Decision-support for Digester-Algae IntegRation for Improved Environmental and Economic Sustainability (DAIRIEES)

User Manual

June 2017

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ABSTRACT

Manure management is a major concern for dairy farms, as manure emits significant quantities of greenhouse gases and contains concentrated nutrients, especially nitrogen and phosphorus. Current manure management practices consist of spreading minimally processed manure on agricultural fields, which releases greenhouse gases directly to the atmosphere and often leads to nutrient overloading on fields and runoff to surface and groundwater. A novel manure treatment system has been proposed that mitigates many of the current environmental concerns and creates value-added products from the manure including bioplastics, electricity, fertilizer, and animal bedding. The Decision-support for Digester-Algae IntegRation for Improved Environmental and Economic Sustainability (DAIRIEES), an Excel-based model, allows users to enter characteristics about a dairy farm's manure, manure management plan, and regional market. Based on these inputs, the five main processes of the integrated system—fermenter, anaerobic digester, bioplastics reactor, algae cultivation, and hydrothermal liquefaction or fast-pyrolysis system—are analyzed in detail using data from laboratory-scale experiments supplemented by information on full-scale processes from the literature. The model can be used to estimate performance of the integrated manure treatment system, including: (1) carbon and nutrient sequestration, (2) quantities and market value of end products, and (3) the system's overall economic viability. The DAIRIEES model outlines the major economic considerations for construction and operation of a full-scale integrated treatment system. This information can be used to inform a more detailed pro forma analysis of the deployed system.

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FIGURES

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ACRONYMS

ACS	Algae Cultivation System
AD	Anaerobic Digester
ATS	Algal Turf Scrubber
BSU	Boise State University
CH_4	Methane
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
DAIRIEES	Decision-support for Digester-Algae Integration for Improved Environmental and Economic Sustainability
eGRID	U.S. Environmental Protection Agency Emissions and Generation Resource Integrated Database
EPA	Environmental Protection Agency
GHG	Greenhouse Gas
HDPE	High-Density Polyethylene
HHV	High Heating Value
HTL	hydrothermal liquefaction
INL	Idaho National Laboratory
IRR	Internal Rate of Return
LDPE	Low-Density Polyethylene
LHV	Low Heating Value
NPV	Net Present Value
OLR	Organic Loading Rate
OPR	Open Pond Raceway
PBR	Photobioreactor
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PHBV	Polyhydroxybutyrate-Co-Valerate
PHV	Polyhydroxyvalerate
RBB	Residual Bacterial Biomass
SRT	Solids Residence Time
TOC	Total Organic Carbon
TSM	Total Slurry Mass
UI	University of Idaho
USDA	United States Department of Agriculture

VFA   Volatile Fatty Acid

C_m Carbon Mass

NOMENCLATURE

D_A anaerobic digester data

D_f fermenter data

$X \%Y_m$ composition by mass (the percent mass of element Y in substance X)

$\%_m$ percent by mass

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1.   INTEGRATED DAIRY MANURE PROCESSING SYSTEM

Subsections below are comprised of an overview, description, and set of calculations and parameters pertaining to the various system components involved in the integrated manure treatment system. Decision-support for Digester-Algae IntegRation for Improved Environmental and Economic Sustainability (DAIRIEES) is a technoeconomic model developed to quantify the mass and nutrient flows between the various subsystems and provide economic information on the integrated system for a specified herd size.

1.1   Overall Process Flow Diagram

1.1.1   Process Overview

Annually, the dairy industry in the United States creates an estimated 226 billion kg of wet manure and 5.8 billion kg of CO_2 equivalents (CO_2 e). Manure management accounts for nearly half of the greenhouse gas emissions in the dairy industry and the dairy industry accounts for 7% of the total greenhouse gas (GHG) emissions. In January 2009, the Innovation Center for U.S. Dairy announced a voluntary goal to reduce GHG emissions by 25% in 2020; however, individual implementation has been slow (Coats 2013).

Over 9 million milk cows are in the U.S. (USDA 2015a). Manure management is a major concern nationally and also for individual dairies, as the average lactating cow produces about 68 kg of manure per day (ASAE 2005). In Idaho, for example, the average dairy has 660 cows, meaning it handles over 16,000 metric tons of manure annually (Informa Economics 2013). Manure is conventionally stored in lagoons or open ponds because of their ease of operation and low costs, but lagoons raise concerns about odor control, water quality, and GHG emissions (EPA 2011).

To address these manure management obstacles faced by dairies, the U.S. Environmental Protection Agency (EPA) and the Innovation Center for U.S. Dairy are promoting installation of anaerobic digesters, which use bacteria to process manure and produce methane as a by-product. Methane is typically burned for electricity and provides a source of power and/or revenue to the dairy farm. However, despite industry support for installing anaerobic digesters, voluntary implementation has been slow. Reasons include higher capital costs, additional operation and maintenance concerns compared to existing methods, and low electricity rates (Zaks et al. 2011). In most cases, the sale of electricity alone is not enough to make digesters profitable. Additional sources of revenue are needed to make manure anaerobic digesters a financially viable option for dairies.

A novel treatment system has been proposed that combines subsequent treatment steps with a plug flow anaerobic digester to create additional products with economic value. This system separates anaerobic digestion into two physically distinct steps. The main purpose of this approach is to be able to capture volatile fatty acids (VFAs) that are produced in the first treatment step (the fermenter) and divert them to a separate polyhydroxyalkanoate (PHA) reactor. The PHA reactor converts the VFAs to a plastic precursor called PHBV (poly(3-hydroxybutyrate-co-3-hydroxyvalerate)), which can have chemical properties similar to the plastics in milk jugs (high density polyethylene [HDPE]) or flexible films (low density polyethylene [LDPE]) (Kessler 1999). By-products from the anaerobic digester may be extracted

and sold as fibrous material suitable for animal bedding and nitrogen and phosphorus-containing fertilizer products (Minnesota Project 2010).

This system also produces algae as a source of added biomass for the fermenter and provides a way to remove the excess nutrients (nitrogen and phosphorus) associated with manure treatment. The algae are grown with CO_2 from the second step of anaerobic digestion as the carbon input. Conversely, when lagoons are used, nitrogen that is present in soils and water bodies feeds the microbial processes of nitrification and de-nitrification, which create nitrous oxide that can be released to the atmosphere. Nitrous oxide is a concern since 1 pound has 300 times the global warming potential of one pound of carbon dioxide (EPA 2013). The nitrogen and phosphorus in manure are both hazardous to our water supply. Nitrogen in soil is converted to nitrates, which can seep into groundwater, causing contamination of drinking water. The phosphorus in manure can runoff into surface water, which leads to eutrophication (Coats 2013). Eutrophication is an excessive richness of nutrients in bodies of water frequently caused by runoff from over-fertilized land, which over-stimulates the growth of aquatic plant life and results in the depletion of dissolved oxygen, causing death of animal life from lack of oxygen.

This integrated manure treatment system provides a way to reduce GHG emissions and adverse impacts to surface and ground water quality, while generating additional revenue. The benefits of this integrated system are twofold: create more high-value products, especially bioplastics, and create a GHG-*negative* system by sequestering carbon in algae biomass and bioplastics. The system modeled by DAIRIEES is designed to be a comprehensive way to treat dairy manure, create high-value products that can be sold or reused, and reduce GHGs from the dairy industry.

The key questions to be answered by the model are:

- What are the carbon and nutrient flows through the system? How much carbon is sequestered in the products?

- What are the amounts and values of the products produced per kg of manure?

- What is the overall cost of operating this system?

This integrated system is currently being tested and optimized at the laboratory scale. The DAIRIEES model provides a way to estimate GHG reduction and costs associated with implementing the full-scale treatment system. Tools are being developed for researchers to better understand the processes and estimate the economics associated with implementation of this system.

1.1.2   Process Description

The process flow diagram gives an overview of how all the processes are linked together. The DAIRIEES process illustrated in Figure 1 is a visual representation of the integrated system. It shows the overall process from cow manure to end products. The major processes considered separately in the model are the fermenter, anaerobic digester, PHA reactor, algae cultivation, and biomass treatment (hydrothermal liquefaction or pyrolysis). The green ovals indicate a *process step*, the brown circles represent *resources*, the lines represent the movement of products from one process to another, and the pictures represent the *products* of the process.
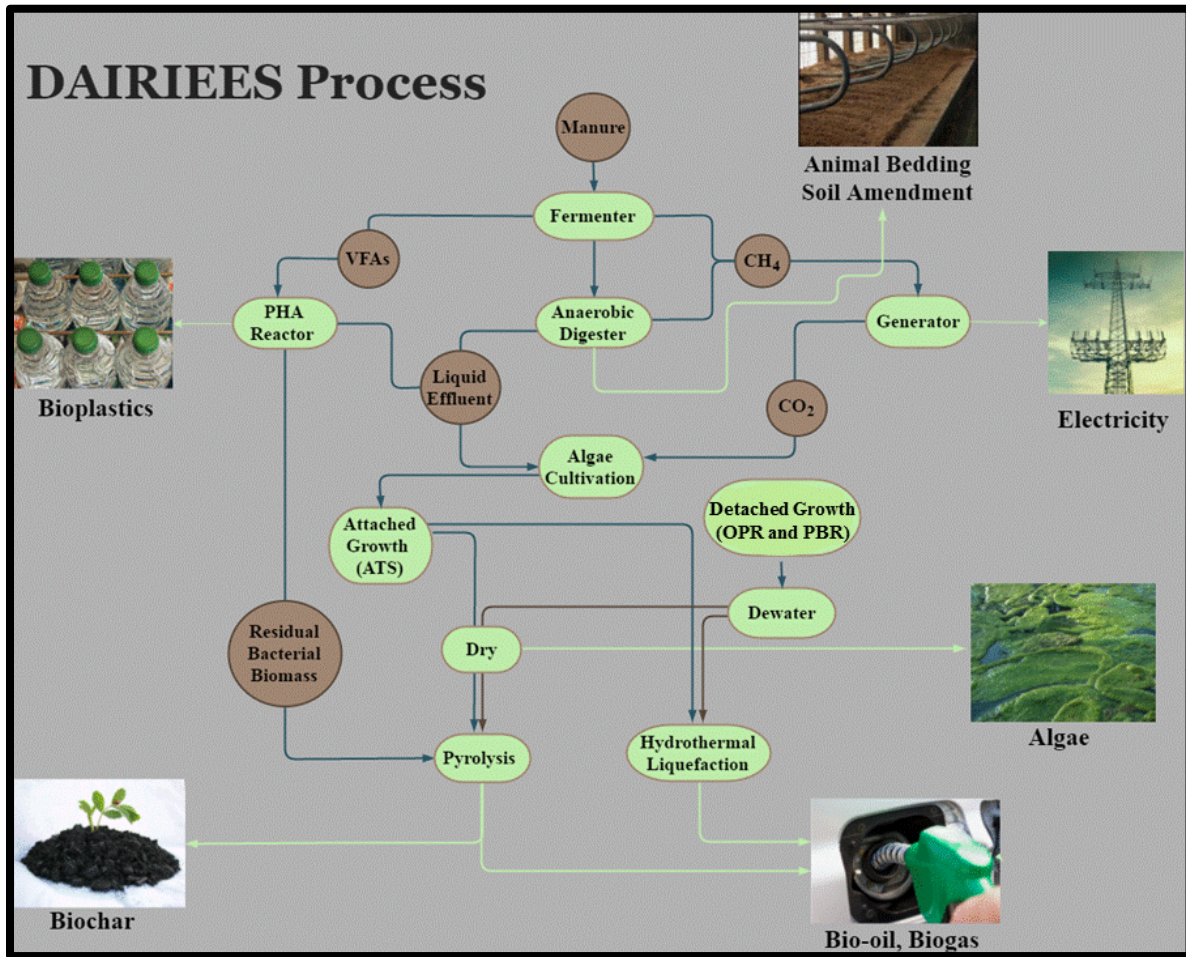
Figure 1. DAIRIEES process flow diagram.

1.1.3   Calculations and Parameters

The DAIRIEES model relies upon University of Idaho (UI) and Boise State University (BSU) laboratory data as the primary source of inputs and parameters. However, since not all of the data needed for the model was provided by the laboratory experiments, the information is supplemented by literature data.

Many of the system processes are fairly new, such as a few algae cultivation types, and the PHA reactor, as well as others. Commercial implementation of these systems is not well established, and so estimates for capital costs of these systems are either based upon a formula from a literature source, or scaled from a case study, using the following equation:

$$model\ system = cost\ of\ case\ system \left(\frac{volume\ of\ model\ system}{volume\ of\ case\ system}\right)^{0.7} \qquad (1)$$

This type of equation is commonly used by engineers for scaling system costs (Perry and Chilton 1973). The concept is that equipment is cheaper per unit in bulk.

Annual costs of most systems were estimated by referencing the published literature using *Equation* 2:

$$annual\ cost\ of\ model\ system = capital\ cost\ of\ model\ system \left(\frac{annual\ cost\ of\ case\ system}{capital\ cost\ of\ case\ system}\right) \qquad (2)$$

1.2   Fermenter

1.2.1   Overview

The fermenter is a reactor that uses raw manure as an input to create VFAs, which are precursors to bioplastics. This is the first stage of a two-stage anaerobic digester (AD), also known as the acid phase (EPA 2006), where hydrolysis and fermentation occur. While the principles are the same whether or not this phase is combined into an AD for the integrated dairy manure processing, the two stages must be separate to properly partition the products after they leave the reactor.

The driving force of the fermenter is a community of bacteria, called acidogenic bacteria, which create VFAs. VFAs in the fermenter effluent are comprised of acetic, propionic, butyric, iso-butyric, valeric, iso-valeric, and caproic acid. Acetic acid is the dominant component, constituting 61% of the total VFA mass, which is in the range of other studies (Coats et al. 2011). The transformation of manure to VFAs is ~95% efficient (Coats et al. 2012). The two most important operating variables for the fermenter are temperature and solids residence time (SRT). The temperature is important because bacterial reactions are highly affected by temperature—reactions generally occur faster at higher temperatures, but if the temperature becomes too high it can inhibit or kill the bacteria. SRT is the amount of the time material stays in the reactor. This is related to the amount of new "food" the bacteria receive and the amount of VFAs that can be produced from a given amount of manure. Each reactor has an ideal operating temperature and SRT to obtain the highest yields, but the ideal values usually vary between reactors. Another parameter that is important for determining how well the fermenter processes the added carbon-containing compounds is the organic loading rate (OLR). OLR is measured in kilograms of volatile solids per cubic meter per day. This quantity tells how much organic matter is added per unit of volume and time, which helps the operator know how much and what concentration of material is being added at a given time (EPA 2006).

1.2.2   Process Description

The experimental data for this model was obtained from the benchtop-scale fermenters at UI as shown in Figure 2. Raw dairy manure was obtained from the UI dairy farm, a small dairy with approximately 100 to 120 dairy cows. Ten gallons of fresh manure was collected on a semi-weekly basis and stored at 4°C until the manure was used (Coats et al. 2012). The reactors were stirred continuously with an axial flow impeller to allow the bacteria to access the organic matter for food (this is referred to as a continuously stirred tank reactor). There are three independent fermenters operated at the same time. These fermenters have a 20 L capacity and a 4-day SRT. Therefore, a 5-L mixture of 2% manure was added to the tanks every day. Fermenter effluent is first centrifuged and then decanted. Of the 5 L produced daily, 2 L were fed to the AD and 3 L were fed to the PHA reactor.

Figure 2. Experimental setup for fermenters at UI.

The fermenters are operated at a temperature of 22.8°C. Figure 3 shows the inflows and outflows from the fermenter. It assumed that the manure is flushed from the stalls and is routed to the fermenter shortly after being excreted. Therefore, it is assumed that there are no nitrogen losses due to volatilization.
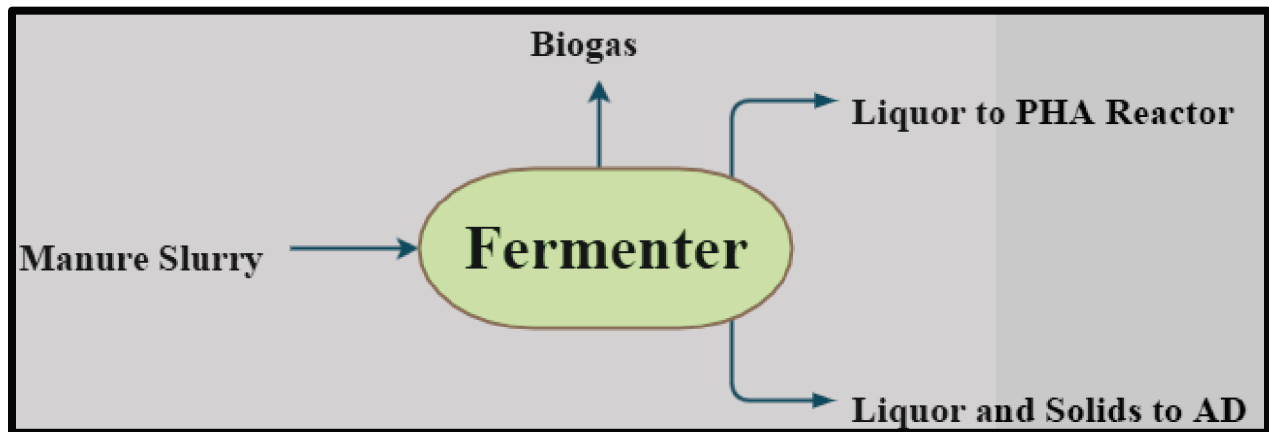
Figure 3. Inflow of manure slurry and outflows of liquor to PHA reactor and solids to AD.

1.2.3. Calculations and Parameters

These computations based on ASAE standards and a value of 68 kg per lactating dairy cow per day (ASAE 2005). These values are for urine and feces combined. The moisture content for the manure is assumed to be 87% (Chen 2003), and the volatile solids content dry manure is assumed to be 84%, derived by dividing the total amount of volatile solids by the total dry cow manure (ASABE 2005). These values are for manure as-excreted instead of as-collected to be consistent with most other measurements for manure content. Values for dairy cattle N and P are 0.66% and 0.115%, respectively (ASABE 2005).

Because of the reduced scale of the laboratory equipment, the data are based upon manure from one-fiftieth (or 0.02) of one cow produced in a day. This number results from *Equation* 3, which uses the total slurry mass (TSM) entering the fermenter divided by the amount a cow excretes per day.

$$\frac{TSMin}{TSMcow} = \frac{1398.17\ g}{68\ kg/cow} * \frac{kg}{1000\ g} = 0.02\ cow \tag{3}$$

$$\text{Daily amount of manure} = \text{Herd size} * 68\ \frac{\text{kg manure}}{\text{cow*day}} \tag{4}$$

$$\text{Solid dry manure} = \text{Total manure} * (1 - \%\ \text{moisture of manure}) \tag{5}$$

$$\text{acids}\ \%_m\ \text{of total mass out} = \frac{\text{total mg acids}/1000\frac{mg}{g}}{\text{total g solids added}} \tag{6}$$

$$CH_4\ \%C_m\ \text{out} = \frac{g\ CH_4 * \%C_m\ of\ CH_4}{(g\ CH_4 * \%C_m\ of\ CH_4) + (g\ CO_2 * \%C_m\ of\ CH_4)} \tag{7}$$

$$CO_2\%C_m\ \text{out} = \frac{g\ CO_2 * \%C_m\ of\ CO_2}{(g\ CH_4 * \%C_m\ of\ CH_4) + (g\ CO_2 * \%C_m\ of\ CO_2)} \tag{8}$$

$$kg\ CO_2 = \frac{CO_2\ \%C_m\ out * kg\ of\ biogas\ C}{CO_2\ \%C_m} \tag{9}$$

$$kg\ CH_4 = \frac{CH_4\ \%C_m\ out * kg\ of\ biogas\ C}{CH_4\ \%C_m} \tag{10}$$

$$kg\ \text{out to PHA} = \frac{(D_f\ TOC, gC\ out - D_A\ \text{solids TOC gC in}) * C\ \text{in to fermenter}}{D_f\ TSMin * (1 - \%\ \text{moisture of manure}) * \%C_m\ \text{of raw manure}} \tag{11}$$

$$kg\ \text{out to AD} = \frac{D_A\ \text{solids TOC gC in} * C\ \text{in to fermenter}}{D_f\ TSMin * (1 - \%\ \text{moisture of manure}) * \%C_m\ \text{of raw manure}} \tag{12}$$

The desired output from the fermentation process, as mentioned above, is VFAs. There are several different types that contain varying amounts of carbon as listed in Table 1. The VFAs are separated and fed to the PHA reactor. The residual solids are transferred to the AD as shown in Figure 3. The mass of each acid is divided by its density and then the volume of each acid is summed. In the UI laboratory-scale system, approximately 0.03 L of VFAs were produced. The VFAs will be part of the liquid stream when the fermenter effluent is separated. Approximately 1.1 to 1.2 L of tap water were added to the manure to generate 5 L of manure slurry. It is assumed that the average density of the liquid fraction is the same as water (1000 g/L). The PHA reactor receives only liquid and no solids. The AD receives all the solids plus some of the liquid. Approximately 3 L of the liquid fraction go to the PHA reactor, and the remaining amount of liquid is added to the solids fraction and sent to the AD. Note that not all of the VFAs from the fermenter are routed to the PHA reactor. Approximately 62.26% of the VFAs go to the PHA reactor and the remaining 37.74% are routed to the AD (Pham et al. 2012). This is necessary to "prime" the AD.

The carbon content of the biogas shown in Figure 3 is obtained by subtracting the total organic carbon (TOC) leaving from the amount entering the fermenter rather than by using the data from the fermenter data sheet. This accounts for the "missing" carbon as done by Coats et al. (2012).

Table 1. Carbon containing compounds produced by the fermenter.

Compound	No. of Carbon Units	Chemical Formula	Density (g/L)
Acetic acid	2	CH_3COOH	1050
Propionic acid	3	CH_3CH_2COOH	995
Iso-butyric acid	4	$(CH_3)_2CHCOOH$	970
Butyric acid	4	$CH_3 (CH_2)_2COOH$	1135
Valeric acid	5	$CH_3 (CH_2)_3COOH$	930
Isovaleric acid	5	$(CH_3)_2CHCH_2COOH$	925
Caproic acid	6	$CH_3 (CH_2)_4COOH$	927
Carbon dioxide	1	CO_2	1.98
Methane	1	CH_4	0.656

1.3 Anaerobic Digester

1.3.1 Overview

The AD takes in the residual, pre-fermented solids from the fermenter. This is the second stage of the two-stage AD process where methanogenesis takes place. For biogas to be produced, the reactions must occur in oxygen-free (anaerobic) conditions. The reactions that take place are driven by a class of bacteria called methanogens that produce methane and carbon dioxide (EPA 2006). Similar to the fermenter, temperature, OLR, and SRT are important operational variables. For the integrated dairy manure treatment system these two steps (fermentation and anaerobic digestion) must be separate. It is desirable to minimize the effluent VFAs and maximize methane production.

The biogas product is composed of approximately 55–60% methane and 35–45% carbon dioxide by weight (Angelidaki and Batstone 2010). The gas may be used to produce electricity that can be sold to the power grid. Biogas produced by the methods outlined here may be more consistent in composition than biogas produced conventional ADs; since power companies often require relatively consistent rates of supply, this is an advantage of this type of system (Coats et al. 2012). Usually a portion of the gas is sold to the power grid, and the remaining portion is burned at the dairy to generate electricity and reduce the electricity consumption of the farm. Carbon dioxide may be diverted to serve as the CO_2 source for the algae cultivation.

The by-products of this process are liquids and digested solids. These are separated and the liquids are allocated to algae cultivation and the solids sold as a soil amendment fertilizer and/or animal bedding. Though these are not very high-value products, they do contribute overall to the economic viability of the system.

1.3.2 Process Description

The data for this model were obtained by bench-scale experiments conducted at the UI as shown in Figure 4. Several different AD reactors were operated over the course of this project, with different reactor volumes, SRTs, and feedstock. Studies were performed to investigate whether the methane yield in the biogas could be increased by separation of the two distinct fractions of fermented solids based on particle size and digestion of each fraction in a separate reactor. Results show that more methane is produced when the combined fermenter effluent solids are fed to the AD rather than processing the different solids fractions separately (Coats et al. 2012).
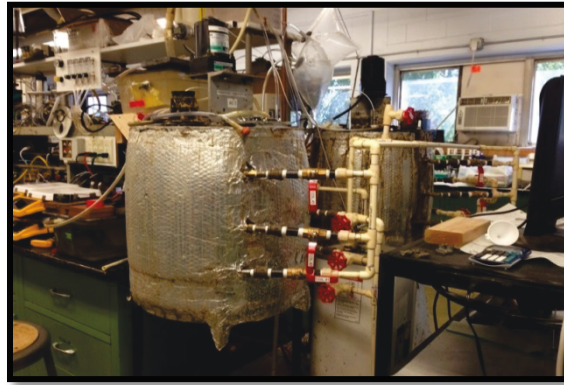
Figure 4. Experimental setup of laboratory-scale AD at UI.

The DAIRIEES model uses the data from the AD6 reactor that has a total volume of 40 L, SRT/HRT of 20 days, and influent volume of 2 L. Note that AD requires a much higher residence time for the biomass and liquid to remain in the reactor than fermenters. The reactor is continuously stirred to allow the bacteria to have adequate access to its food source. Each day, an influent volume of manure and water was added and the same amount removed from the bottom of the reactor. Tipping gas meters were used to measure the amount of biogas produced. Since a mesophilic AD must be heated to operate optimally, the reactor in this experiment was maintained with tight temperature control at 35°C ±0.1°C. In operational ADs, the waste heat from the generator supplies heat to the AD. Figure 5 illustrates the inflows, outflows, and products from the AD process (Passero et al. 2015).
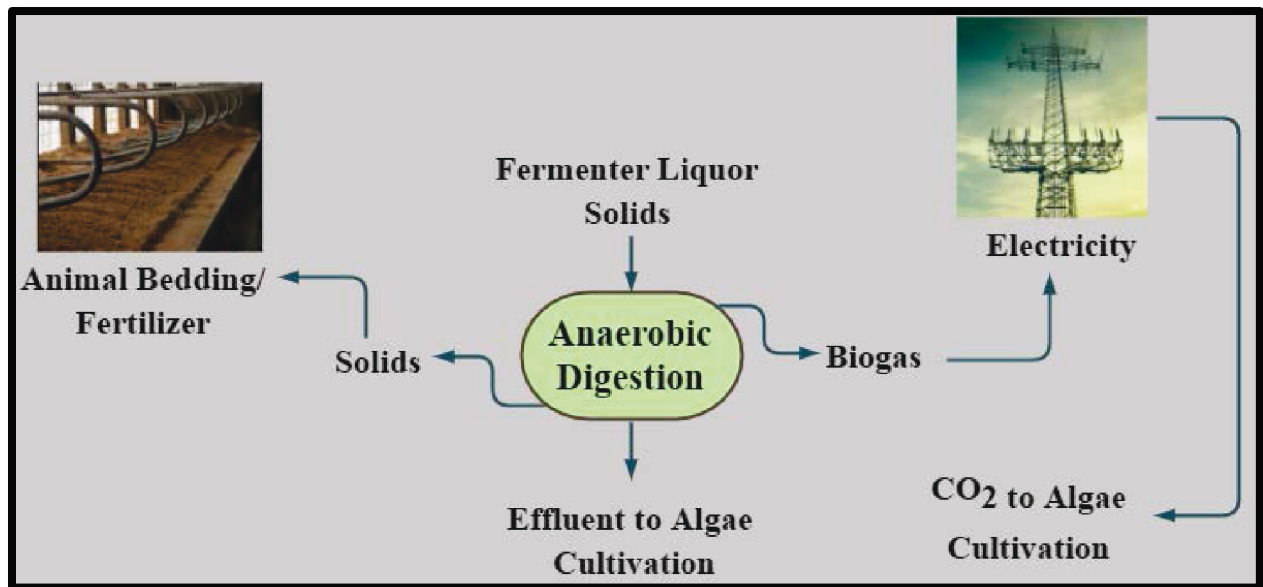
Figure 5. Inflows, outflows, and products from the AD process.

1.3.3 Calculations and Parameters

All of the solid material exiting the fermenter is assumed to enter the AD. An estimation the ratio of mass sent to the AD can be determined by tracking the carbon outflow relative to the carbon inflow from the AD data. The most valuable AD products are the biogas and animal bedding. Husfeldt et al. (2012) cites C, N, and P values in AD separated solids as 45%, 1.42%, 0.44%, respectively. The amount and composition of animal bedding is estimated by tracking carbon flow. The biogas is measured using tipping gas meters. Nitrogen in the effluent is routed to the algae cultivation system (ACS).

$$\text{fermenter kg C out} = \left(\frac{D_A \text{ solids TOC gC in}}{D_f \text{ TSM in} * (1 - \% \text{ moisture of manure}) * \text{manure } \%C_m} \right) \tag{13}$$

$$\text{kg C biogas out} = \left(\frac{D_A \text{ gC } CO_2 \text{ out} + \text{AD gC } CH_4 \text{ out}}{\text{AD solids TOC gC in}} \right) \tag{14}$$

$$\text{animal bedding kg C out} = \left(\frac{D_A \text{ solids TOC gc out}}{D_A \text{ solids TOC gC in}} \right) \tag{15}$$

$$\text{kg N to ACS} = \left(\frac{\%N_m \text{ of AD out to ACS} * 2 \text{ (L out in lab experiments)}}{(D_A \text{ solids TOC gC in}/1000)} \right) \tag{16}$$

The power produced from the biogas from anaerobic digestion can be estimated. Heating value is the amount of heat produced by a complete combustion of fuel and it is measured as a unit of energy per unit mass or volume of substance. The heat of combustion of fuels is expressed by the higher and lower heating values (HHV and LHV). HHV is measured using a bomb calorimeter; and defined as the amount of heat released when fuel is combusted and the products have returned to a temperature of 25°C. The latent heat of condensation of the water is included in the total measured heat. LHV is determined by subtracting the latent heat of vaporization of water vapor (generated during combustion of fuel) from the HHV. Biogas from a digester will always be saturated since the path from the digester to the point of use will be one of lowering temperature that will keep the gas saturated. Because the biogas produced on dairy farms will be used in engines and/or boilers, none of water produced during combustion will be condensed (Ludington 2006).

In determining the heating value of biogas from an anaerobic digester, the assumption is made that the biogas is saturated as it passes through the gas meter. Therefore, the LHV (corrected for methane percentage in the biogas, temperature, and pressure) should be used rather than the HHV.

The heat energy in the biogas is from burning the methane. Table 2 lists the percentage by volume of methane in the biogas from 40% to 70%. The LHV values in middle column are calculated by multiplying the lower calorific heating value of methane at 50,051 J/g by the density of the dry biogas, .66 kg/m³ (Elert 2014). A correction factor of 0.918 was applied to account for an STP pressure (i.e., atmospheric) at a non-STP temperature of 18°C (Elert 2014). A regression of the LHV values yield the following linear expression:

$$\text{Biogas LHV @ 18C } \frac{kWh}{m^3} = 0.0916 * \%CH_4 * 100 - 0.0032 \tag{17}$$

Table 2. Lower heating values for methane (Ludington 2006).

%CH$_4$ by volume	LHV (kWh/m^3)	LHV corrected for temp. (kWh/m^3)
40	3.985	3.658
42	4.192	3.848
44	4.388	4.028
46	4.585	4.209
48	4.792	4.399
50	4.989	4.580
52	5.185	4.760
54	5.382	4.941
56	5.589	5.131
58	5.785	5.311
60	5.982	5.491
62	6.189	5.682
64	6.386	5.862
66	6.582	6.042
68	6.779	6.223
70	6.986	6.413

A study by Atrip et al. (2013) of an AD implementation at a dairy in the Northwest U.S. showed that the actual energy yield was 1.76 kWh/m^3 of biogas added versus the energy contained in the biogas of 5.25 kWh/m^3, so the efficiency was calculated as 1.76/5.25, or 33%. For comparison, the Synergy Biogas plant in Covington, New York (Rankin et al. 2013) uses AD technology from Bigadan (Skanderborg, Denmark) that produces 2.1 kWh/m^3 and the energy contained in the biogas was 3.5 kWh/m^3, or about 60% efficiency.

To size the engine appropriately (and not oversize it), it is assumed that 50% of the methane gas is available to generate electricity:

$$\text{Electricity Produced } \frac{\text{kWh}}{\text{day}} = \text{CH}_4 \text{ produced } \frac{\text{m}^3}{\text{day}} * \text{Biogas LHV } \frac{\text{kWh}}{\text{m}^3} * 0.5 \tag{18}$$

With a 95% capacity factor, the engine size is calculated:

$$Engine\ size\ kW = \frac{Daily\ electricity\ produced \frac{kWh}{day}*0.95}{24\frac{h}{d}} \tag{19}$$

Waste heat from the engine can be used for various applications, including heat, process steam, biomass drying, or maintaining the digester temperature. To estimate the amount of waste heat, it is assumed that the engine efficiency is 40% with 60% of the heat generated being waste heat and that the heat exchangers have an 80% efficiency (Hegde et al. 2005).

$$Waste\ Heat\ Generated\ \frac{kWh}{day} = \frac{Daily\ electricity\ produced \frac{kWh}{day}*0.6*0.8}{0.4} \tag{20}$$

The amount of natural gas displaced annually through the use of waste heat is calculated assuming that 50% of the waste heat is used to heat the digester and the remaining 50% is available for other heating uses or steam production with an average efficiency of 90%.

$$Natural\ gas\ displaced\ \frac{kWh}{day} = Daily\ amt\ waste\ heat\ \frac{kWh}{day} * \frac{0.5}{0.9} \qquad (21)$$

The amount of GHG emissions avoided through the combustion of biogas can be calculated based upon the U.S. average of 1232.52 lb CO_2 equivalent/MWh as reported in the U.S. Environmental Protection Agency Emissions and Generation Resource Integrated Database (eGRID) database (U.S. EPA 2012). eGRID assigns zero CO_2 emissions to generate the combustion of all biomass (including biogas) because these organic materials would otherwise release CO_2 (or other GHGs) to the atmosphere through decomposition via the natural carbon cycle; therefore, the materials do not contribute to global warming.

$$Displaced\ grid\ emissions\ \frac{MT}{day} = electricity\ \frac{kWh}{day} * 1238.52 \frac{lb\ CO_2 equivalent}{MWh} * \frac{MWh}{1000\ kWh} * \frac{metric\ ton}{2200\ lb} (22)$$

The amount of CO_2 produced by on-farm combustion that is available for algae cultivation is calculated using a value of 54 kg CO_2/MMBTU for natural gas per the U.S. Energy Information Administration's Voluntary Reporting of Greenhouse Gases Program (EIA 2011).

$$Available\ CO2\ for\ ACS\ \frac{MT}{day} = 54\ \frac{kg\ CO2}{MMBTU} * \frac{1\ MMBTU}{293\ kWh} * \frac{1\ metric\ ton}{1000\ kg} * electricity\ produced\ \frac{kWh}{day} \qquad (23)$$

1.4   PHA Reactor

1.4.1   Overview

After fermentation VFAs are transferred to the PHA reactor (Endres 2011). The PHAs are the precursor of some forms of bioplastics that have the advantages over petrochemical plastics of being natural, renewable, and biocompatible. Bacteria produce PHAs as a form of carbon and energy that can be stored for later use, similar to how a bear stores up fat for hibernation. An electron microscope image of PHA-containing microorganisms is shown in Figure 6 (Endres 2011). It is synthesized when carbon in the reactor is in excess, but another necessary nutrient (typically nitrogen) is lacking. When that nutrient is available again, the bacteria then degrade the PHA compounds and consume the energy. This is called the feast/famine cycle of PHA synthesis (Dias 2005). The PHA should be harvested when it is present. Figure 7 illustrates the chemical structure of PHA. The polyester linkage creates a molecule with 3-carbon segments separated by oxygen atoms. The remainder of the monomer becomes a side chain off the main backbone of the polymer.
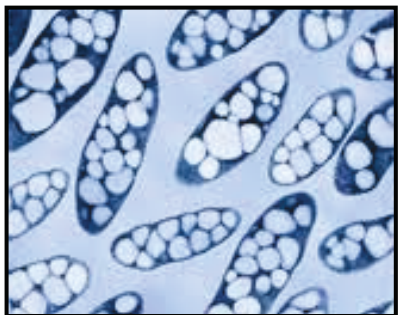
Figure 6. PHA-containing microorganism (Endres and Siebert-Raths 2011).
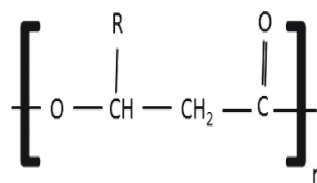
R=CH_3 polyhydroxybutyrate (PHB)
R=CH_2-CH_3 polyhydroxyvalerate (PHV)

Figure 7. The chemical structure and formula for polyhydroxyalkonates (Endres and Siebert-Raths 2011).

The specific PHA polymer of interest in this process is PHBV. This is a co-polymer comprised of two PHA compounds: polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). The resulting polymer composition is a function of the carbon source, with even-carbon VFAs producing 3-hydroxybutyrate and odd-carbon number VFAs producing 3-hydroxyvalerate (Wei et al. 2014). The polymer is desirable because the compounds by themselves have material properties that make them unsuitable for large commercial use. PHBV has advantages over PHB in that the chemical microstructures can be controlled to tailor the physical and mechanical properties, melting and cocrystallization behavior, and biodegradability (Wei et al. 2014). PHBV has potential for use in biodegradable films, utensils, and medical applications (Unknown 1989; Madison and Huisman 1999; Zinn et al. 2001). PHBV with 10% PHV and 90% PHB content has properties similar to the plastic in milk jugs (HDPE), while PHBV with 20% PHV and 80% PHB content has properties similar to the plastic that makes up flexible films (LDPE) (Luzier 1992). In general, most of the VFAs added to the reactor are converted to PHA compounds, so it is a generally efficient process. PHAs can be accumulated by bacteria to levels as high as 90% (w/w) of the dry cell mass (Steinbüchel and Lütke-Eversloh 2003; Coats 2010).

1.4.2 Process Description

The VFA-rich supernatant fraction generated in the hydrolysis/fermentation stage is fed to a PHA reactor. The data for this model was obtained from experiments conducted at UI. PHBV was biosynthesized in a 20-L scale bioreactor inoculated with activated sludge (mixed microbial consortia) obtained from the Moscow, Idaho, wastewater treatment plant as shown in Figure 8. The aerated bioreactor was run continuously for 1 year and was fed a mixture of VFAs from clarified fermented manure from the UI dairy with SRT and hydraulic retention times of 4 days (Wei et al. 2014). Influent to the UI laboratory-scale PHA reactor consists of 3 L of fermenter liquor mixed with 4.5 L of water.

Figure 8. Experimental setup for PHA reactors at UI.

PHAs are produced using a two-stage batch-fed process consisting of an enrichment reactor and a production reactor. Within the enrichment reactor an initial growth phase in a nutritionally enriched medium yields sufficient biomass, which is then fed to a production reactor consisting of a product formation phase in a nitrogen-depleted medium. The polymer-containing microorganisms are separated from the culture medium by classical mechanical techniques, such as filtration and centrifugation. The PHA is then extracted and recovered. The PHA powder is extrusion-granulated for processing to plastics using injection molding equipment. Additives to enhance material properties are typically incorporated (Endres and Siebert-Raths 2011).

1.4.3   Calculations and Parameters

The calculations presented in the model are for the production PHA reactor, which produces PHB and PHV from VFAs. The production reactor receives inputs from the fermenter and from the enrichment reactor. The fermenter serves as the source of VFAs and the enrichment reactor serves as the source of bacteria needed to carry out the reaction. To maximize PHB/PHV productivity, the amount of carboxylate-rich liquid sent to the enrichment reactor should be minimized. For the current state of the model, mass and nutrient movement from the enrichment reactor is not considered due to lack of data; when more data becomes available this should be integrated into the overall process. The enrichment reactor will operate continuously to maintain a bacterial consortium capable of rapidly producing commercial levels of PHA in the production reactor. Research results show that the PHA enrichment reactor can be aerated at an oxygen mass transfer rate as low as $4hr^{-1}$ without compromising PHA production. The enrichment reactor cycles PHA. First, the consortium converts VFAs to PHA, then later in the operational cycle the consortium consumes the PHA for energy and growth. It is the production reactor that sequesters VFAs without subsequent use. This is the element that ultimately sequesters carbon and reduces GHG emissions. A PHA yield of 60–70% can be sustained in the PHA production reactor (i.e., 60–70% of the organic carbon present in the VFAs is sequestered by a mixed microbial consortium as PHA). Wei et al. (2015b) report PHBV content up to 40% of the dry cell weight. Aqueous phosphorus is incorporated into the biomass. Laboratory experiments by Al-Najjar et al. (2011) showed that the quantity of phosphorous removed from a synthetic wastewater solution was ~67%.

The experimental data available at the time of the development of this portion of the model only provided peak production values for PHB and PHV production. This value was used because it was the only estimate available, and because this is considered to be an approximation of actual behavior in the production reactor. Once a certain concentration of PHAs is reached, the bacteria are killed so that they do not start to consume the PHAs that were just produced as a source of energy. The RBB from the lysed bacterial cells (containing proteins, nucleic acids, carbohydrates, and lipids) is sent to the HTL or pyrolysis unit. Figure 9 shows the process flow for the PHA reactors. In addition to the desired production of bioplastic compounds, there is a liquid by-product that is rich in nutrients. This effluent can be provided to the algae raceway to serve as a source of nutrients for algal cultivation. The residual bacterial biomass (RBB) can be recycled back to the fermenter to augment PHA production (Wei et al. 2015a).
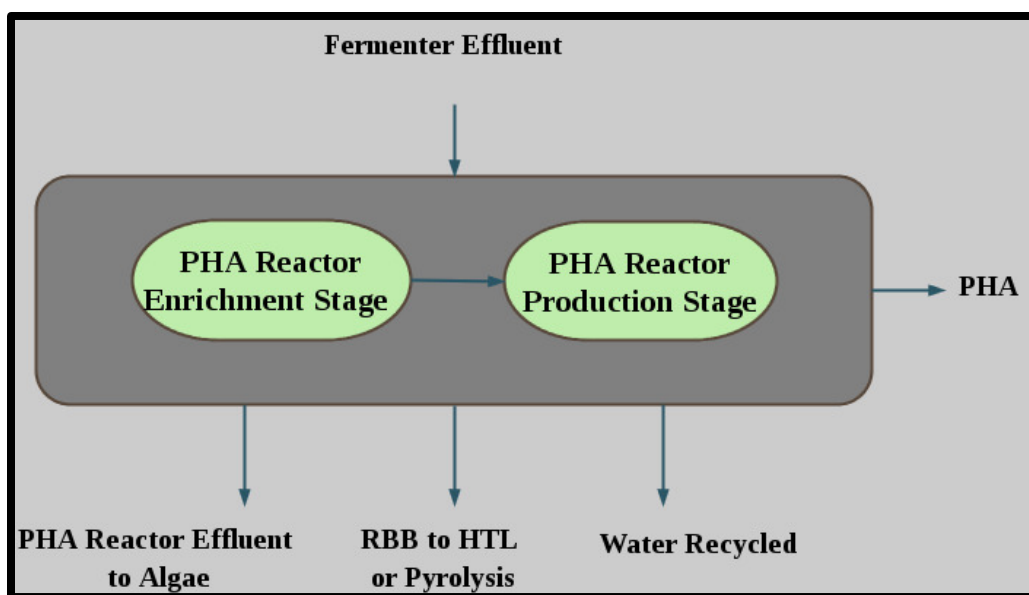
Figure 9. Process flow for the PHA reactors.

The carbon contents of PHB and PHV were provided in the experimental data from the Coats' laboratory at UI. The PHA retains almost all of the carbon of the original feedstock and there is essentially no removal of N or P by the PHA reactors (Smith et al. 2015).

$$VFA\ in = \%_m\ towards\ enrichment * dry\ manure\ in * \left(\frac{(D_F\ mg\ total\ acid\ out/1000)}{D_F\ g\ total\ solids\ in} \right) \tag{24}$$

$$PHB\ produced = VFA\ in * (peak\ g\ PHB/g\ VFA) \tag{25}$$

$$PHV\ produced = VFA\ in * (peak\ g\ PHV/g\ VFA) \tag{26}$$

1.5   Algae Cultivation

1.5.1   Overview

Microalgae production has become a topic of great interest over recent years as it emerges as a promising successor to first-generation biofuels (Quinn et al. 2014). This is due to several factors, including high lipid production rates and use of lower-quality water and land not suitable for other sources (Juenja et al. 2013; Quinn et al. 2014). The ability of microalgae to produce energy with relatively few inputs makes it a promising resource for other applications as well.

In the context of integrated dairy manure management, algae can serve as a source of biomass while serving as a sink for the excess nutrients produced in the rest of the process. The biomass can be fed into the fermenter to increase yields from the fermenter and, by extension, increase yields of the desired products. Carbon dioxide can be diverted from anaerobic digester biogas to serve as the carbon source for algae growth. Nitrogen- and carbon-rich effluent from the anaerobic digester and PHA reactor will be input into the algae reactor to stimulate growth, as shown in Figure 10.
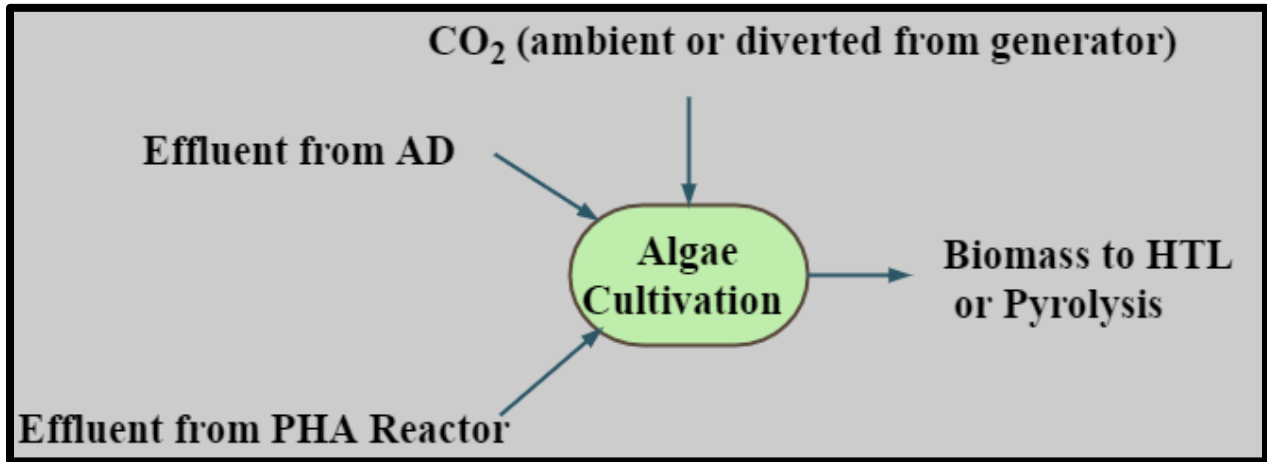
Figure 10. Process flow for algae cultivation system.

This diversion of inorganic nutrients from the waste stream is an important consideration in dairy-production areas. Many of these regions have historically spread nutrient-rich manure on agricultural fields, and the result is nutrient overloading, which has serious environmental impacts. Eutrophication affects the ecology of lakes and streams by degrading water quality and can lead to loss of aquatic life.

Both detached and attached growth scenarios for algae production were examined. There are two main methods for detached growth microalgae production: photobioreactors (PBRs) and open pond raceways (OPR). For the attached growth scenario the algal turf scrubber (ATS) were examined.

PBRs are closed vessels and, since the environment is artificial, all the operational variables are specifically controlled to promote the growth of phototropic algae. Many different types of PBR systems have been proposed, such as tubular (serpentine, manifold, helical, fence arrangement with manifolds) flat plate (flat alveolar panels, glass) airlift column, vertical sleeve, fermenter-type, and attached growth (Burns 2014).

Productivity for these types of systems is given in terms of average overall a real productivity, average illuminated surface productivity, and/or average volumetric productivity. Though these systems sometimes have higher yields because the system can be better optimized, this additional control is accompanied by increased capital and maintenance costs. Another downside of PBRs, is their energy efficiency based upon energy input to the cultivation process according to an assessment compiled on a variety of PBRs (Pegallapati et al. 2014).

A raceway is a series of long oval "tracks" built to circulate water containing the suspended algae. The raceway is open on top, allowing for the necessary sunlight to reach the algae. Carbon dioxide is bubbled in, and water is pumped to replace water that has evaporated. Usually a paddle wheel is used to keep the water-algae mixture moving. At regular time intervals (typically every 21 days) the algae are harvested. A certain amount of algae/water is removed, and the algae are allowed to settle out of the water. Harvesting the algae also serves to ensure that the raceway does not get overcrowded so the necessary amount of light reaches the algae.

Some of the operational concerns for a raceway are the amount of fertilizer/nutrients added, temperature, and the frequency at which the algae are harvested. In this process, open raceways are used because of their relatively low capital costs. They also require fewer energy inputs, although they are more controlled by climatic variables and are more susceptible to contamination by undesired species. However, since the process that already has a low profit margin, the lowest cost process is most desirable.

The ATS treatment technology consists of an attached algal community growing on screens in a sloped trough over which AD effluent flows (Pizarro et al. 2006). The key variables that affect the metabolism of the algal community are water depth and flow rates, presence of grazers (i.e., herbivores), and harvest frequency (which rejuvenates the organisms and increases growth rates). The attached algal community uptakes inorganic compounds and breaks down organic compounds.

1.5.2   Process Description

1.5.2.1   Detached Growth Systems. The data for detached growth of algal cultures is based on research on phototropic growth in photobioreactors and raceways at BSU. The algae species used for most of the initial experiments was Chlorella vulgaris, which is one of the most commonly studied species of microalgae for this type of application. Initial algal cultivation studies for this project utilized monocultures grown in photobioreactors or raceways (Passero et al. 2015). Recent studies have shown that algal polycultures are more resistant to grazers and exhibit more robust productivity (Corcoran et al. 2012). However, later studies focused on polycultures wherein a consortium of species was found to be the most productive.

A depiction of the raceways is shown in Figure 11. Each raceway holds 100 L of liquid, in which the algae are suspended. Diluted PHA or AD effluent was supplied to the algae culture as a source of nutrients. The temperature was maintained at 25–30°C. Half of the algae volume was harvested every 2 days to serve as the source of biomass and to allow the algae in the raceway to continue to grow. The harvested liquid was centrifuged to separate the algae from the liquid.

Figure 11. Experimental setup for algae raceways.

1.5.2.2 ***Attached Growth System.*** The ATS utilizes native algae that grow attached to a screen in a shallow, flowing water system. The ATS system consists of an attached algal community growing on screens in a shallow trough or raceway through which manure slurry from an AD is pumped (Pizarro et al. 2006). The algal community provides water treatment by uptake of inorganic compounds in photosynthesis. Water is pumped from a waterway onto the raceway and algae remove the nutrients through biological uptake for growth as the water flows down the raceway. At the end of the raceway, water is released back into the waterway with a lower nutrient concentration than when it was pumped up onto the top of the raceway (shown in Figure 12 Nitrogen and phosphorus removal rates of approximately 7170 and 900 kg/ha are reported (HydroMentia, Inc., Ocala, Florida). A biomass productivity of 22 g/m^2-d is estimated (Kebede-Westhead et al. 2003). Wilkie and Mulbry (2002) report productivities of dry algae 5 g/m2-d with dairy wastewater.

Figure 12. ATS deployed in Florida (Ref: http://www.algalturfscrubber.com/).

1.5.3   Calculations and Parameters

It is assumed that the elemental C, N, and P are transferred to and taken up by algae biomass with no losses and 100% efficiency. The nutrient content of microalgae is often approximated by the Redfield ratio of C:N:P = 106:16:1 (Weyer et al. 2009). Using the respective molecular weights of C (12 g/mol), N (14 g/mol), and P (31 g/mol), the resulting C:N:P mass ratio is given as:

$$(106 \times 12) : (16 \times 14) : (1 \times 31) = 1272 : 224 : 31 \tag{27}$$

If the algae has a 50% C content by mass, then the mass percentage ratios are:

$$((0.50 \times 1272)/1272) : ((0.50 \times 224)/1272) : ((0.50 \times 31)/1272) = 50\% \, C : 8.8\% \, N : 1.22\% \, P \tag{28}$$

Therefore, for an algae strain with a 50% C content by mass, 88 kg of N and 12.2 kg of P are required to produce a metric ton of dry algae biomass (Pate et al. 2011).

This research presents algae biomass production dependent on the nitrogen source: nitrate or ammonium. Ammonium is the nitrogen source produced as a product in the anaerobic digester, and nitrate is the nitrogen source in the PHA effluent. Algal cultures supplied with PHA effluent tend to exhibit higher productivity (Passero et al. 2015), but cultures supplied with AD effluent tend to exhibit a higher resistance towards grazers as have been observed by the UI. Therefore, the type of effluent fed to the algal production raceways will affect algae biomass growth and composition.

The algae has a carbon mass fraction of about 50%. Therefore, there is ~500 gC in 1 kg of algal biomass. There are 12 gC in 1 mole (44 gCO_2). Therefore, the number of grams of CO_2 needed per gram of algal biomass is:

$$CO_2 \; needed = 500 \; \frac{gC}{kg \; biomass} * \frac{44 \; g \; CO_2}{12 \; gC} = 1833 \; \frac{g \; CO_2}{kg \; biomass} \tag{29}$$

Since the concentration of algae in the ponds is typically 1 g biomass/L, 1.833 g CO_2/L would be the minimum concentration of carbon dioxide in the water to achieve stoichiometric productivity. The solubility of carbon dioxide in water at atmospheric pressure and 18°C is 1.789 g/L (Dean 1999) where solubility decreases as the temperature increases. Estimates presented in the literature state that roughly two mass units of CO_2 to one mass unit of algae is often considered to be the required minimum due to losses and inefficiencies (Slade and Bauen 2013). Outgassing losses are dependent on pond depth, mixing velocity, friction coefficient of the pond bottom, pH, and alkalinity (Weissman et al. 1988). To supply carbon dioxide to an algal raceway, carbonation stations are often placed at certain distances that are a function of the mixing velocity.

The following calculation demonstrates why it is necessary to provide supplemental carbon dioxide to the algae pond. Atmospheric measurements indicate a level of carbon dioxide in atmospheric air of 402.8 ppm or 0.04% (NOAA 2015). To convert to mass percent, the ratio of carbon dioxide to air molecular weights is multiplied by the density of air at 20°C (Incropera et al. 2007).

$$CO_2 \%_m \; of \; air = 0.0004 * \frac{44 \; g \; CO_2}{28.97 g \; air} * 1.194 \; \frac{kg \; air}{m^3} * 1000 \frac{g \; air}{kg \; air} = 0.7254 \; \frac{g \; CO_2}{m^3 \; air} \tag{30}$$

$$Volume \; of \; air \; needed = \frac{1833 \frac{g \; CO_2}{kg \; biomass}}{0.7254 \frac{g \; CO_2}{m^3 air}} = 2527 \frac{m^3 \; air}{kg \; biomass} \tag{31}$$

For the detached growth scenario, water depth is assumed to be 30 cm, based on the parameters given by Slade and Bauen (2013). It is assumed that 100% of the materials (nitrogen, phosphorus, and carbon dioxide) are taken up by the algae. If these materials need to be added in excess because 100% uptake is not possible (which is, of course, the case), the calculations for amounts of materials added need to be adjusted accordingly. Calculations in the algae spreadsheet were performed as follows:

The dewatered algae moisture content of 80% was an operational constant in the Bennion (2015) publication. This same constant assumption is used for this model coupled with an assumption of algae production uptime of 270 days/year (Davis et al. 2012).

Biomass productivity ranges from 6.2 to 16.5 g/ m^2-day with an average biomass productivity of 13.2 g/m^2-day for the harmonized productivity of an open pond raceway. This is in line with large-scale commercial productivity of 10–20 g/m^2-day. Laboratory data from BSU shows productivities for "optimal" polycultures of 4.3 g/m^2-day (*Microcystis aeruginosa*, *Synechococcus leopoliensis*, *Scenedesmus obliquus*) and 4.2 g/m^2-day (Boise River polyculture). These two polycultures exhibit a combination of the highest yields and most resistance to grazers. Biomass productivity will vary greatly dependent upon the algae cultivation system and the regional climate.

A harmonized value for water evaporation from the algal ponds was not reported by Davis et al. (2012), so the average of the pre-harmonization values presented was used. The two values were 0.6 cm/day and 0.3 cm/day for an average of 0.45≈0.5 cm/day. This evaporation rate was converted to a volumetric rate per square meter by the following calculation:

$$Evaporation\ rate\ \left(\frac{\frac{L}{m^2}}{day}\right) = 0.5\ \frac{cm}{day} * \frac{1m}{100cm} * \frac{1000L}{1m^3} = 5\ \frac{L}{m^2*day} \tag{32}$$

$$Water\ evaporation\ \left(\frac{L}{kg*day}\right) = Raceway\ area\ needed\ \left(\frac{m^2}{kg}\right) * Evaporation\ rate\ (L/m^2/day) \tag{33}$$

Nitrogen in the production of algae is considered to be the limiting reagent. Therefore, the amount of algae needed to sequester the nitrogen is the basis used to determine the number of hectares of algae cultivation needed, as shown in Table 3. The following two formulas are based uponupon laboratory fractions of input and output. Volumes of outflow that was put towards algae cultivation was 2 L for AD and 3 L for PHA. Daily manure used in the daily laboratory experiments was equivalent to the manure produced by 0.02 cow or approximately one-fiftieth of that produced by one cow in 1 day.

$$AD\ kg\ N\ out\ = \left(\frac{AD\ N\ \%_m\ out*2\ L}{(AD\ solids\ TOC\ gC\ influent/1000)}\right) \tag{34}$$

$$PHA\ kg\ N\ out = (N\ \%_m\ of\ PHA\ out * 3\ L) * \frac{\#\ of\ cows}{0.02} \tag{35}$$

Biomass productivity rates can be controlled for by the user.

$$Raceway\ area\ needed\ (m^2) = \frac{\left(\frac{kg\ algae}{kg\ N}\right)*[N]\ of\ algae}{biomass\ productivity\ rate\ (g/m^2/day)} \tag{36}$$

Nitrogen and phosphorous data for the AD and PHA effluent was taken from Passero et al. (2015). To scale these numbers to a per-cow basis, they are multiplied by 100 L for AD (i.e., 2 L for 0.02 cow) and 150 L for PHA effluent (i.e., 3 L for 0.02 cow).

Table 3. Nitrogen and phosphorous content of AD and PHA effluent (Passero et al. 2015).

	AD effluent (mg/L)	PHA effluent (mg/L)
Total dissolved nitrogen (N)	1226.0	499.5
Total dissolved phosphorus (P)	96.2	33.3

1.6   Biomass Treatment

1.6.1   Overview

The algal biomass and the RBB from the PHA reactor can be treated by either hydrothermal liquefaction (HTL) (Figure 13) or pyrolysis (Figure 14), or it can be sold without treatment after dewatering and drying.

Figure 13. Laboratory HTL equipment.

Figure 14. Laboratory pyrolysis unit.

1.6.1.1   Hydrothermal Liquefaction. The HTL process converts biomass into four phases (Tian et al. 2014): solid residue, bio-oil, gaseous products, and aqueous products, as shown in Figure 15.
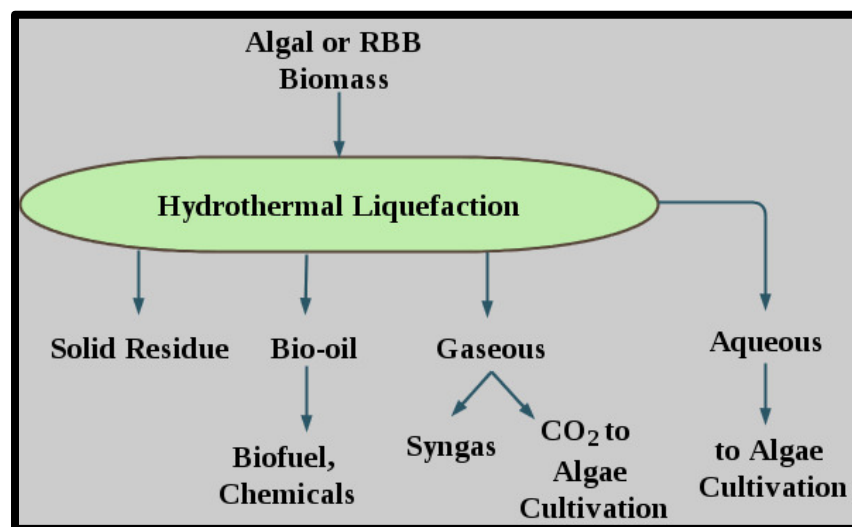
Figure 15. Products derived from the HTL process.

HTL of whole algae is an attractive process since wet slurries are readily accommodated. Thus, dewatering (an energy intensive step) is minimized. The slurry is hydrothermally treated in subcritical water, typically at pressures between 13.8 MPa (2000 psi) and 20.7 MPa (3000 psi) and temperatures ranging from 300 to 350°C (Jones et al. 2014). Primary products are bio-oil and an aqueous phase. The aqueous phase contains residual bacterial biomass, which consists of carbohydrates, protein, lipids, and lignin that can be recycled to the fermenter to augment PHA Biosynthesis. Small amounts of gases and solids are also formed. The solids are high in phosphorus content and can be recycled back to the algae ponds (Figure 15).

HTL of the RBB from the PHA reactor has the potential to generate value-added bioproducts from materials that would otherwise be discarded as waste. The RBB is protein- (i.e., nitrogen) and carbohydrate-rich material comprised of lysed bacterial cells. Freeze-dried biomass containing PHBV stored in the bacterial cells is first batch extracted with acetone to remove lipids, and then Soxhlet extracted with $CHCl_3$ to recover the PHBV. Then, direct HTL is performed to hydrolyze the proteins, nucleic acids, carbohydrates, and lipids at temperatures from 150 to 250°C. This converts the biomass into useful products, such as water-soluble products and organic oils (bio-oils). The water-soluble portion can be recycled to the fermenter as carbon and nitrogen sources to biosynthesize additional PHA (Wei et al. 2015a).

1.6.1.2 ***Pyrolysis.*** Pyrolysis is the heating of an organic material, such as biomass (wood, food wastes, bacterial residuals, etc.), in the absence of oxygen. Without oxygen, combustion does not occur. Rather, the chemical compounds (i.e., cellulose, hemicellulose and lignin) that comprise the material thermally decompose into combustible gases and charcoal. Most of these combustible gases can be condensed into combustible liquid, called pyrolysis oil (bio-oil), though there are gases released in the process (CO_2, CO, H_2, light hydrocarbons). Pyrolysis vapors can be condensed to form bio-oil, used directly as biogas for energy, or treated by steam reforming to produce syngas (Czernik et al. 2007). Biochar is a carbon-based, solid co-product (i.e., charcoal) that has value as a soil amendment. The pyrolysis of biomass produces three products—bio-oil (liquid), bio-char (solid) and syngas (gas)—that are assigned market values in the model. The proportion of these products depends on several factors that include the feedstock composition and process parameters, which is the subject of continuing research. The primary compounds in the bio-oil are hydrocarbons, such as mono-aromatic hydrocarbons and phenolic compounds, which include toluene and phenolic compounds; aliphatic ketone, including pentanone and cyclopentanedione; nitrogen and oxygen containing aromatic compounds, such as pyrrole,

20

indole, and pyridinyl products; aliphatic compounds and amines; and carboxylic acids. Since the biochar contains considerable amounts of inorganic nitrogen, it is suitable for fertilizer. Nitrogen-rich pyrolysis oil could be recycled back to the PHA reactor (shown in Figure 16) or fermenter to augment production since it is highly dispersible in water (Wei et al. 2015b).
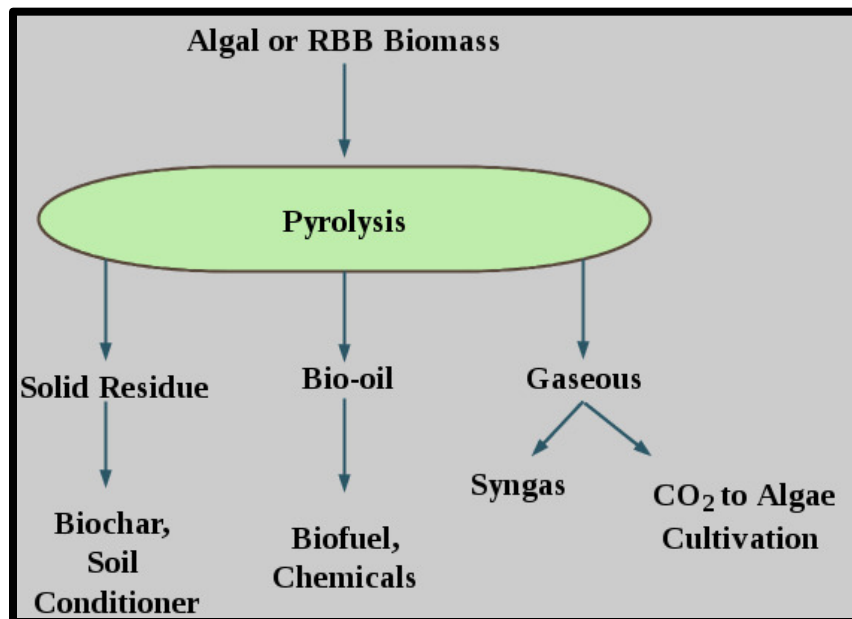
Figure 16. Products from pyrolysis.

1.6.2   Process Description

1.6.2.1   Mechanical dewatering. Before algae can be processed by HTL or pyrolysis it must first be dewatered. Prior to performing HTL on microalgae, dewatering algae from an initial concentration of approximately 1–5% to a concentration of at least 20% is required (Bennion 2015). Concentrations of 10 to 20% can be achieved with physical separation methods, such as centrifugation, screw or belt presses. Once the algae has been dewatered it is ready for HTL, but not for pyrolysis.

1.6.2.2   Drying. For microalgae to be processed by pyrolysis, it not only has to be dewatered, but it also must be dried to a solids concentration of ~80% (Bennion 2015). Drying can be accomplished by solar or thermal drying. Solar drying requires a sunny location, trays on which to spread the algae, and a means to rotate and change out the algae. Solar drying can be a cost-effective method; however, in humid or wet/rainy climates it would be ineffective in drying large quantities of algae since a large surface area and regular turnover is required. Thermal drying, though more expensive, typically employs a gas-fired heater to dry the algae to 80% solids regardless of the weather. Hence, in this analysis, thermal drying is used in the economic calculations.

1.6.3   Calculations and Parameters

1.6.3.1   HTL. The HTL data is for the Chlorella sorokiniana species (Chakraborty et al. 2013), but this data will be used in the model until data on the optimum polyculture is available. Ambient temperature is an important variable that can affect the yield of each product. Table 4 lists the composition of the solid residues after HTL of RBB.

Table 4. Ultimate analysis of solid residues after HTL at 250°C of RBB (Wei et al. 2015a).

Component	Dry weight %
C	33.2 ± 0.05
N	3.9 ± 0.08

1.6.3.2   *Pyrolysis.* Pyrolysis offers much of the same value as HTL does. The yields of biochar and their composition, shown in Table 5, are used to calculate the economic feasibility of performing pyrolysis on harvested algae.

Table 5. Characterization of RBB biomass and biochar product (Wei et al. 2015b).

		% dry basis
Analysis	RBB biomass	Biochar
C	36.1 ± 0.1	27.7 ± 0.4
N	—	5.6 ± 0.0

Once algae has been dried by a thermal dryer, its composition must be analyzed to determine its value as a feedstock for alternative fuels. Results of the bio-oil composition resulting from pyrolysis of two microalgae strains by Miao et al. (2004) are given in Table 6.

Table 6. Elemental compositions (wt%) of bio oils from pyrolysis of two algae strains (Miao et al. 2004).

Algae Strain	C (wt%)	N (wt%)
C. protothecoides	62.07	9.74
M. aeruginosa	60.99	9.83
Average	61.63	9.79

Pyrolysis of RBB was performed at the UI using a laboratory-scale auger reactor operating at 500°C. The RBB feedstock comprised of proteins, carbohydrates, phenolics, and ash were converted to bio-oil and biochar products. The yields of bio-oil and biochar were 28% and 46%, respectively (Wei et al. 2015b).

2. DAIRIEES MODEL

2.1 Description and Implementation

In the DAIRIEES model there are 18 different tabs, which are described in Table 7. The different worksheets in the model are grouped by function, with light blue tabs providing the user with basic information regarding the model, red tabs providing the results of calculations for the different processes, the green tabs presenting GHG and nutrient results, and purple tabs containing the original data from the laboratory experiments.

Table 7. Worksheet descriptions and interactions.

Sheet	Description	Inputs from
Process Flow Diagram	Illustrates the steps of the process	None
User Inputs	Determines the values that will be used by the model either input by the user or through a default value	-Input Selections -Fermenter -HTL, Pyrolysis, PHA -Algae Cultivation -AD data -Fermenter data
Fermenter	Provides process details and calculations on the fermenter	-User Inputs -Fermenter Data -Algae Cultivation
Anaerobic Digester	Provides process details and calculations on the anaerobic digester	-User Inputs -Fermenter -AD Data
PHA Reactor	Provides process details and calculations on the PHA reactor	-User Inputs -Fermenter - HTL, Pyrolysis, PHA
Algae Production	Provides process details and descriptions on algae production	-Anaerobic Digester -User Inputs
Pyrolysis	Provides process details and descriptions on hydrothermal liquefaction and pyrolysis	-Pyrolysis -Algae Cultivation -User Inputs
HTL	Provides process details and descriptions on hydrothermal liquefaction and pyrolysis	-HTL -Algae Cultivation -User Inputs
PHA	Provides process details and descriptions on hydrothermal liquefaction and pyrolysis	-PHA -Algae Cultivation -User Inputs

Table 7. (continued).

Sheet	Description	Inputs from
Results	Shows numerical calculations for processes – reactor inputs and outputs	-User Inputs -Fermenter - HTL, Pyrolysis, PHA -Anaerobic Digester -Algae Cultivation -Economic Analysis
Economic Analysis	Shows charts pertaining to the economic costs of the project	-User Inputs -Results
Economic Graphical Analysis	Describes the economics in a visual way.	-User Inputs -Results
GHG Analysis	Shows charts pertaining to the GHG usage/sequestration of the project	-Fermenter -Anaerobic Digester -User Inputs
Fermenter Data	Provides the data given to us for the fermenter	None
AD Data	Provides the data given to us for the anaerobic digester	None
PHA Data	Shows the only data used in the model	None
PHA Data Raw	Provides the raw data for the PHA reactor	None
Polyculture Data	Provides the data for the Algae cultivation system	None

The color coding for the headings on the data worksheets (purple tabs in the Excel model) is as follows: green for influent, blue for effluent, and red for calculations based upon the data.

To begin using the DAIRIEES model, under the User Inputs tab there is a section where users can customize inputs to predict the costs and earnings based on their specific dairy farm. The drop-down menu shown in Figure 17 provides different choices that are available for Algae Cultivation: OPR, PBRs, ATS, or No Algae Cultivation. The second drop-down menu lists the options for Biomass Treatment, which consist of selling algae, performing pyrolysis or HTL, or None (i.e., no treatment).

INPUT SELECTION		
Select the Algae Cultivation Parameters		
Algae Cultivation Type:	4. No Algae cultivation	
Biomass Treatment	4. None	
*Algae Productivity Rate Slider:		0 g/m²/day
*Algae Nitrogen Content Slider:		8.8 %
*note: If algae productivity rate or nitrogen content is unkown, leave the slider on "0" and estimates dependent on the algae cultivation type will be given		

Figure 17. User input selection choices.

Figure 18 shows a range of cells that are colored green where users can enter custom data. If no values are entered, a default value will be used by the model. The user has the opportunity to choose variables they would like to examine and manipulate one or more at a time to explore sensitivities. In the defaults section, the boxes colored green show the values that the user can affect by customization, whereas boxes colored red indicate fixed values. All worksheets have been purposely locked to prevent a user from inadvertently changing model parameters. To intentionally make changes, the sheets can be unlocked with the password "dairiees."

INPUTS			
Enter in custom values in column shaded green		value	unit
Length of Time	Year	2016	current year
	Time Period Considered (1-30 years)		years
Herd	Size of Herd		head of cattle
Wet Manure	Moisture Content		%
	Volatile Solids composition (% of TS)		% of TS
Dry Manure	Carbon		%
	Nitrogen		%
	Phosphorus		%
Engine Efficiency	Engine Efficiency		%
Individual Capital Costs	AD		$
	Algae Production System		$
	PHA Reactor		$
	Electrical System		$
	Pyrolysis		$
	HTL		$
	Thermal Drying		$
	Mechanical Dewatering		$
Annual Costs for integrated Systems	Integrated Annual Costs for AD and PHA reactor without Algae cultivation		$
	Integrated System Annual Cost Pyrolysis (thermal drying)		$
	Integrated System Annual Costs for HTL options		$
	Integrated Annual Costs for Selling Algae (thermal drying)		$
Project Financing	Interest Rate		%
	Percent of Capital Cost Needed for Down Payment		%
	Length of Loan		years
Product Market Value	Electricity		¢/kWh
	PHBV		$/kg
	Bedding (value on site)		$/cow
	Algae		$/kg
	Biochar		¢/kg
	Bio-oil		¢/kg
	Syngas		$/m^3
	Waste heat		$/head

Figure 18. Section to enter custom inputs.

The "Quick Economic Look" section of the User Inputs sheet shown in Figure 19 displays the years until project pays off, capital cost, annual operation and maintenance cost, annual net market value from system products, net present value, and internal rate of return.

Quick Economic Look	
value	description
5.05	Years until project pays off
$ 1,844,626	Capital cost
$ 110,726	Annual O&M cost
$ 654,512	Annual Net market value from system products
$9,987,210.89	Net Present Value after 30 years at 5% discount rate
34%	Internal Rate of Return

Figure 19. Summary of economic information.

The experimental data from UI was supplemented by literature data, where experimental data was unavailable or for scale-up purposes. The User Input worksheet contains references and hyperlinks to the data used in the model.

2.2 Model Parameters

2.2.1 Herd Size

The average herd size in the state of Idaho is 660 head of lactating cattle (Informa Economics 2013). This does not take into account any other cattle that may be present on the dairy, but not lactating, in contrast to some other estimates of herd size. A project undertaken by Minnesota project, bases its minimum herd size of 500 cows on an estimated capital cost of $563 per cow plus $320,864 for an AD system. After accounting for inflation, the 2016 cost is about $632 per cow plus $360,284 (Minnesota Project 2010). The minimum herd size for the DAIRIEES model is 500 cows, since the integrated manure treatment system will not be profitable at smaller scales (Klavon 2013). According to Informa Economics (2013), the average herd size in the U.S. is ~1500 dairy cows, and this value is used as the default value for the model.

2.2.2 Algal Biomass Productivities

The algae biomass productivity rates can be controlled by the user with the use of a slider bar. However, default values are used when the slider bar is set at 0. Table 8 gives the biomass productivity for each of the different types of algae cultivation.

Table 8. Biomass productivity rates for each algae cultivation system.

Input	Value (g/m^2/day)	Reference
Biomass Productivity (OPR)	13.2	Davis et al. (2012)
Biomass Productivity (PBR)	35.1	Silva et al. (2013)
Biomass Productivity (ATS)	22	Pizarro et al. (2006)

2.2.3 Process Efficiencies

Table 9 lists the efficiencies and constants that are used to determine how much of the theoretical yield will actual be given and used in the economic model.

Table 9. Constants and efficiencies used in Excel model.

Input	Value	Reference
Volatile fatty acid removal efficiency	95%	Davis et al. (2012)
Biogas capture efficiency	99%	None-assumption
Algae harvesting efficiency	85.5%	Davis et al. (2012)
Nitrogen recovery from AD	100%	Topper et al. (2006)
Phosphorus recovery from AD	100%	Topper et al. (2006)
Electricity generation uptime	270 day/yr	Mulbry et al. (2006)

2.2.4 Process Constants

Many of the process constants were already discussed in the calculation and parameters sections of each process and many of the default values were involved in formulas; however, those values that were not part of the formulas previously given are listed in Table 10.

Table 10. Default values used to calculate values used in the Excel model tabs of each system.

Input	Value/units	Reference
Fermenter		
Fermenter production uptime	270 day/yr	Mulbry et al. (2006)
Anaerobic Digestion		
Bedding needed	6.8 kg/cow	Tyson (2011)
%C_m of bedding	45%	Husfeldt (2012)
%N_m of bedding	1.4%	Husfeldt (2012)
AD production uptime	270 day/yr	Mulbry et al. (2006)
Algae Cultivation		
%C_m of algae	49%	Determined by polyculture data
%N_m of algae	8.8%	Pate et al. (2011)
%P_m of algae	1.22%	Pate et al. (2011)
Dewatered algae %$_m$ as moisture	80%	Bennion (2015)
%$_m$ of biogas as CO_2	41.8%	Dalrymple et al. (2013)
%$_m$ of biogas as CH_4	21.3%	Dalrymple et al. (2013)
Water evaporation	5 L/m^2/day	Davis et al. (2012)
Algae production uptime	270 day/yr	Mulbry et al. (2006)
Water depth	30 cm	Slade and Bauen (2013)
Pyrolysis		
%C_m of biochar	27.7%	Wei et al. (2015b)
%C_m of bio-oil	59.5%	Sadaka and Boateng (2009)
%N_m of RBB	5.2%	Wei et al. (2015b)
Bio-oil yield	29.3%	Bennion (2015)
Biochar yield	13.6%	Bennion (2015)
Biogas yield	22.9%	Bennion (2015)
HTL		
Bio-oil yield	37%	Bennion (2015)
Biogas yield	30%	Bennion (2015)
Solids yield	16%	Bennion (2015)

2.2.5 Baseline Emissions and Nutrient Release

2.2.5.1 GHG Emissions. GHG emissions are taken from a study at a commercial dairy located in southern Idaho with 10,800 milking, maternity and sick cows and 2200 dry cows and replacement heifers, for a total of 13,000 cows. For the baseline scenario, the GHG production for a dairy with an open lot, wastewater pond and compost is 5.2 metric tons of CO_2e cow^{-1} yr^{-1} (Leytem et al. 2011). Average emissions from the open lot were 179 kg CH_4 cow^{-1} yr^{-1} and 3.65 kg N_2O cow^{-1} yr^{-1}. The integrated manure treatment system described here would reduce the CH4 emissions to 9%. Because the U.S. EPA does not consider CO_2 production from manure storage systems to be anthropogenic, it would not typically be reported. Only the contributions from CH_4 and N_2O are included. GHG generation from enteric fermentation is not included.

It should be noted that worldwide GHG emission measurements vary widely (Owen and Silver 2014). This is due to variations in field measurements that are affected by herd characteristics (number of lactating versus total cows, average mass, animal diet), manure characteristics and handling practices (C and N content, volatile solid content, management schedule, storage configuration), and climate (temperature, humidity). The U.S. EPA (2011) estimates that implementation of anaerobic digesters can reduce the total CH_4 emissions from manure management at dairies by 85% (Owen and Silver 2014).

2.2.5.2 ***Nutrient Release from Lagoons.*** Lagoon systems are ponds used to store and treat parlor and free-stall flush water. Anaerobic lagoons utilize bacteria in the absence of oxygen and are deeper than aerobic lagoons. Aerobic lagoons require aeration and tend to be very shallow, requiring more land area. Manure enters at one end and the effluent is removed at the other. The lagoons operate at psychrophilic or ground temperatures. Consequently, the reaction rate is affected by seasonal variations in temperature. Since the reaction temperature is quite low, the rate of conversion of solids to gas is also low.

Anaerobic lagoons are commonly used because of their low cost and smaller land area requirement. The low cost is offset by the lower energy production and poor effluent quality. Without mixing, solids tend to settle to the bottom where decomposition occurs in a sludge bed. Little contact of bacteria with the bulk liquid occurs, resulting in very low solids conversion to gas. Solids may be screened and removed prior to entering the lagoon. A considerable amount of energy potential is lost with the removal of particulate solids. Periodically, the lagoons must be cleaned at considerable cost and accompanied by nuisance odors. Nitrogen losses from anaerobic lagoon releases are approximately 70 to 80%.

2.3   Economic Analysis

The ability to perform an economic analysis is useful to determine preliminary feasibility of the overall system. If this system were proposed for implementation, a more thorough economic analysis would be necessary to support the business plan. The green Economics Analysis tab contains the economic calculations. To change any of the values on this worksheet, the user can unlock the sheet and see how the results change using different values of the specified parameters.

In basic economics, there are two tests that are usually undertaken to determine if an investment is good or not. One test is Net Present Value (NPV) and the other is Internal Rate of Return (IRR). NPV is the amount of money an investor will get back over the duration of the investment based upon the discount rate. NPV is used to determine profitability while accounting for the discounted time value of the projected revenues. The discount rate is the interest rate that the Federal Reserve loans out to commercial banks. Currently, the discount rate is 1%. Usually, if this value is greater than zero, the investment is accepted; whereas, if it is equal to or below zero it is rejected. IRR calculations use the NPV to generate the IRR. The IRR is the rate of return that investors would receive if they invested their money in this project, rather than somewhere else. The IRR is when one determines the discount rate at which the NPV would equal zero, in other words the breakeven point. IRR is another tool that investors use to determine if an investment should be made. If the percentage is greater than 0%, then the investment is accepted; otherwise, if it is equal to or below 0%, it is rejected. Both NPV and IRR are necessary to determine if the investment should be made. On the Economic Analysis tab of the Excel model, the user is able to determine the NPV and IRR for every DAIRIEES process.

When monetary values are used in the model, they are normalized to 2016 monetary values by assuming a price increase based upon an estimate of 1.95% annual inflation. Analyses can be conducted for up to 30 years. Shorter time periods can be considered. The capital investment paid in full is the down payment of the capital cost in the first year and 10% of the capital cost every 10 years after that. The loan payment is the total capital cost minus the down payment.

The analysis assumes one payment annually. The payment pays down the interest that has accrued first and then pays down the principal. The next year's interest is calculated from the remaining principal of the previous year. Interest is assumed to be compounded once annually.

Operations and maintenance values and all product values are increased at approximate inflation rate of 1.195% per year to the year 2016. For the products produced, a certain portion is assumed to be used on the farm (a cost savings) and the rest are assumed to be sold (income). Both the cost savings and the income are included in the total value of the product. All bedding produced is assumed to be used on the farm. Electricity is assumed to be 60% used on farm and 40% sold (Lazarus and Rudstrom 2007). The percentage split is not changed by the user directly, but the user can specify the monthly amount of electricity and bedding used on the farm. These are converted to annual values. The amount sold for these products is the total amount minus the amount normally used on the farm annually. Some aspects of uncertainty in the data are the prices of PHBV and syngas, as widely varying prices were found for how much they cost to produce and how much they can be sold for.

Installing the integrated dairy manure treatment system involves a significant upfront capital cost. The costs and benefits of this system are weighed against the conventional treatment system of an anaerobic lagoon with the effluent spread on a field. For cost comparison purposes, it is assumed that the conventional treatment system is already paid for in full.

The payback period is defined as the amount of time it takes for the profits to outweigh the combined capital and annual costs. The payback period is defined as the total capital cost divided by the annual product market value. The internal rate of return is calculated the Excel function "IRR", which selects an array of values that reflect the net cumulative income/loss for every year minus the capital cost.

Total revenue over the loan period is calculated by the summing the product market values minus operating and maintenance costs, the lump sum capital cost and loan payments. For certain combinations of algal cultivation and processing methods, the project net present value will not be positive for the discount rate range specified in the model (1% to 15%).

2.3.1 Operational Period

The default start year for the model computations is 2016. All costs have been adjusted to 2016 U.S. dollars. Also, on the default dairy farm is comprised of 1500cows. The default financing period is 30 years.

2.3.2 Capital Costs

The cost for the anaerobic digester is for a two-stage AD, which means that the cost includes the cost for the fermenter. In our model, these two systems are separate and therefore costs would be a bit higher. However, 60% of the fermenter effluent is diverted to the PHA reactor. This means that the size needed for the anaerobic digester is 40% of the size assumed to be used by the formula provided by Lazarus and Rudstrom (2007). Therefore, we assume that the cost of separating these two processes is offset by the smaller anaerobic digester.

A formula for the cost of the PHA reactor was found (Roland-Holst et al. 2013). The formula is based upon a plant with the given cost scaled to 2016 dollars with a capacity of 0.0567 metric ton. A multiplier of 1.5 is applied to avoid underestimating the capital cost of the system. HTL, pyrolysis, and PHA capital costs were calculated similarly. Different equations are used for each of the different algae cultivation systems. The formulas for each are listed in Table 11, along with the corresponding reference.

Table 11. Formulas used to determine capital cost of each system.

Process	Reference	
$Anaerobic\ Digester = (\$632 * \#\ of\ cows) + 360{,}284$	Minnesota Project (2010)	(37)
$PHA\ Reactor = 1.5 * \$6{,}460{,}675 * \left(\dfrac{reactor\ capacity\ MT}{0.0567\ MT}\right)^{0.7}$	Roland-Holst et al. (2013)	(38)
$Pyrolysis\ Reactor = \$124{,}187{,}678 \left(\dfrac{reactor\ capacity\ MT}{2000\ MT}\right)^{0.7}$	Wright et al. (2010)	(39)
$HTL\ Reactor = \$230{,}187{,}871 \left(\dfrac{reactor\ capacity\ MT}{2000\ MT}\right)^{0.7}$	Ou et al. (2015)	(40)
$ACS\ (OPR) = \$11.18 * \text{m}^2$	Huntley et al. (2007)	(41)
$ACS\ (PBR) = \$131.05 * \text{m}^2$	Hallenbeck et al. (2002)	(42)
$ACS\ (ATS) = (\$1{,}634{,}500 * 1.0195^{10}) * \left(\dfrac{\#\ of\ cows}{1000}\right)^{0.7}$	Pizarro et al. (2006)	(43)

2.3.3 Annual Costs

Many of the annual costs are estimated based upon a percentage of the capital cost which can be seen in Table 12. This percentage is found from dividing the annual cost by the capital cost in various technoeconomic analyses. Feedstock is a common contributor to annual costs that does not apply to our model and so it has been eliminated from the calculations.

Table 12. Formulas used to determine annual cost of each system.

Description	Formula	Reference	
AD/Fermenter	7% of capital cost	USDA NRCS (2007)	(44)
PHA Reactor	19% of capital cost	Roland-Holst et al. (2013)	(45)
Pyrolysis Reactor	30% of capital cost	Thilakaratne et al. (2014)	(46)
HTL Reactor	55% of capital cost	Ou et al. (2015)	(47)
ACS (OPR)	9% of capital cost	Richardson et al. (2012)	(48)
ACS (PBR)	5% of capital cost	Richardson et al. (2012)	(49)
ACS (ATS)	$ATS = 778 * \#\ of\ cows$	Mulbry et al. (2008)	(50)

2.3.4 Project Financing and Economic Constants

Default values related to taking out a loan include interest rate, percent of capital cost needed for down payment and length of loan. Every cost value received was inflated to 2016 dollars through the formula:

$$2016\ dollars = original\ cost * (1.0195)^{(2016 - source\ of\ info\ year)} \tag{44}$$

where an inflation rate of 1.95%.was derived by averaging the inflation rates over the past 10 years (Federal Reserve Bank 2014). In the Excel user model, all numbers have been brought up to the year 2016 using the formula above. Table 13 lists the default project values that were used to compute project financing. Many of these values will vary by locality and by size of farm.

Table 13. Project financing and economic default values.

Description	Value/units	Reference
Interest Rate	3.9%	USDA FSA (2014) Farm Ownership - Direct Loan Pricing Valid for loans up to $300,000.00 for "farm improvements"
Percent of Capital Cost Needed for Down Payment	15%	USDA (2015b)
Length of Loan	30 years	None-assumption
Annual Inflation Rate	1.95%	The Federal Reserve Bank of Minneapolis (2014)
Capital Cost Needed to Reinvest Every 10 years	10%	The Federal Reserve Bank of Minneapolis (2014)
Portion of reinvestments paid in full	100%	None-assumption

2.3.5   Product Market Values

Values for the products produced by the integrated manure treatment system are listed in Table 14. Product values were derived from literature sources, but are dependent upon market conditions.

Table 14. Default values of system products.

Input	Value/Units	Reference
Electricity (U.S. average)	6.91 ¢/kWh	U.S. Energy Information Administration (2016)
PHBV	21.10 $/kg	Sigma Aldrich (2016)
Syngas	0.1 $/ m^3	LNG Industry (2015)
Bedding (value on site)	59.11 $/cow	Minnesota Project (2010)
Algae	0.182 $/kg	Bryant et al. (2012)
Biochar	30.87 ¢/kg	Goteti (2010)
Bio-oil	40.59 ¢/kg	Goteti (2010)
Waste Heat	11.77 $/cow	EPA (1999)
Nitrogen trading credit	7.01 $/kg	Pennsylvania General Assembly (2013)
Phosphorus trading credit	13.34 $/kg	Passero et al. (2015)

3.   GLOSSARY

Anaerobic. Reactions that take place without oxygen.

Anaerobic digester (AD). A reactor that uses prefermented manure to produce biogas.

Biogas. A combination of carbon dioxide and methane produced by a biological process.

Bioplastic. A plastic produced biologically, for example by bacteria.

Carbon sequestration. The process of effectively "tying up" carbon so it cannot be readily emitted back into the atmosphere.

Fermenter. A reactor that uses raw manure to produce volatile fatty acids via bacteria.

Organic loading rate (OLR). The amount of material added to a reactor for a given volume and amount of time.

PHA reactor. A reactor that uses volatile fatty acids to produce compounds that are precursors to bioplastics.

Photobioreactor (PBR). A reactor where algae are cultivated within containers.

Poly3hydroxyalkanoates (PHA). A group of compounds used to make bioplastics.

Polyhydroxybutyrate (PHB). A type of PHA that forms a brittle plastic; it is more valuable when combined with PHV to create PHBV.

Polyhydroxybutyrate-Co-Valerate (PHBV). A polymer of two types of PHAs that is the desired end product of the PHA reactor; it is a form of bioplastic that has potential for commercial uses.

Polyhydroxyvalerate (PHV). A type of PHA that is combined with PHB to create PHBV.

Solids residence time (SRT). The time it takes for all the material in the reactor to cycle through.

Total solids (TS). Weight of residue left in the vessel after evaporation of liquid from a sample and subsequent drying in an oven at 103°C to 105°C.

Volatile fatty acid (VFA). A class of compounds produced by fermentation.

Volatile solids (VS). Weight of a sample after it is heated to dryness at 550°C.

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Appendix A

Experimental Data Variables List

Variable	Units	Definition
Ferm_Operational_Date	—	Fermenter date on which operational data was collected
Ferm_SRT_HRT	days	Fermenter Solids Residence Time, Hydraulic Residence Time = The time, on average, that the biomass and liquid resides within a bioreactor (typically measured as days). SRT and HRT are operational control variables.
Ferm_OLR	gVS/L-d	Fermenter Organic Loading Rate = The quantity of organic matter, measured as VS, that a bioreactor receives on both a volumetric and time basis.
VS	g	Volatile Solids = Measurement of organic matter - solids that volatilize at 550 deg C in a muffle furnace
TS	g	Total Solids = total mass of dry solids
Ferm_Influent_Volume	L	Fermenter Influent Total volume of slurry added to a reactor per operational cycle
Ferm_Operating_Temperature	C	Fermenter Measured operating temperature of the reactor.
FI_solids_TIN	g	Fermenter Influent mass of the weighing dish used to determine solids (TS, VS) masses
FI_solids_sample	g	Fermenter Influent mass of the sample added from the reactor to the TIN
FI_solids_dried	g	Fermenter Influent mass of the dried sample
FI_solids_muffled	g	Fermenter Influent residual mass of solids following volatilization at 550 deg C
FI_TS%	%	Fermenter Influent % dry solids within the reactor
FI_VS%	%	Fermenter Influent % volatile solids within the reactor
FI_Total_Slurry_Mass	g	Fermenter Influent total wet mass of slurry added to the reactor per operational cycle
FI_solids_TOC	g C	Fermenter Influent total organic carbon within the dry solids, measured as grams of carbon
FI_solids_TOC_conc	g/g	Fermenter Influent concentration of TOC within the dry solids sample
FI_soluble_TOC_conc	g/g	Fermenter Influent concentration of TOC within the liquid sample
FI_soluble_TOC	g C	Fermenter Influent total organic carbon within the liquid, measured as grams of carbon
FI_Hac_mg_L	mg/L	Fermenter Influent acetic acid, mg/L

Variable	Units	Definition
FI_Hac_mgCOD_L	mgCOD/L	Fermenter Influent acetic acid, COD basis
FI_Hac_gC	gC	Fermenter Influent acetic acid, gC
FI_Hpr_mg_L	mg/L	Fermenter Influent propionic acid mg/L
FI_Hpr_mgCOD_L	mgCOD/L	Fermenter Influent propionic acid, COD basis
FI_Hpr_gC	gC	Fermenter Influent propionic acid, gC
FI_Hbu_mg_L	mg/L	Fermenter Influent butyric acid, mg/L
FI_Hbu_mgCOD_L	mgCOD/L	Fermenter Influent butyric acid, COD basis
FI_Hbu_gC	gC	Fermenter Influent butyric acid, gC
FI_HiBu_mg_L	mg/L	Fermenter Influent iso-butyric acid, mg/L
FI_HiBu_mgCOD_L	mgCOD/L	Fermenter Influent iso-butyric acid, COD basis
FI_HiBu_gC	gC	Fermenter Influent iso-butyric acid, gC
FI_Hva_mg_L	mg/L	Fermenter Influent valeric acid, mg/L
FI_Hva_mgCOD_L	mgCOD/L	Fermenter Influent valeric acid, COD basis
FI_Hva_gC	gC	Fermenter Influent valeric acid, gC
FI_HiVa_mg_L	mg/L	Fermenter Influent iso-valeric acid, mg/L
FI_HiVa_mgCOD_L	mgCOD/L	Fermenter Influent iso-valeric acid, COD basis
FI_HiVa_gC	gC	Fermenter Influent iso-valeric acid, gC
FI_Hca_mg_L	mg/L	Fermenter Influent caproic acid, mg/L
FI_Hca_mgCOD_L	mgCOD/L	Fermenter Influent caproic acid, COD basis
FI_Hca_gC	gC	Fermenter Influent caproic acid, gC
FI_EtOH_mg_L	mg/L	Fermenter Influent ethanol, mg/L
FI_EtOH_mgCOD_L	mgCOD/L	Fermenter Influent ethanol, COD basis
FI_EtOH_gC	gC	Fermenter Influent ethanol, gC
FE_solids_TIN	g	Fermenter Effluent mass of the weighing dish used to determine solids (TS, VS) masses
FE_solids_sample	g	Fermenter Effluent mass of the sample added from the reactor to the TIN
FE_solids_dried	g	Fermenter Effluent mass of the dried sample
FE_solids_muffled	g	Fermenter Effluent residual mass of solids following volatilization at 550 deg C
FE_TS%	%	Fermenter Effluent % dry solids within the reactor
FE_VS%	%	Fermenter Effluent % volatile solids within the reactor
FE_Total_Slurry_Mass	g	Fermenter Effluent total wet mass of slurry added to the reactor per operational cycle
FE_solids_TOC	g C	Fermenter Effluent total organic carbon within the dry solids, measured as grams of carbon
FE_solids_TOC_conc	g/g	Fermenter Effluent concentration of TOC within the dry solids sample
FE_soluble_TOC_conc	g/g	Fermenter Effluent concentration of TOC within the liquid sample

Variable	Units	Definition
FE_soluble_TOC	g C	Fermenter Effluent total organic carbon within the liquid, measured as grams of carbon
FE_Hac_mg_L	mg/L	Fermenter Effluent acetic acid, mg/L
FE_Hac_mgCOD_L	mgCOD/L	Fermenter Effluent acetic acid, COD basis
FE_Hac_gC	gC	Fermenter Effluent acetic acid, gC
FE_Hpr_mg_L	mg/L	Fermenter Effluent propionic acid mg/L
FE_Hpr_mgCOD_L	mgCOD/L	Fermenter Effluent propionic acid, COD basis
FE_Hpr_gC	gC	Fermenter Effluent propionic acid, gC
FE_Hbu_mg_L	mg/L	Fermenter Effluent butyric acid, mg/L
FE_Hbu_mgCOD_L	mgCOD/L	Fermenter Effluent butyric acid, COD basis
FE_Hbu_gC	gC	Fermenter Effluent butyric acid, gC
FE_HiBu_mg_L	mg/L	Fermenter Effluent iso-butyric acid, mg/L
FE_HiBu_mgCOD_L	mgCOD/L	Fermenter Effluent iso-butyric acid, COD basis
FE_HiBu_gC	gC	Fermenter Effluent iso-butyric acid, gC
FE_Hva_mg_L	mg/L	Fermenter Effluent valeric acid, mg/L
FE_Hva_mgCOD_L	mgCOD/L	Fermenter Effluent valeric acid, COD basis
FE_Hva_gC	gC	Fermenter Effluent valeric acid, gC
FE_HiVa_mg_L	mg/L	Fermenter Effluent iso-valeric acid, mg/L
FE_HiVa_mgCOD_L	mgCOD/L	Fermenter Effluent iso-valeric acid, COD basis
FE_HiVa_gC	gC	Fermenter Effluent iso-valeric acid, gC
FE_Hca_mg_L	mg/L	Fermenter Effluent caproic acid, mg/L
FE_Hca_mgCOD_L	mgCOD/L	Fermenter Effluent caproic acid, COD basis
FE_Hca_gC	gC	Fermenter Effluent caproic acid, gC
FE_EtOH_mg_L	mg/L	Fermenter Effluent ethanol, mg/L
FE_EtOH_mgCOD_L	mgCOD/L	Fermenter Effluent ethanol, COD basis
FE_EtOH_gC	gC	Fermenter Effluent ethanol, gC
FE_Biogas_L	L	Fermenter Effluent biogas
FE_CO2_L	L	Fermenter Effluent carbon dioxide, L
FE_CO2_gC	gC	Fermenter Effluent carbon dioxide, gC
FE_CH4_L	L	Fermenter Effluent methane, L
FE_CH4_gC	gC	Fermenter Effluent methane, gC
AD_Operational_Date	—	Anaerobic Digester date on which operational data was collected
AD_SRT_HRT	days	Anaerobic Digester Solids Residence Time, Hydraulic Residence Time = The time, on average, that the biomass and liquid resides within a bioreactor (typically measured as days). SRT and HRT are operational control variables.

Variable	Units	Definition
AD_OLR	gVS/L-d	Anaerobic Digester Organic Loading Rate = The quantity of organic matter, measured as VS, that a bioreactor receives on both a volumetric and time basis.
AD_Influent_Volume	L	Anaerobic Digester Influent Total volume of slurry added to a reactor per operational cycle
AD_Operating_Temperature	C	Anaerobic Digester Measured operating temperature of the reactor.
ADi_solids_TIN	g	Anaerobic Digester Influent mass of the weighing dish used to determine solids (TS, VS) masses
ADi_solids_sample	g	Anaerobic Digester Influent mass of the sample added from the reactor to the TIN
ADi_solids_dried	g	Anaerobic Digester Influent mass of the dried sample
ADi_solids_muffled	g	Anaerobic Digester Influent residual mass of solids following volatilization at 550 deg C
ADi_TS%	%	Anaerobic Digester Influent % dry solids within the reactor
ADi_VS%	%	Anaerobic Digester Influent % volatile solids within the reactor
ADi_Total_Slurry_Mass	g	Anaerobic Digester Influent total wet mass of slurry added to the reactor per operational cycle
ADi_solids_TOC	g C	Anaerobic Digester Influent total organic carbon within the dry solids, measured as grams of carbon
ADi_solids_TOC_conc	g/g	Anaerobic Digester Influent concentration of TOC within the dry solids sample
ADi_soluble_TOC_conc	g/g	Anaerobic Digester Influent concentration of TOC within the liquid sample
ADi_soluble_TOC	g C	Anaerobic Digester Influent total organic carbon within the liquid, measured as grams of carbon
ADi_Hac_mg_L	mg/L	Anaerobic Digester Influent acetic acid, mg/L
ADi_Hac_mgCOD_L	mgCOD/L	Anaerobic Digester Influent acetic acid, COD basis
ADi_Hac_gC	gC	Anaerobic Digester Influent acetic acid, gC
ADi_Hpr_mg_L	mg/L	Anaerobic Digester Influent propionic acid mg/L
ADi_Hpr_mgCOD_L	mgCOD/L	Anaerobic Digester Influent propionic acid, COD basis
ADi_Hpr_gC	gC	Anaerobic Digester Influent propionic acid, gC
ADi_Hbu_mg_L	mg/L	Anaerobic Digester Influent butyric acid, mg/L
ADi_Hbu_mgCOD_L	mgCOD/L	Anaerobic Digester Influent butyric acid, COD basis
ADi_Hbu_gC	gC	Anaerobic Digester Influent butyric acid, gC
ADi_HiBu_mg_L	mg/L	Anaerobic Digester Influent iso-butyric acid, mg/L
ADi_HiBu_mgCOD_L	mgCOD/L	Anaerobic Digester Influent iso-butyric acid, COD basis

Variable	Units	Definition
ADi_HiBu_gC	gC	Anaerobic Digester Influent iso-butyric acid, gC
ADi_Hva_mg_L	mg/L	Anaerobic Digester Influent valeric acid, mg/L
ADi_Hva_mgCOD_L	mgCOD/L	Anaerobic Digester Influent valeric acid, COD basis
ADi_Hva_gC	gC	Anaerobic Digester Influent valeric acid, gC
ADi_HiVa_mg_L	mg/L	Anaerobic Digester Influent iso-valeric acid, mg/L
ADi_HiVa_mgCOD_L	mgCOD/L	Anaerobic Digester Influent iso-valeric acid, COD basis
ADi_HiVa_gC	gC	Anaerobic Digester Influent iso-valeric acid, gC
ADi_Hca_mg_L	mg/L	Anaerobic Digester Influent caproic acid, mg/L
ADi_Hca_mgCOD_L	mgCOD/L	Anaerobic Digester Influent caproic acid, COD basis
ADi_Hca_gC	gC	Anaerobic Digester Influent caproic acid, gC
ADi_EtOH_mg_L	mg/L	Anaerobic Digester Influent ethanol, mg/L
ADi_EtOH_mgCOD_L	mgCOD/L	Anaerobic Digester Influent ethanol, COD basis
ADi_EtOH_gC	gC	Anaerobic Digester Influent ethanol, gC
ADe_solids_TIN	g	Anaerobic Digester Effluent mass of the weighing dish used to determine solids (TS, VS) masses
ADe_solids_sample	g	Anaerobic Digester Effluent mass of the sample added from the reactor to the TIN
ADe_solids_dried	g	Anaerobic Digester Effluent mass of the dried sample
ADe_solids_muffled	g	Anaerobic Digester Effluent residual mass of solids following volatilization at 550 deg C
ADe_TS%	%	Anaerobic Digester Effluent % dry solids within the reactor
ADe_VS%	%	Anaerobic Digester Effluent % volatile solids within the reactor
ADe_Total_Slurry_Mass	g	Anaerobic Digester Effluent total wet mass of slurry added to the reactor per operational cycle
ADe_solids_TOC	g C	Anaerobic Digester Effluent total organic carbon within the dry solids, measured as grams of carbon
ADe_solids_TOC_conc	g/g	Anaerobic Digester Effluent concentration of TOC within the dry solids sample
ADe_soluble_TOC_conc	g/g	Anaerobic Digester Effluent concentration of TOC within the liquid sample
ADe_soluble_TOC	g C	Anaerobic Digester Effluent total organic carbon within the liquid, measured as grams of carbon
ADe_Hac_mg_L	mg/L	Anaerobic Digester Effluent acetic acid, mg/L
ADe_Hac_mgCOD_L	mgCOD/L	Anaerobic Digester Effluent acetic acid, COD basis
ADe_Hac_gC	gC	Anaerobic Digester Effluent acetic acid, gC
ADe_Hpr_mg_L	mg/L	Anaerobic Digester Effluent propionic acid mg/L
ADe_Hpr_mgCOD_L	mgCOD/L	Anaerobic Digester Effluent propionic acid, COD basis

Variable	Units	Definition
ADe_Hpr_gC	gC	Anaerobic Digester Effluent propionic acid, gC
ADe_Hbu_mg_L	mg/L	Anaerobic Digester Effluent butyric acid, mg/L
ADe_Hbu_mgCOD_L	mgCOD/L	Anaerobic Digester Effluent butyric acid, COD basis
ADe_Hbu_gC	gC	Anaerobic Digester Effluent butyric acid, gC
ADe_HiBu_mg_L	mg/L	Anaerobic Digester Effluent iso-butyric acid, mg/L
ADe_HiBu_mgCOD_L	mgCOD/L	Anaerobic Digester Effluent iso-butyric acid, COD basis
ADe_HiBu_gC	gC	Anaerobic Digester Effluent iso-butyric acid, gC
ADe_Hva_mg_L	mg/L	Anaerobic Digester Effluent valeric acid, mg/L
ADe_Hva_mgCOD_L	mgCOD/L	Anaerobic Digester Effluent valeric acid, COD basis
ADe_Hva_gC	gC	Anaerobic Digester Effluent valeric acid, gC
ADe_HiVa_mg_L	mg/L	Anaerobic Digester Effluent iso-valeric acid, mg/L
ADe_HiVa_mgCOD_L	mgCOD/L	Anaerobic Digester Effluent iso-valeric acid, COD basis
ADe_HiVa_gC	gC	Anaerobic Digester Effluent iso-valeric acid, gC
ADe_Hca_mg_L	mg/L	Anaerobic Digester Effluent caproic acid, mg/L
ADe_Hca_mgCOD_L	mgCOD/L	Anaerobic Digester Effluent caproic acid, COD basis
ADe_Hca_gC	gC	Anaerobic Digester Effluent caproic acid, gC
ADe_EtOH_mg_L	mg/L	Anaerobic Digester Effluent ethanol, mg/L
ADe_EtOH_mgCOD_L	mgCOD/L	Anaerobic Digester Effluent ethanol, COD basis
ADe_EtOH_gC	gC	Anaerobic Digester Effluent ethanol, gC
ADe_Biogas_L	L	Anaerobic Digester Effluent biogas
ADe_CO2_L	L	Anaerobic Digester Effluent carbon dioxide, L
ADe_CO2_gC	gC	Anaerobic Digester Effluent carbon dioxide, gC
ADe_CH4_L	L	Anaerobic Digester Effluent methane, L
ADe_CH4_gC	gC	Anaerobic Digester Effluent methane, gC
PHA_Operational_Date		PHA date on which operational data was collected
PHA_SRT	d	PHA solids residence time
PHA_HRT	h	PHA hydraulic residence time
PHA_Operating_Temperature	C	PHA operating temperature
PHAi_solids_filter+TIN	g	PHA influent filter + weighing dish mass
PHAi_solids_sample	g	PHA influent filter + weighing dish + sample mass
PHAi_solids_dried	g	PHA influent solids mass
PHAi_solids_muffled	g	PHA influent residual muffled solids mass
PHAi_MLSS	g/L	PHA influent MLSS
PHAi_MLVSS	g/L	PHA influent MLVSS
PHAi_solids_TOC	g	PHA influent solids total organic carbon
PHAi_solids_TOC_conc	g/L	PHA influent solids total organic carbon concentration

Variable	Units	Definition
PHAi_soluble_TOC_conc	g/L	PHA influent soluble total organic carbon concentration
PHAi_soluble_TOC	g	PHA influent soluble total organic carbon
PHAi_Hac_mg_L	mg/L	PHA influent acetic acid, mg/L
PHAi_Hac_mgCOD_L	mgCOD/L	PHA influent acetic acid, COD basis
PHAi_Hac_gC	gC	PHA Influent acetic acid, gC
PHAi_Hpr_mg_L	mg/L	PHA Influent propionic acid mg/L
PHAi_Hpr_mgCOD_L	mgCOD/L	PHA Influent propionic acid, COD basis
PHAi_Hpr_gC	gC	PHA Influent propionic acid, gC
PHAi_Hbu_mg_L	mg/L	PHA Influent butyric acid, mg/L
PHAi_Hbu_mgCOD_L	mgCOD/L	PHA Influent butyric acid, COD basis
PHAi_Hbu_gC	gC	PHA Influent butyric acid, gC
PHAi_HiBu_mg_L	mg/L	PHA Influent iso-butyric acid, mg/L
PHAi_HiBu_mgCOD_L	mgCOD/L	PHA Influent iso-butyric acid, COD basis
PHAi_HiBu_gC	gC	PHA Influent iso-butyric acid, gC
PHAi_Hva_mg_L	mg/L	PHA Influent valeric acid, mg/L
PHAi_Hva_mgCOD_L	mgCOD/L	PHA Influent valeric acid, COD basis
PHAi_Hva_gC	gC	PHA Influent valeric acid, gC
PHAi_HiVa_mg_L	mg/L	PHA Influent iso-valeric acid, mg/L
PHAi_HiVa_mgCOD_L	mgCOD/L	PHA Influent iso-valeric acid, COD basis
PHAi_HiVa_gC	gC	PHA Influent iso-valeric acid, gC
PHAi_Hca_mg_L	mg/L	PHA Influent caproic acid, mg/L
PHAi_Hca_mgCOD_L	mgCOD/L	PHA Influent caproic acid, COD basis
PHAi_Hca_gC	gC	PHA Influent caproic acid, gC
PHAi_EtOH_mg_L	mg/L	PHA Influent ethanol, mg/L
PHAi_EtOH_mgCOD_L	mgCOD/L	PHA Influent ethanol, COD basis
PHAi_EtOH_gC	gC	PHA Influent ethanol, gC
PHAe_solids_filter+TIN	g	PHA effluent filter + weighing dish mass
PHAe_solids_sample	g	PHA effluent filter + weighing dish + sample mass
PHAe_solids_dried	g	PHA effluent solids mass
PHAe_solids_muffled	g	PHA effluent residual muffled solids mass
PHAe_MLSS	g/L	PHA effluent mixed liquor suspended solids (MLSS)
PHAe_MLVSS	g/L	PHA effluent mixed liquor volatile suspended solids (MLVSS)
PHAe_solids_TOC	g	PHA effluent solids total organic carbon
PHAe_solids_TOC_conc	g/L	PHA effluent solids total organic carbon concentration
PHAe_soluble_TOC_conc	g/L	PHA effluent soluble total organic carbon concentration
PHAe_soluble_TOC	g	PHA effluent soluble total organic carbon

Variable	Units	Definition
PHAe_Hac_mg_L	mg/L	PHA effluent acetic acid, mg/L
PHAe_Hac_mgCOD_L	mgCOD/L	PHA effluent acetic acid, COD basis
PHAe_Hac_gC	gC	PHA effluent acetic acid, gC
PHAe_Hpr_mg_L	mg/L	PHA effluent propionic acid mg/L
PHAe_Hpr_mgCOD_L	mgCOD/L	PHA effluent propionic acid, COD basis
PHAe_Hpr_gC	gC	PHA effluent propionic acid, gC
PHAe_Hbu_mg_L	mg/L	PHA effluent butyric acid, mg/L
PHAe_Hbu_mgCOD_L	mgCOD/L	PHA effluent butyric acid, COD basis
PHAe_Hbu_gC	gC	PHA effluent butyric acid, gC
PHAe_HiBu_mg_L	mg/L	PHA effluent iso-butyric acid, mg/L
PHAe_HiBu_mgCOD_L	mgCOD/L	PHA effluent iso-butyric acid, COD basis
PHAe_HiBu_gC	gC	PHA effluent iso-butyric acid, gC
PHAe_Hva_mg_L	mg/L	PHA effluent valeric acid, mg/L
PHAe_Hva_mgCOD_L	mgCOD/L	PHA effluent valeric acid, COD basis
PHAe_Hva_gC	gC	PHA effluent valeric acid, gC
PHAe_HiVa_mg_L	mg/L	PHA effluent iso-valeric acid, mg/L
PHAe_HiVa_mgCOD_L	mgCOD/L	PHA effluent iso-valeric acid, COD basis
PHAe_HiVa_gC	gC	PHA effluent iso-valeric acid, gC
PHAe_Hca_mg_L	mg/L	PHA effluent caproic acid, mg/L
PHAe_Hca_mgCOD_L	mgCOD/L	PHA effluent caproic acid, COD basis
PHAe_Hca_gC	gC	PHA effluent caproic acid, gC
PHAe_EtOH_mg_L	mg/L	PHA effluent ethanol, mg/L
PHAe_EtOH_mgCOD_L	mgCOD/L	PHA effluent ethanol, COD basis
PHAe_EtOH_gC	gC	PHA effluent ethanol, gC
PHAe_Biogas_L	L	PHA Effluent biogas
PHAe_CO2_L	L	PHA Effluent carbon dioxide, L
PHAe_CO2_gC	gC	PHA Effluent carbon dioxide, gC
PHAe_CH4_L	L	PHA Effluent methane, L
PHAe_CH4_gC	gC	PHA Effluent methane, gC
TOC	—	Total Organic Carbon
Effluent type	AD or PHA	Type of effluent used to create the algal cultivation medium
Effluent concentration	percent	Concentration of anaerobic digester or PHA reactor effluent used as a nutrient source for algal cultivation
Species	species name, wild type, or consortia name	Species name indicates a known species that was used as an inoculum, wild type indicates a consortia of algae enriched from a municipal wastewater treatment facility, consortia indicates an undefined or partially defined consortia of algal species

Variable	Units	Definition
Treatment	numerical	Effluent type/concentration and polyculture consortium
Dry weight	grams per liter	Algal biomass yield produced over the course of a batch experiment measured as dry weight using standard methods