved process described by PMB3 would be less exothermic and have less lost work than PMB2. This process still, however, does not match the performance of the original PMB 1, where no CO_2 was emitted.

We could then ask how we might improve PMB3 even further? Without having a process target, one cannot decide if design decisions were made that impose unnecessary constraints on the process described by PMB 3. One could, for example, falsify the proposition that PMB 3 is optimal by proposing that the CO2 and H_2O in the product be recycled back into the process. If this were done, then PMB 3 would be transformed to PMB 1. Notice that introducing the recycles would result in reduced flowrates of CH_4 to the process and simultaneously reduce the heat and work losses. This seems to be a win-win for increasing plant profitability and reducing environmental impact.

PMB1 is better than PMB2 or PMB3 in terms of feed utilization, less lost work, and lower CO_2 emissions. However, is PMB1 the "best" PMB? The "best" PMB is the TMB which requires that either ΔH or ΔG be zero, and PMB1 does not satisfy this. The process target for this system is work-limited and the TMB for ΔG=0 corresponds to $\varepsilon_I^*=1$ and $\varepsilon_{II}^*=-0.141$; giving:

$$0.859\ CH_4 + 0.217\ O_2 + 0.141\ CO_2 + 0.283\ H_2O_{(l)} \rightarrow CH_3OH_{(l)} \qquad \text{(TMB)}$$

with ΔH=-35.5 kJ/mol and ΔG=0 kJ/mol

The TMB corresponds to the process target – no process based on IMB's (i) and (ii) can perform better than this. Furthermore, the TMB can be used to compare processes via the PMB to identify if there are opportunities for improvement in process performance. Any improvements will result in improved CH_4 utilizing, and simultaneously reduce heat and work losses.

Examining the TMB, we see that both CO_2, and H_2O are consumed and, by doing so, the reversible process would convert 0.859 moles of methane to 1 mole of methanol. It might appear, because of the negative value of ε_{II}^*, that the TMB requires a unit operation where methane is "un-combusted" or equivalently where CO_2 and H_2 are converted to CH_4. However, (I) and (II) are IMBs and may not correspond to actual reactions occurring in the process. Although PMB1 was better than either PMB2 or PMB3, it is still very far from the TMB.

In summary, the TMB describes the PMB for a reversible process, and so we would not expect a real process to match the TMB. However, the TMB gives information about how much room there is for improvement in the PMB. It can be used as a guide against which design decisions are made, so that as we take irreversibilities in the process into account by modifying the process and thus the PMB, we can benchmark the impact of the decision on the PMB by comparing it to the TMB.

This approach can also be used on sections of a plant to define the TMB across sections of the plant is and, thus, gives insights on how to integrate the mass, heat, and workflows between sections so as to approach the TMB of the overall process.

Example: Analyzing the process subsections in the conversion of methane to methanol

Methane to methanol plants typically consist of two subsections, namely a section which generates the synthesis gas, a mixture of CO, CO_2 and H_2, which we will call the reformer section followed by a methanol synthesis section where the syngas is converted to methanol as shown in Fig. 2.

We will again use a production rate 1mol/s of methanol as a basis. Looking further into the process details, we need to include the components of syngas in the definition of $\underline{A}$. Furthermore, water will exist in both the liquid and vapor phases (and thus have different G and H), and so we will include these as two separate species.

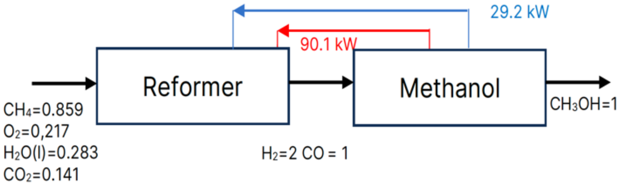

Figure 2. The methane to methanol process broken in a reformer and methanol synthesis section. Molar flowrates (mol/s) corresponding to the TMB are indicated in black, heat flows in red and workflows in blue

We therefore define $\underline{A}^T$= {CH_4, O_2, CH_3OH (l), $H_2O_{(l)}$, $H2O_{(v)}$, CO_2, CO, H_2}.

There are 5 IMBs in this case, and we will define the IMBs in terms of reactions or unit operations that may be occurring in the process, namely:

$$CH_4 + H_2O_{(v)} \rightarrow CO + 3H_2 \qquad (III)$$

ΔH_{III}= 206.1 kJ/mol; ΔG_{III}=142.2 kJ/mol

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(v)} \qquad (IV)$$

ΔH_{IV}=-802.4 kJ/mol; ΔG_{IV}=-800.7 kJ/mol

$$CO_2 + H_2 \rightarrow CO + H_2O_{(v)} \qquad (V)$$

ΔH_V= 41.2 kJ/mol; ΔG_V= 28.6 kJ/mol

$$H_2O_{(l)} \rightarrow H_2O_{(v)} \qquad (VI)$$

ΔH_{VI}= 44.0 kJ/mol; ΔG_{VI}= 8.56 kJ/mol

$$CO + 2H_2 \rightarrow CH_3OH_{(l)} \qquad (VII)$$

ΔH_{VI}= -128.1 kJ/mol; ΔG_{VI}= -29.6 kJ/mol

We can calculate the extent of these IMBs that correspond to the overall TMB. In order to achieve the TMB we require $\underline{\varepsilon}^{*T}$= {$\varepsilon_{III}^*$,$\varepsilon_{IV}^*$,$\varepsilon_V^*$,$\varepsilon_{VI}^*$,$\varepsilon_{VII}^*$} = {0.75, 0.109, 0.25,0.283,1}. For illustrative purposes, we will specify the composition of the syngas, leaving the reformer section as having ratio CO:H_2 = 1:2. We will further assume that the liquid feed water is evaporated in the reformer section. Thus, IMBs III, IV, V, and VI will occur in the reformer section, while only IMB VII will occur in the methanol section because of the specified composition of the intermediate syngas is in the stoichiometric ratio defined by IMB (VII). This allows us to determine the TMB of the individual sections of the plant that will be consistent with the overall TMB. Conditions (5) and (6) can be lifted for process subsections, with the understanding that a plant subsection with $\Delta H>0$ implies that heat integration needs to be done between this plant subsection and the other, which will be exothermic, namely with $\Delta H<0$. Similarly, a plant subsection with $\Delta G>0$ implies that work integration needs to be done between this plant subsection and another with $\Delta G>0$.

The TMB for the reformer section, TMB_{Ref}, can be calculated using $\underline{\varepsilon}^{*T}$= {$\varepsilon_{III}^*$,$\varepsilon_{IV}^*$,$\varepsilon_V^*$,$\varepsilon_{VI}^*$,$\varepsilon_{VII}^*$} = {0.75, 0.109, 0.25,0.283,0} giving:

$$0.859\ CH_4 + 0.217\ O_2 + 0.141\ CO_2 + 0.283\ H_2O_{(l)} \rightarrow CO + 2H_2 \qquad (TMB_{Ref})$$

with ΔH= 90.14 kJ/mol and ΔG=29.23 kJ/mol

Similarly, the TMB for the methanol synthesis section, TMB_{Meth}, can be calculated using $\underline{\varepsilon}^{T*}$= {$\varepsilon_{III}$,$\varepsilon_{IV}$, ε_V, ε_{VI}, ε_{VII}} = (0,0,0,0,1}, giving:

$$CO + 2H_2 \rightarrow CH_3OH \qquad (TMB_{Meth})$$

with ΔH= -128.1 kJ/mol and ΔG=-29.23kJ/mol

We see that both work and heat will need to be transferred from the methanol synthesis to the reformer section, as indicated in Fig. 2. We will consider the reformer section further to show how we can use the TMB_{Ref} to develop a flowsheet and related PMB.

Example: Development of the Reformer Flowsheet using the TMB_{Ref}

The development of the reformer flowsheet is iterative in terms of setting up the flows and recycles and the heat and work integration. This paper will focus on setting up the mass flows (Fig. 3) and will show an example where heat and mass integration has been incorporated (Fig. 4).

The reformer section consists of a combustion process where CH_4 is combusted to provide the work to drive the reforming reaction, a steam reforming reaction and a water gas shift (WGS) reaction to shift the gas to the correct CO:H_2 ratio of 1:2. The extents of reforming, WGS and combustion are initially set by the TMB_{Ref}.

There are two exothermic, work producing reactions, namely combustion and methanol synthesis. The amount of work that can be recovered from a process is given by $\Delta H(1- T^0/T)$ [16], where T is the temperature of the heat (ΔH) added or rejected by the reaction. The combustion process is particularly irreversible, as the Carnot temperature for combustion of methane is very large (~147000K). Thus, the amount of O_2 fed to the process for combustion must be increased so that the recovered work from both the combustion and the methanol synthesis subprocess is sufficient to supply the overall process work. This is done by increasing the extent of combustion ($\varepsilon_{IV} > \varepsilon_{IV}^*$) and, consequently, increasing the amount of oxygen and methane fed to the combustion reaction. This design decision introduces process irreversibility which results in the PMB moving away from the target TMB. We describe how the new PMB is calculated below.

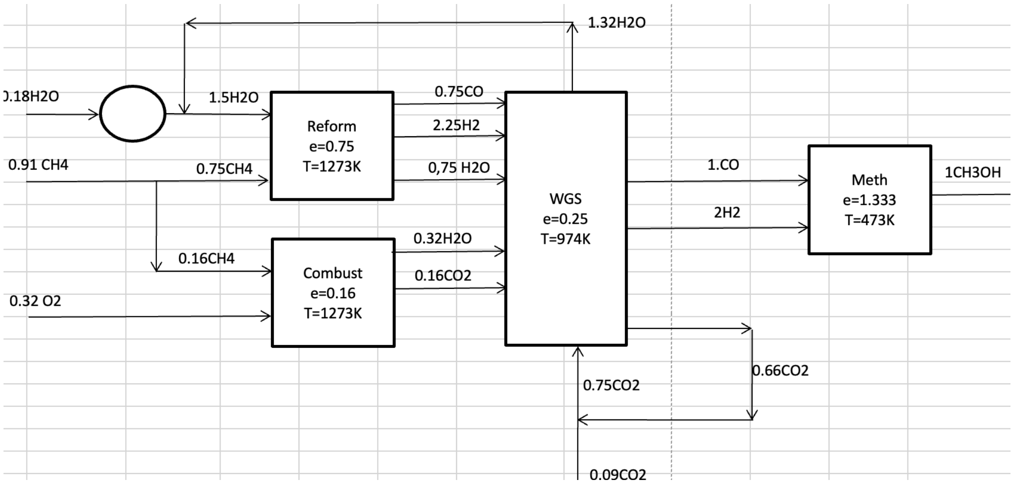

Figure 3: Example of the molar flows around the reformer section (mol/s) corresponding to PMB 4.

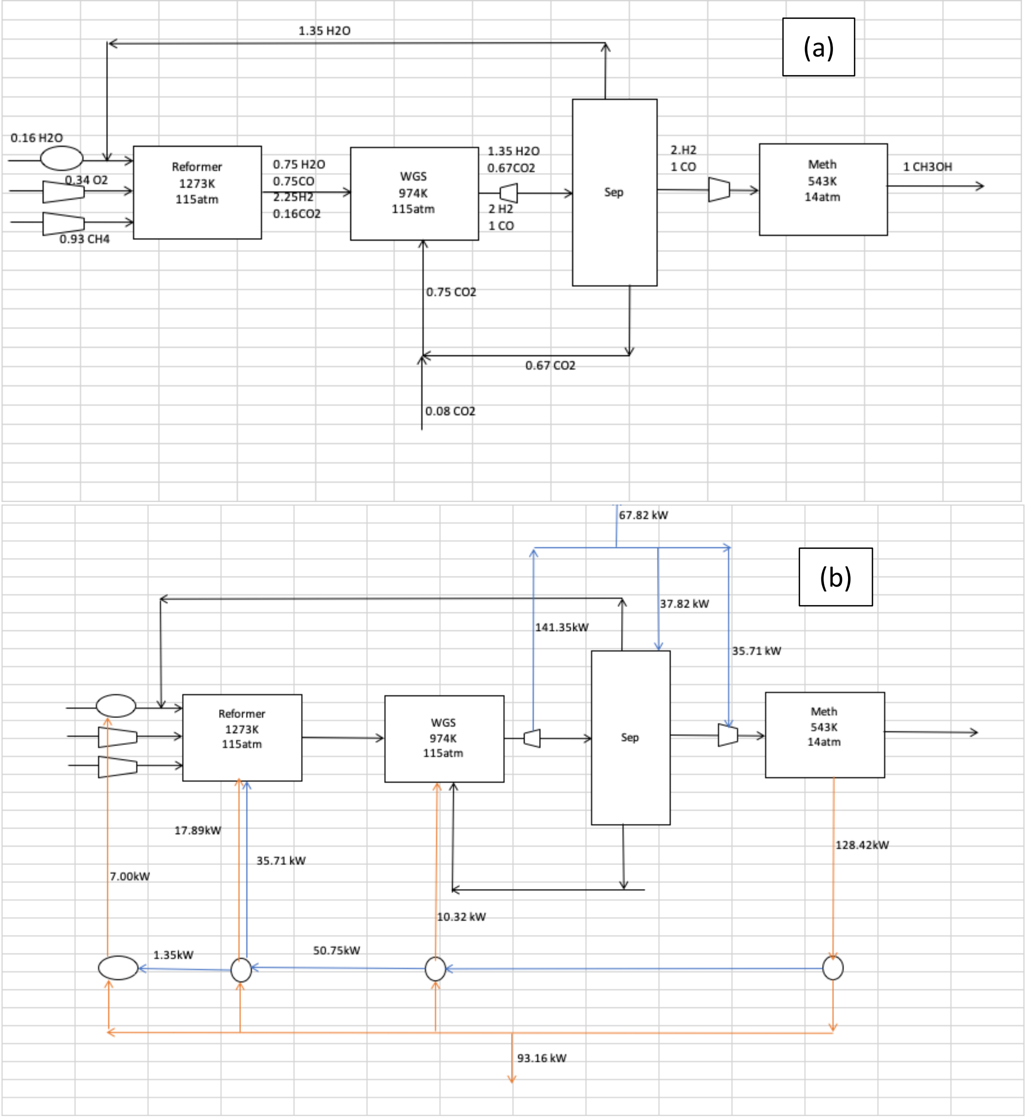

Figure 4: (a) Mass flows and (b) heat flows in red and work flows in blue for a process producing 1 mol/s methanol which has been heat and work integrated.

Further design constraints can to specified; for example, we set the reforming temperature at 1273K and specify the ratio of H_2O:CH_4=2:1 entering the reformer in order to suppress carbon depositing; as we know the flow rate of methane entering the reformer (ε_{III}) this then sets the water flowrate entering the reformer $(2\varepsilon_{III})$, and consequently the flowrate of water in the stream leaving the reformer as well as the water recycle flowrate. Setting the reforming temperature sets ε_{IV} as we require that the work rejected by the combustion when the heat is rejected at 1274K, and methanol synthesis reactions must supply the work for the reforming process, i.e.:

$$\varepsilon^*_{III}\Delta G_{III} = \varepsilon^*_{VII}\,\Delta G_{VII} + \varepsilon_{IV}\Delta H_{IV}\left(1 - {T^o}/{1274}\right) \qquad (7)$$

Solving eq.(7) gives that $\varepsilon_{IV} = 0.16$, thus setting the flowrate of O_2 to 0.32 mol/s, and the flowrate of methanol entering the combustion process as 0.16 mol/s, which ensures that sufficient work is supplied to the process once the irreversibility of work transfer from combustion is taken into account, as shown in Fig. 3.

In order for the WGS reaction to operate at its Carnot Temperature *Tc*, we require that the WGS equilibrium constant, K_{WGS}, be 1 (i.e. $\Delta G(Tc, p) = 0$), which corresponds to an operating temperature of Tc= 974 K. As we know the flow rate of CO, H_2 and H_2O leaving the WGS reactor, we can then determine the amount of CO_2 in the product stream of the WGS reactor so as to meet the requirement that (K_{WGS} =1); this then allows us to subsequently calculate the CO_2 recycle flowrate. The resulting flowsheet is shown in Figure 3. The PMB for the overall process in Fig. 3 is given by:

$$0.91\ CH_4 + 0.32\ O_2 + 0.09\ CO_2 + 0.18\ H_2O_{(l)} \rightarrow CH_3OH \qquad (PMB4)$$

with ΔH= -83.65kJ/mol and ΔG=-42.38 kJ/mol

The PBM for the reformer section is described by:

$$0.91\ CH_4 + 0.32\ O_2 + 0.09\ CO_2 + 0.18\ H_2O_{(l)} \rightarrow CO + 2H_2 \qquad (PMB_{Ref})$$

with ΔH= 44.4 4kJ/mol and ΔG=-12.8 kJ/mol

The PMB_{IV} consumes less CO_2 than the TMB; however, it is considerably better than the PMB's 1, 2 or 3 given earlier. This is mainly due to the use of recycles to ensure that we approach the TMB more closely than in the previous processes. The process flowsheet can be iteratively developed to ensure that the workflows to each section are such that $\Delta G \leq 0$ for each reaction system. Work can, for example, be *added* to a process by operating at high pressure when there is a decrease in moles of gas across the process. The exact operating pressure can be calculated to ensure that the correct amount of work is added via this route. The flow sheet can be developed, taking temperature constraints and work flows to ensure that $\Delta G \leq 0$ in each reactor, and an example of the flow sheet that is mass, heat and work integrated is given in Figure 4 [8]. This process not only consumes CO_2, but also produces 67 kW of work (based on a production rate of 1 mol/s methanol).

CONCLUSION

The TMB represents the overall process material balance for either a reversible process (in the case of a G-limited process) or an adiabatic process (in the case of an H-limited process). The TMB also sets the limiting process heat and work flows. The TMB represents the limit of performance of the process; thus the overall material balance across a process, which we refer to as the PMB, may at best, in the limit approach the TMB. The further the PMB is from the TMB, the more room for improvement there may be. Any design decision that results in a sizable departure of the new PMB from the TMB therefore represents the introduction of irreversibility which constrains the performance limits for subsequent design steps.

The TMB can be calculated using only the Gibbs Free Energy and Enthalpies of formation of the feed and product species. The TMB in the case of a G-limited process corresponds to the situation where the chemical potential of the feed (s) is conserved in the product. It also represents the limiting amount of CO_2 that is emitted from a process.

A design procedure can, therefore, reliably and falsifiably search for optimal processes by first defining the TMB and comparing the subsequent PMBs resulting from subsequent design decisions against that benchmark. In this way, the TMB can be used as a tool for iterative design, which conserves as much of the feasible optimization space as possible through each stage of design.

The TMB can also be modified by the inclusion of specific constraints that may reduce the optimization space, such as heat transfer occurring at temperatures other than the process or reaction Carnot temperature. Thereafter, in the case of reversible reactions, recycles can be introduced to ensure that the desired extent of reaction is achieved. In this way one can work toward the desired TMB rather than accepting the PMB given by a simulation.

While the TMB represents a performance benchmark that might not be achievable in real processes, it is useful as a means of identifying, and hopefully avoiding, design decisions that prematurely constrain the optimization space for design which can in some case result in both carbon release and inefficient utilization of the feed. It is also a useful basis of comparison between processes of differing levels of technological maturity, where it can identify which processes have the most inherent potential regardless of current levels of optimization and equipment design, making them a useful tool for long-range planning and R&D investment decisions.

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