BIOMASS AS A SUSTAINABLE ENERGY SOURCE:

an Illustration of ChE Thermodynamic Concepts

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

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has been used in thermodynamics courses[5] because it resembles problem-solving situations encountered in industry.[6]

The objectives of this paper are to present an open-ended problem given as a final project to a graduate process thermodynamics class, describe how one student tackled it, and demonstrate how it was a useful addition to the thermodynamics concepts taught in the class. Portions of the problem may be suitable in an undergraduate thermodynamics, modeling,[3] or design class,[7] if presented in a less open-ended manner or as a continuing problem integrated in a series of courses using the approach of Shaeiwitz.[8] The problem given to students, with three references on anaerobic digestion,[9-11] is shown below. Students were instructed on literature research methods using online libraries and Internet sites, 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.

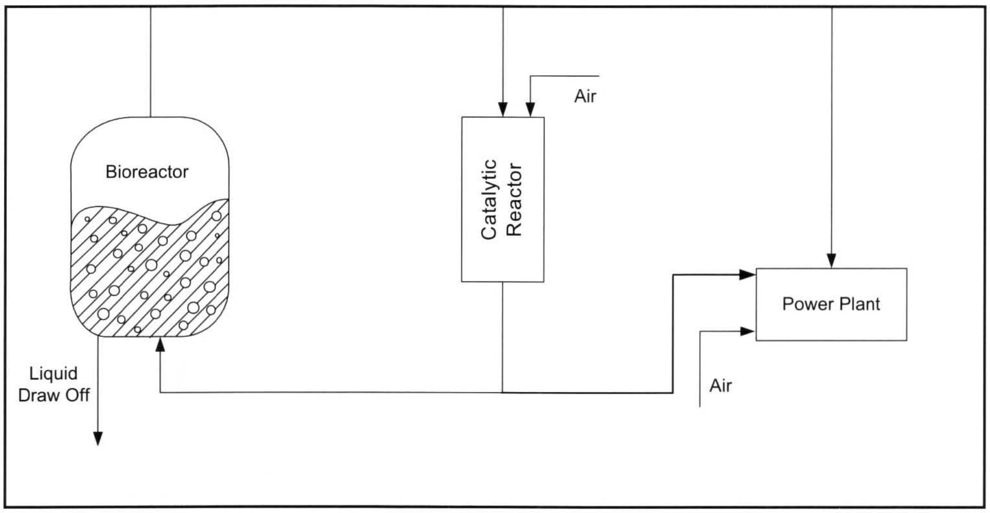

Figure 1. *Schematic of system components.*

TABLE 1 **Overview of Course Syllabus** (The chapters refer to the class textbook[13])	
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); computer assignment discussed
8	Ch. 7 (parts)
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

PROBLEM STATEMENT

As shown in Table 1, the students had about six weeks to complete the project and were expected to work independently. By the time the computer assignment was issued, the students were exposed to solution equilibrium theory, which begins with Chapter 6.

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 uses 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 flow rate and energy content. It has been proposed to accelerate the decomposition of the biomass to generate more CH_4, or at least a higher flow rate of the CH_4/CO_2 mixture. One way to do this is to "feed" the bacteria that is decomposing the biomass a warm stream of CO_2 and hydrogen (H_2). In addition, this CO_2 can serve as a carbon source for the bacteria. This allows the bacteria population to increase and the decomposition of the biomass to occur faster. The supply of CO_2 and H_2 is secured by another reactor placed upstream to convert some of the bioreactor product stream (CH_4 and CO_2) to 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 liquid and gas phases. In addition, you also need to determine the preferred concentrations of 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 students assessing how this type of a project impacts their understanding of the subject and overall learning experience.

BACKGROUND AND THEORY

Anaerobic digestion, or methane fermentation, is the process by which microorganisms convert biomass to methane in the absence of oxygen. Often, a water layer serves as a blanket to exclude oxygen and promote growth of the appropriate anaerobes.[14] 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.[14]

Methane fermentation is a three-step process that utilizes three main categories of bacteria: fermentative, acetogenic, and methanogenic.[14, 15] In the first step, the fermentative bacteria convert complex polysaccharides, proteins, and lipids present in biomass to lower molecular weight fragments, such as carbon dioxide and hydrogen,[14] according to the main reactions shown.[14]

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, hydrogen-producing acetogenic bacteria catabolize the longer chain organic compounds formed in the first step to yield acetate, carbon dioxide, and hydrogen. Also, some carbon dioxide and hydrogen are converted to acetate by the acetogens, according to the main acetogenic reactions considered below[14]:

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, according to Reference 14:

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.[14]

As evidenced by the reactions, there are a number of intermediate acids generated. Since all reactions do not go to completion, a certain amount of these compounds builds up within the bioreactor, changing the solution pH, poisoning the bacteria, or inhibiting 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 presented thus far on biochemical reactions taking place in the bioreactor can now be applied to solve the problem at hand. 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 and exposes them to realistic processes in industry, where thought must be given to system startup and shutdown, as well as adjustments that must be made on the way to a targeted operational condition. As was previously discussed, the problem statement is open-ended; therefore, there are several possible approaches and solutions.

ONE STUDENT'S SOLUTION

A computer solution was created in Mathematica to perform the calculations described in the Background and Theory section, and can be obtained, in Mathematica format, upon request.

Traditional Bioreactor

The objective of this project was to determine if it is possible to increase the total power that may be harnessed from a traditional bioreactor system. Therefore, the logical starting point is to calculate the amount of power actually generated from a traditional system, which consists solely of a batch bioreactor set to operate in the mesophilic 30 °C – 38 °C temperature range, at a pH within the range 6.6 – 7.4 to maintain the proper alkalinity. Furthermore, a high-rate digestion is assumed, and an appropriate residence time of 10 days is specified. The volume of the reactor is estimated using values from the literature,[1] and it is assumed that approximately two-thirds of the total volume is charged with an initial amount of municipal solid waste (MSW). The MSW is simplified to a 50% (by weight) glucose suspension in water, and its volume, along with the density of the waste (a weighted density of water and glucose), allows the calculation of the total amount of MSW in the reactor or the total amount of glucose initially charged (S_0). Once the initial amount of glucose is calculated, three sets of reactions (Rxn 1–13) are assumed to occur, and the resulting biogas (vapor product stream) may be evaluated. Its composition (which is directly proportional to the power generated) is noted. This will serve as the control to which all subsequent biogas compositions will be compared.

Catalytic Reforming Reactor

The next aspect of the solution is the introduction of additional equipment (the catalytic reforming reactor and the shift reactor) that, along with the bioreactor, constitute a modified system that may be used to meet the objective of increasing the total power harnessed as specified in the problem statement. The product stream from the bioreactor is split: 90% is sent to a power generation plant, and the remaining 10% is routed to a catalytic reforming reactor which is brought online 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 generate a higher flow rate of methane and carbon dioxide. This was one of the major outcomes of the investigation. That is, once the student developed the computer routine that 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 10% split, an air stream is fed 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:

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

where

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

After testing various equivalence ratios, an $\phi = 3.0$ is chosen, and a partial oxidation reaction follows:

$$\begin{gathered} 4CH_4(g) + 2.67O_2(g) + 10.0N_2(g) \rightarrow 0.449CO_2(g) + \\ 3.55CO(g) + 0.901H_2O(g) + 7.21H_2(g) + 10.0N_2(g) \\ (\text{Rxn}\,14) \end{gathered}$$

The stoichiometry of the above partial oxidation reaction was obtained through the use of the thermodynamic equilibrium software, GasEQ.[17] At the adiabatic flame temperature (1020 K), Rxn (14) has an equilibrium conversion, X_{eq}, of 0.9969.

Shift Reactor

The effluent of the catalytic reforming reactor contains a significant amount of 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 according to:

$$CO(g) + H_2O \Leftrightarrow CO_2 + H_2(g) \qquad (\text{Rxn}\,15)$$

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

Modified Bioreactor

The next step in the solution involves returning to the bioreactor (which will now be referred to as the modified bioreactor). This bioreactor operates as a semi-batch reactor since the waste that is decomposed by the bacteria is charged in as necessary (this is dictated by the residence time), while the stream of hydrogen and carbon dioxide produced from the other reactors (catalytic reforming and shift) is fed continuously.

The same assumptions as in the traditional system regarding the MSW are made, and once the total amount of glucose initially charged is calculated, it is further assumed that at the end of the charge life all of the glucose will have decomposed, reaching a final concentration of S1 = 0. Assuming a residence time of 10 days, which is typical for high-rate anaerobic digestion, and assuming that glucose decomposes at a constant rate throughout the 10-day period, the rate of glucose decomposition may be calculated and 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 to allow all of the fermentative and most of the acetogenic reactions to occur. As this decomposition 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. The benefits of introducing this external feed stream into the bioreactor are three-fold: first, the H_2 and CO_2 provide an immediate electron and carbon source for the bacteria; second, the gas stream increases the contact area between the bacteria and the available food sources; and third, since the external feed stream is at an elevated temperature, it enhances the digestion rate within the bioreactor.

As this stream feeds into the bioreactor, the solubilities of its components in water must be considered. Most of those (N_2, H_2, and the acid vapors) are gaseous and insoluble in water. The solubility of CO_2 is of particular interest, however, 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 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.

Acid Phase Distribution

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—acetic, butyric, and propionic acids—produced in the fermentation and acetogenic reactions, and if their levels in the liquid continue to increase, the alkalinity of the bioreactor will change. As a result, the pH may drop outside of the allowable range for methane fermentation. In order to find the distribution of acids between the liquid and vapor phases, chemical thermodynamic concepts are applied using the assumptions summarized in Table 2 (next page). The first concept used is the equilibrium criterion:

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

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

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

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 and the fugacity of the standard state is defined as:

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

The Poynting pressure correction factor and the fugacity coefficient, φ_i^{sat}, are assumed to be 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 nongaseous components formed from the bioreactor reactions are water and 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, which is a function of composition, temperature, and pressure as seen in Eq. (3). Unless the pressure is very high, however, its effect on the activity coefficient may be neglected, as is done in this solution, and the van Laar equation used 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,

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 = $1\ e^{\left[\frac{1}{R\cdot T}\cdot\int_{P_i^{sat}}^{P}\bar{V}\cdot dP\right]}$ 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. When it is employed, however, 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.

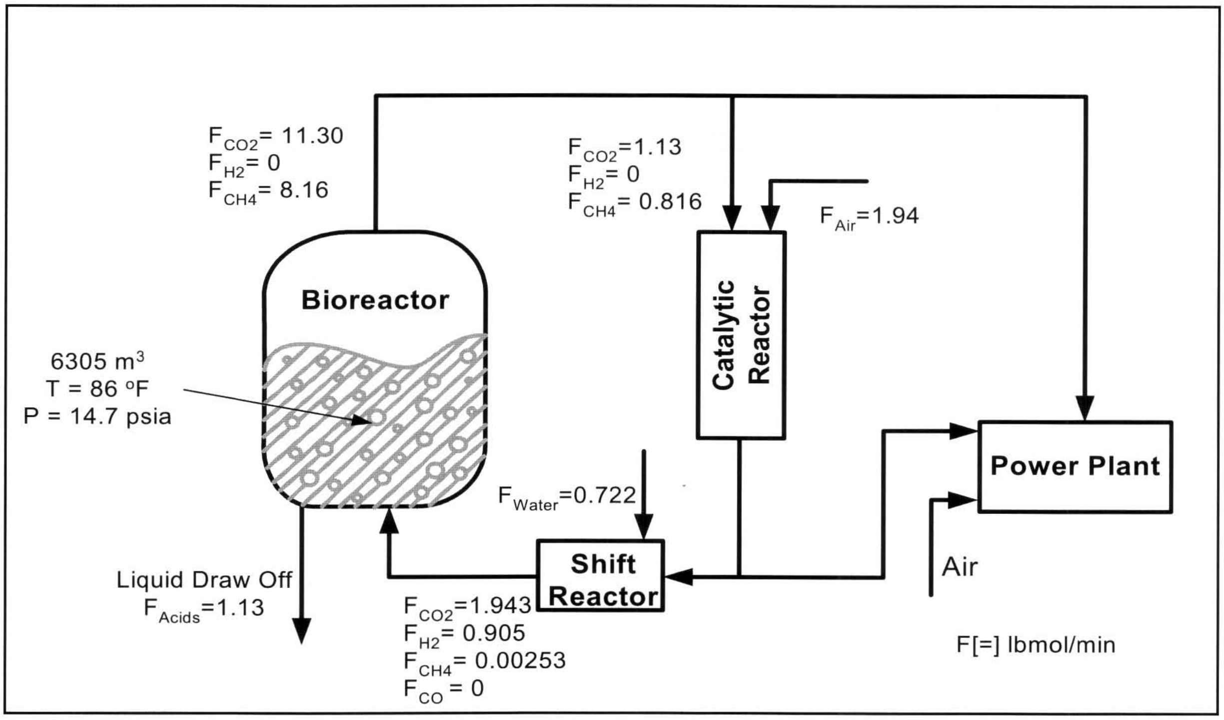

Figure 2. *Flow rates (in lbmol/min) of major components using modified system.*

TABLE 3
Mathematica Model: Traditional vs. Modified Bioreactor

	Traditional BR	Modified BR Single Pass
CH_4 Produced, lbmol/min	7.65	8.16
CH_4 Sacrificed, lbmol/min	--	0.765
CH_4 Sent to Power Plant, lbmol/min	7.65	7.40
Biogas CH_4/CO_2	0.89/1	0.72/1

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

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. According to this rule, the fugacity coefficient of i is independent of the composition of the mixture and of the nature of the other components of the mixture, at constant temperature and pressure. As a result, the fugacity of component i in a vapor mixture is expressed as:

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

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

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

$$\varphi_i = e^{\left(\ln\left(\left[\frac{v_i}{v_i \cdot b_i}\right]\right) - \frac{a_i}{R \cdot T \cdot v_i} + \left(\frac{P \cdot v_i}{R \cdot T} - 1\right) - \ln\left(\frac{P \cdot v_i}{R \cdot T}\right)\right.} \quad \text{where } v_i = \frac{R \cdot T}{P} + b_i - \frac{a_i}{R \cdot T}$$

$$(7)$$

In this solution, φ was calculated and was close to unity.

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

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

Eq. (8) is used to solve for the composition of the vapor phase and allows the calculation of the composition of the liquid phase in equilibrium with this vapor.

RESULTS

While not all students followed the above development, the results obtained from the students were generally satisfactory, in that most of them analyzed the entire system. Figure 2 depicts the flow rates (in lbmol/min) of the most important components as they move through the modified system in a single pass, and Table 3 illustrates how the external feed stream of H_2 and CO_2 (*i.e.*, the modified system) affects the power generated and summarizes the comparison of the traditional and modified systems. The results shown in Table 3 indicate that the current modified system does meet the objective of accelerating the decomposition of the biomass by producing more methane: 8.16 lbmol/min vs. 7.65 lbmol/min produced from the modified bioreactor and the traditional bioreactor, respectively. Although the quantity of the methane produced increases in the modified system, the quality of the biogas (defined as CH_4 to CO_2 ratio) decreases from 0.89/1 to 0.72/1 in the traditional and modified system, respectively.

COURSE ASSESSMENT

Once the projects were submitted, the students were asked to assess the overall success of the assignment. The student answers to questions 2 and 3 indicate that they overwhelmingly found the project to have enhanced their understanding of thermodynamics (n = 8). In Table 4 (next page), a score of 5 indicates agreement with the statement, and 1 indicates disagreement.

In addition to the four questions listed in Table 4, students were asked for their comments on two other topics. When answering the question, "What sources (*e.g.*, World Wide Web, online libraries, handbooks, publications) were useful in obtaining thermodynamic data, bioreactor information, etc.?," students listed a variety of sources including the Web (more specifically <www.uspto.gov> and Web sites linked to chemical engineering departments at large universities, *e.g.*, Texas A&M). Students also indicated the use of the Manhattan College and Columbia University online libraries, *Vapor/Liquid Equilibrium Data* handbooks, the research articles handed out with the assignment, and microbiology and bioreaction engineering textbooks. In their answer to the question, "Did you program the solution yourself or use a computer program in your solution? If computer program was used, which one and why?," students reported using a variety of programming tools including Mathematica (especially for its useful indexing feature and for repetitive and iterative calculations),

TABLE 4
Course Assessment

Question	5	4	3	2	1
1. Overall, do you feel that the class lectures and homework provided you with the necessary background for developing a solution to the computer project?	12.5%	75%	12.5%	- - -	- - -
2. Did the computer project give you a better understanding of thermodynamic principles such as fugacity, solubility, and multi-phase equilibrium, and how they are used in practical situations?	12.5%	75%	12.5%	- - -	- - -
3. Was the computer project a relevant, practical, and open-ended application of the principles taught in the class?	75%	25%	- - -	- - -	- - -
4. Did the computer project enhance your research skills?	12.5%	12.5%	50.0%	12.5%	12.5%

Excel (for both programming and graphing), and the Pro/II Simulation Package.

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 experimental anaerobic bioreactor —is the subject of another study in preparation. The requirement given to the students was to only 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 students to apply sometimes-abstract thermodynamic concepts to an important problem while training them to focus on the big picture: how to find a solution to the problem. An additional benefit is that students obtain an appreciation for what commercially available thermodynamic packages involve, as well as their capabilities, since students find the need to obtain property information not found in literature. Also, the exercise gives 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, 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 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 J.W. Sutherland, *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.

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