

Systems Approach to Reducing Energy Usage and Carbon Dioxide Emissions

David Glasser, Diane Hildebrandt, Brendon Hausberger, and Bilal Patel

Centre of Material and Process Synthesis, Dept. of Chemical and Metallurgical Engineering,
University of the Witwatersrand, Johannesburg, South Africa

Benjamin J. Glasser

Dept. of Chemical and Biochemical Engineering, Rutgers University, Piscataway, NJ 08854

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Introduction

Some of the sunlight reaching earth is stored chemically (as carbonaceous material) by plants, and over the past billions of years some of this plant material has been converted by geological processes to coal and oil. These fossil fuels and the current carbonaceous biological materials represent energy reserves, and this energy is in the form of chemical potential.

Unlocking this chemical potential as best as we can means using and transforming energy efficiently. Hence, if we do not develop processes to effectively unlock this chemical potential, we produce more carbon dioxide for a given amount of product (whether it be fuel, electricity or chemicals). If we do not use this chemical potential when the transformations are taking place it is lost forever. Effectively utilizing this chemical potential and limiting carbon dioxide and other greenhouse gas emissions presents significant challenges and opportunities for chemical engineers. In this article we will discuss a systems approach to increasing process efficiency, reducing energy usage and limiting greenhouse gas emissions. Recent theoretical tools are discussed that allow one to look at the chemical plant as a whole, and, thus, identify more efficient ways to run chemical processes.

The available strategies for reduction in carbon footprints were discussed by Sheppard and Socolow.¹ They looked at carbon capture and sequestration but made the point that there were other issues that needed to be addressed. In particular, process efficiency and carbon dioxide emission reduction were mentioned, which are largely the domain of chemical engineering.

Careful design and operation of chemical plants can lead to reductions in waste generation, work consumption and carbon dioxide emissions. If the generation of pollutants can be minimized at the source one reduces the need for extra materials and extra equipment used in subsequent purification steps. In many cases, progress is hindered by a lack of a quantitative description of what is the highest efficiency, least amount of energy (heat and work), or lowest amount of carbon dioxide that can be achieved for a particular process. Without being able to answer such simple questions it is hard to make good decisions.²

A chemical plant is a complex system made up of many units each of which have their own operating conditions and constraints. Chemical engineering has traditionally looked at the plant as a collection of these units.^{3,4} The way these are put together into a flow sheet is usually via experienced designers who, since the advent of the computer, use simulation packages to try to optimize the operating conditions. There have been attempts to automate flow sheet design by defining superstructures that include many units with complex interconnections. Mathematical programming is then used to solve for the optimum flow sheet.^{5,6,7} These are very large and complex problems, and one is often not sure the program has converged to the best solution or that the original superstructure was rich enough. Thus, the question that often remains is, was there a better flow sheet? Is there one that can use less energy or work and emit less carbon dioxide? In order to be able to come up with an optimum flow sheet new tools are needed to be able to synthesize and compare different flow sheets. One may ask how this state of affairs came about and how are we to remedy it?

Another approach involves utilizing physical and thermodynamic principles to set targets prior to synthesizing a flow sheet. Pinch analysis in one of the most well known means

Correspondence concerning this article should be addressed to D. Glasser at David.Glasser@wits.ac.za

of setting targets.⁸ It is based primarily on the first law of thermodynamics. Initially pinch analysis was applied to the synthesis of heat exchanger networks for fixed processes (processes with an existing mass and energy balance). Based on the mass and energy balance, targets for the minimum energy consumption can be determined ahead of the detailed design of the heat exchanger network. In recent years, the use of pinch analysis has become much more extensive.⁹ It has been applied to utility targeting, low refrigeration system design, distillation column profiles, cogeneration systems and total site integration, emission targeting and batch process integration.^{10,11} Another important development was the synthesis of mass exchange networks (MEN).¹² The purpose of these mass exchange networks is to transfer certain species from a set of rich streams to a set of lean streams. Mass exchangers are units, which employ mass separating agents in a countercurrent fashion to effect a transfer of wastes from a waste stream to the mass separating agent (for example, absorbers, strippers, ion-exchange units). The MEN concept has been extended to solve a much broader range of problems, including pollution prevention and water and wastewater minimization.^{13,14}

How the individual units and subsections of a chemical plant and their operating conditions interact is not so well understood. If we are to try to identify these interactions and the consequences for improved operation of the plant, in particular energy and work utilization and carbon dioxide emissions, new tools that can look at the plant as a whole have to be developed. Instead of looking at the plant with a microscope and focus on optimizing equipment we need to use a telescope and focus on the chemical plant as a system. Thus, before deciding whether we can transform a plant that is say 60% carbon efficient to 65% efficient we should be able to answer the question, can we make it 100% carbon efficient or even 120% carbon efficient, i.e., actually consume carbon dioxide in the process. This article looks at some of these developments and how they can and should be used to increase process efficiency and thus reduce carbon dioxide emissions.^{15,16,17,18,19} In the first instance one would like to understand, for a process, what is the best that one is able to achieve (for instance, minimum energy or work flows or carbon dioxide emissions) for a particular chemical plant? We call this the target for the process. If we are in a position to calculate these targets we will be in a position to compare different flow sheets on a consistent basis.

We will illustrate what can be done via a case study. Let us assume we are to make methanol from methane and see how we may go about synthesizing such a process and see how the decisions we make either consciously or by default affect the carbon dioxide emissions. We choose this as a case study because it is fairly simple in principle, but rich enough to show many of the benefits of computing targets. Clearly if we are to calculate targets for a new process we want to do this with the minimum of information and not spend too long doing this. For an established process we would also like to be able to assess what has caused our carbon dioxide or other emissions to be higher than the target, and, thus, try to assess what actions, if any, we can take to reduce them.

Tools

The tools that can be used to evaluate a process are essentially four.^{17,20} These are as follows:

1. The process mass balance.
2. The process energy balance.
3. The process work balance. This is based on entropy and Gibbs energy.
4. The thermodynamics of the reactions in the system through the method of Solvay clusters.

The information needed to use these tools are the molecular masses, enthalpies and Gibbs energies of formation and the heat capacities of the substances involved. For most common substances these data is usually available in databases. Even though mass and energy balances are commonly used in designing chemical processes, the way they can be used to do process synthesis is somewhat different from the traditional approach. The question is not what is the mass balance for the plant? Rather we ask what we would like the mass balance to be. This will become clearer in the case study.

Although the first law of thermodynamics (or energy balance) can provide one with a target for the minimum energy requirement (in terms of heat and work), it has its limitations in that it does not allow one to differentiate between different forms of energy, and does not allow one to determine if the energy is being used efficiently. The use of the second law of thermodynamics, in conjunction with the first law is more useful for analyzing chemical processes. It has been successfully applied in analyzing and improving existing flow sheets.^{21,22,23,24} Unfortunately, its use in the synthesis and design of processes has not been extensive.

If we consider a chemical plant operating in an ambient environment where all the mass and energy flows are accounted for, we can consider this to be our universe. If the plant is to operate at all, the second law of thermodynamics insists that the entropy change must be greater than or equal to zero, where zero refers to a reversible process and is the limit of operation. This can be shown to be equivalent to the Gibbs energy for the process being less than or equal to the work added to the process.²⁵ If we add more work than is necessary and do not recover it we degrade this work and waste energy, and the usual consequence of this is we emit more carbon dioxide than is necessary. This is because in order to make up for this unutilized (lost) work, we needed to have burnt some fuel. Thus, the second law provides us with a feasible target, to try to achieve, in order to increase efficiency and reduce carbon dioxide emissions.

Now it is extremely unlikely that any particular process will initially be close to reversible. Furthermore, even reversible processes may need work to be added or removed from the process, and one will almost certainly also have to either add or remove heat from the process. It, therefore, makes sense to first ask if we can either supply or remove the required work with this heat. Remember that the work content or quality of the heat depends on its temperature, thus, in order to assess the work content of a stream we need to know its temperature. Or looking at this in reverse we may ask what must the temperature of the stream be in order to

Table 1. Process Mass, Enthalpies, Gibbs Energies and Carnot Temperatures for Processes 1 and 2

Process Mass Balance	$\Delta H_{\text{process}}$ (kJ/mol)	$\Delta G_{\text{process}}$ (kJ/mol)	T_{carnot} (K)
1. $\text{CH}_{4(\text{g})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{CH}_3\text{OH}_{(\text{l})} + \text{H}_{2(\text{g})}$	122.03	121.58	80811
2. $\text{CH}_{4(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})} \rightarrow \text{CH}_3\text{OH}_{(\text{l})}$	-163.81	-115.55	1012

match the heat and work requirements of the process, and, thus, without adding extra work, make it reversible. Putting in or removing heat at a temperature other than ambient is analogous to using a heat engine to supply or remove the work we require to run the system reversibly. This tells us that we can view a chemical plant as a heat engine.¹⁷

By looking at the overall process we may come up with a scheme where the reactions we propose are not thermodynamically feasible or do not give us the product we require in the correct proportions. The method of Solvay clusters can be used to solve this problem. This will also help us to decide and understand why certain processes cannot be done in a single step but must be broken down into multiple steps. This again involves the idea of a heat engine. This point should again become clearer from the case study.

The main reason for doing a case study is that it is easier to illustrate the ideas and the methodology than to stipulate a set of guidelines to use these methods.

Case Study

Let us suppose we have a natural gas feed that we will approximate as methane and we wish to make methanol from it. We suppose we will use as our source of oxygen either air or water. In the former case it is only the oxygen that enters the process mass balance although if we do not remove the nitrogen it will act as a diluent. The process mass balances are given in Table 1. There are other possible mass balances including linear combinations of the two in Table 1, but we will not consider them here as we assume we only have access to oxygen and water as feed materials. We note these are the mass balances for the entire process, and do not necessarily represent individual reactions occurring in the process.

Let us consider a simple process where both the feed to the process and the products from the process are at ambient conditions (both pressure and temperature). In this case our energy balance for the plant is

$$\Delta H_{\text{process}} = Q + W \quad (1)$$

where $\Delta H_{\text{process}}$ is the enthalpy change of the process from feed to products, Q is the actual heat added to the process, and W is the work added to the process.

The work balance (or G balance) becomes

$$\Delta G_{\text{process}} - W \leq 0 \quad (2)$$

where $\Delta G_{\text{process}}$ is the Gibbs energy change of the process from feed to products.

The first thing we note is that Process 1 (see Table 1) needs a lot of heat to be added to it as it is an endothermic process. In order to add this heat we might need to burn some of our methane. This would need to be taken into account in our overall mass balance as it would effectively be producing carbon dioxide. In order to perform a proper analysis of the plant it is imperative to take into account the carbon dioxide emissions of the utilities such as electricity, even if they are imported, and, therefore, do not at first sight appear to be an integral part of the plant. The point is that for instance the electricity would not have been made if we did not need it, and, therefore, its emissions are part of our responsibility.

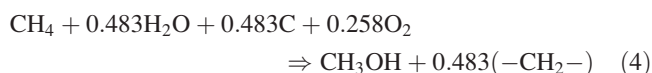
Furthermore as it stands Process 1 is also not a feasible mass balance for the plant as it has a $\Delta G_{\text{process}}$ with a positive value. One would need to add very large amounts of work to make it possible as it stands. Let us not discard Process 1 as we could envisage it to be part of a more complex process.

Because we have spare hydrogen in Process 1 we could envisage burning it to produce the energy we need



This supplies 285.84 kJ/mol of heat, which is more than enough for the energy requirements for the process as evidenced by the value of $\Delta H_{\text{process}}$ (see Table 1). Furthermore, this provides 237.13 kJ/mol of work as compared to the 121.58 kJ/mol required for Process 1. We further note that we now have water as the product of the process given by Eq. 3 and we need water as a feed for Process 1, thus, we can recycle the water and if we do this we get the process shown in Figure 1a. What we have done is to achieve the overall mass balance of Process 2 (see Table 1) without trying to oxidize the methane directly. This now has the mass balance of Process 2, and, thus, is overall exothermic and so no external heat needs to be added and it also has a feasible (negative) $\Delta G_{\text{process}}$. We do, however, note that Process 2 produces a lot of excess heat and work and we would like to be able to use these.

One can use linear programming¹⁸ to show that in principle one can produce a plant that makes hydrocarbons (represented as $-\text{CH}_2-$), as well as methanol in a plant that produces zero carbon dioxide emissions and is feasible ($\Delta G_{\text{process}} = 0$) and produces 38 kJ/(mol of methane feed) of exothermic heat. Such a plant is shown in Figure 1b, and the overall mass balance is given in Eq. 4



It is an exciting prospect to realize that by combining plants one can potentially make significant savings in carbon dioxide emissions. Of course how one designs such a plant in detail is not yet clear, but what this gives is a target against which to evaluate a more detailed design.

Getting back to our original processes we may ask the question, by adding heat at some temperature is it possible to match the heat and work requirements of the system. One can show that Eq. 5 can be derived for this situation¹⁷

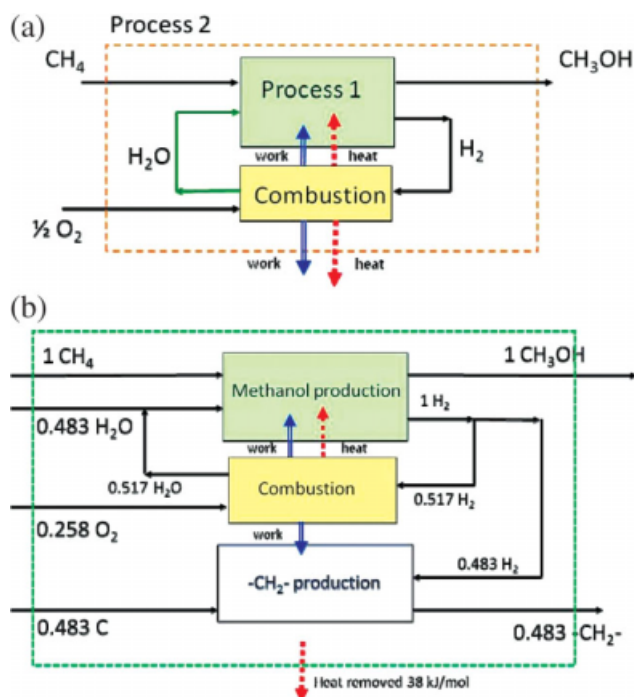


Figure 1. (a) A process not using direct oxidation of the methane to methanol that achieves the same overall mass balance, and (b) plant structure target for maximum feasible combined production of methanol and hydrocarbons with no carbon dioxide production, using process described in Figure 1a as a starting point.

$$\Delta G_{\text{process}}(T_0) + T_0 S_{\text{generated}} = \Delta G_{\text{process}}(T_0) \left(1 - \frac{T_0}{T}\right) \quad (5)$$

For a reversible process $S_{\text{generated}}$ is zero and so we have a relationship between $\Delta H_{\text{process}}$ and $\Delta G_{\text{process}}$ with our only free variable being T . The temperature at which this relationship holds is called the Carnot temperature. For Processes 1 and 2 the Carnot temperatures are shown in Table 1. Clearly the Carnot temperature for Process 1 is not feasible, while that for Process 2 is quite high but in principle possible.

What we have not done up to now is to evaluate the feasibility of the process in terms of the actual reactions that might take place. In order for a reaction to take place to a reasonable extent we would need the equilibrium to be favorable. Thus, we need the Gibbs energy of reaction, $\Delta G_R \leq \epsilon$ where ϵ is some small positive number. We can then use this fact to try to assess what reactions are thermodynamically possible. What the method of Solvay clusters does is break the reaction species up into collections of species that all satisfy the same atom balances and plot ΔG for each Solvay cluster vs. temperature for each of these clusters.²⁰ If these lines cross then we have a temperature range to one side where the reaction is possible and a temperature range to the other side where it is not. If they do not cross then one of the clusters is not thermodynamically favored to form from the other.

We can easily understand this by drawing the diagrams for the reactions for the two previous processes (see Figure 2). For Process 2 the results are shown in Figure 2b. The line labeled $\text{CH}_4 + \frac{1}{2}\text{O}_2$ represents the ΔG of these components as a function of temperature. Similarly the line labeled CH_3OH represents the value of ΔG for this component. Both $\text{CH}_4 + \frac{1}{2}\text{O}_2$ and CH_3OH are Solvay clusters as they contain all the same atoms as do all the other clusters ($\text{CO} + 2\text{H}_2$ and $\frac{3}{4}\text{CH}_4 + \frac{1}{4}(\text{CO}_2 + 2\text{H}_2\text{O})$) shown on the diagram. From the diagram it is clear that going from methane and oxygen to methanol has a negative ΔG_R as the curve for $\text{CH}_4 + \frac{1}{2}\text{O}_2$ is always above that for CH_3OH . There is, therefore, the possibility of making methanol directly from methane and oxygen, but a catalyst that can do this with high selectivity has not yet been found. An examination of the $\text{CH}_4 + \frac{1}{2}\text{O}_2$ and $\frac{3}{4}\text{CH}_4 + \frac{1}{4}(\text{CO}_2 + 2\text{H}_2\text{O})$ clusters on the diagram shows that if we start with methane and oxygen and allow some of the methane to go to carbon dioxide and water, this is even more favorable (than going directly to methanol), namely has an even lower ΔG_R . However, we can see that at a high enough temperature (above about 630°C —see point A on Figure 2b) the $\text{CO} + 2\text{H}_2$ cluster becomes favored over the $\frac{3}{4}\text{CH}_4 + \frac{1}{4}(\text{CO}_2 + 2\text{H}_2\text{O})$ cluster. If the $\text{CO} + 2\text{H}_2$ cluster is now taken to a low enough temperature (below about 140°C —see point B on Figure 2b), and using a catalyst that would not favor carbon dioxide and water production one can make methanol. This would be a two step process where we start with CH_4 and O_2 and

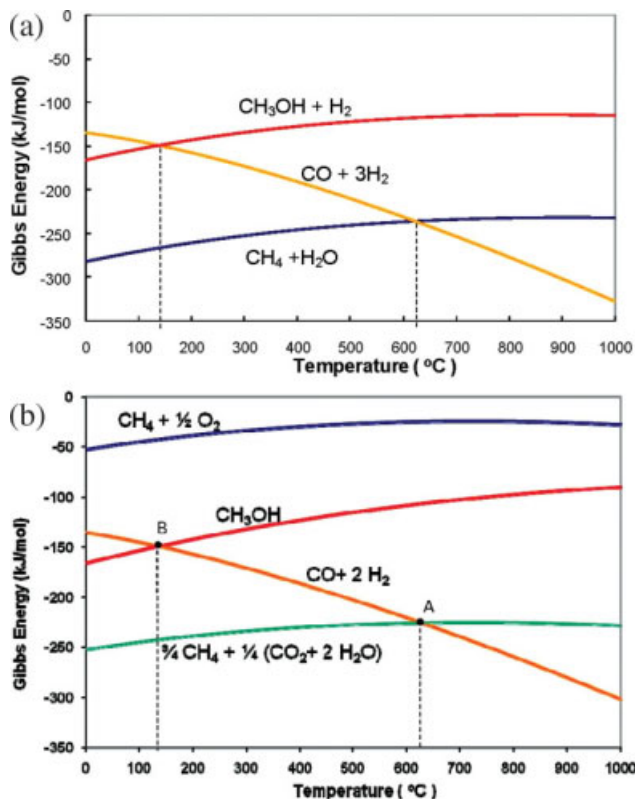


Figure 2. Plot of ΔG vs. temperature for the Solvay clusters associated with (a) Process 1, and (b) Process 2.

first produce CO and H₂ (syngas) at high-temperature, and then produce CH₃OH at low-temperature.

We can repeat the analysis for Process 1 and the results are shown in Figure 2a. Here it is not in principle possible to do the reaction in one step as ΔG_R is positive, but the two step process is very similar to that for Process 2. Here, the two-step process involves starting with CH₄ and H₂O and producing CO and H₂ at high-temperature and then producing CH₃OH and H₂ at low-temperature.

We may ask why is it that the two-step process in the latter case is now feasible. This is because if we examine it closely we see that we have a high-temperature endothermic process followed by a low-temperature exothermic process. We can deduce this from the slopes of the lines for the Solvay clusters as these slopes are given by the Gibbs-Helmholtz equation whose sign is determined by the enthalpy of reaction, ΔH_R . Putting in heat at a high-temperature, and removing it, a low-temperature is nothing more than happens in a heat engine. In this case, instead of the work being removed as shaft work it goes into supplying the work that the process needs to make it feasible. This work is not put in as shaft work and so does not appear directly in the G balance, however, the heats that supply this virtual work do appear in the energy balances. This idea of a chemical plant being viewed as heat engine is a very powerful one and will be explored further.

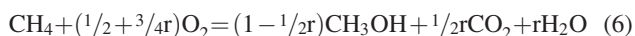
What we now have is a process that instead of having just a single temperature in which we add or take away heat has two such temperatures. In principle we could look at processes with three or more temperatures, but the more of these we have the more irreversibilities we are likely to have, and so we should probably stay with those with the smallest possible number.

Practical application

We can see that the ideas that have been used can lead to targets for a process. How do we use these? Clearly we would like to compare real or proposed processes with these targets, and then try to identify why these have not met the targets, and then use this information to improve the process.

Now for Process 1 as used in Figure 1a, we have shown the potential benefit of recycling the water. In fact there is no need to do this to achieve this objective as putting in fresh water and removing the same amount later achieves the same objective. The sting in the tail is actually in the words “the same amount”. In a complex plant with a complicated process it may not be that easy to identify all the water streams and check that we have “the same amount”.

Let us examine the consequences of not having “the same amount”. Suppose we remove more water than we have put in. This has an immediate consequence for the overall process mass balance in the following way. If we remove more water than we put in we are removing more oxygen and hydrogen. As carbon cannot build in the process we have to remove it and the only way this can be done is by removing carbon dioxide to give the following mass balance



We can see the unintended consequence of removing r molecules of extra water is that we have needed to add $3/4r$

of extra oxygen to the process; we make $1/2r$ less methanol and make $1/2r$ of unnecessary carbon dioxide. In a big and complex plant it may not be easy to see this without making a conscious effort to find this out. This not only affects the mass balance but it will affect the energy and work balances as well. The consequence of removing too much water is that we have effectively burnt some of our methane to water and carbon dioxide and turned a process that already was a net heat and work producer into one that was even more so and reduced the carbon efficiency from one to $(1 - 1/2r)$. If we want to improve the position we need to recycle both carbon dioxide and water. The problem is that they have to be in the proportions in Eq. 6. This may not be as easy as it seems, as one must remember that one has to include the amount burnt in the utilities in the analysis, and the carbon dioxide and the water for recycling may be recovered in different places. The consequences of not doing it correctly, however, will be more carbon dioxide than is necessary being emitted.

From this analysis we can see that in principle the methane to methanol process should not emit any carbon dioxide. In fact it should be a potential work and heat source. The fact that the literature gives a carbon efficiency of about 75%, and a thermal efficiency of 60% suggests there is large room for improvement.²⁶ By looking at the flow sheet without understanding the targets it would be very difficult to realize the need for these recycles.

In fact for the methane to methanol process, from a mass balance point of view, one could in principle use a feed of $3/4 \text{ CH}_4 + 1/4 (\text{CO}_2 + 2 \text{ H}_2\text{O})$, thus, using up carbon dioxide. In fact this could be a more efficient process overall as there is a significant loss in ΔG in starting from $\text{CH}_4 + 1/2 \text{ O}_2$. However, to complete the evaluation of this process we need to also focus on the value of $\Delta H_{\text{process}}$.

We note that for processes that do not work spontaneously, namely $\Delta G_{\text{process}} \geq 0$ we can in principle make them work via adding work as shown by Eq. 2. Thus, for instance a process that results in a decrease in the number of moles of gas, can have work added to it by running at a higher pressure. We can do a similar thing by running a recycle process in which we are effectively adding the work of separation.¹⁸

Conclusions

As discussed at the beginning, what we believe is needed is rather than examine the process through a microscope, it needs to be looked at through a telescope. What this means is one needs to adopt a systems approach. The consequence of this is one is able to calculate targets for the process; that is what is theoretically possible. By doing this it is possible to compare different processes or flow sheets or evaluate the process relative to what is done in practice. One is now in a position to see what has been done that leads to high emissions. This opens up opportunities to put the process together in such a way that emissions can be reduced, in particular carbon dioxide. It turns out that many of the savings are likely to come not from improving the individual pieces of equipment but improving their interaction.

Literature Cited

1. Sheppard MC, Socolow RH. Sustaining fossil fuel use in a carbon constrained world by rapid commercialization of carbon capture and sequestration. *AIChE J.* 2007; 53(12):3022–3028.
2. Shinnar R, Citro F. Up front, efficient technology evaluation: It's what's needed to prevent futile Investments. *Chem Eng Prog.* 2007;103(2):10–13.
3. Perry RH, Green DW. *Perry's Chemical Engineers' Handbook*. 7th ed. New York: McGraw-Hill; 1997.
4. McCabe W, Smith J, Harriot P. *Unit Operations of Chemical Engineering*. New York: McGraw-Hill; 2000.
5. Biegler LT, Grossmann IE, Westerberg AW. *Systematic Methods of Chemical Process Design*. NJ: Prentice Hall; 1997.
6. Flores-Tlacuahuac A, Biegler LT. Simultaneous mixed-integer dynamic optimisation for integrated design and control. *Comput Chem Eng.* 2007;31(5–6):588–600.
7. Caballero JA, Grossmann IE. An algorithm for the use of surrogate models in modular flowsheet optimization. *AIChE J.* 2008;54(10):2633–2650.
8. Linnhoff B, Hindmarsh E. The pinch design method for heat exchanger networks. *Chem Eng Sci.* 1983; 38(5):745–763.
9. Smith R. State of the art in process integration. *Appl Thermal Eng.* 2000;20(15–16):1337–1345.
10. Rossiter AP, Rutkowski MA, McMullan A S. Pinch technology identifies process improvements. *Hydrocarbon Proc.* 1991;70(1):3–66.
11. Linnhoff B. Use pinch analysis to knock down capital costs and emissions. *Chem Eng Prog.* 1994;90(8):33–57.
12. El-Halwagi MM, Manousiouthakis V. Synthesis of mass exchange networks. *AIChE J.* 1989;35(8):1233–1244.
13. El-Halwagi MM, Spriggs D. Solve design puzzles with mass integration. *Chem Eng Prog.* 1998;94(8):25–44.
14. Dunn RF, El-Halwagi MM. Process Integration technology review: background and applications in the chemical process industry. *J Chem Technol Biotechnol.* 2003; 78(9):1011–1021.
15. Shinnar R. Thermodynamic analysis in chemical reactor and process design. *Chem Eng Sci.* 1988;43(8):2303–2318.
16. Ishida, M. The role and limitations of endoreversible thermodynamics. *Energy.* 1999;24(12):1009–1014.
17. Patel B, Hildebrandt D, Glasser D, Hausberger B. Thermodynamics analysis of processes: implications of work integration. *Ind Eng Chem Res.* 2005;44(10):3529–3537.
18. Patel B. Fundamental targets for the synthesis and evaluation of chemical processes.. University of the Witwatersrand, Johannesburg, South Africa; 2007. PhD Thesis.
19. Hildebrandt D, Glasser D, Hausberger B, Patel B, Glasser BJ. Producing transportation fuels with less work. *Science.* 2009;323:1680–1681.
20. May D, Rudd DF. Development of Solvay clusters of chemical reactions. *Chem Eng Sci.* 1976;31(1):59–69.
21. Hinderink AP, Kerkhof FPJM, Lie ABK, de Swaan Arons J, Van der Kooi HJ. Exergy analysis with a flowsheet simulator -II. Application: Synthesis gas production from natural gas. *Chem Eng Sci.* 1996;51(20):4701–4715.
22. Cornelissen RL. Thermodynamics and Sustainable Development. University of Twente, The Netherlands; 1997. PhD Thesis.
23. Leites IL, Sama DA, Lior N. The theory and practice of energy saving in the chemical industry: some methods for reducing thermodynamic irreversibility in chemical technology processes. *Energy.* 2003;28(1):55–97.
24. Dincer I, Rosen MA. *Exergy: Energy, Environment and Sustainable Development*. Amsterdam: Elsevier; 2007.
25. De Nevers N, Seader JD. Lost Work: A measure of thermodynamic efficiency. *Energy.* 1980;5(8–9):757–769.
26. Cheng W-H, Kung HH. *Methanol Production and Use*. New York: Marcel Dekker; 1994.

