To the Graduate Council:

I am submitting herewith a dissertation written by Anthony DeWayne Turner entitled "Determining the Optimum Conditions for Catalytic Steam Gasification of Broiler Litter." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Atul Sheth, Major Professor

We have read this dissertation
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Interim Vice Provost and
Dean of The Graduate School

DETERMINING THE OPTIMUM CONDITIONS FOR CATALYTIC STEAM GASIFICATION OF BROILER LITTER

A Thesis Presented for the Master of Science Degree

The University of Tennessee, Knoxville

Anthony Turner

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ABSTRACT

In the United States in 1996, approximately 7.6 billion head of broiler chickens were produced. This number has continuously risen over the last few years, with more than 75% of the production accounted in the southeastern United States. Because of the significant growth in the rate of production, the amount of litter produced is substantial. Unfortunately, much of the litter is not used for fertilizer and ends up polluting the rivers and surface waters. Because of the decreased availability of land and potential federal regulations, appropriate actions must be taken to find a better way to handle the poultry waste.

Recently, catalytic steam gasification has been considered as an alternative to manage the broiler litter. The process requires and alkali metal or alkaline earth metal salt and steam to convert the feedstock to a fuel gas consisting primarily of carbon monoxide, carbon dioxide, hydrogen, and methane. The gas may be used as a possible energy source or chemical feedstock. The broiler litter is a good candidate for catalytic steam gasification because it contains potassium and several other alkali metal salts that can be used as a catalyst. Even if the inherent salts are not sufficient, additional sources, such as potassium carbonate and langbeinite, can be used with minimal additional cost. The broiler litter also produces low quantities of unwanted hydrogen sulfide. The residue left after gasification can also be used as fertilizer or in the concrete/cement manufacturing industries.

A preliminary study was carried out to determine the concept's feasibility. In that study, a bench-scale high-pressure, fixed bed gasification system was designed and assembled to carry out experiments up to a temperature of 1400^0F and pressures up to 250 psig. Also, in that study, a limited number of experiments were conducted at different temperatures, pressures, and catalyst loadings to prove the technical and economic viability of handling broiler liter.

Additional work has now been carried out to validate the optimum conditions for handling the broiler litter. In this work, a screening test matrix has been developed to assess the different process variables so as to determine the optimum conditions for treating the broiler litter. Comparative analyses are also carried out in this work to see if the process is economically viable for stationary as well as mobile applications.

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LIST OF SYMBOLS

$A_{cal,i}$	Calibration peak area
A_i	Peak area of individual gas component
$C_{correct}$	Reconciled mass of carbon
C_o	Initial mass of carbon in bed (grams)
C_{gas}	Mass of carbon gasified
$[CH_4]_j$	Moles of methane
$[CO]_j$	Moles of carbon monoxide
$[CO_2]_j$	Moles of carbon dioxide
dV	Change in volume of exit gases (liter)
E_1	Activation energy for gasification reaction
E_2	Heat of adsorption for steam adsorption step
$G_{exit,j}$	Cumulative moles of the exit gases (moles)
$[H_2]_j$	Moles of hydrogen
$H_2O_{out,j}$	Amount of steam condensed at time interval j (moles)
$H_2O_{avg,j}$	Average amount of steam in bed at time, j (moles)
$H_2O_{in,j}$	Amount of water entering reactor at time interval of j (moles)
k_1	Reaction rate constant
k_2	Adsorption constant
k_{1o}	Frequency factor
k_{2o}	Frequency factor
M_c	Atomic weight of carbon
$m_{initial}$	Mass of sample prior to drying (grams)

m_{final}	Mass of sample after drying (grams)
N	Number of data points
pH_2O_j	Partial pressure of steam at time, t_j
P_{atm}	Atmospheric pressure
$P_{reactor}$	Operating pressure of reactor
R	Ideal gas constant
T_{cond}	Condenser temperature (^0F)
t_j	Gasification time at interval j (minutes)
V_j	Cumulative volume of exit gases (liter)
w_{H2O}	Mass fraction of moisture in the broiler litter
$X_{c,char}$	Fractional carbon conversion in bed
$X_{correct}$	Reconciled fractional carbon conversion in bed
X_{gas}	Cumulative conversion of carbon via gas chromatograph
X_{TGA}	Cumulative conversion of carbon from TGA analyzer
$x_{c,i}$	Specific carbon conversion at particular time
$x_{c,f}$	Final carbon conversion at particular time
$y_{cal,i}$	Mole fraction of calibration standard
y_i	Mole fraction of individual gas component
$y_{H20,j}$	Mole fraction of steam in fixed bed at time, t_j
$(dC/dt)_j$	Gasification rate
ϕ_i	Fuel gas fraction at specific carbon conversion
ρ	Total molar density (mol/liters)
ρ_c	Cumulative molar density (mol/liter)

ρ_i	Molar density of individual gas component (mol/liter)
ρ_{CH4}	Molar density of methane (mol/liter)
ρ_{CO}	Molar density of carbon monoxide (mol/liter)
ρ_{CO2}	Molar density of carbon dioxide (mol/liter)
τ	Total gasification time period (minutes)

LIST OF ABBREVIATIONS

BTU	British thermal unit
C	Celsius
DOE	Department of Energy
EPA	Environmental Protection Agency
F	Fahrenheit
kJ	Kilojoules
kPa	Kilopascal
ml	Milliliters
mol	Moles
min	Minutes
psig	pounds per square inch
RCWF	Remaining carbon weight fraction
TGA	Thermogravimetric Analyzer
USDA	United States Department of Agriculture
UTSI	University of Tennessee Space Institute
wt	Weight

CHAPTER 1

INTRODUCTION

The production of broiler chickens has become one of the largest industries in the United States' agriculture. In 1996, the production of broiler chickens reached approximately eight million. The growing demand for poultry has led to an annual growth rate of about five percent. Over 70 percent of the production can be traced to the Southeastern United States.

Along with the increased demands, waste disposal and management have become major challenges in the agricultural industry. These challenges have not met the needs of the increased production. Over five million tons of manure is produced in the Southeastern United States. This statistic is more phenomenal considering this region only has about 20 percent of the total farm land in the country, yet accounts for the majority of the broiler production (1, 2).

When handling broiler litter, it is regularly removed from a broiler house. The litter consists of manure, wood shavings, and other bedding material. After the litter is removed, it is used primarily as a supplemental fertilizer for pastures, hay, and crop producing fields. In one ton of broiler litter, there may be approximately 60 pounds of nitrogen, 60 pounds of phosphate, and 40 pounds of potash (3, 4). Although the litter is very rich in nutrients, most broiler producers do not have adequate land in close proximity to handle the useful application of the litter, which is as fertilizer. Hence, the

litter brings diminishing returns since it does not have any other useful or profitable alternatives. Since there is not sufficient land to spread the litter as fertilizer, the chances of land and water pollution increase significantly due to excess application.

Due to decreased availability of land, the environmental impact of the broiler litter must be considered. Not only is the ecosystem compromised, but also the people and animal life in those communities are directly affected. One example of the environmental impact was a recent outbreak of *Pfiesteria* in the Chesapeake Bay in 1996 (5). This incident was linked to poultry producers, and led to the deaths of some aquatic life and serious illnesses suffered by several people in the community. Another high-profile incident that occurred was the outbreak of Mad Cow's Disease. Although cattle were affected and it did not become an international catastrophe, its widespread consequences and environmental risks forced the agricultural and private industrial sectors to become more proactive than reactive in handling animals and properly disposing of waste. Even the *E. Coli* bacterial outbreaks have forced industries to take a serious look at how livestock and its litter are handled (7). With the health consequences, potential environmental legislation, and legal actions being considered, it has become necessary to look at feasible alternatives to handle the litter without compromising the needs of the agricultural industry and the nearby communities. Various industries are now looking at alternatives so that major fines are avoided and customer relations remain strong.

Previous work at the University of Tennessee Space Institute (UTSI) was carried out to assess the feasibility of using broiler litter as an energy source. Preliminary experiments

were conducted to see if the process was technically feasible. The results showed that a gasifier operating at a low pressure (approximately 50 psig) and high temperature (approximately 1400° F) produced a gas with significant amounts of carbon monoxide and hydrogen (8). The gas has the potential to be used as an energy source, thus being able to use the litter for potential savings and not becoming an environmental threat. Despite the potential success, the feasibility study was performed with very limited criteria. A complete range of conditions was not applied in that study. Therefore, a full screening test matrix must be designed and implemented to find the optimum conditions that will convert the broiler litter into the desired products. Finding the best operating conditions will also allow a comparative economic analysis to be performed for transportable and stationary gasification systems. A previous study was conducted for a transportable unit, bringing a profitable return within a couple of years. However, other alternatives, such as using a centralized stationary unit, may prove more beneficial in certain situations. A complete study with optimal conditions will help determine the best conditions for handling broiler litter and determining the economic potential that may assist agricultural communities and private industries.

CHAPTER 2

BACKGROUND

The quantity of broiler litter produced in the United States has increased at a significant rate throughout the 1990's. This quantity is more phenomenal since over 75% of the litter comes from the Southeastern United States (9, 10). This region includes the following states: Alabama, Arkansas, Florida, Georgia, Kentucky, Louisiana, Mississippi, Missouri, North Carolina, South Carolina, Tennessee, Virginia, and West Virginia.

The increase in broiler litter is due to the increased demand of poultry, especially chicken. Chicken meat has been widely seen and reported to be a healthier alternative to other meats. Cholesterol, fat, and other nutritional factors are not as high in chicken as in other meats. The increased demand of poultry has translated into $25 billion contributing to the economy (2). The increased demand can also be seen in the increased efforts of genetic testing using poultry. This testing includes ways to produce healthier poultry and eliminating some of the common health risks that are encountered.

Despite the increase in broiler production, the negative side of this production is the increase in broiler litter produced. This is further compounded by the fact that land availability on and around broiler farms is decreasing. These negative trends also bring a negative outcome for the extra broiler litter produced. The litter often ends up in streams or other waterways due to surface run-off. Too much litter when applied to the land as

fertilizer also restricts the effectiveness of the litter, possibly over saturating the land and rendering the areas useless.

The increasing average broiler litter farm size currently is a disadvantage, but could become advantageous in the future. The larger farms must transport their broiler litter through long distances to dispose it properly. However, economics usually prevail over ecology, leading to a negative environmental impact (2, 11). Instead of properly disposing the litter, much of it is often dumped into streams or placed in deserted land areas. Due to lack of proper monitoring, the litter often remains in the streams of surface run-off and is not always detected. Consequently, the likelihood of catching a serious bacterial infection significantly increases. If an alternative disposal method such as catalytic steam gasification is used, the growing farm size will become advantageous. This alternative disposal method will not only allow the broiler litter to be handled properly, it will also reduce the serious consequences associated with the contamination of water, air, and land sources. Proper disposal of the broiler litter will also bring financial benefits if it is designed to properly accommodate the needs of the agricultural communities and industries that produce a lot of waste. The economics will result in lower conversion costs if the litter is properly treated and converted by appropriate disposal methods. The growing farm sizes could be the deciding factor in adopting an alternative disposal technology. Proper disposal of the broiler litter would also lead to using it as a favorable, alternative fuel source (2, 3).

These alternatives must be addressed due to increasing pressure from the federal government to find an acceptable solution. Poultry processors have already begun looking at the alternatives before the government mandates them. One alternative is being researched by private industries, which are taking an active role in resolving the situation (12, 13). Some of the private industries include Tyson Foods, Owens Corning, Inc., and Excel Corporation. Under the private industries' plan, chicken companies would work with their farmers to develop litter management plans. The farmers would keep records of how they are storing and using the litter and then submit an annual report to the appropriate state agency. The private companies could make the procedures a required condition to continue the business relationships. The private industries hope that their proactive stance would help curtail some of the controversy that has risen in recent years, when animal waste runoff was heavily targeted for some of the pollution in the nation's rivers and streams (14).

While the private industries seek voluntary cooperation, the federal government has worked to implement their own plan to handle the animal waste. The U.S. Agriculture Department (USDA) and Environmental Protection Agency (EPA) have drafted a proposal that would rein in large livestock feeding operations that confine thousands of animals in a small space and produce enormous amounts of waste (14). The large operations would have to get permits from their respective states to ensure their compliance in waste disposal. Guidelines would have to be developed on what animals are fed and how waste is handled. These permits would be issued on an annual basis (9, 15). Regardless of who leads the waste management efforts, it is hoped that all farmers

and agricultural communities will work to put environmental acceptability on a higher priority while still keeping a financially viable operation.

Biomass Gasification

Biomass gasification is a critical concept that is gaining more attention as it is being researched as a viable option for handling waste. Biomass gasification is gaining more acceptance because gasifiers can be connected to advanced power systems with high efficiencies and low emissions (16).

Biomass gasifiers operate by heating the biomass in an oxygen-starved environment until the biomass breaks into its constituent components. The process requires the input of heat energy for the endothermic chemical reaction to proceed and split the molecules apart (17).

According to feasibility studies conducted by the U.S. Department of Energy (DOE) and private industry, there are three types of gasifiers that are economically sound when used in conjunction with gas-turbine generators (16, 18). The gasifiers are fixed-bed, fluidized-bed, and entrained-flow. These gasifiers are used in a direct-fired mode in which air or oxygen is fed directly to the gasifier, or indirect mode in which the externally supplied heat is used to gasify the biomass.

Gasification with air produces a low-BTU gas that has a heating value of about one-fifth of that of natural gas. Indirectly heated gasification and direct gasification with oxygen

produce a medium-BTU gas with heating values just under one-half of that of natural gas. Product gas from either of these gasification methods provides a suitable fuel (17).

Biomass Gasification Background

Gasification is a two-step, endothermic process in which a solid fuel (such as biomass) is thermochemically converted into a low- or medium-BTU gas. This conversion allows the fuel to be used for different power systems without being an environmental detriment in the industrial and residential sectors (13, 19). Before anything is gasified, the solid must be pyrolyzed. Pyrolysis allows the volatile components of the solid to vaporize under inert conditions at temperatures below 900^0C through a series of complex reactions. These volatile vapors include hydrocarbon gases, hydrogen, carbon monoxide, tar, and water vapor. Char, which is the fixed carbon, and ash are the solid by-products of the pyrolysis that do not get vaporized (13, 17).

After pyrolysis is complete, catalytic steam gasification is the next step. Catalytic steam gasification has received serious attention because of its potential for high carbon conversion at relatively moderate operating conditions. This process involves the use of an alkali salt, which helps in lowering the reaction temperature (17). This process also involves several key reactions that help determine the composition of the gasified products. They are:

Steam-carbon reaction	$C + H_2O \rightarrow CO + H_2$	(2-1)
Steam-carbon reaction	$C + 2\,H_2O \rightarrow CO_2 + 2\,H_2$	(2-2)

Water-gas shift reaction	$CO + H_2O \rightarrow CO_2 + H_2$	(2-3)
Methanation reaction	$CO + 3\,H_2 \rightarrow CH_4 + H_2O$	(2-4)
Hydrogasification reaction	$C + 2\,H_2 \rightarrow CH_4$	(2-5)
Boudouard reaction	$C + CO_2 \rightarrow 2\,CO$	(2-6)

The reactor's temperature and operating pressure and the catalyst loading determine the equilibrium composition of the gasified products. Catalytic gasification is applicable to broiler litter since some of the alkali salts are already present in the feedstock and can serve as potential catalysts (17). The conversion time can also be reduced if additional catalyst is mixed with the broiler litter.

Air-blown fixed-bed and fluidized-bed gasifiers appear to have several advantages for biomass power systems. The oxidant for the gasification process can be atmospheric air or pure oxygen. Oxygen-blown gasifiers offer a higher-BTU gas and faster reaction rates than air-blown systems, but they have the disadvantage of additional capital costs associated with the oxygen plant. The air-blown gasifier is preferred for biomass integrated gasifier power systems (20). The air-blown gasifiers produce a gas diluted with nitrogen from the atmosphere, and as a result have a lower heating value.

In considering different types of gasifiers, one must look at the choice between dry-ash and slagging gasifier designs. The slagging gasifier requires substantially less blast steam injection for the gasification process and it has the potential for greater throughput

capacity. This occurs because the slagging gasifier operates at higher temperatures than the dry-ash design.

Alternative methods can also be considered when transferring the heat from the char combustion to the gasifier feedstock. In direct combustion gasifiers, some of the char is burned in the vessel where thermochemical reactions occur. However, indirect gasifier systems utilize a separate combustor for char combustion, which allows heat to be transferred to the gasifier reactor (20, 21). The indirect gasifier system also has the advantage of not allowing the nitrogen from the atmosphere used during the combustion step to combine with the product fuel gas, thereby avoiding the dilution of the product gas.

Types of Gasifiers Used in Biomass Gasification

Fixed-Bed Gasifier

The most successful fixed-bed design is the updraft gasifier, which allows the biomass to be fed from the top of the gasifier and allowing it to successively undergo drying, pyrolysis, char gasification, and char combustion as it settles to the bottom of the gasifier. The product gas is removed from the top of the gasifier and the ash from the bottom. Blast air and steam are injected into the gasifier to keep the ash below melting temperatures (in a dry-ash gasifier) and to facilitate char conversion. The product gas from this scheme has a low velocity and low temperature. The low operating temperature creates a considerable amount of condensable oils and tars in the product gas. However,

the filtering effect of the bed and low stream velocities create a product gas with low particulate concentrations.

Because of the volatility of biomass, the excellent heat transfer design, and high peak temperatures used in the fixed-bed design, the achieved carbon conversion is typically around 99%. Furthermore, the design and operation of the fixed-bed is relatively simple and is the most widely used commercially. However, one disadvantage of the fixed-bed gasifier is that it requires large, dense, uniformly sized fuels to be most effective. This puts agricultural residues and products at a disadvantage since they are not uniform all the time (2, 22). They would require densification, which would increase the fuel handling costs and make the process less economically viable. This would prove to be challenging when dollars overrule ecology (2).

Fixed-bed gasifiers also exist as either an updraft or downdraft design. Updraft gasifiers allow the gases to flow in a countercurrent direction to the fuel. Updraft gasifiers can accommodate fuels with moisture content being 35 to 50 percent of the fuel. Although the product gas leaves the reactor with a high tar and condensable aqueous content, it is usually low in particulates. The main disadvantage with updraft fixed-bed gasifiers is the frequent tar condensation in the upper reactor. Downdraft gasifiers allow the gases to flow in a cocurrent mode with the fuel. A constriction is often designed into the gasifier to accommodate the cocurrent flow. Downdraft gasifiers require a low moisture content and fuel of relatively large particle size. Downdraft gasifiers also generate product gas loaded with ash and char particulate. The main disadvantage of downdraft gasifiers is the

fuel quality. Other disadvantages include bridging in the upper part of the reactor, slagging from high ash content, bed plugging from high fines content, and poor gas quality due to excessive fuel moisture.

Fluidized-Bed Gasifiers

In a fluidized-bed gasifier, a continuous feed of biomass and inert heat-distributing material are "fluidized" by and oxidant and/or steam. There are two options for supplying heat to the gasifier. In a directly heated fluidized-bed gasifier, heat required for gasification comes from part of the char combustion in the gasifier reactor. In an indirectly heated fluidized bed gasifier, partially gasified char is removed from the gasifier and burned in a separate vessel. The resulting heat is transferred to the gasifier by either in-bed heat exchangers or by recirculating the inert bed material heated in the char combustor. The primary advantage to indirect heating of the gasifier is the gasification product is not diluted with the char combustion by-products (e.g. N_2 and CO_2).

Regardless of which design is chosen, pyrolysis occurs throughout the bed and is not localized. As in the up draft fixed-bed design, the product gas is drawn from the top of the gasifier. The superior mixing which occurs in the fluidized-bed gasifier provides for excellent heat and mass transfer, which subsequently yield uniform temperatures; better fuel-moisture to keep bed temperatures below the ash melting temperatures; and faster reactions. These benefits allow higher throughput capabilities, which, in turn, can reduce the size and capital cost of the gasifier. Also, the temperature is more uniform, and the

average temperature in a fluidized-bed gasifier is greater than in the fixed-bed design. A significant amount of tars and oils are also converted into permanent gases, reducing the amount of unwanted by-products.

There are some significant differences between the fluidized and fixed-bed gasifiers. Fluidized-bed gasifiers are capable of handling much smaller, less dense, and less uniform feedstock. This is especially advantageous for broiler litter and other solid fuels whose samples can vary in many ways. With fluidized-bed designs, the fuel and fuel handling systems are more likely to set lower limits for acceptable bulk density. However, a close particle size is required to keep the bed fluidized. A shortcoming of the fluidized-bed gasifier is that the raw gas has a high particulate level.

CHAPTER 3

EXPERIMENTAL PROCEDURES

Analysis of the Broiler Litter, Char, and Ash

When analyzing any samples of broiler litter, the moisture, volatiles, and ash content must be determined. These factors were studied to verify the analyses performed in the previous studies and ensure replication of the results (3). To determine the moisture content of the litter, a 20-gram sample was heated under nitrogen in a Precision Gravity Convection Oven for 72 hours at 105^0C. The sample mass before and after drying was measured with a Mettler PM2000 analytical balance. The percent moisture content was calculated from the initial and final masses, $m_{initial}$ and m_{final} respectively (3). This value represents the percentage of the original sample mass attributed to moisture.

$$\text{Percent Moisture} = \frac{m_{initial} - m_{final}}{m_{initial}} * 100\% \qquad (3\text{-}1)$$

The determinations of volatile content and ash content were performed using a Perkin-Elmer TGA 7 Thermogravimetric Analyzer. The TGA is essentially a temperature-controlled furnace equipped with an internal microbalance. The composition of the TGA furnace atmosphere can be controlled by the addition of both inert and reactive gases. The volatiles content was measured by heating the furnace and a fresh broiler litter sample to 1000^0C at a rate of 7.5^0C per minute. The pyrolysis reaction was achieved by maintaining an inert atmosphere of argon gas. Any weight loss was attributed to the loss

of both moisture and volatiles. To determine the percent volatiles content in the fresh sample, the moisture contribution must be removed from the weight loss (3, 4). This is shown in equation 3-2.

$$\% \text{ Volatiles} = \frac{(1 - w_{H2O})\, m_{initial} - m_{final}}{m_{initial}} * 100\% \qquad (3\text{-}2)$$

where w_{H2O} is the mass fraction of moisture in the broiler litter. The ash content was also found using the TGA, but with oxygen being fed to the system. The reproduced results are consistent with the previous results obtained from Andrew Jones' experiments (3).

Pyrolysis of Broiler Litter

The primary gasification, or pyrolysis, of carbonaceous compounds generates both char and volatiles. In a bench-scale apparatus, products from this pyrolysis process may interfere with the subsequent secondary gasification. For example, tars and oils, which are volatile at pyrolysis temperatures, may condense at lower temperatures. These compounds may then foul the apparatus or even interfere with the operating procedures. For this reason, the production of pyrolyzed char was performed in an apparatus devoted to the task (4).

The pyrolysis was conducted in a Barnstead Thermolyne - Model F48015 muffle furnace at atmospheric pressure. The muffle furnace housed a cylindrical stainless steel container to maintain a complete inert atmosphere during pyrolysis. The container had a heavy lid

that had an inlet for the inert gas (N_2) and an outlet for the volatiles and tar to escape. Tests were always performed on the container to ensure that there were no leaks in or around the cylindrical steel container. These leak tests were always performed before any pyrolysis to ensure the results would be as accurate as possible under the most ideal conditions. Equipment was also regularly maintained and cleaned to make sure the most accurate results were obtained for every run. A 20-gram sample of the litter was used for every pyrolysis and purged with grade 5.0 N_2. The muffle furnace was then set to a temperature of 750^{0}C for the pyrolysis to begin. There was a continuous purging of the inert gas to help remove the volatiles from the container. The outgoing gases were bubbled into a conical flask partially filled with water to allow the tars and other heavy volatile compounds to condense before the gases were released into the atmosphere through the exhaust hood's vent. The pyrolysis was carried out for three hours from the time the desired temperature (750^{0}C) was reached in the muffle furnace. The desired temperature was regularly reached within approximately 20 minutes. At the end of the pyrolysis, the furnace was cooled to room temperature by continuous purging with the inert gas. This process usually took six to seven hours since the furnace was always closed during this stage. This was done so that minimal reaction with the air would occur if the furnace were left open for a faster cooling (4). Otherwise, oxidation of the sample would be a serious challenge and may significantly alter any results from further analyses.

After cooling, the pyrolyzed broiler litter was crushed in an agate mortar and sieved. A standard particle size of the char sample used in the gasifier was between 30 and 100

mesh. Anything outside of that range would be too big to fit in the reactor or would slip through the sieve baskets. After sieving, the char was placed in small bottles and stored in the glove box under the inert conditions so that oxidation would not occur.

Steam Gasification

The catalytic steam gasification experiments were carried out in the bench scale high-pressure, high-temperature fixed-bed gasifier system. The gasifier in this system was typically operated with a downdraft gas flow regime and in a differential fixed bed mode. The gasifier was designed to operate at the desired constant temperature, pressure and steam/water flow conditions.

The core part of this bench scale gasification unit was the gasifier reactor. The reactor body was constructed of a 3/4-inch Type 304 stainless steel tubing, with a wall thickness of 0.0065-inch. This allowed a working a pressure greater than 1500 psi at 1400^0F. The reactor was sealed with an end cap on one end and filled with ceramic beads on a 200-mesh stainless steel screen (4). This provided support for the char sample. The char sample to be gasified was supported by two 200-mesh stainless steel screen baskets placed above the ceramic packing, closer to the center of the reactor. A Type K thermocouple was introduced from the other end cap and was placed close to the top of the char bed. The thermocouple was used to monitor the bed temperature throughout the entire experiment. A schematic of the differential fixed-bed reactor is shown in Figure 3.1. The high-pressure fixed-bed gasifier system was operated in the start-up mode to bring the system to required operating conditions of temperature and pressure.

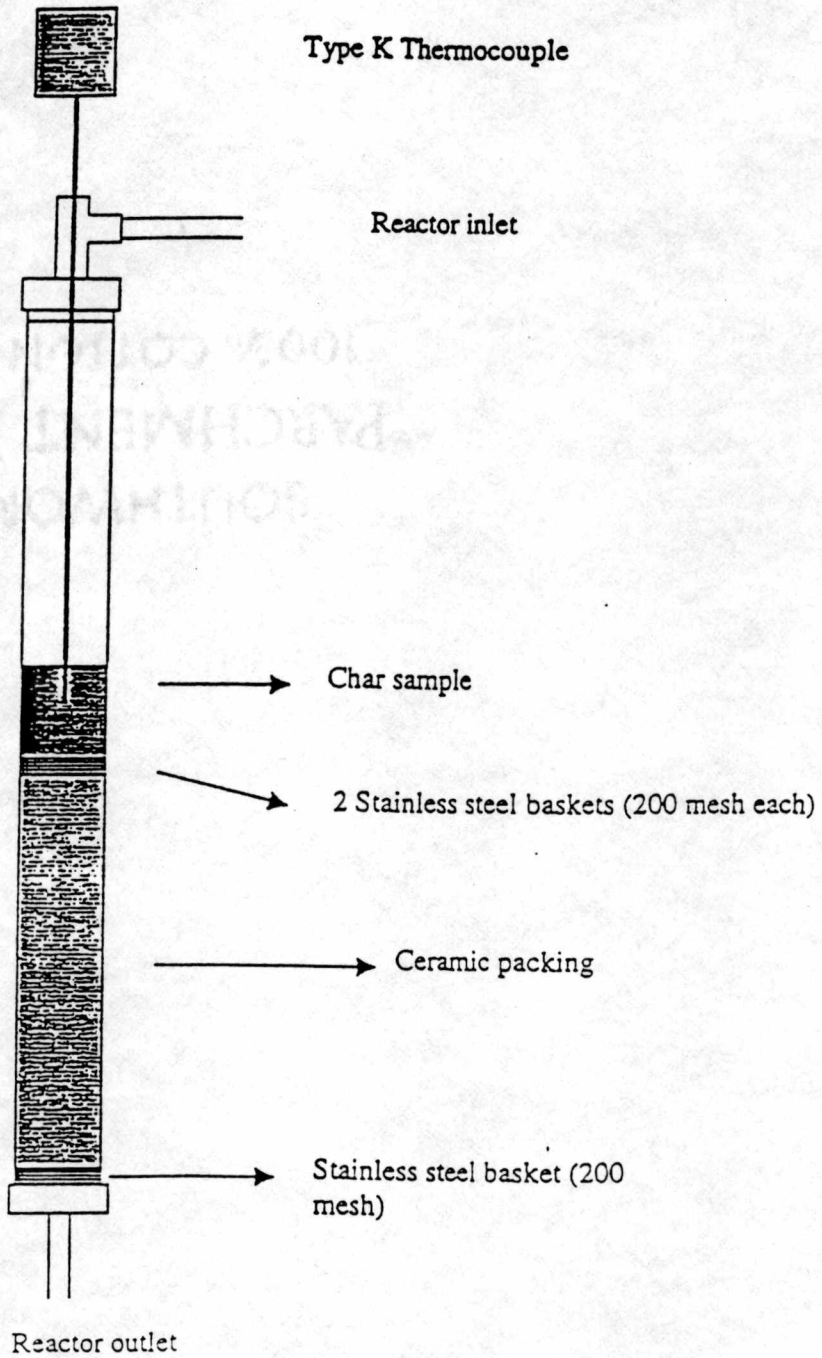

Figure 3.1: Schematic of Differential Fixed-Bed Reactor

The reactor was continuously purged with nitrogen, from the start-up through the gasification steps, to maintain inert conditions. The reactor was heated using a long vertically mounted Lindberg Sola Basic Model 123 split-tube furnace. The differential char bed accommodated about 2.5 grams of char during each experimental run. Once the system was ready for gasification, steam was introduced into the reactor. Distilled water was introduced to the system using an Eldex Laboratories, Inc. Model A-10-S metering pump. The total amount of water entering the apparatus was measured by the burette from which the water entered the pump. The water was preheated to provide steam to the reactor using a separate Lindberg Sola Basic Model 123 split-tube furnace. The preheater furnace was placed directly above the gasifier reactor to provide better heat transfer and to minimize heat loss. This was a slight modification made from previous work done on the broiler litter, in which the preheater was placed far from the reactor, decreasing the efficiency in effectively carrying out the experiments (4). The change in set-up also worked well in maintaining the required operating temperature in the reactor throughout the carbon-steam gasification. This revised set-up also allowed for more efficient use of time since one person could now handle all of the required tasks or goals for completing the experimental run. The pressure in the whole system was regulated by a Tescom Industrial Controls Model backpressure regulator, which was placed at the reactor outlet. Pressure was monitored at both ends of the reactor using Ashcroft pressure gauges, with a reading up to 400 psig, to maintain constant pressure conditions during gasification. A schematic of the high-pressure high-temperature fixed-bed gasifier set-up is shown in Figure 3.2.

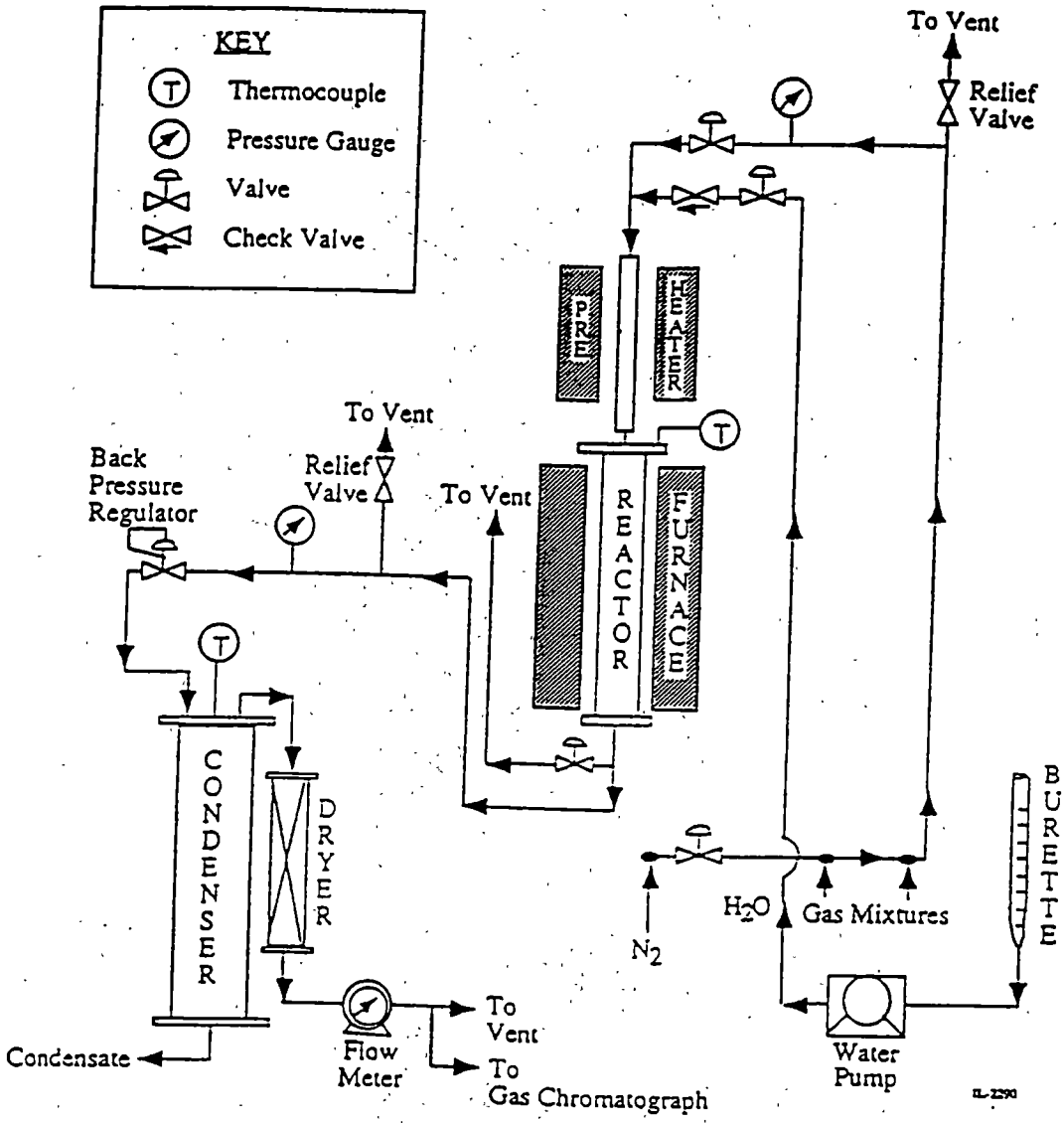

Figure 3.2: Schematic of High-Pressure High-Temperature Fixed Bed Gasifier

The water was pumped into the system once the reactor reached the desired operating conditions. The nitrogen, unreacted steam, and products from the gasifier entered the condenser after passing through the backpressure regulator. Most of the unreacted steam was condensed at this point and collected at the end of the gasification run. A drying tube packed with silica gel removed any traces of water left from the condenser outlet gases. This allowed the dry gas to enter the analytical section of the system.

The flow rate of the nitrogen gas was maintained throughout the start-up, gasification, and cooling stages of the experimental runs. The steam gasification step was carried out for about four hours. During the progress of the run, the process variables required to calculate the rate of gasification were measured. A Rockwell cumulative gas flowmeter determined the total volume of the dry gas from the reactor. The exit gases were collected at set time intervals in SKC sample bags. Before any gases were collected, the bags were always vacuumed to ensure no residual air was in the bag, possibly altering the results from the gas analysis data. After the gases were collected, an SRI 8610C gas chromatograph was used to analyze the exit gases. The gas chromatograph analyzed the gases to help determine the mole fractions of oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, and hydrogen. A Gateway 2000 computer with the Peaksimple 1.44 software controlled the gas chromatograph operation and analyzed the exit gas.

The cumulative gas volume, water burette reading, and temperature of the reactor and condenser were continuously monitored and recorded at the same time the exit gases

were collected. This helped in ensuring consistency, and also making sure that the apparatus did not behave in an unusual manner. The inlet gas flow rate was also considered, but was not measured due to mechanical problems with the measuring equipment. The carbon-steam gasification rate was calculated from the cumulative gas volume and from the gas analysis results obtained from the gas chromatograph in the form of mole fractions of the various components in the exit gas.

At the end of the gasification step, the system was cooled to room temperature under the nitrogen flow. Further oxidation of the char was thus prevented by the flow of the inert gas. After cooling, the remaining char was removed from the reactor, weighed and stored in sealed, glass bottles for further analyses in the TGA.

Use of Raw Data

The data based on the reactor's parameters and the gas chromatograph analysis were collected at set time intervals. These data were used to calculate the gasification rate. The gas chromatograph was used to calculate the mole fractions of the exit gas components, based on the standard calibration gas. The standard calibration consisted of 4 mol% hydrogen, 5 mol% oxygen, 5 mol% nitrogen, 4 mol% methane, 5 mol% carbon monoxide, 5 mol% carbon dioxide, and the balance containing helium. The mole fractions of the exit gas components were found using helium as the carrier gas. The carbon dioxide that was in the exit gas was assumed to be mainly from the gasification reactions that occurred during the steam gasification process. The amount of oxygen in the peak may have been slightly affected by small amounts of the air that entered the gas

chromatograph during sample injection. Hydrogen peaks were analyzed when nitrogen was used as the carrier gas and the gas chromatograph operated at low voltages. This was done because hydrogen peaks are affected by helium as a carrier gas. Using the gas chromatograph results, the mole fractions of the individual gas component, y_i with the peak area, A_i, at each time interval is given by

$$y_i = (y_{cal,i} / A_{cal,i}) A_i \qquad (3\text{-}3)$$

The mole fraction of the calibration standard and the corresponding calibration peak areas are symbolized by $y_{cal,i}$ and $A_{cal,i}$ respectively. A small amount of air inadvertently entered the gas chromatograph when the sample gases were injected into the unit. However, this incident was corrected through appropriate normalization for the components.

The cumulative flow meter measured the total volume of the dry exit gas mixture from the condenser. The total molar density, ρ, of the mixture was calculated at the condenser temperature, T_{cond} and at the atmospheric pressure, P_{atm} representing the conditions of the flow meter. The condenser temperature remained fairly constant, ranging in value from 71^0F through 76^0F.

$$\rho = \frac{P_{atm}}{RT_{cond}} \qquad (3\text{-}4)$$

The molar density of each gas species, i, is the product of the component mole fraction and the total molar density.

$$\rho_i = y_i \rho \tag{3–5}$$

The cumulative molar density of the carbonaceous components is represented by ρ_c and is equal to the sum of the individual molar densities of these constituents.

$$\rho_c = \sum \rho_i = \rho_{CH4} + \rho_{CO} + \rho_{CO2} \tag{3-6}$$

The moles of carbon gasified in the overall reaction process from time equal to zero up to the gasification time, t_j, is the integral of the carbon molar density with respect to the cumulative volume of the exit gases, V_j. It is then multiplied by the atomic weight of carbon, M_c, to give the mass of gasified carbon, C_{gas}.

$$\text{Moles of carbon gasified} = \int_0^{Vj} \rho_c \, dV \tag{3-7}$$

$$\text{Mass of carbon gasified, } C_{gas} = M_c \int_0^{Vj} \rho_c \, dV \tag{3-8}$$

The data being collected at the regular time intervals can be approximated using a numerical summation of the number of data points, N. Equation 3-9 is used since the data were taken at discrete time intervals.

$$\text{Mass of carbon gasified, } C_{gas} = M_c \sum_{j=1}^{N} \rho_c (V_j - V_{j-1}) \qquad (3\text{-}9)$$

where V_j and V_{j-1} are the cumulative volumes of the effluent gases measured at times t_j and t_{j-1} respectively. The molar density of carbon was taken as an arithmetic average of the molar densities at these consecutive time intervals so that there would be no discrepancies in the data obtained.

$$\rho_c = (\rho_{c,j} + \rho_{c,j-1}) / 2 \qquad (3\text{-}10)$$

which was then substituted accordingly into Equation 3-9. The initial mass of carbon in the bed, C_o, was determined from the oxidation of the pyrolyzed char in the TGA and verified through repeated experimental runs. The carbon left in the fixed-bed at any time, t_j, is given as:

$$C = C_o - C_{gas} \qquad (3\text{-}11)$$

The remaining carbon weight fraction (RCWF) in the bed at any time is then given as

$$RCWF = (C_o - C_{gas}) / C_o \quad (3\text{-}12)$$

The fractional carbon conversion in the bed based on the amount of fixed carbon in the pyrolyzed char is presented as:

$$X_{c,char} = 1 - RCWF \quad (3\text{-}13)$$

Reconciliation

Data were reconciled using the results from the TGA and from the gas chromatograph. The total carbon content of the pyrolyzed litter was determined before and after gasification. The correction was then implemented using the following formula:

$$X_{correct} = (X_{gas} / X_{TGA}) * X_{c,char} \quad (3\text{-}14)$$

X_{gas} is the cumulative conversion of carbon at the end of gasification using the gas chromatograph and X_{TGA} is the value found from the TGA analysis. To find X_{TGA}, the amount of fixed carbon was determined from the TGA analysis of the char before and after gasification. The amount found after the gasification was then subtracted from the amount before gasification and divided over the amount prior to gasification to find the conversion. The corrected conversions were used to recalculate the amount of carbon gasified in the bed and the volume of gases flowing between the consecutive time intervals. The correction factor was usually about 0.98.

$$RCWF_{correct} = 1 - X_{correct} \quad (3\text{-}15)$$

$$C_{correct} = RCWF_{correct} * C_o \quad (3\text{-}16)$$

The amount of gasified carbon in the bed is now:

$$C_{gas,correct} = C_o - C_{correct} \quad (3\text{-}17)$$

Using the reconciled values, the gasification rate was calculated using the 3-point numerical differentiation formula.

$$(dC/dt)_j = (-3C_j + 4C_{j+1} - C_{j+2}) / 2\,\Delta t \quad (3\text{-}18)$$

where $j = 0$ when $t = 0$ and $j = j - 2$ when $t = \tau$, the total gasification time period. When determining the gasification rates at the end points, the following equation was used.

$$(dC/dt)_j = (C_{j+1} - C_{j-1}) / 2\,\Delta t \quad (3\text{-}19)$$

The reconciled data were used to find the moles of gasified carbon products that existed as carbon monoxide, methane, and carbon dioxide between the consecutive times of t_j and t_{j-1}.

$$\text{Moles of CO} = [CO]_j = \frac{(\rho_{CO,j} + \rho_{CO,j-1})}{2} * \Delta V_{j,correct} \quad (3\text{-}20)$$

$$\text{Moles of } CH_4 = [CH_4]_j = \frac{(\rho_{CH4,j} + \rho_{CH4,j-1})}{2} * \Delta V_{j,correct} \quad (3\text{-}21)$$

$$\text{Moles of } CO_2 = [CO_2]_j = \frac{(\rho_{CO2,j} + \rho_{CO2,j-1})}{2} * \Delta V_{j,correct} \quad (3\text{-}22)$$

In these experiments, the amount of gasified carbon that formed CO and CH_4 was also determined. This amount reflected the total amount of carbon gasified in the bed to fuel gas constituents at a particular time interval of t_j.

$$\text{Fuel Gas Fraction of } CO + CH_4 + H_2 = \sum_{1}^{j} ([CO]_j + [CH_4]_j + [H_2]_j)(M_c / C_{j,correct}) \quad (3\text{-}23)$$

Partial Pressure of Steam During Gasification

The previous calculations were carried out on a dry basis at the exit of the condenser. However, the components in the product gas also contained unreacted steam. The amount of steam present in the bed was calculated as the average of the amount entering and leaving the reactor (4). The unreacted steam exiting between time t_{j-1} and t_j was calculated from the average amount collected in the condenser over the total gasification time period, τ. The amount of steam that condensed at a time, t_j, was determined on a molar basis. This quantity is defined as $H_2O_{out,j}$.

$$H_2O_{out,j} = \{\text{Condensate} * (t_j - t_{j-1})\} / (\tau * 18) \quad (3\text{-}24)$$

The average moles of steam in the bed at a time, t_j, is then shown by:

$$H_2O_{avg,\,j} = (H_2O_{in,\,j} + H_2O_{out,\,j}) / 2 \qquad (3\text{-}25)$$

where $H_2O_{in,j}$ represents the amount of water in moles entering the reactor at the time, t_j.

The mole fraction of the amount of steam in the fixed bed was calculated from the total moles of all the exit gases. This included the steam, too. Cumulative moles of the exit gases, $G_{exit,j}$, for the time frame between t_j and t_{j-1} is given by:

$$G_{exit,j} = (y_{CO} + y_{CH4} + y_{CO2} + y_{H2} + H_2O_{avg})_j \qquad (3\text{-}26)$$

The basis for the calculations is one mole of dry gases at the exit conditions. The mole fraction is the same as the number of moles at the exit on a dry basis. The mole fraction of the steam in the bed and the partial pressure of steam in the bed are then,

$$y_{H20,j} = H_2O_{avg} / G_{exit,j} \qquad (3\text{-}27)$$

$$pH_2O_j = y_{H2O,j} * P_{reactor} \qquad (3\text{-}28)$$

where,

$y_{H2O,j}$ is the mole fraction of the steam in the fixed bed at time, t_j

pH_2O_j is the partial pressure of steam at time, t_j, in kPa

$P_{reactor}$ is the operating pressure of the reactor

These parameters were calculated during the interpretation of the raw data to determine the effects of various variables on the gasification kinetics.

CHAPTER 4

RESULTS AND DISCUSSION

In determining the optimum conditions to handle the broiler litter, the catalytic steam gasification of the broiler litter was carried out using K_2CO_3 and langbeinite as the catalysts. Langbeinite is an inexpensive mineral used in the fertilizer industry. It contains potassium and magnesium sulfate, and it comes in a crystalline form. The chemical formula for langbeinite is $K_2Mg_2(SO_4)_3$. The catalyst was physically mixed with the broiler litter, then the entire sample was pyrolyzed into the char used for the gasification experiments. The next step in determining the optimum conditions to handle the broiler litter was to set up a screening matrix that evaluated several variables affecting the gasification. The following variables were evaluated: temperature, pressure, steam flow rate, and catalyst loading. The operating conditions used for the experimental runs carried out using K_2CO_3 are provided in Table 4.1. For each run, the initial amount of char in the bed was 2.5 grams and the gasification was carried out for 255 minutes. The following sections highlight the effects of different variables studied during the experiments. Comparisons are then made using two different catalysts, potassium carbonate and langbeinite.

Studies with Potassium Carbonate

Temperature

In providing an accurate gauge on the effect of temperature in catalytic steam gasification, three runs were performed. The samples were separately tested at 1200^0F,

Table 4.1: Process Variables for Catalytic Gasification Runs Using K_2CO_3

Run	Temperature (^{0}F)	Pressure (psig)	Catalyst Loading (wt%)	Steam/Water Flow Rate (ml/min)
1	1200	100	10	0.25
2	1350	100	10	0.25
3	1420	100	10	0.25
4	1350	50	10	0.25
5	1350	300	10	0.25
6	1350	100	5	0.25
7	1420	100	15	0.25
8	1420	100	10	0.084
9	1420	100	10	0.0145

1350^{0}F, and 1420^{0}F. At 1200^{0}F, the carbon conversion, based on pyrolyzed char, reached approximately 86%, while at higher temperatures it approached 100% carbon conversion. The results on the carbon conversions are presented in Figure 4.1. As shown in the figure, the carbon conversions at 1350^{0}F and 1420^{0}F mirrored each other closely, showing that good conversion does not have to be reached at the highest temperature. However, the conversion is not as good at low temperature, making the gasification rate unfavorable. At a lower temperature, the conversion of the char sample is not complete, indicating some of the reactions may be slow or not completed. However, the gasification reactions are more likely to be completed at 1350^{0}F and higher temperatures. This minimum in temperature also allows the gasification rates to be high enough to let the reactions go to completion and produce desirable by-products in a reasonable time. Based on the experimental runs, it can be stated that a temperature of at least 1350^{0}F is sufficient for the gasification of broiler litter under given pressure and steam flow rate conditions. Since the results are very similar at 1420^{0}F, it does not appear beneficial to operate at any higher temperature than 1350^{0}F. To further evaluate the effect temperature has on the gasification reaction, the conversion of carbon to carbon monoxide, methane and hydrogen was estimated. Figure 4.2 shows a plot of the amount of gasified carbon that existed as CO, CH_4 , and H_2 at a particular time interval. The gasified carbon is converted into carbon dioxide, carbon monoxide, and methane. However, only carbon monoxide, methane, and hydrogen comprise the mole fraction of by-products formed as fuel gas constituents from the total carbon. A plot of the fuel gas fraction of CO, CH_4, and H_2 against the conversion is shown for the different temperatures in Figure 4.2. Since there were different values at each carbon conversion, an average of the fuel gas

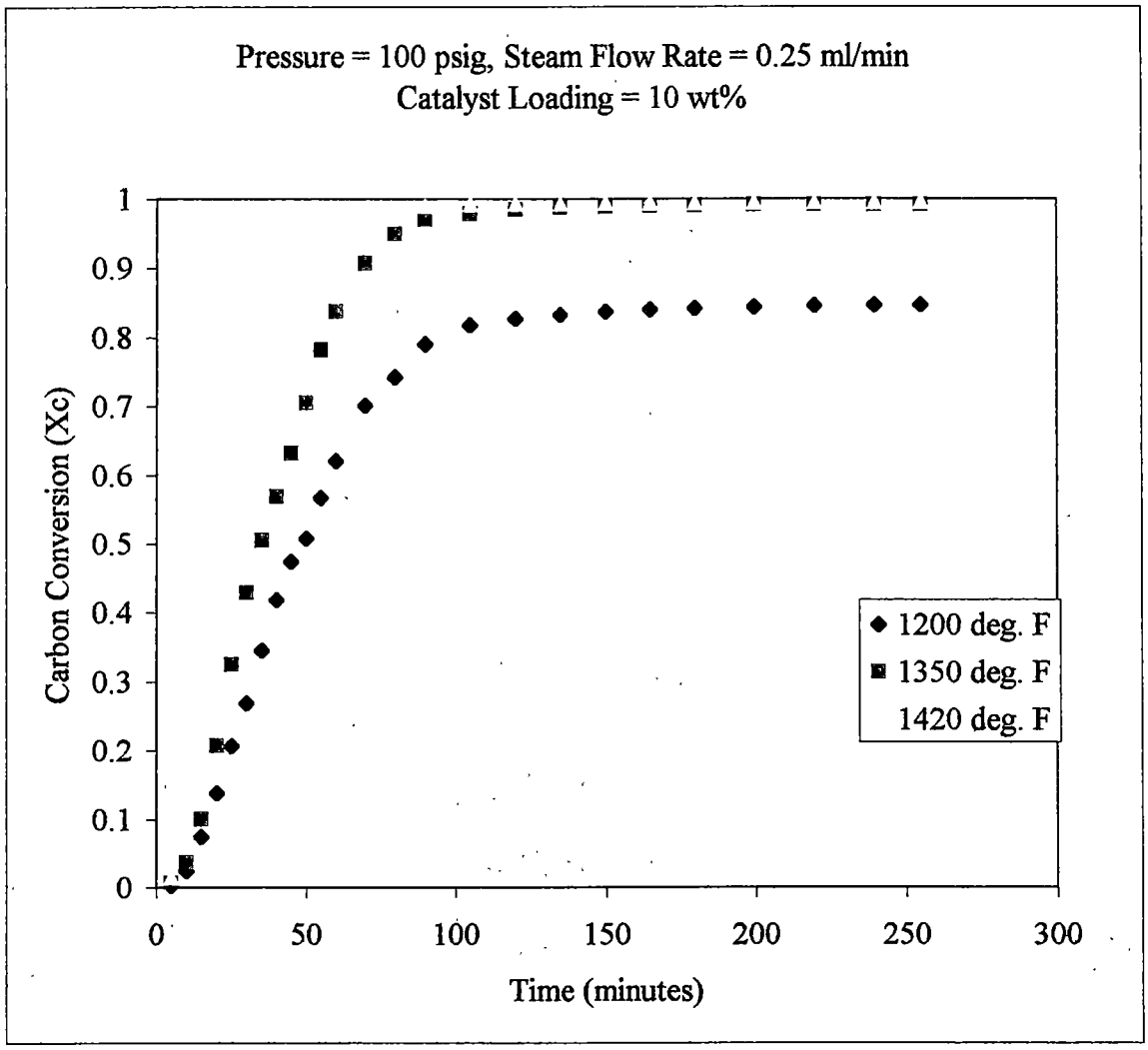

Figure 4.1: Catalytic Gasification of Broiler Litter with K_2CO_3 at Various Temperatures

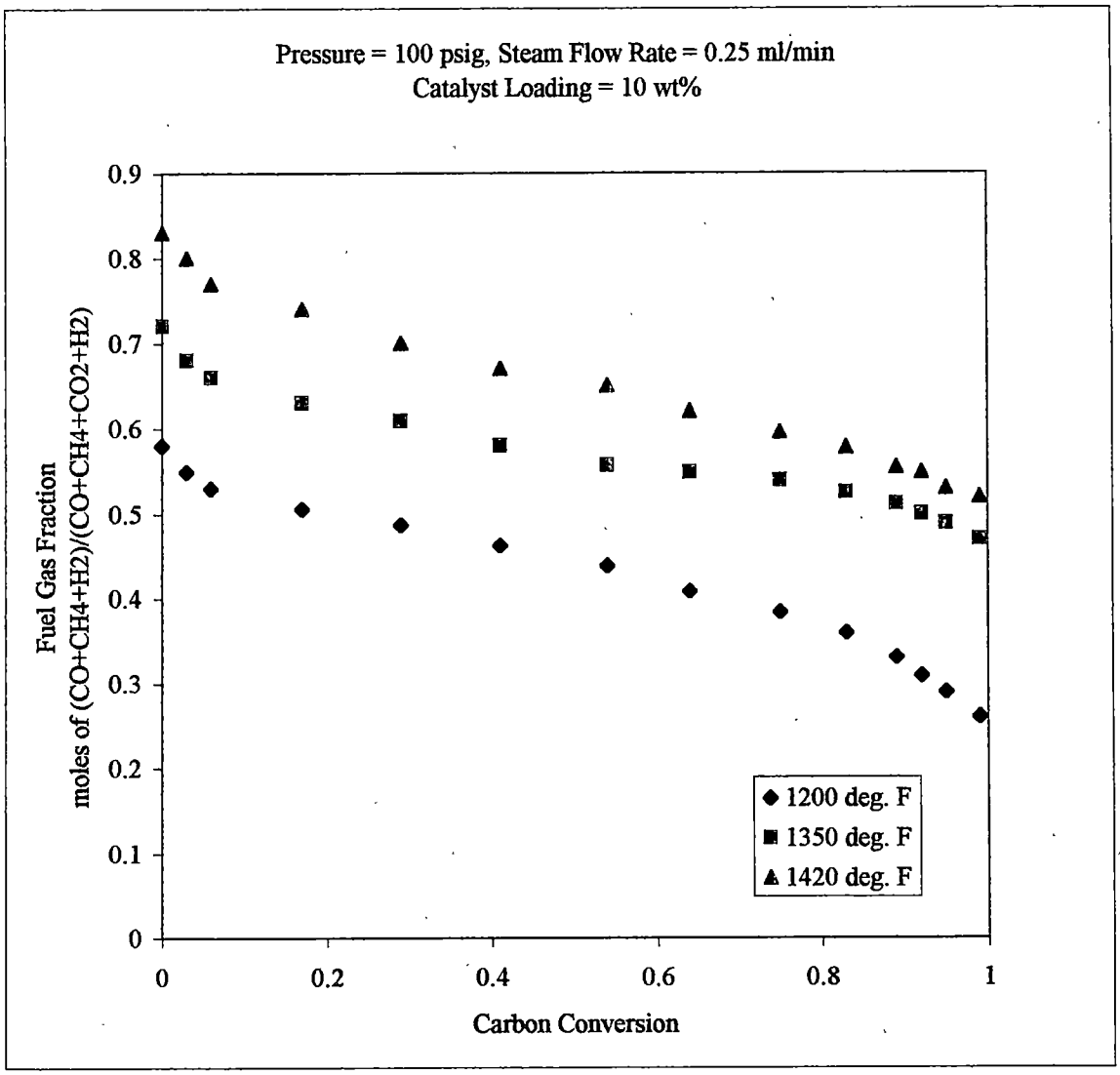

Figure 4.2: Fuel Gas Fraction as a Function of Temperature Using K_2CO_3

fraction was taken for each temperature for comparison purposes. The following equation was used to determine this average fuel gas fraction:

$$\text{Average Fuel Gas Fraction} = \frac{\sum_{i=0}^{N} \phi_i \, x_{c,i}}{x_{cf} - 0} \qquad (4\text{-}1)$$

where ϕ_i represents the fuel gas fraction at a particular carbon conversion and $x_{c,i}$ represents that carbon conversion. This equation was used to find the analytical average since the area of the curve just above and below the average should be nearly the same. At 1200^0F, the average mole fraction formed as fuel gas constituents was 0.44, while at the highest temperature of 1420^0F, the average mole fraction was just under 0.66. At 1350^0F, the average fraction was 0.57. The conversion of the carbon into useful fuel gas constituents is quite relevant at the lowest tested temperature, but it is even more profound at the higher temperatures. From these experiments, the higher temperatures allow for better conversion of the carbon into useful by-products. Finding alternative uses for the broiler litter may be very beneficial if a significant percentage of the carbon is converted into useful fuel gas constituents, such as carbon monoxide, methane, and hydrogen.

Pressure

Pressure was adjusted to see if carbon conversion would be affected in any significant manner. Three runs were conducted at pressures of 50 psig, 100 psig, and 300 psig.

The results are presented in Figure 4.3, which show that the ultimate conversion was reached around the same time, although the initial rates varied slightly. These runs showed that the gasification rates are probably independent of the pressure at the conditions used in this study.

The effects of pressure on the fractional conversion of carbon are presented. Those values were found as an average over the entire run, as discussed earlier when temperature was the tested variable. As seen in Figure 4.4, the average fractional conversion to carbon monoxide, methane, and hydrogen is just under 53% at 50 psig. At 100 psig, the average fractional conversion was 64.3%, while the conversion was 61.2% at 300 psig. Although the gasified char reached the similar maximum carbon conversion at each pressure, there does appear to be some relevance in adjusting the pressure to about 100 psig if one wants to achieve a slightly higher conversion to useful fuel gas constituents. However, the difference in conversion from 100 psig to 300 psig is minimal, thus making an increase in pressure unnecessary beyond 100 psig.

Catalyst Loading

Potassium carbonate (K_2CO_3) and langbeinite were used to study the effect of catalysts during steam gasification of the broiler litter. The results with langbeinite are discussed in a later section. Potassium carbonate was added to the broiler litter at 5 wt%, 10 wt%, and 15 wt% levels. A run was also conducted with no additional catalyst being added to the litter. An increase in the catalyst loading increased the number of potassium atoms available for catalytic activity. With no additional catalyst, the

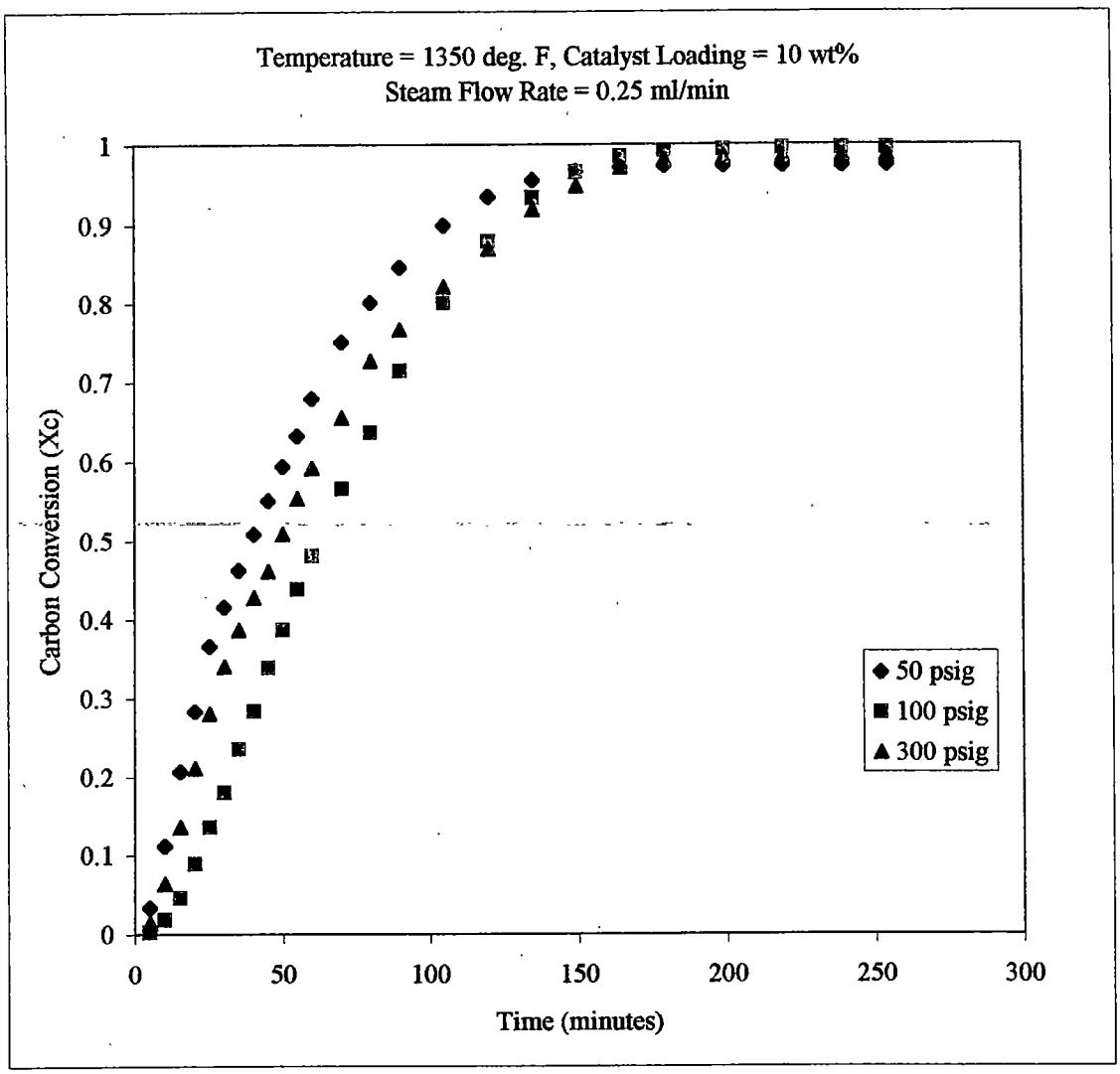

Figure 4.3: Catalytic Gasification of Broiler Litter with K_2CO_3 at Various Pressures

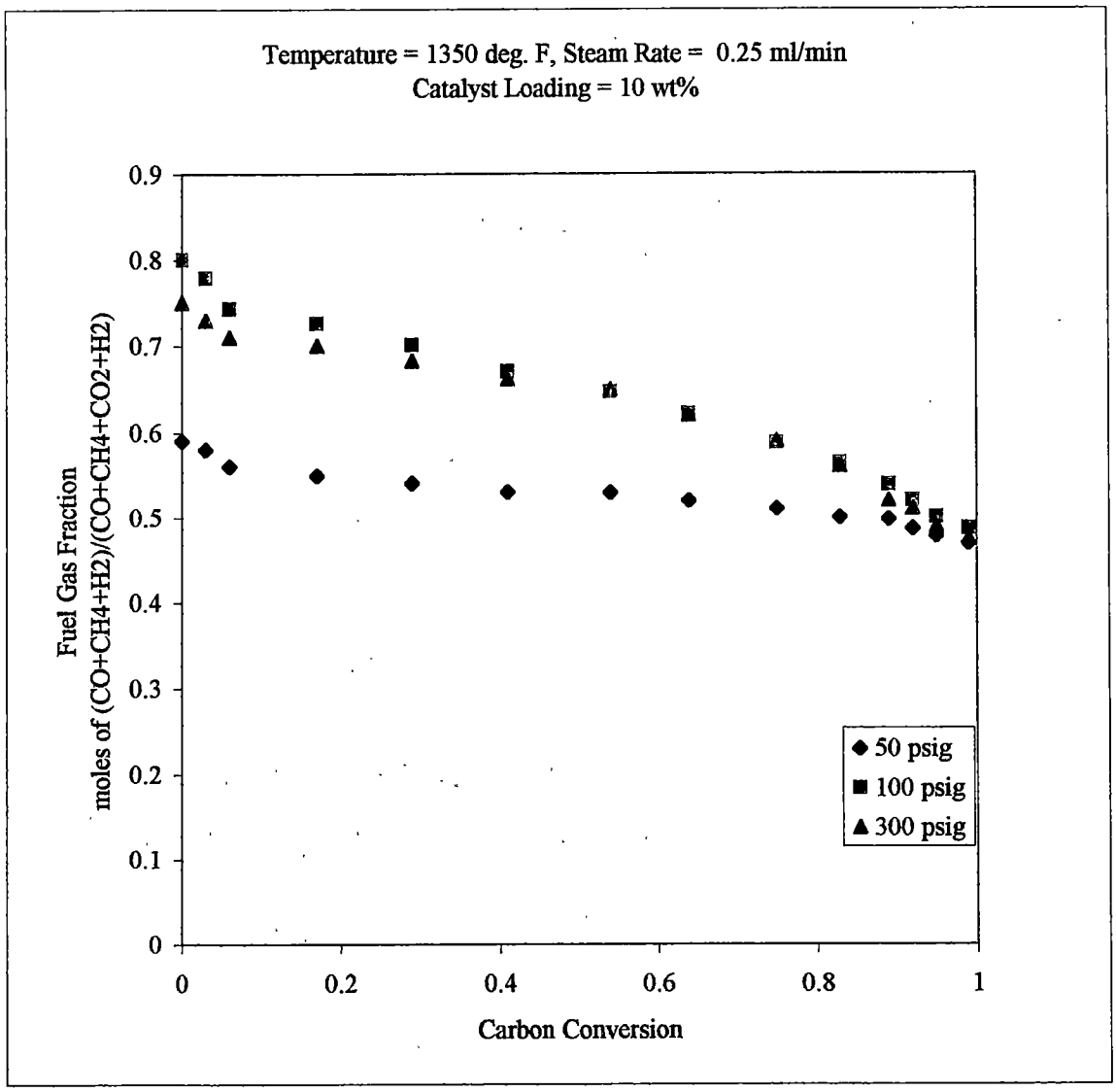

Figure 4.4: Fuel Gas Fraction as a Function of Pressure Using K_2CO_3

conversion only reached just under 75% after 240 minutes. However, adding catalyst at 5 wt% loading did increase the final carbon conversion to 85%, and 10 wt% and 15 wt% loadings allowed the conversion to reach over 95%. These results are shown in Figure 4.5. At a lower catalyst loading, it is likely that the catalyst might have been deactivated to a greater extent by the reaction of the catalyst with the mineral matters in the litter, thus slowing the gasification process and producing lower carbon conversion for the run. When the catalyst loading was 10 wt% and 15 wt%, the gasification rates increased significantly. However, an increase in catalyst loading from 10 to 15 wt% did not proportionately increase the conversion or the rate of conversion. The specific gasification rates, defined as (1/C)(dC/dt), were obtained from the slopes of first order plots of the carbon conversions in the bed versus the time for each run and are shown as a function of the atomic K/C ratio in Figure 4.6. The increased activity could be due to the increased number of potassium atoms (from the catalyst) available in the bed at the higher loadings. However, loadings higher than 10 wt% did not produce any substantial increase in the gasification performance. This could be due to possible saturation of the alkali metal atoms in the carbon matrix, thus leading to a point of diminishing returns. Catalyst loadings were also varied to show what happens to the conversion of carbon to carbon monoxide and methane. Again, the conversion to useful fuel gas constituents was calculated as an average of the samples collected throughout the entire experimental run. Figure 4.7 shows that the average conversion of carbon was around 57% at 10 wt% and 62% at 15 wt% loading, while 5 wt% loading produced a conversion just under 50%. When no additional catalyst was used, this fractional conversion value dropped to 13%.

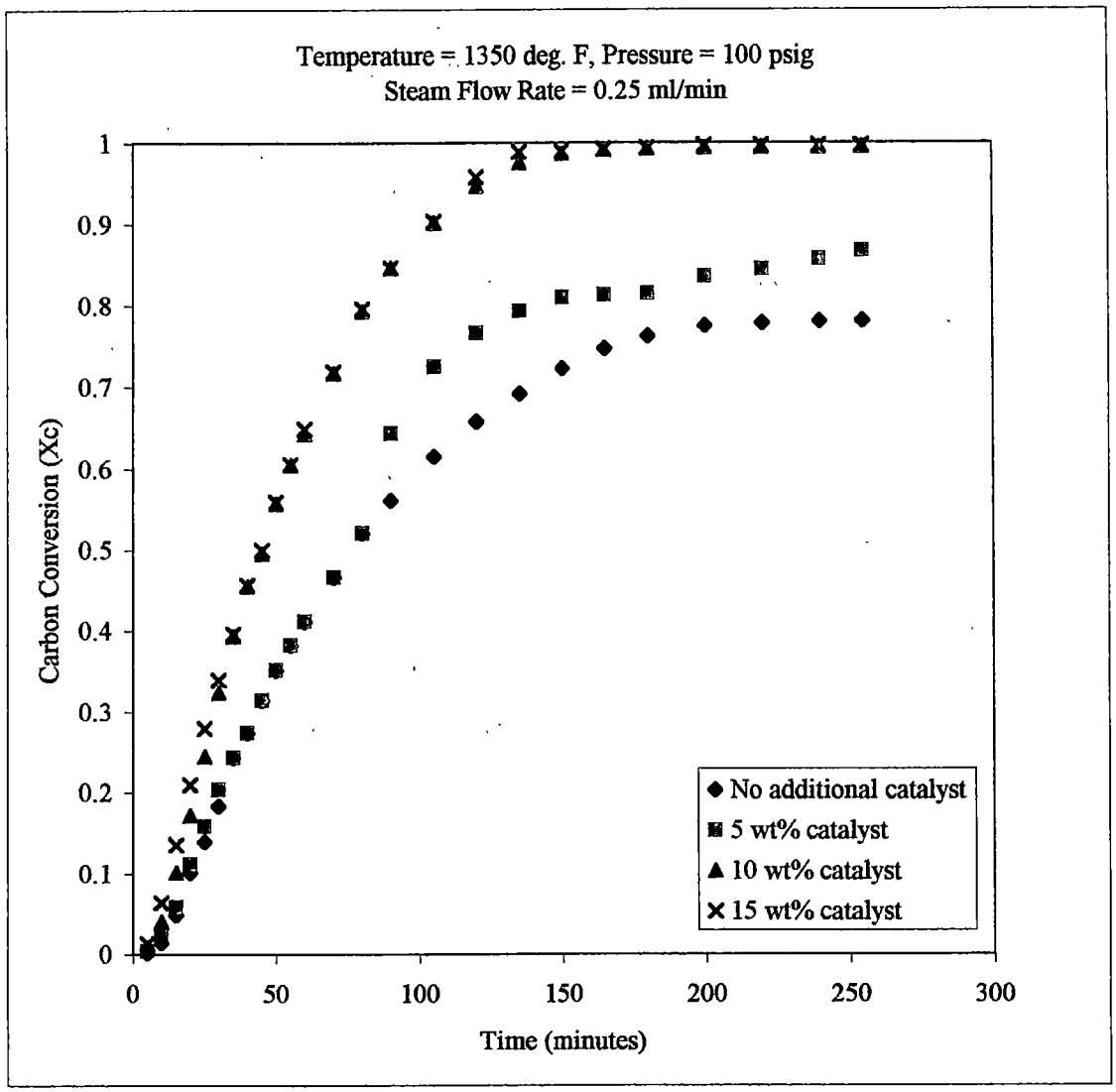

Figure 4.5: Catalytic Gasification of Broiler Litter with K2CO3 at Various Loadings

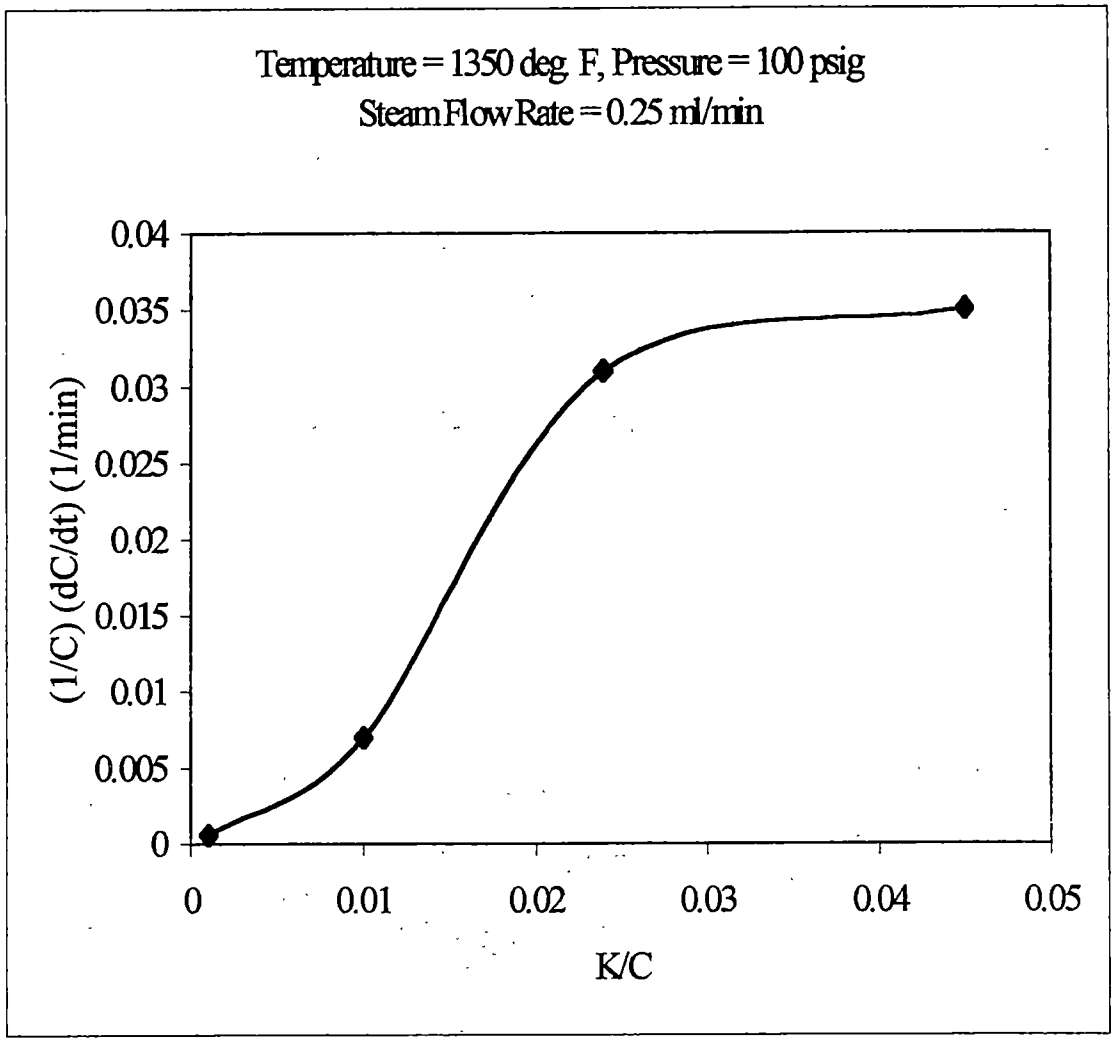

Figure 4.6: Specific Gasification Rates vs. K/C Ratio (using K_2CO_3)

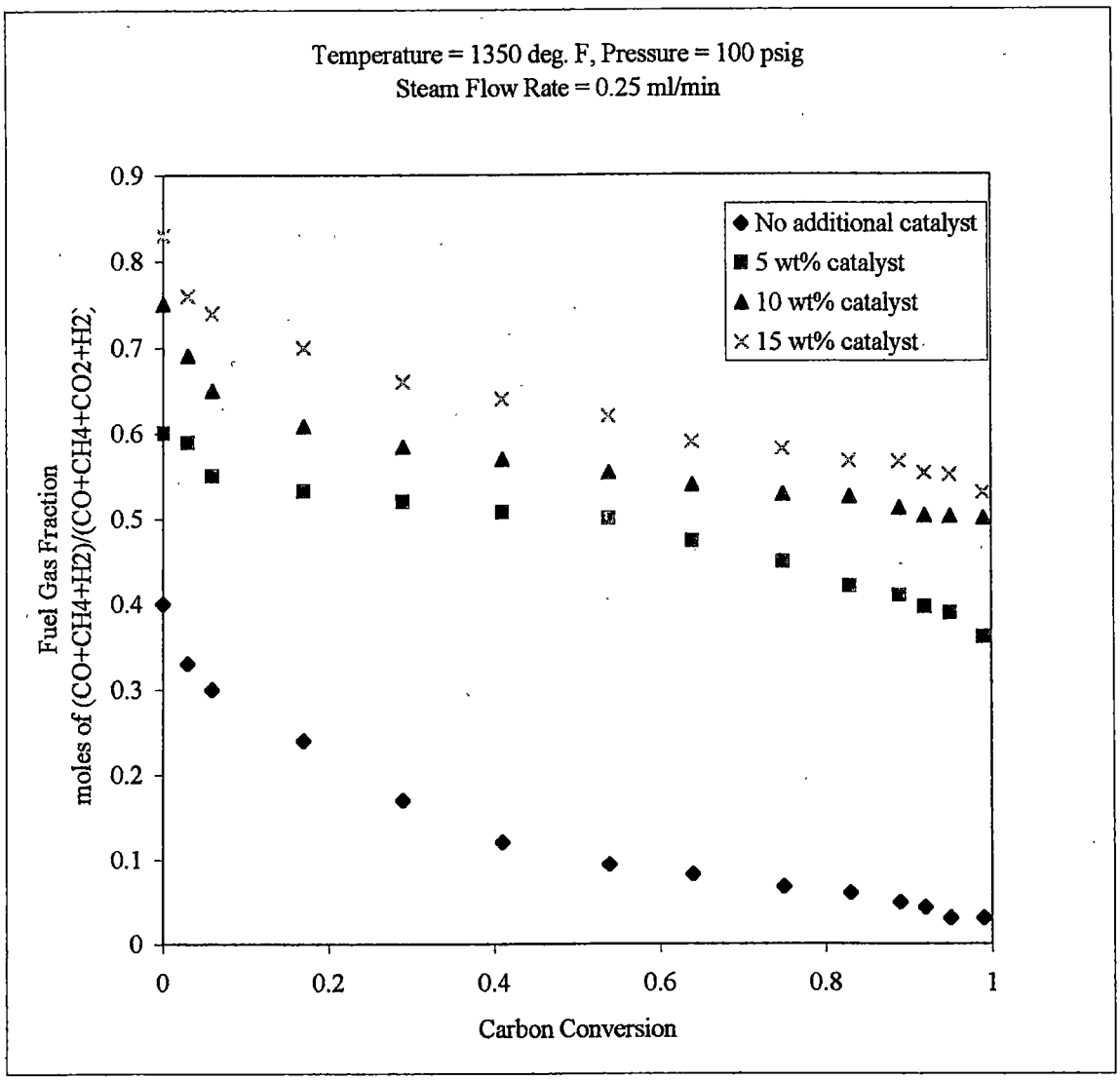

Figure 4.7: Fuel Gas Fraction as a Function of Catalyst Loading Using K_2CO_3

Therefore, the catalyst loading does appear to affect the fuel gas fraction of the carbon monoxide and methane in a significant way. Increasing the catalyst loading does improve the fuel gas conversion, although the improvement is less drastic when the loading is increased over 10 wt%. However, further testing may be needed to determine when an increase in the catalyst loading no longer improves the conversion to CO, CH_4, and H_2.

Steam Flow Rate

Experiments were conducted at different steam/water flow rates corresponding to sufficient amounts of steam required for gasifcation reaction (based on stoichiometry) to a large excess of steam. These experiments were carried out at 0.084 ml/min, 0.145 ml/min, and 0.25 ml/min, and the results are presented in Figure 4.8. At a lower steam/water flow rate, only 77% conversion of carbon was reached during the duration of the run. When excess steam was provided, broiler litter char reached 96% conversion in less than 100 minutes at a rate of 0.25 ml/min. At 0.145 ml/min, the same conversion was reached in about 220 minutes. Based on the steam gasification reactions, it is known that 2 moles of water are required for every mole of carbon to complete the overall gasification reaction. When one provides excess moles, it can favor the gasification reaction to a certain extent. However, beyond that point, the excess steam probably saturates the active sites in the carbon matrix without further improving the gasification rates, suggesting a Langmuir-Hinshelwood type of mechanism. The overall gasification rates calculated from the first order fit to the conversion data were also very low when 2 moles/hr of steam was provided for every mole of carbon. That rate was

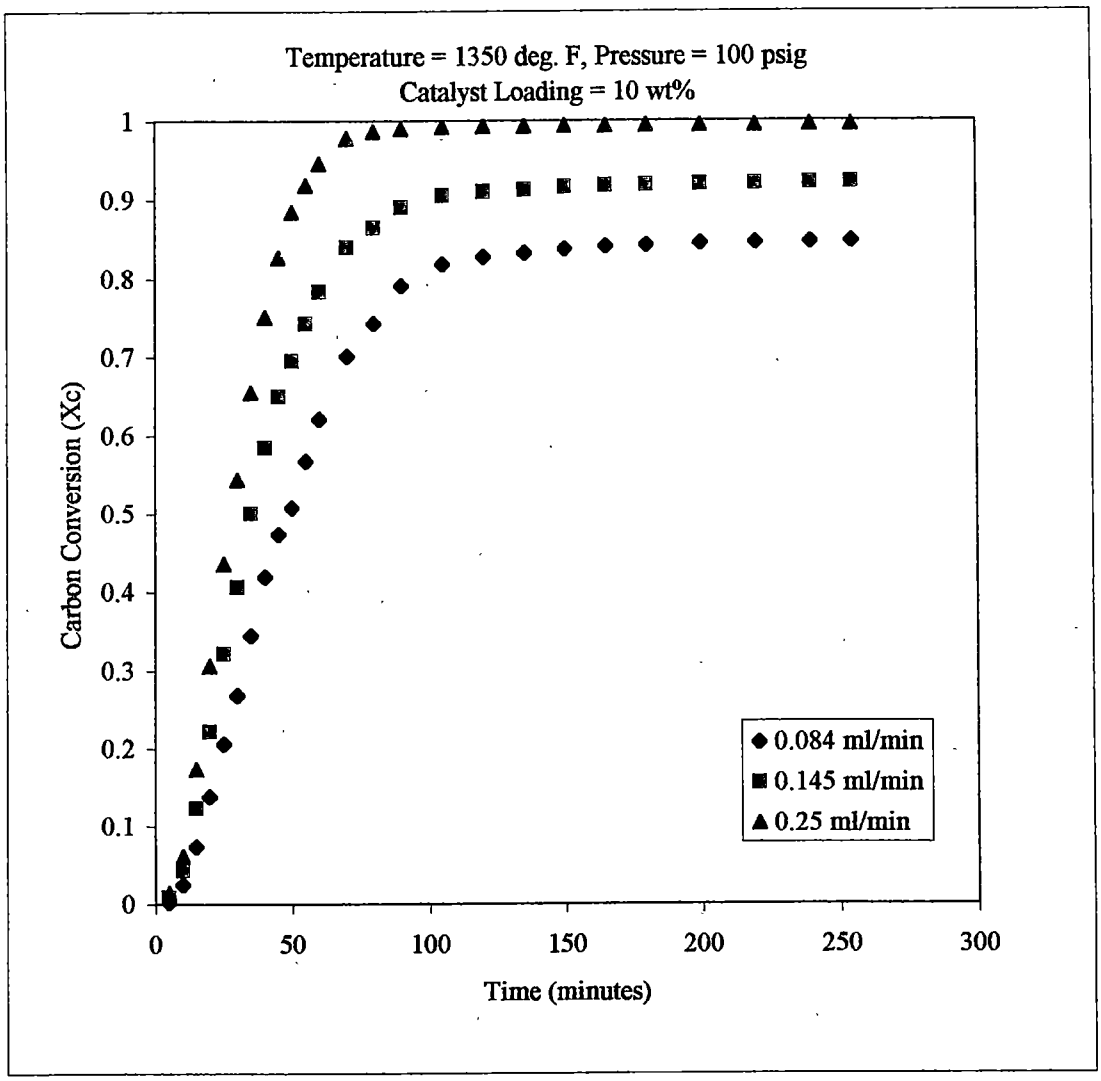

Figure 4.8: Catalytic Gasification of Broiler Litter with K_2CO_3 at Various Steam Flow Rates

0.0011 min^{-1}. The overall rate increased to about ten times (0.0135 min^{-1}) when the flow rate was increased to 0.145 ml/min. Upon providing excess steam, the gasification rates seemed to increase. However, increasing the steam flow rate to 0.25 ml/min did not provide any significant additional increase in the overall rate. The excess unreacted steam was condensed and collected as the bottoms condensate in each run. The amount of carbon monoxide, methane, and hydrogen produced on a molar basis was determined for each steam flow rate. The average fractional conversion of the fuel gas constituents was just under 55% at a flow rate of 0.084 ml/min, while at a flow rate of 0.145 ml/min and 0.25 ml/min, the average fractional conversions were 66% and 70% respectively. This shows that an increase in the amount of steam favors the carbon conversion into useful by-products. However, the increase is not as dramatic when the steam flow rate was increased from 0.145 ml/min to 0.25 ml/min. It is possible that this occurs due to possible saturation of the steam in the carbon matrix. These results are shown in Figure 4.9.

Studies with Langbeinite

Temperature

In providing an accurate gauge on the effect of temperature in catalytic steam gasification, three runs were performed with langbeinite. The experimental procedures and data analysis methods employed were the same as those employed for potassium carbonate. The char samples were again tested at 1200^{0}F, 1350^{0}F, and 1420^{0}F. The complete matrix of experimental conditions is presented in Table 4.2.

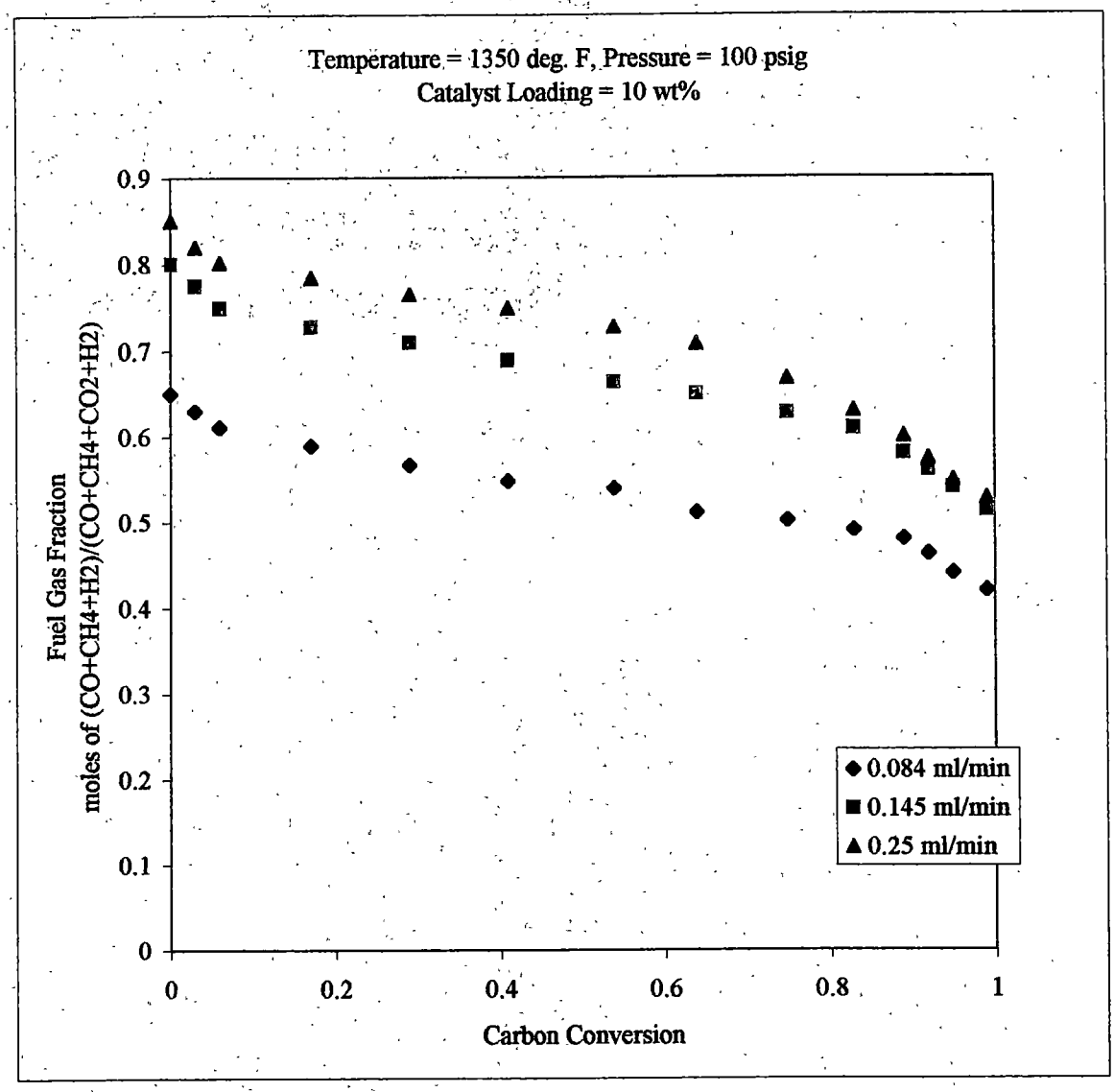

Figure 4.9: Fuel Gas Fraction as a Function of Steam Flow Rate Using K_2CO_3

Table 4.2: Process Variables for Catalytic Gasification Runs Using Langbeinite

Run	Temperature (^{0}F)	Pressure (psig)	Catalyst Loading (wt%)	Steam/Water Flow Rate (ml/min)
1	1200	100	10	0.25
2	1350	100	10	0.25
3	1420	100	10	0.25
4	1350	50	10	0.25
5	1350	300	10	0.25
6	1350	100	5	0.25
7	1420	100	15	0.25
8	1420	100	10	0.084
9	1420	100	10	0.0145

At 1200^{0}F, conversion was around 85%, while the gasification approached 100% at the higher temperatures. The results of the conversions are presented in Figure 4.10. As shown in this figure, the carbon conversions at 1350^{0}F and 1420^{0}F mirrored each other closely, showing that good conversion again does not have to be reached at the highest temperature. However, the conversion is not as good at a low temperature of 1200^{0}F, making the gasification rate undesirable. The low temperature likely prevents the reaction of the char sample from going to completion and obtaining desirable by-products. Just like the analysis with K_2CO_3, favorable gasification reactions are more likely to occur at 1350^{0}F. This minimum in temperature also allows the gasification rates to be high enough to let the reactions go to completion. Based on the experimental runs, it can be stated that a temperature of at least 1350^{0}F will be sufficient for gasification of the broiler litter using langbeinite as a catalyst. Since the results are very similar at 1420^{0}F, it again would not be beneficial to operate at temperatures higher than 1350^{0}F. Economics do play a vital role in determining what operating conditions work best for the trials, and operating at higher conditions is not always the best solution. To further show the effect of temperature on the gasification reaction, the conversion of carbon to carbon monoxide, methane, and hydrogen was studied. Figure 4.11 provides the supporting data for this evaluation. A plot of the fuel gas fraction of CO, CH_4, and H_2 against the carbon conversion is shown for the different temperatures. Once again, an average of the fuel gas fraction for the entire experimental run is used. At 1200^{0}F, the average mole fraction formed as fuel gas constituents was 0.40, while at the highest temperature of 1420^{0}F, the average mole fraction was just 52%. At 1350^{0}F, the average fuel gas fraction was 45%.

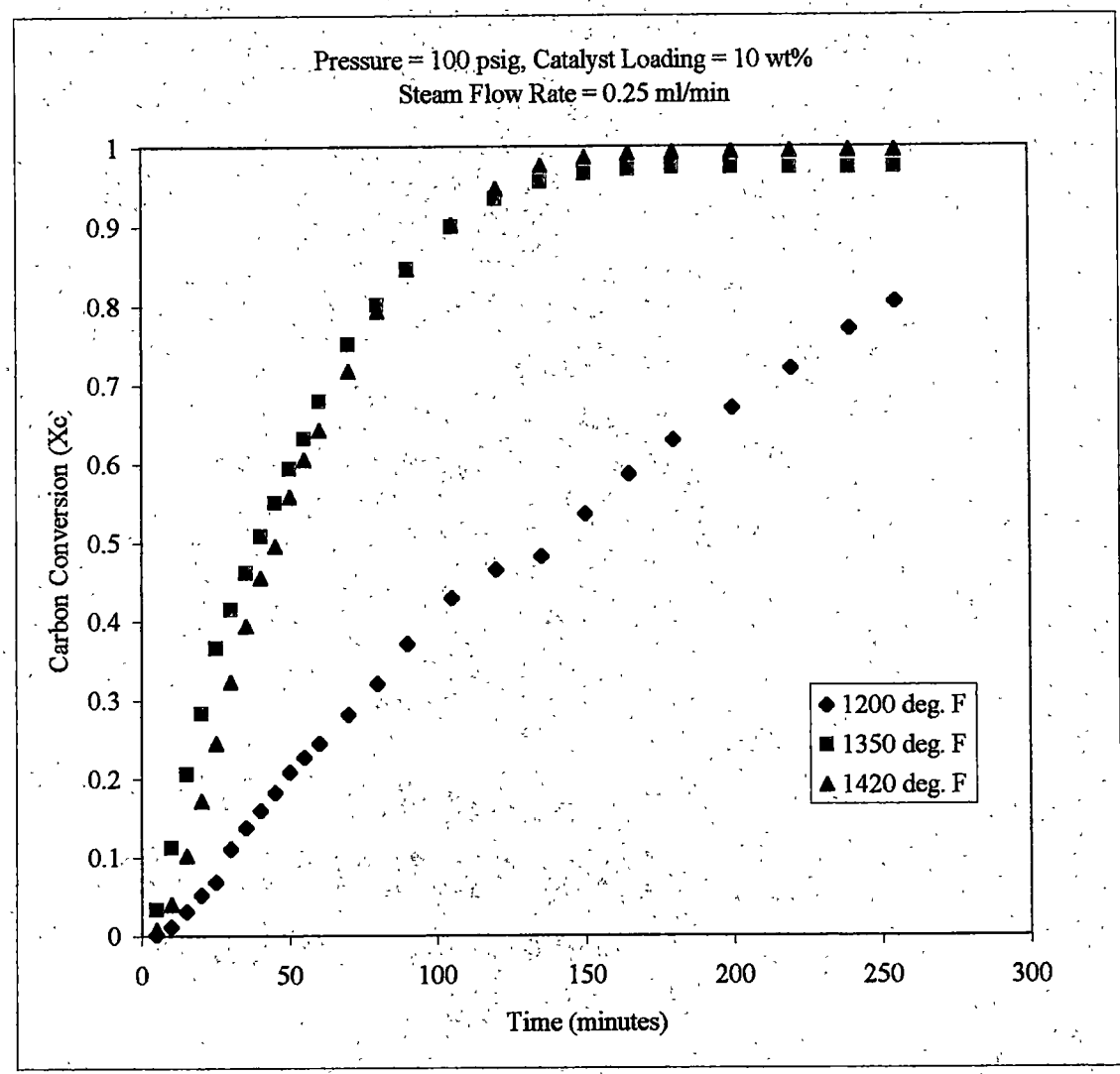

Figure 4.10: Catalytic Gasification of Broiler Litter with Langbeinite at Various Temperatures

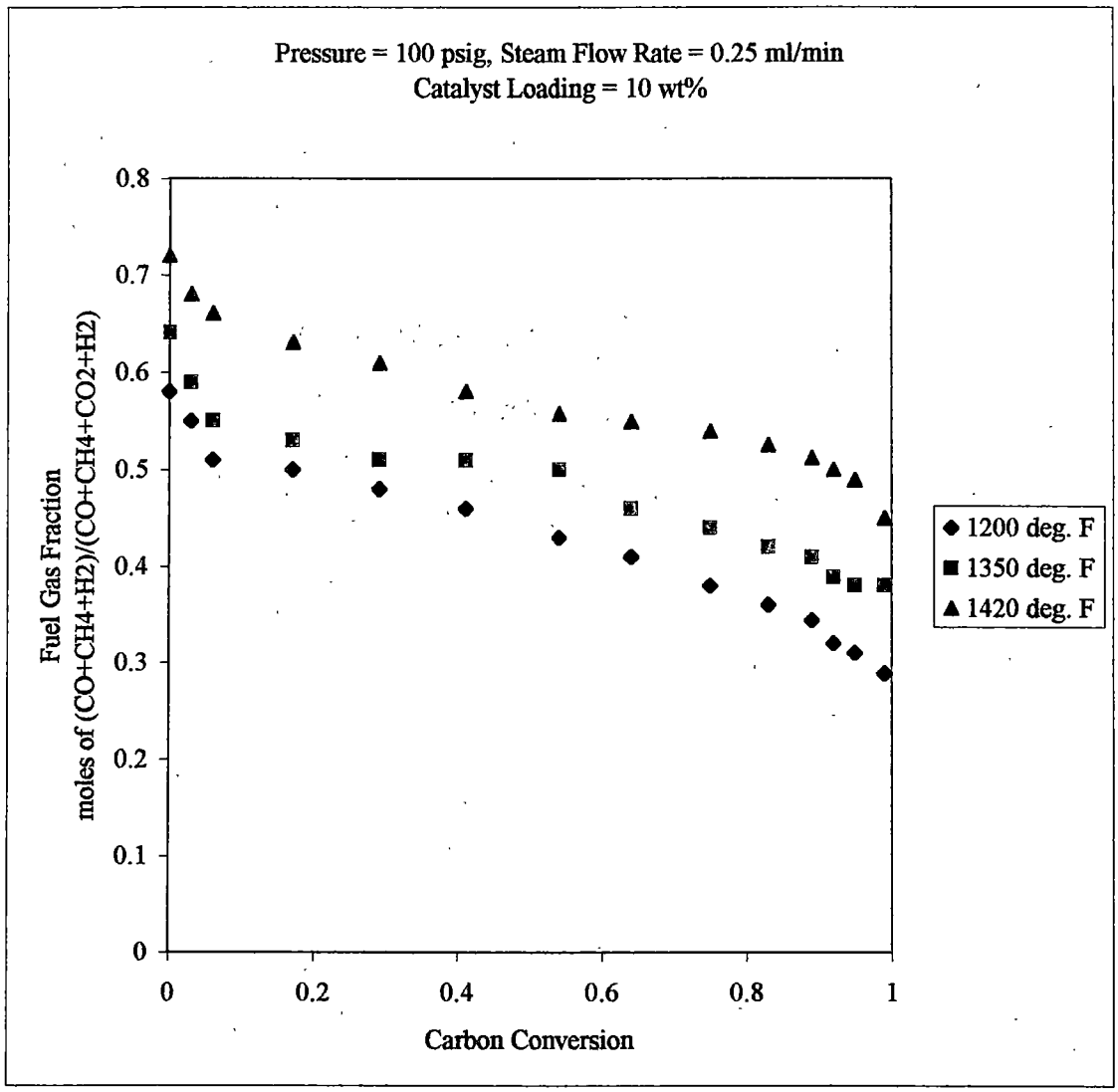

Figure 4.11: Fuel Gas Fraction as a Function of Temperature Using Langbeinite

Although there was some conversion to fuel gas at each temperature, the conversion was not as strong as it was when potassium carbonate was used. This average fraction was 57% at 1350^{0}F and 66% at 1420^{0}F using potassium carbonate as the catalyst. While the average fuel gas fraction reached only 52% at 1420^{0}F when langbeinite was used as the catalyst, the fractions were under 50% at 1200^{0}F and 1350^{0}F. This may occur because potassium exists in a higher atomic percentage in potassium carbonate than in langbeinite at similar weight loadings. The potassium atoms in potassium carbonate may also react more quickly since it is in more abundance.

Pressure

Pressure was adjusted to see if carbon conversion would be affected in any significant manner. Three runs were conducted at pressures of 50 psig, 100 psig, and 300 psig. The results are presented in Figure 4.12, which show that complete conversion was reached in each case but at somewhat different times. The complete conversion was reached after 200 minutes at 50 psig, while it took just over 90 minutes at 100 psig and 300 psig. While the maximum conversion of 99% was reached at different times, the initial gasification rates showed very little variation between the lower and higher pressures.

The fuel gas fraction of carbon monoxide and methane shows the fractional conversion of carbon into these two components. Once again, the conversion was calculated as an average. As seen in Figure 4.13, the average fractional conversion to carbon monoxide, methane, and hydrogen at 50 psig was about 17% of the overall carbon conversion, while it was 35% and 46% at 300 and 100 psig respectively. These low figures may suggest

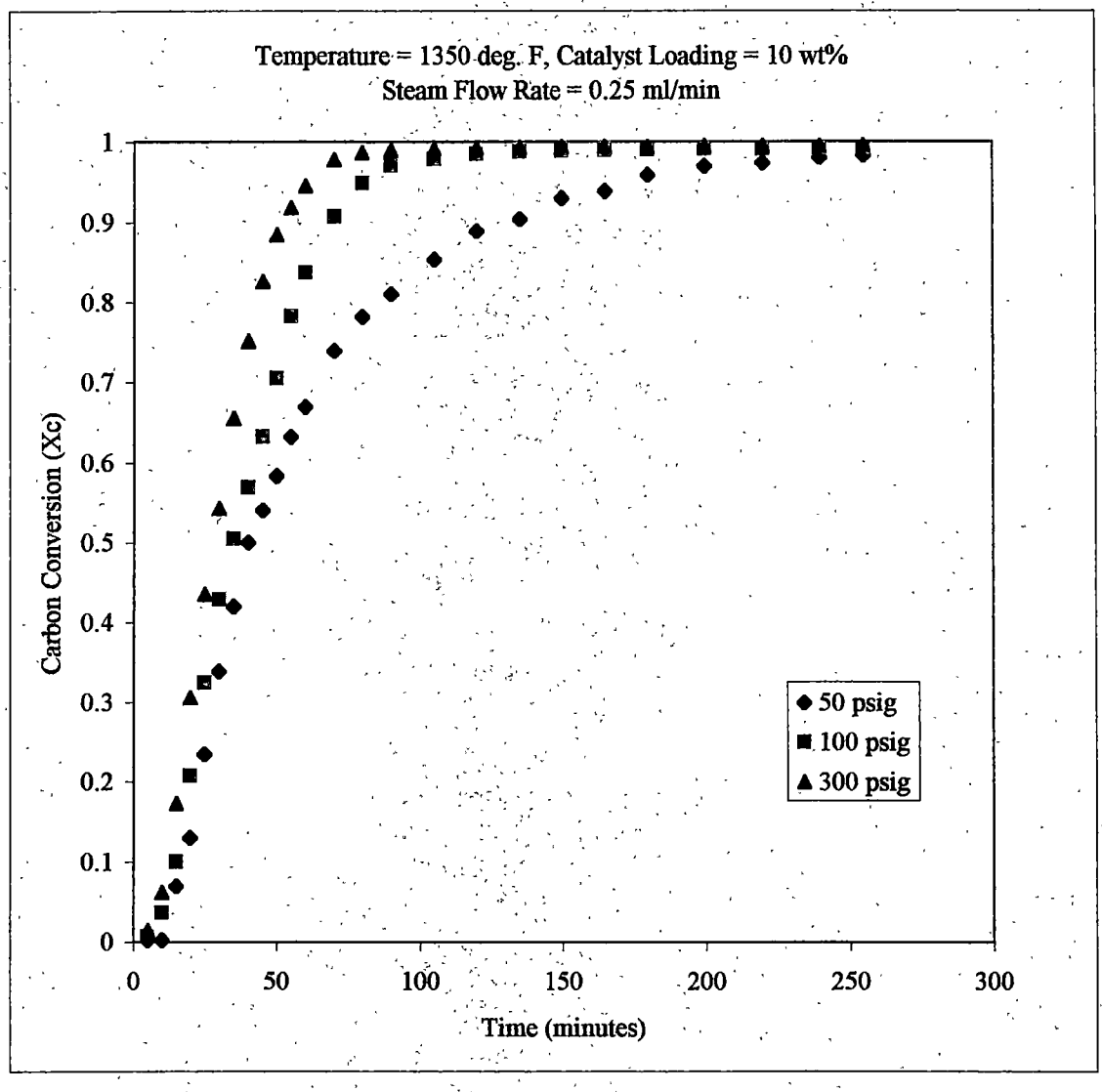

Figure 4.12: Catalytic Gasification of Broiler Litter with Langbeinite at Various Pressures

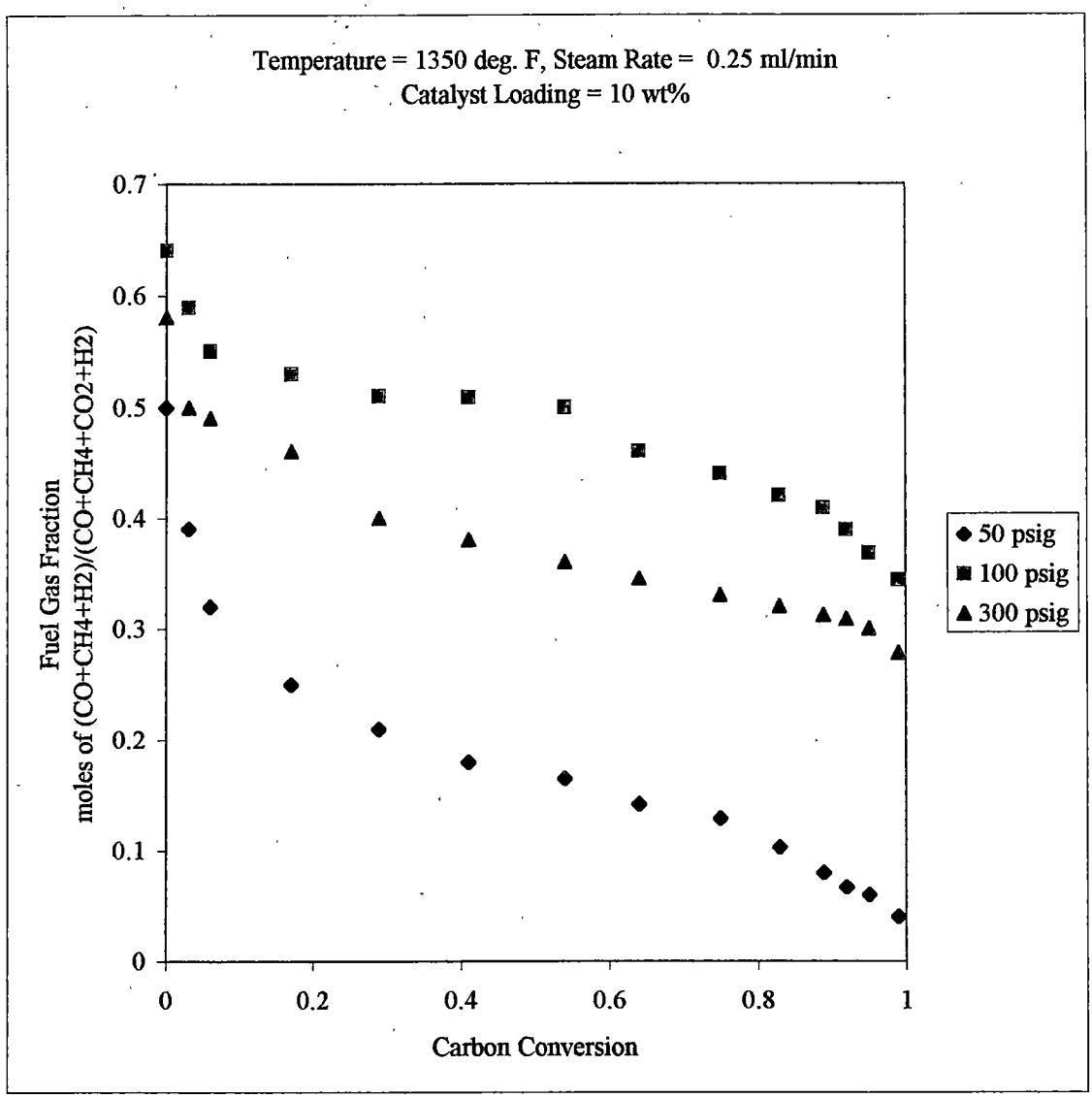

Figure 4.13: Fuel Gas Fraction as a Function of Pressure Using Langbeinite

that significantly higher pressures may be needed to reach an acceptable fraction in order to promote fuel gas production. A significantly higher pressure may also affect the carbon conversion rate and overall carbon conversion.

Catalyst Loading

Langbeinite was added to the broiler litter at 5 wt%, 10 wt%, and 15 wt% levels. These results were compared to an experimental run with no additional catalyst provided. The results are presented in Figure 4.14. As discussed earlier for K_2CO_3, an increase in the catalyst loading increased the number of potassium and magnesium atoms available for catalytic activity. When no catalyst was added, conversion reached 75%. At a low loading of 5 wt%, the conversion only reached 80% after 240 minutes, while 10 wt% and 15 wt% loading levels allowed the conversion to reach over 95%. At a lower catalyst loading, it is likely that the catalyst will again be deactivated to a greater extent by the reaction of the catalyst with the mineral matters present in the litter, thus slowing the gasification process and producing lower gasification performance. When the catalyst loading level was 10 wt% or 15 wt%, the gasification rates increased significantly. However, loadings higher than 10 wt% did not produce any substantial increase in the gasification rate. This could be due to saturation of the potassium and magnesium atoms in the carbon matrix, thus leading to a point of diminishing returns.

Catalyst loadings were also varied to show what happens to the conversion of carbon to carbon monoxide, methane, and hydrogen. Again, the averages were used to determine the conversion rate. Figure 4.15 shows that the conversion of carbon to carbon monoxide

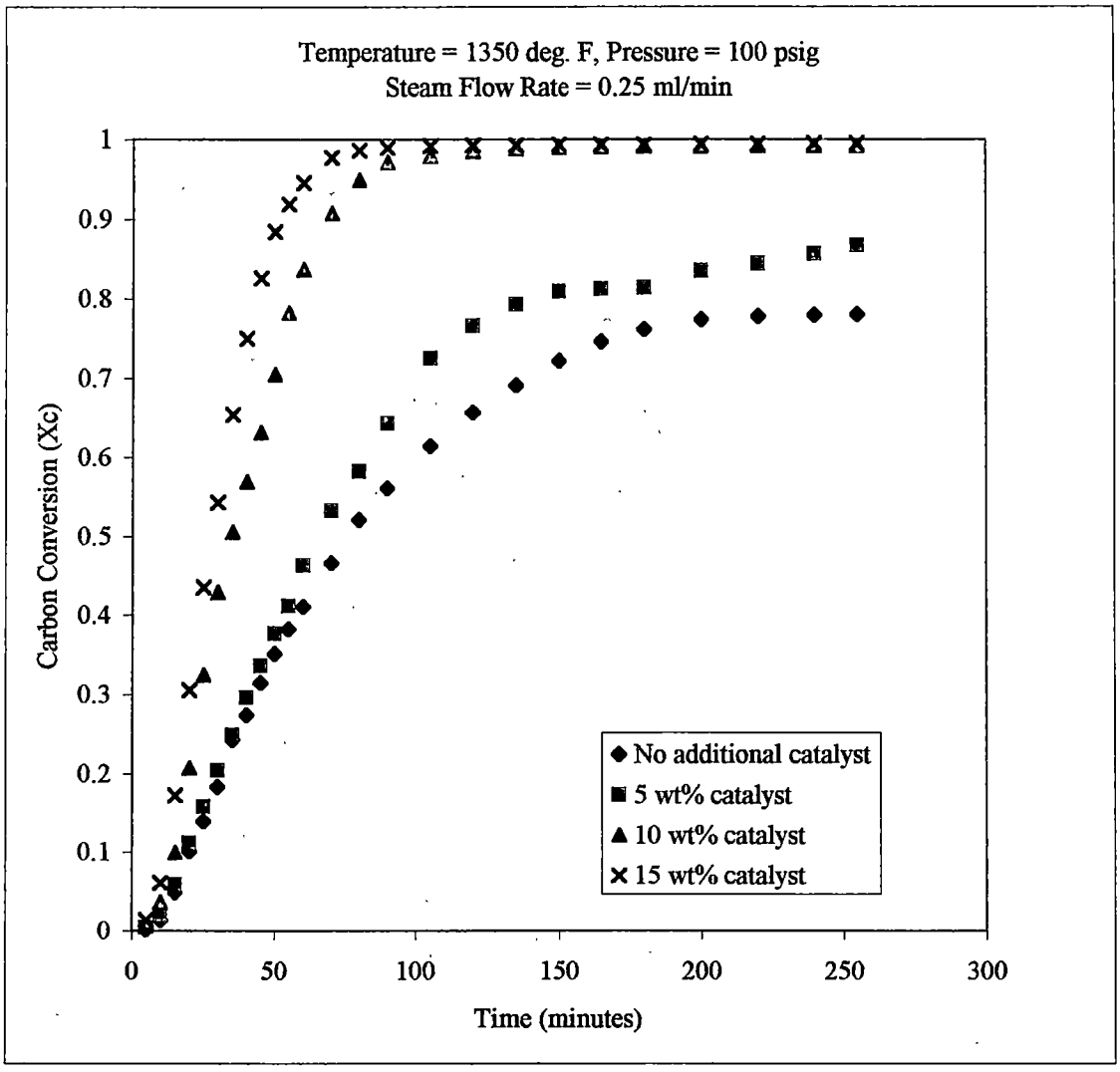

Figure 4.14: Catalytic Gasification of Broiler Litter with Langbeinite at Various Catalyst Loadings

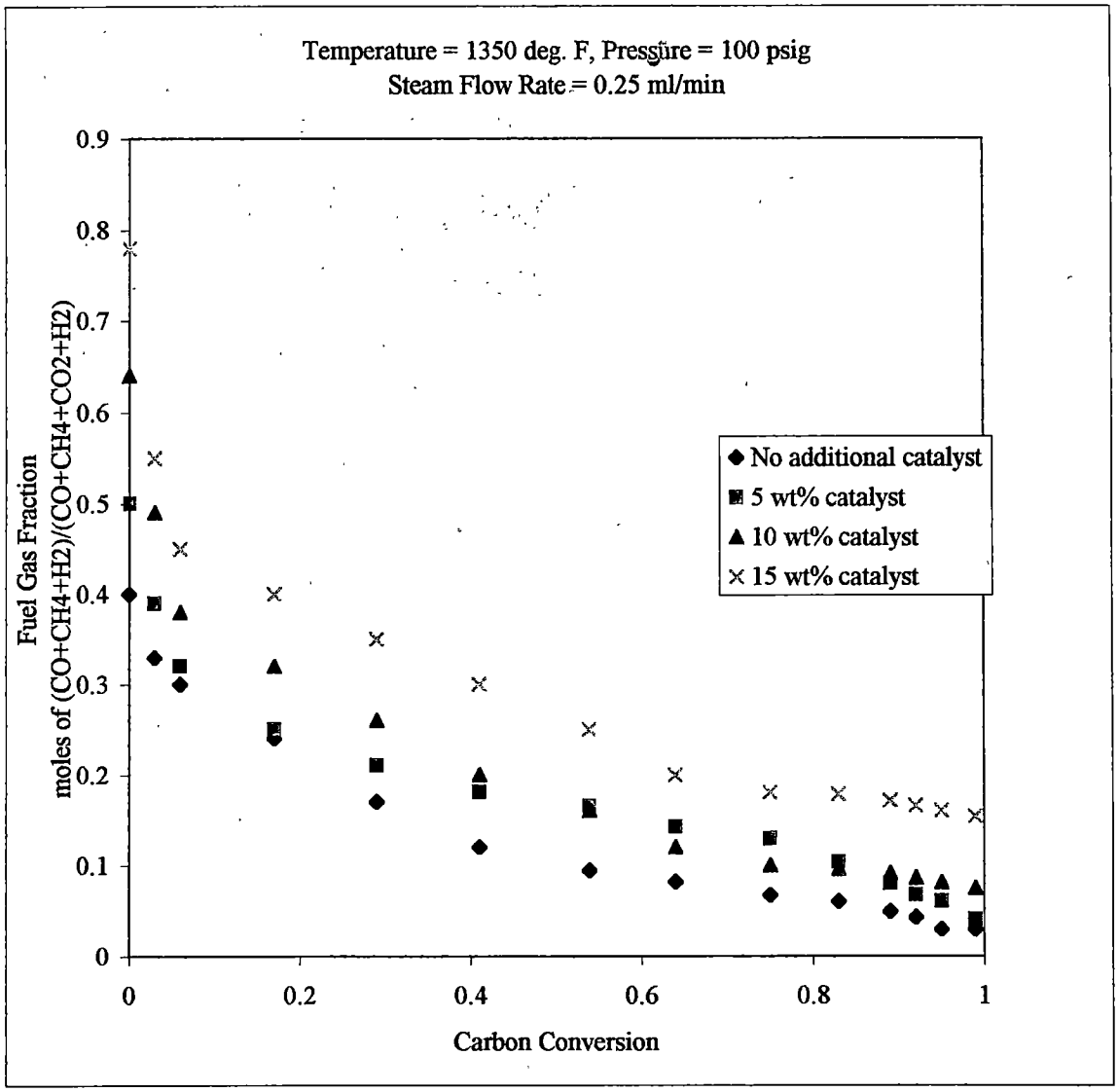

Figure 4.15: Fuel Gas Fraction as a Function of Catalyst Loading Using Langbeinite

and methane was low for all of the loadings tested. With no catalyst, the average fraction was just under 13%, while at 5, 10, and 15 wt%, the average fractions were 18%, 22%, and 30% respectively. Although the average fraction increased with each loading, more tests may be needed to see how far the loading should be increased to yield a very high fraction and rate. The effect of the atomic (K + 0.5 Mg)/C ratio on the specific gasification rate did show an increase with the increased catalyst loading. However, after 10 wt% loading, the rate seemed to level off, showing probably an overabundance of potassium and magnesium atoms. This is shown in Figure 4.16. The effects of atomic metal-to-carbon ratio for K_2CO_3 and langbeinite on the specific gasification rate were combined from Figures 4.6 and 4.16. This combined plot is shown in Figure 4.17. As shown in Figure 4.17, the plots fit each other within 10% of their values. This justified the assumed equivalency of 0.5 for the magnesium atom, in comparison to one for the potassium atom.

Steam Flow Rate

Experiments were conducted at different steam/water flow rates corresponding to sufficient amounts of steam required for gasification reaction to a large excess of steam. These experiments were carried out at 0.084 ml/min, 0.145 ml/min, and 0.23 ml/min. The results are shown in Figure 4.18. At a lower steam/water flow rate, only 75% conversion of carbon was reached during the duration of the run. When excess steam was provided, broiler litter char reached 96% conversion in less than 100 minutes at a rate of 0.25 ml/min. At 0.145 ml/min, the maximum conversion reached was only 92%, and remained at that level until the experiment was completed. These differences suggest

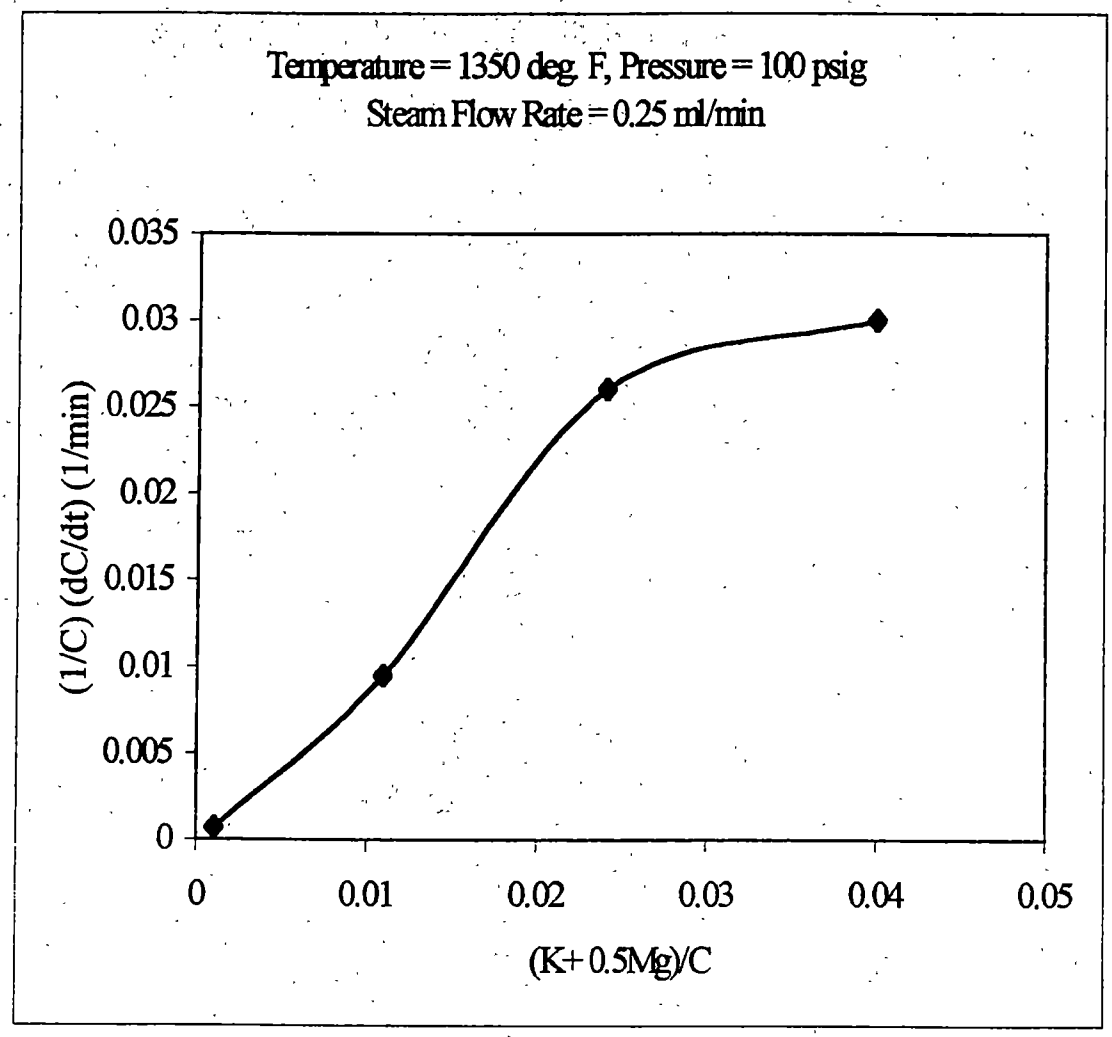

Figure 4.16: Specific Gasification Rates vs. (K+0.5Mg)/C Ratio (using Langbeinite)

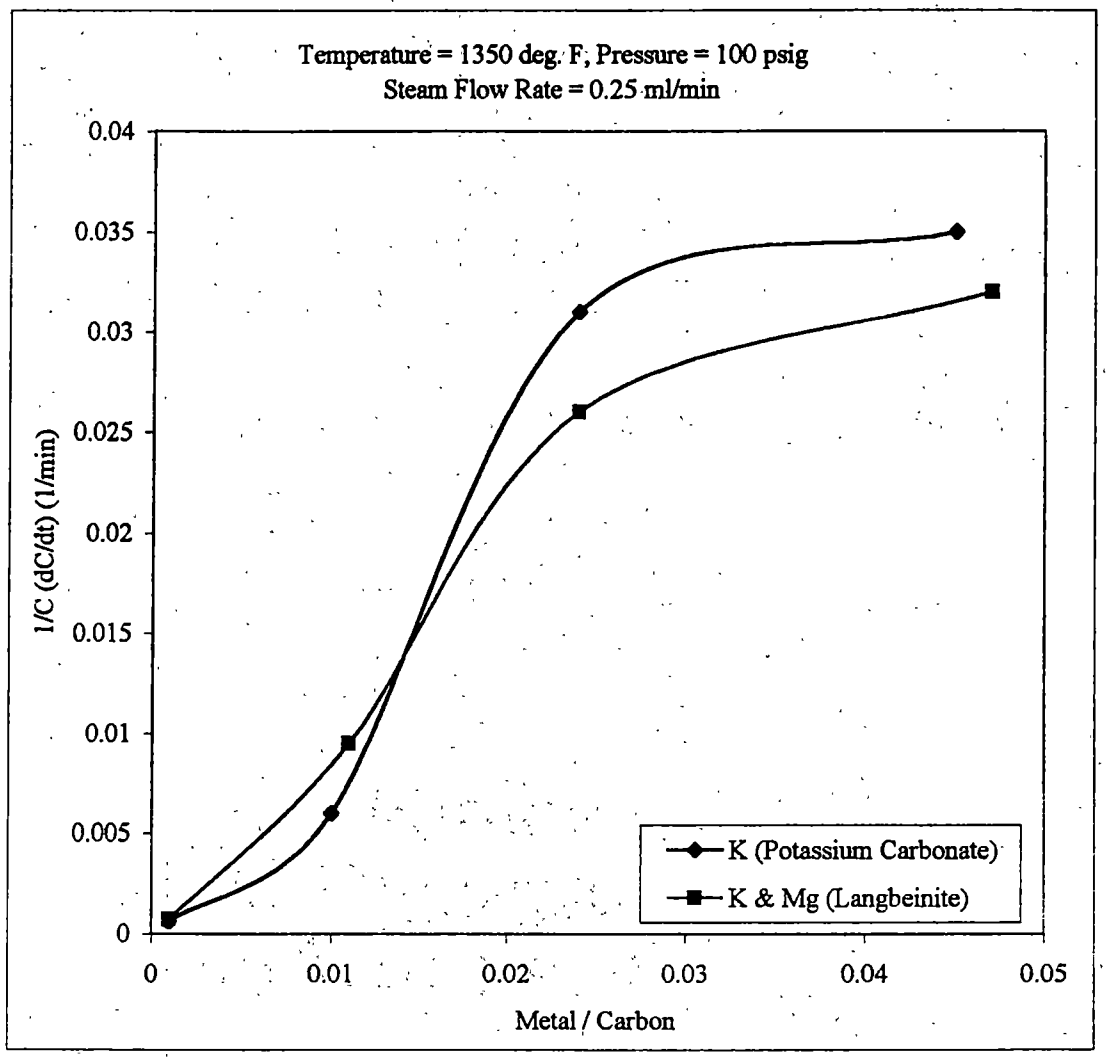

Figure 4.17: Specific Gasification Relationship for K_2CO_3 and Langbeinite

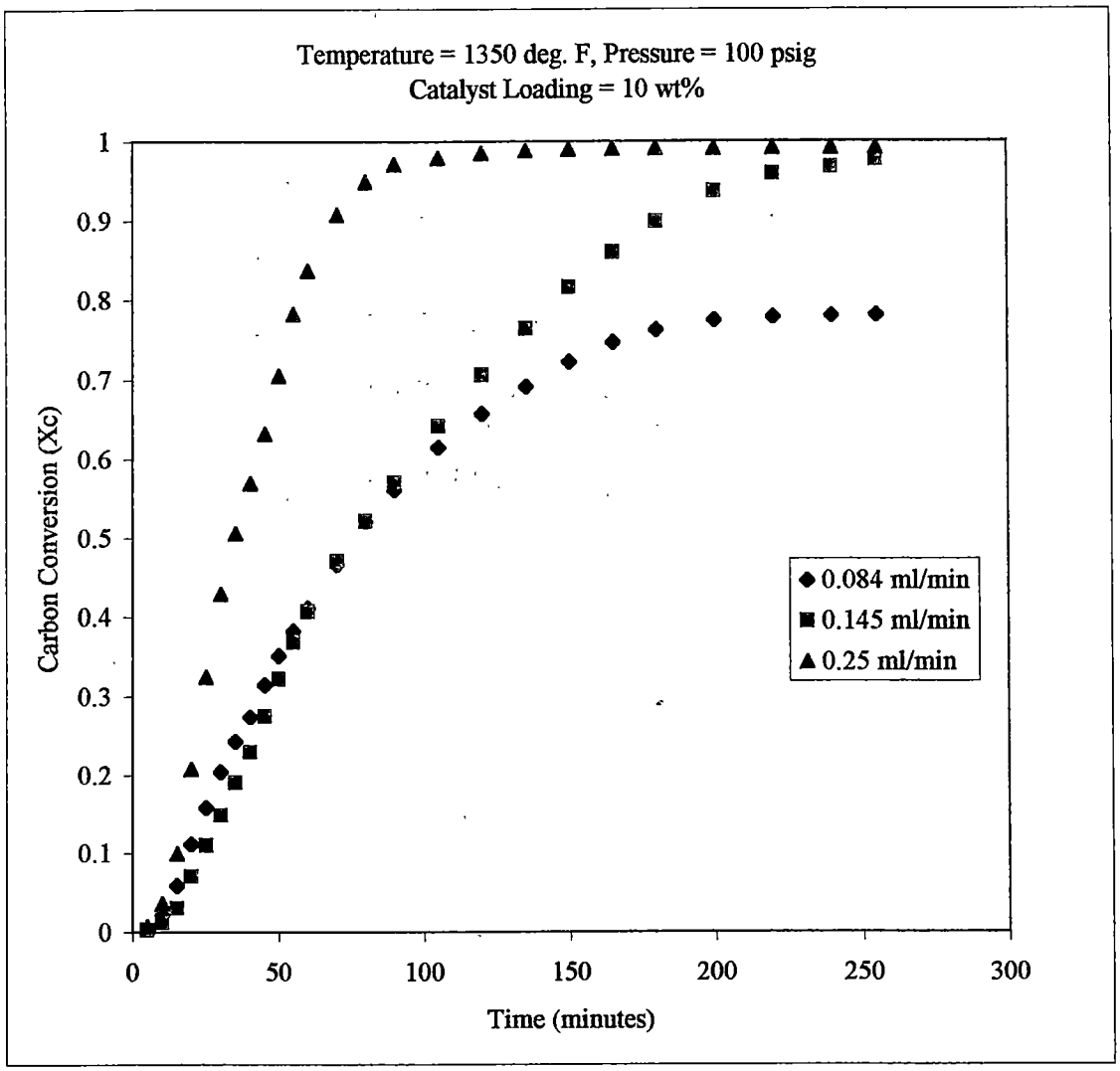

Figure 4.18: Catalytic Gasification of Broiler Litter with Langbeinite at Various Steam Flow Rates

the possible existence of some side reactions at the lower steam rate, preventing 100% carbon conversion to be reached within four hours. The amount of carbon monoxide, methane, and hydrogen produced as a percentage of the total amount of converted carbon was calculated as an average since none of the runs produced a constant value. The results are shown in Figure 4.19. The average fuel gas fraction at the low steam rate of 0.084 ml/min was 41%, and increased to 54% and 60% at steam flow rates of 0.145 ml/min and 0.25 ml/min respectively. From these results, it appears that an increase in the amount of steam flow rate does influence the carbon conversion to useful end products such as CO and H_2. However, the rate of increase is not as sharp between 0.145 ml/min and 0.25 ml/min as it is between 0.084 ml/min and 0.25 ml/min, suggesting that the average fuel gas fraction may not increase significantly after a certain steam/water flow rate.

Kinetic Modeling for K_2CO_3 and Langbeinite

Kinetics of catalytic steam gasification of broiler litter follows a similar pattern to gasification of coal since both coal and biomass possess a similar carbonaceous composition (1). Hence, many of the energy conversion processes utilizing coal can be modified to handle the biomass. In previous catalytic gasification studies using coal, the kinetics were studied at various operating conditions using different types of coal (17). In studying the kinetics, all of the models attempting to fit the experimental results used a Langmuir-Hinshelwood type rate expression (5). When using a Langmuir-Hinshelwood type rate expression to fit and study the steam gasification rate data, various factors, such as product inhibition and catalyst deactivation, are included. In many instances, the

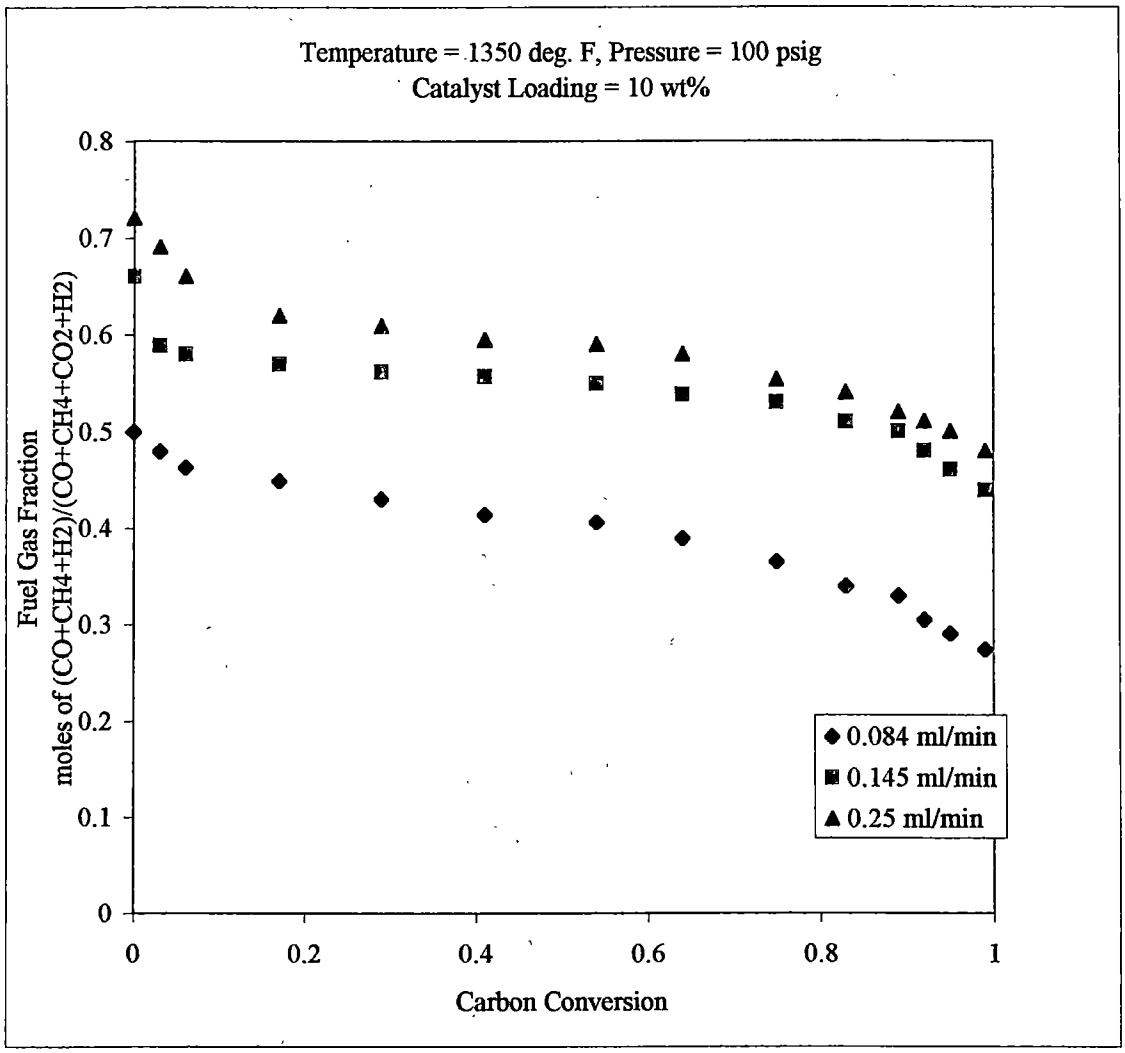

Figure 4.19: Fuel Gas Fraction as a Function of Steam Flow Rate Using Langbeinite

inhibition of the char due to hydrogen adsorption may be neglected because of the small amounts of hydrogen detected in the experimental runs with steam (23). The linearity of the typical first order plots of $-\ln(1-X_c)$ as a function of gasification time is illustrated in Figures 4.20 and 4.21 for the K_2CO_3 and langbeinite catalyst system respectively. The following equations show what was used to construct such plots.

$$dC/dt = -kC \tag{4-2}$$

$$-kC = -kC_o\,(1- X_c) \tag{4-3}$$

$$-kC_o\,(1- X_c) = -C_o\,(dX_c/dt) \tag{4-4}$$

$$(dX_c/dt) = k\,(1-X_c) \tag{4-5}$$

$$-\ln\,(1-X_c) = kt \tag{4-6}$$

where k is the first order rate constant and is equal to (1/C)(dC/dt), the specific gasification rate. The value of the slope that determines the respective specific gasification rate is presented in Table 4.3 for each run. These values were determined from the best first-order fit that forced the data to not go through the origin. These values also show that steam gasification probably followed a first-order rate behavior with respect to the unreacted char in the reactor bed. In addition to catalytic gasification, the gasification reaction may also occur thermally. The overall gasification rate is therefore:

$$(-dC/dt)_{overall} = (-dC/dt)_{catalytic} + (-dC/dt)_{thermal} \tag{4-7}$$

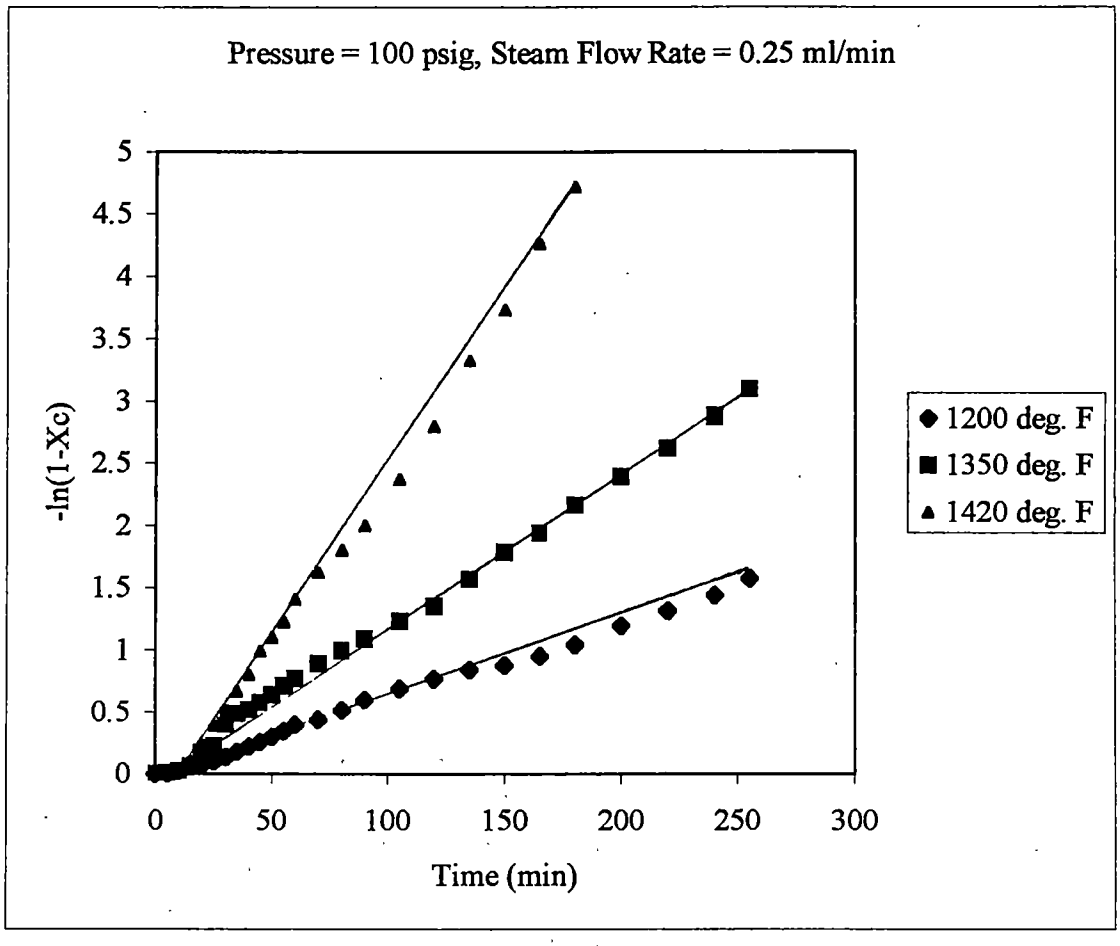

Figure 4.20: Fitted 1st Order Data for Carbon Conversion vs. Gasification Time with K_2CO_3

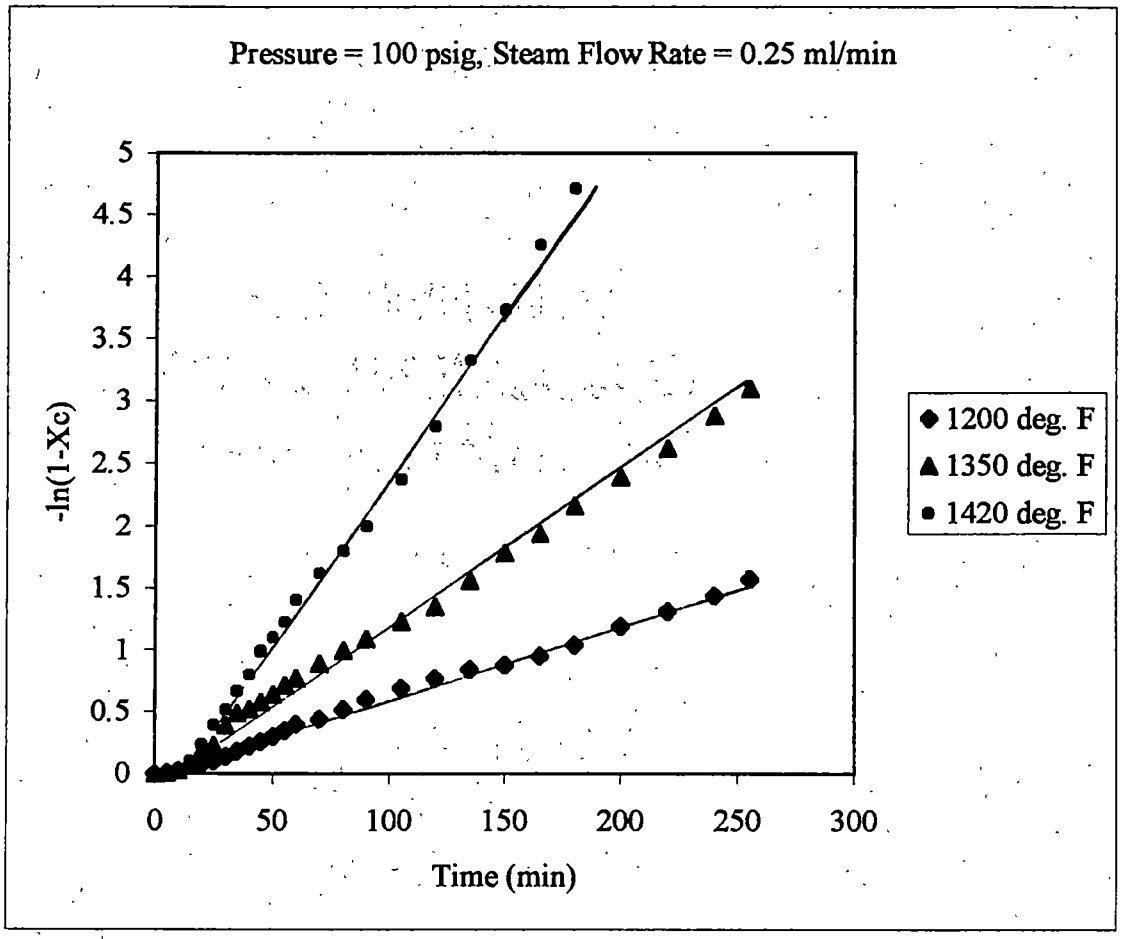

Figure 4.21: Fitted 1st Order Data for Carbon Conversion vs. Gasification Time with Langbeinite

Table 4.3: Specific Gasification Rates for Individual Runs

Run	Catalyst	(1/C)(dC/dt) (min^{-1})
1	K_2CO_3	0.0019
2	K_2CO_3	0.028
3	K_2CO_3	0.034
4	K_2CO_3	0.0234
5	K_2CO_3	0.0194
6	K_2CO_3	0.0038
7	K_2CO_3	0.0392
8	K_2CO_3	0.00103
9	K_2CO_3	0.0157
10	Langbeinite	0.003
11	Langbeinite	0.0206
12	Langbeinite	0.037
13	Langbeinite	0.0024
14	Langbeinite	0.029
15	Langbeinite	0.044
16	Langbeinite	0.0028
17	Langbeinite	0.035
18	Langbeinite	0.030

The thermal gasification is usually very small compared to the catalytic gasification, but it could still slightly affect the overall conversion. Although thermal gasification merits serious consideration, the kinetics of such mixed gasification cannot be determined easily. The contribution of thermal gasification to the overall gasification rate may be evident in Figures 4.20 and 4.21, where the plots show that all lines do not necessarily pass through the origin. This behavior probably accounts for thermal gasification as well as other induction, transient type phenomena. Hence, the data were forced through the origin to simplify the kinetic expression and to obtain a nearly first-order rate expression. Such forced linear fits are believed to give slope values that are about 5% - 10% different in values from the slopes of the lines that did not pass through the origin. Hence, the actual slope values for those lines not going through the origin would be about 5% - 10% off of the forced values. The Langmuir-Hinshelwood expression is given by:

$$r/C = k_1 pH_2O / (1 + k_2 pH_2O) \qquad (4\text{-}8)$$

where,

pH_2O is the partial pressure of steam in the bed (kPa)

k_1 is the reaction rate constant (kPa^{-1} min^{-1})

k_2 is the adsorption constant (kPa^{-1})

r is the gasification rate of carbon in the bed (g/min)

C is the remaining carbon in the bed at any instant time, t (g)

r/C is the specific gasification rate (min^{-1})

As a function of temperature, k_1 and k_2 are given by the Arrhenius expressions as:

$$k_1 = k_{1o} \exp(-E_1/RT) \quad (4\text{-}9)$$

$$k_2 = k_{2o} \exp(-E_2/RT) \quad (4\text{-}10)$$

where k_{1o} is the frequency factor; E_1 is the activation energy for the gasification reaction; k_{2o} is the frequency factor and E_2 is the heat of adsorption for the steam adsorption step. Equation 4-8 is then inverted to give the linearized relation as:

$$C/r = k_2/k_1 + (1/k_1)(1/pH_2O) \quad (4\text{-}11)$$

The calculated specific gasification rate data from the experimental results for different temperatures were used to obtain the rate expression. The partial pressure of steam, pH_2O, was calculated from the average moles of steam/water entering and leaving the reactor bed at each instant time, t_j. The calculation for this procedure was discussed earlier under Experimental Procedures.

The resulting linearity following equation 4-11 is shown in Figure 4.22 and Figure 4.23 using potassium carbonate and langbeinite respectively. The regressed values of the slope and intercept for both catalysts are shown in Table 4.4 and Table 4.5.

From these values, the rate constants, k_1 and k_2, were obtained and used to determine the activation energies and frequency factors for the respective Arrhenius plots.

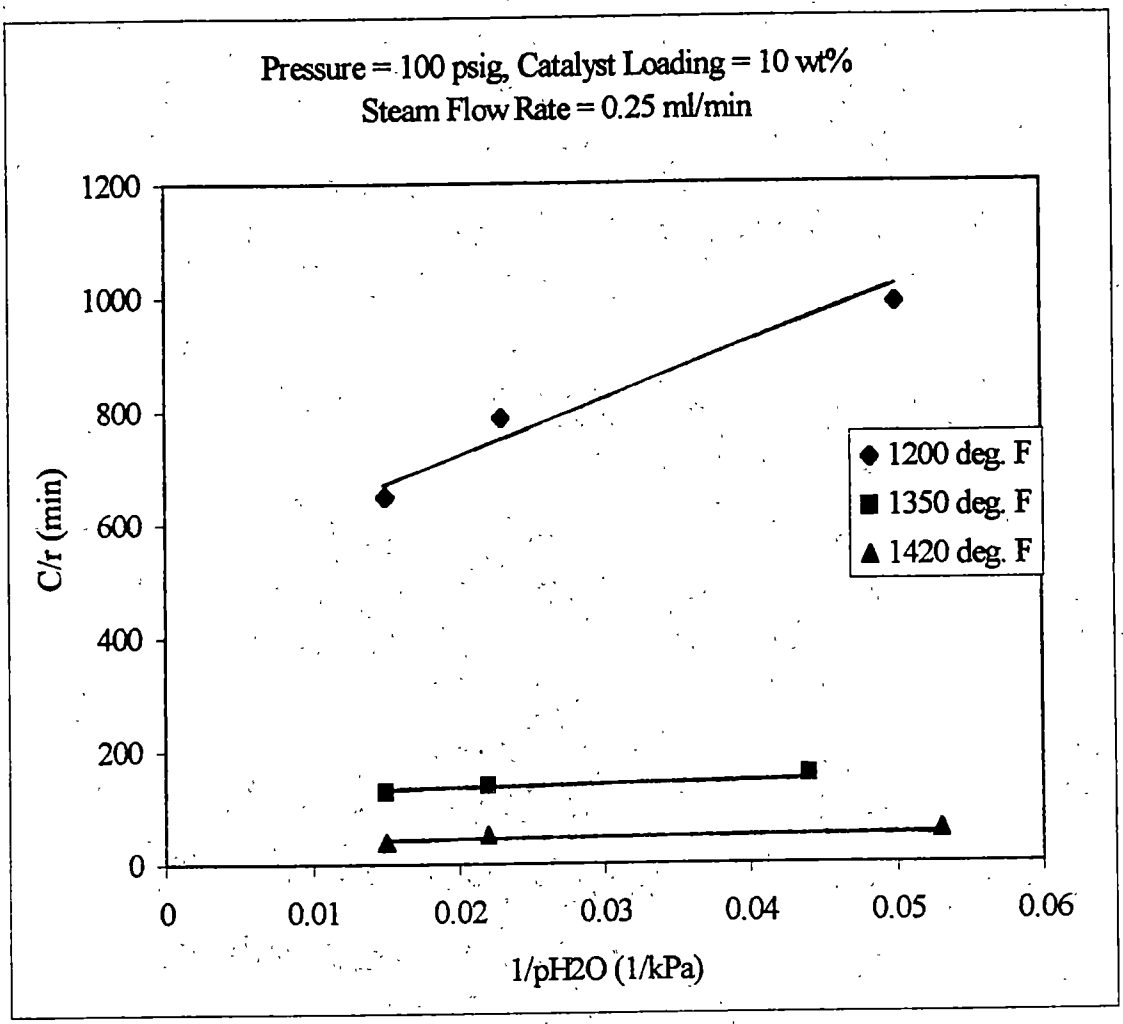

Figure 4.22: Linearized Plot of Langmuir-Hinshelwood Expression Using K_2CO_3

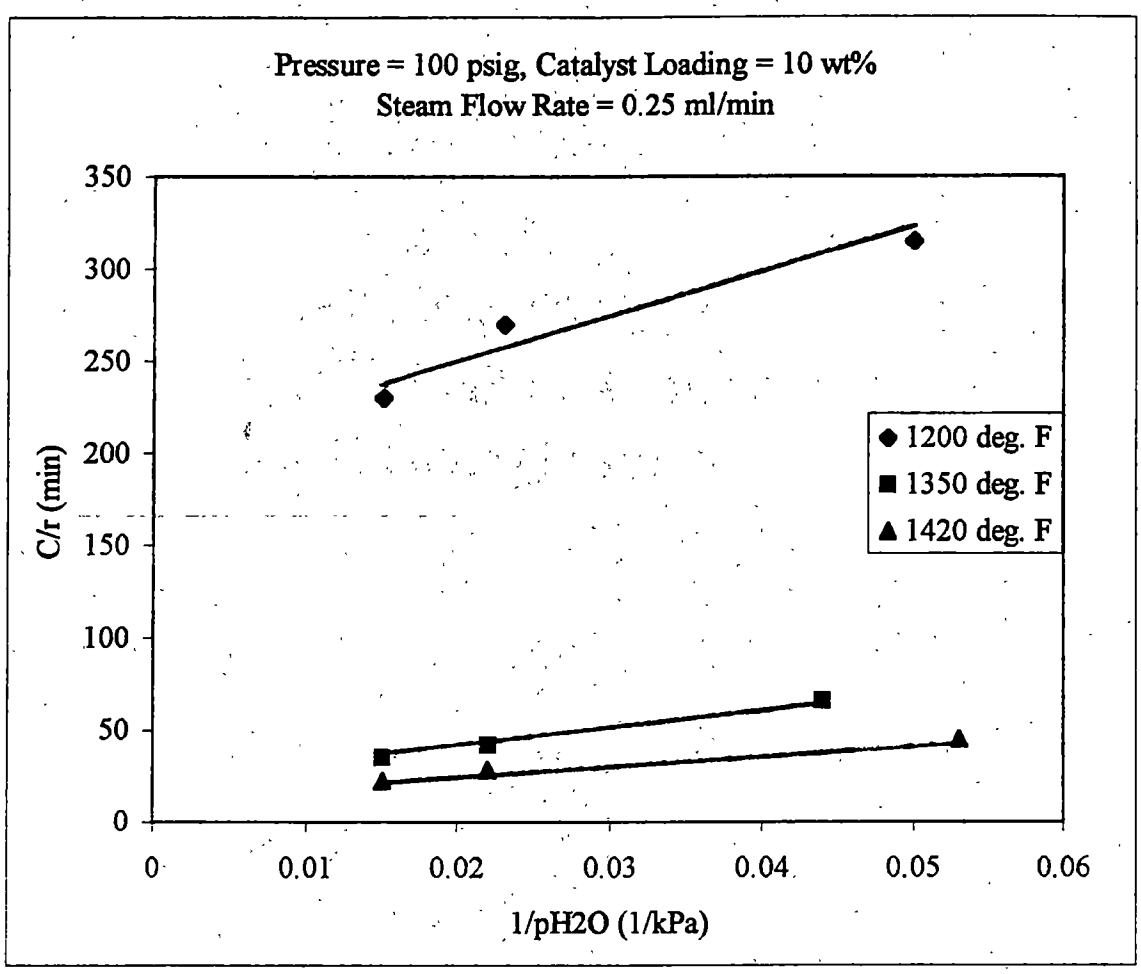

Figure 4.23: Linearized Plot of Langmuir-Hinshelwood Expression Using Langbeinite

Table 4.4: Rate Constants for Broiler Litter with K_2CO_3 at Different Temperatures

Temperature	Slope ($1/k_1$) (kPa min.)	Intercept (k_2/k_1) (min.)
1200	9685.71	530.78
1350	1004.48	69.83
1420	678.6	14.61

Table 4.5: Rate Constants for Broiler Litter with Langbeinite at Different Temperatures

Temperature	Slope ($1/k_1$) (kPa min.)	Intercept (k_2/k_1) (min.)
1200	2833.54	609.62
1350	1413.79	140.49
1420	793.10	44.36

These Arrhenius plots are presented in Figures 4.24 and 4.25, while the values of the activation energies and frequency factors for both of the catalysts are presented in Table 4.6. Based on the calculated values of the activation energies, E_2 was found to be negative in this system. The negative value may indicate an adsorption type phenomenon, leading to exothermic heat of reaction. The low activation energy may also indicate that temperature is not as sensitive with when analyzing and looking at possible trends (17, 23).

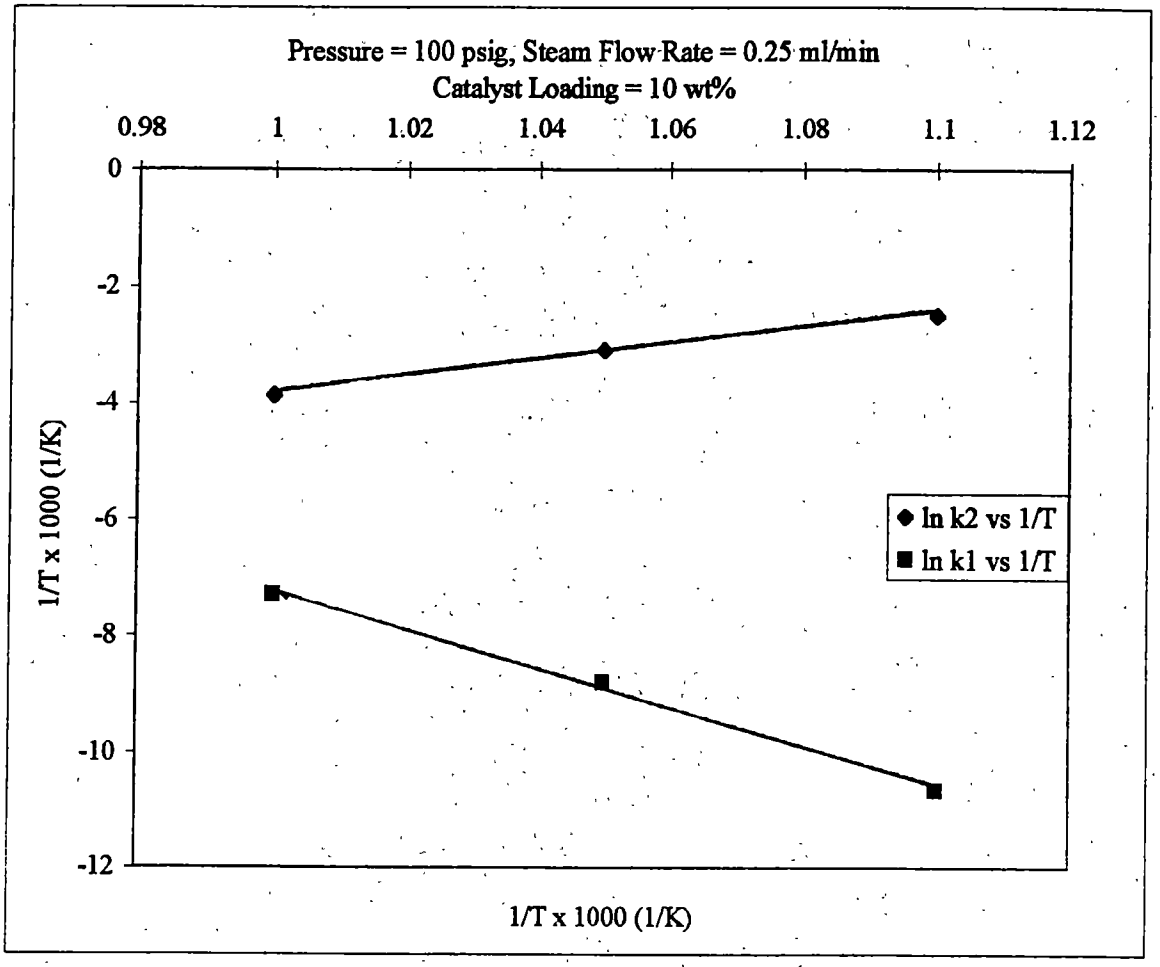

Figure 4.24: Arrhenius Plot for Langmuir-Hinshelwood Rate Expression Using K_2CO_3

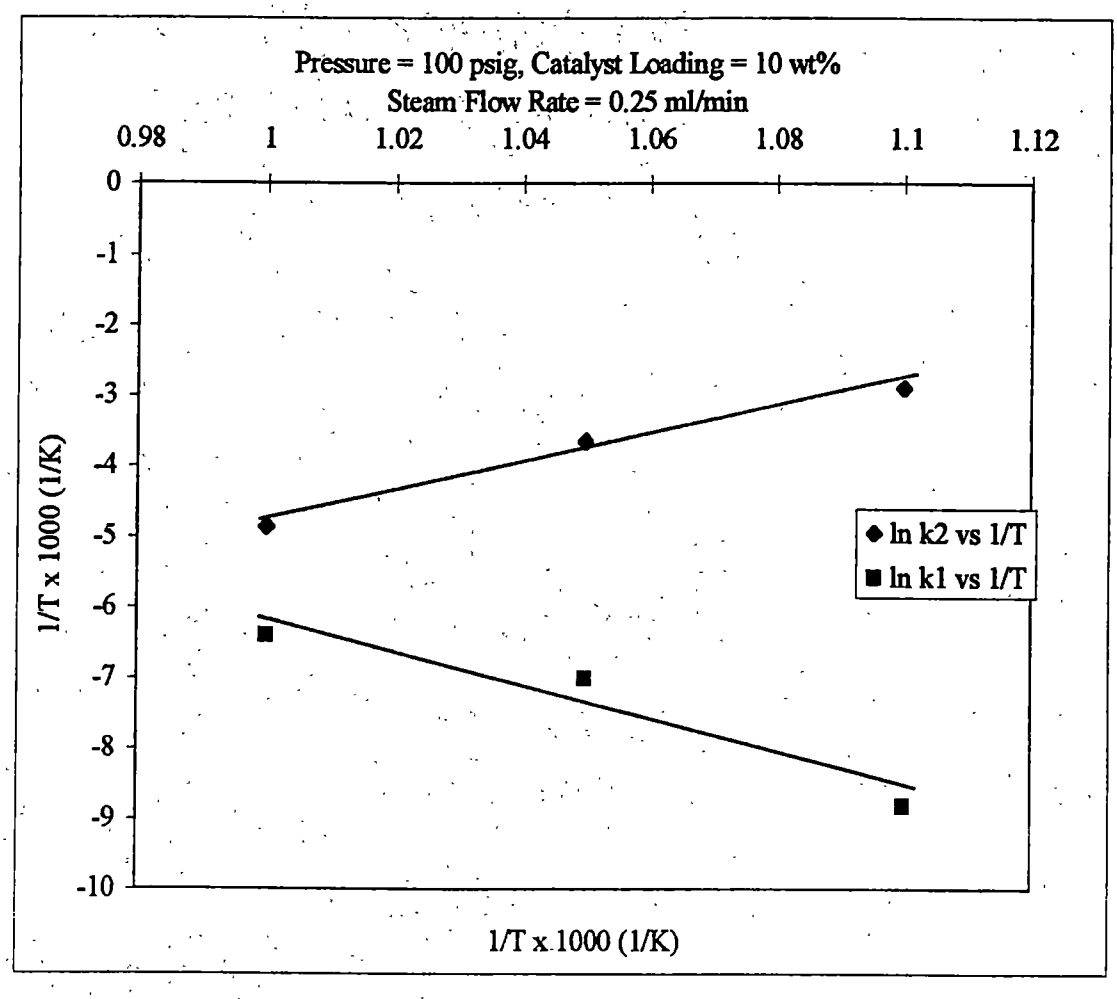

Figure 4.25: Arrhenius Plot for Langmuir-Hinshelwood Rate Expression for Langbeinite

Table 4.6: Rate Parameters for Catalytic Steam Gasification

Parameter	$k_{1,K2CO3}$	$k_{2,K2CO3}$	$k_{1,Langbeinite}$	$k_{2,Langbeinite}$
k_{1o}	$3.77*10^{7}$ kPa^{-1} min^{-1}	$4.01*10^{-7}$ kPa^{-1}	190.47 kPa^{-1} min^{-1}	$4.25*10^{-12}$ kPa
E_i (kJ/mol)	220.45	-108.56	113.92	-147.23

Based on these calculated values, the derived Langmuir-Hinshelwood rate equation for the K_2CO_3 system is:

$$(-dC/dt) = \frac{3.77*10^{7}\, C \exp\left(\frac{-26515.52}{T}\right) pH_2O}{1 + 4.01*10^{-7} \exp\left(\frac{17708.68}{T}\right) pH_2O}$$

where

pH_2O is the partial pressure of steam in the bed (kPa)

C is the remaining carbon in the bed at any instant time, t (g)

T is the gasification temperature (K)

(dC/dt) is the overall gasification rate (g/min)

Similarly, the derived Langmuir-Hinshelwood rate equation for the langbeinite system is:

$$(-dC/dt) = \frac{190.47\, C \exp\left(\frac{-13702.19}{T}\right) pH_2O}{1 + 4.25 * 10^{-12} \exp\left(\frac{8931.92}{T}\right) pH_2O}$$

The derived rate model is applicable only to the region where the first order fit is possible as shown in Figures 4.20 and 4.21. The proposed mechanism that explains the model is given as:

$$C_{(s)} + H_2O_{(g)} \text{ --> } CO_{(g)} + H_{2(g)} \quad (4\text{-}12)$$

$$H_2O_{(g)} \text{ --> } H_2O_{(ad)} \quad (4\text{-}13)$$

$$C_{(s)} + H_2O_{(ad)} \text{ --> } H_{2(ad)} + CO_{(ad)} \quad (4\text{-}14)$$

$$H_{2(ad)} \text{ --> } H_{2(g)} \quad (4\text{-}15)$$

$$CO_{(ad)} \text{ --> } CO_{(g)} \quad (4\text{-}16)$$

In the above mechanism, equation 4-12 is the overall gasification step. From these equations, we observe that the rate is directly proportional to the amount of carbon in the bed. In terms of steam/water, it reacts with the carbon to produce carbon monoxide and hydrogen gas. The derived expression was then used to compare the model specific gasification rates to those values presented in Table 4.3. This comparison is presented in Table 4.7. Table 4.7 shows that the values are within 10% of each other, indicating a satisfactory relationship between the experimental results and the results calculated from the model.

To show the validity of these rate parameters, a comparison was then made between this study and the results from the thesis, "Catalytic Coal Gasification Using Eutectic Salt Mixtures," by Anuradha Godavarty (4). This comparison is presented in Table 4.8, where the ternary eutectic catalyst mixture such as LNK (lithium, sodium and potassium)

Table 4.7: Comparison of Specific Gasification Rates Derived from Experimental Data and Predicted Values by Rate Model

Run	Catalyst	r/C (experimental) (min^{-1})	r/C (model predicted) (min^{-1})
1	K_2CO_3	0.0019	0.0024
2	K_2CO_3	0.028	0.033
3	K_2CO_3	0.034	0.039
9	Langbeinite	0.003	0.0025
10	Langbeinite	0.0206	0.0231
11	Langbeinite	0.037	0.031

and the binary catalyst mixture such as NK (sodium and potassium carbonates) were used to carry out steam gasification of Illinois #6 coal (17). The predicted specific gasification rates used from Godavarty's experiments with coal also were within 10% of her experimental values based on the parameters used in Table 4.8.

Table 4.8: Rate Parameters Used for Steam Gasification of Coal and Poultry Litter

Steam Gasification of...	Catalyst/Parameter	k_{io}	E_i (kj mol^{-1})
Coal	LNK/k_1	154.08 kPa^{-1} min^{-1}	98.63
Coal	LNK/k_2	$3.7*10^{-12}$ kPa^{-1}	-180.3
Coal	NK/k_1	$32.835*10^{6}$ kPa^{-1} min^{-1}	201.5
Coal	NK/k_2	$3.347*10^{-7}$ kPa^{-1}	-91.87
Poultry Litter	K_2CO_3/k_1	$3.77*10^{7}$ kPa^{-1} min^{-1}	220.45
Poultry Litter	K_2CO_3/k_2	$4.01*10^{-7}$ kPa^{-1}	-108.56
Poultry Litter	Langbeinite/k_1	190.47 kPa^{-1} min^{-1}	113.92
Poultry Litter	Langbeinite/k_2	$4.25*10^{-12}$ kPa^{-1}	-147.23

CHAPTER 5

ECONOMIC ASSESSMENT

In the thesis, "From Waste to Energy - Catalytic Gasification of Broiler Litter" by Andrew Jones, he demonstrated the economic feasibility of the catalytic steam gasification process for a transportable broiler litter gasification system. This system was constructed on a flatbed trailer. The payback period for producing a low to medium BTU gas was estimated to be about 27 months, or just over two years. In order to determine whether a larger stationary gasification plant would be economically feasible, a similar preliminary economic assessment was performed. The basis for the stationary design was developed with the help of the Excel Corporation in Kansas (24). Two engineers, Michael Dreyfuss and Scott Percy of Excel Corporation, were consulted for determining the parameters needed to compare the cost of producing a viable fuel gas for distribution at different poultry litter feed rates. Both gentlemen work in the process design group of the Excel Corporation, and conduct computerized simulations on various projects to determine their feasibility. For the stationary plant, it was assumed to operate 330 days per year, with a base feed rate of 100 tons per day. The feed rate was chosen on the basis that the litter would be transported from a 100-mile radius of the centralized plant. The plant capacity was set at 85%. Based on experiments conducted at UTSI, the feed would be fed to the gasifier at certain conditions, operating at a temperature of 1350^0F and a pressure of 100 psig. Langbeinite was used as additional catalyst, and was loaded into the feed at 10 wt% level. For the stationary apparatus, the study was conducted on the basis that any broiler litter would be collected from different farmers and then sent to one

site instead of building several, separate smaller units within a particular area. Hence, transportation costs become an important factor since the litter would be transported from various farmers to the centralized location. Building costs must also be considered since the gasification system would be permanent in a primary area instead of being transported to different sites. A schematic of the stationary gasification system is provided in Figure 5.1.

Once the broiler litter is transported to a common area, it is stored in a receiving tank. From the tank, the litter is sent to a feed hopper via a conveyor. For the base case, 10 wt% of langbeinite was added to the litter. Later, a comparison will be made to see what effect the feed rate of the litter has on the costs and revenues of operating a gasification plant. The broiler litter then leaves the feed hopper and enters a fixed bed gasifier, which handles the pyrolysis and steam gasification. The output gas is then carried to a cyclone separator, where the desired product gases are separated from the entrained char and transferred to a scrubber. The unreacted entrained char exits the cyclone and enters an air-fed combustor, which burns off the carbon from the char and sends the ash to a separate receiver before being sent for disposal. The ash container is emptied on a regular basis to prevent unnecessary accumulation. Once the char enters the combustor, off-gases, which may contain some SO_2, will also be produced and treated in a scrubber. This SO_2 scrubber is fed with a sodium hydroxide solution and would remove all sulfur compounds. Once the sulfur compounds are removed, the rest of the off-gases can be vented. The unreacted steam, volatiles, and hot product gases leave the cyclone, and enter a heat exchanger for heat extraction. Any condensable species are then separated

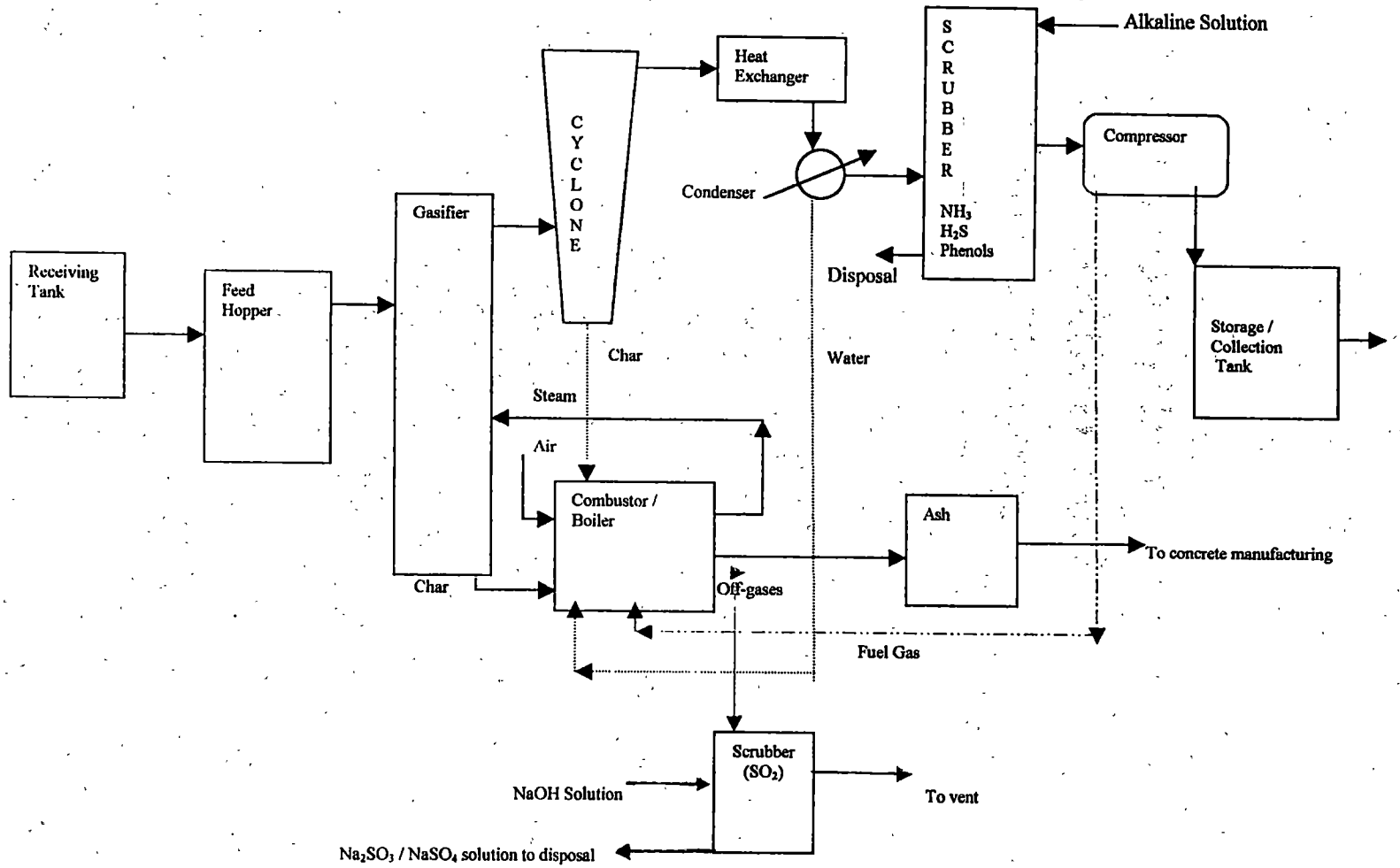

Figure 5.1: Schematic of Stationary Gasification System

from cooled product gases and other light hydrocarbons in a condenser, and the product gases then go to the scrubber to remove NH_3, H_2S, phenol, etc. The condensate, mostly unreacted water, exits the condenser and will be sent to the char combustor, for conversion to steam. The resulting steam is then fed back to the gasifier. Using the alkaline solution fed scrubber, the product gases are scrubbed off any ammonia and phenols for sale or disposal while the rest of the cleaned product gases goes to a compressor. After the gases enter through the compressor, part of the fuel gas is sent back to the combustor for steam production, and the remainder is collected in a storage tank for future distribution as a low to medium-energy fuel gas.

The heating value of the product gas is found using the average fuel gas fraction to carbon monoxide and methane and their respective heats of combustion. Contributions from hydrogen were also considered. The average fuel gas fraction used to find the heating value was 0.73. The average heating value was 304.7 BTU per standard cubic foot. The gasifier also operates at 1350^0F and 100 psig with 10 wt% langbeinite as additional catalyst.

Part of the annual cost comes from operating expenses. These costs include labor, materials, transportation, and utilities. These costs are presented in Table 5.1. The langbeinite costs \$0.024/lb, and it is assumed that the broiler litter already has inherent catalyst. 3% is assumed, with the remaining 7% being added to the litter. An additional 10% charge is added for other materials used for the process. That total is \$122,000. Transportation cost is at \$0.36/mile and accounts for a truck making 10 trips, hauling 10

Table 5.1: Operating Costs

Item	Price ($/year)
Labor	$600,000.00
Materials	$122,000.00
Transportation	$118,800.00
Utilities	$98,000.00
Total	**$938,800.00**

tons of litter per trip. Each trip is around 100 miles round-trip, and will be the basis for all costs. The transportation cost is at $118,800. Labor covers 9 employees and totals $600,000 annually. Utility costs include operating the facility and using power and using the local utility company. In this case, the Tennessee Valley Authority is the supplier.

Capital costs include purchase prices for equipment, instrumentation, and piping. These costs are presented in Table 5.2. The capital costs were estimated using the charts and correlation from Peters and Timmerhaus (12), and were adjusted for inflation using the Marshall and Swift index for industries. The index is applicable for 1999 since values for 2000 were not available. Various pieces of equipment were assumed to be made from steel to accommodate the abrasion and corrosive behavior of the litter. Other materials, such as aluminum, would probably fatigue quickly and lead to costly replacements.

Table 5.3 shows the additional capital costs of installing the equipment so that the plant will be operable. These additional costs are assumed as a percentage of the total purchase

Table 5.2: Capital Costs for the Broiler Litter Gasification Equipment

Item	Purchase Cost
Two Receiving Tanks	$80,000
Feed Hopper	$60,000
Fixed Bed Gasifier (1500 gal)	$250,000
Cyclone Separator (800 cu. ft)	$60,000
Heat Exchanger (150 sq. ft)	$13,000
Condenser (1500 gpm)	$9,000
Combustor for Steam and Char	$130,000
Ash Container	$75,000
Two Gas Scrubbers	$120,000
Multi-Stage Compressor	$94,000
Building	$40,000
Fuel Gas Storage Tank (for distribution)	$58,000
Total Purchase Costs	**$989,000**

cost of the broiler litter equipment from Table 5.2. The equipment costs and additional fees for installing and operating equipment represent the direct costs associated with the capital investments. Table 5.4 provides information on the indirect capital costs. These costs include supervision and construction expenses. The costs are assumed to be a percentage of the total purchase price of the equipment listed in Table 5.2. The total capital cost is shown in Table 5.5. It includes the totals from Tables 5.2, 5.3, and 5.4, and includes the contractor's fee and project contingency. The project contingency factor accounts for unexpected events and expenses, such as weather, labor issues, price changes, and estimation errors. A process contingency of 12% is used to account for incomplete development of the entire scheme.

To figure annual cost, factor 25% for depreciation, tax, etc. of the capital costs. That total equals $766,000. Add that to the operating cost and the annual cost is $1,704,800. To determine the payback period, the gross revenue must be determined. From that value, the net average is divided into the original capital investment to find the payback period. For the gross revenues, 100 tons of litter will be produced per day, with the fuel gas being sold at $14.52 per million BTU. Also, assume that some of the litter can be recovered as residue. We will only assume 10% recovery and sell at $29 per ton. That total is $95,700. The total gross revenue is $2,460,900, leading to a net revenue of approximately $755,900. The payback period is around 4.1 years, compared to 2.25 years for a mobile unit. This case is representative for high demand of gas. Under normal operations, fuel gas would be available at $9.85 per million BTU. The total gross revenue is $1,700,300, showing no chance of payback at these particular conditions.

Table 5.3: Additional Costs for Installing Plant Equipment

Item (% Purchase Price)	**Purchase Cost**
Purchased Equipment Installation (52%)	$514,280
Instrumentation and Controls (12%)	$118,680
Piping (18%)	$178,020
Electrical (13%)	$128,570
Buildings (include services)(29%)	$14,000
Land	$10,000
Yard Improvements	$10,000
Total	**$973,550**

Table 5.4: Indirect Capital Costs

Item (% Purchase Price)	Purchase Cost
Engineering and Supervision (36%)	$356,000
Construction Expenses	$360,000
Total	**$716,000**

Table 5.5: Total Capital Cost for Broiler Litter Plant

Item	Cost
Total Purchase Cost	$989,000
Additional Costs to Install Equipment	$973,550
Indirect Cost	$716,000
Process Contingency	$321,000
Contractor's Fee	$60,000
Total	**$3,066,550**

Under "normal" conditions, a feed rate of 100 tons/day would not provide a sufficient turn-around for profit. Hence, an increased feed rate may prove to be the best option. The cost analysis was also considered for daily feed rates of 500 and 1000 tons. The annual cost was scaled up to accommodate the increased feed rates. The values in expense, gross revenue, and payback period are presented in Table 5.6. The gross revenue had a linear increase. The total capital cost increased exponentially, while the operating cost increased linearly when determining the payback period.

Table 5.6: Comparison of Economics for Various Feed Rates

Feed Rate (tons/day)	Annual Cost ($/year)	Gross Revenue @ High Price of Gas	Payback Period w/ High Selling Price	Gross Revenue @ Regular Price of Gas	Payback Period w/ Regular Selling Price
100	$1,704,800	$2,460,900	4.06 years	$1,700,000	----------
500	$6,706,000	$12,304,500	1.44 years	$8,500,970	4.49 years
1000	$12,437,500	$24,609,000	1.00 years	$17,000,000	2.67 years

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Although attention and dialogue have been presented for proper disposal of broiler litter, there are still many challenges to overcome. Land availability continues to decrease as more land is converted into residential and commercial properties, making availability scarce and difficult. That challenge is further magnified by the fact that broiler production continues to grow at an astounding rate, with over three-fourths of the production coming from the Southeastern United States. The increased production of the good product also leads to a major increase in waste production. This is further compounded by the fact that the federal government is working on legislation that will monitor broiler and waste production and levying penalties if corrective actions are not taken.

However, catalytic steam gasification is seen as a viable alternative to handling the waste production from broiler litter. It has the potential to become a major alternative fuel source for companies, both agricultural and non-agricultural. While previous research showed that the process is technically feasible, new studies have provided some operating parameters that will let this application be viable and attractive to many business sectors.

The major conclusions from this study are:

- Using two catalysts, potassium carbonate and langbeinite, various parameters such as temperature and catalyst loading, are found to affect the carbon conversion and/or gasification rates. However, potassium carbonate provided more significant effects on the broiler litter. Because for a given wt% loading, K2CO3 provides more atoms of potassium than the langbeinite. Also, the carbonate form of potassium is believed to be more active than the sulfate form.

- Temperature does have a significant effect on the steam gasification. Gasification is most effective if the temperature is at least 1350^0F. Such a temperature allowed for over 90% conversion, and provided a good fraction of carbon monoxide and methane. On the other hand, conversion was only 85% at 1200^0F. This may be due to the fact that the gasification reaction at the lower temperature may not be completed in four hours.

- Pressure was not such a strong factor in determining the final carbon conversion or the fuel gas fraction. The same conversion and fuel gas fraction were reached after gasification was run for over 240 minutes. Although the conversion was a little faster at a higher pressure, it did not really have any significant advantage.

- Catalyst loading did have a significant effect on the gasification and final carbon conversion. At low loadings (i.e. 5 wt% or less), the conversion did not reach 80%, but at a loading of 10 wt% or higher, this level of conversion was reached well before the duration of the experimental run. A higher catalyst loading does increase the K/C

atomic ratio and gasification performance. However, increasing the catalyst loading above 10 wt% level does not result in a significant increase in the specific gasification rate.

- Steam or water flow rate does alter the gasification performance significantly. At the highest flow rate of 0.25 ml/min, over 99% conversion was reached much sooner than at 0.145 ml/min. This may show the reaction taking place very quickly at the high steam or water flow rate.

- A Langmuir-Hinshelwood type of rate expression was developed and modeled after the behavior of coal. The model did provide a satisfactory fit to the experimental runs at various temperatures and using both langbeinite and potassium carbonate as catalyst for the broiler litter.

- An economic analysis of a stationary gasification unit showed that at a regular selling price of fuel gas, there would be no opportunity to achieve any profit unless there is a minimal feed rate of 500 tons per day. However, if the fuel gas is sold at a higher rate, such as $14.52 per million BTU, then there will be a profit after four years at the lower feed rate of 100 tons per day. However, the payback period reduces to less than two years if the feed rate is increased to 500 tons per day.

Recommendations

For continuing work in this area of catalytic steam gasification of the broiler litter, the following areas are suggested for further analysis.

- Evaluating broiler litter gasification studies with updraft and downdraft flow patterns. There could be significant differences in results when comparing both alternatives.

- Using the economic studies, compare the benefits and challenges related to different types of communities.

- Expand the kinetic rate studies to see if and how other process variables, such as catalyst loading and steam flow rate, affect the rate expression.

- Evaluate other types of animal waste to determine the applicability of steam gasification.

- Study the effects of carbon monoxide and hydrogen in the feed gas to determine the effect on production of methane.

- Determine the fate of ammonia and phenol during steam gasification of broiler litter.

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APPENDICES

Appendix I

Operating Procedure for Pyrolysis of Poultry Litter Sample in Muffle Furnace

1. A cylindrical reactor is used in the muffle furnace for maintaining complete inert conditions in the devolatilization process.
2. The reactor has an inlet for the nitrogen to flow into the broiler litter sample and an exit to remove the generated volatile matter and tars from the poultry litter sample.
3. Around 20 grams of the broiler litter sample is pyrolyzed for each run. The reactor is filled with the sample and has a heavy lid placed on the top to maintain inert conditions.
4. The system is purged with nitrogen gas at 20 psig for about 20 minutes. This removes any oxygen in the reactor.
5. The temperature is set to 750^0C in the muffle furnace and the hood fan is turned on to remove the outlet gases from the reactor.
6. The outlet line from the reactor enters a conical flask, partially filled with water. The tars coming out of the pyrolysis process is condensed in the water as the gases bubble through it before they are vented to the hood. This prevents the outlet lines from being clogged with the tars that would otherwise condense in the line.
7. The nitrogen flow is maintained constant throughout the process as a carrier gas for the volatile matter from the sample without any blockage in the line.
8. The process is carried out for three hours from the time the temperature reaches the operating temperature of 750^0C.

9. At the end of three hours, the temperature is reduced to the room temperature, during which the nitrogen flow is still maintained.
10. The sample is removed after the reactor is cooled and the nitrogen flow is stopped.
11. The sample is crushed in an agate mortar and sieved to the required mesh size to provide feed for the gasification reactor.
12. The char samples obtained are stored in inert atmosphere in a glove box to avoid any unexpected oxidation of the sample.

Appendix II

Operating Procedure for the High-Pressure, High-Temperature Fixed-Bed Gasifier Unit

Pre-Gasification Preparation Mode

1. The internal surfaces of the reactor are cleaned with acetone.
2. An end cap is attached to the bottom of the reactor. Above it is placed a stainless steel basket of 200 mesh to hold the ceramic beads that are filled up to the center of the reactor.
3. Two stainless steel baskets of 200 mesh are placed on top of each other and then on the packing to support the char sample.
4. The reactor is filled with 2.5 grams of the char sample. The top end of the reactor is closed with the end cap that has the thermocouple assembly attached to it.
5. The reactor is connected to the inlet and outlet lines using quick connect couplings. The whole apparatus is tested for leaks by opening all the valves and bringing the system to the operating pressure.
6. The burette is filled with distilled water to the zero milliliter graduation. The pump settings are adjusted to provide the required flow rate into the reactor.
7. The silica gel is changed in the adsorber after every experimental run to avoid saturation of the silica bed. This avoids entry of water particles into the cumulative flow meter, which is very sensitive to the water.
8. The sample bags are vacuumed with a vacuum pump to remove any air or gases trapped in the bag.

9. The gas chromatograph is calibrated with the Scotty Specialties calibration gas prior to the analysis of the gasification product gases.

Gasification Mode

1. The nitrogen flow is started into the whole apparatus at a pressure that is slightly above the atmospheric pressure.
2. The temperature of the system is brought to the required operating value by raising the preheater and reactor temperatures.
3. The temperatures of the reactor and condenser are monitored continuously using the thermocouples. Once the reactor is about to reach the operating pressure, pressurize the apparatus to the operating pressure using the backpressure regulator.
4. As the system reaches the operating conditions, switch on the water pump for the water flow into the apparatus.
5. Start the stopwatch simultaneously and note the initial cumulative flow meter reading at the start of the gasification experiment.
6. Collect the sample gases at regular intervals as required and inject them into the gas chromatograph for analysis. The carbonaceous compounds are determined using helium as the carrier gas in the gas chromatograph.
7. At every time interval, record the reactor temperature, condenser temperature, burette reading, and cumulative gas flow meter reading.
8. At the end of four hours or when no more carbonaceous compounds are detected from the gas chromatograph results, the gasification experiment is considered over.

Post-Gasification Mode

1. Turn the pump off and reduce the temperature of the preheater and the reactor.
2. Turn on the hood fan to cool the apparatus and open the split furnace to reduce the temperature of the reactor to room temperature at a faster rate.
3. When the reactor has reached room temperature, adjust the backpressure regulator to bring the apparatus to atmospheric pressure.
4. Now, stop the nitrogen flow through the reactor. Remove the gasified char sample from the reactor. Weigh the sample and perform further analysis as necessary or store it under inert atmosphere.
5. The gas samples that are collected in the sample bags are analyzed for their hydrogen content using nitrogen as the carrier gas and injecting the gas sample into the gas chromatograph.

Appendix III

Raw Data for the Different Operating Conditions

Table III.1: Experimental Data for Run 1, No Additional Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.15	779.019	5.258	5.934	12598.44	0.993	12.948	102.857
10	2.3	779.346	7.829	4.984	13934.93	1.002	12.843	94.837
15	3.45	779.691	8.812	5.290	13548.94	0	11.892	110.477
20	4.6	779.877	9.203	7.209	13973.58	0.381	12.460	143.891
25	5.8	780.105	8.995	6.882	12780.34	0	11.923	162.779
30	7.0	780.438	8.391	6.093	13843.09	0	13.002	139.843
35	8.15	780.778	9.034	4.871	12984.34	0	12.746	105.983
40	9.3	781.026	8.106	4.409	13489.86	0	18.239	120.802
45	10.5	781.392	8.692	5.691	12994.08	0	12.032	101.773
50	11.65	781.649	9.438	6.820	13085.87	0	11.746	130.902
55	12.9	781.905	9.926	5.583	14002.15	0	12.000	129.880
60	14.0	782.304	10.028	5.974	13980.05	0	11.904	115.782
70	16.85	783.035	9.783	5.762	13892.89	0	11.993	108.732
80	20.0	783.694	8.942	5.082	13667.82	0	12.107	120.087
90	22.9	784.322	8.087	4.982	12999.03	0	10.992	108.349
105	27.5	785.453	6.832	5.957	14001.98	0	11.096	94.973
120	32.0	785.995	6.090	5.029	13092.84	0	9.092	100.204
135	36.3	787.103	5.832	4.845	13782.77	0	10.338	89.459
150	40.2	788.245	5.103	6.853	12678.93	0	9.014	80.054
165	44.5	789.140	4.329	5.845	11998.74	0	8.934	77.483
180	48.7	790.391	3.894	8.348	13009.92	0	5.024	43.928
200	54.35	792.655	4.086	5.657	13668.48	0	3.002	15.737
220	59.85	794.933	2.984	6.347	13772.36	0	1.671	7.303
240	65.9	797.101	1.627	4.683	12903.84	0	0.843	4.501
255	68.1	799.833	1.049	5.568	13017.34	0	0	3.896

Temperature = 1350^0F
Pressure = 100 psig
Steam Flow Rate = 0.25 ml/min

Table III.2: Experimental Data for Run 2, 10 Wt% K_2CO_3 Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.05	805.019	5.498	11.934	14698.44	2.564	11.948	199.857
10	2.2	805.346	7.239	12.984	15034.93	1.834	11.843	184.837
15	3.4	805.691	10.832	10.042	14848.94	1.023	10.892	170.477
20	4.65	805.877	10.503	10.623	14973.58	0.594	9.460	173.891
25	5.8	806.105	14.975	9.886	13780.34	0.674	9.923	172.779
30	7.1	806.438	26.594	9.355	14843.09	1.290	7.002	129.843
35	8.15	806.778	15.832	9.302	14094.34	0	10.746	155.983
40	9.3	807.137	12.344	9.522	13999.86	0	10.239	140.802
45	10.45	807.392	12.574	8.998	13984.08	0	15.032	131.773
50	11.75	807.649	11.576	8.693	14785.87	0.494	8.427	130.902
55	12.9	807.905	9.926	7.736	15002.15	0.203	9.340	109.880
60	14.0	808.304	14.211	8.397	14280.05	0.110	12.904	105.782
70	16.8	809.035	10.837	9.203	14622.89	0	15.993	125.732
80	20.0	800.694	9.484	8.935	15167.82	0	8.107	120.087
90	22.9	810.322	8.619	5.982	14899.03	0	9.742	117.349
105	27.5	811.453	6.401	5.957	16001.98	0	16.096	122.973
120	32.0	812.995	6.924	6.029	14192.84	0	7.092	112.204
135	36.3	814.103	5.452	5.845	14882.77	0.104	9.338	81.459
150	40.2	815.378	5.851	6.853	14578.93	0	8.004	70.054
165	44.5	816.140	4.411	5.565	15098.74	0	5.136	59.483
180	48.9	817.391	6.843	8.048	14009.92	0	4.001	25.928
200	54.6	818.655	5.832	4.257	14868.48	0	0	15.737
220	59.9	820.933	3.857	3.347	13772.36	0	1.048	12.303
240	65.9	822.101	3.627	3.683	14303.84	0	0	3.501
255	67.7	824.765	2.049	2.568	14517.34	0	0	4.896

Temperature = 1200^0F
Pressure = 100 psig
Steam Flow Rate = 0.25 ml/min

Table III.3: Experimental Data for Run 3, 10 Wt% K_2CO_3 Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	0.85	834.019	4.258	6.034	15598.44	0	12.948	102.857
10	1.9	834.346	4.829	6.779	15934.93	0.702	12.843	94.837
15	3.0	834.691	6.498	6.290	16548.94	0	11.892	110.477
20	4.45	834.877	8.203	5.209	14973.58	0	12.460	143.891
25	5.6	835.105	7.995	7.882	14380.34	0	11.923	162.779
30	6.8	835.438	6.391	6.093	16343.09	0	13.002	139.843
35	7.95	835.778	8.034	5.871	15884.34	0	12.746	105.983
40	9.5	836.026	9.106	6.409	16989.86	0	18.239	120.802
45	10.7	836.392	7.692	6.691	16694.08	0	12.032	101.773
50	11.8	836.649	6.438	4.820	14885.87	0	11.746	130.902
55	12.95	836.905	7.926	7.583	16102.15	0.208	12.000	129.880
60	13.9	837.304	8.028	6.974	15980.05	0	11.904	115.782
70	16.25	838.035	8.783	3.762	16992.89	0	11.993	108.732
80	18.75	838.694	9.034	4.082	16767.82	0	12.107	120.087
90	21.9	840.322	9.287	4.982	16499.03	0	10.992	108.349
105	26.5	841.453	5.332	4.957	15801.98	0	11.096	94.973
120	30.4	842.995	6.569	4.029	16492.84	0	9.092	100.204
135	35.0	844.103	7.832	3.845	16982.77	0	10.338	89.459
150	39.5	845.245	6.103	5.853	17378.93	0.340	9.014	80.054
165	44.5	846.140	5.329	4.845	15798.74	0	8.934	77.483
180	48.95	847.391	4.894	7.348	17009.92	0	5.024	43.928
200	55.25	848.655	5.086	4.657	14968.48	0	3.002	15.737
220	60.85	849.933	3.984	5.347	15202.36	0.205	1.671	7.303
240	65.9	852.101	2.627	3.683	15903.84	0	0.843	4.501
255	69.05	853.833	2.049	4.568	16017.34	0	0	3.896

Temperature = 1350^0F
Pressure = 100 psig
Steam Flow Rate = 0.25 ml/min

Table III.4: Experimental Data for Run 4, 10 Wt% K_2CO_3 Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.16	858.32	5.31	5.99	12724.42	1.00	13.08	103.89
10	2.32	858.65	7.91	5.03	13684.43	1.01	12.97	95.79
15	3.48	859.00	8.90	5.34	14113.32	0.00	12.01	111.58
20	4.65	859.19	9.30	7.28	12908.14	0.38	12.58	145.33
25	5.86	859.42	9.08	6.95	13981.52	0.00	12.04	164.41
30	7.07	859.75	8.47	6.15	13114.18	0.00	13.13	141.24
35	8.23	860.10	9.12	4.92	13624.76	0.00	12.87	107.04
40	9.39	860.35	8.19	4.45	13124.02	0.00	18.42	122.01
45	10.61	860.72	8.78	5.75	13216.73	0.00	12.15	102.79
50	11.77	860.98	9.53	6.89	14142.17	0.00	11.86	132.21
55	13.03	861.23	10.03	5.64	14128.94	0.00	12.12	131.18
60	14.14	861.64	10.13	6.03	14033.84	0.00	12.02	116.94
70	17.02	862.38	9.88	5.82	13804.51	0.00	12.11	109.82
80	20.20	863.04	9.03	5.13	13235.07	0.00	12.23	121.29
90	23.13	864.69	8.17	5.03	14142.00	0.00	11.10	109.43
105	27.78	865.83	6.90	6.02	13223.77	0.00	11.21	97.94
120	32.32	867.38	6.15	5.08	13920.60	0.00	10.12	101.21
135	36.66	868.50	5.89	4.89	12896.62	0.00	10.44	90.35
150	40.60	869.66	5.15	6.92	13138.83	0.00	9.10	80.85
165	44.95	870.56	4.37	5.90	12973.37	0.00	9.02	78.26
180	49.19	871.82	3.93	8.43	13805.16	0.00	5.08	44.37
200	54.89	873.10	4.13	5.71	13910.08	0.00	3.08	15.89
220	60.45	874.39	3.01	6.41	13223.81	0.00	1.69	7.38
240	66.56	875.57	1.64	4.73	13618.62	0.00	0.85	4.55
255	68.78	877.32	1.06	5.62	13147.51	0.00	0.00	3.93

Temperature = 1420^0F
Pressure = 100 psig
Steam Flow Rate = 0.25 ml/min

Table III.5: Experimental Data for Run 5, 10 Wt% K_2CO_3 Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.18	881.92	5.42	6.11	12976.39	1.02	13.34	105.94
10	2.37	885.26	8.06	5.13	13955.41	1.03	13.23	97.68
15	3.55	885.61	9.08	5.45	14392.79	0.00	12.25	113.79
20	4.74	885.80	9.48	7.43	13163.75	0.39	12.83	148.21
25	5.97	886.04	9.26	7.09	14258.38	0.00	12.28	167.66
30	7.21	886.38	8.64	6.28	13373.87	0.00	13.39	144.04
35	8.39	886.73	9.31	5.02	13894.56	0.00	13.13	109.16
40	9.58	886.99	8.35	4.54	13383.90	0.00	18.79	124.43
45	10.82	887.36	8.95	5.86	13478.45	0.00	12.39	104.83
50	12.00	887.63	9.72	7.02	14422.21	0.00	12.10	134.83
55	13.29	887.89	10.22	5.75	14408.72	0.00	12.36	133.78
60	14.42	888.30	10.33	6.15	14311.74	0.00	12.26	119.26
70	17.36	889.06	10.08	5.93	14077.86	0.00	12.35	111.99
80	20.60	889.73	9.21	5.23	13497.15	0.00	12.47	123.69
90	23.59	891.41	8.33	5.13	14422.04	0.00	11.32	111.60
105	28.33	892.58	7.04	6.14	13485.63	0.00	11.43	99.88
120	32.96	894.16	6.27	5.18	14196.25	0.00	10.32	103.21
135	37.39	895.31	6.01	4.99	13152.00	0.00	10.65	92.14
150	41.41	896.48	5.26	7.06	13399.00	0.00	9.28	82.46
165	45.84	897.40	4.46	6.02	13230.27	0.00	9.20	79.81
180	50.16	898.69	4.01	8.60	14078.53	0.00	5.18	45.25
200	55.98	899.99	4.21	5.83	14185.53	0.00	3.14	16.21
220	61.65	900.31	3.07	6.54	13485.67	0.00	1.72	7.52
240	67.88	902.51	1.68	4.82	13888.29	0.00	0.87	4.64
255	70.14	904.30	1.08	5.74	13407.86	0.00	0.00	4.01

Temperature = 1350^0F
Pressure = 50 psig
Steam Flow Rate = 0.25 ml/min

Table III.6: Experimental Data for Run 6, 10 Wt% K_2CO_3 Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.18	910.22	5.47	6.17	13102.38	1.03	13.47	106.97
10	2.36	913.56	8.14	5.18	14090.90	1.04	13.36	98.63
15	3.54	913.92	9.16	5.50	14532.52	0.00	12.37	114.90
20	4.72	914.11	9.57	7.50	13291.55	0.40	12.96	149.65
25	5.95	914.35	9.35	7.16	14396.81	0.00	12.40	169.29
30	7.18	914.70	8.73	6.34	13503.71	0.00	13.52	145.44
35	8.35	915.05	9.40	5.07	14029.45	0.00	13.26	110.22
40	9.53	915.31	8.43	4.59	13513.84	0.00	18.97	125.63
45	10.76	915.69	9.04	5.92	13609.30	0.00	12.51	105.84
50	11.94	915.95	9.82	7.09	14562.24	0.00	12.22	136.14
55	13.22	916.22	10.32	5.81	14548.61	0.00	12.48	135.08
60	14.35	916.64	10.43	6.21	14450.69	0.00	12.38	120.41
70	17.27	917.40	10.17	5.99	14214.54	0.00	12.47	113.08
80	20.50	918.08	9.30	5.29	13628.19	0.00	12.59	124.89
90	23.47	919.77	8.41	5.18	14562.06	0.00	11.43	112.68
105	28.19	920.95	7.11	6.20	13616.55	0.00	11.54	100.85
120	32.80	922.55	6.33	5.23	14334.08	0.00	10.42	104.21
135	37.21	923.71	6.07	5.04	13279.69	0.00	10.75	93.04
150	41.21	924.89	5.31	7.13	13529.09	0.00	9.37	83.26
165	45.61	925.83	4.50	6.08	13358.72	0.00	9.29	80.58
180	49.92	927.13	4.05	8.68	14215.22	0.00	5.23	45.69
200	55.71	928.44	4.25	5.88	14323.25	0.00	3.17	16.37
220	61.35	929.77	3.10	6.60	13616.60	0.00	1.74	7.60
240	67.55	930.99	1.69	4.87	14023.13	0.00	0.88	4.68
255	69.80	935.79	1.09	5.79	13538.03	0.00	0.00	4.05

Temperature = 1350^0F
Pressure = 300 psig
Steam Flow Rate = 0.25 ml/min

Table III.7: Experimental Data for Run 7, 5 Wt% K_2CO_3 Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.19	941.52	5.52	6.23	13228.36	1.04	13.60	108.00
10	2.38	941.86	8.22	5.23	14226.39	1.05	13.49	99.58
15	3.57	942.23	9.25	5.55	14672.26	0.00	12.49	116.00
20	4.75	942.42	9.66	7.57	13419.36	0.40	13.08	151.09
25	5.99	942.66	9.44	7.23	14535.24	0.00	12.52	170.92
30	7.23	943.01	8.81	6.40	13633.56	0.00	13.65	146.84
35	8.42	943.37	9.49	5.11	14164.35	0.00	13.38	111.28
40	9.61	943.63	8.51	4.63	13643.78	0.25	19.15	126.84
45	10.85	944.01	9.13	5.98	13740.16	0.00	12.63	106.86
50	12.04	944.28	9.91	7.16	14702.26	0.00	12.33	137.45
55	13.33	944.55	10.42	5.86	14688.50	0.00	12.60	136.37
60	14.47	944.97	10.53	6.27	14589.63	0.11	12.50	121.57
70	17.41	945.74	10.27	6.05	14351.22	0.00	12.59	114.17
80	20.67	946.43	9.39	5.34	13759.23	0.00	12.71	126.09
90	23.67	948.14	8.49	5.23	14702.08	0.00	11.54	113.77
105	28.42	949.33	7.17	6.25	13747.48	0.00	11.65	101.82
120	33.07	950.94	6.39	5.28	14471.91	0.00	10.52	105.21
135	37.52	952.11	6.12	5.09	13407.38	0.00	10.85	93.93
150	41.55	953.31	5.36	7.20	13659.18	0.00	9.46	84.06
165	45.99	954.25	4.55	6.14	13494.17	0.00	9.38	81.36
180	50.33	955.56	4.09	8.77	14351.90	0.00	5.28	46.12
200	56.17	956.89	4.29	5.94	14460.98	0.00	3.20	16.52
220	61.85	958.23	3.13	6.66	13747.52	0.13	1.75	7.67
240	68.11	959.46	1.71	4.92	14157.97	0.00	0.89	4.73
255	70.38	961.27	1.10	5.85	13668.21	0.00	0.00	4.09

Temperature = 1350^0F
Pressure = 100 psig
Steam Flow Rate = 0.25 ml/min

Table III.8: Experimental Data for Run 8, 15 Wt% K_2CO_3 Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.16	966.52	6.20	7.00	14866.16	1.17	15.28	121.37
10	2.32	966.90	9.24	5.88	15994.75	1.18	15.15	111.91
15	3.48	967.29	10.40	6.24	16488.82	0.00	14.03	130.36
20	4.64	967.51	10.86	8.51	15080.80	0.45	14.70	169.79
25	5.86	967.77	10.61	8.12	16334.85	0.00	14.07	192.08
30	7.07	967.15	9.90	7.19	15321.52	0.00	15.34	165.01
35	8.23	968.54	10.66	5.75	15918.03	0.00	15.04	125.06
40	9.39	968.83	9.57	5.20	15333.01	0.00	21.52	142.55
45	10.60	969.25	10.26	6.72	15441.33	0.00	14.20	120.09
50	11.76	969.55	11.14	8.05	16522.54	0.00	13.86	154.46
55	13.02	969.84	11.71	6.59	16507.08	0.00	14.16	153.26
60	14.13	970.30	11.83	7.05	16395.97	0.00	14.05	136.62
70	17.01	971.14	11.54	6.80	16128.04	0.00	14.15	128.30
80	20.19	971.90	10.55	6.00	15462.76	0.00	14.29	141.70
90	23.12	972.77	9.54	5.88	16522.34	0.00	12.97	127.85
105	27.76	973.07	8.06	7.03	15449.55	0.00	13.09	114.43
120	32.30	974.84	7.19	5.93	16263.67	0.00	11.82	118.24
135	36.64	976.12	6.88	5.72	15067.34	0.00	12.20	105.56
150	40.58	977.43	6.02	8.09	15350.31	0.00	10.64	94.46
165	44.92	978.46	5.11	6.90	15157.01	0.00	10.54	91.43
180	49.16	979.90	4.59	9.85	16128.81	0.00	5.93	51.84
200	54.94	981.35	4.82	6.68	16251.38	0.00	3.60	18.57
220	60.42	982.82	3.52	7.49	15449.60	0.00	1.97	8.62
240	66.53	984.17	1.92	5.53	15910.86	0.00	0.99	5.31
255	68.75	986.16	1.24	6.57	15360.46	0.00	0.00	4.60

Temperature = 1350^0F
Pressure = 100 psig
Steam Flow Rate = 0.25 ml/min

Table III.9: Experimental Data for Run 9, 10 Wt% K_2CO_3 Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.20	990.57	6.73	7.60	16126.00	1.27	16.57	131.66
10	2.39	990.96	10.02	6.38	17342.64	1.28	16.44	121.39
15	3.59	991.37	11.28	6.77	17886.18	0.00	15.22	141.41
20	4.78	991.59	11.78	9.23	16358.91	0.49	15.95	191.18
25	6.03	991.86	11.51	8.81	17719.16	0.00	15.26	208.36
30	7.28	992.25	10.74	7.80	16619.96	0.00	16.64	179.00
35	8.47	992.66	11.56	6.23	17267.02	0.00	16.31	135.66
40	9.67	992.95	10.38	5.64	16632.42	0.00	23.35	154.63
45	10.91	993.38	11.13	7.28	16749.91	0.00	15.40	130.27
50	12.11	993.69	12.08	8.73	17922.75	0.00	15.03	167.55
55	13.41	993.99	12.71	7.15	17905.98	0.00	15.36	166.25
60	14.55	994.47	12.91	7.65	17792.46	0.00	15.24	148.20
70	17.52	994.33	12.52	7.38	17494.82	0.00	15.35	139.18
80	20.79	995.11	11.45	6.50	16773.16	0.00	15.50	153.71
90	23.80	996.04	10.35	6.38	17922.53	0.00	14.07	138.69
105	28.59	997.38	8.74	7.62	16758.91	0.00	14.20	124.13
120	33.26	998.21	7.80	6.44	17641.95	0.00	12.82	128.26
135	37.73	999.52	7.46	6.20	16344.23	0.00	13.23	114.51
150	41.79	1006.88	6.53	8.77	16651.19	0.00	11.54	102.47
165	46.26	1007.94	5.54	7.48	16441.50	0.00	11.44	99.18
180	50.62	1009.42	4.98	10.69	17495.65	0.00	6.43	56.23
200	56.50	1011.92	5.23	7.24	17628.62	0.00	3.90	20.14
220	62.21	1013.43	3.82	8.12	16758.89	0.00	2.14	9.35
240	68.50	1015.81	2.08	5.99	17259.24	0.00	1.08	5.76
255	70.79	1016.94	1.34	7.13	16662.20	0.00	0.00	4.99

Temperature = 1350^0F
Pressure = 100 psig
Steam Flow Rate = 0.091 ml/min

Table III.10: Experimental Data for Run 10, 10 Wt% K_2CO_3 Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.04	1021.62	6.25	7.05	14969.47	1.18	15.38	122.21
10	2.09	1023.02	9.30	5.92	16098.92	1.19	15.26	112.69
15	3.13	1023.44	10.47	6.29	16603.41	0.00	14.13	131.27
20	4.17	1023.67	10.94	8.57	15192.60	0.45	14.80	170.97
25	5.26	1023.95	10.69	8.18	16448.36	0.00	14.17	193.41
30	6.35	1024.35	9.97	7.24	15427.99	0.00	15.45	166.16
35	7.39	1024.77	10.73	5.79	16028.65	0.00	15.14	125.93
40	8.43	1025.07	9.63	5.24	15439.57	0.00	21.67	143.54
45	9.52	1025.52	10.33	6.76	15548.63	0.00	14.30	120.93
50	10.56	1025.83	11.21	8.10	16637.35	0.00	13.96	155.54
55	11.70	1026.14	11.79	6.63	16621.79	0.00	14.26	154.32
60	12.70	1026.63	11.92	7.10	16509.91	0.00	14.14	137.57
70	15.28	1027.52	11.62	6.92	16240.12	0.00	14.25	129.20
80	18.14	1028.33	10.62	6.04	15570.21	0.00	14.39	142.69
90	20.77	1030.31	9.61	5.92	16637.15	0.00	13.06	128.74
105	24.94	1031.69	8.12	7.08	15556.91	0.00	13.18	115.22
120	29.02	1033.57	7.24	5.98	16376.69	0.00	11.90	119.06
135	32.92	1034.93	6.93	5.76	15172.04	0.00	12.28	106.30
150	36.45	1036.32	6.06	8.14	15456.98	0.00	10.71	95.12
165	40.35	1037.41	5.14	6.95	15262.33	0.00	10.62	92.07
180	44.16	1038.94	4.63	9.92	16240.89	0.00	5.97	52.20
200	49.28	1040.48	4.92	6.72	16364.32	0.00	3.62	18.70
220	54.27	1042.04	3.55	7.54	15556.96	0.00	1.99	8.68
240	59.76	1043.46	1.93	5.56	16021.43	0.00	1.00	5.35
255	61.75	1045.58	1.25	6.62	15467.20	0.00	0.00	4.63

Temperature = 1350^0F
Pressure = 100 psig
Steam Flow Rate = 0.145 ml/min

Table III.11: Experimental Data for Run 11, 10 Wt% Langbeinite Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.10	1051.67	6.56	7.41	15725.37	1.24	16.16	128.39
10	2.20	1052.08	9.77	6.22	16911.79	1.25	16.03	118.38
15	3.30	1052.52	11.00	6.60	17441.82	0.00	14.91	137.90
20	4.40	1052.75	11.49	9.00	15952.42	0.48	15.55	179.60
25	5.55	1053.04	11.23	8.59	17278.94	0.00	14.88	203.18
30	6.70	1053.45	10.47	7.61	16207.05	0.00	16.23	174.55
35	7.80	1053.88	11.28	6.08	16838.04	0.00	15.91	132.29
40	8.90	1054.19	10.12	5.50	16219.21	0.00	22.77	150.79
45	10.05	1054.65	10.92	7.10	16333.78	0.00	15.02	127.03
50	11.15	1054.97	11.78	8.51	17477.48	0.00	14.66	163.39
55	12.34	1055.30	12.39	6.97	17461.13	0.00	14.98	162.12
60	13.40	1055.80	12.52	7.46	17343.60	0.00	14.93	144.52
70	16.12	1056.71	12.21	7.19	17060.19	0.35	14.97	135.72
80	19.14	1057.54	11.16	6.34	16356.45	0.00	15.11	149.89
90	21.91	1059.58	10.09	6.22	17477.27	0.00	13.72	135.24
105	26.31	1061.00	8.53	7.44	16342.48	0.21	13.92	121.04
120	30.62	1062.94	7.60	6.28	17203.65	0.00	12.50	125.07
135	34.73	1064.33	7.28	6.05	15938.18	0.00	12.90	111.66
150	38.46	1065.76	6.37	8.55	16237.51	0.00	11.25	99.92
165	42.58	1066.89	5.40	7.30	16033.03	0.00	11.15	96.71
180	46.60	1068.46	4.93	10.42	17061.00	0.09	6.27	54.83
200	52.00	1070.04	5.10	7.06	17190.66	0.00	3.80	19.64
220	57.26	1071.65	3.72	7.92	16342.53	0.00	2.09	9.12
240	63.05	1073.11	2.03	5.92	16830.45	0.00	1.05	5.62
255	65.16	1075.29	1.31	6.95	16248.24	0.00	0.00	4.93

Temperature = 1200^0F
Pressure = 100 psig
Steam Flow Rate = 0.25 ml/min

Table III.12: Experimental Data for Run 12, 10 Wt% Langbeinite Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.09	1084.94	6.83	7.71	16367.89	1.29	16.82	133.63
10	2.19	1085.30	10.17	6.48	17602.78	1.30	16.69	123.21
15	3.28	1085.74	11.45	6.94	18154.48	0.00	15.45	143.53
20	4.37	1085.99	11.96	9.37	16604.22	0.49	16.19	193.94
25	5.51	1086.28	11.69	8.94	17991.94	0.00	15.49	211.48
30	6.65	1086.71	10.90	7.92	16939.25	0.00	16.89	181.68
35	7.74	1087.15	11.74	6.33	17526.03	0.00	16.56	137.69
40	8.91	1087.47	10.53	5.73	16881.91	0.00	23.70	156.95
45	9.98	1087.95	11.29	7.39	17001.16	0.00	15.63	132.22
50	11.07	1088.28	12.26	8.93	18191.59	0.00	15.26	170.07
55	12.26	1088.61	12.90	7.25	18174.57	0.00	15.59	168.74
60	13.30	1089.13	13.03	7.76	18052.24	0.00	15.47	150.42
70	16.01	1090.08	12.71	7.49	17757.24	0.00	15.58	141.26
80	19.00	1090.93	11.62	6.60	17024.76	0.00	15.73	156.02
90	21.76	1093.04	10.51	6.47	18191.37	0.00	14.28	140.77
105	26.13	1094.50	8.88	7.74	17010.22	0.00	14.42	125.99
120	30.40	1096.50	7.91	6.53	17906.57	0.00	13.02	130.19
135	34.49	1097.93	7.58	6.29	16589.39	0.00	13.43	116.23
150	38.19	1099.41	6.63	8.90	16900.96	0.00	11.71	104.01
165	42.28	1101.57	5.62	7.59	16688.12	0.00	11.61	100.67
180	46.27	1102.19	5.06	10.92	17758.09	0.00	6.53	57.07
200	51.63	1104.83	5.31	7.35	17893.05	0.00	3.96	20.45
220	56.93	1107.48	3.88	8.25	17010.27	0.00	2.17	9.49
240	62.61	1109.00	2.11	6.08	17518.13	0.00	1.10	5.92
255	64.70	1111.24	1.36	7.23	16912.13	0.00	0.00	5.06

Temperature = 1350^0F
Pressure = 100 psig
Steam Flow Rate = 0.25 ml/min

Table III.13: Experimental Data for Run 13, 10 Wt% Langbeinite Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.14	1124.68	7.36	8.30	17627.74	0.56	18.12	143.92
10	2.28	1125.12	10.95	6.97	18957.68	1.40	17.97	132.70
15	3.42	1125.59	12.33	7.40	19551.83	0.00	16.64	154.58
20	4.55	1125.91	12.88	10.09	17882.25	0.53	17.43	201.33
25	5.74	1126.15	12.59	9.63	19369.25	0.00	16.68	227.76
30	6.93	1126.60	11.74	8.53	18167.69	0.00	18.19	195.67
35	8.07	1127.06	12.64	6.82	18945.01	1.94	17.83	148.29
40	9.21	1127.40	11.34	6.17	18181.32	0.00	25.52	169.03
45	10.40	1127.89	12.16	7.96	18309.75	0.00	16.91	142.40
50	11.53	1128.24	13.21	9.54	19591.81	0.00	16.44	183.16
55	12.77	1128.59	13.89	7.81	19573.48	0.00	16.79	181.73
60	13.93	1129.13	14.03	8.36	19441.73	0.00	16.66	162.00
70	16.68	1130.12	13.69	8.06	19124.03	0.00	16.78	152.14
80	19.80	1131.01	12.51	7.11	18335.16	0.00	16.94	168.03
90	22.67	1133.22	11.32	6.97	19591.57	0.17	15.38	151.60
105	27.23	1134.75	9.56	8.34	18319.50	0.00	15.53	135.68
120	31.68	1136.91	8.52	7.04	19291.92	0.00	14.02	140.21
135	35.94	1138.34	8.16	6.78	17936.29	0.00	14.46	125.17
150	39.80	1139.89	7.14	9.59	18201.83	0.00	12.61	112.01
165	44.06	1141.10	6.06	8.18	17972.61	0.90	12.50	108.41
180	48.21	1142.79	5.45	11.68	19124.94	0.00	7.03	61.46
200	53.81	1144.51	5.72	7.92	19270.29	0.00	4.26	22.02
220	59.25	1146.24	4.18	8.88	18319.56	0.00	2.34	10.22
240	65.24	1147.82	2.28	6.55	18936.50	0.00	1.18	6.30
255	67.42	1150.17	1.47	7.79	18213.93	0.00	0.00	5.45

Temperature = 1420^0F
Pressure = 100 psig
Steam Flow Rate = 0.25 ml/min

Table III.14: Experimental Data for Run 14, 10 Wt% Langbeinite Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.00	1162.03	7.68	8.66	18393.72	1.45	18.90	150.17
10	2.00	1162.48	11.43	7.28	19781.45	1.46	18.75	138.46
15	2.99	1162.97	12.94	7.72	20401.43	0.00	17.36	161.30
20	3.99	1163.23	13.44	10.53	19359.30	0.56	18.19	210.08
25	5.03	1163.55	13.13	10.05	20210.91	0.00	17.41	237.66
30	6.08	1164.01	12.25	8.90	18957.14	0.00	18.98	204.17
35	7.07	1164.49	13.19	7.11	19695.20	0.00	18.61	154.74
40	8.07	1164.91	11.83	6.44	18971.36	0.00	26.63	176.37
45	9.11	1165.35	12.69	8.31	19105.37	0.00	17.57	148.59
50	10.11	1165.71	13.78	9.96	20443.14	0.00	17.15	191.12
55	11.20	1166.07	14.49	8.15	20424.01	0.00	17.52	189.62
60	12.15	1166.63	14.64	8.72	20293.54	0.00	17.38	169.04
70	14.63	1167.65	14.28	8.41	19955.03	0.00	17.51	158.75
80	17.36	1168.57	13.06	7.42	19131.88	0.00	17.68	175.33
90	19.88	1170.92	11.81	7.27	20442.89	0.00	16.05	158.19
105	23.94	1172.43	9.97	8.70	19115.55	0.00	16.20	141.58
120	27.78	1174.59	8.89	7.34	20122.91	0.00	14.63	146.30
135	31.51	1176.14	8.51	7.07	19342.64	0.00	15.09	130.61
150	34.89	1177.74	7.45	10.01	18992.76	0.00	13.16	116.88
165	38.63	1179.00	6.32	8.53	19453.58	0.00	13.04	113.13
180	42.27	1180.75	5.69	12.19	19955.98	0.00	7.34	64.13
200	47.18	1182.52	5.97	8.26	20107.65	0.00	4.45	22.98
220	51.95	1191.31	4.36	9.27	19115.60	0.00	2.44	10.66
240	57.20	1192.94	2.38	6.91	19693.32	0.00	1.23	6.57
255	59.11	1188.37	1.53	8.13	19005.32	0.00	0.00	5.69

Temperature = 1350^0F
Pressure = 50 psig
Steam Flow Rate = 0.25 ml/min

Table III.15: Experimental Data for Run 15, 10 Wt% Langbeinite Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.00	1195.23	7.45	8.41	17930.81	1.41	18.36	145.82
10	2.00	1195.70	11.10	7.07	19208.33	1.42	18.21	134.45
15	2.99	1196.20	12.49	7.50	19810.34	0.00	16.93	156.62
20	3.99	1196.46	13.05	10.22	18118.69	0.54	17.66	203.99
25	5.03	1196.79	12.75	9.76	19625.35	0.00	16.90	230.77
30	6.08	1197.27	11.90	8.64	19107.90	0.00	18.43	198.26
35	7.07	1197.76	12.81	6.91	19124.57	0.00	18.07	150.25
40	8.07	1198.12	11.49	6.25	19121.71	0.00	25.93	171.26
45	9.11	1198.64	12.32	8.07	19251.91	0.00	17.06	144.28
50	10.11	1199.01	13.38	9.67	19920.92	0.00	16.65	192.58
55	11.20	1199.38	14.07	7.92	19832.28	0.00	17.01	191.13
60	12.15	1199.96	14.22	8.47	19698.79	0.00	16.88	164.14
70	14.63	1201.01	13.94	8.17	19376.88	0.00	17.00	154.15
80	17.36	1201.96	12.68	7.20	19277.58	0.00	17.16	170.25
90	19.88	1204.30	11.46	7.06	19920.61	0.00	15.58	153.61
105	23.94	1205.93	9.69	8.45	19261.72	0.00	15.73	137.48
120	27.78	1208.15	8.63	7.13	19539.83	0.00	14.20	142.06
135	31.51	1209.75	8.27	6.94	18102.51	0.00	14.66	126.83
150	34.89	1211.39	7.23	9.72	19142.49	0.00	12.78	113.49
165	38.63	1212.68	6.14	8.29	18210.24	0.00	12.67	109.92
180	42.27	1214.48	5.52	11.83	19377.80	0.00	7.13	62.28
200	47.18	1216.30	5.79	8.02	19525.07	0.00	4.32	22.31
220	51.95	1218.14	4.23	9.00	19261.78	0.00	2.37	10.35
240	57.20	1219.83	2.31	6.64	19115.95	0.00	1.20	6.38
255	59.11	1222.32	1.49	7.89	19154.68	0.00	0.00	5.52

Temperature = 1350^0F
Pressure = 300 psig
Steam Flow Rate = 0.25 ml/min

Table III.16: Experimental Data for Run 16, 5 Wt% Langbeinite Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.14	1228.43	7.98	9.01	19120.65	1.51	19.65	156.11
10	2.28	1228.91	11.88	7.56	20563.23	1.52	19.49	143.93
15	3.42	1229.42	13.37	8.03	21207.70	0.00	18.05	167.67
20	4.55	1229.70	13.97	10.94	19396.72	0.58	18.91	218.38
25	5.74	1230.04	13.65	10.44	21009.66	0.00	18.10	247.05
30	6.93	1230.53	12.74	9.25	19706.33	0.00	19.73	212.24
35	8.07	1231.03	13.71	7.39	20473.56	0.00	19.34	160.92
40	9.21	1231.40	12.30	6.69	19721.12	0.00	27.68	183.34
45	10.40	1231.94	13.19	8.64	19930.42	0.00	18.26	154.46
50	11.53	1232.32	14.32	10.35	21251.06	0.00	17.83	198.67
55	12.77	1232.70	15.06	8.47	21231.18	0.00	18.21	197.12
60	13.93	1233.29	15.22	9.07	21088.27	0.00	18.07	175.72
70	16.68	1234.37	14.92	8.74	20743.67	0.00	18.20	165.02
80	19.80	1235.35	13.57	7.71	19894.99	0.00	18.37	182.26
90	22.67	1237.76	12.27	7.56	21250.81	0.00	16.68	164.44
105	27.23	1239.43	10.37	9.04	19941.00	0.00	16.91	147.18
120	31.68	1241.71	9.24	7.63	20918.11	0.00	15.20	152.08
135	35.94	1243.35	8.92	7.35	19379.41	0.00	15.69	135.77
150	39.80	1245.04	7.74	10.40	19743.36	0.00	13.68	121.50
165	44.06	1246.37	6.57	8.94	19494.74	0.00	13.56	117.60
180	48.21	1248.22	5.91	12.67	20744.65	0.00	7.63	66.67
200	53.81	1250.09	6.20	8.59	20902.31	0.00	4.63	23.88
220	59.25	1251.98	4.53	9.63	19941.06	0.00	2.54	11.08
240	65.24	1253.71	2.47	7.11	20464.33	0.00	1.28	6.83
255	67.42	1256.27	1.59	8.45	19756.42	0.00	0.00	5.91

Temperature = 1350^0F
Pressure = 100 psig
Steam Flow Rate = 0.25 ml/min

Table III.17: Experimental Data for Run 17, 15 Wt% Langbeinite Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.06	1261.63	8.30	9.36	19946.56	1.57	20.43	162.28
10	2.12	1262.13	12.35	7.93	21376.16	1.58	20.26	149.62
15	3.17	1262.65	13.90	8.35	22046.12	0.00	18.76	174.30
20	4.23	1262.93	14.52	11.37	20163.54	0.60	19.66	227.02
25	5.34	1263.28	14.19	10.93	21910.24	0.00	18.81	256.82
30	6.44	1263.79	13.24	9.61	20492.39	0.00	20.51	220.63
35	7.50	1264.30	14.25	7.68	21282.95	0.00	20.11	167.21
40	8.56	1264.68	12.79	6.96	20500.76	0.00	28.78	190.59
45	9.66	1265.24	13.71	8.98	20645.58	0.00	18.98	160.57
50	10.72	1265.63	14.89	10.76	22091.19	0.00	18.53	206.52
55	11.94	1266.02	15.66	8.81	22070.52	0.00	18.93	204.91
60	12.88	1266.62	15.82	9.43	21921.97	0.00	18.78	182.67
70	15.50	1267.73	15.43	9.09	21563.74	0.00	18.92	171.55
80	18.40	1268.73	14.11	8.02	20674.23	0.00	19.10	189.46
90	21.07	1271.21	12.76	7.93	22090.92	0.00	17.34	170.94
105	25.30	1272.93	10.78	9.40	20656.57	0.00	17.51	152.99
120	29.44	1275.27	9.61	7.93	21745.08	0.00	15.81	158.09
135	33.40	1276.96	9.20	7.64	20145.54	0.00	16.31	141.14
150	36.98	1278.69	8.05	10.81	20523.89	0.00	14.22	126.30
165	40.94	1280.05	6.83	9.22	20265.43	0.00	14.10	122.24
180	44.80	1281.95	6.14	13.17	21564.76	0.00	7.93	69.31
200	50.00	1283.88	6.45	8.93	21728.65	0.00	4.81	24.83
220	55.06	1292.82	4.71	10.01	20656.64	0.00	2.64	11.52
240	60.63	1294.59	2.57	7.39	21273.36	0.00	1.33	7.10
255	62.65	1290.23	1.66	8.78	20537.46	0.00	0.00	6.15

Temperature = 1350^0F
Pressure = 100 psig
Steam Flow Rate = 0.25 ml/min

Table III.18: Experimental Data for Run 18, 10 Wt% Langbeinite Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.13	1303.13	7.96	8.98	19071.14	1.50	19.60	155.70
10	2.25	1303.64	11.92	7.54	20509.98	1.52	19.44	143.56
15	3.38	1304.18	13.34	8.01	21152.79	0.00	18.00	167.24
20	4.51	1304.48	13.93	10.91	19346.50	0.58	18.93	217.82
25	5.68	1304.83	13.62	10.42	20955.25	0.00	18.05	246.41
30	6.93	1305.36	12.70	9.22	19655.30	0.00	19.68	211.69
35	7.99	1305.89	13.68	7.37	20420.55	0.00	19.29	160.43
40	9.11	1306.28	12.27	6.67	19670.05	0.00	27.61	182.94
45	10.29	1306.93	13.16	8.61	19809.00	0.00	18.21	154.06
50	11.42	1307.26	14.29	10.32	21196.03	0.00	17.78	198.16
55	12.64	1307.66	15.03	8.45	21176.20	0.00	18.17	196.61
60	13.72	1308.29	15.18	9.04	21033.67	0.00	18.02	175.27
70	16.51	1309.43	14.81	8.72	20689.95	0.00	18.15	164.60
80	19.60	1310.47	13.54	7.69	19836.49	0.00	18.33	181.78
90	22.44	1313.03	12.24	7.54	21195.78	0.00	16.64	164.02
105	26.95	1314.80	10.34	9.02	19819.55	0.00	16.80	146.79
120	31.36	1317.22	9.22	7.61	20933.94	0.00	15.16	151.69
135	35.57	1318.96	8.83	7.33	19329.22	0.00	15.65	135.42
150	39.40	1320.75	7.72	10.37	19692.24	0.00	13.65	121.18
165	43.61	1322.16	6.55	8.92	19444.25	0.00	13.52	117.29
180	47.73	1324.12	5.89	12.64	20690.93	0.00	7.61	66.50
200	53.26	1326.11	6.19	8.56	20918.19	0.00	4.61	23.82
220	58.65	1328.11	4.52	9.61	19819.61	0.00	2.53	11.06
240	64.58	1329.95	2.46	7.09	20411.34	0.00	1.28	6.81
255	66.74	1332.67	1.59	8.43	19705.26	0.00	0.00	5.90

Temperature = 1350^0F
Pressure = 100 psig
Steam Flow Rate = 0.091 ml/min

Table III.19: Experimental Data for Run 19, 10 Wt% Langbeinite Catalyst

Time (min)	Burette Reading (ml)	Gas Flow (ft^3)	H_2	O_2	N_2	CH_4	CO	CO_2
5	1.09	1337.99	7.91	8.92	19489.02	1.48	19.31	153.40
10	2.18	1338.52	11.68	7.43	20206.58	1.49	19.15	141.44
15	3.27	1339.07	13.14	7.89	20839.88	0.00	17.74	164.76
20	4.36	1339.37	13.73	10.75	19060.31	0.57	18.58	214.60
25	5.50	1339.74	13.41	10.26	20645.27	0.00	17.78	242.76
30	6.64	1340.28	12.51	9.09	19364.55	0.00	19.39	208.56
35	7.73	1340.83	13.47	7.26	20118.47	0.00	19.01	158.06
40	8.82	1341.23	12.09	6.58	19379.07	0.00	27.20	180.16
45	9.95	1341.82	12.96	8.49	19515.97	0.00	17.94	151.78
50	11.04	1342.23	14.08	10.17	20882.48	0.00	17.52	195.22
55	12.23	1342.64	14.80	8.33	20932.95	0.00	17.90	193.70
60	13.27	1343.29	14.96	8.91	20722.52	0.00	17.75	172.67
70	15.97	1344.46	14.59	8.59	20383.89	0.00	17.89	162.16
80	18.96	1345.53	13.34	7.58	19543.05	0.00	18.06	179.09
90	21.71	1348.15	12.06	7.43	20882.23	0.00	16.39	161.59
105	26.07	1349.97	10.19	8.88	19526.36	0.00	16.55	144.62
120	30.34	1352.46	9.08	7.50	20555.31	0.00	14.94	149.44
135	34.41	1354.25	8.70	7.23	19043.29	0.00	15.42	133.42
150	38.11	1356.09	7.61	10.22	19400.94	0.00	13.44	119.39
165	42.19	1357.53	6.46	8.72	19156.62	0.00	13.32	115.56
180	46.17	1359.55	5.81	12.45	20391.93	0.00	7.50	65.51
200	51.52	1361.58	6.09	8.44	20539.78	0.00	4.55	23.47
220	56.74	1363.64	4.45	9.47	19526.42	0.00	2.49	10.89
240	62.47	1365.53	2.43	6.98	20109.40	0.00	1.26	6.71
255	64.56	1368.32	1.56	8.30	19413.76	0.00	0.00	5.81

Temperature = 1350^0F
Pressure = 100 psig
Steam Flow Rate = 0.145 ml/min

VITA

Anthony Turner was born in Martin, Tennessee on February 12, 1972. He completed his undergraduate studies in May 1995 at the University of Tennessee - Knoxville, where he earned a Bachelor of Science in Chemical Engineering with a minor in psychology. He then worked for three years for the Westinghouse Savannah River Company and the city of Atlanta. Anthony returned to graduate school to earn his Master of Science in Chemical Engineering. After completion of his graduate studies, Anthony joined the staff of BASF Corporation, working in the Chemicals Division.