TEACHING PROCESS DESIGN THROUGH INTEGRATED PROCESS SYNTHESIS

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What is the minimum amount of carbon dioxide that a process can produce? This may seem like a trivial question but it is not a question usually asked when processes are being designed. In many cases, there is a lack of a quantitative description of what is the highest efficiency, least amount of energy, or lowest amount of carbon dioxide that can be achieved for a particular process, *i.e.*, what is the theoretical achievable target. Without being able to answer such simple questions it is hard to make good decisions in the design of processes.

In this regard, a novel approach to the chemical process design course was recently introduced at the University of the Witwatersrand, Johannesburg, South Africa, called Integrated Process Synthesis. The course aimed to introduce students to systematic tools and techniques for setting and evaluating performance targets for processes as well as gaining insight into how these targets can be achieved. The main objectives, in terms of the targets set for the process design, were efficient use of raw materials and energy and improved environmental performance (reducing CO_2 emissions).

PHILOSOPHY

The decisions made in the early stage of the design process or the conceptual phase are of vital importance as the economics of the process are usually set at this stage. Biegler, et al.[1] estimate that the decisions made during the conceptual design phase fix about 80% of the total cost of the process. Once the process structure has been fixed, only minor cost improvements can be achieved. Thus, the success of the process is largely determined by the conceptual design.[2] There is therefore a need for systematic procedures to generate, as well as identify, the most promising alternatives. Without such procedures, even an experienced designer might not be able to uncover the best process structure and will be stuck with a poorly operating process. Ideally, these procedures should be applied in the early stages of the design and should require minimum information since the use of rigorous design methods to evaluate alternatives can be time and capital intensive.

The philosophy underlying the course is to look at the process holistically. The design of a flow sheet is approached with this overall analysis as its foundation. We address the overall process by tools and techniques developed within

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the framework of process synthesis and integration, which provides a holistic approach to process design, *i.e.*, considering "the big picture first, and the details later."[3] We aim to introduce a method of providing insights and setting targets for the overall process based on fundamental concepts, as well as developing systematic procedures to attain these targets.

Targeting allows one to identify a benchmark for the performance of a system before the actual design of the system is carried out.[4, 5] These benchmarks are the ideal or ultimate performance of such a system and provide useful insight into the process. These targets are usually based on fundamental engineering principles—for example, thermodynamic principles—but can be based on heuristics or cost estimates. Targets are usually independent of the structure of the process, *i.e.*, the ultimate performance of the system can be determined without identifying how it can be reached.[4] Thus, these targets reduce the dimensionality of the problem to a manageable size.[4] These targets are also useful in evaluating existing systems as one can easily compare the current performance of the system to the ideal performance of the system, even identifying ways to minimize waste from a process.[6]

Every chemical process can be considered in terms of a number of inputs and outputs. These inputs or outputs can be classified into three variables: mass, heat, and work. Mass and energy balances are used in the analysis of individual units and flow sheets, as well as in the synthesis of chemical processes. Another tool, the second law of thermodynamics (or the entropy balance) is also useful for synthesizing or analyzing chemical processes, especially since it can quantitatively assess the efficiency and sustainability of processes. The law of mass conservation (mass balance) and the first law of thermodynamics (energy balance), as well as the second law of thermodynamics (work balance), will be employed as the basis of the approach. One can assemble processes through decision making about the mass, energy, and work balance, rather than arbitrarily connecting unit operations. This is useful not only for the design of new processes but for retrofitting as well.

Unlike the traditional approach to process design[7-9] where the flow sheet is normally chosen from existing literature or from prior knowledge, the flow sheet emerges from the analysis. No longer is it necessary for the lecturer to hand out a design brief to the students with the desired process route,[10] but students are challenged to select the most promising synthesis route with limited information, training them for similar instances encountered in industry.[11] One can then use the more detailed design approach to include costing, sizing, etc. In addition, this approach works equally well for product design[12] and to include additional factors such as designing for controllability[13] and risk due to uncertainty,[14] as well as reactor optimization.[15] As always, design is an iterative procedure, so in most cases the assumptions made at this point will need to be revisited, but this approach provides a framework to register those assumptions and provide a philosophy of why they were implemented.

A back-to-front synthesis approach based on determining the target overall mass balance for a process is proposed. The overall mass balance can be determined by applying atomic species balances based on the inputs and outputs of the process. This is referred to as the mass balance subject to atomic balance constraints, *i.e.*, all atoms entering must also exit. In addition, it is also possible to develop a process mass balance subject to energy constraints, by determining the energy requirements of the overall process mass balance. In this work, an adiabatic target is chosen (no heat rejected to or required from the environment). Finally, the work requirements are also determined for each overall mass balance based on the entropy, or work, balance. The target for the work balance is a reversible process that does not require or produce work. An understanding of which of the three variables is the limiting target is also very important, in that it gives insight into what is the important or limiting parameter in the design and operation of the process. Changing the target often results in a change to the overall process mass balance, so these three tools work in conjunction, rather than independently. Therefore, the design is also an iterative process. Regardless, once a mass balance is chosen subject to any constraint, the energy and work requirements of the process are set, and determined through a simple calculation. It is true that cost must always be considered during design, but it is also true that a working process may not be economically feasible, whereas an economically feasible process may not work. Therefore, one must ensure the process is possible first and foremost, and then consider the economic aspects.

Consider a flow process at steady-state as shown Figure 1, operating in an ambient environment where all the mass and energy flows are accounted for. This is our process "universe." The pure component inputs to the process enter with a certain

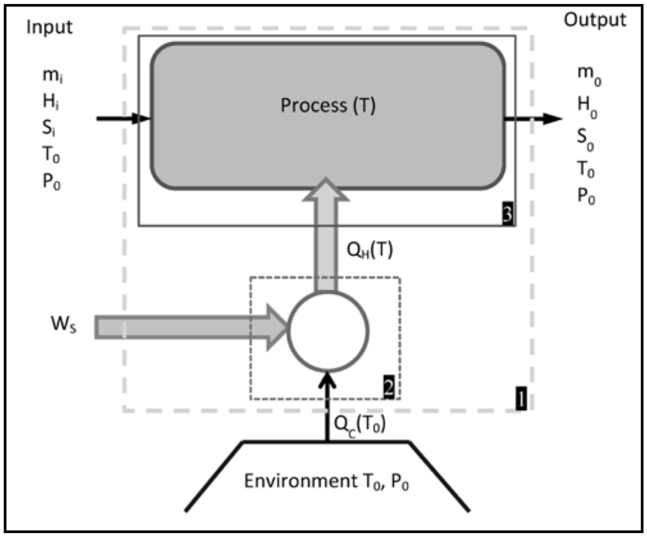

Figure 1. *General schematic of a process "universe."*

flow rate (m_i) at a standard temperature and pressure of the environment (T_0 and P_0), and possess a certain enthalpy (H_i) and entropy (S_i). The pure component outputs leave the process at identical conditions to the inlets, but with potentially different flow rates, enthalpies, and entropies. Mass is conserved across the process, allowing one to develop a process mass balance relating the entering flow rates to the exiting flow rates. Also flowing into (or out of) the system is a heat stream $Q_C(T_0)$and a work stream W_s. The values of these streams are determined using the first and second laws of thermodynamics. The first law of thermodynamics states that the energy flows entering and leaving a system must be equal at steady state. Energy flows can be in the form of heat or work. The energy balance can be applied to individual units as well as entire processes. Therefore, we can write an energy balance over the *entire process* (dashed box number 1) shown in Figure 1, as shown in Eq. (1).

$$\Delta H + \frac{1}{2}\Delta u^2 + g\Delta z = \sum Q + \sum W_S \tag{1}$$

Here ΔH is the difference in enthalpy of the streams leaving and entering ($\Delta H = m_0H_0 - m_iH_i$), Δu is the difference in velocity of the outlet and inlet streams (kinetic energy), Δz is the difference in height of the output and input streams relative to a reference plane (potential energy), g is the gravitational constant, $\sum Q$ refers to all heat flows in or out of the process, which we represent as only $Q_C(T_0)$, and $\sum W_s$ refers to all shaft work entering or leaving the system, which we represent as only W_S. A positive value of $Q_C(T_0)$ would mean that heat is required whereas a negative value indicates that heat has to be released from the process. A positive value of W_s means that work is required to upgrade heat from the environment to the level necessary to run the process, whereas a negative value means that work can be produced by downgrading the heat leaving the process as it returns to the environment. Assuming Δu and Δz are negligible, Eq. (1) reduces to:

$$\Delta H = Q_C(T_0) + W_s \tag{2}$$

Performing the same energy balance over the dotted box number 2 in Figure 1 we can also develop the following relationship:

$$Q_H(T) = Q_C(T_0) + W_s \tag{3}$$

As a result, we can then substitute Eq. (3) into Eq. (2) and find that

$$\Delta H = Q_H(T) \tag{4}$$

or, an identical result to if the energy balance were performed over the solid box number 3. Therefore, the amount of heat that is required to convert the given feeds to the products is equal to the enthalpy difference between the outlet and inlet streams. From this point on $Q_H(T)$ is simplified to Q. Here we note that the difference between $Q_H(T)$ and $Q_C(T_0)$ is the quality of the heat, with $Q_C(T_0)$ having a low quality and $Q_H(T_0)$ having a high quality, meaning that there is work associated with the heat at higher temperature, as given by Eq. (3).

To determine the relationship for W_s, we utilize the second law of thermodynamics and follow the steps outlined by Denbigh.[16] The second law of thermodynamics states that in order for the process in Figure 1 to operate, the entropy change must be greater than or equal to zero, where zero refers to a reversible process and is the limit of operation. The entropy balance over the dashed box number 1 in Figure 1 is shown in Eq. (5).

$$\Delta S + \frac{Q_C(T_0)}{T_0} = S_{gen} \tag{5}$$

where ΔS is the entropy difference between the outlet and inlet streams ($\Delta S = m_0S_0 - m_iS_i$) and S_{gen} is the entropy generated by the process. Replacing $Q_C(T_0)$ in Eq. (5) with the relationship in Eq. (2) and rearranging, we can then write the following expression:

$$W_s + S_{gen} = \Delta H + T_0\Delta S \tag{6}$$

Using the definition of Gibbs free energy ($G=H-TS$), Eq.(6) reduces to

$$W_s + S_{gen} = \Delta G \tag{7}$$

Finally, as $\Delta S_{gen} \geq 0$ (the equality assuming a reversible process), we can determine the limit of operation,

$$W_s \geq \Delta G \tag{8}$$

Thus, for our "process universe," we can determine the amount of work required to run the process reversibly (or amount of work rejected from the process) by calculating the change in Gibbs free energy between the outlet and inlet streams. This "available work" is also called exergy when $T=T_0$. Exergy considers both the quantity and quality of work associated with a process and is particularly useful for identifying sources of thermodynamic inefficiency within a process.[17-19] More information on this derivation and its utility is given elsewhere,[20-23] along with additional case studies and development of this approach.[24, 25]

To demonstrate the procedure of using Integrated Process Synthesis to determine process targets, we will consider the following example of methanol synthesis. The example will go step-by-step through the Integrated Process Synthesis approach, increasing in complexity, starting with a process mass, energy, and work balance and ending with the basic outline of a process flow diagram.

THE PROCESS MASS BALANCE

We wish to produce methanol, while maximizing the amount of carbon, hydrogen, and oxygen that ends up in the desired product, *i.e.*, minimize by-products. As a result, the ideal process to produce 1 mole of methanol will consume only those elements present in methanol and in the correct proportions. A simple mass balance across the process can tell us how to run our process optimally. The ideal methanol production requires 1 mole of carbon, 4 moles of hydrogen, and 1 mole of oxygen, as shown in Figure 2.

If these elements are introduced as feeds to the process in any other ratio besides C:H:O 1:4:1, then another species besides methanol must be produced, reducing the efficiency of the process. Two metrics will be used to compare various processes based upon how much of each element from the feed ends up in the desired product. First, the carbon efficiency is the percentage of the carbon in the feed that ends up as carbon in the desired product, and the calculation is given in Eq. (9).

$$CE = \frac{\text{number of moles of Carbon in the desired product}}{\text{number of moles of Carbon in the feed}} \quad (9)$$

In the schematic shown in Figure 2, 1 mole of carbon is fed into the process and that 1 mole of carbon ends up in the desired methanol product. Therefore, the carbon efficiency is 1 (CE=1/1=1). Similarly, a hydrogen efficiency can be defined, performing the same calculation, but with hydrogen as the element of interest, as given by Eq. (10).

$$HE = \frac{\text{number of moles of Hydrogen in the desired product}}{\text{number of moles of Hydrogen in the feed}} \quad (10)$$

For Figure 2, the hydrogen efficiency is also 1 (HE=4/4=1). A similar function can be described for oxygen efficiency, but that will not be included in this example. Thus, the process described in Figure 2 is ideal from a carbon and hydrogen efficiency standpoint, but how would we create such a process? What resources are readily available as sources of carbon, hydrogen, and oxygen, and how well do they match with the desired C:H:O=1:4:1 ratio?

Let us assume that the compounds available to us that contain some combination of carbon, hydrogen, and oxygen are liquid water (H_2O), coal (we assume this to be pure carbon - C), methane (CH_4), oxygen (O_2), and carbon dioxide (CO_2). These species can be combined in an effort to match the required elemental ratios and begin to develop a mass balance over the entire process, or a process mass balance.

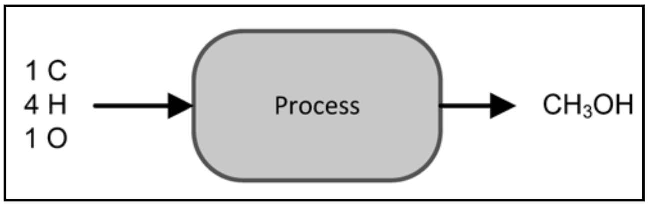

Figure 2. *Schematic representing ideal mass inputs for the production of methanol.*

TABLE 1

Overall process mass balances, carbon efficiences, and hydrogen efficiencies for processes using a single carbon source to produce methanol from readily available species.

Overall Process Mass Balance	Eq. No.	CE	HE
$1C_{(s)}+2H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+0.5O_{2(g)}$	11	1	1
$1.5C_{(s)}+2H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+0.5CO_{2(g)}$	12	0.67	1
$CH_{4(g)}+H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+H_{2(g)}$	13	1	0.67
$CH_{4(g)}+0.5O_{2(g)} \Rightarrow CH_3OH_{(l)}$	14	1	1

Start with coal as a carbon source. One mole of coal meets our requirement of 1 mole of carbon. Water can be used as the source of both hydrogen and oxygen, but one mole of water does not provide enough hydrogen (2 moles and we need 4 moles), so we will need at least 2 moles of water. Now, however, we have an additional mole of oxygen, which must end up as another product. A product of oxygen is possible, as well as a product of CO_2. For an oxygen product, the process mass balance is straightforward: coal plus water makes one mole of methanol, with the balance of oxygen ending up as elemental oxygen. This is shown in Eq. (11).

$$1C_{(s)} + 2H_2O_{(l)} \Rightarrow CH_3OH_{(l)} + 0.5O_{2(g)} \quad (11)$$

An additional amount of carbon is needed, however, to provide the carbon for both methanol and carbon dioxide. The resulting process mass balance is thus,

$$1.5C_{(s)} + 2H_2O_{(l)} \Rightarrow CH_3OH_{(l)} + 0.5CO_{2(g)} \quad (12)$$

Notice the use of ⇒ to denote a process mass balance and not a reaction. We know that at least one reaction will have to take place to chemically convert the feed to the products, but those details are contained within the "Process" box in Figure 2 and are nonessential at this point in the analysis. We can see that the carbon and hydrogen efficiency of the process represented by Eq. (11) are 1, whereas the same values for the process represented by Eq. (12) are 0.67 and 1, for carbon and hydrogen, respectively.

Following the same procedure, one can develop alternative process mass balances using methane as the carbon and hydrogen source and water or atmospheric oxygen as the oxygen source. The resulting set of process mass balances is shown in Table 1, along with their carbon and hydrogen efficiencies.

There are other combinations of the species, but only these three will be considered here. From both a carbon and hydrogen efficiency perspective, the process represented in Eq. (14) (methane plus oxygen yields methanol) is most attractive. The by-product, however, from the process represented by Eq. (13) (methane plus water yields methanol and hydrogen) is hydrogen, which is an attractive product in its own right, so this process is also considered. If one was deciding on processes to produce methanol with minimal environmental impact, by using coal you are forced to have a minimum of 33% of your feed carbon ending up as carbon dioxide, whereas it may be possible to produce methanol with no CO_2 emissions by using methane. This procedure provides a quick and easy methodology to screen potential feeds against one another when deciding on various process routes. All this was possible by just performing a simple mass balance.

The consequence of not providing the desired elements in the desired proportions is the production of unwanted by-products, adversely affecting the efficiency of the overall process. On the other hand, removing products from intermediate steps also adversely affects the overall process efficiency. For example, the industrial approach to methanol synthesis is in a two-step process producing syngas (a mixture of carbon monoxide and hydrogen) from methane, water and oxygen, and then producing both methanol and water from the syngas.[26] None of the overall process mass balances presented in Table 1 have water as a product, which therefore means that additional reactants are required to satisfy the overall process mass balance. Instead, one could identify that recycling the water as a feed to the process would be a more desirable approach, instead of removing what appears to be a harmful by-product. This demonstrates that optimizing each individual part of a process may not be the best for the optimization of the overall process. Therefore, the approach is not only a tool for process designers, but also a tool for process operators.

THE PROCESS ENERGY BALANCE

Although the processes listed in Table 1 seem attractive, they may not be feasible. In order to determine if they are feasible, *i.e.*, do not require additional energy to convert the reactants to the products, one must perform an energy balance over each of those processes. The basic schematic used to calculate the heat requirements for the process combining oxygen and methane to produce methanol is shown in Figure 3.

As discussed earlier, the difference between the enthalpy of the inlet streams and enthalpy of the outlet streams can be used to determine the energy requirements of the process: Q. For reference, the enthalpy of each compound discussed in this text is included in Table 2.

Using the values in Table 2, one can calculate the heat requirements of the process mass balances in Table 1. These values are shown in Table 3.

Remember that $\Delta H_{process} > 0$ means the process is endothermic and requires an external source of heat to convert the reactants into the products, whereas $\Delta H_{process} < 0$ means the process is exothermic and produces heat when converting the reactants into the products. Additionally, heat normally comes from combustion, which results in a change to the overall process mass balance. As a result, the overall process mass balances for producing methanol from coal and methanol from methane and water will be different than those shown in Table 1 and Table 3. Also, note the extremely large value for $\Delta H_{process}$ of the process represented by Eq. (11). This is because the formation of oxygen is highly unlikely from a thermodynamics perspective.

To demonstrate this, consider the production of methanol from methane and water [the process represented by Eq. (13)]. One can see that the by-product from this process is hydrogen, or a potential energy source through combustion. Therefore, it may be possible to combust the extra hydrogen in order to meet the energy requirements of the process. Hydrogen combustion is shown in Eq. (15), along with its enthalpy, calculated using the values in Table 2.

$$H_{2(g)} + 0.5O_{2(g)} \Rightarrow H_2O_{(l)} \qquad \Delta H_{H_2,comb} = -285.8\,kJ/mol \qquad (15)$$

Comparing the heat requirements of the process represented by Eq. (13) to the hydrogen combustion enthalpy, combusting all of the hydrogen results in an energy excess

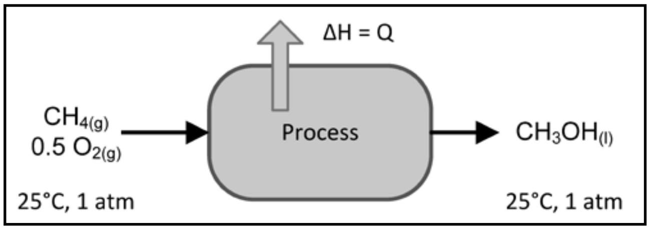

Figure 3. *Energy balance for the production of methanol from the more efficient feed components.*

TABLE 2
Heats of formation and Gibbs free energies for each species used.

Species	ΔH° (kJ/mol)	ΔG° (kJ/mol)
$C_{(s)}$	0.0	0.0
$CH_{4(g)}$	-74.8	-50.7
$O_{2(g)}$	0.0	0.0
$CO_{2(g)}$	-393.5	-394.4
$H_{2(g)}$	0.0	0.0
$H_2O_{(l)}$	-285.8	-237.1
$CH_3OH_{(l)}$	-238.7	-166.9

TABLE 3
Heats of reaction for each of the overall process mass balances presented in Table 1.

Overall Process Mass Balance	Eq. No.	$\Delta H_{process}$ (kJ/mol)
$1C_{(s)}+2H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+0.5\ O_{2(g)}$	11	333.0
$1.5C_{(s)}+2H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+0.5\ CO_{2(g)}$	12	136.2
$CH_{4(g)}+H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+H_{2(g)}$	13	122.0
$CH_{4(g)}+0.5O_{2(g)} \Rightarrow CH_3OH_{(l)}$	14	-163.9

(122 kJ required, 285.8 kJ available). In addition, the overall process mass balance is different as a result of the inclusion of the hydrogen combustion. The resulting schematic of the conversion of methane and water to methanol and hydrogen, producing the required energy from hydrogen combustion, is shown in Figure 4.

Notice that when the overall process feeds and products are considered, the resulting overall process mass balance is identical to that given by Eq. (14), or the conversion of methane and oxygen to methanol. The heat required by the process represented by Eq. (4) is provided by combusting the hydrogen by-product, with the excess energy produced (Q) equal to the overall of $\Delta H_{process}$ of Eq. (13). This example demonstrates how one can utilize the Integrated Process Synthesis approach to begin to assemble preliminary process flow sheets with the use of readily available thermodynamic information about the species present and the process requirements.

The same approach can be applied to each of the overall process mass balances given in Table 3 to determine the overall process mass balance for a feasible process converting the given feeds to the desired products, with the energy requirements coming from either combusting additional amounts of the carbon source or combusting a combustible by-product, *e.g.*, hydrogen. For each case, the target of the analysis is to combust only enough of a fuel source to provide enough energy to make the overall process adiabatic ($\Delta H_{process} = 0$), because combusting additional amounts of fuel will also result in the conversion of a usable fuel source into undesired by-products (some combination of CO_2 and/or H_2O). To do this, the enthalpy of the process as given in Table 3 is divided by the absolute value of the enthalpy of combustion to determine the amount of combustion required to make the process adiabatic. Then the two resulting mass balances are summed to produce the results in Table 4.

Eq. (16) represents the overall process mass balance that, from a heat point of view, is feasible to convert coal and water into methanol. This result is obtained from the analysis considering both processes represented by Eqs. (11) and (12). The oxygen produced in the process represented by Eq. (11) is used to combust additional coal, which produces an identical process mass balance for the adiabatic result from Eq. (12). This is a powerful result showing that some rules of thumb (*e.g.*, oxygen is normally not a product) come naturally from the analysis, rather than through assumptions. In addition, one can see that the carbon efficiency of the coal to methanol process has decreased from 1 and 0.67 to 0.54, as compared to Eqs. (11) and (12), as more coal is combusted to provide the necessary energy, resulting in an increase in CO_2 production. Eq. (17) represents the methane and water to methanol and hydrogen process, where instead of combusting the hydrogen by-product, additional amounts of methane are combusted to provide the necessary energy. As a result, the carbon efficiency decreases, whereas the hydrogen efficiency remains unchanged. Eq. (18) represents a process very similar to that shown in Figure 4, but only the amount of hydrogen necessary to yield an adiabatic process is combusted. Therefore, both hydrogen and methanol are products and the overall mass balance is different than that given by Eq. (14). At this point, the methane plus oxygen to methanol [Eq. (14)] is still the most attractive process, as it has a carbon and hydrogen efficiency of unity and $\Delta H_{process} < 0$, meaning that there is excess heat produced, which may be used for other purposes.

A process produces excess work, requires additional work, or is reversible if $\Delta G_{process} < 0$, $\Delta G_{process} > 0$, or $\Delta G_{process} = 0$, respectively.

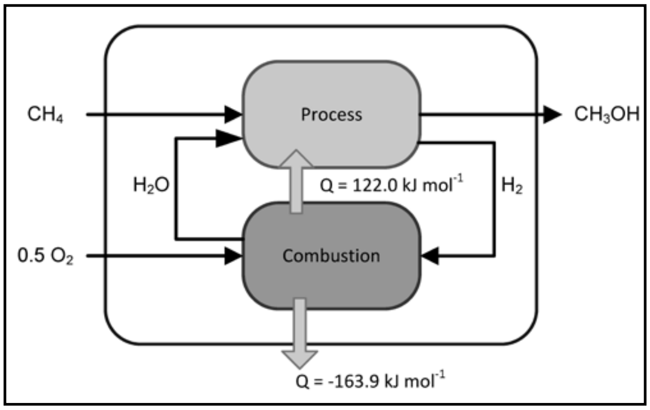

Figure 4. *Schematic representing the production of methanol from methane and water, burning the hydrogen by-product to provide the required additional energy. Resulting overall process mass balance is identical to the methane plus oxygen to methanol process.*

TABLE 4
Overall process mass balances, carbon efficiencies, and hydrogen efficiencies for heat neutral processes.

Overall Process Mass Balance	Eq. No.	$\Delta H_{process}$ (kJ/mol)	CE	HE
$1.85\ C_{(s)} + 0.35 O_{2(g)} + 2\ H_2O_{(g)} \Rightarrow CH_3OH_{(l)} + 0.85\ CO_{2(g)}$	16	0.0	0.54	1
$1.14\ CH_{4(g)} + 0.28\ O_{2(g)} + 0.73\ H_2O_{(l)} \Rightarrow CH_3OH_{(l)} + H_{2(g)} + 0.14\ CO_{2(g)}$	17	0.0	0.88	0.67
$CH_{4(g)} + 0.22\ O_{2(g)} + 0.57\ H_2O_{(l)} \Rightarrow CH_3OH_{(l)} + 0.57\ H_{2(g)}$	18	0.0	1	0.78

THE PROCESS WORK BALANCE

So far we have looked at the mass and heat balance as design tools, but we must also consider the process work balance. Since a process that requires heat is not feasible, a process that requires work will also not be feasible. To determine if a process is feasible from a work perspective, a difference in the Gibbs free energy of the products and reactants is used. The basic schematic used to calculate the work requirements for the process combining oxygen and methane to produce methanol is shown in Figure 5.

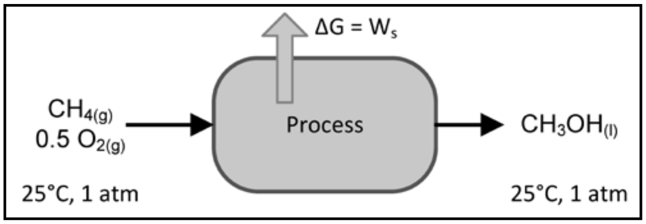

Figure 5. *Schematic representing the entropy/work balance over the process to produce methanol from methane, water, and oxygen at the adiabatic target.*

A process produces excess work, requires additional work, or is reversible if $\Delta G_{process} < 0$, $\Delta G_{process} > 0$, or $\Delta G_{process} = 0$, respectively. Using the values for Gibbs free energy given in Table 2, the value for $\Delta G_{process}$ for the process represented by Eq. (14) is $\Delta G_{process} = -116.2$ kJ/mol. Therefore, when 1 mole of methane is converted to 1 mole of methanol with 0.5 moles of oxygen, the conversion releases 116.2 kJ of work for use elsewhere. This is thus an attractive process from a mass (ideal elemental ratio), energy ($\Delta H_{process} < 0$), and work ($\Delta G_{process} < 0$) perspective.

What about the other processes shown in Table 4? $\Delta G_{process}$ of each of the process mass balances given in Table 3 and Table 4 is shown in Table 5.

One can see that all processes except those in Eq. (14) and Eq. (16) require additional work ($\Delta G_{process} > 0$). The process represented by Eq. (18) is shown schematically in Figure 6.

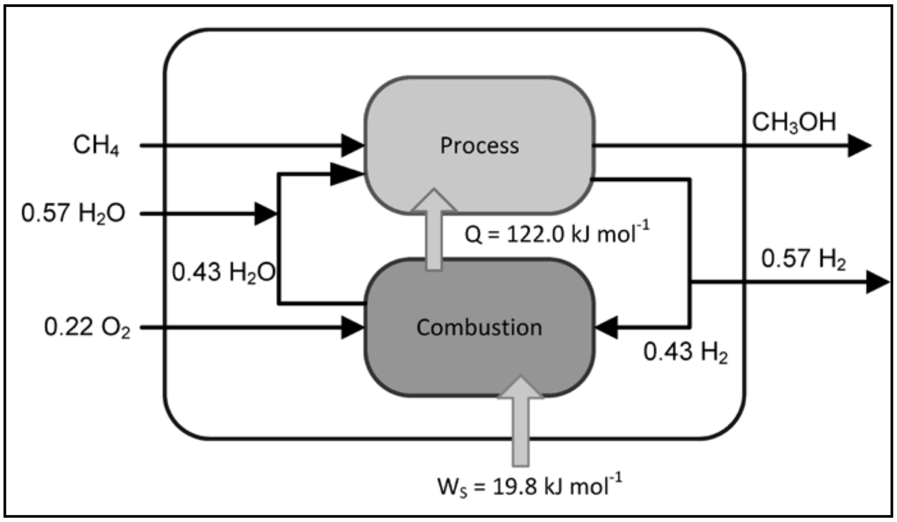

Figure 6. *Schematic representing methanol production from methane, water, and oxygen at the adiabatic limit, with the additional heat required produced by combusting additional hydrogen.*

The energy required for the process to proceed comes from combusting the hydrogen by-product in the presence of oxygen, with the water produced sent to the process to make methanol. This process is infeasible because the $W_S = 19.8$ kJ/mol of work must come from somewhere, usually from combustion, which will result in a different mass balance. For those processes represented by Eqs. (17) and (18), they are feasible from an energy or heat perspective, but not so from a work perspective. These processes are referred to as work limited, *i.e.*, $\Delta G_{process} > 0$ when $\Delta H_{process} = 0$. They will not proceed without the additional amount of work required, and this additional work comes from additional combustion.

The work target is a process with $\Delta G_{process} = 0$, or a reversible process. Therefore, additional combustion is performed to produce only the amount required by the overall process. The procedure for this is similar to that to determine the amount to combust to provide the required excess heat. Taking the process represented by Eq. (18), the amount of additional work

TABLE 5
Overall process mass balances and work requirements for methanol production processes.

Overall Process Mass Balance	Eq. No.	$\Delta G_{process}$ (kJ/mol)
$1C_{(s)}+2H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+0.5\ O_{2(g)}$	11	307.4
$1.5C_{(s)}+2H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+0.5CO_{2(g)}$	12	110.2
$CH_{4(g)}+H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+H_{2(g)}$	13	121.0
$CH_{4(g)}+0.5O_{2(g)} \Rightarrow CH_3OH_{(l)}$	14	-116.2
$1.85C_{(s)}+0.35O_{2(g)}+2H_2O_{(g)} \Rightarrow CH_3OH_{(l)}+0.85CO_{2(g)}$	16	-26.4
$1.14CH_{4(g)}+0.28O_{2(g)}+0.73H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+H_{2(g)}+0.14CO_{2(g)}$	17	8.9
$CH_{4(g)}+0.22O_{2(g)}+0.57H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+0.57H_{2(g)}$	18	19.8

required is 19.8 kJ. There is still some excess H_2 produced, so we can combust this as the fuel following Eq. (15). 19.8/237.1 = 0.08, so an additional 0.08 moles of hydrogen are combusted and the mass balances are integrated again to produce the process shown schematically in Figure 7.

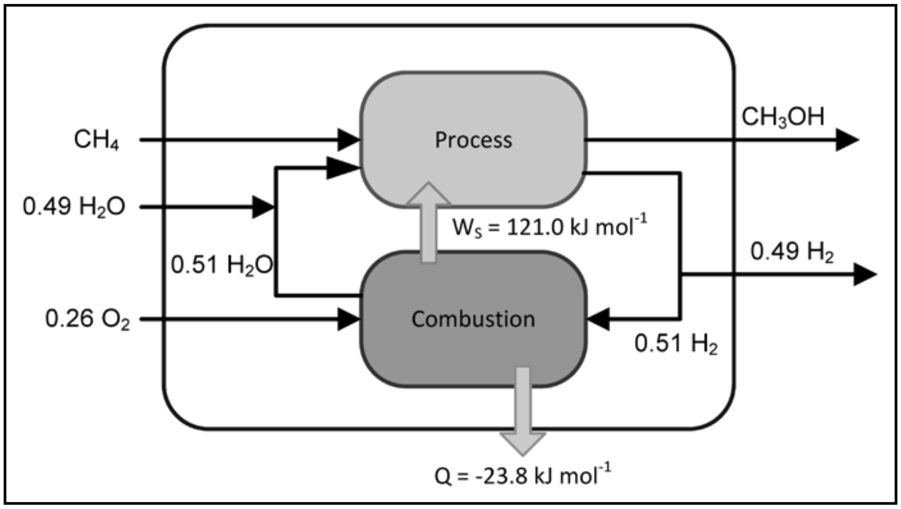

Figure 7. *Schematic representing methanol production from methane, water, and oxygen at the reversible limit, with the additional work required produced by combusting additional hydrogen.*

Notice now that there is an excess heat stream leaving the process (Q = –23.8 kJ/mol), but all of the work necessary to run the process is provided by the combustion of the hydrogen by-product. This excess heat can be used for other purposes or lost to the environment. In order for the process to operate, however, this is the minimum amount of heat to be released. Inputting additional work through additional combustion (of the hydrogen or another fuel) will result in additional heat produced.

TABLE 6
Heat and work specifications and carbon and hydrogen efficiencies for each of the reversible overall process mass balances.

Overall Process Mass Balance	Eq. No.	$\Delta H_{process}$ (kJ/mol)	$\Delta G_{process}$ (kJ/mol)	CE	HE
$1.78C_{(s)}+0.28O_{2(g)}+2H_2O_{(g)} \Rightarrow CH_3OH_{(l)}+0.78CO_{2(g)}$	19	26.3	0.0	0.56	1
$1.15CH_{4(g)}+0.30O_{2(g)}+0.70H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+H_{2(g)}+0.15CO_{2(g)}$	20	-9.7	0.0	0.87	0.67
$CH_{4(g)}+0.26O_{2(g)}+0.49H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+0.49H_{2(g)}$	21	-23.8	0.0	1	0.80

This procedure can be repeated for all processes represented in Table 4. For the process represented by Eq. (17), it assumed that the additional work comes from combustion of additional methane, rather than combustion of the hydrogen by-product. The results are shown in Table 6.

The processes represented by Eqs. (20) and (21) are work limited ($\Delta H_{process} \leq 0$ when $\Delta G_{process} = 0$) but the process represented by Eq. (19) is heat limited ($\Delta H_{process} > 0$ when $\Delta G_{process} = 0$). Therefore, for this process, it is necessary to meet the heat requirements of the process, whereby the process will produce excess work.

We can now look at all processes that are feasible and have some benefit, as shown in Table 7.

One can see that the process represented by Eq. (14) is still the most desirable process, as it has the highest carbon and hydrogen efficiency and produces both heat and work. The technology to perform this conversion does not exist, however, as combining oxygen with methane results in combustion of the methane and the production of CO_2 and H_2O (not CH_3OH and H_2). Therefore, if one were to develop a catalyst that could perform this conversion (in one or many steps) it could greatly increase the efficiency of methanol production. Regardless, the process synthesis approach has identified the process shown in Eq. (14) as the optimal process and further development to achieve such a conversion is warranted. Eq. (14) is now the process target, to which all other alternatives should be compared.

TABLE 7
Heat and work specifications and carbon and hydrogen efficiencies for each of the most attractive, feasible, overall process mass balances.

Overall Process Mass Balance	Eq. No.	$\Delta H_{process}$ (kJ/mol)	$\Delta G_{process}$ (kJ/mol)	CE	HE
$CH_{4(g)}+0.5O_{2(g)} \Rightarrow CH_3OH_{(l)}$	14	-163.9	-116.2	1	1
$1.85C_{(s)}+0.35O_{2(g)}+2H_2O_{(g)} \Rightarrow CH_3OH_{(l)}+0.85CO_{2(g)}$	16	0.0	-26.4	0.54	1
$1.15CH_{4(g)}+0.30O_{2(g)}+0.70H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+H_{2(g)}+0.15CO_{2(g)}$	20	-9.7	0.0	0.87	0.67
$CH_{4(g)}+0.26O_{2(g)}+0.49H_2O_{(l)} \Rightarrow CH_3OH_{(l)}+0.49H_{2(g)}$	21	-23.8	0.0	1	0.80

The process represented by Eq. (16) shows the best one can hope to do in converting coal to methanol. Particularly undesirable about this process is the fact that almost half of the carbon in the feed ends up as carbon dioxide. Such an analysis justifies the perception of coal as a "dirty" fuel. On the other hand, producing methanol from methane is a much more environmentally friendly pathway, in that one can either produce a small amount of CO_2 with an equal amount of useful by-product of hydrogen [Eq. (20)], or produce no CO_2 with a smaller amount of useful hydrogen by-product [Eq. (21)].

Industrially, the preferred path to methanol synthesis from methane is following Eq. (21), in a two-step process using syngas (a mixture of carbon monoxide and hydrogen) as an intermediate. Such industrial processes operate well below their theoretical target carbon efficiency, however, with actual carbon efficiency closer to 0.75 rather than 1.[27] As a result, the process mass balance shown in Eq. (21) can be used as a target to identify and eliminate sources of inefficiency in industrial methanol synthesis routes. At this point, one can return to the traditional approaches to teaching process design to incorporate reaction pathways, equipment size and cost, separation equipment, return on investment, etc. Therefore, the proposed framework fits naturally as a first step in the selection of potential design routes to achieve a goal, incorporating a broad range of engineering skills to develop the big picture first, and then enforcing the concepts through the steps included in the more detailed design.

STRUCTURE OF COURSE

These synthesis techniques are offered as part of a senior-level design course, taught over half a semester. Students are required to apply these tools to projects chosen from literature, working through the examples in class, where they are encouraged to develop their own process alternatives and discuss the merits of each with the class. Recent projects include the synthesis of ammonia and Fischer-Tropsch synthesis. Each project begins by following the targeting approach presented here for the initial design and then follows more traditional design approaches for process economics, life-cycle analyses, etc., as provided in such classic texts of Turton, et al.,[7] Douglas,[8] and Peters and Timmerhaus.[9] Some projects involve validating the resulting flow sheets using ASPEN®. A three-day course covering these techniques is also given to post-graduate students and members of industry. More recently, a full-day workshop was incorporated at the end of the course to test the students' grasp of the concepts. The task was to design a methanol synthesis plant, using the concepts presented here to identify the most promising route, followed by the inclusion of reactions and the selection of optimal operating conditions. This approach ensures that the fundamentals of engineering design are utilized (hand-calculations, assumptions, and evaluation of those assumptions) along with the new design approaches of teamwork and computer simulation.[28]

Student feedback on these techniques was very positive. The students filled out a questionnaire asking them to respond to the following statements about their experience in the course. The options given were 1 = strongly disagree, 2 = disagree, 3 = neutral, 4 = agree, and 5 = strongly agree. No control group was tested.

- *Q1: I learned a great deal in this course.*
- *Q2: I feel I had adequate thermodynamics background to understand the material in this class.*
- *Q3: This course taught me to evaluate process alternatives and understand the consequences of various choices.*
- *Q4: This course helped me understand that decisions made early on in the design process are often the most important decisions.*
- *Q5: This course gave me the tools to make early process decisions.*
- *Q6: From this course, I learned one should design the process to obtain the overall process mass balance one wants.*
- *Q7: I would recommend this course to another student.*

The results from the questionnaire are included in Table 8.

TABLE 8

Results from the questionnaire given to students to evaluaate the course.

			Q1	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**	**Q7**
Senior Design	Fall 2011	Average	4.1	3.1	4.3	4.3	3.9	4.1	4.4
59 students		Stdev	0.8	1.1	0.8	0.7	0.8	1.0	0.8
			Q1	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**	**Q7**
Post-graduate Short Course	Fall 2011	Average	4.3	4.1	4.4	4.7	4.4	4.5	4.6
24 students		Stdev	1.0	1.2	0.7	0.5	1.0	0.6	0.7
			Q1	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**	**Q7**
Overall		Average	4.2	3.4	4.3	4.4	4.0	4.2	4.4
		Stdev	0.8	1.2	0.8	0.7	0.9	0.9	0.7

Generally, the opinion of the course was favorable from both groups, with the strongest agreement in response to "decisions early on affect the overall process design" and in regards to recommending the course to other students. Across the board, the students claim their thermodynamics background was lacking. Generally, the negative comments from the students were focused around three main areas: the need for more detailed design aspects, assignments being too open-ended, and requests for more examples. In response to these comments the lecturers emphasized that the more detailed aspects of design were covered in the third-year design course, and this approach was meant to develop the "bigger picture." Along those lines, assignments were purposefully kept broad to resemble poorly constrained problems encountered in industry, which most likely led to the second batch of criticism. To address this point, the broader questions were broken down into smaller pieces, which were then solved in stages to keep the class moving towards the solution together. Finally, to incorporate more examples, recently published postgraduate research (<5 years) was worked into the lecture material, connecting the undergraduate students with real applications of the approach.

The authors believe this course should be presented shortly following the traditional thermodynamics courses as a way to utilize the concepts learned and discussed but not implemented to their fullest extent. Once these tools are used to decide on the most promising process path, then the students can dig deeper into the important design information related to sizing, economics, and safety. The approach is not suggested as a replacement for the traditional approach to teaching design and does not include all relevant aspects of a complete design, *e.g.*, economics, safety measures, life-cycle analysis. Rather, the approach should complement the traditional approach as a means to decide on preliminary process flow sheets for further development. This analysis is only a high-level starting point and much more work is required to develop a realistic flow sheet. With that in mind, more complex problems can be broken down into smaller pieces, focusing on the mass, energy, and work balances containing only the major components. From that point, the way forward depends on requirements/restrictions on the particular task at hand in order to choose the most attractive process arrangement.

CONCLUSION

A new design approach was introduced that presents a unique and systematic approach to the conceptual design of chemical processes. The approach focuses on the synthesis aspects of chemical engineering design and provides a comprehensive analysis of mass, energy, and work flows in a process. The approach allows students to develop a better understanding of developing processes that are efficient and environmentally friendly. The responses from students towards the course content and structure were very favorable.

The authors believe this course should be presented shortly following the traditional thermodynamics courses as a way to utilize the concepts learned and discussed but not implemented to their fullest extent.

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