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THE GASIFICATION OF BIOMASS IN A FLUIDIZED BED REACTOR

by

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You can fuel all the people some of the time

and

You can fuel some of the people all the time

but

You can not fuel all the people all of the time.

Peter Chapman in "Fuel's Paradise"

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CHAPTER I

INTRODUCTION

Rising costs and the instability and uncertainty in the supply of fossil fuels, combined with dwindling reserves has increased the need to develop alternate energy resources. In this regard, the utilization of agricultural, forest, municipal, and industrial wastes as potential energy sources has gained attention. Despite their different sources, they all have the same advantages of being renewable, abundant, and generally low in sulphur.

The concept of using biomass as a primary energy source is not new. Wood was a major source of primary energy and chemicals in the U.S. till only a relatively few years ago. As late as 1880, over 50 % of the U.S. energy demand was supplied by wood. After 1880, fossil fuels began to dominate as primary energy suppliers and have continued to be our largest source of energy to the present time. Now, as the costs of fossil energy increase and the available supplies, especially of petroleum and natural gas, shrink, we are beginning to return to a renewable source of fixed carbon in the form of biomass to assure a continuous supply of organic liquid and gaseous fuels and chemicals. It is generally not realized that the contribution by biomass, in all its forms, for the production of heat, steam, electric power, and synfuels for 1979 (in the U.S.) was about 1.9 quads (1 quad = 10^{15} BTU), or a contribution of about 2.3 % to the total primary energy consumption. Thus, biomass energy consumption is already equivalent to about one million barrels of oil per day (Klass, 1979).

Regarding the availability of biomass, a conservative estimate of the total continental production of the world puts the figure at 100 billion tons per year, or about 65 % of the total continental and oceanic value of 155 billion tons annually (Goldstein, 1981). The figure for the U.S. is about 3.5 billion tons/year, not counting unproductive or reserved forest land,

pasture or range land, swamp land, and industrial and urban areas. The actual available annual production of woody biomass which is harvested in the U.S. amounts to about 1.4 billion tons (plus 550 million tons of agricultural residue and 160 million tons of municipal waste). Over 700 million tons of this woody biomass is not used because it is not of the right species, size, fiber length, fiber morphology etc. (Goldstein, 1978). In contrast to the traditional procurement and usage restrictions, the form or nature of wood for conversion to energy or chemicals is not important.

The main disadvantage of biomass as compared to fossil fuels is their low energy density. This makes it uneconomical to use directly as fuels since large quantities have to be handled. Direct usage also results in significant air pollution problems. Thus, various processing options are being explored. Among these is gasification in a fluidized bed to produce a clean transportable gas suitable for use either as a chemical synthesis gas or more directly as a fuel gas.

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

A review of the literature on the gasification of various biomasses is presented in Chapter II. The review emphasizes experimental studies conducted using fluidized bed gasifiers. Basic devolatilization studies on cellulose pyrolysis are also discussed.

Chapter III presents the results of an experimental study of gasification of cottonwood (branchwood). This work focussed on the effect of reactor temperature on the product gas composition, heating value, gas yield, energy recovery, and carbon conversion.

Chapter IV deals with the attempts to gasify lignin in the fluidized bed reactor. Modifications on the system have been proposed to enable this study to be done.

Chapter V summarizes the major conclusions of this thesis and outlines the recommendations for extensions of this work.

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CHAPTER II

GASIFICATION –

A LITERATURE REVIEW

Introduction

Rising costs and the instability and uncertainty in the supply of fossil fuels combined with dwindling reserves has increased the need to develop alternate energy resources. In this regard, the utilization of agricultural, forest, municipal, and industrial wastes as potential energy sources has gained attention. Agricultural and forest wastes constitute biomass while municipal and industrial wastes can be classified as organic wastes. Despite their different sources, they all have the same advantages of being renewable, abundant, and generally low in sulphur. Also, the technology for their utilization as energy sources is the same since their thermochemical properties are similar. The main disadvantage stems from the fact that their energy density is very low compared to fossil fuels, making them uneconomical to use directly as fuels.

Various processing options are being explored to convert biomass into fuels or chemicals. The technologies for this conversion can be generally classified into two categories – thermochemical and biochemical. Figure 1 (Ward, 1981) illustrates the alternative conversion routes and the possible products from biomass and wastes. Thermochemical conversion denotes technologies that use elevated temperatures to convert the fixed carbon of the biomass materials by : 1) combustion to produce heat, steam, and/or electricity; 2) pyrolysis to produce gas, pyrolytic liquids, chemicals, and char; 3) gasification to produce low or medium BTU gas; 4) liquefaction to produce heavy fuel oils. Biochemical conversion entails energy yielding enzymatic breakdown of biomass by microorganisms via : 1) anearobic digestion to produce fuel gas (methane); 2) fermentation to produce liquid fuels (mainly ethanol).

In this thesis, one aspect of thermochemical conversion, namely gasification, is considered. Gasification may be defined as the process by which organic materials (biomass as well as solid fossil fuels) are degraded by thermal reactions in the presence of controlled amounts of oxidizing agents (oxygen, water, carbon dioxide, or a mixture of these) to provide, when carried to completion, a gaseous phase comprised of H_2, water, CO, CO_2, CH_4, and trace amounts of heavier hydrocarbons. A solid phase made up of carbonaceous or inorganic residues is also obtained.

Gasification can be distinguished from pyrolysis in that pyrolysis is performed in a completely inert environment, producing a complex volatile phase and char. On a practical basis, gasification is normally carried out at a higher temperature than pyrolysis. To accomplish gasification, it is always necessary to pass through a pyrolytic stage. Moreover, in practice gasification processes are seldom carried to completion as defined above, and both the amount and complexity of volatile products and carbonaceous residues increase as the conditions used for gasification are moderated towards those for pyrolysis.

Several types of reactors have been used to gasify biomass. They include packed (fixed) beds, entrained beds, moving beds, rotary kilns, and fluidized beds. Wan and Cheng (1978) have compared a number of thermochemical gasification technologies for biomass. Their paper presents a condensation of the major factors to be considered in the selection of a process for gasification. They have compared three basic types of commercial reactor beds : fixed, entrained, and fluidized. A summary of gasification reactors representing the state-of-technology is given. They have also compared three promising gasification technologies from coal gasification, municipal waste gasification, and catalytic hydrogasification.

Fluidized bed reactors have many advantages over other devices to gasifiy biomass. The more important ones are :

1) flexibility, with respect to feed materials, permits use of a wide range of liquid and solid feed stocks;

2) uniform temperature in the bed allows good control of the process resulting in consistent yields;

3) very high heat transfer rates between the bed and feed materials maximizes gas production and narrows the product distribution;

4) systems can be designed to be self sufficient in energy;

5) the system is easy to maintain and simple to operate, and it is flexible as far as operating conditions are concerned;

6) the system can be easily adapted to large or small scale operations; and

7) proper selection of feed materials, operating conditions, and/or catalysts can produce synthesis gas of specified qualities to be used as feedstock for further chemical processing.

To successfully design a commercial fluidized bed system which is economically viable, a vast amount of research and development is needed. While the technology for gasification had been available for quite some time, its development was superceded by the growth in importance of petroleum. Only in the last ten years have extensive studies on gasification of biomass, particularly in fluidized beds, been done.

The literature review presented here attempts to summarize the experimental work that has been done in this field, though it is not comprehensive in any respect. It attempts to present the operating conditions and the results obtained in various studies in a form so as to be easily compared with each other and with the work in this thesis. Although most of the emphasis is on the gasification of biomass materials, gasification of pure cellulose is also considered. Only fluidized bed systems are

considered except for the work on cellulose directed at investigating the basic pyrolysis mechanism. Detailed reviews of fixed and moving bed systems are presented by Reed and Jantzen (1979) and Brink (1981). For a review of the literature on theoritical and modelling aspects of fluidized bed reactors the readers are referred to Raman et al. (1981).

Before presenting results from different studies on biomass gasification, a review of the terminology involved will be helpful. When studying the gasification of carbonaceous materials, most investigators are interested in the characteristics of the gas such as its composition, yield (mass or volumetric), higher heating value, energy recovery, and carbon conversion. Different investigators present their results on different basis. Gas yield can be reported as off-gas yield or produced gas yield. Off-gas yield includes gas produced from the biomass feed plus the gas used to fluidize the bed itself. The produced gas yield represents the actual product from biomass by gasification. The produced gas yield is used primarily to report results obtained under partial oxidation conditions. Gas yields are normally reported in volumetric units produced per unit mass of dry ash-free (DAF) feed used. Gas composition involves reportingthe mole or volume fractions of the gas components present. The components depend on whether off-gas or produced gas is being considered. The higher heating value of the gas is calculated using the gas composition and the higher heating value of the individual components. The basis is important again. An attempt has been made to present the results from all the different studies in a uniform fashion in this review. Some results though could not be recalculated due to lack of pertinent information. A factor to be considered when dealing with volumetric units is the temperature and pressure used as a basis. All volumetric units reported throughout this

thesis have been calculated at the standard conditions of 101.3 kPa
(1 atm.) and 288 K unless stated otherwise.

Two other results which are frequently reported are the energy rec-
overy and the carbon conversion. Energy recovery of the product gas is a
measure of the effectiveness of the process. It is the ratio of the
heating value of the produced gas from a unit mass of DAF feed to the
heat of combustion of a unit mass of feed, also on a DAF basis. Another
measure of this conversion effeciency is the carbon conversion. It measures
the effectiveness of the process in converting carbon in the feed to carbon
in the gas. It is defined as the ratio of the moles of carbon in the pro-
duced gas from a unit mass of DAF feed to the moles of carbon in a unit
mass of DAF feed.

Gasification Studies in Single Fluidized Bed Systems

Among the early work done on fluidized bed systems was that of
Morgan et al. (1953) on the distillation of hardwood in a fluidized bed.
The unit consisted of a 0.0508 m pipe in which powdered hardwood was flui-
dized by preheated nitrogen. A preweighed amount of the feed was charged
for a batch operation at a given temperature. After operation for 30 mins.
at 673 K, they reported a charcoal yield of 32 wt. % of the dry charge, a
liquid yield of 29 wt. %, and a total gas production of 16 wt. %. The
23 wt. % loss was attributed to accumulation of tars and solids in the
product recovery train and inaccuracies in measurement of gas yield. The
gas was reported to contain significant amounts of CO, CO_2, and CH_4.

Kilburn and Levelton (1963) of the British Columbia Research Council
conducted tests on the charcoal production from fluidized bed. A 0.1524 m
I.D. reactor with a bed of incandescent charcoal was fluidized with
preheated air (or oxygen) and recycled wood gas. Sawdust was fed into the

reactor continuously and charcoal removed by an overflow system. Under
their best gasification conditions (1000 K, 1 atm.), the unit produced
approximately 1.1 m^3/kg. of dry feed of off-gas with a heating value bet-
ween 8.1 to 9.1 MJ/m^3. The charcoal yield was about 5 % of the feed. The
gas consisted of 10.5 % CO_2, 54.8 % CO, 18.9 % H_2, 11.3 % CH_4, and 4.3 %
illuminants.

Among the contemporary researchers, Bailie and Burton at West Virginia
University were the first in this country to study fluidized bed gasifi-
cation of biomass comprehensively. Burton's masters thesis (Burton, 1972)
reports on the gasification of ten different feed materials including
municipal solid waste, chicken manure, cow manure, and digested sewage
sludge. A 0.38 m I.D. reactor bed with an expanded disengaging zone was
used. Silica sand or limestone was used as the bed material. Hot fluidi-
zing gas was supplied by burning methane or propane under starving air
conditions. They studied the influence of temperature on the composition,
heating value, and yield of the produced gas for different feed materials.
The 15 experiments reported on biomass were done with reactor temperatures
ranging between 966 K and 1160 K. The produced gas had a H_2 composition
ranging from 23 % to 58 % over this temperature range. The percentage CO_2
ranged from 2 to 30 %, CO between 21 and 45 %, and CH_4 between 3 and 12 %.
The heating value of the gas varied from 10 MJ/m^3 at 966 K to 17 MJ/m^3 at
1160 K. The gas yield increased from 0.6 to 1.2 m^3/kg. DAF feed for the
 same temperature range. The energy recovery ranged between 38 and 91 %
and the carbon conversion from 34 to 97 %.

Maa and Bailie (1978) continued the pyrolysis studies at West
Virginia University with more fundamental studies with wood in the same
reactor. They studied the pyrolysis of individual wood cylinders over a

bed temperature range of 713 K to 1273 K. This study showed that pyrolysis rate increased with temperature of the bed. It also demonstrated the validity of the shrinking core model for large feed particles undergoing pyrolysis. Their experimental work verified Maa and Bailie's (1973) shrinking core reaction model proposed for the pyrolysis of cellulosic materials. The reaction time obtained experimentally agreed quite well with the predicted times calculated using their model and the parameters obtained from an independent TGA (thermogravimetric analysis) study.

Epstein et al. (1978) studied the potential of energy production from different crop wastes. They used a 0.5 m diameter reactor with the bed composed of sand. The system was operated between 773 K and 1273 K with the heat and fluidizing gas being supplied by burning natural gas. Among the various materials gasified, the results for corn cobs were presented in the most detail. The gas yield, reported as the mass fraction of feed, ranged from 17 % to 60 %, and tar yield decreased from 22 % to 3 %. The gas had a heating value varying from 5.4 MJ/m^3 to 10.9 MJ/m^3 and contained large amounts of CO and H_2. The complete composition was not reported.

Chen and Rei (1980) studied the gasification of rice husk in a 0.05 m diameter fluidized bed reactor. The reactor was heated electrically and fluidized with super heated steam. The bed was made up of fused alumina sand. They obtained a gas yield of 0.38 m^3/kg. DAF feed at 873 K and 0.55 m^3/kg. DAF feed at 973 K. For the same temperatures, the gas composition was found to be : H_2 3.6 and 13.1 %; CO 52.2 and 51.1 %; CH_4 14.4 and 13.5 %; CO_2 23 and 14.6 %. Small amounts of higher hydrocarbons $C_2 - C_4$ were also detected. By conducting an energy balance around the system, they estimated the heat of reaction of dry rice husk feed in pyrolytic gasification to be 0.84 MJ/kg. of dry rice husk (endothermic).

Researchers at Texas Tech University studied the partial oxidation of cattle manure in a 0.15 m I.D. pilot reactor (Beck et al., 1979). An air-steam mixture was used as the fluidizing gas and the bed was made up of only the feed materials and char. With temperature variations of as high as 500 K along the axis of the reactor, the quality of their fluidization is in doubt. Feldmann (1978) reported a similar case where a bed of wood chips alone, resulted in poor fluidization. Beck et al., reported nine experiments over a temperature range of 790 K to 909 K. Their gas yield increased with temperature, the off-gas yield ranging from 0.36 m^3/kg. DAF feed at 790 K to 1.18 m^3/kg. DAF feed at 909 K. The off-gas heating value varied between 9 and 12 MJ/m^3 and the energy recovery ranged from 20 % to 60 % at 790 and 909 K respectively. Carbon conversion also increased with temperature and varied from 27 % to 60 %. Their off-gas composition did not show any consistent pattern although it had significant amounts of CH_4 and C_2H_4.

Beck and Wang (1980) used the same reactor to study the gasification of oak sawdust. The total off-gas yield for operation between 893 K and 1053 K ranged from 1.2 m^3/kg. DAF feed to 1.52 m^3/kg. DAF feed. They compared their gas yields obtained from sawdust to those from the earlier feedlot manure runs in Beck et al. (1979), and noted that the yield from sawdust was significantly greater. Inert-free off-gas compositions were also reported at 893 and 1053 K : H_2 16.7 and 16.5 %, CO 38.1 and 40.1 %. CO_2 30.9 and 21.5 %, CH_4 8.2 and 16.0 %, C_2H_4 4.3 and 5.3 %, C_2H_6 1.7 and 0.6 %.

Schoeters et al. (1981) gasified linden wood shavings in a 0.15 m fluidized bed reactor. The bed was made of sand and fluidized with air or anair-steam mixture. They studied the influence of the air-factor, steam

rate, and reactor freeboard temperature on the gasification results between 923 K and 1123 K. The air-factor was defined as the ratio of the actual flow rate of air to the flow rate required for complete stochiometric combustion of the feed. The off-gas yield varied between 2 and 3 kg. gas per kg. fuel. The higher heating value of the off-gas ranged from 4 to 5 MJ/m^3, and optimum energy recovery was about 60 %. An increase in the air-factor caused the yield to increase, the HHV to pass through a maximum, and the energy recovery to be almost unchanged. They found that high steam rates lowered the HHV, the gas yield, and the energy recovery. The freeboard temperature influence was studied by varying it from 25 K above the reactor bed temperature to 150 K below. It was shown that the freeboard temperature had a considerable influence on gas yield, composition, and heating value. The concentrations of CO_2 and H_2 increased while that of CO decreased with an increase in freeboard temperature. This was explained by the water-gas-shift reaction where CO reacted with steam to produce CO_2 and H_2. They expected that above 1123 K, the CO should start increasing due to a reversal in the direction of the reaction.

van den Aarsen et al. (1982) investigated beechwood pyrolysis in a 0.03 m I.D. fluidized bed reactor with nitrogen as the fluidizing agent. Heat was provided by electrical furnaces surrounding the reactor body. Their objectives were to deduce and interpret kinetic data on the pyrolysis of small wood particles at heating rates of 250 - 1000 K/s., such as those found in fluidized beds, and to study the product distribution. For temperatures between 973 K and 1273 K, they obtained gas yields ranging from 0.6 m^3/kg. feed to 0.817 m3/kg. feed. The CO concentration in the gas ranged from 51.2 % at 973 K to 45.3 % at 1173 K while H_2 varied from 15.7 to 26.3 %; CO_2 from 14.1 to 11.2 %; CH_4 from 14.1 to 12.4 %; and the C_2 - C_3

volatiles from 4.7 to 4.1 % over the same range of temperatures. Energy recovery was found to be essentially constant between 70 and 72 %.

Using kinetic data evaluated from their results and applying it to a first order Arrhenius type expression, they predicted that the pyrolysis of a 1 mm wood particle is essentially completed in 2 seconds, for heating rates of about 500 K/s. Further, they correlated char yield as a function of particle diameter by combining their data and that from Epstein et al. (1978) and Sakoda et al. (1981). For a reactor at 1173 K, char yield increases linearly with particle size (5 % for 1 mm dia. to 22 % for 10 mm dia.). For an operation temperature of 973 K, the variation is parabolic (10 % for 1 mm dia. particle, 22 % for 5 mm dia., and 26 % for 7 mm).

Lian et al. (1982) at the University of Missouri studied air-blown wood gasification in a set of different sized fluidized bed reactors. The four reactor sizes used were 0.15 m I.D., 0.56 m I.D., 1.02 m I.D. (bottom feed), and 1.02 m I.D. (top feed). The beds were made up of sand and gravel while the feed was screened oak sawdust. The fluidizing gas was preheated air which also supplied oxygen for gasification and partial combustion to bring and maintain the bed at reaction temperature.

Their combined char and tar yields decreased with increasing bed temperature from about 6 % by weight of dry wood at 923 K to 0 % at 1073 K. After examining a number of operating variables (temperature, flow rate of wood, air, residence time etc.) they found that the ratio of total carbon-to-nitrogen in the dry gas correlated best with the important properties of the product gas including % C, % H, and heating value. Their results indicated that at a given total carbon-to-nitrogen ratio, the gas quality is only slightly affected by wide variations in the type of reactor, the existence

of thermal steady state, the type of feed, the moisture content, the residence time, and the bed temperature. However, these variables did affect the char and tar formation and the total carbon-to-nitrogen ratio. Correlation equations were also given for heating value, total carbon in dry gas, and the gas component fractions. Steps to estimate the requirements (reactor volume and inlet air temperature for choosen feed rate, air flow, bed temperature, and moisture content) for an air-blown wood gasification were also suggested based on these correlations.

Researchers at Kansas State University have conducted extensive studies on the gasification of carbonaceous materials in fluidized bed reactors. Walawender and Fan (1978) reported preliminary results on the gasification of feedlot manure in a 0.23 m I.D. fluidized bed reactor similar to the system at West Virginia University. The sand filled bed was fluidized by a mixture of steam and flue gas generated from burning propane under starving air conditions. They found that the produced gas yield ranged from 0.44 to 1.02 m^3/kg. DAF feed 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 %. Further investigations on this system were reported by Raman et al. (1980a) for feedlot manure over a temperature range of 900 K to 977 K. Their produced gas yield increased from 0.4 m^3/kg. DAF feed at 900 K to 0.62 m^3/kg. DAF feed at 977 K. The produced gas heating value increased with temperature from 12.5 to 21.5 MJ/m^3. Energy recovery ranged from 20 % at 900 K to 58 % at 977 K. Their results compared favourably with those obtained from the gasification of municipal waste (Tsukishima, 1975). The trends for produced gas compositions and yields with temperature were similar for both materials.

One of the problems discussed in the gasification of manure by

Walawender and Fan (1978) was agglomeration of the bed when the system was
operated in a reducing atmosphere for more than 7 to 8 hours. Others who
reported similar problems were Burton (1972) for municipal sewage sludge
and Araki et al. (1979) for tires. The agglomeration of the bed was suspec-
ted to be a consequence of the alkali salts present in the feed. These salts
react with the sand to form low melting silicates which could cause the bed
to become bound after a sufficient amount of time. It was observed that
fluidization could be re-established with the system being operated under
oxidizing conditions (Walawender and Fan, 1978). Walawender et al. (1981)
then tested the influence of limestone as a bed additive in steam gasific-
ation of manure in a 0.05 m I.D. bench-scale reactor. Limestone was found to
prevent the agglomeration and subsequent choking of the bed. Differences in
the quality and quantity of the gas were observed when the additive was used
over when it was not. The differences were attributed to the quality of
fluidization or the catalytic influence of limestone (see also Feldmann,
1978) or a combination of the two factors.

Work at Kansas State University continued with an investigation into
the effects of superficial gas velocity and feed size fraction on the gasifi-
cation results. Raman et al. (1980b) found that superficial velocity did not
have a significant influence on gas yield, composition or heating value. On
the other hand, the feed size fraction significantly influenced the results.
The produced gas yield at a particular temperature increased with a decrease
in feed size fraction. The yield for the smallest size studied (-14 +40 mesh)
ranged from 0.05 m^3/kg. DAF feed at 800 K to 0.85 m^3/kg. DAF feed at 1025 K.
For the largest size fraction (-2 +8 mesh), the yield ranged from 0.1 m^3/kg.
DAF feed at 900 K to 0.6 m^3/kg. DAF feed at 1010 K. The heating value of the
produced gas was also influenced by the feed size fraction. All heating

value - temperature plots were parabolic in shape with the temperature for the maximum heating value shifting to the right with an increase in feed size. The heating value of the largest feed size ranged from 12.0 to 19.75 MJ/m^3 with a maximum at 980 K; that of the smallest fraction ranged from 10.4 to 18.3 MJ/m^3 with a maximum at 910 K. Gas composition, particularly CO, H$_2$, and CO$_2$ were also affected although the trends with respect to temperature were the same for the different sized feeds.

Among the other feed materials gasified in the same reactor were cane, sewage sludge, manure, and rubber tires (Walawender et al., 1980). The results of gasification were found to be dependent on both temperature of gasifier and feed material. For temperatures below 1000 K, the gas yield was the highest for cane, followed by manure, sludge, and tires respectively. Above 1000 K, cane still showed the highest yield followed by manure, tires, and sludge in that order. The produced gas higher heating value (HHV) was the highest for tires and then sludge, manure, and cane respectively.

The same group also studied the gasification of corn stover (Raman et al., 1980c) and wheat straw (Walawender et al., 1982a). They found that over a reactor temperature range of 825 K to 1030 K in a 0.23 m I.D. reactor, corn stover gave a higher volumetric yield than wheat straw, but a lower heating value. Energy recoveries and carbon conversion for both materials were almost the same. Volumetric gas yields also increased with increasing temperature for both feeds.

Another investigation was done on the steam gasification of corn grain dust in the 0.05 m I.D. bench-scale fluidized bed reactor (Hoveland et al., 1982). Experiments were conducted over a temperature range of 867 K to 1033 K and the gas yield was found to be strongly dependent on temperature. It increased linearly from 0.13 m^3/kg. DAF feed at 867 K to 0.73 m^3/kg. DAF

feed at 1033 K. The produced gas heating value increased from 9.4 to 11.5 MJ/m^3 over this same range with a maximum of 11.6 MJ/m^3 at 1002 K. The principal components of the gas were H_2, CO, CO_2, and CH_4. The H_2 concentration increased linearly from 41.3 % to 49 %; CO decreased from 24.3 % to 11.8 %; CO_2 ranged from 33.4 % to 31.9 % with a minimum of 25.2 % at 955 K; and CH_4 increased linearly from 3.1 % to 5.7 %. Energy recovery varied from 8 % at 867 K to 55 % at 1033 K.

Gasification Studies in Dual Fluidized Bed Systems

The pyrolysis of municipal waste was evaluated by Tsukishima Kikai Co. in a twin bed system with solids circulation between the beds (Tsukishima, 1975). Char residue from pyrolysis in the first bed was carried by the circulating sand to the second bed where it was burned. The heat was gained by the sand and recirculated back to the gasifier. Experiments were performed over a temperature range of 723 K and 1123 K using steam as the fluidizing agent. Their produced gas (raw) yield increased with temperature from 30 to 85 wt. % of the feed over this temperature range. The composition of the raw gas showed that H_2 increased from 4 % to 35 % over the temperature range; CO decreased from 16 to 12 %; CH_4 passed through a maxima and ranged from 5 % to 16 %; C_2H_6 from 2 to 6 % and C_3H_8 from 2 to 13 % also showed maximas. The rest of the gas was composed of CO_2, varying between 20 to 40 %. Traces of H_2S and NH_3 were also detected. The higher heating value of the raw gas (including CO_2, H_2S, NH_3) also had a maximum value of 27 MJ/m^3 at 993 K and varied from 19 to 18.5 MJ/m^3. The weight percent (of original matter) yield of char and tar were also reported: Char 60 % at 723 K and 6 % at 1123 K; tar 11 % at 723 K, 12.5 % at 773 K, and 2 % at 1123 K.

Among the advantages reported for twin bed systems were:

1) since the pyrolysis of refuse and the heating of the heat transfer media (to supply heat for pyrolysis) proceed in separate beds, the combustion gas does not mix with the product gas. Consequently, the gas obtained has a higher HHV than gas from a single bed;

2) it is possible to separate the inorganics mixed in the feed;

3) heat of pyrolysis in the reactor is distributed evenly. The pyrolysis thus occurs at a relatively uniform rate and temperature.

Hasagewa et al. (1979), also from Tsukishima Kikai Co. later reported on gasification experiments in three different sized reactors. The first was a 0.05 m single fluidized bed reactor which used alumina particles as the solid media, and was fluidized by super heated steam. Using municipal solid waste as feed, they obtained gas yields of 0.09 m^3/kg. dry feed at 773 K increasing to 0.8 m^3/kg. at 1073 K. The second unit studied was a 0.1 m I.D. bed coupled with a fluidized bed regenerator with sand circulation between the two. Gas yield from this twin-bed system was higher than from the single bed operated at the same temperature. With the same feed, 0.30 m^3/kg. dry feed of gas was produced at 823 K, which increased to 0.7 m^3/kg. dry feed at 973 K. The heating value of the produced gas ranged from 14.6 to 18.0 MJ/m^3. Finally, a scaled-up twin bed system with a 2 m I.D. bed was used. Feed materials tested included organic sludge from paper and pulp plants, waste plastics, municipal solid waste, and tires. With municipal solid waste as feed at 973 K, the gas yield was 1.3 m^3/kg. dry feed with a heating value of 16 MJ/m^3. The volumetric composition of the gas was H_2 18.5 %, CO 34.6 %, CO_2 17.0 %, and CH_4 5.6 %. The energy recovery was 67 % and carbon conversion 63 %.

At Arizona State University, Kuester (1979) gasified cellulosic wastes in a dual fluidized bed reactor system with a capacity of 11 kg./hour. His reactor was similar to the one reported in Tsukishima (1975). The bed, made up of inert solids was fluidized with recycled product gas. Kuester studied the gasification of several feedstocks including paper, kelp residue, and guayule bagasse over a temperature range of 873 to 1073 K. He obtained gas yields as large as 95 wt. % of the feed. The product gas had a heating value of 18.6 MJ/m^3, and a volume fraction of H_2 17 - 33 %; CO 40 - 55 %; CH_4 13 - 17 %; C_2H_4 5 - 10 %; and CO_2 3 - 8 %. The produced gas was subsequently converted to liquid fuels via the Fischer Tropsch synthesis.

Among the others who used the twin (dual)- bed concept were Feldmann et al. (1981) who studied the steam gasification of wood in a multi-solid fluidized bed (MSFB) gasifier. Their system consisted of a 0.15 m I.D. dense-phase fluidized bed reactor coupled with a 1 m I.D. fluidized bed combustor. Operation involved feeding wood and a mixture of steam and recycled product gas into the dense-phase reactor with entrainment of wood-char and sand into the combustor. Char was burned in this bed with air and the heat was transferred back to the gasifier with the recirculating sand. The dense phase itself was made up of larger sized inert particles. The advantage of this system was that the entrained-phase passing through the dense-phase fluidized bed created bubble free fluidization and increased heat and mass transfer in the reactor. Since the entrained-phase was made up of char and sand, coarser wood particles could be used as feed.

The objective of this study was to characterize the system and study the influence of gasifier temperature, wood feed rate, steam rate, entrained-phase recycle rate, wood particle size and moisture content, and dense-phase particle size and height on gasifier performance. Silica pebbles and alumina

pellets were tested as the dense-phase material but these were rapidly ground up in the bed and elutriated. Subsequent experiments were then run with only the entrained-phase providing mixing and transport while the search for a good dense-phase material went on.

The gasifier temperature was found to have the most influence on gasification of all the variables studied. Increasing temperature increased carbon conversion from 30 % at 963 K to 70 % at 1171 K although feed moisture content (20 %) was also a factor in the results. Wood with a lower moisture content (6 %) gave carbon conversions up to 80 %. Conversion was limited by the maximum temperature reached by the wood and the time it took the wood to dry which is a function of the moisture content. Energy recovery of the gasifier ranged from 25 % at 963 K to 70 % at 1171 K. Heating value increased from 15.8 MJ/m^3 to 17.7 MJ/m^3 with a maximum of 18.1 at 1116 K. Typical produced gas compositions were also given. Methane ranged from 13.3 % at 977 K to 15.5 % at 1088 K. The corresponding compositions of the other components were H_2 11.2 % and 13.3 %, CO 50.5 % and 49.2 %, C_2H_6 1.6 % and 0.8 %, C_2H_4 4.9 % and 5.9 %, CO_2 18.5 % and 15.7 %.

Cellulose Pyrolysis and Gasification

With the accumulation of data on the gasification of biomass and wastes, it became obvious that there was an apparent correlation between the quantity and quality of the produced gas and the feed composition, especially its cellulose content.

Beck and Wang (1980) found significantly greater yields from sawdust than from feedlot manure (Beck et al., 1979). The difference was attributed to the difference in composition of manure and sawdust. Sawdust had 43 % cellulose, 25 % hemicellulose, and 22 % lignin. Manure contained 16 % protein along with 7.7 % fat, and 75 % fiber (cellulose, hemicellulose, lignin).

Cattle manure was higher in lignin and lower in cellulose compared to wood due to digestion of cellulose by the cow. Cellulose is also easier to gasify than lignin.

TGA studies by Antal et al. (1978) on steam gasification of organic wastes showed an apparent correlation between cellulose content of the feed and the extent of devolatilization it undergoes. Pure cellulose devolatilized about 90 % when exposed to high heating rates. Paper devolatilized about 85 % under similar conditions. Hardwood (cherry), which contains between 54 and 62 % cellulose lost 80 % of its weight. Softwood (southern yellow pine) with 53 % cellulose lost approximately 70 % of its weight. Manure devolatilized the least at 60 % and had the least amount of cellulose.

Walawender et al. (1980), in their gasification of cane, feedlot manure, and sewage sludge indicated qualitatively that yield appeared to correlate well with the cellulose content of the materials. The higher the cellulose content, the higher the yield and the easier the gasification. High cellulose feeds also seemed to produce a lower quality gas. Raman et al. (1980b) in their study on different feed size fractions of manure, found that the different sizes produced different gas yields. This difference was again attributed to the different cellulose contents of the various fractions as the material make-up of each fraction was different.

It was evident that in order to understand the gasification of biomass; to be able to predict, however approximately, the yield from a particular feed, condition and process combination, the gasification of pure components that make up biomass should be studied. This data-base, while helping in designing gasification plants, would also provide a datum which could serve as a bench mark in gauging biomass gasification processes.

A short discussion of the pyrolysis chemistry of cellulose is in order

here. This subject has been extensively studied by many people and the material presented here has been based on two review papers by Shafizadeh (1968, 1982). Cellulose is a macro-molecule composed of linearly linked β- (1 - 4) - D - glucopyranose units as shown in Figure 2. The structure is the same in all types of biomass except for their degree of polymerization. Pyrolysis of cellulose proceeds through a complex series of cocurrent and consecutive chemical reactions. It is highly influenced by the temperature and period of heating, particle size (rate of mass and heat transfer), and the environment in which the process is carried out. Shafizadeh (1968) proposed the general reaction scheme for cellulose pyrolysis shown in Figure 3. The process is divided into two sets of reactions-primary and secondary, occuring at different stages.

Primary Reactions (1, 2, 3)

Thermal degradation of cellulose proceeds through two types of reactions - a gradual degradation, decomposition, and charring on heating at the lower temperatures (below 523 K, reaction 1, Figure 3); and a rapid volatilization accompanied by the formation of levoglucosan on pyrolysis at the higher temperatures. The rates of these two reactions and of the overall decomposition process are also highly dependent on the pyrolysis atmosphere.

The initial degradation reactions include depolymerization (bond scission), formation of free radicals, elimination of water, formation of carbonyl, carboxyl, and hydroperoxide groups (especially in air), evolution of carbon monoxide and carbon dioxide, and finally, production of charred residue. It has been found that water and oxygen have a profound effect in enhancing thermal degradation of cellulose. Degradation is more pronounced in air/oxygen than in nitrogen.

At temperatures above 523 K, vacuum pyrolysis of cellulose provides,

in addition to water, CO, CO_2 (depolymerization, decomposition), a volatile tar which contains mainly levoglucosan (1, 6, anhydro - D - glucopyranose), and leaves a charred residue. Under these conditions, the oxidation reactions are eliminated or minimized, and the levoglucosan is rapidly removed from the heated area where it could undergo further decomposition. It has also been shown that pyrolysis of cellulose in a nitrogen atmosphere proceeds at almost the same rate as pyrolysis under vacuum, but a lower yield of tar and a greater yield of the lighter fraction results. This is because of appreciable secondary reactions involving the intermediate fragments. The purity and physical properties of cellulose also appear to have a significant effect on the yield of levoglucosan.

Secondary Reactions (4, 5, 6, 7)

Products from the primary reactions, if not rapidly removed from the heated environment, can further react and decompose to provide a series of secondary components of low molecular weight. For temperatures greater than 515 K, the degradation products of cellulose and levoglucosan are essentially identical including char. For a big enough particle, the layer of hot char that is formed on the surface covers the path of the volatile compounds evolving from pyrolysis of the inner materials, and would be expected to participate in the secondary reactions. The participation could be either as a catalyst, or more directly as a reacting material (reaction 6, Figure3). It has been shown that hydrogen, methane, ethane, and propane are formed at the later stage of pyrolysis, when the char layer becomes hot enough (above 873 K) to react endothermically with the pyrolysis products. This observation indicates the reduction of the pyrolysis products by the hot char, to form CO and other compounds mentioned before. The H_2 could be derived from water by the water-gas-shift reaction, and the hydrocarbons could originate

from the reduction of heavier organic compounds (Shafizadeh, 1968). The author alsomentions that little is as yet known about the catalytic effect of hot char in promoting secondary reactions such as cracking of levoglucosan and tarry materials of higher molecular weight to give lighter compounds.

He indicates that there is indirect evidence to show that these low molecular weight materials are formed from the secondary reactions of tar and from the high temperature interaction of char with water and CO_2 (Shafizadeh, 1982). However, the possibility of direct conversion of cellulose molecules to the low molecular weight products cannot be entirely eliminated. Under the conditions in which the molecule is physically torn to pieces, it is very probable that more than one mechanism or set of mechanisms are involved, thus producing a multitude of degradation products.

A report was presented by Lipska and Parker (1966) on the kinetics of pyrolysis of cellulose in the temperature range 523 - 573 K. They isothermally pyrolyzed α- cellulose in a fluidized bath in a nitrogen environment. Their findings showed three distinct stages of pyrolysis; 1) an initial period of rapid decomposition and devolatilization; 2) a range in which both the devolatilization and decomposition are of zero-order; 3) a stage in which the devolatilization follows a first-order expression leaving a char deposit that undergoes no further pyrolysis.The transition between the zero and first order behavior occurs at a greater degree of pyrolysis as the temperature is increased. At 563 K, initial volatilization leaves about 94 % of the original weight and the zero to first-order transition occurs at about a point where 50 % of the original weight remains. The residual char is around 16 % between 549 K and 573 K and is substantially greater at lower temperatures.

An important observation they made was that pyrolysis of cellulose is kinetically similar whether the cellulose is in the form of paper or cotton and whether the experiment is performed in vacuum or in nitrogen.

Antal et al. (1978) studied the pyrolysis/gasification characteristics of cellulose and cellulosic materials in a modified Dupont 951 Thermal gravimetric analyzer, in atmospheres of steam and nitrogen. The objective was to determinethe conditions which favor the formation of hydrocarbons from biomass using thermochemical techniques. This was accomplished by studying the effects of various reactor conditions (residence time, heating rate, and temperature) on the rates of the primary pyrolysis reactions and the rates and products of the secondary gas phase reactions. They reported that gasification occurs in three steps. The first involves devolatilization producing volatiles and char. This step starts at about 573 K and is complete around 723 K. Cellulose looses about 90 % of its weight during this step. The second step involves cracking and reforming of volatile matter formed in the first step. This step occurs at temperatures greater than 873 K and produces a hydrocarbon rich synthesis gas. The third step is char gasific- ation above 1073 K. This step is not very important for cellulose since the amount of char formed from cellulose is very small.

Although each of these steps plays a role in commercial reactors designed for biomass gasification, the ultimate product distribution is largely determined by the second step of the gasification process. Careful control of reactor conditions (i.e. gas phase residence time and temperature) can favor the formation of one set of products over another.

Antal et al. (1978) also presented a schematic which attempts to summarize the findings of various workers on the mechanism of cellulose pyrolysis, as shown in Figure 4. The first step is a decrease in the degree

of polymerization (DP) to about 200 with no detectable weight loss. From this point on, the mechanism appears to branch on the assumption that a molecule as complex as cellulose should have more than one chemical decomposition pathway available, and the implentation of one of these pathways increases or decreases the likelihood of another taking place. A dehydration or thermal auto-crosslinking reaction leads to the formation of anhydrocellulose. This may continue to react further to form most of the char and some volatiles.

Competing with anhydrocellulose reaction is a series of sequential depolymerization reactions which eventually produce a levoglucosan tar. This tar may either form char and some volatiles, or mainly volatiles depending upon the experimental conditions. The presence of acids or bases may catalyze the conversion of levoglucosan tar to char. Pyrolysis conditions utilizing high temperatures virtually eliminate the tar forming route and bring about the complete conversion of cellulose to volatiles.

Antal (1979) also studied the secondary reactions of the volatiles derived from cellulose pyrolysis in a quartz plug flow reactor. Cellulose was pyrolyzed by super heated steam and the evolved gases then passed into a gas phase reactor where its residence time could be controlled. The experiments focussed on the effect of temperature and residence time on these reactions. His results indicated that gas phase reaction temperatures affect gasification results most significantly. The role of primary pyrolysis conditions and the gas phase residence times are much less important. For temperatures above 923 K, the initial rate of species formation is very high so that much of the gas formation is complete in less than 0.5 seconds. Over the temperature range used (773 K to 1023 K), the yield of gases and the carbon conversion increased with temperature. At 1023 K, the carbon

conversion was about 80 %, energy recovery 83 %, and tar yield about 2 % of initial feedstock weight (residence time 3.5 s). An investigation into the effect of increased pressure showed that this inhibited gasification.

Diebold (1980) used an entrained flow pyrolysis reactor to investigate the pyrolysis of pure cellulose under steady state operating conditions. The system consisted of a metered amount of carrier-gas conveying a solid feed at a known rate into a steam ejector. The solid feed, carrier-gas, and the super heated steam then passed through a helical pyrolysis tube located in a gas fired kiln. The products were quenched after separation of the solids. Residence times were calculated as the amount of time spent in the helical tube, and were of the order of fractions of a second. Problems were reported with pressure fluctuations in the system which caused the feeding to be intermittent. The performance of the set-up was quite unsatisfactory and some changes were being made at the time the report was written. Of the six runs performed with cellulose using CO_2 as the carrier-gas, only two produced data useful for quantitative evaluation. Gas yield at 1017 K was reported as 0.07 m^3/kg. feed and at 1027 as 0.12 m^3/kg. feed. The produced gas consisted of: CO (60 and 53 %), H_2 (19 and 23 %), CH_4 (8 %), C_2H_4 (6 %), CO_2 (3 and 5 %), at 1017 K and 1027 K respectively. The high CO content of the gas was attributed to the high oxygen - to - carbon ratio of the cellu-lose feedstock and the near absence of free carbon or char in the product stream.

Most of the available information on cellulose was from batch processing experiments and under transient conditions. Researchers at Kansas State Univ. (Walawender et al., 1982b) focussed their attention on gasification of pure μ- cellulose in a fluidized bed reactor, with the gasification being examined under steady state conditions. The gas composition and yield were

studied as functions of temperature with the gas residence time being held fairly constant (1.26 - 1.54 s). A 0.05 m I.D. bench-scale reactor was used. The fluidizing media was steam. The freeboard and the reactor bed temperatures were kept the same by controlling the heaters surrounding the reactor. The major components of the produced gas were CO, CO_2, H_2, and CH_4, comprising over 90 % of the gas. The gas yield ranged from 0.5 m^3/kg. DAF feed at 865 K to 1.4 m^3/kg. DAF feed at 1060 K. The higher heating value of the gas averaged 11.8 MJ/m^3. The energy recovery increased with temperature from 32 % to 82 % while the carbon conversion increased from 32 % to 89 % over the temperature range studied.

A mechanistic model was proposed which described the gasification of cellulose between 865 and 1060 K as being composed of two distinct regimes. The first regime, up to 940 K, was described as being controlled by the cracking of volatile matter and it showed a rapid rise in gas yield with increasing temperature. The gas yield rose much more slowly with temperature above 940 K. The water-gas-shift reaction was considered to be the dominant reaction in this regime. These regimes, with their distinctly different slopes were evident in the energy recovery and carbon conversion vs. temperature plots also.

This hypothesis could qualitatively explain the various trends observed in the results. It was further tested quantitatively by assuming that the increase in gas yield above 940 K was solely due to the water-gas-shift reaction. The rate of increase in gas yield was related to the rate of change in mole fractions of H_2, CO, CO_2. Good agreement was found between the calculated rates of change in mole fractions of these components and the experimental data above 940 K.

This work was extended by examining the effect of elevated freeboard

temperature on the steam gasification of α-cellulose (Hoveland, 1982). This involved controlling the operation of the system so that the temperature in the expanded freeboard section was higher than the bed temperature. The freeboard elevation reported was the difference between these two temperatures. Two freeboard elevations 28 ± 1 K and 83 ± 2 K were used. Since the final results are mainly determined by the secondary gas phase reactions occuring in the freeboard, this type of experiment was useful in confirming the nature of these reactions, when compared with the 0 K elevation (flat profile) results in Walawender et al. (1982b).

The two regimes reported in Walawender et al. (1982b) - cracking dominated and water-gas-shift dominated were evident again. Both elevations showed changes in apparent slopes of the results around 940 K. In the first regime (below 940 K), the higher freeboard temperatures (for the same bed temperature) resulted in increased cracking of the volatiles, and thus, increased gas yield, energy recovery, and carbon conversion. The gas compositions for 28 K elevations were similar to those reported in Walawender et al. (1982b). Gas compositions for the 83 K elevations were significantly different from the 0 K elevation results, but no explanation for this behavior could be found.

In the second regime (above 940 K), where the water-gas-shift reaction dominates, an 83 K elevation in freeboard produced a lower gas yield and energy recovery when compared to the 0 K elevation results above 1000 K. An elevation of 83 K placed the freeboard above 1083 K for bed temperatures above 1000 K. Since the equilibrium of the water-gas-shift reaction shifts to the left above 1083 K, this would have a tendency to reduce the yield and the energy recovery as was observed. Thus the observation was consistent with the hypothesis. For the 28 K elevation results above 1055 K, a similar

effect could be seen in the results. The gas composition results, especially for the 83 K elevation, also agreed well with the hypothesis. Above 1000 K, the 83 K elevation showed lower molar concentrations of H_2, CO_2, and higher concentrations of CO, than the 0 K results at the same bed temperatures.

A review of the literature has shown that there are several groups studying the gasification of biomass in fluidized bed reactors. It is generally agreed that the reactor temperature is the major factor influencing the process and the results of gasification. As the temperature increases, the gas yield tends to increase while the heating value of the gas goes down. Many researchers have also found an apparent correlation between gasification results and cellulose content of the feed : as the cellulose content increases so does the gas yield. It has been realized that in order to understand gasification and ultimately, to properly design such a system, information from the gasification of pure components of biomass would be needed. This data base can also serve as a basis for characterizing biomasses and biomass gasification processes.

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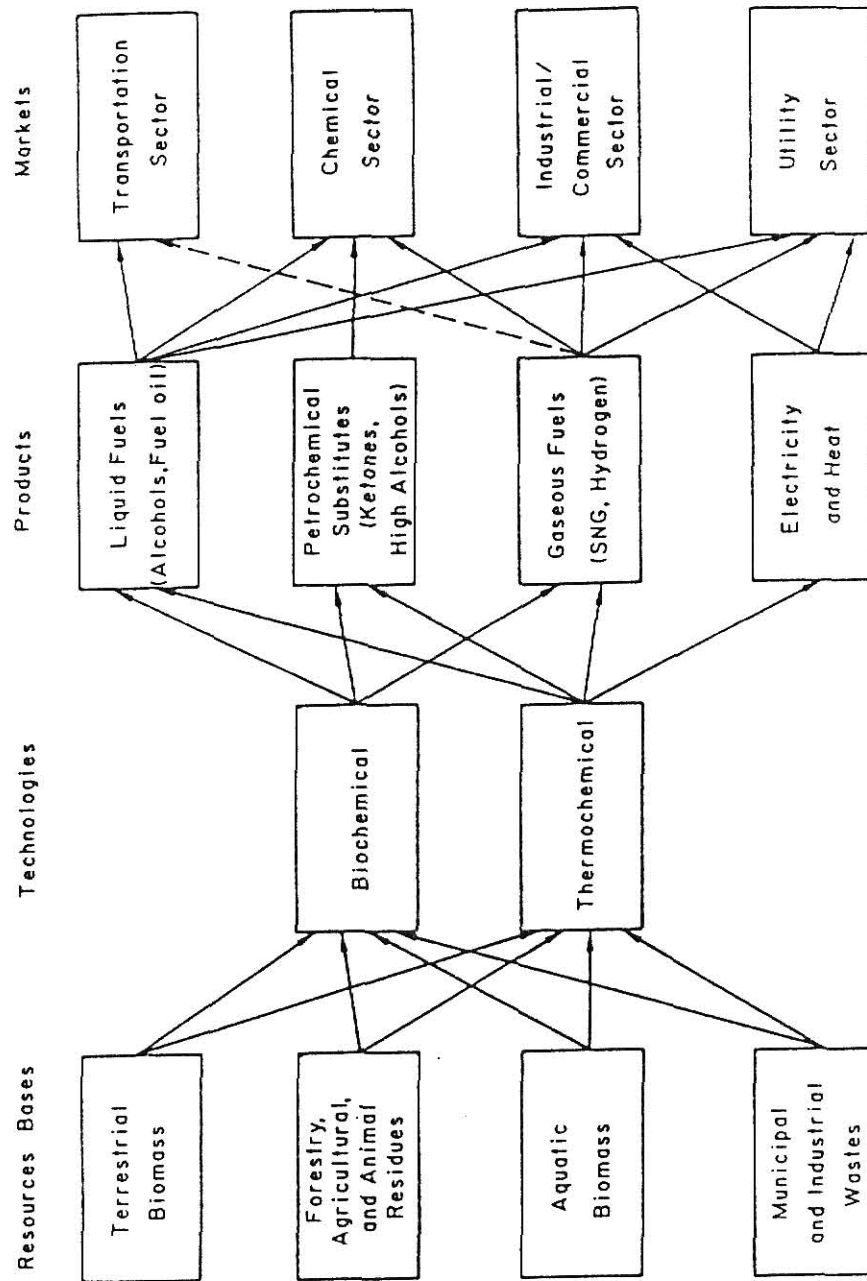
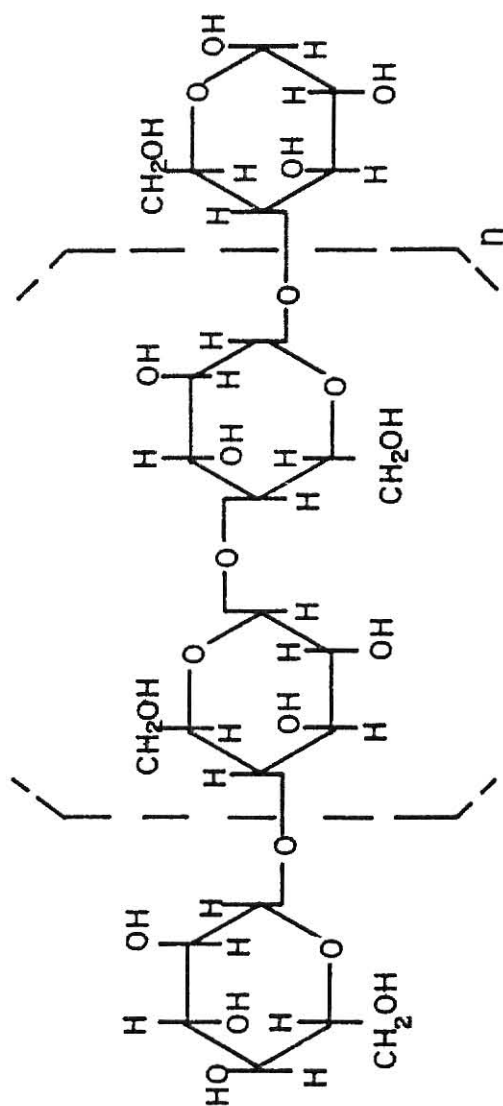Figure 1. Possible Conversion Routes and Products from Biomass and Wastes (Ward, 1981).

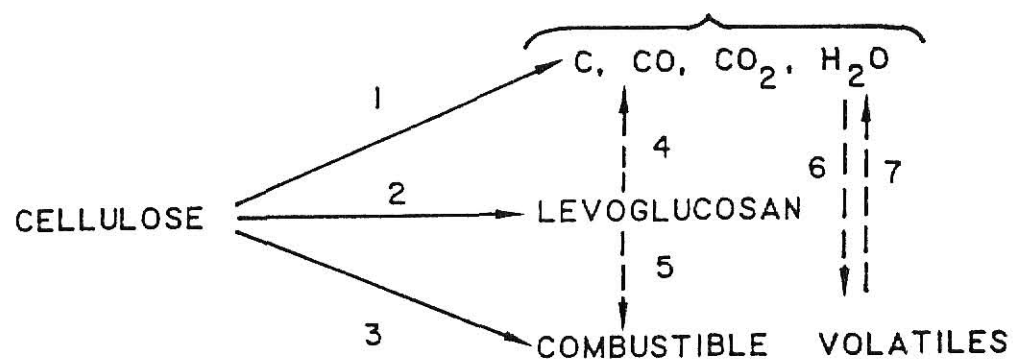Figure 2. Molecular structure of alpha cellulose.

Figure 3. General Reactions Scheme in Pyrolysis of
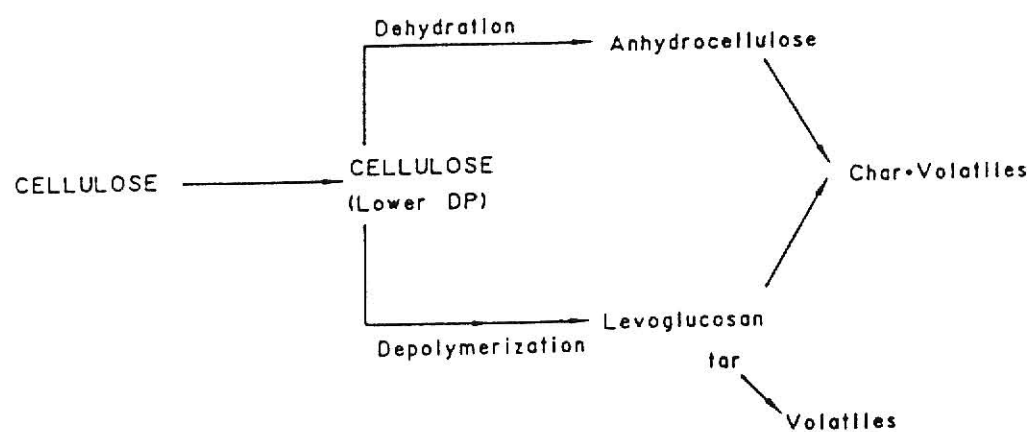Cellulose   (Shafizadeh, 1968).

Figure 4. Mechanism of Cellulose Pyrolysis
(Antal et al., 1978).

CHAPTER III

STEAM GASIFICATION OF COTTONWOOD

(BRANCHWOOD) IN A FLUIDIZED BED REACTOR

Introduction

Gasification is an attractive method for converting wood or any biomass into a clean gas, usable for either chemical synthesis or directly as a fuel. Currently, wood provides about 2 % of our total energy needs and could contribute up to 8 % within the next decade (Zerbe, 1981). The actual available annual production of woody biomass which is harvested amounts to about 1.4 billion tons in the U.S. alone. Over 700 million tons of this production is not used because it is not of the right species, size, fiber length, fiber morphology etc. (Goldstein, 1978). Branchwood is a prime example of this type of wood waste. Thus the potential for the utilization of wood to ensure a continuous supply of organic liquid and gaseous fuels and chemicals is undeniable.

Some advantages of wood as a gasification feedstock over solid fossil fuels (coal, oil shale) are its higher gasification reactivity, its lower sulphur content, and its lower ash content. Most important is the fact that it is renewable. Its disadvantages stem from its lower heating value, lower bulk density, and its higher moisture content which makes handling and processing facilities more expensive.

Destructive distillation of wood has been practiced for centuries. The process was originally used to produce charcoal but emphasis shifted towards the production of methanol, acetic acid, and acetone in the later part of the nineteenth century. With the advent of petrochemicals, the use of wood as a source of organic chemicals declined, although it is still important in the soviet bloc countries.

Fluidized beds came to be used for wood pyrolysis about 30 years ago. Among the early reports on fluidized bed gasification was a study by Morgan et al. (1953). Their bed, fluidized by nitrogen, was used in a batch

operation to gasify powdered hardwood. The charcoal yield after 30 minutes of operation at 673 K was 32 % by weight of the dry charge. Kilburn and Levelton (1963) used a bed of incandescent charcoal, fluidized by air or oxygen, to produce charcoal from sawdust. Their unit was operated with continuous feed and overflow of charcoal and yielded about 5 % of the feed weight as charcoal at 1000 K.

More recently, the gasification of wood has been studied in fluidized bed reactors as an alternate means of utilizing wood for energy. Feldmann et al. (1981) studied the gasification of wood in a multi-solid fluidized bed (MSFB) gasifier. The system consisted of two fluidized beds with solids circulation between them, one serving as a reactor, the other as a combustor. The process has been considered in some detail in Chapter II of this thesis. The process variables considered were the gasifier temperature, the wood feed rate, the steam rate, the entrained-phase recycle rate, dense-phase particle size, and the wood particle size and moisture content. Cherry and mixed hardwoods were used as feedstocks. The gasifier temperature was found to have the most influence on the performance of the system. The heating value of the produced gas increased with gasifier temperature up to 18.1 MJ/m^3 at 1116 K and then showed a tendency to level off. The decrease in the gas heating value was more than compensated for by increases in the gas yield. Thus the total energy recovery in the form of the product gas continued to increase with temperature. The carbon conversion showed a similar trend.

Among the other factors studied, solids feed rate (a maximum tested of 113 kg. dry wood/hr.) and wood particle size (0.635 to 3.8 cm) did not have an appreciable effect on the performance of the gasifier. These factors would however influence the design of the gasifier by fixing the cross

section area of the gasifier and combustor, maximum heat load, and minimum gas velocity. They also mentioned that the solid conversion with higher moisture wood chips was limited by the time it took the wood to dry. For small residence times in the gasifier (1 - 3 s), the maximum temperature reached by the moist wood chips would be much lower than the measured temperature of the gasifier. Another important observation was that tar production was negligible, and that for the steam/wood ratio used (0.8 kg. steam to 1 kg. wood), there was no net steam consumption (operation temperature range 963 K to 1172 K). No results were presented to support this conclusion.

Schoeters et al. (1981) gasified linden wood shavings in a fluidized bed reactor under partial oxidation conditions. The bed was made up of sand and fluidized with air or a mixture of air and steam. They studied the influence of air-factor, and reactor freeboard temperature on the gasification between 923 K and 1123 K. The air-factor was defined as the ratio of actual flow rate of air to the flow rate required for complete combustion of feed. An increase in the air-factor caused the yield to increase, the higher heating value (HHV) of the gas to pass through a maximum, and the energy recovery to be almost unchanged. They found that high steam rates lowered the HHV, the gas yield, and the energy recovery. The influence of the freeboard temperature on the gasification was studied by changing it from 25 K above the reactor bed temperature to 150 K below. It was shown that freeboard temperature had considerable influence on the gas yield, gas composition, and HHV. The concentrations of CO_2 and H_2 increased while that of CO went down with an increase in freeboard temperature. This was explained by the water-gas-shift reaction where CO reacted with steam to produce CO_2 and H_2. They expected that above 1123 K, the CO would start increasing due

to the system approaching equilibrium.

van den Aarsen et al. (1982) investigated beechwood pyrolysis in a
0.03 m I.D. fluidized bed reactor with nitrogen as the fluidizing gas. The
study was concerned with the interpretation of kinetic data on small
particle wood pyrolysis at fast heating rates (250 - 1000 K/s) and with the
product distribution therefrom. The gas yield was found to increase with
temperature, at the cost of condensate yield, indicating further breakdown
of tar at higher temperatures. They predicted that the pyrolysis of a 1 mm
wood particle is essentially completed in 2 seconds with a heating rate of
about 500 K/s.Further they correlated char yield as a function of particle
diameter and found the results to be in agreement with predictions that
char yield decreases with an increase in heating rates and reduction in
particle size.

Lian et al. (1982) studied air-blown wood gasification in a set of
different sized fluidized bed reactors. The feed was screened oak sawdust.
The fluidizing gas was preheated air which also supplied oxygen for partial
combustion to maintain the bed at the reaction temperature. After examining
a number of variables (temperature, flow rate of wood, air, residence time
etc.), they found that the ratio of total carbon - to - nitrogen in the dry
gas correlated best with the important properties of the produced gas
including % C, % H_2, and heating value. Their results indicated that at a
given total carbon - to - nitrogen ratio, the gas quality was only slightly
affected by wide variations in the type of reactor, the existence of thermal
steady state, the type of feed, the residence time, and the bed temperature.
However, these variables did influence the char and tar formation, and the
total carbon - to - nitrogen ratio. Equilibrium calculations indicated that
the more reduced forms of carbon (CH_4 and CO) were in greater than

equilibrium concentrations in the homogenous gas-phase reactions.

Rensfelt et al. (1978) conducted basic gasification studies on biomass fuel characteristics in a flash pyrolysis unit. The gas yield (as percent mass of feed) was observed to be strongly dependent on the residence time and temperature of the volatiles. For flash pyrolysis of poplar wood at 1073 K, the weight percent gas yield increased from 10 % at 0.5 s to 70 % at 0.75 s. At 973 K, the corresponding numbers were 5 % at 0.5 s and 55 % at 0.8 s. Results from these experiments also showed the importance of secondary reactions of the primary heavy hydrocarbons produced during rapid heating. The secondary reactions depend on residence time in the heated zone, the temperature and temperature profile in this zone, and the chemical composition of the environment. It was concluded that steam was a very active gasification agent and was consumed in the process due to steam reforming of the hydrocarbons produced in the primary reactions and/or char gasification. DTG analysis was used to calculate kinetic data on the gasification. They concluded that entrained and fluidized beds with indirect heating for partial gasification of biomass can give a good medium BTU gas. The partially gasified char can be used for producing the necessary process heat.

Apart from using the produced gas for fuels, the other major use can be as a source of synthesis gas for methanol or ammonia. The produced gas normally has to be treated to make it suitable for synthesis. Mudge et al. (1981) studied the economics of using catalysts to promote gasification and shift reactions to obtain a methanol synthesis gas with a favourable CO/H_2 ratio. They studied headrig sawdust containing a mixture of alder and maple in a laboratory scale quartz continuous flow reactor and in a fluidized bed process development unit (PDU). Catalysts used were Ni:SiAl (1 : 1);

Ni on SiAl; and Ni-Cu-Mo on Alumina. Comparing the results of gasification in the PDU with and without catalysts, an improvement in carbon conversion to gas was observed. The H_2/CO ratio without catalyst was 1 : 1 while that with catalyst was around 2 : 1. The cold gas efficiency also improved substantially. Production of methanol and methane (SNG) from wood via catalytic gasification was considered technically feasible and economically advantageous over conventional steam-oxygen gasification.

In addition to wood sawdust which is a waste product, branchwood which does not satisfy the requirements of the traditional wood users (lumber, paper, furniture, and construction industries) also represents a source of wood for conversion to energy. The objective of this work therefore was to examine the steam gasification of wood (cottonwood branchwood) in a fluidized bed reactor under continuous steady state conditions. The gas composition and other properties of the gas were examined as functions of temperature with the gas residence times being held relatively constant. Specific characteristics of the gasification that were examined included the gas heating value, the gas yield, carbon conversion, and energy recovery. Comparision was also made with data for α - cellulose on the same system.

Experimental Facilities and Procedure

Facilities

A schematic of the bench-scale fluidized bed reactor system used in this study is shown in Figure 1. The reactor was constructed from a 5.08 cm I.D. by 50 cm length of schedule 40 Inconel 600 pipe, fitted on top with a 10.16 cm I.D. by 15 cm length of pipe of the same material. The upper 15 cm served as a disengaging zone for the reactor. The lower 23 cm, which served as the gas preheater and distributor, was packed with aluminum oxide pellets (0.5 cm diameter). The fluidized bed section was separated from the packed

bed section by a 0.025 mm (60 mesh) SS 304 screen. The bed was composed of
a mixture of 25 wt. % limestone and 75 wt. % silica sand. The limestone
ranged in size from 2.82 mm to 0.297 mm (-7 +50 mesh); the sand varied
between 0.595 mm and 0.297 mm (-30 +50 mesh). The bed had a static height
of 8 cm and an expanded height of about 11 cm. The reactor was heated by
means of four pairs of semi-cylindrical electrical resistence heaters, each
capable of delivering up to 2300 watts, with a maximum operating temperature
of 1743 K. The top three pairs were controlled by three Omega (model 49K-814)
three-mode controllers, each having a range of 273 K - 1273 K. The lowest
pair of heaters for the distributor/preheater zone was controlled by a
simple thermostat. Feedback to these controllers was from thermocouples
placed inside the reactor at appropriate points.

Steam, the sole fluidizing agent, wasgenerated in a Sussman Hot Shot
electric boiler (model MB-6) and was supplied to the distributor/preheater
section at approximately 400 K and 202.6 kPa (2 atm). A heating tape was
wrapped around the pipe leading from the boiler to the preheater to prevent
steam from cooling and condensing in the pipe. The feed was introduced into
the reactor by gravity flow through a vertical feed-pipe which discharged
7 cm above the static bed. A Vibra Screw (model SCR-20) feeder with a solid
core flight screw transported the feed from the hopper to the feed-pipe. A
known volumetric flow rate of nitrogen was used to aid flow through the
feed-pipe and to prevent back-flow of gas and steam and subsequent conden-
sation of vapor in the feed-pipe and the hopper.

The off-gas from the reactor passed through a cyclone where entrained
char was separated from the gas. The temperature in the cyclone was maint-
ained at about 600 K with a heating tape to prevent condensation of tars.
The gas stream leaving the cyclone then passed through two water-cooled

double-pipe heat exchangers in series. This resulted in the condensation of steam and tar, which were collected in a condensate receiver. The gas subsequently passed through a bed of glass-wool to remove the oily mist entrained in it. A wet-test meter connected to a strip-chart recorder was used to measure the flow rate of the gas before and during the experiment. A side draw of the off-gas was passed through a drying column packed with Drierite ($CaSO_4$) and then sent to an on-line process gas chromatograph for analysis. The remaining gas was vented to the atmosphere.

Temperatures in the bed and at three points in the freeboard section were monitored by thermocouples connected to temperature controllers. The axial temperature profile in the reactor was measured by a sliding (91 cm long) thermocouple, which was moved vertically to measure the temperatures from the bottom of the bed to the top of the disengaging zone. Temperatures of the cyclone, the two heating tapes, the nitrogen purge, and the cooled exit gas were monitored. A pressure probe, connected to a manometer, indicated the bed pressure and the state of fluidization.

Procedure

For start-up of each experimental run, the reactor heaters, the steam generator, the cyclone and inlet pipe heating tapes were turned on. The controllers were set at the desired operating temperatures. During the heat-up period, air was used as the fluidizing gas and as the feed-pipe purge. The steam generator was set up so that it supplied steam at a constant pressure. Once steam was available, the fluidizing air flow was gradually replaced by steam. The volumetric flow rate of steam required to maintain fluidization was measured by collecting condensate downstream from the heat-exchangers and controlled by a needle valve on the steam line.

When the bed and the freeboard reached the selected operating temperature

the axial temperature profile was measured and minor corrections made with the controllers to ensure a uniform profile. The exit-gas from the system was analyzed to ensure that the system was purged of air. At this point, the system was ready for the feeding to begin. Total start-up time from a cold start was about two hours and about one hour from a warm start. Normally at the end of a run, the heaters were not turned off but just turned down so that the system stayed warm overnight.

A slight drop in the temperature of the reactor occured when feeding was initiated, but was corrected automatically by the controllers. A gas sample was taken about 5 minutes after feeding began and every 11 minutes thereafter. Condensate and nitrogen flow rates were measured every ten minutes throughout the run. A typical experiment at a given temperature lasted 100 to 130 minutes with the last 40 - 50 minutes yielding steady gas chromatograph readings. The feed rate was evaluated by disconnecting the lower section of the feed-pipe and weighing the effluent collected over three 3-minute time intervals. This was done at the start and end of the run.

It was not possible to measure the total char produced in the exper- iment because of hold-up of char in the bed. It was also not possible to measure the total tar produced due to lack of adequate separation facilities. Also, significant quantities of tar were held up in the heat-exchangers. Thus, an overall material balance was not possible with the present system.

Chemical Analysis

Analyses of the dry off-gas were conducted by an Applied Automation (Optichrom 2100) on-line process gas chromatograph. The components of interest were H_2, CO, CO_2, CH_4, C_2H_6, C_3H_8, C_3H_6, O_2, C_2H_4, and N_2. The chromatograph had a cycle time of 11 minutes. Moisture and ash analyses of the feed material were performed according to standard ASTM procedures in a

ventilated oven and muffle furnace respectively. Elemental analyses of the feed were done using a Perkin-Elmer (model 240) elemental analyzer. Analyses of the feed for cellulose, hemicellulose, and lignin were conducted by an independent laboratory. Neutral-detergent (cell wall), Acid-detergent fiber, and Permanganate lignin tests, as described by Goering and Van Soest (1970), were used for these determinations. The same laboratory also conducted ash and heat of combustion analyses of the feed.

Operating Conditions

The operating conditions for all the experimental runs are summarized in Table 1. By adjusting the steam rate with the temperature of the run, it was possible to maintain a fairly constant mean volatiles residence time over all the runs. The gas phase mean residence time ranged from 2.00 to 2.35 seconds. The residence time was estimated on the basis of reactor temperature, total dry gas flow rate, and steam rate.The observed average feed rate varied between 1.56 and 1.98 g/min. although the screw-feeder setting was the same for all the experimental runs. An average calculated over all the experiments gave a feed rate of 1.77g/min. (1.55 g dry ash-free/min.). The principal experimental variable was the reactor temperature. All the experiments were performed with the temperature of the freeboard section the same as that of the reactor bed, resulting in a uniform axial temperature profile over the length of the reactor. A typical temperature profile is shown in Figure 2.

Feed Material

The cottonwood (Populus deltoides Bartr) used in this study was obtained from the branches of three trees.- all 12 years old with trunk diameters about 30.5 cm. Branches up to 7.6 cm in diamete were used. These branches (including the bark) were first run through a M bark chipper and then fine

ground in a hammer mill. The -28 +50 mesh fraction was separated by sifting and used as the feed material. A typical elemental and component analysis of the feed is presented in Table 2.

Results

All results presented here are based on the average of gas composition data obtained during the last 40 to 50 minutes of each run. The GC readings were corrected for the nitrogen purge to give the produced gas composition. The composition in turn was used to evaluate the higher heating value (HHV) of the gas using the standard heat of combustion for each component. The feed rate used in the calculation of gas yield, energy recovery, carbon conversion, and mass yield was the average value for all the experiments (1.77 g/min., 1.55 g DAF/min.). The average was used because the screw-feeder setting was the same for all the experiments. The volumetric flow rate of the produced gas was determined from the difference in the rates measured by the wet-test meter with and without feeding to the gasifier. The volumetric gas yield of dry produced gas at 288 K and 101.3 kPa per unit mass of DAF feed was calculated by dividing the produced gas volume flow rate by the feed rate. The energy recovery was calculated as the ratio (expressed as a percentage) of the product of the gas yield per unit mass of DAF feed and HHV to the heat of combustion of a unit mass of DAF feed. The carbon conversion was determined as the ratio (expressed as a percentage) of the moles of carbon in the gas produced from a unit mass of DAF feed to the moles of carbon in a unit mass of DAF feed. Finally, the mass yield of the gas was calculated by converting volumetric yield to a mass basis to give the mass of produced gas per unit mass of DAF feed.

All the results were fit by polynomial functions of temperature using the SAS (Statistical Analysis System) package. For each dependent variable,

the square of the correlation coefficient (R^2), the probability of falsely
rejecting the proposed regression model (Pr. > F-statistic in F-test for
significance of regression), and the significant regression model are
tabulated in Table 3. In addition, the gas composition data (H_2, CO, CO_2,
CH_4) were fit by splines (two lines with a common join point) for comparision
with cellulose data from Walawender et al. (1982). For this purpose, a
linear regression model with different parameters in each temperature region
was used to determine the common point. This common point was estimated
using a search technique in which various points were tested to find one
which gave the minimum sum of the squares of the residuals (Hudson, 1966).
The common point was found to be close to 930 K for all the four major
components and thus 930 K was used. The model coefficients and statistics
are given in Table 4.

Produced Gas Composition

The variations in the concentrations of H_2, CO, CO_2, and CH_4 as functions
of temperature are shown in Figure 3. The solid lines represent the spline
regression of the data, while the dot-and-dash lines, the polynomial
regression. The concentration of H_2 increased with an increase in temperature
from 32.3 % at 850 K to 48.9 % at 1075 K. The concentration of CO_2 ranged
from 33.7 % at 850 K to 32.4 % at 1075 K with a minimum of 28.6 % at 930 K.
The CO concentration in the produced gas decreased linearly with increasing
temperature from 20.6 % at 850 K to 8.9 % at 1075 K. Methane decreased from
9.3 % at 850 K to 6.9 % at 1075 K. The minor components of the gas C_2H_6,
C_3H_6, and C_2H_4, decreased with increasing temperature. Their compositions
are not plotted since they represent a small part of the total gas yield
(C_2H_6 0.82 % to 0.24 %; C_3H_6 0.91 % to 0.30 %; C_2H_4 2.9 % to 1.5 %). The
broken lines shown on the figure are the corresponding gas compositions

from Walawender et al. (1982) for α- cellulose gasification in the same reactor.

Produced Gas Higher Heating Value

The HHV of the gas as a function of temperature is shown in Figure 4. The solid line represents the polynomial regression analysis results. The HHV decreased continuously with temperature from 12.4 MJ/m^3 at 850 K to 11.6 MJ/m^3 at 1075 K. The variation in the heating values of the gas was small, with an average of 11.8 MJ/m^3. The broken line represents the cellulose results from Walawender et al. (1982).

Produced Gas Yield

The variation in the volumetric yield of produced gas is shown in Figure 5 as a function of temperature. The solid line again represents the polynomial regression results. The gas yield increased from 0.23 m^3/kg at 850 K to 1.59 m^3/kg at 1075 K. The broken lines are the results from α- cellulose gasification (Walawender et al., 1982).

Energy Recovery

The energy recovery represents the energy content of the feed that is converted to combustible gas. Figure 6 shows the energy recovery plotted against temperature and fitted by the polynomial regression (solid) curve. The energy recovery increased from 15.0 % at 850 K to 96.8 % at 1075 K. The broken lines are the α- cellulose results from Walawender et al. (1982).

Carbon Conversion

The carbon conversion is the ratio, presented as a percentage (Figure 7) of the moles of carbon in gas to the moles of carbon in feed, both on a unit mass (DAF) basis, The polynomial regression is shown by the solid curve. The carbon conversion increased with temperature from 16.9 % at 850 K to 87.1 %

at 1075 K. The broken lines are the corresponding results from cellulose gasification from Walawender et al. (1982).

Produced Gas Mass Yield

The mass yield as a function of temperature is shown in Figure 8. The polynomial regression is represented by the solid curve. The mass yield increased from 0.24 kg gas/kg DAF feed at 850 K to 1.35 kg gas/kg DAF feed at 1075 K. The corresponding results for α- cellulose are presented by the broken lines.

Discussion

Raman et al. (1981a, 1981b) have indicated that devolatilization of biomass in a fluidized bed reactor is nearly instantaneous for small particles. Antal et al. (1978) and Antal (1979) have also confirmed that the initial devolatilization and char forming step is completed in less than 0.5 s for particles between 75 - 250 μm in size at high heating rates. They also stated that secondary gas phase reactions determine the composition and yield of the products. van den Aarsen et al. (1982) stated that less than 10 % char is produced from fast pyrolysis of a 1 mm wood particle in a fluidized bed. Particle heating rate becomes the rate limiting factor at particle diameters between 5 and 10 mm. Maa and Bailie (1973) in their study on cellulosic materials theorized that for particle sizes less than 0.2 cm in diameter, pyrolysis is reaction controlled and particle size has no influence.

The secondary gas phase reactions have been suggested to be combinations of reforming, cracking, and water-gas-shift reactions. On the basis of his experiments, Antal (1979) has suggested that reforming reactions are not as important as cracking. Walawender et al. (1982) explained their cellulose results for operation above 940 K on the basis of the water-gas-shift reaction. They hypothesized that the shift reaction dominates above 940 K with the resultant increase in H_2 and CO_2 and the decrease in CO. Their gas yield (increased), HHV (decreased slightly), carbon conversion (unchanged), and energy recovery (increased) with temperature, supporting their hypothesis. For operation below 940 K, the mechanism which determined the composition was proposed to be primarily tar cracking. By assuming that the water-gas-shift reaction was the sole reaction above 940 K, they were also able to relate the slope of the gas yield - temperature line to the

slopes of the mole fraction - temperature lines for CO, CO_2, and H_2. Using the experimental gas yield data, they could then predict the slopes of the mole fraction - temperature lines. The predicted slopes and the experimentally observed slopes corresponded reasonably well considering the complexity of the system.

All the experiments in the present study were conducted under steady state conditions with a well defined temperature profile and volatiles residence time. The feed particles were small (0.595 mm to 0.297 mm) resulting in essentially instantaneous devolatilization. Also, the range of temperatures used was such that gasification of char was not important in the process (Antal et al., 1978, Rensfelt et al., 1978). Consequently, the results reflect the influence of temperature on the secondary gas phase reactions. The results could also be compared with those from Walawender et al. (1982) for alpha-cellulose which was gasified in the same reactor under very similar conditions.

Gas Compositions

Comparing the gas compositions from cellulose and wood (using splines for wood), it can be seen that the general trend above 940 K is similar in both cases. Moreover, the CO and CO_2 lines for wood above 930 K are nearly parallel to the corresponding lines above 940 K for cellulose. This correspondence in the slopes and the similarity in the trends suggests that the water-gas-shift reaction may dominate in this region for wood gasification too. A way of checking this hypothesis is to compare the slopes of CO, CO_2, H_2 lines in this regime. The ratio of the slopes of CO : CO_2 : H_2 is -1.54 : 1 : 0.5. If the water-gas-shift is the only major reaction influencing these components, the ratios should theoretically be in a -1 : 1 : 1 proportion from the stochiometry of the reaction. While the agreement may

not seem so good, it must be recalled that these slopes are influenced by the points in the first regime also, from the simultaneous statistical analysis of both regions.

To further investigate this, it was decided to check how well could the CO, CO_2, and H_2 data above 930 K be represented by lines with a common absolute slope. The slopes would then be in theoretical proportion as required by the hypothesis. Using the slope of one component, R^2's for fitting the data of the other two were determined. The original slope of CO_2 gave the best results which are plotted as the dot-and-dash lines in Figure 9. These lines have the same absolute slope as the original CO_2 line and gave R^2's of 0.24 for H_2 and 0.74 for CO. There does not seem to be any substantial difference between the original best fit lines and the lines with slopes in theoretical proportion. Maximum deviation between the two lines was 2.5 %. A similar analysis on cellulose data gave similar results.

The preceding analysis adds more evidence to the hypothesis that the water-gas-shift reaction dominates above an operating temperature of 930 – 940 K. The transition point of 930 K for wood is close enough to 940 K for cellulose that in light of the complexity of the system, they may be considered the same. This conclusion though, is seemingly contradicted by two observations – increasing carbon conversion, although at a steadily decreasing rate, over the entire temperature range (rate refers to the slope of the curve); and visual observation of higher levels of tar from wood than from cellulose in all the experiments. These tar levels in the condensate were observed to decrease with increasing temperature through changes in the color of the condensate. This raised the question as to why the gas composition data implies that the shift reaction was the dominant gas phase reaction in this temperature range. The analysis of Walawender et al. (1982)

was based on the requirement that tar cracking be complete. Evidently the extent of tar cracking in the higher temperature region was not significant enough to mask the influence of the shift reaction on the gas composition. Since the carbon conversion in case of cellulose did not change appreciably above 940 K and the observed tar was also very small, the explanation rests on the differences in the nature of the volatiles produced from the two feeds.

Order-of-magnitude calculations, using data from Antal (1982) and Shafizadeh (1982) and the wood composition, showed that while the tar from the lignin component of wood was present even at 1023 K, its amount (as percent feed) did not change much : from 10 % at 923 K to 8 % at 1023 K. This indicates that a nearly constant amount of lignin tar was produced over this temperature range. The incremental amount of tar cracked between any two temperatures was small relative to the increment in the produced gas yield. Furthermore, the total lignin tar produced relative to mass yield of gas decreased considerably with increasing temperature. Similar order-of-magnitude calculations for cellulose showed that while the amount of tar from cellulose was large at 873 K, it decreased rapidly with increasing temperature up to 940 K. The amount of tar from cellulose between 940 K and 1023 K was unchanged. This implies that cracking of cellulose tar was complete by 940 K although not all the tar was cracked. While these calculations could not be done for hemicellulose, it was expected that hemicellulose would give even less tar than cellulose (Milne, 1979). The behavior of hemicellulose and cellulose tar was expected to be similar because of the structural similarities between the two polysacharides.

It could thus be concluded that due to the lignin component of wood, small amounts of tar cracking did occur at the temperatures above 930 K but

the extent of this cracking was too small to be reflected in the gas composition. Evidently the water-gas-shift reaction is not the sole reaction above 930 K for wood but it is dominant in determining the product gas composition. The small tar cracking reactions, however, by necessity, show up in the carbon conversion.

Comparing the mole fractions of CO, CO_2, H_2 from the two feeds, the difference between them is interesting. Wood gives slightly more CO_2 and less CO than cellulose at the same temperatures although the sum of the CO and CO_2 mole fractions for the two feeds is relatively close. Cellulose, because of the higher concentrations of CO and steam (steam concentration is related to residence times: 1.3 - 1.6 s for cellulose compared to 2.00 to 2.35 s for wood) had a much higher driving force for the shift reaction. But from the calculated partial pressure ratio $PCO_2 \cdot PH_2/PCO \cdot PH_2O$ in Figure 10, it can be seen that the wood gas came closer to equilibrium. This is possibly due to the shift reaction being catalyzed by carbon surfaces (Graboski, 1979) and/ or wood ash (Feldmann, 1978). The system under investigation had large quantities of carbon (in the form of char) for wood and possibly wood ash (formed by combustion of char in bed after an experimental run was completed, and held up in the bed material). The higher residence time in the wood experiments may also have been a factor. This greater extent of the shift reaction is also evident in the greater slope of the gas yield line for wood as compared to that for cellulose (Figure 5).

While the extent of the water-gas-shift reaction may be important in determining the product distribution, it is not the only factor. The amounts of these gas components are also dependent on the reactions in the primary devolatilization stage. These in turn are dependent on the nature and composition of the feed material.

In contrast to the composition above 930 K, that below 930 K behaves quite differently. A sharp increase in H_2 and decrease in CO, CO_2, and CH_4 fractions was observed with increasing temperature. Walawender et al. (1982) ascribed this regime to cracking reactions of tar. Visual observation of the color of condensate in the experiments also suggested that the tar production decreased with increasing temperature. The order-of-magnitude calculations mentioned before also showed that tar cracking was important in this temperature region. The large excess of steam at these temperatures implies that the water-gas-shift reaction was also possible but was not as important as cracking in determining the product characteristics in this temperature range.

Comparing the compositions in this regime to those from cellulose, the general trends for CO and CO_2 are similar while H_2 differs substantially. This reflects the basic differences in the make-up of the two feeds. Antal, (1982) showed that Hardwood (cherry) produced less H_2 than cellulose while lignin produced significantly larger amounts. Cellulose produced the most CO followed by wood and lignin. Wood gave slightly higher CO_2 compared to cellulose, while lignin gave the least. The relative results for wood and cellulose correspond broadly to those in the tar cracking regime in this thesis. A comparision of Antal's cellulose and Hardwood gasification results and those for cellulose from Walawender et al. (1982) and for wood from this study is given in Table 5.

The differences in trends of gas composition from wood and cellulose in the first regime and the similarity in the second suggests that while gasification at higher temperatures, in the presence of large amounts of steam, normalizes the behavior of the products from different feeds, products at the lower temperatures are dependent on the feed, more strongly.

Higher Heating Value

The Higher Heating Value (HHV) results also support the hypothesis that the water-gas-shift reaction determines the products in the second regime. The heating value of the gas corresponds almost exactly with that obtained from cellulose in this temperature region. Dilution of the gas due to the CO_2 produced by the shift reaction lowers the HHV since the heating values of CO and H_2 are almost identical (283.1 MJ/kmole for CO and 285.9 MJ/kmole for H_2). The HHV decreases slowly with increasing temperature which agrees well with the concept of secondary gas phase reactions decreasing the heating value of the product while the yield is increased (Soltes and Elder, 1981).

Gas Yield, Carbon Conversion, and Energy Recovery

The composition of cottonwood (branchwood) on a dry basis is 37.2 % cellulose, 25.1 % lignin, 13.2 % hemicellulose, 5.5 % ash, and 18.9 % extractives (volatile oils, resins, fatty acids, pigments, starch etc.). Shafizadeh and McGinnis, (1971) conducted a TGA study on cottonwood and its components and showed that while cellulose and hemicellulose were almost completely devolatilized at 773 K, lignin lost only half of its weight at this temperature. The heating rates used by them were of the order of 15 K/min. In contrast, the heating rates in a fluidized bed are of the order of 1000 K/s. Consequently, extent of devolatilization is expected to be higher and the char yield less than the 12 % shown by them (van den Aarsen et al., 1982, Rensfelt et al., 1978). Char yields of the order of 6 - 8 % can be expected for wood in a fluidized bed. Similarily, for cellulose, negligible char yields are expected. Visual observation of char and tar produced in the experiments confirmed that the yields from wood were higher than those from cellulose. Also, char gasification was not

important in these experiments since the highest temperature was 1075 K (Antal et al., 1978). Consequently, carbon conversion and mass yield for wood were expected to be lower than those for cellulose at thesame temperatures. Figures 7 and 8 show that cellulose had a higher carbon conversion and mass yield at all temperatures.

The volumetric gas yield from cottonwood, on the other hand was higher than cellulose for temperatures above 970 K. This was probably a result of the greater reactivity of the wood gas due to the catalytic influence of char and/or wood ash. Volume yield is slightly misleading as it depends on the distribution of components in the gas.

All these results show a qualitative trend which agrees well with the conclusions drawn from the gas compositions. The gas yield increased rapidly with temperature below 930 K and then increased at a continuously slowing rate. This parallels the conceptual mechanism proposed by Walawender et al. (1982) for cellulose gasification. In the lower temperature regime, a large part of the tar was cracked to gas resulting in the rapid increase in gas yield. With higher temperatures, the extent of cracking diminished with respect to the water-gas-shift reaction, giving the reduced slope with increasing temperature. Gas yield increased because of the conversion of steam through the shift reaction and the minor amount of tar cracking. This mechanism is also supported by the observed trend in carbon conversion and energy recovery. Carbon conversion increased, depending on extent of tar cracking reactions occuring in the system at the particular temperature. Since water-gas-shift does not influence carbon conversion, the slow increase

above 930 K is due to the lignin tar cracking discussed earlier. The HHV of the gas dropped, but the gas yield compensated for it, resulting in the increase in energy recovery.

It may be pertinent at this point to remark on the presentation of gas yield, carbon conversion, energy recovery, and mass yield data by continuous curves while the gas compositions were fit by two lines. From the discussion of gas compositions, it was noted that, for wood, there did not seem to be any temperature beyond which the tar cracking was negligible as was the case for cellulose beyond 940 K. Beyond this point for cellulose, no appreciable cracking occured. For wood, tar cracking, although at decreasing levels of importance, occurs even up to 1023 K. There is no clear cut transition point for the two mechanisms and thus in order to present the continuous transition from tar cracking to shift reaction dominated regions, curves have been used to correlate the data. Gas Compositions have been correlated by splines, solely to be able to make comparisions with cellulose.

Mass Yield

These data also provide evidence to support the hypothesis that the shift reaction dominated in the second regime. For both cellulose and wood, mass yields greater than 1 kg gas/kg DAF feed were obtained at the higher temperatures. These high yields were simply due to steam becoming a part of the produced gas through the shift reaction. The greater-than-1 yields do not seem contradictory in this light. Antal et al. (1978) in their experiments found that cellulose loses about 90 % of its weight in the devolatilization step. This implies that with complete tar cracking, the maximum expected mass yield from cellulose would be 0.9 kg gas/kg DAF feed. Thus, in the cellulose gasification, nearly 0.5 kg steam/kg DAF feed was converted to produced gas. The levels of steam consumption for wood may well be higher because a larger part of the feed goes to form char and tar. As much as 50 % of the gas yield may come from steam at the higher temperatures. While the actual condensate rate observations were not accurate enough to

give an estimate of the amount of steam consumed, a drop in the condensate rate was observed in all experiments.

Steam plays an important role in the gasification process, especially when present in large excess. Figure 10 shows the calculated partial pressure ratio $P_{CO_2}.P_{H_2}/P_{CO}.P_{H_2O}$ values for wood and the cellulose experiments. The large excess of steam provides a high driving force for the forward reaction in the water-gas-shift. Antal (1982) presented his results from steam gasification of cellulose and wood. On comparing his results with those obtained here (in Table 5), it can be noted that the produced gas in his case always had higher levels of CO and lower levels of CO_2 and H_2 at the corresponding temperatures. The steam to DAF feed ratios used by Antal were of the order of 1.4 : 1 while those used in these experiments were closer to 6 or 10 : 1. In light of the differences in these ratios, Antal's gas compositions are expected. The shift reaction was not an important reaction in his case thus resulting in higher CO and lower CO_2 and H_2. His experimental system did not contain char or wood ash which could have catalyzed the water-gas-shift. Unpublished data from the gasification of cottonwood in a pilot-scale fluidized bed reactor at Kansas State Univ. corresponds closely to the data in Antal (1982) for wood. The pilot scale reactor was fluidized by combustion gases from propane and the steam to feed ratio was less than 1 : 1. The mass yield was found to be less than 1 at 1010 K. Antal (1979) from steam gasification of biomass also concluded that steam dilution ratios higher than 1.4 g steam per g feed had little effect on gasification results. On the other hand, Schoeters et al. (1981), working on a system similar to the one reported here implied that steam takes part in gasification. The observations reported here also contradict Antal's findings – steam, in large excess, appears to be a major factor in

determining the gas composition and yield. These experiments showed that steam is an active gasification agent.

Conclusions

Steam gasification experiments were conducted with cottonwood (branchwood) in a bench-scale fluidized bed reactor over a temperature range of 850 K to 1075 K. The volumetric yields of the produced gas increased with increasing temperature. The major components of the produced gas were CO, CO_2, H_2, and CH_4 which comprised over 90 % of the gas. The HHV of the gas averaged 11.8 MJ/m^3. Both the carbon conversion and energy recovery increased with an increase in temperature.

The gas composition data suggested the existence of two regimes in the gasification process as postulated by Walawender et al. (1982). The first regime is dominated by tar cracking and the second, at higher temperatures (> 930 - 940 K), by the water-gas-shift reaction. Unlike cellulose, there is no distinct transition point from one mechanism to the other. Tar cracking reactions for wood occur above 930 K - 940 K also, but their extent is small relative to water-gas-shift reaction, and hence the shift reaction dominates the product characteristics in this range of temperatures.

Steam is an important gasification agent when present in large excess. It is converted to the product gas in significant amounts through the water-gas-shift reaction.

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Table 1.

Reactor Operating Parameters

Reactor Temperature Range   850 - 1075 K

Fluidizing Gas   Steam

Superficial Velocity   0.15 - 0.20 m/s.

Condensate Rate   9.5 - 15.6 cc./min.

Feed Rate (average)   1.55 DAF g./min.

Particle Size (Feed)   -28 +50 mesh

Particle Size (Bed)
    Sand (75 weight %)   -30 +50 mesh
    Limestone (25 weight %)   -7 +50 mesh

Gas Residence Time   2.00 - 2.35 s.

Table 2.

Analysis of Feed - Cottonwood (branchwood)

Ultimate Analysis (% dry basis)		Component Analysis (% dry basis)	
Ash	5.9	Ash	5.5
C	48.6	Cellulose	37.2
H	6.0	Hemicellulose	13.2
N	0.5	Lignin	25.1
O[1]	39.0	Extractives[1]	19.0

Average Moisture Content   4.8 %

Empirical Formula $C_6H_{8.82}O_{3.62}$

Heat of Combustion (DAF basis)[2]   19.124 MJ/kg.

[1]   by difference

[2]   Dulong's Formula

TABLE 3
Statistical Analysis

y	R^2	Prob. > F-value	Significant Regression Model
mole % CO	0.95	0.0001	$y = 64.98 - 5.22*10^{-2} T^a$
mole % CO_2	0.82	0.0001	$y = 2566.35 - 7.66T + 7.68*10^{-3} T^2 - 2.55*10^{-6} T^3$
mole % H_2	0.97	0.0001	$y = -4246.43 + 12.89T - 1.29*10^{-2} T^2 + 4.31*10^{-6} T^3$
mole % CH_4	0.86	0.0001	$y = 142.78 - 2.73*10^{-1} T + 1.36*10^{-4} T^2$
HHV	0.47	0.0033	$y = 6.12 + 1.60*10^{-2} T - 1.01*10^{-5} T^2$
Gas Yield	0.96	0.0001	$y = -21.86 + 4.17*10^{-2} T - 1.85*10^{-5} T^2$
Energy recovery	0.94	0.0001	$y = -1500.01 + 2.90T - 1.32*10^{-3} T^2$
Carbon conversion	0.93	0.0001	$y = -1240.59 + 2.40T - 1.08*10^{-3} T^2$
Mass yield	0.95	0.0001	$y = -17.14 + 3.27*10^{-2} T - 1.44*10^{-5} T^2$

[a] T is reactor temperature in Kelvin

TABLE 4

Statistical Analysis (splines)

y^1	Model Parameters				R^2	t-test Ho: $\beta_1=0$ Prob $> |t|$	t-test Ho: $\beta_2=0$ Prob $> |t|$	F-test Ho: $\beta_1=\beta_2$ Prob $> F$
	α_1	β_1	α_2	β_2				
CO	73.235	$-6.14 * 10^{-2}$	61.30	$-4.86 * 10^{-2}$	0.96	0.0001	0.0001	0.2885
CO_2	86.56	$-6.27 * 10^{-2}$	-1.10	$3.15 * 10^{-2}$	0.76	0.0001	0.0001	0.0001
H_2	-104.78	$1.62 * 10^{-1}$	31.85	$1.51 * 10^{-2}$	0.96	0.0001	0.0092	0.0001
CH_4	42.88	$-3.93 * 10^{-2}$	3.98	$2.58 * 10^{-3}$	0.89	0.0001	0.1597	0.0001

$$1 \quad y = \begin{bmatrix} \alpha_1 + \beta_1 \cdot T \; \forall \; T < T^* \\ \alpha_2 + \beta_2 \cdot T \; \forall \; T \geq T^* \end{bmatrix} \quad T^* = 930 \; K$$

Table 5

Comparison of gasification results

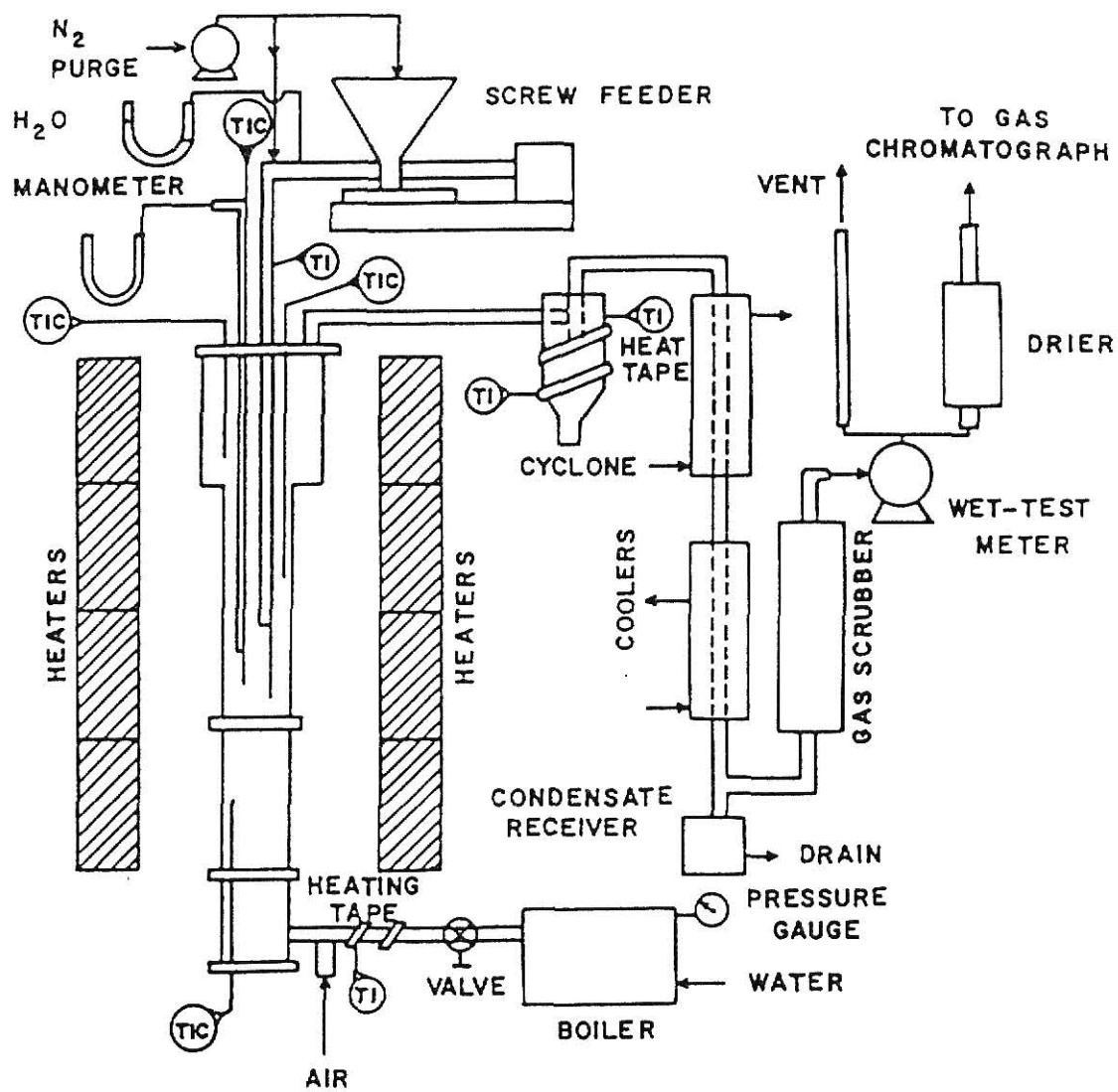| | cellulose ($\tau \sim 1.5s$) | | | | wood ($\tau \sim 2.2s$) | | | |
| | Antal (1982) | | Walawender et al. (1982) | | Antal (1982) | | This work | |
	873 K	973 K	873 K	973 K	873 K	973 K	873 K	973 K
mole % CO	54.0	53.4	25.7	20.0	43.1	46.7	19.6	14.0
mole % CO_2	21.1	10.7	26.7	26.3	28.7	16.7	31.8	29.5
mole % H_2	13.4	14.5	42.0	44.5	9.2	11.1	36.6	46.5
mole % CH_4	7.3	13.3	3.2	4.2	14.3	17.8	8.6	6.5
Carbon conversion (%)	20	60	39	75	15	42	29	74
Mass yield (kg. gas/kg. feed)	0.23	0.57	0.47	0.88	0.25	0.45	0.43	1.10

Figure 1. Bench-Scale Reactor.
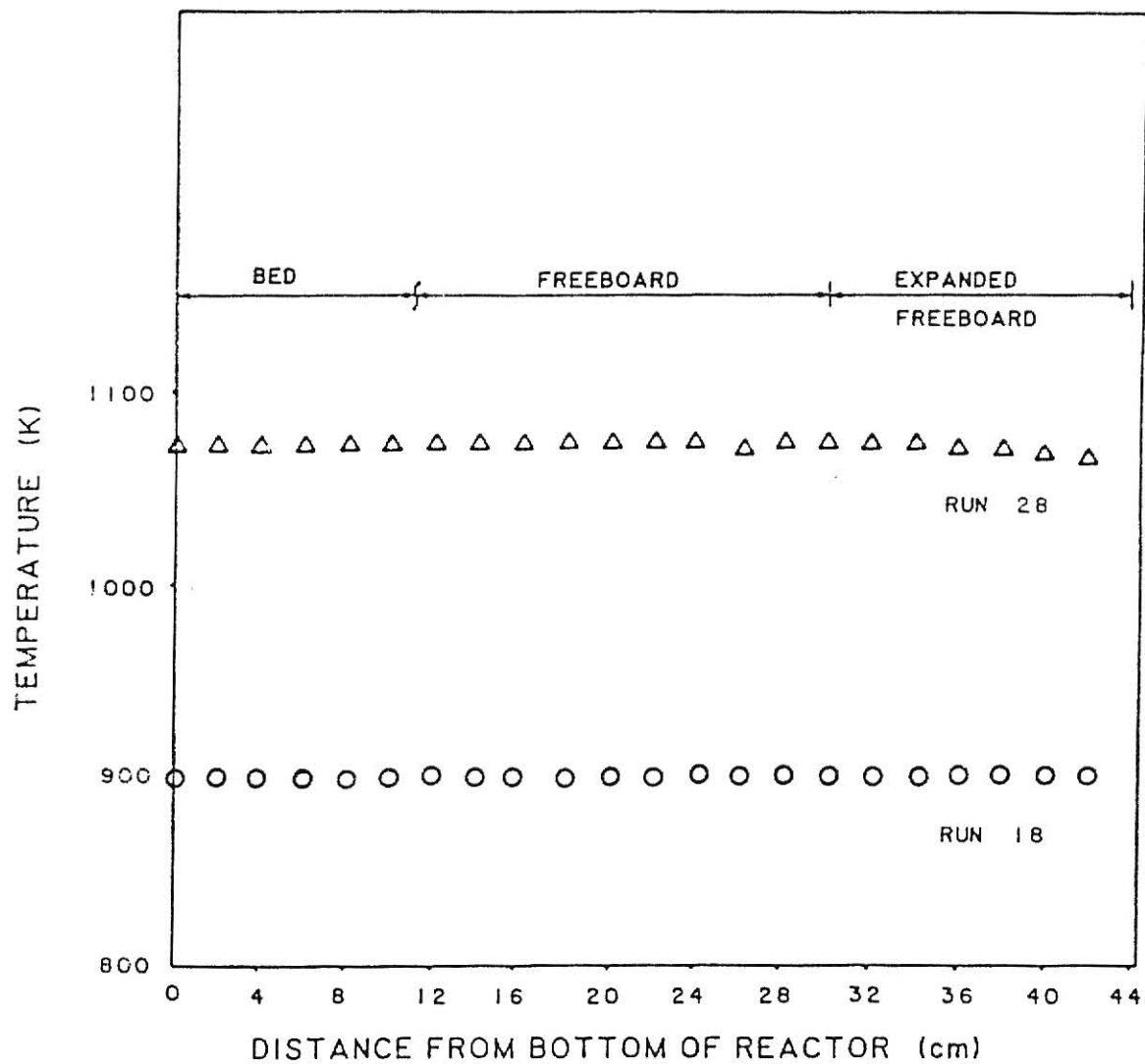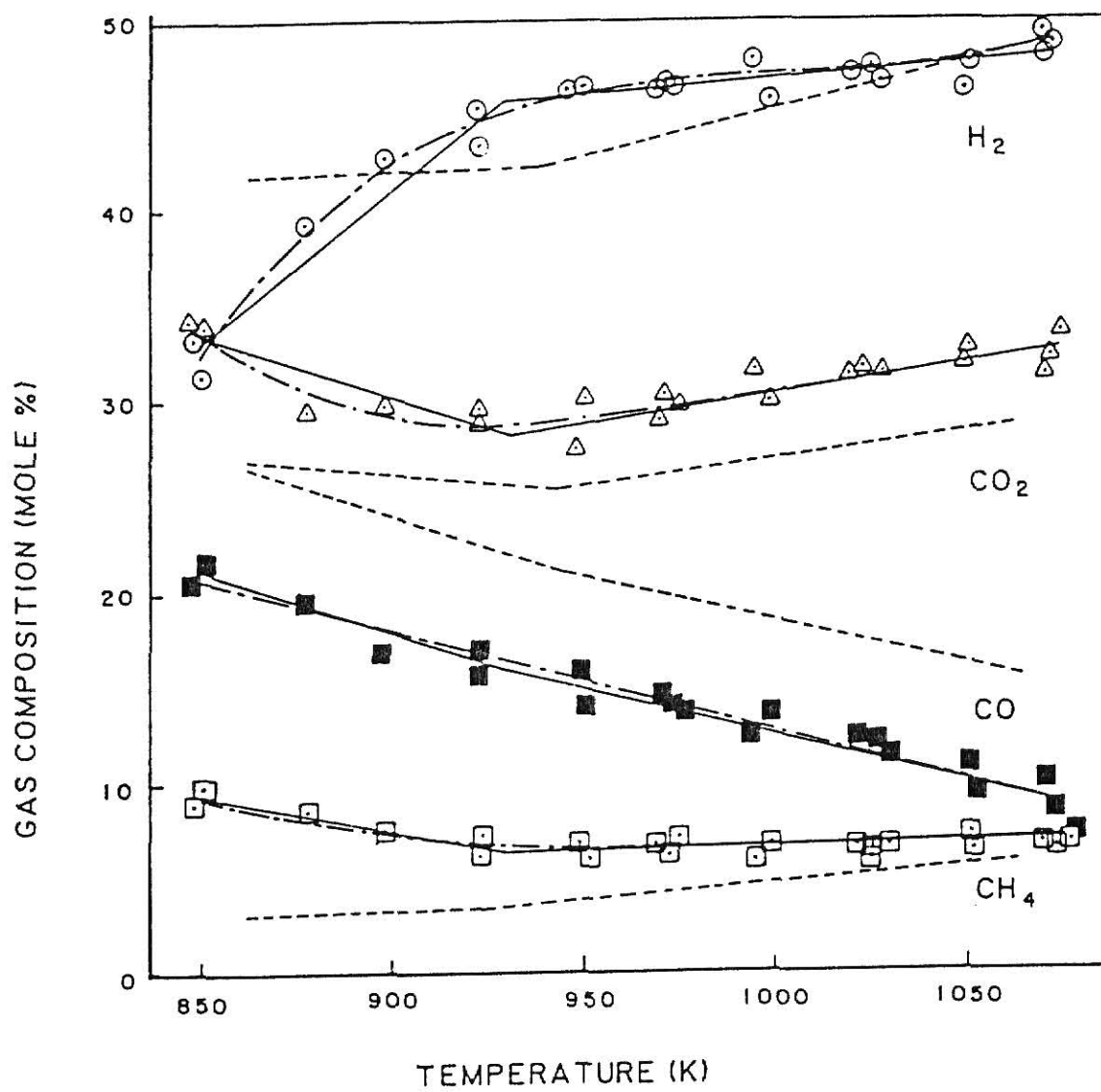
Figure 2. Typical Reactor Temperature Profiles.

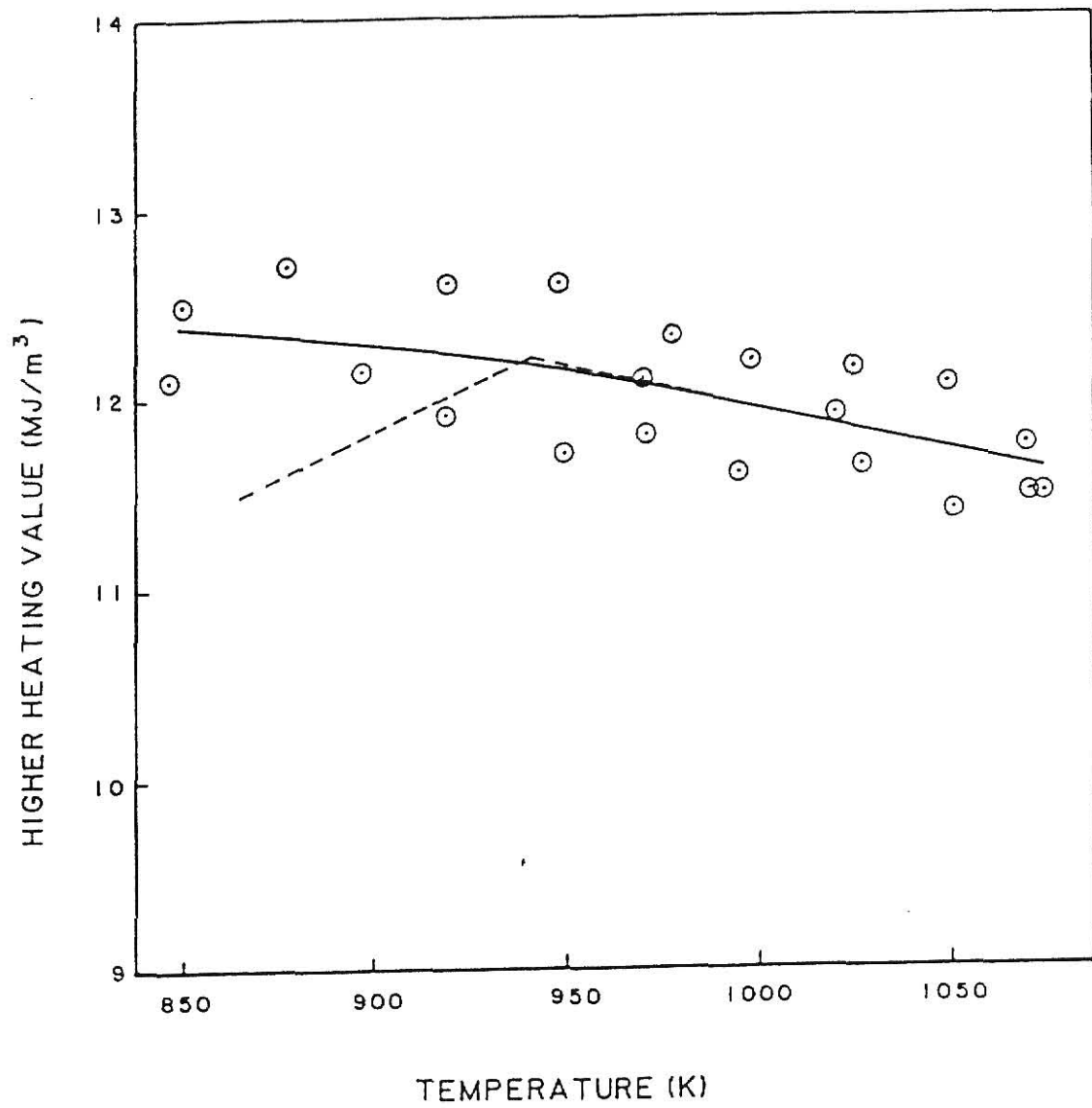Figure 3. Gas Composition vs. Temperature.

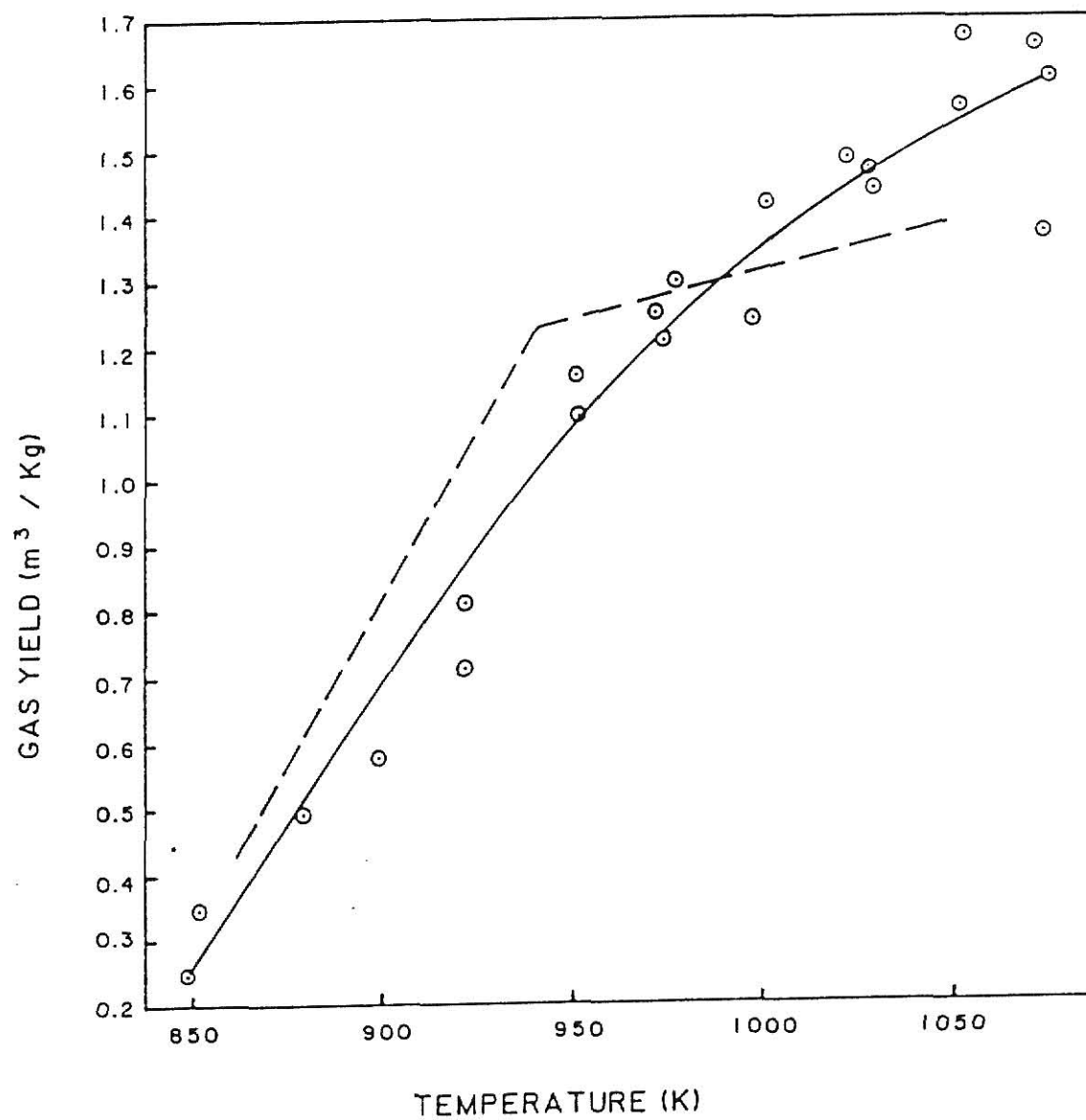Figure 4. Gas Heating Value vs. Temperature.

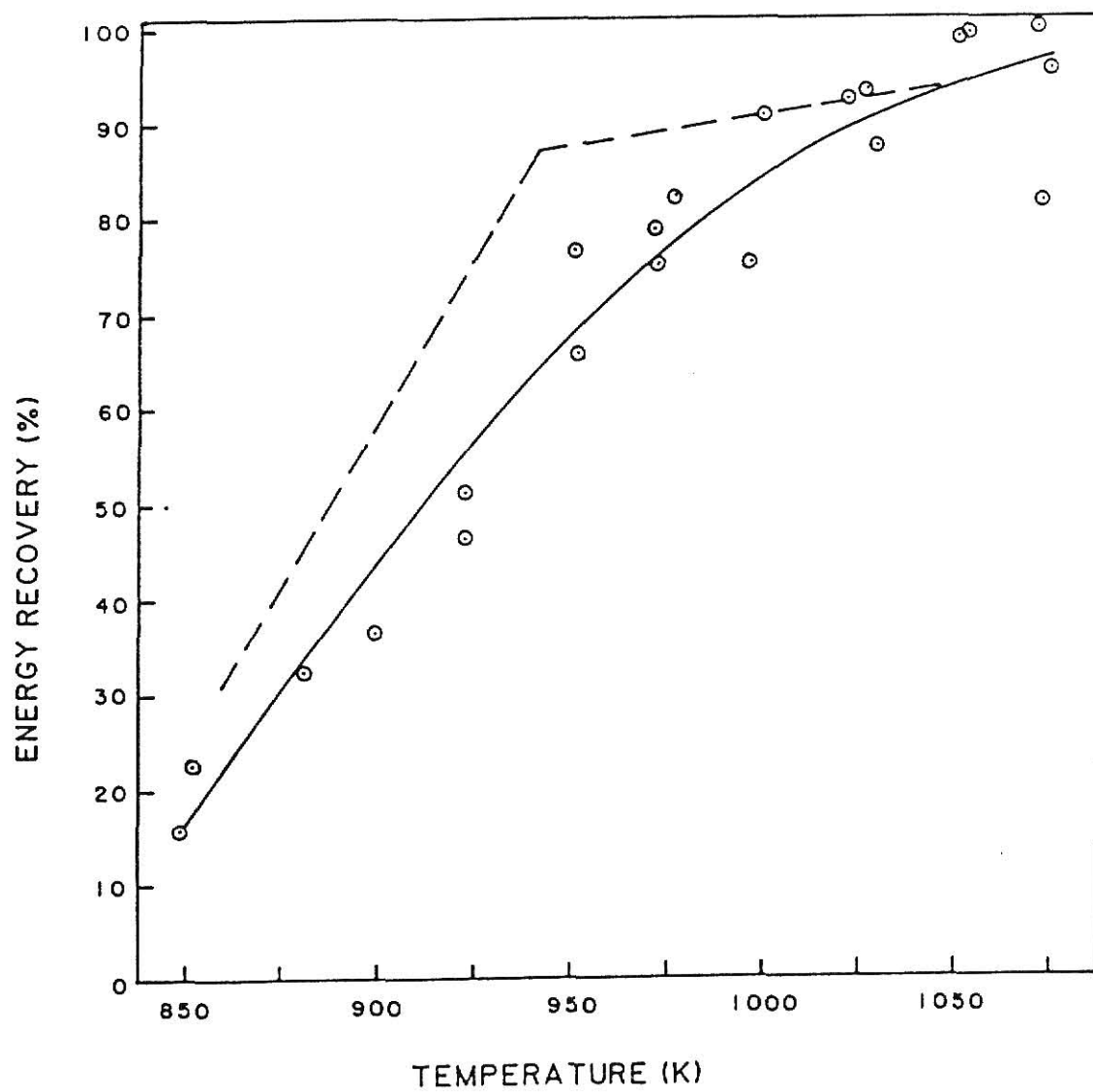Figure 5. Gas Yield vs. Temperature.
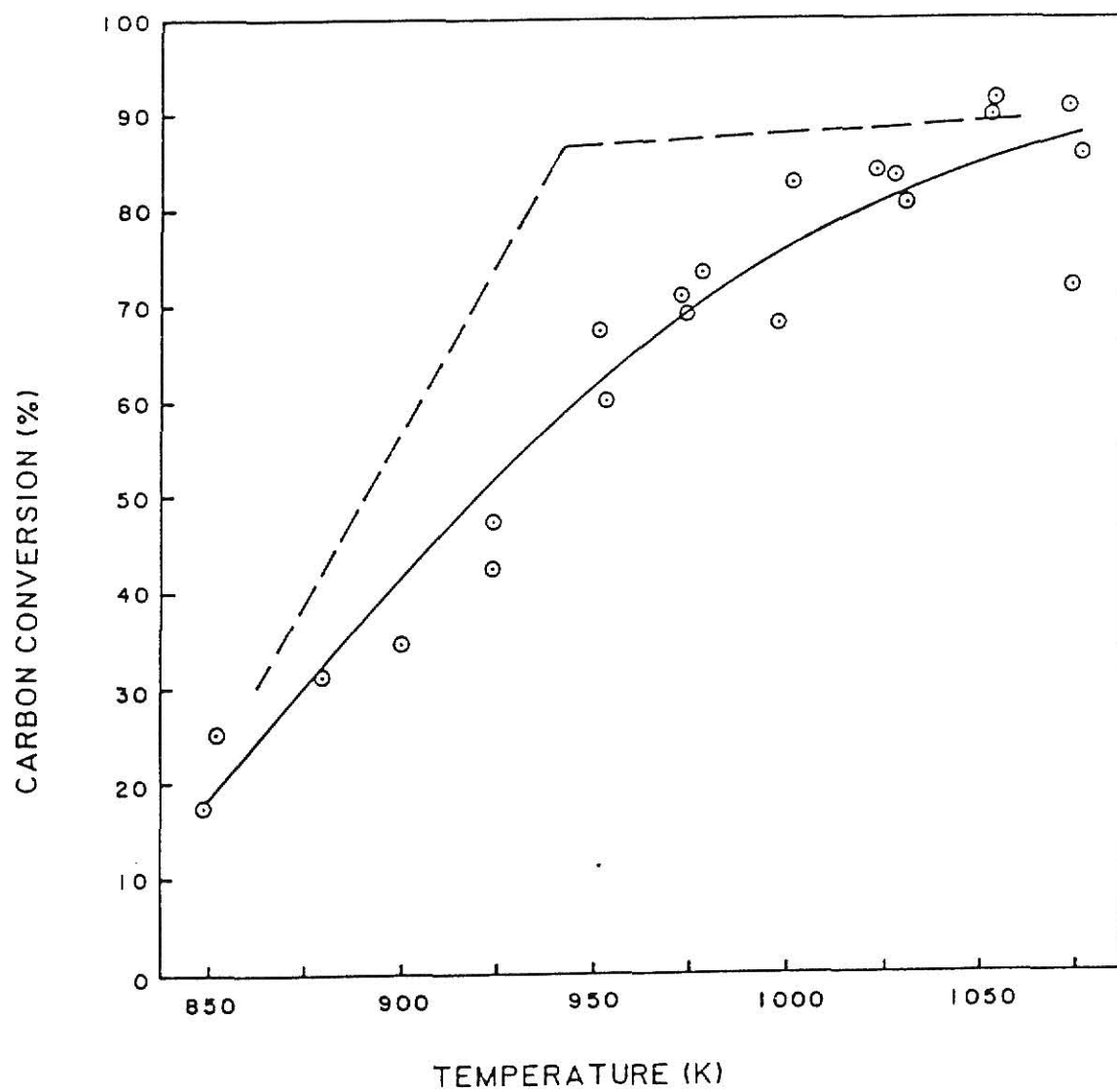
Figure 6. Energy Recovery vs. Temperature.
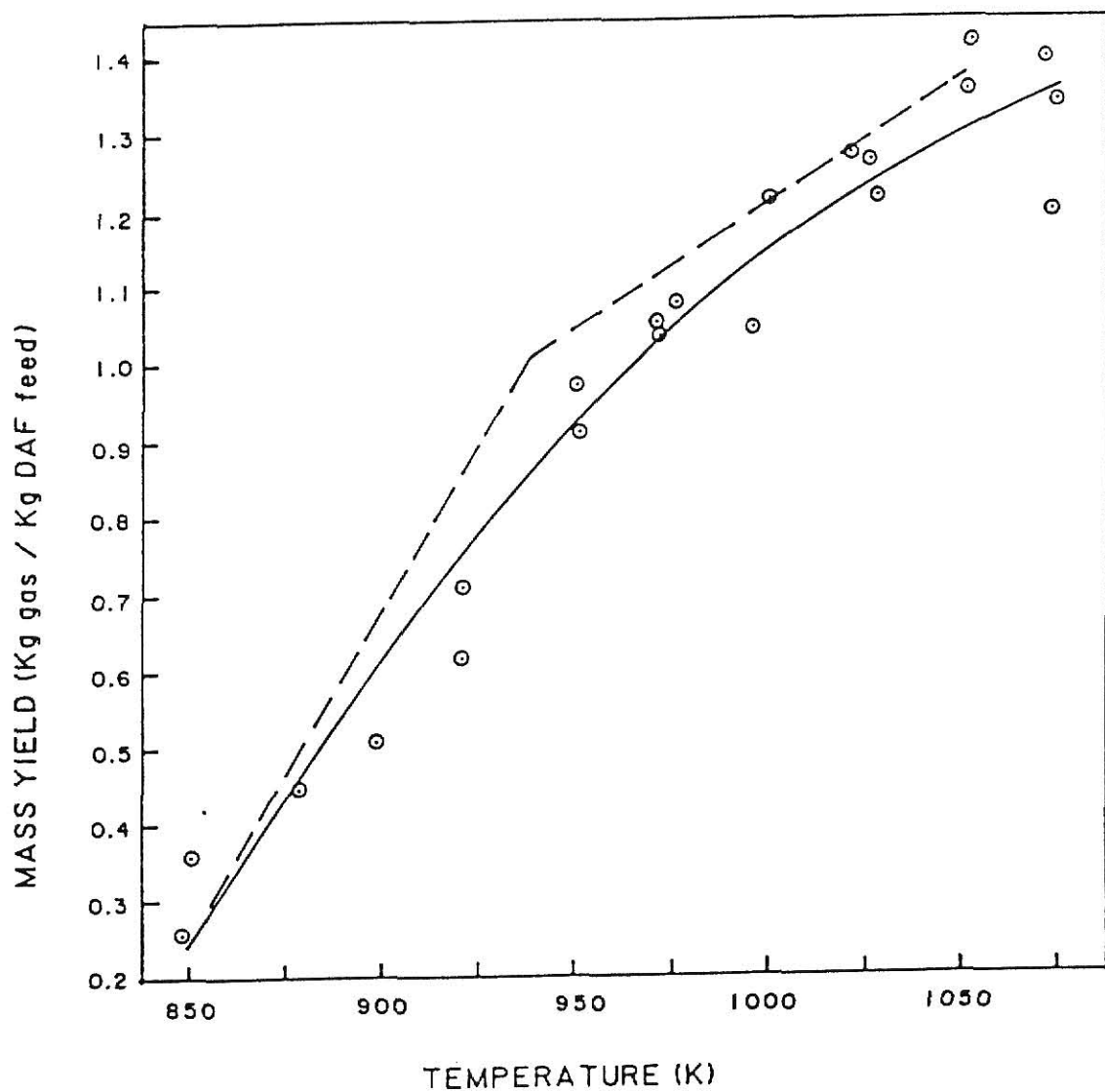
Figure 7. Carbon Conversion vs. Temperature.

Figure 8. Mass Yield vs. Temperature.

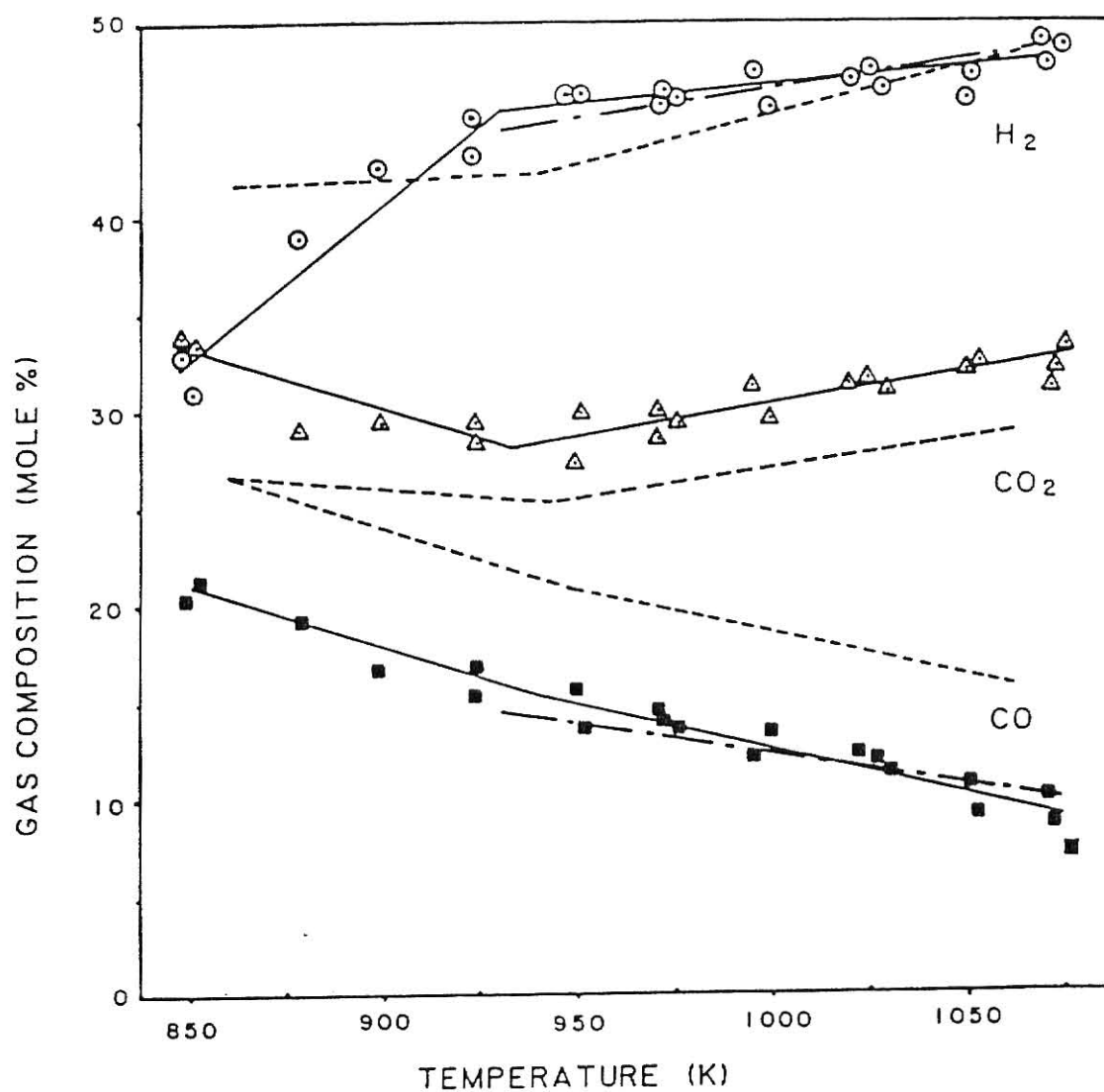Figure 9. Gas Composition (Theoretical Proportion
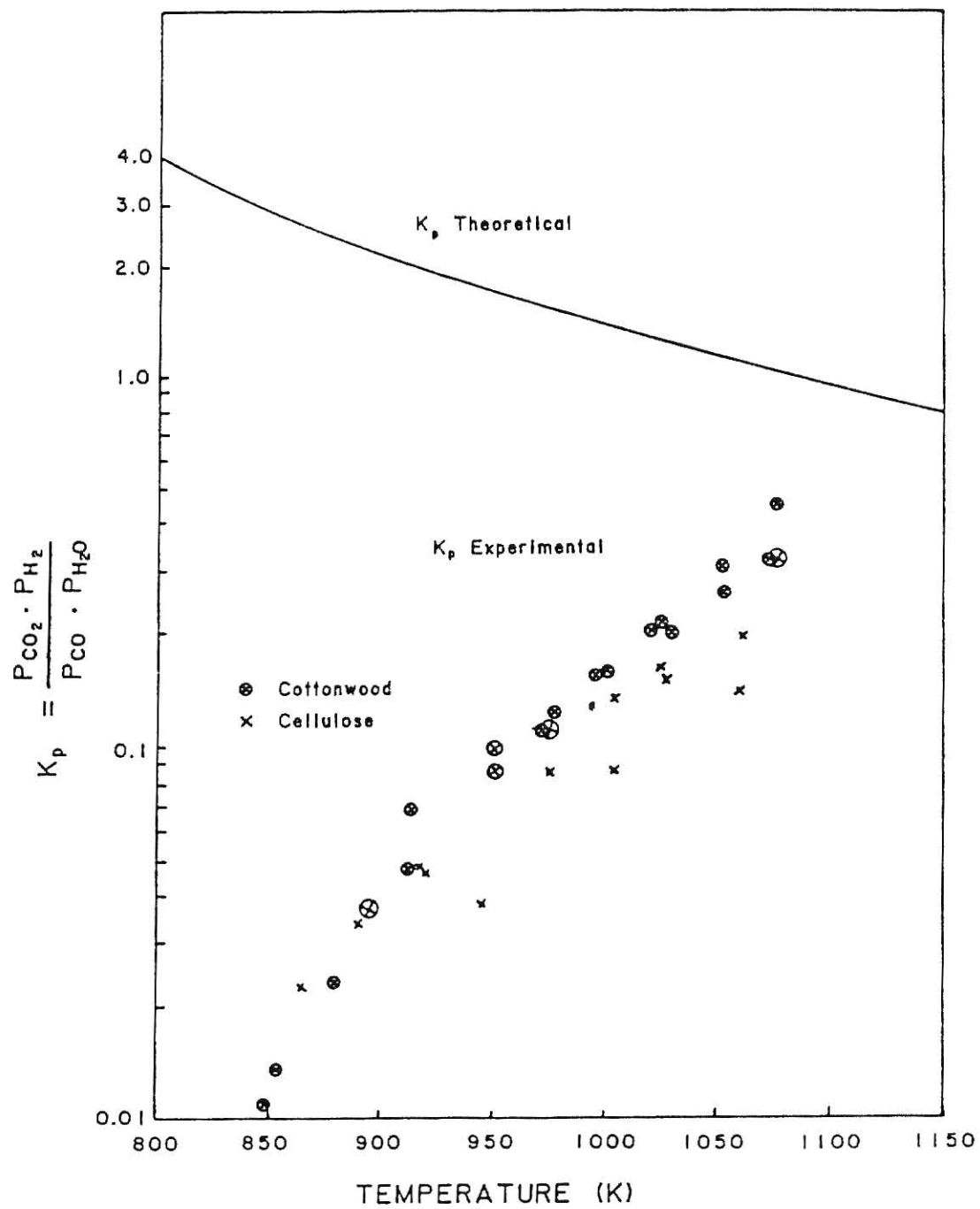Fit) vs. Temperature.

Figure 10. Reactor $P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$
vs. Temperature.

CHAPTER IV

STEAM GASIFICATION OF LIGNIN

Introduction

The gasification of cellulose in various pyrolysis and gasification processes has been extensively studied (Bradbury et al., 1979, Lewellen et al., 1976, Shafizadeh, 1968, Walawender et al., 1982). The product distribution and kinetic data for different reactors and under different operating conditions is relatively abundant. All this is to be expected since cellulose comprises approximately 50 % of all biomass from an annual production of 100 billion tons throughout the world. But while cellulose is the most abundant organic material on earth, products obtained from the gasification of any biomass will be significantly influenced by its other major components – lignin and hemicellulose also.

It has been reported that gas yield and composition are related to the feed composition, among other factors in a gasification process (Antal et al., 1978, Walawender et al., 1980, Raman et al., 1980, Beck and Wang, 1980). Upon being subject to pyrolytic conditions, wood has been suggested to behave much like a mixture of its three major components : cellulose, lignin and hemicellulose. Thus, if wood was completely pyrolyzed, resulting products are about what would be expected by pyrolyzing the three components separately (Browne, 1958). This belief in the additive nature of the products is not supported by Wenzl (1970), who considers that more interaction takes place between the products of pyrolysis from wood components. It is expected that the conditions of pyrolysis such as the surrounding atmosphere, residence time etc. may affect the interaction between components. Shafizadeh (1968) also points out that it is difficult to extend the data obtained from pyrolysis of cellulosic material to wood or plant materials because the latter contain not only a substantial amount of cellulose but also some hemicellulose and lignin. The high lignin content of most biomass is evident

from Table 1 which gives the composition of various types of biomass and wastes.

In this context, it is obvious that if we are to be able to characterize biomass feed material and their products under different operating conditions in various processes, extensive studies, similar to those on cellulose may be necessary.

Lignin is a major component in woody plant cell walls, comprising approximately 25 % of the cell wall material. In fact, lignin is the necessary component for a plant to be classified as woody. Lignin serves as a cement between the wood (cellulose) fibers and as a stiffening agent within the fibers. Hydrophobic lignin in conjunction with hydrophilic hemicellulose gives plants their structure. It also serves as a barrier to enzymatic degradation of the cell wall (Falkehag, 1975).

Apart from these important functions, lignin is a major participant in energy flows in the biosphere. More solar energy is stored in lignin than in other functional components in plants. For softwood with 42 % cellulose, 27 % hemicellulose, 28 % lignin and 3 % lipid extractives, the lignin contributes to the heat of combustion of wood by about 39 %, while the contributions by cellulose and hemicellulose amount to 34 % and 22 % respectively.

Lignins are three-dimensional network polymers formed from phenyl-propane units that have randomly grown into a complicated large molecule with many different kinds of linkages between the monomers. The lignins from grasses, softwoods, and hardwoods differ somewhat in composition and the degree of carbon-carbon linkage between phenyl groups. However their common structural features predominate. An abbreviated schematic structure of kraft pine lignin is shown in Figure 1. The aromatic and phenolic character is apparent.

The molecular weight and chemical properties of any lignin sample depend on its history. It is not possible, with the present knowledge, to remove lignin from wood without some degradation. Lignins, which are byproducts of different pulping processes are different from each other. This is why lignin samples used in various studies are identified by the source or process they were obtained from (Goldstein, 1981).

At this point it will be pertinent to recapitulate the difference between gasification and pyrolysis. Gasification is degradation by thermal reaction in the presence of controlled amounts of oxidizing agents. Pyrolysis, on the other hand, is carried out in the absence of these agents. Also, gasification is normally carried out in a higher temperature region than pyrolysis. The aromatic nature of lignin makes it a good potential source of chemicals and this is the objective of most of the pyrolysis studies on pure lignin.

Katzen et al. (1943) performed destructive distillation on lignin extracted from maple wood. After 5.5 hours at 712 K, they obtained 55.8 % char, 12.5 % aqueous distillate, 7.1 % tars, and 24.7 % gas. The gas was composed of CO_2, O_2, CO, CH_4, H_2, N_2. The concentrations of individual components was not reported. The process was carried out in a retort heated by a gas-fired cast-iron oven burner. Fletcher and Harris (1952) also performed destructive distillation on Douglas-Fir lignin in an externally heated retort packed with dry lignin. The retort had copper tubes welded lengthwise inside to produce uniform heating throughout the mass. Heating at 673 - 718 K for about 7.5 hours yielded 53 - 64.5 % char, 15 - 25 % aqueous distillate, a settled tar, and gases. The aqueous distillate and tar contained a wide range of organic acids and phenolic compounds. The gas composition was not reported.

Goheen and Henderson (1978) conducted rapid, high temperature pyrolysis of kraft lignin in a batch reactor. Lignin was introduced into a hot reactor and the product gas purged with helium. A series of runs with temperature ranging between 1313 and 2033 K were made. They found that the gas contained CH_4, C_2H_4, and C_2H_2. Yields based on lignin feed were CH_4 22.1 % to 13.5 %; C_2H_4 6.5 % to 2.1 %; and C_2H_2 3.2 % to 7.9 %. No other products were reported as the objective of the study was to produce unsaturated hydrocarbons from lignocellulosic materials.

Iatridis and Gavalas (1979), pyrolyzed Douglas-Fir lignin precipated kraft lignin by a captive sample technique. A small sample was placed between two folds of stainless steel wire cloth and heated electrically. The process was conducted in a helium environment with provision to keep gas contents in the reactor below 373 K, and thus restricting secondary gas phase reactions. Various reaction times were used. The authors reported that for pyrolysis times greater than 30 seconds, the total weight loss ranged from 22 % at 673 K to 65 % at 1023 K. The tar yield increased from 8 % of original lignin loading at 673 K to 15 % at 1023 K. Yield of methane ranged from 0.5 % at 673 K to 4.8 % at 923 K (based on original lignin weight). The gas evolved, for a 30 second reaction time, comprised of 15.2 % CO_2 at 773 K and 9.8 % CO_2 at 923 K. CO within this same temperature range varied rom 4.9 % to 11.2 % of the gas. The C_1 - C_4 fraction was essentially constant at about 6.8 %. The detailed product distributions in this study did not account for 100 % of the lignin.

Graef et al. (1979) studied the product distributions from rapid pyrolysis of Pinewood kraft lignin. They obtained 33 - 36 % solid residuals, approximately 10 % volatiles, and 54 % permanent gases. The permanent gases contained about 44 % CO, 2 % CO_2, 43 % H_2, 2 % CH_4, 14 % C_2H_2, and traces

of ethane and higher hydrocarbons. It must be noted that lignin, in this study, was pyrolyzed in a microwave plasma reactor which induces extremely rapid heating at a high temperature. Rapid quenching of the products was done by sweeping them from the reaction zone in a stream of helium. Residence time of the gas phase in the reaction zone varied from 0.1 to 2 seconds, depending on the helium purge rate. Peak surface temperature of the small lignin pellet was observed to be between 923 K - 1023 K. The authors compared their product distribution to conventional pyrolysis and noted that the nature of the two reactions was radically different. The objective of using the microwave plasma process was to narrow the product distribution through the use of high heating rates.

Antal (1982) studied the gas phase pyrolysis reactions of volatiles generated from kraft pine lignin (Indulin AT). The samples were devolatilized in a flowing steam environment at 773 K and the gas phase reactions studied in a quartz plug flow reactor, where reaction temperature and residence times could be controlled. His results showed a maximum carbon conversion of 20 % at 1023 K. For the maximum temperature studied (1023 K) with approximately 2 seconds of residence time, the gas analysis gave 15 % CO, 63 % H_2, 6.3 % CO_2, 13 % CH_4 and small amounts of C_2 - C_3 compounds. Gas phase reaction temperatures had a more significant effect on results than residence times. He also tried to explain yields from wood in terms of a linear superposition of yields obtained from experiments on individual wood components (lignin, cellulose, and D - mannose). His conclusion was that wood gasification probably does not simply reflect the independent behavior of its components.

In considering the kinetics of lignin pyrolysis, it has been suggested that the major components of biomass degrade in separate pathways

delayed in temperature (Shafizadeh et al., 1979, Milne, 1979). When one examines the thermal behavior of each component as indicated by weight loss as a function of slowly increasing temperature in Figure 2, it is evident that the lignin undergoes degradation over a wider range of temperatures than cellulose and hemicellulose (Shafizadeh and McGinnis, 1971). These observations imply that lignin exhibits a wider distribution of bond strengths and a large number of reactive volatiles. It seems that no single intermediate dominates the pyrolysis pathways of lignin as levoglucosan does in the pyrolysis of cellulose (Shafizadeh, 1968). The products of lignin pyrolysis reflect the complexity of the lignin molecule in which many repeating units are present with a variety of possible linkages. This is why no simple model for lignin pyrolysis, comparable to that for cellulose (Antal et al., 1978), is available nor is there any kinetic data in the literature.

There is no report of lignin being gasified in a fluidized bed reactor with the specific purpose of characterizing it as a parameter in gasification of biomass wastes. Thus the objective of this study was to focus on the gasification of pure lignin in a fluidized bed - the gasification being examined under continuous steady state conditions. The primary experimental variable was temperature and its effect on produced gas composition, yield, and energy recovery and carbon conversion were to be studied. This would generate datum lines under well defined conditions, which in conjunction with the already available data on cellulose from the same system (Walawender et al., 1982), could be used to understand the gasification of biomass as it is influenced by the material make-up.

Experimental Facilities and Procedure

The experimental facilities used for experiments on lignin were the same as reported for wood in Chapter III. The experimental procedure was also similar up to the point where the feeding was initiated. From there on, all the attempted runs on lignin were unsuccessful. The feed material sintered, bubbled, and then solidified to form a hard brittle plug in the feed-pipe. This effectively prevented the feed and the nitrogen purge from entering the reactor and thus disrupted the run. The top of the feed-pipe had to be disconnected and air blown into the reactor to oxidize the lignin plug out of the pipe.

Feed material preparation

Lignin to be used in this study was obtained from Westvaco (chemicals div. polychemicals dept.) Charleston Heights, S.C. It had a trade name Indulin AT and was derived from kraft alkaline pulping process. It was obtained as a free flowing fine powder, with a flash point of 450 K and a sintering temperature of 461 K.

The as-received lignin was pelletized by extruding it through a screw-feeder with steam being added to it in the screw. It came out as clumps which were then broken in a grinder. The -28 +50 mesh size fraction was collected after sifting to be used as the feed for the reactor.

An ultimate analysis of the lignin is given in Table 2.

Other Methods of Feed Preparation

The first attempts to gasify lignin were made with pure lignin in the form of powder and pellets. These attempts were unsuccessful as the pure lignin sintered and blocked the feed-pipe within a minute of initiating feeding. The plug normally formed between 1 to 4 cm below the top plate of the reactor.

In order to facilitate feeding, the feed rate was reduced and the nitrogen purge rate in the feed-pipe increased. This arrangement enabled the system to work, but the feed rate was so small that coupled with the diluting effect of N_2, the gas chromatograph did not detect any significant changes in the gas composition. The large volume of the total system as compared to the gas generated also contributed to the problem. A plug would eventually be formed in 15 - 20 minutes, at these small feed rates also before any meaningful data could be obtained.

A second set of attempts was made by pelletizing a 50 % by weight each, lignin and fine sand (-80 +200mesh) mixture. This sand was so choosen that under normal operating conditions, it would be entrained in the off-gas to the cyclone. Pelletization was done as before by extruding the mixture a screw feeder with a steam feed. Clumps of the mixture had to be ground and the -28 +50 mesh fraction collected. This mixture did not turn out to be any better than the pure lignin feed.

The next tactic tried was to combine lignin with pure α - cellulose and feed the pelletized mixture. Two combinations were tried - 75 % cellulose, 25 % lignin; and 90 % cellulose, 10 % lignin (by weight). Pelletization was done by blending the mixture with water to make a paste which was then pressed through a 2 mm. screen. The resulting pellets were dried at 323 K for 48 hours and then seived to extract the -28 +50 mesh particles.

The 75 % - 25 % mixture was not successful. The 90 % - 10 % mixture could be fed for about 20 minutes before the feed-pipe got plugged. 20 mins. was not long enough to get good steady gas chromatograph (GC) readings. Data from a representative run on this mixture after 20 minutes is given in Table 3. These results were obtained before the steady state gas composition was recorded by the GC. A disadvantage of this mixture was that while feeding could be prolonged by reducing the feed rate, it would be difficult to separate the effects of cellulose and lignin.

On heating pure lignin in a muffle furnace at 463 - 473 K, it was observed that if the sample was removed from the furnace after it had sintered and fused, the pellets would cool to a hard brittle mass. This mass could be broken into small pieces and on reheating to and beyond 473 K, the sintering would not reoccur. The small pieces would not fuse together again. This suggested that if the weight loss was not substantial, lignin could be sintered in a furnace, repelletized and then used as a feed material for the reactor. The data bulletin on Indulin AT from Westvaco gave the percentage weight loss on heating in air at 422 K to be 1 %; at 477 K to be 7 %. This magnitude of weight loss was considered acceptable.

Quantities of lignin powder were then heated on aluminum foils in a ventilated oven at temperatures between 443 K and 453 K for 20 minutes. The material smoked and blackened into a hard mass but did not appear to have undergone sintering. A weight loss of about 1.5 % (dry basis) was recorded. This pretreated lignin, on feeding immediately plugged the feed-pipe.

The temperature of the pretreatment was then raised to between 453 - 463 K. Parts of this material sintered and a weight loss of approximately 2.5 % (dry basis) was observed. There was no success in feeding this material either.

Finally, pretreatment was done at 463 - 473 K (5 % weight loss) and at 473 - 483 K (10 % weight loss), with no success. Samples of this oven pretreated material, on heating in a muffle furnace showed slight amounts of sintering. The main problem with the pretreatment was that the heating was not uniform in the oven. Depending on the thickness of the lignin layer on the foil, parts of the lignin would undergo sintering while others would not. The portion of lignin which did not get heated to the sintering temperature would then cause a plug in the reactor.

It was then decided to abandon the attempts to gasify lignin. The problem had to approached from a different direction. Instead of trying to modify the lignin feed, modifications were needed on the reactor.

Discussion

The only other report on the gasification of lignin in a continuous flow reactor is from SERI (Diebold, 1980). He attempted to gasify lignin in an entrained flow reactor but encountered similar problems in feeding lignin. His procedure involved entrainment of a metered amount of lignin in a carrier gas (CO_2), into a helical pyrolysis tube. Steam was added to the tube and the whole tube was placed inside a furnace. Lignin in his case sintered and blocked the entrance to the pyrolysis tube. He did not report any successful runs with lignin.

In order to be able to gasify pure lignin, either the experiments will have to be of the batch-type or major modifications in the present system will be needed. Since the basic problem lies in the feed-pipe being too hot, a jacketed pipe with cooling water to keep the temperature inside the pipe below 463 K may work. This may enable the lignin to drop into the bed before sintering. A problem with such a system will be the difficulty

in maintaining a uniform or an elevated temperature profile in the reactor. A 0.1016 m I.D. bed reactor with just such an arrangement has been constructed, and is currently being installed at Kansas State University, for studies on liquefaction of coal and oil-shale. Experiments on lignin could be performed on this system in the future.

An alternative arrangement can be to introduce the feed from the side of the reactor, directly into the bed. A screw feeder in a jacketed pipe may do the job. This would avoid the problem of maintaining a temperature profile in the reactor. A side or top feed can also be used with the feed being entrained in a jet of nitrogen. This arrangement may be better than using a screw feeder on the side as the pellets would then be forced in at high speeds.

While these suggested modifications remain to be tested, it must be noted that a 90 % - 10 % mixture of cellulose - lignin could be fed for about 20 minutes in the present set-up. While this is too short a time to get steady GC readings, it is enough to give a steady state gas analysis as the reactor comes to equilibrium in this time. By making arrangements to collect the gas evolved in the last 10 minutes and analyzing it in a bench GC, some useful data may be obtained. More uniform presentering may also work, but this has the disadvantage of weight losses and other changes which may occur in the lignin.

Conclusions

Attempts were made to gasify lignin in a bench-scale fluidized bed reactor. Gasification could not be studied as the lignin sintered and blocked the feed-pipe. The feed material was then modified by mixing with sand/cellulose in different amounts. Pretreatment of lignin by heating in a ventilated oven to sintering temperatures was also tried. All these attempts were unsuccessful but the 90 % - 10 % cellulose - lignin mixture could be fed for approximately 20 minutes. Modifications to the existing system have been proposed.

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Table 1.

Composition of Various Types of Biomass (% dry weight)

Material	Cellulose	Hemicellulose	Lignin
Cotton, Flax etc.	80 – 95	5 – 20	–
Grasses (including palms, bamboo, sugar-cane etc.)	25 – 40	25 – 50	10 – 30
Temperate Hardwoods	45 ± 2	30 ± 5	20 ± 4
Softwoods	42 ± 2	27 ± 2	28 ± 3
Animal Manure	18	–	–
Corn cobs	41	36	6
Corn stalks	29	28	3
Wheat straw	40	29	14
Newspapers	40 – 55	25 – 30	18 – 30
Chemical Pulps	60 – 80	20 – 30	2 – 10

Table 2.

Ultimate Analysis of Pure Lignin (% dry Basis) Indulin AT.

Ash	1.0
C	64.3
H	5.7
N	0.03
O[1]	29.0

Average Moisture Content	2 %
Empirical Formula	$C_6H_{6.38}O_{2.09}$
Heat of Combustion (DAF basis)[2]	25.0145 MJ/kg.

[1]   by difference

[2]   Dulong's Formula

Table 3.

Results of Gasification of 90 % cellulose - 10 % lignin mixture

at 873 K after 20 minutes of operation

Gas Composition (mole % dry gas)

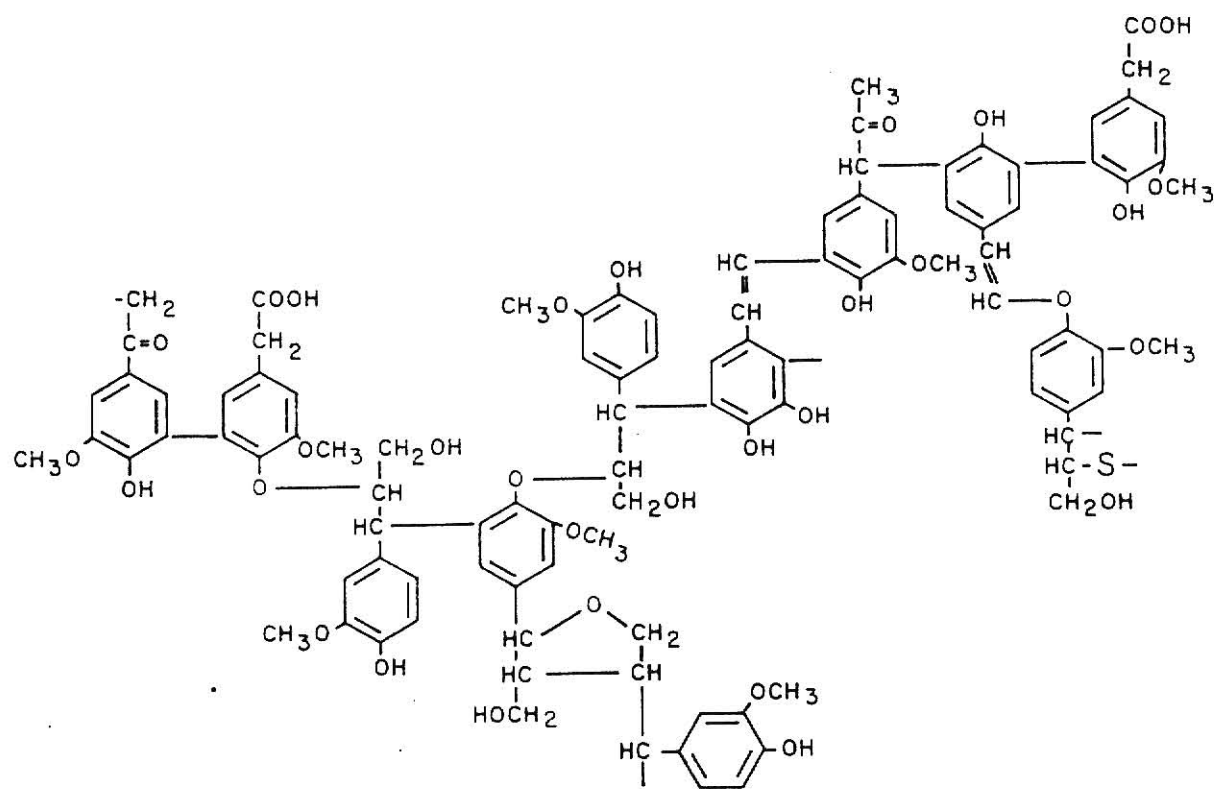|	
H_2	30.9
CO	28.5
CO_2	32.0
CH_4	5.76
C_2H_6	0.56
C_2H_4	1.37
C_3H_6	0.87
Gas Yield	0.23 m^3/kg. DAF feed
Carbon Conversion	13.1 %
Energy Recovery	16.3 %
Produced Gas Heating Value	11.36 MJ/m^3

Figure 1. Abbreviated Schematic of Kraft Pine Lignin
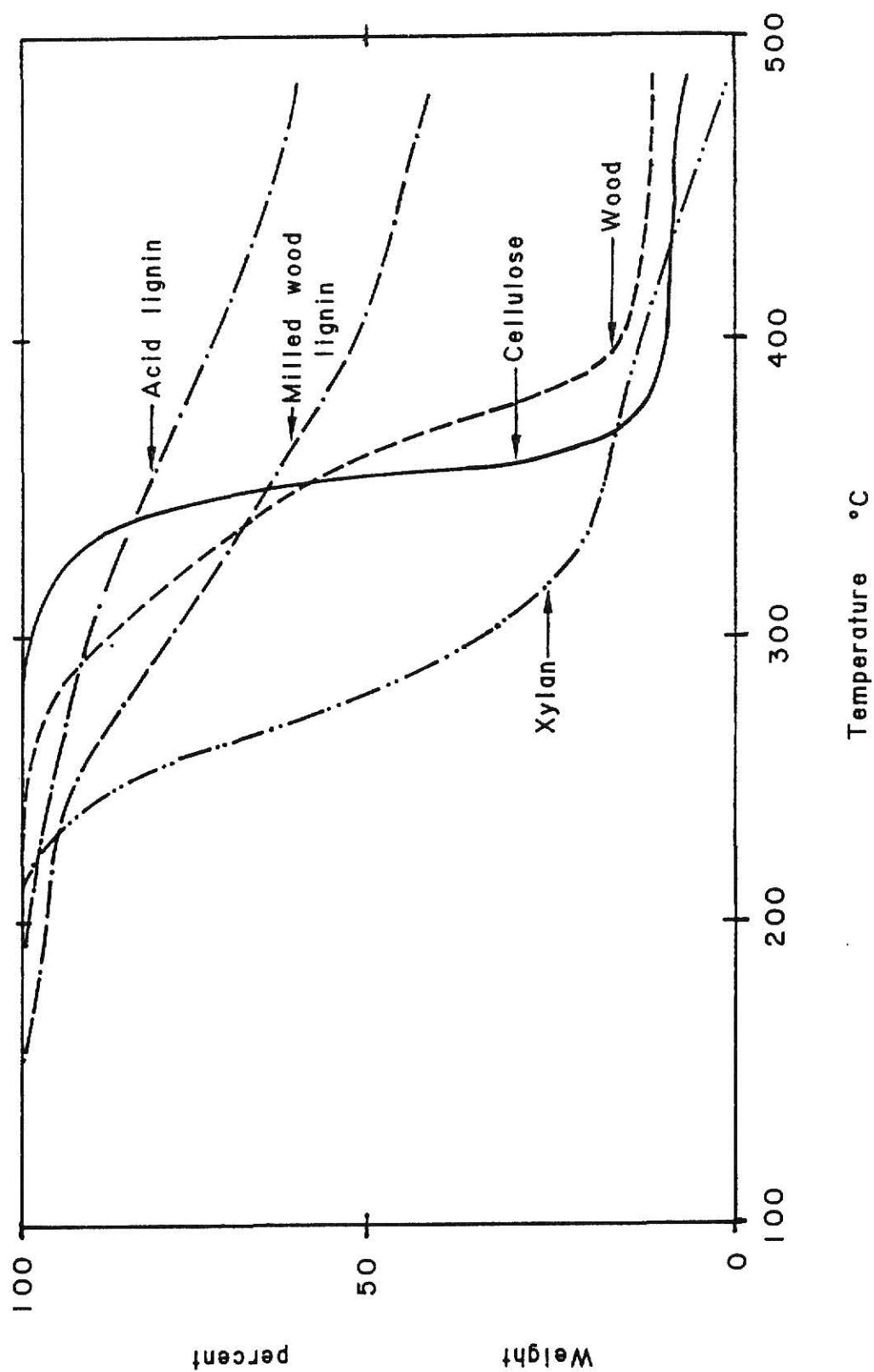(Data Bulletin on Indulin AT).

Figure 2. Thermogravimetric Analysis of Cottonwood and its Components (Shafizadeh and McGinnis, 1971).

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Gasification experiments were conducted on cottonwood (branchwood) in a 0.0508 m I.D. fluidized bed reactor. Steam was used as the fluidizing and gasification agent. The objective was to examine the steam gasification of wood under steady state conditions. The produced gas characteristics were examined as functions of temperature, in the range 850 - 1075 K with the gas residence time being held fairly constant. The major components of the produced gas were CO, CO_2, H_2, and CH_4, comprising over 90 % of the gas. The gas yield increased with temperature from 0.23 to 1.59 m^3/kg. Energy recovery and carbon conversion also increased with increasing temperature from 15.0 to 96.8 % and 16.9 to 87.1 % respectively. The higher heating value of the gas decreased from 12.4 to 11.6 MJ/m^3.

The behavior of the gas composition data indicated the existence of two regimes in the gasification process. The first regime was dominated by tar cracking and the second, at higher temperatures ($>$ 930 - 940 K), by water-gas-shift reaction. Tar cracking reactions for wood occured above 930 - 940 K also, but their extent was small relative to water-gas-shift, and hence the shift reaction determined the product characteristics in this range of temperatures. The existence of these regimes was supported by the other results obtained. Steam was found to be an important gasification agent when present in large amounts. It was converted to the product gas in significant amounts through the shift reaction.

Similar gasification experiments were attempted on lignin. The objective was to generate datum lines under well defined conditions to serve as a bench-mark in gauging biomass and biomass gasification processes. All the experiments were unsuccessful as the lignin sintered, bubbled, and solidified, effectively blocking the feed-pipe and disrupting the run. Various other methods of feed preparation were tried to no avail.

Modifications on the existing experimental system are proposed.

Further modifications may be required on the system to provide a more uniform feed rate. A better method of estimating the feed rate is also needed. This will reduce some of the experimental data scatter and make it more suitable for analysis. Modifications are also needed to be able to conduct mass balance analysis on the system. For this purpose, improved steam and condensate rate estimation techniques are needed. Char estimation will have to be done by indirect methods like elemental balance or ash balance unless char hold-up can be estimated or eliminated. Analysis of tar will help in confirming the existence of tar cracking regime and may show the possibility of extracting a range of useful products from it.

This work can be extended by studying the gasification of wood beyond 1075 K. Data in this range will be influenced by steam gasification of char. The water-gas-shift reaction will start to be less and less important as the extent of the reverse reaction increases. The influence of residence time can also be tested by changing the steam rate at a particular temperature. The present experimental technique gives different steam to DAF feed ratios at various temperatures with constant volatiles residence times. It can be easily modified to give a constant steam to DAF feed ratio by adjusting the residence time using different N_2 purge rates.

The work on cellulose can be extended by gasifying lignin and hemicellulose in the same system. Gasification of lignin will help confirm the statements about the cracking of lignin tar made in Chapter III. Hemicellulose contains two to four different polymeric sugars. Xylans, polymers of d - xylose $C_5H_{10}O$, which are the most abundant, will be the most representative ones to study. With this data base, it will be possible to test the hypothesis that products from gasification of biomass are the sum

of the products from its components.

The data base can also be used to characterize the various biomasses as to their effectiveness in producing a particular product (fuel gas or synthesis gas or liquid or even a particular organic chemical), from a certain process or treatment condition. Further investigation can also be done by studying different parts of the biomass like stem, branches, leaves, and bark etc. separately as there is enough evidence to believe that each of these behaves differently in gasification due to their different compositions, age, density, moisture content, and morphology. These may differ from species to species also. Ultimately, by correlating the data, an empirical model may be built to predict product distributions, given certain information about the feed and process.

THE GASIFICATION OF BIOMASS IN A FLUIDIZED BED REACTOR

by

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The steam gasification of wood was studied in a 0.0508 m I.D. bench scale fluidized bed reactor. The overall objective of the work was to investigate the effect of reactor temperature on the produced gas composition, yield, and heating value. The energy recovery and carbon conversion were also determined and the results were compared with data from cellulose gasification in the same reactor.

Cottonwood (branchwood) was gasified over a temperature range of 850 – 1075 K. The major components of the produced gas were CO, CO_2, H_2, and CH_4, comprising over 90 % of the gas. The gas yield, energy recovery, and carbon conversion increased with temperature from 0.23 to 1.59 m3/kg., 15.0 to 96.8 %, and 16.9 to 87.1 % respectively. The heating value of the gas decreased from 12.4 to 11.6 MJ/m^3.

The behavior of the gas composition data indicated the existence of two regimes in the gasification of wood. The first regime was dominated by tar cracking and the second, at higher temperatures ($>$ 930 – 940 K), by the water-gas-shift reaction. Tar cracking reactions for wood occured above 930 – 940 K also but their extent was small relative to the shift reaction and hence the shift reaction determined the gas composition in this range of temperatures. Steam, in large excess, was found to be an active gasification agent and participated in the gasification process through the shift reaction. Mass yields greater than 1 kg. gas/kg. DAF feed were consequently found at high temperatures.

Gasification experiments were also attempted on pure lignin. All the experiments were unsuccessful because the lignin sintered, bubbled, and solidified in the feed-pipe preventing its introduction into the reactor. Various methods of lignin preparation and cellulose – lignin mixtures were also tried without success.