UNIVERSITY OF THE WITWATERSRAND

A Graphical Approach to Analyze Processes Using Thermodynamics

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DECLARATION

I declare that this thesis in 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

Efficient use of energy and efficient use of raw materials are among the key factors for sustainability in the process industries. In the field of process synthesis and integration much progress has been made in developing design and optimization tools in order to improve the efficiency of chemical processes. Techniques such as hierarchical decomposition, pinch analysis and mathematical programming (MINLP) have made possible the development of improved processes in terms of energy and mass efficiency, environment and economics. However there is still room for improvement. The work in this thesis is part of the many efforts that are being made to develop systematic methods for synthesizing more efficient processes.

It has been shown that most of the features and cost of a process are usually fixed in the early stage of process design; therefore decisions made during this stage are crucial and thus there is a need for systematic methods that would guide decision making toward more efficient processes using as little information as possible. We have developed tools that combine fundamental thermodynamic concepts and a graphical approach in order to gain insight and provide a systematic way for not only determining process *targets* but understanding what is required in order to meet these *targets*. The approach used in this thesis is based on the idea that every process in which certain feed materials are converted into products has a certain amount of *heat* and *work* associated with it. Understanding the relationship between the *heat* and *work* can provide insight into the process and can give an indication of what the process structure would be.

Chemical processes are analyzed in terms of their *heat* and *work* requirement using the analogy of heat engine and a graphical approach. This approach looks at chemical processes holistically, where only the inlet and outlet streams are considered. Processes are represented and classified in different thermodynamic regions in a ΔH - ΔG space (gh-diagram) where their feasibility and reversibility are analyzed. This allows determining whether heat at an appropriate temperature is sufficient to meet the work requirement for a process, or if other means should be considered.

The gh-diagram is used to understand how process conditions such as pressure and temperature can be manipulated in order to meet heat and work requirements more reversibly. The relationship between process heat and work requirement and process complexity is revealed. The approach is applied to ammonia processes to understand the implications of process conditions and catalyst choice, on the heat and work requirement, process complexity and process efficiency.

The approach has been also used to analyze combustion processes and it has been shown that it is not possible to combust carbon based materials efficiently and a considerable amount of work potential is lost during the combustion process. However other substances have been explored and it has been showed that some of these have the potential for more reversible combustion. Opportunities to produce valuable chemicals such as fertilizers in addition to power production have been revealed.

This approach does not require much information or complex calculations and is suitable to be used in the early stage of process design for a quick insight into the process and analysis of alternatives.

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1 INTRODUCTION

1.1 Sustainable development and the process industry

Dincer and Rosen (2004) have noted that '*The world is changing rapidly due in part to the increasing wealth and size of the population.'* This goes along with increasing production in industrial processes and most importantly in the consumption of raw materials and energy, in order to meet the growing needs of the population. However concerns have been raised on the limited availability of our natural resources and the impact of the use of non-renewable energy on the ecosystem. The trend of human activities leads the earth to be stressed beyond its carrying capacity (Stuart January - February 1997). Among the most important issues that the world is facing today include:

- The growth and dynamics of the world population: the growth of the world population has been estimated at about 90 million people per year, and most of it occurs in the developing nations. Economic development in these nations is driven by the need of alleviating poverty and improving living standards. This will lead to increased global energy demand up to 10 times by 2050 (Stuart January - February 1997, Dincer 2000, World Energy Council 1995).
- Diminishing natural resources and degradation of the environment: currently human survival and development is built on a one way flow use of natural resources. Industrialization and excessive dependency on fossil fuels, is believed to be responsible for many environmental problems including global climate change due to CO_2 emissions, acid rains, ozone depletion and

emission of a wide range of pollutants including toxic substances in water streams and underground waters; excessive use of arable land and deforestation in most developing nations, are among other elements that threaten the survival of current and most importantly of future generations (Fells 1990, Dincer, Rosen 2005).

- The non-sustainable nature of current industrial practices: industrial production has played an important part in meeting current life style needs and improving living standards. However the trend in most industry is the one that leads to resource depletion and environmental destruction. Sustainability questions are being raised concerning the current approach in the process industry where large amount of raw materials are consumed as feedstock and as energy source (Hinderink, van der Kooi & de 1999, Dewulf et al. 2000, Gong, Wall 2001, Wall 2002).

The solution for sustainable development can only be found in a complex combination of the ecosystem, natural sciences and different aspects of human kinds including socio-cultural, economic and political aspect (Dewulf et al. 2000, Wallner 1999). However there is no doubt that industrial revolution will play a bigger part in addressing the issues of sustainability (Korhonen 2004). Stuart (January - February 1997) noted that '*The more we learn about the challenges of sustainability, the clearer it is that we are poised at the threshold of a historic moment in which many of the world's industries may be transformed'.*

In order for the process industry to take a move toward sustainable development, there are a number of issues that need to be addressed. Among the most important ones include:

- Energy efficiency: with diminishing energy resources and the environmental impact arising from energy utilization, there is a greater need to use energy more efficiently in the process industry. One of the requirements for sustainable development is the use of sustainable energy resources which must be assisted by efficient use of these resources (Dincer, Rosen 2004, Rosen, Dincer 2001). A number of studies are being conducted in the framework of energy integration in order to develop techniques that will help reduce energy consumption in process industries.

- Efficient use of raw materials: it has become clear that any feed material to a process that is not transformed into desirable products will end up as waste which, in a short or long term, could be detrimental to the environment. Following strict environmental regulations, most process industries have adopted the end of pipe approach, where waste is first created then treated in another process to bring it to an acceptable level of toxicity before it is discharged in the environment. This usually tends to worsen the situation as, in addition to capital cost increase, the energy consumption increases as well, making the overall process less efficient (Van Berkel 2000). Therefore strategies are needed to conserve resources and reduce discharges from industrial processes. These could include material recycle, material reuse or material substitution and process modification (El-Halwagi, Gabriel & Harell 2003).

1.2 Contribution and Approach

In the field of process synthesis and integration, efforts have been made to develop new ways of analyzing and designing processes so as to reduce energy consumption and waste production. Many authors have agreed that, the tools and techniques developed within this field are of great importance in addressing sustainability issues in process industries (O'Young, Natori 1996, Johns 2001, Kalitventzeff, Maréchal & Closon 2001, Dunn, Bush 2001, Dunn, El-Halwagi 2003). Some of the tools have already been successfully applied in the industry and have resulted in savings up to 60% as a consequence of improved efficiency.

The work in this thesis is part of the many efforts that are being made in the field of process synthesis and integration in order to meet the challenges of energy and material efficiency in the chemical and energy production industry. Since most of the features and cost of a process are usually fixed in the early stage of process design, decisions made during this stage are crucial (Biegler, Grossmann & Westerberg 1997). We have developed tools that combine fundamental thermodynamics concepts and a graphical approach in order to gain insight and provide a systematic method that allows not only determining process *targets* but gives an understanding of what is required in order to meet these targets. A holistic approach has been adopted, where processes are first analyzed at their highest level by looking at the inlet and outlet streams only; details are considered at a later stage. These tools can be useful in the early stage of process design in particular, the conceptual design phase, as they are able to guide decision making toward more efficient processes.

The approach adopted in this work is based on the *second law of thermodynamics*; we use the concept of '*work'* commonly known as '*exergy'* which is a kind of *necessary energy* required in order to transform certain feed materials into products. Thus a process becomes inefficient when more '*work'* is consumed than necessary due to many factors including:

- Production of undesirable products along with desirable ones. The potential impact of this on the environment and economics is twofold; firstly the undesirable products could become waste which could potentially be detrimental to the environment, secondly the process would require additional energy in the production of these waste products leading to unnecessary CO_2 emissions. This goes along with increased operating cost of the process in a sense that the amount of feed material must be increased since part of it is turned into waste and the required rate of production of desirable products must be met. In addition the energy cost of the process is increased as well since part of it is consumed to produce these waste products.

- Loss of energy within the process as a result of poor energy integration or poor interconnections between different parts of the process, bad choice of operating conditions such as pressure and temperature or even bad choice of material transformation path or reaction path.

We see that the concept of *work* could provide a more integrated way of assessing a process. It could help developing valuable tools for use in the design and retrofit of industrial processes in order to reach sustainability.

Thermodynamic concepts have been found to be a tangible basis in assessing different aspects of industrial processes. Cornelissen (1997) has demonstrated exergy analysis as a powerful instrument to obtain sustainable development in production processes. Dewulf (2000) have performed the assessment of the sustainability of technological processes in a quantitative way based on the laws of thermodynamics; they use the concept of *exergy* to reflect the extent to which renewable sources are used, to assess the efficiency of a technology taking into account the generation of waste products and the exergy required to transform the waste into desirable products. Dincer and Rosen (2004) have also shown that exergy analysis is an important tool for achieving sustainable development by noting that energy can never be “lost” as it is conserved according to the first law of thermodynamics, while exergy can be lost due to internal irreversibilities. They suggest that exergy losses, particularly due to the use of nonrenewable energy forms, should be minimized to attain sustainable development. Ayres (1998) has shown that the economic significance of the second law lies in the fact that exergy is not conserved and that exergy is a useful common measure of resource quality as well as quantity, applicable to both materials and energy; it can be used to measure and compare resource inputs and outputs, including wastes and losses. Many other authors have also shown the ties between sustainability, economics and thermodynamics (Dincer, Rosen 2005, Dewulf et al. 2000, Gong, Wall 2001, Wall 2002, Szargut 1980, Rosen 2002, Rosen, Dincer 2003, Hammond 2004, Tonon et al. 2006). Thermodynamic concepts, especially the *second law* and *exergy*, have been applied in a number of fields and it has been shown that the number of fields could be even greater in the future and could lead to savings in human effort to achieve sustainability in the use of land, water, energy and natural resources (Hirs 2003).

1.3 Process Synthesis

Process synthesis generally deals with developing process flowsheets with the aim of finding the best flowsheet that meets certain objectives. Chemical processes are made up of a set of parts, known as unit operations, connected in an organized manner in order to transform raw materials into desirable products. While the operation of each part has been well understood, the connecting them together in order to achieve the best arrangement, in terms of energy efficiency, environment and economics, is a major challenge and the focus of process synthesis. The number of possible arrangements for a typical chemical process has been estimated to be in the order of 10^4 to 10^9; only less than 1% of these alternatives are commercialized (Douglas 1988, Kirkwood, Locke & Douglas 1988); analyzing each arrangement and choosing the one that will work better seems to be impossible. Therefore it is clear that in order to achieve sustainability in the process industry, there is a need to develop *systematic methods* of generating the most energy efficient, environmental friendly and economic arrangement.

The economic and environmental benefits of process synthesis are enormous. Conceptual process synthesis is becoming an increasingly important field of activity in the industry and academia (Li, Kraslawski 2004). The application of process synthesis in the industry has led to cost savings ranging from 20 to 60% (Harmsen 1999).

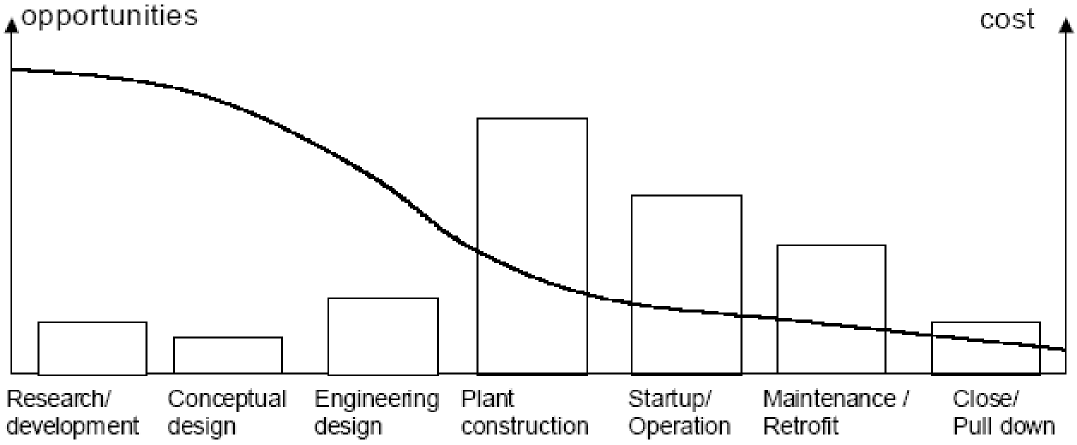

Fig. 1-1: Opportunities for environmental impact minimization along process life cycle (Yang, Shi 2000)

Fig. 1-1 depicts the stages in a process life cycle along with the opportunities for environmental considerations and cost (Yang, Shi 2000). We can see in Fig. 1-1 that during the conceptual design of the process there are more degrees of freedom and this provides more opportunities to minimize the environmental impacts of the process. As the process development progresses it becomes more and more difficult to make changes to the original design. The cost increases, the number of degrees of freedom decreases and the opportunities for environmental considerations decrease as well. We also see that once the plant has been constructed and put in operation retrofitting to improve the plant performance becomes more costly and offers little environmental improvement compared to the conceptual design phase. Another representation of process design economics is shown in Fig. 1-2 (Korevaar 2004), we can see that most of the money assigned to the process is fixed during the conceptual design phase. Note that the cost during this stage is low and that the degrees of freedom are high. There is limited information available during conceptual design phase and that this phase often happens quickly (Sueranan 2006). Therefore the decisions taken during this stage are of a great importance as they determine both the environmental impact as well as the economics of the process. This provides a good incentive to '*getting it right from the beginning'* as it results in enormous savings in the long run. There is therefore the need for systematic methods that require as little information as possible and that are able to guide decision making in conceptual design toward more sustainable processes.

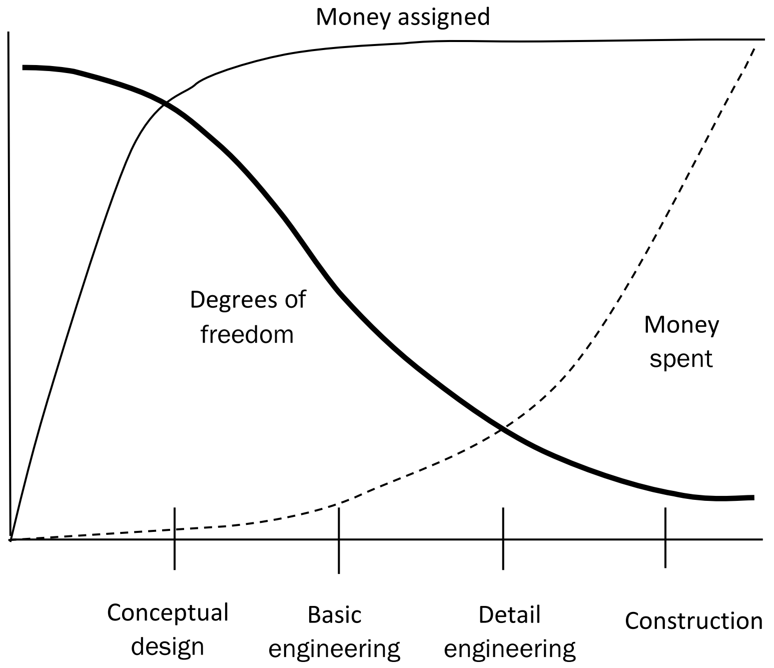

Fig. 1-2: Financial characteristics and degrees of freedom of the various stages in process design (Korevaar 2004)

Previously designing a chemical process was an act of guessing and knowing how others did it before, or comparing with other processes. This approach is still much used and has led to sophisticated designs. However it does not guarantee that the design obtained is the best (Hendry, Rudd & Seader 1973). Progress has been made in developing systematic approaches to process design; a number of techniques have been developed which provide guidance in the selection of equipment and the interconnection between them as well as provide means of evaluating the process and finding alternatives. Reviews on developments in the area of process synthesis can be found in Hendry et al. (1973), Hlavacek (1978), Nishida et al. (1981), Westerberg (1980, 1989) and Grossmann and Daichendt (1996).

The numerous techniques for process synthesis can be classified in three categories according to the approach used (Grossmann 1985, Gundersen 2002). 1) *Heuristics:* make use of rules-of –thumb that are based on engineering judgment or experience. 2) *Thermodynamics*: based on setting up performance targets, usually energy type targets. 3) *Optimization*: uses mathematical formulations to represent a process, and searches for a solution by optimizing an objective function. There is significant overlap between the various approaches and today there is a strong tendency to using all three categories in order to exploit their respective strengths. For example, the amount of structural alternatives for a process is reduced by the use of insight, heuristics and thermodynamics, and the rest of the problems are addressed by using optimization techniques (Grossmann 1985, Gundersen 2002).

1.3.1 Hierarchical Analysis

Hierarchical analysis consists of decomposing the design problem into smaller manageable tasks (Hendry, Rudd & Seader 1973, Barnicki, Siirola 2004). Design decisions at each sub-task are taken using heuristics and short cut calculations. Heuristic method seeks the discovery of the solution to a problem by means of plausible but fallible guesses (Hendry, Rudd & Seader 1973). Douglas (1988, 1985) proposed a systematic method for flowsheet development by hierarchical decision procedure which breaks the design problem into the following five main decision levels:

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 recovery system
- 4d: Solid recovery system

Level 5: Energy integration

The economic potential of the complete process is considered at each decision level, but additional fine structure is added as the flowsheet proceeds to the later decision levels. The procedure uses heuristics, short-cut design procedures and physical insight to develop an initial base-case design. Initially this procedure was based on economic consideration, it has subsequently been extended to identify and solve waste minimisation problems as well as other objective (Douglas 1992). This approach allows quick location of flowsheet structures that are often near optimal solution (Grossmann 1985). Since only 1% of all designs are ever implemented in practice, this procedure allows avoiding detailed evaluation of most alternatives (Grossmann, Daichendt 1996). One of the drawbacks of this method is the dependency on the guesses of the design variables and alternatives which may lead to a solution far from the best possible design (Douglas 1985, Colmenares, Seider 1989). Furthermore, its sequential nature may not allow to properly accounting for the interaction among the design variables at various decision levels.

The onion model (Linnhoff et al. 1982, Smith, Linnhoff 1988) as shown in Fig. 1-3 is another way of representing the hierarchical approach to process synthesis. The diagram emphasizes the sequential nature of process design.

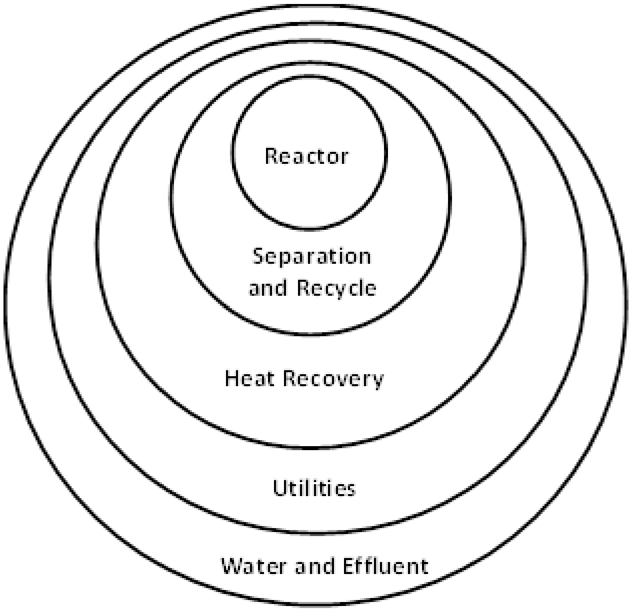

Fig. 1-3: The onion model of process design

The design of the process begins with the reactor at the center of the onion, and proceeds outward. The design of the reactor determines the structure of the separation and recycles system which comes in second position in the design process. Next the reactor, the separation and recycles system dictate the overall heat requirement which is designed in the third position. The utility system is then designed to provide additional cooling or heating requirements that cannot be satisfied through heat recovery of the process. Finally the water and effluent treatment is considered in case it is required. Heuristics and detailed process analysis tools and optimization tools are used at each layer. The sequential nature of the model does not guarantee optimal solution as interactions between layers may be overlooked.

1.3.2 The Use of Thermodynamics

The use of thermodynamic insights in process synthesis is based on the idea that before starting the design process, one must first establish performance *targets*, such as minimum energy consumption, least number of heat transfer equipment, minimum total heat transfer area, minimum annual cost, minimum shaft work in low temperature processes, minimum wastewater, minimum emissions, maximum power production, etc. All these targets have two important features (Gundersen 2002):

1) Any design can be objectively compared with the “best possible”.
2) The way some targets are calculated provides guideline for design.

This approach can be powerful in reducing the combinatorial problem if the quality of the target is good, that is if it is near the optimal solution for the flowsheet.

The pinch technology (Linnhoff, Flower 1978, Umeda, Harada & Shiroko 1979) is one of the most know design techniques which was originally based on identifying energy targets in heat recovery problems and has been used in the design of heat exchanger network (HEN) (Linnhoff et al. 1982). The concept has been extended to mass recovery problems and has been applied in areas such as Waste water Minimization, mass exchanger network (MEN) design (El-Halwagi, Manousiouthakis 1989) and work exchanger network (WEN) design (Huang, Fan 1996).

Other methods based on performance targets include the synthesis of reactor networks using the attainable regions concept (Glasser, Crowe & Hildebrandt 1987, Hildebrandt, Glasser & Crowe 1990, Balakrishna, Biegler 1992) and residue curve maps for the design of separation systems (Doherty, Malone 2001).

The use of the pinch concept (Linnhoff, Flower 1978, Umeda, Harada & Shiroko 1979) in the design of heat recovery systems has resulted in one of the most successful design techniques that have found real life applications in industry. It was initially used to determine minimum energy requirements for a fixed process, that is given mass and energy balance for a set of process streams, before the design of the heat recovery system. Further developments have included targets for minimum number of heat exchangers, minimum heat transfer area, and minimum total annual costs (Linnhoff, Ahmad 1990). The minimum energy consumption is determined by using numerical procedures (Heat Cascade) or by using *Composite curves* (Fig. 1-4), a graphical representation depicting the heat contents and temperatures of all process streams that require heating or cooling. The hot and cold *Composite Curves* are established by adding enthalpy changes for the hot and cold streams separately for each temperature interval in the process. Thus the minimum external heating, the minimum external cooling and the location of the heat recovery Pinch for a given value of ΔT_{min} can be determined. The Pinch point constitutes the transfer bottleneck where heat exchange cannot be done effectively given a certain minimum temperature difference ΔT_{min}. Once these have been determined, the initial heat exchanger network is designed by following a set of rules to ensure that the targets are reached. These rules are: 1) Heat must not be transferred across the pinch, 2) no external cooling utility must be used above the pinch and 3) no external heating utility must be used below the pinch. The initial design can be modified to allow integration of other process aspects. The *Grand Composite* curve (Linnhoff et al. 1982) is another graphical representation that is used to identify possible modifications. In the industry the *Grand Composite Curve* can be used to qualitatively and to some extent quantitatively address the following tasks (Gundersen 2002):

- Identify near-optimal set of utility types
- Identify potential for steam production
- Identify potential for power production
- Identify scope for using heat pumps

Identify opportunity for integration of other equipment such as distillation columns or evaporators.

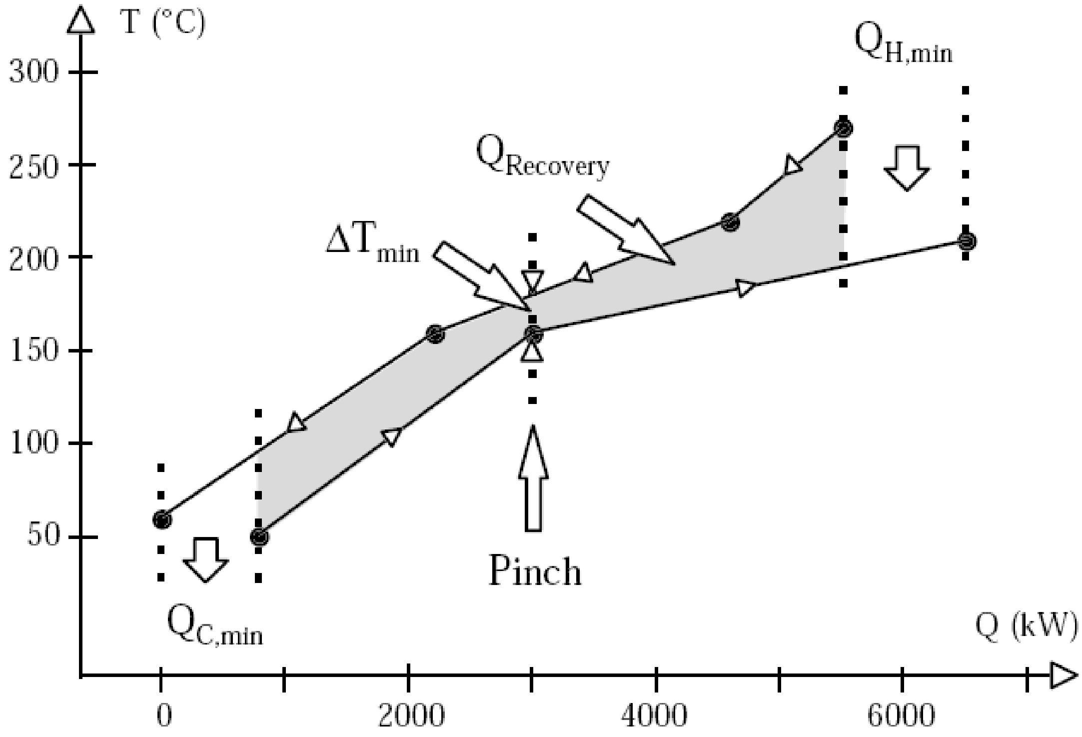

Fig. 1-4: Example of hot and cold composite curves for heat recovery (Gundersen 2002)

In summary the Pinch analysis concept is a valuable tool for setting up performance targets. It is applicable in other areas than heat recovery. Among other applications of Pinch analysis include utility targeting, refrigeration system design, distillation column profiles, cogeneration systems and total site integration, emission targeting and batch process integration (Linnhoff 1994, Rossiter, Rutkowski & McMullan 1991). A detailed review on heat exchanger network design can be found in Gundersen and Naess (1990).

The second law of thermodynamics analysis is a useful tool that can offer insight into the design of new processes and indicate opportunities for improvement of old ones (Shinnar 1988, Szargut, Morris & Steward 1988). The importance of the second law in process synthesis has been demonstrated many years ago by Denbigh (1956), and recently there has been a growing interest to apply the concept in many areas. Exergy is one of the most known concepts, based on the second law that has led to the development of various tools used in process synthesis and process integration. It has been often used as an analysis tool to assess the performance of processes and identify possible ways for improvement (Rosen 2002, Ishida, Zheng & Akehata 1987, Rosen, Bulucea 2009, Koroneos et al. 2004, Taniguchi et al. 2005, Woudstra et al. 2010). Many authors have also agreed that exergy is an essential concept for the design of more environmental friendly processes, to ensure sustainable development (Dincer, Rosen 2004, Dincer, Rosen 2005, Hinderink, van der Kooi & de 1999, Gong, Wall 2001, Wall 2002, Hammond 2004). Some of the developments in the use of exergy concept include:

- Grossmann Diagrams: graphical representation of exergy and exergy losses in a process (Kotas 1985).
- Combination of Pinch analysis and exergy in heat exchanger network design (Umeda, Harada & Shiroko 1979, Linnhoff, Dhole 1992, Aspelund, Berstad & Gundersen 2007).
- Exergetic life cycle assessment used for environmental considerations in process design (Gong, Wall 2001, Cornelissen 1997).

Eco-thermodynamics, thermoeconomics or exergoeconomics, combines economic analysis and the second law (Ayres 1998, Sciubba 2005).

1.3.3 The Use of Mathematical Formulation

In this approach the synthesis of a flowsheet is handled as an optimization problem. Optimization techniques are used to select the configuration and parameters of the process (Grossmann 1985). The optimal process structure is found by optimizing a certain objective function, which is typically some economic criteria, subjected to some equality and inequality constraints. Design and synthesis problems give rise to discrete and continuous optimization problems which can be represented in a mathematical form and solved as mixed-integer optimization problem with the following form (Grossmann, Caballero & Yeomans 2000):

$$\min f(x,y)$$
$$\text{Constraints } h(x,y) = 0$$
$$g(x,y) \leq 0$$
$$x \in X, y \in \{0,1\}$$

Where *f(x,y)* is the objective function (e.g. cost, number of equipment, surface area, etc.), *h(x,y) = 0*, are the equations that describe the performance of the system (e.g. mass and energy balance), and *g(x,y) ≤ 0* are inequalities that define the specifications or constraints for feasible choices. *x* are generally continuous variables (e.g. flowrates, equipment sizes, pressures, temperatures, etc.) and *y* are the discrete variables which take a value of 0 or 1 to define a selection of an item or an action. The problem can be classified as: 1) Mixed-integer nonlinear programming (MINLP) when any of the functions involved are nonlinear. 2) Mixed-integer linear programming (MILP) if all functions are linear. 3) Nonlinear programming (NLP) or linear programming (LP) if there are no discrete variables (0, 1) and depending whether or not the functions are linear.

The advantage of Mathematical Programming approach is that it provides a systematic way of handling a variety of process synthesis problems and takes into account different aspects of the process such as interactions and capital cost. It also has the ability to generate automatically the process flowsheet structures (Grossmann 1985). Furthermore many options can be considered simultaneously, and alternatives can be generated quickly and effectively (Smith 2005).

When using this approach to synthesize a process flowsheet, the final result will depend on the following three important activities (Gundersen 2002, Grossmann 2002, Floudas 1995):

1. The process alternatives must be represented in what is called a Superstructure from which the optimum solution is selected. The Superstructure must contain all promising solutions but not too wide to create prohibitive combinatorial problems. The superstructure can be defined for a specific class of problems (heat exchanger network, or reactor network, etc.) or must be specified by the designer with the use of heuristics and thermodynamics targets (Grossmann 1985).
2. The Superstructure must then be converted into a mathematical model which could be classified as an MINLP, MILP, NLP or LP. This modeling phase is almost an art, and the same problem can be formulated differently (Gundersen 2002).
3. An algorithm must be developed to numerically solve the mathematical model for the optimum solution.

Some of the limitations that can be encountered with Mathematical approach include (Smith 2005, El-Halwagi 2006).

1. They cannot guarantee “true” optimality because potentially optimal alternatives may not have been included in the problem representation.
2. The mathematical problem can be very large and nonlinear with possibility of finding local optimal solutions. Therefore the global optimum is not guaranteed. (Kravanja, Grossmann 1997).
3. It does not provide insight as to why decisions are made and the designers’ input into the problem is usually not included.

A detailed review on mathematical programming can be found in Grossmann (2002).

As was mentioned earlier, currently there is a strong tendency of making use of a combination of all the above mentioned process synthesis techniques. Furthermore the use of complex process simulators has drastically increased the speed at which calculations are made and thus allows many alternatives to be studied. However Glasser et al. (2000) have noted that all these powerful tools that have been developed relates to the traditional sequential way in which new processes have been design or improved. They also noted that problems with developing and design new processes often arise because of this sequential approach used to manage the development process. Glasser et al (2000) have studied a number of cases in which problems were encountered and have summarized the problems with the traditional approach of process design as shown in Table 1-1.

Table 1-1: Traditional process design and some of the problems that can arise

Traditional Approach	Problems
Opportunity identified	Choice of chemical route decided before the engineers have had input
Process chemistry identified	Experiments that have been performed limit the process that can be designed
Laboratory results handed over to engineers to design process	All the opportunities for the process design not fully investigated

The question that can arise from the above problems is that, with all the new tools and computing power that is available, are there better and efficient ways to develop new processes. The solution that Glasser et al. (2000) proposed can be summarized as follows:

- A quick and simple process design is required to enable and initial costing to be done to evaluate if the product can produced and sold for a profit.

- It is required a very simple design is required. The design must be based on a minimum amount of laboratory results. These results need not be of high accuracy.
- It is advantageous for the design engineer to collaborate with the laboratory and help to specify the experimental results that are required to proceed further. This suggests that the design engineer needs to be involved in the specification of the laboratory test programme.
- The laboratory needs to have available a range of simplified techniques for rapidly measuring quantities such as reaction rates, heat effects, liquid-liquid and vapor-liquid equilibrium.

In summary Glasser et al. (2000) suggested that the approach for designing a new process must be based on asking, “What is the simplest calculation that can be done that will still adequately differentiate between the alternatives?”

Patel (2007) has recently introduced an approach which uses mass, energy, and entropy balance to synthesis chemical processes. The approach begins by setting performance target based on mass, energy and entropy balance and these targets are based only on the input and output from the process. The targets are independent of the process structure i.e. no information regarding individual units and the interconnections is required. The approach also gives insight into how the targets can be achieved. The approach does not need much information or complex calculations, and can be used in the early stage of process design.

The work in this thesis follows the same line of ideas as in Patel (2007). The approach taken in this work is based on the idea that every process in which certain feed materials are converted into products has a certain amount of *heat* and *work* associated with it. Understanding the relationship between the *heat* and *work* can provide insight into the process and can give an idea of what the process structure would be. The approach uses fundamental thermodynamic concepts and a graphical technique where any number of processes can be represented and analyzed for reversibility and feasibility. The approach also does not require much information or complex calculations and is suitable to be used in the early stage of process design for a quick insight into the process and alternatives.

1.4 Thesis Outline

In chapter 2, we introduce a graphical representation of chemical processes where they are classified in different thermodynamic regions defined in the ΔH-ΔG space (gh-diagram) and their feasibility in terms of heat and work requirement is discussed. This approach allows one to determine whether heat at an appropriate temperature is sufficient to meet the work requirement of a chemical process, or if other means should be considered. In Chapter 3, the gh-diagram is used to investigate alternative ways of supplying *work* to a process when heat alone is not sufficient. While, for most processes, the amount of heat required can be easily satisfied, supplying the amount of work required is a major challenge and usually the determinant of the process complexity. The gh-diagram is used to determine which method of supplying work is suitable in order for the process to be feasible and reversible. An analysis of an ammonia process is done as a case study where a comparison of different methods of supplying work is made in terms of reversibility and process complexity. In Chapter 4 the gh-diagram is used to analyze combustion processes and power production. It is shown that major inefficiencies in power production processes originate from the chemical transformation that produces heat and that the combustion of most carbon based fuel cannot be done efficiently. It is also shown that other substances have the potential for more reversible combustion and an alternative route for coal combustion is proposed. Chapter 5 discusses the application of the gh-diagram in the analysis and design of Liquefied Natural gas (LNG) processes. Chapter 6 concludes the thesis.

References

Aspelund, A., Berstad, D.O. & Gundersen, T. 2007, "An Extended Pinch Analysis and Design procedure utilizing pressure based exergy for subambient cooling", *Applied Thermal Engineering,* vol. 27, no. 16, pp. 2633-2649.

Ayres, R.U. 1998, "Eco-thermodynamics: economics and the second law", *Ecological Economics,* vol. 26, no. 2, pp. 189-209.

Balakrishna, S. & Biegler, L.T. 1992, "Targeting strategies for the synthesis and energy integration of nonisothermal reactor networks", *Industrial & Engineering Chemistry Research,* vol. 31, no. 9, pp. 2152-2164.

Barnicki, S.D. & Siirola, J.J. 2004, "Process synthesis prospective", *Computers & Chemical Engineering,* vol. 28, no. 4, pp. 441-446.

Biegler, L.T., Grossmann, I.E. & Westerberg, A.W. 1997, *Systematic Methods of Chemical Process Design,* Prentice Hall, New Jersey.

Colmenares, T.R. & Seider, W.D. 1989, "Synthesis of utility systems integrated with chemical processes", *Industrial & Engineering Chemistry Research,* vol. 28, no. 1, pp. 84-93.

Cornelissen, R.L. 1997, *Thermodynamics and Sustainable Development*, University of Twente.

Denbigh, K.G. 1956, "The second-law efficiency of chemical processes", *Chemical Engineering Science,* vol. 6, no. 1, pp. 1-9.

Dewulf, J., Van Langenhove, H., Mulder, J., van, d.B., van, d.K. & de, S.A. 2000, "Illustrations towards quantifying the sustainability of technology", *Green Chemistry,* vol. 2, no. 3, pp. 108-114.

Dincer, I. 2000, "Renewable energy and sustainable development: a crucial review", *Renewable and Sustainable Energy Reviews,* vol. 4, no. 2, pp. 157-175.

Dincer, I. & Rosen, M.A. 2005, "Thermodynamic aspects of renewables and sustainable development", *Renewable and Sustainable Energy Reviews,* vol. 9, no. 2, pp. 169-189.

Dincer, I. & Rosen, M.A. 2004, "Exergy as a Driver for Achieving Sustainability", *International Journal of Green Energy,* vol. 1, no. 1, pp. 1-19.

Doherty, M.F. & Malone, M.F. 2001, *Conceptual design of distillation systems,* McGraw-Hill, New York.

Douglas, J.M. 1988, *Conceptual Design of Chemical Processes,* McGraw-Hill, New York.

Douglas, J.M. 1985, "A hierarchical decision procedure for process synthesis", *AIChE Journal,* vol. 31, no. 3, pp. 353-362.

Douglas, J.M. 1992, "Process synthesis for waste minimization", *Industrial & Engineering Chemistry Research,* vol. 31, no. 1, pp. 238-243.

Dunn, R.F. & Bush, G.E. 2001, "Using process integration technology for CLEANER production", *Journal of Cleaner Production,* vol. 9, no. 1, pp. 1-23.

Dunn, R.F. & El-Halwagi, M.M. 2003, "Process integration technology review: background and applications in the chemical process industry", *Journal of Chemical Technology & Biotechnology,* vol. 78, no. 9, pp. 1011-1021.

El-Halwagi, M.M. 2006, *Process Integration,* Academic Press, Amsterdam.

El-Halwagi, M., Gabriel, F. & Harell, D. 2003, "Rigorous Graphical Targeting for Resource Conservation via Material Recycle/Reuse Networks", *Industrial & Engineering Chemistry Research,* vol. 42, no. 19, pp. 4319-4328.

El-Halwagi, M.M. & Manousiouthakis, V. 1989, "Synthesis of mass exchange networks", *AIChE Journal,* vol. 35, no. 8, pp. 1233-1244.

Fells, I. (ed) 1990, *The problem. In: J. Dunderdale Editor, Energy and the environment Royal Society of Chemistry, UK (1990).*, Energy and the Environment Royal Society of Chemistry, UK.

Floudas, C.A. 1995, *Nonlinear and Mixed-Integer Optimization: Fundamentals and Applications,* Oxford University Press, New York.

Glasser, D., Crowe, C. & Hildebrandt, D. 1987, "A geometric approach to steady flow reactors: the attainable region and optimization in concentration space", *Industrial & Engineering Chemistry Research,* vol. 26, no. 9, pp. 1803-1810.

Glasser, D., Hildebrandt, D. & McGregor, C. 2000, "CONTRIBUTED PAPERS - CONCEPTUAL DESIGN AND SYNTHESIS - There is More to Process Synthesis than Synthesising a Process", *AIChE symposium series.,* vol. 96, no. 323, pp. 311.

Gong, M. & Wall, G. 2001, "On exergy and sustainable development—Part 2: Indicators and methods", *Exergy,An International Journal,* vol. 1, no. 4, pp. 217-233.

Grossmann, I.E., Caballero, J.A. & Yeomans, H. 2000, "Advances in mathematical programming for the synthesis of process systems", *Latin American Applied Research,* vol. 30, pp. 263-284.

Grossmann, I.E. 2002, *Review on Nonlinear Mixed-Integer and Disjuctive programming Techniques*, Department of Chemical Engineering Carnegie Mellon University, Pittsburgh.

Grossmann, I.E. 1985, "Mixed-integer programming approach for the synthesis of integrated process flowsheets", *Computers & Chemical Engineering,* vol. 9, no. 5, pp. 463-482.

Grossmann, I.E. & Daichendt, M.M. 1996, "New trends in optimization-based approaches to process synthesis", *Computers & Chemical Engineering,* vol. 20, no. 6-7, pp. 665-683.

Gundersen, T. 2002, *A Process Integration Primer*, SINTEF Energy research, Trondheim.

Gundersen, T. & Naess, L. 1990, "The synthesis of cost optimal heat exchanger networks : An industrial review of the state of the art", *Heat Recovery Systems and CHP,* vol. 10, no. 4, pp. 301-328.

Hammond, G.P.G.P. 2004, "Towards sustainability: energy efficiency, thermodynamic analysis, and the ‘two cultures’", *Energy Policy,* vol. 32, no. 16, pp. 1789-1798.

Harmsen, G.J. 1999, "Industrial applied process synthesis method creates synergy between economy and sustainability", *Proceedings of the conference FOCAPD99*FOCAPD, Breckenridge, USA, July, 18-23, 1999.

Hendry, J.E., Rudd, D.F. & Seader, J.D. 1973, "Synthesis in the design of chemical processes", *AIChE Journal,* vol. 19, no. 1, pp. 1-15.

Hildebrandt, D., Glasser, D. & Crowe, C.M. 1990, "Geometry of the attainable region generated by reaction and mixing: with and without constraints", *Industrial & Engineering Chemistry Research,* vol. 29, no. 1, pp. 49-58.

Hinderink, A.,P., van der Kooi, H.,J. & de, S.A. 1999, "On the efficiency and sustainability of the process industry", *Green Chemistry,* vol. 1, no. 6, pp. G176-G180.

Hirs, G. 2003, "Thermodynamics applied. Where? Why?", *Energy,* vol. 28, no. 13, pp. 1303-1313.

Hlavácek, V. 1978, "Synthesis in the design of chemical processes", *Computers & Chemical Engineering,* vol. 2, no. 1, pp. 67-75.

Huang, Y.L. & Fan, L.T. 1996, "Analysis of a Work Exchanger Network", *Industrial & Engineering Chemistry Research,* vol. 35, no. 10, pp. 3528-3538.

Ishida, M., Zheng, D. & Akehata, T. 1987, "Evaluation of a chemical-looping-combustion power-generation system by graphic exergy analysis", *Energy,* vol. 12, no. 2, pp. 147-154.

Johns, W.R. 2001, *Process synthesis: poised for a wider role*, Chemical Engineering Progress.

Kalitventzeff, B., Maréchal, F. & Closon, H. 2001, "Better solutions for process sustainability through better insight in process energy integration", *Applied Thermal Engineering,* vol. 21, no. 13-14, pp. 1349-1368.

Kirkwood, R.L., Locke, M.H. & Douglas, J.M. 1988, "A prototype expert system for synthesizing chemical process flowsheets", *Computers & Chemical Engineering,* vol. 12, no. 4, pp. 329-343.

Korevaar, G. 2004, *Sustainable Chemical Processes and Products*, Delft University of Technology.

Korhonen, J. 2004, "Industrial ecology in the strategic sustainable development model: strategic applications of industrial ecology", *Journal of Cleaner Production,* vol. 12, no. 8-10, pp. 809-823.

Koroneos, C., Haritakis, I., Michaloglou, K. & Moussiopoulos, N. 2004, "Exergy Analysis for Power Plant Alternative Designs, Part I", *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects,* vol. 26, no. 13, pp. 1277-1285.

Kotas, T.J. 1985, *The Exergy Method of Thermal Plant Analysis,* Butterworths, London.

Kravanja, Z. & Grossmann, I.E. 1997, "Multilevel-hierarchical MINLP synthesis of process flowsheets", *Computers & Chemical Engineering,* vol. 21, no. Supplement 1, pp. S421-S426.

Li, X. & Kraslawski, A. 2004, "Conceptual process synthesis: past and current trends", *Chemical Engineering and Processing,* vol. 43, no. 5, pp. 583-594.

Linnhoff, B. 1994, "Use Pinch Analysis to Knock Down Capital Costs and Emissions", *Chemical Engineering Progress,* vol. 90, no. 8, pp. 33-57.

Linnhoff, B., Townsend, D.W., Boland, D., Hewitt, G.F., Thomas, B.E., Guy, A.R. & Marsland, R.H. 1982, *A user guide on process integration for the efficient use of energy,* The Institution of Chemical Engineers, Rugby.

Linnhoff, B. & Ahmad, S. 1990, "Cost optimum heat exchanger networks—1. Minimum energy and capital using simple models for capital cost", *Computers & Chemical Engineering,* vol. 14, no. 7, pp. 729-750.

Linnhoff, B. & Dhole, V.R. 1992, "Shaftwork targets for low-temperature process design", *Chemical Engineering Science,* vol. 47, no. 8, pp. 2081-2091.

Linnhoff, B. & Flower, J.R. 1978, "Synthesis of heat exchanger networks: I. Systematic generation of energy optimal networks", *AIChE Journal,* vol. 24, no. 4, pp. 633-642.

Nishida, N., Stephanopoulos, G. & Westerberg, A.W. 1981, "A review of process synthesis", *AIChE Journal,* vol. 27, no. 3, pp. 321-351.

O'Young, D.L. & Natori, Y. 1996, "Process Synthesis: technology, environment and applications", *Computers & Chemical Engineering,* vol. 20, no. Supplement 1, pp. S381-S387.

Patel, B. 2007, *Fundamental Targets for the Synthesis and Evaluation of Chemical Processes*, University of the Witwatersrand.

Rosen, M.A. & Dincer, I. 2003, "Exergy–cost–energy–mass analysis of thermal systems and processes", *Energy Conversion and Management,* vol. 44, no. 10, pp. 1633-1651.

Rosen, M.A. 2002, "Assessing energy technologies and environmental impacts with the principles of thermodynamics", *Applied Energy,* vol. 72, no. 1, pp. 427-441.

Rosen, M.A. & Dincer, I. 2001, "Exergy as the confluence of energy, environment and sustainable development", *Exergy, An International Journal,* vol. 1, no. 1, pp. 3-13.

Rosen, M. & Bulucea, C.A. 2009, "Using Exergy to Understand and Improve the Efficiency of Electrical Power Technologies", *Entropy,* vol. 11, no. 4, pp. 820-835.

Rossiter, A.P., Rutkowski, M.A. & McMullan, A.S. 1991, "Pinch technology identifies process improvements", *Hydrocarbon Processing,* vol. 70, no. 1, pp. 63-66.

Sciubba, E. 2005, "Exergo-economics: thermodynamic foundation for a more rational resource use", *International Journal of Energy Research,* vol. 29, no. 7, pp. 613-636.

Shinnar, R. 1988, "Plenary paper received too late to be included at front of issue: Thermodynamic analysis in chemical process and reactor design", *Chemical Engineering Science,* vol. 43, no. 8, pp. 2303-2318.

Smith, R. 2005, *Chemical Process Design and Integration,* John Wiley & Sons, West Sussex.

Smith, R. & Linnhoff, B. 1988, "The design of separators in the context of overall processes", *Chemical Engineering Research and Design,* vol. 66, pp. 195-228.

Stuart, L.H. January - February 1997, "Beyond Greening: Strategies for a sustainable world", *Havard Business Review,* , pp. 67-76.

Sueranan, T. 2006, *Studies on Computer-aided conceptual process design*, Helsinki University of Technology, Finland.

Szargut, J., Morris, D.R. & Steward, F.R. 1988, *Exergy Analysis of Thermal, Chemical and Metallurgical Processes,* Hemisphere Publishing Corporation, New York.

Szargut, J. 1980, "International progress in second law analysis", *Energy,* vol. 5, no. 8-9, pp. 709-718.

Taniguchi, H., Mouri, K., Nakahara, T. & Arai, N. 2005, "Exergy analysis on combustion and energy conversion processes", *Energy,* vol. 30, no. 2-4, pp. 111-117.

Tonon, S., Brown, M.T., Luchi, F., Mirandola, A., Stoppato, A. & Ulgiati, S. 2006, "An integrated assessment of energy conversion processes by means of thermodynamic, economic and environmental parameters", *Energy,* vol. 31, no. 1, pp. 149-163.

Umeda, T., Harada, T. & Shiroko, K. 1979, "A thermodynamic approach to the synthesis of heat integration systems in chemical processes", *Computers & Chemical Engineering,* vol. 3, no. 1-4, pp. 273-282.

Van Berkel, R. 2000, "Cleaner production for process industries", *CHEMECA 2000*, July, 9-12, 2000.

Wall, G. 2002, "Conditions and tools in the design of energy conversion and management systems of a sustainable society", *Energy Conversion and Management,* vol. 43, no. 9-12, pp. 1235-1248.

Wallner, H.P. 1999, "Towards sustainable development of industry: networking, complexity and eco-clusters", *Journal of Cleaner Production,* vol. 7, no. 1, pp. 49-58.

Westerberg, A.W. 1980, "A review of process synthesis", *ACS Symposium Series,* vol. 124, pp. 53-87.

Westerberg, A.W. 1989, "Synthesis in engineering design", *Computers & Chemical Engineering,* vol. 13, no. 4-5, pp. 365-376.

World Energy Council 1995, *Global energy perspectives to 2050 and beyond*, World Energy Council, London.

Woudstra, N., Woudstra, T., Pirone, A. & Stelt, T.v.d. 2010, "Thermodynamic evaluation of combined cycle plants", *Energy Conversion and Management,* vol. 51, no. 5, pp. 1099-1110.

Yang, Y. & Shi, L. 2000, "Integrating environmental impact minimization into conceptual chemical process design — a process systems engineering review", *Computers & Chemical Engineering,* vol. 24, no. 2-7, pp. 1409-1419.

2 CLASSIFICATION OF CHEMICAL PROCESSES

A Graphical Approach to Process Synthesis to Improve Reactive Process Work Efficiency

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2.1 Abstract

In order to reduce carbon dioxide emissions for chemical processes one would like to make them as reversible as possible. Patel et al. (2005) have shown that in some cases one can analyze processes in terms of their work and heat requirements. In particular, for processes there exists a temperature that is called '*the Carnot Temperature'*, at which one can satisfy the work requirement for the process, by using the heat that needs to be added or removed.

The analogy of a heat engine and Carnot temperature is applied to chemical processes, particularly on reactive processes, using a graphical approach. This approach looks at chemical processes holistically, where only the inlet and outlet streams are considered. The process is represented in a *ΔH-ΔG* space. Chemical processes are classified in different thermodynamics regions as defined in the *ΔH-ΔG* space and their feasibility in terms of heat and work requirement is discussed. This approach allows one to determine whether heat at an appropriate temperature is sufficient to meet the work requirement of a chemical process, or if other means should be considered. The approach is used to investigate and discuss the possibility

of combining reactive chemical processes classified in different thermodynamic regions in the ΔH-ΔG space, with the purpose of making infeasible processes possible, or to minimize or even eliminate the work requirement of the combined process.

2.2 Introduction

Growing concerns regarding emissions of green-house gases, depletion of raw materials and energy resources have created the need to reassess the efficiency of chemical processes. A large portion of energy used in the chemical industry originates from fossil fuels. Energy production from fossil fuels is believed to be one of the major contributors to green-house gas emissions and particularly the emission of carbon dioxide. It is therefore important to develop design techniques that emphasize minimizing the consumption of raw materials and energy.

In the spirit of reducing waste production and energy consumption, a number of practices such as process optimization, mass and energy integration have been explored. The pinch analysis (Linnhoff et al. 1982) is an example of one of the most popular heat integration techniques used to generate optimal heat exchanger systems within a process. The combination of pinch technology and exergy analysis has been also used (Staine, Favrat 1996). Computer aided mathematical techniques are also used to systematically generate integrated, energy efficient and economical flowsheets. The Mixed-Integer Non-linear Programming (MINLP) is one of the mathematical techniques used for heat integration (Kovač Kralj, Glavič & Kravanja 2005); it is also used in combination with the hierarchical decomposition technique in process synthesis (Daichendt, Grossmann 1998). Gundersen (1997) gives an overview of numerous energy saving techniques used in process integration.

Most of the above mentioned techniques aim to reaching a certain performance target; however, it is important to know what the optimal target is or what is achievable for a particular process. The second law of thermodynamics has been found to be a tangible basis upon which process efficiency could be effectively assessed. Denbigh (1956) developed equations for calculating the thermodynamic efficiency of chemical processes, using as a basis the second law of thermodynamics, which sets a certain limit on the conversion of heat into work. He used the notion of heat engine efficiency, calculated relative to the concept of a reversible heat engine, to assess the efficiency of chemical processes. Previous work by Yamamoto and Ishida (2002) has shown that process features such as exergy and enthalpy can be represented on a single diagram to create a functional classification of processes in a system. Chemical processes could be classified as refrigerants type, heating type, heat source type, mixing and separation type, etc. on the diagram. The classification could then be used in developing a chemical plant structure. A similar classification has been developed by Oaki and Ishida (1982) where processes are represented as vectors on a ΔH-$T_O\Delta S$ plan to identify their functions and in addition to determine their performance by calculating a certain factor called the 'Dissipation Factor'. Patel et al. (2004) have shown that chemical processes can be analyzed in terms of their heat and work requirement and in particular that for chemical processes which can be defined as '*simple* processes', there exists a temperature which he called 'Carnot temperature', at which one can satisfy the work requirement using the heat that needs to be added or removed from the process. This temperature may or may not be physically meaningful, in which case the process would be irreversible or may require work in other forms to be added.

This paper uses the notion of "heat engine" and Carnot temperature as applied to chemical processes. The paper shows that one can look at chemical processes in terms of the inlet and outlet streams only, and represent the process in the ΔH-ΔG space. A process classification similar to those developed by Yamamoto and Ishida (2002) and Oaki and Ishida (1982) can then be produced. Processes can be classified in different thermodynamic regions as defined by the ΔH-ΔG space, and their feasibility in terms of their heat and work requirement can be determined. This approach gives a more convenient way of representing and analyzing processes at their highest level where much valuable information can be obtained for different processes on a single diagram and possibly even on a single point or line on the diagram. This approach can be used as a starting point in developing more reversible process flowsheets; it can be used to determine the best method of supplying or recovering energy from a process. In particular the approach can be used to analyze and synthesize integrated processes to improve process reversibility.

2.3 A Simple Chemical Process

Traditionally mass and energy balances are performed on individual pieces of equipment to assess the performance of a unit process. However, understanding the influence of the interaction between the pieces of equipment in a process, on performance, can be a challenging task. The approach taken in this paper has been used by several authors including Patel et al. (2005), Smith (2000) and Westerberg (2004), where one looks at the process at its highest level, and only considers the streams in and out of the process. This will allow setting the performance target for the process and will allow understanding what is achievable in respect of the thermodynamics. Then one can determine which piece of equipment is required and how it should be designed, connected and operated, in such a way as to get the overall process as close to the target as possible. This can be done by first considering the process as a simple process then determine whether the process is feasible under normal operating conditions; in case the process is not feasible, then one could look at other alternatives such as changing the mass balance of the process or introducing complexity in the process. Before we explore this further let us first define what a '*simple process*' is.

Consider a simple representation of a chemical process as shown in Fig. 2-1. The process could comprise several unit operations such as reactors, separation units, heat exchangers etc. Let us however consider only the inlet and the outlet streams of the process which we assume to be at ambient conditions T_O and P_O.

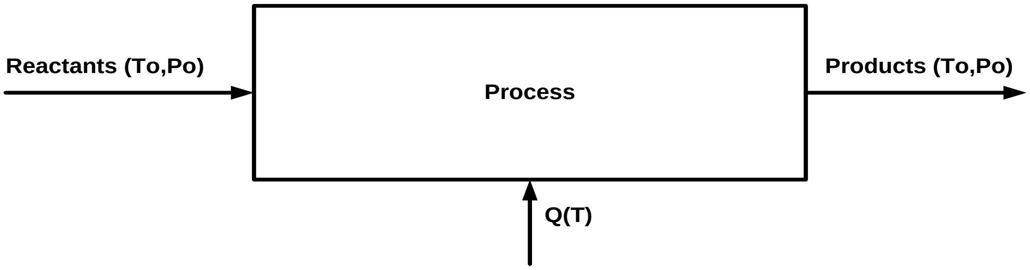

Fig. 2-1: A simple chemical process

We could describe a simple chemical process in more detail as shown in Fig. 2-2, where it is assumed that the reactants and the products have approximately equal heat capacities such that heat can be exchanged between the product and the reactant streams to bring them to their required temperatures without needing extra cooling or heating; this may not be possible in practice, since an infinitely large heat exchanger may be required and the process may not be economically feasible. However the extra heat quantities required to remove or add may be negligible compared to the heat of the reactor, therefore their effect on the overall process may also be negligible. In case the quantities of the extra heat are considerably high then their effect on the overall process will need to be considered, however this is beyond the scope of the present manuscript. It is also assumed that the reactor is the major heat load in the process and that other process equipment have negligible heat load compared to the reactor.

We therefore define a simple chemical process as the one in which the heat Q is added or removed at a single temperature T which is the reactor temperature.

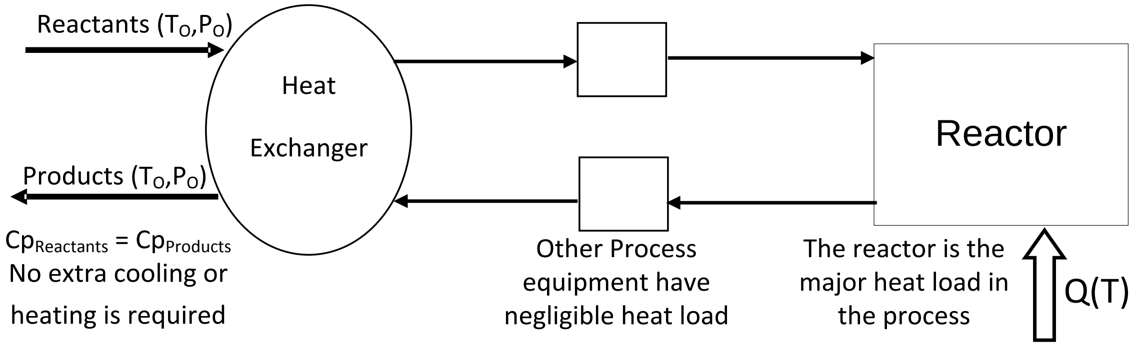

Fig. 2-2: A simple chemical process: description and assumptions

Given the reactants and the products, the net chemical reaction (or the overall mass balance) for the process can be determined. The mass balance across the process can determine how much product will be obtained from a given amount of reactants. The energy balance will determine how much heat and work is needed to make the process possible. However in a simple process only heat *Q* is supplied to the process. It can be shown that Q is determined by the enthalpy change across the process, ΔH_P. That is:

$$Q = \Delta H_P \tag{2.1}$$

The entropy balance will determine how reversible or efficient the process is and this will constitute the basis of our discussion throughout the paper.

The heat requirement *Q* of the process can be provided by an external source such as burning fuel or applying steam; but it could theoretically also be provided from the environment using a heat engine[1]. The heat engine can be provided with mechanical work to absorb a quantity of heat Q_O from the environment at ambient

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[1] The term 'Heat Engine' is generally referred to a device that converts thermal energy (heat) into mechanical energy (work) while the term 'Heat Pump' is referred to a device that converts work into heat. Here the term 'Heat engine' is generalized and refers to both heat engine and heat pump; in a sense that a heat pump is essentially a heat engine running in reverse.

temperature T_O and reject a quantity of heat Q_H at a higher temperature T_H as shown in Fig. 2-3.

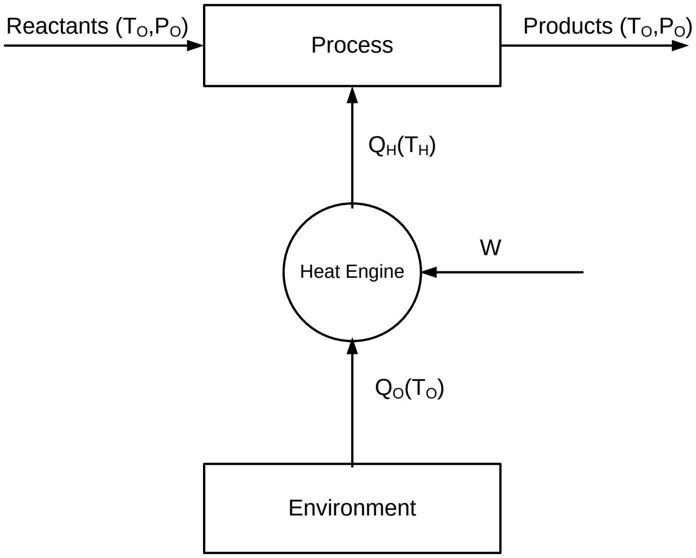

Fig. 2-3: Heat engine a heat source for a chemical process

The work requirement for a reversible heat engine is given by the following equation:

$$W = Q_H \left(1 - \frac{T_O}{T_H}\right) \qquad 2.2$$

This equation is usually referred to as the Carnot equation (Smith, van Ness & Abbott 2001).

Patel et al. (2004), have shown that for a simple process to be reversible, the temperature, referred to as the *Carnot Temperature (T_{Carnot})*, at which heat is transferred to the process must satisfy the following equation:

$$\Delta G_P(T_O, P_O) = \Delta H_P(T_O, P_O)\left(1 - \frac{T_O}{T_{Carnot}}\right) \qquad 2.3$$

ΔG_P and ΔH_P are the Gibbs Energy change and the enthalpy change between the inlet and outlet process streams.

Let us assume that the process and the heat engine in Fig. 2-3 are both reversible and satisfy Equations 2.3 and 2.2 respectively; then T_H corresponds to T_{Carnot} in Equation 2.3. From the energy balance of the process it can be shown that $\Delta H_P = Q_H$, and by comparing Equation 2.2 with 2.3 it is clear that $\Delta G_P = W$. From this result it can be concluded that:

The Gibbs Energy change across a reversible chemical process as described in Fig. 2-1, *is equivalent to the work W required by a heat engine when absorbing a quantity of heat* Q_O *from the environment at ambient temperature, and supplying a quantity of heat* ΔH_P *at the Carnot temperature to the process. Where* $\Delta H_P = W + Q_O$.

The concept of considering chemical processes as heat engines, has been expressed in many other ways by several authors, including Denbigh (1956), who stated that when the initial and final conditions of a process are at the same temperature and pressure as the atmosphere, then minimum amount of work which must be applied is equal to the increase in its Gibbs energy. He then used this idea as a basis for assessing the efficiency of chemical processes. Shinnar (1988) also assessed the value of heat of chemical processes in terms of the possibility of recovering the Gibbs Energy as useful work.

Patel et al. (2004) referred to the Gibbs Energy change as the process work requirement which they also called virtual work, because it does not appear in the energy balance. They defined T_{Carnot} in Equation 2.3 as the temperature at which the work, carried in with process heat requirements, by virtue of the temperature of the heat, matches the work requirement of the process; hence no additional work (which would appear in the energy balance) is needed. Patel et al. (2004) also explained the implications of transferring heat at a temperature other than T_{Carnot}. This will be discussed in detail later in the paper.

It is important to note that, although the energy requirement of the process, as determined by the energy balance, might be satisfied, the process would not proceed if the work requirement is not satisfied. As we will see later in the paper this work can be supplied, directly as mechanical work, which will appear in the energy balance, or through heat which it could be understood as being supplied by a heat engine and which will not appear in the energy balance, or a combination of both.

If it is further assumed, in addition to the assumptions for a simple chemical process in Fig. 2-2, that there is only one reactor, then the process mass balance is the same as that occurring in the reactor. However the extent of reaction may be different as the reaction may not go to completion and in that case, a separation-recycle system would be needed; however, for the purpose of this discussion we will further assume that the separation-recycle system is part of the reactor such that the reaction is complete and that the products out of the process are pure components. In this case the Gibbs energy and the enthalpy change for the process can be approximately equal to the Gibbs energy and enthalpy change across the reactor; we can therefore write: $\Delta G_P \approx \Delta G_{rxn}$ and $\Delta H_p \approx \Delta H_{rxn}$ and Equation 2.3 for the process can be rewritten as follows:

$$\Delta G_{rxn}(T_O, P_O) = \Delta H_{rxn}(T_{O,} P_O)\left(1 - \frac{T_O}{T_{Carnot}}\right) \qquad 2.4$$

We therefore see that there is a relationship between ΔG_{rxn}, ΔH_{rxn} and the Carnot temperature of the process T_{Carnot}. We will now investigate alternative ways of representing this information and in particular look at the usefulness of this information in the *ΔH-ΔG* space.

2.4 The ΔH-ΔG Domain (gh-Diagram)

A chemical process with a single net reaction and a single heat input can be graphically represented in a ΔH-ΔG domain which we will refer to as the '*gh-Diagram'*. A combination of Equation 2.4 and a plot of ΔG versus ΔH can provide us with insights and information regarding the process. To demonstrate this, let us look at the dehydration of methanol to form dimethyl-ether (DME).

The overall process reaction, the specific enthalpy $\Delta\hat{H}_{rxn}$ and the specific Gibbs Energy $\Delta\hat{G}_{rxn}$ change of reaction are given as follows:

$$\begin{aligned} &2CH_3OH \rightarrow CH_3OCH_3 + H_2O \\ &\Delta\hat{H}_{rxn}(T_O, P_O) = -24.05\,\tfrac{kJ}{mol} \\ &\Delta\hat{G}_{rxn}(T_O, P_O) = -16.75\,\tfrac{kJ}{mol} \end{aligned} \qquad 2.5$$

Suppose *n* moles of DME is produced in simple process, then the enthalpy change across the process is $\Delta H_{rxn} = n\Delta\hat{H}_{rxn}$, and the Gibbs Energy across the process is $\Delta G_{rxn} = n\Delta\hat{G}_{rxn}$; a linear relationship can be obtained between ΔH_{rxn} and ΔG_{rxn} by varying the number of moles *n* of DME produced as shown in Fig. 2-4.

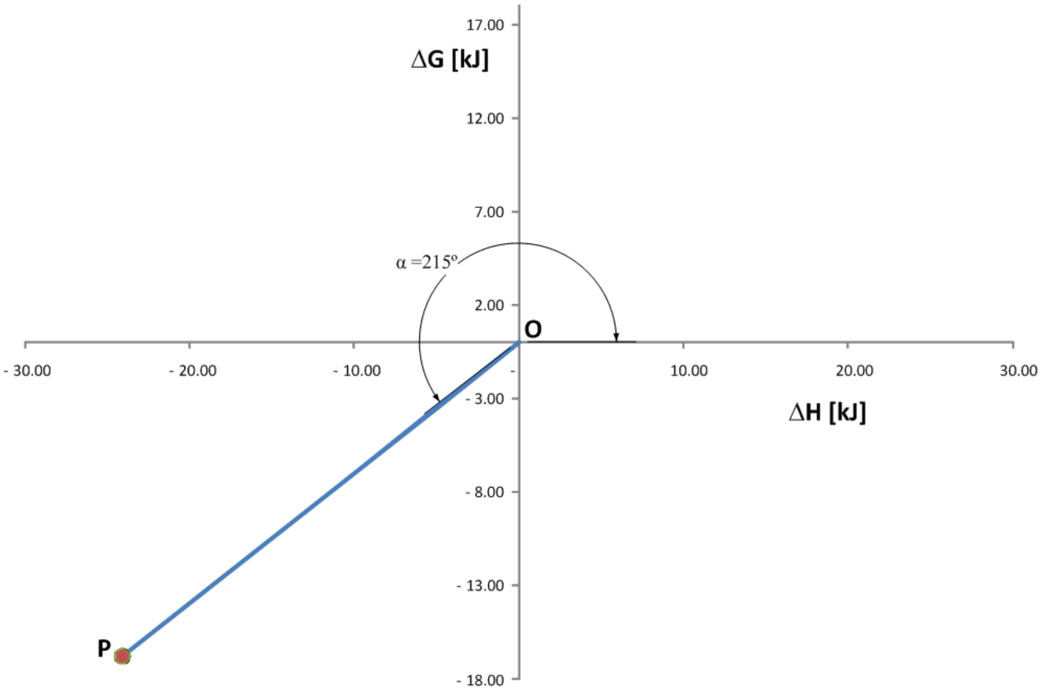

Fig. 2-4: Representation of a simple process on the gh-diagram

In Fig. 2-4 the origin (O) corresponds to zero DME produced, as the production of DME is increased the process will lie at any point along line OP or on the extension of the line. Point (P) represents one mole of DME produced.

Equation 2.4 can be rearranged to obtain:

$$T_{Carnot} = \frac{T_O}{1 - \dfrac{\Delta G_{rxn}}{\Delta H_{rxn}}} \qquad 2.6$$

- Note that the quotient $\frac{\Delta G_{rxn}}{\Delta H_{rxn}}$ in Equation 2.6 is constant and independent of the number of moles of DME produced.
- The Carnot temperature of any DME process is the same and independent of the number of moles of DME produced, as long as the overall mass balance is described by Equation 2.5. Furthermore T_{Carnot} is the same for any process

such that when ΔG_{rxn} and ΔH_{rxn} plotted on the diagram in Fig. 2-4, the point lies on line OP or the extension of this line.

On the diagram in Fig. 2-4, T_{Carnot} is represented by the angle α, where $\tan\alpha = \frac{\Delta G_{rxn}}{\Delta H_{rxn}}$ hence equation 2.6 can be written in terms of α as follows:

$$T_{Carnot} = \frac{T_O}{1-\tan\alpha} \tag{2.7}$$

For the dehydration of methanol to DME $\tan\alpha = 0.69647$ hence $\alpha = 214.86^O$ and from Equation 2.7 $T_{Carnot} = \frac{298.15K}{1-0.69647} = 982.26K$

2.4.1 Variation of *T_{Carnot}* on the gh-Diagram

The variation of T_{Carnot} with α is cyclic and similar to that of tan α tan αas shown in Fig. 2-5. T_{Carnot} starts at ambient temperature at α = 0, increases rapidly and tends to infinity as αα reaches 45°; at this point *ΔG* and *ΔH* are positive and equal in magnitude. When α goes above 45°, *ΔG* becomes greater than *ΔH*, T_{Carnot} starts from negative infinity then increases rapidly and reaches zero at α equal to 90° where *ΔH* equal zero. After this point T_{Carnot} continues increasing at a slower pace until it reaches ambient temperature at α equal 180° and *ΔG* equal to zero, then increases again rapidly toward infinity; then the same behaviour repeats itself in a cycle every 180°. The magnitude and sign of T_{Carnot} is determined by the magnitudes and directions of *ΔH* and *ΔG*; as we will see in section 4, T_{Carnot} is an indicator of how difficult it would be to meet the work requirement for a particular process; for example a negative T_{Carnot} indicates that the process would be infeasible and a high T_{Carnot} indicates that it might be difficult to achieve the targeted operation, hence indicating how complex the process would be.

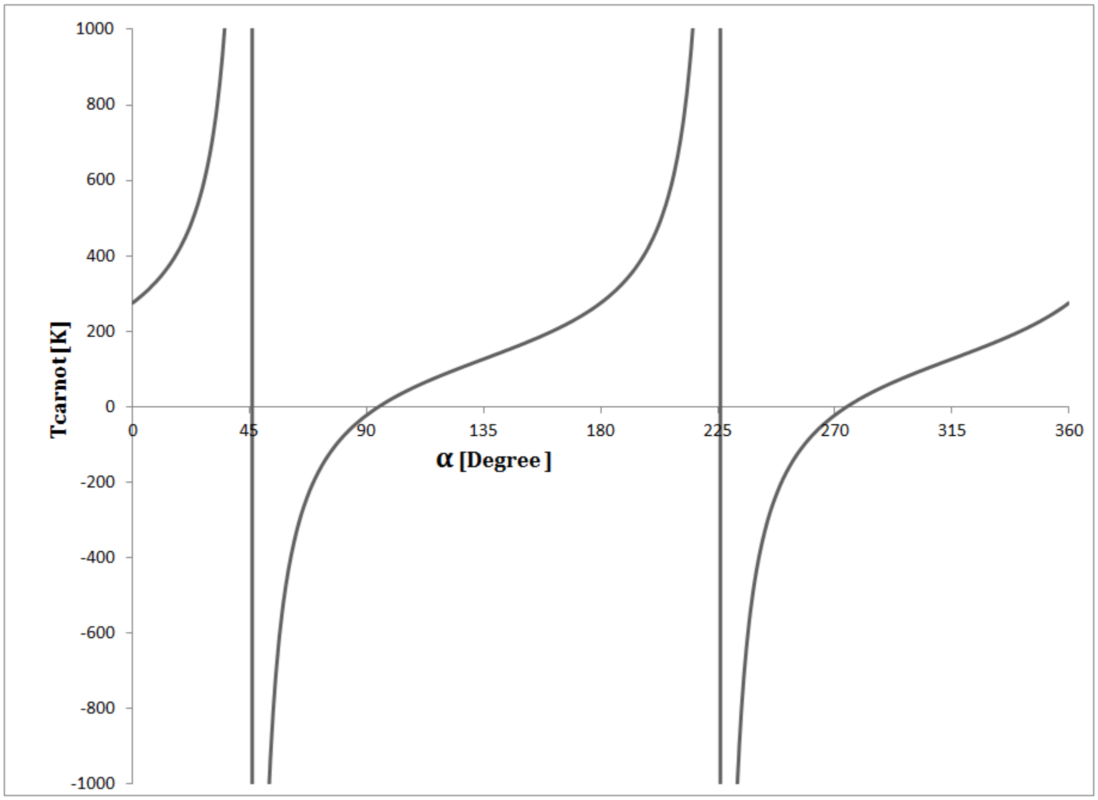

Fig. 2-5: Variation of T_{Carnot} with α on the gh-diagram is similar to that of tan α

We can represent the variation of T_{Carnot} on the gh-diagram as a temperature scale as shown in Fig. 2-6.

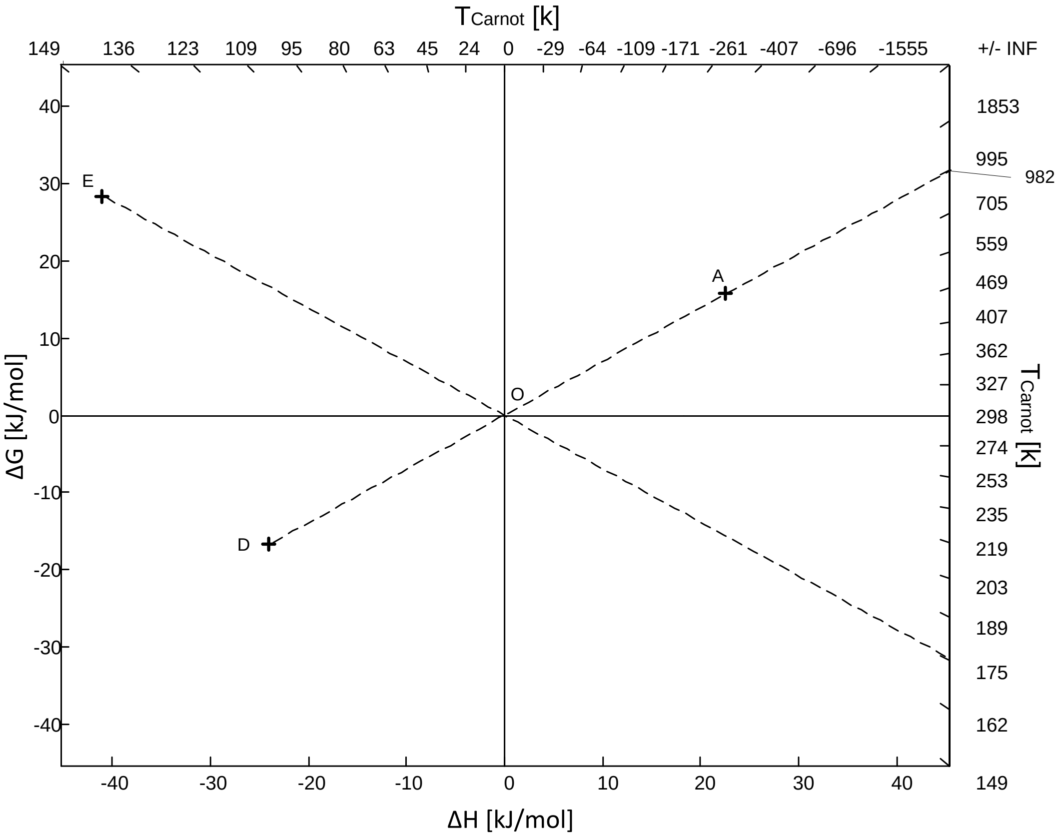

Fig. 2-6: Temperature scale representing the Carnot temperature for processes on the gh-diagram

In Fig. 2-6 a chemical process is represented by points such as D or E. The Carnot temperature of the process is determined by the intersection of the temperature scale with a line linking the origin O, and a point that represents the process. Thus if D represents the DME process as described by Equation 2.5, then the point of intersection of line DO with the temperature scale gives the Carnot temperature of the DME process which is 982 K. A process at a point such as E would similarly have a Carnot temperature of approximately 175 K given by the intersection of line EO with the temperature scale.

Note that any process, that is represented by a point such as A, lying on line DO, would have the same Carnot temperature as D. The reverse DME process, where DME and water form methanol, is an example of a process that would be represented by point A. Both lines AO and DO intercept the temperature scale at 982 K.

2.5 T_{Carnot} and the Process as a Heat Engine

In light of the behaviour of T_{Carnot} with respect to α, a number of thermodynamic regions, numbered 1 through to 4 can be identified on the gh-Diagram as shown in Fig. 2-7. Each region is identified by the magnitude and direction of heat and work flows to the process. The regions are grouped in pairs as shown by the different line patterns, indicating the range of the Carnot temperatures; for example, regions 1A and 3A have the same range of T_{Carnot} starting from 298 K to + INF (infinity), while the T_{Carnot} range for regions 1B and 3B starts from - INF to 0 K. So far we have only looked at a case where the directions of heat and work flows to the process are the same. We will now consider each region in more detail.

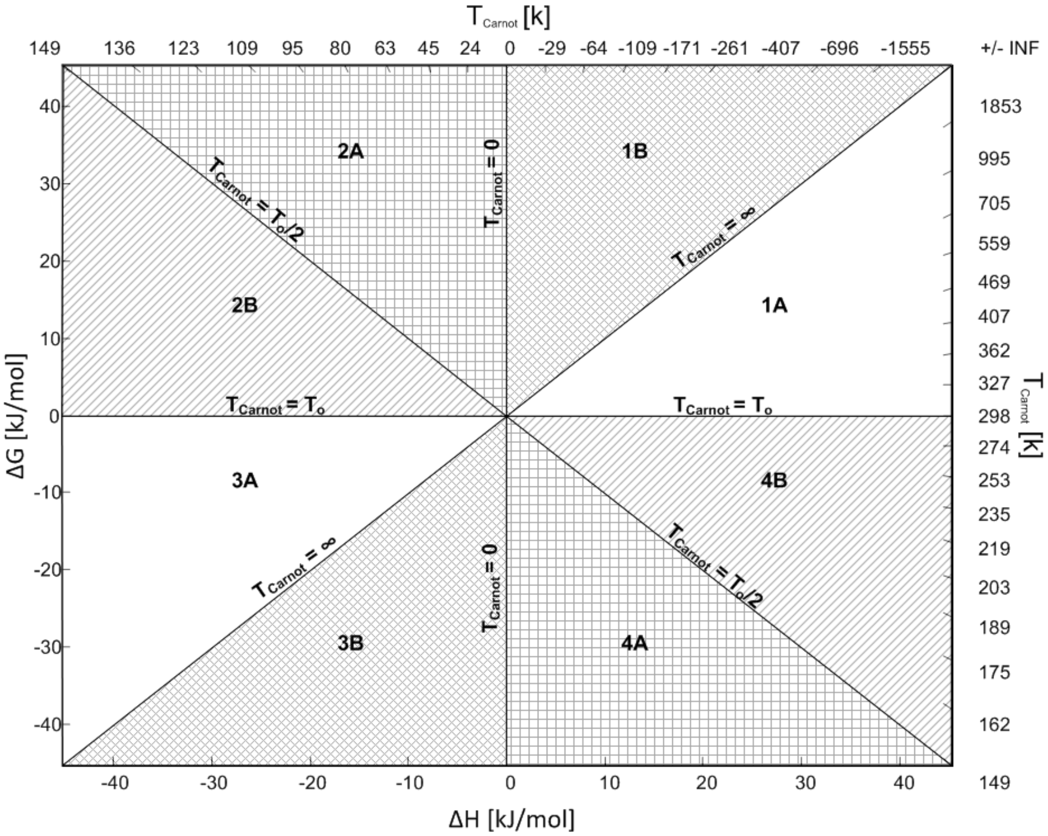

Fig. 2-7: Thermodynamic regions on the gh-diagram

2.5.1 Region 1: Processes which require *heat* and *work* input

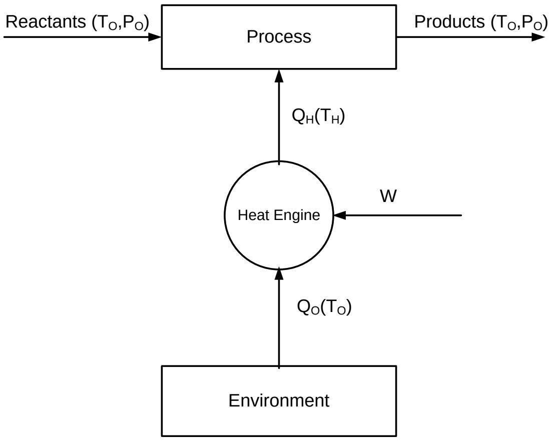

Fig. 2-8: Heat engine for processes that require *heat* and *work* input (Region 1)

Processes in regions 1 are those that have a positive ΔH and a positive ΔG. A positive ΔH signifies that the process is endothermic, that is the process requires heat input; and a positive ΔG means that there must be an increase in the Gibbs free energy for the process to occur; hence work must be applied to the process (Denbigh 1956). A heat engine (or a heat pump) as shown in Fig. 2-8 could be used to supply both the heat and work requirement to the process. For processes in region 1 to be reversible, heat must be supplied at the process Carnot temperature. However if we look at the Carnot Temperature for processes in region 1A, we can see from Fig. 2-7 that this varies from ambient temperature to infinity. As an example of a process in region 1A, consider the reverse water gas shift (RWGS) process described by the following equation:

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{2.8}$$

The work and heat requirements for this process are, $\Delta G = 28.52 \frac{kJ}{mol}$ and $\Delta H = 41.16 \frac{kJ}{mol}$ respectively. Using the temperature scale in Fig. 2-6, the Carnot temperature for the process is found to be 970 K. This implies that:

- If 41.16 kJ/mol of heat is supplied to the RWGS process at a temperature of 970 K it will satisfy the work requirement (28.52 kJ/mol) such that no additional work will need to be added or removed from the process; and therefore the process will be reversible.
- If a reversible heat engine, such as in Fig. 2-8 is used to supply the heat requirement (41.16 kJ/mol) at 970 K for the RWGS process, then the minimum work requirement for the heat engine would be 28.52 kJ/mol.

This means that it is possible to run processes in region 1A (Fig. 2-7) as reversible simple processes where the work requirement is satisfied by supplying heat at the Carnot temperature. However for processes close to the 45° line, one becomes limited by the availability of materials that can withstand high temperatures. In this case other methods of supplying the work reversibly must be considered and therefore a simple process will not be possible.

On the other hand, processes in region 1B (Fig. 2-7) require heat to be supplied at negative temperatures for them to be reversible; however negative absolute temperatures have no physical meaning. In this case they are simply a result of ΔG being greater than ΔH in magnitude. The implications of this result are as follows:

- ΔG and ΔH for a process are fixed and if they are equal in magnitude, then T_{Carnot} must go to infinity to satisfy Equation 2.3 However if ΔG > ΔH then there is no physically feasible T_{Carnot} that will satisfy Equation 2.3, that is $\Delta G > \Delta H\left(1 - \frac{T_O}{T = \infty}\right)$. In addition, Fig. 2-8 and Equation 2.2 show that it is impossible to have a heat engine such that $W > Q_H$. Therefore, for processes in region 1B, the maximum amount of work that can be transferred through heat is equal to the heat requirement of the process and this can only occur at infinite temperature. Hence:
- *Processes in region 1B will always be work deficient irrespective of the temperature at which heat is added and would require additional work input by other means such as pressure work or electro-chemical work and therefore cannot be run as simple processes*.

2.5.2 Region 2: Processes which reject *heat* and require *work* input

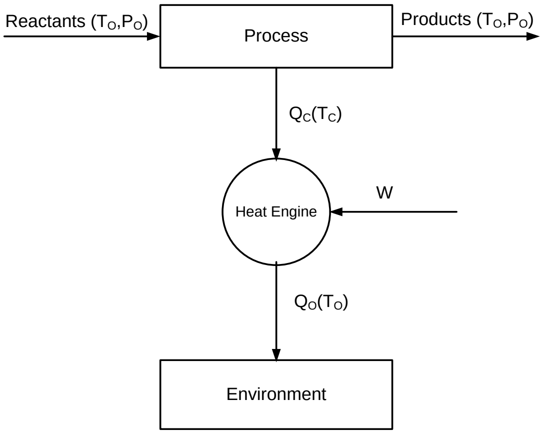

Fig. 2-9: Heat engine for processes which reject heat and require work input (Region 2)

Region 2 in Fig. 2-7 represents processes where the work requirement is reversibly supplied by removing heat at temperatures below ambient temperature T_O. A heat engine as shown in Fig. 2-9 can be supplied with work to extract an amount of heat Q_C from the process and reject an amount of heat Q_O at ambient temperature T_O to the environment. This corresponds to refrigeration processes where work is supplied to remove heat from substances at low temperatures and reject it at ambient temperature. The work requirement (W) for reversible refrigeration is given by (Smith, van Ness & Abbott 2001):

$$\left|\frac{W}{Q_C}\right| = \frac{T_O}{T_C} - 1 \qquad 2.9$$

T_C and T_O are the cold and hot temperatures at which heat is absorbed and rejected respectively. In this case the hot temperature is the ambient temperature T_O, while T_C is the sub-ambient temperature at which a quantity of heat Q_C is removed from the process.

It can be shown that *W* in Equation 2.9 is equivalent to *ΔG* across the process in Fig. 2-9, if the process is reversible. Hence one can say that:

- Rejecting heat below ambient temperature is one way of equivalently supplying work to a process. Hence the amount of work supplied is equivalent to the work needed by a refrigeration process to absorb the same amount of heat as the process heat requirement, at the process temperature.
- Region 2 represents all processes that run below ambient conditions, that reject heat and that require a refrigeration process, where the *ΔH* axis gives the amount of heat to be absorbed, the *ΔG* axis gives the minimum work needed to absorb the heat and the temperature scale gives the reversible refrigeration temperature. As an illustration consider a process at point *m* in Fig. 2-10.

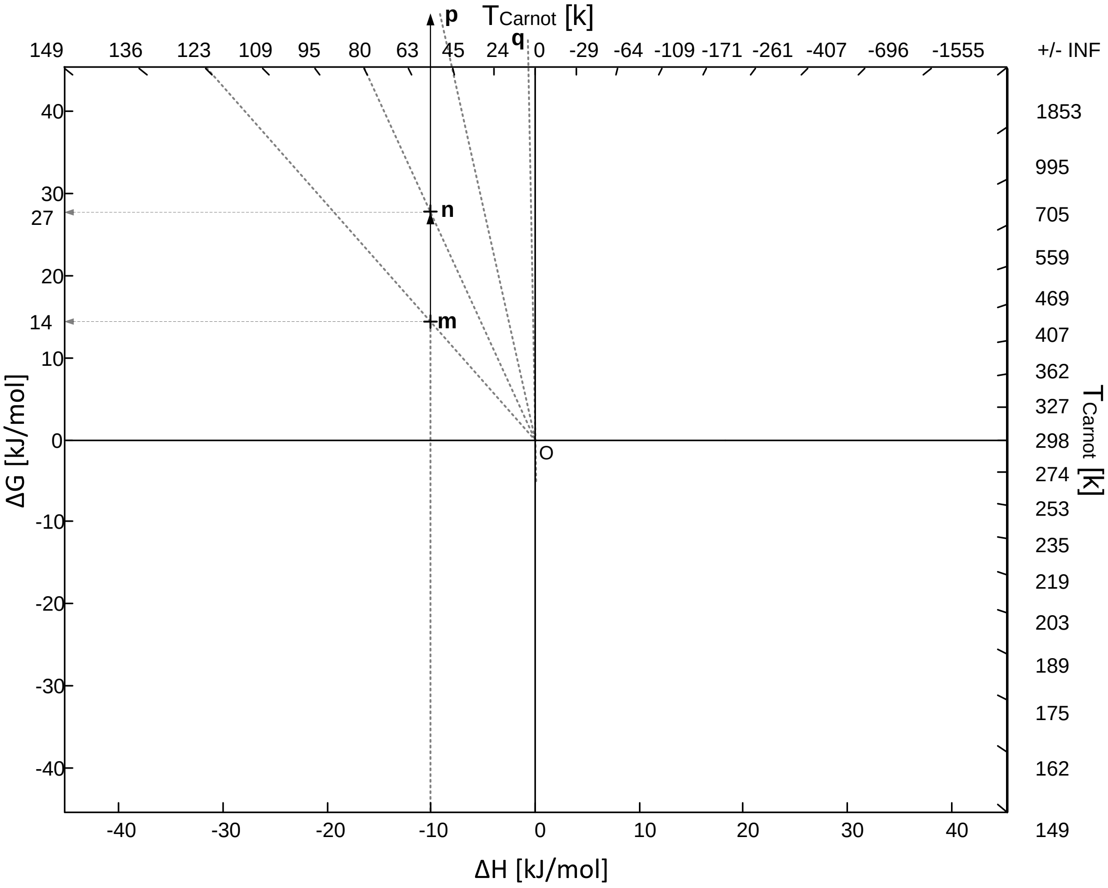

Fig. 2-10: Refrigeration processes are represented in Region 2 on the gh-diagram

At point *m* if 10 kJ/mol of heat needs to be absorbed then a minimum amount of work equivalent to 14 kJ/mol (at the intersection of line *o-m* and line *m-n*) is required to operate reversibly at a temperature of 123 K (as indicated by the intersection of line *o-m* and the temperature scale). However if the process operates at a temperature of 80 K (Intersection of line *o-n* and the temperature scale) with the same amount of heat dissipation, at point *n*, then the minimum amount of work required will be 27 kJ/mol (at the intersection of line *o-n* and line *m-n*); similarly at an operating temperature of 45 K, the amount of work required will be found at the intersection of line *m-n* and line *o-p* which is beyond the scale of the diagram. We can see that as the operating temperature decreases the amount of work required increases and as we approach a temperature of 0 K, line *o-q* tends to be parallel to line *m-n* signifying that the amount of work required tends to be infinitely large.

- Processes in region 2A (Fig. 2-7), require more work input than the amount of heat to be absorbed by the process and therefore reaching lower temperatures than those in region 2B. In particular processes in region 2A operate reversibly between $\frac{T_O}{2}$ and 0 K temperature. However these processes would be expensive to operate as they would require a large amount of work.
- On the other hand, processes in region 2B require less work for a larger amount of heat to be absorbed, hence operating reversibly at higher temperatures, between $\frac{T_O}{2}$ and T_O. These processes are consequently more feasible to implement.

2.5.3 Region 3: Processes which reject *heat* and *work*

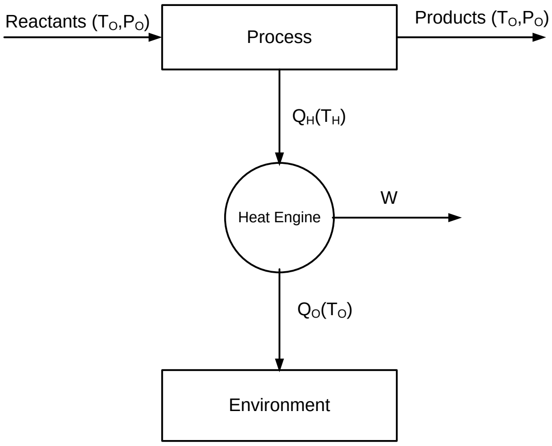

Fig. 2-11: Heat engine for processes which reject both heat and work (Region 3)

Processes in region 3 reject heat and have the potential to produce work. The heat rejected from the process could be used, for example, in a heat engine to produce work as shown in Fig. 2-11. Processes in region 3A can be run reversibly by removing heat at the process Carnot temperature which varies from ambient to infinite temperature.

As an example of a process in region 3A, consider the DME process as described by Equation 2.5. This process can reversibly reject all its work, ΔG = -16.75 kJ/mol, by removing heat, ΔH = -24.05 kJ/mol, from the process at T_{Carnot} = 983.04K. Similar to region 1A, for processes that are close to the 45° line in region 3A, one is also limited by the availability of materials that can handle these high temperatures.

For processes in region 3B to be reversible, it is required that heat be removed at negative temperatures, which has no physical meaning, for them to be reversible. This is a case similar to that encountered in region 1B. Here the absolute value of ΔH is less than that of ΔG. This means that:

- The maximum amount of work that can be recovered from the process, using a reversible heat engine, is equal to the amount of heat that the process can reject. This can only occur at infinite temperature. Therefore $\Delta G > W = \Delta H\left(1 - \frac{T_O}{T = \infty}\right)$ There is no heat engine capable of fully recovering the work from processes in region 3B irrespective of the temperature at which heat is removed.
- *Processes in region 3B will therefore always lose part of their work potential; they will always be irreversible if the only means of work recovery is from the quality of heat by, for example, a heat engine. Other means of recovering work should be considered.*
- Almost all commonly used processes, involving reaction with oxygen, in particular combustion and oxidation, are located in region 3B. Hence there is

no physically feasible temperature at which these processes can be run reversibly as simple processes. Power production processes, for example, involve the transformation of heat into mechanical power. While the mechanical side of this transformation has been much improved, these processes remain inefficient as a result of using combustion as heat source.

2.5.4 Region 4: Processes which require *heat* input and which could reject *work*

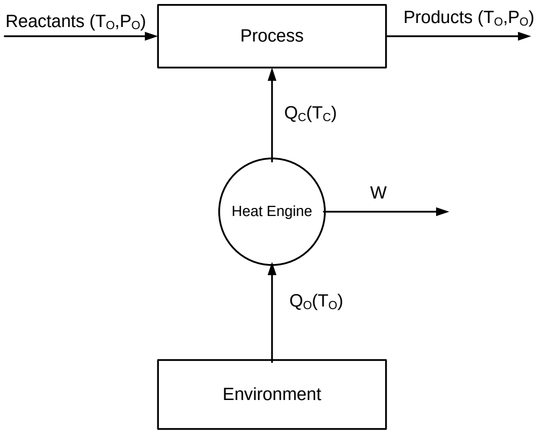

Fig. 2-12: Heat engine for processes which require heat input and that reject work (Region 4)

In order for processes in region 4 to reject work and input heat, sub-ambient temperatures are required for them to operate reversibly. As shown in Fig. 2-12, a heat engine can be used to recover work from processes in region 4, by absorbing a quantity of heat Q_O at a temperature T_O, from the environment, and rejecting a quantity of heat Q_C to the process at the process temperature T_C, where $T_C < T_O$.

Processes in region 4A operate reversibly between $0 < T < \frac{T_O}{2}$ while those in region 4B operate reversibly between $\frac{T_O}{2} < T_C < T_O$.

2.6 Process Irreversibility on the gh-Diagram

T_{Carnot} in Equation 2.4 was said to be the temperature at which heat must be added or removed from the process for it to be reversible; this means that if the process is operated at T_{Carnot} there is no entropy generation. If the only transfer of energy between the process and the surroundings occur as heat and if heat is added or removed at any other temperature *T*, then the process will generate entropy and will become irreversible. In that case Equation 2.4 becomes:

$$\Delta G_{rxn}(T_O, P_O) + T_O S_{generated} = \Delta H_{rxn}(T_O, P_O)\left(1 - \frac{T_O}{T}\right) \qquad 2.10$$

The reference temperature and pressure, *To* and *Po,* are the ambient temperature and ambient pressure respectively and *T* is the temperature at which heat is removed from the process.

The term $T_O S_{generated}$ in Equation 2.10 represents the additional work that is lost or needs to be added to the process as a result of the process irreversibility. This term can be quantified by subtracting Equation 2.4 from 2.10 to give:

$$T_O S_{generated} = W_{lost} = T_O \Delta H_{rxn}\left(\frac{1}{T_{Carnot}} - \frac{1}{T}\right) \qquad 2.11$$

A positive value for W_{lost} means that the process is producing extra work that cannot be recovered and which is lost, therefore generating entropy. A negative value for W_{lost} means that the process is work deficient; part of its minimum work requirement is being consumed to generate entropy, hence extra work must be added to make up for the lost work.

This can be represented on the gh-diagram as shown in Fig. 2-13.

As an illustration, consider Fig. 2-13; the ammonia process (A) is capable of delivering a maximum of 32 kJ/mol of work when it runs reversibly at 461 K. If it is run at 327 K it will only deliver 8 kJ/mol of work from the heat rejected and therefore 24 kJ/mol will be lost. When it is run at 900 K then 61 kJ/mol of work will be removed by the heat which is above the maximum that the process can deliver, therefore the process will be work deficient by 29 kJ/mol. This will have to be supplied by other methods for the process to occur.

Consider also the partial oxidation of methane in Fig. 2-13 (B); it could only occur reversibly if heat was rejected at -211 K, (which is impossible), 87 kJ/mol of work would be recovered. If it is run at 800 K, only 23 kJ/mol can be recovered from the heat and the remaining work, 64 kJ/mol, will be lost in generating entropy.

Methanol can also be cracked to form syngas (Fig. 2-13 C); if heat is absorbed at 412 K only 25 kJ/mol of work is required, at 970 K, 63 kJ/mol will be required and at 235 K the process would be work deficient, the work supplied by the heat would not be enough, the process would not happen unless work is added in other ways such as compression.

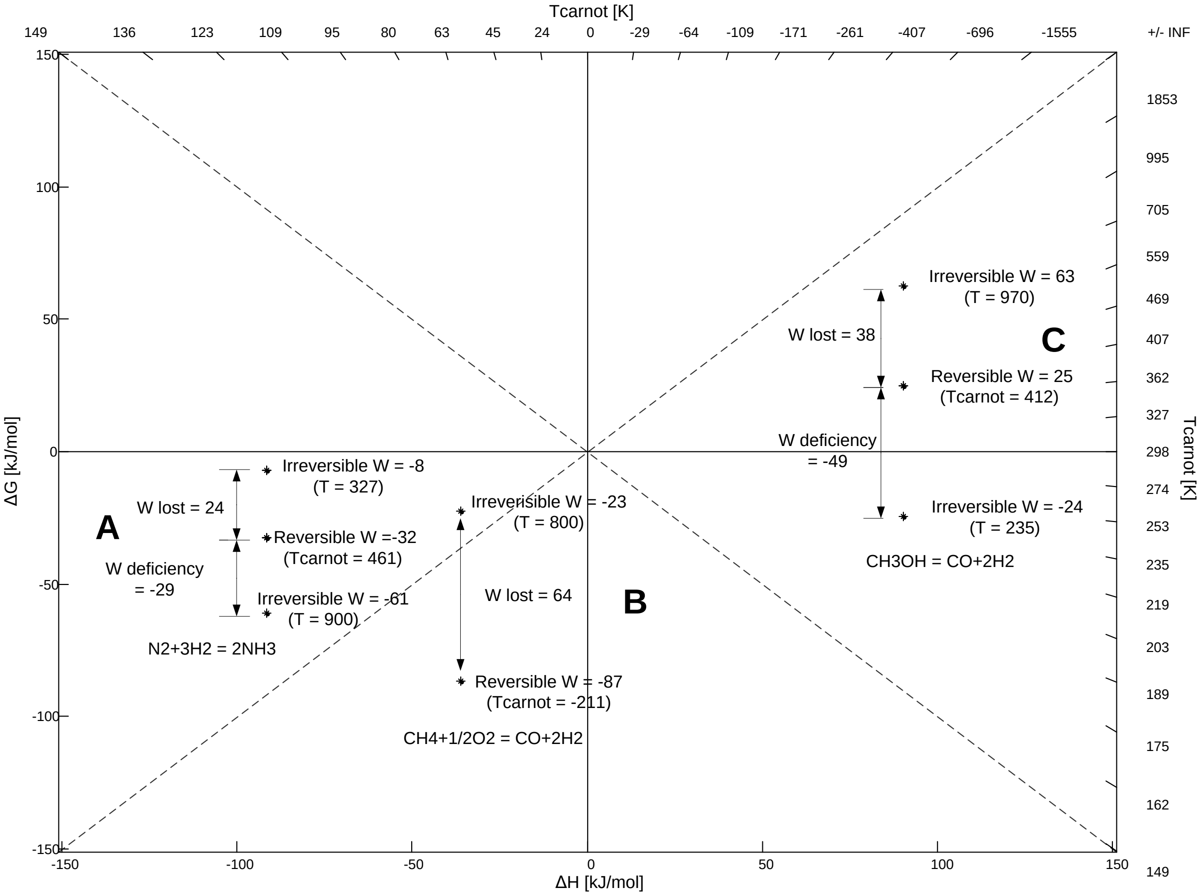

Fig. 2-13: Process irreversibility on the gh-diagram. A: Ammonia process. B: Methane partial oxidation. C: Methanol cracking

As a general rule on the gh-Diagram, if the process runs vertically above its reversible point (T_{Carnot}) work will be lost and if it runs vertically below the reversible point then there will be deficiency of work.

2.7 Combining Reactive Processes on the gh-Diagram

Glasser and King (1973) suggested using a combination of two reactions of opposite heat effect occurring on different catalysts, to control temperature in an adiabatic reactor, such that the heat released by one reaction is absorbed by the other. This is an alternative way of dealing with heat transfer problems in packed bed reactors as opposed to using heat exchanger surfaces which has been unsuccessful in efficiently solving the above problem.

This idea can be extended to combining chemical processes where not only the heat effect but also the work and temperature effects are used to achieve a certain target. As we will see in the gh-diagram, when processes are combined, one could either target reducing or even eliminating the heat or the work requirement or shifting the Carnot temperatures from very low or very high values to easily achievable temperatures. However this can only be achieved when the chemical processes are combined in a single unit.

As an illustration consider three processes represented by the following overall mass balances:

$CH_4 + H_2O \rightarrow CO + 3H_2$ (Rxn1)

$CO + 2H_2 \rightarrow CH_3OH$ (Rxn2)

$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$ (Rxn3)

These processes are represented on the gh-diagram as shown in Fig. 2-14. They can be run individually to obtain line O-Rxn1 for the first process, line O-Rxn2 and line O-Rxn3 for the second and third process respectively. Any point along line O-Rxn1 is given by $\Delta H = E_1 \Delta H_{Rxn1}$ and $\Delta G = E_1 \Delta G_{Rxn1}$ where E_1 is the extent of the first process (Rxn1). Similarly points on line O-Rxn2 and O-Rxn3 are represented by the pairs ($E_2 \Delta H_{Rxn2}, E_2 \Delta G_{Rxn2}$) and ($E_3 \Delta H_{Rxn3}, E_3 \Delta G_{Rxn3}$) respectively.

Suppose process Rxn1 and Rxn3 are combined and their extents of reaction are such that $E_1 + E_3 = 1$ based on 1 mole of methane used. The combined process is represented by line Rxn1-Rxn3 and each point on the line is given by $\Delta H = E_1 \Delta H_{Rxn1} + E_3 \Delta H_{Rxn3}$ and $\Delta G = E_1 \Delta G_{Rxn1} + E_3 \Delta G_{Rxn3}$. Therefore the triangle O-Rxn1-Rxn3 defines a region of possible combinations of these two processes. Line

Rxn1-Rxn3 represents points where the combined processes go to completion, any other point in the triangle corresponds to incomplete processes where some of the reactant appears in the product stream, therefore $E_1 + E_3 < 1$.

Note that *ΔG* = 0 on line O-A inside the triangle, this line represents solutions for *E1* and *E3* if the target is to have zero work requirements. This means that if there exists active catalysts at 298 K for the reactions in process Rxn1 and Rxn3, one could run them at no work cost with heat provided by the environment at 298 K. However if the target is to run the processes at zero heat requirement then it must run along line O-B at zero absolute temperature which is clearly difficult to achieve.

Process Rxn1 is the production of syngas by methane and water. This process requires large amount of heat and work input. These can be provided by an external source or one can react some of the methane with oxygen to provide the heat and work while producing more syngas as well. Methane oxidation to provide heat and work to process Rxn1 can be done in two ways:

- The first option consists of running a separate methane oxidation process (process Rxn3 in Fig. 2-14). For this process to be able to supply the work requirement of process Rxn1, it must be run at a temperature close enough to the Carnot temperature of process Rxn1 (958 K). However running process Rxn3 at 958 K would be highly irreversible, since methane oxidation is in region 3B and has a negative Carnot temperature (-211 K). This option could be feasible but it would be inefficient as well.
- The second option is running a reversible combined process of Rxn1 and Rxn3. The extent of both reactions must be adjusted so that the process falls in region 1-3 (Fig. 2-14) where one can reach reversible temperatures using available resources such as steam. If the process is run along line O-A then no work input would be required and heat would be obtained freely from the

environment provided of course that an active catalyst exists at these conditions.

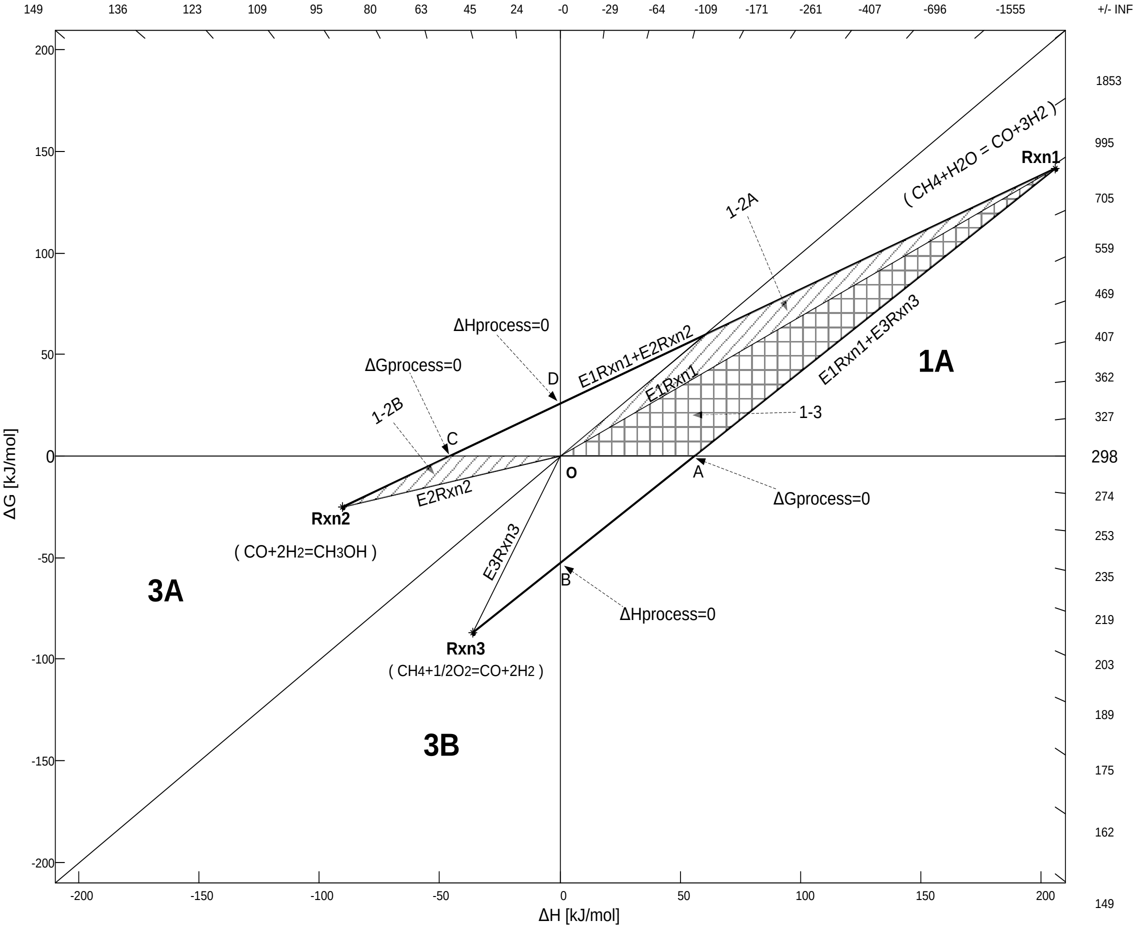

Fig. 2-14: Processes can be combined on the gh-diagram allowing them to be more feasible and reversible

In the same way heat can be recovered from the methanol process (Rxn2) and be used to run the syngas production process (Rxn1). If these processes are run separately and for process Rxn2 to be able to supply sufficient heat and work to process Rxn1, it must run at a temperature close to Rxn1 Carnot temperature (958 K) and as a consequence process Rxn2 will be irreversible for operating at a higher temperature than its Carnot temperature (412 K).

However if Rxn1 and Rxn2 are combined as shown by line Rxn1-Rxn2 then one has many options as to where the combined process can reversibly operate. Regions 1-2A and 1-2B give the possible easily achievable temperatures at which the combined process can be reversible. The combined process can also be run along line O-C at no work cost while heat is rejected at ambient temperature. Again there must exist active catalysts for both reactions at these conditions.

In conclusion, for heat integration in a system of chemical processes, there are advantages to combining reactions in a single unit as opposed to running them in separate processes. It is unlikely to integrate heat between separate processes reversibly, whereas reversibility can be achieved over a range of temperatures when processes are combined in a single unit.

2.8 Analysis of Existing Processes on the gh-Diagram

Shinnar (1988) stated that inefficiency in most existing chemical processes results not from the second law of thermodynamics, but from design decisions and lack of better technology. Let us investigate this further by analyzing a few chemical processes on the gh-diagram in Fig. 2-15.

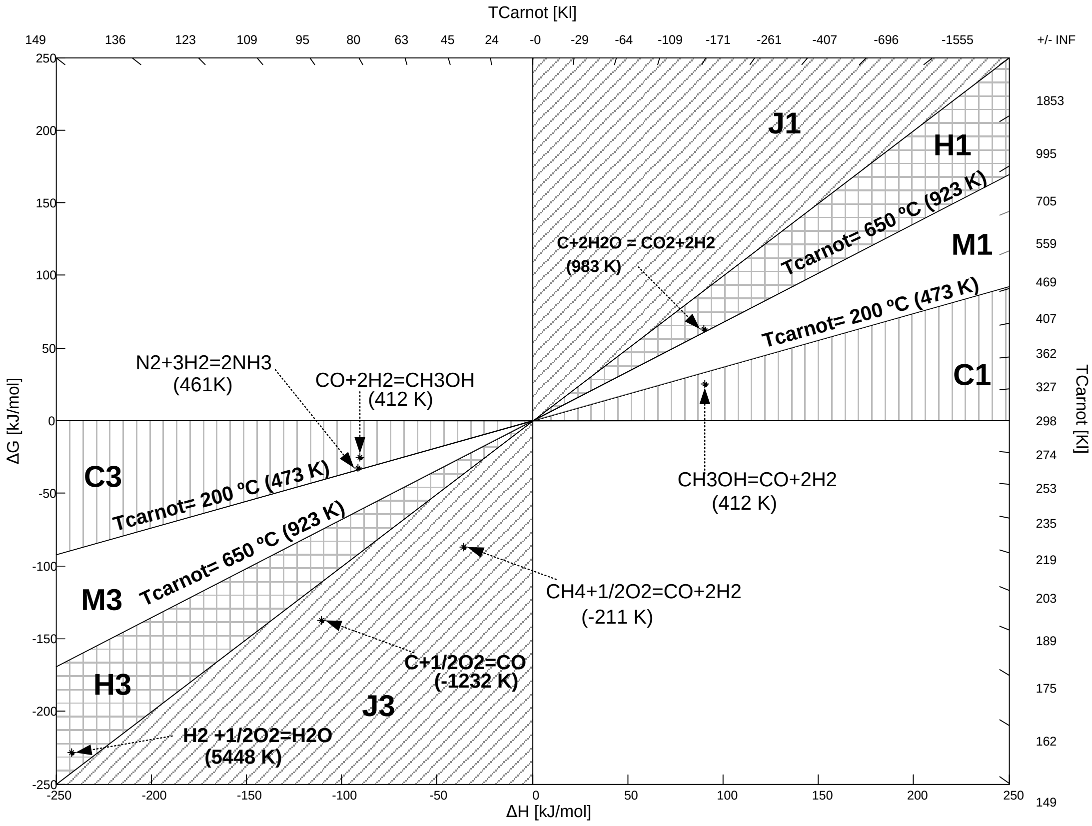

Fig. 2-15: Thermodynamic regions on the gh-diagram based on the use of steam for transferring heat

Most processes use steam and steam cycles to transfer heat from one operation unit to another and to recover work from the process. Steam production is usually restricted to a maximum temperature of about 650 ^{o}C, to allow the use of low cost material such as steel for boilers and turbines; high temperature (above 650 ^{o}C) steam production requires the use of expensive alloys which would lead to high capital costs.

Let us consider the first and third quadrants in Fig. 2-15. The regions M1 and M3 are enclosed between T_{Carnot} = 650 ^{o}C and T_{Carnot} = 200 ^{o}C, the upper and the lower steam temperature limits respectively. The lower steam temperature limit is set to be the lowest temperature at which work can be efficiently produced from heat using available heat engine technology (Shinnar 1988). If it is decided to use low cost material so as to use steam for heat transfers then one would be forced to operation in region M1 or M3. As a consequence, only processes whose Carnot temperatures fall in regions M1 and M3 will potentially be reversible, any other process will fall in one of the following cases:

- If the process is in region C3 (Regions C1 and C3, are the low temperature regions, representing processes with Carnot temperatures between 25 ^{o}C and 200 ^{o}C), there is no possibility to recover work reversibly using a heat engine; hence heat removed from the process will lose its work potential. If it is decided to run the process in region M3 in order to recover the work through a heat engine, heat will then be rejected at a higher temperature (below the reversible point), taking with it more work than the process can provide. Hence the process will require additional work input as was explained in Fig. 2-13. This is the case for ammonia processes which can be reversibly operated in region C3 (Fig. 2-15) at 188 °C. However in the industry ammonia processes are conducted at 500°C and most of the heat recovered from the process is used to produce steam (Austin 1984). By removing heat at 500 ^{o}C, the process will be work deficient as explained earlier, and additional work input is required. Therefore, in the industry higher pressures (between 15 and 30MPa) (Austin 1984) are required to drive ammonia processes. The higher operating pressures provide work to compensate for the lost work during heat removal.
- If the process operates in region H3 (Regions H1 and H3, are the High temperature regions, representing processes with Carnot temperatures between 650 ^{o}C and infinitely high temperature), then steam will need to be generated at high temperatures to recover work reversibly using a heat engine. As an example, let us suppose that the combustion of hydrogen (Fig. 2-15) is used to provide heat for steam generation, the process would need to operate in region H3 at 5175 ^{o}C (5448 K) for it to be reversible hence expensive alloys will be required for the equipment. If the process is

operated in region M3 to avoid the cost of generating steam at high temperatures, then the process will be running at lower temperatures than its Carnot temperature (above the reversible point); hence not all the available work will be recovered and will therefore be lost and the process will be irreversible.

- If the process is operated in region H1, such as the production of hydrogen by reacting carbon and water (Fig. 2-15), then high temperature steam (983 K) will be needed to provide the required work reversibly; and again to avoid the cost of generating steam at high temperatures the process would be run in region M1 at lower temperatures than its Carnot temperature. Therefore, the work provided by steam would be insufficient to drive the process and additional work input would be required in order to make the process feasible. To avoid the use of steam one could supply the heat by burning coal together with water in a single unit as it is usually done in gasification of coal.

An interesting point to note is the production of methanol from carbon monoxide and hydrogen, as illustrated in Fig. 2-15. This process has a Carnot temperature of 412 K and can be reversibly operated in region C3, however with the current heat engine technology it is not possible to efficiently recover the work with low temperature steam. Note however that its reverse process, with the same Carnot temperature in region C1, can be reversibly run by using low temperature steam to provide the work needed. It is therefore clear that there is no lower limit for processes that use steam in region C1 because there is no need for special equipment to supply work to the process at these low temperatures.

Note also that most of the oxidation processes, including combustion, such as oxidation of carbon to carbon monoxide or carbon dioxide and partial oxidation of methane are located in region J3 (Regions J1 and J3, are the infeasible regions, representing processes with negative Carnot temperatures between), In practice oxidation and combustion processes are operated at high temperatures in region M3, where heat is removed via steam at about 650°C, far above their reversible point. Therefore they are always irreversible. Combustion processes are known to have a high exergy loss (Yamamoto, Ishida 2002).

2.9 Conclusion

The discussion in this paper implies that for every chemical process there are two dimensions of energy, which need to be satisfied for the process to be feasible. These are heat and work requirement of the process. Since heat is the easiest way of transferring energy, it is almost always used in any chemical process. On the other hand, satisfying the work requirement for a process is the major challenge for chemical engineers. Heat, by virtue of its temperature, carries a certain amount of work; however it has been shown in the gh-diagram that, heat must be at an appropriate temperature in order to efficiently transfer work to the process. It has also been shown that for some processes it is impossible to efficiently transfer work via heat irrespective of the temperature at which heat is transferred to the process.

Although the concept of transferring work to a process via heat is not well understood, it is extensively used in industry. The incorrect application of the concept is a major source of irreversibility in most existing processes. With the gh-diagram, the process designer can identify where the concept can be applied without or with less work losses. Since the gh-diagram only requires knowledge of the enthalpy and the Gibbs energy change across the process, any number of processes can be simultaneously analyzed on a single diagram, hence it allows scanning of many possible routes for desired products.

References

Austin, G.T. 1984, *Shreve's Chemical Process Industries,* McGraw-Hill, New York.

Daichendt, M.M. & Grossmann, I.E. 1998, "Integration of hierarchical decomposition and mathematical programming for the synthesis of process flowsheets", *Computers & Chemical Engineering,* vol. 22, no. 1-2, pp. 147-175.

Denbigh, K.G. 1956, "The second-law efficiency of chemical processes", *Chemical Engineering Science,* vol. 6, no. 1, pp. 1-9.

Glasser, D. & King, R.P. 1973, "Optimal catalyst concentration profile for bifunctional catalyst: Langmuirian kinetics", *Chemical Engineering Science,* vol. 28, no. 9, pp. 1685-1689.

Gundersen, T. 1997, *A worldwide catalogue on process integration,* International Energy Agency.

Kovač Kralj, A., Glavič, P. & Kravanja, Z. 2005, "Heat integration between processes: Integrated structure and MINLP model", *Computers & Chemical Engineering,* vol. 29, no. 8, pp. 1699-1711.

Linnhoff, B., Townsend, D.W., Boland, D., Hewitt, G.F., Thomas, B.E., Guy, A.R. & Marsland, R.H. 1982, *A user guide on process integration for the efficient use of energy,* The Institution of Chemical Engineers, Rugby.

Oaki, H. & Ishida, M. 1982, "Study of chemical process structures for process synthesis", *Journal of Chemical Engineering of Japan,* vol. 15, no. 1, pp. 51-56.

Patel, B., Hildebrandt, D. & Glasser, D. 2004, "Overcoming the Overall Positive Free Energy of a Process: Using the Second Law to understand how this is Achieved", *AIChE Annual Meeting*AIChE, Austin, November.

Patel, B., Hildebrandt, D., Glasser, D. & Hausberger, B. 2005, "Thermodynamics Analysis of Processes. 1. Implications of Work Integration", *Industrial & Engineering Chemistry Research,* vol. 44, no. 10, pp. 3529-3537.

Shinnar, R. 1988, "Plenary paper received too late to be included at front of issue: Thermodynamic analysis in chemical process and reactor design", *Chemical Engineering Science,* vol. 43, no. 8, pp. 2303-2318.

Smith, J.M., van Ness, H.C. & Abbott, M.M. 2001, *Introduction to Chemical Engineering Thermodynamics,* McGraw-Hill, New York.

Smith, R. 2000, "State of the art in process integration", *Applied Thermal Engineering,* vol. 20, no. 15-16, pp. 1337-1345.

Staine, F. & Favrat, D. 1996, "Energy integration of industrial processes based on the pinch analysis method extended to include exergy factors", *Applied Thermal Engineering,* vol. 16, no. 6, pp. 497-507.

Westerberg, A.W. 2004, "A retrospective on design and process synthesis", *Computers & Chemical Engineering,* vol. 28, no. 4, pp. 447-458.

Yamamoto, M. & Ishida, M. 2002, "Process vectors both to create functional structures and to represent characteristics of an entire system", *Energy Conversion and Management,* vol. 43, no. 9-12, pp. 1271-1282.

3 WORK TO CHEMICAL PROCESSES

The Relationship between Heat, Temperature, Pressure and Process Complexity

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3.1 Abstract

In order for a chemical process to be feasible, two levels of energy must be met; these are the *heat* and the *work* requirement of the process. While, for most processes, the amount of heat required can be easily satisfied, supplying the amount of work required is a major challenge and usually the determinant of the process complexity. In some cases, heat by virtue of its temperature can satisfy the work requirement for a process; it is the simplest method for supplying work but could result in major irreversibility when applied inappropriately to a process. This manuscript discusses different techniques that can be used to supply work to a process. A graphical approach, namely the *gh-diagram*, is used to analyse the heat and work requirement of chemical processes and to determine which method of supplying work is suitable in order for the process to be feasible and reversible. An analysis of an ammonia process is done as a case study where a comparison of different methods of supplying work is made and where an attempt is made to bring to light the consequences of operating conditions, namely temperature, on the reversibility and complexity of the process. This is a novel approach to process

synthesis which requires the knowledge of ΔH and ΔG only to determine the target for a process in terms of heat and work requirement, to determine which method of supplying work is suitable, to give ways of manipulating the process in order to use available technology and get as close to reversibility as possible and also to give an early understanding of what the process structure would be. It also allows assessing irreversibilities and where they occur within a process; therefore it can be applied to existing processes to reveal opportunities for improvement and attempts to determine how this can be achieved.

3.2 Introduction

Previous work by Sempuga et al. (2010), has shown that in order for a chemical process to be feasible two levels of energy must be met; these are the heat requirement, given by the enthalpy change, $\Delta H(T_O,P_O)$, and the work requirement, given by the Gibbs free energy change, $\Delta G(T_O,P_O)$, across the process; both taken at ambient conditions of pressure and temperature T_O and P_O respectively. Processes were classified on a ΔH - ΔG diagram, which is called '*gh-Diagram'*, where from a single point representing a process, one could predict how feasible and how complex the process would be. This approach is useful in the early stage of process development as it provides an idea of how the reversibility of a process can be achieved and thereby giving an indication of what the structure of a chemical process would be by simply looking at the magnitude and direction of both the heat and the work requirement. It is a potentially useful tool for decision makers as it gives direction toward more energy efficient processes.

While transferring heat to a process is relatively easy, supplying work is usually a major challenge for engineers. The work requirement (or work potential) for a process is generally referred to as 'Exergy' and several authors (Aljundi 2009, Ganapathy et al. 2009, Caton 2000, Taniguchi et al. 2005) have analyzed the 'exergy efficiency' of a number of processes, such as those involving combustion, in search for more efficient ways of utilizing the work potential or supplying the work requirement of processes. It is believed that a better understanding of exergy can be economically profitable and is the key to reducing the negative effect that most chemical processes have on the environment (Rosen 2002, Tonon et al. 2006, Ayres 1998). This manuscript combines a graphical approach, introduced by Sempuga et al. (2010), in order to analyze some of the methods for supplying work to, or removing work from chemical processes. Using a more fundamental approach, an attempt is made to bring to light the implications arising from using available technologies which set limits on operating conditions namely pressure and temperature and thereby impacting the efficiency of energy utilization in industry.

Thermodynamic equations, such as the Gibbs/Duhem equation, are often used as means of calculating thermodynamic properties of chemical substances. These equations, however, can also reveal different ways the flow of energy occurs across a process. One particular example is the fundamental equation (Equation 3.1) relating the Gibbs free energy to temperature, pressure and composition.

$$dG = VdP - SdT + \sum_i \mu_i dx_i \qquad 3.1$$

Equation 3.1 describes how the Gibbs free energy of a substance changes with changing pressure, temperature and composition. When this equation is applied to a process, it shows different ways *work* is transferred across the process. The first term of the right hand side of the equation shows that work can be transferred directly as mechanical work via pressure; the second term shows that heat by virtue of its temperature can transfer work across a process and the third term shows that work can also be transferred by mixing or separating different species in the process. Thus in order to satisfy the work requirement for any existing chemical process, one would either use one of the three ways to transfer work or a combination of them. Throughout this manuscript we will ignore the work associated with mixing and separation, since, in principle, the work of mixing can be reintegrated in the process to cover for the work of separation. In existing processes the amount work associated with separation can be large and requires a particular attention; however this is beyond the scope of the present analysis. Therefore we will only explore work flows via pressure and heat.

3.3 Work Transfer across a Process via Heat

In some cases, heat, by virtue of its temperature, can satisfy the work requirement for a process; this could be the simplest way of meeting the work requirement and is almost always used; but it is also a major route of inefficiencies in most chemical processes. Previous works by Sempuga et al. (2010) and Patel et al. (2005), have shown that when work is transferred via heat only, this can be described by Equation 3.2 where $\Delta G_P(T_O,P_O)$ is the change in Gibbs free energy between the inlet and outlet streams, and represents the work requirement for the process; $\Delta H_P(T_O,P_O)$ is the enthalpy change representing the heat requirement of the process and (T_{Carnot}) is the *'Carnot Temperature'* defined as the unique temperature for a process at which maximum or minimum amount of work is transferred via heat.

$$\Delta G_P(T_O,P_O) = \Delta H_P(T_O,P_O)\left(1-\frac{T_O}{T_{Carnot}}\right) \tag{3.2}$$

In the case where heat is transferred at any other temperature (T), than the Carnot temperature, the process will either be irreversible or work deficient depending on whether it is run above or below the Carnot temperature. The work loss or work deficiency (W_{lost}) can be evaluated using Equation 3.3, where a positive value for

W_{lost}, means the process is consuming more work than needed and therefore becomes irreversible, and a negative value for W_{lost} means that the process is work deficient and therefore becomes infeasible.

$$W_{lost} = T_O \Delta H_P \left(\frac{1}{T_{Carnot}} - \frac{1}{T} \right) \tag{3.3}$$

Sempuga et al. (2010) have shown that chemical processes can be represented and classified on the *gh-diagram* according to the direction and magnitude of their heat and work requirement. The *gh-diagram* was subdivided in different regions numbered 1 through to 4, as shown in Fig. 3-1, indicating where it is possible to transfer work efficiently across a process via heat.

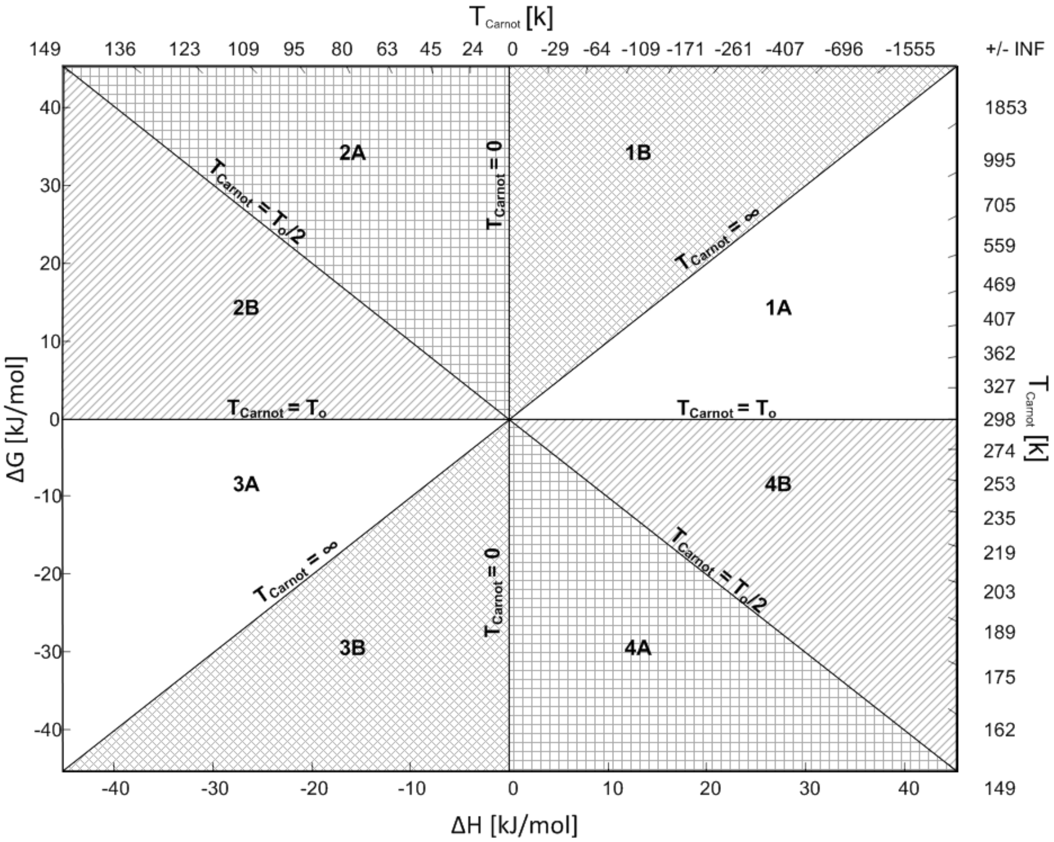

Fig. 3-1: The gh-diagram subdivided in different thermodynamic regions according to the direction of work and heat requirement and the Carnot temperature for a process

We defined a *'Simple Process'* as the one in which heat is transferred at a single temperature and at a single point, which could be the reactor; it is a process described by Equation 3.2. Consequently, processes that can be run as '*simple processes'* are those whose work requirement (ΔG) and heat requirement (ΔH) are such that the Carnot temperature (T_{Carnot}), as shown in Equation 3.2, is positive and achievable. The regions in the *gh-diagram*, where it is possible to reversibly run chemical processes as '*Simple Processes'* are; 1A, 2A, 2B and 3A; Processes in regions 1B, 3B, 4A and 4B cannot be run reversibly as '*Simple Processes'* due to their impracticable Carnot temperatures .

The currently available technology and the usage of utilities, such as steam, only permit operation of most existing chemical processes in regions 1A and 3A where temperatures are positive and above ambient temperature. Therefore processes which are not inherently located in region 1A and 3A will not be practically feasible or efficient when run as *simple processes* unless some sort of manipulations are employed. In that case these processes will be run as '*Non Simple processes'* or *'Complex Processes'* and might require work to be supplied using other methods than that of supplying work using heat at single temperature. In general, any process whose work and heat requirement are such that Equation 3.2 requires an extra term on the right hand side, would be considered as a *complex process* and will be described by an equation of the form in Equation 3.4, where W_{ex} is the extra work that is needed for the process to be feasible and reversible. As we will see later in the paper, W_{ex} will depend on the method used to supply work. Note also that; 1) in order for a process to feasible and reversible when it is run in any other region than the one it inherently belongs to, the process must be run as a *complex process*; 2) If the process is run in its original region but at another temperature than the Carnot temperature it must also be run as a *complex process* for it to be feasible and reversible.

$$\Delta G_P(T_O, P_O) = \Delta H_P(T_O, P_O)\left(1 - \frac{T_O}{T}\right) + W_{ex} \tag{3.4}$$

Thus a process that is described by Equation 3.4 is a *complex process* and might need multiple steps and extra equipment for it to be feasible; and in some cases each step of the *complex process* might be a *simple process*. This is the case encountered in some reactive processes, where the chemistry of the complex process is such that a number of chemical transformations occur from feed to product where each chemical transformation is a simple process.

In this paper we are going to investigate two main methods that are commonly used in the industry. The first method uses more than one point to transfer heat to and from the process; the heat transfer configuration constitute a virtual heat engine which removes or add work to the process. The second technique consists of adding or removing work from the process mechanically via pressure. Other techniques which are not discussed here comprise, work transfer electrochemically in galvanic cells or fuel cells, and work transfer by light such as photosynthesis. Using the *gh-diagram*, we will show that these techniques can make it possible, in principle, to reversibly run a number of chemical processes in other regions than those they inherently belong to. These techniques will, for example, allow processes with negative or extremely high Carnot temperatures, to be run using commonly available utilities and technology at industrially achievable conditions.

3.3.1 Work Transfer across a Process by Heat Engine Configuration

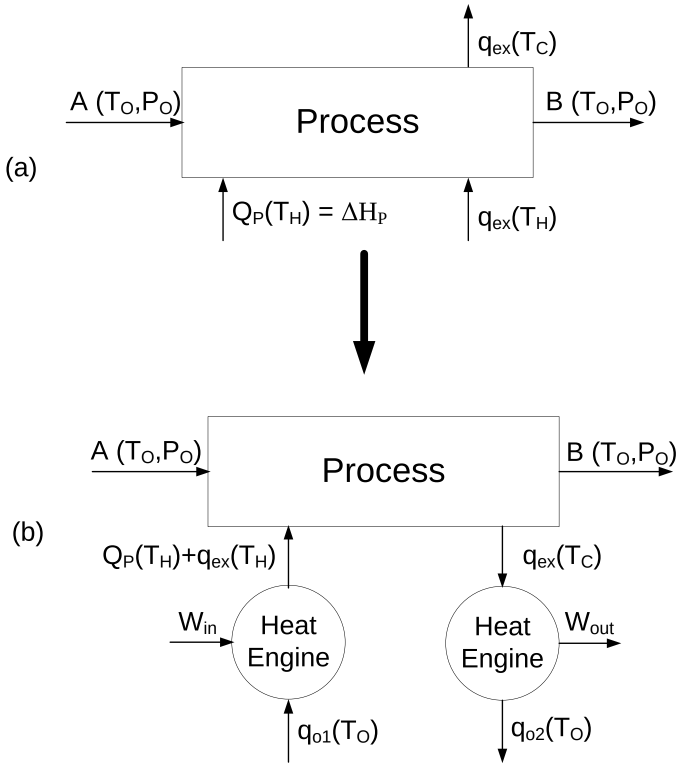

Fig. 3-2: (a) Work addition by adding heat at high temperature and rejecting heat at lower temperature. (b) Work flows associated with each heat transfer across the process

For a process requiring work input this technique will consist of adding a larger amount of heat at high temperature at one point of the process and removing a smaller amount of heat at a lower temperature at another point of the process. On the other hand, for a process that releases heat the inverse will apply; that is a smaller amount of heat at low temperature is added at one point of the process and a larger amount of heat at high temperature is removed at another point of the process (Patel et al. 2005).

Let us consider a process where a substance A is converted to another substance B as shown in Fig. 3-2 (a); the process heat requirement Q, equivalent to the enthalpy change across the process (ΔH_P), is supplied at a temperature T_H; if an extra amount of heat q_{ex}, is added then the same amount of heat must be removed at some point of the process in order to meet the overall energy balance. Note that we can choose to remove the extra amount of heat at a different temperature than that it was added at; hence suppose that we add the extra amount of heat q_{ex}, at T_H, and remove it at a lower temperature T_C. The work that flows together with the heat in and out of the process can be understood as being supplied by heat engines as shown in Fig. 3-2 (b). Hence the work flowing in the process is given by:

$$W_{in} = Q_P\left(1-\frac{T_O}{T_H}\right)+q_{ex}\left(1-\frac{T_O}{T_H}\right) \tag{3.5}$$

And the work flowing out of the process is given by:

$$W_{out} = q_{ex}\left(1-\frac{T_O}{T_C}\right) \tag{3.6}$$

Therefore the total amount of work transferred to the process is given by:

$$W_T = W_{in} - W_{out} = Q_P\left(1-\frac{T_O}{T_H}\right)+q_{ex}T_O\left(\frac{1}{T_C}-\frac{1}{T_H}\right) \tag{3.7}$$

The first term on the right hand side of the equation is the work that would be transferred to the process if the process was given just the amount of heat it requires. The second term is the extra amount of work added to the process resulting from adding and removing an extra amount of heat at a higher then a lower temperature respectively. This method is useful when the heat requirement alone is not capable of satisfying the work requirement of the process irrespective of the temperature at which it is supplied. This is the case of processes with negative Carnot temperatures in region 1B and 3B on the *gh-diagram*. Note that although the heat requirement may be satisfied the process would not proceed if the work requirement is not satisfied. Therefore the remaining amount of work that is needed for the process to proceed can be supplied by adding an extra amount of heat at a higher temperature then removing the same amount of heat at a lower temperature. Since the process in Fig. 3-2 has certain amounts of heat being transferred at different points of the process and at two different temperatures, it is not a *simple process*. Therefore the process is a *complex process* and would be reversible if it is described by Equation 3.8; the second term on the right hand side is equivalent to W_{ex} in Equation 3.4.

$$\Delta G_P(T_O, P_O) = \Delta H_P(T_O, P_O)\left(1 - \frac{T_O}{T_H}\right) + q_{ex} T_O \left(\frac{1}{T_C} - \frac{1}{T_H}\right) \tag{3.8}$$

However each point of heat transfer, with the temperature and work associated with it can be treated as a *simple process,* and can be located on the *gh-diagram.* The implication of this is as illustrated in Fig. 3-3; if the heat requirement of a certain process X cannot satisfy the work requirement at any reasonable temperature, for example when it requires heat to be supplied at a negative or an extremely high temperature to meet the work requirement, then one can split it into two processes Y and Z, such that Y is a heat accepting process with a positive and achievable Carnot temperature $\mathrm{T_H}$, and Z is a heat releasing process also with a positive and achievable Carnot temperature $\mathrm{T_C}$, where $\mathrm{T_H}$ is greater than $\mathrm{T_C}$ and both Y and Z can be run reversibly as simple processes.

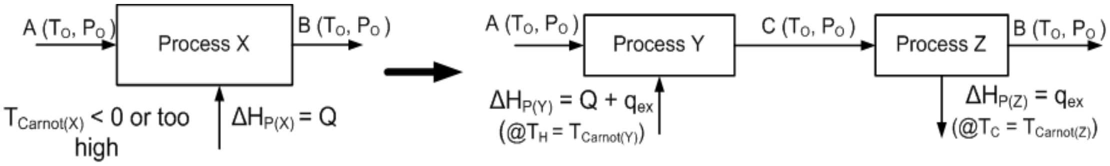

Fig. 3-3: A non-simple process can be split into multiple simple processes

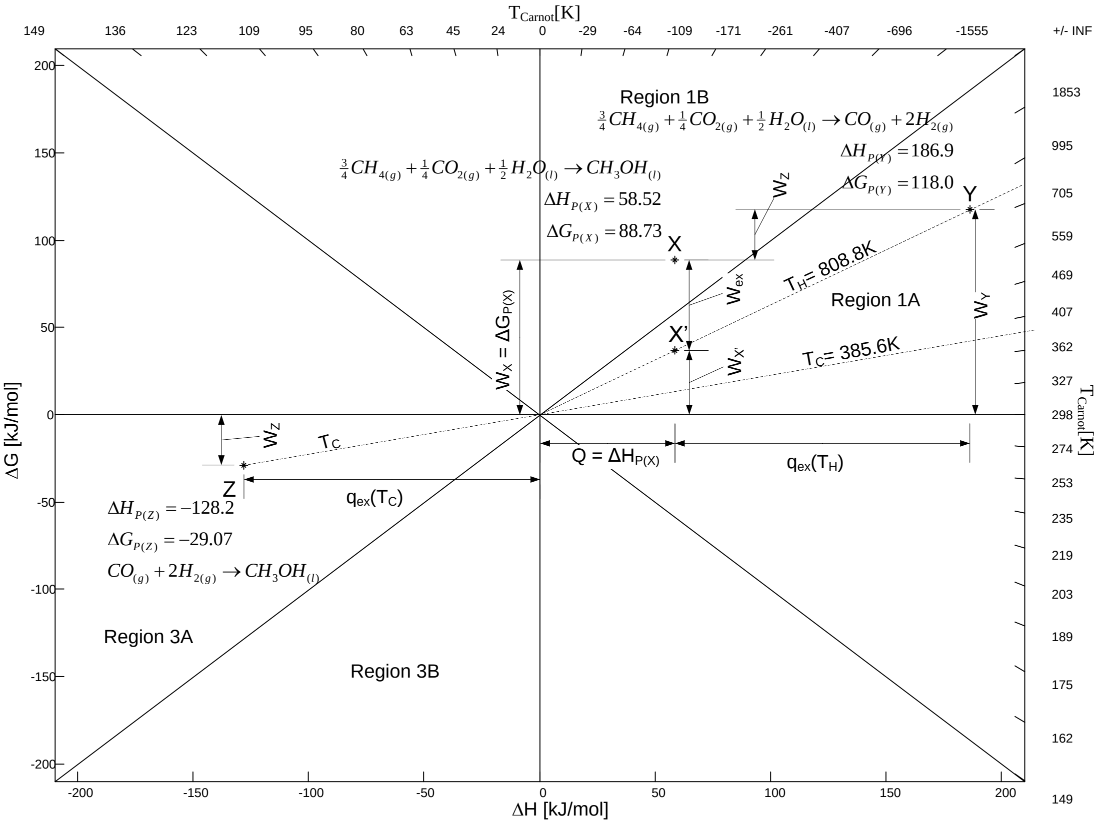

Fig. 3-4: gh-Diagram showing how a process can be made feasible where work is supplied via heat at two different temperatures by splitting the process (X) into two simple processes (Y) and (Z).

As an illustration consider a process for the production of methanol from methane, carbon dioxide and water according to the following equation:

$$\begin{aligned}&\tfrac{3}{4}CH_{4(g)}+\tfrac{1}{4}CO_{2(g)}+\tfrac{1}{2}H_2O_{(l)}\rightarrow CH_3OH_{(l)}\\&\Delta H(T_O,P_O)=58.52\tfrac{kJ}{mol}\\&\Delta G(T_O,P_O)=88.73\tfrac{kJ}{mol}\end{aligned} \qquad 3.9$$

This process is represented by point X in Fig. 3-4 and is situated in region 1B on the *gh diagram* and has negative Carnot temperature of -577.5 K. The process requires 88.73 kJ of work ($\Delta G_{P(X)}$) and 58.52 kJ of heat ($\Delta H_{P(X)}$) to produce one mole of methanol. Since the process has a negative Carnot temperature, there is no real single temperature at which heat can be added to the process in order to satisfy the work requirement and the process cannot be feasible if it is run as a *simple process* where the only way of supplying work is by heat at a single temperature. As an example, if heat is supplied at a single temperature of 808.8 K, then the amount of work supplied would be given by point X’ (Fig. 3-4), and the process would be work deficient by an amount W_{ex} = 51.78 kJ/mol shown as the difference between point X and X’. The process would still be work deficient even if heat is supplied at infinite temperature, it would lie on the 45° line below point X. Therefore we see that the process would not proceed by supplying the heat requirement alone no matter the temperature at which heat is supplied. Other methods of supplying work must be used as well in order for the process to be feasible.

Suppose, instead of directly making methanol we start by making syngas ($CO + 2H_2$) as follows:

$$\begin{aligned} &\tfrac{3}{4}CH_{4(g)} + \tfrac{1}{4}CO_{2(g)} + \tfrac{1}{2}H_2O_{(l)} \rightarrow CO_{(g)} + 2H_{2(g)} \\ &\Delta H(T_O, P_O) = 186.9 \tfrac{kJ}{mol} \\ &\Delta G(T_O, P_O) = 118.0 \tfrac{kJ}{mol} \end{aligned} \tag{3.10}$$

This process is located at point Y in region 1A, it is an endothermic process and requires 186.9 kJ/mol of heat and 118.0 kJ/mol of work to be supplied. It has a positive Carnot temperature of 808.8 K, which implies that supplying heat at this temperature is sufficient to meet the process minimum work requirement. Therefore the process can be feasible and reversible when it is run in a single step as a *simple process* with heat supplied at 808.8 K.

Syngas can be converted to methanol according to the following equation:

$$\begin{aligned} &CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(l)} \\ &\Delta H(T_O, P_O) = -128.2 \tfrac{kJ}{mol} \\ &\Delta G(T_O, P_O) = -29.07 \tfrac{kJ}{mol} \end{aligned} \tag{3.11}$$

This process is located at point C in region 3A on the *gh-diagram*, it is an exothermic process and can reject 128.2 kJ/mol of heat and can also reject 29.07 kJ/mol of work. It has a positive Carnot temperature of 385.6 K, which implies that removing heat at this temperature is sufficient to recover maximum amount of work from the process, therefore the process can be feasible and reversible when it is run in a single step as a *simple process* with heat removed at 385.6 K.

We see that if process X is infeasible, where work cannot be supplied via heat at single temperature alone due to a negative Carnot temperature, we can make it feasible by splitting it into two different *simple processes* where work can be transferred via heat alone, this is equivalent to having two points of heat transfer at two different temperatures for process X. The first *simple process* would be at point Y where heat in excess, $Q_P + q_{ex} = \Delta H_{P(Y)}$, is added to the overall process at a higher temperature, T_H = 808.8 K, thereby transferring work in excess, $W_Y = W_X + W_Z = \Delta G_{P(Y)}$, to the overall process. The second simple process would be at point Z where the extra amount of heat, $q_{ex} = \Delta H_{P(Z)}$, added in the first stage is removed at a lower temperature, T_C = 385.6 K, thereby removing the extra amount of work, $W_Z = \Delta G_{P(Z)}$, that was transferred in the first stage. Therefore the net heat and work supplied to the process are $Q = \Delta H_{P(X)}$ and $W_X = \Delta G_{P(X)}$ respectively.

3.3.2 Implication on Current Technology

Since the currently available technology forces processes to run only in region 1A and 3A, we see that this technique allows us to move any process from any infeasible region to the feasible regions 1A and 3A and allows to run the process reversibly in these regions; however two or more separate processes would be required instead of one, thereby increasing the process complexity.

This method is similar to Solvay Clusters, where intermediate steps are used to bypass thermodynamic infeasibility of chemical reactions. The intermediate steps are a set of reactions that are stoichiometrically consistent with the overall reaction and must be feasible and have a favorable equilibrium at industrial conditions (May, Rudd 1976).

Solvay clusters can also be used in the *gh-diagram* where the intermediate steps are not considered as reactions but as processes. In order to use Solvay clusters as a way of supplying work to an infeasible process, several conditions must be met; 1) the intermediate steps must be stoichiometrically consistent with the overall mass balance. 2) Each intermediate step must be in one of the feasible regions ($1A$ or $3A$), in other words, they must be able to be run as *simple processes*, their Carnot temperatures must be within achievable range with available technology. 3) The individual ΔH and ΔG of the intermediate steps must add up to the overall ΔH and ΔG of the process.

The main challenge using this method is to identify the appropriate intermediate steps. Lopez and Manousiouthakis (2001) have developed a methodology to automatically generate intermediate steps for a reaction using the lexicographic approach. The methodology has proven to be useful for certain reactions such as the decomposition of water to hydrogen and oxygen (Choi 2004) and can be used as starting point for the search of intermediate steps for any chemical process.

Chemical looping (McGlashan 2008, Ishida, Zheng & Akehata 1987) is an example of a method of recovering work reversibly from a process by adding and removing an extra amount of heat at different temperatures. We can show on the *gh-diagram* that most combustion processes are located in region $3B$ with negative Carnot temperatures or close to the $45°$ line with extremely high Carnot temperatures; however in the industry combustion processes are inefficient since they are conducted as *simple processes* in region $3A$ at temperatures lower than their Carnot temperatures. In order for combustion processes to be efficient they must be run as complex processes. Chemical looping uses a metal to react the fuel with oxygen indirectly, thus allowing running combustion processes reversibly when they are moved from the infeasible region 3B to feasible regions 1A and 3A. We will use methane and Zinc as an example of chemical looping. Consider the combustion of methane according to Equation 3.12

$$\begin{aligned} &CH_{4(g)} + 2O_2 \rightarrow CO_2 + 2H_2O_{(g)} \\ &\Delta H_{P(X)} = -802.6 \tfrac{kJ}{mol} \\ &\Delta G_{P(X)} = -801.1 \tfrac{kJ}{mol} \end{aligned} \qquad 3.12$$

As shown in Fig. 3-5, the process is represented by point X and is located in region 3A almost at the 45° line with a Carnot temperature of 163894 K. This temperature is beyond reach for any available technology; therefore methane combustion cannot be run reversibly in a single step as a *simple process*. As we see in Fig. 3-5 when methane combustion is conducted at 1839.4 K with a single point of heat transfer, the amount of work ($W_{X'}$)that can be recovered is indicated by point X' in Fig. 3-5; the process will lose about 16% of work potential and therefore will be irreversible. Chemical looping for methane combustion allows having two points of heat transfer instead of one; this is equivalent to splitting the process into two processes that can be run reversibly as simple processes. The first process, at point Y, is located in region 1A and is an endothermic process where methane reacts with zinc oxide (Equation 3.13), representing the first point of heat transfer where an amount of heat q_{ex} (equivalent to $\Delta H_{P(Y)}$ = 1120.9 kJ/mol) is transferred to the overall process at a lower Carnot temperature T_C = 1077 K, the heat transferred also carries an amount of work W_Y (equivalent to $\Delta G_{P(Y)}$ = 810.6 kJ/mol) to the process (Fig. 3-5).

$$\begin{aligned} &CH_{4(g)} + 4ZnO_{(s)} \rightarrow CO_{2(g)} + 2H_2O_{(g)} + 4Zn_{(g)} \\ &\Delta H_{P(Y)} = 1120.9 \tfrac{kJ}{mol} \\ &\Delta G_{P(Y)} = 810.6 \tfrac{kJ}{mol} \end{aligned} \qquad 3.13$$

The second process, at point Z, is exothermic and is located in region 3A (Fig. 3-5) where oxygen reacts with its carrier, zinc (Equation 3.14) representing the second point of heat transfer where an amount of heat q_{ex} + Q (equivalent to $\Delta H_{P(Z)}$ = -1923.5 kJ/mol) is removed at a higher Carnot temperature T_H = 1839.4 K; the heat removed carries an amount of work $W_Z = W_X + W_Y$ (equivalent to $\Delta G_{P(Z)}$ = -1611.7 kJ/mol).

$$\begin{aligned} &4Zn_{(g)} + 2O_2 \rightarrow 4ZnO_{(s)} \\ &\Delta H_{P2} = -1923.5 \tfrac{kJ}{mol} \\ &\Delta G_{P2} = -1611.7 \tfrac{kJ}{mol} \end{aligned} \qquad 3.14$$

We see that it is possible to make combustion processes reversible by having more than one point of heat transfer across the process. The integrated gasification combine cycle is another example where work recovery from coal combustion is made more reversible by splitting the process into two simple processes: coal gasification to syngas where heat is added to the process at a lower temperature, followed by syngas combustion where heat is removed from the process at a higher temperature.

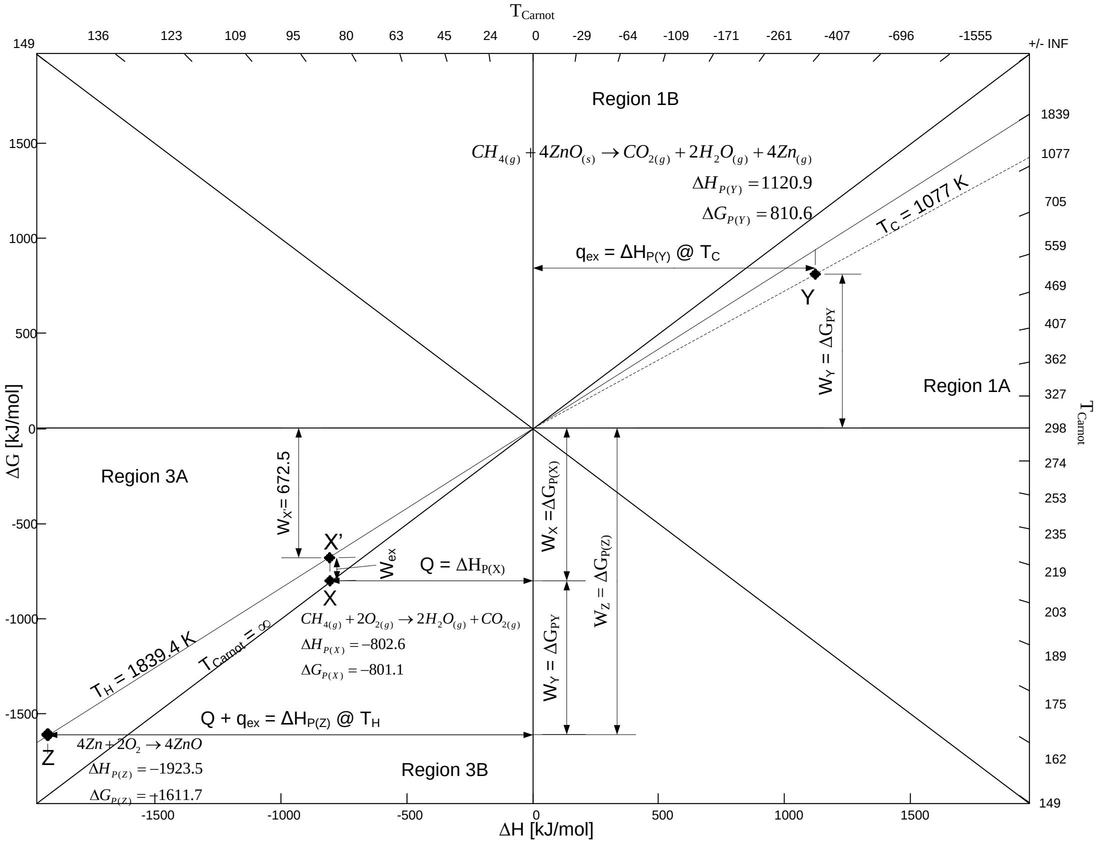

Fig. 3-5: Chemical looping on the gh-diagram: Methane combustion

3.4 Work Addition by Shaft Work

Another way of transferring extra amount of work to a process is by adding or removing mechanical work or shaft work directly to the process. This technique will also apply to those processes that cannot be reversible or feasible in their inherent regions on the *gh-diagram* as well as those processes running at another temperature than the Carnot temperature. In order to understand how mechanical work can be directly transferred across a process, consider a process as shown in Fig. 3-6 where the heat requirement Q_P is supplied at a certain temperature T_{Rev}; since for this process the work requirement cannot be satisfied by heat alone, let us suppose that a certain amount of mechanical work W_S is also added. However in order to keep the energy balance of the process unchanged, an amount of heat q_S equivalent to W_S must also be removed from the process; let us suppose that q_S is removed at ambient temperature T_O.

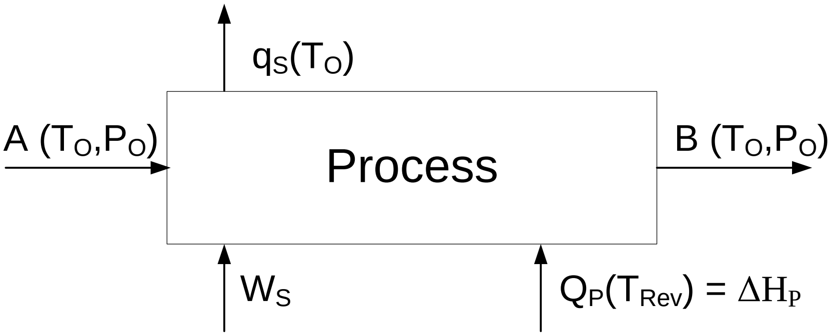

Fig. 3-6: Work addition by combination of heat and shaft work

The energy balance for the process is given by the following equation:

$$\Delta H_P(T_O, P_O) = Q_P \qquad 3.15$$

Where, ΔH_P is the enthalpy change across the process taken at ambient conditions T_O and P_O. If the process is reversible, then the entropy balance gives:

$$\Delta S_P(T_O, P_O) = \frac{\Delta H_P(T_O, P_O) - \Delta G_P(T_O, P_O)}{T_O} = \frac{Q_P}{T_{\mathrm{Rev}}} - \frac{q_S}{T_O} \qquad 3.16$$

Where, ΔS_P and ΔG_P are the entropy and Gibbs energy change across the process respectively, taken at ambient conditions T_O and P_O. Keeping in mind that $q_S = W_S$, combining Equation 3.15 and 3.16 results in the following equation:

$$\Delta G_P(T_O, P_O) = \Delta H_P(T_O, P_O)\left(1 - \frac{T_O}{T_{\mathrm{Rev}}}\right) + W_S \qquad 3.17$$

We see that Equation 3.17 has the form of Equation 3.4 and therefore it describes complex processes where the extra amount of work W_{ex} required to make the process feasible and reversible, is supplied by adding a certain amount of mechanical work W_S; however the process must have a second point of heat transfer q_S occurring at ambient temperature T_O. On the other hand if q_S is removed at any other temperature T_S rather than T_O, we can show that the process will be described by Equation 3.18; this implies that not all the amount of mechanical work added will take effect in satisfying the process work requirement; part of it will leave the process with heat and might become an irreversibility if there are no means of recovering it.

$$\Delta G_P(T_O,P_O)=\Delta H_P(T_O,P_O)\left(1-\frac{T_O}{T_{\mathrm{Rev}}}\right)+W_S\left(\frac{T_O}{T_S}\right) \qquad 3.18$$

In Equation 3.17 $\Delta G(T_O,P_O)$ and $\Delta H(T_O,P_O)$ for a particular process are fixed, therefore one can solve for the reversible temperature T_{Rev} for a given value of W_S or vice versa; the implications of Equation 3.17 can be well understood as shown on the *gh-diagram* in Fig. 3-7. Three cases can be identified which we will explore by considering a hypothetical process represented by point X in Fig. 3-7.

1. When W_S is zero, no mechanical work is being added to the process then T_{Rev} is the same as T_{Carnot} in Equation 3.2. In this case the reversible temperature for process X will be determined by a temperature scale as defined by point O. Therefore when W_S is zero then T_{Rev} for process X is 749 K. In this case the process is a *simple process*.
2. If W_S is a positive value, mechanical work is being added to the process, and then a different reversible temperature can be obtained. Let us suppose that 100 kJ/mol of mechanical work is added the process X. T_{Rev}, in this case, is determined by a temperature scale as defined by point **n** along the ΔG axis. Therefore T_{Rev} for X becomes 373 K; this means that the amount of work to be supplied via heat decreases, however the same amount of heat must be supplied. We also see that the process is moved from a high reversible

temperature point to a low reversible temperature point in the same region of the *gh-diagram*.

3. If W_S is a negative value, mechanical work is being removed from the process and again we obtain a different value for T_{Rev}. Let us suppose that 100 kJ/mol of mechanical work is removed from process X, then T_{Rev} is determined by a temperature scale as defined by point **m**; in this case T_{Rev} for process X is infinity; this means that the amount of work to be supplied via heat will increase in order to compensate for the mechanical work removed from the process. However in this case, since T_{Rev} is infinity, it is impossible to meet the process work requirement by supplying heat. This means that process X cannot be feasible if 100 kJ/mol of mechanical work is removed.

In light of the above three cases we see that the reversible temperature of a process is no longer fixed as suggested by Equation 3.2, one can freely choose the temperature at which heat is added and still remains reversible as long as some mechanical work is added or removed accordingly. Adding mechanical work is another way of moving a process from an infeasible to a feasible region by shifting the temperature scale on the *gh-diagram*. In reactive processes, this technique is useful when the temperature of heat to be transferred is dictated by the catalyst activity; if the temperature is not the same as the Carnot temperature, and in order for the process to be feasible and reversible, one would simply find the amount of mechanical work that must be added or removed so that the operating temperature becomes the reversible temperature. This is equivalent to moving the process from one point to another or from one region to another on the *gh-diagram* by shifting the temperature scale.

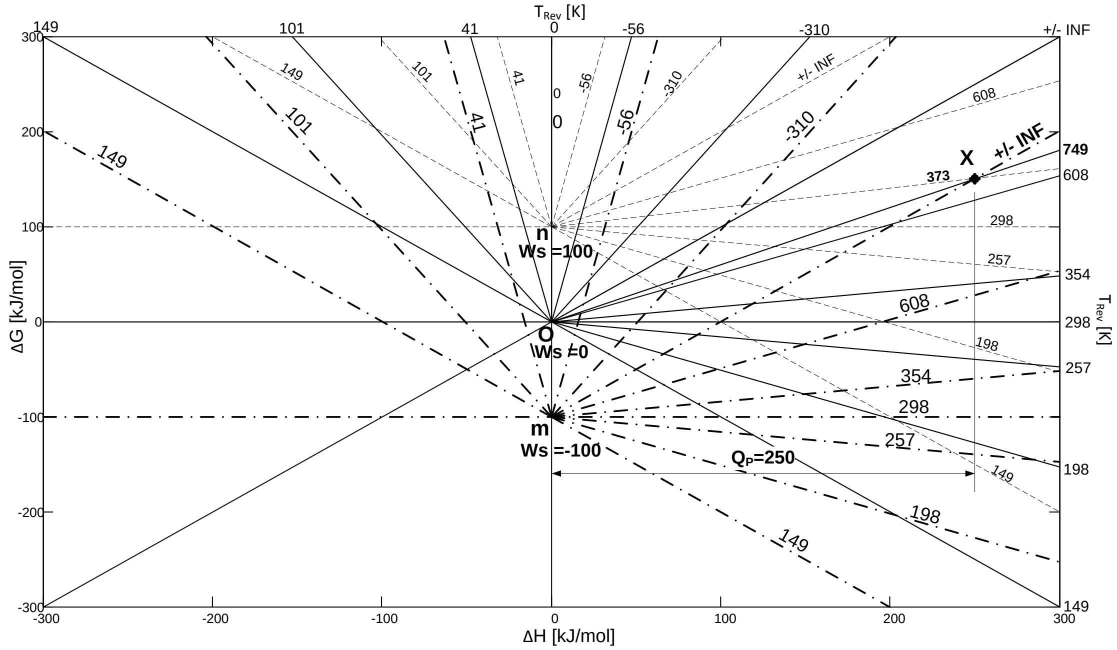

Fig. 3-7: Effect of mechanical work transfer on the reversible temperature of a process; the center point of the temperature scale moves along the ΔG axis leading to the process being moved from one point to another or from one region to another on the gh-diagram. The reversible temperature for reversible processes, where W_S is either added or removed, is indicated on the constant temperature lines.

Compression is generally the major way mechanical work is added to a process. However this may not be possible in all cases as we would need a change in the number of moles of gas between the input and the output of the process, in order to put work or remove work by compression. The proof of this statement is given in the following section:

3.4.1 Isothermal Compression

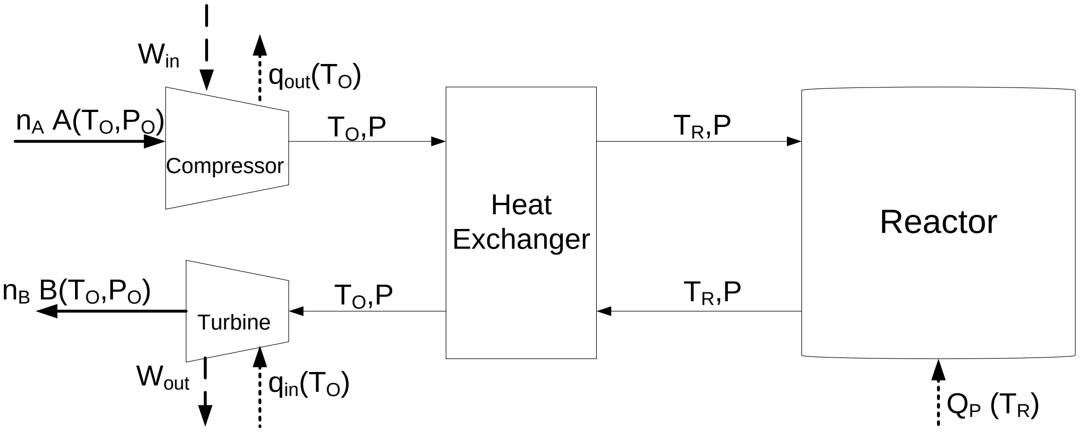

Fig. 3-8: Mechanical work transfer across a process via isothermal compression and expansion

Consider the process as shown in Fig. 3-8, where n_A moles of substance A is converted to n_B moles of substance B. We will start by assuming that the heat capacities at constant pressure (Cp) of substance A and substance B are such that $n_A Cp_A = n_B Cp_B$, thus heat can be exchanged between them without requiring extra heating or cooling given that the heat exchanger in Fig. 3-8 has sufficient area to get the streams to their required temperature. This assumption also implies that the enthalpy of reaction (ΔHrxn) is constant and equal to the enthalpy change across the process ($\Delta H_P(T_O,P_O)$). Let us suppose that a quantity of mechanical work W_{in} is transferred to the process by compressing A from ambient pressure P_O to the process pressure P at constant temperature T_O. Assuming ideal gas behavior the energy balance across the compressor is given by:

$$\begin{aligned}&\Delta H_{Compressor} = n_A Cp_A (T_O - T_O) = W_{in} - q_{out}\\ &\text{therefore}\\ &W_{in} = q_{out}\end{aligned} \qquad 3.19$$

The entropy balance across the compressor gives:

$$\begin{aligned}&\Delta S_{Compressor} = -n_A R T_O \ln\frac{P}{P_O} = -\frac{q_{out}}{T_O}\\&\text{since } q_{out} = W_{in}\\&W_{in} = n_A R T_O \ln\frac{P}{P_O}\end{aligned} \tag{3.20}$$

Similarly another quantity of mechanical work is transferred from the process by expanding the product B from P to $\mathrm{P_O}$ at constant temperature $\mathrm{T_O}$; the energy and entropy balance across the turbine will show that:

$$\begin{aligned}&W_{out} = q_{in}\\&\text{and}\\&W_{out} = -n_B R T_O \ln\frac{P}{P_O}\end{aligned} \tag{3.21}$$

The energy and entropy balance across the entire process in Fig. 3-8 shows that:

$$\begin{aligned}&\Delta H_P(T_O,P_O) = Q_P\\&\Delta S_P(T_O,P_O) = \frac{\Delta H_P(T_O,P_O) - \Delta G_P(T_O,P_O)}{T_O} = \frac{Q_P}{T_{\mathrm{Rev}}} + \frac{q_{in}+q_{out}}{T_O}\end{aligned} \tag{3.22}$$

Thus combining Equations 3.19 through to 3.22 gives:

$$\Delta G_P(T_O,P_O) = \Delta H_P(T_O,P_O)\left(1 - \frac{T_O}{T_{\mathrm{Rev}}}\right) + (n_A - n_B) R T_O \ln\frac{P}{P_O} \tag{3.23}$$

Therefore we see that a net amount of mechanical work equivalent to $\mathrm{W_S}$ in Equation 3.17 is transferred across the process by subjecting the process to a certain pressure P. Thus the net amount of work transferred is:

$$W_S = (n_A - n_B) R T_O \ln\frac{P}{P_O} \tag{3.24}$$

If $P > P_O$ we see that when there is a decrease in the number of moles of gas between the input and the output of the process, that is $n_A > n_B$, then work is being added, and when there is an increase in the number of moles, that is $n_A < n_B$, work is being removed from the process and when $n_A = n_B$, no mechanical work is being transferred irrespective of the pressure at which the process is subjected to. We also see that Equation 3.23 gives us one degree of freedom between pressure P and the temperature T_{Rev}, allowing us to match any temperature to a pressure in order for the process to be feasible and reversible.

3.4.2 Adiabatic Compression

Fig. 3-9 shows work flows across a process when work is transferred via adiabatic compression; where a stream containing n_A moles of A is compressed from ambient pressure P_O to the process pressure P accompanied by a raise in temperature from T_O to T. The stream is then brought to the reactor temperature, T_{Rev}, by exchanging heat with the product stream from the reactor containing n_B moles of B which, after heat exchange, is brought to temperature T, with the assumption that $n_A Cp_A = n_B Cp_B$ and that the exchanger is given sufficient area. The product stream is expanded from the process pressure P to ambient pressure P_O, followed by a decrease in temperature from T to T_B, and then the product stream is brought to ambient temperature T_O by passing through a device, labeled E, which could be regarded as a heat engine; the device produces a certain amount of work W_E and rejects a certain amount of heat q_E at ambient temperature as it cools the product stream from T_B to T_O.

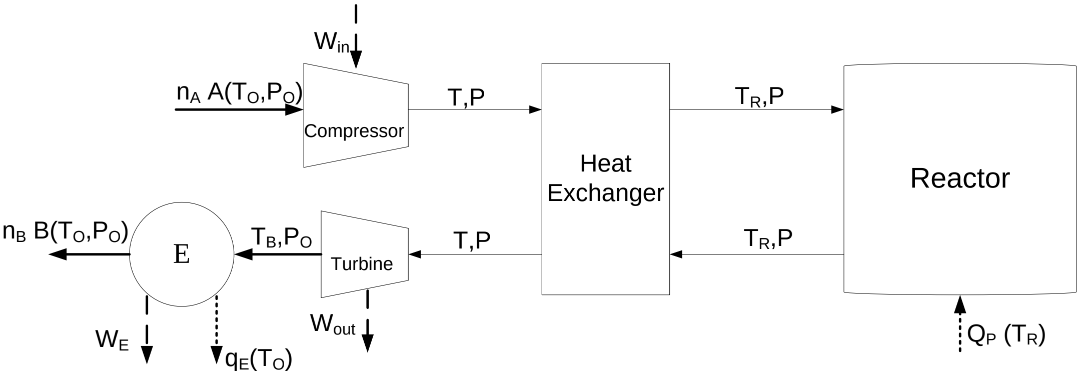

Fig. 3-9: Mechanical work transfer across a process via adiabatic compression with two points of heat transfer across the process

The energy and entropy balance around the process in Fig. 3-9 can show that the process is also described by Equation 3.23; we could also show that:

$$\begin{aligned} &W_E + q_E(T_O) = W_{in} + W_{out} \\ &thus \\ &q_E(T_O) = (W_{in} + W_{out}) - W_E \end{aligned} \qquad 3.25$$

Thus the process is effectively equivalent to the process in Fig. 3-8 where compression is done isothermally. Therefore we see that the net mechanical work transferred across the process will take effect in satisfying the process work requirement as long as heat at ambient temperature is removed at some point of the process. If the device, E, does not produce work, it will act as a heat exchanger where heat will be rejected at some average temperature between T_B and T_O, and therefore the process will lose an amount of work, W_E, and will become irreversible if this work potential is not recovered or integrated. The amount of work, W_E, can be quantified by combining the energy and entropy balance around the device. This will give for a reversible process assuming constant heat capacities:

$$W_E = n_B Cp_B (T_B - T_O) - n_B Cp_B T_O \ln \frac{T_B}{T_O} \qquad 3.26$$

Existing compressors and turbines do not have the ability of operating isothermally; thus compression is conducted adiabatically, in multiple steps with inter-stage cooling; if the cooling between steps is done by heat engine devices such as E in Fig. 3-9, we can show that this will be equivalent to isothermal compression; however since such devices are currently not available, cooling is done by rejecting heat to the environment. Therefore work that would have been produced by the heat engine device E is lost in the heat which is removed at some average temperature between the outlet temperature of the previous stage and inlet temperature of following compression stage.

One of the possible ways of avoiding work losses in a process with adiabatic compression is doing the inter-stage cooling in such a way that heat is removed at the same temperature as the reactor. In that way heat can be reintegrated to the reactor so that the overall heat requirement of the process is reduced; the equivalent of such a process is shown in Fig. 3-10. Therefore the process will be described by Equation 3.27, where W_S is the net work transferred and is given by Equation 3.28 where R is the ideal gas constant.

$$\Delta G_P(T_O,P_O)=\Delta H_P(T_O,P_O)\left(1-\frac{T_O}{T_{\mathrm{Rev}}}\right)+W_S\left(\frac{T_O}{T_{\mathrm{Rev}}}\right) \tag{3.27}$$

$$W_S=W_{in}+W_{out}=n_A Cp_A T_O\left[\left(\frac{P}{P_O}\right)^{R/Cp_A}-1\right]+n_B Cp_B T_O\left[1-\left(\frac{P}{P_O}\right)^{R/Cp_B}\right] \tag{3.28}$$

For the special case where $n_A Cp_A = n_B Cp_B = nCp$, W_S will be given by:

$$W_S=W_{in}+W_{out}=nCpT_O\left[\left(\frac{P}{P_O}\right)^{R/Cp_A}-\left(\frac{P}{P_O}\right)^{R/Cp_B}\right] \tag{3.29}$$

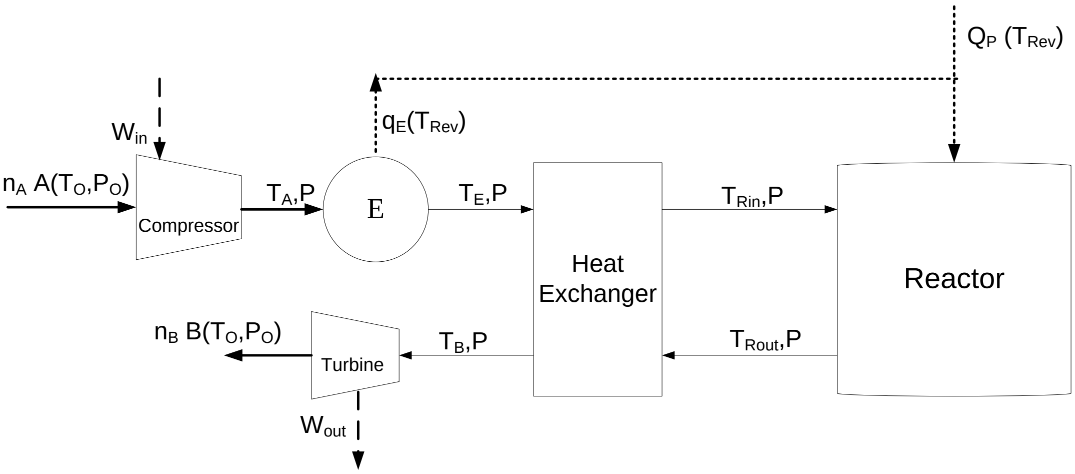

Fig. 3-10: Mechanical work transfer via adiabatic compression with a single point of heat transfer across the process (MWSH)

We see that in this case mechanical work is added and the process has a single point of heat transfer occurring at a single temperature. Thus the heat requirement is different from those of the processes in Fig. 3-8 and Fig. 3-9 and is given by:

$$Q_P = \Delta H_P(T_O, P_O) - W_S \qquad 3.30$$

From Equation 3.27 we see that this technique also gives us means of moving processes from one point to another or from one region to another on the *gh-diagram* by moving the temperature scale as shown in Fig. 3-11; this time the centre point of the temperature scale is determined by the coordinate (W_S, W_S) on the *gh-diagram*.

Note that the net mechanical work transferred across the processes in Fig. 3-8 and Fig. 3-9 is accompanied by an equivalent amount of heat transferred at ambient temperature in the opposite direction (see Equations 3.19, 3.21 and 3.25) and the energy balance shows that the heat requirement for these processes is not affected by the net amount of mechanical work transferred across the process. Consequently the centre point for the reversible temperature scale on the *gh-diagram* (Fig. 3-7) moves along ΔG axis only (Indicating that the work requirement for the process varies with W_S) and does not move along the ΔH axis (Indicating that the heat requirement for the process does not vary with W_S). Therefore the coordinates for the temperature scale centre point are (0, W_S).

On the other hand, the net mechanical work transferred across the process in Fig. 3-10 is not accompanied by an equivalent amount of heat transferred in the opposite direction, thus the energy balance shows that the heat requirement of the process is affected by the net mechanical work transferred (see Equation 3.30). Consequently, in this case, the centre point for the reversible temperature scale on the *gh-diagram* (Fig. 3-11) moves along both the ΔH and ΔG axis (that is along the 45^o line), indicating that both the heat and the work requirement for the process vary with W_S. Therefore, for this case, the coordinates for the temperature scale centre point are (W_S, W_S).

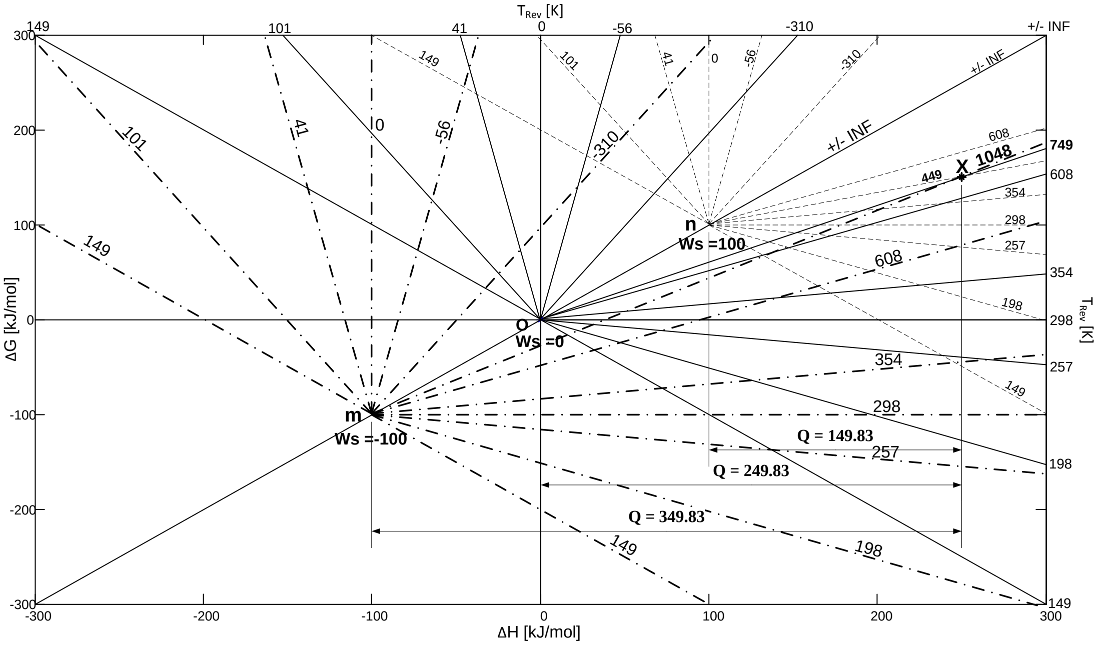

Fig. 3-11: Variation of the reversible temperature of a process as a result of having mechanical work transfer and heat transfer at a single temperature; the centre point of the temperature scale moves along the 45^o line on the gh-diagram

In Fig. 3-11 we see that for the same hypothetical process X and the same amount of work transferred as in Fig. 3-7, we have different reversible temperatures and heat requirements for the process. Therefore we have two cases involving mechanical work transfer across a process; these are: 1) mechanical work transfer with multiple heat transfers at different temperatures (MWMH); this case concerns processes such those in Fig. 3-8 and Fig. 3-9 where mechanical work is added with two points of heat transfer occurring at two different temperatures of which one is at ambient temperature. 2) Mechanical work transfer with a single heat transfer at a single temperature (MWSH) across the process, this case concerns processes such as that in Fig. 3-10. A comparison between MWMH and MWSH in terms of heat requirement and the reversible temperature is summarised in Table 3-1.

Table 3-1: Comparison between mechanical work transfer with multiple heat transfer (MWMH) and mechanical work transfer with a single heat transfer (MWSH) across a reversible process

$\Delta G(T_o,P_o)(W_{Requirement})$	150.35 kJ/mol				
$\Delta H(T_o,P_o)$	249.83 kJ/mol				
W_S [kJ/mol]	**$W_{Thermal}$ [kJ/mol]**	**Q_P [kJ/mol]**		**T_{Rev} [K]**	
		MWSH	**MWMH**	**MWSH**	**MWMH**
0	150.35	249.83	249.83	749	749
100	50.35	149.83	249.83	449	373
-100	250.35	349.83	249.83	1048	Infinity

Table 3-1 shows the heat requirements (Q_P) and the reversible temperatures (T_{Rev}) of the hypothetical process X in Fig. 3-7 and Fig. 3-11, as mechanical work is added and removed from the process. The minimum amount of work that process X requires is given by the Gibbs energy change ($\Delta G\ (T_o,P_o)$) across the process taken at ambient temperature and pressure. Let us consider the following three cases for process X referring to Table 3-1, Fig. 3-7 and Fig. 3-11; 1) If no mechanical work is transferred, then the entire work requirement (150.35 kJ/mol) for the process must be satisfied via heat (249.83 kJ/mol) at 749 K for both MWSH and MWMH; this is the case where the number of moles of gas does not change between the input and output of the process ($n_A = n_B$), resulting in no work being added irrespective of the pressure at which the process is subjected to. The work supplied via heat is referred to as $W_{Thermal}$ in Table 3-1. Therefore process X must be run as a *simple process*, and will be described by Equation 3.2. 2) If out of 150.35 kJ/mol of work requirement, 100 kJ/mol of work is supplied via mechanical work then the additional 50.25 kJ/mol of work must be supplied via heat; for MWSH a smaller amount of heat (149.83 kJ/mol) at a higher temperature (449 K) will be required while for MWMH a larger amount of heat (249.83 kJ/mol) at a lower temperature (373 K) will be required; this is the case where the number of moles of gas entering the process exceed that of gas leaving the process ($n_A > n_B$). 3) If 100 kJ/mol of work is removed via mechanical work, the process will be work deficient and then 250.35 kJ/mol of work will need to be supplied via heat for the process to be feasible; in this case, for MWSH, a larger amount of heat (349.83 kJ/mol) at a lower temperature (1048 K) will be required while for MWMH a smaller amount of heat (249.83 kJ/mol) at a higher temperature (infinity) will be required; this is the case where the number of moles of gas entering the process is less than that of gas leaving the process ($n_A < n_B$). In this particular case we see that with MWMH it is impossible to satisfy the work since it requires supplying heat at an infinitely high temperature.

This approach is one of the ways of manipulating a process using pressure in order to meet the availability of utilities in terms of heat and temperature; it is also useful in the case where the process operating temperature is dictated by the catalyst. One would opt to use MWSH or MWMH to supply a certain amount of work to the process to match the amount and temperature of heat required that will make the process reversible. However this can only be useful when there is a change in the number of moles between the input and the output of the process. A similar approach has been used in the Expand method developed by Aspelund et al. (2007), which includes the effect of pressure (via exergy analysis) in the pinch analysis for optimal heat exchanger network development.

3.5 Case Study: Ammonia Processes

In this section we are going to look at the work and heat requirement for an ammonia process in a general manner. The aim in this discussion is to identify different ways the minimum amount of work and heat for an ammonia process can be achieved, and further explore the implications of operating conditions such as temperature and pressure on the process in a more fundamental way. Thus we will start by ignoring all the inefficiencies associated with the equipment and we will assume that the feed to the process does not contain impurities. We will further assume that the reactor system is such that it includes reaction, separation and recycle and that the work of mixing is reintegrated back to the work of separation; this is equivalent to assuming that the conversion across the reactor system is 100% and that the system is fully heat and work integrated internally such that the only energy required is for the transformation of the reactants into products; of course the energy associated with the recycle and separation in existing ammonia processes could be large and deserves particular attention, however this is beyond the scope of the present manuscript. These assumptions have been taken in order to simplify the analysis and understand the applicability of the approach being presented in this manuscript.

$$\begin{aligned} &\tfrac{1}{2}N_{2(g)} + \tfrac{3}{2}H_{2(g)} \rightarrow NH_{3(g)} \\ &\Delta H(T_O, P_O) = -45.90\,\tfrac{kJ}{mol} \\ &\Delta G(T_O, P_O) = -16.40\,\tfrac{kJ}{mol} \end{aligned} \qquad 3.31$$

Equation 3.31 represents an ammonia process where the reactants, nitrogen and hydrogen, and the product, ammonia, are at ambient temperature T_O and pressure P_O as gases. The process is exothermic and has a negative Gibbs energy; the process is located in region 3A on the *gh-diagram*, thus in principle the process is capable of producing a maximum amount of work equivalent to -16.40 kJ/mol, this work can be recovered (using a reversible heat engine system) by removing -45.90 kJ/mol of heat at the process Carnot temperature 190.8^{0}C (464 K) as represented at point R in Fig. 3-12.

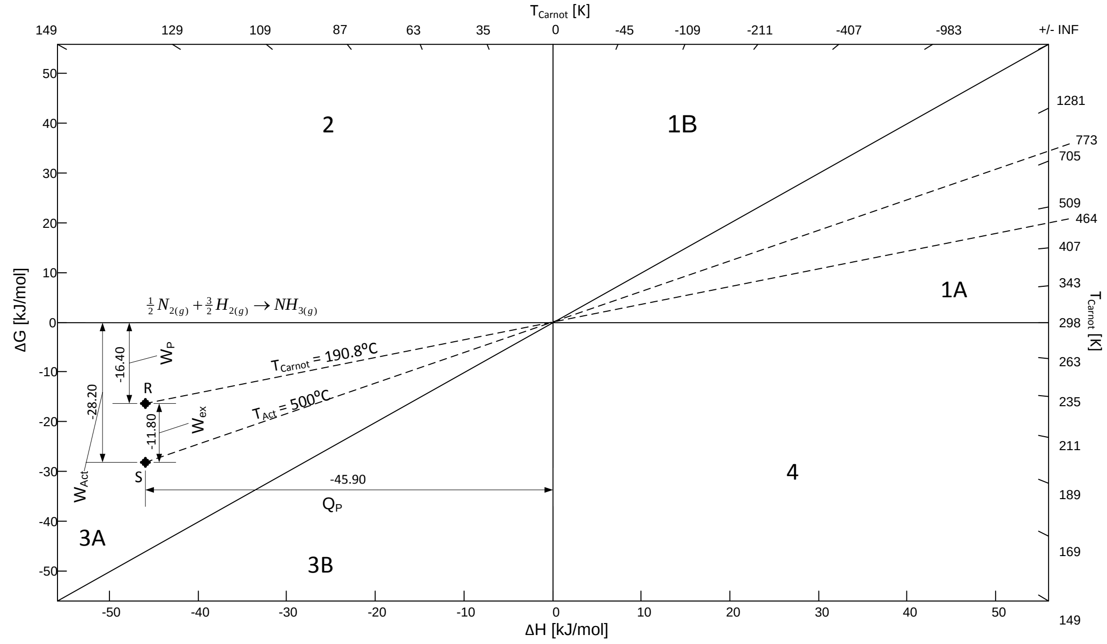

Fig. 3-12: Work deficiency in an ammonia process running at a higher temperature than the Carnot temperature. At point 'R' heat is removed from the ammonia process at the Carnot temperature (190.8^{o}C), maximum amount of work is recovered and the process is a simple process and reversible. At Point 'S' heat is removed at a higher temperature than the Carnot temperature (500^{o}C), more work than the maximum available is removed and the process becomes work deficient.

Industrial ammonia processes are conducted on an iron catalyst active at temperatures ranging from 350 ^{0}C to 550 ^{0}C (Efma 2000). Let us suppose that the process is operated at a temperature T_{Act}= 500 ^{0}C (773 K), temperature at which the heat of the process Q_P (-45.90 kJ/mol) is removed; this is equivalent to point S on the *gh-diagram* in Fig. 3-12, where the amount of work W_{Act} = -28.20 kJ/mol is removed from the process via heat. We see that at the actual temperature T_{Act} the amount of work W_{Act} removed is greater than the maximum amount of work W_P (-16.40 kJ/mol) that the process can deliver. Therefore the process will be work deficient by -11.80 kJ/mol if it is run as a simple process where work is transferred via heat only. In principle the process would not be feasible unless an extra amount of work W_{ex} equivalent to the process work deficiency is added according to Equation 3.4 therefore the process would be complex. We can see from Equation 3.31 that there is a decrease of 1 mole of gas, between the reactants and product for ammonia synthesis; hence there is an opportunity to supply the extra amount work W_{ex} via mechanical work which can be supplied either by MWMH or MWSH. We will now explore three cases involving the method and equipment used to supply the extra amount of work and how these influence the pressure requirement of the ammonia process. We will then explore how inefficiencies in the major equipment (the compressors, expanders and heat engine system) affect the reversibility of the process.

3.5.1 Work transfer across an ammonia process by (MWMH).

Fig. 3-13 shows that in order to supply work by MWMH, the center point for the temperature scale must be shifted along the ΔG axis from point **o** to point **n**, such that the actual operating temperature T_{Act}, which is infeasible in the previous temperature scale (inner scale labelled T_{Carnot}), becomes a reversible temperature T_{Rev} in the new temperature scale (outer scale labelled T_{Rev}). This indicates that the total amount of mechanical work W_S that must be supplied is 11.80 kJ/mol. This is the net amount of work required by the compressor - expander system of the process. The heat removed from the ammonia process at T_{Rev} carries with it a total amount of work W_{Rev}, which could be fully recovered in a reversible heat engine system and could be reintegrated to the process to supply for the work of the compressor-expander system. If that is the case then the process would be 100% reversible and would produce a net amount of work W_P equivalent to -16.40 kJ/mol.

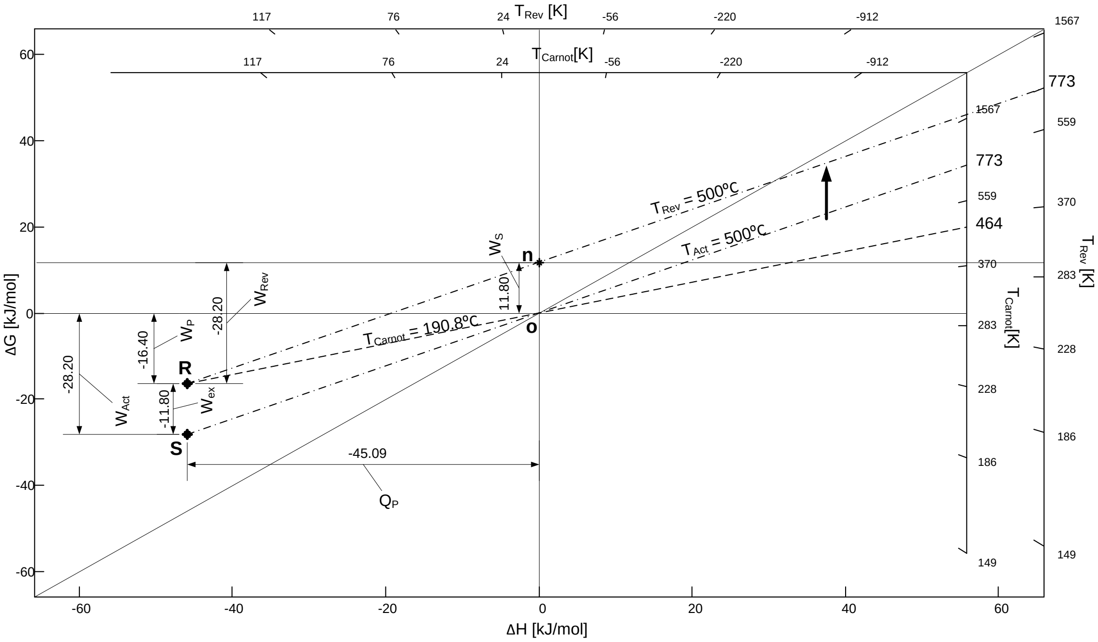

Fig. 3-13: Ammonia process: adding work by mechanical work transfer with multiple heat transfers (MWMH); the temperature scale is shifted such the actual operating temperature becomes the reversible temperature. The temperature of point 'S' in the inner scale (T_{Carnot}) becomes the temperature of point 'R' in the outer scale (T_{Rev}). The process becomes a complex process and could be reversible.

3.5.1.1 *MWMH with Isothermal Compression*

When the compressor-expander system is operated at constant ambient temperature, as shown in Fig. 3-8, heat is removed and absorbed at ambient temperature. Thus heat generated due to inefficiencies in the compressor-expander system will be transferred across the system at ambient temperature. Therefore these inefficiencies will have no effect on the reversibility of the process since heat transferred at ambient temperature does not carry any work value with it.

The reversibility of the process is expressed as the ratio of the net work produced from the process over the work potential of the process given by the change in Gibbs free energy at ambient conditions across the process. Therefore the percentage reversibility is given by:

$$\%\text{Reversibility} = \frac{\text{net-work}}{\Delta G(T_O, P_O)} \times 100 \qquad 3.32$$

Note that for a process that requires work supplied, the inverse will apply; the reversibility will be expressed as the ratio of the minimum work requirement ($\Delta G(T_O,P_O)$) over the net work consumed.

We therefore see that for this case, the major irreversibility in the process is driven by the ability of recovering work from the heat produced by the process (W_{Rev} in Fig. 3-13), in other words, the reversibility of the process will mostly depend on the efficiency of the heat engine system and not on the efficiency of the compressor – expander system. The work produced by the heat engine system, W_{HE} is given by:

$$\begin{aligned} &W_{HE} = \eta_{Work} Q_P \left(1 - \frac{T_O}{T_{\mathrm{Rev}}}\right) \\ &or \\ &W_{HE} = \eta_{Work} W_{\mathrm{Rev}} \end{aligned} \qquad 3.33$$

Where η_{Work} is the work efficiency of the heat engine system. When η_{Work} is less than 1, then it is not possible to fully recover the amount of work W_{Rev} from the heat produced by the process and then the process may not be able to satisfy its work requirement and might need an external source of work depending on the work requirement of the compressor-expander system. In this particular case, where the process is operated at 500°C, in order for the process to be self-sustaining with zero net work consumed and zero net work produced the value for η_{Work} must be at least 0.42, which means that the heat engine system must be able to recover at least 42%

of the total work available from the process heat. Thus out of -28.20 kJ/mol of work available -11.80 kJ/mol of work is recovered, which when reintegrated in the process would be enough to cover the work required for the compressor-expander system. Therefore for this case the process would be 0% reversible. Several authors, including Aljundi (2009) and Amari et al. (2009), have shown that heat engine systems that operate with steam cycles could go up to 70% work efficient (η_{Work} = 0.7), some authors have reported even 82.9% work efficient (Ray, Ganguly & Gupta 2007) .

3.5.1.2 *MWMH with Adiabatic Compression*

We have shown that mechanical work transfer across a process via MWMH with adiabatic compression and expansion, as illustrated in Fig. 3-9, is equivalent to MWMH with isothermal compression as long as a quantity of heat q_E, equivalent to the total amount of mechanical work transferred across the process (Equation 3.25), is removed at some point of the process at ambient temperature. However this is only valid when the heat capacities at constant pressure of the feed and product are equal; that is when $n_ACp_A = n_BCp_B$. For the ammonia process the heat capacity of the feed (nitrogen and hydrogen) is not equal to the heat capacity of the product (ammonia) that is $n_ACp_A \neq n_BCp_B$. Thus for this case we could show that:

$$\Delta G(T_O,P_O) = \Delta H(T_O,P_O)\left(1-\frac{T_O}{T_R}\right)+W_S\left(\frac{T_O}{T_R}\right)-\left(W_E+q_E(T_O)\right)\left(\frac{T_O}{T_R}\right)+q_E(T_O) \quad 3.34$$

Where W_E and q_E are the heat and work removed from the process via the device E as shown in Fig. 3-9, and W_S is the work required by the compressor – expander system and is given by:

$$W_S = W_{in}+W_{out} = n_ACp_AT_O\left[\left(\frac{P}{P_O}\right)^{R/Cp_A}-1\right]+n_BCp_BT_O\left(\frac{P}{P_O}\right)^{R/Cp_A}\left[\left(\frac{P}{P_O}\right)^{-R/Cp_B}-1\right] 3.35$$

We could also show that:

$$W_E + q_E(T_O) = W_S + \left(n_B Cp_B - n_A Cp_A\right)\left(T - T_O\right) \qquad 3.36$$

Where T is the temperature after the compressor, and is the same temperature as the one before the turbine, as shown in Fig. 3-9; this can be achieved if the heat exchanger is given sufficient area and if $n_A Cp_A \geq n_B Cp_B$.

The total work requirement for the process is given by:

$$W_{Stotal} = W_S - W_E \qquad 3.37$$

Since compression and expansion are conducted adiabatically, inefficiencies in the equipment, which include isentropic and mechanical inefficiency, will lead to some of the work supplied being turned into heat and therefore the work requirement for the compressor – expander system will increase in order to achieve the required pressure. For this discussion we will only consider the isentropic efficiency and we will assume that the mechanical efficiency is 1. Thus, taking into consideration the isentropic efficiencies, we can show that the work required by the compressor-expander system W_S is given by:

$$W_S = \frac{1}{\eta_{IC}} W_{in} + \eta_{IT} W_{out} \qquad 3.38$$

Where η_{IC} and η_{IT} are the isentropic efficiencies of the compressor and the turbine respectively. For most compressors η_{IC} varies between 0.7 and 0.8 and for turbines η_{IT} varies between 0.7 and 0.9 (Smith, van Ness & Abbott 2001).

We see that when work is supplied to the ammonia process via MWMH with adiabatic compression, the reversibility of the process will be influenced by the efficiencies of both the compressor – expander system and the heat engine system. Thus for this case, we can show that in order for the ammonia process, operating at 500^oC, to be self-sustaining with no work consumed and no work produced η_{Work} for the heat engine system must have a value of at least 0.61 assuming that both η_{IC} and η_{IT} for the compressor – expander system are equal to 1. If we consider the values for η_{IC} and η_{IT} to be 0.8 and 0.9 respectively, then η_{Work} for the heat engine system must have a value of at least 0.84 in order for the process to be self-sustaining. This means that the heat engine system must be able to recover at least 84% of the total amount of work available in the process heat. We therefore see that the process could be a net work consumer since most heat engine systems are able to recover only about 70% of the total work available in heat.

3.5.2 Work transfer across an ammonia process by MWSH

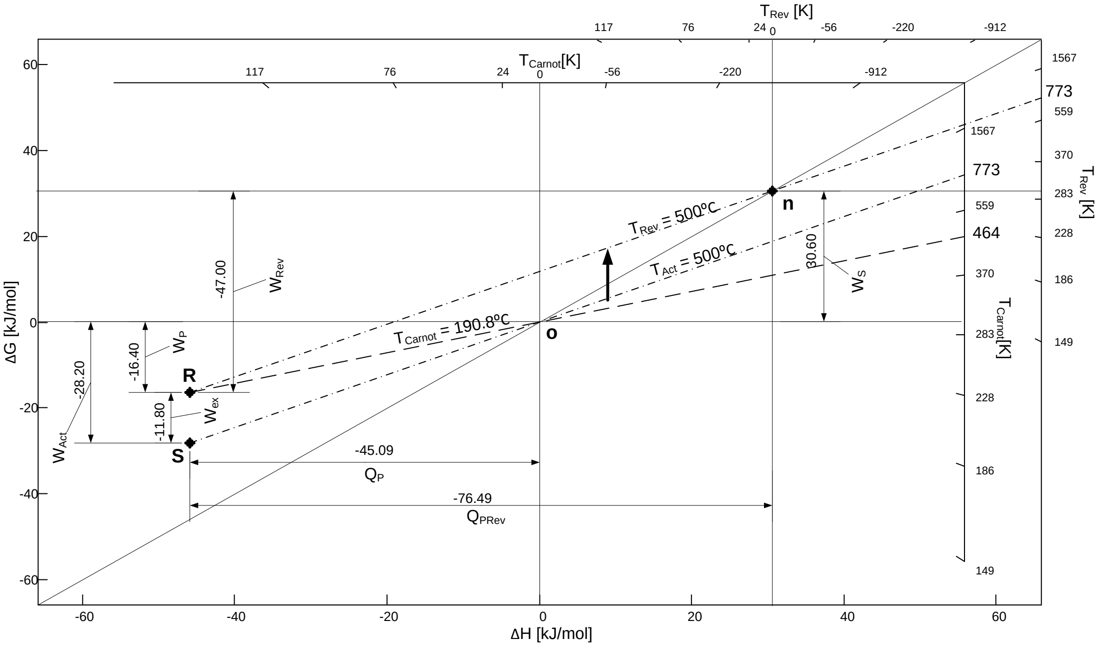

Fig. 3-14: Ammonia process: adding work by mechanical work transfer with single heat transfer (MWSH). The temperature scale is shifted along the 45° line by move the center point from 'O' to 'n'. The effective extra amount of work added to the process is the same as with MWMH, but here more mechanical work for compression is required.

In the similar way as in the previous case, Fig. 3-14 shows that in order to supply work to the ammonia process by MWSH, the center point of the temperature scale must be shifted along the 45^o line from point **o** to point **n**, such that the actual operating temperature T_{Act}, which is infeasible in the previous temperature scale (inner scale labelled T_{Carnot}), becomes a reversible temperature T_{Rev} in the new temperature scale (outer scale labelled T_{Rev}). This indicates that the total amount of mechanical work W_S that must be supplied is 30.60 kJ/mol. This is the net amount of work required by the compressor - expander system of the process. For this case the amount of heat to be removed is Q_{PRev} (-76.49 kJ/mol) instead of Q_P (-45.90 kJ/mol); and the total amount of work removed with heat is W_{PRev} (-47.00 kJ/mol).

Since this case also involves adiabatic compression, then the reversibility of the process will also be influenced by the isentropic efficiency of the compressor–expander system (η_{IC} and η_{IT}) and the work efficiency of the heat engine system (η_{Work}). If these efficiencies are all equal to 1 then the total amount of work removed with heat (W_{PRev} = -47.00 kJ/mol) could be fully recovered and reintegrated to the process to supply for the work of the compressor-expander system, and then the process would be 100% reversible and would produce a net amount of work W_P equivalent to -16.40 kJ/mol. Otherwise η_{Work} for the heat engine system must have a value of at least 0.65 assuming that both η_{IC} and η_{IT} for the compressor – expander system are equal to 1. If we consider the values for η_{IC} and η_{IT} to be 0.8 and 0.9 respectively, then η_{Work} for the heat engine system must have a value of at least 0.82 in order for the process to be self-sustaining. This means that the heat engine system must be able to recover at least 82% of the total amount of work available in the process heat. Therefore for this case we also see that the process could be a net work consumer since most heat engine systems are able to recover only about 70% of the total work available in heat.

The above three cases show that the reversibility for an ammonia process depends mainly on the following four elements: 1) the operating temperature which is dictated by the catalyst used, 2) the method used to supply mechanical work to the process, 3) the efficiency of the heat engine system used to recover work from the heat of the process and 4) the efficiency of the compressors and turbines through which mechanical work is supplied via pressure.

If an active catalyst for ammonia synthesis exists at the Carnot temperature (190.8 ^{0}C) no mechanical work will be needed, at least in principle, and the process would run at atmospheric pressure. At this point the process would be at its highest reversibility which will be limited mostly by the efficiency of the heat engine system used to recover work from the heat of the process.

Above 190.8 ^{0}C the ammonia process becomes work deficient and requires additional work to be supplied for it to be feasible. When this work is supplied as mechanical work via pressure and if the compression-expansion system and the heat engine system are reversible, then the ammonia process would be 100% reversible for all the three methods of transferring work discussed earlier. If the compression-expansion system and the heat engine system are not reversible, then the following cases can be considered.

1) If the heat engine system is not reversible, we can see, from Fig. 3-15 where the value for η_{Work} is 0.7 and the value for both η_{IC} and η_{IT} is 1 that the reversibility of the process decreases with increasing operating temperature for all three methods of transferring work. We can also see that MWMH with isothermal compression offers less irreversibility compared to MWMH with adiabatic compression and MWSH. We also see that when work is transferred by MWMH with adiabatic compression and by MWSH the process becomes a net work consumer, indicated by negative percent reversibility in Fig. 3-15, above certain temperatures while with MWMH with isothermal compression the process remains a net work producer over the range of temperatures considered; we can also see that the percent reversibility seems to remain unchanged at high temperatures. Furthermore

we see that the process becomes a net work consumer at lower temperature (about 570 ^oC) when work is transferred by MWSH, compared to when it is transferred by MWMH with adiabatic compression (about 650 ^oC).

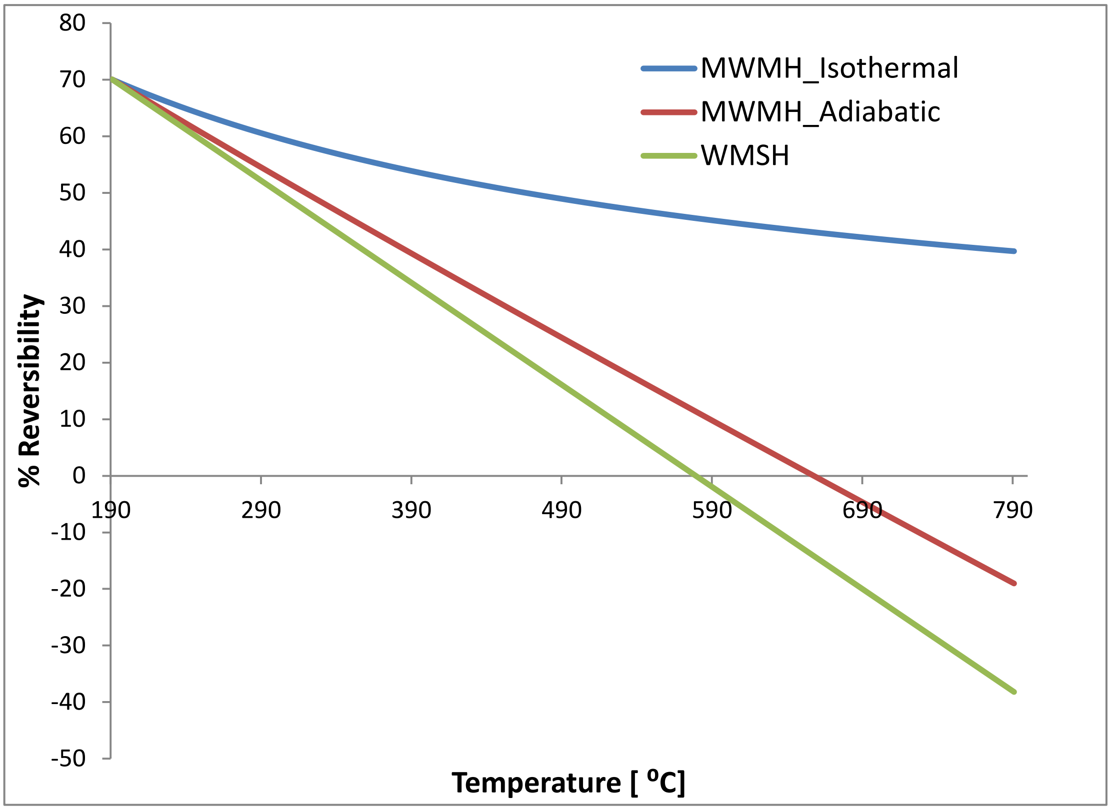

Fig. 3-15: Comparison of the effect of operating temperature on the reversibility of an ammonia process between mechanical work transfer with a single heat transfer (MWSH) and mechanical work transfer with multiple heat transfer (MWMH), assuming that the heat engine system to recover work from the process heat is 70% work efficient.

2) The effect of the isentropic efficiencies of the compressor-expander system for both MWMH with adiabatic compression and MWSH is shown in Fig. 3-16. This is the case where η_{Work} for the heat engine system is 1 and η_{IC} and η_{IT} for compressor-expander system are set to 0.8 and 0.9 respectively (HE 1, C 0.8, T 0.9). We can see that at these efficiencies the reversibility of the ammonia process decreases with increasing operating temperature and

remains positive, meaning that the process is a net work producer, even at high temperatures; and we can also see that isentropic efficiencies have a greater effect on MWMH with adiabatic compression compared to MWSH. Furthermore it is clear that the efficiency of the heat engine system has a greater effect on the reversibility of the process compared to the efficiencies of the compressor-expander system for both MWMH with adiabatic compression and MWSH. This can be seen in Fig. 3-16 where the effect of the heat engine system efficiency is shown when η_{Work} is 0.7 and η_{IC} and η_{IT} are 1 (HE 0.7, C 1, T 1) and as discussed earlier, with these efficiencies the process becomes a net work consumer above certain temperatures.

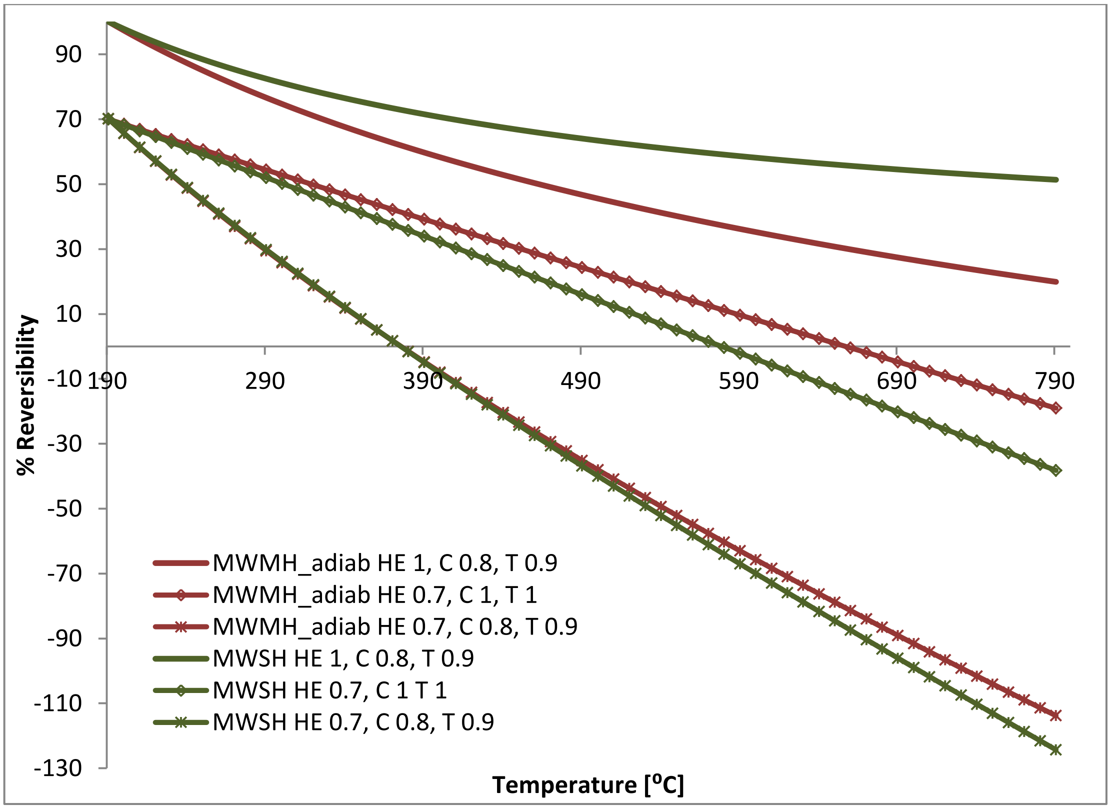

Fig. 3-16: Reversibility of an ammonia process as a function of operating temperature for work transfer by MWMH with adiabatic compression (MWMH_adiab) and for work transfer by MWSH at different efficiencies of the heat engine system (HE) and the compressor-expander system (C and T).

3) The combined effect of the heat engine system and the compressor-expander system efficiencies is also shown in Fig. 3-16. This is the case where η_{Work} is 0.7 and η_{IC} and η_{IT} are 0.8 and 0.9 respectively (HE 0.7, C 0.8, T 0.9). Below about 500 ^{o}C both MWMH with adiabatic compression and MWSH show almost the same behavior and both make the ammonia process a net work consumer at operating temperatures above about 380 ^{o}C. Existing ammonia processes operate by MWMH with adiabatic compression, where compression is done adiabatically with inter-stage cooling. These processes are equivalent to the process in Fig. 3-9; but in this case the device E rejects only heat at a temperature $\mathrm{T_S}$ higher than ambient temperature and the work W_E that would have been produced is lost. Therefore the reversibility of existing ammonia processes is expected to be much lower than that of MWMH with adiabatic compression for combined efficiencies (HE 0.7, C 0.8, T 0.9) as shown in Fig. 3-15.

While temperature plays a major role on the reversibility of the ammonia process, the pressure requirement is a consequence of the operating temperature, in a sense that the operating temperature determines the amount of mechanical work required (Equations 3.17 and 3.27) which in turn determines what pressure is needed according to Equation 3.24, 3.28 and 3.35.

Fig. 3-17 shows the minimum pressure requirement of an ammonia process as a function of operating temperature for MWMH with isothermal compression, MWMH with adiabatic compression and MWSH. In this case we see that there is no much difference in pressure requirement between MWMH with isothermal compression and MWSH, however this results may not be generalized as differences may exist in other processes.

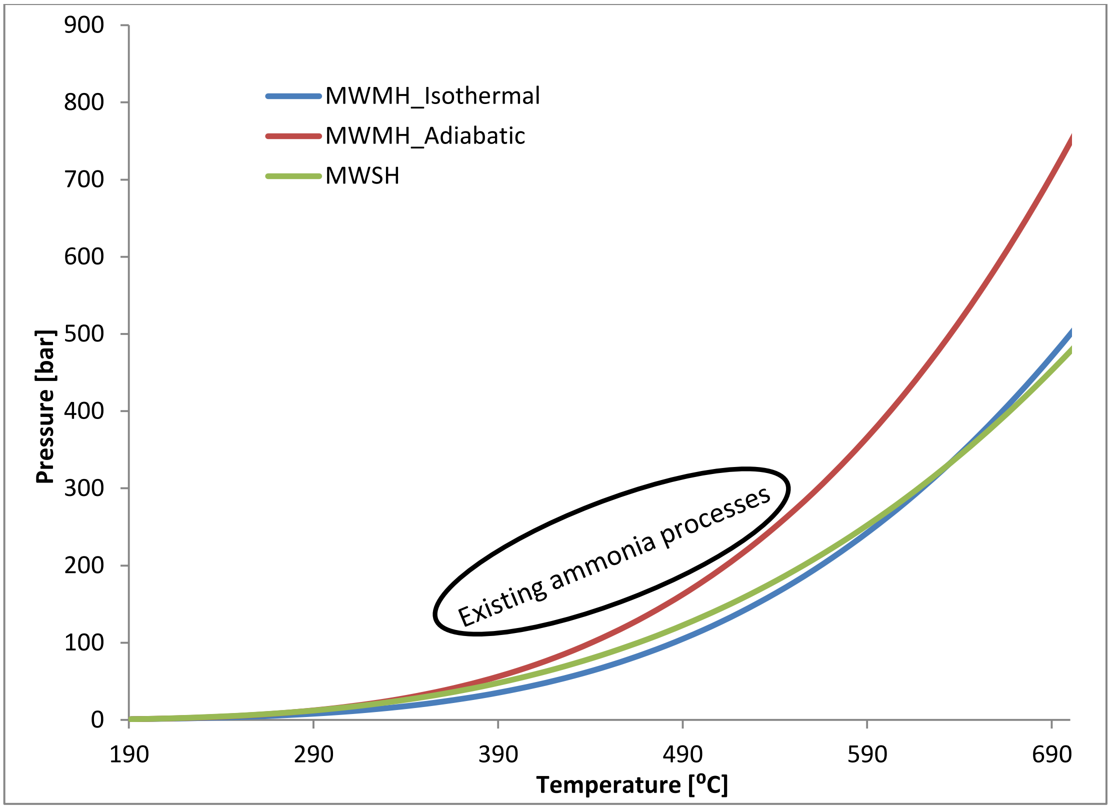

Fig. 3-17: The effect of operating temperature on pressure requirement for an ammonia process

Existing ammonia processes operate by MWMH with adiabatic compression, where compression is done adiabatically with inter-stage cooling. These processes are equivalent to the process in Fig. 3-9 but in this case device E does not produce work and rejects only heat at a temperature T_S higher than ambient temperature. Thus the work requirement for the compressor-expander system would be higher and would lead to higher pressures than that of MWMH with adiabatic compression in Fig. 3-17. Most existing ammonia processes operates at higher pressures (Efma 2000, Appl 1999, Austin 1984) as indicated in Fig. 3-17. One of the main reasons for higher pressures is to allow easy ammonia recovery by condensation (Efma 2000). However this could also be attributed to inefficiencies arising from mechanical imperfections or heat losses; in the sense that inefficiencies lead to increased work losses in the process and these losses must be compensated through pressure for the process to be feasible, in addition the compression work will also increase to compensate for work loss around the device E, and therefore this will lead to higher pressures.

3.6 Conclusion

For every chemical process there is a certain amount of heat and a certain amount of work associated with it. It is important to understand how work is transferred across a process in order to make chemical processes more reversible. Heat by virtue of its temperature is the easiest method of transferring work and could result in a structurally simple process; however this is not possible in all cases. A graphical approach, namely the *gh-diagram*, has been used to classify chemical processes in different thermodynamic regions allowing determining processes where a single point of heat transfer at a certain temperature is sufficient to transfer work across reversibly. These are the processes that could potentially have the simplest structure. In cases where this is not possible, we have shown, using the *gh-diagram*, two other methods that can be used to transfer work across a process reversibly. 1) Work can be transferred reversibly by having multiple points of heat transfer across the process. Different amounts of heat at different temperatures are transferred in a sort of a heat engine configuration thereby transferring work across the process. For a chemical process that cannot be feasible or reversible in a single step, the above technique is equivalent to having multiple steps for the process where each step represents a process which could potentially be a *simple process*. Therefore processes in this category would be structurally complex. 2) Work can also be transferred by adding mechanical work accompanied by multiple heat transfer across the process (MWMH) or by adding mechanical work accompanied with a single point of heat transfer across the process (MWSH); however this would require a change in number of moles of gas between the input and the output of the process. This technique provides, to some extent, one degree of freedom between the pressure and the temperature at which heat is transferred. This results in multiple pairs of temperature and pressure where the process could be feasible and reversible. Processes in this category would also be structurally complex.

These techniques have been applied to an ammonia process, where from the knowledge of ΔH and ΔG and the use of the *gh-diagram*, the following conclusions could be drawn: 1) the simplest structure for an ammonia process can be derived when heat is transferred across the entire process at 190.8 °C and the process can be run reversibly. 2) The pressure requirement for an ammonia process is a result of transferring heat at temperatures above 190.8 °C. Each operating temperature chosen can be matched with a certain pressure in order for the process to be reversible. We could also show that, ammonia processes seems to be more reversible when work is transferred by MWMH with isothermal compression compared to when work is transferred by MWMH with adiabatic compression and by MWSH due to inefficiencies in the compressor-expander system and the heat engine system.

This manuscript provides the process developer with a tool, that does not require much information or complex computations and allows to determine the target for a process in terms of heat and work requirement, to determine which method of supplying work is suitable, to give ways of manipulating the process in order to use available technology and get as close to reversibility as possible and also to give an early understanding of what the process structure would be. It also allows assessing irreversibilities and where they occur within a process; therefore it can be applied to existing processes to reveal opportunities for improvement and attempts to determine how this can be achieved.

This approach would guide decision making toward more energy efficient chemical processes.

References

Aljundi, I.H. 2009, "Energy and exergy analysis of a steam power plant in Jordan", *Applied Thermal Engineering,* vol. 29, no. 2-3, pp. 324-328.

Ameri, M., Ahmadi, P. & Hamidi, A. 2009, "Energy, exergy and exergoeconomic analysis of a steam power plant: A case study", *International Journal of Energy Research,* vol. 33, no. 5, pp. 499-512.

Appl, M. 1999, *Ammonia: Principles and Industrial Practice,* Wiley-Vch, New York.

Aspelund, A., Berstad, D.O. & Gundersen, T. 2007, "An Extended Pinch Analysis and Design procedure utilizing pressure based exergy for subambient cooling", *Applied Thermal Engineering,* vol. 27, no. 16, pp. 2633-2649.

Austin, G.T. 1984, *Shreve's Chemical Process Industries,* McGraw-Hill, New York.

Ayres, R.U. 1998, "Eco-thermodynamics: economics and the second law", *Ecological Economics,* vol. 26, no. 2, pp. 189-209.

Caton, J.A. 2000, "On the destruction of availability (exergy) due to combustion processes — with specific application to internal-combustion engines", *Energy,* vol. 25, no. 11, pp. 1097-1117.

Choi, S.H. 2004, "A lexicographic search algorithm for synthesis of four reaction clusters for water decomposition", *Korean Chem. Eng. Res,* vol. 42, pp. 121-123.

Efma, E. 2000, "Production of ammonia" in *Best Available Techniques for Pollution Prevention and Control in the European fertilizer Industry*, ed. E. Efma, European Fertilizer Manufacturers Association, Brussel.

Ganapathy, T., Alagumurthi, N., Gakkhar, R.P. & Murugesan, K. 2009, "Exergy analysis of operating lignite fired power plant", *Jest,* vol. 2, no. 1, pp. 123-130.

Ishida, M., Zheng, D. & Akehata, T. 1987, "Evaluation of a chemical-looping-combustion power-generation system by graphic exergy analysis", *Energy,* vol. 12, no. 2, pp. 147-154.

Lopez, T. & Manousiouthakis, V. 2001, *A lexicographic approach to the automatic generation of thermodynamically feasible reaction clusters*, UCLA.

May, D. & Rudd, D.F. 1976, "Development of Solvay clusters of chemical reactions", *Chemical Engineering Science,* vol. 31, no. 1, pp. 59-69.

McGlashan, N.R. 2008, "Chemical-looping combustion- a thermodynamic study", *Journal of Mechanical Engineering Science,* vol. 222, no. 6, pp. 1005-1019.

Patel, B., Hildebrandt, D., Glasser, D. & Hausberger, B. 2005, "Thermodynamics Analysis of Processes. 1. Implications of Work Integration", *Industrial & Engineering Chemistry Research,* vol. 44, no. 10, pp. 3529-3537.

Ray, T.K., Ganguly, R. & Gupta, A. 2007, "Exergy Analysis for Performance Optimization of a Steam Turbine Cycle", *Power Engineering Society Conference and Exposition in Africa, 2007. PowerAfrica '07. IEEE*, pp. 1.

Rosen, M.A. 2002, "Assessing energy technologies and environmental impacts with the principles of thermodynamics", *Applied Energy,* vol. 72, no. 1, pp. 427-441.

Sempuga, B.C., Hausberger, B., Patel, B., Hildebrandt, D. & Glasser, D. 2010, "Classification of Chemical Processes: A Graphical Approach to Process Synthesis To Improve Reactive Process Work Efficiency", *Industrial & Engineering Chemistry Research,* vol. 49, no. 17, pp. 8227-8237.

Smith, J.M., van Ness, H.C. & Abbott, M.M. 2001, *Introduction to Chemical Engineering Thermodynamics,* McGraw-Hill, New York.

Taniguchi, H., Mouri, K., Nakahara, T. & Arai, N. 2005, "Exergy analysis on combustion and energy conversion processes", *Energy,* vol. 30, no. 2-4, pp. 111-117.

Tonon, S., Brown, M.T., Luchi, F., Mirandola, A., Stoppato, A. & Ulgiati, S. 2006, "An integrated assessment of energy conversion processes by means of thermodynamic, economic and environmental parameters", *Energy,* vol. 31, no. 1, pp. 149-163.

4 EFFICIENT COMBUSTION

A Process Synthesis Approach to Improve the Efficiency of Coal Fired Power Stations

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4.1 Abstract

Much of our energy reserves are locked in the chemical potential of chemicals such as fossil fuels. The majority of CO_2 emissions caused by human activities come from the combustion of these fuels. Typically the fuel is burnt with oxygen (air) and heat is released. This heat is then used to drive power cycles to produce, for example, electricity in a power plant or motion in the motor car engine. Very often we look at the efficiency of these process in terms of how much of the heat that is released in the combustion process can be turned into work. This however is not a very good representation of how efficient the process is, as an idealized Carnot engine is reversible and thus takes all the work potential (exergy) of the heat and converts this to work. Thus the Carnot engine might only have efficiency in term of converting heat to work of 40%, but it is fully reversible and thus generates no entropy. Thus in effect the Carnot engine is 100% efficient.

However there is a much more fundamental efficiency that we should consider; *namely how much of the chemical potential that was in the fuel are we able to turn into work*. When we look at combustion processes in this way we see that some of

the major inefficiencies are in the chemical transformations that produce the heat rather than in the power cycles that convert heat to work.

A very important question is can we do these transformations more efficiently and thereby conserve the work potential or chemical potential in fuel. *We will show from a very fundamental thermodynamic analysis that it is not possible to combust carbon based materials efficiently*, that is that the process of combustion of carbon based materials is irreversibly, and that a considerable amount of the chemical potential of the fuel is lost during the combustion process. However we will explore other substances or chemistries and show that some of these have the potential for more reversibly combustion. We will explore these options, what it means and how it could be implemented by looking at a coal based power plant as an example. In particular we will show that there is the potential to significantly reduce CO_2 emissions by using different chemical pathways to do the combustion and by combining power and chemical production.

4.2 Introduction

Chemical energy is by far the most important source of power; although other alternatives, such as solar energy, hydroelectric power and wind power, exist these contribute only a small portion to the power used worldwide. The use of chemical energy is a major source of greenhouse gases, namely CO_2 which is believed to have significant environmental impact. Therefore the efficient use of chemical energy is necessary not only to ease environmental degradation but to also conserve diminishing energy resources for future generations (Rosen 2002)

It is important to understand how '*energy* efficiency' is defined and how, does the definition influence different approaches to improving energy production and utilization. Patterson (1996) has reviewed different energy efficiency indicators and their use at the policy level. Several authors (Rosen 2002, Rosen, Bulucea 2009, Szargut 1980, Taniguchi et al. 2005, Ganapathy et al. 2009, Ameri, Ahmadi & Hamidi 2009) have shown that energy conservation and the efficiency of energy utilization and their environmental impact, are well described by the concept of exergy rather than a mere first law energy balance.

Current practice for converting chemical energy into power consists of combusting fuel with oxygen (air) to produce heat. Heat is then converted to mechanical power using heat engine systems such as, steam cycles or internal combustion engines. Much attention has generally been directed to the transformation of heat into work rather than to the chemical transformation that produces heat. The process for converting heat into work (Fig. 4-1) is described by the well-known Carnot engine relation, given by Equation 4.1, which set a certain thermodynamic limit to the conversion. The performance of power production processes is generally assessed by looking at the Carnot relation, generally referred to as '*thermal efficiency*'; this is essentially looking at how much heat is converted into mechanical work.

$$\eta_{thermal} = \frac{|W_{out}|}{|Q_H|} = 1 - \frac{T_O}{T_H} \qquad 4.1$$

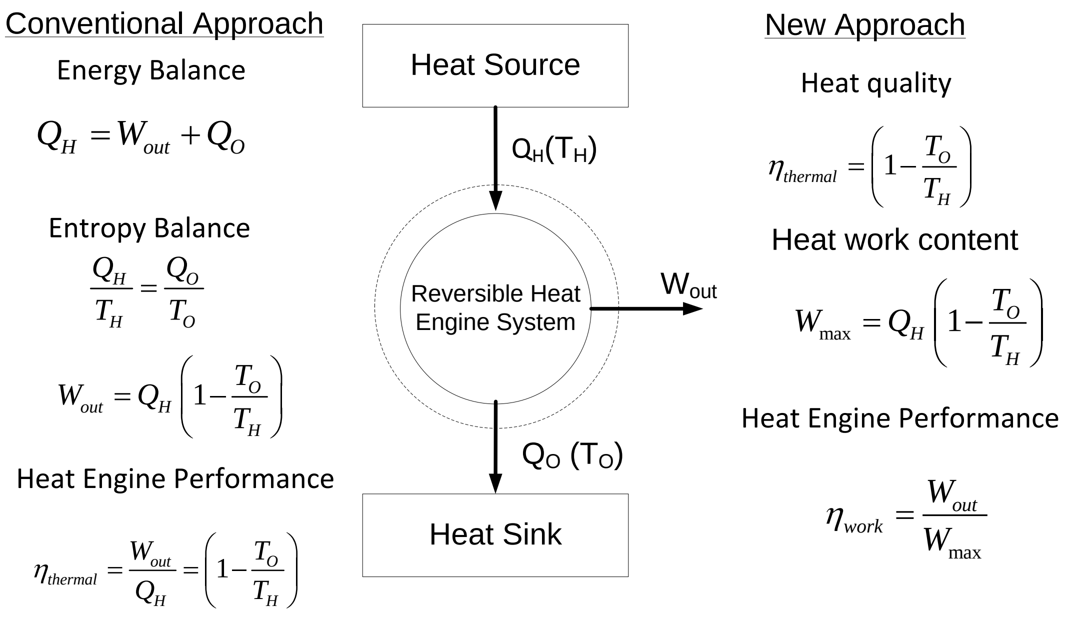

Fig. 4-1: Schematic representation of a heat engine: Conventional approach and novel approach to heat engine performance

Equation 4.1 is a relation describing a reversible Carnot engine, where $\eta_{thermal}$ is the thermal efficiency of the Carnot transformation, W_{out} is the mechanical work produced, Q_H is the amount of heat absorbed by the engine from a heat source at a temperature T_H and T_O is the temperature at which the quantity of heat Q_O is released from the heat engine to a heat sink (in this case the environment). Thus traditionally no heat engine, even an idealized reversible heat engine, can be 100% efficient; however in the traditional way of power plant design, efforts are made to increase the thermal efficiency $\eta_{thermal}$ (Manninen, Zhu 1998) by optimizing the heat engine system configuration but mostly by increasing the temperature of the heat source T_H, that is the temperature of the working fluid in the heat engine system, to as a high value as possible. The limit to which the temperature T_H can be increased is mostly determined by the material resistance to high temperatures and pressures. Thus improving a power plant performance in a traditional approach would simply mean finding high temperature resistant materials for boilers, turbines and pipelines transporting the working fluid. This approach can be misleading as to what the heat engine performance is and what improvement can be achieved. In fact as we approach metallurgical limitations, it appears that there is no more room for improvement to power plant designs. However, in this paper we will show that much improvement can be achieved when we look at Equation 4.1 in a different way.

Equation 4.1 should be understood as the *quality* of heat Q_H (which is also referred to as exergy) indicating how much work is contained in the heat; hence the higher the temperature of heat, the better its *quality* and the higher its *work content* with respect to the reference temperature *To* (in this case the ambient temperature). We will refer to the work content of heat as W_{max}, it is the maximum amount of work, given by Equation 4.2, that can be recovered by converting a quantity of heat Q_H at temperature T_H, to mechanical work. Thus the performance of a heat engine, which we will refer to as the work efficiency (η_{work} in Equation 4.3), is assessed by looking at how much work we are able to recover from the maximum amount available. Since a reversible heat engine is capable of recovering all the work content of heat, it is 100% work efficient and therefore cannot undergo any further improvement. Thus increasing the temperature T_H will only improve the quality of heat and not the performance of the heat engine in terms of η_{work}. Thus for a reversible heat engine $\eta_{work} = 1$ irrespective of the value of T_H.

$$W_{\max} = Q_H\left(1 - \frac{T_O}{T_H}\right) \qquad 4.2$$

$$\eta_{work} = \frac{W_{out}}{W_{\max}} \qquad 4.3$$

Energetic and exergetic analyses have been performed on a number of existing power plants (Ganapathy et al. 2009, Ameri, Ahmadi & Hamidi 2009, Aljundi 2009, Hussein, Yusoff & Boosroh 2001, Koroneos et al. 2004, Mitrović, Zivkovic & Laković 2010); it was reported that up to 90% of the total irreversibility in the plant occurs in the boilers. This suggests that the power production part, where heat is transformed into mechanical work, is sufficiently efficient considering the number of equipment involved and that it only accounts for about 10% of the total irreversibility in the plant. Most of this irreversibility could be associated with mechanical imperfections in turbines, pumps, boilers, piping as well as with operating parameters such as mass flowrate, temperature and pressure. Methods for determining optimal operating parameters have been developed (Rosyid et al. 2010, Regulagadda, Dincer & Naterer 2010, Manninen, Zhu 1999), which can lead to even higher efficiency in the transformation of heat to power. It was also reported (Aljundi 2009) that heat losses in boilers account for about 6%, thus about 94% of the heat produced by combustion is transferred to the working fluid, therefore irreversibility due to heat losses in boilers account for a small portion. In some cases heat losses are reduced by pre-heating the working fluid with the exhaust gas before it enters the boiler. We therefore see that major inefficiencies in power plants are found in the chemical transformation, namely combustion, that produces heat, rather than in the cycles that convert heat into mechanical work. Other literatures refer to combustion inefficiency as '*destruction of availability*' and detailed thermodynamic analysis in this regard exists (Caton 2000).

Curzon and Ahlborn (1975) have shown that the efficiency of Carnot Engine operating at maximum power output is given by:

$$\eta_{thermal} = 1 - \sqrt{\frac{T_o}{T_H}} \qquad 4.4$$

It has been shown that this model matches better the observed thermal efficiency of real heat engines. This therefore indicates that the transformation of heat into mechanical work in existing processes is almost at the highest possible efficiency;

this means that power plants are able to recover almost all the entire work content of heat.

In light of the above discussion, the analysis in the following sections will therefore consider that the transformation of heat into work in a coal based power plant is almost 100% efficient; this means that the entire work content of heat is recovered as mechanical work. However we will focus on the heat production part where we believe there is much room for improvement as described in Fig. 4-2.

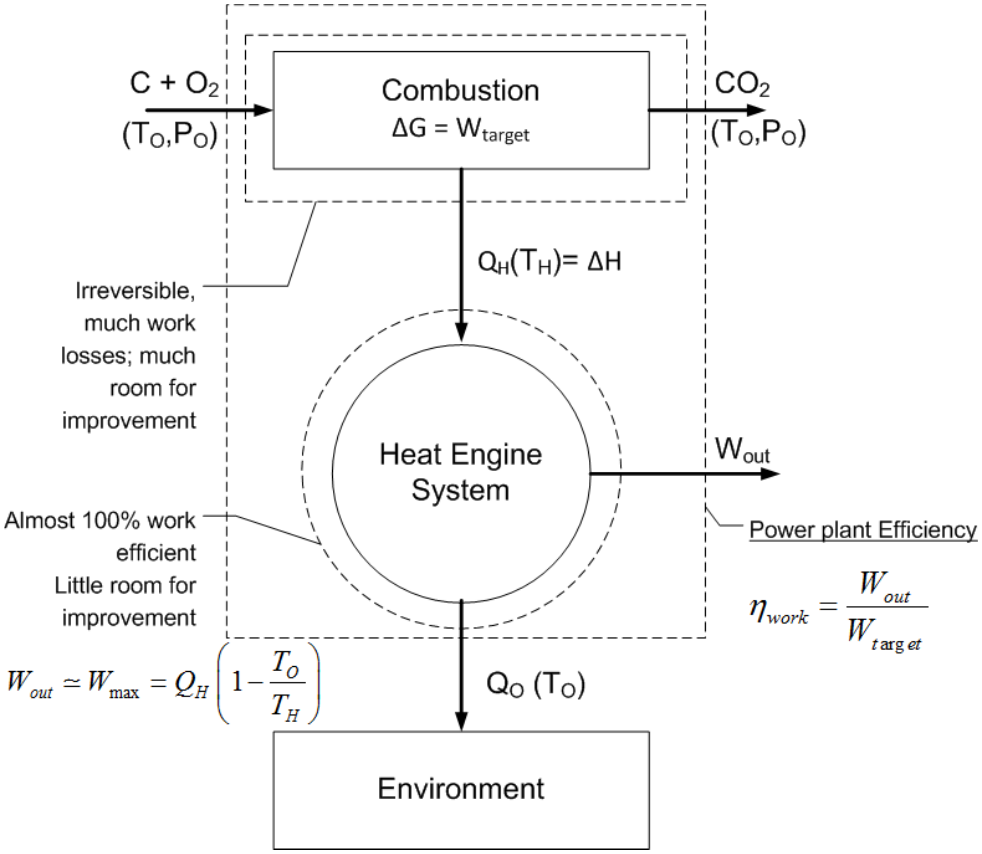

Fig. 4-2: Schematic representation of a coal fired power plant: There is much room for improvement in the combustion section and there is little room for improvement in the heat engine system section of the process. Power plant performance is assessed with respect to the work target, W_{target} which is the maximum amount of work that can be obtained from the chemical transformation

4.3 A More Fundamental Approach to Power Plant Efficiency

Chemical transformations are always accompanied with a certain amount of work; if the Gibbs energy of the transformation is negative, it means useful work (mechanical or electrical work) can be recovered and if it is positive, work must be supplied for the transformation to take place (Caton 2000, Denbigh 1956). Taking advantage of this aspect is the key to making chemical processes more efficient. The major challenge that chemical engineers have, is to design systems that will allow unlocking as much work potential contained within chemical molecules as possible.

Our main focus in this paper is to look at the performance of the transformation of chemical energy into mechanical work; this leads us to defining a more fundamental efficiency, as shown in Fig. 4-2, which looks at how much of the work potential in chemical transformations are we able to turn into mechanical work. This is defined as follows:

$$\eta_{Work} = \frac{W_{out}}{W_{target}} \qquad 4.5$$

Where W_{out} is the work recovered by the heat engine system, and W_{target} is the maximum amount of work that the power plant could produce and therefore is used as the basis for performance; W_{target} is the maximum amount work that can be obtained from the chemical transformation; it is the chemical potential and is given by the change in Gibbs free energy at ambient temperature To and pressure Po (Caton 2000, Denbigh 1956). That is:

$$W_{target} = \Delta G(T_O, P_O) \qquad 4.6$$

As an example, if we consider coal combustion as the transformation of carbon (C) to carbon dioxide (CO_2), as described in Equation 4.7, then the work target is 394.36

kJ/mol. Thus any coal fired power station should aim at producing 394.36 kJ of work per mol of carbon.

$$\begin{aligned} &C + O_2 \rightarrow CO_2 \\ &\Delta H(T_O, P_O) = -393.51 \tfrac{kJ}{mol} \\ &\Delta G(T_O, P_O) = -394.36 \tfrac{kJ}{mol} \end{aligned} \qquad 4.7$$

It is important to note that in cases where the values of ΔH and ΔG are close to each other, then the values for thermal efficiency $\eta_{thermal}$, and work efficiency η_{work}, as defined above, will also be close to each other, and in some cases they can be so close that comparing the two approaches to power plant efficiency would seem to make no difference. However they give different interpretations to power plant performance. A typical example would be a coal fired power plant. If heat is extracted from coal combustion say at 620°C and work is recovered in a reversible heat engine system; then the thermal efficiency (Equation 4.1) would be 66.6% and the work efficiency (Equation 4.5) would be 66.4%. $\eta_{thermal}$ is an indication of how much of the energy produced is turned into mechanical work, hence leading to the conclusion that the rest of the energy is lost mostly as heat; as a consequence the designer would try to optimize the process by finding points where larger amount of energy is lost (usually at the condenser) and will try minimize the losses. On the other hand η_{work}, indicates how much work was recovered from the maximum amount of work available, hence leading to the conclusion that the rest of the work is lost due to irreversibilities; these include any heat lost at a higher temperature than the reference temperature, but not the heat lost at the reference temperature. As a consequence the designer would not focus on minimizing heat transfer from the process occurring at the reference temperature, for example if the heat transferred at the condenser is at the reference temperature, then it would not be considered as lost since it has no work value even if it is a larger amount of heat. The designer would consider the process as being at the highest performance if all heat transfers across the process occur at the reference temperature and would therefore find other solutions for reducing irreversibilities, for example using alternative fuels.

In other cases one can clearly see the difference between the thermal and work efficiency. Let us consider a power plant using ammonia as fuel and the combustion products are nitric dioxide and water according to the Equation 4.8

$$\begin{aligned} &NH_3 + \tfrac{7}{4}O_2 \rightarrow NO_2 + \tfrac{3}{2}H_2O \\ &\Delta H(T_O, P_O) = -349.45\,\tfrac{kJ}{mol} \\ &\Delta G(T_O, P_O) = -287.93\,\tfrac{kJ}{mol} \end{aligned} \qquad 4.8$$

If the heat from combustion is transferred to the working fluid in a reversible heat engine system at 620°C, then the thermal efficiency (Equation 4.1) would be 66.6% and the work efficiency (Equation 4.5) would be 80.9%. We clearly see that there would be different indications of how much effort is needed and what solution should be considered in order to improve the process. An important element to note is that, if the heat is extracted at 1420°C, the process would be 100% work efficiency. However the traditional approach would indicate a thermal efficiency of 82% hence giving a false impression that the process needs further improvement.

In this paper, we will adopt the new approach to power plant performance and we will use a simple tool that we call *gh-diagram* (Sempuga et al. 2010), to show from a fundamental thermodynamic analysis that it is not possible to combust carbon based materials efficiently, that is that the process of combustion of carbon based materials is irreversible, and a considerable amount of the chemical potential of the fuel is lost during the combustion process; this has also been shown by Caton (2000). However we will explore other substances or chemistries and show that some of these have the potential for more reversible combustion and we will use these as an opportunity to make power plants more efficient. Several other authors including, McGlashan (2008) and Ishida at al. (1987), have shown that it is possible to indirectly combust carbon based materials reversibly, through other chemical routes such as chemical looping combustion. This is one of the best methods for reaching the work target for coal and natural gas combustion.

In the same spirit of improving efficient use of energy resources, some work have considered co-production of electricity and chemicals (Liu et al. 2010, Normann, Thunman & Johnsson 2009), or co-production of power and chemicals such as ammonia and methanol (Kaggerud, Bolland & Gundersen 2006, Gao et al. 2004, Li et al. 2010). These have shown considerable advantages in efficient use of energy and capital cost savings associated with CO_2 capture. However these systems all have an element of inefficient combustion of carbon based fuels or hydrogen fuels, in the power production part of the system.

This paper uses a process synthesis approach to explore opportunities to improve the reversibility of power production, as well as explore other ways of reaching the work target for power production by combustion of other substances whose by-products could eventually be converted into valuable chemicals. We will explore these options, what it means and how it could be implemented by looking at a coal based power plant as an example.

4.4 Combustion and the gh-Diagram

When we look at the change in Gibbs free energy and enthalpy between the input and the output streams for combustion processes, (that is, between the fuel +oxygen and CO_2 and water), we can represent them as points, on a ΔH-ΔG diagram which we will refer to as the 'gh-diagram'. For example in Fig. 4-3, the points shown in the third quadrant represent combustion processes of various substances.

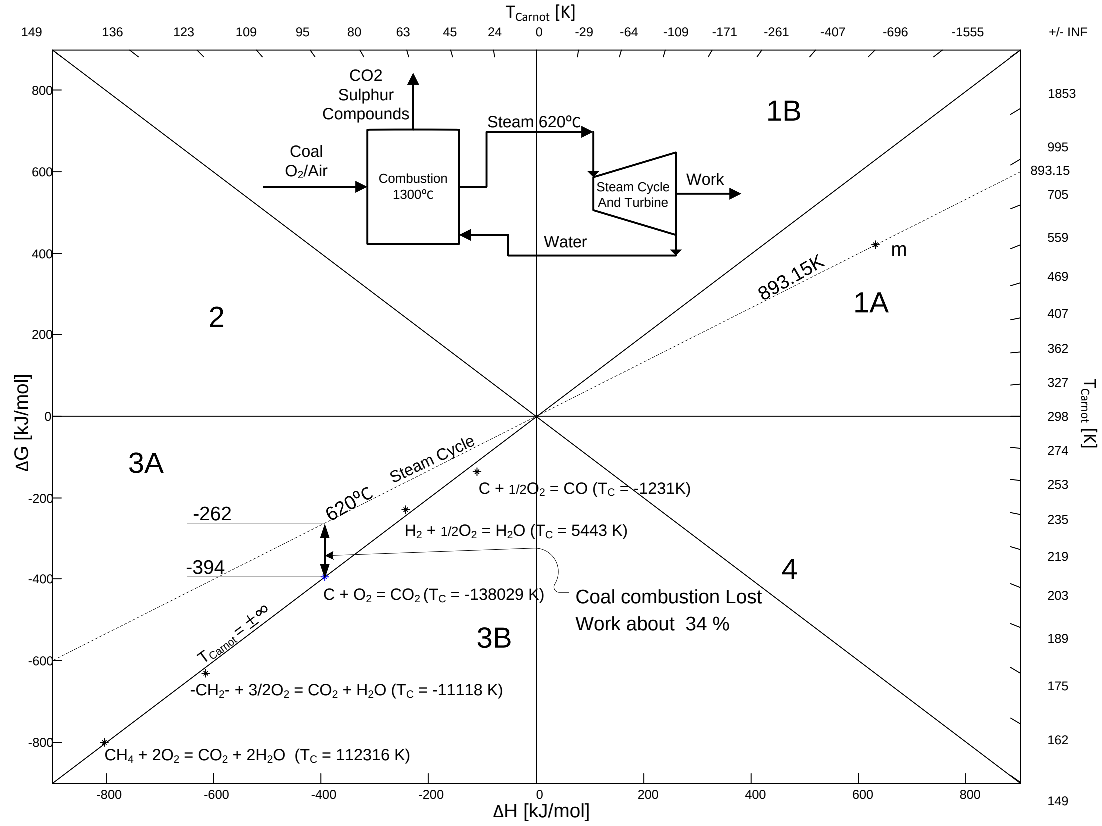

Fig. 4-3: A graphical representation of chemical processes: the combustion of most carbon based fuels and other conventional fuels are located in region 3B on the gh-diagram. If a steam cycle operating at highest temperature of about 620 °C the process would depart from their work target as indicated by the arrow. Thus a portion of the work potential will be lost.

As we can see all these processes have negative ΔG, which means they have the potential to produce work. The maximum amount of work that can be obtained from these combustion processes is given by their Gibbs free energy at ambient temperature and pressure To and Po (Caton 2000, Denbigh 1956). Recovering this work potential as useful work is one of the most challenging tasks for engineers. This is usually done by first producing heat which is then converted into work. Since heat transfer from processes can be done relatively easily, work from combustion processes is almost always recovered via heat. However when the production of heat is not done properly it becomes a major source of irreversibility in the process. Patel et al. (2004) have shown that in order to recover the maximum amount of work from a process via heat, the quality (or the work content) of the heat of the process (ΔH), by virtue of its temperature, must match the work potential of the process (ΔG). For any process there is a unique temperature at which this is possible. This temperature is referred to as the '*Carnot Temperature'*.

The gh-diagram is subdivided in regions, labeled 1 through to 4, depending on the Carnot temperature and on the directions of heat and work. Each process is represented as a point by the value of ΔG and ΔH taken at ambient temperature and pressure. To determine the Carnot temperature for a process, one would draw a line passing through the point representing the process and through the origin, then the Carnot temperature is read off where the line intercept the temperature scale. As an example let us consider a process represented by point m, the interrupted line in Fig. 4-3 shows us that the process has a Carnot temperature of 893.15 K. Note that processes on the 45^{o} line, have an infinite Carnot temperature.

From Fig. 4-3 we see that processes in region 3B have negative Carnot temperatures and that ΔG is greater than ΔH in magnitude. This implies that there is no temperature at which maximum work can be recovered from these processes via heat. We also see that most of the combustion processes involving carbon based substances are either located in region 3B or close to the 45^{o} line. For example, coal combustion has a work potential of 394 kJ/mol, but has a negative Carnot temperature (-138029K), therefore it is practically impossible to recover this amount of work via heat. Methane combustion is close to the 45 line, thus requires almost infinite temperature (112316K) for maximum work recovery.

The majority of existing coal-fired power plants are based on conventional steam cycle operating at sub-critical conditions with temperature range 535-565°C. However the best available technology operates at super-critical conditions with temperature range 600-620°C; future development is expected to reach up to a steam temperature of 720°C and would require special alloys, such as nickel alloys, for turbines and boilers (Dti 2006). Fig. 4-3 shows that, for a coal fired power station, a reversible steam cycle operating at 620°C can only recover 262 kJ/mol out of 394 kJ/mol of work available. This represents η_{work} (as defined by Equation 4.5) being 66%; it is the maximum efficiency that the best current coal fired power stations can achieve. In real processes η_{work} is much lower (46-48%) due to the steam cycle being irreversible and heat losses through the chimney and through other process equipment. Thus about 34% of efficiency of power plant is lost in combustion and about 20% due to equipment. We can also see from Fig. 4-3 that in order to approach the target work for coal combustion, the temperature of the steam cycle must be increased (the interrupted line must move closer to the 45° line); however this may not be possible, as one could quickly reach metallurgical limitations when operating with steam in the supercritical region above 300 bar and 620°C. Moreover, even with the highest temperature gas turbine that exists (± 1300°C); the maximum work efficiency can only be pushed up to 80%. This would require a combined cycle system where the combustion gas is passed directly into the turbine followed by a steam cycle to recover the rest of the work. However this may not be possible as solid particulates found in coal combustion gas may be detrimental to the turbine. Thus current coal fired power plants are bound to operate with steam cycles leading to a minimum of 34% of work loss.

Much improvement can be achieved by adopting chemical routes that allow reaching the work target at lower temperatures. The integrated Gasification Combined Cycle (IGCC) is an attempt to this approach.

4.5 The Integrated Gasification Combined Cycle (IGCC)

The IGCC evolved as a cleaner and more effective alternative to coal fired power stations; this produces synthesis gas (Syngas), a mixture of hydrogen and carbon monoxide, that can be cleaned prior to combustion hence making it possible to use high temperature gas turbines. This also allows capturing of CO_2 and other harmful substances, such as sulfur containing compounds, preventing them from being discharged into the environment. This section will focus on analyzing current application of the IGCC, how efficient it is in recovering the work potential from coal.

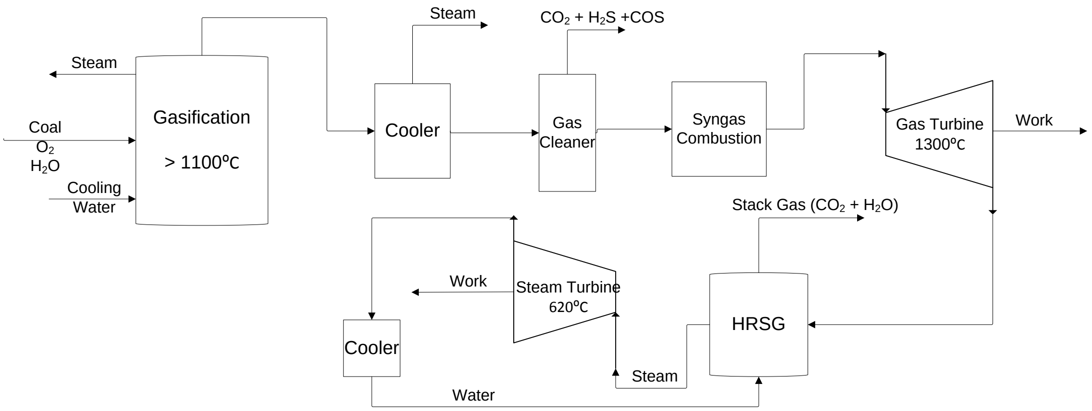

Fig. 4-4: A flow-diagram representing an IGCC process

Fig. 4-4 is a simplified schematic diagram of an IGCC process. Here instead of combusting coal to produce steam, coal is gasified to syngas which is burned as fuel to produce power. Before syngas can be burned, impurities in the gas must be removed; these include solid particulates, CO_2 and sulfur containing compounds such as H_2S and COS. Syngas is burned at high temperature (± 1300^{o}C) and is passed through a gas turbine to produce work. The exhaust gas from the gas turbine (± 600^{o}C) contains energy which is recovered in the heat recovery steam generator (HRSG). The steam from the HRSG is then passed in a steam turbine to produce more work. About 70% of work is recovered in the high temperature gas turbine and 30% is recovered in the steam cycle (Franco, Casarosa 2002).

The IGCC process could be understood as indirect coal combustion, subdivided in two steps. The first step, gasification, consists of a chemical potential or a work potential transfer from coal to syngas; and the second step, consists of syngas combustion followed by work recovery. Since direct coal combustion is in Region 3B with a negative Carnot temperature, it cannot be done efficiently in one step. On the other hand, syngas combustion is in Region 3A with a positive Carnot temperature, making it possible to be done efficiently if its Carnot temperature can be reached using available technology. We will see that by splitting coal combustion in multiple steps we can be able to reach its work target more efficiently. However this will require that each step can be operated reversibly at reasonable conditions of temperatures; this means that each step must be located in Region 1A or 3A and must have an easily achievable Carnot temperature.

4.5.1 Gasification Process

Fig. 4-5 represents a coal gasification process on the gh-diagram.There are many reactions involved in coal gasification however let us consider that the main reaction that produces syngas is the gasification reaction, as described by Equation 4.9. This reaction is found in region 1A on the gh-diagram and is endothermic and requires work input for it to be feasible. The necessary heat and work requirement for this reaction is supplied by combustion of coal, in Equation 4.10 situated in Region 3B. Another important reaction found in gasification is the water gas shift reaction, given by Equation 4.11, which could be located in Region 3A or 1A on the gh-diagram, depending on the direction of equilibrium. A combination of these three reactions results in the ‘gasification’ line ($a - b$) on the gh-diagram in Fig. 4-5 obtained by varying the amount of oxygen at a fixed amount of water per mole of carbon (Coal) in the feed. This produces syngas (pCO + qH_2) with varying CO/H_2 ratio along line *a* – *b* in Fig. 4-5.

$$C + H_2O \rightarrow CO + H_2 \qquad 4.9$$

$$C + O_2 \rightarrow CO_2 \qquad 4.10$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad 4.11$$

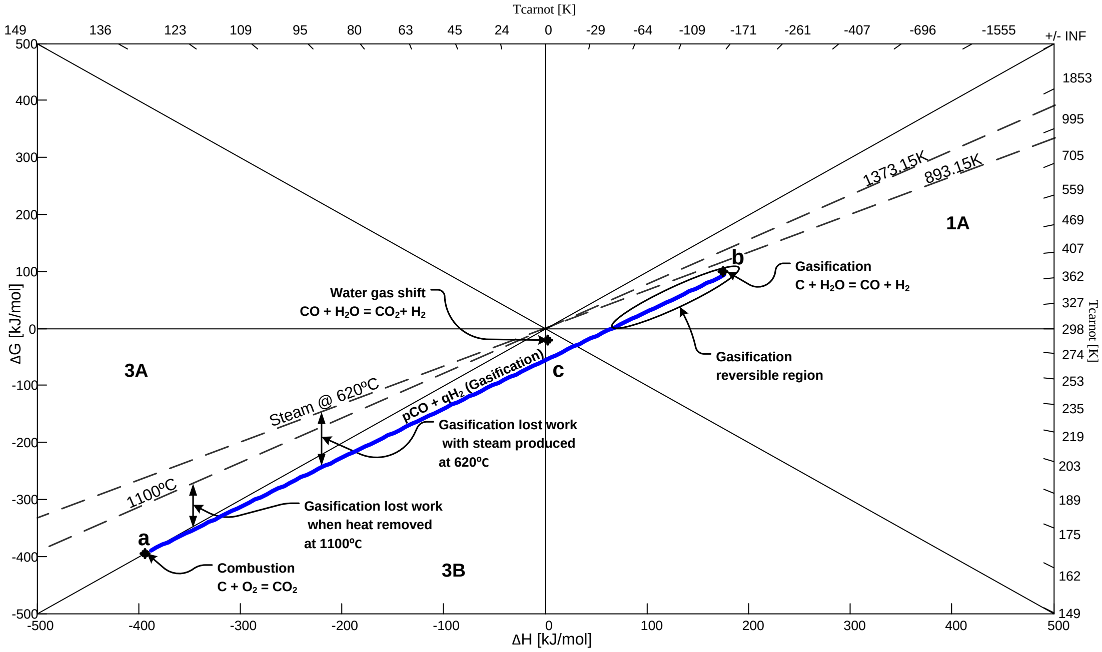

Fig. 4-5: Coal gasification (line a – b) on the gh-diagram as a combination of gasification, water gas shift and combustion reaction. Coal gasification process can be reversible when operated in region 1A. Work is lost when coal gasification is operated in region 3A where heat is removed at 1100°C; much work is lost (about 33% - 97%) when heat is removed by producing steam at 620°C.

Existing gasification processes operate at a temperature of about 1100°C and heat is released from the process. Thus on the gh-diagram these processes are located in region 3B where combustion is dominant and where Carnot temperatures are negative. Since the operating temperature is about 1100°C (this means the process is operated in region 3A instead of 3B), and if heat is removed at this temperature work will be lost due to irreversibility caused by the departure of the operating temperature from the Carnot temperatures along line *a – b*; These Carnot temperatures are negative from the point (**c**) where heat is released from the process. If the heat released is recovered by making steam say at 620°C, work losses could range between 34% and 99% as the process operates near complete combustion or toward syngas production in region 3B.

Work losses in gasification could be prevented by operating in the reversible region as shown in Fig. 4-5 situated in region 1A where the gasification reaction is dominant and where instead of heat being released, the process requires heat and work to be supplied. Processes located in region 1A on the gh-diagram require heat and work to be supplied; these processes have positive Carnot temperatures within reasonable range (except for processes near the 45° line with Carnot temperature approaching infinity); thus the work requirement can be reversibly satisfied by supplying heat at their respective Carnot temperatures. Operating gasification in region 1A means that, heat at temperatures ranging from 25°C to about 360°C must be supplied to the process in order to meet the work requirement; this can be done by feeding a correct amount of steam at a temperature within the range 25°C - 360°C so as to supply the correct amount of heat and work that the process would require. The temperature inside the gasifier could still be at 1100°C but there should not be any external heat exchange other than the one supplying heat to the process within the temperature range given above. In a combined cycle process, the steam to run the gasifier can be produced in the heat recovery steam generator unit (HRSG).

4.5.2 Syngas Combustion in a Steam Cycle

If we assume that syngas is produced by running gasification in the reversible region (line *a – b*)as show in Fig. 4-6, then the corresponding syngas combustion producing water as a vapor (Equation 4.12), is represented by line $e - f$, and has Carnot temperatures of about 4000 ^{o}C for all CO/H_2 ratios obtained.

$$pCO + qH_2 + rO_2 \rightarrow pCO_2 + qH_2O_{(gas)} \qquad 4.12$$

$$pCO + qH_2 + rO_2 \rightarrow pCO_2 + qH_2O_{(liquid)} \qquad 4.13$$

It is important to note that the Carnot temperature for syngas combustion will depend on the ratio CO/H_2. We can show that for syngas rich in H_2 the combustion Carnot temperature is about 5200 ^{o}C and decreases to about 3000 ^{o}C as syngas becomes leaner in H_2 and richer in CO.

Therefore we see that in order to reach the *work target* (defined in section 4.3) in power production and if combustion of syngas produces water as vapor, heat must be produced at temperatures near 4000^{o}C. If the power plant uses a steam cycle operating at maximum temperature of 620^{o}C we could show that η_{work} (Equation 4.5) could reach a maximum of about 65% taking into account the work required to produce syngas. Therefore about 34% of work potential of coal to CO_2 would be lost. Thus in this case direct coal combustion would be more advantageous since the process could be much simpler than the syngas route and could reach almost the same work efficiency.

However if syngas combustion produces water liquid (Equation 4.13). This corresponds to line $c - d$ in Fig. 4-6 with Carnot temperatures of approximately 1800^{o}C. As we can see line $c - d$ in Fig. 4-6 is closer to the 620 ^{o}C temperature line which means that less work would be lost compared to syngas combustion to water vapor (line $e - f$) and direct coal combustion. In this case we can show that η_{work} could reach a maximum of about 73%. However this may require condensing the water in the stack gas, before it is released, and integrating the heat back to the process; for example by preheating the water in the steam cycle before it goes to the boiler.

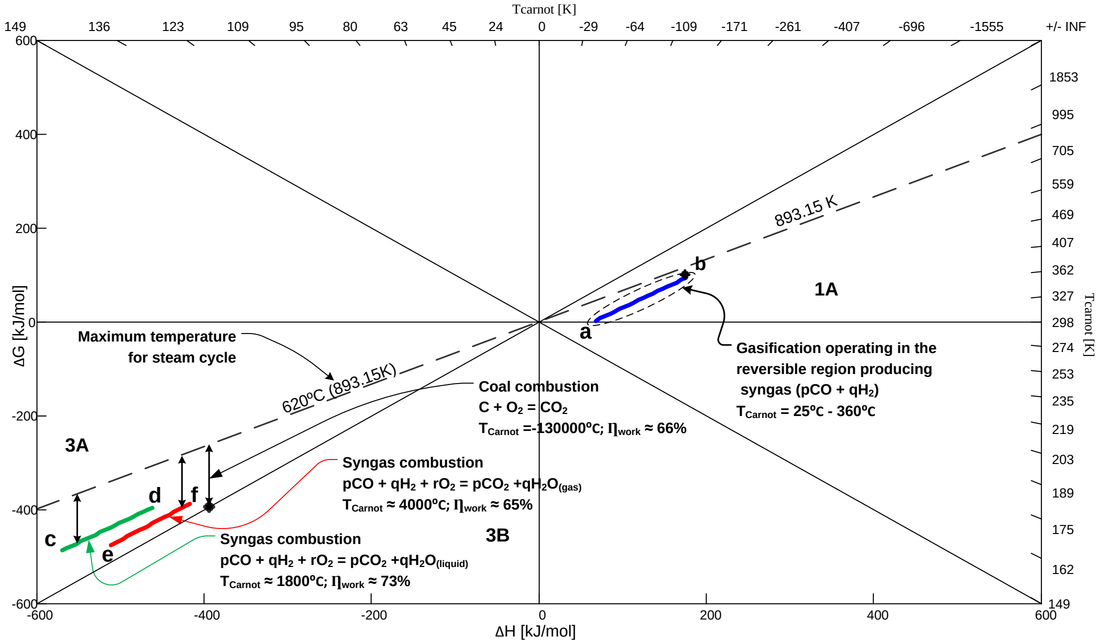

Fig. 4-6: Coal gasification (line a-b) operating in the reversible region (1A) to produce syngas. In a steam cycle operating at 620°C, combustion of coal (T_{Carnot} = -130000°C) could reach η_{work} (Eq. 4.5) of 66%, combustion of syngas producing water vapor (line e-f) (T_{Carnot} = 4000°C) could reach η_{work} of about 65% and combustion of syngas producing water liquid (line c-d) (T_{Carnot} = 1800°C) could reach η_{work} of about 73%.

We see that with syngas there are real temperatures (1800 °C to 4000°C) at which combustion can be conducted reversibly; which means that our ability to reach the *work target* for syngas combustion is not limited by thermodynamics but is limited by technological availability thereby offering more opportunities for improvement. On the other hand, direct coal combustion, as we have seen in section 4.4, is thermodynamically limited and that there is no real temperature at which the *work target* can be reached.

4.5.3 The combined cycle process (CC)

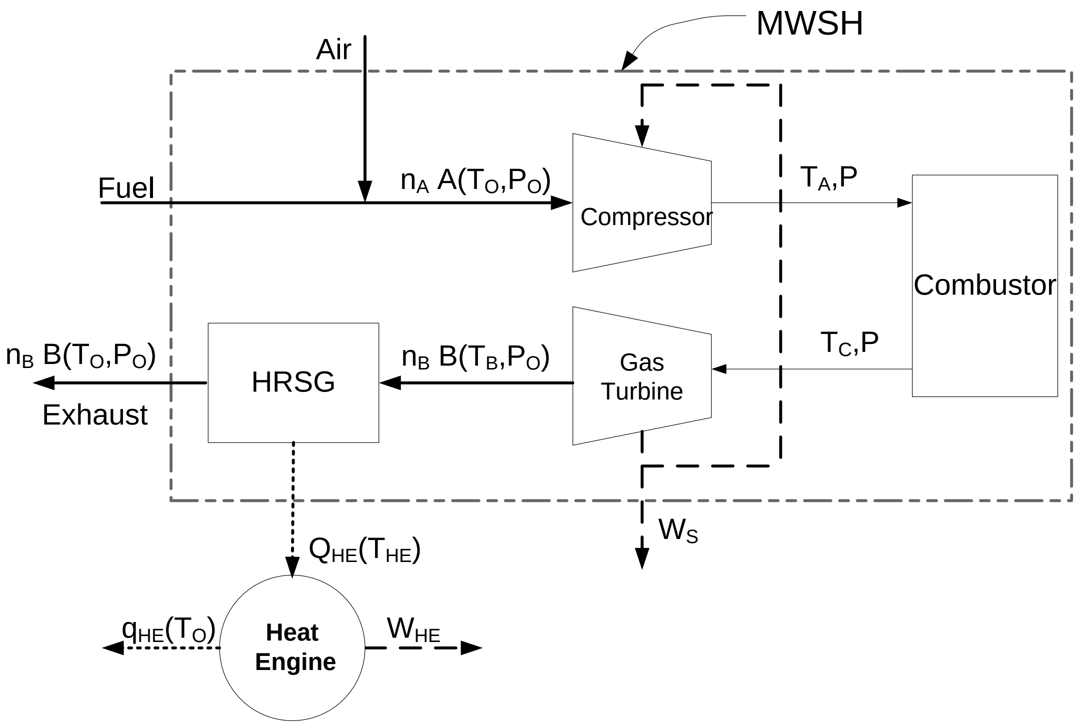

Fig. 4-7: Schematic representation of a combined cycle where work is recovered from the heat of combustion using a combination of a gas turbine and a heat engine. The process in the boundary can be considered as a process with Mechanical Work transfer with a Single Heat transfer (MWSH, refer to Chapter 3).

Fig. 4-7 is a simple representation of a combined cycle (CC) where a fuel is burned with air and work is recovered by a combination of a gas turbine and a heat engine. A mixture of fuel and air (which we will refer to as substance A) at ambient conditions (T_O, P_O) is compressed to a pressure P and reaches a temperature T_A; the mixture is then fed to a combustor, where the fuel is completely combusted with oxygen at constant pressure. The gas leaving the combustor (which we will refer to as substance B containing the combustion products, inert nitrogen and the remaining oxygen if the air in the feed is in excess) at a temperature T_C and pressure P is expanded in a gas turbine to produce work; a portion of this work is reintegrated to the compressor and the net work produced from the gas turbine is W_S. The gas leaving the gas turbine at a pressure P_O and a temperature T_B, is then brought to ambient temperature T_O by passing it through a heat recovery steam generation unit (HRSG) where a quantity of heat, Q_{HE} is removed in the form of steam and then passed to a heat engine system to produce more work W_{HE}.

If we consider the portion of the CC process as indicated by the boundary line (Fig. 4-7) we can see that there is mechanical work transfer and a single heat transfer across the boundary. This corresponds to a *complex process* where energy is transferred by mechanical work with a single heat transfer (MWSH), this is discussed in more detail by Sempuga et al. (2011). For *complex processes* we have shown (in Chapter 3) that for every amount of mechanical work transferred (W_S), there is a single reversible temperature (T_{Rev}) at which heat must be transferred for the process to be reversible. When there is no mechanical work transfer then the single reversible temperature is the Carnot temperature (T_{Carnot}) of the process. This temperature is given by the temperature scale determined by a point at the origin on the gh-diagram. As mechanical work is added or removed from the process the temperature scale on the gh-diagram is shifted accordingly resulting in a new reversible temperature for the process. As an example consider process X on the gh-diagram in Fig. 4-8. When no mechanical work is transferred across the process then the reversible temperature is 749 K as indicated by the temperature scale determined by the origin. If 100 kJ/mol of mechanical work is added then the reversible temperature becomes 449 K as indicated by the temperature scale determined by the center point ***n***; and if 100 kJ/ mol of mechanical work is removed then the reversible temperature becomes 1048 K as indicated by the temperature scale determined by center point ***m***.

We therefore see that in order for the CC process in Fig. 4-7 to be reversible the temperature, T_{HE}, at which the quantity of heat Q_{HE} is removed from the HRSG unit must correspond to the reversible temperature T_{Rev} as determined by the amount of work W_S removed from the process; if $T_{HE} \neq T_{Rev}$ then the CC process will be irreversible and a certain quantity of work will be lost.

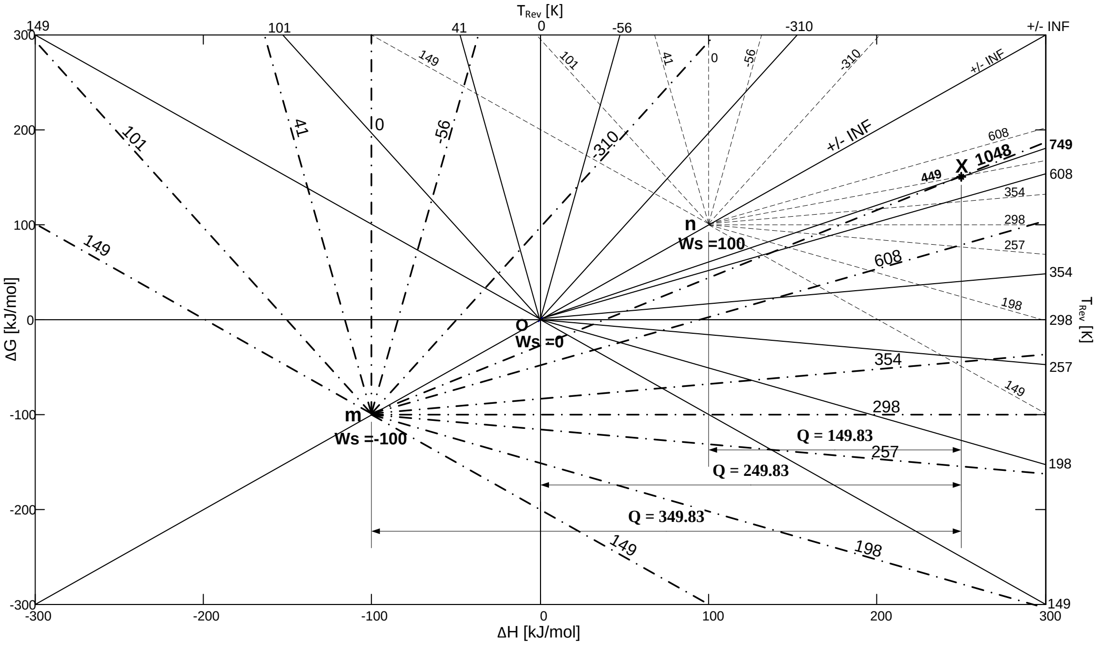

Fig. 4-8: Reversible temperature for a process as a function of mechanical work transfer. The temperature scale on the gh-diagram shifts according to the amount of mechanical work added or removed from the process.

We could show that the temperature T_{HE} is the log mean temperature between the inlet and outlet temperatures of the HRSG unit, T_B and T_O respectively. Therefore T_{HE} is given by:

$$T_{HE} = \frac{(T_B - T_O)}{\ln \frac{T_B}{T_O}} \qquad 4.14$$

4.5.4 Syngas Combustion in the CC process

Previously we have explored the efficiency of syngas combustion in steam cycles. In this section we will explore some of the possibilities and requirements for making syngas combustion more reversible using a CC process.

The calculations in the rest of the analysis were based on 1 mole of carbon (Coal) being transformed to CO_2 via different routes. If we assume that coal gasification is operated in the reversible region as shown in Fig. 4-6, then we can choose to run the process at any point along line *a* – *b* and each point corresponds to a certain H_2 and CO composition as well as a certain temperature, in the range 25 - 360^oC, at which heat must be supplied for the process to be reversible and feasible. If we choose to supply heat to the gasifier at 360^oC the results obtained are summarized in Table 4-1

Table 4-1: Result summary for work recovery when 1 mol of Coal (Carbon) is transformed to CO2 via a reversible steam cycle and via IGCC with 4 times the stoichiometric amount of air for syngas combustion in the CC process. Assuming gasification and the steam cycle in the HRSG are reversible

Gasification								
Feed [mol]			Product [mol]			Heat (ΔH)[kJ]	Work (ΔG)[kJ]	T_{Carnot} [^oC]
C	H_2O	O_2	H_2	CO	CO_2	176.13	93.463	362.07
1	1.3177	1e-4	1.3177	0.6821	0.3179			

Syngas Combustion									
Feed [mol]			Product [mol]				Heat ΔH [kJ]	Work ΔG [kJ]	T_{Carnot} [^oC]
H_2	CO	Air	$H_2O_{(l)}$	CO_2	O_2	N_2	-569.63	-487.86	1803.85
1.3177	0.6821	19.046	1.3177	0.6821	2.9997	15.0461			

Steam Cycle with heat removed at 620 ^oC					
Q_{HE}[kJ]	T_{HE} [^oC]	W_{CC} [kJ]	η_{SC}	W_{Ptotal}[kJ]	η_{work}
-569.63	620	-379.48	0.78	-289.02	0.73

Combined Cycle Process (CC)									
T_C [^oC]	W_S[kJ]	P_{CC}[bar]	Q_{HE}[kJ]	T_{Rev}[^oC]	T_{HE} [^oC]	W_{CC} [kJ]	η_{CC}	W_{Ptotal}[kJ]	η_{work}
2889	-431.72	3951	-137.91	229.9	90.10	-456.40	0.94	-362.94	0.92
1300	-304.88	42.69	-264.76	692.40	172.30	-392.54	0.80	-299.08	0.76

We have previously mentioned that one of the ways for improving work recovery from combustion processes is to reduce the temperature at which the target work can be reached (the Carnot temperature or reversible temperature) using available technologies. This can be achieved in a CC process as it combines mechanical and heat transfer across the process and thereby shifting the reversible temperature.

We have also mentioned that in order for the CC process (Fig. 4-7) to be reversible the temperature (T_{HE}) at which heat (Q_{HE}) is removed from the process via the HRSG unit must match the reversible temperature (T_{Rev}) of the process which depends on the amount of mechanical work W_S removed from the process. We can see from Fig. 4-9 that the more mechanical work is removed the more T_{HE} approaches T_{Rev}, however at pressures above approximately 200 bar W_S tends to be constant leading to the departure of T_{HE} from T_{Rev} to be also constant and therefore the irreversibility of the CC process remains almost unchanged as pressure is increased.

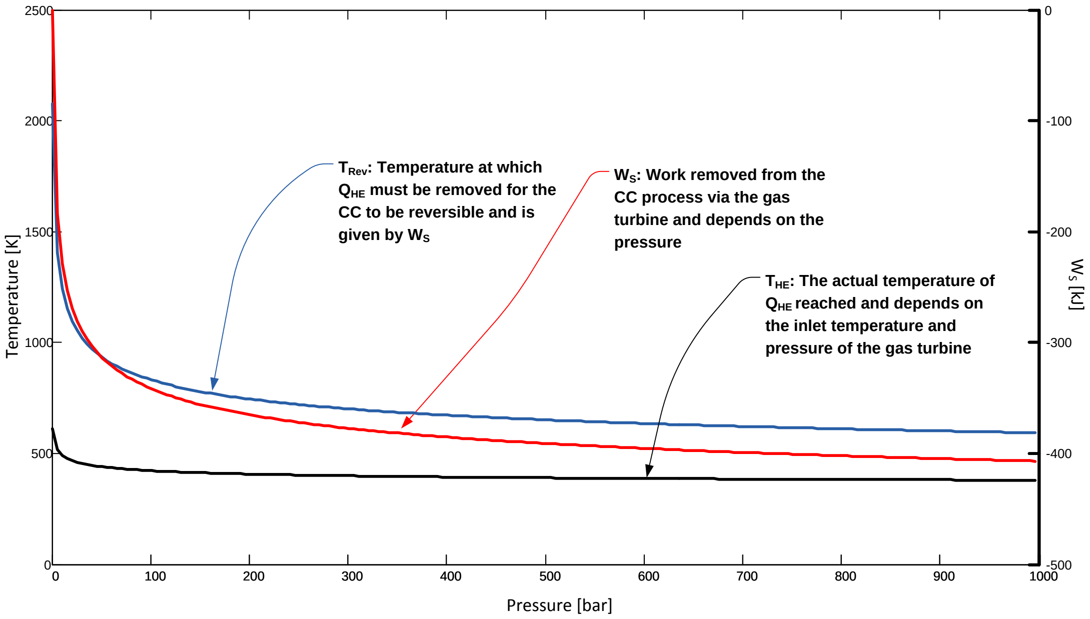

Fig. 4-9: Variation of W_S, T_{Rev} and T_{HE} with pressure for syngas combustion to CO_2 and $H_2O_{(l)}$ in a CC process with air fed at 4 times the stoichiometric amount. W_S, T_{Rev} and T_{HE} tend to be constant as the pressure is increased to higher value. Thus the departure of T_{HE} from T_{Rev} as well as the irreversibility of the CC process remain constant and do not reach zero.

We can see from Fig. 4-10 that by using a CC process we can shift the reversible temperature for syngas combustion from 1804°C to 230°C by removing about -432 kJ of mechanical work (W_S) from the gas turbine (Fig. 4-7), thus only a small amount of heat (Q_{HE}) will go to the heat engine system at a much lower temperature. Although we cannot match T_{HE} to T_{Rev}, we see from Fig. 4-9 that the CC process allows lowering T_{Rev} and brings it as close as possible to T_{HE}. As shown in Table 4-1, at inlet gas turbine temperature and pressure of 2889 °C and 3951 bar respectively, the amount of work removed is -432 kJ and the reversible temperature for Q_{HE} (T_{Rev}) is about 230 °C, but under these conditions the actual temperature for Q_{HE} (T_{HE}) that can be reached is about 90 °C; therefore only 94% of the work target for syngas combustion (η_{CC}) can be reached and about 92% of the work target for coal to CO_2 (η_{work}) via the syngas route.

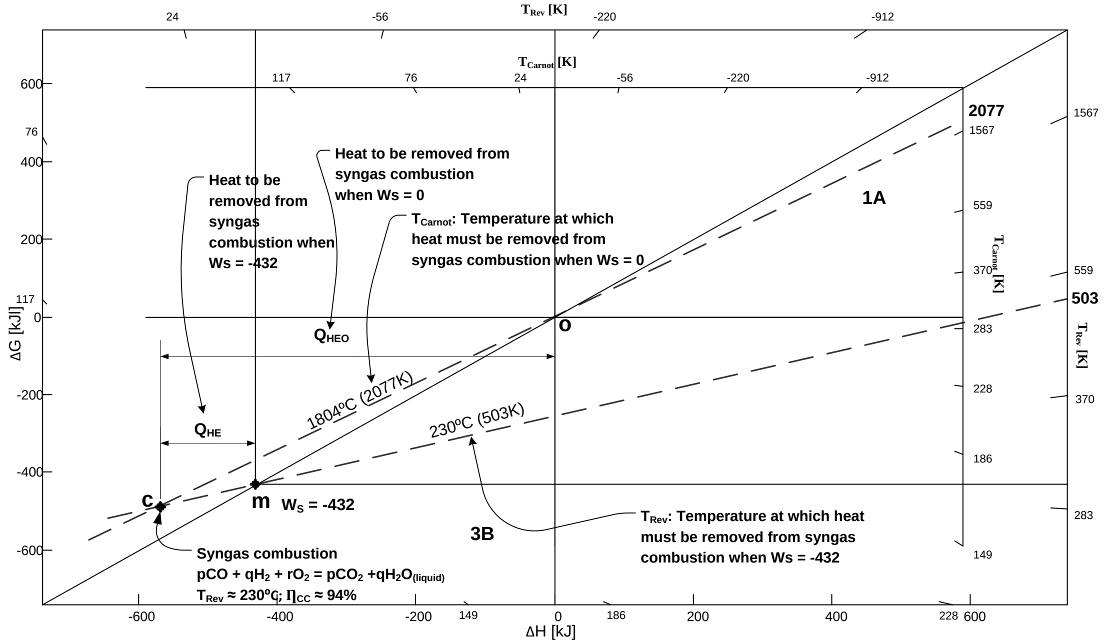

Fig. 4-10: Combining mechanical work and heat removal from a process results in the reversible temperature being shifted by shifting the center point for the temperature scale from point o to m on the gh-diagram. Using a CC process, the reversible temperature for syngas combustion can be shifted from 1804°C to 230°C by removing -432 kJ of mechanical work, this could allow reaching almost 94% work target for syngas combustion

Current technology for CC processes allows inlet gas turbine temperature of about 1300°C (Franco, Casarosa 2002). For the CC process being considered, where syngas is fed with air at 4 times the stoichiometric amount, we can show that in order to reach inlet gas turbine temperature (T_C) of 1300°C, the operating pressure must be approximately 42.69 bar. This would produce about -304.88 kJ of work (W_S) and the resulting amount and temperature of heat in the HRSG are -264.76 kJ (Q_{HE}) and 172.30°C (T_{HE}) respectively. However Fig. 4-11 shows that when W_S = -304.88 kJ the reversible temperature (T_{Rev}) is 692.40°C; since this temperature is higher than the actual temperature (T_{HE}) of the process then approximately 20% of work potential is lost. Thus only a maximum of 80% (η_{CC}) of the work target for syngas combustion can be reached using existing CC technology. We can also show that this could allow reaching a maximum of 76% (η_{work}) of the work target for coal to CO_2.

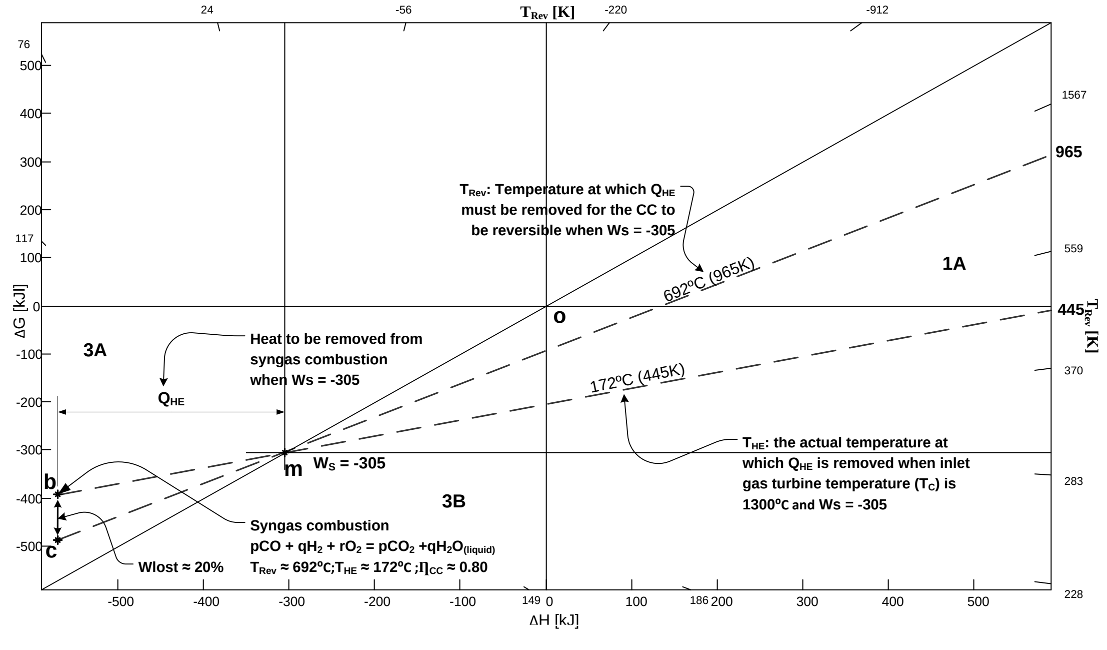

Fig. 4-11: Efficiency of a CC process when syngas is fed with air at 4 times the stoichiometric amount and the inlet gas turbine temperature is 1300°C and the pressure is 42.69 bar. The resulting temperature (T_{HE}) of the heat to be removed does not correspond to the reversible temperature (T_{Rev}) on the gh-diagram therefore about 20% of work potential is lost.

We therefore see that work recovery from the transformation of coal to CO_2 can be greatly improved when other routes, which are not limited by thermodynamic constraints, than direct coal combustion are adopted. This requires coal to be transformed into a fuel that can allow reaching the *work target* at lower temperatures using available technology such as the IGCC. Another fuel, beside syngas, that can meet the above criteria using the IGCC technology is ammonia.

4.6 The Ammonia Route

Ammonia can be produced from syngas by introducing a shift process to convert the CO in the syngas to hydrogen, followed by an ammonia synthesis process where the hydrogen is reacted with nitrogen to form ammonia.

The process for making ammonia from hydrogen and nitrogen, as represented by Equation 4.15, is exothermic and lie in Region 3A of the gh-diagram with a Carnot temperature of about 191^{o}C, thus the process can produce work if it is run reversibly. An active catalyst must exist to achieve a reasonable conversion at 191^{o}C. Existing ammonia catalysts require temperatures in the range 350^{o}C – 500^{o}C and pressures ranging from 15 to 30 Mpa (Austin 1984, Efma 2000); under these conditions it is possible for ammonia processes to be self-sustaining with regard to energy. Low temperature catalysts need to be developed in order to run ammonia processes reversibly, and if we assume that such catalysts exist, we can run the ammonia process in Region 3A where work can be produced.

$$\begin{aligned} &\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightarrow NH_{3(g)} \\ &\Delta H(T_O, P_O) = -46.11\tfrac{kJ}{mol} \\ &\Delta G(T_O, P_O) = -16.45\tfrac{kJ}{mol} \end{aligned} \qquad 4.15$$

The hydrogen and nitrogen required for ammonia synthesis can be produced by the gasifier. Coal is gasified with air and steam to produce syngas and CO_2. Syngas can undergo the shift reaction to produce more hydrogen and more CO_2. In this way the work potential in the transformation of coal to CO_2 is passed to hydrogen, then to ammonia production and finally recovered in a combined cycle by burning ammonia. Coal gasification for ammonia synthesis only requires an air feed which supplies the oxygen needed for gasification and the nitrogen for the ammonia synthesis. This is an advantage compared to conventional IGCC, where an air separation unit (ASU) is needed to avoid diluting syngas with inert nitrogen from air, which reduces the gas heating value, and increases the gas volume during treatment. However if the gasifier is run reversibly in region 1A, then the amount of oxygen needed will be small and therefore the ASU would not be necessary in any case.

If we assume that the gasifier is operated reversibly with heat supplied at 360°C then we can summarize the results of the transformation of coal to CO_2 via ammonia combustion as shown in Table 4-2.

The combustion of ammonia to form nitrogen and liquid water (Equation 4.16) has a Carnot temperature of about 2352°C. This is the temperature at which heat must be removed in order to recover an amount of work close to the *work target* ($\Delta G(T_O,P_O)$) for ammonia combustion using a heat engine system. However this temperature is too high for currently used heat engine systems.

$$\begin{aligned} &NH_{3(gas)} + \tfrac{3}{4}O_2 \rightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2O_{(liquid)} \\ &\Delta H(T_O,P_O) = -382.64\tfrac{kJ}{mol} \\ &\Delta G(T_O,P_O) = -339.24\tfrac{kJ}{mol} \end{aligned} \qquad 4.16$$

Table 4-2: Result summary for work recovery when 1 mol of Coal (Carbon) is transformed to CO2 via ammonia combustion to nitrogen and water, with 3 times the stoichiometric amount of air for combustion in the CC process. Assuming gasification and the steam cycle in the HRSG are reversible

Gasification

Feed [mol]			Product [mol]			Heat (ΔH)[kJ]	Work (ΔG)[kJ]	T_{Carnot} [^oC]
C	H_2O	O_2	H_2	CO	CO_2	176.13	93.463	362.07
1	1.3177	1e-4	1.3177	0.6821	0.3179			

The shift Process

Feed [mol]			Product [mol]		Heat ΔH [kJ]	Work ΔG [kJ]	T_{Carnot} [^oC]
H_2	CO	$H_2O_{(l)}$	H_2	CO_2	1.9099	-31.922	-256.32
1.3177	0.6821	0.6821	1.9998	0.6821			

Ammonia Synthesis Process

Feed [mol]		Product [mol]	Heat ΔH [kJ]	Work ΔG [kJ]	T_{Carnot} [^oC]
H2	N2	NH3	-61.461	-21.998	191.20
1.9998	0.6666	1.3332			

Ammonia Combustion to N_2 and $H_2O_{(l)}$

Feed [mol]		Product [mol]			Heat ΔH [kJ]	Work ΔG [kJ]	T_{Carnot} [^oC]
NH3	Air	N_2	$H_2O_{(l)}$	O_2	-510.08	-452.15	2352.3
1.3332	19.045	15.713	1.9998	2.9997			

Steam Cycle with heat removed at 620 ^oC

Q_{HE}[kJ]	T_{HE} [^oC]	W_{SC} [kJ]	η_{SC}	W_{Ptotal}[kJ]	η_{work}
-510.08	620	-339.81	0.75	-268.34	0.68

Combined Cycle process

T_C [^oC]	W_S[kJ]	P_{CC}[bar]	Q_{HE}[kJ]	T_{Rev}[^oC]	T_{HE} [^oC]	W_{CC} [kJ]	η_{cc}	W_{Ptotal}[kJ]	η_{work}
2611	-361.87	2000	-148.22	489.90	82.20	-385.69	0.85	-314.22	0.79
1300	-263.79	45.77	-246.29	994.60	166.10	-342.85	0.76	-271.38	0.69

We can show that using ammonia as fuel in a steam cycle power plant operating at a maximum temperature of 620^{o}C will result in approximately 25% of work potential being lost. We can also show that 68% (η_{work}) of the *work target* for coal to CO_2 can be reached via this route, taking into account the work required for gasification as well as the work that can be recovered in the ammonia production process. This does not show great improvement compared to syngas combustion to CO_2 and water liquid (η_{work} = 74%), also compared to direct coal combustion (η_{work} = 66%). Thus if a steam cycle is used to recover work then one would rather use direct coal combustion or the syngas route instead the ammonia route since it increases the process complexity and does not sensibly improve the work efficiency for coal to CO_2.

In a similar way as we have shown with syngas combustion (Fig. 4-10 and Fig. 4-11), one can shift the reversible temperature for ammonia combustion by combining mechanical work and heat transfer from the process, so as to approach the *work target* at low temperatures. We can show (Table 4-2) that by using a CC process one could move the reversible temperature for ammonia combustion from 2352 ^oC to about 490 ^oC by removing -361.87 kJ of mechanical work through the gas turbine. This would require the inlet gas turbine temperature and pressure to be approximately 2611 ^oC and 2000 bar respectively. If it is possible to reach these conditions then one could reach almost 85% work target for ammonia combustion (η_{CC}) and 79% work target for coal to CO_2 (η_{work}) via the ammonia route. However we can see from Table 4-2 that by using the current CC technology with inlet turbine temperature of 1300 ^oC, one can only reach η_{CC} and η_{work} of about 76% and 69% respectively. These efficiencies are close to those of ammonia combustion in a steam cycle operating at 620^oC (75% and 68%); therefore we see that the CC process in this case will have no impact in improving the process efficiency; this is mainly due to the large departure of T_{HE} from T_{Rev} when the inlet turbine temperature is 1300 ^oC (Table 4-2).

4.7 Co-production of Chemicals and Power

An alternative approach is ammonia combustion to form water and nitric acid, as shown in Equation 4.17, this process has a Carnot temperature of 823.7 ^oC; this temperature is closer to the steam cycle temperature (620 ^oC) and would be more efficient than the other routes considered earlier. The transformation of Coal to CO_2 via the nitric acid route is summarized in Table 4-3.

$$\begin{aligned} &NH_3 + 2O_2 \rightarrow HNO_{3(l)} + H_2O_{(l)} \\ &\Delta H(T_O, P_O) = -413.80 \tfrac{kJ}{mol} \\ &\Delta G(T_O, P_O) = -301.30 \tfrac{kJ}{mol} \end{aligned} \qquad 4.17$$

We can see from Table 4-3 that by using a steam cycle operating at 620 ^oC we can reach up to 92% (η_{SC}) of the work target for the combustion of ammonia to nitric acid and water liquid and up to 75% (η_{work}) the work target for coal to CO_2. On the other hand, by using a CC process with inlet gas turbine temperature of 1300 ^oC one can only reach 89% η_{SC} and 72% η_{work}. This is another case where work recovery with a steam cycle is more efficient than with a CC process. Table 4-3 also shows that the CC process would be advantageous if it could handle higher temperatures and pressures. As we can see at 2163 ^oC and 906 bar the CC process could reach 100% η_{SC} and 84% η_{work}.

Although syngas combustion seems to have a slightly higher efficiency (76% η_{work} in CC process) than ammonia combustion to nitric acid (75% η_{work} in a steam cycle), the advantage of this route is that, in addition to the work recovered one has a useful product that could eventually be converted to fertilizers. In fact if we take into consideration the work value of the end product, we can show that η_{work} for nitric acid route is 96% hence making it far more efficient than any other route we have considered. This illustrates the advantages of co-production of power and chemicals, as we can see, by combining power and nitric acid production from coal; it is possible to store about 21% of coal work potential into nitric acid, which would otherwise be lost by adopting other routes such as syngas combustion.

Table 4-3: Summary for work recovery when 1 mol of Coal (Carbon) is transformed to CO2 via ammonia combustion to nitric acid and water, with the stoichiometric amount of air for combustion in the CC process. Assuming gasification and all the intermediate steps are reversible. The steam cycle in the HRSG is also assumed to be reversible.

Gasification								
Feed [mol]			Product [mol]			Heat (ΔH)[kJ]	Work (ΔG)[kJ]	T_{Carnot} [^oC]
C	H_2O	O_2	H_2	CO	CO_2	176.13	93.463	362.07
1	1.3177	1e-4	1.3177	0.6821	0.3179			

The shift Process							
Feed [mol]			Product [mol]		Heat ΔH [kJ]	Work ΔG [kJ]	T_{Carnot} [^oC]
H_2	CO	$H_2O_{(l)}$	H_2	CO_2	1.9099	-31.922	-256.32
1.3177	0.6821	0.6821	1.9998	0.6821			

Ammonia Synthesis Process					
Feed [mol]		Product [mol]	Heat ΔH [kJ]	Work ΔG [kJ]	T_{Carnot} [^oC]
H2	N2	NH3	-61.461	-21.998	191.20
1.9998	0.6666	1.3332			

Ammonia Combustion to $HNO_{3(l)}$ and $H_2O_{(l)}$							
Feed [mol]		Product [mol]			Heat ΔH [kJ]	Work ΔG [kJ]	T_{Carnot} [^oC]
NH3	Air	$HNO_{3(l)}$	$H_2O_{(l)}$	N_2	-551.68	-401.68	823.51
1.3332	12.697	1.3332	1.3332	10.031			

Steam Cycle with heat removed at 620 ^oC					
Q_{HE}[kJ]	T_{HE} [^oC]	W_{SC} [kJ]	η_{SC}	W_{Ptotal}[kJ]	η_{work}
-551.68	620	-367.52	0.92	-296.05	0.75

Combined Cycle process									
T_C [^oC]	W_S[kJ]	P_{CC}[bar]	Q_{HE}[kJ]	T_{Rev}[^oC]	T_{HE} [^oC]	W_{CC} [kJ]	η_{CC}	W_{Ptotal}[kJ]	η_{work}
2163	-334.02	906.39	-217.66	159.68	158.53	-401.29	100	-329.83	0.84
1300	-213.67	22.28	-338.01	398.91	241.81	-358.18	0.89	-286.72	0.72

4.8 Summary

Table 4-4 compares the work efficiency as well as the resulting reduction in CO_2 emission for different chemical routes from coal to CO_2. The reference for reduction in CO_2 is determined by direct coal combustion because it has the lowest work efficiency. Hence its CO_2 reduction is zero. A chemical route capable of recovering the entire work target for coal to CO_2 will have 33.5% CO_2 reduction.

Table 4-4: Summary of various coal combustion routes: Comparison of work efficiencies and reduction of CO_2 emission.

	Work Recovered kJ/mol	η_{work} overall efficiency from Coal to CO_2	Main Products	% CO_2 Reduction
Work Target C to CO_2	-394.36	1		33.5
Direct Coal Combustion	-262.15	0.66	CO_2	0
IGCC (Syngas combustion)	-299.08	0.76	CO_2, H_2O	12.3
Ammonia combustion to Nitrogen	-271.38	0.69	CO_2, H_20, N_2	3.4
Ammonia combustion to nitric acid	-296.05(-376.75)	0.75 (0.96)	CO_2, H_20, HNO_3 (Fertilizers)	11.5 (30.4)

Among the chemical routes we have discussed, the Syngas route (IGCC) has the highest work efficiency and the highest reduction in CO_2 emissions; it has the potential to improve coal combustion by about 10% and has relatively low process complexity as shown in Fig. 4-12.

The ammonia route leading to nitrogen and water has the lowest efficiency and lowest reduction in CO_2 emissions. This route seems to have no advantage since it only improves coal combustion by 3% and leads to increased process complexity.

The ammonia route leading to nitric acid and water seems to be the most attractive, having the potential to improve coal combustion by 9% it also has the potential to produce nitric acid which could eventually be converted to fertilizers. Therefore in principle this route has the highest efficiency and highest reduction in CO_2 emission, since it allows locking the work that is not recovered as mechanical work into a useful product. The other chemical routes are not capable of recovering or saving this work potential.

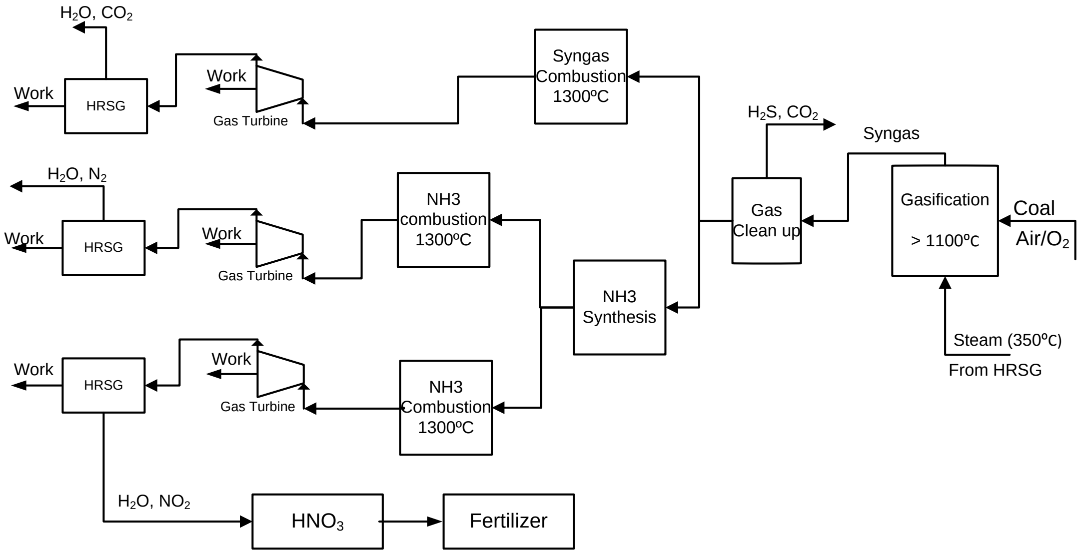

Fig. 4-12: Flow-digaram representing alternative routes for coal combustion

4.9 Conclusion

Coal potential is twofold: energy and useful products. We have shown that it is impossible to produce work efficiently from coal combustion as well as from most carbon based materials. By adopting other chemical routes for coal combustion, it is possible to efficiently recover work using available technology and there is opportunity to produce useful products, which would otherwise be lost in direct combustion. This manuscript has demonstrated the potential benefits of co-production of power and chemicals. Power plants should not be limited to energy production only, but research must be conducted to identify which chemical path will allow better work recovery in addition to useful by-products. Ammonia is one of the possible paths which could lead up to 9% CO_2 reduction in power plants in addition to fertilizers production. This is a possible win-win situation in addressing the issues of environmental sustainability associated with increasing food and energy demand. A study by Zamfirescu et al. (2009), has also shown that ammonia is a potential fuel with better environmental and economic advantages compared to conventional fuels.

It is important to note that finite-time thermodynamics models provide a better match for observed efficiency in energy production processes; however it interprets efficiency in the same way as the classical Carnot type model, notably looking at how much heat is converted into work. This manuscript proposes a more fundamental approach to efficiency which looks at how much of the work contained in a chemical transformation can be recovered as useful mechanical work. This approach has shown that significant improvement can be achieved by selecting appropriate routes for chemical transformations; therefore research should focus more on this aspect of power production. However it would be interesting to look at the results that can be obtained by applying finite-time thermodynamics to the analysis presented in this manuscript; this could be the object of another study.

References

Aljundi, I.H. 2009, "Energy and exergy analysis of a steam power plant in Jordan", *Applied Thermal Engineering,* vol. 29, no. 2-3, pp. 324-328.

Ameri, M., Ahmadi, P. & Hamidi, A. 2009, "Energy, exergy and exergoeconomic analysis of a steam power plant: A case study", *International Journal of Energy Research,* vol. 33, no. 5, pp. 499-512.

Austin, G.T. 1984, *Shreve's Chemical Process Industries,* McGraw-Hill, New York.

Caton, J.A. 2000, "On the destruction of availability (exergy) due to combustion processes — with specific application to internal-combustion engines", *Energy,* vol. 25, no. 11, pp. 1097-1117.

Curzon, F.L. & Ahlborn, B. 1975, "Efficiency of a Carnot engine at maximum power output", *American Journal of Physics,* vol. 43, no. 1, pp. 22-24.

Denbigh, K.G. 1956, "The second-law efficiency of chemical processes", *Chemical Engineering Science,* vol. 6, no. 1, pp. 1-9.

Dti, U. 2006, *Advanced Power Plant Using high Efficiency Boiler/Turbine,* UK Department for Business, Innovation and Skills, Oxfordshire.

Efma, E. 2000, "Production of ammonia" in *Best Available Techniques for Pollution Prevention and Control in the European fertilizer Industry*, ed. E. Efma, European Fertilizer Manufacturers Association, Brussel.

Franco, A. & Casarosa, C. 2002, "On some perspectives for increasing the efficiency of combined cycle power plants", *Applied Thermal Engineering,* vol. 22, no. 13, pp. 1501-1518.

Ganapathy, T., Alagumurthi, N., Gakkhar, R.P. & Murugesan, K. 2009, "Exergy analysis of operating lignite fired power plant", *Jest,* vol. 2, no. 1, pp. 123-130.

Gao, L., Jin, H., Liu, Z. & Zheng, D. 2004, "Exergy analysis of coal-based polygeneration system for power and chemical production", *Energy,* vol. 29, no. 12-15, pp. 2359-2371.

Hussein, I.b., Yusoff, M.Z.b. & Boosroh, M.H. 2001, "Exergy analysis of a 120 MW thermal power plant", *Proceesings of the BSME-ASME International Conference on Thermal Engineering*Dhaka, Bangladesh, pp. 177.

Ishida, M., Zheng, D. & Akehata, T. 1987, "Evaluation of a chemical-looping-combustion power-generation system by graphic exergy analysis", *Energy,* vol. 12, no. 2, pp. 147-154.

Kaggerud, K.H., Bolland, O. & Gundersen, T. 2006, "Chemical and process integration: Synergies in co-production of power and chemicals from natural gas with CO2 capture", *Applied Thermal Engineering,* vol. 26, no. 13, pp. 1345-1352.

Koroneos, C., Haritakis, I., Michaloglou, K. & Moussiopoulos, N. 2004, "Exergy Analysis for Power Plant Alternative Designs, Part I", *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects,* vol. 26, no. 13, pp. 1277-1285.

Li, H., Hong, H., Jin, H. & Cai, R. 2010, "Analysis of a feasible polygeneration system for power and methanol production taking natural gas and biomass as materials", *Applied Energy,* vol. 87, no. 9, pp. 2846-2853.

Liu, G., Li, Z., Wang, M. & Ni, W. 2010, "Energy savings by co-production: A methanol/electricity case study", *Applied Energy,* vol. 87, no. 9, pp. 2854-2859.

Manninen, J. & Zhu, (.X.X. 1999, "Optimal flowsheeting synthesis for power station design considering overall integration", *Energy,* vol. 24, no. 6, pp. 451-478.

Manninen, J. & Zhu, X.X. 1998, "Thermodynamic analysis and mathematical optimisation of power plants", *Computers & Chemical Engineering,* vol. 22, no. Supplement 1, pp. S537-S544.

McGlashan, N.R. 2008, "Chemical-looping combustion- a thermodynamic study", *Journal of Mechanical Engineering Science,* vol. 222, no. 6, pp. 1005-1019.

Mitrović, D., Zivkovic, D. & Laković, M.S. 2010, "Energy and Exergy Analysis of a 348.5 MW Steam Power Plant", *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects,* vol. 32, no. 11, pp. 1016.

Normann, F., Thunman, H. & Johnsson, F. 2009, "Process analysis of an oxygen lean oxy-fuel power plant with co-production of synthesis gas", *Energy Conversion and Management,* vol. 50, no. 2, pp. 279-286.

Patel, B., Hildebrandt, D. & Glasser, D. 2004, "Overcoming the Overall Positive Free Energy of a Process: Using the Second Law to understand how this is Achieved", *AIChE Annual Meeting*AIChE, Austin, November.

Patterson, M.G. 1996, "What is energy efficiency? : Concepts, indicators and methodological issues", *Energy Policy,* vol. 24, no. 5, pp. 377-390.

Regulagadda, P., Dincer, I. & Naterer, G.F. 2010, "Exergy analysis of a thermal power plant with measured boiler and turbine losses", *Applied Thermal Engineering,* vol. 30, no. 8-9, pp. 970-976.

Rosen, M.A. 2002, "Assessing energy technologies and environmental impacts with the principles of thermodynamics", *Applied Energy,* vol. 72, no. 1, pp. 427-441.

Rosen, M. & Bulucea, C.A. 2009, "Using Exergy to Understand and Improve the Efficiency of Electrical Power Technologies", *Entropy,* vol. 11, no. 4, pp. 820-835.

Rosyid, H., Koestoer, R., Putra, N., Nasruddin, Mohamad, A.A. & Yanuar 2010, "Sensitivity analysis of steam power plant-binary cycle", *Energy,* vol. 35, no. 9, pp. 3578-3586.

Sempuga, B.C., Hausberger, B., Patel, B., Hildebrandt, D. & Glasser, D. 2010, "Classification of Chemical Processes: A Graphical Approach to Process Synthesis To Improve Reactive Process Work Efficiency", *Industrial & Engineering Chemistry Research,* vol. 49, no. 17, pp. 8227-8237.

Sempuga, B.C., Hildebrandt, D., Patel, B. & Glasser, D. 2011, "Work to Chemical Processes: The Relationship between Heat, Temperature, Pressure, and Process Complexity", *Industrial & Engineering Chemistry Research,* vol. 50, no. 14, pp. 8603-8619.

Szargut, J. 1980, "International progress in second law analysis", *Energy,* vol. 5, no. 8-9, pp. 709-718.

Taniguchi, H., Mouri, K., Nakahara, T. & Arai, N. 2005, "Exergy analysis on combustion and energy conversion processes", *Energy,* vol. 30, no. 2-4, pp. 111-117.

Zamfirescu, C. & Dincer, I. 2009, "Ammonia as a green fuel and hydrogen source for vehicular applications", *Fuel Processing Technology,* vol. 90, no. 5, pp. 729-737.

5 A MODIFIED APPROACH OF THE gh-DIAGRAM

Liquefied Natural Gas (LNG) Process

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5.1 Abstract

In previous chapters the *gh-diagram* has been used to analyse reactive processes where it was assumed that the reactor is the major source or sink of work and where the feed and the product enters and leaves at ambient temperature and pressure. This chapter introduces the *eh-diagram*, a modified approach to the gh-diagram, where processes are represented in an exergy-enthalpy space. The eh-diagram allows analyzing the heat and work requirement for processes where the reactor is not necessarily the main source or sink of energy and where the feed and product are not restricted to ambient conditions. Processes can be classified in different thermodynamic regions on the eh-diagram in the same manner as on the gh-diagram. The approach is applied to liquefied natural gas process (LNG) to determine the optimum work target for the process as well as determine the optimal paths for refrigeration systems.

5.2 Introduction

Natural gas is one of the most important commodities in the global market. Oil is the leading source of energy; however coal and natural gas contribute almost 50% of the energy source (Al-Sobhi, Alfadala & El-Halwagi 2009). Natural gas is becoming more attractive due to its environmental advantages compared to other fossil fuels such as coal and oil. CO_2 is produced from coal and oil at an approximate rate of 1.4 to 1.75 higher than that produced from natural gas. Furthermore NO_X produced from burning natural gas are approximately 20% less than those produced from burning coal and oil (Kidnay, Parrish 2006). Natural gas is often found in remote locations and sometimes requires long distance transportation to utilization sites. It is either transported as a gas by pipeline or as Liquefied Natural Gas (LNG) using insulated tankers. The mode of transportation used is much dependent on the distance over which natural gas must be transported as well as on the cost of transportation (Delano, Gulen & Foss 2003).

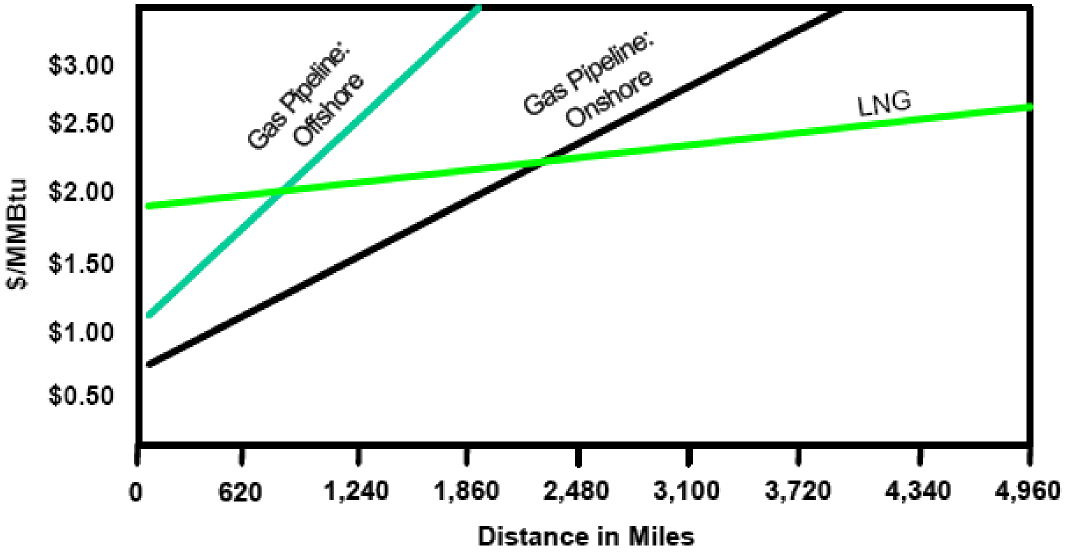

Fig. 5-1: Transportation cost of Natural Gas (NG) and Liquefied Natural Gas (LNG) as a function of distance (Delano, Gulen & Foss 2003).

We can see from Fig. 5-1 that as the distance over which natural gas must be transported increases, LNG has low transportation cost compared to the usage of pipelines. Since most of the natural gas reserves are located in remote area, LNG offers greater trade flexibility than pipeline transport, allowing natural gas to be delivered where the need is greatest and the commercial terms are most competitive.

LNG is produced by condensation of natural gas. Methane is the principal element of natural gas but may also contain ethane, propane and heavier hydrocarbons. Small quantities of nitrogen, oxygen, carbon dioxide, sulfur compounds and water may also be found in natural gas. The typical natural gas composition is approximately 82% methane (Delano, Gulen & Foss 2003). LNG is produced by a sequence of processing steps that transform natural gas from gas phase to liquid phase while getting rid of the undesirable substances (Shukri 2004). The final composition for LNG is usually determined by the market specifications (Al-Sobhi, Alfadala & El-Halwagi 2009).

5.3 The LNG Process

LNG is produced by cooling and liquefying natural gas, and is stored at a temperature of about -161^{o}C and at atmospheric pressure. The process and utility requirement depend on the site conditions, feed gas quality and product specification. An example of a typical LNG process is shown in Fig. 5-2 (Shukri 2004).

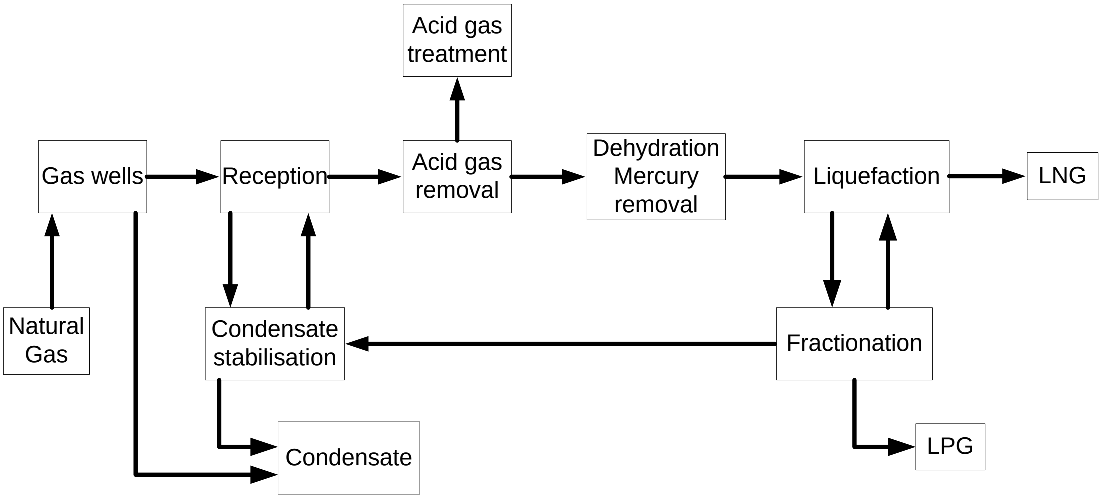

Fig. 5-2: Flow diagram for a typical LNG process (Shukri 2004).

The feed gas is delivered at high pressure (up to 90 bar) from upstream gas fields. Any condensate associated with the gas is removed, and then the gas is pre-treated to remove any impurities that are undesirable in the final product or that could cause problems in the process. These impurities include acid gas, sulfur compounds, water and mercury. The gas is then cooled to separate heavier hydrocarbons. The remaining gas, containing mainly methane, is further cooled to approximately -161^{o}C and is completely liquefied and is stored at atmospheric pressure.

In this manuscript we will focus on the refrigeration and liquefaction part which is the key element of the LNG process.

The cooling and liquefaction of natural gas is generally done in a sequence of refrigeration cycles. The number of cycles is a key factor in the success of liquefaction process. To make the cold temperatures required for the LNG, work must be supplied to the refrigeration cycles and heat must be rejected from the cycles. The process is work intensive, and thus energy efficiency is important as feed gas is consumed in order to carry out the liquefaction process (Remeljej, Hoadley 2006). Most of the existing LNG technologies use closed cycles, where external source of refrigeration is used to cool the natural gas in a number of steps until it liquefies. The external source of refrigeration uses a refrigerant (mixed or pure component) to create the cooling effect by compressing and expanding the refrigerant in a cycle. Among the known existing LNG technologies include (Shukri 2004):

- *APCI Propane pre-cooled mixed refrigerant process*: this process uses two main refrigerant cycles. The precooling cycle uses a pure component, propane, to cool the natural gas down to - 40°C. The liquefaction and sub-cooling cycle uses a mixed refrigerant composed of nitrogen, methane, ethane and propane, to cool the gas from -40°C to between -150°C and -160°C.
- *Phillips optimized cascade process*: In this process refrigeration and liquefaction on natural gas is achieved in a cascade process using three pure component refrigerants; propane ethylene and methane, each at two or three pressure levels.
- *Black & Veatch PRICO process*: This process uses a single mixed refrigerant composed of nitrogen, methane, ethane, propane and iso-pentane. The cooling and liquefaction is carried out at several pressure levels in cold boxes. The refrigerant is compressed and circulated using a single compression train.
- *Statoil/Linge mixed fluid cascade process*: In this process three refrigerants are used to provide the cool and liquefy natural gas. The first mixed refrigerant is used for precooling and the other two refrigerants are used for liquefaction and sub-cooling. The refrigerants are composed of components selected from methane, ethane, propane, and nitrogen.
- *Axens Liquefin process*: This process uses two mixed refrigerants composed of components selected from methane, ethane, propane, butane and nitrogen. The first mixed refrigerant is used to precool natural gas and

precool and liquefy the second mixed refrigerant. The second mixed refrigerant is used to liquefy and sub-cool the natural gas.

The basic principle behind all the above mentioned LNG processes consists of matching as closely as possible the cooling and the heating curves of natural gas and the refrigerant, so as to reduce thermodynamic inefficiency. Fig. 5-3 shows the cooling curve for natural gas and the heating curves for a refrigeration system using a mixed components refrigerant and a cascade refrigeration system using three different pure component refrigerants. We can see from Fig. 5-3 that the mixed refrigerant system comes closest to the natural gas cooling curve and therefore results in reduced thermodynamic inefficiencies because it minimizes the temperature different between the two fluids compared to pure component refrigerants (Kidnay, Parrish 2006).

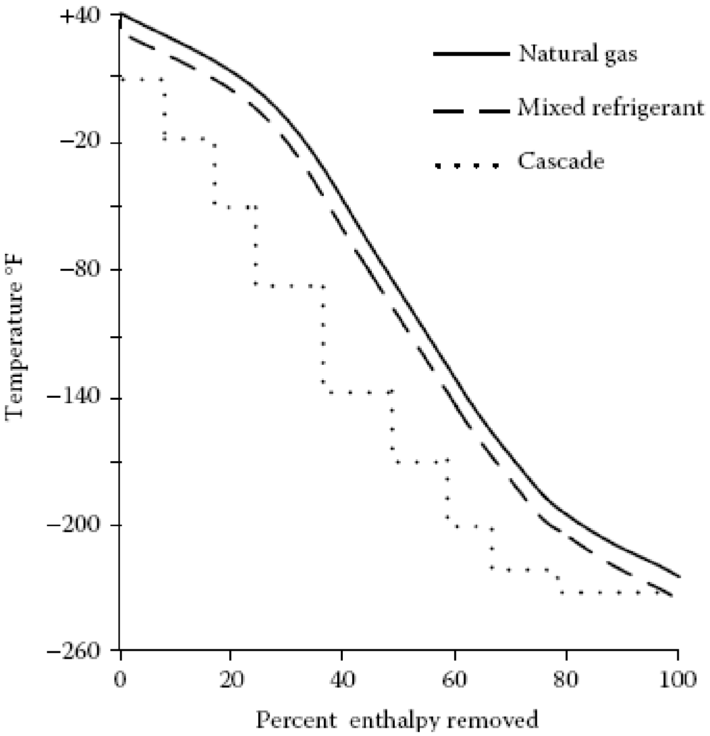

Fig. 5-3: Cooling curve for natural gas and the corresponding heating curves for the mixed refrigerant and cascade cycle with pure component refrigerants (Kidnay, Parrish 2006).

This manuscript presents an alternative way of analyzing LNG processes. The approach used is based on fundamental thermodynamic concepts and a graphical representation which can provide insight and information regarding the LNG process. The approach helps determining the targets for the process and can provide an idea of how these targets can be achieved. This approach is not only applicable to LNG processes but to any process that requires refrigeration.

5.4 LNG Process in the gh-diagram

Sempuga et al. (2010) have introduced a graphical representation of processes in the ΔH-ΔG space (gh-diagram) where processes are classified in different thermodynamic regions according to the directions of their work and heat requirements (Fig. 5-4).

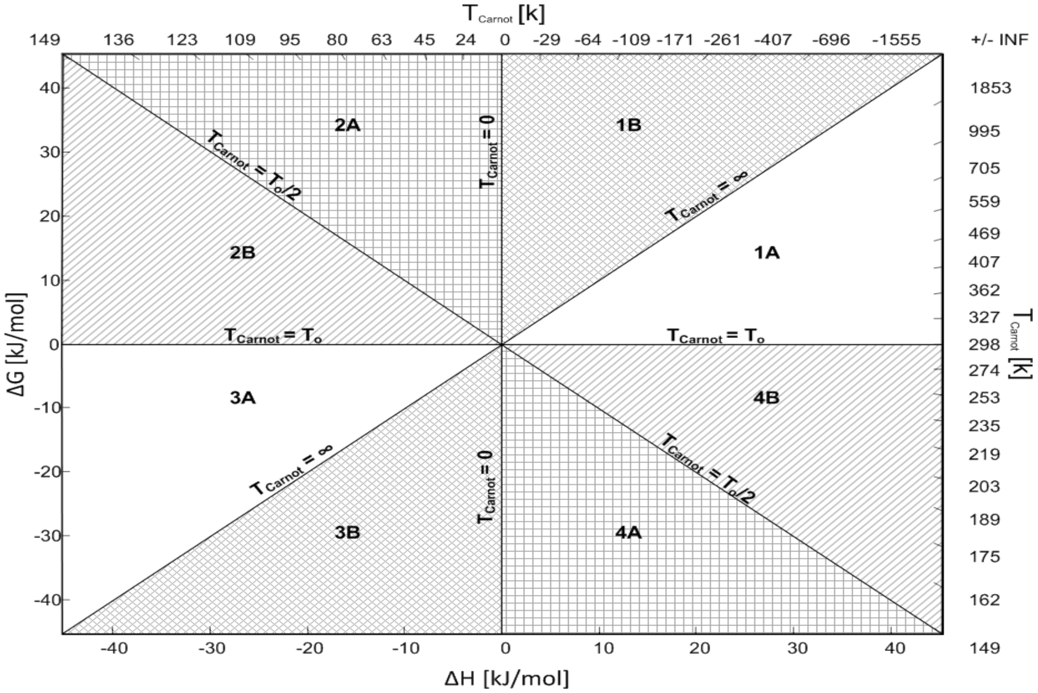

Fig. 5-4: Thermodynamic regions and process classification on the gh-diagram. Each region is identified by the direction of heat and work and the Carnot temperatures (Sempuga et al. 2010).

Previously we have mostly looked at processes in region 1 and 3. Now we will consider at process in region 2. It has been shown that Region 2 (that is 2A and 2B) of the gh-diagram represents processes that run below ambient temperature and reject heat and require a refrigeration system. LNG is one of these processes as It requires refrigeration systems in order to liquefy natural gas. The ΔH axis of region 2 on the gh-diagram gives the amount of heat to be absorbed, the ΔG axis gives the minimum amount of work needed to absorb the heat and the temperature scale gives the reversible refrigeration temperature. This can be shown in Fig. 5-5; a process located at point *m* (given by ΔH and ΔG across the process) would require that 14 kJ/mol of work be supplied, and this can be achieved by removing 10 kJ/mol of heat at 123 K; if this is done using a reversible refrigeration system then the net amount of work that would be consumed is 14 kJ/mol. The amount of work will increase as the temperature at which heat is removed decreases. For example at point *n* 10 kJ/mol of heat is removed at 80 K, therefore the minimum work required is 27 kJ/mol given by the intersection of line *o-n* and line *m-n*; we can see that if the same amount of heat needs to be removed at 0 K then an infinitely large amount of work will be required, this is shown by line *o-q* which can intercept line *m-n* only at an infinitely large value of ΔG.

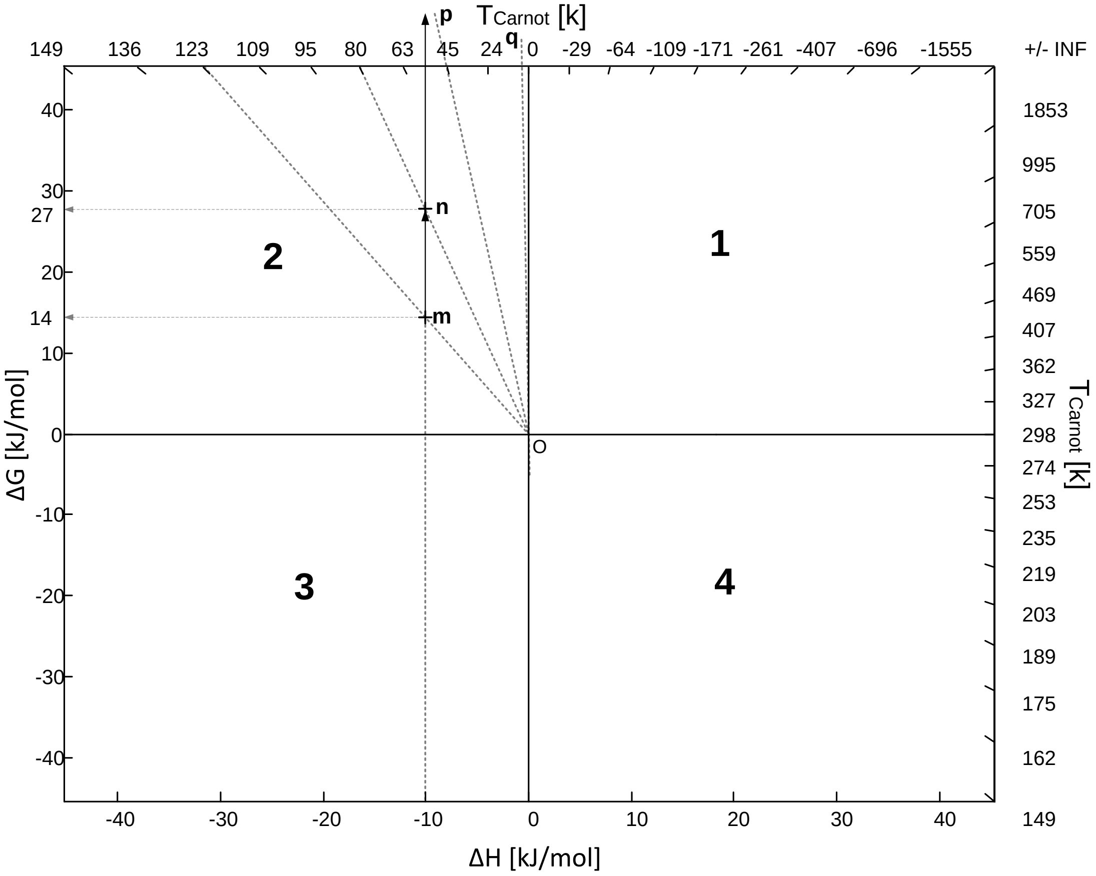

Fig. 5-5: Example of a refrigeration process represented in region 2. Points m and n shows the amount of work needed (ΔG axis) to remove heat (ΔH axis) at the Carnot temperature (Temperature scale)

So far the gh-diagram has been used to represent processes where the input and output streams are at ambient conditions of temperature and pressure, T_O and P_O respectively. In this case the amount of work required in order for the process to proceed is given by the change in Gibbs free energy at T_O and P_O (ΔG (T_O, P_O)) (Denbigh 1956). *Let us now consider processes where the input and output streams are at some other temperatures and pressures than T_O and P_O, as shown in Fig. 5-6.*

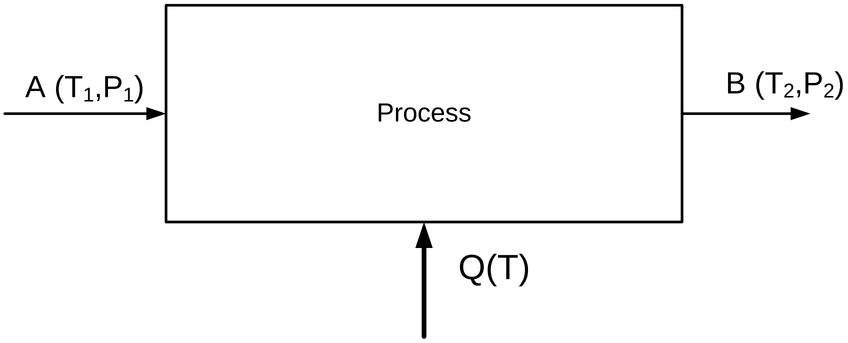

Fig. 5-6: A Simple process with input and output stream at other temperatures and pressures than ambient temperature and pressure T_O and P_O.

In this case, the work required to transform A to B is given by the change in exergy (ΔE) across the process (Remeljej, Hoadley 2006).

The energy and entropy balance across the process are given by Equations 5.1 and 5.2 where H(T,P) and S(T,P) are the enthalpy and entropy respectively, at temperature T and pressure P, and Q is the process heat requirement.

$$\Delta H = H(T_2, P_2) - H(T_1, P_1) = Q \tag{5.1}$$

$$\Delta S = S(T_2, P_2) - S(T_1, P_1) = \frac{Q}{T} \tag{5.2}$$

Exergy (E) is given by the following equation:

$$E = H(T, P) - T_O S(T, P) \tag{5.3}$$

Therefore the change in exergy (ΔE) is given by the following equation:

$$\Delta E = \Delta H - T_O \Delta S \tag{5.4}$$

Combining Equation 5.1 through to 5.5 gives:

$$\Delta E = \Delta H \left(1 - \frac{T_O}{T}\right) \tag{5.5}$$

If the input and the output of the process are given, then ΔE and ΔH are known and therefore there is a unique value of T at which Equation 5.5 will hold. We will refer to this temperature as the Carnot temperature (Sempuga et al. 2010) it is the unique temperature at which the heat requirement must be supplied in order to satisfy the work requirement of the process. In a similar way as processes are represented in ΔH-ΔG diagram (gh-diagram), we can also represent processes in the ΔH-ΔE diagram (eh-diagram); here the input and output to the process are not restricted to ambient conditions. We can also identify the same thermodynamic regions in the eh-diagram as in the gh-diagram.

We will now see that when we represent the LNG process in the eh-diagram, this can provide insight regarding the process and also provide a framework where alternatives can quickly be evaluated.

Since natural gas is mainly composed of methane, in the following discussion we will use the thermodynamic properties of methane to represent natural gas.

When we represent natural gas at various temperatures and pressures in the ΔH-ΔE domain this will form a surface which will be located in region 1 and region 2 of the eh-diagram. However, in this discussion we will only look at the part of the surface which is in region 2 as shown in Fig. 5-7.

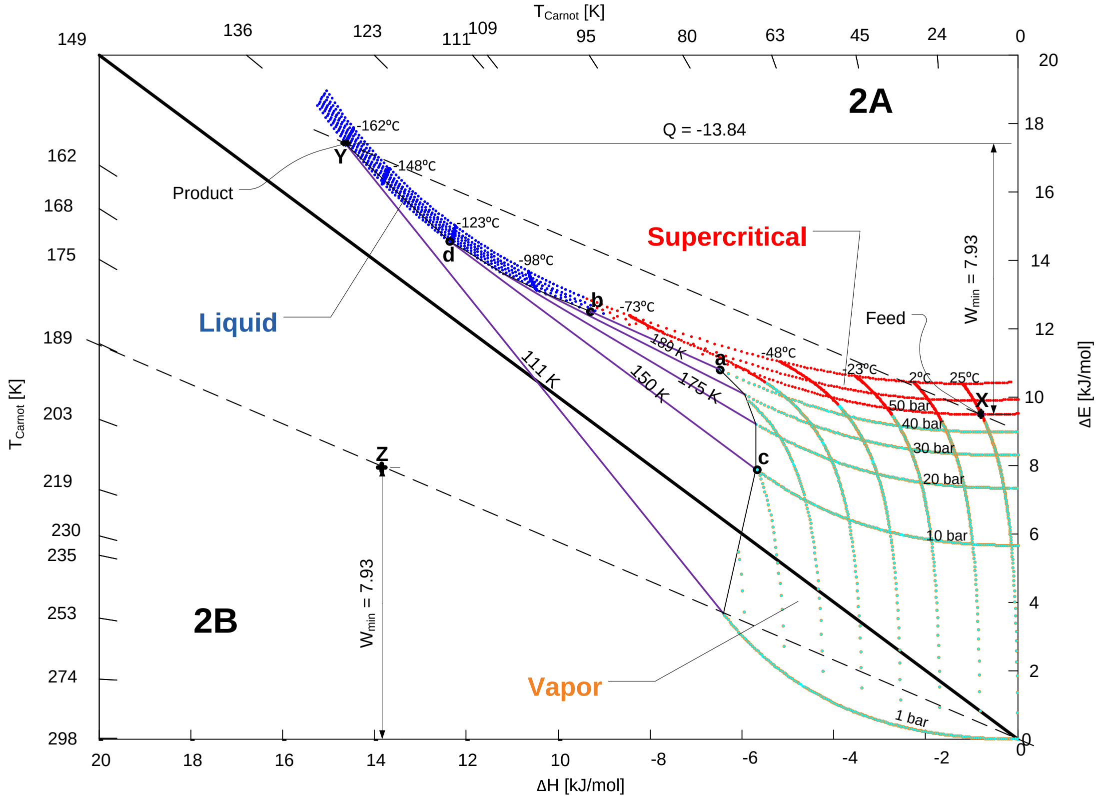

Fig. 5-7: Natural gas at different temperatures and pressures represented on the eh-diagram. The basis is the natural gas enthalpy (H) and entropy (E) are zero at T_O and P_O. Colors are used to distinguish the different phases. Liquid, vapor, and supercritical

We will explore the usefulness of the eh-diagram (Fig. 5-7) in the LNG process by looking at an example. Let us suppose that the feed to the process is natural gas (NG) at 25°C and 50 bar; this is located at point *X* on the eh-diagram in Fig. 5-7. The product is liquefied natural gas (LNG) at -161°C and 1 bar; this is located at point *Y* on the eh-diagram. The minimum amount of work that the process requires to move from *X* to *Y* is given by the change along the ΔE axis and is W_{min} = 7.93 kJ/mol. This represents the work target for any route chosen to go from *X* to *Y*.

W_{min} can be supplied to the process by removing heat at the Carnot temperature. This can be seen on the eh-diagram in Fig. 5-7; the Carnot temperature is obtained by subtracting *X* from *Y* to get point *Z*, and then the temperature is found at the intersection of line *O* – *Z* with the temperature scale. Note that line O – Z is parallel to line *X* – *Y*. Thus the Carnot temperature can be alternatively obtained by drawing a line parallel to *X* – *Y* from the origin to the temperature scale. This will give a temperature of 189 K (-84°C). This means that if we are able to remove the process heat (-13.83 kJ/mol) at the Carnot temperature (189 K), we would be able to reversibly liquefy NG. However we might need to manipulate the process stream to get it to the final state (111 K and 1 bar) by using heat exchangers and expanders and the process must be fully heat and work integrated internally such that only the process heat (-13.83 kJ/mol) at the Carnot temperature (189 K) is exchanged with an external refrigeration system as shown in Fig. 5-8. On the other hand, in order for the refrigeration system to be reversible it must absorb the heat from the process at the process temperature and heat must be rejected from the refrigeration system at ambient temperature. In that case the refrigeration system will require an amount of work equivalent to W_{min}.

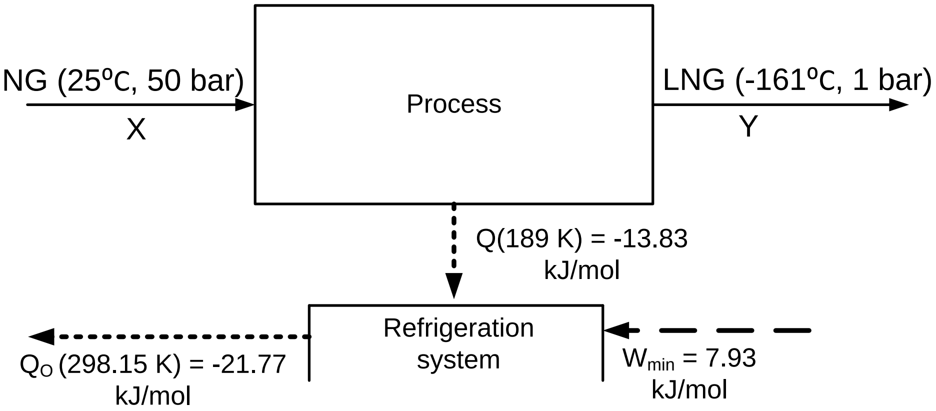

Fig. 5-8: Schematic diagram Supplying work to a LNG process using a refrigeration system: Minimum work is supplied to the LNG process by removing heat at an appropriate temperature

Note that heat can be transferred at single temperatures only in the two-phase region of the natural gas envelop in Fig. 5-7. Thus for the process in Fig. 5-8, heat must be exchanged with the refrigeration system along line *a* – *b* (at 189 K) on the eh-diagram (Fig. 5-7) and the process route will be as follows: *X* – *a* – *b* – *Y*. However the process must be manipulated internally such that the amount of heat between *X* – *a* and between *b* – *Y* are rejected from the process only along line *a* – *b*; this might require a certain combination of recycles, heat exchangers, expanders and flashes as well as multiple points of heat transfers with the refrigeration system all happening at 189 K.

Alternatively the process could be split into multiple processes using different refrigeration systems. For example the process could be split into three processes (Fig. 5-8); the first process would go from *X* to *c*, the second from *c* to *d* and the third process, from *d* to *Y*. Each process with its own refrigeration system as shown in Fig. 5-9

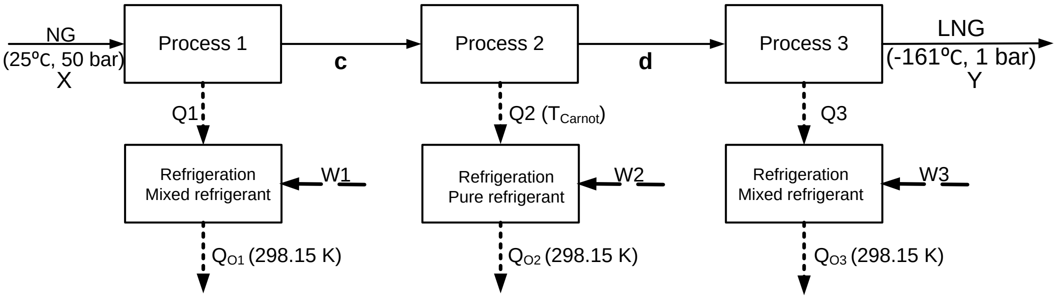

Fig. 5-9: The LNG process split into three different processes, each with its own refrigeration system

Operations in Process 1 might involve expanding and cooling NG to move it from *X* to *c*. However cooling in this region must be done over a range of temperatures; this could be a source of irreversibility. In light of the diagram in Fig. 5-3 it would be preferable to use a refrigeration system with a mixed refrigerant in order to reduce irreversibilities. Process 2 would operate in the two-phase region (*c* – *d*) where heat is removed at a single temperature. Thus in order for the process to be reversible, it would be preferable to use a refrigeration system with a pure refrigerant, since both the refrigerant and the process gas would change phase at a single temperature. Process 3 will also require cooling over a range of temperatures to move from *d* to *Y*. Thus in a similar way as in process 1, a mixed refrigerant system would be preferable in order to reduce irreversibilities.

Note that the temperature of any point in the two-phase region on the eh-diagram corresponds with its Carnot temperature; this can be seen in Fig. 5-10: line $e - Y$ is the vapor-liquid line of NG at 1 bar and 111 K, this line is parallel to line $O - p$ indicating that each point of line $e - Y$ has a Carnot temperature of 111 K. Similarly the vapor-liquid line at 10 bar and 150 K, line $c - d$, is parallel to line $O - q$ indicating that each point on line $c - d$ has a Carnot temperature of 150 K. This means that it is only in this region where work can be transferred reversibly to the process by removing heat at a single temperature and in one step. In other words, the two-phase region is the only region in the envelope where cooling can be done reversibly; thus a pure refrigerant system must be used in order to transfer heat at a single temperature. The other regions (liquid, vapor, and supercritical), will require cooling to be done over a range of temperatures, and therefore mixed refrigerants that approximate the cooling curves in these regions must be used in order to reduce irreversibilities.

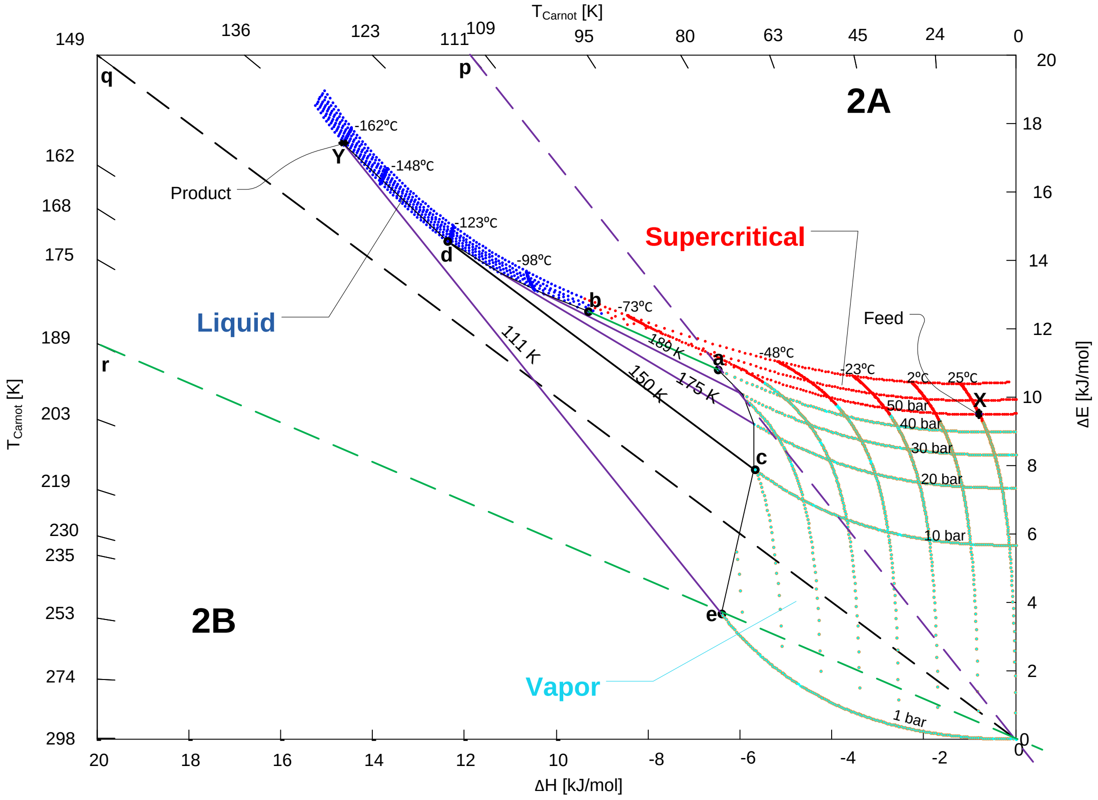

Fig. 5-10: Natural gas on the eh-diagram: The temperatures in the two-phase region correspond to the Carnot temperatures

Furthermore minimum work requirement for refrigeration systems is achieved when the cycle operates in the two phase region at all times. Consequently the refrigerant must be partially evaporated before compression and partially liquefied before expansion. Irreversibilities occur when liquefaction and evaporation are not conducted at a single temperature.

Fig. 5-11 (A) is a schematic representation of existing refrigeration cycles. The refrigerant in vapor phase is compressed to a pressure P_h and reaches a temperature T_{h1}; the gas is then liquefied by cooling it to a temperature T_{h2}. The liquefied refrigerant is then expanded, through a valve, to a pressure P_C where it evaporates partially. The mixed phase is then evaporated completely (usually at constant temperature) reaching a temperature T_C and pressure P_C before it is recompressed. The major source of inefficiency in these processes is in the liquefaction part since it occurs over a range of temperatures. We can show that the resulting temperature (T_{hot}) at which heat (Q_{out}) is removed during liquefaction is given by the log mean temperature between T_{h1} and T_{h2} (Equation 5.6).

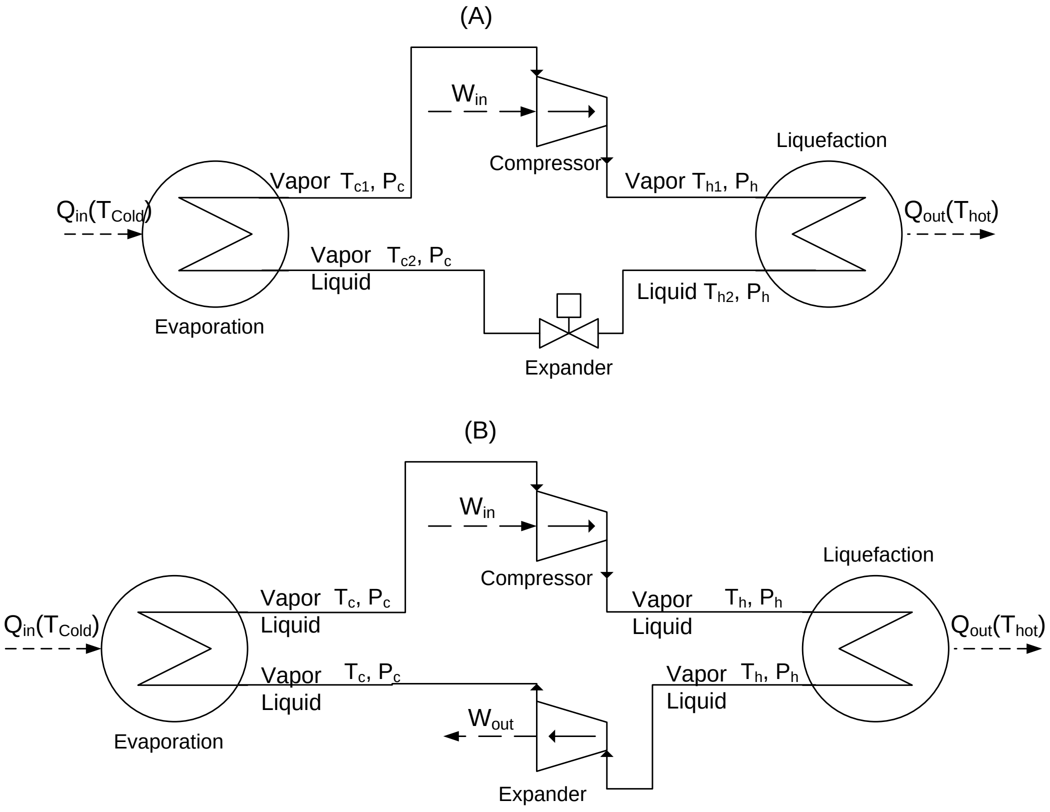

Fig. 5-11: Schematic representation of refrigeration cycles. (A) In conventional refrigeration cycle the refrigerant is compressed in the vapor region consequently liquefaction and evaporation are conducted at multiple temperatures. (B) Compression and expansion are conducted in the two phase region consequently liquefaction and evaporation are conducted a single temperature and thus minimum work requirement is achieved

$$T_{hot} = \frac{\left(T_{\mathrm{h1}} - T_{\mathrm{h2}}\right)}{\ln \dfrac{T_{\mathrm{h1}}}{T_{\mathrm{h2}}}} \qquad 5.6$$

In most cases irreversibility arises because T_{hot} does not match the Carnot temperature (T_{Carnot}) of the liquefaction unit. T_{Carnot} has been previously defined as the temperature at which heat must be transferred for the process to be reversible and can be obtained by rearranging Equation 5.5 as follows:

$$T_{Carnot} = \frac{T_O}{1 - \frac{\Delta E}{\Delta H}} \quad 5.7$$

Where T_O is the ambient temperature and ΔE and ΔH are the change in exergy and change in enthalpy across the unit respectively.

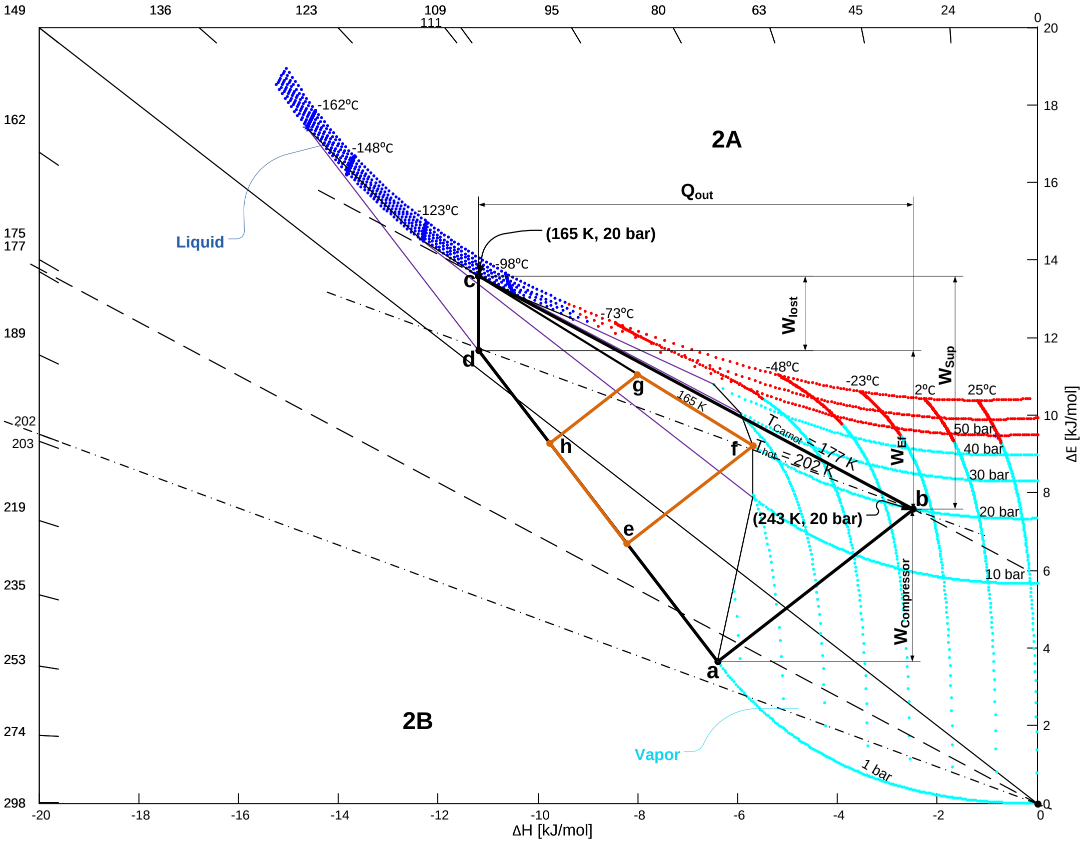

Fig. 5-12: Refrigeration cycle on the eh-diagram. For path a-b-c-d, work is lost when cooling is done at multiple temperatures between b and c T_{Carnot} does not correspond to the actual temperature T_{QH} at which heat is removed, therefore more work (W_{Sup}) than necessary (W_{Ef}) is supplied to the process, and the process becomes irreversible. Every point in path e-f-g-h corresponds with the Carnot temperature; therefore no work is lost and the process is reversible.

As an illustration consider a refrigeration cycle represented on the eh-diagram in Fig. 5-12 where the refrigerant is methane. The refrigeration path, a-b-c-d corresponds to the path on the diagram in Fig. 5-11 (A). The gas is compressed isentropically from

1 bar (a) to 20 bar (b) reaching a temperature T_{h1} = 243 K. The gas is then cooled at constant pressure and liquefies at a temperature T_{h2} = 165 K (c). The Carnot temperature between b and c is T_{Carnot} = 177 K and the log mean temperature is T_{hot} = 202 K. We therefore see that the work supplied to move directly from b to c is W_{Sup} = 6.01 kJ/mol which correspond to heat (Q_{out} = -8.75 kJ/mol) being removed at 177 K. However in the actual process heat (Q_{out}) is being removed at 202 K and this corresponds to the effective work requirement of the process W_{Ef} = 4.17 kJ/mol. The work lost during liquefaction is W_{lost} = 1.84 kJ/mol. This work lost is the penalty for moving from b to c in one step. The work lost could be minimized if the gas is cooled progressively between b and f until it reaches the dew point, followed by liquefaction at constant temperature of 165 K.

On the other hand the refrigeration path e-f-g-h (Fig. 5-12) is in the two phase region and corresponds to the path on the diagram in Fig. 5-11 (B). We can see that liquefaction and evaporation occur at constant temperatures 165 K and 111 K, and these temperatures correspond to their respective Carnot temperatures, therefore there is no work lost in the path. However to ensure that minimum work requirement is achieved one must use an expander that allows recovering the work of expansion which would otherwise be lost if a simple valve is used as in Fig. 5-11 (A) and thereby increasing the process irreversibility.

The major problem that could arise in implementing refrigeration in the two phase region is that most existing compressors and expanders operate efficiently only with vapor, and could result in major work losses when used in the two phase region. However screw compressors and expanders have shown to be able to handle two phase fluids at a relatively high efficiency (75%) (Smith, Stosic & Kovacevic 1999). With further studies these equipment have the potential to be adapted to refrigeration systems. More studies (Hundseid et al. 2008) are also being conducted on centrifugal compressors and expanders for their possible efficient use in handling two phase fluids.

5.5 Conclusion

We have introduced a graphical approach to analyze LNG processes. The use of the eh-diagram can allow determining the optimum work target for the process and how this can be achieved as well as determine the optimum temperatures at which heat must be removed from the process. Furthermore the approach can be useful in scanning different routes from NG to LNG and help determine the appropriate refrigerant for each step of the process in a more systematic way. The eh-digram can be used in the analysis and design of refrigeration cycles and can be used to match refrigerants in cascade refrigeration for optimum operation. We have also shown, by using the eh-diagram, that one of the possible ways for reaching minimum work requirement in refrigeration cycle is to operate in the two phase region at every point in the cycle. While most existing compressors and expanders cannot handle two phase fluids, numerous studies are being conducted in this regard and we see that the outcome of these studies could potential lead to much improved refrigeration systems.

References

Al-Sobhi, S.A., Alfadala, H.E. & El-Halwagi, M.M. 2009, "Simulation and energy integration of a Liquefied Natural Gas (LNG) plant", *1. Proceedings of the 1st Annual Gas Processing Symposium*, ed. A. Hassan, ELSEVIER, Quatar, 10-12 January.

Delano, F., Gulen, G. & Foss, M.M. 2003, *Introduction to LNG: An overview on Liquefied Natural Gas, its properties, the LNG industry, safety consideration*, Institute for Energy Law and Enterprise, University Houston.

Denbigh, K.G. 1956, "The second-law efficiency of chemical processes", *Chemical Engineering Science,* vol. 6, no. 1, pp. 1-9.

Hundseid, O., Bakken, L.E., Gruner, T.G., Brenne, L. & Bjorge, T. 2008, "Wet Gas Performance of a Single Stage Centrifugal Compressor", *1. Proceedings of ASME Turbo expo: Power for Land, Sea and Air, Berlin, 2008*International Gas Turbine Institute, Berlin, 9-13 June.

Kidnay, A.J. & Parrish, W.R. 2006, *Fundamentals of natural gas processing,* Taylor & Francis, Florida.

Remeljej, C.W. & Hoadley, A.F.A. 2006, "An exergy analysis of small-scale liquefied natural gas (LNG) liquefaction processes", *Energy,* vol. 31, no. 12, pp. 2005-2019.

Sempuga, B.C., Hausberger, B., Patel, B., Hildebrandt, D. & Glasser, D. 2010, "Classification of Chemical Processes: A Graphical Approach to Process Synthesis To Improve Reactive Process Work Efficiency", *Industrial & Engineering Chemistry Research,* vol. 49, no. 17, pp. 8227-8237.

Shukri, T. 2004, *LNG technology selection*, Palladian Publications, http://www.palladian-publications.com

Smith, I.k., Stosic, N. & Kovacevic, A. 1999, *Power Recovery from Low Cost Two-phase Expanders*, Centre for Positive Displacement Compressor Technology, Northampton Square, London.

6 CONCLUSION

This thesis presents a process synthesis tool that can provide insight and valuable information regarding a process without going into details. The tool allows determining the optimum target for a process and helps understanding what is required to achieve the target. The tool is suitable to be used in the early stage of process design as it could guide decision making toward more efficient processes.

The approach adopted in this thesis is based on the idea that for every process where certain feed materials are transformed into products, there are certain amounts of *heat* and *work* associated with it. Understanding the relationship between the *heat* and *work* for a process and how these can be transferred across the process is among the key factors to attain sustainability in the process industry.

In many cases, a process becomes inefficient because it consumes more *work* than necessary due to many factors including:

- Setting up wrong targets for the process or not setting/knowing what the targets are. These targets could be energy, mass, number of units which are set to obtain the most economic and environmental friendly process. However when one does not know what is achievable, then the targets set cannot guarantee optimality and may results in a much less efficient process.
- Production of undesirable products along with desirable ones. The potential impact of this on the environment and economics is twofold; firstly the undesirable products could become waste which could potentially be detrimental to the environment, secondly the process would require additional energy in the production of these waste products leading to unnecessary CO_2 emissions. This goes along with increased operating cost of

the process in a sense that the amount of feed material must be increased since part of it is turned into waste and the required rate of production of desirable products must be met. In addition the energy cost of the process is increased as well since part of it is consumed to produce these waste products.

- Loss of energy within the process as a result of poor energy integration or poor interconnections between different parts of the process, bad choice of operating conditions such as pressure and temperature or even bad choice of material transformation path or reaction path.

The tool developed in this work can be useful in tackling these above mentioned issues from the beginning of process design.

The tool uses fundamental thermodynamic concepts such as enthalpy, entropy and Gibbs free energy, combined with a graphical approach, to analyze the feasibility and reversibility of processes in terms of the *heat* and *work* associated with them.

It has been shown that chemical processes can be represented in the ΔH -ΔG space, which has been referred to as the '*gh-diagram*,' where the processes can be classified in different regions depending on the magnitude and direction of their heat and work requirements. While transferring heat across a process is relatively easy, transferring work is a major challenge and in many cases a major source of inefficiencies in the process. Heat by virtue of its temperature can transfer work across the process; it is the simplest way of transferring work, however this is not applicable in all cases. The incorrect use of the concept can results in major irreversibilities in the process. With the gh-diagram, the process designer can identify where the concept can be applied without or with less work losses. The gh-diagram requires knowledge of the enthalpy and the Gibbs energy change across the process only, and therefore any number of processes can be simultaneously analyzed on a single diagram, hence it allows scanning of many possible routes for desired products.

Further works, still in progress, have used the gh-diagram to synthesis a Fischer Tropsch flowsheet which has more than 100% carbon efficiency; a patent application for the proposed flowsheet has been submitted. More works in progress have used the gh-diagram to analyze reactions in a methanol synthesis reactor; the work has demonstrated that the mass region in an extent of reaction domain can be extended to the gh-diagram to analyze the feasibility of reaction paths and to study how the paths can be manipulated in order to achieve the desired extents of reaction. We believe that the gh-diagram has a wide range of applications many of which are still to be discovered.

We have used the gh-diagram to analyze different ways work can be transferred across a process and the following results were observed:

1. Work can be transferred reversibly by having multiple points of heat transfer across the process. Different amounts of heat at different temperatures are transferred in a sort of a heat engine configuration thereby transferring work across the process. This technique is equivalent to having multiple steps for a process that cannot be feasible or reversible in a single step. The process can be split into multiple processes where work can be transferred efficiently using heat at an appropriate temperature. This is equivalent to moving a process in an infeasible region on the gh-diagram to a feasible one.
2. Work can also be transferred by adding mechanical work accompanied with multiple heat transfer across the process (MWMH) or by adding mechanical work accompanied with a single point of heat transfer across the process (MWSH); however this would require a change in number of moles of gas between the input and the output of the process. This technique provides, to some extent, one degree of freedom between the pressure and the

temperature at which heat is transferred. This results in multiple pairs of temperature and pressure where the process could be feasible and reversible.

The above two cases have allowed establishing the relationship between heat, work, temperature, and pressure and process structure complexity, the following can be concluded:

- The simplest structure for a process can be obtained when work is transferred via heat at a single temperature across the process. For every process there is a unique temperature (The Carnot temperature) at which heat can be transferred in order for the process to be feasible and reversible.
- When any other methods for transferring work (other than transferring work via heat at a single temperature) are used, then the process will be structurally complex. This is the case for processes with relatively high Carnot temperatures and those with negative Carnot temperatures. The higher the Carnot temperature and the less negative the Carnot temperature, the more difficult it is to transfer work and therefore the more complex the process structure would be.
- In some cases the pressure requirement for a process is a result of transferring the process heat at other temperatures than the Carnot temperature. As a consequence the process will become structurally complex.

An example of an ammonia process was used to demonstrate the above points and it was found that: 1) the simplest structure for an ammonia process can be derived when heat is transferred across the entire process at 190.8 °C and the process can be run reversibly. 2) The pressure requirement for an ammonia process is a result of transferring heat at temperatures above 190.8 °C, this is dictated by the activity temperature of the catalyst; therefore process pressure requirement will be influenced by the choice of the catalyst. We could also show that, ammonia processes seems to be more reversible when work is transferred by MWMH compared to when work is transferred by MWSH.

The gh-diagram was also used to analyze combustion in power production processes. It was found that for most carbon based fuels, combustion with oxygen cannot be run reversibly in one step. It has been shown that by adopting other chemical route for coal combustion (other than direct combustion with oxygen), it is possible to efficiently recover work using available technologies and that there could be opportunity to produce useful products. For example it has been shown that ammonia is one of the possible routes for coal combustion which could lead up to 17% CO_2 reduction in power plants in addition to fertilizers production.

Finally the gh-diagram was considered to analyze Liquefied Natural Gas (LNG) processes. This has led to the development of the eh-diagram (exergy and enthalpy space), which has the same properties as the gh-diagram, and does not limit the input and output streams of the process to ambient temperature and pressure as is the case with the gh-diagram. It was shown how the eh-diagram can be used to systematically identify possible steps in the liquefaction of natural gas and how one can systemically identify appropriate refrigerant for each step. For example it was shown that pure refrigerants would be preferable to use in the liquefaction step while mixed refrigerant would be preferable in the pre-cooling and sub-cooling steps of the process. Furthermore it was shown, by using the eh-diagram, that one of the possible ways for reaching minimum work requirement in refrigeration cycle is to operate in the two-phase region at every point in the cycle. While most existing compressors and expanders cannot handle two phase fluids, numerous studies are being conducted in this regard and we see that the outcome of these studies could potential lead to much improved refrigeration systems.

6.1 Final Remarks

It is important to note that some of the results obtained using this approach may not be practical due to lack of appropriate technology; however the approach could help identify where much improvement is needed and thereby identifying the focal points for research.

The approach has been used to analyze processes at the highest level with little details. Further developments are recommended which will possibly allow using the tool in detailed process design which could incorporate economic evaluation.

Separation is one of the most inefficient and energy consuming processes in the current process industry. For example distillation columns account for about 40% of energy involved in refining and other continuous chemical processes and this represent about 4% of the total energy consumption in the USA in 1998 (Olujic et al., 2003) and they have a low second law efficiency (5-20%) (Koeijer and Kjelstrup, 2000). Furthermore it has been estimated that a saving of 10% of the energy consumed in distillation applications is equivalent to the natural gas consumption of about 200,000 households annually (Olujic et al., 2003). Therefore there is strong need to improving energy efficiency of distillation.

We believe that the approach presented in this thesis could be valuable in analyzing the work requirement for distillation processes. We therefore recommend further development of the approach in order to identify possible ways of improving the efficiency of separation processes.

References

1. Koeijer, de G.; Kjelstrup, S. Minimising entropy production reate in binary tray distillation, International Journal of Applied Thermodynamics, 2000, 3 (3), 105 – 110.

2. Olujic, Z.; Fakhri, F.; Rijke, de A.; Graauw, de J.; Jansens, P.J. Internal heat integration – the key to an energy-conserving distillation column, Journal of Chemical Technology and Biotechnology, 2003, 78, 241 – 248.