Modeling of Biogas Formation and Utilization using Aspen Plus

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Kurzfassung

Im Rahmen dieser Arbeit wurde ein Modell zur Beschreibung der Bildung und Nutzung von Biogas mittels der Simulations-Software Aspen Plus erstellt. Die drei verschiedenen Konzepte zur Modellierung der Biogasbildung basieren auf Ansätzen aus der Literatur - dem Chemischen Sauerstoffbedarf (CSB), der Busswell-Gleichung und stöchiometrischen Reaktionsgleichungen. Die Biogasnutzung baut sich ebenfalls aus drei Berechnungsmöglichkeiten - einem Gasmotor-Modell, einer adiabaten Verbrennung und einer Berechnungroute, an welche die Aufbereitung des Biogases angeschlossen werden kann - auf.

Ziel der Modellentwicklung ist eine grobe Abschätzung der Sinnhaftigkeit einer Integration eines Biogasprozesses zum Zweck der Wärmeintegration. Das Modell betrachtet keine wirtschaftlichen Faktoren und berechnet den theoretisch maximal möglichen Biogas-, Strom- und Wärmeoutput aus verschiedenen Substraten. Eine Validierung des Modells erfolgt über den Vergleich mit Literaturdaten, der Abtastung von potentiellen Grenzen des Modells durch den Einsatz verschiedener Substrate, sowie dem Vergleich der Ergebnisse mit denen eines Modells aus der Literatur.

Abstract

A flexible model for biogas generation and utilization was developed using simulation tool Aspen Plus. It is based on two interacting submodels, describing the process of biogas generation via anaerobic digestion and biogas utilization. Three possible approaches to model biogas production have been employed - calculation via chemical oxygen demand (COD), calculation according to Buswell's equation, and implementing stoichiometric reactions. For purpose of biogas utilization three paths are included - combined heat and power generation (CHP) by means of a gas engine, a second path which could further be used for biogas upgrading, and adiabatic combustion of generated biogas.

The model can be used for a rough estimate whether integration of a biogas process with systems processing organic waste material streams is beneficial or not. An economic approach is no target of this work. This model simply calculates how much biogas can maximal be obtaind out of a specific organic feedstock and how much heat and power can be generated by the use of a gas engine or a simple combustion process. Because of its flexible and simple configuration, the model can be adapted to various types of substrate with respect to model setup. The difference between the calculation methods used have been discussed. The model was evaluated in terms of comparing with results from literature, comparing the results of the model with results of a model from literature, and sensing potential limits by appling several kinds of input data.

Chapter 1

Introduction

Environmental and resource conservation are increasingly interesting at a time in which natural resources are scarce, since they are limited determined by nature. The topic 'waste management' is closely tied to responsibility for resources and the environment. Guiding principle for the treatment of waste and material flows, written in the Waste Management act [BMLFUW, 2006], implies that avoidance is preferred over material and energy recovery, which is preferred over disposal of waste. Material recovery describes the principle of waste management, which present work is subject to. In making use of the material recovery task, engineering processes are extended and optimized in order to achieve greater material utilization rates. This optimization also provides economic benefits, since disposal costs can be avoided and heat and power can be generated.

However, process optimization necessitates additional investment costs which have to be balanced against financial savings. Waste is a valuable raw material which is, among other possibilites, convertible to useful energy carriers/forms such as biogas, heat, and electrical energy which are high-quality energy sources [Kirchmeyr and Anzengruber, 2008] and [Helwig et al., 2002]. Since present thesis deals exclusively with renewable organic raw materials, generated energy in the form of heat and power is CO_2-neutral which points out an additional advantage of the 'waste to energy' concept. In order to prevent emissions of greenhouse gases (GHG) it is important to apply optimal recycling measures. Anaerobic digestion provides a great opportunity for converting waste material to a valuable energy carrier, since biogas can be produced from nearly any kind of biological feedstock [Holm-Nielsen et al., 2009]. In order to achive a responsible management of natural resources and environment, attainment of optimal material utilization rates of (natural) resources cannot be avoided.

The intention of this thesis is to present a simple and flexible model for anaerobic digestion in order to generate biogas, and for biogas utilization. In this context, flexible is meant in terms of the variety of the input data. Most prior research has concentrated on building comprehensive models of anaerobic digestion, and little attention has been paid to coupled physical models for biogas generation and utilization. Comprehensive models are sophisticated since an increasing degree of detail of modeling increases needed input information [Pröll, 2013]. However, in this way also a higher extent of output information is obtained. Contrary to sophisticated models, simple models are based on a manageable quantity of data.

[Buswell and Müller, 1952] and [Baserga, 1998] are good examples for simple, time-independent ways to calculate biogas production [Gerber and Span, 2008]. This models are based on a simple approach, which only take the elemental composition [Buswell and Müller, 1952] or the class of substrate [Baserga, 1998] into account in order to predict quantitative biogas yields. Comprehensive biogas models are best exemplified by [Batstone et al., 2002], and [Mather, 1986]. The model presented in [Batstone et al., 2002] tries to be as widely applicable as possible. It is limited to the main relevant processes occouring during anaerobic digestion, in order to make it more applicable. However, the amount of required input data is extensive since equillibrium and kinetic processes are considered. The work of [Mather, 1986] describes a mathematical model of anaerobic digestionon on the basis of laboratory tests with acidic acid. Table 1.0.1 indicates main differences between simple and comprehensive physical models of anaerobic digestion according to [Gerber and Span, 2008]. Comprehensive models usually contain unknown parameters which have to be estimated from experimental data. Also, models published in literature do not supply a clear procedure for modeling anaerobic digestion. Published literature data rarely show thourogh analysis of paramater accuarcy, which severely restricts application of published information [Donoso-Bravo et al., 2011].

	SIMPLE MODEL	COMPREHENSIVE MODEL
input requirements		
substrate composition	x	x
restriction to adapted substrate	-	x
kinetic parameters	-	x
yield coefficients	-	x
physio-chemical constants	-	x
conversation factors	rarely	x
considered parameters		
temperature conditions	-	rarely
inhibition processes	-	rarely
growth rate of microorganisms	-	rarely
death rate of microorganisms	-	mostly
stages of anaerobic digestion	-	x
stoichiometric equations	x	x
various bacteria groups involved	-	x
pH or ionic equillibrium	-	mostly
gas-liquid equillia	rarely	x
output information		
CH_4 yield	x	x
CO_2 yield	mostly	mostly
H_2S yield	mostly	mostly
NH_3 yield	mostly	mostly
H_2O yield	mostly	mostly
time-dependent parameters	-	x
yield of substrate to microorganisms	-	mostly
yield of substrate to energy	-	rarely

Table 1.0.1: Difference between simple and comprehensive models for anaerobic digestion

The major disadvantage of simple physical models is that no prediction of time-dependent parameters such as required retention time is possible. Conversely, the major advantage of simple models is the higher flexibility in utilization, which means flexible application on various substrates. A simple anaerobic digestion model is appropriate for almost any kind of substrate, whereas a comprehensive model is tied to a certain kind of substrate since it is adapted properly [Gerber and Span, 2008]. Figure 1.0.1 sketches the biogas generation and -utilization model of present work.

Present model for biogas generation and utilization does not consider any kinetics, processes of inhibition, and effects of pH or temperature. Neither the biological and chemical stages of anaerobic digestion are considered. Degradable substrate components are interpreted as soluble. At some points vapor-liquid-equillibrium is considered which is influenced by temperature. The model is time-independent and is a collection of simple models from literature. It includes stoichiometric reactions, conversion factors, and distinguishes between degradable and nondegradable components. Biogas utilization model does not picture desulphurization and dehumidification properly, since physiochemical processes aren't considered. However, biogas combustion models are modeled in more detail, including humidity of combustion air, excess air ratio, and Gibbs free energy minimization. Since the model neglects several aspects, present model provides results which must be considered as maxium possible biogas, heat, and energy yields. The question which will be answered in this thesis is whether or not created model pictures biogas formation and utilization properly.

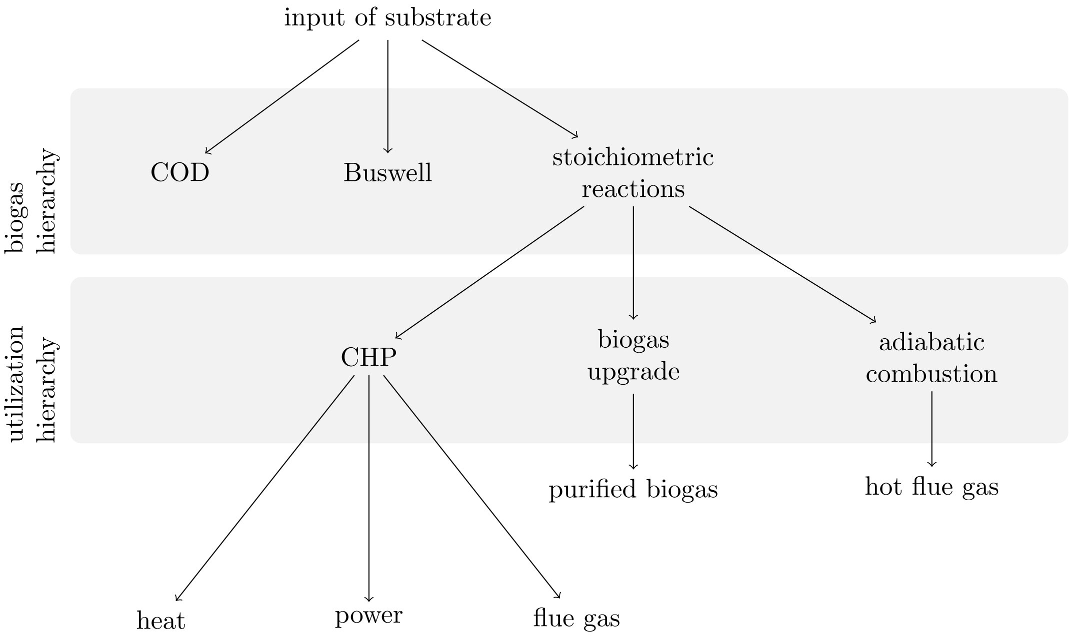

Figure 1.0.1: Scheme of complied biogas generation and -utilization model in Aspen Plus

Model results can be applied to make a rough estimate whether biogas generation out of waste material streams is advantageous or not, in order to cover heat and power demand of an overall process. However, it is important to notice that no economic aspects are taken into account and investment costs have to be balanced against financial savings during process integration. The study of [Wukovits et al., 2013] applied present biogas and utilization model in order to investigate whether or not implementing anaerobic digestion into a two-step biohydrogen process, presented in [Foglia et al., 2011], is beneficial.

The thesis begins by briefly reviewing theoretical aspects of biogas generation and utilization in chapter 2. Section 2.1 introduces the term anaerobic digestion and goes on describing the microbiology, physiology, and environmental influences of/on anaerobic digestion in section 2.2. Section 2.3 goes on to discuss the biogas potential of various substrates and also defines the term biogas. In section 2.4, various pretreatment and utilization possibilities of biogas are itemized. Also a briefly review on combined heat and power generation units (CHP) is given. Chapter 3 is divided into five sections, starting with section 3.1 which is shorty introducing the simulation tool Aspen Plus. Section 3.2 goes on discribing required settings, such as property method, component list, component parameters, etc. Section 3.3 depicts the model development and gives an overview on the implemented calculation routes of the two hierarchies *biogas* and *utilization*. In sections 3.4 and 3.5 the modeling of biogas formation and utilization is discribed in detail, which includes theoretical aspects and implementation procedures of each calculation path. Chaper 4 addresses the model evaluation and the results. Section 4.1 presents evaluation of the present biogas generation and utilization model by making use of different evaluation stategies. Also a systematic and clear procedure for implementing additional substrate components is discribed. Section 4.2 presents simulation results when applying data provided by project partners of HYVOLUTION project [EU, 2010] and comparing them with literature data which are summarized in section 2.3. Evaluation and the results of the biogas generation and utilization model are discussed at this point. Finally, chapter 5 summarizes the present work and gives an outlook.

Chapter 2

Biogas formation and utilization

2.1 Microbiology of anaerobic digestion

Microorganisms have, like every living organism, the endeavor to maintain life functions and to reproduce. Therefore energy and build-up material is needed, which is provided by organic material. The degradation of organic material by microorganisms into smaller low-energy molecules releases energy in form of ATP and heat. ATP stands for adenosine triphosphate which is the essential energy carrying form for all microorganisms. Gibbs free energy ΔG^{o}' [kJ/mol] characterizes the amount of energy released at the breakdown process of the macromolecules which is usable for the synthesis of ATP. A chemical reaction can only take place when ΔG^{o}' approaches negative values. The larger the value, the more rapidly the reaction will take place.

The essential difference between aerobic and anaerobic degradation of organic material is the amount of energy released, by means of change in metabolism [Bischofsberger et al., 2009]. Change in metabolism consequences a change in carbon conversion according to figure 2.1.1 [Jördening and Winter, 2005] and subsequently changes in energy conversion release.

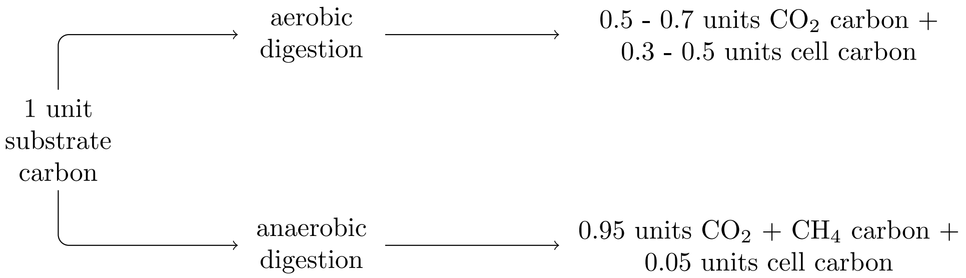

Figure 2.1.1: Carbon conversion of aerobic and anaerobic digestion

Anaerobic digestion describes the complete breakdown of organic material in the absence of oxygen to CO_2 and H_2O (biogas formation), illustrated in the simplified reaction 2.1.1. Aerobic digestion is simplified in reaction 2.1.2 where cell mass is built up by respitation forming products CO_2 and H_2O. Both processes are exothermic, but aerobic degradation releasas more heat energy than anaerobic degradation. However, the heat released during anaerobic digestion does not cover the heat demand of the process when operating at constant temperature conditions. Therefore process energy from external sources has to be supplied in order to maintain a constant (mesophilic) temperature level [Jördening and Winter, 2005].

$$\text{organic material} \quad \rightarrow \quad CH_4 + CO_2 + H_2 + NH_3 + H_2S + \text{heat energy} \tag{2.1.1}$$

$$\text{organic material} \quad \rightarrow \quad \text{cell mass} + CO_2 + H_2O + \text{heat energy} \tag{2.1.2}$$

$$CH_4 + 2\,O_2 \quad \rightarrow \quad CO_2 + 2\,H_2O \quad + \text{heat energy } \Delta G^{o\prime} \ (-891.6 \text{ kJ/mol } CH_4) \tag{2.1.3}$$

During anaerobic degradation approximately 6.9 % of the combustion energy is available for growth and maintenance, and only 4.6 % are lost during anaerobic metabolism. The remaining 88.5 % are bonded to the produced biogas which can further be used as fuel for gas engines to generate electric power and heat related to equation 2.1.3. During aerobic degradation of 1 mol glucose via glycolysis, approximately 69 % of the combustion energy is available for growth and maintenance. Approximately 31 % is lost in form of heat during respiration forming CO_2 and H_2O.

Above observed facts represent the main differences between anaerobic and aerobic degradation, whereby only anaerobic digestion produces biogas. Figure 2.1.2 pictures mass and energy dissipation during anaerobic digestion of glucose according to [Jördening and Winter, 2005].

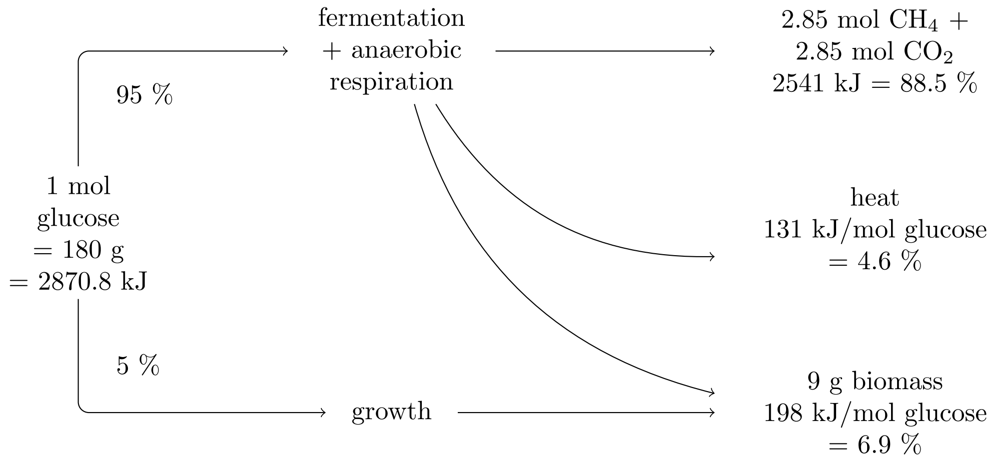

Figure 2.1.2: Mass and energy dissipation during anaerobic fermentation of glucose at pH 7

The anaerobic digestion process involves a complex consortium of microorganisms. According to present state of knowledge, anaerobic digestion processes are performed in four biological and chemical stages: *hydrolysis*, *acidogenesis*, *acetogenesis*, and *methanogenesis* [Bischofsberger et al., 2009], [Kaltschmitt et al., 2009], [Mudhoo, 2012], [Cimochowicz-Rybicka, 2013], [Batstone et al., 2002], and [Zahoransky et al., 2010]. However, some authors (namely [Evans and Furlong, 2003], [Antranikian et al., 2006], [Jördening and Winter, 2005], [Braun, 1982], [Klass, 1998], and [Jung et al., 2000]) combine acidogenesis and acetogenesis. Subdividing this two processes highlights the importance of acetic acid, which accounts to approximately 75 % of the produced methane [Evans and Furlong, 2003]. The biogas that has its source in anaerobic digestion is mainly consisting of methane and carbon dioxide. Biological gasifcation is usually incomplete, which points out the major limitation of anaerobic digestion. Depending on the type of substrate, up to 50% of the organic matter remains unconverted [Chynoweth et al., 2001]. Degradation during a multistage anaerobic digestion process is pictured in figure 2.1.3, according to [Bischofsberger et al., 2009].

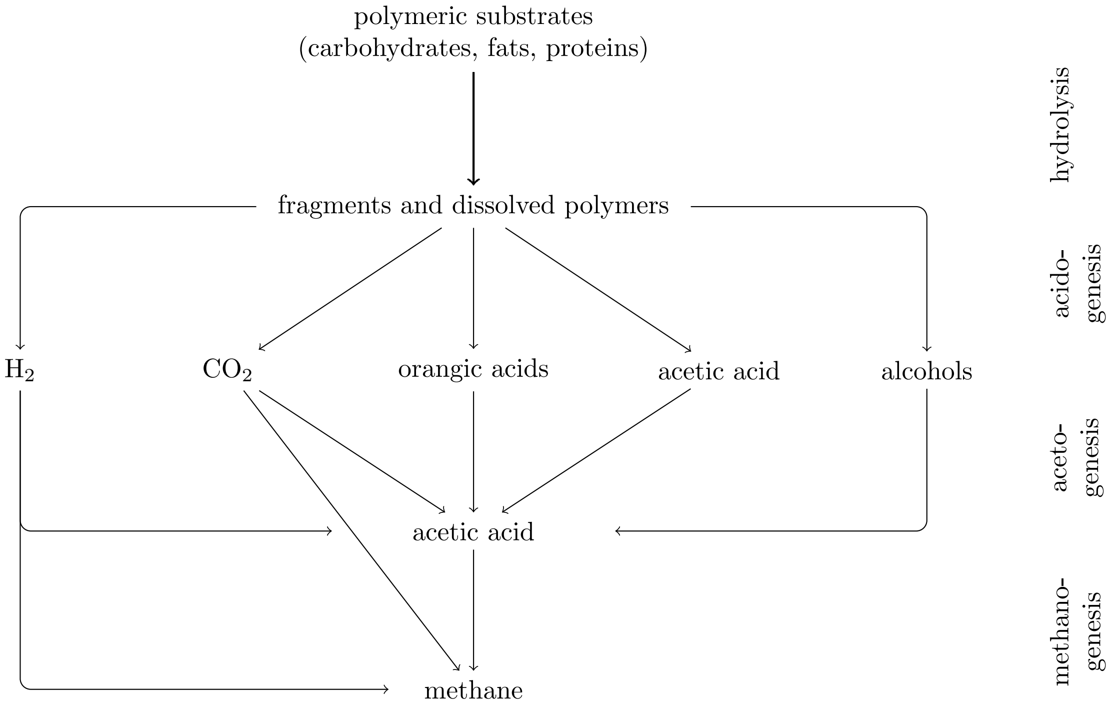

Figure 2.1.3: Scheme of multistage anaerobic digestion process

Microorganisms involved in the process of anaerobic digestion form a microbial anaculture which have strong mutual influences among themselves. [Jördening and Winter, 2005] names hydrogen partial pressure as most sensitive switch of the carbon flow of substrates to biogas. Hydrogen, an intermediate product of acetogenesis, inhibits at the same time growth of the acetogenic microoganisms. However, hydrogen is a basic material for methanogenesis. It is for this reason very important to spacial couple acetogenesis and methanogenesis, so that formed hydrogen is simultaneously consumed. Hydrogen partial pressure limits the area where both processes simultaneously can take place. As this area is very small concerning degradation of propionic acid to acetic acid, propionic acid metabolism (a subprocess of acetogenesis) is frequently referred to as limiting step of anaerobic digestion [Thome-Kozmiensky and Beckmann, 2011], [Ziganshin et al., 2011] and [Bischofsberger et al., 2009]. At the same, [Watter, 2009] states hydrolysis as rate-determining step, when sparingly degradable substances occure. Methanogenesis of acetic acids is also stated as rate-limiting step [Jördening and Winter, 2005]. Hence, it can be supposed that the rate-limiting step depends on compounds of the feedstock which is utilized in the process [Weiland, 2010].

2.1.1 Hydrolysis

During hydrolysis insoluble biopolymers such as carbohydrates, fats and proteins are broken down into water-soluble monomeric fragments by exoenzymes [Jördening and Winter, 2005]. The high molecular weight components of the input biomass are decomposed into low molecular weight components. Hydrolytic exoenzymes are for instance cellulase, cellobiase, xylanase, amylase, lipase, and protease which are excreted by hydrolytic microorganisms [Weiland, 2010]. Carbohydrates are decomposed to oligo- and monosaccharides, fats to their monomeric fragments fatty acids and glycerol, and proteins to peptides and amino acids [Watter, 2009]. Hydrolysis is inhibited by lignocellulose-containing materials, which are decomposed incompletely or very slowly [Jördening and Winter, 2005].

2.1.2 Acidogenic phase

During acidogenesis, hydrolysis products are transformed into hydrogen, carbon dioxide, acetic acid, various other organic acids (including volatile fatty acides VFA), and alcohols. Only the intermediate products hydrogen, carbon dioxide, and acetic acid can be transformed into carbon dioxide and methane by methane-forming microorganisms [Bischofsberger et al., 2009]. Hydrolysis and acidogenesis form together the inital stages of anaerobic digestion, which are usually combined in one stage and separated from the acetogenesis/methanogenesis stage [Ziganshin et al., 2011].

2.1.3 Acetogenic phase

The fermentation products of acidogenesis which can not directly be decomposed by methanogenic microorganisms, namely volatile fatty acids and alcohols, are further converted by acetogenic bacteria to mainly acetic acid [Ziganshin et al., 2011]. Therefore acetogens represent the connection between fermentative and methanogenic microorganisms. Since acetogenesis can only take place at low hydrogen partial pressure, the acetogenic phase has to be coupled with methanogenesis due to interspecies hydrogen transfer [Mudhoo, 2012]. Methanogenic microoganisms consume the hydrogen which acetogenic microoganisms produce.

2.1.4 Methanogenic phase

Methanogenic microorganisms are accountable for forming biogas after organic feedstock is degraded via fermentation. Methanogens are strictly anaerobic microorganisms classified as *archaea*, a group very similar to bacteria. Some major differences between bacteria and archaea can be found in [Wang et al., 2010].

Archaea were splitted off from other life forms during evolution very early, thus they have very unique properties [Bischofsberger et al., 2009]. Owing to their proximity to the origin of life, they require anaerobic conditions. Some of them require temperatures near water´s boiling point, low pH values, and high salt concentrations for optimal growth [Antranikian et al., 2006]. Archaea also are able to grow under 'normal' conditions. Methanogenic microoganisms are usually divided into acetoclastic methanogens which strictly metabolize acetate or formiate, and hydrogenotropic methanogens which use hydrogen and carbon dioxide for their metabolism [Mudhoo, 2012]. During methanogenesis mainly biological conversion of acetic acid, hydrogen, and carbon dioxide into methane takes place. According to [Roedinger et al., 1990], approximately 70% of the methane formed stems from the decomposition of acetic acid and about 30% is formed via redox reaction of hydrogen and carbon dioxide [Speece, 1983].

2.2 Physiology and environmental influences

Microorganisms involved in the anaereobic digestion process steps (hydrolysis, acidogenesis, acetogenesis, and methanogenesis) have various physiology and nutrient requirements. However, in a stable operated process all kinds of microorganisms participating anaerobic digestion are well balanced [Jung et al., 2000]. They require certain nutrients, trace elements, and vitamis for metabolism and maintainance. The limiting concentration depends on species specific requirements. If there are too few nutrients available, the assessible carbon can not be converted entirely. In the opposite position, an excess of nutrients can induce the formation of potentially inhibiting substances [FNR, 2006]. Essential nutrients, such as nitrogen-, phosphorus-, and sulfur compounds, are considered in relation to available carbon (so-called carbon source), in order to set minimum requirements. [FNR, 2006] recommends a nutrient requirement ratio C:N:P:S of 600:15:5:1, [Kaltschmitt et al., 2009] a C:N:P ratio of 100-200:4:1, [Ammary, 2004] a C:N:P ratio of 250:5:1, and [Deublein and Steinhauser, 2011] a C:N:P:S ratio of 500-600:15:5:3. In order to compensate low nitrogen and/or phosphorous concentrations, nitrogen (in the form of urea $(NH_2)_2CO$) and/or phosphorous (in the form of phsophoric acid H_3PO_4) can be added to obtain the minimum nutrient ratio, if neccesary [Jördening and Winter, 2005].

Besides other factors affecting methane production (e.g. temperature, mixing, type of substrate, etc.), the value of pH plays a central role. The pH of fermentation results mainly from alkaline or acidic products of metabolism and a natural buffer system. Anaerobic digestion is sensitve to both, low and high pHs. If the pH value of acetogenenis/methanogenesis sinks below pH value 4.5, the production of organic acids leads to a further decrease of the pH value by the hydrolytic microorganisms. Values of $pH > 10$ in a reactor leads to an irreversible loss of activity of the microorganisms. However, the pH value is held within the neutral range by natural buffering procedures in the fermenter [Deublein and Steinhauser, 2011]. The most significant buffer system in anaerobic digestion is represented by CO_2 - HCO_3^- - system [Braun, 1982]. The optimal pH ranges widely and varies with substrate and digestion technique [Liu et al., 2008].

In hydrolysis/acidogenesis phase, the optimal pH range is 4.5 - 6.3 according to [FNR, 2006], and 5.7 - 5.9 according to [Klass, 1998]. The optimum range of pH (to obtain maximal biogas yield) in acetogenic/methanogenic phase is 6.5 - 7.5 according to [Liu et al., 2008], 6.5 - 8.5 according to [Weiland, 2010], 6.8 - 7.5 according to [Wang et al., 2011], 6.6 - 8.0 according to [Braun, 1982], 6.5 - 8.0 according to [van Lier et al., 2001], and 6.7 - 7.5 according to [Deublein and Steinhauser, 2011]. The study of [Liu et al., 2008] focuses on increasing the methane production by adjusting the optimal pH (which is predicted by a computer circulation program). Results show that the methane production has an average increase of about 35% operating at optimal pH, which brings out the pivotal influence of an optimal pH.

In principle, the higher the temperature, the faster a chemical reactions takes place. However, biological systems do not necessarily follow this rule. Various groups of microorgansims involved in anaerobic digestion processes have various temperature optima. Exceedance or undercut can result in inhibition or irreversible damage of the participating microorganisms [FNR, 2006]. According to [Batstone et al., 2002] temperature affects biochemical reactions in several ways. When increasing the temperature up to the temperature optimum of the involved organisms, the reaction rates are increasing according to Arrhenius equation. However, when the temperature exceedes the optimum, the reaction rate decreases rapidely down to zero. There are three operation temperature ranges in accordance with the optimal temperature range of the different groups of microorgansisms - physiophilic (up to 25°C), mesophilic (30 to 40°C) and a moderate thermophilic temperature range (50 to 60°C) [van Lier et al., 2001]. At physiophilic temperature conditions, the degradation capacity and biogas production is strongly limited. The majority of methanogens have their optimum temperature for growth at mesophilc conditions, which results in high biogas yields. Thermophilic operation mode is appropriate when there is a need for killing pathogens by hygienization [FNR, 2006].

Inhibition of biogas formation or anaerobic digestion process can have several reasons. Firstly, operational parameters such as mixing or residence time have to be followed in order to ensure smooth operation. Secondly, inhibitors can delay progress in biochemical process of biogas formation. Small amounts of inhibitors can be acutely toxic and hamper the degradation process. It is useful to differentiate between inhibitors entering the system via substrate, and inibitors emerging from different degradation steps as intermediate products. It is important to understand that any compound of substrate can harm the biochemical system, since an excessive concentration can inhibit fermentation. This is pariculary true for antibiotics, disinfectants, solvents, herbicides, salts, and heavy metals. Even small amounts of these substances have toxic effects on microorganisms [FNR, 2006]. Mechanism and the controlling factors of inhibition are identyfied and investigated in [Chen et al., 2008], whereby inhibitors include ammonia, sulifides, light metals (Na, K, Mg, Ca, and Al), heavy metals, and organics. Identifying the inibiting concentration limits is very challenging, since a variety of factors (pH, temperature, presence of other substances/ions, acclimation, etc.) influences inhibition. [Braun, 1982] and [Bischofsberger et al., 2009] investigated this comlexity of inhibition extensively.

Optimal environmental conditions for all microorganisms participating anaerobic degradation of a two - stage plant can only be set in one stage for hydrolysis/acidogenesis and one stage for acetogenenis/methanogenesis [Deublein and Steinhauser, 2011]. Table 2.2.1 summarizes microbial process parameters accoring to [Deublein and Steinhauser, 2011], which have to be taken into account in order to ensure an optimum fermentiation process. Enviromental requirements of fermentative microorganisms of hydrolysis/acidogenesis differ from methane-forming microorganisms in acetogenenis/methanogenesis.

Parameter	Hydrolysis/acidogenesis	Acetogenenis/methanogenesis
Temperature	25 - 35 °C	Mesophilic: 32 - 42 °C Thermophilic: 50 - 58 °C
pH value	5.2 - 6.3	6.7 - 7.5
C:N ratio	10 - 45	20 - 30
DM content	< 40% DM	< 30% DM
Required C:N:P:S ratio	500 : 15 : 5 : 3	600 : 15 : 5 : 3
Trace elements	No special requirements	Essential: Ni, Co, Mo, Se

Table 2.2.1: Environmental requirements (DM = dry matter)

2.3 Biogas yields and composition

Anaerobic degradation of different feedstocks provides various amounts of biogas and biogas yields. Studies of [Roedinger et al., 1990] (a), [Linke et al., 2006] (b), [Baserga, 1998] (c), [Jördening and Winter, 2005] (d), [FNR, 2006] (e), [Bischofsberger et al., 2009] (f), [Weissbach, 2009] (g), [Weiland, 2010] (h), and [Hornbachner et al., 2005] (i) published maximum biogas yields stemming from anaerobic degradation of simple carbohydrates, fats, and proteins as listed in table 2.3.1.

	biogas yields [m^3/kg ODM]								
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)
carbohydrates	0.79	0.75	0.79	0.79	0.70 - 0.80	0.79	0.79 - 0.80	0.79 - 0.80	0.70 - 0.80
fats	1.27	1.39	1.25	1.27	1.00 - 1.25	1.27	1.34 - 1.36	1.20 - 1.25	1.00 - 1.25
proteins	0.70	0.79	0.70	0.70	0.60 - 0.70	0.70	0.71 - 0.88	0.70	0.60 - 0.70

Table 2.3.1: Biogas yields of different organic components (ODM = organic dry matter)

Since the feedstock consists of a multitude of compounds besides carbohydrates, fats, and proteins, a biogas yield prediction requires fermentation experiments. Biogas yields of different substrates (organic residue, animal manure, and energy crops) have been investigated in [Görisch and Helm, 2007] (a), [Kaiser, 2007] (b), [Linke et al., 2006] (c), [Braun, 1982] (d), [IFA-Tulln and GERBIO, 2009] (e), [FNR, 2006] (f), [Wetter and Brügging, 2008] (g), and [Deublein and Steinhauser, 2011] (h). Parts thereof are summarized in table 2.3.2. The studies of [Gunaseelan, 1997], [Weiland, 2010], [Amon et al., 2007], and [Braun et al., 2009] provide comprehensive biogas yield data on various substrates related to m^3 biogas/kg VS (volatile solids). Test results for specific biogas yields out of renewable raw material are subject to wide fluctuations due to incomparable factors such as fermetation conditions and point of harvest. Therefore a large range of variation of biogas outcome and methane yield has to be expected [Kaiser, 2007].

	biogas yield [m^3/kg ODM]							
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
organic residue								
clover	0.50-0.65	0.50-0.66	-	0.45	-	-	-	0.60-0.80
potato peelings	-	-	0.88	-	-	-	-	0.30-0.90
molasses	0.45	-	0.51	-	0.36-0.49	0.36-0.49	-	0.30-0.70
farm fertilizer								
cow manure	-	-	0.45	0.14-0.36	0.20-0.5	0.21-0.30	0.40	0.60-0.80
pig manure	-	-	0.37	0.50-0.72	0.30-0.7	0.27-0.45	0.40	0.27-0.45
energy crops								
sugar beet	-	-	0.66	-	-	0.80-0.86	-	0.70
grass silage	0.60-0.60	0.50-0.60	0.54	0.56	0.55-0.62	0.55-0.62	-	0.60-0.70
wheat sillage	0.40-0.50	-	-	-	-	-	0.50	-
rye sillage	-	0.79	0.73	-	-	0.17-0.22	0.56	-
corn sillage	-	0.59-1.13	0.68-0.81	-	0.45-0.70	0.45-0.70	0.54	0.60-0.70
barley sillage	-	-	0.92	-	-	-	0.61	-
crop straw	0.25-0.35	-	-	-	-	-	-	-
corn straw	0.50	0.50-0.66	-	-	-	-	-	0.40-1.00
wheat straw	-	0.34	0.48	0.37	-	-	-	-
oat straw	-	0.33	-	0.40	-	-	-	-
rye straw	-	0.28	-	0.34	-	-	-	-
barley straw	-	0.25-0.35	-	0.39	-	-	-	-

Table 2.3.2: Biogas yields stemming from various substrate matter (ODM = organic dry matter)

Biogas consists mainly of CH_4 and CO_2 besides typical impurities as H_2O, H_2S, NH_3, and N_2. Each gas component has its impact on the gas quality. CO_2 lowers the calorific value of the biogas, causes corrosion if the gas is wet, and it (as well as N_2 and NH_3) increases anti-knock properties of engines. H_2O causes corrosion in condensed state. H_2S spoils catalysts and also has a corrosive effect, wherefore many manufacturers of engines set upper limits of 0.05 vol-% [Deublein and Steinhauser, 2011]. Table 2.3.3 lists average biogas compositions from anaerobic digestion and heating values H_u according to [FNR, 2006] (a), [Scharf, 2007] (b), [Deublein and Steinhauser, 2011] (c), [Braun, 1982] (d), [Cimochowicz-Rybicka, 2013] (e), [Zahoransky et al., 2010] (f), [Thome-Kozmiensky and Beckmann, 2011] (g), and [Bischofsberger et al., 2009] (h). The work of [Lehtomäki et al., 2008], [Ward et al., 2008], [Vintila et al., 2012], [Bischofsberger et al., 2009], [FNR, 2006], [Weiland, 2003], and [IFA-Tulln and GERBIO, 2009] additionally provides data concering CH_4 yields on various substrates, which are in the range of approximately 45 - 75 vol-% methane.

comp. [vol-%]	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
CH_4	50 - 75	55 - 75	45 - 75	52 - 85	55 - 75	50 - 75	45 - 70	60 - 70
CO_2	25 - 45	25 - 45	25 - 55	14 - 48	25 - 45	25 - 45	25 - 50	30-40
H_2O	2 - 7 *	-	-	-	-	2 - 7	3 **	-
H_2S	< 2	0 - 3	-	0.08-6	0.01-1	-	< 1	0 - 0.7
N_2	< 2	0 - 0.3	0.01 - 5	0.6 - 8	2 - 6	-	0 - 4	0 - 0.2
O_2	< 2	0.1 - 0.5	0.01 - 2	0 - 1	-	-	0 - 1	-
H_2	< 1	1 - 5	0.5	0 - 5	0.1 - 2	< 1	< 0.1	0 - 0.2
H_u [MJ/kg]	18.00-18.60	-	15.00-23.28	-	-	> 15.00	-	18.00-24.83

Table 2.3.3: Average biogas composition and heating value (* at 20 - 40 °C; ** at 25 °C)

2.4 Upgrading and utilization of biogas

The high-quality energy carrier biogas can be utilized in several ways. Depending on further usage opportunities, different processing steps are necessary. The minimum pretreatment procedure of biogas is dehumidification and desulphurization. Figure 2.4.1 gives an overview on common utilization options of biogas and their needful pretreatment steps according to [Linke et al., 2006]. Various utilization paths require different processing efforts. [TUV, 2013] provides a tool for calculating biomethane formation based on different feedstock including the technologic and economic aspects of upgrading raw biogas to produce biomethane.

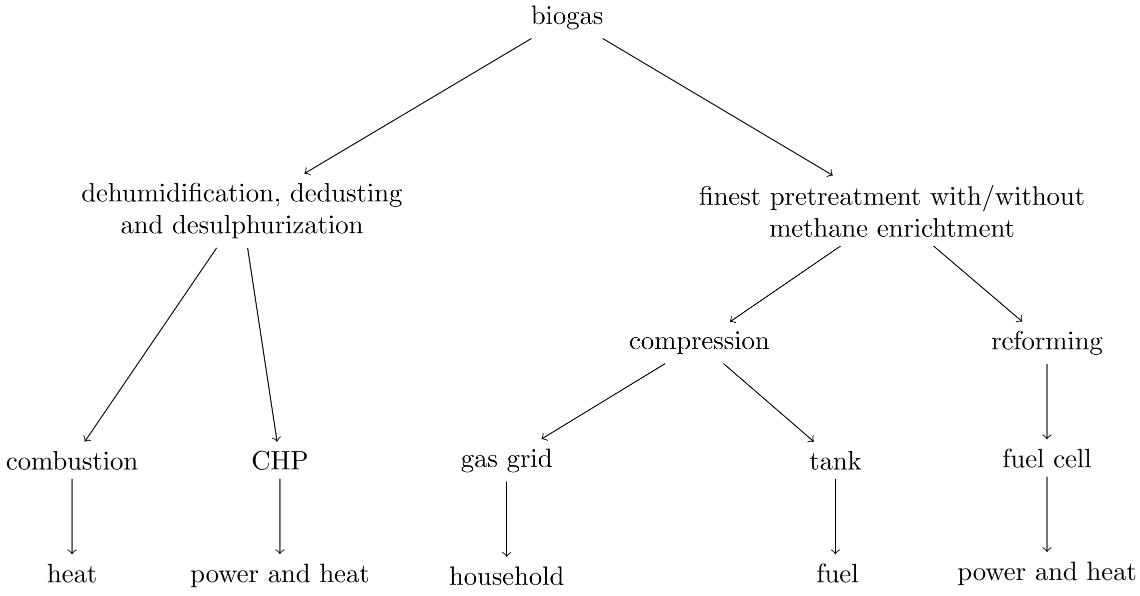

Figure 2.4.1: Utilization options and processing routes of raw biogas

Hydrogen sulphide is formed during anaerobic digestion. H_2S reacts to sulphurous acid during combustion, which has strongly corrosive properties [Linke et al., 2006]. For desulphurization three principles are available [FNR, 2006]: *Biological desulphurization* removes sulphur via sulphur-oxidizing microorganisms (under aerobic conditions). *Desulphurization via absorption* works through katalytic oxidation for instance on iron ore. During *chemical desulphurization* trivalent iron salts are added to the fermenter where sparingly soluble iron sulphide is formed. None of these processes removes the entire H_2S and up to 100 ppm may remain in the biogas. Water vapor is removed via a cooling system which is either consisting of pipelines that are laid underground or by using an external cooling aggregat. Investment costs, operationg costs, and installation size decide which dehumidification option is used [Linke et al., 2006].

Figure 2.4.2 gives an overview of various biogas treatment processes in order remove undesired biogas compounds such as CO_2, H_2O, H_2S, NH_3, oxygen, and nitrogen [Hornbachner et al., 2005]. Since CO_2 amounts about 50 % of the raw biogas, technologies for CO_2 removal possess a high level of interest. Conventional processes are *pressurized water scrubbing*, *pressure swing adsorption (PSA)*, *cryogenic-*, and *membrane processes*, in which pressurized water scrubbing and PSA are most common at present. All these processes result in purified biogas of a methane content of up to 98 % [Linke et al., 2006].

Pressurized water scrubbing is a simple process and it is for this reason one of the most frequent used principles for biogas upgrading. The easy handling, simple regeneration, and the low price of the washing agent water are major advantages of this principle. Pressurized water scrubbing provides the opportunity for simultaneous separation of H_2S and CO_2. Pessure Swing Adsorption (PSA) is the second most employed techniques for biogas upgrading. The adsorbent is a porous solid with a high surface area. Carbon molecular sieves (CMS) but also activated carbons or zeolites are applied as adsorbent. Through PSA, biogas can be upgraded (via CO_2 separation) to a quality similar to natural gas. An overview on possible biogas upgrading technologies in order to produce biomethane is given in [TUV, 2012], [Deublein and Steinhauser, 2011], and [Thrän, 2012]. Reformig of biogas leads to generation of syngas which can further be used in fuel cells.

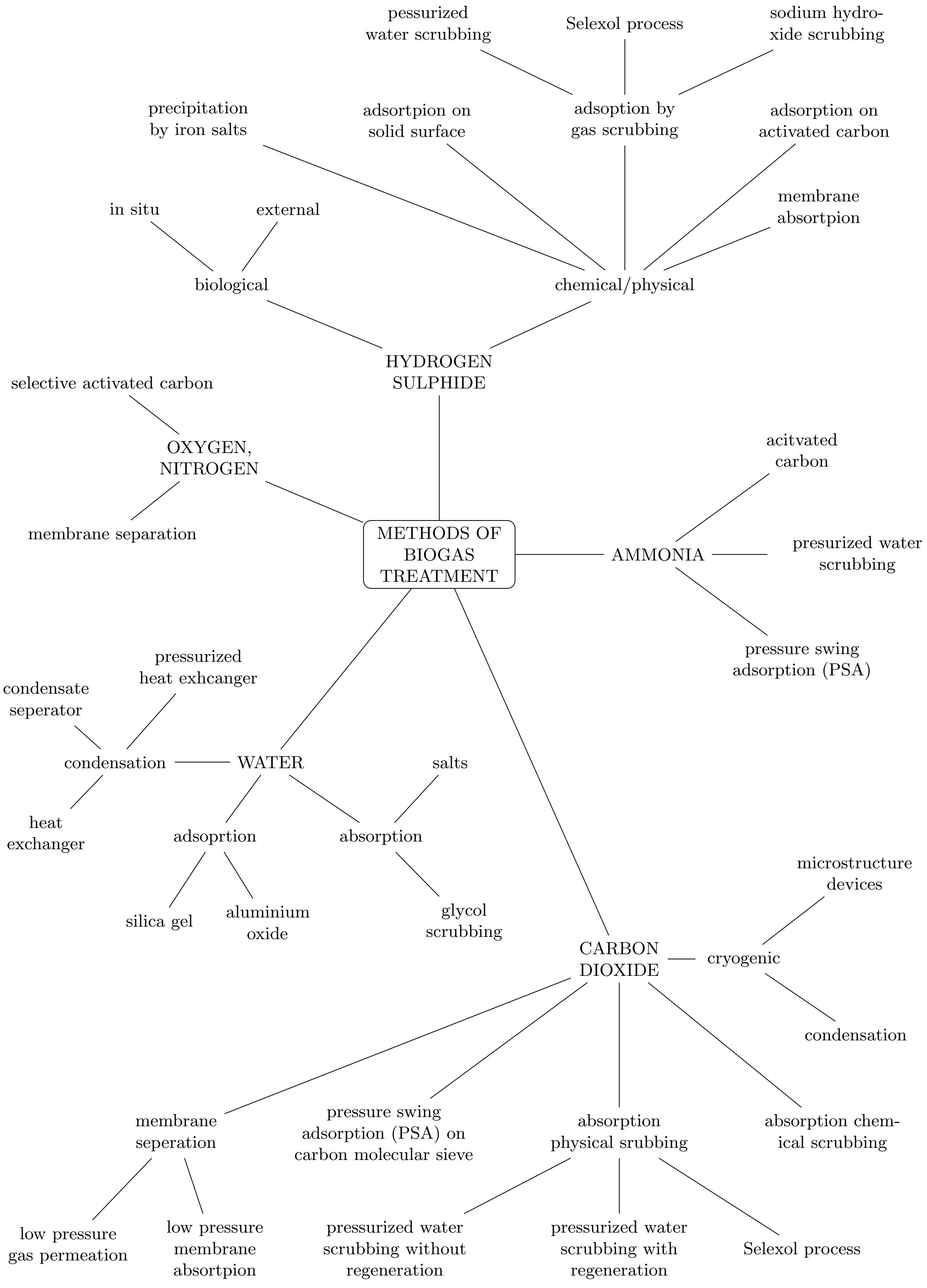

Figure 2.4.2: Biogas treatment routes

Since combined heat and power (CHP) generation represents the most common application of biogas, further details are given in this section. Figure 2.4.3 offers an overview on implementing a CHP unit to a biogas process [Elsenbruch, 2011]. After pretreatment, the biogas is converted to electrical and thermal energy in CHP unit which is consisting of an internal combustion engine, a generator for electrical power generation, and a heat carrier system which cools the engine. Several heat carrier media are interconnected to a global cooling circuit which is sketched in figure 2.4.3.

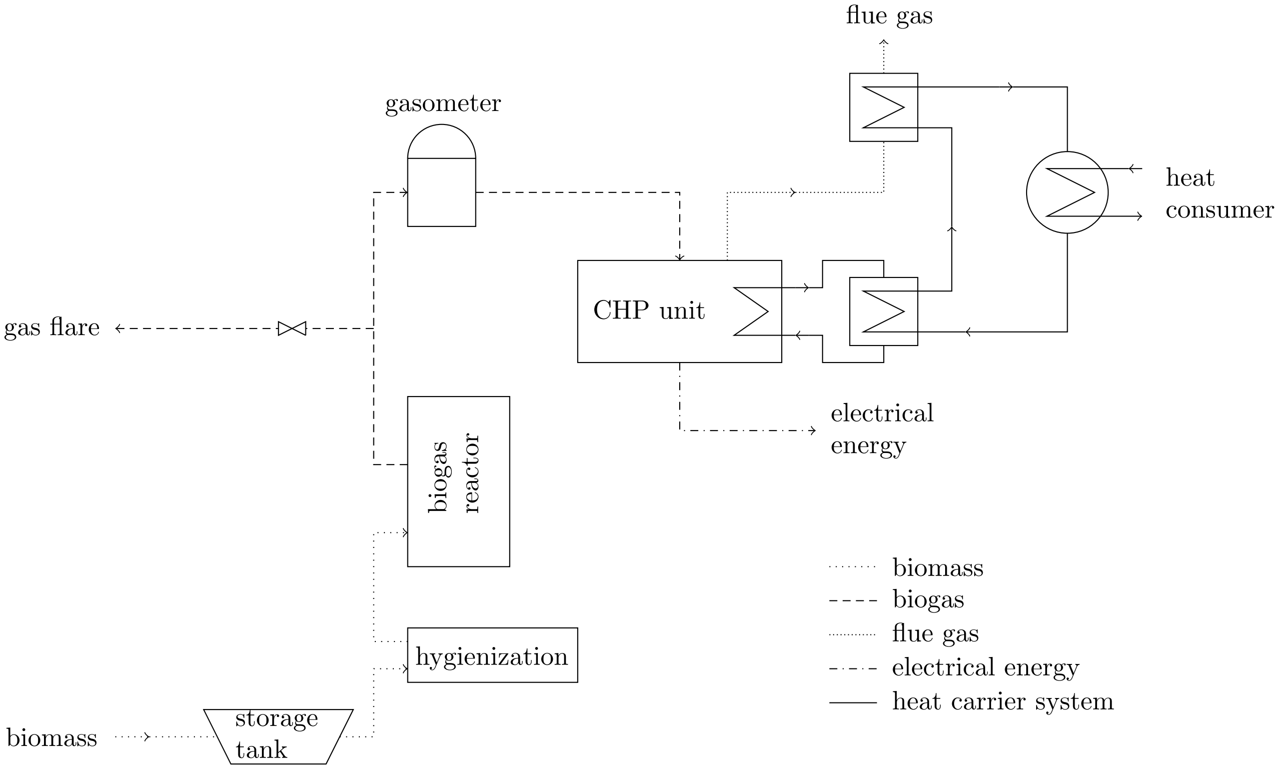

Figure 2.4.3: Schematic implemetion of CHP unit in a biogas process

Figure 2.4.4 illustrates the cooling circuit forming a global hot water circuit, according to [Jenbacher, 2005], which is at a temperature level of approximately 90 °C and can for instance be used for district heating or for heat integration in a global process (such as it is discussed in [Wukovits et al., 2013]).

The heat exchangers (*biogas/air mixture*, *oil*, *engine*, and *flue gas*) are built-in components of the CHP unit. The thermal output of these heat exchangers amout 13 % (biogas/air mixture heat exchanger), 10 % (oil heat exchanger), 26 % (engine heat exchanger), and 51 % (flue gas heat exchanger) of the total thermal output [Jenbacher, 2005].

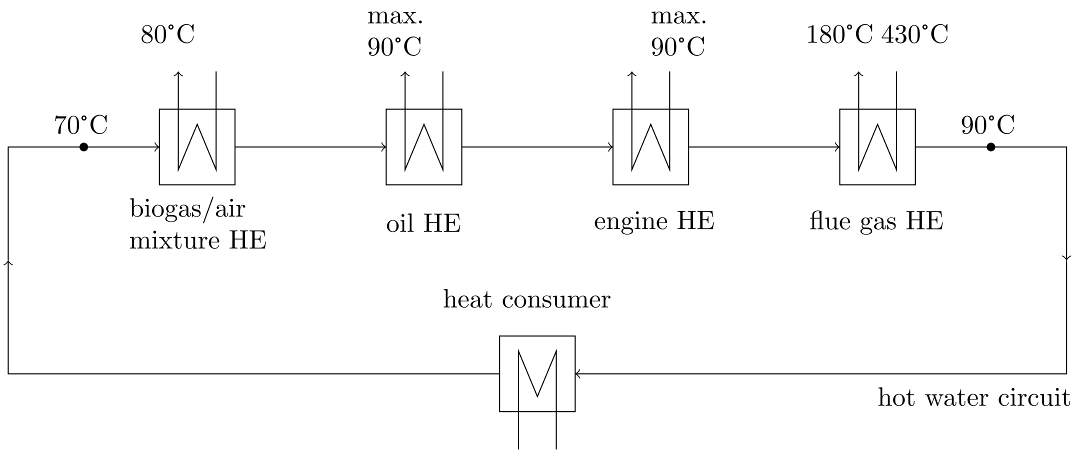

Figure 2.4.4: Heat exchanger water circuit of CHP unit

Chapter 3

Modeling of anaerobic digestion and biogas utilization

3.1 Simulation tool Aspen Plus

Aspen Plus (Advanced System for Process Engineering) is a steady state flowsheeting tool for process simulation which is used to quantitatively model characteristic equations of a particular (chemical) process. Therefore mass and energy balances, equillibrium relationships, and rate correlations for chemical reactions or mass- or heat transfer are linked. The balancing results in prediction of stream attributes (flow rates, compositions, properties), operation conditions, and equipment size. Concerning solution strategy Aspen Plus provides both, an equation-oriented (EO) and a modular-sequencial (SM) approach, which is the default setting and further used in this work.

There are particular advantages of modular-sequentcial approches, namely easily comprehensible calculation, an easily localisation of errors/problems, low requirements for the computer (memory- and computing capacity), and powerful unit-operation models [Friedl et al., 2010]. In order to translate a process into an Aspen Plus simulation model, the following procedure has to be performed [AspenTech, 2001c]. First, the process flowsheet has to be defined, which includes unit operations and process streams. Then chemical components in the process have to be determined. Components have specific thermodynamic properties which have also to be set. After specifying both, component flow rates and operating conditions of unit operations, a simulation can be performed. All specifications can interactively be changed.

At this point some useful Aspen Plus features are explained only shortly. *Property sets* are a collection of several properties (thermodynamic, transport, and others) that can be used to access obtained properties in stream reports, physical property tables, unit operation models, and in design specifications and calculator blocks. Aspen Plus provides several built-in property sets, which are usually sufficient for many applications [AspenTech, 2001e]. Examples for property sets used in this work are listed in table 3.2.3. A *calculator block* provides the possibility to insert FORTRAN statements or excel spreadsheets into flowsheet computations to perform user-defined tasks [AspenTech, 2013]. Calculator blocks are used in order to implement calculations which manipulate process streams and unit operation blocks. A *design specification* allows to set a process variable that is normally calculated during simulation [AspenTech, 2013].

3.2 Components and properties

It is important to chose a suitable *property method* properly. Aspen Plus provides a large range and recommends property methods for different applications. According to [AspenTech, 2001e] and [AspenTech, 2001b] the activity coefficient model NRTL (non-random two-liquid model) has been chosen. NREL (National Renewable Energy Laboratory) [Aden et al., 2002] developed a Aspen Plus model including an anaerobic digestion unit based on NRTL property methode, which correlates the activity coefficients of a component with its mole fractions in the liquid phase.

Table 3.2.1 lists the components used in the developed biogas model, whereby marked components (*) are considered as degradable. The input data originate from project partners of HYVOLUTION project [EU, 2010]. The exact elemental composition of component LIGNIN is $C_{7.3}H_{13.9}O_{1.3}$, of component BIOMASS is $CH_{1.64}O_{0.39}N_{0.23}S_{0.0035}$, and of CELLULAS is $CH_{1.57}O_{0.31}N_{0.29}S_{0.007}$ [Wooley and Putsche, 1996]. The component list includes components for an input of molasses and barley straw, which have been the basis for the model development. A summary of the input data of the two possible feedstocks are listed in Appendix A.1. NREL provides a comprehensive Aspen Plus model describing the chemical conversion process and its economic consideration of the conversion of biomass to ethanol [Aden et al., 2002]. This model includes a *physical property database for biofuels components* [Wooley and Putsche, 1996] developed in a former work of the NREL. This database is now integrated in Aspen Plus, namely *NREL_DB INHSPCD*, and is further used upon others in this work.

In order to evaluate the developed model in chapter 4.1, the original component list has therefore to be extended to include components listed in table 3.2.2. The marked components (*) represent degradables. According to [Wooley and Putsche, 1996] the exact elemental composition of component ZYMO is $CH_{1.8}O_{0.5}N_{0.2}$.

Component ID	Type	Component name	Formula
H2	CONV	HYDROGEN	H2
O2	CONV	OXYGEN	O2
CO2	CONV	CARBON-DIOXIDE	CO2
H2O	CONV	WATER	H2O
*GLUCOSE	CONV	GLUCOSE	C6H12O6
*SUCROSE	CONV	SUCROSE	C12H22O11
NH3	CONV	AMMONIA	H3N
*HAC	CONV	ACETIC-ACID	C2H4O2-1
ASH-WS	SOLID	CALCIUM-OXIDE	CAO
CALDI	SOLID	BIOMASS	CHXNXOXSX-1
RHODO	SOLID	BIOMASS	CHXNXOXSX-1
KOH	CONV	POTASSIUM-HYDROXIDE	KOH
*PECTINE	SOLID	CELLULOS	C6H10O5
*PROTEIN	SOLID	CELLULAS	CHXNXOXSX-2
HCL	CONV	HYDROGEN-CHLORIDE	HCL
K2HPO4	CONV	DIPOTASSIUM-PHOSPHATE	K2HPO4
KH2PO4	CONV	POTASSIUM-DIHYDROGEN-PHOSPHATE	KH2PO4
CH4	CONV	METHANE	CH4
H2S	CONV	HYDROGEN-SULFIDE	H2S
*XYLOSE	CONV	XYLOSE	C5H10O5
*GALACTOS	CONV	GLUCOSE	C6H12O6
*ARABINOS	CONV	XYLOSE	C5H10O5
*GLUCAN	SOLID	CELLULOS	C6H10O5
*XYLAN	SOLID	XYLAN	C5H8O4
*GALACTAN	SOLID	CELLULOS	C6H10O5
N2	CONV	NITROGEN	N2
NO2	CONV	NITROGEN-DIOXIDE	NO2
O2S	CONV	SULFUR-DIOXIDE	O2S
*ARABINAN	SOLID	XYLAN	C5H8O4
LIGNIN	SOLID	LIGNIN-1	CXHXOX-1

Table 3.2.1: Component list (* degradables)

Component ID	Type	Component name	Formula
*ETHANOL	CONV	ETHANOL	C2H6O-2
*FURFURAL	CONV	FURFURAL	C5H4O2
*GLYCEROL	CONV	GLYCEROL	C3H8O3
CELLULOS	CONV	CELLULOS	C6H10O5
*GLUTARIC	CONV	XYLAN	C5H8O4
*DXYLOSE	CONV	XYLOSE	C5H10O5
*DEXTROSE	CONV	GLUCOSE	C6H12O6
ENZYMES	CONV	ZYMO	CHXOXNX
SILICON	CONV	SILICON-DIOXIDE	SIO2
*EXTRACT	CONV	LINOLEIC-ACID	C18H32O2
*PROT	CONV	L-GLUTAMIC-ACID	C5H9NO4
*C3H6O	CONV	PROPIONIC-ACID	C3H6O2-1
*FURFURAL	CONV	FURFURAL	C5H4O2
ENZYMES	CONV	ZYMO	CHXOXNX
H2SO4	CONV	SULFURIC-ACID	H2SO4
CA(OH)2	CONV	CALCIUM-HYDROXIDE	CA(OH)2
*NON-VOL	CONV	OLEIC-ACID	C18H34O2

Table 3.2.2: Extended component list (* degradables)

Aspen Plus requires the *pure component parameters* DHFORM (standard free energy of formation of ideal gas at 298.15 K [J/kg mole]) and DGFORM (standard heat of formation of ideal gas at 298.15 K [J/kg mole]) for the components CALDI, RHODO, PROTEIN, LIGNIN, XYLOSE, and ARABINOS, which can be found in listing A.4.1 in lines 108 to 120. The *pure component parameters* PLXANT (extended Antoine vapor pressure parameters) for the components CALDI, RHODO, PROTEIN, LIGNIN, ARABINAN, XYLAN, and GALACTAN are also required for calculation. The adjusted parameters can be found in listing A.4.1 in lines 127 to 136. The *pure component parameter* CPIG (ideal gas heat capacity coefficitents) of the component LIGNIN, in listing A.4.1 in Appendix A.4 in lines 122 to 125, has to be added to complete the required pure component input data. Parameters regarding to *binary interaction* (lines 138 to 229 in listing A.4.1) of the components, for instance the HENRY coefficients, need to be determined too. Aspen Plus provides a large collection of Henry's law constants, which are generated automatically when the appropiate property methods are used [AspenTech, 2001a]. The following *property-sets* (provided by Aspen Plus), listed in table 3.2.3, were selected for further calculations in the developed model.

Physical properties	Description	Units
COD	chemical oxygen demand for a pure component	[-]
CODMX	chemical oxygen demand for a mixture	[-]
MASSFRC	mass fraction of carbon atoms	[-]
MASSFRH	mass fraction of hydrogen atoms	[-]
MASSFRN	mass fraction of nitrogen atoms	[-]
MASSFRO	mass fraction of oxygen atoms	[-]
MASSFRS	mass fraction of sulfur atoms	[-]
MOLEFRC	mole fraction of carbon atoms	[-]
MOLEFRH	mole fraction of hydrogen atoms	[-]
MOLEFRN	mole fraction of nitrogen atoms	[-]
MOLEFRO	mole fraction of oxygen atoms	[-]
MOLEFRS	mole fraction of sulfur atoms	[-]
QVALNET	net heating value	[kJ/kg]
RELHUMID	relative humidity	[%]

Table 3.2.3: Included property-sets

3.3 Model development

A scheme of the compiled anaerobic digestion and biogas utilization model is depicted in figure 3.3.1. The model consists of two main hierarchies, first is the biogas generation hierarchy, second the biogas utilization hierarchy. When the input stream enters the model, the biogas generation is calculated in three ways, namely via COD (chemical oxygen demand), stoichiometric reactions, and Buswell´s equation. Further calculations of biogas utilization only follow the stoichiometric pathway. Three possible ways for utilization are considered, combined heat and power generation (CHP) via a gas engine, combustion at adiabatic conditions, and biogas upgrading (only minimum pretreatment of drying and desulphurization is implemented). After passing the gas engine, the output streams (heat, power, and flue gas) can further be used by integrating heat and power output into a specific process. In this way it can be assessed whether or not an integration of the biogas process (for heat recovery and power generation) into an existing process is beneficial (as shown in [Wukovits et al., 2013]). The simulation of the biogas combustion ends when the adiabatic flame temperature is calculated. The parameter *adabatic flame temperature* offers the opportunity to compare this parameter with other biogas types. After the utilization steps, figure 3.3.1 shows the outcome at the exit of the biogas model. The remaining paths are residue streams as fermentation residues, water, separated sulphur, etc.

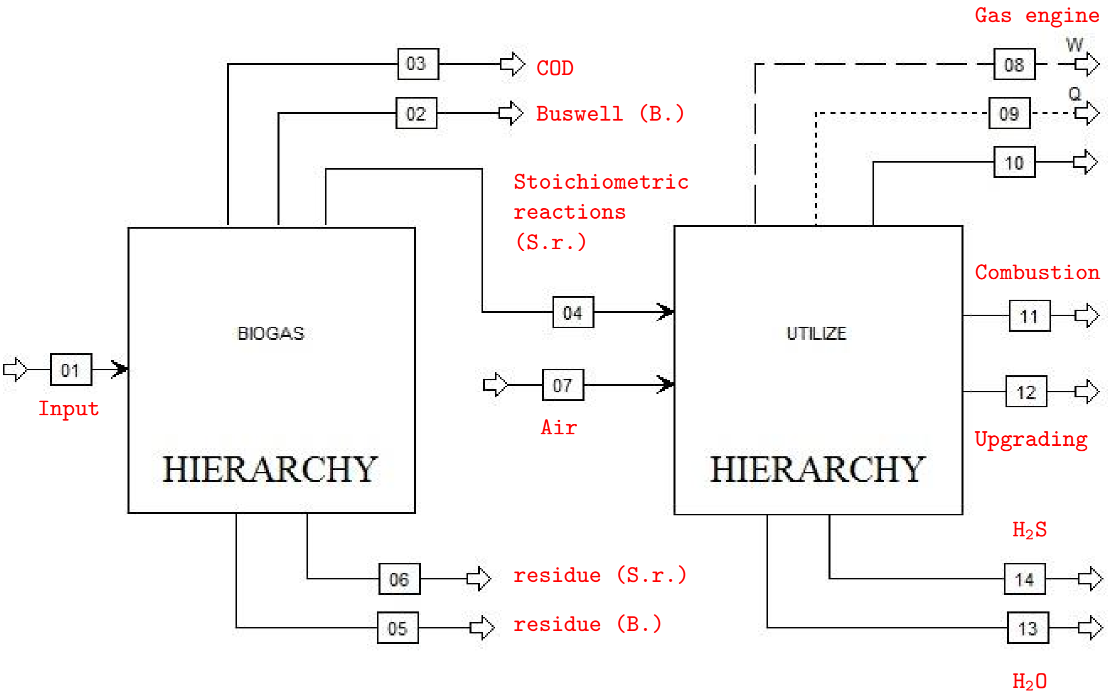

Figure 3.3.1: Hierarchies of the total flowsheet in Aspen Plus

3.4 Modeling of biogas formation

Literature provides some useful approaches for modeling biogas formation. As the aim of this thesis is to build a simple and flexible model, no chemical kinetics were included. Chemical kinetics would require informations concerning reactor design and dimension [Pröll, 2013]. [Serrano, 2011], [Gerber and Span, 2008], and [Donoso-Bravo et al., 2011] give an overview of the latest models for anaerobic digestion. Most of them are very comprehensive, like ADM1 (anaerobic digestion model no.1) [Batstone et al., 2002], [Lidholm and Ossiansson, 2008], [Kiely et al., 1997], or the model presented in [Mather, 1986]. The following sections present some fundamental and steady state approaches for biogas calculation.

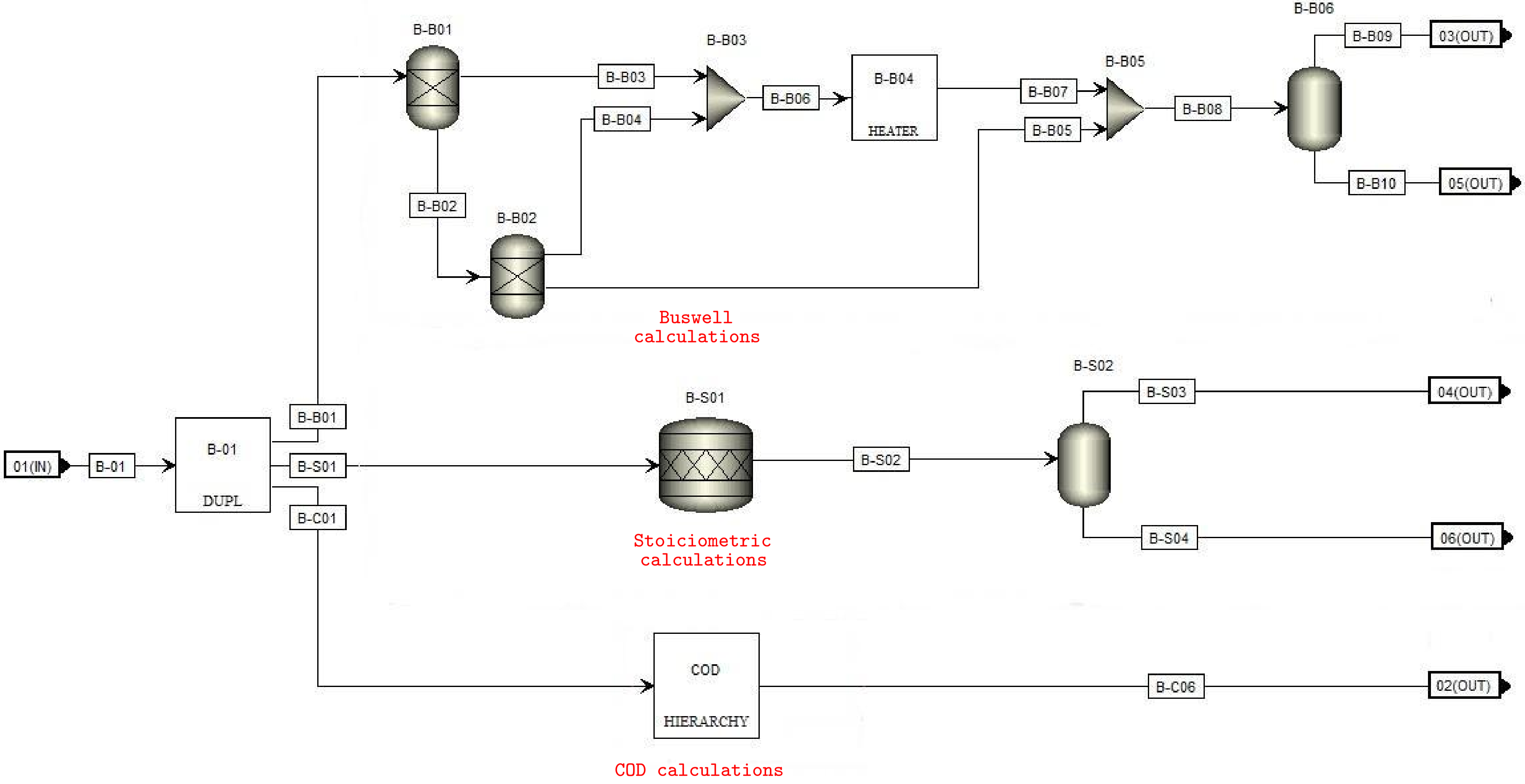

Figure 3.3.2: BIOGAS hierarchy

One approach for calculating biogas generation is via COD (chemical oxygen demand), where it is possible to calculate the amount of methane, but not the composition of biogas. Buswell´s equation [Buswell and Müller, 1952] allows to calculate the amount and composition of biogas, but only for an overall stream not considering the degradability of the components. Via stoichiometric reactions the amount and composition of the biogas, by definition of fractional conversion factors of different components, can be obtained. Fractional conversion factors for anaerobic biodegradation are listed in [J. B. Healy and Young, 1979] and [Aden et al., 2002]. Conversion data of the second study were implemented in the biogas model of [Lassmann, 2012]. Since 92 % of all biogas plants operate at mesophilic temperature conditions [Deublein and Steinhauser, 2011], the temperature of the biogas model is set to 35°C. Figure 3.3.2 illustrates the Aspen Plus model of the biogas hierarchy. The input stream *B-01* is tripled, thus streams *B-B01*, *B-S01*, and *B-C01* are identical with the global input stream *01.* The model runs for both substrates, molasses and barley straw, whose exact compositions are listed in Appendix A.1. After that, each stream follows its calculation path described in detail below.

3.4.1 Chemical Oxygen Demand COD

Due to the fact, that the exact chemical composition of a feedstock is rarely known, the expected methane yield can be calculated via degradation of the COD of a substrate while biogas is formed [Linke et al., 2006] and [Bischofsberger et al., 2009]. Since COD calculation does not distinguish between degradable and non-degradable components, it has to be handled with particular caution. However, Aspen Plus provides a *property set* called *CODMX* (chemical oxygen demand of a mixture) which calculates the theoretical oxygen demand (kg O_2/kg feedstock; equal to the chemical oxygen demand) of a chemical substance $C_CH_HCl_{Cl}N_NNa_{Na}O_OP_PS_S$ or stream of molecular weight MW with a defined composition [AspenTech, 2013].

The mass flow of methane can be easily obtained from equation 3.4.1 based on COD, the mass flow of feedstock and a stoichiometric factor of 0.25 obtained from oxygen demand of chemical oxidation of methane (0.25 kg CH_4 are oxidized by 1 kg O_2 [Wang et al., 2010]). The calculator block of the COD based biogas model can be easily connected to any process stream to analyze its biogas potential.

$$\text{mass flow}(\mathrm{CH_4}) = 0.25 \cdot \text{mass flow}(\text{feedstock}) \cdot CODMX \tag{3.4.1}$$

As mentioned before, in the Aspen Plus model for biogas production only degradable components are considered to be converted to methane. Therefore, a split unit *B-C01* is used to separate degradable (stream *B-C02*) from non-degradable components (stream *B-C03*). COD calculation is implemented with a FORTRAN code in *calculator block* COD. The methane calculation on basis of COD is situated in the *COD-HIERARCHY* depicted in figure 3.4.1. The fact that the COD calculator block can calculate methane output at any point of the flowsheet is based on the prerequisite that the input stream (into COD calculator) only contains degradable components. Otherways, methane calculation would be incorrect, as described earlier.

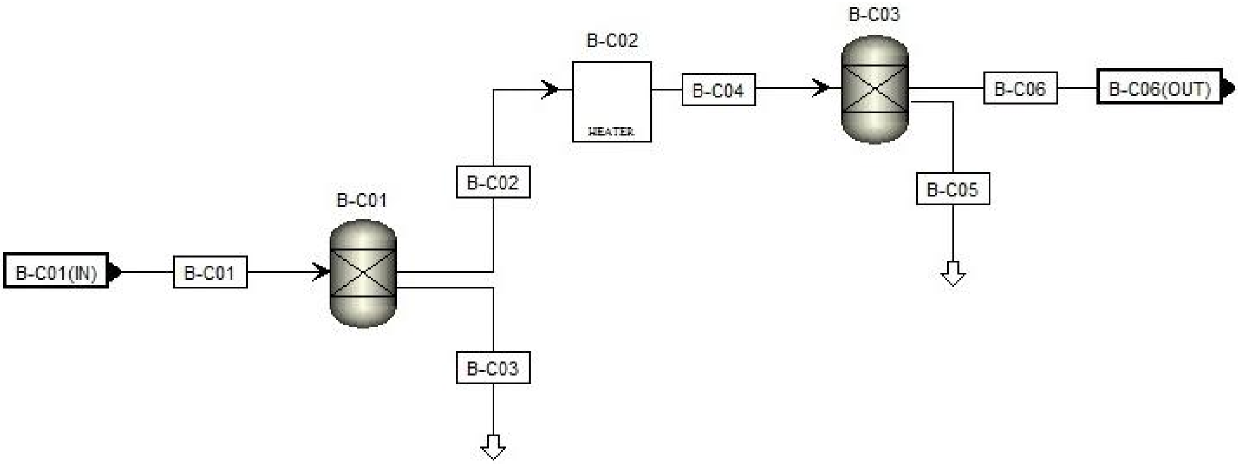

Figure 3.4.1: COD hierarchy

In Appendix A.4, lines 786 to 829 show variable definitions and lines 830 to 850 the FORTRAN code, which is also depicted in listing 3.4.1. In order to fulfill mass balance, all components have to be set to zero at the output (stream *B-C04*) of calculator block *B-C02*. Calculation of the CO_2 flow (stream *B-C05*) is a fake stream which stands for all biogas components except CH_4. It is splitted off from the methane flow (stream *B-C06*) and further not taken into account.

```
830 F     O2BEDARF = CODMX*MASSFLOW
    F
    F     CH4 = O2BEDARF*0.25
    F
    F     GLUCOSE = 0
835 F     SUCROSE = 0
    F     HAC = 0
    F     PECTINE = 0
    F     PROTEIN = 0
    F     XYLOSE = 0
840 F     GALACTOS = 0
    F     ARABINOS = 0
    F     GLUCAN = 0
    F     XYLAN = 0
    F     ARABINAN = 0
845 F     GALACTAN = 0
    F     ASH = 0
    F     LIGNIN = 0
    F     WATER = 0
    F
850 F     CO2 = MASSFLOW - CH4
```

Listing 3.4.1: FORTRAN code of COD calculator block

In order to evaluate the developed model in chapter 4.1, the original FORTRAN code has therefore to be extended to include components listed in table 3.2.2 according to listing 3.4.2.

```
F
F     ETOH = 0
F     FURFURAL = 0
F     GLYCEROL = 0
F     GLUTARIC = 0
F     DXYLOSE = 0
F     DEXTROSE = 0
F     EXTRACT = 0
F     PROT = 0
F     C3H6O = 0
F
```

Listing 3.4.2: Additional definitions and FORTRAN code of adapted COD calculator block

3.4.2 Buswell´s equation

If the chemical composition of a degradable steam is known, [Buswell and Müller, 1952] provide a formula for calculating methane and carbon dioxide yield with a uncertainty of about 5 %. The empirical equation 3.4.2 takes only carbon, hydrogen, and oxygen atoms into account.

$$\mathrm{C_cH_hO_o} + \left(\mathrm{c} - \frac{\mathrm{h}}{4} - \frac{\mathrm{o}}{2}\right)\mathrm{H_2O} \rightarrow \left(\frac{\mathrm{c}}{2} - \frac{\mathrm{h}}{8} + \frac{\mathrm{o}}{4}\right)\mathrm{CO_2} + \left(\frac{\mathrm{c}}{2} + \frac{\mathrm{h}}{8} - \frac{\mathrm{o}}{4}\right)\mathrm{CH_4} \tag{3.4.2}$$

A more comprehensive approach based on Buswell´s equation was publisherd by [Boyle, 1976] and can also be found in [Jördening and Winter, 2005]. This approach additionally includes nitrogen and sulphur atoms and will further be used for calculation.

$$\begin{aligned} \mathrm{C_cH_hO_oN_nS_s} + \left(\mathrm{c} - \frac{\mathrm{h}}{4} - \frac{\mathrm{o}}{2} + \frac{3\,\mathrm{n}}{4} + \frac{\mathrm{s}}{2}\right)\mathrm{H_2O} \rightarrow \left(\frac{\mathrm{c}}{2} - \frac{\mathrm{h}}{8} + \frac{\mathrm{o}}{4} + \frac{3\,\mathrm{n}}{8} + \frac{\mathrm{s}}{4}\right)\mathrm{CO_2} \\ + \left(\frac{\mathrm{c}}{2} + \frac{\mathrm{h}}{8} - \frac{\mathrm{o}}{4} - \frac{3\,\mathrm{n}}{8} - \frac{\mathrm{s}}{4}\right)\mathrm{CH_4} + \mathrm{n}\cdot\mathrm{NH_3} + \mathrm{s}\cdot\mathrm{H_2S} \end{aligned} \tag{3.4.3}$$

[Weissbach, 2009] gives a review on stoichiometric gas production potentials of a multitude of compounds calculated according to Buswell´s equation, assuming total degradation. When dealing with 1 mole of a pure component - like for instance glucose - equation 3.4.3 is easy to handle, due to stoichiometric coefficients c, h, o, n, and s are defined and known. When dealing with more than 1 mole (mole flow in this models case), this is taken into account by multiplying the stoichiometric coefficients with the mole flow. Since the input stream is a combination of pure components, an overall pseudo-component can be formed. The difficulty is to create pseudo stoichiometric coefficients. Therefore a complex calculation, considering the mole flows and the stoichiometric coefficients of the individual components, has to be performed. These calculations are implemented with a FORTRAN code in a calculator block BUSWELL. In Appendix A.4, lines 644 to 730 show variable definitions and lines 731 to 778 the FORTRAN code, which is also pictured in listing 3.4.3.

```
    F
    C   CALCULATION OF THE COEFFICIENT FOR CHEMICAL FORMULA OUT
730 C   OF EMPIRICAL FORMULA
    F
    F     XXC  = 5*GLU+12*SUC+2*HA+6*PEC+PRO+5*XYL+6*GAL+5*ARA+6*GLN
    F     XC   = (XXC+5*XYN+6*GAN+5*ARN)*0.95
    F     XXH  = 10*GLU+22*SUC+4*HA+10*PEC+1.57*PRO+10*XYL
735 F     XH   = XXH+12*GAL+10*ARA+10*GLN+8*XYN+10*GAN+8*ARN
    F     XXO  = 5*GLU+11*SUC+2*HA+5*PEC+0.31*PRO+5*XYL+6*GAL
    F     XO   = XXO+5*ARA+5*GLN+4*XYN+5*GAN+4*ARN
    F     XN   = 0.29*PRO
    F     XS   = 0.007*PRO
740 F
    F     MOLE = XC+XH+XO+XN+XS
    F     FACTOR = MOLE/(GLU+SUC+HA+PEC+PRO+XYL+GAL+ARA+GLN+XYN+GAN+ARN)
    F
    C   CALCULATION OF MOLEFLOWS OF THE BIOGAS
745 F
    F     CMOL = MOLEFRC*MOLEFLOW*FACTOR
    F     HMOL = MOLEFRH*MOLEFLOW*FACTOR
    F     OMOL = MOLEFRO*MOLEFLOW*FACTOR
    F     NMOL = MOLEFRN*MOLEFLOW*FACTOR
750 F     SMOL = MOLEFRS*MOLEFLOW*FACTOR
    F
    F     CO2 = ((CMOL/2)-(HMOL/8)+(OMOL/4)+(3/8)*NMOL +(SMOL/4))
    F     CH4 = ((CMOL/2)+(HMOL/8)-(OMOL/4)-(3/8)*NMOL -(SMOL/4))
    F     NH3 = NMOL
755 F     H2S = SMOL
    F
    C   MASS BALANCE
    F
    F     GLUCOSE = 0
760 F     SUCROSE = 0
    F     HAC = 0
    F     PECTINE = 0
    F     PROTEIN = 0
    F     XYLOSE = 0
765 F     GALACTOS = 0
    F     ARABINOS = 0
    F     GLUCAN = 0
    F     XYLAN = 0
    F     ARABINAN = 0
770 F     GALACTAN = 0
    F     H2O = MASSFLOW-(CO2*MWCO2)-(CH4*MWCH4)-(NH3*MWNH3)-(H2S*MWH2S)
    F
    C   FORMATION OF BIOMASS
    F
775 F     CALDI = CALDIMOL*1.05
    F     RHODO = RHODOMOL*1.05
    F
```

Listing 3.4.3: FORTRAN code of BUSWELL calculator block

In listing 3.4.3, lines 733, 735, 737, 738, and 739 relate stoichiometric coefficients with the mole flows of the pure components. Line 741 summarizes all moles and line 742 devides this moles by the sum of all moleflows, by forming the socalled FACTOR. In order to finally create the pseudo stoichiometric coefficients (CMOL, HMOL, OMOL, NMOL, and SMOL in lines 746 to 750), this FACTOR has to be multiplied with the mole fractions of the individual atoms and the mole flow of the dry stream of degradable components (stream *B-B03*).

In order to evaluate the developed model in chapter 4.1, the original FORTRAN code has therefore to be extended to include components listed in table 3.2.2 according to listing 3.4.4.

```
C    CALCULATION OF THE COEFFICIENT FOR CHEMICAL FORMULA OUT
C    OF EMPIRICAL FORMULA
F
F      XXXC = 5*GLU+12*SUC+2*HA+6*PEC+PRO+5*XYL+6*GAL+5*ARA+6*GLN
F      XXC  = XXXC+2*ETO+5*FUR+3*GOL+5*GRC+5*DXY+6*DEX+18*EXT+5*POT+3*C3H
F      XC   = (XXC+5*XYN+6*GAN+5*ARN)*0.95
F
F      XXXH = 10*GLU+22*SUC+4*HA+10*PEC+1.57*PRO+10*XYL+6*C3H
F      XXH  = XXXH+6*ETO+4*FUR+8*GOL+8*GRC+10*DXY+12*DEX+32*EXT+9*POT
F      XH   = XXH+12*GAL+10*ARA+10*GLN+8*XYN+10*GAN+8*ARN
F
F      XXXO = 5*GLU+11*SUC+2*HA+5*PEC+0.31*PRO+5*XYL+6*GAL
F      XXO  = XXXO+ETO+2*FUR+3*GOL+4*GRC+5*DXY+6*DEX+2*EXT+4*POT+2*C3H
F      XO   = XXO+5*ARA+5*GLN+4*XYN+5*GAN+4*ARN
F
F      XN   = 0.29*PRO+POT
F
F      XS   = 0.007*PRO
F
F      MOLE = XC+XH+XO+XN+XS
F
F      SUM1 = GLU+SUC+HA+PEC+PRO+XYL+GAL+ARA+GLN+XYN+GAN+ARN
F      SUM  = SUM1+ETO+FUR+GOL+GRC+DXY+DEX+EXT+POT+C3H
F
F      FACTOR = MOLE/SUM
F
C    CALCULATION OF MOLEFLOWS OF THE BIOGAS
F
F      CMOL = MOLEFRC*MOLEFLOW*FACTOR
F      HMOL = MOLEFRH*MOLEFLOW*FACTOR
F      OMOL = MOLEFRO*MOLEFLOW*FACTOR
F      NMOL = MOLEFRN*MOLEFLOW*FACTOR
F      SMOL = MOLEFRS*MOLEFLOW*FACTOR
F
F      CO2 = ((CMOL/2)-(HMOL/8)+(OMOL/4)+(3/8)*NMOL +(SMOL/4))
F      CH4 = ((CMOL/2)+(HMOL/8)-(OMOL/4)-(3/8)*NMOL -(SMOL/4))
F      NH3 = NMOL
F      H2S = SMOL
F
C    MASS BALANCE
F
F      GLUCOSE = 0
F      SUCROSE = 0
F      HAC = 0
F      PECTINE = 0
F      PROTEIN = 0
F      XYLOSE = 0
F      GALACTOS = 0
F      ARABINOS = 0
F      GLUCAN = 0
F      XYLAN = 0
F      ARABINAN = 0
F      GALACTAN = 0
F      ETOH = 0
F      FURFURAL = 0
F      GLYCEROL = 0
F      GLUTARIC = 0
F      DXYLOSE = 0
F      DEXTROSE = 0
F      EXTRACT = 0
F      PROT = 0
F      C3H6O = 0
F
F      H2O = MASSFLOW-(CO2*MWCO2)-(CH4*MWCH4)-(NH3*MWNH3)-(H2S*MWH2S)
F
C    FORMATION OF BIOMASS
F
F      CALDI = CALDIMOL*1.05
F      RHODO = RHODOMOL*1.05
```

Listing 3.4.4: Additional definitions and FORTRAN code of adapted BUSWELL calculator block

After creating this pseudo stoichiometric coefficients, calculation of amount and composition of the biogas according to equation 3.4.3 can be performed. In order to fulfill mass balance, all components have to be set to zero at the output (stream *B-B07*) of calculator block *B-B04*. Calculator block *B-B04* includes in line 733, 775, and 776 carbon conversion of anaerobic digestion. According to [Jördening and Winter, 2005] 1 unit of substrate carbon is used to form 0.95 units of CH_4 and CO_2. Only 0.05 units of substrate carbon is converted to biomass. Section 2.1 describes this occurence in detail. The calculation of biogas includes, as told before, mole fractions of the individual atoms which are considered in equation 3.4.3. The mole fractions are provided by the property sets called MOLEFRC, MOLEFRH, MOLEFRO, MOLEFRN, and MOLEFRS. In order to calculate these mole fractions properly, all non-degradable components inclusive water have to be splitted off in block *B-B01*. The mole fractions refer to stream *B-B04*. Since Buswell´s equation involves water for biogas formation, component H_2O is conducted back after the mole fraction calculation via block *B-B02*. After bringing together all streams in block *B-B05*, the biogas is separated from the liquid residues by a flash-unit (block *B-B06*) which operates at 10 °C, separating biogas from residues. The buswell model pathway is depicted in figure 3.3.2.

3.4.3 Stoichiometric reactions

Calculating the amount and composition of biogas via stoichiometric reactions is represented by degradation reactions for each component of the feedstock. The chemical reactions of the stoichiometric model are based on Buswell´s equation 3.4.3. There is also the option of implementing stoichiometric reactions from literature like [Deublein and Steinhauser, 2011],[Gavala et al., 2003], and [Aden et al., 2002] (as was the case in [Lassmann, 2012]). Fractional conversion factors for each component can be defined, considering input from experiments or literature. In order to keep the model simple, no fractional conversion factors are implemented in this model. [Aden et al., 2002] provides comprehensive data according to reactions and fractional conversions in fermentation. Based on the reactions defined in table 3.4.1, it is possible to calculate the amount and composition of a biogas stream.

Rxn #	Stoichiometry	fractional conversion	of component
1	GLUCOSE → 3 CO_2 + 3 CH_4	1	GLUCOSE
2	SUCROSE + H_2O → 6 CO_2 + 6 CH_4	1	SUCROSE
3	HAC → CO_2 + CH_4	1	HAC
4	PECTINE + H_2O → 3 CO_2 + 3 CH_4	1	PECTINE
5	PROTEIN + 0.6735 H_2O → 0.4918 CO_2 + 0.5083 CH_4 + 0.29 NH_3 + 0.007 H_2S	1	PROTEIN
6	XYLOSE → 2.5 CO_2 + 2.5 CH_4	1	XYLOSE
7	GALACTOS → 3 CO_2 + 3 CH_4	1	GALACTOS
8	ARABINOS → 2.5 CO_2 + 2.5 CH_4	1	ARABINOS
9	GLUCAN + H_2O → 3 CO_2 + 3 CH_4	1	GLUCAN
10	XYLAN + H_2O → 2.5 CO_2 + 2.5 CH_4	1	XYLAN
11	GALACTAN + H_2O → 3 CO_2 + 3 CH_4	1	GALACTAN
12	ARABINAN + H_2O → 2.5 CO_2 + 2.5 CH_4	1	ARABINAN

Table 3.4.1: Stoichiometric reactions included in block *B-S01*

In order to evaluate the developed model in chapter 4.1, the original stoichiometric reactions have therefore to be extended to include components listed in table 3.2.2 according to table 3.4.2.

Rxn #	Stoichiometry	fractional conversion	of component
13	ETHANOL $\rightarrow$ 5 CO_2 + 1.5 CH_4	0.9	ETHANOL
14	FURFURAL + 3 H_2O $\rightarrow$ 2.5 CO_2 + 2.5 CH_4	0.9	FURFURAL
15	GLYCEROL $\rightarrow$ 1.25 CO_2 + 0.5 H_2O + 1.75 CH_4	0.9	GLYCEROL
16	GLUTARIC + H_2O $\rightarrow$ 2.5 CO_2 + 2.5 CH_4	0.5	GLUTARIC
17	DXYLOSE $\rightarrow$ 2.5 CO_2 + 2.5 CH_4	0.9	DXYLOSE
18	DEXTROSE $\rightarrow$ 3 CO_2 + 3 CH_4	1	DEXTROSE
19	EXTRAKT + 9 H_2O $\rightarrow$ 5.5 CO_2 + 12.5 CH_4	0.5	EXTRACT
20	PROT + 1.5 H_2O $\rightarrow$ 2.75 CO_2 + 2.25 CH_4	0.9	PROT
21	C3H6O + 0.5 H_2O $\rightarrow$ 1.25 CO_2 + 1.75 CH_4	1	C3H6O

Table 3.4.2: Additional stoichiometric reactions

This pathway for calculating biogas is very simple, because no non-degradable components have to be splitted off. However, the reaction has to be defined for each degradable component. The input stream *B-S01* enters the stoichiometric reactor block *B-S01* (represented by *RStoic* unit operation model supplied by Aspen Plus). After reacting to biogas according to table 3.4.1, biogas and fermentation residue enter a flash unit (block *B-S02*) which operates at 10 °C, separating biogas from liquid fractions. Stream *B-S03* has been selected for further calculations in hierarchy UTILIZATION. The stoichiometric model pathway is depicted in figure 3.3.2.

3.5 Modeling of biogas utilization

For the purpose of biogas utilization three paths are included into the biogas utilization model, namely biogas combustion forming hot flue gas, combined heat and power generation by means of a gas engine, and a third path which could further be used for biogas upgrading. Figure 3.5.1 pictures the biogas utilization hierarchy. The cogeneration calculation route (gas engine) ends with the output streams of heat, power, and flue gas. These streams can further be used by integrating heat and power output into a specific process. In this way it can be assessed whether or not an integration of the biogas process (for heat recovery and power generation) into an existing process is beneficial (as shown in [Wukovits et al., 2013]). The simulation of combustion ends when the adiabatic flame temperature is calculated. The parameter adiabatic flame temperature offers the opportunity to compare this parameter with other biogas types.

Stream *04* turns into *U-01* by entering the UTILIZE hierarchy. The biogas has to be at least drained, cooled, dryed and cleared from the content of H_2S before utilization [Holm-Nielsen et al., 2009], because sulfur would harm the engine. At a first step H_2S is removed via a split unit *U-01* (modeled by a separator unit in Aspen Plus). A realistic desulfurization process is not implemented into this model. In a next step in block *U-03* a flash model is implemented (at temperature level of 10 °C) to adjust an appropriate dew point. After that pretreatment of the biogas, the stream *U-07* is multiplied in order to calculate the two possible pathways. For both utilization routes, combustion and cogeneration an air stream is required. The combustion air in this model is consisting of 79 mole % N_2 and 21 mole % O_2, whereby N_2 is treated as inert. Gaseous fuels burn at near stoichiometric conditions, therfore a low excess air is required. According to [Lehmann, 2000] an excess air ratio λ of 1.1 is common and sufficient. Since mole flow of the combustion air is built upon the input of biogas, calculation is implemented with a FORTRAN code in the calculator block AIR based on reactions listed in table 3.5.1.

$1\ CH_4 + 2\ O_2$	→	$1\ CO_2 + 2\ H_2O$
$1\ NH_3 + 1.75\ O_2$	→	$1\ NO_2 + 1.5\ H_2O$
$1\ H_2S + 1.5\ O_2$	→	$1\ SO_2 + 1\ H_2O$

Table 3.5.1: Oxidation reactions implemented in calculator block AIR

Appendix A.4, lines 619 to 630 show variable definitions and lines 631 to 640 the FORTRAN code, which is also pictured in listing 3.5.1. Line 628 indicates the implementation of reactions in table 3.5.1, and lines 633 and 634 the calculation of O_2 and N_2 flow forming the stream of combustion air.

```
    F      O2 = (CH4FLOW*2+NH3FLOW*1.75+H2SFLOW*1.5)
    F      N2 = O2*(0.79/0.21)
630 F
    C   Luftüberschuss von 1.1 nach Dampferzeugerpraxis - Grundl.&Betrieb
    F
    F      O2FLOW = O2*1.1
    F      N2FLOW = N2*1.1
635 F
    C   vereinfachte Luftzusammensetzung: 21% O2 + 79% N2;
    C   Luft: N2/O2 = 0.79/0.21
```

Listing 3.5.1: FORTRAN code of AIR calculator block

Combustion air also includes water in form of vapor water expressed by relative humidity. In order to meet realistic conditions, the relative humidity is set to 30 % via *design specification* RELHUM presented in listing 3.5.2. 30 % relative humidity corresponds to standard reference conditions [Jenbacher, 2006]. Listing 3.5.2 is an extract from the input summary in Appendix A.4 lines 608 to 608.

```
    DESIGN-SPEC RELHUM
        DEFINE RELHUM STREAM-PROP STREAM="UTILIZE.U-04"  &
610         PROPERTY=RELHUM
        SPEC "RELHUM" TO "30"
        TOL-SPEC "0.3"
        VARY STREAM-VAR STREAM="UTILIZE.U-03" SUBSTREAM=MIXED  &
            VARIABLE=MASS-FLOW
615     LIMITS "0.000000001" "1"
```

Listing 3.5.2: Design specification - RELHUM

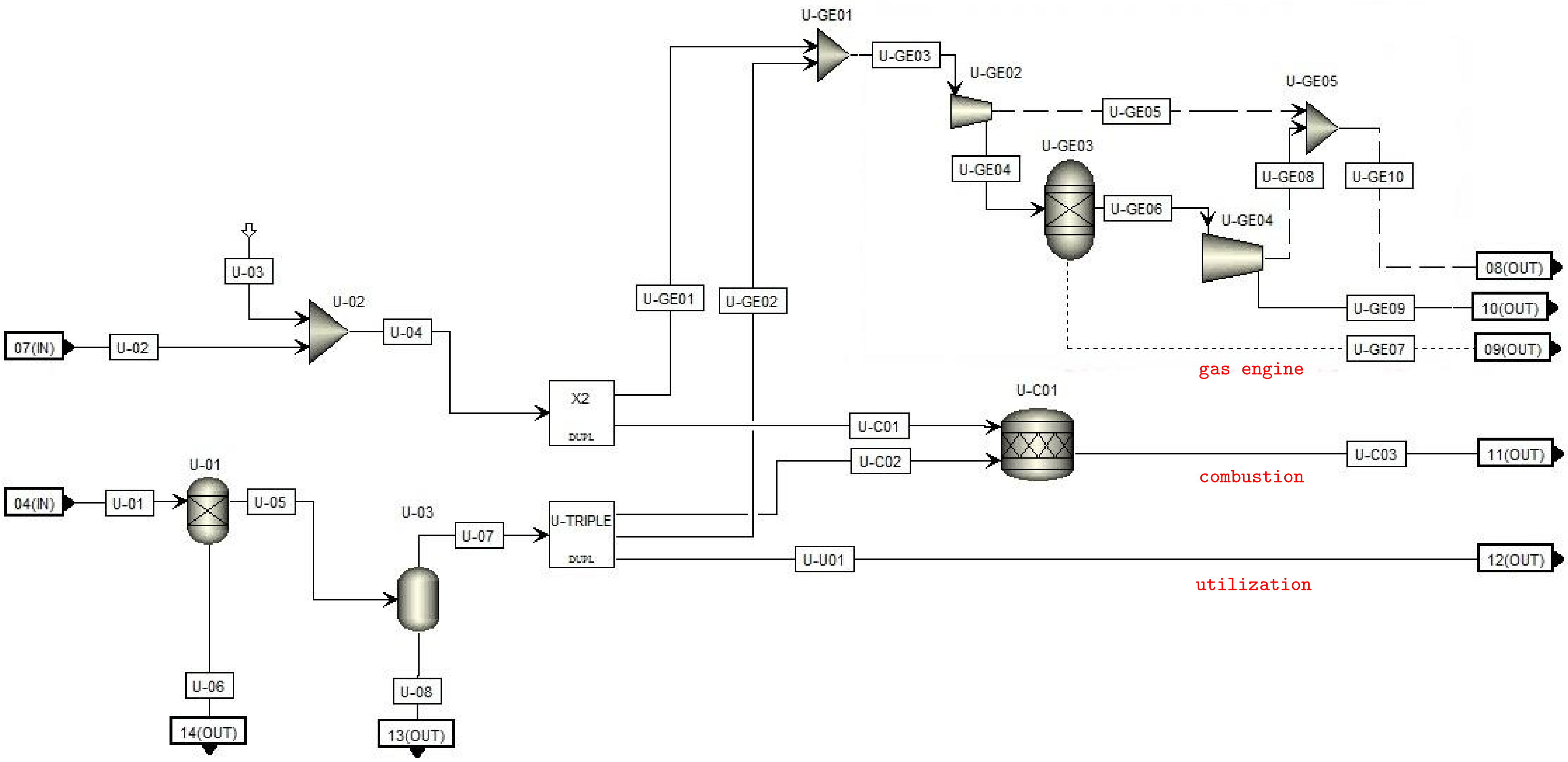

Figure 3.5.1: UTILIZE hierarchy

3.5.1 Combustion

In order to calculate the combustion process of biogas, two possibile unit operation models are available. Since Aspen Plus provides two options for simulating combustion, both were used. Unit operation model *RGibbs* calculates the combustion processes by minimizing the total Gibbs free energy, which proceedes without determining stoichiometric reactions. This method was used in [Khoshnoodi, 1995] and will also be used in section 3.5.2 for modeling cogeneration. Aspen Plus also provides the unit operation model *RStoic* including the setup-sheet *combustion* to be used for calculating combustion reactions [AspenTech, 2001d]. Aspen Plus recommends this method in [AspenTech, 2010] for modeling volatile combustion, and also in the work of [Ahrens and Weiland, 2007] *RStoic* unit operation model was selected to simulate a volatile combustion process. Hence, it is further used to model the combustion process at adiabatic conditions in order to calculate the adiabatic flame temperature. This approach also has no need to specify stoichiometry for chemical reactions, since combustion routines are generated automatically. Advantages and disadvantages of both unit operation models (RGibbs and RStoic) regarding applicability for this particular work are discussed in chapter 4.

Figure 3.5.1 pictures the combustion pathway in the biogas utilization hierarchy. The combustion air (stream *U-C01*) and the pretreated biogas (stream *U-C02*) enter the combustion unit *U-C01* where the combustion takes place. N_2 stemming from combustion air is treated as inert, but nitrogen stemming from biogas (in form of NH_3) is oxidized to NO_2. The calculation of combustion takes place at adiabatic conditions, since no heat is supplied or discharged.

3.5.2 Cogeneration - gas engine

A gas engine is an internal combustion engine and works on the principle of the Otto Cycle. The process is described by the cyclic steps pictured in the temperature - entropy diagram 3.5.2 and also represented in the Aspen model in figure 3.5.1.

An ideal Otto cycle starts at point *1* in figure 3.5.2 where the cylinder is filled up with a combustible mixture at ambient conditions. The mixture is compressed along an isentropic line reaching point *2*. By electric ignition the pressure increases until reaching point *3*. This combustion process happens very rapidly, whereby it can be treated as an isochoric process. In order to simplify the system, it is assumed that the properties of the gas are not changing and the heat created by combustion stems from an external source. At point *3* the gas expands along an isentropic line until reaching point *4*, from where the heat exchange at isochoric conditions takes place until reaching point 1 [Mollenhauer and Tschöke, 2005].

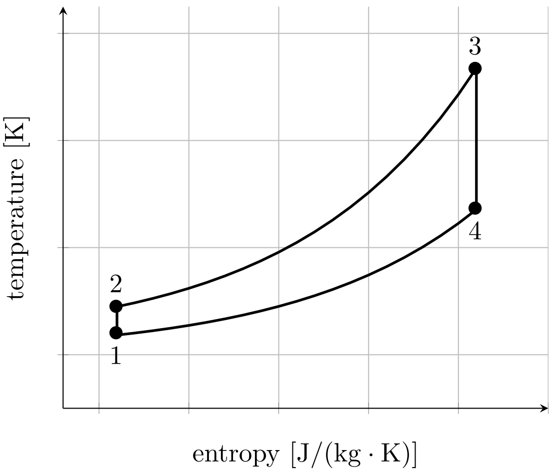

Figure 3.5.2: Temperature - entropy diagram of an idealized Otto - process

Process *(1 - 2)* in figure 3.5.2 is represented in the Aspen Plus model by a *compressor/turbine* unit operation model in compressor mode (block *U-GE02*), whereby the specifications are simply initial values. Block *U-GE03* represents the combustion process *(2 - 3)*, which is consisting of a *RGibbs* reactor unit operation model supplied by Aspen Plus. *RGibbs* minimizes Gibbs free energy, depending on atom balance constraints. Since this model does not require reaction stoichiometry, *RGibbs* can determine phase equilibrium without chemical reaction [AspenTech, 2001e]. Reactor block *U-GE03* considers all components (defined in *components - specifications*) as products, which is set in product - specification section of a *RGibbs* reactor. Process *(3 - 4)* appears in the Aspen Plus model as *compressor/turbine* unit operation model in turbine mode (block *U-GE04*). The specifications are, as in block *U-GE02*, initial values. The input data are required but are however irrelevant for the process. Heat exchange is described by process *(4 - 1)*, represented by stream *U-GE07*. Heat exchange is calculated via calculator block ENGINE, same with units compressor *U-GE02* and turbine *U-GE04*.

In order to obtain power and heat output of the gas engine, mean values of the efficiency data provided in table A.2 (electric and thermic efficiency), supplied by [Jenbacher and IWK, 2007], were calculated. This data connect energy input data of biogas with heat/power output data of the gas engine, which were implemented in calculator block ENGINE. Appendix A.4, lines 856 to 865 show variable definitions and lines 866 to 880 the FORTRAN code of ENGINE calculator block, which is also pictured in listing 3.5.3. Line 881 sets the temperature of the output stream *U-GE09* of the combustion unit to the minimum of 180 °C, which is required due to acid dew point of biogas [Jenbacher, 2006].

```
F
C    Mittelwert von elektrischem und thermischen Wirkungsgrad über
C    Leistungsbereiche von 249 - 2425 kW_el:
C    eta_el = 40.35 %
C    eta_th = 43.85 %
C    aus IWK&Jenhacher Datenblatt für Gasmotoren BHKW Module für
C    Biogas
F
F      ETAEL = 0.4035
F      ETATH = 0.4385
F
F      BE = HU*MASSFLOW*1000
F
F      CHPWORK = ETAEL*BE
F      CHPHEAT = ETATH*BE
F
F      CHPFLUE = 453.15
F
```

Listing 3.5.3: FORTRAN code of ENGINE calculator block

The biogas generation and utilization model includes features which are listed in table 3.5.2. Since Aspen Plus requires chemical component specifications, all three biogas generation routes have chemical composition as input requirement. *Buswell* and *COD calculation path* additionally require information about whether a component is degradable or not. Since stoichiometric reactions have to be defined in *stoichiometric reactions calculation route*, degradability information is integrated in this route indirectly. Conversion factors of carbon/components may be integrated in *Buswell/stoichiometric reactions calculation route*, but are not obliged. Utilization output data are accessible for *stoichiometric reactions calculation route* only, since solely this route is connected to utilization hierarchy.

	STOIC.	COD	BUSWELL
input requirements			
substrate chemical composition	x	x	x
component degradability information	(x)	x	x
additional input information			
carbon conversion factors			x
component conversion factors	x		
output features			
biogas flow rate/composition	x		x
methane flow rate/composition	x	x	x
heat/power output	x		
flue gas composition/temperature	x		

Table 3.5.2: Biogas model features

Chapter 4

Model evaluation and results

4.1 Model evaluation

Three different strategies for model evaluation are selected. On the one hand, two individual models (the model presented in this work and a model from literature) are applied to the same data set. This method provides a quantitative tool for model evaluation with respect to biogas results (see section 4.1.1). On the other hand, various feedstocks at various component concentrations are applied to this model in order to sense potential limits for biogas calculation. Since the first two strategies don´t include the evaluation of the model of biogas utilization, the third one compares the model results of the utilization hierarchy with literature data.

4.1.1 Validation modeling approach of biogas model

In order to analyse the plausibility of the developed model, data of [Lassmann, 2012] were used to compare biogas yield and composition. [Lassmann, 2012] developed a model for anaerobic digestion which is based on stoichiometric reactions and includes fractional conversion factors according to [Barta et al., 2010] listed in table A.3.3. The model splits the anaerobic digestion process into fermentation and methanogenesis. In the block fermentation the steps hydrolysis, acidogenesis, and acetogenesis are included. In this step intermediate products as propionic acid, acidic acid and hydrogen are formed, in the methanogenesis step only methane and carbon dioxide are taken into account as reaction products. Table A.3.2 shows the input data used for the calculation, which is a residual stream of an ethanol production process from lignocellulosic residues, such as wheat straw.

Since an extended component list affects biogas calculation, several additional settings have to be determined. They thermodynamic adjustments are summarized in listing A.3.1. After adapting each individual split-unit to the new component list, the new components need to be included in calculator blocks COD and BUSWELL and in the stoichiometric calculations (in form of additional stoichiometric reactions listed in table 3.4.2). The adjustments result in a comparability of the model described in [Lassmann, 2012] (hereinafter referred to as *model B*) and the model presented in present work (hereinafter referred to as *model A*). Two runs were performed, one without taking the fractional conversion factors into account, which means all fractional conversion factors equal 1, and one where they were included. Table 4.1.1 compares biogas yield and composition of model A and B by applying the same data set, with and without considering fractional conversion factors according to A.3.3. Therefore fractional conversion factors are only taken into account in the stoichiometric calculation path, (see CASE B respectively CASE G), because individual fractional conversion factors can only be implemented in stoichiometric reactors (*RSoic*) in Aspen Plus software. No biogas composition is listed in CASE E, since COD calculation path only calculates CH_4 flow rates (see CASE J).

		biogas composition in mole fraction			
model	fractional conversion	CH_4	CO_2	H_2S	NH_3
model B	acc. table 2	0.53	0.45	0.00	0.02
model A	acc. table 2	0.54	0.46	0.00	0.00
model A	1 (Stoichiometric)	0.56	0.43	0.00	0.01
model A	1 (Buswell)	0.57	0.41	0.00	0.02
model A	1 (COD)	-	-	-	-

		flow rates [kg/hr]			
model	fractional conversion	CH_4	CO_2	H_2S	NH_3
model B	acc. table 2	7100.86	16640.30	0.00	300.50
model A	acc. table 2	7099.20	16642.80	0.00	302.40
model A	1 (Stoichiometric)	9698.21	20122.10	0.00	305.74
model A	1 (Buswell)	9705.60	20098.80	0.00	324.00
model A	1 (COD)	9702.00	-	-	-

Table 4.1.1: Maximum biogas flow rate and composition of model A and B (dry basis)

Results from model evaluation based on comparison with [Lassmann, 2012] (table 4.1.1) show that different *models* (*A* and *B*) used for determining biogas composition and maximum biogas flow rate are in a good agreement with each other. Both models give comparable results for the same feedstock. Biogas flowrate obtained from *model A* (CASE G) and *B* (CASE F) are in good agreement for all biogas components. *Model B* is built up as a detailed two stage process which includes stoichiometric reactions and degradation of intermediate products as propionic acid, acidic acid, and hydrogen. Although biogas composition slightly varies depending on yields of individual biogas components, composition is situated in an average range according to table 2.3.3. However, attention is focused on methane, with regards to heat and power generation. The biogas model presented in this work provides comparable results in terms of methane yield and composition. Differences in results of *model A* and *B* stem from diverse stoichiometric reactions, whereby such good match in methane yields was unexpected. Since the degree of the correspondence between the results of model A and already evaluated *model B* is satisfying, it is assumed that present model describes the real process in a sufficient way. Since [Lassmann, 2012] does not provide any model for heat and power generation, only biogas generation model can be evaluated with this data set.

4.1.2 Identification of biogas model limits

[Foglia et al., 2011] provides data of a two-step fermentation process in order to produce biohydrogen from various biomass feedstock, which consist of four main steps: pretreatment (*PTR*), thermophilic fermentation (*TH-FERM*), photoheterotrophic fermentation (*PH-FERM*), and gas upgrading (*GAS-UPG*) as depicted in figure 4.1.1.

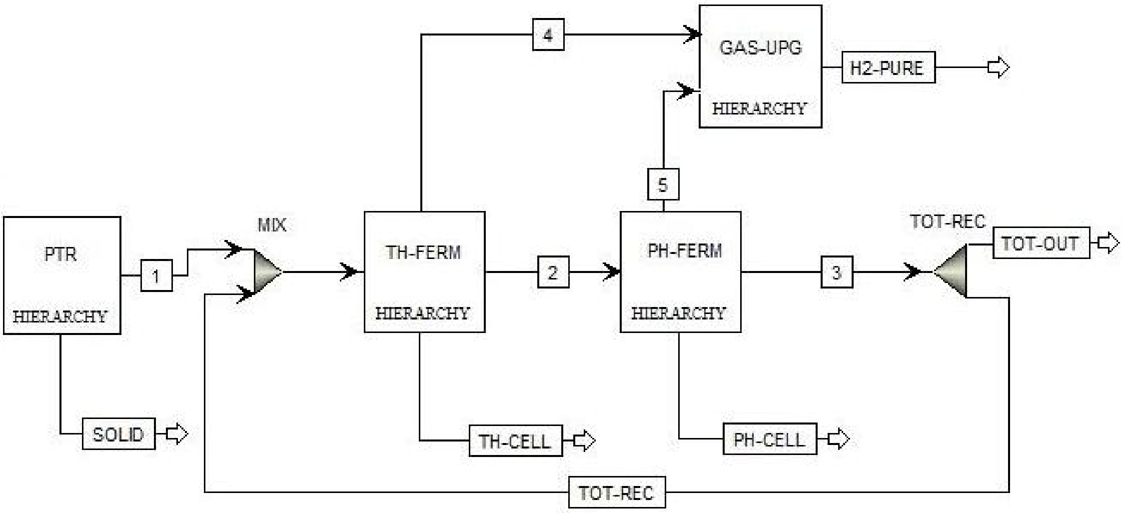

Figure 4.1.1: Scheme of biohydrogen process

Residual streams of this biohydrogen process are used to evaluate the model by applying differing feedstocks and component concentrations. Table A.3.4 summarizes the obtained residues from the biohydrogen process based on feedstock *barley straw*, *potato steam peels (PSP)*, and *thick juice*, which each consist of streams *SOLID*, *TH-CELL*, *PH-CELL*, and *TOT-OUT*. The biohydrogen process is designed to produce 2 MW thermal power (in form of biohydrogen), by an energy input of 0.92 MW for barley straw and PSP and 0.74 MW for thick juice [Foglia et al., 2011]. In a first step the residues of this biohydrogen process are applied to present biogas generation and utilization model in order to sense potential calculation limits. After that, the present model is used to calculate whether or not the heat and power demand of the biohydrogen process can be covered by utilization of produced biogas.

The original component list has therefore be extendend to include additional components listed in table 3.2.2. Since an extended component list affects biogas calculation, some additional settings have to be determined. The thermodynamic settings when applying data from [Foglia et al., 2011] are equal to the changes when applying data from [Lassmann, 2012], which are summarized in listing A.3.1. Furthermore, each individual split-unit has to be adapted to the new component list. Finally, the new components need to be included to the calculator blocks COD and BUSWELL, what is exemplarily implemented in listing 3.4.2 and 3.4.4. Also stoichiometric reactions have to be extended according to table A.3.5.

	PSP			BARLEY STRAW			THICK JUICE		
	buswell	COD	stoic.	buswell	COD	stoic.	buswell	COD	stoic.
biogas composition [mol frac]									
CH_4	0.83	1.00	0.80	0.87	1.00	0.86	0.00	1.00	0.00
CO_2	0.17	0.00	0.20	0.13	0.00	0.14	0.00	0.00	0.00
NH_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
biogas flow rate [kg/hr]									
CH_4	182	384	171	2	221	5	*0.00*	33	*0.00*
CO_2	102	0.00	110	1	0.00	2	0.00	0.00	0.00
NH_3	0.02	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00
H_2S	0.15	0.00	0.14	0.00	0.00	0.00	0.00	0.00	0.00
biogas flow rate [m^3/hr] *									
CH_4	155	326	145	2	188	4	0.00	29	0.00
CO_2	87	0.00	94	1	0.00	2	0.00	0.00	0.00
NH_3	0.02	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00
H_2S	0.1	0.00	0.1	0.00	0.00	0.00	0.00	0.00	0.00
total biogas flow rate [m^3/hr] *									
biogas	343	-	239	3	-	6	0.00	-	0.00
biogas yield [m^3/kg ODM] *									
biogas	0.15	-	0.15	0.002	-	0.005	0.00	-	0.00

Table 4.1.2: Model limits - Biogas flow rates and compositions (dry basis) (* calculated manually)

	PSP			BARLEY STRAW			THICK JUICE		
	buswell	COD	stoic.	buswell	COD	stoic.	buswell	COD	stoic.
biogas composition [mol frac]									
CH_4	0.50	1.00	0.45	0.51	1.00	0.50	0.50	1.00	0.50
CO_2	0.42	0.00	0.45	0.49	0.00	0.49	0.50	0.00	0.50
NH_3	0.078	0.00	0.098	0.00	0.00	0.01	0.00	0.00	0.00
H_2S	0.002	0.00	0.002	0.00	0.00	0.00	0.00	0.00	0.00
biogas flow rate [kg/hr]									
CH_4	401	384	383	214	221	221	32	33	33
CO_2	928	0.00	1037	559	0.00	594	88	0.00	90
NH_3	68	0.00	86	0.00	0.00	9	0.00	0.00	0.00
H_2S	4	0.00	4	0.41	0.00	0.43	0.00	0.00	0.00
biogas flow rate [m^3/hr] *									
CH_4	340	326	325	182	188	188	28	29	29
CO_2	787	0.00	879	474	0.00	504	75	0.00	77
NH_3	58	0.00	73	0.00	0.00	8	0.00	0.00	0.00
H_2S	3	0.00	3	0.4	0.00	0.4	0.00	0.00	0.00
total biogas flow rate [m^3/hr] *									
biogas	1188	-	1280	656	-	700	103	-	106
biogas yield [m^3/kg ODM] *									
biogas	0.71	-	0.77	0.52	-	0.55	0.46	-	0.47

Table 4.1.3: Model limits - Maximum biogas flow rates and compositions (dry basis) (* calculated manually)

Table 4.1.2 represents the results of the performed calculations when applying the three feedstocks *potato steam peals*, *barley straw*, and *thick juice* in sense of biogas flow rate, composition (dry basis), and yields. Since simulation software Aspen Plus has difficulties in dealing with density calculations, volume flow rate calculations were avoided during simulation. Results including volume flow rates were performed manually via recalculation of mass flow rates (calculated by Aspen Plus) by applying density data from literature (see A.3.1). Average biogas densitiy data at standard conditions are provided by [Deublein and Steinhauser, 2011], [Jensen and Jensen, 2000], and [FNR, 2006]. Volume flow rates in tables 4.1.2 and 4.1.3 are marked (*), since they are calculated manually. The biogas density lies in the area of 1.16 - 1.20 kg/m^3. The maximum biogas flow rates and relating compositions (dry basis) are summarized in table 4.1.3. Therefore calculation is interrupted before flash separation *B-B06* and *B-S02* of vapor/liquid mixture in *Buswell* and *Stoichimetric calculation path* pictured in figure 3.3.2. Since *COD calculation path* only calculates a methane flow rate, no flash unit is required and COD´s methane flow rate in table 4.1.2 represents already maximum achievable flow rate. Compared to the maximum biogas flow rate, the actual biogas flow rate is reduced by the amount of biogas which is absorbed due to vapor-liquid equilibrium. In the case where substrate is extensively diluted, vapor-liquid equilibrium has a strong influence. That´s why maximum biogas flow rate is calculated. For a comparison with literature data in 4.2, the maximum biogas flow rate has to be used, since literature does not consider strong diluted substrates.

As it can be seen, biogas compositions obtained from the different calculation routes are in good agreement with each other. In all cases almost equimolar amounts of CH_4 and CO_2 are obtained. Compared to the other feedstock options *PSP* shows a considerable high NH_3 content. No H_2S formation is observed. However, mole fractions of CH_4 are relatively low, especially when compared to *barley straw* in table 4.2.1. Since applied feedstock represents a mixture of residual streams of the originally feedstock, a comparison with literature data makes no sense.

The model evaluation applying data from [Foglia et al., 2011] is supposed to sense potential calculation limits of the described biogas model. As can be seen in table 4.1.2, the dilution rate of feedstock *thick juice* is too high in order to obtain any vapor fraction after the flash unit. Also the other feedstocks obtain only fractional amounts of the maximum achievable flow rates listied in table 4.1.3. It is shown that the flash unit marks a limit of this biogas model. The solubility of the product gas components CO_2, H_2S, or NH_3 are significantly higher than solubility of CH_4, which effects the enrichment of methane in vapor phase [Antranikian et al., 2006]. According to [Ahrens and Weiland, 2007] methane solubility in water at atmospheric pressure and 10°C amounts 0.04 L_N CH_4/kg H_2O, which is equivalent to about 3E-5 kg CH_4/kg H_2O. Carbon dioxide solubility is listed at 1.16 L_N CO_2/kg H_2O, amounting approximately 2.3E-3 kg CO_2/kg H_2O. This data are approved by [NIST, 2013]. Apart from flash separation, no other limit of presented model was detected so far.

In the work of [Wukovits et al., 2013], the utilization of process residual streams of the biohydrogen process, published in [Foglia et al., 2011], were investigated in order to cover the heat demand of the overall process via heat and power generation out of biogas. The analyses showed that residuals from barley straw and PSP seem to be promising in terms of producing additional heat from biogas and its integration with a total process. For the process with thick juice, the heat output is not sufficient to cover the total heat input in the process and additional solutions should be investigated.

4.1.3 Validation of utilization model

Since efficiency data of the simulation were set according to literature data (see [Jenbacher and IWK, 2007]), the adiabatic flame temperature, the heating value, and the flue gas composition were the only factors to consider when comparing the model to literature data. Table 4.1.4 compares utilization hierarchy results presented in table 4.2.2 with literature data according to [Khoshnoodi, 1995] (a) and [Gaydon and Wolfhard, 1979] (b) in order to evaluate the biogas utilization hierarchy of the present model. Adiabatic flame temperature of a CH_4/air mixture is calculated at a stoichiometric ratio [Khoshnoodi, 1995].

	SIMULATION		LITERATURE	
	molasses	barley straw		
adiabatic flame temp. [K]				
biogas/air	1953 - 2014	2028 - 2084	-	-
CH_4/air	2224	2224	2207 - 2225	(a) (b)
flue gas composition [mol frac]				
H_2	0.00 - 0.0003	0.00 - 0.001	0.004	(a) (b)
O_2	0.02	0.02	0.004	(a) (b)
CO_2	0.15	0.13	0.09	(a) (b)
H_2O	0.17	0.17 - 0.18	0.18	(a) (b)
N_2	0.66	0.67	0.71	(a) (b)
NO_2	0.00 - 0.003	0.00	-	-

Table 4.1.4: Comparison of utilization model results (molasses and barley straw) with literature data

The reaction of biogas and air in equillibrium at appropriate adiabatic flame temperature (at excess air ratio of 1.1) is compared with the reaction of CH_4 and air at stoichiometric conditions. Also the reaction of CH_4 and air at stoichiometric conditions is calculated with Aspen Plus. The adiabatic flame temperature of CH_4/air combustion is higher than at biogas/air combustion since CO_2, which represents the largest fraction of biogas besides CH_4, lowers heating value and thus the adiabatic flame temperature. Taking this into account, adiabatic flame temperatures go well together. The CH_4/air combustion fits perfectly with literature data. Although literature characterizes stoichimetric combustion of a CH_4/air mixture, the flue gas composition of simulation and literature are in good agreement with each other. It can be noted that created biogas utilization model pictures the real process more than sufficient.

4.2 Model results

The intention of this thesis is to present a simple and flexible model for anaerobic digestion in order to generate biogas, and for biogas utilization. For the development of the present model, two typical input compositions for the thermophilic section of a biohydrogen process have been provided. The two types of input are molasses and barley straw. Table 3.2.1 lists the components, whereby marked components (*) are considered as degradable. Input data originate from project partners of HYVOLUTION project [EU, 2010], which are in comparison to validation data in 4.1.2 no process residues but untreated molasse and pretreated barley straw.

	MOLASSES			BARLEY STRAW		
calculation model	stoic.	COD	Buswell	stoic.	COD	Buswell
block designation	*B-S01*	*B-C02*	*B-B04*	*B-S01*	*B-C02*	*B-B04*
max. biogas yield						
[kg/kg ODM]	1.10	-	1.06	0.50	-	0.43
[m^3/kg ODM]	0.94 *	-	0.90 *	0.42 *	-	0.37 *
max. CH_4 yield						
[kg/kg ODM]	0.29	0.29	0.30	0.18	0.20	0.17
[m^3/kg ODM]	0.25 *	0.25 *	0.25 *	0.16 *	0.17 *	0.15 *
heating value						
[MJ/kg]	13.46	-	14.04	18.11	-	19.85
total biogas output						
[kg/hr]	1230	-	1185	1458	-	1275
[m^3/hr]	1043 *	-	1005 *	1236 *	-	1081 *
COD [kg COD/kg input]		0.78			0.14	
biogas composition						
[mol fraction]						
CH_4	0.49	1.00	0.51	0.61	1.00	0.64
CO_2	0.48	0.00	0.47	0.38	0.00	0.35
H_2S	0.001	0.00	0.001	0.001	0.00	0.001
NH_3	0.02	0.00	0.01	0.00	0.00	0.00
H_2O	0.01	0.00	0.01	0.01	0.00	0.01
max biogas flow rates						
[kg/hr]						
CH_4	326	326	330	530	586	508
CO_2	883	-	841	917	-	756
H_2S	0	-	0	0	-	0
NH_3	14	-	7	0	-	0
H_2O	7	-	7	11	-	11
[m^3/hr]						
CH_4	453 *	453 *	458 *	736 *	814 *	706 *
CO_2	446 *	-	425 *	463 *	-	382 *
H_2S	0 *	-	0 *	0 *	-	0 *
NH_3	17 *	-	8 *	0 *	-	0 *
H_2O	9 *	-	9 *	14 *	-	14 *

Table 4.2.1: Biogas hierarchy simulation results (* calculated manually)

Table 4.2.1 summarizes results from biogas hierarchy of the model described above. As discussed in 4.1.2, results including volume flow rates were performed manually via recalculation of mass flow rates (calculated by Aspen Plus) by applying density data from literature. Flue gas density of the streams *U-GE09* and *U-C03* for molasses and barley straw (listed in table 4.2.2) is calculated using density data listed in table A.3.1. Density of flue at standard conditions were taken from [Brandt, 1999] and [Cerbe, 2008]. Since the flue gas outlet temperature of the adiabatic combustion block is equal to the adiabatic temperature, no heat and power output can be calculated. The heat and power output in table 4.2.2, marked with (**), are estimated assuming flue gas output temperature is set to 453.15 K. The amount by which the flue gas outlet temperature of the CHP caluculation is decreased (in comparison to the adiabatic flame temperature) is considered in the power output.

Aspen Plus provides two unit operation models to simulate a combustion process, which have both been used in this model. *RStoic* is less demanding, since *RGibbs* can have convergence problems if defined components are insufficient in order to meet equilibrium. Comparing flue gas composition of calculation route *adiabatic combustion* and *CHP* of molasses respectively barley straw, similar results are achieved in table 4.2.2. However, flue gas flow rates vary in terms of NO_2. This can be attributed to the difference in calculation (*stoichiometric reactions* versus *total Gibbs free energy minimization*). Also the heat an power output of the two calculation routes go well together.

	MOLASSES		BARLEY STRAW	
calculation model	adiabatic combustion	CHP	adiabatic combustion	CHP
block designation	*U-C01*	*U-GE03*	*U-C01*	*U-GE03*
total flue gas output				
[kg/hr]	7588	7588	11503	11503
[m^3/hr]	9794 *	9779 *	14625 *	14621 *
adiabatic flame temperature				
[K]	1953	2014	2028	2084
flue gas outlet temperature				
[K]	1953	453.15	2028	453.15
heat output				
[MW]	1.94 **	2.01	3.11 **	3.22
power output				
[MW]	1.78 **	1.85	2.86 **	2.96
flue gas density				
[kg/m^3]	1.29 *	1.29 *	1.27 *	1.27 *
total flue gas output				
[kg/hr]	7588	7588	11503	11503
[m^3/hr]	9794 *	9779 *	14625 *	14621 *
flue gas composition				
[mol fraction]				
H_2	0.00	0.0003	0.00	0.001
O_2	0.02	0.02	0.02	0.02
CO_2	0.15	0.15	0.13	0.13
H_2O	0.17	0.17	0.18	0.17
N_2	0.66	0.66	0.67	0.67
NO_2	0.003	0.00	0.00	0.00
flue gas flow rates				
[kg/hr]				
H_2	0	0.1	0	0.4
O_2	134	159	212	216
CO_2	1776	1776	2371	2371
H_2O	805	804	1277	1274
N_2	4838	4849	7642	7642
NO_2	35	0.02	1	0.03
[m^3/hr]				
H_2	0 *	2 *	0 *	5 *
O_2	94 *	112 *	148 *	151 *
CO_2	897 *	897 *	1198 *	1198 *
H_2O	1007 *	1005 *	1597 *	1592 *
N_2	3870 *	3879 *	6114 *	6114 *
NO_2	17 *	0 *	0 *	0 *

Table 4.2.2: Utilization hierarchy simulation results (* calculated manually)

Table 4.2.3 summarizes simulation results and literature data according to various sources of table 2.3.2 (a), [Bischofsberger et al., 2009] (b), [FNR, 2006] (c), [Vintila et al., 2012] (d), [Fang, 2010] (e), [Satyawali and Balakrishnan, 2008] (f), [Zeng, 2010] (g), and [Jördening and Winter, 2005] (h) in order to give an overview. The different methods (*COD*, *Buswell*, and *stoichiometric reactions*) used for determining biogas outcome in the biogas hierachy are in good agreement with each other. Therefore, the results of all three calculation routes are combined to one overall range in the following discussion, in order to compare them with literature data.

	SIMULATION		LITERATURE	
	molasses	barley straw		
biogas composition [vol-%]				
CH_4	49 - 51	61 - 64	45 - 88	(a)
CO_2	47 - 48	35 - 38	25 - 55	(a)
H_2O	0.01	0.01	2 - 7	(a)
NH_3	0.01 - 0.02	0	-	(a)
H_2S	0.001	0.001	0 - 1	(a)
$\mathbf{H_u}$ [MJ/kg]				
biogas	13.46 - 14.04	18.11 - 19.85	15.00 - 24.83	(a)
max. biogas yield [m^3/kg ODM]				
molasses	0.88 - 0.95	-	0.30 - 0.70	(a)
barley straw	-	0.36 - 0.43	0.25 - 0.39	(a)
max. $\mathbf{CH_4}$ **yield** [m^3/kg ODM]				
molasses	0.24 - 0.25	-	0.25 - 0.37	(b) (c)
barley straw	-	0.15 - 0.17	0.29	(d)
COD [kg COD/kg input]				
molasses	0.78	-	0.06 - 0.99	(e) (f) (g)
barley straw	-	0.14	-	-

Table 4.2.3: Comparison of biogas model results (molasses and barley straw) with literature data

Biogas composition (except the water content) lies within the average values obtained from literature. The low H_2O value stems from bypassing the flash units, since maximum biogas outcome is discussed. Biogas yields of molasses are somewhat higher than literature data, but barley straw lies right in the same area as literature data. Methane yield of molasses a comparable to literature data. Because input data for barley straw stem from a process where a pretreatment step is lokated upstream, this does not apply for barley straw. However, the lower heating value of both substrates are slightly lower than the literature data. This may be because formed biogas contains a relatively high share of CO_2 which lowers the heating value of formed biogas and rises the biogas yield. The CH_4 yield of molasses fit very well with literature data. Considering the fact that barley straw is pretreated, barley straw is in good agreement with unpretreated CH_4 yield from literature. It is difficult to make any statement on COD, since appropriate literature data are rare and diverge widely.

Chapter 5

Summary and Outlook

The intention of this thesis is to present a simple and flexible model for anaerobic digestion in order to generate biogas, and for biogas utilization. Furthermore, it should be possible to use this model to decide whether or not a process integration of a biogas process and, for instance, a biohydrogen process is beneficial in order to cover heat and power demand. It is important to notice that an economic approach is no target of this work. This model should simply calculate how much biogas out of a specific organic feedstock can be obtaind at maximum and how much heat and power can be generated by the use of a gas engine or a simple combustion step. The question which is answered in this thesis is whether or not the created model pictures biogas formation and utilization properly.

In order to achieve this target, a model for biogas generation and utilization without considering any kinetics, processes of inhibition, effects of pH or temperature, and physiochemical processes as desulphurization and dehumidification was built up. In doing so, the model keeps simple enough to meet flexibility and simplicity targets. Including these excluded effects would guide to an increase of input data that are required to run the model [Pröll, 2013]. Additionally, these data are difficult to obtain. In order to model the biological process of anaerobic digestion und utilization, two time-independent interacting submodels, describing the process of biogas generation and biogas utilization, are created.

The *biogas model*, which is a collection of simple models from literature, includes three paths - calculation via chemical oxygen demand (COD), calculation according to Buswell's equation, and implementing stoichiometric reactions. For the development of the present model, two typical input compositions for the thermophilic section of a biohydrogen process have been provided. The two types of input are molasses and barley straw (provided by [EU, 2010]). The *biogas utilization model* is located downstream the biogas generation model. For the purpose of biogas utilization three paths are included - combined heat and power generation (CHP) by means of a gas engine, a second path which could further be used for biogas upgrading, and adiabatic combustion of the generated biogas. Aspen Plus provides two unit operation models to simulate a combustion process, which have both been used in this model in oder to compare them. The biogas generation model includes stoichiometric reactions, conversion factors, and distinguishes between degradable and non-degradable components. The biogas utilization model includes humidity of combustion air, excess air ratio, Gibbs free energy minimization, and efficiency data for the gas engine. Since the model neglects several aspects, the present model provides results which must be considered as maximum possible biogas, heat, and energy yields.

For *model evaluation*, three different strategies are selected. On the one hand, two individual models (the model presented in this work and a model from literature according to [Lassmann, 2012]) are applied to the same data set. On the other hand, various feedstocks at various component concentrations (provided by [Foglia et al., 2011]) are applied to this model in order to sense potential limits for biogas calculation. The scenarios are calculated with process residues of a two-stop fermentation process. Since the first two strategies don´t include the evaluation of the utilization model, the third one compares the model results of the utilization hierarchy with literature data.

Results from model evaluation based on the *first evaluation method* show that both models give comparable results (in terms of methane) for the same feedstock. Biogas composition varies depending on yields of individual biogas components, but composition is situated in an average range according to table 2.3.3. However, this method can only be used to evaluate the biogas generation model, since heat an power generation is not considered in the model from literature.

Residual streams of a biohydrogen process (see figure 4.1.1) are used to evaluate the model (according to the *second evaluation method*) by applying differing feedstock (barley straw, potato steam peels, and thick juice) and component concentrations. In a first step the residues of this biohydrogen process are applied to the present biogas generation and utilization model in order to sense potential calculation limits. After that, the present model is used to calculate whether or not the heat and power demand of the biohydrogen process can be covered by a biogas process. It was established that the dilution rate of the applied feedstocks is too high in order to obtain the maximum achievable flow rates after the flash units (see figure 3.3.2). Hence, the flash unit marks a limit of this biogas model (when dilution rate is to high). This bottleneck can be avoided by bypassing the flash units in order to achieve maximum biogas yields. Apart from flash separation, no other limit of the presented model was detected so far. The utilization of process residual streams of the just discribed biohydrogen process in order to cover the heat demand of the overall process via heat and power generation out of biogas was established und published in [Wukovits et al., 2013]. The analyses showed that residuals from barley straw and PSP seem to be promising in terms of producing additional heat from biogas and its integration with a total process. For the process with thick juice, heat output is not sufficient to cover total heat input in the process and additional solutions should be investigated.

In order to evaluate the biogas utilization model according to the *third evaluation method*, very limited options are available. Since efficiency data of the simulation were set according to literature data (see [Jenbacher and IWK, 2007]), the adiabatic flame temperature, the heating value, and the flue gas composition were the only factors to consider when comparing the model to literature data. The adiabatic flame temperature of CH_4/air combustion is higher than at biogas/air combustion since CO_2, which represents the largest fraction of biogas besides CH_4, lowers the heating value and thus the adiabatic flame temperature. Taking this into account, adiabatic flame temperatures go well together. Comparing the flue gas compositions of the combustion of CH_4/air mixture of simulation and literature show that they are in good agreement with each other.

Comparing the results of the different methods (*COD*, *Buswell*, and *stoichiometric reactions*) used for determining the biogas outcome in the *biogas hierachy* show that they are in good agreement with each other, which leads to the conclusion that biogas generation is modeled properly. In comparison with barley straw, the biogas outcome from feedstock molasses is comparable to literature data, since no pretreatment step is located upstream. However, the biogas composition of both feedstocks (except the water content) lies within the average values obtained from literature. The CH_4 yield of molasses fits very well with literature data. Considering the fact that barley straw is pretreated, barley straw is in good agreement with CH_4 yield from literature. As the aim of this thesis is to present a simple and flexible physical model, the simulation of the biogas process has achieved this target.

Results show, that comparing the two unit operation models to simulate a combustion process in the *biogas utilization hierarchy*, leads to the conclusion that *RStoic* is less demanding, since *RGibbs* can have convergence problems if defined components are insufficient in order to meet equilibrium. Flue gas composition of calculation route *adiabatic combustion* and *CHP* of molasses respectively barley straw, show according to table 4.2.2 that similar results are achieved. However, flue gas flow rates vary in terms of NO_2, which comes from the difference in calculation (*stoichiometric reactions* versus *total Gibbs free energy minimization*). Also the heat an power output of the two calculation routes go well together.

It can be noted that the created biogas formation and utilization model pictures the real process more than sufficient. The model appears to be appropriate for a rough estimation, which was the main objective of present study. However, limitations pointed out by evaluation need to be taken into consideration and results have to be interpreted with caution.

Although the presented model provides a tool for estimating maximal biogas, heat, and power outcome out of organic feestock, the flexibility should be improved. Up to now, for each new component (means not included to the component list of the model), a list of settings have to be placed. The model could be improved when a comprehensive component list would be inplemented (including all the settings) in order to avoid this procedure for the user. Furthermore, the flash units have to be improved, since bypassing is not the proper way.

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Appendix A

A.1 Input data barley straw and molasses

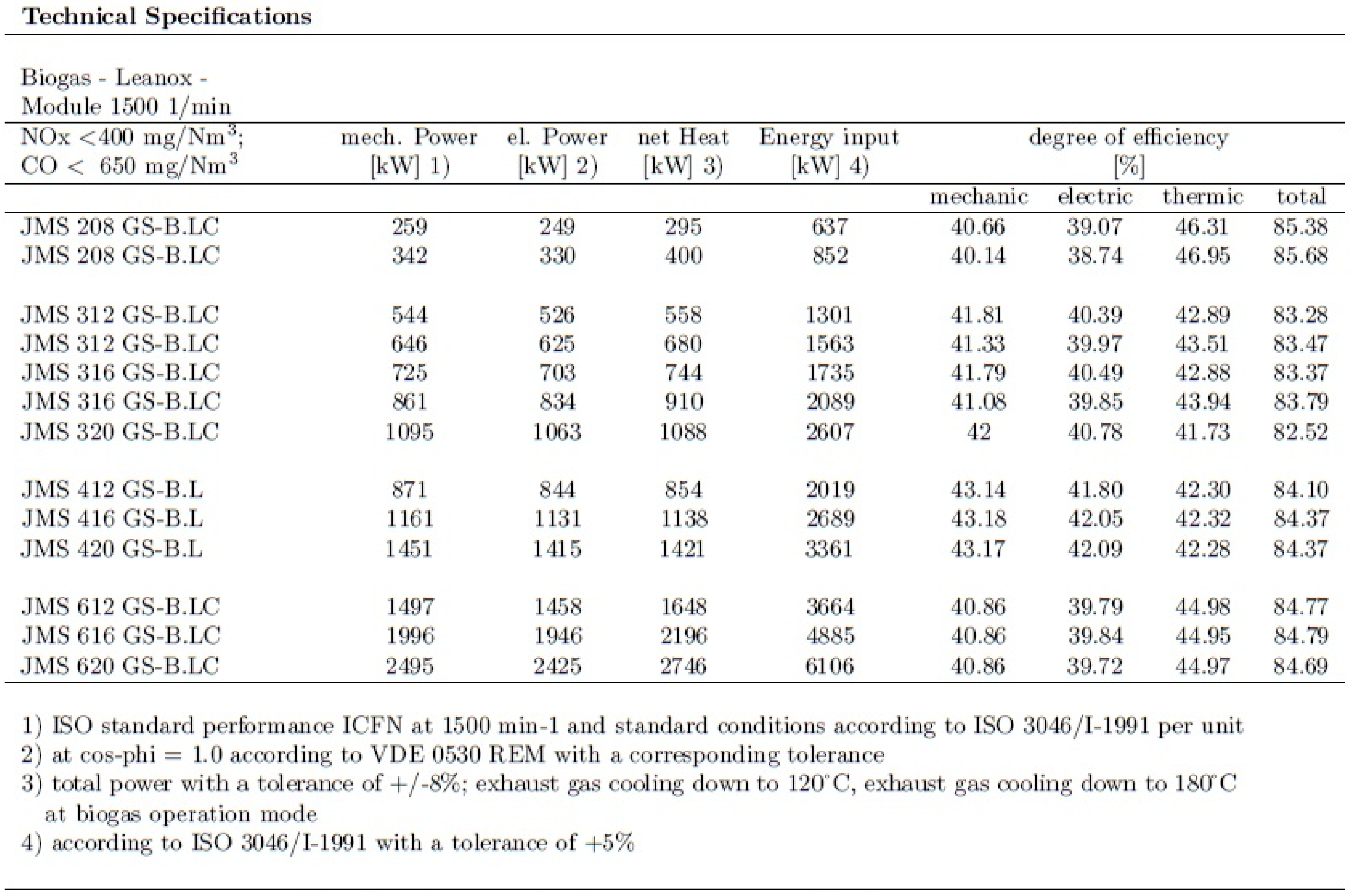
	Feedstock; Stream: TH-FEED ***molasse***			
	Substream: MIXED		Substream: CISOLID	
Temperature C				12.62
Pressure bar				1
	Mole Flow kmol/hr	Mass Flow kg/hr	Mole Flow kmol/hr	Mass Flow kg/hr
Total Flow	23.93	1204.71	9.73	467.00
H2O	21.51	387.48	0	0
GLUCOSE *	0.07	13.00	0	0
SUCROSE *	2.35	804.26	0	0
ASH-WS	0	0	3.01	168.64
PECTINE *	0	0	1.04	168.64
PROTEIN *	0	0	5.68	129.72

Table A.1.1: Input data molasses (* factored in ODM)

	Exit PRT; Stream: TH-FEED ***barley straw***			
	Substream: MIXED		Substream: CISOLID	
Temperature C				50.00
Pressure bar				1
	Mole Flow kmol/hr	Mass Flow kg/hr	Mole Flow kmol/hr	Mass Flow kg/hr
Total Flow	1817.77	33768.73	28.16	1604.41
H2O	1811.13	32627.93	0	0
GLUCOSE *	4.72	849.66	0	0
XYLOSE *	1.64	245.67	0	0
GALACTOS *	0.06	11.60	0	0
ARABINOS *	0.23	33.89	0	0
GLUCAN *	0	0	0.83	133.74
XYLAN *	0	0	1.80	238.29
GALACTAN *	0	0	0.07	11.50
ARABINAN *	0	0	0.25	32.87
LIGNIN *	0	0	6.14	752.40
PROTEIN *	0	0	19.07	435.60

Table A.1.2: Input data barley straw (* factored in ODM)

A.2 Efficiency data provided by GE Jenbacher



Technical Specifications

Biogas - Leanox - Module 1500 1/min NOx <400 mg/Nm^3; CO < 650 mg/Nm^3	mech. Power [kW] 1)	el. Power [kW] 2)	net Heat [kW] 3)	Energy input [kW] 4)	degree of efficiency [%]			
					mechanic	electric	thermic	total
JMS 208 GS-B.LC	259	249	295	637	40.66	39.07	46.31	85.38
JMS 208 GS-B.LC	342	330	400	852	40.14	38.74	46.95	85.68
JMS 312 GS-B.LC	544	526	558	1301	41.81	40.39	42.89	83.28
JMS 312 GS-B.LC	646	625	680	1563	41.33	39.97	43.51	83.47
JMS 316 GS-B.LC	725	703	744	1735	41.79	40.49	42.88	83.37
JMS 316 GS-B.LC	861	834	910	2089	41.08	39.85	43.94	83.79
JMS 320 GS-B.LC	1095	1063	1088	2607	42	40.78	41.73	82.52
JMS 412 GS-B.L	871	844	854	2019	43.14	41.80	42.30	84.10
JMS 416 GS-B.L	1161	1131	1138	2689	43.18	42.05	42.32	84.37
JMS 420 GS-B.L	1451	1415	1421	3361	43.17	42.09	42.28	84.37
JMS 612 GS-B.LC	1497	1458	1648	3664	40.86	39.79	44.98	84.77
JMS 616 GS-B.LC	1996	1946	2196	4885	40.86	39.84	44.95	84.79
JMS 620 GS-B.LC	2495	2425	2746	6106	40.86	39.72	44.97	84.69

1) ISO standard performance ICFN at 1500 min-1 and standard conditions according to ISO 3046/I-1991 per unit
2) at cos-phi = 1.0 according to VDE 0530 REM with a corresponding tolerance
3) total power with a tolerance of +/-8%; exhaust gas cooling down to 120°C, exhaust gas cooling down to 180°C at biogas operation mode
4) according to ISO 3046/I-1991 with a tolerance of +5%

Table A.2.1: Extract from delivery program 2007 Jenbacher gas engines

A.3 Model evaluation

A.3.1 Input evaluation

Average biogas densitiy data at standard conditions are provided by [Deublein and Steinhauser, 2011], [Jensen and Jensen, 2000], and [FNR, 2006]. Density of flue gas at standard conditions were taken from [Brandt, 1999] and [Cerbe, 2008].

biogas components	CH_4	0.72	kg/m^3
	CO_2	1.98	kg/m^3
	H_2S	1.53	kg/m^3
	NH_3	0.85	kg/m^3
	H_2O	0.80	kg/m^3
flue gas components	H_2	0.09	kg/m^3
	O_2	1.43	kg/m^3
	CO_2	1.98	kg/m^3
	H_2O	0.80	kg/m^3
	N_2	1.25	kg/m^3
	NO_2	2.05	kg/m^3

Table A.3.1: Density literature data of biogas and flue gas components at standard conditions

A.3.2 Input data - Validation modeling approach of biogas model

In order to analyse the plausibility of the developed model (chapter 4.1.1), data of [Lassmann, 2012] were used to compare biogas yield and composition.

Component Mass Flow		
H2O	KG/HR	220907.31
HAC	KG/HR	1965.79
CALDI	KG/HR	86.98
LIGNIN	KG/HR	648.97
ETHANOL	KG/HR	2.90
FURFURAL	KG/HR	926.99
GLYCEROL	KG/HR	264.67
CELLULOS	KG/HR	89.82
GLUTARIC	KG/HR	42.84
DXYLOSE	KG/HR	14558.76
ENZYMES	KG/HR	561.53
SILICON	KG/HR	216.33
EXTRACT	KG/HR	5768.37
PROT	KG/HR	2884.50

Table A.3.2: Input data - Validation modeling approach of biogas model

Rxn #	Stoichiometry	frac.conv.	of component
1	PROTEIN + 2 H_2O → 2 CO_2 + C_3H_6O + NH_3 + 2 H_2	0.9	PROTEIN
2	2 ETHANOL + 2 H_2O → 2 ACETAT + 4 H_2	0.9	ETHANOL
3	GLYCEROL → 1.25 CO_2 + 0.5 H_2O + 1.75 CH_4	0.9	GLYCEROL
4	CO_2 + 4 H_2 → 2 H_2O + CH_4	1	H_2
5	0.5 H_2O + C_3H_6O → 1.25 CO_2 + 1.75 CH_4	1	C_3H_6O
6	ACETAT → CO_2 + CH_4	0.9	ACETAT
7	2 XYLOSE → 5 CO_2 + 5 CH_4	0.9	XYLOSE
8	FURFURAL + 3 H_2O → 2.5 CO_2 + 2.5 CH_4	0.9	FURFURAL
9	GLUCOSE → 3 CO_2 + 3 CH_4	0.9	GLUCOSE
10	EXTRAKT + 9 H_2O → 5.5 CO_2 + 12.5 CH_4	0.5	EXTRACT
11	XYLAN + H_2O → 2.5 CO_2 + 2.5 CH_4	0.5	XYLAN

Table A.3.3: Model validation - stoichiometric reactions and fractional conversion factors

```

PROP-DATA PURE-1
    IN-UNITS MET MOLE-ENTHALP='kcal/mol'
    PROP-LIST DHFORM
    PVAL LIGNIN -217
    PVAL ENZYMES -217

PROP-DATA PURE-1
    IN-UNITS MET
    PROP-LIST DGFORM
    PVAL CALDI -200
    PVAL RHODO -200
    PVAL PROTEIN -200
    PVAL ENZYMES -200
    PVAL DXYLOSE -200

PROP-DATA DHVLWT-1
    IN-UNITS SI TEMPERATURE=C
    PROP-LIST DHVLWT
    PVAL SILICON 502 24.85 0 0 -73.15

PROP-DATA PLXANT-1
    IN-UNITS MET
    PROP-LIST PLXANT
    PVAL ENZYMES -1E20
```

Listing A.3.1: Additional thermodynamic settings of validation modeling approach of biogas model

A.3.3 Input data - Identification of biogas model limits

In order to sense potential limits for biogas calculation, data of resides of a two-step fermentation process of [Foglia et al., 2011] were used.

		Residue streams		
Component Mass Flow		PSP	Barley straw	Thick juice
H2	KG/HR	0.110	0.110	0.100
CO2	KG/HR	215.07	220.21	197.71
H2O	KG/HR	90623.65	91546.49	80697.45
GLUCOSE *	KG/HR	86.92	99.07	0
SUCROSE *	KG/HR	0	0	24.07
XYLOSE *	KG/HR	0	36.18	0
GALACTOS *	KG/HR	0	12.21	0
ARABINOS *	KG/HR	0	22.00	0
HAC *	KG/HR	55.93	105.30	50.13
KOH	KG/HR	0	0	302.94
K2HPO4	KG/HR	152.45	155.79	140.78
KH2PO4	KG/HR	119.12	121.72	110.00
GLUCAN *	KG/HR	583.20	122.63	0
XYLAN *	KG/HR	51.62	174.42	0
GALACTAN *	KG/HR	0	13.36	0
LIGNIN *	KG/HR	256.50	444.84	0
ASH-WS	KG/HR	299.26	175.59	20.59
CALDI *	KG/HR	55.56	59.03	58.47
RHODO *	KG/HR	38.70	46.27	46.51
ENZYME	KG/HR	0.81	688.72	0
KOH	KG/HR	332.71	340.46	0
PECTINE *	KG/HR	47.74	0	42.77
PROTEIN *	KG/HR	396.06	40.97	0
NH3	KG/HR	0.003	0	0
ARABINAN *	KG/HR	0.277	0	0
GALACTOS *	KG/HR	0.108	24.50	0
HCL	KG/HR	0.005	0.752	0.0004
NON-VOL *	KG/HR	0	9.76	0
FURFURAL *	KG/HR	0	60.40	0
H2SO4	KG/HR	0	20.53	0
CA(OH)2	KG/HR	0	34.06	0

Table A.3.4: Input data PSP, barley straw and thick juice - Identification of biogas model limits (* factored in ODM)

Rxn #	Stoichiometry	fractional conversion.	of component
13	FURFURAL + 3 $H_2O \rightarrow 2.5\ CO_2 + 2.5\ CH_4$	1	FURFURAL
14	NON-VOL + 3 $H_2O \rightarrow 5.25\ CO_2 + 12.75\ CH_4$	1	NON-VOL

Table A.3.5: Model validation - additional stoichiometric reactions

A.4 Input summary Aspen Plus

```
;
;Input Summary created by Aspen Plus Rel. 24.0 at 11:21:47 Wed Feb 20, 2013
;Directory C:\Users\ehilby\Desktop\Aspen Simulations Filename
;C:\Users\ehilby\AppData\Local\Temp\~ap100b.txt
;


DYNAMICS
    DYNAMICS RESULTS=ON

TITLE ’biogas + utilization’

IN-UNITS SI

DEF-STREAMS CONVEN ALL

SIM-OPTIONS
    IN-UNITS MET VOLUME-FLOW=’cum/hr’ ENTHALPY-FLO=’Gcal/hr’ &
        HEAT-TRANS-C=’kcal/hr-sqm-K’ PRESSURE=bar TEMPERATURE=C &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY=’kmol/cum’ &
        MASS-DENSITY=’kg/cum’ MOLE-ENTHALP=’kcal/mol’ &
        MASS-ENTHALP=’kcal/kg’ HEAT=Gcal MOLE-CONC=’mol/l’ &
        PDROP=bar
    SIM-OPTIONS PARADIGM=SM OLD-DATABANK=NO

DATABANKS ’NREL_DB INHSPCD’ / ’APV72 PURE24’ / ’APV72 AQUEOUS’ &
         / ’APV72 SOLIDS’ / ’APV72 INORGANIC’ / ’APV72 PURE20’ &
         / ’APV72 PURE13’ / ’APV72 COMBUST’ / ’NISTV72 NIST-TRC’ &
         / ’APV72 AQU92’ / ’APV72 ASPENPCD’ / ’APV72 ELECPURE’ &
         / ’APV72 EOS-LIT’ / ’APV72 ETHYLENE’ / ’APV72 INITIATO’ &
         / ’APV72 NRTL-SAC’ / ’APV72 PC-SAFT’ / ’APV72 POLYMER’ &
         / ’APV72 POLYPCSF’ / ’APV72 PURE10’ / ’APV72 PURE11’ &
         / ’APV72 PURE12’ / ’APV72 PURE22’ / ’APV72 PURE856’ / &
        ’APV72 PURE93’ / ’APV72 SEGMENT’ / ’FACTV72 FACTPCD’

PROP-SOURCES ’NREL_DB INHSPCD’ / ’APV72 PURE24’ / &
        ’APV72 AQUEOUS’ / ’APV72 SOLIDS’ / ’APV72 INORGANIC’ / &
        ’APV72 PURE20’ / ’APV72 PURE13’ / ’APV72 COMBUST’ / &
        ’NISTV72 NIST-TRC’ / ’APV72 AQU92’ / ’APV72 ASPENPCD’ / &
        ’APV72 ELECPURE’ / ’APV72 EOS-LIT’ / ’APV72 ETHYLENE’ / &
        ’APV72 INITIATO’ / ’APV72 NRTL-SAC’ / ’APV72 PC-SAFT’ / &
        ’APV72 POLYMER’ / ’APV72 POLYPCSF’ / ’APV72 PURE10’ / &
        ’APV72 PURE11’ / ’APV72 PURE12’ / ’APV72 PURE22’ / &
        ’APV72 PURE856’ / ’APV72 PURE93’ / ’APV72 SEGMENT’ / &
        ’FACTV72 FACTPCD’

COMPONENTS
    H2 H2 /
    O2 O2 /
    CO2 CO2 /
    H2O H2O /
    GLUCOSE C6H12O6 /
    SUCROSE C12H22O11 /
    NH3 H3N /
    HAC C2H4O2-1 /
    ASH-WS CAO /
    CALDI CHXNXOXSX-1 /
    RHODO CHXNXOXSX-1 /
    KOH KOH /
    PECTINE C6H10O5 /
    PROTEIN CHXNXOXSX-2 /
    HCL HCL /
    K2HPO4 K2HPO4 /
    KH2PO4 KH2PO4 /
    CH4 CH4 /
    H2S H2S /
    XYLOSE C5H10O5 /
```

```
    GALACTOS C6H12O6 /
    ARABINOS C5H10O5 /
    GLUCAN C6H10O5 /
    XYLAN C5H8O4 /
    GALACTAN C6H10O5 /
    N2 N2 /
    NO2 NO2 /
    O2S O2S /
    ARABINAN C5H8O4 /
    LIGNIN CXHXOX-1

HENRY-COMPS HC-1 H2 O2 CO2 NH3 HCL CH4 H2S N2 NO2 O2S

MOIST-COMPS NO2 O2S N2 CH4 H2S CO2 O2 H2 HCL

SOLVE
    PARAM

FLOWSHEET
    HIERARCHY BIOGAS
    CONNECT $C-1 IN=01 OUT="BIOGAS.B-01"
    CONNECT $C-3 IN="BIOGAS.B-B09" OUT=02
    CONNECT $C-11 IN="BIOGAS.B-S04" OUT=06
    CONNECT $C-7 IN="BIOGAS.B-S03" OUT=04
    CONNECT $C-13 IN="BIOGAS.B-B10" OUT=05
    CONNECT $C-2 IN="BIOGAS.B-C06" OUT=03
    HIERARCHY UTILIZE
    CONNECT $C-4 IN=04 OUT="UTILIZE.U-01"
    CONNECT $C-8 IN=07 OUT="UTILIZE.U-02"
    CONNECT $C-9 IN="UTILIZE.U-C03" OUT=11
    CONNECT $C-5 IN="UTILIZE.U-U01" OUT=12
    CONNECT $C-6 IN="UTILIZE.U-06" OUT=14
    CONNECT $C-10 IN="UTILIZE.U-08" OUT=13
    CONNECT $C-16 IN="UTILIZE.U-GE10" OUT=08
    CONNECT $C-15 IN="UTILIZE.U-GE09" OUT=10
    CONNECT $C-14 IN="UTILIZE.U-GE07" OUT=09

PROPERTIES NRTL
    PROPERTIES PENG-ROB / PR-BM / STEAMNBS

PROP-DATA PURE-1
    IN-UNITS MET MOLE-ENTHALP='kcal/mol'
    PROP-LIST DHFORM
    PVAL CALDI -217
    PVAL RHODO -217
    PVAL PROTEIN -217

PROP-DATA PURE-1
    IN-UNITS MET
    PROP-LIST DGFORM
    PVAL LIGNIN -200
    PVAL XYLOSE -200
    PVAL ARABINOS -200

PROP-DATA CPIG-1
    IN-UNITS SI
    PROP-LIST CPIG
    PVAL LIGNIN 207

PROP-DATA PLXANT-1
    IN-UNITS MET
    PROP-LIST PLXANT
    PVAL CALDI -1E20
    PVAL RHODO -1E20
    PVAL PROTEIN -1E20
    PVAL LIGNIN -1E20
    PVAL ARABINAN -1E20
    PVAL XYLAN -1E20
    PVAL GALACTAN -1E20

PROP-DATA HENRY-1
```

```
    IN-UNITS ENG PRESSURE=bar PDROP=psi
    PROP-LIST HENRY
    BPVAL H2 H2O 195.5318583 -12588.31790 -26.31190000 &
        8.35727785E-3 33.53000373 150.5300028 0.0
    BPVAL CH4 H2O 198.4980181 -16401.00587 -25.03790000 &
        7.96855562E-5 35.33000372 175.7300026 0.0

PROP-DATA HENRY-1
    IN-UNITS ENG
    PROP-LIST HENRY
    BPVAL O2 H2O 157.8962297 -13995.10789 -18.39740000 &
        -5.2464112E-3 33.53000373 166.7300027 0.0
    BPVAL CO2 H2O 175.2762325 -15734.78987 -21.66900000 &
        6.12550005E-4 31.73000375 175.7300026 0.0
    BPVAL NH3 H2O 94.16754801 -1974.257984 -16.56020000 &
        .0334703336 31.73000375 211.7300023 0.0
    BPVAL HCL H2O -49.78140336 2186.999983 8.370700000 &
        -5.3294445E-3 -3.999995968 68.00000346 0.0
    BPVAL H2 NH3 9.764484410 0.0 0.0 0.0 67.73000346 &
        67.73000346 0.0
    BPVAL H2 HAC 56.22730316 -843.3899933 -7.442700000 &
        6.81166672E-3 65.48000348 166.6400027 0.0
    BPVAL O2 NH3 11.20948341 0.0 0.0 0.0 67.73000346 &
        67.73000346 0.0
    BPVAL O2 HAC 10.39098341 0.0 0.0 0.0 68.00000346 &
        68.00000346 0.0
    BPVAL CO2 HAC -81.05949581 3892.140057 12.88900000 0.0 &
        64.40000348 96.80000323 0.0
    BPVAL HCL HAC 106.4952893 1846.979942 -22.59800000 &
        .0689944450 -3.999995968 122.1800030 0.0
    BPVAL H2S H2O 164.1148189 -14807.69988 -20.23070000 &
        -7.1891667E-4 31.73000375 139.7300029 0.0
    BPVAL H2S HAC 12.37018341 -3290.759885 0.0 0.0 77.00000338 &
        140.0000029 0.0

PROP-DATA NRTL-1
    IN-UNITS ENG
    PROP-LIST NRTL
    BPVAL H2O NH3 -6.268400000 2745.817718 .3000000000 0.0 0.0 &
        0.0 50.00000360 196.7000024
    BPVAL NH3 H2O 9.612100000 -5819.068573 .3000000000 0.0 0.0 &
        0.0 50.00000360 196.7000024

PROP-DATA PRKBV-1
    IN-UNITS MET DENSITY='kg/cum' ENERGY=kJ ENTHALPY='J/kmol' &
        ENTROPY='J/kmol-K' VOLUME-FLOW='cum/hr' ENTHALPY-FLO=kW &
        FORCE=Newton MOLE-HEAT-CA='kJ/kmol-K' &
        HEAT-TRANS-C='kW/sqm-K' PRESSURE=bar TEMPERATURE=C &
        THERMAL-COND='kW/m-K' VOLUME=cum DELTA-T=C HEAD=meter &
        MOLE-DENSITY='kmol/cum' MASS-DENSITY='kg/cum' &
        MOLE-ENTHALP='kJ/kmol' MASS-ENTHALP='kJ/kg' &
        MOLE-ENTROPY='kJ/kmol-K' MASS-ENTROPY='kJ/kg-K' &
        MOLE-VOLUME='cum/kmol' MASS-HEAT-CA='kJ/kg-K' UA='kJ/sec-K' &
        WORK=kJ HEAT=kJ MOLE-CONC='mol/l' &
        MASS-TRANS-C='kg/s-sqm-kg/cum' PDROP=bar &
        VOL-HEAT-CAP='kJ/cum-K' HEAT-FLUX='Watt/m' &
        VFLOW-LENGTH='sqm/hr' INVERSE-HT-C='sqm-K/kW' &
        VOL-ENTHALPY='kJ/cum' MASS-VOLUME='cum/kg'
    PROP-LIST PRKBV
    BPVAL H2 CO2 -.1622000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL CO2 H2 -.1622000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL H2 CH4 .0156000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL CH4 H2 .0156000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL CO2 H2O .1200000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL H2O CO2 .1200000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL CO2 CH4 .0919000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL CH4 CO2 .0919000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL CO2 H2S .0974000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL H2S CO2 .0974000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL H2O NH3 -.2589000000 0.0 0.0 -273.1500000 &
        726.8500000
```

```
    BPVAL NH3 H2O -.2589000000 0.0 0.0 -273.1500000 &
        726.8500000
    BPVAL H2O H2S .0400000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL H2S H2O .0400000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL H2 N2 .1030000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL N2 H2 .1030000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL O2 N2 -.0119000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL N2 O2 -.0119000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL CO2 N2 -.0170000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL N2 CO2 -.0170000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL NH3 N2 .2193000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL N2 NH3 .2193000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL CH4 N2 .0311000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL N2 CH4 .0311000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL H2S N2 .1767000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL N2 H2S .1767000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL CH4 O2S .1356000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL O2S CH4 .1356000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL N2 O2S .0800000000 0.0 0.0 -273.1500000 726.8500000
    BPVAL O2S N2 .0800000000 0.0 0.0 -273.1500000 726.8500000

PROP-SET COD
    IN-UNITS MET
    PROPNAME-LIS COD UNITS=’fraction’ SUBSTREAM=MIXED

PROP-SET CODMX
    IN-UNITS MET
    PROPNAME-LIS CODMX UNITS=’fraction’ SUBSTREAM=MIXED

PROP-SET MOLEFRC
    IN-UNITS MET
    PROPNAME-LIS MOLEFRC SUBSTREAM=MIXED

PROP-SET MOLEFRH
    IN-UNITS MET
    PROPNAME-LIS MOLEFRH SUBSTREAM=MIXED

PROP-SET MOLEFRN
    IN-UNITS MET
    PROPNAME-LIS MOLEFRN SUBSTREAM=MIXED

PROP-SET MOLEFRO
    IN-UNITS MET
    PROPNAME-LIS MOLEFRO SUBSTREAM=MIXED

PROP-SET MOLEFRS
    IN-UNITS MET
    PROPNAME-LIS MOLEFRS SUBSTREAM=MIXED

PROP-SET QVALNET QVALNET UNITS=’kJ/kg’ SUBSTREAM=MIXED

PROP-SET RELHUM
    IN-UNITS MET DENSITY=’kg/cum’ ENERGY=kJ ENTHALPY=’J/kmol’ &
        ENTROPY=’J/kmol-K’ VOLUME-FLOW=’cum/hr’ ENTHALPY-FLO=kW &
        FORCE=Newton MOLE-HEAT-CA=’kJ/kmol-K’ &
        HEAT-TRANS-C=’kW/sqm-K’ PRESSURE=bar TEMPERATURE=C &
        THERMAL-COND=’kW/m-K’ VOLUME=cum DELTA-T=C HEAD=meter &
        MOLE-DENSITY=’kmol/cum’ MASS-DENSITY=’kg/cum’ &
        MOLE-ENTHALP=’kJ/kmol’ MASS-ENTHALP=’kJ/kg’ &
        MOLE-ENTROPY=’kJ/kmol-K’ MASS-ENTROPY=’kJ/kg-K’ &
        MOLE-VOLUME=’cum/kmol’ MASS-HEAT-CA=’kJ/kg-K’ UA=’kJ/sec-K’ &
        WORK=kJ HEAT=kJ MOLE-CONC=’mol/l’ &
        MASS-TRANS-C=’kg/s-sqm-kg/cum’ PDROP=bar &
        VOL-HEAT-CAP=’kJ/cum-K’ HEAT-FLUX=’Watt/m’ &
        VFLOW-LENGTH=’sqm/hr’ INVERSE-HT-C=’sqm-K/kW’ &
        VOL-ENTHALPY=’kJ/cum’ MASS-VOLUME=’cum/kg’
    PROPNAME-LIS RELHUMID SUBSTREAM=MIXED

STREAM 01
    IN-UNITS MET
    SUBSTREAM MIXED TEMP=35. <C> PRES=1. <bar>
```

```
    MOLE-FLOW H2O 21.5081489 / GLUCOSE 0.07200359 / SUCROSE &
        2.34958753 / ASH-WS 3.00720076 / PECTINE 1.04004875 / &
        PROTEIN 5.67958513

STREAM 07
    IN-UNITS MET DENSITY='kg/cum' ENERGY=kJ ENTHALPY='J/kmol' &
        ENTROPY='J/kmol-K' VOLUME-FLOW='cum/hr' ENTHALPY-FLO=kW &
        FORCE=Newton MOLE-HEAT-CA='kJ/kmol-K' &
        HEAT-TRANS-C='kW/sqm-K' PRESSURE=bar TEMPERATURE=C &
        THERMAL-COND='kW/m-K' VOLUME=cum DELTA-T=C HEAD=meter &
        MOLE-DENSITY='kmol/cum' MASS-DENSITY='kg/cum' &
        MOLE-ENTHALP='kJ/kmol' MASS-ENTHALP='kJ/kg' &
        MOLE-ENTROPY='kJ/kmol-K' MASS-ENTROPY='kJ/kg-K' &
        MOLE-VOLUME='cum/kmol' MASS-HEAT-CA='kJ/kg-K' UA='kJ/sec-K' &
        WORK=kJ HEAT=kJ MOLE-CONC='mol/l' &
        MASS-TRANS-C='kg/s-sqm-kg/cum' PDROP=bar &
        VOL-HEAT-CAP='kJ/cum-K' HEAT-FLUX='Watt/m' &
        VFLOW-LENGTH='sqm/hr' INVERSE-HT-C='sqm-K/kW' &
        VOL-ENTHALPY='kJ/cum' MASS-VOLUME='cum/kg'
    SUBSTREAM MIXED TEMP=35. PRES=1. MASS-FLOW=1.
    MOLE-FRAC O2 0.21 / CO2 0. / N2 0.79

DEF-STREAMS HEAT 09

DEF-STREAMS WORK 08

HIERARCHY BIOGAS


DEF-STREAMS CONVEN ALL

SOLVE
    PARAM METHOD=SM
    RUN-MODE MODE=PAR

FLOWSHEET
    HIERARCHY COD
    CONNECT $C-1 IN=B-C01 OUT="COD.B-C01"
    CONNECT $C-2 IN="COD.B-C06" OUT=B-C06
    BLOCK B-S02 IN=B-S02 OUT=B-S03 B-S04
    BLOCK B-S01 IN=B-S01 OUT=B-S02
    BLOCK B-B06 IN=B-B08 OUT=B-B09 B-B10
    BLOCK B-B05 IN=B-B07 B-B05 OUT=B-B08
    BLOCK B-B04 IN=B-B06 OUT=B-B07
    BLOCK B-B01 IN=B-B01 OUT=B-B03 B-B02
    BLOCK B-01 IN=B-01 OUT=B-B01 B-S01 B-C01
    BLOCK B-B03 IN=B-B03 B-B04 OUT=B-B06
    BLOCK B-B02 IN=B-B02 OUT=B-B04 B-B05

PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES
    PROPERTIES PENG-ROB / PR-BM / STEAMNBS

STREAM B-01
    IN-UNITS MET
    SUBSTREAM MIXED TEMP=35. <C> PRES=1. <bar>
    MOLE-FLOW H2O 21.5081489 / GLUCOSE 0.07200359 / SUCROSE &
        2.34958753 / ASH-WS 3.00720076 / PECTINE 1.04004875 / &
        PROTEIN 5.67958513

BLOCK B-B03 MIXER
    IN-UNITS MET DENSITY='kg/cum' ENERGY=kJ ENTHALPY='J/kmol' &
        ENTROPY='J/kmol-K' VOLUME-FLOW='cum/hr' ENTHALPY-FLO=kW &
        FORCE=Newton MOLE-HEAT-CA='kJ/kmol-K' &
        HEAT-TRANS-C='kW/sqm-K' PRESSURE=bar TEMPERATURE=C &
        THERMAL-COND='kW/m-K' VOLUME=cum DELTA-T=C HEAD=meter &
        MOLE-DENSITY='kmol/cum' MASS-DENSITY='kg/cum' &
        MOLE-ENTHALP='kJ/kmol' MASS-ENTHALP='kJ/kg' &
        MOLE-ENTROPY='kJ/kmol-K' MASS-ENTROPY='kJ/kg-K' &
        MOLE-VOLUME='cum/kmol' MASS-HEAT-CA='kJ/kg-K' UA='kJ/sec-K' &
        WORK=kJ HEAT=kJ MOLE-CONC='mol/l' &
        MASS-TRANS-C='kg/s-sqm-kg/cum' PDROP=bar &
```

```
        VOL-HEAT-CAP=’kJ/cum-K’ HEAT-FLUX=’Watt/m’ &
        VFLOW-LENGTH=’sqm/hr’ INVERSE-HT-C=’sqm-K/kW’ &
        VOL-ENTHALPY=’kJ/cum’ MASS-VOLUME=’cum/kg’

BLOCK B-B05 MIXER
    IN-UNITS MET
    PARAM PRES=0. <bar>

BLOCK B-B01 SEP
    IN-UNITS MET
    PARAM
    FRAC STREAM=B-B03 SUBSTREAM=MIXED COMPS=H2 O2 CO2 H2O &
        GLUCOSE SUCROSE NH3 HAC ASH-WS CALDI RHODO KOH &
        PECTINE PROTEIN HCL K2HPO4 KH2PO4 CH4 H2S XYLOSE &
        GALACTOS ARABINOS GLUCAN XYLAN GALACTAN N2 NO2 O2S &
        ARABINAN LIGNIN FRACS=0. 0. 0. 0. 1. 1. 0. 1. 0. &
        0. 0. 0. 1. 1. 0. 0. 0. 0. 0. 1. 1. 1. 1. 1. &
        1. 0. 0. 0. 1. 0.

BLOCK B-B02 SEP
    IN-UNITS MET
    PARAM
    FRAC STREAM=B-B04 SUBSTREAM=MIXED COMPS=H2 O2 CO2 H2O &
        GLUCOSE SUCROSE NH3 HAC ASH-WS CALDI RHODO KOH &
        PECTINE PROTEIN HCL K2HPO4 KH2PO4 CH4 H2S XYLOSE &
        GALACTOS ARABINOS GLUCAN XYLAN GALACTAN FRACS=0. 0. &
        0. 1. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. &
        0. 0. 0. 0. 0. 0. 0. 0.

BLOCK B-B04 HEATER
    IN-UNITS MET
    PARAM TEMP=35. <C> PRES=0. <bar> NPHASE=2
    BLOCK-OPTION FREE-WATER=NO

BLOCK B-B06 FLASH2
    IN-UNITS MET
    PARAM TEMP=10. <C> PRES=0. <bar>

BLOCK B-S02 FLASH2
    IN-UNITS MET
    PARAM TEMP=10. <C> PRES=0. <bar>

BLOCK B-S01 RSTOIC
    IN-UNITS MET
    PARAM TEMP=35. <C> PRES=0. <bar>
    STOIC 1 MIXED GLUCOSE -1. / CO2 3. / CH4 3.
    STOIC 2 MIXED SUCROSE -1. / H2O -1. / CO2 6. / CH4 &
        6.
    STOIC 3 MIXED HAC -1. / CO2 1. / CH4 1.
    STOIC 4 MIXED PECTINE -1. / H2O -1. / CO2 3. / CH4 &
        3.
    STOIC 7 MIXED PROTEIN -1. / H2O -0.6735 / CO2 0.49175 / &
        CH4 0.50825 / NH3 0.29 / H2S 0.007
    STOIC 8 MIXED XYLOSE -1. / CO2 2.5 / CH4 2.5
    STOIC 9 MIXED GALACTOS -1. / CO2 3. / CH4 3.
    STOIC 10 MIXED ARABINOS -1. / CO2 2.5 / CH4 2.5
    STOIC 11 MIXED GLUCAN -1. / H2O -1. / CO2 3. / CH4 &
        3.
    STOIC 12 MIXED XYLAN -1. / H2O -1. / CO2 2.5 / CH4 &
        2.5
    STOIC 13 MIXED GALACTAN -1. / H2O -1. / CO2 3. / CH4 &
        3.
    STOIC 5 MIXED ARABINAN -1. / H2O -1. / CO2 2.5 / CH4 &
        2.5
    CONV 1 MIXED GLUCOSE 1.
    CONV 2 MIXED SUCROSE 1.
    CONV 3 MIXED HAC 1.
    CONV 4 MIXED PECTINE 1.
    CONV 7 MIXED PROTEIN 1.
    CONV 8 MIXED XYLOSE 1.
    CONV 9 MIXED GALACTOS 1.
```

```
    CONV 10 MIXED ARABINOS 1.
    CONV 11 MIXED GLUCAN 1.
    CONV 12 MIXED XYLAN 1.
    CONV 13 MIXED GALACTAN 1.
    CONV 5 MIXED ARABINAN 1.
    PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 &
        TRUE-COMPS=YES

HIERARCHY COD


DEF-STREAMS CONVEN ALL

SOLVE
    PARAM METHOD=SM
    RUN-MODE MODE=PAR

FLOWSHEET
    BLOCK B-C01 IN=B-C01 OUT=B-C02 B-C03
    BLOCK B-C02 IN=B-C02 OUT=B-C04
    BLOCK B-C03 IN=B-C04 OUT=B-C06 B-C05

PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES
    PROPERTIES PENG-ROB / PR-BM / STEAMNBS

BLOCK B-C01 SEP
    IN-UNITS MET
    PARAM
    FRAC STREAM=B-C02 SUBSTREAM=MIXED COMPS=H2 O2 CO2 H2O &
        GLUCOSE SUCROSE NH3 HAC ASH-WS CALDI RHODO KOH &
        PECTINE PROTEIN HCL K2HPO4 KH2PO4 CH4 H2S XYLOSE &
        GALACTOS ARABINOS GLUCAN XYLAN GALACTAN N2 NO2 O2S &
        ARABINAN LIGNIN FRACS=0. 0. 0. 1. 1. 1. 0. 1. 0. &
        0. 0. 0. 1. 1. 0. 0. 0. 0. 0. 1. 1. 1. 1. 1. &
        1. 0. 0. 0. 1. 0.

BLOCK B-C03 SEP
    IN-UNITS MET
    PARAM
    FRAC STREAM=B-C06 SUBSTREAM=MIXED COMPS=H2 O2 CO2 H2O &
        GLUCOSE SUCROSE NH3 HAC ASH-WS CALDI RHODO KOH &
        PECTINE PROTEIN HCL K2HPO4 KH2PO4 CH4 H2S XYLOSE &
        GALACTOS ARABINOS GLUCAN XYLAN GALACTAN N2 NO2 O2S &
        ARABINAN LIGNIN FRACS=0. 0. 0. 0. 0. 0. 0. 0. 0. &
        0. 0. 0. 0. 0. 0. 0. 0. 1. 0. 0. 0. 0. 0. 0. &
        0. 0. 0. 0. 0. 0.

BLOCK B-C02 HEATER
    IN-UNITS MET
    PARAM TEMP=35. <C> PRES=0. <bar> NPHASE=2
    BLOCK-OPTION FREE-WATER=NO

ENDHIERARCHY COD

BLOCK B-01 DUPL
    IN-UNITS MET DENSITY='kg/cum' ENERGY=kJ ENTHALPY='J/kmol' &
        ENTROPY='J/kmol-K' VOLUME-FLOW='cum/hr' ENTHALPY-FLO=kW &
        FORCE=Newton MOLE-HEAT-CA='kJ/kmol-K' &
        HEAT-TRANS-C='kW/sqm-K' PRESSURE=bar TEMPERATURE=C &
        THERMAL-COND='kW/m-K' VOLUME=cum DELTA-T=C HEAD=meter &
        MOLE-DENSITY='kmol/cum' MASS-DENSITY='kg/cum' &
        MOLE-ENTHALPY='kJ/kmol' MASS-ENTHALP='kJ/kg' &
        MOLE-ENTROPY='kJ/kmol-K' MASS-ENTROPY='kJ/kg-K' &
        MOLE-VOLUME='cum/kmol' MASS-HEAT-CA='kJ/kg-K' UA='kJ/sec-K' &
        WORK=kJ HEAT=kJ MOLE-CONC='mol/l' &
        MASS-TRANS-C='kg/s-sqm-kg/cum' PDROP=bar &
        VOL-HEAT-CAP='kJ/cum-K' HEAT-FLUX='Watt/m' &
        VFLOW-LENGTH='sqm/hr' INVERSE-HT-C='sqm-K/kW' &
        VOL-ENTHALPY='kJ/cum' MASS-VOLUME='cum/kg'

ENDHIERARCHY BIOGAS
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HIERARCHY UTILIZE


DEF-STREAMS CONVEN ALL

SOLVE
   PARAM METHOD=SM
   RUN-MODE MODE=SIM

FLOWSHEET
   BLOCK U-01 IN=U-01 OUT=U-05 U-06
   BLOCK U-TRIPLE IN=U-07 OUT=U-U01 U-C02 U-GE02
   BLOCK U-03 IN=U-05 OUT=U-07 U-08
   BLOCK U-GE03 IN=U-GE04 OUT=U-GE06 U-GE07
   BLOCK X2 IN=U-04 OUT=U-C01 U-GE01
   BLOCK U-GE01 IN=U-GE01 U-GE02 OUT=U-GE03
   BLOCK U-GE02 IN=U-GE03 OUT=U-GE04 U-GE05
   BLOCK U-GE04 IN=U-GE06 OUT=U-GE09 U-GE08
   BLOCK U-GE05 IN=U-GE08 U-GE05 OUT=U-GE10
   BLOCK U-C01 IN=U-C02 U-C01 OUT=U-C03
   BLOCK U-02 IN=U-02 U-03 OUT=U-04

PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES
   PROPERTIES PENG-ROB / PR-BM / STEAMNBS$

STREAM U-02
   IN-UNITS MET
   SUBSTREAM MIXED TEMP=25. <C> PRES=1. <bar> MOLE-FLOW=1.
   MOLE-FRAC O2 0.21 / N2 0.79

STREAM U-03
   SUBSTREAM MIXED TEMP=25. <C> PRES=1. <bar> &
      MASS-FLOW=0.1 <kg/hr>
   MOLE-FRAC H2O 1.

DEF-STREAMS HEAT U-GE07

DEF-STREAMS WORK U-GE05

DEF-STREAMS WORK U-GE08

DEF-STREAMS WORK U-GE10

BLOCK U-02 MIXER

BLOCK U-GE01 MIXER

BLOCK U-GE05 MIXER

BLOCK U-01 SEP
   IN-UNITS MET
   PARAM PRES=0. <bar>
   FRAC STREAM=U-05 SUBSTREAM=MIXED COMPS=H2 O2 CO2 H2O &
      GLUCOSE SUCROSE NH3 HAC ASH-WS CALDI RHODO KOH &
      PECTINE PROTEIN HCL K2HPO4 KH2PO4 CH4 H2S XYLOSE &
      GALACTOS ARABINOS GLUCAN XYLAN GALACTAN N2 NO2 O2S &
      ARABINAN LIGNIN FRACS=1. 1. 1. 1. 0. 0. 1. 0. 0. &
      0. 0. 0. 0. 0. 0. 0. 0. 1. 0. 0. 0. 0. 0. 0. &
      0. 1. 1. 1. 0. 0.

BLOCK U-03 FLASH2
   IN-UNITS MET DENSITY=’kg/cum’ ENERGY=kJ ENTHALPY=’J/kmol’ &
      ENTROPY=’J/kmol-K’ VOLUME-FLOW=’cum/hr’ ENTHALPY-FLO=kW &
      FORCE=Newton MOLE-HEAT-CA=’kJ/kmol-K’ &
      HEAT-TRANS-C=’kW/sqm-K’ PRESSURE=bar TEMPERATURE=C &
      THERMAL-COND=’kW/m-K’ VOLUME=cum DELTA-T=C HEAD=meter &
      MOLE-DENSITY=’kmol/cum’ MASS-DENSITY=’kg/cum’ &
      MOLE-ENTHALP=’kJ/kmol’ MASS-ENTHALP=’kJ/kg’ &
      MOLE-ENTROPY=’kJ/kmol-K’ MASS-ENTROPY=’kJ/kg-K’ &
      MOLE-VOLUME=’cum/kmol’ MASS-HEAT-CA=’kJ/kg-K’ UA=’kJ/sec-K’ &
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        WORK=kJ HEAT=kJ MOLE-CONC=’mol/l’ &
        MASS-TRANS-C=’kg/s-sqm-kg/cum’ PDROP=bar &
        VOL-HEAT-CAP=’kJ/cum-K’ HEAT-FLUX=’Watt/m’ &
        VFLOW-LENGTH=’sqm/hr’ INVERSE-HT-C=’sqm-K/kW’ &
        VOL-ENTHALPY=’kJ/cum’ MASS-VOLUME=’cum/kg’
    PARAM TEMP=10. PRES=0.

BLOCK U-C01 RSTOIC
    PARAM PRES=0. <bar> DUTY=0. HEAT-OF-REAC=NO COMBUSTION=YES &
        PROD-NOX=NO2

BLOCK U-GE03 RGIBBS
    PARAM PRES=0. <bar> CHEMEQ=YES DUTY=1. <kW> HYDRATE=RIGOROUS

BLOCK U-GE02 COMPR
    PARAM TYPE=ISENTROPIC PRES=2. <bar> NPHASE=2
    BLOCK-OPTION FREE-WATER=NO

BLOCK U-GE04 COMPR
    PARAM TYPE=ISENTROPIC PRES=1. <bar> NPHASE=2 &
        MODEL-TYPE=TURBINE
    BLOCK-OPTION FREE-WATER=NO

BLOCK U-TRIPLE DUPL
    IN-UNITS MET DENSITY=’kg/cum’ ENERGY=kJ ENTHALPY=’J/kmol’ &
        ENTROPY=’J/kmol-K’ VOLUME-FLOW=’cum/hr’ ENTHALPY-FLO=kW &
        FORCE=Newton MOLE-HEAT-CA=’kJ/kmol-K’ &
        HEAT-TRANS-C=’kW/sqm-K’ PRESSURE=bar TEMPERATURE=C &
        THERMAL-COND=’kW/m-K’ VOLUME=cum DELTA-T=C HEAD=meter &
        MOLE-DENSITY=’kmol/cum’ MASS-DENSITY=’kg/cum’ &
        MOLE-ENTHALP=’kJ/kmol’ MASS-ENTHALP=’kJ/kg’ &
        MOLE-ENTROPY=’kJ/kmol-K’ MASS-ENTROPY=’kJ/kg-K’ &
        MOLE-VOLUME=’cum/kmol’ MASS-HEAT-CA=’kJ/kg-K’ UA=’kJ/sec-K’ &
        WORK=kJ HEAT=kJ MOLE-CONC=’mol/l’ &
        MASS-TRANS-C=’kg/s-sqm-kg/cum’ PDROP=bar &
        VOL-HEAT-CAP=’kJ/cum-K’ HEAT-FLUX=’Watt/m’ &
        VFLOW-LENGTH=’sqm/hr’ INVERSE-HT-C=’sqm-K/kW’ &
        VOL-ENTHALPY=’kJ/cum’ MASS-VOLUME=’cum/kg’

BLOCK X2 DUPL

ENDHIERARCHY UTILIZE

DESIGN-SPEC RELHUM
    DEFINE RELHUM STREAM-PROP STREAM="UTILIZE.U-04" &
        PROPERTY=RELHUM
    SPEC "RELHUM" TO "30"
    TOL-SPEC "0.3"
    VARY STREAM-VAR STREAM="UTILIZE.U-03" SUBSTREAM=MIXED &
        VARIABLE=MASS-FLOW
    LIMITS "0.000000001" "1"

EO-CONV-OPTI

CALCULATOR AIR
    IN-UNITS MET
    DEFINE CH4FLOW MOLE-FLOW STREAM="UTILIZE.U-C02" &
        SUBSTREAM=MIXED COMPONENT=CH4
    DEFINE NH3FLOW MOLE-FLOW STREAM="UTILIZE.U-C02" &
        SUBSTREAM=MIXED COMPONENT=NH3
    DEFINE H2SFLOW MOLE-FLOW STREAM="UTILIZE.U-C02" &
        SUBSTREAM=MIXED COMPONENT=H2S
    DEFINE N2FLOW MOLE-FLOW STREAM=07 SUBSTREAM=MIXED &
        COMPONENT=N2
    DEFINE O2FLOW MOLE-FLOW STREAM=07 SUBSTREAM=MIXED &
        COMPONENT=O2
F     O2 = (CH4FLOW*2+NH3FLOW*1.75+H2SFLOW*1.5)
F     N2 = O2*(0.79/0.21)
F
C  Luftüberschuss von 1.1 nach Dampferzeugerpraxis - Grundl.&Betrieb
F
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F     O2FLOW = O2*1.1
F     N2FLOW = N2*1.1
F
C  vereinfachte Luftzusammensetzung: 21% O2 + 79% N2;
C  Luft: N2/O2 = 0.79/0.21
    READ-VARS CH4FLOW NH3FLOW H2SFLOW
    WRITE-VARS N2FLOW O2FLOW

CALCULATOR BUSWELL
    IN-UNITS MET
    DEFINE MOLEFRC STREAM-PROP STREAM="BIOGAS.B-B03" &
        PROPERTY=MOLEFRC
    DEFINE MOLEFRH STREAM-PROP STREAM="BIOGAS.B-B03" &
        PROPERTY=MOLEFRH
    DEFINE MOLEFRO STREAM-PROP STREAM="BIOGAS.B-B03" &
        PROPERTY=MOLEFRO
    DEFINE MOLEFRN STREAM-PROP STREAM="BIOGAS.B-B03" &
        PROPERTY=MOLEFRN
    DEFINE MOLEFRS STREAM-PROP STREAM="BIOGAS.B-B03" &
        PROPERTY=MOLEFRS
    DEFINE CH4 MOLE-FLOW STREAM="BIOGAS.B-B07" SUBSTREAM=MIXED &
        COMPONENT=CH4
    DEFINE CO2 MOLE-FLOW STREAM="BIOGAS.B-B07" SUBSTREAM=MIXED &
        COMPONENT=CO2
    DEFINE NH3 MOLE-FLOW STREAM="BIOGAS.B-B07" SUBSTREAM=MIXED &
        COMPONENT=NH3
    DEFINE H2S MOLE-FLOW STREAM="BIOGAS.B-B07" SUBSTREAM=MIXED &
        COMPONENT=H2S
    DEFINE GLUCOSE MOLE-FLOW STREAM="BIOGAS.B-B07" &
        SUBSTREAM=MIXED COMPONENT=GLUCOSE
    DEFINE SUCROSE MOLE-FLOW STREAM="BIOGAS.B-B07" &
        SUBSTREAM=MIXED COMPONENT=SUCROSE
    DEFINE HAC MOLE-FLOW STREAM="BIOGAS.B-B07" SUBSTREAM=MIXED &
        COMPONENT=HAC
    DEFINE PECTINE MOLE-FLOW STREAM="BIOGAS.B-B07" &
        SUBSTREAM=MIXED COMPONENT=PECTINE
    DEFINE PROTEIN MOLE-FLOW STREAM="BIOGAS.B-B07" &
        SUBSTREAM=MIXED COMPONENT=PROTEIN
    DEFINE H2O MASS-FLOW STREAM="BIOGAS.B-B07" SUBSTREAM=MIXED &
        COMPONENT=H2O
    DEFINE XYLOSE MOLE-FLOW STREAM="BIOGAS.B-B07" &
        SUBSTREAM=MIXED COMPONENT=XYLOSE
    DEFINE GALACTOS MOLE-FLOW STREAM="BIOGAS.B-B07" &
        SUBSTREAM=MIXED COMPONENT=GALACTOS
    DEFINE ARABINOS MOLE-FLOW STREAM="BIOGAS.B-B07" &
        SUBSTREAM=MIXED COMPONENT=ARABINOS
    DEFINE GLUCAN MOLE-FLOW STREAM="BIOGAS.B-B07" &
        SUBSTREAM=MIXED COMPONENT=GLUCAN
    DEFINE XYLAN MOLE-FLOW STREAM="BIOGAS.B-B07" SUBSTREAM=MIXED &
        COMPONENT=XYLAN
    DEFINE GALACTAN MOLE-FLOW STREAM="BIOGAS.B-B07" &
        SUBSTREAM=MIXED COMPONENT=GALACTAN
    DEFINE ARABINAN MOLE-FLOW STREAM="BIOGAS.B-B07" &
        SUBSTREAM=MIXED COMPONENT=ARABINAN
    DEFINE GLU MOLE-FLOW STREAM="BIOGAS.B-B03" SUBSTREAM=MIXED &
        COMPONENT=GLUCOSE
    DEFINE SUC MOLE-FLOW STREAM="BIOGAS.B-B03" SUBSTREAM=MIXED &
        COMPONENT=SUCROSE
    DEFINE HA MOLE-FLOW STREAM="BIOGAS.B-B03" SUBSTREAM=MIXED &
        COMPONENT=HAC
    DEFINE PEC MOLE-FLOW STREAM="BIOGAS.B-B03" SUBSTREAM=MIXED &
        COMPONENT=PECTINE
    DEFINE PRO MOLE-FLOW STREAM="BIOGAS.B-B03" SUBSTREAM=MIXED &
        COMPONENT=PROTEIN
    DEFINE XYL MOLE-FLOW STREAM="BIOGAS.B-B03" SUBSTREAM=MIXED &
        COMPONENT=XYLOSE
    DEFINE GAL MOLE-FLOW STREAM="BIOGAS.B-B03" SUBSTREAM=MIXED &
        COMPONENT=GALACTOS
    DEFINE ARA MOLE-FLOW STREAM="BIOGAS.B-B03" SUBSTREAM=MIXED &
        COMPONENT=ARABINOS
    DEFINE GLN MOLE-FLOW STREAM="BIOGAS.B-B03" SUBSTREAM=MIXED &
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        COMPONENT=GLUCAN
    DEFINE XYN MOLE-FLOW STREAM="BIOGAS.B-B03" SUBSTREAM=MIXED &
        COMPONENT=XYLAN
    DEFINE GAN MOLE-FLOW STREAM="BIOGAS.B-B03" SUBSTREAM=MIXED &
        COMPONENT=GALACTAN
    DEFINE ARN MOLE-FLOW STREAM="BIOGAS.B-B03" SUBSTREAM=MIXED &
        COMPONENT=ARABINAN
    DEFINE CALDIMOL MOLE-FLOW STREAM="BIOGAS.B-B02" &
        SUBSTREAM=MIXED COMPONENT=CALDI
    DEFINE RHODOMOL MOLE-FLOW STREAM="BIOGAS.B-B02" &
        SUBSTREAM=MIXED COMPONENT=RHODO
    DEFINE MOLEFLOW STREAM-VAR STREAM="BIOGAS.B-B03" &
        SUBSTREAM=MIXED VARIABLE=MOLE-FLOW
    DEFINE MASSFLOW STREAM-VAR STREAM="BIOGAS.B-B06" &
        SUBSTREAM=MIXED VARIABLE=MASS-FLOW
    DEFINE CALDI MOLE-FLOW STREAM="BIOGAS.B-B08" SUBSTREAM=MIXED &
        COMPONENT=CALDI
    DEFINE RHODO MOLE-FLOW STREAM="BIOGAS.B-B08" SUBSTREAM=MIXED &
        COMPONENT=RHODO
    DEFINE MWCH4 UNARY-PARAM VARIABLE=MW ID1=CH4 ID2=1
    DEFINE MWCO2 UNARY-PARAM VARIABLE=MW ID1=CO2 ID2=1
    DEFINE MWNH3 UNARY-PARAM VARIABLE=MW ID1=NH3 ID2=1
    DEFINE MWH2S UNARY-PARAM VARIABLE=MW ID1=H2S ID2=1
    DEFINE MWW UNARY-PARAM VARIABLE=MW ID1=H2O ID2=1
C   CALCULATION OF THE COEFFICIENT FOR CHEMICAL FORMULA OUT
C   OF EMPIRICAL FORMULA
F
F     XXC = 5*GLU+12*SUC+2*HA+6*PEC+PRO+5*XYL+6*GAL+5*ARA+6*GLN
F     XC  = (XXC+5*XYN+6*GAN+5*ARN)*0.95
F     XXH = 10*GLU+22*SUC+4*HA+10*PEC+1.57*PRO+10*XYL
F     XH  = XXH+12*GAL+10*ARA+10*GLN+8*XYN+10*GAN+8*ARN
F     XXO = 5*GLU+11*SUC+2*HA+5*PEC+0.31*PRO+5*XYL+6*GAL
F     XO  = XXO+5*ARA+5*GLN+4*XYN+5*GAN+4*ARN
F     XN  = 0.29*PRO
F     XS  = 0.007*PRO
F
F     MOLE = XC+XH+XO+XN+XS
F     FACTOR = MOLE/(GLU+SUC+HA+PEC+PRO+XYL+GAL+ARA+GLN+XYN+GAN+ARN)
F
C   CALCULATION OF MOLEFLOWS OF THE BIOGAS
F
F     CMOL = MOLEFRC*MOLEFLOW*FACTOR
F     HMOL = MOLEFRH*MOLEFLOW*FACTOR
F     OMOL = MOLEFRO*MOLEFLOW*FACTOR
F     NMOL = MOLEFRN*MOLEFLOW*FACTOR
F     SMOL = MOLEFRS*MOLEFLOW*FACTOR
F
F     CO2 = ((CMOL/2)-(HMOL/8)+(OMOL/4)+(3/8)*NMOL +(SMOL/4))
F     CH4 = ((CMOL/2)+(HMOL/8)-(OMOL/4)-(3/8)*NMOL -(SMOL/4))
F     NH3 = NMOL
F     H2S = SMOL
F
C  MASS BALANCE
F
F     GLUCOSE = 0
F     SUCROSE = 0
F     HAC = 0
F     PECTINE = 0
F     PROTEIN = 0
F     XYLOSE = 0
F     GALACTOS = 0
F     ARABINOS = 0
F     GLUCAN = 0
F     XYLAN = 0
F     ARABINAN = 0
F     GALACTAN = 0
F     H2O = MASSFLOW-(CO2*MWCO2)-(CH4*MWCH4)-(NH3*MWNH3)-(H2S*MWH2S)
F
C FORMATION OF BIOMASS
F
F     CALDI = CALDIMOL*1.05
```

```
F     RHODO = RHODOMOL*1.05
    READ-VARS MOLEFRC MOLEFRO MOLEFRN MOLEFRS MOLEFRH MOLEFLOW &
        MASSFLOW MWCH4 MWCO2 MWNH3 MWH2S MWW GLU SUC HA PEC &
        PRO XYL GAL ARA GLN XYN GAN CALDIMOL RHODOMOL ARN
    WRITE-VARS CH4 CO2 NH3 H2S GLUCOSE SUCROSE HAC CALDI &
        RHODO PECTINE PROTEIN H2O XYLOSE GALACTOS ARABINOS &
        GLUCAN XYLAN GALACTAN ARABINAN

CALCULATOR COD
    IN-UNITS MET
    DEFINE CODMX STREAM-PROP STREAM="BIOGAS.COD.B-C02" &
        PROPERTY=CODMX
    DEFINE MASSFLOW STREAM-VAR STREAM="BIOGAS.COD.B-C02" &
        SUBSTREAM=MIXED VARIABLE=MASS-FLOW
    DEFINE CH4 MASS-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=CH4
    DEFINE GLUCOSE MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=GLUCOSE
    DEFINE SUCROSE MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=SUCROSE
    DEFINE HAC MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=HAC
    DEFINE CALDI MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=CALDI
    DEFINE RHODO MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=RHODO
    DEFINE PECTINE MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=PECTINE
    DEFINE PROTEIN MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=PROTEIN
    DEFINE CO2 MASS-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=CO2
    DEFINE ARABINAN MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=ARABINAN
    DEFINE XYLOSE MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=XYLOSE
    DEFINE GALACTOS MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=GALACTOS
    DEFINE ARABINOS MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=ARABINOS
    DEFINE GLUCAN MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=GLUCAN
    DEFINE XYLAN MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=XYLAN
    DEFINE GALACTAN MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=GALACTAN
    DEFINE ASH MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=ASH-WS
    DEFINE LIGNIN MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=LIGNIN
    DEFINE WATER MOLE-FLOW STREAM="BIOGAS.COD.B-C04" &
        SUBSTREAM=MIXED COMPONENT=H2O
F     02BEDARF = CODMX*MASSFLOW
F
F     CH4 = 02BEDARF*0.25
F
F     GLUCOSE = 0
F     SUCROSE = 0
F     HAC = 0
F     PECTINE = 0
F     PROTEIN = 0
F     XYLOSE = 0
F     GALACTOS = 0
F     ARABINOS = 0
F     GLUCAN = 0
F     XYLAN = 0
F     ARABINAN = 0
F     GALACTAN = 0
F     ASH = 0
F     LIGNIN = 0
F     WATER = 0
```

```
F
F    CO2 = MASSFLOW - CH4
    READ-VARS CODMX MASSFLOW
    WRITE-VARS CH4 GLUCOSE SUCROSE HAC CALDI RHODO PECTINE &
       PROTEIN CO2 ARABINAN XYLOSE GALACTOS ARABINOS GLUCAN &
       XYLAN GALACTAN ASH LIGNIN WATER

CALCULATOR ENGINE
    DEFINE CHPWORK INFO-VAR INFO=WORK VARIABLE=POWER &
       STREAM="UTILIZE.U-GE10"
    DEFINE CHPHEAT INFO-VAR INFO=HEAT VARIABLE=DUTY &
       STREAM="UTILIZE.U-GE07"
    DEFINE CHPFLUE STREAM-VAR STREAM="UTILIZE.U-GE09" &
       SUBSTREAM=MIXED VARIABLE=TEMP
    DEFINE HU STREAM-PROP STREAM="UTILIZE.U-07" PROPERTY=QVALNET
    DEFINE MASSFLOW STREAM-VAR STREAM="UTILIZE.U-07" &
       SUBSTREAM=MIXED VARIABLE=MASS-FLOW
C   Mittelwert von elektrischem und thermischen Wirkungsgrad über
C   Leistungsbereiche von 249 - 2425 kW_el:
C   eta_el = 40.35 %
C   eta_th = 43.85 %
C   aus IWK&Jenhacher Datenblatt für Gasmotoren BHKW Module für Biogas
F
F    ETAEL = 0.4035
F    ETATH = 0.4385
F
F    BE = HU*MASSFLOW*1000
F
F    CHPWORK = ETAEL*BE
F    CHPHEAT = ETATH*BE
F
F    CHPFLUE = 453.15
    READ-VARS HU MASSFLOW
    WRITE-VARS CHPWORK CHPHEAT CHPFLUE

CONV-OPTIONS
    PARAM TEAR-VAR=YES

REPORT INPUT

STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC PROPERTIES=COD &
       CODMX MOLEFRC MOLEFRH MOLEFRN MOLEFRO MOLEFRS QVALNET &
       RELHUM

PROPERTY-REP PCES
;
;
;
;
;
```

Listing A.4.1: Input Summary Aspen Plus