

## WOOD ASH COMPOSITION AS A FUNCTION OF FURNACE TEMPERATURE

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**Abstract-** The elemental and molecular composition of mineral matter in five wood types and two barks was investigated as a function of temperature using thermal gravimetric analysis, differential thermal analysis, inductively coupled plasma emission spectroscopy, and X-ray diffraction. Low temperature ash was prepared at 500°C, and samples were heated in a tube furnace at temperature increments to 1400°C. The dissociation of carbonates and the volatilization of potassium, sulfur, and trace amounts of copper and boron were investigated as a function of temperature. Overall mass loss of the mineral ash ranged from 23-48% depending on wood type. The mass of K, S, B, Na, and Cu decreased, whereas Mg, P, Mn, Al, Fe, and Si did not change with temperature relative to Ca which was assumed to be constant. Sintering of the ash occurred, but fusion of the ash did not occur. In the 600°C ash CaCO<sub>3</sub> and K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub> were identified, whereas in 1300°C ash CaO and MgO were the main compounds. The implications for ash deposition in furnaces is discussed.

**Keywords-** Ash, Wood, Furnaces.

### 1. INTRODUCTION

Wood fuel for generating heat and power is of interest because wood is a renewable fuel with low ash and sulfur content. However, as with coal, the problems of ash deposition on heat transfer surfaces in boilers and on internal surfaces in gasifiers still remain. Even though mineral matter transformations during coal combustion have been extensively investigated,<sup>1-3</sup> little information is available on mineral matter behavior in wood.

Studies of chemical composition of wood ash in the past have primarily been restricted to the elemental composition<sup>4-12</sup> as the focus was largely on the agricultural use of wood ash. These include utilization of wood ash as a source for potash production,<sup>4</sup> as a liming agent, a source of nutrients for agricultural plants,<sup>5-7</sup> and as a tannin neutralizing agent in high-tannin sorghums to increase the growth rates of chickens.<sup>8</sup> Determination of elemental composition in ash of leaves and stems has also been carried out to correlate nutrient uptake by plants with the nutrient content of the soil as a means to monitor plant growth and effect of fertilizer supplementation.<sup>9-12</sup> A common assumption in most of these analyses has been that the minerals present are oxides of different elements.<sup>13</sup> This assumption may be sufficient to identify the extent of alkalinity of wood ash, but gives little information on the thermal/chemical

stability of the actual compounds that may be present in context with the deposition of ash particles in combustor and gasifiers.

In view of the problems associated with mineral matter in wood, there exists a need to identify the forms of the minerals, which transformations occur at higher temperatures when the wood is burned or gasified, which minerals initiate ash deposition, and which improvements in combustor design and operation need to be made to alleviate the problems associated with ash deposition. In this paper we present the results on the chemical composition of mineral matter in wood after heating the ash from five wood species: pine (*Pinus ponderosa* Dougl. ex Laws), aspen (*Populus tremuloides* Micx.), white oak (*Quercus alba* L.), red oak (*Quercus rubra*), and yellow poplar (*Liriodendron tulipifera* L.), and two bark species [white oak and Douglas-fir (*Pseudotsuga menziesii* (Marib.) Franco)]. Results on the extent of mineral matter transformations with temperatures to 1400°C in air are discussed in context of ash deposition in boilers utilizing wood and wood waste as fuel.

### 2. EXPERIMENTAL PROCEDURES

#### 2.1. Ash preparation

Low temperature wood ash was prepared in two stages. In the first stage, approximately 150 g of woodchips were pyrolyzed in a box

Table 1, Low temperature ash content of different wood species

Wood species	Ash, dry basis (%)
Aspen	0.43
Yellow poplar	0.45
White oak	0.87
White oak bark	1.64
Douglas-fir bark	1.82

furnace by heating to 500°C in a closed container. At the termination of devolatilization, the container lid was removed and the residual char burned at 350°C, which took 5--8 h to completely burn at this low temperature. The yield of ash was between 0.75 g and 1.5 g, depending on the ash content of the wood. The amount of ash obtained by this method from some of the woods is listed in Table 1 as a percentage of the initial mass of wood.

The low temperature ash (LTA) formed by the procedure outlined above was used for thermal and chemical analyses. For chemical analyses samples were obtained by heating the low temperature ash to the required temperature in a tube furnace (Lindberg, Model 54233-V). For temperatures lower than 800°C, an alumina crucible was used to heat the ash. For temperatures over 800°C, the ash volume was first reduced by heating it to 800°C in the alumina crucible and then heating to the required temperature in a platinum crucible. This was done primarily to eliminate any possibility of alumina reacting with the alkali compounds present in the ash at elevated temperatures and therefore affecting the results of chemical analysis. The samples were held at the required temperatures for over an hour to allow adequate heat-up time and to ensure completion of any transformation that may have been initiated at the sample holding temperature. This is particu-

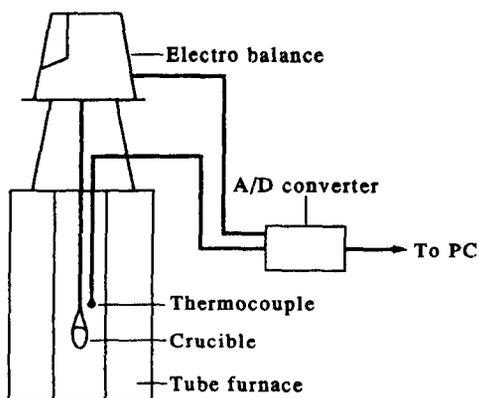


Fig. 1. Schematic of experimental set-up for thermogravimetry.

larly important for pine and aspen ash that contain relatively higher proportions of potassium carbonate which dissociates at a slow rate. Ash samples, for most cases, were prepared at temperatures of 600, 800, 1000, 1200, and 1400°C.

Most of the ash types did not show any sign of melting when heated. At temperatures over 800°C, the ash showed signs of sintering but the lump of ash formed would crumble under a slight pressure. The extent of sintering increased with the increase in temperature and was related to the amount of alkali metals present in the ash. Some of the ash types, especially those of pine, when heated to over 1300°C for long enough time, showed signs of melting and re-solidification when cooled.

## 2.2. Thermal analysis

The weight loss of the low temperature ash (LTA) as a function of temperature by thermogravimetric analysis (TGA) is shown in Fig. 1. A platinum crucible containing LTA was suspended in a tube furnace by means of a platinum wire from an electronic balance (Cahn Electrobalance Model 7500). Outputs from the furnace thermocouple and the balance were stored in a PC by means of a data acquisition system (Metrabyte DAS8). The amount of ash placed in the crucible was about 40 mg which was small enough to minimize the temperature lag between the sample and the furnace, and yet the observed change in the mass was significant compared to the background noise. Furnace control parameters were set such that the heating rate was about 45°C min<sup>-1</sup> in the first stage ( $T < 600^\circ\text{C}$ ) and about 25°C min<sup>-1</sup> in the final stage of the heat-up. Noise levels were significantly reduced by using two low-stiffness springs to suspend the platinum crucible from

tube furnace, which contained air at atmospheric pressure.

Differential thermal analysis (DTA) of the ash samples was carried out in a Perkin-Elmer DTA System 1700 instrument to determine the presence of exothermic or endothermic reactions. Approximately 20 mg of the sample

Table 2, Parameter values used for the DTA

Heating rate (°C min <sup>-1</sup> )	10-3
Cooling rate (°C min <sup>-1</sup> )	30
Min. temp. (°C)	300-500
Max. temp. (°C)	1000-1300
Temp. increment	10 @ 0.5°C cm <sup>-1</sup>

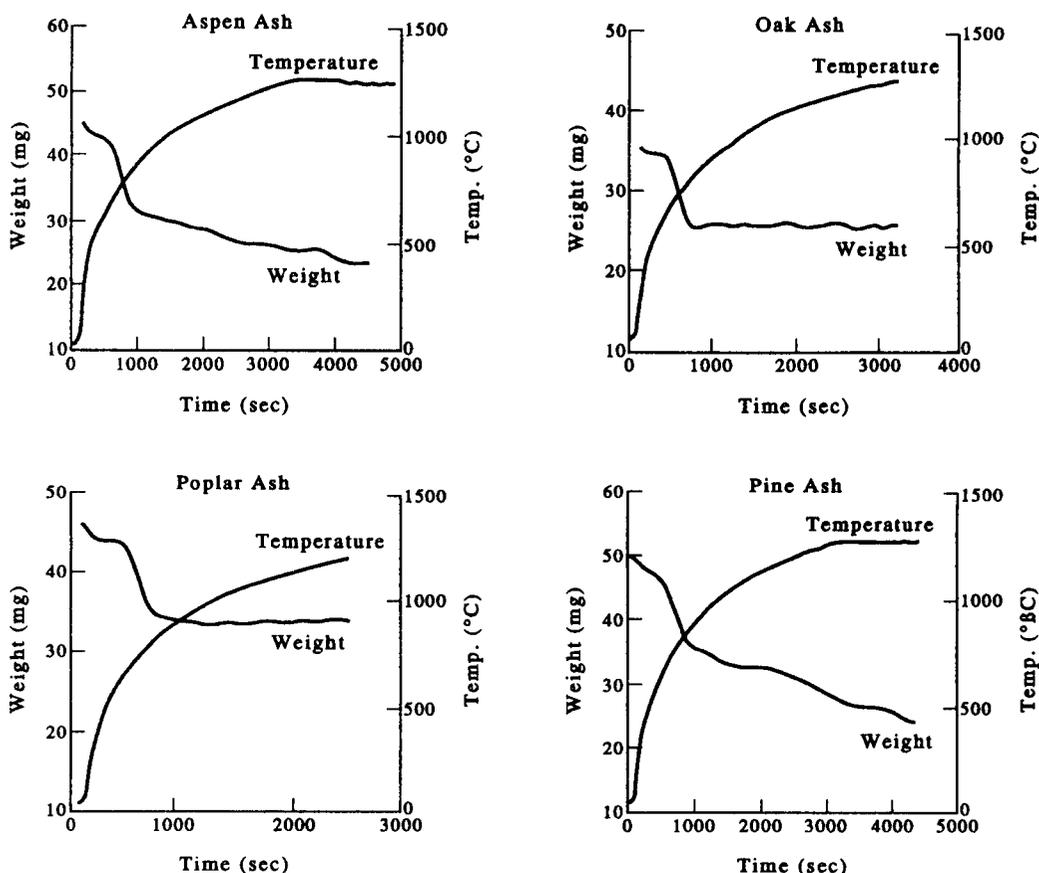


Fig. 2(a), TGA results for low temperature ash prepared from different wood species.

30 mg of aluminum oxide (reference material) were heated in the instrument furnace under controlled conditions and in an inert environment provided by argon at a constant purge rate of  $20 \text{ cc min}^{-1}$ . Values of different parameters used in these experiments are listed in Table 2. Heat-up temperatures were restricted to a maximum of  $1300^{\circ}\text{C}$  as the samples were contained in small alumina cups and keeping the temperatures below  $1300^{\circ}\text{C}$  ensured that the samples did not react with the liners.

### 2.3. Chemical analyses

Elemental and chemical compositions of the wood ash were obtained using Inductively Coupled Plasma Emission Spectroscopy (ICPES) and X-Ray Diffraction (XRD). Samples for ICPES were prepared by first drying the ash in an oven and then dissolving approximately 100 mg of the dried ash in 4 ml of reagent grade, concentrated hydrochloric acid. The mixture was left standing for a couple of hours for complete dissolution. This solution was later diluted to approximately 100 g using

distilled, deionized water so that the concentration of various elements was within the linear range of detection for the ICPE Spectrometer. The solution was analyzed for concentrations of P, K, Ca, Mg, S, Zn, Mn, B, Al, Fe, Si, and Na at the Soil & Plant Analysis Laboratory in Madison, WI.

Samples for XRD were first finely ground and then mounted on a glass slide using an adhesive layer to hold the ash on to the glass surface. The powder was ground fine to ensure random orientation of the crystals so that there are sufficient amount of crystals to generate detectable signals at all angles and that the background noise is kept to a minimum. The samples were analyzed in a Scintag/USA X-Ray Diffractometer using a copper target to generate the X-rays (wavelength =  $0.154 \text{ nm}$ ).

## 3. RESULTS OF ASH ANALYSIS

### 3.1. Thermal analysis

Results of the thermogravimetric analysis and differential thermal analysis are presented in

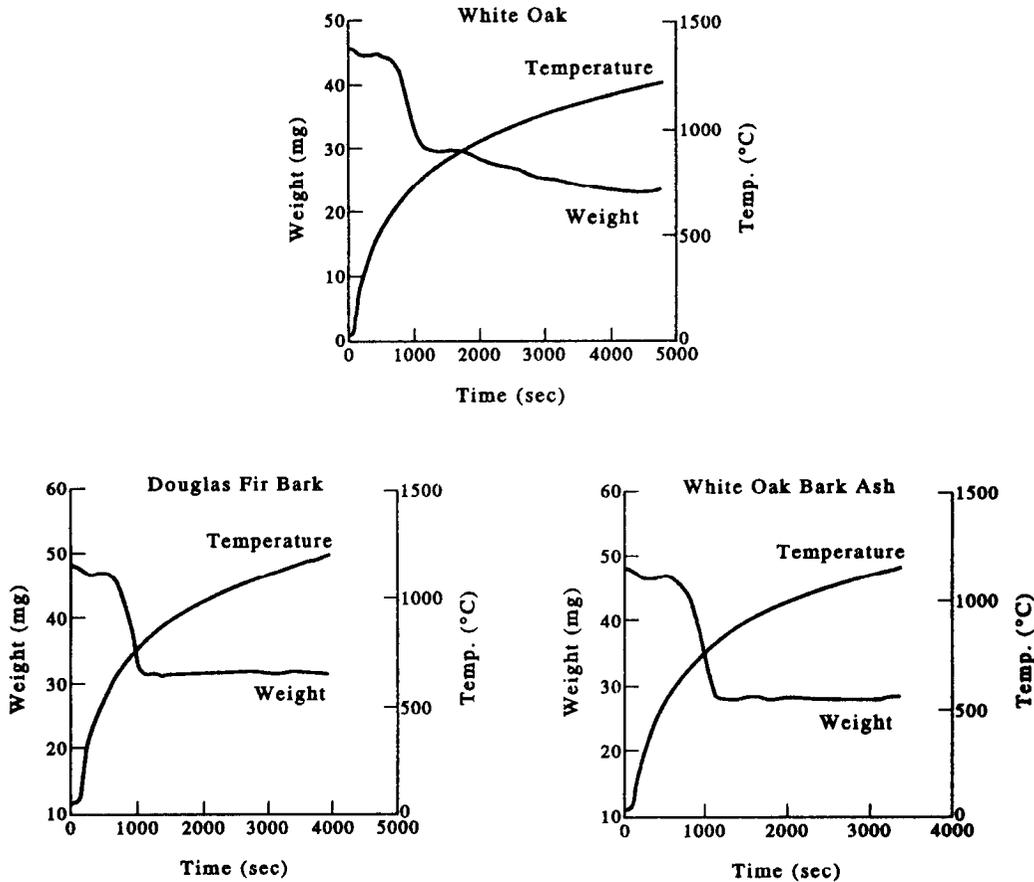


Fig. 2(b). TGA results for low temperature ash prepared from different wood species.

Figs 2 and 3. TGA results shown in Fig. 2 were obtained after filtering out the high frequency components (noise) and smoothing the raw data using the Fourier transform method. These results, in general, show an initial small mass loss at low temperatures and a more significant mass loss at temperatures over 650°C. For pine, aspen, and white oak, the mass loss at higher temperatures appears to be taking place in two or more steps. The observed mass loss for different ash types at different stages are listed in Table 3.

The initial mass loss observed at temperatures lower than 200°C is due to the evaporation of

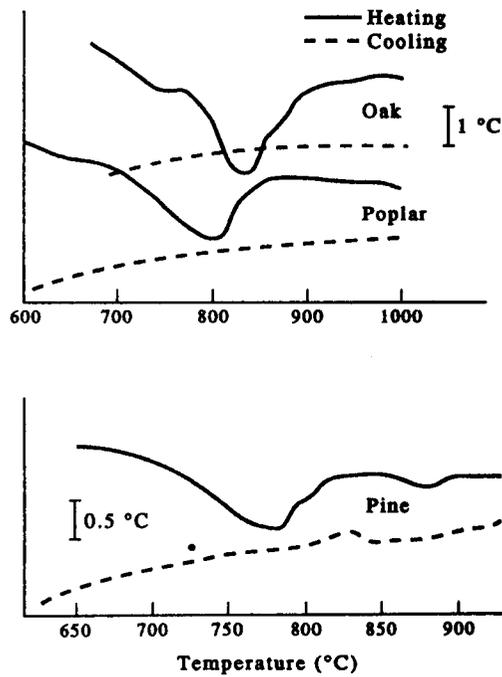


Fig. 3. DTA results for low temperature ash prepared from different wood species.

\* Mass loss was insignificant compared to background noise.

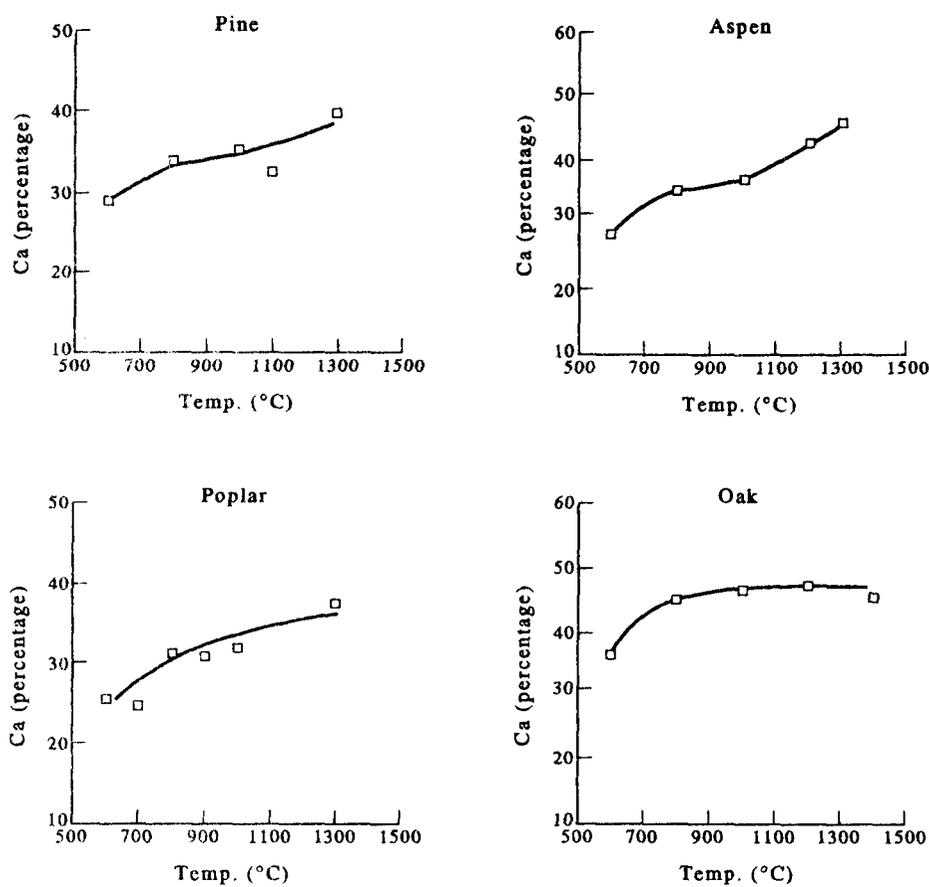


Fig. 4(a). Variation of calcium concentrated with themerature for different ash types.

water adsorbed by the ash when stored for a period of time after preparation. The mass loss observed at temperatures over 600°C has been found to be due to the decomposition of carbonates of both calcium and potassium. This was confirmed by the DTA results shown in Fig. 3. The heating cycle in the DTA results for all ash show a downward deviation of the temperature difference line indicating occurrence of an endothermic process. This process is irreversible as it does not show up in the cooling cycle carried out immediately after the heating cycle. The onset and duration of the processes in Fig. 3 coincide well with the TGA observations shown in Fig. 2. It is interesting to note that the temperature range over which the reaction (decomposition) occurs, as seen from both TGA and DTA results, is similar for all ash types. It will be shown later that the mass loss observed in the temperature range of 650-900°C is predominantly due to the decomposition of  $\text{CaCO}_3$ , and that beyond 900°C is due to the decomposition of  $\text{K}_2\text{CO}_3$  and in some cases, due to the dissociation of calcium and magnesium sulfate.

The mass loss observed beyond 900°C in TGA results for pine and aspen ash do not show up as endothermic peaks in the DTA results for these ash types. This is probably because of the slower rates of dissociation of  $\text{K}_2\text{CO}_3$  compared to that of  $\text{CaCO}_3$  and the thermal load accompanying decomposition of potassium carbonate is not significant enough to alter the heat-up profiles. The DTA curve corresponding to pine ash in Fig. 3 shows a melting process at 850°C as the endothermic peak associated with this process appears during both the heating and cooling cycles. This process appears to be due to the melting of  $\text{K}_2\text{CO}_3$ , since cooling is started immediately following the heating cycle, thereby not allowing sufficient time for complete dissociation of this compound.

### 3.2. Chemical analysis

The concentration of different elements and the variation with temperature for different ash types was determined by ICPES, and the results are presented in Figs 4 to 11. Table 4 lists the measured concentrations of various elements in low temperature ash heated to 600°C. The

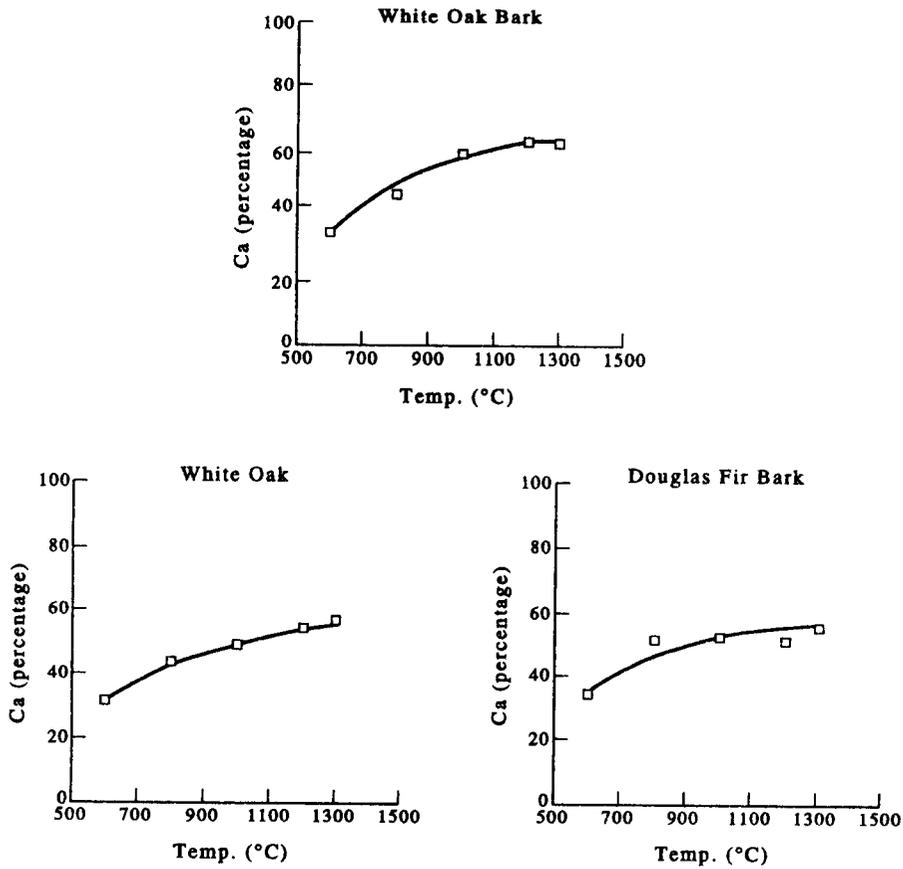


Fig. 4(b). Variation of calcium concentration with temperature for different ash types.

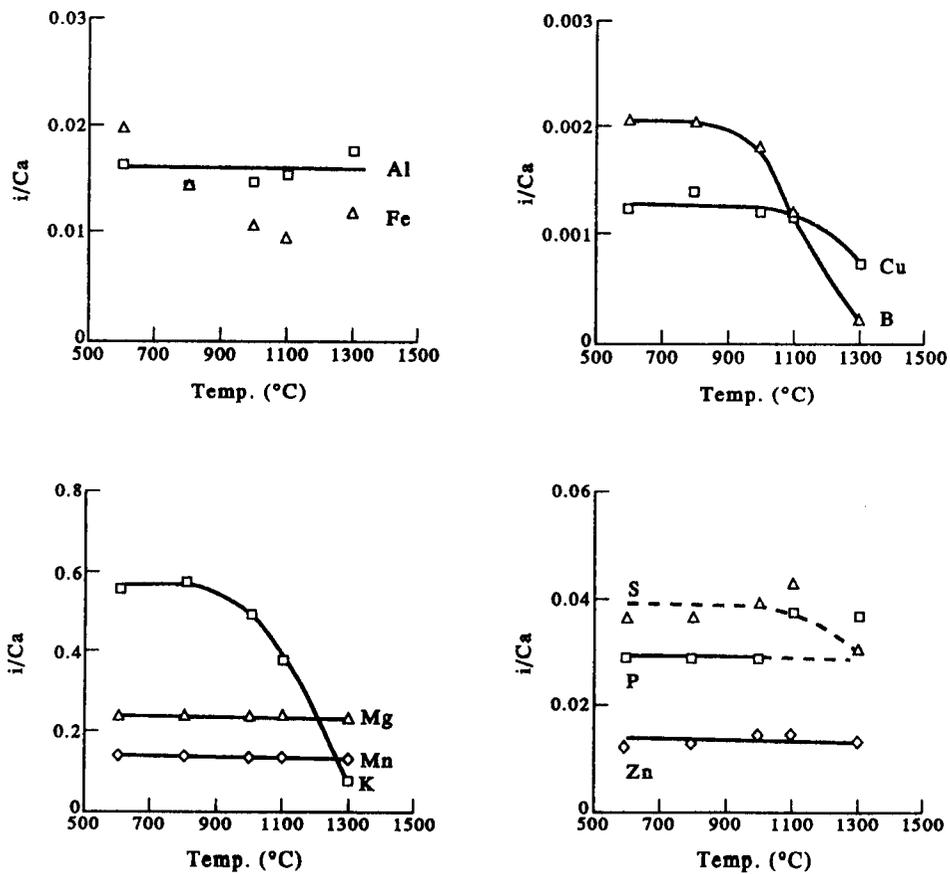


Fig. 5. Variation of normalized concentrations of different elements in pine ash with temperature.

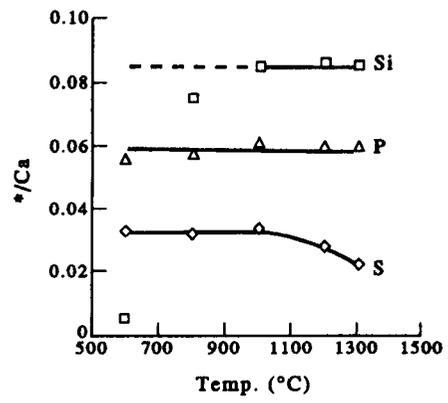
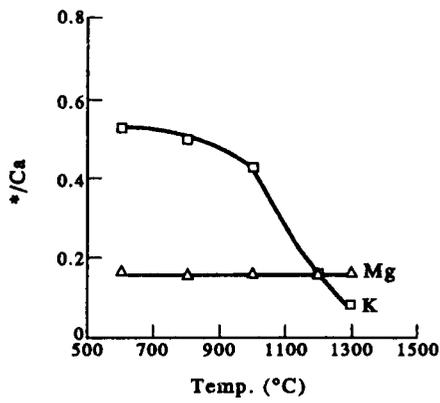
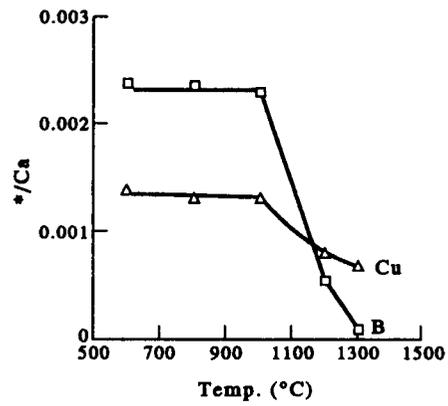
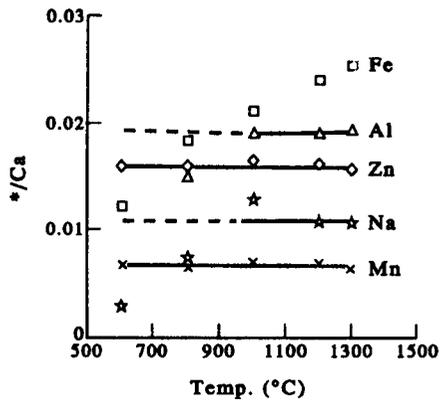
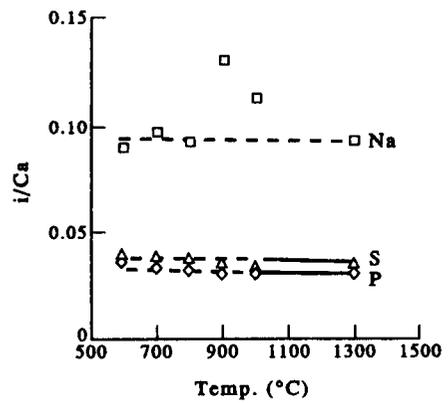
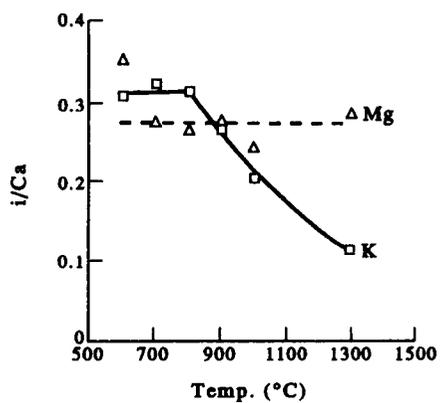
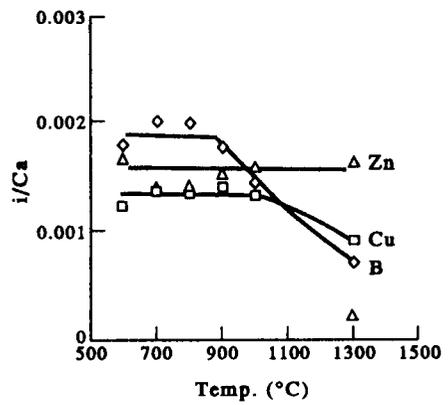
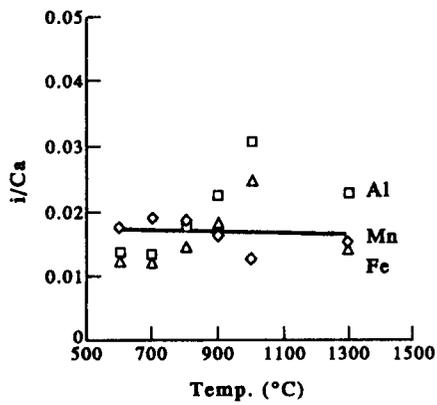


Fig. 6. Variation of normalized concentrations of different elements in aspen ash with temperature.



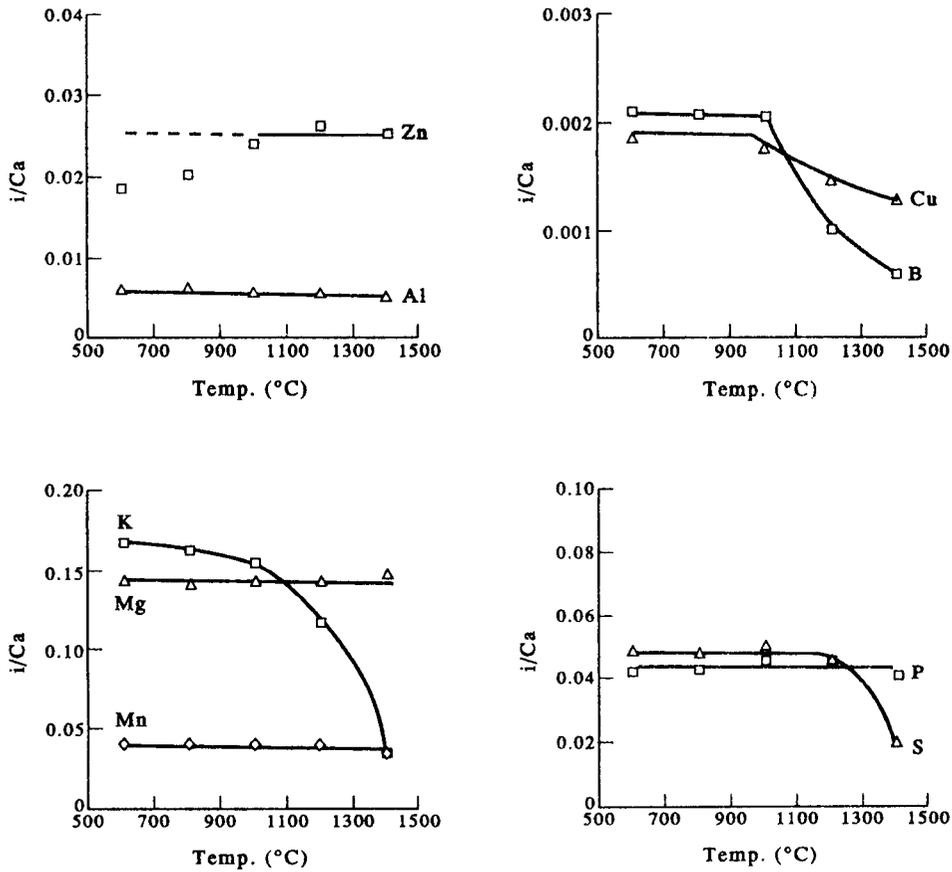


Fig. 8. Variation of normalized concentrations of different elements in red oak ash with temperature.

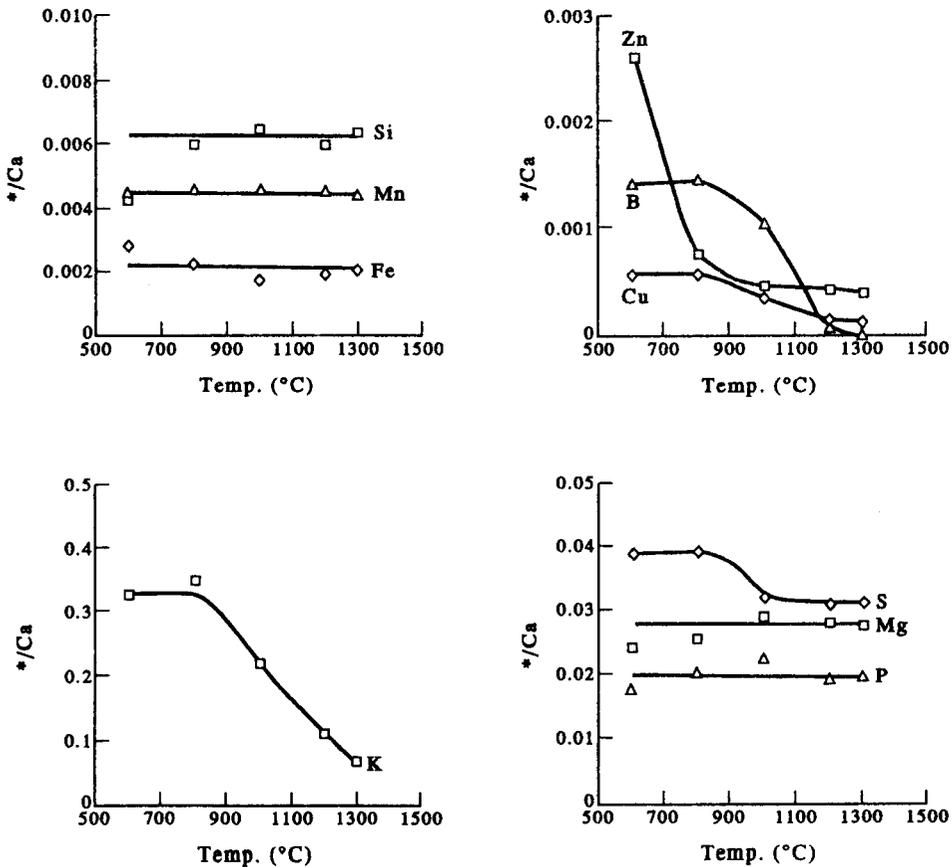


Fig. 9. Variation of normalized concentrations of different elements in white oak ash with temperature.

Table 4. Elemental analysis of ash at 600°C (wt% of ash)

Element	Pine	Aspen	Poplar	R. Oak	W. Oak	W. Oak Bark	D. F. Bark
Calcium	29.05	21.17	25.67	36.58	31.35	36.14	34.26
Potassium	16.24	11.25	7.93	6.08	10.25	0.97	2.78
Magnesium	7.03	3.55	9.09	5.20	7.57	0.34	0.37
Sulfur	1.07	0.70	1.02	1.80	1.21	0.40	0.52
Phosphorus	0.84	1.18	0.95	1.56	0.56	0.08	0.51
Manganese	4.04	0.14	0.45	1.49	0.14	0.16	0.37
Zinc	0.36	0.34	0.04	0.22	0.08	0.05	0.07
Iron	0.58	0.26	0.32	n.d.	0.09	0.01	0.26
Aluminum	0.47	0.14	0.35	0.68	<0.03	<0.03	0.59
Sodium	0.06	0.06	2.30	0.08	<0.06	<0.06	<0.06
Silicon	n.d.	0.11	n.d.	n.d.	0.13	0.12	0.24
Boron	0.06	0.05	0.05	0.08	0.04	0.007	0.07
Copper	0.04	0.03	0.03	0.07	0.02	<0.002	0.02

n.d.—not determined.

major elements in the wood ash are calcium, potassium and magnesium. Sulfur, phosphorus and manganese are present at around 1%. Iron, aluminum, copper, zinc, sodium, silicon, and boron are present in relatively smaller amounts. Oxygen and carbon are also present but are not determined by ICPES. The nitrogen content in wood ash is normally insignificant due to the conversion of most of the wood nitrogen to  $\text{NH}_3$ ,  $\text{NO}_x$  and  $\text{N}_2$  during the combustion of

wood.<sup>14,15</sup> Pine and aspen ash have higher amounts of potassium compared to poplar or oak ash. The other alkali metal, sodium, is generally low in all ash types with the exception of the poplar which had 2.3% Na.

Figure 4 shows the variation of calcium with temperature for different species, and Figs 5 to 11 show the variation of other elements normalized with respect to calcium, because elemental calcium is assumed not to volatilize from the

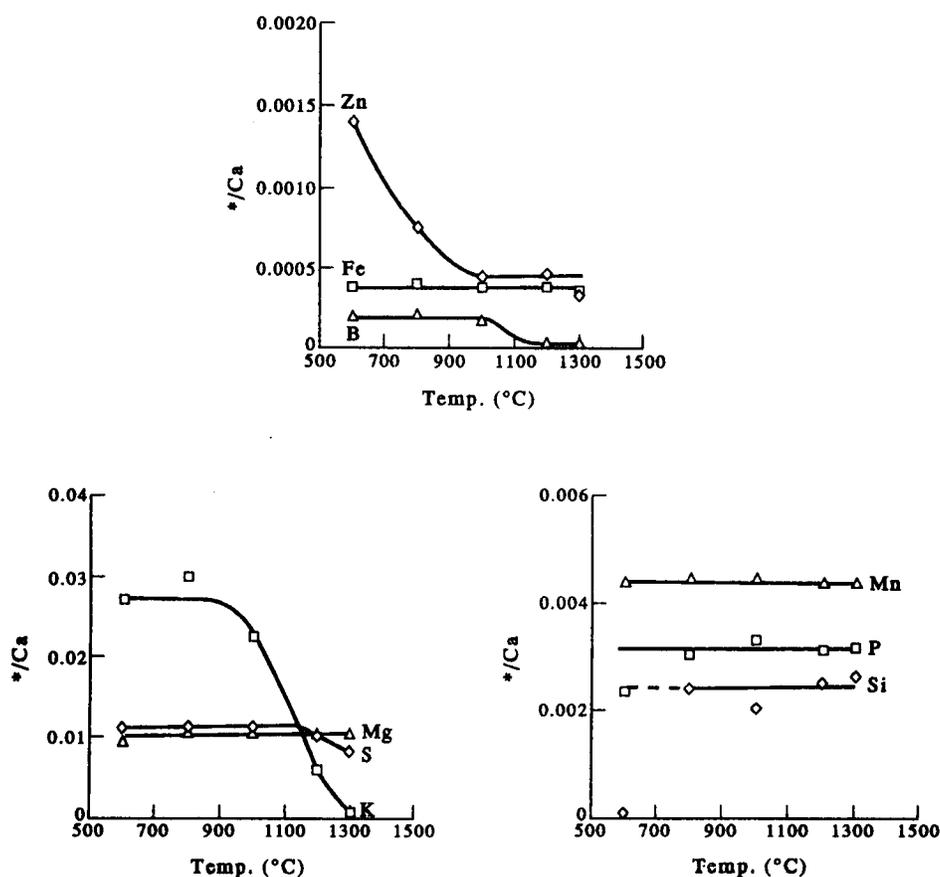


Fig. 10. Variation of normalized concentrations of different elements in white oak bark ash with temperature.

Table 5. XRD analysis of wood ash showing relative intensity of the strongest peaks (%)

Compound	Pine		Aspen		Poplar		White Oak		W. Oak Bark		D. Fir Bark	
	600 C	1300 C	600 C	1300 C	600 C	1300 C	600 C	1300 C	600 C	1300 C	600 C	1300 C
CaCO <sub>3</sub>	100		100		100		100		100		100	
K <sub>2</sub> Ca(CO <sub>3</sub> ) <sub>2</sub>	86		21				11					
Ca(OH) <sub>2</sub>	24	34			40	*		3				8
MgO	8	100		26	4	49		4				
CaO		19		100	16	100		100		100		100
Ca <sub>4</sub> Mn <sub>3</sub> O <sub>10</sub>	21											
Ca <sub>2</sub> MnO <sub>4</sub>		75										
Mg <sub>6</sub> MnO <sub>8</sub>		12										
K <sub>2</sub> Ca <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		12										
K <sub>2</sub> SO <sub>4</sub>		11	9			2		*				
K <sub>2</sub> MgSi <sub>3</sub> O <sub>8</sub>					46							
CaSiO <sub>3</sub>					*							
Na <sub>2</sub> CaSiO <sub>4</sub>					*	17						
Ca <sub>2</sub> SiO <sub>4</sub>				23		22						11

\*May be present.

ash, and any decrease in the concentrations of other elements will become evident in such plots. The normalized concentrations of most elements, with the exception of potassium, boron, and sulfur, remain constant with an increase in temperature, and hence are retained in the ash at higher temperatures. The normalized concentrations of potassium, sulfur, boron, and copper initially remain constant and then

ecline. A significant decrease in the potassium concentration is observed at temperatures greater than 900°C. Decrease in the boron concentration is observed for temperatures beyond 1000°C. Sulfur decreases beyond 1000–1100°C in pine, aspen, and white oak ash, but must be heated to higher temperatures to volatilize sulfur from poplar and red oak ash

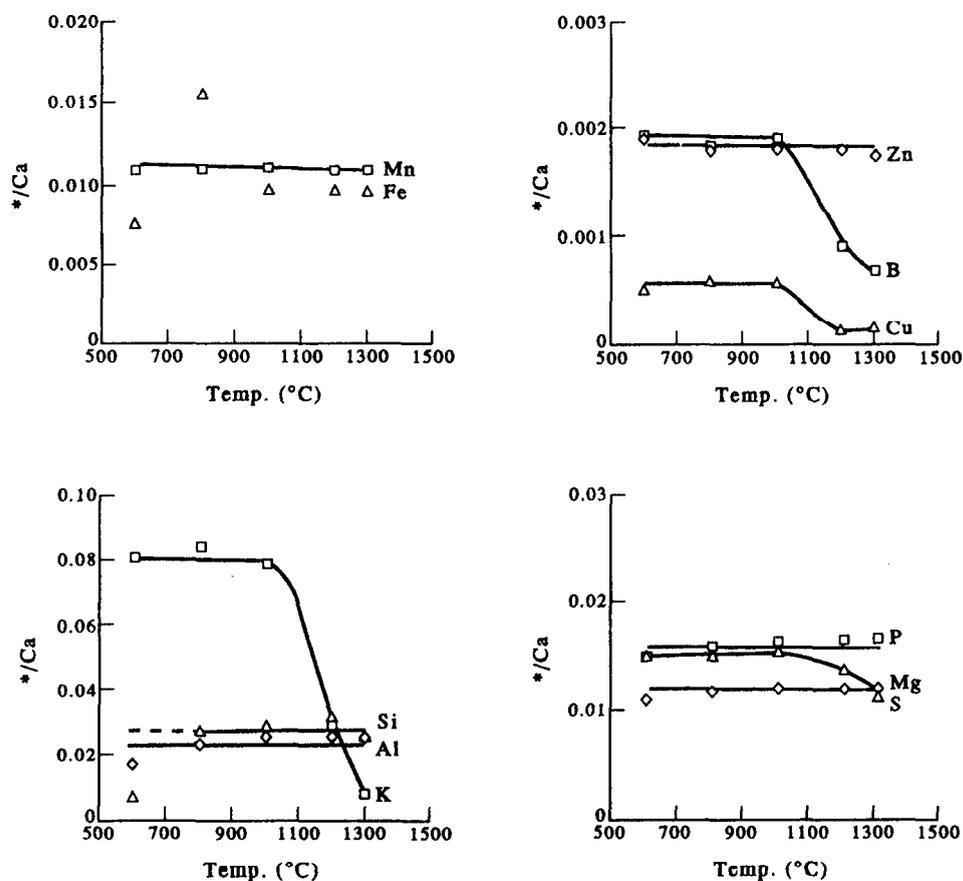


Fig. 11. Variation of normalized concentrations of different elements in Douglas-fir bark ash with temperature.

Table 6. Volatilization of elements in wood ash when heated to 1300°C

Ash type	Potassium (%)		Sulfur (%)		Sodium (%)		Boron (%)	
	K <sub>o</sub>	K/K <sub>o</sub>	S <sub>o</sub>	S/S <sub>o</sub>	Na <sub>o</sub>	Na/Na <sub>o</sub>	B <sub>o</sub>	B/B <sub>o</sub>
Pine	16.24	85.3	1.07	15.1	0.06	25.1	0.06	88.7
Aspen	13.29	83.5	0.83	28.6	0.09	0	0.06	97.0
Poplar	7.93	62.7	1.01	7.6	2.30	0	0.05	58.3
Red oak	6.09	77.9	1.65	55.5	0.07	68.9	0.07	68.9
White oak	10.25	78.3	1.21	18.5	<0.06	<sup>a</sup>	0.04	100.0 <sup>b</sup>
W. oak bark	0.98	96.5	0.40	24.9	<0.06	<sup>a</sup>	0.007	100.0 <sup>b</sup>
D. Fir bark	2.78	90.4	0.52	24.9	<0.06	<sup>a</sup>	0.07	62.2

<sup>a</sup>Initial concentration below detection limit of ICPE spectrometer.

<sup>b</sup>Final concentration below detection limit of ICPE spectrometer.

The increase in calcium concentrations in Fig. 4 at temperatures below 900°C is primarily due to the decomposition of calcium carbonate and at temperatures beyond 900°C the increase is due to the dissociation of potassium carbonate and simultaneous volatilization of potassium oxide formed after dissociation. The latter also leads to a decrease in potassium concentration in the ash. The decrease in sulfur concentration is thought to be due to the dissociation of calcium sulfate and potassium sulfate. The reason for the decrease in boron and copper concentrations was not investigated because only trace quantities were present.

The results of ICPEs were used with XRD analysis to identify the minerals present in wood ash. Typical XRD patterns at temperatures of 600 and 1300°C are shown in Fig. 12, and a list of the compounds identified in ash from different woods is given in Table 5. The low temperature ash shows strong peaks corresponding to calcium carbonate. Pine and aspen ash contain relatively higher amounts of potassium compared to poplar ash and show strong peaks corresponding to K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>. Pine ash contains calcium manganese oxide, aspen ash has sulfates of calcium and potassium, and poplar ash, silicates of K, Mg, and Ca. At higher temperatures, with the dissociation of carbonates, XRD patterns show predominant presence of calcium and magnesium oxides. In addition, pine ash being richer in manganese shows the presence of calcium manganese oxide and manganese oxide. Similarly, poplar, being richer in sodium, displays weak peaks corresponding to sodium calcium silicate. It appears that when the ash is left standing in air, calcium oxide reacts with atmospheric water vapor to form calcium hydroxide, however calcium hydroxide is unstable at temperatures over 600°C.<sup>16</sup> Table 5 also indicates that small amounts of potassium may be present as (K<sub>2</sub>SO<sub>4</sub>) as the peaks corresponding to this

compound become distinct at higher temperatures. Low temperature ash produced from the wood bark appears to contain predominantly calcium carbonate at high temperatures the content changes to predominantly calcium oxide.

## 4. DISCUSSION

### 4.1. Effect of potassium carbonate

The effect of potassium on other compounds is seen in the results obtained in the DTA of ash from different wood species. The second order variations seen in the mass loss profiles with ash type (Fig. 2) is reflected in the DTA results (Fig. 3) as a shift in the temperature of the minima of the valleys (maximum temperature difference between the sample and reference). Since the sample weight and other experimental conditions were the same for all ash, the shift in the temperature of minima was associated with the difference in chemical composition, particularly the relative amounts of potassium and calcium. The justification for this argument is based on the observations of Malik *et al.*<sup>17</sup> and Huang and Daugherty<sup>18</sup> that a trace amount of potassium carbonate in limestone (K/Ca~0.01 and 0.07, respectively) can accelerate the decomposition of calcium carbonate.

The variation in the temperature at maximum temperature difference with K/Ca, observed in Fig. 3, is shown in Fig. 13. It is seen that the temperature at the maximum temperature difference is 836°C for oak which has a K/Ca = 0.165, and this temperature reduces to 788°C for pine which has a K/Ca ratio of 0.56. These results indicate that the presence of increasing amounts of alkali compound can lower the decomposition temperature of CaCO<sub>3</sub>. This was confirmed in separate experiments where temperatures at the minima for pure CaCO<sub>3</sub> and for a CaCO<sub>3</sub>/K<sub>2</sub>CO<sub>3</sub> mixture were compared. The temperature at the maximum temperature

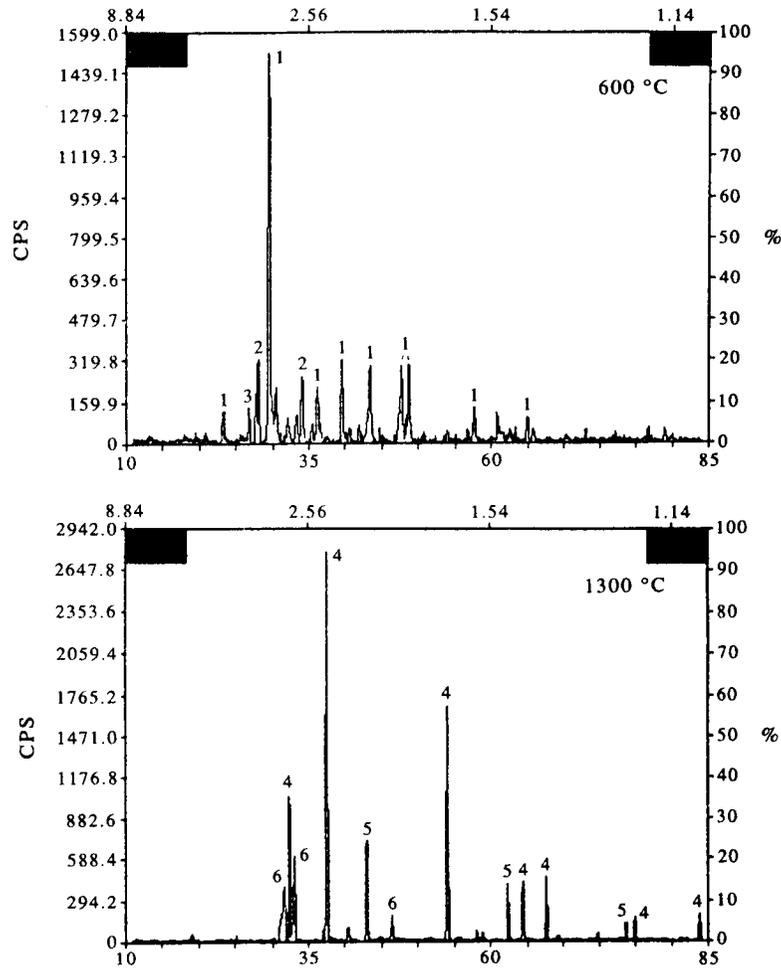


Fig. 12. X-ray diffraction pattern for aspen ash at temperatures of 600 and 1300°C. The possible compounds present are: 1.  $\text{CaCO}_3$ , 2.  $\text{K}_2\text{Ca}(\text{CO}_3)_2$ , 3.  $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ , 4.  $\text{CaO}$ , 5.  $\text{MgO}$ , 6.  $\text{Ca}_2\text{SiO}_4$ .

difference for  $\text{CaCO}_3/\text{K}_2\text{CO}_3$  mixture ( $\text{K}/\text{Ca} = 0.95$ ) is also shown in Fig. 13. Although the trend shown by the mixture appears to be different from that shown by ash, and this may be due to other elements in ash, it is clear that a presence of alkali carbonate accelerates the decomposition of calcium carbonate. Dissociation of calcium carbonate appears to be enhanced with an increase in heat transfer rate.<sup>19</sup> The acceleration of  $\text{CaCO}_3$  dissociation in the presence of alkali compounds has been attributed to improved thermal contact due to melting of alkali compounds,<sup>18</sup> thereby enhancing the heat transfer rate to calcium carbonate.

#### 4.2. Relative amounts of volatile elements

Upon dissociation at temperatures beyond 900°C,  $\text{K}_2\text{CO}_3$  forms  $\text{CO}_2$  and  $\text{K}_2\text{O}$ , both existing as gases at these temperatures. The dissociation is hence associated with a simultaneous decrease in the potassium content of

the ash. The amount of potassium present as potassium carbonate or any other volatile compound can be estimated from the amounts of potassium present in the low temperature ash and in the high temperature ash. In general, the

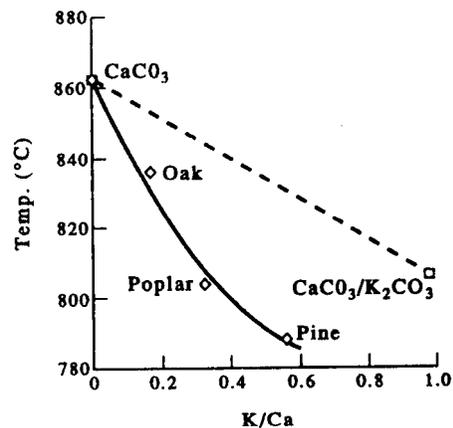


Fig. 13. Variation of temperature at maximum temperature difference with  $\text{K}/\text{Ca}$ .

fraction of any volatile element with respect to its content in low temperature ash, i.e.  $i/i_o$  can be calculated from,

$$\frac{i}{i_o} = 1 - \left(\frac{i_f}{i_o}\right) \left(\frac{Ca_o}{Ca_f}\right)$$

where subscript *o* refers to concentration in low temperature ash, subscript *f* denotes concentration in high temperature ash, and Ca represents concentration of calcium. The derivation of this expression is based on the reasonable assumption that all of calcium is retained in the ash at high temperatures, and hence can be used as a factor to account for mass change as a result of dissociation of carbonates at higher temperatures. Estimates of volatile potassium as a percentage of total potassium present in different wood ash are listed in Table 6 along with sodium, sulfur, and boron. Unlike potassium, these latter elements are present in much smaller quantities and their contribution, if any, to the initiation of ash deposition may be overshadowed by that of potassium compounds.

In the absence of substantial XRD evidence, the process leading to a reduction in sodium concentrations in pine and oak ash is presumed to be similar to that of potassium, namely, dissociation of sodium carbonate and subsequent volatilization of sodium oxide. Reduction in sulfur concentration at high temperatures is probably due to the dissociation of sulfates of calcium, magnesium and potassium, however the form of the sulfur cannot be substantiated in the low temperature ash analyzed so far.

#### 4.3. Deposition characteristics of ash in combustors

Potassium, sodium and sulfur in the wood ash play a key role in formation of deposits. Some of the calcium, potassium, and magnesium may be taken up from the soil as sulfates and phosphates. These minerals are then transported and stored both in organic and inorganic forms. It is reported that potassium is present primarily in solution in cell vacuoles.<sup>14</sup> calcium is present either in combined form in the cell wall or as crystalline calcium oxalate in cytoplasm,<sup>14,20</sup> magnesium primarily in combined form in organic molecules of which chlorophyll and proteins are examples,<sup>14</sup> and silicon as deposits on cell wall.<sup>14,20</sup> The mechanism by which the minerals are released as ash during the combustion of wood is not clear, but it is reasonable to assume that the conversion depends upon the

combustion temperature and the immediate environment. Carbonates are presumably formed at low temperatures in a quiescent atmosphere when the combustion products, primarily carbon dioxide, surround the wood grains. High yields of carbonates indicate that these conditions are prevalent during the low temperature ashing procedure followed in this study. Ash formed at high temperatures in an oxidizing atmosphere consist primarily of metal oxides. Ash composition can also be modified by the presence of silicon, manganese, iron, or aluminum which are capable of forming acidic oxides when the basic oxides are present in association with these oxides to give ceramic-like compounds in the ash. This is evident in the results obtained for both aspen and pine when the presence of silicon in the former yields silicates and the presence of manganese in the latter yields manganates.

Ash deposition in combustors and gasifiers may be initiated by alkali compounds that generally have low melting points. At temperatures starting at about 900°C, deposition can be initiated by the molten potassium carbonate and sulfate which adhere to the colder metallic surfaces and provide a sticky layer to trap other solid particulates such as oxides of calcium and magnesium. Other XRD tests of aspen ash deposits which we have done have clearly identified  $K_2SO_4$ , CaO and MgO as the predominant compounds in the deposits. The undissociated potassium carbonate may dissociate on the metallic surface after prolonged exposure to high temperatures, and the potassium oxide formed may react with the surface elements to form a chemical bond that holds the deposits to the surface. At higher temperatures, dissociation of potassium carbonate and subsequent formation of potassium oxide vapor will be accelerated. On lower temperature heat transfer surfaces  $KOH$ <sup>21</sup> and  $K_2CO_3$  are formed.

With regard to furnace design, the wood ash test results suggest that in order to minimize deposit formation, the furnace temperature should be held below 900°C wherever possible so that the volatilization of potassium and sulfur compounds will be restricted.

## 5. CONCLUSIONS

When low temperature wood ash was heated to 1300°C, a mass loss of 22.9-47.8% was observed depending on the wood type. For

600°C ash CaCO<sub>3</sub> and K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub> were identified, whereas in the 1300°C ash CaO and MgO were the main compounds. Bark ash at 600°C is primarily CaCO<sub>3</sub> at 600°C and CaO at 1300°C. Carbonates of calcium and potassium dissociated at 700-900°C depending on the wood type. Potassium volatilization began at 800-900°C, and sulfur volatilization began at 1000-1200°C. Copper and boron began volatilization at about 1000°C. When heated to 1300°C, potassium decreased by 63% to 90% and sulfur by 7% to 55% depending on the wood type. Potassium and sulfur compounds in wood ash play a key role in the formation of deposits.

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