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Graphical Techniques to biomass gasification

Busisiwe Patience Sekwambane

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

Johannesburg, 2012.

DECLARATION

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

Busisiwe Patience Sekwambane

----------Day of ----------2012

ABSTRACT

A notable way to reduce pollution for a friendly environment is to make use of clean fuels. Biomass has been identified as a potential alternative clean fuel and it will play a significant role providing energy in the years to come.

We will need efficient processes to convert biomass into fuel; therefore this study utilized a process synthesis approach i.e. a graphical targeting tool to determine the optimal operating conditions for biomass gasification. Gasification is the conversion of carbon based material into combustible gases by reacting the solid fuel at high temperatures with a controlled amount of oxygen, steam or air.

The technique of graphically representing gasification allows one to make simple assumptions and represent the mass balance, energy balances and the reaction equilibria around a gasifier graphically to determine a stoichiometric subspace (region) within which we can understand, operate and optimise biomass gasification. The approach allows one to easily screen the various options and thus determine processes that are efficient and environmentally friendly, before a large investment is made on equipment and expensive laboratory testing.

The graphical approach was used to maximise the conversion of biomass, to minimise the carbon dioxide production and to minimise as much energy consumption as possible simultaneously. The result of this approach shows that the best place to operate gasification process is in the region where heat and work are required to be added. This is because in this region when heat is added work

can also be added to meet the energy requirement of the process and there is a point within the region where the process does not emit carbon dioxide.

Furthermore we illustrated the use of the thermodynamic regions in the Enthalpy-Gibbs free energy space to provide the heat and work that gasification requires. This method allows one to determine whether heat at an appropriate temperature is sufficient to meet the work requirement of a chemical process or other means should be considered. This is done with the goal to identify ways to make infeasible processes possible, or minimize or even nullify the work requirements of the combined process.

This work identifies the best operating point in the gasification region as the point where the work requirement of the process is zero, there is no carbon dioxide emission and heat is required to be added. This is the reason why studying biomass gasification process is always welcome, especially if the intention is to save energy. Today, because of increased fuel prices and environmental concern, there is renewed interest in this century old technology.

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NOMENCLATURE

ΔH	Change in Enthalpy
ΔG	Change in Gibbs free energy
υ_i	Stoichiometric coefficient of component *i*
$\Delta H^0_{f,i}$	Enthalpy of formation of substance *i* at standard conditions
$\Delta G^0_{f,i}$	Gibbs free energy of formation at standard conditions
ε_i	Extent of reaction *i*
ΔH^0_{rxn}	Enthalpy of reaction at standard conditions
ΔG^0_{rxn}	Gibbs free energy of reaction at standard conditions
$n_i°$	Moles component *i* entering the system
n_i	Moles component *i* leaving the system
T	Temperature
T_0	Ambient temperature (298K)
P	Pressure
P_0	Ambient pressure (1 atmosphere)

x_i	Mole fraction of component *i*
W	Work
s	Solid phase
l	Liquid phase
g	Gas phase
kJ/mol	Kilo-joule per mole
^oC	Degrees Celsius/centigrade
K	Degrees Kelvin
atm	Atmospheres
K_i	Equilibrium constant of reaction *i*
WGS	Water gas shift reaction
g-h space	The Enthalpy-Gibbs free energy plot

Chapter 1

1General Introduction

1.1Background

1.1.1 Energy source: past, present and future

Gasification is a flexible, reliable, and clean energy technology that can turn a variety of low-value feedstocks into high-value products. It can also help reduce our dependence on foreign oil and natural gas, and can provide a clean alternative source of base load electricity, fertilizers, fuels, and chemicals. It is a century old technology which flourished quite well before and during the Second World War. The technology disappeared soon after the Second World War when liquid fuel became easily available. Biomass, in particular wood, has historically been an important energy source for fires, ovens and stoves. During the Industrial Revolution, coal became a good substitute for biomass owing to its high energy content and its availability in large quantities at low mining cost. Today, the increasing fuel prices and environmental concern have brought about a renewed interest in this century old technology, that is, gasification.

1.1.2 Biomass

Biomass is a very general term which comprises all organic matter that originates from photosynthesis. As such, it is not a well-defined feedstock and is often

inhomogeneous. To name few factors, its chemical and mineralogical composition depends on the origin, the physical location, the age, and the season. Biomass types include many types of wood, plants, vegetable oils, green waste, and materials such as manure and sewage sludge. Numerous aspects account for the large differences in these biofuels. Amongst others are their availability, cost, suitability as a gasifier fuel, and also their acceptance by the public.

Prins (2005) reported that annually, photosynthesis stores 5 – 8 times more energy in biomass than man currently consumes from all sources. Prins (2005) also stated that biomass is currently the fourth largest energy source in the world, making it in principle the main energy source of the future. Several scenarios for the future predict a strong increase in the use of biofuels between 2025 and 2050.

There are a number of fundamental reasons why energy from biomass appears to be an attractive agricultural, industrial and economic option.

Firstly, it utilizes renewable resources as fuel which could be sustainably developed in the future. The only physical constraint is the availability of productive land for cultivation and the current development relating to biomass species which determines productivity.

Secondly, it has the attractive environmental property of recycling carbon by the photosynthesis. The latter leads to no net release of carbon dioxide and only limited sulphur emissions.

Thirdly, it has a very significant potential, at least in some regions in the European Union and in most developing countries.

Finally, wastes will continue to be produced by modern society and industry while agricultural and forestry operations result in large quantities of residues (Maniatis, Millich 1998).

1.1.3 Biomass Gasification

Gasification can be defined as a method of extracting energy from organic materials. There exist two main types of organic materials: fossil fuels and biomass.

For a long time fossil fuels has been used with great environmental consequences expressed over the release of carbon dioxide (CO_2) due to their burning. Kirubakaran et al. (2009) have argued that when fossil fuels are burnt, carbon from fuels reacts with oxygen to produce CO_2. This is the reason for the steady increase of CO_2 content recorded in the atmosphere. Furthermore, carbon dioxide contributes for about 50 % of green house effect. The reduction of CO_2 emission becomes a paramount necessity. Recent trends suggest that biomass can be considered as a good alternative to fossil fuel that would limit the rising concentration of CO_2 in the atmosphere.

The conversion of biomass materials into gaseous component requires a process known as biomass gasification. This process takes place at high temperature typically ranging between 600˚C and 1200˚C. Under these conditions, the complex hydrocarbon present in the biomass material is decomposed. As a result, a producer gas containing carbon monoxide, hydrogen, methane and some other

inert gases is produced. Mixed with air, the producer gas can be used in gasoline or diesel engine with little modifications.

Biomass gasification could play a significant role in a renewable energy economy. The reason for this is that plant photosynthesis is believed to remove more CO_2 than emitted from gasification and combustion i.e. nearly zero balance of CO_2 because the amount of carbon dioxide in emissions is very close to the amount of the CO_2 gas consumed with the plants growth (Kirubakaran et al., 2009). On top of that biomass is widely considered to be the potential fuel and renewable resource for the future that is more likely to make positive contribution to limiting the greenhouse effect.

Environmentally, biomass has some advantages over fossil fuels such as coal and petroleum. Biomass contains little sulphur and nitrogen, so it does not produce the pollutants that cause acid rain. Growing plants for use as biomass fuels may also help keep global warming in check. That is because plants remove carbon dioxide, one of the greenhouse gases from the atmosphere when they grow.

1.1.4 Theoretical considerations

Biomass gasification is the incomplete combustion of biomass resulting in the production of combustible gases such as carbon monoxide, hydrogen and traces of methane and not so useful products like char and tars. The combustible gases mixture is called producer gas. Producer gas can be used to run internal combustion engines as a substitute for furnace oil in direct heat applications and can be used to produce in an economically viable way, methanol, an extremely

attractive chemical which is used both as fuel for heat engines as well as chemical feedstock in industries. Since biomass gasification is a high temperature process, it refines out corrosive ash element such as chloride and potassium, allowing clean gas production (Rajvanshi, 1986).

According to Li and Ma (2009), biomass gasification is the gasification of solid biomass material at high temperatures with a gasification agent such as air, oxygen and water vapour to obtain combustible gases. There are many factors which can affect biomass gasification results, such as reaction temperature, pressure, feed particle size, catalyst addition, the characteristics of the biomass feedstock and so on.

Gasification reaction temperature is the key control parameter with regards to the biomass gasifier. However, Long-long et al. (2003) have argued that temperature should not increase indefinitely because the higher the temperature, the more raw materials are required for oxidation. At the same time, more heat needs to be taken away from the furnace wall and dissipated with the gas energy causing higher energy losses, but also the size of the furnace needs to be increased. As a general consideration, the biomass gasification reaction temperature should be controlled between 600°C ~ 1000°C.

The chemical composition of the feedstock also influences the constituents in the product gas therefore the gasification design and product gas cleanup method must be matched to the intended use. In general, feedstock should have a high carbon to nitrogen ratio, relatively little sulfur and a moisture content of less than fifty percent.

In most fuels there is very little choice in moisture content since it is determined by the nature of fuel, its origin and treatment. But we can always dry the material or add additional water or steam to the gasifier to control the moisture content. However it is desirable to use fuel with low moisture content because heat loss due to its evaporation before gasification is considerable and the heat budget of the gasification reaction is impaired. Besides impairing the gasification heat budget, high moisture content also puts load on cooling and filtering equipment by increasing the Pressure drop across these units because of condensing liquids (Rajvanshi, 1986).

1.2 Research Objective

The aim of this research project is to assess graphical techniques to biomass gasification. This can be achieved by examining the type of information that we can get out of the technique besides what is known from previous coal gasification techniques. Following this, the graphical techniques will be applied to biomass gasification in order to ascertain their benefit.

It is understood that the core of this work lies in the use of fundamental mass balance, energy balance and thermodynamic properties to define a stoichiometric space, within which we can attempt to better understand, operate and optimize biomass gasification process. Different gasifier feeds and operating conditions will also be investigated using this method and the application of this technique will be evaluated.

It is our intention to use the principle of biomass gasification in the conversion of a chosen biomass material to produce gaseous components. Then, using the graphical tool at hand, the investigation will try to determine how far the process can be optimized. Eventually, the accessible region of the process will be validated against theory and compared to coal gasification predictions. This study is a purely theoretical investigation to determine theoretical targets for actual operations.

The choice of this feedstock is motivated by the fact that biomasses are generally far better energy sources, environmentally friendly and still to be proven as more economically viable.

Lastly in this thesis the graphical approach will be used for the following:

- to maximise the conversion of biomass.
- to minimise the carbon dioxide production and
- also to minimise as much energy as possible.

This will help in identifying the best operating point in the gasification region.

1.3 Outline of the thesis

In respect to the graphical approach to biomass gasification, this research work will first review the theory of biomass gasification with emphasis of the techniques of analysis currently used.

An application of graphical analysis in Process Synthesis will then be done to circumscribe the need for sophisticated tools of analysis of the process. In Chapter 3, the proposed graphical approach will be thoroughly presented. The gasification region will be determined using the principles of mass and energy balance, the Gibbs free balance and fundamental thermodynamics. From there, an attempt to understand and optimise the gasification process will be undertaken. Moreover, different gasifier feeds and operating conditions will be evaluated to establish the graphical technique of analysis. Chapter 4 will look into the thermodynamic properties of Enthalpy and Gibbs free energy. This will enable one to develop a process that operates as close to reversible as possible. The use of the g-h plot to describe the relationship between heat and work requirements of the process will also be attempted for validation purposes.

Finally, Chapter 5 will wrap up the research work with sound conclusions, recommendations and an outlook for the graphical analysis of biomass gasification.

Chapter 2

2 Application of graphical analysis in process synthesis

In developing a graphical tool that will enable us to define, optimize and operate a gasification region, an approach is needed for analyzing and comparing alternatives from the early stages of development. In this study, process synthesis is the route adopted to achieve this goal.

A case study together with the target which is based on the fundamental concepts of mass, energy and Gibbs free balance will be used as an approach for the biomass gasification process. These targets also give insights, at a very early stage, into integration of the process. This will then aid in determining the region of operation for gasification process within which we can get an optimal point of operation and determine the effect of temperature on equilibrium.

2.1 Introduction

Gasification is defined as the reaction of solid fuels with air, oxygen, steam, carbon dioxide, or a mixture of these gases at temperatures exceeding 800°C in a reducing environment where the air: oxygen ratio is controlled.

Gasification occurs in sequential steps, namely:

- drying to evaporate moisture
- pyrolysis to give gas, vaporized tars or oils and a solid char residue

- gasification or partial oxidation of the solid char, pyrolysis tars and pyrolysis gases (Bridgwater 1995).

Gasifiers are reactors used in the gasification process and can be designed to gasify almost any kind of organic feed. A wide variety of fuels, such as many types of wood, agricultural residues, peat, coal, anthracite, oil residues and municipal solid waste may be considered.

During the oil crisis in the late 1970's and through to the middle of the 1980's, coal was regarded as a very important substitute for oil. Reserves of coal are abundant and more geographically spread over the world than crude oil. In this period, several coal gasifiers were developed and commercialized. However, due to a large drop in the oil price, coal gasification did not gain a much larger share of the energy market, although heavy oil gasification is commercially practiced at several refineries (Prins, 2005).

During the last decennium, there has been renewed interest in gasification. Focus is less on coal, but more on biomass gasification as a form of renewable energy. With the rapid development of economic population, the problem of energy shortages and environmental pollution is increasingly severe. Therefore introduction of biomass as a renewable energy source is vital for the transition to a more sustainable society.

2.2 Biomass as an alternative energy source

To prevent climate change induced by human activity, greenhouse gas emissions must be dramatically reduced. Renewable energy e.g. solar, wind and biomass could play a major role in achieving this. Biomass is a renewable energy source where carbon dioxide emissions caused by its use are absorbed by newly grown biomass.

With the depletion of fossil fuel sources as well as the global warming issues, the utilization of biomass has been more and more concerned. Han (2008) has shown that at present, biomass share in world's total primary energy consumption is about 12%, see in Figure 2.1 below.

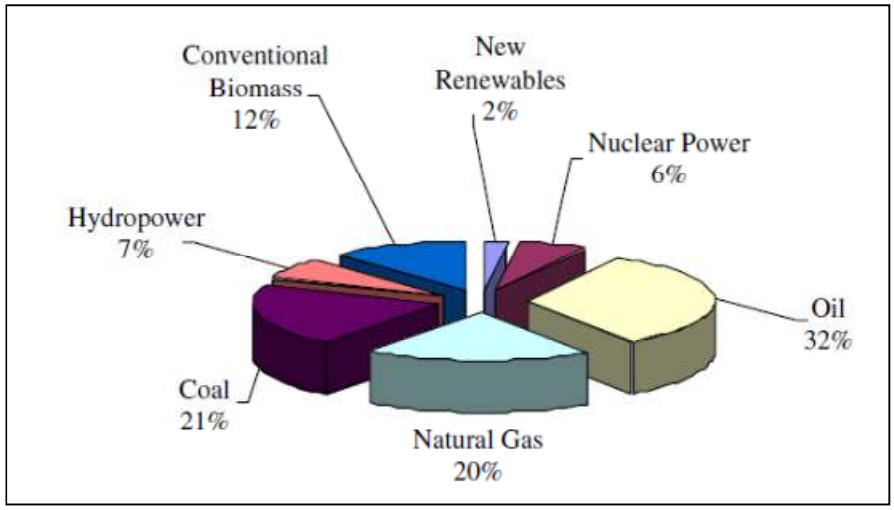


Figure 2.1 The shares of current world's primary energy consumption, (Han, 2008).

Biomass is currently being used worldwide, but its consumptions in developing nations have a significant proportion of the energy. Figure 2.2 below shows the energy consumption in both the developed and developing countries. It can be noted that the use of biomass is improved in the developing countries which makes studying biomass gasification a useful subject.

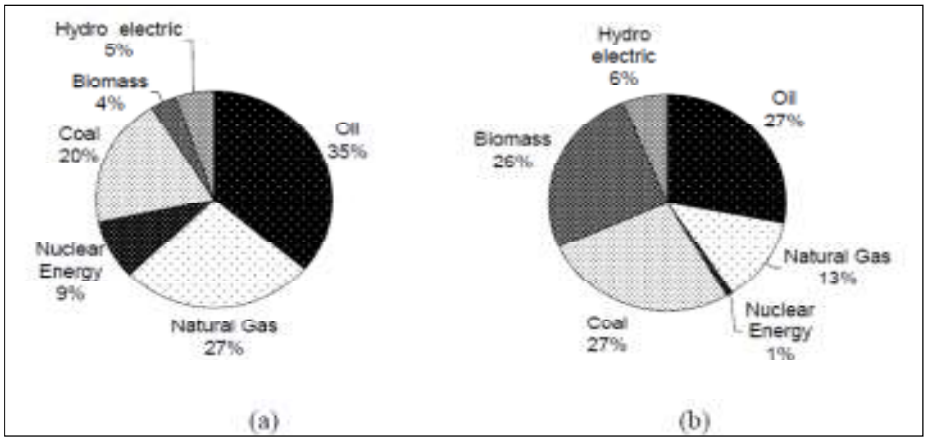


Figure 2.2 Primary energy consumption in a) developed countries, b) developing countries (BP Statistical Review of World Energy, June 2003; biomass consumption from Hall and House, 1995).

A wide variety of biomass resources can be used as feedstock. Wood, agricultural wastes, organic wastes, and sludges are each potential fuels. Theoretically, almost all kinds of biomass with moisture content of 5-30% can be gasified (Knoef, 2000). It was recognized that fuel properties such as surface, size, shape as well as moisture content, volatile matter and carbon content influence gasification.

Maniatis (1998) stated that while not all alternative energy sources can be placed on the same footing, they offer undoubted benefits in terms of protection of the environment and can help to combating global warming problems.

There are different types of biomass and each type of biomass has its own specific properties, which determines its performance as a fuel in gasification plants. The most important properties for gasification are:

- moisture content
- ash content and ash composition
- elemental composition
- heating value
- bulk density and morphology
- volatile matter content
- other fuel related contaminants like N, S, Cl, alkalies, heavy metals, etc.

The substance of a solid fuel is usually composed of the elements carbon, hydrogen and oxygen. In the gasifiers considered, the biomass is heated by combustion. Three different processes can be distinguished in gasification: drying, pyrolysis and oxidation. From a chemical point of view, the process of biomass gasification is quite complex. It includes a number of steps like

- thermal decomposition to non-condensable gas, vapours and char (pyrolysis);
- subsequent thermal cracking of vapours to gas and char or gasification of char by steam or carbon dioxide;

- partial oxidation of combustible gas, vapours and char.(Knoef, 2000)

2.2.1 Reactions involved in gasification

The chemistry of biomass gasification is complex. Biomass gasification proceeds primarily via a three-step process i.e. drying, pyrolysis followed by gasification but Figure 2.3 shows only two steps. Pyrolysis is the decomposition of the biomass feedstock by heat. This step, also known as devolatilization, is endothermic and produces 75 to 90% volatile materials in the form of gaseous and liquid hydrocarbons. The volatile gasification products contain CO_2, CO, H_2, CH_4, N_2, H_2O and un burnt carbon. In our analysis we will assume that reactions participate in equilibrium. The remaining non-volatile material after pyrolysis, containing high carbon content, is referred to as char (Ciferno et al., 2002). Biomass is represented by the general formula $C_xH_yO_z$.

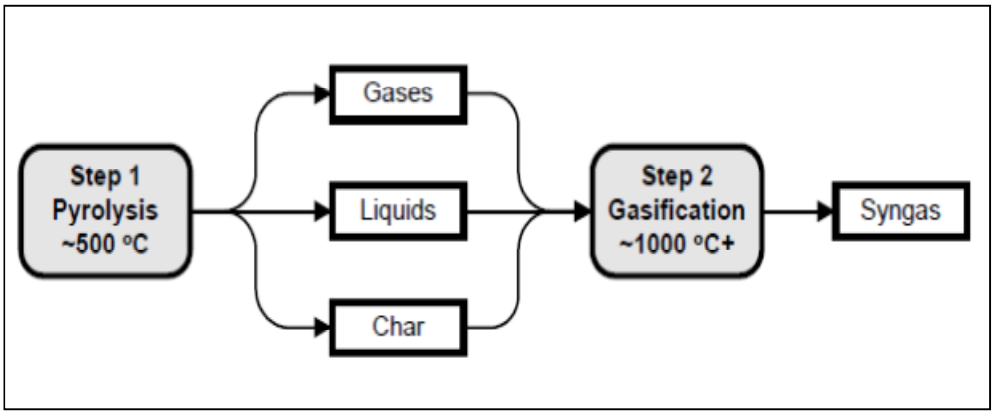


Figure 2. 3 Gasification steps.

From the major volatile material we can derive the following general overall reaction of biomass with air and steam is written as follows:

$C_xH_yO_z + r(pO_2 + p_xN_2) + kH_2O = aCO_2 + bCO + cH_2 + dCH_4 + eN_2 + fH_2O + gC$ (1)

Where: x, y and z are the C/C, H/C and O/C mole ratio respectively.

a ,b, c, d, e, f, g, k and r are coefficients of each component represented

p and p_x represents the amount of the percentage of oxygen and nitrogen in air.

The moisture content of the biomass is neglected and the product quality depends on the y and z. The reaction above will then represents an overall reaction but there are a number of competing intermediate reactions taking place during the process. These are shown by reactions (2) to (6) but it should be noted that the reactions below are used for coal gasification but can be used to analyse biomass gasification because biomass gasification reactions have not yet been established. Since we do not have actual biomass reactions we will use mass balance approach to analyse biomass gasification.

- Oxidation : $C + O_2 = CO_2$ (2)
- Steam gasification : $C + H_2O = CO + H_2$ (3)
- Bouduard reaction : $C + CO_2 = 2CO$ (4)
- Methanation reaction : $C + 2H_2 = CH_4$ (5)
- Water gas-shift reaction: $CO + H2O = CO2 + H2$ (6)

Out of these only four reactions are independent reactions, which are chosen as oxidation, steam gasification, bouduard reaction, and the methanation reaction. Biomass does not appear in any of equations, this is because the above reactions are the standard analysis for coal gasification. The water gas shift reaction can be

considered as the subtraction of the steam gasification and bouduard reactions. Oxidation reaction is typically assumed to be very fast and goes to completion and three reactions namely bouduard reaction, steam gasification and methanation are in equilibrium. (Khadse et al., 2006)

However, in this study clean wood with a chemical formula of cellulose $C_6H_{12}O_6$ is assumed to be used as feedstock. Clean wood gives a relatively clean syngas, with low levels of contaminants. On the longer term, wood from dedicated plantations may become a major source of renewable biomass (Tijmensen et al., 2002). In view of the fact that there is no simple standard enthalpy and Gibbs free energy of formation i.e. $\Delta H_f°$ and $\Delta G_f°$, for cellulose we simplified it by considering the $\Delta H_f°$ and $\Delta G_f°$ of glucose since it has the same chemical formula.

2.2.2 Reaction equilibrium

In a chemical reaction, chemical equilibrium is the state in which the concentrations of the reactants and products have not yet changed with time. It occurs only in reversible reactions and not in irreversible reactions. Usually this state results when the forward reaction proceeds at the same rate as the reverse reaction.

In this way we will look at how equilibrium in the gasifier further limits the region of operation.

For the reaction: $A_{(g)} + B_{(g)} = C_{(g)} + D_{(g)}$ (7)

It is known that the equilibrium constant K for any ideal gas-phase reaction, can be expressed as follows:

$$K = \frac{[C][D]}{[A][B]} \quad (8)$$

Where the quantity in the square brackets is the partial pressure of each species. For solid components concentrations are taken as unity. The partial pressures can also be replaced by:

$$[\mathrm{C}] = \mathrm{x_c}\frac{\mathrm{P}}{\mathrm{P^*}} \quad (9)$$

Where x_c is the mole fraction of component C, P^* is the atmospheric pressure in bar and P is the system total pressure also in bar. In practice, the equilibrium composition of the gas will only be reached in cases where the reaction rate and the time for reaction are sufficient.

Since the standard state temperature is that of the equilibrium mixtures, the standard property changes of reaction, such as $\Delta G°$ and $\Delta H°$, vary with the equilibrium temperature. The dependence of ΔG°on T is given by the following equation:

$$\Delta G° = \Delta H°_0 - \frac{T}{T_0}(\Delta H°_0 - \Delta G°_0) + R\int_{T_0}^{T}\frac{\Delta C_P°}{R}dT - RT\int_{T_0}^{T}\frac{\Delta C_P°}{R}\frac{dT}{T} \quad (10)$$

Therefore: $K = exp\left[\frac{\Delta G^o(T)}{RT}\right]$ (11)

Equation 11 establishes the effect of temperature on the equilibrium constant, and hence on the equilibrium conversion (Salaices et al., 2010). If ΔH° is negative, that is, if the reaction is exothermic, the equilibrium constant will be reduced if the temperature increases. The equilibrium constant, K, increases with temperature, for an endothermic reaction. This reaction equilibrium analysis will be used in the Chapters ahead to determine biomass gasification system.

2.3 Process synthesis alternative approaches

Process synthesis is the step in design where the chemical engineer selects the component parts and how to interconnect them to create the flowsheet. This section includes developing a representation that evaluates alternatives and possible approaches used in process synthesis. In the process synthesis literature, two types of approach exist:

- begin with and seek to improve a feasible flowsheet
- no flowsheet exists, thus find a good candidate.

The first real issue in synthesis is how to represent the design space of alternatives. The wrong representation can make the problem impossible to formulate and/or solve, while the right may make formulation straightforward and may allow one to see how to solve efficiently. Using targeting as in heat exchanger network synthesis or reactor synthesis, one may impose some very strong constraints that will eliminate major portions of the design space quickly. Using abstraction i.e. model, one may make high level decisions that remove major portions of a space. Therefore it is very important to choose the right approach.

Firstly let us take a look at different approaches and understand its implication towards flowsheet design so that we can evaluate which one will be applied in this dissertation.

The superstructure has proved an effective tool for the synthesis of chemical-engineering process flowsheets. The superstructure is assumed to contain all possible alternatives of a potential treatment network, including the optimal solution that is hidden. A common approach for formulating superstructures for process-synthesis problems involving heat and mass exchange has been to use the state-space framework. In this way, unit operations, utility units, and utility streams can be embedded in such a way that all the process synthesis alternatives can be realized. Such a framework has been applied to water and wastewater synthesis problems. (Saif et al., 2009)

The most common approaches for optimizing process-synthesis problems are hierarchical decomposition, superstructures, and targeting techniques (Grossmann et al., 1996). Saif et al. (2009) mentioned that despite its considerable value, the hierarchical technique cannot evaluate process alternatives simultaneously, nor can it accommodate multiple objectives. On the other hand, the superstructure approach can handle a wide range of practical synthesis problems. Targeting techniques apply physical knowledge to understand features of a feasible design without explicit construction of a process network. Each of these techniques has its advantages and disadvantages. Nevertheless, there has been some agreement that the superstructure approach is the most favorable for process-synthesis problems (Westerberg 2004).

According to Grossmann et al. (1996), he concluded that the major methodologies that have emerged and continue to be used in synthesis are Heuristics,

Optimization and Targeting. The first two approaches are mainly directed to the generation and search of flowsheet structures, while the latter is directed to exploiting the physical knowledge of the system. A representative example of the heuristic search approach is the hierarchical decomposition method by Douglas (1985), whose major strength lies in the use of engineering knowledge, and the successive refinement and generation of design alternatives. Its weakness lies in its lack of a systematic framework for process modeling, its inability to perform simultaneous optimization and its reliance on heuristics which may not always be valid.

Another example of the optimization approach is the MINLP (Mixed-Integer Non-linear Programming) optimization of superstructures which was publicized by Grossmann. Its strength lies in providing a systematic framework for modeling and simultaneous optimization, and providing automated capabilities for synthesis problems. Its weaknesses lie in the fact that superstructures must be postulated explicitly there are difficulties in solving large-scale problems and depending on the nature of the model, there is the possibility of getting trapped into poor suboptimal solutions. Nevertheless, a large fraction of the recent research work in the area has followed this approach.

A representative example of the targeting approach is pinch analysis. Its strength lies in being able to use physical and geometric insight to predict a priori certain features that a feasible design should exhibit. Its reliance on graphs and plots makes this approach interesting to designers. Its weakness lies on the fact that the

approach offers only guidelines and the user still has to do all the search work. Another representative example of this type of approach is the synthesis of azeotropic columns which relies on the use for residue curves, and the synthesis of reactor networks by that relies on the use of attainable regions (Grossmann et al., 1996).

As for specific synthesis problems, it is clear that HENS (Heat Exchanger Network Synthesis) has become a mature area. Due to the simplicity and appeal of the ideas behind pinch analysis, the HENS area has been successfully transferred to industry and it is taught in undergraduate design courses (Saif et al., 2009). In terms of research, there is still room for improvement, particularly when it comes to automatically synthesizing large networks or taking layout considerations into account. As for distillation sequences, there is still need of handling more realistic column configurations as well as incorporating rigorous thermodynamic computations for the synthesis.

As for reactor networks, there has been progress with the representations for the attainable region and the modeling of yield targets. There is, however, still a significant gap with respect to the variety and complexity of reactors encountered in industrial situations: the analysis thus far has been restricted to homogenous (or pseudo-homogenous), single-phase systems.

Considering the above mentioned reasons a case study together with targeting methods which is based on the fundamental concepts of mass, energy and Gibbs free balance will be used as an approach for the biomass gasification process.

2.4 Process target

There exist three major principles in process synthesis that the process depends on, these are mass balance, energy balance and entropy balance. These concepts are usually used in analysis or design of equipment and flow sheets. But these will be employed on a process without considering the details of the equipment or flowsheet. They are rather going to be used in setting the overall balance which will then be utilized to find the mass balance reactions involved in the gasification process and to design the flowsheet (Patel et al. 2007).

The approach allows one to screen the various options easily and thus determine processes that are efficient and environmentally friendly. The three major principles, i.e. mass, energy and entropy balance will hence be used to set the process targets which is the minimum amount of feedstock needed in order to make a certain amount of the product. The by-products will be ignored because an idea of the major components needs to be determined.

This study utilises a process synthesis approach i.e. the graphical targeting tool to determine optimal operating conditions for biomass gasification. The following

mass, energy and Gibbs free balance target are tools used to achieve the goal of this research.

2.4.1 Mass balance target

This section will allow us to better understand how certain feeds for the process are chosen and how to determine their respective outputs. This will be determined by the use of mass balance together with the arbitrary selection of feed, where the mass balance is a powerful tool that allows one to determine the minimum amount of inputs needed to produce a specific product. It also establishes the minimum waste products from the process.

The use of mass balance to set a target has been used in the synthesis of methanol hence this will be reviewed as to better understand how to determine the process target. Patel et al. (2007) established a case study of the synthesis of methanol from natural gas (which is assumed to be methane) will be used to demonstrate the approach. However this approach can be applied in any system. Consider Figure 2.4 below:

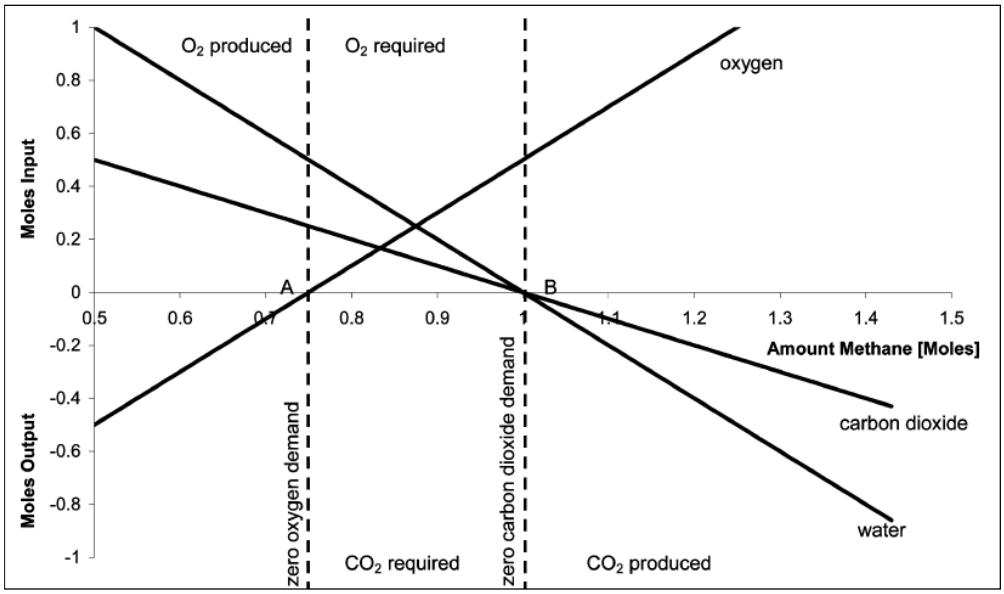


Figure 2.4 Molar amounts of each component required/produced as a function of the amount of methane fed to the process that produces one mole of methanol is varied (Patel et al. 2007).

Figure 2.4 represents the mass balance for all possible methanol processes that use the above feeds i.e. methane, water and carbon dioxide. Each set of values shown in Figure 2.4 corresponds to an overall mass balance for a possible process that produces one mole of methanol. It should be noted that a negative value for a component corresponds to the component being an output, whereas a positive coefficient for a coefficient corresponds to the component being an input. From these results it is possible to examine the possible mass balances that describe these processes and decide which one better match to the sensible processes that is of interests.

However, Patel et al. (2007) have shown that one will only consider processes that are described by mass balances that lie between point A and B in Figure 2.3. This

is because processes that lie before point A will produce oxygen and it is practically very unlikely. While processes that lie after point B will produce carbon dioxide as a waste product, which is undesirable, from an environmental perspective. Therefore a range of possible operation points to meet the process can be established between point A and B. Now that the range of feeds and products has been determined, this can be used to choose the equipment, technology and operating conditions to achieve these targets. It is then decided the reaction which will be suitable for a specific process depending on the requirements and the process targets.

From this analysis the mass balance is a very instructive tool for targeting the entire process but it cannot be isolated as other balances i.e. energy and work (Gibbs free balance) need to be analyzed in search for a suitable process that satisfy the process target.

2.4.2Energy balance target

Despite the fact that the mass balance tool is very useful, the mass aspects of the process cannot be isolated, because energy and work aspects also must be considered. The energy aspects can be taken into account using an energy balance and the work aspect of it can be taken into account by using the Gibbs free energy balance.

Consider a chemical process which will be defined to be a process where the feeds enter and products leave the process at ambient conditions. This process is

referred as an adiabatic process and the one that gives off heat or allows additional heat is called non-adiabatic process. An adiabatic process is shown in Figure 2.5 below:

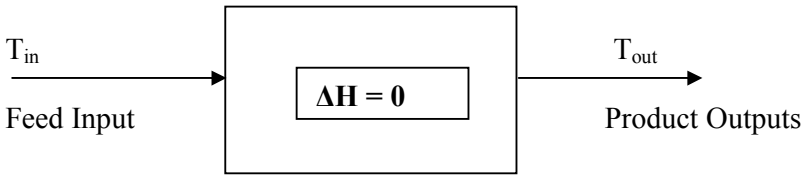


Figure 2. 5 Adiabatic process.

In such a situation, the energy balance across the process gives:

$$\Delta H = 0 \quad (12)$$

$$\Delta H_{rxn} = H_{products} - H_{reactants} \quad (13)$$

Therefore:

$$\Delta H^{0}_{reaction} = \left(\sum_{i} \upsilon_i \Delta H^{0}_{f,i} \right)_{products} - \left(\sum_{i} \upsilon_i \Delta H^{0}_{f,i} \right)_{reactants} \quad (14)$$

Where:

- υ_i (Symbol Upsilon) is the stoichiometric coefficient in the component i.
- The subscript f represents "of formation"
- The superscript 0 represents standard conditions.
- The subscript i represents species i

Equation 14 implies that ΔH, which is the net heat flow requirement of the process, is given by the difference of the enthalpies of formation of the products

and feeds. This is because the products and feeds both enter and leave at ambient conditions, which removes the enthalpy change due to heat capacity. But in the case where the system is non-adiabatic the energy balance will include a heat (Q) term, i.e. $\Delta H = Q$.

Energy must be removed from the process when the enthalpy change for the process is negative which implies that the process is exothermic. On the other hand, energy must be added or supplied to the process when the enthalpy change for the process is positive, implying that the process is endothermic. Thus, the endothermic process is not feasible unless this energy is added. From Patel et al. (2007) case study the process is endothermic and this energy could be supplied by the combustion of a further amount of methane, in the process described by the mass balance, which would result in the production of heat as well as carbon dioxide.

The quantity of extra methane needed to make the overall process adiabatic can be calculated and if more heat is supplied then there will be extra moles of components fed, in this case CO_2 and H_2O.Then a new overall adiabatic equations will be established. Patel et al. (2007) has shown that it is clear that opportunities for mass integration exist as H_2O and CO_2 will be recycled to make the process adiabatic. If the energy balance target was placed to the left of the mass balance target point A in Figure 2.4 above, then the process target would have been the mass balance target and a process that was operating at this limit would have been exothermic. If, as in the present case, the energy balance line intersected the *x*-axis to the right of the mass balance target point A in Figure 2.4 i.e. lying between

point A and B, then the energy balance target sets the process target. Then the minimum methane consumption for a methanol process and the target for the methanol process is limited by the energy balance target, rather than by the mass balance target. The energy balance limit line is shown in Figure 2.6 below.

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

It is possible to deduce from Figure 2.6 that one could continue to improve plant performance until the overall process is adiabatic and that this was the overall target for the process when considering the mass and energy balance targets. There is a third target that must be considered before one can decide on the ultimate target for the process and this will be entropy or work balance target.

2.4.3 Gibbs free energy balance target

Gibbs free energy balance (ΔG) will also be calculated, which represents the minimum work requirement, of the Simple process by:

$$\Delta G^0_{reaction} = \left(\sum_i \upsilon_i \Delta G^0_{f,i} \right)_{products} - \left(\sum_i \upsilon_i \Delta G^0_{f,i} \right)_{reac\,tan\,ts} \qquad (15)$$

Similarly with the mass and energy balance the Gibbs energy change for a methanol synthesis process can also be calculated and plotted as a function of the methane fed to the process. The Gibbs energy change will give insights into the maximum work produced or minimum work required by the process. Work is produced when the Gibbs energy is negative while work is consumed when the Gibbs energy is positive.

There is also a point between the energy balance line and the point B as shown in Figure 2.6 below:

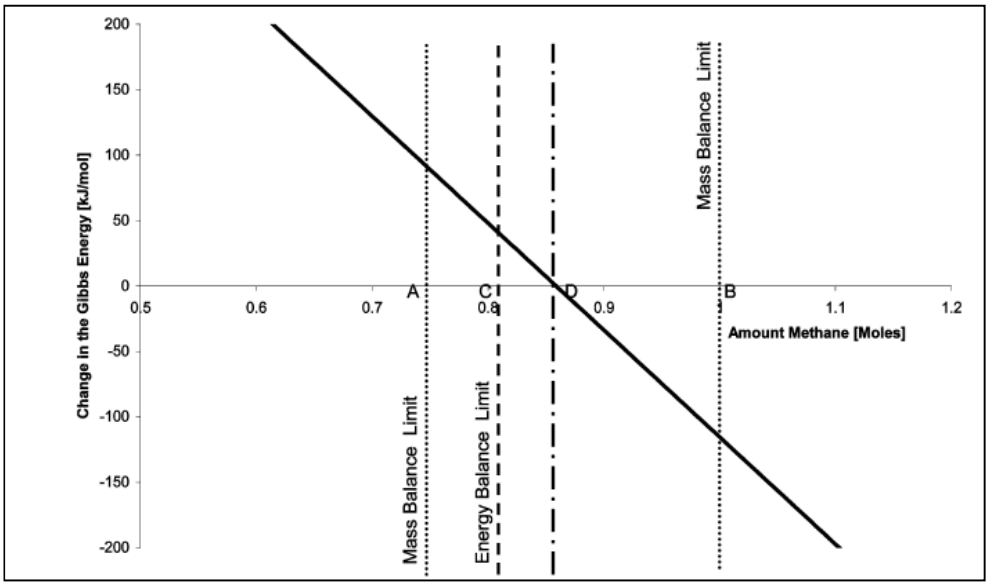


Figure 2.6 Gibbs energy change for the methanol synthesis process, as a function of the methane fed to the process. (A negative change in the Gibbs free energy would correspond to a work-consuming process, whereas a positive change in the Gibbs energy would mean a process would produce work).(Patel et al. 2007)

Figure 2.6 shows a plot of mass, energy and Gibbs free energy balance limits. The point D on the diagram represents the Gibbs free energy change to the process where it becomes zero meaning that there is no net work input or output. Processes that lie to the left of point D in Figure 2.6 correspond to infeasible processes or processes that would require work to be added to them. Processes to the right of point D correspond to feasible processes that would reject work to the surroundings or else be irreversible. Processes that are operating at point D would correspond to a reversible process that, overall, does not consume or emit work.

Therefore by using targets one is also able to identify how far away a process is from being mass, energy or entropy limited and how good or worse the reaction is operating in comparison to other possible reactions. This makes the use of targets to be of great significance in evaluating the performance of a system in its early design.

This analysis illustrate that the mass, energy and entropy balance is a very instructive tool for targeting the entire process as it provides a specific region in which one can focus the search for a suitable process. Therefore a back-to-front synthesis approach based on determining the target overall mass, energy and Gibbs free balance for a process will be used together with the arbitrary feeds for biomass gasification process.

2.5 The ε_1 vs. ε_2 space

The ε_1 vs. ε_2 space is a two dimensional space that enable us to use a graphical approach and visualize the set of all possible gasification outputs from a gasifier. The benefit of presenting biomass gasification on the ε_1 vs. ε_2 space is because:

- the use of graphical methods to asses and predict gasification is viable
- it is also the most economical way of investigating gasification
- finally it allows an easy way of representing the process target and its application.

Research has shown that a graphical tool has been developed for coal gasification. Attempts to use the tool to improve the efficiency of the process have been made and research is still under way. So far, Ngubevana et al. (2011) has shown that the underlined method has been able to establish that the extent to which the gasification reactions occur. In addition, it has successfully shown that the gasification reactions occur in a region and not a specific point.

Firstly in order to use the above mention method, the set of all possible inputs and outputs from the gasifier will be determined. A target will also be established as it was shown in the above section which will aid in selecting the number of moles of component in the feed streams. The reactions in the gasifier occur in many different combinations and amounts. However we are limited by the constraint that all the reactions must occur so that the compositions of all species in the gasifier must always be positive.

Now using graphical techniques one would have to work in a stoichiometric subspace defined by the energy and mass balance. Firstly, reasonable assumptions have to be made to set up mass and energy balance:

- Coal is a pure carbon
- Combustion reaction goes to completion and provides the energy necessary for the other gasification reactions
- The gasifier is assumed to have no heat loses and the heat transfer is perfect when $\Delta H = 0$ case is considered in the energy balance.

Secondly, suitable mass and energy balance as well as reaction equilibra should be applied around a biomass gasifier. The first independent mass balance to be considered is the combustion reaction:

1. $C + O_2 = CO_2$ (16)

The second independent mass balance is a gasification reaction, which is represented as follows:

2. $C + H_2O = CO + H_2$ .....ε_1 (17)

This reaction may not occur to completion and we define the extent of the reaction or mass balance to be ε_1.

The third and final independent mass balance is the water gas shift reaction:

3. $CO + H_2O = CO_2 + H_2$ ..... ε_2 (18)

This reaction will also not occur to completion and we define the extent of this reaction to be ε_2.

Even though there are three independent reactions and therefore a three dimensional mass balance space, by using the assumption that the first reaction which is the combustion reaction, goes to completion; it will reduce the dimension of the space that we will work in to a two dimensional space.

Lastly, a plot will be presented that identifies the accessible region i.e. the gasification region as shown in Figure 2.7 below:

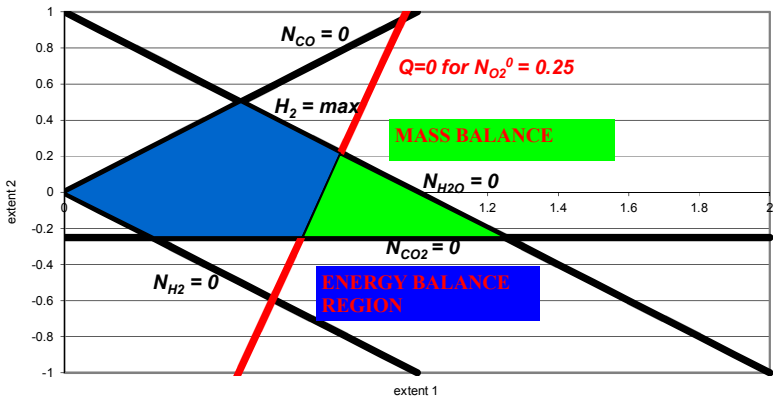


Figure 2.7 Combination of the mass and energy balance for a feed of N_{O2}^{O} = 0.25 and N_{H2O}^{O} = 1.(Ngubevana et al., 2011)

Taking everything into consideration, Figure 2.7 shows us that:

(i) We can achieve gasification in the blue area as it satisfies the mass and energy balance; the energy balance region may be further restricted by the work balance region.

(ii) We cannot reach the green area as gasification here is energy balance limited.

The Ngubevana approach will be further studied by looking at biomass gasification. To analyze the graphical tool, biomass gasification will be studied on equilibrium terms in order to describe the process and to present its energetic performance. This will be done by analyzing operational parameters such as water feed, oxygen feed and temperature.

2.5.1 The effect of temperature on equilibrium

The mass, energy and work balances have been established and now we will take a look at the thermodynamics of the reactions. In this way we will look at how equilibrium in the gasifier further limits the region of operation.

Several equations have been shown by Ngubevana et al. (2011) which will be considered in analyzing the effect of temperature on equilibrium. These equations are the water gas shift, methane producing reaction and the carbon depositing reaction. Each of this reaction has its own plot but for this example we will look at the plot of the equilibrium curve on the effect of temperature on WGS reaction.

The equilibrium curve for the water gas shift reaction (WGS) in the ε_1-ε_2 space is then plotted by using a simple quadratic that can then be solved numerically, which is shown as follows:

$$(1-K)*\varepsilon_2{}^2+\left(N_{CO_2}{}^O+N_{H_2O}{}^O*K+\varepsilon_1\right)*\varepsilon_2+\left(\varepsilon_1{}^2*K+\varepsilon_1*\left(N_{CO_2}{}^O-K\right)\right)=0 \qquad (19)$$

The equilibrium constant K, can be computed using equation 11 above. Figure 2.8 is a plot of the WGS in the ε_1-ε_2 space and it can be seen on Figure 2.8 that the WGS reaction is bound by the $N_{CO} = 0$ and the $N_{H2O}=0$ mass balance lines. The

curve shown in Figure 2.8 initially follows the N_{CO} = zero line and end along the N_{H2O} = zero line. Thus if we assumed that the gasifier was isothermal at 1200K and that the gas as it flows through the gasifier quickly gets to WGS equilibrium and thereafter stays in equilibrium, the composition in the gasifier then would roughly follow the curve shown in Figure 2.8.

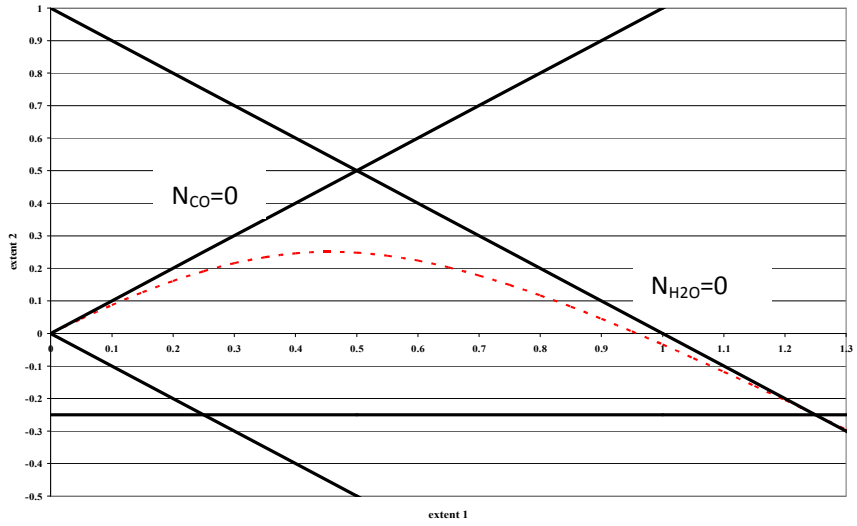


Figure 2.8 Equilibrium plot for WGS reaction at 1200 K for a feed of N_{H2O}^{O} = 1, N_{O2}^{O} = 0.25.(Ngubevana et al., 2011)

It is evident from Figure 2.8 that temperature has a significant effect on the WGS reaction. The reaction is exothermic and therefore an increase in temperature by Le Chatellier's principle drives the reverse reaction.

This implies that more CO and H_2O are formed, at the cost of CO_2 and H_2 formation and this can be clearly seen in Figure 2.8 as ε_2 decreases with an increase in temperature at any chosen ε_1 value. For this reaction, the profile is a

strong function of temperature as it has a relatively low, negative Gibbs' energy of formation and thus a relatively low equilibrium constant.

2.6 The g-h space

Now that the gasification region has been established we will look at the enthalpy and the Gibbs free energy and also determine their respective gasification region. Thermodynamics can be used to describe any process or system of processes that have the properties of Enthalpy and Gibbs free energy. Sempuga et al. (2010) proposed that the ΔG and ΔH of reactions and process units could be drawn on a plot of ΔG and ΔH, hereafter referred to as the g-h space.

We will assume there is a simple process that can be represented as a single reaction. Also we will assume that the feed and products enter and leave as pure components. The mass balance of this simple process, or reaction, can be described by:

$$\sum_i \upsilon_i M_{i,products} - \sum_i \upsilon_i M_{i,reactants} = 0 \qquad (20)$$

Where:

- υ_i is the stoichiometric coefficient in the component *i*.
- The subscript *i* represents species *i*
- M is the mass of component *i*

The change in Gibbs-free energy and the change in enthalpy of simple processes or reactions can be calculated using the following well-known equations:

$$\Delta G^0_{reaction} = \left(\sum_i \upsilon_i \Delta G^0_{f,i} \right)_{products} - \left(\sum_i \upsilon_i \Delta G^0_{f,i} \right)_{reac\tan ts} \quad (21)$$

$$\Delta H^0_{reaction} = \left(\sum_i \upsilon_i \Delta H^0_{f,i} \right)_{products} - \left(\sum_i \upsilon_i \Delta H^0_{f,i} \right)_{reac\tan ts} \quad (22)$$

Where:

- υ_i is the stoichiometric coefficient in the component *i*.
- The subscript *f* represents "of formation"
- The superscript 0 represents standard conditions.
- The subscript *i* represents species *i*

To illustrate the use of the g-h plot, we will consider the coal gasification process. Before one can begin using the g-h space on the coal gasification reaction, we will first define the independent mass balances or reactions that will be used. The feed species to this gasification process will be considered to be coal, which will be represented as pure carbon C, liquid water and oxygen. For this simplified case the products will be considered to be carbon monoxide, hydrogen and carbon dioxide.

Previously we explained the system by three independent reactions; in these three reactions we can add one more reaction i.e. phase change. Phase change has been added because we consider the water liquid and water gas (vapour) as two different components. Therefore there will be four independent mass balances that describe the system. These reactions are the gasification, combustion, WGS and the phase change reactions as shown below.

The gasification reaction is represented as:

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \quad (23)$$

The heat and work requirements for reaction (23) can be determined by applying Equations (21) and (22).

The second reaction is combustion which is:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad (24)$$

Again the heat and work requirements of the process are similar to the reaction above.

To modify the ratio of carbon monoxide to hydrogen another reaction is required, namely the water-gas shift reaction:

$$CO(g) + H_2O(v) \leftrightarrow CO_2(g) + H_2(g) \quad (25)$$

Gasification and WGS use vapour phase water as a reactant. At ambient conditions liquid water is easily obtained. The phase change needs to be considered.

$$H_2O(l) \rightarrow H_2O(v) \quad (26)$$

Having defined all the reactions in gasification and using the heat and work requirements, it is now possible to plot all the gasification reactions into the g-h space. The four reactions are drawn onto the g-h space as presented in Figure 2.9.

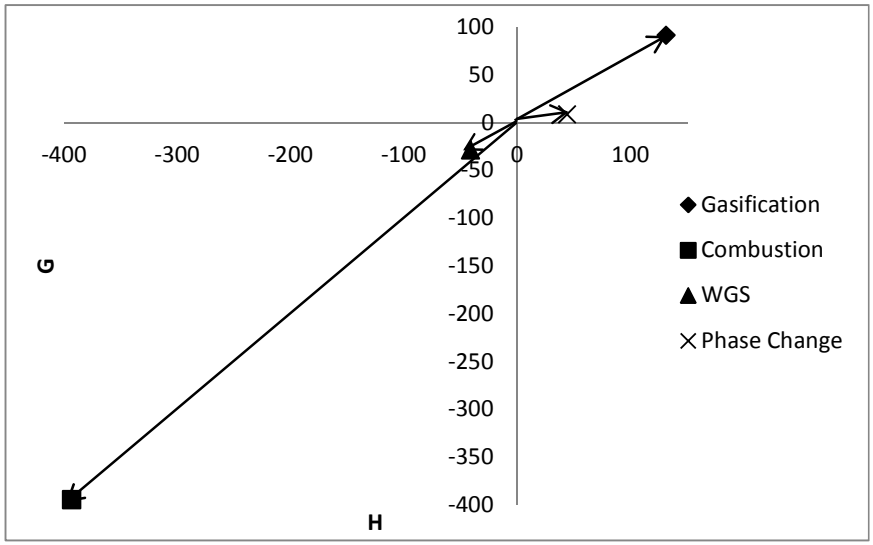


Figure 2. 9 The four gasification reactions as vectors on the g-h space.

Looking at the coal gasification reaction from the graph above, it can be seen that this reaction is endothermic and work deficient; in other words, both heat and work must be added to the process. This means a source of heat and work is required in order for the reaction to proceed. A heat engine as shown in Figure 2.10 could be used to supply both the heat and work requirement to the process.

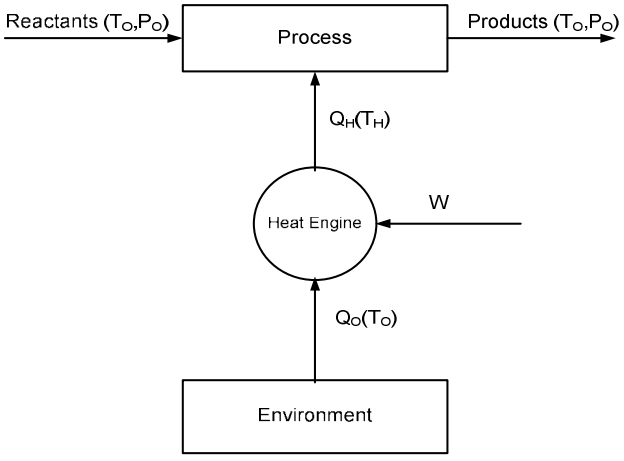


Figure 2.10 Heat Engine for processes that require Heat and Work input.

The most convenient source of heat would come from combusting some of the carbon feedstock (coal) in oxygen to produce the heat; hence the second reaction to be considered is the combustion reaction.

This reaction is exothermic and work producing and it will be used to provide the heat and work to gasification reactions. In fact, burning a unit of coal in combustion will provide much heat and work for gasification reaction. Having such an excess will cause the process to become irreversible if the excess work is not recovered. Hence the combustion reaction has a negative Carnot temperature of -14000^{o}C. A Carnot temperature is the temperature at which all the work required/rejected by the process will be carried with the heat of the process; this means that if the process is operated at Carnot temperature there is no entropy generation. This is a physically impossible temperature; therefore combustion reaction cannot be run reversibly on its own.

The maximum amount of work that can be recovered from the process, using a reversible heat engine, is equal to the amount of heat that the process can reject; and this can only occur at infinite temperature. There is no heat engine capable of fully recovering this work irrespective of the temperature at which heat is removed.

To modify the ratio of carbon monoxide to hydrogen another reaction is required, namely the water-gas shift reaction. This water-gas shift reaction is also an exothermic work producer with a Carnot temperature of 700^{o}C. So if WGS were run at 700^{o}C, removing the excess heat of the reaction would also remove the excess work and the process would be reversible

And finally gasification and water gas shift use vapour phase water as a reactant. At ambient conditions liquid water is easily obtained. The last reaction that will be considered is the phase change. The reaction is an endothermic and work deficient process with a Carnot temperature of 97^{o}C.

Four reactions or simple processes have been defined and it is clear that all four of them could be integrated to interact with one another. By using the g-h space it will be possible to investigate how the reactions interact with one another and to make the process more reversible despite the combustion reaction being shown to be highly irreversible.

The process synthesis approach enabled to identify parametric constraints and objective functions needed to optimize and decide on the best processes involved. This approach is going to be used to examine biomass gasification process on the g-h plot and determine their energy requirements.

Chapter 3

3Identifying attainable region for biomass gasification using graphical approach

A graphical representation of coal gasification has recently been proposed by Ngubevana et al. (2011). In this chapter, we apply a similar approach to investigate the gasification of biomass as a feedstock.

It has been found that the extent to which the gasification reactions occur for coal is not limited by work balance on the reactants but by mass and energy balances. In addition, it has been observed that coal gasification reactions occur in a region and not on a specific point, meaning that for a fixed feed, gasification occurs over a specific region called a mass balance region. It has been found that biomass gasification also occurs in a region and it is a reversible process and work limited i.e. work has to be added before biomass gasification occurs.

3.1 Introduction

In operating chemical reactions there are different reactors involved which differs according to the reactions occurring in them. In a gasification process a reactor used is a gasifier. Gasifier is too often thought of as simple device that can generate a combustible gas from any biomass fuel.

Gasifiers are amongst the very expensive and energy consuming operations in the chemical industry (Turare, 2002). They are also known to be large carbon dioxide

producers. That is the reason why studying the gasification process is always welcome, especially if the intention is to save energy. Today, because of increased fuel prices and environmental concern, there is renewed interest in this century old technology.

The current trend state that biomass gasification is operating in 27 countries, the Asia/Australia region, with 34 percent of the total capacity, is now the leading region in the world for syngas production and uses biomasses rather than fossil fuels like coal and petroleum. Biomass has been an alternative source of energy and could play a significant role in a renewable energy economy (Kirubakaran et al., 2009).

To come back to the gasification process, studies have been mainly conducted empirically and experimentally and not much theoretically. This is due to the complexity of the process at hand. Attempts to use graphical techniques to improve the efficiency of the process have been made and research is still under way. Recently, these techniques have provided a breakthrough allowing a successful description of the various processes taking place in a gasifier (Ngubevana et al., 2011).

The authors used coal as their feedstock and presented a thorough analysis of the gasification process. In the end, they proved the approach to be far more versatile than anything else seen before and less complex to use than pure analytical techniques. The same approach will be employed in this dissertation except that a different feedstock will be studied, that is a biomass.

3.2 The Mass Balance

3.2.1 Simplifying assumptions

In gasifiers, chemical reactions occur in such a way that the input undergoes a transformation to result in some form of outputs. Since we do not have specific reactions we will use mass balance approach to determine a set of independent reactions from which any other process happening could be derived. Firstly mass balance will be used to generate gasification equations within which we can try to simulate the equations and form a region where we will better understand, optimise and operate the gasification process.

As a starting point, we use wood which contain cellulose with a chemical formula of $C_6H_{12}O_6$ as the feedstock. The wood constitutes 40 – 50 percent of the cellulose which then the cellulose will be referred as a biomass (Nishiyama et al., 2002). The remaining percentage accounts to hemicellulose, lignin, pectin and starch.

It is difficult to understand the process from looking at the flowsheet; hence we need to extract the essence by first looking at major inputs and outputs to the overall process. An optimum process will have few extra inputs and outputs as possible because each additional component will have to be removed at some stages which will in turn results as a waste.

If we start with wood as a biomass i.e. $C_6H_{12}O_6$ it contains C, H and O therefore the water and oxygen used as a feedstock needs to be fed in proportionally because the required atoms have to be in the correct ratio. Consider the diagram below where one looks at the overall process (the black box) without looking at process details.

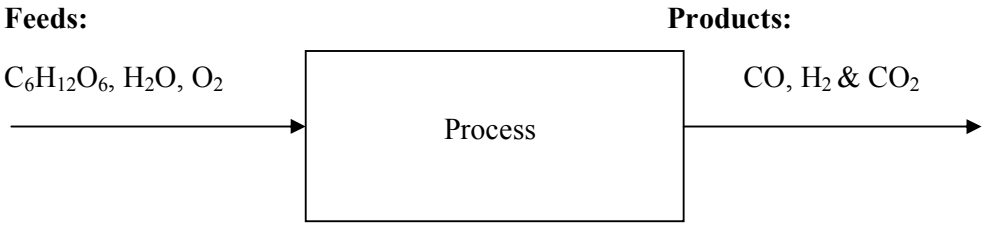


Figure 3.1 The overall process.

Only major input and outputs are considered, not interested at this stage what happens in the process i.e. box. Using the available feed materials we will write mass balances for the process by firstly considering the overall balance as follows, assuming that we are feeding one mole of cellulose:

$$C_6H_{12}O_6 + aO_2 + bH_2O + cH_2 + dCO + eCO_2 = 0 \quad (1)$$

Where: a, b, c, d and e are the respective amounts of oxygen, water, hydrogen, carbon monoxide and carbon dioxide in the overall reaction.

If the coefficient is positive it means that the component is required and must be a feed i.e. it is a reactant and if a coefficient is negative the component is produced. This is achieved by assuming a feed of one mole of cellulose. Note that equation 1 is not the reaction that occurs but the overall mass balance for the process, the individual reactions that occur in the process may be different from the overall mass balance. Since the equation consists of three atomic species i.e. C, H and O, a balance can be written for each species as follows:

$$C: 6 + d + e = 0 \quad (2)$$

$$H: 12 + 2b + 2c = 0 \quad (3)$$

$$O: 6 + 2a + b + d + 2e = 0 \quad (4)$$

From the equation 2 – 4 above, given that the amount of oxygen can be varied, it can be seen that we have five unknowns and three equations, giving us two degrees of freedom. The mass balance equation can be solved by varying the amount of oxygen and water expressed as constants (a) and (b) respectively hence other variables can be solved.

After obtaining the overall mass balance equations one can find the possible reactions involved. Since there are six numbers of species, namely $C_6H_{12}O_6$, O_2, H_2O, H_2, CO and CO_2 as shown in Figure 3.1 above and three atomic components i.e. C, H and O, the number of independent equations can be obtained by subtracting the atomic components from the number of species i.e. *# of independent eqns = # of species - # of atomic eqns*. Hence there are three independent reactions which will be involved in the biomass gasification process. Note that mass balances do not describe the actual reactions occurring in the gasifier but are simply mathematical descriptions of the entire process in the reactor.

Using the available species from the overall mass balance, there can be different combination reactions that describe the biomass gasification process. Using the feed stream components and the products, candidate mass balance equations are generated whether they are feasible or not. Then, some of the candidates are retained whilst others are discarded. The choice is dictated by the fact that an adequate amount of cellulose should be consumed. This is done so that the other two reactions i.e. gasification and WGS reaction can occur since cellulose is used

as a feedstock in gasification reaction. An example of the set of equations is as follows:

Set 1: The gasification reaction: $C_6H_{12}O_6 + H_2O \rightarrow 7H_2 + CO_2 + 5CO$

The water gas shift (WGS): $CO + H_2O \leftrightarrow CO_2 + H_2$

The combustion reaction: $C_6H_{12}O_6 + 3O_2 \rightarrow 6CO_2 + 6H_2$

Set 2: The gasification reaction: $C_6H_{12}O_6 + H_2O \rightarrow 7H_2 + CO_2 + 5CO$

The water gas shift (WGS): $CO + H_2O \leftrightarrow CO_2 + H_2$

The combustion reaction: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

Set 3: The gasification reaction: $C_6H_{12}O_6 + H_2O + O_2 \rightarrow 4H_2 + 3CO_2 + 3CO$

The water gas shift (WGS): $CO + H_2O \leftrightarrow CO_2 + H_2$

The combustion reaction: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

Set 4: The gasification reaction: $C_6H_{12}O_6 + H_2O \rightarrow 7H_2 + CO_2 + 5CO$

The water gas shift (WGS): $CO + H_2O \leftrightarrow CO_2 + H_2$

The pyrolysis reaction: $C_6H_{12}O_6 \rightarrow 6CO + 6H_2$

Set 5: The gasification reaction: $C_6H_{12}O_6 + H_2O \rightarrow 7H_2 + CO_2 + 5CO$

The water gas shift (WGS): $CO + H_2O \leftrightarrow CO_2 + H_2$

The combustion reaction: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

The other equations required more O_2 as a feed which will in turn consume lot of cellulose; this is the reason why they are discarded. Having said this, Set 5 i.e. the combustion, gasification and water gas shift reactions have been retained to constitute the main reactions in the transformation of the cellulose.

The three main gasification equations are presented below:

- The gasification reaction: $C_6H_{12}O_6 + H_2O \rightarrow 7H_2 + CO_2 + 5CO$ (5)
- The water gas shift (WGS): $CO + H_2O \leftrightarrow CO_2 + H_2$ (6)
- The combustion reaction: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ (7)

In order to express symbolically the transformation, several assumptions are to be made:

- First, the moles of material that have reacted via a given reaction per unit time will be denoted by the extent of the reactionε. It follows for instance that the gasification and the WGS reaction may not occur to completion but the extent of the reaction/mass balance will be defined as ε_1 and ε_2 respectively. This means that ε_1 moles of $C_6H_{12}O_6$ and ε_2 moles CO react to produce respectively ε_1 moles of CO_2 from the WGS and ε_2 moles of H_2 per unit time.

- Second, the combustion reaction is known to be exothermic while the gasification reaction is endothermic. The WGS, on the other hand, is a reversible reaction. It can either be exothermic or endothermic depending on the reaction direction.

- For simplicity in the analysis, we assume that the combustion reaction goes to completion to provide energy for the other two reactions. This assumption effectively reduced the dimension of the space that we will work in to a two-dimensional space far easier to study.

The three main reactions will then deduce to the following:

- $C_6H_{12}O_6 + H_2O \rightarrow 7H_2 + CO_2 + 5CO$.....$\varepsilon_1$ (8)
- $CO + H_2O \leftrightarrow CO_2 + H_2$.....$\varepsilon_2$ (9)
- $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ .....ε_3 (10)

From the equations above each reaction is expressed in terms of an extent (ε_1 - ε_3). These extents are the conversion at which each reaction occurs to form the required products. In this manner, the graphical approach will enable the visualization of the set of all possible outputs from a gasifier.

Next, it is required that the molar flowrate of each component in the reactor or gasifier be always positive. If a continuous gasifier is considered, the feed of each component in the gasifier will be expressed as $N_{feed}°$ moles per time of feed and the product as $N_{product}$ moles per time of product. The combustion reaction, on the other hand, has been assumed to go to completion. As a result of this, the amount of oxygen fed will be converted to some of the carbon dioxide produced. The latter will be considered as the carbon dioxide feed into the gasifier which equates as follows

$$N_{O_2}{}^0 = N_{CO_2}{}^0 \quad (11)$$

In order to understand how the overall reaction is linked with the individual mass balance equation described above and hence the extents, consider the following schematic diagram:

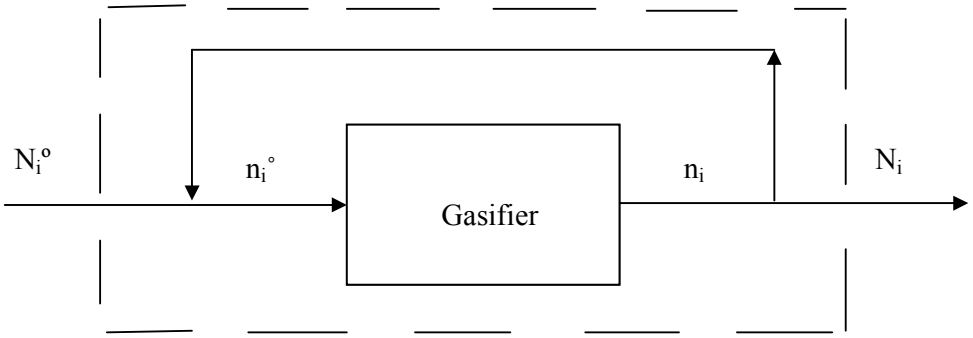


Figure 3.2 Representation of the moles fed and produced in a process

From the diagram N_i^o and N_i represents the number of moles of a specific component coming in and out of the overall process respectively and n_i° and n_i are the moles fed in and out of the reactor (gasifier) respectively. Hence the molar flowrate can be expressed as follows:

$$N_i = n_i^o - n_i \tag{12}$$

If we let N_{CO} be the molar flowrate of CO into the overall process, then n_{CO}° will be the molar flowrate of CO fed in the reactor and n_{CO} will be the molar flowrate out of the reactor. And consequently, the mole balance on CO can be written as

$$N_{CO} = -5\varepsilon_1 + \varepsilon_2 \geq 0 \tag{13}$$

Considering the combustion reaction, an oxygen balance can be constructed and expressed as $N_{O2} = 6\varepsilon_3 \geq 0$

Applying the same approach to the rest of the components taking part in the three reactions (Equations 8 – 10), one can obtain the following:

$$N_{H_2} = -7\varepsilon_1 - \varepsilon_2 \geq 0 \quad (14)$$

$$N_{H_2O} = \varepsilon_1 + \varepsilon_2 - N_{O_2}{}^{o} \geq 0 \quad (15)$$

$$N_{C_6H_{12}O_6} = \varepsilon_1 + \frac{1}{6} N_{O_2}{}^{o} \geq 0 \quad (16)$$

$$N_{CO_2} = -\varepsilon_1 - \varepsilon_2 - N_{O_2}{}^{o} \geq 0 \quad (17)$$

From the inequalities (13) to (17), the key problem reduces to representing the mass balance on a ε_1 versus ε_2 plot and determine the gasification region.

Once the gasification region has been graphically plotted, the objective will be to see how it changes with feed and other factors. That is what the next section focuses on.

3.2.2 Gasification region

As a starting point, let us view inequalities 13 to 17 and refer to them as Equations 13 to17. These inequalities will be expressed as mass balance boundaries where the respective components are zero i.e. for carbon monoxide it is: $N_{co} = 0$. It can be seen that each equation represents a straight line graph in the ε_1-ε_2 space (Figure 3.3 below) for a feed of $N_{O2}{}^{0} = 0.5$ mole, $N_{H2O}{}^{0} = 0.5$ mole and $N_{C6H12O6}{}^{0} =$ 1mole in the reactor which is chosen randomly for simplicity purposes, in order to make a certain amount of syngas but real processes may use considerably more feedstock to make the syngas. One aspect shared by all the line charts is that their respective slopes are constant and do not depend on the feed composition.

Each component line as it is defined by the inequality represents both the positive and the negative moles of that component depending on the direction of the inequality. The negative moles are not feasible therefore they will not be considered. As it can be seen from the Figure 3.3 below the mass balance region is formed by positive moles of all the components involved in the process. Similarly for the case where the feeds are $N_{O2}^{0} = 0$ mole, $N_{H2O}^{0} = 0.5$ mole and $N_{C6H12O6}^{0} = 1$mole and $N_{O2}^{0} = 0.1$ mole, $N_{H2O}^{0} = 0.5$ mole and $N_{C6H12O6}^{0} = 1$mole, the graph will still maintain the same form with a change with the position of a cellulose line along the ε_1 axis.

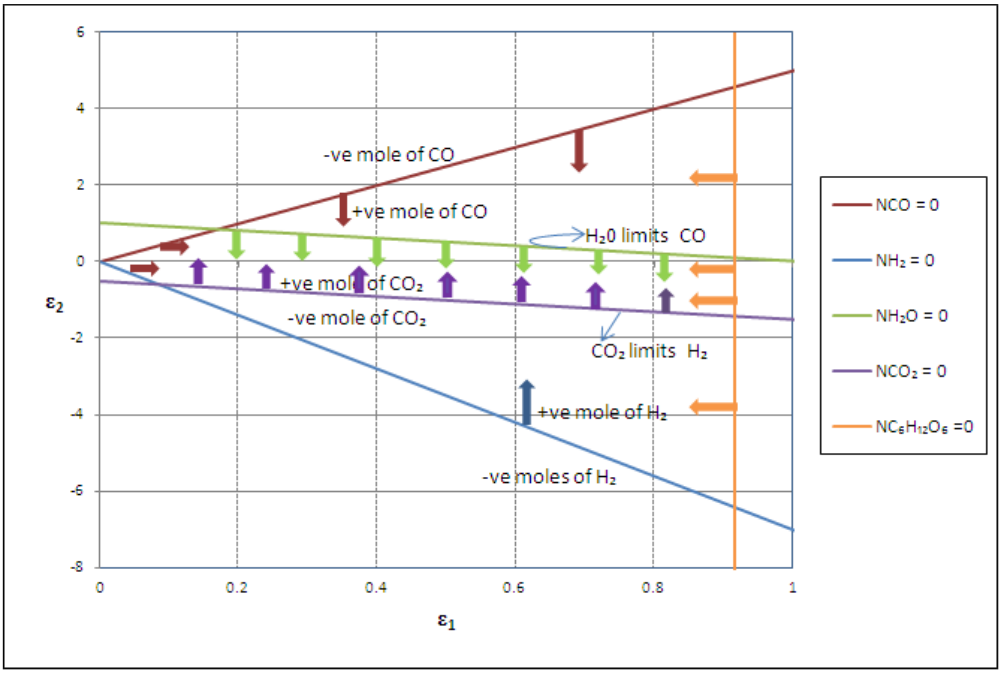


Figure 3.3 The mass balance region.

To move forward in the construction of the gasification region, we go back to the inequalities 13 to 17. When considering for instance Equation (13) i.e. the CO

line, one would see that the straight line divides the ε_1-ε_2 space into two regions: one above the CO line and the other below it. The point above the inequality line represents negative moles of CO and not feasible. The region of positive number of moles for each species (as stated by inequality 13) is considered and used to construct the mass balance region. From this, region below the CO graph will be retained while region above will be discarded. If we operate the gasifier on or very close to this line we run out of CO and the further away we are from the $N_{CO} = 0$ line, the more CO we have. Similarly with the remaining inequalities, Figure 3.3 will be represented in detail in Figure 3.4 with the gasification region clearly represented as follows.

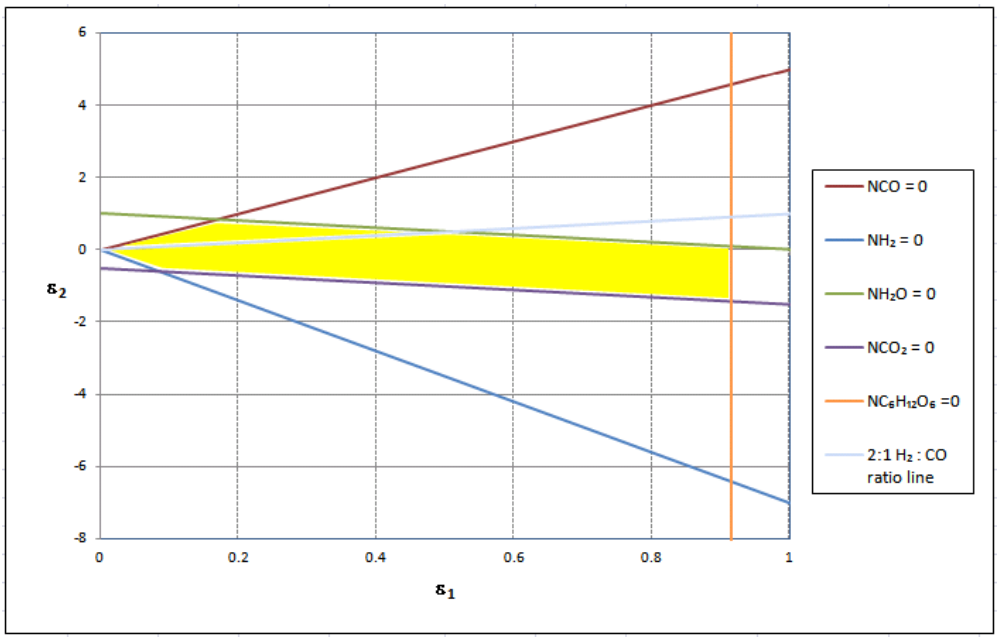


Figure 3.4 The gasification region

Taking everything into consideration, Figure 3.4 shows the following:

(i) Every component is represented by a solid line and the number of moles of that particular component is zero on that line.

(ii) The points that lie below the inequality line of water for an example correspond to positive moles of the component. Physically, this implies that if we operate the gasifier on or very close to this line, the particular component may not be present in the resultant gas or that stage in the reactor.

(iii) The further away is the operation from the component line, the more is the component present in the reactor.

Figure 3.4 also indicates that the enclosed gasification region can be attained by mass balance equations and inequalities. We can deduce that from a mass balance point of view, gasification is only possible within the enclosed region. Any composition that falls outside of this region is not possible, as this would mean negative composition for one or more of the components, which is physically not possible.

The operating region also explains that, for example, if an operator wants to produce syngas that is rich in CO and H_2, they should operate close to the point where the $N_{CO_2} = 0$ line and $N_{C_6H_{12}O_6} = 0$ line meet. Nonetheless, this may be limited by the energy balance, work balance or reaction equilibrium, as we will see later in the chapter.

3.2.3 Effect of the feed composition on the mass balance region

In this section, we investigate the effect of feed composition on the operating region. To this end, the only things that can change in the feed stream are the amounts of H_2O and O_2 fed into the gasifier because they will be involved in a reaction to form the products, $C_6H_{12}O_6$ will not be changed because it has been assumed that 1 mole is fed in the process. In order to investigate the effect of feed composition on the mass balance region we will consider the case where we are feeding: $N_{O2}^0 = 0.5$ mole, $N_{H2O}^0 = 0.5$ mole and $N_{C6H12O6}^0 = 1$mole.

This is achieved by setting a CO: H_2 ratio of 1: 2. Ratios of 1:2 are often favoured by coal-to-liquids processes and methanol processes; and ratios of 1:3 are favoured by ammonia processes. Higher or lower ratios may be desired depending on the intended application. The production of fuels, for instance usually uses a ratio of no more than 2:1 Hydrogen: Carbon Monoxide (Raju et al., 2009).

Consider a case where the amount of water is increased from 0.5 to 1 mole and to 2 moles while the amount of cellulose and oxygen are both kept constant at 1 mole and 0.5 moles respectively. This is shown in Figure 3.5 below:

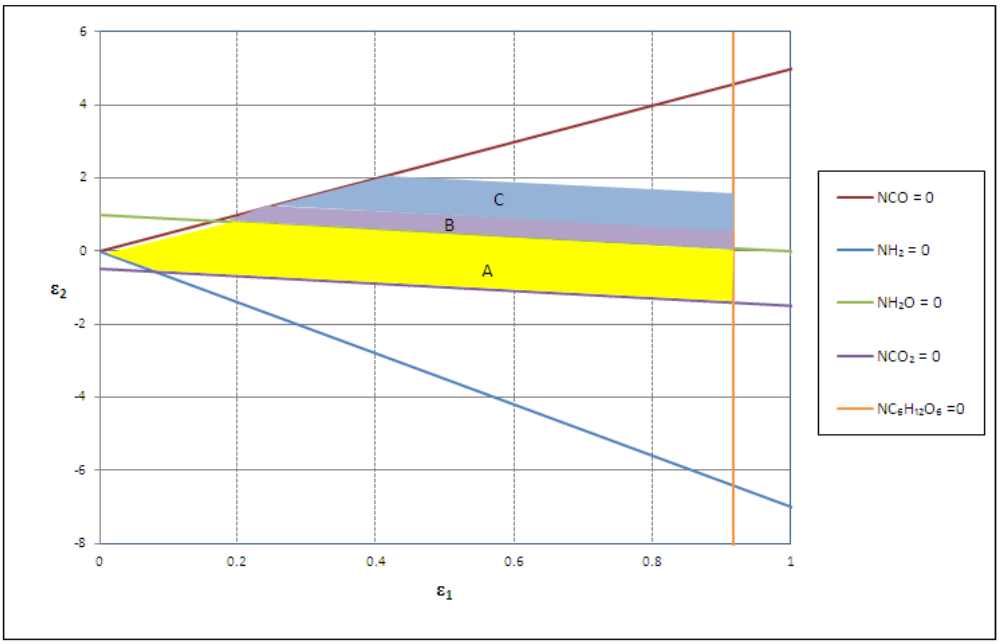


Figure 3.5 The effect of increasing water in the feed stream.

From the graph area A represents 0.5 mole of water and area B and C are 1 mole and 2 moles of water respectively.

The water line increases upwards along the *y*-axis, as shown in Figure 3.5 above. It can be noted that only the water line changes and other components stays constant. The minimum amount of water that can be fed in the gasifier is 0 mole and there is no maximum amount that can be fed. This is because if you feed more than what the process requires i.e. feeding such that the water line will be out of the gasification region, this means is that water will no longer be a limit of operation as it was when it was within the gasification region but water will be in excess . From this scenario, one clearly sees that increasing the amount of water (steam) increases the size of the mass balance region. To put it another way, if one wants to increase either ε_1 (the amount of gasification) or ε_2 (the amount of

WGS), all that needs to be done is to increase the amount of water fed into the gasifier. However, this has its own limitations which are as follows:

- The limit will depend on target i.e. if you feed more water the process in the gasifier is likely to lose the H_2: CO ratio of 2:1
- Also it depends on the product specification i.e. if the aim is to produce syngas, adding more water will be desirable as more syngas will be produced.

Again the amount of oxygen is increased from 0.5 to 1 mole while the water is kept constant at 0.5 mole and cellulose at 1 mole. The results are shown below:

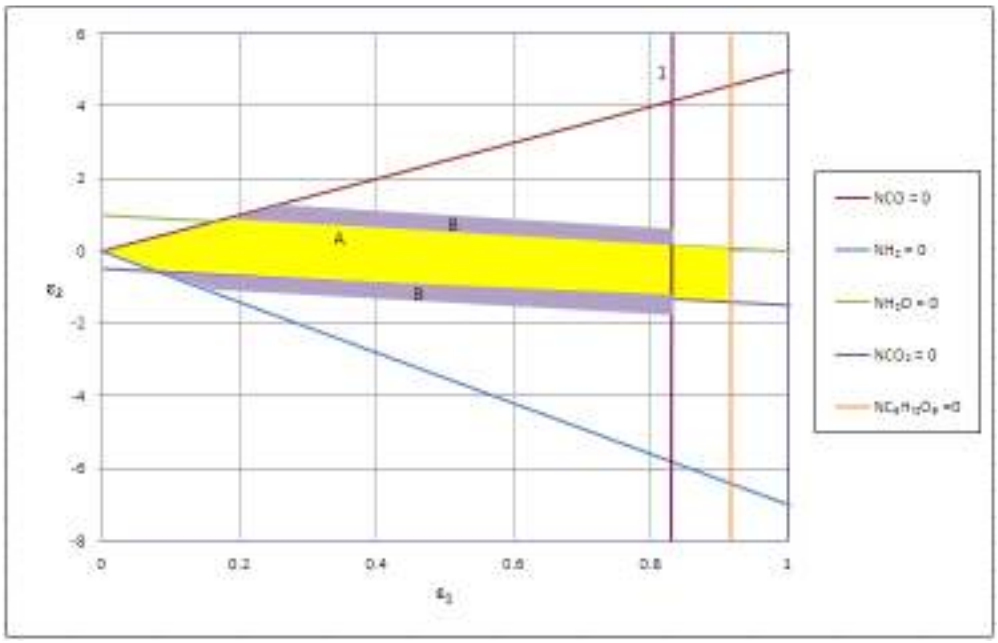


Figure 3.6 The effect of increasing oxygen in the feed stream.

Figure 3.6 shows the effect of increasing oxygen from 0.5 mole to 1 mole. From the graph it can be seen that as we increase oxygen the water line moves upwards

along the positive y-axis and the CO_2 line moves downwards along the negative *y*-axis as represented by area B. The cellulose line will therefore decrease along the ε_1 axis which is shown by line 1 on the graph, which implies that as we increase oxygen it will favour combustion reaction and more cellulose will be consumed. Therefore ε_3 will increase and hence ε_1, the gasification reaction will decrease as shown on the graph. This will as a result cause the area of operation to increase.

To sum up, in order to maximise the gasification region, the amount of water and oxygen should be increased, despite that there is a certain amount of oxygen when increased it may impose some limitation to this. Oxygen should not be increased above 6 moles because at this point all the cellulose is reacting in the combustion reaction hence gasification and WGS will not occur.

Similarly when the feeds of $N_{O2}^0 = 0$ mole, $N_{H2O}^0 = 0.5$ mole and $N_{C6H12O6}^0 =$ 1mole and $N_{O2}^0 = 0.1$ mole, $N_{H2O}^0 = 0.5$ mole and $N_{C6H12O6}^0 = 1$mole are used to evaluate the effect of feed on mass balance region, similarly results are obtained.

We will discuss how these set a constraint on the mass balance region and determine the final gasification region. But first, let us discuss in the next section the use of the energy balance in the determination of the set of achievable extents of reaction.

3.3 Energy Balance

3.3.1 Background

We have figured out in the previous section what the mass balance constraints are. We now attempt to establish whether there are any other constraints on the extent of gasification as a result of the energy balance. We apply the energy balance in a very similar manner to the mass balance described above. The difference is that the energy balance requires precise mathematical modelling of gasification and its dynamics. The bright side to this is that an energy balance over the gasifier provides an estimate of the amount of the energy and work potential that is being used for gasification.

The energy balance is performed around the overall process and it requires an additional factor than the mass balance. The factor includes the temperature of the gasifier and the enthalpy of the gasifier can therefore be modelled.

To proceed with the energy balance calculations, we consider both the adiabatic, where the system is assumed to have no heat loses and the heat transfer is perfect and non-adiabatic case where there system is assumed to have heat loses. The first simplifying assumption is that all species entering and leaving the process are pure components. By this, we mean, there is no heat of mixing in the system. In the adiabatic case $\Delta H = 0$ and the non-adiabatic case heat Q is either removed or added so that $\Delta H = Q$.

Firstly, let us look at the adiabatic case ($\Delta H = 0$) and assume that the temperature in the process is equal with the temperature out, that is $T_{in} = T_{out}$. The ambient

temperature at 298 K will be considered to be the temperature in and out of the process. ΔH = 0 assumes no heat loses.

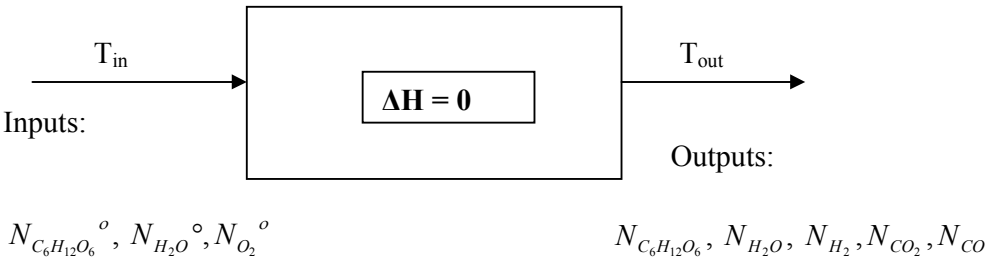


Figure 3.7 Adiabatic process.

In such a situation, the energy balance across the process gives:

$$\Delta H + \Delta U + g\Delta z + \Delta u^2/2 = q + w_s \quad (18)$$

Where ΔH is the change in enthalpy

ΔU is the change in internal energy

gΔz is the change in potential energy

$\Delta u^2/2$ is the change in kinetic energy

q is the heat energy in the system

w_s is the shaft work

The other terms are equals to zero, therefore the energy balance becomes:

$$\Delta H = 0 \quad (19)$$

$$\Delta H = H_{products} - H_{reactants} \quad (20)$$

Then equation 20 will be expressed fully in equation 21, with the unreacted water and biomass in the product stream as follows:

$$N_{C_6H_{12}O_6}{}^{o}.H_{f,C_6H_{12}O_6}{}^{\circ}+N_{H_2O}{}^{\circ}.H_{f,H_2O}+N_{O_2}{}^{o}.H_{f,O_2}{}^{o}=N_{C_6H_{12}O_6}.H_{f,C_6H_{12}O_6}{}^{\circ}+N_{H_2O}.H_{f,H_2O}{}^{\circ}$$
$$+N_{H_2}.H_{f,H_2}{}^{\circ}+N_{CO_2}.H_{f,CO_2}{}^{\circ}+N_{CO}.H_{f,CO}{}^{\circ} \quad (21)$$

where $H_{f,i}$ is the standard enthalpy of formation of species i.

N_i is the number of moles of species i in the product stream.

$N_i{}^{\circ}$ is the number of mole species i in the feed stream.

Equation 21 will deduce to 22, where the moles will be substituted by equation 13 to 17 as follows:

$$(-\varepsilon_1-\frac{1}{6}N_{O_2}{}^{\circ}).H_{f,C_6H_{12}O_6}{}^{\circ}+(-\varepsilon_1-\varepsilon_2+N_{O_2}{}^{\circ}).H_{f,H_2O}$$
$$+(7\varepsilon_1+\varepsilon_2)H_{f,H_2}{}^{\circ}+(N_{O_2}{}^{\circ}+\varepsilon_1+\varepsilon_2)H_{f,CO_2}{}^{\circ}+(5\varepsilon_1-\varepsilon_2)H_{f,CO}{}^{\circ}=0 \quad (22)$$

This then reduces to the final adiabatic energy balance expressed as:

$$\varepsilon_2=-\varepsilon_1\frac{\Delta H_{rxn,1}}{\Delta H_{rxn,2}}-\frac{1}{6}\frac{N_{CO_2}\times\Delta H_{comb}}{\Delta H_{rxn,2}} \quad (23)$$

where $\Delta H_{rxn,1}=-H_{f,C_6H_{12}O_6}{}^{o}-H_{f,H_2O}{}^{o}+H_{f,CO_2}{}^{o}+5H_{f,CO}{}^{o}$

$\Delta H_{rxn,2}=-H_{f,H_2O}{}^{o}+H_{f,CO_2}{}^{o}-H_{f,CO}{}^{o}$

$\Delta H_{comb}=6H_{f,H_2O}{}^{o}+6H_{f,CO_2}{}^{o}-H_{f,C_6H_{12}O_6}{}^{o}$ ….the heat of combustion

Secondly, let us consider a non-adiabatic case where ΔH = Q. Using the same procedure as with the adiabatic case but this time allowing for heat losses into the surroundings, we get the following:

$$\Delta H+\Delta U+g\Delta z+\Delta u^2/2=q+w_s \quad (24)$$

The other terms are equals to zero, therefore the energy balance becomes:

$$\Delta H = q \tag{25}$$

Where q: can be any value, if negative it is exothermic i.e. releasing heat off. If positive it represent an endothermic reaction where heat input is required before the reaction can proceed and if it is zero it is an adiabatic reaction.

ΔH: is the change in enthalpy between the reactant and the products expressed as

$$\Delta H = H_{products} - H_{reactants} \tag{26}$$

Equation 26 then yields to equation 27 below where $N_{H2}°$, $N_{CO2}°$ and $N_{CO}°$ are equals to zero since they are products:

$$\begin{aligned}(N_{C_6H_{12}O_6} - N_{C_6H_{12}O_6}{}^{o}).H_{f,C_6H_{12}O_6}° + (N_{f,H_2O} - N_{f,H_2O}°).H_{f,H_2O} \\ + N_{H_2}H_{f,H_2}° + N_{CO_2}H_{f,CO_2}° + N_{CO}H_{f,CO}° = q\end{aligned} \tag{27}$$

where $H_{f,i}$ is the standard enthalpy of formation of species i

N_i is the number of moles of species i in the product stream

$N_i°$ is the number of mole of species i in the feed stream

Using equation 13 to 17 to substitute the moles in equation 27, this yields the following:

$$\begin{aligned}&(-\varepsilon_1 - \frac{1}{6}N_{O_2}°).H_{f,C_6H_{12}O_6}° + (-\varepsilon_1 - \varepsilon_2 + N_{O_2}°).H_{f,H_2O} \\ &+ (7\varepsilon_1 + \varepsilon_2)H_{f,H_2}° + (N_{O_2}° + \varepsilon_1 + \varepsilon_2)H_{f,CO_2}° + (5\varepsilon_1 - \varepsilon_2)H_{f,CO}° = q\end{aligned} \tag{28}$$

This then reduces to the final energy balance expressed as:

$$\varepsilon_2 = q - \varepsilon_1 \frac{\Delta H_{rxn,1}}{\Delta H_{rxn,2}} - \frac{1}{6}\frac{N_{CO_2} \times \Delta H_{comb}}{\Delta H_{rxn,2}} \tag{29}$$

where $\Delta H_{rxn,1} = -H_{f,C_6H_{12}O_6}{}^{o} - H_{f,H_2O}{}^{o} + H_{f,CO_2}{}^{o} + 5H_{f,CO}{}^{o}$

$$\Delta H_{rxn,2} = -H_{f,H_2O}{}^{o} + H_{f,CO_2}{}^{o} - H_{f,CO}{}^{o}$$

$$\Delta H_{comb} = 6H_{f,H_2O}{}^{o} + 6H_{f,CO_2}{}^{o} - H_{f,C_6H_{12}O_6}{}^{o}$$ ….the heat of combustion

The results which are obtained from the energy balance can be represented and analysed graphically as shown in the next section.

3.3.2 Representation of the non-adiabatic system

The energy balance line has been plotted at the following amount of feeds: H_2O and O_2 are at 0.5 moles while $C_6H_{12}O_6$ is at 1 mole. We can now plot equation 29 as shown in Figure 3.8 to understand how the energy balance constraints affect the mass balance region. The heat (q) in the process can be either supplied or rejected depending on the heat requirements of the process. It can also be zero where it is considered as adiabatic.

In this section, an idealised case is assumed in which there is no loss of heat i.e. no heat transfer. In addition, the inlet and outlet temperature are assumed to be the same. Figure 3.8 below represents the case where q = 0 i.e. adiabatic condition.

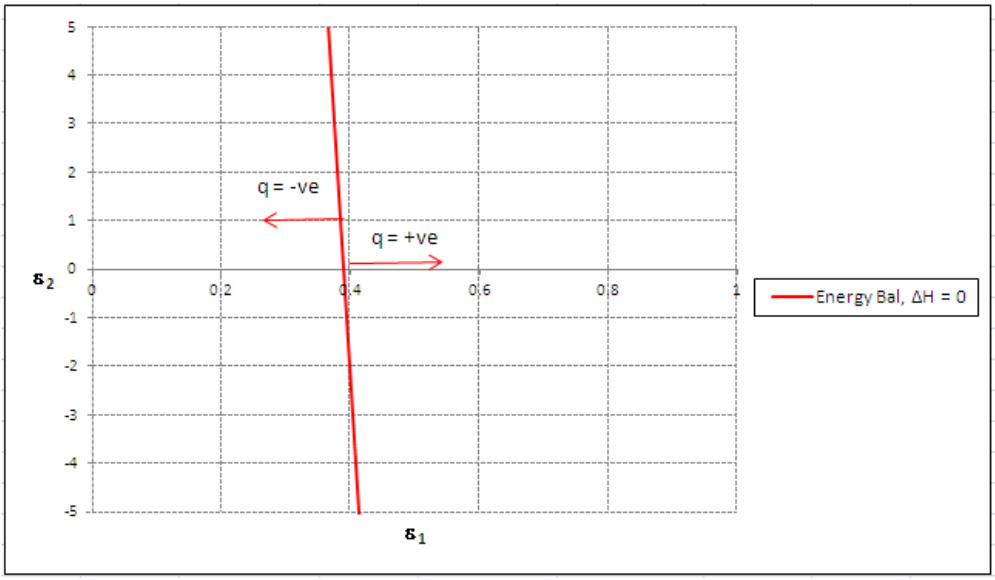


Figure 3.8 Plot of energy balance when ΔH = 0.

Note that the energy balance line is a straight line with a fixed slope in the ε_1-ε_2 space. From the graph above, it can be seen that we have a negative slope. For this case the heat (q) is 0 kJ/mol, and will aid in determining where the reaction requires or rejects heat. If the reaction is on the right of the energy balance line, heat is required i.e. the reaction is endothermic and on the other hand if the reaction is on the left side of the energy balance line, heat is rejected from the process i.e. the reaction is exothermic.

3.3.3 Effect of the feed composition on the energy balance

The energy balance line is not affected by the change of the amount of feed of H_2O but instead it is affected by the change of the amount of feed of O_2. We will consider the feed to the gasifier to be of $N_{O2}^0 = 0.5$ mole, $N_{H2O}^0 = 0.5$ mole and $N_{C6H12O6}^0 = 1$mole but similar results are also obtained when the feeds are: $N_{O2}^0 =$

0 mole, $N_{H2O}^0 = 0.5$ mole and $N_{C6H12O6}^0 = 1$mole or $N_{O2}^0 = 0.1$ mole, $N_{H2O}^0 = 0.5$ mole and $N_{C6H12O6}^0 = 1$mole.

When the amount of oxygen is increased from 0.5 to 1 mole, the energy balance line shifts to the right. The same applies when it's increased to 2 moles it shifts further to the right meaning that the extent of combustion (ε_3) increases. This results in the production of more CO_2 and H_2O and more energy will also be produced as a result there will be a decrease in the process energy demands. The limitation in adding more oxygen is that all the cellulose will be consumed and therefore gasification reaction will not occur since it uses cellulose as a feedstock and also the WGS reaction will not also occur because it depends on the gasification reaction. The increase in oxygen is shown in the Figure 3.9 below:

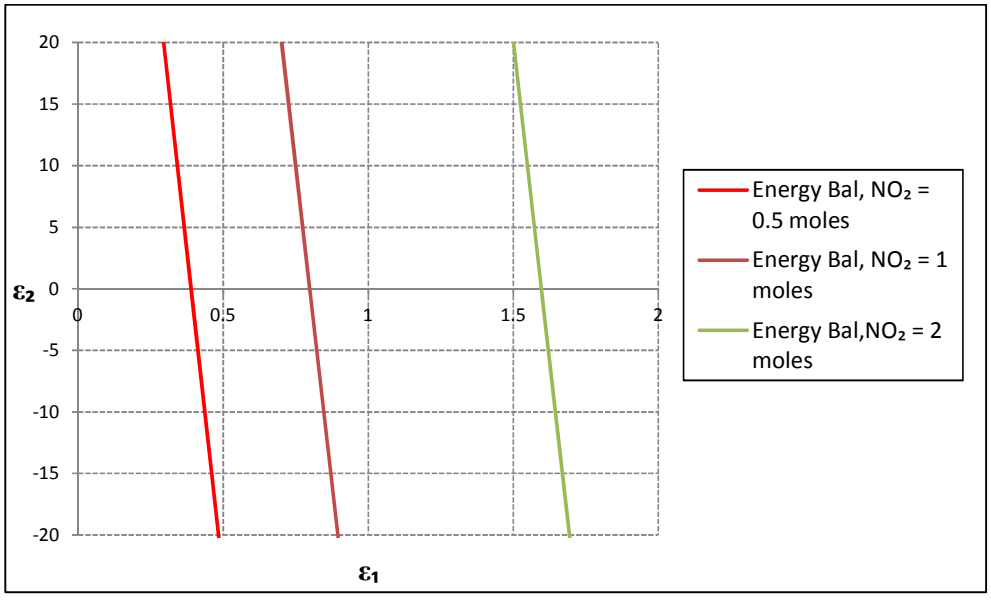


Figure 3.9 The feed effect on the Energy Balance.

As more oxygen is fed, the process will become less endothermic hence it shifts to the right where q is positive as shown by Figure 3.9. More oxygen feed reduces energy demands of the process which make it appears to become less endothermic.

3.4 Gibbs Free Balance

The Gibbs free energy provides one with information about the work requirements of the process. By performing a Gibbs free energy balance across the overall process, one can determine the work flows in the process. The components will enter and leave at the temperature of 298 K and the pressure of 1atm as it was with the energy balance. The same procedure with energy balance will be applied to derive the Gibbs free energy balance equations as shown below:

$$(N_{C_6H_{12}O_6} - N_{C_6H_{12}O_6}{}^{o}).G_{f,C_6H_{12}O_6}\circ + (N_{f,H_2O} - N_{f,H_2O}\circ).G_{f,H_2O} + N_{H_2}.G_{f,H_2}\circ + N_{CO_2}.G_{f,CO_2}\circ + N_{CO}.G_{f,CO}\circ = 0 \quad (30)$$

where $G_{f,i}$ is the Gibbs free energy of formation of species i

N_i is the number of moles of species i in the product stream

$N_i\circ$ is the number of mole of species i in the feed stream

When simplifying the Gibb Free energy balance, Equation (31) is obtained:

$$\varepsilon_2 = -\varepsilon_1 \frac{\Delta G_{rxn,1}}{\Delta G_{rxn,2}} - \frac{1}{6}\frac{N_{CO_2} \times \Delta G_{comb}}{\Delta G_{rxn,2}} \quad (31)$$

Where $\Delta G_{rxn,1} = -G_{f,C_6H_{12}O_6}{}^{o} - G_{f,H_2O}{}^{o} + G_{f,CO_2}{}^{o} + 5G_{f,CO}{}^{o}$

$$\Delta G_{rxn,2} = -G_{f,H_2O}{}^{o} + G_{f,CO_2}{}^{o} - G_{f,CO}{}^{o}$$

$$\Delta G_{comb} = 6G_{f,H_2O}{}^{o} + 6G_{f,CO_2}{}^{o} - G_{f,C_6H_{12}O_6}{}^{o}$$

With these equations, the Gibbs energy graph can be represented in the following graph.

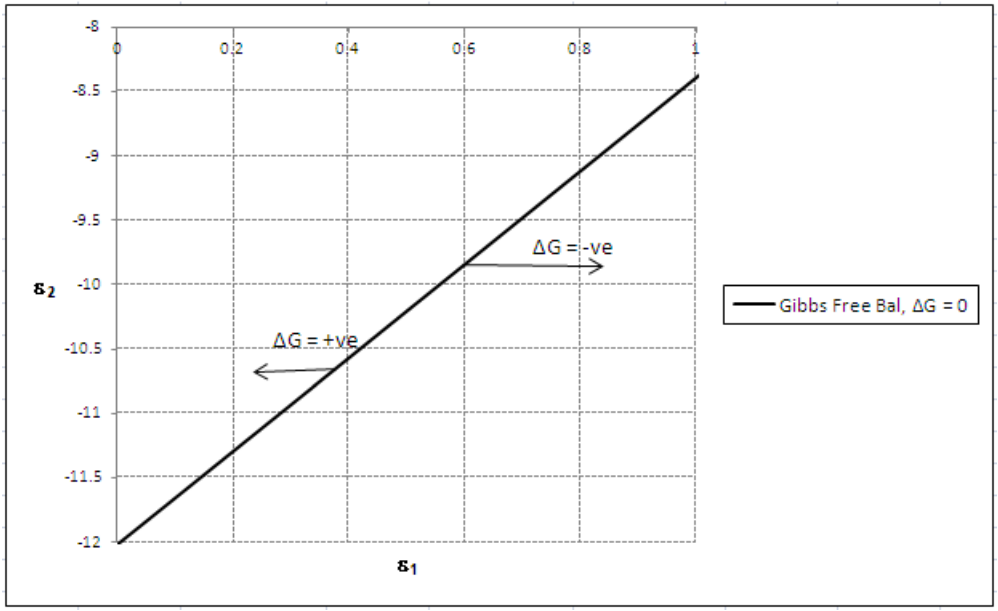


Figure 3.10 Plot of Gibbs free energy Balance, ΔG = 0.

3.4.1 The significance of the Gibbs free energy Balance on the ε_1-ε_2 space

As we have seen in Section 3.2, the mass balance tells us of the possible region of gasification. However, to get a more complete picture, we need to consider the energy and work balance.

The result obtained in Figure 3.10 shows that a positive slope graph is obtained which intercepts at the negative *y*-axis. This signifies that ε_2 is changing rapidly i.e. slight change in ε_1 in order to keep $\Delta G = 0$ will greatly varying ε_2. It is important to operate at a minimum ΔG because the more work is required, the

more heat, pressure and chemical potential you must supply, which increases energy usage and decreases efficiency.

The next case is to consider the effect of oxygen feed on the Gibbs free energy graph since the other feed components does not have an effect. When the amount of oxygen is increased from 0.5 moles to 1mole and finally 2 moles, the graph shifts down and changes the intercept to a more negative value as shown in Figure 3.11 below.

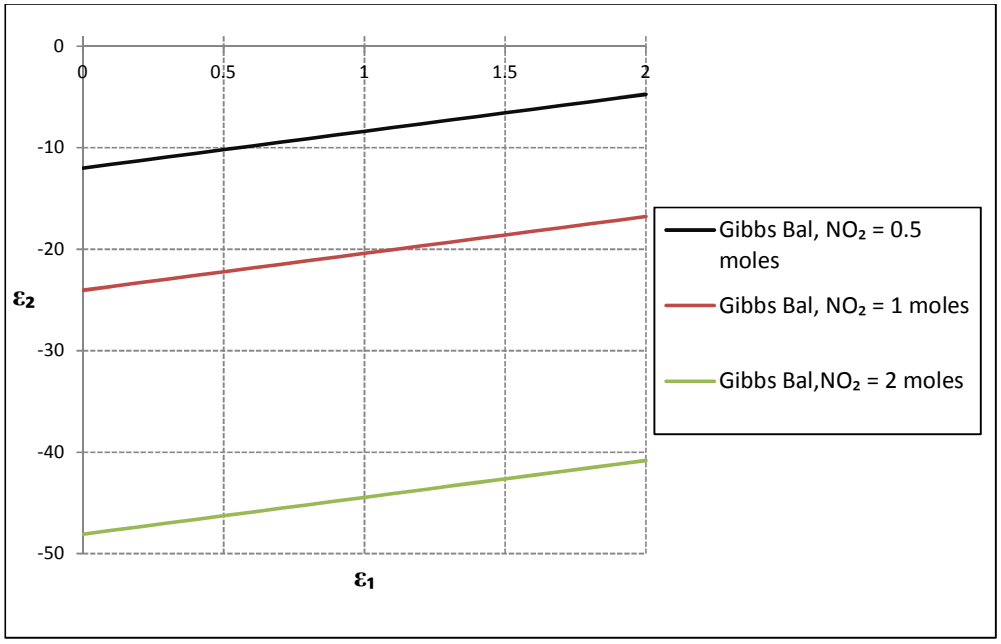


Figure 3.11 Gibbs free energy balance at different NO_2 feed.

Operating on the left (upper) side of the Gibbs free energy constraints would either be irreversible or work could be required to be added in terms of other sources to the gasifier. On the contrary, operating on the right (lower) side of the line would require work to be rejected in order to be feasible. This work could be

added in many ways by heat or by combusting more biomass (cellulose) for example but this will depend on the temperature of the heat.

3.4.2 Combining Mass, Energy and Gibbs free energy Balance

From the discussion above it was shown that the components involved in gasification process and hence the mass balance region will vary significantly with the change in oxygen. Therefore we will be varying the amount of oxygen only at different case studies as it will be shown in Figures 3.12, 3.13 and 3.14 below.

Figures 3.12, 3.13 and 3.14 combines the mass, energy, and Gibbs free energy balance at the different feeds at standard conditions i.e. 25ºC and 1 atm and is therefore a comprehensive tool in providing visual insights into the gasification process. Now let us look at the gasification process when feeding $N_{O2}^{0} = 0.5$ mole, $N_{H2O}^{0} = 0.5$ mole and $N_{C6H12O6}^{0} = 1$mole as shown in Figure 3.12 below:

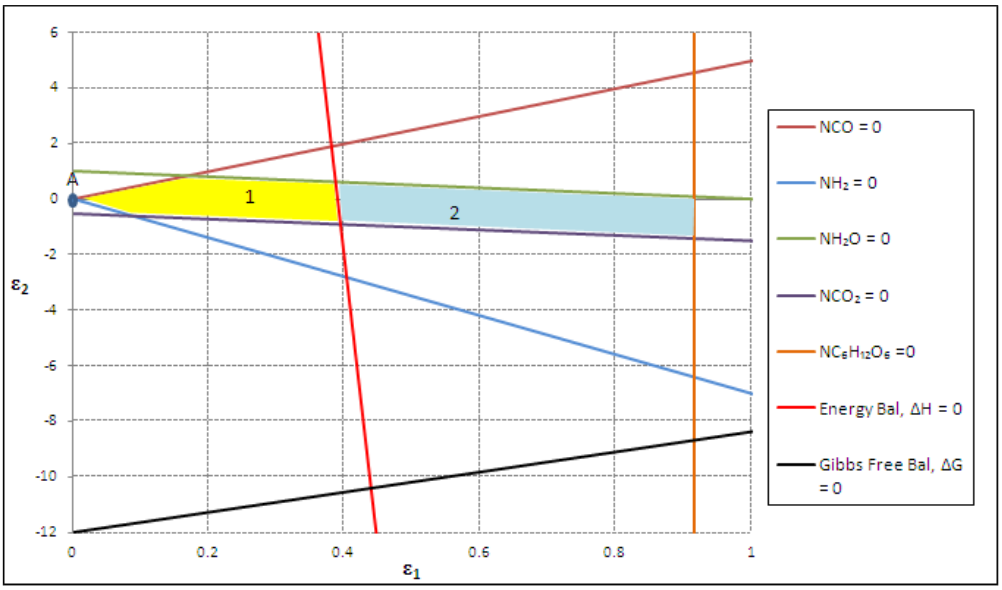


Figure 3.12 Combining Mass, Energy and Gibbs Free Energy balance at the feed of N_{O2}^0 = 0.5 mole, N_{H2O}^0 = 0.5 mole and $N_{C6H12O6}^0$ = 1mole.

The left side of ΔH=0 line is where heat is rejected and the right side of ΔH=0 line, heat is required to be added to the process. On the contrary the left (lower) part of ΔG=0 line is where work is rejected and the right (upper) part of ΔG=0 line, work is required to be added.

From Figure 3.12, the following can be estimated:

- Point A represents the feed point where CO and H_2 = 0 lines meets meaning at this point there is no reaction.
- The H_2O and the CO_2 = 0 lines are parallel because they are proportional i.e. If less CO_2 is to be produced, water should be recycled and if water is taken out of the stream more CO_2 will be produced.
- The gasification region is represented by area 1and 2.

- It can be seen that the cellulose line does not lie in 1 mole on the ε_1 axis, this is because the plot shows reaction 1 (gasification) and reaction 2 (WGS) meaning that the remaining cellulose will be used by the combustion reaction 3.
- Figure 3.12 shows that 0.917 mole of cellulose is consumed by the gasification reaction and from this equation: $\varepsilon_1 + \varepsilon_3 = 1$ it means the remaining 0.083 mole of cellulose is used by the combustion reaction.

- Operating in area 1 is not the best option because even though heat is rejected which looks attractive, work also needs to be added to the process for gasification to occur. In this case it is difficult to add work when heat is rejected because most time work is added by heat.
- Gasification is achieved in the area 2 where it satisfies the mass, energy and the work balances. In this region heat and work are required to be added, therefore when heat is added work can also be added to meet the energy requirement of the process but at different points within area 2 heat and work required to be added differs in quantity.
- Operating in region 2 on the $CO_2 = 0$ line implies that there is no CO_2 produced in the reactor. At this line heat is required and also the extent of reaction 2 is negative meaning that the WGS is going in the opposite direction where more CO is being formed. This is achieved at these feed conditions 0.5 moles of oxygen, 0.5 moles of water and 1 mole of biomass.

In this case when operating the gasifier work will be required to be added in order to achieve any point within the gasification region. This work can be added by external heat at appropriate temperatures.

Next us consider a case where we are feeding $N_{O2}^{0} = 0$ mole, $N_{H2O}^{0} = 0.5$ mole and $N_{C6H12O6}^{0} = 1$mole. The graph for this case is represented by Figure 3.13 below:

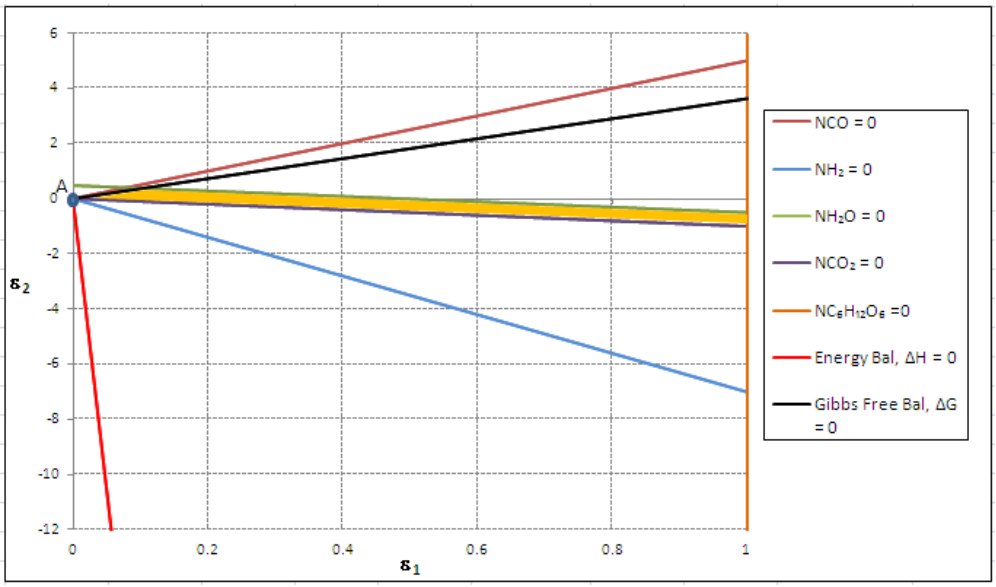


Figure 3.13 Combining Mass, Energy and Gibbs free Energy balance at the feed of $N_{O2}^{0} = 0$ mole, $N_{H2O}^{0} = 0.5$ mole and $N_{C6H12O6}^{0} = 1$mole.

Note that point A on Figure 3.13 is the feed point. If we are not feeding oxygen to the gasification process it implies that combustion reaction is not occurring hence the reactions which will be involved in the process are gasification and WGS reaction.

From the graph the following results are obtained:

- Cellulose line lies exactly at 1mole in the ε_1 axis, implying that all the cellulose is consumed in the gasification reaction at the given feed, this is true since ε_3 (combustion reaction) is zero.

- From the point above this means that we can operate gasification process without feeding oxygen but this has disadvantage because combustion reaction provide most energy requirement of the process.

- The energy balance line shifts to the left side as compared to Figure 3.12 above and intercept the ε_1 axis at the origin. At this feed gasification process will require energy to be added before it can operate i.e. the process will always be endothermic.

- Gibbs free energy line will move further up to the region as compared to when we are feeding 0.5 moles of oxygen in Figure 3.12. This is because combustion is not occurring and therefore the Gibbs free energy line is influenced by gasification and WGS reaction as shown in reaction 31 above.

- Given that the left (lower) part of $\Delta G = 0$ line is where work is rejected it means that at the given feed work will be rejected in the process.

- With the given feed gasification process is operated where heat is required and work is rejected, therefore gasification process will be difficult to operate and will not be efficient. This means that we will not be able to recover work released by the process therefore the process will require to be run at temperature below ambient

- In this case study the process will always operate irreversibly.

Again we will investigate a case study where we are feeding 0.1moles of oxygen, 0.5 moles of water and 1 mole of cellulose. This is represented by Figure 3.14 as follows:

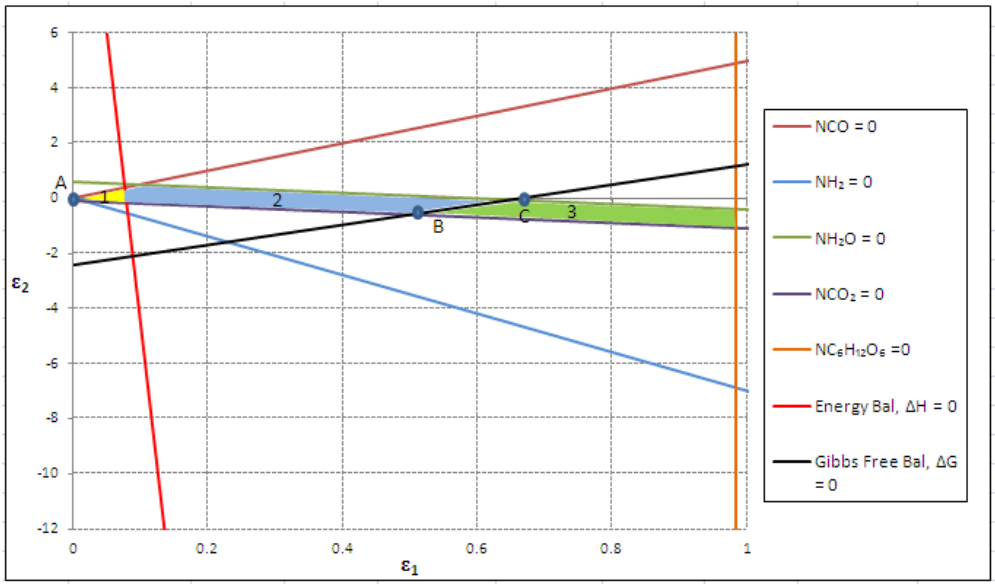


Figure 3.14 Combining Mass, Energy and Gibbs free Energy balance at the feed of $N_{O2}^0 = 0.1$ mole, $N_{H2O}^0 = 0.5$ mole and $N_{C6H12O6}^0 = 1$mole.

Figure 3.14 shows that at the given feeds we can achieve three gasification region i.e. area 1, 2 and 3. At these feeds all the three gasification reactions namely: combustion, gasification and WGS reactions are involved in the process. The following results are obtained from the graph:

- It can be seen that the cellulose line does not lie in 1 mole on the ε_1 axis like it did when we were feeding no oxygen, this is sensible since the graph shows reaction 1(gasification) and reaction 2 (WGS) meaning that the remaining cellulose will be used by the combustion reaction.

- In Figure 3.14 it shows that 0.983 mole of cellulose is consumed by the gasification reaction and from this equation: $\varepsilon_1 + \varepsilon_3 = 1$ it means the remaining 0.017 mole of cellulose is used by the combustion reaction.

- In area 1 heat is rejected while area 2 and 3 heat is required to be added in the process. Also work is required to be added in area 1 and 2 and it is rejected in area 3.

- In area 1 heat is rejected and work is required to be added. Operating in area 1 is not the best option because even though heat is rejected which looks attractive, work also needs to be added to the process for gasification to occur. In this case it is difficult to add work when heat is rejected because most time work is added by heat. Therefore process will require a system like the refrigeration for it to proceed, this will probably not happen because of kinetics of temperatures below ambient. Therefore the process will be infeasible.
- Area 2 is the best place to operate the gasification process, this is where heat and work are required to be added to the process. At this area gasification is possible because it is easier to add work in the process; this work will be added by the heat requirements of the process.

- In area 3 heat is required to be added while work needs to be rejected by the process. This is not the best area to operate gasification because it will have to run below ambient temperatures.

- In area 2 where heat and work are added gasification can either be operated reversibly or irreversibly. This is because within some part of the region the change in enthalpy is greater than the change in Gibbs free energy ($\Delta H > \Delta G$) which implies that gasification will be operated reversibly whereas some part of the gasification region the change in enthalpy is less than the change in Gibbs free energy ($\Delta H < \Delta G$) which implies that gasification can be operated irreversibly.
- The best place to operate gasification process in area 2 is point B. Along the line represented by point B to C Gibbs free energy line crosses the CO_2 and H_2O line and at this line we do not require to add any work in the process i.e. $\Delta G = 0$. The process does not release any CO_2 at point B which is the reason point B is the best point to operate gasification.

From the results analysed in all the Figures 3.12, 3.13 and 3.14 above, biomass gasification will require both heat and work to be added, therefore biomass gasification is work limited because in order to run the gasification process, work needs to be added.

Again in order to operate gasification process there is no need to feed more oxygen in the process. From the analysis above it can be deduced that only a small amount of oxygen is required to be added in the gasification process in order to

operate efficiently. The water fed in the process simply shows that there will be more water in the process and recycle streams will need to be considered.

With all the above mentioned reasons we firmly believe that point B is the best place in the ($\varepsilon_1 - \varepsilon_2$) space to operate biomass gasification because it meet the energy requirement of the process and also there is no carbon dioxide produced in this point. In this study the target was setting a CO: H_2 ratio of 1:2 which produced CO_2 (carbon dioxide) but as it can be seen from the results in Figure 3.14 that operating next to the Gibbs free energy balance line at point B implies that there is no CO_2 produced in the reactor because point B lies on $NCO_2 = 0$ line. At this point the calculated CO: H_2 ratio is 1:1 and a corresponding overall mass balance is calculated as follows:

$$zC_6H_{12}O_6 + aO_2 + bH_2O + cH_2 + dCO + eCO_2 = 0 \quad (31)$$

Where coefficient a = 0.11 moles, represents the amount of water fed in. Since at this point carbon dioxide is zero the coefficient e = 0 mole and the other components are calculated as shown in the equations below:

$$N_{CO^\circ} - N_{CO} = -5\varepsilon_1 + \varepsilon_2 = d \quad (32)$$

$$N_{H2^\circ} - N_{H2} = -7\varepsilon_1 - \varepsilon_2 = c \quad (33)$$

$$N_{H2O^\circ} - N_{H2O} = \varepsilon_1 + \varepsilon_2 - a = b \quad (34)$$

$$N_{C6H12O6^\circ} - N_{C6H12O6} = \varepsilon_1 + 1/6*a = z \quad (35)$$

From these equations the number of moles of each component is as follows:

z = 0.52 moles

b = -0.22 moles

c = -2.90 moles

d = -3.12 moles

These sums up to give an overall mass balance at point B which is as expressed below in equation (36).

$$0.52C_6H_{12}O_6 + 0.11O_2 = 0.22H_2O + 2.90H_2 + 3.12CO \quad (36)$$

3.5 The effect of temperature on reaction equilibrium

We have investigated mass, energy and Gibbs free balance where temperature was assumed constant i.e. it does not have effect. We now want to explore the effect of temperature on reaction equilibrium. Thermodynamics is used to calculate the values of equilibrium constant at any given temperature.

A variation in temperature has a varied effect on the reactions depending on their respective enthalpies of formation and hence their equilibrium constants. In this case the water gas shift and the gasification reaction will be evaluated since combustion reaction was assumed to react completely. In order to calculate the equilibrium curve for the gasification and the water gas shift (WGS) reaction, firstly thermodynamics must be used to calculate the value of the equilibrium constant at any given temperature.

The equilibrium constant at any temperature T using the equation of van't Hoff can be calculated as follows:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^0_{rxn}(T)}{RT^2} \quad (37)$$

where ΔH_{rxn}^{0} is the Enthalpy of the WGS reaction and is a function of temperature

R is the gas constant

T is temperature

K is the equilibrium constant

The van't Hoff equation in equation (37) with the limits of the integral T_o and T_f, which are at 25°C and 1000°C respectively can be simplified as follows:

$$K(T) = \exp\left[In(K^{\circ}) + \int_{T0}^{Tf} \frac{\Delta H_{rxn}(T)}{RT^2} dT \right] \tag{38}$$

Where the equilibrium constant K° can be expressed n terms of the Gibbs free energy of formation (G_{rxn}°), temperature (T) and the gas constant(R) as follows:

$$K^{\circ} = \exp\left[\frac{-\Delta G_{rxn}^{\circ}}{RT^{\circ}} \right] \tag{39}$$

After calculating the equilibrium constant, the equilibrium constant expression for the water gas shift and the gasification reaction can be expressed as follows:

$$K_{WGS} = \frac{[CO_2][H_2]}{[CO][H_2O]} \tag{40}$$

$$K_{GASF} = \frac{[CO_2][CO]^5[H_2]^7}{[H_2O]} \tag{41}$$

Each of the concentration expressed above depends on the value of extent of reaction 1and hence this value is a parameter, see in equations below. We can now plot the equilibrium curve for the water gas shift reaction (WGS) and gasification reaction in the ε_1-ε_2 space using Equations (40) and (41). These can be substituted by mole balance equations (13) to (17) to give equation (42) and (43) respectively:

$$K_{WGS} = \frac{\left[N_{O_2}\circ + \varepsilon_1 + \varepsilon_2\right]\left[7\varepsilon_1 + \varepsilon_2\right]}{\left[5\varepsilon_1 - \varepsilon_2\right]\left[N_{H_2O} - \varepsilon_1 - \varepsilon_2 + N_{O_2}\circ\right]} \tag{42}$$

$$K_{GASF} = \frac{\left[N_{O_2}\circ + \varepsilon_1 + \varepsilon_2\right]\left[5\varepsilon_1 - \varepsilon_2\right]^5\left[7\varepsilon_1 + \varepsilon_2\right]^7}{\left[N_{H_2O} - \varepsilon_1 - \varepsilon_2 + N_{O_2}\circ\right]} \tag{43}$$

These then simplify to Equations (44) and (45) below, respectively:

$$\begin{aligned}&(K-1).\varepsilon_2^{\,2} + \left(-K.N_{H2O}{}^{o} - 4.K.\varepsilon_1 - K.N_{O2}{}^{o} - N_{O2}{}^{o} - 8.\varepsilon_1\right)\varepsilon_2 \\ &\quad + \left[\left(5.K.N_{H_2O}{}^{o} + 5.K.N_{O_2}{}^{o} - 7.N_{O_2}{}^{o}\right)\varepsilon_1 + \left(-5.K - 7\right).\varepsilon_1^{\,2}\right] = 0\end{aligned} \tag{44}$$

$$\begin{aligned}&\left(N_{O2}{}^{o} + \varepsilon_1 + \varepsilon_2\right)\left(7.\varepsilon_1 + \varepsilon_2\right)^7.\left(5.\varepsilon_1 - \varepsilon_2\right)^5 \\ &\quad - K.N_{H_2O}{}^{o} + K.\varepsilon_1 + K.\varepsilon_2 - K.N_{O_2}{}^{o} = 0\end{aligned} \tag{45}$$

These quadratic equations can be solved and hence represented graphically retaining the feed of H_2O = 0.5 moles, O_2 = 0.5 moles and $C_6H_{12}O_6$ = 1 mole. The equilibrium constant for the gasification reaction is very large at these conditions and hence the gasification reaction goes to completion. Also it has been assumed that combustion reaction goes to completion. Therefore from this, WGS reaction will be considered since there is significant change at different temperatures.

Figure 3.15 shows a plot of WGS equilibrium curves in the ε_1-ε_2 space with the reactions bound in the mass balance space. Since ε_1 is a parameter, it will then be fixed at a certain range i.e. from 0 to 1 at different values. The temperature has been increased from 100°C to 800°C and their effects are evaluated as follows:

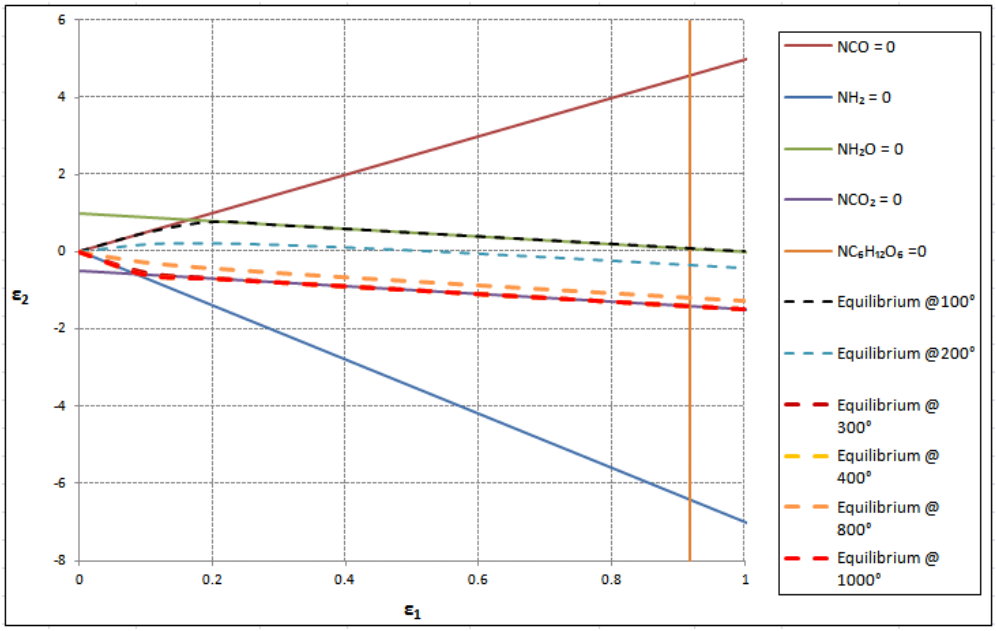


Figure 3.15 Effect of Temperature on the equilibrium.

From the results it can be seen that as you increase temperature, you get closer to the $CO_2 = 0$ line. This means that operating at high temperatures minimises the CO_2 production, therefore it is favourable that biomass gasification be operated at high temperatures from 800ºC to 1200ºC.

3.5.1 Equilibrium plot for WGS reaction at different Temperatures

The effects of gasifier temperature on the reaction equilibria is evaluated and discussed in the following section. From the equilibrium equation (42) and the graph obtained, it can be seen that the temperature lines cross through the following points:

- The 100°C line cross through the CO = 0 and H_2O = 0 line
- The 200°C line cross through the CO = 0 and H_2 = 0 line
- The 300°C line cross through the CO_2 = 0 and H_2 = 0 line
- From the 400°C to 800°C, the lines cross through the CO_2 = 0 and H_2 = 0 line

This can be seen on the following graph represented on Figure 3.16 below:

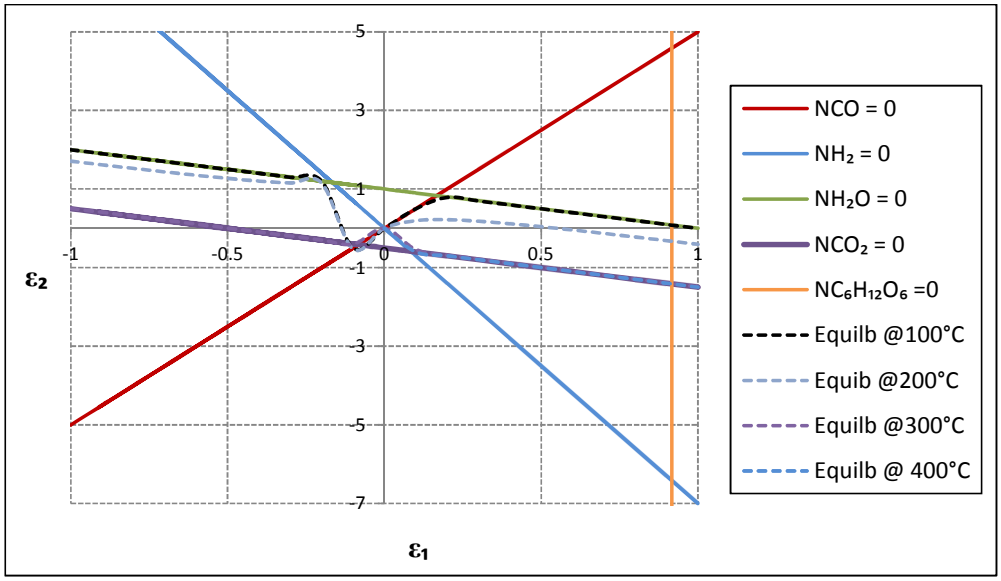


Figure 3.16 Temperature lines crossing through components zero lines.

Figure 3.16 show that temperature has a significant effect on the WGS reaction. From the temperature of 400°C to 1000°C the graphs are superimposed, meaning that the equilibrium constant K become constant. This can be explained as

follows: the reaction is exothermic; therefore, an increase in temperature by Le Chatellier's principle drives the reverse reaction. The consequence of this is that more CO and H_2O are formed from the gasification reaction, at the cost of CO_2 and H_2 formation. This is supported graphically by the fact that ε_2 decreases with an increase in temperature at any chosen ε_1 value.

Figure 3.15 and 3.16 also suggests that as temperature increases the line where gasification is operated within the region shift to the lower part of the gasification region. For this reaction, the profile is a strong function of temperature as it has a relatively low, negative Gibbs' energy of formation and thus a relatively low equilibrium constant. This implies that when operating the gasifier one needs to monitor and control changes in temperature quite carefully as small changes in temperature can shift the WGS equilibrium in the opposite direction.

Lastly it can be seen that the biomass equilibrium trends are the same with the coal equilibrium trends, that is, as temperature increases the line where gasification is operated moves to the lower part of the gasification region. With all these biomass gasification is better than coal gasification because the process reduces carbon dioxide emissions as the feedstock is environmentally friendly. Also the optimal point for operation which is subject to reduction in energy requirement for the process and no carbon dioxide emission has been established.

3.6 Summarized findings

The graphical analysis of the gasification process has shown that one can confidently assess and predict whether gasification is viable. On top of that,

graphical methods suggest ways that offer a more environmental way of investigating gasification.

In our case study, we have been able to determine the operating region within which the gasification of the cellulose will take place. We have established that the extent to which the gasification reactions occur is limited by the work balance. The line where gasification is possible starts at the upper part of the gasification region at lower temperatures and as temperature increases the line moves to the lower part of gasification region next to the $CO_2 = 0$ line, implying that it is favourable to operate biomass gasification at higher temperatures.

The implication of this work on how a gasifier should be designed is that in order to achieve the results obtained in this Chapter, it is not dependent on a specific gasifier i.e. you can run any gasifier to achieve the results.

Chapter 4

4The application of the thermodynamic properties of Enthalpy and Gibbs free energy on the gasification process

In this chapter the thermodynamic properties enthalpy (ΔH) and Gibbs free-energy (ΔG) are applied to the gasification of biomass with the goal of creating a gasification system that is as close to reversible as possible and therefore having minimal environmental impact. The methodology introduced in Chapter 2 together with the approach of the ε_1- ε_2 space in Chapter 3 will be applied to find a gasification region and each biomass gasification process will be evaluated according to its energetic performance in the enthalpy and Gibbs free energy graph.

From the previous chapter mass balance equations have been established and therefore a set of three gasification reactions were chosen. In this chapter the same gasification reactions will also be used. The gasification process is an example that is used to demonstrate and explain the methods used in this chapter, but the approach is general and can be applied to any process.

4.1 Introduction

Thermodynamics can be used to describe any process or system of processes. The resolution of linear problems which contains two or three decision variables can

be illustrated graphical by a method called graphical technique. Graphical technique is the method of scientific analysis and solving of a mathematical equation by using a curve to find and interpret results. In this Chapter the graphical technique uses the thermodynamic properties, enthalpy and Gibbs free energy to develop a system of processes that operates as close to reversible as possible. Energy production from fossil fuels is believed to be one of the major contributors to green house gas emissions and particularly the emission of carbon dioxide. The more reversible a process is, the less energy it will consume and the less emissions it will produce, hence this is the reason why it is desirable to operate the processes in this manner.

The g-h space is a representation of the Gibbs free energy denoted by ΔG and the enthalpy denoted by ΔH. The enthalpy represents the heat requirement of a process while the Gibbs free energy represents the work requirements of a process. By using these two thermodynamic characteristics together as vectors on a diagram of Gibbs free energy against enthalpy, it becomes possible to develop the operating gasification region where components compositions can be found. It should be noted that the quantities $\Delta H_{process}$ and $\Delta G_{process}$ are called process quantities. These quantities are simply the difference in the values of G and H between the products and the reactants entering and leaving the process at ambient conditions.

This graphical technique to gasification is based on the use of mass balance equations and not actual reactions; hence we will be focused on the process. The process mass balance that will be used to calculate these values might be

associated with a reaction that occurs in the process. It should be noted that it is not necessary that the reaction that is described by the process mass balance actually occurs in the process. In this case the sum of all the reactions that occur in the process must give the process mass balance. The heat and work flows of a process will be represented on the g-h space and later a g-h region will be established.

4.2 Application of gasification to the g-h space

4.2.1 The Simple process

The approach of using the g-h space allows all simple unit operations or reactions, for which ΔG and ΔH can be calculated, to be easily represented on a single set of axes.

A simple process is one where the reactants enter the process at $25^{o}C$ and 1atm; the chemical transformations happen at a temperature T; and the products of the process then leave at $25^{o}C$ and 1 atm. We therefore define a simple chemical process as the one in which the heat Q is added or removed at a single temperature T which is the reactor temperature.

Consider a diagram below which represents a simple process and it must be noted that the process could comprise several unit operations such as reactors, separation units, heat exchangers etc. The feed and the product are assumed to be at ambient conditions.

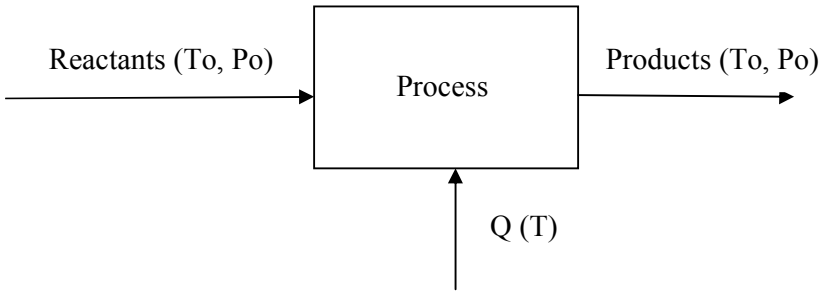


Figure 4.1 A simple process.

It should be noted that we are looking at the process and not the reactor. The difference between a simple process and a reaction is that a reaction can be represented on its own but a simple process could contain many individual reactions. In some cases "process" and "reaction" can be used interchangeably, for instance where the simple process contains only one reaction.

We can perform an energy balance over a process. It is assumed that the process is adiabatic i.e. no heat is required or rejected in the process. Also there is no shaft work, no height change, and no change in internal, kinetic and potential energy. Given the reactants and the products, the nett chemical reaction for the process can be determined. When an Energy Balance is performed on the process the change in Enthalpy can be calculated by:

$$\Delta H^0_{reaction} = \left(\sum_i \upsilon_i \Delta H^0_{f,i} \right)_{products} - \left(\sum_i \upsilon_i \Delta H^0_{f,i} \right)_{reactants} \quad (1)$$

where:

- υ_i (Symbol Upsilon) is the stoichiometric coefficient in the component i.
- The subscript f represents "of formation"
- The superscript ° represents the standard conditions.

- The subscript i represents species i

Now let us consider the Gibbs free energy balance which represents the work requirements of the process. It is assumed that the components enter and leave at the temperature of 298 K and the pressure of 1atm. Similarly the procedure with energy balance will be applied on the Gibbs free balance which represents the work requirements of the process as follows:

$$\Delta G^0_{reaction} = \left(\sum_i \upsilon_i \Delta G^0_{f,i} \right)_{products} - \left(\sum_i \upsilon_i \Delta G^0_{f,i} \right)_{reac\,tan\,ts} \qquad (2)$$

Equations (1) and (2) will be used to calculate the energy and work requirements of the gasification process. This also allows any gasification reaction to be represented as a single point on the g-h space.

4.2.2 Gasification reactions

The g-h plot will now be used to describe the relationship between heat requirements of a process and the work requirements of a process. This will be done by first defining the equations that plays an important role in the process and then calculating ΔH and ΔG for each gasification reactions.

Using the available species from the overall mass balance just as we did in Chapter3, there can be different combination reactions that describe the biomass gasification process. Having said this, from the previous Chapter, the combustion,

gasification and water gas shift reactions have been retained to constitute the main reactions in the transformation of the biomass (cellulose).

The first reaction that will be considered is the combustion of cellulose with oxygen; this is considered because it will provide the heat and work required by the process. The following assumption was proposed: since the chemical formula for cellulose is similar to that of glucose, the heat of formation and the Gibbs free energy of glucose were used for cellulose. This is because there is no simple heat of formation and the Gibbs free energy of cellulose; it is complicated depending on the source, type and conditions.

The combustion of cellulose is as follows:

- $C_6H_{12}O_6 + 6\ O_2 \Rightarrow 6\ CO_2 + 6\ H_2O$ (3)

When Equation (1) and (2) are used on the combustion reaction along with the thermodynamic data provided in the Appendix B it is found that the reaction is exothermic and work producing, therefore ΔH and ΔG are both negative values. The calculated values for ΔH = -2562.04 kJ/mol and ΔG = -2487.86 kJ/mol. This reaction will provide heat and work required by other reactions because large amount of heat is given off, therefore it is the main source of providing heat in the reactor.

The second equation is the gasification reaction which will produce syngas needed in the process, it is expressed as follows:

- $C_6H_{12}O_6 + H_2O \Rightarrow 7\ H_2 + CO_2 + 5\ CO$ (4)

The same enthalpy and Gibbs free energy calculations are also carried on the gasification reaction, it is found that the reaction is endothermic and requires work input i.e. ΔH and ΔG are both positive. The calculated values for $\Delta H = 545.69$ kJ/mol and $\Delta G = 397.86$ kJ/mol. This reaction requires additional heat and work for the process to occur.

The third equation that will be considered is the Water Gas Shift equation which is expressed as follows:

- $CO + H_2O \Leftrightarrow CO_2 + H_2$ (5)

This equation can be either endothermic or exothermic depending on the direction of the reaction, it can be considered in the forward or backward direction. From the above equation it is established that the reaction is exothermic and rejects work. The values for $\Delta H = -41.163$ kJ/mol and $\Delta G = -28.52$ kJ/mol. The WGS is an equilibrium reaction and also rejects heat and work for the reaction to occur, this condition applies for the forward direction as written above.

The last equation is the water conversion. The gasification reaction requires gas phase water (steam) as feed, but liquid water is the phase that is available at the simple process inlet and output conditions. This is the reason steam has to be produced and it is represented by a phase change reaction as shown below:

- $H_2O_{(l)} \Rightarrow H_2O_{(g)}$ (6)

The reaction is endothermic i.e. both heat and work input is required. The values for $\Delta H = 44.01$ kJ/mol and $\Delta G = 8.56$ kJ/mol. This is because water has to be heated before it can be used. Again, we are considering a simple process where

the reactants and products enter and leave at ambient conditions; therefore, each species must be processed to reach the reactor temperature and then processed again to reach ambient outlet conditions.

From the above calculations the ΔH and the ΔG of all the equations can be represented in one diagram i.e. the g-h plot.

Before the g-h graph is presented there are certain thermodynamic regions that need to be established and explained. The following diagram in Figure 4.2 illustrates all the thermodynamic regions.

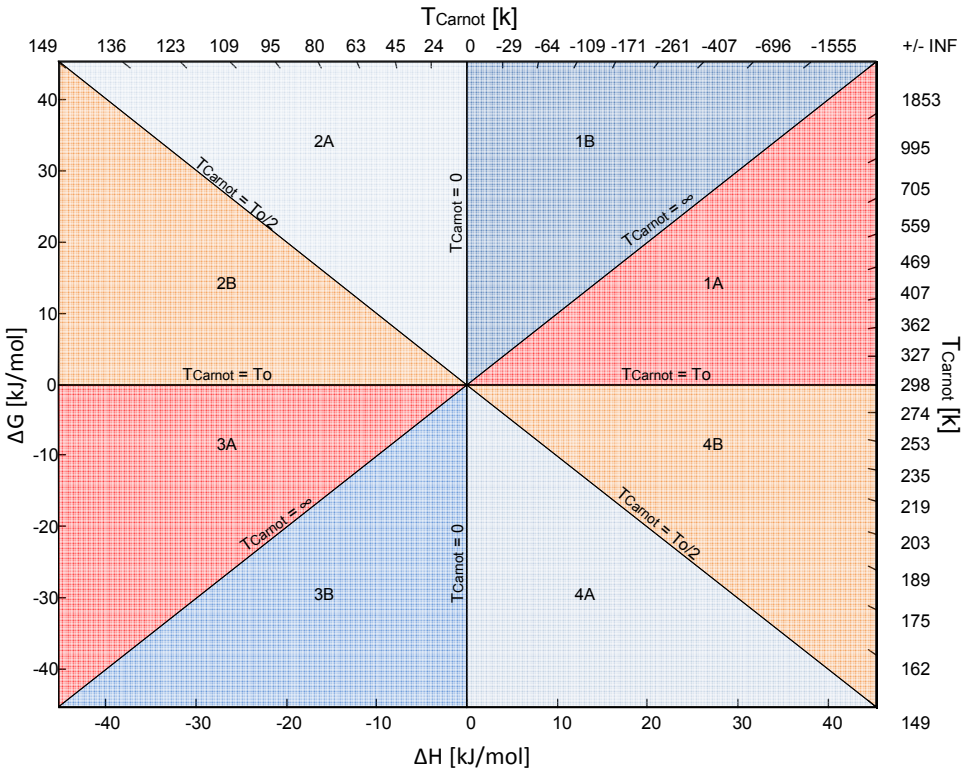


Figure 4.2 Thermodynamic regions on the g-h diagram. (Sempuga et al. 2010)

There are four thermodynamic regions on the g-h diagram. The first region lies between the 0° to 90° line in the first quadrant going anticlockwise and in this region are processes which require heat and work input, the second region lies between 90° to 180° line in the second quadrant and deals with processes which reject heat and require work input. The third region lies between 180° to 270° and are the processes which reject heat and work and lastly is the fourth region in the fourth quadrant and lies between 270° to 360° and in it are processes which require heat input and which could reject work.

For a simple process to become reversible, the temperature at which heat is transferred to the process is called the Carnot Temperature (T_{Carnot}). T_{Carnot} is the temperature at which heat must be added or removed from the process for it to be reversible; this means that if the process is operated at T_{Carnot} there is no entropy generation. If the only transfer of energy between the process and the surrounding occur as heat and if heat is added or removed at any other temperature T, then the process will generate entropy and will become irreversible.

From the regions described above; a 45° line can be drawn in each quadrant to identify whether each reaction will lie below or under the line. What this line implies is that in the third quadrant below the 45° line and in the first quadrant above the line moving anticlockwise, Carnot temperature is negative. This means that processes falling in the mentioned region would not be able to meet the energy requirement i.e. if work is required to be transferred this can be done by compression and other means.

The gasification process will be found in one of the regions; hence the energy requirement of the process and the process reversibility will also be determined by the aid of thermodynamic regions.

4.2.3 Representation of reactions in the g-h plot

Now that the thermodynamic regions have been established, the g-h plot for the four independent reactions will be drawn and we will determine which regions they fall under and find out if they are reversible or not. Figure 4.3 represents the heat requirements and the Gibbs free energy for each independent reaction. It is plotted using the heat and the Gibbs free energy formation data.

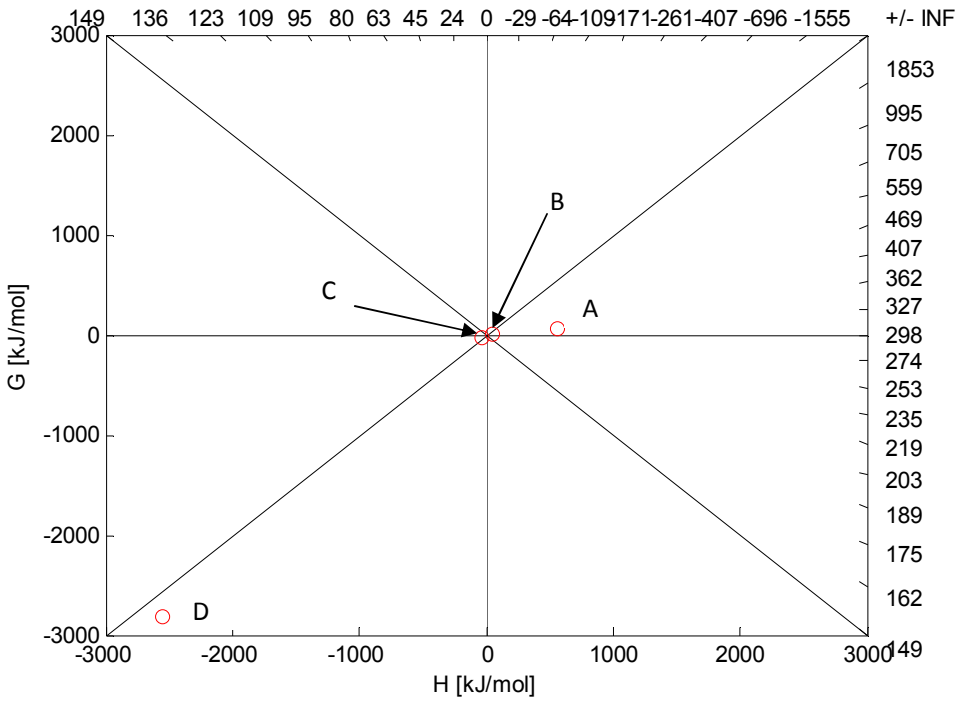


Figure 4.3 Gasification reactions in the thermodynamic regions.

In the above mentioned graph the point A, B, C and D represents the gasification reaction involved in the process with their Carnot temperatures. Point A, B, C and D represents the gasification, phase change, WGS and combustion reactions respectively. Their Carnot temperatures are represented in Table 4.1 below:

Table 4.1 Reaction Carnot Temperatures.

Reactions	Carnot temperatures
Gasification	362K
WGS	995K
Combustion	-1565K
Phase Change	639K

Now that the Carnot temperatures have been specified we will take a closer look at each reaction. This is represented in Figure 4.4.

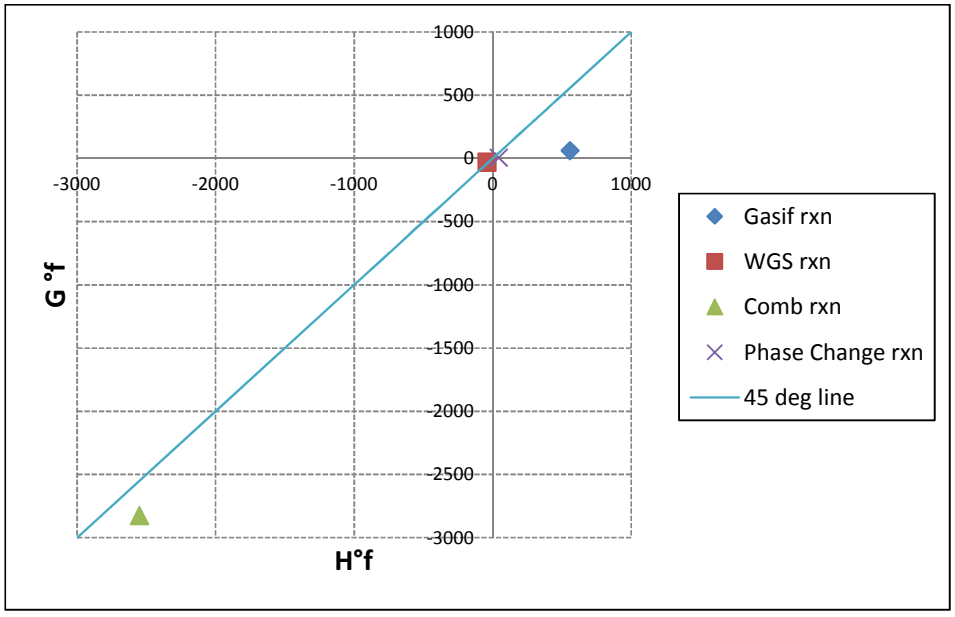


Figure 4.4 Reactions involved in the gasifier.

Different reactions are represented in the g-h plot as points according to their Gibbs free energy and Enthalpy of formation. They will then be evaluated if they are reversible or irreversible. From the explanation of regions above each reaction lies in a certain region as defined by the heat and work requirements.

We know that the gasification and phase change reaction lies in the first quadrant, region 1A as these reactions are both endothermic and have positive Gibb free energy. These two processes will require heat and work input to be supplied in order for the reactions to be reversible. This means that it is possible to run processes in region 1A represented in Figure 4.2 as reversible simple processes where the work requirement for the process is satisfied by supplying heat at the Carnot temperature.

The same applies to the remaining reactions WGS and combustion reaction lies in the third quadrant region. These reactions reject heat and have the potential to produce work. The heat rejected from the process could be used to supply the other two reactions so that a balanced heat network is obtained.

The water gas shift reaction is above the 45°line; hence it falls under region 3A. Processes in region 3A can be run reversibly by removing heat at the process Carnot temperature which varies from ambient temperature to infinity. In this case it is possible to run the WGS reaction reversibly.

On the other hand the combustion reaction lies below the 45°line meaning it is in region 3B. Processes in region 3B require that heat be removed at negative Carnot temperatures, which have no physical meaning for them to be reversible. This Carnot temperature is found in region 1B and 3B only and reversibility cannot be

obtained under this circumstances. Processes in region 1B and 3B will always be work deficient irrespective of the temperature at which heat is added and would require additional work input by other means such as pressure work or electro-chemical work and therefore cannot be run as simple processes. In this case the absolute value of ΔH is less than that of ΔG. The maximum amount of work that can be recovered from the process, using a reversible heat engine, is equal to the amount of heat that the process can reject; and this can only occur at infinite temperature. Therefore processes in region 3B will always loose part of their work potential, they will always be irreversible if the only way of work recovery is from the quality of heat by, for example, a heat engine. A heat engine is a system that performs the conversion of heat or thermal energy to mechanical work. It does this by bringing a working substance from a high temperature state to a lower temperature state. Other means of recovering work should be considered. (Sempuga et al. 2010)

It should be noted that most combustion reactions have similarly infeasible Carnot temperatures, meaning combustion is irreversible by its very nature. Combustion is responsible for most irreversibility in processes.

4.2.4 Reaction lines on the g-h space

Now that the gasification reactions in the gasifier are specified, they will be drawn as a line that represents all possible extents. This will be achieved by assuming that we are feeding 1 mole of cellulose as the basis of the calculations. The extents can be defined at different range, since we have set 1 mole of cellulose that we are

feeding the extent cannot be more than 1 mole because there will not be any cellulose to react. From this then the extent has been set from 0 moles to a maximum of 1 mole. The other feeds involved are oxygen and water. On the contrary it is possible to have an extent of more than 1mole by adding greater amounts of feed rather than less, also they can be negative values implying that the reaction is happening in a reverse meaning that the reaction is shifting to the opposite direction.

Again the reactions involved in the gasifier in addition with phase reaction are described as follows:

- The gasification reaction: $C_6H_{12}O_6 + H_2O \Rightarrow 7H_2 + CO_2 + 5CO.....\varepsilon_1$ (7)
- The water gas shift (WGS): $CO + H_2O \Leftrightarrow CO_2 + H_2$ ……..ε_2 (8)
- The combustion reaction: $C_6H_{12}O_6 + 6O_2 \Rightarrow 6CO_2 + 6H_2O.....\varepsilon_3$ (9)
- The phase change reaction: $H_2O_{(l)} \Rightarrow H_2O_{(g)} .....\varepsilon_4$ (10)

The Equations below are used to calculate the line processes or rather line reactions described in equation (7) to (10) above together with Gibbs free energy of formation and heat of formation; they are expressed as follows:

- $\Delta H°_{rxn} = \varepsilon_1 * \Delta H°_{rxn1} + \varepsilon_2 * \Delta H°_{rxn2} + \varepsilon_3 * \Delta H°_{rxn3} + \varepsilon_4 * \Delta H°_{rxn4}$ (11)
- $\Delta G°_{rxn} = \varepsilon_1 * \Delta G°_{rxn1} + \varepsilon_2 * \Delta G°_{rxn2} + \varepsilon_3 * \Delta G°_{rxn3} + \varepsilon_4 * \Delta G°_{rxn4}$ (12)

With the information a g-h line for combustion reaction can be drawn as shown in Figure 4.5 and then the combination of all the reactions involved in gasification reaction are also illustrated in Figure 4.6 below.

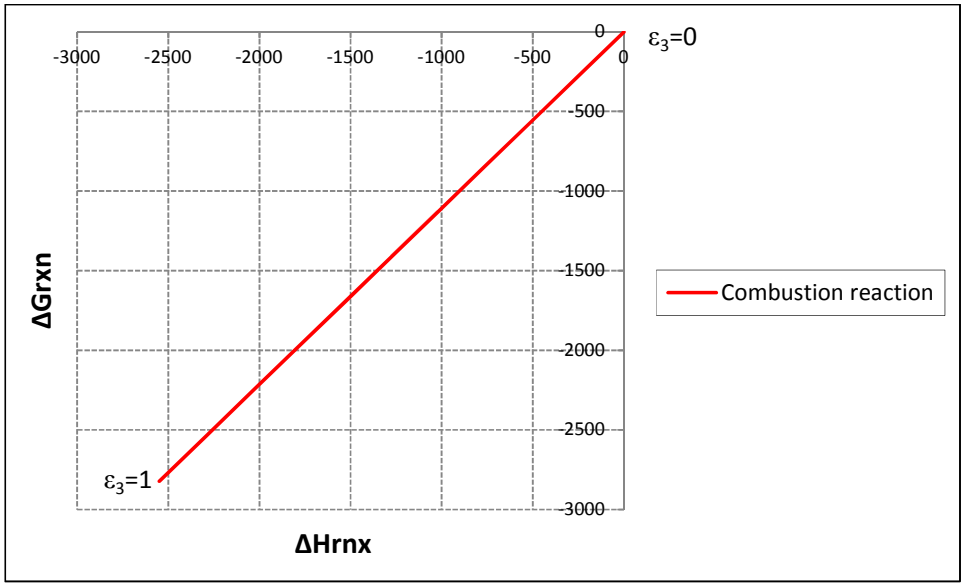


Figure 4.5 Reaction line for the combustion reaction by plotting the overall ΔH_{rxn} and ΔG_{rxn} over a range of extents.

The graph above shows the combustion reaction at different range of extents from extent 0 to 1.As it can be seen from the graph that at the extent of 1 the ΔH_{rxn} and ΔG_{rxn} are at maximum. This is because at the extent of 1 the reaction has gone to completion and therefore its full amount of heat and work is available.

Similar approach will be used to plot the reaction line for all the independent gasification reaction. This is shown in Figure 4.6.

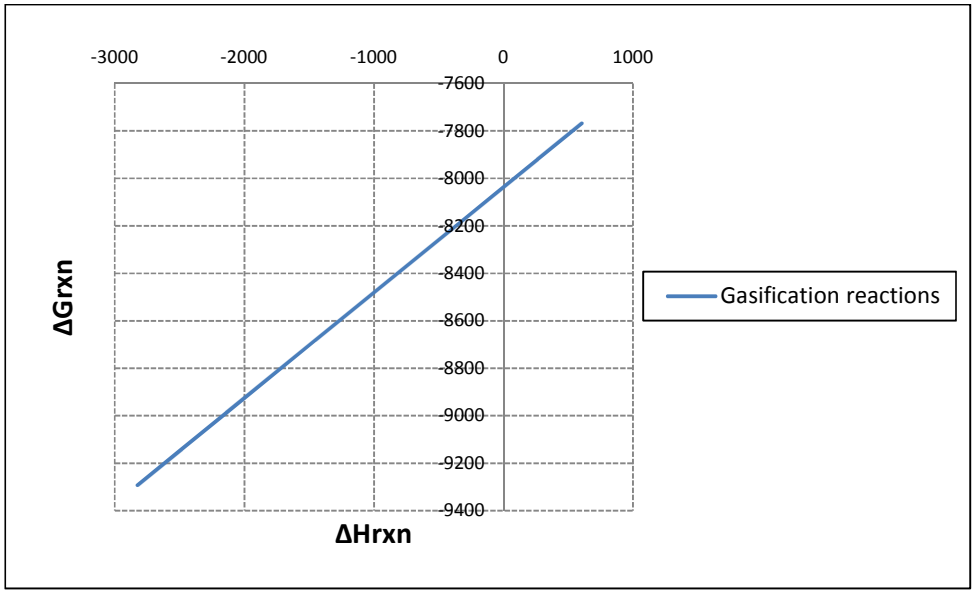


Figure 4.6 Reaction line for all the independent gasification reaction by plotting the overall ΔH_{rxn} and ΔG_{rxn} over a range of extents.

The line drawn in Figure 4.6 represents all the reactions that are occurring in the gasifier at a particular temperature. Figures 4.4 and 4.6 give the same results the difference between Figure 4.4 and 4.6 is that Figure 4.4 represents independent combustion reaction at maximum and minimum extent, while Figure 4.6 represents gasification reactions defined by extents and represented by a line and along the line reactions are not complete. It can also be noted that again the reactions lies in the first and third region as explained in the section above.

4.3 The mass balance region

To illustrate the use of the g-h plot, we will consider the mass balance. Before one can begin using the g-h space in determining a mass balance region it would be

convenient to first define the independent mass balances equations that will be used throughout the development of the region.

The next thing to be established is the mass balance region as it was done in the ε_1- ε_2 space in the previous Chapter. This will help us to be able to compare the gasification region of ε_1- ε_2 space with that of the g-h space. With the previous ε_1- ε_2 gasification space, mass balance calculations were used to get ε_1 and ε_2, but with the g-h space the heat of enthalpy and the Gibb free energy will have to be accounted for.

By using Equations (7) to (10) it can be assumed that we are feeding one mole of cellulose, therefore the following equation will be feasible based on the three independent gasification reactions (7) to (10):

- $\varepsilon_1 + \varepsilon_3 = 1$ (13)

Also by assuming that we are using the H_2 to CO ratio of 2:1 the following equation is obtained:

- $\varepsilon_1 = \varepsilon_2$ (14)

Lastly by performing a mass balance on phase change it is found that:

- $\varepsilon_4 = \varepsilon_1 - 6*e_3 + e_2$ (15)

and we simplify equation (15) by substituting Equation 13 and 14 and we can finally obtain:

- $\varepsilon_4 = 8* \varepsilon_1 - 6$ (16)

With the use of these equations each component can be represented on the g-h plot together with the heat of formation and Gibbs free energy, this is shown in the equations below:

- $\Delta H_{rxn} = \varepsilon_1 * \Delta H_{rxn1} + \varepsilon_2 * \Delta H_{rxn2} + \varepsilon_3 * \Delta H_{rxn3} + \varepsilon_4 * \Delta H_{rxn4}$ (17)
- $\Delta G_{rxn} = \varepsilon_1 * \Delta G_{rxn1} + \varepsilon_2 * \Delta G_{rxn2} + \varepsilon_3 * \Delta G_{rxn3} + \varepsilon_4 * \Delta G_{rxn4}$ (18)

Each component on the g-h space is represented by its independent equation which is shown as follows:

$$N_{CO} = -5\varepsilon_1 + \varepsilon_2 \geq 0 \quad (19)$$

$$N_{H_2} = -7\varepsilon_1 - \varepsilon_2 \geq 0 \quad (20)$$

$$N_{H_2O} = \varepsilon_1 + \varepsilon_2 - N_{O_2}{}^{o} \geq 0 \quad (21)$$

$$N_{C_6H_{12}O_6} = \varepsilon_1 + \frac{1}{6} N_{O_2}{}^{o} \geq 0 \quad (22)$$

$$N_{CO_2} = -\varepsilon_1 - \varepsilon_2 - N_{O_2}{}^{o} \geq 0 \quad (23)$$

Using all these equations a gasification region in the g-h space can be obtained as shown in Figure 4.7 below. This is achieved at the feed of 0.5 mole oxygen, 0.5 water and 1 mole cellulose.

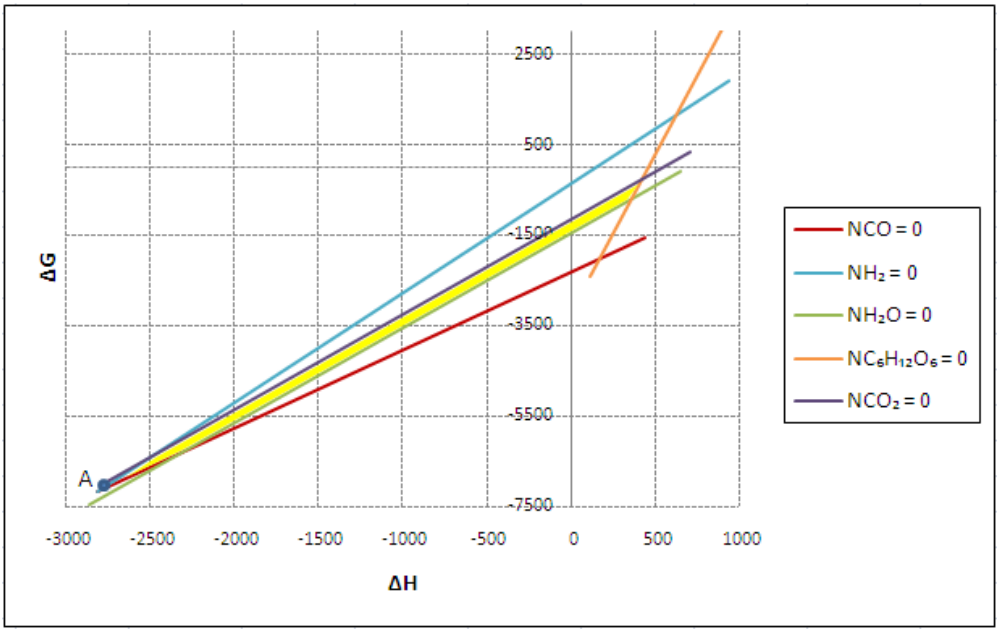


Figure 4.7 The mass balance region on the g-h space.

The results show that a gasification region is also achievable in the g-h space. As it was with the ε_1- ε_2 space, each component is still maintaining its own state i.e. each component is still in the same position and direction. The difference is that in this section the extents are used together with the enthalpy and Gibbs free energy to plot the graph above. It can be seen that the graph lies in the third region where the enthalpy and Gibbs free energy are negative; this is because the combustion reaction has a big negative ΔH and ΔG because it is exothermic. This will hence influence the plot to lie in the third region and from the thermodynamic regions on the g-h diagram the third region lies between 180° to 270° and are the processes which reject heat and work.

Since the gasification region is in region 3B of the thermodynamic regions this signifies that the process is irreversible. This means that in operating the gasifier,

we will always operate irreversibly and that work is potentially lost in the form of heat and can be recovered from the gasifier. The gasification region is only defined by the mass balance while the enthalpy and Gibbs free energy plot will only show where the region lies in the thermodynamic region on the g-h diagram. The feed point for the g-h plot is where the CO and H_2 lines meet at point A. Like the ε_1- ε_2 space in the previous Chapter as the feed is increased the gasification region becomes larger and vice versa.

Each and every reaction in the particular reactor occurs to minimise the Gibbs free energy and also the equilibrium is achieved at minimum Gibbs free energy. At a minimum Gibbs free energy, products are formed. In order to achieve desirable products, conditions need to be adjusted to meet the set goal. From the results it can be seen that the feed point is at the minimum Gibbs free energy and enthalpy of heat. What this implies is that heat and work needs to be supplied before the reaction can occur. This was also established from the previous chapter.

The difference between this region and mass balance is the regions in which the plot lies i.e. in the ε_1- ε_2 space it was in the first quadrant of the ε_1- ε_2, whereas in the g-h plot it lies mainly in the third and a small part of the graph lies the fourth quadrant.

It has been established from the results obtained that biomass gasification is an irreversible process. Since the gasification region lies on the third region and below the 45° line, the Carnot temperature is negative. In order to move the graph above the 45° line so that we can achieve a positive Carnot temperature, reasonable amount of oxygen needs to be added but the disadvantage is that more

cellulose will be consumed, therefore less products (syngas) will be produced. In conclusion the combustion reaction provides more heat and work than is actually needed by the other 3 reactions put together. It would be wasteful to provide too much heat and work. The combustion reaction will need to be controlled so as to provide sufficient heat and work, this is done by feeding enough oxygen so that the process moves to region 3A in order to make it reversible.

4.4 The effect of temperature in the gasifier

Now that we have looked at the overall process, we will now take a look at the gasifier so that we can understand and analyse which factors affect the reactions. In this section we will study the effect of temperature on the gasifier. In the above sections the reactions were calculated based on the heat and Gibbs free energy of formation, considering the overall process. This is because the inlet and outlet temperature of the overall process (T_o), analysed above were equal hence only the energy of formation was considered as the temperature terms were cancelling out. Temperature effect will be considered and their effect will be examined. This will be done by considering the specific heat capacity on the reaction with change in temperature and how it affects the gasification region. The enthalpy and the Gibbs free energy are calculated using the following equations:

$$\Delta H_{rxn}(T) = \Delta H_{rxn}^{\circ} + \int C_p dT \tag{24}$$

Where:

- ΔH_{rxn}° is the change in heat of formation at standard conditions

- C_p is the specific heat capacity
- dT is change in temperature

$$\Delta G_{rxn} = -R * T * InK_{eq} \quad (25)$$

Where:

- R is the gas constant
- T is temperature
- K_{eq} is the Equilibrium Constant for Reaction

The effect of temperature on the gasifier is represented in the Figure 4.8 below. Figure 4.8 analyses temperature effect at 400°C and at each component line the number of moles is zero as it was in the previous Chapter. Each component line as it is defined by the inequality represents the positive moles of that component, the negative moles are not feasible therefore they will not be considered.

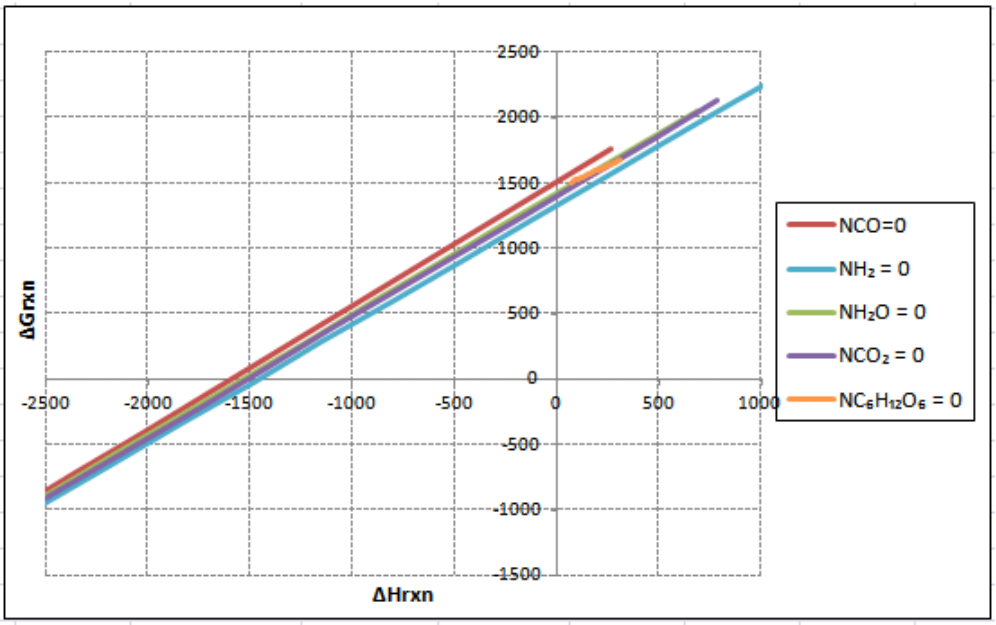


Figure 4.8 The effect of temperature on the gasification region at 400°C.

The figure above shows how the temperature at 400°C affects the gasification region. As we know that gasification can be operated up to 1000˚C we will therefore analyse what happens as we increase the temperature from 400˚C as shown above to 800°C.

Figure 4.9 is the same graph as in Figure 4.8 the difference is that it shows the expanded upper gasification region.

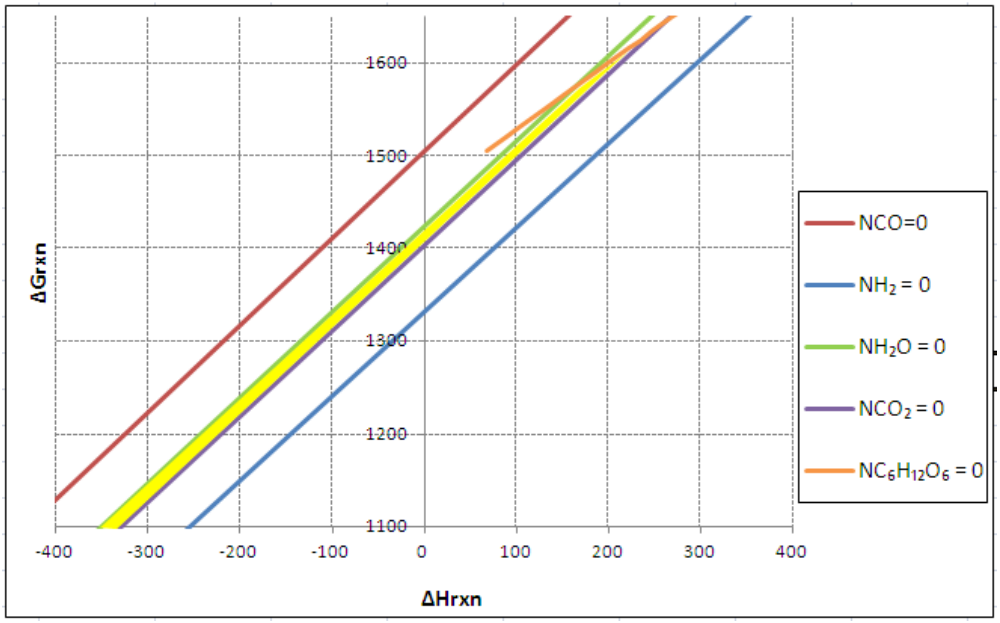


Figure 4.9 The expanded upper region of the effect of temperature on the gasification region at 400˚C.

From Figure 4.9, the shaded region represents the gasification region on the g-h plot. As it was established in Chapter 3 that as the feed streams are increased the gasification region also increases, the same results are also applicable on the g-h plot i.e. as water and oxygen are increased the gasification region becomes enlarged.

Now that we have looked at the effect of temperature at 400˚C we will take a look at what happens as we increase the temperature to 800˚C. Figure 4.10 shows the results of an increased temperature.

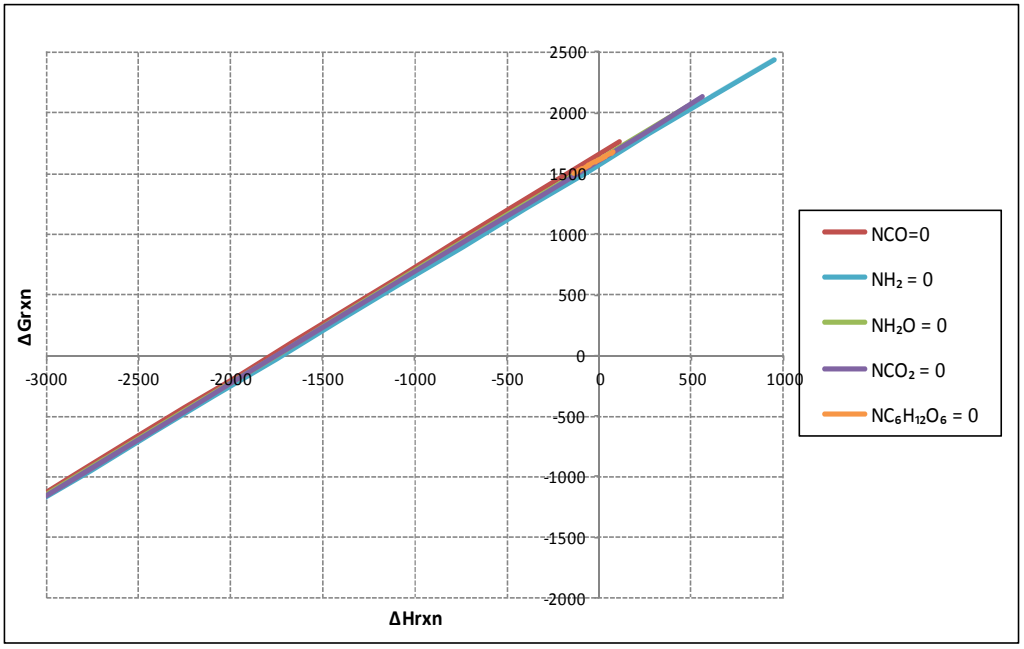


Figure 4.10 The effect of temperature on the gasification region at 800˚C.

From Figures 4.8, 4.9 and 4.10 it can be seen that the g-h plot still has the same form with a decrease in gasification region. So then how does the effect of temperature affect the region?

It can be noted that only mass balance can determine the attainable gasification region, hence if the region needs to be increased or decreased this can be done by mass balance as it was shown in the previous chapter. The graph presented above is plotted when the temperature is 800°C. When temperature is increased from 400°C to 800°C and 1000°C, the gasification region becomes narrower as the component lines becomes closer to each other, this is shown in the graph above when temperature is increased to 800°C. The decrease in the gasification region is caused by the fact that as temperature increases in the gasifier, the combustion

extents decrease and drive endothermic reaction which is the gasification reaction more to completion; therefore there will be the deficiency in the amount of water. This becomes a challenge because operating on a narrow region makes the operation difficult. This can be solved by increasing oxygen in the feed stream which will in turn increase the products formed in the combustion reaction and more water will be formed. As the products are formed the gasification region will therefore increase.

5.6 Evaluation between biomass and coal gasification process

Since it has been assumed that the Gibbs free energy of the cellulose will be the same with that of the glucose which is ΔG = -915.9 kJ/mol, the coal Gibbs free energy is roughly about ΔG = -1300kJ/mol. What this mean is that in the coal gasifier there will be less work input than in biomass, hence this makes the coal a stable energy source than biomass but before a conclusion can be made certain factors need to be considered.(Bridgewater, 1995)

Looking at a biomass (cellulose) it can be noted that it is easier to convert it to a product as compared to coal therefore what this implies is that we can run a biomass gasifier at lower temperature. This is not the case for coal gasifiers because coal gasification should be run at high temperatures, to minimise carbon deposition and methane production, which is also possible with biomass gasification (Maniatis, 2001).There is a limit as to what temperature a biomass gasifier should be operated for example we cannot operate at low temperatures which are from 100-400℃ because there will be slow reactions, which means low

conversion, which means a large recycle to consume all of the biomass. Hence this will demand a lot of energy for the recycle. Lowering the temperature too much will also have the additional negative effect of preventing complete gasification.

Lastly both the coal and biomass gasification are irreversible processes.

5.7 Summarized findings

Gasification on the g-h plot is achievable and mainly occurs on the third region, which means that both heat and work are rejected. This is because of the influence of the combustion reaction as it has large negative values of ΔH and ΔG. This means that heat and work needs to be rejected by the process, this is also expected since the feed point is at the minimum Gibbs free energy. It has been found that biomass gasification is an irreversible process and occurs below the 45 degree line on region 3B with a negative Carnot temperature.

The effect of temperature on the gasifier has also been analysed and it has been found that as temperature increases the gasification region becomes narrow because of insufficient water, this is solved by adding more oxygen which will in turn increase the products i.e. water in the process, and hence the region will increase.

Again combustion reaction provides more heat than what is actually needed to other three reactions, which are the gasification reaction, water gas shift and the phase change reaction. Therefore it is required that we run combustion reaction to

only partial completion and gasify the rest of the biomass. It should be noted that most combustion reactions have similarly infeasible Carnot temperatures, meaning combustion is irreversible by its very nature. Combustion is responsible for most irreversibility in processes. Therefore combustion reaction will need to be controlled so as to provide just enough heat and work, which is done by feeding just enough oxygen for the combustion.

Chapter 5

5 Conclusions

This dissertation presents a graphical technique tool that can provide insight and valuable information regarding a process without going into microscopic detail but rather looking at the overall balance. Firstly the tool uses systematic analysis and solving of a mathematical equation which are inequalities from mass balance, secondly it allows us to determine the optimum target for a process and lastly helps understanding what is required to achieve the target. Analysis were made on the $\varepsilon_1 - \varepsilon_2$ space and on the g-h plot in the previous Chapters using cellulose, water and oxygen as a feed in order to find a region where gasification is achievable.

5.1 Gasification region on the ε_1- ε_2 space

The main objectives of this study were to assess graphical techniques to biomass gasification. This was achieved by using the mathematical modelling to obtain mass balance equations which will describe the gasification reactions. Following these analyses one will find gasification region and optimise the gasification process.

These issues have been addressed by a thermodynamic approach described in Chapters 3 and 4, which formed the main part of this dissertation. The main findings in this part were as follows:

- A graphical approach was used to identify attainable region for biomass gasification. A case study was considered where the numbers of moles of the feed components were selected arbitrarily and used to determine the overall balance for the process. The case study together with the target that is based on the fundamental concepts of mass, energy and Gibbs free balance were used to solve biomass gasification.
- As wood consists of 40 – 50% cellulose we therefore used cellulose as a representative substance for biomass with a chemical formula of $C_6H_{12}O_6$. In view of the fact that there is no simple $\Delta H_f°$ and $\Delta G_f°$ for cellulose we simplified it by considering the $\Delta H_f°$ and $\Delta G_f°$ of glucose since it has the same chemical formula. We understand that this is a generalization, but it allows us to do an easy analysis of the problem to determine what the critical factors are.
- An overall mass balance was constructed and it was found that there were six species and three atomic equations. The three independent equations were obtained which may not describe the actual reactions occurring in the gasifier but are simply independent reactions that can represent all possible reactions that can occur in the gasifier. The three independent reactions that were chosen are the combustion, gasification and water gas shift reactions.

Different case studies were considered where the number of moles for oxygen were varied, the first was for a feed of $N_{O2}^0 = 0.5$ mole, $N_{H2O}^0 = 0.5$ mole and $N_{C6H12O6}^0 = 1$ mole, the second was for a feed of $N_{O2}^0 = 0$ mole, $N_{H2O}^0 = 0.5$ mole and $N_{C6H12O6}^0 = 1$ mole and finally $N_{O2}^0 = 0.1$ mole, $N_{H2O}^0 = 0.5$ mole and

$N_{C6H12O6}^{0}$ = 1 mole in the reactor. Using mass balance inequality equations, an enclosed region was established by positive moles of all the components involved in the process. From a mass balance point of view, gasification is only possible within the enclosed region. The region satisfies the mass, energy and the work balances and heat and work are required to be added. In this region oxygen and cellulose will always be a reactant and carbon dioxide will always be a product while water, carbon monoxide and hydrogen can vary depending on the amount of oxygen fed and the reaction occurring at that certain point.

The combination of mass, energy, and Gibbs free energy balance is a comprehensive tool in providing visual insights into the gasification process within which we can attempt to better understand, operate and optimize biomass gasification process. Therefore the following are the findings in regard to biomass gasification:

- When operating the gasifier, both heat and work will be required to be added in order to achieve any point within the gasification region. This work can be added by external heat at appropriate temperature.
- The additional energy supplied through burning will change the overall mass balance, which then affects the size or location of the region. The benefit of using this approach is that we can consider both the energy required by the process, as well as the resulting mass balance.
- There are three possible areas within which the gasification process can occur: the first are is where heat is rejected and work required to be added and the second area is where heat and work are added and lastly is area 3

where heat is required to be added while work needs to be rejected by the process.

- The best operating area is where the process satisfies the mass, energy and the work balances. In this region heat and work are required. Therefore, when heat is added, work can also be added to meet the energy requirement of the process.
- When evaluating biomass gasification process in area 2 where the Gibbs free energy line crosses the CO_2 line, there exist a point where we do not require adding any work in the process and the process does not release any CO_2, it has been found that at this point biomass gasification can be operated efficiently. This is achieved at the CO: H_2 ratio of 1:1
- It has been found that temperature has a significant effect on equilibrium in the operating region; this implies that when operating the gasifier one needs to monitor and control changes in temperature quite carefully as small changes in temperature can shift the WGS equilibrium in the opposite direction. This means that more water and carbon monoxide will be produced.
- When evaluating the effect of temperature on equilibrium it shows that operating at high temperatures minimises the CO_2 production, therefore it is favourable that biomass gasification be operated at high temperatures from 800ºC to 1200ºC.
- In order to maximise the gasification region, the amount of water (steam) and oxygen should be increased but this has its own limitations:

- The limit will depend on set target for example if the target is H_2: CO ratio of 2:1 then increasing water is likely to deviate from the ratio of 2:1.
- Also the limit depends on the product specification for example in our case study the aim is to produce syngas, adding more water will be desirable as more syngas will be produced. This is because as we add water according to Figure 3.5 in Chapter 3 the region increases and the point moves further away from hydrogen, meaning that we have more rich hydrogen syngas.
- The limitation in adding more than the required amount of oxygen is that all the cellulose will be consumed and therefore according to the case study gasification reaction will not occur since it uses cellulose as a feedstock and also the WGS reaction will not occur because it depends on the gasification reaction and therefore oxygen in the feed should not exceed 6 moles.

- The example above was applicable for biomass gasification process and if a different process is to be analysed the analysis may change. The efficient gasification process was obtained when we are feeding less amount of oxygen i.e. 0.1 moles of oxygen, 0.5 mole of water and 1 mole of cellulose.
- Therefore it is required that we run combustion reaction to partial completion and gasify the rest of the biomass.

Biomass gasification is work limited because in order to run the gasification process, work needs to be added, and (Ngubevana et al., 2011) has shown that coal gasification is energy and not work limited. It is known that in the coal gasifier there will be less work input than in biomass gasification, hence this makes the coal a stable energy source than biomass, this is supported by the fact that it has been assumed that the Gibbs free energy of the cellulose will be the same with that of the glucose which is ΔG = -915.9 kJ/mol, the coal Gibbs free energy is about ΔG = -1300kJ/mol. But before a conclusion can be made certain factors need to be considered, looking at a biomass (cellulose) it can be noted that it is easier to convert it to a product because of the component constituents as compared to coal therefore what this imply is that we can run a biomass gasifier at lower temperature as compared to coal gasifiers which is one form of saving energy.

5.2 Gasification on the g-h plot

Furthermore the dissertation was aimed to investigate the g-h plot in addition to the ε_1- ε_2 space. The g-h diagram which is the area formed by enthalpy and Gibbs free energy was used to represent chemical processes where the processes can be classified in different regions depending on the magnitude of enthalpy and Gibbs free energy which translate to their heat and work requirements. Heat can be transferred across a process by its temperature and heat can also carry work into the process. Transferring work is a major challenge and in many cases, it is a major source of inefficiencies in the process. The approach of using the g-h space

allows all simple unit operations or reactions, for which ΔG and ΔH can be calculated, to be easily represented on a single set of axes. The following results were established:

- The g-h plot was used to describe the relationship between heat requirements of a process and the work requirements of a process.
- The gasification and phase change reaction lies in the first quadrant as these reactions are both endothermic, they require heat and work input to be supplied at the Carnot temperature in order for the reactions to be reversible.
- The WGS and combustion reaction lies in the third quadrant region. These reactions reject heat and have the potential to produce work. The heat rejected from these processes could be used to supply the other two reactions so that a balanced heat network is obtained.
- The water gas shift reaction is above the 45° line; where heat and work are rejected, it can therefore be run reversibly by removing heat at the process Carnot temperature.
- On the other hand the combustion reaction lies below the 45° line in the region where processes require that heat be removed at negative Carnot temperatures, which have no physical meaning for them to be reversible, therefore it is irreversible.
- The gasification region is also achievable in the g-h space. As it was with the ε_1- ε_2 space, each component is still in the same position and direction.
- The gasification region lies on the third region where processes reject heat and work and the enthalpy and Gibbs free energy are negative; this is

because the combustion reaction has a big negative ΔH and ΔG because it is exothermic.

- Since the gasification region lies on the third region and below the 45° line, because of the ratio of enthalpy and Gibbs free values the Carnot temperature is negative. In order to move the graph above the 45° line so that we can achieve a positive Carnot temperature, reasonable amount of oxygen needs to be added but the disadvantage is that more cellulose will be consumed, therefore less products (syngas) will be produced. In conclusion the combustion reaction provides more heat and work than is actually needed by the other 3 reactions put together. Therefore the gasification process will be run irreversibly.

Processes where heat and work is required to be added and processes where heat and work is rejected in regions B will always be work deficient irrespective of the temperature at which heat is added and would require additional work input by other means such as pressure work or electro-chemical work and therefore cannot be run as simple processes. Therefore processes where heat and work are rejected in region B will always lose part of their work potential, they will always be irreversible if the only way of work recovery is from the quality of heat by, for example, a heat engine. It should be noted that most combustion reactions have similarly infeasible Carnot temperatures, meaning combustion is irreversible by its very nature and responsible for most irreversibility in processes.

Therefore a general conclusion from this dissertation is that; since the gasification region for biomass is in region B where heat and work are rejected, this signifies that the process is irreversible. This means that in operating the biomass gasifier, we will always operate irreversibly and that work is potentially lost in the form of heat and can be recovered from the gasifier. This is also applicable in the coal gasification.

5.3 Recommendations

Although graphical techniques to biomass gasification have been studied to an extent, more research is needed in this area of the study as it very promising. This graphical techniques has been used to analyze processes at the highest level with only the most basic assumptions, therefore it is important to note that some of the results obtained using this approach may not be practical due to lack of appropriate technology. But the approach could help identify where much improvement is needed and thus where future research should be devoted.

This is a theoretical or fundamental work and in order to make it possible experimental work should be considered where we can run a gasifier at these conditions:

- Mass of feed i.e. cellulose, water and oxygen should be considered as a variable.
- Temperature should be operated between 800ºC to 1200ºC. Although we can run the gasifier at lower temperatures i.e. 100ºC to 700ºC depending

on the desires of the process, larger temperatures are recommended for increased energy and recycle demands. This is because at lower temperatures there will be big recycle streams. Hence this will demand a lot of energy for the recycle and also it means that the conversion is small.

- The ratio of H_2: CO of 2:1 must also be considered as a variable.
- To optimize the process, the feeds need to be changed as it was shown in the previous Chapters 3 and 4.
- In order to obtain or run a gasification process which does not give off carbon dioxide, one has to consider a ratio of H_2: CO of 1:1 at the overall energy balance of :

$$0.52C_6H_{12}O_6 + 0.11O_2 = 0.22H_2O + 2.90H_2 + 3.12CO$$

5.4 Future work

Although graphical technique of biomass gasification has been briefly studied, more research is needed in the area of developing a recycle stream and finding its extents and composition, and then therefore recalculating the number of moles into the reactor. The recycle stream helps when we are working with the process and we want to look at the reactor; to achieve this mass balance, we will need to look at the recycle and work on the components composition since some reaction does not occur to completion. Also the development of a biomass flowsheet must be considered.

In using the graphical techniques simplifying assumptions were made in order to make the calculations simple but the assumptions does not necessarily happen in reality. For example it was assumed that combustion reaction goes to completion, but now let us look at the detailed analysis of the process without the assumption.

- Instead of having a two dimensional space on the ε_1- ε_2 space we will instead have three dimensional spaces which is ε_1 the gasification extent, ε_2 the WGS extent and the ε_3 the combustion reaction.
- With the 3D space, the graphical technique might not make sense or rather it may be difficult to interpret the results therefore it will require that we built the algorithm and find the extents.

Therefore more improvements should be made on the assumptions used since real processes that are limited by current technology or equipment will perform much worse, when compared to the ideal limit, because of the inefficiencies that are associated with these processes.

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Appendices

Appendix A: Mass balance

The following are the three reactions involved in the gasification process, namely gasification reaction, water gas shift and combustion reaction:

- $C_6H_{12}O_6 + H_2O \rightarrow 7H_2 + CO_2 + 5CO$.....$\varepsilon_1$ (A1)
- $CO + H_2O \leftrightarrow CO_2 + H_2$.....$\varepsilon_2$ (A2)
- $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ .....ε_3 (A3)

The molar flowrate of each component involved in the gasification process above is expressed in terms of inequality as follows:

$$N_{CO} = -5\varepsilon_1 + \varepsilon_2 \geq 0 \quad \text{(A4)}$$

$$N_{H_2} = -7\varepsilon_1 - \varepsilon_2 \geq 0 \quad \text{(A5)}$$

$$N_{H_2O} = \varepsilon_1 + \varepsilon_2 - N_{O_2}{}^{o} \geq 0 \quad \text{(A6)}$$

$$N_{C_6H_{12}O_6} = \varepsilon_1 + \frac{1}{6} N_{O_2}{}^{o} \geq 0 \quad \text{(A7)}$$

$$N_{CO_2} = -\varepsilon_1 - \varepsilon_2 - N_{O_2}{}^{o} \geq 0 \quad \text{(A8)}$$

Where the molar flowrate of each component can be defined as feed subtract product as follows:

$$N_i = n_i{}^{o} - n_i \quad \text{(A9)}$$

Now that the reactions and components involved in the gasification process have been defined we will look at the different feed conditions for gasification reaction, they are represented in the Table A1below:

Table A1: Variable amount of feed components in the process.

Feed (moles)	Case1	Case2	Case 3
CO	0	0	0
H_2	0	0	0
H_2O	0.5	0.5	0.5
O_2	0.5	0	0.1
$C_6H_{12}O_6$	1	1	1
CO_2	0	0	0

Since we have three study cases we will therefore use study case 1 to illustrate the calculations involved in constructing a mass balance region. Similar approach can also be used for the remaining case studies. The inequalities in equations A4 to A8 together with the feed will be used to express a mass balance boundary. It can be seen that each inequality equation represents a straight line graph and the values of each component with the given feed will be calculated.

The values of ε_1 are varied while the values for ε_2 are calculated by using the components inequalities equations A4 to A8 shown above. Table A2 shows the values of each component used to construct a mass balance region involved in the gasification of biomass for study case 1.

Table A2: The values of components involved in the construction of the mass balance region.

	CO	H_2	H_20	CO_2	$C_6H_{12}0_6$
e_1	e_2	e_2	e_2	e_2	e_2
0	0	0	1	-0.5	0.917
0.1	0.5	-0.7	0.9	-0.6	0.917
0.2	1	-1.4	0.8	-0.7	0.917
0.3	1.5	-2.1	0.7	-0.8	0.917
0.4	2	-2.8	0.6	-0.9	0.917
0.5	2.5	-3.5	0.5	-1	0.917
0.6	3	-4.2	0.4	-1.1	0.917
0.7	3.5	-4.9	0.3	-1.2	0.917
0.8	4	-5.6	0.2	-1.3	0.917
0.9	4.5	-6.3	0.1	-1.4	0.917
1	5	-7	0	-1.5	0.917
1.1	5.5	-7.7	-0.1	-1.6	0.917
1.2	6	-8.4	-0.2	-1.7	0.917
1.3	6.5	-9.1	-0.3	-1.8	0.917
1.4	7	-9.8	-0.4	-1.9	0.917
1.5	7.5	-10.5	-0.5	-2	0.917
1.6	8	-11.2	-0.6	-2.1	0.917
1.7	8.5	-11.9	-0.7	-2.2	0.917
1.8	9	-12.6	-0.8	-2.3	0.917
1.9	9.5	-13.3	-0.9	-2.4	0.917
2	10	-14	-1	-2.5	0.917

With the values given above the mass balance boundry was plotted in excell spreadsheet.

Appendix B: Energy balance

In the energy balance calculation both the adiabatic and the non-adiabatic case will be considered. Firstly, let us look at the adiabatic case ($\Delta H = 0$) and assume that the temperature in the process is equal with the temperature out, that is $T_{in} = T_{out}$.

In such a situation, the energy balance across the process is given as:

$$\Delta H = 0 \tag{B1}$$

$$\Delta H = H_{products} - H_{reactants} \tag{B2}$$

Then equation B2 will be expressed fully in equation B3, with the unreacted water and biomass in the product stream as follows:

$$N_{C_6H_{12}O_6}{}^{o}.H_{f,C_6H_{12}O_6}\circ + N_{H_2O}\circ.H_{f,H_2O} + N_{O_2}{}^{o}.H_{f,O_2}{}^{o} = N_{C_6H_{12}O_6}.H_{f,C_6H_{12}O_6}\circ + N_{H_2O}.H_{f,H_2O}\circ + N_{H_2}.H_{f,H_2}\circ + N_{CO_2}.H_{f,CO_2}\circ + N_{CO}.H_{f,CO}\circ \tag{B3}$$

Then equation B3 will deduce to B4, where the number of moles which is shown in Appendix A, equation A4 to A8 as inequalities will be substituted into Equation B3 as follows:

$$(-\varepsilon_1 - \frac{1}{6}N_{O_2}\circ).H_{f,C_6H_{12}O_6}\circ + (-\varepsilon_1 - \varepsilon_2 + N_{O_2}\circ).H_{f,H_2O} + (7\varepsilon_1 + \varepsilon_2)H_{f,H_2}\circ + (N_{O_2}\circ + \varepsilon_1 + \varepsilon_2)H_{f,CO_2}\circ + (5\varepsilon_1 - \varepsilon_2)H_{f,CO}\circ = 0 \tag{B4}$$

This then reduces to the final adiabatic energy balance expressed as:

$$\varepsilon_2 = -\varepsilon_1 \frac{\Delta H_{rxn,1}}{\Delta H_{rxn,2}} - \frac{1}{6}\frac{N_{CO_2} \times \Delta H_{comb}}{\Delta H_{rxn,2}} \tag{B5}$$

where $\Delta H_{rxn,1} = -H_{f,C_6H_{12}O_6}{}^{o} - H_{f,H_2O}{}^{o} + H_{f,CO_2}{}^{o} + 5H_{f,CO}{}^{o}$

$\Delta H_{rxn,2} = -H_{f,H_2O}{}^{o} + H_{f,CO_2}{}^{o} - H_{f,CO}{}^{o}$

$\Delta H_{comb} = 6H_{f,H_2O}{}^{o} + 6H_{f,CO_2}{}^{o} - H_{f,C_6H_{12}O_6}{}^{o}$ ….the heat of combustion

Secondly, let us consider a non-adiabatic case where ΔH = Q. Using the same procedure as with the adiabatic case but this time allowing for heat losses into the surroundings, we get the following overall energy balance equation:

$$\Delta H + \Delta U + g\Delta z + \Delta u2/2 = q + w_s \quad \text{(B6)}$$

Where: ΔH is the change in enthalpy

ΔU is the change in internal energy

gΔz is the change in potential energy

Δu2/2 is the change in kinetic energy

q is the heat energy in the system

w_s is the shaft work

The other terms are equals to zero, therefore the energy balance becomes:

$$\Delta H = q \quad \text{(B7)}$$

Equation B7 then yields to equation B8 below where $N_{H2}°$, $N_{CO2}°$ and $N_{CO}°$ are equals to zero since they are products:

$$(N_{C_6H_{12}O_6} - N_{C_6H_{12}O_6}{}^{o}).H_{f,C_6H_{12}O_6}° + (N_{f,H_2O} - N_{f,H_2O}°).H_{f,H_2O} + N_{H_2}H_{f,H_2}° + N_{CO_2}H_{f,CO_2}° + N_{CO}H_{f,CO}° = q \quad \text{(B8)}$$

Where: $H_{f,i}$ is the standard enthalpy of formation of species i

N_i is the number of moles of species i in the product stream

$N_i°$ is the number of mole of species i in the feed stream

Using the inequalities equation in Appendix A to substitute the number of moles in equation B8, this yields the following:

$$(-\varepsilon_1 - \frac{1}{6}N_{O_2}°).H_{f,C_6H_{12}O_6}° + (-\varepsilon_1 - \varepsilon_2 + N_{O_2}°).H_{f,H_2O} + (7\varepsilon_1 + \varepsilon_2)H_{f,H_2}° + (N_{O_2}° + \varepsilon_1 + \varepsilon_2)H_{f,CO_2}° + (5\varepsilon_1 - \varepsilon_2)H_{f,CO}° = q \quad \text{(B9)}$$

This then reduces to the final energy balance expressed as:

$$\varepsilon_2 = q - \varepsilon_1 \frac{\Delta H_{rxn,1}}{\Delta H_{rxn,2}} - \frac{1}{6}\frac{N_{CO_2} \times \Delta H_{comb}}{\Delta H_{rxn,2}} \quad \text{(B10)}$$

where $\Delta H_{rxn,1} = -H_{f,C_6H_{12}O_6}{}^{o} - H_{f,H_2O}{}^{o} + H_{f,CO_2}{}^{o} + 5H_{f,CO}{}^{o}$

$$\Delta H_{rxn,2} = -H_{f,H_2O}{}^{o} + H_{f,CO_2}{}^{o} - H_{f,CO}{}^{o}$$

$\Delta H_{comb} = 6H_{f,H_2O}{}^{o} + 6H_{f,CO_2}{}^{o} - H_{f,C_6H_{12}O_6}{}^{o}$ ….the heat of combustion.

Using the Equations above together with the standard of heat of formation shown in table B1 the energy balance lines were plotted both adiabatic and non-adiabatic.

Table B1: The standard heat of formation of each component in kJ/mol.

Hf_{CO}	Hf_{H2}	$Hf_{H2O(l)}$	Hf_{O2}	$Hf_{C6H12O6}$	Hf_{CO2}
-110.53	0	-285.84	0	-1262.19	-393.51

The values for the non-adiabatic and adiabatic energy balances as expressed by Equation B5 and B10 are calculated in the Table B2 below at the feed of H_2O and

O_2 at 0.5 moles and $C_6H_{12}O_6$ at 1 mole. The value of ε_1 is constant and varied, the table below shows the value of ε_2:

Table B2: The values for adiabatic and non adiabatic energy balance lines in kJ/mol.

ΔH=0	ΔH=q
82.25	4.25
61.14	-16.86
40.03	-37.97
18.92	-59.08
-2.20	-80.20
-23.31	-101.31
-44.42	-122.42
-65.53	-143.53
-86.64	-164.64
-107.75	-185.75
-128.87	-206.87
-149.98	-227.98
-171.09	-249.09
-192.20	-270.20
-213.31	-291.31
-234.42	-312.42
-255.54	-333.54
-276.65	-354.65
-297.76	-375.76
-318.87	-396.87
-339.98	-417.98

With the values obtained the Energy balance graphs for the adiabatic and non-adiabatic was plotted.

For the non-adiabatic graph when the oxygen feed is changed from 0.5 moles to 1 and 2 moles the following values are obtained:

Table B3: The values for non adiabatic energy balance when the oxygen feed is varied in kJ/mol.

ΔH=0 at O_2 = 1 mol	ΔH=0 at O_2 = 2 moles
165.21	330.43
144.53	309.74
123.85	289.06
103.16	268.38
82.48	247.69
61.80	227.00
41.11	206.32
20.42	185.64
-0.26	164.95
-20.94	144.27
-41.63	123.58
-62.31	102.90
-83.01	82.22
-103.68	61.53
-124.36	40.85
-145.05	20.16
-165.73	-0.52
-186.42	-21.20
-207.10	-41.89
-227.78	-62.57
-248.47	-83.26

Appendix C: Gibbs free energy balance

By performing a Gibbs free energy balance across the overall process, one can determine the work flows in the process. It is assumed that the components enter and leave at the temperature of 298 K and the pressure of 1atm. Therefore:

$\Delta G = 0$ (C1)

The same procedure with energy balance will be applied to derive the Gibbs free energy balance equations as shown below:

$$(N_{C_6H_{12}O_6} - N_{C_6H_{12}O_6}{}^{o}).G_{f,C_6H_{12}O_6}\circ + (N_{f,H_2O} - N_{f,H_2O}\circ).G_{f,H_2O} + N_{H_2}.G_{f,H_2}\circ + N_{CO_2}.G_{f,CO_2}\circ + N_{CO}.G_{f,CO}\circ = 0 \quad \text{(C2)}$$

Where: $G_{f,i}$ is the Gibbs free energy of formation of species i

N_i is the number of moles of species i in the product stream

$N_i\circ$ is the number of mole of species i in the feed stream

When simplifying the Gibb Free energy balance in Equation C2 together with the inequality equations from Appendix A, Equation A4 to A8, Equation C3 is obtained:

$$\varepsilon_2 = -\varepsilon_1 \frac{\Delta G_{rxn,1}}{\Delta G_{rxn,2}} - \frac{1}{6}\frac{N_{CO_2} \times \Delta G_{comb}}{\Delta G_{rxn,2}} \quad \text{(C3)}$$

Where: $\Delta G_{rxn,1} = -G_{f,C_6H_{12}O_6}{}^{o} - G_{f,H_2O}{}^{o} + G_{f,CO_2}{}^{o} + 5G_{f,CO}{}^{o}$

$$\Delta G_{rxn,2} = -G_{f,H_2O}{}^{o} + G_{f,CO_2}{}^{o} - G_{f,CO}{}^{o}$$

$$\Delta G_{comb} = 6G_{f,H_2O}{}^{o} + 6G_{f,CO_2}{}^{o} - G_{f,C_6H_{12}O_6}{}^{o}$$

The equations above together with the standard of heat of formation shown in Table C1 were used to plot the Gibbs free energy balance lines as shown below:

Table C1: The Gibbs free energy of formation values in kJ/mol.

Gf_{CO}	Gf_{H2}	$Gf_{H2O(l)}$	Gf_{O2}	Gf_{C6}	Gf_{CO2}
-137.27	0	-237.19	0	-915.9	-394.38

The values of Gibbs free energy balance line that are calculated by using Equation C3 are shown below:

Table C2: Gibbs free energy values in kJ/mol.

ΔG = 0
-12.02
-11.66
-11.30
-10.93
-10.57
-10.20
-9.84
-9.48
-9.11
-8.75
-8.39
-8.02
-7.66
-7.30
-6.93
-6.57
-6.21
-5.85
-5.48
-5.12
-4.76

With the calculated values in Table above the Gibbs free energy balance line was then plotted.

Appendix D: The effect of temperature on reaction equilibrium

Thermodynamics will be used to calculate the value of the equilibrium constant at any given temperature.The equilibrium constant at any temperature T using van't Hoff equation can be calculated as follows:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^0_{rxn}(T)}{RT^2} \qquad \text{(D1)}$$

where ΔH^0_{rxn} is the Enthalpy of the WGS reaction and is a function of temperature

R is the gas constant

T is temperature

K is the equilibrium constant

The van't Hoff equation in equation (D1) with the limits of the integral T_o and T_f, which are at 25ºC and 1000ºC respectively can be simplified as follows:

$$K(T) = \exp\left[In(K^\circ) + \int_{T0}^{Tf} \frac{\Delta H_{rxn}(T)}{RT^2} dT \right] \qquad \text{(D2)}$$

Where the equilibrium constant Kº can be expressed in terms of the Gibbs free energy of formation (G_{rxn}°) , temperature(T) and the gas constant(R) as follows:

$$K^\circ = \exp\left[\frac{-\Delta G_{rxn}^\circ}{RT^\circ} \right] \qquad \text{(D3)}$$

After calculating the equilibrium constant, the equilibrium constant expression for the water gas shift and the gasification reaction can be represented as follows:

$$K_{WGS} = \frac{[CO_2][H_2]}{[CO][H_2O]} \tag{D4}$$

$$K_{GASF} = \frac{[CO_2][CO]^5[H_2]^7}{[H_2O]} \tag{D5}$$

Each of the concentration expressed above depends on the value of extent of reaction 1(ε_1)and hence this value is a parameter. The equation above can be substituted by inequality mole balance equations in Appendix A, reaction A4 to A8 to give equation (D6) and (D7) respectively:

$$K_{WGS} = \frac{\left[N_{O_2}\circ + \varepsilon_1 + \varepsilon_2\right][7\varepsilon_1 + \varepsilon_2]}{[5\varepsilon_1 - \varepsilon_2]\left[N_{H_2O} - \varepsilon_1 - \varepsilon_2 + N_{O_2}\circ\right]} \tag{D6}$$

$$K_{GASF} = \frac{\left[N_{O_2}\circ + \varepsilon_1 + \varepsilon_2\right][5\varepsilon_1 - \varepsilon_2]^5[7\varepsilon_1 + \varepsilon_2]^7}{\left[N_{H_2O} - \varepsilon_1 - \varepsilon_2 + N_{O_2}\circ\right]} \tag{D7}$$

These then simplify to Equations (D8) and (D9) below, respectively:

$$\begin{aligned}&(K-1).\varepsilon_2^{\,2} + \left(-K.N_{H2O}{}^{o} - 4.K.\varepsilon_1 - K.N_{O2}{}^{o} - N_{O2}{}^{o} - 8.\varepsilon_1\right).\varepsilon_2 \\ &\quad + \left[\left(5.K.N_{H_2O}{}^{o} + 5.K.N_{O_2}{}^{o} - 7.N_{O_2}{}^{o}\right).\varepsilon_1 + \left(-5.K - 7\right).\varepsilon_1^{\,2}\right] = 0\end{aligned} \tag{D8}$$

$$\begin{aligned}&\left(N_{O2}{}^{o} + \varepsilon_1 + \varepsilon_2\right)(7.\varepsilon_1 + \varepsilon_2)^7.(5.\varepsilon_1 - \varepsilon_2)^5 \\ &\quad - K.N_{H_2O}{}^{o} + K.\varepsilon_1 + K.\varepsilon_2 - K.N_{O_2}{}^{o} = 0\end{aligned} \tag{D9}$$

Equation D9 is assumed to react to completion because the equilibrium constant K is large, therefore by using equation D8 the reaction equilibrium will be determined for the water gas shift reaction by varying the temperature and using the solver in excel, the calculations are shown in the table below from 100º-1000ºC:

Table D1: The effect of temperature on equilibrium from 100º to 1000ºC.

100 °C		
ε_1	ε_2	**guess value**
-1	4.39231E-07	1.99919523
-0.9	-4.57389E-07	1.899225377
-0.8	7.39346E-08	1.799261765
-0.7	7.94753E-07	1.699306557
-0.6	4.14014E-07	1.599363042
-0.5	-1.26055E-07	1.499436487
-0.4	-8.07067E-08	1.399535879
-0.3	2.41283E-07	1.29967791
-0.2	-6.07353E-07	1.199897497
-0.1	6.77678E-07	-0.500056381
0	0	0
0.1	-2.01351E-07	0.497546302
0.2	-3.48547E-07	0.788432606
0.3	-3.0294E-07	0.696090477
0.4	-1.25359E-07	0.59727553
0.5	-5.1217E-07	0.49775322
0.6	-1.74658E-07	0.398011152
0.7	-4.07523E-07	0.298172588
0.8	-6.29998E-07	0.198283138
0.9	-5.70799E-08	0.098363583
1	-6.4353E-07	-0.001575253

200 °C		
ε_1	ε_2	**guess**
-1	6.26458E-07	1.704443
-0.9	2.13468E-07	1.611282
-0.8	2.58154E-07	1.519867
-0.7	1.90315E-07	1.430954
-0.6	-4.678E-07	1.345804
-0.5	-1.5486E-07	1.266673
-0.4	-2.8685E-07	1.197994
-0.3	-3.79E-07	1.149604
-0.2	8.39145E-07	1.147033
-0.1	7.45371E-07	-0.53063
0	0	0
0.1	-3.4392E-07	0.19108
0.2	-9.3684E-07	0.215062
0.3	-6.3964E-08	0.177278
0.4	-2.9949E-08	0.113615
0.5	-4.3414E-07	0.037197
0.6	3.82162E-07	-0.04634
0.7	-1.4106E-07	-0.13421
0.8	-5.6707E-07	-0.22492
0.9	-7.1778E-07	-0.31759
1	5.15738E-07	-0.41165

250°C		
ε_1	ε_2	guess
-1	1.37E-07	0.676214
-0.9	4.66E-07	0.574239
-0.8	4.84E-07	0.471762
-0.7	4.68E-07	0.368568
-0.6	5.23E-07	0.264293
-0.5	2.43E-07	0.158283
-0.4	3.36E-08	0.049231
-0.3	-2.07E-07	-0.06588
-0.2	-3.89E-07	-0.19567
-0.1	5.03E-07	-0.37445
0	0.00E+00	0
0.1	5.37E-07	-0.27797
0.2	3.84E-07	-0.43065
0.3	7.04E-07	-0.55327
0.4	7.62E-07	-0.6656
0.5	8.07E-07	-0.77331
0.6	4.07E-07	-0.87858
0.7	9.99E-07	-0.9824
0.8	8.19E-07	-1.0853
0.9	6.14E-07	-1.18757
1	4.09E-07	-1.2894

300°C		
ε_1	ε_2	guess
-1	5.21162E-07	0.508354
-0.9	7.68613E-07	0.408202
-0.8	5.99406E-07	0.308016
-0.7	6.02308E-08	0.207782
-0.6	4.19968E-09	0.10748
-0.5	9.45645E-07	0.007073
-0.4	3.44147E-07	-0.09351
-0.3	-6.5279E-07	-0.19439
-0.2	3.00075E-07	-0.2959
-0.1	-4.8673E-07	-0.39909
0	0	0
0.1	3.4566E-07	-0.53881
0.2	5.05215E-07	-0.67737
0.3	7.01519E-07	-0.78303
0.4	7.5821E-07	-0.88523
0.5	3.59304E-07	-0.98639
0.6	6.51605E-07	-1.08711
0.7	4.38476E-07	-1.1876
0.8	7.47929E-07	-1.28796
0.9	6.75191E-07	-1.38823
1	8.38139E-07	-1.48844

400 °C		
ε_1	ε_2	guess
-1	8.60E-07	5.00E-01
-0.9	7.28E-07	4.00E-01
-0.8	2.95E-07	3.00E-01
-0.7	1.03E-07	2.00E-01
-0.6	1.21E-11	1.00E-01
-0.5	-3.34E-07	1.33E-05
-0.4	2.39E-07	-1.00E-01
-0.3	-8.45E-07	-2.00E-01
-0.2	6.21E-07	-3.00E-01
-0.1	-9.58E-07	-4.00E-01
0	0.00E+00	0.00E+00
0.1	9.84E-07	-6.00E-01
0.2	9.66E-07	-7.00E-01
0.3	3.42E-07	-8.00E-01
0.4	6.39E-07	-9.00E-01
0.5	5.30E-07	-1.00E+00
0.6	2.36E-07	-1.10E+00
0.7	6.32E-07	-1.20E+00
0.8	9.50E-07	-1.30E+00
0.9	7.75E-07	-1.40E+00
1	8.15E-07	-1.50E+00

1000 °C		
ε_1	ε_2	guess
-1	1.00E+00	0.657669
-0.9	1.00E+00	0.574662
-0.8	1.00E+00	0.495854
-0.7	1.00E+00	0.423382
-0.6	9.99E-01	0.360289
-0.5	1.00E+00	0.313797
-0.4	1.00E+00	0.299937
-0.3	1.00E+00	0.382078
-0.2	7.22E-01	0.571
-0.1	-3.17E+25	5.63E+12
0	6.25E-02	-0.251
0.1	8.19E-04	-0.691
0.2	1.08E-01	-1.171
0.3	3.51E-01	-1.71803
0.4	-5.91E+25	-7.7E+12
0.5	1.00E+00	-1.49998
0.6	9.99E-01	-1.46547
0.7	1.00E+00	-1.49342
0.8	1.00E+00	-1.54659
0.9	9.99E-01	-1.61325
1	9.99E-01	-1.68813

With the values calculated on the tables above the effect of temperature on equilibrium graph was plotted.

Appendix E: Gasification on the g-h space

The g-h plot will now be used to describe the relationship between heat requirements of a process and the work requirements of a process. This will be done by first defining the equations that plays an important role in the process and then calculating ΔH and ΔG for each gasification reactions. The following reactions will take place in the process:

- $C_6H_{12}O_6 + H_2O \rightarrow 7H_2 + CO_2 + 5CO$.....$\varepsilon_1$ (E1)
- $CO + H_2O \leftrightarrow CO_2 + H_2$.....$\varepsilon_2$ (E2)
- $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ .....ε_3 (E3)

These reactions will occur at the following feed conditions:

Table E1: Feed conditions for a gasification process.

FEED	**(moles)**
CO	0
H_2	0
H_2O	0.5
O_2	0.5
$C_6H_{12}O_6$	1
CO_2	0

To calculate the heat and work requirement of a process the enthalpy of formation and the Gibbs free energy of formation are used as shown in the Table E2:

Table E2: The enthalpy and Gibbs free energy of formation in kJ/mol.

$\mathbf{Hf_{CO}}$	$\mathbf{Hf_{H2}}$	$\mathbf{Hf_{H2O}}$	$\mathbf{Hf_{O2}}$	$\mathbf{Hf_{C6H12O6}}$	$\mathbf{Hf_{CO2}}$
-110.525	0	-241.826	0	-1262.19	-393.514
$\mathbf{Gf_{CO}}$	$\mathbf{Gf_{H2}}$	$\mathbf{Gf_{H2O}}$	$\mathbf{Gf_{O2}}$	$\mathbf{Gf_{C6H12O6}}$	$\mathbf{Gf_{CO2}}$
-137.269	0	-228.593	0	-915.9	-394.384

Table E3: Heat and work requirements of each reaction in kJ/mol.

ΔH_{rxn1}	557.877	ΔG_{rxn1}	63.764
ΔH_{rxn2}	-41.163	ΔG_{rxn2}	-28.522
ΔH_{rxn3}	-2549.85	ΔG_{rxn3}	-2821.96
ΔH_{rxn4}	44.01	ΔG_{rxn4}	8.56

In order to represent all the reactions on the g-h plot, the following Matlab programming code was used and when it has run according to the heat and work requirement of each reaction it will give a plot on the g-h space with their respective Carnot temperatures.

```
%Plot for the temperature scale
%Units are in kJ/mol
deltaH1 = 557.877;
deltaH2 = -41.163;
deltaH3 = -2549.85;
deltaH4 = 44.01;

deltaG1 = 63.764;
deltaG2 = -28.522;
deltaG3 = -2821.6;
deltaG4 = 8.56;
tscale(3000);
plot( deltaH1,deltaG1, 'ro')
plot( deltaH2,deltaG2, 'ro')
plot( deltaH3,deltaG3, 'ro')
plot( deltaH4,deltaG4, 'ro')
```

The Carnot temperature of each reaction is as follows:

Table E4: Reaction Carnot Temperatures.

Reactions	**Carnot temperatures**
Gasification	362K
WGS	995K
Combustion	-1565K
Phase Change	639K

Now that the individual reactions are represented on the g-h plot we will look at the reaction line for all the independent gasification reaction by plotting the

overall ΔH_{rxn} and ΔG_{rxn} over a range of extents, e_1 is kept constant and varied while e_2, e_3 and e_4 are calculated by their respective equation as shown below.

Since we are assuming that we are feeding 1mole of $C_6H_{12}O_6$:

$$\varepsilon_3 + \varepsilon_1 = 1 \quad \text{(E4)}$$

For the 2:1 ratio of H_2: CO:

$$\varepsilon_1 = \varepsilon_2 \quad \text{(E5)}$$

And finally the mass balance on the phase change:

$$\varepsilon_4 = 8*\varepsilon_1 - 6 \quad \text{(E6)}$$

The following equations are used to plot reaction line for all the gasification reactions.

- $\Delta H°_{rxn} = \varepsilon_1 * \Delta H°_{rxn1} + \varepsilon_2 * \Delta H°_{rxn2} + \varepsilon_3 * \Delta H°_{rxn3} + \varepsilon_4 * \Delta H°_{rxn4}$ (E7)
- $\Delta G°_{rxn} = \varepsilon_1 * \Delta G°_{rxn1} + \varepsilon_2 * \Delta G°_{rxn2} + \varepsilon_3 * \Delta G°_{rxn3} + \varepsilon_4 * \Delta G°_{rxn4}$ (E8)

The values of the reaction lines are shown in Table E5 which are then used to plot a reaction line graph.

Table E5: Values for reaction lines for all independent gasification reactions.

ε_1	ε_2	ε_3	ε_4	ΔH	ΔG
0	0	1	-6	-2813.91	-7183.82
0.1	0.1	0.9	-5.2	-2472.05	-6505.8
0.2	0.2	0.8	-4.4	-2130.18	-5827.78
0.3	0.3	0.7	-3.6	-1788.32	-5149.76
0.4	0.4	0.6	-2.8	-1446.45	-4471.75
0.5	0.5	0.5	-2	-1104.59	-3793.73
0.6	0.6	0.4	-1.2	-762.724	-3115.71
0.7	0.7	0.3	-0.4	-420.86	-2437.69
0.8	0.8	0.2	0.4	-78.99	-1759.67
0.9	0.9	0.1	1.2	262.87	-1081.66
1	1	0	2	604.73	-403.64

Mass balance on the g-h plot

To illustrate the use of the g-h plot, we will consider the mass balance. It is similar to the one expressed in Appendix A but the difference is that it will be done on the g-h plot.

The equation E4 to E6 will be used together with equation E7 to E8 and the inequality equations A4 to A8 in Appendix A to formulate a mass balance equation in the g-h plot. Using all these equations a gasification region in the g-h space can be obtained with the values as shown in Table E6 for each component involved in the reaction.

Table E6: The values for the gasification region on the g-h plot.

CO line					
ε_1	ε_2	ε_3	ε_4	**ΔH**	**ΔG**
0	0	1	-6	-2813.91	-7183.82
0.1	0.5	0.9	-5.2	-2488.51	-6621.24
0.2	1	0.8	-4.4	-2163.11	-6058.66
0.3	1.5	0.7	-3.6	-1837.71	-5496.07
0.4	2	0.6	-2.8	-1512.31	-4933.49
0.5	2.5	0.5	-2	-1186.91	-4370.91
0.6	3	0.4	-1.2	-861.515	-3808.33
0.7	3.5	0.3	-0.4	-536.116	-3245.75
0.8	4	0.2	0.4	-210.716	-2683.17
0.9	4.5	0.1	1.2	114.6828	-2120.58
1	5	0	2	440.082	-1558

H_2 line					
ε_1	ε_2	ε_3	ε_4	**ΔH**	**ΔG**
0	0	1	-6	-2813.91	-7183.82
0.1	-0.7	0.9	-5.2	-2439.12	-6274.93
0.2	-1.4	0.8	-4.4	-2064.32	-5366.04
0.3	-2.1	0.7	-3.6	-1689.53	-4457.15
0.4	-2.8	0.6	-2.8	-1314.73	-3548.25
0.5	-3.5	0.5	-2	-939.936	-2639.36
0.6	-4.2	0.4	-1.2	-565.141	-1730.47
0.7	-4.9	0.3	-0.4	-190.346	-821.581
0.8	-5.6	0.2	0.4	184.4484	87.3107
0.9	-6.3	0.1	1.2	559.2432	996.202
1	-7	0	2	934.038	1905.093

H_2O line					
ε_1	ε_2	ε_3	ε_4	**ΔH**	**ΔG**
0	1	1	-6	-2855.07	-7472.41
0.1	0.9	0.9	-5.2	-2504.98	-6736.67
0.2	0.8	0.8	-4.4	-2154.88	-6000.94
0.3	0.7	0.7	-3.6	-1804.78	-5265.2
0.4	0.6	0.6	-2.8	-1454.69	-4529.46
0.5	0.5	0.5	-2	-1104.59	-3793.73
0.6	0.4	0.4	-1.2	-754.491	-3057.99
0.7	0.3	0.3	-0.4	-404.394	-2322.26
0.8	0.2	0.2	0.4	-54.297	-1586.52
0.9	0.1	0.1	1.2	295.8	-850.782
1	0	0	2	645.897	-115.046

$C_6H_{12}O_6$ line					
ε_1	ε_2	ε_3	ε_4	ΔH	ΔG
0.916667	-14	0.083333	1.333333	933.8618	3336.168
0.916667	-12	0.083333	1.333333	851.5358	2758.985
0.916667	-10	0.083333	1.333333	769.2098	2181.803
0.916667	-8	0.083333	1.333333	686.8838	1604.62
0.916667	-6	0.083333	1.333333	604.5578	1027.438
0.916667	-4	0.083333	1.333333	522.2318	450.2549
0.916667	-2	0.083333	1.333333	439.9058	-126.928
0.916667	0	0.083333	1.333333	357.5798	-704.11
0.916667	2	0.083333	1.333333	275.2538	-1281.29
0.916667	4	0.083333	1.333333	192.9278	-1858.48
0.916667	6	0.083333	1.333333	110.6018	-2435.66

CO_2 line					
ε_1	ε_2	ε_3	ε_4	ΔH	ΔG
0	-0.5	1	-6	-2793.33	-7039.52
0.1	-0.6	0.9	-5.2	-2443.23	-6303.79
0.2	-0.7	0.8	-4.4	-2093.13	-5568.05
0.3	-0.8	0.7	-3.6	-1743.04	-4832.31
0.4	-0.9	0.6	-2.8	-1392.94	-4096.58
0.5	-1	0.5	-2	-1042.84	-3360.84
0.6	-1.1	0.4	-1.2	-692.747	-2625.1
0.7	-1.2	0.3	-0.4	-342.65	-1889.37
0.8	-1.3	0.2	0.4	7.4475	-1153.63
0.9	-1.4	0.1	1.2	357.5445	-417.895
1	-1.5	0	2	707.6415	317.8412

The effect of temperature in the gasifier on the g-h plot

Temperature effect will be considered and their effect will be examined on a gasifier. This will be done by considering the specific heat capacity on the reaction with change in temperature and how it affects the gasification region. The enthalpy and the Gibbs free energy are calculated using the following equations:

$$\Delta H_{rxn}(T) = \Delta H_{rxn}° + \int C_p dT \quad \text{(E9)}$$

Where:

- $\Delta H_{rxn}°$ is the change in heat of formation at standard conditions
- C_p is the specific heat capacity
- dT is change in temperature

$$\Delta G_{rxn} = -R * T * InK_{eq} \quad \text{(E10)}$$

Where:

- $\Delta G_{rxn}°$ is the change Gibbs free energy of formation at standard conditions
- R is the gas constant
- T is temperature
- K_{eq} is the Equilibrium Constant for Reaction

The temperature was varied from 100ºC to 1000ºC and the specific heat constant Cp will be calculated as follows and their values are shown in Table E7;

$$Cp = a + bT + cT^2 + dT^3 \quad \text{(E11)}$$

Table E7: The values of the specific heats constants of each component in kJ/mol.

	a	**b**	**c**	**d**
CO_2	3.61E-02	4.23E-05	-2.9E-08	7.46E-12
H_2	2.88E-02	7.65E-08	3.29E-09	-8.70E-13
CO	2.90E-02	4.11E-06	3.55E-09	-2.22E-12
O_2	2.91E-02	1.16E-05	-6.1E-09	1.31E-12
H_2O	3.35E-02	6.88E-06	7.60E-09	-3.59E-12

The specific heats constant for the cellulose are as follows:

Table E8: Specific heat for cellulose at different temperatures.

Cp $C_6H_{12}O_6$ @25°C	0.224169
Cp $C_6H_{12}O_6$ @100°C	0.295888
Cp $C_6H_{12}O_6$ @150°C	0.350669
Cp $C_6H_{12}O_6$ @200°C	0.411036
Cp $C_6H_{12}O_6$ @250°C	0.444734
Cp $C_6H_{12}O_6$ @300°C	0.548889
Cp $C_6H_{12}O_6$ @400°C	0.709087
Cp $C_6H_{12}O_6$ @500°C	0.89181
Cp $C_6H_{12}O_6$ @800°C	1.1
Cp $C_6H_{12}O_6$ @1200°C	1.5

The heat of formation for the enthalpy and Gibbs free energy represented in Table E2 were also used to calculate the heat and the Gibbs free energy of formation at standard conditions for each reaction in the gasification process. The values of the change in heat of formation at standard conditions for each reaction are shown in Table E9.

Table E9: The change in heat of formation at standard conditions.

	$H°_f$	**$G°_f$**
Gaification reaction	557.877	63.764
WG reaction	-41.163	-28.522
Combustion reaction	-2549.85	-2821.96

With the value given in the tables above the effect of temperature on the gasifier was plotted and the values of each component at 800ºC are shown. The values are ranged according to the change in Temperature but we will show the values at 800ºC.

Table E10: The values of the effect of temperature on the gasifier at 800ºC.

Feed	NCO = 0			
ε_1	**ε_2**	**ε_3**	**H**	**G**
0	0	2	-5794.64	-3728.12
0.1	0.5	1.9	-5499.51	-3453.81
0.2	1	1.8	-5204.39	-3179.5
0.3	1.5	1.7	-4909.26	-2905.19
0.4	2	1.6	-4614.13	-2630.88
0.5	2.5	1.5	-4319.01	-2356.57
0.6	3	1.4	-4023.88	-2082.25
0.7	3.5	1.3	-3728.75	-1807.94
0.8	4	1.2	-3433.63	-1533.63
0.9	4.5	1.1	-3138.5	-1259.32
1	5	1	-2843.38	-985.008
1.1	5.5	0.9	-2548.25	-710.696
1.2	6	0.8	-2253.12	-436.385
1.3	6.5	0.7	-1958	-162.073
1.4	7	0.6	-1662.87	112.2384
1.5	7.5	0.5	-1367.74	386.55
1.6	8	0.4	-1072.62	660.8616
1.7	8.5	0.3	-777.489	935.1732
1.8	9	0.2	-482.362	1209.485
1.9	9.5	0.1	-187.236	1483.796
2	10	0	107.8909	1758.108

Feed	$NH_2 = 0$			
ε_1	**ε_2**	**ε_3**	**H**	**G**
0	0	2	-5794.64	-3728.12
0.1	-0.7	1.9	-5457.51	-3419.59
0.2	-1.4	1.8	-5120.37	-3111.05
0.3	-2.1	1.7	-4783.24	-2802.51
0.4	-2.8	1.6	-4446.1	-2493.97
0.5	-3.5	1.5	-4108.97	-2185.43
0.6	-4.2	1.4	-3771.83	-1876.9
0.7	-4.9	1.3	-3434.7	-1568.36
0.8	-5.6	1.2	-3097.56	-1259.82
0.9	-6.3	1.1	-2760.43	-951.282
1	-7	1	-2423.29	-642.744
1.1	-7.7	0.9	-2086.16	-334.206
1.2	-8.4	0.8	-1749.02	-25.668
1.3	-9.1	0.7	-1411.89	282.87
1.4	-9.8	0.6	-1074.75	591.408
1.5	-10.5	0.5	-737.618	899.946
1.6	-11.2	0.4	-400.483	1208.484
1.7	-11.9	0.3	-63.3478	1517.022
1.8	-12.6	0.2	273.7871	1825.56
1.9	-13.3	0.1	610.922	2134.098
2	-14	0	948.0569	2442.636

Feed	$NH_2O = 0.5$			
ε_1	**ε_2**	**ε_3**	**H**	**G**
0	1.5	2	-5847.15	-3770.91
0.1	1.4	1.9	-5531.02	-3479.48
0.2	1.3	1.8	-5214.89	-3188.06
0.3	1.2	1.7	-4898.76	-2896.63
0.4	1.1	1.6	-4582.63	-2605.21
0.5	1	1.5	-4266.5	-2313.78
0.6	0.9	1.4	-3950.37	-2022.36
0.7	0.8	1.3	-3634.24	-1730.93
0.8	0.7	1.2	-3318.11	-1439.51
0.9	0.6	1.1	-3001.97	-1148.08
1	0.5	1	-2685.84	-856.659
1.1	0.4	0.9	-2369.71	-565.234
1.2	0.3	0.8	-2053.58	-273.809
1.3	0.2	0.7	-1737.45	17.6154
1.4	0.1	0.6	-1421.32	309.0402
1.5	0	0.5	-1105.19	600.465
1.6	-0.1	0.4	-789.059	891.8898
1.7	-0.2	0.3	-472.929	1183.315
1.8	-0.3	0.2	-156.798	1474.739
1.9	-0.4	0.1	159.3328	1766.164
2	-0.5	0	475.4635	2057.589

Feed	$NCO_2 = 0$			
ε_1	**ε_2**	**ε_3**	**H**	**G**
0	-1	2	-5759.63	-3699.6
0.1	-1.1	1.9	-5443.5	-3408.18
0.2	-1.2	1.8	-5127.37	-3116.75
0.3	-1.3	1.7	-4811.24	-2825.33
0.4	-1.4	1.6	-4495.11	-2533.9
0.5	-1.5	1.5	-4178.98	-2242.48
0.6	-1.6	1.4	-3862.85	-1951.05
0.7	-1.7	1.3	-3546.72	-1659.63
0.8	-1.8	1.2	-3230.59	-1368.2
0.9	-1.9	1.1	-2914.46	-1076.78
1	-2	1	-2598.33	-785.354
1.1	-2.1	0.9	-2282.2	-493.929
1.2	-2.2	0.8	-1966.07	-202.504
1.3	-2.3	0.7	-1649.93	88.9204
1.4	-2.4	0.6	-1333.8	380.3452
1.5	-2.5	0.5	-1017.67	671.77
1.6	-2.6	0.4	-701.542	963.1948
1.7	-2.7	0.3	-385.411	1254.62
1.8	-2.8	0.2	-69.2807	1546.044
1.9	-2.9	0.1	246.8501	1837.469
2	-3	0	562.9808	2128.894

Feed	$C_6H_{12}O_6 = 2$			
ε_1	ε_2	ε_3	H	G
1.833333	-1	0.166667	-28.0831	1590.896
1.833333	-0.8	0.166667	-35.0845	1585.191
1.833333	-0.6	0.166667	-42.0859	1579.487
1.833333	-0.4	0.166667	-49.0872	1573.782
1.833333	-0.2	0.166667	-56.0886	1568.078
1.833333	0	0.166667	-63.09	1562.374
1.833333	0.2	0.166667	-70.0914	1556.669
1.833333	0.4	0.166667	-77.0928	1550.965
1.833333	0.6	0.166667	-84.0942	1545.26
1.833333	0.8	0.166667	-91.0955	1539.556
1.833333	1	0.166667	-98.0969	1533.852
1.833333	1.2	0.166667	-105.098	1528.147
1.833333	1.4	0.166667	-112.1	1522.443
1.833333	1.6	0.166667	-119.101	1516.738
1.833333	1.8	0.166667	-126.102	1511.034
1.833333	2	0.166667	-133.104	1505.33
1.833333	2.2	0.166667	-140.105	1499.625
1.833333	2.4	0.166667	-147.107	1493.921
1.833333	2.6	0.166667	-154.108	1488.216
1.833333	2.8	0.166667	-161.109	1482.512
1.833333	3	0.166667	-168.111	1476.808