A thermodynamic approach to biogas production

By

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Declaration

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Abstract

This dissertation determines theoretical targets for producing biogas. Calculations were based on the relationship between the mass of substrate used (assumed to be glucose) versus the amount and composition of gas produced. Methane, hydrogen and carbon dioxide were considered as gases produced by biogas processes. The calculations undertaken to determine the production rates and environmental targets of the biogas production system were based on mass and energy balances as well as the second law of thermodynamics. These were applied to determine the limits of performance of the process. These limits are important due to the fact that they cannot be exceeded even if we genetically engineer organisms or change the equipment design or operation. Combining the results enabled us to plot an attainable region that showed the achievable composition of the gas as well as the minimum work and energy requirements for biogas production. It shows that the process is hydrogen and enthalpy (heat) limited. Furthermore the results show that a maximum of 3 moles of methane per mole of glucose are produced sustainably which in turn produces a large heat load of 142 kJ/mol of glucose.

***Key words*:** Thermodynamics, Glucose, Biogas production, Limits, Methane, Carbon Dioxide, Hydrogen, Digester, Biomass, Anaerobic.

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Chapter 1: Introduction

1.1. Dissertation Outline

The outline of this Masters Dissertation is as follows:

The scope of the project is discussed in Chapter 1 where the reasons to why it is important to study the thermodynamics of biogas production are discussed. This section also outlines the research questions in this study and the scientific contribution of the results obtained.

In Chapter 2, the literature review provides information on the background of biogas. It shows the mechanism of biogas production as well as the benefits of using biogas as a renewable source of energy. Several factors that affect the biomethanation process are also explained.

Chapter 3 outlines the theoretical procedure used to obtain the results. It shows the major reactions that take place in biogas production and how these reactions were used with thermodynamic data to obtain mass and energy limits. It also illustrates a series of mathematical calculations used to obtain the attainable regions using the overall mass balance.

The results obtained showing the limitations of biogas production are shown graphically in Chapter 4. The logical reasoning and justification of the findings is well explained in this section. This is mainly centred on mass, energy considerations and environmental sustainability.

Chapter 5 summarises the important findings of this research project. It also shows the need for future research on experimental work to undertake.

1.2.Executive Introduction

Currently, a great deal of research is being focused on the production of biogas by breaking down biomass material in the absence of oxygen (Steinhauser and Deublein, 2011; Ashrafi *et al*., 2008). The main reasons for the interest in developing biogas technology are due to concerns around global warming, the resulting attempts to limit CO_2 emissions, and a growing awareness of the decline in conventional fossil fuel reserves (Teodorita *et al*., 2008). There is also a need to make society sustainable by looking at alternative sources and design of efficient processes. The alternative sources of energy under development include electricity produced by generators combusting organic fuels such as biogas, biodiesel, biopetrol, wind, hydro and solar energy. However, biodiesel and biopetrol are expensive, and are available mainly in urban areas. Solar panels have potential as alternative sources and have very low operating costs, but the price of installation is still costly (IEA, 2013). This leaves us with biogas, which offers a feasible method of bringing energy within the means of ordinary people, wherever they may live.

Biodigestion is not a new idea. Biogas was used over 200 years ago for gas street lights in the more developed countries before electricity became available (re.energy.ca, 2003-2011; Meynell, 1976; McCabe and Eckenfelder, 1957). However since then little interest or capital has been devoted to developing biogas production technology, especially in African states. In most African nations, this was mainly due to the communities being reluctant to change from mineral/non-renewable to renewable energies. In addition to this, there was lack of financial means coupled with a complex process of decision making involved when moving from traditional practices (firewood/coal burning) to a modern way of producing energy sustainably. Mauritz Lindeque, a biodigester specialist from CSIR, Pretoria, South Africa

confirmed the resistance in trying to bring the biodigester technology to South Africa via a Skype video conversation in May 2012 with Engineers Without Borders-Witwatersrand University, South Africa. He stated that the South African government was not willing to approve this technology as they argued saying that it was not the way forward to end electricity problems in the country (Personal Communication, May 2012). However, a change in attitude is being brought about through research and education. This has led to establishment of the National Biogas Platform as a key resolution of the 2013 National Biogas Conference to address the lessons learnt from existing biogas projects (National Biogas Platform, 2013). One of the aims of the platform is to reveal and bundle the financing options for the biogas projects in order to lift up the industry.

In many developing nations like India, Indonesia and China, use of biogas as a source of clean energy has become very popular, and it is probable that African countries will soon recognise the merits of biogas as means to address their energy and waste management problems. There has been a growth in thermodynamic studies on chemical process as a way of increasing efficiency. This has led to the successful operation of many processes, the Haber process, methanol synthesis process and a lot other processes. However this approach has not been applied to the biogas processes hence the necessity to carry out this research. The long-term aim of biogas research is to create a greener earth by developing a renewable source of energy from waste materials that simultaneously reduces greenhouse gas emissions.

1.3. Application of Thermodynamics

One of the aims of this study was to apply the general laws of thermodynamics to the biological systems. Thermodynamics can be used as a powerful tool for setting and evaluating process and environmental targets (Patel *et al*., 2005). It has also been applied to

understanding microbial processes (Roels, 1983 & Westerhoff et al., 1982). Numerous thermodynamic studies of other processes have been made and have been shown to be applicable in chemical process synthesis and design, for example the fermentation of lactose and methanol synthesis (Griffiths, 2013), but to date little research has been focused on the thermodynamics of biogas production.

Thermodynamic principles were used to analyse the feasibility of producing biogas, and to determine the limits on the production and composition of the gas. This was intended to help find the best possible region for biogas production: that is, the precise conditions that would result in a greater proportion of feed material being converted into the desired product, reducing both the amount of undesirable product and the energy consumption of the process. This approach involved the use of mass and energy balances and the second law of thermodynamics as these are general restrictions which nature imposes on all transformations.

It is important that biochemical engineers understand the thermodynamics of chemical systems and processes. This helps them to design processes that operate close to the performance target. The closer a process operates to the performance target the more efficiently it can use raw materials, reduce unwanted products and emissions, thus the more sustainable the process.

The primary aim of the work described here is to advance scientific knowledge for the benefit of the biogas industry, so as to provide other researchers with a basis for carrying out further experiments on biogas. Another was to emphasise the importance of carrying out theoretical research using existing thermodynamic laws and process synthesis to predict results.

1.4. Why use Biogas?

Biogas can provide an answer to many of the hardships experienced by the rural people. For many of those who live in the urban areas, life without electricity is unimaginable, because almost every aspect of our way of life depends on it. However some people live in rural areas that are not supplied with electricity because the power network does not extend so far. Homes without electricity have to supply the needs of the family without assistance of electrical devices such as lighting and refrigeration. Most of them are still using firewood or coal for cooking. Neither is easy to find, which makes for long and arduous periods spent collecting fuel. Also, once it has been ignited, both, but coal in particular can produce harmful gases like carbon monoxide which can result in long term illness, such as asthma.

The use of biodigestion also helps to bring us closer to a complete cycle of food and provides a way to capture the uncontrolled methane emissions waste. Methane is the second most important contributor to greenhouse gas. Anaerobic digestion processes, as compared to normal aerobic compost processes, also produce elements apart from nitrogen that are more beneficial to plant growth because the process carried out in the digester is not exposed to sunlight which may cause the loss of some nutrient to the atmosphere. Another advantage is that the nutrients contained in bio fertiliser can be made available to crop farmers in large quantities (Fraenkel, 1986). Sludge, which is the solid that collects at the bottom of the biodigestor, also improves soil structure. In addition, because the sludge is 99 % pathogen free, Dunagan (2012) claims that digested animal waste can be used as regular fertilizer, unlike undigested animal waste. Another disadvantage is that a settlement that uses firewood can cause large scale deforestation in the surrounding areas. This is (obviously) unsustainable, leads to environmental degradation, and contributes to global warming. Biogas reduces deforestation, as people who normally use firewood to meet their domestic needs

would be able to switch to biogas. While solar and wind energy do not harm the environment, biogas improves the environment by processing waste material and capturing energy value.

To a large extent, human activities are responsible for most of the deterioration that can be observed in the earth's natural environment. For example the phenomenon of global warming is a direct result of the ever-rising levels of industrial emissions. We have used the earth's minerals such as oil, clean coal and natural gas reserves without considering how we will deal with the waste produced by our industrial applications of them, or whether nature can regenerate the supply of these valuable resources. If no remedial action is taken, then slowly but surely we will reach a point where these resources have reached an irreversible state of depletion. On the other hand, only if we discover alternatives to supplement the traditional sources, will we be able to maintain our current lifestyles. One solution is to replace the fuels mentioned above with renewable energy sources like biogas which reduce the emissions that cause global warming, for two reasons. It produces only carbon dioxide and water vapour on ignition, and the fodder supplied to the animals that produce the faeces from which biogas can be made consumes an amount of carbon dioxide that is almost equal to that combusted in the ecological cycle (Castro and Hurry, 2008).

If biogas technology were to be developed, it could contribute significantly to the nation's electricity supply; it would reduce the carbon emissions that cause global warming; and it holds great promise for alleviating the plight of the rural poor.

As shown in Table 1 below, biogas generates a reasonably high power value. The use of biogas fuel is economically feasible and can contribute to both a country's energy supply and also to its efforts towards curbing harmful emissions reducing greenhouse gas emissions. Methane emissions can be reduced by capturing and combusting it to produce carbon dioxide, which is less harmful. Table 1 below makes a comparison between biogas and other forms of

energy in terms of approximate caloric value when combusted: Although 1 m^3 of biogas is the energy equivalent of 5.5 kg firewood, this amount of biogas emits about 1.6 kg of carbon dioxide, whereas 5.5 kg of firewood emits 11 kg of carbon dioxide (ICAR., 2011). This clearly shows that biogas reduces carbon dioxide emissions by about eightfold, which is a far more desirable option in environmental terms. This leads to the intense of biogas production processes study through application of thermodynamics.

Table 1: Comparison of biogas with other fuel source alternatives.

http://www5.gtz.de/gate/techinfo/biogas/framecond/environ.html

Material	Amount	Power generated (kw/(kg/m^3))
Biogas	1 m^3	6
Cow dung	1 kg	4.17
Wood	1 kg	3.46
Hard coal	1 kg	12.14
Natural gas	1 m^3	10.83
Diesel, Kerosene	1 kg	24

1.5. Aims of the Project

The main aim of this project is to determine theoretically, the conditions required to optimize biogas production. This will be achieved by investigating the theoretical limits of performance on biogas production, drawing up an attainable region and thereafter come up with the mass and energy limits of the process.

1.6. Research Questions

The research questions examined in this project are as follows.

1. What is the relationship between the mass of substrate used versus the amount of methane produced for a given feedstock?
2. Is it possible to produce methane in a biodigester from waste (glucose/cellulose) in a process that does not require external power input or work to be supplied?
3. What is the maximum amount of methane that can be produced sustainably?
4. What are the mass and energy limits of the anaerobic biodigestion process?

Chapter 2: Literature Review

2.1. Background

Researchers have developed different models for biogas production to determine the amount of methane in relation to amount and type of waste used. A relationship between methane yield and digester temperature was suggested by Safely and Westerman (1992), and the model is expressed as $B = 0.216 + 0.00934T$, where B = methane production per mass of volatile solids (m^3/kg VS) and T = temperature of manure (^oC).

Buswell and Mueller (1962) developed a model based on the chemical composition of the degraded waste to predict methane production and this is expressed as

$$C_nH_aO_b + (n - \frac{a}{4} - \frac{b}{2})\,H_2O \Rightarrow (\frac{n}{2} - \frac{a}{8} + \frac{b}{4})\,CO_2 + (\frac{n}{2} + \frac{a}{8} - \frac{b}{4})\,CH_4$$

Where $C_nH_aO_b$ = organic matter and a, b and n are stoichiometric coefficients. This model did not include the production of hydrogen.

2.2. Biogas

Biogas fuel is typically gas produced by the biological breakdown of organic matter in the absence of oxygen. Its components are primarily methane and carbon dioxide, but it may contain small amounts of hydrogen, hydrogen sulphide and moisture (Yadava and Hesse, 1981). It is a low-cost energy source derived from renewable resources because it can be produced from any organic waste, including household food stuffs, animal excreta and human faeces. These are wastes that will continue to be produced as long as humans live on earth and keep livestock. Animals that feed on plant material, like grazers, produce waste that contain a great deal of methane (Austin, 2003), which constitutes the largest

component of biogas. Cow dung, for example, is known to contain the necessary micro-organisms, such as acid and methane formers, for biogas production (Momoh, *et al.*, 2008). Methane produced through biodigestion of this waste material is subjected to combustion, producing water and carbon dioxide. The reason is biogas production is a natural process because waste dumps and animal and human waste release methane, which can be harnessed (and made environmentally innocuous) by converting it to a fuel. Thus combusting biogas to produce carbon dioxide reduces environmental degradation by about 23 times as much compared to releasing methane into the atmosphere directly (David *et al.*, 1997). The carbon dioxide produced from combustion of methane is re-up taken by plants during photosynthesis thus a way of reducing greenhouse gases. Any excess energy produced this way can be added to the national power grid.

2.3. The Composition of Biogas

Table 2 below shows a typical composition of biogas. Biogas is about 20 % lighter than air and has an ignition range of 650 -750 °C (Sathianathan, 1975). It is colourless and odourless, burns with a clear blue flame at 60 % efficiency, and has a calorific value of about 20 kJ/m^3 (Sathianathan, 1975).

Table 2: Composition of biogas (Yadava and Hesse, 1981)

Compound	%
Methane	50-70
Carbon dioxide	30-40
Hydrogen	5-10
Nitrogen	1-2
Water vapour	0.3
Hydrogen sulphide	Traces

2.4. Process and Mechanism of Biomethanation

Anaerobic digestion is the microbial fermentation that converts organic matter to methane in the absence of oxygen (Smith *et al*., 1979). There are two types of anaerobic bacteria: facultative and obligate. Facultative bacteria can metabolise in both oxygen (small amounts) and non-oxygen environments. However obligate anaerobes thrive in non-oxygenic environments. The methane-forming bacteria are an example of the latter i.e. they work at their best in oxygen-free environments. This in turn means that they cannot do their job if there is an appreciable amount of oxygen (House, 1978).

Anaerobic digestion occurs in four steps as shown in Figure 1 below.

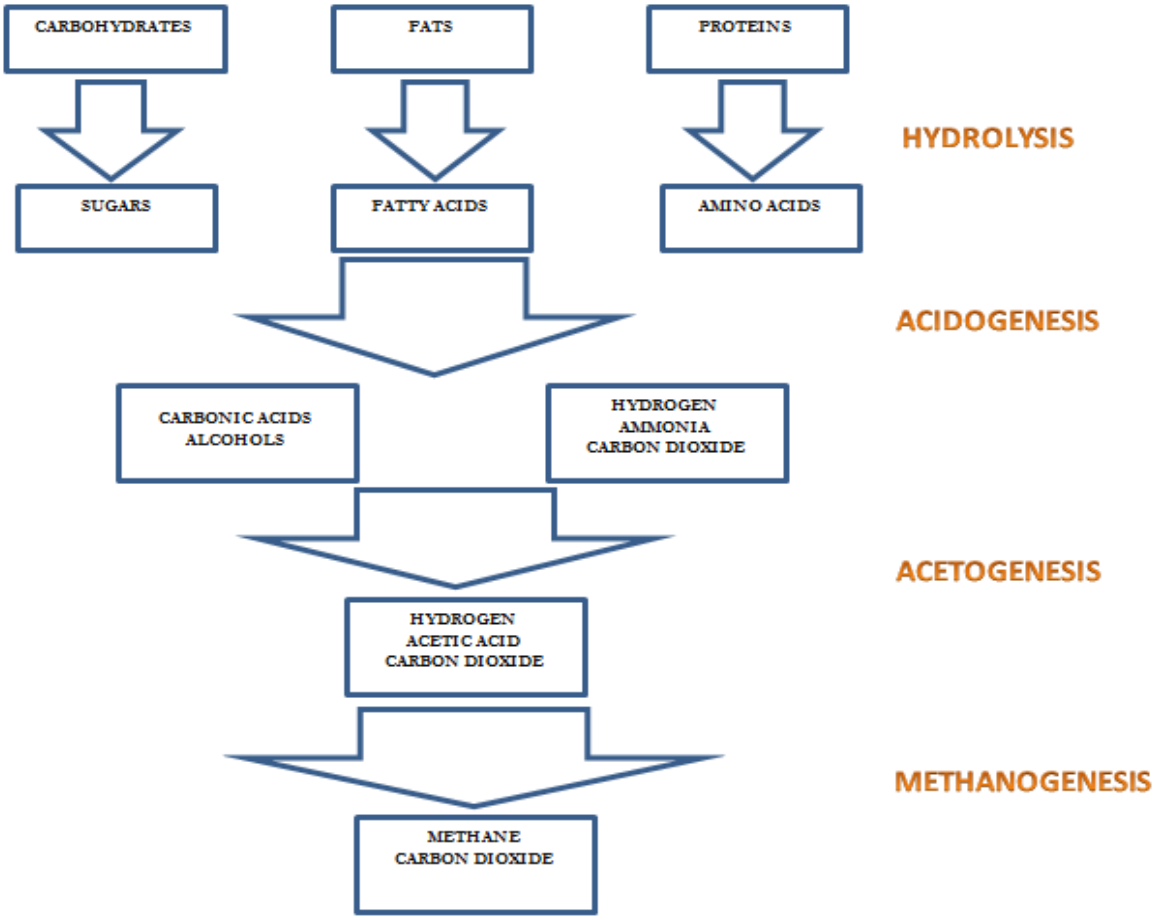

Figure 1: Process and Mechanism of biogas production, Kashyap et al (2003),

2.4.1. Hydrolysis

Hydrolysis is the enzyme catalysed conversion of large complex insoluble organic material and higher molecular mass compounds like fats, lipids and nucleic acids into small soluble organic materials. This is carried out by hydrolytic anaerobic bacteria like *clostridia*, *bactericides* and facultative bacteria like *streptococci*. This makes compounds available for use as energy. Hydrolysis is also known as the polymer break-down stage (Yadvika *et al*., 2004).

2.4.2. Acidogenesis

Another group of micro-organisms ferments the break-down products of the hydrolysis stage to carbonic acids, hydrogen, carbon dioxide and ammonia (Yadvika *et al*., 2004).

2.4.3. Acetogenesis

Propionic and butyric acid formed during acidogenesis are converted to acetic acid, in a process is called acetogenesis. Hydrogen and carbon dioxide gases are also formed in this stage (Yadvika *et al*., 2004).

2.4.4. Methanization

Acetic acid, water and carbon dioxide are then converted into a mixture of methane and carbon dioxide by the methanogen bacteria. *Methanosarcina* and *methanothrixssp* utilize the acetate while*methanobacterium* and *methanococcus*are species that utilize hydrogen and formate (Yadvika *et al*., 2004).

As shown by Yadvika *et al*, (1994), the major reactions that take place during this stage can be expressed as shown In Equations (1) and (2) below.

$$CH_3COOH_{(aq)} \rightarrow CH_{4(g)} + CO_{2(g)} \qquad \text{Equation (1)}$$

and

$$CO_{2(g)} + 4H_{2(g)} \rightarrow CH_{4(g)} + 2H_2O_{(g)} \qquad \text{Equation (2)}$$

2.5. Factors Affecting Anaerobic Digestion

The economic viability of digesters depends upon specific physical properties of the feed used. The major factors affecting anaerobic digestion are temperature, pH, oxygen content, pressure, water content and the carbon to nitrogen ratio (C/N). Because bacterial behaviour depends on these, the quality and quantity of biogas production are determined by them (House, 1978). Another factor that may reduce biogas production is lack of process stability with regard to the physical factors. The factors are discussed in greater detail below. However all these factors depend on the overall thermodynamics of the process, mass and energy limits.

2.5.1. Oxygen content

From the definition of anaerobic digestion, we can infer that the environment in the digestor should be oxygenless. The greater the oxygen content, the longer it will take for methane to be produced because it has to wait until the atmosphere is oxygen-free. The aerobic bacteria have to consume all the oxygen in the digester before the anaerobic bacteria can start working (House, 1978).

2.5.2. Temperature

Temperature affects the rate of production of methane gas in anaerobic digestion. According to Parker (2000), there are two temperature ranges required 25- 40°C for mesophilic and45-60°C for thermophilic methane production. Methanogens are the bacteria that help decompose the substrate in the mesophilic temperature range, but they are inactive at extremely high and low temperatures. Gas production will stop at temperatures below 10°C (Kathmandu, 1997), while the upper range at which bacterial activity slows down is about 70°C (Hobson *et al.*, 1981).

It can be noted that there is an increase in degradation of organic matter at higher temperatures, resulting in higher volatile solid conversion to gaseous form. This leads to a greater biogas yield. However, because very high temperatures reduce bacterial activity, a rise in temperature will in turn increase the loading rate, which will curtail the retention time. Fraenkel (1986) states that the optimum temperature for methane production is 35°C, which puts satisfactory gas production in the mesophilic range. Also the digestion process is exothermic and as a result generates heat but in small amounts. This heat produced should also be considered when setting up operating conditions of temperature. In the work presented in this dissertation the results show the heat needed/produces by the digestion process per given feed.

Although production in the mesophilic range is stable and inhibits ammonia production, these temperatures do not kill potentially harmful bacteria.

Methanogens are sensitive to sudden temperature changes. Even a drop of 2°C in the digestate slurry occurring unexpectedly will affect bacterial growth significantly and hence lessening gas production (Langrage, 1975). Therefore to maintain moderate bacterial activity, drastic changes in temperature should be avoided.

2.5.3. pH

The pH in the digester is a function of retention time. Initially the conditions are acidic due to the production of carbon dioxide and organic acids by the bacteria, and can reach a low pH as about 5. However after the digestion of nitrogen into the ammonium compounds the pH increases to about 8. This indicates that the pH is dependent on carbon dioxide, acetic acid and ammonia concentrations. When methane production is stable, pH ranges between 7.2 - 8.2 (Kathmandu, 1996).

Banks (2003) claims that the optimum values of pH for mesophilic and thermophilic ranges are 7.3-7.78 and 6.82-7.81respectively, while Momoh *et al* (2008) suggested a thermophilic range of 6.6 - 7.6. Methanogenic bacteria are very sensitive to pH and are inactive at pH values below 6.5 (Kathmandu, 1996). They do not favour sudden increases in pH, even if they are within the range of their operation. However they can also regulate the pH if the environment becomes too acidic so that their environment may be suitable for them by using fatty acids as their food source. However, a pH below 5.5 causes the bacteria activity to decrease drastically (House, 1978).

2.5.4. Carbon to Nitrogen Ratio (C/N)

Carbon and nitrogen are vital for both cell synthesis and the metabolism of anaerobic digestion. Austin (2003) and Banks (2003) documented the optimum carbon to nitrogen ratio

as (25-30):1. This means that micro-organisms use carbon about 25-30 times faster than they use nitrogen. The nitrogen is required by the bacteria for growth while carbon is necessary to supply them with energy (Austin, 2003) and to enable them to produce methane and carbon dioxide. If one has a substrate that has a low carbon content, it can be mixed with substances that have high carbon content, to bring the ratio to an average. If the carbon to nitrogen ratio is very low, nitrogen will be liberated and accumulated in the form of ammonia. This will increase the pH of the slurry (Kohli *et al*., 2003). The actual ratio is not a major factor, as there are wide ranges of permissible ratios and the system tends to be self-regulatory in that more ammonia is produced when the C/N ratio is high. On the other hand, in such a case more carbon dioxide is produced, which means that there will be less methane, so creating an acidic environment that will slow the process down, as explained above (House, 1978).

2.5.5. Water Content

Water is used as a transporting medium in the anaerobic digester, and also plays a role in the biological and chemical processes. High water content also increases the conversion performance of the digester (House, 1978). Biogas theory holds that to obtain the highest production of biogas, the contents of a digester should amount to 10% solid by weight and 90% liquid (House, 1981). However, a higher proportion of moisture has been found to result in an increase in the gas produced in the digester. Zennaki *et al* (1996) wrote that the ideal amount of fermentable material of the substrate should be 7- 9% of slurry, because a greater percentage of solid will cause overloading of the fermenter and consequently clogging of the digester because of solidification of the material. A greater percentage of solid will also affect mixing. Yadvika *et al* (2004) reported that the use of urine-soaked substrate doubled the production of gas regardless of the ammonia presence.

2.5.6. Pressure above the Slurry and Surface Area of Digestion

This section concerns the pressure of the gas that lies above the substrate mixture in the biodigester. According to House (1978), this pressure increases the amount of dissolved carbon dioxide and in turn reduces the pH of the slurry, which will slow the productivity of methane. As a result, increasing the pressure is detrimental if the optimal conditions are to be met. Babbit and Bauman (1958) advise that, the preferred pressures should not be greater than 15 cm to 18 cm of water.

2.5.7. Toxins Available

The acid-forming bacteria produce acids and carbon dioxide which are in turn used as food by the methane-forming bacteria (House, 1978). Ammonia is one of the most common toxins found in digesters (House, 1978). However if faeces are to be used as feed on a large scale then it becomes important to take ammonia into account when considering the effect of toxins. Urine contains a high proportion of ammonia, in the form of urea, which increases the pH significantly when mixed with animal faeces. Theoretically, it is assumed that a high proportion of ammonia reduces the amount of biogas produced as it increases the pH of the solution to values inappropriate for the operation of methane bacteria (House, 1978). However, the pH can be reduced by diluting the substrate with water. This may be problematic in water scarce areas.

Other sources of toxins occur when the animal wastes contain antibiotics which in turn are harmful to the bacteria within the digester. This results in biogas containing no methane. Thus, if animal waste is used, the plant operator must take care to ensure that the feed used creates an environment that allows methane production. If the biodigester is contaminated by toxins, it must be emptied and cleaned thoroughly before it can be used again (House, 1978).

2.5.8. Agitation

Agitation is vital to maintain intimate contact between the bacteria and the substrate in order to encourage more active metabolism (Yadvika *et al*., 2004). It is also useful in setting free gases that will be trapped in the substrates, and exposing fresh bacteria to fresh substrates. Yadvika *et al* (2004) also point out that smaller particles provide a larger surface area for adsorbing the substrate, which results in increased microbial activity and hence a rise in gas production.

2.6. Concluding Remarks

From the review of the literature we see that there are various issues that are important in the operation of anaerobic biodigesters.

Firstly we see from Table 2 that there is a wide range of gas compositions that can be achieved in biodigesters. The questions that arise from this is what are the range of gas compositions, yields possible and what is the impact of this on the operation of the digester?

Secondly it has been shown that the operating temperature of the digester has a large impact on the performance of the digester. It is also reported in the literature that the production of biogas is exothermic but the question is how much heat is produced and also what does this depend on.

These issues are ones that we will consider in the following chapters.

Chapter 3: Methodology

This research involved theoretical calculations and two cases are considered.

1. In the first case it is assumed that the overall process is anaerobic. The gas composition range that can be achieved as well as the heat and work flows either into or out of the process were calculated.
2. In the second case, the overall process is assumed to be aerobic and adiabatic. Enough oxygen is added to the overall system in order to supply enough heat through the combustion process in order to make the overall process adiabatic. The remainder of the glucose is assumed to be converted to biogas by anaerobic digestion.

3.1. Defining the Process

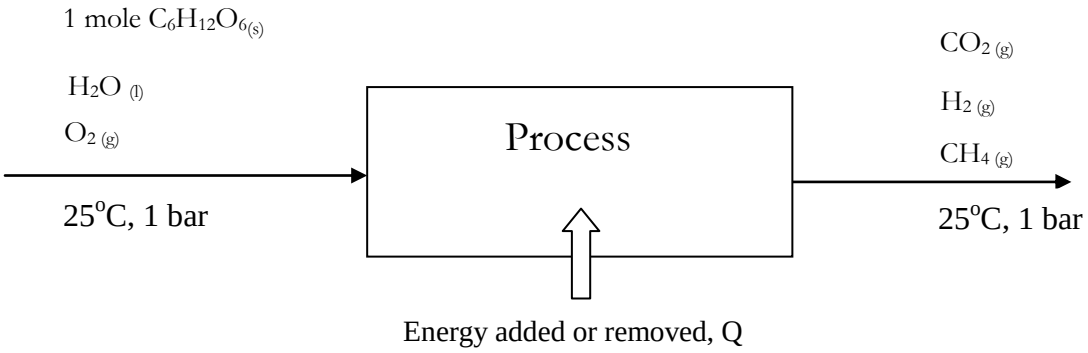

Figure 2: Representation of a process for the synthesis of biogas.

In the process shown in Figure 2 above, we will assume a continuous flow system that is at steady state.

In the first case the feed is considered to be glucose and products are carbon dioxide, methane and hydrogen at 25 °C and 1 bar. Water can either be added as a feed or removed as a product. Heat can be either removed or supplied to the system.

In the second case we looked at a system with a feed of glucose and oxygen which produced carbon dioxide, methane and hydrogen at 25 ^{o}C and 1 bar. Water can either be added as a feed or removed as a product. Enough oxygen process is supplied in order to make the overall system adiabatic.

The carbon efficiency which is defined as the amount of carbon in glucose that is converted to methane, is also used to analyse the overall system. Selectivity is defined as the ratio of desired product to undesired product (Fogler, 2006).

3.2. The Feed

All calculations are based on 1 mole of glucose ($C_6H_{12}O_6$). Cellulose, which is probably the main component of biomass material, could have been used as a feed substrate for this research, but the standard thermodynamic data for Gibbs Free Energy for this substrate proved difficult to obtain. However, since glucose and cellulose are carbohydrates and of comparable chemical structure, the researchers reasoned that similar mass and energy balance results could be obtained for either cellulose or glucose as the feed substrate. Buswell and Boruffl (1932) claim that when cellulose, starch and hemicelluloses decompose, they render about 110 % of their weight in biogas, at 50 % CO_2, 50 % CH_4 because for every mole of cellulose decomposed, the water in the cellulose adds to the weight of biogas.

3.3. Products

The range of products formed from glucose must satisfy the overall mass balance for the process. In other words the moles of C, H and O entering and leaving the system must be the

same. This must always be satisfied irrespective of the biological agents, the reactions occurring or the equipment design. We have assumed that methane, carbon dioxide and hydrogen are the main products of anaerobic digestion. Note that many other products such as acids and alcohols can also be produced during anaerobic digestion. These are usually produced in small quantities and as such will not have a large effect on the mass balance. Thus they can be ignored in the analysis and discussion for simplicity.

3.4. Mass Balance Target

A mass balance provides the foundation for creating a flow sheet. It allows one to set different process targets, contingent on the choice of feed and its stoichiometry. Examples of possible process targets include environmental limits, for example minimizing CO_2 emissions, or production targets such as maximizing methane production from a given feed.

There are many reactions involved in the formation of biogas. There are also complex biochemical pathways but the physical limits imposed by the mass balance define the feasible envelope. The atomic species balance allows one to perform a mass balance over the entire process without considering equipment, process design such as recycles, the biological agents or pathways (Patel, 2007).

Case 1:

In this case there are five species either being fed into or produced by the process, namely CH_4, H_2O, $C_6H_{12}O_6$, CO_2, and H_2, and three atom balances (C, H, and O). We set the amount of feed material $C_6H_{12}O_6$ to one mole; therefore the overall mass balance for the process has one degree of freedom.

Equation (3) below shows the overall mass balance for the process. In the mass balance, ***b, c, d, and e*** are the amounts of carbon dioxide, methane, water, and hydrogen produced per mole of glucose (***a***= 1) respectively.

$$aC_6H_{12}O_6 + bCO_2 + cCH_4 + dH_2O + eH_2 = 0 \qquad \text{Equation (3)}$$

There is only one independent parameter in the above mass balance and we can determine the relationship between the parameters by using the atomic balances, as follows:

C*: 6 + b + c = 0*

H*: 12 + 4c + 2d + 2e = 0*

O*: 6 + 2b + d = 0*

We can thus relate the parameters *b, d* and *e* to the moles of methane produced *c* giving:

b = -(6+c)

d = -(6+2b)

e = -(2c +d+ 6)

Thus we can plot the number of moles of hydrogen, carbon dioxide and water produced from 1 mole of glucose as a function of the number of moles of methane produced. We can plot these on a moles of product produced versus moles of methane produced diagram as shown in Figure 3.

We note that the mass balances are fundamental; thus Figure 3 does not depend on the bacteria, the process or the equipment design. We will discuss the implications of Figure 3 in Chapter 4.

Case 2:

In this case there are six species either being fed into or produced by the process, namely CH_4, H_2O, $C_6H_{12}O_6$, CO_2, H_2 and O_2, and three atom balances (C, H, and O). We again set

the amount of feed material $C_6H_{12}O_6$ to one mole; therefore the overall mass balance for the process has two degrees of freedom.

Equation. (4) below shows the overall mass balance for the process. In the mass balance, ***b, c, d, e*** and ***f*** are the amounts of carbon dioxide, methane, water, hydrogen and oxygen produced per mole of glucose (***a***= 1) respectively.

$$aC_6H_{12}O_6 + bCO_2 + cCH_4 + dH_2O + eH_2 + fO_2 = 0 \qquad \text{Equation (4)}$$

There are now two independent parameters in the above mass balance. We can again determine the relationship between the parameters by using the atomic balances and remembering that a=1,

C*: 6 + b + c = 0*

H*: 12 + 4c + 2d + 2e = 0*

O*: 6 + 2b + d+2f = 0*

We are now able to relate three of the parameters, say *b*, *d* and *e* to two parameters, for example moles of methane produced *c* and moles of O_2 consumed *f*, thus relate the parameters *b*, *d* and *e* to the moles of methane produced *c* giving:

b =-(6+c)

d = -(6+2b+2f)

e = -(6+2c+d)

In order to determine the amount of O_2 used in order to make the process overall adiabatic, we need to determine the overall energy balance across the process. We do this in the next section.

3.5. The Energy (Enthalpy) Limit

The overall energy balance (like the mass balance) must also be taken into account when deciding on feasible outputs from biogas production, because these impose limitations on the system.

The overall energy balance can be applied to the overall process to show the minimum amount of energy required or produced by the process.

The change in enthalpy across the process, $\Delta H°(\text{reaction})$, is calculated by Equation (5)

$$\Delta H°(\text{reaction}) = \sum \Delta H°(\text{products}) - \sum \Delta H°(\text{reactants}) \quad \text{Equation (5)}$$

where the "reaction" referred to is the overall mass balance for the process.

The energy required by the process, Q, is related to the $\Delta H°(\text{reaction})$ by the overall energy balance:

$$Q = \Delta H°(\text{reaction}) \quad \text{Equation (6)}$$

If the change in enthalpy across the process ($\Delta H°(\text{reaction})$) is positive, it means that the system requires heat to be added and when $\Delta H°(\text{reaction})$ is negative, heat has to be rejected from the system in order for the system to be at steady state.

Case 1:

In case 1 the heat load on the system Q was calculated by using the overall mass balance Equation (3) to define the reaction. Thus the heat load could be determined as a function of the amount of methane produced. This is plotted in Figure 3 in Chapter 4 and the interpretation and implications will be discussed in the next Chapter.

Case 2:

In case 2 the heat load on the system Q was set to zero, and the energy balance was used to relate the values of the two parameters *c* (moles of methane produced) and *f* (moles of O_2 used) in Equation (4). Thus the overall mass balance for an adiabatic process could be calculated and the moles of products produced as a function of the amount of methane produced could be determined and is plotted in Figure 6 in Chapter 4.

3.6. The Entropy (Gibbs Free Energy) Limit

In order for a process to be feasible, the change in entropy of the universe must be greater or equal to zero. The entropy limit is somehow different to the mass and energy balance in that entropy is generated in real processes and thus in order for the entropy balance to "balance" the entropy generation term, S_{irr}, must be included If we consider the system shown in Figure 2, the entropy balance becomes:

$$\sum \Delta S^\circ \text{ (reactants)} + Q/T + S_{irr} = \sum \Delta S^\circ \text{(products)} \qquad \text{Equation (7)}$$

where T is the temperature of the heat added to the process. We have neglected the entropy of mixing as this term is usually small compared to the entropy change of reaction.

We can combine this with the energy balance Equation (6) and to rewrite it in terms of Gibbs Free Energy rather than entropy. Thus:

$$\sum \Delta G^\circ \text{ (reactants)} + Q(1-T^o/T) - W_{lost} = \sum \Delta G^\circ \text{(products)} \qquad \text{Equation (8)}$$

Where $W_{lost} = T^o S_{irr} \geq 0$. Biological processes operate close to ambient temperatures ($T \cong T^o$) and thus the heat added or removed does not carry much work with it. Thus the equation simplifies to Equation (9):

$$\Delta G°(\text{reaction}) = \sum \Delta G°(\text{products}) - \sum \Delta G°(\text{reactants}) = -W_{lost} \quad \text{Equation (9)}$$

In order for the process to be spontaneous, $\Delta G°(\text{reaction}) \leq 0$. However, if the Gibbs Free Energy across the process ($\Delta G°(\text{reaction})$) is negative, it indicates that the system has potential to do work and thus is irreversible if this work is not recovered. Furthermore if the lost work is not recovered, the more negative $\Delta G°(\text{reaction})$ is, the more of the chemical potential in the feed is lost and thus less of this chemical potential is stored in the product. Thus there is less work potential in the product which means that if the product is used to drive an engine, less power would be produced from the gas.

The change in Gibbs Free Energy across the process $\Delta G°(\text{reaction})$ as a function of moles of methane produced is plotted in Figure 4 for Case 1 and in Figure 6 for the adiabatic situation (Case 2).

Chapter 4: Results and Discussion

4.1. Anaerobic system

We will firstly consider Case 1, the anaerobic system, and consider the overall mass, energy and Gibbs Free Energy balances for the process. Because of the approach used, it should be remembered that we are considering the outputs from all possible anaerobic processes (normalised for 1 mole of glucose consumed). These results include all possible process designs, all equipment designs and even all types of biological agents, as long as they only produce methane and/or hydrogen.

4.1.1. Mass balance

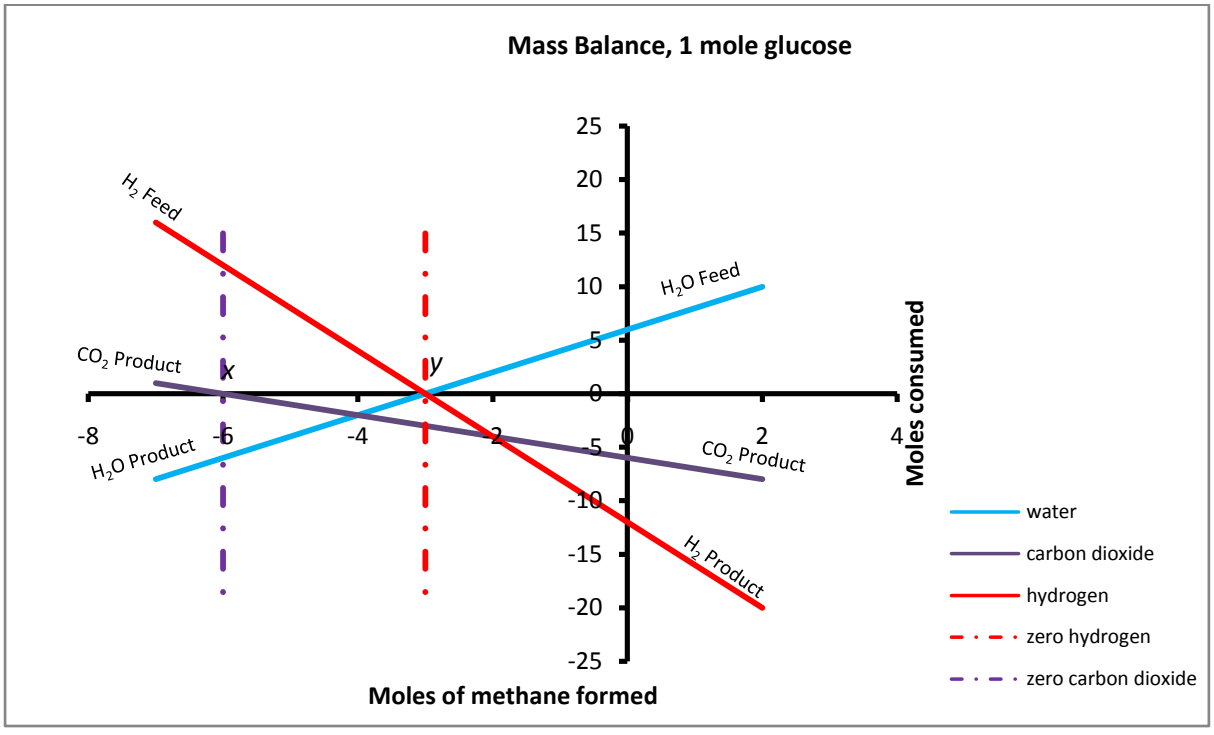

Figure 3: The amount of each component consumed/produced per mole of glucose.

We have plotted Equation (3) in Figure 3. We are thus looking at the number of moles of carbon dioxide, water and hydrogen produced (or consumed) per mole of methane produced

(or consumed) in an anaerobic digestion process. The mass balance also shows whether the substance is a feed or a product. On the mass balance plot; Figure. 3, the positive axes show that the substance is being consumed, while the negative axes represent the substance as a product. The mass balance lines are all straight lines as the equations all depend linearly on the moles of methane produced.

Note that each vertical line defines a feasible mass balance. Thus this diagram represents all possible mass balances, namely the Attainable Region. If there are constraints on the system these will limit what is attainable. Looking at the diagram we can set vertical lines that identify a target of zero for carbon dioxide (the purple dotted line) and hydrogen (the red dotted line) separately. We further note that water can act both as a product (to the left of the red dotted line corresponding to zero hydrogen produced) or a reactant (to the right of the red dotted line corresponding to zero hydrogen produced). Thus water is consumed when hydrogen is produced but is a by-product of methane production.

There are four regions in which the signs of the species are the same. We will look at each of them, starting from the right.

- The area to the right of the y-axis is the region where methane is consumed (i.e. methane would be a feed to the system) and this region is not of interest as we are looking at producing methane, not consuming it. In this region glucose, methane and water would be fed to the process and carbon dioxide and hydrogen would be produced.
- The region between the red dotted line (zero hydrogen and zero water) and the y-axis is the region in which glucose and water would be fed to the process and hydrogen, methane and carbon dioxide would be produced. This region is of interest for biogas production.

- The region between the purple dotted line (zero carbon dioxide) and the red dotted line (zero hydrogen and water) is the region in which glucose and hydrogen would be fed to the process and water, methane and carbon dioxide would be produced. This region is not of interest for biogas production.
- The region to the left of the purple dotted line (zero carbon dioxide) is the region in which glucose, carbon dioxide and hydrogen would be fed to the process and water and methane would be produced. This region is also not of interest for biogas production.

Thus the only region that is of interest for biogas production is that lying between the zero hydrogen line (the red dotted line) and the y-axis.

Each vertical line corresponds to a particular overall mass balance. In the case of zero carbon dioxide (point *x* in Figure. 3), 6 moles of methane and 6 moles of water are produced from a feed of 12 moles of hydrogen and one mole of glucose, as described in Equation (10):

$$C_6H_{12}O_6 + 12H_2 \Rightarrow 6CH_4 + 6H_2O \qquad \text{Equation (10)}$$

The mass balance shows hydrogen is consumed and it is therefore not reasonable to operate at a process with a mass balance corresponding to point *x*.

If the aim is to operate with zero hydrogen (point *y*), three moles of carbon dioxide and three moles of methane are produced from one mole of glucose. This mass balance is given in Equation (11).

$$C_6H_{12}O_6 \Rightarrow 3CH_4 + 3CO_2 \qquad \text{Equation (11)}$$

If we define carbon efficiency as moles of methane in the product gas to moles of carbon in the feed, then the maximum carbon efficiency for an anaerobic biodigestor is 50 %. The mass balance shows that we cannot reduce the amount of carbon dioxide produced relative to methane unless hydrogen is a feed. It also shows that the more hydrogen produced, the less methane is produced and the more carbon dioxide produced.

Methane production stops when 12 moles of hydrogen are produced as given in Equation (12).

$$C_6H_{12}O_6 + 6H_2O \Rightarrow 12\,H_2 + 6CO_2 \qquad \text{Equation (12)}$$

Thus in the region where hydrogen is a product, as long as there is a conversion of glucose to methane, carbon dioxide will always be a product.

4.1.2. Enthalpy and Gibbs Free Energy

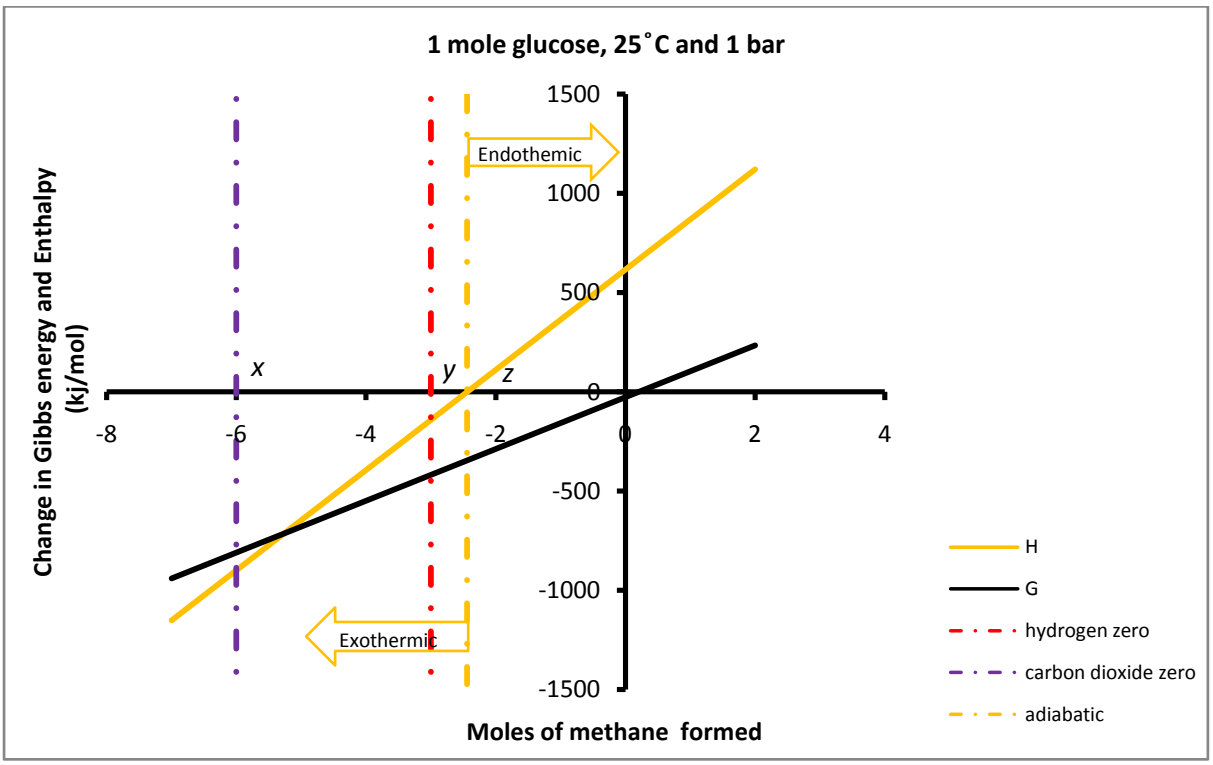

Figure 4: Enthalpy and Gibbs Free Energy change plot as a function of methane produced per mole of glucose.

A mass balance also sets the Enthalpy and Gibbs Free Energy balances and these can also limit the attainable mass balances. Figure 4 show that all the processes that produce methane are feasible from a Gibbs Free Energy (Entropy) point of view, that is its value is negative. This means they are all thermodynamically favourable but do not conserve the chemical potential of the feed material. Unless some mechanism can be devised to recover this work potential it is lost forever. It can be seen the closest to a reversible process occurs when no methane is formed. This occurs when we only make hydrogen and carbon dioxide as shown in Equation (12).

However this process is very endothermic and requires large amounts of heat to be supplied (616 kJ/mole). Thus the design and operation of the reactor for the production of hydrogen Equation (12) requires heat addition and the question that arises is where this heat comes from. If waste heat from some other process is available this could be used in the hydrogen production process. If this was possible, this would be a good process, indeed the best process in terms of reversibility and thus conserving the chemical potential in the feed.

There are three situations that are of particular interest

- **Production of Methane**

When methane is the main product (and thus hydrogen production is zero), three moles of methane are produced per mole of glucose corresponding to the overall mass balance in Equation (13) and the target carbon efficiency is thus 50 %.

$C_6H_{12}O_6 \Rightarrow 3CO_2 + 3CH_4$, ΔH = -141.9kJ/mol, ΔG = -418.68kJ/mol Equation (13)

Such a process would produce around 142 kJ/mole of glucose of heat. This raises the question of how do we design and operate the digesters that produce mainly methane to account for the large heat load removal. The lost work for this target is approximately -420

kJ/mole, and thus a biodigester producing methane would lose about 15 % of the chemical potential in the feed due to irreversibilties.

- **Adiabatic Operation**

For an adiabatic process ΔH = 0 kJ/mol which corresponds to point *z* on Figure, 4. In this situation the mass balance for the digester would be:

$C_6H_{12}O_6 + 1.12H_2O \Rightarrow 2.24H_2 + 3.56CO_2 + 2.44CH_4$, ΔH = 0 kJ/mol, ΔG = -345 kJ/mol Equation (14)

Thus the production of methane would be reduced from the target of 3 discussed previously to 2.44 moles of methane per mole of glucose.

This mass balance is interesting in that if the biodigestor was designed or operated such that there was no or very little heat loss (if cooling systems had not been included in the design), the digester would need to operate with a mass balance close that described above in order for the reaction to be adiabatic. Thus in this case one would co-produce hydrogen and methane in a ratio of close to 1:1 and the carbon efficiency would be 41 %.

- **No Carbon Dioxide Emissions**

The mass balance for a target of zero carbon dioxide emissions is given in Equation (15) below.

$C_6H_{12}O_6 + 12H_2 \Rightarrow 6CH_4 + 6H_2O$, ΔH = -900 kJ/mol ΔG = -810 kJ/mol Equation (15)

A process operating with this mass balance would be exothermic with and would reject 900 kJ/mol of heat. Furthermore the process is irreversible as the change in Gibbs Free Energy is -810 kJ/mole. Thus this process would be both very exothermic and also very irreversible and would require hydrogen as a feed material. This would not be the usual operating mode

of a digester and thus we can conclude that anaerobic digesters would produce carbon dioxide.

4.1.3. Digester performance limits

We should at this point note there are in principle two types of digester that one finds in practice. The first is essentially an uncontrolled passive one that operates in the environment with minimal control, that is the biomass is loaded into a container/ vessel; inoculated and the organisms digest the biomass and the gas is collected. The second is an industrial one in which much more control can and is exercised. While when viewed from fundamental principles the two are the same, the industrial one allows for more flexibility in operation and so where appropriate we will discuss them separately. We will consider passive digesters in this section.

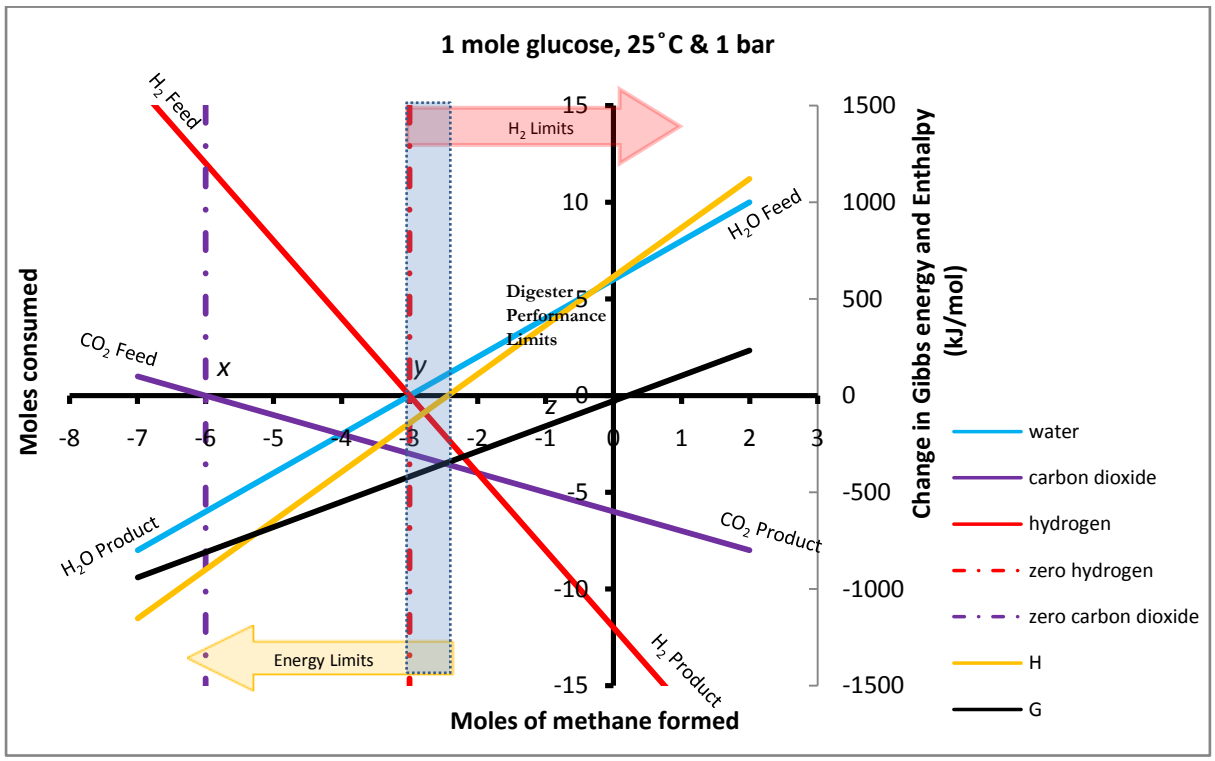

Figure 5: Digester performance limits shown on Mass balance, Enthalpy and Gibbs Free Energy change plot as a function of methane produced per mole of glucose (Case 2).

Passive digesters operate at ambient or above ambient temperatures and thus must loose heat to the surroundings. From Figure 5 we see that this therefore limits the mass balances that can be achieved to those lying in the shaded area, namely between the adiabatic limit and the limit of zero hydrogen production.

In order to understand the magnitude of the heat removal problem in a passive digester we can consider what the temperature increase would be if the reaction occurred and there was no heat removal, namely what the adiabatic temperature rise would be. For instance, if we have cellulose mixed with water the mixture would have a heat capacity between 1 and 4 kJ/(mole cellulose per ^{o}C). The actual value of the heat capacity would depend on the proportion of cellulose to water. We see from Figure 5 that $\Delta H^{o}_{reaction}$ for the production of methane is of the order of 100 kJ/mole which gives rise to adiabatic temperature change of around 100 ^{o}C. Thus in order to ensure a reasonable operating temperature in the reactor, the reaction rate will have to match the rate of heat transfer. Thus the overall reaction rate in a passive digester will need to be slow enough to match the heat transfer rate to the environment. It is an interesting question in this situation as to what determines the observed overall production rate, namely is the rate of the process heat transfer controlled or controlled by the rate of the inherent biological processes.

The energy balance sets the lower limit of operation of the biodigester and the hydrogen production sets the upper limit. Therefore the maximum amount of methane that can be produced from 1 mole of glucose is 3 moles (point *y*). This is the point at which hydrogen is zero hence the overall process is hydrogen limited. At these conditions there is a large heat load of -142 kJ of heat per mole of glucose on the digester that must be rejected. If we consider operating at minimum selectivity of methane to conserve the chemical potential of the feed we would make 2.24 moles of hydrogen and 2.44 moles of methane. This would

reduce the heat load on the digester and conserve the chemical potential of the feed (i.e. be more reversible.)

We must also consider that a significant amount of hydrogen is produced from the mass balance at ΔH >0 kJ/mol. From Figure 5, it is shown that the less CH_4 produced, the more $H_2$is produced. One should not look at the carbon efficiency alone, for H_2 is also a fuel, thus instead of storing all the energy in CH_4 some can be stored in H_2.

To produce hydrogen, the process becomes increasingly complex and the investigator will need to consider how this extra heat (energy) can supplied. One can consider using waste heat from other processes or another source of energy like solar, wind to supply heat in order to favour hydrogen production, Grey, 2012. However it is also difficult to harness the hydrogen in a cheap way as it can easily leak from a simple passive biodigester. We can also see from the figure, that the more hydrogen we can produce, the more carbon dioxide is emitted. In order to reduce CO2 production we need to increase methane production.

4.2. Anaerobic digesters that require heat input.

Hydrogen production in anaerobic digesters is endothermic and thus heat needs to be supplied to the process. There are two possibilities. If heat is available from another source this could be used to supply the heat for the production of hydrogen. In that case the target mass balance would be:

$$C_6H_{12}O_6 + 6H_2O \Rightarrow 12\ H_2 + 6CO_2 \quad \Delta H = 616\ \text{kJ/mol} \quad \Delta G = -27\ \text{kJ/mol} \qquad \text{Equation (15)}$$

Thus we would need to supply 616 kJ/mol of heat and we could produce 12 moles of H_2 per mole of glucose consumed. There is an advantage to this process as it consumes waste heat (where available) and conserves that chemical potential of the feed and thus is more reversible than using the same feed to make methane.

However if heat is not available then we have to get the heat from the process itself. Effectively in this case we have to burn some material, be it feed or product, in the process to produce the heat required by the digester. Under these circumstances oxygen becomes an extra feed to the system and we need to take the burning process into account when modelling the overall system. Furthermore we would not like to add more heat to the process than required so even though there is an extra degree of freedom relative to the anaerobic process we will only examine cases for which ΔH is zero. Thus this is the situation that we called Case 2 previously.

The mass and energy balances when oxygen is added to the system and ΔH = 0 kJ/mol are plotted on the same kind of diagram in Figure. 6. The species are plotted as before as a function of methane to show the set of all possible mass balances for an adiabatic process. Addition of oxygen changes the mass balance, hence the selectivity of products are also changed as shown in Figure 6.

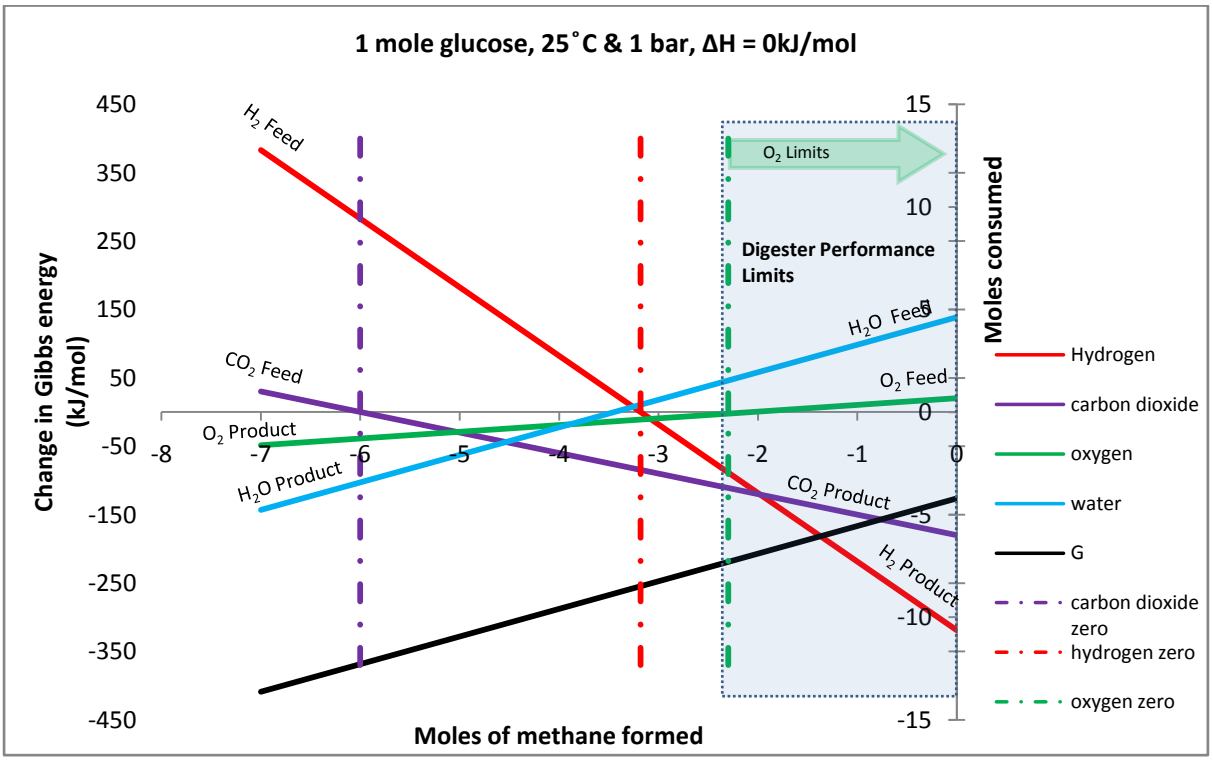

Figure 6: Digester performance limits shown on Mass balance, Enthalpy and Gibbs energy change plot as a function of methane produced per mole of glucose when oxygen is added to the overall process (Case 2).

It is shown that the processes are feasible as the Gibbs Free Energy is negative. As mentioned before adding hydrogen to the process as a feed is undesirable and thus we would not consider the mass balances that require this action.

However a more stringent limit is that the process should consume oxygen rather than produce it as this lies to the right of the zero hydrogen limit. The other limit for possible mass balances corresponds to the mass balance where no methane is produced and hydrogen and carbon dioxide are the only products. Thus the shade region in Figure 6 corresponds to the region of all feasible mass balance for digesters that are overall adiabatic.

The mass balances for the two limits are:

- **Zero Oxygen limit**

In this situation no oxygen is added to the system and it is overall adiabatic. This corresponds to the mass balance found in the previous case (Case 1) namely Equation (3)

This also corresponds to the maximum amount of methane that could be produced in a system that is overall adiabatic, namely 2.4 mole of methane per mole of glucose. In this case the carbon efficiency is 41 % and 88 % of the chemical potential of the feed is retained in the methane

- **Hydrogen production**

In this case we would maximize hydrogen production in an adiabatic digester. The overall mass balance for the process would be shown in Eq. (16):

$C_6H_{12}O_6 + 4.6H_2O + \ 0.7O_2 \Rightarrow 10.6\ H_2 + 6CO_2$ ΔH = 0 kJ/mol ΔG = -126 kJ/mol Equation (16)

In this case we would produce 10.6 moles of hydrogen per mole of glucose and 96 % of the chemical potential of the feed is retained. Thus production of hydrogen is more attractive in terms of the reversibility of the process and the conservation of chemical potential.

Anaerobic bacteria cannot produce methane or hydrogen in the presence of oxygen in a biological system. Thus in this situation the oxygen would need to be kept separated from the anaerobic part and the combustion and heat exchange done externally so as to keep the overall process adiabatic. Thus there will need to be extra equipment such as heat exchangers, heat pumps, heat engines in addition to the digester.

4.3. Mass and Energy Balance plot using Estimated Gibbs Free Energy values of Cellulose

The analysis has been done on glucose because we have good values for the enthalpy and the Gibbs Free Energy of formation for glucose. Such data are not readily available for cellulose. We however have drawn Figure. 7 based on some estimated values (ΔH = -955 kJ/mol, ΔG = -650 kJ/mol), calculated by (Alberty 1998; Griffiths 2013; Perks and Liebman 2000). We can see that the results in Figure. 7 do not differ significantly from Figure. 5 and so our general conclusions remain unchanged though some of the detailed values may change, for example for adiabatic operation our equation now becomes Eq. (17).

$C_6H_{10}O_5 + 2.32H_2O \Rightarrow 2.64H_2 + 3.66CO_2 + 2.34CH_4$, ΔH = 0 kJ/mol, ΔG = -362 kJ/mol Equation (17)

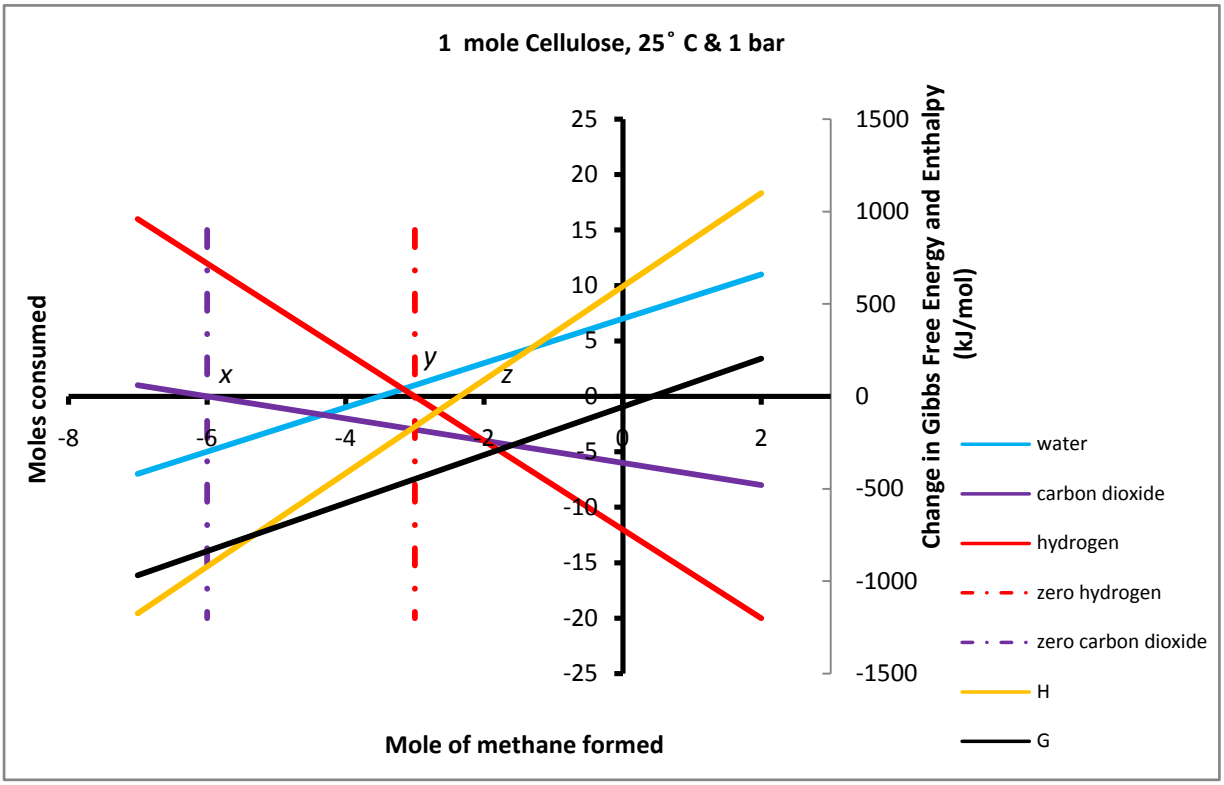

Figure 7: Digester performance limits shown on Mass balance, Enthalpy and Gibbs Free Energy change plot as a function of methane produced per mole of Cellulose

Chapter 5: Conclusions

Anaerobic digesters offer a way of turning waste biomass into biogas. This technology is fairly simple to build and operate and offers a way of supplying poor and rural communities with a renewable source of energy.

It is important to know what limits the performance of these units. For example one could ask what the maximum amount of biogas is that one could produce from a given amount of feed. Alternative questions could be what is the advantage of making methane rich biogas as opposed to hydrogen rich, what are the heat loads on the equipment and what is the best product to make in order to conserve as much of the chemical potential of the feed to the digester in the biogas product as possible. We are able to answer these questions by finding the performance targets of the digester.

We used glucose as a surrogate feed material to the biodigester and the possible products from the digester were assumed to be methane, hydrogen and carbon dioxide. We used the overall mass balance, the overall energy balance and the second law of thermodynamics to determine the set of all possible mass balances across a digester. We were able to plot these and thus determine the attainable set of overall mass balances. From this we could determine all the achievable composition of the gas as well as the minimum work and energy requirements for biogas production Thus we were able to determine the limits of performance of the process. These limits are important as they cannot be exceeded even if we genetically engineer organisms or change the equipment design or operation.

We found that the production of methane is exothermic and a target of 3 moles of methane can be produced per mole of glucose. The heat load on a digester operating at this target mass balance is very high at 142 kJ/mol and it is interesting as to how this is managed in the

design and operation of a digester producing methane. Furthermore the process is fairly irreversible and only 66 % of the chemical potential on the feed is conserved in the product.

The production of hydrogen is very endothermic and 616 kJ/mol of heat would need to be supplied per mol of glucose consumed. Furthermore a target of 12 moles of hydrogen could be produced per mole of glucose if heat was available from another process or method (e.g. solar heat). This process would be the most reversible way to operate a biodigester and conserve 99 % of the chemical potential in the feed would be conserved in the biogas.

If there was no external source of heat to the biodigester then energy would need to be supplied by the process itself. This could be done by combusting either some of the feedstock or the biogas produced which would be the energy source for the digester. We thus looked at the limits of operation of a biodigester where enough oxygen was supplied to maintain the system overall adiabatic.

If the digester could be run to produce a 1:1 mixture of methane to hydrogen, this would make the digester overall adiabatic and no combustion would need to take place. In this case about 88 % of the chemical potential in the feed would be conserved in the product. However if the digester was run so as to make hydrogen, then 0.7 moles of oxygen would need to be supplied to keep the process overall adiabatic and 10.6 moles of hydrogen could be made per mole of glucose. This process would conserve 96 % of the chemical potential in the feed in the hydrogen and thus in terms of reversibility it would be preferred compared to the case of making a 1:1 mixture of hydrogen and methane. However the process complexity would be much more and thus it would probably not be practical option.

We finally looked at the impact of choosing glucose as a surrogate feed. We used the values of enthalpy and entropy of formation of cellulose reported by Alberty 1998; Griffiths 2013; Perks and Liebman 2000, and redid the calculations. We found that the graphs did not change in shape although the actual values of the overall mass balance and heat loads were slightly different to those found using glucose.

A final result from this work is the importance of heat transfer in the operation of a biodigester. In industrial systems we require reasonable rates of reaction and we need to design and operate the process so that we can get a rate as high as possible. Thus if heat transfer rate becomes limiting, then the production rate in the digester would be determined by the heat transfer rate rather than the intrinsic rate of the biological pathways. It is thus very important to ensure that one understands and has calculated the energy balance for the digester and ensures that the heat transfer is sufficient to ensure that the digester operates isothermally.

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Appendix

A.1. Thermodynamic Data

The thermodynamic data used in this research project were obtained from Perry, (2007). These were at standard temperature and pressure conditions of 1 bar, 25 °C. The Enthalpy and Gibbs free energy for the reactions were calculated from the formation data of the species shown in Table A1 below.

Table A1: Thermodynamic Data

Component	$\Delta H°_f$(kJ/ mol)	$\Delta G°_f$ (kJ/mol)	Mr (g/mol)
Methane (g) CH_4	-74.52	-50.49	16.04
Water (l) H_2O	-285.83	-237.15	18.01
Carbon dioxide (g) CO_2	-393.51	-394.37	43.99
Hydrogen (g) H_2	-	-	2.010
Glucose (s) $C_6H_{12}O_6$	-1262.19	-915.9	180.16

1kcal/mol = 4.1868kJ/mol

The Enthalpy and Gibbs free energy for the reaction was calculated using Equations (A1) and (A2) below.

$\Delta H°(\text{reaction}) = \sum \Delta H°(\text{products}) - \sum \Delta H°(\text{reactants})$. Equation (A1)

$\Delta G°(\text{reaction}) = \sum \Delta G°(\text{products}) - \sum \Delta G°(\text{reactants})$. Equation (A2)

B.1. Mass Balance Calculations

The two mass balance reactions below were used as the base reactions for this research project.

Rxn1- $C_6H_{12}O_{6(s)} + 6H_2O_{(l)} \rightarrow 12H_{2(g)} + 6CO_{2(g)}$, $\Delta H°$=616.11 kJ/mol, $\Delta G°$=-27.42 kJ/mol

Rxn 2 - $C_6H_{12}O_{6(s)} \rightarrow 3CO_{2(g)} + 3CH_{4(g)}$, $\Delta H°$ = -141.9kJ/mol$\Delta G°$ = -418.68kJ/mol

B.2. Mass Balance and Energy Balance Plot

Table B1 below shows the nomenclature that was used to carry out the mass balance calculations

Table B1: Element Nomenclature

Coefficient	Component
a	Glucose
b	Water
c	Carbon dioxide
d	Methane
e	Hydrogen
f	Oxygen

And Equation (B1) below was established when no oxygen is added to the system.

$$aC_6H_{12}O_6 + bH_2O + cCO_2 + dCH_4 + eH_2 = 0 \qquad \text{Equation (B1)}$$

From this, all the mass balances were established through elemental balances as follows;

$$C:\ 6a + c + d = 0$$

$$H:\ 12a + 2b + 4d + 2e = 0$$

$$O:\ 6a + b + 2c + d = 0$$

Putting b, c and d in terms of a, d and e we get;

$$d = -(c + 6a)$$

$$b = -(6a + 2d + e)$$

$$c = 2d + 0.5e + 6a$$

All the mass balance calculations were made in terms of 1 mole of glucose ($a = 1$) and estimates of hydrogen moles. Mass balances were calculated using Microsoft Excel spread sheet by means of the linear equations above. Table B2 below shows the limits in number of moles that was used to plot the mass balance graph shown in Figure 3 in Chapter 4.1.1.

Table B2: Figures for mass balance linear plot

a-glucose	b-water	c-carbon dioxide	d-methane	e-hydrogen	ΔH (kj/mol)	ΔG (kj/mol)
1	10	-8	2	-20	1121.45	233.42
1	-8	1	-7	16	-1152.58	-940.36

Figure B1 below shows the mass balance region for calculations done using 1 mole of cellulose ($C_6H_{10}O_5$) at standard conditions. The mass balance region is almost similar to that obtained from the glucose calculations shown in Chapter 4.1.1.

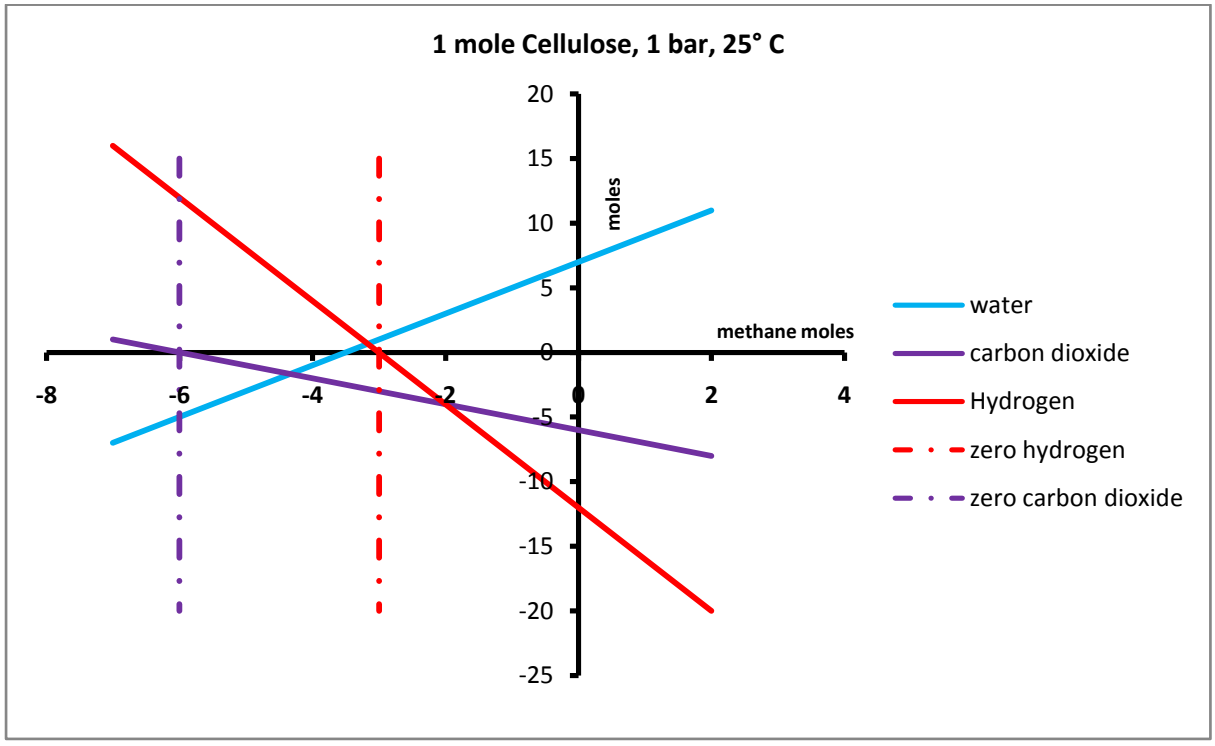

Figure B1: The amount of each component required/produced per mole of glucose.

The same procedure was used for the scenario when oxygen was added to the system.

$$aC_6H_{12}O_6 + bCO_2 + cCH_4 + dH_2O + eH_2 + fO_2 = 0 \qquad \text{Equation (B2)}$$

In addition the enthalpy of reaction

$\Delta H°(reaction) = \sum \Delta H°(products) - \sum \Delta H°(reactants) = 0$

was also used in the calculations. The overall mass balance makes it possible to establish all the atomic mass balances through elemental balances (oxygen in the system), as follows:

C: $6a + b + c = 0$

H: $12a + 4c + 2d + 2e = 0$

O: $6a + 2b + d + 2f = 0$

C.1. Calculation of Enthalpy and Gibbs Free Energy for Cellulose

Table C1: Estimation of cellulose G and H values

		Enthalpy	Gibbs
		[kJ/mol]	[kJ/mol]
monosaccharides	Glucose	-1262.19	-915.9
	fructose	-1259.38	-915.51
		-1260.79	-915.705
disaccharides	sucrose	-2199.87	-1564.7
	lactose	-2233.08	-1567.33
		-2216.48	-1566.02
	water	-285.83	-237.19
	dehydration	19.265	28.205
polysaccharide		**-955.69**	**-650.31**

The calculation shows a simple estimation which removes water and estimated the dehydration term for cellulose (Alberty 1998; Griffiths 2013; Perks and Liebman 2000). The values where used to plot Figure 7.

D.1. Calculation of Chemical Potential

Considering production of methane from Equation (13) shown below

$C_6H_{12}O_6 \Rightarrow 3CO_2 + 3CH_4$, ΔH = -141.9 kJ/mol, ΔG = -418.68 kJ/mol

Chemical potential lost is referred to $\frac{(\Delta G_{\text{combustion of reactant}} - \Delta G_{\text{combustion of product}}) = \Delta G_{\text{reaction}}}{\Delta G_{\text{combustion of reactant}}}$

And the combustion of reactants and product is shown by Equations (D1) and (D2)

$C_6H_{12}O_6 + 6O_2 \Rightarrow 6CO_2 + 6H_2O$ ΔG = -2873 kJ/mol Equation (D1)

$3CH_4 + 6O_2 \Rightarrow 3CO_2 + 6H_2O$ ΔG = -2454.5 kJ/mol Equation (D2)

$$= \frac{2873 - 2454.5}{2873}$$

=15 %

Hence the process would conserve 85 % of the chemical potential in the feed