A Thermodynamic Approach Toward Defining the Limits of Biogas Production

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DOI 10.1002/aic.15016
Published online August 25, 2015 in Wiley Online Library (wileyonlinelibrary.com)

In this article, the authors present theoretical thermodynamic targets for producing biogas. The research shows the relationship between the mass of substrate used vs the methane produced from a feedstock of glucose and an estimate for that of cellulose. Calculations based on material and energy balances are used to determine the performance target (material and energy limits) of an anaerobic digestion system. These limits cannot be exceeded even if one genetically engineer organisms to increase yield. The results show that all processes that produce methane are feasible from a Gibbs free energy point of view but do not conserve the chemical potential of the feed material. The thermodynamics show that methane production is material and energy limited. The maximum amount of methane that can be formed sustainably is 3 moles per mole of glucose, producing 142 kJ of heat per mole of glucose which needs to be rejected.

Keywords: thermodynamics, biogas production, limits

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.[1,2] The main reasons for the interest in developing biogas technology are concerns about global warming, the resulting attempts to limit CO_2 emissions, and a growing awareness of the decline in conventional fossil fuel reserves.[3] 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, and solar energy. Taking the last three in order, 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.[4] This leaves us with biogas, which offers a feasible method of bringing energy within the means of ordinary people, wherever they may live. 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. Biogas produces only carbon dioxide and water vapor on combustion unlike firewood which would produce soot and ash thus leading to less particulate emissions. The fodder supplied to the animals that produce the feces from which biogas can be made consumes an amount of carbon dioxide that is almost equal to that combusted in the ecological cycle leading to a more sustainable process.[3]

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,[5] and the proc regression model (a statistical model equation that shows the relationship between an outcome variable and another set of variables where the parameters are estimated so that a measure of fit is obtained) 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 (°C). Masse and Droste,[6] proposed a mathematical model for a batch reactor as $Q_{CH_4}=V_{TP}*V_L(\sum \rho_i)_{bio}$, where Q_{CH_4} = volumetric flow rate of methane (l/day), V_{TP} = volume of one mole of gas (L/mole), V_L = volume of liquid in reactor (L), and $(\sum \rho_i)_{Bio}$ = rate of change of methane (i) production caused by biological activity (mole/day*L).

Buswell and Mueller[7] developed a model based on the chemical composition of the degraded waste to predict methane production and this is expressed as

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

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

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In this research, the thermodynamic properties of the material balance equations that occur during the production of biogas were examined. Gibbs free energy and Enthalpies of reaction for the decomposition of glucose for the proposed material balances were determined under standard state conditions to determine a thermodynamic attainable region; namely the set of all possible outcomes.

Application of thermodynamics

One of the aims of this study was to apply the general laws of thermodynamics to biological systems. Thermodynamics can be used as a powerful tool for setting and evaluating process and environmental targets.[8] It has also been applied to understanding microbial processes.[9,10] 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,[11] but to date little research has been focused on the thermodynamics of biogas production.

Thermodynamic principles were used to analyze 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 material 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 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 is to emphasize the importance of carrying out theoretical research using existing thermodynamic laws and process synthesis to predict results.

Theoretical Procedure

The research involved theoretical calculations in which

1. In the first case, it is assumed that the overall process is anaerobic. The gas composition ranges 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 to supply enough heat through the combustion process to make the overall process adiabatic. The remainder of the glucose is assumed to be converted to biogas by anaerobic digestion.

Defining the process

The process target is defined as the maximum amount of methane that can be produced from 1 mole of glucose. The idea is to use process synthesis to find a sustainable process that can convert raw materials to the desired products. The system is a continuous process at steady state. The feed and products are both at 25°C and 1 bar as shown in Figure 1. Heat can be either removed or supplied to the system. The carbon efficiency which is defined as the amount of carbon in glucose that is converted to methane, is also used to analyze the overall system. Selectivity is defined as the ratio of desired product to undesired product.[12] Chemical potential is defined as, the rate of change of the Gibbs free energy of the system with respect to the change in the number of moles of a particular component at constant temperature and pressure.

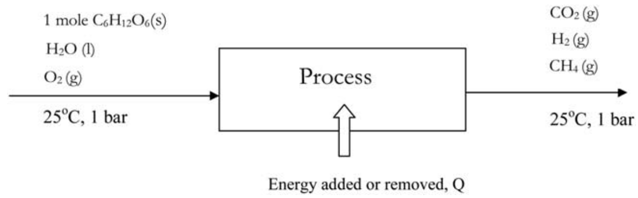

Figure 1. Representation of a process for the synthesis of methane.

The Feed. The feed material comprises of 1 mole of glucose ($C_6H_{12}O_6$). The reaction occurs in water, which therefore forms part of the feed material. 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 on Gibbs free energy for this substrate proved difficult to obtain. However, as glucose and cellulose are carbohydrates and of comparable chemical structure, the researchers reasoned that almost similar material and energy balance results would be obtained if cellulose was used as a feed substrate. Buswell and Boruff 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, one mole of water gets into act and adds to the weight of biogas.[13] In the first scenario glucose and water are the only feed substrates whereas oxygen is added as a feed in the second scenario.

Products. The range of products formed from glucose is limited by the material balance. Methane, carbon dioxide and hydrogen have been considered to be the main products of anaerobic digestion. Note that many other products such as acids and alcohols can also be produced during anaerobic digestion, however, these are usually in small quantities and are ignored in the discussion for simplicity.

Material Balance Target. A material balance provides the foundation for creating a flow sheet. It allows one to set different process (e.g., environmental or production) targets, depending on the choice of feed and its stoichiometry. The more feed that is added, the more product becomes available only if the process is mass efficient.

There are many reactions involved in the formation of biogas. There are also complex biochemical pathways but the thermodynamics involved in these calculations represent the feasible envelope. This is why the thermodynamics holds and is used to simplify the complexity through atomic species balances, hence there is no need to consider each pathway. The atomic species balance allows one to perform a material balance without considering each individual unit or recycle but only the entire process.[14] It can be shown for these products there are two independent material balances that relate the feed material to the possible products when no oxygen is added to the system as there are five species (CH_4, H_2O, $C_6H_{12}O_6$, CO_2, and H_2) and three atoms (C, H, O). $C_6H_{12}O_6$ is set at one mole therefore the material balance has one degree

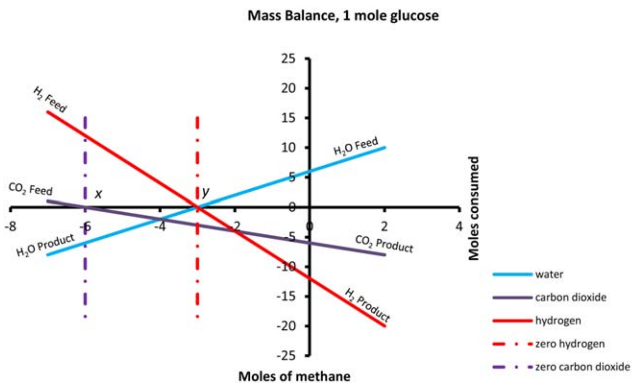

Figure 2. The amount of each component consumed/ produced per mole of glucose.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of freedom. When oxygen is included in the system, a new overall material balance is used, which has six species and three atoms hence two degrees of freedom. The material balance limits are when the moles of CH_4, H_2O, O_2, CO_2, and H_2 are zero. This can be plotted on a moles of product produced vs moles of methane produced diagrams.

It is noted that the material balances are fundamental; thus the amount of CH_4 made per mole of CO_2 or H_2 produced is set by the balances given in the results section. Even if one genetically engineers the bacteria, clearly no organism can disobey these rules and these limits cannot be exceeded. Eq. 1 below shows the overall material balance when no oxygen is added to the system and Eq. 2 when oxygen is included. In the material balance, ***b, c, d, e,*** and ***f*** are the amounts of carbon dioxide, methane, water, hydrogen, and oxygen produced per mole of glucose ($\boldsymbol{a}$=1 mole), respectively.

$$\text{Case 1: } aC_6H_{12}O_6+bCO_2+cCH_4+dH_2O+eH_2=0 \quad (1)$$

$$\text{Case 2: } aC_6H_{12}O_6+bCO_2+cCH_4+dH_2O+eH_2+fO_2=0 \quad (2)$$

The overall material balance makes it possible to establish all the atomic balances through elemental balances (no oxygen in the system), as follows

$$\mathbf{C}: \; 6a+b+c=0$$

$$\mathbf{H}: \; 12a+4c+2d+2e=0$$

$$\mathbf{O}: \; 6a+2b+d=0$$

and when oxygen is added to the material balance, the atomic balance for oxygen is changed to

$$\mathbf{O}: \; 6a+ \; 2b+d+2f=0$$

A number of calculations are used to analyze and evaluate the thermodynamically feasible regions for biogas production. One mole of $C_6H_{12}O_6$ was converted, and the amounts of CH_4, CO_2, O_2, H_2O, and H_2 produced or consumed were plotted as linear functions of the moles of methane produced or consumed. This helps to locate the point at which the maximum amount of methane can be obtained after considering mass limits.

The Energy (Enthalpy) and Entropy (Gibbs Free Energy) Limits. The energy balance (like the material balance) and the second law of thermodynamics must also be taken into account when deciding optimal conditions for biogas production, because all three, impose limitations on the system. The energy balance can also be applied to the overall process to show the minimum amount of energy required or produced. When the change in Enthalpy (ΔH) is positive, it means that the system requires heat to be added and when ΔH is negative, heat has to be rejected from the system. However, if the change in Gibbs free energy (ΔG) is negative, it indicates that the system has potential to do work and when positive the system requires work. The two material balances (Eqs. 1 and 2) represent the basis for the calculations made when no oxygen and when oxygen was added to the overall process respectively. This data was used to plot enthalpy and Gibbs free energy as a function of methane. The plots are used to determine the theoretical energy limits. Combinations of the energy, entropy limits for the system with the material balance limits produce the digester attainable region.

Results and Discussion

Anaerobic system

The overall material, energy and Gibbs free energy balances for the anaerobic system in Case 1 were considered first. Because of the approach used, it should be remembered that the outputs are considered from all possible anaerobic processes (normalized 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.

Material Balance. Equation 1 has been plotted in Figure 2 and 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 material balance also shows whether the substance is a feed or a product. On the material balance plot; Figure 2, the positive axes show that the substance is being consumed, while the negative axes represent the substance as a product. The material 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 material balance. Thus this diagram represents all possible material balances, namely the Attainable Region. If there are constraints on the system these will limit what is attainable. Looking at the diagram vertical lines are set that identify a target of zero for carbon dioxide (the purple broken line) and hydrogen (the red broken line) separately. It is further noted that water can act both as a product (to the left of the red broken line corresponding to zero hydrogen produced) or a reactant (to the right of the red broken line corresponding to zero hydrogen produced). Thus water is consumed when hydrogen is produced but is a by-product of methane production.

From Figure 2, there are four regions in which the species are present and looking 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 producing methane is only considered, 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 material balance. In the case of zero carbon dioxide (point *x* in Figure 2), 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 Eq. 3

$$C_6H_{12}O_6 + 12H_2 \Rightarrow 6CH_4 + 6H_2O \quad (3)$$

The material balance shows that hydrogen is consumed and it is therefore not reasonable to operate at a process with a material 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 material balance is given in Eq. 4

$$C_6H_{12}O_6 \Rightarrow 3CH_4 + 3CO_2 \quad (4)$$

If carbon efficiency is defined as the number of moles of carbon in the methane product gas to the moles of carbon in the feed, then the maximum carbon efficiency for an anaerobic biodigestor is 50%. The material balance shows that one 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 Eq. 5

$$C_6H_{12}O_6 + 6H_2O \Rightarrow 12H_2 + 6CO_2 \quad (5)$$

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.

Enthalpy and Gibbs Free Energy. A material balance also sets the enthalpy and Gibbs free energy balances, and these can also limit the attainable material balances. Figure 3 shows that all the processes that produce methane are feasible from a Gibbs free energy point of view, that is, its value is negative. This means they are all thermodynamically favorable 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 one only make hydrogen and carbon dioxide as shown in Eq. 5.

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 Eq. 5 requires heat addition and the question that

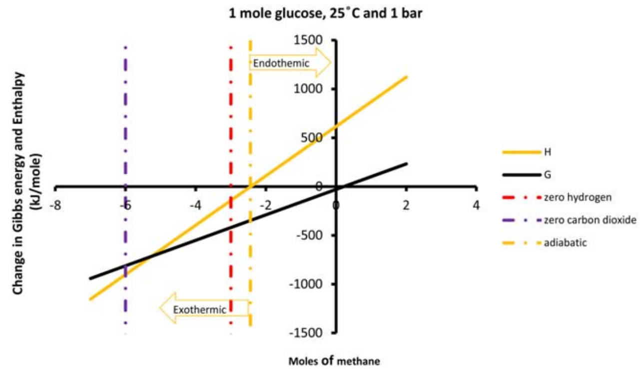

Figure 3. Enthalpy and Gibbs free energy change plot as a function of methane produced per mole of glucose.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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 material balance in Eq. 6 and the target carbon efficiency is thus 50%

$$C_6H_{12}O_6 \Rightarrow 3CO_2 + 3CH_4, \ \Delta H = -141.9 \ \text{kJ/mol}, \ \Delta G = -418.68 \ \text{kJ/mol} \quad (6)$$

Such a process would produce around 142 kJ/mole of glucose of heat. This raises the question of how does one design and operates 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. What is being said is that it is easy to calculate and show that the chemical potential of combustion of the methane made from the glucose is 15% less than the chemical potential of the combustion of the original glucose.

- No carbon dioxide emissions

The material balance for a target of zero carbon dioxide emissions is given in Eq. 7 below

$$C_6H_{12}O_6 + 12H_2 \Rightarrow 6CH_4 + 6H_2O, \ \Delta H = -900 \ \text{kJ/mol}, \ \Delta G = -810 \ \text{kJ/mol} \quad (7)$$

A process operating with this material balance would be exothermic with and would reject 900 kJ/mole 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 concluding that anaerobic digesters would produce carbon dioxide.

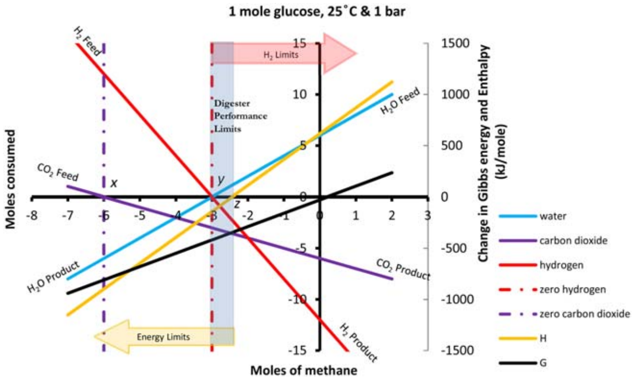

Figure 4. Digester performance limits shown on material balance, enthalpy, and Gibbs free energy change plot as a function of methane produced per mole of glucose.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

- Adiabatic operation

For an adiabatic process, $\Delta H = 0$ kJ/mole which corresponds to point z on Figure 3. In this situation, the material balance for the digester would be expressed in Eq. 8

$$C_6H_{12}O_6 + 1.12H_2O \Rightarrow 2.24H_2 + 3.56CO_2 + 2.44CH_4, \quad \Delta H = 0 \text{ kJ/mol}, \ \Delta G = -345 \text{ kJ/mol} \tag{8}$$

Thus the production of methane would be reduced from the target of 3 discussed previously (at zero hydrogen limit) to 2.44 moles of methane per mole of glucose.

This material 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 material balance close to that described by Eq. 8 in order for the reaction to be adiabatic. Thus in this case one would coproduce hydrogen and methane in a ratio of close to 1:1 and the carbon efficiency would be 41%.

Digester Performance Limits. At this point it is noted that there are in principle two types of digester that one finds in practice. The first is essentially an uncontrolled passive one that operates in an 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. When viewed from fundamental principles the two are the same, the industrial one allows for more flexibility in operation and so where appropriate they are discussed separately. The passive digester is considered in this section.

Passive digesters operate at ambient or above ambient temperatures and thus must lose heat to the surroundings. From Figure 4, it can be seen that this therefore limits the material balances that can be achieved to those lying in the shaded area, namely between the adiabatic limit and the limit of zero hydrogen production.

To understand the magnitude of the heat removal problem in a passive digester, one 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 cellulose is mixed with water the mixture would have a heat capacity between 1 and 4 kJ/(mole cellulose per °C). The actual value of the heat capacity would depend on the proportion of cellulose to water. From Figure 4, $\Delta H^{\circ}_{\text{reaction}}$ for the production of methane is of the order of 100 kJ/mole which gives rise to adiabatic temperature change of around 100°C. Thus 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. Is the overall rate of the process heat-transfer controlled or is it 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 one consider operating at minimum selectivity of methane to conserve the chemical potential of the feed, 2.24 moles of hydrogen, and 2.44 moles of methane would be made. This would reduce the heat load on the digester and conserve the chemical potential of the feed (i.e., be more reversible.)

It is also important to consider that a significant amount of hydrogen is produced from the material balance at $\Delta H > 0$ kJ/mole. From Figure 4, 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 to favor hydrogen production.[15] However, it is also difficult to collect and store the hydrogen in a cheap way as it can easily leak from a simple passive biodigester. It can also be seen from Figure 4 that the more hydrogen that one can produce, the more carbon dioxide is emitted. To reduce CO_2 production, increase in methane production is encouraged.

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 material balance would be shown as Eq. 9

$$C_6H_{12}O_6 + 6H_2O \Rightarrow 12H_2 + 6CO_2, \ \Delta H = 616 \text{ kJ/mol}, \quad \Delta G = -27 \text{ kJ/mol} \tag{9}$$

Thus one would need to supply 616 kJ/mol of heat and 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 one has to get the heat from the process itself. Effectively in this case some material were burnt, 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 thus need to take the burning process into account when modeling the overall system. Furthermore, it is not beneficial to add more heat to the process than required so even though there is an extra degree of freedom relative to the anaerobic process. The cases for which ΔH is zero are examined only. Thus this is the situation that is referred to as Case 2.

The material and energy balances when oxygen is added to the system and $\Delta H = 0$ kJ/mol are plotted on the same kind of diagram in Figure 5. The species are plotted as before as a function of methane to show the set of all possible material balances for an adiabatic process. Addition of oxygen changes the material balance, hence the selectivity of products are also changed as shown in Figure 5.

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 the material balances that require this action are not considered.

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 material balances corresponds to the material balance where no methane is produced and hydrogen and carbon dioxide are the only products. Thus the shaded region in Figure 5 corresponds to the region of all feasible material balances for digesters that are overall adiabatic.

The material 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 material balance found in the previous case (Case 1) namely Eq. 1. This also corresponds to the maximum amount of methane that could be produced in a system that is overall adiabatic, namely 2.44 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, one would maximize hydrogen production in an adiabatic digester. The overall material balance for the process would be shown in Eq. 10

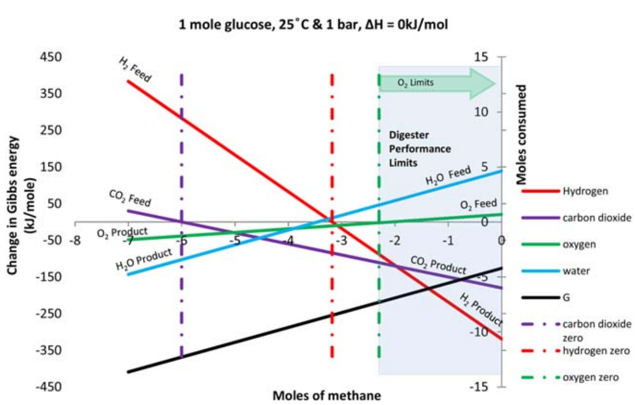

Figure 5. Digester performance limits shown on material balance, enthalpy, and Gibbs free energy change plot as a function of methane produced per mole of glucose when oxygen is added to the overall process.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

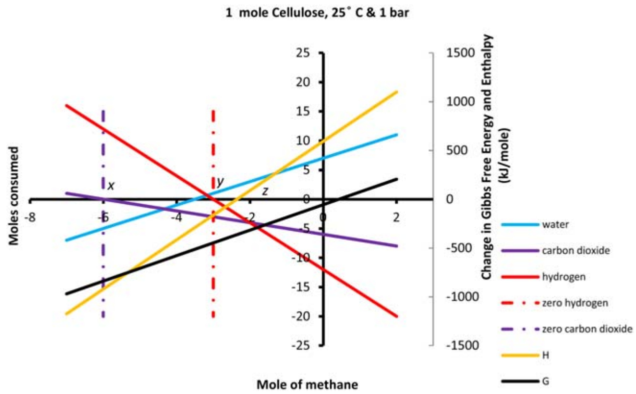

Figure 6. Digester performance limits shown on material balance, enthalpy, and Gibbs free energy change plot as a function of methane produced per mole of cellulose.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$C_6H_{12}O_6+4.6H_2O+0.7O_2 \Rightarrow 10.6\ H_2+6CO_2 \quad \Delta H=0\ \text{kJ/mol}, \Delta G=-126\ \text{kJ/mol} \tag{10}$$

In this case, the system would produce 10.6 moles of hydrogen per mole of glucose and 96% of the chemical potential of the feed is retained. This is obtained using the Gibbs free energy values from combusting glucose rather than hydrogen. 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 be need for extra equipment such as heat exchangers, heat pumps, heat engines in addition to the digester.

Material and energy balance plot using estimated Gibbs free energy values of cellulose

The analysis has been done on glucose because data for the enthalpy and the Gibbs free energy of formation for glucose is available. Such data are not readily available for cellulose. However, Figure 6 has been drawn based on some estimated values ($\Delta H = -955$ kJ/mol, $\Delta G = -650$ kJ/mol), calculated by Refs. 11,16,17. It can be seen that the results in Figure 6 do not differ significantly from Figure 4 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. 11

$$C_6H_{10}O_5+2.32H_2O \Rightarrow 2.64H_2+3.66CO_2+2.34CH_4, \quad \Delta H=0\ \text{kJ/mol}, \Delta G=-362\ \text{kJ/mol} \tag{11}$$

Conclusions

The limits of the thermodynamics of the anaerobic digestion of glucose and cellulose have been examined. The implications of adding heat by burning products were then considered. This was done by plotting a graph that shows all possible process outputs, which have called an Attainable Region. All the anaerobic processes that produce methane from glucose (and cellulose) are feasible from a thermodynamic point of view. At zero emissions of carbon dioxide, hydrogen is required as a feed material, and this is not regarded as a feasible operating point. The attainable region obtained show that the process is limited if hydrogen cannot be added to the digester and enthalpy limited in the sense that large Enthalpy values imply significant heating or cooling of the contents. It is shown that the maximum amount of methane that can be produced sustainably in the absence of oxygen from one mole of glucose is 3 moles, and the remaining carbon is used to produce an equal amount of carbon dioxide. Heat addition or removal can be used to change the selectivity of the products between hydrogen and methane. The economy for both these products is also quite established. However, from a thermodynamic perspective, unless waste heat is available, producing hydrogen may not be the most energy efficient process.

Acknowledgments

The authors would like to thank Materials and Process Synthesis (MaPS) Research Unit at the UNISA Florida Campus, Johannesburg, South Africa for providing financial support for carrying out this work. The work was also supported by the THRIP project.

Literature Cited

1. Steinhauser A, Deublein D. *Biogas from Waste and Renewable Sources: An Introduction*, 2nd ed. Wiley VCH, 2010.
2. Ashrafi M, Proll T, Pfeifer C, Hofbauer H. Experimental study of model biogas catalytic steam reforming: 1 Thermodynamic optimisation. *Energy Fuels*. 2008;22(6):4182–4189.
3. Teodorita A, Dominik R, Heinz P, Michael K, Tobias F, Silke V, Rainer J. *Biogas Handbook*, Esbjerg, Denmark: University of Denmark Esbjerg 2008:11. ISBN 978-87-992962-0-0
4. International Energy Agency. *Tracking Clean Energy Progress*. International Energy Agency, 2013:23–27. Available at www.iea.org. Accessed on December 2013.
5. Safely LM, Westerman PW. Perfomance of a low temperature lagoon digester. *Bioresour Technol*. 1992;41:167–175.
6. Masse DI, Droste. Comprehensive model of anaerobic digestion of swine manure slurry in a sequencing batch reactor. *Waste Res*. 2000; 34(12):3087–3106.
7. Buswell AM, Mueller HF. Mechanisms of methane fermentations. *Ind Eng Chem*. 1952;44:550–552.
8. Patel B, Hildebrandt D, Glasser D, Hausberger B. Thermodynamic analysis of processes I; Implications of work integration. *Ind Eng Chem Res*. 2005;44:3529–3537.
9. Roels, J. *Energetics and Kinetics in Biotechnology*. Amsterdam: Elsevier Biomedical Press, 1983.
10. Westerhoff HV, Lolkema JS, Otto R, Hellingwerf K.J. Thermodynamics of growth non-equilibrium thermodynamics of bacterial growth, the phenomenological and the mosaic approach. *Biochim Biophys Acta*. 1982;683:181–220.
11. Griffiths C. A thermodynamic analysis of biological system using process synthesis, PhD thesis. WIReD Space, University of Witwatersrand, Johannesburg, South Africa, 2013.
12. Fogler SH, *Elements of Chemical Reaction Engineering*, 4th ed. Pearson Education Inc., Prentice Hall PTR, 2006:305–376.
13. Buswell AM, Boruff CS. The relation between the chemical compositions of organic' matter and the quality and quantity of gas produced during sludge digestion. *Sewage Works*. 1932;4:454.
14. Patel B. Fundamental targets for the synthesis and evaluation of chemical processes, PhD thesis. WIReD Space, University of Witwatersrand, Johannesburg, South Africa, 2007.
15. Grey VM, Ngoma L, Obazu FO. Interrelationships between bioreactor volume, effluent recycle rate, temperature, Ph, % hydrogen, hydrogen productivity and hydrogen yield with undefined bacterial cultures. *Int J Hydrogen Energy*. 2012;37:5579–5590.
16. Alberty RA. Calculation of standard transformed Gibbs energies and standard transformed enthalpies of biochemical reactant. *Arch Biochem Biophys*. 1998;353(1):116–130.
17. Perks MH, Joel FL. Estimation of the enthalpies of formation of some common, solid phase compounds of considerable theoretical importance. *J Struct Chem*. 2000;11(5):325–329.

Manuscript received Aug. 19, 2014, and revision received June 24, 2015.