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# Modeling Of USS Gasification To Evaluate New Gasifier Design In Aspen Plus

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# MODELING OF USS GASIFICATION TO EVALUATE NEW GASIFIER DESIGN IN ASPEN PLUS

by
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Bachelor of Science, Bangladesh University of Engineering and Technology, 2004

A Thesis

Submitted to the Graduate Faculty

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This thesis, submitted by Taskin Binte Karim in partial fulfillment of the requirements for the degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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This thesis meets the standards for appearance, conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

Joseph N. Benoit
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Date 19th July, 2007.

## TABLE OF CONTENTS

CHAPTER

# LIST OF FIGURES

# LIST OF TABLES

Table Page

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# ABSTRACT

Evaluation of ultra-superheated-steam (USS) gasification efficiency of coals to produce hydrogen enriched syngas is the research motive of this joint project between the University of North Dakota and Ohio University. A new USS bubbling fluidized bed gasifier was built in Ohio and several tasks were assigned to assess the gasifier's performance and the feasibility of producing tar-free and hydrogen-rich producer gas.

This thesis presents a thermo-equilibrium model of USS gasification. The model calculates the syngas composition and heating value for the base case fuel Clarion 4A coal using input data from experiments completed at Ohio. The RGIBBS reactor module in ASPEN PLUS, which performs calculation using the Gibbs free energy minimization concept, is used to simulate the gasification process. The model compositions were then compared with the experimental syngas composition. The simulation was performed with four other coals and the output for all coals is compared on both wet and dry basis. A sensitivity analysis estimated the effect of temperature and steam flow rate variation on syngas composition and heating value on a wet and dry basis.

The model estimates the syngas composition of mainly 39% $H_2$, 19% CO, 13% $CO_2$ and 28% $H_2O$ and a heating value of 4300 Btu/lb (254 Btu/scf). The composition comparison among all coals provided a favorable syngas composition trend for the low-moisture Clarion 4A and Pittsburgh #8 coals, but gave almost the same $H_2$ composition when gas compositions were compared on a dry basis. This implies that drying of high moisture coal before gasification would improve gas composition. Temperature variation for all coals gives the same trend for gas composition and heating value. The data on temperature variation suggests that gasification at 1320°F gives the maximum $H_2$ composition in the syngas and a gasification temperature of 1410°F produces the highest heating value syngas for this gasifier. The steam flow rate was varied and the effect of $H_2O/C$ on syngas composition and heating value was evaluated and compared with experimental data. $H_2$ concentrations decreased with an increasing $H_2O/C$ ratio on a wet basis due to dilution of the syngas with $H_2O$, but increased by 6 mole% for simulation and 4 mole% for experiment over the $H_2O/C$ range of 0.85 to 3.5 compared on a dry basis.

Comparisons of model results to experimental data indicate a higher CO and lower $H_2$ composition for the experimental data as compared to the model. This indicates the water-gas shift reaction may not be in equilibrium. Since this is a fast reaction it indicates there may be transport/diffusion limitations in the experimental gasifier.

This work tested two hypotheses. The first hypothesis, that a zero-order thermo-equilibrium model accurately predicts the performance of experimental set-up of USS gasifier at Ohio with syngas composition and heating value calculation was not valid. A three-dimensional model that includes both kinetics and transport phenomena is required. The model sensitivity analysis determined the maximum gasification temperature and $H_2O$ to carbon ratio for maximum hydrogen concentration in syngas. This proves the hypothesis that the model provides useful information for improvement of the experiment.

# CHAPTER 1

# INTRODUCTION

Development of methods for gasification of coal into a hydrogen enriched syngas for distributed combined-heat-and-power and hydrogen production is a contemporary research issue. The price volatility of natural gas enhances the interest to study the development of distributed hydrogen infrastructure. Life-cycle cost drivers are now changing the negative impression for coal gasification, making it a research priority. An ultra-superheated-steam (USS) gasifier at Ohio University was built to evaluate its efficiency on hydrogen production.

The USS reforming process produces an extremely hot steam flame (4000°F) and when it is injected into a coal fluidized bed it rapidly converts the coal into syngas enriched with hydrogen. The high temperature steam is able to cleave the high molecular weight tar components and convert it to gas resulting in low-tar syngas which is important for uses in a turbine. The USS gasification process is also expected to produce a higher heating value syngas as compared to current gasification processes.

Ohio University proposed several tasks to the Department of Energy (DOE) -State Technologies Advancement Collaborative (STAC) program designed to develop a comprehensive understanding of the USS process on Ohio Coals. Experimental work was done at Ohio University and modeling of USS gasification process to develop a complete understanding of the thermodynamics and kinetics of the process was performed at the

University of North Dakota. The author is involved with the thermodynamic equilibrium modeling.

Coal gasification produces a syngas composed of mainly CO, $H_2$, $CO_2$, $H_2O$, $CH_4$ and small amounts of other hydrocarbons. The most desired components are CO and $H_2$. Higher temperature increases the CO generation and produces less $CO_2$ which is an important factor from a carbon management viewpoint. Moreover, the syngas enriched in CO and $H_2$ has a higher heating value which is one of the considerations in case of combustion turbines.

This hypothesis of my work is the model will accurately predict the performance of the experimental setup of the USS gasifier operating at Ohio and the model will provide information to allow evaluation and improvement of experiment. This hypothesis was evaluated using thermodynamic equilibrium modeling with ASPEN PLUS as the modeling platform. The model generated gives the output of syngas composition and the heating value. For this study the gasification temperature and steam flow rate was varied to study the effect of these parameters.

## 1.1 The Report Overview

Chapter two presents the background of gasification and a brief literature review on modeling. The gasification background includes the definition of gasification, gasifying agent, heating method and gasifier types. It also contains a short description of USS gasification and ASPEN PLUS features used in modeling. A review of relevant literature on equilibrium and kinetic modeling is presented. The third chapter gives a brief description of the experimental set-up and procedure used by Ohio University during gasification. Chapter four describes the model development with mass and energy balance in detail. Chapter 5 presents the results from the model, its application for several coals and sensitivity analysis. Conclusions and recommendation for future works are detailed in Chapter 6.

# CHAPTER 2

# BACKGROUND

This chapter provides background information related to gasification in general, ultra superheated steam gasification and modeling. It also summarizes previous gasification and modeling work.

## 2.1 Coal Gasification

Gasification is the conversion of solid fuel containing carbon into a clean gaseous fuel, typically called syngas. Usually coal, coke, biomass from different sources and waste material like municipal solid waste are used as feed or fuel for gasification along with one or more gasifying agents. Oxygen, air, steam or mixtures of these are the most common gasifying agents but some gasifiers use hydrogen, carbon dioxide or mixture of these gases [1]. Sometimes a catalyst is used to enhance the process and to get the desired composition. Basically, gasification can be described as the reaction of fuel with an oxidant at a substoichiometric fuel-to-oxygen ratio and elevated temperature designed to produce syngas which is composed of mainly CO, $H_2$, $CO_2$, $CH_4$ and $H_2O$ [2]. Coal is the feedstock and ultra superheated steam is the gasifying agent in the subjected research of ultra superheated steam (USS) gasification addressed here.

Gasification takes place over a temperature range from 1200°F with catalyst to about 2700°F for entrained flow gasifiers, with differences based on gasifier type, fuel and gasification agent. The syngas, mainly composed of CO and $H_2$, can be used to produce electricity, to provide electric power and heat in a combined heat and power (CHP) system, on a fuel cell and or other uses such as to produce synthetic natural gas, liquid fuel like methanol and gaseous fuel like $H_2$ [2, 3].

### *2.1.1 Reactions*

The gasification process was first developed in the early 1800s. In 1850 coal gasification was used to produce 'town gas' for light and heat in London [40]. However the development of natural gas supply and transmission lines hindered for that gasification technology use. During World War II, due to an acute shortage in petroleum supplies German scientists revived the gasification process to produce fuel [41]. In the early 1950s, gasification techniques were used in refineries [42]. The rise in natural gas prices in 1970 was another stage in gasification evolution. The U.S. government provided financial support for several proof-of-concept gasification projects. Shell, Texaco, and Dow Chemical started research projects to develop gasification with solid fuel. Eastman Chemical Company built the first commercial scale gasification plant in 1984 [42]. Dakota Gasification Company started their Synfuels plant operation in 1984 [43]. In the early 1990s, government agencies in the United States and Europe initiated programs to provide financial support to build commercial integrated combined cycle gasification (IGCC) projects. Currently, commercial developers are building IGCC power plants without government subsidies [40].

There are numerous reactions occurring during the gasification process. Not all of the reactions are reported and the same reactions do not occur for each fuel and are dependent on the gasification agent employed. The reactions typically taking place within the gasifier during the various stages of gasification are listed in Table 1 [2, 3].

Table1. List of Typical Gasification Reactions [2, 3]

| Reaction name | Reaction | $\Delta H^{\circ}_{f}$, MJ/Kmol | Reaction Type | Reaction No. |
|---|---|---|---|---|
| Combustion | $C + \frac{1}{2}O_2 \rightarrow CO$ | -111 | exothermic | 1 |
| | $C + O_2 \rightarrow CO_2$ | -394 | exothermic | 2 |
| | $CO + \frac{1}{2}O_2 \rightarrow CO_2$ | -283 | exothermic | 3 |
| Water-Gas Shift Reaction | $CO + H_2O \rightarrow CO_2 + H_2$ | -41 | exothermic | 4 |
| Steam Gasification | $C + H_2O \rightarrow CO + H_2$ | +131 | endothermic | 5 |
| Secondary Reactions | $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ | -242 | exothermic | 6 |
| | $C + CO_2 \rightarrow 2CO$ | +172 | endothermic | 7 |
| | $C + 2H_2O \rightarrow CO_2 + 2H_2$ | 90 | endothermic | 8 |
| Methanation Reactions | $C + 2H_2 \rightarrow CH_4$ | -75 | exothermic | 9 |
| | $CO + 3H_2 \rightarrow CH_4 + H_2O$ | -75 | exothermic | 10 |
| | $2CO + 2H_2 \rightarrow 2CH_4 + 2CO_2$ | -247 | exothermic | 11 |
| Methane Decomposition | $CH_4 + H_2O \rightarrow CO + 3H_2$ | +206 | endothermic | 12 |
| | $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ | -803 | exothermic | 13 |
| | $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ | +247 | endothermic | 14 |
| | $2CH_4 + O_2 \rightarrow 2CO + 4H_2$ | -72 | exothermic | 15 |

### *2.1.2 Stages in Gasification*

Carbonaceous materials mainly go through two processes during gasification: pyrolysis and char gasification. If the fuel is combusted to provide heat for gasification there is one more stage, combustion.

Pyrolysis is the decomposition of organic matter by heat. When the coal is heated, volatile materials such as CO, $CO_2$, $CH_4$ plus other hydrocarbon gases from tar and oils are released and the char, fixed carbon and mineral matter is left behind. 'Devolatalization' and 'carbonization' are used as alternative names of coal pyrolysis. The amount and product composition of pyrolysis depend on coal composition, temperature, heating rate, pressure and particle size distribution [4].

Pyrolysis is represented by the general reaction:

Coal $\rightarrow$ Char + Tar, Light Oil, $H_2O$, $H_2$, CO, $CO_2$, and HC gases ................ (16)

Tar, Light Oil$\rightarrow$ $CH_4$ and other HC gases + CO+ $H_2$ + $CO_2$ ........................ (17)

After pyrolysis, volatile matter and some of the char reacts with oxidant to produce CO and $CO_2$. In direct heating, the heat from the partial combustion of fuel provides heat for the endothermic gasification reactions (reactions 1-3). This step is considered as a combustion stage in the gasification process and is exothermic.

In the gasification stage char goes through several reactions with the oxidant/gasifying agent and produces the syngas (reactions 4-15). The syngas is mainly composed of CO, $H_2$, $CO_2$, $H_2O$ and some hydrocarbons. In this research, the heat for gasification was provided externally through ultra superheated steam (USS), eliminating the need for combustion reactions of fuel. Details about USS are discussed latter in this chapter. The reactions mainly considered during USS gasification are:

Steam gasification: $C + H_2O \rightarrow CO + H_2O$ .................................................. (5)

Water-gas shift: $CO + H_2O \rightarrow CO_2 + H_2$ ......................................................... (4)

Boudouard: $C + CO_2 \rightarrow 2\,CO$ ...................................................................... (7)

Methane Decomposition: $CH_4 + H_2O \rightarrow CO + 3H_2$ ...................................... (12)

### *2.1.3 Method of Supplying Heat*

To drive the endothermic reactions within the gasifier, energy in the form of heat must be supplied either directly (internal) or indirectly (external). The gasifier design also varies with heating arrangements. In direct heating, the exothermic reaction between the gasifying media, typically air or oxygen, and the fuel supplies the heat for both pyrolysis and gasification.

The problem with the use of air is that nitrogen in the syngas will dilute the syngas and results in a lower calorific value syngas, typically less than 10 MJ/m$^3$ [4]. Air blown gasifiers usually produce a syngas gas with a calorific value ranging from 5 to 7 MJ/m$^3$ [5]. The calorific value can be increased by using oxygen instead of air. Direct heating also consumes a portion of the carbon.

In indirect heating, the energy is supplied from an external source, usually an inert solid or fluid carrier that is heated in a separate reactor or furnace. Steam, steam/air or steam/oxygen is generally used in indirect heating. The heat also may be supplied by heat transfer through the hot wall of furnace, from an electrical or a nuclear energy source [4]. In steam reforming, the heat is sometimes provided with superheated steam. The product gas from indirect heated gasification is expected to have calorific values between 10 and 15 MJ/m$^3$ [4].

In the current thesis, the heat was assumed to be provided through production of ultra-superheated steam, consisting of $H_2O$ and $CO_2$, in a separate burner. The temperature of USS steam achieved from model calculations is 3718°F (2048°C). The details of USS generation are described latter in this chapter.

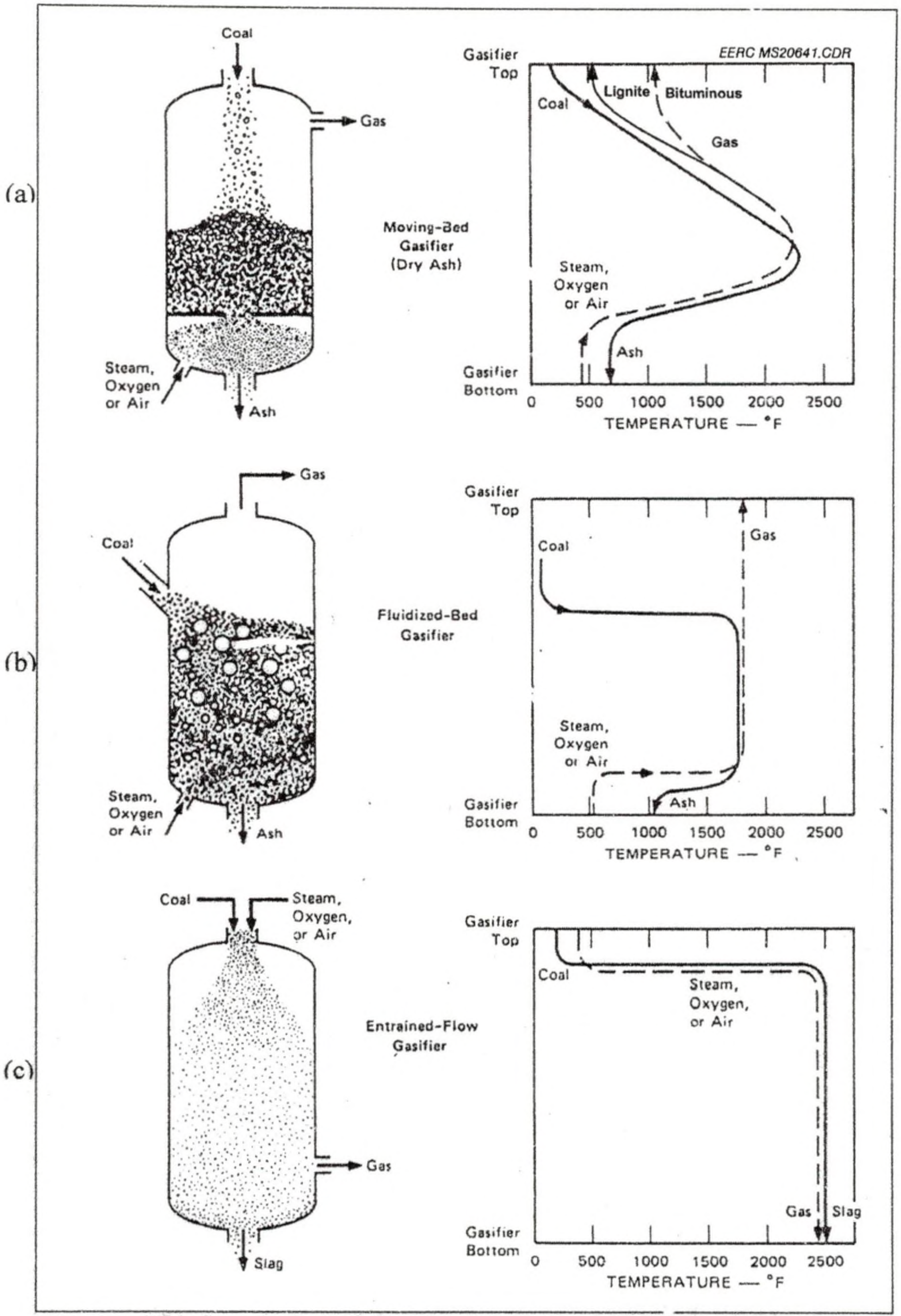
### *2.1.4 Gasifier*

The fuel type, the gasifying media and method of transport of the fuel and media through the gasifier, fuel size and condition, temperature and pressure play a crucial role in choosing the gasifier. Basically, gasifiers are categorized as fixed-bed, entrained-flow and fluidized-bed gasifiers. Those are further classified based on feed conditions, either dry or slurry, and discharged ash, either dry or agglomerated.

#### *2.1.4.1 Fixed-Bed Gasifiers*

The gasifier consists of a fixed bed of carbonaceous fuel through which the gasification agent flows in the counter-current or co-current manner. Figure 1(a) shows a gasifier of this type. The Lurgi dry-ash fixed bed gasifiers were first demonstrated in Germany in 1936. Lurgi gasifiers are currently in operation in major installation at SASOL in South Africa and the Dakota Gasification Great Plains Plant in North Dakota [3].The other prominent suppliers include Riley-Morgan, Kellog and Woodall-Duckham [1].

Updraft gasification is the oldest and simplest gasification process. The fuel particles, ranging from ¼ to 2 ¼ inches in diameter, are introduced into the reactor from the top and move downward through a drying zone, pyrolysis zone, reduction zone and hearth zone. Oxidant is introduced at the bottom of the reactor [6]. The counter-current contact of fuel and oxidant results in high carbon conversion if fuel residence time is long enough for large particles to be consumed. High carbon conversion and low gas exit temperature are the advantages of this type gasifier. Product gas leaves the reactor around 1100°F and this temperature is not high enough for cracking of all tars and oils. A high tar yield is a critical drawback of the gasifier. Both fuel input and syngas output occur at



*This figure is obtained from Sondeal's Report, EERC, UND (2006).

Figure 1.The Main Three Gasifiers and Their Temperature Variations with Height: (a) Fixed –Bed (b) Fluidized-Bed (c) Entrained-Flow) [3].

the top of the gasifier; fine particles will be entrained with syngas and will not be converted. Cyclones are typically used to capture the fine particles.

There are a number of co-current gasifiers, named as downdraft gasifiers, in which both the fuel and the gasifying agents move in the same direction. The solids move downward through the same zones as updraft gasifiers. This gasifier yields low tar gas. The feature of non-uniform radial temperature profiles and local slagging problems makes the fixed bed gasifier unsuitable for large scale uses [1]. That's why the fixed bed gasifier is considered a low throughput type design.

#### *2.1.4.2 Entrained- Flow Gasifier*

In the entrained-flow gasifier, the fine feedstock, either a dry-pulverized solid or an atomized liquid fuel or fuel slurry, flows co-currently with oxidant and/or steam from the top of the vessel and reaction occurs. The gasification takes place in a dense cloud of very fine particles and converts the feedstock mainly to $H_2$, CO, and $CO_2$ with no liquid hydrocarbons in the syngas. The syngas leaves from the bottom of the reactor at high temperature (2300 °F or greater) [7]. The high temperature system produces low amounts of methane and no tars. This type of gasifier is a high pressure, high temperature, and high throughput plug-flow reactor.

The entrained flow reactor usually uses oxygen as the oxidant and operates at temperatures above ash slagging conditions to ensure high carbon conversion. Ash slag removal mechanisms exist in the gasifier. The high temperature and high pressure allow a low residence time design compared to other types of the gasifiers. The gasifier uses more oxygen because of high temperature gasification.

Entrained-flow gasification can gasify all types of coal irrespective of rank or caking tendency by taking advantage of the gasifier's high temperature. The thermal efficiency of the entrained flow gasifier is low because of the cooling requirement of syngas. Figure 1(c) shows an example of an entrained flow gasifier.

Texaco and Destec gasifiers are typical examples of entrained flow gasifiers [7]. The GE gasifier and the Conoco Phillips E-gasifier use coal slurry as feedstock. In the Shell pressured gasifier, dry pulverized coal is fed to the burners of an upward-fired gasifier and oxygen along with steam are added to the burners to control temperature.

### *2.1.4.3 Fluidized- Bed Gasifiers*

Excellent gas-solid mixing and a uniform temperature within the bed make the fluidized bed gasifier attractive for many processes. The feed, oxidant and steam are introduced to the lower part of the reactor and back-mixing of solids results in uniform distribution of all components [7]. When the minimum fluidizing velocity is exceeded and the fuel gas flow rate reaches turbulent flow, the coal bed is fluidized. Fuel is gasified in the central zone of the reactor. Since the particle residence time is non-uniform and solid is entrained with gas, high carbon conversion is not achieved in a single fluidized bed [1]. Fuel throughput is higher than for the fixed bed gasifier but lower than that of entrained flow gasifier.

Fuel particles can be reduced in size to achieve uniform mixing and rapid conversion during gasification. Carry over of fines necessitates a cyclone to capture the entrained and unreacted particles from the syngas and return them to the gasifier. Figure 1(b) shows a fluidized bed gasifier. Most bubbling fluidizing beds are equipped with an internal or external separator like a cyclone to improve carbon conversion and to reduce tar yield in the syngas. The extension of the bubbling bed concept to high fluidization velocities is the circulating fluidized bed (CFB). The bubbling fluidized bed with cyclone separator is used for USS gasification in this work.

The ash removed from the fluidized bed may be either dry or agglomerated. The temperatures are relatively low in the dry ash gasifier making it suitable for high reactive, low-rank coal. The temperature is high in an agglomerated ash gasifier making it more suitable for high-rank coal.

The U-gas, KRW (KELLOG-RUST-Westinghouse), and high throughput Winkler (HTW) process are well renowned examples of fluidized bed gasifiers [3]. Considering the above mentioned features, the bubbling fluidized bed with cyclone separator was a good choice for the USS gasifier built in Ohio.

## 2.2 Ultra Superheated Steam Gasification

Ultra superheated steam is a high temperature steam flame containing $CO_2$ and steam. Steam reforming is another name for USS gasification. The USS gasification differs from other gasification in the sense that the oxygen is not the reactant to convert the fuel into syngas. The sensible heat in superheated steam is used to provide the external heat required for the endothermic C-$H_2O$ reaction [8]:

$$C_a H_bO_c + (a-c)*H_2O \rightarrow a*CO + (a+b/2-c)*H_2 \quad \text{................} (18)$$

In the late 1970s, The University of Illinois at Urbana Champaign performed research on coal gasification with 2060°F (1127°C) steam. In the mid 1980's, the University of Sheffield also started steam gasification research with steam of 1736°F (947°C) [8]. In both cases, a very high fraction of excess steam was required to provide the sensible heat for the endothermic gasification reactions, resulting in low process efficiency [illegible] the added moisture [illegible] am [5]. The USS process (Patents pending) which is under development by the University of Sheffield and F. Michael Lewis Inc. combines high exit temperature and high water vapor mole fraction to get benefits over conventional oxygen blown systems [5]. This would convert the high molecular weight tar and oils to low molecular weight syngas.

The basis of USS gasification is enhancing the C-$H_2O$ reaction through increasing the steam temperature to about 4000°F (2204°C). The process is a conventional burner that utilizes "synthetic air" , usually consisting of 21% $O_2$ and 79% $H_2O$, to burn fuel gas and produce a clear, colorless flame of 3389°F (1865°C) containing mainly $CO_2$ and $H_2O$ [8]. The USS is contacted with a carbonaceous material for rapid gasification. In the present research, the steam is injected into a bubbling fluidized bed where it reacts with coal to produce syngas. The resulting syngas has a high fraction of hydrogen which can be separated out for use in a fuel cell or other uses. This simple concept of increasing steam temperature helps to overcome the problem of higher cost in fabrication of a small scale gasifier.

There are some features of the USS gasification systems that make the process unique. The carbon conversion increases through the cleaving of high molecular weight tars and oils and results in a low tar yield. Avoiding tar is important for both conversion efficiency and syngas quality. The CO and $H_2$ yields are higher than $O_2$ based gasification and $H_2$ yield exceeds the amount of original hydrogen in the coal because of the hydrogen in the USS [10].

The burner based USS process offers the end user a flexible choice of reactor designs. No exothermic oxidization reaction occurs in the reactor and gasification through steam reforming resists tar formation [5]. Fushimi et al. describes the effect of steam gasification on C, $H_2$ yield and energy distribution using Yallourn and Taiheiyo coals. In pyrolysis, 40-70% of the carbon remained as char. The yield of $H_2$ was increased by high temperature steam gasification. It also increased the yield of CO at the expense of $CO_2$ implying that the syngas composition is affected by the equilibrium conversion of the water-gas shift reaction. Fushimi defines the energy distribution as the calculated ratio of higher heating value (HHV) of products to that of original coal. Figure 2 shows, pyrolysis converts 15-25% of the coal energy into gas and 50% of the energy remains in the char. Coal gasification converted 40-80% of the energy to hydrogen energy [9].

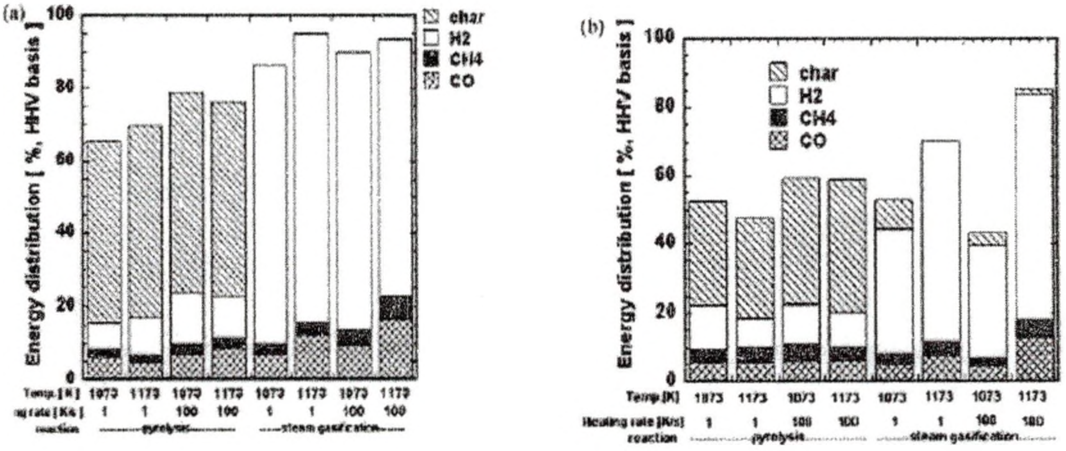


Figure 2. Energy Distribution with Temperature and Processes in Gasification [9]

## 2.3 Overview of Modeling in ASPEN PLUS Software

ASPEN PLUS is a widely used modeling software for steady state simulation, design, performance monitoring and optimization. It was originally developed by the researchers at MIT's Energy Laboratory in 1970 as a prototype for process simulation and named the Advanced System for Process Engineering (ASPEN). It was commercialized in 1980 with the establishment of the ASPEN TECH Company [11]. The simulation helps engineers predict the process behavior using the basic engineering relationships like mass and energy balances, phase and chemical equilibrium and reaction kinetics. Choosing an appropriate property method and thermodynamic data, and using real operating data as inputs help to simulate the actual plant more precisely.

In ASPEN PLUS, simulation is accomplished with three major steps: creating a flow sheet, specifying the components and operating conditions and running the simulation [12]. ASPEN PLUS uses preprogrammed unit operation blocks, user defined FORTRAN blocks, and design specifications to go through all three steps to get the simulation output.

There are several built-in unit operation blocks that represent the processes in actual plants like reactors, heat exchangers, pump, separators. There are also some blocks for the sake of simulation that may not be present in the actual process. The FORTRAN block and design specifications are used for iterative calculations and for inserting user created code. The FORTRAN block allows the user to enter some in-line statements for defined variables within the design specification value to get the specified value with feed-forward control. The design specification allows the user to set values for flow sheet variables like block and streams. The input block variable or stream value data is designed to go through manipulation to achieve the set value with the feed backward control. After all of those specifications, necessary calculations are executed to solve the process output [6, 7].

ASPEN uses a sequential-modular approach for flow-sheet convergence. Mass and energy balances are executed sequentially as in the process flow. When a recycle stream is encountered in the process, ASPEN assumes an initial guess value for the stream. Then it solves the variables iteratively until it converges to get the final value. A stream of this type is called a tear stream in ASPEN [6, 7].

ASPEN has some attractive features as a simulation tool. It has a vast built-in property databank containing thermodynamic and physical parameters. The databank contains parameters for more than 8500 components including organic, inorganic, aqueous and salt species and more than 37,000 sets of binary interaction parameters for 4000 binary mixtures. ASPEN uses convergence analysis to analyze the flow-sheet. It selects a convergence method and then solves sequentially the blocks in the flow-sheet to calculate the tear stream.

ASPEN has a sensitivity analysis option that allows users to generate tables and plots to show the effect of operating parameter variation on output. The case study feature in ASPEN provides the advantage of allowing multiple simulations run with different inputs for comparison and analysis purposes.

## 2.4 Modeling

Mathematical modeling through computer simulation is based on fundamental equations of mass, momentum and energy and the established empirical correlations on those parameters. According to Souza –Santos, the significant and important properties of mathematical modeling are as follows [13]:

- Modeling requires less financial resources than experiments and can be extended to predict the process behavior far beyond the experimental range.
- Modeling can be applied to investigate conditions of inaccessible in experiment or real system where measurements are uncertain.

- Modeling helps to get a better understanding of the experimental data and results.
- Modeling can be used to predict the optimized experimental condition and to avoid the experiments in the range of unexpected situations.
- Modeling can reduce the need of immediate pilot plant installation through its scale-up feature.
- The model can be updated to include an extended range of application, reliability without spending much time in experiments.
- Improvement of models is possible with more reliable experimental data.

Mathematical simulations based on thermodynamics, mass, energy and conservation laws and including constitutive equations are called phenomenological models. If the model considers space dimension as a variable then it can be one, two or three dimensional; otherwise, it is zero dimensional. The time consideration leads to a dynamic model and with exclusion of time as variable the model becomes steady state [13]. The model developed in this thesis is zero-dimensional steady state.

The typical gasification model has two parts, equilibrium and kinetic. The kinetic model handles the reaction rates, mechanism and the concentration of the components in the system at any point and time. It represents the phenomena occurring inside the process and includes the change with time and dimension, axial or radial or both. On the other hand, an equilibrium model does not take dimension and time as variables. It predicts the conversion at equilibrium. The distribution of components in the product stream, temperature, and the enthalpy are based on thermodynamic and mass transfer constraints [14].

### *2.4.1 Equilibrium Modeling*

Schuster et al. [15] developed a model for a dual fluidized-bed steam gasifier using equilibrium calculations based on thermodynamics. Heat and mass balances were employed for both combustion and gasification zones. For the gasification zone, three independent reactions were considered for chemical equilibrium calculations. Gibbs energy minimization was the basis of equilibrium determination. They also showed the effects of gasification temperature, amount of fluidizing agent, water content in biomass, amount of char after the gasification zone, and fuel composition on product output.

Zainal et al. [16] predicted the performance of a downdraft gasifier for different biomass through equilibrium modeling. They employed the global gasification reaction, methane formation reaction, another reaction which was a combination of primary shift reaction and Boudouard reaction for mass balance, energy balance, and equilibrium constant calculation to predict the producer gas composition and the heating value. The predicted value is quite close to the experimental value. They also studied the variation of moisture content in biomass and the gasification temperature on gas composition and calorific values.

Babu and Sheth et al. [17] used Zainal's model and performed sensitivity analysis of the model through variation of oxygen enrichment of air, preheated temperature of air, and the steam to air ratio and presented the effect of those on gas composition, reaction temperature and calorific values of gas. This model also compared reasonably well with experimental data as with the Zainal model.

Fang et al. [18] choose the district model for modeling of a bench scale CFB gasifier that is useful to describe the hydrodynamics and reaction in the CFB gasifier.

They employed several equations and computational algorithms to calculate the model output in hydrodynamics and gasification kinetics parts with some general assumptions during the starting of model. They also studied the effect of variations in temperature, gas velocity, solids circulating rate and oxygen concentration on model output.

Mathieu et al. [19] presented a biomass gasification model with a fluidized bed gasifier which is based on Gibbs free energy minimization in the ASPEN PLUS simulator. The gasification process was split in four basic processes: pyrolysis, combustion, the Boudouard reaction and the gasification processes. They also performed a sensitivity analysis to study the influence of the $O_2$ amount, air temperature, oxygen enrichment in air, operating pressure and steam injection on gasification efficiency, reaction temperature, syngas composition and air temperature.

Altafani et al. [20] developed an equilibrium model based on Gibbs free energy minimization. They did not consider the gasification reactions. They included the atomic balances for elements(C, H, O, N, and S), equation for total mole balance, the Gibbs free energy equations for the species and the energy balance equation. The equations were solved using numerical methods programmed in FORTRAN. The model prediction compared well with experimental data. They also performed sensitivity studies to show the effect of moisture content on product gas composition, heating value and efficiency. The study has been extended with a sensitivity study performed on a model developed with Cycle-tempo software.

Mountouris et al. [21] employed the Gasif Eq model to predict the syngas production and an energy and exergy analysis. The process was externally heated, high-temperature gasification with waste material. They chose three equilibrium reactions, heterogeneous water shift, water-gas-shift, and methane decomposition reaction among the four reactions considered for this model. According to references from previous work, only two reactions are considered when no carbon formation is considered. In the case of solid carbon remaining after gasification, three independent equilibrium reactions are considered. Another consideration includes the favor of methane decomposition reaction in steam gasification. They used the global gasification reaction and three reactions for mass balance, energy balance and equilibrium constant expression and used the database of the Chemical Properties Handbook by Professor Carl L. Yaws of Lamar University, Texas. The model equilibrium constant values matched well with the literature values. They explained soot formation with the molar ternary of C-H-O diagram.

Melgar et al. [22] developed an equilibrium model based on thermal balance and chemical equilibrium. They used the global gasification reaction along with methane formation and the water-gas-shift reaction to predict the reaction temperature with energy balance and product composition at the reaction temperature. They were also able to calculate the moisture dissociated into hydrogen, the heating value of the product gas, and the cold gas efficiency. The model was validated with experimental data and after validation, the effect of moisture content and fuel/air ratio variation on product gas composition and the process characteristic was determined.

Kinchin [2] in his master's thesis developed an equilibrium model using CHEM CAD software. His model comprised two sub-level models, a gasification model and a fuel cell model, based on Gibbs free energy minimization. In his model, he determined the moisture level and equivalence ratio that caused carbon deposition in fuel cells. He identified no carbon deposition for fuel containing 28% moisture or greater regardless of equivalence ratio and for equivalence ratios of 0.23 or greater regardless of the fuel moisture content.

Marek Sciazko [34] presented a static model of coal pyrolysis in a circulating fluidized-bed reactor. He assumed a quasy-equilibrium state based on process parameters within the range studied. He considered two events in a circulating fluidized-bed, partial gasification of circulating char and coal devolatilization. He developed an empirical correlation for Boudouard equilibrium using the carbon monoxide and carbon dioxide concentrations in the product gas from experimental data. He also determined correlations for volatile matter evolution using data for carbon burn-off and volatile matter content in char. He compared the calculated value with the measured value. He studied the effects of air/coal ratio on pyrolysis temperature, char and gas yield, volatile matter, ash content in char and calorific value.

H.-M. Yan et al. [35] extended their previously developed model for a bubbling fluidized-bed coal gasifier inserting an overall energy balance and some new features. The fluidized bed consists of two phases, the dilute phase and an emulsion phase. The gases in both phases were considered to be in plug flow. The dilute phase had jet and bubble phases to consider gas-solid mixing and the transport phenomena in the space above the bed distributor. The overall energy balance around the fluidized bed predicts the bed operating temperature. The simulation prediction of overall carbon conversion, operating bed temperature and gas composition for three pilot-scales and a full-scale fluidized bed gasifier compared well with experimental data as compared to two other models used for comparison. It was found that the water-gas-shift reaction regardless of kinetically driven or equilibrium in the dilute phase has significant effects on the model prediction for the pilot-scale air-blown gasifiers but little on a commercial-scale oxygen-blown gasifier. This implied the much faster oxidation rate of $H_2$ and CO near the distribution for oxygen-blown gasifier to attain equilibrium state faster.

### *2.4.2 Kinetic Modeling*

Kinetic modeling is very significant to evaluate a gasification process in a specific gasifier. Though the author did not develop a kinetic model, she did some literature study on this topic. This section presents the review of several models of various gasification processes.

Knutson [23] in his master's thesis focused on kinetic modeling for a transport coal gasifier with North Dakota lignite coal. He made modifications to a model spreadsheet based on mass and energy balances previously developed by Sondreal to make it more flexible for users. Knutson used the reaction rate parameters and reaction rate constant data from two UND CHE theses by Hossain [37] and Carpenter [36] and also a TGA study performed by Timpe and Jacobson [38] to model the gasification mechanisms and the reaction rate in the gasification zone. He also tried to determine whether the gasification reaction was diffusion or kinetically controlled. His modeling efforts established the feasibility of Transport Reactor Development Unit (TRDU) as a gasifier.

Sanz and Corella [24] studied a kinetic model based on their previous developed model and calculated some process variables using the results from that model. The model predicted the gas composition, lower heating value (LHV), tar content and char concentration. They calculated the variables at the gasifier exit such as gas composition on dry basis, LHV, tar content, C content in fly ash and gas yield. They also showed the effects of total equivalence ratio, 2nd air inlet height, percentage of second air inlet flow, biomass moisture and flow rate. ER values of greater than 0.35 may cause the presence of $O_2$ in the product gas. The second air inlet height does not have significant effect on gas composition and LHV. The increase in secondary air percentage, for the same ER, results in high tar content at the exit, high gas yield and less carbon content in the fly ash. $H_2$, $CO_2$ and $H_2O$ contents increase with biomass moisture while CO decreases. The increase in biomass flow rate can decrease the tar content.

Watanabe et al. [25] developed a numerical model of coal gasification in an entrained flow gasifier. They simulated a three-dimensional model using three processes: pyrolysis, char gasification and gas phase reactions. To model the char gasification they used the Random Pore Model and used several transport equations to calculate mass and energy balances. The coal particle behavior was studied in a Lagrangian manner and radiative heat transfer using the discrete transfer equation. The equations were solved with the finite volume program, CFX. The model calculation on variation of gas temperature and product gas composition coincides well with the results of experiments. It also predicts the change of gasifier performance like the carbon conversion efficiency per pass, the heating value and cold gas efficiency with the gasifier air ratio.

Yu et al. [26] employs the kinetic theory of granular flow (KTGF) to simulate bubbling fluidized bed coal gasification. The model was based on the two-fluid model. The gasification behavior for the bubbling fluidized bed was derived using mass and momentum conservation equations. Particle collision and bed fluctuation was explained with KTGF. The three processes pyrolysis, heterogeneous char reactions and homogenous gas phase reactions were simulated. Heterogeneous reactions are modeled with the combination of Arrhenius rate, diffusion rate while homogenous reactions were modeled with turbulent mixing rate.

Liu et al. [27] clarified their previous work on char gasification kinetics at elevated temperature through modeling and characterization of char. The two phase modeling was performed using the gasification reaction rate data in the fluidized bed from experiments. The modeling revealed that increase in mass transfer resistance with temperature is not the main factor that contributes to a decrease in gasification rate at higher temperature. For char with an ash that has a high fusion temperature, the porosity and specific surface area increase with pyrolysis temperature and no ash accumulation occurs. At high temperature, char with ash having a low temperature ash fusion becomes smooth and ash accumulates near the surface. Char characterization performed in this work included pore structure characterization with nitrogen adsorption, surface morphology examination with Surface Electron Microscope (SEM) analysis and Electron Probe Microanalysis (EPMA).

This modeling review, both equilibrium and kinetic, helped the author to learn details about the gasification process. The assumptions regarding the process prior to modeling can affect the model output as described in the above models. The effect of gasifying agent, fuel on gasification reactions, syngas composition, and heating value was studied. The models approach helps to choose the reactions for modeling based on presence of carbon in syngas. Modeling the gasification process by splitting it into several steps helps to perform the modeling with more ease through modeling individual process phenomena with separate unit operation block. In some of the models, the approach of minimizing the Gibbs free energy minimization at equilibrium was explained in detailed which helped provide a clear understanding of the mathematical relation to reach at equilibrium. The effect of operating variables on tar content in syngas helped the author to choose which parameters to vary for sensitivity analysis.

No process reaches at steady state in real situation. However equilibrium models predict the thermodynamic limit which is very useful during evaluation and improvement of a process. Though a kinetic model gives the mechanism, rates and takes time consideration, it can not predict the thermodynamic limit. Moreover, equilibrium modeling can save money and time with its prediction for a wide operating range with its sensitivity analysis.

Comparison of equilibrium model output with experimental data helps to determine the deviation from equilibrium in experimental runs. This is the considered behind choosing the equilibrium model to evaluate the newly built USS gasifier at Ohio University. Moreover kinetic modeling needs more experimental data than equilibrium modeling and these experimental data were not available.

# CHAPTER 3

# EXPERIMENTAL PROCEDURE

This chapter summarizes the experimental procedures for the gasification work performed at Ohio University. This thesis work is part of a larger joint project between Ohio University and the University of North Dakota. The project purpose is to evaluate the USS gasification efficiency on Ohio coals in a controlled setting. Four tasks were proposed to provide data for evaluation of the gasification process: 1) construction of an ultra superheated steam reactor; 2) modeling of the gasification process; 3) testing of product yields and ash LOI as a function of bed temperature; and 4) testing of product yields and ash LOI as a function of $O_2$ in the oxidizing agent. The second task, gasification modeling was done at UND. The other three experimental tasks were done and will be done by the lead research team at Ohio University.

The objective of the work in this thesis was to develop an equilibrium model to predict the product gas composition and heating value. A summary of the experimental methodology is described here since data collected at Ohio University is used to verify the model developed. Input data for the gasifier's operation is used in the model and model output is compared with the experimental output data. The author was not involved with the experiments performed at Ohio University.

## 3.1 Coal Analysis

Clarion 4A seam coal was used as fuel for the USS gasifier. The proximate and ultimate analyses are presented in Table 2.

Table 2. Proximate and Ultimate Analysis for Clarion 4A Seam Coal

| Proximate Analysis, wt% | |
|---|---|
| Moisture | 6 |
| Fixed Carbon | 53 |
| Volatile Matter | 38 |
| Ash | 9 |
| **Ultimate Analysis, dry basis, wt%** | |
| Carbon | 71 |
| Hydrogen | 5 |
| Oxygen | 9.5 |
| Nitrogen | 1.3 |
| Sulfur | 4.2 |
| Ash | 9 |

## 3.2 Procedure

Gasification process consists of two main steps, ultra superheated steam (USS) reforming and coal gasification.

### *3.2.1 USS Steam Reformation*

Superheated steam at 356°F (180°C) is burnt with a fuel gas at 80°F (26°C) and oxidizer at 80°F (26°C) to create a steam flame of very high temperature, around 4000°F (2200°C). The model predicts 3718°F (2048°C). Figure 3 shows the patent pending USS burner technology from Enercon Systems. Usually recycled syngas is used as fuel gas; but since this study was done at the lab scale, natural gas was used. Oxygen was used as the oxidizer. The flow rate for methane, oxygen and steam were 5, 20 and 34 lb/h respectively.

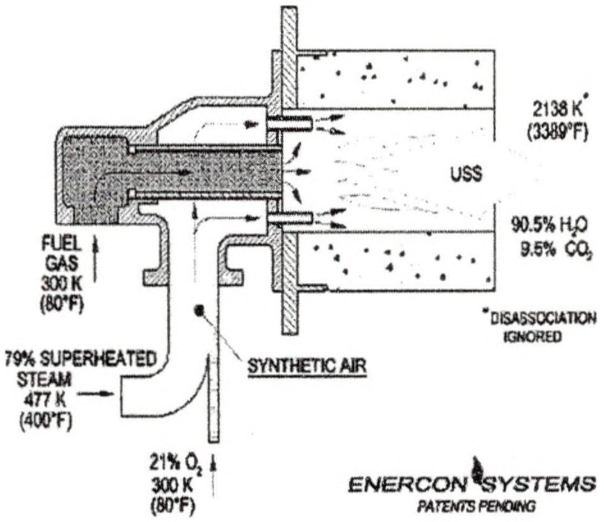


Figure 3. Ultra Superheated Steam Generation in a Burner [10]

### *3.2.2 Coal Gasification*

The coal was first dried and sized to -1/4 to +1/16 inch. Coal is fed using a pressurized hopper. The fluidized bed is made with sand, coal ash and coal. The hot steam flame is injected through lances into the fluidized bed. The reaction zone near the lances rapidly converts the coal to synthesis gas. Then the syngas is sent to the cyclone where some of the ash components and unreacted carbon is separated from the syngas and recycled back to the bed. In this lab scale gasifier, recycling of unreacted char was not done yet. Figure 4 shows the schematic of the gasification process system at Ohio University.

The gasifier unit is approximately 12 inches in diameter with 48 injection lances and is approximately 14 feet high. The initial burn gas is supplied from the lab's pressurized natural gas. The steam is supplied from Ohio University's internal steam network at 1 atm and 356°F. The oxygen is supplied from a liquid oxygen dewer located near the Ohio Coal Research Center. Figure 5 is a photograph of the gasifier.

Experimental conditions and data are presented in chapter 5 along with results from the modeling work.

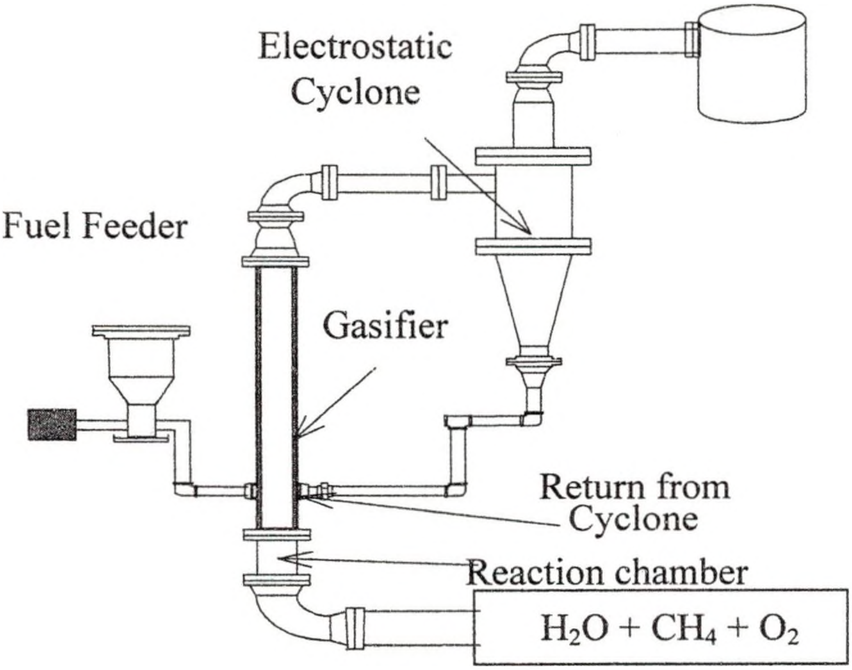


Figure 4. Schematic Presentation of USS Gasification Process at Ohio University [Personal Communication with Dr. David Bayless, Ohio University].

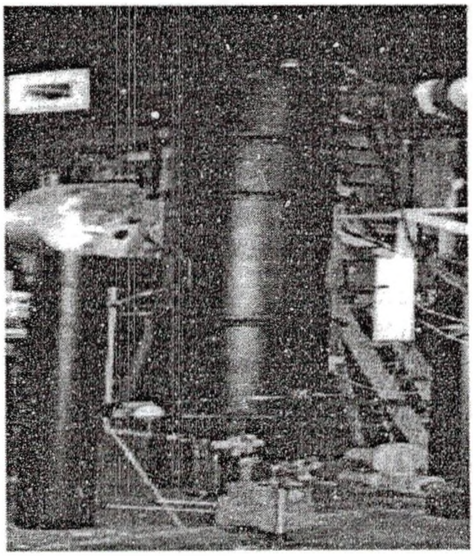


Figure 5. The Ohio University USS Reactor [10]

# CHAPTER 4

# MODEL

This chapter describes the details of the methodology followed during the model development. In this modeling effort I built a zero-dimensional equilibrium model for USS gasification in a bubbling fluidized bed using the simulation software ASPEN PLUS 2004.1. The model output has the gas composition and heating value of the product gas. Since it is zero-dimensional, no design information for the unit operation units was provided nor was hydrodynamic related output generated from the model. The mass and energy balance data for each block is shown in tabular form using the base case data to give the reader more comfort with the model development results.

## 4.1 Equilibrium Model

The modeling effort of this thesis evaluates a new gasifier built at Ohio University which uses the USS technique for its bubbling fluidized bed reactor. The author has followed the suggestions of Souza-Santos [13]: "It is advisable to go from simple to complex, not the other way around." A few numbers of effects should be considered and simplifications can be done based on several hypothesis. If the simulation results do not compare with experimental data well, then the hypothesis should be eliminated and checked the simulation results gradually. Therefore, a zero-dimensional equilibrium model was chosen as the model.

ASPEN PLUS was chosen as the model platform. ASPEN PLUS is a good choice because it has a rich database containing the properties of large number of compounds, can define the components outside the database using predictors, performs mass and energy balances using the thermodynamic property method and performs calculations for each unit operation section in sequential order. The steps followed for this modeling exercise included process flow-sheet development, stream specification, component specification, particle size range insertion if needed, property method selection, design specification, FORTRAN block insertion, convergence method selection and performance analysis if desired.

### *4.1.1 Flow-Sheet Development*

The process flow sheet was developed as the initial step of the modeling. There are some built in blocks in ASPEN PLUS which can be inserted to create the process flow sheet. Each block represents the individual unit operation phenomena occurring in the actual process. Reactors, columns, heat exchangers, separators are examples of several unit operation blocks. There are some blocks which are convenient for calculations which do not exist in real processes. The blocks can be connected to the next block with streams. There are three types of streams: material streams, heat streams and work streams. Material streams connect unit operation models and transfer material flow. Heat streams are used to supply heat to a unit operation block, to specify heat duty for a block and to provide information for heat duty calculation. Work streams are used to supply power specification to pump or compressor block. The streams are used to specify the feed and the initial estimate for tear streams are specified with stream specification. The function of unit operation blocks used in the model is described briefly in table 3. The process flow sheet of the model is illustrated in figure 6.

Table 3. A Brief Description of ASPEN PLUS Blocks Used in the Model

| Block Name | Description |
|---|---|
| RYIELD | Used to model a reactor when its yield distribution is known but reaction stoichiometry and kinetics are unknown. It yields the components specified in the yield distribution. The model may have multiple numbers of inlet and one product material stream. |
| RSTOICH | Used to simulate a reactor when reaction kinetics is unknown but reaction stoichiometry and molar extent of conversion is known for each reaction. It can have any number of inlet material streams but one product material stream. It can handle any number of reactions. It can also generate combustion reactions. |
| RGIBBS | Used to model a reactor when all of the reactions occurring inside the reactor are not known or too many components are involved in the process. It determines the phase and chemical equilibrium based on Gibbs free energy. It is specified with pressure and temperature or heat duty. It can perform three phase flash calculations. |
| REQUIL | Used to calculate phase and chemical equilibrium when reaction stoichiometry is known and some or all reactions reach equilibrium. It can have any number of inlet and two product material streams. It calculates the equilibrium constants for the reactions specified for this block. |
| CYCLONE | Separates an inlet gas stream containing solids into a solid stream and a gas stream containing the remaining solid. It can have one inlet stream and two outlet material streams. |
| SSPLIT | Used to split the inlet streams into two or more outlet streams based on specific split fractions. |
| HEATER | Used to model heater, cooler, valves and pumps. Can have any number of material streams and one outlet material stream. |
| CLCHNG | Used to change the stream class. It should have one inlet and one outlet material stream. |
| DUPL | Copies one inlet material stream into multiple numbers of duplicate streams. It is required when one stream needs to be used in different processing units. It can duplicate heat and work streams also. Mass and energy balance are not maintained in this block. |

### *4.1.2 Stream Specification*

In ASPEN PLUS the stream class is defined based on component type specified by the simulator. It defines conventional components as "CONVEN", non-conventional components as "NC", conventional solids as "CIPSD" and non-conventional solids as "NCPSD". When a component is defined in the ASPEN PLUS database and it is not a solid except those salts defined with chemistry, then it is considered conventional and defined as CONVEN. Oxygen and water are examples of CONVEN. The solid components outside the database are defined as non-conventional and defined as NC. Biomass and coal are examples of stream NC. The solid components which are defined in the database are conventional solids and defined as CIPSD. The solid components with known particle size distribution outside the database are non-conventional components and defined as NCPSD. Coal and solid wastes are examples of NCPSD stream.

ASPEN also allows users to define the stream having multiple type of components as "MIXNC", "MIXCILSD", "MIXNCPSD", "MIXCIPSD", "MIXCINC" and "MCINCPSD" as per as users required.

The stream class was specified as "MCINCPSD" in this model which signifies streams having both conventional and non-conventional solids with known particle size distribution along with conventional stream [29].

### *4.1.3 Coal Property Characterization*

Though ASPEN can handle non-conventional components such as coal or waste materials, it has no molecular structure for those compounds in its database. To define these components, the user needs to enter ultimate, proximate and sulfur analysis data. The ultimate analysis gives the elemental composition of carbon, hydrogen, oxygen, nitrogen, sulfur, chlorine and ash. The proximate analysis defines on the basis of fixed carbon, volatile matter, ash and moisture. The sulfur analysis provides the analysis data in pyritic, sulfate and inorganic sulfur forms. The Clarion 4A seam coal was defined with the ultimate and proximate analysis data provided by the Ohio University [Table 2]. For sulfur analysis, the Penn State coal database record for sample PSOC-198 was used [44]. The particle size distribution (PSD) data for coal and ash were taken from previous work [32]. Tables 4 and 5 show the PSD data for Blacksville bituminous coal used in this model.

Table 4. Particle Size Distribution for Blacksville Bituminous Coal [32]

| Interval | Lower Limit (μm) | Upper Limit (μm) | Weight Fraction |
|---|---|---|---|
| 1 | 0 | 100 | 0 |
| 2 | 100 | 200 | 0 |
| 3 | 200 | 500 | 0.2 |
| 4 | 500 | 1000 | 0.1 |
| 5 | 1000 | 2000 | 0.2 |
| 6 | 2000 | 5000 | 0.4 |
| 7 | 5000 | 10000 | 0.1 |

Table 5. Particle Size Distribution for Blacksville Bituminous Coal Ash [32]

| Interval | Lower Limit ( μm) | Upper Limit ( μm) | Weight Fraction |
|---|---|---|---|
| 1 | 0 | 100 | 0 |
| 2 | 100 | 200 | 0 |
| 3 | 200 | 500 | 0.2 |
| 4 | 500 | 1000 | 0.1 |
| 5 | 1000 | 2000 | 0.2 |
| 6 | 2000 | 5000 | 0.4 |
| 7 | 5000 | 10000 | 0.1 |

Property method choice is one of the most crucial parts of the modeling from a thermodynamics point of view. The property method allows the property calculation for each unit operation block. Fugacity and enthalpy are required for thermodynamic equilibrium calculation. Those are sufficient for mass and heat balance as well.

Thermodynamics provides two property methods to represent fugacities from the phase equilibrium relationships with measurable state variables: the equation of state method and the activity coefficient method. Enthalpy and molar volume are calculated using phase equilibrium. The help topic of ASPEN PLUS 2004.1 recommends SYNFUEL as process type for coal gasification and it was selected in this model. There is a property method option choice for a specific process type which is considered the base. For SYNFUEL PR-BM, RKS-BM, BWR-LS were the options for the base property method. Both PR-BM and RKS-BM are cubic equations of state. PR-BM signifies the Peng Robinson cubic equation of state with the Boston-Mathias alpha function and RKS-BM signifies the Redlich-Kwong-Soave (RKS) equation of state with Boston-Mathias alpha function. BWR-LS uses the Benedict-Webb-Rubin equation of state which is a virial equation of state. Both PR-BM and RKS-BM are suitable as property methods for non-polar and mildly polar mixtures like hydrocarbons and light gases such as carbon dioxide, hydrogen sulfide and hydrogen. BWR-LS is also suitable for non-polar and slightly non-polar mixtures but it is more accurate for liquid molar volume and enthalpy calculations than PR-BM and RKS-BM. It gives good results for coal liquefaction applications. So either PR-BM or RKS-BM is preferred for the model and both of them gave the same output. PR-BM was chosen for this model using Pickett's thesis as reference [6].

For non-conventional component coal, ASPEN needs a model specified for enthalpy and density calculations. HCOALGEN is a general method in ASPEN for enthalpy calculation and was chosen for enthalpy calculations. DCOALIGT is preferred for calculating the density which was the default choice for coal. The HCOALGEN model has several correlations that are used for heat of combustion and heat of formation calculations. The preferred correlation is selected using numbered option codes [31].

Six correlations exist in HCOALGEN for heat of combustion calculations:

- Boie correlation
- Dulong correlation
- Grummel and Davis correlation
- Mott and Spooner correlation
- IGT correlation
- User input value of heat combustion

The author prefered to enter heat of combustion values directly from experimental measurements but this were not available. Therefore, the Dulong formula was used for heat of combustion calculations gave reasonably accurate result for coal. The formula is:

$$\Delta_c h_i^{dm} = [\, a_{1i} w_{C,i}^{\ dm} + a_{2i} w_{H,i}^{\ dm} + a_{3i} w_{S,i}^{\ dm} + a_{4i} w_{O,i}^{\ dm} + a_{5i} w_{N,i}^{\ dm}]10^2 + a_{5i} \text{ .........(19)}$$

Where defaults coefficient values are:

- $a_{1i} = 145.44$
- $a_{2i} = 620.28$
- $a_{3i} = 40.5$
- $a_{4i} = -77.54$
- $a_{5i} = -16.0$

Where the function terms are:

- $w_{C,i}^{\ dm}$ = weight fraction of Carbon on a dry, ash free basis
- $w_{H,i}^{\ dm}$ = weight fraction of Hydrogen on a dry, ash free basis
- $w_{S,i}^{\ dm}$ = weight fraction of Sulfur on a dry, ash free basis

- $w_{O,i}^{dm}$ = weight fraction of Oxygen on a dry, ash free basis
- $w_{N,i}^{dm}$ = weight fraction of Nitrogen on a dry, ash free basis

Two correlations exist for standard heat of formation calculations. Those are:

- Heat of combustion based
- Direct

The help topics mention that 1% error in the heat of combustion based correlation may cause 50% error in heat of formation calculations [31]. Direct correlation is selected in this case. The direct correlation was developed using data from the Penn State Data Base and it uses ultimate, proximate and sulfur analysis data to calculate the heat of formation.

The Kirov correlation was chosen for heat capacity calculation from two options. Those are:

- Kirov Correlation
- Cubic Temperature Equation

The Kirov correlation is preferred because it considers coal proximate analysis and calculates the heat capacity as a weighted sum of those components from analysis. On the other hand, for the cubic temperature equation the data was selected from three lignites and a sub bituminous coal to develop the coefficient parameter in the formula. So it may not be suitable for all coals.

The enthalpy basis is:

- Elements at their standard states at 298.15 K and 1 atm
- Component at 298.15 K

The DCOALIGT model was selected for density calculation. It determines the density of coal on dry basis using ultimate and sulfur analysis based on equations from IGT (1976).

### *4.1.4 Component Specification*

All components including intermediates, both conventional and non-conventional should be in the component list with ID and specific type. Twenty components were listed which contains 17 conventional components, 2 non-conventional components and one conventional solid. Table 6 presents the list of components used as input and output in the model.

Table 6. Components in the USS Gasification Model

| Component Name | Type |
|---|---|
| Coal | Non-conventional |
| Methane | Conventional |
| Steam | Conventional |
| Oxygen | Conventional |
| Carbon | Solid |
| Hydrogen | Conventional |
| Nitrogen | Conventional |
| Sulfur | Conventional |
| Ash | Non-conventional |
| Carbon Monoxide | Conventional |
| Carbon Dioxide | Conventional |
| Hydrogen Sulfide | Conventional |
| Ammonia | Conventional |
| Sulfur Dioxide | Conventional |
| Sulfur Trioxide | Conventional |
| Phenol | Conventional |
| Naptha | Conventional |
| Oil | Conventional |
| Nitric Oxide | Conventional |
| Nitrogen Dioxide | Conventional |

### *4.1.5 Syngas Composition and Heating Value Determination*

The process flow-sheet created in ASPEN is quite different from the real flow-sheet because additional operation units are required for the sake of simulation purposes. The process flow-sheet is shown in figure 6 and all block specification and functions are

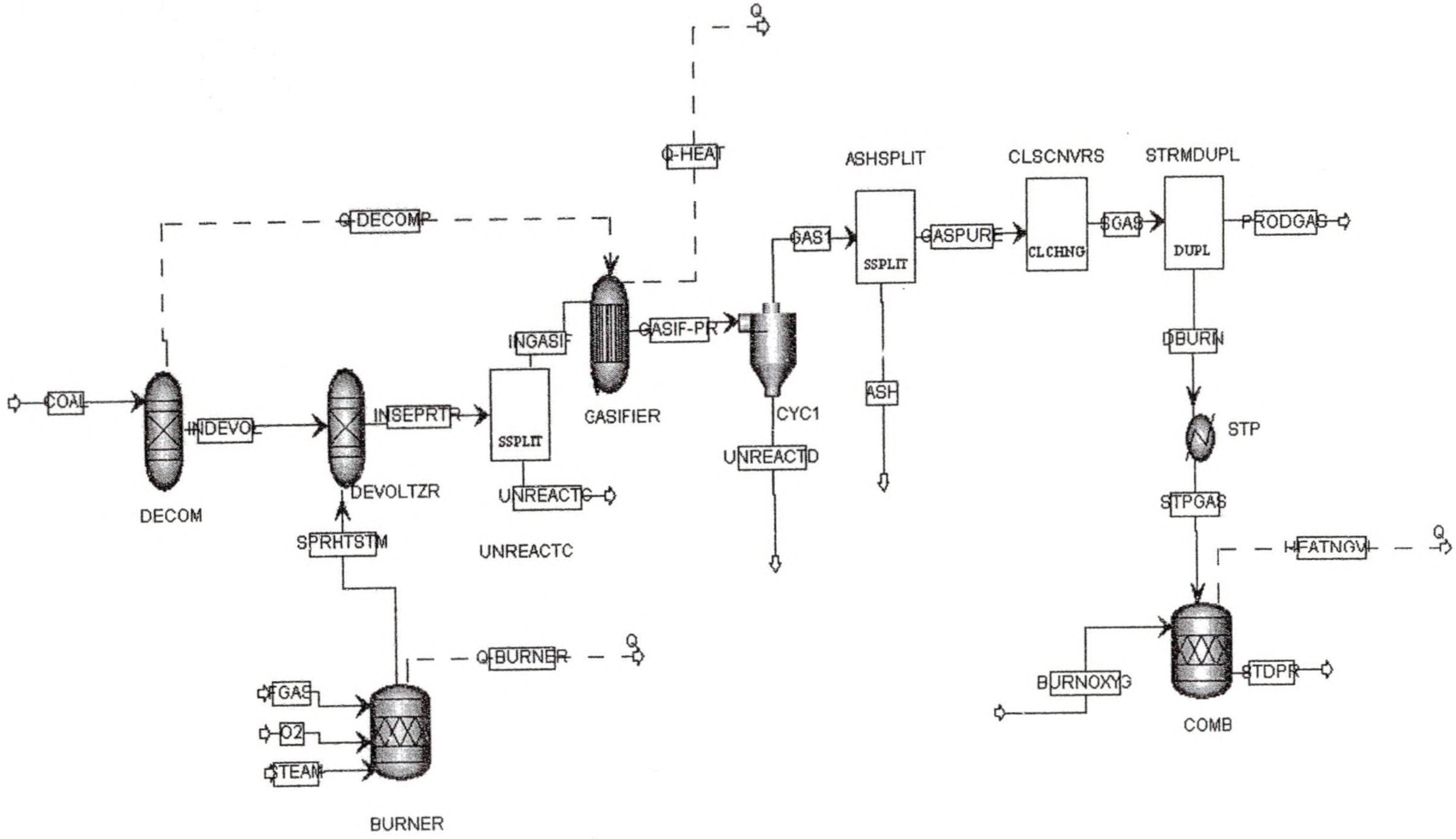


Figure 6. ASPEN PLUS Model Flow Diagram of the USS Gasification Process

Table 7. ASPEN Block Descriptions for Gasification Unit Operations in the USS Model

| Flow-Sheet Units | Specifications | Functions |
|---|---|---|
| DECOM(RYIELD) | P= 1 atm ,<br>T = 298.15K | Gives the yields of coal constituents like carbon, hydrogen, oxygen, nitrogen, sulfur and water using FORTRAN block GASIF. The heat stream Q-DECOMP is set by FORTRAN block DCOMP. |
| DEVOLTZR(RYIELD) | P= 1 atm ,<br>Heat Duty = 0 | Calculates the formation of phenol, naphtha and oil. It also yields the carbon, hydrogen, oxygen, nitrogen, sulfur, ash, water and carbon dioxide. The yields are set with FORTRAN block DEVOL. |
| BURNER(RSTOIC) | P= 1 atm ,<br>Heat Duty = 0 | Simulates the stoichiometric reaction between methane and oxygen and generates USS steam consisting of carbon dioxide and steam. |
| UNREACT(SSPLIT) | Stream UNREACTC<br>Split Fractions:<br>MIXED=0,<br>CIPSD=0.05,<br>NCPSD=0 | Separates the 5% unreacted carbon from the stream, entering to the GASIFIER. |
| GASIFIER(RGIBBS) | P = 1 atm ,<br>T = 1116 K | Simulates the equilibrium calculation of gasification process based on minimum Gibbs free energy. |
| CYC1(CYCLONE) | Efficiency = 0.7 | Separates the ash from stream GASIF-FR produced from GASIFIER block. It is specified at design mode and Shepherd and Lapple correlations as calculation options. |
| ASHSPLIT(SSPLIT) | Stream UNREACTC<br>Split Fractions:<br>MIXED=0,<br>CIPSD=0.05,<br>NCPSD=0 | Separates the remaining amount of non-conventional component ash from the stream allowing the stream class changing. |
| CLSCNVRS(CLCHNG) | - | Changes the stream class from MCINCPSD to MIX. |

Table 7. (Continued.)

| Flow-Sheet Units | Specifications | Functions |
|---|---|---|
| STRMDUPL(DUPL) | - | Duplicates the steam SGAS and allows to calculate the heating value. |
| STP(HEATER) | P = 1 atm ,<br>T = 298.15 K | Cools the stream DBURN to STP condition. |
| COMB(RSTOIC) | P= 1 atm ,<br>Heat Duty = 0 | Performs the combustion reaction of syngas with oxygen and generated the heat stream HEATNGVL which is used for heating value calculation. |
| GASFRWQ(REQUIL) | P = 1 atm ,<br>T = 1116 K | Performs equilibrium calculation based on stoichiometric approach. It calculates the equilibrium constants for the defined reactions in this block. |

described in table 7. The components of this flow sheet are broken down into process steps and discussed individually. The gasification process is simulated using the RGIBBS reactor that uses the approach of minimum Gibbs free energy. The RGIBBS reactor can not simulate non-conventional components; therefore the coal fuel needs to be converted to conventional components before entering to the RGIBBS reactor. To meet the requirement of being conventional for the RGIBBS reactor, the coal fuel is introduced to the RYIELD reactor named as DECOM (see figure7). This reactor gives the output for each element of coal using its ultimate and proximate analysis. A FORTRAN block, GASIF, performs the calculation of mass yield. FORTRAN blocks are calculator blocks and are not shown on the flow diagram. The code for each FORTRAN block is included in Appendix A. Now all of the elements in the stream INDEVOL are conventional except ash. Since ash does not participate in any reactions, it can be assumed as inert. The enthalpy of the stream INDEVOL is not same as that of the stream COAL. The differences in enthalpy of these two streams are calculated using the FORTRAN block DCOMP and then the heat stream Q-DECOMP is added to the gasifier. DECOM was specified at 77°F temperature and 1 atmospheric pressure. The mass and energy balance of the DECOM reactor for the base case using Clarion 4A coal are shown in table 8. The figure 7 shows the block DECOM.

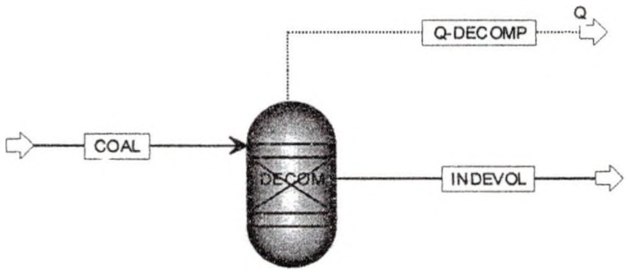


Figure 7. The Unit Operation Block DECOM

Table 8. Mass and Energy Balance for DECOM

| Streams | COAL | INDEVOL | Q-DECOMP |
|---|---|---|---|
| Mass Flow, lb/hr | 22 | 22 | N/A |
| Volume Flow, cuft/hr | 0 | 240 | N/A |
| Enthalpy, Btu/hr | -873,000 | -7,000 | -866,000 |
| Density, lb/ft$^3$ | 90 | 0 | N/A |
| Temperature,°F | 80 | 80 | 80 |
| Component Mass Flow lb/hr | | | |
| Carbon | 0.0 | 14.6 | N/A |
| Hydrogen | 0.0 | 1.0 | N/A |
| Oxygen | 0.0 | 1.9 | N/A |
| Nitrogen | 0.0 | 0.3 | N/A |
| Sulfur | 0.0 | 0.9 | N/A |
| Moisture | 0.0 | 1.3 | N/A |
| Ash | 0.0 | 1.8 | N/A |

*N/A means not applicable

USS generation was modeled using a RSTOICH reactor which is named as BURNER. Figure 8 shows the block with input and output streams. The operating condition is set at 1 atm pressure and 0 Btu/hr. The mass and energy balance for this block is presented in table 9. The reaction for the reactor was:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

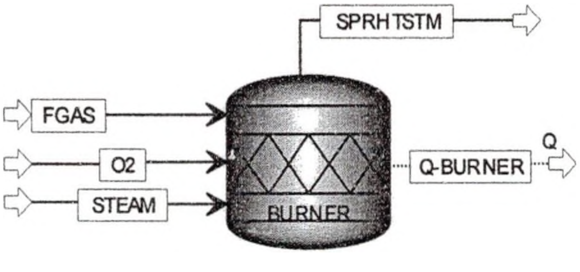


Figure 8. The Unit Operation Block BURNER

Table 9. Mass and Energy Balance for BURNER

| Streams | FGAS | $O_2$ | STEAM | SPRHTSTM | Q-BURNER |
|---|---|---|---|---|---|
| Mass Flow, lb/hr | 5 | 20 | 34 | 60 | N/A |
| Volume Flow, cuft/hr | 120 | 250 | 1200 | 8800 | N/A |
| Enthalpy, Btu/hr | -10,000 | 0 | -194,000 | -204,000 | 0.0 |
| Density lb/ft$^3$ | 0 | 0 | 0 | 0 | N/A |
| Temperature,° F | 80 | 80 | 360 | 3720 | - |
| Component Mass Flow, lb/hr | | | | | |
| Carbon Dioxide | 0.0 | 0.0 | 0.0 | 13.9 | N/A |
| Steam | 0.0 | 0.0 | 0.0 | 45.7 | N/A |
| Oxygen | 0.0 | 20.3 | 34.4 | 0.1 | N/A |
| Methane | 5.0 | 0.0 | 0.0 | 0.0 | N/A |

*N/A means not applicable

The high molecular weight hydrocarbon formation, tars, was simulated using a RYIELD reactor named as DEVOLTZR. The FORTRAN block DEVOL was used to execute the formation calculation. DEVOLTZR is specified with 1 atm pressure and 0 heat duty. The block in the model is shown in figure 9 and table 10 shows the mass and energy balance. The USS steam is introduced to the DEVOLTZR to provide heat for those hydrocarbon formations. The formation formula was taken from Pickett's master's thesis [6]:

$$\mathrm{PHENOL} = 0.002463 \times \mathrm{COAFW} \qquad \text{.......................} (20)$$

$$\mathrm{NAPTHA} = 0.007450 \times \mathrm{COAFW} \qquad \text{.......................} (21)$$

$$\mathrm{OIL} = 0.02031 \times \mathrm{COAFW} \qquad \text{.............................} (22)$$

Where,

COAFW = mass flow rate of coal to the DEVOLTZR,

PHENOL = mass flow rate of phenol,

NAPTHA = mass flow rate of naphtha,

OIL = mass flow rate of oil.

These three compounds were chosen because they are the typical tar compounds for the gasifier.

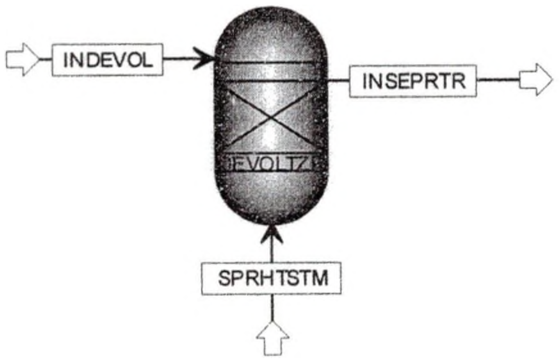


Figure 9. The Schematic of Block DEVOLTZR

Table 10. Mass and Energy Balance for DEVOLTZR

| Streams | INDEVOL | SPRHTSTM | INSEPRTR |
|---|---|---|---|
| Mass Flow, lb/hr | 22 | 60 | 82 |
| Volume Flow, cuft/hr | 240 | 8800 | 8000 |
| Enthalpy, Btu/hr | -7,000 | -204,000 | -212,000 |
| Density, lb/ft$^3$ | 0 | 0 | 0 |
| Temperature,°F | 80 | 3720 | 2610 |
| Component Mass Flow, lb/hr | | | |
| Carbon | 14.6 | 0.0 | 14.0 |
| Hydrogen | 1.0 | 0.0 | 1.0 |
| Oxygen | 1.9 | 0.1 | 2.0 |
| Nitrogen | 0.3 | 0.0 | 0.3 |
| Sulfur | 0.9 | 0.0 | 0.9 |
| Steam | 1.3 | 45.7 | 47.0 |
| Carbon Dioxide | 0.0 | 13.9 | 13.9 |
| Ash | 1.8 | 0.0 | 1.8 |
| Phenol | 0.0 | 0.0 | 0.1 |
| Naphtha | 0.0 | 0.0 | 0.2 |
| Oil | 0.0 | 0.0 | 0.4 |

The output stream INSEPRTR contains both USS components and coal elements including hydrocarbons. 5% carbon loss occurs in the gasification process and this carbon is separated using the block SSPLIT named as UNREACTC. Figure 10 shows the block and table 11 shows the mass and energy balance.

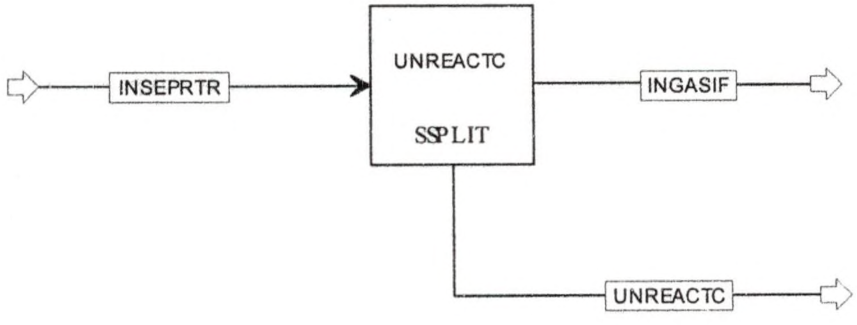


Figure 10. The Figure of Block UNREACTC

Table 11. Mass and Energy Balance for UNREACTC

| Streams | INSEPRTR | INGASIF | UNREACTC |
|---|---|---|---|
| Mass Flow, lb/hr | 82 | 81 | 1 |
| Volume Flow, cuft/hr | 7950 | 7950 | 0 |
| Enthalpy, Btu/hr | -212,000 | -213,000 | 1,000 |
| Density, lb/cuft | 0 | 0 | 141 |
| Temperature,°F | 2610 | 2610 | 2610 |
| Component Mass Flow lb/hr | | | |
| Carbon | 14.0 | 13.3 | 0.7 |
| Hydrogen | 1.0 | 1.0 | 0.0 |
| Oxygen | 2.0 | 2.0 | 0.0 |
| Nitrogen | 0.3 | 0.3 | 0.0 |
| Sulfur | 0.9 | 0.9 | 0.0 |
| Steam | 47.0 | 47.0 | 0.0 |
| Carbon Dioxide | 13.9 | 13.9 | 0.0 |
| Ash | 1.8 | 1.8 | 0.0 |
| Phenol | 0.1 | 0.1 | 0.0 |
| Naptha | 0.2 | 0.2 | 0.0 |
| Oil | 0.4 | 0.4 | 0.0 |

The gasification zone where the reaction between coal and USS takes place is modeled with a RGIBBS reactor named as GASIFIER. GASIFIER calculates the product composition based on Gibbs free energy of minimization with phase splitting. The equilibrium based on minimum Gibbs free energy implies in terms of thermodynamics is:

$$\sum dG/dn_i = 0 \quad \text{.......} \quad (23)$$

where, G is the Gibbs free energy and $n_i$ is the composition of the species i.

The gasifier was specified at 1atm pressure and 1550°F temperature. The option of phase equilibrium and chemical equilibrium options is used to calculate equilibrium so that reactions do not need to be specified. The RGIBBS is the only reactor in ASPEN PLUS that can candle solid-liquid-gas phase equilibrium. Figure 11 shows the GASIFIER block and Table 12 presents the mass and energy balance.

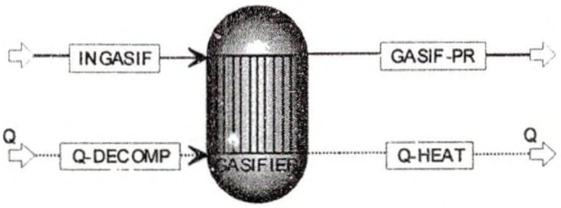


Figure 11. The Block GASIFIER

Table 12. Mass and Energy Balance for GASIFIER

| Streams | INGASIF | GASIF-PR | Q-DECOMP | Q-HEAT |
|---|---|---|---|---|
| Mass Flow, lb/hr | 81 | 81 | N/A | N/A |
| Volume Flow, cuft/hr | 7950 | 6780 | N/A | N/A |
| Enthalpy, Btu/hr | -213,000 | -222,000 | -866,000 | -857,000 |
| Density, lb/ft$^3$ | 0 | 0 | N/A | N/A |
| Temperature, °F | 1550 | 1550 | 80 | - |
| Component Mass Flow lb/hr | | | | |
| Carbon | 13.3 | 0.0 | N/A | N/A |
| Hydrogen | 1.0 | 3.6 | N/A | N/A |
| Oxygen | 2.0 | 0.0 | N/A | N/A |
| Nitrogen | 0.3 | 0.0 | N/A | N/A |
| Sulfur | 0.9 | 0.0 | N/A | N/A |
| Steam | 47.0 | 23.5 | N/A | N/A |
| Carbon Dioxide | 13.9 | 26.1 | N/A | N/A |
| Carbon Monoxide | 0.0 | 24.5 | N/A | N/A |
| Methane | 0.0 | 0.0 | N/A | N/A |
| Phenol | 0.1 | 0.0 | N/A | N/A |
| Naptha | 0.2 | 0.0 | N/A | N/A |
| Oil | 0.4 | 0.0 | N/A | N/A |
| Hydrogen Sulfide | 0.0 | 0.9 | N/A | N/A |
| Ammonia | 0.0 | 0.3 | N/A | N/A |
| Ash | 1.8 | 1.8 | N/A | N/A |

***N/A means not applicable**

In a fluidized bed gasifier some of the char and ash is entrained with the product gas. To capture those solids and recycle them to the gasifier a cyclone is added next to the gasifier. The CYCLONE is shown in figure 12 and table 13 presents the mass and energy balance. In the currently employed lab-scale gasification process, recycling of

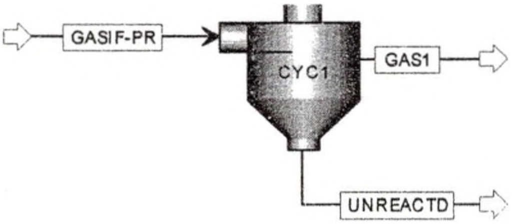


Figure 12. The Block CYC1

Table 13. Mass and Energy Balance for CYC1

| Streams | GASIF-PR | GAS1 | UNREACTD |
|---|---|---|---|
| Mass Flow, lb/hr | 81 | 80 | 1 |
| Volume Flow, cuft/hr | 6780 | 6780 | 0 |
| Enthalpy, Btu/hr | -222,000 | -222,000 | 0 |
| Density, lb/cuft | 0 | 0 | 218 |
| Temperature, °F | 1550 | 1550 | 1550 |
| Component Mass Flow, lb/hr | | | |
| Carbon | 0.0 | 0.0 | 0.0 |
| Hydrogen | 3.6 | 3.6 | 0.0 |
| Oxygen | 0.0 | 0.0 | 0.0 |
| Nitrogen | 0.0 | 0.0 | 0.0 |
| Sulfur | 0.0 | 0.0 | 0.0 |
| Steam | 23.5 | 23.5 | 0.0 |
| Carbon Dioxide | 26.1 | 26.1 | 0.0 |
| Carbon Monoxide | 24.5 | 24.5 | 0.0 |
| Methane | 0.0 | 0.0 | 0.0 |
| Phenol | 0.0 | 0.0 | 0.0 |
| Naptha | 0.0 | 0.0 | 0.0 |
| Oil | 0.0 | 0.0 | 0.0 |
| Hydrogen Sulfide | 0.9 | 0.9 | 0.0 |
| Ammonia | 0.3 | 0.3 | 0.0 |
| Ash | 1.8 | 0.6 | 1.2 |

solids was not performed. The cyclone is specified at design mode and efficiency was set at 70%. The Shepherd and Lapple correlation was used to calculate the solid removal efficiency.

The gas output from the cyclone still contains some ash. This remaining ash is separated using the block SSPLIT named as ASHSPLIT. Only the ash, which is 0.6 lb/hr in mass, is separated in stream ASH. The other components are the same as the stream GAS1. Figure 13 shows the block ASHSPLIT. It is necessary to make this split because the gas stream needs to be ash free for accurate heating value calculation.

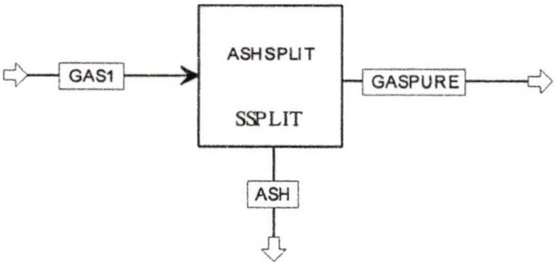


Figure 13. The Block ASHSPLIT

Now all the components of the gas in the stream GASPURE are conventional. The stream class is changed from "MCINCPSD" to "MIX" inserting the manipulating block "CLCHNG" named as CLSCNVRS. The output is then duplicated using another manipulator named as STRMDUPL. This allows calculation of the heating value of the product gas. The output stream SGAS from the block CLSCNVRS and the stream DBURN from the STRMDUPL will be the same as the steam GASPURE. The stream DBURN will be cooled with a HEATER block named as STP (figure 14) and the output condition is 1 atm pressure and 77°F. The gas at standard condition is combusted in the RSTOICH block COMB with oxygen to produce $CO_2$ and $H_2O$. The COMB is specified

Figure 14. The Block STP

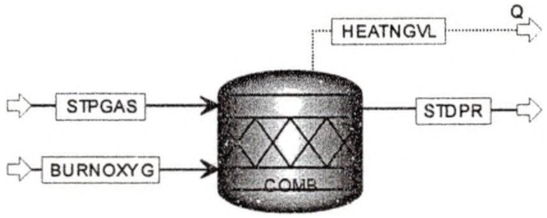


Figure 15. The Block COMB

Table 14. Mass and Energy Balance for COMB

| Streams | STPGAS | BURNOXYG | STDPR | HTNGVL |
|---|---|---|---|---|
| Mass Flow, lb/hr | 79 | 48 | 124 | N/A |
| Volume Flow, cuft/hr | 1330 | 580 | 640 | N/A |
| Enthalpy, Btu/hr | -302,000 | 0 | -677,000 | 338,000 |
| Density, lb/cuft | 0 | 0 | 0 | N/A |
| Temperature, °F | 80 | 80 | 80 | 80 |
| Component Mass Flow, lb/hr | | | | |
| Hydrogen | 3.6 | 0.0 | 0.0 | N/A |
| Oxygen | 0.0 | 45.0 | 0.2 | N/A |
| Steam | 23.5 | 0.0 | 56.9 | N/A |
| Carbon Dioxide | 26.1 | 0.0 | 64.6 | N/A |
| Carbon Monoxide | 24.5 | 0.0 | 0.0 | N/A |
| Methane | 0.0 | 0.0 | 0.0 | N/A |
| Hydrogen Sulfide | 0.9 | 0.0 | 0.0 | N/A |
| Ammonia | 0.3 | 0.0 | 0.0 | N/A |
| Sulfur Dioxide | 0.0 | 0.0 | 1.7 | N/A |
| Nitrogen Oxide | 0.0 | 0.0 | 0.6 | N/A |

*N/A means not applicable

at 1 atm pressure and 0 BTU/hr heat duty. The block COMB is shown in figure 15 and Table 14 presents mass and energy balance. The heat stream from this block will give the heating value that will be divided by the mass flow rate of the gas entering to the burner COMB to get the heating value per unit mass. For the base case, the heating value was determined to be 4300 Btu/lb. This is equivalent to 250 Btu/ft$^3$.

### *4.1.6 Equlibrium Constants Determination*

The GIBBS reactor is useful if all of the reactions taking place within the reactor are not known or they are too numerous because of so many components are involved in reactions. But the major four reactions for USS gasification are taken into consideration for modeling as follows:

Steam gasification: $C + H_2O \rightarrow CO + H_2O$ ................................................... (5)

Water-gas shift: $CO + H_2O \rightarrow CO_2 + H_2$ ........................................................ (4)

Boudouard: $C + CO_2 \rightarrow 2\ CO$ ............................................................................ (7)

Methane Decomposition: $CH_4 + H_2O \rightarrow CO + 3H_2$ .................................... (12)

There is another equilibrium reactor in ASPEN PLUS, REQUIL that solves reaction equilibrium calculations to compute combined phase and chemical equilibrium when reaction stoichiometry is known. It calculates the reaction equilibrium constant ($K_{eq}$) from the Gibbs free energy of the participating components in the reactions. These $K_{eq}$ values help to explain the model better and are presented in chapter 5.

Another process flow-sheet was generated modifying the former one which is described above. Everything including the specifications are the same except the replacement of the RGIBBS reactor GASIFIER with a REQUIL reactor named GASFREQ. The REQUIL reactor does the same job but it works based on different specifications. This reactor can not perform a three-phase flash calculation. The pressure and temperature were specified the same as the RGIBBS reactor. Only the four major reactions listed above were considered for this modeling and provided in the reaction specification. The equilibrium constants are defined as:

$$K_{eq} = \prod_{i=\text{products}} a_i \bigg/ \prod_{i=\text{reactants}} a_i \quad \text{..................................(24)}$$

where, a is activity coefficient and defined as:

$$a_i = f_i\,(\text{mixture}) / f_i\,(\text{pure, standard state}) \quad \text{.................(25)}$$

where, $f$ represents the fugacity. For chemical equilibrium calculation, the fugacity at standard state is 1 atm. So $a_i$ is the $f_i$ in the mixture. Thus:

$$K_{eq} = \prod_{i=\text{products}} f_i \bigg/ \prod_{i=\text{reactants}} f_i \quad \text{...................(26)}$$

The fugacities are in atm. Activities are unitless and so is $K_{eq}$.

# CHAPTER 5

# RESULTS AND DISCUSSION

In this section, the syngas composition and the heating value of the gasification process for the base case at which the gasifier is operated are presented. The operating conditions and flow rates of the input components are shown in tabular form. Results from a sensitivity analysis for the model with variation of gasifier temperature, steam flow rate and coal type are also described.

## 5.1 Results for Base-case Conditions

The baseline gasification experiments at Ohio University were performed at 1550°F and 1atm. The input data is shown in table 15. The data were used as the base condition for the modeling efforts.

Table 15. The Model Input Data for Clarion 4A Coal

| Feed Rate | lb/hr |
|---|---|
| Coal | 21.78 |
| Methane | 5.04 |
| Oxygen | 20.22 |
| Steam | 34.32 |
| Gasification Temperature(°F) | 1550 |
| $H_2O/C$ Ratio (Molar) | 1.25 |

On the basis of the above input data, the simulation results from ASPEN PLUS in the form of product composition and heating value on both wet and dry basis are presented in table 16.

Table 16. The Product Composition and Heating Value at 1550°F

| Molar Composition of Product Gas in % | Wet Basis |  | Dry Basis |  |
|---|---|---|---|---|
|  | Simulation | Experimental | Simulation | Experimental |
| CO | 19 | 32 | 26 | 38 |
| $H_2$ | 39 | 36 | 54 | 43 |
| $CO_2$ | 13 | 17 | 18 | 20 |
| $H_2O$ | 28 | 14 | N/A | N/A |
| $CH_4$ | 90 PPM | NA | 0.0 | NA |
| $H_2S$ | 0.6 | 0.8 | 0.8 | 0.9 |
| $NH_3$ | 0.4 | NA | 0.6 | NA |
| $SO_2$ | 9 PPB | NA | - | NA |
| Higher Heating Value of Synthesis Gas (BTU/lb) | 4300 | NA | - | NA |
| Higher Heating Value of Coal (BTU/lb) | 13300 | NA | - | NA |
| USS Temperature (°F) | 3720 | NA | N/A | NA |

*NA indicates that the data is not available
*N/A indicates not applicable

The gas concentration for $H_2$ and $CO_2$ from the simulation is quite similar to the experimental composition on a wet basis. But for CO and $H_2O$, simulation and experimental data give somewhat different concentrations. The CO concentration from the model was 13 mole % less than that of the experimental while for $H_2O$, it was the opposite.

The gas compositions were compared on a dry basis. The comparison shows more CO and less $H_2$ from the experiment than the simulation. One explanation could be that the water-gas shift reaction did not reach at equilibrium in the experiment. An elemental mole balance of input components and product components for both simulation and experiment was done to further investigate the differences between simulation and experiment results. Table 17 presents the elemental mole balance.

Table 17. Elemental Mole Balance for the Base Case Input, Output and Adjusted Experimental Compositions (Values Are in Mole Percent, Normalized to 100%).

| | | | | Adjusted Experiment | | | |
|---|---|---|---|---|---|---|---|
| Gas Composition | Input Data | Simulation | Experiment | 1 | 2 | 3 | 4 |
| CO | 0 | 19 | 32 | 32 | 26 | 24 | 22 |
| $CO_2$ | 0 | 13 | 17 | 17 | 14 | 13 | 12 |
| $H_2$ | 0 | 39 | 36 | 36 | 30 | 28 | 26 |
| $H_2O$ | N/A | 28 | 14 | 14 | 28 | 28 | 28 |
| $CH_4$ | N/A | 0 | - | 1.6 | 1.6 | 7.6 | 11.3 |
| $O_2$ | N/A | 0 | 0 | N/A | N/A | N/A | N/A |
| Coal | N/A | 0 | 0 | N/A | N/A | N/A | N/A |
| Δ in % | Input Data | Simulation | Experiment | 1 | 2 | 3 | 4 |
| CO | N/A | 0 | 51 | 51 | 33 | 24 | 18 |
| $CO_2$ | N/A | 0 | 26 | 26 | 7 | -1 | -8 |
| $H_2$ | N/A | 0 | -8 | -8 | -26 | -34 | -41 |
| $H_2O$ | N/A | 0 | -68 | -68 | -1 | -1 | 0 |
| $CH_4$ | N/A | 0 | | 200 | 200 | 200 | 200 |
| Elemental Balance | Input Data | Simulation | Experiment | Adjusted Experiment | | | |
| | | | | 1 | 2 | 3 | 4 |
| C | 13 | 13 | 21 | 21 | 17 | 17 | 17 |
| O | 30 | 30 | 35 | 34 | 33 | 30 | 27 |
| H | 56 | 56 | 44 | 45 | 50 | 54 | 56 |
| Δ in % | Input Data | Simulation | Experiment | 1 | 2 | 3 | 4 |
| C | | 0 | 46 | 46 | 24 | 24 | 23 |
| O | 0 | 0 | 13 | 10 | 9 | -3 | -11 |
| H | 0 | 0 | -24 | -22 | -12 | -5 | 0 |

*N/A indicates not applicable

* Δ = (experiment-simulation)*100/experiment

The table shows that the fraction of C in the experimental product exceeds the fraction of C in the input. In the case of simulation output on wet basis the C is 0.52% less than the input accounting for the 5% C loss assumed in the model.

The molar percent of $CH_4$ and $H_2O$ for the experiment was adjusted and then the difference (Δ) between experimental and simulation were compared. The adjusted compositions are highlighted on table 17. The same comparison and difference calculation was done for the elemental mole balance. Nitrogen and sulfur were ignored from the comparison calculation shown on table 17 because those are considered as minor species. For the first adjusted experimental composition, only $CH_4$ was added as 1.6 mole %. $CH_4$ might be the reason of imbalance because the $CH_4$ concentration for the experiment was not reported for the base case. However, $CH_4$ was measured in the product gas from subsequent tests. Also, it is expected that the gasifier does not operate at equilibrium. $CH_4$ would be expected to be present in the product due to this non-equilibrium condition. The difference ($\Delta$) from the elemental mole balance shows that $CH_4$ at the measured value of 1.6% does not change the mole balance much.

Next, the experimental $H_2O$ value was adjusted from 14 mole % to 28 mole % along with the 1.6 mole % $CH_4$ adjustment. It was suspected that the measured $H_2O$ values may be low. 28% was chosen as it represents the equilibrium $H_2O$ content from the product gas. The elemental values obtained from the comparison determined that change of $H_2O$ to the simulation value brings the mole balance into reasonable agreement with those of simulation values.

Two more adjustments in experimental composition were done keeping the $H_2O$ value the same but varying the $CH_4$ concentration 7.6 mole% and 11.3 mole %. The adjustments to $H_2O$ and $CH_4$ content from the data bring the elemental balance into reasonable agreement. This indicates that the $H_2O$ and $CH_4$ may be under reported for the experimental data.

These adjustments were made to allow a better comparison between the simulated and experimental data. For this purpose, adjusted experiment number 2 was used. Number 2 was chosen for the comparison since the $CH_4$ is in line with what was measured in other tests. Adjusted experiment number 2 shows the experimental data are high in CO and low in $H_2$ when compared to the simulated results. This implies the water-gas-shift reaction may not be in equilibrium. This could be due to channeling of steam from the steam lances, rather than creating a well mixed reactor.

The gasifier was not run for long periods of time and may not have reached equilibrium conditions. A continuous NOVA $CO/CO_2/O_2/H_2$ analyzer was used to measure the gas composition and $H_2$ composition was calculated by TCD differentiation. So any error in other components analysis, including $H_2O$, would be reflected in the $H_2$ concentration. A moisture free gas is needed for the analyzer. The gas is condensed and weighed to obtain the moisture content. While this technique gives a run average for moisture content, it may have low accuracy if the gasifier is not at steady-state operation. Also, for varying operation, the conditions for the product gas measurements may not represent the "average" operating conditions.

The equilibrium constant for major four reactions were determined using the REQUIL block. The values for each individual reaction are listed in table 18. The data show that the water-gas shift reaction (#2) plays a significant role in the component yield

Table18. The Equilibrium Constant Values at 1550°F and 1 atm.

| Reaction No. | Reactions | Thermo Equilibrium constant | Kinetic Rate Constant | Kinetic Rate |
|---|---|---|---|---|
| 1 | $C + H_2O \rightarrow CO + H_2$ | 12 | 1.1E-04 | slow |
| 2 | $CO + H_2O \rightarrow CO_2 + H_2$ | 0.9 | 1.6E05 | very fast |
| 3 | $C + CO_2 \rightarrow 2\ CO$ | 13 | 1.4E-09 | very slow |
| 4 | $CH_4 + H_2O \rightarrow CO + 3\ H_2$ | 439 | 3.1E-06 | Moderately slow |

*kinetic rate constant for reactions 1-3 was taken from Mann's Paper [39]
*kinetic rate constant for reaction 4 was calculated from Probstein and Hicks [4]

and reaches equilibrium fast, producing more $CO_2$ and $H_2$ and consuming the CO. Under good mixing conditions, it is expected that the water-gas shift reaction will reach equilibrium. Mass diffusion limitations, or poor mixing, could explain a non-equilibrium water gas shift. The kinetic rate constant for Boudouard reaction shows that it takes longer to reach equilibrium and if it does not achieve equilibrium it would consume less $CO_2$, producing less CO. Moreover reaction (4) might not reach equilibrium which produces both CO and $H_2$. The presence of $CH_4$ in the product gas is an indication that the gasification reactions are not at equilibrium. Non-equilibrium of reaction (4) results in less CO in the product gas.

## 5.2 Comparison of Several Coal Types

Table 19. Proximate, Ultimate and Sulfur Analysis Data for Various Coals [6, 39]

| Coal Types | Clarion 4A | Pittsburgh #8 | Illinois #6 | Spring Creek | North Dakota Lignite |
|---|---|---|---|---|---|
| Proximate Analysis, wt% | | | | | |
| Moisture | 6 | 6 | 18 | 24 | 33 |
| Fixed Carbon | 53 | 49 | 45 | 51 | 45 |
| Volatile Matter | 38 | 39 | 44 | 43 | 44 |
| Ash | 9 | 12 | 11 | 6 | 11 |
| Ultimate Analysis,dry basis, wt% | | | | | |
| Carbon | 71 | 73 | 69 | 70.3 | 63 |
| Hydrogen | 5 | 5 | 5 | 5 | 4.5 |
| Oxygen | 10 | 5 | 10 | 18 | 19 |
| Nitrogen | 1 | 1 | 1 | 1 | 1 |
| Sulfur | 4.2 | 3.3 | 4.3 | 0.4 | 1.2 |
| Chlorine | 0 | 0.1 | 0 | 0 | 0 |
| Ash | 9 | 12 | 11 | 6 | 11 |
| Sulfur Analysis, wt% | | | | | |
| Pyritic | 1.8 | 1.6 | 1.9 | 0.1 | 0.4 |
| Sulfate | 0.1 | 0.1 | 0.1 | 0.1 | 0.4 |
| Organic | 2.3 | 1.6 | 2.4 | 0.1 | 0.4 |

The same input data was applied to four other coals along with base case fuel, Clarion 4A coal. The coals were Pittsburgh#8 and Illinois #6 Bituminous, Spring Creek Subbituminous, and North Dakota Lignite. Pittsburgh #8 is similar to Clarion 4A in its composition. The analysis data for the five types of coals are shown in table 19. The simulation results for these five coals are presented in the tables 20 and 21 and figures 16 through 20.

The motive behind the USS gasification at Ohio University is to enhance hydrogen production compared to other gasifiers. Syngas with a high heating value is desirable especially for electricity production. The figures show that when considered on

Table 20. Product Composition and Heating Values for Various Coals on Wet Basis

| Molar Composition of Product Gas in % | Clarion 4A | Pittsburgh #8 | Illinois #6 | Spring Creek | ND Lignite |
|---|---|---|---|---|---|
| CO | 19 | 20 | 15 | 13 | 9 |
| $H_2$ | 39 | 40 | 35 | 33 | 28 |
| $CO_2$ | 13 | 12 | 14 | 15 | 15 |
| $H_2O$ | 28 | 26 | 35 | 39 | 48 |
| $CH_4$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $H_2S$ | 0.6 | 0.4 | 0.5 | 0.0 | 0.1 |
| $NH_3$ | 0.4 | 0.4 | 0.3 | 0.3 | 0.2 |
| Higher Heating Value – Ash Free, Wet Basis (BTU/lb) | 4300 | 4500 | 3600 | 3200 | 2500 |

Table 21. Product Composition and Heating Values for Various Coals on Dry Basis

| Molar Composition of Product Gas in % | Clarion 4A | Pittsburgh #8 | Illinois #6 | Spring Creek | ND Lignite |
|---|---|---|---|---|---|
| CO | 26 | 28 | 23 | 22 | 18 |
| $H_2$ | 54 | 55 | 54 | 54 | 53 |
| $CO_2$ | 18 | 17 | 22 | 24 | 29 |
| $CH_4$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $H_2S$ | 0.8 | 0.6 | 0.8 | 0.0 | 0.2 |
| $NH_3$ | 0.6 | 0.5 | 0.4 | 0.4 | 0.5 |
| Higher Heating Value – Ash Free, Dry Basis (BTU/lb) | 5900 | 6100 | 5500 | 5100 | 4600 |

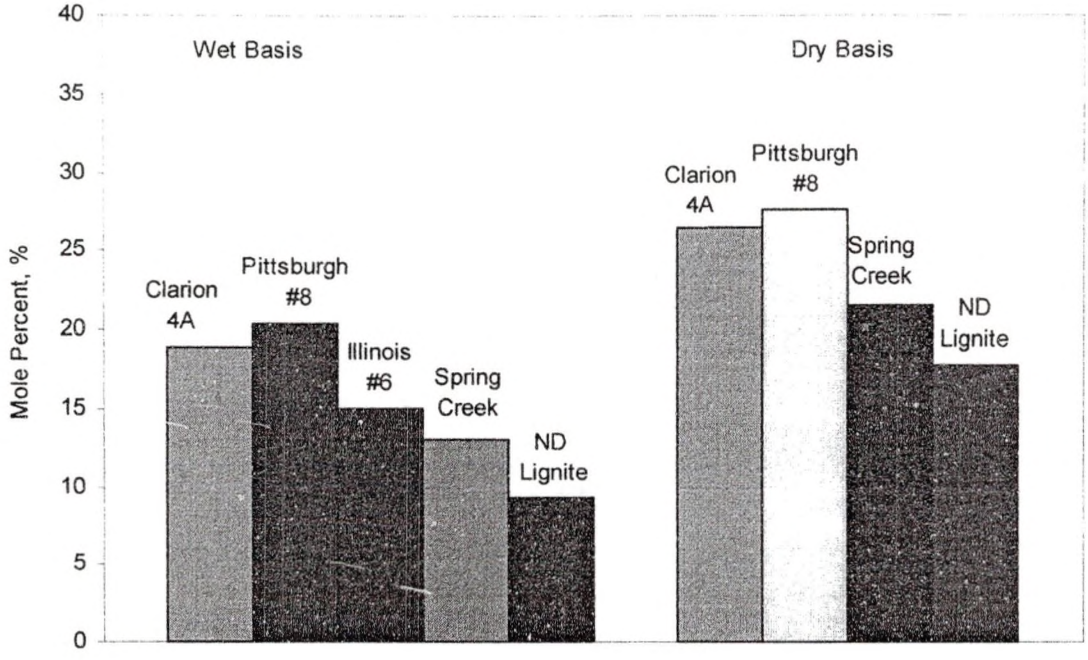


Figure 16. CO Concentration for Coals from ASPEN Simulation of USS Gasifier at 1550°F

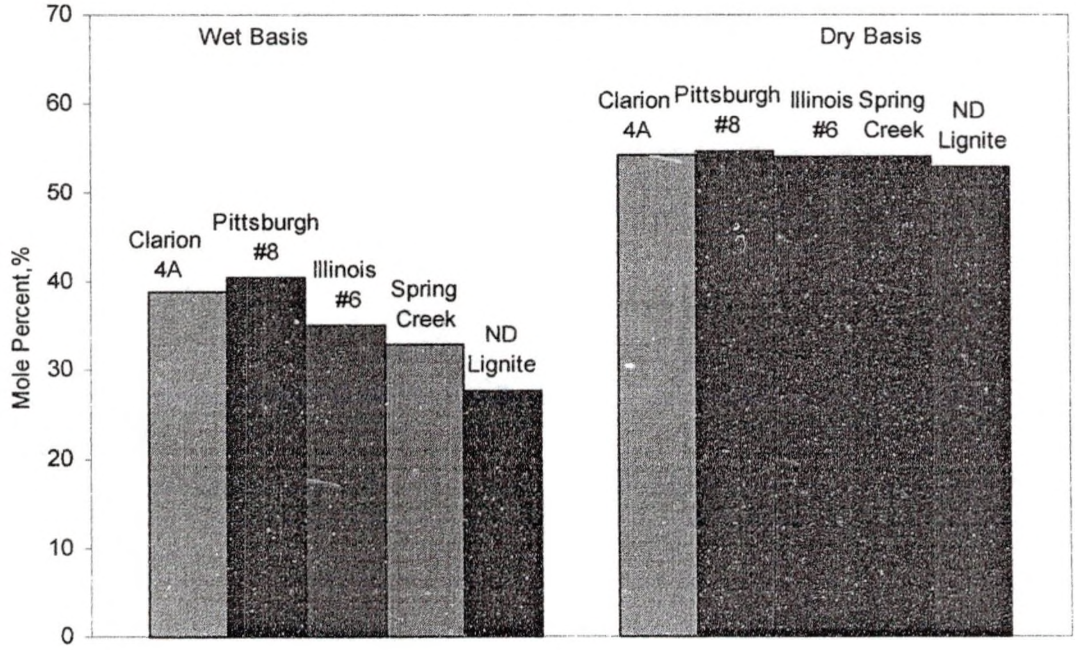


Figure 17. $H_2$ Concentration for Coals from ASPEN Simulation of USS Gasifier at 1550°F

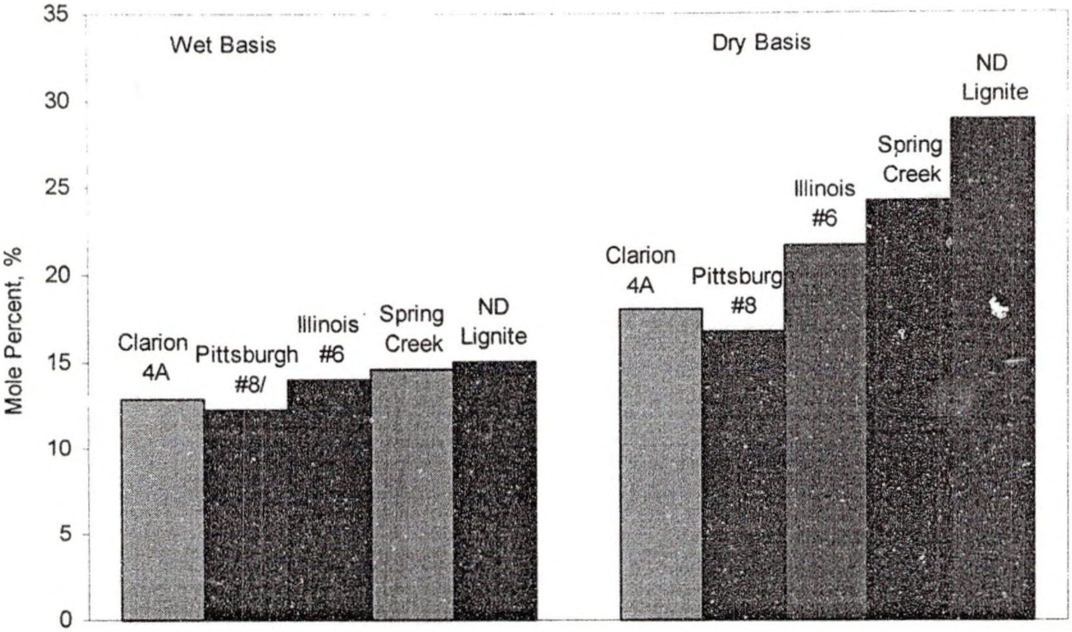


Figure18. $CO_2$ Concentration for Coals from ASPEN Simulation of USS Gasifier at 1550°F

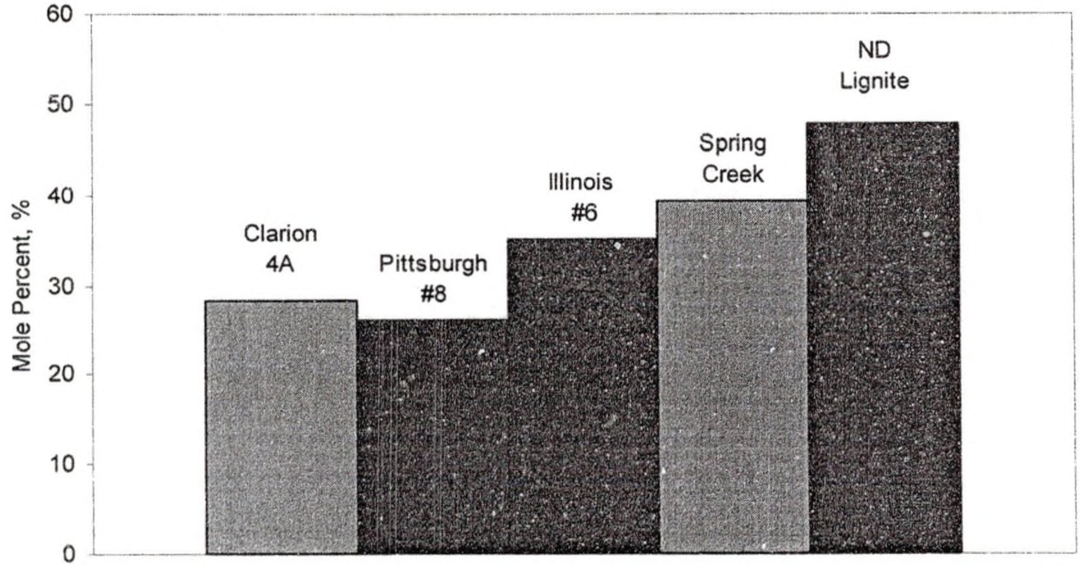


Figure19. $H_2O$ Concentration for Coals from ASPEN Simulation of USS Gasifier at 1550°F

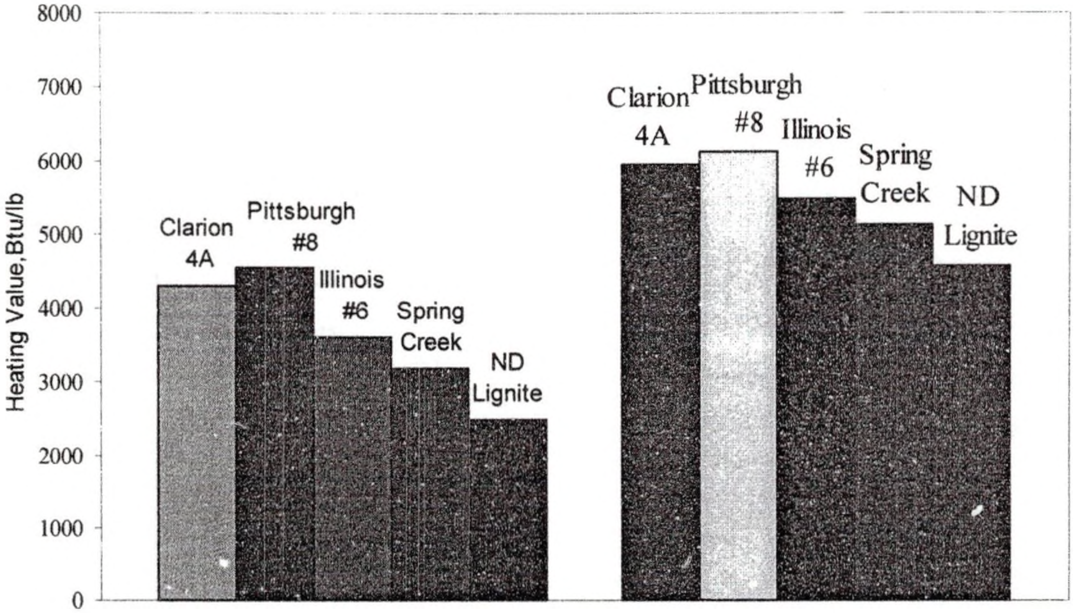


Figure 20. Heating Value Comparison for Product Gas from ASPEN Simulation of USS Gasifier at 1550°F

a wet basis, Clarion 4A and Pittsburgh #8 coals favor the production of syngas containing more CO and $H_2$ which are considered as the main components of syngas. The lignite coal gives the highest composition for $H_2O$ and $CO_2$. The lowest heating value for product gas was for lignite coal also. For lignite coal, drying of coal before gasification may improve the syngas composition and the heating value, too. In that case, the heat provided for gasification is not wasted to vaporize the moisture in coal.

An alternative way to utilize the syngas is to condense the water from the product and use the dry gas. In this the comparison between heat needed to condense the moisture and the increase of heating value for syngas after moisture separation are needed to check the energy efficiency of this technique. The gas composition was compared on dry basis. A comparison on dry basis shows higher concentrations for CO and $H_2$. For CO, the Pittsburgh coal still gives the highest molar percent in the gas output. For $H_2$, all coals give almost the same output as Pittsburgh #8. ND lignite gives the highest $CO_2$ yield than other four coals on dry basis as well as on wet basis. This is probably due to the higher oxygen content in the coal converting more CO to $CO_2$. On the basis of all plots 16 through 20, Pittsburgh # 8 is found to produce the maximum CO and $H_2$ and the minimum $CO_2$ and $H_2O$ and also has the maximum heating value.

## 5.3 Sensitivity Analysis

A sensitivity analysis was performed varying the gasification temperature and the steam flow rate to the BURNER ($H_2O/C$). The effect of those variations on product gas composition and heating value were studied. The temperature variation was performed for all of the above mentioned coals. Steam flow rate were varied only for Clarion 4A coal which is the base fuel for this modeling and compared with the experimental results for the same steam flow rates.

### *5.3.1 Temperature Variation*

Figure 21 shows the syngas composition for the base case fuel Clarion 4A as a function of gasification temperature. It shows $H_2$ content increasing with temperature up to $1320^0$F and then it starts to decline resulting in an increase in $H_2O$ concentration. The reaction equilibrium for the exothermic water gas shift reaction decreases with increasing temperature and may be the reason for the decrease in $H_2$ composition. The increase in temperature favors CO production with consumption of $CO_2$ produced in the water gas-shift reaction and the secondary gasification reaction. The $CH_4$ composition diminishes from a negligible amount to zero. The syngas enriched in CO and $H_2$ provides more heat when it is combusted in a turbine and results in a higher heating value. Figure 22 illustrates the heating value trend with increase in temperature. For Clarion 4A, the

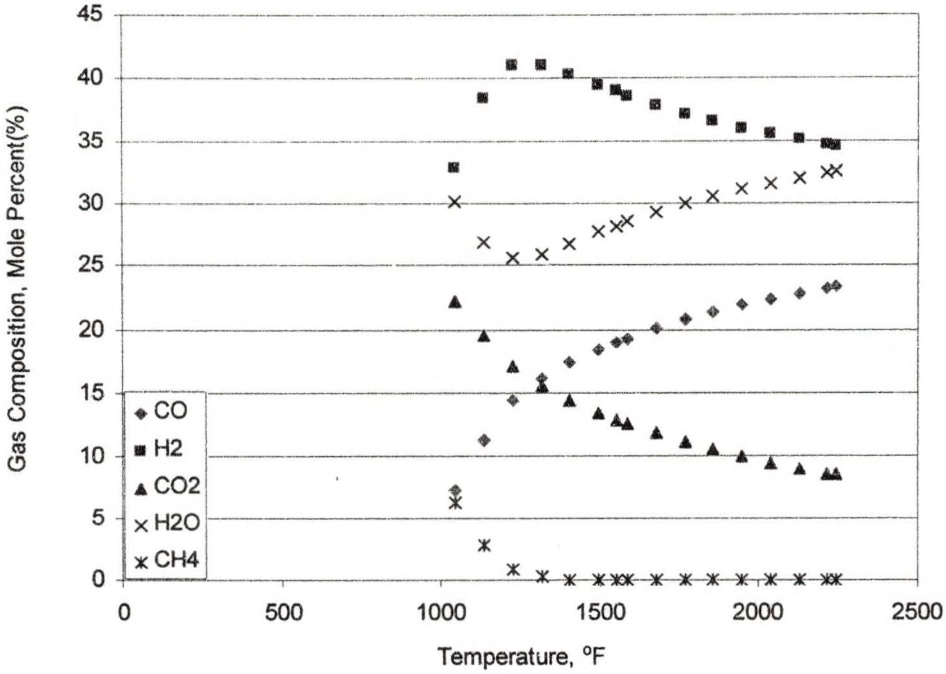


Figure 21. Syngas Composition of Clarion 4A Seam Coal with Temperature on Wet Basis

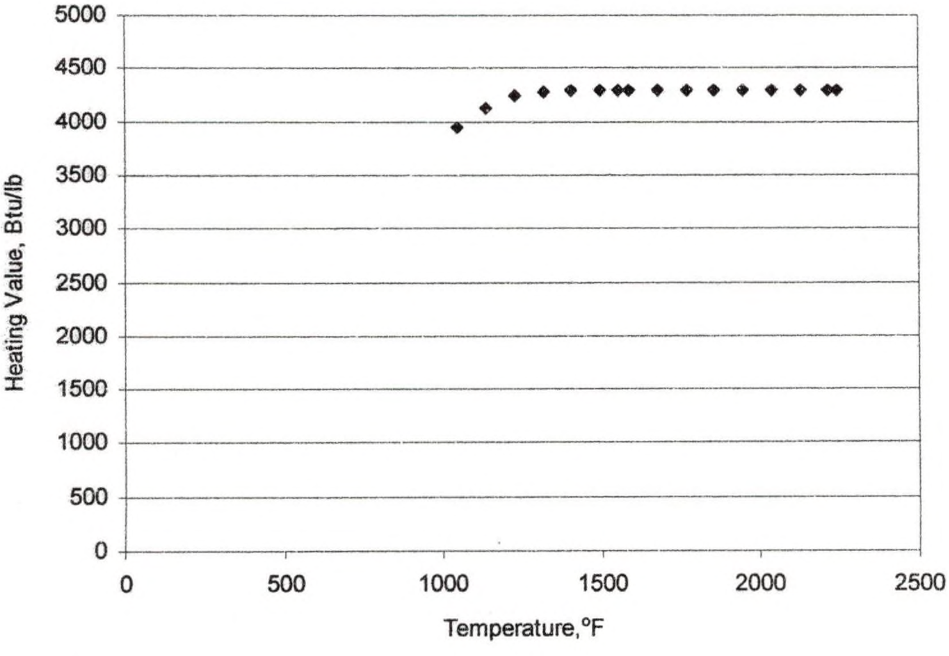


Figure 22. Heating Value of Syngas for Clarion 4A Coal with Temperature on Wet Basis

heating value increases with temperature up to 1500°F and remains steady. The increase in heating value trends to 1320°F and less can be explained with the increasing trend of both CO and $H_2$. After 1320°F the rate of increase declines with the decrease in $H_2$ composition, and for this portion the increasing CO composition is the cause of the increasing trend of heating value up to 1410°F. After 1410°F, the CO composition increase is offset by the decreasing $H_2$ and the heating value remains relatively constant. Figures 23 through 28 show the comparison among different coals for increasing temperature and its effect on syngas composition and heating value. Each coal has similar trends as the base Clarion 4A coal. Tables containing the composition and heating values for respective temperatures for all coals on wet basis found in Tables 22 through 26 of Appendix B.

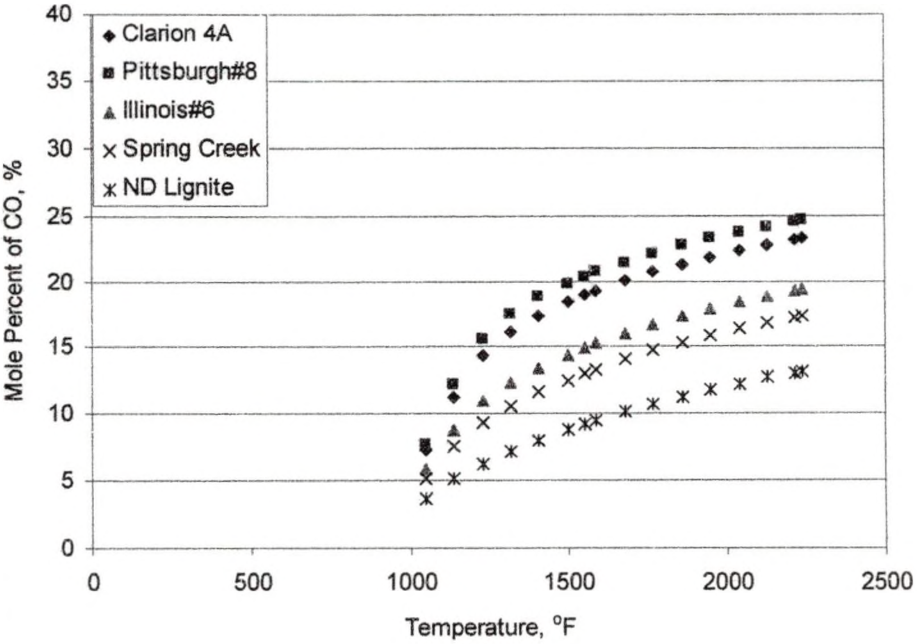


Figure 23. CO Concentration for Various Coals with Temperature on Wet Basis

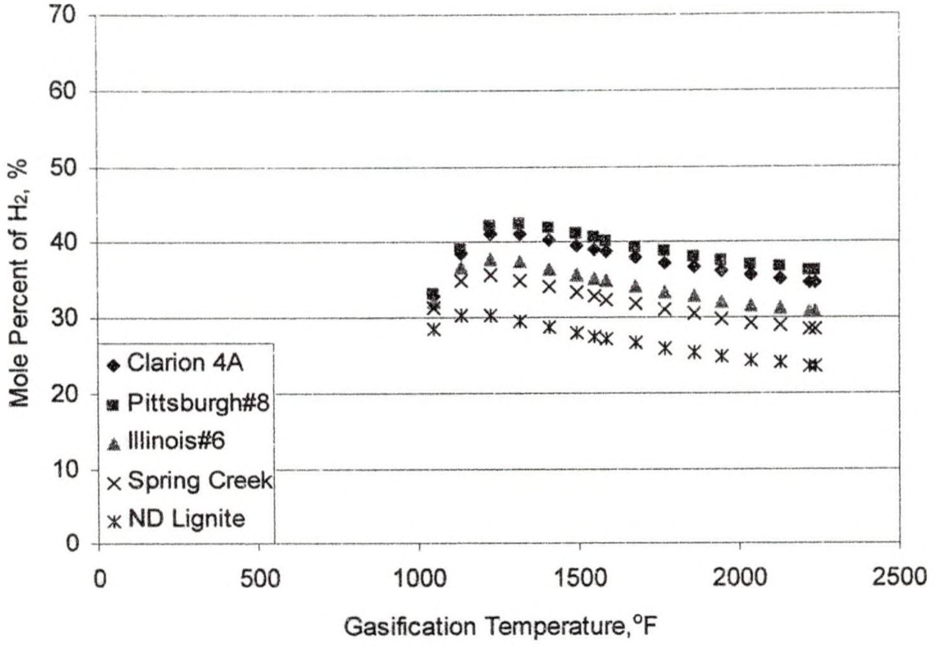


Figure 24. $H_2$ Concentration of Various Coals with Temperature on Wet Basis

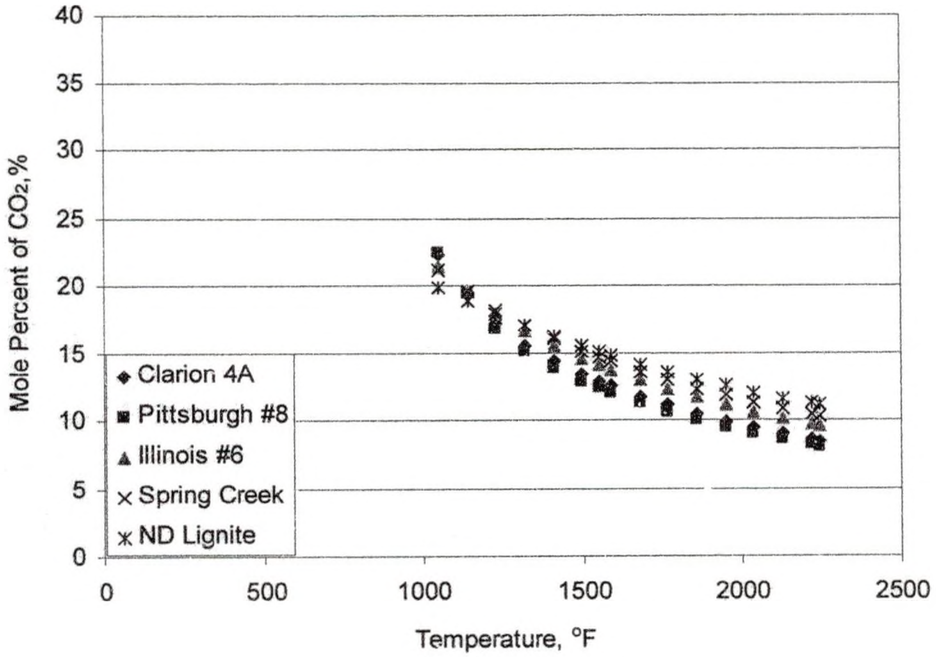


Figure 25. $CO_2$ Concentration of Various Coals with Temperature on Wet Basis

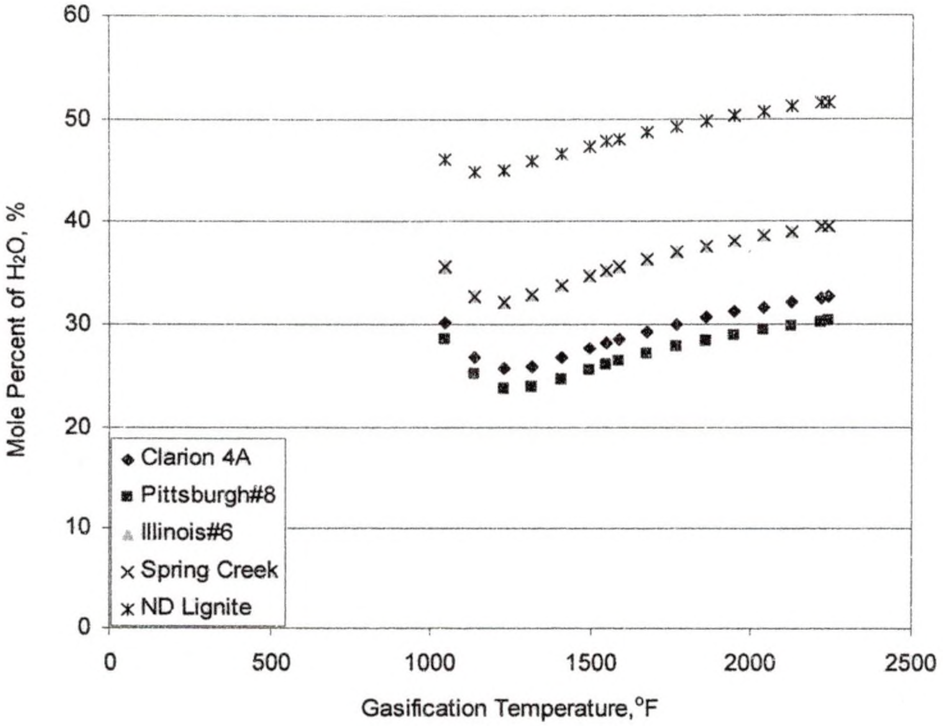


Figure 26. $H_2O$ Concentration of Various Coals with Temperature on Wet Basis

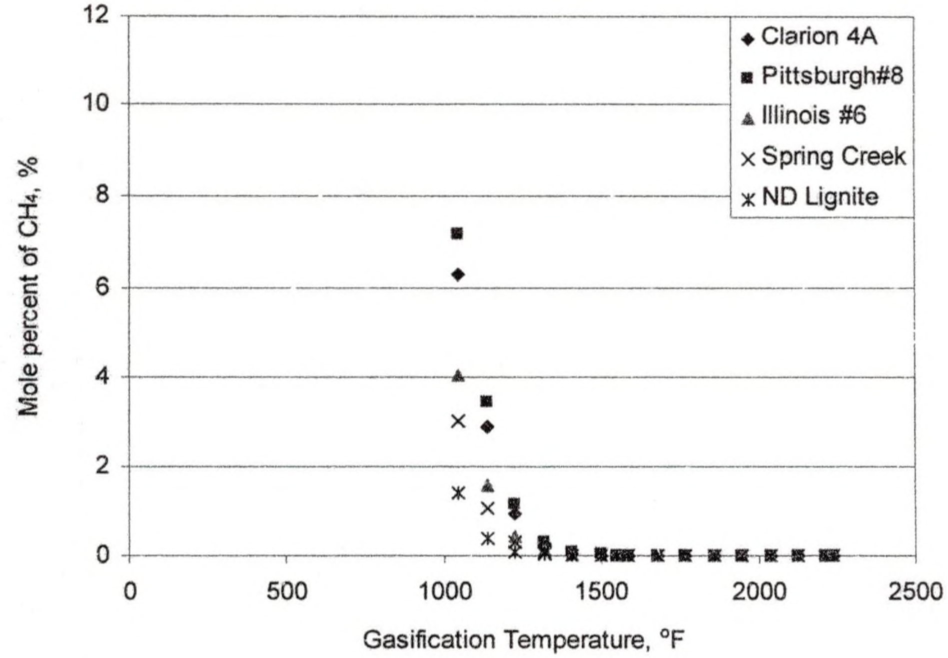


Figure 27. $CH_4$ Concentration of Various Coals with Temperature on Wet Basis

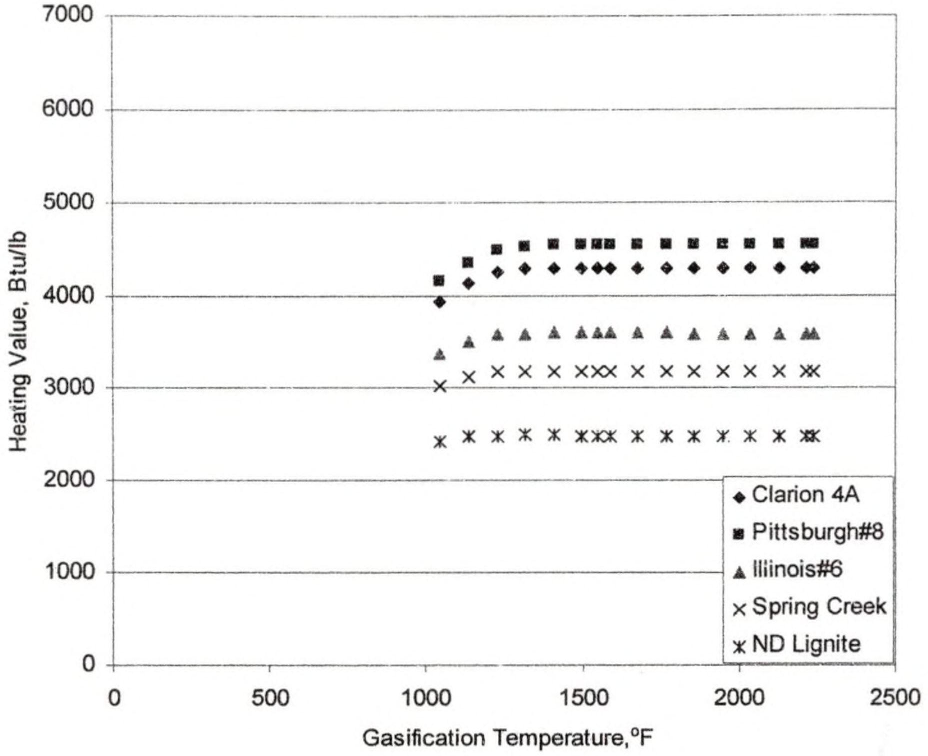


Figure 28. Heating Value of Syngas for Various Coals with Temperature on Wet Basis

The product composition for the coals was also calculated on a dry basis and these give the same trends as with the wet basis. Figures 29 through 33 illustrate the trend of syngas composition and heating value as a function of temperature on a dry basis and tables 27 through 31 in Appendix B show the numerical values. In this case, it gives the CO composition ranging from 6 to 36 percent. The output for $H_2$ ranges from 46-58 percent and for $CO_2$ it is 10-38 percent. On a wet basis, the CO composition ranges from 13-25 % and $H_2$ from 24-37 for different coals and temperatures. The comparison of CO and $H_2$ trends and heating value on wet and dry bases showed that the dry basis trends are less variable with respect to coal types but have the same general trend as on a wet basis.

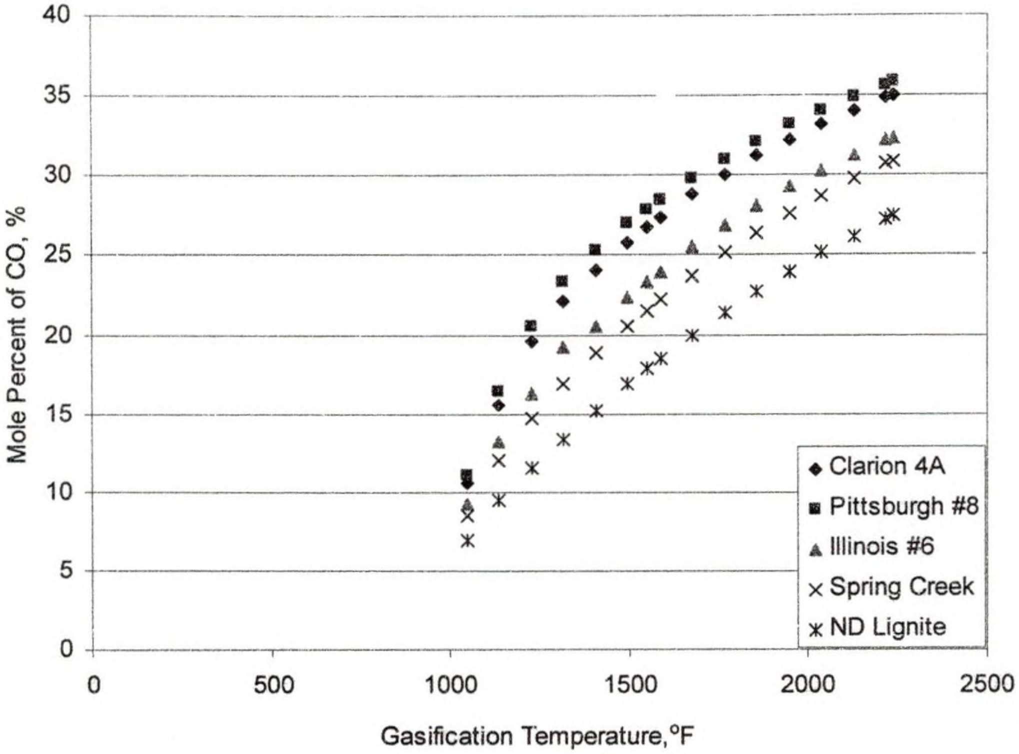


Figure 29. CO Concentration for Various Coals with Temperature on Dry Basis

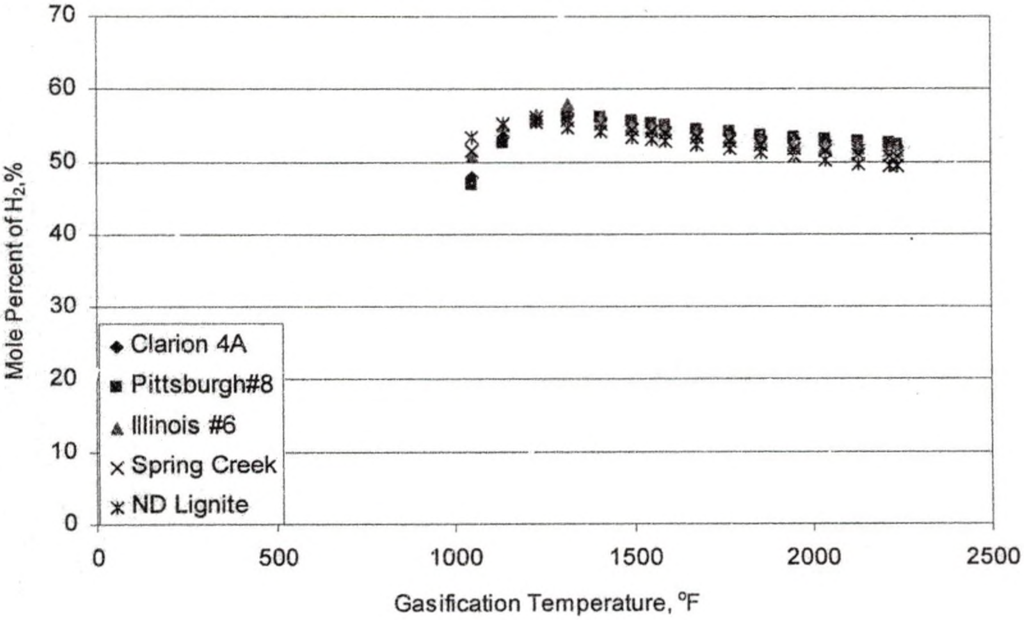


Figure 30. $H_2$ Concentration of Various Coals with Temperature on Dry Basis

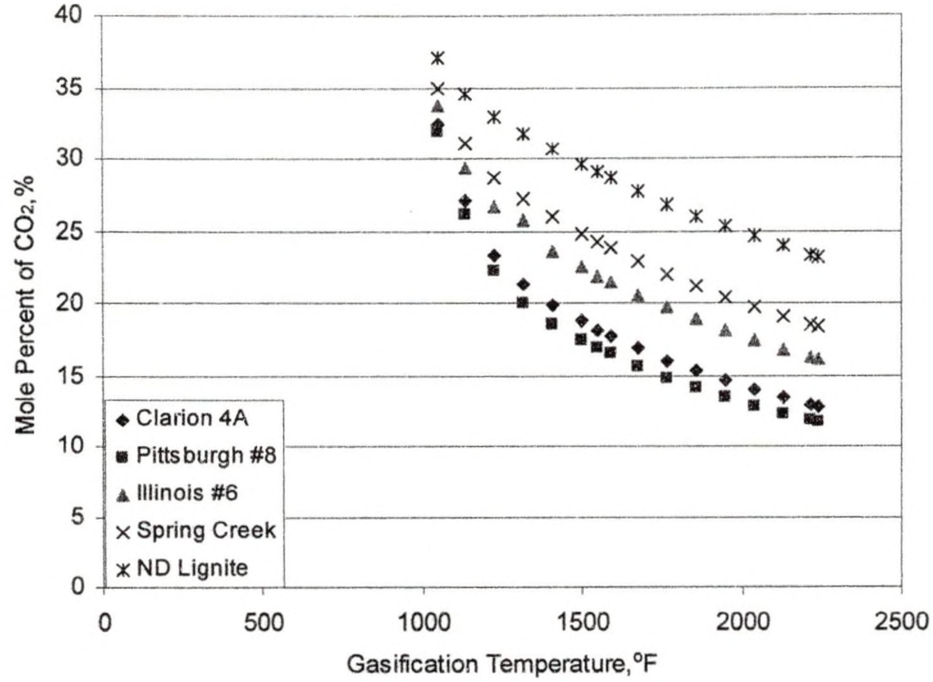


Figure 31. $CO_2$ Concentration of Various Coals with Temperature on Dry Basis

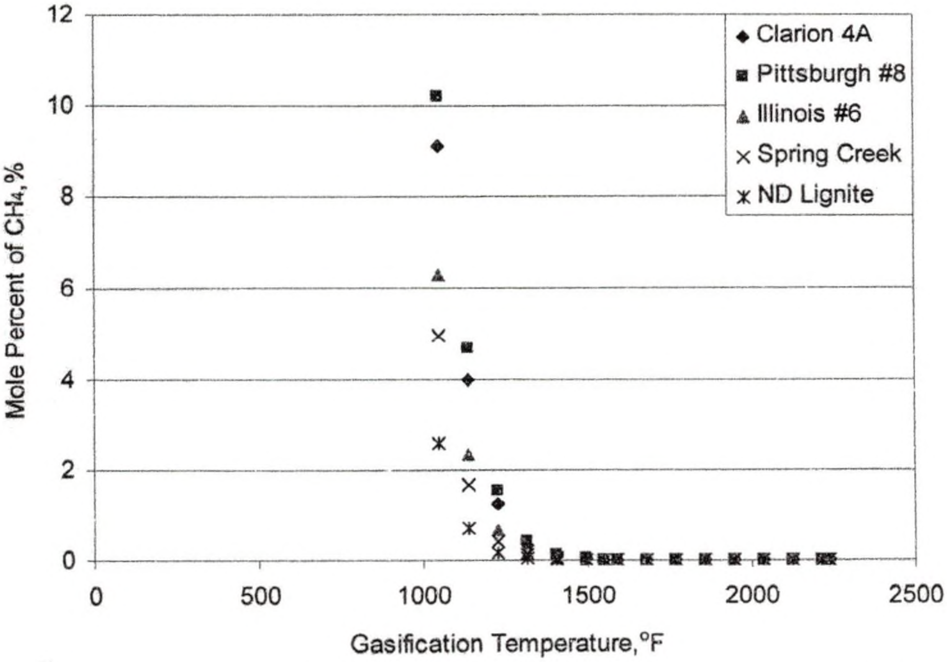


Figure 32. $CH_4$ Concentration of Various Coals with Temperature on Dry Basis

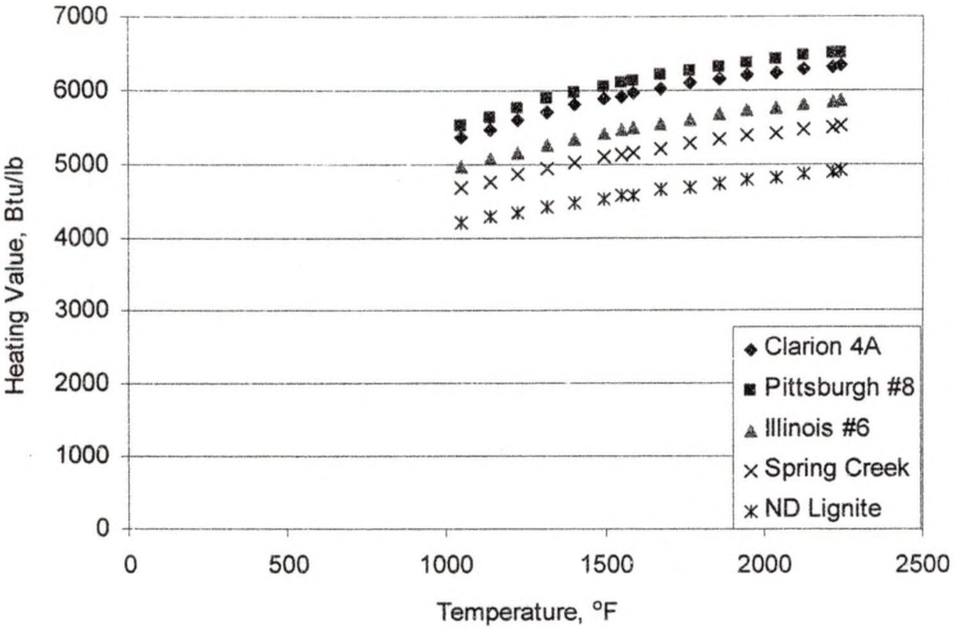


Figure 33. Heating Value of Syngas for Various Coals with Temperature on Dry Basis

On the basis of the above discussions, it can be said that 1320°F (715°C) is the maximum temperature if $H_2$ production is the main focus such as for use in a fuel cell. The gasification temperature of 1500°F (815°C) is the optimal temperature to generate syngas with a higher heating value for use in turbines.

### *5.3.2 Steam Flow Rate Variation*

The simulation for Clarion 4A was performed at different steam flow rates to check the effect of the $H_2O$ to carbon ratio on produced syngas composition. These simulation results were compared with the experimental data. In all cases, the trend of concentration with steam flow rate was the same but the numerical values were different. Figures 34 through 40 illustrate the trend for burner temperature, syngas composition and heating value change with increase in $H_2O/C$ ratio on wet basis. Table 32 in appendix C presents the numerical values. There are several possible explanations for these

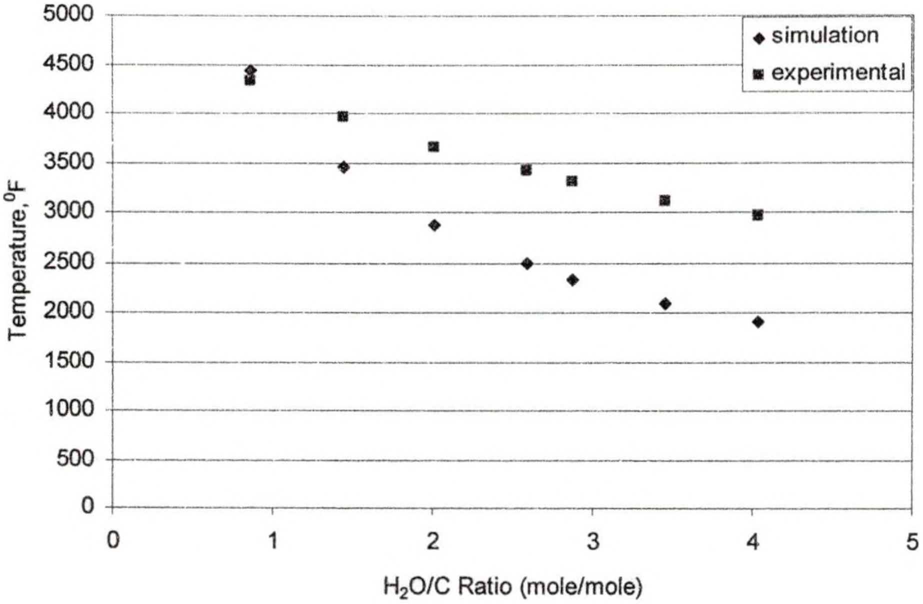


Figure 34. BURNER Temperature Variation with Steam Flow Rate

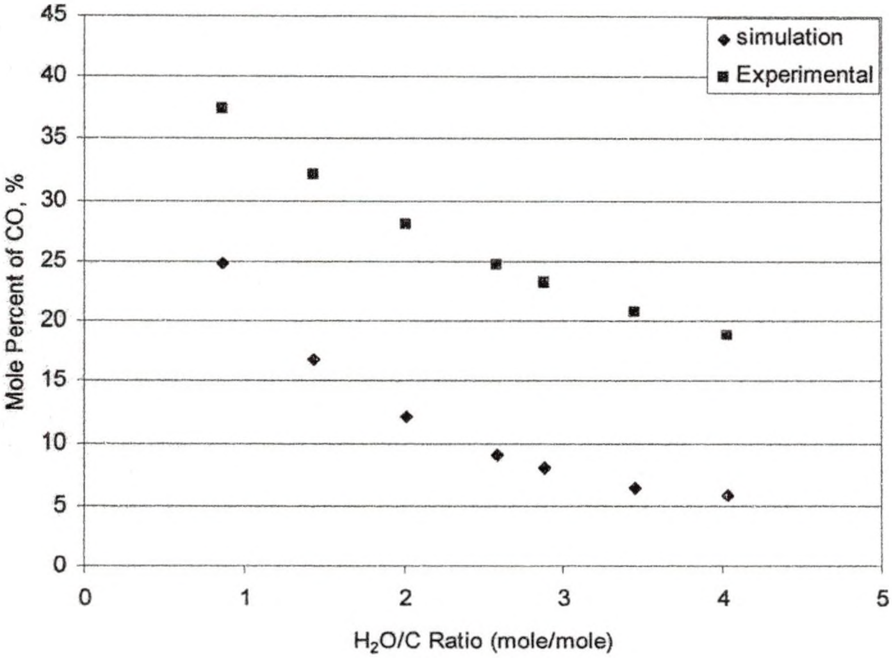


Figure 35. CO Concentration Variation with Steam Flow Rate on Wet Basis

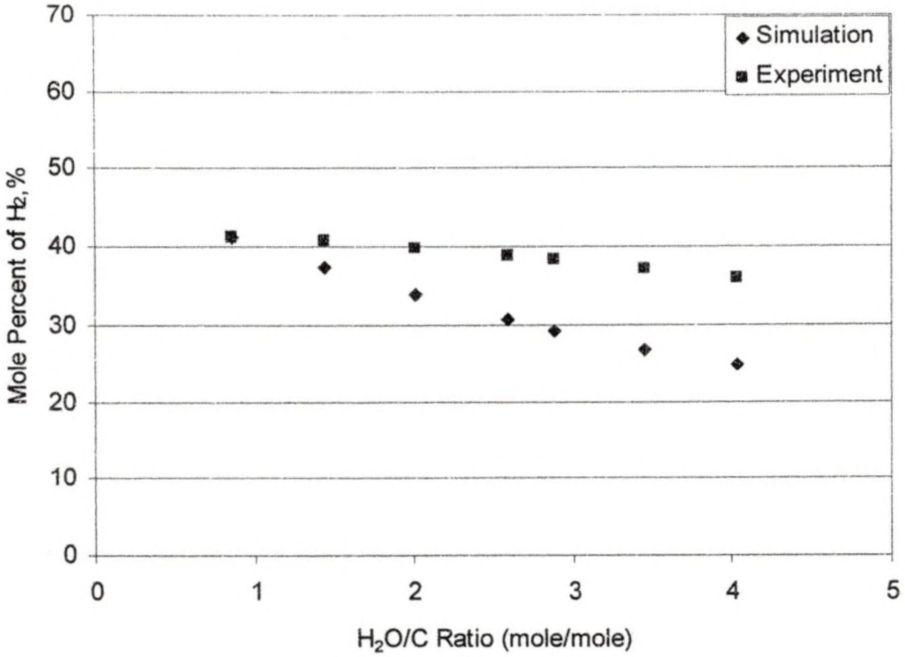


Figure 36. $H_2$ Concentration Variation with Steam Flow Rate on Wet basis

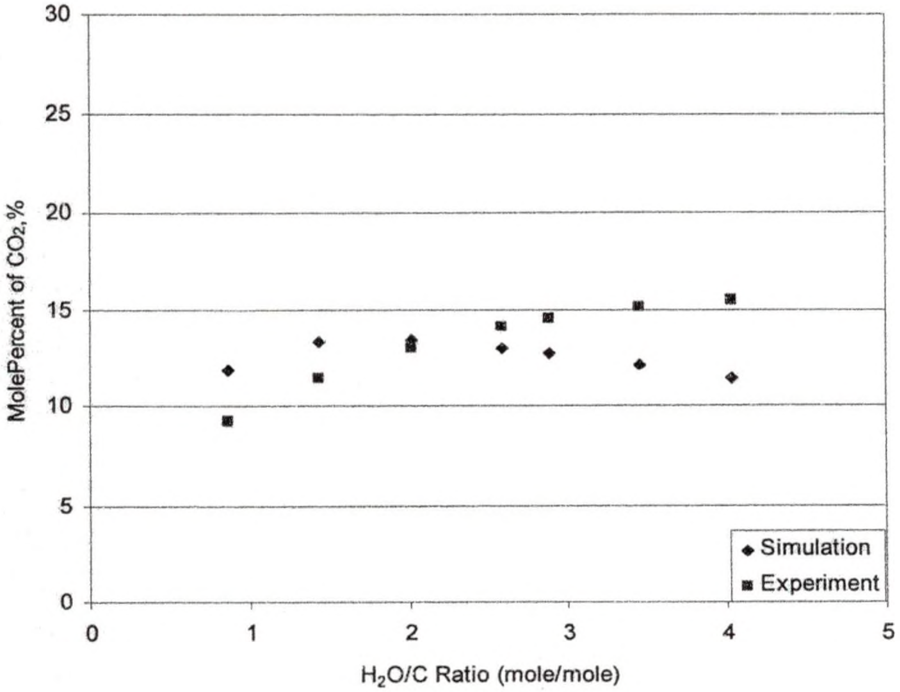


Figure 37. $CO_2$ Concentration Variation with Steam Flow Rate on Wet Basis

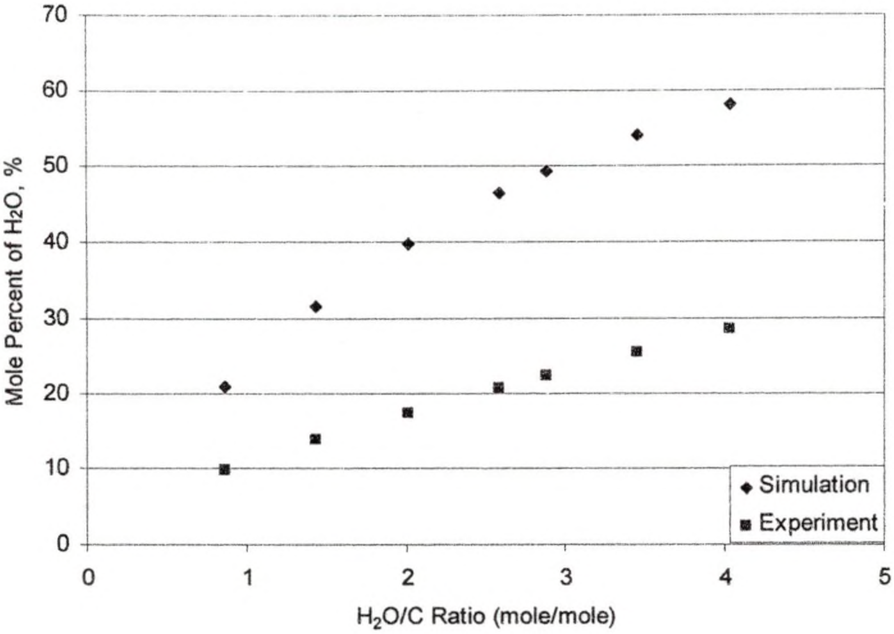


Figure 38. $H_2O$ Concentration Variation with Steam Flow Rate on Wet Basis

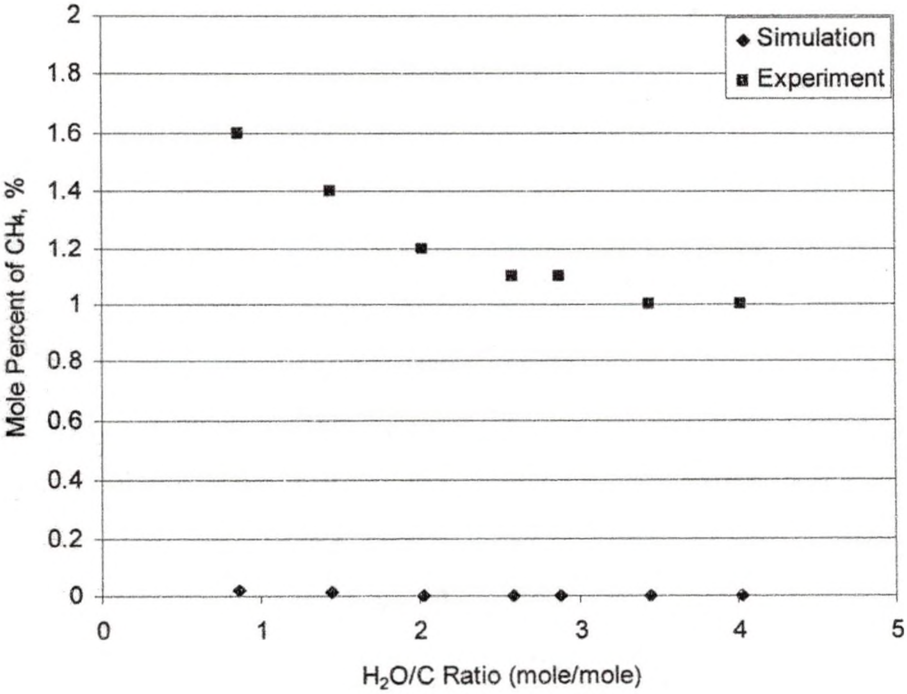


Figure 39. $CH_4$ Concentration Variation with Steam Flow Rate on Wet Basis

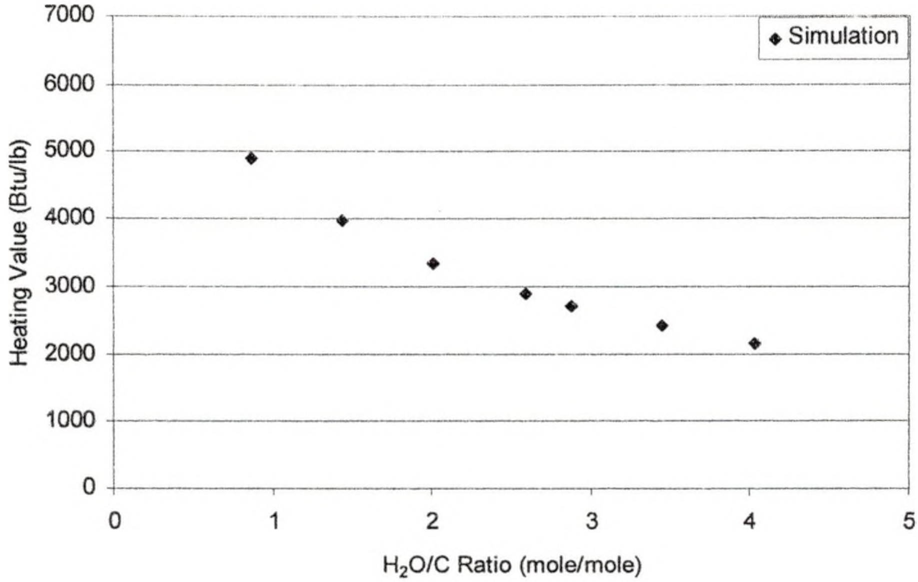


Figure 40. Heating Value Variation with Steam Flow Rate for Model Output on Wet Basis

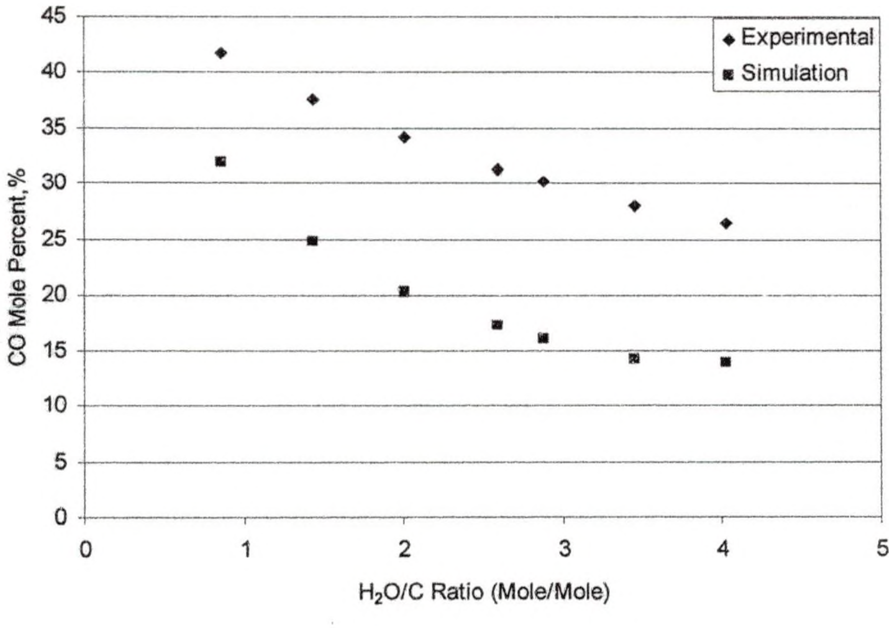


Figure 41. CO Concentration Variation with Steam Flow Rate on Dry Basis

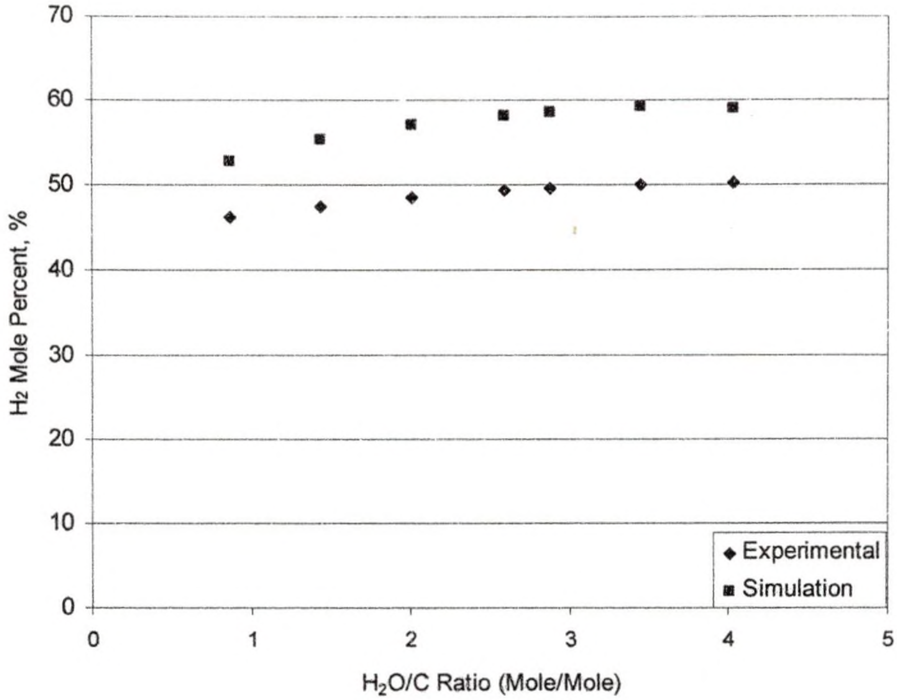


Figure 42. $H_2$ Concentration Variation with Steam Flow Rate on Dry basis

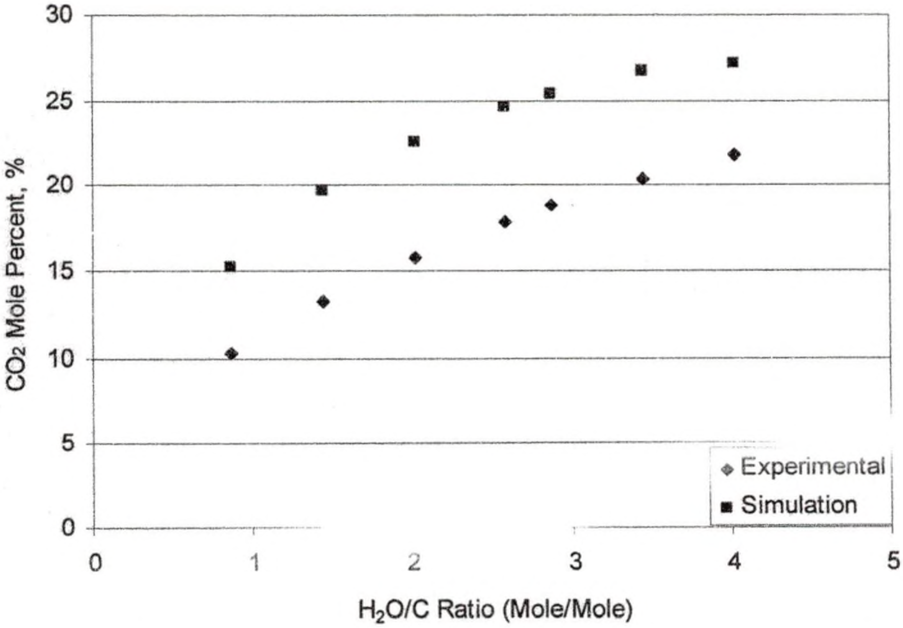


Figure 43. $CO_2$ Concentration Variation with Steam Flow Rate on Dry Basis

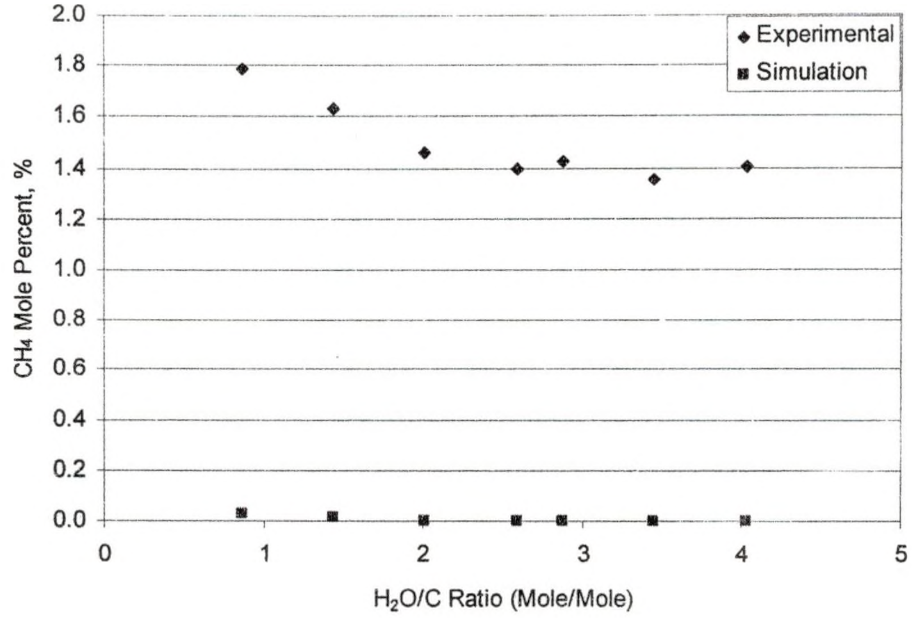


Figure 44. $CH_4$ Concentration Variation with Steam Flow Rate on Dry Basis

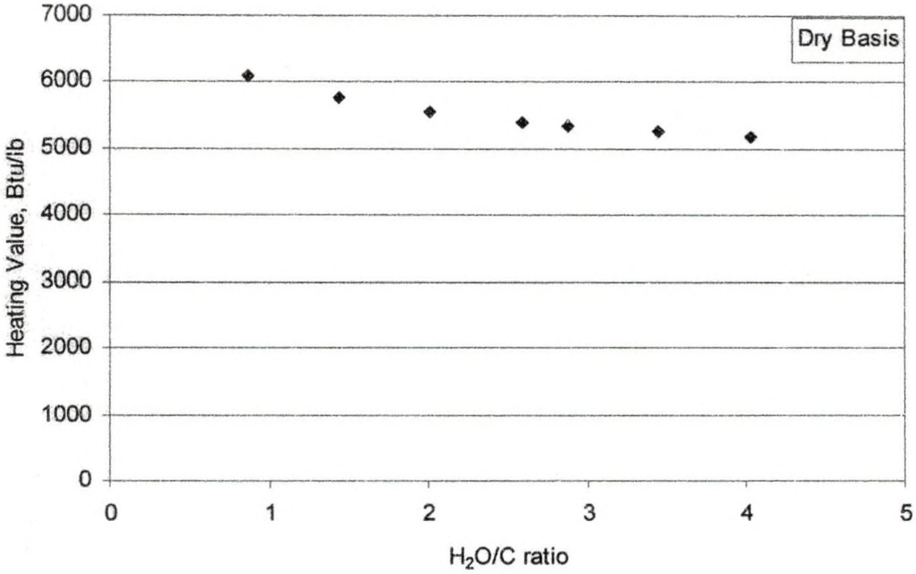


Figure 45. Heating Value Variation with Steam Flow Rate on Dry Basis

differences. The presence of $CH_4$ in the experimental output indicates the experimental data was not equilibrium conditions and might be one of the significant reasons behind the differences. Figure 39 predicts the $CH_4$ composition for the base case experimental condition at a $H_2O/C$ ratio of 1.4 mole%.

Figure 34 shows the experimental burner temperature higher than the simulation result. The model calculates the adiabatic temperature, so the opposite should be true since in the real situation heat losses were experienced. If the steam flow rate is over reported in the experimental data then it might give the higher burner temperature than the simulated burner temperature calculated using the same steam flow rate data. Another possibility may be localized hot spots in the flame due to less than perfect mixing. There may have been some problems with the thermocouples used for temperature measurements in the burner section.

For CO, the trend for both simulation and experiment was the same but concentrations were different. This difference might be explained with the same component mole balance approach. Ohio University used a Nova $CO/CO_2/O_2/H_2$ analyzer to measure gas concentration and $H_2$ concentration is determined by TCD differentiation. The gas was dried with a condenser and the moisture was measured by condensation. This presents the run average $H_2O$ composition and may give a moisture concentration with low accuracy which could explain the lower $H_2O$ concentration in the experimental product gas. The error in $H_2O$ analysis technique would impact the reported $H_2$, CO and $CO_2$ concentrations. More importantly, the trend of $H_2$ composition was decreasing in both simulation and experimental output. As discussed previously, the high CO and low $H_2$ values from the experiment as compared to the model indicates the water-gas shift reaction was probably not at equilibrium.

For $CO_2$, the concentration trend from simulation with $H_2O/C$ differs from the experiment. For simulation, the $CO_2$ maintained its increasing trend for a $H_2O/C$ ratio up to 2 and within that range the model concentration for $CO_2$ was higher than experimental $CO_2$. After a $H_2O/C$ ratio of 2, the $CO_2$ component gave a decreasing trend and the concentration values were less than the $CO_2$ concentration from the experiment.

The $CH_4$ concentration decreases with $H_2O/C$ ratio, which favors the hypothesis that steam gasification favors the methane decomposition reaction. The presence of $CH_4$ in the experimental output indicates the gasification reactor did not achieve equilibrium. The heating value trend with an increase in $H_2O/C$ ratio in figure 40 shows that it decreases due to $H_2O$ in the product gas for the model. The experimental heating value was not available.

To separate the effects of dilution due to the higher flow rates of $H_2O$, the gas analysis was compared on a dry basis. Figures 41 through 45 compare the dry gas composition and heating value for the simulation and experimental results. Table 33 in appendix C presents the numerical values of syngas composition and heating values on dry basis. For CO concentration, the dry basis gives almost the same trend and concentration difference between experimental and simulation results. The CO decreases with increasing $H_2O/C$ ratio. For $H_2$, the dry basis presents an increasing trend and the trend was similar for both simulation and model concentration while the trend was decreasing on a wet basis. This implies that increasing steam flow rate offsets the increase of $H_2$ concentration when it was calculated on wet basis and demonstrates that higher steam flow rate favors $H_2$ production.

For $CO_2$ concentration, the dry basis gives an increasing trend for both experimental and simulation output while the trend for simulation after a $H_2O/C$ ratio of 2 was decreasing on a wet basis. This can be explained with the same offsetting reason for $H_2$ with increase in $H_2O$ at high $H_2O/C$ ratio. As the $H_2O$ feed concentration increases, the water-gas shift reaction moves to the right favoring higher $H_2$ and $CO_2$ at the expense of CO.

The $CH_4$ concentration gives the similar trend on both wet and dry basis which again supports the assumption that steam gasification favors the methane decomposition reaction.

The heating value gives the decreasing trend on dry basis same as on wet basis. On dry basis, the heating value ranges from 5200 Btu/lb to 6100 Btu/lb while the heating value range was 2200 Btu/lb to 4900 Btu/lb on a wet basis.

It can be concluded that steam gasification favors $H_2$ production in the sense that $H_2$ in the product gas exceeds the original $H_2$ in the coal because of using steam. But increasing the steam flow rate ($H_2O/C$ ratio) gives a syngas higher in $H_2O$ and lower in $H_2$ and decreases the heating value due to the dilution effect of the $H_2O$. If the extra moisture can be condensed and separated from the syngas then, $H_2$ concentration is found to give a higher yield and a higher heating value as the $H_2O/C$ ratio increases.

On a wet basis, $H_2$ concentration for the experimental output varies in the decreasing range from 41 to 35% and for simulation output $H_2$ gives the range of 41 to 24% for $H_2O/C$ ratios from 0.9 to 4. On a dry basis, $H_2$ varies from 46 to 50% for experimental data and varies from 53 to 59% for simulation output over the same range of $H_2O/C$ ratios. $H_2$ concentration increases most rapidly for a $H_2O/C$ ratio up to 2.6, after which the concentration increases little followed a nearly constant concentration for $H_2O/C$ ratios of 3.5 and 4 on a dry basis. This implies an optimized $H_2O/C$ ratio of 3.5 for $H_2$ enriched syngas.

# CHAPTER 6

# CONCLUSIONS AND FUTURE RECOMMENDATIONS

## 6.1 Conclusions

The research issue of this project was to evaluate the new gasifier built at Ohio University which performs USS gasification. A thermo equilibrium model was developed in ASPEN PLUS to predict the syngas composition and heating value. Results from this modeling were used to test the following hypotheses:

- The zero-order thermodynamic equilibrium model will accurately predict the performance of experimental set-up of USS gasifier at Ohio with syngas composition and heating value calculation.
- The model will provide information to allow evaluation of the experiment with sensitivity analysis.

The model determined the product composition calculation first and then combusted the gas with oxygen lowering its temperature to 77°F (25°C). The base case fuel Clarion 4A coal gives the syngas composition of 39% $H_2$, 19% CO, 13% $CO_2$ and 28% $H_2O$. The comparison gives the different syngas composition for experimental and simulation output. The difference was explained with dry gas analysis data, elemental mole balance and adjusted experimental data, equilibrium constant values. This analysis indicated that a zero-order model cannot predict the performance of the USS gasifier and a 3-dimensional model that includes both kinetic and transport capabilities is required.

This model proves the feasibility of USS gasifier for $H_2$ enriched syngas. 3.5 moles $H_2$ was present in the syngas for every mole of hydrogen in the coal because of using USS as gasifying agent.

The USS gasifier produces a medium calorific value gas with a higher heating value of 4300 Btu/lb (254 Btu/scf) on ash free basis for the base case of a 1.25 $H_2O/C$ ratio and 1550°F gasification temperature. Typical air blows gasifiers produce syngas with a higher heating value ranging from 130 Btu/scf to 190 Btu/scf. This supports the use of USS gasifier as energy efficient for producing higher heating value gas with USS gasification compared to air gasification.

The gasification simulation was done with Pittsburgh #8, Illinois # 6, Spring Creek Subbituminous and ND Lignite coals. The gas composition and heating value were compared for all five coals on a dry and weight basis. Pittsburgh# 8 and Clarion # 4A were quite similar in composition and gave more favorable syngas compositions consisting of more CO and $H_2$ compared with the others. These coals also produce of higher heating value syngas. A comparison of the product gas on a moisture free basis indicates the simulation gives nearly the same $H_2$ composition for all coals. So it implies that drying of coals before gasification can improve the syngas composition and also the heating value due to absence of the dilution effect of $H_2O$ in the syngas.

A sensitivity analysis was performed varying the temperature and steam flow rate. The temperature variation for the base fuel Clarion #4A suggests the gasification at 1320°F gives the maximum $H_2$ in the product gas. Gasification at 1410°F produces the highest heating value for syngas and after 1407°F, the heating value remains the same.

For the other four coals used in this modeling, the trend for composition and heating value was found similar to that found for the Clarion 4A coal.

The steam flow rate was varied and the effect of $H_2O$ to carbon ratio on gas composition was compared between model and experimental data. The trend was similar on a wet basis for both model and experimental output except for $CO_2$. For $CO_2$, the model trend was increasing up to a $H_2O/C$ ratio of 2 that was similar with the trend of the experiment. Above a $H_2O/C$ ratio of 2, the $CO_2$ concentration for the model exhibits a decreasing trend. The heating value also decreases with increase in $H_2O/C$ ratio primarily due to the dilution effect of extra moisture.

A comparison between experimental and simulation composition on a dry basis shows a similar trend for both but gives different trends for some components from the wet basis. On dry basis, the $CO_2$ keeps an increasing trend even after $H_2O/C$ ratio of 2 and for $H_2$ it gives the increasing trend which was decreasing on a wet basis. The increasing trend of $H_2$ and $CO_2$ for the $H_2O/C$ ratio of 0.9 to 4.0 can be explained with the absence of $H_2O$ in syngas composition on a dry basis. The increase of steam flow rate offsets the increasing trend of $H_2$ and $CO_2$ above a $H_2O/C$ ratio of 2 with increase of $H_2O$ in syngas on a wet basis. The calculation on a dry basis implies that the $H_2O/C$ ratio of 3.5 is the optimal for $H_2$ enriched syngas.

On the basis of the above discussion based, the sensitivity analysis is found to be useful for operating conditions preferable for higher $H_2$ concentration in syngas. This proves the hypothesis that the model provides useful information for improvement of the experiment.

## 6.2 Recommendations

The model presented in this report performs its calculation for the USS gasification process based on minimum Gibbs free energy which conveys the system at equilibrium. In practical situations, no process reaches equilibrium. Moreover, the experimental tests are short tests and may not be at steady state. This could cause a big difference between experimental composition and that of simulation output. Only the flow-rates and pressure and temperature of gasification were known. To get a complete idea about the process, including kinetic of reaction mechanisms and continuous product composition, several more experiments should be performed. The kinetic rate constants and equlibrium constants from the results indicates the water-gas-shift and methane decomposition reaction reaches equlibrium faster using all reactants than the Boudouard reaction. So development of a kinetic model with transport phenomena consideration with data verified by the required experiments would provide a valuable tool for complete evaluation of the USS gasifier.

Though USS gasification is expected to convert all hydrocarbons into syngas, some tars are still formed during gasification. If tar formation could be measured spontaneously then it might be possible to develop predictors for some of the major tars. In the present model one unit operation block, a RYIELD reactor named as DEVOLTZR is inserted to calculate the tars using equations presented by Pickett [6]. Actual data from the USS gasifier would help predict the tar formation and allow development of the required cleaning measures.

The model does not give detailed information about the reaction mechanisms for either the major reactions or other reactions involving undesired side products. A three-dimensional model which can show the events taking place during gasification within the fluidized bed reactor is the suitable tool to give a clear understanding along with the present equilibrium model. Since water-gas-shift reaction plays a significant role in gasification and it reaches equilibrium fast, the equlibrium of this reaction is supposed to be controlled by diffusion limitation. To develop an accurate three-dimensional model some experimentation would be needed to get the data for model input.

The temperature is assumed to be constant throughout the whole gasifier because of uniform mixing characteristics of fluidized bed. Several thermocouples could be added along with bed height to check the temperature. If the temperature is not the same in the top, middle and bottom part of the reactor then each section of the gasifier can be modeled with each individual unit operation block with its own design specification.

# APPENDICES

# APPENDIX A

## FORTRAN STATEMENTS

In this section the FORTRAN statements used in the model are reported. The statements with variable definition for FORTRAN blocks DCOMP, GASIF and DEVOL are presented.

### CALCULATOR BLOCK: DCOMP

```
-------------------------

 SAMPLED VARIABLES:
   HCOAL    : MOLE ENTHALPY IN STREAM COAL SUBSTREAM NCPSD
   HCOMP    : MASS ENTHALPY IN STREAM INDEVOL SUBSTREAM MIXED
   HDCOMP   : SENTENCE=PARAM VARIABLE=NET-DUTY IN UOS BLOCK
DECOM
   MCOAL    : TOTAL MASSFLOW IN STREAM COAL SUBSTREAM NCPSD

 FORTRAN STATEMENTS:

      HDCOMP = (HCOAL - HCOMP)* MCOAL
```

```
                    CALCULATOR BLOCK:   GASIF
                    -------------------------

                       SAMPLED VARIABLES:
 ULT     : COMPONENT-AT VEC IN STREAM COAL SUBSTREAM NCPSD ID:
     ULTANAL
 WAT      : COMP-ATTR-VA IN STREAM COAL SUBSTREAM NCPSD ID:
     PROXANAL
 WATR     : SENTENCE=MASS-YIELD VARIABLE=YIELD ID1=MIXED
     ID2=STEAM IN UOS
       BLOCK DECOM
 ASH      : SENTENCE=MASS-YIELD VARIABLE=YIELD ID1=NCPSD ID2=ASH
     IN UOS
       BLOCK DECOM
 CARB     : SENTENCE=MASS-YIELD VARIABLE=YIELD ID1=CIPSD ID2=C IN
     UOS BLOCK
       DECOM
 H2       : SENTENCE=MASS-YIELD VARIABLE=YIELD ID1=MIXED ID2=H2 IN
     UOS
       BLOCK DECOM
 N2       : SENTENCE=MASS-YIELD VARIABLE=YIELD ID1=MIXED ID2=N2 IN
     UOS
       BLOCK DECOM
 SULF     : SENTENCE=MASS-YIELD VARIABLE=YIELD ID1=MIXED ID2=S IN
     UOS BLOCK
       DECOM
 O2       : SENTENCE=MASS-YIELD VARIABLE=YIELD ID1=MIXED
     ID2=OXYGEN IN UOS
       BLOCK DECOM

FORTRAN STATEMENTS:
C    FACT IS THE FACTOR TO CONVERT THE ULTIMATE ANALYSIS TO
C    A WET BASIS.
     FACT = (100 - WAT) / 100
     WATR = WAT/100
     ASH  = ULT (1) / 100 * FACT
     CARB = ULT (2) / 100 * FACT
     H2   = ULT (3) / 100 * FACT
     N2   = ULT (4) / 100 * FACT
     CL2  = ULT (5) / 100 * FACT
     SULF = ULT (6) / 100 * FACT
     O2   = ULT (7) / 100 * FACT
```

## CALCULATOR BLOCK: DEVOL

### SAMPLED VARIABLES:

PHENOL : PHENOL MASSFLOW IN STREAM INGASIF SUBSTREAM MIXED
NAPTHA : NAPTHA MASSFLOW IN STREAM INGASIF SUBSTREAMMIXED
OIL : OIL MASSFLOW IN STREAM INGASIF SUBSTREAM MIXED
CDVOL : C MASSFLOW IN STREAM INGASIF SUBSTREAM CIPSD
H2DVOL : H2 MASSFLOW IN STREAM INGASIF SUBSTREAM MIXED
O2DVOL : OXYGEN MASSFLOW IN STREAM INGASIF SUBSTREAM MIXED
COAFW : TOTAL MASSFLOW IN STREAM INDEVOL SUBSTREAM MIXED
FUSSTM : TOTAL MASSFLOW IN STREAM SPRHTSTM SUBSTREAM MIXED
USTR : STEAM MASSFLOW IN STREAM SPRHTSTM SUBSTREAM MIXED
UCO2 : CO2 MASSFLOW IN STREAM SPRHTSTM SUBSTREAM MIXED
STDVO : STEAM MASSFLOW IN STREAM INGASIF SUBSTREAM MIXED
CO2DVO : CO2 MASSFLOW IN STREAM INGASIF SUBSTREAM MIXED
UO2 : OXYGEN MASSFLOW IN STREAM SPRHTSTM SUBSTREAM MIXED
N2DVO : N2 MASSFLOW IN STREAM INGASIF SUBSTREAM MIXED
SDVO : S MASSFLOW IN STREAM INGASIF SUBSTREAM MIXED
ASHDVO : ASH MASSFLOW IN STREAM INGASIF SUBSTREAM NCPSD
CDCOM : C MASSFLOW IN STREAM INDEVOL SUBSTREAM CIPSD
O2DCOM : OXYGEN MASSFLOW IN STREAM INDEVOL SUBSTREAM MIXED
H2ODCO : STEAM MASSFLOW IN STREAM INDEVOL SUBSTREAM MIXED
N2DCOM : N2 MASSFLOW IN STREAM INDEVOL SUBSTREAM MIXED
SDCOM : S MASSFLOW IN STREAM INDEVOL SUBSTREAM MIXED
ASDCOM : ASH MASSFLOW IN STREAM INDEVOL SUBSTREAM NCPSD
H2DCO : H2 MASSFLOW IN STREAM INDEVOL SUBSTREAM MIXED

### FORTRAN STATEMENTS:

```
C     FACT2 IS THE FACTOR TO CONVERT THE MASS FLOW TO
C     MASS FRACTION.

      FACT2 = 1 / (COAFW + FUSSTM)
      PHENOL = 0.002463 * COAFW * FACT2
      NAPTHA = 0.007450 * COAFW * FACT2
      OIL = 0.02031 * COAFW * FACT2
      CDVOL = CDCOM*FACT2 - PHENOL*72/94 - NAPTHA*132/142 -
       OIL*120/138
      H2DVOL = H2DCO*FACT2 - PHENOL*6/94 - NAPTHA*10/142 - OIL*18/138
      O2DVOL = O2DCOM*FACT2 + UO2*FACT2 - PHENOL*16/94
```

```
STDVO = (USTR + H2ODCO)*FACT2
CO2DVO = UCO2*FACT2
N2DVO = N2DCOM*FACT2
SDVO = SDCOM*FACT2
ASHDVO = ASDCOM*FACT2
```

# APPENDIX B

## MODEL OUTPUT FOR TEMPERATURE VARIATIONS

In this section the product gas composition and heating value with temperature variation is presented for various coals in tables 22 through 31 will show those results.

Table 22. Effect of Temperature Variation on Clarion 4A Coal on Wet Basis

| Gasifier Temperature | Molar Composition in Percent | | | | | Heating Value |
|---|---|---|---|---|---|---|
| °F | CO | $H_2$ | $CO_2$ | $H_2O$ | $CH_4$ | Btu/lb |
| 1050 | 7 | 33 | 22 | 30 | 6 | 3940 |
| 1140 | 11 | 38 | 19 | 27 | 3 | 4120 |
| 1220 | 14 | 41 | 17 | 26 | 1 | 4240 |
| 1320 | 16 | 41 | 16 | 26 | 0.24 | 4280 |
| 1410 | 17 | 40 | 14 | 27 | 0.06 | 4290 |
| 1500 | 18 | 39 | 13 | 28 | 0.02 | 4290 |
| 1550 | 19 | 39 | 13 | 28 | 0.01 | 4290 |
| 1590 | 19 | 39 | 12 | 29 | 0.01 | 4290 |
| 1680 | 20 | 38 | 12 | 29 | 0.00 | 4290 |
| 1770 | 21 | 37 | 11 | 30 | 0.00 | 4290 |
| 1860 | 21 | 37 | 10 | 31 | 0.00 | 4290 |
| 1950 | 22 | 36 | 10 | 31 | 0.00 | 4280 |
| 2040 | 22 | 36 | 10 | 32 | 0.00 | 4280 |
| 2130 | 23 | 35 | 9 | 32 | 0.00 | 4280 |
| 2220 | 23 | 35 | 9 | 32 | 0.00 | 4280 |
| 2240 | 23 | 35 | 8 | 33 | 0.00 | 4280 |

Table 23. Effect of Temperature Variation on Pittsburgh #8 Coal on Wet Basis

| Gasifier Temperature | Molar Composition in Percent | | | | | Heating Value |
|---|---|---|---|---|---|---|
| °F | CO | $H_2$ | $CO_2$ | $H_2O$ | $CH_4$ | Btu/lb |
| 1050 | 8 | 33 | 22 | 29 | 7.2 | 4140 |
| 1140 | 12 | 39 | 19 | 25 | 3.5 | 4340 |
| 1230 | 16 | 42 | 17 | 24 | 1.2 | 4470 |
| 1320 | 18 | 42 | 15 | 24 | 0.3 | 4520 |
| 1410 | 19 | 42 | 14 | 25 | 0.1 | 4530 |
| 1500 | 20 | 41 | 13 | 26 | 0.0 | 4540 |
| 1550 | 20 | 40 | 12 | 26 | 0.0 | 4540 |
| 1590 | 21 | 40 | 12 | 26 | 0.0 | 4540 |
| 1680 | 21 | 39 | 11 | 27 | 0.0 | 4540 |
| 1770 | 22 | 39 | 11 | 28 | 0.0 | 4530 |
| 1860 | 23 | 38 | 10 | 28 | 0.0 | 4530 |
| 1950 | 23 | 37 | 9 | 29 | 0.0 | 4530 |
| 2040 | 24 | 37 | 9 | 29 | 0.0 | 4530 |
| 2130 | 24 | 37 | 9 | 30 | 0.0 | 4530 |
| 2220 | 25 | 36 | 8 | 30 | 0.0 | 4530 |
| 2240 | 25 | 36 | 8 | 30 | 0.0 | 4530 |

Table 24. Effect of Temperature Variation on Illinois #6 Coal on Wet Basis

| Gasifier Temperature | Molar Composition in Percent | | | | | Heating Value |
|---|---|---|---|---|---|---|
| °F | CO | $H_2$ | $CO_2$ | $H_2O$ | $CH_4$ | Btu/lb |
| 1050 | 5.83 | 32.19 | 21.46 | 35.62 | 4.01 | 3380 |
| 1140 | 8.79 | 36.53 | 19.52 | 32.73 | 1.57 | 3510 |
| 1230 | 10.95 | 37.78 | 17.84 | 32.16 | 0.44 | 3580 |
| 1320 | 12.38 | 37.34 | 16.55 | 32.79 | 0.11 | 3600 |
| 1410 | 13.48 | 36.47 | 15.48 | 33.71 | 0.03 | 3600 |
| 1500 | 14.44 | 35.58 | 14.53 | 34.61 | 0.01 | 3600 |
| 1550 | 14.95 | 35.08 | 14.03 | 35.11 | 0.00 | 3600 |
| 1590 | 15.28 | 34.75 | 13.69 | 35.45 | 0.00 | 3600 |
| 1680 | 16.04 | 34.00 | 12.93 | 36.20 | 0.00 | 3600 |
| 1770 | 16.72 | 33.32 | 12.26 | 36.88 | 0.00 | 3600 |
| 1860 | 17.33 | 32.71 | 11.64 | 37.49 | 0.00 | 3600 |
| 1950 | 17.88 | 32.16 | 11.09 | 38.04 | 0.00 | 3600 |
| 2040 | 18.38 | 31.66 | 10.60 | 38.54 | 0.00 | 3600 |
| 2130 | 18.83 | 31.22 | 10.15 | 38.98 | 0.00 | 3600 |
| 2220 | 19.24 | 30.81 | 9.74 | 39.39 | 0.00 | 3600 |
| 2240 | 19.34 | 30.71 | 9.64 | 39.49 | 0.00 | 3600 |

Table 25. Effect of Temperature Variation on Spring Creek Coal on Wet Basis

| Gasifier Temperature | Molar Composition in Percent | | | | | Heating Value |
|---|---|---|---|---|---|---|
| °F | CO | $H_2$ | $CO_2$ | $H_2O$ | $CH_4$ | Btu/lb |
| 1050 | 5 | 31 | 21 | 39 | 3.0 | 3020 |
| 1140 | 8 | 35 | 20 | 36 | 1.1 | 3130 |
| 1230 | 9 | 36 | 18 | 36 | 0.3 | 3170 |
| 1320 | 11 | 35 | 17 | 37 | 0.1 | 3180 |
| 1410 | 12 | 34 | 16 | 38 | 0.0 | 3190 |
| 1500 | 13 | 33 | 15 | 39 | 0.0 | 3190 |
| 1550 | 13 | 33 | 15 | 39 | 0.0 | 3190 |
| 1590 | 13 | 32 | 14 | 40 | 0.0 | 3180 |
| 1680 | 14 | 32 | 14 | 40 | 0.0 | 3180 |
| 1770 | 15 | 31 | 13 | 41 | 0.0 | 3180 |
| 1860 | 15 | 30 | 12 | 42 | 0.0 | 3180 |
| 1950 | 16 | 30 | 12 | 42 | 0.0 | 3180 |
| 2040 | 16 | 29 | 11 | 43 | 0.0 | 3180 |
| 2130 | 17 | 29 | 11 | 43 | 0.0 | 3180 |
| 2220 | 17 | 29 | 10 | 43 | 0.0 | 3180 |
| 2240 | 17 | 28 | 10 | 44 | 0.0 | 3180 |

Table 26. Effect of Temperature Variation on ND Lignite on Wet Basis

| Gasifier Temperature | Molar Composition in Percent | | | | | Heating Value |
|---|---|---|---|---|---|---|
| °F | CO | $H_2$ | $CO_2$ | $H_2O$ | $CH_4$ | Btu/lb |
| 1050 | 4 | 29 | 20 | 46 | 1.4 | 2420 |
| 1140 | 5 | 30 | 19 | 45 | 0.4 | 2480 |
| 1230 | 6 | 30 | 18 | 45 | 0.1 | 2500 |
| 1320 | 7 | 30 | 17 | 46 | 0.0 | 2500 |
| 1410 | 8 | 29 | 16 | 47 | 0.0 | 2500 |
| 1500 | 9 | 28 | 15 | 47 | 0.0 | 2500 |
| 1550 | 9 | 28 | 15 | 48 | 0.0 | 2500 |
| 1590 | 10 | 27 | 15 | 48 | 0.0 | 2500 |
| 1680 | 10 | 27 | 14 | 49 | 0.0 | 2500 |
| 1770 | 11 | 26 | 14 | 49 | 0.0 | 2500 |
| 1860 | 11 | 25 | 13 | 50 | 0.0 | 2490 |
| 1950 | 12 | 25 | 12 | 50 | 0.0 | 2490 |
| 2040 | 12 | 25 | 12 | 51 | 0.0 | 2490 |
| 2130 | 13 | 24 | 12 | 51 | 0.0 | 2490 |
| 2220 | 13 | 24 | 11 | 52 | 0.0 | 2490 |
| 2240 | 13 | 24 | 11 | 52 | 0.0 | 2490 |

Table 27. Effect of Temperature Variation on Clarion 4A Coal on Dry Basis

| Gasifier Temperature | Molar Composition in Percent | | | | Heating Value |
|---|---|---|---|---|---|
| °F | CO | $H_2$ | $CO_2$ | $CH_4$ | Btu/lb |
| 1050 | 11 | 48 | 32 | 9.1 | 5370 |
| 1140 | 16 | 53 | 27 | 4.0 | 5480 |
| 1230 | 20 | 56 | 23 | 1.2 | 5600 |
| 1320 | 22 | 56 | 21 | 0.3 | 5710 |
| 1410 | 24 | 56 | 20 | 0.1 | 5800 |
| 1500 | 26 | 55 | 19 | 0.0 | 5890 |
| 1550 | 27 | 55 | 18 | 0.0 | 5930 |
| 1590 | 27 | 55 | 18 | 0.0 | 5960 |
| 1680 | 29 | 54 | 17 | 0.0 | 6030 |
| 1770 | 30 | 54 | 16 | 0.0 | 6090 |
| 1860 | 31 | 53 | 15 | 0.0 | 6150 |
| 1950 | 32 | 53 | 15 | 0.0 | 6200 |
| 2040 | 33 | 53 | 14 | 0.0 | 6240 |
| 2130 | 34 | 52 | 13 | 0.0 | 6290 |
| 2220 | 35 | 52 | 13 | 0.0 | 6330 |
| 2240 | 35 | 52 | 13 | 0.0 | 6330 |

Table 28. Effect of Temperature Variation on Pittsburgh #8 Coal on Dry Basis

| Gasifier Temperature | Molar Composition | | | | Heating Value |
|---|---|---|---|---|---|
| °F | CO | $H_2$ | $CO_2$ | $CH_4$ | Btu/lb |
| 1050 | 11 | 47 | 32 | 10.2 | 4200 |
| 1140 | 16 | 53 | 26 | 4.7 | 4270 |
| 1230 | 21 | 56 | 22 | 1.5 | 4340 |
| 1320 | 23 | 56 | 20 | 0.4 | 4400 |
| 1407 | 25 | 56 | 19 | 0.1 | 4470 |
| 1497 | 27 | 56 | 17 | 0.0 | 4530 |
| 1550 | 28 | 55 | 17 | 0.0 | 4560 |
| 1590 | 28 | 55 | 16 | 0.0 | 4580 |
| 1680 | 30 | 55 | 16 | 0.0 | 4640 |
| 1770 | 31 | 54 | 15 | 0.0 | 4690 |
| 1860 | 32 | 54 | 14 | 0.0 | 4730 |
| 1950 | 33 | 53 | 13 | 0.0 | 4780 |
| 2040 | 34 | 53 | 13 | 0.0 | 4820 |
| 2130 | 35 | 53 | 12 | 0.0 | 4860 |
| 2220 | 36 | 53 | 12 | 0.0 | 4890 |
| 2240 | 36 | 52 | 12 | 0.0 | 4900 |

Table 29. Effect of Temperature Variation on Illinois #6 Coal on Dry Basis

| Gasifier Temperature | Molar Composition | | | | Heating Value |
|---|---|---|---|---|---|
| °F | CO | $H_2$ | $CO_2$ | $CH_4$ | Btu/lb |
| 1050 | 9 | 51 | 34 | 6.3 | 4970 |
| 1140 | 13 | 55 | 29 | 2.4 | 5060 |
| 1230 | 16 | 56 | 27 | 0.7 | 5160 |
| 1320 | 19 | 58 | 26 | 0.2 | 5260 |
| 1410 | 21 | 56 | 24 | 0.0 | 5340 |
| 1500 | 22 | 55 | 23 | 0.0 | 5420 |
| 1550 | 23 | 55 | 22 | 0.0 | 5460 |
| 1590 | 24 | 55 | 21 | 0.0 | 5490 |
| 1680 | 25 | 54 | 21 | 0.0 | 5550 |
| 1770 | 27 | 53 | 20 | 0.0 | 5610 |
| 1860 | 28 | 53 | 19 | 0.0 | 5670 |
| 1950 | 29 | 53 | 18 | 0.0 | 5720 |
| 2040 | 30 | 52 | 17 | 0.0 | 5770 |
| 2130 | 31 | 52 | 17 | 0.0 | 5810 |
| 2220 | 32 | 52 | 16 | 0.0 | 5850 |
| 2240 | 32 | 51 | 16 | 0.0 | 5860 |

Table 30. Effect of Temperature Variation on Spring Creek Coal on Dry Basis

| Gasifier Temperature | Molar Composition | | | | Heating Value |
|---|---|---|---|---|---|
| °F | CO | $H_2$ | $CO_2$ | $CH_4$ | Btu/lb |
| 1050 | 8 | 52 | 35 | 4.9 | 4670 |
| 1140 | 12 | 55 | 31 | 1.7 | 4760 |
| 1230 | 15 | 56 | 29 | 0.4 | 4850 |
| 1320 | 17 | 56 | 27 | 0.1 | 4940 |
| 1410 | 19 | 55 | 26 | 0.0 | 5010 |
| 1500 | 21 | 55 | 25 | 0.0 | 5090 |
| 1550 | 22 | 54 | 24 | 0.0 | 5130 |
| 1590 | 22 | 54 | 24 | 0.0 | 5150 |
| 1680 | 24 | 53 | 23 | 0.0 | 5220 |
| 1770 | 25 | 53 | 22 | 0.0 | 5270 |
| 1860 | 26 | 52 | 21 | 0.0 | 5330 |
| 1950 | 28 | 52 | 20 | 0.0 | 5380 |
| 2040 | 29 | 52 | 20 | 0.0 | 5420 |
| 2130 | 30 | 51 | 19 | 0.0 | 5470 |
| 2220 | 31 | 51 | 19 | 0.0 | 5500 |
| 2240 | 31 | 51 | 18 | 0.0 | 5510 |

Table 31.Effect of Temperature Variation on ND Lignite on Dry Basis

| Gasifier Temperature | Molar Composition | | | | Heating Value |
|---|---|---|---|---|---|
| °F | CO | $H_2$ | $CO_2$ | $CH_4$ | Btu/lb |
| 1050 | 7 | 53 | 37 | 2.6 | 4200 |
| 1140 | 9 | 55 | 34 | 0.7 | 4270 |
| 1230 | 12 | 55 | 33 | 0.2 | 4340 |
| 1320 | 13 | 55 | 32 | 0.0 | 4400 |
| 1410 | 15 | 54 | 31 | 0.0 | 4470 |
| 1500 | 17 | 54 | 30 | 0.0 | 4530 |
| 1550 | 18 | 53 | 29 | 0.0 | 4560 |
| 1590 | 18 | 53 | 29 | 0.0 | 4580 |
| 1680 | 20 | 52 | 28 | 0.0 | 4640 |
| 1770 | 21 | 52 | 27 | 0.0 | 4690 |
| 1860 | 23 | 51 | 26 | 0.0 | 4730 |
| 1950 | 24 | 51 | 25 | 0.0 | 4780 |
| 2040 | 25 | 50 | 25 | 0.0 | 4820 |
| 2130 | 26 | 50 | 24 | 0.0 | 4860 |
| 2220 | 27 | 49 | 23 | 0.0 | 4890 |
| 2240 | 27 | 49 | 23 | 0.0 | 4900 |

# APPENDIX C

## MODEL OUTPUT FOR STEAM VARIATIONS

In this section, the effect of steam flow rate on the product composition and USS steam temperature is presented. Table 31 shows the comparison between the experimental output and simulation output on a wet basis. Table 32 shows the comparison on a dry basis.

Table 32. Effect of $H_2O$/C ratio on Syngas for Clarion 4A Coal at 1550°F on Wet Basis

| Steam Flow Rate | $H_2O$/C Ratio | Burner Temperature (°F) | | Heating Value,Btu/lb | CO, mole% | |
|---|---|---|---|---|---|---|
| Kg/h | | Experiment | Model | Model | Experiment | Model |
| 11 | 0.9 | 4329 | 4450 | 4893 | 37 | 25 |
| 18 | 1.4 | 3958 | 3474 | 3978 | 32 | 17 |
| 25 | 2.0 | 3659 | 2896 | 3351 | 28 | 12 |
| 32 | 2.6 | 3414 | 2511 | 2893 | 24 | 9 |
| 36 | 2.9 | 3306 | 2361 | 2710 | 23 | 8 |
| 43 | 3.4 | 3117 | 2120 | 2403 | 21 | 6 |
| 50 | 4.0 | 2955 | 1933 | 2159 | 19 | 6 |

| Steam Flow Rate | $H_2O$/C Ratio | $H_2$,mole% | | $CO_2$, mole% | |
|---|---|---|---|---|---|
| Kg/h | | Experiment | Model | Experiment | Model |
| 11 | 0.9 | 41 | 41 | 9 | 12 |
| 18 | 1.4 | 41 | 37 | 11 | 13 |
| 25 | 2.0 | 40 | 34 | 13 | 13 |
| 32 | 2.6 | 39 | 31 | 14 | 13 |
| 36 | 2.9 | 38 | 29 | 14 | 13 |
| 43 | 3.4 | 37 | 27 | 15 | 12 |
| 50 | 4.0 | 36 | 25 | 16 | 11 |

Table 32. (Continued)

| Steam Flow Rate | $H_2O/C$ Ratio | $H_2O$, mole% | | $CH_4$, mole% | |
|---|---|---|---|---|---|
| Kg/h | | Experiment | Model | Experiment | Model |
| 11 | 0.9 | 10 | 21 | 1.6 | 0.02 |
| 18 | 1.4 | 14 | 32 | 1.4 | 0.01 |
| 25 | 2.0 | 17 | 40 | 1.2 | 0 |
| 32 | 2.6 | 21 | 47 | 1.1 | 0 |
| 36 | 2.9 | 22 | 49 | 1.1 | 0 |
| 43 | 3.4 | 26 | 54 | 1 | 0 |
| 50 | 4.0 | 28 | 58 | 1 | 0 |

Table 33. Effect of $H_2O/C$ ratio on Syngas for Clarion #4A Coal at 1550°F on Dry Basis

| Steam Flow Rate, Kg/h | $H_2O/C$ Ratio | CO, mole% | | $H_2$, mole% | |
|---|---|---|---|---|---|
| | | Experiment | Model | Experiment | Model |
| 11 | 0.9 | 42 | 32 | 46 | 53 |
| 18 | 1.4 | 38 | 25 | 48 | 55 |
| 25 | 2.0 | 34 | 20 | 49 | 57 |
| 32 | 2.6 | 31 | 17 | 49 | 58 |
| 36 | 2.9 | 30 | 16 | 50 | 59 |
| 43 | 3.5 | 28 | 14 | 50 | 59 |
| 50 | 4.0 | 26 | 14 | 50 | 59 |

Table 33. (Continued)

| Steam Flow Rate, Kg/h | $H_2O/C$ Ratio | $CO_2$, mole% | | $CH_4$, mole% | | Heating Value, Btu/lb |
|---|---|---|---|---|---|---|
| | | Experiment | Model | Experiment | Model | Model |
| 11 | 0.9 | 10 | 15 | 1.8 | 0.0 | 6100 |
| 18 | 1.4 | 13 | 20 | 1.6 | 0.0 | 5770 |
| 25 | 2.0 | 16 | 23 | 1.5 | 0.0 | 5550 |
| 32 | 2.6 | 18 | 25 | 1.4 | 0.0 | 5410 |
| 36 | 2.9 | 19 | 25 | 1.4 | 0.0 | 5350 |
| 43 | 3.5 | 20 | 27 | 1.4 | 0.0 | 5260 |
| 50 | 4.0 | 22 | 27 | 1.4 | 0.0 | 5180 |

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