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MEASUREMENT OF THE MASS AND ENERGY BALANCE  
IN CONTACT FAST PYROLYSIS OF WOOD

by

Craig Cowdery

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Chemical and Petroleum-Refining Engineering)

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ABSTRACT

Contact fast pyrolysis is a method of converting biomass to a liquid fuel product by bringing it into contact, under mechanical pressure, with a heat source. This work involves the measurement of the mass and energy balance around two contact wood pyrolyzers; a pyrolysis mill and a heat flux concentrator.

High yields of oils (35-80% with some water) were produced with the heat flux concentrator. It was found that high heat flux and low interface pressures favor the production of liquid products and retard the production of char and pyrolysis gases. The formation of "coke" from pyrolytic oils was found to increase under higher pressures because it inhibited vaporization.

The heat for pyrolysis was measured as a function of temperature on the heat flux concentrator and the heat for pyrolysis ranged between 644 and 1840 J/g between 473 and 598 degrees Celsius. From this the heat of pyrolysis was derived using sensible heat data and ranged from -440 to 190 J/g over the same temperature range.

Preliminary measurements were made on the pyrolysis mill. The heat for pyrolysis was measured and a value of

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2871 J/g was obtained. The liquid yields averaged about 30%, but low char yields suggest that this apparatus could be optimized to produce high yields.

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## 1. INTRODUCTION

### 1.1 Biomass Pyrolysis

Increasingly, as mankind witnesses the depletion of non-renewable resources, the utilization of renewable resources once again emerges as a viable alternative to fossil fuels. Although biomass can't currently supply all of U.S. energy demands, Inman (1979) derives the figure of 14.4 Quads per year for potential biomass energy sources. Reed (1986) estimated that at two to five dollars per MMBTU, the potential value of 15 quads of biomass energy is 30 to 75 billion dollars in energy costs. It has been estimated that between 6 and 17 Quads per year could foreseeably be produced by the year 2000 as opposed to 1.5 Quads per year generated in 1980 (Slesser and Lewis, 1979). Six Quads alone represent about 2.7 million barrels of oil (Probstein and Hicks 1982).

There are many other advantages to the utilization of biomass. Environmental concerns are a major factor in considering biomass. Biomass itself is generally low in sulfur, ash, nitrogen, radioactive materials and heavy metals. Likewise, fuels produced from biomass tend to be low in these pollutants as compared to coal or hydrocarbons. Also combustion of fuels produced from biomass are much

are consumed in more efficient conversion processes. Since a good deal of municipal waste tends to be one form or another of biomass material then the burden currently put on landfills could be reduced by recycling this material into a useable form of energy. Furthermore, wastes from agriculture and lumber industries make ideal sources and unlike municipal wastes tend to be free of metals and polymers. A final advantage is that biomass is renewable resource and less subject to depletion. Virtually every country in the world has its own supply free from the control of a foreign power. It is a resource currently not used as a fuel or a feedstock; thus its incorporation into our society as a fuel may free other fuels for use as chemical feedstocks.

Pyrolysis, in a general sense, is a chemical change in a substance through heating. In the field of fuel processing, its definition has become to mean a process in which a chemical change occurs with heating in the absence of oxygen or in a reduced oxygen environment. The scope of this study is limited to the pyrolysis of wood, although pyrolysis isn't limited to wood or even to biomass. Furthermore, the ultimate purpose of the pyrolyzers used in this work is to pyrolyze wood such that the production of organic liquids is maximized.

In order to maximize pyrolysis oils, the pyrolysis has

In order to maximize pyrolysis oils, the pyrolysis has to occur in such a way that wood is decomposed into pyrolysis oils but that the heat used doesn't destroy these oils in the same process. In fast pyrolysis, the heat is supplied in enough quantity that the wood rapidly "depolymerizes". These high rates of decomposition allow the vapors and gases to have less exposure to the heat source and so they retain their chemical structure. This is opposed to slow pyrolysis. In slow pyrolysis the wood is devolitalized and no oil is produced.

The type of fast pyrolysis dealt with here is contact fast pyrolysis. In fast pyrolysis, high heat transfer rates must be obtained. Convection doesn't offer much promise for fast pyrolysis since the heat transfer coefficients aren't high enough. Radiative heat transfer has shown some promise Antal (1982, 1983), but conduction seems to offer the most potential for success. Contact pyrolysis is fast pyrolysis through conduction. For contact fast pyrolysis to work, the heat source in contact with wood must be able to maintain a high heat flux, the interface between the wood and the heat source must maintain physical contact, and reaction products must be removed from the interface area to reduce their decomposition and because they lower the heat conduction. Contact pyrolysis offers many advantages over pyrolysis

induced by other methods. Since ash and char are constantly removed from the pyrolysis interface, a greater degree of heat transfer via conduction is possible and in some cases physical grinding of the biomass produces more surface area per mass of feedstock.

This thesis involves the use of two different types of contact pyrolysis. The experimental work involved measurement of mass and energy balances on both these systems as well as some work towards qualitatively evaluating these systems. It is expected that the results reported may be of use to the biomass conversion industry.

## 1.2 Need For A Mass Balance

In the various types of pyrolysis, there is in general one product that can be optimized. For producing liquid fuels, pyrolysis oil is the desired product. For gasifiers, maximum output of pyrolysis gas is the goal. Obviously, for charcoal production, charcoal is the main product. The mass balance is important since it is a measurement of success in optimizing the yield of a given pyrolysis product. The mass balance is also of value because it can give evidence of the kinetics and reaction path of a process. Furthermore, the distribution of the reaction products relates back to wall temperature, pressure, and other physical parameters. Therefore mass

balance information is very important in analyzing the efficiency and utility of a given system.

### 1.3 Need For An Energy Balance

One aid to the design of contact fast pyrolyzers is a knowledge of their heat requirements. In evaluating the heat required for a given pyrolyzer, some knowledge of the heat of pyrolysis and the sensible heats is required. Due to the wide diversity of reaction conditions and reaction products, there is no single value of the heat of pyrolysis. Roberts (1971) showed that the heat of pyrolysis can be either endothermic or exothermic depending on the reaction conditions. In particular, the temperature, rate of heating, and the effect of secondary reactions have an effect on the heat of pyrolysis.

Although a great many of the products produced in pyrolysis have been documented, there is very little actual experimental data concerning the change in enthalpy of pyrolysis. Since a number of different reactions are occurring, and therefore, a wide variety of products are produced, it is extremely difficult to calculate heat of reaction by difference using heats of combustion or formation. Reed (1980) did estimate the heat required for pyrolysis of cellulose converted to an idealized

pyrolysis oil to be 2000 J/g but this is only a rough estimate. The development of fast pyrolysis processes requires more accurate values for both the sensible heat and the heat of pyrolysis. Since pyrolysis is a basic component of the combustion process, good thermodynamic data is also useful for the study of fire retardation, industrial combustion processes, and the general study of wood fires.

## 2. PREVIOUS WORK

### 2.1 Historical Background

Biomass was the first fuel source known to man. Combustion is the earliest chemical reactions used by hominoids. Pyrolysis is essentially at the heart of the combustion process in that the wood actually pyrolyzes prior to oxidation (Reed 1986), therefore pyrolysis, like combustion is one of the earliest chemical reactions used by mankind.

Wood pyrolysis products, likewise, go back a long way. The first "synthetic fuel" was charcoal, a pyrolysis product. The ancient Egyptians and Chinese used tarry products for embalming (Shafizadeh 1975). In 1792, the first fuels other than charcoal were made from pyrolyzing wood were produced by Robert Mudoch (Brink et al. 1976). By 1850, an estimated 91% of U.S. fuel needs were supplied by wood (Slesser and Lewis 1979). By the 1950's, the use of processed wood fuels and chemicals in the industrial world was extremely limited due to the emergence of the petro-chemical industry.

One limited use of pyrolysis has been in the generation of smoke for smoked meats, smoked fishes, and other smoked foods. Smoke generators need to optimize the amount of

liquid product vapor, so a form of fast pyrolysis was used. In 1961, patents were granted to R.A. Hawley (1961) and also H.R. Ramussen and H.J. Rasmussen (1961) for a smoke generator based solely on friction. This is an early form of contact pyrolysis.

## 2.2 Recent Work

In recent years, much emphasis has been placed on developing new techniques for pyrolyzing biomass. Much of the progress has been made in more efficient means of heating, in particular, heat transfer through conduction and radiation. Antal (1982, 1983) used concentrated solar energy to flash pyrolyze cellulosic materials. Iredale and Hatt (1982) dissolve wood in heated molten salts. Choi (1976) used heated rollers to pyrolyze filter paper. This is also a form of mechanically induced contact pyrolysis. He also theorized about using a tumbler with heated ceramic spheres similar to the Shell oil shale process except with direct heat applied to the tumbler as opposed to recirculation of the ceramic balls. Diebold (1985) has developed a vortex reactor that maximizes the pyrolysis interface for small particles and short residence times.

Lede et al. (1985) experimented with contact pyrolysis using a moving interface to reduce char buildup, in particular a rotating plate that was heated to constant



temperature by the use of four Bunsen burners. A diagram of this apparatus is shown in Fig. 1. The work of Lede (1985) had a lot of influence in the design of the two pyrolyzers discussed in this work. Unlike Lede's apparatus, both the heat flux concentrator and the pyrolysis mill involve more mechanical action to remove char buildup. Reed (1986) used a heated cylinder with a rotating wood dowel forced into a parabolic opening. This device was the prototype for the heat flux concentrator used in major portion of this study.

Another area of advancement in recent years has been in improved methods of upgrading the gas and liquid vapor that pyrolysis produces. Sundaram et al. (1982) used methane and hydrogen (hydrolysis). This is particularly interesting since they have the potential to increase the hydrogen to carbon ratio and thus increase the value of pyrolytic products as fuels. Catalytic upgrading of pyrolytic products is increasingly being investigated also (Reed, 1986, Ekstrom et al., 1985). Of particular interest as catalyst are zeolites and oxides.

### 2.3 Wood Chemistry

In order to evaluate the general characteristics of the pyrolysis process, the chemical composition of the reactant needs to be described. Wood is generally a polymeric

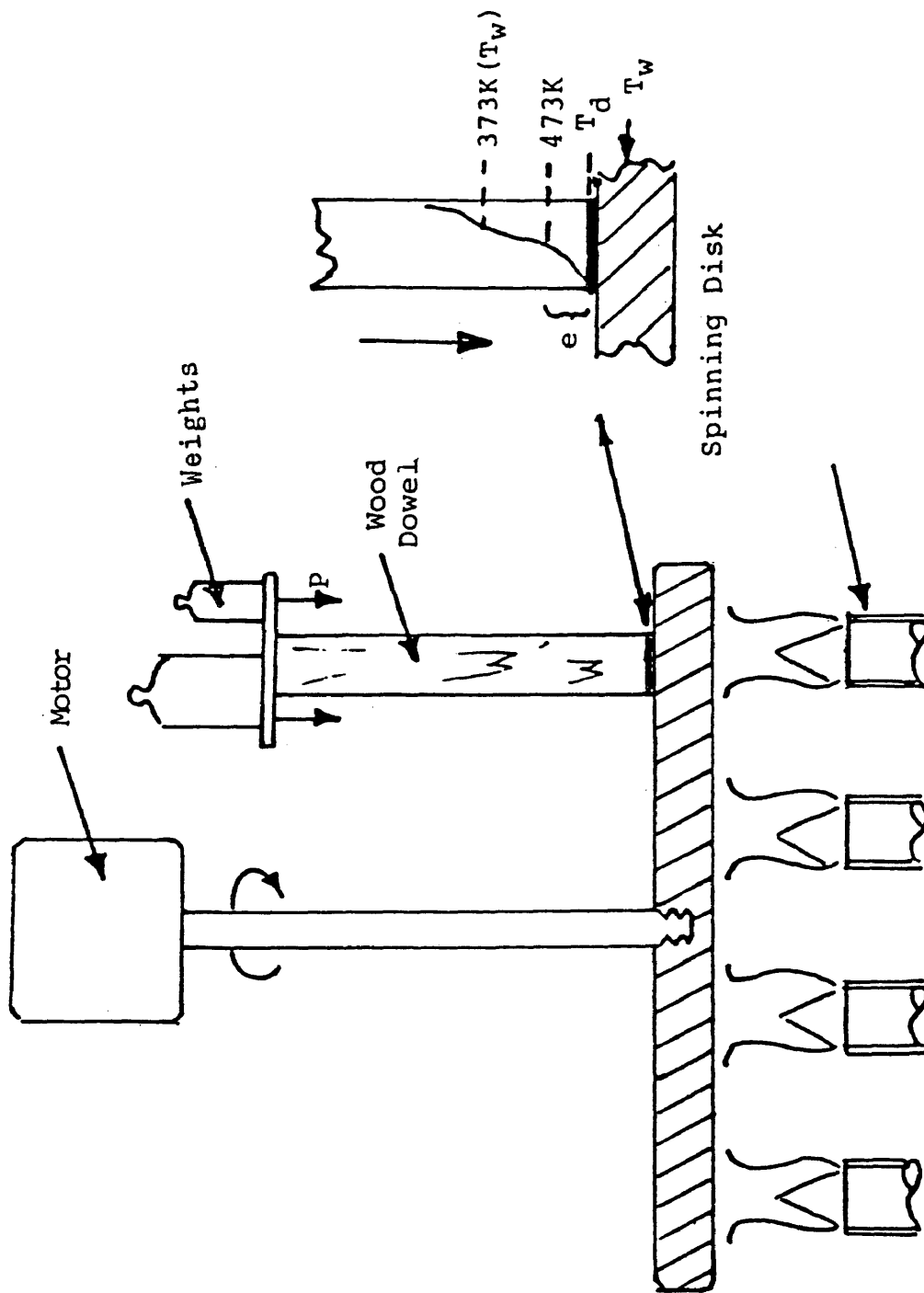


Figure 1: Spinning Disk Apparatus Used By Lele  
(1985)

compound that consists of cellulose, hemicellulose, lignin, extractables, water, and ash. For a typical hardwood, Shafizadeh (1980) reported 39% cellulose, 35% hemicellulose, 19.5% lignin, 0.3% ash, and 3.1% extractables. The polymers in wood are very large molecules. Wood celluloses can have molecular weights in excess of 100,000 (Graboski and Bain 1980). Due to the size of its molecules and the multitude of chemical compounds present in wood, it is difficult to characterize it in terms of all its components.

The ultimate analysis is a simpler chemical representation of wood. According to Bunbury (1929), as in Table 1, for twelve different woods, the ultimate analysis for carbon was between 48.5% and 50.2%, for hydrogen; the range was between 6.1 and 6.9%, and for oxygen (including a small amount of nitrogen); the range is 43.4 to 45.2 percent. Since the variation in these differences is small, a representative empirical formula for wood can be derived. Averaging these values and converting to an elemental basis yields 31.3% carbon, 47.79% hydrogen, and 20.91% oxygen. This corresponds to an empirical ratio of one carbon to 1.52 hydrogen to 0.668 oxygen. This formula compares favorably to Reed (1980) who uses a ratio of 1.4 and 1.66 hydrogen and 0.6 and 0.83 oxygen to one carbon. A ternary diagram showing the relationship of biomass and some of its

Table 1: Proximate Analysis Of Wood on a Weight Percent  
Basis (from Bunbury, 1926 except for averages)

Wood Type	Carbon(%)	Hydrogen(%)	Oxygen(%)
Oak	49.4	6.1	44.5
Beech	48.5	6.3	45.2
Birch	48.6	6.4	45.0
Maple	49.7	6.3	43.9
Elm	50.2	6.4	43.4
Ash	49.4	6.1	44.5
Lime	49.4	6.9	43.7
Poplar	49.7	6.3	44.0
Spruce	49.6	6.4	44.0
Scots Pine	49.9	6.3	43.8
Silver Fir	50.0	6.4	43.6
Larch	50.1	6.3	43.6
Average	49.55	6.35	44.1
Standard Dev.	0.54	0.20	0.58

components to other fuels is displayed in Fig. 2. Also shown are some biomass conversion processes.

Since the main component of wood is cellulose, and cellulose has been more thoroughly investigated and has a greater degree of homogeneity than wood and its other components, wood reactions are often explained relative to those of cellulose. Cellulose is a linear molecule of about 10,000 glucose units (Chornet and Overend, 1985). A section of a typical cellulose molecule is shown in Fig.3. Pure cellulose, as derived from cotton has the elemental formula of 44.2% carbon, 6.3% hydrogen and 49.5% oxygen (Bunbury, 1929). This corresponds to an empirical formula of 1.70 hydrogen and 0.84 oxygen to every carbon.

## 2.4 Reaction Products

### 2.4.1 Liquid Phase

The products of wood pyrolysis are generally separated into three different groups, each a different phase: A solid phase, consisting of the char left behind; a gaseous phase; and a liquid phase, consisting of water and organic products. The relative masses of each of these phases is shown in phase diagrams in Fig. 4(a) for slow pyrolysis and Fig. 4(b) for fast pyrolysis. They show the general inclination toward the production of charcoal at low heating

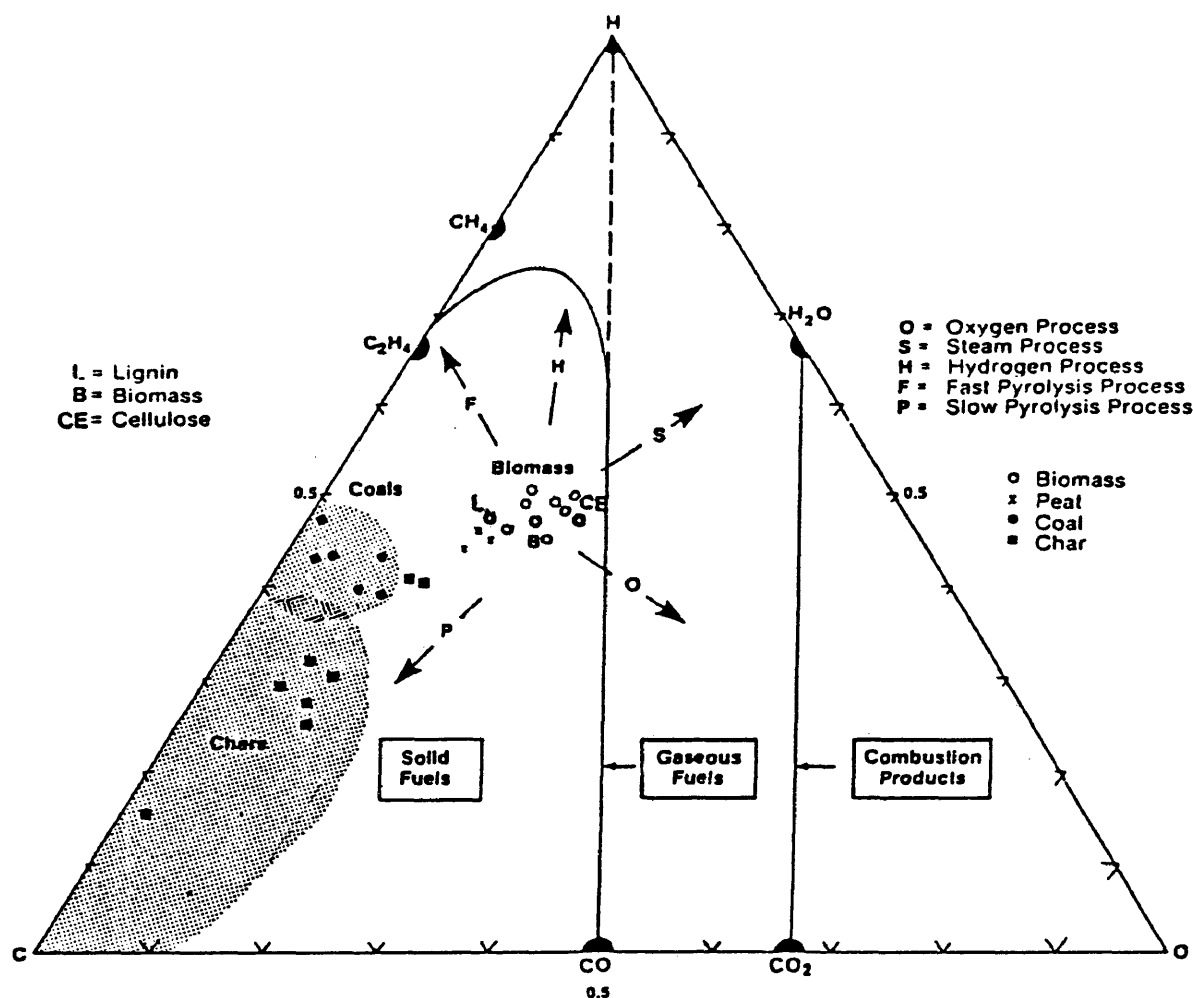


Figure 2: Ternary Plot of the Chemical Composition of Fuels -(Reed 1980).

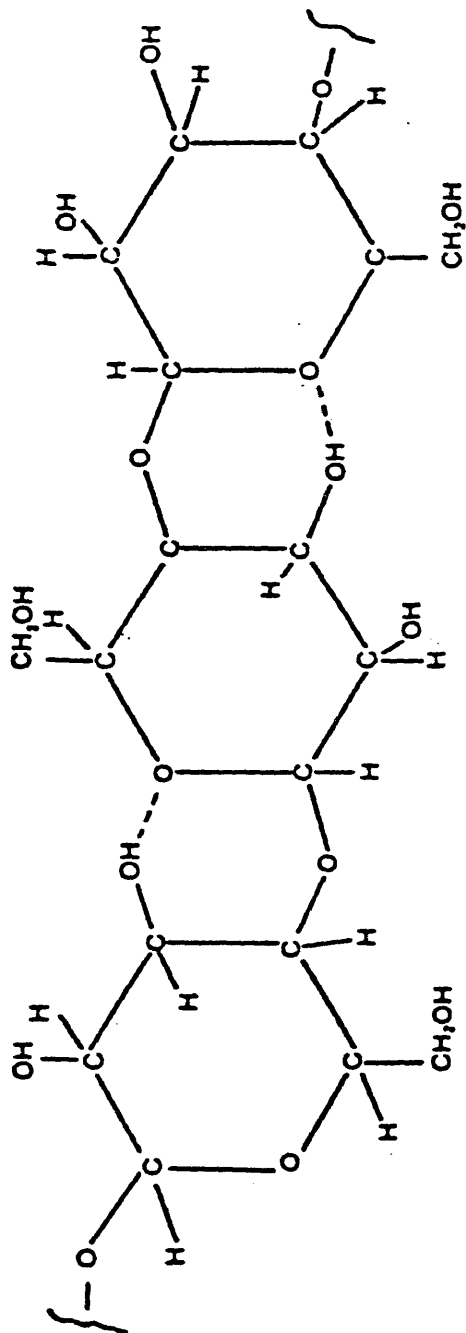


Figure 3: The Structure of the Cellulose Molecule  
-(Graboski and Bain 1980).

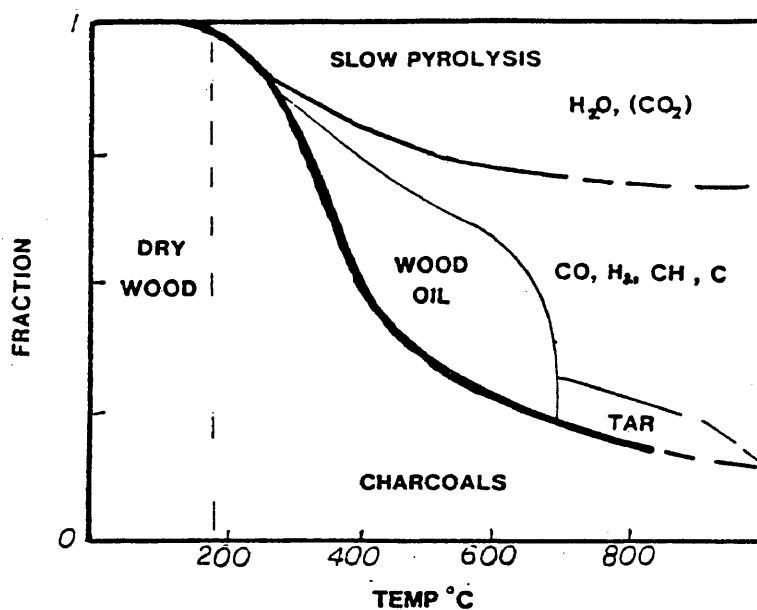


Figure 4(a): Pyrolysis Products as a Function of Temperature For Slow Pyrolysis  
-(Reed 1986).

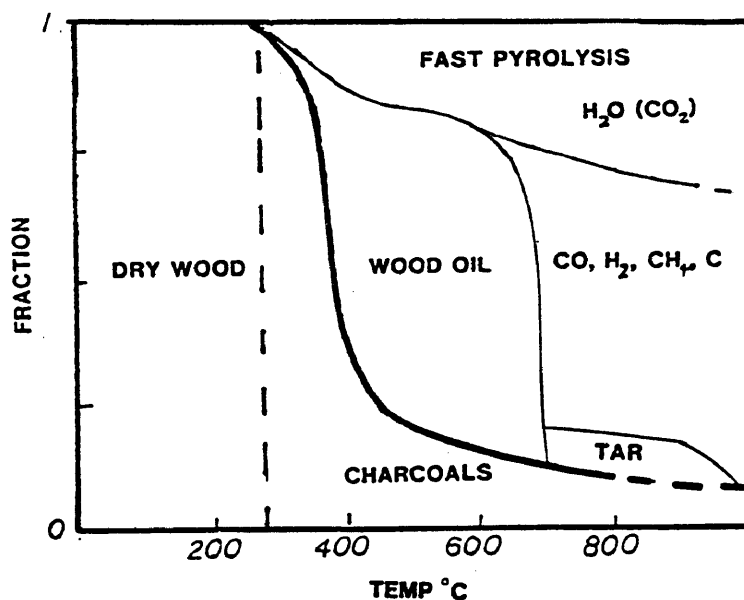


Figure 4(b): Pyrolysis Products as a Function of Temperature For Fast Pyrolysis  
-(Reed 1986)



rates as opposed to a tendency to produce oils at higher heating rates. At one time in the past, the char was of greater interest due to its use as a fuel, although currently the gas and liquid products are of greater interest because of their potential as both fuels and as chemical feedstocks. In this paper, char production is important since there is some evidence of a direct relationship between char production and the heat of pyrolysis (Antal 1982).

The liquid fraction of the pyrolysis products is the most complex of the three phases. Soltes and Elder (1981) compiled a list of 226 compounds found in the liquid fraction. They range from single carbon molecules such as methanol to molecules with as many as 30 carbon atoms such as melene. The majority of these compounds are oxygenated hydrocarbons. A mass spectrum of vapors produced by pyrolysis of birch is shown Fig. 5. It demonstrates the complexity of the liquid fraction. The variation of chemical species in the liquid product increases the difficulty of estimating its physical properties.

#### 2.4.2 Gas Phase

The gas phase is less complicated in terms of composition than the liquid phase. It consists primarily of carbon monoxide, carbon dioxide, hydrogen, methane,

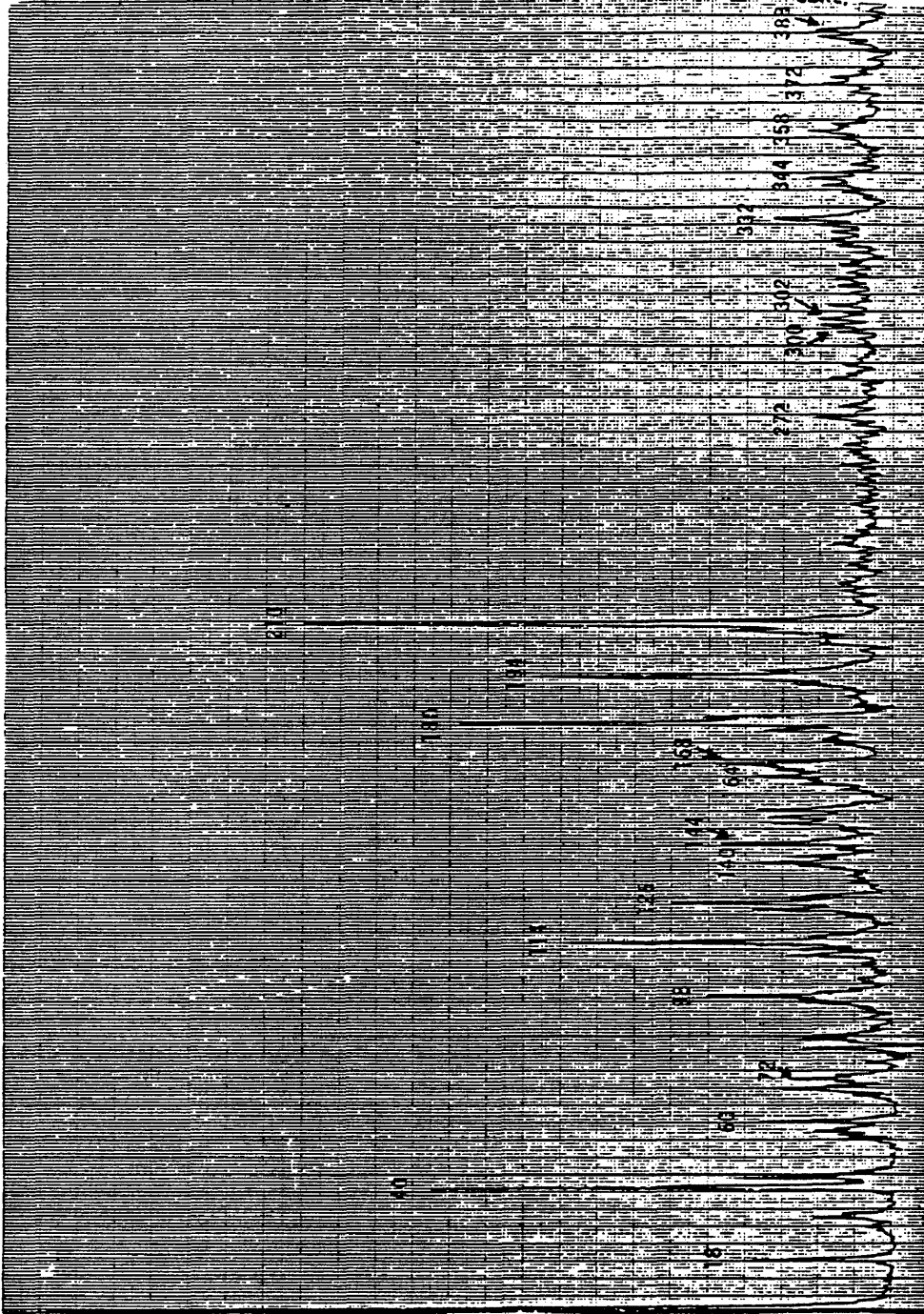


Figure 5: Mass Spectrometry of Wood Oil Derived  
From Birch - (Milne and Soltes 1982).

formaldehyde, ethane, ethylene, propane, propylene, butane, and butylene. From a fuel-oriented viewpoint, the amounts of carbon monoxide and carbon dioxide in relation to the amount of gaseous hydrocarbons gives an indication to the quality of the liquid product because the more carbon and oxygen relative to hydrogen tied up in the gas phase, the higher the hydrogen to carbon ratio in the liquid product and the lower the oxygen to carbon ratio. As is the case with char, the relative of amounts of gas produced tend to be higher for slower, low temperature types of pyrolysis. This relationship also indicates the degree of thermal degradation, since larger quantities of gas are generally favored by successive reactions which are due to the cracking of larger monomers. Therefore the gas phase composition gives some indication as to the reaction pathways.

#### 2.4.3 Solid Phase

Unlike the gas and liquid phases, the char can't be analyzed for distinct chemical compounds as is the case for macro-molecules found in coal. The composition of the char varies with the conditions under which the pyrolysis takes place. The effect of temperature on char composition is documented in Table 2 (data from Shafizadeh (1985) and Soltes and Elder (1981)).

The word "charcoal" covers a wide variety of

Table 2: The Effect Of Temperature On Char Composition

Temp. (deg. C)	Char yield (wt%)	Ultimate Analysis (%)				
		C	H	O	H/C	O/C
200(1)	91.8	52.3	6.3	41.4	1.44	0.59
300	51.4	73.2	4.9	21.9	0.80	0.22
400	37.8	82.7	3.8	13.5	0.55	0.12
500	33.0	89.6	3.1	6.7	0.41	0.06
600	31.0	92.6	2.6	5.2	0.33	0.04
800	26.7	95.8	1.0	3.3	0.12	0.03
1000	26.5	96.6	0.5	2.9	0.06	0.02
300(2)	89.4	44.0	6.4	41.4	1.73	0.71
325	63.3	47.9	6.0	46.1	1.49	0.72
350	31.8	59.9	5.2	34.9	1.03	0.44
400	16.6	76.5	4.7	18.8	0.73	0.18
450	10.5	78.8	4.3	16.9	0.65	0.16
500	8.7	80.4	3.6	16.0	0.53	0.15

(1) - Data of Shafizadeh (1985); unknown residence time

(2) - Data of Soltes and Elder (1981); 5 minute residence  
time

compositions. It is important in studying pyrolysis to differentiate between these compositions. The Van Krevelin diagram of char plotted for various temperatures, Fig. 6, indicates a loss of hydrogen and oxygen with increasing reaction temperature in the ratio of 2:1, corresponding to a loss of water. Edrich (1980) found that the heat capacity of char was almost the same as that of pure carbon but that hydrogen in the char did affect that heat capacity. Shafizadeh (1985), Fig. 7, shows increasing aromaticity with increasing temperature along with decreasing char yields. This combined with smaller hydrogen to carbon ratios and smaller oxygen to carbon ratios leads to the conclusion that at higher temperatures there is a greater tendency towards cross linking of the carbon atoms in the char even though less char is produced and the kinetics of the cross-linking reaction favor lower temperatures and slower rates of pyrolysis.

Iredale and Hatt (1982) concluded that it was possible to produce zero char using molten NaOH-KOH mixture to decompose the wood prior to pyrolysis. Zero char production would be beneficial in reducing accumulation in a pyrolytic device, but since the char is a good sink for excess carbon, reducing the char will also decrease the hydrogen to carbon ratio. This effect could be offset by increased carbon

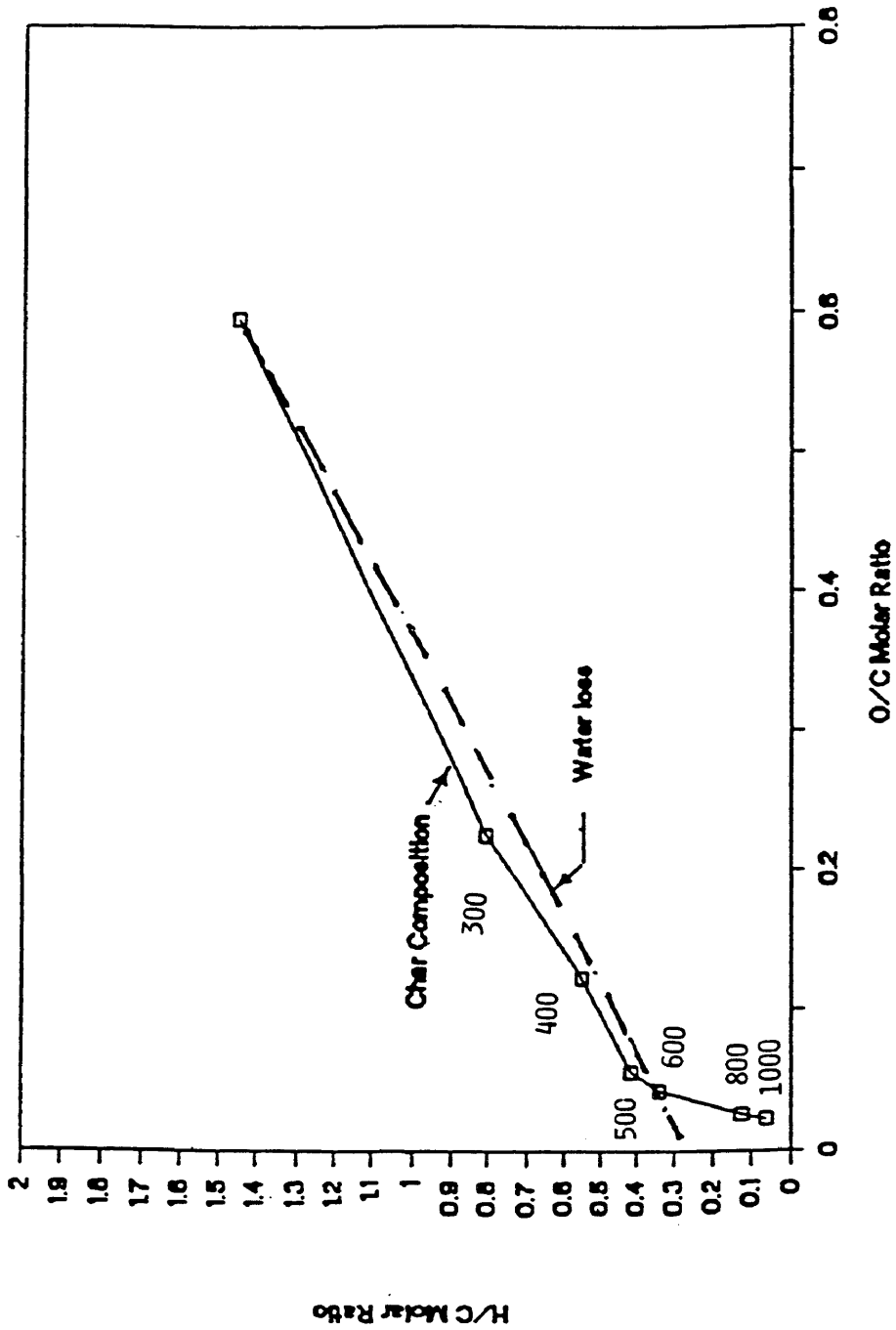


Figure 6: Van Krevelin Diagram Illustrating the Effect of Temperature on Char Composition -(Reed 1986).

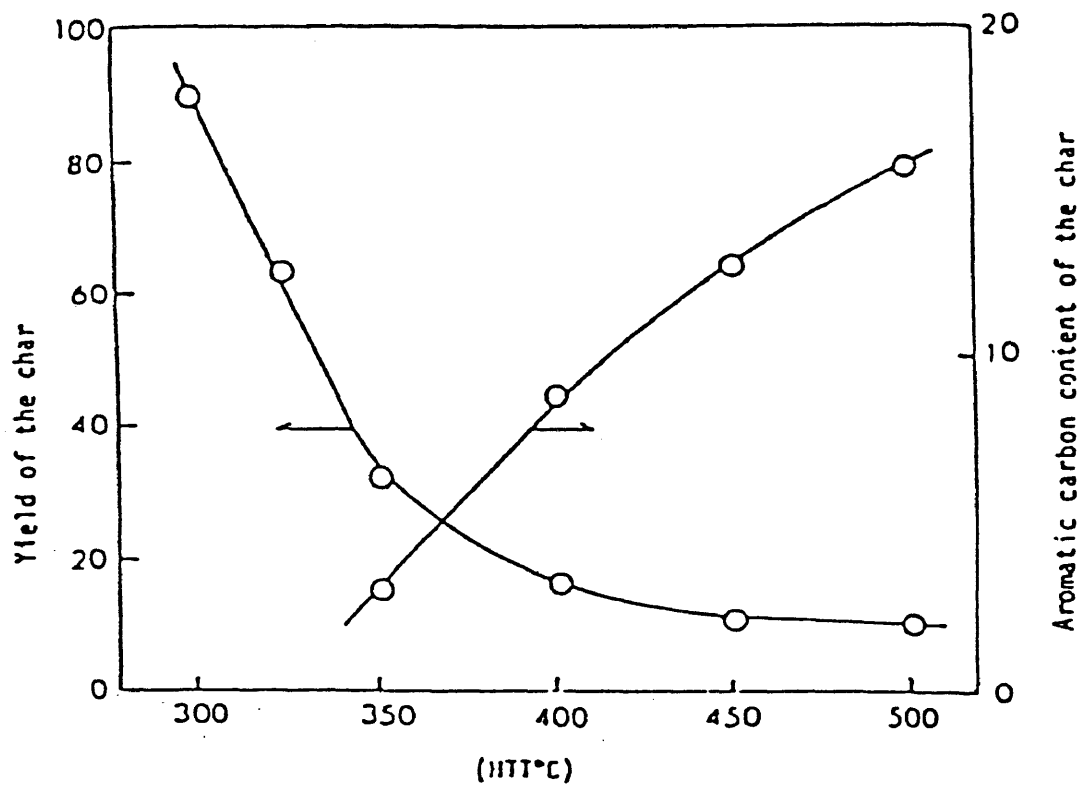


Figure 7: The Effect Of Temperature on Char Yield and Aromaticity -(Shafizadeh 1985)

dioxide production. Charcoal could be a desired by-product of a pyrolysis process either as a fuel to heat a pyrolyzer or to be sold as charcoal, so zero char production could be a disadvantage.

## 2.5 Energy Considerations

### 2.5.1 Heat For Pyrolysis

At this point, a major distinction must be made between the "heat of pyrolysis" and the "heat for pyrolysis".

The heat of pyrolysis,  $\Delta h_p$ , is the heat of reaction at a specific temperature. The heat for pyrolysis,  $\Delta h_{tot}$ , is the heat required to take the reactant to the reaction temperature plus the heat of reaction at that temperature. The heat for pyrolysis can be defined as follows,

$$\Delta h_{tot} = \int_{T_o}^{T_p} \hat{C}_{p_{wood}} dT + \Delta h_{pyr} + \sum_{i=1}^n \int_{T_p}^{T_w} \hat{C}_{p_i_{prod}} dT \quad (1)$$

where  $T_o$  is the initial temperature,  $T_p$  is the temperature at which pyrolysis occurs, and  $T_w$  is the final temperature of the products and the wall temperature of the pyrolyzer. The temperature of pyrolysis,  $T_p$ , is the temperature at which the wood undergoes a solid to fluid transition, although it occurs over a range of temperatures, it is



treated as if it is a single temperature.

The heat for pyrolysis,  $\Delta h_{tot}$ , is the value measured in this thesis and represents the overall heat required. It is this value that is necessary to the design of a pyrolysis apparatus. The heat of pyrolysis,  $\Delta h_p$ , is the heat required or generated for the pyrolysis reaction itself. Its value lies more in a theoretical understanding of pyrolysis reactions.

### 2.5.2 Heat Of Pyrolysis

A wide range of values for the heat of pyrolysis have been documented in past studies. Values of the heat of pyrolysis used in the past are given in Table 3. Many of these values are assumed or estimated, although some are based on experimental work. Since the kinetics of wood pyrolysis allows for a number of reactions to take place depending on the amount of time the sample is exposed to a given temperature and other reaction variables, there are severe limitations to basing the heat of reaction on temperature alone.

Since enthalpy is independent of path, given the initial condition of the reactant and the final condition of the products, theoretically, the heat required for the whole process can be defined. Therefore, the best method of

Table 3: Heat Of Pyrolysis For Wood And Cellulose

Heat of Pyrolysis	Description	Reference
250 to -340 (J/g)	Steam pyrolysis of cellulose, pressure varied between one and six bars.	Antal (1981)
340 to -150 (J/g)	Cellulose, shows the relationship to the amount of char produced	Antal (1982)
-380 (J/g)	Obtained by Differential Thermal analysis. Researcher: Tang and Neil(1964)	Kung and Kalekar (1973)
1760 (J/g)	Obtained from experimental work with wood cylinders in an inert atmosphere.	Roberts and Clough (1963)
84-138 (J/g)	First reaction of a consecutive series of reactions in the combustion of wood dowels.	Tinney (1965)
840-2100 (J/g)	Second reaction of a consecutive series in the combustion of wood dowels is really the oxidation rxn of char produced by release of volatiles	Tinney (1965)
-203 (J/g)	Derrived from one set of data from Roberts and Clough	Kung and Kalekar
330 (J/g)	Guess used as a parameter in for a model of large particle wood pyrolysis	Chan et al. (1982)
0 to 795 (J/g)	Determined by the integration of of the differential scanning calorimetry of cellulose.	Shafizadeh (1977)

Table 3 continued:

Heat of Pyrolysis	Description	Reference
-180-0.031* exp(4600T) (J/kg)	Fitted from data from Roberts (1971). Temp. range 250-450 degrees Celsius, only for exothermic reaction, generates extremely large numbers	Becker et al. (1984)
0.0 (J/g)	Conclusion reached by comparing a model that precludes a heat of reaction to experimental data, white pine, temp. range: 100-400 degrees Celsius	Pyle and Zaror (1984)
368 (J/g)	Cellulose, Researcher: Tang and Eickner	Robisin-Herman (1981)
360 (J/g)	Cellulose, Researcher: Muhlenkamp and Walter	Robisin-Herman (1981)
-352 to -527 (J/g)	Cellulose, Researcher: Roberts	Robisin-Herman (1981)
199 (J/g)	Pine, Researcher: Havens et al.	Robisin-Herman (1981)
111 (J/g)	Oak, Researcher: Havens et al.	Robisin-Herman (1981)
330.0 (J/g)	Cellulose, estimated, temp. range 360-400 degrees Celsius	Edrich (1980)
335 (J/g)	Yellow Pine, estimated, temp. range 280-420 degrees Celsius	Edrich (1980)
337 (J/g)	Birch, estimated temp. range: 290-425 degrees Celsius	Edrich (1980)

Table 3 continued:

Heat Of Pyrolysis	Description	Reference
-220 (J/g)	Wood, experimentally determined Researcher: Bamford, Crank, and Malin	Roberts (1971)
-136 (J/g)	Wood speres, Researcher: Akita	Roberts (1971)
-340 (J/g)	Wood fiber board at 175 deg. Celsius; Researcher: Thomas and Bowes	Roberts (1971)

determining the heat of reaction would be one based on the products as opposed to those methods using reaction parameters. Figure 8 shows the relationship between char yield and the heat of pyrolysis. This plot shows a regression that is fairly linear. An equation fitted to this curve is given by Reed and Cowdery (1986), (see Appendix C)

$$\Delta h_{\text{pyr}} = 553 - 3142 F_c \quad (\text{kJ/g}) \quad (2)$$

where  $F_c$  is the weight fraction of carbon in the char. A similar equation for wood could likewise be derived given that the data existed. It might be possible to combine this equation with data on the char's ultimate analysis and aromaticity. Furthermore, the limits on the heat of reaction may be derived given heat of formation data on the products from the most severe reaction and the least severe reaction for a given set of design specifications.

The most extensive study of pressure effects on the heat of pyrolysis of cellulose was conducted by Mok and Antal(1983). The relationship between heat of pyrolysis and pressure is detailed in Fig. 9. Antal (1981) concluded that increased pressure inhibited gasification. Also it tended to increase char production (Antal 1983). From Fig. 9, it

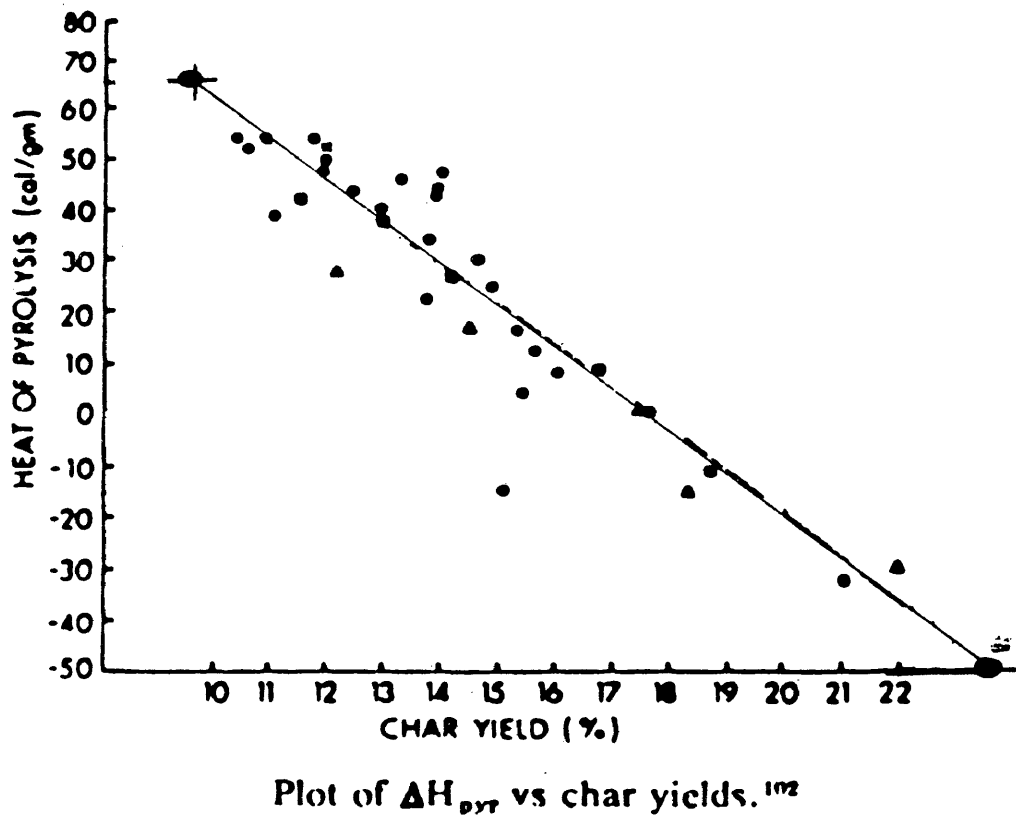


Figure 8: Heat of Pyrolysis Versus Char Yield For Cellulose -(Antal 1982).

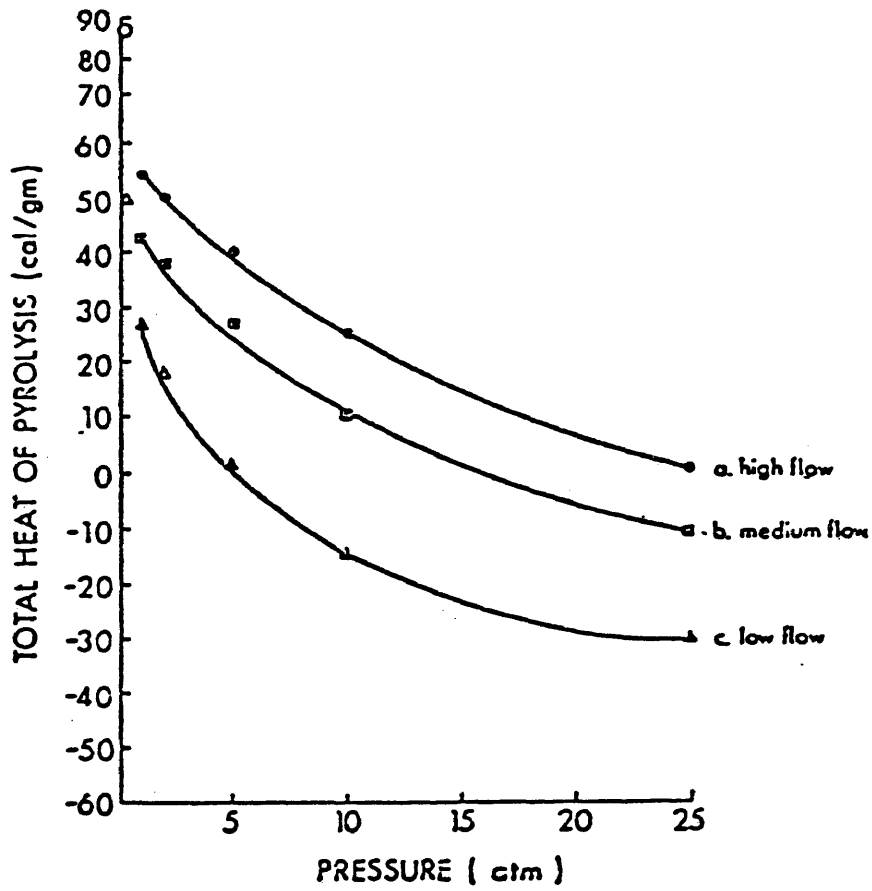


Figure 9: Heat of Pyrolysis of Cellulose as a Function of Pressure for Three Purge Gas Flow Rates -(Antal 1983).

can be noted that with increasing pressure there is a decrease in the heat of pyrolysis for cellulose. The flow rate of purge gas, like pressure, has an effect on the heat of pyrolysis reflecting back on the effect of convective heat transfer.

### 2.5.3 Sensible Heat

An even less established area of wood pyrolysis, than heat of reaction, is the sensible heat. At the time of this writing, there was no heat capacity data available to this author at fast pyrolysis temperatures. Edrich (1980) experimentally produced heat capacity data up to 200 degrees Celsius, but it is extremely temperature dependent and at higher temperatures the heat capacity becomes unreasonably large and probably includes pyrolysis reactions. Edrich (1980) mentions a value of 0.500 cal/g-deg.C from a Russian abstract by Agronskin et al., but no further information was available. In calculating the sensible heat for fast pyrolysis, the heat capacity needs to be integrated from the initial wood temperature up to 466 degrees Celsius, Lede's (1985) solid to fluid transition temperature, and then the heat capacities of the products need to be integrated from 739K to the wall temperature. Like wood itself, there is no data for wood pyrolysis products at



these temperatures except for the gases.

#### 2.5.4 Thermogravimetric Measurements

There are three different major techniques in use today for the thermal analysis of wood; thermogravimetry (TG or TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). In thermogravimetry, the weight of a sample is measured as a function of time at a fixed temperature or as a function of time at a fixed heating rate. The thermogravimetry of wood and some of its components is plotted in Fig. 10. A related measurement is differential thermogravimetry (DTG) which measures the first derivative of the weight with respect to time or, in other words, the rate of weight loss. The plots of the relative weights of wood and cellulose at a heating rate of 15 deg. Celsius per minute are shown in Figs. 11 and 12.

While thermogravimetry is typically used for kinetic studies, DSC and DTA supply more information about the change in enthalpy associated with the reactions. Differential thermal analysis is the measurement of the change in temperature of the sample relative to a standard as a function of temperature. Such a plot shows whether a reaction has an exothermic or endothermic tendency. In Fig. 11 the influence of wood components on the general tendency of the wood pyrolysis reaction can be seen.

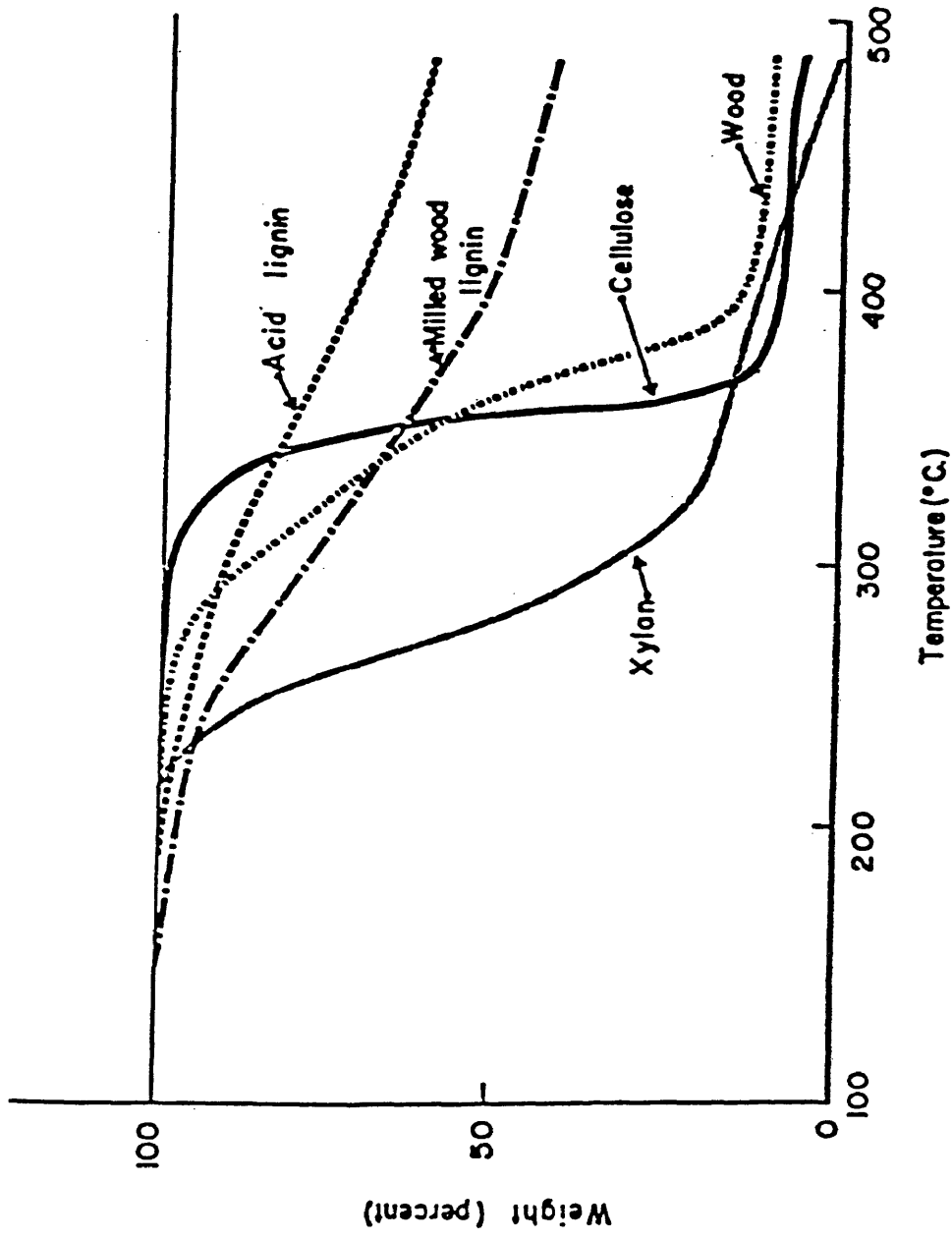


Figure 10: Thermogravimetry of Wood and it's Components -(Shafizadeh 1985).

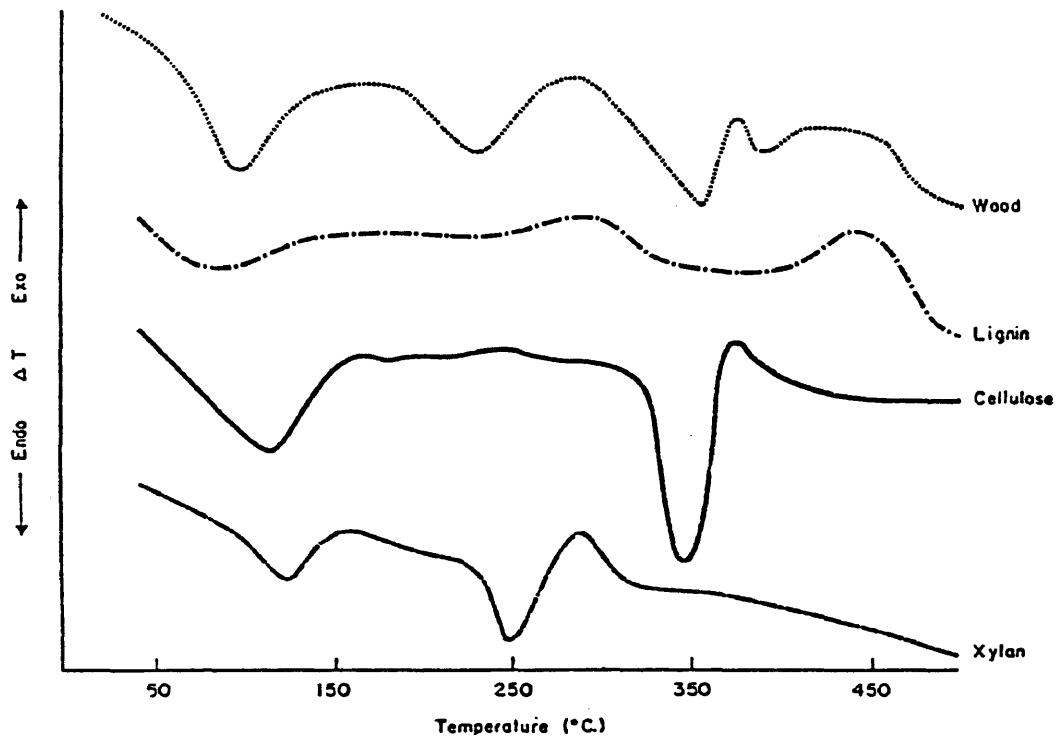


Figure 11: Differential Thermogravimetric Analysis of Wood and it's Components -(Shafizadeh and DeGroot 1977).

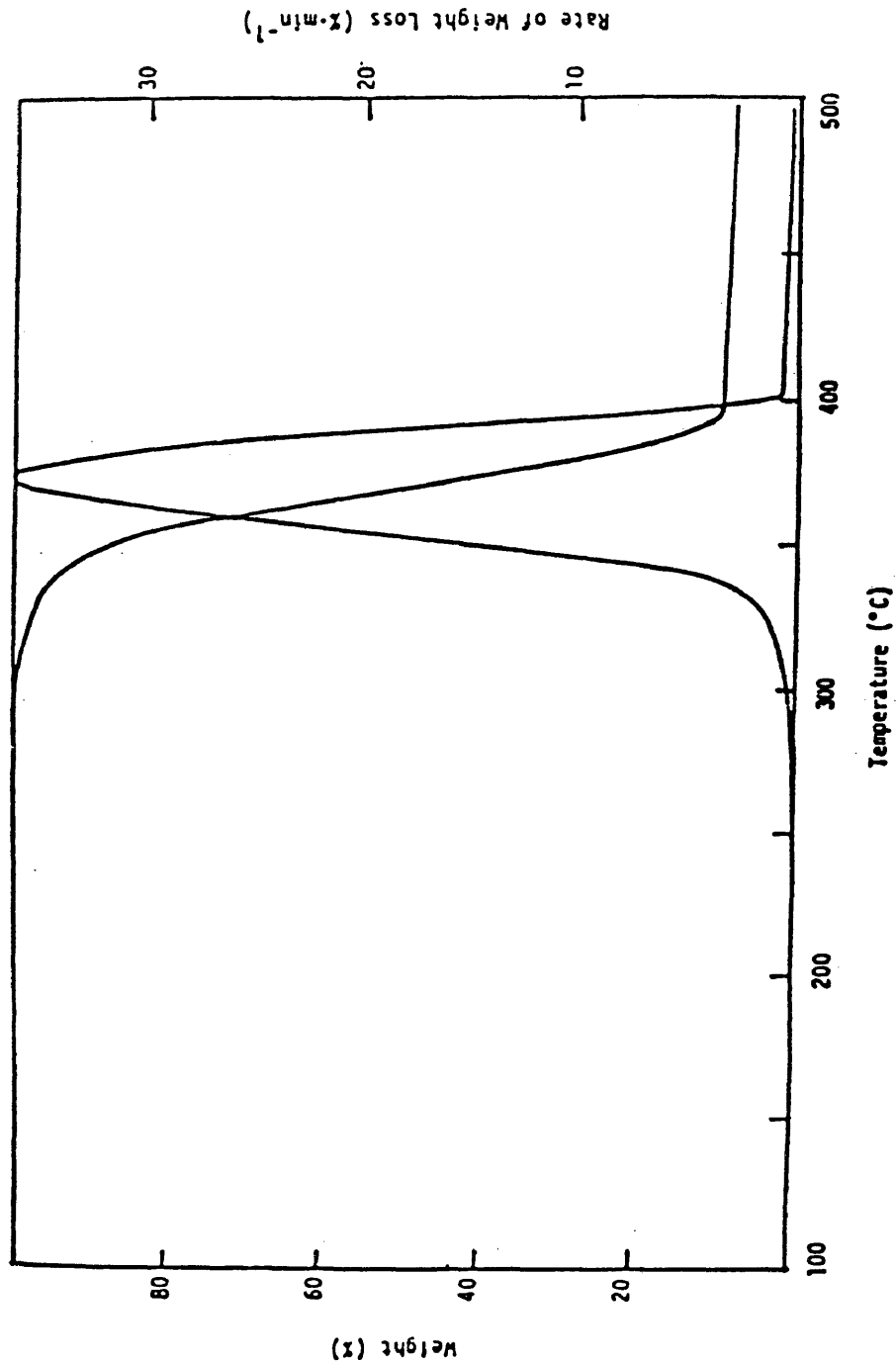


Figure 12: TGA and DTA of Cellulose (Heating Rate = 15 Deg. C /Min) -(Shafizadeh and DeGroot 1977).

The most useful thermogravimetric measurement in the study of reaction heats is differential scanning calorimetry, which has now largely replaced DTA. DSC measures the derivative of the enthalpy with respect to time. In the absence of chemical reactions and phase changes, DSC is a measure of the energy capacity of a sample. Integrating this function over a specific temperature range yields the change in enthalpy per unit weight of the sample. Typically, this measurement is made with a constant rate of temperature rise and as a function of time. A DSC scan for cellulose and the integration of that function is shown in Fig.13.

These plots are particularly useful for examining the relationship between temperature and the heat for pyrolysis and for determining a heat of reaction for a batch type pyrolyzer with a constant heating rate. However, their use for evaluating the heat of pyrolysis at varied pressures, temperatures or continuous systems is limited. Edrich (1980) derived values for heat of pyrolysis from DSC data over a 80-200 deg.Celsius range.

Shafizadeh (1985) notes that above 300 C, glycoisidic linkage breaks in cellulose to produce sugar derivatives and little char. The plot of DSC data reaffirms this (Figure 13). Somewhere between 330 and 380 degrees Celsius, there is

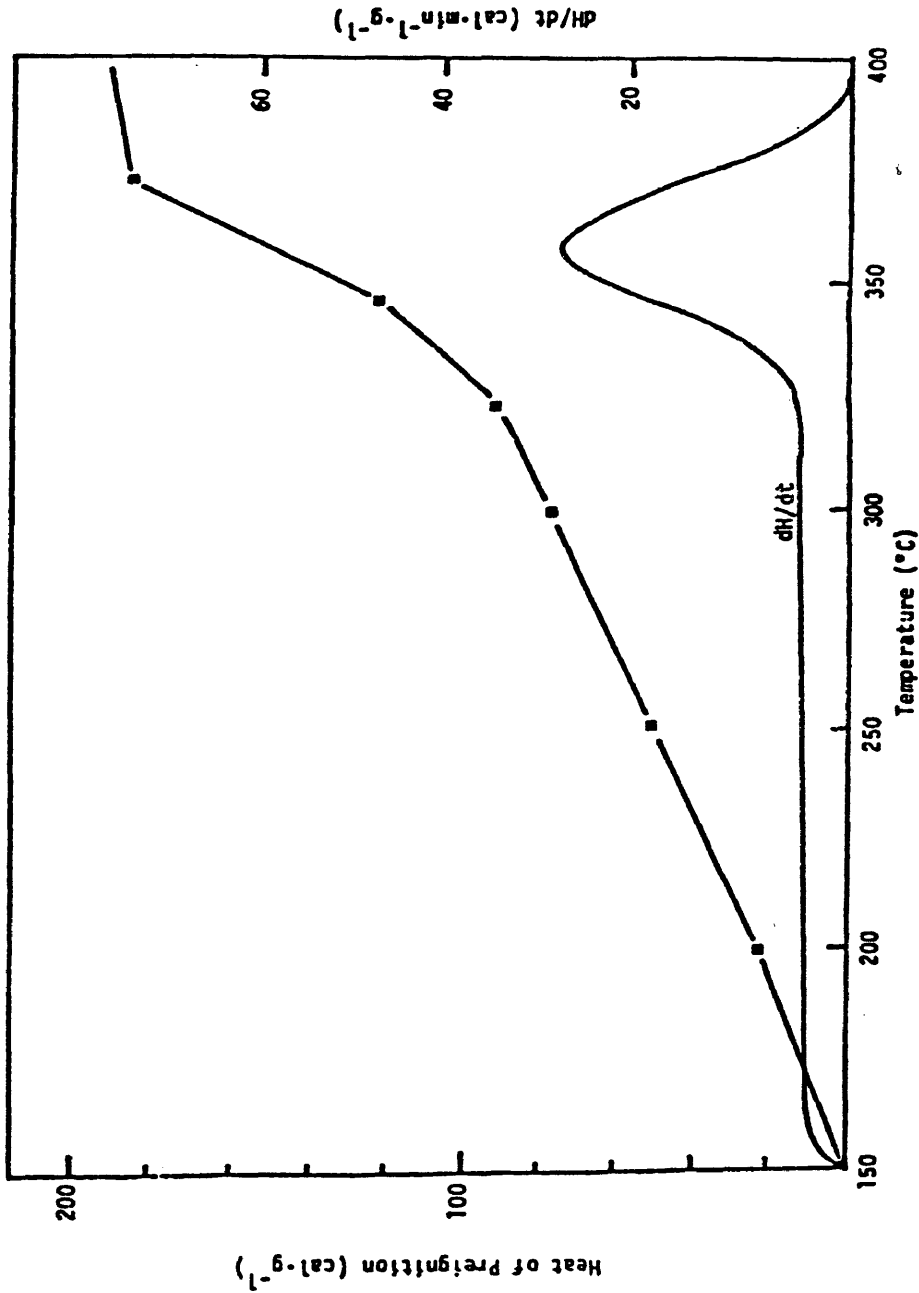


Figure 13: Differential Scanning Calorimetry of Cellulose (Heating Rate = 15 Degree Celsius/Min) --(Shafizadeh and DeGroot 1977).

a significant increase in enthalpy which is associated with this reaction. Another interesting phenomenon to note in this figure is that somewhere around 400 degrees Celsius the change in enthalpy equals zero since because the cellulose is completely gone except for 5-10% residual charcoal, thus the total heat levels off at this point.

#### 2.5.5 Pyrolysis Temperature

The temperature at which all the components of wood have depolymerized is currently under investigation. The individual components decompose at different temperatures. Lignin doesn't decompose to a significant amount until it reaches temperatures above 280 degrees Celsius and hemicellulose decomposes somewhere between 150-210 degrees Celsius (Chornet and Overend 1982). Lede et al. (1985) reports the "melting" point of wood as measured is 466 degrees Celsius with a heated rotating disk. Since wood is not a crystalline solid, rather than call this temperature a melting point it might be better to call it the solid to fluid transition point. Needless to say, it does have some of the same characteristics as a melting point in that wood exposed to a higher temperature will maintain this temperature at it's surface much like ice. These transitional characteristics are further documented in Zhi(1984).

### 2.5.6 Heat Transfer For Prolysis

In fast pyrolysis, the heat transfer becomes of interest because often the interface between the wood and it's heat source can not supply enough energy to maintain a constant temperature. Shafizadeh (1980) noted the reaction rate is dominated by the heating rate, as opposed to kinetics, when materials have high surface to mass ratios or when rapid evaporation at the surface cools the sample.

The heat transfer can be defined over two regimes, the heat flux to the surface of the wood and the heat flux from the surface. There are a couple of schemes for determining the controlling factor in a pyrolysis process. Reed and Cowdery (1986) use the Biot number, the relationship between convective and conductive heat transfer coefficients;

$$Bi = hL/k \quad (3)$$

where  $h$  is the heat transfer coefficient across the reaction interface,  $L$  is the characteristic length, and  $k$  is the thermal conductivity of the wood. If the Biot number is greater than one, then the internal heat flux becomes the controlling factor and if it is less than one then, conductive heat transfer inside the wood has less resistance



conductive heat transfer inside the wood has less resistance and the heat flux to the surface is the controlling factor. These two zones of control and the relationship between heat transfer and heating rate are shown in Fig.14. The effect of the heating rate on heat of pyrolysis and also heat for pyrolysis is shown in Fig. 15.

Pyle and Zaror (1984) define two new dimensionless groups, the pyrolysis numbers,  $Py$  and  $Py'$ ;

$$Py = k/k_r C_{pr}^2 \rho \quad (4)$$

$$Py' = h/k_r C_{pr} \rho \quad (5)$$

Dividing  $Py'$  by  $Py$  will give the Biot number. The following table shows the relationship between the controlling factor and these three dimensionless groups:

Table 4:

Controlling Factors and Dimensionless Groups  
-(Pyle and Zaror 1984)

<u>Controlling Factors</u>	<u>Bi</u>	<u>Py</u>	<u>Py'</u>
External Heat Transfer	Small		Small
Kinetics	Small		Large
Internal Heat Transfer	Large	Small	

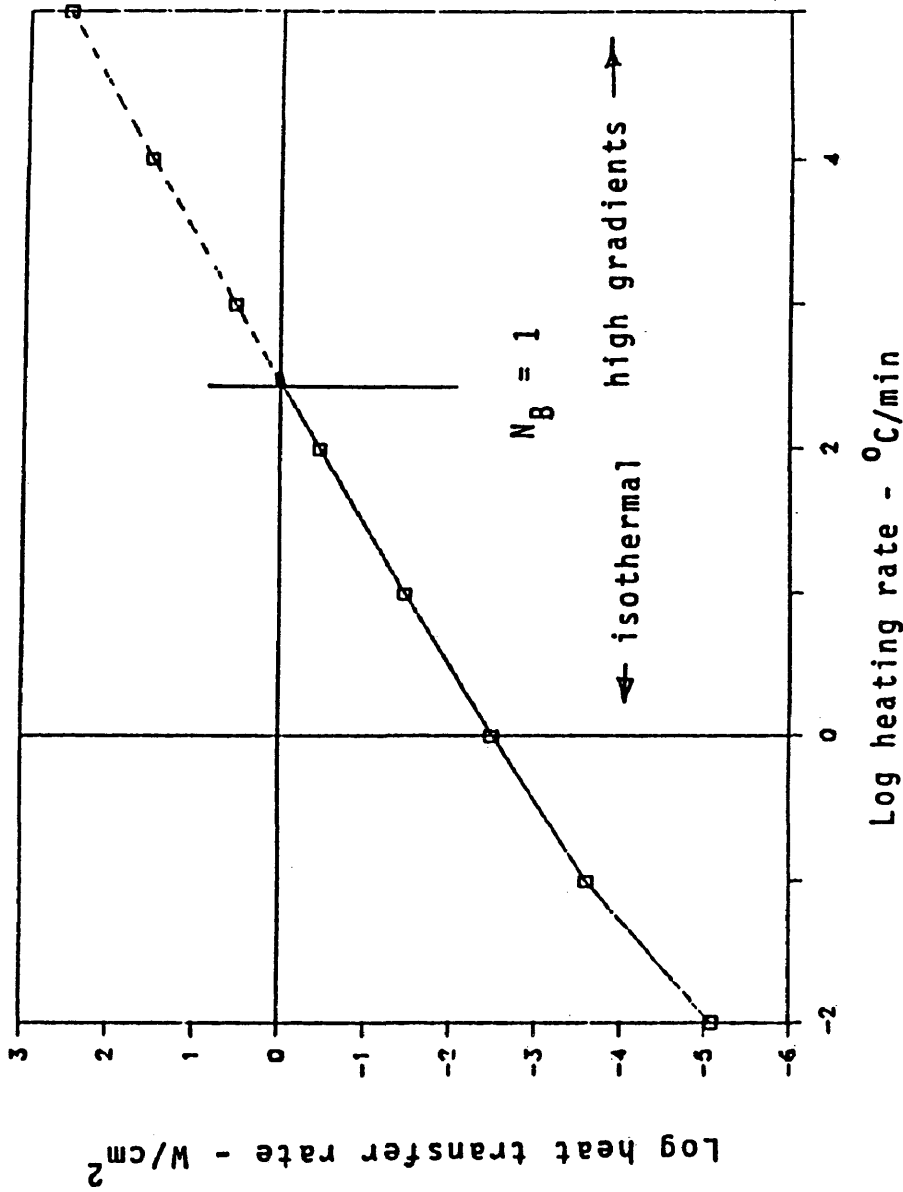


Figure 14: The Effect of the Heat Transfer Rate on the Heating Rate - (Reed and Cowdery 1986).

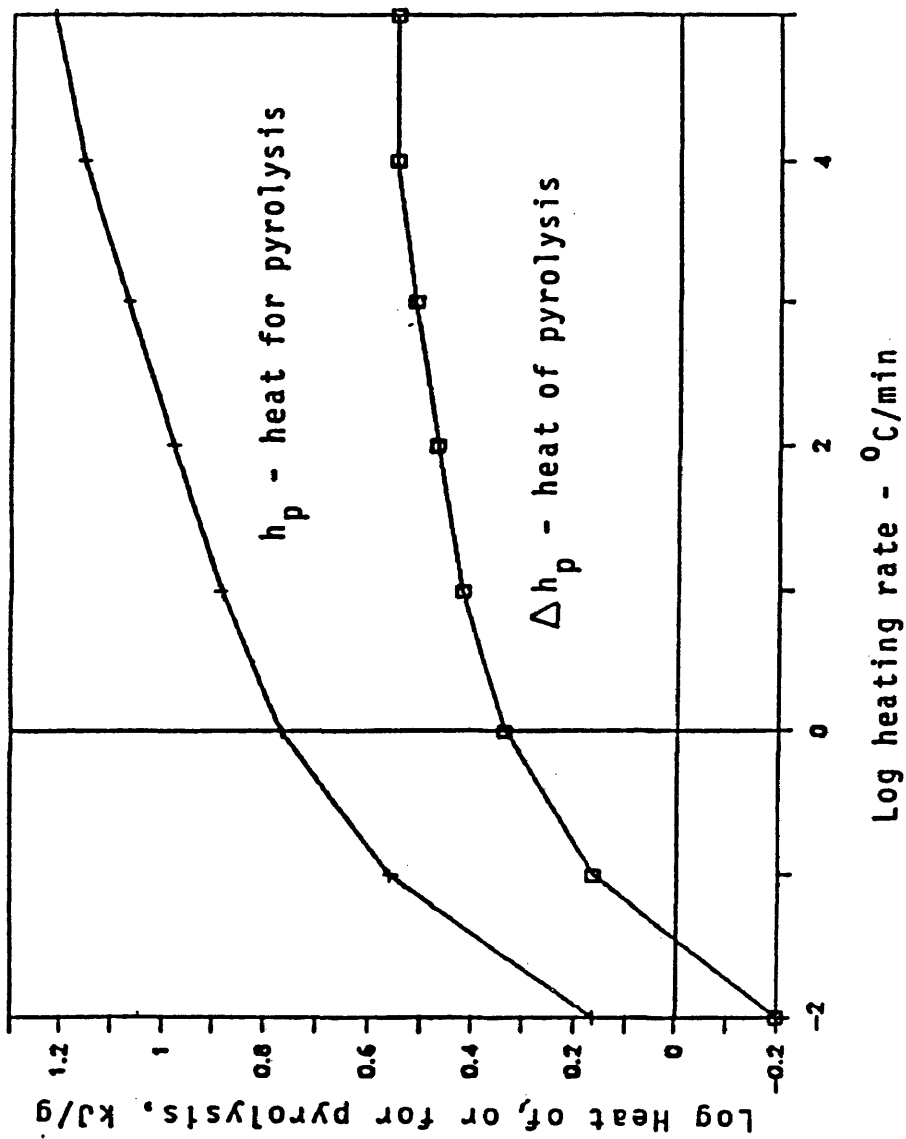


Figure 15: Heating rate and the change in enthalpy  
--(Reed and Cowdery 1986).

In fast pyrolysis the heat flux is obtained as follows;

$$q = h_c(T_w - 739) \quad (6)$$

where  $T_w$ , the temperature of the heat source, is defined in Kelvin. This equation is based on Lede's (1985) work since it assumes that the wood maintains its solid to fluid transition temperature.

## 2.6 Reaction Kinetics

There are two major groups of reactions competing with each other in the pyrolysis of wood and cellulose. Only cellulose has been studied in detail. The global reaction kinetics as defined by Diebold (1985) for the pyrolysis of cellulose are shown in Fig. 16. The "active" state is defined by Bradbury et al. (1979) to be cellulose that has passed through an initiation period and is in a form that can be depolymerized. The dominant depolymerization reactions involving cellulose are a group of reactions known as transglycolization reactions. It is generally believed that a free radical mechanism induces the depolymerization process. Figure 17 shows one possible mechanism for the formation of free radicals. Other mechanisms have been postulated. The reaction paths to the formation of several glucoses are demonstrated in Fig. 18,

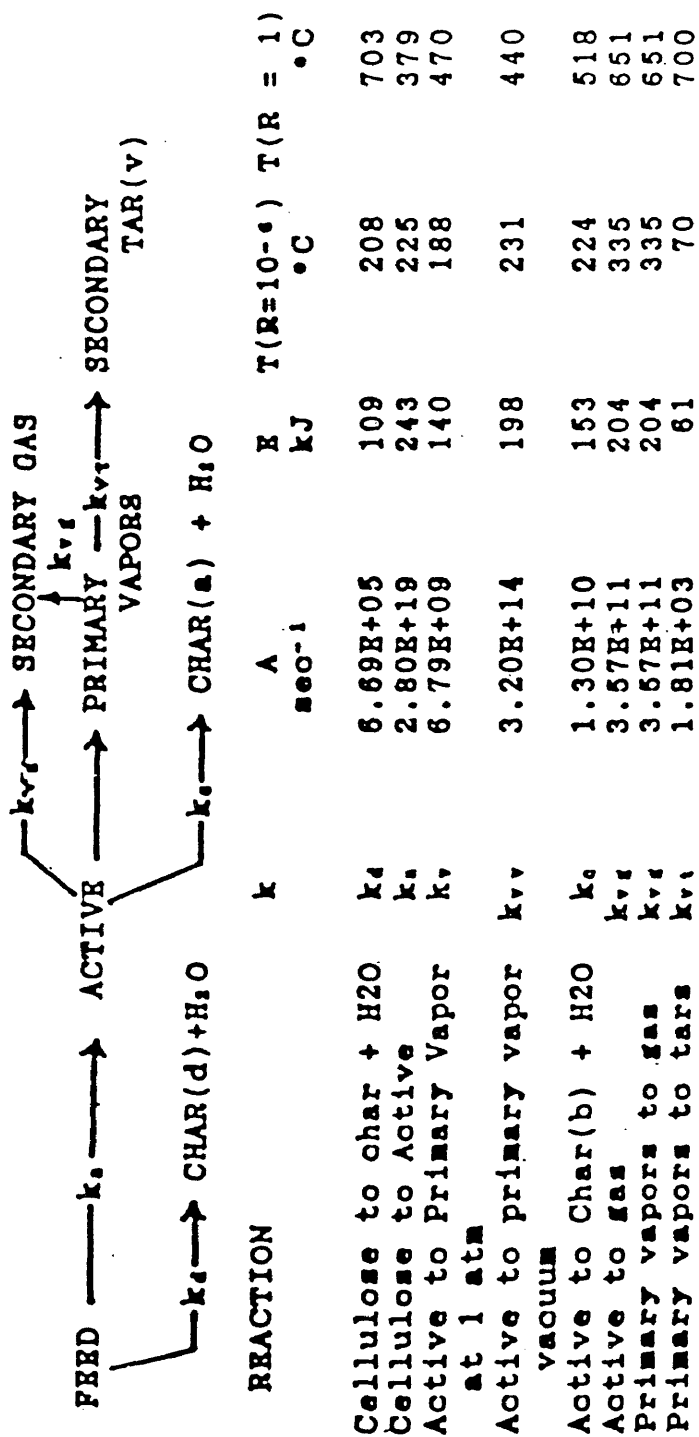


Figure 16: Reaction kinetics of the Diebold model  
-(Reed and Cowdery 1986).

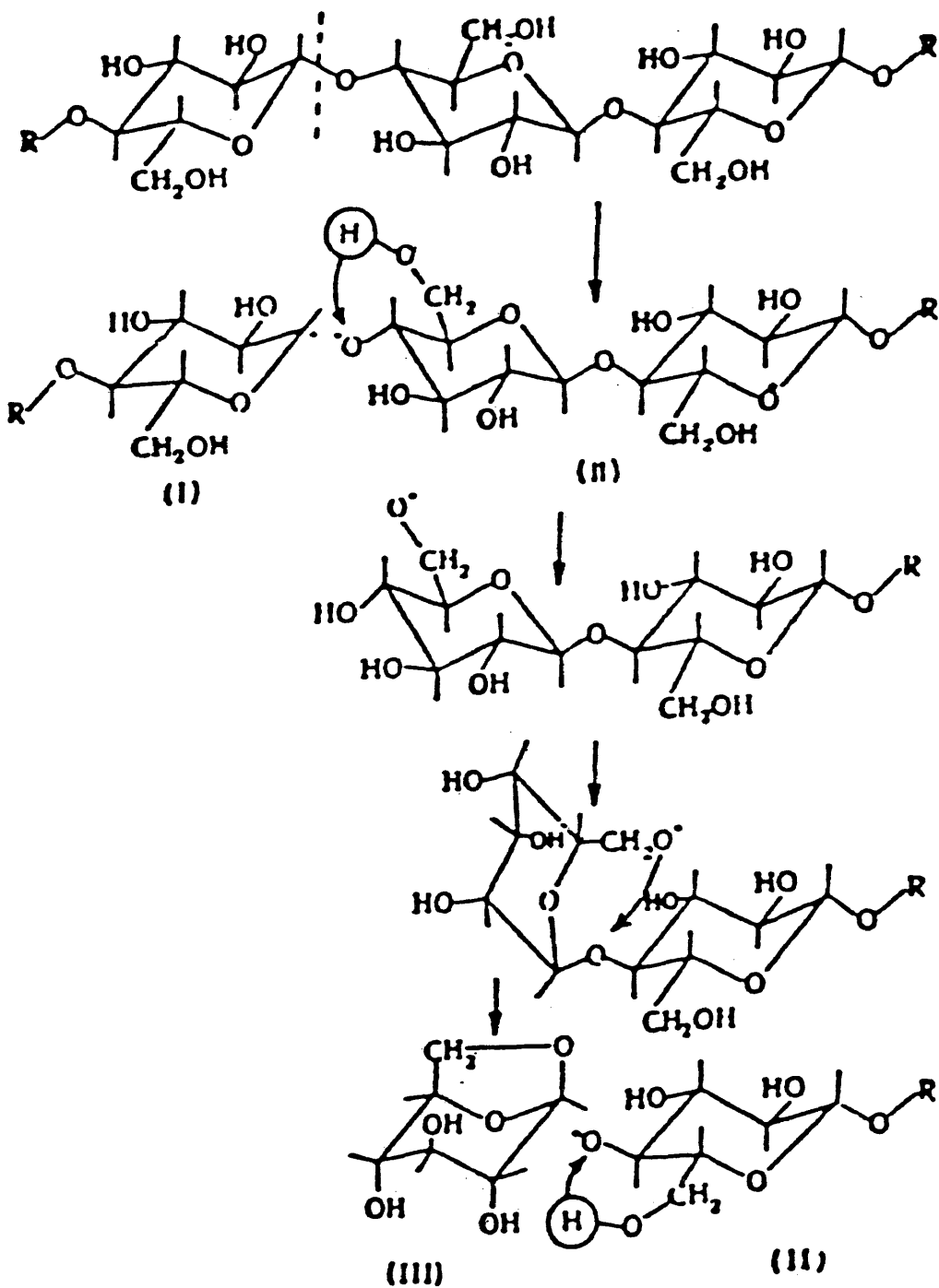


Figure 17: Free radical mechanism of cellulose depolymerization -(Antal 1982).

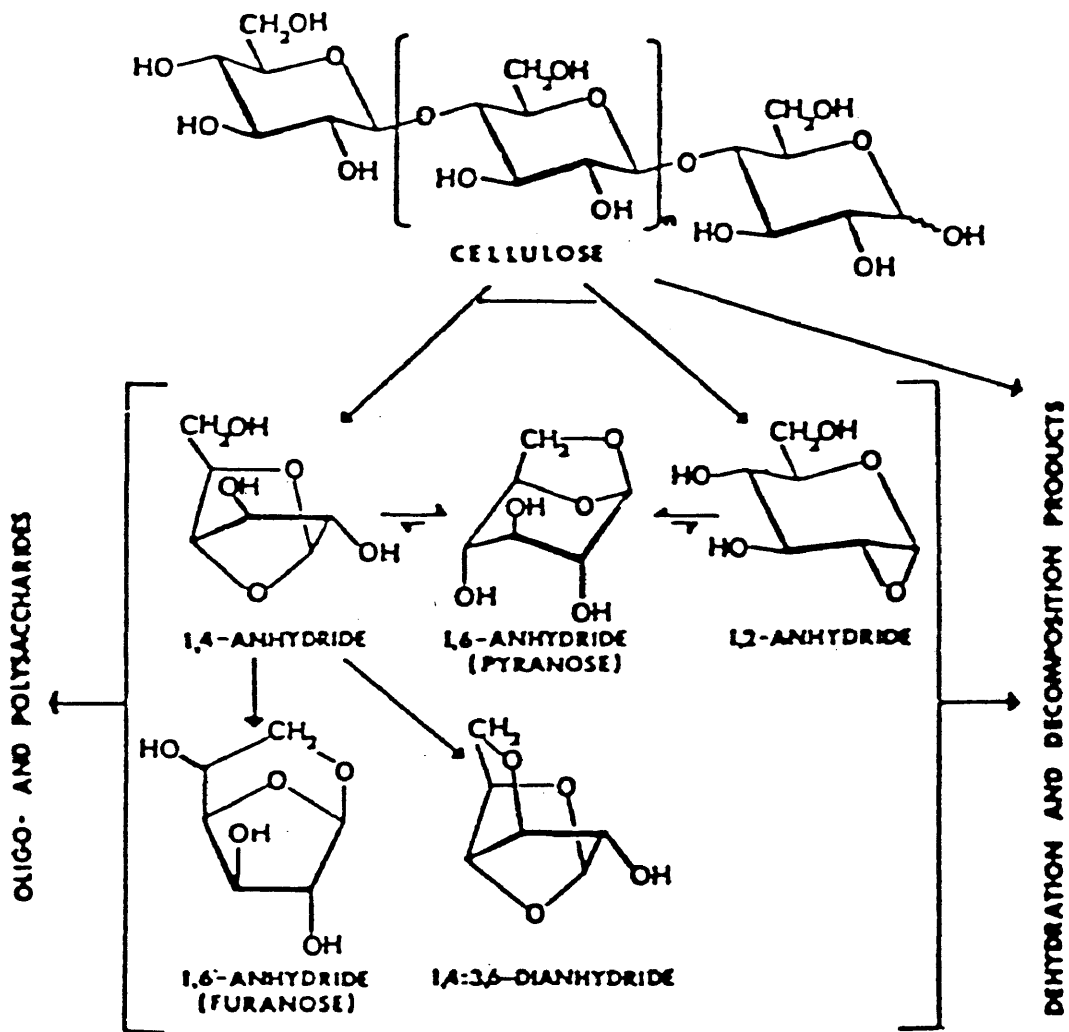


Figure 18: Products of cellulose depolymerization  
 -(Antal 1932).

the most likely being the formation of levoglucosan (pyranose). These reactions compete with cross linking reactions that favor the formation of more char and less hydrocarbons.

The kinetics have an increased influence on the heat for pyrolysis with increased residence times since there is a greater capacity for successive reactions to occur in the products. Diebold (1985) noted the existence of over 200 possible free radical reactions for the pyrolysis of cellulose alone. If the heat of reaction were known for each reaction path, then the pyrolysis products and the heat of pyrolysis could give insight into the kinetics.

## 2.7 Effect Of Mechanical Pressure On Pyrolysis

Pressure in a pyrolyzer has several effects. The most significant is the physical pressure of the wood against the heat source i.e. the pressure against the ablation layer. Since this pressure regulates the thickness of the fluid layer that the heat must travel across, it affects the heat transfer coefficient. Lede (1985) came up with a fitted a curve to this relationship of the following form:

$$h = 0.020 p^{0.995} \text{ (W/m}^2 \text{ K)} \quad (7)$$

where  $p$  is in Pascals. Another relationship that



Lede (1985) developed for a dowel pressed against a rotating stainless steel disk was between the pressure and the ablation rate (at 1073 K);

$$V = 6.10 \times 10^{-9} p \quad (\text{m/s}) \quad (8)$$

where  $p$  is in Pascals. The ablation rate is the rate at which the dowel moves perpendicular to the plate or the linear velocity of the dowel perpendicular to the plates surface. Since this value is geometrically dependent on the dowel and it's surface area, an equivalent ablation rate can be used base on the feed rate;

$$V = m_f / (t A \rho) \quad (9)$$

where  $A$  is the cross sectional area of the dowel. So equations (8) and (9) become:

$$p = m_f / (6.10 \times 10^{-9} t A \rho) \quad (10)$$

(Pa)

This is a very useful equation in cases where the pressure can't be measured directly. Lede then related the wall temperature of the pyrolyzer to ablation rate and pressure

and found another very near linear relationship;

$$V/p = 2.36 \times 10^{-11} T_w - 1.75 \times 10^{-8} \quad (11)$$

(m/s Pa)

where  $T_w$  is in Kelvin,  $V$  is in m/s, and  $p$  is in Pascals.  
which permits one to calculate the pressure or the ablation  
rate at any wall temperature.

### 3. EXPERIMENTAL EQUIPMENT

#### 3.1 Heat Flux Concentrator

The maximum rate of pyrolysis in moving and fluidized beds is limited because of convective heat transfer through a boundary layer of evolving gases around each particle (Reed and Cowdery, 1986). The experiments of Lede (1985) and Diebold and Reed (1980) demonstrate that the heat transfer can be increased 10-100 times by a sliding contact with mechanically induced pressure between biomass and a heated surface. This type of heat transfer is defined as "contact pyrolysis".

Two separate pieces of experimental apparatus were employed in this research, a heat flux concentrator and a pyrolysis mill. Both pieces of equipment pyrolyzed wood using the same basic principle of heat transfer of conduction across moving interfaces. Both physically abraded the wood or charcoal that might form and both produced a pyrolysis vapor and gas that was collected in traps.

In 1986, Reed at the Solar Energy Research Institute (SERI) demonstrated the production of pyrolysis vapor by pressing a rotating birch dowel into a parabolic opening in a heated copper cylinder. Five grams of oil

was collected in a one minute period (Reed 1986). This heat flux concentrator prototype led to the apparatus described in this thesis.

A SERI contract given to Reed at the Colorado School Of Mines in February, 1986 to characterize the heat flux concentrator and to operate it as a source of pyrolysis vapor for evaluating the effect of various catalysts on wood vapor. The characterization of HFC operation is reflected in the mass and energy balances presented in this thesis.

A flow diagram of the of the concentrator apparatus is shown in Fig. 19. A diagram of the complete system with the catalyst bed is shown in Fig. 20. The catalyst tube is optional as is the catalyst furnace. The heat flux concentrator apparatus consisted of a wooden dowel fitted into the bit of a 1/2" "Shopcraft" drill press (Model T6742-20P) which then could be placed into the concentrator through the upper feed assembly. The upper feed assembly is a series of fittings including an upper seal and a gas port which can be used for introducing an inert gas or for sampling the pyrolysis vapor.

The concentrator itself consists of a copper cylinder with a parabolic hole at the top for the dowel and twelve holes at the bottom to vent the pyrolysis vapor. Six of the holes formed an inner circle and the other six surrounded

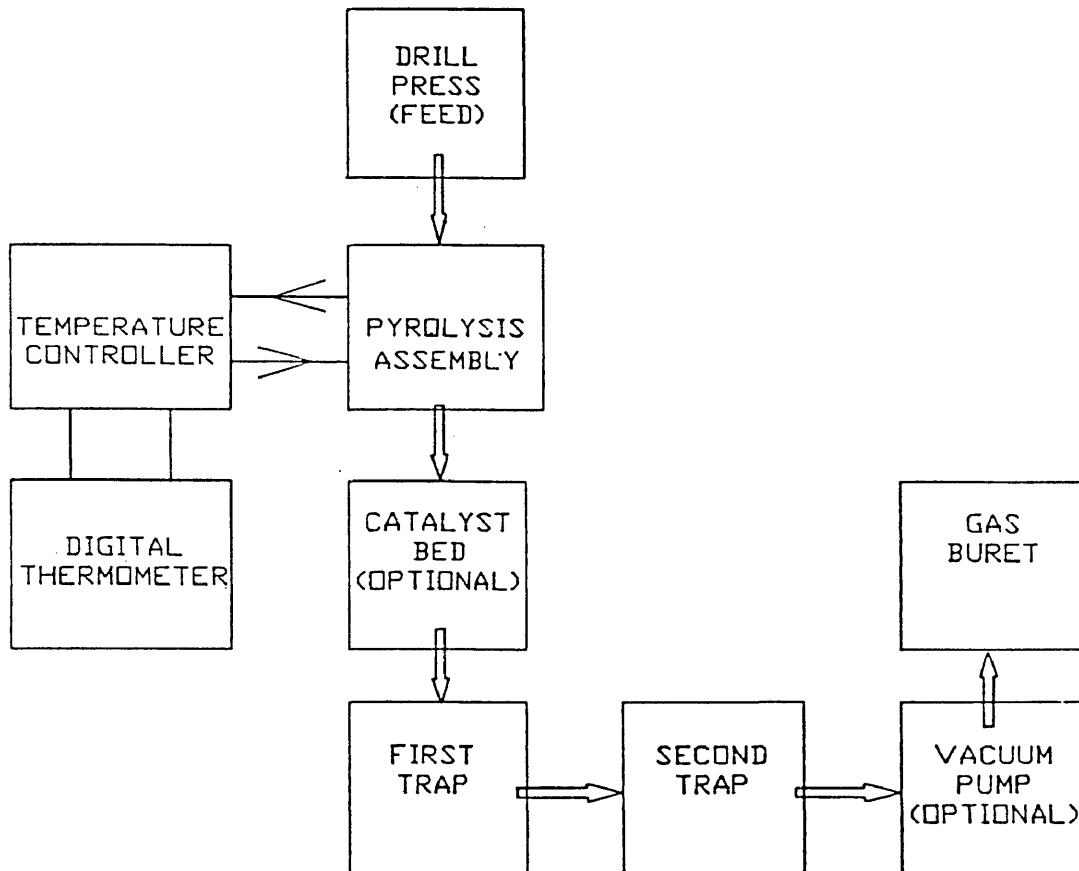


Figure 19: Flow Sheet of Heat Flux Concentrator Apparatus

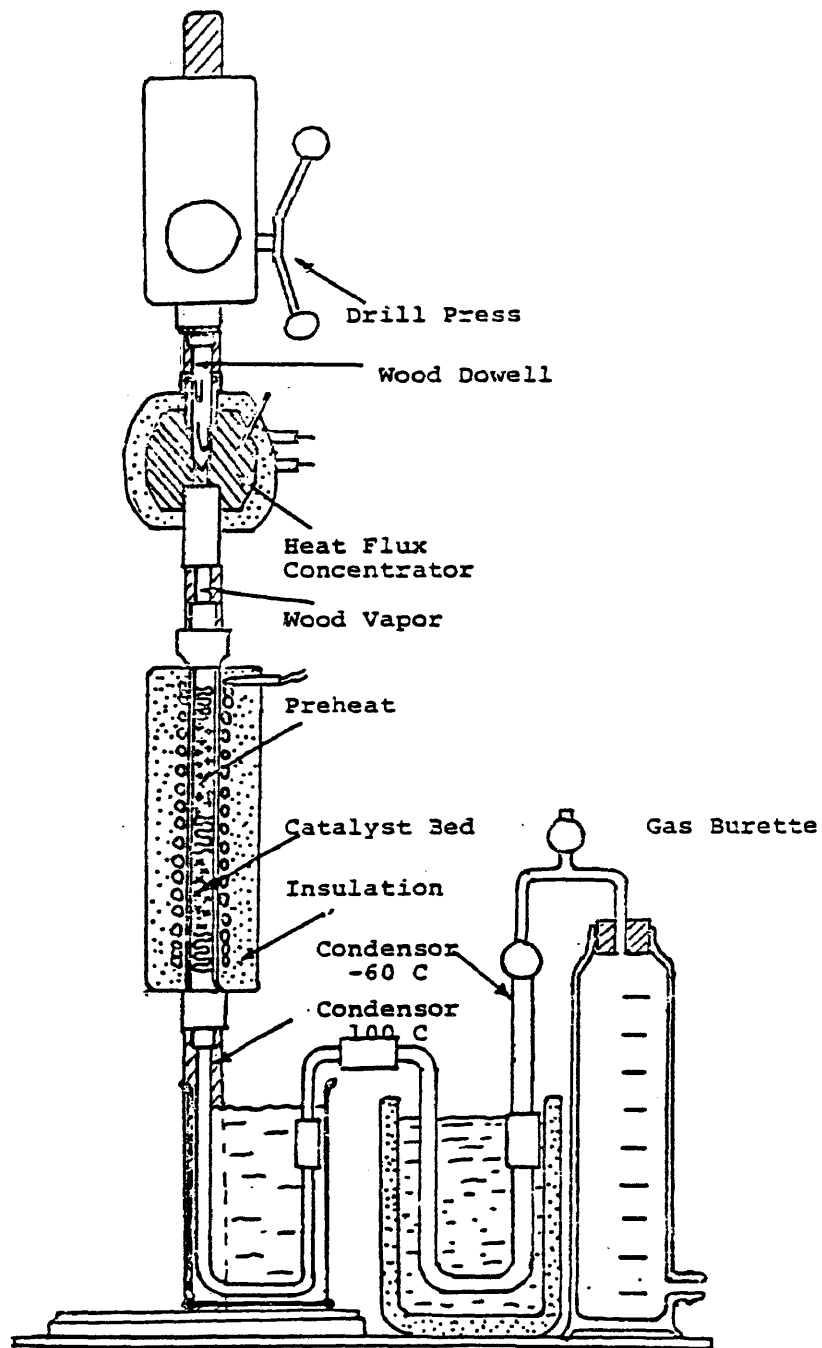


Figure 20: Heat Flux Concentrator Apparatus

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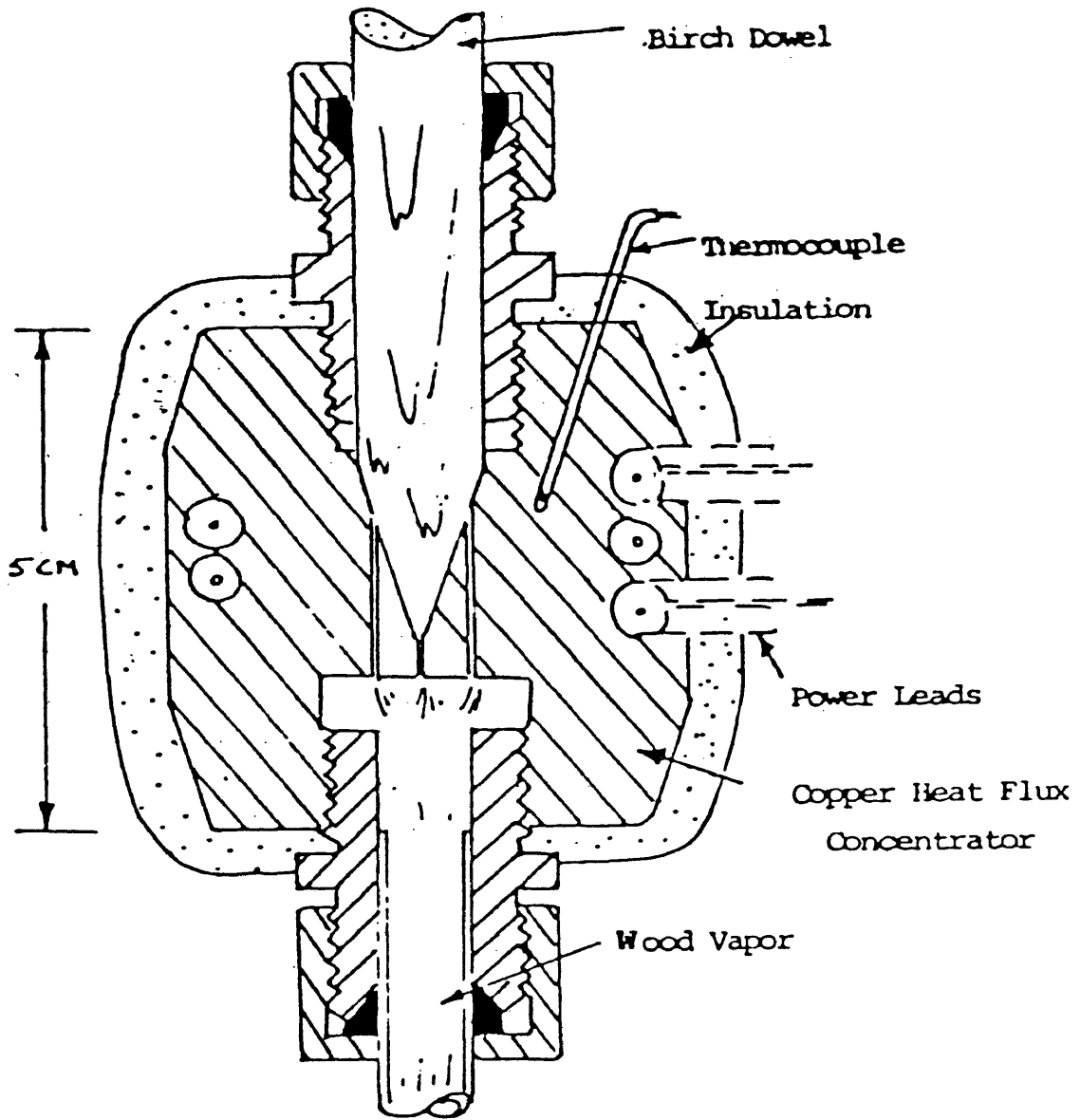


Figure 21: Exposed View of Heat Flux Concentrator  
-(Reed and Cowdery 1986)



bottom of the flux concentrator to catch any solids driven through the system. The first trap consists of a Pyrex tube fitted into a Pyrex manometer tube. The bath surrounding this trap consisted of either ice water or dry ice in an isopropyl alcohol, butyl alcohol, and ethylene glycol mixture. A rubber hose connects the first trap to the second trap.

Like the first trap, the second trap is also an old manometer tube with a fitted glass tube, but it is filled with quartz wool, since it is the final trap and needs to catch all the vapor to protect the vacuum pump. It sits in an ice water bath. The second trap was connected to a vacuum pump (Cole-Parmer Air Cadet model 7530-40) in later runs. From the exit nozzle, the gas is passed on to a glass buret filled with water. As the water is displaced in the buret the gas is collected. The displaced water is collected in a separatory funnel from which it can be used to refill the column or to give a nominal amount of head for pressurizing the gas in the buret. At the top of the buret is a valve that has been adapted so that a small sample cylinder can be attached for taking gas samples.

### 3.2 Pyrolysis Mill

The pyrolysis mill came about because in order to be

comercially useful a contact pyrolysis apparatus would need to accept random size particles rather than dowels as used in the HFC. In November, 1986, Dr. Thomas Reed was awarded a continuing contract from SERI to design and construct a "pyrolysis mill" to apply contact pyrolysis to random sized particles of wood and other types of biomass such as municipal solid waste.

The pyrolysis mill differs from the heat flux concentrator in several ways. The heat flux concentrator is designed to take only wood as a feed. Furthermore, this wood must be a solid mass and cylindrical in form. The pyrolysis mill is designed to take a pulverized feed such as sawdust. It can also accomodate municipal solid waste, rice hulls, pulverized rubber and plastics, and many other materials which produce hydrocarbons in the presence of heat. The pyrolysis mill is not as susceptible to clogging as the flux concentrator. It also is capable of producing a larger mass flow rate of vapor at a more consistant and even rate.

A flow diagram for the entire pyrolysis mill apparatus is shown in Fig. 22. An exposed view of the inside of the pyrolysis mill is shown in Fig. 23 The two plates are made of copper due to its high thermal conductivity. The plates are scored so that particles between them are driven

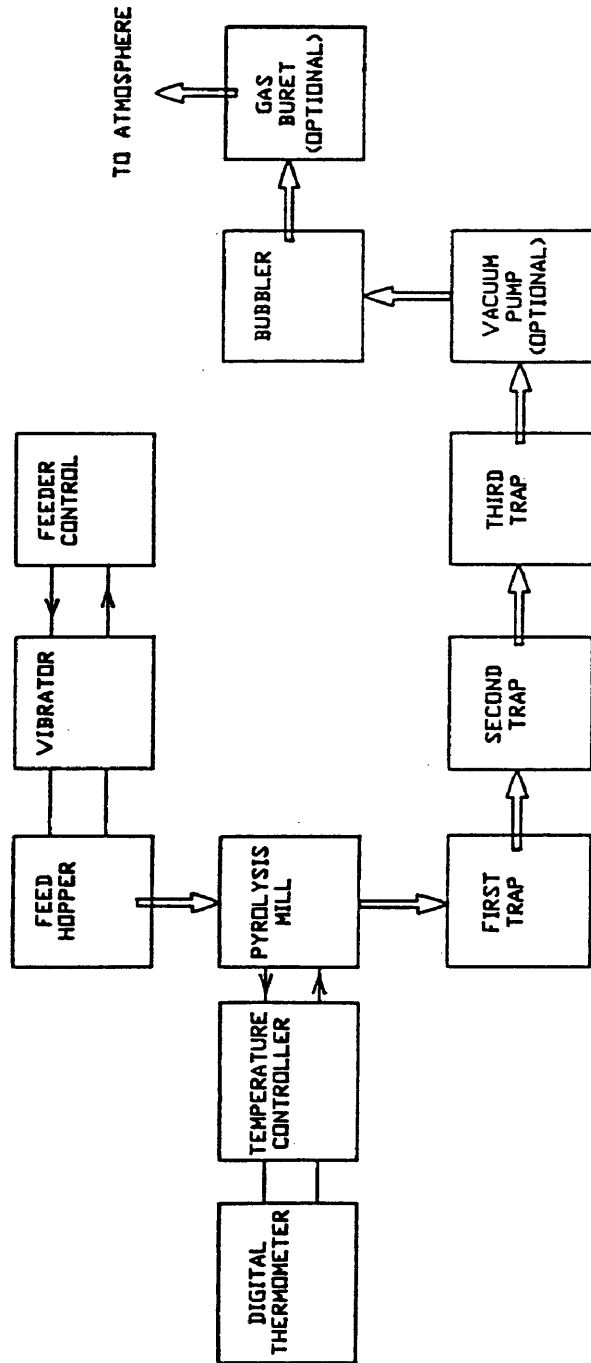


Figure 22: Flow Sheet of Pyrolysis Mill Apparatus

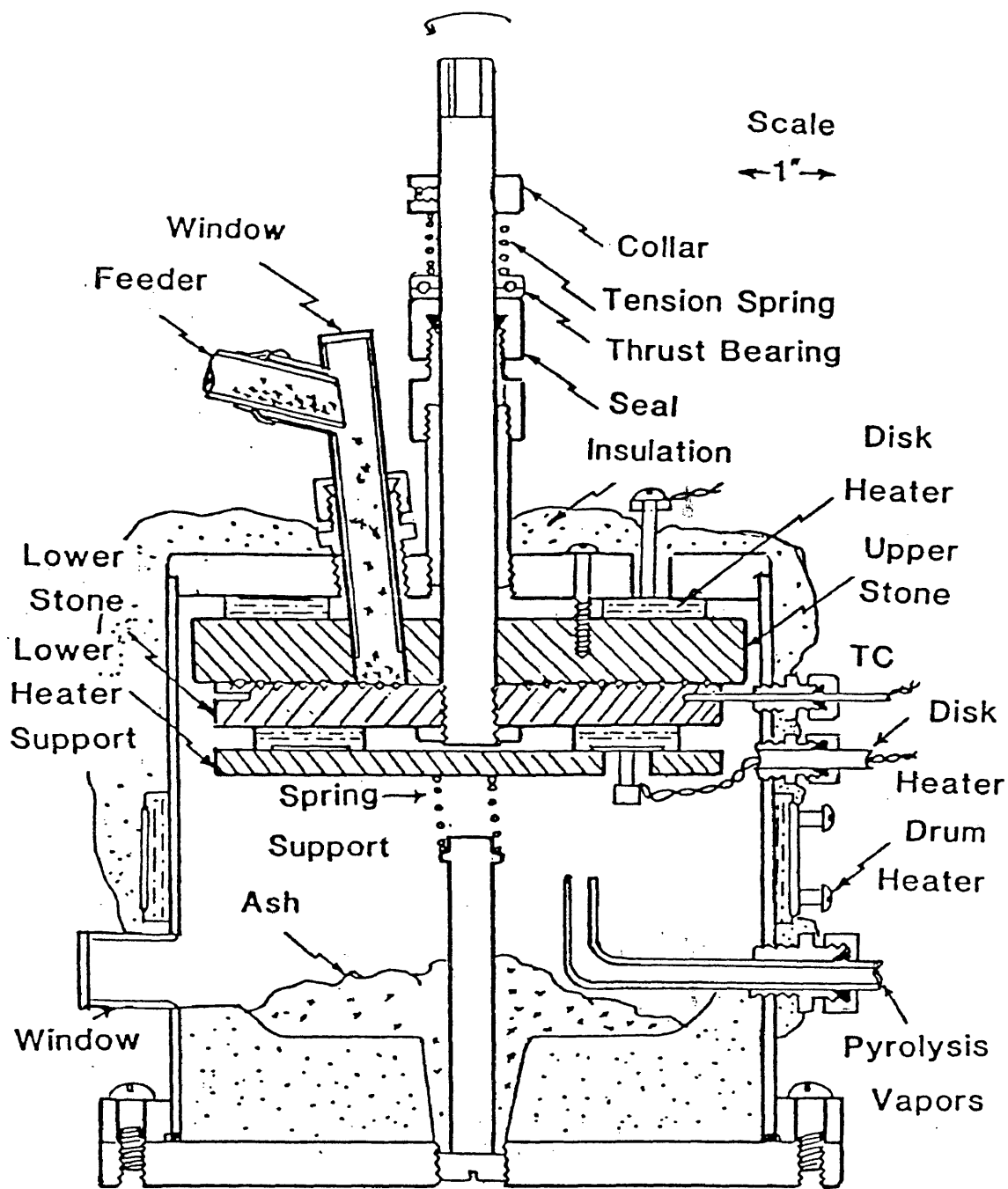


Figure 23: Exposed View of Pyrolysis Mill

outward. The effect of the scoring and the plate motion on particles is demonstrated in Fig. 24. The score patterns are such that not only do they aid in crushing the particle, but by working in combination with the circular motion of the bottom plate, they push char particles to the outside of the plate and so, unlike the flux concentrator, there is little char or coke build-up. The score pattern of the bottom plate is shown in Fig. 25. The bottom plate is scored with a different pattern on its bottom side and is made so that it can be turned over to test a different score pattern. The shaft comes through the top plate and a screw and roll pin holds the lower plate onto the the shaft.

The shaft is sealed with a Swagelock fitting and a nylon ferrule. The drill press used for the heat flux concentrator is the same as that used for the pyrolysis mill, but unlike the heat flux concentrator the drill press is used to drive the plates inside of the mill, instead of as a means of rotating the feed. A speed reducer supported by a 1/2" aluminum rod connected to the drill press support connects the bit to the main shaft. The speed reducer gave an eleven to one speed reduction. The speed of the drill press could be varied to give shaft speeds of between 35.5 and 72 rpm.

Heat is maintained on the top plate with a fixed 750

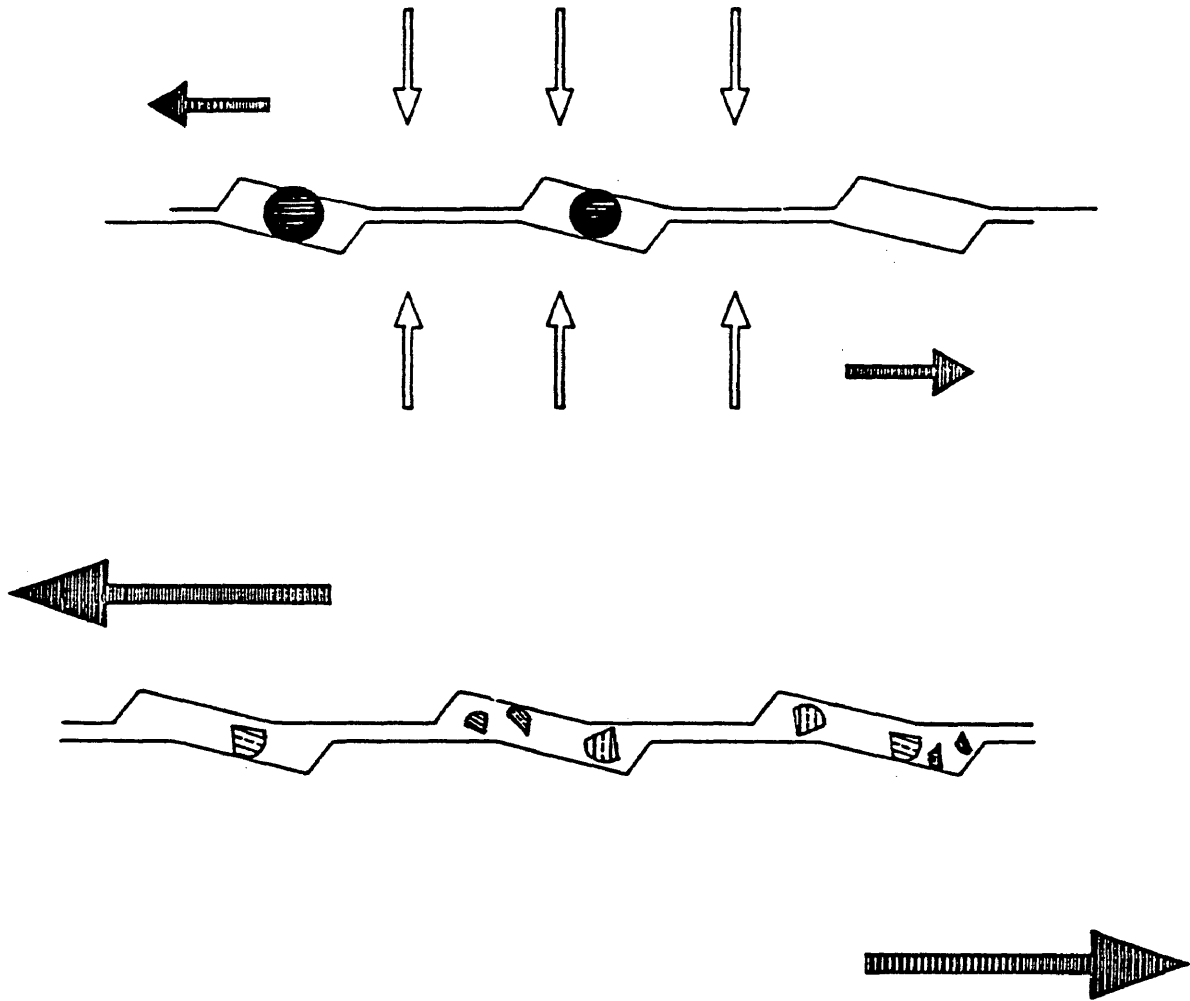


Figure 24: The Effect of Scoring and Plate Motion on Particle Abrasion

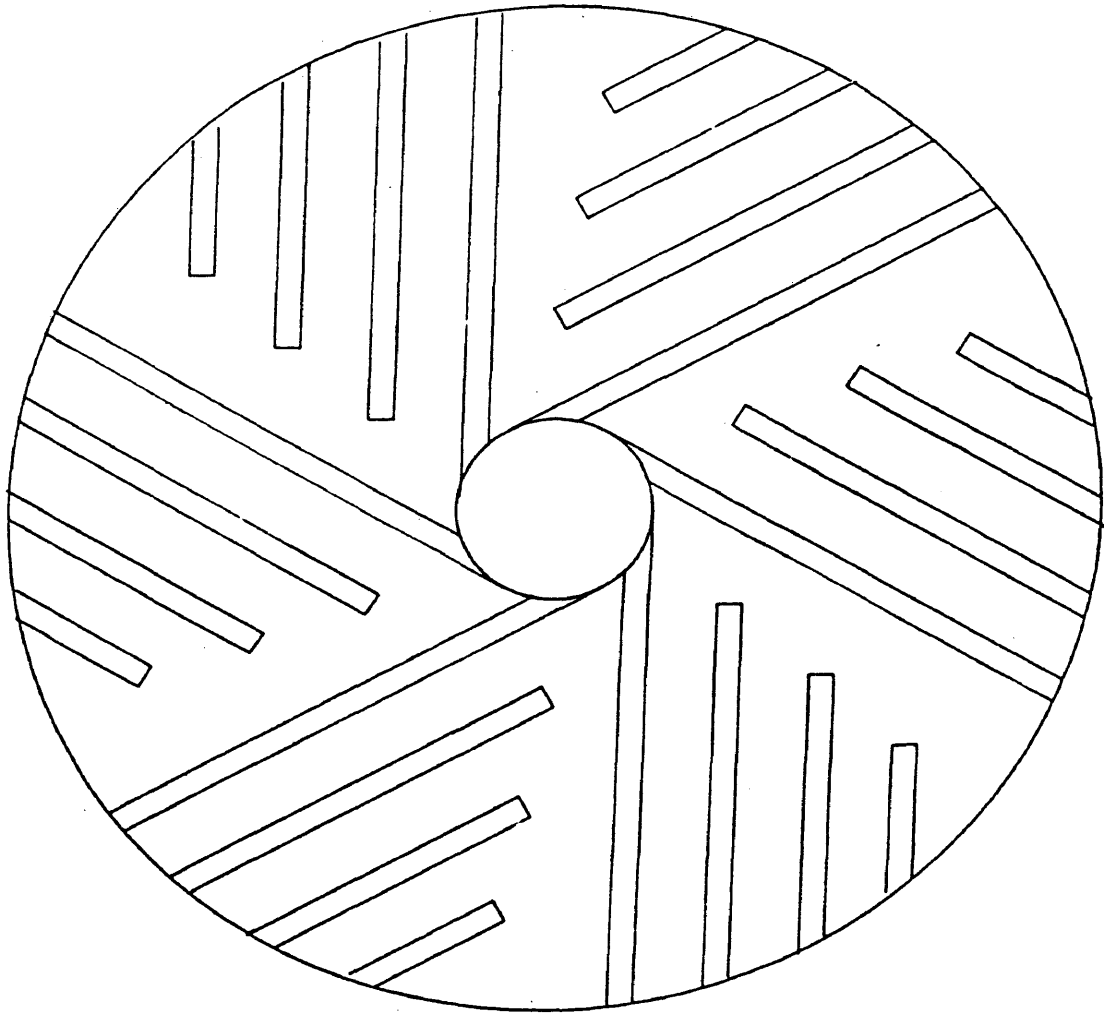


Figure 25: Score Pattern Used on Pyrolysis Mill

watt disc heater. A thermocouple port enters the side of the drum and extends about 1/2" into the top plate. The temperature is measured with a type "K" thermocouple. The bottom plate has a fixed 550 watt disk heat, which is supported by a 1/2" stainless steel plate and presses against the rotating copper disk. Since the bottom plate has to be free to turn, a slot extends around the circumference of the lower plate for a thermocouple. A model 6103 Omega controller maintains the temperature of both plates or a pair of Omega time proportional controllers (models 6103 and 6102) controls each plate individually. Like the flux concentrator, the power to the controller comes through the power meter built by Tipi Workshop and, as before, the power meter draws it's power from a voltage stabilization transformer. The temperature of either plate, the drum temperature, the bath temperature, and ambient temperature can be read from the digital thermometer.

Pressure between the two plates is maintained by a collar near the top of the shaft that compresses a spring sitting on top of a compression bearing. The compression bearing rides on the top of the Swagelock fitting for the shaft seal. Pressure between the plates can also be applied by a spring assembly that pushes upward from the bottom of



the drum onto the bottom heater support plate. The spring tension can be adjusted from outside of the mill by turning a threaded rod at the bottom of the mill.

The drum itself has a 1100 watt band or drum heater encircling its midsection. Unlike the disk heater, there is no temperature control on the band heater and, generally, it is used only for preheating the unit. The bottom of the drum is sealed with a brass flange. This makes possible the removal of char, ash, and any non-combustible material that may be left behind. A teflon ring seals the flange. Built into the bottom plate of the drum is an even smaller plate sealed with a teflon ring. The entire drum is supported about 5 " above the bench by four posts and these in turn are bolted down directly into the bench.

The feed assembly is supported by a Uni-strut bar attached to the support pole of the drill press. The hopper consists of a clear plastic juice bottle with a pyrex tube extending from its bottom. At the top of the bottle is a hole and a rubber stopper from which the feed can be replenished. The pyrex tube goes into a rubber boot attached to a 3/4" copper tee. At the top end of the copper tee is an opening which either a solid stopper or a stopper with a 1/4" tube for a nitrogen carrier gas can be placed. A 1/4" plastic hose connects the 1/4" tubing via "Swagelock"

fittings to a metering valve, a gas regulator, and a 10.75 cu. ft. tank of nitrogen.

The feed is propelled through the pyrex tube by a vibrator attached to the bottom of the juice bottle by a 1/2" threaded aluminum rod. The vibrator is controlled by a Vibratory Feeder Company type 5 controller. The feeder control calibration curve is shown in Fig. 26. The feeder control could not be operated below a setting of 26 because there was no flow rate or above a setting of 80 because the hopper would shake apart.

Quarter inch stainless steel tubing takes the pyrolysis vapors out of the drum and into the first trap. The first and second traps are Erlenmeyer type filter flasks with 1/4" steel tubing inserted through rubber stoppers. The traps are in ice water baths. The third trap is exactly the same as the first two traps except that it is also filled with quartz wool and has a valve attached to a 1/2" steel tubing held by a 1/2" Swagelock fittings. Finally, the pyrolysis gases and vapors are directed into a bubbler, which like the other traps, is an Erlenmeyer type filter flask but is filled with water. This cleans the gas and allows rough estimates of the total volumetric flow rate. From the bubbler, the pyrolysis vapors are released to the atmosphere but the option does exist of collecting the gas

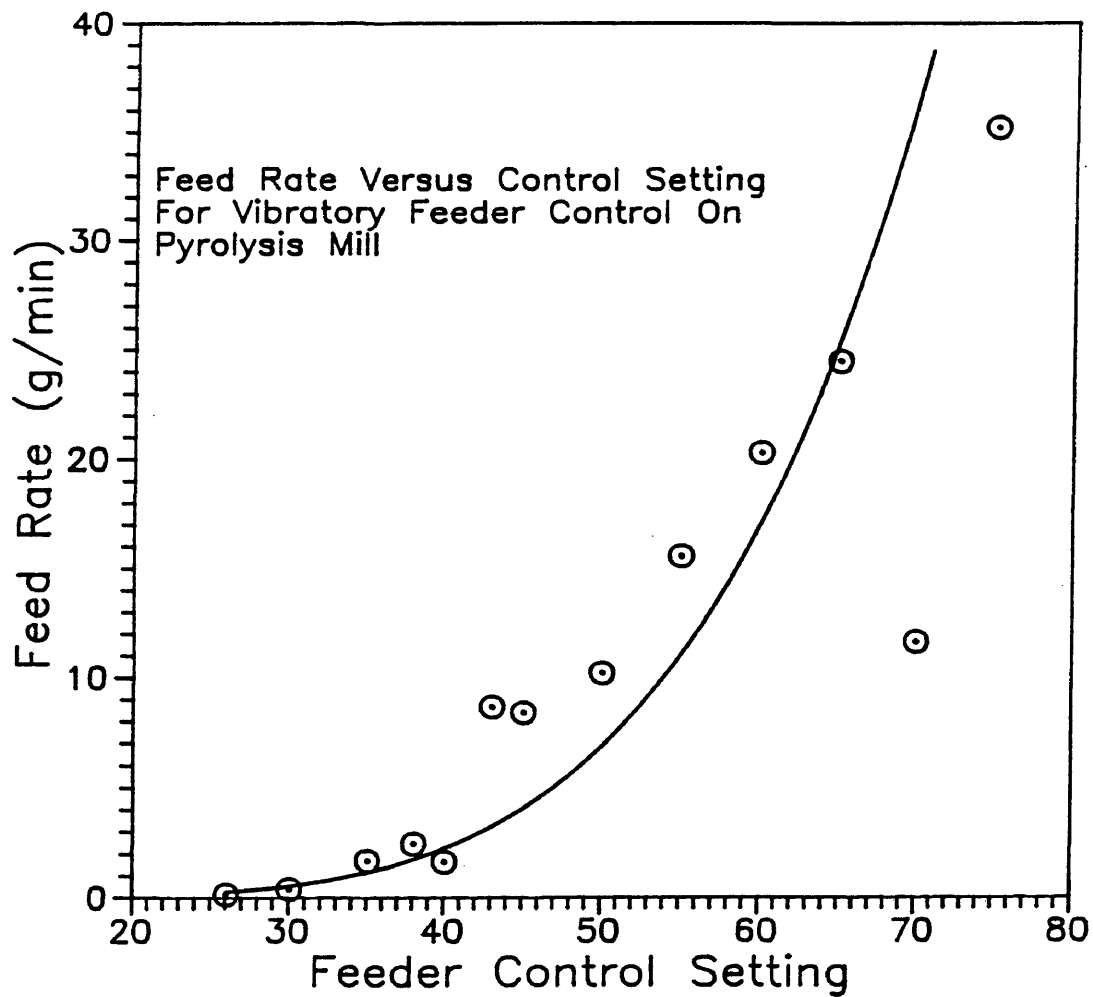


Figure 26: Feed Rate Versus Control Setting for  
Vibratory Feeder Control on Pyrolysis  
Mill

in the gas buret apparatus used with heat flux concentrator for flow rate measurement or for taking a gas sample.

### 3.3 Power Meter Calibration

In order to determine the effectiveness of the power meter built by Tipi Workshop, some knowledge of its accuracy is needed. A resistor with a measured resistance of 52.2 ohms was placed in two liters of water. The power was supplied through a regular 120 volt outlet. The temperature rise of the water with time is shown in Fig. 27. After 435 seconds the power was shut off. The rise in the water temperature prior to the power being shut off gave a value of 279.4 watts. Since the average temperature over which this calibration took place was close to room temperature, the heat losses were neglected. The reading on the power meter was 274 watts. A multimeter was used to calculate the wattage on the same resistor and it measured 277.8 watts.

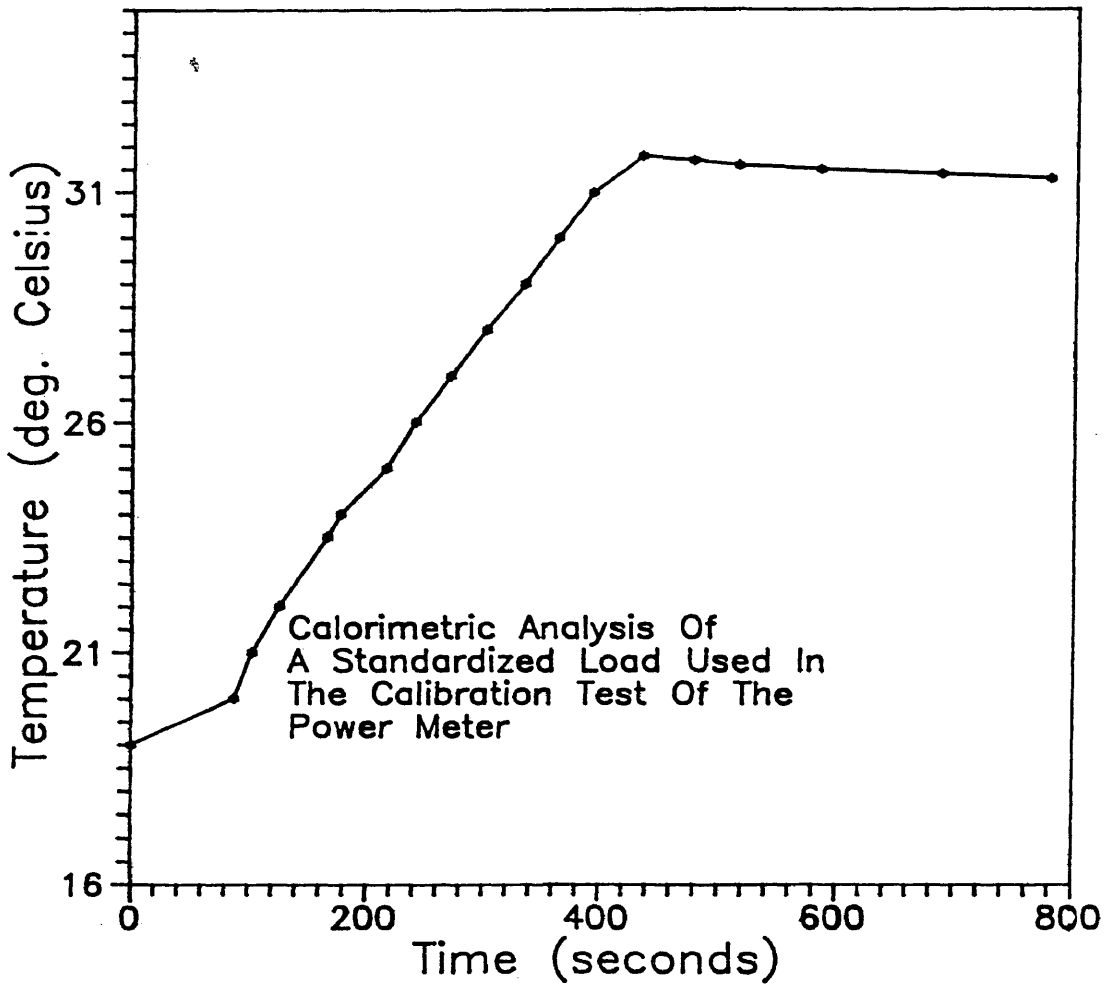


Figure 27: Temperature Versus Time for the Calibration of a Power Meter Using Standardized Resistor in a Water Bath

## 4. EXPERIMENTAL PROCEDURE

### 4.1 Heat Flux Concentrator

#### 4.1.1 Feed Preparation

The feed for all of the runs on the heat flux concentrator was 1/2" birch dowels. The only main variation in the feed was that some of the dowels were pre-dried in an oven at 160 degrees Celsius for approximately one week. The dowels were then put in the drill press and sanded since they were slightly larger than the upper seal and to ensure a smooth surface so that there was a good seal. The dowels were generally about 20 inches long and could be used for two to four runs before they became too short.

#### 4.1.2 Apparatus Preparation

The weight of the feed was recorded as was the weight of the two traps, the lower assembly, the upper assembly, and the flux concentrator prior to assembly. The screen was weighed with the flux concentrator instead of with the lower assembly since it collected principally solids and the change in weight of the lower assembly was due to liquid product coating its inner walls. The upper assembly was then screwed into the flux concentrator. The lower assembly was screwed into the bottom of the flux concentrator such that it fit through the insulation block and the support

bar. It was then fastened to the support bar with two screws to keep it from turning. The traps were assembled and fitted into the lower assembly and the gas buret was filled.

The controller was then connected and the thermocouples were attached. The concentrator was allowed to reach its operating temperature. Once the operating temperature was reached, the ambient temperature, the temperature of both baths, and the temperature at both the top and bottom of the flux concentrator were recorded. The chart recorder was then turned on and zeroed. The chart speed was set at 10 cm./min. The date and run number were marked on the recorder paper. The chart recorder was allowed to run for ten minutes or so to get a baseline value for the energy balance. In other words, the power, as a function of time, required to maintain the concentrator at the set temperature was measured on the recorder via the power meter. This power represented heat loss mainly through radiation and convection to the environment.

#### 4.1.3 The Experimental Run

To start the experimental run, the wood was clamped into the chuck of the drill press and the other end was inserted into the top assembly far enough to get a good

seal, but not far enough to touch the heated flux concentrator. The ferrule was then tightened down enough to make a good seal, but not so tight as to restrict the rotation of the dowel. At approximately the same time as the wood was lowered into the concentrator, the chart paper was marked to show the beginning of the run for the power measurement, the valve to the gas buret was opened and, if the vacuum pump was used, it was then turned on. The wood was pushed into the concentrator using the gear built into the drill press. Generally, the run was halted when the holes at the bottom of the concentrator becomes so clogged that it forced pyrolysis vapor back out of some joint, either in the upper part of the concentrator or in the upper assembly. At this point the chart paper was again marked and the wood was pulled out of the concentrator. The top ferrule was plugged with a rubber stopper since lost vapor couldn't be accounted for in the mass balance and since oxygen could get into the system and cause combustion of the products.

#### 4.1.4 Post Run Procedure

After the run, the apparatus remained fairly close to it's reaction temperature. Since the liquid product was constantly evaporating, the apparatus was broken down immediately and weighed. The oil in the first trap was



poured into a sample bottle and sealed. On some runs a gas cylinder was cooled with dry ice and then attached to the gas buret to collect a sample. The cylinder was then allowed to reach room temperature and was then hooked to a gas chromatograph for sample analysis.

After all measurements were made and the unit was cooled down to room temperature the concentrator was cleaned. Since the insulation on the outside of the concentrator tended to absorb moisture from the air and lose this moisture during the heating of the unit, an apparent heat loss would appear in the calculations. To get around this problem, the solids pushed out of the concentrator were weighed and recorded as the change in weight of the flux concentrator, therefore the concentrator had to be cleaned thoroughly after each run.

After the weights of the traps and the volume of gas in the gas buret were recorded, the chart paper was removed from the recorder. The baseline energy was calculated by integrating the power versus time line made by the recorder. Since the peaks were square, the integration of the curve could be obtained by multiplying the width of each peak (time) by it's height (power). This gave the energy consumed over a given time period. To get a baseline power measurement, the energy was then divided by the total time

period over which the peaks were measured. In a likewise manner, the power during the actual run was determined. The difference between these powers was then multiplied by the run time and divided by the mass of wood pyrolyzed. This gave the heat for pyrolysis on a weight basis.

## 4.2 Pyrolysis Mill

### 4.2.1 Apparatus Set Up

The pyrolysis mill, being very similar in principle to the heat flux concentrator, had very similar operating procedures. Unlike the concentrator, there was no feed preparation. The feed was simply put into the feed hopper and sealed with a rubber stopper. Generally, the pyrolysis mill had to be partially reassembled prior to operation. When this was completed, the drum heater was plugged in to start heating the unit. The voltage stabilization transformer was kept plugged in, since it took at least fifteen minutes warm up. The top and bottom plate heaters were plugged into the transformer via the power meter and allowed to reach operating temperature.

The feeder bottle was weighed and the feeder apparatus was assembled. The three traps and bubbler were weighed and assembled. The three baths were filled with ice water. Nitrogen was introduced into the system at this point at

about 1 cubic centimeter per second. The nitrogen was added early to preheat the pyrolysis vapor out take tube and to replace the air in the system with an inert environment. There was a great deal of trouble maintaining and measuring the nitrogen flow since the metering valve and gas regulator generally had to be turned down about ten times before each run because the lines would clean themselves, thereby reducing the restriction to flow.

Insulation was then placed around the outside of the drum, the pyrolysis out-take tube, and the copper feed tube. The bearings around the drive shaft were wrapped with a paper towel soaked with water. This was to reduce thermal expansion in the shaft which caused binding. Throughout the run the towel had to be resoaked due to evaporation. Temperatures were recorded for room, the three baths, the drum, and the upper and lower plates.

The chart recorder was turned on, zeroed, and set at either 5 or 10 cm. per minute. The chart paper was marked with the date and run number. Then the recorder was allowed to run for about ten minutes to get a baseline for the energy balance.

#### 4.2.2 Experimental Run Procedure

The drill press was turned on and set for rotational

speed (35 to 75 rpm). The feed was started by setting the feeder control at forty. The recorder paper was marked for the start of the run. Any leaks in the system generally became very apparent at this point and if small enough, were patched using a high temperature silicone cement. An optional gas sample and a gas flow rate could be measured at this point by removing the rubber hose to the bubbler and hooking it up to the gas buret. The mill could be run for much longer periods of time than the flux concentrator. Unless the out take tube clogged, the run was generally stopped when the time objective set before the run was reached. At this point the drill press, the recorder, and the controllers were shut off.

#### 4.2.3 Post-run Procedure

The traps and bubbler were disassembled and weighed. The oil in traps one and two was collected, put in a sample bottle, and labeled. After the unit had cooled down, the bottom flange plate was removed and all the ash and char was cleaned out, weighed, and recorded. The power requirements with and without the feed were calculated for the energy balance in the same manner as the heat flux concentrator. As before, the difference in power was calculated and multiplied by the length of the run time. It was then divided by the weight of the wood pyrolyzed to get the

heat for pyrolysis.

## 5. RESULTS AND DISCUSSION

### 5.1 Heat Flux Concentrator

#### 5.1.1 Feed Characteristics

The birch dowels were a consistent feed source, although there was some variation in cross-sectional area due to over sanding. A breakdown of some of the dimensions and densities of the feed is given in Table 5. In most of the calculations involving these dimensions an average was used rather than making the measurement on each piece of wood.

#### 5.1.2 Effect of Operating Parameters

##### 5.1.2.1 Overall Analysis Of Parameter Effects

For the heat flux concentrator, there were only three independent variables, temperature, the mechanically induced pressure at the interface, and the pressure below the reaction area. The temperature had an electronic proportional controller and varied over a range of only a few degrees Centigrade during a run at lower temperatures. At the highest temperature of 700 degrees Centigrade the temperature dropped about twelve degrees (due to the heaters' inability to maintain the heat flux requirements at this temperature). On the other hand, the interface

Table 5: Physical Characteristics Of Birch Dowel Feed For Flux Concentrator .

	Cross-sectional Area (sq cm)	Length (cm)	Weight (g)	Density (g/cu cm)
1-	1.22	38.08	29.81	0.643
2-	1.10	13.74	10.13	0.672
3-	1.28	12.71	11.69	0.720
4-	1.12	7.09	4.38	0.552
5-	1.10			
Average	1.16			0.647
Std. Dev.	0.08			0.071

pressure was a loosely controlled variable, in that the pressure was mechanically controlled by the operator and his or her judgement of the force exerted on the handle of the drill press without any kind of feedback. This led to a wide variation in pressure since even if there is an equivalent force exerted, the surface area of the interface can vary between dowels and throughout a run due to the build up of char.

The principle variable to be investigated was the effect of the variation of temperature on heat for pyrolysis and the heat of pyrolysis. Since one variable, the mechanical pressure, changed independently of the principle variable being investigated this led to a scattering of the data. One way around this, was to examine the effect of the effect of the feed rate, since the feed rate was dependent on both the temperature and the mechanical pressure.

The mass balance data taken on the heat flux concentrator was an attempt to get an accounting of both the material input and material output of the concentrator. Many previous studies on pyrolyzers measured the feed and the liquid and solid products. The mass of gas was then calculated by difference. Although this is a much easier method, it easily leads to error in the gas



measurement and gives no indication of the error involved in the other mass balance measurements. The data on all the flux concentrator runs and the percent closure of the mass balance where applicable is given in Table 6. In some cases, it was only possible to measure some of the product components due equipment malfunctions i.e. leaks in the traps, gas buret, or weight gain due to moisture absorption by the insulation.

#### 5.1.2.2 Effect of Temperature

Although the temperature of the concentrator was being varied the actual temperature at the surface of the wood, probably remains constant over the range of this study as detailed by Lede (1985). The real effect of increasing the temperature is to increase the driving force in the heat flux equation (equation 6). This allows for higher yields of the liquid product because it supplies more heat for the endothermic reaction going from the active cellulose. This in turn allows for a higher feed rate and less residence time at high temperature. The lower the residence time, the less time for the kinetics to continue towards the coking of the oil (as shown in Fig. 16).

The relationship between temperature and weight percent of the product as based on the feed is shown in Table 7.

Table 6: Mass and Energy Balance Measurements on the  
Heat Flux Concentrator

Run No.	Temperature (deg C)	Wood (g)	Liquid (g)	Gas (g)	Char (g)	Mass Bal. Closure (%)	Power w/o Wood (Watts)	Power With Wood (Watts)
A-17	394	3.33	1.93	0.63	0.49	91.6		
A-15	397	5.43	4	0.60	0.48	93.6		
B-2	432	5.11			0.75			
A-16	438	3.31	2.31	0.56	0.48	101.2		
A-32	450	2.77	1.34	1.04	0.58	106.7		
A-29	473	2.57	0.78	0.76	0.59	83.0	172.63	187.36
A-14	475	4.21	0.64					
A-31	498	3.91	1.35	0.79	0.86	76.7	179.26	215.65
A-36	499	4.81	2.62	1.05	0.75	91.8	195.34	222.63
A-9	500	6.1	3.96	0.69	0.75	88.5		
A-24	504	1.94			0.5			
B-8	520	6.95			0.19			
A-20	521	3.99	1.67	0.66				
A-39	526	2.49	1.28	0.84	0.56	107.5	166.41	190.58
A-30	548	3.4	1.54		0.58		200.33	226.95
A-4	550	2.65	1.39					
A-6	550	3.18			0.53			
A-28	598	3.73	1.67	1.04	0.59	88.5	222.85	279.4
A-8	600	5.59	3.84	0.53				
A-38	624	3.21			0.5			
A-34	648	4.66	1.64	0.93	0.58	67.7		
A-35	648	6.58	3.23	1.04				
A-12	650	5.47	3.56	0.44	0.47	81.8		
A-13	650	4.65	3.75	0.42	0.43	98.9		
A-26	677	3.51	1.85	1.08	0.32	92.7		
A-10	700	5.65			0.49			
A-11	700	4.21	2.71	0.52	0.42	86.7		

Table 7: Temperature and Product Weight Percent From  
the Heat Flux Concentrator

Run No.	Temperature (deg C)	Liquid (%)	Gas (%)	Char (%)
A-17	394	58.0	18.9	14.7
A-15	397	73.7	11.1	8.8
B-2	432			14.7
A-16	438	69.8	16.9	14.5
A-32	450	48.4	37.4	20.9
A-29	473	30.4	29.7	23.0
A-14	475		15.1	
A-31	498	34.5	20.2	22.0
A-36	499	54.5	21.7	15.6
A-9	500	64.9	11.3	12.3
A-24	504			25.8
A-20	521	41.9	16.6	
A-39	526	51.4	33.6	22.5
A-30	548	45.3		17.1
A-4	550	52.5		
A-6	550			16.7
A-28	598	44.8	27.9	15.8
A-8	600	68.7	9.4	
A-38	624			15.6
A-34	648	35.2	20.0	12.4
A-35	648	49.1	15.8	
A-12	650	65.1	8.1	8.6
A-13	650	80.6	9.0	9.2
A-26	677	52.7	30.9	9.1
A-10	700			8.7
A-11	700	64.4	12.4	10.0

These values are demonstrated graphically in Figs. 28 and 29. The dashed line was fitted using linear regression and doesn't accurately describe a trend since there is too much scattering of the data , but rather shows an approximate average.

There is a stronger relationship between feed rate and temperature, although the amount of scatter still had a effect on the quality of the data. The data for feed rate and temperature is given in Table 8. This data was plotted as shown in Fig. 30. The scatter in this data, as before, is probably due to the variation in pressure.

#### 5.1.2.3 Effect of Pressure

There were several areas in the whole concentrator apparatus where pressure played an important role. Basically, there were three operating pressures, in the upper assembly and in the pyrolyzer itself above the reaction interface, the pressure exerted at the reaction interface, and the pressure directly below the interface and on through the system. None of these pressures were measured directly but the interface pressure was derived using other relations from Lede (1985). The pressure below the interface was varied through the use of a vacuum pump.

The pressure above the interface wouldn't normally be important to the efficiency of the system if weren't for a

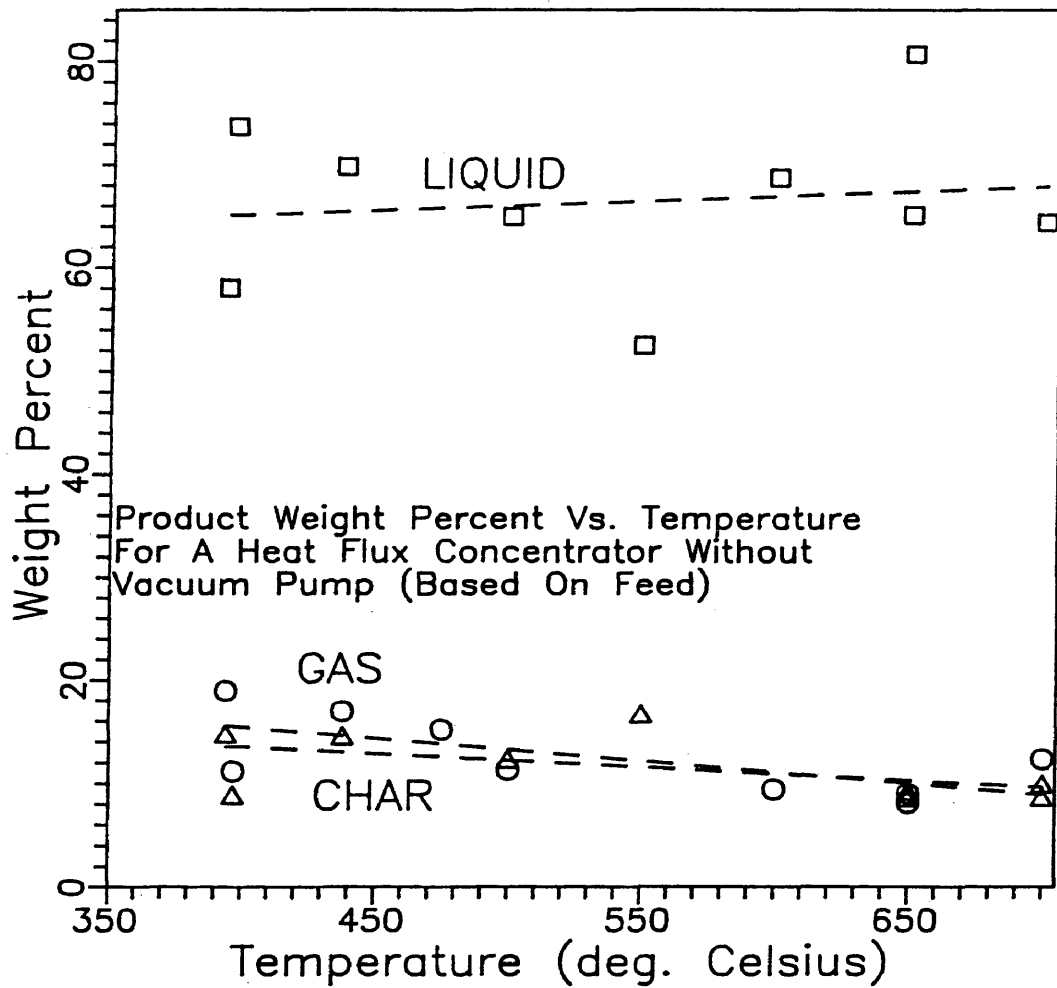


Figure 28: Product Weight Percent Versus Temperature for a Heat Flux Concentrator Without a Vacuum Pump

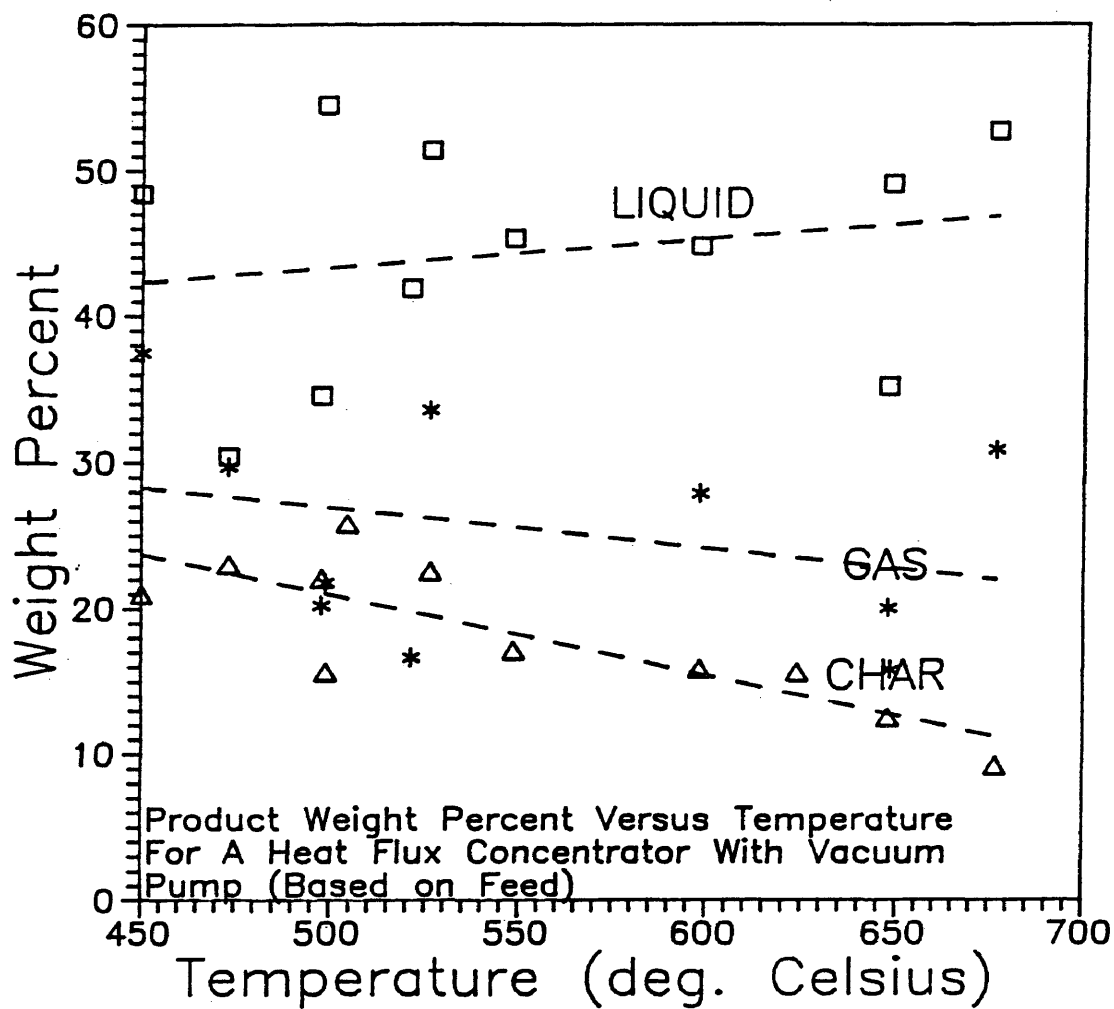


Figure 29: Product Weight Percent Versus Temperature for a Heat Flux Concentrator With a Vacuum Pump

Table 8: Feed Rate and Run Time of Experiments on a Heat Flux Concentrator

<u>Run No.</u>	Temperature (deg C)	Feed Rate (g/s)	Run Time (s)
A-32	450	0.027	101.4
A-29	473	0.028	93
A-31	498	0.050	78
A-36	499	0.038	126
A-24	504	0.025	78
A-39	526	0.033	74.4
A-30	548	0.025	135
A-28	598	0.031	121.2
A-38	624	0.041	78
A-35	648	0.046	142.2
A-26	677	0.057	61.8
A-16	438	0.042	78.6

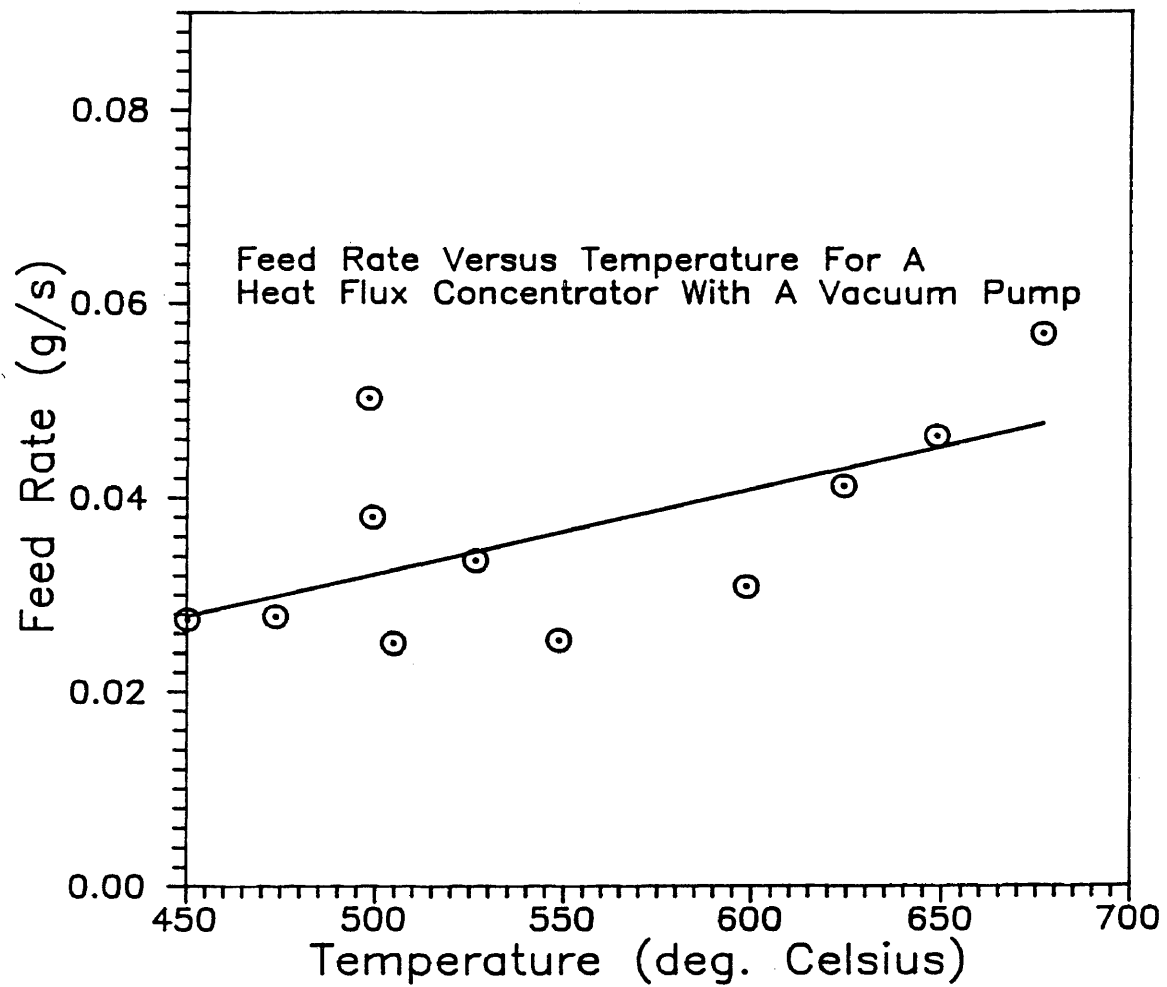


Figure 30: Feed Rate Versus Temperature for a Heat Flux Concentrator With a Vacuum Pump



tendency for this area to leak. The leaks in this area had two effects. As the pressure in this area increased, there was more of a tendency to lose a small amount of the vapor phase (both oil and gases). On the other hand, the increasing pressure also kept air from entering the system. An influx of air, of course, could have caused a combustion reaction and make the overall system more exothermic and lower the amount of oil produced and its value as a fuel. On one run, the system had a leak and the char in the reactor continued to burn for several minutes. This upper pressure was influenced by the heat flux and, thus, the feed rate, since increasing the feed rate increased the volumetric flow of gases. It also seemed to be affected by the vacuum pump in that the vacuum pump lowered the overall pressure of the system. The only evidence of variation in this pressure may be the exothermic nature of the system at lower temperatures.

A rough estimate of the pressure at the interface was made using a small stress gage to measure the approximate force exerted. The area of the interface was calculated using the formula for the surface area of a prolate spheroid and dividing it in half. From Perry (1978) the surface area is:

$$A = 2(\pi)L_b^2 + 2(\pi)(L_a L_b/e) \sin^{-1}e \quad (12)$$

where  $e$  is the eccentricity and  $L_a$  is half the length of the major axis and  $L_b$  is half the length of the minor axis. This yielded a value of 6.00 sq cm. Combined with the approximate force, this exerted a pressure of 166.7 psi or 1,150,000 Pascals.

An alternative method of obtaining the interface pressure was through the relationships experimentally derived by Lede (1985). Using equations 9 and 11, the pressure and an ablation rate equivalent to the geometry of Lede's spinning disk experiment were calculated. The values obtained are summarized in Table 9. The negative value is due to a wall temperature below 739K, which is the temperature at which the ablation rate should go to zero according to the Lede model. These values correspond favorably to the estimate of pressure as presented above.

A plot of the calculated interface pressure and the weight percent of the products produced is shown in Fig. 31. A plausible explanation for the reduction in liquid product and the increase in char and gas is that higher pressures promote coking. This is logical since higher pressures will reduce the ability of the oil to vaporize and pass out of the reaction area. Liquid product in the

Table 9: Feed Rate, Calculated Ablation Rate and Calculated Interface Pressure of a Heat Flux Concentrator

Run No.	Feed Rate (g/s)	Equivalent Ablation Rate (m/s)	Pressure ( $\times 10^6$ Pa)
A-32	0.027	0.000368	-1.71
A-29	0.028	0.000368	3.64
A-31	0.050	0.000667	1.54
A-36	0.038	0.000508	1.13
A-24	0.025	0.000331	0.63
A-39	0.033	0.000446	0.55
A-30	0.025	0.000335	0.30
A-28	0.031	0.000410	0.23
A-38	0.041	0.000548	0.26
A-35	0.046	0.000616	0.25
A-26	0.057	0.000756	0.26

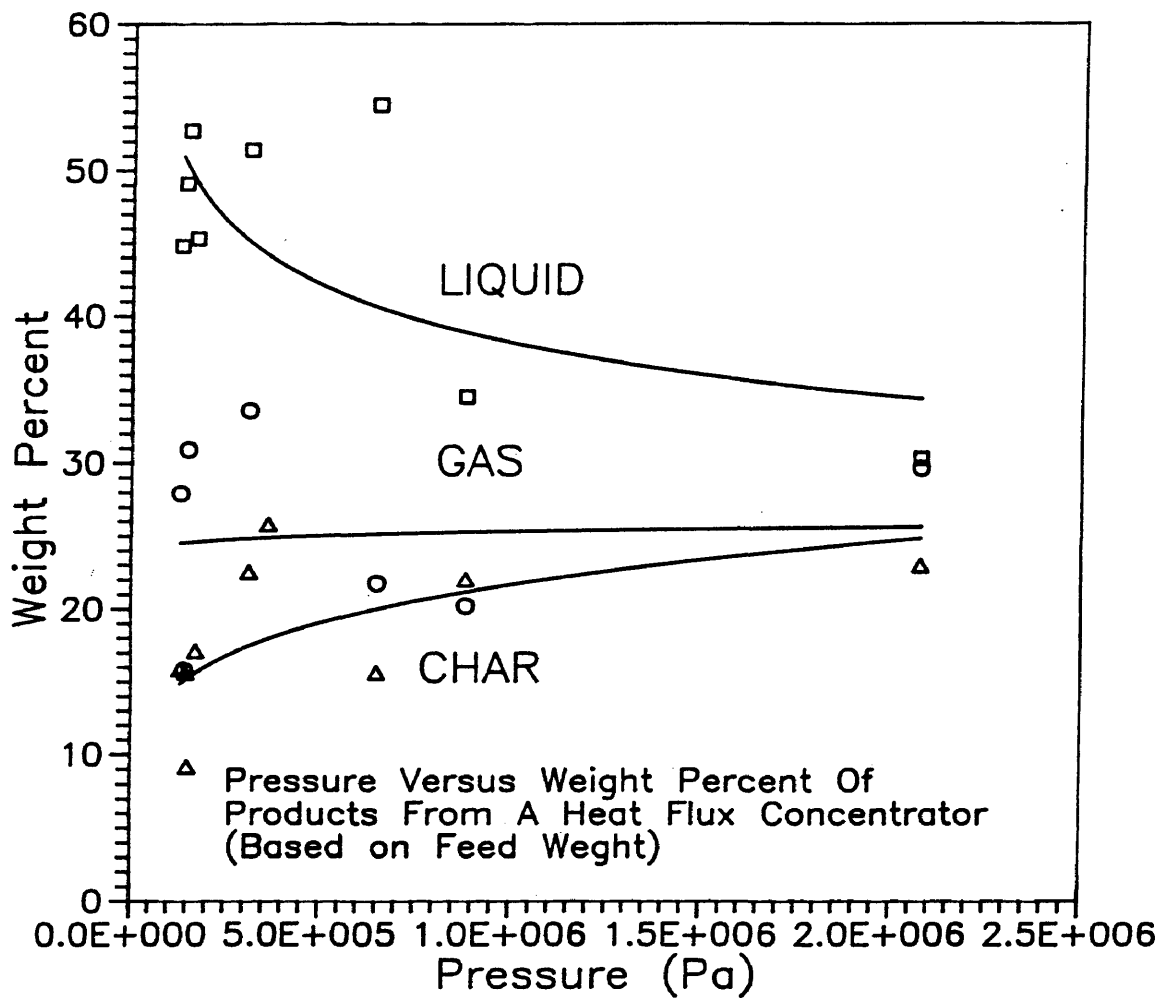


Figure 31: Product Weight Percent Vesus Mechanically Induced Pressure for a Heat Flux Concentrator

reaction area will have greater residence times and will undergo the coking reaction. A more dramatic plot of this effect can be seen in Fig. 32, which shows the ratio of char to liquid versus pressure. Another effect which decreased the oil vapor produced at higher pressures was oil forced into the pores of the birch dowel. This pressure was great enough to drive the oil up through the dowel where it condensed on the wood just above the upper assembly. These effects are somewhat offset by a thinner liquid-vapor layer between the wood's ablation layer and the copper. This thinner layer increases the heat conduction coefficient and thereby, the heat flux.

The effect of pressure below the reaction interface was evaluated through the application of a vacuum pump. The differences in product due to reduced pressure is shown in Figs. 28 and 29. The difference in liquid and gas products can be explained in part by colder bath temperatures since a dry ice bath was used on the runs without a vacuum pump and some of the gases condensed. Also the vacuum pump decreased the amount of residence time and the pressure in the traps and thus, is possible that not all of the oil vapor may have condensed. Also some of the effect may, in part, be due to air leaks allowing for the combustion of the liquid product.

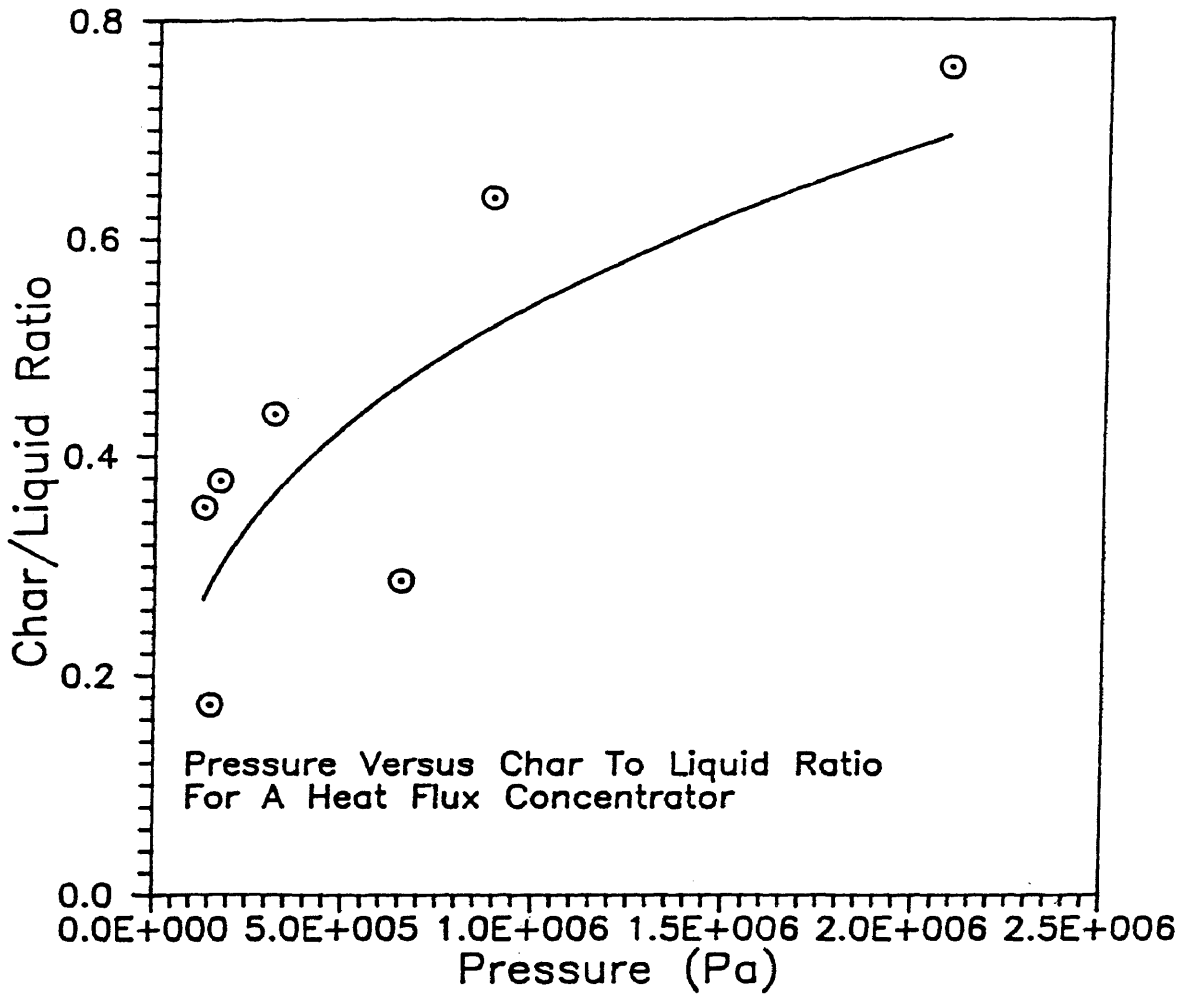


Figure 32: Char to Liquid Ratio Versus Mechanically Induced Pressure for a Heat Flux Concentrator

None of these explanations explain the increase in char production with a vacuum pump. One possibility is that the increased air pulled what ever oil that had condensed down into the holes below the reaction area faster than without the pump. Since there is a greater surface area and smaller total cross-sectional area, the holes may have become clogged sooner, as opposed to the coke forming above the holes where it could be broken up by the rotating dowel. The clogging allowed the pressure to increase and more liquid would then condense.

#### 5.1.3 Heat Flux And Feed Rate

The pressure and temperature can be looked at simultaneously by calculating the heat flux from equations 6 and 7. The calculated heat fluxs and the heat transfer coefficients as a function of temperature are given in Table 10. The effect of the heat flux can be examined throught the feed rate, since the feed rate is totally dependent on the heat flux. The relation between feed rate and the weight percent of the products is shown in Fig. 33. A very similar graph results if the heat flux is plotted.

#### 5.1.4 Energy Balance

##### 5.1.4.1 Frictional Heat

The amount of frictional heat added by the rotation of

Table 10: Calculated Heat Transfer Coefficient and  
Calculated and Measured Heat Flux of a  
Heat Flux Concentrator

Run Number	Temperature (deg C)	Measured Heat Flux (W/sq cm)	Calculated Heat Flux (W/sq.cm)	Calculated Heat Transf Coefficient (W/sq.m K)	Char (%)
A-29	473	2.46	6.01	41511	22.96
A-31	498	6.07	10.90	17641	21.99
A-36	499	4.55	8.30	12983	15.59
A-24	504		5.41	7242	25.77
A-39	526	4.03	7.27	6241	22.49
A-30	548	4.44	5.47	3431	17.06
A-28	598	9.43	6.69	2610	15.82
A-38	624		8.95	2926	15.58
A-35	648		10.06	2850	
A-26	677		12.35	3027	9.12



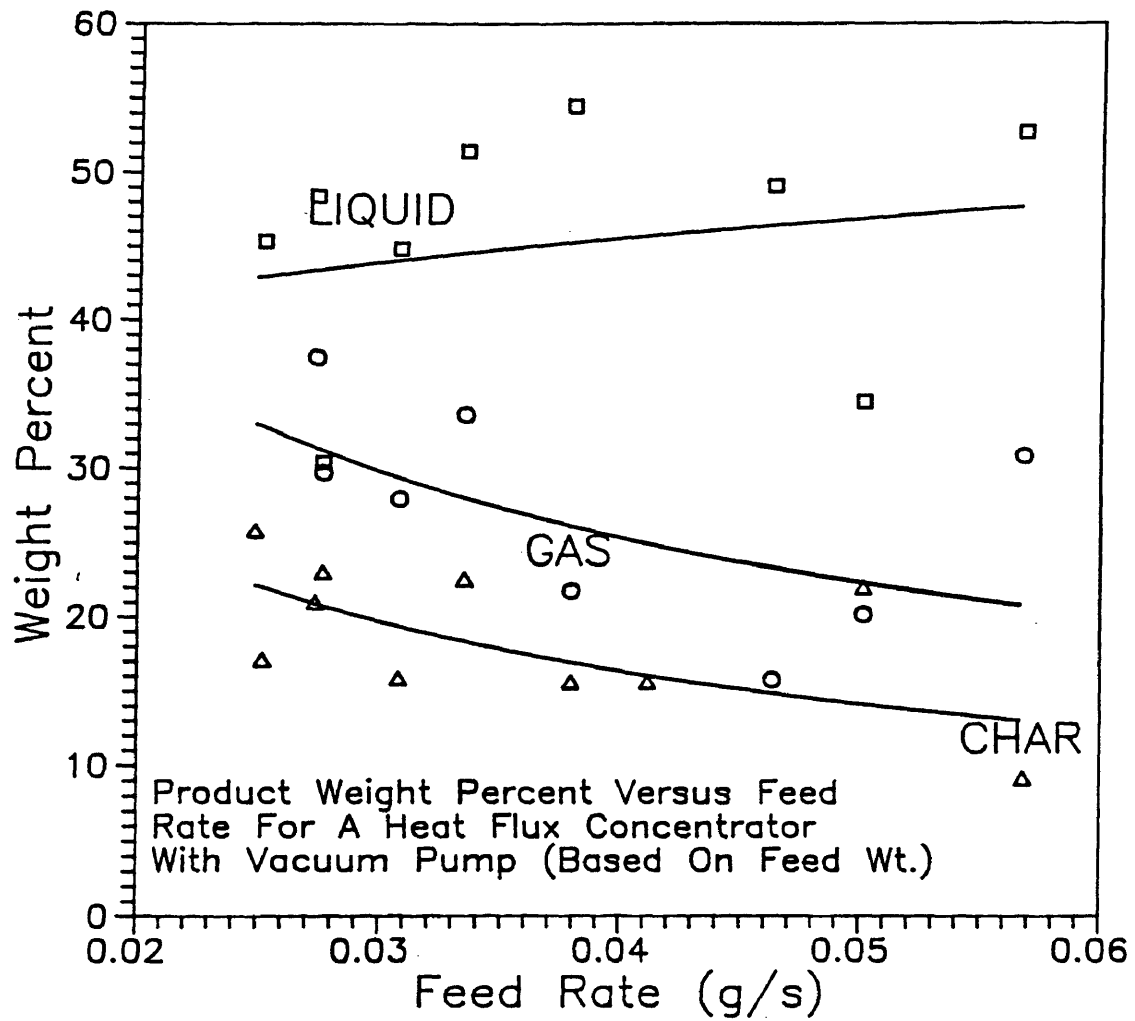


Figure 33: Product Weight Percent Versus Feed Rate for a Heat Flux Concentrator

the wood is not independently measured by the power meter. The question of whether this heat is significant must be addressed, since it affects the heat for pyrolysis measurement. Without heat, but with rotation, the pyrolyzer temperature increased only 5 degrees Centigrade in a 5 minute period. With heat, the drag coefficient will be reduced since there is a lubricating cushion of evolving gases and oil vapor between the interface. Therefore, the frictional heat was considered negligible.

considered negligible.

#### 5.1.4.2 Heat For Pyrolysis

The heat for pyrolysis was measured over a temperature range of between 473 and 598 degrees Celsius and ranged between 644 J/g and 1841 J/g. The heat for pyrolysis values are shown in Table 11. As can be seen from these values, the heat for pyrolysis almost triples over a relatively small range of temperature of 150 degrees Celsius. This is due to different reaction products being produced due to higher heat fluxes at higher temperatures and thereby altering the heat of pyrolysis.

#### 5.1.4.3 Sensible Heat

As can be seen from Table 11, the sensible heat is the largest component of the heat for pyrolysis. The heat of

Table 11: Calculation of Heat of Pyrolysis From Measured Heat for Pyrolysis and Estimated Sensible Heat Requirements of Wood and it's Products

Run No.	Temperat (deg C)	Heat For Pyrolysis (J/g)	Wood Sensible Heat (J/g)	Char Sensible Heat (J/g)	Oil Vapor Sensible Heat (J/g)	Gas Sensible Heat (J/g)	Heat Of Pyrolysis (J/g)
A-29	473	644.09	1045.63	31.92	4.11	3.47	-441.05
A-31	498	752.91	1045.63	146.90	26.21	10.96	-476.79
A-36	499	660.02	1045.63	90.14	35.83	10.21	-521.80
A-39	526	989.96	1045.63	208.33	54.46	24.69	-343.16
A-30	548	1377.00	1045.63	238.98	72.17	40.47	-20.26
A-28	598	1840.80	1045.63	418.29	132.03	55.54	189.31

pyrolysis can be derived from equation 1, if the sensible heat of the reactants and the products can be measured or estimated. The sensible heat had to be calculated in two parts; the heat required to take the wood to 466 degrees Celsius and the heat required to take the reaction products up to the reactor wall temperature, as shown in Table 11. This was true for both the heat flux concentrator and the pyrolysis mill. The sensible heat of the wood was calculated by integrating the heat capacity equation in Edrich (1980) for birch flour. Although this equation was derived from measurements measured at much lower temperatures, it was deemed the best value available. The Edrich heat capacity equation is as follows:

$$C_p = 0.289 + 2.09 \times 10^{-4} T + 2.94 \times 10^{-6} T^2 \quad (13)$$

(cal/g deg C)

Integration of this equation between 295.7K and 739K yielded 1045.6 J/g as the sensible heat required to bring the wood to 466 deg. Celsius.

The sensible heat of the char was calculated in the same manner as it was for the wood. Edrich (1980) gives the following equation for the sensible heat of yellow pine char:

$$C_p = 0.172 + 7.82 \times 10^{-4}T - 3.78 \times 10^{-7}T^2 \quad (14)$$

(cal/g deg C)

Integration of this equation from 466 deg C to the reactor temperature (deg. C) yielded the following equation for the sensible heat:

$$\Delta h = 0.172T + 3.91 \times 10^{-3}T^2 - 1.26 \times 10^{-7}T^3 - 916.48$$

(cal/g)

(15)

This change in enthalpy is then multiplied by the weight fraction of char and converted to Joules.

The sensible heat of the oil vapor was calculated using levoglucosan as a model compound since it is the principle product of cellulose depolymerization, has many of the functional groups of the oil and has roughly the same ultimate analysis as the oil. The Dobrantz method (Perry 1980) was used to calculate a heat capacity equation;

$$C_p = -0.155 + 0.135T - 4.82 \times 10^{-5}T^2 \quad (16)$$

(cal/g-mole K)

Integrating this equation from 739 K to the wall temperature

yielded:

$$\Delta H = -0.155T + 0.067T^2 - 1.61 \times 10^{-5}T^3 - 30357$$

(cal/g-mole) (17)

There was much more reliable heat capacity data for the gases and the heat capacity was calculated on a mole averaged basis from a sample gas analyzed on the gas chromatograph. These values and their averages, given in Table 12, yielded this equation:

$$C_p = 5.84 + 8.03 \times 10^{-3}T - 2.84 \times 10^{-6}T^2 + 2.81 \times 10^{-9}T^3$$

(cal/gmol K) (18)

Like the other equations this was integrated to yield:

$$\Delta H = 5.84T + 4.01 \times 10^{-3}T^2 - 9.47 \times 10^{-7}T^3$$

+ 7.02 \times 10^{-11}T^4 - 6145.7 \quad (\text{cal/mol K}) \quad (19)

This equation was converted to a gram weight basis by using an average molecular weight of 33.37 based on the same sample gas.

Table 12: Calculation of a Heat Capacity Equation of the Gaseous Products of the Fast Pyrolysis of Birch in a Heat Flux Concentrator (Based on Mole Fraction)

Compound	Mole Percent	Fractional Contribution To Heat Capacity Constants			
		a	b	c	d
Hydrogen	7.86	0.567	-0.004	0.008	-0.016
Methane	9.99	0.475	0.120	0.030	-0.263
Ethane	0.87	0.014	0.036	-0.013	0.015
Ethene	1.64	0.015	0.061	-0.033	0.069
Propane	0.27	-0.003	0.020	-0.010	0.021
Propene	0.68	0.006	0.038	-0.020	0.040
CO <sub>2</sub>	35.97	1.912	0.514	-0.301	0.642
CO	42.72	2.873	0.017	0.055	0.227
Total	100.00	5.839	0.803	-0.284	0.281

where  $C_p = a + bx10^{-2}T + cx10^{-5}T^2 + dx10^{-8}T^3$   
(cal/g-mol K)

(Based on data from Kyle 1984)

#### 5.1.4.4 Heat of Pyrolysis

The sensible heat and the heat for pyrolysis plotted together are shown in Fig. 34. The gap between these lines represents the heat of pyrolysis. The heat of pyrolysis presented is in Table 11 and includes the heat of vaporization of the pyrolysis oil. The heat of pyrolysis as a function of temperature is plotted in Fig. 35. The exothermic nature at lower temperatures corresponds to increased coking at lower temperatures. Since the char produced from the coking of the oil is similar to char produced from slow pyrolysis and also since change in enthalpy is independent of path, these heats of reaction can be compared to those of slow pyrolysis. Table 13 gives values as predicted by Antal (1982) in comparison with the experimentally determined values of this work. There is a similar relationship but the magnitude of the change is much greater in this work. Antal's work was on cellulose only, it doesn't take into consideration oil and gas production, and it is for much slower pyrolysis, therefore the qualitative agreement is satisfactory.

#### 5.1.5 Operating Performance

The heat flux concentrator had numerous problems associated with its operation and its performance. The main problem was a tendency to coke enough of the oil it



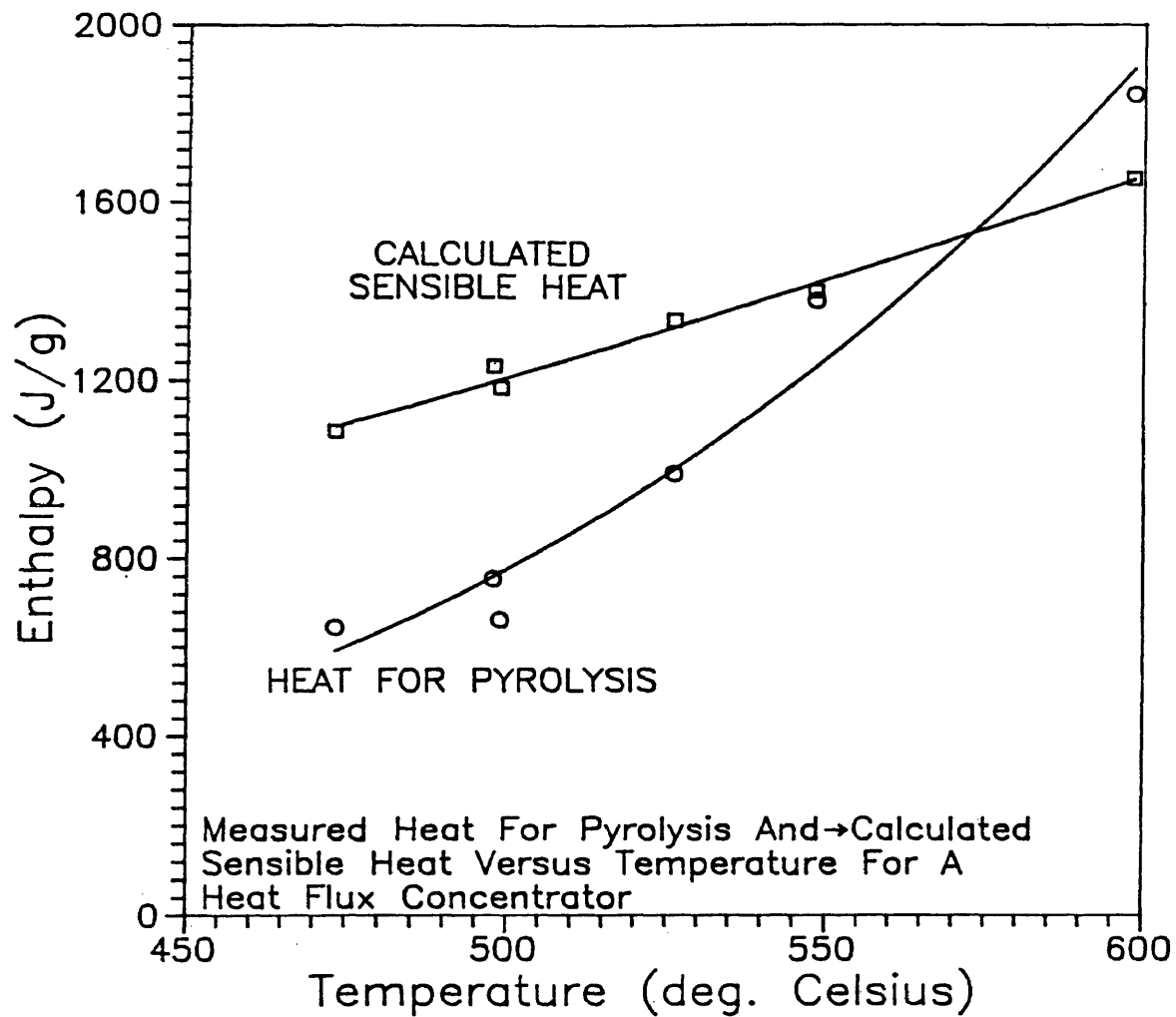


Figure 34: Heat For Pyrolysis and Calculated Sensible Heat of Birch in a Heat Flux Concentrator

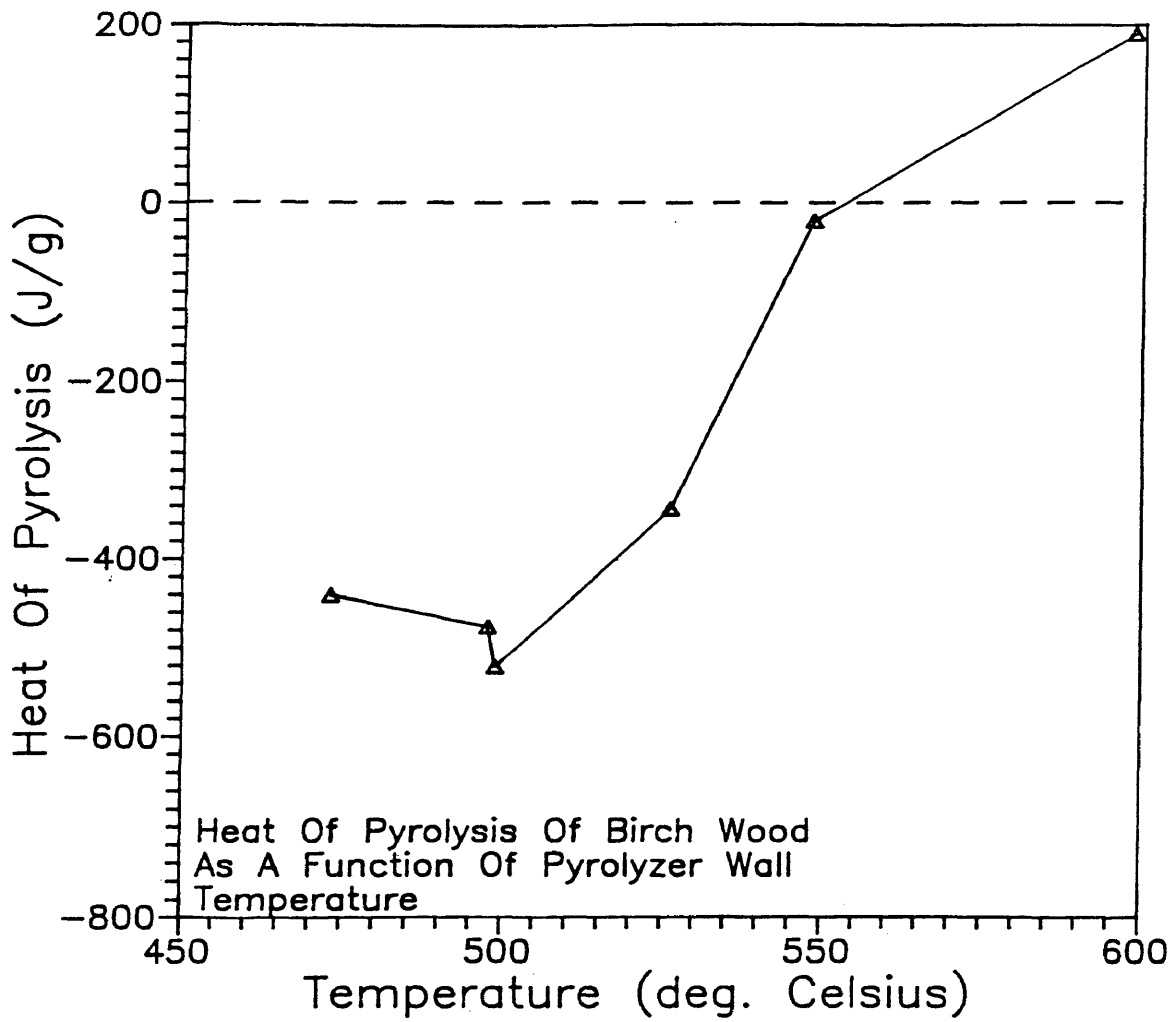


Figure 35: Heat of Pyrolysis of Birch Wood as a Function of Wall Temperature

Table 13: Comparison of Experimental Derived Heat of Pyrolysis and the Heat of Pyrolysis Calculated From Char Yield (Based on Data From Antal 1982)

Run No.	Temperature (deg C)	Heat Of Pyrolysis (J/g)	Antal Heat Of Pyrolysis (J/g)	Char (%)
A-29	473	-441.05	-168.32	22.96
A-31	498	-476.79	-138.08	21.99
A-36	499	-521.80	63.08	15.59
A-39	526	-343.16	-153.63	22.49
A-30	548	-20.26	17.01	17.06
A-28	598	189.31	56.01	15.82

produced to close the exit holes, generally in one or two minutes. In spite of this problem, the oil yields were very high. All of the char produced displayed a structure that suggested that it had flowed as opposed to displaying the original structure of wood. To be more specific, the char had a smooth, almost vitreous surface that resembled petroleum coke or graphite. Also the char had taken the form of the inside of the pyrolyzer including minute cracks and crevices.

## 5.2 Pyrolysis Mill

### 5.2.1 Mass Balance

Compared to the heat flux concentrator the oil yields were much lower. A preliminary mass balance on the mill is given in Table 14. The mass of the gas was calculated by difference. Since the mass of the gaseous products was not actually measured the closure of the mass balance could not be determined. There was some evidence of condensation inside the mill especially in areas with heats lower than the drum temperature. These areas included the ceramic tubes that carried the lower heater's power supply and the view ports. Due to the size of the mill, it wasn't possible to get these values by weight. Higher oil yields would normally be expected, judging from the low char yields.

Table 14: Mass Balance on a Pyrolysis Mill

Run Number	Wood (g)	Total Liquid (g)	Char (g)	Gas (by diff. (g))	Liquid (%)	Char (%)	Gas (%)
C-3	30.47	10.84	2.35	17.28	35.58	7.71	56.71
C-6	25.34	6.2	3.02	16.12	24.47	11.92	63.61
C-8	22.18	4.49	1.42	16.27	20.24	6.40	73.35
C-9	22.76	3.11	2.21	17.44	13.66	9.71	76.63
C-10	15.45	4.6	1.66	9.19	29.77	10.74	59.48
C-11	42.12	12.5	2.41	27.21	29.68	5.72	64.60
Average	26.39	6.96	2.18	17.25	25.57	8.70	65.73

The data in Table 15 shows the results of gas chromatograph analysis for gas produced in the heat flux concentrator, the pyrolysis mill, a gasifier sample and data collected by Zhi (1984) on the spinning disk. The gas from the pyrolysis mill had negligible amounts of hydrogen and had a lesser degree of saturation. This suggests that the oil produced may have had a higher hydrogen to carbon ratio. Also of interest is the high yield of carbon monoxide and carbon dioxide since this would indicate a less oxygenated oil. These two factors suggest that the oil has a more utilitarian value as a fuel with present technology that is adapted to petroleum based fuels as opposed to that produced with the heat flux concentrator.

#### 5.2.2 Energy Balance

An energy balance was attempted on only two runs. For run number C-10, the recorder stopped and the length of the run was not recorded. For run number C-11, 2871 J/g was calculated as the heat for pyrolysis. Using the same sensible heat for wood as the heat flux concentrator of 1045 J/g and the same sensible heat equations as that for the char and the liquid plus a derived equation for the gas yields the heat of pyrolysis. Table 16 shows how the heat capacity of the gas was calculated.

Table 15: Comparison of Gas Compositions of  
Wood Pyrolyzers and Gasifiers

Compound	Heat Flux Concentrator	Pyrolysis Mill	Gasifier	Spinning Disk (1)
Hydrogen	7.9	---	6.5	6.1
Methane	10.0	8.8	4.4	13.5
Ethane	0.9	---	1.3	---
Ethene	1.6	0.2	1.8	0.7
Propane	0.3	---	0.8	0.3
Propene	0.7	0.6	---	---
CO <sub>2</sub>	36.0	24.2	45.9	4.4
CO	42.7	66.3	39.3	75.0

Table 16: Calculation of the Heat Capacity Equation of Gaseous Products of the Fast Pyrolysis of Birch in a Pyrolysis Mill (Based on Mole Fraction)

Compound	Mole Percent	Fractional Contribution To Heat Capacity Constants			
		a	b	c	d
Methane	8.80	0.418	0.106	0.027	-0.232
Ethene	0.18	0.002	0.007	0.004	0.007
Propene	0.53	0.004	0.030	-0.015	0.031
CO <sub>2</sub>	24.18	1.235	0.345	-0.202	0.431
CO	66.31	4.460	0.027	0.035	-0.351
Total	100.00	6.169	0.514	-0.109	-0.113

where  $C_p = a + bx10^{-2}T + cx10^{-5}T^2 + dx10^{-8}T^3$   
(cal/g-mole K)

(Based on data from Kyle 1984)



The heat capacity of the gas is as follows:

$$C_p = 6.1693 + 0.00514T - 1.09 \times 10^{-6} T^2 - 1.14 \times 10^{-9} T^3$$

(cal/g-mol K) (20)

This led to the following equation for the sensible heat of the gas.

$$\Delta H = 6.16T + 7.72 \times 10^{-4} T^2 - 3.65 \times 10^{-7} T^3$$

$$- 2.84 \times 10^{-11} T^4 - 4824 \quad (\text{cal/g-mol K}) \quad (21)$$

The heat of pyrolysis, including the heat of vaporization of the oil and water, was 1726 J/g. It is possible that a cracking reaction of the pyrolysis vapor may have occurred. If cracking did take place it would make the heat of pyrolysis more endothermic. This could explain in part why the heat of pyrolysis in the pyrolysis mill is higher than in the heat flux concentrator.

### 5.2.3 Overall Performance

One essential feature of the pyrolysis mill was the use of a flow nitrogen. The nitrogen kept an inert atmosphere inside the mill and kept the oil vapor out of the feed tube.

One run was attempted without the use of nitrogen and no feed made it to the mill plates. One drawback of the nitrogen is that it took a larger amount of heat for normal operation although this had no effect on the mass or energy balance measurements. It is possible that the nitrogen flow rate could be reduced if an auger was installed on the feed tube.

When compared to the heat flux concentrator, the liquid yields were lower, the experimental runs were longer and there was little mechanical failure once the shaft binding was cured. After the shaft binding problem was fixed, the unit could easily run for an hour and a half as compared to no more than two and a half minutes with the heat flux concentrator. This advantage alone made the mill a much more useful apparatus. The mill was much easier to clean since the char fell to the bottom of the unit. Overall the pyrolysis mill proved itself of greater value due to its reliability.

### 5.3 Uncertainties In The Results

Rather than calculate the error in the mass balance through estimation techniques, the real error can be seen as the difference between the percent closure, as given in Table 6 and 100 percent. It can be assumed that a similar error is implicit in the pyrolysis mill mass balance.

Although the error in the scale used in all the weights can easily be estimated, the estimation of losses inside the mill of oil, water, and char is likely to be inaccurate.

The error in the heat for pyrolysis measurement was estimated using propagation of error and found to range between 61 and 148 Joules per gram. This error is large enough to significantly alter the calculated heat of pyrolysis even with good sensible heat calculations. Unfortunately, there is no basis for calculating an estimate of the error on the sensible heat calculations and therefore, propagation of error can't be used on the heat of pyrolysis.

## 6. CONCLUSIONS

1- The dominating factors in producing oil in the heat flux concentrator was a high heat flux in combination with low pressures at the reaction interface. The high flux is for rapid depolymerization of the biomass. The low pressure is to allow the vaporization of the oil before it comes in contact with the heat source.

### Heat Flux Concentrator:

2 - A high heat flux was produced in the heat flux concentrator until the holes below the reactor clogged and reduced the heat transfer.

3 - The heat for reaction measured at 600 deg C was 1840J/g. The heat of pyrolysis at 466 deg.Celsius was -441 J/g.

4 - The high pressure and small exit holes didn't allow rapid vaporization of the oil so high coke yields occurred (10-20%).

5 - The grinding action of the heat flux concentrator allowed for lower pyrolysis temperatures (394 deg. C) than predicted by Lede (1985) due to the abrasion at the interface.

6 - Lower pressures on the down side of the reaction interface increased coking rather than decreased it.

- 7 - The heat flux concentrator had yields of pyrolysis oil beteen 35 and 80% in terms of liquid product (oil and water) than the pyrolysis mill.
- 8 - The measured preeesure was consistant with that estimated using equations form Lede (1985).

Pyrolysis Mill:

- 9 - The pyrolysis mill had a greater utilitarian value as a pyrolyzer than the flux concentrator in that there was no coking and little mechanical malfunctions .
- 10- The heat for pyrolysis was measured to be 2871 J/g.
- 11- Low char yields and negligible coke yields were measured for the pyrolysis mill.
- 12- The pyrolysis mill could operate over periods of time longer than 1 1/2 hours.

## 7. RECOMENDATIONS FOR FUTURE WORK

- 1 - Other kinds of feed, such as municipal solid waste and coal, should be investigated for use in the pyrolysis mill.
- 2 - Since the pyrolysis mill has a different geometry than the flux concentrator the vacuum pump could have an entirely different effect and this should be investigated.
- 3 - The effect of plate pressure on the pyrolysis mill should be determined.
- 4 - Pressure gauges should be installed on both systems since change in pressure was seen to have a dramatic effect.
- 5 - Coating of the copper in either pyrolyzer could prove whether there is a catalytic effect and what that effect is.
- 6 - For measurement of thermal quantities in fast pyrolysis, better heat capacity and heat of vaporization data needs to be determined. For wood itself the heat capacity needs to be measured above 200 degrees Celsius. There isn't any reliable data on the liquid product at any temperature or pressure for either heat capacity or heat of vaporization.

7 - Gas samples at different temperatures and pressures should be analyzed on the gas chromatograph for variation in composition, especially since what isn't in the gas generally ends up in the oil.

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## Appendix A: Nomenclature

a	- Heat Capacity Constant (cal/g-mole K)
A	- Cross-Sectional Area ( $m^2$ )
b	- Heat Capacity Constant (cal/g-mole $K^2$ )
Bi	- Biot Number (dimensionless)
c	- Heat Capacity Constant (cal/g-mole $K^3$ )
CL	- Confidence Limit
Cp	- Heat Capacity (cal/g-mole $^{\circ}C$ )
$\hat{C}_p$	- Heat Capacity (cal/g $^{\circ}C$ )
d	- Heat Capacity Constant (cal/g-mole $K^4$ )
e	- Eccentricity (dimensionless)
Fc	- Char Fraction Of Pyrolysis Products (dimensionless)
h	- Convective Heat Transfer Coeff. (W/sq m K)
$\Delta h_{pyr}$	- Heat of Pyrolysis
$\Delta h_{tot}$	- Heat for Pyrolysis (J/g)
$\Delta h$	- Sensible Heat (cal/g)
$\Delta H$	- Sensible Heat (cal/g mole)
$h_c$	- Conductive Heat Transfer Coeff. ( $W/m^2K$ )
k	- Thermal Conductivity (W/m K)
$k_r$	- First Order Velocity Constant ( $s^{-1}$ )
L	- Characteristic Length (m)

## Table Of Nomenclature cont'd.

$L_a$	- Length of Major Axis Of A Spheroid (m)
$L_b$	- Length of Minor Axis of a Spheroid (m)
$p$	- Pressure (Pa)
$Py$	- Pyrolysis Number (Dimensionless)
$Py'$	- Pyrolysis Number (Dimensionless)
$q$	- Heat Flux (W/sq m)
$r$	- Radius Of Particle (m)
$t$	- time (s)
$T$	- Temperature (K or C)
$T_o$	- Initial Temperature of Wood ( C)
$T_p$	- Pyrolysis Temperatue ( C)
$T_w$	- Pyrolyzer Wall Temperature ( C)
$\rho$	- Density Of Particle ( $kg/m^3$ ) or ( $g/cm^3$ )

Appendix B: Sample Calculation of Heat for Pyrolysis

This is an example showing how the heat for pyrolysis was obtained. The data used for this sample calculation is from run number A-30. A sample of the chart paper showing the power used by the heaters as a function of time is shown in Figs. B-1 and B-2. The chart in Fig. B-1 is the heat flux concentrator's power without any wood in the system or the baseline power. The chart in Fig. B-2 is the power with wood in the system.

First a time period was selected from the area of the chart where the baseline power was measured and where steady state had been reached. The time period selected always began at the start of a peak and ended at the start of another peak. For run #A-30, a time period of 1.908 minutes was selected and contained six peaks. The height of the peaks was measured to get the power, 383 watts. The baseline power was calculated as follows:

$$P_{\text{base}} = \frac{(P_{\text{heater}}) \times \sum_{n=1}^i t_{\text{peak}^i}}{(t_{\text{total}})}$$

where  $t_{\text{peak}}$  is the length of time of each peak as calculated from the peak width. For run #A-30, this

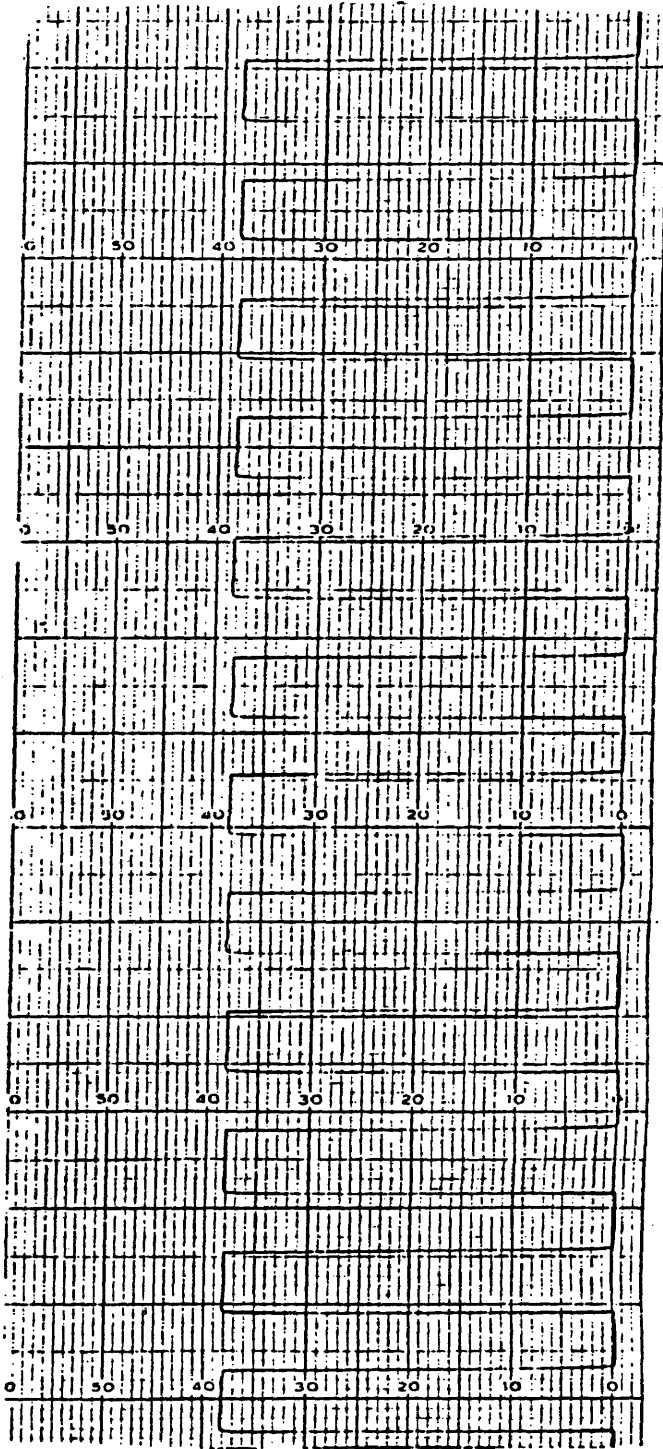


Figure B-1: Power Versus Time for Heat Flux  
Concentrator Without Wood (Sample From  
Chart Recorder on Run #A-30)



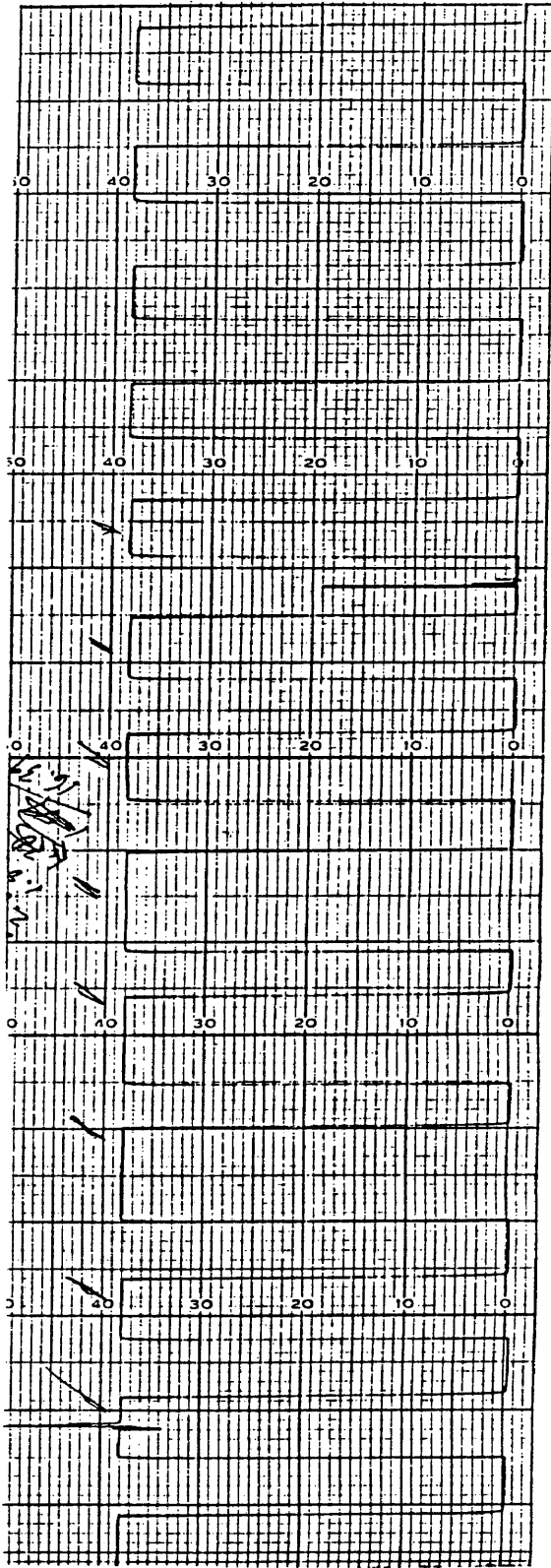


Figure B-2: Power Versus Time for Heat Flux Concentrator During Experimental Run With Birch Dowel (Sample From Chart Recorder on Run #A-30)

equation becomes,

$$P_{\text{base}} = (383 \text{ watts}) \times (1.00 \text{ min.}) / (1.91 \text{ min.})$$

$$= 200.3 \text{ watts}$$

The power with wood in the system was calculated in a similar manner, except that the time period selected was the inclusive of the run time. For run # A-30,

$$P_{\text{tot}} = (383 \text{ watts}) \times (1.31 \text{ min.}) / (2.12 \text{ min.})$$

$$= 237.2 \text{ watts}$$

The difference between these two power terms is the power required for the pyrolysis of wood. The heat for pyrolysis is calculated as follows,

$$h_{\text{tot}} = \frac{(P_{\text{tot}} - P_{\text{base}}) \times (t_{\text{total w/wood}})}{mf}$$

Note  $t_{\text{total w/wood}}$  isn't the same as the run time since their isn't a whole number of cycles inside the length of the run time. For run #A-30, the heat for pyrolysis is:

$$h_{\text{tot}} = \frac{(36.9 \text{ watts}) \times (126.9 \text{ seconds})}{(3.4 \text{ g})}$$

$$= 1377 \text{ J/g}$$

Error analysis was performed by estimating 98% confidence levels on the basic measurements and using propagation of error techniques to find the 98% confidence level on the heat of pyrolysis. Since there was a limited number of measurements made, statistical techniques of error analysis were not possible. From Shoemaker et al (1974), the confidence limit can be found on the difference between the baseline power and the power with wood in the concentrator as follows,

$$CL_{(P_{tot} - P_{base})} = ((CL_{P_{tot}})^2 + (CL_{P_{base}})^2)^{-2}$$

The confidence level for the two power measurements was estimated to be two watts based on calibration measurements at both CSM and Tipi Workshop. Therefore,

$$\begin{aligned} CL_{(P_{tot} - P_{base})} &= ((2)^2 + (2)^2)^{-2} \\ &= 2.83 \text{ watts} \end{aligned}$$

The confidence level on the heat for pyrolysis is found by (Shoemaker et al, 1974),

$$\begin{aligned} CL_{h_{tot}} &= \left( (h_{tot})^2 \times \left[ (CL_t/t)^2 + (CL_{mf}/mf)^2 \right. \right. \\ &\quad \left. \left. + (CL_{(P_{tot}-P_{base})}/(P_{tot}-P_{base}))^2 \right] \right)^{-2} \end{aligned}$$

The confidence level on the time measurement was estimated to be one second and the confidence level on the wood pyrolyzed was 0.03 grams, so the above equation becomes:

$$\begin{aligned} \text{CL}_{\text{htot}} &= \left( (1377 \text{ J/g})^2 \times \left[ (1\text{s}/126.9\text{s})^2 \right. \right. \\ &\quad \left. \left. + (.03\text{g}/3.4\text{g})^2 + (2.83/36.9)^2 \right] \right)^{-2} \\ &= 107 \text{ J/g} \end{aligned}$$

## Appendix C:

Copy of "Heat Flux Requirements For Fast Pyrolysis", by  
T.B.Reed and C.D.Cowdery, as presented at the American  
Chemical Society meeting, April 5-10, 1987, Denver, Colorado

HEAT FLUX REQUIREMENTS FOR FAST PYROLYSIS  
AND A NEW METHOD FOR GENERATING BIOMASS VAPOR

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**ABSTRACT**

The term "fast pyrolysis" has been used to describe a pyrolysis regime in which vapor production is enhanced and char minimized by rapid heating. It has been found in the last decade that high yields of primary pyrolysis oil can be achieved using fast pyrolysis. More recently it has been found that the pyrolysis vapors can be converted to high grade fuels using a catalyst. This makes fast pyrolysis of biomass desirable for synthetic fuel manufacture.

We present here results derived from the Diebold Integrated Kinetic Model (DKM) that predict the time, the temperature, and the products of pyrolysis and the heat for pyrolysis of cellulose as a function of heating rates between 0.01 and  $10^5$ °C/min. This range covers very slow pyrolysis requiring days to fast pyrolysis occurring in fractions of a second. The predictions are in good qualitative agreement with experimental measurements.

We then compare the heat flux required for slow and fast pyrolysis for particles with that which can be obtained with practical heating devices. The comparison shows that convective and radiative heat transfer is adequate for fast pyrolysis of small particles, but not for large particles, due to conduction to the interior. We derive the heat flow requirements for large bodies, the time for onset of pyrolysis, and the depth of heat penetration in that time. We compare the heat flux from various practical devices with those observed in "contact pyrolysis" experiments of Diebold and Lede on large particles. The comparison shows that higher heat flux methods are required for fast pyrolysis of larger particles.

We have designed a "heat flux concentrator", based on the experiments of Diebold and Lede to generate wood vapors for upgrading to gasoline-like liquids. A rotating birch dowel is fed into a heated copper block. Vapors emerge from the bottom and are condensed and collected, or passed over a catalyst to establish optimum conversion conditions. The pyrolysis rates and results of catalytic conversion in these experiments will be described.

**INTRODUCTION**

Pyrolysis of biomass is a very old and complex process producing variable quantities of charcoal, pyrolysis liquids and gases from biomass, peat or coals (1). Pyrolysis was the principle source of chemicals in Western society for about a century and could gain become a major source, particularly if the products can be tailored to modern needs through better understanding of the pyrolysis process or improved upgrading of the products.

The relative amounts of charcoal, liquid and gas obtained from pyrolysis depend on the time-temperature-pressure history of the sample in a way which may never be completely understood. This has led to apparent controversy over the magnitudes of kinetic factors, energies and products when investigators compare results from different experiments. Nevertheless great progress has been made in the last decade in understanding the role of these variables in controlling the nature and quantity of the products.

The term "fast pyrolysis" has been used to describe a pyrolysis regime in which vapor production is maximized and the formation of char is minimized by rapid heating. It has been found in the last decade that it is possible to obtain high yields of pyrolysis oils or

gas using high heat flux (1-3). It has more recently been found that pyrolysis oil can be converted catalytically to high grade, high octane motor fuel. Thus there is a strong motivation to understand these relations.

While there is no hard boundary between "slow" and "fast" pyrolysis, it is necessary to understand the relation between the time and energy required for each and the different chemistry and the possible mechanisms available for supplying this heat. We hope this paper will help draw together the apparently disparate results using a time-temperature-pressure kinetic model and lead toward more effective methods of pyrolysis.

#### CELLULOSE AND BIOMASS PYROLYSIS KINETICS

Biomass is a composite plastic, consisting of cellulose, hemicellulose and lignin with cellulose constituting more than half the total and giving most of the mechanical strength. Cellulose has the best defined structure and thus has been studied more than lignin or hemicellulose. Furthermore it constitutes more than half the substance of most biomass and contributes most of the strength. Much of the following discussion applies primarily to cellulose, but qualitatively to all biomass.

The rates of pyrolysis reactions are usually represented in the form of a first order Arrhenius rate equation

$$dX/dt = -X A \exp(-E/RT) \quad 1)$$

where X represents the quantity of any reactant X at time t and temperature T. (A is the pre-exponential and E is the activation energy. R is the gas constant). If the biomass is heated at a constant rate of R °C/sec, simple substitution leads to

$$dX/dT = (-AX/R) \exp(-E/RT) \quad 2)$$

The values for A and E in Eqs. 1 and 2 are usually measured by thermogravimetric analysis (TGA) and describe the global pyrolysis (including all solid state reactions) in terms of a single A-E pair (2,3). While this oversimplification may be justified over a narrow temperature range for engineering purposes, the global approach ignores preliminary solid state reactions and thus is not able to predict the change of products with heating rate, the time required for pyrolysis or the temperature of pyrolysis.

Several reaction schemes for cellulose pyrolysis have been proposed involving competing parallel and consecutive reactions (2,3,5,6). Cellulose pyrolysis now appears to involve an initial drying step (not discussed here), followed by two parallel reactions which for instance differentiate between two subsequent paths as shown in Table 1. The first reaction involves cross linking (transglycolization) of the cellulose and leads to the formation of charcoal. The second reaction is a depolymerization leading to a low molecular weight liquid or solid depending on temperature and rate of formation. This was called the "active state" by Bradbury and Shafizadeh (4). These more volatile components may either immediately evaporate at low pressure or evaporate subsequently at higher pressures.

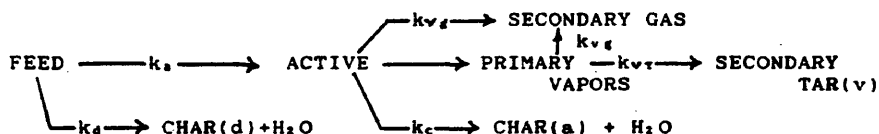
#### AN INTEGRATED MODEL OF CELLULOSE BIOMASS PYROLYSIS KINETICS

The justification for studying the various pyrolysis reactions is to predict the detailed course of pyrolysis under a wide variety of conditions. Diebold has recently collected previous work on various aspects of cellulose pyrolysis into a single integrated model of cellulose pyrolysis (5,6). The six reactions included are shown in Table 1. The temperature at which the reaction rate reaches  $10^{-6}/s$  and  $1/s$  is listed for convenience in evaluating the relative strength of each reaction. Note that the reaction producing char reaches a rate of

10<sup>-6</sup>/s at 208 °C, while the depolymerization reaction does not reach 10<sup>-6</sup>/s until 225 °C. Thus slow pyrolysis favors charring. However the depolymerization reaction reaches a rate of 1/s at 379 °C, while the charring reaction does not reach a rate of 1/s until 703 °C. Thus rapid heating favors depolymerization and volatilization over charring.

The Diebold Kinetic Model (DKM) permits calculation of the relative amounts of the products of pyrolysis as a function of time-temperature history. The kinetic equation 1) using values in Table 1 are integrated using the Runge-Kutta technique on a microcomputer. A second-derivative test is used to determine the time increment. The model permits any type of heating history, but the results given here are those for a constant heating rate as given in Eq. 2).

Table 1 - Simplified Cellulose Pyrolysis Reaction Scheme



REACTION	k	A sec <sup>-1</sup>	E kJ	T(R=10 <sup>-6</sup> ) °C	T(R = 1) °C
Cellulose to char + H2O	k <sub>d</sub>	6.69E+05	109	208	703
Cellulose to Active	k <sub>a</sub>	2.80E+19	243	225	379
Active to Primary Vapor at 1 atm	k <sub>v</sub>	6.79E+09	140	188	470
Active to primary vapor vacuum	k <sub>v,v</sub>	3.20E+14	198	231	440
Active to Char(b) + H2O	k <sub>c</sub>	1.30E+10	153	224	518
Active to gas	k <sub>v,g</sub>	3.57E+11	204	335	651
Primary vapors to gas	k <sub>v,g</sub>	3.57E+11	204	335	651
Primary vapors to tars	k <sub>v,t</sub>	1.81E+03	61	70	700

Notes: Kinetic constants used in Diebold kinetic model. T(R = 10<sup>-6</sup>) is the temperature where the rate constant R = 10<sup>-6</sup>; T(R = 1) is the temperature at which R = 1.

While this model may not explain all aspects of cellulose pyrolysis, it goes a long way toward predicting the changes observed with time-temperature-pressure. Other values for kinetic factors and other pathways should be substituted as they become known. In particular, an improved model should include the effect of pressure explicitly in the vaporization rates given by k<sub>v</sub> and k<sub>v,v</sub>. The nature and role of the "active" state needs to be better defined, since it plays a key role in this and other schemes. We will use this model here to predict heat flux requirements for slow and fast pyrolysis of cellulose.

**DEPENDENCE OF TIME, TEMPERATURE AND PRODUCTS ON HEATING RATE**

The dependence of the pyrolysis time, t<sub>p</sub>, and pyrolysis temperature, T<sub>p</sub>, on heating rate predicted by the DKM are shown in Table 2 and Fig. 1. The dependence of products on heating rate is shown in Fig. 2. (It is the nature of an exponential decay that it is never complete. We have therefore arbitrarily taken the time and temperature of pyrolysis as that time and temperature where the reaction is more than 99.9% complete.)



=====  
 Table 2 - Cellulose Pyrolysis Time, Temperature and Products  
 predicted by Kiebold Kinetic Model  
 =====

PYROLYSIS CONDITIONS			PYROLYSIS PRODUCTS		
R	t <sub>p</sub>	T <sub>p</sub>	Char-	Oil, Gas	Water
Heat Rate	Pyr Time	Pyr Temp	coal-%	%	%
R-°C/min	sec	°C			
0.01	1650000	275	23.9	46.2	29.9
0.1	181200	302	12.4	73.2	14.9
1	19800	330	6.9	84.6	8.7
10	2142	357	4.2	90.3	5.4
100	234.6	391	2.6	94.3	3.1
1000	25.5	425	1.2	97.2	1.5
10000	2.778	463	0.005	98.7	0.007
100000	0.3042	507	0.003	99.4	0.003

Notes: Values calculated from Diebold model.

=====  
 Here it is seen that pyrolysis temperatures vary between 280 and over 500°C as heating rates increase from 10<sup>-2</sup> to 10<sup>5</sup> °/min. In slow "commercial" pyrolysis, char yields are still increasing with pyrolysis times of over a month, and pyrolysis is complete at temperatures below 300°C. These correspond to the conditions that have been used classically for the manufacture of charcoal (1). Most of the kinetic data of Table 1 were acquired in experiments using convenient "laboratory" heating rates of 1-100°C/min. The predicted char yields of 2.6-6.9% and temperatures of 330-390°C correspond to those observed experimentally in this range.

At even higher "heroic" heating rates, gas and oilyields are still increasing with rates of over 10<sup>4</sup> °C/min where pyrolysis occurs at about 460°C. These conditions correspond to the experimental conditions of Diebold, Lede and Reed (7-9) produced by contact pyrolysis (see below). Thus it is clear that heating rate is a primary variable for controlling products in pyrolysis.

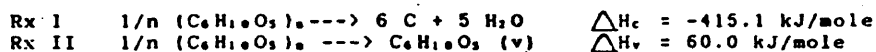
While the calculations in this paper are for cellulose, we believe the conclusions are qualitatively valid for all biomass.

#### HEAT OF PYROLYSIS AND HEAT FOR PYROLYSIS:

The energy required for pyrolysis,  $\Delta h_p$ , has long been a subject of interest to those involved in pyrolysis; yet no commonly accepted value is available to an engineer wishing to design a pyrolysis reactor, and even now it is not clear from the literature whether pyrolysis is endothermic or exothermic. It has been reported to vary from +370 J/g (endothermic) to -1700 J/g (exothermic)(5). One reason there is no commonly accepted value is that it is a difficult measurement to make under many of the conditions of pyrolysis (very slow or very rapid heating, large quantities of condensable vapors present, large temperature gradients in the sample). A more fundamental reason however is that the value depends on the particular form of biomass, the conditions of the experiment and the products formed, so that there is a unique value for each experiment. We will give here a method of calculating the heat of pyrolysis for known heating rates and products which, while approximate, underlines the factors that must be taken into account.

We define the "heat of pyrolysis" of biomass,  $\Delta h_p$ , as that heat required to effect the phase change from biomass to char-liquid-gas at

the temperature where pyrolysis occurs. (We define the "heat of pyrolysis as the heat required for the phase change plus the heat required to reach this temperature - see below.) A thermodynamic calculation of  $\Delta h_p$  can be made for cellulose based on the idealized reactions shown in Table 1. The idealized charring reaction for cellulose can be written as Rx I:



(Here we use the notation  $1/n (\text{C}_6\text{H}_{10}\text{O}_5)_n$  for cellulose to emphasize its polymeric nature. The values above are calculated from the heats of combustion or formation of the products and reactants.) The second reaction represents the depolymerization of cellulose to levoglucosan, with simultaneous vaporization. (Levoglucosan is the principal decomposition product of cellulose.)

These two reactions can be combined in the appropriate ratio to give a value for the heat of pyrolysis depending on the relative amount of carbon formed, eg

$$\begin{array}{ll} \Delta H_p = 59.96 - 475.1 F_c \text{ kJ/mole} & 3) \\ \text{or} \quad \Delta h_p = 370 - 6603 F_c \text{ J/g} & 4) \end{array}$$

where  $F_c$  is the weight fraction of carbon produced in the charring reaction. These values of the heat of pyrolysis should be considered as idealized because pyrolysis of cellulose gives charcoal (not exactly carbon) and other products beside levoglucosan. Nevertheless they illustrate the necessity for knowing the products in measuring the heat of pyrolysis.

Antal recently used a high pressure scanning calorimeter to measure the  $\Delta h_p$  of cellulose (2). He varied the amount of char formed by changing the pressure of the experiment. He found an approximately linear change in the  $\Delta h_p$  of cellulose from -170 kJ/g with a char production of 23% (typical of slow pyrolysis) to +270 kJ/g with a char production of 9% (typical of fast pyrolysis)(5).

These values can be used in a linear equation to predict the heat of pyrolysis on the basis of char content  $F_c$ , ie

$$\Delta h_p = 553 - 3142 F_c \text{ kJ/g} \quad 5)$$

where  $F_c$  is the fraction of charcoal produced. Note that the values for the coefficients resulting from the experimental values are similar in magnitude to those predicted from thermodynamic calculation in Reaction 4). The heats of pyrolysis calculated from the predicted char production and pyrolysis temperatures are listed in Table 3.

A quantity of more interest to the engineer is the heat for pyrolysis. We define the "heat for pyrolysis",  $h_p$  as the sensible heat required to raise a biomass particle to pyrolysis temperature, ( $= c T_p$ , where  $c$  is the heat capacity of the biomass) plus the heat required to pyrolyse it,  $\Delta h_p$ . (If the products of pyrolysis are then heated above this temperature, this heat must also be included.) Table 3 also shows values of  $h_p$  for pyrolysis of cellulose calculated from 2) and the heat capacity of cellulose, 1.31 J/g-°C (0.32 Btu/lb-F). Note that the variation of  $h_p$  with heating rate is small compared with the variation of  $\Delta h_p$ .

Table 3 - Heat of Pyrolysis and Heat For Pyrolysis of cellulose Calculated from char production

BYROLYSIS CONDITIONS Heat Rate R-°C/min	Pyro Temp °C	Char-coal-%	$\Delta H_p$ J/g	hp J/g
0.01	275	23.9	-198	162
0.1	302	12.4	163	559
1	330	6.9	336	769
10	357	4.2	421	889
100	391	2.6	471	984
1000	425	1.2	515	1072
10000	463	0.005	553	1159
100000	507	0.003	553	1217

Notes: Char yield calculated from Diebold Model.  $\Delta h_p$  calculated from  $\Delta h_p = 553 - 3142F_c$ ;  $h_p$  calculated from  $h_p = \Delta h_p = c(T_p - T_a)$  with  $c = 1.3 \text{ J/g-°C}$  for cellulose

HEAT FLUX REQUIRED FOR SLOW AND FAST PYROLYSIS  
A. Small Particles & Slow Heating

The average heat flux required to pyrolyse a particle is given by

$$\dot{q} = \Delta h_p \rho V / t_p A \tag{6}$$

where  $\dot{q}$  is the rate of heat supply per unit area,  $\rho$  is the density,  $V$  is the volume and  $A$  is the heated surface area of the particle. If the particle is a cube, this simplifies to

$$\dot{q} = h_p \rho L / 6 t_p \tag{7}$$

where  $L$  is the length of the cube edge.

The data in Table 2 and 3 can be combined with this equation to predict the magnitude of heat flux required for slow and fast pyrolysis. Table 4 shows the heat flux required to pyrolyse a 1 cm cube of cellulose (or biomass). The values shown are calculated for heating the particle just to pyrolysis temperature. They assume that the particle is approximately isothermal and pyrolysis occurs everywhere at once.

The above calculation assumes that there is no resistance to heat transfer, and the particle will be essentially isothermal. However most forms of wood and biomass are relatively poor conductors of heat and at higher heating rates the results shown above will not be valid. The validity of these assumptions is tested by the Biot number, given by

$$N_b = \text{Heat flux to surface} / \text{Heat flux to interior} = H L / K \tag{8}$$

(where  $H$  is the heat transfer coefficient, characteristic of whatever method of heating is used;  $L$  is a characteristic length of the particle, typically the cube root of the volume; and  $K$  is the thermal conductivity.)

Unfortunately the heat transfer coefficient  $H$  is generally applied to convection or radiation heating with small temperature differences, where heat transfer is a strong function of  $\Delta T$ . However for high temperature radiation and contact pyrolysis sources, the

change in  $\Delta T$  is relatively small and the Biot number is approximated by

$$N_b = \frac{\dot{q}L}{K\Delta T} \quad 9)$$

The maximum heat transfer coefficients for the various heating mechanisms are also shown in Table 6.

Table 4 - Heat flux requirements and Biot number for heating of a 1 cm cube

PYROLYSIS CONDITIONS					
R	T <sub>p</sub>	h <sub>p</sub>	q̇	N <sub>b</sub>	
Heat Rate	Pyr Temp		to 1 cm <sup>3</sup>	Biot No.	
R-°C/min	°C	J/g	W/cm <sup>2</sup>		
0.01	275	162	8.20E-06	7.1E-06	
0.1	302	559	2.57E-04	2.2E-04	
1	330	769	3.23E-03	2.8E-03	
10	357	889	0.035	0.030	
100	391	984	0.35	0.304	
1000	425	1072	3.50	3.0	
10000	463	1159	34.78	30.2	
100000	507	1217	333.41	289.9	

Note: Heat flux calculated from  $\dot{q} = h_p \rho L/6 t_p$   
 Biot number calculated from  $N_b = h_p \rho L^2/6 t_p K \Delta T$   
 $K = 0.0023 \text{ J/s-cm-}^\circ\text{C}$

For Biot numbers less than 1, the particle will be nearly isothermal and will dry, then pyrolyse in sequence. For Biot numbers larger than 1, the resistance to heat transfer within the particle becomes large compared to that of the heat source and steep gradients exist in the particle. In this case the pyrolysis wave travels from the outside of the particle to the inside, producing simultaneous drying and pyrolysis.

The Biot number for a 1 cm cube is also shown in Table 4, calculated for the particle heating rates shown and assuming an average temperature difference of 500 K in. Here it can be seen that the assumption of an isothermal particle is valid for slow heating rates and small particles. However for a heating rate larger than 100 °C/min and a heating rate of 0.35 W/cm<sup>2</sup> there will be steep gradients in the particle, so that the heat flux will be altered and the drying and pyrolysis will occur simultaneously.

**B. Large Particles & Rapid Heating**

For high heat flux and larger particles, when the Biot number exceeds 1, it is necessary to calculate the non-steady state heat transfer for the particular particle geometry and surface temperature. While this can be quite complex for most cases, it is relatively simple for the one dimensional steady state case experiment described by Lede in contact pyrolysis (8). In this case a heated disk supplies sufficient heat to a beech dowel to pyrolyse and vaporize it at a rate V. The steady state temperature distribution in the rod is given by

$$T(x) = T_0 + (q/\rho c V) \exp(-Vx/\alpha) = (T_s - T_0) \exp(-Vx/\alpha) + T_0 \quad 10)$$

where T(x) is the temperature at a distance x from the heat source of strength q, T<sub>p</sub> is the temperature at the pyrolysing interface and T<sub>0</sub> is the initial temperature of the rod. The density of the wood is ρ, c

is the heat capacity,  $\alpha$  the thermal diffusivity and  $V$  the rate of pyrolysis. (Here we have taken the following values used by Lede for consistency; heat capacity,  $c = 2.80 \text{ J/g-}^\circ\text{C}$ ; density =  $\rho = 0.70 \text{ g/cm}^3$ ; thermal conductivity =  $K = 0.0023 \text{ J/s-cm-}^\circ\text{C}$ ; thermal diffusivity =  $\alpha = 0.0012 \text{ cm}^2/\text{s}$

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Table 5 - Steady State Fusion-Pyrolysis of Birch Rod

HEAT FLUX	$\dot{q}$	10.00	100	1000	W/cm <sup>2</sup>
Velocity (b)	$V$	0.01	0.11	1.14	cm/s
Penetration (c)	$X(1/e)$	0.10	0.01	0.001	cm
Heat stored	$Q$	89.76	8.98	0.90	J/cm <sup>2</sup>
Induction Time (e)	$t_i$	9.0	0.09	0.0009	s

Notes and assumptions: (a)  $T_p = 466 \text{ }^\circ\text{C}$ ,  $T_o = 20 \text{ }^\circ\text{C}$   
 (b) The pyrolysis velocity,  $V$  was calculated from  $V = q/(\rho c)(T_p - T_o)$   
 (c) The heat penetration  $X(1/e)$  was taken to be the distance at which the temperature had fallen to  $1/e$  of  $T_p$ ,  $VX/\alpha = 1$ ,  $X = \alpha/V$ .  
 (d) The heat stored in the rod,  $Q$ , was calculated as the integral of the sensible heat between  $x=0$  and  $x=\infty$ ,  $= \alpha c \rho (T_p - T_o)/V$   
 (e) The induction time  $t_i$  is the time required to establish the steady state temperature gradient,  $t_i = Q/\dot{q}$ . This assumes the heat transfer intensity is constant before steady state is reached.  
 (f) Temperature Distribution  $T = T_p \exp(-Vx/\alpha) + T_o$

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 Note in Table 5 that the velocity and heat penetration increase linearly with heat flux. However, the induction time required to reach steady state varies inversely as the square of heat flux. At low flux, considerable char may build at the interface so that the steady state condition may never be reached.

#### HEAT TRANSFER MECHANISMS FOR FAST PYROLYSIS

The magnitudes of heating rates which can be obtained from various methods of heat transfer are shown in Table 6 (Reed, 1981 Cu Mtn.). Comparing the fluxes shown in Table 4 to the values in Table 5, it can be seen that the high heating rates required for fast pyrolysis of small particles can be achieved with convection, radiation or conduction.

Convection is the least satisfactory heat transfer mechanism for fast pyrolysis because the water and pyrolysis vapors produced during pyrolysis interfere with heat transfer. Also convection from gas sources with temperatures above  $600 \text{ }^\circ\text{C}$  is unsuitable for oil production because they crack the pyrolysis oils which are only stable to about  $600 \text{ }^\circ\text{C}$ . Low temperature radiation sources (below  $1000 \text{ }^\circ\text{C}$  are also unsatisfactory for fast pyrolysis of larger particles.

The production of pyrolysis oil is favored by radiation from a high temperature source or by "contact pyrolysis" (see below). In the case of radiation, the solid is heated rapidly, but the vapors are largely transparent and transient and so are not overheated (12). Unfortunately black body sources with temperatures above  $2000 \text{ }^\circ\text{C}$  are expensive and difficult to use.

#### CONTACT PYROLYSIS

A new method of heat transfer, "contact pyrolysis", has been developed in the 1980's and appears to be especially suited for the production of pyrolysis oil vapor.

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 Table 6 - Heat Transfer Rates and Heat Transfer  
 Coefficients from Various Devices

	Typical Temp diff $\Delta T$ K	Maximum Ht Transf $\dot{q}$ W/cm <sup>2</sup>	Maximum Ht tr coef H W/cm <sup>2</sup> -K
<b>CONVECTION</b>			
Gas Free Convection	500	10	0.02
Gas forced convection	500	300	0.6
Air-Gas Flame	1500	200	0.13
Oxy-Acetylene flame	3000	3000	1.00
<b>CONVECTION, ELECTRONIC</b>			
Electric arc	10,000	20,000	2
<b>RADIATION</b>			
	Surface T °K		
Black Body	773	20	0.026
	1,273	150	0.12
	2,273	1,500	0.66
	5,273	44,000	8.3
Focused CO2 laser		100,000	NA
CONTACT PYROLYSIS	873	3,000	3.2

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 In 1980 Diebold showed that a moving hot wire would cut through a piece of wood at rates of several cm/sec with apparently no production of charcoal (7). Ledé et al have since shown that a wood dowel can be consumed at rates up to 3 cm/sec corresponding to heat transfer rates of 3000 J/cm<sup>2</sup> by pressing it against a heated disk (8). Furthermore the heat transfer rate is directly proportional to pressure, and a pressure of 30 atmospheres was used to attain the above heat transfer rate. The heat transfer is also proportional to the difference between the disk temperature and 466 °C. This was interpreted to show that the wood had a "fusion behavior" above 466°C (8,13). Reed has now developed a "heat flux concentrator" (see below) using a copper block to produce vapors for catalytic conversion to fuel (9).

Contact pyrolysis has several interesting and non-obvious features:

- o The thermal conductivity of metals is typically 3-4 orders of magnitude higher than that of hot gases or biomass, and so the heat transfer produced by direct contact is proportionally high.
- o The use of pressure at the heated interface retards the vaporization of the pyrolysis products so that they do not interfere with heat transfer, and instead the biomass pyrolyses to an oil or foam
- o When the resulting oil or foam is squeezed out of the interface region, it is immediately in a low pressure region and can vaporize very rapidly
- o The rubbing contact removes char or ash which would otherwise interfere with heat transfer

#### A HEAT FLUX CONCENTRATOR FOR CONTACT PYROLYSIS PRODUCTION OF PYROLYSIS OIL VAPOR

In order to produce vapors for catalytic conversion to hydrocarbon fuels, we have developed a "heat flux concentrator" shown

in Fig. 5 and 6. In operation, a wood dowel is rotated in a drill press and forced into a 1.2 cm diameter tapered hole in the heated copper block shown in Fig. 5. The rod is fed at a rate of 0.2 - 0.25 cm/sec. The vapors escape through 12 holes through the bottom of the block and are then captured in traps and in a gas burette. Alternatively, the vapors travel without cooling to a catalyst test furnace as shown in Fig. 6 where the products are captured (9).

The heat flux concentrator has been operated to produce pyrolysis vapor as an end product, or to test the operation of various catalysts. A preliminary mass balance on pyrolysis oil production is shown in Table 7 for pyrolysis runs. We observe that the walls of the pyrolyser and the exit holes become coated with a hard, shiny form of carbon like petroleum coke. We now believe that there is a high resistance to vaporization which causes plugging of the pyrolyser after the feeding of about 5 g. We are currently modifying the design to improve vaporization. A few catalyst runs have also been made and they will be described in more detail later.

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 Table 7 - Preliminary Mass Balance on Contact Pyrolysis Experiments

Pyrolysis Run	T <sup>o</sup> °C	Wood Consumed	g liq/ g wood	g gas/ g wood	g coke/ g wood	Mass out/ Mass in
5p	550	2.56	0.61	0.10	0.27	0.98
8p	600	5.59	0.57	0.10	0.33	1.00
9p	500	6.10	0.52	0.12	0.25	0.89
11p	700	4.21	0.57	0.13	0.14	0.85

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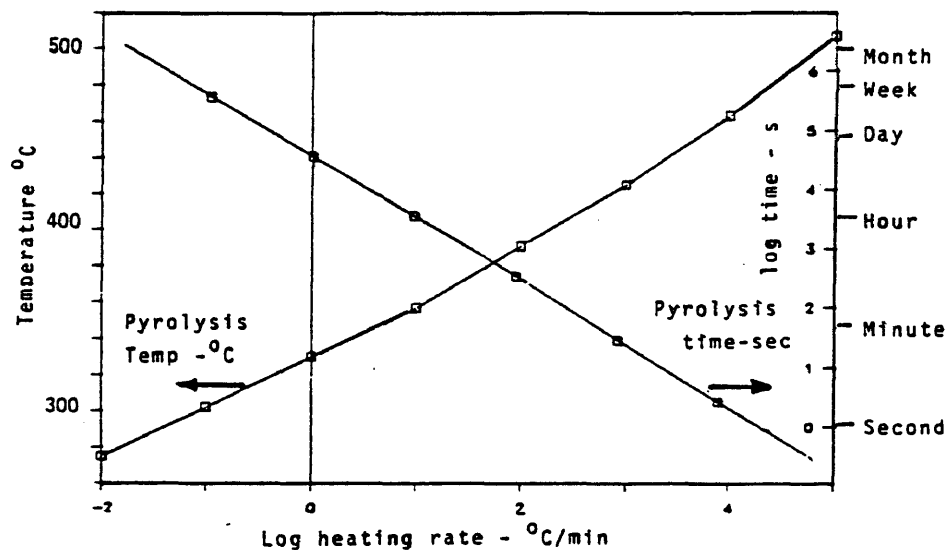


Figure 1 - Time and temperature for pyrolysis of cellulose as predicted by Diebold Kinetic Model

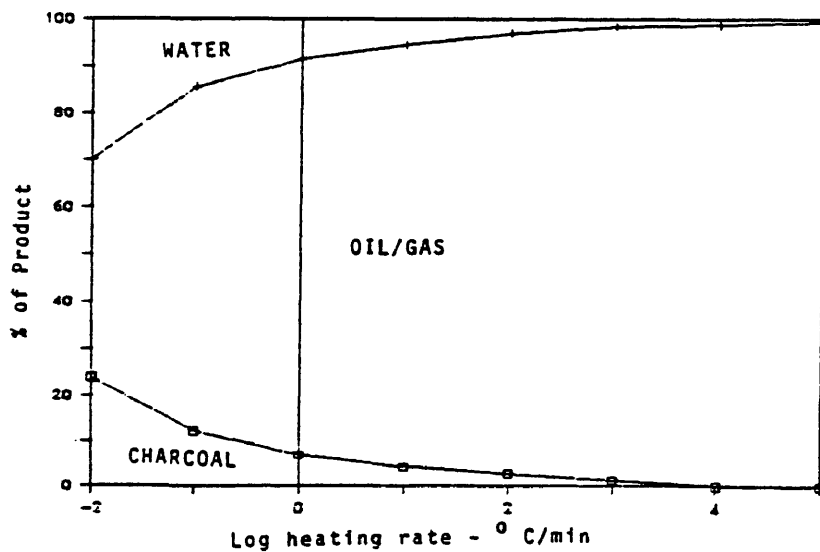


Figure 2 - Products of cellulose pyrolysis as predicted by Diebold Kinetic Model

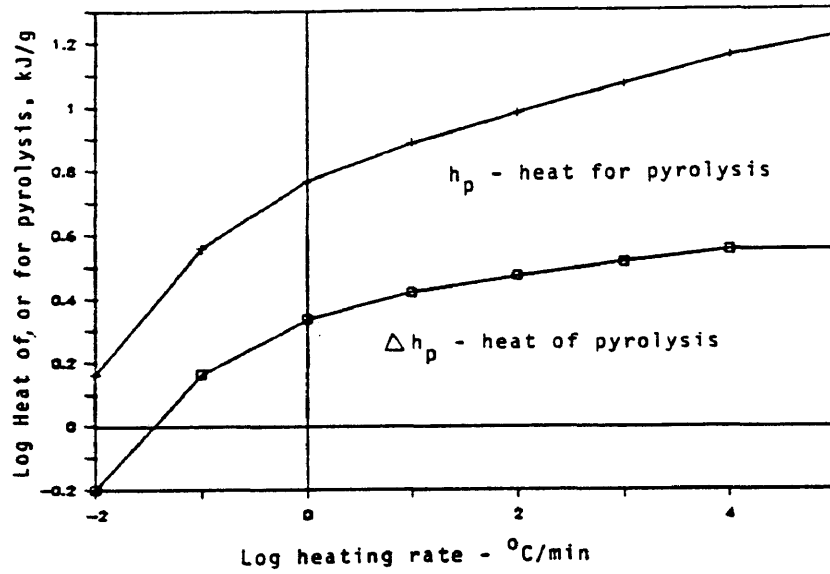


Figure 3 - Heat of pyrolysis and heat for pyrolysis as predicted from char yields and pyrolysis temperature

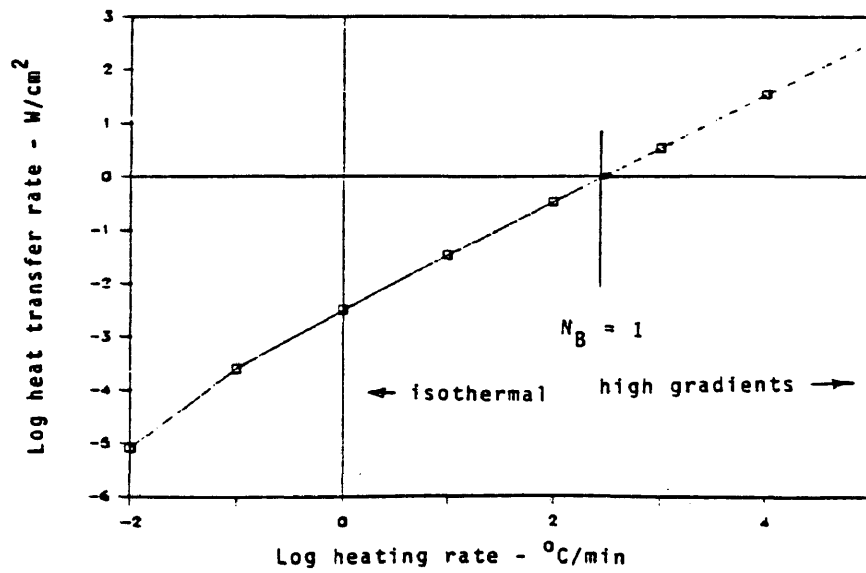


Figure 4 - Heat transfer rate required to support heating rate

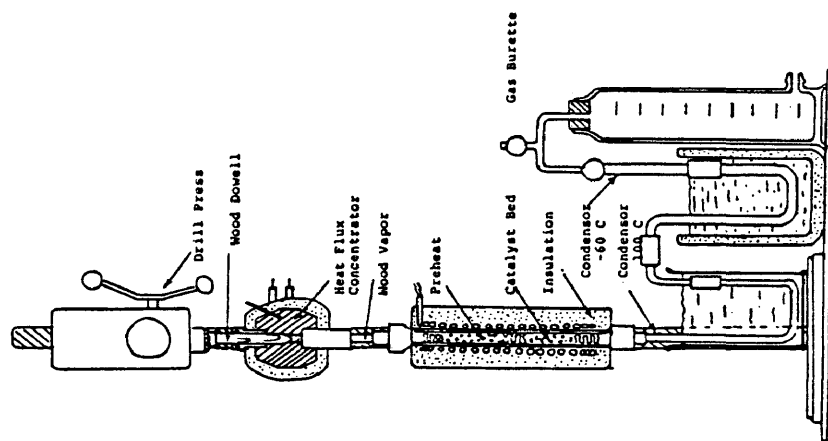


Figure 6 - Microanalytic test apparatus for catalyst testing

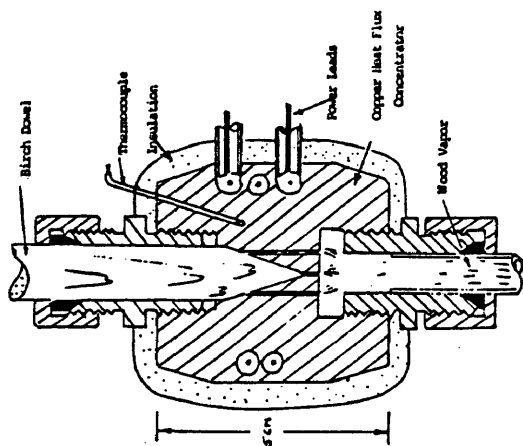


Figure 5 - Contact pyrolysis furnace for producing wood vapor