

STEAM GASIFICATION OF WOOD IN A FLUIDIZED BED

by

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CHAPTER I  
INTRODUCTION

Currently, U.S. industries are considering alternative energy sources to meet future demands. This search has been prompted by the facts that: (1) the world's oil reserves are being rapidly depleted, and (2) the U.S. is highly dependent on foreign oil; the supply of which has proven unreliable in the past (for example, the 1973 oil crisis). Biomass offers an alternative source of renewable energy either through direct combustion or through conversion into liquid or gaseous fuels.

Wood is the largest potential source of biomass energy. However, the use of wood for energy on a large scale is still in the early stages of development. Much of the research in this area is directed toward forest management and energy conversion processes.

Gasification offers an attractive method to convert wood into gases for either low to medium heating value fuel gas or synthesis gas for methane, methanol or ammonia production. The addition of steam in the gasification process has been found to increase the gas yield and carbon conversion through char gasification and the water-gas shift reaction. The water-gas shift reaction can play an important role in adjusting the  $H_2/CO$  ratio for specific chemical syntheses.

In this thesis, steam gasification experiments with different tree species were performed in a fluidized-bed reactor to investigate the effect of differences in wood chemical composition on the gas composition and product yields. In addition, the influence of the steam-to-feed ratio and the gas phase residence time were assessed.

In Chapter II, literature relevant to steam gasification technology is reviewed along with the viability of wood as a renewable energy source. The topics included in the review are (1) wood energy potential, (2) short rotation forestry programs, (3) overview of thermochemical conversion processes, (4) theoretical considerations for thermochemical wood conversion and (5) recent steam gasification studies.

Chapter III presents a statistical comparison of the steam gasification of Siberian elm and cottonwood in a fluidized-bed reactor. The comparison provides an assessment of the effects of differences in the wood chemical composition on various gasification characteristics. The results are also compared to those from related studies to elucidate the effects of varying the steam-to-feed ratio and the gas phase residence time on the product yields and distributions.

Chapter IV presents a statistical comparison of the steam gasification of four cottonwood clones in a fluidized-bed reactor. Comparisons are performed as a preliminary screening to determine whether or not differences in the gasification characteristics exist between the clones.

In Chapter V, the major conclusions from the experimental work presented in Chapters III and IV are summarized. In addition, recommendations for future work are presented.

CHAPTER II

GASIFICATION OF WOOD - A LITERATURE REVIEW

## INTRODUCTION

With continuing depletion of the world's oil reserves and the U.S.'s high demand for crude oil, U.S. industries are looking for alternative energy sources. This search is further prompted by the fact that the U.S. is highly dependent on foreign oil; the supply of which has proven unreliable in the past, (for example, the 1973 oil crisis). Biomass offers an alternative source of renewable energy either through direct combustion or through conversion into liquid or gaseous fuels.

Wood is the largest potential source of biomass energy. However, the use of wood for energy on a large scale is still in the early stages of development. Much of the research in this area is directed toward the growth of woody biomass and wood energy conversion processes.

This thesis is concerned with one particular area of wood energy conversion; i.e., steam gasification in a fluidized bed. In this chapter, literature relevant to this technology is reviewed along with the viability of wood as a renewable energy source. The topics included in the review are (1) wood energy potential, (2) short rotation forestry programs, (3) overview of thermochemical conversion processes, (4) theoretical considerations for thermochemical conversion including wood chemical composition and the thermodynamics and kinetics of wood pyrolysis/gasification and (5) steam gasification process development studies.

## WOOD ENERGY POTENTIAL

The potential of wood as an alternative energy source depends on the extent of the forest reserves. Estimations of the forest reserves vary greatly. The wide variation in estimates is due, in part, to the methods employed to obtain the estimates and/or their interpretation. In fact, most of the estimates tend to be overly optimistic.

Nevertheless, some of the current estimates will be given. The world reserves have been reported to be in the range of 230 billion metric tons to 1.65 trillion metric tons (Smil, 1983). Using an energy to mass conversion factor of 19 MJ/kg and an intermediate value of 1 trillion metric tons for the forest reserves, the energy potential is  $1.9 \times 10^{22}$  J, which is three times the known crude oil reserves in 1980 or the approximate equivalent of the total known coal reserves (Smil, 1983). Two estimates for the U.S. forest reserves are  $3.2 \times 10^{12}$  metric tons (Young *et al.*, 1986) and  $11.2 \times 10^{12}$  metric tons (Lipinsky, 1985). Using the energy-mass conversion factor of 19 MJ/kg, the energy potential of the U.S. reserves range from 62 EJ to 212 EJ (1 EJ =  $10^{18}$  J).

However, it is totally unrealistic to consider the entire forest reserves as a potential energy source since rapid conversion of the world's forests into energy would have a devastating effect on the ecosystem. Consideration must also be given to the fact that wood is used primarily for construction materials and paper products. Consequently, the energy potential from wood is far lower than projections based on reserves. In addition, the energy requirements

for harvesting, drying, transporting and processing need to be considered in determining the net energy conversion factor. Hence, the net energy yield from a wood-energy conversion process along with the extent of implementation of these processes will give the true potential.

Smil (1983) has presented a detailed review of the potential of plant life to store the sun's energy. Here, a brief summary of his report will be presented. Only a small fraction of the sun's total energy or 0.00021% ever reaches the earth. Out of this small fraction, 47% of the sunlight which reaches the earth ( $2.6 \times 10^{26}$  EJ/yr) is absorbed by the earth's surface. The fraction of the solar energy that can be converted by plants is relatively small. The maximum theoretical efficiency for the conversion of the sun's energy by plants has been determined to be 27.5%. However, plants can use only 43% of the sunlight absorbed by the earth. Hence, the upper limit for sunlight conversion is 12% of that absorbed by the earth's surface.

This limit represents a sizeable energy source, but the actual conversion for most plants and trees is of the order of a few tenths of a percent. Consequently, annual yields of converted sunlight in the U.S. are approximately 100 EJ (Smil, 1983; Parnell, 1985). In comparison, U.S. consumption was 83.2 EJ in 1982 (Stout, 1985). Young et al. (1986) conducted a study to estimate the amount of land that would need to be allocated for forests to replace the liquid and gaseous fuels consumed by the U.S. in 1982. In the study, they considered the production of methanol or SNG (synthetic natural gas)



from wood gasification as the means to replace conventional liquid or gaseous fuels. They concluded that 253% more forest land than is currently in existence would be needed to replace our liquid fuels and 108% more forest land than is currently in existence would be needed to replace our gaseous fuels. Thus, it is impractical to consider biomass as a long term energy replacement for crude oil and coal.

However, it is appropriate to view biomass as a viable source of supplemental energy. Several studies give estimates for the annual wood energy potential in the range from 2 to 5 EJ with optimistic values ranging from 10 to 18 EJ (Anderson, 1977; Smil, 1983; Kulp, 1985; Lipinsky, 1985; Schiefelbein, 1985; Stout, 1985). Smil (1983) has estimated a practical limit for energy deriveable from wood to be 5 to 10% of the current U.S. annual energy demand and Parnell (1985) has given a practical limit of 4 EJ/yr or about 5%.

Presently, energy from wood has been estimated to provide anywhere from 230 PJ (PJ =  $10^{15}$  J) to 2.3 EJ (Smil, 1983; Kulp, 1985). Thus, significant potential exists for increasing the use of wood as an energy source. The pulp and paper industry already derives 78% of its energy needs from wood wastes (Ostermeier et al., 1985). Hence, increasing the use of wood for energy in this sector will have little impact on the overall energy picture.

#### SHORT ROTATION FORESTRY PROGRAMS

One method for increasing the potential of wood for energy is by developing new approaches to manage its growth. One such technique is the short-rotation energy plantation concept (i.e.; 2 to 8 yr cutting

cycles) that has received attention over the last decade (Geyer et al., 1985). The wood used for the experiments in this thesis was obtained from this type of program.

The main goal of the short rotation concept is to manage wood production in the same manner as conventional farming; i.e., to achieve control of the variables influencing growth and thus maximize economic gain. However, the program is still in the experimental stage. Research programs are addressing several areas including the selection of species, selection and breeding of clones, optimum spacing, effect of soil conditions, harvesting times in the year and length of the cutting cycle, application of fertilizers, disease and insect control, and economic viability.

Some of the species that hold promise in the U.S. midwest are populus clones, box elder, silver maple, Siberian elm and European black elder (Geyer et al., 1985). In the south, the European elder, cottonwood, sycamore and Eucalyptus grandis are favored (Dippon et al., 1985; Howland et al., 1985; Ranney et al., 1985; Reddy et al., 1985; Rockwood, 1985). Yields from this program have been reported to be as high as 20 to 30 dry metric tons/ha/yr (Geyer et al., 1985; Hummel, 1985; Kulp, 1985; Ranney et al., 1985).

There are still many technical problems that remain to be resolved. First, short cutting cycles increase the rate of soil nutrient depletion; thus the application of appropriate amounts and types of fertilizers are under study. Also, the biomass yields reported from experimental studies tend to be optimistic, since growing

trees under experimental conditions lends itself to controlling growth factors to an extent not possible in full scale operations. Probably the most overlooked drawback of the short-rotation program is that the young wood being harvested has a relatively high moisture content, and consequently a reduced energy content (Smil, 1983).

Furthermore, economic considerations could limit the extent of adoption of this program for energy production. High cost factors include labor, drainage and harvesting (Hummel, 1985; Ranney *et al.*, 1985). In addition, economics may favor pulp wood production over energy production for the short-rotation concept (Smil, 1983; Kulp, 1985).

#### OVERVIEW OF THERMOCHEMICAL CONVERSION PROCESSES

There are three major technologies for the conversion of biomass into energy: biological, extraction and thermochemical. Processes related to these three categories and their main products are shown in Figure II-1 (Etout, 1985). Since this thesis is concerned with the steam gasification of wood, the review in this section will be limited to thermochemical conversion processes in an attempt to provide insight into the relationship between steam gasification and the other processes.

Schiefelbein (1985) has given a breakdown of the various thermochemical conversion processes and their major products as shown in Figure II-2. Pyrolysis, gasification and combustion make up a spectrum of related thermochemical processes (thermal liquefaction is also a thermochemical process but will not be considered here).

Pyrolysis involves heating biomass in the absence of oxygen. Gasification involves partial oxidation with steam/O<sub>2</sub> as the reactant. Combustion concerns complete oxidation with excess air/O<sub>2</sub>. The primary products from pyrolysis or gasification processes are gases, namely, H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O; tars and solid char constitute secondary products. The reactor operating conditions and type of reactor generally determine product species and their distributions.

Before discussing the three major categories for thermochemical conversion processes in greater detail, a brief summary of the advantages of wood over coal will be presented, since many of the conversion processes can use either wood or coal as feed materials. Wood has low ash content (less than 3.0%), low sulfur content (less than 0.2%) and high volatility (70-90%) (La Fontaine, 1985; Schiefelbein, 1985). Coal, however, has high ash content (5-10%), high sulfur content (1-3%) and low volatility (30-45%) (Graboski and Bain, 1979). These differences result in fewer problems (less ash handling and slagging, less SO<sub>2</sub> formation and subsequently lower requirements for gas clean-up, fewer problems with corrosion) and a greater rate of production or lower operating temperatures with wood than with coal. In addition, wood char has a higher reactivity than coal char (Graboski, 1979). This feature is important in gasification processes.

### Pyrolysis

Depending on the operating conditions, pyrolysis can favor the production of either char, tar or gases (LePori and Soltes, 1985). To favor the production of char, the reactor is operated at low

temperatures (500-700 K), long residence times and slow heating rates. Tars are favored at slightly higher temperatures (750-900 K), with very rapid heating rates and very short residence times. These conditions also favor the production of olefins such as ethylene and propylene. The operating conditions favoring gases are high temperatures (greater than 900 K) and long gas phase residence times.

There are two general classifications for pyrolysis reactors: countercurrent flow reactors and cocurrent flow reactors (LePori and Soltes, 1985). Countercurrent flow reactors include multiple hearth and updraft systems. Cocurrent flow reactors include the downdraft systems. Fluidized beds can fall under either classification depending on the location of the feed. For a countercurrent mode of operation, the feed is introduced near the top, and for the cocurrent mode the feed is introduced near the bottom.

Updraft gasifiers are more conducive to tar production than downdraft gasifiers. However, updraft gasifiers may not be ideal, since heating rates are relatively low. Fluidized beds, on the other hand, have relatively high heating rates. Thus, operating a fluidized bed in the countercurrent mode at moderate temperatures and high fluidization velocities will favor tar production.

There are some major drawbacks to tar production, since biomass tar has undesirable physical properties (LePori and Soltes, 1985). It is gummy, corrosive, carcinogenic, viscous and has a high oxygen content which lowers its heating value and its stability. Furthermore, it does not mix well with conventional petroleum fuels and the tar



properties change with time which creates problems in performance reliability after storage.

### Gasification

The objective of gasification is to convert biomass into low to medium heating value fuel gas or synthesis gas for methane, methanol or ammonia production (LePori and Soltes, 1985). Producer gas, composed mainly of  $H_2$ , CO,  $CO_2$  and  $CH_4$ , may be synthesized into diesel fuel via the Fisher-Tropsch process or to gasoline through reforming (Kuester, 1983). Methanol can also be converted into gasoline via the Mobil process (Soltes, 1985). Gasification of biomass occurs at temperatures that fall in between those for pyrolysis and combustion (900-1300 K).

Gasifiers are classified as fixed beds, moving beds, fluidized beds, rotary kiln and multiple hearth types (LePori and Soltes, 1985). Moving beds can be further classified as downdraft, updraft and crossflow. Downdraft gasifiers produce little tar but are limited to small scale operation (Soltes, 1985).

Fluidized beds can provide nearly isothermal conditions with good operating control and high heat transfer rates. In addition, fluidized beds can handle a wide variation in feed types and sizes. Introducing the feed at the bottom will produce less tar than introducing it at the top.

Char and ash are relatively easily handled and disposed of using cyclones, but tar is more difficult to remove due to its properties. Thus, gasification systems need off-gas treatment, such as condensation or scrubbing, to reduce the amount of tar in the product gas.

## Combustion

A few of the various types of combustion systems are the pile burner, semi-pile burner, suspension burner and fluidized bed. Georgia Institute of Technology (1984) has reviewed the different types of boilers and combustion systems for generating process steam and/or heat from biomass and has presented the advantages and disadvantages of each type. Some of the problems with direct combustion of biomass are associated with the ash. If the biomass contains large amounts of ash, then there may be problems with either ash slagging or corrosion. Biomass combustion also requires a larger amount of air than conventional liquid or gaseous fuels due to the inefficiency of air-fuel mixing. As a consequence of the greater air flow, more heat is lost with the stack gases and a greater amount of particulate matter is carried out as well. High moisture content presents another problem since it reduces the net energy output due to water evaporation.

## Industrial Practices in Thermochemical Conversion

Pyrolysis, gasification and combustion processes have been briefly summarized. In this section, the extent of current usage of these processes by the industrial sector will be considered.

A survey conducted by Ostermeier et al. (1985) has shown that 92% of the non-forest product industries that employed wood as an energy source used direct combustion in relatively small boilers to produce either process steam or a combination of process steam and process/space heat. Bulpitt and Walsh (1985) cited 10 wood-fired power plants in the U.S. with outputs ranging from 2.5 to 50 MW. In fact,

the most practical size for wood-fired power plants is 20-30 MW with the cost of gathering and transporting the low energy density wood being the limiting factor (Smil, 1983). Compared to modern day 500-1200 MW fossil fuel or nuclear power plants, wood-fired power plants will potentially contribute only a small fraction of our electrical energy demand.

Programs involving the development of biomass conversion processes include all of the types of processes previously mentioned; however, the major portion of funding has been directed towards the development of pilot-scale to small industrial size facilities that use direct combustion of wood as the means of conversion (Badger, 1985; Bergman, 1985; Stinson, 1985; Tuvell, 1985). As a result of California's SAFRUA funding (State Agricultural and Forestry Residue Utilization Act), 97 direct combustion facilities used by the forest industries and 10 used by the agricultural sector were built in 1983. During the same year, only one gasification facility was built (Tuvell, 1985).

From the above review, it appears that the predominate method for wood energy conversion in the near future is direct combustion to generate steam, heat and/or electricity. This is largely due to the fact that long term operating experience with the other technologies is lacking.

#### THEORETICAL CONSIDERATIONS FOR THERMOCHEMICAL WOOD CONVERSION

Understanding the chemical make-up and physical behavior of wood in a thermochemical conversion process is important for evaluating the process performance. In this section, three areas are considered:



(1) the chemical composition of wood, (2) thermodynamic considerations and (3) reactions and kinetics for pyrolysis and gasification of wood.

#### Chemical Composition of Wood

Defining the chemical composition of the wood is accomplished in several ways. One method is through the gross chemical composition. There are two different types of gross chemical analyses: proximate analysis and ultimate analysis. Proximate analysis determines the percent of volatile matter, fixed carbon and ash content and is reported on a dry basis (Graboski and Bain, 1979). This type of analysis gives an indication of the degree of flaming and glowing combustion that can be expected. Most woods have 80-90 wt% volatile matter, 10-20 wt% fixed carbon and 1-2 wt% ash (Graboski and Bain, 1979; Georgia Institute of Technology, 1984; Rossi, 1984). Ultimate analysis gives a breakdown of the weight percentages of the elements C, H, N, O and S, and the ash content and is reported on a dry basis (Graboski and Bain, 1979). A typical ultimate analysis for wood is 50-55 wt% carbon, 5.5-6.5 wt% hydrogen, 40-45 wt% oxygen, 0.1-0.3 wt% nitrogen, less than 0.1 wt% sulfur and 1-2 wt% ash (Graboski and Bain, 1979; Georgia Institute of Technology, 1984; Rossi, 1984).

The energy content of wood is generally reported as the higher heating value which is the heat released by complete combustion with the water produced in the liquid state. The higher heating value (HHV) or gross heating value is reported either on a wet or dry basis and ranges from 18-21 MJ/kg (8000-9000 Btu/lb) for wood on a dry basis (Graboski and Bain, 1979). The higher heating value can be estimated

from empirical formulas if the ultimate analysis is available.

Graboski and Bain (1979) presented three methods: (1) Dulong-Berthelot, (2) Tillman and (3) IGT. The IGT method was reported to be the best of the three for wood.

Another way of characterizing the chemical make-up of wood is to report the percentage of its major chemical constituents. The constituents that comprise wood are cellulose, hemicellulose, lignin and extractives, where the first three are contained in the cell wall material (Graboski and Bain, 1979; Shafizadeh, 1982). The percentages of these components differ between softwoods and hardwoods. Extracted hardwood contains 40-45 wt% cellulose, 33-37 wt% hemicellulose and 20-25 wt% lignin. Extracted softwood contains 40-45% cellulose, 25-30 wt% hemicellulose and 27-32 wt% lignin. Extractives make up 5-20 wt%, with the lower amounts applicable to hardwoods.

Cellulose is a macromolecule composed of  $\beta$  (1-4) D-glucose and has molecular weights of the order of 100,000. The chemical nature of the cellulose is the same in all woods, but the chemical nature of the hemicellulose and lignin differ. Crystalline cellulose is highly inert and inaccessible to chemical reactants (Graboski and Bain, 1979).

Hemicellulose is composed of two main types in woods: xylan and mannans (Graboski and Bain, 1979; Shafizadeh, 1982). Xylan, made from polymers of D-xylose (a pentose sugar) and having a molecular weight of 30,000 or less, is dominant in hardwoods. Mannans, composed primarily of D-mannose (a hexose sugar with low crystallinity) is found mainly in softwoods. Lignin is a three dimensional polymer composed of phenyl

propane units that are randomly linked and is more abundant in softwoods than hardwoods. Extractives vary widely in nature and quantity in woods. Softwoods contain more resins and volatile oils than the hardwoods. Waxes, fatty acids, pigments and carbohydrates are commonly found in all woods (Graboski and Bain, 1979).

#### Thermodynamic Considerations

Equilibrium calculations for wood pyrolysis and gasification processes can aid in providing an understanding of the effects of various operating parameters. Factors such as temperature, pressure and chemical composition of the inputs can influence the system performance and product quality. These calculations also establish limits for product yields.

Numerous chemical reactions can be formulated to account for all of the products associated with the char, tars and the gases, but generally a simple set of independent chemical reactions will be sufficient for describing the product species from pyrolysis or gasification processes at equilibrium. The major chemical reactions are the following (Desrosiers, 1979):

- 1)  $C + O_2 = CO_2$  , carbon oxidation
- 2)  $C + H_2O = CO + H_2$  , steam gasification
- 3)  $C + 2H_2 = CH_4$  , methanation
- 4)  $C + CO_2 = 2CO$  , Boudard reaction
- 5)  $CO + H_2O = CO_2 + H_2$  , water-gas shift reaction

In these reactions, solid carbon C represents the char fraction.

Notice that combination of reactions 2 and 4 gives reaction 5. For

pyrolysis or gasification processes, reaction 1 need not be considered, since oxygen is not an equilibrium product. Consequently, only three independent chemical reactions coupled with mass and energy balances are required for these cases.

In the remainder of this section, three thermodynamic equilibrium studies will be briefly summarized.

Double and Bridgewater (1985) used the equilibrium model to study the performance of biomass gasification under a wide range of operating conditions. As a base case, they considered the feed to have a composition of  $\text{CH}_1.5\text{O}_0.7$  on a dry-ash free basis (DAF) with 1% ash and 25% moisture both on a dry basis. The pressure was 100 kPa and a heat loss of 5% of the HHV of the feed was assumed. Air or oxygen at ambient conditions was considered as the base case gasifying agent. The study included variations of the base case as well as additions of varying amounts of steam, CO,  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{CH}_4$  as alternative gasifying agents. Their study indicated that increasing the  $\text{H}_2\text{O}$  content by either increasing the feed moisture content or the steam amount resulted in lowering the operating temperature, decreasing CO and  $\text{H}_2$ , increasing  $\text{CH}_4$ , decreasing  $\text{CO}_2$  slightly and increasing the HHV of the product gas. Increasing the pressure resulted in little effect on the CO and  $\text{CO}_2$  concentrations. However, the  $\text{H}_2$  concentration decreased initially and then leveled off at higher pressures. The  $\text{H}_2\text{O}$  and  $\text{CH}_4$  concentrations and the HHV increased slightly with increasing pressure.

Desrosiers (1979) performed equilibrium calculations by using a computer program called "GASEQ" and the JANAF tables. For the study,

he considered a DAF chemical composition of  $C_6H_{8.09}O_{3.54}N_{0.1}$  (or for a C=1 basis:  $CH_{1.4}O_{0.59}N_{0.017}$ ) as typical for wood. The calculations were grouped into five series in which the effects of one or more system variables were investigated. In reporting the results, the theoretical gasifier performance was generally plotted against the equivalence ratio (ER); i.e., the oxidant-to-fuel weight ratio divided by the stoichiometric ratio for complete combustion.

For Series 1, a full range of adiabatic operation from pyrolysis to combustion as determined by the ER ( $0 < ER < 1.2$ ) was examined. Air or oxygen was considered as the oxidant and the feed was either dry or wet (80% moisture). Calculations were performed at pressures of 100, 790 and 2170 kPa for  $O_2$  gasification with dry wood.

In Series 2, oxygen gasification of dry wood in a system that could be operated at constant temperatures and pressures with varying levels of feed and oxygen inputs was investigated.

For Series 3, the effect of water addition to  $O_2$  gasification with an ER ranging from 0 to 0.3 was considered. Water was added either as a liquid at ambient conditions or as steam at 1000 K. Calculations were performed at pressures of 100 and 1480 kPa.

In Series 4, the effects of adding varying amounts of steam (at 1000 K and at 1144 K) to the pyrolysis (ER=0) of wet wood (40%) was investigated. Equilibrium values were calculated at pressures of 100, 2860 and 6990 kPa.

In Series 5, the author considered the effect of pressure on the pyrolysis of wet wood (40%) and dry wood with steam at 1144 K added at



a steam-to-feed mass ratio of 1. The pressure ranged from 100 to 790 kPa.

For the various series described above, only some of the more significant findings will be reviewed. First, the only hydrocarbon present in the gas in significant amounts was methane. Other hydrocarbons, such as ethylene and higher hydrocarbons typically found in the product gas are not equilibrium products. For air gasifiers with an ER ranging between 0.2 to 0.3, the optimum operating point was found to occur where solid carbon just disappeared, since the chemical energy stored in the product gas was maximum. With additional amounts of air/O<sub>2</sub> beyond the point of carbon uptake, H<sub>2</sub> and CO were consumed to combustible end products. The addition of water as a liquid or steam was found to promote solid carbon uptake and increase the chemical energy stored in the product gas. It also promoted the formation of CO<sub>2</sub> and H<sub>2</sub> via the water-gas shift reaction and lowered the adiabatic flame temperature which, in turn, increased CH<sub>4</sub> and decreased H<sub>2</sub>. Increasing the pressure had little effect on CO and CO<sub>2</sub> formation, but decreased H<sub>2</sub> and increased CH<sub>4</sub>. The adiabatic flame temperature and the lower heating value increased slightly.

Antal et al. (1978) used equilibrium calculations to predict the products from cellulose pyrolysis as functions of temperature, pressure and steam-to-feed ratio. The calculations were made with a computer program developed by NASA based on minimizing Gibb's free energy of a mixture of chemical species subject to mass balance constraints. The ranges for the variables in their investigation were 570-1070 K for

temperature, 101.3-1013 kPa for pressure and 0 or 7 moles of steam per mole of cellulose.

They found that char, represented by  $C_s$  (graphite), existed in equilibrium but its amount was reduced by increasing temperature and by increasing pressure. For the gas species,  $H_2$  and CO were favored at high temperatures and low pressures.  $CH_4$ ,  $CO_2$  and  $H_2O$  were favored by low temperatures and high pressures. Higher molecular weight hydrocarbons, such as  $C_2H_2$ ,  $C_2H_4$ , etc. were considered in the calculations, but were not found to be equilibrium products.

The addition of steam decreased the amount of solid carbon, increased  $H_2$  and CO and increased the HHV of the gas. With the disappearance of  $CH_4$  and  $C_s$  at approximately 1070 K, the gas composition was determined solely by the water-gas shift reaction.

#### Reactions and Kinetics for Pyrolysis/Gasification of Wood

Shafizadeh (1968, 1983) has proposed general reaction pathways for the pyrolysis of cellulose as shown in Figure II-3. This scheme can be divided into primary and secondary reactions. The primary reaction is the direct degradation of cellulose and the secondary reactions are the subsequent degradation of intermediate tars, char and higher molecular weight hydrocarbons. Alternatively, the scheme can be classified as two general pathways. The first pathway is the dehydration and formation of char occurring at low temperatures and long residence times. The second pathway is the fragmentation and formation of combustible products that occur at higher temperatures and shorter residence times.

Shafizadeh (1968, 1983 and 1985) also demonstrated that an induction period existed prior to any thermal degradation of cellulose under vacuum over the temperature range of 530-610 K. To interpret his findings, Shafizadeh (1983) proposed the scheme shown in Figure II-4 in which the formation of an active intermediate accounted for the induction period. However, Simmons and Lee (1985) investigated the pyrolysis of cellulose over the temperature range of 590-710 K and found no observable induction period.

The above schemes proposed by Shafizadeh were for the pyrolysis of cellulose. However, this thesis is concerned with the steam gasification of wood. Raman et al. (1981) have proposed a scheme for the steam gasification of manure. Here, their scheme is adapted to the steam gasification of wood as shown in Figure II-5. The scheme is based on the work of Antal et al. (1978). The specific reactions in this scheme will be discussed in detail below.

Pyrolysis. The first step in gasification, as shown Figure II-5, is the devolatilization or pyrolysis of wood. Hence, it is important to understand the behavior of wood and its components under pyrolytic conditions to elucidate the behavior of wood and its components under gasification conditions.

As stated previously, there are two broad classifications for pyrolysis: slow pyrolysis and fast pyrolysis. For slow pyrolysis, the operating conditions are slow heating rates (0.01 to 2 K/s), long residence times (hours) and low temperatures (520-670 K). These operating conditions yield relatively large amounts of char. For fast



pyrolysis, the heating rates are from 1000 to 10,000 K/s and the residence times vary from a few milliseconds to seconds. These conditions favor the production of tars, unsaturated low molecular weight hydrocarbons and little or no char. Milne (1979) has given an extensive review of pyrolytic studies conducted below 870 K on wood and its major components. Several significant findings will be discussed below.

*Cellulose.* Cellulose has received the most extensive study, since this compound is the least complicated and best defined of the three major components of wood. At moderate heating rates, cellulose is stable up to 570 K. However, it decomposes rapidly over the next 50 K and yields 5-15% char.

The nature of the product distributions depends on the rate of heating, temperature, residence time of the primary products within the wood structure and additives. Between 550-610 K, cellulose degradation results in the formation of levoglucosan which constitutes the major tar component. For moderately fast pyrolysis, the ambient atmosphere ( $N_2$ , air, steam,  $H_2$ , etc.) has little effect on product yields. Pressure is not a major factor except at low pressures where higher yields of olefins are produced. It has been postulated that the atmosphere surrounding a pyrolyzing substance imposes a resistance to the escaping gases. This resistance results in a greater residence time for the molecular fragments within the wood structure where they may undergo repolymerization.

*Hemicellulose.* Most of the pyrolytic studies conducted on hemicellulose used xylan as a model compound. Hemicellulose has been found to be the least stable of the three wood components because of its noncrystalline structure. Consequently, hemicellulose decomposes at lower temperatures than cellulose. In addition, hemicellulose has been found to produce more gases and less tar than cellulose.

*Lignin.* The most complicated and least understood component of wood is lignin. Lignin is also the most difficult to isolate without changing its chemical structure. In fact, findings of pyrolytic studies vary with the different procedures used in the preparation of the lignin feed. Pyrolytic studies on lignin have revealed that minor degradation of the lignin begins at temperatures lower than for cellulose, but most of the degradation occurs at higher temperatures. Also, lignin is responsible for most of the char production and the aromatics found in the tar.

*Wood.* Pyrolytic studies on the major components of wood have found that the order of reactivity from high to low is hemicellulose, cellulose and lignin. These studies have also revealed that generally and at least qualitatively, the pyrolysis of wood and its major components is endothermic.

As a predictive model for the pyrolysis of wood, it has been suggested to combine the results for the pyrolysis of its three components with proper weighting. Milne (1979) reported that many researchers claim that the pyrolysis of wood qualitatively resembles the additive effect of its components. However, no quantitative evidence

has been provided to support this hypothesis with respect to the volatiles. Antal (1985) attempted to interpret gas yields from wood in terms of fractional contributions from its components. He used a linear programming optimization algorithm with data from the pyrolysis of cellulose, kraft lignin and d-mannose; no satisfactory fit was obtained.

Most of the pyrolytic studies reviewed by Milne (1979) were conducted at temperatures below 870 K and at slow heating rates of 10-100 K/min. The conditions at which gasification occurs in a fluidized-bed reactor are typically temperatures of 900-1300 K and heating rates of 500-1000 K/s. These operating conditions significantly affect the pyrolytic products.

van den Aarsen et al. (1985) conducted experiments on the rate of pyrolysis of wood in a fluidized bed and found that a 1 mm diameter wood particle was completely volatilized in 2 seconds at 500 K/s. For temperatures typical of fluidized bed gasification, tar formation is favored over char production (Shafizadeh, 1985). Cellulose tar, composed mainly of levoglucosan (Shafizadeh, 1985), was found to undergo extensive cracking as temperature increases (Milne and Soltys, 1985).

At temperatures greater than 670 K, fresh char is highly reactive, but it becomes quickly stabilized and further decomposition through thermal degradation and char gasification reactions becomes relatively slow (Graboski, 1979; Shafizadeh, 1985). The stabilization of char will be discussed in greater detail later. In addition, at ultra-rapid

heating rates, the production of char becomes negligible (Graham *et al.*, 1986).

Secondary Gas Phase Reactions. As indicated in Figure II-5, the volatiles produced from the primary pyrolysis reactions can undergo subsequent cracking and/or reforming reactions in the presence of steam; the extent of these reactions depends on both residence time and temperature. Understanding these reactions is important in controlling the product distribution and for meeting specific product requirements. In this section of the review, the work of two investigators that have explored these reactions will be presented.

Jonsson (1985) conducted thermal cracking experiments on tars,  $\text{CH}_4$  and higher molecular weight hydrocarbons in the presence of steam/ $\text{O}_2$  in a cracking reactor. His experimental system consisted of a pyrolysis reactor operating at 1020 K and a gas phase cracking reactor operating at 1170-1470 K. Steam was added at levels of 0.2 or 0.3 kg/kg feed and  $\text{O}_2$  was added at either 0 or 0.1 kg/kg feed.

The results indicated that tar conversion increased with increasing temperature in the cracking zone and increased to a lesser extent with increasing steam/ $\text{O}_2$  additions. The thermal cracking of  $\text{CH}_4$  and higher molecular weight hydrocarbons increased with increasing temperature, but cracking was not affected by addition of steam/ $\text{O}_2$ . Hydrogen and carbon monoxide were the predominate gas species at higher temperatures. Hydrogen was believed to have inhibited the cracking of tar as well as other hydrocarbon species.

Antal (1985) studied vapor phase pyrolysis of volatile matter generated from biomass. He conducted experiments in a series of quartz tubular reactors where the first one served as a steam preheater. The second one in the series was the pyrolysis reactor where a sample of biomass in a boat was inserted. The temperature of the pyrolyzer was maintained at 770 K. This temperature was sufficiently high to devolatilize the biomass sample at a good rate, but low enough to minimize any secondary reactions. The last reactor in the series served as the secondary gas phase cracking reactor. The volatile matter produced in the pyrolysis zone was swept into the cracking reactor by steam. Normally, a steam rate of 0.34 g/min was used with a 0.25 g sample. Cracking was conducted at 870 to 1020 K.

The results of his experiments indicated that all of the gaseous species formed approached an asymptotic yield with increasing gas phase residence time (approximately 5 seconds). This asymptotic yield increased with increasing temperature. An increase in steam dilution had no effect on the formation of CO and char. However, increasing steam dilution by a factor of six resulted in a methane yield reduction of 6% and an ethylene yield increase to a maximum of 24%.

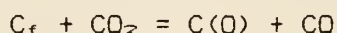
In addition to the above results, Antal (1985) examined various ratios of different gas species yields and ratios of specific gas species yields to the carbon conversion to elucidate the effect of temperature on the competition between various gas species formation reactions. For cellulose generated volatiles,  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  competed with  $\text{CO}_2$  for cellulosic carbon atoms at higher temperatures, strongly

favoring  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  over  $\text{CO}_2$ . Also, the fraction of cellulosic carbon atoms dedicated to CO remained constant over the experimental temperature range of 770-1020 K. For lignin, the competition appeared to be only between  $\text{C}_2\text{H}_4$  and  $\text{CO}_2$ .

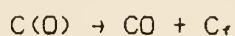
Char Gasification Reactions. The next group of reactions in Figure II-5 that will be covered are the char gasification reactions. These reactions are important to the overall gasification process, since the goal of gasification is to convert the wood into a gaseous product. The rates of the char gasification reactions depend on temperature, particle size and structure, source of the char, the thermal history of the char, mass and heat transfer resistances, and catalysts (Graboski, 1979).

Theoretical mechanisms for the carbon-carbon dioxide and the carbon-steam reactions have been developed and are discussed by Graboski (1979). The carbon-carbon dioxide reaction has been studied most extensively, since the products do not enter into side reactions as with the carbon-steam reaction. The qualitative mechanism for this reaction as originally proposed by Ergun (Graboski, 1979; van den Aarsen *et al.*, 1985) has the following steps:

1) adsorption



2) desorption



where  $\text{C}(\text{O})$  is a surface oxide

$\text{C}_r$  is an active carbon site



In the first step, it has been found that the exchange of oxygen occurs reversibly at temperatures applicable to gasification processes and the interchange between the surface carbon atoms and the carbon atoms in the CO that is generated occurs only at temperatures above 1770 K. In addition, the second step has been found to be the controlling factor at lower temperatures.

For the carbon-steam reaction, a similar two step mechanism has been proposed:

- 1)  $C_r + H_2O = C(O) + H_2$
- 2)  $C(O) \rightarrow CO + C_r$

A high partial pressure of either  $CO_2$  or  $H_2O$  saturates the surface with the oxide, and hence the second step becomes the controlling factor. Also, the carbon-steam reaction rate has been found to be 3-5 times faster than the carbon-carbon dioxide reaction (Graboski, 1979; van den Aarsen *et al.*, 1985).

Considering the reactivity of char, it has been proposed that only carbon atoms along crystal defects or adjacent to mineral matter are sufficiently reactive to be gasified (Graboski, 1979). With an increase in temperature to 970-1370 K and an increase in residence time, thermal annealing or the loss of active sites by surface reorganization results in the char structure becoming more stabilized. Thus, chars with high pretreatment temperatures will have lower reactivity (Graboski, 1979).

However, the conclusions reported by Graboski (1979) were based on data obtained from coal chars. van den Aarsen *et al.* (1985) found that

wood char with different temperature histories had no differences in reactivity. They based their conclusions on data from chars with temperature histories varying from 993-1158 K. They also concluded that the char reactivity in a fluidized bed was depended only on the char hold-up and reactor temperature.

Another factor that effects the char gasification reaction rate is mass transfer resistance. Graboski (1979) determined the temperature regions where external mass transfer, pore diffusion and surface kinetics are the controlling factors. External mass transfer becomes the controlling factor at temperatures above 2700 K. Pore diffusion becomes important at temperatures between 1900-2700 K, and surface kinetics become the controlling factor at temperatures below 1900 K. However, for particle sizes below 20 mesh, pore diffusion effects are not important at any temperature. The apparent activation energy when external mass transfer controls is of the order of 8000 kJ/kmol; whereas, the apparent activation energy is approximately 200,000 kJ/kmol when surface kinetics control.

Effects of Catalysts on Gasification Reactions. As with many chemical reactions, the use of catalysts in gasification has potential benefits. Catalysts can either increase the reaction rates or lower the temperature for significant reaction. A catalyst is often chosen because it favors or inhibits certain product species, thus with a proper selection of one or a combination catalysts, desirable product distributions can be obtained. This section reviews work on the effects of catalysts on (1) char yields and char gasification



reactions, (2) gas phase reactions and (3) the selection of catalysts to promote desired product gas compositions.

Shafizadeh (1985) showed that inorganic materials present in wood ash or inorganic additives could lower the temperature at which thermal degradation occurs and could increase the amount of char formed from wood. His studies were directed towards flame proofing and fire protection. Recent studies on the use of inorganic catalysts are directed towards promoting gas formation via char gasification reactions.

Hallen *et al.* (1985) performed experiments to investigate the effects of alkali carbonates on the steam gasification of Douglas fir in a ball-valve batch reactor with temperatures varying from 820-1120 K. Their experiments investigated gasification in the presence and absence of  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and  $\text{Cs}_2\text{CO}_3$  at concentrations of  $1.5 \times 10^{-3}$  and  $3.0 \times 10^{-3}$  kmol alkali/kg wood. The results showed that the alkali carbonates all had similar catalytic activities, and that the gas production rate as well as the total gas produced varied slightly between the two concentration levels. Also, the alkali carbonates increased the char yield in the devolatilization stage, but the char yield decreased with increasing residence time indicating that the char-steam reaction was taking place. Reactions took place over a time span of 5 to 40 minutes.

DeGroot and Shafizadeh (1985) conducted experiments on the  $\text{CO}_2$  and steam gasification of Douglas fir and cottonwood and their chars with catalysts in a semi-batch reactor. The wood was treated with an aqueous

solution of inorganic salts and dried to give a  $1.0 \times 10^{-4}$  kmol/kg wood concentration. The char samples were prepared at a heat treatment temperature of 1273 K.

Their results indicated that the addition of alkali metals (Na, K) gave substantial increases in char yields and that the addition of Mg, Fe and Ni resulted in only a slight change in the char yield as compared with the uncatalyzed case. The additives had only a slight effect on the char composition.

The authors also conducted treated and untreated char gasification experiments over a temperature range of 870-1170 K. For the purpose of comparison, the authors assumed a zero order Arrhenius rate expression. Their comparisons revealed that the alkali metals (Na, K) lowered the apparent activation energy for both char-CO<sub>2</sub> and char-steam gasification reactions. Magnesium, however, significantly increased the apparent activation energy for the CO<sub>2</sub> gasification of cottonwood char, but produced only a slight increase for Douglas fir char. The authors suggested that this increase was the result of ion exchange of magnesium with the calcium naturally present in the wood. Also, the gasification reactions were essentially complete after a time period of 1000 to 3000 seconds (15-50 min).

Hallen et al. (1985) also conducted experiments to study the effects of Na<sub>2</sub>CO<sub>3</sub> on the secondary gas-phase reactions. The scope of their experiments included the reaction of methane, ethane and ethylene with steam in the presence of the catalyst, the effect of the catalyst on the water-gas shift reaction, and investigation of the reaction of

model compounds to simulate the pyrolysis of cellulose in steam at 870 K.

The results of their experiments showed that the simple hydrocarbons did not react with steam at 870 K and that methane reforming occurred only at temperatures greater than 1070 K. The water-gas shift reaction was found to be significantly catalyzed by  $\text{Na}_2\text{CO}_3$ . For the model compounds, it appeared that  $\text{Na}_2\text{CO}_3$  catalyzed the dehydrogenation of alcohols and decarboxylation of carboxylic acids but had little effect on the reactions of aldehydes and ketones.

Magne et al. (1985) investigated the effect of sand, and decarbonated and carbonated dolomite on the fast pyrolysis of tar generated from pine bark over a temperature range of 870-1070 K. Their results showed that not only did the decarbonated dolomite absorb the  $\text{CO}_2$ , but it also increased the  $\text{H}_2$  and  $\text{CH}_4$  fractions and lowered  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{CO}$  as compared to the carbonated dolomite.

In addition, their results showed that the reaction rates with the decarbonated dolomite were 17-30 times faster than those with sand and 41-126 times faster than those with no catalyst. The relative reaction rates were found to decrease with increasing temperature. At 917 K, the reaction rate with the decarbonated dolomite was 8 times as fast as the reaction rate with carbonated dolomite. However, the authors pointed out that dolomite may not be a practical catalyst, since dolomite is too soft and will crumble into dust.

Baker et al. (1985) conducted experiments on the steam gasification of wood to select the best catalysts and operating

conditions to favor the production of ammonia synthesis gas, hydrogen-rich gas, methane-rich gas and methanol synthesis gas in a fixed bed reactor. They also investigated the lifetime of the catalysts selected for methane-rich gas and methanol synthesis gas production. They found that a Co-Mo metal catalyst supported on alumina favored the formation of ammonia synthesis gas, and a combination of a Ni supported and a Fe-Cr, Ni supported catalyst favored H<sub>2</sub>-rich gas formation. No long lived catalyst was found for the production of methane-rich gas. The best results were obtained with a 50 wt% Ni and a 10 wt% Fe on alumina catalyst which had a life of 73 kg wood/kg catalyst. The deactivated catalyst was found to contain 15 wt% deposited carbon. The authors noted that the catalysts favoring methane-rich gas were the ones with a Ni concentration of 25 wt% or more, a high surface area for the support of 100 m<sup>2</sup>/g and a Ni surface area of 30 m<sup>2</sup>/g. A trimetallic nickel alloy of Ni-Co-Mo on a silica-alumina support was found to be the best supported nickel catalyst in terms of lifetime for methanol synthesis gas production. This catalyst achieved a lifetime of 1470 kg wood/kg catalyst before the experiment was terminated.

In addition to the Ni-Co-Mo catalyst, catalysts containing either 25 wt% Na<sub>2</sub>CO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub> on alumina were tested for the production of methanol synthesis gas. Although these catalysts produced a lower quality gas in terms of H<sub>2</sub> and CO concentration compared to the trimetallic catalyst, their catalytic activity increased slightly with time; whereas, the Ni-Co-Mo catalyst decreased. Additionally, the alkali carbonate catalysts had no carbon deposited on them as compared

to the trimetallic catalyst which was found to have 4-8 wt% carbon deposited. As a final note, the investigators found that as long as the catalysts were active, no tar was observed.

#### RECENT STEAM GASIFICATION STUDIES

In this section, some of the recent investigations on steam gasification processes will be reviewed.

Singh *et al.* (1986) conducted experiments on the steam gasification of cottonwood branches in a bench-scale, fluidized-bed reactor to determine the effect of temperature on the product yields and distributions. The temperature effect was described in terms of linear regression and spline curve fits. They also compared their results with data obtained from steam gasification of  $\alpha$ -cellulose in the same reactor.

The fluidized bed used in their study had a bed of 5.08 cm I.D. and a freeboard of 10.16 cm I.D. The bed material was a limestone-sand mixture. The reactor was electrically heated to temperatures between 850 and 1075 K. Steam was injected in the bottom at rates to give steam-to-feed mass ratios ranging 10 to 6 over the temperature range. All experiments were run at atmospheric pressure.

Their results showed that  $H_2$ ,  $CO_2$ , CO and  $CH_4$  comprised 95% of the product gas. The gas yield, the carbon conversion and the energy recovery increased with increasing temperature from 0.23 to 1.59  $m^3/kg$  DAF feed, 15 to 96.8% and 16.9 to 87.1%, respectively. Their results suggested that two temperature regimes existed for the secondary gas phase reactions with a transition point between 930 and 950 K. The



lower temperature regime was dominated by tar cracking reactions and the upper temperature regime was dominated by the water-gas shift reaction. Their contentions were supported by the results from the  $\alpha$ -cellulose experiments and studies conducted by other investigators.

Walawender et al. (1985) conducted experiments on the steam gasification of Siberian elm in a fluidized bed at temperatures ranging from 850 to 1160 K and at atmospheric pressure to investigate the effects of the steam-to-feed mass ratio on the gasification characteristics. They statistically compared regression models for the gasification characteristics with temperature as the independent variable at different steam-to-feed mass ratios. They also compared their results with data for the steam gasification of  $\alpha$ -cellulose.

Their fluidized-bed reactor had a bed of 10.16 cm I.D. and a freeboard of 15.24 cm I.D. The reactor was electrically heated, and the bed material was the same limestone-sand mixture used by Singh et al. (1986). Where statistical comparisons could be made, it was shown (at the 95% confidence level) that a significant difference existed between the different steam-to-feed mass ratios. For the cases where the statistical comparisons could not be performed, it was observed by the authors that apparent differences existed between the varying levels of the steam-to-feed mass ratio. Statistical comparisons conducted for  $\alpha$ -cellulose revealed the same findings; i.e., the steam-to-feed mass ratio is a significant parameter in steam gasification.



Richard et al. (1985) conducted experiments to determine the operating conditions for the optimum generation of methanol synthesis gas from the steam gasification of wood char. In their experiments, the temperature was varied from 1070-1190 K, the pressure from 100-2000 kPa and the water vapor fraction between 0.16 and 0.90. They conducted the experiments in a tubular quartz, fixed bed reactor. The water vapor was mixed with  $N_2$  to increase the gas velocity which, in turn, reduced the external mass transfer resistance.

The results of their experiments revealed that the effect of temperature on the rate of gasification was described by an Arrhenius rate expression. An increase in the water vapor fraction increased the reaction rate linearly. However, no clear pattern existed for the effect of pressure on the reaction rate. At 1070 K, increasing the pressure from 100-1000 kPa increased the rate by a factor of 2. However, at 1190 K, increasing the pressure from 100-1000 kPa resulted in a rate decrease and a further pressure increase to 2000 kPa resulted in little change.

The main components in the product gas were  $H_2$ , CO and  $CO_2$ , while  $CH_4$  was present in noticeable amounts (0.01-0.02%) only at 2000 kPa. The CO molar fraction increased while the molar fractions of  $H_2$  and  $CO_2$  decreased with increasing temperature. Also, the  $CO_2$  molar fraction increased while the  $H_2$  and CO molar fractions decreased with increasing pressure. The desired  $H_2/CO$  molar ratio of 2 for the synthesis gas was obtained when the temperature was high (1190 K), and both the steam fraction and pressure were low.

Elliott and Baker (1986) investigated the effect of catalysts in both a primary steam gasification reactor and in a secondary gas phase reactor on tar yields and tar components obtained from wood. The scope of their experiments consisted of four cases: (1) uncatalyzed steam gasification, (2) potassium catalyzed steam gasification, (3) potassium catalyzed steam gasification followed by a nickel tar treatment bed and (4) uncatalyzed steam gasification followed by a nickel tar treatment bed.

Their experimental system consisted of two bench-scale fluidized-bed reactors in series with the first fluidized bed serving as the steam gasifier and the second serving as the secondary gas phase reactor. The fluidized beds had a 60 cm bed zone height with a 7.8 cm I.D. and a 90 cm disengaging zone height with a 12.8 cm I.D. The bed material for the steam gasifier was either silica sand or bauxite. The reactors were operated at 1020 K with feed rates of either 0.8 kg/h or 1.2 kg/h and with steam rates of 0.8 kg/h. Gas phase residence times were 1 s in the bed zone and 8 s in the disengaging zone for both reactors.

The catalyst employed for steam gasification was 8 wt% (dry basis)  $K_2CO_3$  impregnated into the wood. For the tar treatment bed, two types of nickel catalysts were used. A 14 wt% Ni on a support composed of  $SiO_2$ ,  $Al_2O_3$ , MgO, CuO and  $K_2O$  was used in case 3, and a 9.5 wt% Ni, 4.25 wt% CuO and a 9.25 wt%  $MoO_3$  on a  $SiO_2/Al_2O_3$  support was used in case 4.

Their results indicated that the alkali catalyst reduced the tar production by a factor of 5 to 10 with a stronger activity towards polycyclic aromatic compounds and ketone/furan oxygenates. The addition of Ni resulted in a strong activity towards the deoxygenation and the demethylation of the tar. Hence, phenolic compounds were nearly non-existent and the remaining aromatics were demethylated. Benzene, toluene and naphthalene were the primary products with the combined catalysts.

Liinanki *et al.* (1985) investigated the yield of  $\text{CH}_4$  from biomass gasification with secondary steam reforming and  $\text{O}_2$  additions at high temperatures and pressures. They noted that the production of  $\text{CH}_4$  is an important consideration, since its yield must be high for fuel gas and low for synthesis gas. The scope of their experiments included (1) steam reforming of peat gasification products with  $\text{O}_2$ , (2) steam reforming of tar-free synthesis gas with  $\text{O}_2$  and (3) steam reforming of tar-free synthesis gas without  $\text{O}_2$ .

Their experimental system consisted of a fluidized bed, a high temperature filter and secondary reformer in-series. The fluidized bed had a 10 cm I.D. and was 60 cm high with steam/ $\text{O}_2$  serving as the fluidizing agent. The fluidized bed was designed to operate at temperatures of 1020-1170 K and the reformer could be operated at temperatures up to 1370 K. The system was designed for pressures up to 3000 kPa. The steam rate was adjusted to give a linear velocity of about 10-15 cm/s. For the tar-free synthesis gas experiments, a gas feed mixture of 55%  $\text{H}_2$ , 15%  $\text{CH}_4$  and 30%  $\text{CO}_2$  was added with steam at the

reformer. For these experiments, the fluidized-bed gasifier served as a steam preheater and operated at 770 K.

Their results indicated that an increase in pressure significantly increased the CH<sub>4</sub> yield. The CH<sub>4</sub> yield was found to be maximum at 1070 K. In all the experiments, the CH<sub>4</sub> yield was higher than predicted from the methane reforming equilibrium reaction:  $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$ . In addition, their results supported two hypotheses: (1) the tar reacts with steam to form H<sub>2</sub>, CO and CO<sub>2</sub>, and reacts with H<sub>2</sub> to form mainly CH<sub>4</sub> and (2) methane decomposition to a solid carbon and H<sub>2</sub> exists in a pseudo-equilibrium state with the solid carbon having a greater activity than graphite.

Elliott and Sealock (1985) investigated the influence of sodium carbonate and a Ni metal supported catalyst in maximizing the production of methane at low temperatures and high pressures. They conducted experiments in a batch autoclave with temperatures between 520-720 K and the pressure initialized at 2168 kPa with run times up to 1 hr. Experiments were conducted on four different feeds: cellulose, holocellulose, lignin and wood flour.

Only the findings for the wood flour will be summarized here. The combined sodium carbonate and nickel catalyst gave a substantial increase in the carbon conversion (over 90% after 1 hr at 720 K). Although the Ni catalyst alone gave the highest CH<sub>4</sub> production, the combined catalysts gave only slightly less CH<sub>4</sub> yield, but gave the highest CH<sub>4</sub> concentration in the product gas.

A comparison of their experiments with high temperature and low pressure steam gasification processes revealed that the wood flour with the combined catalysts in the autoclave achieved an 80% carbon conversion at 620 K; whereas, high temperature steam gasification processes achieved the same carbon conversion at 1020 K. Also, the batch system had four times the CH<sub>4</sub> yield as the high temperature steam gasification process. The authors pointed out that there was a significant difference in residence times between the two systems, since the autoclave had a residence time of 1 hr and the steam gasification process swept the products out of the system shortly after they were formed.

Tanaka *et al.* (1984) determined operating temperatures, water addition amounts, and the most suitable catalysts to favor methanol synthesis gas production for the steam gasification of wood. They conducted their experiments on sawdust from hemlock and spruce in two different reactors: a batch reactor to screen catalysts and a continuously fed, fixed bed, catalytic reactor that operated at temperatures between 770 and 1070 K with a water vapor fraction of 13.7%.

From their investigation, they found that 20 wt% NiO supported on Al<sub>2</sub>O<sub>3</sub> with micropore sizes ranging from 60 to 300 Å and a temperature of 970 K was the most suitable condition for methanol synthesis gas production. At these conditions, the H<sub>2</sub>/CO molar ratio was near 2, the CH<sub>4</sub> yield was small, and the carbon conversion was 89%. They also found that the gas composition was strongly influenced by the metal



oxide catalyst employed.  $\text{MoO}_3$ ,  $\text{CuO}$  and  $\text{V}_2\text{O}_5$ , which are often used for oxidation reactions, resulted in a decrease in  $\text{CO}$  and an increase in  $\text{CO}_2$  indicating that the water-gas shift reaction took place.  $\text{NiO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ , used primarily for hydrogenation reactions, resulted in a  $\text{H}_2/\text{CO}$  molar ratio close to 2 and small amounts of  $\text{CO}_2$  suggesting that both the carbon-steam reaction and the water-gas shift reaction were occurring.

With increasing water vapor fractions, it was discovered that the carbon-steam reaction was more strongly catalyzed, thus increasing the carbon conversion to 90% while the  $\text{H}_2/\text{CO}$  molar ratio remained constant. As a final note, no olefins or tar-like fragments were produced during the gasification process.

Mudge *et al.* (1985) followed up on their catalytic studies (summarized previously in this chapter) and performed steam gasification pilot studies in their process development unit (PDU) with catalysts determined to be good candidates from the previous studies. They investigated the effectiveness of the alkali carbonates (Na, K) and the trimetallic Ni-Co-Mo on a support composed of silica-alumina as catalysts favoring the production of methanol synthesis gas and methane-rich gas. The PDU was a fluidized bed with a 20.32 cm I.D. and a 1.22 m height for the bed zone and a 30.48 cm I.D. and 1.83 m height for the disengaging zone. Tests were conducted at pressures of 101.3, 505.6 and 1013 kPa with the operating temperature ranging between 1008 and 1023 K.



They concluded that sodium was not an effective catalyst. Potassium, however, was an effective catalyst, but there were operational problems encountered. In addition, the trimetallic catalyst, found to have a long lifetime (greater than 1470 kg wood/kg catalyst) in the laboratory studies, deactivated after 10 kg wood/kg catalyst or 2 hr of operation and had 20 wt% carbon deposited. In comparison, the catalyst after the laboratory experiments had 4 wt% carbon deposited. The authors concluded that thermal cycling and intimate mixing of the catalyst contributed to the accelerated deactivation.

They also found that an increase in pressure from 101.3 to 1013 kPa reduced the tar yields from 7 to 2 wt% and increased the CH<sub>4</sub> concentration from 13 to 20%. They operated at a steam-to-feed ratio of approximately 1.2. This ratio was higher than they desired but was necessary to maintain fluidization. They concluded that a proper steam-to-feed ratio would have been about 0.7.

Garg et al. (1987) investigated the gasification of wood over nickel-alumina supported catalysts at 101.3 kPa of hydrogen to produce high yields of methane. They varied the percentage of nickel content in the catalysts from 3 to 30% and the operating temperature from 670 to 920 K to study the effect of these parameters on the gasification products. Their results indicated that the yield of both CO and CO<sub>2</sub> decreased with increasing percentage of nickel in the catalyst, while the yield of methane increased with increasing nickel content. The percentage of carbon converted to methane increased from 52% with 3%

nickel content to 87% with catalysts containing at least 8.8% nickel. In addition, in the presence of a catalyst containing 17% nickel, the conversion of carbon to methane was found to increase with temperature up to 820 K to a maximum of 71%.

Based on results of their study, the authors have proposed a novel integrated gasification process to produce synthesis gas from wood. The conceptual gasification process consists of a hydrogasification step at 770-820 K followed by steam reforming of the methane at 1020 K and a membrane separation step to yield a product synthesis gas (CO and H<sub>2</sub> mixture) and a H<sub>2</sub>-rich gas which may be recycled to the hydrogasification step. The overall process can convert wood to its equivalent yield of CO and H<sub>2</sub> with the addition of steam.

#### SUMMARY

This chapter has presented a review of the viability of wood as a renewable energy source, theoretical aspects pertaining to the pyrolysis/gasification of wood and the development of steam gasification processes for wood. Estimates have shown that wood can provide a practical limit of 5 to 10% of the U.S. energy demand. Short-rotation energy plantation programs may increase the potential of wood as an energy source, but are still in the developmental stage. Three thermochemical conversion techniques for wood are pyrolysis, gasification and combustion. Currently, wood combustion is the conversion method being used to the greatest extent in industry.

The review of the theoretical and technical aspects for the pyrolysis/gasification of wood included the chemical composition of

wood, thermodynamic considerations, and reaction and kinetic considerations. The chemical composition of wood can be characterized by a proximate analysis, an ultimate analysis or by the percentages of its major constituents: cellulose, hemicellulose and lignin. Thermodynamics provides insight to the effects of operating parameters on the yields from pyrolysis/gasification systems. The reactions involved in the gasification of wood can be categorized into primary reactions (the devolatilization of the wood) and secondary reactions that include tar cracking, char gasification and product gas reforming via the water-gas shift reaction.

Studies conducted on the pyrolysis of wood at temperatures below 870 K have shown that the cellulose fraction is responsible for tar formation. Lignin, the least reactive wood component, is responsible for a large fraction of the char produced. Hemicellulose, the most reactive component, is essentially converted to gaseous products. Quantifying product yields obtained from wood in terms of the fractional contributions of its major constituents has been demonstrated to have poor predictive value. At operating conditions applicable to gasification in a fluidized bed, (temperatures between 900-1300 K and heating rates of 500-1000 K/s), devolatilization of wood favors tar formation over char, and the tar produced is extensively cracked. The char formed becomes quickly stabilized, hence reactivity reduces within a few seconds after it is formed.

For the secondary reactions, the extent of thermal cracking of tars is dependent on temperature and residence time. Steam addition has little effect on tar cracking.

The addition of alkali carbonates (Na, K) as catalysts results in an increase in char yield during the rapid devolatilization phase, but promotes char gasification reactions at long char residence times. The water-gas shift reaction is catalyzed by the presence of sodium carbonate. Although the alkali carbonates are less effective than metal catalysts, they do not deactivate as with the metal catalysts.

Recent steam gasification process development efforts have investigated the effects of temperature, pressure, O<sub>2</sub>/steam additions and catalysts. These studies indicate that methane-rich gas is favored at low temperatures and high pressures. With steam addition, the water-gas shift reaction dominates at higher temperatures, thus controlling the gas composition. In addition, catalysts can be used to promote desirable product gas and/or tar distributions for synthesis gas, fuel gas or liquid fuel production.

## REFERENCES CITED

- Anderson, L. L., "A Wealth of Waste: A Shortage of Energy," pp. 1-16 in: Fuels from Waste, L. L. Anderson and D. A. Tillman, eds., Academic Press (1977).
- Antal, M. J., Edwards, W. E., Friedman, H. L., and Rogers, F. E., "A Study of the Steam Gasification of Organic Wastes," Project Report to EPA, Princeton University Grant No. R804836010, W. W. Liberick, Project Officer, Industrial Environmental Research Laboratory, Cincinnati, Ohio (1978).
- Antal, M. J., "A Review of the Vapor Phase Pyrolysis of Biomass Derived Volatile Matter," pp. 511-537 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Badger P. C., "Regional Efforts to Promote Biomass Energy Technologies," pp. 17-27 in: Biomass Energy Development. W. H. Smith, ed., Plenum Press (1985).
- Baker, E. G., Mudge, L. K., and Wilcox, W. A., "Catalysis of Gas-Phase Reactions in Steam Gasification of Biomass," pp. 863-874 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Bergman, M. K., "Public Power Research in Bioenergy," pp. 135-165 in: Energy Applications of Biomass, M. Lowenstein, ed., Elsevier Applied Science Publishers, London (1985).

- Bulpitt, W. S., and Walsh, J. L., "Utilization of Biomass Fuel for Production of Electric Power," pp. 349-361 in: Biomass Energy Development, W. H. Smith, ed., Plenum Press (1985).
- DeGroot, W. F., and Shafizadeh, F., "Kinetics of Wood Gasification by Carbon Dioxide and Steam," pp. 275-292 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Desrosiers, R. "Thermodynamics of Gas-Char Reactions," pp. 132-174 in: A Survey of Biomass Gasification Volume II - Principles of Gasification, T. Reed, ed., SERI/TR-33-239 (1979).
- Dippon, D. R., Rockwood, D. L., and Comer C. W., "Cost Sensitivity Analysis of Eucalyptus Grandis Woody Biomass Systems," pp. 143-156 in: Biomass Energy Development, W. H. Smith, ed., Plenum Press (1985).
- Double, J. M., and Bridgewater, A. V., "Sensitivity of Theoretical Gasifier Performance to System Parameters," pp. 915-919 in: Energy from Biomass, 3rd ed., W. Pulz, J. Coombs and D. C. Hall, eds., Elsevier Applied Science Publishers, London (1985).
- Elliott, D., and Sealock, L. J., "Low Temperature Gasification of Biomass Under Pressure," pp. 937-950 in: Fundamentals of Thermochemical Biomass Conversion. R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).



- Elliott, D. C., and Baker, H. G., "The Effect of Catalysis of Wood-Gasification Tar Composition," *Biomass*, 9, 195-203 (1986).
- Garg, M., Piskorz, J., Scott, D. S., and Radlein, D., "A Novel Catalytic Gasification Process for Production of High Methane Gases," Presented at IGT Symposium on Energy from Biomass and Wastes XI, Orlando, FL, March 16-20 (1987).
- Geyer, W. A., Naughton, G. G., and Melichar, M. W., "Biomass Gains in Coppicing Trees For Energy Crops," pp. 269-273 in: Energy from Biomass, 3rd ed., W. Pulz, J. Coombs and D. C. Hall, eds., Elsevier Applied Science Publishers, London (1985).
- Georgia Institute of Technology, The Industrial Wood Energy Handbook, pp. 8-59, Van Nostrand Reinold Company, Inc., New York (1984).
- Graboski, M., and Bain, R., "Properties of Biomass Relevant of Gasification," pp. 23-65 in: A Survey of Biomass Gasification Volume II - Principles of Gasification, T. Reed, ed., SERI/TR-33-239 (1979).
- Graboski, M., "Kinetics of Char Gasification Reactions," pp. 177-218 in: A Survey of Biomass Gasification Volume II - Principles of Gasification, T. Reed, ed., SERI/TR-33-239 (1979).
- Graham, R. G., Frell, B. A., Overend, R. P., Mok, L. K., and Bergougnou, M. A., "The Ultra-Rapid Fluid (URF) Reactor: Applications to Determine the Kinetics of the Fast Pyrolysis (Ultrapyrolysis) of Cellulose," Proposed for Presentation at the World Fluidization Conference (May 1986).

- Hallen, R. T., Sealock, L. J., and Cuello, R., "Influence of Alkali Carbonates on Biomass Volatilization," pp. 157-166 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Howland, G. P., Meskimen, G., and Constantin, M. J., "Micropropagation of Eucalytus Cloning Candidates in Florida," pp. 111-118 in: Biomass Energy Development, W. H. Smith, ed., Plenum Press (1985).
- Hummel, F. C., "The Use of Forests as a Source of Biomass Energy," pp. 90-98 in: Energy from Biomass, 3rd ed., W. Pulz, J. Coombs and D. C. Hall, eds., Elsevier Applied Science Publishers, London (1985).
- Jönsson, O., "Thermal Cracking of Tars and Hydrocarbons by Addition of Steam and Oxygen in the Cracking Zone," pp. 733-746 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Kuester, J. L., "Catalytic Conversion of Biomass-Derived Synthesis Gas to Diesel Fuel in a Slurry Reactor," in: Proceedings of the Third Annual Solar and Biomass Workshop, USDA, Atlanta, GA (1983).
- Kulp, J. L., "Biomass for Energy in the Forest Products Industry," pp. 43-51 in: Energy Applications of Biomass, M. Lowenstein, ed., Elsevier Applied Science Publishers, London (1985).

- La Fontaine, H., "Simple Inexpensive Gasifiers for Emergency Use Applications," pp. 397-413 in: Biomass Energy Development, W. H. Smith, ed., Plenum Press (1985).
- LePori, W. A., and Soltes, E. J., "Thermochemical Conversion for Energy and Fuel," pp. 9-75 in: Biomass Energy, E. A. Hiler and B. A. Stout, eds., Texas A&M University Press (1985).
- Liinanki, L., Lindman, N., Siöberg, S. O., and Ström, E., "Methane Yield from Biomass Gasification at High Temperature and Pressure," pp. 923-936 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Lipinsky, E. S., "What is the Biomass Energy Resource Base and at What Price?," pp. 13-19 in: Energy Applications of Biomass, M. Lowenstein, ed., Elsevier Applied Science Publishers, London (1985).
- Magne, P., Donnot, A., and Deglise, X., "Kinetics of Wood Tar Pyrolysis," pp. 822-826 in: Energy from Biomass, 3rd ed., W. Pulz, J. Coombs and D. C. Hall, eds., Elsevier Applied Science Publishers, London (1985).
- Milne, T., "The Thermal Behavior of Biomass Below 600 °C," pp. 177-218 in: A Survey of Biomass Gasification Volume II - Principles of Gasification, T. Reed, ed., SERI/TR-33-239 (1979).

- Milne, T., and Soltys, M., "The Direct, Mass-Spectrometric Study of the Primary and Secondary Pyrolysis Behavior of Biomass and its Constituents," pp. 361-383 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Mudge, L. K., Baker, E.G., Mitchell, D. H., and Brown, M. D., "Catalytic Steam Gasification of Biomass for Methanol and Methane Production," Journal of Solar Energy Engineering, 107, 88-92 (1985).
- Ostermeier, D. M., Young, T. M., and Walsh, D. F., "Characteristics of Industrial Wood Energy Users," pp. 29-42 in: Biomass Energy Development, W. H. Smith, ed., Plenum Press (1985).
- Parnell, C. B., "Systems Engineering of Biomass-Fueled Energy Alternatives," pp. 213-247 in: Biomass Energy, E. A. Hiler and B. A. Stout, eds., Texas A&M University Press (1985).
- Raman, P., Walawender, W. P., Fan, L. T., and Chang, C. C., "Mathematical Model for the Fluid-Bed Gasification of Biomass Materials. Applications to Feedlot Manure." Ind. Eng. Chem. Proc. Des. Dev., 20, 686-692 (1981).
- Ranney, J. W., Trimble, J. L., Wright, L. L., and Perlack, R. D., "Research on Short-Rotation Woody Crops in the South," pp. 71-83 in: Biomass Energy Development, W. H. Smith, ed., Plenum Press (1985).

- Reddy, K. V., Rockwood, D. L., Comer, C. W., and Meskimen, G. F.,  
"Genetic Improvement of Eucalyptus Grandis Woody Biomass  
Production in Florida," pp. 103-118 in: Biomass Energy  
Development, W. H. Smith, ed., Plenum Press (1985).
- Richard, J., Cathonnet, M., and Rouan, J., "Gasification of Charcoal:  
Influence of Water Vapor," pp. 589-599 in: Fundamentals of  
Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and  
L. K. Mudge, eds., Elsevier Applied Science Publishers, London  
(1985).
- Rockwood, D. L., "Development of Woody Biomass Cultural Systems for  
Florida," pp. 85-94 in: Biomass Energy Development, W. H. Smith,  
ed., Plenum Press (1985).
- Rossi, A., "Fuel Characteristics of Wood and Nonwood Biomass Fuels,"  
pp. 69-99 in: Progress in Biomass Conversion, Vol. 5, D. A.  
Tillman and E. C. John, eds., Academic Press (1984).
- Schiefelbein, G. F., "Thermal Conversion of Biomass: Progress and  
Prospects," pp. 275-290 in: Energy Applications of Biomass,  
M. Lowenstein, ed., Elsevier Applied Science Publishers, London  
(1985).
- Simmons, G. M., and Lee, W. H., "Kinetics of Gas Formation from  
Cellulose and Wood Pyrolysis," pp. 385-395 in: Fundamentals of  
Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and  
L. K. Mudge, eds., Elsevier Applied Science Publishers, London  
(1985).

- Singh, S. K., Walawender, W. P., Fan, L. T., and Geyer, W. A., "Steam Gasification of Cottonwood (Branches) in a Fluidized Bed," *Wood and Fiber Sci.*, 18, 327-344 (1986).
- Shafizadeh, F., "Pyrolysis and Combustion of Cellulosic Materials," pp. 419-474 in: Advances in Carbohydrate Chemistry, Vol. 23, M. S. Wolfrom and R. S. Tipson, eds., Academic Press, New York (1968).
- Shafizadeh, F., "Introduction to Pyrolysis of Biomass," *Journal of Analytical and Applied Pyrolysis*, 3, 283-305 (1982).
- Shafizadeh, F., "Alternative Pathways for Pyrolysis of Cellulose," *American Chemical Society*, 28, 285-290 (1983).
- Shafizadeh, F., "Pyrolysis Reactions and Products of Biomass," pp. 183-217 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Smil, V., Biomass Energies: Resources, Links and Constraints, Plenum Press, New York (1983).
- Soltes, E. J., "Thermochemical Processes for Bioenergy Production," pp. 321-331 in: Biomass Energy Development, W. H. Smith, ed., Plenum Press (1985).
- Stinson, J. M., "TVA Biomass Fuels Program," pp. 65-73 in: Energy Applications of Biomass, M. Lowenstein, ed., Elsevier Applied Science Publishers, London (1985).
- Stout, B. A., "Introduction," pp. 3-7 in: Biomass Energy, E. A. Hiler and B. A. Stout, eds., Texas A&M University Press (1985).



- Tanaka, Y., Yamaguchi, T., Yamasaki, K., Ueno, A., and Kotera, Y.,  
"Catalyst for Steam Gasification of Wood to Methanol Synthesis  
Gas," *Ind. Eng. Chem. Prod. Res. Dev.*, 23, 225-229 (1984).
- Tuvell, R., "Progress in the California Energy Commission Biomass  
Demonstration Program," pp. 119-134 in: Energy Applications of  
Biomass, M. Lowenstein, ed., Elsevier Applied Science Publishers,  
London (1985).
- van den Aarsen, F. G., Beenackers, A. A. C. M., and van Swaaij, W. P.  
M., "Wood Pyrolysis and Carbon Dioxide Char Gasification Kinetics  
in a Fluidized Bed," pp. 691-715 in: Fundamentals of  
Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and  
L. K. Mudge, eds., Elsevier Applied Science Publishers, London  
(1985).
- Walawender, W. P., Eriksson, M. A., Neogi, D., Singh, S., Fan, L. T.,  
and Geyer, W. A., "Effect of Steam-to-Feed Ratio on Biomass  
Gasification," Presented at AIChE Annual Meeting, Chicago,  
IL (1985b).
- Young, J., Griffin, E., and Russell, J., "Feasibility of Biomass-Based  
Fuels and Chemical Production in the USA," *Biomass*, 10, 9-25  
(1986).

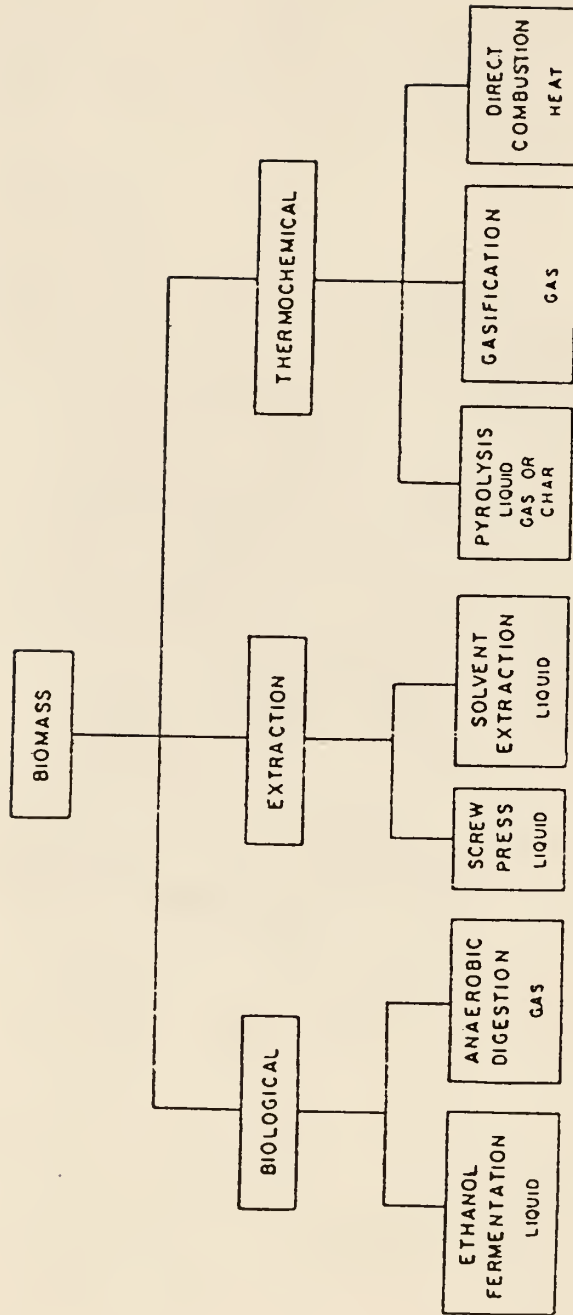


Figure II-1. Major Processes in the Conversion of Biomass into Energy Products (Stout, 1985).

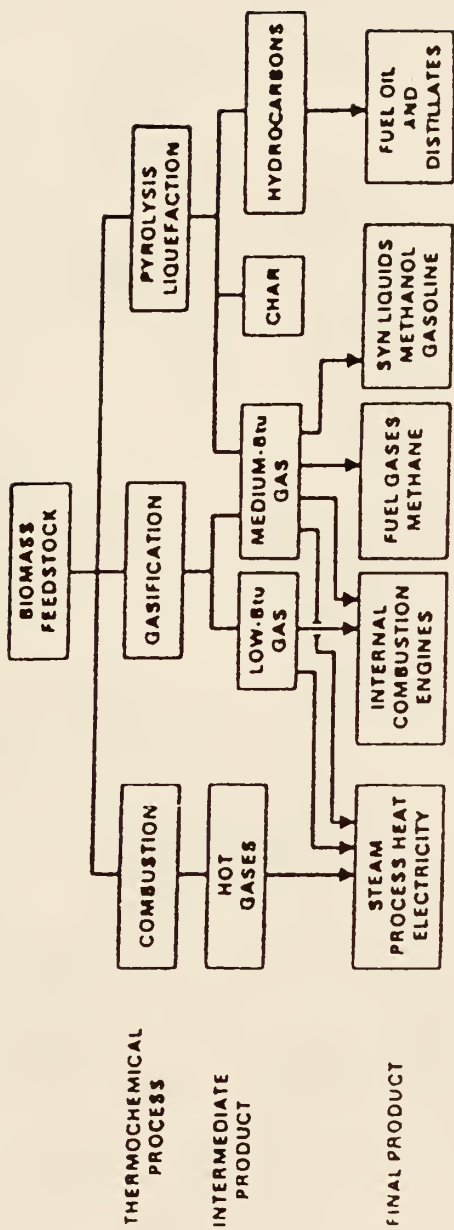


Figure II-2. Biomass Thermochemical Conversion Processes and Their Products (Schiefelbein, 1985).

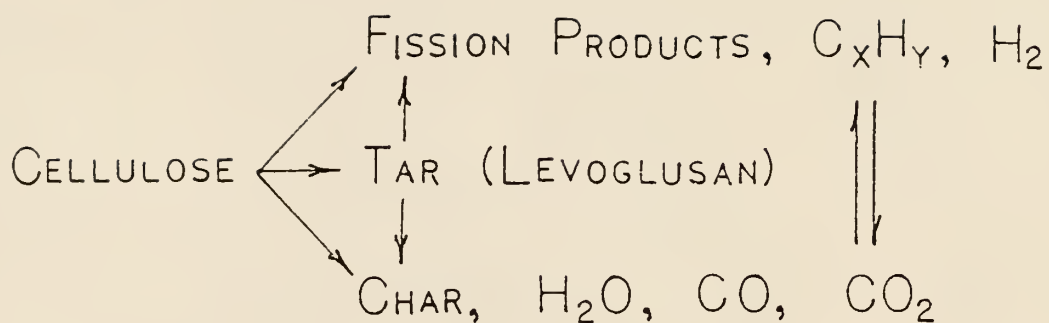
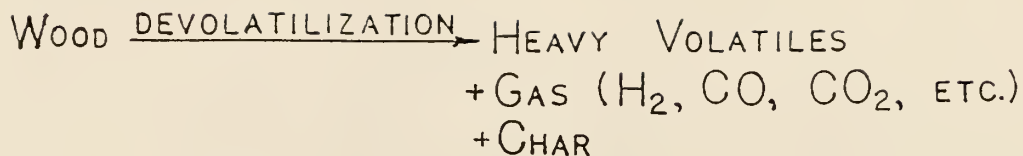


Figure II-3. General Reactions in the Pyrolysis of Cellulose (Shafizadeh, 1968 and 1983).

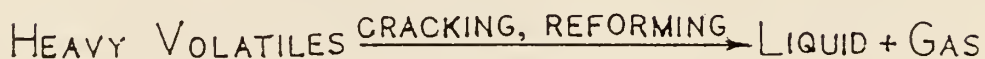


Figure 11-4. General Reaction Scheme for the Pyrolysis of Cellulose with an Active Intermediate (Shafizadeh, 1983).

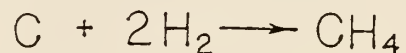
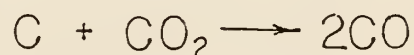
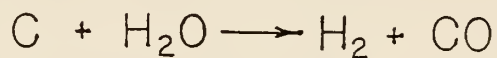
## (1) PRIMARY



## (2) SECONDARY



## (3) CHAR GASIFICATION



## (4) WATER-GAS SHIFT REACTION

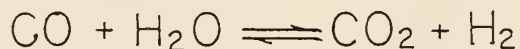


Figure II-5. Reaction Scheme for the Steam Gasification of Wood  
(Adapted from Raman *et al.*, 1981).



CHAPTER III

STEAM GASIFICATION OF SIBERIAN ELM AND COTTONWOOD

## INTRODUCTION

Gasification is an attractive method for converting wood into either low to medium heating value fuel gas or synthesis gas for liquid fuel production. The inclusion of steam in the gasification process has been found to increase the gas yield and carbon conversion through char gasification and the water-gas shift reaction. The water-gas shift reaction is particularly important in adjusting the  $H_2/CO$  ratio for methanol synthesis.

Several researchers investigated the effects of various operating parameters and the chemical composition of biomass on steam gasification. Reactor temperature has been found to be the major parameter influencing gas yield (Antal, 1983); pressure has been shown to have a strong influence on methane formation (Liinanki *et al.*, 1985). However, the role of the steam-to-feed ratio has not been clearly established.

Antal *et al.* (1978) investigated the secondary gas phase reactions of volatile matter derived from cellulose in a quartz, plug flow reactor. The results indicated that steam-to-feed mass ratios up to 1.4 had little effect. Hence, they have concluded that the gasification process is dominated by cracking reactions and that the presence of steam is not important below 1023 K. Feldman *et al.* (1981) conducted wood gasification experiments in a multi-solid fluidized bed, consisting of two beds with solids circulation between them. For a steam-to-feed ratio of 0.8, they observed no net steam consumption over a temperature range from 963 to 1172 K.

Walawender et al. (1985b) studied the steam gasification of Siberian elm in a fluidized bed over a temperature range of 850 to 1160 K with levels of the steam-to-feed mass ratio ranging from 3 to 11. They statistically compared regression models for various gasification characteristics at different levels of the steam-to-feed ratio with temperature as the independent variable. They also investigated the effect of the steam-to-feed ratio with  $\alpha$ -cellulose as the feed for comparison. They concluded that the steam-to-feed ratio had a significant effect on both biomass and cellulose gasification.

Singh et al. (1986) investigated the steam gasification of cottonwood branches in a fluidized-bed reactor over a temperature range of 850 to 1075 K with a steam-to-feed ratio that varied from 6 to 10 over their temperature range. Their study was a follow-up on the work performed by Walawender et al. (1985a) who investigated the steam gasification of  $\alpha$ -cellulose in the same reactor and found that two distinct temperature regimes existed; one where tar cracking reactions dominated below 940 K, and the other where the water-gas shift reaction dominated at temperatures above 940 K. The results of Singh et al. (1986) also indicated that two temperature regimes existed with the transition temperature between 930 and 950 K; however, the transition was not as distinct as found for cellulose by Walawender et al. (1985a). They concluded that the lignin present in the cottonwood caused the difference, since lignin tar cracking, although weakly affected by temperature, continued over the experimental temperature range whereas cellulose tar cracking was essentially complete at 940 K.

Prasad and Kuster (1988) performed regression modeling on pine sawdust process data obtained from a dual fluidized-bed gasifier. They established multiple regression models for the molar yields of the gas components ( $H_2$ , CO,  $CO_2$ ,  $CH_4$ ,  $C_2H_4$  and  $C_2H_6$ ) with temperature (1000-1100 K) and steam-to-feed ratio (1-10) as the independent variables. The results indicated that both variables were significant and that there was strong interaction between them. In addition, their results indicated that two regions existed over the temperature range of 1000 to 1100 K; a residence time or reaction rate dominated regime at lower temperatures (1000-1040 K) and an equilibrium dominated regime at higher temperatures (1060-1100 K) where the water-gas shift reaction and steam dilution were prevalent. In their work, as the steam-to-feed ratio was increased at a given temperature, the gas phase residence time decreased; whereas, Walawender *et al.* (1985a, 1985b) and Singh *et al.* (1986) reduced the steam flow rate with increasing temperature in order to maintain a fairly uniform residence time while the steam-to-feed ratio decreased.

Differences in the chemical composition of different forms of biomass have been found to influence the product yields and distributions from gasification. Kuester (1984) gasified a number of different feedstocks and indicated that the H/O ratio in the feed strongly effected the  $H_2/CO$  ratio and that ethylene production increased with increasing H/O ratio. DeGroot and Shafizadeh (1985) investigated  $CO_2$  and steam gasification of Douglas fir and cottonwood chars. Their results indicated that the ash percentage in the original

wood sample as well as its composition had an effect on steam and CO<sub>2</sub> gasification rates of its char. Higher ash content increased the char gasification rates. The alkali metals Na, K and Ca in ash were effective as catalysts but Mg, also found in ash, was shown to have little effect. Studies conducted by Antal et al. (1978), Walawender et al. (1980) and Beck and Wang (1980) indicate that biomass materials with higher cellulose contents tend to produce higher gas yields. While Milne (1979), DeGroot and Shafizadeh (1985), Antal (1983) and Koufopoulos et al. (1985) indicated that higher lignin contents tend to produce higher char yields.

In this work, steam gasification of Siberian elm and cottonwood was conducted in a fluidized bed to investigate the effect of composition differences associated with tree species on the yields of gas, tar and char; the gas composition; the conversion of carbon to gas, tar and char; and other gasification characteristics. The results of this study were also compared to results from prior related steam gasification studies to elucidate the effects of varying the steam-to-feed ratio and the gas phase residence time on the product yields and distributions.

## EXPERIMENTAL

### Facilities

The fluidized bed used in this work was designed for investigating the gasification of carbonaceous materials at temperatures up to 1400 K under atmospheric pressure conditions. Details of the bench-scale gasifier are given by Neogi (1984). The equipment consisted of three

major sections: (1) the reactor, (2) the gas clean-up section and (3) the gas sampling section as shown in Figure III-1.

The system consisted of a fluidized bed (constructed from Inconel 600) surrounded by electrical resistance heaters, a screw feeder and a steam generator. Figure III-2 presents a detailed schematic of the reactor section. The figure depicts four zones: (1) gas inlet, (2) packed bed, (3) fluidized bed and (4) disengaging. The bed material was composed of 25% of limestone and 75% of silica sand by weight. The limestone particle size ranged from -7 to +50 mesh (2.82 to 0.287 mm) and the silica sand particle size ranged from -30 to +50 mesh (0.59 to 0.287 mm). The static bed height was 8 to 10 cm, and the expanded bed height was 12 to 14 cm. Aluminum oxide pellets, with a diameter of 0.5 cm, were used in the packed bed zone to provide uniform distribution of the fluidizing gas (steam/air). Both the packed bed and the gas inlet zones served as preheaters for the fluidizing gas. The bed section contained a pressure probe, connected to a manometer, to indicate the state of fluidization and the bed pressure.

Twelve, quarter cylindrical, electrical resistance heaters, arranged in three sets of four, were used to heat the reactor. The top set was connected with all four heaters in parallel and the bottom two sets contained two pairs of heaters in series, connected in parallel. The parallel circuit in top set was used to compensate for the greater heat loss from the disengaging zone due to the water jacketed feed pipe. Three Omega, three-mode, PID controllers (model 49K-814) were used to control the voltage to each set of heaters. Five chromel



alumel thermocouples with 1/8 inch sheaths were installed in the reactor. Three thermocouples measured the temperature of the active zone; i.e., the disengaging and fluidized bed zones, and provided feedback to the controllers. They were located in the freeboard, the top of the fluidized bed zone and the bottom of the bed. Another thermocouple, inserted through the top, was able to slide freely to permit measurement of the axial temperature profile. A fifth thermocouple was located in the inlet zone and monitored the temperature of the fluidizing gas.

A Vibra Screw Feeder (model SCR-20), with a solid core flight screw, supplied the feed material at a uniform volumetric flow rate to the vertical feed pipe, thus providing a gravity flow. A nitrogen purge was applied to prevent the backflow of condensibles into the feed pipe and to aid the flow of fine feed particles. The feed pipe was enclosed by a water jacket to prevent premature devolatilization of the feed material.

Steam was generated externally by a Sussman Hot Shot electric boiler (model MB-6) and provided steam to the inlet zone at 400 K and 200 kPa. Steam flow was regulated with a needle valve.

The gas clean-up section consisted of a cyclone, water jacketed condensers and a filter. The hot cyclone removed the particulate char from the product gas. The product gas then passed through a series of countercurrent, water cooled, condensers to remove the steam and tar which were collected in a condensate receiver. Finally, the product gas was passed through a dry filter, packed with glass wool. This

filter was effective in removing remaining particulates and fine tar mist that bypassed the cyclone and the condensers.

A wet-test meter and a Perkin-Elmer strip chart recorder were used to measure the volumetric flow rate of the gas. A sample of the off-gas was drawn through a drying column packed with drierite ( $\text{CaSO}_4$ ) and sent to an on-line process gas chromatograph (GC) for analysis.

#### Procedure

The experimental procedure was similar to that used by Neogi (1984), consequently, only a brief description of it will be given. Reactor heat-up required 6 to 8 hours. During this time, air was used as the fluidizing gas and feed pipe purge. Water flow was initiated to the jacketed feed pipe at the beginning of preheat. The feed rate was calibrated and measured by disconnecting the feed pipe from the top of the fluidized bed, and weighing effluent collected over three minute intervals. Once the desired feed rate had been achieved, at least three measurements were taken and averaged. When the preheat was completed, nitrogen purge was established and the fluidizing air was gradually replaced with steam. Total time for the start-up was 8 to 10 hours.

After initiating feeding for 15 to 20 minutes, the system was ready for data collection to begin. Gas samples were taken every 11 minutes (GC cycle time) for 60 to 90 minutes. For each GC cycle, the axial temperature profile (measured in 4 cm increments from the bottom of the bed to near the top of the disengaging zone), the condensate rate and the gas flow rate were measured. Minor adjustments were made

manually during the course of the run to the nitrogen purge rate and the heater controller set points; especially, the bottom set of heaters which would experience a large range of variation without the adjustments.

At the conclusion of the measurement period, the system was shut down and samples of the char and tar were taken from the cyclone receiver and the condensate receiver, respectively. The feed rate was remeasured using the procedure employed at the start of the run. The average of the two feed rates was used as the mass feed rate for the run.

#### Chemical Analyses

The product gas, feed, char and tar were analyzed for each experimental run. An Applied Automation on-line process gas chromatograph (Optichrom 2100) was used to determine the composition of the dry product gas. The components of interest were  $H_2$ , CO,  $CO_2$ ,  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ ,  $C_3H_8$ ,  $O_2$  and  $N_2$ . Moisture and ash in the feed and char were determined in a ventilated oven and muffle furnace respectively, according to standard ASTM procedures. Elemental analyses were conducted on samples of the feed, char and tar with a Perkin-Elmer elemental analyzer (model 240B).

#### Feed Materials

Siberian elm (Ulmus pumila L.) and cottonwood (Populus deltoides Bartr.) were the tree species for this investigation. The Siberian elm was obtained from 10 seven-year-old trees selected randomly from a one hectare short-rotation "energy plantation" during the dormant season of

1984. The trees were chipped in their entirety with a Morbark chipper. The cottonwood was obtained from branches of twelve-year-old trees. Branches up to 8 cm in diameter were used and were run through a Morbark chipper. Each chip source was ground in a hammermill with a 0.6 cm screen. The resulting ground materials were separated by sieves to obtain the -28 to +50 mesh (0.595 to 0.287 mm) fraction. Fibrous materials, that would result in bridging in the feed hopper, were removed in the separation process. Further reduction of the particle size for both species was accomplished by passing the sieved fractions through a Fritzmill with a 0.508 mm (0.020 in.) screen. The ultimate and component analyses, moisture content and heat of combustion for each species are presented in Table III-1.

#### Operating Conditions

The operating conditions for the experimental runs are summarized in Table III-2. The principle variable was the reactor temperature which ranged from 870 to 1070 K. Typical axial temperature profiles are presented in Figure III-3. The steam rate varied from 9 to 14 g/min, and the feed rate varied from 1.6 to 2.4 g/min. Thus, the steam-to-feed mass ratio ranged from 5.7 to 6.6. The flow rate for the nitrogen purge (at 288 K and 101.3 kPa) varied from 0.0022 to 0.0023 m<sup>3</sup>/min. As a consequence of varying the steam rate with the reactor temperature, a fairly constant gas phase residence time of about 5 s was obtained, since the steam constituted approximately 80% of the gas phase.

## Statistical Design of Experiments

The experiments were planned with the reactor temperature varying at five levels from 870 to 1070 K in increments of 50 K. The order in which the experiments at the various temperatures were performed for the Siberian elm was randomized. In the latter stage of experimentation, cottonwood was also used as a feed to permit direct comparisons with the results obtained from Siberian elm. The order in which the tree species-temperature level combinations were performed was randomized. Randomization of the order of experiments was used to reduce the influences of biases that might result from performing the experiments over time. Possible sources for biases include changes in the performance of the equipment and the learning experience of the operators.

## METHODS OF DATA ANALYSIS

### Gasification Characteristics

In general, data obtained during each gas chromatograph cycle over the last 50 to 60 minutes of steady-state operation in each run were used for analysis. The results consisted of the dry gas composition, the gas higher heating value (HHV), the dry gas volumetric yield, the energy recovery, the mass yields of gas, tar and char, the steam consumed and the conversion of carbon to gas, tar and char. The standard conditions for the volumetric gas yield were 288 K (60 °F) and 101.3 kPa (1 atm).

The dry gas was divided into its major components:  $H_2$ ,  $CO_2$ ,  $CO$  and  $CH_4$ , and its minor components:  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$  and  $C_3H_8$ . The gas

higher heating value was calculated using all of the components and the standard heat of combustion for each component. The volumetric flow rate of the dry gas was determined from the difference between the wet-test meter flow rates before and after feeding. The dry gas volumetric yield was calculated as the volume of dry gas per unit mass of dry-ash-free (DAF) feed. The energy recovery was determined as the ratio (expressed as a percentage) of the product of the volumetric gas yield per unit mass of DAF feed and the gas higher heating value to the heat of combustion (measured by calorimetry) of a unit mass of DAF feed. This value represents the ratio of the energy contained in the cool dry product gas to the energy contained in the feed.

The mass yield of gas was determined by converting the volumetric gas yield to a mass basis. The char and tar mass yields were estimated from ash and carbon balances, respectively. Here, it was assumed that all the ash originally in the wood was contained in the char and that the fraction of tar miscible in the condensate was negligible. In addition, the moles of steam consumed per mole of carbon in the wood was estimated from ash, carbon and oxygen balances. The carbon conversions were determined as the ratio (expressed as a percentage) of the weight of carbon in either the gas, tar or char obtained from a unit mass of DAF feed to the weight of carbon in a unit mass of DAF feed.

#### Statistical Analyses

Effect of temperature. The regression procedures in the SAS package (Statistical Analysis System; version 82.3) were used to



determine polynomial models (up to third order) with the reactor temperature as the independent variable and the various gasification characteristics as the dependent variables for Siberian elm and cottonwood. The simplest polynomial that adequately described the data over the experimental temperature range was chosen as the "best fit" model.

Criteria for selecting the "best fit" models were the F-test, the parameter significance level and the R-Square value. If the significance probability, denoted as  $PR > F$ , was equal to or less than 0.05, the model was considered to be significant. Parameters of the model were accepted as being significant by the t-test at the 5% significance level.

Statistical comparison of Siberian elm and cottonwood. Siberian elm and cottonwood were statistically compared for significant differences by a method that uses both continuous and categorical variables in the multiple regression analysis (see Pedhazur, 1982). By the use of an indicator variable  $w$  for tree species, it was possible to describe the temperature dependence of a given gasification characteristic ( $Y$ ) for both species with one model. The full third order polynomial model considered in this analysis was

$$Y = A + A'w + BT + B'wT + CT^2 + C'wT^2 + DT^3 + D'wT^3 + \epsilon \quad (\text{III-1})$$

where  $Y$  = gasification characteristic

$T$  = reactor temperature

$w$  = tree species; {1 = Siberian elm and 0 = cottonwood}

$\epsilon$  = error

The regression parameters for cottonwood are A, B, C and D. The regression parameters for Siberian elm are  $A + A'$ ,  $B + B'$ ,  $C + C'$  and  $D + D'$ . Hence, the parameter  $A'$  represents the effect of tree species on the dependent variable Y and the parameters  $B'$ ,  $C'$  and  $D'$  represent the effects of species-temperature interactions. By determining which of the parameters in equation (III-1) are significant, statistical inferences can be made regarding how a given gasification characteristic differs as a function of temperature between the two species. For example, if the parameters A,  $A'$ , B and C are found significant, it can be concluded that both species show a second order temperature dependence for Y and that the species are significantly different by a constant amount  $A'$ . Parameters B and C become the pooled or common regression parameters for both species.

The regression procedures in SAS were again used to determine "best fit" models for the combined data from both species. Criteria for selecting the "best fit" models were the same as used to select the "best fit" models with temperature as the sole independent variable.

## RESULTS

### Regression Models for Gasification Characteristics

For Siberian elm, the results from 10 runs were used in the statistical analyses and, for cottonwood, a total of 5 runs were used. The results of the regression analyses with the reactor temperature as the independent variable are summarized in Table III-3. The table contains estimates for the model parameters, the R-Square value, the F-value, the probability of falsely rejecting the regression model

( $PR > F$ ), and the number of data points for each of the gasification characteristics. The results are graphically presented in Figures III-4 through III-10. In the figures, the solid lines represent the regression models for Siberian elm and the dashed lines represent the regression models for cottonwood. The points represent the experimental observations. Results for each of the gasification characteristics will be presented in turn.

Product gas composition. The mole percentages of the major components of the dry gas ( $H_2$ ,  $CO_2$ ,  $CO$  and  $CH_4$ ) showed similar variations with temperature for each tree species as shown in Figure III-4. The  $H_2$  concentration increased with temperature and leveled off at higher temperatures. Its temperature dependence was described by second order models. For Siberian elm, the  $H_2$  concentration ranged from 36.6% at 870 K to 50.5% at 1070 K and, for cottonwood, it increased from 36.8% at 870 K to 52.7% at 1070 K. The concentration of  $CO_2$  was nearly independent of temperature and was described by third order models for each species. It ranged from 27.8% at 870 K to 28.3% at 1070 K with a minimum of 26.7% at 920 K and a maximum of 28.7% at 1040 K for Siberian elm. For cottonwood, the  $CO_2$  concentration varied from 27.6% at 870 K to 30.3% at 1070 K with a minimum of 27.0% and a maximum of 30.8%, occurring at about the same temperatures as for Siberian elm. For  $CO$ , the temperature dependence was described by third order models for each species. The  $CO$  concentration ranged from 22.7% at 870 K to 10.8% at 1070 K with a minimum of 10.6% at 1050 K for Siberian elm and ranged from 22.7% at

870 K to 8.7% at 1070 K with a minimum of 8.3% at 1050 K for cottonwood. For  $\text{CH}_4$ , the concentration varied linearly from 8.2% at 870 K to 7.2% at 1070 K for Siberian elm and from 8.8% at 870 K to 6.4% at 1070 K for cottonwood.

Gas higher heating value. The temperature dependence of the gas higher heating value (HHV) is presented in Figure III-5. For both Siberian elm and cottonwood, the temperature dependence of the gas HHV was described by third order models. Values for the gas HHV ranged from 13.1  $\text{MJ/m}^3$  at 870 K to 11.9  $\text{MJ/m}^3$  at 1070 K for Siberian elm and from 13.6  $\text{MJ/m}^3$  at 870 K to 11.7  $\text{MJ/m}^3$  at 1070 K for cottonwood. Maxima and minima occurred at approximately 885 K and 1065 K, respectively, for both species.

Volumetric gas yield. The dry gas volumetric yield as a function of temperature for each species is shown in Figure III-6. The temperature dependence of the volumetric yield for each species was described by second order models. It increased from 0.77  $\text{m}^3/\text{kg DAF}$  at 870 K to 1.76  $\text{m}^3/\text{kg DAF}$  at 1070 K for Siberian elm and from 0.66  $\text{m}^3/\text{kg DAF}$  at 870 K to 1.57  $\text{m}^3/\text{kg DAF}$  at 1070 K for cottonwood.

Energy recovery. The temperature dependence of the energy recovery for Siberian elm and cottonwood is shown in Figure III-7. Second order models described the temperature dependence for each species. The energy recovery increased from 51% at 870 K to 104% at 1070 K for Siberian elm and from 45% at 870 K to 91% at 1070 K for cottonwood.

Product mass yields. The mass yields of gas, tar and char as functions of temperature for Siberian elm and cottonwood are presented in Figure III-8. The temperature dependence of the mass yield of gas for both species was described by second order models. Gas yield increased from 0.71 kg/kg DAF at 870 K to 1.37 kg/kg DAF at 1070 K for Siberian elm and from 0.62 kg/kg DAF at 870 K to 1.23 kg/kg DAF at 1070 K for cottonwood. Both the tar and char mass yields varied linearly with temperature for each tree species. For Siberian elm, the tar mass yield decreased from 0.14 kg/kg DAF at 870 K to near zero at 1070 K, and the char mass yield decreased from 0.12 kg/kg DAF at 870 K to 0.05 kg/kg DAF at 1070 K. For cottonwood, the tar mass yield decreased from 0.14 kg/kg DAF at 870 K to 0.08 kg/kg DAF at 1070 K, and the char mass yield decreased from 0.18 kg/kg DAF at 870 K to 0.03 kg/kg DAF at 1070 K.

Steam consumption. The steam consumption as function of temperature for each species is shown in Figure III-9. The temperature dependence of the steam consumption for each species was described by third order models. For Siberian elm, it increased from 0.02 mol/mol C at 870 K to 0.56 mol/mol C at 1070 K. For cottonwood, the steam consumption increased from near zero at 870 K to 0.43 mol/mol C at 1070 K.

Carbon conversion. The temperature dependence of the conversion of carbon to gas, tar and char for Siberian elm and cottonwood is presented in Figure III-10. For both species, second order models described the carbon conversion to gas and linear models described the

conversion of carbon to both tar and char. The carbon conversion to gas ranged from 54% at 870 K to 94% at 1070 K for Siberian elm and from 48% at 870 K to 82% at 1070 K for cottonwood. The carbon conversion to tar decreased from 22% at 870 K to near zero at 1070 K for Siberian elm and from 22% at 870 K to 9.7% at 1070 K for cottonwood. The carbon conversion to char decreased from 20% at 870 K to 10% at 1070 K for Siberian elm and from 28% at 870 K to 4.9% at 1070 K for cottonwood.

#### Statistical Comparisons of Siberian Elm and Cottonwood

Table III-4 presents the results of the multiple regression analyses with the independent variables temperature (T) and tree species (w). It represents a statistical comparison between Siberian elm and cottonwood. Although the full third order model as given by equation (III-1) was considered, only the effect of tree species represented by the parameter A' and the first order species-temperature interaction represented by the parameter B' were found to be significant in the regression analyses.

For the major gas components, the H<sub>2</sub> concentration for cottonwood was found to be higher than for Siberian elm by a constant amount as indicated by the parameter A'. Both the effect of tree species and the first order species-temperature interaction were found significant for the gas components CO<sub>2</sub>, CO and CH<sub>4</sub>. For CO<sub>2</sub>, cottonwood had the higher concentration in which the difference increased with increasing temperature. For CO, the opposite was found; i.e., Siberian elm had the higher concentration with the difference increasing at higher temperatures. Cottonwood had the higher CH<sub>4</sub> concentration at low



temperatures, while Siberian elm had the higher CH<sub>4</sub> concentration at high temperatures.

For the gas heating value, both the tree species effect and first order species-temperature interaction were found significant with cottonwood gas having a greater HHV over Siberian elm gas at low temperatures. The difference in the gas HHV between cottonwood and Siberian elm became insignificant at high temperatures.

The comparisons between the two tree species also indicated that Siberian elm had the greater volumetric and mass yields of gas, energy recovery, steam consumption and carbon conversion to gas by a constant amount over the entire temperature range.

For the tar mass yield and the carbon conversion to tar, the effect of tree species was also found significant with cottonwood exceeding Siberian elm. There were no significant differences in the char mass yields and carbon conversions to char between Siberian elm and cottonwood.

## DISCUSSION

### Comparison of Siberian elm and Cottonwood

Comparisons of the two tree species indicated that differences existed in their gasification characteristics. One of the objectives of this work was to determine if wood composition differences between species influenced the gasification results. Table III-1 illustrates that the elemental compositions and the ash weight percentages for Siberian elm and cottonwood were very similar. Thus, the elemental composition cannot be considered as a factor in the observed

differences in the gasification results. However, Table III-1 also indicates that differences in the weight percentages of hemicellulose, cellulose and lignin existed between the two tree species. These component differences are believed to be responsible for differences in the gasification characteristics between Siberian elm and cottonwood.

Table III-4 shows that the volumetric gas yield, the mass yield of gas and the carbon conversion to gas were significantly different for the two species. Figures III-6, III-8 and III-10, as well as Table III-4, indicate that these characteristics were significantly higher for Siberian elm than for cottonwood over the entire temperature range. Since Siberian elm has a higher cellulose content than cottonwood, the results are consistent with the findings of Antal et al. (1978), Walawender et al. (1980) and Beck and Wang (1980), who suggested that biomass materials with higher cellulose contents produce higher gas yields.

Table III-4 also indicates that no significant difference existed between the char yields from the two woods. These results are not consistent with the findings of Milne (1979), DeGroot and Shafizadeh (1985), Koufopoulos et al. (1985) and Antal (1983), who reported that char yield increases with increasing lignin content. However, inspection of the regression lines in Figure III-8 indicates that for the low temperature range, the char yield from cottonwood, which has the higher lignin content, is greater than that from Siberian elm. Only in the upper temperature range are the two char yields very similar. This implies that for the high steam-to-feed ratios used in

the present experiments, the char from cottonwood is more reactive than the char from Siberian elm. This is reasonable since cottonwood is a more porous wood than Siberian elm.

Statistically, the tar mass yields for the two species are significantly different as indicated in Table III-4. Figure III-8 indicates that the tar yields for each species are nearly the same at 870 K and significantly higher for cottonwood at 1070 K. It is possible to explain the observed behavior in terms of differences in the cellulose and lignin contents between the two species. Singh et al. (1986) estimated tar yields from the cellulose and lignin portions of their cottonwood using Antal's data (Antal, 1983, 1985). Their calculations indicated that the cellulose tar yield at 870 K (0.2 kg/kg DAF feed) was significantly greater than the tar yield from lignin (0.07 kg/kg DAF feed). However, the cellulose tar yield decreased rapidly with increasing temperature up to 940 K. Above 940 K, it remained fairly constant at 0.02 kg/kg DAF feed. In contrast, lignin tar yield decreased slightly from 0.07 kg/kg DAF feed at 870 K to 0.04 kg/kg DAF feed at 1020 K. Therefore, the higher cellulose content in Siberian elm compensates for its lower lignin content in tar production at low temperatures, and differences in the tar yields between species are reduced at temperatures below 940 K. However, above 940 K, differences in the lignin content becomes a major factor in the differences in the tar yields between species, since lignin tar yield is greater than the tar yield from cellulose at these temperatures.

The higher  $H_2$  and  $CO_2$  and the lower  $CO$  concentrations from cottonwood at the higher temperatures (see Figure III-4) might tend to suggest that the water-gas shift reaction occurred to a greater extent relative to the gas produced from cottonwood; especially since the composition differences become larger for temperatures above 940 K. Singh *et al.* (1986) and Walawender *et al.* (1985a) have indicated that the water-gas shift reaction dominates above 940 K. However, Figure III-9 as well as Table III-4 indicate that steam consumption was higher for Siberian elm. It is possible that the differences in the contents of cellulose and lignin between the two species may have contributed to the differences in gas component concentrations. The results of Antal (1985) showed that lignin yielded three times the amount of  $H_2$  as compared to cellulose at 1020 K. Also, the mass ratio of  $CO_2/CO$  at 1020 K was about 0.6 for lignin and about 0.3 for cellulose. Since cottonwood has more lignin and less cellulose than Siberian elm, the higher concentrations of  $H_2$  and  $CO_2$  and lower concentration of  $CO$  for cottonwood are consistent with Antal's observations.

Additionally, the results of Antal (1985) are also consistent with the differences found between the  $CH_4$  concentrations for the two species. Antal observed that lignin yields slightly more  $CH_4$  than cellulose at lower temperatures and yields slightly less  $CH_4$  than cellulose at higher temperatures. Cottonwood with a higher lignin content and a lower cellulose content had a higher  $CH_4$  concentration at low temperatures and a lower  $CH_4$  concentration at high temperatures compared to Siberian elm.

The above discussion suggests that the steam gasification behavior of wood can be qualitatively explained in terms of the amounts of the major chemical constituents, cellulose and lignin. However, it should be pointed out that the gasification of wood or other biomass cannot be quantitatively represented by the fractional contributions from its components. Milne (1979) reported that many researchers claim that the pyrolysis of wood qualitatively resembles the additive effect of its components. However, no quantitative evidence has been provided to support this hypothesis. Antal (1985) attempted to use a linear programming optimization algorithm with data from the pyrolysis of cellulose, kraft lignin and d-mannose to interpret gas yields from wood in terms of fractional contributions from the components; however, no satisfactory fit was obtained.

#### Effect of High Steam-to-Feed Ratio

The results of this investigation were compared with previous related studies to assess the effects of a high steam-to-feed mass ratio. Equilibrium calculations have projected that increasing the water vapor fraction promotes solid carbon uptake and produces  $H_2$  and CO gas through the carbon-steam gasification reaction at temperatures applicable to gasification processes; i.e., 870 to 1170 K (Antal, 1978; Antal et al., 1978; Desrosiers, 1979). Antal's calculations (Antal, 1978) indicated that solid carbon would be exhausted between 770 and 870 K for a steam-to-feed (cellulose) mass ratio of 0.8.

In contrast to the equilibrium calculations, solid char, composed mainly of carbon, was present throughout the experimental temperature



range. Hence, the steam gasification process did not achieve thermodynamic equilibrium. Furthermore, the minor gas components  $C_2H_4$ ,  $C_2H_6$  and  $C_3H_6$  were present at all temperatures investigated, whereas the equilibrium analyses of Antal *et al.* (1978) and Desrosiers (1979) indicate that these components should not be present.

The water-gas shift reaction is exothermic, and the forward reaction is favored at low temperatures; however, the rate is reduced at low temperatures. Since the equilibrium constant for this reaction is equal to 1 at 1103 K (Antal *et al.*, 1978) and the law of mass action tends to drive the forward reaction to favor  $H_2$  and  $CO_2$  formation with high steam-to-feed ratios, operating a steam gasification system below 1100 K with high water concentrations favors the production of  $H_2$  and reduces the amount of CO.

Experimental studies with relatively low steam-to-feed ratios; i.e., approximately 1, have suggested that steam has little effect on the gas yield (Antal *et al.*, 1978; Feldman *et al.*, 1981). While other studies with relatively high steam-to-feed ratios (6 or greater) have suggested that the presence of steam is important in increasing the gas yield (Walawender *et al.*, 1985b; Singh *et al.*, 1986). Both of the above observations are consistent with the behavior of the shift reaction.

The results of this work with a steam-to-feed ratio of 6 show that steam is consumed in significant quantities in the gasification process, particularly at the higher temperatures. Figure III-9 shows that steam consumption for both species increased over the experimental



temperature range. For Siberian elm, steam consumption was detected at a temperature of 870 K.

Table III-5 presents a summary of the results of this work and those of several other researchers (Walawender *et al.*, 1983; Antal, 1985; Jönsson, 1985; Mudge *et al.*, 1985; van den Aarsen *et al.*, 1985) involving pyrolysis or low steam-to-feed ratio gasification of wood for comparative purposes. Inspection of the contents of the table clearly indicates that both steam-to-feed ratio and temperature are important in establishing the gas composition. Table III-5 also indicates that high steam-to-feed ratios result in higher H<sub>2</sub> and CO<sub>2</sub> concentrations and lower CO concentrations compared to the low steam-to-feed ratio gasification.

Figure III-7 shows that the energy recovery for Siberian elm exceeded 100% for temperatures greater than 1045 K. This would not have been possible if steam was consumed solely through the shift reaction. The gain in the energy content of the gas (based on a unit mass of wood) from the production of H<sub>2</sub> would be offset by the consumption of CO, since the heating value of H<sub>2</sub> and CO, on a molar basis, are nearly equal (0.286 MJ/mol for H<sub>2</sub> and 0.283 MJ/mol for CO). Therefore, the fact that the energy recovery for Siberian elm exceeded 100% implies that a portion of the steam was reacting with the char to yield additional H<sub>2</sub> and CO.

Comparison with the Work of Singh *et al.*

The work of Singh *et al.* (1986) was compared with the present work, since both studies were conducted with the same cottonwood

feedstock, the same bed matrix mix and similar experimental equipment. These comparisons permitted assessment of the influences of both the steam-to-feed ratio and the gas phase residence time, since these operating parameters were not the same in the two investigations.

The significant regression models for cottonwood from this work and those from Singh et al. (1986) are plotted for the gas composition, the volumetric gas yield and the carbon conversion in Figures III-11, III-12 and III-13, respectively. Figure III-11 shows that small differences existed in the gas compositions between this study and the work of Singh et al. For temperatures below 900 K, the CO<sub>2</sub> concentration for this work was slightly less than the CO<sub>2</sub> concentration found by Singh et al., and the CO concentration for this work was slightly greater than the CO concentration found by Singh et al. At temperatures greater than 1030 K, the H<sub>2</sub> concentration for this work was slightly greater than the H<sub>2</sub> concentration found by Singh et al. However, as show in Figures III-12 and III-13, notable differences existed in the volumetric gas yield and carbon conversion at the lower temperatures, with the results of this study exceeding those found by Singh et al.

Two of the operating parameters, the steam-to-feed mass ratio and the gas phase residence time were significantly different between the two investigations. These factors were considered in the interpretation of the differences found in the gas yield and the carbon conversion. In the study by Singh et al. (1986), the steam-to-feed ratio decreased from 10 to 6 with increasing temperature in order to

maintain a uniform gas phase residence time with the feed rate held fairly constant. The steam-to-feed ratio of 6 for this work was held fairly constant over the entire temperature range by varying both the steam rate and the cottonwood feed rate. The residence times for both studies were maintained fairly uniform since the steam constituted approximately 80 % of the gas volume. The gas phase residence time for Singh *et al.* ranged from 2 to 2.4 s and it ranged from 5 to 5.6 s for this work.

The greatest difference in steam-to-feed ratios between the two studies occurred at the lowest temperature (870 K). At this temperature, the steam-to-feed ratio for Singh *et al.* (1986) exceeded that of the present work by a factor of 1.7. However, even with this significantly higher steam-to-feed ratio, the gas yield and carbon conversion were lower. Figure III-9 indicates that in the present work, steam consumption with cottonwood was negligible at 870 K. Consequently, the steam-to-feed ratio appears to have little influence at low temperature.

The differences in the gas yield and the carbon conversion below about 940 K can be attributed to tar cracking reactions. The work of Antal (1985) indicated that light permanent gases derived through the cracking of volatile matter displayed asymptotic yields which were approached in approximately 5 s. Although Singh *et al.* (1986) did not measure the tar yield directly, a cellulose tar yield of 0.2 kg/kg DAF feed and a lignin tar yield of 0.07 kg/kg DAF feed at 870 K were estimated by them using the wood component tar yields from the work of

Antal (1983, 1985), their wood composition and their experimental residence time. While a tar yield from hemicellulose could not be estimated in a similar fashion, Singh *et al.* expected the tar yield from hemicellulose to be less than cellulose based on the study of Milne (1979). Thus, the total tar yield from these two components was estimated to be 0.27 kg/kg DAF feed at 870 K. This yield is significantly greater than the tar yield of 0.15 kg/kg DAF feed at 870 K (determined from a carbon balance) for this study. Hence, the longer gas phase residence time of 5.3 s used in this work as compared to 2.2 s used in the work of Singh *et al.* is responsible for the greater degree of tar cracking and the subsequently higher gas yield and carbon conversion.

From Figure III-12, it appears that the difference in gas residence time between the two studies has little influence on the gas yield at the higher temperatures. The works of Walawender *et al.* (1985a) and Singh *et al.* (1986) indicate that the water-gas shift reaction dominates for temperatures greater than 940 K and that tar cracking is secondary. Figure III-9 illustrates that significant steam is consumed in the gasification of cottonwood at the higher temperatures. Since both studies were conducted at nearly the same steam-to-feed ratio for the high temperature range, it appears from Figure III-12 that the degree of completion of the shift reaction is not significantly altered by the residence time difference between the two sets of experiments (approximately 3 s). It should also be noted

that equilibrium calculations indicate that the shift reaction is not complete under the conditions of the experiments.

Actually, at the higher temperatures, the gas yield obtained by Singh *et al.* (1986) is slightly higher than that obtained in the present work as illustrated in Figure III-12. Additionally, as shown in Figure III-13, the carbon conversion to gas obtained by Singh *et al.* at the higher temperatures is even more noticeably higher even though the residence time was lower than in this work. An explanation for these differences may be associated with the fact that the wood samples studied by Singh *et al.* contained a higher percentage of ash (5.9% vs 3.9%). DeGroot and Shafizadeh (1985) have observed that the rate of char gasification increases with an increase in the ash content of the wood. The higher ash content in the wood studied by Singh *et al.* is most likely due to a higher proportion of bark in their wood samples. Enhancement of char gasification increases both carbon conversion and gas yield, although it can be shown that the apparent effect on carbon conversion is much greater than it is on the gas yield at the higher temperatures.

#### CONCLUDING REMARKS

Steam gasification experiments with Siberian elm and cottonwood were conducted in a fluidized-bed reactor over a temperature range of 870 to 1070 K with a steam-to-feed ratio of 6 to investigate the effect of differences in the chemical composition of two tree species on the product yields and distributions. Statistical comparisons between Siberian elm and cottonwood indicated that Siberian elm yielded more

gas and a higher carbon conversion than cottonwood. The higher cellulose content and the lower lignin content in Siberian elm, as compared to cottonwood, qualitatively explains these differences. In addition, cottonwood had a greater tar yield than Siberian elm at the higher temperatures, primarily due to its higher lignin content.

A comparison with other related studies revealed that a high steam-to-feed ratio relative to pyrolysis or low steam-to-feed gasification resulted in a higher percentages of  $H_2$  and  $CO_2$  and a lower percentage of CO in the product gas as a consequence of the water-gas shift reaction.

A comparison with the work of Singh *et al.* (1986) indicated that increasing the steam-to-feed ratio from 6 to 10 in the tar cracking dominated regime (below 940 K) had no significant effect. On the other hand, increasing the gas phase residence time from 2 to 5 s in this regime resulted in greater tar cracking. For higher temperatures (shift dominated regime), the increase in the gas phase residence time had no significant effect on the gas yield suggesting that the degree of completion of the shift reaction is not influenced by small differences in the gas phase residence time. The higher carbon conversion obtained by Singh *et al.* (1986) at the higher temperatures was attributed to the greater ash content in their wood samples.



## REFERENCES CITED

- Antal, M. J., "Synthesis Gas Production from Organic Wastes by Pyrolysis/Steam Reforming," pp. 495-523 in: Symposium Papers: Energy from Biomass and Wastes, IGT, Chicago (1978).
- Antal, M. J., Edwards, W. E., Friedman, H. L., and Rogers, F. E., "A Study of the Steam Gasification of Organic Wastes," Project Report to EPA, Princeton University Grant No. R804836010, W. W. Liberick, Project Officer, Industrial Environmental Research Laboratory, Cincinnati, Ohio (1978).
- Antal, M. J., "Effects of Reactor Severity on the Gas Phase Pyrolysis of Cellulose and Kraft Lignin Derived Volatile Matter," *Ind. Eng. Chem. Prod. Res. Dev.*, 22, 366-375 (1983).
- Antal, M. J., "A Review of the Vapor Phase Pyrolysis of Biomass Derived Volatile Matter," pp. 511-537 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Beck, S. R., and Wang, M. J., "Wood Gasification in a Fluidized Bed," *Ind. Eng. Chem. Process Des. Dev.*, 19, 312-317 (1980).
- DeGroot, W. F., and Shafizadeh, F., "Kinetics of Wood Gasification by Carbon Dioxide and Steam," pp. 275-292 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).

- Desrosiers, R. "Thermodynamics of Gas-Char Reactions," pp. 132-174 in:  
A Survey of Biomass Gasification Volume II - Principles of  
Gasification, T. Reed, ed., SERI/TR-33-239 (1979).
- Feldman, H. F., Choi, P. S., Paisley, M. A., Chauhan, S. P.,  
Robb, C. J., Folsom, D. W. and Kim, B. C., "Steam Gasification  
of Wood in a Multi-solid Fluidized-bed (MSFB) Gasifier," pp. 529-  
547 in: Symposium Papers: Energy from Biomass and Wastes V, IGT,  
Chicago (1981).
- Jönsson, O., "Thermal Cracking of Tars and Hydrocarbons by Addition of  
Steam and Oxygen in the Cracking Zone," pp. 733-746 in:  
Fundamentals of Thermochemical Biomass Conversion, R. P. Overend,  
T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science  
Publishers, London (1985).
- Koufopoulos, C., Maschio, G., Paci, M., and Lucchesi, A., "Some Kinetic  
Aspects on the Pyrolysis of Biomass and Biomass Components,"  
pp. 837-841 in: Energy from Biomass, 3rd ed., W. Pulz, J. Coombs  
and D. C. Halls, eds., Elsevier Applied Science Publishers, London  
(1985).
- Kuester, J. L., "Conversion of Cellulosic Wastes to Liquid Hydrocarbon  
Fuels," Interim Report to Waste Products Utilization Branch,  
Industrial programs Division, DOE Contract No. DE-AC02-76CS40202,  
Tempe, AZ (1984).

- Liinanki, L., Lindman, N., Siöberg, S. O., and Ström, E., "Methane Yield from Biomass Gasification at High Temperature and Pressure," pp. 923-936 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Milne, T., "The Thermal Behavior of Biomass Below 600 °C," pp. 177-218 in: A Survey of Biomass Gasification Volume II - Principles of Gasification, T. Reed, ed., SERI/TR-33-239 (1979).
- Mudge, L. K., Baker, E.G., Mitchell, D. H., and Brown, M. D., "Catalytic Steam Gasification of Biomass for Methanol and Methane Production," Journal of Solar Energy Engineering, 107, 88-92 (1985).
- Neogi, D., "Coal Gasification in an Experimental Fluidized Bed Reactor," M.S. Thesis, Kansas State University (1984).
- Pedhazur, E. J., Multiple Regression in Behavioral Research: Explanation and Prediction, Ch. 12, 2nd ed., Hott, Rinehart and Winston, New York (1982).
- Prasad, Burugupalli V. R. K. and Kuester, J. L., "Process Analysis of a Dual Fluidized Bed Biomass Gasification System," Ind. Eng. Chem. Res., 27, 304-310 (1988).
- Singh, S. K., Walawender, W. P., Fan, L. T., and Geyer, W. A., "Steam Gasification of Cottonwood (Branches) in a Fluidized Bed," Wood and Fiber Sci., 18, 327-344 (1986).

- van den Aarsen, F. G., Beenackers, A. A. C. M., and van Swaaij, W. P. M., "Wood Pyrolysis and Carbon Dioxide Char Gasification Kinetics in a Fluidized Bed," pp. 691-715 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Walawender, W. P., Raman, K. P., and Fan, L. T., "Gasification of Carbonaceous Materials in Fluidized Bed Reactor," p. 575 in: Proceedings of Bio-Energy '80 World Congress and Exposition, The Bio-Energy Council, Washington, D. C. (1980).
- Walawender, W. P., Dybing, K. D., Billquist, K., and Fan, L. T., "Fluid-bed Gasification of Cottonwood," Presented at the Seventh Annual FRPS Industrial Wood Energy Forum '83, Sept. 19-21, Nashville, TN (1983).
- Walawender, W. P., Hoveland, D. A., and Fan, L. T., "Steam Gasification of Pure Cellulose. 1. Uniform Temperature Profile," Ind. Eng. Chem. Process Des. Dev., 24, 813-821 (1985a).
- Walawender, W. P., Eriksson, M. A., Neogi, D., Singh, S., Fan, L. T., and Geyer, W. A., "Effect of Steam-to-Feed Ratio on Biomass Gasification," Presented at AIChE Annual Meeting, Chicago, IL (1985b).

Table III-1. Analyses of Siberian elm and Cottonwood Feed.

Ultimate Analysis (% dry basis)<sup>1</sup>

	Siberian elm	Cottonwood
C	47.80	47.82
H	5.89	5.93
N	0.45	0.23
O <sup>2</sup>	42.16	42.17
Ash	3.70	3.85

Component Analysis (% dry basis)<sup>3</sup>

	Siberian elm	Cottonwood
Cellulose	49.97	45.91
Hemicellulose	11.81	13.79
Lignin	22.87	24.40
Extractives <sup>2</sup>	11.86	13.08
Ash	3.49	2.82

	Siberian elm	Cottonwood
Moisture Content (% wet basis) <sup>4</sup>	6.31	6.90
Heat of Combustion (DAF basis) <sup>5</sup>	18.43 MJ/kg	18.53 MJ/kg
Heat of Combustion (DAF basis) <sup>6</sup>	19.71 MJ/kg	19.82 MJ/kg
Heat of Combustion (DAF basis) <sup>7</sup>	19.96 MJ/kg	20.18 MJ/kg

<sup>1</sup> Average of 13 samples for Siberian elm, except ash which was the average of 14 samples. Average of 10 samples for cottonwood.

<sup>2</sup> By difference.

<sup>3</sup> Average of 3 samples each for Siberian elm and cottonwood.

<sup>4</sup> Average of 14 samples for Siberian elm and 10 samples for cottonwood.

<sup>5</sup> Dulong's formula.

<sup>6</sup> IGT's formula.

<sup>7</sup> Average of 5 samples from calorimetry.

Table III-2. Reactor Operating Parameters.

<u>Tree Species</u>	<u>Siberian elm</u>	<u>Cottonwood</u>
Temperature Range (K)	870 - 1080	860 - 1065
Steam-to-Feed Mass Ratio	5.66 - 6.64 (6.08 ave.)	5.80 - 6.15 (6.01 ave.)
Steam Rate (g/min)	9 - 14	9.5 - 14
Feed Rate (g/min)	1.6 - 2.1	1.5 - 2.4
N <sub>2</sub> Purge Rate (m <sup>3</sup> /min)	0.00218 - 0.00229	0.00218 - 0.00226
<u>Gas Residence Time (sec.)</u>	<u>4.7 - 5.8</u>	<u>5.0 - 5.6</u>



Table III-3, Regression Models for Siberian elm and Cottonwood,

Dependent Variable	Wood	Sample Size, N	R <sup>2</sup>	F-value	Pr>F	Regression Model y=A+BT+CT <sup>2</sup> +DT <sup>3</sup>			
						A	B	C	D
Mole % H <sub>2</sub>	Sib, elm	50	,9438	394,93	,0001	-270,10	0,5826	-0,0002645	---
	Cottonwood	22	,9232	114,26	,0001	-167,41	0,3608	-0,0001449	---
Mole % CO <sub>2</sub>	Sib, elm	50	,2156	4,21	,0103	2038,03	-6,2138	0,006377	-2,173x10 <sup>-6</sup>
	Cottonwood	22	,7445	17,48	,0001	2433,64	-7,5007	0,007756	-2,659x10 <sup>-6</sup>
Mole % CO	Sib, elm	50	,8976	134,46	,0001	-1990,44	6,5550	-0,007035	2,483x10 <sup>-6</sup>
	Cottonwood	22	,9444	101,85	,0001	-3572,27	11,4806	-0,012121	4,2236x10 <sup>-6</sup>
Mole % CH <sub>4</sub>	Sib, elm	50	,2836	19,00	,0001	12,299	-0,00474	---	---
	Cottonwood	22	,6632	39,39	,0001	19,089	-0,01186	---	---
Higher Heating Value (MJ/m <sup>3</sup> )	Sib, elm	50	,7783	53,84	,0001	-493,25	1,5762	-0,001625	5,643x10 <sup>-7</sup>
	Cottonwood	22	,8558	35,61	,0001	-586,92	1,8895	-0,0019677	5,773x10 <sup>-7</sup>
Gas Yield (m <sup>3</sup> /kg DAF)	Sib, elm	50	,9380	355,80	,0001	-10,612	0,01969	-7,600x10 <sup>-6</sup>	---
	Cottonwood	22	,9472	170,30	,0001	-9,741	0,01797	-6,911x10 <sup>-6</sup>	---
Energy Recovery (%)	Sib, elm	50	,9115	242,13	,0001	-776,394	1,5082	-0,0006405	---
	Cottonwood	22	,9479	172,82	,0001	-793,324	1,5613	-0,0006871	---

Table III-3, (Continued)

Dependent Variable	Wood	Sample Size, N	R <sup>2</sup>	F-value	Pr>F	Regression Model y=A+BT+CT <sup>2</sup> +DT <sup>3</sup>			
						A	B	C	D
Mass Gas Yield (kg/kg DAF)	Sib, elm	50	,9136	248,46	,0001	-8,030	0,01552	-6,290x10 <sup>-6</sup>	---
	Cottonwood	22	,9401	149,06	,0001	-8,112	0,0157	-6,509x10 <sup>-6</sup>	---
Mass Tar Yield (kg/kg DAF)	Sib, elm	9	,7279	18,72	,0034	0,789	-0,000744	---	---
	Cottonwood	5	,4926	2,91	,1865	0,432	-0,000331	---	---
Mass Char Yield (kg/kg DAF)	Sib, elm	10	,4312	6,06	,0392	0,445	-0,000371	---	---
	Cottonwood	5	,9741	112,64	,0018	0,816	-0,000734	---	---
H <sub>2</sub> O Consumed (mol/mol C)	Sib, elm	43	,9433	216,11	,0001	50,900	-0,1681	0,00018197	-6,4334x10 <sup>-6</sup>
	Cottonwood	19	,9731	180,96	,0001	165,322	-0,52493	0,0005516	-1,9171x10 <sup>-7</sup>
Carbon Conv. to Gas (%)	Sib, elm	50	,8735	162,26	,0001	-608,31	1,219	-0,000526	---
	Cottonwood	22	,9296	125,50	,0001	-699,14	1,416	-0,000641	---
Carbon Conv. to Tar (%)	Sib, elm	9	,7235	18,32	,0037	120,67	-0,1137	---	---
	Cottonwood	5	,6357	5,24	,1061	76,47	-0,0624	---	---
Carbon Conv. to Char (%)	Sib, elm	9	,4100	4,86	,0632	63,2	-0,0494	---	---
	Cottonwood	5	,9750	116,79	,0017	131,1	-0,1179	---	---

Table III-4. Regression Analysis for the Comparison of Siberian elm and Cottonwood.

Dependent Variable	Sample Size, N	R <sup>2</sup>	F-value	Regression Model $y=A+A'w+BT+B'wT+CT^2+DT^3$					
				A	A'	B	B'	C	D
Mole % H <sub>2</sub>	72	,9297	299,97	-252,25	-0,7215	0,5442	---	-0,0002433	---
Mole % CO <sub>2</sub>	72	,4311	10,00	2066,52	10,226	-6,330	-0,01122	0,006516	-2,223x10 <sup>-6</sup>
Mole % CO	72	,9174	146,62	-2522,65	-12,685	8,2157	0,01462	-0,008747	3,064x10 <sup>-6</sup>
Mole % CH <sub>4</sub>	72	,4987	22,55	19,089	-6,790	-0,01186	0,007121	---	---
Higher Heating Value (MJ/m <sup>3</sup> )	72	,8142	57,83	-483,39	-3,248	1,5560	0,003203	-0,001611	5,507x10 <sup>-7</sup>
Gas Yield (m <sup>3</sup> /kg DAF)	72	,9430	374,95	-9,9107	0,1428	0,01807	---	-6,834x10 <sup>-6</sup>	---
Energy Recovery (%)	72	,9244	277,03	-735,67	9,862	1,4161	---	-0,000599	---

Table III-4. (Continued)

Dependent Variable	Sample Size, N	R <sup>2</sup>	F-value	Regression Model y=A+A'w+BT+B'wT+CT <sup>2</sup> +DT <sup>3</sup>					
				A	A'	B	B'	C	D
Mass Gas Yield (kg/kg DAF)	72	,9267	286,76	-7,7866	0,1206	0,01485	---	-5,988x10 <sup>-6</sup>	---
Mass Tar Yield (kg/kg DAF)	14	,6670	11,02	0,6817	-0,0434	-0,000588	---	---	---
Mass Char Yield (kg/kg DAF)	15	,5945	19,06	0,5720	---	-0,000495	---	---	---
H <sub>2</sub> O Consumed (mol/mol C)	62	,9466	252,64	75,416	0,0765	-0,2441	---	0,000260	-9,103x10 <sup>-9</sup>
Carbon Conv. to Gas (%)	72	,8987	200,99	-504,76	9,314	1,2010	---	-0,000521	---
Carbon Conv. to Tar (%)	14	,6915	12,33	107,53	-5,633	-0,09429	---	---	---
Carbon Conv. to Char (%)	14	,6037	18,28	87,01	---	-0,0734	---	---	---

Table III-5. Comparison of Gasification/Pyrolysis Results.

	Present work		873 K		Walawender <i>et al.</i>	
	Sib.	Cot.	Antal (1985)		(1983)	
mole % H <sub>2</sub>	36.6	36.8	9.2		20.1	
mole % CO <sub>2</sub>	27.8	27.6	28.7		21.0	
mole % CO	22.7	22.7	43.1		41.8	
mole % CH <sub>4</sub>	8.2	8.8	14.3		12.8	
C-Conv. (%)	54	48	15		45	
Steam/Feed	6.1	6.0	1.4		0.2-0.6	

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	Present work		973 K		Jönsson		van den Aarsen	
	Sib.	Cot.	Antal (1985)	Walawender <i>et al.</i> (1983)	(1985)	<i>et al.</i> (1985)	(1985)	<i>et al.</i> (1985)
mole % H <sub>2</sub>	46.2	46.2	11.1	30.8	5.4		16	
mole % CO <sub>2</sub>	27.5	28.8	16.7	16.7	5.2		14.5	
mole % CO	14.8	14.0	46.7	36.2	50.3		55	
mole % CH <sub>4</sub>	7.7	7.6	17.8	11.2	19.4		14.5	
C-Conv. (%)	79	71	42	68	---		---	
Steam/Feed	6.1	6.0	1.4	0.2-0.6	0		0	

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	Present work		1023 K		Mudge <i>et al.</i>	
	Sib.	Cot.	Jönsson (1985)	van den Aarsen <i>et al.</i> (1985)	(1985)	(1985)
mole % H <sub>2</sub>	49.0	50.0	14.6	20.5	36.4	42.7
mole % CO <sub>2</sub>	28.6	30.5	17.1	10.5	23.5	24.6
mole % CO	11.4	9.4	35.1	51	26.4	21.6
mole % CH <sub>4</sub>	7.5	7.0	21.2	13	13	8.7
C-Conv. (%)	89	78	---	---	76	87
Steam/Feed	6.1	6.0	0	0	1.1	1.0

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	Present work		1073 K	
	Sib.	Cot.	Jönsson (1985)	van den Aarsen <i>et al.</i> (1985)
mole % H <sub>2</sub>	50.5	52.7	23.1	26
mole % CO <sub>2</sub>	28.3	30.3	20.6	10.5
mole % CO	10.8	8.7	28.3	48
mole % CH <sub>4</sub>	7.2	6.4	19.7	12
C-Conv. (%)	94	82	---	---
Steam/Feed	6.1	6.0	0	0

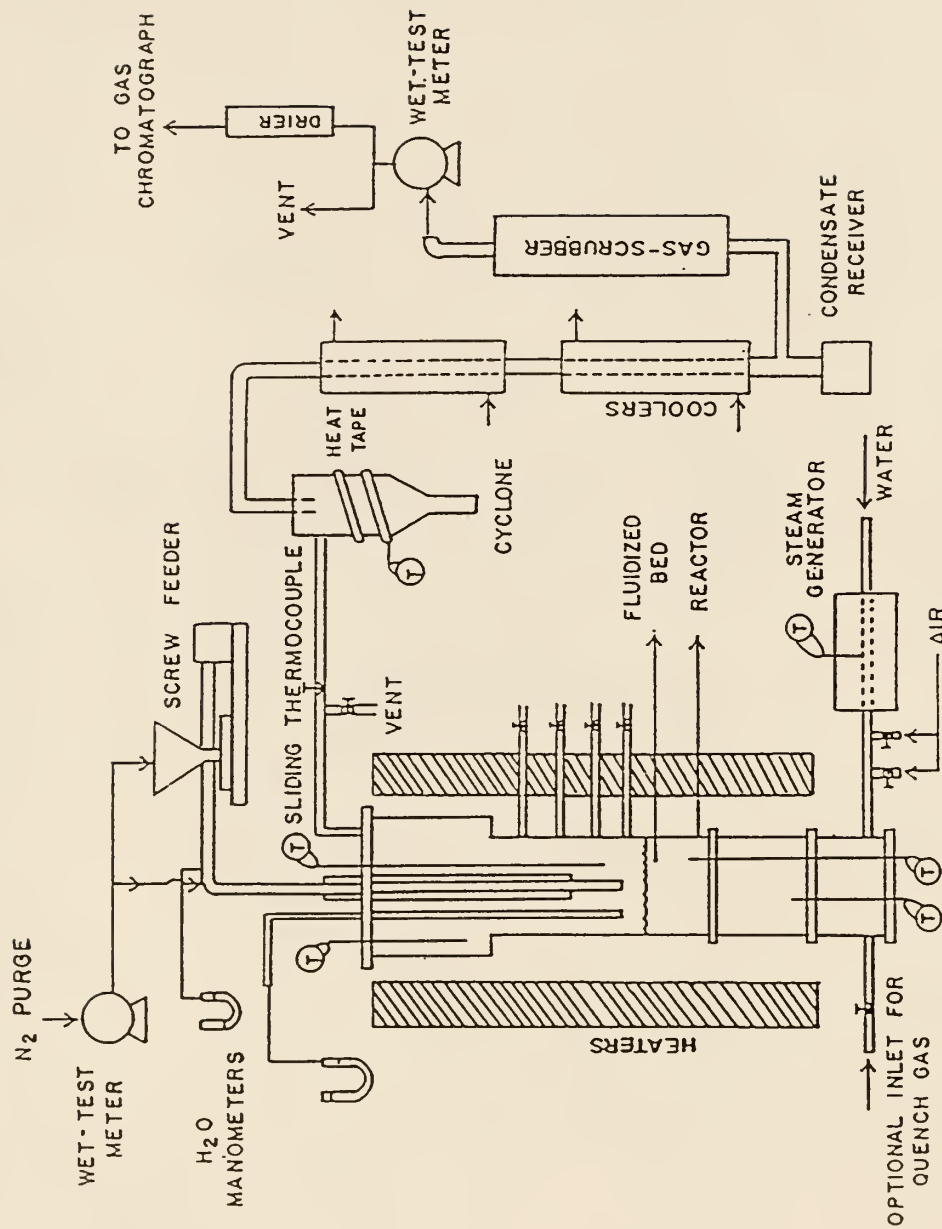


Figure III-1. Bench-Scale Fluidized-Bed Reactor System.



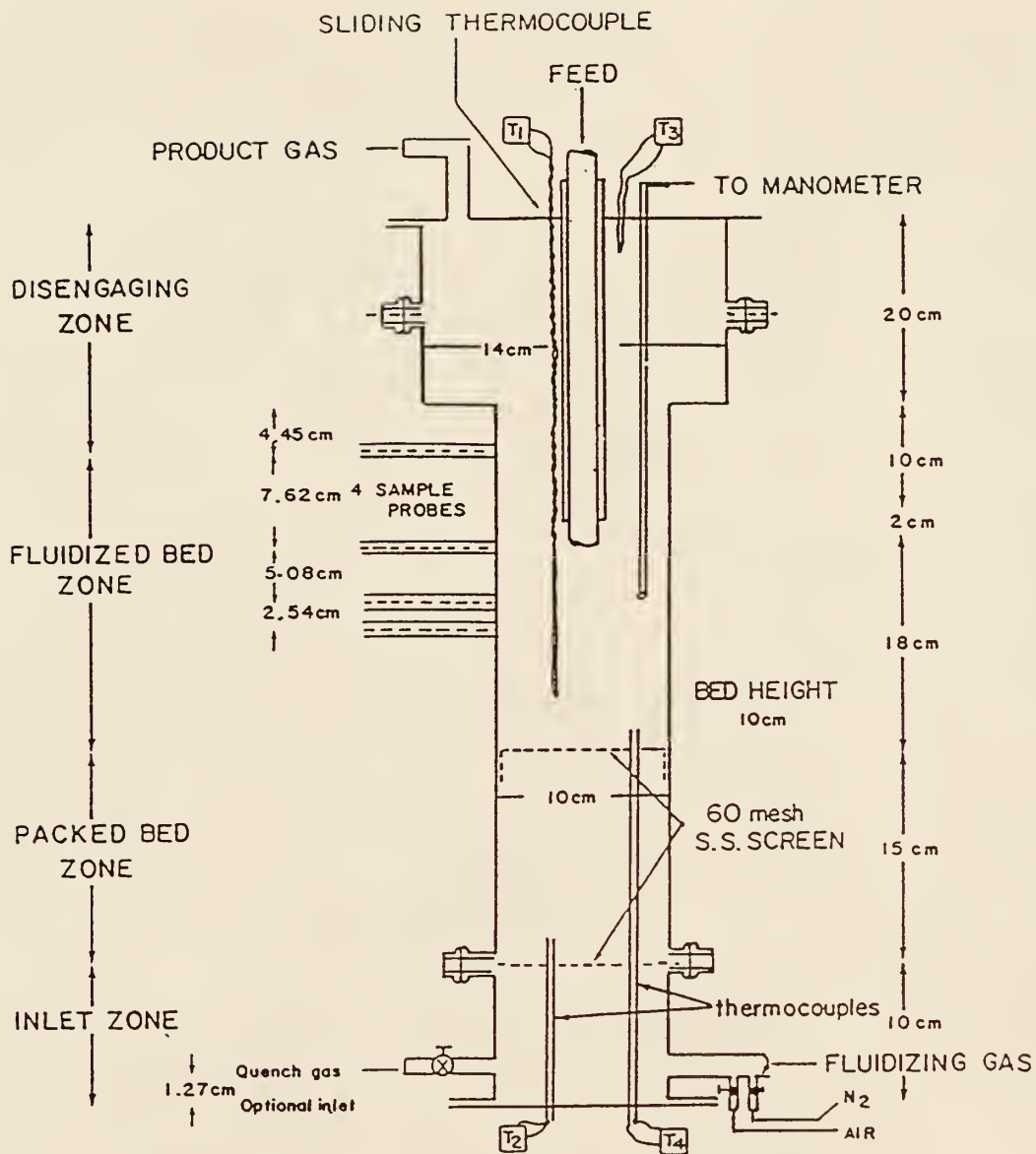


Figure III-2. Fluidized-Bed Reactor Details.

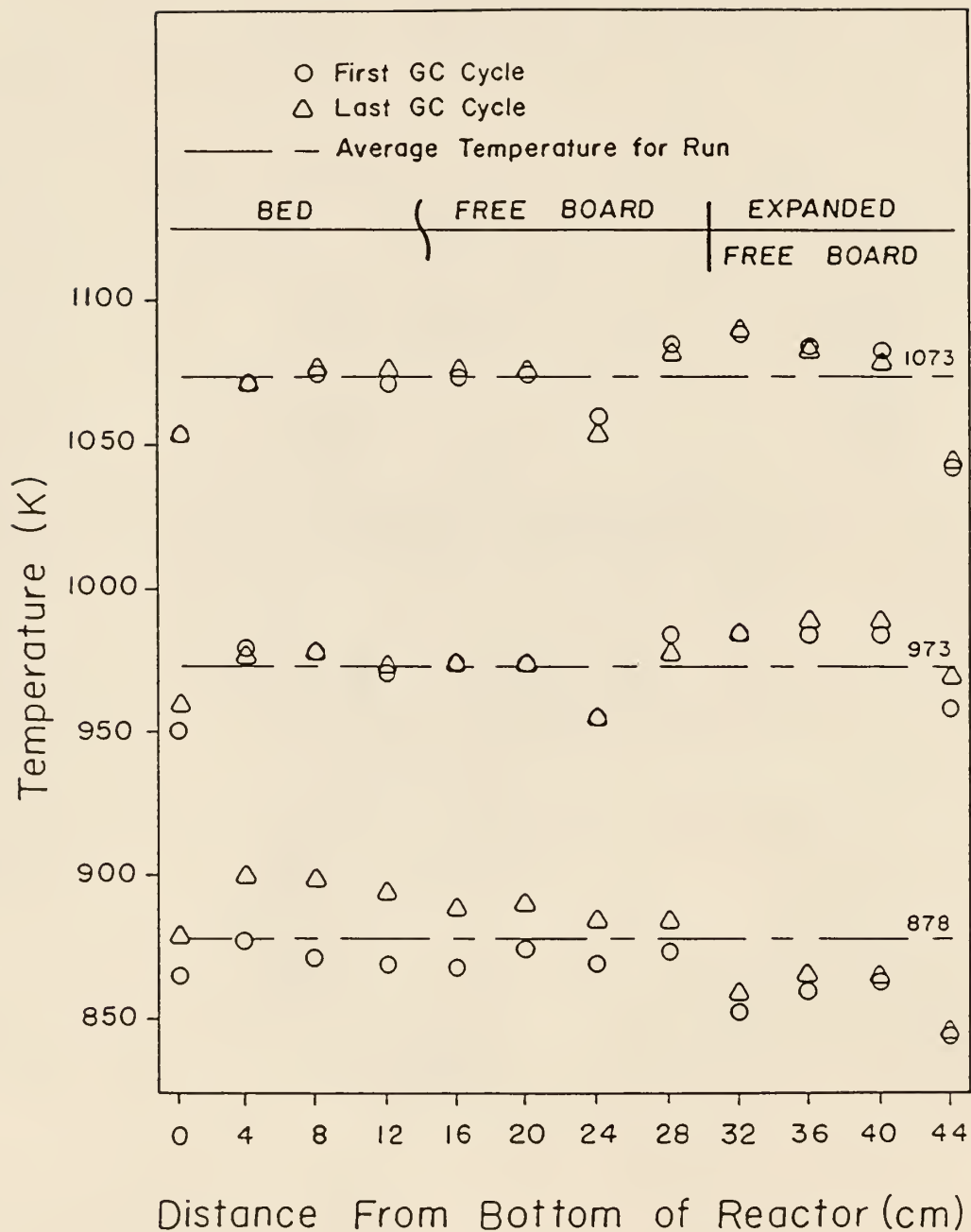


Figure III-3. Typical Reactor Temperature Profiles.

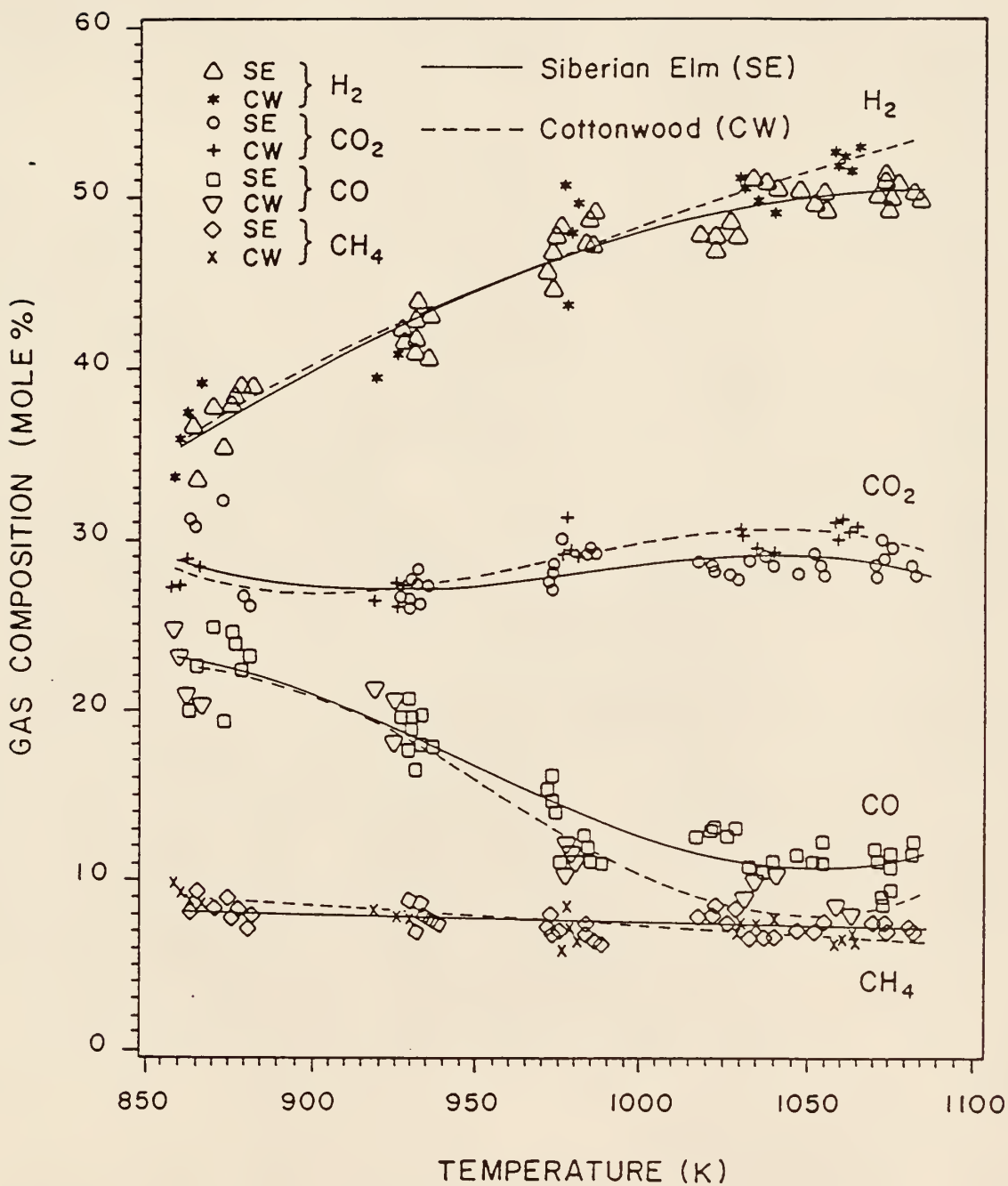


Figure III-4. Effect of Temperature on Gas Composition.

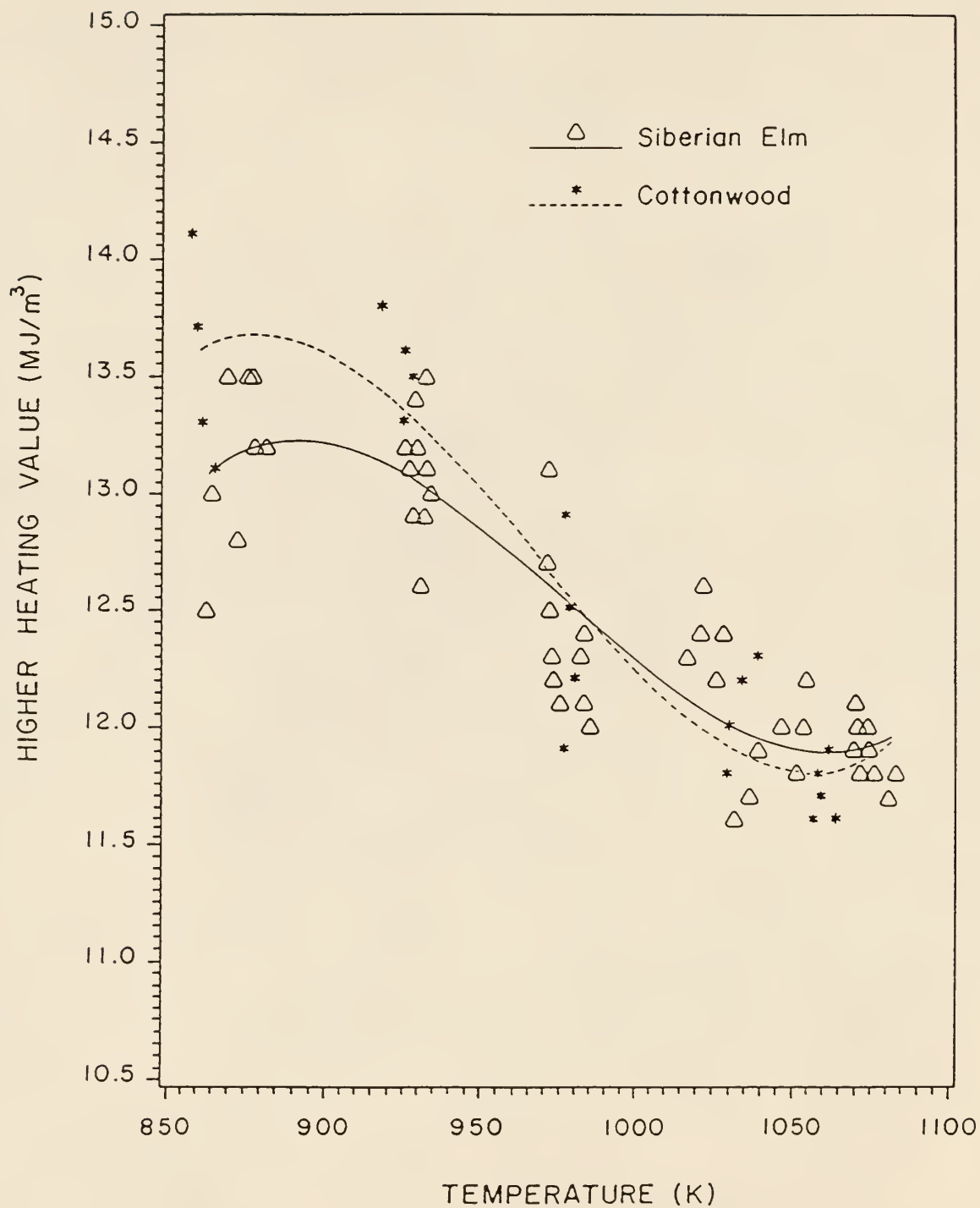


Figure III-5. Effect of Temperature on Gas Higher Heating Value.

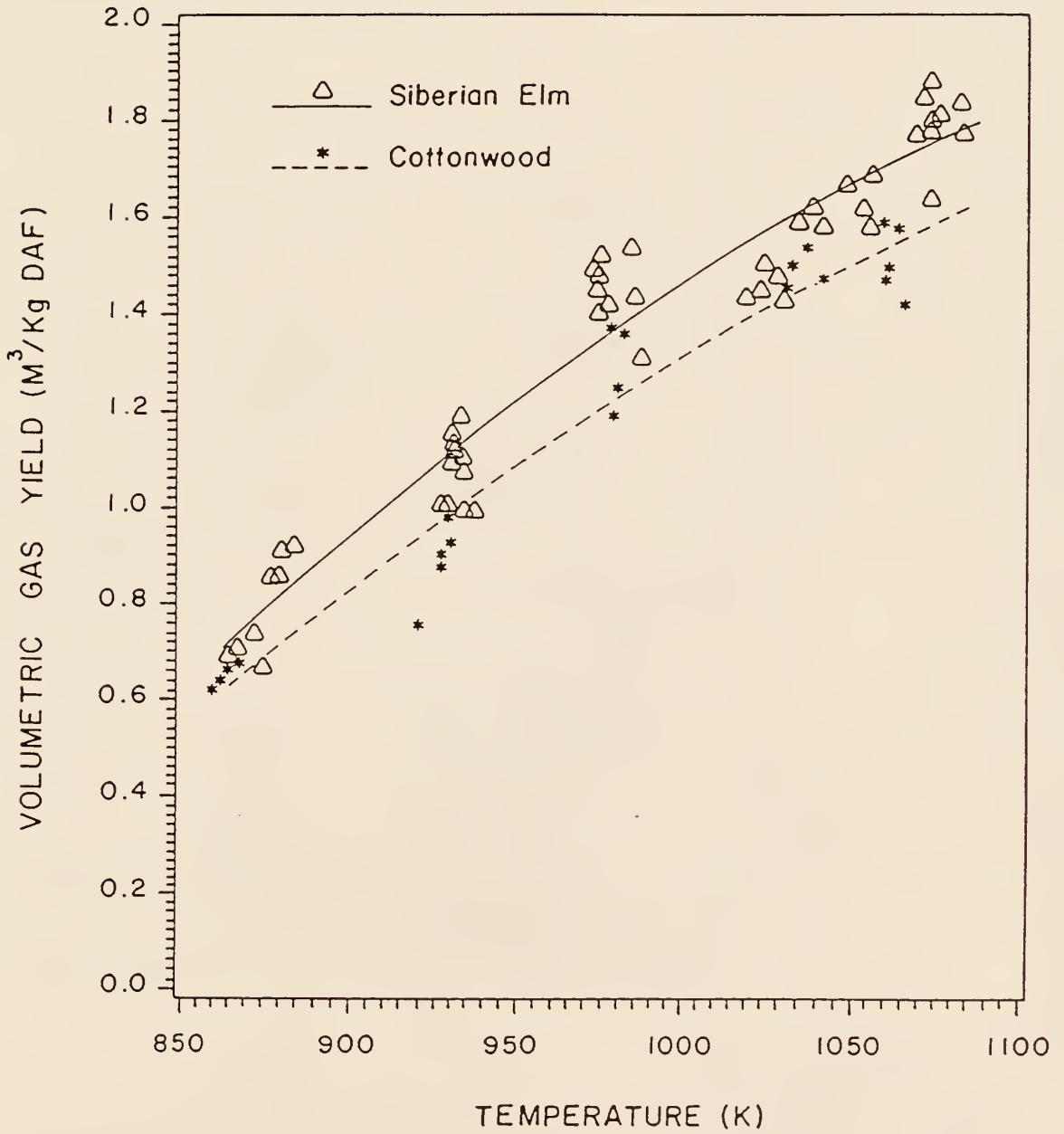


Figure III-6. Effect of Temperature on Volumetric Gas Yield.

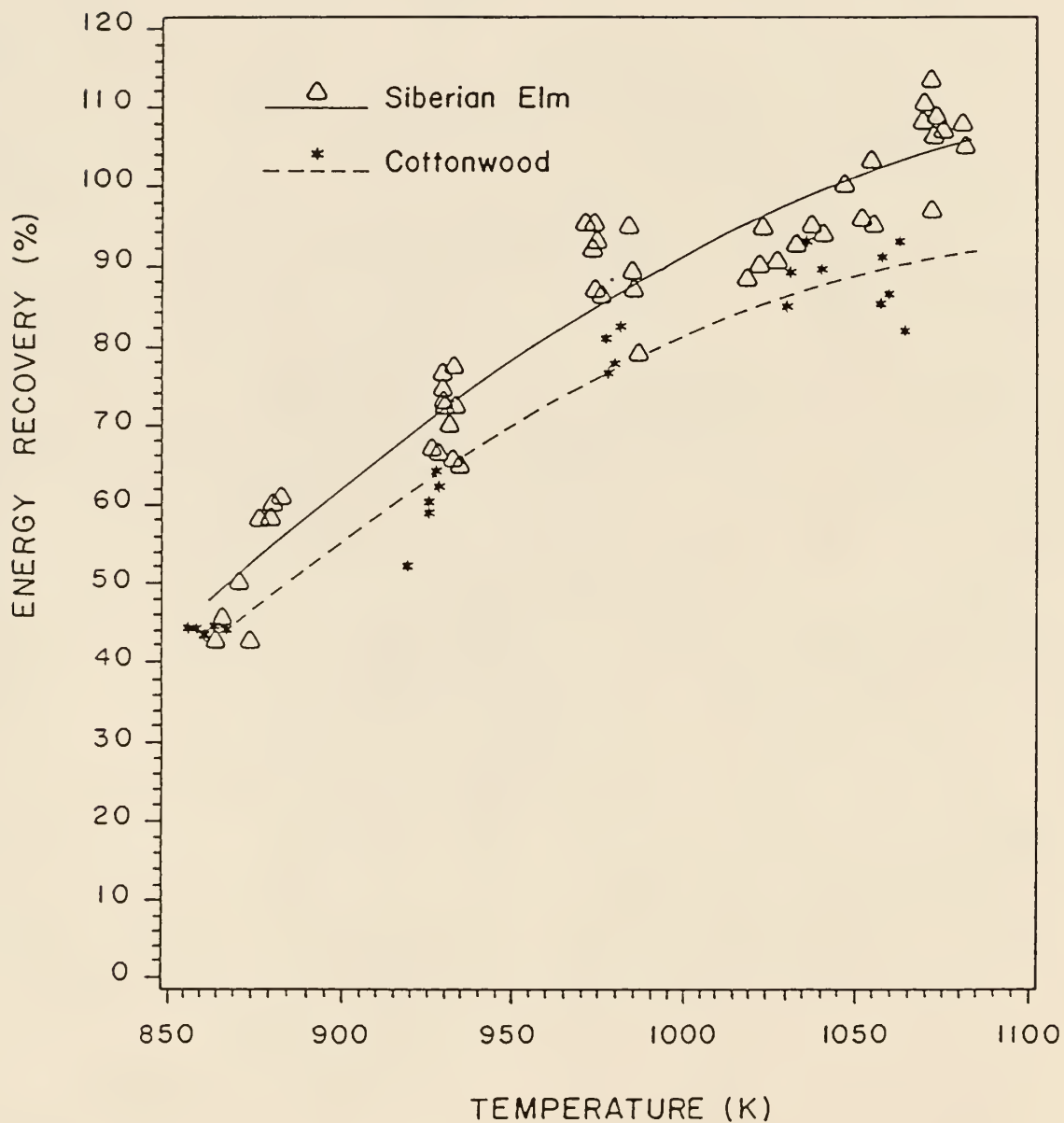


Figure III-7. Effect of Temperature on Energy Recovery.



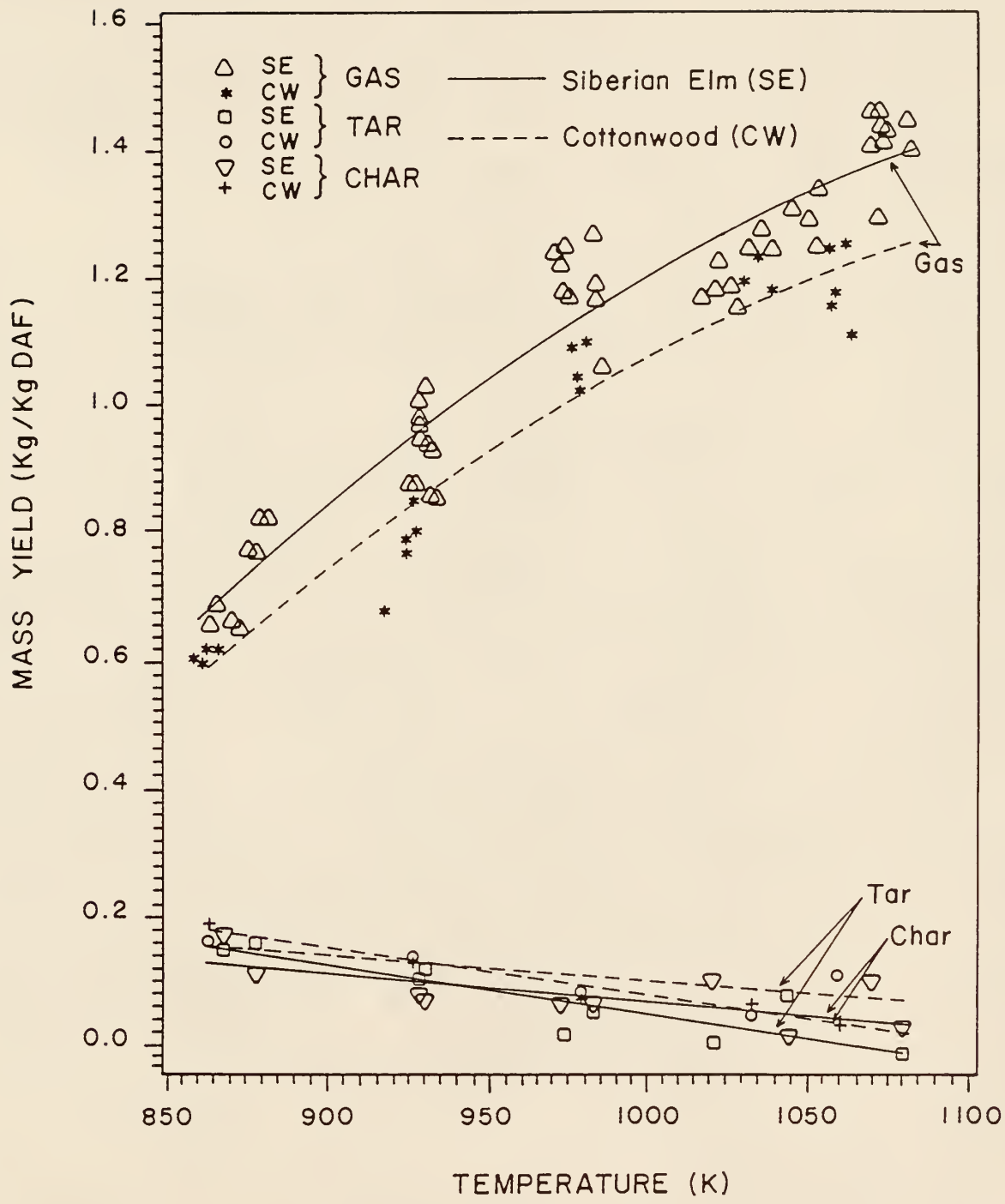


Figure III-8. Effect of Temperature on Mass Yields of Gas, Tar and Char.

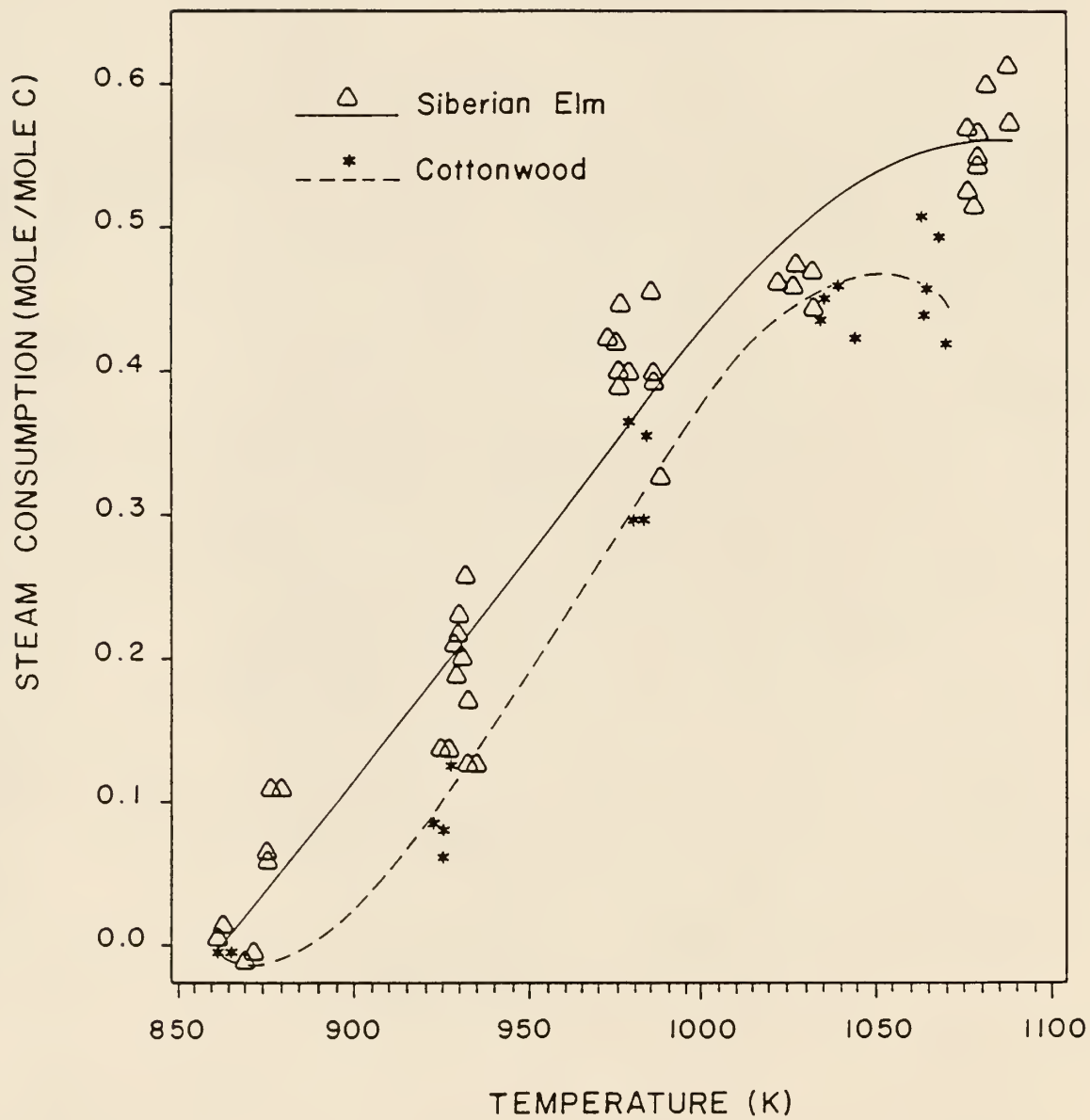


Figure III-9. Effect of Temperature on Steam Consumption.

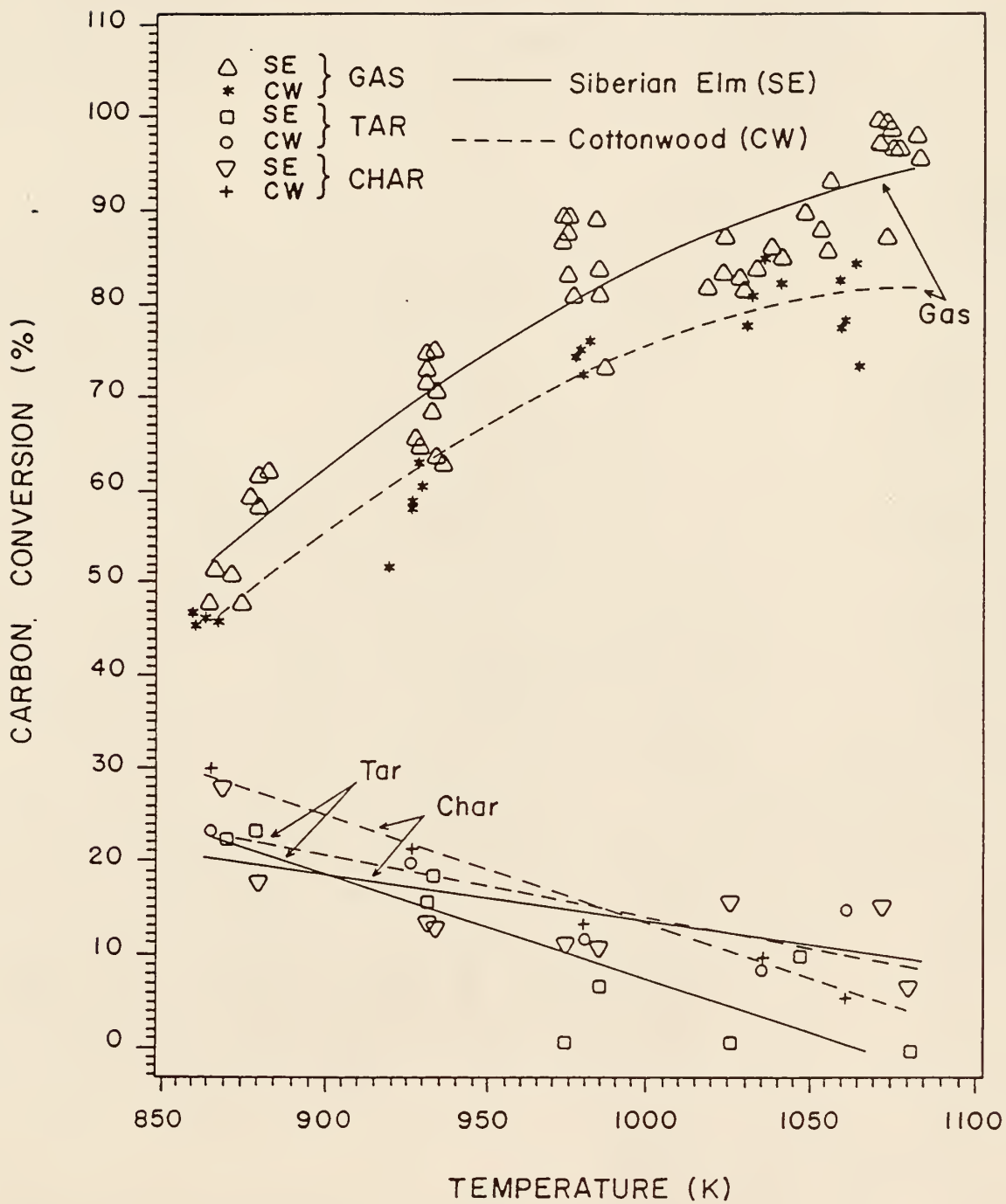


Figure III-10. Effect of Temperature on Carbon Conversion to Gas, Tar and Char.

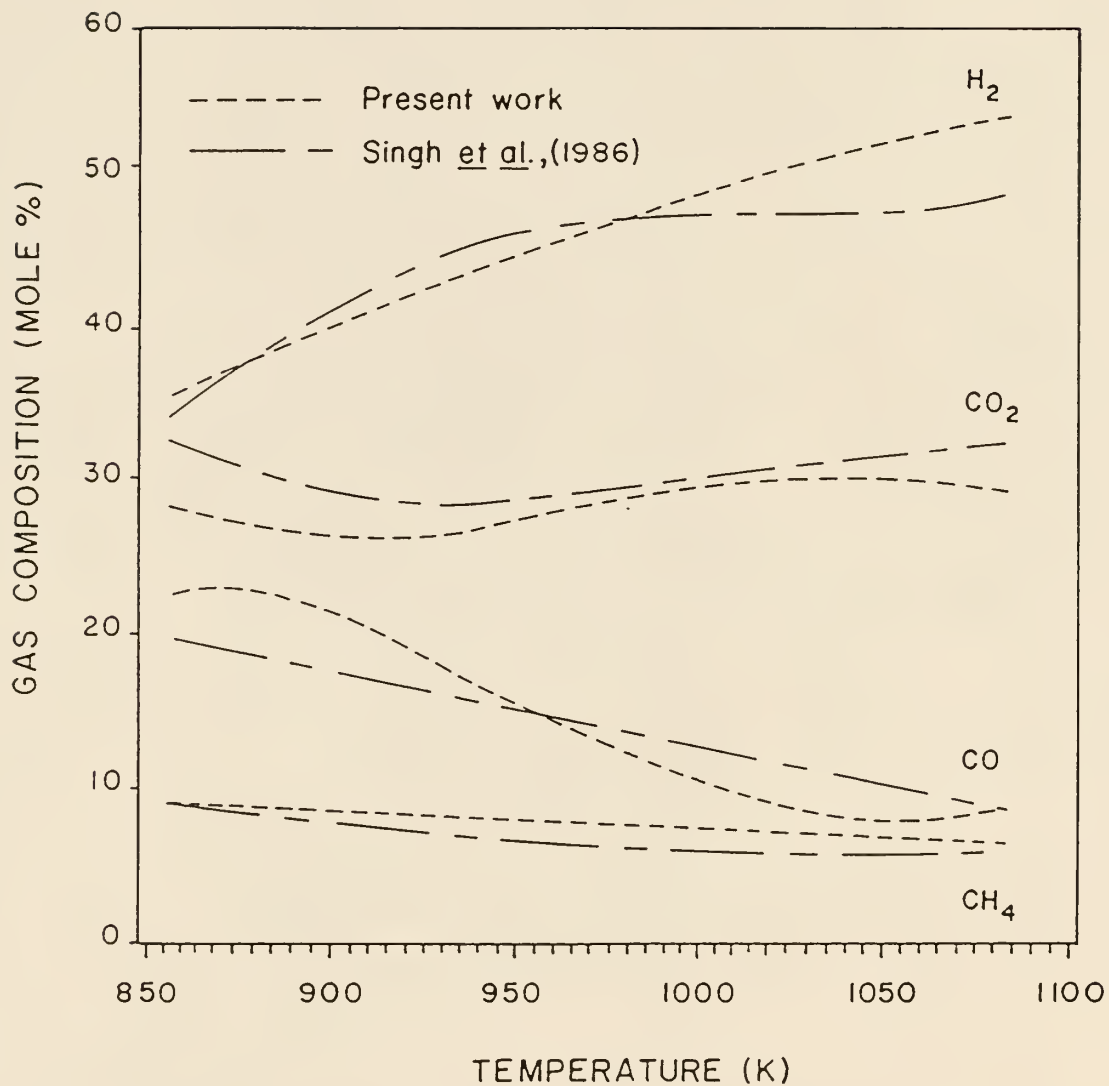


Figure III-11. Comparison of Gas Composition as a Function of Temperature with results from this work and Singh et al. (1986).

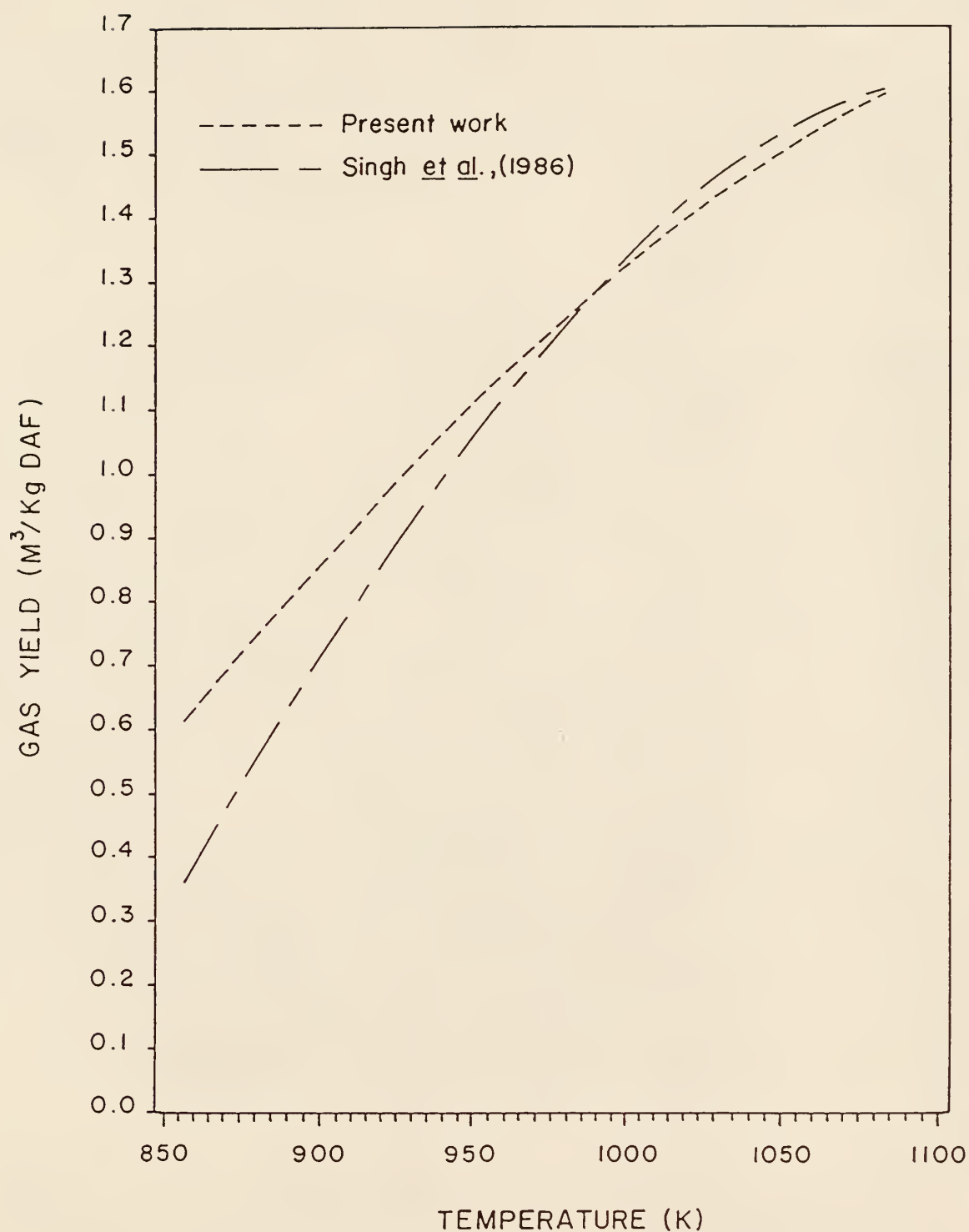


Figure III-12. Comparison of Volumetric Gas Yield as a Function of Temperature with results from this work and Singh et al. (1986).

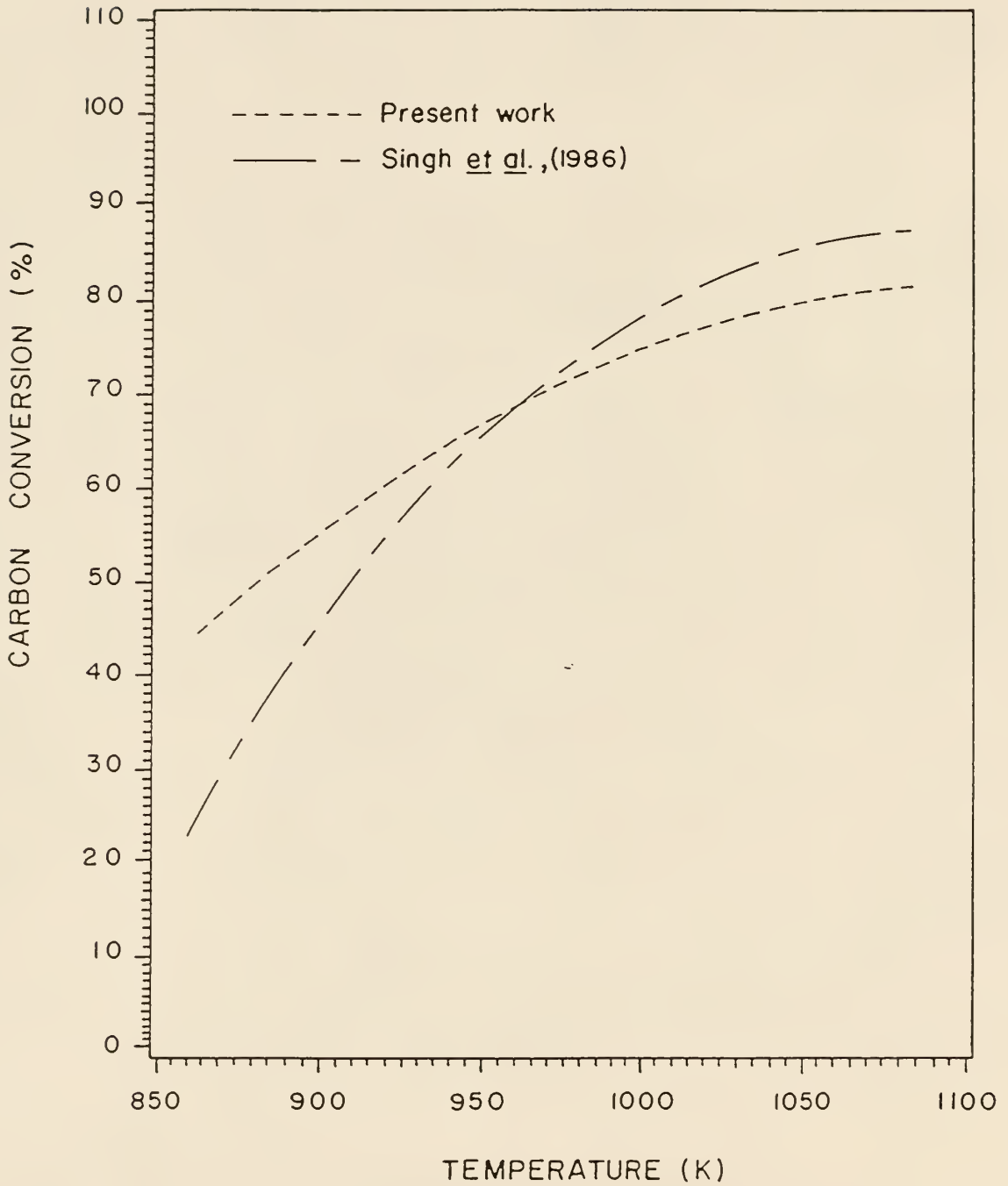


Figure III-13. Comparison of Carbon Conversion as a Function of Temperature with results from this work and Singh et al. (1986).



CHAPTER IV

STEAM GASIFICATION OF COTTONWOOD CLONES

## INTRODUCTION

Wood gasification has been proposed as a source of alternate fuels and chemicals. However, the technology is still in the developmental stage. Commercial implementation will require an understanding not only of the factors affecting the growth characteristics and biomass yields of various tree species but also the effects of chemical differences between wood sources on the product yields and distributions obtained from conversion processes.

Short-rotation intensive culture (SRIC) forestry is a viable method for producing significant amounts of woody biomass for energy/chemical conversion. Research activities in the SRIC forestry program have shown that selection and clonal propagation of species can bring out desirable traits for maximum growth in the first generation (Hummel, 1985; Ranney *et al.*, 1985; Reddy *et al.*, 1985; Rockwood, 1985). Geyer *et al.* (1985) conducted a study on thirty *Populus* clones and reported that coppice production and survival are dependent on clone source. However, little research has been conducted to investigate whether different clones will effect product yields and distributions from gasification processes.

In Chapter III, the effect of chemical differences between Siberian elm and cottonwood on the product characteristics from steam gasification in a fluidized-bed reactor were investigated. The results indicated that Siberian elm had a higher gas yield and carbon conversion than cottonwood as a consequence of its higher cellulose and lower lignin content.

In this work, the steam gasification of four cottonwood clones in a fluidized-bed reactor was investigated in a preliminary screening effort to determine whether or not differences in the gasification characteristics existed between clones.

#### EXPERIMENTAL

A bench-scale fluidized bed was used to conduct the steam gasification experiments on the cottonwood clones. Details of the reactor, the experimental procedure and the chemical analyses conducted on the dry product gas and feed are previously given in Chapter III.

##### Feed Materials

Four cottonwood clones (Populus deltoides Bartr.) were the wood sources for this investigation. The four clones were randomly selected from a set of ten clones available for the preliminary screening. The trees were chipped in their entirety with a Morbark chipper. Further reduction of particle size was accomplished by passing the chips through a Fritzmill with a 1.651 mm (0.065 in.) screen. The ultimate analysis, moisture content and heat of combustion for each of the clones are presented in Table IV-1.

##### Operating Conditions

The operating conditions for the experimental runs are summarized in Table IV-2. All of the operating parameters shown in Table IV-2 were initially planned to be held constant from run-to-run; however, some variations in the operating parameters were experienced. The reactor temperature ranged from 868 to 890 K. The steam rate varied from 13.1 to 14.2 g/min, and the feed rate varied from 2.14 to 2.50

g/min. Thus, the steam-to-feed ratio ranged from 5.6 to 6.6. The flow rate for the nitrogen purge (at 288 K and 101.3 kPa) varied from 0.00226 to 0.00232 m<sup>3</sup>/min, and the gas phase residence time varied from 4.8 to 5.1 s.

#### Statistical Design of Experiments

For each clone, two runs were performed. The order in which clone experiments were conducted was randomized. Randomization of the clone experiments was used to reduce any biases from extraneous factors which could change over time. Possible sources of extraneous factors included changes in the performance of the equipment and the learning experience of the operators.

#### METHOD OF DATA ANALYSIS

##### Gasification Characteristics

In general, data collected for each gas chromatograph cycle were averaged over the last 50 to 60 minutes of steady-state operation in each run. The gasification characteristics or response variables considered in this work were the dry gas composition (major components: H<sub>2</sub>, CO<sub>2</sub>, CO and CH<sub>4</sub>), the gas higher heating value (HHV), the dry gas volumetric and mass yield, the carbon conversion to gas and the energy recovery. Definitions and/or methodology used to determine the above characteristics are presented in Chapter III.

##### Statistical Analysis.

The general linear model procedure in the SAS (Statistical Analysis System; version 82.3) package was used to conduct the statistical comparison between the cottonwood clones. Temperature was

included as a covariate in the analysis, since it varied between 868 and 890 K in the experiments. The F-test was used to determine if significant differences existed between the clones and to determine if temperature had a significant effect on any of the response variables. The F-test was considered to yield a significant effect when the probability of falsely rejecting the parameter, denoted as  $Pr > F$ , was equal to or less than 0.05.

### RESULTS

Table IV-3 presents summaries of the analysis of variance for each of the response variables. Table IV-3 presents the mean for each clone, the overall mean, the mean square error (the estimate of the variance) and the degrees of freedom associated with the mean square error for each response variable. In addition, the degrees of freedom, the F-value and the significance probability ( $Pr > F$ ) for the clone effect and the temperature covariate are included in Table IV-3.

### DISCUSSION

In Chapter III, it was demonstrated that the principal operating factors that can influence the gasification characteristics are temperature, steam-to-feed ratio and gas phase residence time. In the present work, it was not possible to hold each of the above factors constant. For the temperature range involved (868-890 K), tar cracking dominates the secondary gas phase reactions. Since the gas phase residence time for the experiments was approximately 5 seconds, cracking was virtually complete (Antal, 1985). Consequently, the influences of the small variations in the gas phase residence time

(4.8-5.1 s) need not to be considered in the statistical analysis. Furthermore, for the temperatures involved, variations in the steam-to-feed ratio have little effect. In Chapter III, it was determined that significant differences in the steam-to-feed ratio have little influence on the gasification characteristics in the tar cracking regime ( $T < 940$  K). Although the range of temperature variation was small (22 K) for the series of experiments, it was decided to include temperature as a covariate in the statistical comparison of the clones, since some of the gasification characteristics are strong functions of temperature.

As indicated in Table IV-3, none of the response variables had a clone effect or a temperature covariate that was significant at the 0.05 level. The clone effect for the volumetric gas yield, the mass yield of gas, the carbon conversion and the energy recovery came closest to being significant. The temperature covariate was nearly significant for the gas higher heating value, the  $\text{CO}_2$  concentration and the  $\text{CH}_4$  concentration.

Comparison of the results of the present work with regression curves presented in Chapter III for the cottonwood branches revealed that the data points fell within or were very near the 95% confidence intervals. This implies that there was little difference between the cottonwood clones and the cottonwood branches studied in Chapter III.

## CONCLUSIONS

Steam gasification of cottonwood clones in a fluidized-bed reactor was conducted to determine whether or not statistical differences in various gasification characteristics existed between the clones. The analysis revealed that no significant differences existed between clones for the gasification characteristics considered in this investigation. The analysis also indicated that the temperature covariate (which attempted to account for temperature variations in the experiments) was not significant.



## REFERENCES CITED

- Antal, M. J., "A Review of the Vapor Phase Pyrolysis of Biomass Derived Volatile Matter," pp. 511-537 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Geyer, W. A., Naughton, G. G., and Melichar, M. W., "Biomass Gains in Coppicing Trees For Energy Crops," pp. 269-273 in: Energy from Biomass, 3rd ed., W. Pulz, J. Coombs and D. C. Hall, eds., Elsevier Applied Science Publishers, London (1985).
- Hummel, F. C., "The Use of Forests as a Source of Biomass Energy," pp. 90-98 in: Energy from Biomass, 3rd ed., W. Pulz, J. Coombs and D. C. Hall, eds., Elsevier Applied Science Publishers, London (1985).
- Ranney, J. W., Trimble, J. L., Wright, L. L., and Perlack, R. D., "Research on Short-Rotation Woody Crops in the South," pp. 71-83 in: Biomass Energy Development, W. H. Smith, ed., Plenum Press (1985).
- Reddy, K. V., Rockwood, D. L., Comer, C. W., and Meskimen, G. F., "Genetic Improvement of Eucalyptus Grandis Woody Biomass Production in Florida," pp. 103-118 in: Biomass Energy Development, W. H. Smith, ed., Plenum Press (1985).
- Rockwood, D. L., "Development of Woody Biomass Cultural Systems for Florida," pp. 85-94 in: Biomass Energy Development, W. H. Smith, ed., Plenum Press (1985).

Table IV-1. Analyses of Cottonwood Clones.

Clone	<u>Ultimate Analysis (% dry basis)<sup>1</sup></u>			
	S-2	S-21	S-22	S-26
C	46.45	48.11	47.90	48.62
H	5.88	5.89	5.95	5.93
N	0.71	0.56	0.38	0.61
O <sup>2</sup>	45.13	43.85	44.33	43.11
Ash	1.83	1.59	1.44	1.72
Moisture Content <sup>3</sup> (% wet basis)	5.30	5.14	5.45	5.47
Heat of Combustion <sup>4</sup> (MJ/kg DAF)	19.14	19.48	19.25	19.14

<sup>1</sup> Average of 6 samples for C, H, N and O. Average of 12 samples for ash.

<sup>2</sup> By difference.

<sup>3</sup> Average of 12 samples.

<sup>4</sup> Average of 4 samples from bomb calorimetry.

Table IV-2. Reactor Operating Parameters.

Clone	Run	N <sub>2</sub> purge (m <sup>3</sup> /min)	Steam rate (g/min)	Feed rate (g/min)	S/F <sup>1</sup>	$\tau$ <sup>2</sup> (sec)	Temperature (K)
S-2	1	0.00233	14.1	2.44	5.78	4.89	868
	2	0.00233	14.1	2.14	6.59	4.94	877
S-21	1	0.00226	13.1	2.27	5.77	5.12	880
	2	0.00226	14.1	2.27	6.21	4.85	885
S-22	1	0.00230	14.1	2.50	5.64	4.80	879
	2	0.00230	13.7	2.43	5.64	4.83	890
S-26	1	0.00226	14.2	2.40	5.92	4.81	877
	2	0.00230	13.9	2.25	6.18	4.90	886
Average		0.00229	13.9	2.34	5.97	4.89	880

<sup>1</sup> S/F = steam-to-feed mass ratio

<sup>2</sup>  $\tau$  = gas phase residence time

Table IV-3, Analysis of Variance for Cottonwood Clones.

IV-10

Dependent Variable	Clone	Mean	MSE <sup>1</sup>	df <sub>E</sub> <sup>2</sup>	Parameter	df	F-value	Pr>F	
Higher Heating Value (MJ/m <sup>3</sup> )	S-2	13.34	0,0480	3	Clone	3	0,84	0,5543	
	S-21	13,45				Temp	1	9,15	0,0565
	S-22	13,58							
	S-26	13,59							
	overall	13,49							
Mole % H <sub>2</sub>	S-2	34,49	2,252	3	Clone	3	0,63	0,6421	
	S-21	35,81				Temp	1	0,76	0,4463
	S-22	35,06							
	S-26	35,86							
	overall	35,31							
Mole % CO <sub>2</sub>	S-2	26,49	0,4771	3	Clone	3	2,27	0,2590	
	S-21	26,93				Temp	1	8,08	0,0655
	S-22	26,26							
	S-26	25,72							
	overall	26,35							
Mole % CO	S-2	27,00	2,020	3	Clone	3	1,49	0,3756	
	S-21	24,50				Temp	1	1,37	0,3256
	S-22	25,83							
	S-26	25,70							
	overall	25,76							
Mole % CH <sub>4</sub>	S-2	7,579	0,4494	3	Clone	3	0,19	0,8948	
	S-21	8,378				Temp	1	5,02	0,1109
	S-22	8,328							
	S-26	8,277							
	overall	8,140							
Gas Yield (m <sup>3</sup> /kg DAF)	S-2	0,496	1,513x10 <sup>-3</sup>	3	Clone	3	3,31	0,1758	
	S-21	0,590				Temp	1	0,61	0,4307
	S-22	0,634							
	S-26	0,599							
	overall	0,580							
Mass Yield (kg/kg DAF)	S-2	0,474	1,016x10 <sup>-3</sup>	3	Clone	3	4,12	0,1376	
	S-21	0,553				Temp	1	1,05	0,3803
	S-22	0,597							
	S-26	0,556							
	overall	0,545							
Carbon Conv. (%)	S-2	37,84	4,673	3	Clone	3	3,99	0,1427	
	S-21	42,56				Temp	1	0,45	0,5501
	S-22	46,75							
	S-26	42,81							
	overall	42,49							
Energy Recovery (%)	S-2	34,51	4,838	3	Clone	3	4,15	0,1366	
	S-21	40,61				Temp	1	0,00	0,9685
	S-22	44,70							
	S-26	42,46							
	overall	40,57							

<sup>1</sup> MSE = mean square error<sup>2</sup> df<sub>E</sub> = degrees of freedom for mean square error

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

## CONCLUSIONS

Experimental studies on the steam gasification of different tree species and clones of the same species are presented in Chapters III and IV, respectively. The studies were conducted to investigate the effect of differences in the chemical composition of wood on the product yields and distributions. In addition, an assessment of two operating parameters, the steam-to-feed mass ratio and the gas phase residence time, has been made to clarify their influences on the steam gasification process.

In Chapter III, steam gasification experiments with Siberian elm and cottonwood were conducted in a fluidized bed over a temperature range of 870 to 1070 K with a steam-to-feed ratio of 6. Statistical comparisons between Siberian elm and cottonwood revealed that Siberian elm had a higher gas yield and a higher carbon conversion than cottonwood. The higher cellulose content and the lower lignin content in Siberian elm (as compared to cottonwood) qualitatively explained these differences. In addition, cottonwood had a greater tar yield than Siberian elm at the higher temperatures primarily due to its higher lignin content.

A comparison with related steam gasification studies revealed that high steam-to-feed ratio gasification (relative to pyrolysis or low steam-to-feed gasification) resulted in higher percentages of  $H_2$  and  $CO_2$  and a lower percentage of  $CO$  in the product gas as a consequence of the water-gas shift reaction. Comparison with the work of Singh *et al.* (1986) indicated that increasing the steam-to-feed ratio from 6 to 10

in the tar cracking dominated temperature regime (below 940 K) had no significant effect. On the other hand, increasing the gas phase residence time from 2 to 5 s in this temperature regime resulted in greater tar cracking. For higher temperatures (above 940 K), the same increase in the gas phase residence time had no significant effect on the gas yield or its composition suggesting that the degree of completion of the steam gasification process is not influenced by small differences in the gas phase residence time. The higher carbon conversion obtained by Singh *et al.* (1986) at the higher temperatures was attributed to the greater ash content in their wood samples.

In Chapter IV, steam gasification of cottonwood clones was conducted in a fluidized bed to determine whether or not statistical differences in various gasification characteristics existed between the clones. The statistical analysis revealed that no significant differences existed between clones for the gasification characteristics considered in this investigation.

#### RECOMMENDATIONS

The comparisons made in Chapter III have indicated that differences in the major wood constituents between tree species have an effect on the volumetric and mass gas yields, the carbon conversion and the energy recovery. However, as pointed out in Chapter III, the product distributions obtained from the steam gasification of wood cannot be quantitatively predicted by the linear combination of the distributions from its major constituents; cellulose, hemicellulose and lignin. Hence, further experimentation with other tree species is



needed to improve our understanding of the influence of wood's major constituents on its gasification behavior.

In Chapter III, the results indicated that the quantity of ash in the cottonwood had an effect on the mass yield of gas and the carbon conversion. DeGroot and Shafizadeh (1985) have shown that both the composition and quantity of the ash determines its catalytic effectiveness. Therefore, further experimentation with various tree species should include an analysis of the ash composition along with other present analyses.

The determination of mass yields and carbon conversions for tar and char by using ash, carbon and oxygen balances gave reasonable results. However, it was often difficult to obtain sufficiently large tar samples at the higher temperatures. At 1070 K, the wood feed rate was normally set at approximately 1.5 g/min. With a total run time of 2 hrs and a 5% tar mass yield, the total tar produced was about 9 g. Much of this tar was held up in the piping and condensers. Thus, it is recommended to increase the wood feed rate and/or the run time.

Increasing the feed rate with the present system will increase the gas rate. Thus, it may be necessary to procure a flow meter with a higher capacity than the present wet-test meter. In addition, the increase in the gas rate will decrease the gas phase residence time. However, as the results in Chapter III have shown, small decreases in the gas phase residence time will only have significant effects at temperatures below 940 K. Operating a large-scale steam gasification system at such low temperatures would not be attractive economically,

since the gas yields are low and the contribution from the steam is minimal.

The bed material used in the two experimental studies was composed of a limestone and sand mixture. Other researchers have shown that limestone as well as other alkali carbonates have a catalytic effect on the steam gasification process (Hallen *et al.*, 1985; Baker *et al.*, 1985; DeGroot and Shafizadeh, 1985). However, the catalytic effect of the bed material for this system has not been clearly established (Walawender *et al.*, 1981). Thus, in future experiments, the percentage of limestone should be varied to determine its significance.

Consideration should be given to increasing the consumption of steam per unit mass of feed in order to reduce the steam-to-feed ratio. Reduction in the steam-to-feed ratio will have obvious economic benefits. One method that may be explored is to follow the present fluidized bed and cyclone with a catalytic packed bed reactor. With the current system, the wood rapidly devolatilizes as it comes in contact with the hot bed. Hence, this arrangement does not allow for long contact times between gas species and the limestone particles to promote the water-gas shift reaction. A downstream packed bed reactor would increase the gas-solid contact time and various alkali carbonates could be explored as potential catalysts. Hallen *et al.* (1985) have shown that the shift reaction is catalyzed in the presence of sodium carbonate, and Baker *et al.* (1985) have indicated that alkali carbonates are not inclined to deactivate from carbon deposition as with metal catalysts.

## REFERENCES CITED

- Baker, E. G., Mudge, L. K., and Wilcox, W. A., "Catalysis of Gas-Phase Reactions in Steam Gasification of Biomass," pp. 863-874 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- DeGroot, W. F., and Shafizadeh, F., "Kinetics of Wood Gasification by Carbon Dioxide and Steam," pp. 275-292 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Hallen, R. T., Sealock, L. J., and Cuello, R., "Influence of Alkali Carbonates on Biomass Volatilization," pp. 157-166 in: Fundamentals of Thermochemical Biomass Conversion, R. P. Overend, T. A. Milne and L. K. Mudge, eds., Elsevier Applied Science Publishers, London (1985).
- Singh, S. K., Walawender, W. P., Fan, L. T., and Geyer, W. A., "Steam Gasification of Cottonwood (Branches) in a Fluidized Bed," Wood and Fiber Sci., 18 327-344 (1986).
- Walawender, W. P., Ganesan, S., and Fan, L. T., "Steam Gasification of Manure in a Fluid Bed - Influence of Limestone as a Bed Additive," pp. 517-527 in: Symposium Papers: Energy from Biomass and Wastes, IGT, Chicago (1981).

STEAM GASIFICATION OF WOOD IN A FLUIDIZED BED

by

JON DAVID DEWYKE

B.S., Kansas State University, 1984

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

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Experimental studies on the steam gasification of wood from different tree species and clones of the same species were conducted to investigate the effect of differences in the wood chemical composition on the product yields and distributions. Comparisons were also made to related work to assess the influence of two operating parameters, the steam-to-feed mass ratio and the gas phase residence time, on the gasification characteristics.

Steam gasification experiments were conducted with Siberian elm and cottonwood in a fluidized bed over a temperature range of 870 to 1070 K with a steam-to-feed ratio of 6. Statistical comparisons between Siberian elm and cottonwood indicated that Siberian elm produced a higher gas yield and a higher carbon conversion than cottonwood. The higher cellulose content and the lower lignin content in the Siberian elm (as compared to cottonwood) qualitatively explained the differences. In addition, cottonwood yielded more tar than Siberian elm at the higher temperatures primarily due to its higher lignin content.

Comparisons with related studies revealed that high steam-to-feed ratio gasification (relative to pyrolysis or low steam-to-feed gasification) resulted in higher percentages of  $H_2$  and  $CO_2$  and a lower percentage of CO in the product gas as a consequence of the water-gas shift reaction. Increasing the steam-to-feed ratio from 6 to 10 in the tar cracking dominated temperature regime (below 940 K) had no significant effect. On the other hand, increasing the gas phase residence time from 2 to 5 s in this temperature regime resulted in an

increase in tar cracking. For the water-gas shift dominated regime, (above 940 K) the same increase in the gas phase residence time had no significant effect on the gas yield or its composition suggesting that the degree of completion of the steam gasification process is not influenced by small differences in the gas phase residence time.

Steam gasification of several cottonwood clones was conducted in a fluidized bed to evaluate their gasification behavior. An analysis of variance revealed that no significant differences existed between the clones for the gasification characteristics considered in this investigation.





