

EFFECT OF INORGANIC SALTS ON PRODUCT COMPOSITION DURING PYROLYSIS OF BLACK SPRUCE

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ABSTRACT

The effect of inorganic salts on the pyrolysis of black spruce sawdust was determined in the temperature range 400–500 C under 2-mm Hg vacuum.

The major pyrolysis products were: a char residue; light and heavy liquid fractions; volatiles (CH₄, C₂H₄, C₂H₆, and C₃H₆); and gases (H₂, CO, and CO₂). Experiments on untreated and treated sawdust show that salts reduce the proportion of flammable tars, volatiles and gases, and increase the proportion of char.

Keywords: Black spruce, pyrolysis, inorganic salts.

INTRODUCTION

When wood burns, it undergoes thermal decomposition (pyrolysis) and yields volatile products of lower molecular weight. These volatiles react with atmospheric oxygen in the gas phase; this is the combustion stage and is accompanied by flame. Martin (1965) and Shafizadeh et al. (1982) proposed that there are at least two competitive reactions by which wood decomposes thermally. The primary reaction produces mainly water, char, and oxides of carbon; a secondary reaction supplies the bulk of the volatile fuels.

It is difficult to prevent combustion of the volatile material once it has formed; the principal mode of action of fire retardants is to prevent its formation. Fire retardants react with wood constituents, at or below the burning temperature, altering the course of the pyrolysis so that the volatiles formed are noncombustible and largely water vapor.

The principal effects of fire-retardant chemicals are to increase the percentage of char and water and to decrease the percentage of flammable tars. Several theories have been proposed (Brown 1958; Brown and Tang 1963; MacKay 1968; Tang and Eickner 1968) to explain the role of fire-retardant chemicals. It is suggested that coating of fibers by chemicals may prevent the escape of volatile products; these are then converted by secondary pyrolysis to more char and less tar. Dilution of the combustible gases and pyrolysis products by noncombustible gases and catalytic inhibition of flaming by free radicals capable of breaking the reaction chains of normal gaseous combustion are also mechanisms. Catalytic dehydration of cellulose, the major component of wood, is often proposed as a chemical mechanism.

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TABLE 1. *Effect of flame retardants on the amount and composition of the pyrolysis products (at 500 ± 5 C).*

Pyrolysis [‡] products	Sodium tetraborate			Ammonium acid phosphate			Potassium bicarbonate			Sodium chloride		
	Treated [†]	Untreat.	% Change	Treated [†]	Untreat.	% Change	Treated [†]	Untreat.	% Change	Treated [†]	Untreat.	% Change
Total liq.*	41.9	44.0	-2.1	46.0	46.6	-0.6	43.2	44.0	-0.8	44.5	45.4	-0.9
Gases	11.2	28.0	-16.8	13.0	28.6	-15.6	17.9	27.0	-9.1	22.8	24.0	-1.2
Char	46.9	28.0	+18.9	40.5	24.8	+15.7	38.9	29.0	+9.9	32.7	30.0	+2.7
Total light liq.**	27.4	17.5	+9.9	24.5	20.1	+4.4	26.7	17.8	+8.9	32.3	19.1	+13.2
Water	23.1	11.5	+11.6	17.9	12.6	+5.3	24.4	11.8	+12.6	27.3	12.8	+14.5
Light org. liq.	4.3	6.0	-1.7	6.5	7.5	-1.0	2.2	6.0	-3.8	5.0	6.3	-1.3
Tar	14.5	26.5	-12.0	22.1	26.5	-2.4	16.5	26.2	-9.7	12.2	26.3	-14.1
CO	5.1	18.0	-12.9	6.7	15.7	-9.0	7.2	16.0	-8.8	13.5	14.1	-0.6
CO ₂	4.4	4.5	+0.1	3.0	3.3	-0.3	7.2	5.5	+1.7	3.9	3.6	+0.3
H ₂	0.2	1.4	-1.2	0.4	2.0	-1.6	0.6	1.1	-0.5	0.1	1.4	-1.3
CH ₄	1.2	2.5	-1.3	2.4	5.8	-3.4	2.0	2.4	-0.4	3.8	3.8	0.0
C ₂ H ₄	0.3	1.2	-0.9	0.5	1.5	-1.0	0.3	1.1	-0.8	0.9	1.2	-0.3
C ₂ H ₆	0.1	0.3	-0.2	0.1	0.3	-0.2	0.2	0.2	0.0	0.3	0.3	0.0
C ₃ H ₆	0.0	0.1	-0.1	0.0	0.3	-0.3	0.2	0.3	-0.1	0.1	0.2	-0.1

[†] Initial salt content in treated sample = 2.0%, w/w, approx.

[‡] Percent composition of pyrolysis products for treated and untreated samples is based on moisture-free wood.

* Total liquid = total light liquid + tar (heavy liquid).

** Total light liquid = light organic liquid + water.

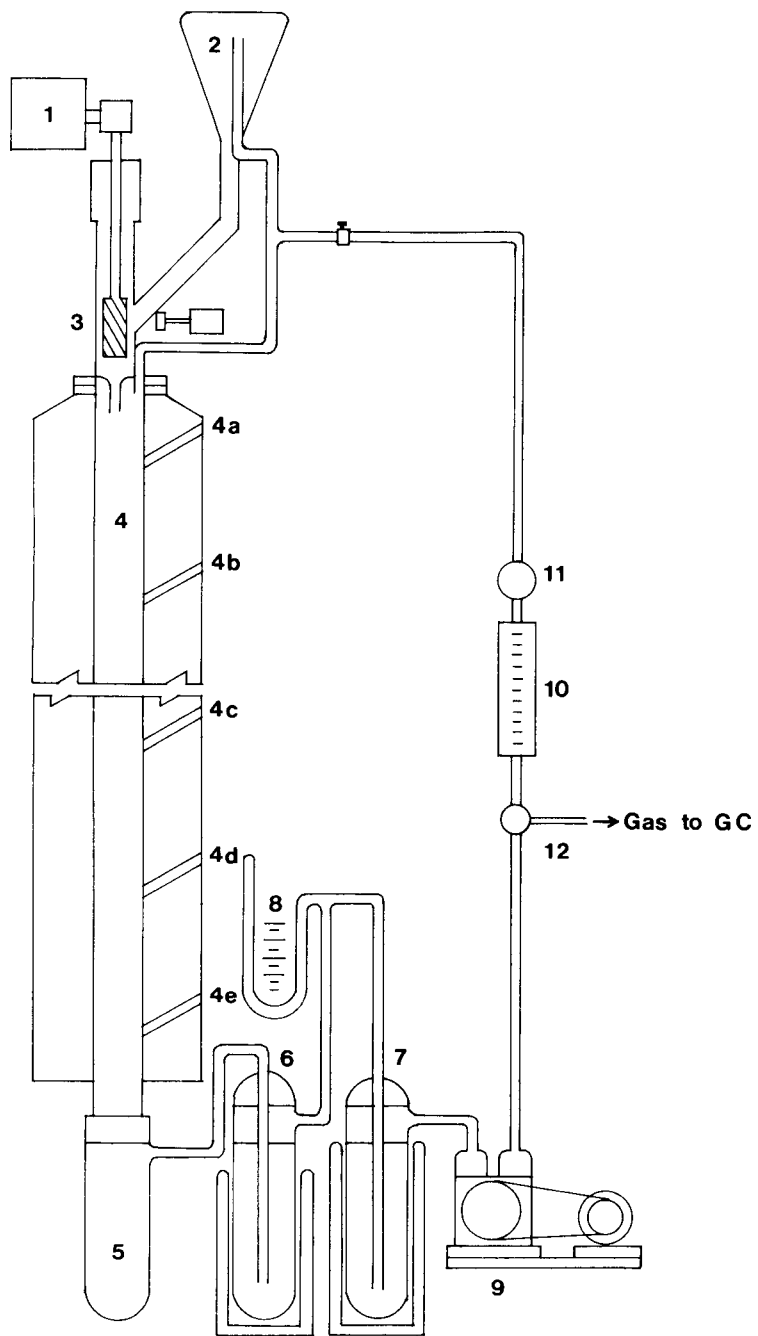


FIG. 1. Experimental setup.

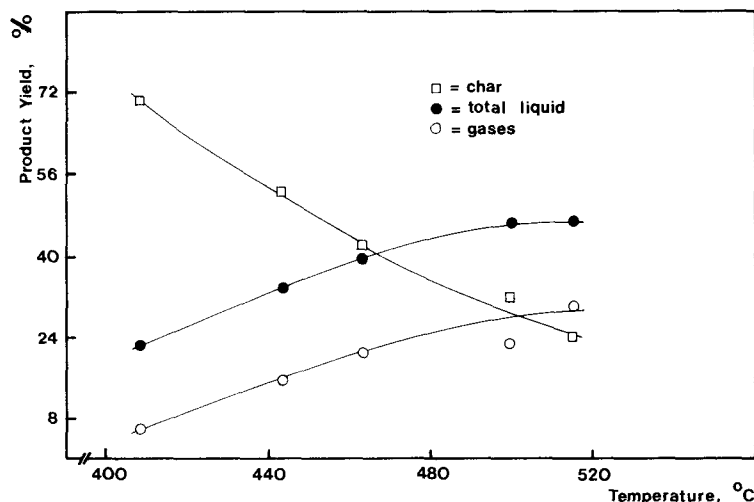


FIG. 2. Gas, liquid, and char yield as percent of untreated wood at different temperatures.

The major products of pyrolysis are water vapor and a carbonaceous solid residue. Knowledge of the composition of the volatiles and the amount of tar and char is needed to evaluate the role of chemicals during pyrolysis of treated wood.

EXPERIMENTAL

Samples of black spruce sawdust (35/200 mesh) either untreated or treated with flame-retardant inorganic chemicals (sodium tetraborate, ammonium acid phosphate, potassium bicarbonate, sodium chloride) were pyrolyzed (Table 1). The wood was treated by soaking the sawdust in a 2% aqueous salt solution, under vacuum, for 20 minutes. The gain in weight of the dried specimen was determined against a blank of sawdust soaked in salt-free water.

The basic equipment is a furnace and pyrolysis tube, and a vacuum manifold to collect and fractionate the pyrolyzed products. The apparatus is shown in Fig. 1. It consists of a variable speed motor [1], a hopper [2], a screw feeder [3], a 3.5 cm I.D. quartz glass reactor pipe [4], thermocouples [4a-4e] to ensure a uniform temperature along the reactor pipe, a char collector [5], a first condenser with ice water [6], a second condenser with dry ice [7], a sampling assembly vacuum gage [8], a vacuum pump [9], a rotameter for back feeder [10], a back feed adjustment needle valve [11] and a sample line connected to a gas chromatograph [12].

The pyrolysis unit is mounted vertically, and the feeder is designed so that each particle of sawdust is heated under identical conditions. The sawdust is fed continuously at a rate of 0.6 g per minute. Gas analysis is started after the system has operated for 40 minutes; this assures that residual air has been purged from the system.

Gas analysis was carried out using a gas chromatograph, Hewlett Packard 5880 equipped with a thermal conductivity detector, under the following conditions: injection temperature 120 C; detection temperature 150 C; 80/100-mesh Porapak Type N, 5 ft, 1/8 in. column used to separate gaseous products. The carrier gas was helium at a rate of 30 cc/min.

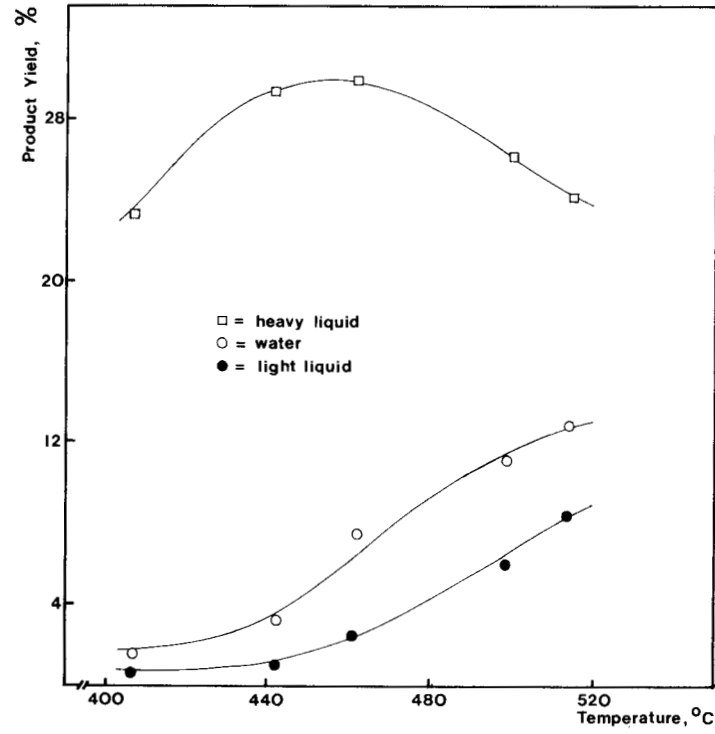


FIG. 3. Liquid yield as percent of untreated wood at different temperatures.

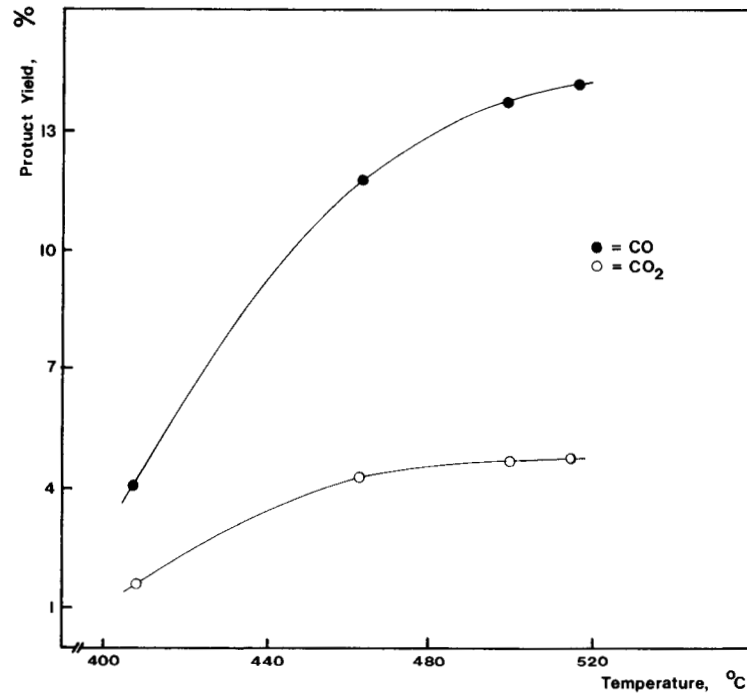


FIG. 4. Carbon oxides yield as percent of untreated wood at different temperatures.

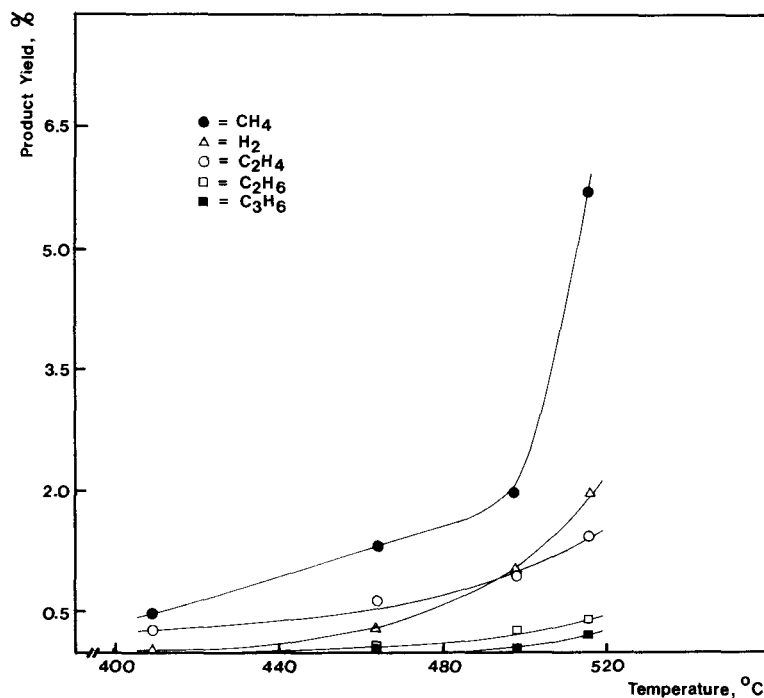


FIG. 5. Some volatile product yield as percent of untreated wood at different temperatures.

RESULTS AND DISCUSSION

The effect of temperature on the yields and composition of char, tar, and light volatiles from untreated wood sawdust, at a feeding rate of 0.06 g/min under 2 mm Hg vacuum, are shown in Figs. 2–5. Figure 2 presents the results for char, total liquid [water + light organic liquids of boiling point 64–68 C + heavy liquid fraction (tar) with boiling point between 260–350 C] and gas; it shows that measurable decomposition of sawdust begins at about 400 C. The extent of decomposition increases with temperature, with the maximum yields of liquid and gas at about 500 C. The char decreases continuously with increasing temperature. At 500 C the product distribution by weight (Figs. 2 and 3), based on moisture free wood, is 28.0% char, 27.4% gas, and 44.6% total liquid. The total liquid is 26.3% heavy liquid (tar) and 18.3% total light liquid. The total light liquid is 12.0% light organic liquid and 6.3% water.

The yield of the two organic liquid fractions, namely light organic liquid and tar, follows different patterns with temperature (Fig. 3). While the amount of light organic liquid increases continuously with temperature, the amount of tar increases to a maximum and then decreases. The maximum tar yield of about 22% is obtained at about 460 C. This yield decreases rapidly at both higher and lower temperatures. This decrease is probably the result of secondary reactions. Water follows the same pattern as light organic liquids (Fig. 3).

The total gas yield (Fig. 2) increases with temperature; the gradient decreases continuously. The increased yield arises from the additional gas generated by tar cracking; compare Fig. 2 and Fig. 3. The gas composition as a function of tem-

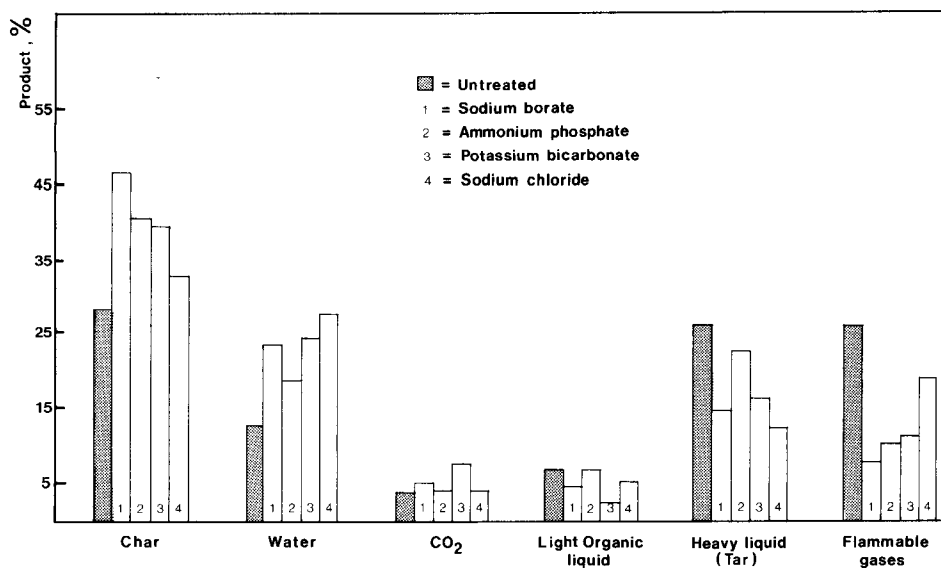


FIG. 6. The effect of inorganic fire retardant salts on the pyrolysis product yield at 500 ± 5 C.

perature is shown in Figs. 4 and 5. From Fig. 4, the rapid increase in decarboxylation reactions at higher temperatures is clearly evident. The corresponding increase in yields of hydrogen and hydrocarbon gases is shown in Fig. 5. It is interesting to note that the yield of hydrogen is at a constant rate from 400 C to about 430 C and thereafter increases steadily.

The effect of inorganic salts was studied at 500 C. The selection of inorganic salts was based on work done by Brown and Tang (1963). Addition of the salts causes a change in the yield of pyrolysis products. Figure 6 is a graphical representation of the results, comparing the effects of the four inorganic salts on the major pyrolysis products from black spruce sawdust at 500 C. Results in Table 1 and Fig. 6 show that the yield of gases was decreased by 1.2 to 16.8%. The major reduction is in carbon monoxide; it was reduced by 0.6 to 12.9%. The amount of hydrogen was reduced by 0.5 to 1.6%; the same trend is observed for hydrocarbon gases. The total liquid was also decreased by 0.6 to 2.1%. The tarry liquid accounts for this reduction of between 2.4 to 14.1%, while the total light liquid was increased between 4.4 to 13.2%. The reason for the increase in the total light liquid is that the increase in water generated during pyrolysis is greater than the accompanying decrease in light organic liquid. The other two products that are increased are CO₂ and char. This verifies that application of flame-retardant inorganic chemicals causes an increase in inert products as CO₂ and water, while the flammable products, either gas or tar, are decreased.

With the decrease in flammable material, namely tar, the percentage of char was increased by 2.7% to 18.9%.

CONCLUSION

The effect of the inorganic fire-retardant salts on the distribution of pyrolysis products is clear, not only on the amount of tars, as reported in the literature, but

also on the amount of gases. This means that the disappearance of flames in the presence of fire retardants is due not only to the decrease of the flammable liquid products, but also to the decrease of the flammable gaseous products, especially CO.

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