# BIOMASS TO ETHANOL: PROCESS SIMULATION, VALIDATION AND SENSITIVITY ANALYSIS OF A GASIFIER AND A BIOREACTOR

By

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# NOMENCLATURE

| | |
|---|---|
| atm | Atmosphere |
| AF | Air Fuel (ratio) |
| bar | bars |
| Btu | British thermal units |
| C | carbon |
| °C | degree centigrade |
| CAA | Clean Air Act |
| cc/min | cubic centimeter per minute |
| $CH_4$ | methane |
| $C_2H_2$ | acetylene |
| $C_2H_4$ | ethylene |
| $C_2H_5OH$ | ethanol |
| CO | carbon monoxide |
| $CO_2$ | carbon dioxide |
| CSTR | continuous stirred tank reactor |
| DOE | Department of Energy |
| E | stoichiometric conversion |
| EOS | equation of state |
| EPA | Environmental Protection Agency |

| | |
|---|---|
| ER | Equivalence Ratio |
| FBN | fuel bound nitrogen |
| GHG | green house gases |
| $H_2$ | hydrogen |
| $H_2O$ | water |
| $HNO_3$ | nitric acid |
| K | kelvin |
| Kg/hr | kilogram per hour |
| Kg/sec | kilogram per second |
| KJ/mol | kilo joule per mole |
| Kmol | kilo mole |
| mol | mole |
| mol frac | mole fraction |
| MTBE | methyl tertiary butyl ether |
| $NH_3$ | ammonia |
| $NO_x$ | nitrogen oxide (x is 1, 2 or 3) |
| $N_2O$ | nitrous oxide |
| NRTL | Non Random Two Liquid |
| $O_2$ | oxygen |
| psi | pounds per square inch |
| $P7^T$ | strain identification of *C. carboxidivorans* species |
| RFG | reformulated gasoline |
| RFS | Renewable Fuel Standard |

| | |
|---|---|
| VOC | volatile organic compounds |
| vol % | percentage by volume |
| wt % | percentage by weight |

# CHAPTER 1

# BIOMASS FERMENTATION TO ETHANOL: AN OVERVIEW

## 1.1 Introduction

Since the 1973-1974 oil embargo, the requirement to conserve petroleum resources has become imminent and new processes for the development of alternate fuels are being investigated (Paul, 1979). The transportation sector with its nearly total dependence on petroleum has virtually no capacity to switch to other fuels in the event of a supply disruption (Lynd et al., 1991). In light of the rapid changes in the regulatory and legislative aspects of government in the past two decades, ethanol has taken an important role in bringing together often conflicting environmental and security concerns (Yacobucci and Womach, 2004).

Production of ethanol from biomass has increasingly gained importance since the supply of biomass from agriculture is readily available in the United States. In 2003, 99% of fuel ethanol consumed in the United States was in the form of “gasohol” or “E 10” which are blends of gasoline with up to 10% of ethanol (Yacobucci and Womach, 2004). Environmental issues limiting the increase of $CO_2$ in the atmosphere and global warming due to burning of petroleum based fuels also argue for increased utilization of ethanol. Use of alternative energy sources instead of petroleum would aid in stabilizing the concentration of $CO_2$ in the atmosphere (Hohenstein and Wright, 1994). The use of fuel ethanol has been stimulated by the Clean Air Act Amendments of 1990, which require emissions of CO and volatile organic compounds (VOCs) to be controlled through the use of oxygenated gasoline (Yacobucci and Womach, 2004). For many years Methyl Tertiary Butyl Ether (MTBE) has been the oxygenate of choice but this is likely to change. MTBE is known to cause health problems and is also a source of ground water contamination (Nadim et al., 2001). Since January 2004, California has banned MTBE from its fuel pool as did the states of New York and Connecticut. A total of 16 states had banned the use of MTBE by July 2005 (Ethanol Industry Outlook, 2005) and this has opened the way for greater ethanol utilization. According to Argonne National Laboratory, 10% ethanol fuel blends reduce green house gases emissions by 12 to 19% (Ethanol Industry Outlook, 2005). Estimated figures for U.S. consumption of fuel ethanol, MTBE and gasoline are shown in Table 1.1.

The total energy used as fuel for transportation in the United States was about 27.1 Quadrillion Btu (quads) in 2001, 99% of which was obtained from fossil fuels (Greene and Schafer, 2003). The domestic ethanol production in 2004 was approximately 3.41 billion gallons (Ethanol Industry Outlook, 2005). Under current laws and incentives, ethanol consumption as fuel has increased from 1.8 billion gallons per year in 2001 to 2.8 billion gallons per year in 2003 (Yacobucci and Womach, 2004). A comparative chart for ethanol production over the past few years is shown in Fig 1.1. Combustion of ethanol in internal combustion engines designed for operation with alcohols will give a higher efficiency than combustion of gasoline in conventional combustion engines (Lynd et al., 2001). Agrarian states like Oklahoma have large amounts of agricultural wastes which can be used as renewable energy resources for production of ethanol. Hence, the production of ethanol from biomass on a large scale holds a huge potential in replacing petroleum based fuels in the transportation sector. The many potential advantages of using ethanol as fuel, in the environmental, economic and energy sectors are discussed in the following sections.

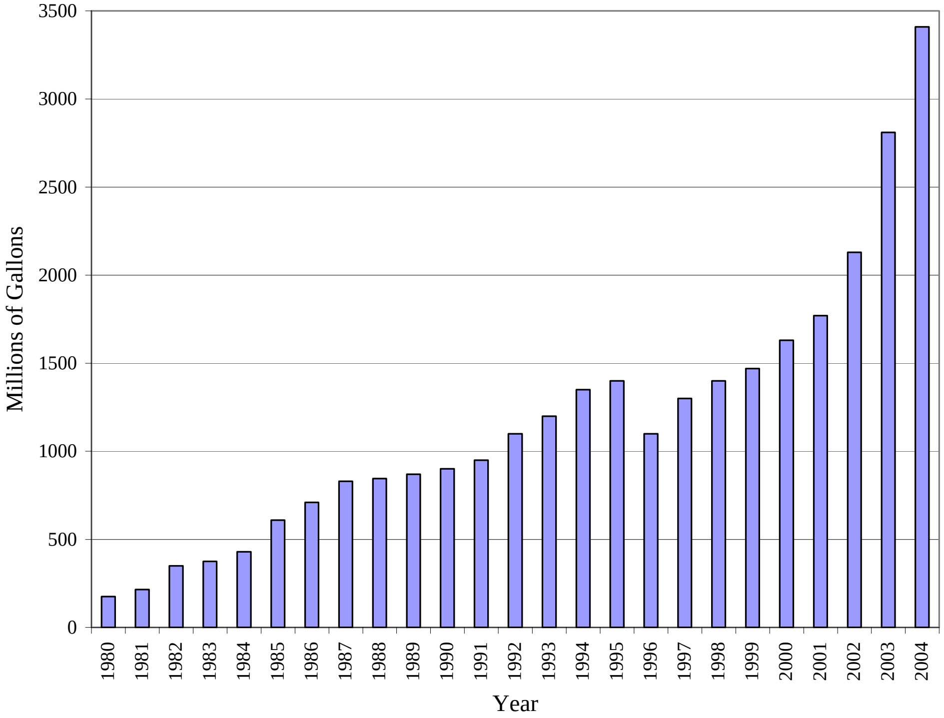


Figure 1.1. Historic U.S. fuel ethanol production (Ethanol Industry Outlook, 2005)

Table 1.1 Estimated U.S consumption of Fuel Ethanol, MTBE and Gasoline (Yacobucci and Womach, 2004)

| | (thousand gasoline-equivalent gallons) | | | |
|---|---|---|---|---|
| | 1996 | 1998 | 2000 | 2002 |
| E 85 | 694 | 1,727 | 7,704 | 10,075 |
| E 95 | 2,669 | 59 | 13 | 0 |
| Ethanol in Gasohol (E 10) | 660,200 | 889,500 | 1,106,300 | 1,118,900 |
| MTBE in Gasoline | 2,749,700 | 2,903,400 | 3,087,900 | 2,531,000 |
| Gasoline[a] | 117,783,000 | 122,849,000 | 125,720,000 | 130,735,000 |

[a] Gasoline consumption includes ethanol in gasohol and MTBE in gasoline

## 1.2 Renewable Source of Energy supply

Biomass is the plant material derived from the reaction between $CO_2$ and air, in the presence of water and sunlight, via photosynthesis to produce carbohydrates that form the building blocks of biomass (McKendry, 2002a). Agricultural biomass is abundant in the United States; it is presently estimated to contribute on the order of 10-14% of the worlds' energy supply (McKendry, 2002a). Hence, fuel ethanol produced from biomass using agricultural crop residues is a renewable source of energy.

## 1.3 Reduction/elimination of MTBE

The Clean Air Act Amendments of the 1990's requires reduction in CO emissions and VOCs through the use of oxygenated fuels (Yacobucci and Womach, 2004). While oxygenates reduce CO and VOC emissions, they lead to higher levels of nitrogen oxides, which are precursors to ozone formation (Yacobucci and Womach, 2004). MTBE use during winter months has proven to cause significant acute health problems and illness in large city residents (Nadim et al., 2001). MTBE moves more rapidly into groundwater than other gasoline compounds and contaminates drinking water. MTBE is much more resistant to biodegradation than other gasoline compounds (Nadim et al., 2001). MTBE has also been identified as an animal carcinogen with further concern of being a human carcinogen as well (Yacobucci and Womach, 2004). Despite the cost differential, ethanol has many advantages over MTBE and will replace it as the gasoline additive in the future. Ethanol contains 35% oxygen by weight which is almost twice the oxygen content of MTBE and is a sustainable fuel; MTBE on the other hand is only produced from fossil fuels (Yacobucci and Womach, 2004). A complete list of states where the use of MTBE has been banned is shown in Table 1.2.

Table 1.2 State MTBE bans
(Ethanol Industry Outlook, 2005)

| State | Effective Date |
|---|---|
| Arizona | Effective |
| California | Effective |
| Colorado | Effective |
| Connecticut | Effective |
| Illinois | Effective |
| Indiana | Effective |
| Iowa | Effective |
| Kansas | Pending federal action |
| Kentucky | 1/1/2006 |
| Maine | 1/1/2007 |
| Michigan | Effective |
| Minnesota | Effective |
| Missouri | 7/1/2005 |
| Nebraska | Effective |
| New Hampshire | Pending federal action |
| New York | Effective |
| Ohio | 7/1/2005 |
| South Dakota | Effective |
| Washington | Effective |
| Wisconsin | Effective |

## 1.4 Environmental Benefits and Climatic change

Due to the requirements of the Clean Air Act (CAA) of 1990, oxygenates were required in gasoline. Although this reduced the CO and VOC emissions to the environment, it also increased the formation of ground level ozone. Ground level ozone was found to be harmful to plants and causes respiratory problems in humans (Nadim et al., 2001). As part of the CAA program, the federal government introduced the use of reformulated gasoline (RFG) which requires the use of 2% oxygenate, met by adding 11% MTBE or 5.7% ethanol by volume. This program was intended to reduce the emission levels of highly toxic aromatic compounds like benzene formed during the combustion of gasoline. In conventional gasoline, aromatics which reach levels as high as 50%, were reduced to 27% by the use of RFG (Nadim et al., 2001). The Environmental Protection Agency (EPA) states that the usage of RFG has led to a 17% reduction in VOCs and a 30% reduction in toxic emissions (Yacobucci and Womach, 2004).

Another environmental factor supporting the use of ethanol as an additive in motor fuels is the emission of green house gases (GHG). Global warming has been an important environmental concern in the past two decades. Global warming occurs when temperatures increase due to the emission of $CO_2$, $CH_4$ and $NO_x$, collectively known as GHG. The U.S. transportation sector accounts for one third of all U.S. $CO_2$ emissions, which is likely to rise to 36% by 2020. Use of E 10 blend of gasoline has reduced the GHG emissions (per mile) by 2-3%, which is much smaller than the reductions with E 85 and E 95 (Wang et al., 1999). In the present scenario, if the production of ethanol from biomass is commercialized and current tax subsidies continued, the use of ethanol blended fuels could reduce transportation sector $CO_2$ emissions by 2% by 2015 and by 7% by 2030 (Greene and Schafer, 2003). $CO_2$ is released into the atmosphere when ethanol is burned with gasoline; however this $CO_2$ is used to produce new biomass which is a cyclical process (McKendry, 2002a). Thus, ethanol used in fuels has a potential to reduce GHG and contribute to the overall reduction of global warming.

Inefficient burning of gasoline causes the emission of carbon particulate and carbon monoxide due to incomplete conversion of gasoline into carbon dioxide. Oxygenated fuels improve the combustion efficiency of motor fuels and hence lead to lower emissions of CO and carbon particulate. The use of 10% ethanol blended fuel (E 10) has led to a reduction of tailpipe fine particulate emission by 50% and a reduction in CO emissions by up to 30% (Greene and Schafer, 2003). The reduction in these emissions would be higher for fuels containing higher blends of ethanol like E 85 (85% ethanol and 15% gasoline) and E 95 (95% ethanol and 5% gasoline). This is a substantial reduction in CO emissions, which is a major atmospheric pollutant and has been a cause for respiratory problems in humans.

### 1.5 Less International Dependence

Political unrest and sabotage attacks on the oil infrastructure in the major oil producing countries, particularly the Middle East, have caused a disruption of oil flow and a record increase in oil prices in the past years (Ethanol Industry Outlook, 2005). Use of ethanol as motor fuel will reduce U.S. reliance on oil imports, thus making the U.S. less vulnerable to an oil embargo like the one in the early 1970s. According to Argonne National Laboratory, the use of E 10 leads to a 3% reduction in fossil fuel usage per vehicle per mile, while usage of E 95 could lead to a 44% reduction in fossil fuel (Yacobucci and Womach, 2004).

### 1.6 Economic Benefits

Producing ethanol for use as fuel also has had many advantages in the U.S. economy. For the year 2004, the ethanol industry has reduced the trade deficit by $5.1 billion by eliminating the need to import 143.3 million barrels of oil. This has added more than 25.1 billion to gross outputs through the combination of operations expense and capital expense for new plants under construction (Ethanol Industry Outlook, 2005). The ethanol industry has created more than 147,000 jobs in all sectors of the economy and boosted the household economy by $4.4 billion. It has also added $1.3 billion of tax revenue for the Federal government and $1.2 billion for State and Local governments (Ethanol Industry Outlook, 2005).

### 1.7 Disadvantages of Ethanol as a Fuel

The primary drawback of ethanol usage as a fuel is its high price. Before 2004, the primary federal incentive to support the ethanol industry was a 5.2¢ per gallon exemption that blenders of gasohol (E 10) received from the 18.4¢ excise tax on motor fuels. This exemption applied to blended fuel which had only 10% of ethanol, thus providing an effective subsidy of 52¢ per gallon of ethanol. It is argued that the ethanol industry could not survive without the tax exemptions on ethanol used as blended fuel, since wholesale ethanol prices before federal subsidies are generally twice that of wholesale gasoline prices (Yacobucci and Womach, 2004). The net effective cost for producing ethanol from agricultural biomass and the economic feasibility of the entire project has been vehemently argued upon recently (Pimentel and Patzek, 2005). Pimentel and Patzek argue upon validity of earlier economic and technological calculations on which the feasibility of this entire research project is based. The paper takes into account the cost factors which were neglected in earlier reports by the DOE and the USDA.

## 1.8 Ethanol Manufacturing Processes

The following sections describe different technological processes for the production of ethanol from biomass.

### 1.8.1 Ethanol Production from Corn

In the United States, corn constitutes for about 90% of the feedstock for ethanol production. The other 10% is largely from grain sorghum, barley, wheat, cheese whey and potatoes. The U.S. Department of Agriculture (USDA) estimates that about 1.4 billion bushels of corn will be used to produce about 3.7 billion gallons of fuel ethanol during the 2004-2005 corn marketing year (Yacobucci and Womach, 2004). Corn is utilized because it is a relatively low cost starch source that can be converted into simple sugars that are then fermented and distilled to produce ethanol (Yacobucci and Womach, 2004). Corn is initially processed by dry milling (grinding process) or wet milling (chemical extraction process) to reduce the size of the feedstock and is then converted to sugars by treatment with enzymes. The sugars are then converted into ethanol by treatment with special strains of yeast. Finally, the ethanol produced is then distilled from the fermented broth to produce fuel grade ethanol (Yacobucci and Womach, 2004).

### 1.8.2 Ethanol Production from Lignocellulosic Feedstock

Lignocellulosic feedstocks are comprised of corn stover, crop residues, grasses and wood chips (Hohenstein and Wright, 1994). These are abundantly available in the United States from the northern plains and the Midwest. These feedstocks are easily procurable and are an inexpensive raw material as compared to sugar and starch based feedstocks. Since, for successful use of ethanol as a fuel, its price has to compete with gasoline, cheaper raw materials play an important role (Yacobucci and Womach, 2004). As the name suggests, lignocellulosic feedstock contains high cellulosic material that need to be broken down into simpler carbohydrates before they can be converted into ethanol. Typically the composition of lignocellulosic biomass is 40-50% cellulose, 20-40% hemi cellulose and 10-30% lignin by weight (Hohenstein and Wright, 1994). Some of the processes used for the production of ethanol from lignocellulosic feedstock are (Rajagopalan, 2001):

- Acid hydrolysis followed by fermentation
- Enzymatic hydrolysis followed by fermentation
- Gasification followed by fermentation

### 1.8.3 Ethanol Production from the Gasification and Fermentation Process

Gasification implies the thermochemical conversion of biomass into gaseous fuel by heating in a gasification medium like steam, oxygen or air (McKendry, 2002b). The fuel gas produced (syngas) comprises chiefly of carbon monoxide, carbon dioxide and hydrogen. The syngas then flows into a cleaning and cooling process, and is subsequently directed to a bioreactor (Cateni et al., 2000). The fuel gas is converted biochemically to ethanol by special strains of bacteria like *Clostridium ljungdahlii* and *Clostridium acetoethanogenum* under anaerobic conditions (Rajagopalan, 2001). From the bioreactor, the fermented broth then undergoes further processing to separate ethanol by distillation, hence producing fuel grade ethanol as a final product.

## 1.9 Purpose of the Study

The ultimate aim of this project is to develop a cost efficient process for conversion of lignocellulosic feedstock into ethanol using gasification. This is a relatively new technology and knowledge is limited in this field. Due to the broad range of science the project encompasses, a combined effort by chemical engineers, agricultural engineers, economists and microbiologists is underway at Oklahoma State University.

This part of the study was undertaken to learn more about the performance of the biomass gasifier and the bioreactor using computer generated models. Process models have been developed using simulation software Aspen Plus™ and the results discussed in the following chapters. The models described herein are relatively simple, and they are designed to predict the steady state performance of the gasifier and the bioreactor in terms of compositions and flowrates in the input and output streams. The models are not kinetic models and they cannot be used to size a reactor or predict the compositional variations or reactor conditions within a reactor. The objectives of this work include:

- Developing process models in Aspen Plus™ for the gasifier and the bioreactor and validating simulation results with experimental results in literature

- Using the developed model to study the performance of the gasifier by manipulating the process variables and characterizing the effect on gas quality and composition
- To study the performance of the bioreactor by manipulating the input syngas components and characterizing the effect on ethanol produced
- To determine maximum outputs from the gasifier and the bioreactor to help solve overall material and energy balances

# CHAPTER 2

# GASIFICATION, FERMENTATION AND PROCESS SIMULATION: LITERATURE REVIEW

## 2.1 Gasification

Gasification technology is not new by any means, even back in the 1850s, most of the city of London was illuminated by the use of “town gas” produced from the gasification of coal (Belgiorno et al., 2003). Gasification can be broadly defined as the thermochemical conversion of solid or liquid carbon based feedstock (biomass) into combustible gaseous fuel by partial oxidation of the biomass using a gasification agent (Belgiorno et al., 2003, McKendry, 2002b). The process is carried out at high temperatures of around 800 ºC – 900 ºC. Biomass gasification using air as the gasifying agent, yields syngas which contains $CO_2$, CO, $H_2$, $CH_4$, $H_2O$, trace amounts of hydrocarbons, inert gases present in the air and biomass and various contaminants such as char particles, ash and tars (Belgiorno et al., 2003, Bridgwater, 2003). Fuel Bound organic Nitrogen (FBN) can also be converted into nitrogen oxides ($NO_x$) during gasification (Furman et al., 1993).

The U.S. Department of Energy (US-DOE) has selected switchgrass as a potential candidate to produce a sustainable energy crop from which a renewable source of transportation fuel, primarily ethanol, can be derived (Sanderson et al., 1996). Switchgrass (*Panicum virgatum*) is a sod forming, warm season grass which is an important constituent of the North American Tallgrass Prairie (McLaughlin and Walsh, 1998). Switchgrass was chosen for further research as a primary herbaceous energy candidate after evaluating the yield and agronomic data on 34 herbaceous species, studied at Oak Ridge National Laboratory (McLaughlin and Walsh, 1998). Switchgrass has demonstrated high productivity across a wide geographic range, requires marginal quality land, low water and possesses many environmentally positive attributes (McLaughlin and Walsh, 1998, Sanderson et al., 1996). The gasification of switchgrass is presently under study at Oklahoma State University.

Gasification of biomass feedstocks is a well studied technology and is amply described in the literature (Narvaez et al., 1996, Natarajan et al., 1998, Reed, 1981). Biomass tends to decompose instantaneously when introduced into a gasifier operating at a high temperature, to form a complex set of volatile and solid matter (Bettagli et al., 1995). The kinetics of char gasification can be classified by the following steps, which occur in series and each of them can limit the rate of reaction (Reed, 1981):

1) diffusion of reactants across the char external film
2) diffusion of gas through the pores of the solid surface
3) adsorption, surface reaction and desorption of gas at the external surface
4) diffusion of the products out of the pores
5) diffusion of the products out of the external film

At the temperatures of gasifier operation, i.e. around 800 ºC – 900 ºC, the pore diffusion and mass transfer rates become quite fast and the third step becomes the rate limiting factor (Bettagli et al., 1995). The type of gasifier and the gasification agent used depends a lot on the type of feedstock that is to be gasified. Fluidized bed gasification technology was primarily developed to solve the operational problems of fixed bed gasification related to feedstocks with high ash content and low combustion efficiency (Belgiorno et al., 2003). Biomass gasification proceeds over the following set of reactions (Beukens and Schoeters, 1989):

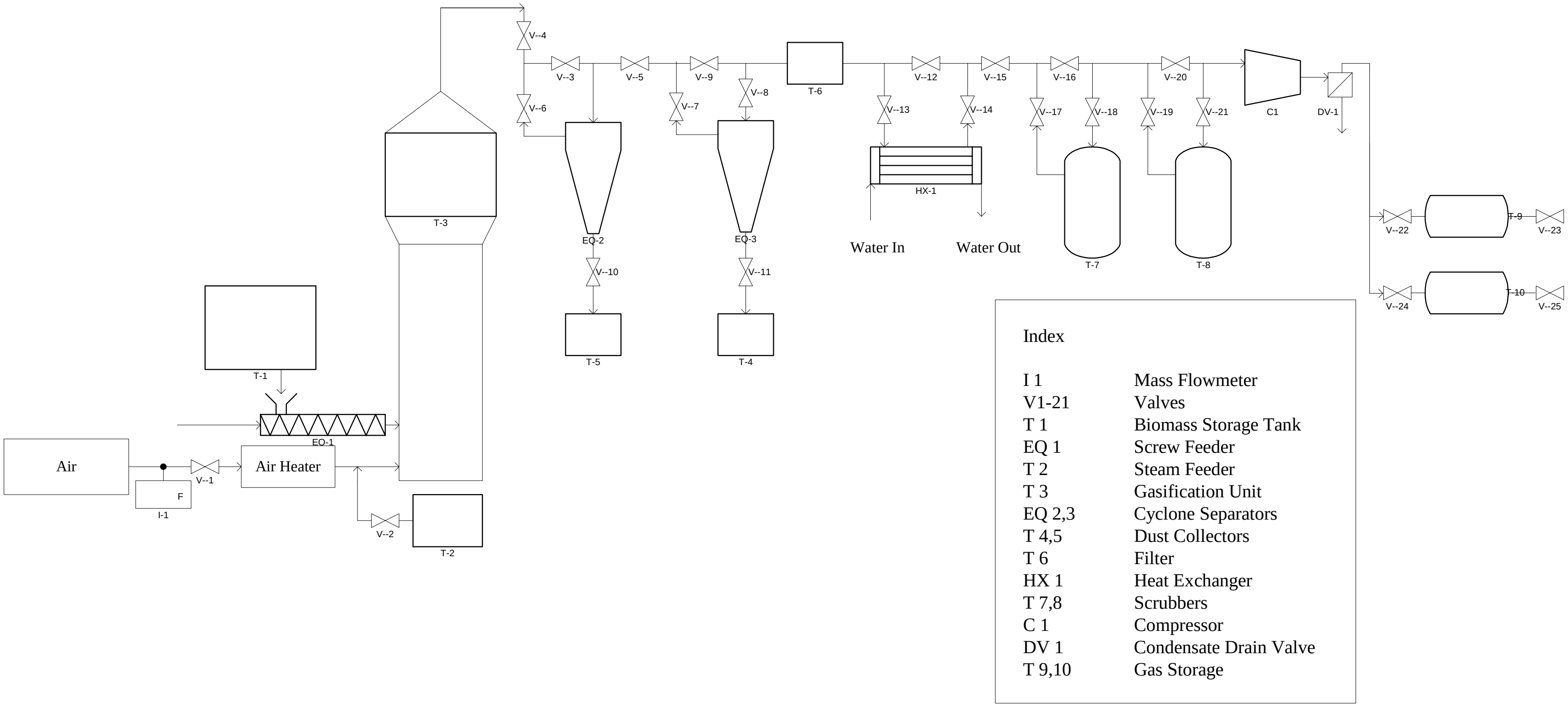
| | H (KJ/mole) | |
|---|---|---|
| Oxidation of carbon | | |
| $C + \frac{1}{2} O_2 \rightarrow CO$ | - 110.6 | (2.1) |
| $C + O_2 \rightarrow CO_2$ | - 393.8 | (2.2) |
| Boudouard reaction | | |
| $C + CO_2 \rightarrow 2\,CO$ | 172.6 | (2.3) |
| Water-gas reaction | | |
| $C + H_2O \rightarrow CO + H_2$ | 131.4 | (2.4) |
| Methane formation | | |
| $C + 2\,H_2 \rightarrow CH_4$ | - 74.93 | (2.5) |
| Water-gas shift reaction | | |
| $CO + H_2O \rightarrow CO_2 + H_2$ | - 41.2 | (2.6) |
| Reverse methanation reaction | | |
| $CH_4 + H_2O \rightarrow CO + 3\,H_2$ | - 201.9 | (2.7) |

### 2.1.1 Gasifier Pilot Plant Set-up

The pilot scale fluidized bed air gasifier at Oklahoma State University was constructed by using a design developed by Carbon Energy Technology, Inc., and the Center for Coal and the Environment at the Iowa State University. It consists of a fuel hopper, feed auger, injection auger, reactor, air blower, and ignition system (Cateni et al., 2000). The biomass is stored in a 5660 L air tight cylindrical fuel hopper and is fed using an injection auger which pushes the material into the reactor (Cateni et al., 2000). The estimated maximum feed rate capacity of the reactor is 34 Kg/hr. The reactor is 25 cm in diameter and is constructed of mild steel with a 5 cm refractory lining. During startup, propane gas is combusted in the reactor to heat it to about 500 ºC. The gas flow is slowly reduced as the biomass flow is increased. Once the temperature inside the gasifier reaches 750 ºC with a constant flow of biomass, the recirculation is activated and the airflow is decreased to starve combustion and maximize carbon monoxide formation. The biomass combusts as it enters the high temperature bed, which is fluidized by a mixture of air and recycled syngas. The fluidized reactor bed consists of sand (90%) and limestone (10%) mixture. The limestone cracks the tars and reduces agglomeration of the sand particles. The gas produced exits from the top of the gasifier where it is filtered through two cyclones (Cateni et al., 2000). A picture of the gasification unit is shown in Figure 2.1 and a detailed plant layout is shown in Figure 2.1. Part of the gas is then recycled into the reactor through a high temperature blower underneath the bed (Cateni et al., 2000). At the exhaust, the gas is filtered by passing it through ceramic wool, where light ashes and tars are collected.

The process is controlled by various sensors, which are connected to a computer for process control and data acquisition. Fourteen thermocouples that are located strategically are connected to the computer to control the reactor temperature. Syngas collected from the exhaust, is cooled, filtered and then injected into a Gas Chromatograph for analysis. The cooled gas is then compressed and filled in storage tanks at 120 psi (Cateni et al., 2000).

Figure 2.1 Gasifier pilot plant set up



Index

| | |
|---|---|
| I 1 | Mass Flowmeter |
| V1-21 | Valves |
| T 1 | Biomass Storage Tank |
| EQ 1 | Screw Feeder |
| T 2 | Steam Feeder |
| T 3 | Gasification Unit |
| EQ 2,3 | Cyclone Separators |
| T 4,5 | Dust Collectors |
| T 6 | Filter |
| HX 1 | Heat Exchanger |
| T 7,8 | Scrubbers |
| C 1 | Compressor |
| DV 1 | Condensate Drain Valve |
| T 9,10 | Gas Storage |

Figure 2.2 Gasifier pilot plant flowsheet

## 2.2 Syngas Fermentation

Synthesis gas is a major building block in the production of fuels and chemicals. Catalytic processes may be used to convert syngas into a variety of fuels and chemicals such as methane, methanol, formaldehyde, acetic acid and, ethanol (Klasson et al., 1992). In 1987, a strict anaerobic mesophilic bacterium was isolated that converted CO, $H_2$, and $CO_2$ to a mixture of acetate and ethanol. The bacterium was identified and characterized as a new clostridial species, named *Clostridium ljungdahlii* (Rajagopalan et al., 2002). In addition to synthesis gas components, it is also capable of using sugars like xylose, arabinose, and fructose (Klasson et al., 1990, Klasson et al., 1992). The metabolic pathway through which CO and $CO_2$ are utilized to produce ethanol is called the acetyl-CoA pathway or the Wood-Ljungdahl pathway (Wood et al., 1986). The overall stoichiometry for ethanol formation from CO, $CO_2$ and $H_2$ is (Rajagopalan et al., 2002):

$$6\ CO + 3\ H_2O \rightarrow C_2H_5OH + 4\ CO_2 \qquad (2.8)$$

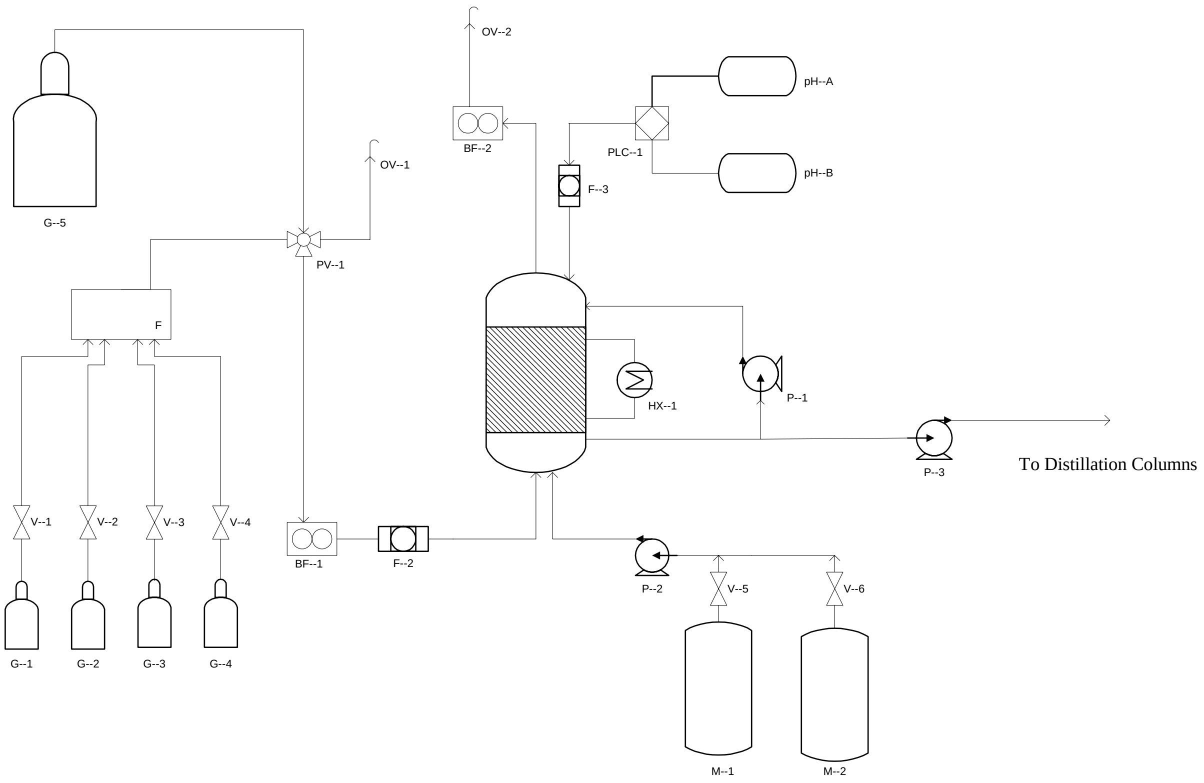
$$2\ CO_2 + 6\ H_2 \rightarrow C_2H_5OH + 3\ H_2O \qquad (2.9)$$

With CO alone as the sole substrate carbon source, one third of the carbon from CO can be theoretically converted into ethanol (Rajagopalan et al., 2002). A novel clostridial bacterium, P7 was demonstrated to produce ethanol and acetic acid from CO, $CO_2$ and $H_2$ through an acetogenic pathway (Datar, 2003, Rajagopalan et al., 2002). The optimum survival growth of P7 is at a pH range of 5-6 (Rajagopalan et al., 2002). The production of ethanol through the acetyl-CoA pathway using P7 is presently under study at Oklahoma State University.

The choice of a suitable bioreactor for synthesis gas fermentations is a question of matching reaction kinetics with the capabilities of various reactors. However, for fermentation processes which involve slightly soluble gases, mass transfer usually controls the reactor size (Klasson et al., 1992). A good reactor design for a fermentation process is one, which can achieve high mass transfer rates and high cell growth under operating conditions in a small reactor volume with minimum operational difficulties and costs (Datar, 2003). The reactor should then be efficiently scaled up to industrial size for the integrated gasifier-bioreactor-distillation column plant. Continuous stirred tank reactors (CSTR) are traditionally used for fermentation processes. A CSTR offers high rates of mass transfer and agitation leading to a higher conversion of CO into ethanol. A bubble column reactor offers greater mass transfer than a CSTR for producer gas fermentations, but initial studies (Rajagopalan, 2001) have indicated that the bioreactor is limited by the intrinsic kinetics of P7 (nutrient limitation) and not by the mass transfer rate of CO from the bulk gas to the cells (Datar, 2003). The chemical composition of the culture medium and nutrient requirements are described elsewhere (Datar et al., 2004).

### 2.2.1 Bioreactor Laboratory Scale Set-up

The present bioreactor set up at Oklahoma State University is a BioFlo 110 Bench top Fermentor (New Brunswick Scientific, Brunswick, NJ) with a 3 liter working volume, which was used for fermentation studies in a continuous operation mode (Ahmed, A. and Lewis, R. S., 2005). A detailed schematic diagram is shown in Figure 2.3. The reactor consists of an agitator, sparger, pH probe, dissolved oxygen probe, ports for liquid inlet and outlet, jacket for temperature control and pumps for feed, product removal and pH control (Ahmed, A. and Lewis, R. S., 2005). A four way valve is used to introduce gas feed into the reactor by switching between bottled gases (CO, $CO_2$, $H_2$ and $N_2$) and syngas using a sparger which bubbles the gas through the reactor volume. The gas removed from the reactor is then sampled and analyzed using a Gas Chromatograph to measure levels of component gases. Two liquid feed tanks supply the sterile nutrient media to the bioreactor during chemostat operation. The two liquid feed tanks are continuously purged with nitrogen to maintain anoxic conditions (Ahmed, A. and Lewis, R. S., 2005).



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| pH A | Acid Storage Tank |
| pH A | Base Storage Tank |
| PLC 1 | pH Controller |
| HX 1 | Heat Exchanger |

Figure 2.3 Bioreactor lab scale set up flowsheet

## 2.3 Process Simulation

Simulation can be defined as the use of a mathematical model to generate the description of the state of a system (Raman, 1985). The biggest advantage of process simulation is that it provides a good insight into the behavior of an actual process system. This is particularly true for complex systems with several interacting variables. Since the computer based mathematical model responds to changes in the same parameters as does a real process, simulation provides a convenient, inexpensive and safe method of understanding the process without actually experimenting on an operating process plant (Raman, 1985). Over the years, computer based process simulation has come a long way from BASIC and FORTRAN algorithms run on large mainframe computers to modern and much more complex software packages like Aspen Plus™, ChemShare, ChemCAD, FLOWTRAN, HYSYS and Pro II that can be run on all types of computers. The evolution of the personal computer over the past two decades has put the power of process simulation in the hands of many engineers. A logic flowchart for development of a process simulation is shown in Figure 2.4.

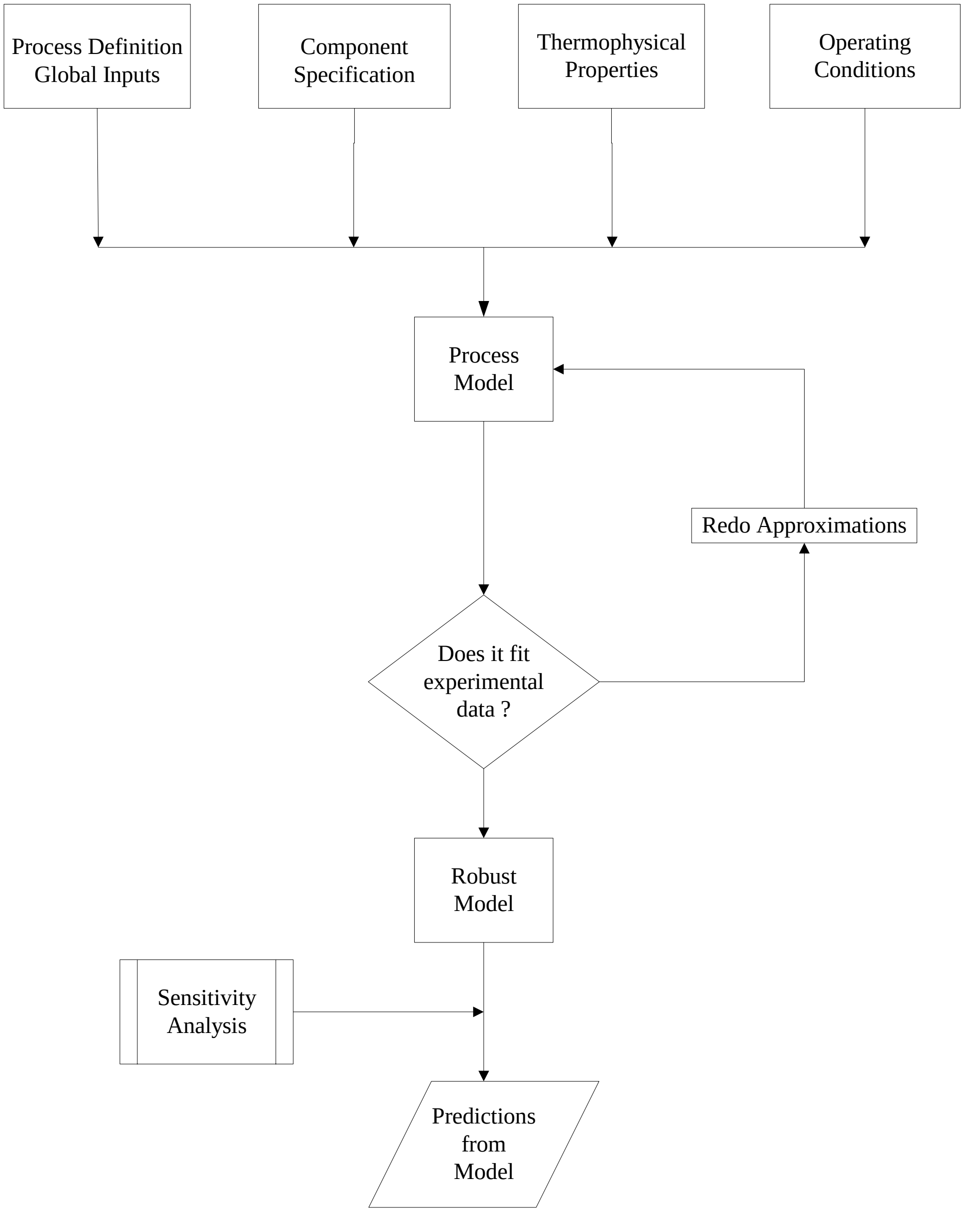


Figure 2.4 Simulation model development algorithm

Steady-state simulation is a powerful tool that enables process engineers to study plant behavior and analyze effects of changes in process parameters by using simulation software. The Chemical Process Industries have benefited by the use of process simulation by analyzing new development projects, studying economic feasibility of upcoming technologies and optimization and de-bottlenecking of existing plants. Process simulation models are developed using parametric data from existing plants or the literature. The advantage of modern simulator packages is the built in thermodynamic models and databanks, which make the task of process calculations on a computer very simple. A detailed process model fit precisely to plant data allows one to study the plant and its inefficiencies in depth and helps the engineer to cut costs, investigate design modifications, optimize the process, increase efficiency, cut down on cumbersome and expensive experimentation and improve the product quality.

Aspen Plus™ has many advantages as a process simulator. The thermodynamic models and the unit operation models are already built in, so there is no need to program them individually. The simulator can easily handle solids, which is a major advantage over many other software packages. Even with all the built in capabilities, Aspen Plus™ is easily customizable when required (Wooley and Ibsen, 2000). Aspen Plus™ is the most widely used commercial process simulation software for steady state simulation (Luyben, 2004). Steady-state simulation in Aspen Plus™ allows the user to predict the behavior of a system by using basic mass and energy balances, reaction kinetics, phase and chemical equilibrium. With Aspen Plus™ one can easily manipulate flowsheet configuration, feed compositions and operating conditions to predict plant behavior and design better plants.

### 2.3.1 Biomass Gasification Modeling and Simulation

For a clear understanding of the design and operation of a gasifier, complete knowledge of the effects of operation parameters like fuel, air and operation temperature is vital. Developing mathematical models for biomass gasification is a complex task due to the presence of multiple reactions at the high operating temperatures at which gasification takes place. Although biomass gasification is not a new technology, pertinent experimental data is incomplete. Consequently, most of the necessary modeling parameters are usually derived from coal gasification (Bettagli et al., 1995).

Many models for the fluidized bed gasifier are demonstrated in the literature. These models can chiefly be divided into kinetic models and thermodynamic equilibrium models. Numerous kinetics based biomass gasification models are illustrated in literature (Bettagli et al., 1995, Bilodeau et al., 1993, Bingyan et al., 1992, Wang and Kinoshita, 1993). Kinetics based models always contain parameters that make them not universally applicable to different plants (Schuster et al., 2001). Hence thermodynamic equilibrium calculations, which are independent of the gasifier design, may be more convenient for process studies on the influence of important process parameters (Schuster et al., 2001), although equilibrium models cannot be used to scale up gasifiers. Many equilibrium based biomass gasifier models are demonstrated in literature (Bridgwater et al., 1989, Schuster et al., 2001, Wang and Kinoshita, 1992, Watkinson et al., 1991). Schuster et al. have used a commercial equation-oriented simulation tool IPSEpro$^{TM}$ for developing an equilibrium model for biomass gasification.

In this study, biomass gasification using switchgrass as feedstock, was simulated using a thermodynamic equilibrium model developed in Aspen Plus™. The gasification model was developed with the following assumptions:

- The gasifier is at steady state operating condition
- The biomass feed is a uniform spherical solids feed
- The biomass undergoes instantaneous devolatilization
- Agglomeration, entrainment and ash formation were neglected
- Ideal mixing of biomass and air inside the reactor
- Ideal gas behavior
- Isothermal behavior of the gasifier

Most of the assumptions are simple and valid, although in practice the ideal mixing is not observed which gives rise to fluctuations in exit gas composition. Also, the gasifier does not perform isothermally, the operating temperature is sensitive to variations in moisture associated with biomass, air feed rate and the biomass feed rate.

### 2.3.2 Syngas Fermentation Modeling and Simulation

A recent report (Pimentel and Patzek, 2005) vehemently argues that the biomass generated ethanol manufacturing technology was over hyped and ethanol production miscalculated, thus rendering the project economically unfeasible. This study aims at simulation of a syngas fermentation model to study the maximum amount of ethanol production possible using switchgrass as feedstock. Many kinetics based models were used earlier to simulate biological reactors (Lee et al., 1983, Mussati et al., 1998, Nihtila et al., 1997), some have also used Finite Element analysis approach for modeling kinetics based reactors (Kalil et al., 2000, Nihtila et al., 1997).

Simulation of biological processes using commercial simulators is a daunting task, since most of the commercial simulators are packaged with technology pertaining to the petroleum industry namely distillation. There are some process simulators like gPROMS and Berkeley Madonna which are specifically designed for simulation of biological reactors. These software packages use integrated traditional kinetics models to simulate the bioreactor. A recent trend in bioreactor simulation is to build a reaction scheme based on the biological reactions and metabolic pathways and represent them as parallel or successive elementary reactions. Such an approach is more naturally integrated into process simulators since they treat reactions in a sequential manner (Pascal et al., 1995). To be rigorous, a simulation model must use equilibrium conditions as boundary values. The equilibrium predictions are far from simple because the liquid phase is a multi component mixture with ionic media (Pascal et al., 1995).

In this study, a fermentation reactor was simulated using two approaches, a thermodynamic equilibrium approach using Gibbs free energy minimization technique to calculate the maximum ethanol yield possible and analyze the effect of feed variations in individual components of syngas and a stoichiometric approach to study the effect of conversion of CO and $H_2$ on ethanol production. The bioreactor models were developed using the following assumptions:

- The bioreactor is at steady state operating condition
- Mass transfer limitations do not hinder reactions
- The presence of biological catalyst was neglected

- The reactions occurring in the reactor are instantaneous
- The reactor is well mixed and the gas phase is well dispersed in the liquid phase
- Isothermal behavior of the bioreactor

For the stoichiometry based reactor, a further assumption was the presence of only two reactions shown by equations 2.8 and 2.9. The assumption of neglecting the biological catalyst essentially treats the bioreactor as a chemical reactor based on two reactions. For the equilibrium based model, all possible reactions possible with the present chemical species at the operating temperature would be taken into account. It was demonstrated earlier (Rajagopalan, 2001) that the present bioreactor set up is not limited by mass transfer between the gas phase and the liquid phase, but was limited by intrinsic kinetics of P7. Thus the assumption of elimination of the microbial catalyst is sound for evaluating the maximum production of ethanol in a chemical reactor.

The simulation technique for modeling the gasifier and the bioreactor using Aspen Plus™ is elucidated in the next chapter.

# CHAPTER 3

# DEVELOPMENT OF PROCESS MODELS IN ASPEN PLUS

In this study, a steady state process simulator Aspen Plus™ (Advanced System for Process ENgineering), which is developed by Aspen Technology was used to develop process models. Aspen Plus™ is one of the most powerful and widely used process simulators in the process industry today. It has several features that make it very intuitive and user friendly. Its Graphic User Interface and Model Manager make an excellent guide for the user and allow for complete specifications and control at every stage of model development.

Although Aspen Plus™ is perhaps the most widely used process simulator in the industry; its usage is not widely reported in literature, since most of the industrial technical reports are proprietary in nature and not available universally.

## 3.1 Process Characterization

The fluidized bed gasification process was modeled as a steady state process in Aspen Plus™. The biomass input stream was assumed to consist of pure elemental solids and modeled as a combined solids feed stream.

The continuously stirred tank reactor process for anaerobic fermentation was modeled as a steady state process in Aspen Plus™.

### 3.2 Component Specification

Aspen Plus™ has an extensive database for pure component specification and properties. The built in database contains parameters for almost 8500 components which include organic, inorganic and salt species (Aspen Tech User Manuals, 2003). The species present in process feed streams and possible products are defined in the components specification form. The components specified in the gasifier and the bioreactor are listed in Table 5.1 and Table 5.3 respectively.

### 3.3 Physical Property Estimation

Estimation of accurate thermodynamic properties of pure components and mixtures in a process is vital for any process (Carlson, 1996). Property estimation in Aspen Plus™ can be performed using more than 80 EOS based thermodynamic models built in the simulator. Binary interaction parameters are determined data from DECHEMA (Aspen Tech User Manuals, 2003).

Properties for the components in the gasifier model were calculated from the SOLIDS Equation Of State (EOS) based property estimator since it is the recommended property estimator for solids. One reason for choosing Aspen Plus™ as a simulator over other simulation softwares was because it allows the user to include solids in the simulated process models. Properties for the components in the bioreactor simulation model were evaluated using the Non-Random Two Liquid (NRTL) model based estimator since the system is a Vapor-Liquid System (VLE) system operating at a pressure of less than 10 atmospheres with an assumption of the media as a non-electrolyte and the NRTL method is recommended for such conditions (Carlson, 1996).

### 3.4 Built-In Reactor Models in Aspen Plus

Aspen Plus™ has a Model Library which is equipped with reactor models chiefly categorized as: (a) Balance or stoichiometry based reactors (b) Equilibrium based reactors (c) Kinetics based reactors. Since reaction kinetics for both the gasifier and bioreactor are not well documented for the experimental studies at Oklahoma State University, kinetics based models were not used. The Gibbs reactor model in Aspen Plus™ is the only reactor model which calculates solid-liquid-vapor equilibrium, considers simultaneous phase and chemical equilibria and has a temperature based approach to equilibrium (Aspen Tech User Manuals, 2003). Hence it makes the most suitable reactor model for simulating the gasifier. For modeling the bioreactor, a balance based stoichiometric reactor model and an equilibrium based Gibbs reactor model were used.

### 3.5 Process Flowsheet Development

The Process Flowsheet Window and the Model Library in Aspen Plus™ allow the user to construct the flowsheet graphically (Aspen Tech User Manuals, 2003). The model library is equipped with an array of process equipments, modifiers and connectors from which a process plant and its sections can be designed. The flowsheet developed for the bioreactor based on the stoichiometric reactor model is shown in Figure 3.1.

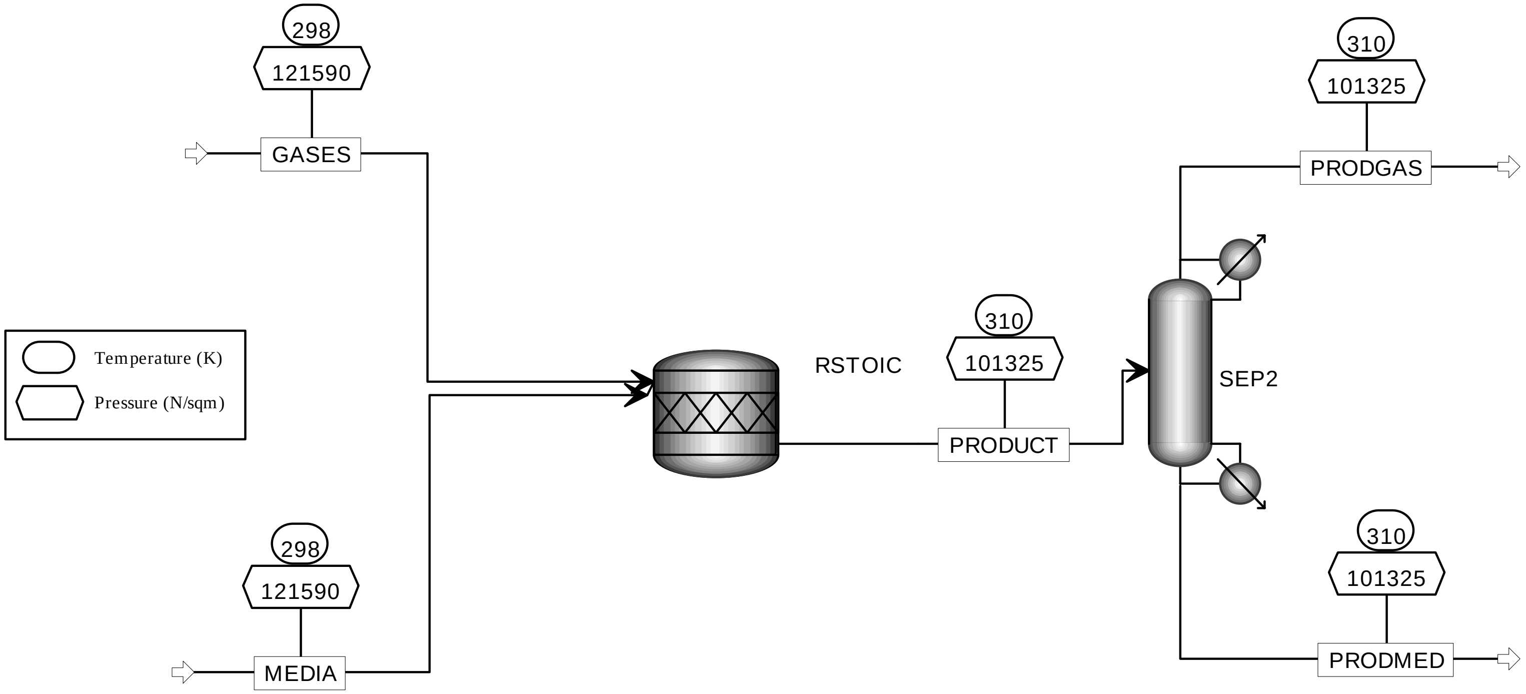


Figure 3.1 Flowsheet of the bioreactor simulation using a stoichiometric reactor model in Aspen Plus$^{TM}$

### 3.6 Process Variables Specification

The state variables for the system like temperature, pressure and flowrate are designated in the specifications input form. Molar compositions of the input gas streams for the gasifier and the bioreactor are defined in this section. A snapshot of a Specification Form is shown in Figure 3.2.

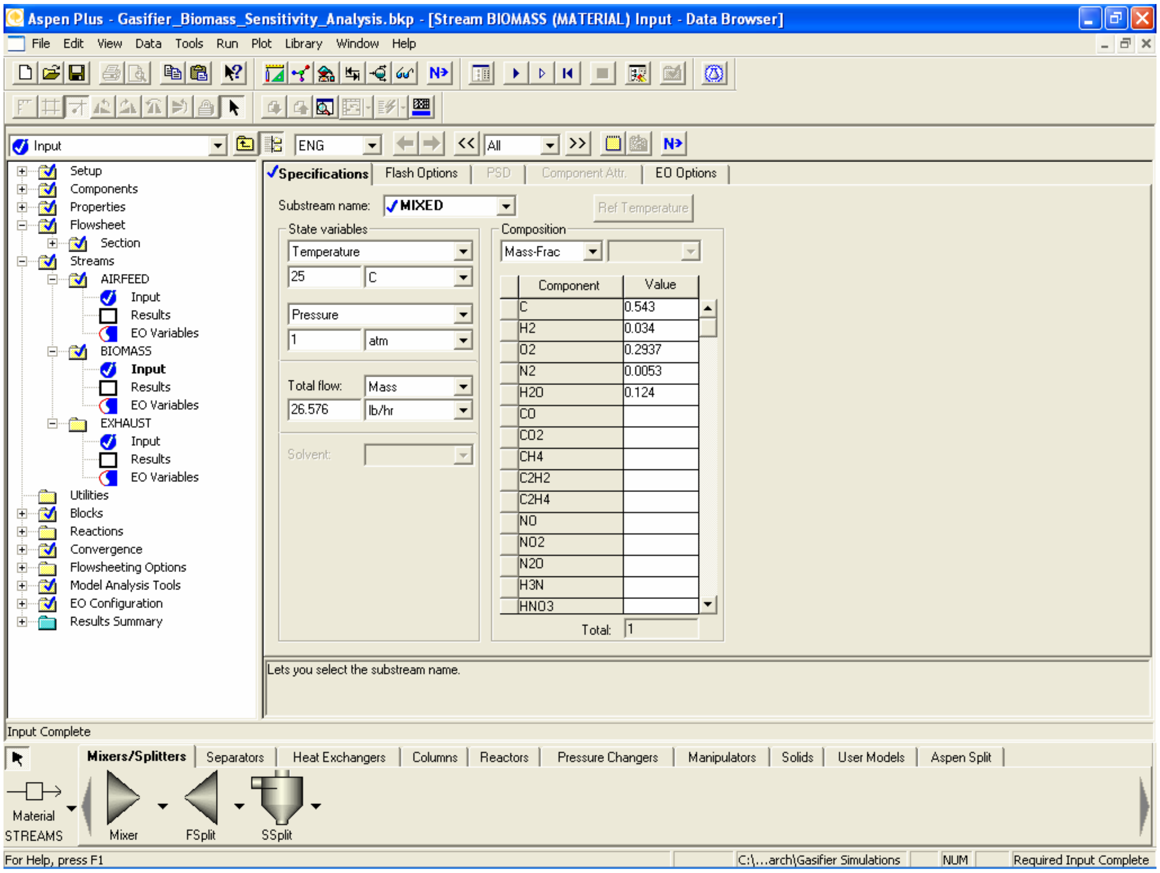
### 3.7 Sensitivity Analysis Tools

Aspen Plus™ equips the user with an array of model analysis tools like Sensitivity Analysis, Data Fit, Optimization and Constraint Analysis (Aspen Tech User Manuals, 2003). The sensitivity analysis tool was used in this study to analyze and predict the behavior of the model to changes in key operating and design variables.

Process variables like temperature and Air Fuel ratio were varied to study the effect on the exhaust gas composition of the gasifier. Feed composition of input gases to the bioreactor was varied to study the effect on ethanol production. These studies are helpful in predicting scenarios over a range of operating variables and provide solutions in a “What-If” analysis.

### 3.8 Simulation Output Data

Simulation results in Aspen Plus™ are reported on the Results Data Form and are segregated as a global output and a streams summary. The global output reports the overall mass balance, overall heat balance, heat duty and, reaction enthalpies. The stream results summarize the stream flowrates, stream compositions, individual stream fractions, stream flowrates, stream entropies, stream enthalpies, average densities and, molecular weights.



Aspen Plus - Gasifier_Biomass_Sensitivity_Analysis.bkp - [Stream BIOMASS (MATERIAL) Input - Data Browser]

Substream name: MIXED

State variables

Temperature: 25 C

Pressure: 1 atm

Total flow: Mass 26.576 lb/hr

Composition: Mass-Frac

| Component | Value |
|---|---|
| C | 0.543 |
| H2 | 0.034 |
| O2 | 0.2937 |
| N2 | 0.0053 |
| H2O | 0.124 |
| CO | |
| CO2 | |
| CH4 | |
| C2H2 | |
| C2H4 | |
| NO | |
| NO2 | |
| N2O | |
| H3N | |
| HNO3 | |

Total: 1

Lets you select the substream name.

Figure 3.2 Snapshot of a typical specifications input form in Aspen Plus$^{TM}$

# CHAPTER 4

# MODELING OF A GASIFIER AND A BIOREACTOR

## 4.1 Modeling a Gasifier as a Gibbs Reactor Model

The gasification process at Oklahoma State University is carried out in a pilot plant scale fluidized bed gasifier. A gasifier model in Aspen Plus™ was used for simulation with the assumption that the gasifier reaches physical and chemical equilibrium at the operating conditions and hence a Gibbs free energy minimization model denoted by RGibbs, can be used to simulate it. The built-in RGibbs reactor model of Aspen Plus™ is the only unit operations model that can compute a solid-liquid-vapor phase equilibrium. The model uses Gibbs free energy minimization with phase splitting to calculate equilibrium without the need to specify stoichiometry or reaction kinetics (Aspen Tech User Manuals, 2003).

RGibbs considers each solid stream component as a pure solid phase unless specified otherwise. The biomass input stream was specified with C, H, N and O as individual components. Reported experimental data shows an absence of sulfur in the standard run, in some other runs of the gasifier a trace amount of less than 0.01 % by weight has been reported. For this study, the presence of sulfur in biomass was assumed to be zero. Possible products of gasification that were identified in the reactor model are C, $H_2$, $N_2$, $O_2$, $H_2O$, CO, $CO_2$, $CH_4$, $C_2H_2$, $C_2H_4$, NO, $NO_2$, $N_2O$, $NH_3$ and $HNO_3$. Oxides of sulfur are ruled out since sulfur was not identified as a component in the reactor. A complete list of input components is shown in Table 5.1.

### 4.1.1 Base Case Simulation

A model was developed on the basis of input data from a standard experimental run of the gasifier. The composition of input biomass stream in the simulation was duplicated from the experimental run and is listed in Table 5.1. The biomass input stream is fed to the reactor at 25 ºC and 1.2 atm pressure. The air input stream was also fed to the reactor at 25 ºC and 1.2 atm pressure. Biomass was fed at a rate of 17.64 Kg/hr and air was fed at a rate of 30.13 Kg/hr. The reactor operating conditions were specified at 815 ºC and 1.0 atm, with a temperature approach to equilibrium for the reactor. Thermodynamic properties of the components were calculated for the model using the SOLIDS EOS based property estimator in Aspen Plus™.

### 4.1.2 Fuel Sensitivity Analysis

This analysis was conducted to study the effect of a change in the biomass feed rate on the exhaust gas composition, while maintaining the biomass elemental composition the same as the base case. A sensitivity analysis tool was implemented as a nested loop in the model developed for the base case scenario. Biomass feed in 34 runs reported by the gasifier research group varied from 12.01 to 23.15 Kg/hr (including moisture). The fuel or biomass input in the sensitivity model was varied from12.0 Kg/hr to 24.0 Kg/hr (including moisture). Operating conditions for all other streams and the reactor remained the same as the base case.

### 4.1.3 Moisture Sensitivity Analysis

The biomass is generally associated with some moisture when fed to the reactor. This analysis was conducted to study the effect of variation in the moisture content of the biomass on the composition of exhaust gases from the gasifier. The experimental range of moisture associated with biomass was 1.13 Kg/hr to 5.99 Kg/hr. The $H_2O$ content in the biomass input stream to the reactor was varied from 0.5 Kg/hr to 8.0 Kg/hr. Operating conditions for the air feed stream and the reactor remained same as the base case.

### 4.1.4 Temperature Sensitivity Analysis

In a gasification process, reactor temperature is a key variable since it affects equilibrium thermodynamics. In this analysis, the reactor temperature was varied to study the effects on the output gas composition and individual gas flowrates in the exhaust stream. The range of temperatures over which the pilot plant was tested is 635 ºC to 850 ºC. In the simulated model the temperature was varied from 600 ºC to 900 ºC. All other operating conditions remained the same as the base case model.

### 4.1.5 Air Fuel Ratio Sensitivity Analysis

A term widely used in gasification technology is Air Fuel Ratio since it has a strong effect on the process. The Air Fuel (AF) ratio is defined as:

$$AF = \frac{Weight\ of\ Air}{Weight\ of\ Dry\ Biomass} \qquad (4.1)$$

The AF ratio is a key variable because an increase in it causes an increase in the amount of oxidant and hence a shift in the gasifier operation from pyrolysis to gasification and further on towards total combustion. A comparative study of the producer gas quality and energy conversion efficiency of various gasifiers shows that these parameters are predicated by the AF ratio (Esplin et al., 1986). In this analysis the AF ratio was varied from a value of 1.1 to 3.31 and the effect on product gas flow rates and mole fractions of individual gas components charted. Other operating parameters for the model remained same as the base case model.

### 4.1.6 Equivalence Ratio Sensitivity Analysis

A concept frequently used in gasification technology is the Equivalence Ratio (ER), which is defined as the oxidant to fuel ratio divided by the stoichiometric ratio.

$$ER = \frac{Weight\ of\ \ Air / Weight\ of\ \ Dry\ Biomass}{Stoichiometric\ Air\ to\ Biomass\ Ratio} \tag{4.2}$$

The ER should be greater or equal to 1.0 for complete combustion of fuel to carbon dioxide and water (Reed, 1981). Complete combustion of wood biomass requires 6.364 g air/g wood (Reed, 1981). For this analysis, switchgrass composition is assumed to be same as the elemental composition of wood as $CH_{1.4}O_{0.59}N_{0.1}$ (Reed, 1981). The ER is frequently manipulated in gasification technological models to study its effect on gasifier performance. The ER determines the fraction of fuel that is gasified in the reactor as well as affects the fluidization quality and the reactor temperature (Natarajan et al., 1998). In this analysis, the ER was manipulated over a range of 0.17 to 0.53 to study its effect on the exhaust gas composition. Other process parameters for reactor operation remained same as the base case model.

## 4.2 Bioreactor Modeling in a Gibbs Reactor Model

Syngas fermentation to produce ethanol is performed in a laboratory scale biofermentor at Oklahoma State University. Kinetics of the fermentation reactions to produce ethanol is not well quantified. A bioreactor model developed in Aspen Plus™ was designed with the assumption that the CSTR attains chemical and phase equilibrium at the operating temperature and pressure and hence it can be simulated using a Gibbs reactor model. The Gibbs reactor model does not take microbial growth into account as a catalyst for the conversion of syngas to ethanol. Although treatment of the bioreactor as a chemical reactor without microbial catalyst is not accurate, this analysis was conducted to study the maximum amount of ethanol that can be produced in a Gibbs free energy model. Sensitivity analyses based on this model were conducted to study the effects of variation in individual feed gas compositions on bioreactor performance. Thermodynamic properties for the components were calculated using an NRTL based property estimator in Aspen Plus™, since the bioreactor is a liquid-liquid equilibrium model, properties for which are best predicted using the NRTL based model (Carlson, 1996).

The syngas stream to the bioreactor model was assumed to be composed only of CO, $CO_2$, $H_2$ and $N_2$. Presence of trace gases and hydrocarbons were neglected since their combined mole fraction contribution to the stream is about 1%. Presence of methane in the exhaust stream of the gasifier has not been taken into account since it causes a drastic reduction in the ethanol produced in the model; this is discussed in a later section.

The media fed to the bioreactor contains a solution of nutrients in water, which are necessary for microbial growth. In the simulated model, the media feed stream is assumed to be pure water. Possible products from the model were identified as $C_2H_5OH$, $H_2O$, CO, $CO_2$, $H_2$ and $N_2$. Butanol and Acetic Acid, which are usually associated as by products in syngas fermentation have not been taken into consideration as possible products, since the focus of this work was on ethanol production. A complete list of input components and specification data is shown in Table 5.3. The product stream from the model was split using a phase separator, into a gas phase output stream containing the gases CO, $CO_2$, $H_2$ and $N_2$ and a liquid phase output stream containing $C_2H_5OH$ and $H_2O$.

### 4.2.1 Base Case Simulation

The model was developed on the basis of data from an experimental run of the bioreactor. Input gas and media streams were fed at 25 ºC and 1.2 atm pressure each. The gas composition and flowrates are tabulated in Table 5.3. The reactor operating conditions were specified at 37 ºC and 1.0 atm pressure, with a temperature approach to equilibrium.

### 4.2.2 Carbon Monoxide Sensitivity Analysis

This analysis was conducted to study the effect of variation in the CO molar composition in the feed gas stream on the ethanol produced in the bioreactor. The analysis was performed using output data from a set of 17 simulation runs of the model developed for the base case scenario. The exhaust gas composition data from the gasifier experimental runs was used for this analysis, due to the lack of a range of data from the laboratory bioreactor runs. Trace gases and hydrocarbons present in the exhaust gas stream of the gasifier were not considered and were compensated by difference in the percentage composition value of $N_2$. In the feed gas stream the mole fraction of CO was varied while keeping the mole fractions of $CO_2$ and $H_2$ constant. A change in the mole fraction of CO was compensated by difference with a change in the mole fraction of $N_2$, since variation of $N_2$ does not affect bioreactor performance as it is an inert component. The mole fraction of CO was varied from 0.1 to 0.2 in the simulation runs while keeping the mole fraction of $CO_2$ at a constant of 0.1871 and the mole fraction of $H_2$ at 0.0525. The mole fraction of $N_2$ was varied to adjust variations in the mole fraction of CO. Other operating conditions in the model remained the same as the base case model.

### 4.2.3 Carbon Dioxide Sensitivity Analysis

This analysis studied the effect of variation in the mole fraction of $CO_2$ in the feed gas on the ethanol produced. The analysis is based on output data from a set of 18 simulation runs of the model developed using the base case. The mole fraction of $CO_2$ was varied in the feed stream while keeping the mole fractions of CO and $H_2$ constant at the average gasifier output level. Presence of trace gases and hydrocarbons in the gasifier exhaust was neglected in the input gas feed stream to the bioreactor as discussed earlier. The mole fraction of $CO_2$ varied in the experimental runs from 0.1774 to 0.2055. In the simulation analysis model, the mole fraction of $CO_2$ was varied from 0.11 to 0.25. The mole fraction of $N_2$ was varied in the feed by a difference to compensate for variation in the mole fraction of $CO_2$. Mole fraction of CO was held at a constant of 0.1407 and mole fraction of $H_2$ was kept constant at 0.0525. All other operating conditions for the streams and reactor remained same as the base case model.

### 4.2.4 Hydrogen Sensitivity Analysis

This study delineated the effect of variation in the mole fraction of $H_2$ in feed gas to the bioreactor on the ethanol produced in the model. The analysis is based on output data from a set of 16 simulation runs of the model developed using the base case. The mole fraction of $H_2$ was varied in the gas feed, while keeping the mole fractions of CO and $CO_2$ constant at 0.1407 and 0.1871 respectively. Presence of trace gases and hydrocarbons in the gasifier exhaust gas was neglected as discussed earlier. In the experimental runs of the gasifier, the composition of $H_2$ varied from a mole fraction of 0.0379 to 0.0627. Mole fraction of $H_2$ in the simulated runs was varied from 0.03 to 0.09 while maintaining CO and $CO_2$ at constant mole fractions of 0.1407 and 0.1871 respectively. All other operating conditions for the streams and the reactor remained same as the base case model.

### 4.2.5 Media Sensitivity Analysis

The media feed to the bioreactor was assumed as a pure water feed stream to the Gibbs reactor model. This analysis presents the effect of variation of water input to the reactor on the liquid phase output composition from the reactor model. The water input to the reactor was varied using a sensitivity analysis tool built as a nested loop in the process model and the exit mole fractions of water and ethanol were charted. In the laboratory experiments on the bioreactor, media feed is usually varied from a flowrate of

0.2 to 2.5 ml/min or 3.3 E-6 Kg/sec to 4.1 E-6 Kg/sec. In this analysis the water input flowrate was varied from 1.0 E-6 Kg/sec to 5.0 E-5 Kg/sec. The gas composition was kept at constant mole fractions of CO: 0.1407, $CO_2$: 0.1871, $H_2$: 0.0525 and $N_2$: 0.6197. All other process parameters remained same as the base case model.

### 4.3 Bioreactor Modeling in a Stoichiometric Reactor Model

Ethanol production from syngas can be stoichiometrically represented by the reactions shown by equations 2.8 and 2.9. The syngas is composed mainly of CO, $CO_2$, $H_2$ and $N_2$ gases. The exhaust gas from the gasifier contains a small fraction of methane but its presence was shown to reduce the production of ethanol in the simulated model, which is discussed in a later section. Other trace hydrocarbons emanating from the gasifier were assumed to be negligible for reactor modeling in Aspen Plus™. Since reaction kinetics for the bioreactor is not well quantified and a kinetic model for the bioreactor not yet developed, a kinetics approach for the reactor cannot be accurately modeled. The stoichiometric reactor model developed in Aspen Plus™ performs mass and energy balances based on the reaction stoichiometry and extent of conversions of the reactants.

For the bioreactor modeling in a stoichiometric reactor model, it was assumed that only the above mentioned reactions are occurring in the bioreactor. The individual effects of the two reactions on ethanol production and reactant consumption were studied in this analysis. The effect of microbial growth and catalytic behavior of the organism on reactant consumption was not taken into consideration. The syngas feed to the bioreactor was assumed to be comprised of pure CO, $CO_2$, $H_2$ and $N_2$ gases. Presence of methane and other hydrocarbons in the gasifier exhaust gas were neglected in the gas feed stream to the model. The media fed to the bioreactor contains nutrients necessary for microbial growth. The media feed stream in the model was defined as a pure water stream.

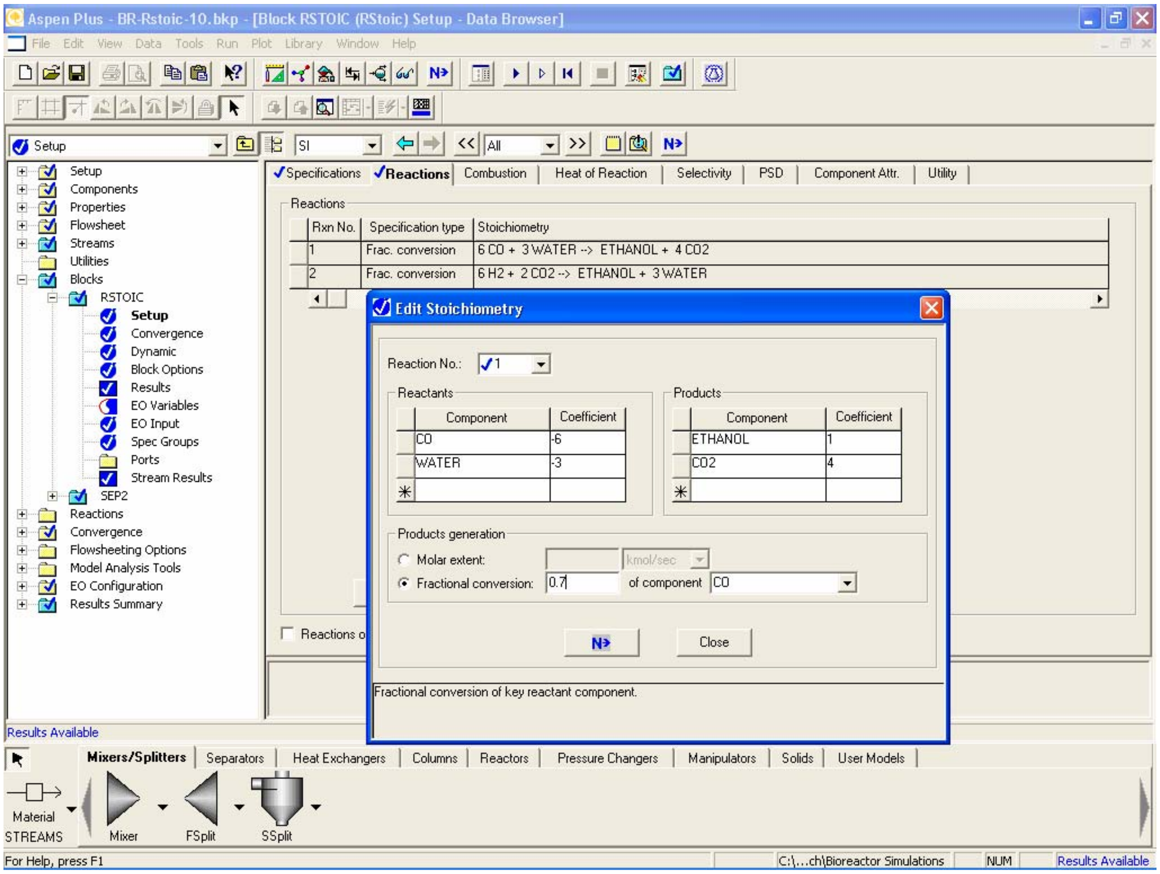
CO, $CO_2$, $H_2$, $N_2$, $H_2O$ and $C_2H_5OH$ were defined as possible products from the bioreactor. Experimental runs of the bioreactor show a production of butanol and acetic acid as well; these have not been taken into consideration in the simulated model since only the production of ethanol was under study. A complete list of input components is specified in Table 5.3. The product stream from the reactor was split into a gas phase containing CO, $CO_2$, $H_2$ and $N_2$ and a liquid phase containing $H_2O$ and $C_2H_5OH$ using a phase separator.

### 4.3.1 Base Case Simulation

A base case simulation was developed on the basis of experimental data from a laboratory run of the bioreactor. The gas and media streams were fed to the reactor at 25 ºC and 1.2 atm pressure each. Stream composition and flowrate specifics are listed in Table 5.3. Reactions 2.8 and 2.9 were specified occurring in the reactor at 37 ºC and 1.0 atm pressure. For reaction 2.8 the limiting reactant is CO and for reaction 2.9 the limiting reactant is $H_2$. The extents of both the reactions were individually varied by trial and error until the composition of exit gases closely matched composition of exit gas in the experimental run. The product stream from the reactor was split into a gas phase containing CO, $CO_2$, $H_2$ and $N_2$ and a liquid phase containing $H_2O$ and $C_2H_5OH$ using a phase separator.

### 4.3.2 Sensitivity of the Model to Stoichiometric Conversions

Extents of reactions 2.8 and 2.9, defined as variables $E_1$ and $E_2$, were manipulated for the base case analysis and output of the experimental results closely matched at $E_1 = 0.1$ and $E_2 = 0.1$. For this analysis, $E_1$ and $E_2$ were varied individually and simultaneously to study the effects on exit gas compositions and ethanol production from the simulated model. Individual extents of reaction can be defined in Aspen Plus™ using the reaction stoichiometry form, shown in Figure 4.1. The extents of reactions were also varied using a sensitivity model built as a nested loop in the simulation.



| Rxn No. | Specification type | Stoichiometry |
|---|---|---|
| 1 | Frac. conversion | 6 CO + 3 WATER --> ETHANOL + 4 CO2 |
| 2 | Frac. conversion | 6 H2 + 2 CO2 --> ETHANOL + 3 WATER |

Reaction No.: 1

Reactants

| Component | Coefficient |
|---|---|
| CO | -6 |
| WATER | -3 |

Products

| Component | Coefficient |
|---|---|
| ETHANOL | 1 |
| CO2 | 4 |

Products generation

○ Molar extent: kmol/sec

● Fractional conversion: 0.7 of component CO

Fractional conversion of key reactant component.

Figure 4.1 A snapshot of a typical reaction stoichiometry input form in a stoichiometric reactor model developed in Aspen Plus$^{TM}$

# CHAPTER 5

# RESULTS AND DISCUSSION

## 5.1 Gasifier Modeling

The results from simulated models are presented and discussed in this chapter. The output from the Gibbs reactor model is presented in the form of charts and data tables, and compared with results from pilot plant studies and the literature.

### 5.1.1 Base Case Simulation Output and Model Validation

The base case simulation of the gasifier was developed on the basis of input data from a standard experimental run of the gasifier pilot plant. The experimental input data for the feed streams and operating conditions were used as input data for the simulation. The input of air and biomass feed streams by mass flowrate is listed in Table 5.1. The results from the simulation are presented in Table 5.2.

Production of CO in the model was at a rate of 10.55 Kg/hr at the operating conditions, which is higher than the observed experimental value of 6.43 Kg/hr. Production of $CO_2$ in the model was 9.727 Kg/hr which is slightly lower than the experimental value of 10.48 Kg/hr. A higher model prediction of CO in the output could be an indication of a potentially theoretical higher possibility of CO production from the pilot plant. Predicted $N_2$ production in the model is 23.25 Kg/hr which is present in the gas phase. The $N_2$ in the exhaust gas of the experimental run was reported as 23.11

Kg/hr. $N_2$ input to the model in the input air stream was 23.11 Kg/hr and in the biomass stream was 0.14 Kg/hr. Hence the theoretical prediction from the model indicates complete conversion of $N_2$ into gas phase and emission as exhaust gas. This indicates that the behavior of $N_2$ is completely inert in the gasification unit. In the experimental run, some amount of $N_2$ might have been lost as solids in ash and tar, which is not present in theoretical calculations of the simulated model. The other possibility is experimental error since $N_2$ is calculated experimentally by difference.

Table 5.1 Experimental input composition of feed streams to gasifier

| | Element/ Gas | Kg/hr |
|---|---|---|
| Air | $N_2$ | 23.11 |
| | $O_2$ | 7.02 |
| | Total | 30.13 |
| Switchgrass | C | 7.18 |
| | H | 0.91 |
| | N | 0.14 |
| | O | 7.77 |
| | S | 0.00 |
| | Ash | 0.55 |
| | $H_2O$ | 1.64 |
| | Total | 18.19 |

$O_2$ was completely utilized in the simulation model for conversion of carbon, and there was no detectable emission of $O_2$ in the exhaust gas. In the experimental run, there was no emission of $O_2$ in the exhaust gas. $H_2$ produced in the simulation was 0.696 Kg/hr, which is greater than the experimental emission of 0.16 Kg/hr. $CH_4$ production in the simulation was 1.4 E-3 Kg/hr, which is much lower than the experimental value of 0.96 Kg/hr. $C_2H_2$ production in the simulation was 1.19 E-10 Kg/hr, which is much less than the experimental production value of 0.06 Kg/hr. The $C_2H_4$ produced in the simulation was 1.93 E-9 Kg/hr which is much less than the experimental production value of 0.62 Kg/hr. $C_2H_6$ produced in the simulated model was 2.45 E-10 Kg/hr, which is far lesser than the experimental production value of 0.05 Kg/hr. This shows that production of hydrocarbons in the model was much lower than actual production in the pilot plant studies. Production of hydrocarbons at higher temperatures of operation of the gasifier is theoretically low, since a thermal cracking of hydrocarbons take place. The presence of a high amount of hydrocarbons in the fluidized gas indicates incomplete combustion, gas bypassing due to the presence of gas pockets at lower temperatures inside the reactor or thermal unevenness.

The production rate of $H_2O$ in the simulation was 3.42 Kg/hr which was quite close to the experimental production value of 3.06 Kg/hr. Some $H_2O$ is lost in association with the ash emanating from the gasifier in the experimental run but the difference can also be accounted for by the incomplete hydrocarbon combustion. A tabular comparison of all the gases is presented in Table 5.2. The experimental values of production for the most pertinent gases (CO, $CO_2$ and $H_2$) in the study closely matched the simulation and can be assumed to be generally predictive. A complete list of components in the product gas is shown in Appendix A.1.

Table 5.2 Comparison of simulation and experimental data

|  | Gas | Experimental Output Kg/hr | Simulation Output Kg/hr |
|---|---|---|---|
| Exhaust Gases | $H_2$ | 0.16 | 0.696 |
|  | $N_2$ | 23.11 | 23.250 |
|  | $O_2$ | 0.00 | 0.000 |
|  | CO | 6.43 | 10.550 |
|  | $CH_4$ | 0.96 | 1.40 E-3 |
|  | $CO_2$ | 10.48 | 9.727 |
|  | $C_2H_2$ | 0.06 | 1.19 E-10 |
|  | $C_2H_4$ | 0.62 | 1.93 E-9 |
|  | $C_2H_6$ | 0.05 | 2.45 E-10 |
|  | $H_2O$ | 3.06 | 3.543 |

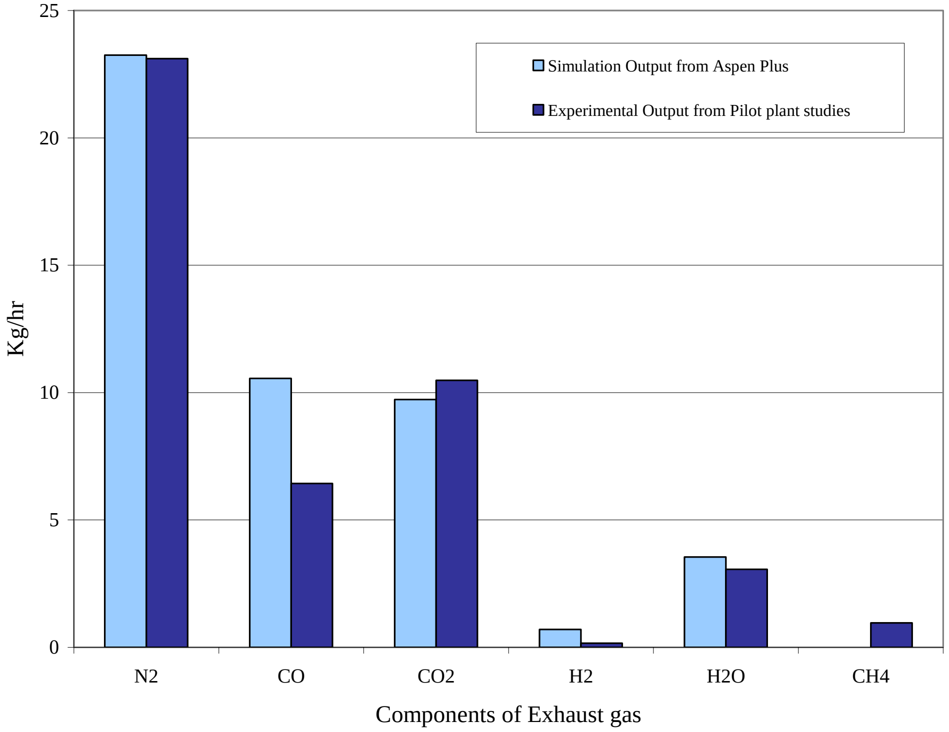


Figure 5.1 Graphical comparison of simulation data with experimental results

### 5.1.2 Effect of Fuel Variation on Production of Syngas

The input biomass feed to the simulation was varied from 12.0 Kg/hr to 24.0 Kg/hr and individual gas production rates in the exhaust gas stream compared with the variation in biomass feed. The results from this sensitivity analysis are charted in Figure 5.2. There was a linear increase in production of CO with an increase in biomass feed. This indicates that the majority of conversion of biomass is predicted to go to CO in a Gibbs reactor model. There was also an increase in the production of $H_2$ with an increase in the biomass feed. There is a slight reduction in $H_2O$ levels produced in the reactor with an increase in the biomass feed. This indicates a prediction of almost complete conversion of elemental H in the biomass feed to gaseous $H_2$; only a small fraction of elemental H gets converted into hydrocarbons. A decrease in the production of $CO_2$ was also shown in the simulation output. This could be partially the result of a decrease in the Air Fuel ratio and hence lesser conversion of the fuel to $CO_2$ by combustion. However a more likely possibility, since there is a simultaneous decrease of $H_2O$ and increase of $H_2$ in the model, is that the changes observed are a result of the effect of the water-gas shift reaction occurring in the reactor at the operating temperature. Production of $CH_4$ in the model increased with an increase in biomass feed. The production figures were extremely small to be compared on the same scale as the other gases and were omitted in the chart. The increase in hydrocarbons with an increase in biomass feed is a result of the change in the Air to Fuel ratio. Production of $N_2$ increased linearly with biomass feed which shows conversion of organic N present in biomass into $N_2$ gas.

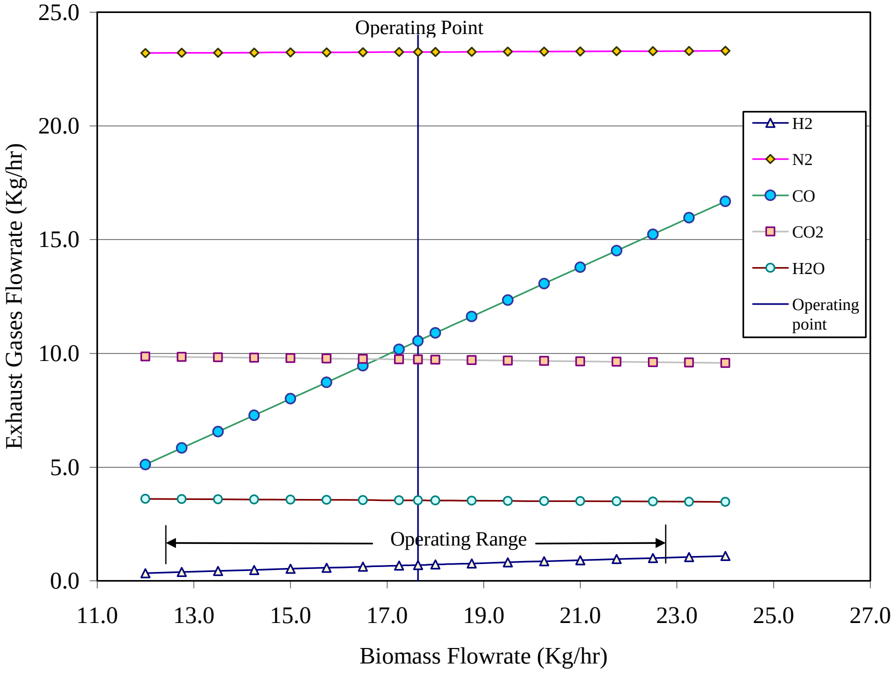


Figure 5.2 Effect of variation in the biomass feed rate on the exhaust gas composition

### 5.1.3 Effect of Moisture Variation on Production of Syngas

The moisture associated with biomass in the feed stream was varied from 0.5 Kg/hr to 8.0 Kg/hr while keeping the biomass (dry basis) at a constant feed of 16.0 Kg/hr and its composition the same as the base case model to model natural moisture content variability and effect on syngas composition. The results from this analysis are charted in Figure 5.3. An increase of $H_2O$ in the exhaust gas was noted, although the increase was not linearly proportional with the input of $H_2O$ to the model. An increase in $CO_2$ shows strong indication of the action of the water-gas shift reaction in the model since it is accompanied by a decrease in CO output. There is also an increase in production of $H_2$

which further supports the action of the water-gas shift reaction. An increase of $CO_2$ could also mean an increase in combustion due to increased amount of oxidant in the reactor. A part of the decrease in CO production could be attributed to the conversion of CO to $CO_2$ due to higher oxidation in the model. This is also shown by a decrease in the production of $CH_4$ with an increase in the moisture associated with the biomass feed. The curve trends for all the gases in this analysis completely match with results from a computer generated equilibrium model for a fluidized bed gasifier found in literature (Bridgewater et al., 1989).

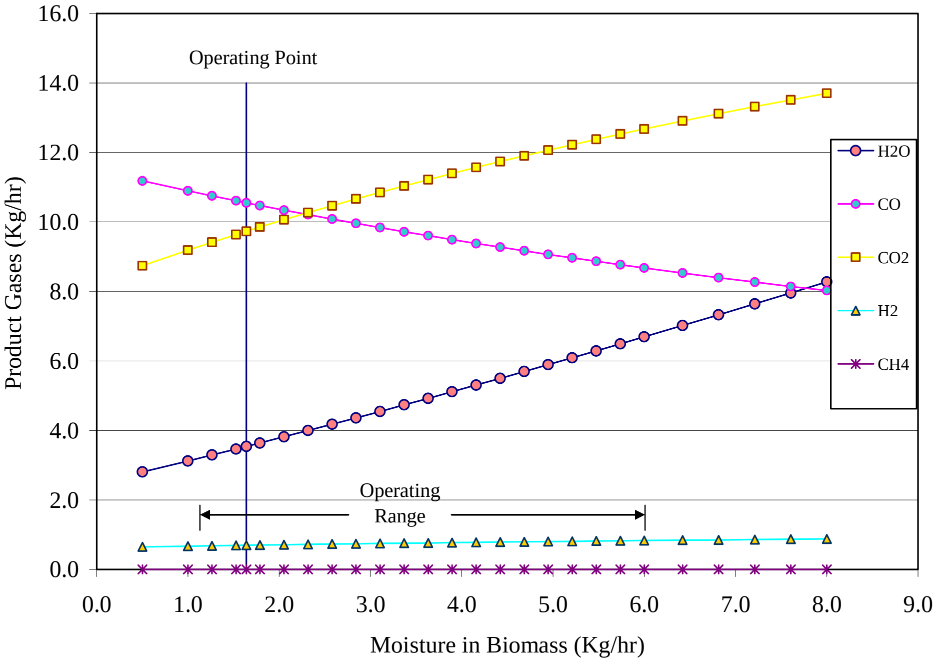


Figure 5.3 Effect of variation in the moisture associated with biomass feed rate on the exhaust gas composition

### 5.1.4 Effect of Temperature Variation on Syngas Production

Temperature is a key variable in a gasification process since most of the reactions occurring in the reactor are sensitive to temperature and the gasifier operates over a broad range of temperatures. In this analysis, the temperature was varied from 873 K to 1123 K while keeping the biomass and air feed rates at the base case values. Operational variables of the reactor remained same as the base case simulation. Production of CO increased from 7.219 Kg/hr to 11.05 Kg/hr over the range of 300 K with the same biomass input. This indicates the sensitivity of CO production to temperature and suggests the possibility to control CO production by manipulating temperature. The production of $CO_2$ dropped from 13.469 Kg/hr to 8.946 Kg/hr in the temperature interval. Production of $N_2$ remained constant at a value of 23.250 Kg/hr. Since this is a very high value as compared to the production values of other gases, it was not included in the following production profile charts. A production chart on mass basis of gases is compared with the increase in operation temperature and shown in Figure 5.4.

To better understand the relative behavior of the individual gases, a mole fraction basis chart is shown in Figure 5.5. An increase in the mole fraction of CO is observed with an increase in the operating temperature which is similar to the trends found in the literature (Wang and Kinoshita, 1992, Wang and Kinoshita, 1993). A decrease in the mole fraction of $CO_2$ in the output correlated with an increase in the operating temperature, a trend that is also found in the literature (Wang and Kinoshita, 1992, Bingyan et al., 1992, Wang and Kinoshita, 1993). The mole fraction of $H_2$ reaches a maximum value a temperature of 948 K but then decreases on a further increase in temperature.

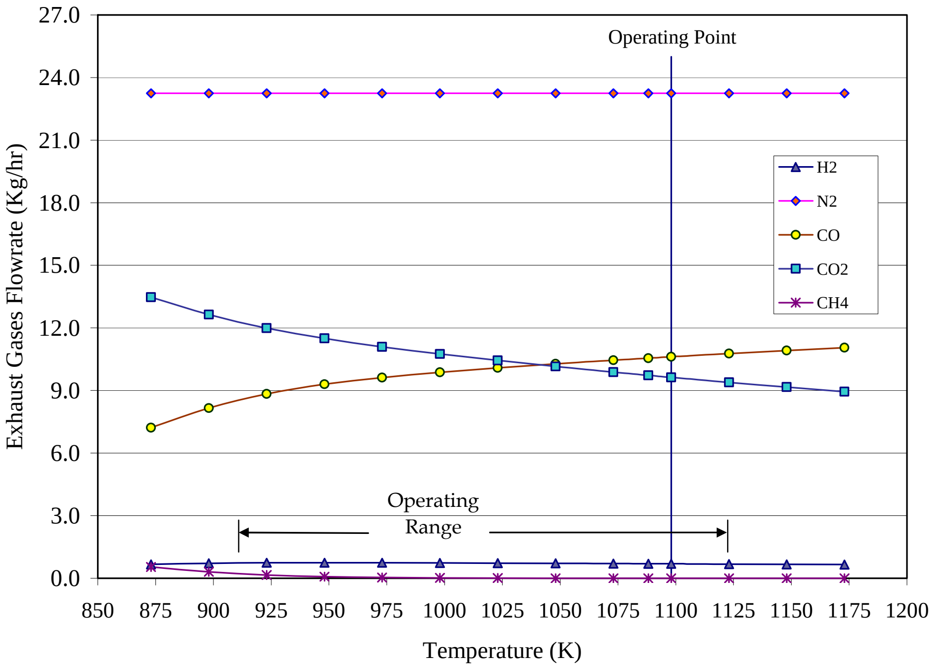


Figure 5.4 Effect of variation in the operation temperature on the exhaust gas composition: mass basis

Since the temperature range is above our experimental pyrolysis temperature (< 873 K) and lower than the total combustion temperature (>1200 K), the effect of water-gas shift reaction is most visible. The curve characteristics of gas mole fractions closely match those found in literature for biomass gasification in air (Reed, 1981, Wang and Kinoshita, 1992, Watkinson et al., 1991), and are in complete agreement with a modeling study using IPSEpro$^{TM}$ simulator (Schuster et al., 2001) and a computer program developed for simulation of biomass gasification under equilibrium conditions (Kinoshita et al., 1991). The variation in the mole fractions of CO, $H_2$ and $CH_4$ is closely matched with previous studies using a mathematical model for biomass gasification (Bilodeau et al., 1993, Watkinson et al., 1991) and experimental studies on biomass gasification (Wang and Kinoshita, 1992). The mole fraction of $CH_4$ decreases with an increase in temperature, which is also seen in experimental studies in the literature (Wang and Kinoshita, 1992, Watkinson et al., 1991). This could be attributed to a reverse methanation reaction occurring in the gasifier at the operation temperature.

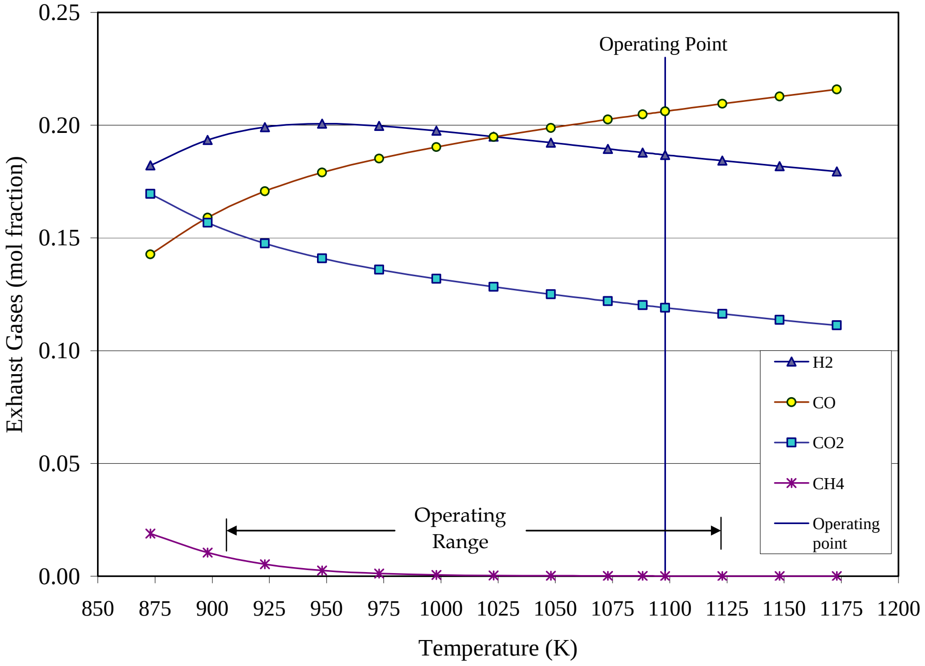


Figure 5.5 Effect of variation in the operation temperature on the exhaust gas composition: mole basis

Although in this analysis a simple change in temperature has been used to study a variation in output gas composition, such a change is not possible in actual operation. To vary the temperature, a change in the Air Fuel ratio is required which changes the amount of combustion and hence the thermal output in the reactor which in turn affects the operation temperature.  However there are thermal losses from the gasifier, either due to operational heat losses or due to calorific loss to the moisture present (Bridgewater et al., 1989).  Results from this analysis can be used to study other biomass feeds which may have a different moisture content and hence a different operational temperature for the same Air Fuel ratio.  The hydrocarbons $C_2H_2$, $C_2H_4$ and $C_2H_6$ were produced in trace quantities in the simulation and decreased with an increase in the operation temperature. The variation in the mole fraction of these three hydrocarbons on a logarithmic scale is charted against the variation in temperature and is shown in Figure 5.6.

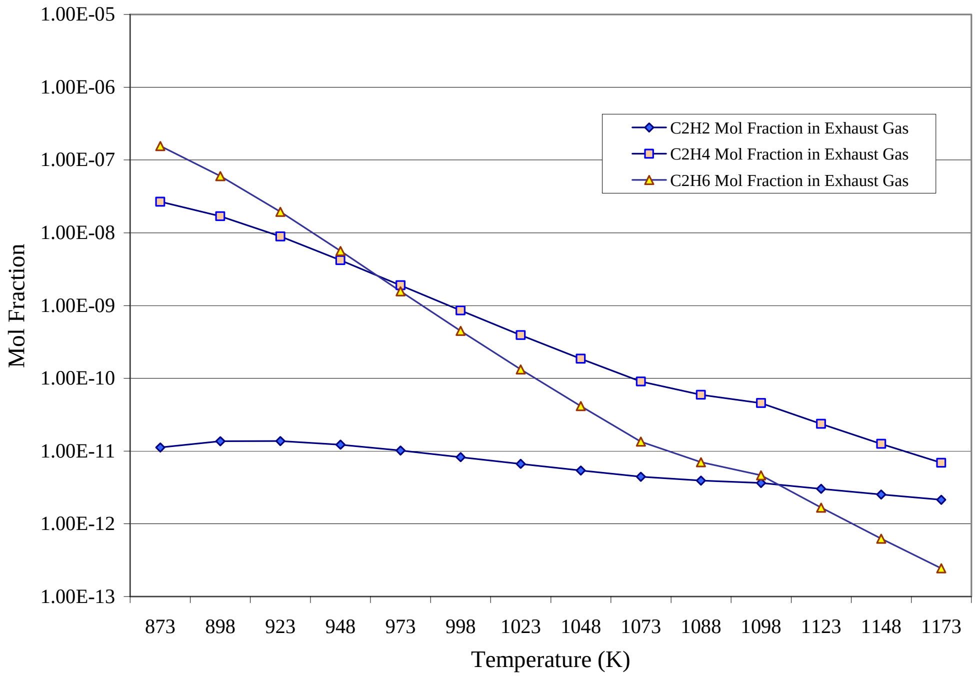


Figure 5.6 Effect of variation in the operation temperature on the hydrocarbons in the exhaust gas

### 5.1.5 Effect of Air Fuel Ratio on Syngas Production

Air Fuel (AF) ratio is an important variable in gasifier operation. In this analysis, the air feed rate was varied from 20.0 Kg/hr to 61.0 Kg/hr while keeping the biomass feed rate constant at the base case value; thus varying the AF ratio from 1.10 to 3.36. The reactor temperature and all other operating conditions were kept constant at the base case values. Production of CO decreased from 12.715 Kg/hr to 3.965 Kg/hr over the manipulated range of AF ratios. Production of $CO_2$ increased from 6.314 Kg/hr to 20.079 Kg/hr. The $O_2$ output remained zero at all times. The variation of individual gases on a mass flow basis is charted against the AF ratio in Figure 5.7.

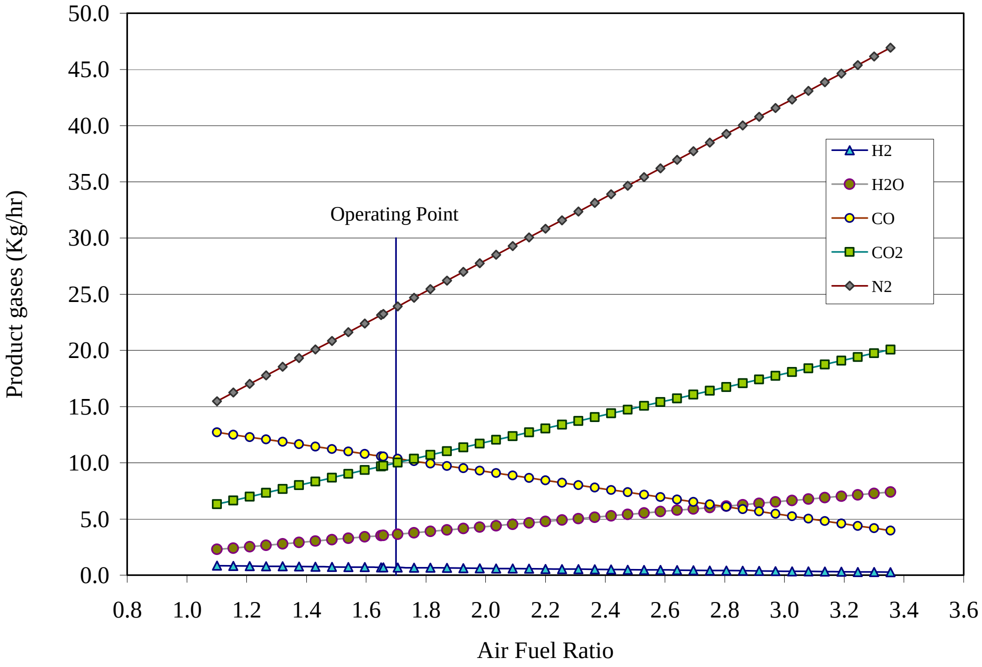


Figure 5.7 Effect of variation in the Air – Fuel Ratio on the exhaust gas composition: mass basis

To better understand the relative changes of the individual gases a mole fraction basis chart for the major product gases is shown in Figure 5.8. The mole fraction of $N_2$ increases with an increase in the AF ratio; this indicates the increase in $N_2$ production which is associated with an increase in the air feed to the reactor. An increase in the AF ratio suggests an increase in oxidation of the fuel, hence a higher production of $CO_2$ from elemental C and more conversion of CO into $CO_2$. This is also indicated by the decrease in the mole fraction curve of CO with a simultaneous increase in the mole fraction of $CO_2$. A high amount of $CO_2$ present in the reactor tends to shift the equilibrium of the water gas shift reaction towards greater production of $H_2O$ at higher temperatures. This is seen in the increasing trend of the $H_2O$ mole fraction curve with an increase in AF. The amount of $CH_4$ produced decreased from 0.006 Kg/hr to 0.0 Kg/hr with an increase in the AF ratio. This could be either the effect of increased combustion or an effect of thermal cracking due to a higher internal energy of the reacting species, since the reactor temperature is kept at the base case constant of 815 °C. Similar trend of $CH_4$ variation were seen for coal gasification at 800-900 °C and 1 bar (Richard et al., 1989).

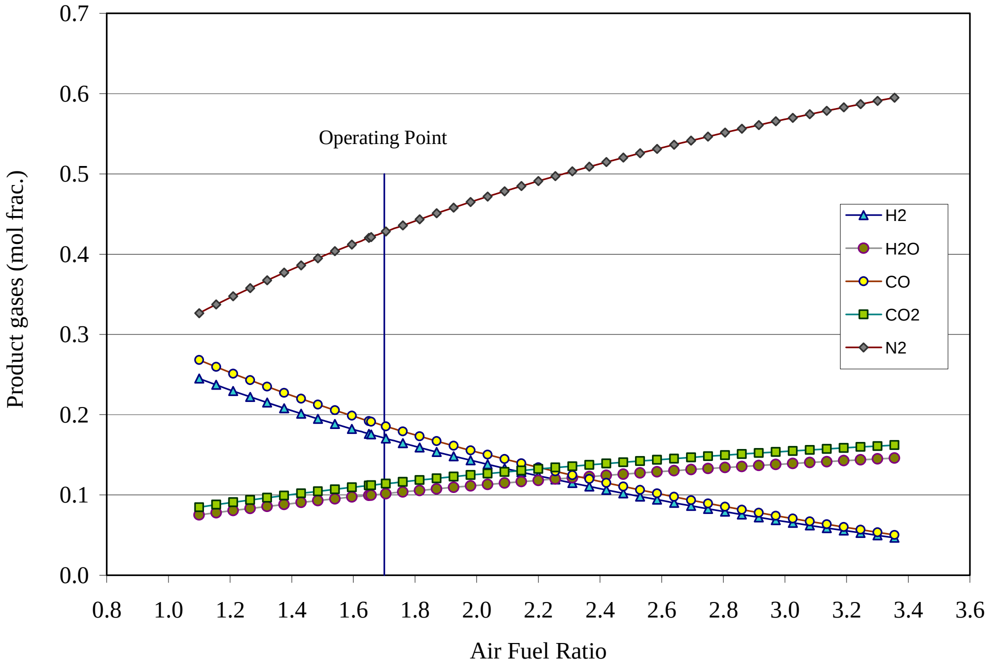


Figure 5.8 Effect of variation in the Air – Fuel Ratio on the exhaust gas composition: mole basis

### 5.1.6 Effect of Variation of Equivalence Ratio on Syngas Production

The equivalence ratio (ER) is defined as the ratio of actual AF ratio to the AF ratio required for complete combustion. The AF ratio required for complete combustion is a fixed number for any given type of biomass provided that the moisture associated with it remains constant. Hence, for this analysis the effect of variation in ER has the same effect as variation in AF ratio. ER is the standard which is used universally to compare different types of biomass and study gasification.

This section describes the effect of variation of ER on the mole fractions of individual components of produced syngas. The AF required for complete combustion of wood chips or sawdust equivalent, which closely matches the composition of biomass from crop residue is 6.36 (Reed, 1981). For this analysis the AF required for complete combustion has been assumed to be the same as the AF required for complete combustion of wood.

The ER was varied from 0.17 to 0.53 using a sensitivity analysis tool in Aspen Plus™. The operating ER for the base case is 0.268. The mole fractions of gases in the gasifier output are compared with the variation in ER and are shown in Figure 5.9.

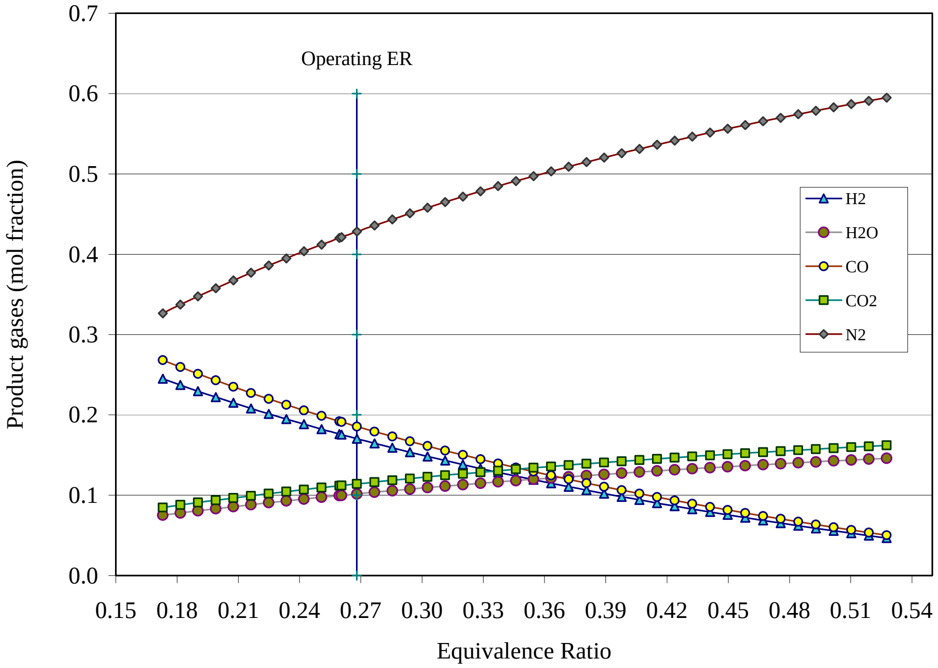


Figure 5.9 Effect of variation in the Equivalence Ratio on the exhaust gas composition

The product gases from the gasifier are CO, $CO_2$, $H_2$, $N_2$, $H_2O$ and $CH_4$. The mole fraction of CO decreases from 0.27 to 0.05 and there is a simultaneous increase in the mole fraction of $CO_2$ from 0.08 to 0.16. These changes indicate an apparent increase in oxidation of elemental C and CO in the reactor to $CO_2$, which is a direct effect of increasing the ER. A part of this effect could also be attributed to the presence of the water-gas shift reaction in the model. The trend of mole fraction curves in this analysis closely matches previous studies on ER sensitivity using kinetic modeling reported in literature (Bettagli et al., 1995, Bingyan et al., 1992, Wang and Kinoshita, 1992).

Similar ER sensitivity analyses were run at operating temperatures of 750 °C, 875 °C and 925 °C. A set of curves for comparison of relative CO-$CO_2$ and $H_2$-$N_2$ production on a mole fraction basis over an ER range of 0.17 to 0.53 is shown in Figure 5.10 and Figure 5.11.

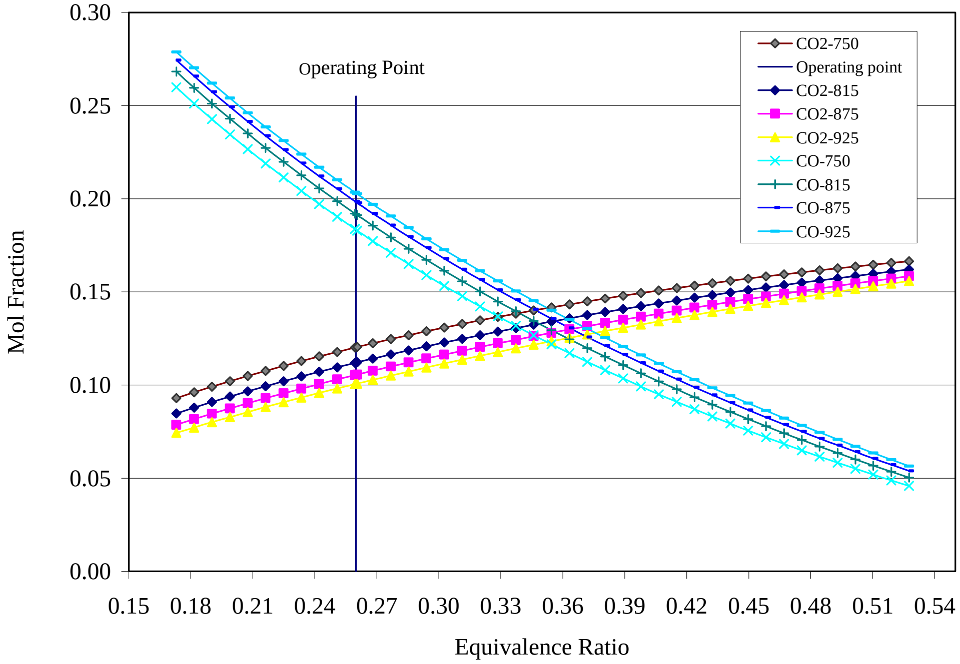


Figure 5.10 Effect of variation in the Equivalence Ratio on the production of CO and $CO_2$ at other temperatures

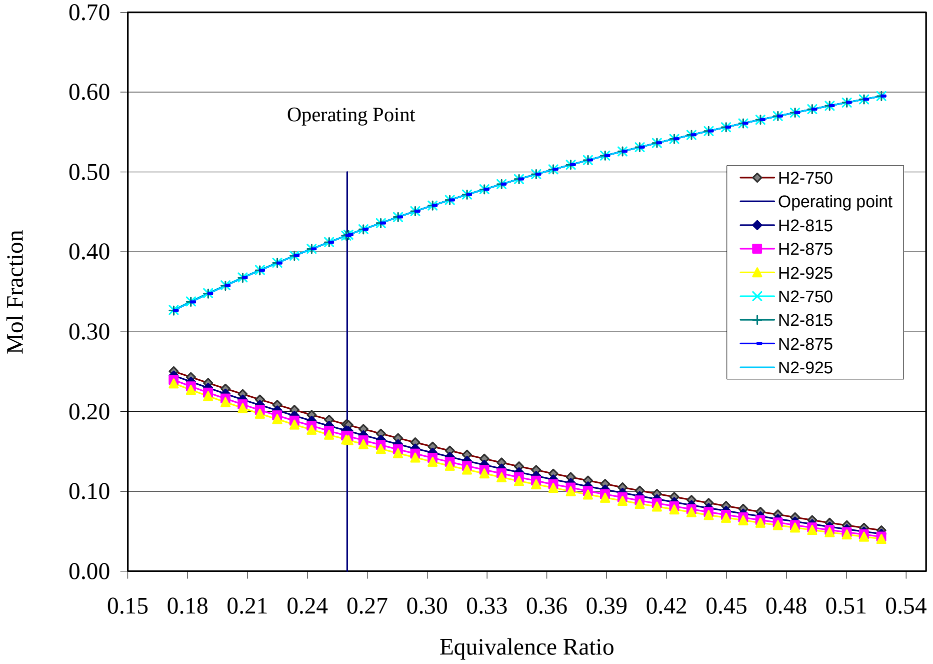


Figure 5.11 Effect of variation in the Equivalence Ratio on the production of $H_2$ and $N_2$ at other temperatures

### 5.1.7 Energy Balance

The energy balance of the gasifier model shows a net heat duty of - 113902.21 Kcal/hr for the base case, which shows the highly exothermic operation condition of the gasifier.

## 5.2 Bioreactor Modeling

As described in Chapter 4, the bioreactor was simulated in Aspen Plus™ using two approaches, a Gibbs free energy model approach and a stoichiometric model approach for reactor modeling. Results and analysis from both these approaches are discussed in the following sections.

### 5.2.1 Base Case Simulation Output and Model Validation: Gibbs Reactor

The base case simulation was developed on the basis of input data from a standard experimental run of the bioreactor in a laboratory set-up. The experimental input data and operating conditions were used for the simulation. The composition and flowrate of gas feed stream and the media feed stream are listed in Table 5.3. The results from simulation are presented in Table 5.4 and compared with experimental results.

Table 5.3 Experimental input data to the bioreactor

| | | Mole % | Kmol/sec |
|---|---|---|---|
| Gases[a] | CO | 16.52 | 2.1608 E-8 |
| | $CO_2$ | 15.45 | 2.0208 E-8 |
| | $H_2$ | 5.21 | 6.8146 E-9 |
| | $N_2$ | 62.82 | 8.2168 E-8 |
| Media | $H_2O$ | 5.961 E-6 Kg/sec | |

[a] At a flowrate of 160 cc/min at 25 °C and 1.2 atm

Table 5.4 Comparison of simulation and experimental data: Gibbs reactor model

| | | Input | | Output | | | |
|---|---|---|---|---|---|---|---|
| | | Experimental Results | | Experimental Results | | Simulation Results | |
| | | Mole % | Kmol/sec | Mole % | Kmol/sec | Mole % | Kmol/sec |
| Gases | CO | 16.52 | 2.1608 E-8 | 15.55 | 2.0339 E-8 | 2.85 E-5 | 3.284 E-14 |
| | $CO_2$ | 15.45 | 2.0208 E-8 | 16.53 | 2.1621 E-8 | 28.22 | 3.248 E-8 |
| | $H_2$ | 5.21 | 6.8146 E-9 | 4.89 | 6.396 E-9 | 0.368 | 4.244 E-10 |
| | $N_2$ | 62.82 | 8.2168 E-8 | 63.03 | 8.2168 E-8 | 71.41 | 8.2168 E-8 |
| Media | $H_2O$ | 5.961 E-6 Kg/sec | | 5.961 E-6 Kg/sec | | 5.82 E-6 Kg/sec | |
| Ethanol | $C_2H_6O$ | | | 0.073 wt. % (max) | | 3.56 wt. % | |

The observed CO output from the model was at a rate of 3.284 E-13 Kmol/sec which is much less than the observed experimental output of 2.0339 E-8 Kmol/sec. Production of $CO_2$ in the model was 3.248 E-8 Kmol/sec, which is higher than the experimental production of 2.1621 E-8 Kmol/sec. Ethanol production in the model was 2.149 E-7 Kg/sec, which is much higher than the experimental production rate of 4.38 E-9 Kg/sec. This indicates that in a Gibbs free energy model, operating at physical and chemical equilibrium, the CO is almost completely converted into $CO_2$ and $C_2H_5OH$ according to equation 2.8. The $H_2$ output from the model was 4.244 E-10 Kmol/sec which is less than the experimental production of 6.396 E-9 Kmol/hr, which shows that at equilibrium $H_2$ is expected to convert largely into $C_2H_5OH$ and $H_2O$ according to equation 2.9. The production of $H_2O$ in the simulation results is 5.82 E-6 Kg/sec which is less than the experimental output value of 5.961 E-6. Since equations 2.8 and 2.9 combined show no net molar production of $H_2O$ for similar conversions for both the reactions, this could possibly be the effect of the water gas shift reaction in the reactor or that different conversions of the two reactions are occurring. The $N_2$ feed to the reactor was 8.2168 E-8 Kmol/sec, which was the same as the output stream in the simulation results as well as the experimental results.

The production of ethanol is reported in weight fraction in the liquid output from the bioreactor on a media feed basis. In the experimental run, a maximum production of ethanol was reported at 0.073 wt %, which is much less than the 3.56 wt % production of ethanol in the simulation model. Since the model computes the maximum production of ethanol by minimizing the Gibbs free energy for the reactor, the ethanol production indicated can be considered the maximum feasible production at the operating conditions.

Since, the simulation output does not match the experimental results closely, the Gibbs reactor model is not accurate for modeling the bioreactor at present. Instead the simulation shows that there is much room for improvement of operations of the bioreactor. The Gibbs reactor is also very useful to study the effect of variation in individual feed gases on ethanol production.

### 5.2.2 Effect of Variation of Carbon Monoxide on Ethanol Production

The molar fraction of CO in the feed gas was varied from 0.1 to 0.2, while keeping the mole fractions of $CO_2$ and $H_2$ feed at constants of 0.1871 and 0.0525 respectively. Mole fraction of $N_2$ was varied by difference to accommodate variation in the mole fraction of CO. The production of ethanol increased linearly from 1.42 E-5 Kmol/hr to 1.85 E-5 Kmol/hr with the increase in the mole fraction of CO. The linear curve of ethanol production in the model versus the mole fraction of CO was charted and is shown in Figure 5.12. The data fits a linear equation represented mathematically as:

$$A = 0.737\ B + 0.038 \qquad (5.1)$$

Where, A: Ethanol output (E-4 Kmol/hr)

B: Mole fraction of CO

This linear variation indicates production of ethanol in the reactor is linear with variation in CO, and hence is produced stoichiometrically according to equation 2.8.

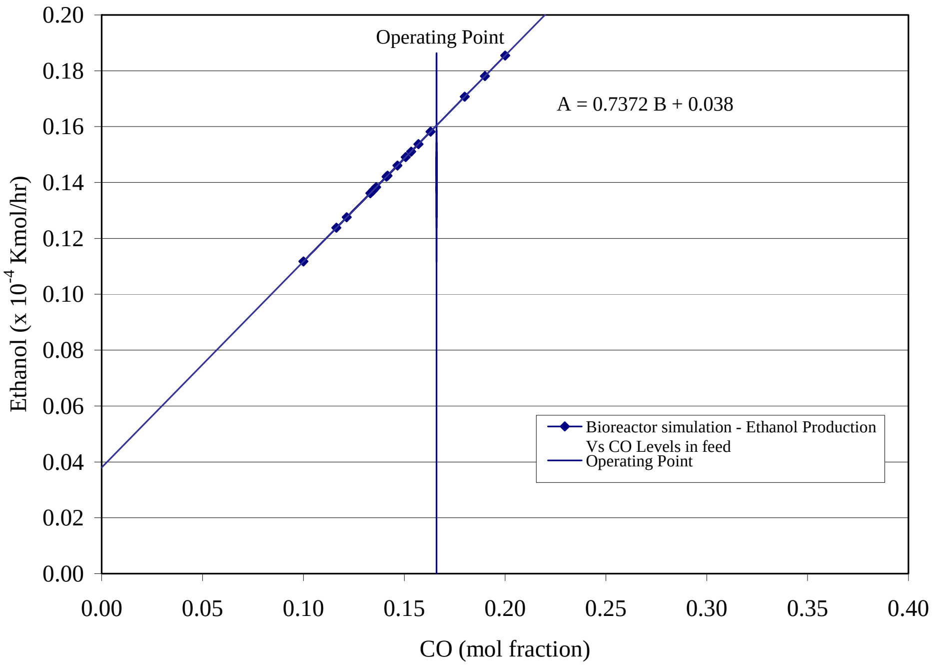


Figure 5.12 Effect of the variation in CO levels in feed gas on the ethanol produced

### 5.2.3 Effect of Variation of Carbon Dioxide on Ethanol Production

The mole fraction of $CO_2$ in the feed gas to the model was varied from 0.11 to 0.25, while keeping the mole fractions of CO and $H_2$ at constants of 0.1407 and 0.0525 respectively. Mole fraction of $N_2$ was varied by difference to accommodate the variation in the mole fraction of $CO_2$. The production of ethanol remains virtually constant at 1.417 E-5 Kmol/hr. The linear curve of ethanol production versus the mole fraction of $CO_2$ is shown in Figure 5.13. The data fits the linear equation:

$$C = - 6.0 \text{ E-7 } D + 0.141 \qquad (5.2)$$

Where, C: Ethanol output (E-4 Kmol/hr)

D: Mole fraction of $CO_2$

This indicates that the ethanol produced in a Gibbs reactor model is independent of variation in mole fraction of $CO_2$ and the intercept shows the effect of CO and $H_2$.

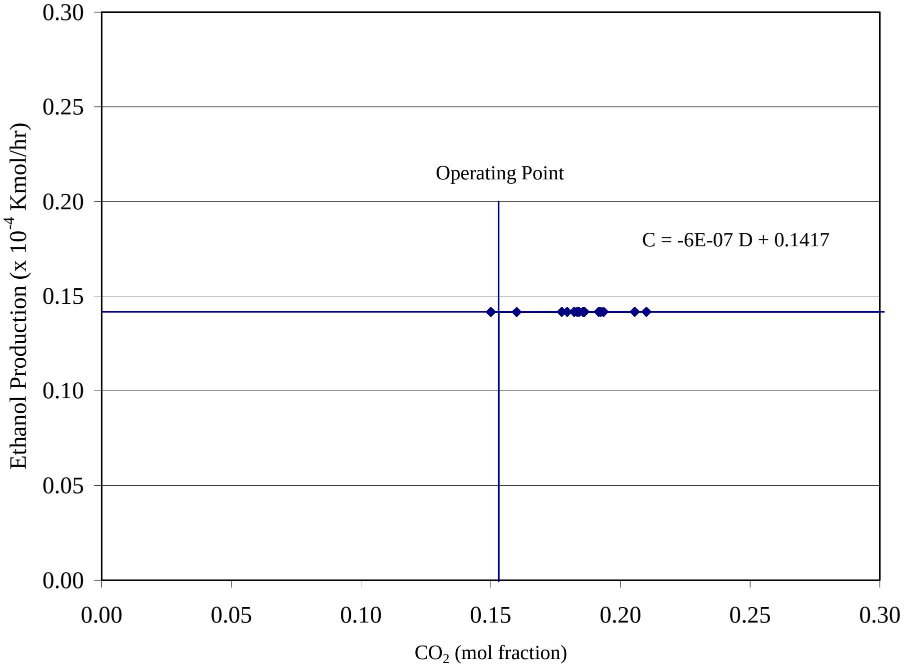


Figure 5.13 Effect of the variation in $CO_2$ levels in feed gas on the ethanol produced

### 5.2.4 Effect of Variation of Hydrogen on Ethanol Production

The mole fraction of $H_2$ in the feed gas to the model was varied from 0.03 to 0.09, while keeping the mole fractions of CO and $CO_2$ at constants of 0.1407 and 0.1871 respectively. Mole fraction of $N_2$ was varied by difference to accommodate the variation in the mole fraction of $H_2$. The production of ethanol increased linearly from 0.125 E-4 Kmol/hr to 0.169 E-4 Kmol/hr over the range of mole fraction increase from 0.03 to 0.09.

The variation in ethanol produced versus the variation in mole fraction in $H_2$ is shown in Figure 5.14.

The data fits the linear equation:

$$E = 0.737\ F + 0.103 \qquad (5.3)$$

Where, E: Ethanol output (E-4 Kmol/hr)

F: Mole fraction of $H_2$

This indicates that the ethanol production in a Gibbs reactor model is in linear variance with a variation in the mole fraction of $H_2$, and hence it is produced stoichiometrically in a single reaction given by equation 2.9.

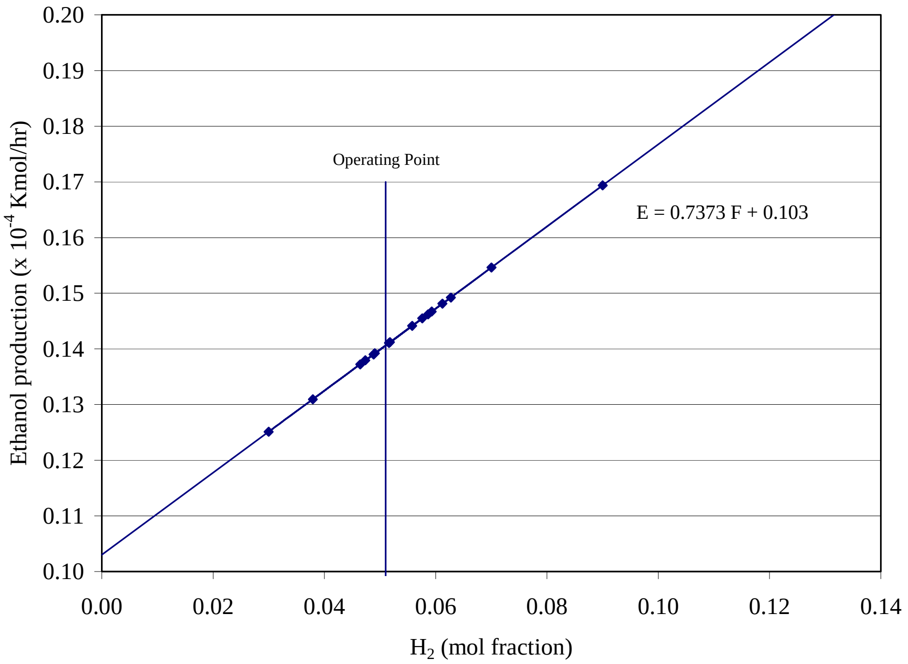


Figure 5.14 Effect of the variation in $H_2$ levels in feed gas on the ethanol produced

When equations 5.1, 5.2 and 5.3 are observed together, the linear variation in equation 5.1 and equation 5.3 shows that the conversion of CO and $H_2$ to form ethanol is stoichiometrically similar. The intercept of equation 5.2 indicates that when no $CO_2$ is present in the reactor model, there is a production of 0.141 E-4 Kmol/hr of ethanol. The intercepts of equation 5.1 and equation 5.3 add up to 0.141 E-4 Kmol/hr, which shows that when $CO_2$ is absent in the model, the net ethanol produced is due to the combined individual effects of CO and $H_2$. This validates the presence of a single reaction in the reactor which is responsible for production of ethanol, in a Gibbs reactor model. This reaction is a summation of equation 2.8 and equation 2.9, which can be represented as:

$$6\,CO + 6\,H_2 \rightarrow 2\,C_2H_5OH + 2\,CO_2 \qquad (5.4)$$

This also shows that the simulated model can be used more accurately in prediction of ethanol production if both the reactions are modeled individually in a reactor using Aspen Plus™.

### 5.2.5 Effect of Variation of Media on Ethanol Production

The media feed to the reactor was increased from 1.0 E-6 Kg/sec to 5.0 E-5 Kg/sec while keeping the gas stream input at mole fractions of CO: 0.1407, $CO_2$: 0.1871, $H_2$: 0.0525 and $N_2$: 0.6197. The production of ethanol in the model increased from 1.748 E-7 Kg/sec to 1.763 E-7 Kg/sec on increasing the media input. This indicates that the $H_2O$ is being consumed in the reactor according to equation 2.8. The mole fraction of ethanol in the liquid output stream decreases exponentially due to dilution effects. A chart of mole fractions of water and ethanol versus the media input to the reactor model is shown in Figure 5.15.

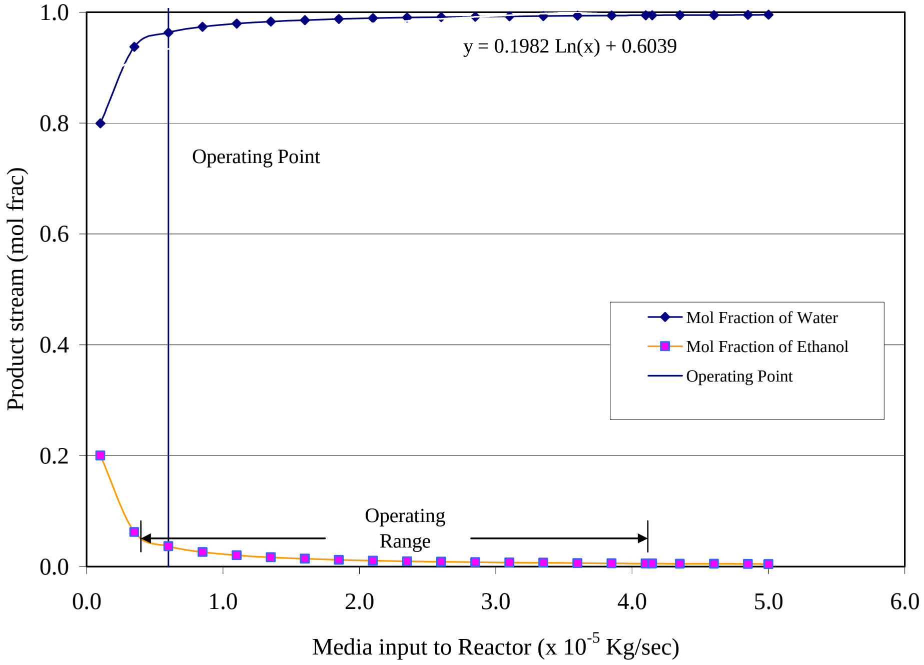


Figure 5.15 Effect of the variation in the media feed on the ethanol produced

### 5.2.6 Presence of Methane in the Model

In the model, when methane was defined as a possible product in the Gibbs reactor mode, ethanol production was reduced drastically. In the absence of methane, the base case model showed a production rate of ethanol of 2.149 E-7 Kg/sec. This is reduced to 1.026 E-24 Kg/sec in the presence of 0.001 volume percent of $CH_4$ in the feed gas. An excessive amount of $CH_4$ was produced in the model. This can be explained by the thermodynamic stability of $CH_4$ and preferential production of $CH_4$ over ethanol. The

Gibbs reactor model assumes infinite reaction time and complete attainment of equilibrium, which indicates that eventually most of the feed gases might get converted to methane as the preferred product. For this reason, $CH_4$ was excluded as an inlet or outlet component for all bioreactor simulations using the Gibbs reactor model.

### 5.2.7 Base Case Simulation Output and Model Validation: Stoichiometric Reactor

A base case simulation was developed on the basis of input data from a standard experimental run of the bioreactor in a laboratory set-up. The composition of the feed gas stream and media stream are listed in Table 5.3. The reaction stoichiometry of equation 2.8 and equation 2.9 were specified for the reactor model. The stoichiometric conversions for both the reactions were varied simultaneously from 0.05 to 0.95 and output results were matched to the experimental output. The output data from the model at a conversion of 0.1 for both the reactions was found to closely fit the experimental output. The results from the simulation are presented in Table 5.5 and compared with experimental results.

The CO output from the model was at a rate of 1.944 E-8 Kmol/sec which is close to the experimental output of 2.033 E-8 Kmol/sec. $CO_2$ production in the model was 2.142 E-8 Kmol/sec which is close to the experimental production value of 2.162 E-8 Kmol/sec. $H_2$ production in the model was 6.133 E-9 Kmol/sec which is close to the experimental output value of 6.396 E-9 Kmol/sec. Ethanol production in the model was 2.182 E-8 Kg/sec which was higher than the experimental output of 4.38 E-9 Kg/sec. A chart indicating the variation of output gases with the variation in $E_1$ and $E_2$ is shown in Figure 5.16. A close fit of output data from the simulation indicates that the laboratory set-up of the bioreactor is comparable to a stoichiometric reactor model working at 10% efficiency.

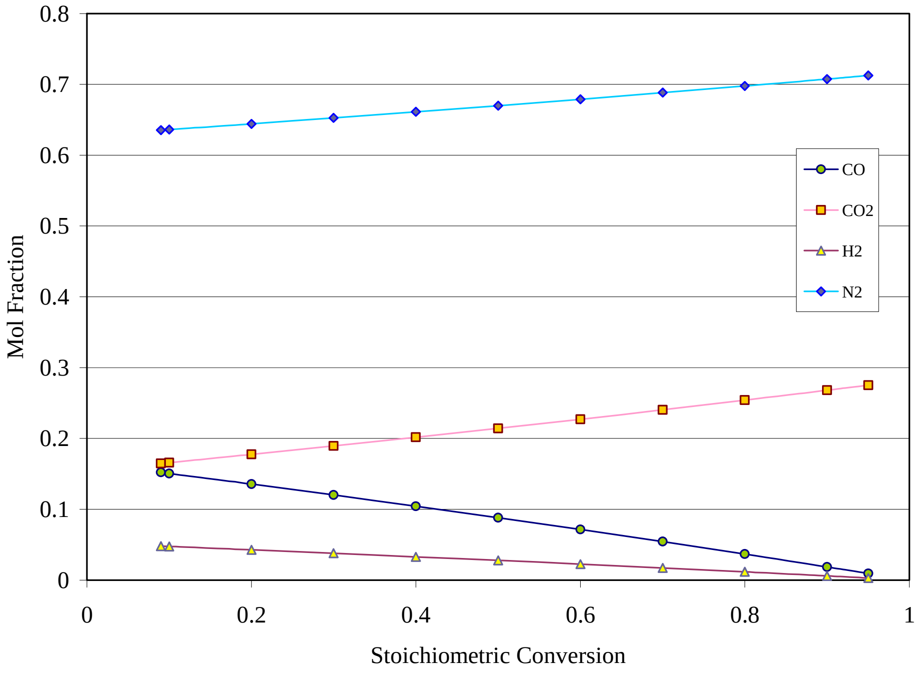


Figure 5.16 Effect of variation in the stoichiometric conversions on the exit gas composition

Table 5.5 Comparison of simulation and experimental data: Stoichiometric reactor model

| | | Input | | Output | | | |
|---|---|---|---|---|---|---|---|
| | | Experimental Results | | Experimental Results | | Simulation Results | |
| | | Mole % | Kmol/sec | Mole % | Kmol/sec | Mole % | Kmol/sec |
| Gases | CO | 16.52 | 2.1608 E-8 | 15.55 | 2.0339 E-8 | 15.06 | 1.944 E-8 |
| | $CO_2$ | 15.45 | 2.0208 E-8 | 16.53 | 2.1621 E-8 | 16.58 | 2.142 E-8 |
| | $H_2$ | 5.21 | 6.8146 E-9 | 4.89 | 6.396 E-9 | 4.75 | 6.133 E-9 |
| | $N_2$ | 62.82 | 8.2168 E-8 | 63.03 | 8.2168 E-8 | 63.61 | 8.2168 E-8 |
| Media | $H_2O$ | 5.961 E-6 Kg/sec | | 5.961 E-6 Kg/sec | | 5.947 E-6 Kg/sec | |
| Ethanol | $C_2H_6O$ | | | 0.073 wt. % (max) | | 0.365 wt. % | |

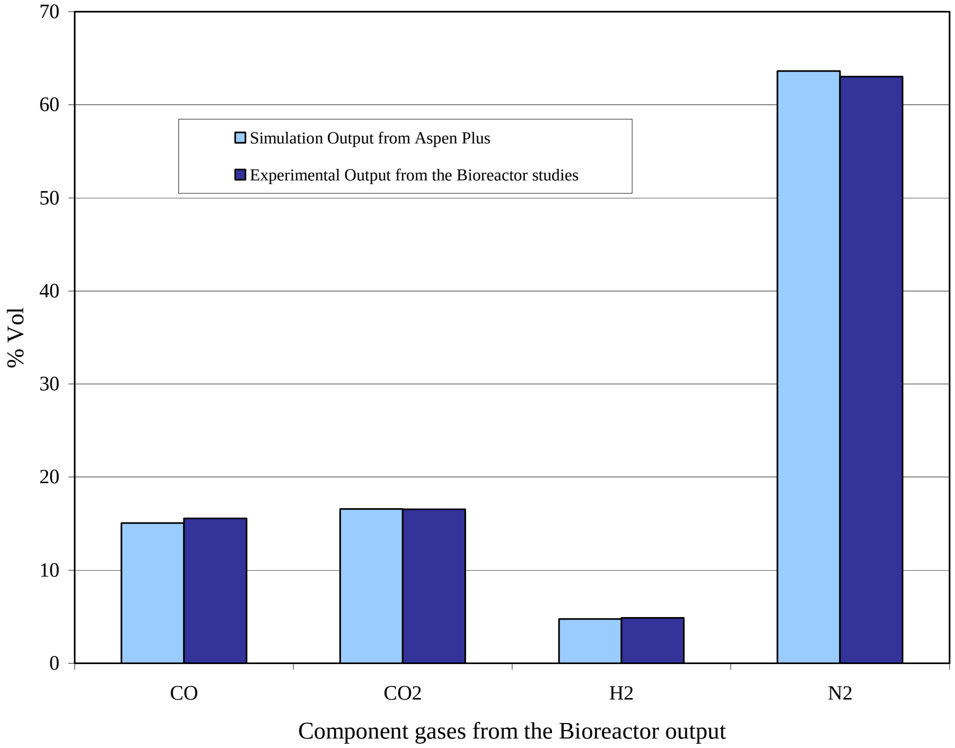


Figure 5.17 Graphical comparison of simulation data with experimental results

### 5.2.8 Effect of Stoichiometric Conversion on Ethanol Production

In this analysis, stoichiometric conversions for reactions 2.8 and 2.9, defined as $E_1$ and $E_2$, were varied independently of each other to study their individual effects on ethanol production as shown in Figure 5.20. A sensitivity tool was used to vary $E_1$ while keeping $E_2$ at 0.1. The output mole fractions of CO, $CO_2$, $H_2$ and $N_2$ were plotted against $E_1$, as shown in Figure 5.18. The production of ethanol increased linearly with an increase in $E_1$. The sensitivity analysis was run again by varying $E_2$ while keeping $E_1$ at 0.1. The variation in output mole fractions of CO, $CO_2$, $H_2$ and $N_2$ were plotted against $E_2$ and are depicted in Figure 5.19. The production of ethanol increased linearly with an increase in $E_2$, although with a lesser influence when compared to variation in $E_1$. A comparison between variations in both $E_1$ and $E_2$ and their effect on ethanol production is shown in Figure 5.20.

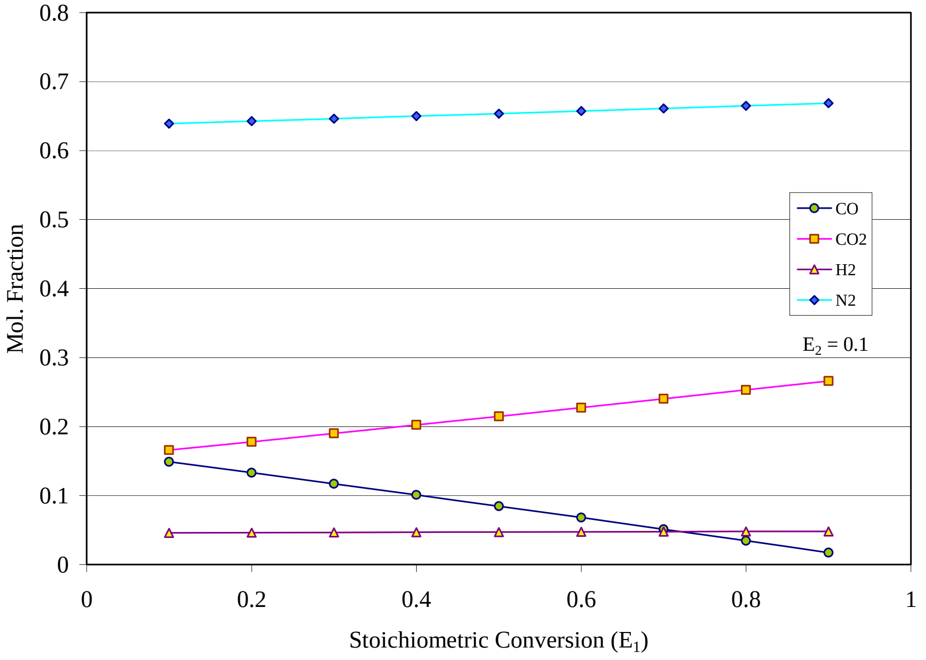


Figure 5.18 Effect of variation in the stoichiometric conversion ($E_1$) on the exit gas composition

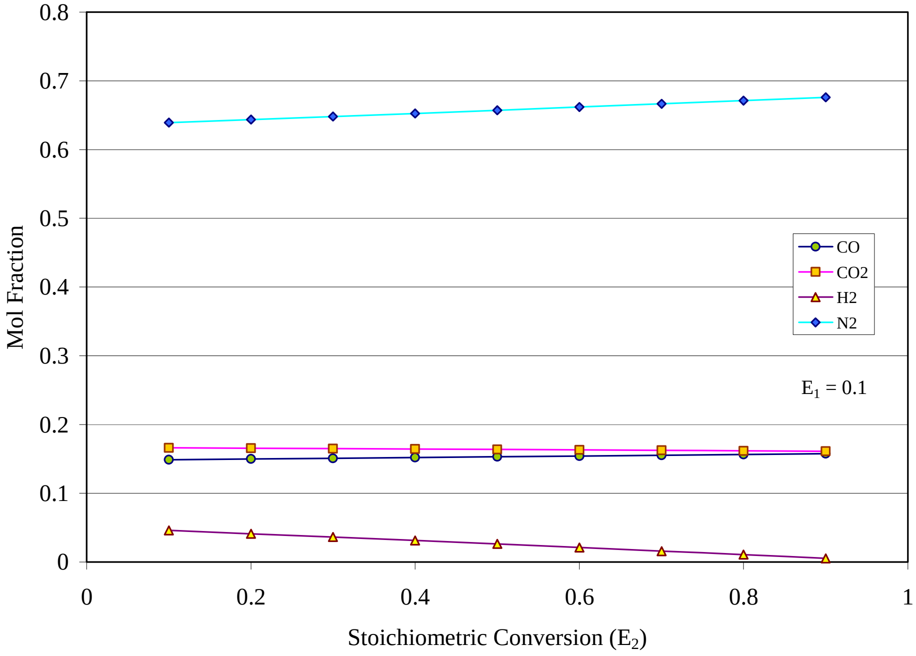


Figure 5.19 Effect of variation in the stoichiometric conversion ($E_2$) on the exit gas composition

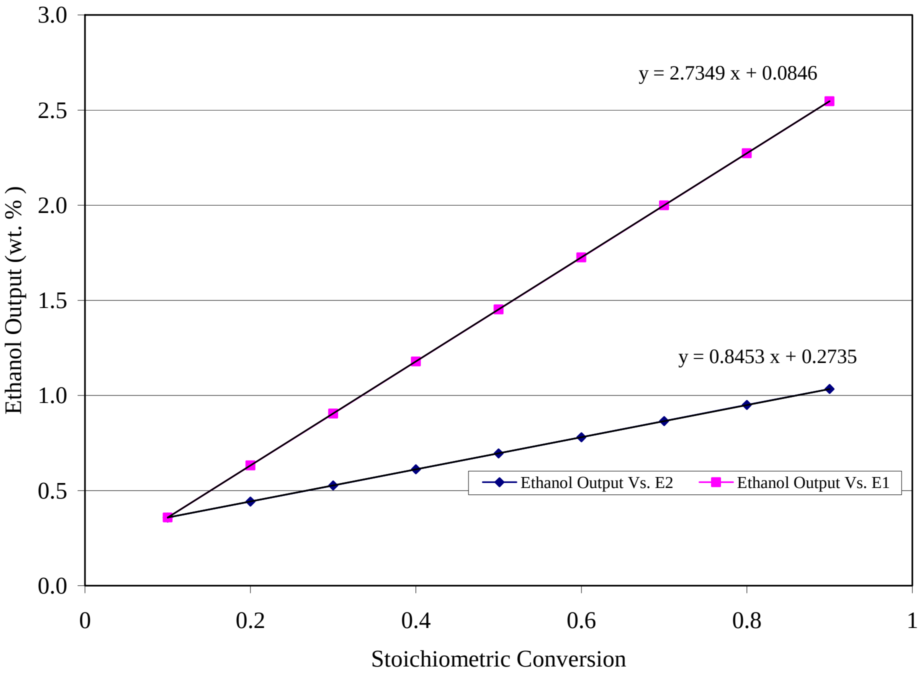


Figure 5.20 Effect of variation in the stoichiometric conversions on the ethanol produced

### 5.2.9 Energy Balance for the Bioreactor Model

The energy balance for the Gibbs reactor model of the bioreactor shows a net heat duty of – 0.7616 Kcal/hr for the base case. The energy balance for the stoichiometric reactor model shows a net heat duty of 0.4629 Kcal/hr for the base case.

# CHAPTER 6

# CONCLUSIONS AND RECOMMENDATIONS

## 6.1 Conclusions

A pilot plant gasifier and a laboratory bioreactor at Oklahoma State University, used to study the production of ethanol from switchgrass, were simulated in this study. Aspen Plus™, a commercial process simulation software was used to develop simulation models for the gasifier and the bioreactor, based on experimental parameters of operation. The results described in this thesis, based on the Aspen Plus™ simulations can be used to help reduce time consuming and expensive experimentation. The conclusions from the study are discussed in the following sections.

### 6.1.1 Gasifier simulation

The gasifier was modeled using a Gibbs free energy minimization model in Aspen Plus$^{TM}$. The Gibbs model is based on thermodynamic equilibrium and gave results which were close to the experimental values. Sensitivity was tested based on varying operation parameters and the results from the model were similar to other studies on gasifier performance found in the literature. Since the model is an equilibrium model, it cannot be used for scale up and design purposes. However, the sensitivity studies can be used to predict the performance of the gasifier at unknown operating conditions. This work can be used to:

- Predict exhaust composition of syngas at various biomass feed rates
- Predict exhaust gas composition at various moisture contents associated with the biomass
- Predict exhaust composition of syngas and individual flowrates of gases at various gasification temperatures
- Predict composition and variation of trace hydrocarbons produced during biomass gasification
- Predict effect of the Air Fuel ratio on the syngas composition and the individual gas flowrates
- Predict effect of the Equivalence Ratio on the syngas composition
- Predict effect of the Equivalence Ratio on the syngas at 750 ºC, 815 ºC, 875 ºC and 925 ºC.

Some of the chief conclusions are:

1) The base case simulation results show a 10.55 Kg/hr production of CO, which is 64.1% greater than the experimental production of 6.43 Kg/hr. This indicates a theoretical higher potential for CO production in the gasifier.

2) The base case simulation results show a 0.696 Kg/hr production of $H_2$ which is more than four times greater than the experimental production of 0.16 Kg/hr $H_2$. This indicates a theoretical higher potential for $H_2$ production in the gasifier.

3) Production of CO drops with an increase in the moisture content of biomass. Hence, preparation and drying of biomass are critical for greater CO production.

4) The Equivalence Ratio was found to be the most influential variable on syngas composition. An increase in the ER leads to a decrease in the production of CO and $H_2$.

### 6.1.2 Bioreactor simulation

The bioreactor model was modeled in Aspen Plus$^{TM}$ using two approaches, an equilibrium approach and a stoichiometric approach. The equilibrium model was based on Gibbs free energy minimization and was used to estimate the maximum theoretical ethanol production. The results from the equilibrium model were much greater than the observed values from the laboratory studies, indicating that there is a potential for great improvement in the laboratory reactor. The equilibrium model was also used to study the sensitivity of the bioreactor model to changes in the composition of syngas. This work can be used to benchmark the production of ethanol possible out of the present reactor set up. The simulation studies can also be used to:

- Predict the maximum ethanol production possible
- Study the effect of changes in the feed syngas composition on the ethanol produced

The stoichiometric model in Aspen Plus™ was based on the two main reactions occurring in the bioreactor. The results from the model were close to the experimental results. The stoichiometric conversions were varied for the two main reactants in the reactions simultaneously and individually to study the effect on ethanol production and output gas composition. These results can be used to:

- Predict the ethanol production at various stoichiometric conversions of the two combined reactions

- Predict the influence of the stoichiometric conversion of the combined reactions on the output gas composition from the bioreactor
- Predict the ethanol production with variation in individual stoichiometric conversion of each reaction
- Predict the influence of stoichiometric conversion of each reaction individually on the output gas composition from the bioreactor

Some of the chief conclusions are:

1) The base case analysis using the gibbs reactor model shows an ethanol production of 3.56% by weight which is much greater than the experimental production of 0.073% by weight. This shows that there is room for improvement in the ethanol production in laboratory studies.

2) A higher input of CO and $H_2$ results in an increase in the ethanol production in the sensitivity analysis. This indicates that we can increase the production of ethanol by increasing the composition of CO and $H_2$ in the syngas. This could be achieved by steam gasification.

3) A higher ethanol production results from increasing the stoichiometric conversion in the stoichiometric reactor model. This indicates that CO and $H_2$ are not completely utilized in the bioreactor for ethanol production and we can improve the consumption of CO and $H_2$ further.

## 6.2 Recommendations for future work

The reactor models developed in this work were built in Aspen Plus™ and are generic in nature. Although the gasifier model gives accurate predictions of gasifier performance at unknown operation parameter ranges, it cannot be used for scale up or design purposes. For scale up of the gasifier, kinetic data on biomass gasification is required. With the help of kinetic data, a gasifier model could be developed in Aspen Plus™ using the kinetic reactor, which would be useful for scaling up the gasifier for industry level production.

For a precise fit of the reactor model for the bioreactor simulation, kinetic data and biochemical equations governing the production of ethanol are required and need to be programmed into Aspen Plus™ using FORTRAN subroutines. Future work on bioreactor simulations could include user defined subroutines in Aspen Plus™ for local use and a better fit of the model to laboratory experimentation for syngas conversion using P7. With the use of kinetic data, this reactor model could be used for scale up purposes.

A distillation model is required for complete simulation of the entire process of conversion of switchgrass to ethanol. An integrated design of the entire plant at an industry level of production is needed to successfully study the performance of the entire plant. An optimization study aimed at optimizing performance of the gasifier, bioreactor and distillation units is required as well as an optimization for the entire process as an integrated plant. In such an optimization study, the amount of ethanol produced could be used as an objective function and the effects of process parameters on the objective function could be analyzed, thus developing a generalized correlation for the objective function.

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# APPENDIX A

# SIMULATION DATA TABLES

A.1 Complete list of exhaust gas components from the gasifier

| Component | Flowrate (Kg/hr) |
|---|---|
| C | 4.8061 E-27 |
| $H_2$ | 0.6966 |
| $O_2$ | 1.9237 E-17 |
| $N_2$ | 23.25 |
| $H_2O$ | 3.5437 |
| CO | 10.5504 |
| $CO_2$ | 9.7278 |
| $CH_4$ | 0.4016 E-3 |
| NO | 4.4215 E-12 |
| $NO_2$ | 2.4309 E-22 |
| $C_2H_2$ | 1.1908 E-10 |
| $C_2H_4$ | 1.9396 E-9 |
| $C_2H_6$ | 2.4551 E-10 |

A.2 Simulation data from the gasifier model for biomass sensitivity analysis

| Biomass Input | Product Gases | | | | | |
|---|---|---|---|---|---|---|
| | $H_2$ | $N_2$ | CO | $CO_2$ | $CH_4$ | $H_2O$ |
| (Kg/hr) | (Kg/hr) | (Kg/hr) | (Kg/hr) | (Kg/hr) | (Kg/hr) | (Kg/hr) |
| 12.000 | 0.339 | 23.205 | 5.116 | 9.862 | 0.000 | 3.608 |
| 12.750 | 0.387 | 23.211 | 5.838 | 9.846 | 0.000 | 3.598 |
| 13.500 | 0.434 | 23.217 | 6.561 | 9.829 | 0.000 | 3.589 |
| 14.250 | 0.482 | 23.223 | 7.283 | 9.812 | 0.000 | 3.580 |
| 15.000 | 0.529 | 23.229 | 8.006 | 9.795 | 0.001 | 3.571 |
| 15.750 | 0.576 | 23.235 | 8.729 | 9.777 | 0.001 | 3.562 |
| 16.500 | 0.624 | 23.241 | 9.452 | 9.759 | 0.001 | 3.553 |
| 17.250 | 0.671 | 23.247 | 10.175 | 9.741 | 0.001 | 3.544 |
| 17.640 | 0.696 | 23.250 | 10.551 | 9.732 | 0.001 | 3.540 |
| 18.000 | 0.718 | 23.253 | 10.898 | 9.723 | 0.002 | 3.536 |
| 18.750 | 0.766 | 23.259 | 11.621 | 9.705 | 0.002 | 3.528 |
| 19.500 | 0.813 | 23.265 | 12.344 | 9.687 | 0.002 | 3.519 |
| 20.250 | 0.860 | 23.271 | 13.067 | 9.668 | 0.003 | 3.511 |
| 21.000 | 0.907 | 23.277 | 13.790 | 9.650 | 0.003 | 3.503 |
| 21.750 | 0.955 | 23.283 | 14.513 | 9.631 | 0.004 | 3.495 |
| 22.500 | 1.002 | 23.288 | 15.236 | 9.613 | 0.005 | 3.487 |
| 23.250 | 1.049 | 23.294 | 15.958 | 9.594 | 0.005 | 3.479 |
| 24.000 | 1.096 | 23.300 | 16.681 | 9.576 | 0.006 | 3.471 |

A.3 Simulation data from the gasifier model for moisture sensitivity analysis

| Biomass Input | Exhaust Gases | | | | | | |
|---|---|---|---|---|---|---|---|
| $H_2O$ (Kg/hr) | $H_2$ (Kg/hr) | $N_2$ (Kg/hr) | CO (Kg/hr) | $CO_2$ (Kg/hr) | $O_2$ (Kg/hr) | $CH_4$ (Kg/hr) | $H_2O$ (Kg/hr) |
| 0.5000 | 0.6503 | 23.2499 | 11.1800 | 8.7432 | 0.0000 | 0.0016 | 2.8058 |
| 1.000 | 0.6708 | 23.2499 | 10.8951 | 9.1911 | 0.0000 | 0.00152 | 3.1223 |
| 1.263 | 0.6812 | 23.2499 | 10.7509 | 9.4179 | 0.0000 | 0.00147 | 3.2926 |
| 1.526 | 0.6914 | 23.2499 | 10.6104 | 9.6388 | 0.0000 | 0.00142 | 3.4653 |
| 1.639 | 0.6957 | 23.2499 | 10.5512 | 9.7318 | 0.0000 | 0.00140 | 3.5400 |
| 1.789 | 0.7013 | 23.2499 | 10.4734 | 9.8541 | 0.0000 | 0.00137 | 3.6402 |
| 2.053 | 0.7109 | 23.2499 | 10.3400 | 10.0639 | 0.0000 | 0.00132 | 3.8174 |
| 2.316 | 0.7203 | 23.2499 | 10.2098 | 10.2685 | 0.0000 | 0.00128 | 3.9968 |
| 2.579 | 0.7294 | 23.2499 | 10.0829 | 10.4680 | 0.0000 | 0.00124 | 4.1782 |
| 2.842 | 0.7384 | 23.2499 | 9.9590 | 10.6628 | 0.0000 | 0.00120 | 4.3616 |
| 3.105 | 0.7471 | 23.2499 | 9.8382 | 10.8528 | 0.0000 | 0.00116 | 4.5470 |
| 3.368 | 0.7556 | 23.2499 | 9.7202 | 11.0383 | 0.0000 | 0.00112 | 4.7341 |
| 3.632 | 0.7639 | 23.2499 | 9.6049 | 11.2194 | 0.0000 | 0.00109 | 4.9231 |
| 3.895 | 0.7720 | 23.2499 | 9.4924 | 11.3963 | 0.0000 | 0.00105 | 5.1138 |
| 4.158 | 0.7800 | 23.2499 | 9.3824 | 11.5692 | 0.0000 | 0.00102 | 5.3062 |
| 4.421 | 0.7877 | 23.2499 | 9.2750 | 11.7381 | 0.0000 | 0.00099 | 5.5001 |
| 4.684 | 0.7953 | 23.2499 | 9.1699 | 11.9033 | 0.0000 | 0.00096 | 5.6957 |
| 4.947 | 0.8027 | 23.2499 | 9.0672 | 12.0647 | 0.0000 | 0.00093 | 5.8927 |
| 5.211 | 0.8099 | 23.2499 | 8.9668 | 12.2226 | 0.0000 | 0.00090 | 6.0912 |
| 5.474 | 0.8170 | 23.2499 | 8.8685 | 12.3771 | 0.0000 | 0.00087 | 6.2911 |
| 5.737 | 0.8240 | 23.2499 | 8.7723 | 12.5283 | 0.0000 | 0.00085 | 6.4923 |

A.3 Simulation data from the gasifier model for moisture sensitivity analysis (cont'd)

| Biomass Input | Exhaust Gases | | | | | | |
|---|---|---|---|---|---|---|---|
| $H_2O$ (Kg/hr) | $H_2$ (Kg/hr) | $N_2$ (Kg/hr) | CO (Kg/hr) | $CO_2$ (Kg/hr) | $O_2$ (Kg/hr) | $CH_4$ (Kg/hr) | $H_2O$ (Kg/hr) |
| 6 | 0.8307 | 23.2499 | 8.6782 | 12.6762 | 0.0000 | 0.00082 | 6.6949 |
| 6.4211 | 0.8413 | 23.2499 | 8.5318 | 12.9064 | 0.0000 | 0.0008 | 7.0217 |
| 6.8158 | 0.8509 | 23.2499 | 8.3988 | 13.1154 | 0.0000 | 0.0007 | 7.3308 |
| 7.2105 | 0.8602 | 23.2499 | 8.2700 | 13.3179 | 0.0000 | 0.0007 | 7.6426 |
| 7.6053 | 0.8692 | 23.2499 | 8.1450 | 13.5144 | 0.0000 | 0.0007 | 7.9569 |
| 8.0000 | 0.8779 | 23.2499 | 8.0237 | 13.7051 | 0.0000 | 0.0007 | 8.2736 |

A.4 Simulation data from the gasifier model for temperature sensitivity analysis: mass basis

| TEMP (K) | $H_2$ (Kg/hr) | $N_2$ (Kg/hr) | $O_2$ (Kg/hr) | $H_2O$ (Kg/hr) | CO (Kg/hr) | $CO_2$ (Kg/hr) | $CH_4$ (Kg/hr) | NO (Kg/hr) | $NO_2$ (Kg/hr) |
|---|---|---|---|---|---|---|---|---|---|
| 873 | 0.663 | 23.250 | 0.000 | 0.000 | 7.219 | 13.469 | 0.545 | 0.000 | 0.000 |
| 898 | 0.714 | 23.250 | 0.000 | 0.000 | 8.158 | 12.644 | 0.309 | 0.000 | 0.000 |
| 923 | 0.742 | 23.250 | 0.000 | 0.000 | 8.835 | 11.995 | 0.157 | 0.000 | 0.000 |
| 948 | 0.750 | 23.250 | 0.000 | 0.000 | 9.296 | 11.496 | 0.075 | 0.000 | 0.000 |
| 973 | 0.746 | 23.250 | 0.000 | 0.000 | 9.621 | 11.095 | 0.035 | 0.000 | 0.000 |
| 998 | 0.738 | 23.250 | 0.000 | 0.000 | 9.873 | 10.750 | 0.017 | 0.000 | 0.000 |
| 1023 | 0.727 | 23.250 | 0.000 | 0.000 | 10.086 | 10.439 | 0.008 | 0.000 | 0.000 |
| 1048 | 0.715 | 23.250 | 0.000 | 0.000 | 10.276 | 10.152 | 0.004 | 0.000 | 0.000 |
| 1073 | 0.703 | 23.250 | 0.000 | 0.000 | 10.450 | 9.883 | 0.002 | 0.000 | 0.000 |
| 1088 | 0.697 | 23.250 | 0.000 | 0.000 | 10.550 | 9.728 | 0.001 | 0.000 | 0.000 |
| 1098 | 0.692 | 23.250 | 0.000 | 0.000 | 10.614 | 9.630 | 0.001 | 0.000 | 0.000 |
| 1123 | 0.681 | 23.250 | 0.000 | 0.000 | 10.767 | 9.389 | 0.001 | 0.000 | 0.000 |
| 1148 | 0.671 | 23.250 | 0.000 | 0.000 | 10.913 | 9.162 | 0.000 | 0.000 | 0.000 |
| 1173 | 0.661 | 23.250 | 0.000 | 0.000 | 11.050 | 8.946 | 0.000 | 0.000 | 0.000 |

A.5 Simulation data from the gasifier model for temperature sensitivity analysis: mol basis

| TEMP (K) | $H_2$ (mol frac) | $N_2$ (mol frac) | $O_2$ (mol frac) | $H_2O$ (mol frac) | CO (mol frac) | $CO_2$ (mol frac) | $C_2H_2$ (mol frac) | $C_2H_4$ (mol frac) | $C_2H_6$ (mol frac) |
|---|---|---|---|---|---|---|---|---|---|
| 873 | 0.182 | 0.460 | 0.000 | 0.143 | 0.169 | 0.019 | 1.12E-11 | 2.68E-08 | 1.55E-07 |
| 898 | 0.193 | 0.453 | 0.000 | 0.159 | 0.157 | 0.010 | 1.36E-11 | 1.69E-08 | 6.00E-08 |
| 923 | 0.199 | 0.449 | 0.000 | 0.171 | 0.147 | 0.005 | 1.37E-11 | 8.91E-09 | 1.93E-08 |
| 948 | 0.201 | 0.448 | 0.000 | 0.179 | 0.141 | 0.003 | 1.22E-11 | 4.20E-09 | 5.61E-09 |
| 973 | 0.200 | 0.448 | 0.000 | 0.185 | 0.136 | 0.001 | 1.02E-11 | 1.90E-09 | 1.57E-09 |
| 998 | 0.198 | 0.448 | 0.000 | 0.190 | 0.132 | 0.001 | 8.26E-12 | 8.54E-10 | 4.48E-10 |
| 1023 | 0.195 | 0.449 | 0.000 | 0.195 | 0.128 | 0.000 | 6.68E-12 | 3.92E-10 | 1.33E-10 |
| 1048 | 0.192 | 0.450 | 0.000 | 0.199 | 0.125 | 0.000 | 5.42E-12 | 1.85E-10 | 4.13E-11 |
| 1073 | 0.189 | 0.451 | 0.000 | 0.203 | 0.122 | 0.000 | 4.43E-12 | 9.05E-11 | 1.35E-11 |
| 1088 | 0.188 | 0.451 | 0.000 | 0.205 | 0.120 | 0.000 | 3.93E-12 | 5.94E-11 | 7.02E-12 |
| 1098 | 0.187 | 0.452 | 0.000 | 0.206 | 0.119 | 0.000 | 3.65E-12 | 4.55E-11 | 4.63E-12 |
| 1123 | 0.184 | 0.452 | 0.000 | 0.210 | 0.116 | 0.000 | 3.03E-12 | 2.36E-11 | 1.67E-12 |
| 1148 | 0.182 | 0.453 | 0.000 | 0.213 | 0.114 | 0.000 | 2.54E-12 | 1.26E-11 | 6.26E-13 |
| 1173 | 0.179 | 0.454 | 0.000 | 0.216 | 0.111 | 0.000 | 2.14E-12 | 6.90E-12 | 2.44E-13 |

A.6 Simulation data from the gasifier model for ER sensitivity analysis at 815 °C: mass basis

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Air | $O_2$ | $N_2$ | $H_2$ | $N_2$ | $O_2$ | $H_2O$ | CO | $CO_2$ | $CH_4$ |
| (Kg/hr) | (Kg/hr) | AF | ER | (Kg/hr) | (Kg/hr) | (Kg/hr) | (Kg/hr) | (Kg/hr) | (Kg/hr) | (Kg/hr) | (Kg/hr) | (Kg/hr) | (Kg/hr) |
| 20.000 | 18.18 | 1.10 | 0.17 | 20.000 | 4.660 | 15.340 | 0.836 | 15.479 | 0.000 | 2.289 | 12.715 | 6.314 | 0.006 |
| 21.000 | 18.18 | 1.16 | 0.18 | 21.000 | 4.893 | 16.107 | 0.822 | 16.246 | 0.000 | 2.413 | 12.502 | 6.651 | 0.005 |
| 22.000 | 18.18 | 1.21 | 0.19 | 22.000 | 5.126 | 16.874 | 0.808 | 17.013 | 0.000 | 2.536 | 12.289 | 6.988 | 0.005 |
| 23.000 | 18.18 | 1.27 | 0.20 | 23.000 | 5.359 | 17.641 | 0.795 | 17.780 | 0.000 | 2.660 | 12.075 | 7.325 | 0.004 |
| 24.000 | 18.18 | 1.32 | 0.21 | 24.000 | 5.592 | 18.408 | 0.781 | 18.547 | 0.000 | 2.784 | 11.862 | 7.662 | 0.003 |
| 25.000 | 18.18 | 1.38 | 0.22 | 25.000 | 5.825 | 19.175 | 0.767 | 19.314 | 0.000 | 2.907 | 11.648 | 7.999 | 0.003 |
| 26.000 | 18.18 | 1.43 | 0.22 | 26.000 | 6.058 | 19.942 | 0.754 | 20.081 | 0.000 | 3.031 | 11.434 | 8.337 | 0.003 |
| 27.000 | 18.18 | 1.49 | 0.23 | 27.000 | 6.291 | 20.709 | 0.740 | 20.849 | 0.000 | 3.155 | 11.220 | 8.674 | 0.002 |
| 28.000 | 18.18 | 1.54 | 0.24 | 28.000 | 6.524 | 21.476 | 0.726 | 21.616 | 0.000 | 3.279 | 11.006 | 9.011 | 0.002 |
| 29.000 | 18.18 | 1.60 | 0.25 | 29.000 | 6.757 | 22.243 | 0.712 | 22.383 | 0.000 | 3.403 | 10.792 | 9.348 | 0.002 |
| 30.000 | 18.18 | 1.65 | 0.26 | 30.000 | 6.990 | 23.010 | 0.698 | 23.150 | 0.000 | 3.528 | 10.578 | 9.685 | 0.001 |
| 30.130 | 18.18 | 1.66 | 0.26 | 30.130 | 7.020 | 23.110 | 0.697 | 23.249 | 0.000 | 3.544 | 10.550 | 9.729 | 0.001 |
| 31.000 | 18.18 | 1.71 | 0.27 | 31.000 | 7.223 | 23.777 | 0.684 | 23.917 | 0.000 | 3.652 | 10.364 | 10.022 | 0.001 |
| 32.000 | 18.18 | 1.76 | 0.28 | 32.000 | 7.456 | 24.544 | 0.671 | 24.684 | 0.000 | 3.776 | 10.150 | 10.359 | 0.001 |
| 33.000 | 18.18 | 1.82 | 0.29 | 33.000 | 7.689 | 25.311 | 0.657 | 25.451 | 0.000 | 3.900 | 9.935 | 10.695 | 0.001 |
| 34.000 | 18.18 | 1.87 | 0.29 | 34.000 | 7.922 | 26.078 | 0.643 | 26.218 | 0.000 | 4.025 | 9.721 | 11.032 | 0.001 |
| 35.000 | 18.18 | 1.93 | 0.30 | 35.000 | 8.155 | 26.845 | 0.629 | 26.985 | 0.000 | 4.149 | 9.507 | 11.369 | 0.001 |
| 36.000 | 18.18 | 1.98 | 0.31 | 36.000 | 8.388 | 27.612 | 0.615 | 27.752 | 0.000 | 4.274 | 9.293 | 11.705 | 0.001 |
| 37.000 | 18.18 | 2.04 | 0.32 | 37.000 | 8.621 | 28.379 | 0.601 | 28.519 | 0.000 | 4.398 | 9.079 | 12.041 | 0.001 |
| 38.000 | 18.18 | 2.09 | 0.33 | 38.000 | 8.854 | 29.146 | 0.587 | 29.286 | 0.000 | 4.523 | 8.866 | 12.378 | 0.000 |

A.6 Simulation data from the gasifier model for ER sensitivity analysis at 815 °C: mass basis (cont’d)

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (Kg/hr) | (Kg/hr) | AF | ER | Air (Kg/hr) | $O_2$ (Kg/hr) | $N_2$ (Kg/hr) | $H_2$ (Kg/hr) | $N_2$ (Kg/hr) | $O_2$ (Kg/hr) | $H_2O$ (Kg/hr) | CO (Kg/hr) | $CO_2$ (Kg/hr) | $CH_4$ (Kg/hr) |
| 39.000 | 18.18 | 2.15 | 0.34 | 39.000 | 9.087 | 29.913 | 0.573 | 30.053 | 0.000 | 4.648 | 8.652 | 12.714 | 0.000 |
| 40.000 | 18.18 | 2.20 | 0.35 | 40.000 | 9.320 | 30.680 | 0.559 | 30.820 | 0.000 | 4.773 | 8.438 | 13.050 | 0.000 |
| 41.000 | 18.18 | 2.26 | 0.35 | 41.000 | 9.553 | 31.447 | 0.545 | 31.587 | 0.000 | 4.897 | 8.224 | 13.386 | 0.000 |
| 42.000 | 18.18 | 2.31 | 0.36 | 42.000 | 9.786 | 32.214 | 0.531 | 32.354 | 0.000 | 5.022 | 8.011 | 13.721 | 0.000 |
| 43.000 | 18.18 | 2.37 | 0.37 | 43.000 | 10.019 | 32.981 | 0.517 | 33.121 | 0.000 | 5.147 | 7.797 | 14.057 | 0.000 |
| 44.000 | 18.18 | 2.42 | 0.38 | 44.000 | 10.252 | 33.748 | 0.503 | 33.888 | 0.000 | 5.272 | 7.583 | 14.393 | 0.000 |
| 45.000 | 18.18 | 2.48 | 0.39 | 45.000 | 10.485 | 34.515 | 0.489 | 34.655 | 0.000 | 5.397 | 7.370 | 14.728 | 0.000 |
| 46.000 | 18.18 | 2.53 | 0.40 | 46.000 | 10.718 | 35.282 | 0.476 | 35.422 | 0.000 | 5.522 | 7.157 | 15.064 | 0.000 |
| 47.000 | 18.18 | 2.59 | 0.41 | 47.000 | 10.951 | 36.049 | 0.462 | 36.189 | 0.000 | 5.647 | 6.943 | 15.399 | 0.000 |
| 48.000 | 18.18 | 2.64 | 0.42 | 48.000 | 11.184 | 36.816 | 0.448 | 36.956 | 0.000 | 5.772 | 6.730 | 15.734 | 0.000 |
| 49.000 | 18.18 | 2.70 | 0.42 | 49.000 | 11.417 | 37.583 | 0.434 | 37.723 | 0.000 | 5.898 | 6.517 | 16.069 | 0.000 |
| 50.000 | 18.18 | 2.75 | 0.43 | 50.000 | 11.650 | 38.350 | 0.420 | 38.490 | 0.000 | 6.023 | 6.304 | 16.404 | 0.000 |
| 51.000 | 18.18 | 2.81 | 0.44 | 51.000 | 11.883 | 39.117 | 0.405 | 39.257 | 0.000 | 6.148 | 6.091 | 16.739 | 0.000 |
| 52.000 | 18.18 | 2.86 | 0.45 | 52.000 | 12.116 | 39.884 | 0.391 | 40.024 | 0.000 | 6.274 | 5.878 | 17.073 | 0.000 |
| 53.000 | 18.18 | 2.92 | 0.46 | 53.000 | 12.349 | 40.651 | 0.377 | 40.791 | 0.000 | 6.399 | 5.665 | 17.408 | 0.000 |
| 54.000 | 18.18 | 2.97 | 0.47 | 54.000 | 12.582 | 41.418 | 0.363 | 41.558 | 0.000 | 6.524 | 5.452 | 17.742 | 0.000 |
| 55.000 | 18.18 | 3.03 | 0.48 | 55.000 | 12.815 | 42.185 | 0.349 | 42.325 | 0.000 | 6.650 | 5.239 | 18.076 | 0.000 |
| 56.000 | 18.18 | 3.08 | 0.48 | 56.000 | 13.048 | 42.952 | 0.335 | 43.092 | 0.000 | 6.776 | 5.027 | 18.410 | 0.000 |

A.6 Simulation data from the gasifier model for ER sensitivity analysis at 815 °C: mass basis (cont’d)

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (Kg/hr) | (Kg/hr) | AF | ER | Air (Kg/hr) | $O_2$ (Kg/hr) | $N_2$ (Kg/hr) | $H_2$ (Kg/hr) | $N_2$ (Kg/hr) | $O_2$ (Kg/hr) | $H_2O$ (Kg/hr) | CO (Kg/hr) | $CO_2$ (Kg/hr) | $CH_4$ (Kg/hr) |
| 57.000 | 18.18 | 3.14 | 0.49 | 57.000 | 13.281 | 43.719 | 0.321 | 43.859 | 0.000 | 6.901 | 4.814 | 18.744 | 0.000 |
| 58.000 | 18.18 | 3.19 | 0.50 | 58.000 | 13.514 | 44.486 | 0.307 | 44.626 | 0.000 | 7.027 | 4.602 | 19.078 | 0.000 |
| 59.000 | 18.18 | 3.25 | 0.51 | 59.000 | 13.747 | 45.253 | 0.293 | 45.393 | 0.000 | 7.153 | 4.389 | 19.412 | 0.000 |
| 60.000 | 18.18 | 3.30 | 0.52 | 60.000 | 13.980 | 46.020 | 0.279 | 46.160 | 0.000 | 7.278 | 4.177 | 19.746 | 0.000 |
| 61.000 | 18.18 | 3.36 | 0.53 | 61.000 | 14.213 | 46.787 | 0.265 | 46.927 | 0.000 | 7.404 | 3.965 | 20.079 | 0.000 |

A.7 Simulation data from the gasifier model for ER sensitivity analysis at 815 °C: mol basis

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Air | $O_2$ | $N_2$ | $H_2$ | $N_2$ | $O_2$ | $H_2O$ | CO | $CO_2$ | $CH_4$ |
| (Kg/hr) | (Kg/hr) | AF | ER | (Kg/hr) | (Kg/hr) | (Kg/hr) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac |
| 20.000 | 18.18 | 1.10 | 0.17 | 20.000 | 4.660 | 15.340 | 0.25 | 0.33 | 0.00 | 0.08 | 0.27 | 0.08 | 0.00 |
| 21.000 | 18.18 | 1.16 | 0.18 | 21.000 | 4.893 | 16.107 | 0.24 | 0.34 | 0.00 | 0.08 | 0.26 | 0.09 | 0.00 |
| 22.000 | 18.18 | 1.21 | 0.19 | 22.000 | 5.126 | 16.874 | 0.23 | 0.35 | 0.00 | 0.08 | 0.25 | 0.09 | 0.00 |
| 23.000 | 18.18 | 1.27 | 0.20 | 23.000 | 5.359 | 17.641 | 0.22 | 0.36 | 0.00 | 0.08 | 0.24 | 0.09 | 0.00 |
| 24.000 | 18.18 | 1.32 | 0.21 | 24.000 | 5.592 | 18.408 | 0.22 | 0.37 | 0.00 | 0.09 | 0.24 | 0.10 | 0.00 |
| 25.000 | 18.18 | 1.38 | 0.22 | 25.000 | 5.825 | 19.175 | 0.21 | 0.38 | 0.00 | 0.09 | 0.23 | 0.10 | 0.00 |
| 26.000 | 18.18 | 1.43 | 0.22 | 26.000 | 6.058 | 19.942 | 0.20 | 0.39 | 0.00 | 0.09 | 0.22 | 0.10 | 0.00 |
| 27.000 | 18.18 | 1.49 | 0.23 | 27.000 | 6.291 | 20.709 | 0.19 | 0.39 | 0.00 | 0.09 | 0.21 | 0.10 | 0.00 |
| 28.000 | 18.18 | 1.54 | 0.24 | 28.000 | 6.524 | 21.476 | 0.19 | 0.40 | 0.00 | 0.10 | 0.21 | 0.11 | 0.00 |
| 29.000 | 18.18 | 1.60 | 0.25 | 29.000 | 6.757 | 22.243 | 0.18 | 0.41 | 0.00 | 0.10 | 0.20 | 0.11 | 0.00 |
| 30.000 | 18.18 | 1.65 | 0.26 | 30.000 | 6.990 | 23.010 | 0.18 | 0.42 | 0.00 | 0.10 | 0.19 | 0.11 | 0.00 |
| 30.130 | 18.18 | 1.66 | 0.26 | 30.130 | 7.020 | 23.110 | 0.18 | 0.42 | 0.00 | 0.10 | 0.19 | 0.11 | 0.00 |
| 31.000 | 18.18 | 1.71 | 0.27 | 31.000 | 7.223 | 23.777 | 0.17 | 0.43 | 0.00 | 0.10 | 0.19 | 0.11 | 0.00 |
| 32.000 | 18.18 | 1.76 | 0.28 | 32.000 | 7.456 | 24.544 | 0.16 | 0.44 | 0.00 | 0.10 | 0.18 | 0.12 | 0.00 |
| 33.000 | 18.18 | 1.82 | 0.29 | 33.000 | 7.689 | 25.311 | 0.16 | 0.44 | 0.00 | 0.11 | 0.17 | 0.12 | 0.00 |
| 34.000 | 18.18 | 1.87 | 0.29 | 34.000 | 7.922 | 26.078 | 0.15 | 0.45 | 0.00 | 0.11 | 0.17 | 0.12 | 0.00 |
| 35.000 | 18.18 | 1.93 | 0.30 | 35.000 | 8.155 | 26.845 | 0.15 | 0.46 | 0.00 | 0.11 | 0.16 | 0.12 | 0.00 |
| 36.000 | 18.18 | 1.98 | 0.31 | 36.000 | 8.388 | 27.612 | 0.14 | 0.46 | 0.00 | 0.11 | 0.16 | 0.12 | 0.00 |
| 37.000 | 18.18 | 2.04 | 0.32 | 37.000 | 8.621 | 28.379 | 0.14 | 0.47 | 0.00 | 0.11 | 0.15 | 0.13 | 0.00 |
| 38.000 | 18.18 | 2.09 | 0.33 | 38.000 | 8.854 | 29.146 | 0.13 | 0.48 | 0.00 | 0.11 | 0.14 | 0.13 | 0.00 |

A.7 Simulation data from the gasifier model for ER sensitivity analysis at 815 °C: mol basis (cont’d)

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Air | $O_2$ | $N_2$ | $H_2$ | $N_2$ | $O_2$ | $H_2O$ | CO | $CO_2$ | $CH_4$ |
| (Kg/hr) | (Kg/hr) | AF | ER | (Kg/hr) | (Kg/hr) | (Kg/hr) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) |
| 39.000 | 18.18 | 2.15 | 0.34 | 39.000 | 9.087 | 29.913 | 0.13 | 0.48 | 0.00 | 0.12 | 0.14 | 0.13 | 0.00 |
| 40.000 | 18.18 | 2.20 | 0.35 | 40.000 | 9.320 | 30.680 | 0.12 | 0.49 | 0.00 | 0.12 | 0.13 | 0.13 | 0.00 |
| 41.000 | 18.18 | 2.26 | 0.35 | 41.000 | 9.553 | 31.447 | 0.12 | 0.50 | 0.00 | 0.12 | 0.13 | 0.13 | 0.00 |
| 42.000 | 18.18 | 2.31 | 0.36 | 42.000 | 9.786 | 32.214 | 0.11 | 0.50 | 0.00 | 0.12 | 0.12 | 0.14 | 0.00 |
| 43.000 | 18.18 | 2.37 | 0.37 | 43.000 | 10.019 | 32.981 | 0.11 | 0.51 | 0.00 | 0.12 | 0.12 | 0.14 | 0.00 |
| 44.000 | 18.18 | 2.42 | 0.38 | 44.000 | 10.252 | 33.748 | 0.11 | 0.51 | 0.00 | 0.12 | 0.12 | 0.14 | 0.00 |
| 45.000 | 18.18 | 2.48 | 0.39 | 45.000 | 10.485 | 34.515 | 0.10 | 0.52 | 0.00 | 0.13 | 0.11 | 0.14 | 0.00 |
| 46.000 | 18.18 | 2.53 | 0.40 | 46.000 | 10.718 | 35.282 | 0.10 | 0.53 | 0.00 | 0.13 | 0.11 | 0.14 | 0.00 |
| 47.000 | 18.18 | 2.59 | 0.41 | 47.000 | 10.951 | 36.049 | 0.09 | 0.53 | 0.00 | 0.13 | 0.10 | 0.14 | 0.00 |
| 48.000 | 18.18 | 2.64 | 0.42 | 48.000 | 11.184 | 36.816 | 0.09 | 0.54 | 0.00 | 0.13 | 0.10 | 0.15 | 0.00 |
| 49.000 | 18.18 | 2.70 | 0.42 | 49.000 | 11.417 | 37.583 | 0.09 | 0.54 | 0.00 | 0.13 | 0.09 | 0.15 | 0.00 |
| 50.000 | 18.18 | 2.75 | 0.43 | 50.000 | 11.650 | 38.350 | 0.08 | 0.55 | 0.00 | 0.13 | 0.09 | 0.15 | 0.00 |
| 51.000 | 18.18 | 2.81 | 0.44 | 51.000 | 11.883 | 39.117 | 0.08 | 0.55 | 0.00 | 0.13 | 0.09 | 0.15 | 0.00 |
| 52.000 | 18.18 | 2.86 | 0.45 | 52.000 | 12.116 | 39.884 | 0.08 | 0.56 | 0.00 | 0.14 | 0.08 | 0.15 | 0.00 |
| 53.000 | 18.18 | 2.92 | 0.46 | 53.000 | 12.349 | 40.651 | 0.08 | 0.56 | 0.00 | 0.14 | 0.08 | 0.15 | 0.00 |
| 54.000 | 18.18 | 2.97 | 0.47 | 54.000 | 12.582 | 41.418 | 0.07 | 0.56 | 0.00 | 0.14 | 0.08 | 0.15 | 0.00 |
| 55.000 | 18.18 | 3.03 | 0.48 | 55.000 | 12.815 | 42.185 | 0.07 | 0.57 | 0.00 | 0.14 | 0.07 | 0.15 | 0.00 |
| 56.000 | 18.18 | 3.08 | 0.48 | 56.000 | 13.048 | 42.952 | 0.07 | 0.57 | 0.00 | 0.14 | 0.07 | 0.15 | 0.00 |

A.7 Simulation data from the gasifier model for ER sensitivity analysis at 815 °C: mol basis (cont'd)

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (Kg/hr) | (Kg/hr) | AF | ER | Air (Kg/hr) | $O_2$ (Kg/hr) | $N_2$ (Kg/hr) | $H_2$ (mol frac) | $N_2$ (mol frac) | $O_2$ (mol frac) | $H_2O$ (mol frac) | CO (mol frac) | $CO_2$ (mol frac) | $CH_4$ (mol frac) |
| 57.000 | 18.18 | 3.14 | 0.49 | 57.000 | 13.281 | 43.719 | 0.06 | 0.57 | 0.00 | 0.14 | 0.07 | 0.16 | 0.00 |
| 58.000 | 18.18 | 3.19 | 0.50 | 58.000 | 13.514 | 44.486 | 0.06 | 0.58 | 0.00 | 0.14 | 0.06 | 0.16 | 0.00 |
| 59.000 | 18.18 | 3.25 | 0.51 | 59.000 | 13.747 | 45.253 | 0.06 | 0.58 | 0.00 | 0.14 | 0.06 | 0.16 | 0.00 |
| 60.000 | 18.18 | 3.30 | 0.52 | 60.000 | 13.980 | 46.020 | 0.05 | 0.59 | 0.00 | 0.14 | 0.06 | 0.16 | 0.00 |
| 61.000 | 18.18 | 3.36 | 0.53 | 61.000 | 14.213 | 46.787 | 0.05 | 0.59 | 0.00 | 0.14 | 0.05 | 0.16 | 0.00 |

A.8 Simulation data from the gasifier model for ER sensitivity analysis at 750 °C: mol basis

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Air | $O_2$ | $N_2$ | $H_2$ | $N_2$ | $O_2$ | $H_2O$ | CO | $CO_2$ | $CH_4$ |
| (Kg/hr) | (Kg/hr) | AF | ER | (Kg/hr) | (Kg/hr) | (Kg/hr) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac |
| 20.000 | 18.18 | 1.10 | 0.17 | 20.000 | 4.660 | 15.340 | 0.25 | 0.33 | 0.00 | 0.07 | 0.26 | 0.09 | 0.00 |
| 21.000 | 18.18 | 1.16 | 0.18 | 21.000 | 4.893 | 16.107 | 0.24 | 0.34 | 0.00 | 0.07 | 0.25 | 0.10 | 0.00 |
| 22.000 | 18.18 | 1.21 | 0.19 | 22.000 | 5.126 | 16.874 | 0.24 | 0.35 | 0.00 | 0.07 | 0.24 | 0.10 | 0.00 |
| 23.000 | 18.18 | 1.27 | 0.20 | 23.000 | 5.359 | 17.641 | 0.23 | 0.36 | 0.00 | 0.08 | 0.23 | 0.10 | 0.00 |
| 24.000 | 18.18 | 1.32 | 0.21 | 24.000 | 5.592 | 18.408 | 0.22 | 0.37 | 0.00 | 0.08 | 0.23 | 0.10 | 0.00 |
| 25.000 | 18.18 | 1.38 | 0.22 | 25.000 | 5.825 | 19.175 | 0.22 | 0.38 | 0.00 | 0.08 | 0.22 | 0.11 | 0.00 |
| 26.000 | 18.18 | 1.43 | 0.22 | 26.000 | 6.058 | 19.942 | 0.21 | 0.39 | 0.00 | 0.08 | 0.21 | 0.11 | 0.00 |
| 27.000 | 18.18 | 1.49 | 0.23 | 27.000 | 6.291 | 20.709 | 0.20 | 0.40 | 0.00 | 0.09 | 0.20 | 0.11 | 0.00 |
| 28.000 | 18.18 | 1.54 | 0.24 | 28.000 | 6.524 | 21.476 | 0.20 | 0.40 | 0.00 | 0.09 | 0.20 | 0.12 | 0.00 |
| 29.000 | 18.18 | 1.60 | 0.25 | 29.000 | 6.757 | 22.243 | 0.19 | 0.41 | 0.00 | 0.09 | 0.19 | 0.12 | 0.00 |
| 30.000 | 18.18 | 1.65 | 0.26 | 30.000 | 6.990 | 23.010 | 0.18 | 0.42 | 0.00 | 0.09 | 0.18 | 0.12 | 0.00 |
| 30.130 | 18.18 | 1.66 | 0.26 | 30.130 | 7.020 | 23.110 | 0.18 | 0.42 | 0.00 | 0.09 | 0.18 | 0.12 | 0.00 |
| 31.000 | 18.18 | 1.71 | 0.27 | 31.000 | 7.223 | 23.777 | 0.18 | 0.43 | 0.00 | 0.09 | 0.18 | 0.12 | 0.00 |
| 32.000 | 18.18 | 1.76 | 0.28 | 32.000 | 7.456 | 24.544 | 0.17 | 0.44 | 0.00 | 0.10 | 0.17 | 0.12 | 0.00 |
| 33.000 | 18.18 | 1.82 | 0.29 | 33.000 | 7.689 | 25.311 | 0.17 | 0.44 | 0.00 | 0.10 | 0.16 | 0.13 | 0.00 |
| 34.000 | 18.18 | 1.87 | 0.29 | 34.000 | 7.922 | 26.078 | 0.16 | 0.45 | 0.00 | 0.10 | 0.16 | 0.13 | 0.00 |
| 35.000 | 18.18 | 1.93 | 0.30 | 35.000 | 8.155 | 26.845 | 0.16 | 0.46 | 0.00 | 0.10 | 0.15 | 0.13 | 0.00 |
| 36.000 | 18.18 | 1.98 | 0.31 | 36.000 | 8.388 | 27.612 | 0.15 | 0.46 | 0.00 | 0.10 | 0.15 | 0.13 | 0.00 |
| 37.000 | 18.18 | 2.04 | 0.32 | 37.000 | 8.621 | 28.379 | 0.15 | 0.47 | 0.00 | 0.11 | 0.14 | 0.13 | 0.00 |
| 38.000 | 18.18 | 2.09 | 0.33 | 38.000 | 8.854 | 29.146 | 0.14 | 0.48 | 0.00 | 0.11 | 0.14 | 0.14 | 0.00 |

A.8 Simulation data from the gasifier model for ER sensitivity analysis at 750 °C: mol basis (cont'd)

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Air | $O_2$ | $N_2$ | $H_2$ | $N_2$ | $O_2$ | $H_2O$ | CO | $CO_2$ | $CH_4$ |
| (Kg/hr) | (Kg/hr) | AF | ER | (Kg/hr) | (Kg/hr) | (Kg/hr) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) |
| 39.000 | 18.18 | 2.15 | 0.34 | 39.000 | 9.087 | 29.913 | 0.14 | 0.48 | 0.00 | 0.11 | 0.13 | 0.14 | 0.00 |
| 40.000 | 18.18 | 2.20 | 0.35 | 40.000 | 9.320 | 30.680 | 0.13 | 0.49 | 0.00 | 0.11 | 0.13 | 0.14 | 0.00 |
| 41.000 | 18.18 | 2.26 | 0.35 | 41.000 | 9.553 | 31.447 | 0.13 | 0.50 | 0.00 | 0.11 | 0.12 | 0.14 | 0.00 |
| 42.000 | 18.18 | 2.31 | 0.36 | 42.000 | 9.786 | 32.214 | 0.12 | 0.50 | 0.00 | 0.11 | 0.12 | 0.14 | 0.00 |
| 43.000 | 18.18 | 2.37 | 0.37 | 43.000 | 10.019 | 32.981 | 0.12 | 0.51 | 0.00 | 0.12 | 0.11 | 0.14 | 0.00 |
| 44.000 | 18.18 | 2.42 | 0.38 | 44.000 | 10.252 | 33.748 | 0.11 | 0.51 | 0.00 | 0.12 | 0.11 | 0.15 | 0.00 |
| 45.000 | 18.18 | 2.48 | 0.39 | 45.000 | 10.485 | 34.515 | 0.11 | 0.52 | 0.00 | 0.12 | 0.10 | 0.15 | 0.00 |
| 46.000 | 18.18 | 2.53 | 0.40 | 46.000 | 10.718 | 35.282 | 0.11 | 0.53 | 0.00 | 0.12 | 0.10 | 0.15 | 0.00 |
| 47.000 | 18.18 | 2.59 | 0.41 | 47.000 | 10.951 | 36.049 | 0.10 | 0.53 | 0.00 | 0.12 | 0.10 | 0.15 | 0.00 |
| 48.000 | 18.18 | 2.64 | 0.42 | 48.000 | 11.184 | 36.816 | 0.10 | 0.54 | 0.00 | 0.12 | 0.09 | 0.15 | 0.00 |
| 49.000 | 18.18 | 2.70 | 0.42 | 49.000 | 11.417 | 37.583 | 0.09 | 0.54 | 0.00 | 0.13 | 0.09 | 0.15 | 0.00 |
| 50.000 | 18.18 | 2.75 | 0.43 | 50.000 | 11.650 | 38.350 | 0.09 | 0.55 | 0.00 | 0.13 | 0.08 | 0.15 | 0.00 |
| 51.000 | 18.18 | 2.81 | 0.44 | 51.000 | 11.883 | 39.884 | 0.09 | 0.55 | 0.00 | 0.13 | 0.08 | 0.16 | 0.00 |
| 52.000 | 18.18 | 2.86 | 0.45 | 52.000 | 12.116 | 39.117 | 0.08 | 0.56 | 0.00 | 0.13 | 0.08 | 0.16 | 0.00 |
| 53.000 | 18.18 | 2.92 | 0.46 | 53.000 | 12.349 | 40.651 | 0.08 | 0.56 | 0.00 | 0.13 | 0.07 | 0.16 | 0.00 |
| 54.000 | 18.18 | 2.97 | 0.47 | 54.000 | 12.582 | 41.418 | 0.07 | 0.57 | 0.00 | 0.13 | 0.07 | 0.16 | 0.00 |
| 55.000 | 18.18 | 3.03 | 0.48 | 55.000 | 12.815 | 42.185 | 0.07 | 0.57 | 0.00 | 0.13 | 0.06 | 0.16 | 0.00 |
| 56.000 | 18.18 | 3.08 | 0.48 | 56.000 | 13.048 | 42.952 | 0.07 | 0.57 | 0.00 | 0.14 | 0.06 | 0.16 | 0.00 |

A.8 Simulation data from the gasifier model for ER sensitivity analysis at 750 °C: mol basis (cont'd)

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (Kg/hr) | (Kg/hr) | AF | ER | Air (Kg/hr) | $O_2$ (Kg/hr) | $N_2$ (Kg/hr) | $H_2$ (mol frac) | $N_2$ (mol frac) | $O_2$ (mol frac) | $H_2O$ (mol frac) | CO (mol frac) | $CO_2$ (mol frac) | $CH_4$ (mol frac) |
| 57.000 | 18.18 | 3.14 | 0.49 | 57.000 | 13.281 | 43.719 | 0.06 | 0.58 | 0.00 | 0.14 | 0.06 | 0.16 | 0.00 |
| 58.000 | 18.18 | 3.19 | 0.50 | 58.000 | 13.514 | 44.486 | 0.06 | 0.58 | 0.00 | 0.14 | 0.06 | 0.16 | 0.00 |
| 59.000 | 18.18 | 3.25 | 0.51 | 59.000 | 13.747 | 45.253 | 0.06 | 0.59 | 0.00 | 0.14 | 0.05 | 0.16 | 0.00 |
| 60.000 | 18.18 | 3.30 | 0.52 | 60.000 | 13.980 | 46.020 | 0.05 | 0.59 | 0.00 | 0.14 | 0.05 | 0.17 | 0.00 |
| 61.000 | 18.18 | 3.36 | 0.53 | 61.000 | 14.213 | 46.787 | 0.05 | 0.60 | 0.00 | 0.14 | 0.05 | 0.17 | 0.00 |

A.9 Simulation data from the gasifier model for ER sensitivity analysis at 875 °C: mol basis

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Air | $O_2$ | $N_2$ | $H_2$ | $N_2$ | $O_2$ | $H_2O$ | CO | $CO_2$ | $CH_4$ |
| (Kg/hr) | (Kg/hr) | AF | ER | (Kg/hr) | (Kg/hr) | (Kg/hr) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) |
| 20.000 | 18.18 | 1.10 | 0.17 | 20.000 | 4.660 | 15.340 | 0.24 | 0.33 | 0.00 | 0.08 | 0.27 | 0.08 | 0.00 |
| 21.000 | 18.18 | 1.16 | 0.18 | 21.000 | 4.893 | 16.107 | 0.23 | 0.34 | 0.00 | 0.08 | 0.27 | 0.08 | 0.00 |
| 22.000 | 18.18 | 1.21 | 0.19 | 22.000 | 5.126 | 16.874 | 0.22 | 0.35 | 0.00 | 0.09 | 0.26 | 0.08 | 0.00 |
| 23.000 | 18.18 | 1.27 | 0.20 | 23.000 | 5.359 | 17.641 | 0.22 | 0.36 | 0.00 | 0.09 | 0.25 | 0.09 | 0.00 |
| 24.000 | 18.18 | 1.32 | 0.21 | 24.000 | 5.592 | 18.408 | 0.21 | 0.37 | 0.00 | 0.09 | 0.24 | 0.09 | 0.00 |
| 25.000 | 18.18 | 1.38 | 0.22 | 25.000 | 5.825 | 19.175 | 0.20 | 0.38 | 0.00 | 0.09 | 0.23 | 0.09 | 0.00 |
| 26.000 | 18.18 | 1.43 | 0.22 | 26.000 | 6.058 | 19.942 | 0.20 | 0.39 | 0.00 | 0.10 | 0.23 | 0.10 | 0.00 |
| 27.000 | 18.18 | 1.49 | 0.23 | 27.000 | 6.291 | 20.709 | 0.19 | 0.39 | 0.00 | 0.10 | 0.22 | 0.10 | 0.00 |
| 28.000 | 18.18 | 1.54 | 0.24 | 28.000 | 6.524 | 21.476 | 0.18 | 0.40 | 0.00 | 0.10 | 0.21 | 0.10 | 0.00 |
| 29.000 | 18.18 | 1.60 | 0.25 | 29.000 | 6.757 | 22.243 | 0.18 | 0.41 | 0.00 | 0.10 | 0.21 | 0.10 | 0.00 |
| 30.000 | 18.18 | 1.65 | 0.26 | 30.000 | 6.990 | 23.010 | 0.17 | 0.42 | 0.00 | 0.11 | 0.20 | 0.11 | 0.00 |
| 30.130 | 18.18 | 1.66 | 0.26 | 30.130 | 7.020 | 23.110 | 0.17 | 0.42 | 0.00 | 0.11 | 0.20 | 0.11 | 0.00 |
| 31.000 | 18.18 | 1.71 | 0.27 | 31.000 | 7.223 | 23.777 | 0.16 | 0.43 | 0.00 | 0.11 | 0.19 | 0.11 | 0.00 |
| 32.000 | 18.18 | 1.76 | 0.28 | 32.000 | 7.456 | 24.544 | 0.16 | 0.44 | 0.00 | 0.11 | 0.19 | 0.11 | 0.00 |
| 33.000 | 18.18 | 1.82 | 0.29 | 33.000 | 7.689 | 25.311 | 0.15 | 0.44 | 0.00 | 0.11 | 0.18 | 0.11 | 0.00 |
| 34.000 | 18.18 | 1.87 | 0.29 | 34.000 | 7.922 | 26.078 | 0.15 | 0.45 | 0.00 | 0.11 | 0.17 | 0.11 | 0.00 |
| 35.000 | 18.18 | 1.93 | 0.30 | 35.000 | 8.155 | 26.845 | 0.14 | 0.46 | 0.00 | 0.12 | 0.17 | 0.12 | 0.00 |
| 36.000 | 18.18 | 1.98 | 0.31 | 36.000 | 8.388 | 27.612 | 0.14 | 0.46 | 0.00 | 0.12 | 0.16 | 0.12 | 0.00 |
| 37.000 | 18.18 | 2.04 | 0.32 | 37.000 | 8.621 | 28.379 | 0.13 | 0.47 | 0.00 | 0.12 | 0.16 | 0.12 | 0.00 |
| 38.000 | 18.18 | 2.09 | 0.33 | 38.000 | 8.854 | 29.146 | 0.13 | 0.48 | 0.00 | 0.12 | 0.15 | 0.12 | 0.00 |

A.9 Simulation data from the gasifier model for ER sensitivity analysis at 875 °C: mol basis (cont'd)

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Air | $O_2$ | $N_2$ | $H_2$ | $N_2$ | $O_2$ | $H_2O$ | CO | $CO_2$ | $CH_4$ |
| (Kg/hr) | (Kg/hr) | AF | ER | (Kg/hr) | (Kg/hr) | (Kg/hr) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) |
| 39.000 | 18.18 | 2.15 | 0.34 | 39.000 | 9.087 | 29.913 | 0.12 | 0.48 | 0.00 | 0.12 | 0.15 | 0.12 | 0.00 |
| 40.000 | 18.18 | 2.20 | 0.35 | 40.000 | 9.320 | 30.680 | 0.12 | 0.49 | 0.00 | 0.12 | 0.14 | 0.13 | 0.00 |
| 41.000 | 18.18 | 2.26 | 0.35 | 41.000 | 9.553 | 31.447 | 0.11 | 0.50 | 0.00 | 0.13 | 0.14 | 0.13 | 0.00 |
| 42.000 | 18.18 | 2.31 | 0.36 | 42.000 | 9.786 | 32.214 | 0.11 | 0.50 | 0.00 | 0.13 | 0.13 | 0.13 | 0.00 |
| 43.000 | 18.18 | 2.37 | 0.37 | 43.000 | 10.019 | 32.981 | 0.10 | 0.51 | 0.00 | 0.13 | 0.13 | 0.13 | 0.00 |
| 44.000 | 18.18 | 2.42 | 0.38 | 44.000 | 10.252 | 33.748 | 0.10 | 0.51 | 0.00 | 0.13 | 0.12 | 0.13 | 0.00 |
| 45.000 | 18.18 | 2.48 | 0.39 | 45.000 | 10.485 | 34.515 | 0.10 | 0.52 | 0.00 | 0.13 | 0.12 | 0.14 | 0.00 |
| 46.000 | 18.18 | 2.53 | 0.40 | 46.000 | 10.718 | 35.282 | 0.09 | 0.53 | 0.00 | 0.13 | 0.11 | 0.14 | 0.00 |
| 47.000 | 18.18 | 2.59 | 0.41 | 47.000 | 10.951 | 36.049 | 0.09 | 0.53 | 0.00 | 0.13 | 0.11 | 0.14 | 0.00 |
| 48.000 | 18.18 | 2.64 | 0.42 | 48.000 | 11.184 | 36.816 | 0.08 | 0.54 | 0.00 | 0.14 | 0.10 | 0.14 | 0.00 |
| 49.000 | 18.18 | 2.70 | 0.42 | 49.000 | 11.417 | 37.583 | 0.08 | 0.54 | 0.00 | 0.14 | 0.10 | 0.14 | 0.00 |
| 50.000 | 18.18 | 2.75 | 0.43 | 50.000 | 11.650 | 38.350 | 0.08 | 0.55 | 0.00 | 0.14 | 0.09 | 0.14 | 0.00 |
| 51.000 | 18.18 | 2.81 | 0.44 | 51.000 | 11.883 | 39.884 | 0.07 | 0.55 | 0.00 | 0.14 | 0.09 | 0.14 | 0.00 |
| 52.000 | 18.18 | 2.86 | 0.45 | 52.000 | 12.116 | 39.117 | 0.07 | 0.56 | 0.00 | 0.14 | 0.09 | 0.15 | 0.00 |
| 53.000 | 18.18 | 2.92 | 0.46 | 53.000 | 12.349 | 40.651 | 0.07 | 0.56 | 0.00 | 0.14 | 0.08 | 0.15 | 0.00 |
| 54.000 | 18.18 | 2.97 | 0.47 | 54.000 | 12.582 | 41.418 | 0.06 | 0.57 | 0.00 | 0.14 | 0.08 | 0.15 | 0.00 |
| 55.000 | 18.18 | 3.03 | 0.48 | 55.000 | 12.815 | 42.185 | 0.06 | 0.57 | 0.00 | 0.14 | 0.08 | 0.15 | 0.00 |
| 56.000 | 18.18 | 3.08 | 0.48 | 56.000 | 13.048 | 42.952 | 0.06 | 0.57 | 0.00 | 0.14 | 0.07 | 0.15 | 0.00 |

A.9 Simulation data from the gasifier model for ER sensitivity analysis at 875 °C: mol basis (cont’d)

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (Kg/hr) | (Kg/hr) | AF | ER | Air (Kg/hr) | $O_2$ (Kg/hr) | $N_2$ (Kg/hr) | $H_2$ (mol frac) | $N_2$ (mol frac) | $O_2$ (mol frac) | $H_2O$ (mol frac) | CO (mol frac) | $CO_2$ (mol frac) | $CH_4$ (mol frac) |
| 57.000 | 18.18 | 3.14 | 0.49 | 57.000 | 13.281 | 43.719 | 0.05 | 0.58 | 0.00 | 0.15 | 0.07 | 0.15 | 0.00 |
| 58.000 | 18.18 | 3.19 | 0.50 | 58.000 | 13.514 | 44.486 | 0.05 | 0.58 | 0.00 | 0.15 | 0.06 | 0.15 | 0.00 |
| 59.000 | 18.18 | 3.25 | 0.51 | 59.000 | 13.747 | 45.253 | 0.05 | 0.59 | 0.00 | 0.15 | 0.06 | 0.16 | 0.00 |
| 60.000 | 18.18 | 3.30 | 0.52 | 60.000 | 13.980 | 46.020 | 0.05 | 0.59 | 0.00 | 0.15 | 0.06 | 0.16 | 0.00 |
| 61.000 | 18.18 | 3.36 | 0.53 | 61.000 | 14.213 | 46.787 | 0.04 | 0.59 | 0.00 | 0.15 | 0.05 | 0.16 | 0.00 |

A.10 Simulation data from the gasifier model for ER sensitivity analysis at 925 °C: mol basis

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (Kg/hr) | (Kg/hr) | AF | ER | Air (Kg/hr) | $O_2$ (Kg/hr) | $N_2$ (Kg/hr) | $H_2$ (mol frac) | $N_2$ (mol frac) | $O_2$ (mol frac) | $H_2O$ (mol frac) | CO (mol frac) | $CO_2$ (mol frac) | $CH_4$ (mol frac) |
| 20.000 | 18.18 | 1.10 | 0.17 | 20.000 | 4.660 | 15.340 | 0.24 | 0.33 | 0.00 | 0.09 | 0.28 | 0.07 | 0.00 |
| 21.000 | 18.18 | 1.16 | 0.18 | 21.000 | 4.893 | 16.107 | 0.23 | 0.34 | 0.00 | 0.09 | 0.27 | 0.08 | 0.00 |
| 22.000 | 18.18 | 1.21 | 0.19 | 22.000 | 5.126 | 16.874 | 0.22 | 0.35 | 0.00 | 0.09 | 0.26 | 0.08 | 0.00 |
| 23.000 | 18.18 | 1.27 | 0.20 | 23.000 | 5.359 | 17.641 | 0.21 | 0.36 | 0.00 | 0.09 | 0.25 | 0.08 | 0.00 |
| 24.000 | 18.18 | 1.32 | 0.21 | 24.000 | 5.592 | 18.408 | 0.20 | 0.37 | 0.00 | 0.10 | 0.25 | 0.09 | 0.00 |
| 25.000 | 18.18 | 1.38 | 0.22 | 25.000 | 5.825 | 19.175 | 0.20 | 0.38 | 0.00 | 0.10 | 0.24 | 0.09 | 0.00 |
| 26.000 | 18.18 | 1.43 | 0.22 | 26.000 | 6.058 | 19.942 | 0.19 | 0.39 | 0.00 | 0.10 | 0.23 | 0.09 | 0.00 |
| 27.000 | 18.18 | 1.49 | 0.23 | 27.000 | 6.291 | 20.709 | 0.18 | 0.39 | 0.00 | 0.10 | 0.22 | 0.09 | 0.00 |
| 28.000 | 18.18 | 1.54 | 0.24 | 28.000 | 6.524 | 21.476 | 0.18 | 0.40 | 0.00 | 0.11 | 0.22 | 0.10 | 0.00 |
| 29.000 | 18.18 | 1.60 | 0.25 | 29.000 | 6.757 | 22.243 | 0.17 | 0.41 | 0.00 | 0.11 | 0.21 | 0.10 | 0.00 |
| 30.000 | 18.18 | 1.65 | 0.26 | 30.000 | 6.990 | 23.010 | 0.16 | 0.42 | 0.00 | 0.11 | 0.20 | 0.10 | 0.00 |
| 30.130 | 18.18 | 1.66 | 0.26 | 30.130 | 7.020 | 23.110 | 0.16 | 0.42 | 0.00 | 0.11 | 0.20 | 0.10 | 0.00 |
| 31.000 | 18.18 | 1.71 | 0.27 | 31.000 | 7.223 | 23.777 | 0.16 | 0.43 | 0.00 | 0.11 | 0.20 | 0.10 | 0.00 |
| 32.000 | 18.18 | 1.76 | 0.28 | 32.000 | 7.456 | 24.544 | 0.15 | 0.44 | 0.00 | 0.12 | 0.19 | 0.11 | 0.00 |
| 33.000 | 18.18 | 1.82 | 0.29 | 33.000 | 7.689 | 25.311 | 0.15 | 0.44 | 0.00 | 0.12 | 0.18 | 0.11 | 0.00 |
| 34.000 | 18.18 | 1.87 | 0.29 | 34.000 | 7.922 | 26.078 | 0.14 | 0.45 | 0.00 | 0.12 | 0.18 | 0.11 | 0.00 |
| 35.000 | 18.18 | 1.93 | 0.30 | 35.000 | 8.155 | 26.845 | 0.14 | 0.46 | 0.00 | 0.12 | 0.17 | 0.11 | 0.00 |
| 36.000 | 18.18 | 1.98 | 0.31 | 36.000 | 8.388 | 27.612 | 0.13 | 0.46 | 0.00 | 0.12 | 0.17 | 0.11 | 0.00 |
| 37.000 | 18.18 | 2.04 | 0.32 | 37.000 | 8.621 | 28.379 | 0.13 | 0.47 | 0.00 | 0.12 | 0.16 | 0.12 | 0.00 |
| 38.000 | 18.18 | 2.09 | 0.33 | 38.000 | 8.854 | 29.146 | 0.12 | 0.48 | 0.00 | 0.13 | 0.16 | 0.12 | 0.00 |

A.10 Simulation data from the gasifier model for ER sensitivity analysis at 925 °C: mol basis (cont’d)

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Air | $O_2$ | $N_2$ | $H_2$ | $N_2$ | $O_2$ | $H_2O$ | CO | $CO_2$ | $CH_4$ |
| (Kg/hr) | (Kg/hr) | AF | ER | (Kg/hr) | (Kg/hr) | (Kg/hr) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) |
| 39.000 | 18.18 | 2.15 | 0.34 | 39.000 | 9.087 | 29.913 | 0.12 | 0.48 | 0.00 | 0.13 | 0.15 | 0.12 | 0.00 |
| 40.000 | 18.18 | 2.20 | 0.35 | 40.000 | 9.320 | 30.680 | 0.11 | 0.49 | 0.00 | 0.13 | 0.15 | 0.12 | 0.00 |
| 41.000 | 18.18 | 2.26 | 0.35 | 41.000 | 9.553 | 31.447 | 0.11 | 0.50 | 0.00 | 0.13 | 0.14 | 0.12 | 0.00 |
| 42.000 | 18.18 | 2.31 | 0.36 | 42.000 | 9.786 | 32.214 | 0.10 | 0.50 | 0.00 | 0.13 | 0.14 | 0.13 | 0.00 |
| 43.000 | 18.18 | 2.37 | 0.37 | 43.000 | 10.019 | 32.981 | 0.10 | 0.51 | 0.00 | 0.13 | 0.13 | 0.13 | 0.00 |
| 44.000 | 18.18 | 2.42 | 0.38 | 44.000 | 10.252 | 33.748 | 0.10 | 0.51 | 0.00 | 0.13 | 0.13 | 0.13 | 0.00 |
| 45.000 | 18.18 | 2.48 | 0.39 | 45.000 | 10.485 | 34.515 | 0.09 | 0.52 | 0.00 | 0.14 | 0.12 | 0.13 | 0.00 |
| 46.000 | 18.18 | 2.53 | 0.40 | 46.000 | 10.718 | 35.282 | 0.09 | 0.53 | 0.00 | 0.14 | 0.12 | 0.13 | 0.00 |
| 47.000 | 18.18 | 2.59 | 0.41 | 47.000 | 10.951 | 36.049 | 0.08 | 0.53 | 0.00 | 0.14 | 0.11 | 0.13 | 0.00 |
| 48.000 | 18.18 | 2.64 | 0.42 | 48.000 | 11.184 | 36.816 | 0.08 | 0.54 | 0.00 | 0.14 | 0.11 | 0.14 | 0.00 |
| 49.000 | 18.18 | 2.70 | 0.42 | 49.000 | 11.417 | 37.583 | 0.08 | 0.54 | 0.00 | 0.14 | 0.10 | 0.14 | 0.00 |
| 50.000 | 18.18 | 2.75 | 0.43 | 50.000 | 11.650 | 38.350 | 0.07 | 0.55 | 0.00 | 0.14 | 0.10 | 0.14 | 0.00 |
| 51.000 | 18.18 | 2.81 | 0.44 | 51.000 | 11.883 | 39.884 | 0.07 | 0.55 | 0.00 | 0.14 | 0.09 | 0.14 | 0.00 |
| 52.000 | 18.18 | 2.86 | 0.45 | 52.000 | 12.116 | 39.117 | 0.07 | 0.56 | 0.00 | 0.14 | 0.09 | 0.14 | 0.00 |
| 53.000 | 18.18 | 2.92 | 0.46 | 53.000 | 12.349 | 40.651 | 0.06 | 0.56 | 0.00 | 0.15 | 0.09 | 0.14 | 0.00 |
| 54.000 | 18.18 | 2.97 | 0.47 | 54.000 | 12.582 | 41.418 | 0.06 | 0.57 | 0.00 | 0.15 | 0.08 | 0.15 | 0.00 |
| 55.000 | 18.18 | 3.03 | 0.48 | 55.000 | 12.815 | 42.185 | 0.06 | 0.57 | 0.00 | 0.15 | 0.08 | 0.15 | 0.00 |
| 56.000 | 18.18 | 3.08 | 0.48 | 56.000 | 13.048 | 42.952 | 0.05 | 0.57 | 0.00 | 0.15 | 0.07 | 0.15 | 0.00 |

A.10 Simulation data from the gasifier model for ER sensitivity analysis at 925 °C: mol basis (cont'd)

| Air Feed | Biomass Feed | Air Fuel Ratio | Equivalence Ratio | Air Input | | | Product Gases | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Air | $O_2$ | $N_2$ | $H_2$ | $N_2$ | $O_2$ | $H_2O$ | CO | $CO_2$ | $CH_4$ |
| (Kg/hr) | (Kg/hr) | AF | ER | (Kg/hr) | (Kg/hr) | (Kg/hr) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) | (mol frac) |
| 57.000 | 18.18 | 3.14 | 0.49 | 57.000 | 13.281 | 43.719 | 0.05 | 0.58 | 0.00 | 0.15 | 0.07 | 0.15 | 0.00 |
| 58.000 | 18.18 | 3.19 | 0.50 | 58.000 | 13.514 | 44.486 | 0.05 | 0.58 | 0.00 | 0.15 | 0.07 | 0.15 | 0.00 |
| 59.000 | 18.18 | 3.25 | 0.51 | 59.000 | 13.747 | 45.253 | 0.05 | 0.59 | 0.00 | 0.15 | 0.06 | 0.15 | 0.00 |
| 60.000 | 18.18 | 3.30 | 0.52 | 60.000 | 13.980 | 46.020 | 0.04 | 0.59 | 0.00 | 0.15 | 0.06 | 0.15 | 0.00 |
| 61.000 | 18.18 | 3.36 | 0.53 | 61.000 | 14.213 | 46.787 | 0.04 | 0.59 | 0.00 | 0.15 | 0.06 | 0.16 | 0.00 |

A.11 Simulation data from the bioreactor model for CO sensitivity analysis

| CO (mol frac) | $CO_2$ (mol frac) | $H_2$ (mol frac) | $N_2$ (mol frac) | Ethanol Production (x $10^{-4}$ Kmol/hr) |
|---|---|---|---|---|
| 0.141 | 0.187 | 0.053 | 0.619 | 0.142 |
| 0.153 | 0.187 | 0.053 | 0.607 | 0.151 |
| 0.142 | 0.187 | 0.053 | 0.619 | 0.142 |
| 0.116 | 0.187 | 0.053 | 0.644 | 0.124 |
| 0.136 | 0.187 | 0.053 | 0.624 | 0.138 |
| 0.133 | 0.187 | 0.053 | 0.627 | 0.136 |
| 0.135 | 0.187 | 0.053 | 0.626 | 0.137 |
| 0.147 | 0.187 | 0.053 | 0.614 | 0.146 |
| 0.163 | 0.187 | 0.053 | 0.597 | 0.158 |
| 0.121 | 0.187 | 0.053 | 0.639 | 0.128 |
| 0.151 | 0.187 | 0.053 | 0.610 | 0.149 |
| 0.134 | 0.187 | 0.053 | 0.626 | 0.137 |
| 0.157 | 0.187 | 0.053 | 0.603 | 0.154 |
| 0.100 | 0.187 | 0.053 | 0.660 | 0.112 |
| 0.180 | 0.187 | 0.053 | 0.580 | 0.171 |
| 0.190 | 0.187 | 0.053 | 0.570 | 0.178 |
| 0.200 | 0.187 | 0.053 | 0.560 | 0.185 |

A.12 Simulation data from the bioreactor model for $CO_2$ sensitivity analysis

| CO (mol frac) | $CO_2$ (mol frac) | $H_2$ (mol frac) | $N_2$ (mol frac) | Ethanol Production (x $10^{-4}$ Kmol/hr) |
|---|---|---|---|---|
| 0.141 | 0.184 | 0.053 | 0.623 | 0.14171 |
| 0.141 | 0.182 | 0.053 | 0.625 | 0.14171 |
| 0.141 | 0.179 | 0.053 | 0.627 | 0.14171 |
| 0.141 | 0.177 | 0.053 | 0.629 | 0.14171 |
| 0.141 | 0.182 | 0.053 | 0.625 | 0.14171 |
| 0.141 | 0.183 | 0.053 | 0.623 | 0.14171 |
| 0.141 | 0.186 | 0.053 | 0.621 | 0.14171 |
| 0.141 | 0.192 | 0.053 | 0.614 | 0.14172 |
| 0.141 | 0.192 | 0.053 | 0.615 | 0.14172 |
| 0.141 | 0.205 | 0.053 | 0.601 | 0.14174 |
| 0.141 | 0.186 | 0.053 | 0.621 | 0.14171 |
| 0.141 | 0.193 | 0.053 | 0.613 | 0.14172 |
| 0.141 | 0.186 | 0.053 | 0.621 | 0.14171 |
| 0.141 | 0.150 | 0.053 | 0.657 | 0.14167 |
| 0.141 | 0.160 | 0.053 | 0.647 | 0.14168 |
| 0.141 | 0.210 | 0.053 | 0.597 | 0.14170 |
| 0.141 | 0.110 | 0.053 | 0.697 | 0.14170 |
| 0.141 | 0.250 | 0.053 | 0.557 | 0.14170 |

A.13 Simulation data from the bioreactor model for $H_2$ sensitivity analysis

| CO (mol frac) | $CO_2$ (mol frac) | $H_2$ (mol frac) | $N_2$ (mol frac) | Ethanol Production (x $10^{-4}$ Kmol/hr) |
|---|---|---|---|---|
| 0.14 | 0.19 | 0.09 | 0.58 | 0.169 |
| 0.14 | 0.19 | 0.06 | 0.61 | 0.146 |
| 0.14 | 0.19 | 0.06 | 0.61 | 0.147 |
| 0.14 | 0.19 | 0.05 | 0.62 | 0.141 |
| 0.14 | 0.19 | 0.04 | 0.63 | 0.131 |
| 0.14 | 0.19 | 0.05 | 0.62 | 0.139 |
| 0.14 | 0.19 | 0.05 | 0.62 | 0.141 |
| 0.14 | 0.19 | 0.05 | 0.62 | 0.138 |
| 0.14 | 0.19 | 0.06 | 0.62 | 0.144 |
| 0.14 | 0.19 | 0.06 | 0.61 | 0.149 |
| 0.14 | 0.19 | 0.05 | 0.63 | 0.137 |
| 0.14 | 0.19 | 0.06 | 0.61 | 0.145 |
| 0.14 | 0.19 | 0.05 | 0.62 | 0.139 |
| 0.14 | 0.19 | 0.06 | 0.61 | 0.148 |
| 0.14 | 0.19 | 0.03 | 0.64 | 0.125 |
| 0.14 | 0.19 | 0.07 | 0.60 | 0.155 |

A.14 Simulation data from the bioreactor model for media sensitivity analysis

| Media Flowrate (x $10^{-5}$ Kg/sec) | Water in Product Stream (mol frac) | Ethanol production (x $10^{-5}$ Kg/sec) | Ethanol production (mol frac) |
|---|---|---|---|
| 0.10 | 0.800 | 0.017482 | 0.2004 |
| 0.35 | 0.938 | 0.017524 | 0.0623 |
| 0.60 | 0.963 | 0.017546 | 0.0369 |
| 0.85 | 0.974 | 0.017560 | 0.0262 |
| 1.10 | 0.980 | 0.017571 | 0.0203 |
| 1.35 | 0.983 | 0.017579 | 0.0166 |
| 1.60 | 0.986 | 0.017586 | 0.0140 |
| 1.85 | 0.988 | 0.017592 | 0.0122 |
| 2.10 | 0.989 | 0.017597 | 0.0107 |
| 2.35 | 0.990 | 0.017601 | 0.0096 |
| 2.60 | 0.991 | 0.017605 | 0.0087 |
| 2.85 | 0.992 | 0.017609 | 0.0079 |
| 3.10 | 0.993 | 0.017612 | 0.0073 |
| 3.35 | 0.993 | 0.017615 | 0.0067 |
| 3.60 | 0.994 | 0.017618 | 0.0063 |
| 3.85 | 0.994 | 0.017621 | 0.0059 |
| 4.10 | 0.994 | 0.017623 | 0.0055 |
| 4.15 | 0.995 | 0.017624 | 0.0055 |
| 4.35 | 0.995 | 0.017625 | 0.0052 |
| 4.60 | 0.995 | 0.017628 | 0.0049 |
| 4.85 | 0.995 | 0.017629 | 0.0047 |
| 5.00 | 0.995 | 0.017631 | 0.0045 |

A.14 Simulation data from the bioreactor model for stoichiometric conversion sensitivity analysis

| Fractional conversion of main reactant | | Output from the Bioreactor | | | | |
|---|---|---|---|---|---|---|
| CO (Rxn 1) | $H_2$ (Rxn 2) | CO (mol frac) | $CO_2$ (mol frac) | $H_2$ (mol frac) | $N_2$ (mol frac) | Ethanol (wt. %) |
| 0.95 | 0.95 | 0.009 | 0.275 | 0.003 | 0.712 | 3.431 |
| 0.9 | 0.9 | 0.019 | 0.268 | 0.006 | 0.707 | 3.253 |
| 0.8 | 0.8 | 0.037 | 0.254 | 0.012 | 0.698 | 2.895 |
| 0.7 | 0.7 | 0.054 | 0.240 | 0.017 | 0.688 | 2.537 |
| 0.6 | 0.6 | 0.071 | 0.227 | 0.023 | 0.679 | 2.177 |
| 0.5 | 0.5 | 0.088 | 0.214 | 0.028 | 0.670 | 1.817 |
| 0.4 | 0.4 | 0.104 | 0.202 | 0.033 | 0.661 | 1.456 |
| 0.3 | 0.3 | 0.120 | 0.189 | 0.038 | 0.653 | 1.093 |
| 0.2 | 0.2 | 0.136 | 0.177 | 0.043 | 0.644 | 0.730 |
| 0.1 | 0.1 | 0.151 | 0.166 | 0.047 | 0.636 | 0.365 |
| 0.09 | 0.09 | 0.152 | 0.165 | 0.048 | 0.635 | 0.329 |

A.15 Simulation data from the bioreactor model for stoichiometric conversion (E1) sensitivity analysis

| Fractional conversion of main reactant | | Output from the Bioreactor | | | | |
|---|---|---|---|---|---|---|
| CO (Rxn 1) | $H_2$ (Rxn 2) | CO (mol frac) | $CO_2$ (mol frac) | $H_2$ (mol frac) | $N_2$ (mol frac) | Ethanol (wt. %) |
| 0.9 | 0.1 | 0.017 | 0.266 | 0.048 | 0.669 | 2.546 |
| 0.8 | 0.1 | 0.034 | 0.253 | 0.048 | 0.665 | 2.273 |
| 0.7 | 0.1 | 0.051 | 0.240 | 0.048 | 0.661 | 1.999 |
| 0.6 | 0.1 | 0.068 | 0.227 | 0.047 | 0.657 | 1.726 |
| 0.5 | 0.1 | 0.085 | 0.215 | 0.047 | 0.653 | 1.452 |
| 0.4 | 0.1 | 0.101 | 0.202 | 0.047 | 0.650 | 1.179 |
| 0.3 | 0.1 | 0.117 | 0.190 | 0.047 | 0.646 | 0.905 |
| 0.2 | 0.1 | 0.133 | 0.178 | 0.046 | 0.643 | 0.632 |
| 0.1 | 0.1 | 0.149 | 0.166 | 0.046 | 0.639 | 0.358 |

A.16 Simulation data from the bioreactor model for stoichiometric conversion (E2) sensitivity analysis

| Fractional conversion of main reactant | | Output from the Bioreactor | | | | |
|---|---|---|---|---|---|---|
| CO (Rxn 1) | $H_2$ (Rxn 2) | CO (mol frac) | $CO_2$ (mol frac) | $H_2$ (mol frac) | $N_2$ (mol frac) | Ethanol (wt. %) |
| 0.1 | 0.9 | 0.157 | 0.161 | 0.005 | 0.676 | 1.034 |
| 0.1 | 0.8 | 0.156 | 0.162 | 0.011 | 0.671 | 0.950 |
| 0.1 | 0.7 | 0.155 | 0.162 | 0.016 | 0.666 | 0.865 |
| 0.1 | 0.6 | 0.154 | 0.163 | 0.021 | 0.662 | 0.781 |
| 0.1 | 0.5 | 0.153 | 0.164 | 0.026 | 0.657 | 0.696 |
| 0.1 | 0.4 | 0.152 | 0.164 | 0.031 | 0.652 | 0.612 |
| 0.1 | 0.3 | 0.151 | 0.165 | 0.036 | 0.648 | 0.527 |
| 0.1 | 0.2 | 0.150 | 0.165 | 0.041 | 0.643 | 0.443 |
| 0.1 | 0.1 | 0.149 | 0.166 | 0.046 | 0.639 | 0.358 |

# APPENDIX B

# ASPEN PLUS™ INPUT AND OUTPUT FILES

The simulation output data in Aspen Plus$^{TM}$ is displayed in an output table form on the process flowsheet. The input and the output from the Base Case simulation for the Gibbs gasifier model is shown in Appendix B.1 and the input and the output from the Base Case simulation for the stoichiometric bioreactor model is shown in Appendix B.2.

# B1. Simulation output data table from the Gibbs Gasifier model

| Gsfr-RGIBBS-12 | | | | |
|---|---|---|---|---|
| Stream ID | | AIR | BIOMASS | PRODUCT |
| From | | | | RGIBBS |
| To | | RGIBBS | RGIBBS | |
| Phase | | VAPOR | MIXED | VAPOR |
| Substream: MIXED | | | | |
| Mole Flow | kmol/hr | | | |
| C | | 0.0 | .5977854 | 4.0015E-28 |
| H2 | | 0.0 | .4514158 | .3455666 |
| O2 | | .2193832 | .2428216 | 6.0119E-19 |
| N2 | | .8249600 | 4.99759E-3 | .8299576 |
| H2O | | 0.0 | .0910338 | .1967083 |
| CO | | 0.0 | 0.0 | .3766608 |
| CO2 | | 0.0 | 0.0 | .2210372 |
| CH4 | | 0.0 | 0.0 | 8.73577E-5 |
| NO | | 0.0 | 0.0 | 1.4735E-13 |
| NO2 | | 0.0 | 0.0 | 5.2839E-24 |
| C2H2 | | 0.0 | 0.0 | 4.5733E-12 |
| C2H4 | | 0.0 | 0.0 | 6.9141E-11 |
| C2H6 | | 0.0 | 0.0 | 8.1647E-12 |
| Mole Frac | | | | |
| C | | 0.0 | .4306643 | 2.0312E-28 |
| H2 | | 0.0 | .3252148 | .1754129 |
| O2 | | .2100681 | .1749367 | 3.0517E-19 |
| N2 | | .7899319 | 3.60043E-3 | .4212945 |
| H2O | | 0.0 | .0655837 | .0998510 |
| CO | | 0.0 | 0.0 | .1911966 |
| CO2 | | 0.0 | 0.0 | .1122006 |
| CH4 | | 0.0 | 0.0 | 4.43436E-5 |
| NO | | 0.0 | 0.0 | 7.4798E-14 |
| NO2 | | 0.0 | 0.0 | 2.6822E-24 |
| C2H2 | | 0.0 | 0.0 | 2.3214E-12 |
| C2H4 | | 0.0 | 0.0 | 3.5096E-11 |
| C2H6 | | 0.0 | 0.0 | 4.1445E-12 |
| Mass Flow | kg/hr | | | |
| C | | 0.0 | 7.180000 | 4.8061E-27 |
| H2 | | 0.0 | .9100000 | .6966208 |
| O2 | | 7.020000 | 7.770000 | 1.9237E-17 |
| N2 | | 23.11000 | .1400000 | 23.25000 |
| H2O | | 0.0 | 1.640000 | 3.543755 |
| CO | | 0.0 | 0.0 | 10.55042 |
| CO2 | | 0.0 | 0.0 | 9.727804 |
| CH4 | | 0.0 | 0.0 | 1.40146E-3 |
| NO | | 0.0 | 0.0 | 4.4215E-12 |
| NO2 | | 0.0 | 0.0 | 2.4309E-22 |
| C2H2 | | 0.0 | 0.0 | 1.1908E-10 |
| C2H4 | | 0.0 | 0.0 | 1.93965E-9 |
| C2H6 | | 0.0 | 0.0 | 2.4551E-10 |
| Mass Frac | | | | |
| C | | 0.0 | .4070295 | 1.0061E-28 |
| H2 | | 0.0 | .0515873 | .0145828 |
| O2 | | .2329904 | .4404762 | 4.0271E-19 |
| N2 | | .7670096 | 7.93651E-3 | .4867071 |
| H2O | | 0.0 | .0929705 | .0741836 |
| CO | | 0.0 | 0.0 | .2208587 |
| CO2 | | 0.0 | 0.0 | .2036383 |
| CH4 | | 0.0 | 0.0 | 2.93376E-5 |
| NO | | 0.0 | 0.0 | 9.2559E-14 |
| NO2 | | 0.0 | 0.0 | 5.0887E-24 |
| C2H2 | | 0.0 | 0.0 | 2.4927E-12 |
| C2H4 | | 0.0 | 0.0 | 4.0604E-11 |
| C2H6 | | 0.0 | 0.0 | 5.1394E-12 |
| Total Flow | kmol/hr | 1.044343 | 1.388054 | 1.970018 |
| Total Flow | kg/hr | 30.13000 | 17.64000 | 47.77000 |
| Total Flow | l/min | 354.8593 | 249.7050 | 2931.692 |
| Temperature | K | 298.1500 | 298.1500 | 1088.150 |
| Pressure | atm | 1.200000 | 1.200000 | 1.000000 |
| Vapor Frac | | 1.000000 | .5051573 | 1.000000 |
| Liquid Frac | | 0.0 | .4948427 | 0.0 |
| Solid Frac | | 0.0 | 0.0 | 0.0 |
| Enthalpy | cal/mol | 7.0286E-13 | 60663.34 | -15074.27 |
| Enthalpy | cal/gm | 2.4362E-14 | 4773.469 | -621.6574 |
| Enthalpy | cal/sec | 2.0390E-13 | 23390.00 | -8249.049 |
| Entropy | cal/mol-K | .6587547 | 113.9860 | 16.11036 |
| Entropy | cal/gm-K | .0228332 | 8.969319 | .6643853 |
| Density | mol/cc | 4.90496E-5 | 9.26463E-5 | 1.11996E-5 |
| Density | gm/cc | 1.41512E-3 | 1.17739E-3 | 2.71572E-4 |
| Average MW | | 28.85067 | 12.70844 | 24.24851 |
| Liq Vol 60F | l/min | .9322121 | .7258234 | 1.642086 |

## B.2 Simulation output data table from the stoichiometric bioreactor model

| BR-Rstoic-7 | | | | | | |
|---|---|---|---|---|---|---|
| Stream ID | | GASES | MEDIA | PRODGAS | PRODMED | PRODUCT |
| From | | | | SEP2 | SEP2 | RSTOIC |
| To | | RSTOIC | RSTOIC | | | SEP2 |
| Phase | | VAPOR | LIQUID | VAPOR | LIQUID | MIXED |
| Substream: MIXED | | | | | | |
| Mole Flow | kmol/sec | | | | | |
| ETHANOL | | 0.0 | 0.0 | 0.0 | 4.7371E-10 | 4.7371E-10 |
| WATER | | 0.0 | 3.30891E-7 | 0.0 | 3.30151E-7 | 3.30151E-7 |
| H2 | | 6.81463E-9 | 0.0 | 6.13317E-9 | 0.0 | 6.13317E-9 |
| N2 | | 8.21680E-8 | 0.0 | 8.21680E-8 | 0.0 | 8.21680E-8 |
| CO | | 2.16080E-8 | 0.0 | 1.94472E-8 | 0.0 | 1.94472E-8 |
| CO2 | | 2.02085E-8 | 0.0 | 2.14218E-8 | 0.0 | 2.14218E-8 |
| Mole Frac | | | | | | |
| ETHANOL | | 0.0 | 0.0 | 0.0 | 1.43277E-3 | 1.03027E-3 |
| WATER | | 0.0 | 1.000000 | 0.0 | .9985672 | .7180397 |
| H2 | | .0521000 | 0.0 | .0474813 | 0.0 | .0133389 |
| N2 | | .6282000 | 0.0 | .6361218 | 0.0 | .1787057 |
| CO | | .1652000 | 0.0 | .1505549 | 0.0 | .0422953 |
| CO2 | | .1545000 | 0.0 | .1658420 | 0.0 | .0465899 |
| Mass Flow | kg/sec | | | | | |
| ETHANOL | | 0.0 | 0.0 | 0.0 | 2.18234E-8 | 2.18234E-8 |
| WATER | | 0.0 | 5.96109E-6 | 0.0 | 5.94776E-6 | 5.94776E-6 |
| H2 | | 1.37375E-8 | 0.0 | 1.23637E-8 | 0.0 | 1.23637E-8 |
| N2 | | 2.30181E-6 | 0.0 | 2.30181E-6 | 0.0 | 2.30181E-6 |
| CO | | 6.05249E-7 | 0.0 | 5.44724E-7 | 0.0 | 5.44724E-7 |
| CO2 | | 8.89370E-7 | 0.0 | 9.42770E-7 | 0.0 | 9.42770E-7 |
| Mass Frac | | | | | | |
| ETHANOL | | 0.0 | 0.0 | 0.0 | 3.65576E-3 | 2.23343E-3 |
| WATER | | 0.0 | 1.000000 | 0.0 | .9963442 | .6087000 |
| H2 | | 3.60548E-3 | 0.0 | 3.25219E-3 | 0.0 | 1.26532E-3 |
| N2 | | .6041233 | 0.0 | .6054737 | 0.0 | .2355696 |
| CO | | .1588510 | 0.0 | .1432855 | 0.0 | .0557475 |
| CO2 | | .2334202 | 0.0 | .2479886 | 0.0 | .0964840 |
| Total Flow | kmol/sec | 1.30799E-7 | 3.30891E-7 | 1.29170E-7 | 3.30625E-7 | 4.59795E-7 |
| Total Flow | kg/sec | 3.81017E-6 | 5.96109E-6 | 3.80167E-6 | 5.96959E-6 | 9.77125E-6 |
| Total Flow | cum/sec | 2.66667E-6 | 6.00000E-9 | 3.28734E-6 | 6.08510E-9 | 3.49050E-6 |
| Temperature | K | 298.1500 | 298.1500 | 310.1500 | 310.1500 | 310.1500 |
| Pressure | N/sqm | 1.21590E+5 | 1.21590E+5 | 1.01325E+5 | 1.01325E+5 | 1.01325E+5 |
| Vapor Frac | | 1.000000 | 0.0 | 1.000000 | 0.0 | .2977827 |
| Liquid Frac | | 0.0 | 1.000000 | 0.0 | 1.000000 | .7022173 |
| Solid Frac | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Enthalpy | J/kmol | -7.9057E+7 | -2.8568E+8 | -8.1535E+7 | -2.8483E+8 | -2.2691E+8 |
| Enthalpy | J/kg | -2.7139E+6 | -1.5858E+7 | -2.7703E+6 | -1.5775E+7 | -1.0677E+7 |
| Enthalpy | Watt | -10.34056 | -94.52996 | -10.53191 | -94.17258 | -104.3322 |
| Entropy | J/kmol-K | 22259.69 | -1.6269E+5 | 23567.62 | -1.6014E+5 | -1.0576E+5 |
| Entropy | J/kg-K | 764.1518 | -9030.528 | 800.7625 | -8869.457 | -4976.398 |
| Density | kmol/cum | .0490496 | 55.14843 | .0392932 | 54.33350 | .1317276 |
| Density | kg/cum | 1.428812 | 993.5145 | 1.156457 | 981.0171 | 2.799387 |
| Average MW | | 29.12993 | 18.01528 | 29.43148 | 18.05547 | 21.25134 |
| Liq Vol 60F | cum/sec | 7.00531E-9 | 5.97258E-9 | 6.91807E-9 | 5.98678E-9 | 1.29049E-8 |

# VITA

Sirigudi Rahul Rao

Candidate for the Degree of

Master of Science

Thesis: BIOMASS TO ETHANOL: PROCESS SIMULATION, VALIDATION AND SENSITIVITY ANALYSIS OF A GASIFIER AND A BIOREACTOR

Major Field: Chemical Engineering

Biographical Information:

Personal Data: Born in Mumbai, India, on the 24th of September, 1979, the son of Sirigudi Ramakrishna Rao and Sirigudi Vijayalakshmi Rao.

Education: Graduated from Holy Cross Higher Secondary School, Byron Bazar, Raipur, India in May 1997; received Bachelor of Engineering degree in Chemical Engineering from National Institute of Technology, Karnataka, India, in June 2002. Completed the requirements for the Master of Science degree in Chemical Engineering at Oklahoma State University, Stillwater, Oklahoma, in December, 2005.

Experience: Summer Internship at Bhilai Steel Plant, India, 2000; employed as a Graduate Engineer Trainee at Bharat Aluminum Company, Korba, India, June 2002 to May 2003; employed by Oklahoma State University, Department of Chemical Engineering as a Research Assistant, August 2003 to August 2005; Teaching Assistant, August 2003 to December 2003, August 2004 to December 2004 and January 2005 to May 2005.

Name: Sirigudi Rahul Rao Date of Degree: December, 2005

Institution: Oklahoma State University Location: Stillwater, Oklahoma

Title of Study: BIOMASS TO ETHANOL: PROCESS SIMULATION, VALIDATION AND SENSITIVITY ANALYSIS OF A GASIFIER AND A BIOREACTOR

Pages in Study: 128 Candidate for the Degree of Master of Science

Major Field: Chemical Engineering

Scope and Method of Study: The Gasification-Fermentation process for the production of fuel-grade ethanol from agricultural biomass is being investigated at Oklahoma State University, Stillwater. Process simulation software, Aspen Plus™ was used to study the gasifier and the bioreactor set-ups in this research. Process models were developed and validated with experimental data. Sensitivity studies were conducted for the gasifier by manipulating important process parameters like biomass feed rate, moisture content, operating temperature and equivalence ratio. Sensitivity of the bioreactor model was studied by manipulating the input gas composition of carbon monoxide, carbon dioxide and hydrogen gases, media flow rate, and stoichiometric conversion of substrates.

Findings and Conclusions: The results from this work indicate that, the amount of carbon monoxide and hydrogen gases produced in the gasifier and the amount of ethanol produced in the bioreactor can theoretically be improved further.

ADVISER'S APPROVAL: Arland H. Johannes