

Effects of Fire Retardant Addition on the Combustion Properties of a Charring Fuel

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ABSTRACT

Results are presented which show the effect of fire retardant addition on the fuel related properties used in diffusion flame calculations. Samples of cellulose retarded with up to 3 wt. percent of sodium hydroxide were subjected to a radiant heat flux of 40 kW/m² in a special apparatus designed for this purpose. The volatile products of pyrolysis were analyzed using a gas chromatograph to determine the concentration of inert gases (carbon dioxide and water). Retardant addition was found to increase both the char yield and the production of inert gases. This results in a decrease in the fuel fraction in the pyrolysate from 69 wt. percent for pure cellulose to 35 wt. percent for retarded cellulose. The corresponding change in the stoichiometric oxygen/fuel ratio is from 1.6 for pure cellulose to a maximum of 2.3 for retarded cellulose. Retardant addition also causes a decrease in the heat of gasification (defined as the energy input to generate a unit mass of volatiles) and an increase in the heat of combustion of the combustible gases in the pyrolysate.

Keywords: (1) materials properties (2) retardants (3) heat of gasification (4) heat of combustion

INTRODUCTION

In this paper we examine the effects of a solid-phase fire retardant (sodium hydroxide) on the combustion properties of a charring fuel (cellulose). After tests with wood and commercial plastics, cellulose was chosen as an "ideal" charring material for basic studies because of its dimensional stability during combustion and the reproducibility of the results obtained. Sodium hydroxide was selected from a ranked list of retardants given by Shifazadeh et al. [1]. The method devised for preparing

homogeneous samples containing a known amount of retardant is described in Sibulkin and Tewari [2]. Measurements of flaming combustion presented in that paper showed that sodium hydroxide is an effective retardant in the sense that addition of 0 to 3 wt. percent of NaOH raised the oxygen index from 0.18 to over 0.30.

Diffusion flame theory, e.g., Sibulkin [3], can be used to predict the burning behavior of solid fuels including extinction limits. However, in order to obtain useful results from such a theory, a set of inputs must be provided which specify the material properties of the fuel and ambient gas mixture. (Experience suggests that the measurement of material properties is a more arduous task than the creation of theoretical models.) Since changes in fuel properties affect the extinction limits predicted by diffusion flame theory, one can investigate how a fire retardant acts to suppress burning by determining its effects on the combustion properties of the fuel to which it is added. This is the motivation for the work described here.

The fuel related properties which must be specified to predict burning behavior are:

$\Delta h[\text{comb vol}]$ = heat of combustion (gas-to-gas) per unit mass of combustible volatiles

h_g = heat of gasification per unit mass of volatiles

Y_{FP} = mass fraction of combustible volatiles (fuel) in the total volatile products of pyrolysis

$v_s[\text{comb vol}]$ = stoichiometric oxygen/fuel mass ratio of the combustible volatiles

Much of the recent progress in understanding diffusion flames has been based on the use of PMMA (polymethyl methacrylate) in both calculations and experiments. Since PMMA completely volatilizes to combustible gas, its value of $Y_{FP}=1$. For cellulosic materials the volatile products of pyrolysis include water and carbon dioxide giving values of $Y_{FP}<1$. The heat of combustion which is normally measured for these charring materials is

$\Delta h[\text{vol}]$ = heat of combustion per unit mass of volatile, so that

$\Delta h[\text{vol}] = Y_{FP}\Delta h[\text{comb vol}]$.

It would simplify the description of charring combustion if burning behavior depended on $\Delta h[\text{vol}]$ rather than on $\Delta h[\text{comb vol}]$ and Y_{FP} . Unfortunately, calculations we have made (unpublished) show that this is not the case; therefore both of these quantities must be measured. In the remainder of the paper, results are given for the effects of retardant addition on $\Delta h[\text{comb vol}]$, h_g , Y_{FP} , and v_s .

EXPERIMENTAL METHODS

The apparatus used in these experiments is shown in Figs. 1 and 2. The system is designed to simulate the unsteady pyrolysis process which occurs during flaming combustion. The samples used were *dry* cylinders of pure and fire retarded cellulose having a diameter of 2.5 cm and a length of 5 cm. The sample is placed in a horizontal position in a ceramic sample holder which sits on a top-loading electronic balance (see Fig. 1). The heat flux from a diffusion flame to the surface of the sample is simulated

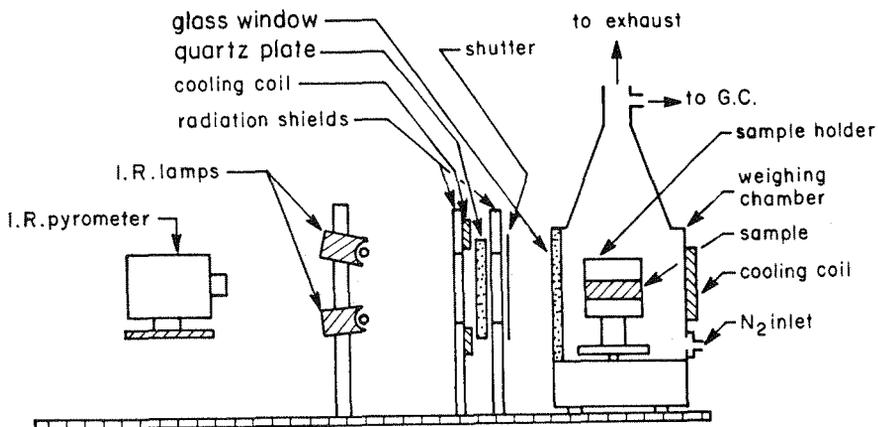


FIGURE 1. Schematic drawing showing weighing chamber and pyrolysis apparatus.

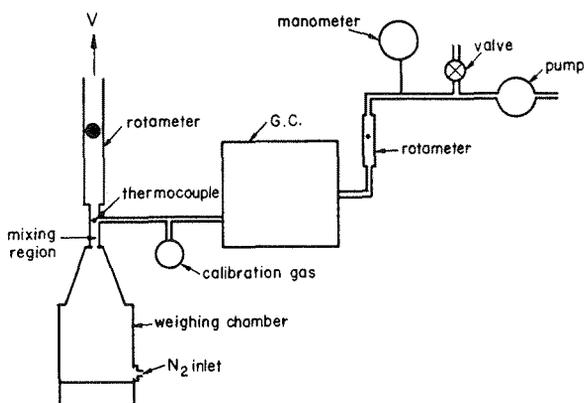


FIGURE 2. Schematic drawing showing gas analysis apparatus.

by a pair of tungsten filament, quartz-envelope infrared lamps. Pyrolysis takes place inside of a weighing chamber which is a modified glass draft shield attached to the top of the electronic balance. A nitrogen purge is used to eliminate all but a trace of oxygen from the chamber (as determined by gas chromatograph measurements). An oxygen free environment is desired to simulate flaming combustion of a solid fuel surrounded by a diffusion flame, since for such flames measurements have shown that little or no oxygen diffuses through the flame to fuel surface. This is discussed in Seshadri and Williams [4] and Chen et al. [5]. Diffusion flame calculations using finite rate chemistry also illustrate this point, for an example see Sibulkin et al. [6].

The portion of the apparatus used to measure the inert gases (carbon dioxide and water) produced by pyrolysis is shown in Fig. 2. The weighing chamber was purged with nitrogen before each run. During the run a reduced flow of nitrogen was used to dilute the volatiles by a factor of 100:1. The gas flow leaving the weighing chamber entered the mixing region by passing through a sharp-edged orifice plate. The relationships between the length and diameter of the mixing region and the orifice diameter were chosen to give a well mixed sample as described by Heskestad [7]. The flow rate of the diluted volatiles V (which is 99% nitrogen) was measured by the rotameter directly above the mixing region. Values of V were calculated from the rotameter reading using the temperature measured by the thermocouple shown in the mixing region. (The measured temperatures varied from 55 to 75°C.) This system was used to draw off a small sample (less than 1%) of the diluted volatiles for analysis by the GC (gas chromatograph). Details about the sampling and calibration procedures are given in Chen [8].

RESULTS AND DISCUSSION

Major Products of Pyrolysis

For the purpose of obtaining combustion properties, the major products of cellulose pyrolysis are *char, inert gases and combustible volatiles*.

The mass fraction of char Y_{ch} was obtained in the following manner. A thin (3 mm) disk was cut from the end of a 2.5 cm diameter test specimen. The disk was then replaced at the end of the test specimen facing the radiant heaters (see Fig. 1) and held there by a spring-loaded clamp which is needed to maintain tension during sample shrinkage. The composite sample was irradiated for 5 to 10 minutes with a flux of 40 kW/m² which was sufficient time for the pyrolysis wave to move through the disk leaving it completely charred. Values of Y_{ch} were obtained as the ratio of the weight of the sample after pyrolysis to its initial weight. (Both weight measurements were made on a dry basis.) The inert gases in the products of pyrolysis are carbon dioxide and water. Their mass fractions were obtained from the concentrations of carbon dioxide and water vapor measured by the gas chromatograph and the flow rate measured by the rotameter (see Fig. 2). The equations used to calculate these results are given in [5]. The mass fraction of combustible volatiles is found by subtracting the inert gases from the (total) volatile products of pyrolysis; the volatile production rate is the sample mass loss rate measured in the weighing chamber.

The results of these measurements are summarized on Fig. 3 which shows how retardant addition modifies the products obtained from a unit mass of sample (cellulose plus retardant). Retardant addition causes the mass fraction of char to increase from $Y_{ch} = 0.09$ for pure cellulose to $Y_{ch} = 0.30$ for cellulose retarded with 3 wt. percent of NaOH ($Y_R = 0.03$). This trend of increasing char production with retardant addition is a well known effect of many solid-phase fire retardants. However, the amount of char produced depends on the thermal history of the sample. For example, Shafizadeh and Sekiguchi [9] found for isothermal pyrolysis of pure cellulose that Y_{ch} varied from

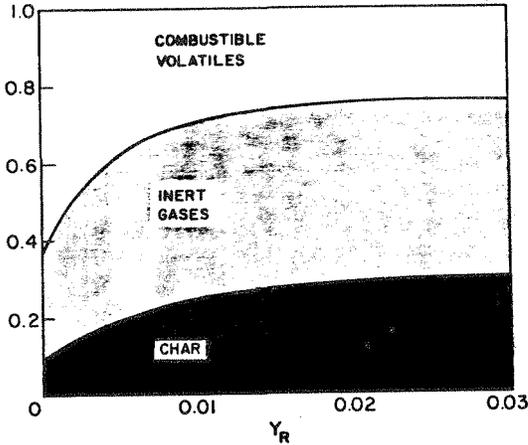


FIGURE 3. Effect of retardant concentration on major products of pyrolysis.

0.33 at 350°C to 0.05 at 600°C. The mass fraction of inert gases Y_{in} produced by pyrolysis is shown by the middle band on Fig. 3. These results are obtained from the concentration measurements of CO_2 and H_2O given in [5]. The value of Y_{in} increases from 0.28 for pure cellulose to 0.46 for $Y_R = 0.03$. The mass fraction of combustion volatiles Y_{cv} is given by

$$Y_{cv} = 1 - Y_{ch} - Y_{in} \quad (1)$$

Retardant addition causes Y_{cv} to decrease from 0.63 for pure cellulose to 0.24 for $Y_R = 0.03$ where most of the reduction occurs for 1 percent retardant addition. These results show that one of the major ways in which sodium hydroxide acts to suppress burning is by reducing the supply of combustible volatiles. In order to obtain the material properties needed for diffusion flame calculations of extinction limits, these composition results are now used to calculate values of Y_{FP} and v_s .

Mass Fraction of Fuel in Pyrolysate Y_{FP}

Whereas Y_{cv} is the mass fraction of combustible volatiles in the original fuel, Y_{FP} is the mass fraction of combustible volatiles in the (total) volatiles. Therefore

$$Y_{FP} = Y_{cv} / (1 - Y_{ch}), \quad (2)$$

and its value is plotted in Fig. 4 as a function of Y_R . Diffusion flame theory shows, as expected, that a decrease in Y_{FP} favors extinction.

Stoichiometric Oxygen/Fuel Ratio v_s [comb vol]

The stoichiometric ratio v_s is defined as the mass of oxygen required for combustion of a unit mass of combustible volatiles. It is calculated from the reaction equation



where $C_xH_yO_z$ represents the elemental composition of the combustible volatiles. The values of x , y , and z were determined from the known composition of cellulose, the measured concentrations of CO_2 and H_2O , the value of Y_{ch} , and the elemental composition of the char. The composition results and specific equations used are given in [5]. The resulting values of v_s are shown in Fig. 4. The effect of retardant addition is to increase v_s from 1.6 for pure cellulose to a maximum of 2.3 at $Y_R = 0.015$ which is an increase of 40 percent. Diffusion flame theory shows that an increase in v_s favors extinction.

Heat of Gasification h_g

The heat of gasification is defined by

$$h_g \equiv q''_{net}/m'' \quad (4)$$

where q''_{net} is the sum of the heat flux inputs and losses at the fuel surface and m'' is the mass flux of gaseous products leaving the sample surface (i.e., the pyrolysis rate). The electronic balance measured the sample mass as a function of time, and the results were numerically differentiated to obtain $m''(t)$. The net heat flux is found from

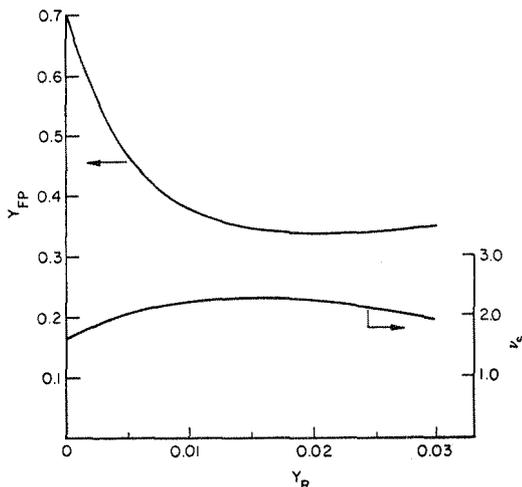


FIGURE 4. Variation of fuel fraction in pyrolysate and stoichiometric ratio.

$$q''_{\text{net}} = \epsilon q''_{\text{ex}} - \epsilon \sigma [T_w^4 - T_\infty^4] - q''_{\text{conv}} \quad (5)$$

by the following procedures. The value of the external heat flux q''_{ex} which is incident on the sample surface was calibrated against the power input to the I.R. lamps before and after each run by placing a water-cooled radiation flux gage at the sample location. The surface temperature $T_w(t)$ was obtained from a calibration curve of the voltage output of the I.R. pyrometer against surface temperature. The convective heat loss q''_{conv} could not be measured. Its value was calculated from heat transfer theory for free-convection from a vertical surface with blowing using the measured values of T_w and m'' .

The effect of retardant addition on the heat of gasification h_g calculated from Eqs. (4) and (5) is shown in Fig. 5. The combination of retardant effects discussed above reduces h_g by a factor of 2 below its value for pure cellulose with most of the reduction taking place for 1 percent retardant addition. Based upon diffusion flame theory, this reduction in h_g opposes extinction since less energy is needed to pyrolyse a unit mass of fuel.

Heat of Combustion Δh [comb vol]

The burning characteristics of solid fuels depends upon the heat of combustion of the volatile products of pyrolysis. For use in diffusion flame models the specific property needed is the heat of combustion (on a gas-to-gas basis) of the combustible products of pyrolysis. In this work a subtraction method introduced by Yeh et al. [10]

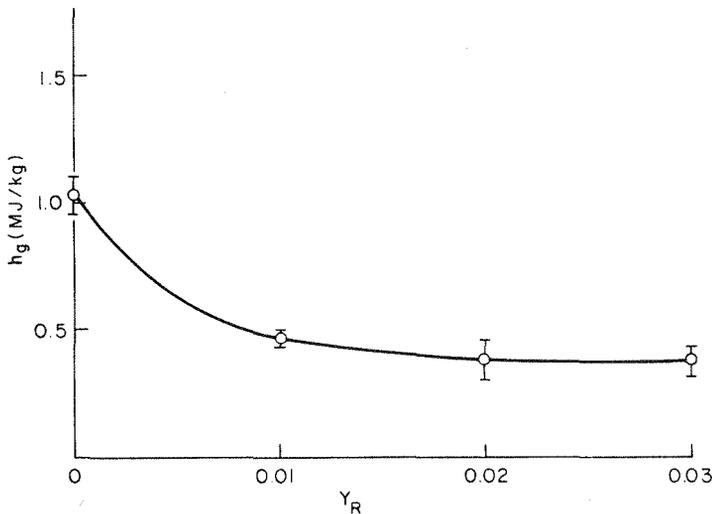


FIGURE 5. Effect of retardant concentration on heat of gasification.

was used. In the subtraction method the heat of combustion (per unit mass of volatiles) is calculated from

$$\Delta h[\text{vol}] = \Delta h[\text{cell} + \text{ret}] - Y_{\text{ch}}\Delta h[\text{char}] / (1 - Y_{\text{ch}}) \quad (6)$$

where $\Delta h[\text{cell} + \text{ret}]$ is the heat of combustion of the original material, cellulose plus retardant, measured in a bomb calorimeter, and $\Delta h[\text{char}]$ is the heat of combustion of the char from that material obtained by a separate bomb calorimeter measurement. The value for the combustible volatiles is then found from

$$\Delta h[\text{comb vol}] = \Delta h[\text{vol}] / Y_{\text{FP}} \quad (7)$$

where the measurements of Y_{ch} and Y_{FP} have been described above. The bomb calorimeter measurements were carried out at 25°C. The corresponding results on a gas-to-gas basis were obtained by correcting the heats of combustion for both cellulose and char to 400°C as described in Susott et al. [11].

The effects of retardant addition are shown in Fig. 6. For the (total) volatiles, retardant addition decreases the heat of combustion by up to 30 percent. This decrease in $\Delta h[\text{vol}]$ is primarily due to the increase in the inert gas fraction of the volatiles as Y_{R} increases. For the combustible volatiles, retardant addition *increases* the heat of combustion by up to 35 percent. This increase in $\Delta h[\text{comb vol}]$ is due to an increase in

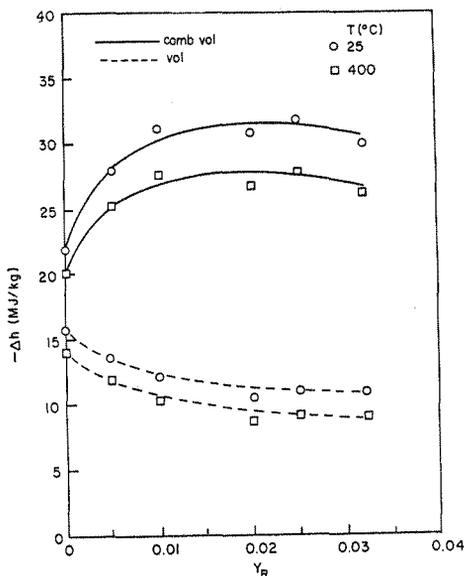


FIGURE 6. Heat of combustion of volatiles and of combustible volatiles.

the carbon content of the combustible volatiles as Y_R increases. Based upon diffusion flame theory this increase in $\Delta h[\text{comb vol}]$ is a retardant effect which *opposes* extinction.

CONCLUSIONS

The results of this investigation are summarized in Table 1 which shows the effects of retardant addition on the combustion properties of cellulose. (Values of T_w are also tabulated.) Table 1 shows that most of the changes take place for a retardant concentration Y_R less than 0.02. Some of these changes tend to *promote* flaming combustion, i.e., the increase in the heat of combustion $-\Delta h$ and the decrease in the heat of gasification h_g . However, as noted in the Introduction, sodium hydroxide is an effective fire retardant. Therefore the retardant action of sodium hydroxide must be due to its effects on the remaining properties. The changes which *oppose* flaming combustion are the decrease in the fuel fraction in the pyrolysate Y_{FP} and the increase in the stoichiometric ratio v_s . Both of these results are closely related to the increases in inert gas production with retardant addition. The increase in T_w with retardant addition also opposed flaming combustion since it increases the radiative heat loss from the fuel surface.

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Table 1. Material Properties for use in Diffusion Flame Calculations ^a

Y_R	$-\Delta h^b$ (MJ/kg)	h_g (MJ/kg)	Y_{FP}	v_s^b	T_w (K)
0	20	1.01	0.69	1.6	826
0.005	26	0.61	0.47	1.9	844
0.010	28	0.46	0.38	2.2	854
0.015	27	0.40	0.35	2.3	856
0.020	27	0.38	0.34	2.2	857
0.025	28	0.38	0.34	2.1	857
0.030	26	0.37	0.35	2.0	857

^a Values for $q''_{ab} = 40 \text{ kW/m}^2$ at $t=180 \text{ s}$. ^b For combustible volatiles.

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