Biomass as an Alternative Energy Source: An Illustration of Chemical Engineering Thermodynamic Concepts

Marguerite A. Mohan[1], Nicole May[1], Nada M. Assaf-Anid[1,2] and Marco J. Castaldi[3]
1. Chemical Engineering Department, Manhattan College, Riverdale, NY/ 2. Earth Engineering Center, Columbia University, New York, NY/ 3. Earth and Environmental Engineering Department, Columbia University, New York, NY

Abstract

The ever increasing global demand for energy has sparked renewed interest within the engineering community in the study of sustainable alternative energy sources. This paper discusses a power generation system which uses biomass as “fuel” to illustrate the concepts taught to students taking a graduate level chemical engineering process thermodynamics course. The students were asked to propose solutions as to how a bioreactor might be used to decompose the biomass anaerobically and subsequently generate power. The purpose of the assignment was to give the students a better understanding of chemical thermodynamics by incorporating abstract thermodynamic principles, such as fugacity, solubility, and multi-phase equilibrium and to give them a chance to apply these principles to a relevant, practical, and open-ended situation. Specifically, the students were required to provide a full understanding of the bioreactor, and to develop the appropriate thermodynamic relationships to determine preferred system conditions which would accelerate the decomposition process. Among the characteristics examined were the types of byproducts formed, how these byproducts distribute themselves between the liquid and vapor phases, and the preferred concentration of carbon in the feed stream as a function of residence time, temperature, and pressure.

Introduction

As discussed in an earlier paper[1], the overall objective of the thermodynamics course sequence at Manhattan College is to allow the students to become confident enough about their understanding of the theoretical material taught and familiar enough with mathematical manipulations to properly and accurately set-up solutions to problems involving thermodynamics. Towards the end of the semester, students have a chance to explore and propose feasible solutions, and conduct what-if scenarios to contemporary problems such as Methyl Tert-Butyl Ether (MTBE) contamination of groundwater[1], or biofuels[2], or thermodynamics of power plants[3]. The desired outcome is to develop the students’ engineering judgment and capabilities along with their mathematical skills in solving fairly complicated equations with many inputs. This major assignment introduces the students to a practical and current problem that they can tackle somehow intuitively rather than by a direct application of formulas as presented by Cengel[4]. The only requirement for a solution is the use of some sort of computer programming, a spreadsheet, Mathematica, or MathCad®, and the thermodynamic principles taught in class (i.e., as phase equilibria, solubility, fugacity, etc). Such an open-ended approach is common in engineering education and has been used in thermodynamics courses[5] because it resembles problem solving situations encountered in industry[6].

The open-ended problem presented in this paper was given as a final project to a graduate process thermodynamics class. However, portions of it could be suitable in an undergraduate thermodynamics, modeling[3] or design class[7] if presented in a less open-ended manner, or as continuing problem integrated in a series of courses using the approach of Shaewitz[8]. The problem assignment given to the students with three references on anaerobic digestion[9,10,11] is shown below. In addition, the students were instructed on literature research methods using online libraries and the Internet, such as About.com[12], to assist them in finding background information. Topics and information searched ranged from gasification of biomass for distributed energy production systems, to physical property data needed to perform calculations, to ideas for possible solutions.

Problem Statement

Below is the problem statement, verbatim, given to the students as the final class project. As shown in Table 1, the students had about 6 weeks to complete the project and were expected to work independently. By the time the computer assignment was issued, the students would have been exposed to solution equilibrium theory which begins with Chapter 6.

Table 1: Overview of Course Syllabus

Week	Subject
1	Review of Classical Thermodynamics
2	Review of Classical Thermodynamics (cont'd)
3	Ch. 2, prepare for Exam #1
4	Ch. 3, Exam #1 (classical thermo and Ch. 2)
5	Ch. 4 (parts)
6	Ch. 5 (parts), Review exam #1
7	Ch. 6 (parts)
8	Ch. 7 (parts); Computer Assignment Discussed
9	Ch. 7 (parts), Exam #2 (Ch. 3, 4, 5, 6)
10	Ch. 8, Ch. 9 (parts)
11	Review exam #2, Ch 9 (parts)
12	Ch. 10 (parts), Ch. 11 (parts) Ch. 12 (parts)
13	Statistical Thermodynamics, Computer Assignment Due, Review
14	Final Exam

The demand for power, especially electricity, has driven many engineers to propose possible ways to generate power. Of course, that power generation must be compatible with environmental regulations and must be fueled by available resources. One novel power generation system is to use a bioreactor to decompose various types of biomass anaerobically. The off-gas from that process will generate methane (CH_4*), which can be used as fuel. However, carbon dioxide (*CO_2*) is also generated. In this gas mixture of *CH_4* and *CO_2*, the latter is* *considered a diluent and effectively lowers the energy content of the gas stream. One could separate out the* CO_2 *from the stream, but the energy requirements are prohibitively high.*

The total power that can be obtained from the system is governed by volumetric flowrate and energy content. It has been proposed to accelerate the decomposition of the biomass to generate more methane, or at least a higher flowrate of CH_4 *and* CO_2*. One way to do this is to "feed" the bacteria that is decomposing the biomass a warm stream of* CO_2 *and hydrogen. In addition to the biomass, this* CO_2 *can serve as a carbon source for the bacteria. This allows the bacteria's population to increase and the decomposition of the biomass to occur faster.*

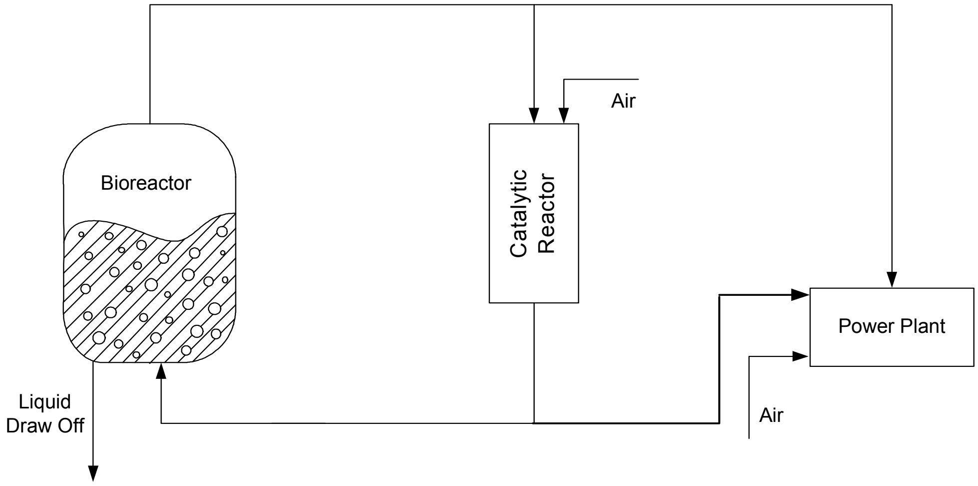
To supply the bacteria with CO_2 *and hydrogen, another reactor is placed upstream to convert some of the bioreactor product stream (*CH_4 *and* CO_2*) to hydrogen (*H_2*), carbon monoxide (CO), and* CO_2*. This second reactor is a catalytic reforming reaction that uses a small amount of air.*

Lastly, it is known that the bacteria will have some waste byproducts as a result of their digestive process. Some of those byproducts could harm the bacteria if they accumulate to dangerous levels.

As an engineer on this job, you need to provide a full understanding of the bioreactor. That is, what types of byproducts will be formed by the bacteria and how will those byproducts distribute themselves between the liquid and the gas phases. In addition, you also need to determine the preferred concentrations of the carbon in the bioreactor feed stream as a function of residence time in the bioreactor to ensure that adequate carbon is dissolved in the liquid phase for the bacteria to access.

In addition to the statement, a conceptual schematic (Figure 1) was provided to show the overall system. Finally, a survey was distributed to the students to determine how this type of a project impacts their understanding of the subject and overall learning experience.

Figure 1: Schematic of System Components



Background and Theory

The derivation presented here relies on an initial set of equations with key intermediate steps. The complete solution to the model developed for this open ended problem can be obtained, in *Mathematica* format, upon request.

Anaerobic digestion, or methane fermentation, is the process by which fermentative microorganisms convert biomass to methane in the absence of oxygen. Often, a water layer serves as a blanket to exclude oxygen and promote the growth of the appropriate anaerobes[13].

The methane produced in the anaerobic digestion has long been recognized as a possibly significant source of energy. With higher (gross) heating values ranging from 15.7 to 29.5 MJ/m^3(n), the gas produced by the anaerobic digestion of biomass, called biogas, is a medium-energy fuel that may be used for heating and power[13].

Methane fermentation is a three step process that utilizes three main categories of bacteria which are; fermentative, acetogenic, and methanogenic[13,14]. In the first step of the digestion, the fermentative bacteria convert complex polysaccharides, proteins, and lipids present in biomass to lower molecular weight fragments such as carbon dioxide, and hydrogen[13]. For the purpose of this paper, the main fermentative reactions that will be considered are[13]:

Reactions	$\Delta G^{o'}$(kJ)	
$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2$	-26	(Rxn 1)
$C_6H_{12}O_6 \rightarrow 2CH_3COCO_2^- + 2H^+ + 2H_2$	-112	(Rxn 2)
$C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2CO_2^- + H^+ + 3CO_2 + 5H_2$	-192	(Rxn 3)
$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2CO_2^- + H^+ + 2CO_2 + 2H_2$	-264	(Rxn 4)

In the second step of the process, hydrogen producing acetogenic bacteria catabolize the longer chain organic compounds formed in the first step to yield acetate, carbon dioxide, and hydrogen. Also during this second stage, some carbon dioxide and hydrogen are converted to acetate by the acetogens. Only the main acetogenic reactions are considered for this paper and are given below [13]:

Reactions	$\Delta G^{o'}$(kJ)	
$CH_3COCO_2^- + H_2O \rightarrow CH_3CO_2^- + CO_2 + H_2$	-52	(Rxn 5)
$2CO_2 + 4H_2 \rightarrow CH_3CO_2^- + H^+ + 2H_2O$	-95	(Rxn 6)
$2HCO_3^- + 4H_2 + H^+ \rightarrow CH_3CO_2^- + 4H_2O$	-105	(Rxn 7)
$C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3CO_2^- + 2HCO_3^- + 4H^+ + 4H_2$	-206	(Rxn 8)
$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3CO_2^- + 2H^+ + 2CO_2 + 4H_2$	-216	(Rxn 9)
$C_6H_{12}O_6 \rightarrow 3CH_3CO_2^- + 3H^+$	-311	(Rxn 10)

In the third and final stage of the fermentation process, methanogenic bacteria convert acetate to methane and carbon dioxide by decarboxylation, and the latter to additional methane upon reaction with hydrogen. The methanogenic reactions considered for the purpose of this paper are [13]:

Reactions	$\Delta G^{o'}$(kJ)	
$CH_3CO_2^- + H^+ \rightarrow CH_4 + CO_2$	-36	(Rxn 11)
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-131	(Rxn 12)
$HCO_3^- + H^+ + 4H_2 \rightarrow CH_4 + 3H_2O$	-136	(Rxn 13)

In the three stages described above, CH_4, H_2, and CO_2 are in the gaseous state. In addition, the standard physiological conditions are atmospheric pressure, unit activity, and a temperature of 25 °C at a pH of 7.0[13].

As evidenced by the reactions, there are a number of intermediate acids and alcohols that are generated. Since all reactions do not go to completion, there is a certain amount of these that buildup within the bioreactor. These components serve to change the solution pH, poison the bacteria, or inhibit the digestion rates. Since the bioreactor usually takes days to digest the initial charge of biomass, an equilibrium is established between the vapor and liquid phases in which the compounds partition.

The information that has been presented thus far is an overview of the biochemistry that is occurring in the bioreactor. This knowledge can now be applied in order to present a solution to the proposed engineering problem. It should be noted that the problem statement is of an open-ended nature; therefore, there are several possible approaches as well as solutions. One solution was chosen that encompassed the whole system.

Student's Solution

One unique feature of this type of problem is the dynamic nature of the system. That is, starting the system with an initial charge results in changing stream composition while steady state is achieved. This requires students to develop a solution that is iterative in nature. This exposes students to realistic processes in industry where thought must be given to system startup and shutdown as well as adjustments that must be made along the way to a targeted operational condition.

The objective of the project was to increase the total power that may be harnessed from a bioreactor system, either by accelerating the decomposition of the biomass to produce more methane, or by generating a higher flowrate of methane and carbon dioxide in the bioreactor product stream. In addition, a complete thermodynamic analysis, using the phase equilibria theory taught, of the bioreactor was done to determine the partitioning of the acids, alcohols and dissolved gases formed during the digestion process.

A computer solution was created in *Mathematica*® to perform the calculations described in the Background and Theory section. The data generated, along with general design guidelines, were used to propose a potential solution.

The iterative nature of the solution requires a choice of starting points. The solution begins at the product stream of the bioreactor. Literature indicates that this stream consists mostly of methane and carbon dioxide (totaling about 80% of the entire stream), and the ratio of the two typically ranges from 40 / 60 to 75 / 25 (CH_4 / CO_2)[13]. In order to start the solution, vapor mole fractions based on the lower limit of this range, as well as a total flowrate, are assumed. The bioreactor is set to operate in the mesophilic 30°C - 38°C temperature range. Furthermore, in order to maintain the proper alkalinity, the pH must remain within the range 6.6 – 7.4[15].

The product stream from the bioreactor is split: 70% is sent to a power generation plant, and the remaining 30% is routed to a catalytic reforming reactor which is brought online in order to generate hydrogen that will be fed continuously to the bioreactor. Hydrogen is used by the bacteria in the bioreactor as an electron donor for methanogenesis. In most cases, the hydrogen is the limiting reactant. Therefore, feeding hydrogen to the bioreactor may help to accelerate the decomposition of the biomass and will generate a higher flowrate of methane and carbon dioxide. This was one of the major outcomes of the investigation. That is, once the student developed the *Mathematica*® routine which accurately predicted the performance of the system, it was discovered that under several scenarios, the hydrogen fed back to the bioreactor was completely consumed long before the other substrates. This result brings into question the entire concept of feeding a warm stream of hydrogen to accelerate the digestion process.

In addition to the 30% split, there is a second air stream feed to the catalytic reforming reactor. The air stream provides the oxygen necessary for a partial oxidation reaction, which will produce (among other things) the desired hydrogen. In order to maximize the concentration of hydrogen in the catalytic reforming reactor's product stream, the equivalence ratio (ϕ) of the system is varied, and the effect on product composition observed. The equivalence ratio is defined as:

$$\phi = \frac{(F/A)_{actual}}{(F/A)_{stoichiometric}} \qquad \text{(Eqn 1)}$$

where

F/A = the fuel (CH_4) to air (O_2) ratio

After testing various equivalence ratios, an ϕ = 4.0 is chosen, and the following partial oxidation reaction follows:

$$4CH_{4(g)} + 2O_{2(g)} + 7.53N_{2(g)} \rightarrow 0.587CO_{2(g)} + 3.41CO_{(g)} + 0.637H_2O_{(g)} + 7.36H_{2(g)} + 7.53N_{2(g)} \qquad \text{(Rxn 14)}$$

The stoichiometry of the above partial oxidation reaction was obtained through the use of the thermodynamic equilibrium software, *GasEQ*[16]. At the adiabatic flame temperature (1020 K), Reaction (1) has an equilibrium conversion, X_{eq}, of 0.765.

The effluent of the catalytic reforming reactor contains a significant amount of carbon monoxide (CO), which is toxic to the bacteria within the bioreactor. In order to avoid feeding this CO to the bioreactor, a shift reactor is added to the process after the catalytic reactor and before the bioreactor to convert, or shift, the CO to CO_2. The reaction taking place in this reactor is the water gas shift reaction:

$$CO_{(g)} + H_2O \Leftrightarrow CO_{2(g)} + H_{2(g)} \qquad \text{(Rxn 15)}$$

The benefits of shifting the CO to CO_2 are twofold. First, it removes the entire amount of poisonous CO from the bioreactor feed stream. Second, it provides the bacteria with the second species necessary for methane production – carbon dioxide (the first species being hydrogen).

The next step in the solution involves examining the bioreactor, which is the heart of the methane producing process. This bioreactor operates as a semi-batch reactor – the waste that is decomposed by the bacteria is charged in every few weeks, while the stream of hydrogen and carbon dioxide created from the other reactors (catalytic reforming and shift) is fed continuously.

We will focus first on the batching aspect of the bioreactor. The bioreactor is charged with a municipal solid waste (MSW) containing an adjusted moisture content. For the purposes of this solution, the MSW is simplified to glucose suspended in water. In order to find the initial loading of MSW, the volume of the reactor was estimated using values from literature and is proportional to the flowrate that was initially assumed for methane production[13]. The reactor volume along with the density of solid waste, are used to calculate the total amount of MSW in the reactor. It is assumed that the substrate (glucose) constitutes 10% of the total (glucose and water) waste. Therefore, the total amount of glucose initially charged (S_0) may be calculated. It is also assumed that at the end of the charge life, all of the glucose will have been decomposed, and therefore has a final concentration $S_1 = 0$. Assuming a residence time of 30 days, which is typical for anaerobic digestion, and assuming that glucose decomposes at a constant rate throughout the 30-day period, the rate of glucose decomposition may be calculated. The significance of finding this rate of decomposition is that it may be compared to the continuous flow of H_2 and CO_2 that is fed to the bioreactor, since both will be on a time basis.

The initial charge of MSW is allowed to start decomposing before the external H_2 and CO_2 stream is fed into the bioreactor and for a duration that is sufficient enough to allow all of the fermentative and most of the acetogenic reactions to occur. As the decomposition of glucose approaches the end of the acetogenic stage and the beginning of the methanogenic stage, the continuous feed of H_2 and CO_2 is introduced.

As the external stream feeds into the bioreactor, the solubilities of its components in water must be considered. Most of the components entering in this stream (CO_2, N_2, H_2 and the acid vapors) are gaseous and the solubility of the stream component CO_2 is of particular interest as it is dictated by the carbonate system. When CO_2 enters an aqueous solution, the following dissolution and dissociation occur:

$$CO_{2(g)} \overset{K_H}{\Leftrightarrow} CO_{2(aq)} \overset{K_m}{\Leftrightarrow} H_2CO_{3(aq)} \overset{K_a}{\Leftrightarrow} HCO_{3(aq)}^{-} \qquad \text{(Rxn 16)}$$

The initial concentration of the $CO_{2(g)}$ entering the bioreactor is used along with Henry's constant, K_H, to find the concentration of $CO_{2(aq)}$. The latter is then used in combination with K_m to find the concentration of carbonic acid H_2CO_3. The concentration of H_2CO_3, along with K_a, and the pH of the system are used to find the concentration of the bicarbonate ion HCO_3^-. Once the concentrations of $CO_{2(aq)}$, H_2CO_3, and HCO_3^- have been calculated, the remaining concentration of the $CO_{2(g)}$ is tabulated.

As the remaining acetogenic and methanogenic reactions take place, CH_4 and CO_2 are continually produced, while most of the other components are consumed. The exceptions to this are the acid byproducts produced in the fermentation and acetogenic reactions. These acids –

acetic, butyric and propionic – are produced but are not completely consumed. If the levels of the acids in the liquid continue to increase, the alkalinity of the bioreactor will change. As a result, the pH may drop outside of the allowable optimal range for methane fermentation.

In order to find the distribution of the acids between the liquid and vapor phases, chemical thermodynamic concepts are applied. The first concept used is the equilibrium criterion:

$$f_{M,i}^{L} = f_{M,i}^{V} \qquad \text{(Eqn 2)}$$

In words, this criterion indicates that at equilibrium, the fugacity of the vapor phase equals the fugacity of the liquid phase.

The fugacity of component *i* in a liquid solution is related to the mole fraction, x_i, according to the following equation[17]:

$$f_{M,i}^{L} = x_i \gamma_i (T,P,x_i) f_i^0 (T,P) \qquad \text{(Eqn 3)}$$

where

γ_i = the activity coefficient

f_i^0 = the fugacity at some arbitrary condition known as the standard state

In this solution, the standard state is assumed to be that of the pure substance. The fugacity of the standard state is defined as:

$$f_i^0 (T,P) = P_i^{sat}(T) \cdot \varphi_i^{sat} \cdot e^{\left[\frac{1}{R\cdot T} \cdot \int_{P_i^{sat}}^{P} \overline{V} \cdot dP\right]} \qquad \text{(Eqn 4)}$$

The exponential term is called the Poynting pressure correction factor, and it accounts for situations where the actual system pressure is different from the saturation pressure. A second correction term is the fugacity coefficient, φ_i^{sat}, which corrects for deviations of the saturated vapor from ideal-gas behavior. Literature suggests that the two corrections are often small, and sometimes negligible. In this solution, it is assumed that both the Poynting pressure correction factor and the fugacity coefficient are negligible (i.e., they equal unity). Another term in the standard state fugacity is the vapor pressure for the pure liquid, $P_i^{sat}(T)$, which can be calculated using the Antoine Equation. The final term needed for the liquid phase fugacity is the liquid mole fraction. In this system, the only non-gaseous components formed from the bioreactor reactions are water and the organic acids, which are assumed to be produced as byproducts in a supernatant layer that is separate from the sludge. Thus, the original liquid mole fraction is known, and the liquid phase fugacity for each component may be calculated.

Once the standard state fugacity is known, the next step in obtaining the liquid phase fugacity is to calculate the activity coefficient, γ_i. The activity coefficient is used to calculate the fugacity of a component in a liquid mixture. As seen in Equation (3), the activity coefficient is a function of composition, temperature, and pressure. However, unless the pressure is very high, its effect on the activity coefficient may be neglected, as is done in this solution. The activity coefficient can be determined from experimental data, or from one of several liquid mixture activity coefficient models. The van Laar equation is used in this solution to calculate the activity coefficients.

The fugacity of component *i* in a gas mixture may be related to the fugacity of pure gaseous *i* at the same temperature and pressure by the following relationship,

$$RT\ln\frac{f_{M,i}^{V}(T,P,y_i)}{y_i f_{\text{pure i}}(T,P)}=\int_0^P(\overline{v_i}-v_i)dP \qquad \text{(Eqn 5)}$$

In order to more easily solve for the vapor phase fugacity, either an equation of state or the principle of corresponding states with a simplifying assumption such as the Lewis Fugacity Rule may be used. In this problem, the Lewis Fugacity Rule is utilized, which assumes that at constant temperature and pressure, the fugacity coefficient of *i* is independent of the composition of the mixture and is independent of the nature of the other components of the mixture. Assuming the Lewis Fugacity Rule, the fugacity of component *i* in a vapor mixture is expressed as:

$$f_{M,i}^{V}(T,P,y_i)=y_i\cdot f_{\text{pure i}}(T,P)=y_i\cdot(P\cdot\varphi) \qquad \text{(Eqn 6)}$$

where

φ = the vapor phase fugacity coefficient of component *i* in the gaseous mixture

The pure phase fugacity can be determined using an equation of state such as the van der Waals equation. The van der Waals equation, shown below, is the simplest non-trivial equation of state, yet it provides a reasonable estimation of volumetric behavior of the vapor phase:

$$\varphi_i=e^{(\ln\left(\frac{v_i}{v_i\cdot b_i}\right)-\frac{a_i}{R\cdot T\cdot v_i}+\left(\frac{P\cdot v_i}{R\cdot T}-1\right)-\ln\left(\frac{P\cdot v_i}{R\cdot T}\right)} \qquad \textit{where} \quad v_i=\frac{R\cdot T}{P}+b_i-\frac{a_i}{R\cdot T} \qquad \text{(Eqn 7)}$$

In this solution, φ was calculated and was close to unity. Therefore the Van der Waals equation was not used in the detailed solution which was programmed in *Mathematica*®.

Once all of the terms in both the liquid and vapor phase fugacities have been tabulated, the criterion for equilibrium may be written as:

$$x_i\cdot\gamma_i(T,P,x_i)\cdot P_i^{sat}(T)\cdot\varphi_i^{sat}\cdot e^{\left[\frac{1}{R\cdot T}\cdot\int_{P_i^{sat}}^{P}\overline{V}\cdot dP\right]}=y_i\cdot P\cdot\varphi_i \qquad \text{(Eqn 8)}$$

Equation (7) is used to solve for the composition of the vapor phase. Subsequently, the composition of the liquid phase in equilibrium with this vapor is calculated. Table 2 summarizes the key thermodynamic model assumptions employed in the student's solution.

Table 2: Summary of Thermodynamic Model Assumptions

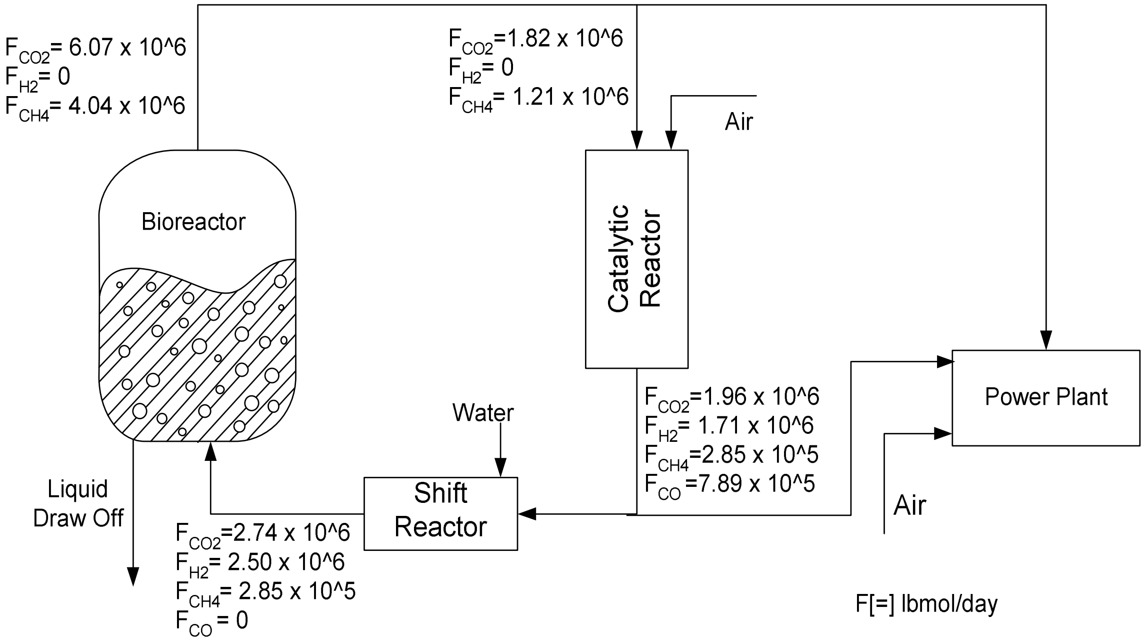
Liquid Phase Assumptions	**Justification**
1) The Standard State is that of the Pure Substance	
2) Poynting Pressure Correction Factor = 1 $e^{\left[\frac{1}{R\cdot T}\cdot\int_{P_i^{sat}}^{P}\overline{V}\cdot dP\right]}$ is negligible	Accounts for situations where the actual system $P \neq P^{sat}$. Since it is an exponential function of P, it is small at low Ps. The bioreactor is operated at low Ps, therefore the Poynting correction factor is assumed to be a negligible term which was confirmed by preliminary calculations.
3) The saturation fugacity coefficient $\varphi_i^{sat} = 1$	Corrects for deviations of the saturated vapor from ideal gas behavior. φ_i^{sat} differs considerably from 1 as $T_{critical}$ is approached. Since the T of the system is not near any of the components critical Ts, it is assumed that this term equals unity.
4) The activity coefficient, γ_i, is not a function of P	The activity coefficient becomes a function of P at very high pressures. Since the system P is low, this term is primarily a function of T and composition.
5) The activity coefficient is calculated from the van Laar Equation	The van Laar equation is typically used for binary systems. However, when it is employed, the concentrations of all other components are so small that a binary system can be assumed.
Vapor Phase Assumptions	**Justification**
1) Lewis Fugacity Rule applies ($f_i = y_i f_{pure,i}$)	The LFR assumes that at a fixed T and P, the fugacity coefficient of species i is independent of the composition of the mixture and is independent of the nature of other components in the mixture. The LFR relies on the assumption that Amagat's rule is valid over the entire range of pressures from 0 → system P. The LFR is a good approximation at sufficiently low Ps where the gas phase is ideal, as is the case in this system.
2) The pure fugacity coefficient, $\varphi_{pure,i}$, and mole fraction, $y_{pure,i} = 1$	For a pure, ideal gas, the fugacity is equal to the pressure (i.e., the fugacity coefficient and mole fraction are both 1). It is assumed that the system follows ideal-gas behavior because it is at low pressure, therefore the coefficient is set to unity. The mole fraction is unity because the species is pure.

Results

While not all students followed the above development, the results obtained from the students were generally very good, in that most of them analyzed the entire system. For example, both the bioreactor and the catalytic reformer were included in the analyses. Most students performed the minimum calculations necessary to support the solution. In addition, some students chose to use simulation packages such as PRO/II® but did not program the details of the reactors the way the students who used a programming software like *Mathematica*®. Most solutions using the above development led to familiar unit operations to achieve the necessary separations and reactions. A couple of solutions did employ flash operations and membrane separators. This is encouraging as it demonstrates that the students are beginning to use thermodynamic calculations to initiate the design of an integrated system for practical problems such as this one. There were no instances where conflicting solutions were found as has been shown to be possible elsewhere[18] In addition, all the students found the use of the Internet to be valuable in finding data and background information on the problem as well as introducing them to new, academic sites that could be used in the future. The discussion of the results will focus on one student's report. The student's analysis was very similar to the development described in the previous section including the incorporation of external research to help focus the analysis. For example, the student's analysis included bounding the problem, i.e. size of bio and catalytic reactor, effluent splits and target yields, a literature search of previously proposed solutions, and a high level of detail in the calculations to support the proposed solution.

After detailed *Mathematica* calculations were made, the flowrates for all streams were calculated to steady state values. Figure 1 depicts the flowrates (in lbmol/day) of the most important components as they move through the process in a single pass. This figure lists the initial guess values for the flowrates of the bioreactor product stream. One important discussion point is that the catalytic reforming reactor meets its objective by converting some of the CH_4 into H_2 (and CO_2 and CO as well). In addition, the shift reactor converts all the toxic CO to CO_2 before the feed stream enters the bioreactor. The values for the methane production and the volume that were used were extracted directly from Klass' book[13].

Figure 2: Flowrates (in lbmol/day) of Major Components using Initial S1 Guesses



In order to more clearly understand how the external feed stream of H_2 and CO_2 has affected the power generated, Figures 2 and 3 are presented. Figure 2 depicts the bioreactor feed and product streams after a single pass with the external stream. Figure 3 depicts the bioreactor system without the external feed. By comparing the two figures, it may be determined whether the project's objectives – accelerating the decomposition of the biomass to produce more methane and/or generating a higher flowrate of methane and carbon dioxide – were met.

When the external feed stream was used in combination with the decomposing biomass to produce methane, the flowrate of CH_4 increased from only 255.09 lbmol/min (Figure 3) to 8.54 x 10^5 lbmol/min (Figure 2). Thus, adding the external feed met the second objective and increased the flowrate of product. However, when the only source of CH_4 is the decomposing biomass, the energy content of the product gas is higher. This is observed by comparing the CH_4/CO_2 ratio in the product stream. In Figure 2, this ratio is 0.39, whereas in Figure 3 it is 0.86. Thus, the first objective is met when the external feed stream is not present. Therefore, the decision as to whether the external H_2 and CO_2 stream should be included depends on whether quantity or quality of product is required.

Figure 3: Bioreactor Flowrates (in lbmol/day) Single Pass with External Feed Stream.

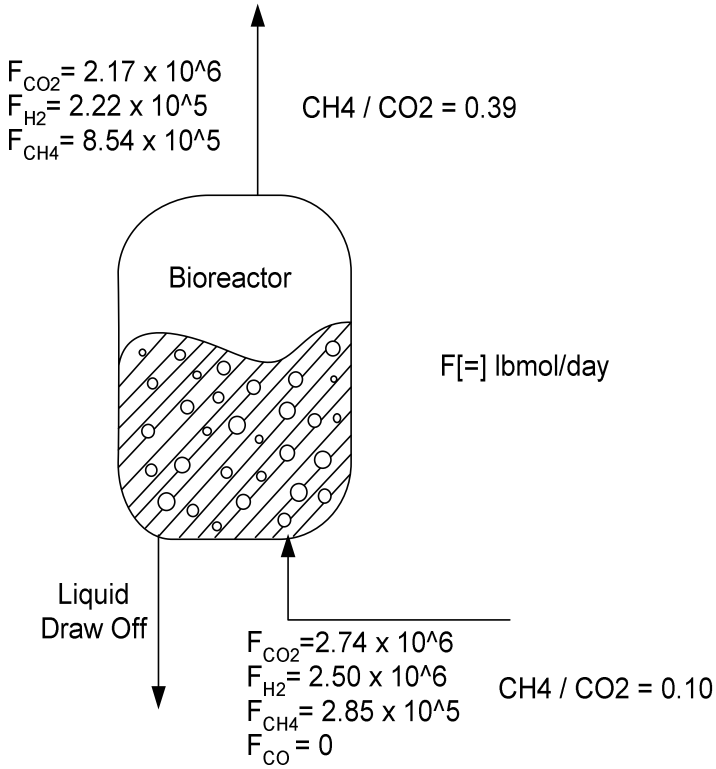
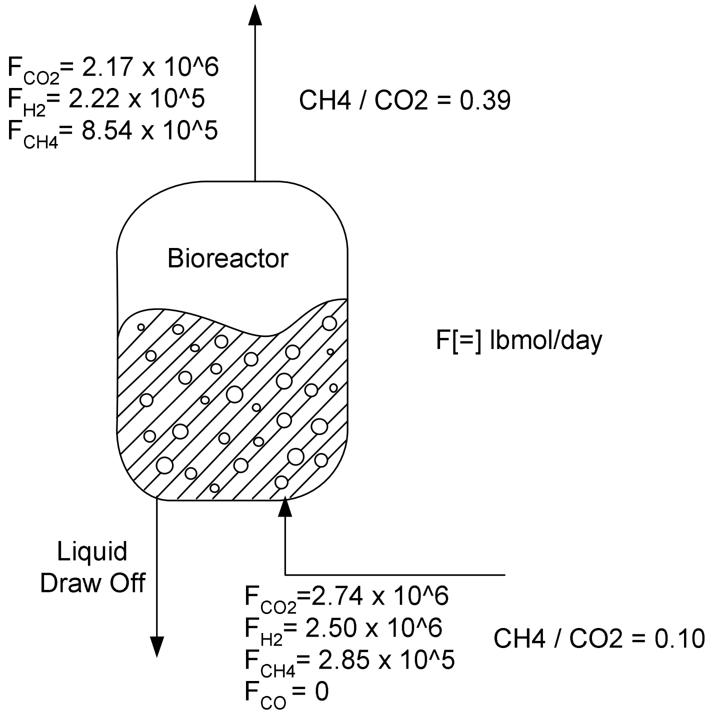


Figure 4: Bioreactor Flowrates (in lbmol/day) Single Pass without External Feed Stream.



Conclusions

This paper presented the results of one student's work for a class-required computer project. Model results validation using Pro/II® and an anaerobic bioreactor is the subject of another study in preparation. The requirements given to the students were only to use the thermodynamic concepts learned during the semester to analyze and propose a feasible solution to a current environmental or industrially significant problem. The outcome of such an exercise allows the students to apply sometimes abstract thermodynamic concepts to an important problem while training them at focusing on the big picture, which is how to find a solution to the problem. An additional benefit is that the students obtain an appreciation for what commercially available thermodynamic packages involve and can do since they find the need to obtain property information that cannot be found in literature. For example, many students use UNIFAC or Pro/II® for property data. Additionally, the exercise gives the students a sense of accomplishment in that they applied the principles of thermodynamics to analyze and propose feasible, realistic solutions to problems they may encounter during their careers.

Lastly, as the need for renewable energy sources grows, and in order to fulfill that need, research and development will require a workforce that is well educated and trained to develop the technologies necessary for a sustainable future. The example presented in this paper demonstrates that such a training is possible through an in-depth approach to a societal problem. It also sets the stage for further development of the Chemical Engineering curriculum at Manhattan College to include grounding in alternative energy sources and sustainability following the call of Sutherland, J.W. et al.,[19] of Michigan Technological University for the need for “globally aware students”.

Nomenclature

$f_{M,i}^{L}$: Fugacity of component *i* in the liquid mixture.
$f_{M,i}^{V}$: Fugacity of component *i* in the vapor mixture.
x_i: Liquid phase mole fraction of species *i*.
$\gamma_i(T,P,x_i)$: Activity coefficient of species *i* as a function of temperature, pressure and liquid phase mole fraction.
$f_i^{0}(T,P)$: Pure component fugacity of *i* in the liquid phase.
$P_i^{vap}(T)$: Vapor pressure of species *i* as a function of temperature.
ϕ_i^{sat}: Fugacity coefficient of the saturated vapor of species i.
$\overline{V}$: Molar volume of the liquid (condensed) phase.
y_i: Gas phase mole fraction of species i.
P: Total pressure of the system
φ: Fugacity coefficient of species i.
ϕ: equivalence ratio

Bibliography

1. Castaldi, M., Dorazio, L., and Assaf-Anid, N. Relating Abstract Concepts of Chemical Engineering Thermodynamics to Current, Real World Problems, *Chemical Engineering Education*, vol 38, no 4, pp. 268-279, 2004.

2. Kauser, J., Hollar, Kathryn; Lau, Fan; Constans, Eric; Von Lockette, Paris R.; Head, Linda Getting students to think about alternate energy sources*, ASEE Annual Conference Proceedings*, *2002 ASEE Annual Conference and Exposition: Vive L'ingenieur*, 2002, p 4593-4600.

3. Farley, Earl T. Ernest, David L., Application of power generation modeling and simulation to enhance student interest in thermodynamics, *Modeling and Simulation, Proceedings of the Annual Pittsburgh Conference*, v 21, n pt part 3, *Computers, Computer Architecture and Microprocessors in Education*, 1990, p 1275-1279

4. Cengel, Y.A. “Intuitive and unified approach to teaching thermodynamics” *Proceedings of the ASME Advanced Energy Systems Division*, **36,** 251 (1996).

5. Lombardo, S., “Open-ended estimation design project for thermodynamics students”, *Chem. Eng. Ed.,* **34**(2),154 (2000)

6. Tsatsaronis, George, Moran, Michael; Bejan, Adrian eds. Education in Thermodynamics and Energy Systems, *American Society of Mechanical Engineers, Advanced Energy Systems Division (Publication) AES*, v 20, *Education in Thermodynamics and Energy Systems*, 1990, 64p.

7. Reistad, Gordon M.; Gaggioli, Richard A.; Bejan, Adrian; Tsatsaronis, George, Thermodynamics and Energy Systems - Fundamentals, Education and Computer Aided Analysis, *American Society of Mechanical Engineers, Advanced Energy Systems Division (Publication) AES*, v 24, *Thermodynamics and Energy Systems -*

Fundamentals, Education and Computer Aided Analysis, 1991, 103p.

8. Shaeiwitz, J. A., "Teaching Design by Integration throughout the Curriculum and Assessing the Curriculum using Design Projects," *International Journal of Engineering Education*, 17, 479-482 (2001).

9. Garcia-Ochoa, F., Santos, V.E., Naval, L., Guardiola, E., and Lopez, B. Kinetic Model for Anaerobic Digestion of Livestock Manure. *Enzyme and Microbial Technology*, 25, 1999, 55-60.

10. Jagadish, K.S., Chanakya, H.N., Rajabapaiah, P., and Anand, V. Plug Flow Digestors for Biogas Generation from Leaf Biomass. *Biomass and Bioenergy*, vol.14, No. 5/6, pp. 415-423, 1998.

11. Castelblanque, Jasmine, Salimbeni, Francesco. Application of membrane systems for COD removal and reuse of waste water from anaerobic digestors. *Desalination*, 126, 1999, 293-300

12. Http://Www.About.com – Chemical engineering section.

13. Klass, Donald L., *Biomass for Renewable Energy, Fuels, and Chemical*, Academic Press, New York, 1998, pages 452 – 458.

14. Michael T. Madigan, John Martinko, and Jack Parker, *Brock Biology of Microorganisms*, Prentice Hall, Upper Saddle River, NJ, 2000, pages 605-615.

15. Muller, E.A. "Thermodynamics problem with two conflicting solutions" *Chem. Eng. Ed.* 34 (4), (2000).

16. Morley, C., Website: http://www.gaseq.co.uk

17. John Prausnitz, Rudiger N. Lichtenthaler, and Edmundo Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice Hall International Series, New Jersey, 1999.

18. Muller, E.A. "Thermodynamics problem with two conflicting solutions" *Chem. Eng. Ed.* **34**(4), (2000).

19. Sutherland, J.W., Kumar, V.; Crittenden, J.C.; Durfee, M.H.; Gershenson, J.K.; Gorman, H.; Hokanson, D.R.; Hutzler, N.J.; Michalek, D.J.; Mihelcic, J.R.; Shonnard, D.R.; Solomon, B.D.; Sorby, S. , An Education Program in Support of a Sustainable Future, *American Society of Mechanical Engineers, Manufacturing Engineering Division, MED*, v 14, 2003, p 611-618.

NADA M. ASSAF-ANID
Dr. Anid is Associate Professor and Chairperson of the Chemical Engineering Department at Manhattan College. She earned her BS and MS in Chemical Engineering from the Royal Institute of Technology in Stockholm, Sweden, and her PhD in Environmental Engineering from the University of Michigan in Ann Arbor. Her research and teaching interests are in separations, biochemical engineering, hazardous chemicals remediation, thermodynamics, and water purification. She is Director of the ASEE Chemical Engineering Division and Director of the Environmental Division of AIChE.

MARGUERITE A. MOHAN
Marguerite is currently working towards her MS in Chemical Engineering at Manhattan College where she obtained a BS in Chemical Engineering. After completing her graduate degree, she will be employed full-time by Merck & Co., Inc. as a Staff Chemical Engineer. Marguerite's research interests include chemical thermodynamics and nanoscale science.

NICOLE MAY
Nicole is currently pursuing her MS in Chemical Engineering at Manhattan College. She also holds a BS in Chemical Engineering from Manhattan College. Her interests include engineering education, bioreaction engineering, and environmental conservation.

MARCO J. CASTALDI
Dr. Castaldi is Assistant Professor in the Earth & Environmental Engineering Department at Columbia University. He received his B.S. ChE from Manhattan College and M.S. and Ph.D. ChE from the University of California, Los Angeles. Prior to joining Columbia University, he worked in industry for 7 years researching and developing novel catalytic reactors. His teaching interests lie in thermodynamics, combustion phenomena and reaction engineering. His research is focused on beneficial uses of CO_2 in catalytic and combustion environments, Waste-to-Energy processes and novel extraction techniques for methane hydrates.