FUNDAMENTAL TARGETS FOR THE SYNTHESIS AND EVALUATION OF CHEMICAL PROCESSES

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DECLARATION

I declare that this thesis is my own, unaided work, unless otherwise stated. It is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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ABSTRACT

In order to ensure industrial sustainability, there is a significant need for conserving natural resources and eliminated the environmental impact associated with industrial processes. This thesis presents an approach to the synthesis and integration of chemical processes by incorporating the aspect of sustainability. 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. In quantifying these variables, the concept of mass and energy conservation has been extensively used. Mass and energy balances have traditionally been used in the *analysis* of individual units and flowsheets. They however can also be used for *synthesizing* 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 approach begins by setting performance targets for a chemical process based on mass, energy and entropy. These targets can be determined in the early stages of the design process based only on the input and output from the process. The targets are independent of the structure of the process i.e. no information regarding the individual units and the interconnections is required. Examples of targets include minimum consumption of raw materials, minimum production of by-products (for example, carbon dioxide) and minimum energy consumption. Both graphical and algebraic techniques are used to determine the targets.

The next step of the approach is to evaluate the targets and gain insight into how the targets can be achieved. Techniques for analyzing the mass, heat and work flows for each overall process target have been developed. The technique is used to determine the minimum heat and work required for a process, gives insight into the

work flows in a process and its allows opportunities for integration of work to be realized. The implications of work integration in terms of capital and operating costs are discussed.

The analysis is illustrated by considering various industrial processes. The synthesis of methanol and ammonia was found to require extra work addition, even after work integration was considered. Methods of putting in the extra work, such as compression, are discussed. The technique is able to predict the minimum pressure required for these processes. Conversely, current Gas-to-Liquid processes, is associated with work rejection. This implies that the process need not be run at high pressures from a work or thermodynamic perspective. Opportunities for reducing the amount of work rejected from the Gas-to-Liquid process are identified.

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INTRODUCTION

1.1   The Challenge: Sustainability

There are many challenges that face the process industries. One of the major challenges is the aspect of sustainability (Anastas, 2001; Barnicki and Siirola, 2004; Jenck et al., 2004; Grossmann, 2004)).

At present, the process industry is unsustainable (Korevaar, 2004). Sustainable industrial development has been defined as "the continuous innovation, improvement and the use of clean technologies to reduce pollution levels and consumption of resources" (OECD, 1998).

One of the ways of addressing the issue of sustainability is by designing efficient processes. Therefore, there is great need for advances in the way processes are designed. These approaches need to incorporate aspects, over and above economic aspects, such as efficient use of material resources, efficient use of energy as well as improved environmental performance.

- Efficient use of raw materials

    The process industry utilizes a large amount of the world's raw materials to produce products that satisfy human needs. At present, the industry is dependent mainly on non-renewable resources. The increase in demand for chemical products, especially in developing nations, and the rapidly increasing cost of oil and natural gas necessitates the efficient use of the world's resources. There is therefore a need for systematic strategies that conserve resources as well as reduce discharges from processes. Such strategies could include material recycle/reuse or material substitution, reaction alteration and process modification (El-Halwagi et al., 2003)

- Efficient use of energy

Energy is essential for all production processes, and these industries are usually one of the biggest users of energy. The demand and consumption of energy continues to rise annually. There is thus a need for the efficient use of energy and the employment of technologies that reduce the consumption of energy in the process industries.

- Improved environmental performance

    One of the most serious challenges facing the process industry is that of pollution. A disregard for the environment has resulted in increased local air, soil and water pollution as well as global effects such as ozone depletion, acid rain and climate change. The reduction of wastes and gaseous emissions (carbon dioxide, toxic emissions etc.) is imperative. Consequently, environmental performance should be a central consideration in the design of processes. Traditionally, end-of-pipe approaches have been employed for pollution treatment. Such approaches usually result in increased cost and do not increase the efficiency of material or energy usage (Van Berkel, 2000). Recently, approaches that reduce or eliminate the emissions at the source, such as green engineering, pollution prevention and waste minimization, have been proposed (Yang and Shi, 2000). These approaches are more cost effective and result in processes that are less of a burden on the environment (Allen and Shonnard, 2001). In this light, systematic design tools for assessing, improving and integrating the environmental performance of processes need to be developed (Allen and Shonnard, 2000).

1.2 The Contribution

The aim of this thesis is to address the issue of industrial sustainability by designing efficient processes from a mass, energy and environment perspective. In particular, we develop tools that can be applied in the *conceptual design phase*. These tools fall within the framework of *process synthesis and integration,* which provides a holistic approach to process design i.e. it considers "the big picture first, and the details later" (Srivinas, 1997). Process synthesis and integration has been recognized as a key approach to pollution prevention and sustainability (El-Halwagi, 1998; Kalitventzeff et al., 2001; Tsoka et al., 2004). We aim to develop 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. The

law of mass conservation (mass balance), the first law of thermodynamics (energy balance) as well as the second law of thermodynamics will be employed as the basis of the approach. The second law of thermodynamics (or exergy analysis) is another powerful tool that has been proposed to address sustainability (Cornelissen, 1997; Hinderink et al, 1999; Wall, 2002; Dincer and Rosen, 2004).

1.3 The Approach: Process Synthesis and Integration

Chemical processes are usually considered to consist of a number of "unit operations" connected together in order to transform raw materials into useful products. Traditionally, each unit operation in the process was designed and optimized individually. Unfortunately, even though each unit is optimized, the overall process may be far from optimal.

In recent years, more attention has been paid to the design of the overall process instead of individual units. In designing the overall process, the designer is faced with many challenges. The designer not only has to choose the various steps (reaction, separation, mixing etc) but also determine the best interconnection of these various steps i.e. the structure of the process. This activity of determining the structure of process is termed *Process Synthesis*.

It is clear that there exist an enormous number of arrangements. Douglas (1988) states that approximately 10^4 to 10^9 process alternatives can be generated for a typical chemical process. The examination of all these alternatives is not possible. 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 very poor process structure. 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 decisions taken in the early stage of the design process or the conceptual phase is of vital importance as the economics of the process is usually set at this stage. Biegler et al. (1997) estimates 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 (Meeuse, 2002). Therefore, it

is imperative that systematic and comprehensive conceptual design tools be developed.

Steady progress has been made over the last few decades in the development of systematic techniques for process synthesis and integration. Many of these tools have also been successfully applied in industry. The use of process synthesis tool in industry has led to cost savings ranging from 20 to 60 % (Harmsen, 2004). Nevertheless, advancement is still required. To quote Barnicki and Siirola (2004), "…the need for systematic process synthesis methods and tools has never been greater. There are many challenges. But we are excited and optimistic that continued progress will be made and that these challenges will be met."

1.4   Outline of Thesis

The thesis begins with a review of concepts and literature relating to the fields of process synthesis and integration in Chapter 2. Chapter 3 presents an overview of the thermodynamics concepts (mass, energy and entropy) that will be employed in this thesis. In particular, it will be shown how valuable these concepts are in synthesizing processes. Chapter 4 will show how to set targets for an overall process, based on mass, energy and entropy. Chapter 5 and 6 focuses on achieving the overall process targets. In these chapters, a specific target, processes with a positive change in the Gibbs energy, will be analysed further in terms of energy flows and work flows. Chapter 7 applies the approach developed to industrial processes (methanol, ammonia and hydrocarbons production) in order to determine any possible energy savings. Chapter 8 applies the concept to a distillation system, in particular, a distillation system with vapour recompression. Chapter 9 concludes the thesis.

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2
LITERATURE SURVEY

2.1 Introduction

In this chapter, we will briefly look at the design process. We will then focus on the role *process synthesis* plays in the design of chemical processes. We discuss the relevance and importance of process synthesis. A review of pertinent literature with regard to the main achievements in the field of process synthesis is then presented.

2.2 The design process

The design process begins with an idea (new product, new technology etc), which must then be translated into a process. In particular, the main objective of a chemical process is to convert a specific feed stream into specified products that are beneficial to society (Seider et al., 2003). The design of such a process is accomplish through a sequence of steps or activities, which vary in detail and complexity.

Siirola (1996) describes the different levels of detail or phases in the design of a chemical process:

    i.   Targeting phase: The first and lowest level of detail in the innovation process, where one determines feasibility

    ii.   Preliminary or Conceptual phase: A provisional and not too detailed solution is proposed

    iii.   Detailed or refined phase: A more detailed solution is produced based on the solution proposed in the conceptual phase and any additional information that has been acquired from the previous levels

    iv.   Final phase: The refined solution is further improved as more information becomes available

This thesis is mainly concerned with the first two levels of details: Targeting and Conceptual design.

Targeting allows one to identify a benchmark for the performance of a system before the actual design of the system is carried out (El-Halwagi, 2006). 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 (El-Halwagi, 2006). Thus, these targets reduce the dimensionality of the problem to a manageable size (El-Halwagi, 2006). 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.

As was mentioned previously, the decisions made in the *conceptual phase of the design* usually have a much greater impact on the economics of the process (Figure 1). Note also that very limited information is available in the conceptual design phase and that this phase has to happen quickly and is a relatively low-expense activity (Seuranan, 2006). In addition, the degrees of freedom available in the conceptual design phase are much greater (Figure 2.1) as compare to the other stages in the design process. It is therefore clear that although very little capital is available for the conceptual design phase, a majority of the investment cost is fixed during this phase (Korevaar, 2004).Thus, the techniques applied in this phase need to systematically provide a good solution of appropriate detail in as short a period as possible.
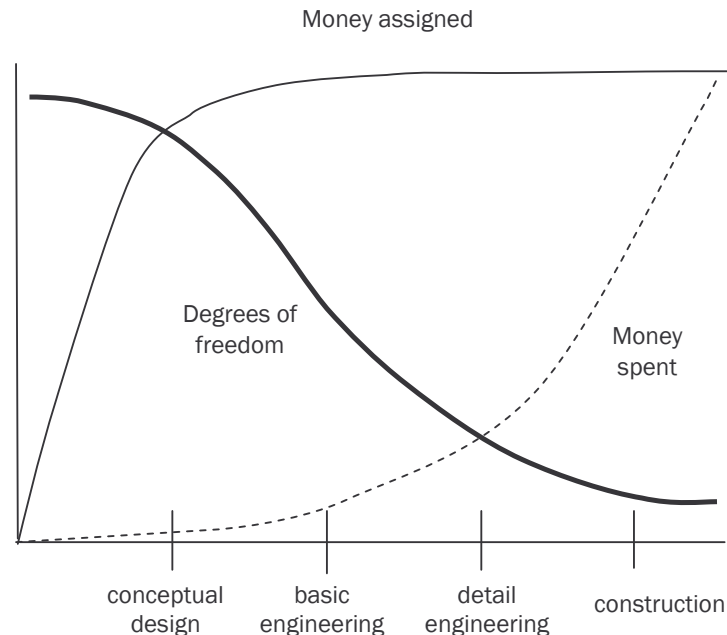
Figure 2.1: Financial characteristics as well as degrees of freedom of the various stages in the design (Adapted from Korevaar, 2004)

Figure 2.2 shows the various stages in the conceptual phase of the design process (Siirola, 1996; Biegler et al., 1997; Cano-Ruiz, 1998)

Abstract Design
Problem

Problem
Formulation

Synthesis

Analysis

Evaluation and
Optimization

Refined
Description
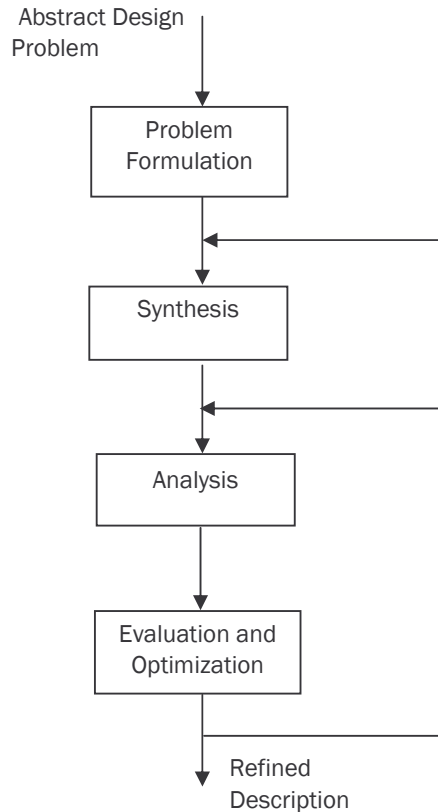
Figure 2.2: Stages in conceptual design

Initially one needs to define the problem. Design problems are usually underspecified, which requires the designer to make various assumptions and decisions (design objectives, constraints etc) such that the design is posed as a well-defined problem.

The next step in the design process is synthesis. In this stage, various alternatives for the design problem formulated are generated. It was mentioned previously that there are numerous possibilities that can be generated and it is often impossible to enumerate all these alternatives (usually due to time constraints). Many different approaches have been applied to develop processes. Traditionally, this involved adapted previously determined solutions for a similar process or brainstorming (El-

Halwagi, 2006). Although these methods have proved to be useful, they have serious limitations and usually never result in the optimum solution (El-Halwagi, 2006). This has prompted the need for systematic tool for synthesizing processes. *Process Synthesis* involves the development of the structure of chemical processes that satisfy the objectives set out for the process. This includes selecting the raw materials, identifying the various process tasks (reactions, separation, etc), determining the sequence of these tasks and establishing the interconnection between tasks, in simple terms determining the flowsheet for the process. Simply put, one is given the inputs and outputs of the process and one is required to determine the flowsheet for the process as shown in Figure 2.3. Note that process synthesis techniques can also be applied to retrofit existing plants as well.
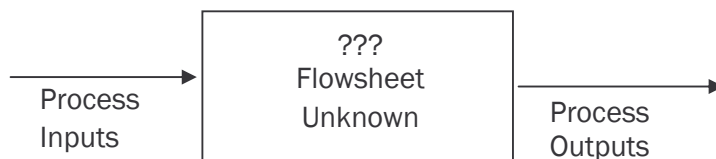
Figure 2.3: Schematic diagram representing process synthesis

A key aspect in the synthesis of processes is how well integrated the process is (Spriggs, 1994). This leads one to the important aspect of Process Integration. *Process Integration* refers to systematic approaches for the design and operation of integrated processes, in contrast to individual units, which aims to reduce energy usage and environmental effects (Gundersen, 2002).

The next step in the design process is analysis, where the alternatives generated are analyzed. Most of us are quite familiar with this stage of the design process. Analysis of processes usually involves performing fundamental engineering analysis, which includes mathematical models, correlations and computer-aided simulations (Aspen Plus, Hysys) of the alternatives. This allows useful information for the various streams in the process (such as flowrates, composition, temperature etc) to be determined as well as information regarding the various units in the process such as equipment size, energy consumption etc. Analysis also includes experimental predictions and validations. Thus, process analysis involves determining the outputs of the process given the inputs and the process structure or flowsheet, as shown in Figure 2.4 (El-Halwagi, 2006).
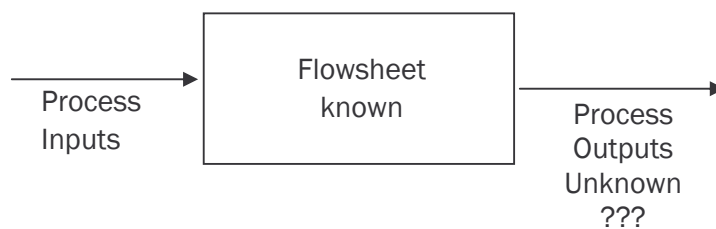
Figure 2.4: Schematic representation of process analysis

Once the various alternatives have been analyzed, each alternative is evaluated. This can be done based on the objective set out in the problem formulation stage. These objectives could be, for example, economic performance, safety or environmental performance and so on (Biegler et al., 1997). Thus, one can rank the various alternatives based on specific indicators. One can then optimize by adjusting or refining to improve the evaluation.

Note that the design process is iterative since there is a strong interaction between the synthesis, analysis and evaluation stages. Thus, the various steps may need to be repeated in order to improve the design.

2.3   Review of Process Synthesis

We will now look at the various methods of synthesizing and integrating a process i.e. generating and search among alternatives. In particular, we concentrate on systematic approaches developed over the past few decades. In the 1960's and early 1970's the *simulation* of chemical processes using computers were developed and became routine (Umeda, 1983). In contrast, the subject of *process synthesis* was largely ignored until the late 1960's when it was introduced by Rudd (1968). Early reviews on the field of process synthesis can be found in Hendry et al. (1973), Westerberg (1980), Nishida et al (1981), Umeda (1983) and Stephanopoulos and Townsend (1986).

Currently, process synthesis and integration approaches can be classified into three main categories (Grossmann, 1985; Hostrup et al, 2001): (a) hierarchical analysis, (b) physical (thermodynamic) insights and (c) mathematical programming. There is also a growing trend of combining these various categories, in order to make use of the advantages of each technique and overcome the disadvantages associated with

each technique (Mizsey and Fonyo, 1990; Daichendt and Grossmann, 1997; Hostrup et al, 2001).

Hierarchical analysis

Owing to the complexity of the design task, one approach suggested for synthesizing processes is to decompose the design decisions into several sub-problems, which are more manageable (Barnicki and Siirola, 2004). The decisions made during each sub-problem are usually based on intuition, engineering knowledge (heuristics) and short-cut calculations. One of the most common hierarchical approaches is the one originally presented by Douglas (1985, 1988). A flowsheet is systematically developed by following a series of hierarchical levels with increasing detail. At each level, heuristic rules are used to guide the search and limit the number of alternatives to be examined and these alternatives are evaluated in terms of their economics. Table 2.1 shows the decision levels used by Douglas (1988):

Table 2.1: Hierarchical procedure proposed by Douglas

Level 1: Input Information
Level 2: Input-Output structure of the flowsheet
Level 3: Recycle structure of the flowsheet
Level 4: Specification of the separation system
4a: general structure: phase splits
4b: vapor recovery system
4c: liquid recover system
4d: solid recovery system
Level 5: Energy integration

Initially the model proposed was based only on economic consideration, the procedure has subsequently been extended to identify and solve waste minimization problems (Douglas, 1992) as well as other objectives. A major limitation of this approach is its sequential nature, which means that the interactions between the various levels are not taken into account. Therefore, these approaches may not always lead to an optimal solution.

Another model that proposed by Linnhoff et al. (1982, 1983) is the "onion model" for process design. The diagram emphasizes the sequential nature of process design. The design begins with the reactor (the core of the onion), followed by the separation system. The two inner layers fix the material and energy balance. The next layer to be designed is the heat exchange network, followed by the utility system (heating and cooling) and finally water and effluent treatment (Figure 2.5).
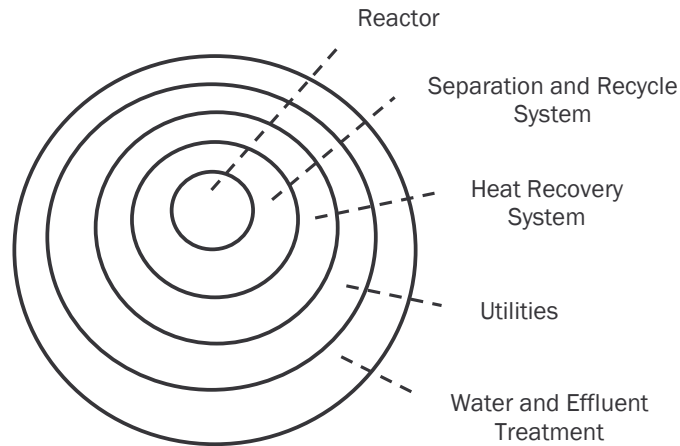
Figure 2.5: Onion model for conceptual process design

Each layer can then be synthesized by using heuristics, graphical or algebraic techniques or detailed process analysis tools. The use of detailed analysis could be time consuming and might not be systematic. As with the Douglas model, the interactions between the various layers may be overlooked.

Physical (Thermodynamic) Insights

This approach involves utilizing physical and thermodynamic principles to set targets prior to synthesizing a flowsheet. These targets can correspond to an upper or lower bound for the optimal flowsheet. These targets can also provide valuable insights for the improving existing flowsheets. By setting targets for the process a priori, one can reduce combinatorial nature of the problem especially in cases where the bounds are close to the optimal solution and hence reduce the search space for the best alternatives. Various means, such as, algebraic, graphical or mathematical optimization techniques, are then employed in order to attain the target or optimum flowsheet (El-Halwagi, 2006).

Pinch analysis in one of the most well known means of setting targets (Linnhoff et al., 1982). It is based primarily on the first law of thermodynamics. Initially pinch analysis was applied to the synthesis of heat exchanger networks (the third layer in the onion diagram) 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. Targets for minimum heat transfer area, minimum number of heat exchanger units or total annual cost have also been developed. These targets are based on the "composite curve" (or algebraically, using the "problem table") (Linnhoff, 1978), which is a temperature-enthalpy diagram, representing the cumulative heating (cold composite curve) and cooling requirements (hot composite curve) of the process (Smith, 2000). A representation of the composite curve is shown in Figure 2.6.
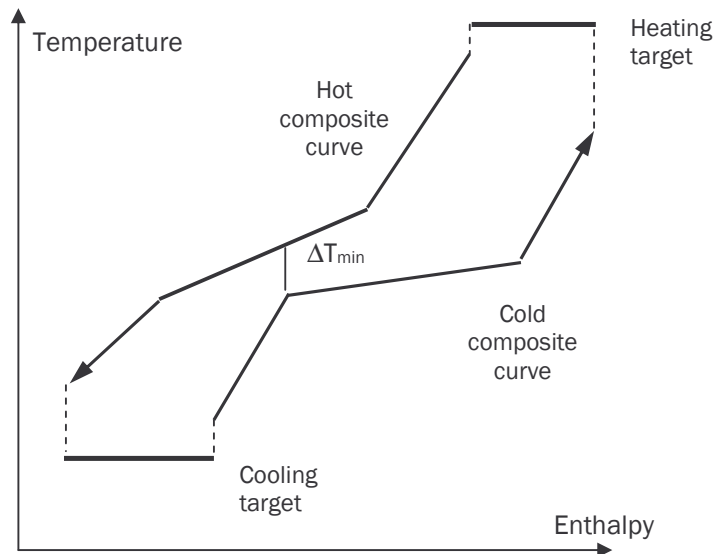
Figure 2.6: The composite curve for determining energy targets and the pinch point

Further extension of the analysis resulted in the Grand Composite Curve (GCC), which is a convenient method for setting multiple utility targets. The grand composite curve shows the overall net heat flow for the process by showing the variation of the heat supply and demand within the process.

Based on the composite curve or grand composite curve, one can attain a target for the heat recovery opportunities as well as targets for the minimum external heating and cooling utilities. The point where the minimum temperature difference, ΔT_{min} is noted is known as the "pinch" (Linnhoff; 1978; Umeda, 1979). The location of the pinch is very significant as it allows targets to be achieved by employing the Pinch Design Method (Linnhoff and Hinnmarsh, 1983). Essentially, this entails observing the following design rules in order to achieve the minimum energy target:

- Heat should not be transferred across the pinch
- No external cooling utility must be employed above the pinch
- No external heating utility must be employed below the pinch

A detailed review of the synthesis of heat exchanger networks is given by Gundersen and Naess (1990).

It is clear that pinch analysis has formed the basis for energy integration. In recent years, the use of pinch analysis has become much more extensive (Linnhoff, 1993; Smith, 2000). 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 (Rossiter et al, 1991; Linnhoff, 1994).

Another important development was the synthesis of mass exchange networks (MEN) (El-Halwagi and Manousiouthakis, 1989). The purpose of these mass exchange networks is to transfer certain species from a set of rich stream to a set of lean streams. Mass exchangers are units, which employ mass separating agents in a counter current fashion to effect a transfer of wastes from a waste stream to the mass separating agent (for example, absorbers, strippers, ion-exchange units). Again, targets are established before the configuration of the network has determined. In analogy to the pinch analysis, a composition pinch point can be located using mass transfer composite curves i.e. plot of cumulative exchanged mass of a specific component vs. composition. The MEN concept has been extended to solve a much broader range of problems (El-Halwagi and Spriggs, 1998; Dunn and El-Halwagi, 2003), including pollution prevention (Spriggs, 1994) and water and wastewater minimization problem (Wang and Smith, 1994; Dhole et al., 1996; Polley and Polley, 2000; Dunn et al, 2001; Hallale, 2002).

Other targeting approaches include residue curve maps for the synthesis of separation systems (Doherty and Malone, 2001) and the synthesis of reactor networks using the attainable regions theory (Glasser et al., 1987; Balakrishna and Biegler, 1992)

Another thermodynamic approach that has been employed is a second law analysis or exergy analysis. The second law analysis is useful for *analyzing* and *assessing* process units or entire flowsheets (Szargut et al., 1988). The use of exergy methods in *process synthesis* is far from developed (Kotas, 1986). The second law analysis (exergy) takes into account not only the quantity but the quality of energy as well, allows thermodynamic inefficiencies to be identified and thus opportunities for improvement ca be proposed. Recently, various tools based on the second law or exergy have been suggested for the analysis and optimization of processes (Wall, 2003). Most of these tools require the system structure to be fixed before the analysis can take place. Grassmann diagrams offer a pictorial representation of exergy and losses in a process (Kotas, 1995). Another graphical method that has been developed is the exergy utilization diagram (EUD) which can be used to improve the efficiency of chemical processes (Ishida and Kawamura, 1982; Ishida and Taprap, 1992). Methods that combine pinch and exergy have also been suggested (Umeda, 1979; Linnhoff and Dhole, 1992; Feng and Zhu, 1997). The use of the principle of equipartition of forces an irreversible thermodynamics has been applied to the design and optimization of processes (Sauar et al., 1996). The exergy load distribution method (Sorin and Brodyansky, 1992; Sorin et al., 2000) has been applied to the synthesis of processes by carrying out an exergy optimization of a superstructure. The exergetic life cycle analysis (ELCA), which combines exergy analysis and life cycle assessment (Cornelissen, 1997; Gong and Wall, 1997) is useful for improving processes from an environmental point of view. Thermoeconomics or exergoeconomics combined economic analysis and the exergy method (see Sciubba for a review, 2005).

Mathematical Programming

The mathematical programming approach to process synthesis and integration employs optimization techniques to determine the best configuration and operating conditions for the process. There are three major steps in this approach (Floudas, 1995):

Step 1: Representation of the alternatives: The alternatives can be represented in various levels of detail (Grossmann and Daicendt, 1996). One form of representation is a superstructure. A superstructure is a very detailed explicit or implicit representation of all processing units and interconnections of interest. Another form of representation is aggregate models, which are simplified by including design targets. Other frameworks for representing the alternatives include process graphs (Friedler et al, 1995) and state space representation (Bagajewicz and Manousiouthakis, 1992).

Step 2: Mathematical model: A model is developed which describes the performance of the process by including mass and energy balances as well as design equations of units and the interconnectivity. The constraints for the unit and their operating conditions are also included. The objective function is also specified, for example, cost minimization or maximizing profit etc. In certain cases i.e. mixed-integer linear program (MILP) or mixed integer non-linear program (MINLP) problems, discrete variable (0-1 values) are required to define the selection of a unit. If these variables are not required, the problem reduced to a nonlinear program (NLP) if the functions are nonlinear or linear program (LP) if the functions are linear. The mathematical model is usually of the following form (Grossmann et al., 2000):

$$\text{Min } Z = f(x, y)$$
$$st. \quad h(x, y) = 0$$
$$g(x, y) \le 0$$
$$x \in X, y \in \{0,1\}$$

where $f(x, y)$ is the objective function, $h(x, y)$ are the various equations describing the system, $g(x, y)$ are the constraints imposed on the system. The variable x is a continuous variable that describes the system (pressure, temperature, flow etc) and y is a discrete variable denoting the inclusion of a unit (0 – not included, 1- included).

Step 3: Obtain the optimal design: The optimal design is extracted from the various alternatives represented in step 1 by solving the mathematical model in step 2 using specific algorithms

An extensive review of optimization techniques applied to process systems engineering problems can be found in Biegler and Grossmann (2004).

The mathematical programming approach has mainly been applied to subsystem: heat–exchanger networks, separation systems, reactor networks and reactor-separator-recycle systems. A review of the use of optimization techniques for process synthesis problems can be found in Biegler et al. (1997), Grossmann et al (2000) as well as Gundersen, 2002.

The mathematical programming approach is useful as many options can be considered simultaneously, and since the entire process is automated, alternatives are generated quickly and effectively (Smith, 2005).

The mathematical programming approach has a few limitations (Smith, 2005; El-Halwagi, 2006):

- Since all the alternatives need to be enumerated, it might be possible that the optimal configuration may not have been included an therefore this approach will not be able to determine the optimal structure
- The mathematical formulation of the problem can be very large and non-linear. Therefore, the global optimum for such an optimization problem is not guaranteed.
- This approach does not provides insight into the process and the designers' input into the problem is usually not included

2.4   Concluding remarks

Much progress has been made in the field of process synthesis over the last few decades. The tools developed have made possible the development of not only economical processes, but also processes that take into account the environment as well as social aspects as well as multiple objectives. There is still a growing need to develop such tools, especially in the early stages of the design, which will aid in conserving resources (raw materials and energy) and will contribute to the sustainability of the chemical industry. Tools that provide physical insights are usually the most useful and by combining these insights with optimization techniques, one can develop powerful methods for synthesizing processes.

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3
THERMODYNAMICS FOR PROCESS SYNTHESIS

3.1 Introduction

This chapter provides an overview of the fundamental thermodynamic concepts that will be employed in this thesis. In particularly, we will show how these principles can be useful for setting targets for processes as well as for synthesizing processes with the objective of sustainability in mind.

3.2 Law of mass conservation

We begin by first introducing the law of mass conservation as it usually precedes any thermodynamic analysis. The law of mass conservation or mass (material) balance is a central concept in chemical engineering and is usually the first principle a chemical engineer is taught as an undergraduate. Simply stated, the law of mass conservation states that the mass flows entering and leaving a system must be equal at steady state. Mass balances are used in the design of new processes or the *analysi*s of existing processes. It can be applied to individual units, for example, a reactor or a distillation column but it can also be applied to an entire flowsheet.

3.2.1 Mass balance for synthesizing processes

Since chemical processes may involve reactions, recycles, bypasses or purges, the mass balances can become quite complex. To overcome this complexity, atomic species balances are usually employed since the mass balance simply reduces to *input = output*. The atomic species balance can be very useful from a synthesis perspective as well. It allows one to perform a mass balance without having to consider each individual unit or the recycle flows instead one can focus on the entire process. To illustrate these points, consider the following simple example:

Traditional Approach
Consider producing methanol from carbon monoxide and hydrogen as follows:

$$CO + 2H_2 \qquad CH_3OH \qquad\qquad\qquad [3.1]$$

The feed to the process consist of 500 kmol /day of carbon monoxide and 1000 kmol /day of hydrogen. A simplified flowsheet of the process is shown in Figure 3.1. It is assumed that the condenser/separator is a perfect separator i.e. all the unreacted material is recycled back to the reactor.

500 kmol/day CO
1000 kmol/day H_2

CH_3OH
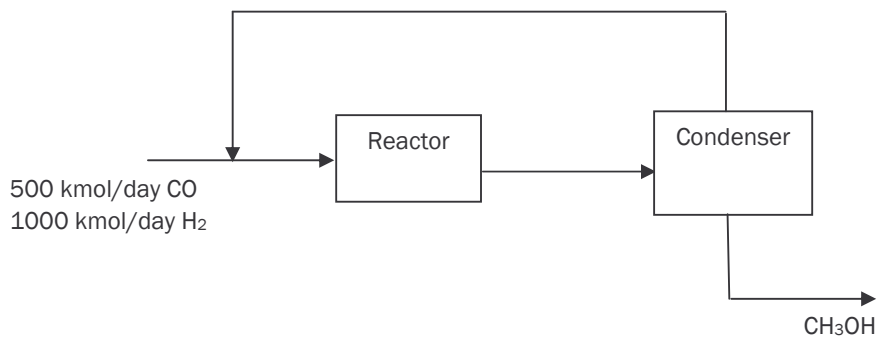
Figure 3.1: Simple flowsheet for the synthesis of methanol

By applying an atomic species balance, say for example a C (carbon) balance, one can determine that the amount of methanol produced will also be 500 kmol/day. One can check this by applying the oxygen (O) balance or hydrogen balance (H). We call this a *mass flow analysis*. If the conversion in the reactor is known, one can then determine the flows of all streams in the process i.e. reactor inlet, reactor outlet and recycle stream. This is an example of an *analysis* problem i.e. given the flowsheet and inlet conditions, one can determine the outlet conditions.

Synthesis approach
Consider now the *synthesis* problem. In this case, we are only interested in a *mass flow analysis*. Given the feed material CO and H_2, produce 500 kmol/day CH_3OH and determine the overall mass balance for the process.

The overall mass balance can be expressed as, assuming a production of 1 kmol of methanol:
a CO + b H_2 – 1 CH_3OH = 0   [3.2]

where a and b is the relevant amounts (in moles) of carbon monoxide and hydrogen required to produce 1 kmol of methanol.

The atomic species balance can be written as follows:

C balance: a = 1

O balance: a = 1

H balance: 2b = 4 or b = 2

Thus, the overall balance corresponds to

$$1CO + 2H_2 - 1CH_3OH = 0 \hspace{4cm} [3.3]$$

We now can scale up the mass balance to determine that a feed of 500 kmol/day CO and 1000 kmol/day H_2 will be required to produce 500 kmol/day CH_3OH. Notice that no information is required regarding the units in the process, such as the reactor or condenser, or the connection between the units.

It is clear from this simple example how the atomic species balance can be used for both analysis and synthesis. We will build on these principles further in Chapter 4.

3.2.2 Mass balance as a targets for a process

The mass balance can also be employed to set targets for a process. The mass balance represents the minimum amount of inputs required to produce a specified product. Also, the mass balance can also give insights into by-products or wastes that may be formed. The mass balance can also be a target for process integration (provides insight into recycling or reuse of materials) as will be shown in Chapter 4.

Consider another example, the synthesis of one kmol of methanol from methane and oxygen. The mass balance can be represented as follows:

$$aCH_4 + b\,O_2 - CH_3OH = 0 \hspace{4cm} [3.4]$$

By applying the atomic species balance, one can determine the minimum amount of methane and oxygen required.

C Balance: a = 1

H balance: 4a = 4 or a = 1

O balance: 2b = 1 or b = 0.5

Thus, the mass balance is given as follows:

$$1CH_4 + \tfrac{1}{2}\,O_2 - CH_3OH = 0 \hspace{4cm} [3.5]$$

In order to produce 1 kmol of methanol, a minimum of 1 kmol of methane and 0.5 kmol of oxygen is required. This is a *target* for the process since it represents the minimum quantities of the various components in the system.

If one, for example, fed excess oxygen (1 kmol instead of 0.5 kmol), the mass balance will need to change and *by-products or wastes will have to be formed*. In this particularly case, the by-product/waste that could be formed are water and carbon dioxide. The mass balance can be written as follows:

$$a\ CH_4 + 1\ O_2 + b\ CO_2 + c\ H_2O - 1\ CH_3OH = 0 \qquad [3.6]$$

The atomic species balance can be used to determine the values of a, b and c.

C balance: $a + b = 1$

H balance: $4a + 2c = 4$

O balance: $2 + 2b + c = 1$

Notice that a negative value for a, b or c would mean that the component occurs as a product since all components were initially specified as feed material. The resulting mass balance is given as follows:

$$1.25\ CH_4 + 1\ O_2 + 0.25\ CO_2 + 0.5\ H_2O - 1\ CH_3OH = 0 \qquad [3.7]$$

By adding more oxygen than required, more methane has to be added to the process and both carbon dioxide and water are produced.

The implications of by-products/waste formation are clear from the example given above. Thus, any process that puts in higher mass flows than the target values implies:

- The formation of waste/by-products which may not be desirable
- Results in the wastage of feed material, which implies more handling i.e. larger equipment and more separation steps. It also results in increased operating cost since more feed material required, additional energy will be required to process feed material and to effect separation steps.

The consequences of waste production are illustrated in Figure 3.2. Hence, we can see the importance of a target mass balance for the process
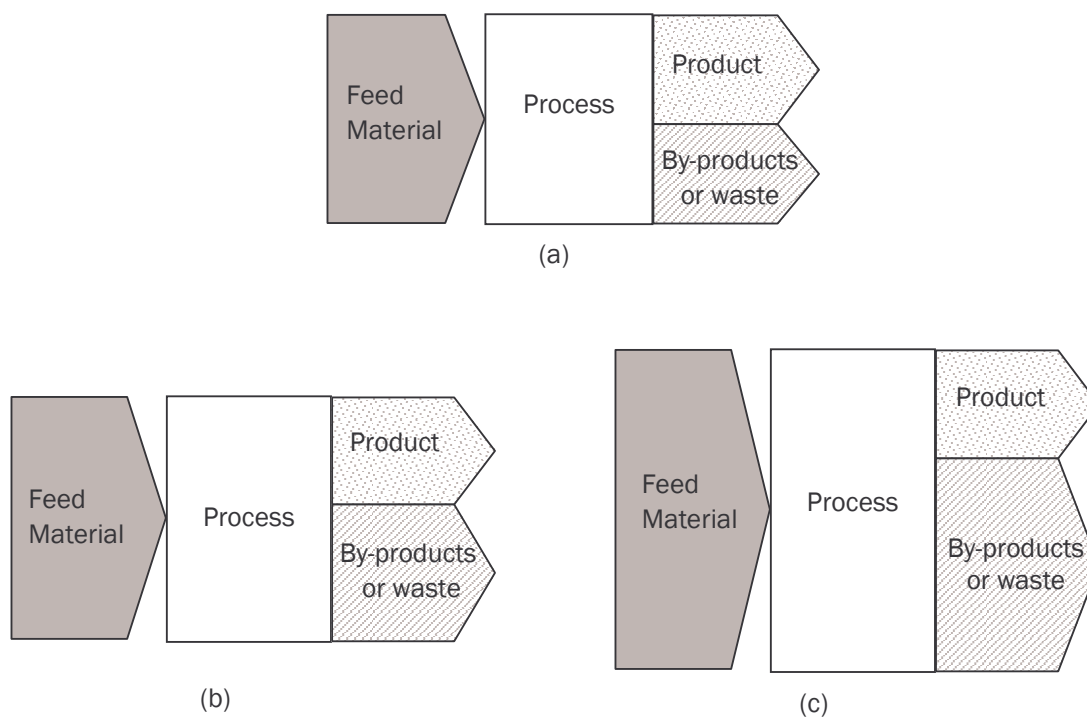
Figure 3.2: Implications of waste product formation (a) fairly selective process (b) low selectivity process (c) very low selectivity process

3.3 First law of thermodynamics (Law of energy conservation)

The first law of thermodynamics or the energy balance 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 first law (energy balance) is the most common method of assessing or analyzing the energy requirements and energy efficiency of processes. The energy balance can be applied to individual units as well as *entire processes*.

Consider a flow process at steady state as shown in Figure 3.3.
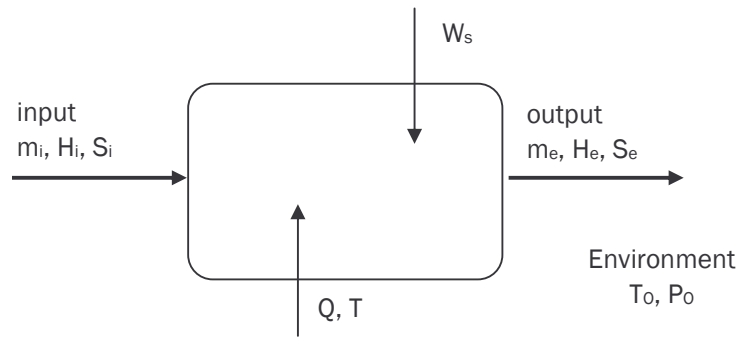
Figure 3.3: General flow process at steady state

The energy balance is given as follows:

$$\Delta H + \tfrac{1}{2}\Delta u^2 + g\Delta z = \sum Q + \sum W_s \qquad\qquad [3.8]$$

where

ΔH is the difference in enthalpy of the output and input streams ($\Delta H = m_e H_e - m_i H_i$)

Δu is the difference in the velocity of the output and input 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

Q refers to the heat flow in or out of the process, (a positive value would mean that heat is required whereas a negative value indicates that work has to be released from the process)

W_s refers to the shaft work entering or leaving the system

The energy balance can also be applied to a process without the details of the flowsheet or units into consideration. Thus, the energy balance gives an indication of the quantity of energy flowing in the process. It can also be used to obtain a target for the minimum amount of energy required or produced by the overall process.

3.4   Second law of thermodynamics

Although the first law 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 allows 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 flowsheets (Denbigh, 1956; Riekert, 1974; Gaggioli and Petit, 1977; De Nevers and Seader, 1980; Rosen, 1996; Hinderink et al, 1996).

Consider again the system (flow process at steady state) shown in Figure 3.3. The entropy balance for the system can be written as follows:

$$\Delta S = \sum \frac{Q}{T} + S_{gen} \qquad [3.9]$$

where

ΔS is the difference in entropy of the output and input streams ($\Delta S = m_e S_e - m_i S_i$)

Q refers to the heat flow in or out of the process, (a positive value would mean that heat is required whereas a negative value indicates that work has to be released from the process)

T is the temperature at which the heat is transferred to the system

S_{gen} refers to the entropy generated in the system (for a reversible process $S_{gen} = 0$, whereas for irreversible processes, $S_{gen} > 0$)

A combined first-second law statement can be obtained by multiplying the entropy balance (equation 3.9) by the environment temperature, T_0, subtracting it from the energy balance (equation 3.8) and rearranging. We will neglect the kinetic and potential terms in the energy balance.

$$\Delta H - T_O \Delta S = Q\left(1 - \frac{T_O}{T}\right) + W_S - T_O S_{gen} \qquad [3.10]$$

We define

$$\Delta B = \Delta H - T_O \Delta S \qquad [3.11]$$

where

ΔB is the difference in the availability function (B = H - T_0S) or exergy of the output and input streams. Availability or Exergy can be defined as the maximum amount of work that can be achieved from a system with respect to its environment. Note also that the availability function can also be related to the Gibbs free energy, G = H – TS when T =T_o.

$Q\left(1 - \frac{T_O}{T}\right)$ can be considered as the work equivalent of heat

$T_o S_{gen}$ is referred to as lost work or irreversibility and is equal to zero for reversible processes

The second law analysis or exergy analysis can also be very useful for the *synthesis* and design of chemical processes. Unfortunately, it use in the synthesis and design of processes has not been extensive. A limited number of direct applications of the second law to the design of chemical processes can be found in the literature (Sama, 1995; Linnhoff, 1981, 1983). Both authors provide only a qualitative approach of applying the second law to process design.

3.4.1 Second law as a target

The second law is also useful for setting targets for a process, even before the structure of the process is known:

- Exergy depend on only the initial and final conditions. One does not require any information regarding the structure of the process or any details of the process.
- Exergy provides a target in terms of reversible processes. It gives a measure of the thermodynamic perfection of the process as it determines the maximum amount of work that could be obtained (or minimum amount of work required)

3.4.2 Second Law and the environment

The second law analysis is an effective tool for addressing environmental issues:

- The second law analysis is linked to the environment, as it is a measure of the departure of the state of a system from that of the environment (Rosen and Dincer, 1997). It is therefore a useful tool for assessing and addressing the environmental impact of a system.
- Since the second law accounts for the quality of the energy, it can give an insight into the efficient usage of energy. It provides a more meaningful measure than the fist law or energy balance since the first law only measures the quantity of energy and states that energy is conserved (cannot be created or destroyed). The second law analysis, on the other hand, identifies imperfections and losses (irreversibilities) and gives clues regarding possible improvements to the process by comparing a process to the ideal. Thus, by increasing the energy efficiency one can reduce the environmental impact since the energy inputs are reduced and the quantity of waste are also reduced.

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4
SETTING TARGETS FOR THE OVERALL PROCESS[*]

4.1 Introduction

Two major steps in the design of chemical processes are process synthesis and process analysis. Synthesis involves determining the structure of the process knowing only the inputs and outputs from the process. Analysis entails determining the outputs given the inputs and the process structure, and is usually associated with modeling or simulating a given process (El-Halwagi, 2006).

The analysis of processes has been performed extensively. The tools used for analysis include mass balances (in order to quantify the flows of materials in and out of individual units and/or a process), energy balances (for quantifying the heat and/or work flows in the process). There also exists another tool, the entropy balance (or exergy analysis) which can be used to assess and improve chemical processes (Szargut, 1988). While these three tools have been used for *analysis* purposes, the combined use of these tools in the *synthesis* of processes has been limited.

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 quality of heat or equivalently work. In order to assess processes there is a need for these variables to be quantified. In this paper, a new approach for systematically synthesizing chemical processes using these three fundamental variables: mass, heat and work will be illustrated. The approach is intended for use in the very early stages of the design process i.e. during the conceptual phase, before the flowsheet exists. The approach aims to systematically:

- Provide global insights into the process,

- Set performance targets well before the flowsheet is designed,

- Identify opportunities to improve the process at a very early stage of the design.

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[*] This chapter has been submitted for publication to Industrial and Engineering Chemistry Research (2006)

It is necessary to have good understanding of the process at a very early stage as the decisions made in these stages impact the performance and cost of the process considerably.

The approach proposes to determine the overall mass balance for a process in the conceptual design phase based on various criteria (which will be discussed in the paper). This overall mass balance sets the energy as well as the "work" requirements for the process. Once this target mass balance has been chosen, the various tasks (i.e. reaction, separation, recycles etc.) can be used to achieve this target.

4.2   Setting Targets for a Process

A target can be defined as the limit of performance or the ultimate potential of the process and it is usually based on fundamental principles. It can be applied to grassroots designs as well as retrofitting applications. Targeting allows one to evaluate how close a process can get to its ultimate potential. Real processes (i.e. processes which are limited by current technology, equipment etc.) will perform much worse, when compared to the ideal limit, due to inefficiencies associated with these processes. These targets are usually determined without knowing the structure or flowsheet of the process. Since these targets look at the process as a whole and do not target individual units, insights into the system and opportunities with regard to the integration of process streams at the conceptual level of the design can be gained. The pinch design method is an example of a graphical technique proposed for targeting heat exchange networks (Linnhoff, 1983). This technique has been extended for targeting mass exchange (El-Halwagi, 1989) as well.

The approach presented in this paper allows targets to be determined for the entire process based only on the inputs and outputs. A case study of the synthesis of methanol from natural gas (assumed to be methane) will be used to demonstrate the approach. At this stage, the main idea is to determine the major factors affecting the process. Minor impurities or feed materials are initially ignored.

4.2.1 The Mass Balance Target

The mass balance is routinely applied in analysis and modeling of processes. However, its use as a tool in synthesizing processes has been somewhat overlooked. This paper will show how the mass balance can be used as a target when synthesizing a process. The mass balance is a powerful tool allowing one to determine the minimum amount of inputs needed to produce a specific product. It also establishes the minimum waste products from the process. The mass balance can also gives insights into the mass integration of various streams by considering a mass balance across the entire process i.e. considering the inputs and outputs of the process.

Consider the synthesis of methanol (CH_3OH). The possible inputs to the process are methane (CH_4), water (H_2O) and oxygen (O_2). It is assumed that the oxygen is freely available. This assumption can be relaxed by accounting for the work of separation required for separating air. Carbon dioxide (CO_2) should also be considered as a possible input or output from the process. Note that various other feed materials could be considered depending on the particular situation. These compounds were chosen in order to illustrate the approach. The *mass balance* for the *entire process*, assuming that one mole of methanol is produced, can be written as follows:

$$a\ CH_4 + b\ H_2O + c\ O_2 + d\ CO_2 - 1CH_3OH = 0 \qquad\qquad [4.1]$$

where a, b, c and d are amounts of methane, water, oxygen and carbon dioxide required (if the coefficient is positive) or produced (for a component with a negative coefficient) in the process in order to produce 1 mole methanol. The mass balance should also give one an insight into whether a component will be an input or an output. It need not be specified explicitly. A representation of the process is given in Figure 4.1.

Note that equation 4.1 is not the *reaction* that occurs but the *overall mass balance* for the process. The individual reaction(s) that occur in the process may be different from the overall mass balance.

CH$_4$: a moles

H$_2$O: b moles

O$_2$: c moles

CO$_2$: d moles

Chemical Process

CH$_3$OH: 1 mole
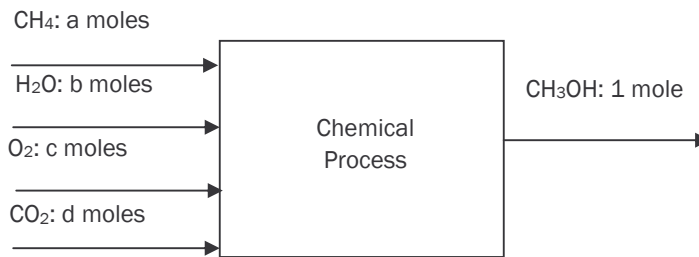
Figure 4.1: A schematic representation of a process for the synthesis of methanol

The process consists of three main atomic species: carbon, hydrogen and oxygen. A balance can be written for each species as follows:

$$\text{Carbon: } a + d = 1 \qquad [4.2i]$$

$$\text{Hydrogen: } 4a + 2b = 4 \qquad [4.2ii]$$

$$\text{Oxygen: } b + 2c + 2d = 1 \qquad [4.2iii]$$

There are four unknown variables and the mass balances (equation 4.2 (i), (ii), and (iii)) provide three equations. Therefore, there is only one degree of freedom in this specific example.

In order to visualize the various options, these mass balances can be plotted by varying the amount of methane fed to the process i.e. choosing values for variable *a* and determining variables *b*, *c*, and *d* using equations 4.2(i), 4.2(ii) and 4.2(iii). Figure 4.2 illustrates the amounts of the various components required/produced as a function of methane fed into the process. Each of the mass balances are *linear* equations and are therefore easy to plot.
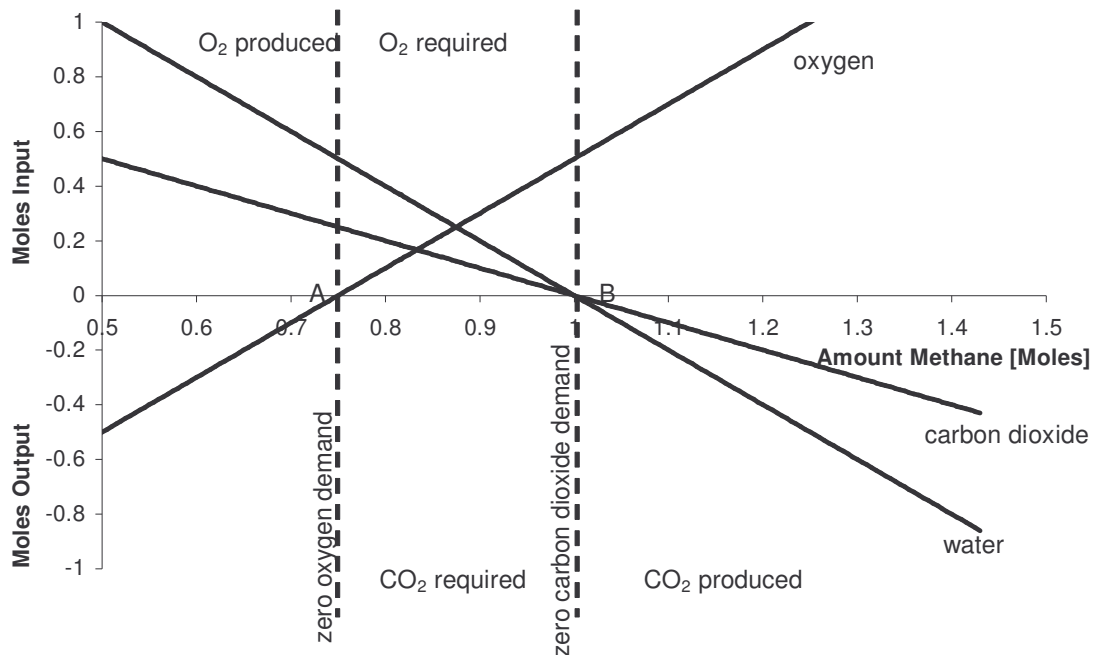
Figure 4.2: The molar amounts of each component required/produced as the amount of methane fed to the process that produces one mole of methanol is varied. (A negative value for a component corresponds to the component being an output while a positive coefficient for a coefficient corresponds to the component being an input)

Figure 4.2 allows one to determine the molar quantities of each component required or produced, in order to produce one mol of methanol, as a function of the methane fed to the process. Although Figure 4.2 appears simple, it has profound significance. Each set of values shown in Figure 4.2 correspond to an overall mass balance for a possible process that produces one mole of methanol. Hence, Figure 4.2 contains the mass balances for all possible methanol processes that use (or produce as the case may be) methane, oxygen, water and carbon dioxide. One can then scan all possible processes by considering all the possible mass balances that describe these processes and decide which ones correspond to sensible process or processes that are of interest. One can, for example, say that processes that produce O_2 are not feasible and thus one will only consider processes that are described by mass balances that lie to the right of point A. Point A represents the point when the amount of oxygen required or produced equals to zero. *Thus one could consider Point A to be a mass balance target for the process since it allows one to determine the minimum amount of methane required to achieve an oxygen neutral process.* One can also

then determine the amount of water and carbon dioxide required to achieve this target. The following mass balance (equation 4.3) can represent this target process:

$$0.75 \ CH_4 + 0.5 \ H_2O + 0.25 \ CO_2 \Rightarrow CH_3OH \qquad [4.3]$$
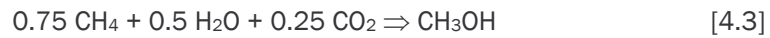
It is interesting that in this target process, carbon dioxide is utilized as a feedstock to the process. Thus, a minimum of 0.75 moles of methane per mole of methanol produced is required in order to satisfy the mass balance.

One could also, for example, consider a process that does not either consume or produce CO_2 such as occurs at point B in Figure 4.2. The target amount of methane for this CO_2 neutral process can be determined as well as the amount water and oxygen required. In this specific case, it turns out that the amount of water required/produced also equals to zero as can be seen in Figure 4.2. Equation 4.4 represents the mass balance at point B in Figure 4.2 for a CO_2 neutral process:

$$1 \ CH_4 + 0.5 \ O_2 \Rightarrow CH_3OH \qquad [4.4]$$

Processes described by mass balances given by Equations 4.3 and 4.4 represent in some sense the lower and upper limit for efficient processes from the mass balance perspective. Processes operating with less methane then that required by the process represented in Equation 4.3 (Point A in Figure 4.2) will emit oxygen, which is practically very unlikely. Processes operating with more methane then that required by the process given by Equation 4.4 (corresponding to Point B in Figure 4.2) will produce carbon dioxide as a waste product, which is undesirable from an environmental perspective.

The mass balance is therefore a very instructive tool for targeting the entire process. The mass balance provides a specific region in which one can focus the search for a suitable process. Although the mass balance tool is very useful, the mass aspects of the process cannot be isolated as energy aspects also need to be considered. The energy aspects can be accounted for using an energy balance which is discussed in section 4.2.2.

4.2.1.1 Identifying opportunities and targets for mass integration

Consider as an example a process that is described by the overall mass balance:

$$0.75 \ CH_4 + 1 \ H_2O + 0.25 \ CO_2 \Rightarrow CH_3OH + 0.5 \ H_2O$$

Thus compared to the process described by the overall mass balance given in equation 4.2, this process takes in an extra 0.5 moles of water as a feed or input and therefore has to reject 0.5 moles of water as an output or by product. This process would be represented on Figure 4.2 by a point corresponding to the water input which lies above the water mass balance line in Figure 4.2. In the simple example given above one can readily identify this opportunity and see that if the 0.5 moles of water produced as an output is returned to the process, the net water input to the process is reduced to 0.5 moles. Thus the lines given in Figure 4.2 are in themselves targets for process operating with a given feed quantity of methane and this target is the *target for Mass Integration* of such a process.

4.2.2 Energy Balance Target

The energy balance is useful in providing one with information regarding the quantity of energy required or produced by the process. By performing an *energy balance over the entire process*, one can determine the energy flows into and out of the process.

Consider the process depicted in Figure 4.1. Assume initially that the inputs enter and outputs leave the process as pure components at temperature T^o (298.15 K) and pressure P^o (1 atm). Each overall mass balance (and hence process) considered (in section 4.2.1.) and described by the mass balance lines in Figure 4.2 will have a corresponding energy balance.

The energy aspects can be considered in terms of the enthalpy change of the process, ΔH to produce 1 mole of methanol. The enthalpy change, ΔH, can be calculated as follows for a steady state process:

$$\Delta H = H^o_{f,CH_3OH} - a H^o_{f,CH_4} - b H^o_{f,H_2O} - c H^o_{f,O_2} - a H^o_{f,CO_2} \qquad [4.5]$$

where $H^o_{f,i}$ is the enthalpy of formation the i th component. Under the assumption that the inputs and outputs are at ambient conditions, the enthalpy of the

components corresponds to the standard enthalpy of formation of each component. The kinetic and potential energy terms are neglected from the energy balance. It is also assumed that water enters the process as a liquid and methanol leaves the process as a liquid. All other components are in the gas phase.

The enthalpy change for a process as a function of the amount of methane fed to the process is given in Figure 4.3.
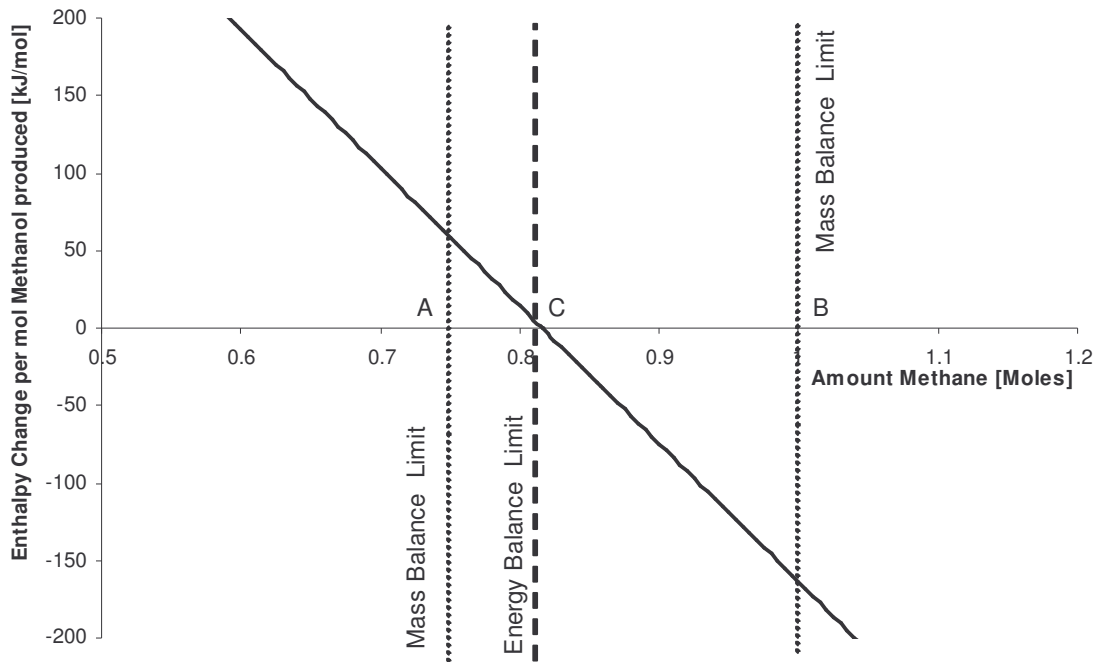
Figure 4.3: The enthalpy change of the process as a function of the amount of methane (in terms of moles) fed to the process which produces 1 mole of methanol. (A negative value corresponds to an overall "exothermic" process and thus heat is released from the process while a positive value corresponds to an overall "endothermic" process and heat must be supplied to the process)

It is clear from Figure 4.3 that there is a linear relationship between the enthalpy change and the amount of methane fed to the process, as was the case with the mass balance relationships.

Figure 4.3 presents information regarding the energy requirements for the overall process and the minimum amount of heat required/produced for each process

represented by the associated mass balance. Energy must be removed from the process (or the process is overall exothermic) when the enthalpy change for the process is negative.

Energy however must be added or supplied to the process (if the process is overall endothermic) when the enthalpy change for the process is positive. Thus, the process is not feasible unless this energy is added. One might next ask how this energy might be added to the process. Typically, this energy could be supplied by the combustion of a further amount of methane in the process described by the mass balance given by equation 4.6, which would result in the production of heat as well as carbon dioxide.

$$CH_4 + 2\ O_2 \Rightarrow CO_2 + 2\ H_2O\ \text{(liquid)} \qquad\qquad [4.6]$$

The enthalpy change for equation 6 can be calculated to be -890.36 kJ/mol. Thus, the quantity of extra methane needed can be calculated so as to make the overall process adiabatic. For example, the process described by equation 4.3 and corresponding to point A on Figures 4.2 and 4.3, is endothermic and the minimum amount of energy required by the process is 58.74 kJ/mol. Hence, the amount of methane that must be combusted in order to supply this heat can be calculated and the minimum amount of methane required, assuming perfect heat transfer, is 0.066 moles. That would mean an extra 0.066 moles of CO_2 and 0.132 moles H_2O is produced. The new overall adiabatic process is shown in Figure 4.4.
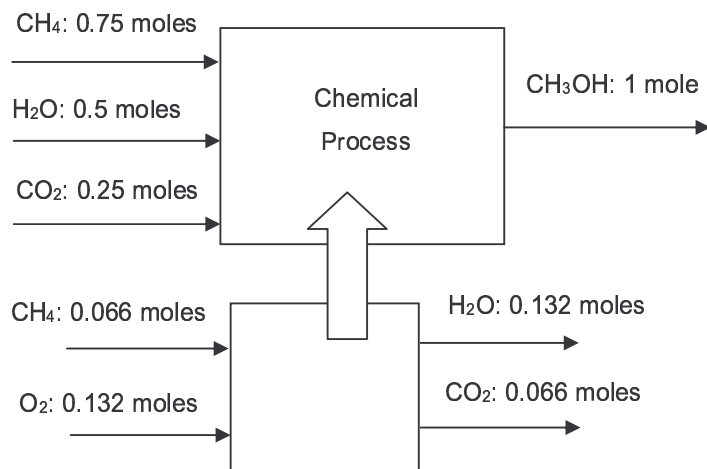
Figure 4.4: Supplying the energy required for an energy deficit process by burning extra methane

The mass balance that describes this overall adiabatic process as given in Figure 4.4 is given in equation 4.7:

$$0.816 \; CH_4 + 0.5 \; H_2O \; (liquid) + 0.132 \; O_2 + 0.25 \; CO_2 \Rightarrow CH_3OH \; (liquid) + 0.132 \; H_2O$$
$$(liquid) \quad + 0.066 \; CO_2 \hspace{6cm} [4.7]$$
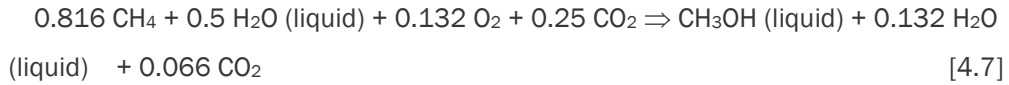
Consider once again the process illustrated in Figure 4.4 or described by equation (4.7). It is clear that opportunities for mass integration exist. If the H_2O and CO_2 produced from burning the methane (to supply the energy) were recycled or introduced to the original process as shown in Figure 4.5, the H_2O and CO_2 inputs will be reduced. We can see that the target for a mass integrated process will be:

$$0.816 \; CH_4 + 0.368 \; H_2O \; (liquid) + 0.132 \; O_2 + 0.184 \; CO_2 \Rightarrow CH_3OH \hspace{1cm} [4.8]$$

Furthermore the mass integrated process is adiabatic. This process is represented by Point C on Figure 4.3 and is the Energy Balance Target for the process.
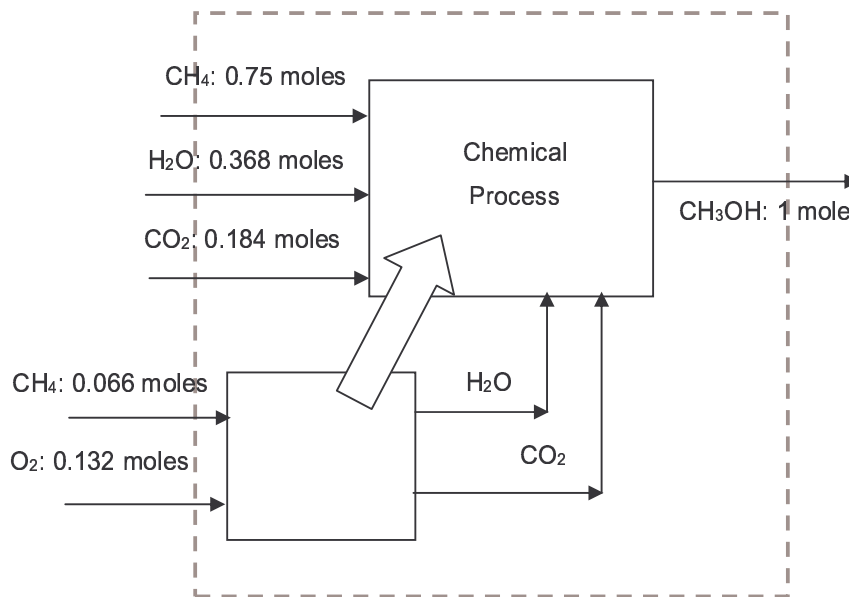
Figure 4.5: Heat and Mass integration of processes effectively changes the overall mass balance

It is apparent from Figure 4.3 that point C would define the minimum methane consumption for a methanol process and that the target for the methanol process is limited by the energy balance target rather than the mass balance target.

It is clear that the mass and energy balances are interlinked. These balances also give one insight into mass and energy integration, which allows one to change the overall process in order to reach a target. Note also that the target that was set by the energy balance is independent of the structure of the process. The target can be reached by different flowsheets if one considers mass and energy integration opportunities.

To illustrate the interpretation of Figure 4.3 consider a process that was described by the mass balance target (Point A in Figure 4.2). The energy requirements for the process can be determined and as a result, the process target is moved to point C on Figure 4.3. Thus, the new process target becomes the Energy Balance Target. However, with this in mind, one could have looked directly at Figure 4.3 and seen where the energy balance line intersected the x-axis (i.e. found point C). If point C lay to the left of the Mass Balance Target, then the process target would have been the Mass Balance Target and a process operating at this limit would have been exothermic. If as in the present case the energy balance line intersected the x-axis to the right of the Mass Balance Target, then the Energy Balance Target sets the process target. One can also see by comparing the Energy Balance Target to the CO_2 target (Point B) that the process that is overall adiabatic will consume CO_2. Thus for a real process which is emitting CO_2, one can immediately recognize that it is not operating near its target and that the CO_2 emissions could be reduced to at least zero if not to a level where the process consumes CO_2. Furthermore, one could also deduce from Figure 4.3 that the real process would also be emitting energy, i.e. be overall exothermic. By reducing the CO_2 emissions one would reduce the amount of energy that the process would reject to the surroundings. Reducing the CO_2 emissions of the process to zero would still mean that the process is overall exothermic. It is also possible to deduce from Figure 4.3 that one could continue to improve plant performance until the overall process was adiabatic and that this was the overall target for the process when considering the Mass and Energy Balance targets. A third target needs to be considered before one can decide on the ultimate target for the process. This third target will be introduced in section 4.2.3.

Thus although these diagrams are extremely easy to construct, their interpretation is surprisingly complex and gives deep insights into the process limits. To reiterate it is possible to scan all possible processes and select those that are mass and energy integrated. One is also able to identify how far away a process is from being mass or energy integrated and how much worse the process is operating compared to the best of all possible processes.

4.2.3   Identifying opportunities and targets for heat integration

The line in Figure 4.3 represents the energy integration target for a methanol process and hence provides one with information regarding the minimum energy input or output for the process. A process that is overall exothermic might need to reject overall a minimum quantity of heat Q according to Figure 4.3, for example. If the process is designed such that a quantity q of heat enters the process at some point, the process therefore must reject a quantity (Q + q) of heat. If δq of this rejected heat could be integrated into the process, this would reduce the amount of heat to be supplied by external sources to (q - δq) and hence reduce the amount of heat to be rejected from the process to (Q + q - δq). The limit of heat integration for the process would be such the energy rejected from the process was Q. Thus, the line in Figure 4.3 corresponds to the energy integration targets for processes and furthermore describes how this target changes with methane consumption.

4.3   Targets based on the Entropy Balance

The second law of thermodynamics states the total entropy change of a process is always positive and that only a reversible process achieves the limiting value of zero (Smith et al, 2001). The second law is also useful for targeting processes as it provides a limit to performance i.e. reversible processes. The second law (or exergy analysis) gives a limit to the amount of work required or produced by a process.

It can be shown that the maximum theoretical work produced (or minimum work required) for a process is related to the change in Gibbs Free Energy of the process, assuming again the inputs and outputs of the process are pure components at standard conditions (Denbigh, 1956; De Nevers and Seader, 1980).

The Gibbs energy change for a process can be calculated as follows:

$$\Delta G = G^o_{f,CH_3OH} - a\,G^o_{f,CH_4} - b\,G^o_{f,H_2O} - c\,G^o_{f,O_2} - a\,G^o_{f,CO_2} \qquad [4.9]$$

where $G^o_{f,\,i}$ is the Gibbs energy of formation of the i th component. Under the assumption that the inputs and outputs are at ambient conditions, the Gibbs energy of the components corresponds to the standard Gibbs energy of formation of each component.

The Gibbs energy change for a methanol synthesis process can thus be calculated and plotted (Figure 4.6) as a function of the methane fed to the process.
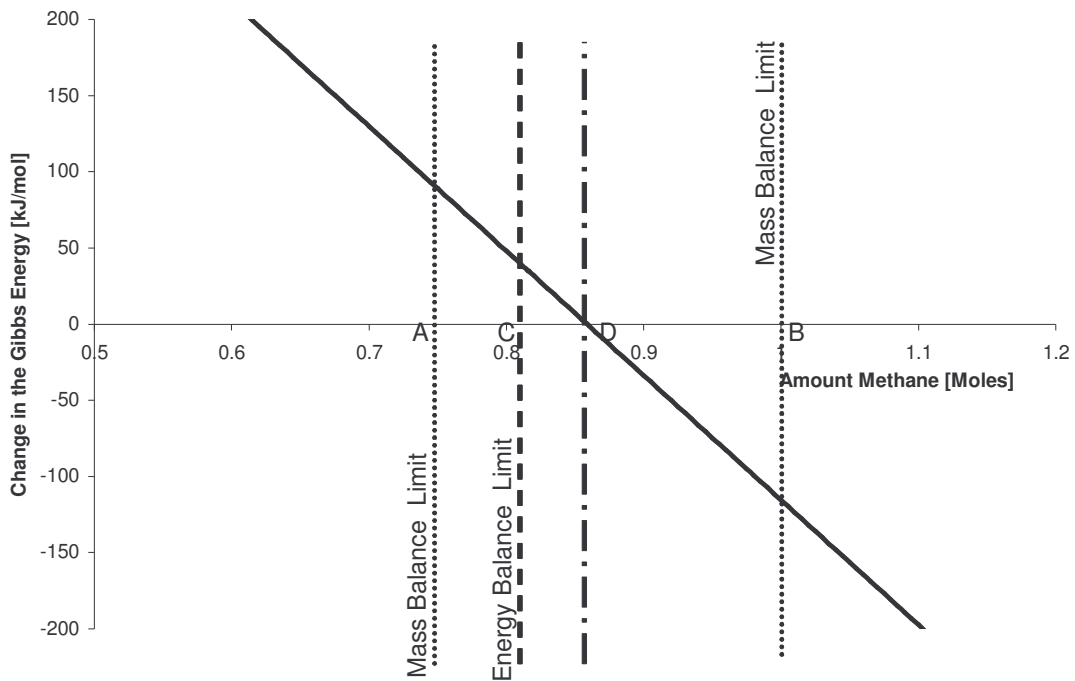
Figure 4.6: The Gibbs energy change for the methanol synthesis process as a function of the methane fed to the process. (A negative change in Gibbs Energy would correspond to a work consuming process whereas a positive change in Gibbs energy would mean a process would produce work)

Figure 4.6 gives insights into the maximum work produced or minimum work required by the process. Work is produced when the Gibbs energy is negative while work is consumed when the Gibbs energy is positive. It is clear that the relationship between the Gibbs energy change and the amount methane fed to the process is also linear. There is also a point D when the Gibbs energy change for the process becomes zero i.e. no net work input or output. Processes that lie to the left of point D in Figure 4.6

correspond to infeasible processes or process that would require work to be added to them. Processes the right of point D corresponds to feasible processes that would reject work to the surroundings, for example via high-pressure steam, or else be irreversible. Processes operating at point D would correspond to a reversible process that overall does not consume or emit work. In cases where it is not the purpose of the process to produce work, this should be the target for the process. Thus, Point D corresponds to the Work or Entropy Balance Target for the process.

The mass balance for a process operating at the Work Balance Target is given by equation 4.10.

$$0.859 \ CH_4 + 0.283 \ H_2O \ (liquid) + 0.217 \ O_2 + 0.141 \ CO_2 \Rightarrow CH_3OH \ (liquid) \qquad [4.10]$$

Consider once again the process given by Equation 4.3. The process described by the overall mass balance in Equation 4.3 has an energy and work deficit. To supply the energy, one can burn an extra amount of methane, as given by Equation 4.6. The process given by Equation 4.6 also has a negative change in Gibbs energy (- 817.9 kJ/mol) and can therefore supply work to the process described by Equation 4.3. In this case, the amount of methane to be combusted is determined by the work requirements of the process and hence the process that is work neutral will be overall exothermic. The heat that is emitted would need to be at ambient temperatures in order not to carry any work potential out with it. This is depicted in Figure 4.7.
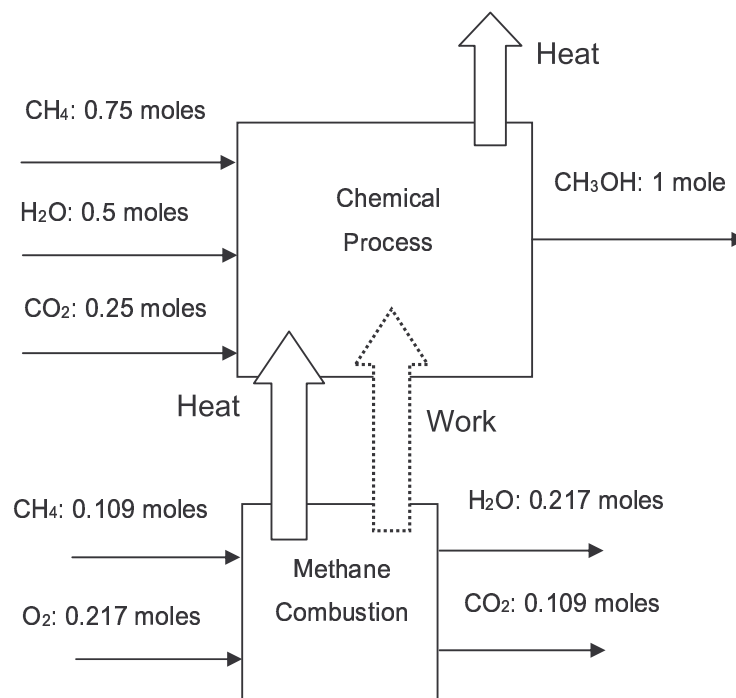
Figure 4.7: Supplying the work and heat to a process by burning an extra amount of methane

Figure 4.7 reveals opportunities for integration (mass, heat and work) within the process. By allowing integration, one can reach the required Work Balance Target (no work input or output) as given by the mass balance in equation 4.10. This is shown in Figure 4.8. Patel et al (2005) explains the concept of work integration in detail (the concept will be discussed in chapters 5 and 6).
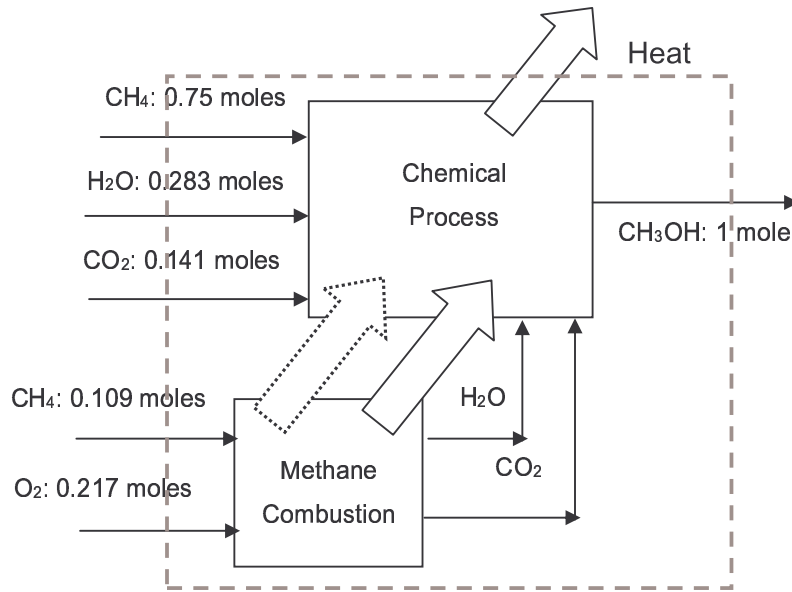
Figure 4.8: Mass, heat and work integration to reach the desired target of no work input or output

Note that the energy balance limit lies to the left of the limit set by the Gibbs energy. This means that although the process (Equation 4.8) does not require or produce energy, it will require a work input. As a result, carbon dioxide will have to be emitted in order to put in this work and therefore Equation 4.10 gives the new and ultimate process target.

4.4   A second example

4.4.1   Synthesis of methanol and hydrogen

In section 4.2, a simple example was used to illustrate the concept of overall process targeting. In this section, a slightly more complex example is considered. The

synthesis of methanol is still considered but another component i.e. hydrogen is added to the system thus allowing for an extra degree of freedom.

Consider the following processes to produce one mole of methanol:

$$aCH_4 + bH_2O + cO_2 + dCO_2 + eH_2 \Rightarrow CH_3OH \qquad [4.11]$$
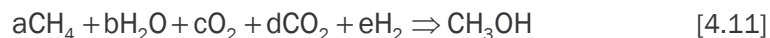
where a, b, c, d, and e are the relevant amounts of each component required or produced. In this example, there are five unknown variables.

Firstly, the *mass balance* can be performed. There are three atomic species in the system: Carbon, Hydrogen and Oxygen, therefore three balances can be written as with the previous example. There are therefore two degrees of freedom in this case. Thus, if the mass balance were to be plotted it will result in a three-dimensional plot with the amounts of each component representing a surface rather then a line (as was the case with the previous example).

Since the interpretation of these surfaces can be complicated, instead of plotting the entire surface one can simply plot the specific case when the amount of each component equals to zero. The problem can therefore be reduced to a two-dimensional problem that is much easier to interpret. The zero lines can provide a great deal of information without one actually having to determine the entire surface.

Consider the zero mass balance lines for the process given by Equation 4.11. These lines are plotted as a function of the amount of methane as well as the amount of oxygen fed to the process, since there are two degrees of freedom in the system. These variables were chosen as they are most likely to be feed material and are unlikely to be found in the product.

Figure 4.9 illustrates the zero lines for hydrogen and water as a function of the methane and oxygen fed to the process (to produce one mole of methanol). Above the zero water line, the amount of water has a negative value, signifying that water occurs as a product. Above the zero hydrogen line, the amount of hydrogen has a positive value and thus hydrogen occurs as a feed. Since the carbon dioxide varies only with methane and is not a function of oxygen, its mass balance line lies on the methane axis as shown in Figure 4.9. Carbon dioxide will be a product when the

amount of methane exceeds one mole and a feed when the amount of feed is below one mole.
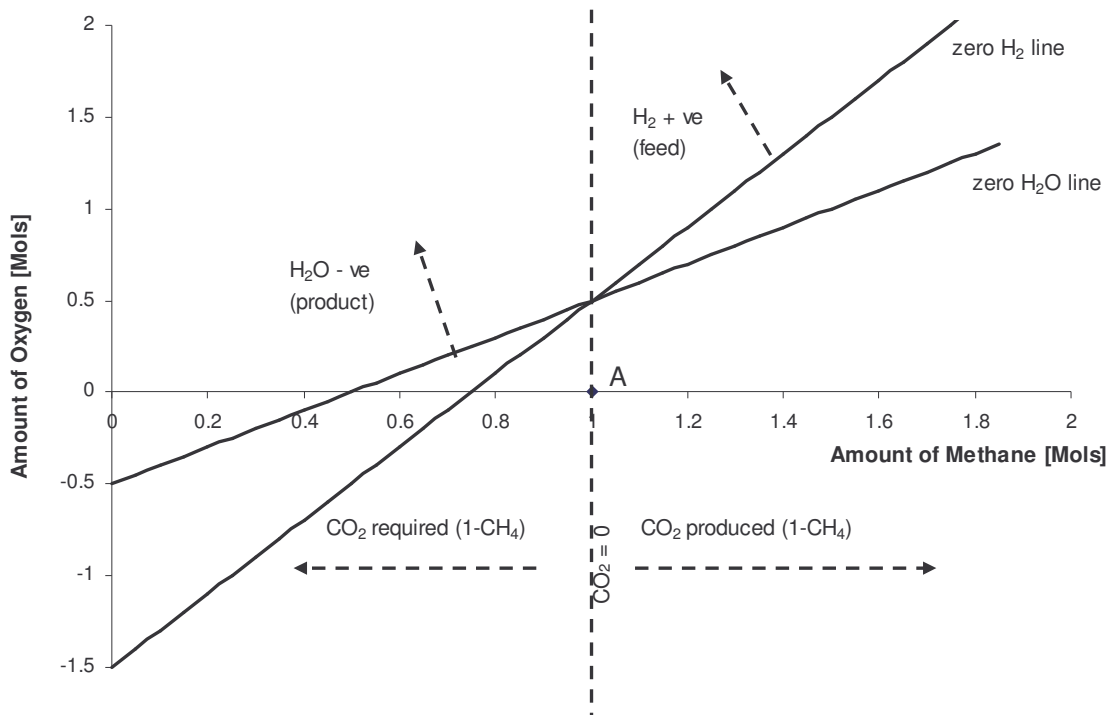
Figure 4.9: The zero mass balance lines for water, hydrogen and carbon dioxide for a process producing one mol of methanol

Figure 4.9 gives one graphical insights into the mass balances that are possible using a methane and oxygen to produce one mole of methanol. It is possible from the figure to determine bounds or targets for the process based on the mass balance. It is unlikely that the process would produce oxygen, therefore all mass balance that lies below the methane axis, when the amount of oxygen is negative, are infeasible. By setting various criteria, one can determine all the feasible mass balances that satisfy these criteria. For example, one would prefer a process that does not emit carbon monoxide; this occurs when the amount of methane equals to one mole (shown as point A on Figure 4.6). Another criterion that could be set is, for example, hydrogen to be a product instead of a feed material and thus one would operate below the hydrogen line, and all mass balances above the line would be regarded as infeasible.

The next step is to evaluate the *energy balance* and the *entropy balance* (work balance) for each of the mass balances, as was done with the previous example. To

simplify the evaluation, only the lines where the enthalpy change and Gibbs energy change equal zero are determined.

Figure 4.10 illustrates the zero mass balance lines as well the lines where the enthalpy change (ΔH) and Gibbs energy change (ΔG) for the process equal zero. Above the '$\Delta H = 0$' line, the enthalpy change for the process is negative. This indicates that processes lying above the line release energy or are exothermic. Processes lying below the '$\Delta H = 0$' line will require energy or are endothermic. Similarly, processes lying above the '$\Delta G = 0$' line, will release work whereas processes lying below the line require a work input.
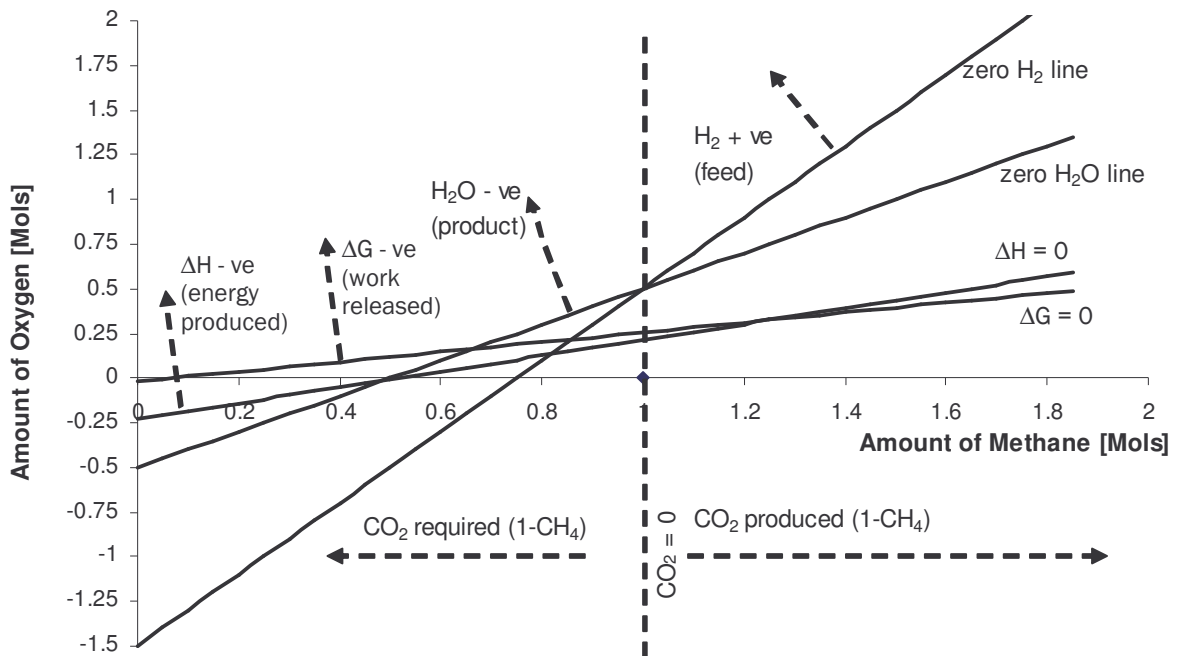
Figure 4.10: The mass balance, energy balance and entropy (work) balance to produce one mole of methanol.

Figure 4.10 combines the mass, energy and entropy balance and is therefore a comprehensive tool in providing visual insights into the process, aids in setting targets and in the selection of suitable processes that satisfy the required criteria.

It is clear from Figure 4.10 that processes with low methane feeds will be work limited since the '$\Delta G = 0$' lies line above the '$\Delta H = 0$'. This occurs until the amount of methane fed to the process exceeds 1.3 moles. Thereafter the process will be energy limited. Notice also that, in this particular example, one can make both $\Delta G = 0$ and

ΔH = 0 (where the 'ΔG = 0' and 'ΔH = 0' lines intersect) but this is only possible at the cost of producing carbon dioxide.

Consider now a process with the following criteria: zero CO_2 emission and that H_2 should occur as a product. One can then determine the region of operation based on these criteria. Based on the zero CO_2 emissions criteria one would have operate in the region where the amount of methane fed to the process is less then one mole. For hydrogen to be a product one will have to operate below the zero hydrogen line, so in fact, the hydrogen mass balance limits the process. This region (Region A) is shown in Figure 4.11. The region is further constrained by the energy and work requirements. One has to operate above the 'ΔG = 0' line so that the process will not require any work. Region B shown in Figure 4.11 illustrates the feasible region. In this region, water will be required as a feed material. One would produce both heat and work in the region. One can also determine from Region B the maximum amount of hydrogen one could produce without requiring heat or work requirements. This occurs at the intersection of the 'ΔG = 0' line with the zero CO_2 line.
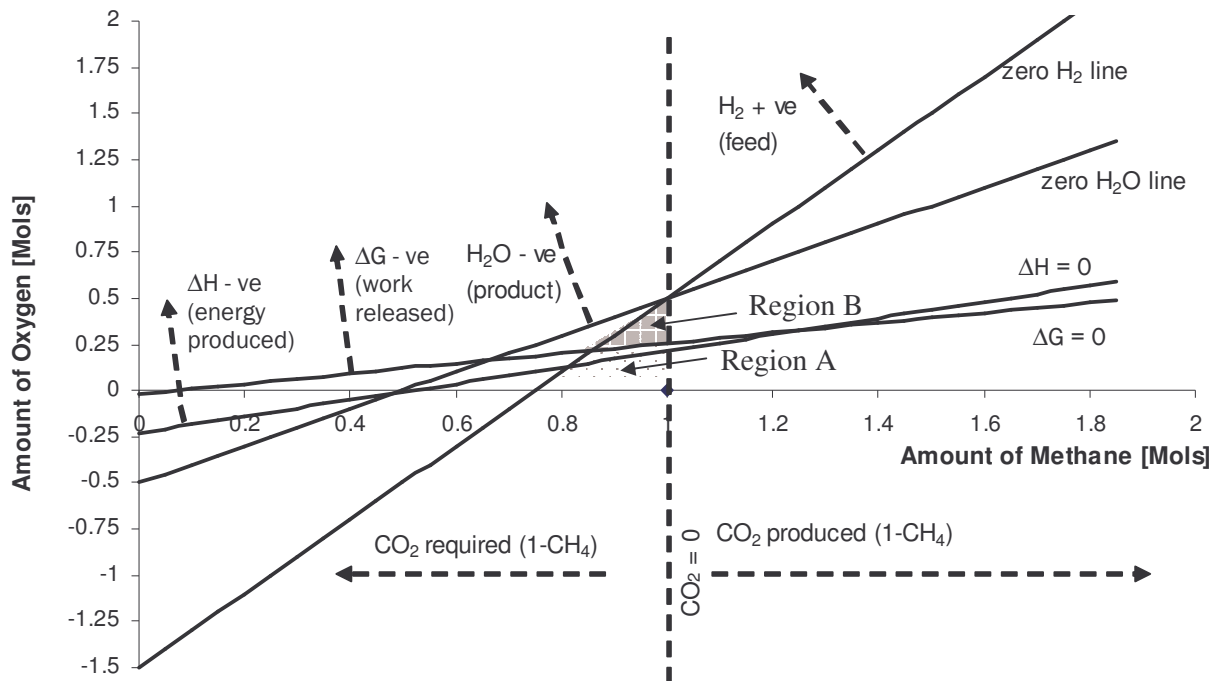
Figure 4.11: Feasible region for the co-production of hydrogen and methanol without the production of carbon dioxide

4.4.2 Mass Integration

Consider the following mass balance for a process that produces methanol and hydrogen:

$$CH_4 + H_2O \Rightarrow CH_3OH + H_2 \qquad [4.12]$$
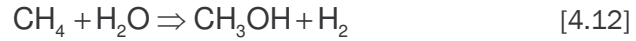
This process can be located on Figure 4.10 as it lies on the methane axis (since the amount of oxygen equals zero) where the amount of methane equals one mole. The process requires both energy as well as work. This is clear from Figure 4.10 since the process lies below the '$\Delta G = 0$' line as well as the '$\Delta H = 0$' line. Consider a process that supplies the energy required by burning the hydrogen produced. This will produce -285.83 kJ/mol of energy. The amount of energy required by the mass balance given in equation 12 is 121.98 kJ/mol. Thus, there is an excess of -163.85 kJ/mol of energy. The process is shown in Figure 4.12.
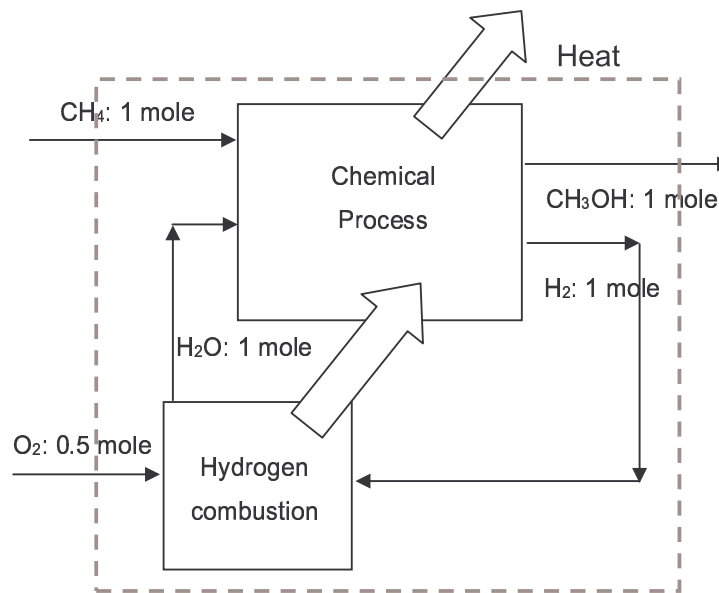
Figure 4.12: Changing the overall mass balance for a methanol process by mass integrating the hydrogen produced

It is clear from Figure 4.12 that by recycling the water produced by burning the hydrogen, one can change the process mass balance from that given by equation 4.12 to that given by equation 4.4.

There are clear opportunities for mass integration and Figure 4.10 can gives insights into the integration of processes as well as the components to be recycled.

4.5   Generalization

The examples considered in the sections 4.2 and 4.3 were of low dimensionality and therefore visual interpretation of the results was possible. Since this approach only considers the inputs and outputs, the dimensionality of the problems will not be too large. In systems with higher dimensions, a *linear program* can be formulated to describe the system. This allows a more general approach to the formulation and solution of the problem. The fact that the mass balances, energy balance as well as entropy balances are all linear is clear from the previous two examples.

The linear program can be formulated as follows:

Given a number of components (A_i) in a system, where the amounts of each component (υ_i) is unknown, it is required to determine all feasible mass balances to produce a specified amount (taken to be one mole) of the desired product (A_K). Let the number of components in the system equal to K. All mass balances can be expressed as follows:

$$\nu_1 A_1 + \nu_2 A_2 + \ldots\ldots - A_K = 0 \qquad\qquad [4.13]$$

The first step is to write the mass balances for each atomic species (n) in the system. Given that there are N atomic species in the system, the mass balance can be formulated as follows:

$$\sum_{i=1}^{K} \nu_i \varepsilon_{i,n} = 0 \qquad \text{for } n = 1, 2, \ldots N \qquad [4.14]$$

where $\varepsilon_{i,n}$ = the number of n atomic species in component *i*

υ_i = the relative amount (in terms of moles) of component *i*

The second step is to write the energy balance for the system (assuming the inputs and outputs occur at standard conditions) in terms of the amounts of each component. The enthalpy change for the system should be either equal to zero (i.e. no energy requirements) or less than zero (energy will be produced from the system)

$$\sum_{i=1}^{K} (-\nu_i) \hat{H}_{f,i} \leq 0 \qquad\qquad [4.15]$$

where $H_{f,i}$ = the standard enthalpy of formation (per mol) of component i

             υ_i = the relative amount (in terms of moles) of component i

The next step is to write the entropy balance (in terms of the Gibbs energy) for the system (assuming input and output at standard conditions) in terms of the amounts of all components. The Gibbs energy change for the system must either be equal to zero (no work requirements) or less than zero (work will be produced from the system)

$$\sum_{i=1}^{K}(-\nu_i)\hat{G}_{f,i} \leq 0 \qquad\qquad [4.16]$$

where $G_{f,i}$ = the standard Gibbs energy of formation (per mol) of component i

             υ_i = the relative amount (in terms of moles) of component i

Finally, one can state the linear programming problem by specifying the objective function and various other constraints. These will depend on the specific problem being solved. The objective function could be, for example, maximizing the yield of a product or minimizing a by-product or could also be related to the profit of the process.

Consider the example discussed in section 4.3. The mass balance for the system can be written as follows

$$\nu_1 CH_4 + \nu_2 H_2O + \nu_3 O_2 + \nu_4 CO_2 + \nu_5 H_2 \Rightarrow CH_3OH \qquad\qquad [4.17]$$
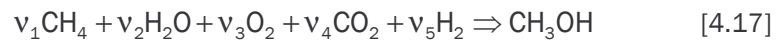
An attempt is made to solve this example using the linear programming formulation described above.

There are three atomic species (carbon, hydrogen and oxygen) in this case and six components (including the methanol product).

One can therefore write three mass balances as follows

$$\text{Carbon Balance} : \nu_1 + \nu_4 = 1 \qquad\qquad [4.18i]$$

$$\text{Hydrogen Balance: } 4\nu_1 + 2\nu_2 + 2\nu_5 = 4 \qquad\qquad [4.18ii]$$

$$\text{Oxygen Balance: } \nu_2 + 2\nu_3 + 2\nu_4 = 1 \qquad\qquad [4.18iii]$$

The energy balance can now be written in terms of the various amount of each component

$$\Delta H = H_{f,CH_3OH} - \nu_1 H_{f,CH_4} - \nu_2 H_{f,H_2O} - \nu_3 H_{f,O_2} - \nu_4 H_{f,CO_2} - \nu_5 H_{f,H_2} \leq 0 \qquad [4.19]$$

where ΔH = the enthalpy change for the system

Similarly, the entropy balance (written in terms of the Gibbs energy) can be written as follows

$$\Delta G = G_{f,CH_3OH} - \nu_1 G_{f,CH_4} - \nu_2 G_{f,H_2O} - \nu_3 G_{f,O_2} - \nu_4 G_{f,CO_2} - \nu_5 G_{f,H_2} \leq 0 \qquad [4.20]$$

where ΔG = the change in the Gibbs energy for the system

It is now possible to formulate the linear programming problem. Consider, as an objective function maximizing the amount of hydrogen that can be co-produced with the methanol product.

The objective function will be as follows

Minimize υ_5

It is required to find the minimum since when hydrogen occurs as a product υ_5 will be a negative number.

The constraint can be written as follows:

Subject to $\upsilon_1 \geq 0$; methane should be a feed material only

$\upsilon_3 \geq 0$; oxygen should appear as a feed

$\upsilon_4 \geq 0$; CO_2 should preferably be zero or appear as a fee

$\upsilon_5 \leq 0$; H_2 should be a product

$\Delta H \leq 0$; energy balance requirement

$\Delta G \leq 0$; entropy (work) balance requirement

No constraint is placed on the amount of water in the system i.e. water can be a feed or a product. The problem can be solved using Microsoft Excel Solver. The amounts of each component required/produced (in addition to the one mol of methanol produced) are summarized in Table 4.1.

Table 4.1: Solution to the linear programming problem (maximizing the amount of hydrogen produced)

(a) Components and the quantities required or produced

Component	Amount Required (moles)	Amount Produced (moles)
CH_4	1.0	-
H_2O	0.487	-
O_2	0.256	-
CO_2	-	-
H_2	-	0.487

(b) The enthalpy and Gibbs Energy change

ΔG (kJ/mol)	0
ΔH (kJ/mol)	-24.69

It is clear that for every mole of methanol produced one can produce almost half a mole of hydrogen without producing carbon dioxide. Oxygen and water are required as feed material. In addition, the process does not require a further input of either energy or work. In fact, it may be possible to produce additional heat from the system as ΔH is negative. The ΔG was determined be equal to zero i.e. no work requirement for the overall process. The same solution could have been obtained using the graphical approach as illustrated by Figure 4.11.

4.6   A further example

4.6.1   Co-feeding coal and methane to produce methanol and hydrogen

In this section, an example that may be difficult to represent graphically is considered. Consider again the synthesis of methanol and hydrogen (as a by-product) using both coal and methane. The mass balance can be represented as follows:

$$a\ C + b\ CH_4 + c\ H_2O + d\ O_2 + e\ CO_2 + f\ H_2 - 1CH_3OH = 0 \qquad [4.21]$$
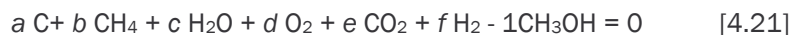
It is assumed that coal is pure carbon, although coal usually contains other elements such as hydrogen and nitrogen. The methanol coefficient is set to one i.e. one mole of methanol is being produced.

There are six unknowns and three mass balances (one for each atomic species: carbon, hydrogen and oxygen). Therefore, there are three degrees of freedom (by adding an additional component one has increased the number of degrees of freedom).

Once again, linear programming is employed to find feasible solutions as well as to screen various options. For example, consider using only coal to produce methanol (i.e. let the amount of methane equal to zero). One can now determine the minimum amount of carbon dioxide produced by letting the objective function to be minimum CO_2 production. The constraints are C and O_2 should be a feed; H_2 should be a product; $\Delta G \leq 0$ and $\Delta H \leq 0$. It turns out it is not possible to produce methanol from coal (taken as pure carbon) without producing carbon dioxide. The minimum amount of carbon dioxide produced is 0.846 moles per mole of methanol produced. This occurs when ΔH equals zero. Thus, it is clear that such a process is limited by the energy balance and not by the work balance as was the case for the methane-to-methanol process.

It is clear that methanol cannot be produced from coal without the production of carbon dioxide but it is possible using methane as a feed. The combination of coal and methane as feedstock could be advantageous in terms of conserving methane resources and utilizing coal without producing carbon dioxide. A linear program with objective function of minimizing carbon dioxide production can be developed using the following constraints: C, O_2 and CH_4 must be a feed (i.e. C, O_2, and CH4 $\geq$ 0); H_2 must be zero or a product ($H_2 \leq 0$); $\Delta G \leq 0$ and $\Delta H \leq 0$. Table 4.2 gives the results obtained by solving the linear program.

Table 4.2: Solution to the linear programming problem (co-feeding coal and methane to produce methanol by minimizing carbon dioxide)

(a) Components and the quantities required or produced

Component	Amount Required (moles)	Amount Produced (moles)
C	0.273	-
CH_4	0.727	-
H_2O	0.546	-
O_2	0.227	-

CO_2	-	-
H_2	-	-

(b) The enthalpy and Gibbs Energy change

ΔG (kJ/mol)	0
ΔH (kJ/mol)	-28.30

It is clear that it is possible to produce methanol by co-feeding coal and methane without the production of carbon dioxide. This is a very interesting result and it can be a possible way of utilizing coal in a clean and efficient manner. The feed requirements are coal and methane in approximately a 1:3 ratio. Water and oxygen are also required as feed material. In this particular example, no hydrogen is produced. It is also clear that the process is work limited process since the zero carbon dioxide solution is achieved when the Gibbs energy equals zero. The enthalpy change for the process is negative for such a process, which means heat will be produced from the process.

4.7   Conclusions

A simple method of determining targets for a process, before the detailed design of the process, has been illustrated by considering the synthesis of methanol as an example. These targets are based on the overall process as it only considers the inputs and outputs from the process. These targets are based on the fundamental concepts of mass, energy and entropy. Ways of calculating the minimum amount of mass inputs, minimum amount of energy (or maximum amount of energy produced) and minimum work required (or maximum work produced) have been shown. There is a strong interrelationship between these three variables (mass, energy, work) and all three variables have to be considered when setting a target.

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, as well as various other criteria (such as environmental aspects, cost etc). The energy and work requirements are also accounted for when determining the target mass balance. An easy method of screening and ranking various mass balances either graphically or algebraically was presented.

These targets also give insights, at a very early stage, into integration of the process. An understanding of which of the three variables is the limiting target is also very important in that gives insight into what is the important or limiting parameter in the design and operation of the process. It has also been shown that targets can be achieved by considering mass, heat and work integration of a process. This is useful not only for the design of new processes but for retrofitting as well.

The approach has been applied to various examples relating to the synthesis of methanol and various interesting results have been discovered relating to such a process.

In particular, the approach presented in this paper is a powerful tool for improving process efficiency and for reducing carbon dioxide emissions in the conceptual design phase.

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5

ANALYSING THE OVERALL PROCESS TARGET[†]

5.1   Introduction

Chemical processes consume a large amount of the world's resources, as raw materials to produce various products as well as energy sources to drive the processes. Therefore, in order to develop energy efficient processes, reduce raw material requirements and alleviate the environmental effects associated with processes, there is growing need to integrate processes in terms of mass and energy (heat and work).

In light of this, two branches of Process Integration have developed: mass integration and energy integration. These tools provide a fundamental understanding of the process, identify targets for the process and provide a means of optimizing the process. The emphasis of these methods is to consider the process as a whole instead of considering individual unit operations. Energy integration is a systematic methodology for analyzing the energy flows within a process, in order to identify targets and determine the optimal system for a minimum consumption of energy. For example, Pinch Analysis is an energy integration tool for designing heat exchanger networks (Linnhoff, 1982). The pinch technique has since been applied to various other aspects of process design such as total site integration, separation systems (distillation columns) and targeting emissions and water minimization problems (Linnhoff, 1993; Rossiter et al., 1991). Mass integration aims at systematically identifying performance targets for the mass flows in a process. The synthesis of mass exchange networks was introduced by El-Halwagi (1988) and the technique has been successfully been extended to solve a wide range of waste reduction problems (El-Halwagi, 2003).

The use of thermodynamic methods, especially the Second Law Analysis, has proved to be a valuable tool in process synthesis and integration (Linnhoff and Turner, 1980; Shinnar, 1988). In particular, the application of the second law to processes involving chemical reactions, first introduced by Denbigh (1956) and then considered by

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[†] This chapter is based on a manuscript submitted for publication to Computers and Chemical Engineering (2005)

numerous researchers reveal that chemical reactors usually are the main cause of thermodynamic inefficiency due to the irreversible manner in which reactions occur. Although present day technology do not allow reactions to be carried out reversibly, not all the exergetic losses are inevitable; it is possible to reduce the irreversibility of chemical processes. One possibility is to carry out chemical processes under a "prescribed degree of irreversibility" (Denbigh, 1956) i.e. the consumption of a specific amount of exergy to account for technological constraints. Glavic et al (1988) performed a thermodynamic analysis of reactors in order to heat integrate the reactors into the process. De Ruyck (1998) also proposed a way in which to include chemical reactions in composite curve theory by defining a 'reversible temperature'. Hinderdrink et al (1996) investigated the exergy losses associated with chemical reactions and suggested ways in which the exergy losses can be minimized. Leites (2003) also suggests various methods of reducing exergetic losses, and in turn energy losses, for chemical reactions and other chemical processes.

In the previous chapter, we proposed a new method for targeting and integrating chemical processes based on fundamental thermodynamic concepts, in particular the first and second law of thermodynamics. The method is applied to a process in the very early stages of the design process, considering only the inputs and outputs of the process, and *does not require a flowsheet*. We set process targets, which are the limit of performance for a process using a specified feed and producing a given product and are independent of the structure of the flowsheet.

In this chapter, we seek to understand the interaction of mass, heat and work flows for the process targets set. This chapter will investigate the specific case of processes which have a positive Gibbs energy change (which means the process requires work) and explore the possibilities of saving energy by considering a mass, energy and entropy (second law) analysis. We will show how these concepts (mass, energy and entropy) gives some very powerful insights and identifies mass- and energy- saving opportunities for the process at a very early stage.

It is important to realize that there are mass and energy balances across a process, even when we only consider feed and product streams rather than individual pieces of equipment and their interconnections i.e. the flowsheet, which is where one traditionally applies mass and energy balances.

In addition to mass and energy balances, entropy should be considered. This can, and we believe should be done, at the conceptual level of the design to look at what the implications of the heat flows are on the potential reversibility as well as the work flows in a process.

5.2 Thermodynamic analysis of a one stage process

Consider the production of methanol from methane. Consider a process as shown in Figure 5.1, the inputs of which are methane, carbon dioxide and steam and the product is liquid methanol.
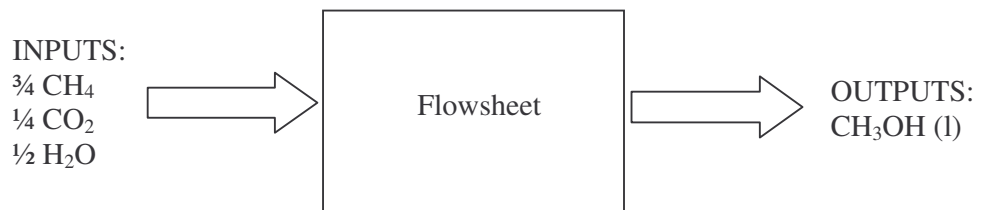
Figure 5.1: The production of methanol from methane, carbon dioxide and steam

The *overall process* can be described by the mole balance:

$$\tfrac{3}{4}\,CH_4 + \tfrac{1}{4}\,CO_2 + \tfrac{1}{2}\,H_2O_{(gas)} \xrightarrow[\text{mole balance}]{\text{process}} CH_3OH_{(liquid)} \qquad [5.1]$$
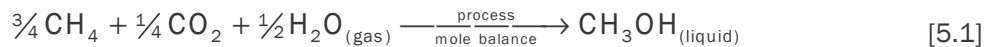
The mass or mole balance is determined simply by balancing each atomic species that occurs in the process. Note that this is the mass balance for the whole plant and *need not be* the actual reaction that takes place in any specific reactor.

However, our assumption at this stage is that the major heat input and removal is at a reactor. We will relax these assumptions later in this chapter. This assumption applies particularly to highly exothermic and endothermic reactions and in these processes the main heat input or output will often be associated with the reactor. We furthermore assume that heat at temperature T is added to the reactor at a point in the reactor where the temperature is also T.

Thus for example a simple process might be represented as shown in Figure 5.2.
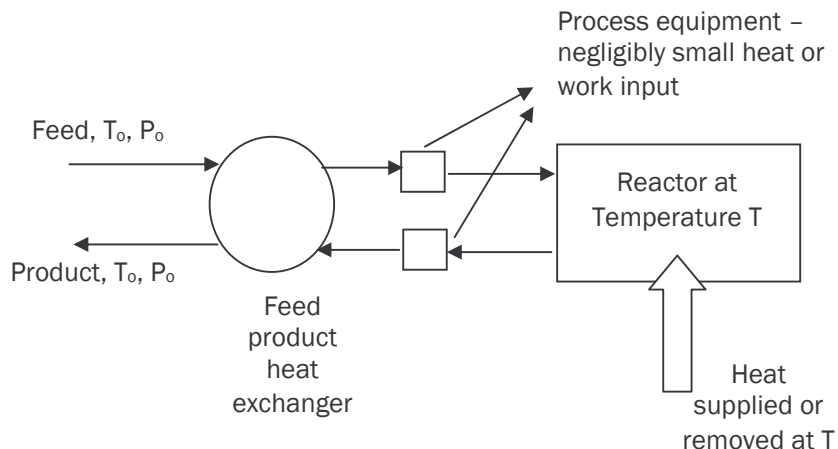
Figure 5.2: Schematic representation of a simple chemical process

Let us consider the limits of performance of a fully integrated reversible process. We will assume that the total energy supplied to heat the feed material from ambient, T_o, to the reactor temperature, T, is the same as the total heat removed when cooling the product from the reactor temperature to the ambient temperature. If, furthermore, the specific heat of the feed ($C_{p\ feed}$) is approximately equal to the specific heat of liquid methanol ($C_{p\ methanol}$), so that the enthalpy-temperature profiles of the feed and products are the same, there will be no entropy generation and hence we can ignore this unit in our analysis. There may be other processes occurring but at this stage we will assume that they do not require any large heat input (compared to the enthalpy of reaction, ΔH_{rxn}) or work inputs (compared to Gibbs Energy of reaction, ΔG_{rxn}) and hence we will neglect these units in our analysis. We will at this stage accept that our process is somewhat imaginary in that it produces liquid methanol from the reactor. We will later release this constraint to make the process more realistic.

Thus if we look at the *overall process* (as described by equation 5.1), we see that the energy load for the process, $\Delta H_{process}$ is:

$$\Delta H_{process} = H_{product} - H_{feed}$$
$$= \Delta H_{eqn\ 1}(T_o)$$

[5.2]

The $\Delta H_{process}$ for the process described by equation 5.1 is calculated to be 36.8 kJ/mol using equation 5.2. Thus, we can see that the process requires heat to be supplied to it and this quantity is fixed although we have not yet looked at the *quality* of the heat.

The process may use more energy than $\Delta H_{process}$ and if the amount of heat supplied is $\Delta H_{process} + \delta Q$, the process will have to reject heat, the quantity being δQ as shown in Figure 5.3. The energy can be rejected in any place i.e. not necessarily at the reactor. Thus, the temperature at which the energy is rejected could be different from the temperature at which the heat is supplied.

Figure 5.3: (a) The minimum quantity of heat added to the process and (b) additional heat added must be rejected

We will now consider the *quality of energy* i.e. the entropy of the process. Let us now consider the process described previously where the heat at temperature T is supplied to a reactor at a point where the temperature is also T. We will assume at this stage that the amount of heat supplied to the process is $\Delta H_{process}$ as given by equation 5.2.

Writing the entropy balance for the process shown in Figure 5.2, under the assumptions stated earlier, gives

$$S_{generation} + \frac{\Delta H_{process}}{T} = S_{product} - S_{feed} \qquad [5.3]$$

The entropy can be written in terms of the Gibbs Energy, G, as follows:

$$G_i = H_i - T_o S_i \tag{5.4}$$

Assuming a reversible process i.e. $S_{generation}$ = 0, equation 5.3 can be rearranged to give

$$\frac{\Delta H_{process}}{T} = \frac{1}{T_o}\Big[(H_{product}(T_o) - H_{feed}(T_o)) - (G_{product}(T_o) - G_{feed}(T_o))\Big] \tag{5.5}$$

Under our assumptions, we have defined

$\Delta H_{process} = \Delta H_{eqn\ 1}(T_o)$

Furthermore

$\Delta G_{process} \approx \Delta G_{eqn\ 1}(T_o)$

If the process is reversible, i.e. $S_{generation}$= 0, then we will define the temperature at which this occurs at to be the Carnot Temperature, T_{carnot}. Substituting these relations into equation 5.5 gives:

$$\Delta G_{process} = \Delta H_{process}\left(1 - \frac{T_o}{T_{carnot}}\right) \tag{5.6}$$

Thus, in order for a process to be reversible the temperature, T_{carnot}, of the heat that we add to the process must satisfy the above equation as $\Delta G_{process}$ (minimum work load) and $\Delta H_{process}$ (minimum heat load) are fixed. Shinnar (1988) also explains the implications of this equation for process design. We call this temperature T_{carnot} because equation (6) is essentially the equation of a heat engine that supplies the work $\Delta G_{eqn\ 1}(T_o)$ reversibly from the heat $\Delta H_{eqn\ 1}(T_o)$. One can imagine the process as a heat pump, since heat is supplied from the surrounding at a low temperature and "pumped" up to a higher temperature by the addition of work. This is shown schematically in Figure 5.4. We note the work supplied is virtual work in that we are not adding any shaft work to the system. If this latter situation were the case, we would have to include it in the energy balance. This virtual work is the notional work

that could have been made using this heat but instead is used to supply the Gibbs Energy to make the process possible, namely to make ΔS_{total} = 0. We note that as with any natural process the best our plant can do (operate reversibly) is to satisfy this condition.
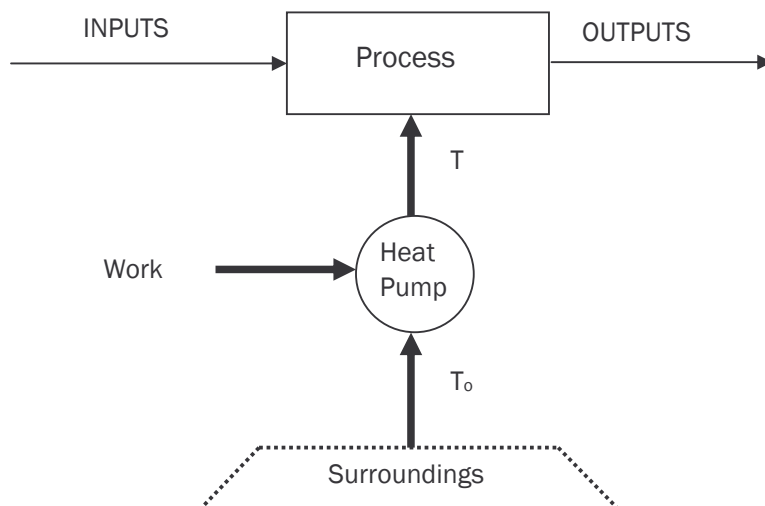
Figure 5.4: Representing the process as a heat pump

If the temperature that we supply the heat at T is greater than the T_{carnot} calculated from equation 5.6, then the process will be irreversible and will generate entropy. This can be described by the following equation:

$$\Delta G_{eqn\ 1}(T_o) + T_o S_{generated} = \Delta H_{rxn}\left(1 - \frac{T_o}{T}\right)$$ [5.7]

Alternatively, the process would have the potential to produce work, the quantity being equal to $T_o S_{generated}$. If this potential work is not recovered, we could consider this as lost work, $W_{lost} = T_o S_{generated}$. If the temperature that we supply the heat at T is less than T_{carnot}, in order to make the process feasible we would need to supply "work" W_{add} or further energy of high enough quality as described by:

$$\Delta G_{eqn\ 1}(T_o) = \Delta H_{eqn\ 1}(T_o)\left(1 - \frac{T_o}{T}\right) + W_{add}$$ [5.8]

We can represent the three cases pictorially as shown in Figure 5.5.
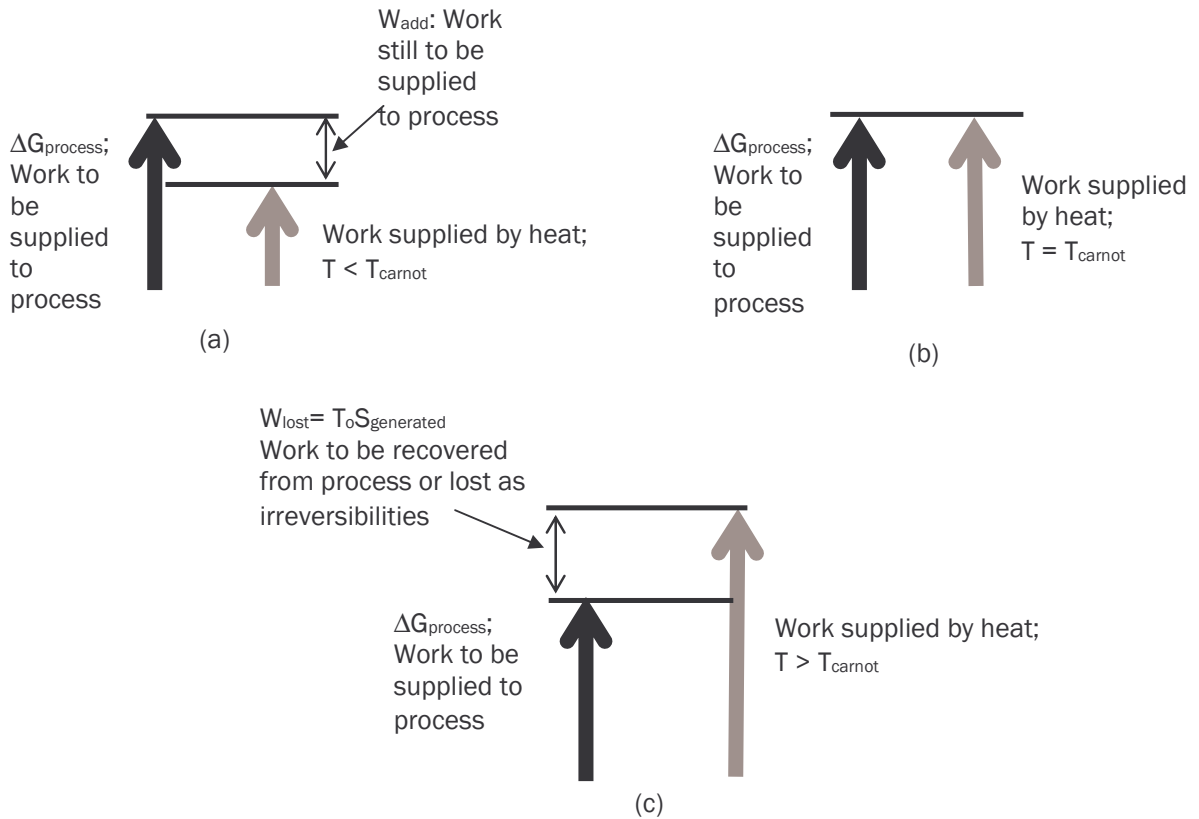
Figure 5.5: Pictorial representation of work flows (a) Temperature is less than Carnot temperature (b) Temperature is equal to Carnot temperature (c) Temperature is greater than Carnot temperature

Let us look at the implications of this analysis on our previously described methanol production process as described by equation 5.1. For our process $\Delta H_{process} \approx \Delta H_{rxn} = 36.8$ kJ/mol methanol and $\Delta G_{process} = 84.8$ kJ/mol. Substituting the values into equation 5.6, we find that

$$T_{carnot} = \frac{T_o}{1 - \dfrac{\Delta G_{eqn\ 1}(T_o)}{\Delta H_{eqn\ 1}(T_o)}}$$

$$= \frac{T_o}{1 - \dfrac{84.8\ ^{kJ}/_{mol}}{36.8\ ^{kJ}/_{mol}}}$$

[5.9]

We can see from equation 5.9 that T_{Carnot} is negative, and hence we can never supply heat at a temperature such that the entropy generated across the process is zero. This occurs because $\Delta G_{process}$ is greater than $\Delta H_{process}$, which means that the addition of the minimum amount of heat alone cannot supply the required work. It should be noticed that the heat and work requirements can be matched only in cases when $\Delta G_{process}$ is less than $\Delta H_{process}$ since

$$\frac{\Delta G_{process}}{\Delta H_{process}} = \left[1 - \frac{T_o}{T}\right] \leq 1$$

We thus need to supply heat or work in other ways to make our process feasible. We will now look at the three main ways of supplying additional work. These will be described in the section 5.3.

5.3   Modes of putting extra work into the process

There are in principle many ways that we can put work into a process. However, three of these are really the only practical methods of use in a conventional plant. We will consider these three modes of adding work, namely:

- Work input by high temperature heat i.e. Carnot engine effect with increased heat addition
- Work of compression
- Work of separation

5.3.1   Work input by Carnot engines

We know from the thermodynamic study of Carnot engines that heat at high temperature has the ability to do work, and the quality or the work potential depends on its temperature. Thus when we add heat to a process we are equivalently adding a certain amount of work to the process that we could access if we designed our process reversibly.

We have seen from our previous example that if we added the minimum amount of heat to the process namely $\Delta H_{process}$, it is not possible to carry out the process reversibly. Alternatively, more work needs to be added to the process. Thus one way of achieving this is by adding more heat, namely $(\Delta H_{process} + \delta Q)$ at temperature $T_{carnot,\delta Q}$, and rejecting an amount δQ of heat at a lower temperature T_o as explained in Figure 5.6.
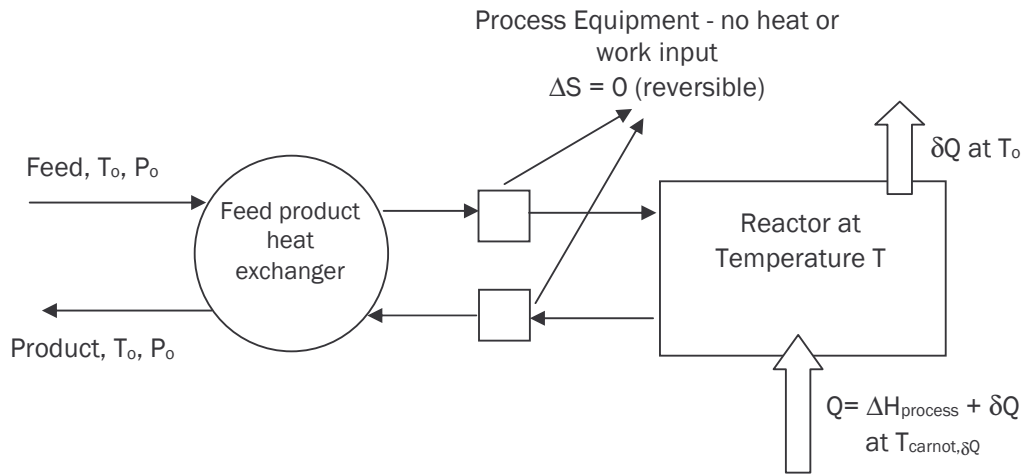
Figure 5.6: Schematic representation of a process where additional heat δQ is added

Writing the entropy balance for Figure 5.6 gives:

$$S_{generation} + \left(\frac{\Delta H_{process} + \delta Q}{T_{carnot,\delta Q}} \right) = \frac{\delta Q}{T_o} + S_{product} - S_{feed} \qquad [5.10]$$

If we assume a reversible process i.e. $S_{generation} = 0$

$$\Delta S_{process} = S_{product} - S_{feed} = \frac{\Delta H_{process} - \Delta G_{process}}{T_o}$$
$$= \frac{\Delta H_{process} + \delta Q}{T_{carnot,\delta Q}} - \frac{\delta Q}{T_o} \qquad [5.11]$$

Rearranging equation 5.11 gives

$$\Delta G_{process} = \Delta H_{process} \left(1 - \frac{T_o}{T_{carnot,\delta Q}} \right) + \delta Q \left(1 - \frac{T_o}{T_{carnot,\delta Q}} \right) \qquad [5.12]$$

Thus, we can see that if we increase the heat input at high temperature to the process we have the potential to make this process feasible.

This however comes at the expense of having to reject heat at a lower temperature. Hence, the heat loads in the process are larger and the equipment, for example the

heat exchangers, are larger which leads to increased capital and operating costs. The process also has to be such that it can absorb the extra energy at high temperature and have ways of producing streams at lower temperatures which can reject the heat. *Thus, this means increased complexity of the process.*

Let us apply this to the process previously considered, namely methanol production from methane (equation 5.1). We will look at how much extra heat needs to be supplied and at what temperature the process should operate to make the process feasible and reversible. Substituting we see that the temperature $T_{Carnot, \delta Q}$ and the quantity of heat required, δQ are related as follows:

$$Q = \frac{\Delta G_{process} - \Delta H_{process}\left(1 - \dfrac{T_o}{T_{carnot,\delta Q}}\right)}{\left(1 - \dfrac{T_o}{T_{carnot,\delta Q}}\right)}$$

$$= \frac{84.8 \,{}^{kJ}\!/\!_{mol} - 36.8 \,{}^{kJ}\!/\!_{mol}\left(1 - \dfrac{T_o}{T_{carnot,\delta Q}}\right)}{\left(1 - \dfrac{T_o}{T_{carnot,\delta Q}}\right)}$$

[5.13]

Equation 5.13 can be plotted to show the relationship between the heat added and the temperature $T_{Carnot,Q}$ for the case of methanol production. This is shown in Figure 5.7.
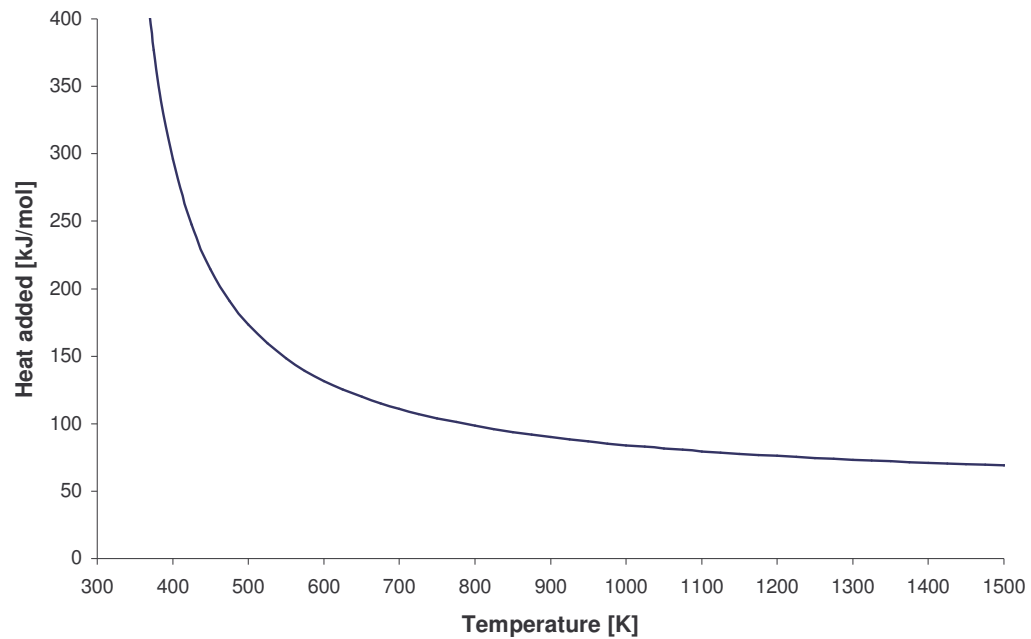
Figure 5.7: The relationship between amount of additional heat required δQ and the temperature $T_{Carnot,\delta Q}$ for a reversible methanol production process.

Thus, we can see that if we can design the process to absorb the extra heat and reject it at low (ambient) temperature that we can potentially find a temperature at which to add the heat that will allow work to be supplied to the process reversibly. Furthermore, the more we can increase the heat flow to the process the lower the temperature at which we added the heat needs to be in order to make the process reversible. However, we see that the amount of heat that needs to be added via this route in this example is an order of magnitude more than the enthalpy of reaction. Designing a process so that this quantity of heat could be input or rejected, if at all possible, would be potentially quite difficult and expensive. Thus, one might conclude that it would not be practical to input the work via this method for this particular case.

5.3.2 Work addition by compression

Now let us consider how we can put work into the process by compression. We have a process with a feed of n moles of gas at temperature T_o and pressure P_o and the product from the process is m moles of gas at T_o and P_o. Let us assume that we compress the feed reversibly and isothermally to a pressure P* and that we run the

reactor at a pressure P* and temperature T. We then cool the products down in a feed product heat exchanger and then decompress the product gas from pressure P* to pressure P_o. This decompression is done reversibly and isothermally. A schematic of this process is shown in Figure 5.8.
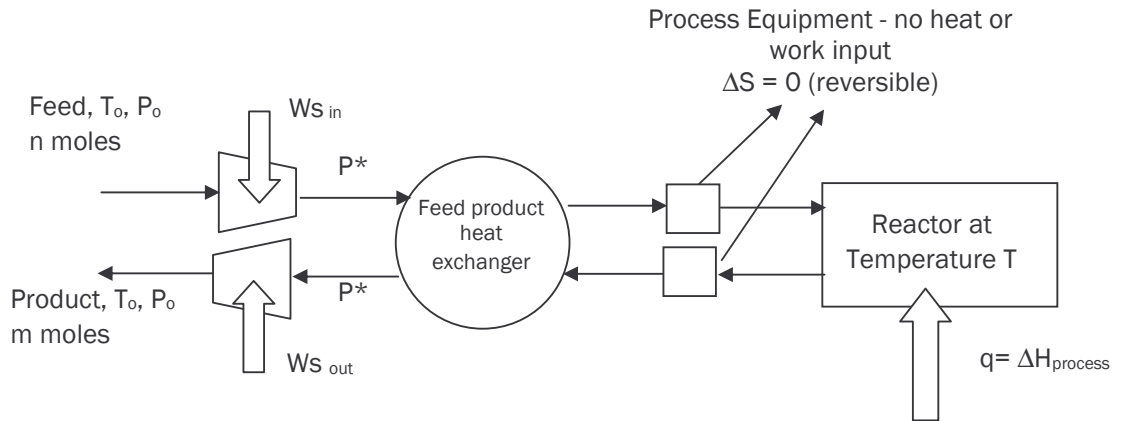
Figure 5.8: Schematic representation of process considering compression of the feed and decompression of the product

We again assume that the molar flowrate of the product multiplied by the specific heat of the product (i.e. $mC_{p\ product}$) is approximately equal to the molar flowrate of the feed multiplied by the specific heat of the feed (i.e. $nC_{p\ feed}$) so that the feed product heat exchanger in the limit is reversible and adiabatic. Under these assumptions, the heat removed from the feed compression process is equal to that added to the product expander and so these heat flows do not add to the entropy generation of the process. If we furthermore assume that the feed and products are ideal gases we can calculate the work of compression.

The work to compress the feed isothermally from pressure P_o to P*, Ws_{in} is given by

$$Ws_{in} = nRT_o \ln \frac{P^*}{P_o}$$ [5.14]

Similarly the work that can be recovered by decompressing the product gas from P* to pressure P_o is

$$Ws_{out} = mRT_o \ln\frac{P_o}{P^*} \qquad\qquad [5.15]$$

Doing an entropy balance over the process, assuming a reversible process we see that

$$\Delta G_{process} = Ws_{in} + Ws_{out} + \Delta H_{process}\left(1 - \frac{T_o}{T}\right)$$
$$= (n-m)RT_o \ln\left(\frac{P^*}{P_o}\right) + \Delta H_{process}\left(1 - \frac{T_o}{T}\right) \qquad [5.16]$$

We see that if the molar flowrate of the feed stream is greater than that of the product, i.e. n > m, then we have a mechanism of putting work into the process. Conversely if n < m, then we have a mechanism for removing work from the process.

Let us consider our previous process (equation 5.1) and look at including the work of compression. For the methanol production the feed was 1.5 mol of gas and the product contained no gas only a liquid. As the decompression of a liquid releases comparatively small qualities of energy we can thus see that Ws $_{out}$ ≈ 0. Applying equation 16 to the methanol production example gives

$$84.8 \, ^{kJ}\!/_{mol} = (1.5)RT_o \ln\frac{P^*}{P_o} + 36.8 \, ^{kJ}\!/_{mol}\left(1 - \frac{T_o}{T}\right) \qquad [5.17]$$

We can see that if we put in the minimum energy into the process i.e. q = $\Delta H_{process}$ then there is a unique relationship between T and P* as shown graphically in Figure 5.9.
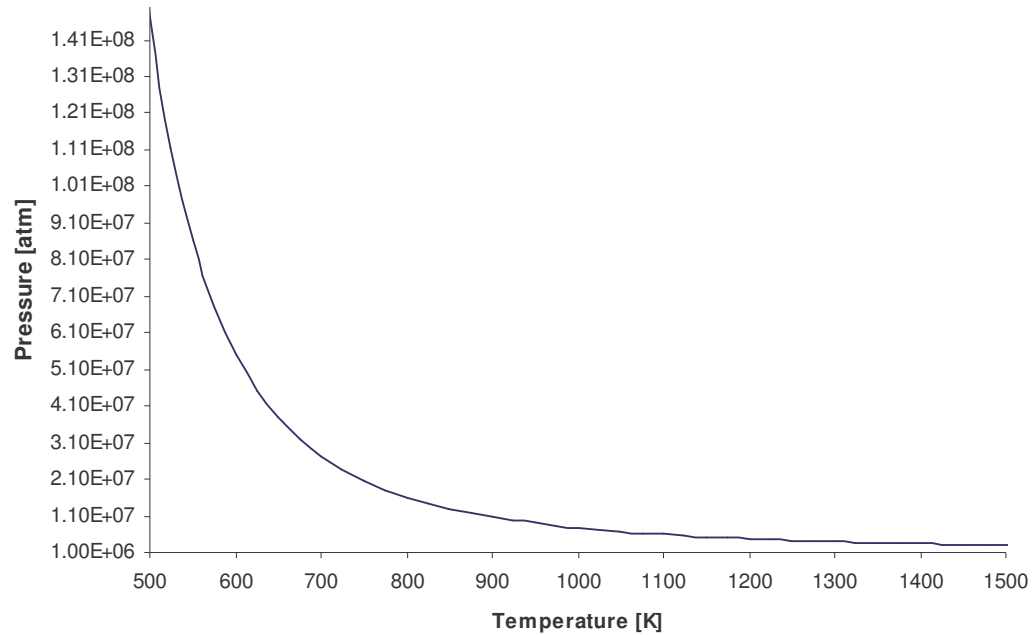
Figure 5.9: The relationship between the isothermal pressure, P* and temperature required for a reversible methanol production process

Thus if we wish to run the process reversibly, we need to match the reaction pressure P*, to the reaction temperature T. We see that the pressures required are unrealistic and that sufficient work could not be put in by compression. Let us however consider what the graph means, even if in this case the numbers are somewhat unrealistic. If the reactor pressure is chosen to be above the curve, then the compressor is using more work than required for a reversible process. Unless this extra work is recovered somewhere in the process as work or high temperature heat, this work will be degraded and will show as an entropy generation i.e. irreversibility in the process. The further the point is above the curve, the greater the work required by the compression resulting in greater irreversibilities if the work is not recovered. If however the pressure P* was chosen to lie beneath the curve, then the compressor is supplying insufficient work. Thus to make the process feasible (i.e. $\Delta S_{process} > 0$) extra work would need to be supplied by another mechanism such as the Carnot engine heat addition described previously.

One can also consider adding additional heat and compressing simultaneously. We will not pursue this route in this chapter. We also note in this case the work of compression is no longer virtual work but shaft work and that if we were to do the process at high pressure we would have to include this shaft work in the energy balance.

5.3.3 Work addition by separation

Separation is also a means of supplying work to a process. The specific work of separation W_{sep} for an ideal mixture is

$$W_{sep} = RT \sum_{i=1}^{N} x_i \ln x_i \qquad [5.18]$$

where R is the ideal gas constant, T is the temperature of the streams entering and leaving the separator and x is the mole fraction of the ith component in the stream.

To consider the magnitude of this term, we will consider separating an equimolar binary mixture (since we are only separating the methanol from the other components) into pure components. This corresponds to x_i = 0.5, which in turn corresponds to the maximum magnitude of W_{sep} for a binary. Let us take a separation temperature of approximately T = 600K.

The magnitude of the separation work W_{sep} is

W_{sep} = 8.315*600*2*0.5*ln (0.5)

   = 3458 J/mol = 3.46kJ/mol

The $\Delta G_{process}$ in this case is of the order of 80 kJ/mol. Thus for this type of process the work of separation cannot be a major means of supplying work. However, in processes where the $\Delta G_{process}$ is small (in the order of 10 kJ/mol) the W_{sep} would need to be considered and could be a way of supplying work. We note that for this situation the work is again virtual work. It may be possible to supply a greater amount of work via the separation if the flowrate to the separator is increased drastically (for example, if there is a very low conversion in the reactor).

5.4 Processes where $\Delta H_{process}$ is not equal to ΔH_{rxn}

   Let us now consider processes where not all the heat is input at the reactor but also in evaporators and condensors. We will again assume that the process is as integrated as possible and that the specific heat C_p of products is roughly equal to the C_p of the feed. In this way the heat required to heat the feed stream up (excluding phase change) would be of the same magnitude as the heat to be removed from the products (again excluding phase change). Thus in the limit we can neglect the sensible heat effects in terms of generating entropy. We would however need to add heat, and thus cause entropy changes, when changing phase.

We will consider this case via an example. We will extend our previous example to make it more realistic. We will use the same feedstocks as before, but assume that the water is supplied as a liquid but enters the reactor as steam. We will also now assume that methanol leaves the reactor as a vapour and we cool it down and condense it so that the methanol product is still a liquid. A diagram of the process is shown in Figure 5.10. HX 1 heats up the feed stream to temperature T_W, the vaporization temperature of water. HX 2 vaporizes water at temperature T_W. HX 3 heats up the feed stream which is all vapor to the reactor temperature T. HX 4 cools down the vapor product to temperature T_M, the condensing temperature of methanol. HX 5 condenses methanol at temperature T_M. HX 6 cools down the vapor products and liquid methanol to ambient temperature T_o.
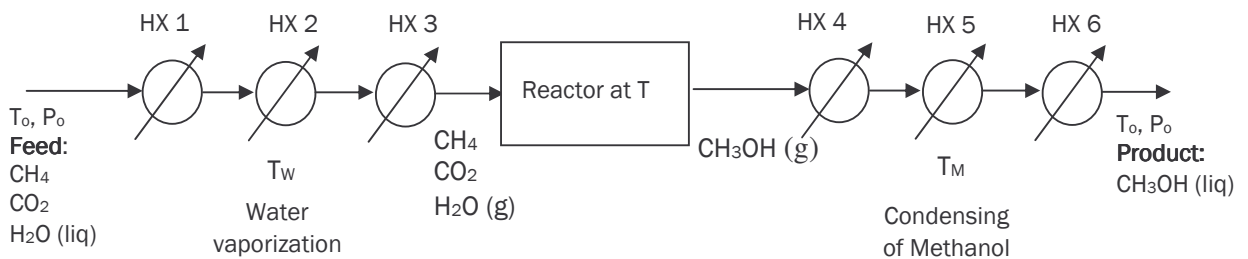
Figure 5.10: Schematic representation of process including phase change

We see that under our assumptions, the heat loads in heat exchangers HX1 and HX2 match those of heat exchangers HX4 and HX6. Furthermore the temperature- heat curves are such that the net entropy generation of these heat exchangers is zero. In

this case, considering the reaction and heat exchangers 2 and 5 only, we can define $\Delta H_{process}$ as well as ΔH_{rxn}

$$\Delta H_{process} = H_{CH_3OH(l)}(T_o, P_o) - \frac{3}{4}H_{CH_4}(T_o, P_o) - \frac{1}{4}H_{CO_2}(T_o, P_o) - \frac{1}{2}H_{H_2O(l)}(T_o, P_o)$$

while

$$\Delta H_{rxn} = H_{CH_3OH(g)}(T_o, P_o) - \frac{3}{4}H_{CH_4}(T_o, P_o) - \frac{1}{4}H_{CO_2}(T_o, P_o) - \frac{1}{2}H_{H_2O(g)}(T_o, P_o)$$

We assume that heat added to increase the temperature of the feed from T_o to T (excluding the vaporization of water) is the same as the heat removed from the product when cooling from T to T_o (excluding the condensation of methanol).

Heat will need to be supplied to the feed stream to vaporize the water. In order to keep the process reversible we assume that heat is supplied at the temperature T_W such that the vapour pressure of water at T_W is P_o. Similarly we assume that the heat is removed from the methanol at its saturation temperature T_M corresponding to a pressure P_o.

The overall entropy balance assuming a reversible process becomes

$$S_{feed} + \frac{q_W}{T_W} + \left(\frac{q_{rxn}}{T}\right) = \frac{q_M}{T_M} + S_{product} \qquad [5.19]$$

where q_W is the heat load for vaporizing water fed into the process and q_M is the heat load for condensing methanol leaving the process. Rewriting equation 5.19 in terms of the entropy change of the process gives:

$$\Delta S_{process} = S_{product} - S_{feed} = \frac{\Delta H_{process} - \Delta G_{process}}{T_o}$$
$$= \frac{q_W}{T_W} + \frac{q_{rxn}}{T} - \frac{q_M}{T_M} \qquad [5.20]$$

Rearranging equation 5.20 in terms of Gibbs Energy gives:

$$\Delta G_{process} = \Delta H_{process} - \frac{T_o}{T_W} q_W - \frac{T_o}{T} q_{rxn} + \frac{T_o}{T_M} q_m$$

$$= \Delta H_{process} - \frac{T_o}{T_W} \Delta H_{L \to V}(water, T_W) - \frac{T_o}{T} \Delta H_{rxn} + \frac{T_o}{T_M} \Delta H_{V \to L}(methanol, T_M)$$

[5.21]

The $\Delta H_{process}$ is as defined above and is related to ΔH_{rxn} by

$$\Delta H_{process} = \Delta H_{L \to V}(water, T_W) + \Delta H_{rxn} - \Delta H_{L \to V}(methanol, T_M)$$ [5.22]

Substituting equation 5.22 into equation 5.21 gives

$$\Delta G_{process} = \Delta H_{L \to V}(water, T_W)\left(1 - \frac{T_o}{T_W}\right) + \Delta H_{rxn}\left(1 - \frac{T_o}{T}\right) - \Delta H_{V \to L}(methanol, T_M)\left(1 - \frac{T_o}{T_M}\right)$$

[5.23]

If the enthalpy of phase change is much less than the enthalpy of reaction, than the phase change terms can be ignored and we simplify the above equation to the case as described previously. If the saturation temperature is close to ambient temperature, then the heat supplied to the process to vaporize the material does not carry much work with it and so is not a way of supplying or removing work from a process. In this situation, the term associated with phase change in equation 5.23 will again be small and can therefore be neglected.

Let us consider how the phase change affects the process that we have been looking at i.e. methanol production from methane, water and carbon dioxide. Let us expand the previous methanol synthesis example so that the *process* is described by:

$$\tfrac{3}{4} CH_4 + \tfrac{1}{4} CO_2 + \tfrac{1}{2} H_2O_{(liquid)} \xrightarrow{\text{process}} CH_3OH_{(liquid)}$$ [5.24]

The *reactor* is described by:

$$\tfrac{3}{4} CH_4 + \tfrac{1}{4} CO_2 + \tfrac{1}{2} H_2O_{(vapour)} \xrightarrow{\text{rxn}} CH_3OH_{(gas)}$$ [5.25]
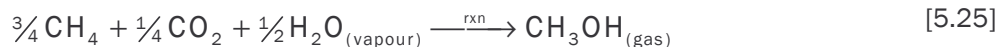
Using equation 5.23, we can calculate the temperature T which satisfies the conditions for a reversible process. Substituting in the numerical values gives the following relationship (equation 5.26), which allows us to solve for the temperature.

$$89.06\,{}^{kJ}\!/_{mol} = 40.79\,{}^{kJ}\!/_{mol}\left(1 - \frac{T_o}{373.15}\right) + 74.24\,{}^{kJ}\!/_{mol}\left(1 - \frac{T_o}{T}\right) - (-35.14\,{}^{kJ}\!/_{mol})\left(1 - \frac{T_o}{337.85}\right)$$

$$[5.26]$$

It was found that no physical temperature satisfies equation 5.26. This means that the addition of the minimum amount of heat cannot supply the work required. Other means of putting work into the process, which were discussed in section 5.3, must be considered.

As was shown previously, we can add additional heat to the process and calculate the temperature required for the heat addition to make the process reversible. Figure 5.11 shows the heat addition and temperature required for the process described by equation 5.24.
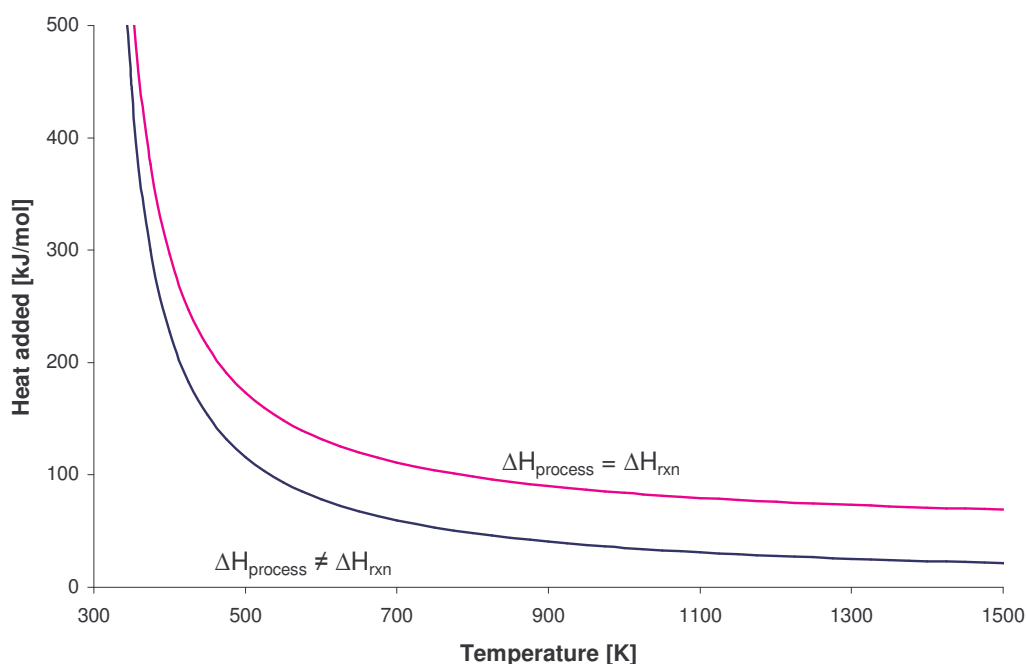
Figure 5.11: The relationship between amount of additional heat required and the temperature for a reversible methanol production process where $\Delta H_{process} \neq \Delta H_{rxn}$ as compared to a process where $\Delta H_{process} = \Delta H_{rxn}$

It is clear from Figure 5.11 that it is possible to make the process reversible by addition of extra work. It is also apparent that at higher temperature, less heat is required. Also, the inclusion of the phase change terms has reduced the heat loads, such that at high temperature the heat required is comparable to the $\Delta H_{process}$. Similarly, the work of compression can also be calculated. In the end, however what the analysis shows that it is not feasible to run this methanol process in a single stage.

5.5   Concluding remarks

In this chapter, we have analysed the overall process, based entirely on the inputs and outputs from the process using mass, energy and entropy. This chapter considers methanol production from methane initially as a one-stage process. It was shown that this process required heat as well as work. It was not possible to match the heat and work requirements for this particular process. In order to overcome this, more work has to be added to the process. The ways of putting in additional work that were considered: (a) adding work via the Carnot engine effect (b) adding work by compression (c) adding work by separation. It was found that methanol production in a one-stage process was not feasible even with the addition of more work.

In the next chapter, we extend the analysis to a two-stage methanol production process and try to determine whether such a configuration is feasible.

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6
DECOMPOSING THE OVERALL PROCESS TARGET[‡]

6.1   Introduction

In the previous chapter, we analyzed an overall process target with regard to mass, energy and entropy. In particularly, we considered a process, producing methanol from methane, which possesses a positive Gibbs energy change. It was shown, for the example considered, that it not feasible to carry out such a process in a single stage. Several methods of overcoming the positive change in Gibbs energy have been suggested [Meissner, 1971; May and Rudd, 1976; Resnick, 1981; Shinnar, 1988]. One of these methods suggests staging the overall process i.e. the feed is first converted into intermediates at certain operating conditions and thereafter these intermediates are converted to the desired product under different operating conditions.

In this chapter, we consider staging the overall process. We will analyze each stage in terms of the concepts (based on mass, energy and entropy) developed in chapter 5. We aim to provide insight into the process and to determine any possible opportunities for material or energy savings.

6.2   Staging the process

Consider the production of methanol from methane, carbon dioxide and water as described in chapter 5. The process is characterized by a positive change in the Gibbs energy and therefore requires a work input. The process also requires a heat input as the enthalpy change for the process is also positive. It was shown, for the process under consideration, that it is not possible to carry the required work using the heat input required for the overall process.   Therefore, an alternative configuration of the process is required i.e. staging the process. Methanol synthesis in practice is done in a two-stage (or two sub-processes) process. In the first stage methane is reformed to produce syngas (CO and H_2) while in the second stage the

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[‡] This chapter is based on a publication: Patel B, Hildebrandt D, Glasser D and Hausberger B, Thermodynamic analysis of processes. 1. Implications of work integration. Ind. Eng. Chem. Res., 44, 2005, pp. 3529 - 3527

synthesis gas is converted into methanol. The two-stage process is shown schematically in Figure 6.1.
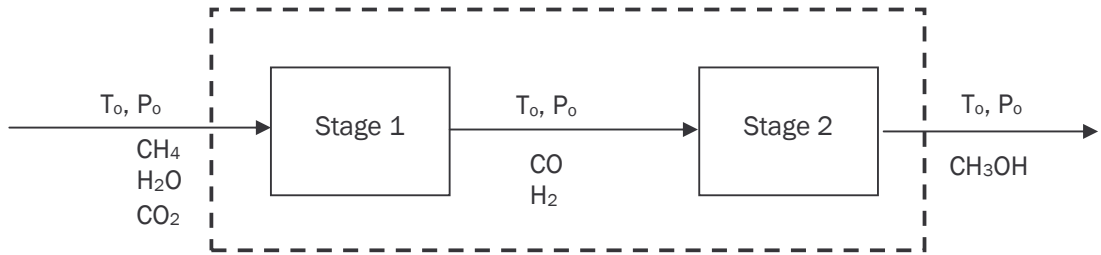
Figure 6.1: Schematic diagram of the two-stage process

We start by considering the mass (or mole) balance for each stage. The mole balances must be such that the addition of the mole balances of the various stages must give the overall mass (or mole) balance as given by equation 5.1.

The first stage of the processor the reforming stage is described by the following mole balance

$$\tfrac{3}{4}CH_4 + \tfrac{1}{4}CO_2 + \tfrac{1}{2}H_2O \xrightarrow[\text{mol bal}]{\text{stage 1}} CO + 2H_2 \qquad [6.1]$$
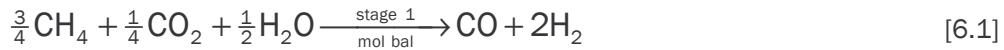
Next we perform an energy balance and entropy balance as discussed in chapter 5. We make the same assumption as stated in chapter 5. The process (stage 1) is endothermic (ΔH_{stage1} = 164.9 kJ/mol) and requires work (ΔG_{stage1} = 113.8 kJ/mol). As ΔG_{stage1} < ΔH_{stage1}, this allows us to potentially supply the required work as high temperature heat. We see for a reversible reforming process operating at $T_{Hcarnot}$

$$\Delta G_{stage1} = \Delta H_{stage1}\left(1 - \frac{T_o}{T_{Hcarnot}}\right) \qquad [6.2]$$

Thus, $T_{Hcarnot}$ is approximately 950 K. This is the temperature at which the minimum amount of heat added (ΔH_{stage1}) to stage 1 (or reformer section) matches the work required. If the reformer section temperature is less than 950 K (i.e. $T_H < T_{Hcarnot}$), then more work will need to be added to the reformer section by some other means. If the reformer section temperature is greater then 950 K (i.e. $T_H > T_{Hcarnot}$), then work could potentially be recovered from the reformer section. This work would then be available for use in other processes (for example, stage 2 (the synthesis section) or

for exporting from the complex). Figure 6.2 illustrates the work potential of stage 1 as a function of temperature.
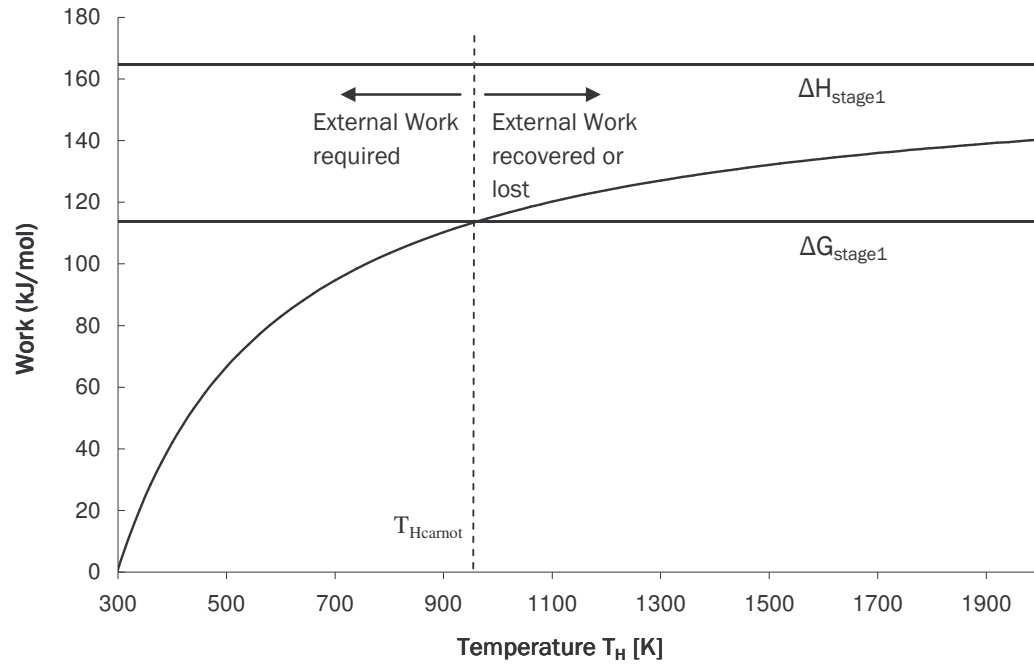
Figure 6.2: The work profile for stage 1 (reforming section) as a function of temperature

The Carnot temperature for stage 1, $T_{Hcarnot}$ could also be modified by adding more heat than required i.e. $Q > \Delta H_{stage1}$ and thus rejecting heat at a lower temperature, for example ambient temperature. In this case, the Carnot temperature will be lower than 950K calculated above. Furthermore, the more heat added to stage 1 over and above ΔH_{stage1}, the lower the Carnot temperature. This is shown in Figure 6.3 which shows how the temperature changes as more heat is added.
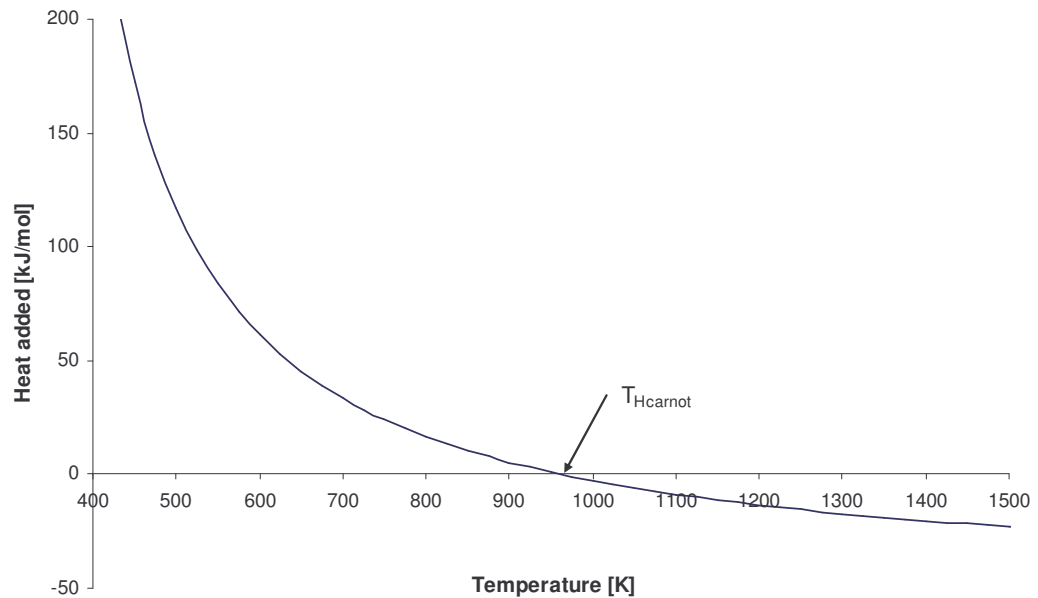
Figure 6.3: The effect of heat addition (over and above the minimum amount of heat, ΔH_{stage1}) on the temperature $T_{HCarnot,Q}$ of the reforming process

We will assume for the purpose of the analysis that stage 1 (the reformer section) has been/or will be designed to consume the minimum amount of energy namely ΔH_{stage1}. In practice, reformers usually run at temperatures greater than the reversible carnot temperature, $T_{Hcarnot}$ hence the reformer section can export work.

The synthesis section can be described by the following mass (or mole) balance

$$CO + 2H_2 \xrightarrow[\text{mol bal}]{\text{stage 2}} CH_3OH_{(liq)}$$

[6.3]

Now this process (stage 2 or the synthesis section) is exothermic i.e. releases energy (ΔH_{stage2} = -128.2 kJ/mol) and produces work (ΔG_{stage2} = -29.07 kJ/mol). If all the work that needs to be removed from the process is exported via a Carnot engine (i.e. by rejecting heat at high temperature), we can see that the synthesis temperature $T_{Ccarnot}$ would need to satisfy:

$$\Delta G_{stage2} = \Delta H_{stage2}\left(1 - \frac{T_o}{T_{Ccarnot}}\right)$$

[6.4]

The Carnot temperature for the synthesis section (stage 2), $T_{Ccarnot}$ can thus be calculated from equation 6.4, and was found to be approximately equal to 400K. If the temperature of the synthesis section is less than $T_{Ccarnot}$, then the process would need to reject the extra work by some other means. However, in practice the synthesis process usually runs hotter than $T_{Ccarnot}$ ($T_C > T_{Ccarnot}$). This means that the synthesis section rejects more work than the for the Gibbs energy change for the synthesis section, ΔG_{stage2}, and hence to satisfy the second law of thermodynamics, more work needs to be added from some other source. This concept is shown pictorially in Figure 6.4.
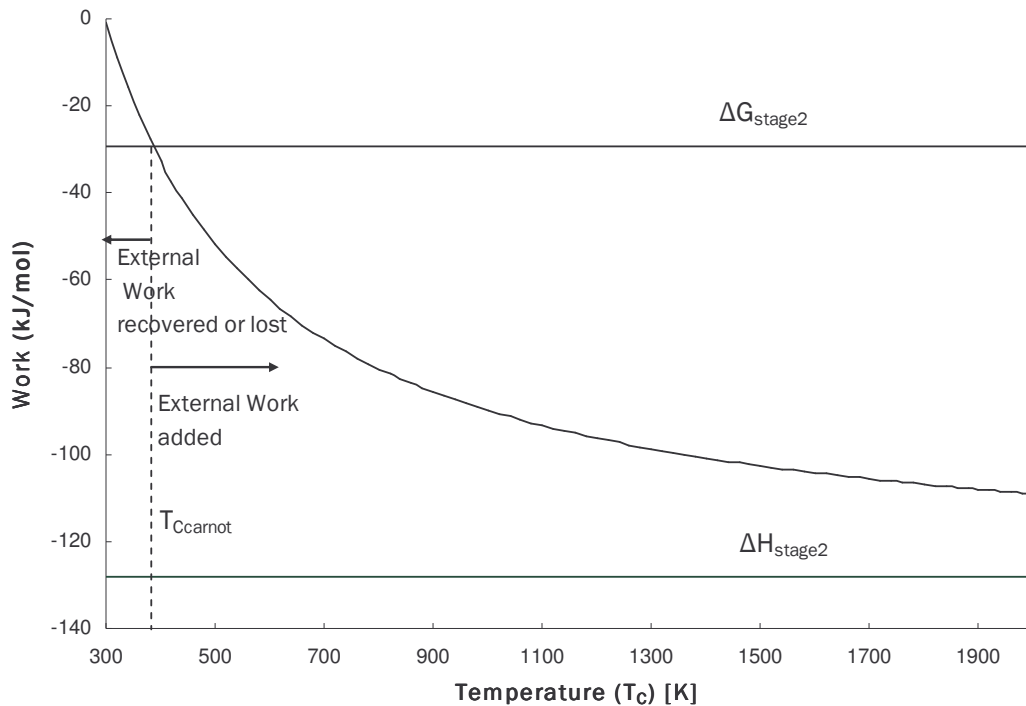
Figure 6.4: Work profile for stage 2 (synthesis section) as a function of temperature

It is clear from the above discussion that the first stage (reforming section), as given by equation 6.1, is energy deficient ($\Delta H_{stage1} > 0$) and work deficient ($\Delta G_{stage1} > 0$) but $\Delta G_{stage1} < \Delta H_{stage2}$. The second stage (synthesis section), as given by equation 6.3, has an excess of energy ($\Delta H_{stage2} < 0$) as well excess work ($\Delta G_{stage2} < 0$) with $\Delta G_{stage2} < \Delta H_{stage2}$. Therefore, it is possible to match the heat and work requirement in the two-stage process. Figure 6.5 summarizes the mass and heat flows in the two stages.
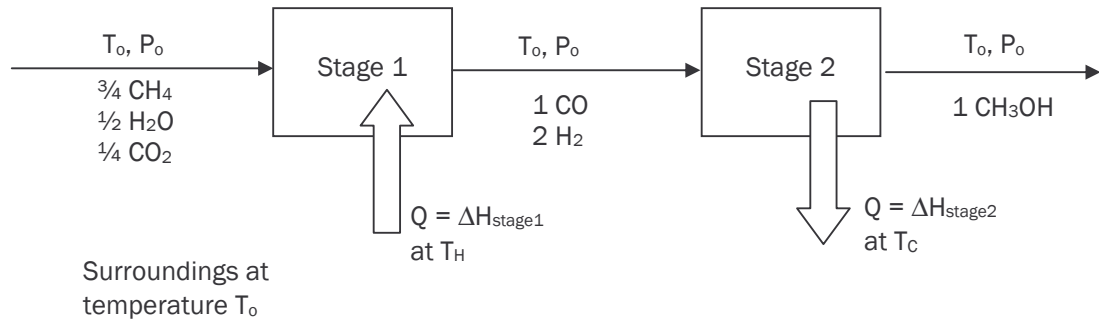
Figure 6.5: Mole flows and heat flows in the two-stage process

In the above discussion, we considered the two stages separately. Let us now consider the process as a whole, in order to determine if opportunities for integration between the stages exist.

We start by performing the energy balance for the two-stage process. We assumed that the minimum energy (ΔH) is to be input into stage 1 and stage 2. Thus, the overall energy balance is

$$Q = \Delta H_{stage1} + \Delta H_{stage2} = \Delta H_{\substack{overall \\ process}} \qquad [6.5]$$

Next, we write the entropy balance for the process. The entropy balance is given by

$$\Delta S_{\substack{overall \\ process}} = S_{gen} + \frac{\Delta H_{stage1}}{T_H} + \frac{\Delta H_{stage2}}{T_C} \qquad [6.6]$$

If we assume reversibility i.e. $S_{gen} = 0$ and we write the overall entropy change in terms of Gibbs energy, we get

$$\Delta G_{\substack{overall \\ process}} = \Delta H_{stage1}\left(1 - \frac{T_o}{T_H}\right) + \Delta H_{stage2}\left(1 - \frac{T_o}{T_C}\right) \qquad [6.7]$$

The above equation (equation 6.7) could also be attained by considering the process as a combination of Carnot engines; stage 1 as a heat pump (since it requires energy) and the stage 2 as a heat engine (since it can potentially supply energy). This is depicted in Figure 6.6.
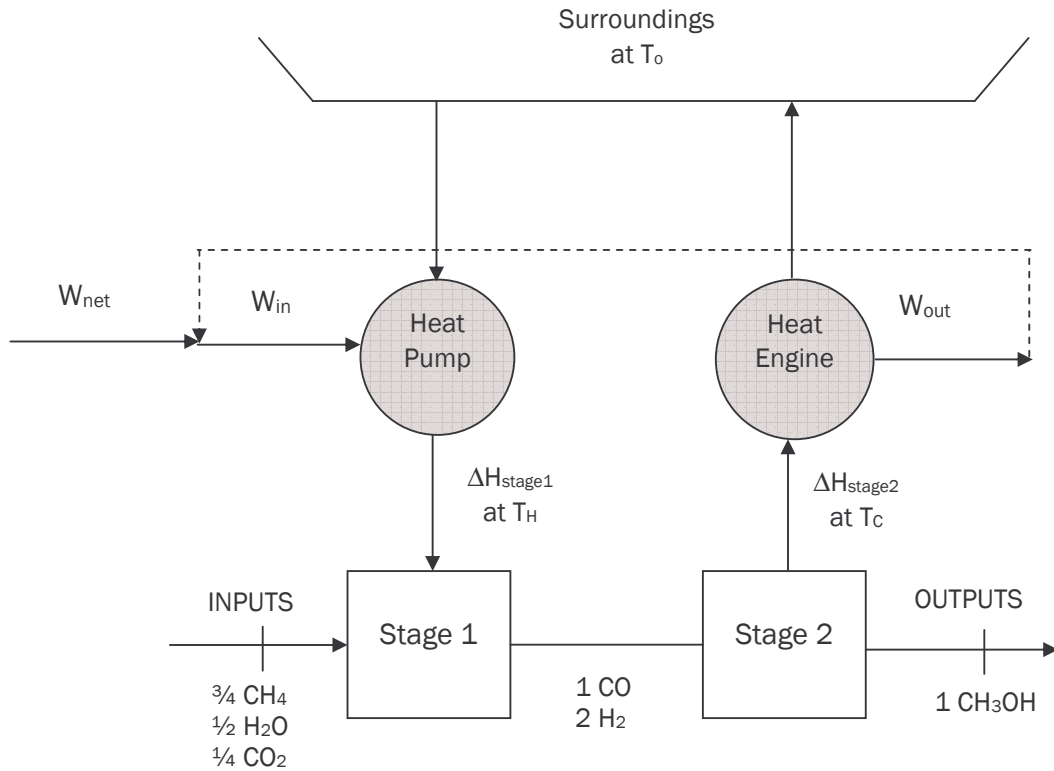
Figure 6.6: The two stage process in terms of Carnot engines

The net work, W_{net} is given as the sum of W_{in} and W_{out}, where W_{in} and W_{out} are given by the Carnot equation. Therefore, W_{net} equals to

$$W_{net} = W_{in} + W_{out} = \Delta H_{stage1}\left(1 - \frac{T_o}{T_H}\right) + \Delta H_{stage2}\left(1 - \frac{T_o}{T_C}\right) \quad \text{[6.8]}$$

It is clear from Figure 6.6 that there is potential to integrate the work flows between stage 1 and stage 2. For a reversible process, the net work, W_{net} must be equal to the change in the Gibbs energy change of the overall process $\Delta G_{process}$. Rearranging leads to equation 6.7. *If the net work, W_{net} is equal to the Gibb energy change of the overall process, the process is defined as being work integrated.*

Consider a plot of the temperature of stage 1 against the temperature of stage 2, as shown in Figure 6.7. One can plot the reversible Carnot temperature of stage 1, $T_{Hcarnot}$ and stage 2, $T_{Ccarnot}$ in order to classify the work flows for the two stages.
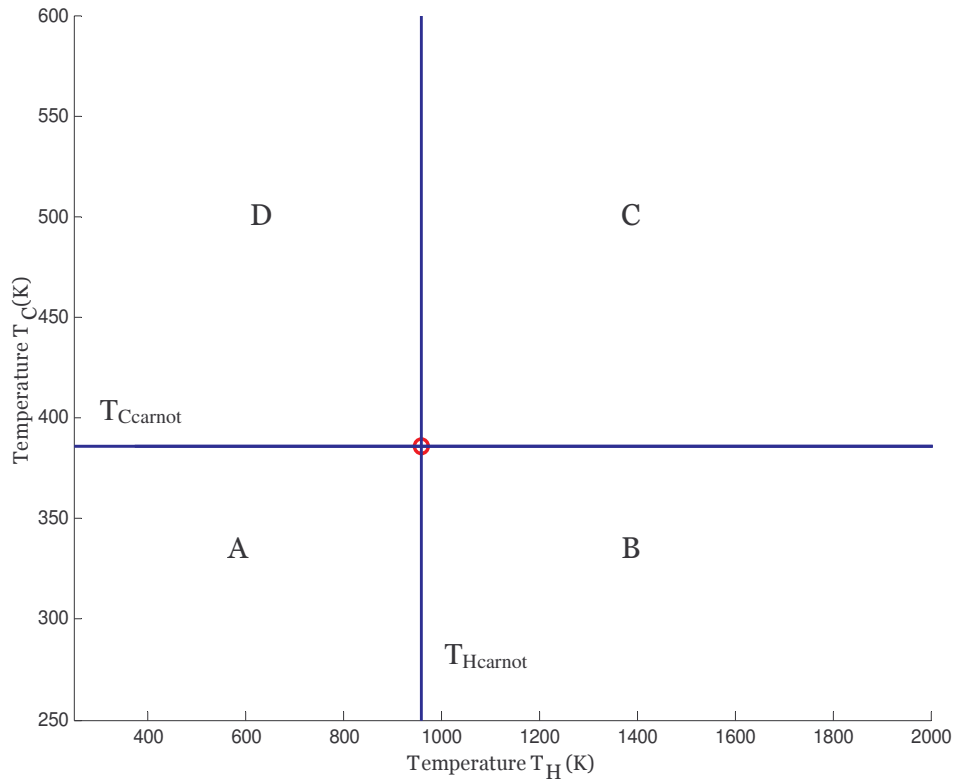
Figure 6.7: The Carnot temperatures of the two staged methanol production process

Figure 6.7 shows the point where both stages are run reversibly in isolation and operate at the Carnot temperature, $T_{Hcarnot}$ (for stage 1) and $T_{Ccarnot}$ (for stage 2). The Carnot temperatures of the two stages ($T_{Hcarnot}$ and $T_{Ccarnot}$) divides the plot (Figure 6.7) into four quadrants labeled A, B, C and D on Figure 6.7:

- Quadrant A is the region where stage 1 requires additional work as the temperature, T_H, is less than $T_{Hcarnot}$. The synthesis section rejects insufficient work via the Carnot engine effect and so this stage must reject extra work ($T_C < T_{Ccarnot}$). This could be lost as irreversibilities or recovered. If it is recovered it can be used in the reformer section (stage 1) as in this quadrant the reformer section is not getting sufficient work from the Carnot engine effect. Thus, there is a possibility to

integrate across the two processes by effectively pumping work from the synthesis stage to the reformer stage.

- In quadrant B both stages export work ($T_H > T_{Hcarnot}$ and $T_C < T_{Ccarnot}$) and hence this work could potentially be recovered. If this work is not recovered then this work would be lost as irreversibilities. There is also no potential to integrate work flows between the two stages in this quadrant.

- In quadrant C we could potentially recover work from the reformer section (stage 1), as the temperature is greater than $T_{Hcarnot}$. Thus, the work supplied is greater than the Gibbs energy change for stage 1, ΔG_{stage1}. The synthesis stage is work short and requires extra work, as the temperatures are greater than $T_{Ccarnot}$. Therefore, the work rejected is greater than the Gibbs energy change for stage 2, ΔG_{stage2}. Again, this allows us to potentially integrate between processes.

- In quadrant D additional work is required for stage 1 (reforming section) since the temperature, T_H is less than $T_{Hcarnot}$, meaning that the work supplied is less than the Gibbs energy change for stage 1, ΔG_{stage1}. Additional work is also required in region A for stage 2 (synthesis section) as the temperature, T_C is greater than the $T_{Ccarnot}$. Thus, the work obtained from stage 2 is greater than the Gibbs energy change, ΔG_{stage2} .A simple integration between the stages is not possible in this quadrant.

Quadrant A and C are the two regions in which there is a possibility of work integrating between the two stages, since these are the regions where one stage rejects work while the other stage requires work. The relationship governing the work integration in these two quadrants can be determined from equation 6.7. This relationship is shown in Figure 6.8.
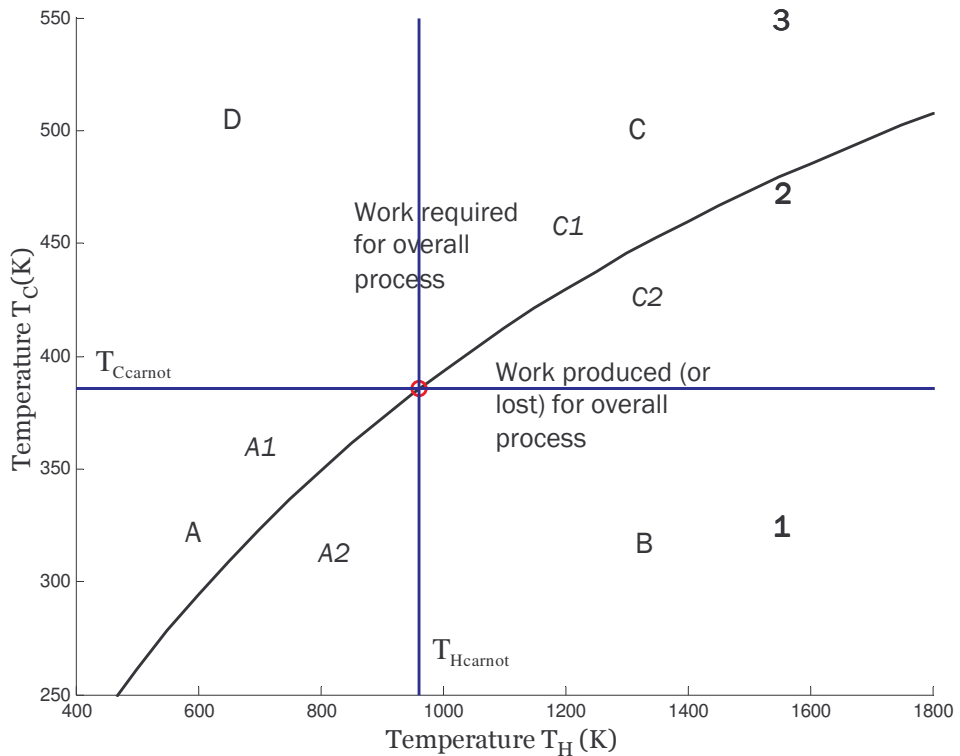
Figure 6.8: Relationship between the temperatures of the two stages for a reversible methanol production process

Figure 6.8 shows how the temperature of the two stages T_H and T_C are related in order for the overall process to be reversible. It is clear that by considering the two stages together as a system allows an entire curve to be defined instead of just a single point where the overall process would be reversible. Above the curve the net work to the process is less than the Gibbs energy change for the overall process (i.e. the minimum work required for the process) and therefore external work has to be supplied to the process. In the region below the curve the net work to the process is greater than the Gibbs energy change for the overall process. Therefore, work can potentially be produced in this region. If this work is not recovered, it will be lost (appear as irreversibilities in the process).

It is clear that the work-integrated curve falls in quadrants A and C. Region A and C can be divided even further into regions A1, A2, C1 and C2 as shown in Figure 6.8. Region C1 corresponds to the region where additional work must be specifically added to the synthesis section (stage 2), since region C1 lies above the reversible

curve. Region C2 is the region where the reforming section (stage 1) will produce (or lose) work as the region lies below the reversible curve. In region A1 additional work must be specifically added to the reforming section (stage 1) while in region A2 work can be produced (or lost) from the synthesis section(stage 2).Thus, it is possible to determine exactly which stage has the work surplus or deficit.

Let us examine what other information Figure 1.8 provides one with. If T_H and T_C are set to lie at point 1 say (shown in Figure 1.8), then for the methanol process to be reversible, work would need to be recovered from both the reformer and synthesis section. The further point 1 is from the curve, the more work could be recovered. If the work is not recovered it would manifest itself as irreversibilities or entropy generation.

Point 2 corresponds to a reversible process where the work exported from the reformer section matches the work deficit of the synthesis section. Hence, there is no surplus work for export nor is there a deficit of work.

Point 3 is interesting in that it corresponds to operating temperatures currently employed by methanol processes. As explained previously the temperature of the synthesis section (stage 2) is such that it exports more work than required with the Carnot engine effect. Thus, the synthesis stage is work deficient. Furthermore, the work that can be exported from the reformer section is less than the work required by the synthesis stage. Thus even if we pumped all the excess work from the reformer section to the synthesis section, the synthesis section would still require work. Thus, this work has to be supplied by some other means. The further point 3 is from the curve, the more work must be supplied externally.

The potential for integration between stages are clarified pictorially in Figure 13.
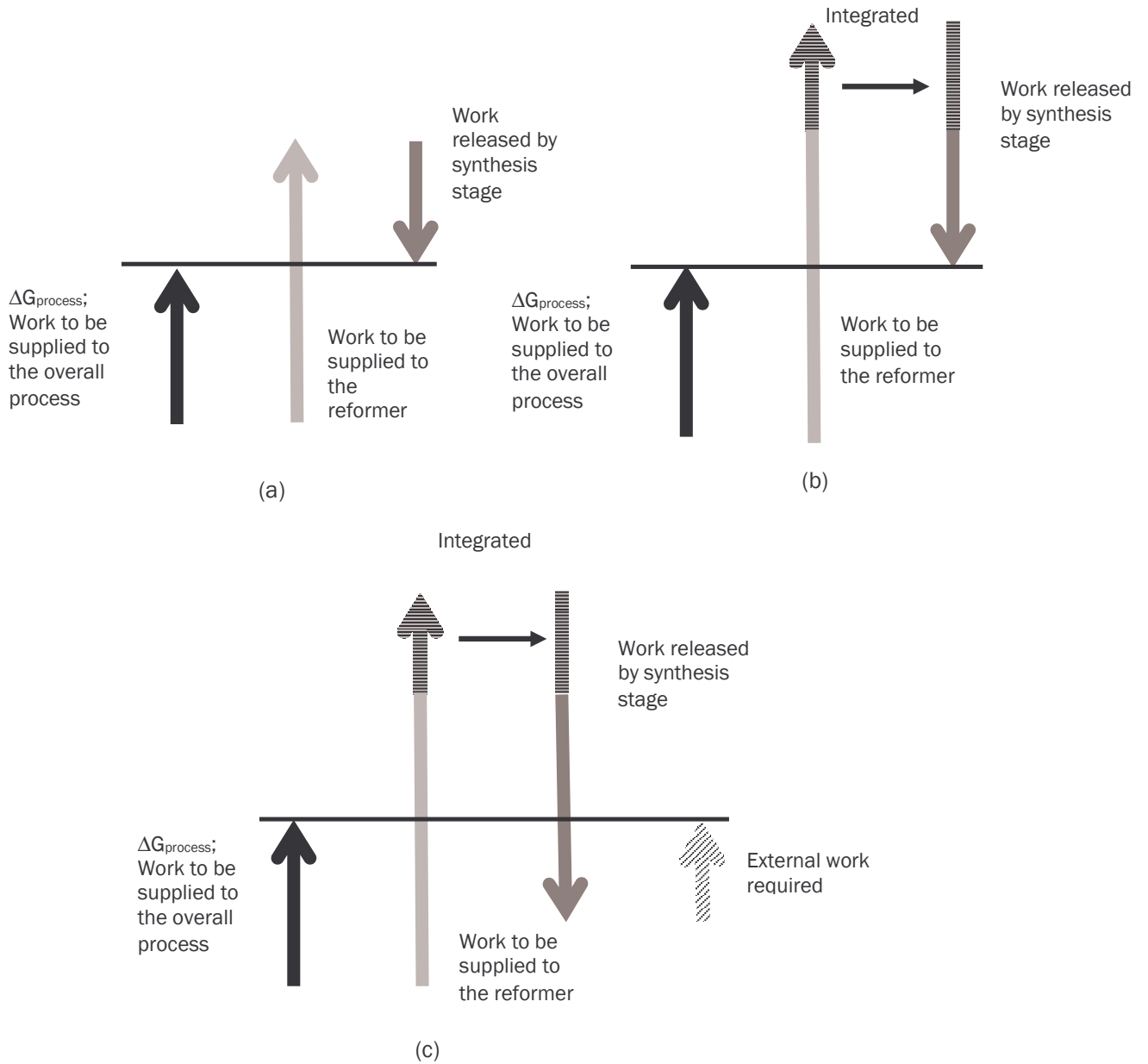
Figure 6.9: Pictorial representation of the work flows for the two-stage methanol production process (a) Reformer section running at $T_{Hcarnot}$ and synthesis section running at $T_{Ccarnot}$ (shown by the circle on Figure 6.8) (b) Process running at point 2 (Figure 6.8) (c) Process running at point 3 (Figure 6.8)

Let us consider processes' operating at point 3 as this is where most commercial methanol processes tend to operate (in terms of temperatures of the reformers and

synthesis sections). Processes operating at point 3 require external work. In the previous chapter, we considered three ways of putting in additional work. We shall again look at putting work in by compression, as this is one of the most common ways of inputting additional work in practice. Work could put in by separation but as explained previously, the work put in by this method is usually rather small (if one does not have large flowrates). Work could be input by the Carnot engine effect and adjusting the heat flows, but this is not considered in this chapter.

6.3 Work addition by compression for multistage processes

An alternative way of supplying the external work is by coupling the two-stage system with a compressor, since the processes usually consists of gaseous feeds and intermediate products. In order to determine where the compressor is to be positioned one needs to consider the number of moles entering the compressor as the work of the compressor is proportional to the number of moles entering the compressor.
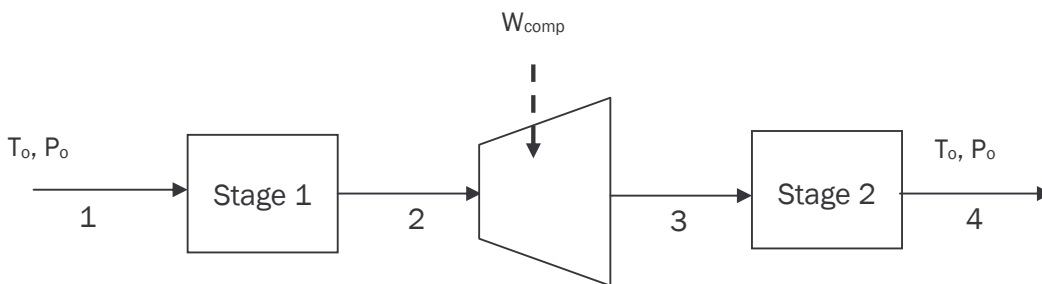
Figure 6.10: Schematic diagram of the two-stage methanol production process with compression between stages

Considering the production of methanol, the reformer section (occurring at temperature T_H) is accompanied by an increase in volume whereas the volume decreases in synthesis section (occurring at temperature T_C). Running the reformer section at high pressure (with the synthesis section at atmospheric pressure) is thus not an option for putting extra work in. Running both stages at high pressure is an option as the overall process is accompanied with a decrease in volume. However, compression of the intermediate product (in this case CO and H_2) will be the most effective way of putting in work as the synthesis section is accompanied with a large decrease in volume. In addition, since the final product (i.e. methanol) is taken as a

liquid, there is no large gain in work in reducing the pressure of the output stream. Therefore, the compressor will be placed between the two stages as shown in Figure 6.10.

The entropy balance can be written to include the work of compression for the two-stage process, as was done for the one stage process. The equation for the process is given by

$$\Delta G_{\substack{overall \\ process}} = \Delta H_{stage1}\left(1 - \frac{T_o}{T_H}\right) + \Delta H_{stage2}\left(1 - \frac{T_o}{T_C}\right) + W_{comp} \qquad [6.9]$$

The compressor is considered to operate isothermally, and is described as discussed in the previous chapter.

Using equation 6.9, the effect of adding work via the compressor can be determined for the two stage process. The effect of compression is plotted in Figure 6.10, which relates the reformer section (stage 1) temperature (T_H) and synthesis section (stage 2) temperatures (T_C). Figure 6.10 shows the work input by means of compression from the ambient pressure to various pressures. The compression is done between the two stages; therefore, it gives an indication of the pressure at which the second stage (the synthesis stage) should operate.
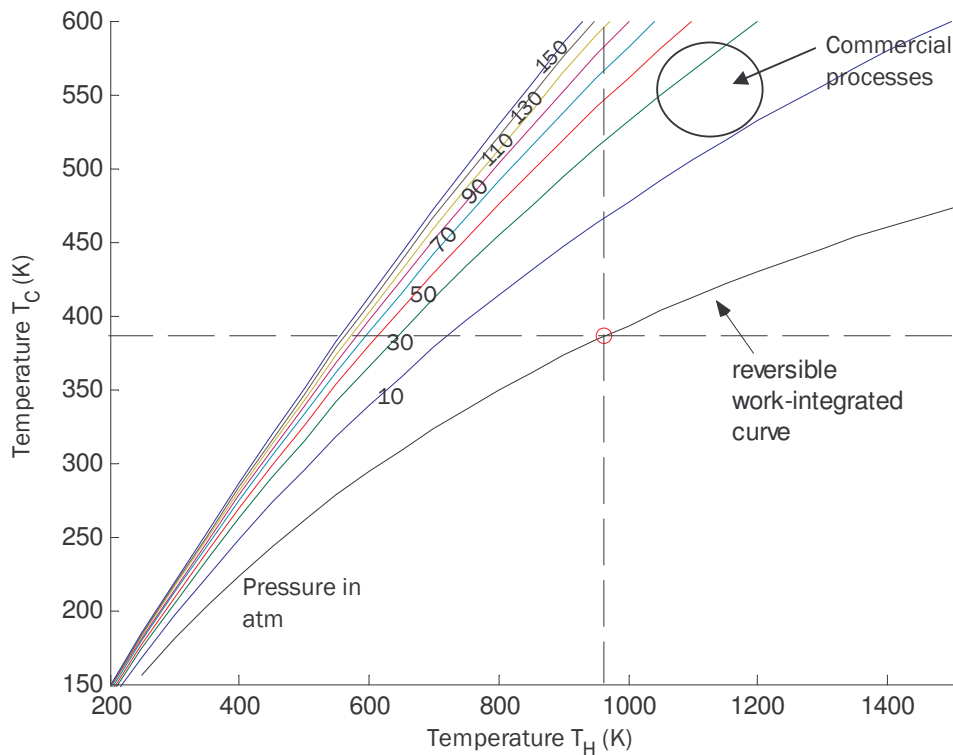
Figure 6.11: The effect of isothermal compression on the work integrated curve for the two-stage methanol production process

It is clear that by compressing the feed to the synthesis stage (i.e. running it at high pressures), one is able to put in enough work for the process to run in regions which were previously unfeasible. It can also be seen from Figure 6.11 by comparing the distances between the pressure curves, that the amount of work gained at low pressures is much greater compared to the worked gained at high pressures. We note that the work added to the process is real shaft work and so the energy balance has to take into account this work.

Most commercial methanol processes operate at high pressures of 50 – 100 bar (Twigg, 1989; Lange, 2001). It is clear that the technique (which only requires simple thermodynamic data) is able to give an initial estimate of the pressure required for the process and the values predicted are close to those used commercially as shown in Figure 6.11. The technique under-predicts the pressure to a certain extent, which may be due to the assumption of an isothermal compression (ideal compression) and the fact that the compression in commercial processes are associated with irreversibilities. Therefore, Figure 6.11 is useful in estimating the pressure at which the process should operate once the temperature limitations (catalyst properties, material limitations etc) of the stages are taken into account. These calculations are simple to carry out and are a good estimate at an early stage in the design process.

We also note that modern commercial methanol processes, with the temperature limitations on the operating regions for the reformer section and synthesis section, appear to be fairly well integrated, as they appear to be recovering the work produced in the synthesis stage and these processes operate at around the minimum predicted pressure.

6.4   Concluding remarks

This chapter proposes a new technique, based on the mass, energy and entropy balance, for process synthesis and integration. The technique is applied during the conceptual phase of the design process, and therefore requires little information regarding the structure of the process.

The technique allows one to determine the minimum work requirements for a process, considers matching the work and heat requirements, systematically analyzes the work flows in a process, determine whether integration of work flows is possible and suggests ways of supplying additional work.

In this chapter, the analysis was then extended to a two-stage methanol production process. We showed how it is possible to integrate work between the two stages. It was shown that commercial methanol process still requires extra work, even after one considers work integration. We therefore also considered adding extra work by compression, and were able to predict the minimum pressure required in order to make the process feasible.

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7

APPLICATIONS§

7.1 Introduction

In the previous chapters, mass, energy and entropy was used to analyze a methanol process. The heat and work flows were calculated using elementary thermodynamic data. This allowed targets to be set for the heat and work flows and from this for operating temperatures and pressures could be calculated. These targets represent the limits of operation for reversible processes, i.e. processes that operate with no entropy generation. The targets are important as processes operating at these targets have minimum heat and work loads, which in turn corresponds to minimum operating costs of the plant. In addition, processes operating at these targets also have we believe, if not minimum, at least reduced capital costs. The simultaneous reduction in both capital and operating costs occurs because as heat and work loads decrease, the process equipment becomes smaller and, in same cases, less complex in order to handle the decreased heat and work flows. Thus, we believe that these targets are useful for synthesis as well as analysis.

This paper will apply the work integration concept to assess and compare various processes using natural gas as a chemical feedstock, viz. methanol synthesis, ammonia synthesis and hydrocarbons production (Fischer-Tropsch synthesis).The use of natural gas in the production of chemicals is becoming increasingly important in the energy market (Rostrup-Nielson, 2002). The need to achieve high efficiencies in such processes in order to reduce both capital and operating costs is therefore a necessity. Improvements in such processes may be attained by investigating the thermodynamics, in particular a second law analysis (exergy analysis), of such processes (Rosen, 1996). We wish to identify operating targets for these processes, compare heat and work flows and finally to show interesting similarities as well as differences in these flows. As a result of the differences, the potential for work integration is different in the various processes. Understanding the interaction between the targets and the heat and work flows allows us to identify areas for future research in order to realize the potential opportunities.

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Usually commercial processes require an indirect conversion of the methane into product via the production of synthesis gas (carbon monoxide and hydrogen). Synthesis gas is usually produced by reforming, which is requires work at standard conditions ($\Delta G > 0$) and energy ($\Delta H > 0$) reaction. The synthesis step (i.e. the production of the required chemical) produces work at standard conditions ($\Delta G < 0$) and energy ($\Delta H < 0$)

The issue of supplying the external work (i.e. in addition to the work that flows in our out of the process with the heat transferred to or from the process) required by processes such as the methanol synthesis process will also be investigated. Ways of putting in external work will be discussed with respect to the various processes. In particular, work can be externally supplied by the work of separation or by compression. Both these methods of supplying work will be considered in this paper.

7.2   Analysis of processes

We will briefly summarize the approach that has been developed in a systematic way, so that the method can be applied more generally.

1) Write the *overall mass balance* for the process by considering the input and outputs of the process. We wish to emphasize that this is for the plant as a whole and need not be for a specific reaction. Furthermore one can look at different process mass balances. For example in making methanol from natural gas, one might not have used carbon dioxide as feedstock as was the case in chapter 5 and 6.

2) Write an *overall energy balance* for the mass balance as given. For the initial analysis, one should not include shaft work. Shaft work may need to be included at a later stage.

3) Write an overall work balance for the process (based on the entropy balance). In the first instance, assume the process is reversible.

4) Check whether there is a feasible temperature at which to operate the single stage process such that the process is reversible. If it is possible then this is likely to be the best and cheapest way to run the process provided the reaction can be run at this temperature (e.g. catalyst available). If cannot run at this temperature then extra work may need to be supplied to the reactor and removed at a later stage.

5) If no feasible temperature, in particular because work needs to be supplied to the process, then check whether this can be done via the three methods commonly available

   a. Check if enough extra heat can be added at the reactor temperature such that the required work can be put in and check that this extra heat can be readily removed at a lower temperature.

   b. Check if by running the system at different pressure one can supply or remove the required work. In this case one needs to add the shaft work to the overall energy balance.

   c. Check whether one can add the extra work to the system by adding the work of separation. One can also check whether one can add the extra work by changing the phases of the reactants and products

6) If the one stage process cannot be achieved, consider a two step process and repeat steps 1) to 5)

We notice that we have only looked at the fundamental process and the utilities have been consigned to only supplying or removing heat. If for instance we provide the heat for gasification or reforming by burning natural gas with oxygen in the main process then this would not be regarded as a utility but part of the main process. We have also not looked at the irreversibilities of the individual pieces of equipment, but rather the structural irreversibilities of the overall process. By this we mean the irreversibilities associated with the mismatch between the operating conditions of the various major components of the flowsheet. These structural irreversibilities could be large and these are ones that the designer could most easily overcome by changes in the flowsheet design.

7.3   Process descriptions: One stage process

A brief simplified description of the three processes will be given in the sections that follow. Details of typical flowsheets, process descriptions and reviews for methanol synthesis, ammonia synthesis and Gas-to-Liquids synthesis can be found in textbooks (Austin, 1984; Twigg, 1989; Kroschwitz, 1991) and the literature and will not be described here. In this chapter, we are rather developing tools for *synthesizing processes* in order eventually to be able to develop the optimal flowsheet and operating conditions.

We will initially consider the overall process. By this, we mean that the input to the process is our feed material; these are converted in the process and the output from the process is the desired product and any byproducts that are formed. In particular, we will analyze the process by considering the mass, energy and entropy flows. We will regard any heat that must be added or removed from the processes a heat flow with an associated temperature. We will not consider the utility streams that absorb or provide the heat at this stage. Hence, we separate utility and process streams.

Initially, to simplify the approach, we will assume that the major transfer of heat occurs at a single process operation, for example a reactor. Other typical process operations with large heat duties could be where phase changes, for example, occur. For simplicity we will assume that the reaction in our process occurs at a single temperature T and that a quantity of heat Q is supplied (or removed) at the temperature T which corresponds to the temperature that the reaction occurs at.

7.3.1 Process mass balance

One can write a mass balance for the *overall process,* relating inputs to outputs. The form of this mass balance looks like a chemical reaction, but it need not correspond to the actual reaction occurring in the reactors in more complex processes. We also for the purposes of clarity indicate the phases of the process inputs and outputs in the mass balance description.

> *Example: Process Mass Balances for Methanol, Ammonia and Gas-to-Liquids Processes*
> We now consider the overall process mass balances for our three example processes, namely methanol, ammonia and Gas-to-Liquids synthesis. A basis of 1 mole of final product is taken in order to compare the various processes. All three processes are based on a methane feed.
>
> *The Process Mass Balance for a Methanol Synthesis Process*
>
> $$\tfrac{3}{4} CH_{4(g)} + \tfrac{1}{4} CO_{2(g)} + \tfrac{1}{2} H_2O_{(l)} \xrightarrow[\text{mol bal}]{\text{process}} 1\, CH_3OH_{(l)} \qquad [7.1]$$
>
> Note that in the previous chapter, we considered water in the vapour form, but in this chapter we will consider liquid water.
>
> *The Process Mass Balance for an Ammonia Synthesis Process*
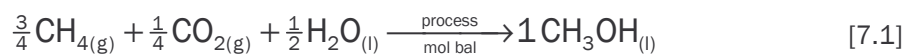
$$\tfrac{3}{8}\,CH_{4(g)} + \tfrac{1}{2}\,N_{2(g)} + \tfrac{3}{4}\,H_2O_{(l)} \xrightarrow[\text{mol bal}]{\text{process}} 1\,NH_{3(l)} + \tfrac{3}{8}\,CO_{2(g)} \qquad [7.2]$$
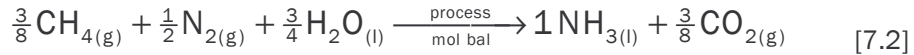
The Process Mass Balance for a Gas-to-Liquids Process

$$nCH_{4(g)} \xrightarrow[\text{mol bal}]{\text{process}} (-CH_2-)_{n(l)} + nH_{2(g)} \qquad [7.3]$$

where n is the average carbon number

We note that the mass balances given above are not unique, in that different feeds and combinations of feeds could be used to produce the products. For example, we could produce methanol from a feed of methane and oxygen, or by combining methane and oxygen produce Fischer Tropsch products with water as a waste by product. We however are not going to examine the effect of different feeds and, for the purpose of this chapter, we will assume that the process mass balances given above are fixed and not open to optimization.

The overall mass balance also provides insights into the carbon dioxide emissions as well as the production of by-products from each process. It is clear that carbon dioxide is required as a feed material in the methanol synthesis process whereas carbon dioxide will be produced in the ammonia synthesis process as all the carbon from the methane will end up as carbon dioxide. The Gas-to-Liquids process will produce hydrogen as a by-product.

7.3.2 Process energy balance

Just as the overall process has a process mass balance, the overall process also has an overall or process energy balance. Assume that the input and output stream are at ambient conditions (T_o and P_o). The process energy balance is described by:

$$\Delta H_{process} = H_{outputs} - H_{inputs} = Q$$
$$= \Delta H(T_0, P_0)$$

where Q is the amount of heat that must be supplied or removed from the process, H_{output} is the total enthalpy of the output streams, H_{input} is the total enthalpy of the input streams, and $\Delta H(T_o, P_o)$ is the enthalpy of reaction as described by the process mass balance calculated at temperature T_o and pressure P_o.

Thus we can see that the amount of heat Q that a process needs either to be supplied to it or removed is related to the enthalpy of the *overall or process mass balance*. Furthermore the amount of heat that needs to be either supplied or removed from a process is unique once the process inputs and outputs have been specified. Again we reiterate that the equation described by the overall mass balance need not be the reactions occurring in the actual process. Furthermore, no matter what the actual reactions are in the process, the nett quantity of energy that needs to be either supplied or removed from the process is fixed by the overall mass balance. The only way for example to reduce the energy requirement of a process is to change the process mass balance and hence the process inputs and outputs. The process energy balance does not tell us about the *quality* of the energy that needs to be supplied; to answer this we need to consider the entropy or exergy balance across the process and this will be done in the next section.

Example: Process Energy Balances for Methanol, Ammonia and Gas-to-Liquids Synthesis

The amount of heat that needs to be added to each of the three processes is calculated from the overall energy balances and is given in Table 1. All three processes are *endothermic* and this heat would need to be supplied by the utilities. We also see that the methanol synthesis process is the most endothermic of the three processes. Hence, one could expect that heat addition is an issue in the methanol synthesis process and that this would increase the capital and running costs of this process as compared to ammonia synthesis and Gas-to-Liquids synthesis processes.

Furthermore the addition of heat is usually done in these processes by combusting feed material, for example methane. Hence supplying this extra heat results in additional CO_2 production over and above the CO_2 target inherent in the process mass balance. If we consider supplying the energy by combusting methane, the amount of CO_2 produced to supply this energy can be calculated. The amount of CO_2 produced can be calculated by dividing the energy requirements of each process by the enthalpy of combustion of methane ($\Delta H_{combustion}$ = -890. 36 kJ/mol). The results are shown in Table 7.1. It is clear that the methanol process will produce the most CO_2 to supply the energy requirements whereas the ammonia synthesis process will produce the least since it requires the least energy. It can also be deduced that the amount of CO_2 produced due to energy requirements are small relative to the

amounts produced due to mass balance requirement. This is clear in terms of the ammonia synthesis process.

Table 7.1: Energy requirements for each process and amount of CO_2 produced to supply the required energy

Process	Energy Requirements (kJ/mol product)	Moles CO_2 produced from the mass balance	Additional moles of CO_2 produced per mol product to supply energy
Methanol synthesis	58.74	0	0.066
Ammonia synthesis	27.84	0.375	0.031
Gas-to-Liquids Process	43.49	0	0.049

Modifying the overall mass balance as described previously, also modifies the overall energy balance and this may have benefits in reducing energy requirements.

We also note that we can always supply more heat then that calculated in Table 7.1 to a process. Thus, for example we could supply 70 KJ/mol of heat per mole of methanol produced to the methanol process, which is 11 KJ/mol over and above that calculated for methanol synthesis. The process would then need to reject 11 kJ/mol of heat per mol of methanol produced, as described previously in Chapter 5.

Adding additional energy (over the minimum required from the energy balance) would increase both the running and capital costs of the process. However, it may increase the flexibility in the design as this extra energy stream is a way of supplying or removing additional work from the process. This flexibility is gained as the extra energy may be supplied at a temperature that is different to the temperature at which the energy is rejected, which allows work to be either added or removed from the process. This will be expanded on in the next section.

7.3.3 Process entropy balance

The *quality* of energy added or removed from a process affects the entropy or exergy generated in the process and hence the degree of irreversibility of the process.

From the second law of thermodynamics, the overall change in entropy of the process and associated heat flows must either be greater or equal to zero.

If the change of entropy is zero (i.e. the entropy "balances") then the process is reversible. This is a limit of operation of the plant. Usually we consider that entropy is generated by driving forces of temperature, pressure and chemical potential. We furthermore consider that all process have to have driving forces in order to keep the size of the equipment reasonable and so keep capital costs down. Thus we usually consider a reversible process to be one where the driving forces are tending to infinitely small.

We speculate that a major source of entropy generation in many chemical processes is by the choice of (incorrect) operating temperatures. We believe in fact that this source of irreversibility typically produces larger entropy losses than the temperature, pressure and chemical potential driving forces that we typically accept in order to keep process equipment size reasonable. We note that operating the process at the reversible temperature, in contrast to making equipment driving forces zero, does not inherently cause infinitely large processes. *We therefore postulate that a goal of synthesizing a process is to try and design processes such that the operating temperature is in fact the reversible temperature.*

It has been shown that the amount of work that must be added or removed from the process, W, is equal to the change in the Gibbs Energy of the overall process mass balance description at the process input conditions, i.e.:

$$W = \Delta G_{process} = G_{outputs} - G_{inputs}$$
$$= \Delta G(T_O, P_O)$$

where G_{input} is the total Gibbs Energy of the input streams, G_{output} is the total Gibbs Energy of the output streams and $\Delta G(T_o, P_o)$ is the Gibbs Energy of the process mass balance at the temperature T_o and pressure P_o. The overall change in Gibbs Energies for the three processes is given in Table 2. We see firstly that all three process require work to be added (i.e. $\Delta G_{process} > 0$) and that the work loads follow a different trend compared to the overall process heat loads in that methanol synthesis has the largest work and heat requirements while the ammonia synthesis process has the smallest work and heat requirements.

Table 7.2: Work requirements for each process

Process	Work Requirements (kJ/mol product)
Methanol Synthesis	88.93
Ammonia Synthesis	38.03
Gas-to-Liquids Process	51.47

The designer has many way of adding or removing work from a process. One way that one can add substantial quantities of work to a process that are highly endothermic i.e. that require energy, is by controlling the temperature of the heat that is added to the process. The higher the temperature of the heat the more "work potential" it carries with it into the process. The designer can determine if there is a temperature T at which the heat supplied can carry all the required work with it. If it is possible to set the temperature so that the energy required for the process carries with it the required work, this temperature is the temperature we previously referred to as the reversible or Carnot temperature.

Example: Analysis of a one stage Ammonia, Methanol and Gas-to-Liquids processes

We will again consider building a one-stage process for methanol, ammonia and Gas-to-Liquids synthesis. By this we mean a process were we take our feeds of methane, carbon dioxide and water and convert them in a one-stage reaction to the desired product. In particular, we will consider the entropy/exergy generation. As stated above, we will assume that the major transfer of heat occurs at the reactor and furthermore for simplicity we will assume that the reactor is at a single temperature.

There is no positive reversible temperature for all three processes i.e. methanol, ammonia and Gas-to-Liquid synthesis (all three processes have $\Delta G/\Delta H$ greater than one) and hence one can conclude that there is no feasible temperature at which the heat can be supplied, which will:

- Allow the entropy change of the of the process to be greater or equal to zero, or alternatively

- Allow sufficient work to be carried in with the energy of the process to meet the process requirements.

Thus a one stage methanol, ammonia or Fischer-Tropsch process in which the heat supplied Q = $\Delta H_{process}$ is not feasible. However, there are interesting differences between the Gas-to-Liquid process and methanol and ammonia synthesis which results in the different work flows in the overall processes as will be shown later.

At this stage there are various options that the designer can consider. The first is that excess heat is supplied to the process (i.e. Q = ($\Delta H_{process}$ + δQ) as described in chapter 5 at temperature $T_{\delta Q}$. If the excess heat, δQ, is rejected at temperature T_c and $T_{\delta Q}$ >T_c, then sufficient work might be added to the process in this way. For a given quantity of excess heat, δQ, added to the process, the most work will be added when the heat is rejected at ambient conditions, i.e. T_c = T_o. Thus, for a reversible process, the relationship between the amount of extra heat added δQ and the reversible Carnot temperature of the heat $T_{carnot,\delta Q}$ was derived in chapter 5. Notice that temperature $T_{carnot,\delta Q}$ too defines a temperature at which the process operates reversibly. The difference from the temperature T_{carnot} that we previously called the Carnot temperature, is that that in the latter case the amount of heat that was added to the process was the minimum, namely Q = ΔH (T_o, P_o) or equivalently δQ = 0.

We would expect that a process operating with excess heat flows will be more expensive than a process where the heat added is the minimum, i.e. δQ = 0 or Q = ΔH (T_o, P_o), because:
- Running cost would be higher as there is more energy (δQ) supplied to the process
- Capital cost would be higher because there is increased heat duty both in supplying heat and in rejecting heat, leading to more and bigger heat exchangers (all other things being the same).

The relationship between quantity of heat δQ and the reversible Carnot temperature, $T_{carnot,\ \delta Q}$, for the methanol, ammonia and Gas-to-Liquid process is given in Figure 7.1 below.
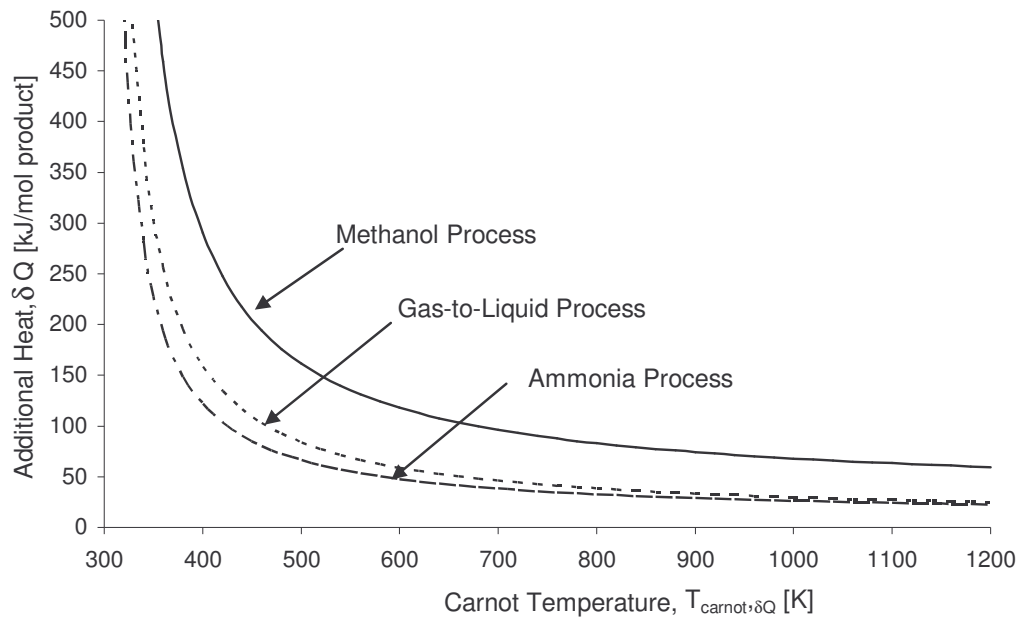
Figure 7.1: The relationship between the amount of additional heat required δQ and the temperature $T_{carnot, \delta Q}$ for a reversible methanol, ammonia and Gas-to-Liquid process

It is clear that by increasing the heat flow to the process, it is possible to design a reversible process which operates at a reversible temperature, $T_{carnot,\delta Q}$ for all three processes. It is also clear from Figure 7.1 that the additional heat required is quite large if we operate at low temperatures for all three processes. Therefore, it may not be practical to operate processes at these low temperatures. At higher temperatures, the heat requirements are comparable to the enthalpy change of the process, $\Delta H_{process}$. From the three processes being considered, the methanol process would require the most additional heat, δQ whereas the ammonia and Fischer-Tropsch process require similar amounts of additional heat.

It important to understand that if the quantity of heat and temperature are chosen so as to lie on the curve shown in Figure 7.1, then the process is such that the increased heat flow to the process carries the required amount of work with it, namely $\Delta G_{process}$. If it is necessary to use increased heat flow to meet the work requirements of the process, *then we believe that a process with an operating temperature on the curve*

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would correspond to the process with the minimum running costs and capital costs within all possible process that operate with the increased heat flow δQ.

Processes that are Work Deficient

If the temperature at which the amount of heat δQ, $T_{\delta Q}$, is added is such that the operating point lies *below* the curve, i.e. $T_{\delta Q} < T_{carnot,\delta Q}$, then the process is work deficient, that is the work supplied by the heat flow is not sufficient and thus additional work will need to be added to the process. The amount of work that needs to be added is given by:

$$W_{deficit} = \Delta G_{process} - \Delta H_{process}\left(1 - \frac{T_o}{T_{\delta Q}}\right) + \delta Q\left(1 - \frac{T_o}{T_{\delta Q}}\right) \qquad [7.4]$$

In order to make the process feasible, and amount of work $W_{deficit}$ would need to be added in alternative ways (i.e. not via the *quality* of heat) to the process. We will later look at how this extra work is added in typical commercial processes. However what should be clear is that having to add extra work increases the complexity of the plant and hence operating and capital costs.

Process Reversibility and Rejecting Work

If temperature at which the amount of heat δQ is added is such that the operating point lies *above* the curve, i.e. $T_{\delta Q} > T_{carnot,\delta Q}$ then the heat carries excess work with it into the process, the amount being W_{excess} given by:

$$W_{excess} = \Delta H_{process}\left(1 - \frac{T_o}{T_{\delta Q}}\right) + \delta Q\left(1 - \frac{T_o}{T_{\delta Q}}\right) - \Delta G_{process} \qquad [7.5]$$

The quantities of work that need to be rejected are typically large (in other words of a similar order to the Gibbs Energy of the process). If this excess work is rejected via irreversibilities in a process, namely temperature, pressure or chemical potential gradients, this work potential is lost.

However, in this situation one might rather be able to design the process so that the excess work that must be rejected can be recovered rather than lost. Thus the process must be designed in such a way, for example, that there is a place in the process where there is a heat flow that carries the excess work out of the process with it. (This also means that the process has to be designed so that the same quantity of heat flows into the process in order to conserve energy across the

process) This again obviously increases the complexity of the process design and operation, and hence we believe operating and capital costs.

We speculate firstly that in the typical process design of processes such as methanol, ammonia and Gas-to-Liquid synthesis where $\Delta G_{process}$ and $\Delta H_{process}$ are large, the quantity of entropy generated or work lost via temperature, pressure and chemical potential gradients *in a well designed process* should be typically small compared to the value of W_{excess}. Thus we can in the limit initially assume that the amount of work lost through driving forces in a well designed process is negligible and hence does not introduce large irreversibilities to the process.

Secondly, as we said previously, the process must be designed to reject the excess work, W_{excess}. In this situation, the irreversibilities arise from how we handle the rejected work, for example, in the form of heat, after it has left the process and hence the irreversibilities are caused by the interaction of the utilities with the heat and work flows from the process.

Thus, lastly, the challenge in designing efficient process lies is in recovering the excess work and designing the process to reject the heat in a way that it can be recovered. The excess work would either need to be recovered from the process (in order to make the process and utilities in the limit reversible) or else would be lost as irreversibilities in the transfer either between the process and utilities or within the utility system itself. The further the process operating conditions are from the curve, the more important the recovery of work is. Thus if we had a choice of process operating temperature, it would be far better to choose an operating temperature closest to the curve in order to reduce the amount of work recovered and hence reduce both capital and running costs of the process and utilities.

Thus we believe that the curves given in Figure 7.1 are potentially useful targets if the operating temperatures are feasible. We therefore claim that if one does use a one-stage process then operating a process as close to these targets as possible is desirable.

It is clear that the conditions for the one stage process can be quite extreme, and in commercial practice another way of supplying work to these processes is utilized. This will be discussed in the next section.

7.4   The two stage process

In many cases, as seen in the previous section, it is not practically possible to supply the required work via the heat flow in a single stage process. In the previous chapter we explained how in the case of methanol, the equivalent of an internal heat engine in the process is used to supply the work. In this case, a more complex process route is used and the process occurs in two stages. Again, these stages need not correspond to the actual reaction occurring in the process. In particular the overall process now occurs via two sub processes or stages as we will call them. The sub-processes or stages that are currently used to achieve this are:

- in the first stage reforming (or gasification in coal based plants), which is endothermic and occurs at high temperature hence carrying work into the process;

- followed by synthesis in the second stage, which is exothermic at lower temperatures and rejects work from the process.

It is important to notice the following:

- The *overall* process mass, energy and work considerations are unchanged by the fact that the process now occurs in two stages as shown schematically in Figure 6.1 (chapter 6). Thus:

  $\Delta H_{process} = \Delta H_{stage\ 1} + \Delta H_{stage\ 2}$

  $\Delta G_{process} = \Delta G_{stage\ 1} + \Delta G_{stage\ 2}$

- Thus the overall process mass balance and hence the overall process energy and work requirements are still as determined previously for the one stage process.

- Work and heat are input into the first stage, i.e. $\Delta H_{stage\ 1} > 0$ and $\Delta G_{stage\ 1} > 0$. The quantity of both work and heat that are input into this stage is more than the overall process requirements i.e. $\Delta H_{stage\ 1} > \Delta H_{process}$ and $\Delta G_{stage\ 1} > \Delta G_{process}$. As a result both heat and work need to be rejected in the second stage, i.e. $\Delta H_{stage\ 2} < 0$ and $\Delta G_{stage\ 2} < 0$.

- If the work rejected from the second stage is recovered, then the process will in the limit be reversible. This work can either be exported as work from the process or else returned to the process.

- If the work recovered from the second stage is returned to the process, we call this *work integration.* The work returned to the process would need to be input to the *first* stage of the process. This would then reduce the amount of

work that need to be added from an external source to stage 1 of the process to $\Delta G_{process}$.

We will summarize the overall and individual stage mass balances for the three processes that we are considering, namely ammonia, methanol and Gas-to-Liquid synthesis. The individual mass balances are chosen such that the sum of all stages must add up to the overall process mass balance.

7.4.1 Two stage process mass balance

Methanol synthesis

The synthesis of methanol can be broken into the following two stages. We again indicate the phase of the phase of the input and output streams as subscripts in the mass balance descriptions.

The overall process mass balance is given by equation 7.1 and is reproduced here

$$\tfrac{3}{4}CH_{4(g)} + \tfrac{1}{4}CO_{2(g)} + \tfrac{1}{2}H_2O_{(l)} \xrightarrow[\text{mol bal}]{\text{process}} 1\,CH_3OH_{(l)}$$
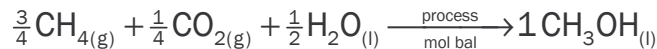
The overall process is divided into two stages as follows:

Stage 1: The production of synthesis gas (a mixture of carbon monoxide and hydrogen) from methane and water:

$$\tfrac{3}{4}CH_{4(g)} + \tfrac{1}{4}CO_{2(g)} + \tfrac{1}{2}H_2O_{(l)} \xrightarrow[\text{mol bal}]{\text{stage 1}} CO_{(g)} + 2H_{2(g)} \qquad [7.6a]$$

Stage 2: The synthesis of methanol from carbon monoxide and hydrogen:

$$CO_{(g)} + 2H_{2(g)} \xrightarrow[\text{mol bal}]{\text{stage 2}} CH_3OH_{(l)} \qquad [7.6b]$$
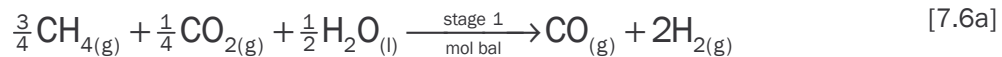
Ammonia synthesis

The overall process mass balance for the synthesis of ammonia (equation 7.2) is given below:

$$\tfrac{3}{8}CH_{4(g)} + \tfrac{1}{2}N_{2(g)} + \tfrac{3}{4}H_2O_{(l)} \xrightarrow[\text{mol bal}]{\text{process}} 1\,NH_{3(l)} + \tfrac{3}{8}CO_{2(g)}$$
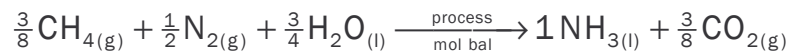
The overall mass balance can be divided into two stages as follows:

Stage 1: The production of hydrogen from methane and water

$$\tfrac{3}{8}CH_{4(g)} + \tfrac{3}{4}H_2O_{(l)} \xrightarrow[\text{mol bal}]{\text{stage 1}} \tfrac{3}{8}CO_{2(g)} + \tfrac{3}{2}H_{2(g)}$$

[7.7a]
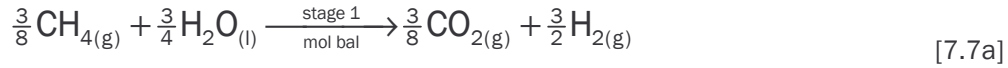
Stage 2: The synthesis of ammonia from nitrogen and hydrogen

$$\tfrac{1}{2}N_{2(g)} + \tfrac{3}{2}H_{2(g)} \xrightarrow[\text{mol bal}]{\text{stage 2}} 1\,NH_{3(l)}$$

[7.7b]
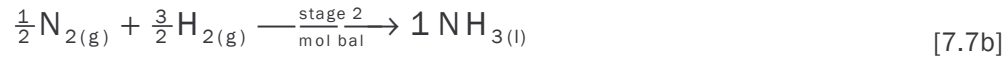
Gas-to-Liquid process

The production of hydrocarbon fuels from methane can be represented by the following overall process (equation 7.3):

$$nCH_{4(g)} \xrightarrow[\text{mol bal}]{\text{process}} (-CH_2-)_{n(l)} + nH_{2(g)}$$
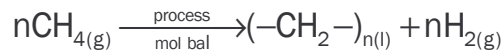
where n is the average carbon number

The overall process can be divided into two stages as follows:

Stage 1: The production of synthesis gas from methane

$$nCH_{4(g)} + nH_2O_{(l)} \xrightarrow[\text{mol bal}]{\text{stage 1}} nCO_{(g)} + 3nH_{2(g)}$$

[7.8a]
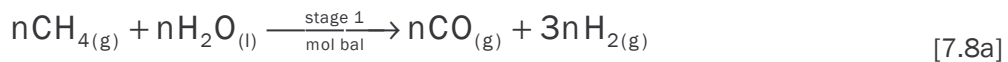
Stage 2: The Fischer-Tropsch synthesis process to produce hydrocarbon fuels from synthesis gas

$$nCO_{(g)} + 2nH_{2(g)} \xrightarrow[\text{mol bal}]{\text{stage 2}} (-CH_2-)_{n(l)} + nH_2O_{(l)}$$

[7.8b]
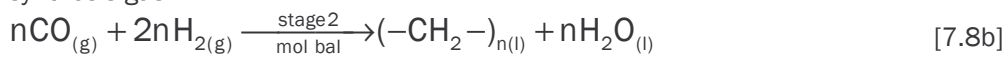
For the purpose of this analysis, we will consider n = 1.

There are many variations of the reforming process where mixtures of oxygen and steam are used and there are similarly many variations of the overall balances as discussed previously. We are not going to consider these in this paper but the various options could be explored using the approach outlined in this paper.

7.4.2 Two stage process heat and work flows

The changes in enthalpy and Gibbs energy for the individual stages and the overall process are given in Table 7.3. These were calculated from standard enthalpies and Gibbs energies of formation of the various compounds (Atkins, 1986; Yaws, 1999).The change in Gibbs energy indicates the amount of work required for the stage (for a positive ΔG) or work released (if ΔG is negative). The change in enthalpy represents the heat requirements of the stage (a positive ΔH means heat is needed while a negative ΔH means heat is released).

Table 7.3: The standard change in the Gibbs energy and standard change in Enthalpy of the various processes and stages as described by equations 7.6, 7.7 and 7.8

	Change in Gibbs energy under standard conditions (kJ/mol)			Change in Enthalpy under standard conditions (kJ/mol)		
	Overall process	Stage 1	Stage 2	Overall process	Stage 1	Stage 2
Methanol synthesis	88.93	118.00	-29.07	58.74	186.90	-128.16
Ammonia synthesis	38.03	48.98	-10.95	27.84	94.86	-67.02
Gas-to-Liquid synthesis	51.47	150.65	-99.18	43.49	250.14	-206.65

It can be seen from Table 7.3 that the change in the Gibbs energy as well as the enthalpy change for the overall reactions is the sum of the individual sub processes, namely reforming (stage 1) and synthesis (stage 2). It is also important to note that the $\Delta G_{stage1} < \Delta H_{stage1}$ for the first stage of all three processes implying that the heat and work requirements can potentially be matched. Thus there is the potential that

the temperature that the heat is added to the stage 1 process can be set so that it carries the required work with it. This will be investigated in the next section. The change in the Gibbs energy for the various stage 1 processes are quite different with the Fischer-Tropsch synthesis process having the largest change whereas the ammonia synthesis process has the smallest change. The same is true concerning the enthalpy change for the various stage 1 processes. This implies that the heat addition to stage 1 of the Fischer –Tropsch process is much more problematic than to the first stage of ammonia and methanol synthesis processes. Hence this adds to the running costs of the Fischer- Tropsch reformers (first stage), making it the most expensive to run.

Stage 2 processes vary both in terms of the change in Gibbs free energy and enthalpy. The Gas-to-Liquids process (described by equation 7.8) has the largest (in terms of magnitude) change in Gibbs energy and enthalpy. This would seem to imply that the removal of heat and work from the Fischer Tropsch synthesis stage (i.e. second stage) is going to more difficult and more capital intensive than for ammonia and methanol synthesis stage. The change in Gibbs energy of the methanol synthesis is almost three times that of ammonia synthesis whilst the change in enthalpy of the methanol synthesis process is also much larger (when comparing the magnitudes). This has some interesting implications for operating temperatures as will be seen later. It is important to note that $\Delta G_{stage\ 2} > \Delta H_{stage\ 2}$ for all the second stage processes. This is important as it means that there is again the potential to set the temperature of the heat that is rejected from the stage 2 process such that the heat flow carries the rejected work with it. We will also investigate this possibility in the next section.

Thus any opportunities for work integration between the two stages will be beneficial, particularly in the case of the Gas-to-Liquids process.

Note that the above discussion applied only to the processes described by equations 7.6, 7.7 and 7.8 and are in no way applicable to all methanol, ammonia and gas-to-liquids processes.

7.4.2.1 Carnot temperatures of the Two Stage Processes

The Carnot temperatures of the individual stages can be calculated as follows. We will now use the subscript "process" for the overall process and "stage i" when referring to a specific stage i. At the reversible temperature:

Work input to stage 1= $\Delta G_{stage\ 1}$
and Work rejected from stage 2 = $\Delta G_{stage\ 2}$ = $\Delta G_{process}$ -$\Delta G_{stage\ 1}$

Similarly:
Heat input to stage 1= $\Delta H_{stage\ 1}$
and Heat rejected from stage 2 = $\Delta H_{stage\ 2}$ = $\Delta H_{process}$ -$\Delta H_{stage\ 1}$

The process equipment where the main heat transfer occurs would be the reactors, which is the reformer in stage 1 and the synthesis reactors in stage 2. It however must be remembered that we are firstly only considering the process streams and not utilities, and secondly that a stage will have many process units, but we are assuming at this stage that the main heat and work flows occur at the reactors.

Table 7.4: The Carnot temperatures for the two stage processes under consideration

Process	Stage 1 Carnot temperature (T_{carnot}) [K]	Stage 2 Carnot temperature (T_{carnot}) [K]
Methanol Synthesis	808.7	385.6
Ammonia Synthesis	616.5	356.4
Gas–to- Liquids Process	749.6	573.3

The Carnot temperatures of the first stage of the processes (endothermic reforming section) correspond to a high temperature process. As expected, the first stage of the methanol synthesis process as the highest reversible temperature while the ammonia synthesis has the lowest reversible temperature. It is interesting that the first stage (reforming section) of the Gas-to-Liquids process has a lower reversible temperature than that of the first stage of the methanol synthesis process despite

work requirements for the Gas-to-Liquids reforming process being 30 % higher than for the methanol process.

The second stage (or synthesis section) Carnot temperatures are lower that the first stage reversible temperatures with the ammonia synthesis stage having the lowest reversible temperature while the Fischer-Tropsch having the highest reversible temperature. The second stage temperature of ammonia synthesis and methanol synthesis are reasonably close to each other.

Running each of the processes at their Carnot temperature has certain advantages. A schematic diagram of work flows when running at the reversible temperature is shown in Figure 7.2. It must be remembered that the overall processes are all endothermic (require an energy input) and require a work input. The work and heat input into the reformer section is greater than that required by the overall process in all three cases. Thus, work and heat must be rejected in the second stage. When the second stage is run at its Carnot temperature, then the heat that is rejected by the second stage carries the correct amount of work with it.

$\Delta G_{process}$ $\qquad$ $\Delta G_{stage\ 1}$ $\qquad$ $\Delta G_{stage\ 2}$
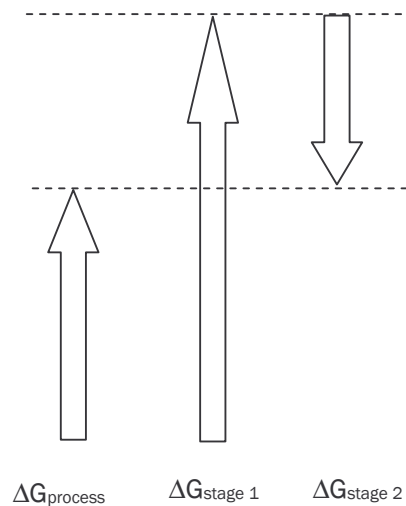
Figure 7.2: Schematic representation of the work flows in the overall process and stage 1 and 2. The length of the arrow is proportional to the quantity of work and the direction indicates where the work is added or rejected.

7.4.2.2 Implications of not operating at the Carnot temperature for the two stage process

Let us firstly consider the implications of not operating the reformer section at the Carnot temperature $T_{1, carnot}$. We will define the work excess of a stage i as $W_{stage\ i}$. By convention an excess of work will have a positive sign, i.e. $W_{stage\ 1} > 0$ implies that stage 1 has a work excess that needs to be rejected. A work deficit for stage 1 will be indicated by $W_{stage\ 1} < 0$ and hence additional work needs to be supplied to stage 1.

Quantity of work that can be recovered from stage 1

Quantity of work still required in stage 1

$\Delta G_{stage\ 1}$

Actual work input by heat flow if $T_1 < T_{1,\ carnot}$

$\Delta G_{stage\ 1}$

Actual work input by heat flow if $T_1 > T_{1,\ carnot}$

(a)

(b)
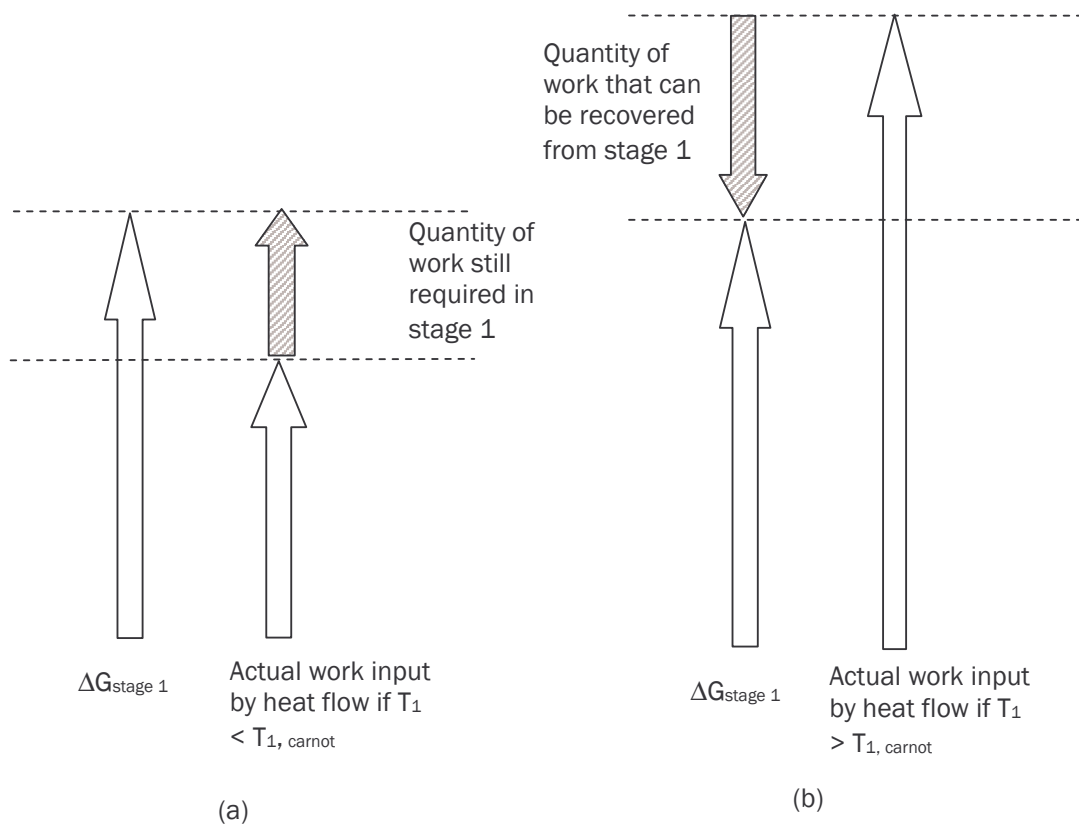
Figure 7.3: Schematic representation of the work flow for stage 1 (a) when $T_1 < T_{1,carnot}$ and (b) when $T_1 > T_{1,\ carnot}$. The length of the arrow is proportional to the quantity of work and the direction indicates whether the work is added or rejected.

- If the reformer operated above its Carnot temperature (i.e. $T_1 > T_{1,carnot}$. See Figure 7.3 (b)), this would imply that the heat added to the reformed carried more than the required work with it. This excess work would need to be

rejected or lost from the reformer section. The quantity of excess work is given by:

$$W_{stage1} = \Delta H_{stage1}\left(T_o, P_o\right)\left(1 - \frac{T_o}{T_1}\right) - \Delta G_{stage1}\left(T_o, P_o\right)$$ [7.9]

where $W_{stage\ 1} > 0$. Rejecting and recovering the work leads to increase complexity and hence capital and energy costs.

- If the reformer section operated below its reversible temperature, (i.e. $T_1 < T_{1,carnot}$. See Figure 7.3(a)), this would mean that the heat added to the reformer section did not carry sufficient work with it, i.e. the reformer section is in work deficit. In order for the reformer to operate, additional ways of adding work to the reformer section would need to be implemented. The amount of work that would need to be added is as defined by equation 1.9 but $W_{stage\ 1} < 0$ in this case. Other ways of adding work may include compressing, separation or increasing the heat load into the reformer to $Q = (\Delta H_{stage\ 1} + \delta Q)$ and therefore rejecting a quantity of heat δQ as discussed previously. Again implementing these options increases the complexity of the stage 1 process and hence capital and energy costs.

There are similarly implications when operating the synthesis stage away from its Carnot temperature $T_{2,\ carnot}$. We consider these now:

- If the synthesis section operates above their reversible temperature, (i.e. $T_2 > T_{2,carnot}$. See Figure 7.4 (a)), this means that the heat rejected from the synthesis section carries with it more work than needs to be rejected. Hence the stage 2 process would be work deficient, and the deficiency being:

$$W_{stage2} = \Delta H_{stage2}\left(T_o, P_o\right)\left(1 - \frac{T_o}{T_2}\right) - \Delta G_{stage2}\left(T_o, P_o\right)$$ [7.10]

where $W_{stage\ 2} < 0$. Other ways of supplying work to the stage 2 process would need to be implemented in order to make this stage feasible. This could mean adding excess heat $Q = (\Delta H_{stage\ 2} + \delta Q)$ and therefore rejecting a quantity of heat δQ somewhere in stage 2. Alternatively, work could be added by compression or separation. Implementing ways of adding work to stage 2

increases the complexity of the stage 2 process and hence capital and energy costs.

- If the synthesis stage operates below its reversible temperature, (i.e. $T_2 <$ $T_{2,carnot}$. See Figure 7.4 (b)) this means that insufficient work is rejected from the stage 2 process. Unless the excess work is recovered, this excess work will be lost as irreversibilities, which is not a desired outcome as this leads to higher operating costs. The amount of work that needs to be rejected (or lost) is given by equation 7.10 but in this case $W_{stage2} > 0$.

Actual work carried out by heat flow if T_2 $>T_{2,carnot}$

$\Delta G_{stage\ 2}$

Work deficiency in stage 2

Actual work carried out by heat flow if T_2 $< T_{2,carnot}$

$\Delta G_{stage\ 2}$

Work lost/rejected in stage 2

(a)

(b)
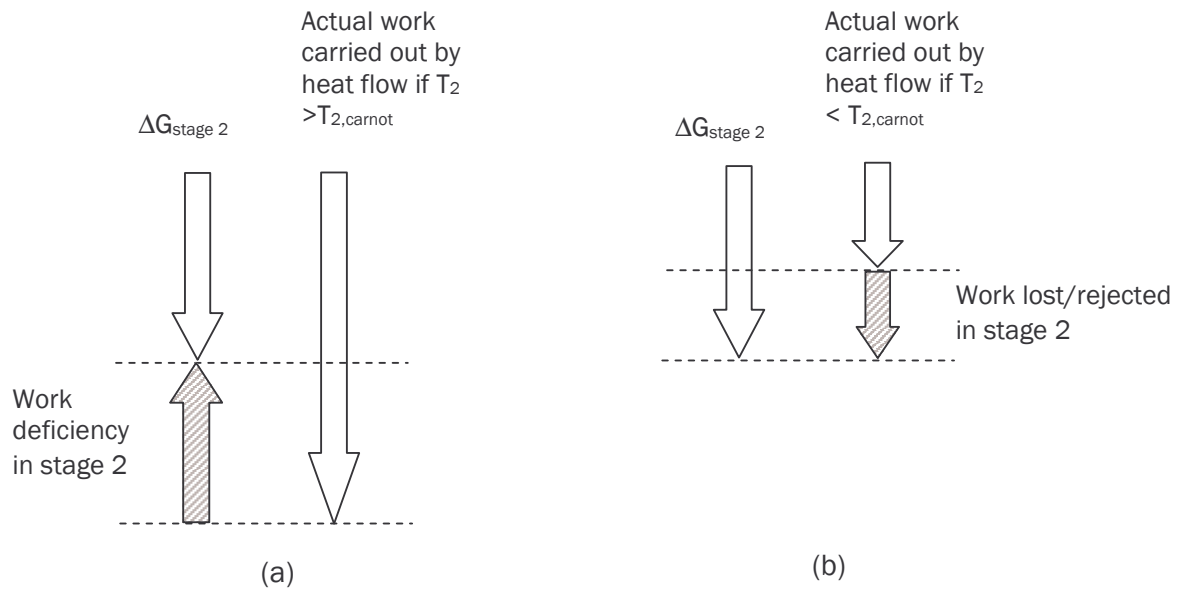
Figure 7.4: Schematic representation of the work flow for stage 2 (a) when $T_2 >$ $T_{2,carnot}$ and (b) when $T_2 < T_{2,carnot}$. The length of the arrow is proportional to the quantity of work and the direction indicates whether the work is added or rejected.

In practice none of the three processes, that is methanol, ammonia and Gas-to-Liquids processes, operate at their Carnot temperature. It is an interesting question if one can design processes to operate at their Carnot temperature. In this chapter, we will look at how to synthesize and operate processes that do not operate at their Carnot temperature as efficiently as possible. In these processes, work integration between the stages is very important and this will be discussed in the next section.

7.4.3 Work integrated two stage processes

Work integrating processes operating at the Carnot temperature.

We note that even when a process runs at its Carnot temperature, there is room to work integrate the process. The work rejected from stage 2 via the heat that is removed from this stage could be recovered and returned to stage 1 as shown schematically in Figure 7.2. In this case the process would be reversible and the net work supplied by an outside source to the reformer is then $\Delta G_{process}$, rather than $\Delta G_{stage\ 1}$ when the process is not work integrated. The other part of the work required to be input to stage 1, namely (ΔG_{stage1} -$\Delta G_{process}$) is recovered from stage 2 ($\Delta G_{stage\ 2}$) and returned to stage 1.

The larger the value of $\Delta G_{stage\ 2}$ is compared to $\Delta G_{process}$ the bigger the reduction of the overall work input into the reformer section will be. Thus, referring to the values of the change in Gibbs energy for the synthesis stage in Table 7.3, we can expect this recovery of work from the synthesis section (stage 2) in the Gas-to-Liquids process to be more important than in the case of methanol or ammonia synthesis. It is however important to realize that the heat that is rejected by the synthesis section carries work potential with it and it is important to try to conserve this work potential and recover it.

Work integrating processes not operating at the Carnot temperature

Even when the individual stages are not working at their Carnot temperatures there is the potential for work integration between the 2 stages in a manner similar to that described above for process operating at the Carnot temperature.

   As shown in chapter 6 one can consider work integrating between the two stages to achieve a process where the net work that needs to be input is in fact the minimum, namely $\Delta G_{process}$. Thus we are identifying systems where the excess work put into a stage is recovered and the quantity of work recovered matches the work deficit of the other stage. This allows the relationship between the temperature of stage 1, T_1, and stage 2, T_2, to be determined for a work integrated, reversible process as described in chapter 6.

In chapter 6 we defined the reversible, work integrated curve, which can be plotted as a function of $T_{WI\ 1}$ and $T_{WI\ 2}$ (the temperatures corresponding to the curve). The values of $\Delta G_{process}$, $\Delta H_{stage\ 1}$, and $\Delta H_{stage\ 2}$ are given in Table 7.3 for the three processes being considered. Thus if the operating temperatures of the individual stages are chosen to lie on this curve, there is the potential for work integrating the overall process and so achieving a process with the minimum virtual input work, namely $\Delta G_{process}$ (i.e. work input by heat) and no additional work. Let us briefly summarize what information one can obtain from the curve means by considering a representation of the curve as shown in Figure 7.4. The shape of the curve depends on the specific values of $\Delta G_{process}$, $\Delta H_{stage\ 1}$, and $\Delta H_{stage\ 2}$.
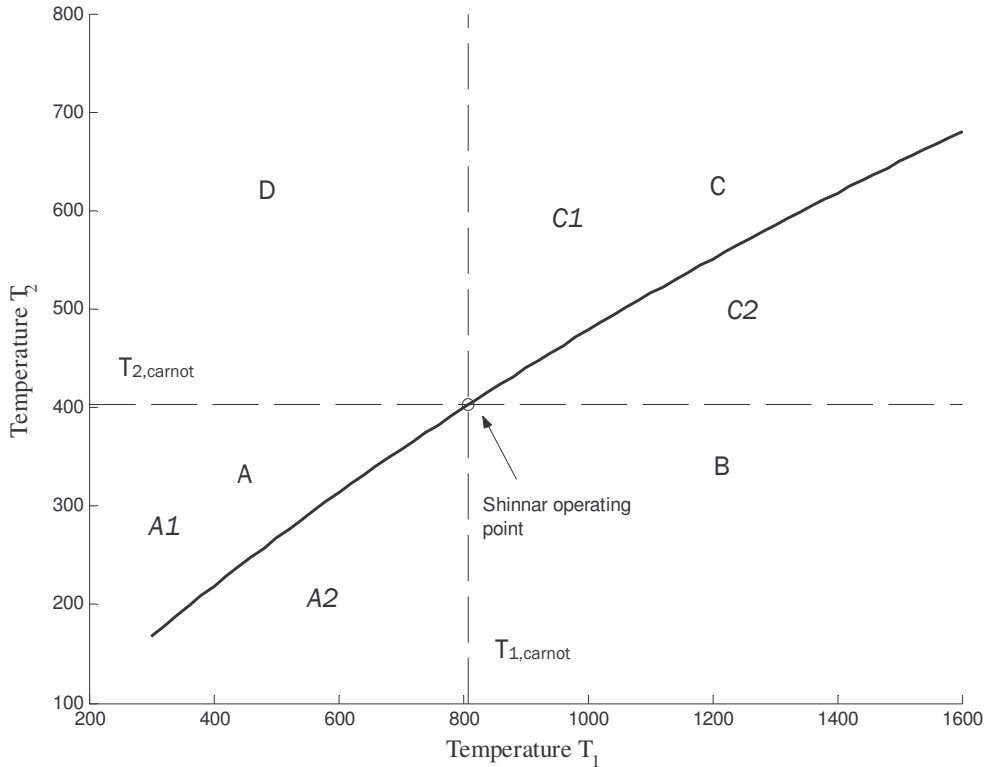

Figure 7.5: A representation of a reversible, work-integrated curve as a function of the temperature of the two stages

Operating points on the reversible, work integrated curve:

We see that the work integrated, reversible curve passes through the Carnot temperatures ($T_{1,carnot}$ and $T_{2,carnot}$) of the process. We will call this point the Shinnar point. The implication of operating at this point has been explained previously.

Operating points on the reversible work integrated curve to the *left* of the Shinnar point (i.e. $T_{WI, 1} < T_{1,carnot}$ and $T_{WI, 2} < T_{2,carnot}$) correspond to situations where:

- The work added to the reformer via the heat flow is insufficient. Therefore the reformer is work deficient and this deficiency has to be met by inputting work from a source other than the heat flow ($Q = \Delta H_{stage\ 1}$). The amount of work that would need to be added is given by:

$$W_{stage1} = \Delta H_{stage1}\left(T_o, P_o\right)\left(1 - \frac{T_o}{T_{WI,1}}\right) - \Delta G_{stage1}\left(T_o, P_o\right) < 0$$

- The work rejected with the heat flow from the stage 2, the synthesis section, is insufficient. Thus there is a surplus of work in the stage 2 process that needs to be rejected in some other way, which is not via the heat (i.e. $Q = \Delta H_{stage\ 2}$). The method of recovering or rejecting this work have to be built into the stage 2 process, and a potential method could be increased heat flows. The amount of work that needs to be rejected from stage 2 is:

$$W_{stage2} = \Delta H_{stage2}\left(T_o, P_o\right)\left(1 - \frac{T_o}{T_{WI,2}}\right) - \Delta G_{stage2}\left(T_o, P_o\right) > 0$$

- The quantity of surplus work available from stage 2 is exactly the same as the quantity of work that is deficit in the reformer (stage 1), i.e.
  $W_{stage\ 2} = -W_{stage\ 1}$.
  Thus one could work integrate the process by inputting the excess work recovered from the synthesis section (Stage 2) to the reformer section (Stage 1). Again this work could not simply be converted to heat at temperature T_1 and more complex situations would need to be considered, for example the more complex heat flow situation as explained in chapter 5.

- Note that over and above this work integration, the transfer of work from the synthesis section to the reforming section, as done at the Shinnar point, could still be done in order to reduce the work requirements of the reformer section to the minimum, namely $\Delta G_{process}$. In other words, the work inherent in the heat rejected from stage 2 could be recovered and input to stage 1. This would reduce the heat requirements of stage 1 to $\Delta H_{process}$ and the work requirements to $\Delta G_{process}$. We regard these two types of work integration

somewhat differently as the type of integration at the Shinnar point does not require design modifications to stage 2 and only requires ways of recovering the work from the heat flow, i.e. design changes in the utilities. However, when the work rejected via the heat flow from stage 2 stream does not match the Gibbs energy change for a stage or process (as occurs when not operating at the Shinnar point), then ways of rejecting this work need to be built into the design of stage 2.

Conversely operating points on the reversible work integrated curve to the *right* of the Shinnar point (i.e. $T_{WI,1} > T_{1,carnot}$ and $T_{WI,2} > T_{2,carnot}$) correspond to situations where:

- The heat flowing into the reformer (stage 1) carries too much work with it into the reformer. The amount of surplus work is:

$$W_{stage1} = \Delta H_{stage1}\left(T_o, P_o\right)\left(1 - \frac{T_o}{T_{WI,1}}\right) - \Delta G_{stage1}\left(T_o, P_o\right) > 0$$

   This excess work would need to be rejected from the reformer in ways other than heat (and hence this would need to be built into the flowsheet) and the work could then be recovered.

- The heat flowing out of the synthesis section (stage 2) carries too much work with it and thus the synthesis reactors are work deficit, the amount given by:

$$W_{stage2} = \Delta H_{stage2}\left(T_o, P_o\right)\left(1 - \frac{T_o}{T_{WI,2}}\right) - \Delta G_{stage2}\left(T_o, P_o\right) < 0$$

   Thus this quantity of work would need to be input into the synthesis section.

- For operating points on the curve, the work recovered from the reformer section (stage 1) is sufficient to match the work deficit of the synthesis section (stage 2), i.e.

   $W_{stage\ 1} = -W_{stage\ 2}$

   Thus in order to work integrate the process, recovered work would need to be transferred from the reformer section to the synthesis section. Again, this would need to involve a plant with more complex heat flows or other methods to recover and supply the work.

- To reduce the overall work supplied to the process to $\Delta G_{process}$, further work integration as discussed for operating at the Shinnar point would need to be done. Thus work would need to be transferred from the synthesis section to the reformer section. This would again introduce further complexity to the process and utilities design.

Thus we can see that the Shinnar point offers in principle the simplest situation for work integrating the overall process, and hence our claim that it is desirable to try to design a process to operate at its Shinnar point. We will show however that current processes do not operate even close to the work integrated reversible curve and we ask now what the implication of this is.

Operating points off the reversible, work integrated curve:

By considering the work flows and in particular the work deficits and excesses, one can define four main regions on the T_1-T_2 plot, where two of the quadrants, namely A and C, are in turn split into two regions. There are therefore six regions overall and each region defines operating temperatures ranges where the work excesses or deficits for the individual stages have the same sign. This in turn means that each of the regions correspond to different scenarios with regards to the work flows between the stages for reversible, work integrated processes. A summary of the six regions defined in chapter 6 and the implications of the operating conditions for the efficiency and design of the process are summarized in Table 7.5.

Table 7.5: Summary of the six regions on the T_1-T_2 plot

Region	Operating Conditions	Implications on Work
A	$T_1 < T_{1,carnot}$ and $T_2 < T_{2,carnot}$	Too little work input by heat supplied to reformer section i.e. reformer section work deficient and thus need additional work supplied, the amount being $W_{stage\ 1}$, where $W_{stage\ 1}$ is as defined above and: $W_{stage\ 1} < 0$ Too little work removed by heat rejected in synthesis section – synthesis section therefore need to reject excess work, the amount being $W_{stage\ 2}$ where $W_{stage\ 2}$ is as defined above and : $W_{stage\ 2} > 0$

		Region A1: $T_1 < T_{WI, 1} < T_{1,carnot}$ and $T_{WI, 2} < T_2 < T_{2,carnot}$ Work rejected by synthesis section less than work deficiency of reformer section, i.e. $W_{stage\ 2} + W_{stage1} < 0$. In a work integrated process, excess work would need to be added to the reformer section, the amount being ($W_{stage\ 1} + W_{stage\ 2}$). *Region A2*: $T_{WI, 1} < T_1 < T_{1,carnot}$ and $T_2 < T_{WI, 2} < T_{2,carnot}$ Work rejected by synthesis section greater than work deficiency of reformer section, i.e. $W_{stage\ 2} + W_{stage\ 1} > 0$. In a work integrated process, excess work would be exported from the synthesis section, the amount being ($W_{stage\ 2} + W_{stage\ 1}$). If this work is not recovered, it will be lost.
B	$T_1 > T_{1,carnot}$ and $T_2 < T_{2,carnot}$	Excess work added by heat supplied to the reformer section i.e. reformer section needs to reject excess work, the amount being $W_{stage\ 1}$ where: $W_{stage\ 1} > 0$. Too little work removed by heat rejected in synthesis section i.e. synthesis section therefore needs to reject additional work, the amount being $W_{stage\ 2}$ where: $W_{stage\ 2} > 0$ Work is rejected by both stages, i.e. stages 1 and 2 both reject work. If the rejected work is not recovered, this leads to entropy generation and increased operating costs. Recovering the work implies increase complexity of process design and increased heat flows in both the synthesis and reformer sections for recovery.
C	$T_1 > T_{1,carnot}$ and $T_2 > T_{2,carnot}$	Too much work added by heat supplied to reformer section i.e. reformers need to reject additional work, the amount being $W_{stage\ 1}$ as defined as above, but with $W_{stage\ 1} > 0$,

		Too much work removed by heat rejected in synthesis section i.e. synthesis section therefore work deficient and need to add additional work to synthesis section, the amount being $W_{stage\ 2}$ as defined above, where :
		$W_{stage\ 2} < 0$
		Region C1: $T_{1,carnot} < T_1 < T_{WI,\ 1}$ and $T_2 > T_{WI,\ 2} > T_{2,carnot}$
		Work rejected by reformers is less than work deficiency of synthesis section, i.e. $W_{stage\ 1} + W_{stage\ 2} < 0$. In a work integrated process, excess work would need to be added to the synthesis section, the amount being $(W_{stage\ 2} + W_{stage\ 1})$ where the work terms are as defined above.
		Region C2: $T_1 > T_{WI,\ 1} > T_{1,carnot}$ and $T_{2,carnot} < T_2 < T_{WI,\ 2}$
		Work rejected by reformers is greater than work deficiency of synthesis section, i.e. $W_{stage\ 1} + W_{stage\ 2} > 0$. In a work integrated process, excess work would be recovered from the reformer section, the amount being $(W_{stage\ 1} + W_{stage\ 2})$, where the work terms are as defined above.
D	$T_1 < T_{1,carnot}$ and $T_2 > T_{2,carnot}$	Insufficient work is added by heat supplied to the reformer and the reformer therefore has a work deficit .Thus we need to add additional work to the reformer, the amount being: $$W_{stage1} = \Delta H_{stage1}(T_o, P_o)\left(1 - \frac{T_o}{T_1}\right) - \Delta G_{stage1}(T_o, P_o) < 0$$ Too much work removed by heat rejected in synthesis section i.e. synthesis section therefore work deficient and need to add additional work to synthesis section, the amount being: $$W_{stage2} = \Delta H_{stage2}(T_o, P_o)\left(1 - \frac{T_o}{T_2}\right) - \Delta G_{stage2}(T_o, P_o) < 0$$ Additional work is required for both the reformer (stage 1) and

		the synthesis process (stage 2) as both are work deficient. This implies increase complexity of process design. Furthermore heat rejected from synthesis reactors carries more work with it than $\Delta G_{stage\ 2}$. This excess work can be recovered which suggest added complexity of the process

7.4.3.1 Work analysis of two-stage methanol, ammonia and Fischer-Tropsch processes

We continue with the analysis of methanol, ammonia and Fischer-Tropsch synthesis processes.

Methanol synthesis

The reversible work integrated curve for the methanol process, together with the Shinnar point and the operating conditions of typical commercial methanol synthesis process is given in Figure 7.6 and 7.7. It can be seen that commercial processes typically run in region C1 which corresponds to the region of operation where the reformer rejects excess work and the synthesis section is work deficient. Let us start by considering the work flows in the synthesis section as it requires work.

The amount of work that must be input into the synthesis section is:

$$W_{stage2} = \Delta H_{stage2}\left(T_o, P_o\right)\left(1 - \frac{T_o}{T_2}\right) - \Delta G_{stage2}\left(T_o, P_o\right) < 0$$

We can superimpose contours of $W_{stage\ 2}$ on Figure 7.6. We see that the contours only depend on the temperature of the second stage and that at the Shinnar point $W_{stage\ 2}$ = 0. For $T_2 < T_{2,carnot}$ the synthesis section would export work and hence the sign of the work term becomes positive. For $T_2 > T_{2,carnot}$ the synthesis section would require work and hence the sign of the work term becomes negative. We see that the further away T_2 (i.e. the hotter) is from $T_{2,carnot}$, the more work has to be added to the synthesis section.

It can be seen that the amount of work needed for such processes i.e. the synthesis section is approximately between 25 and 35 kJ/mol. This represents the limit for the synthesis section where no work integration or work recovery takes places.
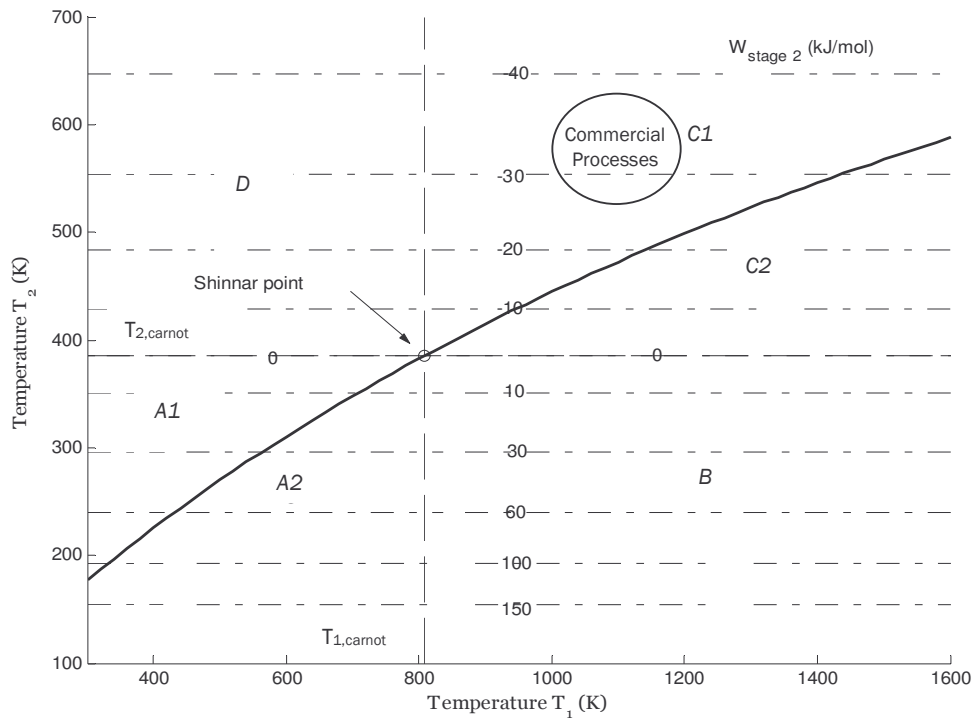
Figure 7.6: The reversible, work integrated curve for a two-stage methanol synthesis process. Also shown are work contours for the un-integrated synthesis stage (stage 2) as described by W_{stage2}; a positive value represents a work surplus while a negative value represents a work deficit.

However, if the process was work integrated, that is the excess work was recovered from the reformer section and work carried by the heat flow from the synthesis section were integrated into the process, the process would still require a further quantity of work W_{WI} to be input to the process, where:

$$W_{WI} = W_{stage1} + W_{stage2} = \Delta H_{stage1}\left(T_o, P_o\right)\left(1 - \frac{T_o}{T_1}\right) - \Delta G_{stage1}\left(T_o, P_o\right) +$$

$$\Delta H_{stage2}\left(T_o, P_o\right)\left(1 - \frac{T_o}{T_2}\right) - \Delta G_{stage2}\left(T_o, P_o\right)$$

[7.11]

We can use equation 7.11 to draw iso–work contours of W_{WI} and these are shown in Figure 7.7. We see that the contours depend on both T_1 and T_2. Furthermore as expected the contour for $W_{IW} = 0$ corresponds to the reversible, work integrated curve. The contours below this curve correspond to $W_{WI} > 0$ which corresponds to the

process exporting work. We can also see that the curves are much more sensitive to the reformer temperature than the synthesis section temperature. In order for the methanol processes to operate near the work integrated curve, one is required to either decrease the temperature of stage 2 (synthesis section) by 50 to 75 K or increase the temperature of stage 1 (reforming section) by 400 to 500 K. This can only be achieved if there is advancement in current technology (materials, catalysts etc) as the temperatures of the reactors are presently constrained by these technologies.
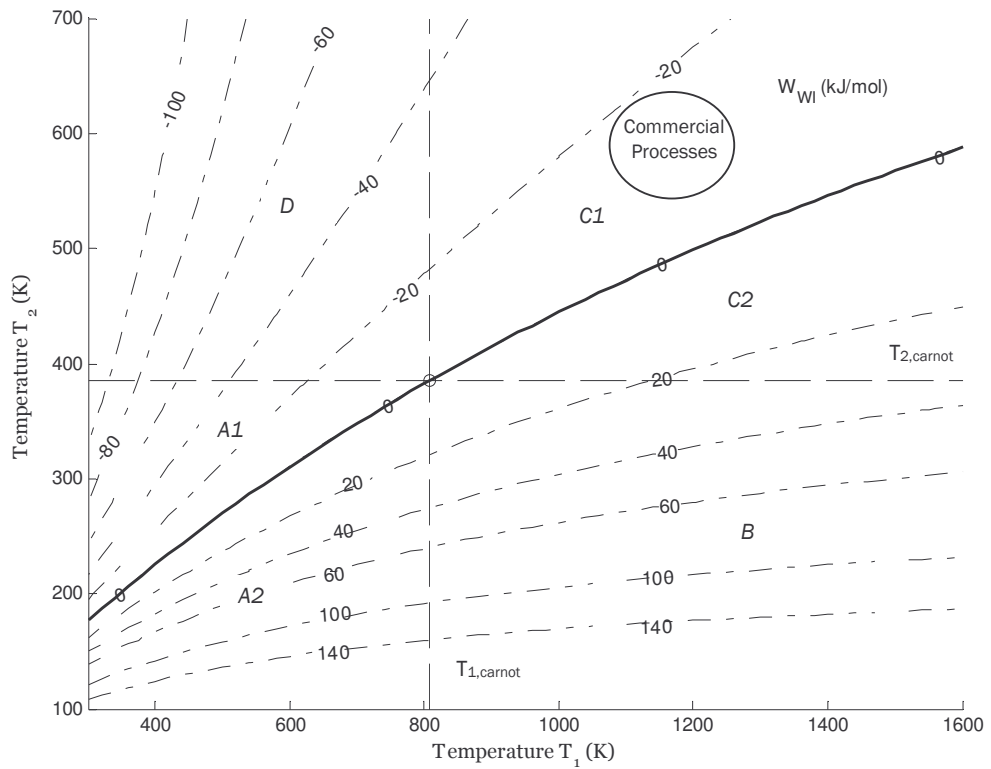
Figure 7.7: Iso-work contours for a work integrated methanol synthesis process as given by equation 7.11; a positive value means work surplus and a negative value means work deficit and process will reject work.

We note that the work input to a work integrated process is approximately between 10 and 20 kJ/mol (compared to between 25 and 35 kJ/mol when no work integration takes place; see Figure 7.6). These values correspond to the lowest limit of work input for processes operating with these temperatures.

To elucidate the matter further, we will now consider, as an example, the work flows for a methanol plant operating at a reformer temperature of 1200 K and the synthesis reactor temperature of about 550K as shown in Table 7.6.

Table 7.6: Work flows in a two-stage methanol synthesis process

	Work Flow (kJ/mol)
Reformer	
A. Work required to be input to reformer	118.00
B. Actual work input via heat flow to reformer	140.46
C. Work that can be recovered from reformer (C = B – A)	22.47
Synthesis Section	
D. Work required to be rejected from synthesis section	29.07
E. Actual work rejected via heat flow from synthesis section	58.69
F. Work deficiency of synthesis section i.e. amount of work that needs to be input to synthesis section (F = E – D)	29.62
Process	
G. Total work input to process if no work recovery/integration done (G = B + F)	170.08
H. Total work input to process if work is recovered from synthesis section and returned to process (H = G – E)	111.39
I. Total work input to process if work is recovered from synthesis section and reformer and returned to process (I = H – C)	88.93

Table 7.6 considers three cases concerning the work flows in the process: no work recovery (G), work recovery from the synthesis section (H) and work recovery from both the synthesis and reformer sections (I). It is clear from Table 7.6 that it is possible to achieve a 33% saving (a saving of 58.69 kJ/mol i.e. E in Table 7.6) if the amount of work is recovered from the synthesis section and returned to the process when compared to a process in which the work is not recovered. A saving of almost 50% (a saving of 88.15 kJ/mol i.e. E + C in Table 7.6) for work that has to be input to the process can be achieved by completely work integrating the two stages. It is clear that there are large opportunities for savings in terms of the work flows in the process.

Ammonia Synthesis

A similar analysis was performed on the ammonia synthesis process as described by equations 7.2, 7.7(a) and 7.7(b).

Figure 7.8 shows the relationship between the reforming section (stage 1) temperature and the synthesis section (stage 2) temperature for the synthesis of ammonia in order to attain a reversible work integrated process. As with the methanol example, above the reversible work integrated curve additional work is required whereas below the reversible curve work is lost (or could potentially be recovered).

The operating range of commercial processes (Vancini, 1971; Austin, 1984) is also shown in Figures 7.8 and 7.9. The ammonia synthesis process is similar to the methanol synthesis as commercial ammonia production processes also operating in region B1, that is $T_{1,carnot} < T_1 < T_{WI,\ 1}$ and $T_2 > T_{WI,\ 2} > T_{2,carnot.}$
This means that:

- the reforming section rejects excess work
- the synthesis section is work deficit,
- in a work integrated process, additional work is required to be added

Also shown in Figure 7.8 is the work input to the second stage (synthesis stage). The amount of work that must be input into the synthesis section is:

$$W_{stage2} = \Delta H_{stage2}\left(T_o, P_o\right)\left(1 - \frac{T_o}{T_2}\right) - \Delta G_{stage2}\left(T_o, P_o\right) < 0$$

As with the methanol synthesis case, we can superimpose contours of $W_{stage\ 2}$ on Figure 7.8. These contours only depend on the temperature of the second stage $W_{stage\ 2} = 0$ at the Shinnar point. For $T_2 < T_{2,carnot}$ the synthesis section would export work and hence the sign of the work term becomes positive. For $T_2 > T_{2,carnot}$ the synthesis section required work (the work term is negative). We see that the further away T_2 (i.e. the hotter) is from $T_{2,carnot}$, the more work has to be added to the synthesis section.
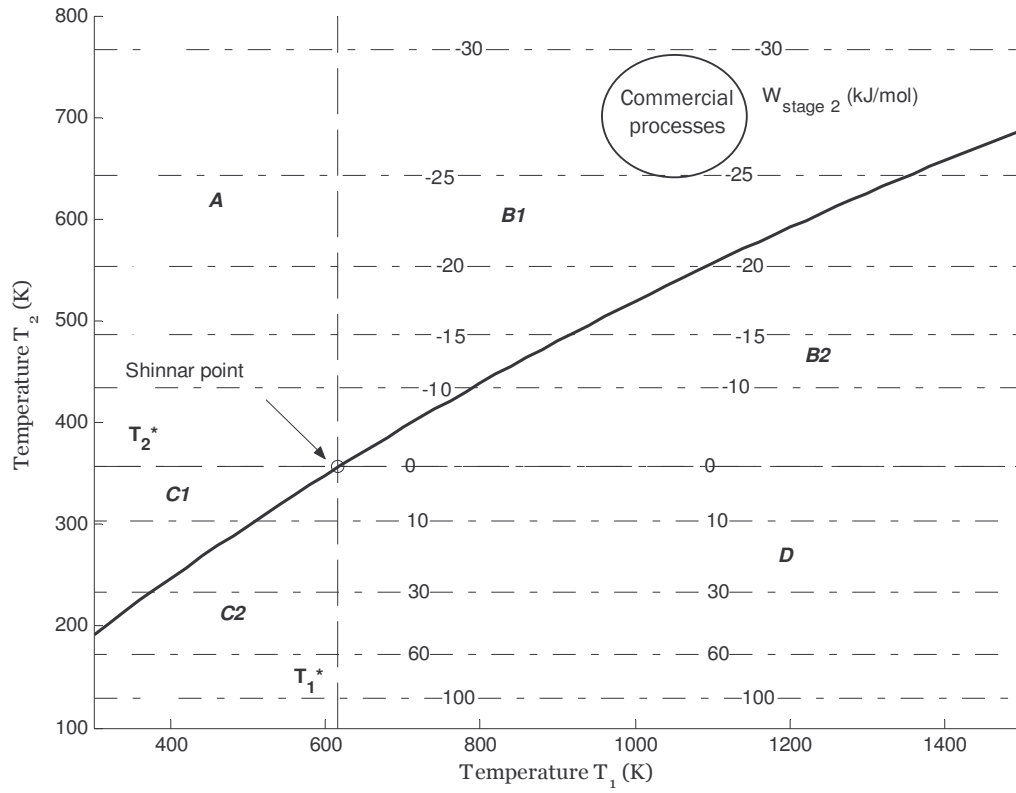
Figure 7.8: The reversible work integrated curve for a two-stage ammonia synthesis process and the corresponding Shinnar operating point. Work ($W_{stage\ 2}$) contours (in kJ/mol) for an un-integrated Stage 2 (synthesis stage) are also shown; a positive value corresponds to a work surplus while a negative value corresponds to a work deficit.

Note that the work required in the synthesis section (based on the given commercial operating temperatures) is between 25 and 30 kJ/mol in the case where no work is recovered or integrated within the process.
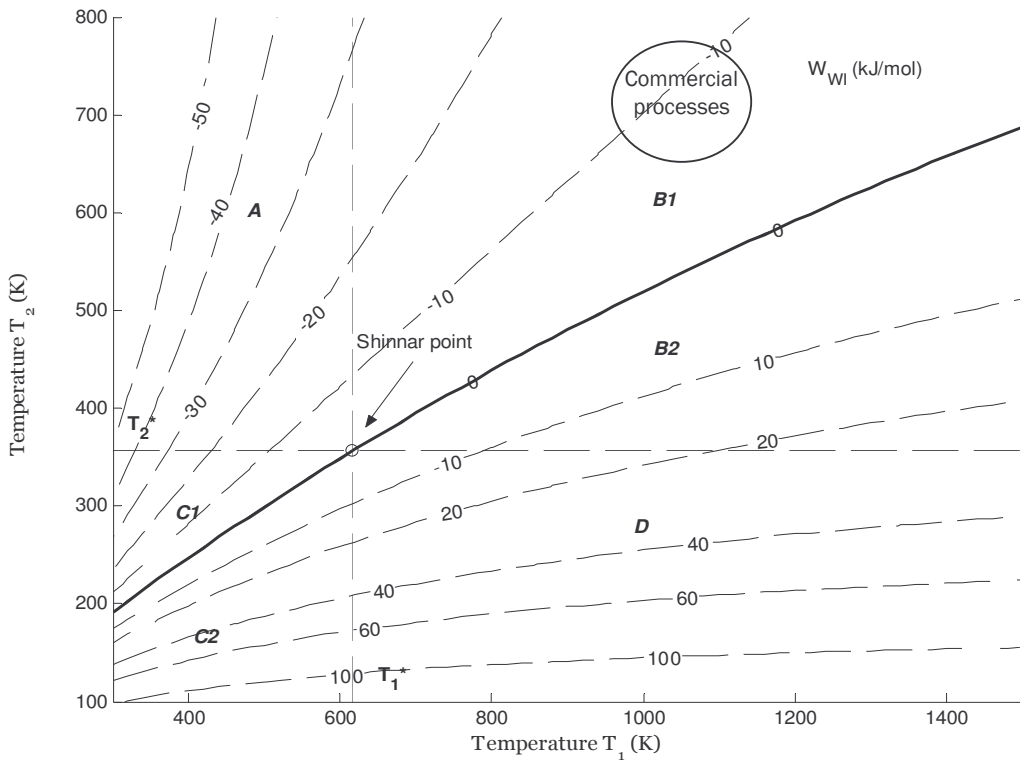
Figure 7.9: The relationship between the temperatures of in the two-stage ammonia synthesis process; also shown is the net work required or produced for the overall work integrated process as described by equation 7.11 (+ work means work deficit and - means work surplus and process will reject work)

Figure 7.9 also shows the "iso-work" curves for the work integrated ammonia synthesis process. These give an indication of the amount of work required/released from the process. It is therefore possible to determine the minimum amount of work (for a completely work integrated process) needed by commercial ammonia synthesis process as shown in Figure 7.9. Note that the minimum work required lies between 5 and 15 kJ/mol depending on the operating temperatures of the reformer and synthesis sections (compared to the previous values of 25 to 30 kJ/mol in the case of no work integration).

Let us now look at the work flows for an ammonia production process with the reformer section operating at 1100 K and the synthesis section operating at 700 K as shown in Table 7.7

Table 7.7: Ideal and actual work flows in an ammonia production process

	Work Flow (kJ/mol)
Reformer	
A. Work required to be input to reformer	48.98
B. Actual work input via heat flow to reformer	69.15
C. Work that can be recovered from reformer (C = B – A)	20.17
Synthesis Section	
D. Work required to be rejected from synthesis section	10.95
E. Actual work rejected via heat flow from synthesis section	38.47
F. Work deficiency of synthesis section; i.e. amount of work that needs to be input to synthesis section (F = E –A)	27.52
Process	
G. Total work input to process if no work recovery/integration done (G = B + F)	96.67
H. Total work input to process if work is recovered from synthesis section and returned to process (H = G – E)	58.19
I. Total work input to process if work is recovered from synthesis section and reformer and returned to process (I = H- C)	38.03

The savings for the ammonia production process, in terms of work, is apparent from Table 7.7. A saving of 40% (a saving of 38.47 kJ/mol can be achieved i.e. E in Table 7.7) can be achieved if one recovers the work from the synthesis section and returns it to the process as compared to a process where no work integration occurs. A 60% saving (a saving of 58.64 kJ/mol can be obtained i.e. E + C in Table 7.7) can be attained if work is recovered from both the reformer and synthesis section and returned to the process when compared to a process where no work integration takes place. It is clear that current ammonia processes (using the above operating temperatures) are putting in much more work than is actually required.

Gas-to-Liquids process

The analysis was finally performed for the synthesis of hydrocarbons (Gas-to-Liquids) as described by reaction 7.3, 7.8 (a) and 7.8 (b).

The plot of the relationship between the temperature of the reformer section (stage 1), as given by equation 7.8 (a) and the temperature of the synthesis section (stage 2), as given by equation 7.8 (b), for the synthesis of hydrocarbons is shown in Figure 7.10.
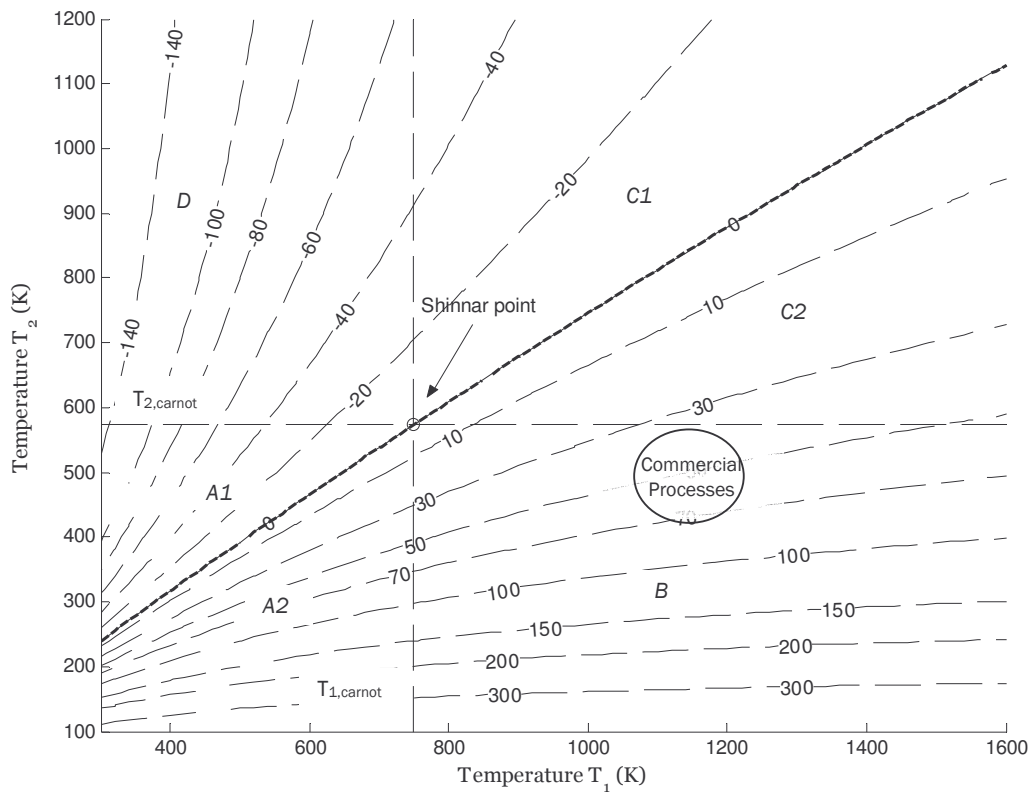
Figure 7.10: The relationship between the temperatures in the two-stage Gas-to-Liquids process for completely work integrated process; also shown is the net work required or produced for a completely work integrated process (+ work means work deficit and - means work surplus and process will reject work)

The operating range for commercial reforming (stage 1) and Fischer-Tropsch processes (stage 2), obtained from literature (Van der Laan and Beenackers, 1999) is also shown on Figure 7.10. It is apparent from Figure 7.10 that the operating range

for commercial Gas-to-Liquids processes falls into the region where work is rejected, i.e. region B. In this region both the reformer section as well as the synthesis section rejects work. The Gas-to-Liquids process is therefore unlike the synthesis of methanol and ammonia, which operate in the region where work needs to be added to the process. In contrast, the Gas-to-Liquids process rejects work from the both the synthesis section as well as the reformer section.

Let us look at the work flows in the process, assuming say that the reformer section operates at a temperature of say 1200 K and the synthesis section temperature of about 520 K.

Table 7.8: Work flows in a typical Gas-to-Liquids process

	Work Flow (kJ/mol)
Reformer	
A. Work required to be input to reformer	150.65
B. Actual work input via heat flow to reformer	187.99
C. Work that can be recovered from reformer (C = B - A)	37.34
Synthesis Section	
D. Work required to be rejected from synthesis section	99.18
E. Actual work rejected via heat flow from synthesis section	88.16
F. Work excess of synthesis section; i.e. amount of work that needs to be rejected by synthesis section (F = D – E)	11.02
Process	
G. Total work input to process if no work recovery/integration done (G = B)	187.99
H. Total work input to process if work is recovered from heat rejected from synthesis section and returned to process (H = G – E)	99.83
I. Total work input to process if all rejected work is recovered from synthesis section and returned to process (I = H – F)	88.81
J. Amount of work to be input to process if all rejected work is recovered from synthesis section and reformer and returned to process (J = I – C or $\Delta G_{process}$)	51.47

In a process where the work associated with the heat is recovered from the synthesis section and integrated into the process, the quantity of work that can possibly be recovered is 99.18 kJ/mol (D in Table 7.8). The total work input can be reduced to 88.81 kJ/mol (I in Table 7.8) if this work is returned to the process. Thus, the work a saving of approximately 50 % can be obtained when compared to a process where no work is recovered or integrated if the work is recovered from the synthesis section. If this is no the case, the 99.18 kJ/mol will be lost. We see that recovering this amount of work is quite a serious design challenge and that if it is not recovered that it will lead to large work losses or entropy increases. For a 1000 ton of ($-CH_2-$)/day process this would equate to recovering 81 MW of work.

In the completely work integrated process, where work from both the reformer section and synthesis section is recovered and integrated into the process, a saving, in terms of work, of about 73% (a saving of 136.52 kJ/mol i.e. C + D in Table 7.8) can be obtained when compared to a process which does not recover/integrate the work. For a 1000 ton of ($-CH_2-$)/day process this would correspond to recovering 112 MW of work.

It should be noted that most commercial Fischer Tropsch synthesis processes operate at low pressures of between 10- 60 bar (Van der Laan and Beenackers, 1999). If compression was used to attain these pressures, then extra work is added to the process and this work need to be recovered or it will be lost from the process. This exacerbates the problem of work rejection and recovery.

Comparison of the three processes considered
The three processes can be compared by plotting the reversible curve for each process on the same set of axes, which is given by Figure 7.11.
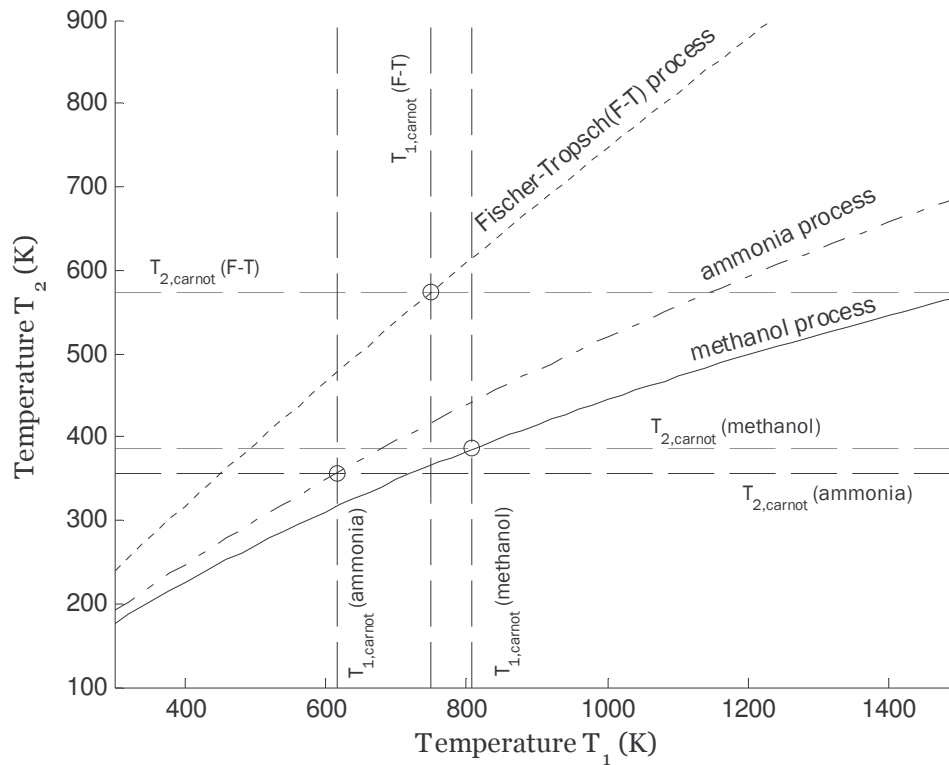
Figure 7.11: A comparison of methanol synthesis, ammonia synthesis and Gas-to-Liquids synthesis based on the reversible work integrated curve.

It is clear from Figure 7.11 that the Gas-to-Liquids process has the highest Shinnar point followed by the methanol process and finally the ammonia process.

It is interesting to note that none of the three processes operates commercially (in terms of their operating temperatures, which were shown in previous figures) close to the Shinnar point or even the curve corresponding to reversible, work integrated processes.

It is clear from Figure 7.11 that the reversible work integrated curve for the Gas-to-Liquids process lies above the curves of both the ammonia and methanol processes. *This means that there is a larger region, in T_1 vs. T_2 space, which work can be produced in Gas-to-Liquids synthesis than in ammonia and methanol synthesis*. If this work is not recovered, this will be lost work and as such result in increased

running costs for the process. The Gas-to-Liquids process also has the largest work requirements in terms of the two-stage process. This means:

- that work flows in the reformer section will be even larger than in the ammonia and methanol case causing increased capital and running costs
- and that the work loads in the Fischer Tropsch synthesis section, which is the largest of the three process, will be even larger based on the process mass balance of the synthesis stage.

Figure 7.11 is useful when comparing the different processes in terms of their energy requirements. Note how these simple graphical (and algebraic) calculations can gives insights into the work flows of the various processes and help in determining the possible opportunities in terms of work integration and savings.

7.5 Supplying further work for the two-stage process

It was determined in the previous sections that the first stage (reforming section) of both the ammonia and methanol synthesis processes rejects work while the second stage (synthesis section) requires extra work. The work rejected from the reformer is less than the work required by the synthesis stage. Hence, a net work input is required for the methanol and ammonia synthesis processes. The amount of work required is dependent on the temperature of stage 1, T_1 and stage 2, T_2 and can be determined using the the iso-work curves plotted in T_1-T_2 space. We next look at the question of how we can put this extra work in.

In the previous chapter we showed that work can be supplied either by the Carnot effect or by the work of separation and/or by compression. We will initially look at adding work by means of compression, as it is a common method used in industry.

7.5.1 Supplying work by compression

In the previous chapter, we discussed how extra work could be put in using compression. We now apply the analysis to the methanol and ammonia process. The Gas-to-Liquids process was shown to reject work and thus does not require further work input.

Methanol synthesis

The effect of compression was determined and plotted in Figure 7.12 and 7.13, which relates the stage 1 temperature (T_1) and stage 2 temperatures (T_2). Figure 7.12 and 7.13 shows the work input by means of compression from the ambient pressure to various pressures or it could be thought of as a pressure ratio between the inlet pressure and outlet pressure. The compression work is calculated in the manner described in chapter 5 (equation 5.13 – 5.16). The compression is done between the two stages; therefore, it gives an indication of the pressure at which the second stage (synthesis section) should operate in order to supply the extra work required. A higher pressure would means a higher work input and can be related to a higher lost work from the process.

We will first consider the case of no work integration as shown in Figure 7.12. Figure 7.12 shows the minimum pressure required in order to obtain a reversible process where the extra work required is supplied by compression. In this case, the pressure is totally dependent on the synthesis section temperature and is independent of the reforming section (stage 1).
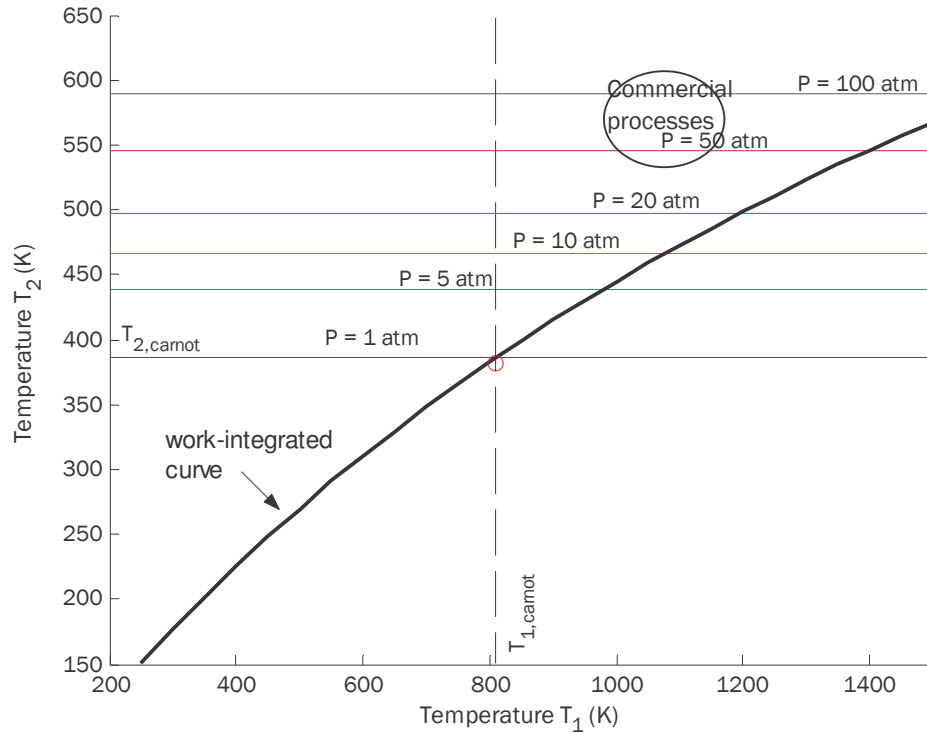
Figure 7.12: Putting in additional work via isothermal compression in an un-integrated two-stage methanol synthesis process

It is clear that by compressing the feed to the synthesis section (i.e. running it at high pressures), one is able to put in work for the process to run in region where most commercial processes currently operate. It is apparent from Figure 7.12 that processes operating at the Shinnar point require no extra work input. The further a process lies from the Shinnar point means a process will require much more work and therefore a higher pressure is needed (if work is supplied by compression). Also shown on Figure 7.12 is the operating range for commercial methanol processes. It is clear from Figure 7.12 that a minimum pressure of between 40 – 100 bar is required if no work integration is considered. Note that commercial methanol processes usually operate at pressure between 50 -100 bar (Twigg, 1989). This suggests that methanol processes are not well integrated. It also suggests that they are fairly reversible from an overall perspective when the process is considered without any work integration.

Figure 7.13 considers the case of a completely work integrated methanol process. Again, one can determine the minimum pressure required for such a process. It is fairly intuitive that such a process will require less work input and therefore a much lower pressure.
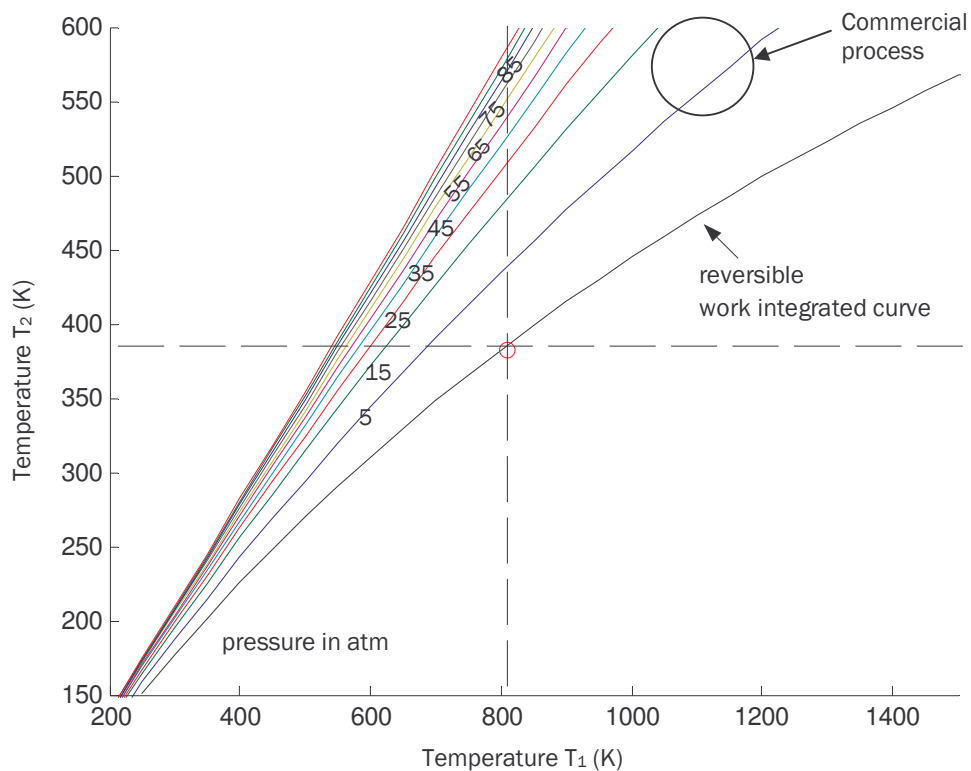
Figure 7.13: The additional of extra work via isothermal compression as shown on the work integrated curve for the two-stage methanol synthesis process

It can be seen from Figure 7.12 by comparing the distances between the pressure curves, that the amount of work gained at low pressures is much greater compared to the worked gained at high pressures.

Figure 7.13 estimates that a pressure of 4-15 atm is required to put in the necessary work. As mentioned, the synthesis section of methanol processes usually operates at pressures of 50- 100 bar. This is far higher than that predicted by the analysis. Also, the minimum pressure required for a completely work integrated process is much lower than for an un-integrated process. This could therefore imply that commercial processes put in much more work than is required by running the compressors at such high pressures. In addition, it is clear that commercial processes are far from being work-integrated i.e. the excess work from the reformer and synthesis sections are not recovered and returned to the process. It is clear from Figure 7.12 and 7.13 that the savings that can be obtained by work integrating processes, in terms of operating costs (lower pressures in compressors) is huge.

Ammonia Synthesis

A similar analysis is performed for the production of ammonia via the two-stage process. The effect of compressing between the two stages on the operating pressure of the synthesis of ammonia is shown in Figure 7.14 and Figure 7.15. Figure 7.14 considers the case of no work integration whereas Figure 7.15 considers the case of a fully work integrated process.
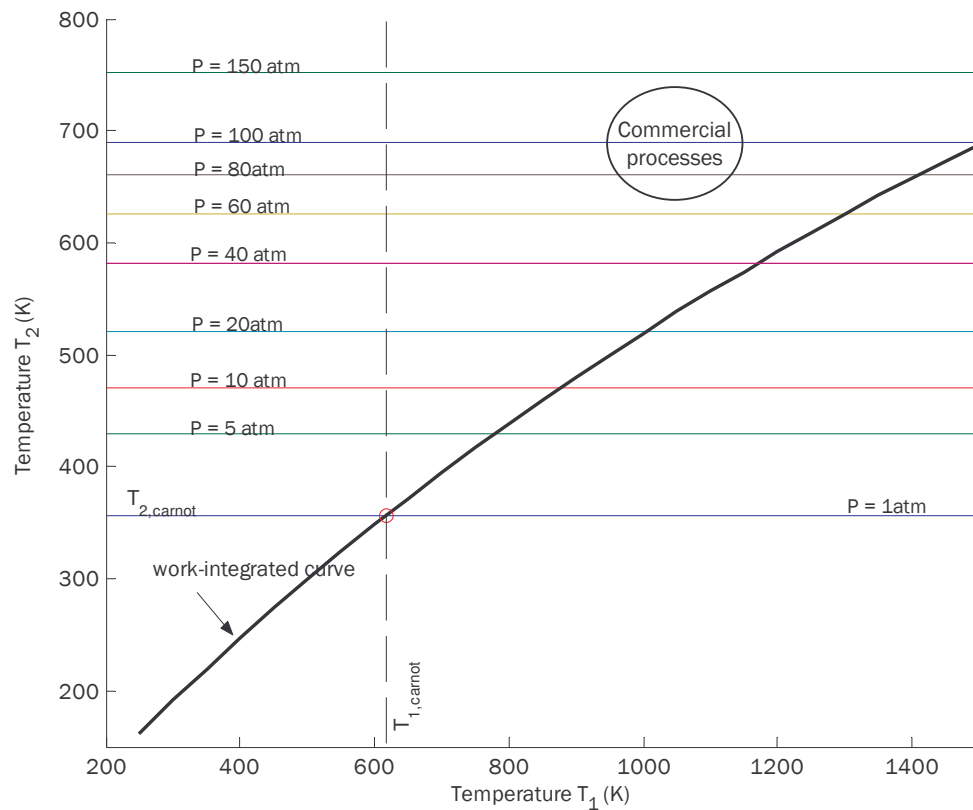
Figure 7.14: Putting in additional work via isothermal compression in an un-integrated two-stage ammonia synthesis process

As with the synthesis of methanol, high pressures are required in order to put in the necessary work for the ammonia synthesis process to operate in the region C1. Figure 7.14 estimates that the minimum pressure required for an un-integrated ammonia process is between 70 – 140 bar. These pressures are higher than that required for an un-integrated methanol process. It therefore appears that the ammonia process requires a higher work input than that of the methanol process. Most commercial ammonia processes operate the synthesis sections at a pressure of between 100 and 250 bar (Vancini, 1971). In the latest technologies pressures have been reduced to between 80 and 150 bar (Greef et al, 2003). We notice the analysis is very close to the pressures at which the latest technologies operate. This suggests that, as with the methanol process, the overall ammonia processes are not well integrated but are fairly reversible if work integration is not considered. The older

technologies were run at too high pressure (high work input) and these processes could be associated with irreversibilities.

Figure 7.15 considers the compression work required for a completely work integrated ammonia process.
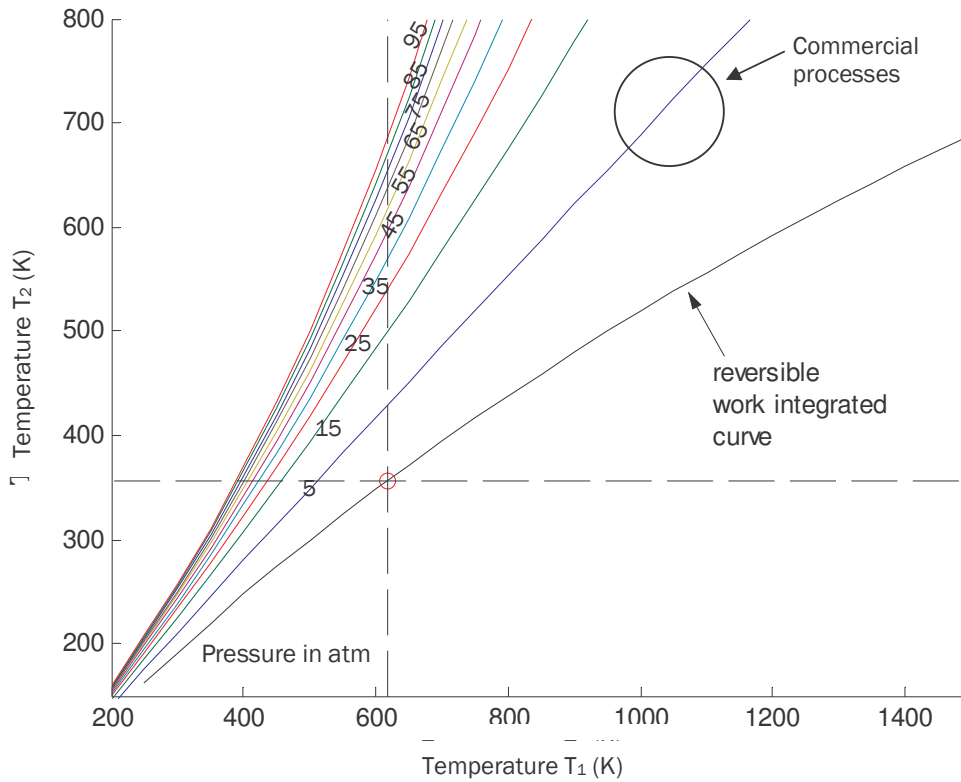
Figure 7.15: The effect of isothermal compression on the work integrated curve for the synthesis of ammonia

It is clear from Figure 7.15 that at low pressures, large gains in work can be obtained but at higher pressures, the gains are much smaller.

Figure 7.13 estimates that a minimum pressure of 3 - 10 atm are required to put in the necessary work. These pressures are far lower then those predicted by the analysis for an un-integrated process and much lower than the pressures used in commercial processes. Also, commercial ammonia processes are not work-

integrated. There is therefore room for improvement in terms of reducing the work input to the process and thus reducing the high-pressure requirement.

7.6   Concluding remarks

In this chapter, we applied the concepts of a mass, energy and entropy flow analysis to industrial processes of interest i.e. the production of methanol, ammonia and Fischer-Tropsch.

The technique illustrated is a simple and useful tool in the synthesis and integration of processes. It can be performed in the earliest stages of the design process as very simple thermodynamic data is required for the analysis. By systematically analyzing the mass, energy and work flows in the processes, one is able to determine the minimum requirements, identify opportunities for process improvements and estimate the potential reduction in work input such that process can be design better and more efficient. The technique also gives insight into design parameters such as operating temperatures and pressures of the various stages of the process. The technique is also useful in analyzing existing process with the aim of improving such processes.

The analysis of the methanol process revealed that such processes operate far from reversibility (and thus is not work integrated) and require large amount of work. A way the work can be inputted is by operating the synthesis section at high pressure. The technique was also able to estimate the pressure required (for a completely work integrated process) to put in the work required for operating conditions of commercial methanol processes.

The analysis of the ammonia process revealed similar results as current technology limitations (materials of construction, catalysts limit etc) do not allow the ammonia process to operate reversibly/work integrated. Work is required to attain these current operating conditions and the work is put in by operating the synthesis section at high pressures. Again, the technique was able to predict the pressure required for the process and the predicted pressures are much lower than the pressure used by commercial processes. This again indicates that commercial ammonia processes are not work integrated and possible savings can be achieved by work integrating processes.

The synthesis of Fischer Tropsch products was found to operate in the region where work is lost and therefore thus not require further work and thus there is no need for high-pressure operations. Work is lost in both reformer and synthesis sections. An interesting question is whether such processes could be designed more efficiently in order to reduce the work lost from the process such that the process operates closer to the reversible curve.

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8

ANALYZING A DISTILLATION SYSTEM[**]

8.1   Introduction

Although distillation is one of the most widely used separation technique in the chemical industry and will continue to be used in the future, improvements in the energy efficiency of the process remains a challenge for the industry, especially due to the rising costs of energy and growing environmental concern.

Various design strategies have been proposed for the minimizing the energy consumption in distillation systems. These include the use of complex distillation arrangements, column coupling, energy integration and heat pumping techniques (Rev et al., 2001).

In this paper, we will consider the use of heat pump techniques to distillation systems. Distillation is based on the principle of supplying work to effect a separation by supplying heat at a high temperature (to the reboiler) and rejecting heat at a lower temperature (in the condenser). The addition of a heat pump to a distillation system allows the reuse of the heat in the condenser by the addition of mechanical work. Thus a vapor recompression system can reduce the amount of energy required considerably (Kenney, 1979; Castells and Ferre, 1984; Meili, 1990).

The heat pump can be applied to a distillation system by means of three possible configurations (Meszaros and Fonyo, 1986): (a) closed cycle process, which involves the use of an external working fluid (b) vapor recompression (c) bottom flashing. In this study, we will focus on the vapor recompression system since it has been found to be the most advantageous and economical of the three configurations (Null, 1976; Fonyo, 1998)

The subject of applying a vapor recompression system to distillation has been studied extensively. The literature has seem to focus mainly on *analyzing or simulating*

[**] This work was carried out in conjunction with the Process Integration and Systems Optimization group, Chemical Engineering Department, Texas A & M University, under the supervision of Prof. M. M El-Halwagi

various systems and the economic optimization of these systems and their operating conditions (Null (1976), Quadri (1981), Omideyi et al (1984), Brousse et al. (1985), Ferre et al. (1985) , Meili and Stuecheli (1987))

Many of these studies have found for the various systems studied that vapor recompression is most feasible for close boiling mixtures, systems which require high heat loads, small column pressure drops and low process temperatures. (Carta et al, 1982)

The approach proposed is to apply fundamental thermodynamic principles to the system i.e. energy and entropy balance. Thermodynamic analyses of distillation columns, mainly employing the first law of thermodynamics, have been performed previously. The second law has also been employed to analyze distillation columns (Fonyo, 1974; Fitzmorris and Mah, 1980; Itoh et al, 1980; Kaiser and Gourlia, 1985; Taprap and Ishida, 1996). A review of the application of thermodynamic analyses to separation systems, in particular, distillation can found in the literature (Demirel, 2004). It has been found that conventional distillation is very inefficient from a thermodynamic point of view (see, for example, Freshwater, 1951; Flower and Jackson, 1964; King, 1980).

Pinch analysis, which is also based on thermodynamic principles, has also been applied to determine the best placement of the heat pump into the distillation system (Bernstead and Sharman, 1990; Rivera-Ortega, 1999). These analyses require the compositions, number of stages and reflux ratio of the column to be known in order to determine the feasibility of implementing the heat pump into the system.

In this paper, we will consider the *synthesis* of a vapor recompression distillation system. In particular, we will also show how one can systematically decide when to use a distillation system with vapour recompression instead of a conventional distillation system.

We will use the thermodynamic equations from a process synthesis and integration perspective, where only the inputs and outputs are known and the details of the process are unknown. We will show that it is possible, using very limited data, to synthesize processes in the early design stages without the need of detailed design.

We set targets for the process based on fundamentals variables ahead of the detailed analysis and the cost optimization.

8.2   Conventional Distillation Column

Consider a conventional distillation column, which includes both a reboiler (heat source), with a heat duty Q_R, and condenser (heat sink), with heat duty, Q_C, as shown in Figure 8.1. The feed to the system is a binary mixture of components A (most volatile) and B (least volatile). Assume a complete separation of components A and B i.e. pure A in the distillate and pure B in the bottoms.
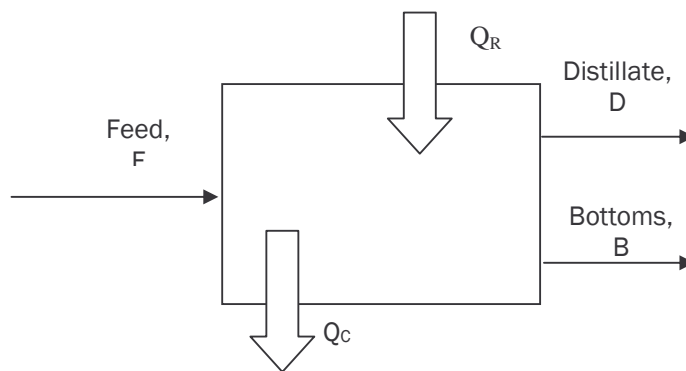

Figure 8.1: Conventional Distillation system

We start by writing the overall mass balance for the system:

$$F = D + B \tag{8.1}$$

where

F is the feed flowrate (in terms of moles) = $N_A + N_B$, where N_A is the number of moles of component A and N_B is the number of moles of component B

D is the distillate flowrate, which, under the assumptions made, will be equal to N_A

B is the bottoms flowrate, which, under the assumptions made, will be equal to N_B

The energy balance for the system can now be written. In order to simplify the analysis, we assume that the enthalpy difference between products streams and the feed stream is negligible. The change in enthalpy due to mixing is also ignored. These are reasonably assumptions, since the heat duties in the condenser and reboiler are usually much larger then these enthalpies. Thus, the energy balance is given as follows:

$$Q_C = Q_R \tag{8.2}$$

where

Q_C is the heat duty associated with the condenser

Q_R is the heat duty associated with the reboiler

According to the energy balance, the quantity of energy entering the system must equal the quantity of energy leaving the system.

An entropy balance for the system can now be employed for the system. It is assumed that the system is reversible i.e. there is no entropy generated within the system.

$$S_{feed} + \frac{Q_R}{T_R} = S_{distillate} + S_{bottoms} + \frac{Q_C}{T_C} \qquad [8.3]$$

where

S_{feed} is the entropy of the feed stream

$S_{distillate}$ is the entropy of the distillate stream

$S_{bottoms}$ is the entropy of the bottoms stream

T_R is the temperature at which the heat, Q_R enters the system

T_C is the temperature at which the heat Q_C leaves the system

The feed, distillate and bottoms entropies can be written in terms of the entropies of the components A and B as follows:

$S_{feed} = N_A S_A + N_B S_B + (N_A + N_B) \Delta S_{MIX}$ [8.3a]

$S_{distillate} = N_A S_A$ [8.3b]

$S_{bottoms} = N_B S_B$ [8.3c]

where ΔS_{MIX} is the entropy change due to mixing. For an ideal mixture, the entropy change of mixing is given by $R\sum (x_i \ln x_i)$ where R is the gas constant and x_i is the mole fraction of component i in the mixture

Substituting equations 8.3 a, b and c into equation 8.3 and simplifying gives the following relationship

$$(N_A + N_B)\Delta S_{MIX} = \frac{Q_C}{T_C} - \frac{Q_R}{T_R} \qquad [8.4]$$

Substituting for Q_C using the energy balance (equation 8.2) gives

$$\Delta \hat{S}_{MIX} = Q_R \left[\frac{1}{T_C} - \frac{1}{T_R} \right] \qquad [8.5]$$

Equation 8.5 is useful as it can provide a target for the heat duty, Q_R required by the system. It provides the minimum heat duty for the reboiler. It is dependent on the temperature of the reboiler and the temperature of the condenser.

8.3 Distillation system with vapor recompression

Consider a distillation system with vapor recompression (heat pump) as shown in Figure 8.2. We will consider, in this paper, the recompression of overhead vapours. In this scheme, the overhead vapours are compressed and then condensed in the reboiler/condenser in order to provide the necessary heat load.
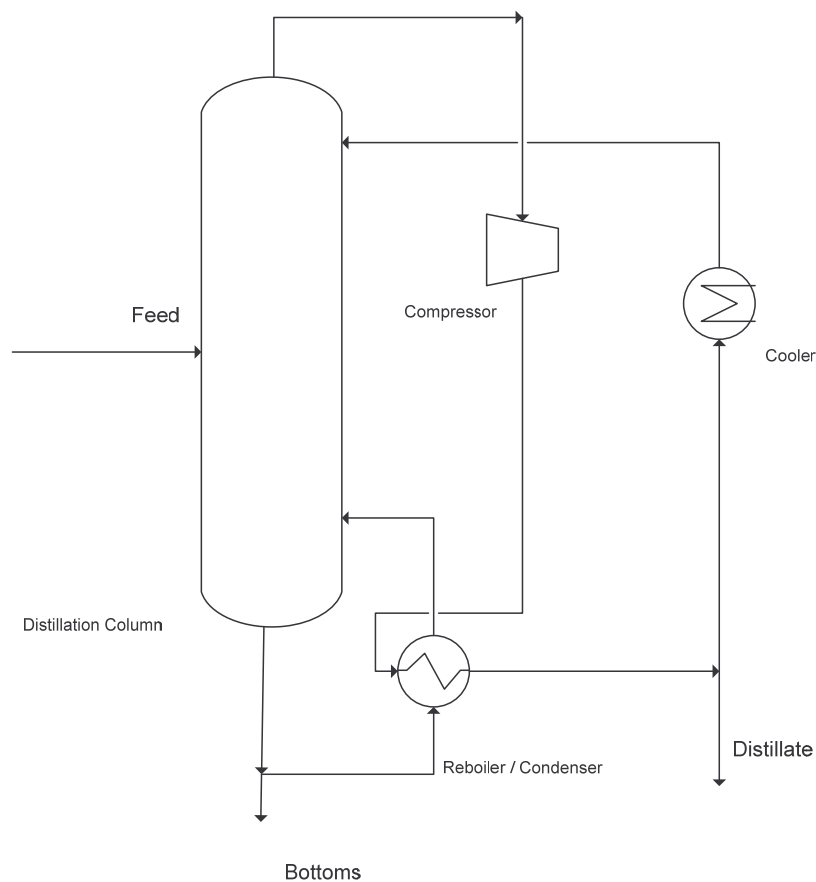

Figure 8.2: Direct recompression of overhead vapor

Let us analyze the overall heat and work flows of the system shown in Figure 8.2. These can be illustrated as shown in Figure 8.3.
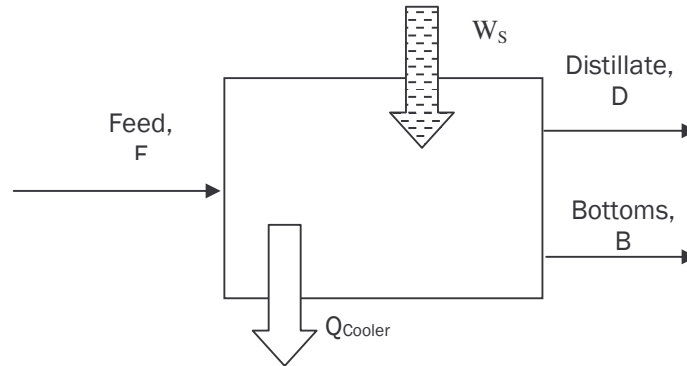
Figure 8.3: Heat and work flows in a vapor recompression system

Work enters the system via the compressor. Heat leaves the system via the cooler. Note that the reboiler heat load is not considered since it is internal to the system.

Assume again, a complete separation of components A and B. The mass balance for the system (shown in Figure 8.2 and 8.3) is identical to that of the conventional distillation system.

The energy balance for the system can be written as follows:

$$W_S = Q_{cooler} \qquad\qquad [8.6]$$

where

W_S is the work of compression

Q_{cooler} is the heat leaving the cooler

Again, it is assumed the enthalpy difference between the product streams and feed streams is negligible compared to heat and work loads.

The entropy balance for the vapor recompression system is given as:

$$S_{feed} = S_{distillate} + S_{bottoms} + \frac{Q_{Cooler}}{T_R} \qquad\qquad [8.7]$$

Once again, reversibility is assumed. It is also assume that the heat in the cooler will be rejected at temperature, T_R. In reality, there could be a range of temperatures and

equation 8.7 could be modified if the specific heat data is known. As we focusing on obtaining a simple target, T_R represents the highest temperature and therefore corresponds to the maximum work. Once again, the entropy of the feed and product streams can be written in terms of the entropies of components, as the analysis for the conventional distillation system.

Simplifying and substituting for Q_{cooler} from the energy balance (equation 8.6), one obtain the following expression:

$$\Delta \hat{S}_{MIX} = \frac{W_S}{T_R} \qquad [8.8]$$

Equation 8.8 provides one for a target for the compression work required for a distillation system with vapour recompression. It is a function of the entropy change of mixing for the system and the reboil temperature (which can be related to the boiling temperature of the components).

8.4 Comparison of the conventional distillation system and the distillation system with vapor recompression

We will base our comparison of the two configurations on a common variable, *work*. In order to do this, we need to find the work equivalent of the heat input, Q_R, to the conventional column. Assume that we supply this heat via a heat engine as shown in Figure 8.4.
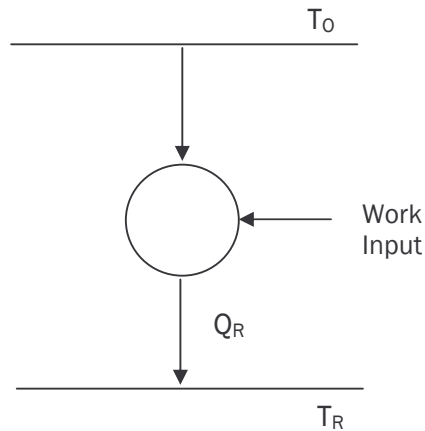

Figure 8.4: Work equivalent of the heat input to the conventional distillation column

We can therefore relate the heat input to a work input as follows:

$$W_Q = Q_R \left(1 - \frac{T_O}{T_R}\right)$$ [8.9]

Substituting for Q_R in equation 5 and rearranging gives the following relationship:

$$\Delta \hat{S}_{MIX} = \frac{W_Q}{T_C} \left[\frac{T_R - T_C}{T_R - T_O}\right]$$ [8.10]

For both configurations, the entropy change of mixing should be equal, assuming an identical separation for both cases. Thus, we can equate equations 8.8 and 8.10 in order to find a relationship between the compression work required in the vapor recompression and the equivalent work required for a conventional distillation system. The ratio between the compressor work and equivalent work for a conventional distillation system is given by:

$$\frac{W_S}{W_Q} = \frac{\left[\frac{T_R}{T_C} - 1\right]}{\left[1 - \frac{T_O}{T_R}\right]}$$ [8.11]

By manipulating equation 8.11 one can find a relationship between T_R and T_C, which are essentially the boiling points of the least volatile and the most volatile components in the system. The relationship between these temperatures is given as

$$T_C = \frac{T_R}{\left(1 + \frac{W_S}{W_Q}\right) - \frac{T_O}{T_R}\frac{W_S}{W_Q}}$$ [8.12]

In interesting case to consider is when the compressor work in the vapour recompression system equal the equivalent work for the conventional distillation system i.e. the ratio $W_S/W_Q = 1$. The relationship between TR and TC is given by:

$$T_C = \frac{T_R}{2 - \frac{T_O}{T_R}} = \frac{T_R^2}{2T_R - T_O}$$ [8.13]

This relationship between T_R and T_C can be plotted and can be used to determine whether vapor recompression is advantageous over a conventional distillation system. Figure 8.5 shows the relationship between T_R and T_C and the region in which vapor recompression is more favourable then a conventional column.
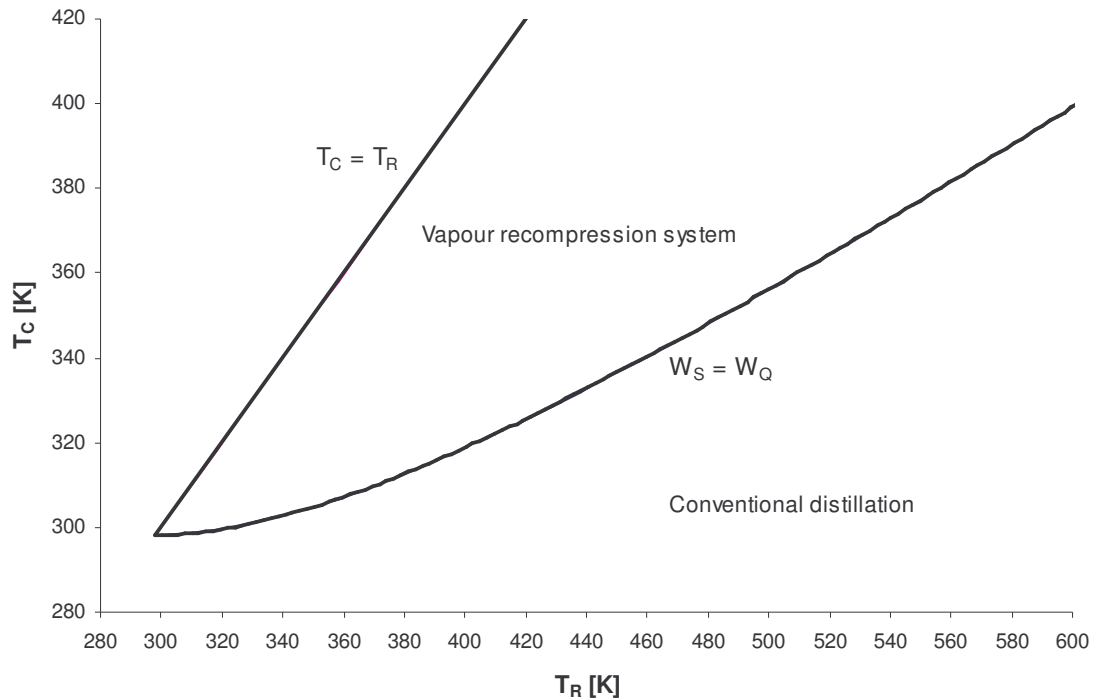
Figure 8.5: Graphical method to determine the feasibility of distillation with vapour recompression

Based on Figure 8.5 and the boiling points of the components in the system, one can determine whether is will be thermodynamically feasible to apply vapour recompression. Thus, Figure 8.5 can be used to screen whether vapour recompression can be applied to various systems or not very simply and effectively.

8.5   Concluding remarks

In this chapter, we have devised a simple method for comparing a conventional distillation system and a distillation system with vapour recompression. This method allows one to quickly determine the factors the choice of the separation equipment. It allows one to set targets for the system and can be used to easily eliminate the bad alternatives and home in on the better alternatives.

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9
CONCLUSIONS AND OUTLOOK

9.1 The approach

The aim of thesis has been to develop techniques in the fields of process synthesis and integration, which takes into consideration sustainability. In particular, the thesis concentrates on accounting for the efficient use of raw materials and energy as well minimizing the environmental impact of chemical processes.

These techniques have been developed mainly for application in the early stages of the design process. In these early stages, only minimum information, time and resources are available but the decisions taken in this stage are extremely crucial.

The main aim of the tools and techniques developed is to identify performance targets for the process. These targets are identified before detailed design is carried out and do not require the structure of the process (i.e. a flowsheet). These targets allow an understanding of the process and thus direct the design of the process.

9.1.1 Old tools for a new purpose

Chemical processes are usually characterised by flows of mass, heat and work (see Figure 9.1.). The flow of mass is usually subjected to the law of mass conservation i.e. a mass balance. The flow of energy (heat and work) is subjected to both the first and second law of thermodynamics. The first law describes the conservation of energy; while the second law (entropy balance) is used to describe the ideal thermodynamic process as well as the extent and magnitude of the loss work or irreversibility of the process, thus giving an indication of where designers need to concentrate their efforts to improve the performance of the process.
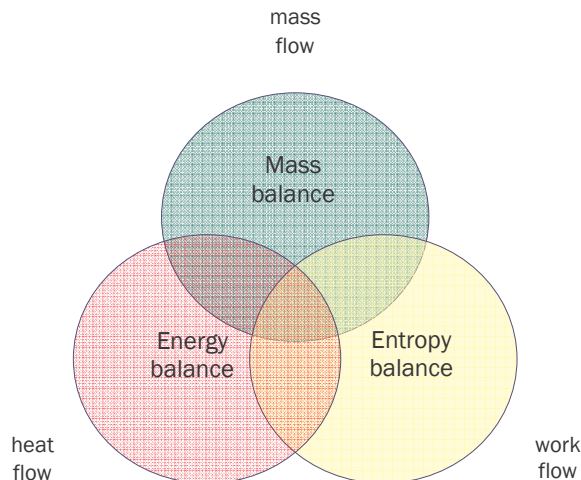
Figure 9.1: Approach for setting targets and synthesizing chemical processes using mass, energy and entropy

9.2 Summary of main results

In this thesis, the mass balance, energy balance and entropy balance are used to set targets for chemical processes. These targets are based on the overall process as it only considers the inputs and outputs from the process i.e. it is independent of the structure of the process or the flowsheet. Ways of calculating the minimum amount of mass inputs, minimum amount of energy (or maximum amount of energy produced) and minimum work required (or maximum work produced) have been shown. There is a strong interrelationship between these three variables (mass, energy, work) and all three variables have to be considered when setting a target. The targets are important as processes operating at these targets have minimum heat and work loads, which in turn corresponds to minimum operating costs of the plant. In addition, processes operating at these targets also have we believe, if not minimum, at least reduced capital costs. The simultaneous reduction in both capital and operating costs occurs because as heat and work loads decrease, the process equipment becomes smaller and, in same cases, less complex in order to handle the decreased heat and work flows.

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, as well as various other criteria (such as environmental aspects, cost etc). The energy requirements are then accounted for by applying the energy balance to the overall mass balance. The work requirements are also determined for each overall mass balance based on the entropy balance. An understanding of which of the three variables is the limiting target is also very important in that gives insight into what is the important or limiting parameter in the design and operation of the process.

These targets also give insights, at a very early stage, into integration of the process. It has also been shown that targets can be achieved by considering mass, heat and work integration of a process. This is useful not only for the design of new processes but for retrofitting as well. These targets also provide an easy method of screening various mass balances either graphically or algebraically.

The approach has been applied to various examples relating to the synthesis of methanol and various interesting results have been discovered relating to such a process. In particular, it has been shown how one can produce methanol from methane (or coal), in the conceptual design phase, with reduced carbon dioxide emissions or no carbon dioxide emissions. The approach can easily be applied to other processes of interest.

It has also been shown how each of the overall mass balances can be analyzed, based entirely on the inputs and outputs from the process, using mass, energy and entropy. A specific case, methanol production from methane, carbon dioxide and water, was considered. As a first step towards achieving the overall mass balance, we considered the process to occur in a single stage. It was shown that this one-stage process required heat as well as work. It was not possible to match the heat and work requirements for this particular process. In order to overcome this, more work has to be added to the process. The ways of putting in additional work that were considered: (a) adding work via the Carnot engine effect (b) adding work by compression (c) adding work by separation. It was found that this particular one-stage methanol production process was not feasible even with the addition of more work. Therefore, an alternative configuration of the overall process was required.

We therefore considered the analysis to a two-stage methanol production process and tried to determine the feasibility of such a configuration. Once again, each stage is analyzed in terms of its mass, heat and work flows. It was shown that the first stage required heat and work (this work can be virtual) whereas the second stage produced heat as well as work. It was shown that each stage could potentially match the heat and work requirement (at a specific temperature) in a reversible manner.

We then considered integrating the heat and work flows between the stages. This led to the introduction of the concept of work integration between the stages. By considering work integration, it is possible to obtain a relationship between the temperatures of the stages (the work-integrated curve) such that the overall process can be reversible. We postulated that processes are most efficient if they operate as close as possible to the work-integrated curve. This can be achieved by considering different overall mass balances.

It was also established that commercial methanol synthesis processes and ammonia synthesis processes require further work as these processes are limited by the operating temperatures of the catalysts as well as the stability of the materials of construction. We looked at how this extra work can be put in via compression for the two examples. The minimum pressure required for putting in this extra work could be determined. An analysis of the Fischer-Tropsch process (Hydrocarbons production from methane) showed that the process rejects works. Thus, the process does not require further work input or high-pressure operation. The rejected work must be recovered or else it will be lost (appear as irreversibilities), resulting in higher operating and capital costs.

Finally, the approach was applied to a distillation system. We showed how one can set targets for a conventional distillation system and a distillation system that employs vapour recompression. A way of deciding between the conventional system and vapour recompression system was also developed.

9.3 Recommendations

This work presents the beginnings of a systematic approach to targeting and synthesizing chemical processes in the earliest design phases.

Further work should focus on developing a systematic framework for achieving the given targets by deducing the various tasks (reaction, mixing, separation etc) required and the how these should be connected. This has only been partially determined in this thesis. One way of achieving this is by using aggregate superstructure models. Other methods (for example, a linear programming approach) are currently being investigated.

In this thesis, we have only considered specific work of separation. Further work is focusing on including the flowrate to the separator which in the case of both methanol and ammonia synthesis id dependent on the recycle flowrate.

The practicalities associated with work-integrated processes need to be considered. Ways in which work can be recovered, for example, from the Fischer-Tropsch process efficiently need to be devised.