THE GASIFICATION OF BIOMASS IN A FLUIDIZED BED REACTOR

by

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CHAPTER I

INTRODUCTION

Rising costs and the instability in the supply of fossil fuels has increased the need for alternative energy sources. One such source being considered is biomass. Biomass is a renewable source of energy derived from plants. Biomass includes agricultural, forestry and municipal waste products. In its natural form biomass is not a practical energy source because of handling and pollution problems. There are several methods of converting biomass into more useful energy sources. One method that has been growing in importance over the last few years is gasification in a fluidized bed reactor.

The objective of this thesis is to report on studies done on the gasification of biomass in a bench-scale fluidized bed reactor. The studies investigated the gasification characteristics of the process, such as gas composition, gas heating value, gas yield and energy recovery.

Chapter II reviews the literature on the gasification of carbonaceous materials. This review emphasizes the experimental studies conducted using fluidized bed gasifiers. Devolatilization studies on cellulose and grain dust are also discussed.

Chapter III presents the results of an experimental study of gasification of corn grain dust. This work studied the effect of reactor bed temperature of a fluidized bed on the gas composition, gas heating value, gas yield and energy recovery of the produced gas.

Chapter IV deals with the gasification of α-cellulose. Alpha-cellulose was studied to provide a bench mark for gauging other biomass gasification processes. This chapter analyzes the influence of reactor bed temperature on the gasification characteristics. It also proposes a mechanism for the gasification of pure cellulose over the temperature range studied.

Chapter V discusses further investigations into the gasification of

α-cellulose. Here the effects of elevated freeboard temperature on the gasification characteristics are presented. This work gives further support for the mechanism developed in Chapter IV.

Chpater VI summarizes the major conclusions of this thesis and outlines the recommendations for extensions of this work.

CHAPTER II

GASIFICATION OF BIOMASS

A LITERATURE REVIEW

A need for an alternative energy source has emerged in this nation. Biomass represents a renewable alternate energy source of tremendous importance if economical conversion processes can be developed. Biomass refers to all renewable products ultimately derived from plants, which converted the sun's energy through photosynthesis to chemical energy. Biomass includes agricultural and forestry products, along with animal and human wastes. Fossil fuels are ultimately derived from plants, but because they take thousands of years to convert they are not considered renewable.

In its natural state biomass is not economical as a fuel because of its handling and pollution problems. There are numerous conversion schemes for changing it into more useful fuels or chemical feedstocks. They include direct combustion, anaerobic digestion, liquefaction, hydrolysis for fermentation to ethyl alcohol and pyrolysis (gasification).

Gasification or pyrolysis is the process by which organic matter is converted to gas through thermal decomposition in an oxygen deficient environment, followed by secondary reactions of the resulting volatiles. The resulting synthesis gas can be utilized for heat or power generation, or it can be used as a feedstock for further chemical processes. There are several devices which can be used to gasify carbonaceous materials. They include packed (fixed) beds, entrained beds, moving beds, rotary kilns and fluidized bed reactors.

There are several advantages of using a fluidized bed reactor over other devices to gasify biomass. The more important being:

1. Flexibility with respect to feed materials permits the use of a wide range of liquid and solid materials.
2. Uniform high temperature in the reactor bed allows good control of the process.

3. Very high heat transfer rates between reactor bed and feed materials maximizes gas production.
4. Product gas can be scrubbed easily to control air emissions.
5. Systems can be designed to be energy self-sufficient.
6. The system is simple to operate and easy to maintain.
7. The system can be adapted to large or small scale applications.
8. Proper selection of feed materials, operation conditions and/or catalysts can produce synthesis gas of specified qualities to be used as feedstock for further chemical processes.

Because of these advantages it appears that the gasification of biomass in a fluidized bed reactor is an attractive method for converting renewable materials into useful products.

To successfully design a commercial fluid-bed system to economically gasify biomass, a vast amount of research and development is needed. The technological development of the gasification process is just beginning. The gasification of biomass in fluidized bed reactors is a topic that appears to only have been studied for the last ten years. The following literature review attempts to summarize the experimental work that has been done in the field. The review attempts to emphasize the operation conditions and the results obtained so that they can be compared with each other and with the work presented in this thesis. Although most of the emphasis is on gasification of biomass materials, the review also considers the gasification behavior of pure cellulose. This review does not include the gasification work done using other reactors such as packed beds, entrained beds, moving beds or rotary kilns. For a review of fixed and moving bed gas producers see Reed and Jantzen (1979). Also this review does not emphasize the theoretical work done with fluidized beds such as reactor modeling. For a review of this topic see Raman et al. (1981).

When studying the gasification of carbonaceous materials most investigators are interested in the characteristics of the gas such as its composition, yield, higher heating value, energy recovery and carbon conversion. The gas composition is the component composition of the gas usually on a volumetric or molar basis. The produced gas yield is defined as the volumetric difference between the off-gas and the fluidized gas, produced from a unit mass of dry ash-free feed. Many investigators report of off-gas yield which includes the fluidized gas of N_2, air or the air combustion products of methane or propane. The off-gas yield will be larger than the produced gas yield because of these dilutants present. The produced gas higher heating value will be larger than the off-gas higher heating value for the same reason. The higher heating value of the gas is calculated from the gas composition and the higher heating values of the individual gas components. Another factor to consider when dealing with volumetric units is the temperature and pressure basis. All volumetric units reported in this work will be reported at the standard condition of 101.3 kPa (1 atm) and 288 K unless otherwise indicated.

The energy recovery of the produced gas is a measure of the effectiveness of the process. It is the ratio of the heating value of the produced gas per unit mass of dry ash-free feed to the heat of combustion of a unit mass of feed, also on a dry ash-free basis. Another measure of the efficiency of the process is the carbon conversion. This is defined as the ratio of the moles of carbon in the produced gas from a unit mass of dry ash-free feed to the moles of carbon in a unit mass of dry ash-free feed.

Bailie and Burton at West Virginia University (Burton, 1972) were the first in this country to study the fluidized bed gasification of biomass. Burton's masters thesis reports the gasification of ten different feed

materials including municipal solid waste, sawmill wood waste, chicken manue and cow manure. They used a 0.38 m I.D. pilot plant with either silica sand or lime as the bed material. Hot fluidizing gas was supplied by burning natural gas under starving air conditions. They studied the influence of temperature on the composition, heating value and yield of the produced gas. Of the 14 pyrolysis experiments reported, all but two operated at reactor temperatures between 966 K and 1088 K. The volume percent composition of H_2 produced ranged from 23% to 58%. The CO_2 composition ranged from 2% to 30%. The composition of CO ranged from 21% to 45%, and the composition of CH_4 ranged from 3% to 12%. The heating value of the produced gas varied from 10 to 17 MJ/m^3, and the gas yield from 0.6 to 1.2 m^3/kg. The energy recovery ranged from 38% to 91%, and the carbon conversion from 34% to 97%.

Maa and Bailie continued the pyrolysis work at West Virginia University with more fundamental studies on the pyrolysis of wood in a fluidized bed reactor (Maa et al., 1978). They studied the pyrolysis of wooden cylinders over a reactor bed temperature range of 713 K to 1273 K. This study demonstrated that the pyrolysis rate increased with an increase in fluidized bed temperature. More importantly it demonstrated that shrinking core phenomenon as being the reaction mechanism of the feed particle. This experimental work was done to demonstrate Maa and Bailie's shrinking core reaction model for the pyrolysis of cellulosic materials (Maa et al., 1973). The reaction time obtained from the pyrolysis of the wood in the fluidized bed reactor agreed quite well with the predicted times calculated using the model and parameters obtained from a TGA unit.

Halligan et al. (1975) at Texas Tech University investigated the effects of temperature on the gasification of feedlot manure in a 0.5 m I.D. fluidized bed reactor. They operated their bench-scale reactor

under partial oxidation conditions using an air-steam mixture as the fluidizing agent. The fluidizing media consisted of only the feed material. Due to the high temperature difference in the reactor bed (as high as 100 K) there is some question as to the quality of fluidization. They reported six experiments over a temperature range of 966 K to 1069 K. Their gas yield increased with temperature and they reported off-gas yields of 0.6 m^3/kg at 966 K to 1.3 m^3/kg at 1069 K. The off-gas heating value was relatively constant and varied from 8.7 to 9.8 MJ/m^3. The volume percent composition of the off-gas fluctuated with temperaure. Energy recovery increased with temperature and ranged from 23% at 966 K to 49% at 1069 K. The carbon conversion also increased with temperature and ranged from 20% at 966 K to 50% at 1069 K.

Texas Tech University continued its study of the partial oxidation of cattle feedlot manure and Beck et al. (1979) reported results obtained in a 0.15 m I.D. pilot plant. The pilot plant was run similar to their bench operations, and the results obtained were also similar. The temperature ranged studied was 790 K to 909 K. The off-gas yield increased with temperature and ranged from 0.36 m^3/kg at 790 K to 1.15 m^3/kg at 909 K. The heating value varied from 9 to 12 MJ/m^3, which was higher than the results obtained on the bench-scale reactor due to the presence of significant amounts of hydrocarbons (C_2's) in the off-gas. The energy recovery increased with temperature and ranged from 20% at 790 K to 60% at 909 K. The carbon conversion also increased with temperature and varied from 27% at 790 K to 60% at 909 K. The gas composition still fluctuated with temperature. Again there was some question as to the quality of the fluidization, because feed was the sole solid in the bed and there were differences as high as 500 K along the longitudinal axis of the reactor.

Associates of Texas Tech University also tried to model the fluid-bed gasification of feedlot manure (Huffman et al., 1977). They assumed two first order reactions, where the feed devolatilized to form char, liquid and gas, and the liquid reactor to produce gas. They treated the fluid-bed as a completely mixed reactor and developed a model which estimated the gas and liquid yields. No attempt was made to include the reactions involving the gases or the char. Also the model did not estimate the composition of the gas produced.

Beck et al. (1980) reported the results from gasification of sawdust in the same pilot plant at Texas Tech University. They reported off-gas yields of 1.1 to 1.3 m^3/kg when the average reactor temperature was 873 K to 1073 K. These results were significantly higher than those for cattle manure. The higher heating value of the sawdust off-gas was reported to be greater than 11.2 MJ/m^3 in all experiments, which was slightly higher than the higher heating values of the off-gas produced from cow manure.

In Japan, Itoh (1975) reported results for gasification of newspaper in a 0.3 m I.D. fluid-bed reactor. Hot gas was generated by burning propane under starving air conditions, and sand was used as the bed media. The study investigated the effect of temperature, which ranged from 823 K to 1173 K, on gas yield, heating value and composition. The produced gas yield increased with temperature and ranged from 0.2 m^3/kg at 823 K to 0.7 m^3/kg at 1173 K. Itoh reported a decrease in heating value of the produced gas with increasing temperature. The CO_2 free heating value varied from 25 MJ/m^3 at 723 K to 17 MJ/m^3 at 973 K. The heating value remained relatively constant at 17 MJ/m^3 from 973 K to 1123 K. The composition of CO remained relatively constant at 55% to 60%. Hydrogen increased in the first 150 K of the temperature range studied, and ranged from 4% at

823 K to 26% at 973 K, and then it remained relatively constant at 26% to 1173 K. The composition of CH_4 decreased in the first 150 K from 42% to 12%, and then remained constant thereafter. The balance of the gas was CO_2 which Itoh did not report, but by difference it comprised less than 5% of the gas.

Tsukishima Kikai Company (1975) in Japan studied the pyrolysis of municipal refuse in a circulating twin-bed system, where the char produced in the first bed was burned in the second bed to heat the sand, which was recirculated back to the first bed to provide the heat to drive the gasification reaction. Their summary reported that experiments were performed over a temperature range of 723 K to 1123 K using steam as the fluidized agent. No indication of the size of the reactor was given. Their results showed that the produced gas yield increased with an increase in temperature and varied from 30 to 85 wt. % gas yield from the organic waste over the temperature range studied. The composition of the raw gas showed that H_2 increased steadily as temperature increasd over the temperature range studied and ranged from 4% to 35%. The composition of CO decreased from 16% at 723 K to 12% at 1123 K. Methane passed through a maximum and ranged from 5% to 16%. Ethane and propane also passed through maxima and ranged from 2% to 6%, and from 2% to 13% respectively. Carbon dioxide made up the balance of the produced gas and varied from 20% to 40%. The produced gas heating value also passed through a maximum over the temperature range studied because of the behavior of the hydrocarbons. It varied from 19 MJ/m^3 at 723 K and 1123 K to a maximum of 27 MJ/m^3 at 993 K. The weight percent yields of char and tar were also presented. The char yield decreased with an increase in temperature from 60% at 723 K and 6% at 1123 K. The tar yield basically decreased with an increase in temperature

and ranged from 12.5% at 773 K to 2% at 1123 K. The tar yield did rise over the first 50 K of the temperature range studied and was 11% at 723 K.

Hasegawa (1979), also from the Tsukishima Kikai Company later reported the experimental results of gasification experiments utilizing three difference sized reactors. The first was a 0.5 m I.D. single fluidized bed reactor which used alumina particles as the solid media, and was fluidized with superheated steam. Municipal solid waste was used as the feed and the gas yield increased with temperature and ranged from 0.09 m^3/kg at 723 K to 0.8 m^3/kg at 1073 K. The second reactor was a 1.0 m I.D. dual fluidized bed reactor with circulating sand. The gas yield from this pilot plant was higher than was obtained from the single fluidized bed operated at the same temperature. Using municipal solid waste as the feed, the gas yield increased with temperature and ranged from 0.3 m^3/kg at 823 K to 0.7 m^3/kg at 973 K. The heating value of the produced gas ranged from 14.6 to 18.0 MJ/m^3. Results from a 2.0 m I.D. demonstration plant which was a scale up of the dual fluidized bed were also reported. Here the feed masterials used were organic sludge from a pulp and paper plants, waste plastic, municipal solid waste and scrap tires. With municipal solid waste at 973 K, the gas yield from the demonstration plant was 1.3 m^3/kg and the heating value was 16.5 MJ/m^3. The volumetric composition of the major gases were: H_2, 18.5%; CO, 34.6%; CO_2, 17.0%; CH_4, 13.4%; and C_2H_4, 5.6%. The energy recovery was 67% and the carbon conversion was 63%.

At Arizona State University, Kuester (1979) gasified cellulosic wastes in a dual fluidized bed reactor with a capacity of 11 kg/hr. His reactor was similar to the one reported by the Tsukishima Kikai Company. The bed, made up of inert solids, was fluidized with recycled product gas. Kuester studied the gasification of several feedstocks including paper

chips, kelp residue and guayule bagasse over a temperature range of 873 K to 1073 K. He found gas yields as high as 95% weight of the feed. The produced gas had a heating value of 18.6 MJ/m^3, and a volume composition of H_2, 17-33%; C_2H_4, 5-10%; CO, 40-55%; CH_4 13-17%; C_2H_6 1-2%; and CO_2, 3-8%. The produced gas was subsequently converted to liquid fuels via the Fischer-Tropsch synthesis.

The Environmental Resources Company (ERCO) (Howard et al., 1979) has also been interested in gasifying biomass in a fluidized bed reactor. The feed materials tested included paper, sawdust, corncobs, municipal solid waste, wood chips and manure. They operated their 0.5 m I.D. pilot plant under a variety of experimental conditions including steam gasification, partial oxidation, combustion, and steam partial oxidation. They studied the effects of reactor temperature, fluidization velocity, feed rate, static bed height and feed particle size on reactor performance. They concluded that temperature had the predominant effect on the various product yields, and that the other variables did not show appreciable affect on the products. The reactor temperature range studied was 873 K to 1273 K. They found that gas yield increased with temperature and ranged from 0.05 kg of product per kg of wet, ash-free feed at 873 K to 0.7 kg of product per kg of wet, ash-free feed at 1273 K for all materials under pyrolysis conditions.

Howard et al. (1979) also developed a model to predict the yield of liquid (tar and oil) as a function of temperature during the gasification of various biomass materials. They assumed first order reaction kinetics for the reactions involved but did not take into account the hydrodynamics associated with a fluid-bed reactor. Their model predicted the general trends observed but there was considerable scatter in their experimental data.

Groves et al. (1979) at Texas A&M University studied the fluid-bed gasification of cotton gin trash in two different reactors. Both of the shallow sand bed reactors used were fluidized with air. The smaller, 0.05 m I.D., reactor generated off-gas having a heating value of 4.5 to 8.2 MJ/m^3 when the bed operating temperature was between 922 K and 1144 K. They found that the heating value of the off-gas from the larger, 0.3 m I.D., reactor was generally lower than in the smaller reactor when operated under similar conditions. It ranged from 3.4 to 4.3 MJ/m^3. They also found that the energy recovery ranged from 30% to 65% in the small reactor and from 27% to 53% in the larger one. At the preferred operating condition (a reactor temperature of between 1033 K and 1144 K) the off-gas yield was 1.1 m^3/kg in the small reactor and 1.7 m^3/kg in the larger one. They concluded that the gas composition was similar in both reactors. They also found little tar formation in both reactors. In the larger reactor at a reactor temperature of 1036 K there was only 0.002 gm tar per gm of feed.

In Belgium, Schoeters et al. (1981) investigated the gasification of wood shavings in a 0.15 m I.D. fluidized bed reactor. Their bench-scale reactor had a bed of sand and was fluidized with either air or a mixture of steam and air. They studied the effects of air factor, steam rate and reactor freeboard temperature on the gasifier's performance. Air factor was defined as the ratio of actual flow rate of air to the flow rate of air required for complete stoichiometric combustion of the feed. They found that at a reactor bed temperature of 1073 K, the off-gas yield varied from 2.5 to 3.0 kg gas per kg fuel. The higher heating value of the off-gas ranged from 4 to 5 MJ/m^3, and the energy recovery was about 60%. They found that the gas composition varied with freeboard temperature (which ranged from 25 K above the reactor bed temperature to 150 K below the

reactor bed temperature). Both CO_2 and H_2 concentrations increased with an increase in freeboard temperature.

At Kansas State University researchers have extensively studied the gasification of carbonaceous materials in fluidized bed reactors. Walawender et al. (1978) reported preliminary results on the gasification of feedlot manure in a 0.23 m I.D. fluid-bed reactor similar to Burton's at West Virginia University. The sand filled bed was fluidized with a mixture of steam and flue gas. They found that the produced gas yield ranged from 0.34 to 0.8 m^3/kg over a temperature range of 1000 K to 1100 K. The heating value ranged from 9 to 16 MJ/m^3 and the energy recovery from 18% to 62%. Raman et al. (1980a) reported on the gasification of feedlot manure in the same reactor using similar procedures over a temperature range of 900 K to 994 K. They found that the produced gas yield increased with temperature from 0.4 m^3/kg at 900 K to 0.63 m^3/kg at 994 K. These produced gas yields are larger than the ones previously reported because of the addition of limestone chips to the feed which eliminated bed agglomeration (Walawender et al., 1981). The produced gas heating value increased with an increase in temperature and ranged from 12.5 MJ/m^3 at 900 K to 22 MJ/m^3 at 994 K. The energy recovery increased with temperature and ranged from 20% to 58% over the temperature ranged studied. The carbon conversion also increased with temperature and varied from 34% at 900 K to 50% at 994 K.

The researchers at Kansas State University expanded their study of the gasification of manure in a fluid-bed reactor to include the study of the effects of superficial gas velocity and feed size fraction at different operating temperatures. Raman et al. (1980b), using the same reactor, found that superficial velocity did not appear to have a significant

influence on the gas yield, composition or heating value of the produced gas. They did find that size fraction of the feed influenced the produced gas. The produced gas yield increased with an increase in temperature and a decrease in the feed size. The produced gas yield of the smallest feed size studied (-14 + 40 mesh) ranged from 0.05 m^3/kg at 800 K to 0.85 m^3/kg at 1025 K. For the largest feed size fraction (-2 + 8 mesh), the yield ranged from 0.1 m^3/kg at 900 K to 0.6 m^3/kg at 1010 K. The heating value of the produced gas was also influenced by the feed size fraction. All of the heating value-temperature plots were parabolic in shape with the maximum shifting to the right for an increase in feed size fraction. The heating value of the largest feed size fraction ranged from 12.0 to 19.75 MJ/m^3 with a maximum at 980 K. The heating value of the smallest feed size fraction varied from 10.4 to 18.2 MJ/m^3 with the maximum at about 910 K. The gas composition of the produced gas was also influenced by feed size fraction, but the composition did show similar trends for the different sizes.

Walawender et al. (1980) reported on the gasification of other feed materials in the same fluidized bed reactor. They studied the gasification of cane, manure, sewage sludge and rubber tires over a temperature range of 800 K to 1060 K. They found that the heating value and the produced gas yield were related to both temperature and feed material. The heating value ranged from 11.2 to 39.1 MJ/m^3, and the produced gas yield ranged from 0.12 to 1.25 m^3/kg. They found an apparent correlation between cellulose content and gas yield.

The same group has also studied the gasification of corn stover (Raman et al., 1980c) and wheat straw (Walawender et al., 1982). They found that over a reactor temperature range of 825 K to 1030 K in a 0.23 m I.D.

fluid-bed reactor, corn stover gave a higher volumetric gas yield than wheat straw, but it gave a lower heating value. Energy recovery and carbon conversion ratios were about the same for both materials. For corn stover, the gas yield ranged from 0.38 m^3/kg at 830 K to 0.82 m^3/kg at 1020 K. The higher heating value was parabolic with respect to temperature and varied from 13.0 MJ/m^3 to a maximum of 16.5 MJ/m^3 at 930 K. For wheat straw, the gas yield ranged from 0.24 m^3/kg at 825 K to 0.73 m^3/kg at 1030 K. The produced gas heating value was parabolic with respect to temperature, and ranged from 12.5 MJ/m^3 to a maximum of 16.3 MJ/m^3 at 945 K. The energy recovery for both feeds increased with an increase in temperature and ranged from about 30% to 70%. The carbon conversion also increased with an increase in temperature and ranged from about 30% to 65% over the temperature range studied.

Raman et al. (1981) have also developed a model to describe fluid-bed gasification of manure to estimate the yield of gas, liquid and solid as well as the gas composition. They found that the model did a reasonable job of predicing experimental results.

Another type of agricultural waste that has created serious problems is grain dust. Grain dust is an undesirable byproduct of grain handling. One method of utilizing this waste could be by gasifying it. From a review of the literature it appears that no work has been conducted on the gasification of grain dust in a fluidized bed reactor. Chiotti et al. (1977) conducted some low temperature pyrolysis of corn grain dust in the presence of oxygen. For their experimental study, they used an Ainsworth Thermogravimetric apparatus over a temperature range of 373 K to 498 K and a time range of 1.75 hr to 72 hr. They found that the primary weight loss of the grain dust, below 473 K, was due to water evaporation. They

also found that at 493 K corn dust exhibits an increasing weight-loss ratio. The primary gases evolved other than water vapor were CO_2, CO and H_2.

During the study of the gasification of biomass several investigators have noted an apparent correlation between the gas yield and the cellulose content of the feed. Walawender et al. (1980), in their gasification of cane, manure and sewage sludge, qualitatively found that the higher the cellulose content of the feed the higher the gas yield. They suggested that materials containing a higher fraction of cellulose were easier to gasify. Raman et al. (1980b), in their study of the gasification of different feed size fractions of manure, found that the different feed size fraction produced different gas yields. They suggested that this difference could be attributed to the difference in the cellulose content of the different feed size fractions.

Raman et al. (1980b) also stated that Antal et al. (1978) studies on thermal degradation of biomass also showed an apparent correlation between cellulose content of the feed material and the extent of devolatilization. They found that pure cellulose devolatilized 90% when exposed to high heating rates. Paper devolatilized 85% when exposed to the same conditions. Cherry (hardwood), which contained between 62% and 54% cellulose devolatilized about 80%. Southern yellow pine (softwood), which contained 53% cellulose devolatilized only about 70%. Manure devolatilized the least at 60%.

Beck et al. (1980) found significantly different gas yield in their study of the gasification of cow manure and sawdust in a fluidized bed reactor. They claimed that this difference was due to the difference in composition of the manure and sawdust. According to their paper, fiber (cellulose, hemicellulose and lignin) decomposed more easily than protein

and fat. Sawdust contains 100% fiber whereas manure from green roughage feeding cattle contains 25% protein and fat, and 75% fiber. Also, sawdust contains more cellulose and less lignin than manure and it has been shown that cellulose gasifies faster than lignin.

From the observation that cellulose content of the feed material and gas yield seem to be correlated, it is apparent that the study of the thermal degradation of pure cellulose is an important aid in the understanding of the gasification of all cellulosic materials in a fluidized bed reactor. The pyrolysis chemistry of cellulosic material has been reviewed by others and will not be presented here (see Shafizadeh, 1968 or Maa et al., 1973). It is important to note that alpha (α) cellulose is an organic polymer formed from D-glucose building blocks and is derived from cotton. Alpha cellulose has a molecular formula of $(C_6H_{10}O_5)_n$ and a molecular weight between 250,000 and 1,000,000. Its structural formula is shown in Figure 1.

Antal et al. (1978) have studied the thermal degradation of cellulose and other cellulosic materials in a Dupont 951 Thermal Gravimetric Analyzer and residence times, in atmospheres of steam and nitrogen. They reported that the gasification of cellulose takes place in three stages. The first step is the devolatilization of the cellulose to produce volatiles and char. This step starts at a temperature of about 573 K and is complete at about 723 K. Cellulose looses about 90% of its weight during this step. The second step is the cracking and reforming of the volatile matter formed in the first step. These secondary reactions occur at temperatures greater than 873 K and the synthesis gas produced is rich in hydrocarbons. The third step occurs at temperature greater than 1073 K.

Antal et al. (1978) and Antal (1979) have also studied the secondary reactions of the volatile matter derived from cellulose pyrolysis using a quartz, plug flow reactor. Their experiments studied the effect of temperature and residence time on the products and rates of secondary gas phase reactions of the volatile matter. They found that for cellulose under steam gasification conditions, that the reaction temperature was the most significant factor in the gasification results, and that the gas phase residence time played a less important role. They found that at temperatures of about 923 K, the gas formation was complete in less than 0.5 sec. For the temperature range studied (773 K to 1023 K) the yield of gases and the carbon conversion ratio of the gas increased with an increase in temperature. At 1023 K the carbon conversion ratio was about 80%. The energy recovery was about 83% and the tar yield produced was 2% of the initial feedstock weight.

A review of the literature has shown that there are several groups studying the gasification of biomass in a fluid-bed reactor. In general, they have found that the reactor temperature has the major effect on the gasification process. Results show that as the reactor temperature increases, the gas yield increases. Many have found an apparent correlation between the gas yield and the cellulose content of the feed; as the cellulose content of the feed increases, they gas yield increases during gasification. Work is continuing to systematically develop a data base to properly design a system to gasify biomass in a fluid-bed reactor on a commercial level. Part of this work is reported in this thesis.

REFERENCES CITED

Antal, M. J., W. E. Edwards, H. L. Friedman and F. E. Rogers, "A Study of the Steam Gasification of Organic Wastes," Project Report to EPA, W. W. Liberick, Project Officer (1978).

Antal, M. J., "The Effects of Residence Time, Temperature and Pressure on the Steam Gasification of Biomass," presented at Symposium on Biomass as a Nonfossil Fuel Source, Division of Fuel Chemistry, American Chemical Society Meeting, Honolulu, April 1-6 (1979).

Beck, S. R., W. J. Huffman, B. L. Landeene, and J. E. Halligan, "Pilot Plant Results for Partial Oxidation of Cattle Feedlot Manure," Ind. Eng. Chem. Process Des. Dev., 18 (2), 328-332 (1979).

Beck, S. R. and M. J. Wang, "Wood Gasification in a Fluidized Bed," Ind. Eng. Chem. Process Des. Dev., 19 (2), 312-317 (1980).

Burton, R. S , "Fluid Bed Gasification of Solid Waste Materials," M.S. Thesis, West Virginia Univ. (1972).

Chiotti, P. and V. Morris, "Low Temperature Pyrolysis of Grain Dust," presented at Grain Dust Explosions International Symoposium hosted by Grain Elevator and Processing Society, Kansas City, MO, October 4-6 (1977).

Groves, J., R. G. Anthony, and W. A. Lepori, "Shallow Fluidized Bed Gasification of Cotton Gin Wastes," presented at the Winter Meeting of ASAE, New Orleans, December 13 (1979).

Halligan, J. E., K. L. Herzog, and H. W. Parker, "Synthesis Gas from Bovine Wastes," Ind. Eng. Chem. Process Des. Develop., 14 (1), 64-69 (1975).

Hasegawa, M., J. Fukuda and D. Kunii, "Gasification of Solid Waste in a Fluidized Bed Reactor with Circulating Sand," Conservation and Recycling, 3, 143-153 (1979).

Howard, J. B., R. H. Stephens, H. Kosstrui, S. M. Ahmed, "Pilot Scale Conversion of Mixed Waste to Fuel, Volume I," Project Report to EPA, W. W Liberick, Project Officer (1979).

Huffman, W. J., C. Lin, S. R. Beck and J. E. Halligan, "Kinetic Analysis of Manure Pyrolyzers," presented at SERI Technical Seminar-Thermchemical Conversion of Biomass Residues, Golden, CO, Nov. 30 - Dec. 31 (1977).

Itoh, K., "Municipal Refuse Pyrolysis with Two Circulating Fluidized Beds," Kankyo Sozo, 6, 42-46 (1974). As reviewed by T. Y. Chen, E. Kojima, W. P. Walawender, and L. T. Fan. "A Review of Waste Gasification Technology as Developed in Japan," System Institute Report 68, Kansas State Univ., Manhattan (1975).

Kuester, J. L., "Conversion of Cellulosic Wastes to Liquid Fuels," presented at Engineering Foundation Conference on Municipal Waste as a Resource - The Problems and the Promise, Henniker, N.H., July 22-27 (1979).

Maa, P. S. and R. C. Bailie, "Influence of Particle Sizes and Environmental Conditions on High Temperature Pyrolysis of Cellulosic Materials - I (Theoretical)," Comb Sc. Tech., 6, 1-13 (1973).

Maa, P. S. and R. C. Bailie, "Experimental Pyrolysis of Cellulosic Material," presented at the AIChE 84th National Meeting, Atlanta, GA (1978).

Raman, K. P., W. P. Walawender, and L. T. Fan, "Gasification of Feedlot Manure in a Fluidized Bed Reactor. The Effect of Temperature," Ind. Eng. Chem. Process Des. Develop., 19 (4), 623-629 (1980a).

Raman, K. P., W. P. Walawender, and L. T. Fan, "Gasification of Feedlot Manure in a Fluidized Bed: The Effects of Superficial Gas Velocity and Feed Size Fraction" Preprints, ACS Div. Fuel Chem 25 (4), 233-244 (1980b).

Raman, K. P. W. P. Walawender, Y. Shimizu, and L. T. Fan, "Gasification of Corn Stover in a Fluidized Bed," in Agricultural Energy, Vol. 2, Biomass Energy Crop Production, ASAE, 335-337 (1980c).

Raman, K. P., W. P. Walawender, L. T. Fan and C. C. Chang, "Mathematical Model for the Fluid-Bed Gasification of Biomass Materials. Application to Feedlot Manure," Ind. Eng. Chem. Process Des. Dev., 20 (4), 686-692 (1981).

Reed, T. B. and D. E. Jantzen, "Generator Gas - The Swedish Experience from 1939 - 1945," transalated from the work of the Swedish Academy of Engineering, SERI/SP-33-40 (1979).

Schoeters, J., K. Maniatis, and A. Buekens, "Fuel Gas from Agricultural Residues in a Fluidised Bed Reactor," in Proceeding 2nd World Congress of Chemical Engineering, 1, 313-317 (1981).

Shafizadeh, F., Advances in Carbohydrate Chemistry, 23, eds. M. L. Wolfrom and R. S. Tipson, Academic Press (1968).

Tsukishima Kikai Co., "Municipal Refuse Pyrolysis Through Two-bed-circulation Fluidized Beds," Kankyo Sozo, 61-67, 6 (1974). As Reviewed by T. Y. Chen, E. Kojima, W. P. Walawender, and L. T. Fan, "A review of Waste Gasification Technology as Developed in Japan," System Institute Report 68, Kansas State Univ., Manhattan (1975).

Walawender, W. P. and L. T. Fan, "Gasification of Dried Feedlot Manure in a Fluidized Bed - Preliminary Pilot Plant Tests," presented at the 84th National Meeting of AIChE, Atlanta, Feb, 27 (1978).

Walawender, W. P., K. P. Raman and L. T. Fan, "Gasification of Carbonaceous Materials in a Fluidized Bed Reactor," in Proceedings of Bio-Energy '80 World Congress and Exposition (Washington, D. C.: The Bio-Energy Council), 575-577 (1980).

Walawender, W. P., S. Ganesan and L. T. Fan, "Steam Gasification of Manure in a Fluid Bed: Influence of Limestone as a Bed Additive," in Symposium Papers Energy from Biomass and Wastes V (Chicago, IL: Institute of Gas Technology), 517-528 (1981).

Walawender, W. P., D. A. Hoveland, D. Arfiwidsson, and L. T. Fan, "Steam Gasification of Wheat Straw in a Fluidized Bed," presented at Industrial Wood Energy Forum '82, Washington, D. C., March 8-10 (1982).

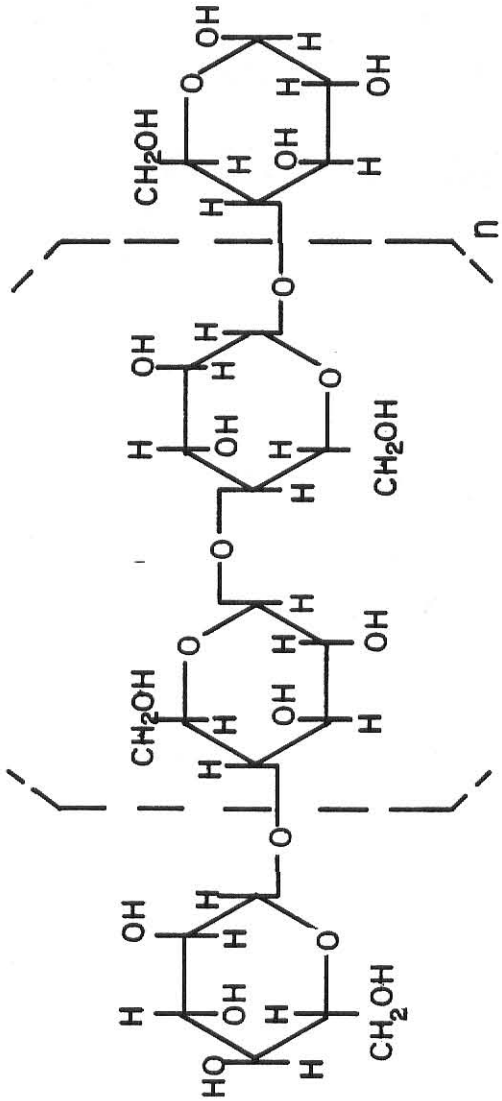

Figure 1. Molecular structure of alpha cellulose.

CHAPTER III

STEAM GASIFICATION OF GRAIN DUST IN A FLUIDIZED BED REACTOR

INTRODUCTION

A need for alternate energy sources is rapidly emerging. Wastes from the processing of agricultural products represent an ideal source of renewable energy because these materials are concentrated at the processing site. Grain dust is one such waste product that has a potential for conversion to a fuel. Possible conversion schemes for grain dust include direct combustion, anaerobic digestion, pyrolysis (gasification), liquefaction and hydrolysis for fermentation to ethyl alcohol. This work is concerned with the steam gasification of grain dust in a fluidized bed reactor.

Grain dust is an undesirable byproduct of grain handling. In the United States, where about 10 billion bushels of grain are handled each year, the dust is collected by dust control equipment to alleviate the potential of explosions and to provide a clean working environment. Assuming that the grain is handled only once and that it generates on the average 0.05% (by weight) dust, the total amount of dust potentially available is 1.4×10^8 kg per year (1.5×10^5 tons per year). The dust is distributed among several thousand elevators of various sizes. A large elevator, one handling 400 millions bushels of grain per year, generates 5.4×10^6 kg of dust per year (6,000 tons per year).

Gasification is the process by which organic matter is converted to gas through thermal decomposition in an oxygen deficient environment, followed by secondary reactions of the resulting volatiles. The process also produces combustible char and tar which can be burned with air to provide the necessary energy for processing. Studies on the fluid-bed gasification of agricultural wastes have been limited in the past but data is beginning to grow rapidly. Bailie and Burton (Burton, 1972) were the first in this

country to study the fluid-bed gasification of agricultural wastes. Burton's master thesis reports the gasification of many different kinds of solid wastes including sawmill wood, chicken manure and cow manure. They used a 38 cm (I.D.) pilot plant to study the effect of temperature on composition, heating value and yield. Halligan et al. (1975) investigated the gasification of feedlot manure in a 5 cm (I.D.) fluidized-bed reactor. Their bench-scale reactor was operated under partial oxidation conditions to study the effects of temperature on gasification. Howard et al. (1979) studied the pyrolysis of a wide range of wastes including manure and corncobs in a 50 cm (I.D.) fluid-bed reactor. They studied the effects of temperature, fluidization velocity, feedrate of pyrolyzable material, bed height (static) and particle size on the final products of pyrolysis. Kuester (1979) developed a fluid-bed system which has been used to gasify bagasse and other materials. The gas produced from his complete pilot plant facility is subsequently converted into liquid fuels via the Fischer-Tropsch synthesis. Le Pori et al. (1979) used a pilot scale, shallow fluidized bed reactor to gasify cotton gin trash. Beck et al. (1979) conducted extensive studies with manure in a variable velocity fluid-bed reactor. Their 15 cm (I.D.) reactor evaluated the gasification of manure by partial oxidation. Walawender and Fan (1978) conducted preliminary pilot plant tests to study the gasification of feedlot manure in a fluid-bed reactor. Walawender et al. (1980) presented gasification data for a variety of carbonaceous materials including cane and rubber in the same reactor. They also (Raman et al., 1980) studied the gasification of corn stover. These works examined the effects of temperature on the gas composition, heating value and yield of produced gas.

It appears that no work has been conducted on the gasification of grain dust. In this paper we consider the steam gasification of corn grain

dust in a fluidized bed. The produced gas composition, heating value, yield and energy recovery are examined as functions of the gasifier temperature.

EXPERIMENTAL FACILITIES AND PROCEDURE

Facilities

The bench-scale fluidized bed reactor used in this study is shown schematically in Figure 1. The reactor was constructed from a 5.08 cm (2 in.) I.D. by 50 cm length of schedule 40 Inconel 600 pipe, fitted on top with a 10.16 cm (4 in.) I.D. by 15 cm length pipe of the same material. The upper 15 cm of the reactor served as a disengaging zone. The lower 23 cm, which served as a gas distributor and gas preheater, was packed with aluminum oxide pellets (0.5 cm in diameter). The fluid-bed section was separated from the packed bed section by means of a 60 mesh (0.025 mm) 304 stainless steel screen. The bed material was composed of a 25% by weight limestone - 75% by weight silica sand mixture. The limestone was used to eliminate the bed agglomeration which typically occurs in a bed composed only of sand (Walawender et al., 1981). The limestone particle size was -7 + 50 mesh (2.82 mm - 0.297 mm); the sand particle size was -30 + 50 mesh (0.595 mm - 0.297 mm). The bed had a static height of 8.4 cm and an expanded height of about 11 cm.

The reactor was heated by means of four parts of semi-cylindrical electrical resistance heaters, each capable of delivering up to 2300 watts of power, at the maximum operating temperature of 1743 K. Voltage to each pair of heaters was controlled by a variable voltage autotransformer. The second pair of heaters from the bottom was also controlled by a thermostat connected to a thermocouple inside the reactor bed. Steam, the sole fluidizing gas, was generated externally in a series of two (600 and 800 watt) electrical furnaces and was supplied to the gas preheater section at apprxoimately 500 K. Heating tape was wrapped around the pipe leading

from the steam generator to the preheater to prevent the steam from cooling and condensing.

The feed was introduced into the reactor by gravity flow through a vertical feedpipe which discharged 6.6 cm above the static bed. A Vibra Screw (Model SCR-20) screw feeder with a solid core flight screw was used to supply the feedpipe at a uniform volumetric rate. A purge flow of helium was used to aid flow through the feedpipe and to prevent backflow through the feedpipe and subsequent condensation of vapor in the feedpipe and feeder.

The product gases from the reactor were sent to a cyclone where entrained fines were separated from the gas. The temperature in the cyclone was maintained at about 600 K to prevent condensation of tar. This was accomplished with a heating tape wrapped around the cyclone. The gaseous stream leaving the cyclone was cooled to approximately 300 K with two water-cooled heat exchangers in series. This resulted in the condensation of the fluidizing steam, which was collected in a receiver. The resultant product gas carried with it a fine mist of condensables, which were removed by passing the gas through a packed bed of glass wool to remove tars and a column packed with Drierite ($CaSO_4$) to remove residual moisture. A known volumetric flow of nitrogen was introduced as a tracer gas just up stream of the drying column. The product gas could bypass the column packed with Drierite and vent to a hood, or a portion could go through the drying column to a gas sample bottle for analysis.

The temperature in the fluidized bed was monitored by a thermocouple placed inside the bed. The temperature in the disengaging zone was monitored by using a sliding (91 cm long) thermocouple, which measured temperatures from the bottom of the fluidized bed to the top of the dis-

engaging zone. Temperature was also monitored in the steam generators, cylcone, heat exchanger outlet, reactor inlet and the two heating tapes. A pressure probe, connected to a water manometer, was used to monitor the bed pressure and as a check on the quality of fluidization. A second pressure probe on the feedpipe was connected to a water manometer and was used to monitor the reactor pressure.

Feedstock

The feedstock was corn grain dust treated with oil (0.025% by weight) obtained from the U.S. Grain Marketing Research Laboratory, Manhattan, KS. As a convenience for introducing the feed into the bed, the grain dust was pelletized without binders and subsequently ground and sieved prior to introduction to the reactor. The size fraction used was -14 + 40 mesh (1.41 mm - 0.42 mm). The grain dust contained a 10.8% (by weight) moisture. The ultimate analysis of the feed (in weight %) on a dry basis was as follows: C, 39.2; H_2, 5.7; N_2, 1.0; O_2, 42.9; ash, 11.2. The heating value on a dry ash-free basis, estimated using the Dulong formula, was found to be 15.4 MJ/kg. Pelletizing had no influence on the elemental composition of the dust.

Procedure

For start-up of the experimental system, the reactor heaters, steam generators, cyclone and inlet heating tapes were turned on. Initially, air was used as the fluidized agent and as the feedpipe purge gas. During the heat-up period, the steam generators, cyclone heater and inlet section heater were brought to their operating temperatures of 670 K, 920 K, 750 K and 700 K, respectively. When the effluent from the steam generators reached about 800 K, the air flow was replaced by steam. The volumetric flow rate of the steam required to maintain the selected fluidization

velocity was measured both by collecting condensate downstream of the heat exchangers and by metering the water flow into the steam generators.

When the reactor temperature stabilized at the selected operating temperature, the air purge was replaced with helium. For this study the same temperature was maintained in the bed and through the disengaging zone. About one half hour after the helium purge was started, feeding and nitrogen tracer were initiated. The nitrogen tracer was introduced just upstream of the drying column at a known rate which averaged about 60% of the flow rate of the dry produced gas. The total start-up time was about two hours from a cold start.

Any change in the temperature of the reactor due to feeding the dust was corrected automatically by the thermostat. A gas sample was taken 15 minutes after feeding began and a second sample was taken after 25 minutes. The condensate and nitrogen rates were measured over ten minute time intervals as the gas samples were being taken. After all of the pertinent data were taken, feeding of the dust was terminated and the reactor temperature was elevated for another run. Feeding was started after the temperatures in the bed and disengaging zone had stabilized. This procedure was repeated for each run in a set of experiments.

The feed rate was evaluated by disconnecting the lower section of the feed pipe and weighing the effluent collected for 10 minute time intervals at a given setting on the feeder. The feed rate was evaluated several times before and after each set of experiments.

It was not possible to measure the total char produced in an experiment because of the hold-up of chair in the bed. Nor was it possible to measure the total tar produced because of hold-up on the inside of the water cooled heat exchangers.

Chemical Analysis

The chemical analysis included the ultimate analysis of the feed as well as the quantitative analysis of the product gas. Ultimate analysis was performed with the aid of a Perkin-Elmer Model 240 B Elemental Analyzer. Ash analyses were performed on the feed material according to the standard ASTM procedure in a muffle furnace and the moisture contents were determined by dring in an oven for ten hours at 423 K.

The product gas was analyzed by using a Packard Model 417 Becker dual column gas chromatograph equipped with thermal conductivity detectors. The gas components of interest included H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, O_2 and N_2. A 1.83 m x 0.0032 m (6' x 1/8") column with No. 5A molecular seive packing (-80 + 100 mesh) was used to separate and analyze H_2, O_2, N_2, CH_4 and CO. The remaining components were analyzed by using a 1.83 m x 0.0032 m (6' x 1/8") column with a -80 + 100 mesh Porapak Q packing preceded by a short lead section of Porapak R. The Porapak R was used to shift the retention time of the water peak so that it could be easily separated from the other components. The gas chromatograph was operated isothermally at 350 K with helium as the carrier gas.

Operating Conditions

The operating conditions for all the experimental runs are summarized in Table 1. The principal experimental variable was the operating temperature. The superficial velocity of the fluidizing gas corresponded to about two times the minimum fluidization velocity and 20% of the terminal velocity of the feed. It corresponded to about three times the minimum fluidization velocity of the bed material.

RESULTS AND DISCUSSION

Calculations and Analyses

From the GC analysis and the nitrogen tracer rate, the volumetric flow rate of the dry produced gas (nitrogen free) was calculated with the aid of a nitrogen balance. The small amount of nitrogen (less than 2% of the produced gas) resulting from the gasification of the feed can be neglected without serious error for the conditions of the experiment. The dry produced gas analysis (nitrogen-free basis) was used to compute the higher heating value of the dry produced gas using the standard heat of combustion for each component. The volumetric gas yield per unit mass of feed was calculated from the volume flow rate of the dry produced gas (at 288 K and 101.3 kPa) and the mass flow rate of the dry ash-free feed. Because of the hold-up of char and tar in the experimental system, it was not possible to conduct an overall material balance on the bench-scale reactor. Consequently, only the yield and properties of the dry produced gas are considered in this report.

Regression analysis was used to determine the relationship between the independent variable, reactor temperature, and the dependent variables: the produced gas compositions, the produced gas heating value, the produced gas yield and the energy recovery. An analysis of variance was also performed on the data to determine the significance of the regression model. The parameters determined by the regression analysis were accepted as being significant on the basis of the F-test at the 10% significance level.

The statistical analysis is summarized in Table 2. For each dependent variable, the number of data points used for the analysis (n), the square of the correlation coefficient (R^2), the F-test statistical value (F-value),

the probability of falsely rejecting the proposed regression model (α) and the significant regression model are tabulated.

Produced Gas Composition

The variations in the concentration of H_2, CO_2, and Co, the major components of the produced gas, as functions of temperature are shown in Figure 2. The mole percent concentration of CO_2 varied parabolically over the temperature range studied. The concentration ranged from 33.4% at 867 K to 31.9% at 1033 K with a minimum of 25.1% at 954 K. The concentration of CO decreased linearly over the temperature range studied, and ranged from 24.3% at 867 K to 11.8% at 1033 K. The concentration of H_2 increased linearly over the temperature range studied, and ranged from 41.3% at 867 K to 49.0% at 1033 K.

The variations in the concentrations of CH_4, C_2H_4 and C_2H_6, the minor components of the produced gas, as functions of temperature are shown in Figure 3. No relationship could be found between the mole percent concentration of C_2H_6 and temperature. However, the amount present was almost negligible. Its average value was 0.1% and it varied from 0.4% to 0.0%. The concentration of CH_4 and C_2H_4 increased linearly with an increase in temperature. The mole percent of CH_4 varied from 3.1% at 867 K to 5.7% at 1033 K. The mole percent of C_2H_4 ranged from 1.0% at 867 K to 3.6% at 1033 K.

The principle gas phase reaction in this system is the water-gas shift reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

In our experiments, water was present in large excess relative to the other components (about two orders of magnitude). Because of this, we

produce a gas that is rich in hydrogen. Equilibrium constants were evaluated from the concentration ratio for each experiment and compared with the theoretical equilibrium constant for each temperature studied. This comparison showed that our system is far removed from equilibrium with the concentration ratio being one to two orders of magnitude smaller than the theoretical equilibrium constant.

Produced Gas Heating Value

The variation in the produced gas heating values as a function of temperature is shown in Figure 4. From the analysis of variance, it was found that the produced gas heating value varied parabolically over the temperature range studied and ranged from 9.4 MJ/m^3 (251 BTU/SCF) at 867 K to 11.5 MJ/m^3 (308 BTU/SCF) at 1033 K with a maximum of 11.6 MJ/m^3 (311 BTU/SCF) at 1002 K. The overall effect of the concentrations of H_2, CH_4 and C_2H_4 increasing and the concentration of CO decreasing is a parabolic curve with a maximum value at about 1000 K.

Produced Gas Yield

The variation in the volumetric yield of the produced gas (on a dry ash-free basis) as a function of temperature is shown in Figure 5. The yield of dry produced gas was a linear function of temperature and ranged from 0.13 m^3/kg (2.0 SCF/lb) at 867 K to 0.73 m^3/kg (11.7 SCF/lb) at 1033 K.

Energy Recovery

The effectiveness of the gasification process can be examined by considering the ratio of the heating value of the produced gas per unit mass of feed, on a dry ash-free basis to the heat of combustion of a unit mass of feed, also on a dry ash-free basis. The ratio, termed the energy recovery, was computed by multiplying the significant regression models of

the gas yield by the gas heating value and dividing by the heating value of the feed. A plot of energy recovery versus temperature is presented in Figure 6.

The energy recovery increased from 8% at 867 K to 55% at 1033 K. The increase observed in the energy recovery is a direct consequent of the increase in the produced gas yield and the relatively constant produced gas heating value with respect to temperature.

If the produced gas were converted to electricity via direction combustion, it would provide about 36% of a grain elevator's electricity needs. This estimate is based on the assumption of a 50% energy recovery ratio for gasification, a 25% electricity generation efficiency, a 0.05% (by weight) generation of grain dust from the grain handled and an electricity need of 2 kilowatt-hour per 100 bushels of grain handled.

CONCLUSION

Steam gasification experiments were conducted with corn dust in a 5.08 cm fluidized bed reactor. The results indicated that the yield of product gas increased linearly with an increase in temperature of the reactor and ranged from 0.13 m^3/kg (2.0 SCF/lb) at 867 K to 0.73 m^3/kg (11.7 SCF/lb) at 1033 K. It was also found that the produced gas heating value ranged from 9.4 MJ/m^3 (251 BTU/SCF) at 867 K to 11.5 MJ/m^3 (308 BTU/SCF) at 1033 K, with a maximum of 11.6 MJ/m^3 (311 BTU/SCF) at 1002 K. The results also indicated that the concentrations of H_2, CH_4 and C_2H_4 increased linearly with an increase in the temperature over the temperature ranged studied. The concentration of H_2 ranged from 41.3% at 167 K to 49.0% at 1033 K; that of CH_4 ranged from 3.1% at 867 K to 5.7% at 1033 K; and that of C_2H_4 ranged from 1.0% at 867 K to 3.6% at 1033 K. The concentration of CO which decreased linearly as temperature was increased ranged from 24.3% at 867 K to 11.8% at 1033 K. The concentration of CO_2 ranged from 33.4% at 867 K to 31.9% at 1033 K, with a minimum of 25.1% at 954 K; that of C_2H_6 averaged 0.1% over the temperature range studied. The energy recovery ranged from 8% at 867 K to 55% at 1033 K. If the produced gas were converted to electricity it would provide about 36% of a grain elevator's needs.

REFERENCES CITED

Beck, S. R., W. J. Huffman, B. L. Landeene and J. E. Halligan, "Pilot Plant Results for Partial Oxidation of Cattle Feedlot Manure," Ind. Eng. Chem. Process Des. Dev., 18, 328 (1979).

Burton, R. S., Fluidized Bed Gasification of Solid Waste Materials, M.S. Report, West Virginia University (1972).

Halligan, J. E., K. L. Herzog and H. W. Parker, "Synthesis Gas from Bovine Wastes," Ind. Eng. Chem. Process Des. Dev., 14, 64 (1975).

Howard, J. B., R. H. Stephens, H. Kosstrin and S. M. Ahmed, "Pilot Scale Conversion of Mixed Wastes to Fuel," Volume I. Project Report to EPA, W. W. Libertick, Project Officer (1979).

Kuester, J. L., "Conversion of Cellulosic Wastes to Liquid Fuels," paper presented at Engineering Foundation Conference on Municipal Waste as a Resource - The Problems and the Promise, Henniker, NH, July 22- 27 (1979).

LePori, W. A., J. Groves, R. G. Anthony and J. D. Craig, "Shallow Fluidized Bed Gasification of Cotton Gin Wastes," paper presented at the Winter Meeting of ASAE, New Orleans, LA, Dec. 13 (1979).

Raman, K. P., W. P. Walawender, Y. Shimizu and L. T. Fan, "Gasification of Corn Stover in a Fluidized Bed," ASAE NATIONAL ENERGY SYMPOSIUM, Vol 2, 335-37 (1980).

Walawender, W. P. and L. T. Fan, "Gasification of Dried Feedlot Manure in a Fluidized Bed - Preliminary Pilot Plant Tests," a paper presented at the 84th National Meeting of AIChE, Atlanta, GA, Feb. 27 (1978).

Walawender, W. P., K. P. Raman and L. T. Fan, "Gasification of Carbonaceous Materials in a Fluidized Bed Reactor," in Proceedings of Bio-Energy '80 World Congress and Exposition (Washington, D. C.: The Bio Energy Council) 575-577 (1980).

Walawender, W. P., S. Ganesan and L. T. Fan, "Steam Gasification of Manure in a Fluid Bed: Influence of Limestone as a Bed Additive," in Symposium Papers Energy From Biomass and Wastes V (Chicago, IL: Institute of Gas Technology) 517-528 (1981).

Table 1. Reactor Operating Parameters

Reactor Temperature Range	867 K - 1033 K
Fluidizing Gas	Steam
Superficial Velocity	0.22 m/sec - 0.32 m/sec
Feed Rate	1.34 g/min - 1.96 g/min
Grain Dust Particle Size	1.41 mm - 0.420 mm (-14 + 40 mesh)
Bed Particle Size	
Sand	0.595 mm - 0.297 mm (-30 + 50 mesh)
Limestone	2.82 mm - 0.297 mm (-7 + 50 mesh)

Table 2. Statistical Analysis

Dependent Variable y	Sample Size n	The Square of The Correlation Coefficient R^2	F-value	Probability > F α	Significant Regression Model
Gas Yield*	8	0.918	66.88	0.0002	$y = -3.01 + 0.00362T$**
Heating value***	8	0.730	6.76	0.0379	$y = -112. + 0.247T - 0.00012T^2$
mole % H_2	8	0.464	5.21	0.0627	$y = 1.05 + 0.0464T$
mole % CO_2	8	0.655	4.75	0.0699	$y = 1020.5 - 2.08T + 0.00109T^2$
mole % CO	8	0.829	29.20	0.0017	$y = 89.7 - 0.0754T$
mole % CH_4	8	0.704	14.28	0.0092	$y = -10.3 + 0.0155T$
mole % C_2H_4	8	0.863	37.89	0.0008	$y = -12.3 + 0.0154T$
mole % C_2H_6	8	0.240	1.89	0.2180	--

* m^3/kg

** T is reactor temperature in Kelvin

*** MJ/m^3

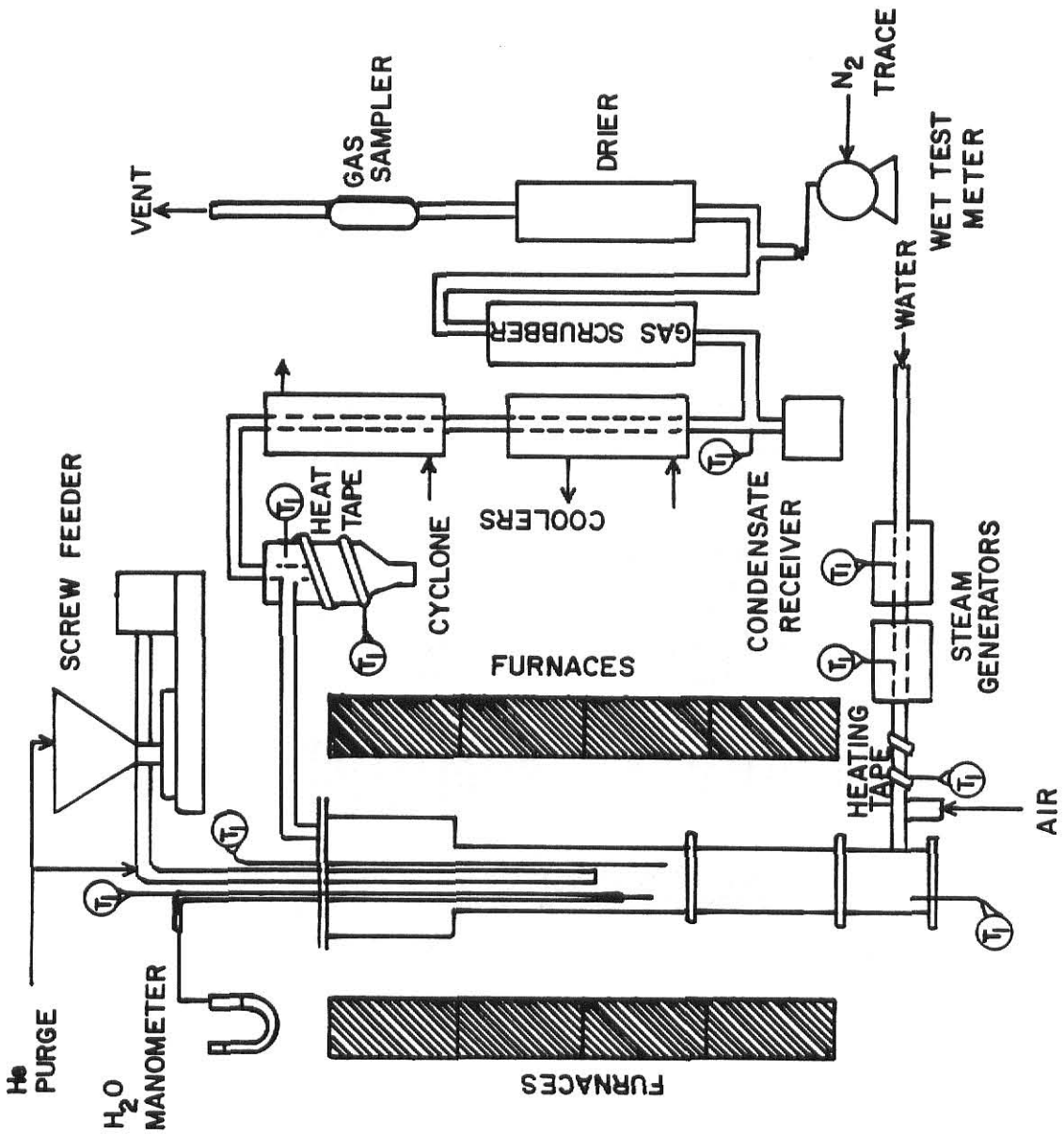

Figure 1. Bench-scale reactor.

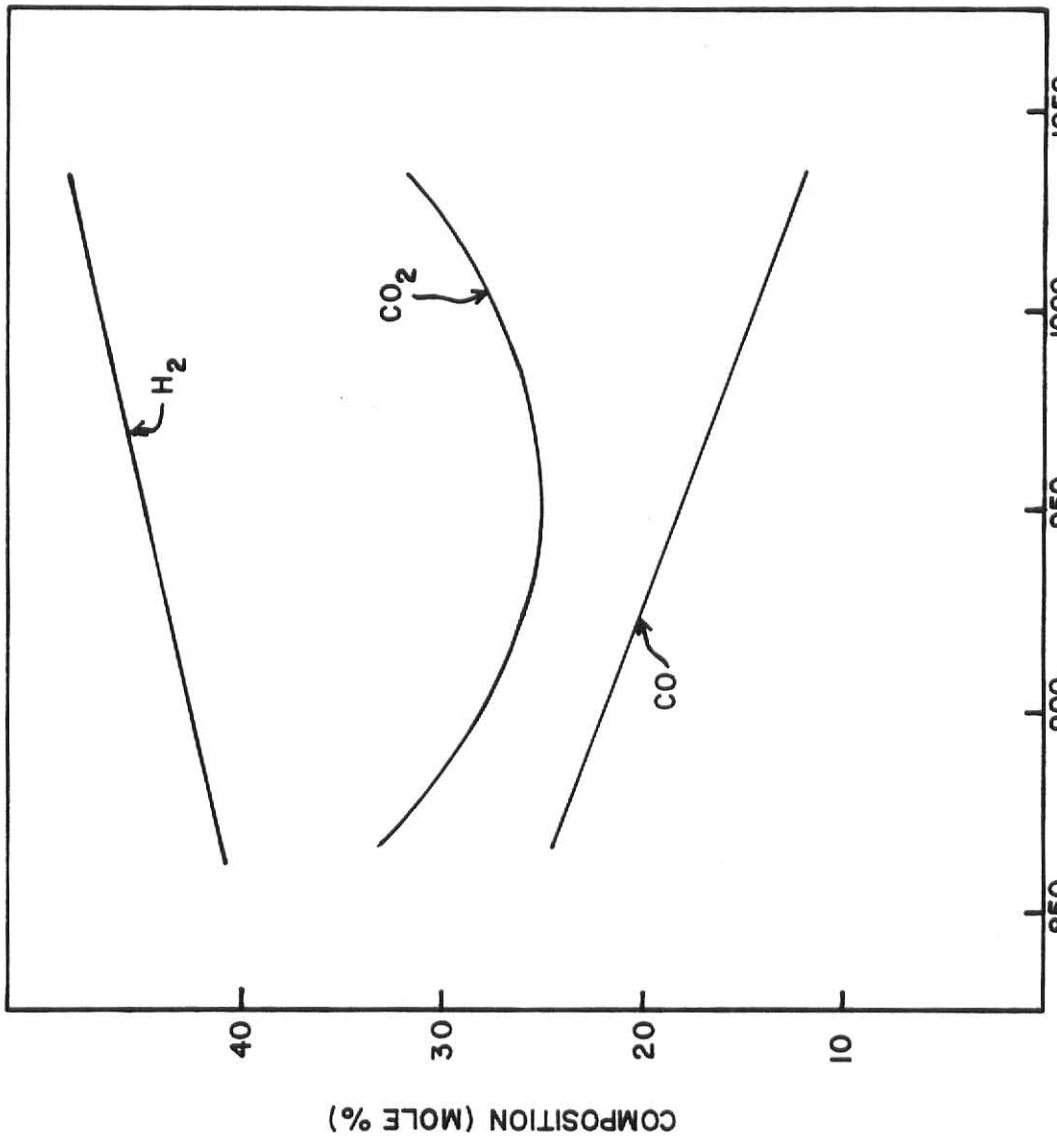

Figure 2. Gas composition versus temperature.

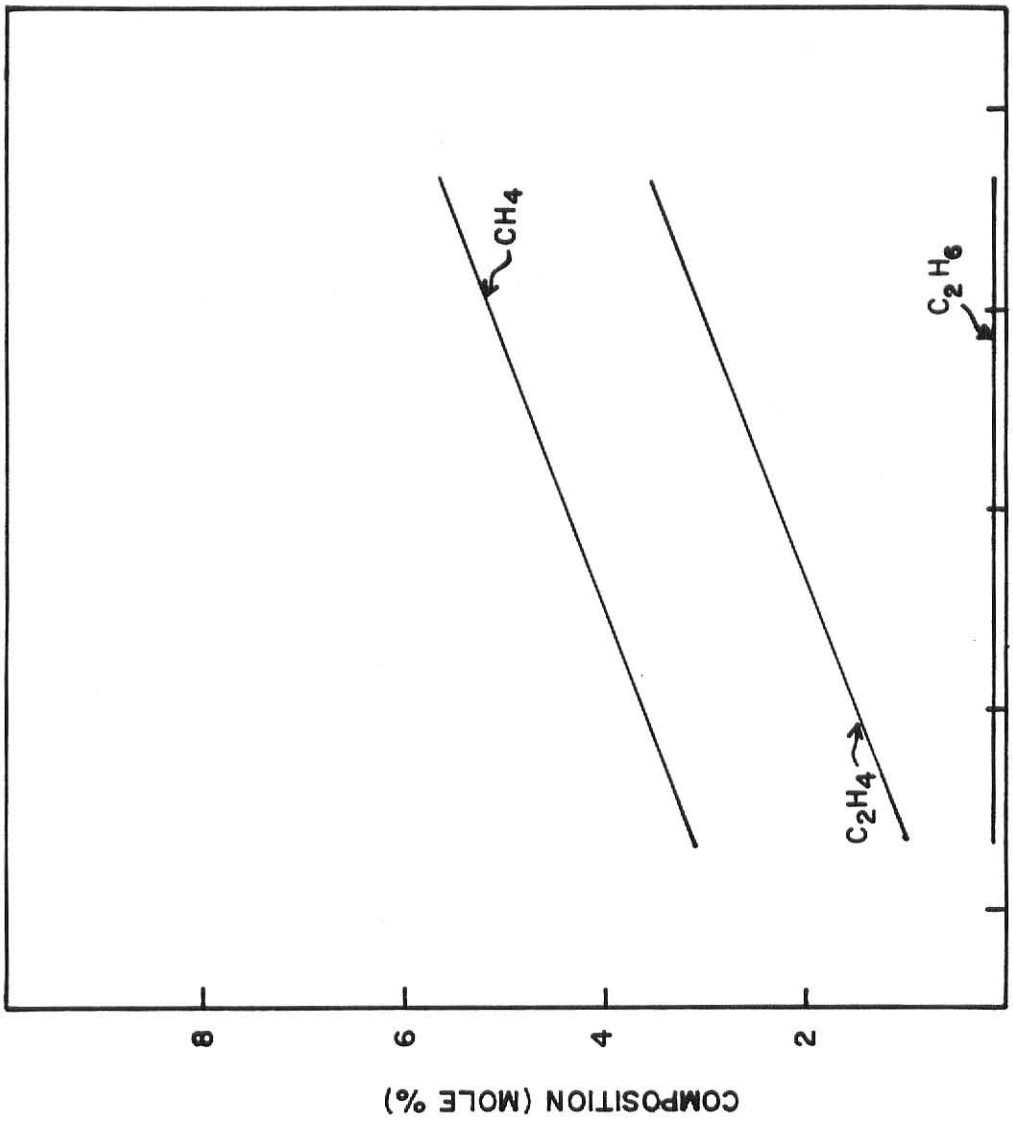

Figure 3. Gas composition versus temperature.

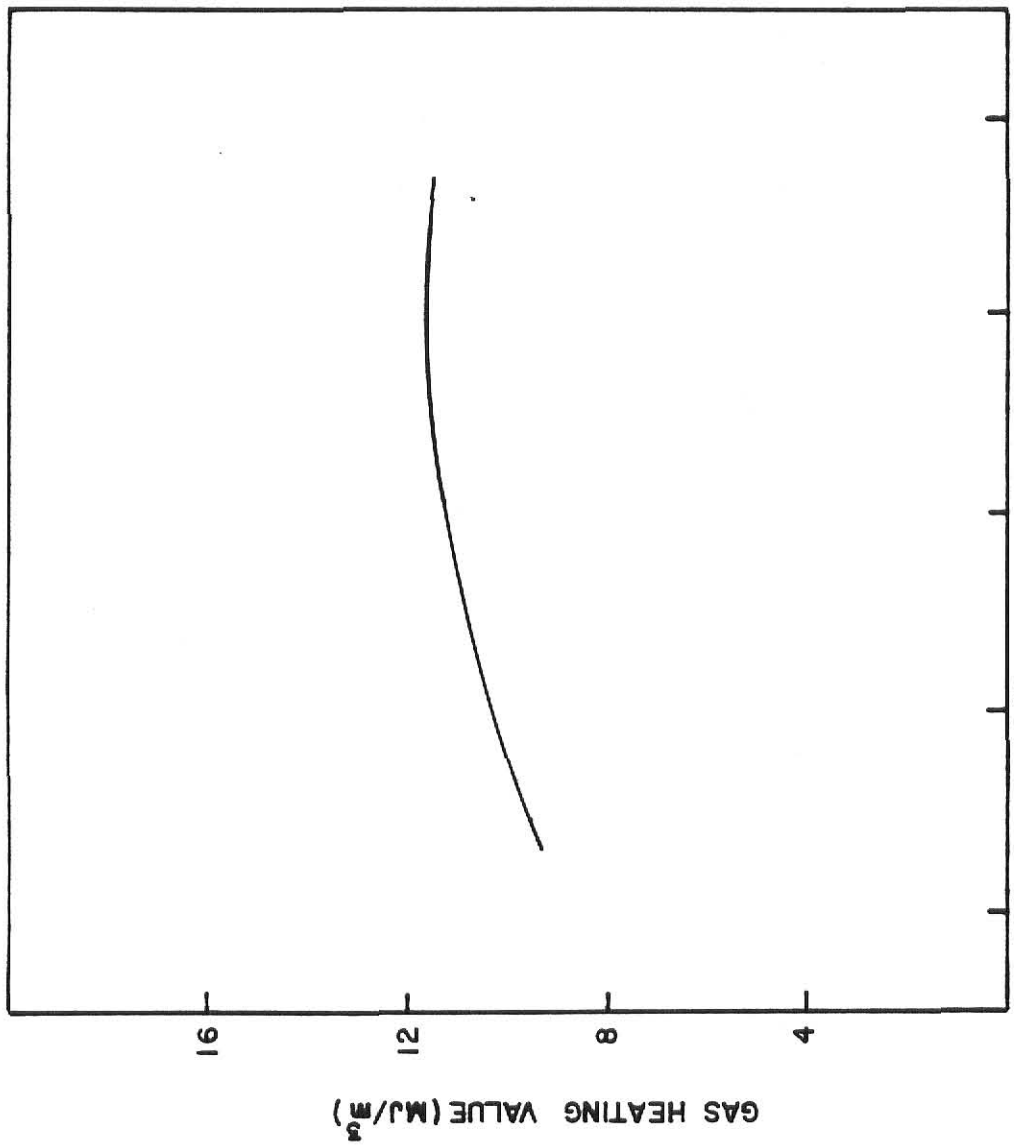

Figure 4. Gas heating value versus temperature.

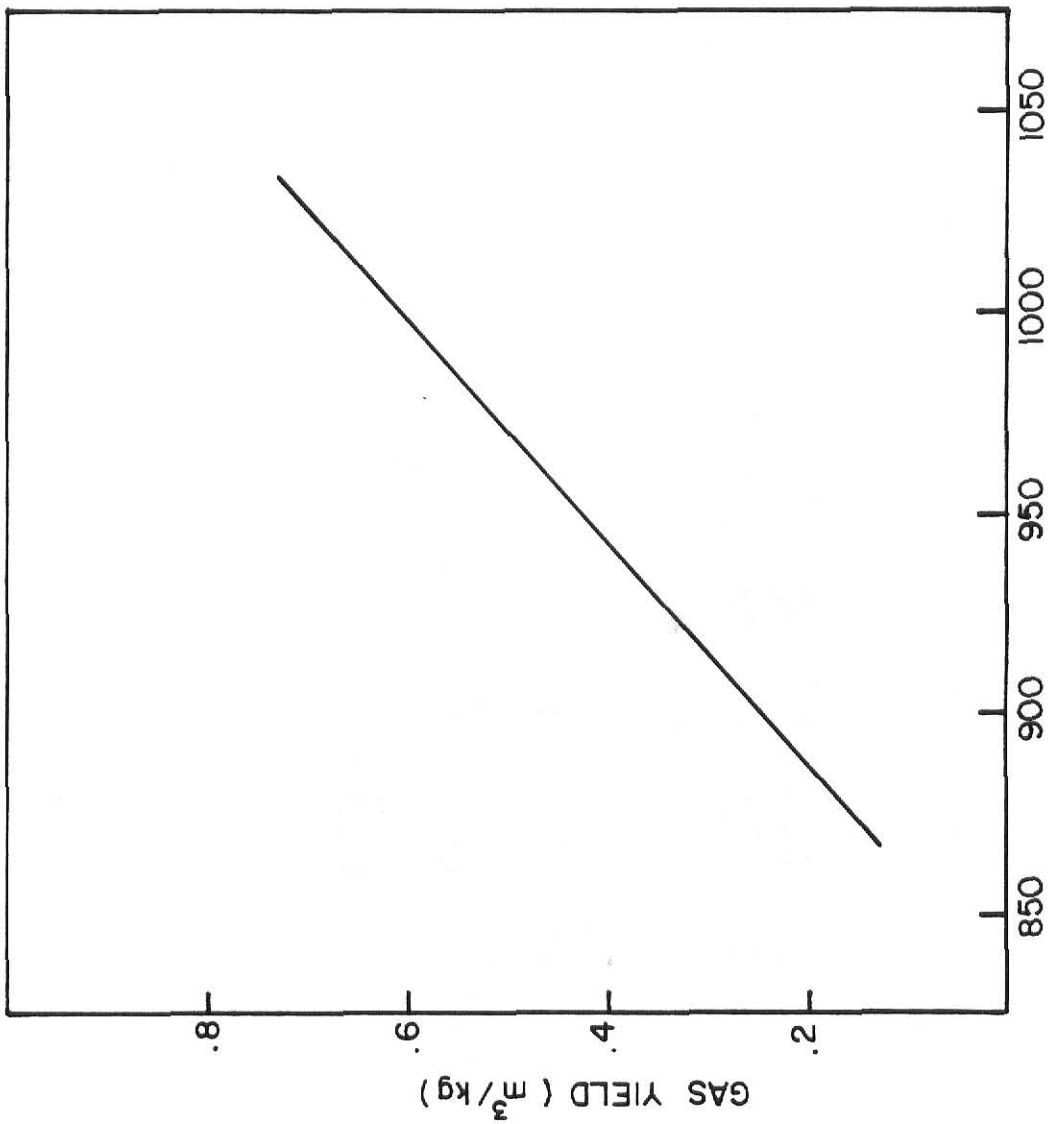

Figure 5. Gas yield versus temperature.

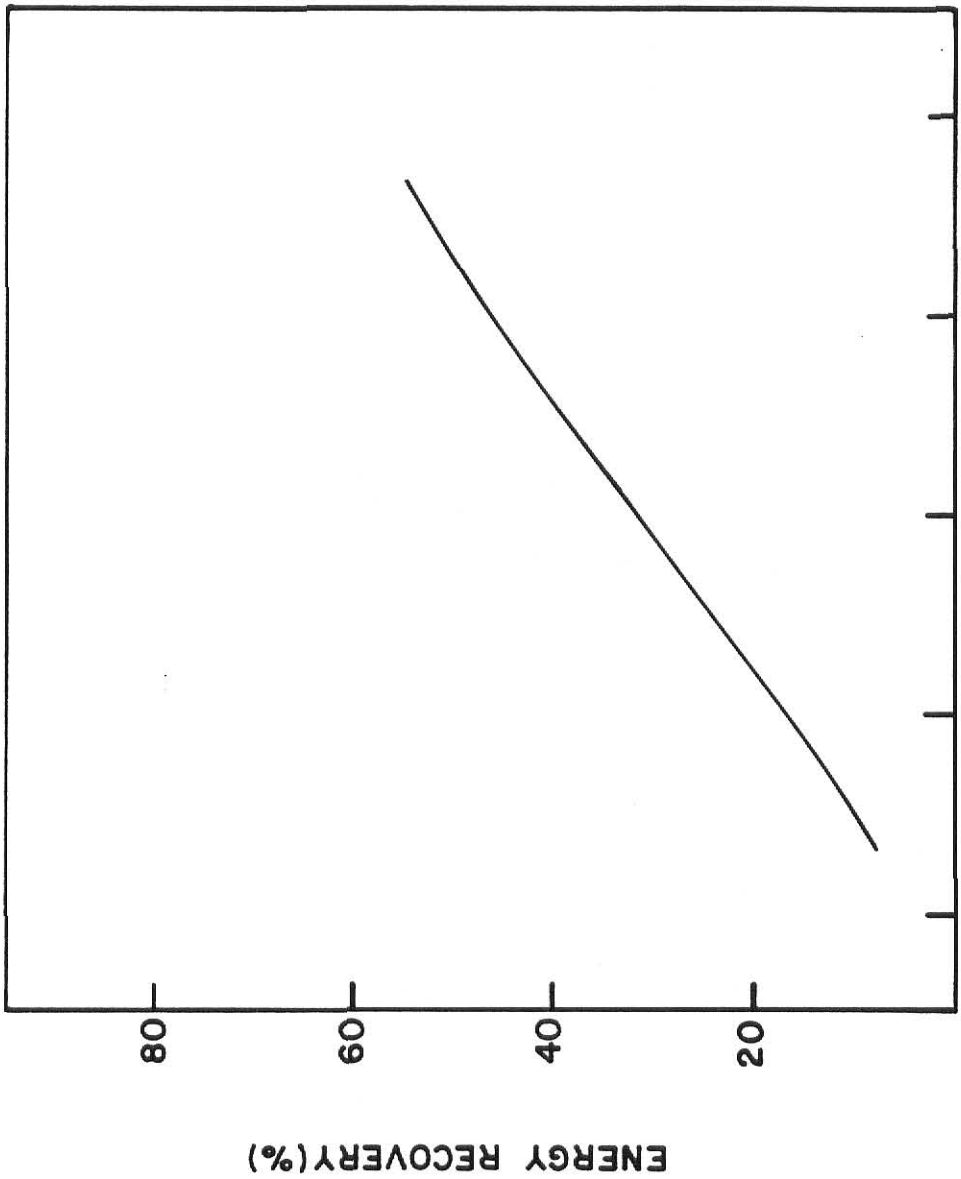

Figure 6. Energy recovery versus temperature.

CHAPTER IV

STEAM GASIFICATION OF PURE CELLULOSE

UNIFORM TEMPERATURE PROFILE

INTRODUCTION

The need for alternate energy sources coupled with the need for disposing of organic wastes has motivated many investigators to study the potential of converting biomass and other carbonaceous materials into fuels. One conversion method that has received increasing attention over the last few years is gasification in fluidized bed reactors.

Gasification is the process by which organic matter is converted to gas through thermal decomposition in an oxygen deficient environment, followed by secondary reactions of the resulting volatiles. The process also produces combustible char and tar which can be recovered and burned to provide the necessary energy for processing. Studies on the fluid-bed gasification of carbonaceous materials have grown rapidly over the last ten years. There are several parameters which influence the gasification process, the most important being the reactor temperature. Several investigators have shown that different feed materials also produce different results when gasified under similar conditions (see Walawender et al., 1980; Raman et al., 1980; Beck and Wang, 1980; Antal et al., 1978; and Howard et al., 1979). Some have postulated that the differences observed are due to differences in the cellulose content of the feed materials used.

Antal et al. (1978) conducted thermogravimetric studies on various materials including pure cellulose, paper, hardwood, softwood and manure. The results suggest a relationship between cellulose content and the extent of devolatilization. They found that pure cellulose devolatilized about 90% whereas manure (which contains significantly less cellulose) devolatilized only 55-60%. The extent of devolatilization of paper (85%), hardwood (80%) and softwood (70%) also appears to vary directly with the cellulose content.

Walawender et al. (1980) gasified various materials in a 0.23 m I.D. fluidized bed reactor including cane, manure and sludge. They found that there was an apparent qualitative correlation between the level of gas yield and the cellulose content of the biomass material. Materials containing a higher percentage cellulose tended to produce a higher gas yield at the same operating temperature than those containing a lower percentage. They also found that higher cellulose containing materials tended to produce gas of lower heating value.

At Texas Tech University, Beck and Wang (1980) gasified sawdust and manure in a 0.05 m I.D. fluidized bed reactor under partial oxidation conditions. They reported that sawdust produced gas in significantly higher yields than cattle manure under similar operating conditions. They also attributed the increase in gas yield to an increase in cellulose content of the feed material.

Raman et al. (1980) studied the effects of feed size fraction on the gasification of manure in a fluid-bed reactor. They found that different feed size fractions produced different gas yields, heating values and compositions when gasified under similar conditions. They suggested that this difference could be attributed to the variation in cellulose content of these fractions since each size fraction had a different material makeup.

Various carbonaceous wastes contain different amounts of cellulose. If cellulose content is a significant parameter in the gasification process, then it is apparent that the study of pyrolytic characteristics of pure cellulose would aid substantially in understanding the gasification of carbonaceous wastes.

A review of the literature indicates that little work has been conducted on the gasification of pure cellulose in a fluidized bed reactor.

Antal et al. (1978) and Antal (1979) examined the gasification of cellulose using a pyrolysis furnace followed by a gas phase reactor. They were mainly concerned with the secondary gas phase reactions. Their experiments involved batch processing and transient conditions, where small samples were gasified in an attempt to study the effects of reactor temperature and gas residence time. The gas samples taken were an average of the conditions for the batch processing. In contrast, this study focused on the gasification of pure cellulose in a fluidized bed reactor, with the gasification being examined under continuous, steady-state conditions. The gas compositions and other properties of the gas were examined as functions of temperature with gas residence times being held relatively constant. The objective of this study was to generate datum lines for gas composition, yield, heating value, energy recovery and carbon conversion under well defined conditions to serve as a bench mark for gauging biomass gasification processes.

EXPERIMENTAL FACILITIES AND PROCEDURE

Facilities

The bench-scale fluidized bed reactor used in this study is shown schematically in Figure 1. The reactor was constructed from a 5.08 cm (2 in.) I.D. by 50 cm length of schedule 40 Inconel 600 pipe, fitted on top with a 10.16 cm (4 in.) I.D. by 15 cm length of pipe of the same material. The upper 15 cm of the reactor served as a disengaging zone. The lower 23 cm, which served as a gas distributor and gas preheater, was packed with alumni oxide pellets (0.5 cm in diameter). The fluid-bed section was separated from the packed bed section by means of a 0.025 mm (60 mesh) 304 stainless steel screen. The bed material was a mixture of 25% by weight limestone-75% by weight silica sand. The diameter of limestone particles ranged from 2.82 mm to 0.297 mm (-7 + 50 mesh); the diameters of sand particles ranged from 0.595 mm to 0.297 mm (-30 + 50 mesh). The bed had a static height of 8.4 cm and an expanded height of about 11 cm.

The reactor was heated by means of four pairs of semi-cylindrical electrical resistance heaters, each capable of delivering up to 2300 W, at the maximum operating temperature of 1743 K. Voltage to each pair of heaters was controlled by a variable voltage autotransformer. The second and fourth pairs of heaters from the bottom were also controlled by thermostats connected to thermocouples inside the reactor bed and freeboard section of the reactor, respectively. Steam, the sole fluidizing gas, was generated externally in a series of two (600 W and 800 W) electrical furnaces and was supplied to the gas preheater section at approximately 500 K. A heating tape was wrapped around the pipe leading from the steam generator to the preheater to prevent the steam from cooling and condensing.

The feed was introduced into the reactor by gravity flow through a vertical feedpipe which discharged 6.6 cm above the static bed. A Vibra Screw (Model SCR-20) screw feeder with a solid core flight screw was used to supply to feed pipe at a uniform volumetric rate. A known volumetric flow of nitrogen was used to aid flow through the feedpipe and to prevent backflow through the feedpipe and subsequent condensation of vapor in the feed pipe and feeder. It was also used as a tracer gas.

The off-gas from the reactor was sent to a cyclone where entrained char was separated from the gas. The temperature in the cyclone was maintained at about 600 K to prevent condensation of tar. This was accomplished with a heating tape wrapped around the cyclone. The gaseous stream leaving the cyclone was cooled to approximately 300 K with two water-cooled heat exchangers in series. This resulted in the condensation of the fluidizing steam, which was collected in a receiver. The resultant off-gas carried with it a fine mist of condensables, which were removed by passing the gas through a packed bed of glass wool. The off-gas was then passed through a wet-test meter to measure the volume flow rate of gas. The off-gas could vent directly to the atmosphere, or a portion could go through a drying column packed with Drierite ($CaSO_4$) and then to an on-line process gas chromatrograph for analysis.

The temperature in the fluidized bed was monitored by a thermocouple placed inside the bed. The temperature profile in the reactor was monitored by using a sliding (91 cm long) thermocouple, which measured temperatures from the bottom of the fluidized bed to the top of the disengaging zone. Temperatures were also monitored in the steam generators, cyclone, heat exchanger outlet, reactor inlet and the two heating tapes. A pressure probe, connected to a water manometer, was used to monitor the bed pressure.

A second pressure probe on the feed pipe, connected to a water manometer, was used to monitor the reactor pressure.

Feedstock

The feedstock used in this experiment was alpha (α) cellulose powder rated at 99.5% pure obtained from the Sigma Chemical Company. The as-received α-cellulose was a fine powder which could not be fed consistently into the reactor through the screw feeder. To facilitate feeding, the α-cellulose was blended with tap water to form a paste which was pressed through a 2 mm screen to form pellets. The resulting pellets were dried at 323 K for 48 hours and then sieved. The size fraction used was 1 mm - 2 mm. The pelletized cellulose contained 4.9% moisture and 1.1% ash. Pure α-cellulose has an empirical formula of $(C_6H_{10}O_5)_n$ and a heating value on a dry ash-free basis of 17.492 MJ/kg DAF.

Procedure

For start-up of each experimental run, the reactor heaters, steam generators, cyclone and inlet heating tapes were turned on. Initially, air was used as the fluidized agent and as the feed pipe purge gas. During the heat-up period, the two steam generators, cyclone heater and inlet section heater were brought to their operating temperatures of 800 K, 750 K, 650 K, and 500 K, respectively. When the effluent from the steam generators reached about 500 K, the air flow was replaced by steam. The volumetric flow rate of steam required to maintain the selected fluidization velocity was measured both by collecting condensate downstream of the heat exchangers and by metering the water flow into the steam generators.

When the reactor bed and the freeboard temperatures stabilized at the selected operating temperature, the air purge was replaced with nitrogen.

The total N_2 introduced was about 40% of the flow rate of the dry produced gas. About one half-hour after the nitrogen was started, feeding was initiated. The total start-up time was about two hours from a cold start.

Any change in the temperature of the reactor bed or freeboard section due to feeding of the cellulose was corrected automatically by the thermostats. A gas sample was taken 5 minutes after feeding began and every 11 minutes thereafter. The condensate and nitrogen rates were measured over ten minutes time intervals as the gas samples were being taken. A typical run lasted about 90 minutes with about the last 30 to 45 minutes yielding steady GC readings. The feed rate was evaluated after every run by disconnecteding the lower section of the feed pipe and weighing the effluent collected for 3, 3-minute time intervals at a given setting on the feeder.

It was not possible to measure the total char produced in an experiment because of the hold-up of char in the bed. Nor was it possible to measure the total tar produced because of hold-up on the inside of the water cooled heat exchangers and other parts of the experimental system. For these reasons, overall materials balances were not possible.

Chemical Analysis

Analyses of the dry off-gas were conducted with the aid of an Applied *Automation* (*Optichrom* 2100) on-line process gas chromatograph. The gas components of interest included H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, O_2 and N_2. The GC had a cycle time of 11 minutes. Moisture and ash analysis were performed on the cellulose according to the standard ASTM procedures in a ventilated oven and muffle furnace respectively.

Operating Conditions

The operating conditions for all the experimental runs are summarized

in Table 1. By adjusting the water rate with temperature, an attempt was made to have nearly constant gas residence times, which ranged from 1.26 to 1.54 sec for all runs. The feed rate was varied from 1.8 to 2.3 g/min although the screw setting was always the same. It is believed that the feed rate variations were due to differences in the size and density of the pelletized cellulose. The principal experimental variable was the reactor bed temperature. The freeboard section of the reactor was operated at the same temperature as the reactor bed for each run. The superficial velocity of the fluidized gas corresponded to about 2 times the minimum fluidization velocity and 7% of the terminal velocity of the feed. It also corresponded to about 3 times the minimum fluidization velocity of the bed material.

RESULTS AND DISCUSSION

Calculations and Analyses

All of the calculations were based on the average of the data obtained during the last 30 to 45 minutes of each run. From the average of the GC analyses and the nitrogen tracer rate for each run, the volumetric flow rate of the dry producd gas (nitrogen-free) was calculated with the aid of a nitrogen balance. The dry produced gas analysis (nitrogen-free basis) was used to evaluate the higher heating value of the dry produced gas using the standard heat of combustion for each component. The volumetric gas yield per unit mass of feed on a dry ash-free basis was calculated from the volume flow rate of the dry produced gas (at 288 K and 101.3 kPa) and the mass flow rate of the dry ash-free feed. Because of the hold-up of char and tar in the experimental system, it was not possible to conduct an overall material balance on the bench-scale reactor. Consequently, only the yield and properties of the dry produced gas are considered in this report.

Model Development

The gasification of cellulose in reality is an extremely complex process involving numerous physical and chemical steps. Experimental investigations of biomass gasification by Antal et al. (1978) have shown that gasification can be described by the following conceptual model: (1) pyrolysis or devolatilization from 574 K to 773 K, which produces volatile matter and char; (2) secondary reactions involving the evoluted volatiles above 873 K; (3) char gasification at temperatures greater than 1073 K. Rensfelt et al. (1978) have noted that char gasification does not significantly affect the gasification process below 1100 K. Raman et al. (1981a) and Raman et al. (1981b) have found that devolatilization of biomass in a fluidized bed reactor is nearly instantaneous. Because of temperature constraints of this work, char gasification is not important to this study. Hence, we are only concerned with the second step of Antal's conceptual model. The secondary reactions of gasification involve many complex reactions such as reforming, cracking and the water gas shift reaction (Antal et al., 1978; Raman et al., 1981b; Schoesters et al., 1981).

A simplified mechanism is presented here based on the observations of others and a preliminary regression analysis of the gas yield, energy recovery and carbon conversion data obtained in this work. This mechanism postulates that the gasification of cellulose between 865 K and 1060 K can be divided into two regimes or zones. The first regime up to 940 K is controlled by cracking of volatile matter and the second, above 940 K, is dominated by the water gas shift reaction.

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Produced Gas Yield

The variation in the volumetric yield of produced gas (on a dry ash-free basis) as a function of temperature is shown in Figure 2. The solid lines have been obtained from regression analysis of the data. Note that the gas yield varied essentially linearly with temperature in both regimes which can be distinctly identified. In the first regime the gas yield rose rapidly from 0.48 m^3/kg at 865 K to 1.25 m^3/kg at 940 K. In the second regime, above 940 K the gas yield rose slowly to 1.41 m^3/kg at 1060 K. The existence of the two distinct regimes were also evident in the energy and carbon conversion data as will be elaborated later.

Produced Gas Composition

The variations in the concentrations of H_2, CO_2, CO, CH_4 and C_2H_4 as functions of temperature are shown in Figure 3. Again the solid lines have been determined from regression analysis of the data. The percent concentration of H_2 increased with an increase in the temperature; it ranged from 41.8% at 865 K to 48.3% at 1060 K, with a transition value of 42.6% at 940 K and then rose to 29.1% at 1060 K. The concentration of CO decreased with an increase in temperature and ranged from 26.4% at 865 K to 14.9% at 1060 K, with a transition value of 21.9% at 940 K. The concentration of CH_4 increased slightly with an increase in the temperature. It varied from 3.6% at 865 K to 5.6% at 1060 K, with a transition value of 4.3% at 940 K. The concentration of C_2H_4 also increased slightly with an increase in the temperature. It varied from 1.5% at 865 K to 2.6% at 1060 K, with a transition value of 2.2% at 940 K. The minor cmponents, C_3H_6, C_2H_6 and C_3H_8, all decreased with an increase in the temperature. Their compositions are not plotted because they represented only a small

portion of the total gas yield. In fact, all had compositions of less than one percent.

Produced Gas Heating Value

The higher heating value of the produced gas as a function of temperature is shown in Figure 4, with the solid lines determined from regression analysis of the data. The heating value increased from 11.5 MJ/m^3 at 865 K to 12.0 MJ/m^3 at 940 K and then decreased to 11.5 MJ/m^3 at 1060 K. Notice the variation in the heating value was small and that its average value was 11.8 MJ/m^3.

Energy Recovery

The effectiveness of the gasification process can be examined by considering the ratio of the heating value of the gas produced per unit mass of the feed, on a dry ash-free basis, to the heat of combustion of a unit mass of feed, also on a dry ash-free basis. This ratio, termed the energy recovery, was determined by dividing the product of the produced gas volumetric yield and heating value by the heat of combustion of the feed. It represents the percentage of the energy content of the feed that is converted to combustible gas. The energy recovery is plotted against the temperature in Figure 5. It shows that the data fit the linear correlations (represented by the solid lines) quite well, especially over the first temperature regime. In the first regime, the energy recovery rose rapidly from 32% at 865 K to 87% at 940 K. Then, it rose only 5% over the next 120 K. The final energy recovery was 92% at 1060 K. Antal et al. (1978) and Antal (1979) obtained energy recoveries as high as 83% when gasifying cellulose in a plug flow pyrolysis furnace. In making the above observation, the reactor furance temperature was 773 K and the gas phase

section of the furnace was at 973 K.

Carbon Conversion

Another way of measuring the effectiveness of a gasification process is to consider the carbon conversion. The carbon conversion is defined as the moles of carbon in the produced gas from a unit mass of feed on a dry ash-free basis to the moles of carbon per unit mass of dry ash-free feed. It represents the percent of the carbon in the feed converted to the gas. The carbon conversion is shown in Figure 6 as a function of temperature. Like the gas yield and energy recovery data, the carbon conversion data are well represented with the linear correlations, represented by the two solid lines, which have been determined from regression analysis. In the first regime the carbon conversion rose sharply from 32% at 865 K to 87% at 940 K. The carbon conversion was essentially constant over the next 120 K and rose to only 89% at 1060 K. Antal et al. (1978) and Antal (1979) obtained carbon conversions as high as 80% when gasifying cellulose at a reactor furance temperature of 773 K and a gas phase reactor temperature of 973 K.

Mechanistic Interpretations

TGA studies by Antal et al. (1978) have shown that devolatilization of cellulose is essentially complete at 773 K with 90% of the feed being volatile and 10% char formation. They have further suggested that cracking and reforming of the volatile materials produced during devolatilization occurs at temperatures greater than 873 K. Additional studies by Antal (1979) have indicated that reforming is probably not important and the secondary reactions are dominated by cracking reactions. Our own data also suggest that reforming is probably not important; no water consumption was noted in this temperature regime and the concentrations of CH_4 did not decrease.

The forward step of the water gas shift reaction, which is supposed to dominate the second regime in the mechanism proposed here, is faster than the reverse step below 1083 K. This is the case that existed in our experiments. Also, the reaction will tend to be driven to the right due to the excess of steam in the system. The molar concentration of steam was ten times the concentration of produced gas in the present study. When this reaction takes place in the forward direction, the dry gas yield would increase as shown by our data. Water would also be consumed as indicated by our measurements. The carbon conversion should remain unchanged because one mole of gaseous carbon as CO is converted to one mole of gaseous carbon as CO_2. The data showed only a 2% increase in the carbon conversion over the second regime. Because of the water gas shift reaction the heating value of the gas should decrease slightly with an increase in the temperature due to the diluent effect of CO_2. Our data indicated a slight decrease in the heating value. Additional calculations showed that if the water gas shift reaction was the only reaction taking place in the second

regime, then the energy recovery above 940 K should have increased with an increase in the temperature, as was observed in our data.

It should also be pointed out that cracking volatile matter is probably not important above 940 K. Antal et al. (1978) and Antal (1979) have shown that the yield of tar decreases with an increase in the reaction temperature. They found that for a reactor furnace temperature of 773 K and a gas phase reactor temperature of 973 K the tar yield was only 2% of the initial feedstock weight, indicating that cracking was essentially complete. Also, if reforming reactions were important in this regime, the compositions of the hydrocarbons should decrease. The compositions of CH_4 and C_2H_4 remained nearly constant during this regime. The other higher order hydrocarbons did decrease, but they composed a very small amount of the total gas yield; it could not be ascertained if the decrease in their concentrations were due to reforming or cracking.

Quantitative Analysis

The hypothesis that the water gas shift reaction dominates the second regime was tested quantitatively by assuming that the increase in the gas yield above 940 K was due solely to the water gas shift reaction. This assumption enables us to relate the slope of the gas yield curve, dY/dT, to that of the mole fraction curve, dy_i/dT, for the components, H_2, CO_2 and CO, over the second temperature regime. Note that the slope of the mole fraction curve is 10^{-2} times that of the mole composition curve shown in Figure 2.

The mole fraction of component i in a gaseous mixture, y_i, is defined as

$$y_i = \frac{n_i}{n_t} \qquad (1)$$

where n_i is the number of moles of component i in the mixture and n_t is the total number of moles of the mixture. Both n_i and n_t can be written, respectively, as

$$n_i = n_{io} + \Delta n_i \tag{2}$$

and

$$n_t = n_o + \Sigma \Delta n_i \tag{3}$$

where n_{io} is the number of moles of component i in the mixture at a reference temperature (it is 940 K is the present work), n_o is the total number of moles of the mixture at the reference temperature, and Δn_i is the difference between the number of moles of component i at the temperature of interest and that at the reference temperature. In the water gas shift reaction one mole of dry gas (CO) produces two moles of dry gas (H_2 and CO_2). Water is not considered as a component of the gas or a part of the gas yield since the present analysis is on a dry basis. Thus, Equation (3) can be simplified as

$$n_t = n_o + |\Delta n_i| \tag{4}$$

The change in the mole fraction of component i, y_i, with respect to temperature, T, is obtained by differentiating Equation (1) with respect to T as

$$\frac{dy_i}{dT} = \left[\frac{d\Delta n_i}{dT}\right]\left[\frac{(n_o + |\Delta n_i|)}{(n_o + |\Delta n_i|)^2}\right] - \left[\frac{d|\Delta n_i|}{dT}\right]\left[\frac{(n_{io} + \Delta n_i)}{(n_o + |\Delta n_i|)^2}\right] \tag{5}$$

Note that only Δn_i is a function of temperature. We can relate dn_i/dT to the slope of the gas yield curve, dY/dT, in Equation (5) by transforming moles to volume at the standard conditions. For components that are

produced during the reaction (H_2 and CO_2), Equation (5) becomes

$$\frac{dy_i}{dT} = \frac{1}{f}\left(\frac{dY}{dT}\right)\left[\frac{(n_o - n_{io})}{(n_o + |\Delta n_i|)^2}\right] \tag{6}$$

where f is the volume of one mole of gas at the standard conditions. A similar expression can be found for the component that is consumed during the reaction (CO)

$$\frac{dy_i}{dT} = -\frac{1}{f}\left(\frac{dY}{dT}\right)\left[\frac{(n_o + n_{io})}{(n_o + |\Delta n_i|)^2}\right] \tag{7}$$

Notice that the slope of the mole fraction curve changes with a change in temperature because Δn_i is a function of the temperature. The change in the slope is not large for the temperature range studied because the total number of moles, n_o, is much greater than the change in the number of moles of component i, Δn_i. The gas composition data may have been better represented with polynomial regression curves, but to be consistent with the proposed mechanistic model, the data have been fitted with a straight line between 940 K and 1060 K (see Figure 3).

Table 2 shows the average of the predicted slopes of the produced gas mole fraction versus temperature curves, calculated from Equations (6) and (7). The average values have been obtained by evaluating the slopes at 940 K and 1060 K, and taking their arithmetic averages. Table 2 also shows the least squares estimates of those slopes using data between 940 K and 1060 K for comparison. Agreement between the predicted (5.63×10^{-4}/K) and experimentally determined (4.75×10^{-4}/K) slopes for H_2 is good. The values for CO and CO_2 are of the same order of magnitude, but the agreement

is surprisingly good in light of the complexity of the system.

Improved agreement was obtained by using an approximate approach, which may be called the forcing technique. The objective of this technique was to obtain the smallest possible difference between the three predicted and actual slopes of the mole fraction curves in the second regime. This was done by parametrically varying the slopes to fit the gas yield and gas composition data in the second regime. This method, however, moves the transition point from 940 K. The resultant correlations are given by the dotted lines on Figures 2 and 3; they have been used along with Equations (6) and (7) to predict the slopes of the mole fraction curves between 950 K and 1060 K. The results are shown in Table 2.

CONCLUSION

Steam gasification experiments were conducted with cellulose in a bench-scale reactor over a temperature range of 865 K to 1060 K. The volumetric yields of the produced gas increased with an increase in temperature and ranged from 0.5 to 1.4 m^3/kg. The major components of the produced gas, which comprised over 90% of the gas were H_2, CO_2, CO and CH_4. The higher heating value of the gas averaged 11.8 MJ/m^3, and the energy recovery increased from 32% to 92% while the carbon conversion increased from 32% to 89%.

The gas yield and other data indicated the existence of two distinct regimes in the gasification process which led to the postulation of a mechanistic model which describes the gasification process between 865 K and 1060 K as being composed of two distinct regimes. The first was due to the cracking of volatile matter and showed a very rapid rise in gas yield with an increase in temperature up to 940 K. The second regime was a secondary reaction controlled regime which showed a dramatically slower rise in gas yield with an increase in temperature above 940 K. These regimes were also evident in the energy recovery and carbon conversion. Both showed dramatic changes in the slopes at 940 K. These observations suggested that the water gas shift reaction may be the dominant secondary gas phase reaction. This hypothesis was further tested quantitatively by assuming that the increase in the gas yield above 940 K was solely due to the water gas shift reaction. The rate of increase in the gas yield with temperature was related to the rate of change in the mole fractions of H_2, CO_2 and CO. Good agreement was found between the calculated rate of change of the mole fractions and the slopes of the mole fraction-temperature curves of the three components above 940 K.

REFERENCES CITED

Antal, M. J., W. E. Edwards, H. L. Friedman and F. E. Rogers, "A Study of the Steam Gasification of Organic Wastes," Project Report to EPA, W. W. Liberick, Project Officer (1978).

Antal, M. J., "The Effects of Residence Time, Temperature and Pressure on the Steam Gasification of Biomass" presented at Symposium on Biomass as a Non-fossil Fuel Source. Division of Fuel Chemistry, American Chemical Society Meeting, Honolulu, April 1-6 (1979).

Beck, S. R., and M. J. Wang, "Wood Gasification in a Fluidized Bed," Ind. Eng. Chem. Proc. Descrip. Devel., 19 (2) 312-317 (1980).

Howard, J. B., R. H. Stephens, H. Kosstrui, S. M. Ahmed, "Pilot Scale Conversion of Mixed Waste to Fuel, Volume I," Project to EPA, W. W. Liberick, Project Officer (1979).

Raman, K. P., W. P. Walawender and L. T. Fan, "Gasification of Feedlot Manure in a Fluidized Bed: The Effects of Superficial Gas Velocity and Feed Size Fraction," Preprints, ACS Div. Fuel Chem. 25 (4), 233-244 (1980).

Raman, K. P., W. P. Walawender, L. T. Fan and J. A. Howell, "Thermogravimetric Analysis of Biomass. Devolatilization Studies on Feedlot Manure," Ind. Eng. Chem. Proc. Descrip. Devel., 20 (4), 630-636 (1981a).

Raman, K. P., W. P. Walawender, L. T. Fan and C. C. Chang, "Mathematical Model for the Fluid-Bed Gasification of Biomass Materials. Application to Feedlot Manure," Ind. Eng. Chem. Proc. Descrip. Devel., 20 (4), 686-692 (1981b).

Rensfelt, E., G. Blomkvist, C. Ekström, S. Engström, B. G. Espenös, L. Liinanki, "Basic Gasification Studies for Development of Biomass Medium-BTU Gasification Processes," in Symposium Papers Energy from Biomass and Wastes (Washington, D.C.: Institute of Gas Technology), 465-494, August 14-18 (1978).

Schoeters, J., K. Maniatis and A. Buekens, "Fuel Gas from Agricultural Residues in a Fluidized Bed Reactor," in Proceedings of 2nd World Congress of Chemical Engineering, 1, 313-317 (1981).

Walawender, W. P., K. P. Raman and L. T. Fan, "Gasification of Carbonaceous Materials in a Fluidized Bed Reactor," in Proceedings of Bio-Energy '80 World Congress and Exposition (Washington, D.C.: The Bio-Energy Council), 575-577 (1980).

Walawender, W. P., S. Ganesan and L. T. Fan, "Steam Gasification of Manure in a Fluid Bed: Influence of Limestone as a Bed Additive," in Symposium Papers Energy from Biomass and Wastes V (Chicago, IL: Institute of Gas Technology), 517-528 (1981).

Table 1. Reactor Operating Parameters

Reactor Temperature Range	865 K - 1060 K
Fluidized Gas	Steam
Superficial Velocity	0.27 m/sec - 0.33 m/sec
Feed Rate	1.8 g/min - 2.3 g/min
Cellulose Particle Size	1 mm - 2 mm
Bed Particle Size	
Sand	0.595 mm - 0.297 mm (-30 + 50 mesh)
Limestone	2.82 mm - 0.297 mm (-7 + 50 mesh)

Table 2. Predicted and Experimentally Determined Slopes of the Produced Gas Mole Fraction Versus Temperature Curves

Calculations based on regression analysis

Component	Average predicted slope of the produced gas mole fraction versus temperature curve between 940 K and 1060 K	Experimentally determined slope of the produced gas mole fraction versus temperature data between 940 K and 1060 K
	(1/K)	(1/K)
H_2	5.63×10^{-4}	4.75×10^{-4}
CO_2	7.29×10^{-4}	2.91×10^{-4}
CO	-11.8×10^{-4}	-5.11×10^{-4}

Calculations based on forcing technique

	Average predicted slope of the produced gas mole fraction versus temperature curve between 950 K and 1060 K	Experimentally determined slope of the produced gas mole fraction versus temperature data used between 950 K
	(1/K)	(1/K)
H_2	3.17×10^{-4}	3.33×10^{-4}
CO_2	4.24×10^{-4}	3.86×10^{-4}
CO	-6.76×10^{-4}	-6.11×10^{-4}

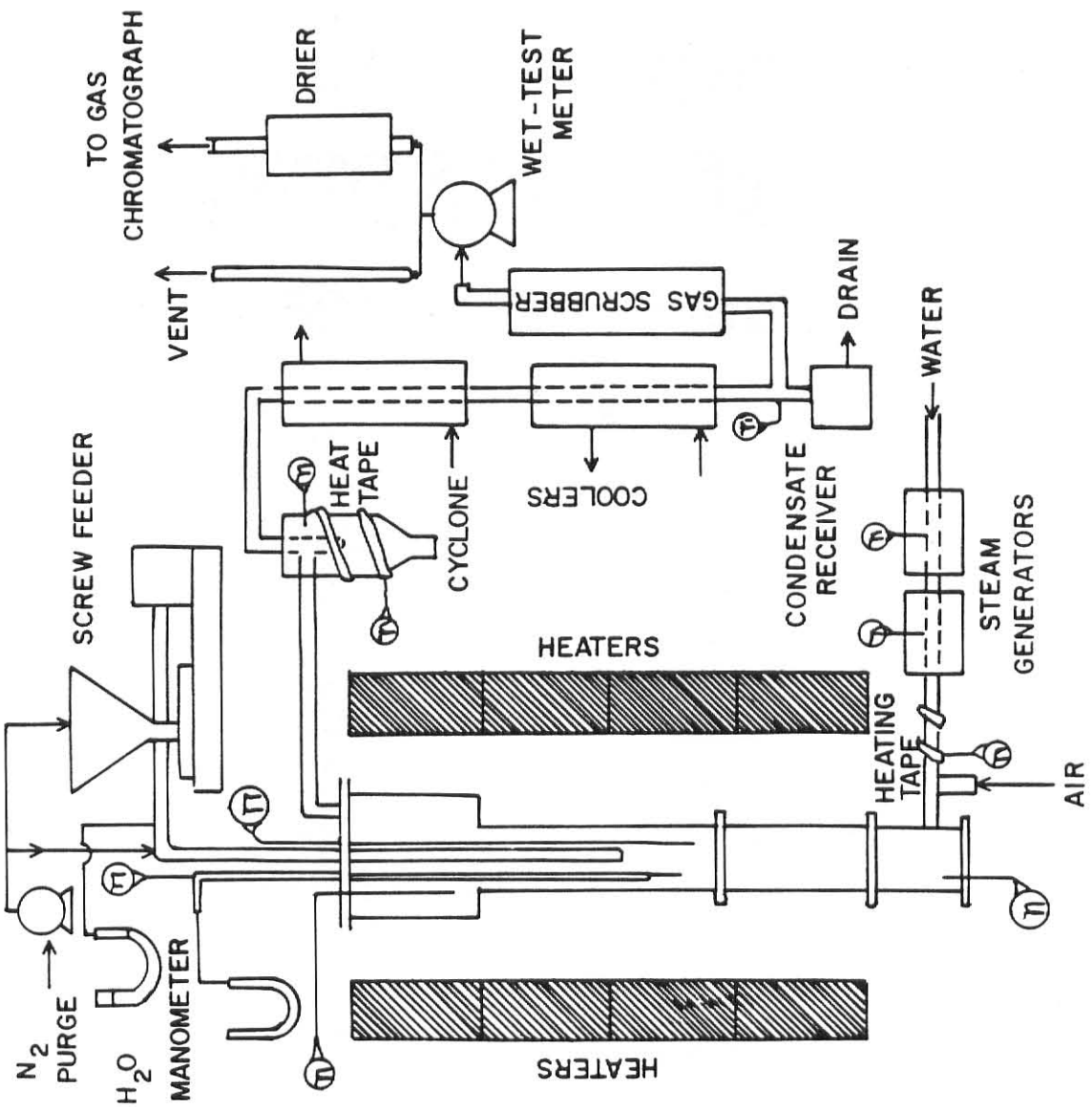

Figure 1. Bench-scale reactor.

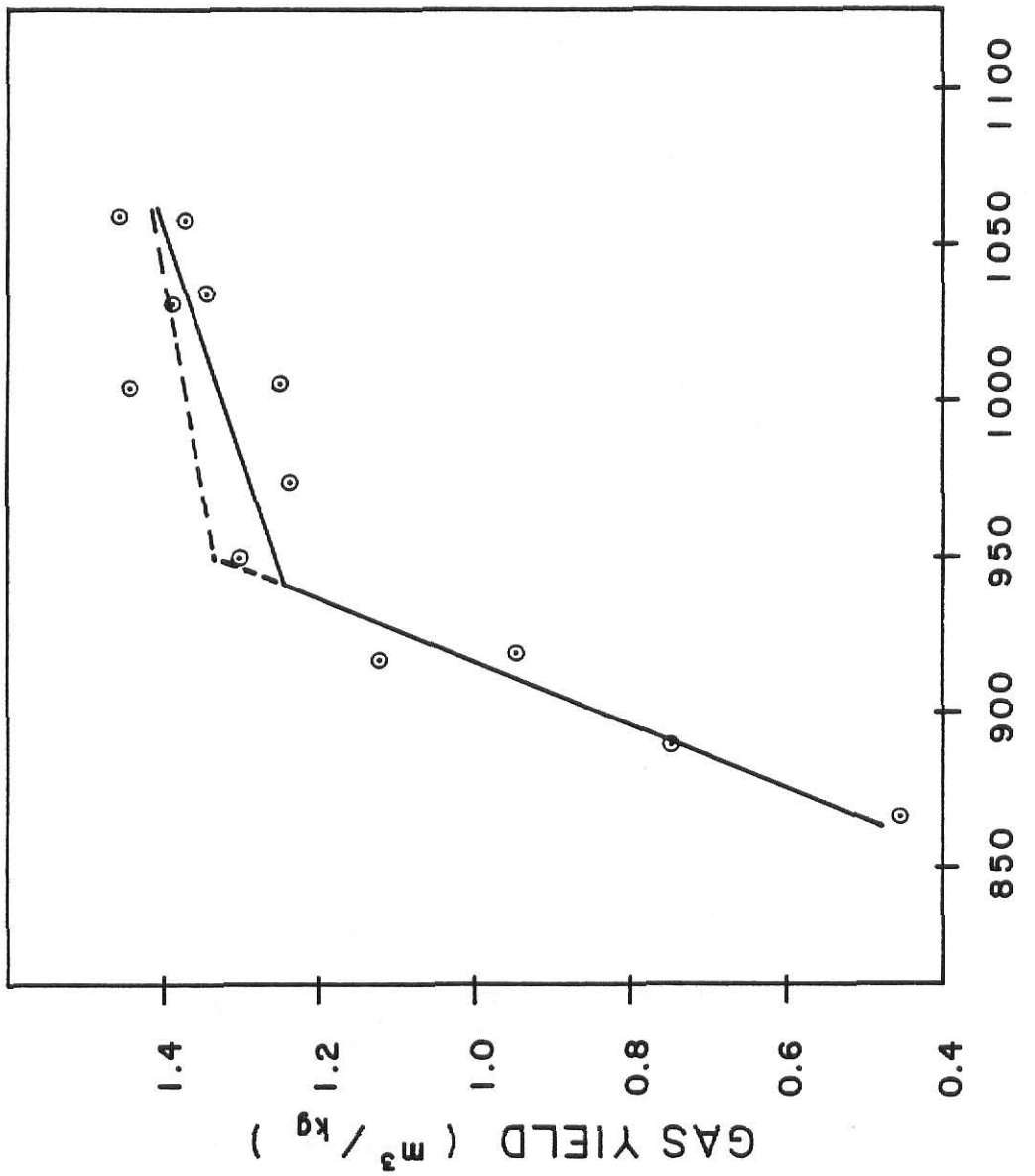

Figure 2. Gas yield versus temperature.

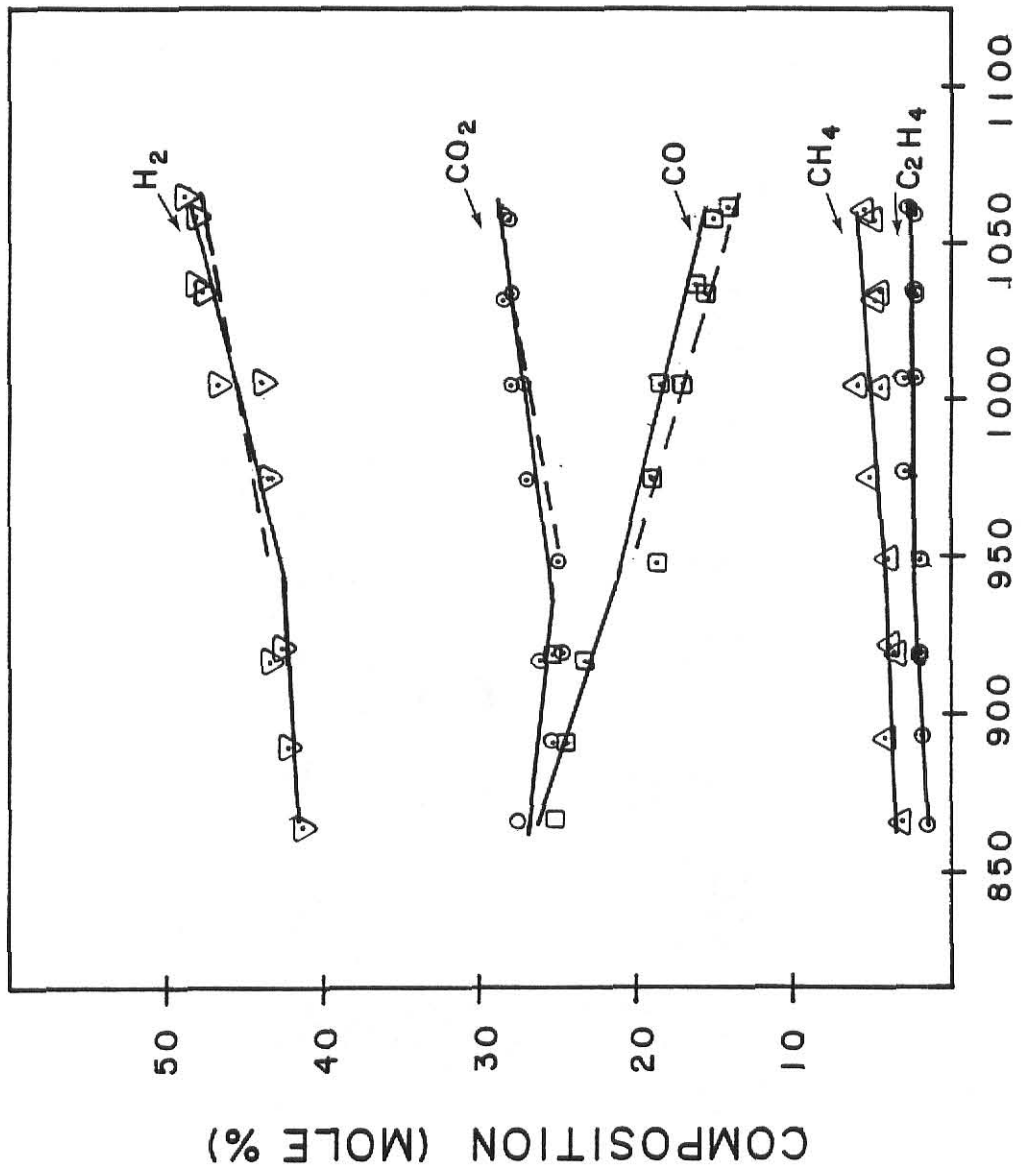

Figure 3. Gas composition versus temperature.

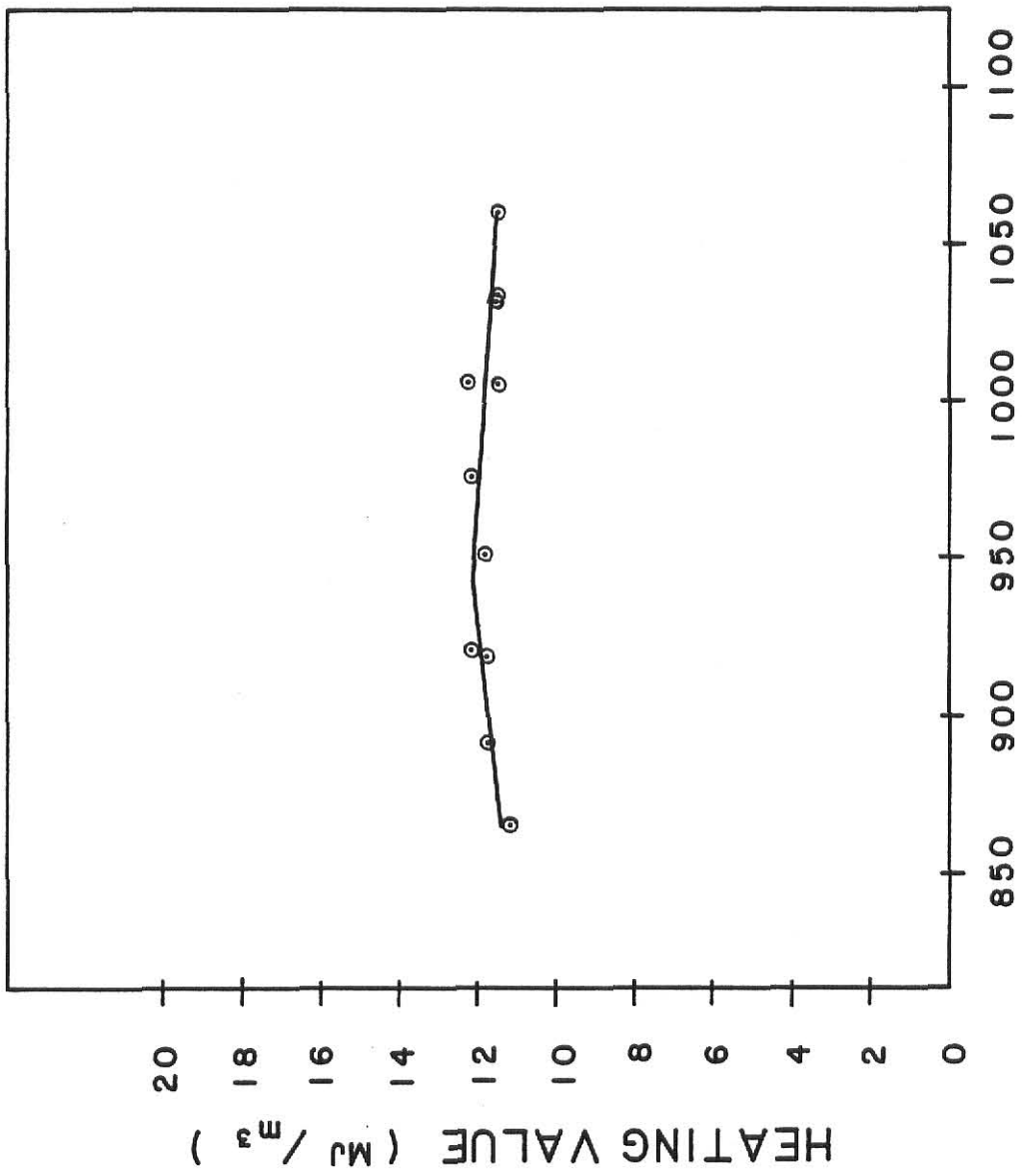

Figure 4. Gas heating value versus temperature.

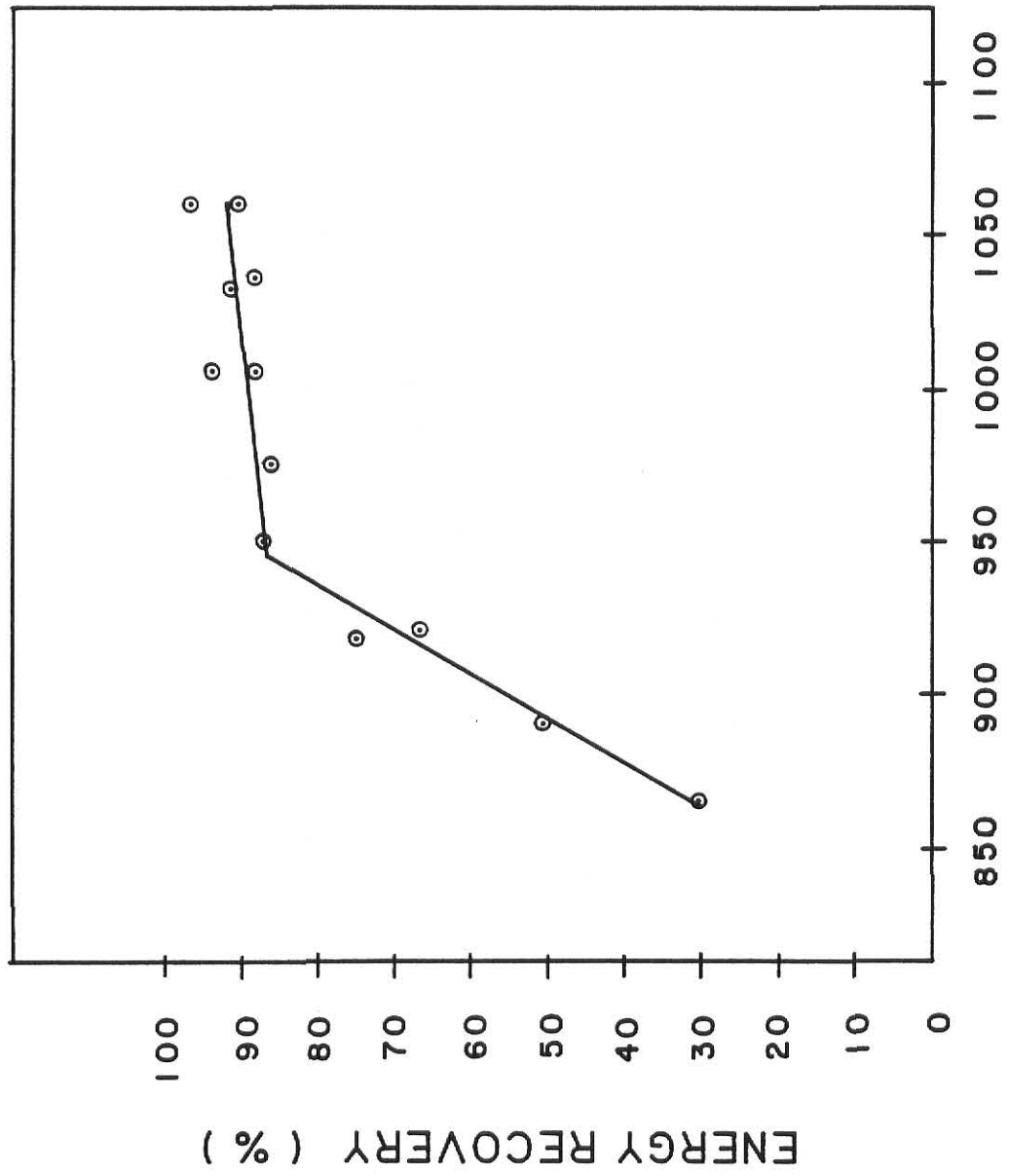

Figure 5. Energy recovery versus temperature.

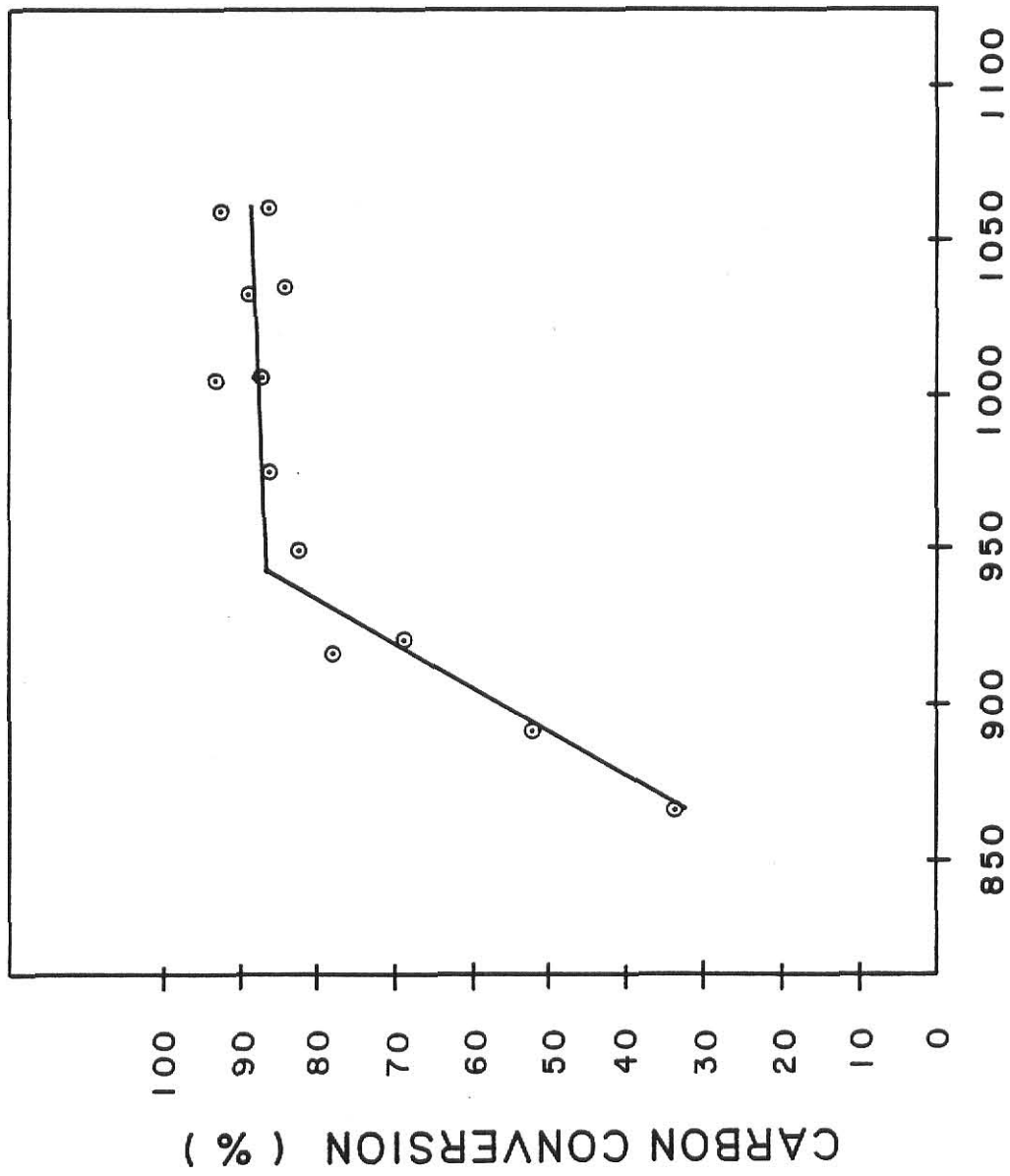

Figure 6. Carbon conversion versus temperature.

CHAPTER V

STEAM GASIFICATION OF PURE CELLULOSE

ELEVATED TEMPERATURE PROFILE

INTRODUCTION

The study of the gasification of pure cellulose is an important step in understanding the gasification of biomass materials. Chapter IV of this thesis reports on the effects of reactor bed temperature on steam gasification of pure cellulose in a fluidized bed reactor. This study proposed that for bed temperatures between 865 K and 1060 K gasification of cellulose takes place in two different regimes. The first regime between 865 K and 940 K is dominated by cracking of volatile matter; it shows a very rapid rise in gas yield with an increase in temperature. The second regime shows a dramatically slower rise in gas yield with an increase in the bed temperature above 940 K; it is dominated by the water gas shift reaction.

Many investigators have found that reactor bed temperature is an important parameter in determining the gasification products for the pyrolysis of biomass in a fluidized bed reactor (Itoh, 1975; Howard et al., 1979; Raman et al., 1980 and Walawender et al., 1980). The closely related freeboard temperature may also be a factor in determining the gasification products. The freeboard temperature may affect the secondary gas phase reactions which dominate the gasification process above 773 K (Antal et al., 1978). Antal (1979) studied the secondary gas phase reaction by heating cellulose produced volatiles in a quartz, tubular plug flow reactor. He examined the effect of gas phase temperature and gas residence time on the product gas composition under transient conditions. Although he found considerable variation in the product composition during the course of his experiments, he concluded that the gas phase reaction temperature significantly affected the gasification results. He also

claimed that the primary pyrolysis conditions and the gas phase residence times affected the results to a lesser degree.

Schoeters et al., (1981) examined the effects of freeboard temperature on the gasification of biomass in a fluidized bed reactor under partial oxidation conditions. In their study, wood shavings were gasified in a 0.15 m I.D. reactor using sand as the bed material and a mixture of air and steam as the fluidizing gas. They studied the effect of freeboard temperature variations on the produced gas composition, heating value, yield and energy recovery. The bed temperature used was 1073 K and the freeboard temperature ranged from 923 K to 1098 K, so that both temperature elevation and reduction were studied. They found that an increase in the freeboard temperature decreased the gas yield slightly from 2.9 to 2.8 kg gas per kg feed. It decreased the off-gas heating value from 4.4 to 3.8 MJ/m^3 and reduced the energy recovery from 65% to 55%. They also found that the gas composition changed with a change in the freeboard temperature. The gas components CO, CH_4, C_2H_4 and C_2H_6 decreased with an increase in the freeboard temperature, while CO_2 and H_2 increased with an increase in the freeboard temperature.

The investigation reported in this chapter is a continuation of the study reported in Chapter IV. The present work examined the effect of elevated freeboard temperature on the steam gasification of pure cellulose in a bench-scale fluidized bed reactor. The object of the study was to determine the effect of reactor freeboard temperature on the produced gas composition, yield, heating value, energy recovery and carbon conversion under steady-state conditions with nearly constant gas residence times.

EXPERIMENTAL FACILITIES AND PROCEDURE

The experimental facilities, feedstock, chemical analysis and procedure used in this investigation were the same as reported in Chapter IV. For their description readers are referred to Chapter IV.

The operating conditions for all the experimental runs of this investigation are summarized in Table 1. The principal experimental variables were the reactor bed temperature and the difference in temperature between the bed proper and expanded freebaord section of the reactor. An attempt was made to keep the gas residence time constant for all experimental runs. This was done by changing the steam rate to compensate for changes in temperature. Gas residence times varied between 1.2 and 1.6 sec. The superficial velocity of the fluidizing gas corresponded to about twice the minimum fluidization velocity and 7% of the terminal velocity of the feed. It also corresponded to about 3 times the minimum fluidization velocity of the bed material.

Typical reactor temperature profiles are shown in Figure 1. Figure 1 also shows a typical flat profile for comparison. For this investigation about half of the experimental runs were made with a temperature difference of 28 K ± 1 K between the reactor bed proper and the expanded freeboard section of the reactor. The other half had a difference of 83 K ± 2 K.

RESULTS AND DISCUSSION

Calculations and Analyses

The volumetric gas yield per unit mass of feed (at 288 K and 101.1 kPa), gas compositions, higher heating value, energy recovery and carbon conversion of the dry produced gas were calculated based on methods described in Chapter IV. The reactor bed temperature used for calculations was an average of six temperatures covering the length of the fluidized section of the reactor, and the expanded freeboard section temperature used was an average of six temperatures covering the length of the expanded section of the freeboard. The freeboard elevation was the difference between these two averages.

The calculated gas characteristics are plotted against the reactor bed temperature in Figures 2 - 7, with the actual data being shown by points. Distinctions are made between runs made with 28 K and 83 K freeboard elevations. The data are compared to the results obtained from the uniform temperature profile reported in Chapter IV, which are represented as solid lines labeled 0 K elevation.

Produced Gas Yield

The variation in the volumetric yield of the produced gas (on a dry ash-free basis) versus reactor bed temperature is shown in Figure 2. The gas yield showed a rapid rise for both freeboard elevations in the cracking controlled regime. The gas yield showed a slow rise over the second part of the bed temperature range, which is dominated by the water gas shift reaction. Compared with the 0 K freeboard elevation profile, which is depicted on the figure by the solid lines, the gas yield in the cracking controlled regime is increased and shifted to the right by an elevation in the freeboard temperature. There was considerable scatter of the data at

the higher bed temperatures, where the water gas shift reaction dominates. It appears however that above 1000 K the 83 K freeboard elevation showed a lower gas yield than the 0 K or 28 K elevation.

The scatter in the data could have occurred because of inaccuracies in the feed rates (these varied over 50% at the same screw setting) or because of variations in gas residence time. Although Antal (1979) concluded that residence time was not as important a parameter as the gas phase temperature in the gasification of cellulose, he found considerable variation in the gas composition data with variation in the gas residence time between 0 and 3 sec. Our gas residence times ranged between 1.2 and 1.6 sec. The lower gas yield observed at the 83 K freeboard elevation for the high bed temperatures was consistent with the findings of Schoeters et al. (1981).

Produced Gas Composition

The variations in the concentrations of H_2, CO, CO_2, CH_4 and C_2H_4 as functions of reactor temperature for the 28 K freeboard elevation are shown in Figure 3. The results were very similar to those obtained with the 0 K freeboard elevation. The 0 K elevation is represented by the solid lines on the figure. The concentrations of H_2 and CO_2 increased with an increase in the temperature, while the concentration of CO decreased. The concentrations of CH_4 and C_2H_4 rose slightly. Little difference could be noted between the gas compositions of runs made with the uniform temperature profile and those made with a 28 K freeboard elevation for bed temperaturesbelow 1055 K.

The variations in the component concentrations for the 83 K freeboard elevation are shown in Figure 4. The concentrations of H_2 and CO_2 increased

with an increase in temperature, while that of CO decreased. Concentrations of CH_4 and C_2H_4 decreased slightly over the temperature range studied. The concentrations of H_2 and CO_2 were lower than those concentrations found with no freeboard elevation at the same bed temperature, while those of CO were higher. The deviations in the concentrations of H_2, CO_2 and CO for bed temperatures below 1000 K could not be explained. The concentrations of CH_4 and C_2H_4 were higher than the concentrations found at the same bed temperature for the uniform temperature profile. The 0 K elevation profile is depicted as the solid line segments on the figure.

The variation in concentrations of C_2H_6, C_3H_6 and C_3H_8 as functions of temperature are not shown. Statistically there was no significant difference at the $\alpha = 0.05$ level between curves fitted for the three different freeboard profiles. All three components decreased with an increase in the bed temperature; however, they amounted to less than 2% of the total gas produced.

Produced Gas Heating Value

The variation in the higher heating value of the produced gas as a function of temperature is shown in Figure 5, for the various profiles studied. There appears to be no difference in the heating values from the 0 K and 28 K elevated profiles. Heating values from the 0 K profile are represented as solid lines on the figure. The 83 K elevated profile however, had higher heating values at the lower bed temperature (about 14.4 MJ/m^3 at 865 K to 925 K compared to about 11.8 MJ/m^3 for the 0 K profile). At the higher temperatures, the heating values variation with bed temperature was similar to the 0 K elevation. The reason for the higher heating values at the lower temperatures for the 83 K elevations

was because of the behavior of the gas compositions. There was more CH_4 and C_2H_4 at the lower bed temperature than for the uniform or 23 K elevated profiles. The 83 K elevated profile also had lower CO_2 concentration. Both CH_4 and C_2H_4 have high heats of combustion which increase the heating value of the produced gas, whereas CO_2 has no heat of combustion, and hence it does not add to the heating value of the gas but the overall heating value increases due to its reduced concentration.

Energy Recovery

Energy recoveries are plotted versus temperature in Figure 6. The energy recoveries from the 0 K elevation are also presented on the figure and are depicted as solid lines. Like the gas yield results, the energy recovery of all three freeboard profiles rose sharply between 865 K and 940 K, and then the slope of the 0 K elevation and the apparent slopes of the other two dramatically decreased; there was only a slight increase in the energy recovery over the second temperature range. Like the gas yield at the lower bed temperature, the higher freeboard elevations produced higher energy recoveries. At bed temperatures above 1000 K however, it appeared as if the 83 K freeboard elevation produced lower energy recoveries. Again, there was more scatter of the data at the higher bed temperatures.

Carbon Conversion

Carbon conversion versus temperature is shown in Figure 7. The carbon conversion for the 0 K elevation is depicted on the figure by solid lines. Like the gas yield and energy recovery, the carbon conversion for all three freeboard profiles rose sharply between 865 K and 940 K, and then the slope of the 0 K elevation and the apparent slopes of the other two

dramatically changed; they were nearly flat between 940 K and 1090 K. The carbon conversions for the higher freeboard elevations were higher at the lower bed temperatures. Although there was considerable scatter of the data, it appeared as if the carbon conversion for the 83 K elevation was lower than the 0 K or 28 K elevations above 1000 K.

Mechanistic Interpretations

The results of this investigation give further support to the mechanistic model developed in Chapter IV. The gas yield, energy recovery and carbon conversion data obtained with the elevated freeboard temperature profiles follow the same trends as the results obtained with the uniform temperature profile. Both elevations show dramatic changes in apparent slopes around 940 K. In the first temperature regime, controlled by cracking of volatile matter, the gas yield, energy recovery and carbon conversion were increased and shifted to the right by an increase in the elevation of freeboard temperature. This is because of the higher temperatures in the gas phase where the cracking reactions are taking place. Antal (1979) noted similar results.

In the second temperature regime, controlled by the water gas shift reaction, an 83 K increase in the elevation of freeboard temperature appears to reduce the gas yield and energy recovery above 1000 K, although there is considerable scatter in the data. This would be consistent with the hypothesis that the water gas shift reaction dominates this temperature regime. At temperatures above 1083 K the reverse water gas shift reaction is faster than the forward reaction. A reactor bed temperature above 1055 K combined with a freeboard elevation of 28 K places the freeboard in the region where the rate of the reverse water gas reaction is equal to the

forward reaction. Above this temperature, the reverse reaction dominates. For the 83 K elevation, a reactor bed temperature above 1000 K is needed. Above 1000 K, the 83 K elevation shows lower molar compositions of H_2 and CO_2, and a higher composition of CO than the 28 K or 0 K elevation for the same bed temperature. This is expected since the rate of the reverse shift reaction increases with temperature. This appears to provide additional credence to the proposition that the second regime is controlled by the shift reaction.

CONCLUSION

Steam gasification experiments were conducted with cellulose in a 5.08 cm fluidized bed reactor over a temperature range of 865 K to 1090 K. The experiments were designed to study the effects of freeboard temperature on the gasification products at nearly constant gas residence times.

The gas yield, energy recovery and carbon conversion for the experiments with the elevated freeboard temperature profiles reinforce the results obtained with the uniform temperature profiles. The results indicate that the steam gasification of cellulose between 965 K and 1090 K takes place in two distinct regimes. The first regime is due to the cracking of volatile matter and it shows a very sharp rise in the gas yield, energy recovery and carbon conversion up to a bed temperature of 940 K. The runs made with the elevated freeboard temperatures have shown greater magnitudes of gas yield, gas recovery and carbon conversion than those made with the uniform profiles at the same bed temperature. This is due to the increased temperature for cracking.

The second regime is dominated by the water gas shift reaction and it shows a dramatically slower rise in gas yield for all profiles above 940 K. In the higher temperature range it appears that the gas yield, energy recovery and carbon conversion of runs made with the 83 K elevated freeboard profile were lower than those made with the 0 K or 28 K profiles at the same bed temperature. These observations are consistent with the fact that at temperatures greater than 1083 K the reverse water gas shift reaction is faster than the forward reaction.

The dominant components of the produced gas for all three freeboard profiles were H_2, CO and CO_2. The same general trends were noted for each

profile. The concentrations of H_2 and CO_2 for the highest freeboard temperature were, for bed temperatures greater than 1000 K, lower at the same bed temperature than for the uniform or 28 K profile. The concentration of CO for the highest freeboard temperature was higher than the 0 K or 28 K profile. Again, these observations are consistent with the fact that at temperatures greater the 1083 K, the reverse water gas shift reaction is faster than the forward reaction. Hence, more CO and less H_2 and CO_2 should be formed when the reaction temperatures are greater than 1083 K.

REFERENCES CITED

Antal, M. J., W. E. Edwards, H. L. Friedman and F. E. Rogers, "A Study of the Steam Gasification of Organic Wastes," Project Report to EPA, W. W. Liberick, Project Officer (1978).

Antal, M. J., "The Effects of Residence Time, Temperature and Pressure on the Steam Gasification of Biomass," presented at Symposium on Biomass as a Nonfossil Fuel Source, Division of Fuel Chemistry, Americal Chemical Society Meeting, Honolulu, April 1-6 (1979).

Howard, J. B., R. H. Stephens, H. Kosstrue, S. M. Ahmed, "Pilot Scale Conversion of Mixed Waste to Fuel, Volume I," Project Report to EPA, W. W. Liberick, Project Officer (1979).

Itoh, K., "Municipal Refuse Pyrolysis with Two Circulation Fluidized Beds," Kankyo Sozo, 6, 42-46 (1974). As reviewed by T. Y. Chen, E. Kojima, W. P. Walawender, and L. T. Fan. "A Review of Waste Gasification Technology as Developed in Japan," System Institute Report 68, Kansas State Univ., Manhattan (1975).

Raman, K. P., W. P. Walawender, and L. T. Fan, "Gasification of Feedlot Manure in a Fluidized Bed Reactor. The Effect of Temperature," Ind. Eng. Chem. Process Des. Develop., 19 (4), 623-629 (1980).

Schoeters, J., K. Maniatis, and A. Buekens, "Fuel Gas from Agricultural Residues in a Fluidised Bed Reastor," in Proceeding 2nd World Congress of Chemical Engineering, 1, 313-317 (1981).

Walawender, W. P., K. P. Raman and L. T. Fan, "Gasification of Carbonaceous Materials in a Fluidized Bed Reactor," in Proceedings of Bio-Energy '80 World Congress and Exposition (Washington, D. C.: The Bio-Energy Council), 575-577 (1980).

Table 1. Reactor Operating Parameters

Reactor Bed Temperature Range	865 K - 1090 K
Difference Between Reactor Bed and Expanded Freeboard Temperature	28 K and 83 K
Fluidizing Gas	Steam
Superficial Velocity	0.27 m/sec - 0.36 m/sec
Feed Rate	1.7 g/min - 2.5 g/min
Cellulose Particle Size	1 mm - 2 mm
Bed Particle Size	
Sand	0.595 mm - 0.297 mm (-30 + 50 mesh)
Limestone	2.82 mm - 0.297 mm (-7 + 50 mesh)

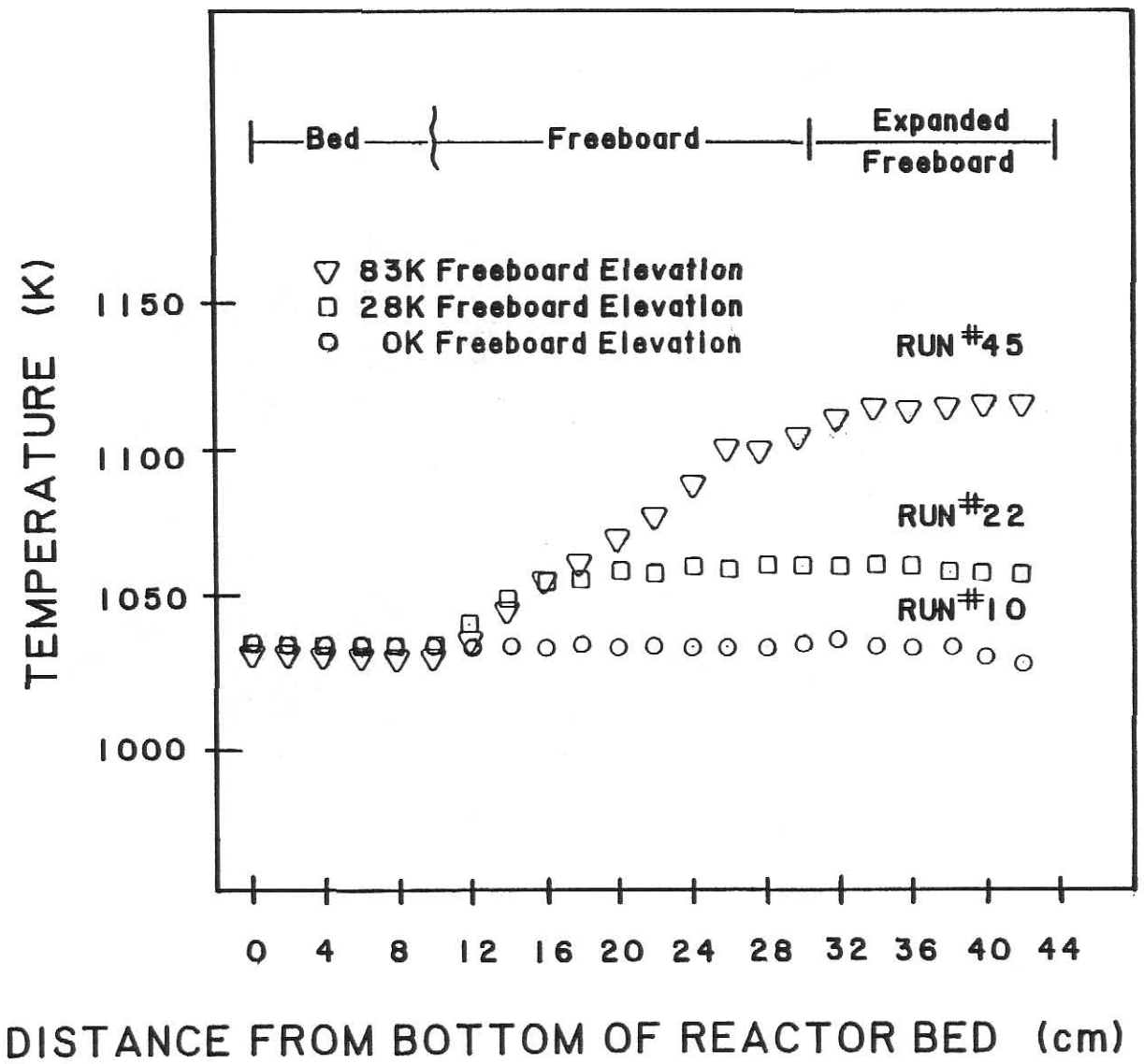

Figure 1. Typical reactor temperature profiles.

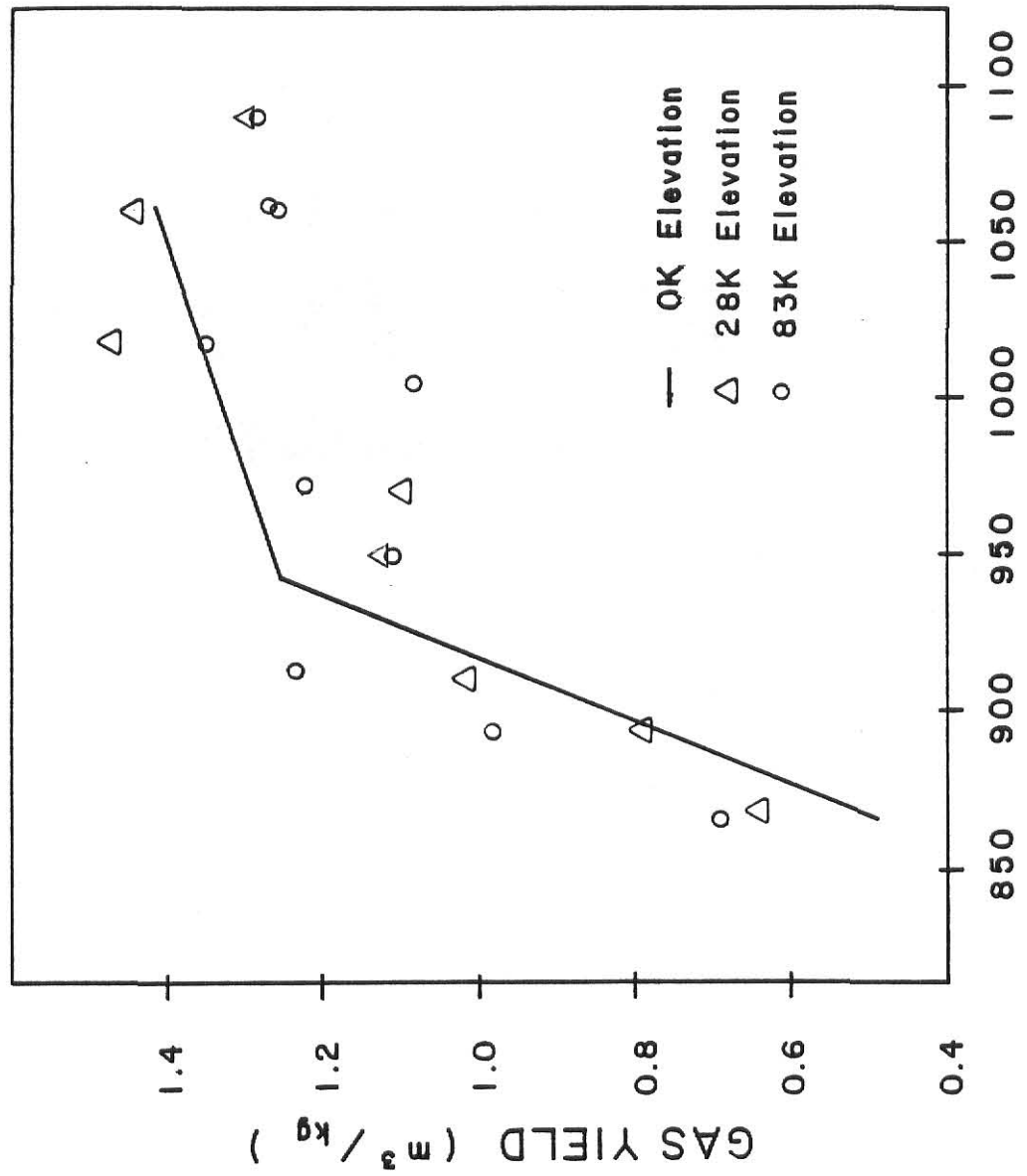

Figure 2. Gas yield versus temperature.

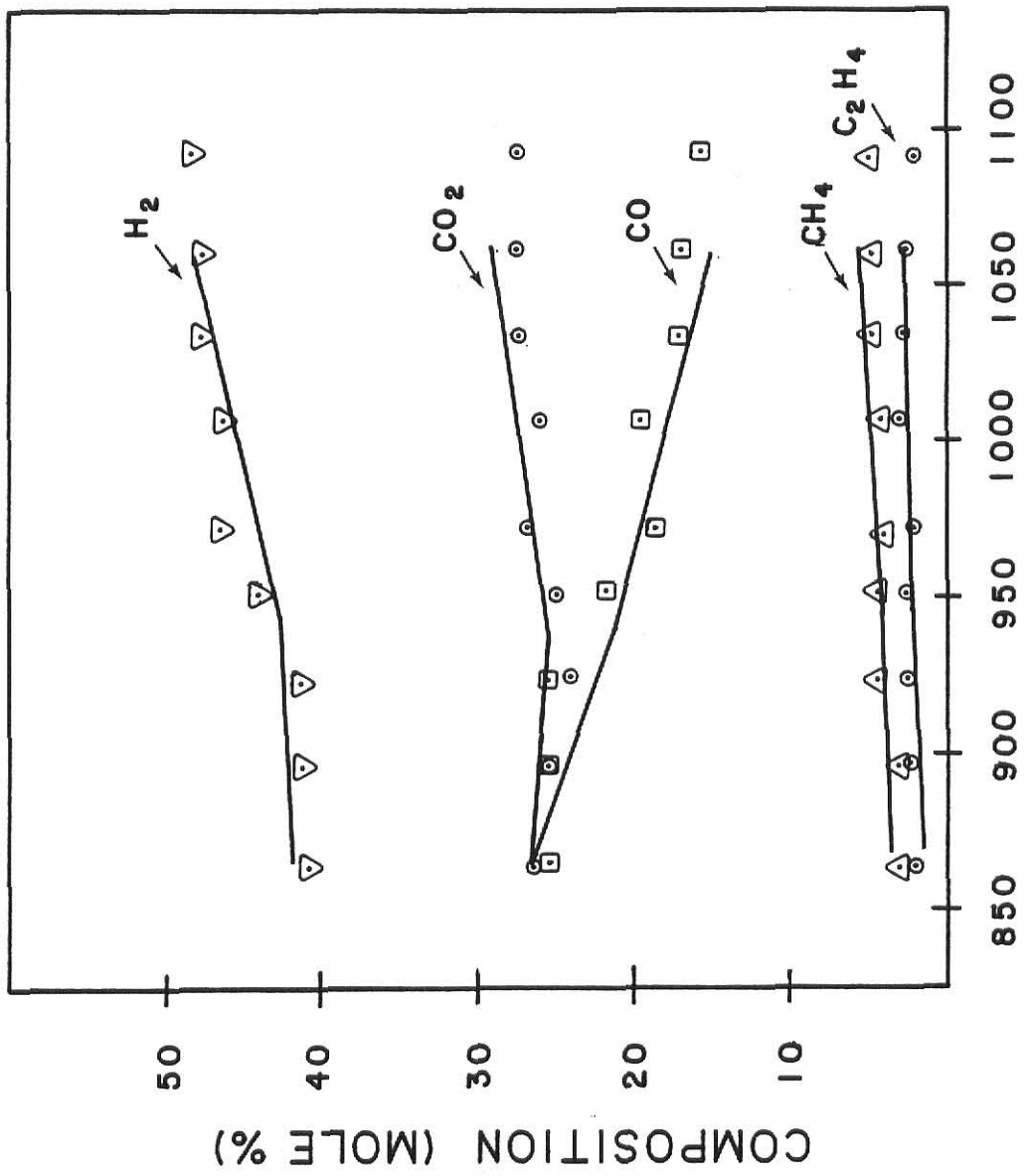

Figure 3. Gas composition versus temperature for 28 K elevation.

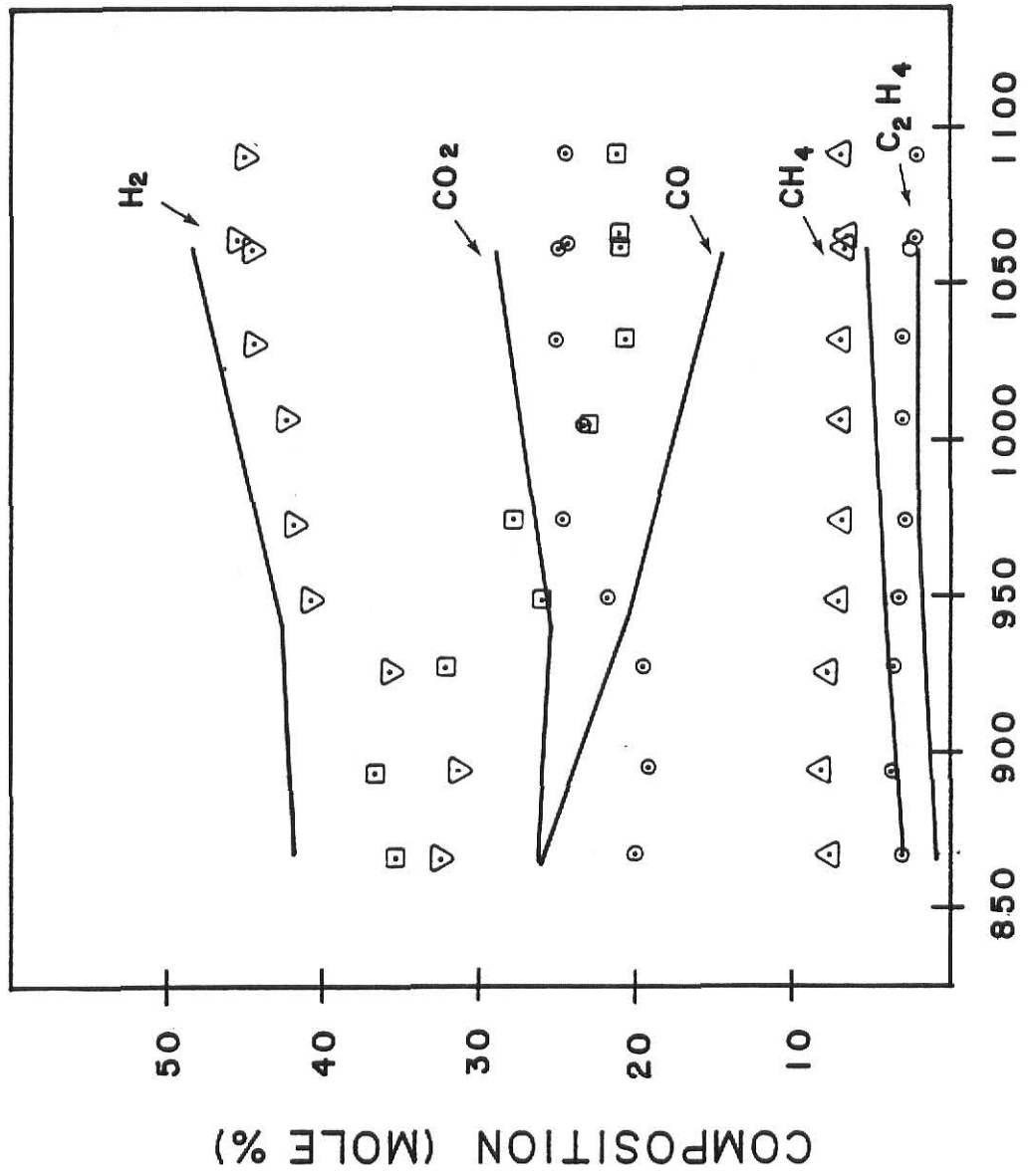

Figure 4. Gas composition versus temperature for 83 K elevation.

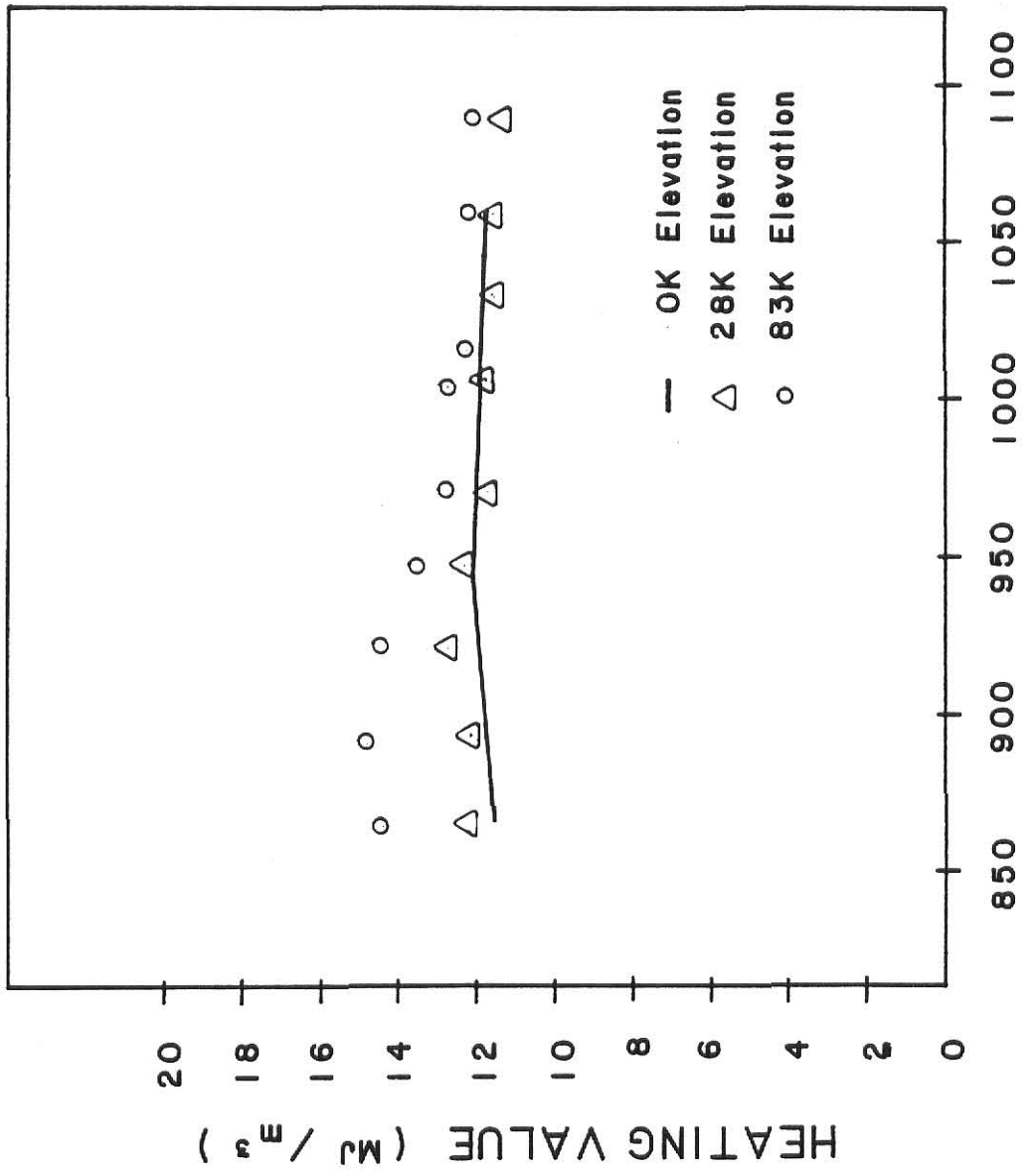

Figure 5. Gas heating value versus temperature.

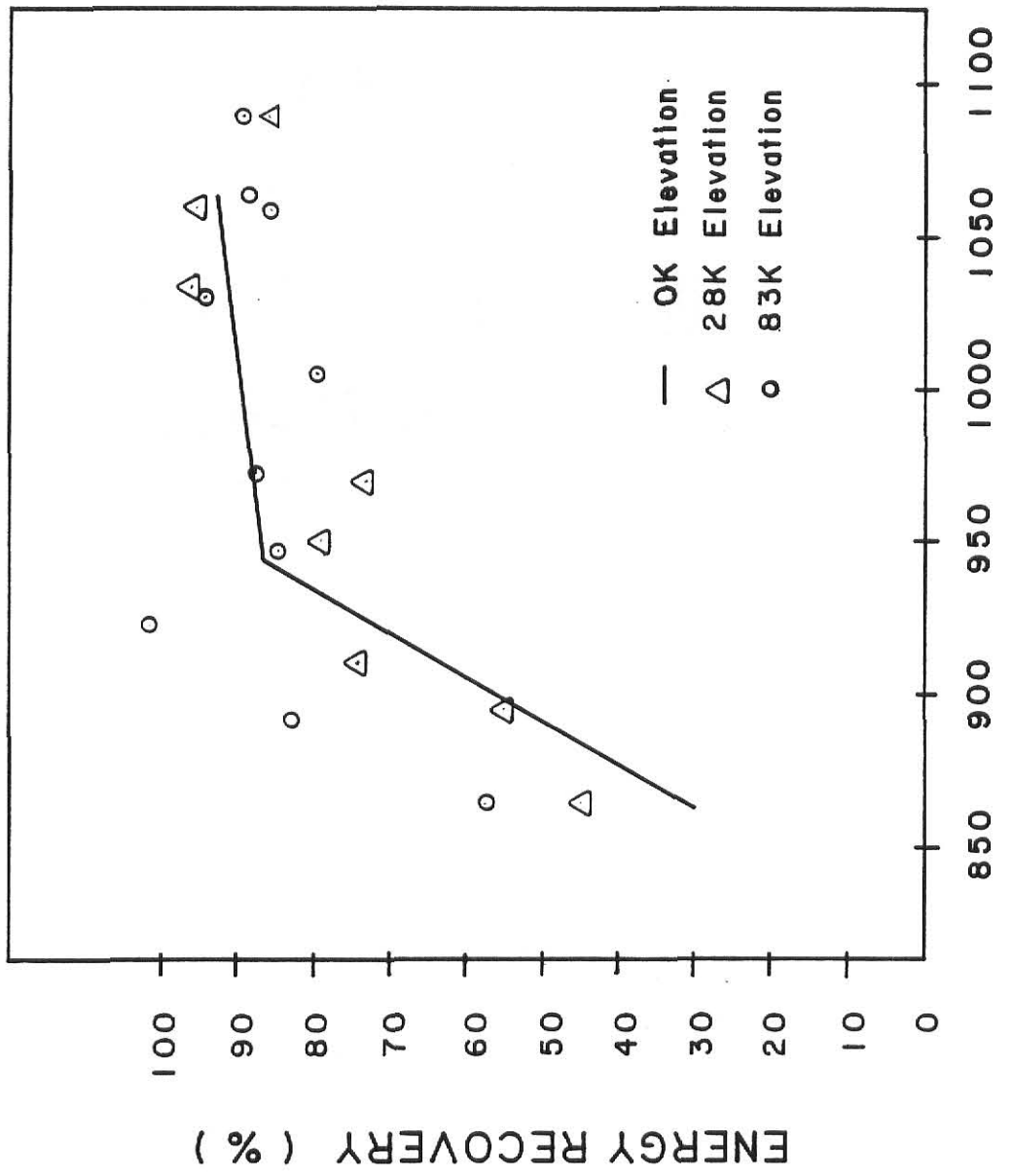

Figure 6. Energy recovery versus temperature.

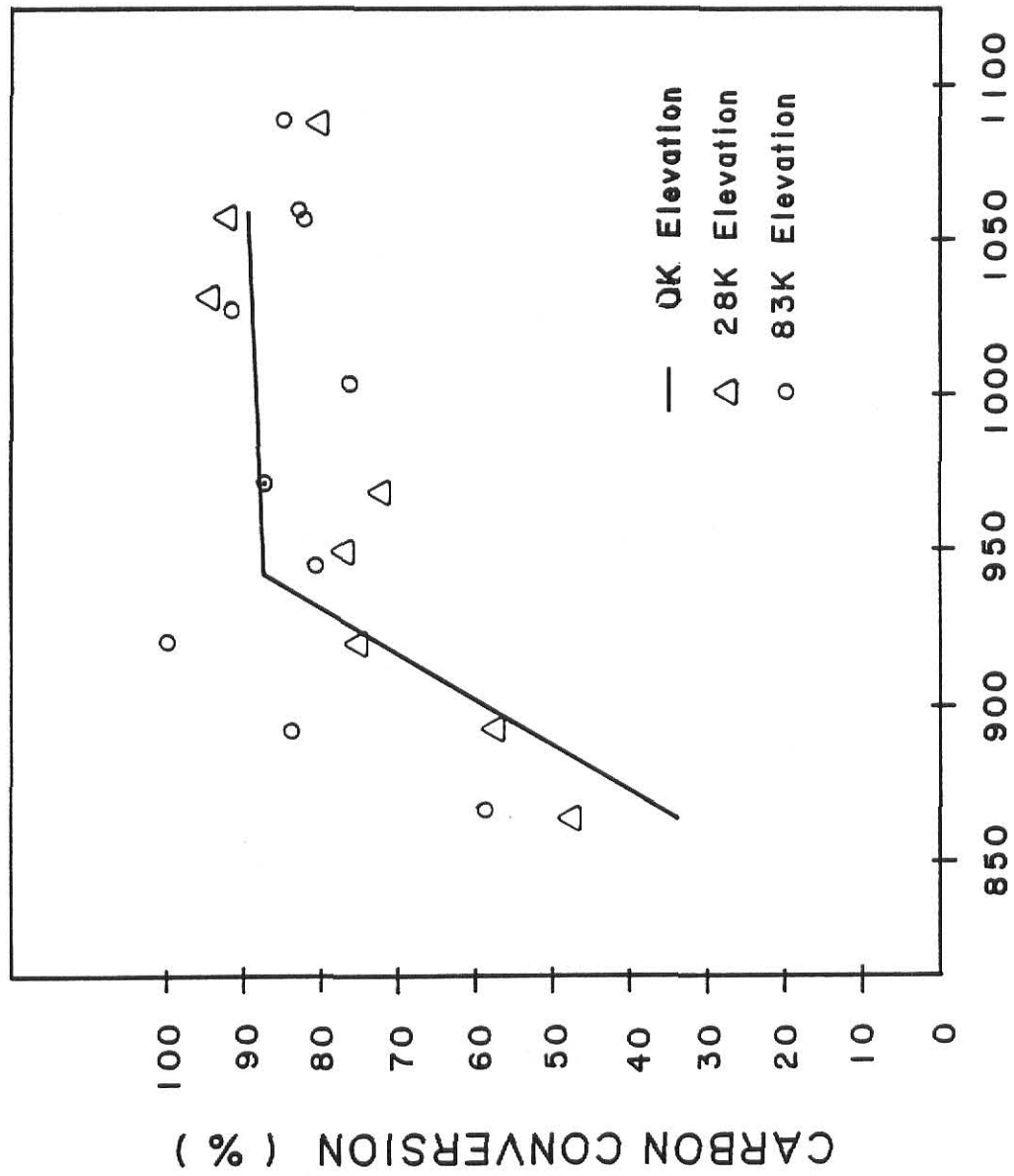

Figure 7. Carbon conversion versus temperature.

CHAPTER VI

CONCLUSION

SUMMARY

Steam gasification experiments were conducted with corn dust and cellulose in a 5.08 cm fluidized bed reactor. The overall objective of the work was to investigate the effects of feed material, reactor temperature and freeboard temperature on the produced gas composition, yield, heating value, energy recovery and carbon conversion.

Corn grain dust was gasified over a reactor temperature range of 867 K to 1033 K to examine the influence of temperature on the produced gas. The principal components of the produced gas were H_2, CO_2 and CO, which comprised over 90% of the produced gas. The minor components of the gas were CH_4, C_2H_4 and C_2H_6. Gas yield increased linearly with an increase in temperature and ranged from 0.13 to 0.73 m^3/kg. The energy recovery also increased linearly with an increase in temperature and varied from 8 to 55%. The heating value varied from 9.4 MJ/m^3 at 867 K to 11.5 MJ/m^3 at 1033 K, with a maximum of 11.6 MJ/m^3 at 1002 K.

Alpha cellulose was gasified over a reactor bed temperature range of 865 K to 1060 K to generate datum lines under well defined conditions to serve as a bench mark for gauging biomass gasification processes. In this study the freeboard temperature was held the same as the reactor bed temperature. The major components of the produced gas were H_2, CO_2, CO and CH_4, which comprised over 90% of the gas. The gas yield increased with an increase in temperature and varied from 0.5 to 1.4 m^3/kg. Energy recovery and carbon conversion also increased with an increase in temperature and ranged from 32 to 92% and 32 to 89% respectively. The heating value varied from 11.5 MJ/m^3 at 865 K to 11.5 MJ/m^3 at 1060 K, with a maximum of 12.0 MJ/m^3 at 940 K. The behavior of the gas yield data indicated the existence of two distinct regimes in the gasification process

between 865 K and 1060 K. The first regime from 865 K to 940 K was the result of cracking of volatile matter, and the second, from 940 K to 1060 K was dominated by the water gas shift reaction. These regimes were also evident in the energy recovery and carbon conversion versus temperature curves.

Alpha cellulose was also gasified to study the effect of an elevated freeboard temperature on the gasification processes. The results of this study were in line with the results obtained for the gasification of cellulose with a uniform temperature in both bed and freeboard. The results also gave further support to the mechanistic model developed in the uniform profile studies. In the cracking controlled regime, and increase in freeboard temperature increased and shifted the produced gas yield to the right. The gas yield decreased with an increase in freeboard temperature in the second regime due to the reverse water gas shift reaction, which dominates above 1083 K. Further support for the domination of the reverse water gas shift reaction in this regime is given by the component composition data. An increase in freeboard temperature decreased the molar composition of H_2 and CO_2, while it increased the composition of CO as would be expected from the reverse shift reaction.

RECOMMENDATIONS

To improve the performance of the experimental facilites, better control of the feed rates and steam condensation rates are needed. Improving the control over the feed rate may reduce some of the experimental scatter. Improving control over the steam condensation rate may also reduce some of the scatter. It will also enable further studies to be made on the effects of gas residence time on the gasification process.

To further study the gasification of cellulose, more work is needed at gasification temperatures less than 865 K and greater than 1090 K. This will allow the investigation of other gasification regimes such as the devolatilization of cellulose and the gasification of char by water.

The gasification of lignin and hemicellulose will continue the systematic study of the gasification of biomass. Along with cellulose, lignin and hemicellulose are major components of biomass. Knowledge of their gasification characteristics will aid in the gauging of biomass gasification processes.

THE GASIFICATION OF BIOMASS IN A FLUIDIZED BED REACTOR

by

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B.S.ChE., Washington University, 1977

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

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KANSAS STATE UNIVERSITY
Manhattan, Kansas

1982

Studies of the steam gasification of biomass materials was conducted in a 5 cm I.D. bench-scale fluid-bed reactor. The overall objective of the work was to investigate the effects of feed material, reactor temperature and freeboard temperature on the produced gas composition, yield, heating value, energy recovery and carbon conversion.

Corn grain dust was gasified over a reactor temperature range of 867 K to 1033 K to examine the influence of temperature on the produced gas. The principal components of the produced gas were H_2, CO_2 and CO which comprised over 90% of the gas. Gas yield and energy recovery increased linearly with an increase in temperature and ranged from 0.13 to 0.73 m^3/kg and 8 to 55% respectively. The heating value varied from 9.4 to 11.6 MJ/m^3.

Alpha cellulose was gasified over a reactor bed temperature range of 865 K to 1060 K to generate datum lines under well defined conditions to serve as a bench mark for gauging biomass gasification processes. In this study the freeboard temperature was held the same as the reactor bed temperature. The major components of the produced gas were H_2, CO_2, CO and CH_4 which comprised over 90% of the gas. The gas yield, energy recovery and carbon conversion increased with an increase in temperature and varied from 0.5 to 1.4 m^3/kg, 32 to 92% and 32 to 89% respectively, The heating value varied from 11.5 to 12.0 MJ/m^3. The behavior of the gas yield with respect to temperature indicated the existence of two distinct regimes in the gasification process. The first regime up to 940 K was the result of cracking of volatile matter, and the second was dominated by the water gas shift reaction.

Alpha cellulose was also gasified to study the effect of an elevated freeboard temperature on the gasification processes. The results of this study were in line with the results obtained for the gasification of cellu-

ose with a uniform temperature in both bed and freeboard. The results also gave further support to the mechanistic model developed in the previous study. In the cracking controlled regime, an increase in freeboard temperature increased and shifted the produced gas yield to the right. The gas yield decreased with an increase in freeboard temperature in the second regime due to the reverse water gas shift reaction, which dominates above 1083 K. Further support for the domination of the reverse water gas shift reaction in this regime is given by the component composition data. An increase in freeboard temperature decreased the molar composition of H_2 and CO_2, while it increased the composition of CO as would be expected from the reverse shift reaction.