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

Thomas B. Reed & Craig D. Cowdery
Colorado School of Mines, Golden CO 80401

ABSTRACT
The term "fast pyrolysis" has been used to describe a pyrolysis regime in which vapor production is enhanced and char mimimized 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 occuring 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, hemi-cellulose 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 hemi-cellulose. 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 Arhennius rate equation

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

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

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

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 oversimplfification may be justified over a narrow temperature range for engineering purposes, the global approach ignores preliminary solid state reactions and 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 (trans-glycolization) 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.ote that the reaction producing char reaches a rate of

69

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

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

```
                              ┌─kvₑ──► SECONDARY GAS
                              │         ↑ kᵥg
   FEED ──────kₐ──────►  ACTIVE ─────► PRIMARY ──kᵥₜ─► SECONDARY
                              │         VAPORS           TAR(v)
      └─k_d─► CHAR(d)+H₂O      └─kc─► CHAR(a) + H₂O
```

REACTION	k	A	E	T(R=10⁻⁶)	T(R = 1)
		sec⁻¹	kJ	°C	°C
Cellulose to char + H2O	k_d	6.69E+05	109	208	703
Cellulose to Active	kₐ	2.80E+19	243	225	379
Active to Primary Vapor at 1 atm	k_v	6.79E+09	140	188	470
Active to primary vapor vacuum	k_vv	3.20E+14	198	231	440
Active to Char(b) + H2O	k_c	1.30E+10	153	224	518
Active to gas	k_vg	3.57E+11	204	335	651
Primary vapors to gas	k_vg	3.57E+11	204	335	651
Primary vapors to tars	k_vt	1.81E+03	61	70	700

Notes: Kinetic constants used in Diebold kinetic model. $T(R = 10^{-6})$ is the temperature where the rate contsant $R = 10^{-6}$; $T(R = 1)$ 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_v and k_{vv}. 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_p and pyrolysis temperature, T_p 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_p	T_p			
Heat Rate	Pyr Time	Pyr Temp	Char-	Oil,Gas	Water
R-°C/min	sec	°C	coal-%	%	%
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^{-2} to 10^5 °/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 oil yields are still increasing with rates of over 10^4 °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 controling products in pyrolysis.
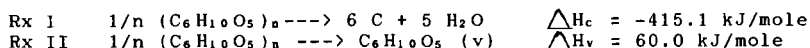
While the calculations in this paper are for cellulose, we believe the conclusions are qualitatively valid for all biomass.

HEAT OF PYROLYSIS AND HEAT FOR PYROLYSIS:

The energy required for pyrolysis, $\triangle h_p$ 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 condensible 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, $\triangle h_p$, as that heat required to effect the phase change from biomass to char-liquid-gas at

71

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 $\triangle h_p$ can be made for cellulose based on the idealized reactions shown in Table 1. The idealized charing reaction for cellulose can be written as Rx I:

Rx I $1/n$ $(C_6H_{10}O_5)_n$ ---> 6 C + 5 H_2O $\triangle H_c$ = -415.1 kJ/mole
Rx II $1/n$ $(C_6H_{10}O_5)_n$ ---> $C_6H_{10}O_5$ (v) $\triangle H_v$ = 60.0 kJ/mole

(Here we use the notation $1/n$ $(C_6H_{10}O_5)_n$ 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 a-mount of carbon formed, eg

$$\triangle H_p = 59.96 - 475.1 \ F_c \ \text{kJ/mole} \tag{3}$$
or $$\triangle h_p = 370 - 6603 \ F_c \ \text{J/g} \tag{4}$$

where F_c is the weight fraction of carbon produced in the charing 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 $\triangle h_p$ 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 $\triangle h_p$ 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

$$\triangle h_p = 553 - 3142 \ F_c \ \ \text{kJ/g} \tag{5}$$

where F_c is the fraction of charcoal produced. Note that the values for the coeficients 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, $\triangle h_p$. (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 $\triangle h_p$.

72

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

PYROLYSIS CONDITIONS Heat Rate $R-°C/min$	Pyr Temp $°C$	Char-coal-%	$\triangle Hp$ 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. $\triangle h_p$ calculated $\triangle hp$ = $553-3142F_c$; h_p calculated from $h_p = \triangle h_p = c(T_p - T_o)$ with c = 1.3 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

$$\dot{q} = \triangle h_p \rho V/t_p A \qquad 6)$$

where $\dot{q}$ is the rate of heat supply per unit area, 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

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

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

$$N_B = \text{Heat flux to surface/Heat flux to interior}$$
$$N_B = H \ L/K \qquad 8)$$

(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 $\triangle T$. However for high temperature radiation and contact pyrolysis sources, the

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

$$N_B = \overset{\bullet}{q}L/K\triangle T \qquad\qquad 9)$$

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_p	h_p	;	$\overset{\bullet}{q}$	N_B
Heat Rate	Pyr Temp		;	to 1 cm3	Biot No.
R-°C/min	°C	J/g	;	W/cm2	
			;		
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 $\overset{\bullet}{q} = h_p\,\rho\,L/6\,t_p$
Biot number calculated from $N_B = h_p\,\rho\,L^2/6\,t_p K\triangle T$
K = 0.0023 J/s-cm-°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^2 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

$$T(x) = T_0 + (q/\rho cV)\exp(-Vx/\alpha) = (T_d - T_0)\exp(-Vx/\alpha) + T_0 \qquad 10)$$

where $T(x)$ is the temperature at a distance x from the heat source of strength q, T_p is the temperature at the pyrolysing interface and T_0 is the initial temperature of the rod. The density of the wood is ρ, c

is the heat capacity, α the thermal diffusivity and V the rate of pyrolysis. (Here we have taken the following values used by Lede for consistancy; heat capacity,c = 2.80 J/g-°C; density = ρ = 0.70 g/cm³.; thermal conductivity $\square$ K = 0.0023 J/s-cm-°C; thermal diffusivity = α = 0.0012 cm²/s

===
Table 5 - Steady State Fusion-Pyrolysis of Birch Rod

HEAT FLUX	$\overset{\bullet}{q}$	10.00	100	1000	W/cm²
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/cm²
Induction Time (e)	t_i	9.0	0.09	0.0009	s

Notes and assumptions: (a) T_p = 466 °C, T_o = 20 °C
(b) The pyrolysis velocity, V was calculated from V = q/(ρc)(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/α = 1, X=α/V.
(d)The heat stored in the rod, Q, was calculated as the integral of the sensible heat between x=0 and x=∞, = αcρ (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/$\overset{\bullet}{q}$. This assumes the heat transfer intensity is constant before steady state is reached.
(f) Temperature Distribution T = T_p exp(-Vx/α) + T_o
===
    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 °C is unsuitable for oil production because they crack the pyrolysis oils which are only stable to about 600 °C. Low temperature radiation sources (below 1000 °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 °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.

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

	Typical Temp diff $\triangle T$ K	Maximum Ht Transf $\overset{\circ}{q}$ W/cm²	Maximum Ht tr coef H W/cm²-K
CONVECTION			
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
CONVECTION, ELECTRONIC			
Electric arc	10,000	20,000	2
RADIATION	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
```
========================================================================
```

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). Ledè 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/cm² 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.

```
================================================================
```
Table 7 - Preliminary Mass Balance on Contact Pyrolysis Experiments

Pyrolysis Run	T_P °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

```
================================================================
```

REFERENCES

1. Stern, A. J. and Harris, E. E., "Chemical Processing of Wood",
    Chemical Publishing Co., New York, 1953

2. Antal, M. J., Jr., "Biomass Pyrolysis: A Review of the
    Literature, Part I-Carbohydrate Pyrolysis", in **Advances in Solar
    Energy**, ed K. W. Boer and J. A. Duffie, American Solar Energy
    Society, Boulder, CO, Vol 1, pp 61-112.

3. Antal, M. J., Jr., "Biomass Pyrolysis: A Review of the
    Literature, Part II-Lignocellulose Pyrolysis, in **Advances in Solar
    Energy**, ed K. W. Boer and J. A. Duffie, American Solar Energy and
    Plenum Press, New York, Vol 2, pp 175-255.

4   Bradbury, A. G., Sakai, Yoshio and Shafizadeh, F., "A Kinetic
    Model for Pyrolysis of Cellulose", J. **Appl. Polymer Science, 23**
    3271 (1979)

5. Diebold, J. P., "The Cracking Kinetics of Depolymerized Biomass
    Vapors in a Continuous Tubular Reactor", Thesis T-3007, Colorado
    School of Mines, Golden, CO 1985.

6. Diebold, J. P., Scahill, "Ablative, Entrained Flow Fast Pyrolysis
    of Biomass", in **Proceedings of the 16th Biomass Thermochemical
    Contractors' Meeting**, Portland, OR May 8-9, 1984, PNL-SA-12403,
    1984. See also, Diebold, J. P. "A unified Global Model for the
    Pyolsis of Cellulose", (in preparation).

7. Diebold, J. P., "Ablative Pyrolysis of Macroparticles of Biomass,"
    **Proceedings of the Specialists Workshop on the Fast Pyrolysis of
    Biomass**, Copper Mountain, CO., Oct. 12 1980, Solar Energy Research
    Institute, Golden, CO. 80401, SERI/CP-622-1096.

8. Lede, J., Panagopoulos, J., Li, H. Z. and
    Villermaux, J., "Fast Pyrolysis of Wood: Direct Measurement and
    Study of Ablation Rate", **Fuel** $\underline{64}$, 1514 (1985)

9. Reed, T. B., Diebold, J. P., Chum, H. L., Evans, R. J.
    Milne, T. A. and Scahill, J. W., "Overview of Biomass Fast
    Pyrolysis and Catalytic Upgrading to Liquid Fuels," in
    Proceedings of the American Solar Energy Society, K. W.
    Boer, Ed., Boulder, CO June 11, 1986.

10. Roberts, A. F., "The Heat of Reaction During the Pyrolysis of
    Wood", **Combustion and Flame** $\underline{17}$, 79 (1971).

11. Reed, T. B., Diebold, J. P. and Desrosiers, R., "Perspectives in
    Heat Transfer for Pyrolysis", **Proceedings of the Specialists
    Workshop on the Fast Pyrolysis of Biomass**, Copper Mountain, CO.,
    Oct. 12 1980, Solar Energy Research Institute, Golden, CO. 80401,
    SERI/CP-622-1096.

12. Chan, W. -C. R., Kelbon, M. and Krieger, B. B., "Product Formation
    in the Pyrolysis of Large Wood Particles", **Fundamentals of
    Thermochemical Biomass Conversion**, ed. R. P. Overend et al,
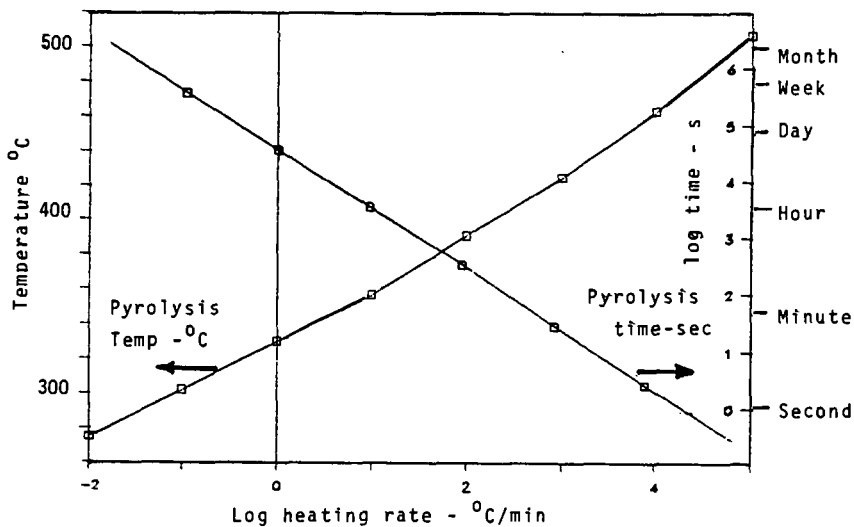   Elsevier, New York, 1985.

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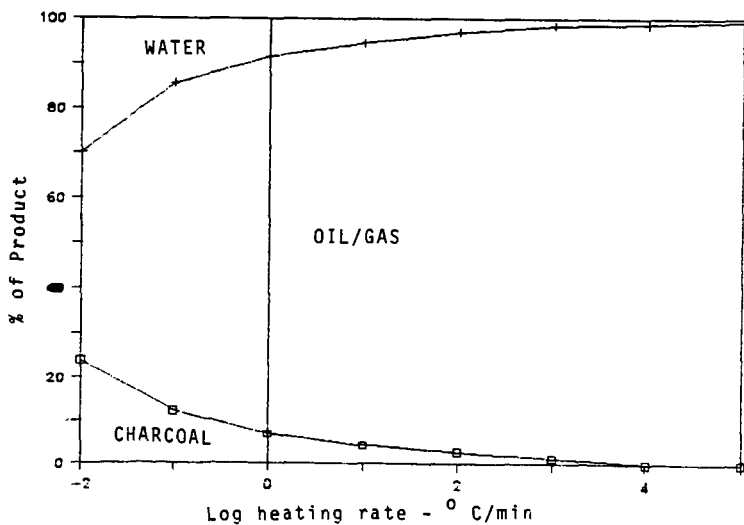

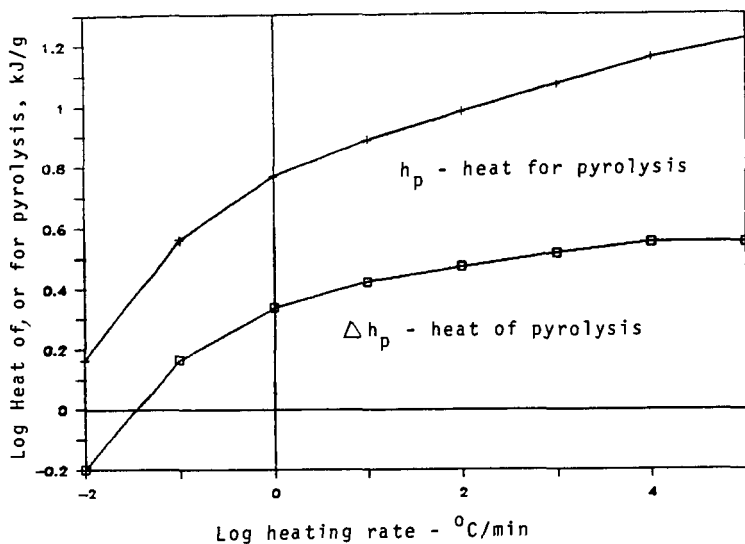Figure 2 - Products of cellulose pyrolysis as predicted by Diebold Kinetic Model

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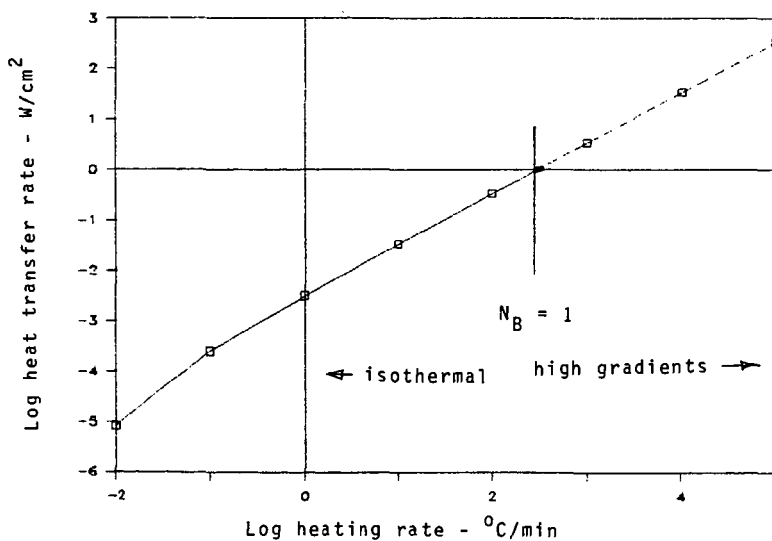from char yields and pyrolysis temperature

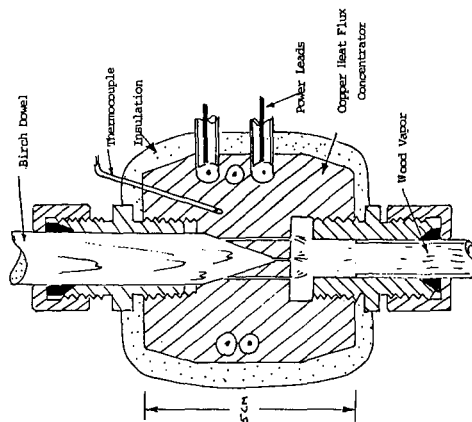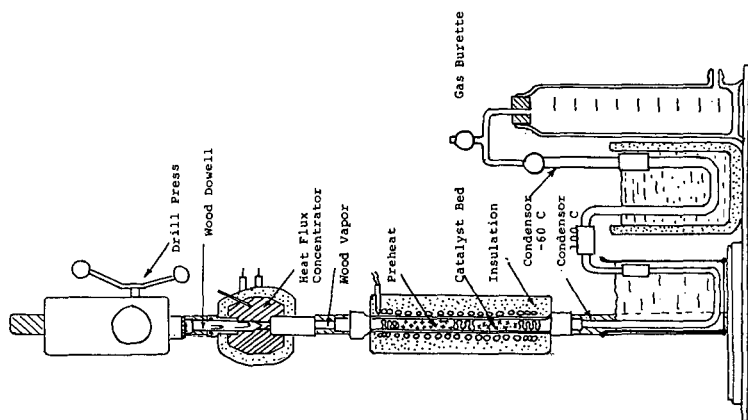Figure 4 - Heat transfer rate required to support heating rate

Figure 6 – Microanalytic test apparatus for catalyst testing

Figure 5 – Contact pyrolysis furnace for producing wood vapor