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BURNING TIMES OF WOOD CUBES

*The University of Nebraska - Lincoln*

PH.D.

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BURNING TIMES OF WOOD CUBES

by

Edward Remick Huff

A DISSERTATION

Presented to the Faculty of  
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In Partial Fulfillment of Requirements  
For the Degree of Doctor of Philosophy

Major: Interdepartmental Area of Engineering

Under the Supervision of Professor William E. Splinter

Lincoln, Nebraska

August, 1979

**TITLE**

Burning Times of Wood Cubes

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CHAPTER I  
ENERGY FROM BIOLOGICAL MATERIALS

THE NEED

In 1953, when advertisements were persuading us to convert to oil and use more gas, Palmer Putnam (1953) wrote the book Energy in the Future in which he says, "The United States and much of the Free World have been living high off accumulated capital energy in the cream of the coal, oil and gas reserves". He then concludes:

If, as is supposed, "low-cost" energy is essential to the liveliness of an economy, then new sources of "low-cost" energy must begin to carry some of the load by A.D. 1975 or sooner, and much of it by A.D. 2000, if we are not to run the risk of seeing economic systems throughout the non-Communist world falter in the face of steeply rising costs of energy.

The next 20 years saw U.S. energy consumption double, with the largest increases being in those fuels in shortest supply, oil and gas. In a national address in 1979, President Carter attributed a part of the U.S. economic difficulty to importation of nearly half of its oil.

There is no easy solution for our energy problems. No single source of energy can meet our needs. Solution of our energy problems, if it comes, will be in the form of many types of contributions, including energy conservation and developing sources of income energy including biological materials. Two examples of the possible use of these materials for energy will illustrate the national need and potential.

Nine-tenths of Maine, or 17,750,000 acres, is forest covered. In 1970, 409 million cubic feet of lumber was cut, resulting in 162 million cubic feet of waste wood from forest operations and wood processing plants. Ferguson and Kingsley (1972) estimated that this waste, if all were retrieved, could heat Maine's 250,000 dwelling units, most of which are now heated with oil.

In 1975, Nebraska irrigated approximately 5.6 million acres, mostly from wells (Fischbach 1976). The energy required to do this varies from 0.5 to 2 million BTU per acre per season. W. E. Splinter of the University of Nebraska (1976, 1977) has suggested using about a third of the approximately 3 tons per acre of corn stover (stalks, leaves, and cobs) to supply energy for irrigation, leaving the other two-thirds for soil protection and cattle feed. At 8,000 BTU per pound of dry material and with combustion, prime mover, and pump efficiencies of 60%, 20%, and 80%, one ton of stover would provide 1.5 million BTU, enough energy for most applications. It thus seems possible to use one-third of the residual material to supply the energy for irrigation of corn.

Because of our need and their availability, it seems desirable to develop the use of biological materials for heat. This work will be directed toward that end.

#### SPECIFIC AREA OF THIS STUDY

Whether the need is to heat houses, irrigate corn, or some other application of the energy from biological materials, it is desirable

to obtain controlled heat release and retrieval from a wide variety of materials. The general problem can be broken down into six aspects: mechanical handling, drying, combustion, ash separation and disposal, heat retrieval, and system behavior and control. Of these six aspects, combustion is the one addressed in this study.

Increasing combustion intensity permits a smaller firebox with a smaller surface area, reducing heat loss. A smaller firebox contains less material to raise in temperature when first starting, which is particularly desirable for comfort heating units with on-off control.

Combustion intensity depends on burning time of particles entering a firebox. It is therefore desirable to determine the effects of such parameters as size, moisture content, shape, material density, and firebox temperature on burning time. While it is desirable to know these things for bulk material, a beginning can be made by determining them for single particles in a known environment. It is this problem that this dissertation addresses.

## CHAPTER 2

### COMBUSTION RESEARCH LITERATURE

This chapter reviews the areas of research most closely associated with the combustion of cellulosic materials and increasing combustion intensity.

#### WOOD COMBUSTION

Reineke (1960) and Koch (1972) summarized the combustion of wood as taking place in three consecutive overlapping stages as follows:

1. Evaporation of water, which absorbs approximately 2300 kJ per kg of water evaporated. Fuel temperature does not much exceed 373°K until moisture content is near zero.
- 2a. Volatilization of combustible gases (Pyrolysis). Volatile matter comprises about 60% of the mass of dry wood. This stage absorbs approximately 465 kJ per kg of gas evolved. Temperature rises during this stage, until the volatile matter is removed.
- 2b. The gases evolved may burn as they are evolved, or they may ignite downstream of the bed. This part of the process is exothermic. This large percentage of volatile matter produces a long flame, requiring a larger combustion space outside of the bed itself than coal requires.

3. Combustion of char. The charcoal remaining after volatilization is now mostly carbon which unites with oxygen to form CO or CO<sub>2</sub>, depending on oxygen availability. This glows at 800°K or higher. This process is exothermic.

When wood is heated in the absence of air, only stages 1 and 2a occur. When heated with insufficient air, stage 2b may only partially take place, and stage 3 may supply heat for the other stages and add CO to the combustible gases.

Browne (1958) described four zones of pyrolysis and the difference in pyrolysis products obtained from slow and fast pyrolysis rates, as summarized in Table 2.1. Lee et al. (1976) also described three pyrolysis zones and approximate temperatures at which they occur. They found that events took place at lower temperatures with slower heating.

Kanury (1970) stated that pyrolysis temperature is a function of depth beneath the heated surface because of incubation of different layers at various temperatures for different durations. Those layers held at higher temperatures for longer times pyrolyze at a lower temperature.

Kanury (1970, 1972) described combustion of a slab undergoing pyrolysis because of heat supplied symmetrically to both sides. He described three phases, called the preheat, infinite body, and finite body phases. When material is burning or otherwise heated from the outside, the preheat phase occurs until the surface starts pyrolyzing. During this phase, the surface temperature is rising and heat is flowing into the interior of the solid. He called this a thermal wave.



TABLE 2.1  
PYROLYSIS ZONES AND THEIR PRODUCTS\*

Zone	Temperature, °K	What Happens
A	< 470	Water vapor, formic and acetic acids, and possibly CO <sub>2</sub> are evolved. Charring may eventually occur at temperatures as low as 370°K.
B	470-550	The reaction becomes exothermic between 420 and 530°K. Ignition may be possible with enough time.
C	550-770	Combustible gases are evolved, blocking oxygen from the surface.
D	> 770	Charcoal glows.

Rate of Heating Through the Pyrolysis Range

Slow (several hours)	Rapid (several seconds or minutes)
Much charcoal	Little charcoal
Little tar	Much tar
Less flammable gases containing much H <sub>2</sub> O + CO <sub>2</sub>	Highly flammable gases, rich in H <sub>2</sub> , CO, & HC's
Decomposition proceeds in an orderly manner, with stepwise formation of increasingly stable molecules, richer in carbon, converging toward hexagonal structure of graphitic carbon.	Macromolecules may be torn into volatile fragments with little orderly arrangement.
Releases energy	Consumes energy

\*From Browne (1958)

In the infinite body phase (so called because the temperature profile would be no different if the body were infinitely thick) the thermal wave continues to penetrate the solid, and now a pyrolysis wave follows it.

When the thermal wave reaches the plane of symmetry, the finite body pyrolysis phase begins. The pyrolysis front continues to move in while the interior solid material continues to preheat.

The gases released in pyrolysis may create a pressure in the material where they are formed and travel in directions where resistances to flow are low. They sometimes flow into cooler regions of the solid as well as out, where some components may recondense, to be gasified again later when the pyrolysis front reaches that point. Those that flow outward are further heated. Thus internal convective heat transfer inhibits the inward heat transfer by conduction.

Behind the pyrolysis wave is char with gases flowing outward through it. When the end of the pyrolysis wave has reached the plane of symmetry, there remains char without the gas flow.

Roberts (1970) described four regions of a pyrolysis wave advancing into wood:

1. Wood structure virtually intact. Pyrolysis begins.
2. Wood structure has failed. Most reactive constituents (cellulose and hemicellulose) pyrolyze.
3. Pyrolysis of cellulose and hemicellulose is complete. Ligin is now pyrolyzing.
4. All wood has pyrolyzed to char. Secondary reactions between char and outward-bound volatiles may occur.

There remains some question as to whether pyrolysis is endothermic or exothermic. Kanury (1972) described pyrolysis as "an endothermic irreversible chemical degradation process in which the virgin wood is transformed into char residue and combustible vapors." Unlike many other workers who reported that pyrolysis is exothermic at some points, Kanury theorized that all pyrolysis is endothermic but that gases passing out through the hot char undergo exothermic catalytic reactions that make the pyrolysis appear exothermic.

By comparing terms in his mathematical expressions, Kung (1973) argued that the basic pyrolysis reaction is endothermic but that the changing heat capacities of wood, char, and gas sometimes give higher temperatures in the middle of pyrolyzing specimens than on the outside. This he said led some prior researchers to regard pyrolysis as sometimes exothermic. Havens et al. (1971) also concluded that decomposition of wood in a non-oxidative atmosphere is endothermic.

Lee et al. (1976) concluded that heat of reaction varies with heating rate, from endothermic at low heating rates to exothermic at high heating rates. This, they said, accounts for the varying heats of pyrolysis in the literature. It may also account for the disagreement on whether pyrolysis is endothermic or exothermic.

#### MATHEMATICAL MODELS OF PYROLYSIS

In 1946, Bamford, Crank, and Malan (1946) performed a pioneer work in describing mathematically the pyrolysis reaction. They "combined the

equations for heat conduction in a solid with those for heat generation by a first order reaction and solved them by a finite difference method for the conditions of a series of experiments which they performed. In their experiments boards of various thickness were heated on both sides by flames, and their surface and center temperatures were measured. The values of activation energy, velocity constant, and heat of reaction which gave the best agreement between experimental and calculated values of the center temperature were then determined" (Roberts 1963).

Many workers since then have tried to develop models to describe mathematically the rate of temperature increase, mass loss, and other variables in the pyrolysis of wood and other cellulosic materials. Most have worked with slabs or cylinders, which can be treated as one dimensional problems.

The two equations most commonly used by these workers are the Arrhenius rate equation and some form of the Fourier conduction equation. The Arrhenius equation, applicable to many chemically controlled reactions, is (Edwards 1974)

$$\frac{dm}{dt} = F e^{-E/RT}, \quad (2.1)$$

where  $dm/dt$  is the rate of change of mass.  $F$  is the frequency factor, and is a measure of the number of effective collisions of gas molecules. It has been called a velocity constant.  $E$  is the activation energy of the material,  $R$  is the universal gas constant, and  $T$  is the absolute temperature.

The Fourier equation for one dimensional conduction in a slab with an internal heat source is

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} - \frac{Q}{c\rho} \frac{\partial \rho}{\partial t}, \quad (2.2)$$

where  $c$  is heat capacity,  $\rho$  is density,  $t$  is time,  $k$  is thermal conductivity,  $\alpha$  is thermal diffusivity, and  $x$  is depth. With no internal heat source, the last term is zero.

Tinney (1965) solved the Fourier conduction equation, including the source term, for temperature at any radius and time in dry wooden dowels heated in air in a constant temperature oven. The dowels received heat from the outside by radiation and convection, and were assumed to react exothermically. The rate of density change was assumed to follow the first-order Arrhenius decomposition equation. He used numerical methods to solve these equations, and determined values for the heat of decomposition and for  $E$  and  $F$  for the Arrhenius equation.

Roberts and Clough (1963) heated wood cylinders in a nitrogen atmosphere in a furnace. Temperature was measured at several internal points in the cylinders, which were weighed continuously while heating. They used an integrated form of the Arrhenius equation at each annulus where a thermocouple was mounted in the specimen, as a basis for determining values of  $E$  and  $F$  in the equation. Then from a heat balance equation on each annulus they arrived at a heat of reaction for the pyrolysis reaction.

Roberts (1971) extended the work of Roberts and Clough (1963) and of Tinney (1965) to include the effect of fissures in the char on escape

of volatiles and on heat transfer. He developed an equation to describe the rate of advance of a steady state pyrolysis wave into a wood slab. To confirm theory, he continuously weighed square specimens of oven dry wood exposed to a known radiant heat flux. He observed a linear relationship between applied heat flux and peak rate of evolution of volatiles.

Blackshear and Kanury (1970) showed that for cellulose cylinders burning under free convection in a pile, the ratio of mass at any time to the original mass is a function of  $t/D^{1.6}$  while the internal temperature profiles correlate with  $t/D^2$ . They assume, and support mathematically, that the influence of temperature on decomposition rate can be described by a simple power law instead of the Arrhenius negative inverse exponential law. They then show that in a pyrolyzing solid, heat transfer by internal convection (the movement of gases in the material) can often be about the same magnitude as that by conduction, and indicate that as specimen size increases the effect of this internal convection increases.

Kanury (1970) cited a model for pyrolysis used earlier, added terms to include internal convection, and gave conditions that dictate significance of the convection term. Increasing specimen size increases the effect of convection by increasing the volume of gases coming out from the inside, retarding heat flow into the specimen. He thought that under most conditions this gives a stronger dependence of burning rate on size than a pure conduction model would suggest.

In discussing kinetics of pyrolysis, Kanury cited previous workers who determined the reaction rate of wood when subjected to nitrogen

atmospheres at 500, 700, and 900°C. They found reaction rate to be twice as fast for disks cut parallel to the grain as for disks cut normal to it. Rate constant was directly proportional to specific surface area and temperature. He noted that the advent of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have greatly increased the study of kinetics. DTA is used to detect compositional changes during breakup, by analysis of the thermograms produced. TGA measures mass vs. temperature of small samples and is used to determine activation energies for the decomposition.

Kanury (1971) attempted to build a model for charring solids. He considered the problem as a heat and mass transfer problem influenced by the chemistry of pyrolysis. His experimental technique included taking x-ray pictures that show changing density as wood dowels burn, and correlating these with continuous weight measurements. He plotted density and rate of density loss vs. time at 8 radii in the rods. He observed that "Layers of solid lying progressively deeper from the exposed surface exhibit a progressively lower maximum pyrolysis rate and a progressively wider range of temperature (and time) in which pyrolysis occurs." Assuming a first-order Arrhenius-type rate law, he determined values for E and F. The activation energy he determined is about half the value commonly expressed in the literature of DTA/TGA measurements.

Kanury (1972) developed an empirical equation to relate pyrolysis rate to thickness of a specimen:

$$t_p = C x^n, \quad (2.3)$$

where  $t_p$  is a characteristic pyrolysis time, initial mass of specimen/

maximum rate of mass loss.  $C$  is a constant, a function of the properties of the solid,  $x$  is the half thickness of the specimen, and  $n$  is a constant.

Havens et al. (1972) listed six parameters that generally must be specified for mathematical models of thermal decomposition processes in solids. These are density, heat capacity, thermal conductivity, heat of decomposition, frequency factor, and activation energy. All of these may vary during decomposition of the material.

Their model did not require the first four parameters above to be constant, and did not use the Arrhenius equation. Instead, the energy effects associated with decomposition were measured directly by differential scanning calorimetry. They solved their equation numerically for temperature and weight loss with time for a cylinder with an axial hole, then heated pine cylinders in a nitrogen atmosphere using a resistance wire centered in the hole. The cylinders were weighed before and after the tests and temperature was measured by thermocouples in the cylinders. They found excellent agreement between predicted and measured temperatures and weight loss, with a model that required fewer assumptions concerning constancy of material properties.

Kung (1972) developed a mathematical model for pyrolysis in a wood slab which includes transient heat conduction, the Arrhenius reaction rate, internal convection by volatiles, endothermicity of pyrolysis, and variable thermal properties. Solving these equations numerically, he showed that the magnitude of the convection term in his equations was equivalent to the conduction term and therefore could not be neglected. He did not verify his model with experiment.