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Work flow in reactive processes: systematic approach to process synthesis

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Work Flow In Reactive Processes

Systematic approach to Process Synthesis

Teta Bahunde

Johannesburg, 2014

A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfillment of the requirements for the degree of Master of Science in Engineering.

DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted to the Degree of Master of Science to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

_____
Teta Bahunde

_____ day of _____ 2014

ABSTRACT

The industrial sector's large energy use presents itself as a vast potential for energy saving and technology improvements, making it an attractive target for industrial sustainability through increased energy efficiency.

Process synthesis is a tool used early in the design stage of a process to generate flowsheets with optimized efficiency, environmentally friendly and economically viable. By understanding flowsheets design and parameters' effects on the flow of heat and work through a reactive process, one is able to create processes capable of utilizing heat and work efficiently.

Energy as heat and work is fundamental in the analysis of process performance. This dissertation therefore proposes two case studies which reflect investigations done on the effect of temperature, conversion and heat capacities on reactive processes.

Findings show that temperature, conversion affect the heat and work use across the process in such a way that they can be adjusted to minimize heat and work lost across the process or a unit. Work lost minimization is an indication that heat and work supplied to the process is being utilized rendering the process efficient. Findings also show that the larger the difference between the heat capacity at the stream going into the process and the heat capacity at the stream going out of the process, the larger the required temperature and conversion manipulations to produce an efficient process by minimizing work lost.

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1 INTRODUCTION

1.1 The Process Industry

For centuries now, fossil fuels (coal, oil, or natural gas) have been a source of energy as well as feedstock to industries. After the beginning of the eighteen hundreds, feedstock to relatively small commodity chemical industries consisted predominantly of coal. The introduction of oil and natural gas only followed during the nineteenth century, triggering a strong dependency of global chemical enterprises to fossil fuels (Narodoslawsky et al., 2006).

As predicted by Robert A. Linn (1984), today's chemical industry which is of interest for this study, is undergoing major changes as the industry's members rethink the way they operate in order to withstand severe constraints and complexities they face. Namely:

- Fierce global competition over the scarceness of the resource. The diminished availability of fossil fuels is driving the chemical industry to think about the way their businesses will function in the future. Narodoslawsky et al. (2006) have predicted a constant increase of crude oil prices as the increase in demand can no longer be offset by increasing production. Consequently, for its relatively global abundance, affordability and reduced greenhouse gas emissions, natural gas is increasingly sought after as feedstock to chemical industries.

- Environmental pollution. There has been growing environmental concerns related to carbon processing industries. In addition to Carbon dioxide (CO_2) emissions, poor management and disposal of wastes are also affecting our ecosystem. Following a decade of research on this topic, Steinberg (1994) believes that improved energy

utilization efficiency is one of the ways to considerably reduce Carbon dioxide emissions which make the largest part of greenhouse gas (GHG) emissions and is believed to be a major cause of global warming.

- Economic performance. The growing scarcity and increasing demand of fossil fuels are reflected by the rising costs of fossil fuels' exploration and exploitation over the years. The diversification of energy sources by the inclusion of renewable sources (water, sun, wind, biomass, geothermal) to the energy mix could be a solution to meet the global energy demand and hinder environmental pollution (Swift, 1999; Nel & Cooper, 2009). A desirable energy mix would guarantee a steady, clean, and low cost supply of energy which satisfies a balanced energy supply-demand model which is a fundamental part of the industrial development as well as a basis to economic growth.

- Global population growth. Global population and energy demand increase hand-in-hand (Abdelaziz et al., 2011). The forecast resulting from global population growth and increasingly scarce resources predicts a cycle of complexities where soon enough more soil will be needed for agriculture to feed the growing population; fossil fuels demand will soar and as a result challenge the supply to energy producers and industries. Integration of renewable resources to the energy mix could be the key in overcoming this challenge.

- Geopolitical forces disturbing the stability of the crude oil and gas market.

Steps toward the transformation of industries in view to synthesize processes with enhanced productivity, conservation of mass and energy, reduced GHG emissions, as well as reduced

operating and capital costs are evidently some of the most important responsibilities and challenges for our civilization.

1.2 The Process Industry's place within a Sustainable Development model

The term *"Sustainable development"* has been defined by the World Commission on Environment and Development (WCED) as

> *"The development that meets the needs of the present without compromising the ability of future generations to meet their needs"* - (WCED, 1987).

Its aim is to reach a balance between an economic viability, social equity, and environmental integrity such that economic growth offers a desirable quality of life to the population without damaging the environment.

A graphical representation of *Sustainability* is illustrated below as a "three circles" model and shows its economic, social and environmental dimensions.

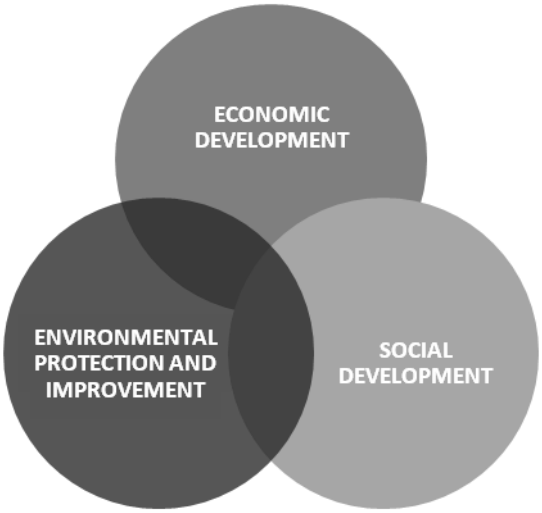

Figure 1-1. Graphical representation of Sustainability (Todorov & Marinova, 2011)

This model is also referred to as the "*Venn"* diagram or the "*three pillars"* model. It illustrates the relationship between economic, social, and environmental development which cannot be addressed individually when sustainable development is desired, but in an integrated manner. For instance, population change, energy, water as well as food demand are interlinked; finding a solution for one aspect of the problem could help solving the others.

Energy is not directly one of the three sustainability components shown in Figure 1-1, it is however linked to each as energy drives majorly -if not most of- the world's economic activities; it is sourced from the environment and its related wastes are released to the environment; and services created from the production and use of energy improve living standards which often support social stability and promote development.

Thus, since the process industry uses a large amount of energy consuming about 37% of the world's total delivered energy (Abdelaziz & al., 2011; Silveria & Luken, 2008) , it presents itself as a significant parameter within the sustainable model for improvements in its

renewability, efficiency, accessibility, distribution, use as well as in lowering its environmental impact tailored based on local social-economic-environmental conditions (Orecchini, 2011).

As a response to the constant population growth, for instance, increasing energy supply to the process industry is not the only solution to an unwavering energy future; reducing energy demand by improving energy and equipments' efficiency as well as industrial efficiency as a whole can also be a solution. Another solution could be to improve energy supply management via the development of an effective energy planning, adoption of energy efficiency and waste minimization incentive policies, as well as the adoption of GHG mitigation policies as other channels to meet the same outcome.

The development of a sustainable energy model that not only ensures steady lowest-priced and constant energy supply, but also avails necessary feedstock to the chemical industry is reinforced under the overall sustainability model in Figure 1-1 through the implementation of energy management frameworks, energy technologies, and tailored policies aiming at regulating the process industry. Such frameworks are often adapted in the form of environment impact assessment, energy auditing, energy pricing, physical control, Research & Development as well as educational methods (Munasinghe, 1983; Berrie, 1978).

On the demand side, applicable policies in aim to regulate the use of energy by the industry include GHG emission taxes, cap and trade schemes, green technology tax reductions, preferential loans, as well as subsidy among others (Tanaka, 2011).

1.3 Government - University - Industry link

Knowledge in the form of intellectual and human quality is a significant contributor to economic development. Similarly to the need for balanced interaction between the three dimensions of Sustainability in Figure 1-1, it is imperative that the three major entities playing a role in economic growth: Government-University-Industry, maintain a strong bond.

For many years now, it is common practice in developed countries as well as developing countries to have a dynamic transfer of knowledge from University to Industry and vice-versa. This flow of knowledge has an important impact on economic growth and supplies the means to meet social needs (Bekkers & Bodas-Freitas, 2008) by transforming knowledge into labor, physical capital, products, as well as processes (Mueller, 2006).

The University takes its place in the society in defining one's opportunity in reference to the quality of the education received, and in defining the level of operation of the labor market. It can also be viewed as a policy tool as it improves social mobility, adjusts the distribution of income within a society, and also helps in channeling compatible skills with their respective fields for optimum output to the industry and enhanced economic performance (Friedman, 2007). The term *University* is used here in its broader sense to refer to a higher level learning and research institutions with direct output to the industry.

A well coordinated relationship between the university and the industry is critical, and so is the role of the Government in ensuring that the flow of knowledge between the University and the Industry through the commercialization of valuable ideas and skills is supported by a favorable incentive structure which promotes schemes such as sponsored researches and consulting agreements with research institutions, as well as support for entrepreneurship

which in turn develops the industry by creating diversification and competitiveness. Other forms of incentives for innovation could also be applied to the inventor via compensation, recognition, royalties and equity.

The flow of knowledge and skills between the University and the Industry thus ensures that innovation is in constant expansion and the development of advanced technologies as well as ideas from both the University and the Industry is collective to improve efficiency and to withstand global competitiveness.

1.4 Scope of the study

The discussions covered in this introductory part of the dissertation highlight the importance of aggregated energy efficiency at the industry level complemented by policy regulations capable of offering a better quality of life, a sustainable economy as well as a preserved environment to the society. Later chapters of this dissertation elaborate on how chemical processes are generated and how specific thermodynamic parameters can be manipulated to reach optimal energy efficiency hence improving industrial performance as a whole.

Previous work by Patel et al. (2005, 2007) and Sempuga et al. (2010) have given methodologies and tools to analyze and set targets for overall processes using thermodynamics. This dissertation goes a step further, where one start putting pieces of equipment into the process and evaluate their effect on the thermodynamics of the overall process. We consider equipments such as the reactor, separator and heat exchange and look at how certain parameters such as temperature and conversion of these equipments will affect the target of the overall process.

Firstly, a basic process example where a specie *(A)* is transformed to produce a specie *(B)* is used to contextualize the theoretical approach used to understand the flow of work across a reactive chemical process. Secondly, a first case study on the isomerization of Butane followed by a second case study on the Reverse Water-Gas Shift (RWGS) process together illustrate how thermodynamic assumptions such as temperature and conversion under heat capacities (*Cp*) hypothesis affect the flow of work across chemical processes.

In the first case study on the isomerization of Butane process, the effect of temperature and conversion on the work flow across the process is evaluated as an example of a reactive process where the heat capacity (*Cp*) of the inlet stream to the process containing iso-butane and the outlet stream of the process containing n-butane have almost the same values and considered to be insignificant with 0.02 KJ/mol.K difference between the inlet and outlet streams of the process at 25 °C (with 37.02 KJ/mol.K at the feed stream and 37.04 KJ/mol.K at the product stream).

The second case study on the Reverse Water-Gas Shift (RWGS) process shows the effect of temperature and conversion on the work flow across the process as an example of one where the heat capacity (*Cp*) of the inlet streams to the process containing Carbon Dioxide (CO_2) and Hydrogen (H_2) and the outlet streams of the process containing Carbon Monoxide (CO), Water in its gas phase (H_2O), and any un-reacted feed as bi-products (CO_2 and H_2) have values that are significantly different from each other around 5 KJ/mol. K average difference between the inlet and outlet streams of the process at 25 °C (with 41.1 KJ/mol.K at the feed stream and 36.2 KJ/mol.K at the product stream).

Both case studies on which this dissertation is based evaluate the effect of temperature and conversion on reactive processes at the difference that the inlet and outlet streams of both processes represented have different magnitudes of heat capacity (*Cp*) between the inlet and outlet streams of the process.

Conclusions drawn from this study will aim at providing clarity and understanding on the effect of specific thermodynamic parameters (such as temperature, conversion, and heat capacity) on reactive chemical processes and prevent further loss of resources across the chemical industry.

2 AN INTRODUCTION TO PROCESS SYNTHESIS

2.1 Introduction

Process Synthesis is the development of process configurations that enables the conversion of raw materials into products meeting the required specifications in aim to improve the overall process performance. Process Synthesis results from a series of decisions made during early stages of the process design and originates from a *unit operation* concept introduced by Little in 1915 which relies on two main dimensions of sustainability: Firstly whether the plant is fit-for-purpose; and secondly whether financial returns are maximized.

Process synthesis is also relying on *unit operations* to satisfy two other dimensions of process sustainability: social and environmental considerations. Social design considerations ensuring that the health & safety factor, provisions for employment have been included as decision features during the conceptual phase of the process, while environmental design considerations such as the minimization of emissions, environmental impact, as well as the amount of feedstock have also been integrated during the process synthesis (Azapagic et al., 2004a).

The modern concept of process synthesis is also based on *unit operations* to develop optimal processes which do not necessarily result from an arrangement of unit operations set at their individual optimal performances, but rather result from an overall process performance concept where optimal equipment geometry, process layouts, and operating conditions are identified. The resulting flowsheet consist of interconnections and equipments organized in their best arrangements with the aim of reducing costs (El-Halwagi, 2012), waste of raw material and energy as well as prevent GHG emission and improve efficiency, safety, and scale (Barnicki & Siirola, 2004).

It is important to note that in the past decades great progress has been recorded in research in the field of process synthesis. The Center Of Material and Process Synthesis (COMPS) at the University of Witwatersrand is among well known research groups worldwide which has devoted for many years a concrete focus on the design of optimal and feasible chemical processes. Innovative approaches by Patel et al. (2005, 2007) have provided insightful methods to determine thermodynamic targets for processes and have introduced an analytical approach to design optimal flowsheets by ways of energy and mass balances. Several other researchers including Sempuga et al. (2010) have brought more light to the importance of the notion of optimization, mass and energy integration in the conceptual phase of a chemical process by illustrating possible performance adjustments that could be applied to inefficient processes to overcome a history of crippled chemical industry.

2.2 Process synthesis methodology

The conceptual phase of process synthesis consists of defining targets and analyzing their outcome and feasibility. For decades now, various approaches have been used in the industry to set targets among which a conceptual design practice known as *System decomposition* (Rudd, 1968) which splits the design into simpler sub-problems to which solutions apply to the overall design. For this approach to be efficient, the point where the design splits into simpler sub-problem must be identified, economic evaluation for the incomplete design problem must also be quantified. These limitations to the system decomposition approach are reflected by its spare use during process synthesis.

Smith and Linnhoff (1988) have introduced an *onion model* which decomposes the chemical process into process design layers where the selection of the inner-most layer of the onion model, defines the requirements of the following layers consecutively. For instance in Figure 2-1, the selection of a reactor directly affects the other layers of *unit operation* namely the separation system, recycle system, heat recovery, utilities, water and effluent.

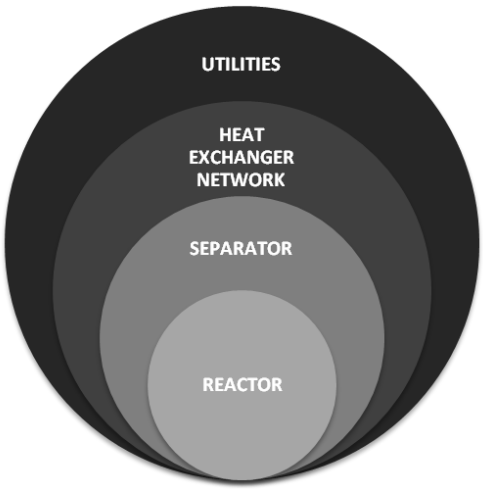

Figure 2-1. Onion model example applied to process synthesis proposed by Zhan et al., 2013

A closely related concept known as the *Hierarchical Decision Procedure* (Douglas, 1985) proposes a design structure where the flowsheet is designed on a trial-and-error basis for decisions at various assessment levels as shown in Figure 2-2.

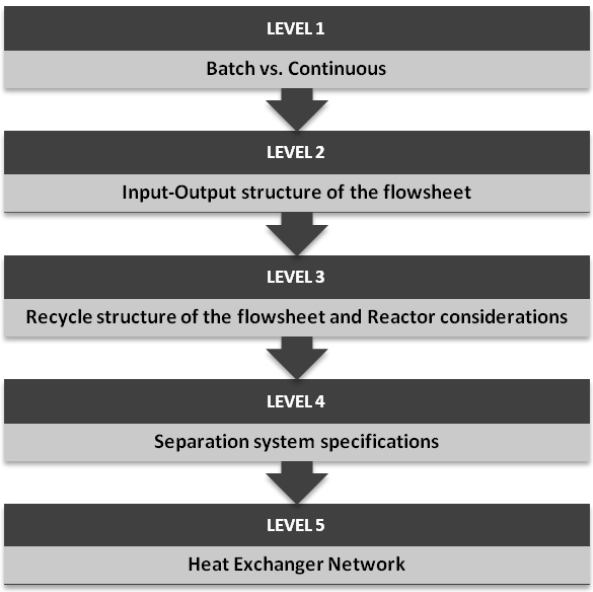

Figure 2-2. Sample Hierarchical Decision Procedure for process synthesis (Smith & Linnhoff, 1988)

Another design practice known as *Evolutionary modification* synthesis approach (King et al, 1972) identifies possible improvements and alternatives before modifying the existing flowsheet. An additional design practice known as *Superstructure optimization* (Ichikawa et al, 1972) aims at improving the performance of the whole system by discarding of less advantageous options and remaining with the best one. The superstructure optimization is very similar to the *Pinch analysis* which suggests ways of setting practically achievable energy targets (Smith, 2000) for the whole process since setting process' equipments at their respective optimal performance would not necessarily improve the overall process performance.

Also, the *Properties hierarchy* (Siirola & Rudd, 1971) which organizes a series of properties (mass, concentration, temperature, pressure, etc) and evaluates subsequently the effect of each on the production of the flowsheet's output.

These design approaches all revolve around the same goals namely the minimization of energy and feedstock consumption as well as prevention of GHG emissions which are among the most common and important basis for setting targets.

For this dissertation, the approach adopted in synthesizing an efficient process flowsheet is based on *Properties Hierarchy* design methodology where the effects of assumptions such as temperature, conversion, and others are evaluated consecutively to identify their respective effects on the flow of work within reactive processes which in turn will identify processes' energy efficiency and determine whether efficiency improvement can be feasible.

2.3 Process Synthesis' economic benefit

While early parts of this dissertation discuss the place of energy within a sustainable development model, this part of the dissertation focuses on the economic benefit associated with Process synthesis.

Process synthesis is a practice which doesn't only creates flowsheets on basis of feasible chemical, physical and unit operation options, but also determines the economic value of the overall chemical process based on prices and costs as it helps in identifying inferior design options and discard of processes with low economic performance (Ichikawa et al, 1972).

With the spread of globalization, an increased pressure to decrease cost and increase productivity has led the industry to justify the cost associated to the construction or modification of an industrial plant by quantifying its benefits in economic terms. Process

Synthesis is a fundamental tool used for business decisions early in the design phase of the project as it fixes 70 to 80% of the total cost of the process (Westerberg, 1989) while achieving an energy saving of 50% and a cost cutting of 35% (Siirola, 1996).

The integration of the thermodynamic feasibility together with business rational can lead to the creation of optimal industrial processes via the promotion of systematic decision frameworks in early conceptual stages of the process.

3 THERMODYNAMIC ANALYSIS OF A PROCESS

Thermodynamics is a basic tool used during the design and analysis phase of a process to find out whether a process is theoretically possible and realizable in practice. The first and second laws of thermodynamics provide a foundation to synthesize an energy efficient flowsheet using basic concepts of energy (heat and work), equilibrium, and their relationships to each other as well as to temperature and conversion.

3.1 Work flow in reactive processes

Chemical processes are always accompanied with a transfer of energy in or out of the process. While ”heat” is the most common and well understood form of energy transfer, ”work” is another important form of energy that has a significant impact on energy efficiency and feasibility of the process; this ”work” does not refer to the mechanical work required to move materials from one unit to another across the process but rather refers to the work related to the chemical transformation of the feed material into products. In this dissertation, a methodology is proposed to identify and analyze work flows across reactive processes.

In order to understand the concept of work flow across a process, a basic example is used where a substance *(A)* is transformed into a substance *(B)* as represented below:

$$A \Rightarrow B \tag{3.1}$$

This process has been chosen as an example for its simple form and to understand how thermodynamic conditions of reactive processes can influence the energy flow and, more specifically for this dissertation, the flow of work within the process.

The process is assumed to be a steady-state *simple* process with inlet and outlet streams to the process at standard state (T_o, P_o) as illustrated below:

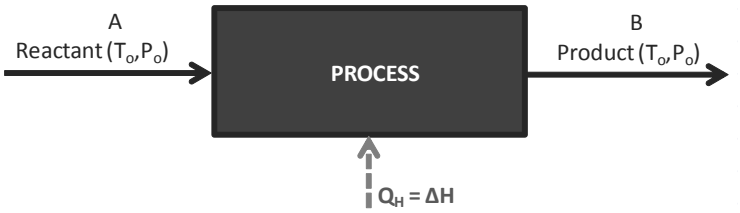

Figure 3-1. Process setup as a Simple process where specie (*A*) reacts to form specie (*B*) at standard state

A *Simple* process as the one shown in Figure 3-1 is defined by Sempuga et al. (2010) as a process in which only heat is exchanged with the surroundings at a single temperature and via a single point (often the reactor). This is only possible if we assume that the inlet and outlet streams to the process have the same heat capacities such that heat can be exchanged between them without requiring extra cooling or heating to bring the product to ambient temperature and/or to bring the feed to the reactor temperature. The effect of removing this assumption is also part of this study and will be discussed as part of the second case study on the Reverse Water-Gas Shift (RWGS) process.

Figure 3-1 is a representation of the case where a process is endothermic and requires work in order to operate. Many other cases such as when heat and work are released, or when work is required to release heat, can also be explored. Evaluations on which this dissertation is based focuses on the case where the process requires heat and work and assess how the flow of work is affected by temperature and conversion around the reactor under the assumption that the heat capacity of the feed (*A*) and that of the product (*B*) are equal.

Material streams in Figure 3-1 are represented by solid black lines carrying the feed *(A)* into the process and the product *(B)* out of the process. The heat stream is represented by a dashed black line directed toward the process indicating that heat *(Q_H)* is supplied or needs to be supplied to the process.

In order for any process to be feasible, both the heat and work requirements of the process must be satisfied. However for the *simple* process shown in Figure 3-1 and by definition, must only have one point of energy transfer in the form of heat. Thus, to satisfy the work requirement of the process, heat alone is used as the only form of energy transfer across the process. Heat by virtue of its temperature carries a specific amount of work given by the Carnot engine equation. Thus when heat is transferred at a certain temperature to the process, it simultaneously carries with it a certain amount of work into the process. In order to meet the work requirement of the process heat must be transferred at an appropriate temperature specific to the process. This can be well understood by considering the illustration in Figure 3-2 below:

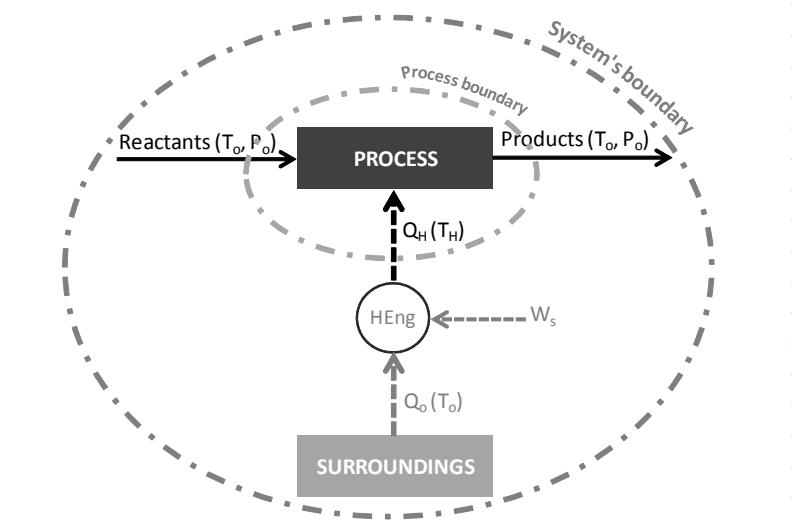

Figure 3-2. Simultaneous transfer of heat and work to a *Simple* process via a heat engine configuration

Where the solid black lines in Figure 3-2 represent material streams for the reactant going in and product going out of the process for which the mass balance is written in equation (3.1); dashed lines represent energy streams supplied to the process as well as to the heat engine *(HEng)*; and the intermittent dotted & dashed lines represent the overall system's boundary and the process' boundary. The term *"Heat Engine"* in this dissertation is used as a general term to refer to both a heat engine (to convert heat to work) and a heat pump (to convert work to heat).

The work carried into the process by the heat (Q_H) at a temperature T_H, can be understood as being supplied by a heat engine. The energy and entropy balance for both the process and the heat engine system in Figure 3-2, will show that the work required by the heat engine to supply the required amount of heat at the required temperature is equivalent to the process change in Gibbs free energy between the inlet and outlet streams of the process.

3.1.1 Energy and Entropy balance across the process

ENERGY BALANCE

An energy balance around the process as shown in Figure 3-2 maintaining the assumptions that the process is an open steady-state process at constant temperature and pressure (T_o, P_o) is written as follow:

$$\Delta H + \Delta E_k + \Delta E_p = Q_H - W \tag{3.2}$$

Where, (ΔH) is the change in enthalpy between the inlet and outlet streams of the process, Kinetic Energy (ΔE_k) as well as Potential Energy (ΔE_p) will not be accounted for to simplify this study and are assumed to be negligible, (Q_H) is the heat supplied to the process, and where

the shaft work (*W*) is nil since no mechanical work is directly supplied to the process. The resulting energy balance from equation (3.2) becomes:

$$\Delta H_{(T_o)} = Q_H \tag{3.3}$$

Thus in this case the amount of heat supplied to the process (Q_H) via the heat engine setup is equivalent to the change in enthalpy (ΔH) between the inlet and outlet streams of the process.

ENTROPY BALANCE

An entropy balance around the process evaluates the quality of energy within the process by assessing the *Entropy generated (S_{gen})* also known as the "*conversion of potentially useful energy into useless thermal energy*" resulting in work that is irrecoverably lost or *Work Lost*. The aim of evaluating the entropy generated *(S_{gen})* at the process –referred to as *($S_{gen(p)}$)*- is to identify the maximum amount of useful work which can be moved across the process and to minimize the amount of irreversible work by manipulation of thermodynamic parameters. An entropy balance around the open steady-state process gives:

$$\Delta S_{(T_o)} = \frac{Q_H}{T_H} + S_{gen(p)} \tag{3.4}$$

Where, *($S_{gen(p)}$)* is the entropy generated at the process, *(Q_H)* is the heat requirement for the process, and *(T_H)* is the temperature at which the heat *(Q_H)* is supplied to the process. For a thermodynamically reversible process as assumed for this process, no entropy will be generated ($S_{gen(p)} = 0$), thus no work will be irreversibly lost. On the other hand, for an irreversible process where $S_{gen(p)} > 0$, entropy will be generated resulting in work that will be irrecoverably lost *(Work Lost)*.

The Energy and entropy balances are combined by eliminating Q_H in both equation (3.3) and (3.4) to yield:

$$\Delta S_{(T_o)} = \frac{\Delta H_{(T_o)}}{T_H} + S_{gen(p)} \tag{3.5}$$

The change in the Gibbs free energy across the process is given by:

$$\Delta G_{(T_o)} = \Delta H_{(T_o)} - T_o \Delta S_{(T_o)} \tag{3.6}$$

Eliminating $\Delta S_{(T_o)}$ between equation (3.5) and (3.6) yields:

$$\Delta G_{(T_o)} = \Delta H_{(T_o)} \left(1 - \frac{T_o}{T_H}\right) - T_o S_{gen(p)} \tag{3.7}$$

For a reversible process $S_{gen(p)}$ = 0 and thus equation (3.7) becomes:

$$\Delta G_{(T_o)} = \Delta H_{(T_o)} \left(1 - \frac{T_o}{T_H}\right) \tag{3.8}$$

3.1.2 **Energy and Entropy Balance of the Heat Engine**

ENERGY BALANCE

An energy balance around the Heat engine is written as:

$$\Delta U + \Delta E_k + \Delta E_p = Q - W_s \tag{3.9}$$

Where, *(Q)* is the heat transferred from the surroundings to the heat engine, *(W_s)* is the shaft work done by the heat engine on its surroundings, Kinetic Energy (ΔE_k) and Potential Energy (ΔE_p) will not be accounted for as they are assumed negligible, internal energy (ΔU) is nil since there is no change in volume within the system. Simplifying equation (3.9) gives:

$$W_s = Q = Q_H - Q_o \tag{3.10}$$

The shaft work *(W_s)* done by the heat engine on its surrounding is equivalent to the difference between the heat supplied to the process *(Q_H)* and the heat supplied by the surroundings or cold reservoir *(Q_o).*

ENTROPY BALANCE

The Heat engine within the system in Figure 3-2 is assumed to be thermodynamically reversible where heat is used to carry the required amount of work to the process by virtue of its temperature. This reversible Heat engine is also called "Carnot Engine" (Smith J.M. et al., 2005). An entropy balance at the stream going into the heat engine *(S_o)* and the stream going out of the heat engine *(S_H)* is written as follow:

$$S_H = \frac{-Q_H}{T_H} \quad \text{and} \quad S_o = \frac{Q_o}{T_o} \tag{3.11}$$

Because the heat engine is operated reversibly, no entropy is generated, thus the total entropy going into the heat engine *(S_o)* is equal to the entropy going out of the heat engine *(S_H)* and as a result the change in entropy *(ΔS)* around the heat engine is nil as shown in the relationship below:

$$\Delta S = S_H + S_o = \frac{-Q_H}{T_H} + \frac{Q_o}{T_o} = 0 \tag{3.12}$$

Where, *(S_H)* is the entropy of the stream going out of the heat engine to the process or hot reservoir, *(S_o)* is the entropy of the stream going into the heat engine from the surroundings or cold reservoir.

We combine the Energy and Entropy balance by eliminating Q_o in equation (3.10) and (3.12) to yield:

$$W_s = Q_H \left(1 - \frac{T_o}{T_H}\right) \tag{3.13}$$

Therefore, by looking at Figure 3-2 and equations (3.3), (3.8) and (3.13) it can be concluded that:

$$\Delta G_{(T_o)} = W_s \tag{3.14}$$

That is, the change in Gibbs free energy across a simple process (a process with a single heat transfer at a single temperature) is equivalent to the amount of work required by a heat engine, in order to absorb heat from the environment at ambient temperature and supply

the required amount of heat to the process at a required temperature. Therefore the change in Gibbs free energy across the process at ambient conditions is equivalent to the work requirement of the process. The temperature at which heat (Q_H) must be supplied to the process is referred to as the Carnot temperature (T_{Carnot}); it is the temperature at which the work carried by heat matches the work requirement of the process.

$$\Delta G_{(T_o)} = \Delta H_{(T_o)} \left(1 - \frac{T_o}{T_{Carnot}} \right) \tag{3.15}$$

For a simple process, when the process heat requirement ($\Delta H_{(T_o)}$) is supplied at T_{Carnot}, no additional work is required and no work will be lost and the process is reversible. However if the process heat requirement is supplied at any other temperature (T) than the Carnot temperature (T_{Carnot}), the process will either be work deficient or will lose work potential depending on whether T is above or below T_{Carnot} and the sign of $\Delta H_{(T_o)}$ and $\Delta G_{(T_o)}$; in this case the process will be irreversible and will generate entropy as described by the following equation:

$$\Delta G_{(T_o)} = \left[\Delta H_{(T_o)} \left(1 - \frac{T_o}{T} \right) \right] - \left[T_o S_{gen(p)} \right] \tag{3.16}$$

Where the term $T_o S_{gen(p)}$ is the additional work that needs to be supplied in order to meet the work requirement ($\Delta G_{(T_o)}$) of the process or the work surplus carried in with heat and is lost. This term is generally referred to as the lost work ($W_{lost(p)}$). Thus:

$$W_{lost(p)} = T_o S_{gen(p)} \tag{3.17}$$

The *Work lost* term written as $W_{lost(p)}$ gives evidence of the irrecoverable work which the chemical engineer can manipulate through mass and energy balance to minimize its quantity. This Work lost -in fact- plays a major role in reducing energy waste across the process industry. As the aim nowadays is to save as much energy as possible, the ideal target for a flowsheet design is to come up with one which does not favor entropy generation so

that the Work lost ($W_{lost(p)}$) is minimized rendering the process thermodynamically reversible and in turn benefiting from the total amount of heat and work potential of the process. However, since such an ideal situation cannot be reached, the aim for the engineer is to design a process as close as possible to an ideal situation of zero $W_{lost(p)}$. It is to note that for all positive values of $W_{lost(p)}$, work will be irreversibly lost; and for all negative values of $W_{lost(p)}$, the process will be work deficient and will require additional work to be supplied by other means in order for the process to be feasible.

An alternative equation used to evaluate the Work lost *($W_{lost(p)}$)* at the process at various temperatures is given by the relationship below:

$$W_{lost_p} = \Delta H_{(T_o)} \times T_o \left(\frac{1}{T_{Carnot}} - \frac{1}{T} \right) \tag{3.18}$$

Where when $T = T_{Carnot}$, the Work lost term *($W_{lost(p)}$)* goes to zero and no work is irreversibly lost. At any other temperature above or below the Carnot temperature respectively, the process is either consuming more work than needed (work lost) or is supplied with less work than required (work deficient). As a result work will either be irreversibly lost ($W_{lost(p)} > 0$, $S_{gen(p)} > 0$) or infeasible ($W_{lost(p)} < 0$, $S_{gen(p)} < 0$). The work lost at the process ($W_{lost(p)}$) written as per equation (3.18) results from a subtraction of equation (3.16) from equation (3.15).

Therefore for a process that requires heat and work to be supplied ($\Delta H_{(T_o)} > 0$ and $\Delta G_{(T_o)} > 0$) work scenarios for equation (3.16) as interpreted above can be illustrated as shown below:

(a) (b) (c)

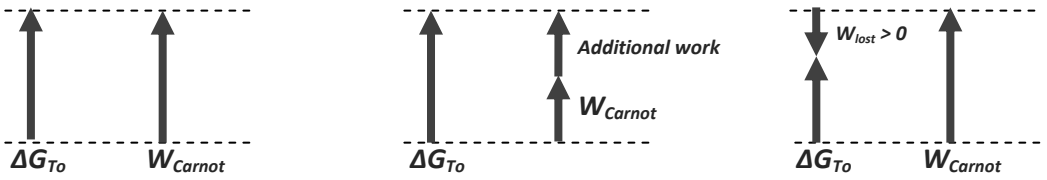

Figure 3-3. Work flow scenarios across the process where in (a) the process' work requirement is met through heat, (b) the process' work requirement is not met through heat alone, (c) the process' work requirement is met with excess work

Where in scenario (a) the process meets its exact work requirement by work supply through heat alone, that is when $T = T_{Carnot}$. In scenario (b) the process does not meet its work requirement through heat alone, the process is work deficient and infeasible as a *simple* process, additional work must be added for the process to be operational, that is when $T < T_{Carnot}$ and $W_{lost} < 0$. In scenario (c) the process receives more work than required and unless this work is recover it will be irreversibly lost to the surroundings, that is when $T > T_{Carnot}$, $W_{lost} > 0$, and a *simple* process is feasible.

3.2 The Effect of Heat capacity (Cp) on process work flow

3.2.1 Heat Capacity of the feed equal Heat Capacity of the product ($Cp_{feed} = Cp_{product}$)

So far we have looked at work flows around a '*simple process'* , where it has been assumed that materials going in and out of the process have equal heat capacities (*Cp*) such that heat could be exchanged between the two streams to bring the inlet stream from ambient temperature to the reactor temperature without requiring external heating and to bring the exit stream from the reactor temperature back to ambient temperature without requiring external cooling as shown in Figure 3-4 below:

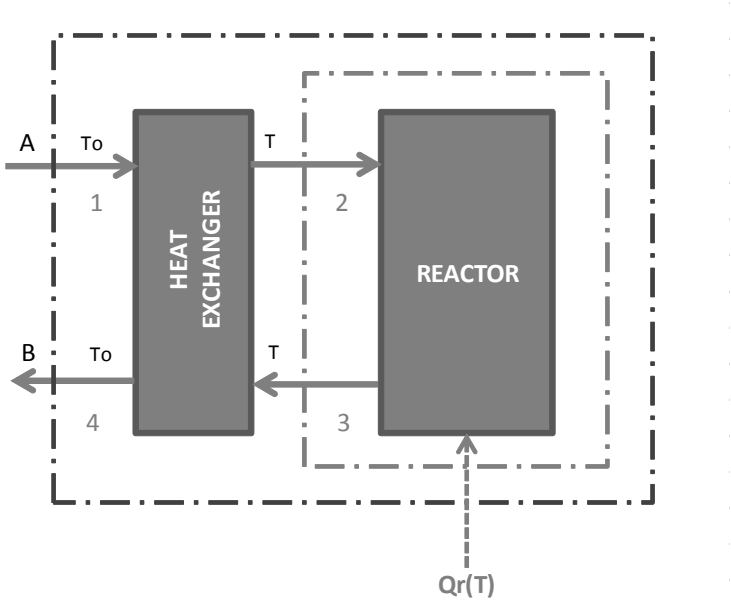

Figure 3-4. Basic equipments set-up for the *Simple* process where specie (*A*) reacts to produce specie (*B*) only

If we consider the process in Figure 3-4 as being a simple process described by the hypothetical mass balance in equation (3.1), then the feed material (specie *A*) is fed to overall process at ambient temperature and constant pressure (T_o, P_o) then goes through a heat exchanger to step up the operating temperature from (T_o) to the reactor's temperature (T) before proceeding through the reactor where the reaction takes place at an assumed complete conversion $(x = 1)$. The product material (specie *B*) exits the reactor at temperature (T) then goes through a heat exchanger once again to step-down the stream's temperature from reactor's temperature (T) to ambient temperature (T_o) then proceeds to exiting the process at temperature (T_o). There are no recycle/reflux streams or byproduct at this point while feed and product materials enter and leave the process as pure components.

Because the heat capacities of the streams in and out of the process are assumed to be equal and no external heating is required, the change in enthalpy across the process is therefore equivalent to the change in enthalpy across the reactor and the change in Gibbs

free energy across the process is equivalent to the change in Gibbs free energy across the reactor. Thus for $Cp_{in} = Cp_{out}$:

$$\Delta H^{o}_{\mathrm{Process}}(T_o) = \Delta H^{o}_{\mathrm{Reactor}}(T) = \left(\sum_i \upsilon i \Delta H^{o}_{f_i}(T_o)\right)_{products} - \left(\sum_i \upsilon i \Delta H^{o}_{f_i}(T_o)\right)_{reactants}$$
$$\Delta G^{o}_{\mathrm{Process}}(T_o) = \Delta G^{o}_{\mathrm{Reactor}}(T) = \left(\sum_i \upsilon i \Delta G^{o}_{f_i}(T_o)\right)_{products} - \left(\sum_i \upsilon i \Delta G^{o}_{f_i}(T_o)\right)_{reactants} \quad (3.19)$$

Where, $(\Delta H^{o}_{\mathrm{Process}}(T_o))$ and $(\Delta G^{o}_{\mathrm{Process}}(T_o))$ are the change in enthalpy between the inlet and outlet streams of the process and the change in Gibbs free energy between the inlet and outlet streams of the process at standard state (T_o, P_o) respectively, where $(\Delta H^{o}_{Reactor}(T))$ and $(\Delta G^{o}_{Reactor}(T))$ are the change in enthalpy of reaction and the change in Gibbs free energy of reaction at standard pressure (P_o) and at the reactor temperature (T) respectively, (υi) is the stoichiometric coefficient for specie (i), where $(\Delta H^{o}_{f_i}(T_o))$ and $(\Delta G^{o}_{f_i}(T_o))$ are the change in enthalpy and Gibbs free energy of formations at standard conditions (T_o, P_o) respectively.

We therefore see that there are no work flows associated with the heat exchanger with its surroundings since no external heat is added or removed from the heat exchanger as a result from *all* the work from the hot stream (along with its heat) being transferred to the cold stream of the heat exchanger; so in this case the process has only one point of heat transfer which is at the reactor and thus only one point of work transfer across the process.

3.2.2 Heat Capacity of feed different than Heat Capacity of product ($Cp_{feed} \neq Cp_{product}$)

In the case where the heat capacity of the feed is not equal to that of the product, the equations in (3.19) will no longer apply. In this case one would need to evaluate the heat

capacity of each specie in order to calculate the enthalpy and Gibbs free energy change across the reactor at the reactor temperature (*T*).

- This case needs to be considered because the inlet and outlet streams not having the same *Cp* will affect the work flow across the process since it implies that external heating or cooling will be required to bring either the feed to the required reactor temperature or to cool down the product stream to ambient temperature; thus, the process will no longer have a single point of heat transfer but multiple points of heat transfers which must be taken into account when analyzing work flows across the process. Additionally, the change in enthalpy *($\Delta H_{reaction}$)* and the change in Gibbs free energy *($\Delta G_{reaction}$)* across the reactor unit will also differ from the change in enthalpy *($\Delta H_{process}$)* and the change in Gibbs free energy *($\Delta G_{process}$)* across the process. Thus for $Cp_{in} \neq Cp_{out}$:

$$\begin{aligned} \Delta H^{o}_{\mathrm{Pr}ocess}(T_o) &\neq \Delta H^{o}_{\mathrm{Re}actor}(T) \\ \Delta G^{o}_{\mathrm{Pr}ocess}(T_o) &\neq \Delta G^{o}_{\mathrm{Re}actor}(T) \end{aligned} \tag{3.20}$$

The assumption that heat capacities between inlet and outlet streams of the process or unit are far different applies to the second case study done in this dissertation on the Reverse Water-Gas Shift (RWGS) process where more than a single heat source will have to be supplied to the process for it to proceed. The change in enthalpy *(ΔH)* between the inlet and outlet streams of the process or unit at temperature *T* in this instance is given by the following equation:

$$\Delta H_{(T)} = \Delta H_{(T_o)} + \int_{T_o}^{T} \Delta C p dT \tag{3.21}$$

Where *(ΔH_{To})* is the change in enthalpy between the inlet and outlet streams of the process or unit at temperature T_o, the term $\int_{T_o}^{T} \Delta CpdT$ accounts for the heat capacity change as a function of temperature between the inlet and outlet streams of the process or unit.

Note that the heat capacity at constant pressure (*Cp*) of a component can be evaluated as a function of temperature using the following temperature dependent power series:

$$Cp_i = A + BT + CT^2 + DT^3 + ET^4 \tag{3.22}$$

Where the subscript (p) refers to the constant pressure heat capacity (Cp), where the subscript (i) represents a specific specie, and where values for coefficients A,B,C,D,E (3.22) are from Table 2 (APPENDIX A: List of Tables) of this dissertation.

The integration using the *Cp* expression in (3.22) in its expanded form is written as:

$$\int_{T_o}^{T} CpdT = A\left(T - T_o\right) + \frac{B}{2}\left(T^2 - T_o^2\right) + \frac{C}{3}\left(T^3 - T_o^3\right) + \frac{D}{4}\left(T^4 - T_o^4\right) + \frac{E}{5}\left(T^5 - T_o^5\right) \tag{3.23}$$

Under the same assumption that heat capacities between inlet and outlet streams of the process are not equal and calculating for the change in entropy (*ΔS*) across the process or unit is given by the equation below:

$$\Delta S_{(T)} = \Delta S_{(T_o)} + \int_{T_o}^{T} \Delta Cp \frac{dT}{T} \tag{3.24}$$

Where (ΔS_{To}) is the change in entropy between the inlet and outlet streams of the process or unit at temperature T_o, the term $\int_{T_o}^{T} \Delta Cp \frac{dT}{T}$ accounts for the heat capacity change as a function of temperature between the inlet and outlet streams of the process or unit. The integration in equation (3.24) in its expanded form is written as:

$$\int_{T_o}^{T} Cp\frac{dT}{T} = A\ln\left(\frac{T}{T_o}\right) + B\left(T - T_o\right) + \frac{C}{2}\left(T^2 - T_o^2\right) + \frac{D}{3}\left(T^3 - T_o^3\right) + \frac{E}{4}\left(T^4 - T_o^4\right) \qquad (3.25)$$

The outcome from both assumptions: that the inlet and outlet streams of the process have equal heat capacities ($Cp_{in} = Cp_{out}$) or does not have equal heat capacities ($Cp_{in} \neq Cp_{out}$), is explained in subsequent parts of this dissertation through two case studies on Butane isomerization and Reverse Water-Gas Shift (RWGS) process respectively. For simplicity *Cp* can be considered to be independent of temperature and in that case the change in enthalpy *(ΔH)* across a particular unit at temperatures other than the reference temperature (T_o) can be estimated as follows:

$$\Delta H_{(T)} = \Delta H_{(T_o)} + Cp\left(T - T_o\right) \qquad (3.26)$$

Similarly, the change in entropy *(ΔS)* between the inlet and outlet streams of process or unit at temperature *T* can also be estimated as follows:

$$\Delta S_{(T)} = \Delta S_{(T_o)} + Cp\ln\left(\frac{T}{T_o}\right) \qquad (3.27)$$

Where (ΔS_{To}) is the change in entropy between the inlet and outlet streams of the process or unit at temperature T_o. The change in Gibbs free energy can then be calculated using (3.26) and (3.27) as follows:

$$\Delta G_{(T)} = \Delta H_{(T)} - T\Delta S_{(T)} \qquad (3.28)$$

3.2.3 **Heat Exchanger energy and entropy balance**

Here we are looking at the Heat Exchanger in Figure 3-4 for the case where $Cp_{feed} \neq Cp_{product}$. In this case the heat exchanger is not able to either step up the temperature of the stream going into the process carrying specie *(A)* (when $Cp_A > Cp_B$) from (T_o) to the reactor's temperature *(T)* and thus would require additional heat to be supplied externally in order to

reach the reactor temperature, or to step-down the stream exiting the reactor carrying specie *(B)* ($Cp_A < Cp_B$) from reactor's temperature *(T)* to ambient temperature *(T_o)* before exiting the process and thus would require more heat to be removed from the process in order to reach ambient temperature.

The energy and entropy balance around the heat exchanger will reveal the work flow associated with the additional heat transfer at the heat exchanger. Let us explore this by considering the Heat Exchanger setup as follows:

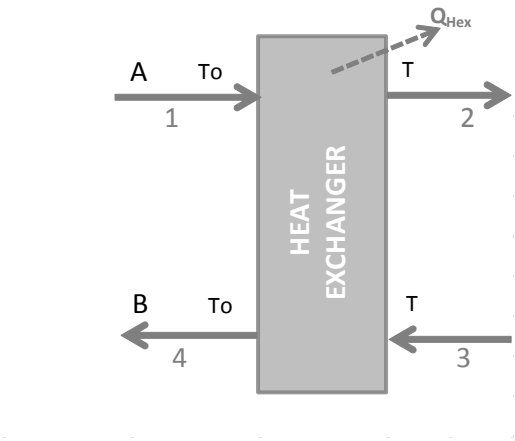

Figure 3-5. Heat Exchanger setup within the process

Where the solid lines in Figure 3-5 represent material streams going in and out of the Heat exchanger and where the dotted line represent the heat stream also carrying the work (W_{hex}) associated with this heat.

ENERGY BALANCE

An energy balance around the heat exchanger unit where $Cp_{in} \neq Cp_{out}$ gives:

$$\begin{aligned} H_1 + H_3 + Q_{hex} &= H_2 + H_4 \\ \Delta H &= Q_{hex} \end{aligned} \tag{3.29}$$

Where the subscripted numbers (1,2,3, and 4) refer to the streams in and out of the heat exchanger as labeled in Figure 3-5, and where the change of enthalpy across the Heat exchanger is equivalent to the heat supplied to the Heat exchanger.

ENTROPY BALANCE

An entropy balance around the heat exchanger where $Cp_{in} \neq Cp_{out}$ gives:

$$S_1 + S_3 + \frac{Q_{hex}}{T_{hex}} = S_2 + S_4$$
$$\Delta S = \frac{Q_{hex}}{T_{hex}} \tag{3.30}$$

Where the subscripted numbers (1,2,3, and 4) refer to the streams in and out of the heat exchanger as labeled in Figure 3-5, where *(S)* is the Entropy of respective streams going in and out of the heat exchanger, where T_{hex} is the temperature at which the heat Q_{hex} is supplied to the Heat exchanger.

In a similar way as was done in Section 3.1, the work associated with external heat (Q_{hex}) transferred at the heat exchanger is equivalent to the mechanical work that a heat engine would require to absorb heat at ambient temperature and provide a quantity of heat Q_{hex} at temperature T_{hex}. That is:

$$W_{hex} = Q_{hex}\left(1 - \frac{T_o}{T_{hex}}\right) \tag{3.31}$$

Also in the similar analysis as in Section 3.1, it can be shown that this work is equivalent to the change in Exergy (ΔB) between the streams coming in and the streams coming out of the heat exchanger.

It is important to note that, the change in Gibbs free energy is equivalent to the work requirement only if all the streams around the process or unit are at ambient conditions T_o,

and P_o. When all the streams are not at ambient conditions, then the work requirement is equivalent to the change in *exergy* around the process or the unit. The Exergy (*B*) of a stream at temperature *T* and pressure *P* is defined as:

$$B_{(T,P)} = H_{(T,P)} - T_o S_{(T,P)} \tag{3.32}$$

Thus by combining the energy and entropy balance around the heat exchanger (equations (3.29) and (3.30)) and eliminating the entropy terms by using equation (3.32), we obtain the follows equation for a reversible heat exchanger:

$$W_{hex} = \Delta B_{hex} = \Delta H_{hex}\left(1 - \frac{T_o}{T_{revhex}}\right) \tag{3.33}$$

We can also show that in the case where the heat exchanger is not reversible, that is when there is entropy generation equation (3.33) becomes:

$$W_{hex} = \Delta B_{hex} = \Delta H_{hex}\left(1 - \frac{T_o}{T_{hex}}\right) - T_o S_{gen(hex)} \tag{3.34}$$

Where $S_{gen(hex)}$ is the entropy generated due to irreversibility coming from transferring heat at a temperature T, different from the reversible temperature $T_{rev(hex)}$. The change in exergy around the heat exchanger in Figure 3-5 is calculated by expanding equation (3.32) to give:

$$\Delta B_{hex} = \left[\int_{T_o}^{T} Cp_A dT - \int_{T_o}^{T} Cp_B dT - T_o\left(\int_{T_o}^{T} Cp_A \frac{dT}{T} - \int_{T_o}^{T} Cp_B \frac{dT}{T}\right)\right] \tag{3.35}$$

Where, (W_{Hex}) is the work requirement at the heat exchanger, subscripts *(A)* and *(B)* refer to the species involved in this process as shown in Figure 3-4, *(Cp)* is the heat capacity term, *T* is the temperature at which the feed stream is raised, and T_o is the ambient temperature at which the product stream is cooled. A positive W_{Hex} for instance would mean that work is done by the surroundings on the heat exchanger.

3.3 The Effect of Conversion

So far we have looked at cases where there is complete conversion of feed material to product in the reactor. In this part we explore the energy and work flow around an additional unit in the process, the separator. The need for a separator occurs when the process shown in the mass balance in equation (3.1) takes place at partial conversion. For this example where specie *(A)* reacts to form specie *(B)* at complete conversion, there is no need for a Separator unit since the stream coming out of the reactor only contains specie *(B)*.

If for instance specie *(A)* reacted to form specie *(B)* at partial conversion and the resulting products -specie *(A)* and *(B)*- needed to be separated, a Separator unit will be required at the exit of the reactor to direct the products in their respective streams as shown in the figure below.

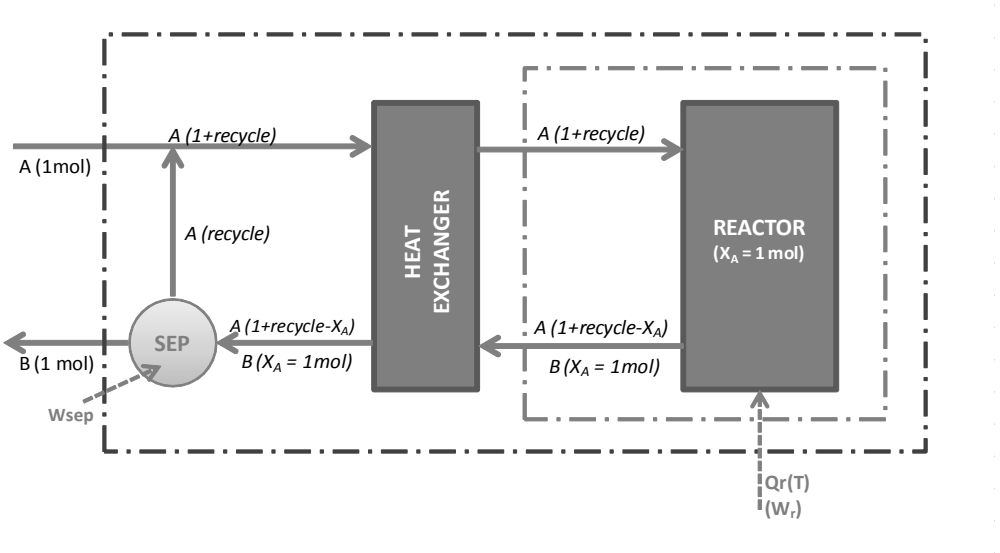

Figure 3-6. Basic equipment setup within a *simple* process which includes a separator to divide specie *(A)* from specie *(B)*

In Figure 3-6, for 1 mole of specie *(A)* fed to the process to produce specie *(B)* at partial conversion (x), at the exit of the reactor: there will be an amount of specie *(A)* exiting the

reactor equivalent to (1-x_A) and an amount of specie *(B)* exiting the reactor equivalent to (x_B). Heat is exchanged between the streams coming in and out of the reactor as was described previously and then the product stream goes into a separator as shown in Figure 3-7.

The separator unit is designed as a reversible unit to prevent any additional work requirement to operate the unit or any work loss to the surroundings. As a result, the heat load at the separator *(Q_{Sep})* is nil and the work of separation *(W_{Sep})* is equivalent to the work of mixing at the reactor *($W_{Reactor}$)* since: at the reactor, specie *(B)* is produced and mixed with any un-reacted amount of specie *(A)*; and at the Separator, the mixed species of *(A)* and *(B)* are un-mixed to their respective forms.

The work of mixing generated at the reactor is virtually supplied to the separator to meet its work requirement as shown in the relationship below:

$$W_{Sep} = -\Delta G_{mix_{(\mathrm{Re}actor)}} = nRT_o \sum xi \ln xi \tag{3.36}$$

Where, (W_{Sep}) is the work of separation at the Separator unit, (ΔG_{mix}) is the work of mixing at the reactor, (n) is the total number of moles present in the unit, (R) is the universal constant with its values available from thermodynamic tables (see Table 1 in APPENDIX A: List of Tables), (T_o) is the ambient temperature, and (x_i) is the molar ratio of a particular specie (i) over the total molar amount.

ENERGY BALANCE

Consider the separator depicted in Figure 3-7, the streams are assumed to come in and out of the separator at ambient temperature and thus their enthalpies are given by:

$$\begin{aligned} H_{4(T_o)} &= H_{A(T_o)} + H_{B(T_o)} + \Delta H_{mixAB(T_o)} \\ H_{5(T_o)} &= H_{A(T_o)} \\ H_{6(T_o)} &= H_{B(T_o)} \end{aligned} \tag{3.37}$$

Therefore the change in enthalpy around the separator is:

$$\begin{aligned} \Delta H_{sep} &= H_{5(T_o)} + H_{6(T_o)} - H_{4(T_o)} \\ &\text{Therefore} \\ \Delta H_{sep} &= -\Delta H_{mixAB(T_o)} \end{aligned} \tag{3.38}$$

The enthalpy change of mixing for most ideal mixtures is negligible. Thus, if we assume ideal mixing then the energy balance around the Separator gives:

$$\Delta H_{sep} = 0 \tag{3.39}$$

ENTROPY BALANCE

Similarly, the entropy of the streams around the separator in Figure 3-7 is:

$$\begin{aligned} S_{4(T_o)} &= S_{A(T_o)} + S_{B(T_o)} + \Delta S_{mixAB(T_o)} \\ S_{5(T_o)} &= S_{A(T_o)} \\ S_{6(T_o)} &= S_{B(T_o)} \end{aligned} \tag{3.40}$$

Therefore the change in entropy around the separator is:

$$\begin{aligned} \Delta S_{sep} &= S_{5(T_o)} + S_{6(T_o)} - S_{4(T_o)} \\ &\text{Therefore} \\ \Delta S_{sep} &= -\Delta S_{mixAB(T_o)} \end{aligned} \tag{3.41}$$

Unlike the enthalpy of mixing, the entropy of mixing is not negligible and is given by:

$$\Delta S_{mix} = -nR\sum xi \ln xi \tag{3.42}$$

Where n is the total number of moles of the mixtures, R is the ideal gas constant (refer to APPENDIX A: List of Tables), and x_i is the mole fraction of component i in the mixture. Thus for the mixture of A and B, the entropy of mixing is:

$$\Delta S_{mixA,B} = -R(n_A + n_B)(x_A \ln x_A + x_B \ln x_B) \tag{3.43}$$

The change in Gibbs free energy across the separator is given by:

$$\Delta G_{sep(T_o)} = \Delta H_{sep(T_o)} - T_o \Delta S_{sep(T_o)} \tag{3.44}$$

From equation (3.39) $\Delta H_{sep} = 0$ therefore:

$$\Delta G_{sep(T_o)} = -T_o \Delta S_{sep(T_o)} = T_o \Delta S_{mixA,B(T_o)} = \Delta G_{mixA,B(T_o)} \tag{3.45}$$

We previously showed that the change in Gibbs free energy between the streams coming in and out of a process or unit at ambient conditions T_o and P_o is equivalent to the work requirement of the process of the unit. Therefore from equation (3.45) we see that the separator requires work, equivalent to the Gibbs free energy of mixing, to be supplied, that is:

$$W_{Sep} = -\Delta G_{mixA,B(T_o)} = RT_o(n_A + n_B)(x_A \ln x_A + x_B \ln x_B) \tag{3.46}$$

We therefore see that although the energy balance suggests that no energy is required for separation, the entropy balance shows that work (work potential) must be supplied for the separation to take place. The minimum amount of work required is equal to the work potential that exist when mixing *A* and *B*, this work potential is the Gibbs free energy of mixing. The work of separation (W_{sep}) can be supplied to the separator in two ways:

(1) By directly supplying mechanical work (W_{Shaft}). For example via pressure in membrane separation) as shown in Figure 3-7.

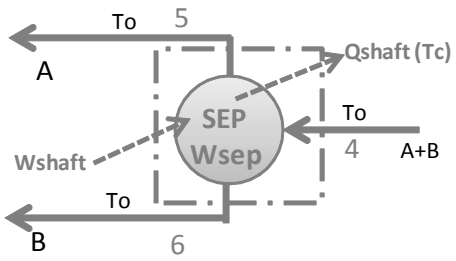

Figure 3-7: Supplying the work of separation by directly adding mechanical work (shaft work) to the Separator

Energy in the form of shaft work (W_{Shaft}) is added to the separator and the same amount of energy is removed from the separator in the form of heat (Q_{Shaft}) at a temperature T_C, in this

way there is no net energy added or removed from the separator according to equation (3.39), however the entropy balance combined with the energy balance around the separator will show that the work of separation, W_{Sep} is left behind in the separator and is given by:

$$W_{Sep} = W_{Shaft}\left(\frac{T_o}{T_C}\right) \tag{3.47}$$

W_{Sep} can be thought of as virtual work or work potential (because it does appear in the energy balance around the separator) needed to do separation. We see from equation (3.47) that the higher T_C is the larger the amount of shaft work is needed for a fixed amount of work separation required. Thus minimum shaft work is needed when heat (Q_{Shaft}) is removed at ambient temperature.

(2) The work of separation can also be supplied by adding and removing the same amount of heat at different temperatures as shown in Figure 3-8. A typical example of this is a distillation column.

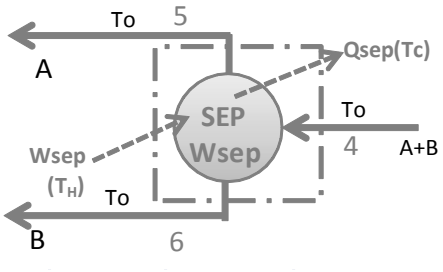

Figure 3-8: Supplying work of separation by adding heat at high temperature and removing heat at low temperature

A quantity of heat, Q_{Sep} at a high temperature T_H is added to the separator and the same quantity of heat is removed from the separator at a temperature T_C lower than T_H. In this way there is no net energy added or removed from the separator according to equation (3.39), however, in the similar way as with the previous case in (1), the entropy balance in

combination with the energy balance will show that work of separation W_{sep} is left behind in the separator and is given by:

$$W_{Sep} = Q_{Sep} T_o \left(\frac{1}{T_C} - \frac{1}{T_H} \right) \tag{3.48}$$

3.4 Heat and Work flow across the Reactor

Following evaluations of heat and work flows at the process, a centered attention is placed on the evaluation of heat and work flow within the reactor. The reactor is the central unit within the process as shown in Figure 3-9below. The inlet stream to the reactor is at the required reactor temperature *T*, after having been raised from ambient temperature by the heat exchanger. The reactor is kept at the same temperature *T* and thus the outlet stream from the reactor is also at *T*. In this discussion the reactor, as well as the other units in the process, is kept at ambient pressure (P_o). Heat (Q_r) at a the reactor *T*, is added to supply the reactor with its energy requirements.

The reactor is setup within the process as shown in the figure below:

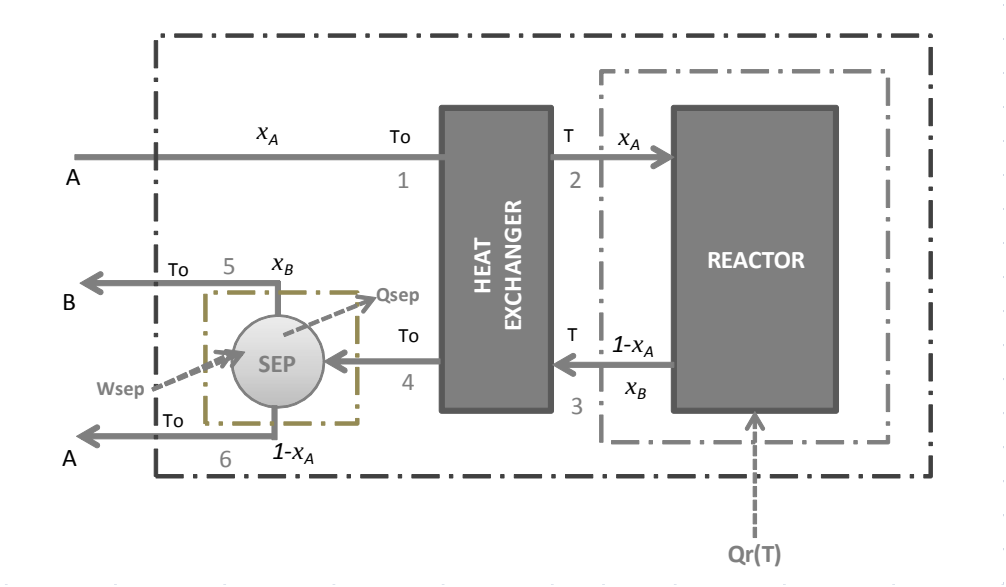

Figure 3-9. Reactor unit setup within a *Simple* process

An energy balance around the reactor will give the following result:

$$\Delta H_{r(T)} + \Delta E_{k_{(T)}} + \Delta E_{p_{(T)}} = Q_r + W_s \tag{3.49}$$

Where, (ΔH_r) is the change in enthalpy between the inlet and outlet streams at the reactor at temperature *T* Kinetic Energy (ΔE_k) as well as Potential Energy (ΔE_p) will not be accounted for as they are assumed to be negligible, (Q_r) is the heat supplied to the reactor, and the shaft work (W_s) is nil since no mechanical work is directly supplied to the reactor. The resulting energy balance from equation (3.49) becomes:

$$\Delta H_{r(T)} = Q_r \tag{3.50}$$

Where, the subscript (*r)* refers to the reactor unit.

An entropy balance around the reactor gives the following relationship:

$$\Delta S_{r(T)} = S_{rout(T)} - S_{rin(T)} = \frac{Q_r}{T} + S_{gen(r)} \tag{3.51}$$

Where $(S_{gen(r)})$ is the entropy generated at the reactor, and (S_{mix}) is the entropy of mixing of specie *(A)* and *(B)* at the stream exiting the reactor at temperature *T*.

We have previously shown that the work requirement (or work potential) across a unit or a process, where the streams coming in and out are not both at ambient conditions, is given by the change in Exergy (*ΔB*) between the streams; thus by combining the energy and entropy balance around the reactor and knowing that $\Delta B_{(T)} = \Delta H_{(T)} - T_o \Delta S_{(T)}$ we obtain:

$$\Delta B_{r(T)} = \Delta H_{r(T)} \left(1 - \frac{T_o}{T} \right) - T_o S_{gen(r)} \tag{3.52}$$

Where, (ΔB_r) is the change in Exergy between the inlet and outlet streams of the reactor at temperature *T*, (ΔH_r) is the change in enthalpy between the inlet and outlet streams of the reactor at temperature *T*, (T_o) is the temperature of the surroundings, and (ΔS_r) is the change in entropy between the inlet and outlet streams of the reactor at temperature *T*. For a reversible reactor, the change in Exergy (ΔB_r) between the inlet and outlet streams of the reactor at temperature *T* can be written as:

$$\Delta B_{r(T)} = \Delta H_{r(T)} \left(1 - \frac{T_o}{T_{\text{Rev}}} \right) \tag{3.53}$$

Where, T_{Rev} is the reactor's reversible temperature. It is the temperature at which the heat requirement of the reactor ($\Delta H_{r(T)}$) must be supplied in order to meet the work requirement of the reactor ($\Delta B_{r(T)}$). T_{Rev} can be evaluated by rearranging equation (3.53) to give:

$$T_{Rev} = \frac{T_o}{\left(1 - \frac{\Delta B_{r(T)}}{\Delta H_{r(T)}} \right)} \tag{3.54}$$

When the heat requirement is supplied at a temperature *T*, other than the reversible temperature T_{Rev}, the reactor work requirement will be described by equation (3.52), where the term $T_o S_{gen(r)}$ represent the work lost due to irreversibility. And thus the reactor will either be work deficient or will lose work depending on the sign of the heat and work

requirement as well as whether *T* is above or below T_{Rev}. The lost work at the reactor can be evaluated by subtraction equation(3.52) from (3.53) to yield:

$$W_{lost_r} = \Delta H_{r(T)} \times T_o \left(\frac{1}{T_{\mathrm{Re}v}} - \frac{1}{T} \right) \tag{3.55}$$

It is to note that the change in Exergy *(ΔB)* at temperature T_o and the change in Gibbs free energy *(ΔG)* at temperature T_o are the same and both refer to the work requirement of a process or a unit at temperature T_o as shown by the relationship below:

$$\Delta B_{(To,Po)} = \Delta G_{(To,Po)} = \Delta H_{(To)} - T_o \Delta S_{(To)} \tag{3.56}$$

Where, *(ΔB)* at temperature T_o is the change in Exergy, *(ΔG)* at temperature T_o is the change in Gibbs free energy, *(ΔH)* is the change in enthalpy between the inlet and outlet streams of a unit or a system at temperature T_o, (T_o) is the temperature of the surroundings, and *(ΔS)* is the change in entropy between the inlet and outlet streams of a unit or a system at temperature T_o.

3.5 Reaction Equilibrium

Following the Second Law of thermodynamics, the total entropy (or level of disorder) has a natural tendency to increase until it reaches its maximum at equilibrium state. Practically speaking, for a chemical process where a reaction takes place in both forward and reverse direction, the feed reacts to form products in proportions which will increase until the reaction reaches a state where the reactants and products concentration ratios no longer change with time and where it is said to have reached the *equilibrium state*.

The magnitude of the equilibrium constant *(K)* is an indication of how far the reaction proceeds toward the product before reaching equilibrium at a specific temperature. A small

value of *(K)* is an indication that the reaction proceeds very little toward the product, that is the product will in a smaller amount at equilibrium or that there is almost no reaction taking place. A large value of *(K)* is an indication that the reaction proceeds almost completely toward the product when it reaches equilibrium. Alternatively, when *(K)* has an intermediate value, the reactant and product are present in significant amount at equilibrium.

The relationship between the Equilibrium constant *(K)* and temperature is shown in the relationship below:

$$\frac{d\ln K}{dT} = \frac{\Delta H^{o}_{(T)}}{RT^{2}} \tag{3.57}$$

Where *($\Delta H^{o}_{(T)}$)* is the standard (at P_o) change in Enthalpy of reaction, *(R)* is the Universal constant, the value of which is available from thermodynamic tables (see Table 1 in APPENDIX A: List of Tables), *(T)* is the reaction temperature, and *(K)* is the Equilibrium constant. It follows from equation (3.57) that for an endothermic reaction with a positive change in enthalpy *($\Delta H^{o}_{(T)}$)* of reaction, the equilibrium constant will increase as a function of temperature. Inversely for an exothermic reaction with a negative change in enthalpy of reaction, the equilibrium constant will decrease as a function of temperature.

The Equilibrium Constant *(K)* at temperature *T* is often estimated on the basis of the equilibrium constant at T_o (written K^o) using the *Van't Hoff* equation. This equation assumes that the change in enthalpy *($\Delta H^{o}_{(T)}$)* of reaction is independent of temperature. The *Van't Hoff* equation is written as follow:

$$\ln\left(\frac{K}{K^{o}}\right) = -\frac{\Delta H^{o}_{(T_o)}}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) \tag{3.58}$$

Where *(K)* is the equilibrium constant at a temperature *T*, (*R)* is the Universal constant from thermodynamic tables (see Table 1 in APPENDIX A: List of Tables), $\Delta H^{o}_{(T_o)}$ is the standard change in Enthalpy of reaction at ambient temperature, and *(K^o)* is the Equilibrium constant at ambient temperature *(T_o)* calculated from the equation below:

$$\Delta G^{o}_{(T_o)} = -RT_o \ln K^o \tag{3.59}$$

Where *($\Delta G^{o}_{(T_o)}$)* is the change in Gibbs free energy of reaction standard temperature and pressure (T_o,P_o), and *(R)* is the universal gas constant. Both *($\Delta G^{o}_{(T_o)}$)* and *(R)* values are available from thermodynamic tables (see APPENDIX A: List of Tables) and K^o given by:

$$K^o = e^{\left(\frac{-\Delta G^{o}_{(To)}}{RT_o}\right)} \tag{3.60}$$

The *Van't Hoff* equation is often used as it gives a good approximation on the equilibrium constant (*K*) at temperature *T* which is an indication of the direction of the reaction without performing lengthy calculations for the change in Gibbs free energy (*ΔG*) at temperature *T* involving heat capacity calculations. The relationship between the change in Gibbs free energy at temperature *T* and reaction's equilibrium is well represented in the equation below:

$$\Delta G_{(T)} = -RT \ln K \tag{3.61}$$

Where *(K)* is the Equilibrium constant at temperature *T*, *(R)* is the Universal gas constant (see Table 1 in APPENDIX A: List of Tables), and *(ΔG)* is the change in Gibbs free energy between the inlet and outlet streams of the reactor at temperature *T* also evaluated from the following relationship:

$$\Delta G_{(T)} = \Delta H_{(T)} - T\Delta S_{(T)} \tag{3.62}$$

Where *(ΔH)* is the change in enthalpy between the inlet and outlet streams of the reactor at a temperature *T* evaluated from the relationship in equations (3.26) or involving heat capacities calculations, *(T)* is the temperature at which the heat is supplied, and *(ΔS)* is the

change in entropy between the inlet and outlet streams of the reactor at a temperature *T* evaluated from the relationship in equation (3.27) also involving heat capacities calculations.

Combining the energy balance and entropy balances in equations (3.50) and (3.51) respectively, and combining them with equation (3.62) above, to solve for the change in Gibbs free energy across the reactor at temperature *T* gives:

$$\Delta G_{(T)} = -TS_{gen(r)} \tag{3.63}$$

In reference to equation (3.63), for a change in Gibbs free energy at a temperature *T* equal to zero *($\Delta G_T = 0$),* The reaction is said to be reversible. However equilibrium is reached at minimum ΔG_T .

Performing a Gibbs free energy balance across the reactor where specie *(A)* enters the reactor at temperature *T* and produces specie *(B)* and un-reacted amounts of specie *(A)* in proportions relative to conversion *(x)* will give:

$$\Delta G_{(T)} = -TSgen = (x)\left[\begin{array}{l}\left(H^{o}_{f_B} + \int_{T_o}^{T} Cp_B dT - H^{o}_{f_A} - \int_{T_o}^{T} Cp_A dT\right) \\ -T\left(S^{o}_{f_B} + \int_{T_o}^{T} Cp_B \frac{dT}{T} - S^{o}_{f_A} - \int_{T_o}^{T} Cp_A \frac{dT}{T}\right)\end{array}\right] - TS_{mix_{(A,B)}} \tag{3.64}$$

Where subscripts *(A)* and *(B)* refer to the reactant and the product respectively; where *(ΔG)* at temperature *T* is the change in Gibbs free energy between the inlet and the outlet streams of the reactor at a reactor's conversion *(x)* to produces the product; where *($TS_{mixA,B}$)* is the work of mixing at the stream exiting the reactor as evaluated below:

$$\begin{aligned} TS_{mix_{(A,B)}} &= -RT\left[(1-x)\ln(1-x) + (x)\ln(x)\right] \\ G_{mix_{(3)}} &= RT\left[(1-x)\ln(1-x) + (x)\ln(x)\right] \\ TS_{mix_{(A,B)}} &= -G_{mix_{(3)}} \end{aligned} \tag{3.65}$$

Where (G_{mix3}) is the work of mixing at the stream going out of the reactor inversely equivalent to $(TS_{mixA,B})$.

The term $-TS_{gen(r)}$ being a function of reaction's equilibrium automatically confirms that the work of mixing (G_{mix3}) at the stream exiting the reactor is also a function of equilibrium. Two consecutive case studies on the isomerization of Butane followed by the Reverse Water-Gas Shift (RWGS) reaction are used to assess and confirm these relationships.

4 CASE STUDY I: BUTANE ISOMERIZATION PROCESS

To better illustrate the concept of work flow in reactive processes, the isomerization of Butane is used as an example. This particular isomerization case study has been chosen for its similarity to our baseline assumptions where the process is an open steady-state process at constant pressure which transforms specie *(A)* to produce specie *(B)* with the heat capacity of the inlet stream of the process being equal to the heat capacity of the process' outlet stream. This example on the Butane isomerization process have almost equal heat capacities at the inlet and outlet streams of the process at temperature T_o with Heat capacities values of 30.92 KJ/mol.K at the inlet stream and 30.97 KJ/mol.K at the outlet stream. For this case study the streams going in and out of the process are assumed to be equal because their difference is insignificant and thus is befitting to be considered as a *simple* process. A comparative evaluation where heat capacities of the streams in and out of the process have a large difference will follow in later chapters of this dissertation.

This case study discusses the isomerization of Butane where iso-butane also called i-butane; trimethylmethane; 1,1-dimethylethane; 2-methylpropane (Gas Encyclopedia, 2009) isomerizes to produce n-butane as illustrated below:

$$\text{Iso-butane} \longleftrightarrow \text{n-butane}$$
$$C_4H_{10} \leftrightarrow C_4H_{10} \tag{4.1}$$

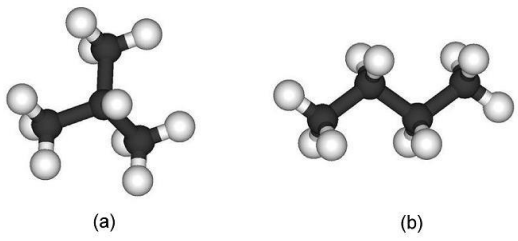

Figure 4-1. Isomerization of iso-butane (a) to n-butane (b) (Barron, 2010)

Figure 4-1 shows the spatial configurations of iso-butane (a) and n-butane (b) where both Iso-butane as well as n-butane have four atoms of carbon (in black) and ten atoms of hydrogen (in white). Both iso-butane and n-butane are isomers of Butane with the molecular formula C_4H_{10}, same empirical formula, same bond structure but different spatial arrangements.

For this case study, one mole of iso-butane is fed as a pure substance to the process to produce n-butane in quantities respective to conversion. The amount of feed to the overall process will remain one mole for the course of this study while temperature and conversion will vary consecutively to illustrate their respective effects on the work flow within the process. The isomerization process of Butane is graphically shown in the figure below:

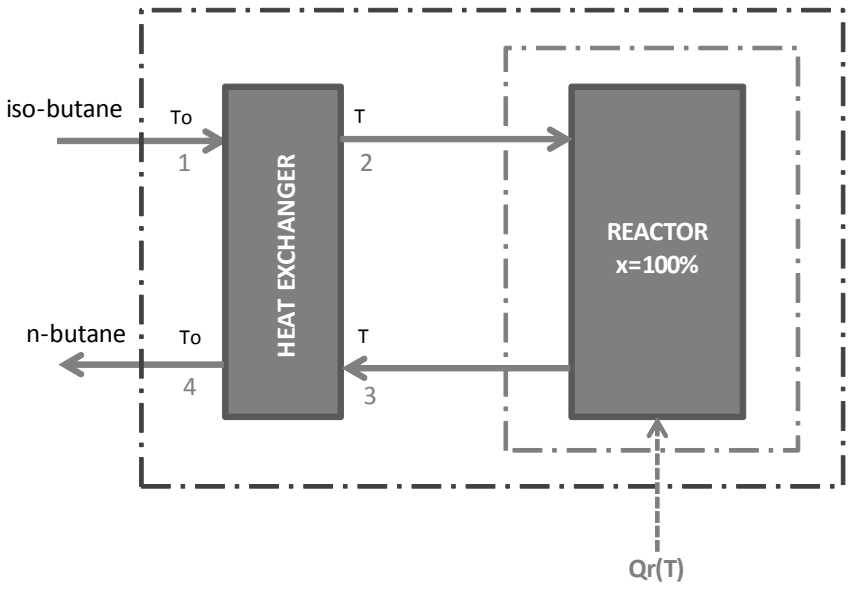

Figure 4-2. Basic equipments set-up for the isomerization process of Butane at complete conversion in the reactor

Figure 4-2 shows the main equipments and streams involved in the Butane isomerization process which is an in-depth reflection of Figure 3-4 and where the feed material to the overall process (iso-Butane) at ambient temperature and pressure (T_o,P_o) goes through a

heat exchanger to step-up the operating temperature from *(T_o)* to the reactor's temperature *(T)* then proceeds through the reactor where the isomerization reaction takes place at complete conversion. The feed and exit streams at the reactor exchange heat and reach their respective temperatures without the need for external heating or cooling since the heat capacities of butane and iso-butane are almost equal.

The product material (n-Butane) exits the reactor at temperature *(T)* before going through a heat exchanger once more to step-down the stream's temperature from reactor's temperature *(T)* to reference temperature *(T_o)* and proceeds to exiting the process at temperature *(T_o)* as a pure substance. There are no recycle/reflux streams for this flowsheet or byproduct at this stage.

The solid black lines in and out of the process in Figure 4-2 represent material streams while the dashed line represents the energy stream, and intermittent dotted & dashed lines represent boundaries of energy balances performed.

Looking at the process as a whole and in order for this process to be operational, energy requirements in the form of Heat (change in Enthalpy, *ΔH* at T_o,P_o) and Work (change in Gibbs free energy, *ΔG* at T_o,P_o) across the process must be met. What Sempuga et al. (2010) calls the *ΔG-ΔH diagram* (or gh-diagram) can be used to establish whether the isomerization process can be feasible and operated as a reversible *simple* process. The gh-diagram is shown below:

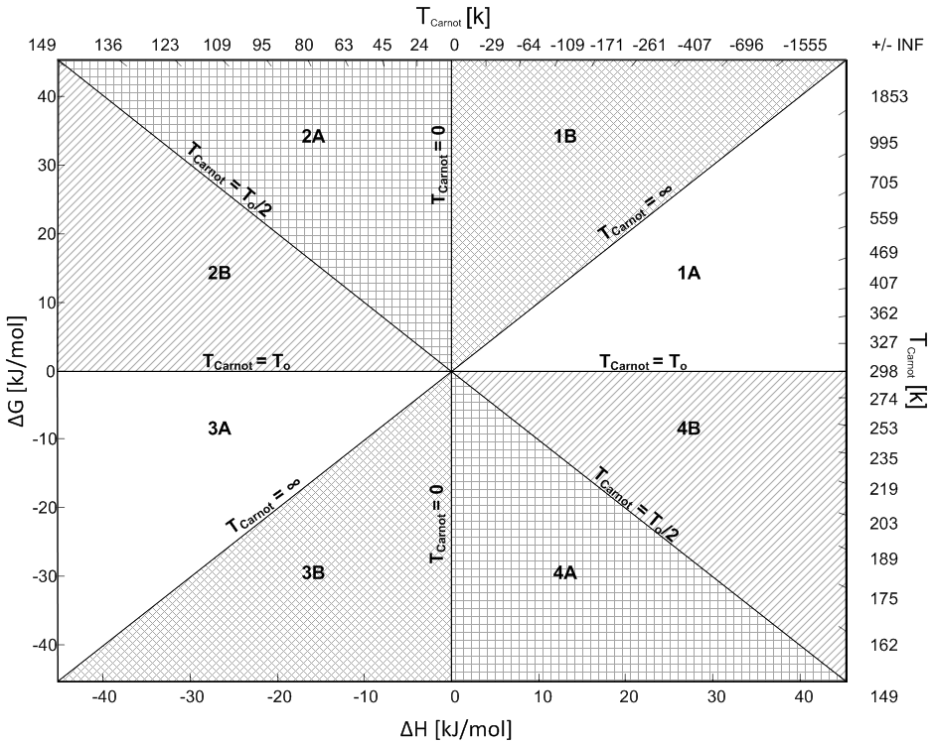

Figure 4-3. gh-diagram subdivided in thermodynamic regions (Sempuga et al, 2010)

The gh-diagram is a graphical tool used to analyze the feasibility of chemical processes in term of heat and work load as well as to establish the most appropriate method of supplying or extracting work. The change in enthalpy across processes lies on the x-axis of the gh-diagram while the change in Gibbs free energy across processes lies on the y-axis of the gh-diagram. In Figure 4-3, the change in enthalpy (*ΔH*) and the change in Gibbs free energy (*ΔG*) are extensive properties that are linked to the mass balance and not directly to each other.

The four main regions (1, 2, 3, and 4) of the gh-diagram show whether the process' heat and work is to be supplied or rejected and they are each subdivided in two regions: Regions 1A-4A and Regions 1B-4B as shown in Figure 4-3. In Regions 1A, 2A, 2B, and 3A of the gh-diagram, it is possible to run chemical processes reversibly as simple processes; while in Regions 1B, 3B, 4A and 4B, chemical processes cannot be run reversibly as simple processes

due to their unfeasible Carnot temperatures. The Butane Isomerization process lies in the gh-diagram as shown below:

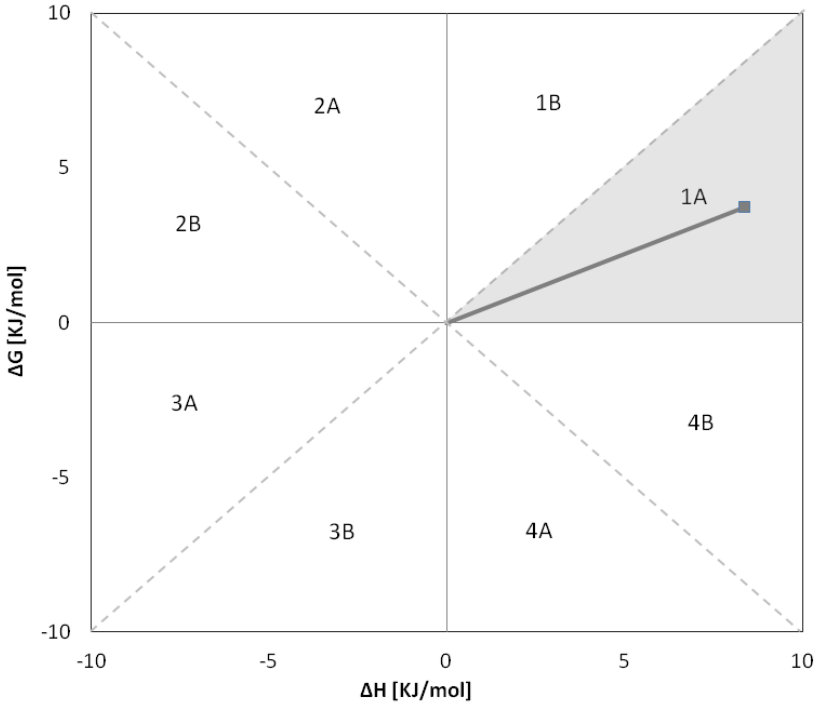

Figure 4-4. Butane isomerization process drawn in the gh-diagram

The isomerization process of Butane is an endothermic process requiring 8.4 KJ of heat and 3.7 KJ of work in order to proceed at complete conversion. The amount of heat requirement being greater than the amount of work requirement for this process is an indication that the process is feasible. Inputting the heat and work requirement values into Figure 4-4 shows that the process lies in region 1A characterized by a positive change in enthalpy as well as a positive change in Gibbs free energy across the process represented on the gh-diagram. Thus in principle supplying heat alone at an appropriate temperature to the process should be sufficient to meet both its heat and work requirement. Heat by virtue of the temperature will carry with it the work to the process as shown in the heat engine configuration in Figure

3-2. In order to meet the work requirement of the process via heat alone, heat must be supplied at least at the process Carnot temperature (538K) calculated from equation (3.15).

4.1 Temperature effect on the process

The approach adopted in synthesizing an efficient process flowsheet for the Butane isomerization process discussed in this dissertation is based on properties hierarchy design methodology where the effects of assumptions such as temperature and conversion are evaluated consecutively to identify their respective effects on the flow of work across a process which in turn will identify the process' overall energy efficiency and feasible efficiency improvements.

Based on targets and assumptions for the synthesis of n-butane from iso-butane, it has been asserted that operating at the process' reversible temperature (or Carnot temperature) would be most beneficial since at the Carnot temperature heat is capable of carrying the minimum work requirement to the process thus the process would not loose work nor will it be work deficient.

Temperature being an influential parameter to the overall process performance as seen in the previous example where specie *(A)* reacts to form specie *(B)*, at Carnot temperature it has been recorded that the work requirement at the process could be achieved.

In this example on the Butane isomerization process, the flow of work across the process will be evaluated at the Carnot temperature where the process' reversibility and equilibrium will be achieved as well as at different temperatures (between 300K and 1000K) and conversions

(from almost no conversion to complete conversion) to assess their respective effect on the flow of work across the process.

4.1.1 Temperature effect on Reaction's Equilibrium

Following the Second Law of thermodynamics, the total entropy (or level of disorder) has a natural tendency to increase until it reaches its maximum at equilibrium state. Practically speaking, for a chemical process such as the isomerization of Butane where a reaction takes place in both forward and reverse direction, the feed (iso-butane) reacts to form the product (n-butane) in proportions which will increase until the reaction reaches a state where the reactants and products concentration ratios no longer change with time where it is said to have reached *equilibrium state*.

The relationship between reaction's equilibrium and temperature has been established in a few equations seen in previous chapters of this dissertation. Applied to the isomerization of Butane reaction, the effect of temperature on the equilibrium constant *(K)* is plotted below:

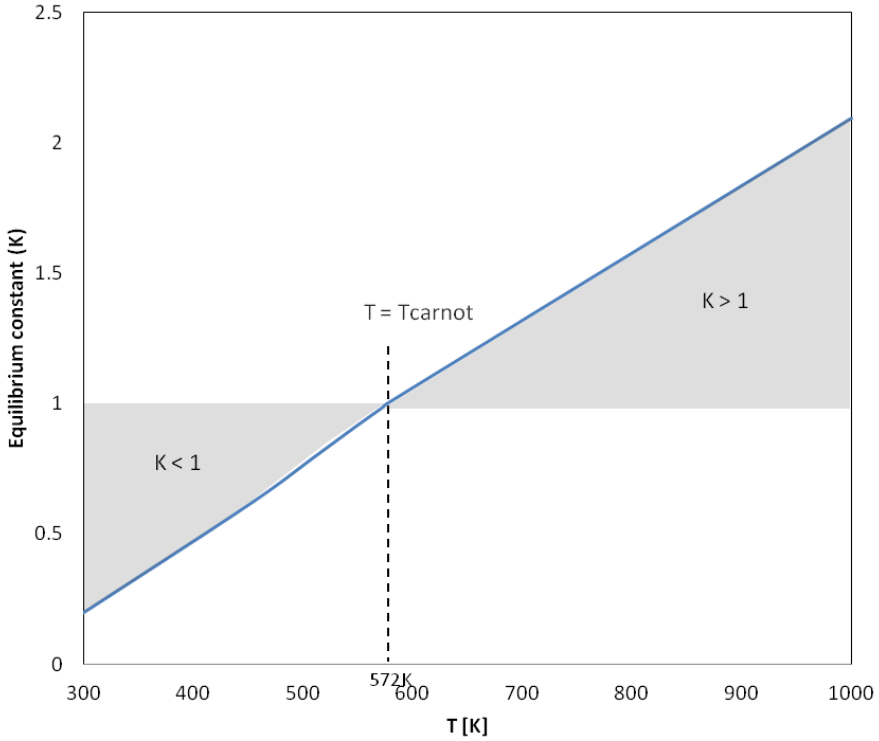

Figure 4-5. Temperature effect Equilibrium constant for the isomerization reaction

Figure 4-5 shows that for the endothermic isomerization reaction, the equilibrium constant (*K*) increases as a function of temperature, thus encouraging the reaction to proceed forward (toward the product). At every point on this increasing line in Figure 4-5, reaction equilibrium is reached.

We notice in Figure 4-5 that at the point where $T = T_{Carnot}$ (538K), $K = 1$, this can also be shown using equation (3.58). We also see that for this case when $K = 1$, the equilibrium conversion is 50% which means that the work of separation would need to be supplied in order to have pure product coming out of the process, and a recycle will be needed to achieve the required production rate. We also know that for a simple process, where heat is added at the reactor only and where it is assumed complete conversion, when heat is transferred at $T = T_{Carnot}$, the process as a whole is reversible. However in this case, because of the limitations

due to equilibrium conversion, the process would not be reversible since the process would require additional work, in order to separate the reactants from the product.

At temperatures above the Carnot temperature, the reaction's equilibrium constant *(K)* is greater than one, therefore the mixture contains more product than reactant and the work of separation decreases, however from the overall process point of view work is lost, which can be evaluated from equation (3.18).

At temperatures below the Carnot temperature, the reaction equilibrium *(K)* is less than one and the work lost at the process will be negative as evaluated from equation (3.18). Thus for this example for $K < 1$, less product will be made and this might require larger recycle stream in order to achieve the required production rate, thus the process might require a large amount of work of separation. From the process point of view the isomerization process will be work deficient or infeasible as is; however if recovered, the large work of separation may serve to compensate for the work deficiency at the reactor.

While the relationship between temperature and reaction equilibrium has been established, the relationship between the change in Gibbs free energy between the inlet and outlet streams of the reactor at temperature *T* and the reaction equilibrium is assessed below.

The change in Gibbs free energy between the streams in and out of the reactor at temperature *T,* (ΔG_T), is an indication of the direction of the reaction equilibrium as defined by the relationship in equation (3.61). Plotting the change in Gibbs free energy (ΔG_T) across the reactor as a function of temperature gives:

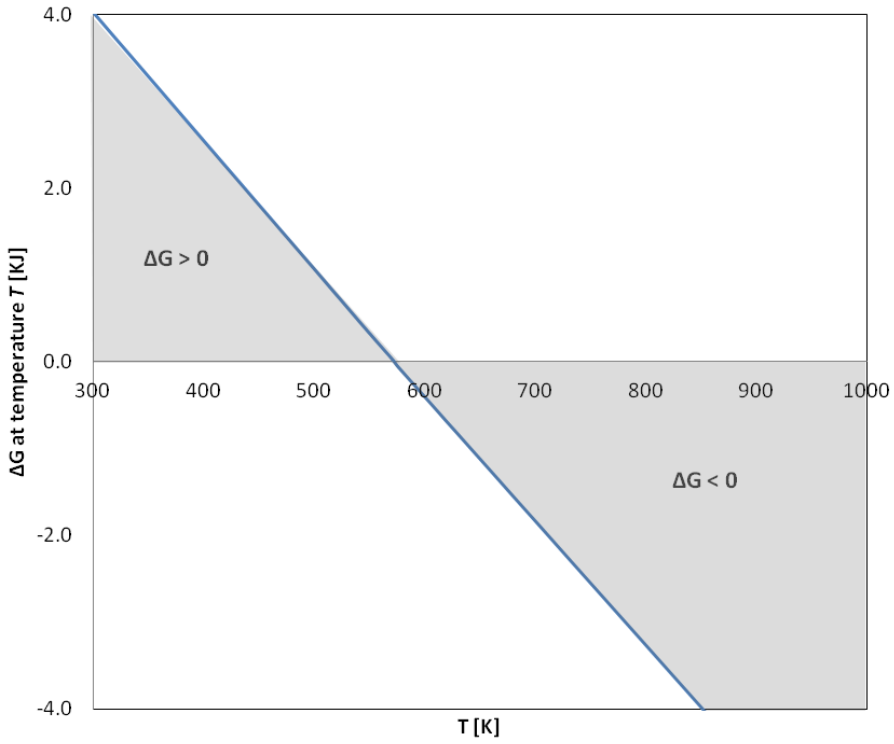

Figure 4-6. Change in Gibbs free energy across the reactor at temperature *T* plotted as a function of temperature

Figure 4-6 shows a decreasing trend of the Gibbs free energy curve as a function of temperature where the change in Gibbs free energy across the reactor at temperature *T* curve crosses the x-axis at the reactor's reversible temperature (572K) evaluated as the temperature at which the difference between the Gibbs free energy at the stream entering the reactor and the Gibbs free energy at the stream exiting the reactor is nil because at this temperature the Gibbs free energy at the streams going in and out of the reactor are the same.

For a negative (ΔG_T), the Gibbs free energy at the stream going into the reactor is greater than the Gibbs free energy at the stream going out of the reactor and -as per equation (3.61) , the corresponding equilibrium constant (K) is greater than one, thus the reaction is proceeding toward the products. For a positive (ΔG_T), the Gibbs free energy at the stream

going out of the reactor is greater than the Gibbs free energy at the stream going into the reactor and -as per equation (3.61), the corresponding equilibrium constant (*K*) is less than one, thus the reaction will not proceed forward.

The close relationship between the change in Gibbs free energy at temperature *T* (ΔG_T) and the $-TS_{gen}$ term established in equation (3.63) is an indication on the direction of the reaction's equilibrium. Plotting the $-TS_{gen}$ term as a function of temperature gives:

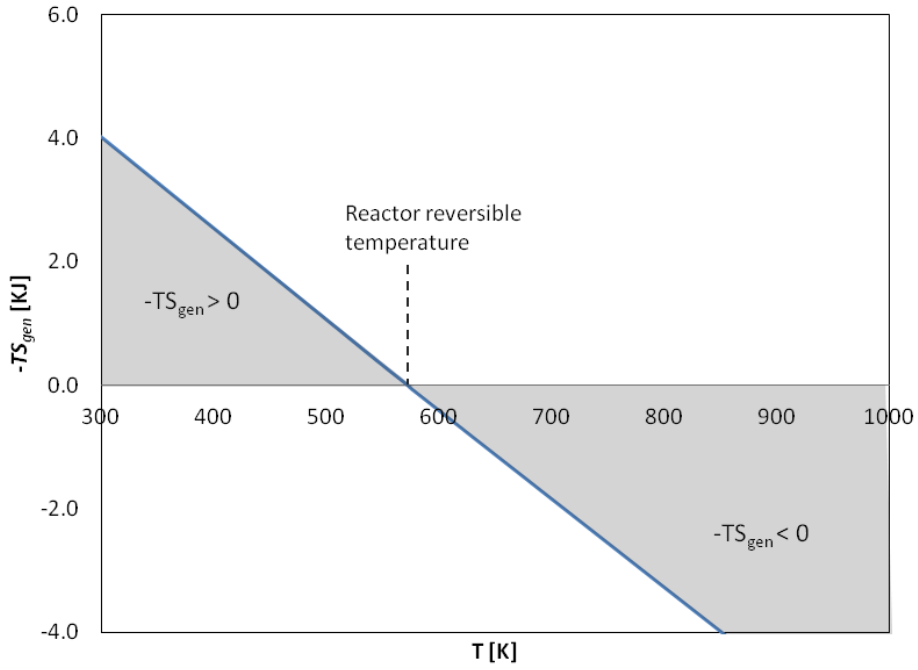

Figure 4-7. -*TSgen* curve as a function of temperature for the Butane isomerization reaction

The $-TS_{gen}$ curve is a decreasing curve crossing the x-axis at the reactor reversible temperature (572K) because at this temperature the Gibbs free energy at the inlet stream of the reactor and the Gibbs free energy at the outlet stream of the reactor are equal.

Consequently, for a positive $-TS_{gen}$ term, the process is proceeding toward the reactant (iso-butane), and for a negative $-TS_{gen}$ term, the process is proceeding toward the product (n-butane). On these findings alone, in order for this process to meet its target and produce n-butane, the change in Gibbs free energy between the inlet and outlet streams of the reactor at temperature *T* will have to be nil or negative, and consequently the $-TS_{gen}$ term will also be nil or negative.

Based on the results on the effect of temperature on the isomerization reaction's equilibrium, additional parameters will have to be included to these findings to make comprehensive decisions. At the process level it is desirable to transfer heat to the process at the Carnot temperature where the process is reversible, while at the reactor level it is desirable to transfer heat to the reactor at the reactor's reversible temperature (572K) where the reactor is reversible and no waste of energy takes place.

A dilemma arises when operating at the process reversible temperature, there are irreversibilities at the reactor and vice versa. But since when the process is operating at the reactor's reversible temperature (572K) irreversibilities occur at the process level, it is preferable to supply heat to the process at its reversible temperature (Carnot temperature, 538K) where there are no irreversibilities occurring at the process and maximize heat and work utilization within the process.

Further investigations on the work flow across the isomerization process will assess how temperature affects the performance of the Butane isomerization process which in turn will provide basis for decision-making during the early stages of its process synthesis.

4.1.2 Temperature effect on Work flow across the overall Process

The flowsheet illustrated in Figure 4-2 shows major equipments involved in the isomerization process of Butane. The temperature of the streams coming in and out of the overall process is intended not to vary and remains at standard temperature and pressure throughout these evaluations, while the temperature at which heat is supplied to the reactor is varied (between 300-1000K) to investigate its effect on the overall work flow across the process at its Carnot temperature (538K) as well as at other temperatures.

The change in Gibbs free energy (*ΔG*) at ambient temperature and pressure *(T_o,P_o)* across the process also called *Ideal work* is the minimum amount of work required at the process and is given by the equation below:

$$\Delta G_{(T_o)} = \Delta H_{(T_o)} - T_o \Delta S_{(T_o)} \tag{4.2}$$

Where (T_o) refers to the standard temperature, *(ΔG)* at temperature T_o is the change in Gibbs free energy across the process also equivalent to the change in exergy *(ΔB)* at temperature T_o as shown in equation (3.56), *(ΔH)* at temperature T_o is the change in enthalpy across the process evaluated as per equation(3.19), and *(ΔS)* at temperature T_o is the change in entropy across the process (refer to APPENDIX B: Calculations).

The change in Gibbs free energy between the inlet and the outlet streams of the process at temperature T_o which is the work requirement for the process does not vary as a function of temperature since the streams in and out of the process are kept at ambient conditions (T_o ,P_o) irrespective of what occurs within the process. Graphically, the change in Gibbs free energy *(ΔG)* between the inlet and outlet streams of the process at ambient temperature and pressure (T_o ,P_o*)* is a constant linear curve at *ΔG* = 4.0 KJ and represents the amount of work required by the isomerization process to produce n-butane from iso-butane at

complete conversion. It will be preferable to supply this amount of work to the process reversibly through a heat engine setup as shown in Figure 3-2.

We therefore see that the work requirement of the process remains the same irrespective of the temperature at which heat is supplied to the process, however there is only one temperature (T_{Carnot}) at which the work supplied with the heat matches the work requirement of the process, thus above T_{Carnot}, more work than required by the process is supplied with the heat this work will be lost if not recovered; below the T_{Carnot} less work than required by the process is supplied with heat, and thus the process would be work deficient unless additional external work is supplied to the process.

4.1.3 Temperature effect on the Work flow at the Heat Exchanger

Evaluating the effect of temperature on the work flow at the heat exchanger will give an indication on whether work is absorbed, rejected, or nil at the heat exchanger. For this case of butane isomerization, it is clear that because the heat capacities of the streams in and out of the process are very close and almost equal, we have assumed them to be equal and therefore there is no need for external heat transfer at the heat exchanger in order to achieve the needed temperatures of the streams going out of the heat exchanger and thus there will be no work associated with the heat exchanger.

For the second case study on the Reverse Water-Gas Shift (RWGS) reaction where heat capacities at the streams going in and coming out of the process are significantly different, the heat and work evaluations at the heat exchanger will be of relevance as it will affect the work flow within the process.

4.1.4 Temperature effect on the Separator

For a *simple* process, it is assumed complete conversion in the reactor and thus no work flow will be associated with the separator. However even though we have used Butane isomerization process to demonstrate a *simple* process, we see that the complete conversion assumption will not hold, because for this process conversion is limited by equilibrium in the reactor even when heat is supplied at T_{Carnot}, the process reversible temperature. Therefore the process deviates from being a *simple* process because of the work of separation and a recycle that are required in order to achieve a complete conversion overall. The work of separation can be calculated using equation (4.3).

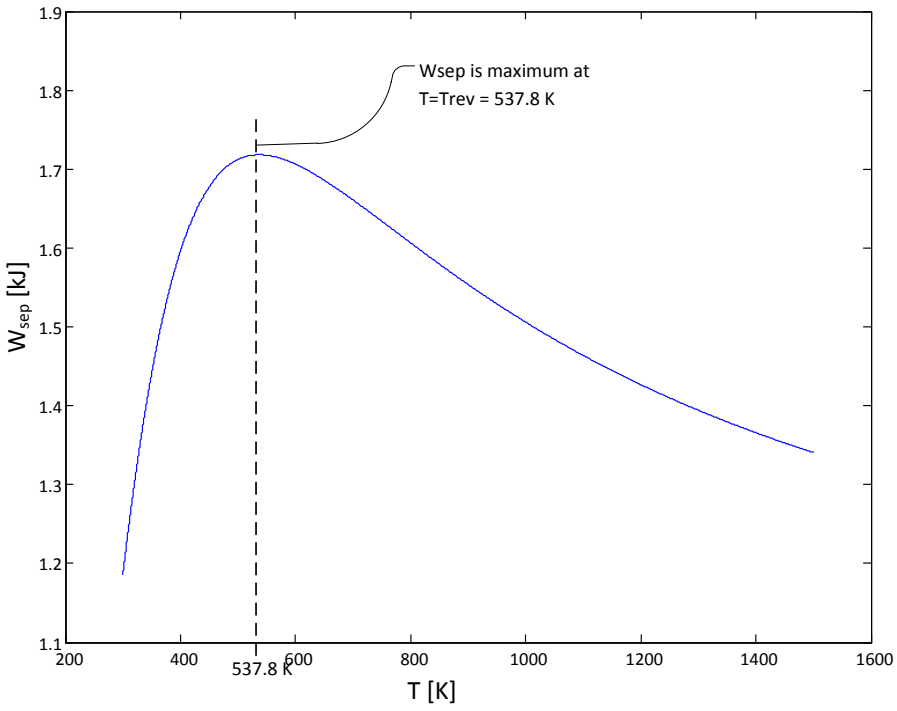

Figure 4-8: Work required by separator as a function of reactor temperature, without recycle

Figure 4-8 shows how the temperature of the reactor affects the work required at the separator when only one pass is considered, that is no recycle. In this case the overall

process has incomplete conversion that is the product (n-butane) production is less than 1 mole.

$$W_{sep} = T_o S_{mix} = -W_{mix(reactor)} = -G_{mix_3} \tag{4.3}$$

Where W_{sep} is the work requirement at the Separator, T_oS_{mix} is a mathematical equivalent to the work requirement at the Separator, $W_{mix(reactor)}$ is the work of mixing at the reactor where the feed and the product generated are mixed, and G_{mix3} is the work of mixing at the stream exiting the reactor. The negative sign preceding the $W_{mix(reactor)}$ term in equation (4.3) indicates that the work of mixing at the reactor is rejected. With an equal amount of work requirement at the separator, it appears as if the work of mixing is rejected at the reactor and absorbed at the separator to split the mixed material in the reactor into separate streams.

From Figure 4-8 we see that maximum work of separation is required at $T = T_{Rev} = T_{Carnot}$ without a recycle stream. However the recycle stream needs to be added in order to achieve complete conversion for the overall process, that is to be able to produce 1 mole of n-butane from 1 mole of iso-butane; in this case the work required at the separator as a function of temperature is as follows:

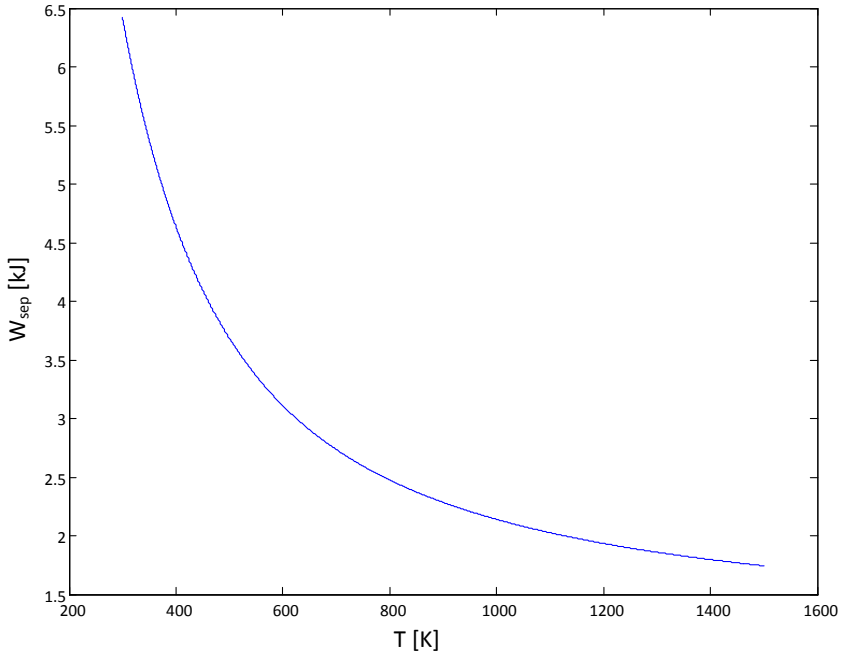

Figure 4-9: Work required by separator as a function of reactor temperature, with recycle

From Figure 4-9, we see that the work of separation in this case decreases with increasing reactor temperature and this is because the size of the recycle also decreases as the conversion increases with the reactor temperature. We will see what this means from the point of view of work flows around the overall process in subsequent sections.

4.1.5 Temperature effect on Work flow at the Reactor

For a *simple* process where it is assumed complete conversion in the reactor, both the stream coming in and that coming out of the reactor are pure substances and thus no work of mixing is involved. For this case, keeping in mind that the heat capacities are also equal, we can show that the heat and the work requirement of the reactor are equal to the heat and work requirement of the entire process. That is:

$$W_{r_required} = \Delta B_{(T)r} = \Delta G_{(T_o)p} \tag{4.4}$$

Where the work required (W_r) by the reactor, $\Delta B_{(T)r}$ is the change in Exergy across the reactor at the reactor temperature (T) and $\Delta G_{(T_o)p}$ is the change in Gibbs free energy across the process taken at ambient temperature.

For the case of Butane isomerization, we saw that the conversion at the reactor is limited by equilibrium and thus, the stream coming out of the reactor is not a pure substance but a mixture of reactant and product at a proportions determined by the reactor temperature. Figure 4-10 is a plot of the work required by the reactor as a function of reactor temperature at complete and incomplete conversion. In both cases the reactor produces 1 mole of n-butane; however for the incomplete conversion case the amount of iso-butane in the feed to the reactor varies with temperature (i.e we allow for recycle) in order to achieve a production of 1 mole of n-butane for all conversion.

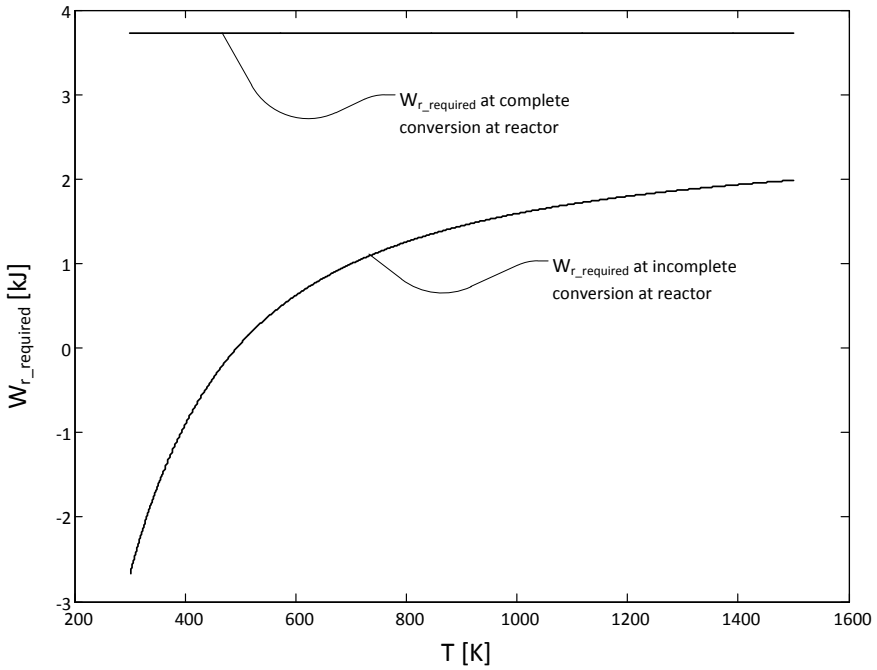

Figure 4-10: The work required by the reactor as a function of reactor temperature at complete and incomplete conversion

Figure 4-10 shows that when the conversion at the reactor is complete the work requirement remain unchanged and is equal to that of the overall process at all temperatures. However when the conversion is incomplete the work requirement increases with increasing temperature but it is less than that of complete conversion at all temperatures; the reason for that is because for incomplete conversion the work of mixing is included in the calculation of the reactor work requirement, this implies that the work of mixing is used to supply for some of the reactor work requirement and thereby reducing the external work that needs to be supplied. In principle the work of mixing is not recovered and is not automatically absorbed by the reactor, thus the plot in Figure 4-10 represents an ideal situation where the work of mixing is recovered and absorbed by the reactor. We will consider that the work of mixing if not recovered; it is simply lost and will be considered as irreversibility in the reactor.

HEAT SUPPLIED TO THE REACTOR AT DIFFERENT TEMPERATURES

Here we are comparing the work that is supplied together with heat to the reactor at the reactor temperature versus the work requirement of the reactor. Remember that the work that is carried with heat at temperature *T* is given by:

$$W_{r_heat} = \Delta H_{(T)_r}\left(1-\frac{T_o}{T}\right) \tag{4.5}$$

Because the work of mixing is not used by the reactor, it will not be taken into account and therefore the work requirement of the reactor for both complete and incomplete conversion will be the same.

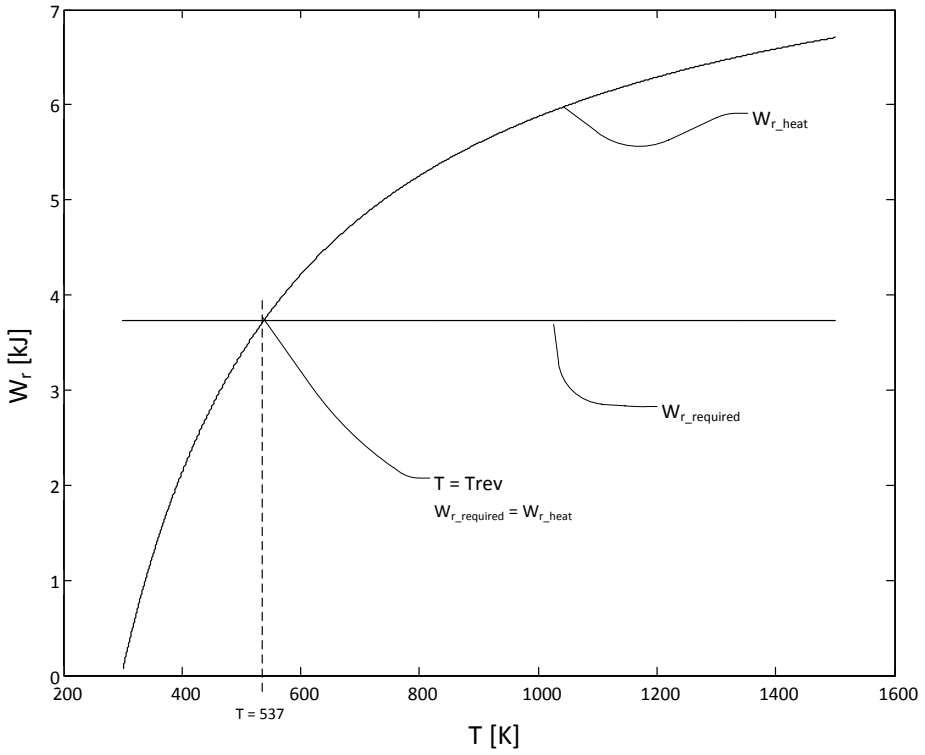

Figure 4-11: Comparison of the work required by the reactor with the work supplied with heat as a function of temperature

Figure 4-11 shows that when the heat supplied to the reactor is at temperature below the T_{Carnot}, the work supplied with heat is less than what the reactor requires and thus the reactor would require additional external work for it to achieve the desired production rate. At T_{Carnot}, the work supplied with heat matches the work required by the reactor and thus in principle no additional work is required at the reactor.

Above T_{Carnot} we see that heat carries more work than required by the reactor and consequently the additional work becomes irreversibility if it is not recovered.

The work deficiency or work lost at the reactor can be evaluated as a function of temperature as follows:

$$W_{lost_r} = \Delta H_{(T)_r} \times T_o \left(\frac{1}{T_{Carnot}} - \frac{1}{T} \right) \tag{4.6}$$

4.2 Work flows interactions within the process

Previously we have shown work requirements and flows around the major equipments of the Butane isomerization process. Since the heat capacity of n-butane and that of iso-butane are close, we have assumed them to be equal and therefore we can ignore external energy transfers across the heat exchanger and only focus on the reactor and the separator.

We have shown that if the reactor can achieve complete conversion of iso-butane to n-butane, there will be no need for a separator and that the reactor heat and work requirement will be the same as for the entire process. In that case the process is a *simple* process which requires a single heat transfer at the T_{Carnot} in order to satisfy the heat and the work requirement of the entire process.

However because the conversion of reaction of iso-butane to n-butane is limited by equilibrium, then there is need for a separator in order and a recycle in order to achieve the required butane production, that is 1 mole of butane from 1 mole of iso-butane. And therefore we see that there is an interaction between the reactor and the separator and in this section we will explore this interaction.

In Figure 4-12, we plot on the same figure the work required for separation, the work required at the reactor, the work supplied by heat at the reactor and conversion as a function of temperature, with conversion axis on the right of the graph.

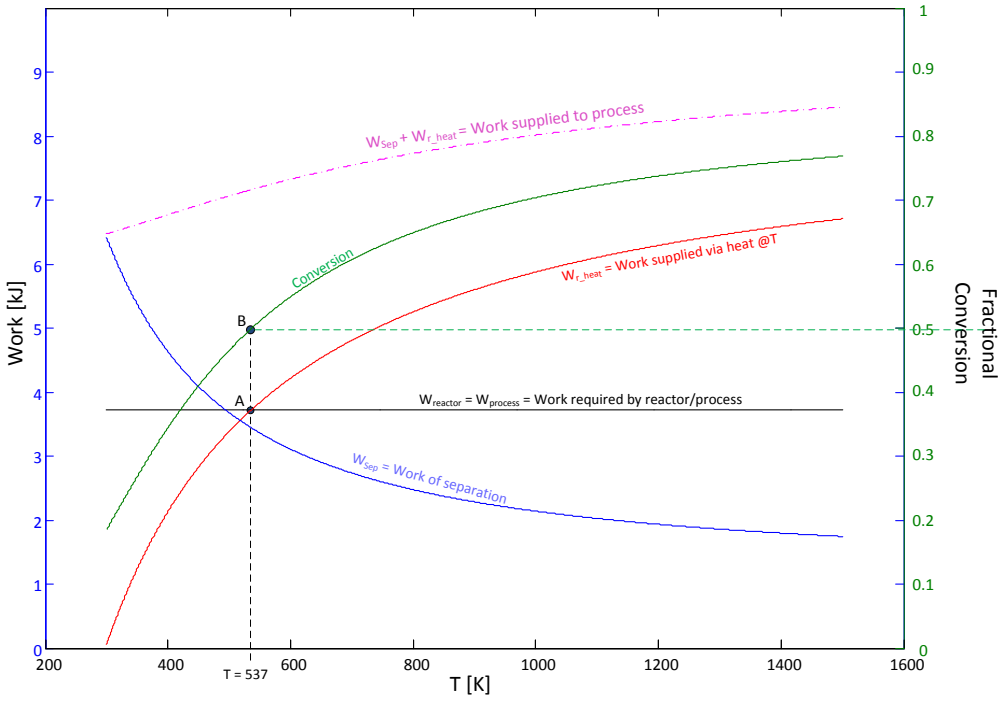

Figure 4-12: Temperature dependence of process parameters: Work of separation, reactor work requirement, work supplied with heat and reactor conversion

In Figure 4-12 we see that equilibrium conversion increases with increasing temperature but does not reach a fractional conversion value of 1; each conversion less than 1 corresponds a certain amount of work of separation required. In fact we can see that even when heat is supplied at the reactor reversible temperature, conversion is only 50% (point B) and thus the process still requires external work to be supplied for separation. We may recall that at the reversible temperature the heat added to the reactor carries with it work matching the work requirement of the process (shown at point A) and thus in principle no additional external work is needed; however we can see from Figure 4-12 that this is not the case, one still needs to supply the work of separation due to conversion limitations at the reversible temperature.

When $T < T_{Carnot}$, the process is normally work deficient since the work supplied with heat at T is less than what the process requires, but we see in Figure 4-13 that even at $T < T_{Carnot}$, the process still receives more work than required; this is because at these temperatures the

conversion is low and thus a large recycle is required in order to maintain the product rate of 1 mole of n-butane per mole of iso-butane, consequently the work of separation is larger because of large amount of material to separate.

We therefore see that for all temperatures at which the reactor operates at, the total work that goes to the process is more than what is required and thus the process is irreversible, that is the total work supplied to the process is greater than the change in Gibbs free energy across the process:

$$\Delta G_{(T_o)p} < \Delta H_{(T)r}\left(1-\frac{T_o}{T_{Carnot}}\right)+W_{Sep} \tag{4.7}$$

Where $\Delta G_{(T_o)p}$ is the work required by the process. The first term on the right hand side of the equation represent the work supplied with heat at the reactor and the second term (W_{Sep}) is the work of separation required given by equation (3.46). We may also recall that for a reversible process:

$$\Delta G_{(T_o)_p} = \Delta H_{(T)_r}\left(1-\frac{T_o}{T_{Carnot}}\right) \tag{4.8}$$

For the isomerization of butane one can therefore conclude that irreversibility in the process is :

- Caused by the loss of work of mixing in the reactor when the reactor is operated at T_{Carnot}. The work of mixing is caused by limitations in conversion due to equilibrium.
- A combination of the loss of work of mixing and irreversibility caused by supplying heat at any other temperature than the T_{Carnot}.

We therefore see that in order to achieve a production of 1 mole of n-butane from 1 mole of iso-butane when the heat is supplied at the reversible temperature, we need to supply additional work of separation and thus this work becomes irreversibility to the process.

In order to make the process reversible we must be able to recover the work of mixing from the reactor and use it to supply for the work required by the separator. Alternatively if the reactor is able to use the work of mixing within itself then, in principle, its work requirement would be reduced by an amount equivalent to the work of separation and this will also make the process reversible. When the reactor uses the work of mixing then the work requirement of the reactor is given by:

$$W_{reactor} = \Delta B_{(T)_r} = \Delta H_{(T)_r} - T_o \Delta S_{(T)_r} \tag{4.9}$$

Where the change in entropy includes the entropy of mixing as follows:

$$\Delta S_{(T)_r} = S^{out}_{A(T)} + S^{out}_{B(T)} + S^{out}_{mix,A,B} - S^{in}_{A(T)} \tag{4.10}$$

And when the reactor is reversible, heat must be supplied to the reactor at the reversible temperature (T_{Rev}). T_{Rev} here is not the same as T_{Carnot} (the process reversible temperature) and T_{Rev} will not necessarily match the current reactor temperature (T). T_{Rev} is calculated from the heat and work requirement across the reactor only. Thus for a reversible reactor the heat and work requirement are related as follows:

$$\Delta B_{(T)_r} = \Delta H_{(T)_r}\left(1 - \frac{T_o}{T_{\mathrm{Re}v}}\right)$$

Therefore (4.11)

$$T_{\mathrm{Re}v} = \frac{T_o}{1 - \dfrac{\Delta B_{(T)_r}}{\Delta H_{(T)_r}}}$$

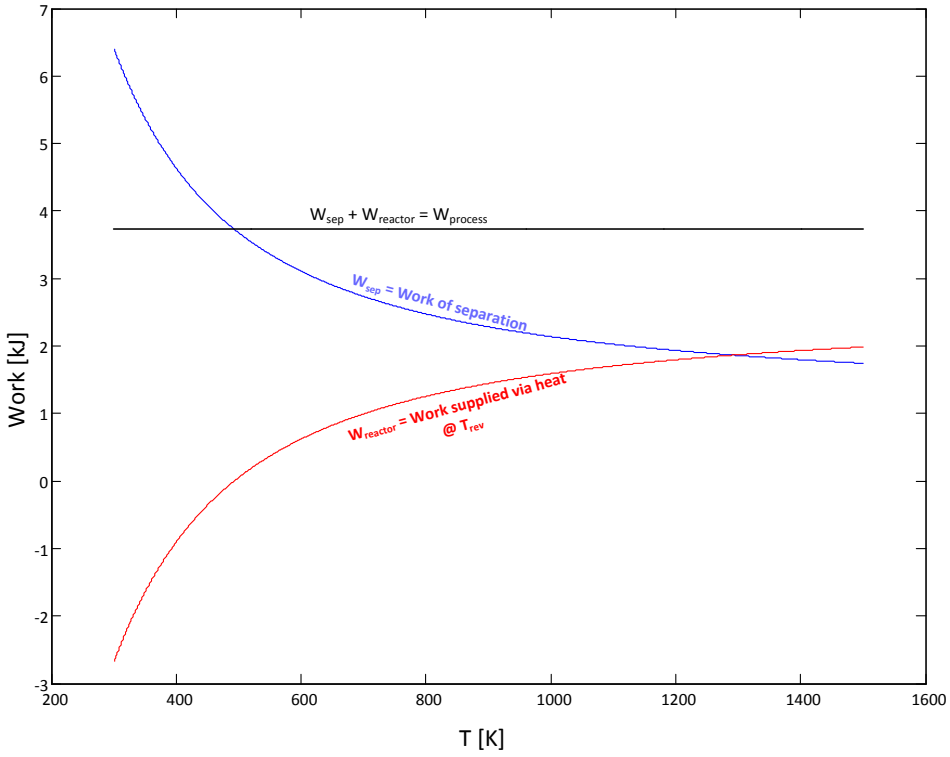

Figure 4-13: Work of separation and work requirement of reactor when work of mixing is reintegrated in the reactor

In Figure 4-13 the work requirement of the reactor (taking into account the work of mixing at the reactor's exit stream) and the work of separation are plotted as a function of the reactor temperature. We can see that the sum of these works matches the work requirement of the process and thus the process is reversible since the total work does not exceed what the process requires.

However this requires that heat be added to the reactor at the reactor reversible temperature (T_{Rev}). From equation (4.11) we can plot the reversible temperature of the reactor as a function the actual reactor temperature as follows:

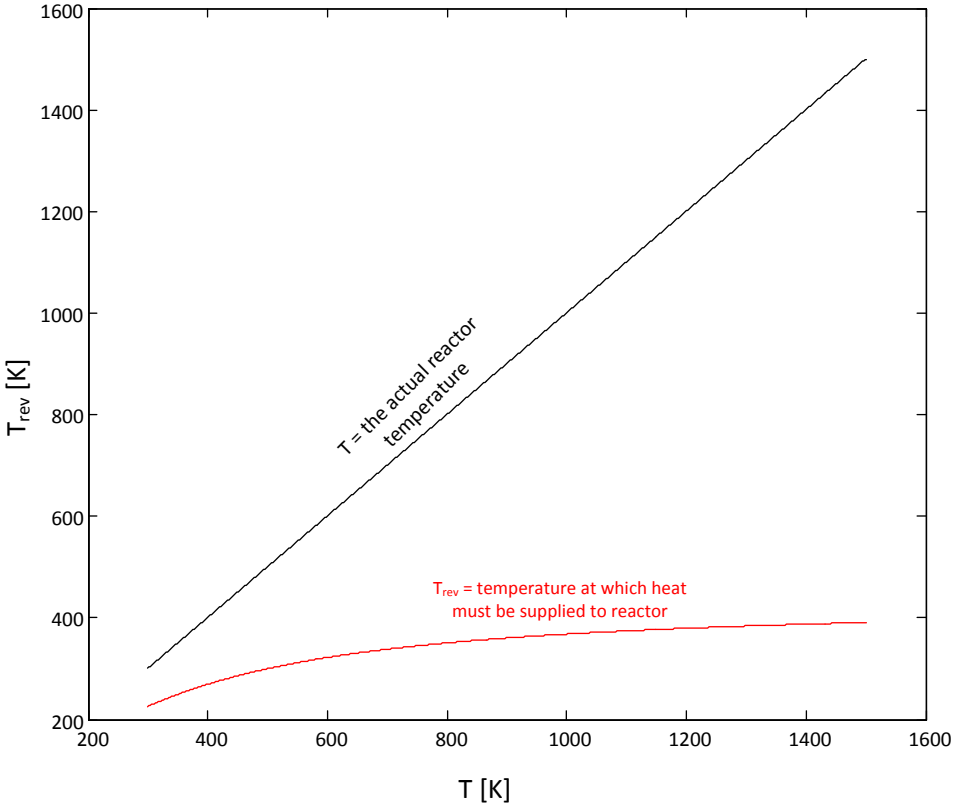

Figure 4-14: Reactor reversible temperature as a function of the actual temperature in the reactor

We may recall that the reactor reversible temperature (T_{Rev}) is the temperature at which heat must be supplied to the reactor in order for work within the heat to match the reactor's work requirement. We can see from Figure 4-14 that T_{Rev} does not match and is below the actual reactor temperature (T, the temperature which determines the work requirement of the reactor in equation (4.9)) at all temperatures, and thus it may not be possible to transfer heat to the reactor while the heat source is at a temperature lower than that of the reactor.

In conclusion, the work flow analysis of the Butane isomerization case, indicates that the process can be run as a *simple* process only if the reactor can achieve complete conversion and if heat is supplied to the process at the Carnot temperature maximum energy efficiency can be achieved. However because the conversion of the Butane isomerization reaction is limited by equilibrium, the process cannot be run as a *simple* process since the energy for

separation needs to be added over and above the work requirement of the process and therefore the process is always irreversible even when heat is supplied at Carnot temperature. The source of irreversibility is mainly due to the work of mixing being lost in the reactor.

5 CASE STUDY II: REVERSE WATER-GAS SHIFT (RWGS) REACTION

The first case study on the isomerization of Butane has been used as an example to illustrate a simple process, and to analyze the effect of temperature on conversion limitations and work flow around a process where the heat capacity of the streams going into the process is very close to the heat capacity of the streams coming out of the process. That is when one can simply assume that the heat capacity of the feed material and that of the product material are equal. This assumption has enabled us to simplify the process by eliminating work flow around the Heat exchanger, and thus enabled us to consider the process as a *simple* process.

For this second case study, the Reverse Water-Gas Shift (RWGS) reaction has be used as an example to illustrate the effect of temperature and conversion on a process where the heat capacity of the stream going into the process containing Carbon Dioxide and Hydrogen is significantly different from the heat capacity of the stream coming out of the process containing Carbon Monoxide and Water steam.

We will first start by assuming complete conversion in the reaction in order to be able to assess the effect of heat capacities of the feed and product stream on work flows around the process; and then we will relax the assumption of complete conversion in order to see the cumulative effect of conversion limitations as well as that of heat capacity differences between the feed and the product streams.

The reverse reaction is called Water-Gas shift and is widely used in the gasification and reforming processes as well as petrochemical industry. The Reverse Water-Gas Shift process

is an endothermic process and is assumed to be an open steady-state process with its mass balance written as shown below:

Carbon Dioxide + Hydrogen <=> Carbon Monoxide + Water Steam

$$CO_{2(g)} + H_{2(g)} \Rightarrow CO_{(g)} + H_2O_{(g)} \tag{5.1}$$

Where Carbon Dioxide *(CO_2)* and Hydrogen *(H_2)* in gas phase are fed to the process at ambient temperature and pressure *(T_o,P_o)* to produce Carbon Monoxide *(CO)* and Water steam *(H_2O)* as shown in the flowsheet below:

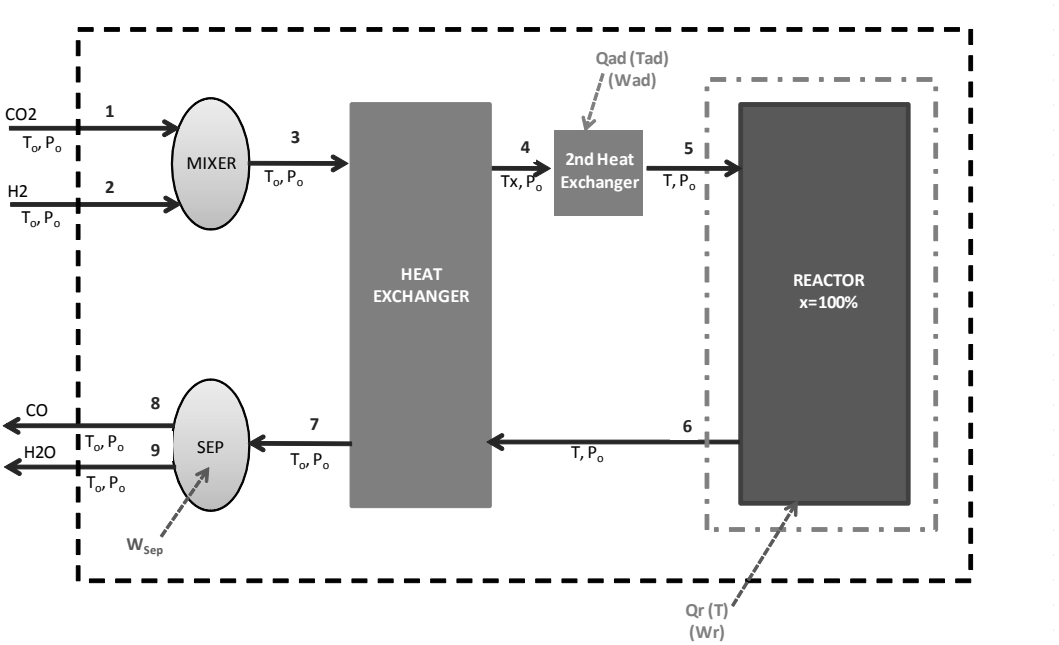

Figure 5-1: Setup of a RWGS process with complete conversion in the reactor

For this case study it is assumed that one mole of Carbon Dioxide and one mole of Hydrogen are fed as pure substances to the RWGS process at ambient temperature and pressure *(T_o,P_o)* to produce 1 mole Carbon Monoxide *(CO)* and 1 mole Water steam *(H_2O)*. The feed streams are first mixed, then fed to a Heat exchanger unit where heat is exchanged between the reactant and product streams. However since the heat capacity of the reactant is greater than that of the product stream (Cp_{in}>Cp_{out}), then the reactant can only be heated up from T_o

to a temperature of T_X lower than the reactor temperature T; while the product stream can be cooled from T to T_o. Therefore in order for the reactant stream to reach the reactor temperature T, additional heat Q_{ad} must be supplied to a second Heat exchanger at T_{ad} to increase the stream temperature from T_x to T before proceeding through the reactor where the Reverse Water-Gas shift reaction takes place. The Products (Carbon Monoxide and Water steam) with byproduct (Carbon Dioxide and Hydrogen) leave the reactor, goes through a heat exchanger once more to step down the temperature from T to T_o then goes through a separator unit to separate each product in their respective streams before exiting the process at ambient temperature and pressure (T_o,P_o). Since it is assumed complete conversion of the reactant into product; There is no recycle/reflux stream, however the product are coming out the process as pure components, therefore there is need for a separator, to separate CO and H_2O.

The solid black lines in and out of the process in Figure 5-1 represent materials streams while the dashed lines represent the energy streams, and intermittent dashed lines represent boundaries of energy balances performed.

The RWGS process is an endothermic process requiring 41KJ of heat and 28KJ of work to proceed at complete conversion. The amount of heat requirement being greater than the amount of work requirement is an indication that the process is feasible. Inputting heat and work requirement values in the gh-diagram gives:

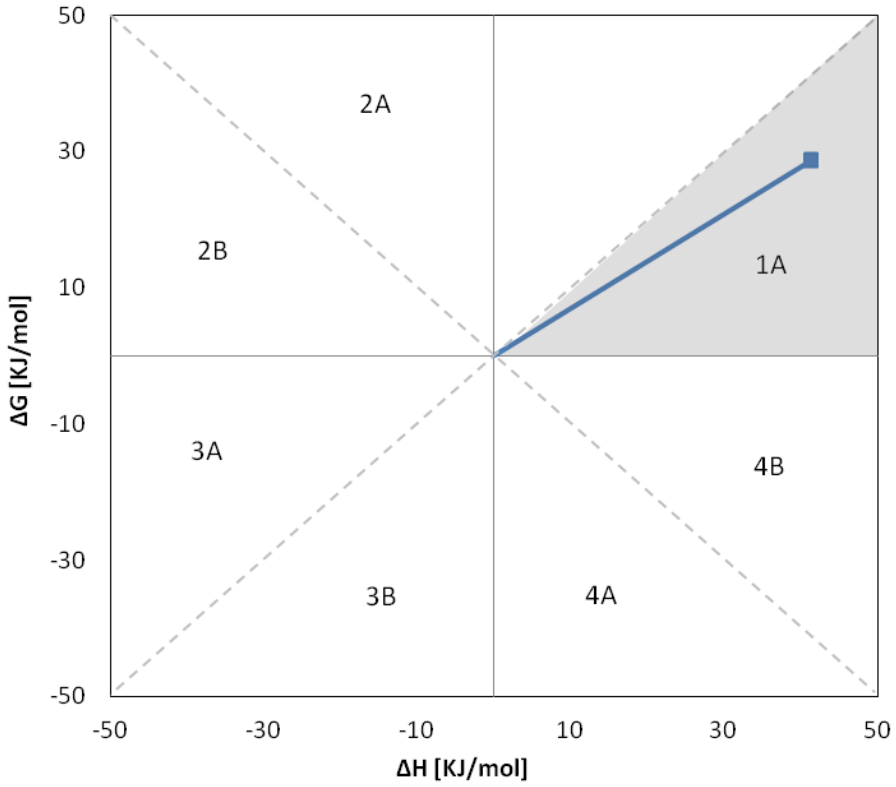

Figure 5-2. RWGS process drawn in the gh-diagram

Figure 5-2 above shows that the RWGS process lies in region 1A of the gh-diagram meaning that the RWGS can be run reversibly as a *Simple process* if one is able to meet the energy requirement of the process by supplying heat alone to the process at its reversible temperature (or Carnot temperature) to meet the process' heat and work requirements. Given the change in Gibbs free energy and enthalpy across the process for complete conversion, the Carnot temperature for this process can be calculated using equation (3.15), and this gives T_{Carnot} = 968.81 K.

5.1 Temperature effect on the process at complete conversion in the reactor

The Properties Hierarchy design methodology is once again used to evaluate the effect on temperature and conversion on the flow of work across the RWGS process and assess the process' overall energy efficiency in this case where the heat capacity of the inlet streams to the process is significantly different from the heat capacity of the outlet streams to the process (~5KJ/mol.K difference).

For this case study, the temperature *T*, at which the reactor is operated, is varied and the effect on the work around the process is analyzed.

5.1.1 Temperature effect on Work flow at the Heat exchanger

Because the difference in heat capacities at the streams in and out of the RWGS process is significant, a certain amount of additional heat must be added or removed from the heat exchanger in order for the streams coming out of the heat exchanger to reach their desired temperatures, *T* for the reactant stream and T_o for the product stream. In this case the heat capacity of the reactant stream is greater than that of the product stream therefore an additional amount of heat Q_{ad} must be added to the heat exchanger in order to heat up the reactant stream to the reactor temperature *T*, as shown in Figure 5-1. The reactant stream is first heated from T_o to an intermediary temperature T_X by exchanging heat with the product stream while it cools from *T* to T_o; and then the stream goes into a second heat exchanger where external heat is added to heat it up from T_X to *T*. The additional heat Q_{ad} is given by the change in enthalpy across the heat exchanger; that is:

$$Q_{ad} = H_{5(T,P_o)} - H_{4(T_X,P_o)} \tag{5.2}$$

If we assume that the second heat exchanger is reversible then we can calculate the work required by the heat exchanger in order to raise the temperature of the stream from T_X to *T*. This work is given by the change in exergy across the second heat exchanger:

$$W_{ad} = B_{5(T,P_o)} - B_{4(T_X,P_o)} \tag{5.3}$$

Then we can calculate the temperature at which Q_{ad} must be added in order to meet the work requirement of the heat exchanger. Assuming that the heat exchanger is reversible T_{ad} is given by:

$$T_{ad} = \frac{T_o}{1 - \frac{W_{ad}}{Q_{ad}}} \tag{5.4}$$

In principle heat is transferred in the heat exchanger at different temperatures, T_{ad} is then an average temperature between T_X and T. In fact we can show that T_{ad} is the logarithmic mean temperature between T_X and T, that is:

$$T_{ad} = \frac{T - T_X}{\ln\left(\frac{T}{T_X}\right)} \tag{5.5}$$

We therefore see that there is work flow associated with the heat exchanger and since this work crosses the process boundary, it is necessary to evaluate the effect of the reactor temperature on the work flow at the heat exchanger. Plotting the work requirement at the Heat Exchanger as a function of temperature gives:

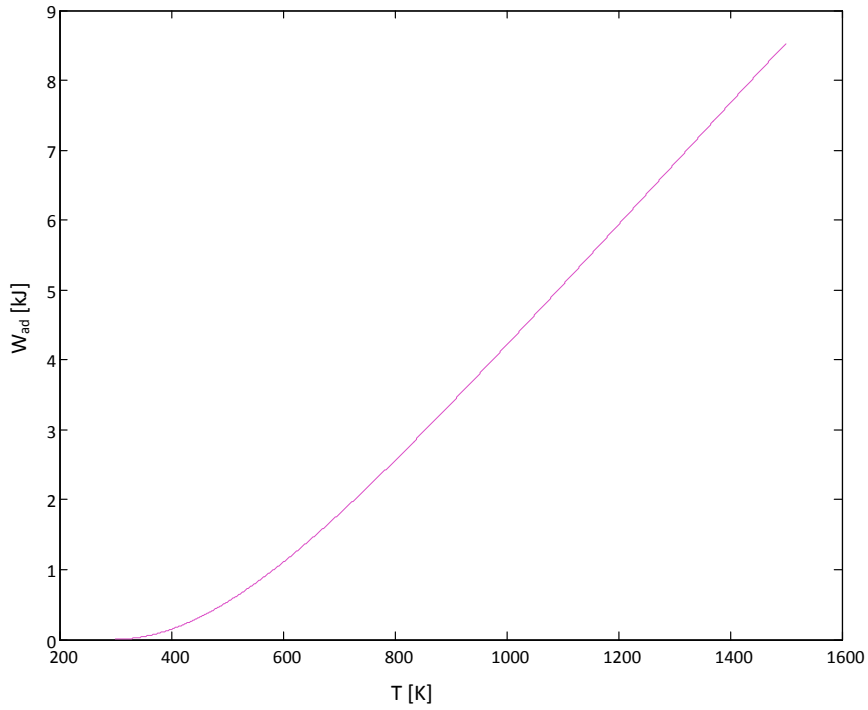

Figure 5-3: Work requirement at the heat exchanger as a function of temperature for the RWGS process

Figure 5-3 shows the increasing work requirement at the heat exchanger as a function of temperature. However one can also see that the amount of work transferred here is less than that of the reactor, thus the reactor will still have a greater influence on the work flow across the entire process. Further evaluations of the work flow across the various process' equipments will provide a clearer map for the flow of work across the process.

5.1.2 Temperature effect on Work flow at the Separator and Mixer

Although at this moment we assume complete conversion in the reactor, two different components are produced and come out of the reactor as a mixture, therefore a separator is required in order to have pure components in the product streams, thus the need for work of separation. Complete conversion means that the production rate of the products is constant and will not depend on the reactor temperature. The work of separation is given by the work of mixing in the product stream.

On the other hand the feed streams come in the process as pure components and are mixed before they enter the heat exchanger, thus there is work of mixing which can potentially be recovered, however in this case this work is not recovered and is considered lost, therefore there is no work crossing the process boundary from the mixer.

5.1.3 Temperature effect on Work flow at the Reactor

Work flow at the reactor is evaluated in order to confirm whether the major amount of work is flowing through the reactor; to assess how this work varies with the temperature at which the reactor is operated; to investigate the conditions at which the reactor can be run reversibly; and to capture how these conditions affect the process as a whole. Calculations on the change in Exergy *(ΔB)* across the reactor will determine the amount of work required

at the reactor ($W_{r_required}$) as per equation (3.32). We can also evaluate the work that is supplied to the reactor via heat (W_{r_heat}) at the reactor operating temperature. The heat requirement of the reactor is given by the change in enthalpy between the reactants stream and the product stream. Thus plotting both works ($W_{r_required}$ and W_{r_heat}) as a function of temperature gives:

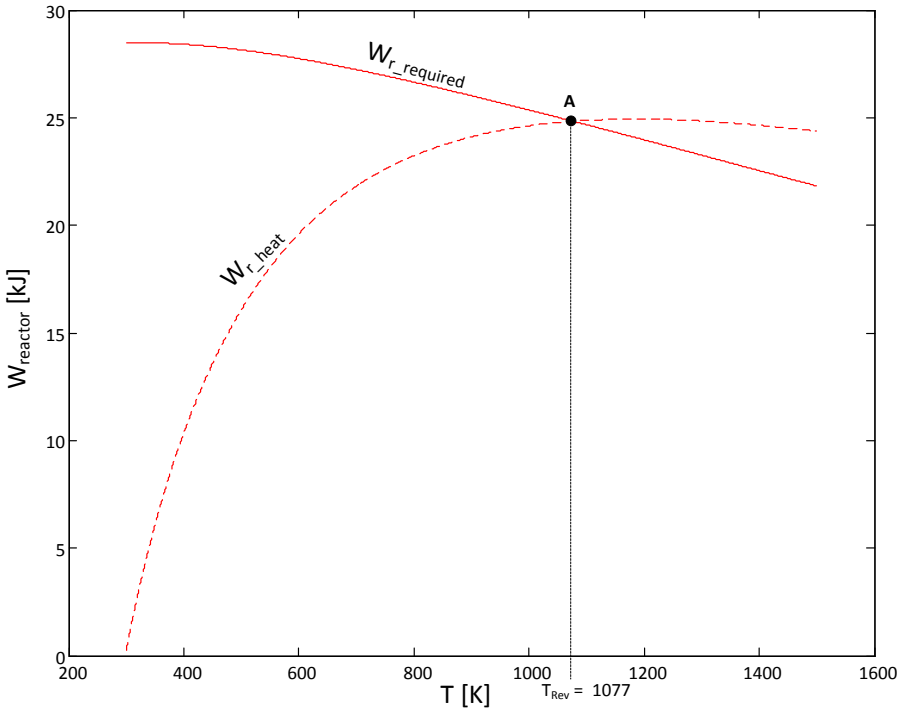

Figure 5-4. Temperature dependence of the work required by the reactor at complete conversion and that of the work supplied to the reactor via heat.

The work required by the reactor ($W_{r_required}$) in Figure 5-4 decreases with increasing temperature, while the work supplied to the reactor via heat (W_{r_heat}) increases with temperature. The temperature at which W_{r_heat} matches $W_{r_required}$, point A in Figure 5-4 is the reactor reversible temperature (T_{Rev}) here equal to 1077 K.

When heat is supplied below T_{Rev}, W_{r_heat} is less than what the reactor requires for complete conversion, and as a consequence the reactor conversion will be limited. The reaction will

proceed but the production rate of 1 mole of CO and 1 mole H_2O per mole of H_2 and per mole of CO_2 will not be achieved.

On the other hand when heat is supplied above T_{Rev}, W_{r_heat} is greater than $W_{r_required}$, thus there will be work surplus in the reactor which will be lost if it is not recovered and the reactor will be irreversible.

5.1.4 Temperature effect on Work flow at the Process

Understanding how the flow of work is affected by temperature for the RWGS process will give insights on the most appropriate temperature at which heat ($\Delta H_{(To)}$) and work (ΔG_{To}) should be supplied to the process. Heat to the process is supplied via the reactor and the second heat exchanger as shown in Figure 5-1. There is no energy associated with the separator as explained in Figure 3-7 and Figure 3-8; therefore:

$$\Delta H_{(T_o)p} = Q_{r(T)} + Q_{ad(Tad)} \tag{5.6}$$

We now see that in this case the heat requirement to the process is supplied at two different points and at two different temperatures, thus the process is not a *simple* process but a complex process. This means that, even if the process has a Carnot temperature (T_{Carnot} = 969 K), the work requirement cannot be satisfied by simply adding heat at a single point at T_{Carnot} as would be possible in a *simple* process. In this case work must be added at different point of the process, which are the heat exchanger, the reactor and the separator. Therefore:

$$\begin{aligned} W_{P_\text{required}} &= \Delta G_{(T_o)p} \\ W_{P_\text{supplied}} &= W_{ad} + W_r + W_{Sep} \end{aligned} \tag{5.7}$$

Where $W_{P_required}$, is the work that the process requires in order to transform the feed material to the product material at the required production rate (for this case 100% conversion overall), $W_{P_supplied}$ is the total work supplied to the process, and W_{ad}, W_r, W_{Sep} are

the works supplied to the process at the heat exchanger, the reactor, and the separator respectively. The process is reversible when $W_{P_supplied} = W_{P_required}$.

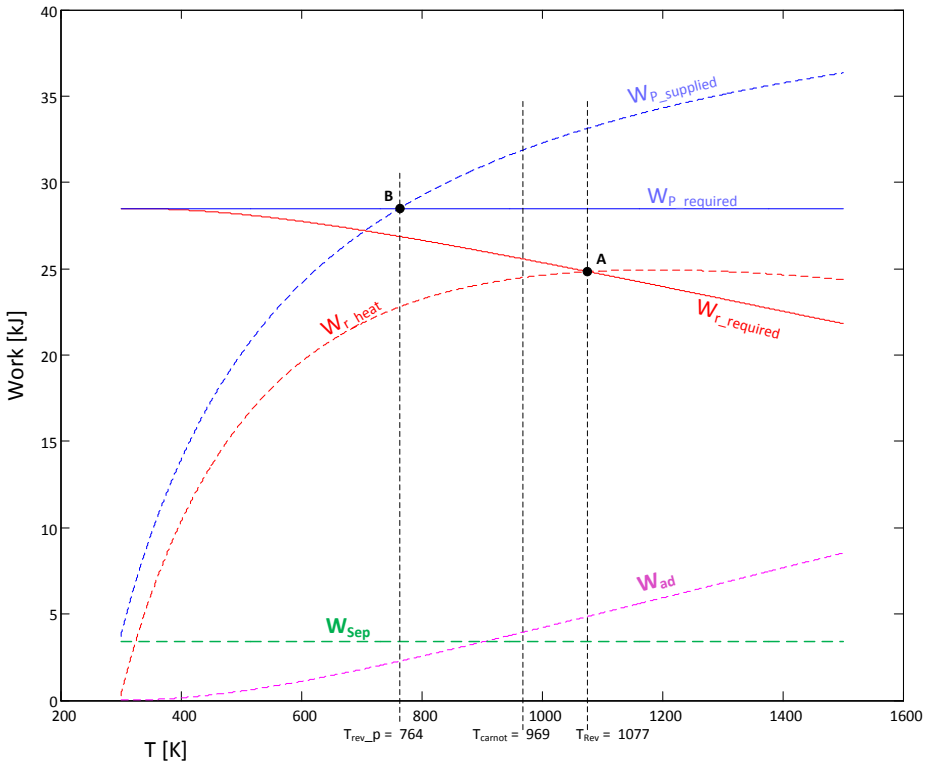

Figure 5-5. Work flows across the process as a function of the temperature at which the reactor is operated with complete conversion

Figure 5-5 puts together the variations of all the work flows and work requirements as a function of *T*, the temperature at which the reactor is operated. We can see from Figure 5-5 that:

- When the reactor is operated at 764 K, the work supplied to the process via its equipments ($W_{P_supplied}$) matches the work required by the process ($W_{P_required}$) as shown at point B. The process at this point is reversible there will be no work loss. We refer to this temperature as the "process reversible temperature" (T_{rev_P}), this is the temperature at which heat is supplied to the reactor to make the process as a whole reversible. It is different from the Carnot temperature (T_{Carnot}) and from the reactor reversible temperature (T_{Rev}). Remember that all other variables of heat,

work and temperatures around the process depend on the temperature of the reactor.

However we can also see that at T_{rev_P}, the work supplied to the reactor via heat (W_{r_heat}) is less than the work required by the reactor for complete conversion ($W_{r_required}$) thus at this point the reactor is work deficient. The reaction will proceed but will only reach a limited conversion and therefore the process as a whole will not achieve the required product rate unless additional work is supplied. This can be done by adding a recycle stream which will increase the work of separation.

- When the reactor is operated at the Carnot temperature (T_{Carnot}), we can see that a surplus of work is supplied to the process ($W_{P_supplied} > W_{P_required}$) which will be lost if not recovered. However at this point the reactor is work deficient ($W_{r_heat} < W_{r_required}$) thus complete conversion cannot be achieved. However if the work surplus of the process is recovered, it can be used to compensate for the work deficiency at the reactor.
- At the reactor reversible temperature (T_{Rev}), the work supplied to the reactor via heat matches the work required by the reactor ($W_{r_heat} = W_{r_required}$) as shown at point A, thus the work of the reactor is satisfied and the reactor is reversible; however the process as a whole has a surplus of work which will be lost if it is not recovered.
- The additional work (W_{ad}) that is required at the second heat exchanger does not increase much with increasing temperature and is much less compared to that of the reactor. Thus the reactor is the part of the process where much energy is supplied.

We therefore see that, in this case where the heat capacity of the feed materials is not equal to that of the products, running the equipments (mainly the reactor) reversibly does not necessarily make the process reversible as a whole, and we also see that conditions that are

required for a reversible process may not be ideal for equipments. So, one needs to find conditions that will at least minimize work losses for the overall process.

5.2 Work flows around the process with incomplete conversion in the reactor

In the previous case, we look at the work flows around the reactor assuming complete conversion in the reactor. This enabled us to simplify the process by eliminating the need to separate the unused reactants from the products and thereby eliminate the work of separation. Although one still has to separate the product components, the work of separation required is fixed and does vary with the reactor temperature. Therefore this allows us to assess the effect of the additional point of heat transfer to the process, which is required due to the difference in heat capacities between the feed and product materials.

Here we relax the complete conversion assumption in the reactor and analyze the combined effect of conversion limitations as well as heat capacity differences. Since the reaction does not go to completion, the unreacted feed material needs to be separated and recycled back to the reactor in order to achieve the required production rate. Thus the process will be depicted as follows:

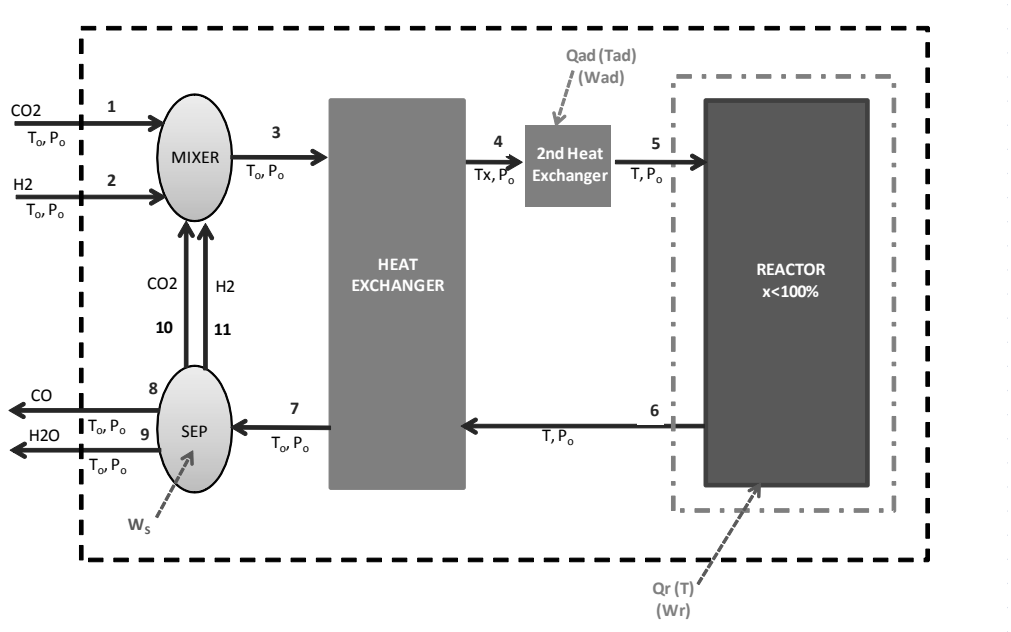

Figure 5-6: Setup of a RWGS process with incomplete conversion in the reactor

Two separate feed streams, one containing Carbon Dioxide as a pure substance and the other containing Hydrogen also as a pure substance enter the open steady-state process at ambient temperature and pressure (T_o,P_o), then goes through a mixer unit to mix both materials into one as well as combine with the recycle streams' materials before going through a heat exchanger which steps up the stream's temperature from T_o to an intermediary temperature T_X then goes into a second heat exchanger where external heat is supplied to raise the stream temperature from T_x to the reactor's temperature T. The material leaving the heat exchanger enters the reactor (at temperature T and ambient pressure P_o) where the Reverse Water-Gas Shift (RWGS) reaction takes place. From the reactor, the material goes through a heat exchanger to step down the stream's temperature to ambient temperature (T_o) and proceed through a separator which separates the reactants (Carbon Dioxide and Hydrogen) from the products (Carbon Monoxide and Water steam). The products leave the separator as pure components.

5.2.1 Temperature effect on Reaction's equilibrium

For the RWGS reaction, the feeds (Carbon Dioxide and Hydrogen) react to form the desired products (Carbon Monoxide and Water steam) in increasing proportions until the reaction reaches a state where the reactants and the products concentration ratios no longer change with time and where, it is said to have reached *equilibrium state*. Plotting the equilibrium constant as a function of temperature gives:

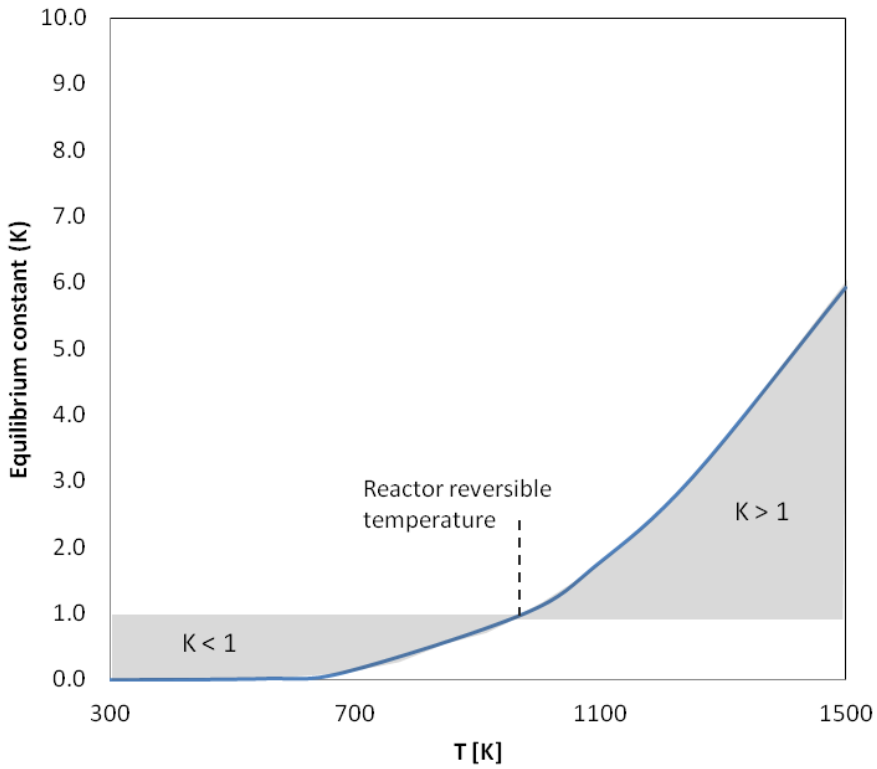

Figure 5-7. Temperature effect on the RWGS reaction's equilibrium

Figure 5-7 shows that the equilibrium constant (*K*) increases as a function of temperature. The equilibrium constant curve goes from close-to-zero change in concentrations of reactants to form products to increasingly higher proportions of reactants forming products. Note that at the reactor reversible temperature T_{Rev} (1077 K) as well as on every point on the

equilibrium constant curve, equilibrium is reached and it is at T_{Rev} that the equilibrium constant is equal to 1 ($K = 1$).

Following the findings on the effect of temperature on reaction's equilibrium, the subsequent evaluation is on the effect on temperature on the change in Gibbs free energy across the reactor at temperature T, (ΔG_T) which is an indication on the direction of the reaction and consequently on the equilibrium state as expressed by the relationship in equation (3.61). The change in Gibbs free energy between the inlet and outlet streams of the reactor plotted as a function of temperature gives:

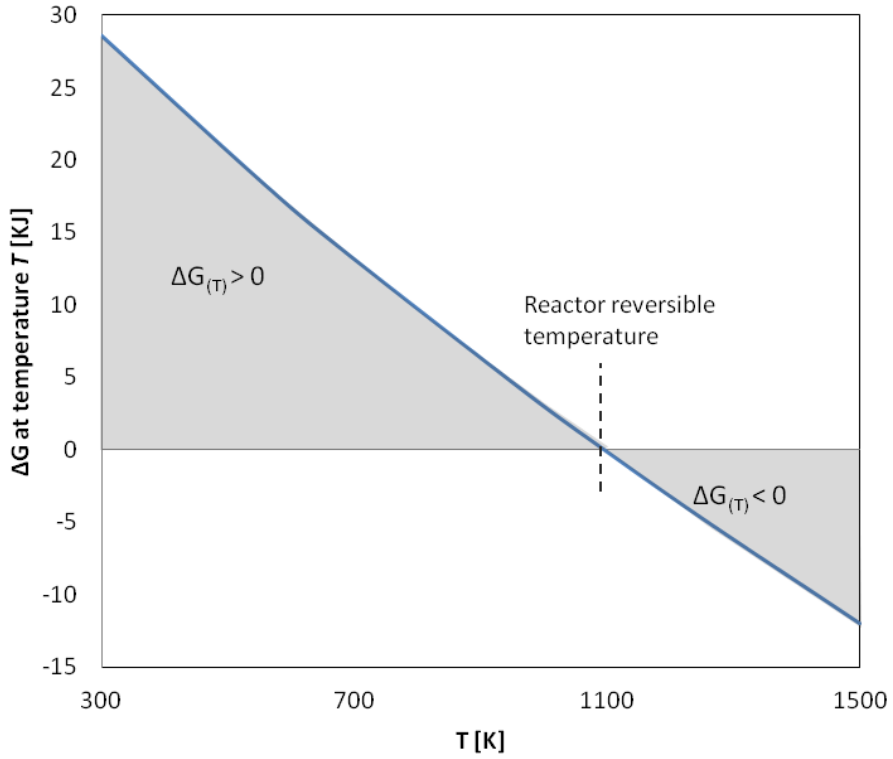

Figure 5-8. Change in Gibbs free energy across the reactor plotted as a function of temperature

Figure 5-8 shows that the change in Gibbs free energy evaluated at temperature T is a decreasing curve crossing the x-axis at the reactor's reversible temperature (1077K) where

the difference between the Gibbs free energy at the inlet stream of the reactor and the Gibbs free energy at the outlet stream of the reactor is nil. For a negative change in Gibbs free energy between the inlet and outlet streams of the reactor ($\Delta G_T < 0$) which corresponds to an equilibrium constant greater than 1 ($K > 1$), the reaction will proceed toward the products; while for a positive change in Gibbs free energy between the inlet and outlet streams of the reactor ($\Delta G_T > 0$), the equilibrium constant is less than 1 ($K < 1$), thus the reaction will proceed toward the reactants.

The $-TS_{gen}$ term as shown in equation (3.63) has also been established as an indication on the direction of the reaction's equilibrium. Shown below is the $-TS_{gen}$ term plotted as a function of temperature.

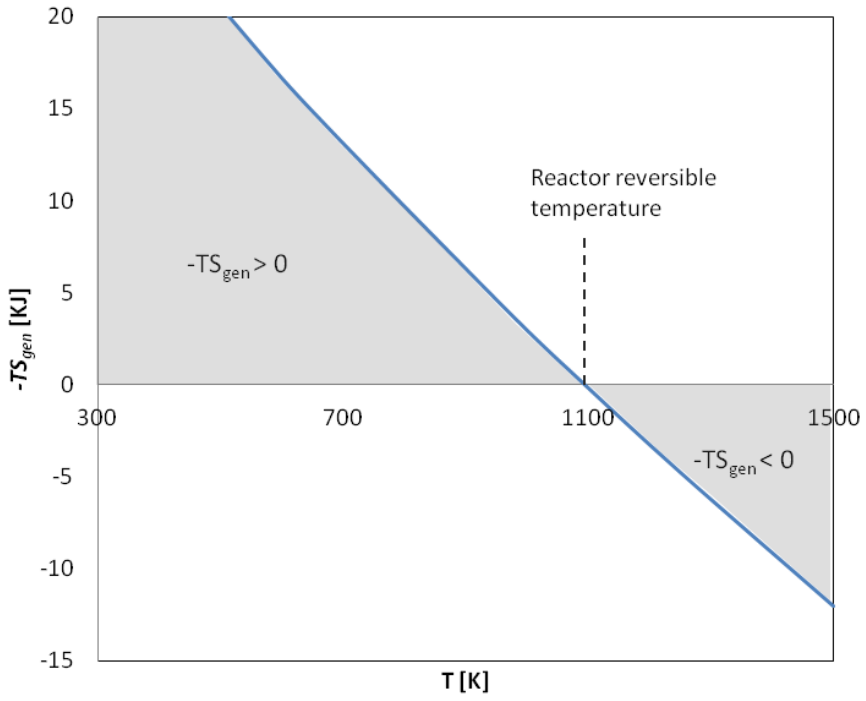

Figure 5-9. -*TSgen* term plotted as a function of temperature for the RWGS process

The $-TS_{gen}$ curve is a decreasing curve crossing the x-axis at the reactor's reversible temperature (1077K) where the difference between the Gibbs free energy at the inlet and that of the outlet streams of the reactor is nil. For a positive $-TS_{gen}$ term, the reaction is proceeding toward the reactants (Carbon Dioxide and Hydrogen), and for a negative $-TS_{gen}$ term, the reaction is proceeding toward the products (Carbon Monoxide, Water steam and perhaps byproducts). In order for this process to meet its target and produce Carbon Monoxide and Water steam, the $-TS_{gen}$ term will have to be negative ($-TS_{gen} < 0$).

5.2.2 Conversion effect on Work flow at the Process

As seen in the first case study on Butane isomerization, and for this case study as well, the work requirement across the process or change in Gibbs free energy at temperature T_o is evaluated as a function of conversion and gives an indication on whether the flow of work across the process is affected by a change in conversion. The change in Gibbs free energy across the RWGS process at temperature T_o is plotted below as a function of conversion:

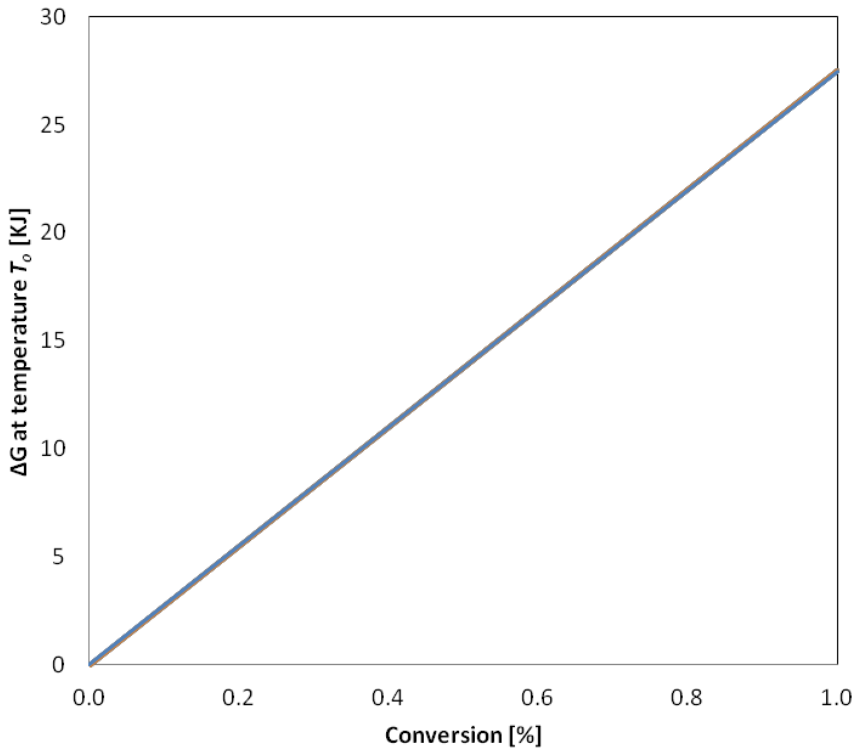

Figure 5-10. Change in Gibbs free energy across the process plotted as a function of conversion

The general trend of the change in Gibbs free energy across the process at temperature T_o at various conversions which represents the work requirement at the RWGS process evaluated at various conversions are superposed increasing linear curves. This is an indication that the change in Gibbs free energy across the RWGS process at temperature T_o does not varies as a function of temperature but varies as a function of conversion which depends on

temperature and which influences the change in Gibbs free energy at temperature T (ΔG_T) such that ΔG_T will increase proportionally with conversion: the higher the conversion, the higher the work requirement by the RWGS process.

5.2.3 Work of separation with incomplete conversion in the reactor

In the previous case, complete conversion is assumed and therefore the work of separation is only that required to separate the products into pure components and thus does not vary with the reactor temperature. Now we look at the case where conversion is incomplete and thus the work of separation required includes that of separating the product streams from the unreacted reactants.

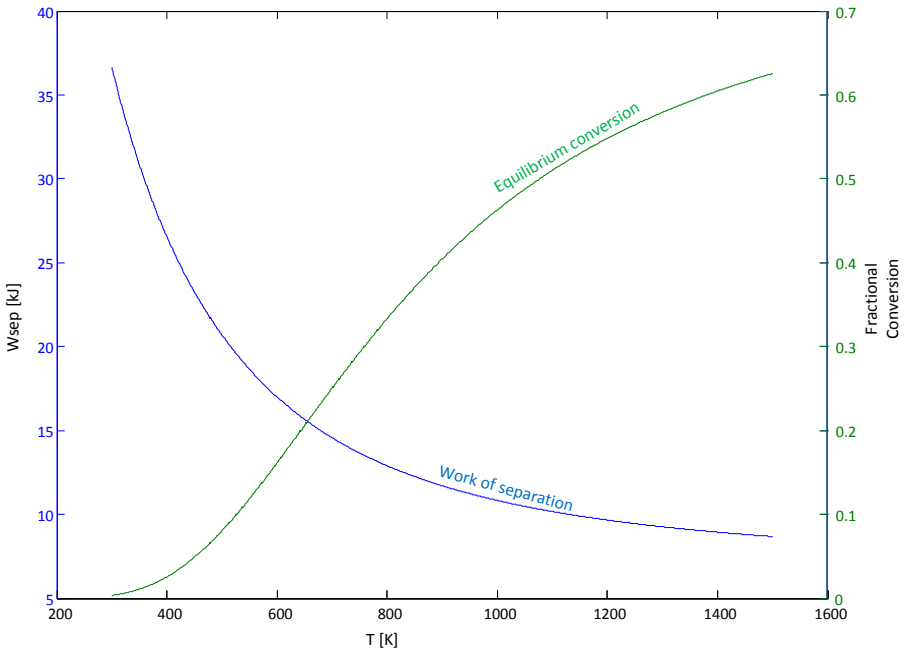

Figure 5-11: Work required for separation and equilibrium conversion as a function of reactor temperature

Figure 5-11 shows the variation of conversion and that of the work of separation with temperature. We can see that the work requirement for separation is much higher at low

temperatures; this is due to the low conversions at low temperatures which lead to large recycles in order to achieve the required production rate. The work of separation increases as the amount of unreacted reactants increases.

5.2.4 Work flows around the process with incomplete conversion in the reactor

In the previous case (section 5.1) we looked at the effect of heat capacities of the reactant and product streams on work flows around the process at complete conversion, now here we now look at the effect of heat capacities of the reactant and product streams on work flows around the process at incomplete conversion in the reactor, which makes the work of separation more significant. The combined effect of all the works around the process is depicted as shown in Figure 5-12.

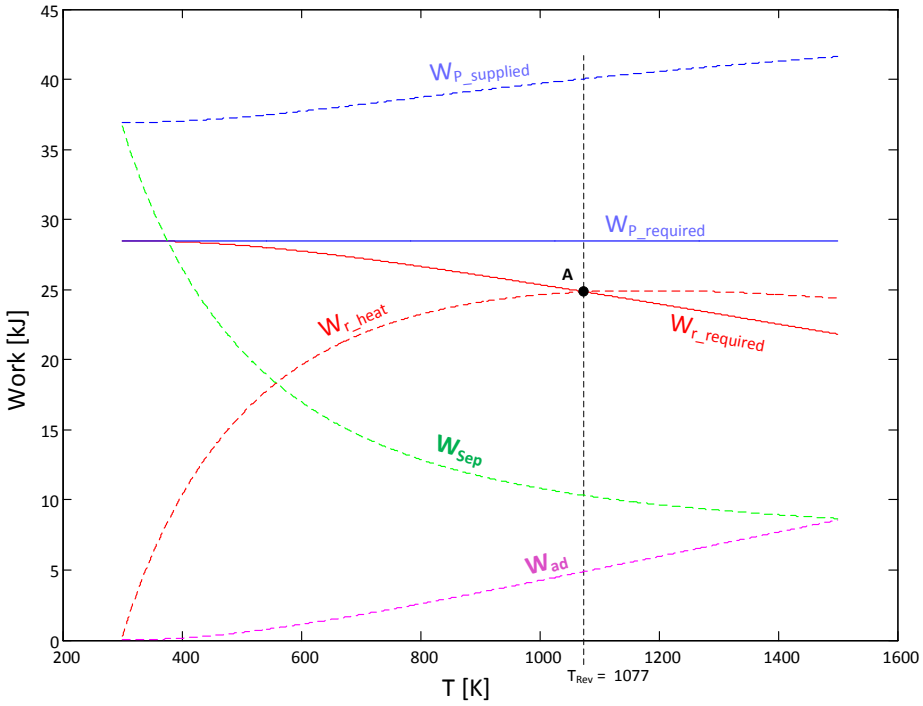

Figure 5-12: Work flows across the process as a function of the temperature at which the reactor is operated with incomplete conversion

In Figure 5-12 the effect of the work of separation is now more significant at low temperatures (because of low conversion) in the same order as that of the reactor is at high temperature. The additional work (W_{ad}) required at the heat exchanger is still much less over the whole range of temperatures compared to that of the reactor and separator. The most significant effect of the combination of all these works is that the process is supplied with a surplus of work ($W_{P_supplied} > W_{P_required}$) over the range of temperatures chosen for the reactor. This means that the process will be irreversible at all temperature unless there is a way of recovering the work surplus.

We also see that $W_{P_supplied}$ does not change much with temperature, and this means that the reactor temperature does not have much effect on the irreversibility of the process, contrary to what we see in Figure 5-3. Therefore even when the reactor is run at its reversible temperature it will have no overall effect on the process. Thus one would want to run the reactor at as high temperature as possible in order to reduce the capital cost of the process; a high temperature in the reactor will lead to high conversion, and therefore will reduce the work of separation and the size of the recycle as well as that of the streams in the process; thereby reducing the size of equipments in the process.

6 GENERAL CONCLUSIONS AND RECOMMENDATIONS

Reducing the amount of energy consumption in the chemical industry is one of the elements toward sustainable development. In this dissertation we present a method of analyzing work flows around a process using fundamental thermodynamic concepts.

We analyze the work flows around a simplified chemical process in order understand where major work losses occur and how they can be minimized, by using fundamental thermodynamic concepts.

The concepts of Gibbs free energy, energy balance and entropy balance as well as temperature and pressure, are closely related with the basic design of a process. Analyzing the effect of temperature at which the reactor and the major equipment in the process are operated, on the work flow in reactive processes have given insights on possible design decisions that the chemical engineer can apply in aim to produce optimal flowsheets. Heat capacity difference of the material going in and out of the process has also been identified as a parameter affecting the flow of work across a reactive process.

Throughout this dissertation, the effect of temperature and that of heat capacities of feed and product material on the flow of work has been evaluated by first looking at a hypothetical process where specie *A* is converted to *B* and then looking at two study cases, one where the effect of heat capacities difference between the feed stream and the product stream of the process is ignored and the other where this effect is taken into account. The following conclusion could be drawn:

- The case where specie *A* reacts to form specie *B*. This case was a simple representation of a basic evaluation of work on a reactive process. This example has shown how the

major pieces of equipments across a reactive process interact with each other and gave the basic flow of work network for the process. In particular this case enabled us to define what we call “a *simple* process” which is a process where heat is supplied at a single point and at a single temperature. In a *simple* process it is assumed that the heat capacity of the feed stream is equal to that of the product stream; in this way heat can be exchanged between these streams without the need of additional external heat to reach their required temperature. We were able to show that, a single heat supply to a *simple* process allows to meet both the energy requirement (given by the change in enthalpy across the process) and the work requirement (given by the change in Gibbs free energy across the process) simultaneously when it is supplied at the Carnot temperature making the process reversible.

- The case study on the Butane isomerization where iso-butane reacts to produce n-butane was used to corroborate the findings of the hypothetical *simple* process. This case was used to show the effect of temperature and conversion on the Butane isomerization process where the difference between the heat capacities at the stream going in the process and the stream going out of the process is insignificant, their heat capacity was considered to be the same to enable us to consider the process to be a *simple* process. It was shown that for such steady-state endothermic reactive processes, it is only when the conversion in the reactor is complete that the process can be operated reversibly as a *Simple* process by supplying the process with its heat requirement at the Carnot temperature. It follows that since the reaction is complete no separator is required and since the heat capacity of the feed stream and that of the product stream are equal, no external energy is required at the heat exchanger, and thus all the work requirement of the process can only be taken in by the reactor; therefore the reversible temperature at the process (Carnot temperature) is almost equal to the reversible temperature at the reactor. However when the conversion in the

reactor is not complete due to equilibrium limitations, it was shown that the process would require additional work for separation which decreases with increasing temperature. The process now has two points where work is added and can no longer be run as a *simple* process. It was also shown that the process will have a work surplus at all temperatures and will be irreversible unless this work can be recovered.

- The case study on the Reverse Water Gas Shift (RWGS) process where Carbon Dioxide and Hydrogen react to produce Carbon Monoxide and Water steam was used to show the effect of temperature and conversion on a process where there is a considerable difference between the heat capacities of the streams going in the process and the streams going out of the process. For such steady-state endothermic reactive processes, operating the process reversibly as a *Simple* process is not possible by supplying the process with heat required alone at the Carnot temperature because of the additional external heat that is required at the heat exchanger. The process has two points of heat transfer at two different temperatures. The heat requirement and the reversible temperature of the process are not the same as those of the reactor. It was shown that if the conversion in the reactor is complete there is a temperature at which the reactor can be operated which results in the total work supplied to the process (via the reactor and the heat exchanger) matching the work requirement of the process. This means that there is no work surplus or deficiency and therefore the process is reversible as a whole at a temperature called the “reversible temperature of the process” which is not to be confused with the Carnot temperature. However it was also shown that at the process reversible temperature, the reactor was work deficient and consequently could not achieve complete conversion and thus the process needed some work of separation in order to achieve the required production rate.

  When the conversion is not complete, it was shown that at all temperatures at which the reactor is operated, the total work supplied to the process (a combination of the

work at the reactor, at the heat exchanger and at the separator) is greater than what the process requires, and thus the process always has work surplus. It was also shown that for the RWGS process the work surplus (or irreversibility) does not change much with temperature and therefore in this case temperature has no effect on reducing fundamental inefficiencies in the process. For this case it is therefore recommended that the reactor be run at as high temperature as possible in order to achieve a high conversion which will then reduce the work of separation required as well as reduce the size of the recycle and potentially reduce the capital and operating cost of the process.

Findings from the above evaluations are conclusive in a way that they provide clear insights on how and by how much a reactive process can be improved by adjusting the temperature which in turn refers to a specific conversion of reactant into product.

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APPENDIX A: List of Tables

Table 1. Table of Constants

Universal gas constant (R)	R= 8.31 J/mol.K or 0.00831 KJ/mol.K

Table 2. Table of Chemical Properties (Yaws, 1999)

HEAT CAPACITY OF GAS					
$Cp = A + BT + CT^2 + DT^3 + ET^4$			**[Cp- Joule/(mol K), T- K (200-1500K)]**		
	A	**B**	**C**	**D**	**E**
Iso-Butane	6.772	3.4147^{e}-01	-1.0271^{e}-04	-3.6849^{e}-08	2.0429^{e}-11
N-Butane	20.056	2.8153^{e}-01	-1.3143^{e}-05	-9.4571^{e}-08	3.4149^{e}-11

ENTHALPY OF FORMATION OF GAS		
	Hf @298K	**Hf @ 500K**
Iso-Butane	-134.52	-148.22
N-Butane	-126.15	-139.99
$Hf = A + BT + CT^2$	**[Hf- KJoule/mol, T- K (298-1000K)]**	
	A	**B**	**C**
Iso-Butane	-106.746	-1.0929^{e}-01	5.2693^{e}-05
N-Butane	-98.186	-1.0974^{e}-01	5.2254^{e}-05

GIBBS ENERGY OF FORMATION OF GAS		
	Gf @298K	**Gf @ 500K**
Iso-Butane	-20.88	60.78
N-Butane	-17.15	61.43
$Gf = A + BT + CT^2$	**[Gf- KJoule/mol, T- K (298-1000K)]**	
	A	**B**	**C**
Iso-Butane	-136.801	3.7641e-01	3.7497e-05
N-Butane	-128.375	3.6047e-01	3.8256e-05

ENTROPY OF FORMATION OF GAS	
	Sf @298K joule/(mol K)
Iso-Butane	-381.150
N-Butane	-365.588

APPENDIX B: *Calculations*

i. CALCULATION SHEET 1: BUTANE ISOMERIZATION

$$C_4H_{10} \longleftrightarrow C_4H_{10}$$

$$\text{Iso-butane} \longleftrightarrow \text{n-butane}$$

$$A \longleftrightarrow B$$

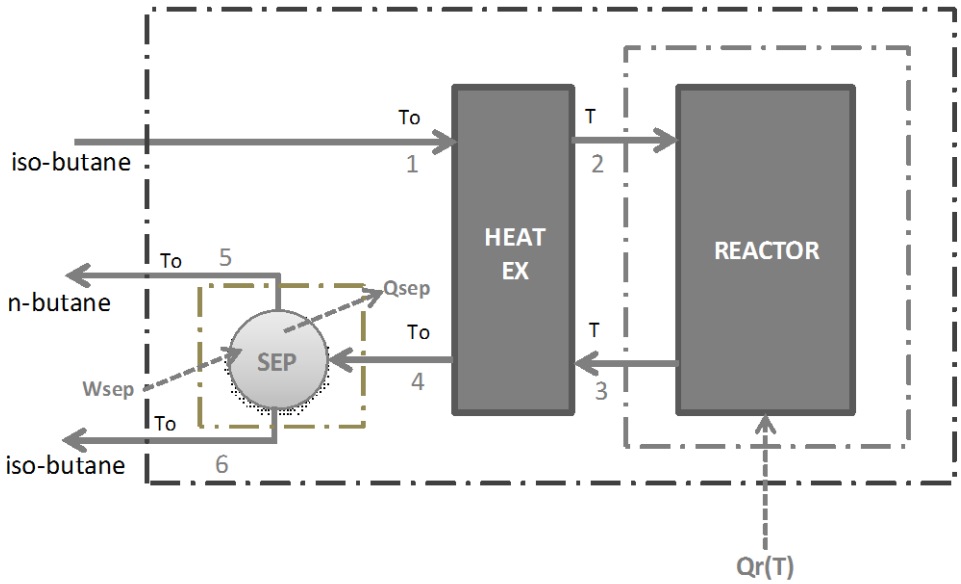

Figure 0-1. Flowsheet for the Butane Isomerization

Butane isomerization process transforms iso-butane into n-butane. This example represents the case where the heat capacity difference between the streams in and out of the process is significant (Cp_{in}=Cp_{out}). It is assumed that the reactant is fed to the process as a pure component at ambient temperature and pressure (T_o,P_o) and that the products are coming out of the process as a pure component at ambient temperature and pressure (T_o,P_o). It is assumed that ΔH_{mix}=0.

1. STREAMS

$H_1 = H_{f_A(T_o,P_o)} = H^o_{f_A}$ $S_1 = S_{f_A(T_o,P_o)} = S^o_{f_A}$ $G_1 = H_1 - T_o S_1$	$H_2 = H^o_{f_A} + \int_{T_o}^{T} Cp_A dT$ $S_2 = S^o_{f_A} + \int_{T_o}^{T} Cp_A \frac{dT}{T}$ $G_2 = H_2 - TS_2$

$$H_3 = (1-x)H^o_{f_A} + (1-x)\int_{T_o}^{T} Cp_A dT + (x)H^o_{f_B} + (x)\int_{T_o}^{T} Cp_B dT$$

$$S_3 = (1-x)S^o_{f_A} + (1-x)\int_{T_o}^{T} Cp_A \frac{dT}{T} + (x)S^o_{f_B} + (x)\int_{T_o}^{T} Cp_B \frac{dT}{T} + S_{mix_{(A,B)_T}}$$

$$G_3 = H_3 - TS_3$$

$$S_{mix_{(A,B)}} = -nR\sum\left[xi \ln xi\right]$$

$$= -R\left[(1-x)\ln(1-x) + (x)\ln(x)\right]$$

$$H_4 = (1-x)H^o_{f_A} + (x)H^o_{f_B}$$

$$S_4 = (1-x)S^o_{f_A} + (x)S^o_{f_B} + S_{mix(A,B)_{T_o}}$$

$$G_4 = H_4 - T_o S_4$$

$$H_5 = (1-x)H^o_{f_A}$$

$$S_5 = (1-x)S^o_{f_A}$$

$$G_5 = H_5 - T_o S_5$$

$$H_6 = (x)H^o_{f_B}$$

$$S_6 = (x)S^o_{f_B}$$

$$G_6 = H_6 - T_o S_6$$

2. PROCESS

REVERSIBLE PROCESS

$$\Delta H_{(T_o)} = H_5 + H_6 - H_1 = Q$$

$$\Delta S_{(T_o)} = S_5 + S_6 - S_1 = \frac{Q}{T_{Carnot}} = \frac{\Delta H_{(T_o)}}{T_{Carnot}}$$

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

$$W_{lost} = 0$$

IRREVERSIBLE PROCESS

$$\Delta H_{(T_o)} = H_5 + H_6 - H_1 = Q$$

$$\Delta S_{(T_o)} = S_5 + S_6 - S_1 = \frac{Q}{T} + S_{gen(p)} = \frac{\Delta H_{(T_o)}}{T} + S_{gen(p)}$$

$$\Delta G_{(T_o)} = \Delta H_{(T_o)} - T_o \Delta S_{(T_o)} = \Delta H_{(T_o)}\left(1 - \frac{T_o}{T}\right) - T_o S_{gen(p)}$$

$$W_{lost} = T_o S_{gen(p)}$$

$$W_{lost} = \Delta H_{(T_o)} T_o \left(\frac{1}{T_{Carnot}} - \frac{1}{T} \right)$$

3. REACTOR

REVERSIBLE REACTOR

$$\Delta H_{(T)} = H_3 - H_2 = Q$$

$$\Delta S_{(T)} = S_3 - S_2 = \frac{Q}{T_{\mathrm{Re}versible}} = \frac{\Delta H_{(T)}}{T_{\mathrm{Re}versible}}$$

$$\Delta B_{(T)} = \Delta H_{(T)} - T_o \Delta S_{(T)} = \Delta H_{(T)} \left(1 - \frac{T_o}{T_{\mathrm{Re}v}} \right)$$

$$W_{lost} = 0$$

IRREVERSIBLE REACTOR

$$\Delta H_{(T)} = H_3 - H_2 = Q$$

$$\Delta S_{(T)} = S_3 - S_2 = \frac{Q}{T} + S_{gen(r)} = \frac{\Delta H_{(T)}}{T} + S_{gen(r)}$$

$$\Delta B_{(T)} = \Delta H_{(T)} - T_o \Delta S_{(T)} = \Delta H_{(T)} \left(1 - \frac{T_o}{T} \right) - T_o S_{gen(r)}$$

$$W_{lost} = T_o S_{gen(r)}$$

$$W_{lost} = \Delta H_{(T)} T_o \left(\frac{1}{T_{\mathrm{Re}v}} - \frac{1}{T} \right)$$

4. SEPARATOR

It is assumed that $\Delta H_{mix}=0$ and if the work of separation (W_{sep}) is recovered or added, then Q_{sep} must also appear such that $W_{sep}=Q_{sep}$, therefore ΔH_{mix} remains zero.

$$H_4 = H_5 + H_6$$

$$W_{sep} = Q_{sep}$$

$$S_4 = S_5 + S_6 + \frac{Q_{(T_o)}}{T_o}$$

$$W_{sep} = Q_{(T_o)} = -T_o S_{mix(A,B)}$$

$$W_{sep} = -RT_o \left[(1-x)\ln(1-x) + (x)\ln(x) \right] = -G_{mix_{(4)}}$$

Work of separation (W_{sep}) is equivalent to the work of separation at the stream going into the separator unit, G_{mix4}

5. HEAT EXCHANGER

Heat capacity of the streams going into the process is different from the heat capacity of the streams going out of the process (Cp_{in}=Cp_{out}).

$$H_3 + H_1 = H_4 + H_2$$
$$H_{in} = H_{out}$$
$$S_3 + S_1 = S_4 + S_2$$
$$S_{in} = S_{out}$$
$$W_{hex} = \Delta G_{(hex)} = (H_{out} - H_{in}) - T_o(S_{out} - S_{in})$$
$$W_{hex} = (x)\left[\int_{T_o}^{T} Cp_A dT - \int_{T_o}^{T} Cp_B dT - To \times \left(\int_{T_o}^{T} Cp_A \frac{dT}{T} - \int_{T_o}^{T} Cp_B \frac{dT}{T}\right)\right]$$
$$W_{hex} = 0$$

6. EQUILIBRIUM

$\Delta G_{(T_o)} = -RT \ln K_o$	$\Delta G_{(T)} = -RT \ln K$
$K_o = e^{\left(\frac{-\Delta G_{(T_o)}}{RT}\right)}$	$K = e^{\left(\frac{-\Delta G_{(T)}}{RT}\right)}$

a. Reversible Reactor

$$\Delta H_{(T)} = Q$$
$$\Delta S_{(T)} = \frac{Q}{T}$$
$$\Delta G_{(T)} = \Delta H_{(T)} - T\Delta S_{(T)} = \Delta H_{(T)} - \Delta H_{(T)} = 0$$

Minimal ΔG at the reactor's reversible temperature

b. Irreversible Reactor

$$\Delta H_{(T)} = Q$$
$$\Delta S_{(T)} = \frac{Q}{T} + S_{gen}$$
$$\Delta G_{(T)} = \Delta H_{(T)} - T\Delta S_{(T)} - TS_{gen}$$
$$\Delta G_{(T)} = -TS_{gen}$$

To include entropy of mixing to streams calculations before proceeding with -TSgen calculations

below:

$$\Delta H_{(T)} = H_3 - H_2$$

$$\Delta S_{(T)} = S_3 - S_2$$

$$-TS_{gen} = \Delta G_{(T)} = (H_3 - H_2) - T(S_3 - S_2)$$

$$-TS_{gen} = (x)\left[\left(H^o_{f_B} + \int_{T_o}^{T} Cp_B dT - H^o_{f_A} + \int_{T_o}^{T} Cp_A dT \right) - T\left(S^o_{f_B} + \int_{T_o}^{T} Cp_B \frac{dT}{T} - S^o_{f_A} + \int_{T_o}^{T} Cp_A \frac{dT}{T} \right)\right] + TS_{mix_{(A,B)}}$$

$$TS_{mix_{A,B}} = -RT\left[(1-x)\ln\frac{(1-x)}{2} + (x)\ln\frac{(x)}{2}\right]$$

$$G_{mix_{(3)}} = RT\left[(1-x)\ln\frac{(1-x)}{2} + (x)\ln\frac{(x)}{2}\right]$$

$$-G_{mix_{(3)}} = TS_{mix_{A,B}}$$

ii. CALCULATION SHEET 2: WATER-GAS SHIFT PROCESS

$$CO_2 + H_2 \longleftrightarrow CO + H_2O$$

$$\text{Carbon Dioxide} + \text{Hydrogen} \longleftrightarrow \text{Carbon Monoxide} + \text{Water Steam}$$

$$A + B \longleftrightarrow C + D$$

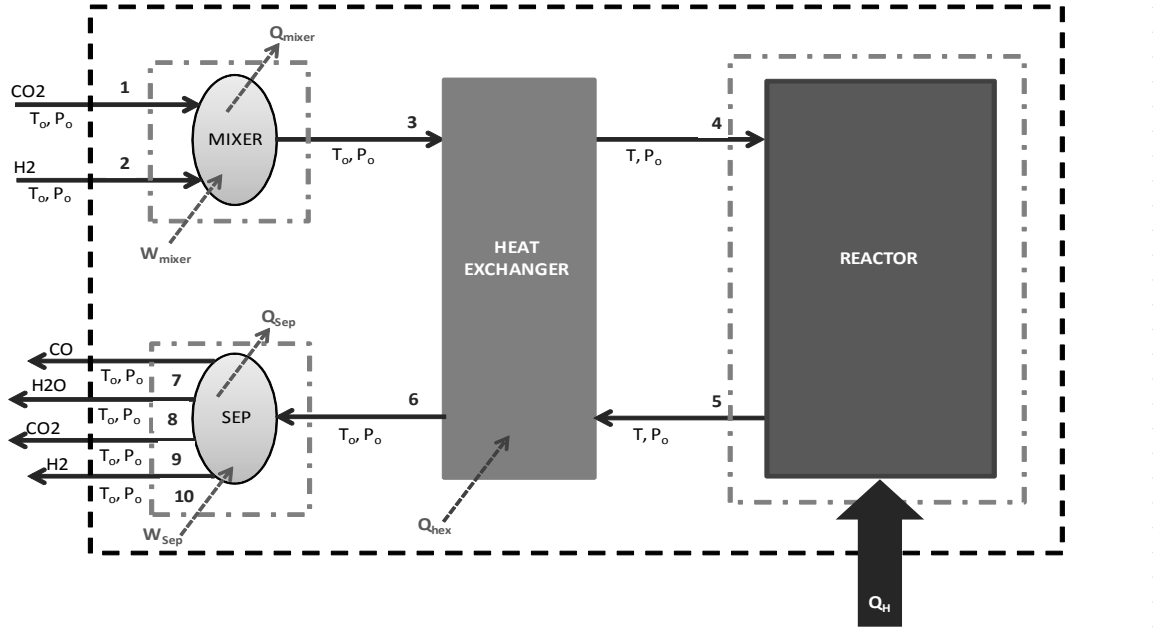

Figure 0-2. Flowsheet for the Reverse Water-Gas shift process

The Reverse Water-Gas Shift (RWGS) process transforms Carbon Dioxide (CO_2) and Hydrogen (H_2) into Carbon Monoxide (CO) and Water steam (H_2O). This example represents the case where the heat capacity of the streams going into the process is significantly different from the heat capacity of the streams coming out of the process ($Cp_{in} \neq Cp_{out}$). It is assumed that the reactants are fed to the process as pure components at ambient temperature and pressure (T_o,P_o) and that the products are coming out of the process as pure components at ambient temperature and pressure (T_o,P_o). It is assumed that $\Delta H_{mix}=0$.

1. STREAMS

$H_1 = H_{f_A(T_o,P_o)} = H^o_{f_A}$ $S_1 = S_{f_A(T_o,P_o)} = S^o_{f_A}$ $G_1 = H_1 - T_o S_1$	$H_2 = H_{f_B(T_o,P_o)} = H^o_{f_B}$ $S_2 = S_{f_B(T_o,P_o)} = S^o_{f_B}$ $G_2 = H_2 - T_o S_2$

$H_3 = H^o_{f_A} + H^o_{f_B}$ $S_3 = S^o_{f_A} + S^o_{f_B} + S_{mix_{(A,B)}}$ $G_3 = H_3 - T_o S_3$	$H_4 = H^o_{f_A} + \int_{T_o}^{T} Cp_A dT + H^o_{f_B} + \int_{T_o}^{T} Cp_B dT$ $S_4 = S^o_{f_A} + \int_{T_o}^{T} Cp_A \frac{dT}{T} + S^o_{f_B} + \int_{T_o}^{T} Cp_B \frac{dT}{T} + S_{mix_{(A,B)}}$ $G_4 = H_4 - TS_4$

$$S_{mix_{(A,B)}} = -nR\sum[xi \ln xi]$$
$$= -2R\left[\ln\frac{1}{2}\right]$$

$$H_5 = (1-x)H^o_{f_A} + (1-x)\int_{T_o}^{T} Cp_A dT + (1-x)H^o_{f_B} + (1-x)\int_{T_o}^{T} Cp_B dT + (x)H^o_{f_C} + (x)\int_{T_o}^{T} Cp_C dT + (x)H^o_{f_D} + (x)\int_{T_o}^{T} Cp_D dT$$

$$S_5 = (1-x)S^o_{f_A} + (1-x)\int_{T_o}^{T} Cp_A \frac{dT}{T} + (1-x)S^o_{f_B} + (1-x)\int_{T_o}^{T} Cp_B \frac{dT}{T} + (x)S^o_{f_C} + (x)\int_{T_o}^{T} Cp_C \frac{dT}{T} + (x)S^o_{f_D} + (x)\int_{T_o}^{T} Cp_D \frac{dT}{T} + S_{mix_{(A,B,C,D)}}$$

$$G_5 = H_5 - TS_5$$

$$S_{mix_{(A,B,C,D)}} = -nR\sum[xi \ln xi]$$
$$= -2R\left[(1-x)\ln\frac{(1-x)}{2} + (x)\ln\frac{(x)}{2}\right]$$

$$H_6 = (1-x)H^o_{f_A} + (1-x)H^o_{f_B} + (x)H^o_{f_C} + (x)H^o_{f_D}$$
$$S_6 = (1-x)S^o_{f_A} + (1-x)S^o_{f_B} + (x)S^o_{f_C} + (x)S^o_{f_D} + S_{mix_{(A,B,C,D)}}$$
$$G_6 = H_6 - T_o S_6$$

$H_7 = (x)H_{f_{C(T_o,P_o)}} = (x)H^o_{f_C}$ $S_7 = (x)S_{f_{C(T_o,P_o)}} = (x)S^o_{f_C}$ $G_7 = H_7 - T_o S_7$	$H_8 = (x)H_{f_{D(T_o,P_o)}} = (x)H^o_{f_D}$ $S_8 = (x)S_{f_{D(T_o,P_o)}} = (x)S^o_{f_D}$ $G_8 = H_8 - T_o S_8$
$H_9 = (1-x)H^o_{f_A}$ $S_9 = (1-x)S^o_{f_A}$ $G_9 = H_9 - T_o S_9$	$H_{10} = (1-x)H^o_{f_B}$ $S_{10} = (1-x)S^o_{f_B}$ $G_{10} = H_{10} - T_o S_{10}$

2. PROCESS

REVERSIBLE PROCESS

$$\Delta H_{(T_o)} = H_7 + H_8 + H_9 + H_{10} - H_1 - H_2 = Q_H + Q_{hex}$$

$$\Delta S_{(T_o)} = S_7 + S_8 + S_9 + S_{10} - S_1 - S_2 = \frac{Q_H}{T_{reactor}} + \frac{Q_{hex}}{T_{hex}}$$

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

$$W_{lost} = 0$$

IRREVERSIBLE PROCESS

$$\Delta H_{(T_o)} = H_7 + H_8 + H_9 + H_{10} - H_1 - H_2 = Q$$

$$\Delta S_{(T_o)} = S_7 + S_8 + S_9 + S_{10} - S_1 - S_2 = \frac{Q}{T} + S_{gen(p)} = \frac{\Delta H_{(T_o)}}{T} + S_{gen(p)}$$

$$\Delta G_{(T_o)} = \Delta H_{(T_o)} - T_o \Delta S_{(T_o)} = \Delta H_{(T_o)} \left(1 - \frac{T_o}{T} \right) - T_o S_{gen(p)}$$

$$W_{lost} = T_o S_{gen(p)}$$

$$W_{lost} = \Delta H_{(T_o)} T_o \left(\frac{1}{T_{Carnot}} - \frac{1}{T} \right)$$

3. REACTOR

REVERSIBLE REACTOR

$$\Delta H_{(T)} = H_5 - H_4 = Q$$

$$\Delta S_{(T)} = S_5 - S_4 = \frac{Q}{T_{\mathrm{Re}versible}} = \frac{\Delta H_{(T)}}{T_{\mathrm{Re}versible}}$$

$$\Delta B_{(T)} = \Delta H_{(T)} - T_o \Delta S_{(T)} = \Delta H_{(T)} \left(1 - \frac{T_o}{T_{\mathrm{Re}v}} \right)$$

$$W_{lost} = 0$$

IRREVERSIBLE REACTOR

$$\Delta H_{(T)} = H_5 - H_4 = Q$$

$$\Delta S_{(T)} = S_5 - S_4 = \frac{Q}{T} + S_{gen(r)} = \frac{\Delta H_{(T)}}{T} + S_{gen(r)}$$

$$\Delta B_{(T)} = \Delta H_{(T)} - T_o \Delta S_{(T)} = \Delta H_{(T)} \left(1 - \frac{T_o}{T} \right) - T_o S_{gen(r)}$$

$$W_{lost} = T_o S_{gen(r)}$$

$$W_{lost} = \Delta H_{(T)} T_o \left(\frac{1}{T_{Rev}} - \frac{1}{T} \right)$$

4. MIXER

It is assumed that $\Delta H_{mix}=0$ and if the work of mixing (W_{mix}) is recovered or added, then Q_{mix} must also appear such that $W_{mix}=Q_{mix}$, therefore ΔH_{mix} remains zero.

$$H_1 + H_2 = H_3$$

$$W_{mix} = Q_{mix}$$

$$S_1 + S_2 = S_3 + \frac{Q_{(T_o)}}{T_o}$$

$$W_{mix} = Q_{(T_o)} = 2RT_o \left[\ln 0.5 \right] = G_{mix_{(3)}}$$

Work of mixing (W_{mix}) is *equivalent to the work of mixing at the stream exiting the mixer unit, G_{mix3}*

5. SEPARATOR

It is assumed that $\Delta H_{mix}=0$ and if the work of separation (W_{sep}) is recovered or added, then Q_{sep} must also appear such that $W_{sep}=Q_{sep}$, therefore ΔH_{mix} remains zero.

$$H_6 = H_7 + H_8 + H_9 + H_{10}$$

$$W_{sep} = Q_{sep}$$

$$S_6 = S_7 + S_8 + S_9 + S_{10} + \frac{Q_{(T_o)}}{T_o}$$

$$W_{sep} = Q_{(T_o)} = T_o S_{mix(A,B,C,D)}$$

$$W_{sep} = -2RT_o \left[(1-x) \ln \frac{(1-x)}{2} + (x) \ln \frac{(x)}{2} \right] = -G_{mix_{(6)}}$$

Work of separation (W_{sep}) is equivalent to the work of separation at the stream going into the separator unit, G_{mix6}

6. HEAT EXCHANGER

Heat capacity of the streams going into the process is different from the heat capacity of the streams going out of the process ($Cp_{in} \neq Cp_{out}$).

$$H_3 + H_5 + Q_{hex} = H_4 + H_6$$

$$\Delta H = Qhex$$

$$S_3 + S_5 + \frac{Q_{(T_o)}}{T} = S_4 + S_6$$

$$\Delta S = \frac{Q_{(T_o)}}{T}$$

$$W_{hex} = \Delta G_{(hex)} = (H_{out} - H_{in}) - T_o(S_{out} - S_{in})$$

$$W_{hex} = \Delta H\left(1 - \frac{T_o}{T}\right)$$

$$W_{hex} = (x)\left[\left(\int_{T_o}^{T} Cp_A dT + \int_{T_o}^{T} Cp_B dT - \int_{T_o}^{T} Cp_C dT - \int_{T_o}^{T} Cp_D dT\right) - T_o\left(\int_{T_o}^{T} Cp_A \frac{dT}{T} + \int_{T_o}^{T} Cp_B \frac{dT}{T} - \int_{T_o}^{T} Cp_C \frac{dT}{T} - \int_{T_o}^{T} Cp_D \frac{dT}{T}\right)\right]$$

7. EQUILIBRIUM

$\Delta G_{(T_o)} = -RT \ln K_o$	$\Delta G_{(T)} = -RT \ln K$
$K_o = e^{\left(\frac{-\Delta G_{(T_o)}}{RT}\right)}$	$K = e^{\left(\frac{-\Delta G_{(T)}}{RT}\right)}$

a. Reversible Reactor

$$\Delta H_{(T)} = Q$$

$$\Delta S_{(T)} = \frac{Q}{T}$$

$$\Delta G_{(T)} = \Delta H_{(T)} - T\Delta S_{(T)} = \Delta H_{(T)} - \Delta H_{(T)} = 0$$

Minimal ΔG at the reactor's reversible temperature

b. Irreversible Reactor

$$\Delta H_{(T)} = Q$$

$$\Delta S_{(T)} = \frac{Q}{T} + S_{gen}$$

$$\Delta G_{(T)} = \Delta H_{(T)} - T\Delta S_{(T)} - TS_{gen}$$

$$\Delta G_{(T)} = -TS_{gen}$$

To include entropy of mixing to streams calculations before proceeding with -TSgen calculations below:

$$\Delta H_{(T)} = H_5 - H_4$$

$$\Delta S_{(T)} = S_5 - S_4$$

$$-TS_{gen} = \Delta G_{(T)} = (H_5 - H_4) - T(S_5 - S_4)$$

$$-TS_{gen} = (x)\left[\left(H^o_{f_C} + \int_{T_o}^{T} Cp_C dT + H^o_{f_D} + \int_{T_o}^{T} Cp_D dT - H^o_{f_A} - \int_{T_o}^{T} Cp_A dT - H^o_{f_B} - \int_{T_o}^{T} Cp_B dT\right) - T\left(S^o_{f_C} + \int_{T_o}^{T} Cp_C \frac{dT}{T} + S^o_{f_D} + \int_{T_o}^{T} Cp_D \frac{dT}{T} - S^o_{f_A} - \int_{T_o}^{T} Cp_A \frac{dT}{T} - S^o_{f_B} - \int_{T_o}^{T} Cp_B \frac{dT}{T}\right)\right] - T\Delta S_{mix}$$

$$T\Delta S_{mix} = S_{mix_{(A,B)}} - S_{mix_{(A,B,C,D)}}$$

$$T\Delta S_{mix} = TS_{mix_{A,B}} - TS_{mix_{A,B,C,D}} = 2RT\left[(1-x)\ln\frac{(1-x)}{2} + (x)\ln\frac{(x)}{2} - \ln\left(\frac{1}{2}\right)\right]$$

$$G_{mix_{(5)}} = 2RT\left[(1-x)\ln\frac{(1-x)}{2} + (x)\ln\frac{(x)}{2}\right]$$

$$-G_{mix_{(5)}} = TS_{mix_{A,B,C,D}}$$

$$G_{mix_{(5)}} = 2RT\left[\ln\frac{1}{2}\right]$$

$$-G_{mix_{(5)}} = TS_{mix_{A,B}}$$