STUDIES ON THE MEAT OF COMBUSTION OF WOOD:

PHYSICAL PROPERTIES AND THERMAL ANALYSIS

BY

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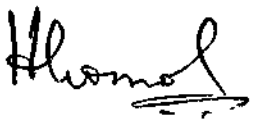
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DECLARATION

I hereby declare that this thesis contains the report of my research work and has not been presented in any previous application for a high degree. All information from other sources have been acknowledged by means references.



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3rd JULY, 2000.

CERTIFICATION

This thesis entitled "Studies on the Heat of Combustion of Wood: Physical Properties and Thermal Analysis" by Musa Momoh, meets the regulations governing the award of Doctor of Philosophy of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

To my father Chief Saliu Momoh Attah-Ibayi, my mother Iya Amina Momoh, my brother Shaibu Momoh and my wives Joyce and Janet whose advice and encouragement have been highly valued for many years of my study.

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ABSTRACT

In this work, the studies are concerned with: -

(i) The burning parameters of wood and the influence of physical properties

(ii) Thermoanalytical analysis and (LOI) of combustion of wood,

(iii) The kinetics of the thermal degradation,

(iv) The mechanism of complex formation between wood and selected flame-retardants on the burning behavior of the wood.

In case (i), four parameters namely ignition, burning rate, afterglow, char yield and degradation pattern were examined for fourteen tropical wood. It was found that the timbers may be ranked differently depending on which of the parameters is considered and no simple correlation of the four parameters exists. These observations were explained in terms of the variation in the composition of the wood and the effect of these on the phenomena of heat and mass transfer. Experiments were conducted to find the influence of physical properties on the burning characteristics. It was found that for the fourteen wood studied there is a highly significant correlation between both time of ignition and flame spread rate and timber oven-diy density. It was also found that the rate of flame spread depends on the orientation of the samples; for each wood, vertical orientation gives a higher flame spread value than horizontal orientation; Moisture content, as

expected reduces ease of ignition and flame spread, and the afterglow time is dependent on char yield and ash residue. The latter observation was interpreted to have arisen from the probable presence of metallic salts known to increase afterglow. Scanning electron micrographs of the wood show that the wood samples have different surface topographies. The wood specimens are seen as having striations, voids and lacunae, which in some samples coalesce to form network structures. .

Thermal analysis was studied. All measurements were made in a static atmosphere of air. By reference to the TG/DTG traces, two-step significant decomposition profile with the first step comprising two adjacent mass loss transitions separated by about 30°C were assigned to all the timbers. It was further found that the start, peak, and end temperatures of degradative transitions are similar for both steps for all wood samples and do not depend on timber density. These observations are interpreted in terms of the mechanisms of the wood pyrolysis/combustion. Differential Thermal Analysis methods (DTA and DSC) were also employed for comparison. Furthermore, experiments were conducted to determine the limiting oxygen index (LOI) of the wood. It was found that these LOI values are between 22% to 32%, and indeed, indicating that wood has some inherent flame tolerant or resistant properties.

The kinetics of the thermal degradation of the timbers were obtained using Broido's analytical procedure. The kinetic behaviour of pyrolysis of all wood in air is very similar and fairly high activation energies are required for the first step involving dehydration and chain scission reactions. The second step which is predominantly secondary product and char oxidations have significantly lower activation energies. The calculated kinetic parameters were also discussed within the context of other published values for wood/cellulose.

The influence that a range of selected inorganic flame-retardants have on the burning parameters, burning behaviour and pyrolysis of the wood were investigated. It was found that the flame retardancy related directly to char-forming tendency for all retardants and their ability to reduce the dominance of flammable volatile formed during the active first stage of wood pyrolysis. Among the flame retardants tested, diammonium phosphate (DAP),diammonium phosphate-borax (DAP:B) and boric acid-borax (B:B) are highly effective for reducing wood flammability as indicated by increased LOI and char yield values and reduced intensity of DTA peaks. Local alum and fertilizer are moderately effective. The possible retandancy mechanisms of these systems are discussed in detail.

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CHAPTER ONE

WOOD: STRUCTURE, PROPERTIES AND STAGES IN FIRE DEVELOPMENT

1.1 INTRODUCTION

From the primitive times to the present days highly advanced technology, man has been very much dependent on wood as a fuel and as a construction material. Further, cellulose, lignin, hemicellulose, resins, tannin, fat, waxes, and some colouring matters (Braus, 1964; Marton, 1966), are constituents of wood and it is the degradation of all these components that leads to the variety of chemicals observed on its pyrolysis. When wood is used for construction, however, its susceptibility to burning when accidentally ignited becomes a decided disadvantage, and the first attempts to render it fire-resistant were made. Combustibility or flammability of wood can therefore be looked at in two perspectives: As a mode by which useful energy as well as chemicals can be derived from wood and as a fire hazard.

Combustion of wood involves a complex series of physical transformation and chemical reactions that are further complicated by the heterogeneity of the substrate. Wood, and cellulosic materials in general, do not burn directly. Under the influence of sufficiently strong heat sources they

decompose to a mixture of volatile, tarry compositions and highly reactive carbonaceous char (Shafizadeh, 1984). Gas-phase oxidation of the combustible volatile and tarry products produces flaming combustion. Solid phase oxidation of the remaining char produces glowing or smouldering combustion, depending on the rate of oxidation (Shafizadeh, 1984). Regarding the flame retardancy of wood, a number of theories have been advanced. Briefly the current belief is that a flame retardant influences the mechanism of decomposition, lowers the temperature of decomposition onset and increases the char yield.

The present research project was undertaken to study wood pyrolysis/combustion and the effects of chemicals on it by the methods of thermal analysis. As an aid to the work and in order to clarify points of contention that may arise and the areas of ignorance, certain aspects of wood structure and physical properties, the important stages of pyrolysis, combustion and retardant action will be discussed. Thus, chapter one contains the background information on wood structure and properties and the pyrolysis and combustion of wood while chapters two and three give an up-to-date summary of the state of the art in flame-retarding wood, and the test methods developed to provide flammability/combustion respectively.

1.2 THE HAZARDS OF WOOD FLAMMABILITY

As already mentioned, combustibility of wood is valued when wood is used as a fuel, but is regarded as a fault when wood is used for construction.

The need to produce fire-resistant woods may be assessed in terms of identifying the hazard to life and property which burning wood and wood products create: Throughout the world, many people die or are injured from burns associated with flammable polymeric materials. Human sufferings and material losses as a result of fires are frightening and staggering. According to the National Fire Protection Association estimate (NFPA, 1967; Shafizadeh, 1968), in the United States in 1966 there were 2,396,550 fires of all types which caused property damage and loss amounting to $1,860,500,000. This included 970,880 building fires and building damage of $1,528,000,000. In the same period, forest and wild land fires in the United States burned a total of 4,574,389 acres (Forest Service, 1966). These simple statistics testify to the awesome toll of fire that in the United States, is estimated at 12,000 lives and five billion dollars a year in monetary value (NFPA, 1967). In comparison with the catastrophe of fires in U.S.A., the hazard of fire in Nigeria, and indeed, other countries cannot be ignored or underestimated. On April 12th, 1985 property worth several millions of naira were destroyed by fire at the headquarters of NNPC in Falomo. Five months later, on August 28th it was the turn of the headquarters of NPA in Marina, Lagos. Other examples of major fire outbreaks are those involving the multi-million naira NECOM building at Marina, Defence headquarters, NEPA headquarters and more recently the fire which engulfed the Onisha main market.

These few examples do not by any means present an exhaustive treatment of all the outstanding fire hazards. Rather they serve to illustrate the dangers that exist when advantages are taken of available technical knowledge. Further information on the tremendous hazards and threat of fire to man and his environment is contained in references (Eboatu, 1992; Fire Statistics U.K., 1994; FOS Nigeria, 1985; Fire Statistics, USA, 1973).

Flammability hazard is a combination of many factors such as heats, smoke, toxic gases, etc. Assessment of the potential flammability hazard is thus a difficult task and can only follow if sources of danger to life and injury are identified at each stage of the burning process. The major hazard of combustion product toxicity is just one parameter which is related to others like ignition, flame spread, afterglow, heat release, smoke emission, lachrymatory effects and oxygen depletion (Horrocks, 1986), all of which may be influenced by flame retardants.

1.3 WOOD IN GENERAL

Wood is a very valuable and versatile material with an extremely wide range of uses in construction/building, furniture, packaging, boat building, railroad ties, power transmission lines, means of transportation, musical instruments, athletic equipment, wood carvings and others (Champion, 1961; Hoadley, 1980; Spencer and Luy, 1975; Tsoumis, 1983, 1987). According to

Dubussy (1978), wood's favourable features which enable it hold its place in competition with other materials are:

- Attractive and varied appearance.
- High strength/weight ratio compared with most materials.
- Ease of machining, working with hand tools and joining with nails, screws, metal connectors, or glues.
- Durability, either natural or enhanced by treatment with preservatives.
- Resistance to corrosive influences and effects of weather.
- Good thermal insulation and acoustic properties.
- Compatibility with paints and other finishes.
- Wide range of properties available by selection of suitable species of tree.
- Low cost.
- Renewable.

Wood is the natural supporting skeleton of larger plants and it is important to understand the basic structure of wood, the variation between softwoods and hardwoods, the differences between species, wood properties and the significance of various features/properties in order to fully appreciate their burning behaviour.

(i) Softwoods and Hardwoods:- Commercial timbers fall into two main classes generally known as softwoods and hardwoods. The softwoods are

derived from coniferous or cone-bearing trees which usually have needle-shaped leaves and seeds that are not enclosed in a seed-case (gymnosperms). The hardwoods are derived from dicotyledons or the broad-leaved trees having seeds that are enclosed in a seed-case (angiosperms). There are important differences in structure between softwoods and hardwoods which affect the properties of the timbers.

(ii) Colour:- Colour in wood is due mainly to extractives. However, the major cell wall components, with the possible exception of cellulose, may also contribute to the colour of exposed wood surface through oxidation. Wood colour varies not only among different kinds of wood but also within a species and often even in the same piece of wood.

1.3.1 Wood Structure

The trunk or stem of the tree is the wood of commerce. The trunk consists of a central pith enclosed by a series of cones, each cone representing the annual growth increment or annual ring. The wood tissue around the pith is the heartwood consisting of dead cells which become filled with various extractives. Around the heartwood is the sapwood of living cells, the inner zone (xylem) conducting water upward to the leaves and the outer or phloem conveying sugars from the leaves to the living cells throughout the tree providing them with energy to sustain life and sugar components to form

cellulose, hemicellulose and starch (Richardson, 1993; Panshin and de Zeeuw, 1980). The interface between the xylem and phloem cells are known as the cambium and are distinctive as they can divide to form new cells. The cambium consists essentially of two types of dividing cells, the fusiform initials and the ray initials. The fusiform initials adjacent to the sapwood give rise to xylem or wood cells which ultimately become the tracheid of conifers or softwoods and the fibres of dicotyledonous or hardwoods. The outer fusiform initials give rise to the bark. The ray initials also produce xylem but in the form of parenchyma or ray cells. In this way the wood is formed so that the vertical tracheid and fibres give longitudinal strength, as well as vertical transport routes within the tracheid in conifers and within the pores surrounded by fibres in dicotyledons. In contrast, the ray cells are orientated along horizontal radial paths in order to provide conducting tissue between the phloem and the cells deep within the sapwood and heartwood, apparently conducting extractive towards the heartwood and sugars to the living cells in the sapwood and also often providing tissue for the storage of starch, (Richardson, 1993), particularly in hardwoods.

The structure and arrangement of the various types of cell differ widely between different wood species and greatly affect the texture and the strength. The thickness of the cell walls, particularly of fibres and tracheid, differs markedly between species (Dubussy, 1978), and is largely responsible for the differences in density between timbers.

1.3.2 Chemical Composition

The chemistry of wood is discussed in detail by Sjostrom (1981). As mentioned before, the wood of any species of tree consists essentially of a large number of fibres which are bonded together to form a solid and rigid structure. These fibres are hollow, cylindrical structures, the walls of which are composed mainly of polysaccharides, while the bonding material which unites them into a solid mass consists essentially of lignin.

The polysaccharides, known collectively as holocellulose, are further divided into cellulose and hemicellulose. The cellulose is a linear polymer composed of glucosan units with a definite chemical composition but variable molecular weight and crystallinity. The degree of polymerisation (DP) of cellulose ranges from 10,000 for wood to 15,000 for cotton and almost 20,000 for certain algal cellulose (Goring and Timell, 1962). The hemicellulose is composed of several polysaccharides without a definite chemical composition. Their degree of polymerisation is small, usually around 200. They also have side chains which prevent them from forming a crystal structure like that of cellulose. These factors contribute to their relatively high rate of pyrolysis compared to that of cellulose. There are two major hemicelluloses present in the softwoods, galactoglucomannan and arabinoglucuronoxylan, called mannan and

xylan respectively. The hemicelluloses present in hardwood consists of glucuronoxylan and glucomannan, also called xylan and mannan. Thus the chemical composition of the mannan and xylan present in hardwoods differs from that in softwoods.

Lignin, on the other hand, does not possess a linear molecule, but is an amorphous material having a 3-dimensional polymerical structure. It thus has the properties necessary for it to perform its function as a bonding or cementing material between the fibres. The unzipping mechanism present in polysaccharides is not available to lignin because of this structure. Consequently, it has a slower rate of pyrolysis.

In addition to these structural components, all woods contain small amounts of extractable organic materials and some inorganic materials which contribute to the ash content when wood is burnt. These extraneous components do not form part of the cell wall structure but may be infiltrated completely or deposited within the cell walls or they may occur as surface deposits or plugs in cell lumina (Dubussy, 1978; Pandhin and de Zeeuw, 1980). They are extracted by means of inert solvents without destroying the structure of the wood, and for this reason they are often called extractive. Wood extractive represent an extremely wide range of classes of organic components consisting of polyphenols - tannin, flavone, catechin and kino, and oleoresin - turpentine, tall oil and resin. Other types of organic materials that commonly

occur are gums, fats, fatty acids, waxes and volatile hydrocarbons (Hillis, 1962).

In general terms, the following ranges are suggested by Sjostrom (1981), for the principal components of the wood: Cellulose 40 to 45 percent in all woods; Lignin in softwood 26-32 percent, in hardwood 20 to 28 percent; mannan in softwood about 20%, in hardwood 2 to 5 percent; xylan in softwoods 5 to 10 percent, in hardwood 15 to 30 percent; the ash content is about 0.1 to 0.5 percent for domestic wood (Panshin and de Zeeuw, 1980), but it may be much greater, and a remaining fraction consisting of resins, tannin, and miscellaneous compounds usually amounting to only a few percent.

Experimental data commonly show considerable variation within the general ranges quoted. This arises from species or generic differences and the fact that the chemical composition of wood from the different parts of the same tree may be quite dissimilar (Panshin and de Zeeuw, 1980; Tamminen, 1964; Taylor and Wooten 1973; Hale and Clermont, 1963). Another cause for differences in data on chemical composition of wood that is botanically similar is due to differences in analytical methods employed. According to Panshin and de Zeeuw (1980), the boundaries separating the classes of compounds are not distinct and minor changes in procedures can alter percentages of the compounds.

1.4 SOME WOOD PROPERTIES

The discussion here will be limited to that needed for this research. Basically most properties of wood are determined by the factors inherent in its structural organisation. These includes (Panshin and de Zeeuw, 1980):

- The amount of cell wall substance present in a given volume of wood.
- The amount of water present in the cell wall.
- The proportionate composition of the primary chemical components of the cell wall and the quantity as well as the nature of the extraneous substance present.
- The arrangement and orientation of the wall materials in the cells and in different tissues.
- The kind, size, proportions, and arrangement of the cells making up the woody tissue.

These factors profoundly affect the total behaviour of wood and are mostly responsible for the large differences found in the responses of wood with respect to fire treatment.

1.4.1 Moisture Content of Wood

The water content has a great influence on the properties of wood, affecting its weight, strength, shrinkage and other non-mechanical properties. The moisture content (M.C.) is stated as

$$M.C.(\%) = \frac{\text{Weight of water present}}{\text{Dry weight of wood substance}} \times 100 \qquad (1.1)$$

$$= \frac{\text{Initial weight of sample - OD weight of sample}}{\text{OD weight of sample}} \times 100 \qquad (1.2)$$

Where the initial weight of sample is the actual weight at the time of test and the dry weight (OD) is the weight of the sample after the moisture has been expelled.

1.4.2 Density of Woods

Density of homogeneous material is defined as its mass per unit volume

$$\rho = \frac{\text{Mass}}{\text{Volume}} \qquad (1.3)$$

The density of a piece of wood depends to a considerable degree on the amount of moisture held in the wood. For this reason it is important, when quoting the density of wood, to state the moisture content to which it refers.

The basic dry wood substance that composes the cell walls has about the same specific gravity of 1.5 (Panshin and de Zeeuw, 1980; Desch, 1977), for all woods. However, there are enormous variations in density of different samples of all woods. This is because different timbers vary enormously in their weight from about 160-1250 kg/m^3. This variation is caused by differences in the ratio of cell wall to air space in different timbers, and to the amount of water in the test piece at the time the density is determined.

1.4.3 Thermal Properties of Wood

Dry wood is one of the poorest conductors of heat and this characteristic renders it eminently suitable for many of the uses to which it is put every day, e.g. as a building material, in the construction of refrigerators, or fireless cookers, and as handles of cooking utensils. The conduction of heat depends on two factors the thermal (or specific) conductivity k and the specific heat of the intervening material.

The thermal conductivity of wood is dependent on several characteristics (Panshin and de Zeeuw, 1980; Desch, 1977):

(i) direction of heat flow with respect to the grain orientation in the wood, (ii) moisture content of the wood, and (iii) specific gravity of wood. It is quite low for dry wood, because wood is a cellular substance, and in the dry state the cell cavities are filled with air, which is one of the poorest conductors known. The conductivity of green unseasoned wood is much higher than that of dry wood as in green wood the cells are filled with water and salts which is a better conductor of heat than air.

The conductivity of dry wood depends greatly on its density; the lighter the wood the better are its insulating properties i.e., the heavier woods conduct heat faster than lighter woods because of the greater amount of solid wall materials in the heavier woods. The cellular structure of wood also partly

explains why heavy woods conduct heat more rapidly than light porous ones.

The transverse thermal conductivity (k) of wood is expressed (Panshin and de Zeeuw, 1980).

$$k = G[1.39 + A\,(M.C.)] + 0.165 \qquad (1.4)$$

where G is specific gravity at a given moisture content, M.C. is moisture content in percent, and A is a constant depending on the M.C. with a value of 0.028 below 40% M.C. and 0.038 above.

The specific heat of a substance is the amount of heat required to raise the temperature of 1g of that substance 1°C. The specific heat of wood is about 50% higher than that of air, and four times as high as that of copper (Desch, 1977). The movement of heat is more rapid in green timber than dry wood of the same species because of the water present, which is a much better conductor than air. Because of the relatively high specific heat and poor conductivity of wood, wooden doors are often effective in preventing the spread of a fire for a considerable period. Wooden doors fail when shrinkage causes the different parts, e.g. panels, styles, and mouldings to pull apart, leaving gaps through which flames can penetrate. Metal doors, on the other hand, conduct heat to the opposite side so quickly, and absorb so little heat themselves in the process, that they tend to pass on a fire with great rapidity.

Thermal diffusivity is a measure of the speed with which a material can absorb heat from its surroundings. This thermal property is defined as the ratio of thermal conductivity to the product of density and specific heat. Wood has a low thermal diffusivity because of the low thermal conductivity and moderate values for both density and specific heat. The low thermal diffusivity values associated with wood account for the comfortably warm feeling of wood furniture in contrast with metals and plastics when these are used for furniture.

1.5 THERMAL DEGRADATION OF WOOD

A large number of investigations (Shafizadeh, 1968; Browne, 1958; Sandermann and Augustin, 1963; Fang et al., 1966; Shafizadeh, 1971; Stamm, 1956; Browne and Tang, 1962), have been published and reviewed pertaining to wood degradation. The work done by Shafizadeh (1984), Shafizadeh and Lai (1972), Shafizadeh and Fu (1973), Lipska and Wodley (1968), and others (Byrne et al., 1966; Tsuchiya and Sumi, 1970), to mention just a few, although pertaining only to cellulose is nevertheless of direct application to wood studies since cellulose constitutes a large percentage of wood.

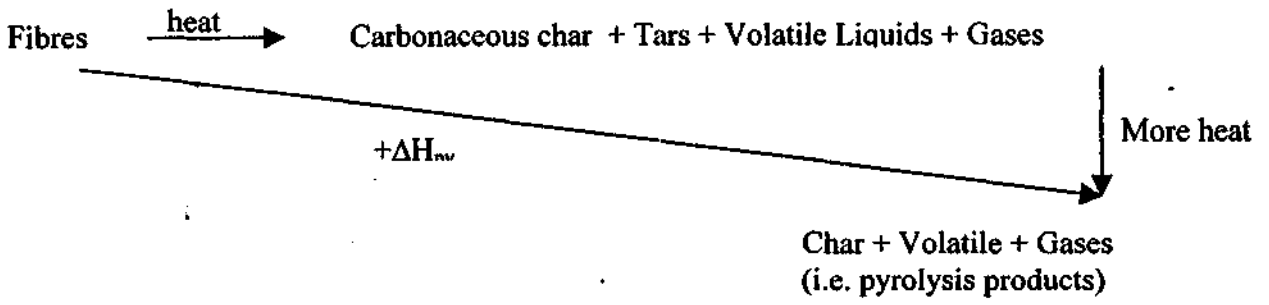
When wood is exposed to a heat source, it will experience a temperature rise as a result of the heat transfer. The heat must progressively raise the temperature of the wood until degradation,often termed pyrolysis, of the polymer structure is initiated. Pyrolysis is the chemical breakdown of the

substance by the influence of heat alone. It can be influenced by the presence or absence of oxygen and occurs in stages.

Initially, the chemical action of heat on any polymer, and in particular wood, is to pyrolyse it once the polymer attains the temperature, T_p, at which major decomposition ensues. At a higher temperature, T_c, oxidation and hence combustion may occur. Investigations of the pyrolysis and combustion of wood or cellulose dealt with the relative amount of gases, chars, and tars produced, and with observations of how flammability varied with the relative proportions of these fractions.

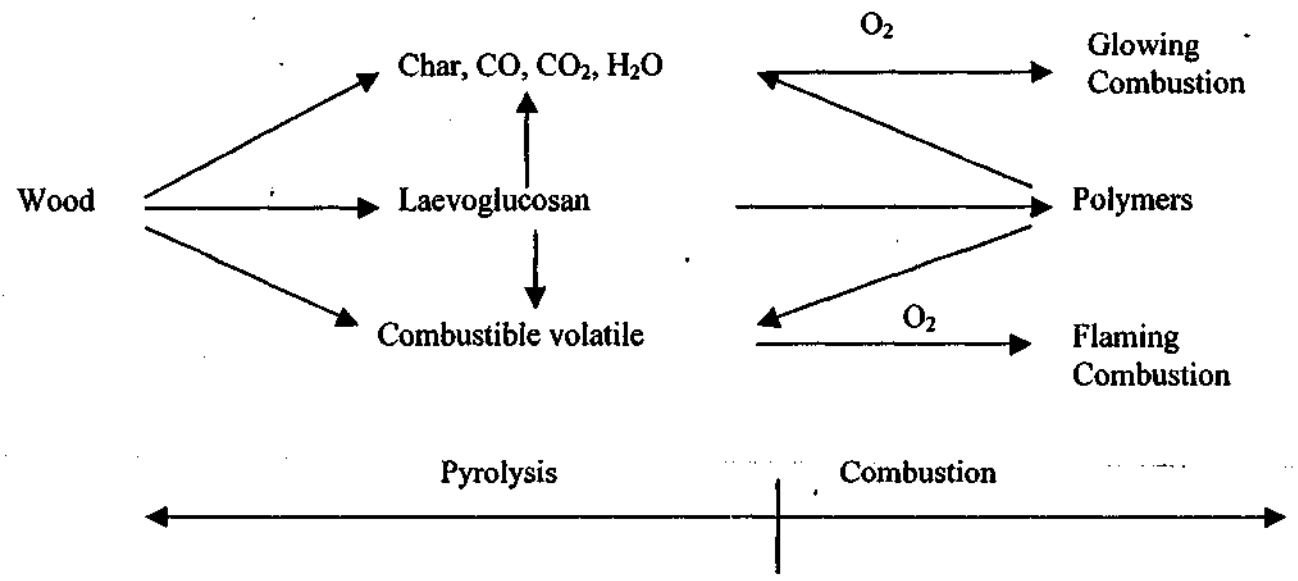
1.5.1 The Course of Pyrolysis

When a piece of wood is heated in the absence of air at temperatures below 280°C, the wood becomes dehydrated and slowly charred (Browne, 1958; Shafizadeh and Lai, 1972). In all woods, a temperature may be reached at which the energy absorbed equals that of a component bond which gives rise to bond rupture and ensuing pyrolysis. Char, water, carbon dioxide, formic and acetic acids and perhaps a little carbon monoxide (Martin, 1956; Othmer and Schurig, 1941), are the major product when there is rupture of bonds in the wood structure. The reactions are endothermic (Weidel, 1949), and the gaseous products are largely non-combustible. Pyrolysis often occurs in stages;



where ΔH_{py} indicates the heat of pyrolysis and is endothermic. At higher temperatures (300-500°C) active pyrolysis begins suddenly and exothermically, (Shafizadeh, 1968; Hawley, 1952; Sergeeva and Vaivads, 1954), and the wood decomposes further, giving a combination of higher molecular weight products (char), low molecular weight products (volatile) and gases. Thus, in addition to depolymerisation and decomposition (with evolution of water, carbon dioxide, and carbon monoxide) a volatile tar, which contains mainly laevoglucosan are evolved and leaves a charred residue (Shafizadeh, 1968; Martin, 1956; Othmer and Schurig, 1941). The primary pyrolysis products undergo further pyrolysis and reactions with one another before they escape (Martin, 1956; Hawley, 1952; Sergeeva and Vaivads, 1954).

Above 500°C there will occur more vigorous secondary reactions in which the gaseous product and tars are further pyrolysed to more highly combustible products. For example, carbon dioxide and water vapour react with carbon to form carbon monoxide, hydrogen and formaldehyde (Martin, 1956).



1.5.2 The Course of Combustion

The course of events when wood is heated in air is similar to that in the inert atmosphere, but is modified by oxidation reactions, and, after ignition, by combustion of pyrolysis and oxidation products (Shafizadeh, 1968; Browne and Tang, 1962). At lower temperatures (<280°C) the wood becomes charred quickly and oxidation reactions occur that are exothermic. Although the gases evolved are not readily ignitable, oxidative degradation proceeds faster than pyrolysis in an inert medium (Shafizadeh and Bradbury, 1979). Oxygen catalyses the formation of volatile as well as the char promoting reactions.

When air is present at higher temperatures (>280°C), the combustible volatile products thus formed react with oxygen in the gas phase, and give rise

to flaming ignition; whereas, the oxidation of the charred residue in the solid phase leads to glowing combustion.

In general, ignition of the volatile pyrolysis products occurs if,

(i) volatiles are flammable or oxidisable, e.g. CO, C_xH_y, H_2S, and NH_3),

(ii) oxygen is available to create the correct oxygen/fuel ratio for combustion;

(iii) the temperature is high enough for the fuel and oxygen to react, this temperature is known as the oxidation temperature, T_{ox}.

For ignition of the initially formed pyrolysis products to give rise to a self-sustained propagating flame, there must be an excess of energy from the combustion stage, ΔH_{exo}, to cause pyrolysis of more wood and maintain the high flame temperature required for oxidation.

$$\text{Wood Material} \xrightarrow[\Delta H_{py}]{200-280^\circ C} \text{Volatile Products} + O_2 \rightarrow \text{char products} + \Delta H_{exo}$$

$$\Delta H_{exo} - \Delta H_{ph} = \Delta H_c \quad \text{(heat of combustion)}$$

Figure 1.1 illusrates a scheme which was proposed by Horrocks (1983), to describe the burning process of a polymer. This scheme and others (Yeh et al., 1976; Bauer, 1978) proposed to describe the polymer burning process show that the process is cyclic (feedback system) and tend to be self-sustaining as long as the fuel and oxygen persist.

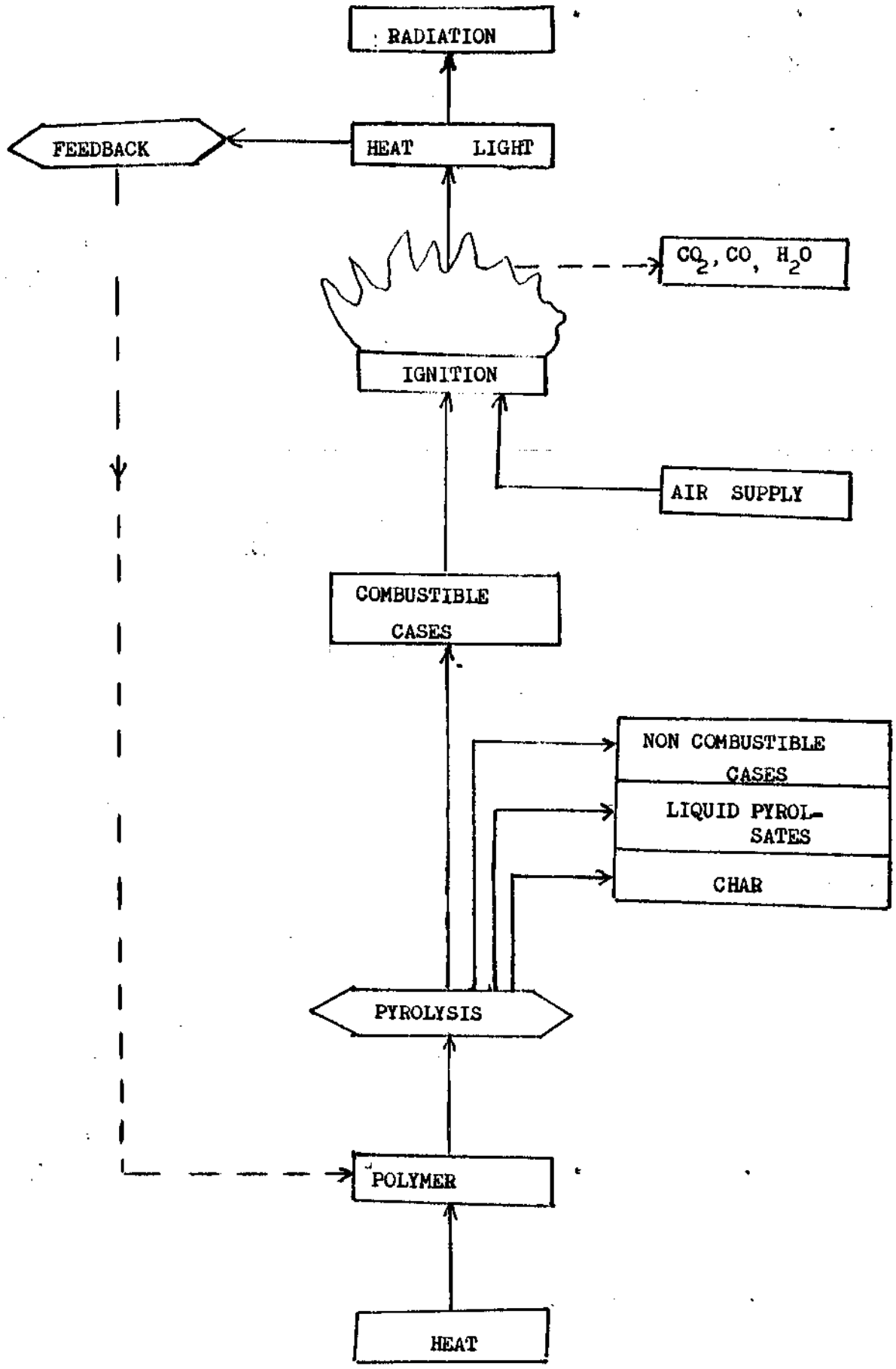


FIGURE 1.1: Combustion process as a feedback system (44)

In practice, simultaneous pyrolysis and combustion of volatile occurs and this reduces char formation to zero in ideal circumstances. Furthermore, this interaction often ensures that piloted flame ignition occurs at a lower temperature than non-piloted ignition. If, in the above model insufficient oxygen is present then the combustion will not be completed and products will be essentially carbonaceous as both char and smoke, unburnt flammable volatile, non-flammable gases (eg.CO_2) or H_20 and CO.

1.6 PARAMETERS THAT DESCRIBE BURNING BEHAVIOUR OF WOOD

When wood burns, the characterisation of its behaviour in terms of the feedback mechanism (Fig.1.1) requires the quantification of certain identifiable parameters such as ignition, burning behaviour/flame spread, heat of decomposition, afterglow, etc. The phenomena of ignition or burning of wood have been the subject of extensive studies.

1.6.1 Ignition

In the literature, generally three types of ignition have been accepted: spontaneous ignition with external heating; piloted ignition and spontaneous ignition by self-heating (Akita, 1959). Spontaneous ignition with external heating is defined as the appearance of a flame at the surface of a material which has been exposed to some type of external heating such as a radiant heat

flux. Piloted ignition is defined as the appearance of a flame at the surface of a material which has been exposed to some type of external heating with the presence of an ignition source in the volatile stream formed as the material is heated. The spontaneous ignition by self-heating is brought about by the generation of heat within the material by means of an exothermic chemical reaction which gradually raises the temperature of the substance until it burst into flames. In both spontaneous ignition with external heating and pilot ignition, two types of flaming have been observed (Akalin, 1979). The flame appears at the surface only momentarily. This is often called "transient ignition". In the second case, the flame is maintained at the surface and the sample continues to burn in the absence of additional heating. This is often called "sustained or persistent ignition".

Another phenomenon should also be mentioned here which has been referred to as "glowing ignition". Glowing ignition is defined as the appearance of red hot or glowing areas at the surface of the material when exposed to external heating. However, no flame appears at the surface . This phenomenon can be observed when an ignition source is either present or absent but is not considered to constitute ignition according to the above definition of spontaneous and pilot ignition.

Whatever the cellulosic material and means of heating or source of ignition, the overall ignition process is generally the same and is shown in

Figure 1.2. As the external heat sources transfers heat to the material, the temperature of the material increases and heat is redistributed simultaneously by conduction. When certain temperature levels are reached within the material, volatiles are formed and proceed to the surface where they are expelled into the surrounding air. These volatiles will consist mainly of water vapour in the early stages resulting from hygroscopic moisture, but as the temperature of the material increases decomposition reactions occur which release combustible products. The volatile stream is hotter and thus less dense than the surrounding air and therefore rises as it mixes with the temperature of the material increases and heat is redistributed simultaneously by conduction. When certain temperature levels are reached within the material, volatiles are formed and proceed to the surface where they are expelled into the surrounding air. These volatiles will consist mainly of water vapour in the early stages resulting from hygroscopic moisture, but as the temperature of the material increases decomposition reactions occur which release combustible products. The volatile stream is hotter and thus less dense than the surrounding air and therefore rises as it mixes with the air. If sufficient heat is supplied, a combustible mixture is eventually formed at some point in this volatile stream and ignition occurs at this spot and flashes back to the surface where it may or may not be stabilised.

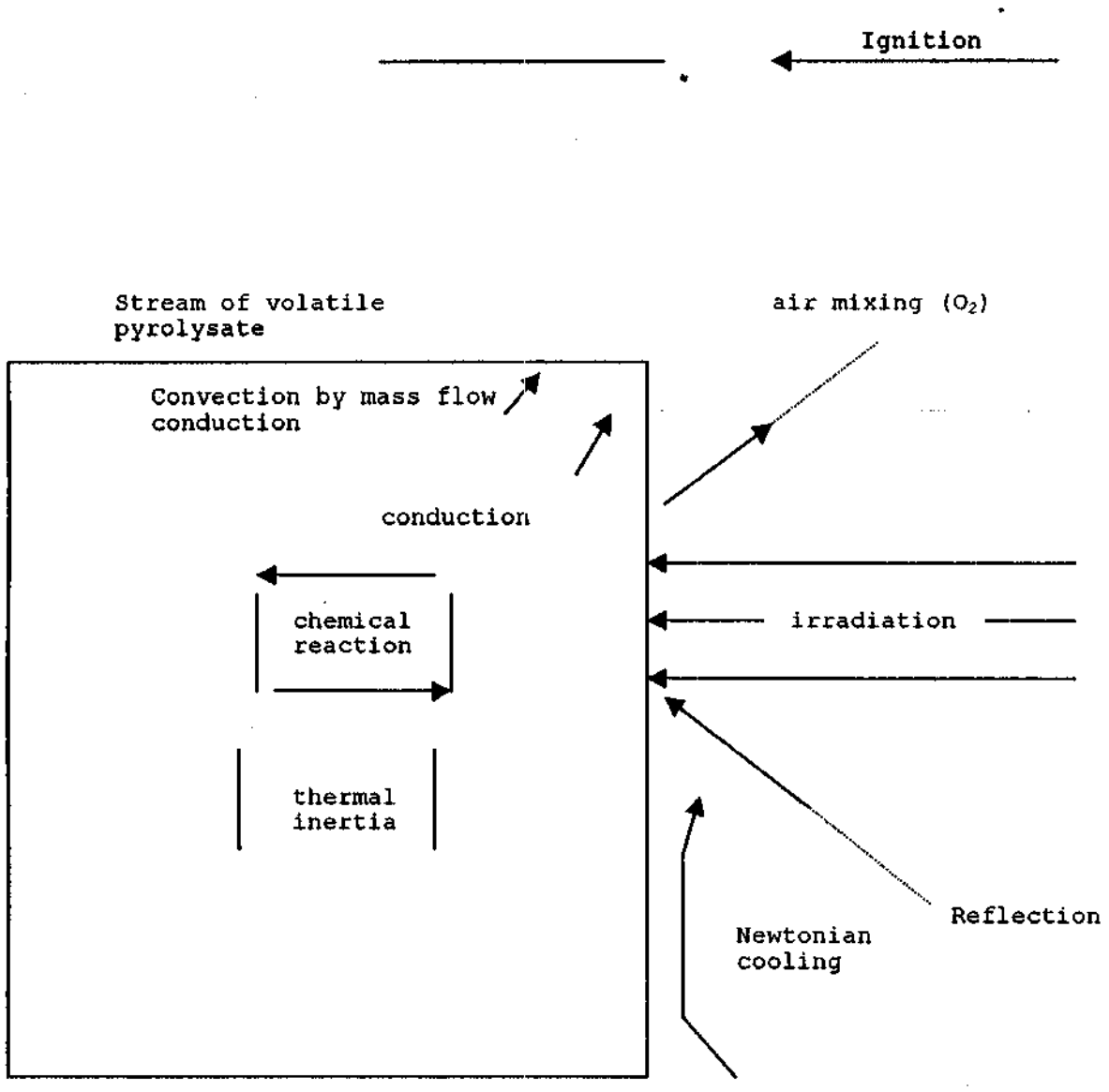


FIGURE 1.2: Ignition of a solid polymer in terms of heat transfer mechanism (Akita, 1959).

Since the fuel concentration is not normally known for pyrolysing cellulose materials, ignition characteristics (Welker, 1976; Alger, 1972), have generally been studied in terms of the critical irradiance i.e. the threshold value of heat input for ignition, the time to ignition, surface temperature and temperature distribution within the specimen, the rate of weight loss from the sample, sample absorptance for radiant energy, sample size, moisture content and convective effects. The incident irradiance has been the primary independent parameter in most studies. The most important of these parameters is the time required for ignition. However, the results of measurements made by the various investigators at different laboratories have not always been in good agreement; even the measurement of the incident irradiance which is fundamental to all ignition tests, is often in error. Smith (1968), has reported a wide variation in calibration of commercially Gardon-type radiometers, for example. Such errors and variations in thermal and absorptance properties in ignition studies accounted for the variation in results.

Both the fuel concentration and the temperature depend on the heating rate, consequently, ignition can occur for various combinations of heating rate, temperature and time (Alger, 1972). Two observations (Butler et al., 1956; Martins, 1965), have contributed substantially to our ability to rationalise and predict ignition behaviour from the knowledge of the heating rate and the thermal properties of the cellulosic samples. First, the time to ignition t_i,was

found to be inversely proportional to the square of the heating rate,

$$\text{i.e. } t_i \quad \propto \quad 1/H^2$$

where H is the irradiance. Second, a solution to the heat conduction problem for radiant energy entering a semi-infinite slab gave the same inverse relationship provided ignition occurred at constant surface temperature (T) i.e

$$t_i \quad \propto \quad (\Delta T/H)^2 \; kpc$$

where kpc are the thermal conductivity, density and specific heat respectively for the slab. With these efforts, considerable success has been achieved in predicting ignition conditions for a variety of cellulosic materials.

1.6.2 Sustained Burning Behaviour(Flame Spread)

After ignition has occurred, it is evident that the rate of burning is of importance in any attempt to determine the general flammability behaviour of cellulosic wood. Burning of wood products may, however, occur in two possible ways, namely: (i) flaming and (ii) smouldering. A flame is the visible combustion of a gas or vapour. Flaming is the exothermic oxidative process which takes place in the combustible vapours above the decomposing wood surface. Smouldering is the exothermic reaction which takes place at the surface and in the gas phase just above the surface. For the flame to be self-sustained and propagate, all the pre-combustion processes in the condensed and gas phase must proceed in consecutive order and at optimum

rates as discussed before. Generally, there should be:

(i) a constant supply of fuel precursors,

(ii) a constant flow of combustible gases,

(iii) sufficient oxygen,

(iv) a positive net heat of combustion, and

(v) no barrier for the heat flux in all phases.

Any disturbance in the sequence of the pre-combustion processes of these five specific requirements will lead to flame retardation and possibly fire extinguishment.

Several research workers have generated useful and interesting information about general wood flammability using the approach of measurement of flame burning rate (Lewin and Sello, 1975). However, as the flame front moves along a specimen in the normal burning process, a variable situation is created with respect to the gaseous environment boundary conditions and the heat transfer process in the vicinity of the flame front. This results in poor reproducibility in burning rate studies. In a 1968 review, Friedman (1968), noted that combustion science is not able to specify mathematically the laws governing this process (flame spread) and indeed there is uncertainty as to which variable exert the dominant effects. In addition to a continuing process of pyrolysis and ignition, flame spread also involves heat transfer and aerodynamics. At this point the geometry, size, and orientation of fuel becomes

an important factor contributing to the pattern and rate of flame spread. The thermal properties Kρc which govern ignition are other factors important for flame spread.

1.6.3 Heat of Decomposition

Heat release has long been recognised as the major reaction to fire parameter because it defines fire size. This in turn defines many of the other reaction to fire quantities e.g. smoke and toxic gas production because they are fire size, i.e. heat release, dependent.

The concern of heat release rate measurement is to determine the heat being released in a fire environment and the ability to accurately measure it in natural fire environments is viewed as essential to fire protection.

Akita (1959), and Klason (1914) studied several woods and cellulose and measured the heat generated during decomposition using the transient heat balance technique. Browne and Brenden (1964), later used Klason's data to estimate the heat of combustion of the volatile materials produced by pyrolysis. Values of the heat of decomposition reported by these authors range from about 30 cal/gm to about 300 cal/gm., all exothermic (Widel, 1949). Some other investigators (Sandermann and Augustin, 1963; Sergeeva and Vaivads, 1954; Tang and Neil, 1964; Broido, 1966; Arseneau, 1961; Iskhahov, 1957; Keylworth and Christoph, 1960), used DTA equipment to measure heat of

decomposition of wood and α - cellulose and found some endothermic regions and some exothermic regions. Their results differ in several respects. According to Welker (1976), and Havens (1969), the lack of agreement among the measurement of various workers for the heat of decomposition of cellulosic materials may most likely be traced to differences in equipment and techniques. The striking contrast between Tang and Neil's (1964), measurements indicating only endothermic reactions and Broido's (1966), measurements indicating both endothermic and exothermic reactions are a case in point.

CHAPTER TWO

FLAME RETARDANCY OF WOOD

2.1 HISTORICAL BACKGROUND

The desire for flammability reduction of wood dates back to the times of alchemy and the Roman era (Schlegel, 1934; Hird and Simms, 1953). Wyld (1735), received a patent in England for a treatment of theatres with alum, ferrous sulphate, and borax. The first systematic investigation of the use of flame retardants was completed by Gay-Lussac (1821). In this study, he disclosed the development of a flame resistant finish for linen and jute based on a mixture of ammonium phosphate, ammonium chloride and borax. He found that mixtures of ammonium phosphate with ammonium chloride or borax (1:1) prevented both flaming and glowing. He also concluded that the most effective flame retardant salts either had low melting points and so formed glassy deposits over the fibre surface, or decomposed into non-flammable vapours which diluted the flammable gases derived from the cellulose. Later, studies on fire-retardant treatments for wood was conducted by the American Forest Products Laboratory (Hunt, et al., 1931, 1932; Truax et al., 1933, 1935).

One hundred and thirty single chemicals or combinations of chemicals in the form of various salts were evaluated for ignition, flame spread reduction, smoke, etc. The most recent references on flame retardancy are cited in Browne (1958), Fang et al (1966), Goldstein (1984), Lyons (1970) and Kandola et al (1995). Essentially, flame etardancy for wood is still based on these old inventions by Gay-Lussac (1821) although several innovative modifications and improvements have been introduced. The more recent achievements concern the introduction of soluble organic compounds in order to reduce the leachability of treated wood which had hitherto hampered the use of flame-retardant wood where they will be exposed to the weather or running water and the synergistic combination of an organic phosphate and boric acid (Oberkey, 1983).

Another important but little understood aspect of flame retardancy is afterglow retardancy. Untreated wood usually show afterglow and the glowing reaction proceeds probably in the following directions (Benisek and Phillips, 1978):

$$C + O_2 \longrightarrow CO \qquad \text{(surface)}$$

$$CO + O_2 \longrightarrow CO_2 \qquad \text{(gas reaction)}$$

$$CO_2 + C \longrightarrow 2CO \qquad \text{(surface)}$$

The reaction to CO_2 is much more exothermic than that to CO, so that prevention of the CO_2 reaction substantially reduces the heat generation and may itself cause glow elimination.

Since flaming combustion and glowing combustion occur at different times and places and by distinctly differing mechanisms, they are therefore different in the means by which they are controlled. Effective flame proofing agents may fail to retard glow and vice-versa.

2.2 THEORIES OF FLAME RETARDANCY AND INFLUENCE OF FLAME RETARDANTS ON WOOD PYROLYSIS

From the previous discussion on the thermal degradation and combustion, the polymer burning process is cyclic and tends to be self-sustaining as long as fuel and oxygen persist. The role of a chemical flame retardant is to interrupt this closed-loop process (Akalin, 1979) by:

(i) shielding of the contact area between 'fuel' and oxygen

(ii) influencing pyrolysis, and/or

(iii) influencing the mechanism of combustion.

The first effect is mainly physical, whereas the second and third are chemical in nature.

However, where two compounds may function as flame retardants, the results may be additive, synergistic or antagonistic. In considering combinations of flame retardants, it is also important to consider the phenomenon of synergism. Synergism is defined as observed effectiveness of combination of compounds greater than the sum of the effects of individual components. Antagonism is not common in the flame retardation of polymers. However, it is defined as observed effectiveness of combinations of compounds smaller than the sum of the effects of individual components.

Traditionally, four main theories have been advanced to explain how to make cellulose and cellulosic materials flame-retardant. These are physical theories (coating theories), thermal theories, chemical theories and gas theories (Browne, 1958; Fang et al., 1966, Lyons, 1970, Kandola et al., 1995; Little, 1947, 1951). Nowadays, flame retardancy is discussed in terms of two major theories: (1) condensed and (2) gas phase mechanisms. Condensed phase retardant activity may be equated with the dehydration theory, where gas forming reaction of the pyrolysing solid are modified, while vapour - phase activity is similar to the gas theory explanation in that the retardant modifies the flame chemistry of the flammable gases (McNaugton, 1945). Retardants which act in the gas

phase exert their effect by functioning as either inert diluents or as free-radical inhibitors which slow the oxidation processes and decrease the heat returned to the polymer surface. Those retardants which act in the condensed phase may operate by several mechanisms (Baker, 1964): They may inhibit the pyrolysis so that it does not break down to produce the small volatile molecules necessary for flame propagation. More commonly, however, they act to alter rather than inhibit this pyrolysis reaction. The alteration is such that the mode of pyrolysis is changed and smaller quantities of flammable gases are produced. In addition, they may exert their effect in a physical rather than a chemical manner in that by enhancing char and/or forming a fused coat which acts as a shield. The shield prevents the transfer of heat from the flame back to the wood surface. Through this, the rate of polymer pyrolysis and fuel production is decreased.

Flame retardants, as already mentioned, may influence the pyrolysis by diminishing the formation of fuel or influence the chain reaction by increasing the rate and/or number of chain termination reactions. In the first case, flame retardant action is mainly confined to the solid phase; in the second case, it takes place in the gas phase.

2.2.1 Condensed Phase Reactions

Many workers (Shafizadeh, 1968; Browne and Tang, 1962; Brenden, 1972; Hirata and Abe, 1973; LeVan, 1984; Madorsky, 1956; Shafizadeh and Chin, 1977; Tang, 1967; Woo and Schniewind, 1987) have shown that in the pyrolysis of chemically treated wood and its components, the onset temperature and the apparent activation energy of the pyrolysis would be lowered, the residual char, water, carbon monoxide and carbon dioxide would be increased, and the volatile products (tar) containing mainly laevoglucosan would be decreased in comparison with those of untreated materials. Madorsky and co-workers (1956) have proposed that these added salts catalyse the dehydration of cellulose by scission of C - O bonds of cellulose, resulting in the destruction of the hexose units and increasing the yield of water and char at the expense of Laevcoglucosan. Shafizadeh et al (1975), have also shown that the presence of an acidic material, whether introduced as an additive or generated during the pyrolysis process, lowers the temperature of decomposition, suppresses the production of the combustible volatile and spreads the evolution of these materials over a wide range of temperatures, resulting in a major reduction in the rate of release of the combustible gases which fuel the flaming combustion reaction.

A possible chemical mechanism for the reduction of these combustible volatile is that fire retardant chemicals somehow inhibited the formation of leavoglucosan (1,6 anhydroglucopyranose), a major volatile fraction obtained from the thermal degradation of cellulose (see chapter 1). Fung et al (1972), analysed the amount of laevoglucosan produced by treated and untreated specimens of cellulose. All the chemicals led to the suppression of laevoglucosan formation but they had different effects on the chain depolymerisation reaction. Shafizadeh and co-workers (1968, 1975), studied the nature of uncatalysed, acid-catalysed, and alkali-catalysed thermal decomposition of leavoglucosan. The results agree with the findings of Fung et al (1972).

Flame retardants may not only catalyse dehydration of the cellulose to more char and fewer volatile but may also enhance the condensation of the char to form cross-linked and thermally stable polycyclic aromatic structures. According to Shafizadeh and Sekiguchi (Shafizadeh and Sekiguchi, 1983; Sekiguchi et al., 1983), the increased char formation is caused by the increased condensation and cross-linking of the carbon skeleton, in addition to any role that inorganic flame retardants play in dehydration of the glucose unit in the cellulose molecule or in lowering the solid phase combustion rate.

2.2.2 Vapour - Phase Reactions

Basically, combustion vapour phase reactions process occurs predominantly by branching chain reactions among free radicals (LeVan, 1984). The major chain branching reactions are:

$$H^{\cdot} + O_2 \longrightarrow HO^{\cdot} + O \qquad (2.1)$$

$$O^{\cdot} + H_2 \longrightarrow HO^{\cdot} + H \qquad (2.2)$$

Certain flame retardants affect vapour-phase reactions by inhibiting the chain reactions 1 and 2. Halogens such as bromine and chlorine are good free radical inhibitors. They have been studied extensively in the plastic industry (Creitz, 1970; Hastie, 1973; Hindersinn and Witschard, 1978), and their efficiency decreases in the order Br > Cl > F. A mechanism for the inhibition of the chain branching reactions (using HBr as the halogen) is:

$$H^{\cdot} + HBr \longrightarrow H_2 + Br^{\cdot} \qquad (2.3)$$

$$OH^{\cdot} + HBr \longrightarrow H_2O + Br^{\cdot} \qquad (2.4)$$

The hydrogen halide consumed in these reactions is regenerated to continue the inhibition. Although this proposed mechanism was based on experiments with premixed hydrocarbon flames, the same order of effectiveness exists with wood.

An alternate mechanism (reactions 5-7) was suggested for halogen inhibition which involves recombination of oxygen atoms (Creitz, 1970).

$$O\cdot + Br\cdot + M \longrightarrow BrO\cdot + M \qquad (2.5)$$

$$O\cdot + Br_2 \longrightarrow BrO\cdot + Br\cdot \qquad (2.6)$$

$$O\cdot + OBr\cdot \longrightarrow Br\cdot + O_2 \qquad (2.7)$$

Thus the inhibitive effect results from the removal of active oxygen atoms ($O\cdot$) from the vapour phase. Additional inhibition can result from removal of $\cdot OH$ radicals in the chain branching reactions:

$$BrO + \cdot OH \longrightarrow HBr + O_2 \qquad (2.8)$$

$$BrO + \cdot OH \longrightarrow Br\cdot + H_2O \qquad (2.9)$$

Reactions (5-9) explain the lack of halogen inhlbition in hydrocarbon nitrous oxide flames where the hydrogen--oxygen chain is not required for oxidation (Creitz, 1970).

2.3 CHEMICALS USED AS FLAME-RETARDANTS

The most common flame-retardants used in the wood industry consist mostly of mixtures of inorganic salts which have been known for centuries. Because such mixtures are no longer patentable, many such formulations have been kept a proprietary secret by the companies preparing them. However some of these formulations used commercially are described in

literature (AWPA, 1965). Bramhall (1966), listed most of them in his review. They include:-

Chromated Zinc Chloride _____ Zinc chloride ($ZnCl_2$) -65.2%, Sodium dichromate ($Na_2Cr_2O_7.\ 2H_2O$) -14.8%, ammonium sulphate [$(NH_4)_2SO_4$] -10% and boric acid (H_3BO_3) - 10%.

Minality_____Diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] -10%, ammonium sulphate [$(NH_4)_2SO_4$] -60%, boric acid -20% and anhydrous sodium tetraborate or borax ($Na_2B_4O_7$) - 10%.

Pyresote_____Zinc chloride-35%, ammonium sulphate -35%, boric acid - 25% and sodium dichromate [$Na_2Cr_2O_7.2H_2O$] -5%.

In addition to these, certain other proprietary formulations being used are composed of approximately equal quatities of monoammonium phosphate and ammonium sulphate, together with sodium fluoride or some other fungicide, and certain corrosion inhibitors. Gray (1959), compiled a list of commercial flame-retardants used in Britain. Some of which are Celcure - ammonium salts, borates, and copper chromate; Pyrolith - monoammonium phosphate and chromate/ arsenate/fluoride; Oxylene - monoammonium phosphate and borax; and Faspes 1 & 2 - monoammonium phase base plus fungicide.

These chemicals have the advantage of relatively low cost, and solubility in low-cost solvent, water. Salts promote the formation of char rather than of combustible gases (Browne, 1958). In efficient loading they are effective flame-retardants. However, they suffer from at least one serious drawback - they are subject to leaching because of their solubility in water and therefore cannot be used where they will be exposed to weather, especially running water (Bramhall, 1966). Therefore leach-resistant chemicals that can be impregnated into wood for use in exterior or high humidity applications were developed. These include chemical combinations that form insoluble complexes, amino-resin system, etc. (Goldstein, 1972; Lyons, 1970; Shafizadeh and Sekiguchi, 1983; Bramhall, 1966), of which are Arban - (triaryl phosphate) and Crebyl - (diphenyl phosphate), etc.

Specific reviews of flame-retardants and some comparison of their effectiveness have also been carried out. Bernhard (1953), and Hunt et al. (1932), categorised the common water borne flame-retardants according to effectiveness and listed their tendency to afterglow, corrode iron, effloresce and pick up moisture. They listed ammonium sulphate, diammonium phosphate, borax, sodium silicate and zinc chloride as very good flame-retardants. Bramhall (1968), using the ASTM E 69 test,

surveyed seventy flame retardant formulations, consisting of water - and organic solvent soluble impregnants, paints and coatings for red cedar. He found that the flame-retardant would be unable to suppress the flame at temperature greater than 315°C. Kollman (1952), and Eicker and Schaffer (1967), studied Douglas fir plywood samples impregnated with diammonium and monoammonium phosphate, zinc chloride, ammonium sulphate, borax and boric acid and ammonium chloride. They found that $(NH_4)HPO_4$ is most effective in retarding flame spread, followed by $ZnCl_2$, $(NH_4)_2SO_4$ and Na_3BO_3.

A durable flame-retardant treatment reported for red cedar involves impregnated with PCl_3, $PSCl_3$, and a vinyl chloride - vinyl acetate copolymer binder (Perirrolo, 1970). Ishihara and Maku (1972), reported the use of mixtures of melamine - formaldehyde resins and strong inorganic acids such as H_3PO_4 , H_2SO_4 and HBr for sliced veneer and papers.

2.4 GLOWING COMBUSTION INHIBITION

As mentioned earlier, glowing combustion is really the oxidation of carbon, which is the main constituent of the charred residue. This oxidation of carbon takes place through both of the following reactions.

$$C_{(S)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H = -110.45KJ\ mol^{-1}$$

$$C_{(S)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -394.95kJ\ mol^{-1}$$

Since the first reaction involves liberation of 110.45 $kJmol^{-1}$ as the heat of formation of CO and second one 395.95$kJ\ mol^{-1}$ as the heat of formation of CO_2 the additional release of 284.5$KJ\ mol^{-1}$ in the latter reaction is more likely to promote self-sustained glowing. In the first reaction, energy liberated is considerably less and is insufficient to propagate the oxidation of carbon, once the initiating source is removed. Hence, it is thought that smoulder and glow retardants accelerate the formation of CO and inhibit the formation of CO_2 either directly from carbon or by subsequent conversion of CO to CO_2 by the following reaction:

$$CO_{(g)} + \tfrac{1}{2}0_{2\,(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -284.5KJmol^{-1}$$

The ratio of CO to CO_2 produced in glowing or smouldering combustion is influenced by various additives (LeVan, 1984; McCarter, 1981; Shafizadeh et al., 1982). Phosphate and borates increase the $CO:CO_2$ ratio. Metal ions such as sodium, potassium, calcium, magnesium and many transition metals, particularly manganese and iron are known to reduce this ratio whilst promoting smouldering/glowing combustion (McCarter, 1981; Shafizadeh et al., 1982; Barker and Drews, 1985). The metal ions aid the

dissociation of the adsorbed molecular oxygen, thereby promoting the smouldering process (Shafizadeh and Sekiguchi, 1983; Barker and Drews, 1985). Ammonium phosphate and boric acid, which are known to inhibit smouldering or glowing may interfere with the active sites thereby blocking the process.

2.5 AIMS, OBJECTIVES AND SCOPE OF THIS WORK

The importance of wood flammability on the loss of human life and properties has been outlined in the foregoing sections. Also the endeavour to fight the dangers associated with wood and wood products fire through the application of flame retardants as well as the published literatures concerning the pyrolysis and combustion mechanisms of wood and flame-retarded wood has been discussed.

Most of these studies tend to centre on temperate and subtropical timbers which find use in the construction industries. There is no doubt that in the near future the wood resources of the temperate zones cannot support an increasing wood demand (Lauer, 1958). The vast resources of the tropical rain forests should therefore become of decisive interest for future timber and forest planning, renewal and development. Within Africa, hardwood and tropical woods have commercial potential although

their combustion behaviours are little understood. For these reasons, it is necessary to undertake study regarding the burning behaviour of both untreated and flame-retardant treated tropical timbers.

The main aim herein is therefore to study the fire properties, degradation characteristics and activation energies of a number of tropical wood under pyrolysis and combustion; and to find out the effects of selected common flame retardant chemicals upon the course and extent of the pyrolysis and combustion under controlled conditions of temperature and stoichiometry.

The objectives of the present investigation are as follows:-

1) To determine the flammability parameters such as ignition time, flame spread/propagation rate, afterglow time, extent of char area and limiting oxygen index for specimen samples made from a range of common tropical wood.
2) While behaviour of wood in response to fire is influenced greatly by many factors, a full characteristics is not possible but the influence of several decisive variables (wood density, moisture content, orientation, etc) will also be investigated.
3) To compare the results obtained for 14 types of tropical wood.
4) To obtain accurate comparative LOI data for the 14 different wood.

5) To obtain continuous plots of TG/DTG, DTA, and DSC to allow thermal analysis data and kinetic parameters to be established. Studies will be carried out on the char yield using the thermal degradation profiles.

6) Study the effect of a variety of common flame retardant treatments on tropical wood fire properties, thermal and burning behaviour. Attempts will be made to compare the effect of the flame retardant additives and composite variables on LOI.

The following techniques will be employed to obtain the various information on fire properties, LOI, thermal and morphological properties of the native (original) and treated samples, so that a probable mechanism of flame proofing can be formulated.

a. Simple match tests to determine the burning parameters such as ignition, burning rate, afterglow and char yield of the wood. Physical properties such as density, moisture content and sample orientation were examined in order to determine their effect on the burning characteristics.

b. FTA to identify the LOI for the different wood.

c. TG, DTG and DSC to determine the thermal decomposition and kinetic parameters for the treated and untreated wood. TG and simultaneous DTA give a possibility to determine the efficiency of inorganic salts. From these studies, the following parameters can be obtained:

(i) The decomposition temperatures for various samples using DTA, DTG and DSC techniques.

(ii) The temperature range where maximum weight loss occurs.

(iii) The percentage of the residue at the final temperature.

(iv) The values of the various kinetic and the thermodynamic parameters, like the enthalpy, the entropy and the free energy of activation.

d. Scanning electron microscopy (SEM) of wood to ascertain the morphological structure and the state of the fibrillar reaction sites on thermal degradation.

CHAPTER THREE

FLAMMABILITY AND ANALYTICAL TECHNIQUES FOR PHYSICAL AND CHEMICAL CHARACTERISATION OF WOOD

3.1 INTRODUCTION

Many techniques (Akita, 1959; Horrocks et al., 1985; Pearce et al., 1981), are often used for the assessment of the processes of combustion and flammability of polymers from various aspects, as is shown in Table 3.1. The fire properties, i.e., ignition, flame spread, afterglow, etc. and the parameters associated with degradation of polymer in the table are influenced by polymer structure, density and dimension; presence of moisture, finishes and impurities; polymer geometry (horizontal or vertical); type and size of ignition source, age and conditioning of samples; and environmental factors such as temperature, relative humidity, air velocity and oxygen availability (Barker and Drews, 1985). To measure all the parameters for a given cellulosic material such as wood would be a mammoth task. Therefore, this chapter will deal with those of particular relevance to this research work.

TABLE 3.1: Parameters describing burning of cellulosic materials

Observable parameters of a burning material	Measurable parameters to characterise burning.
IGNITION	Nature of igniting source Ease of ignition. Effect of environment. Physical character of the material.
FLAME PROPAGATION	Speed of propagation in all directions Influence of mode of ignition Extent of burning. Effect of environment.
FLAME DURATION	Rate at which flame consumes sample. Rate of flame extinction. Presence of afterglow, smouldering etc. Effect of environment. Physical character of the material.
ENERGY EVOLVED	Total thermal(and light) output. Rate of energy evolved. Rate of mass loss. Effect of environment and character of the Material on burning rate.
COMBUSTION PRODUCTS	Gaseous products and concentrations. Particulate (smoke) products and densities Toxicity of products Type of flaming debris. Char formation.

3.2 FLAMMABILITY TESTS

There are considerable numbers of testing methods (Lewin and Sello, 1975), for the determination of flammability of wood materials. Some of these methods have been adopted internationally as standards for official testing while others are used for research and development work only. The commonly used test methods include simple screening tests - Match Test (Israel Standard, 1969), 2-, 8-, and 25- feet tunnel flame-spread tests (ASTM, 1993, 1969; BS, 1968), and oxygen index test (ASTM, 1977). The tunnel flame-spread tests are quite expensive so that the cost of full scale room burns is totally out of the question and therefore except for the simple match test and oxygen index test, other above mentioned tests are not used in this work.

3.2.1 Simple Match Test

The simple match test or its equivalent is one of the easiest to run for screening. Oven-dry specimens are used. A simple match method for measuring flame-spread on wood has been proposed in Switzerland and Israel (Israel Standard, 1969; ASTM, 1977, 1969, 1993; BS, 1968). The specimens (10x10x2.5cm) are mounted vertically and the flame of a lighted match is applied from below to the down edge of the specimen for 30

seconds. The results showed that specimen is classed in group 1-111 if it burns out completely, it is classed in group IV-VI if it does not ignite or does not burn out completely.

Eboatu and co-workers (1992, 1990) have recently used simple match test to investigate the ease of ignition, flame spread and afterglow of some wood. A close linear correlation between the time of ignition, flame spread rate, afterglow and the wood density was found on untreated and alum/fertiliser treated wood.

3.2.2 The Limiting Oxygen Index (LOI)

The concept of limiting oxygen index was introduced in 1966 by Fenimore and Matin (1966), Fenimore (1966) as a means of assessing numerically the relative flammability of polymeric materials. Following the extensive round-robin tests (Isaacs, 1969; Issacs, 1970), the first standard using the LOI method was introduced in 1970 for the determination of the relative flammability of plastics (ASTM, 1977). However, it has been adapted to the testing of wood, and in particular, fire retardant treated wood (Abdel-hameed, 1991; Eboatu et. al., 1992; Yoshinura and Miwa, 1980; Yoshinura and Umemura, 1980).

The LOI of a material is the percentage concentration of oxygen in a mixture of oxygen and nitrogen which will maintain equilibrium burning condition, i.e., the minimal volume fraction of oxygen in a slowly rising gaseous atmosphere that will sustain candle-like burning of a stick of polymer. According to the standard, ASTM D 2863-83 (ASTM, 1977), LOI may be calculated using the following formula;

$$LOI = \frac{(O_2)}{(O_2)+(N_2)} \times 100\%$$

where (O_2) = volumetric flowing oxygen (mls^{-1}) and

(N_2) = " " nitrogen (mls^{-1}).

Although a limited amount of work has been published to date on this method for wood, it seems to offer a new approach to the testing of flammability. The results have been stated to be highly sensitive and when used in association with other tests which measure flame spread, etc. will allow complete characterisation of the properties of that material during combustion.

3.3 PHYSICAL STRUCTURE CHARACTERISATION

Perhaps the most fundamental instrument, particularly in polymer structural analysis is the optical microscope, which has played a very important role in the early work on wood structure. It can be used to study

the gross morphology and surface appearance of a wood, as well as for more basic structure of the woody cell wall, identification and observation of types of elements (cells) and their arrangement, inclusions in vessel elements, damage and imperfections, etc. The use of light microscopy for wood characterisation has been reviewed by Clark (1939). Direct microscopic examination, aided by staining reagents have proved to be suitable for developing structural features in wood. Its main limitation is its poor resolution.

More sophisticated physical structural analysis requires the use of a scanning electron microscope (SEM) which also permits examination of the finer morphology, sub-microscopic features as well as the ultimate chemical structure (Hale and Clermont, 1963; Desch, 1977).

3.4 THERMAL ANALYSIS AND ITS USE IN THE CHARACTERISATION OF WOOD

Thermal analysis comprises a group of techniques in which changes in physical or chemical properties of a substance is measured as a function of temperature while it is subjected to a controlled temperature program (ASTM, 1983). The introduction of modern thermal analytical instrumentation in the last thirty years has made thermal analysis a highly

sophisticated method which is used widely both in research and in production control in laboratories. The enormous development has been due to the possibilities for investigation of physical phenomena (i.e., melting, crystallisation, polymorphic transitions, etc.) and chemical reactions including decomposition and degradation. The various thermal methods commonly used in the evaluation of and in investigating the polymeric materials are shown in Table 3.2.

3.4.1 Differential Thermal Analysis (DTA)

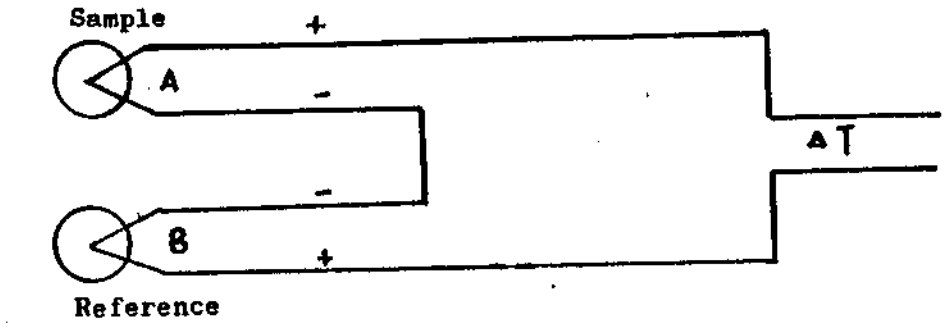
Differential thermal analysis (DTA) is a technique in which the temperature difference between a substance and a reference material is measured as a function of temperature while the substance and the reference material are subjected to a controlled temperature programme. This technique was first used by LeChatelier (1887) and Robert-Austin (1889) (Mackenzie, 1970; Wiedemann and Budolf, 1970). The resulting curve shows increase or decrease in the temperature# difference, from which information on enthalpy changes can be derived and from which it is possible to detect and measure any physical or chemical phenomena which are accompanied by heat change. Such a record indicates the occurrence of endothermic or exothermic reactions at various

Table 3.2. Classification of Thermal Analytical Techniques.

Physical parameter	Derived Technique	Abbreviation
Temperature	Differential thermal analysis	DTA
Energy	Differential scanning calorimetry.	DSC
Mass		TGA
	Thermogravimetry	EGD
	Evolved gas detection	EGA
	Evolved gas analysis	
Mechanical	Thermomechanical analysis	TMA
	Dynamic thermomechanical analysis.	DMA

temperatures. The principle of the measurement is shown in Fig.3.1a. Temperature is measured by registration of outputs from thermocouples situated in or below the sample and the reference. When the temperature of the sample is equal to the reference temperature, the net voltage output produced by the two thermocouples is zero. If an endothermic reaction takes place in the sample leading to a lag in the sample temperature

Fig. 3.1



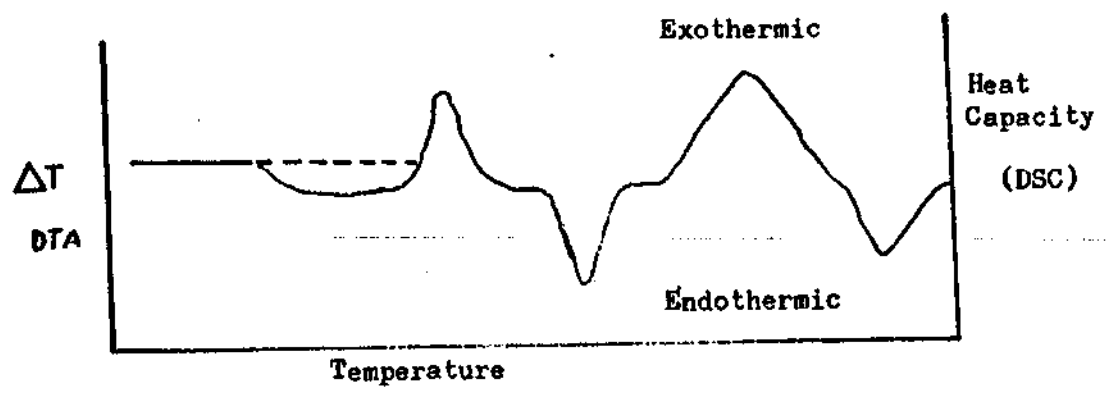


FIGURE 3.1: (a) Principle of DTA

(b) Schematic DTA/DSC curve

compared with the reference temperature, a corresponding temperature difference is measured. By analogy, an opposite temperature difference appears with exothermic effects. In other words. ΔT is usually expressed as (T_{sample} - $T_{reference}$), so exothermic peaks are positive and endothermic peaks are negative. In programmed temperature DTA, ΔT is usually plotted against T_{sample} (see Fig.3.1b).

In quantitative analysis, the measurement of heat is given by the area under the curve obtained by the integration between the beginning of the effect (t_1) and its end (t_2) according to the equation;

$$B = \int_{t1}^{t2} \Delta T dt = \Delta Q A$$

where A is a constant determined experimentally or calculated on the basis of the apparatus parameters. Different methods of integration can be used: planimetry, cutting and weighing, etc. or automation of data handling with an adequate calculatory system.

Differential thermal analysis method has been used by several authors (Sandermann and Augustin, 1963; Sergeeva and Vaivads, 1954; Arseneau, 1961; Keylworth and Christoph, 1960; Domansky and Rendois, 1962; Hienrich and Kaesche, 1962; Hirata and Abe, 1973), to follow the thermal

decomposition of wood, wood treated with inorganic salts, wood components such as cellulose, hemicellulose, and lignin, in air and in inert atmospheres. It has been shown that the behaviour of wood is a composite of the behaviour of its components (Arseneau, 1961; Domansky and Rendois, 1962). According to Havens et al. (1976), detailed comparison of the authors results is difficult since the investigations were made with different experimental conditions; wood types were different, sample preparation (drying particularly) was not always specified, heating rates varied from $1^{\circ}Cmin^{-1}$. to $16^{\circ}Cmin^{-1}$ and most importantly different purge gases used, including air, nitrogen, and hydrogen. However, certain similarities in the results do exist. Most of these investigators concluded that:-

(i) weight loss was small and the decomposition was endothermic up to a temperature of 250° (Ý $30^{\circ}C$), and results in the evolution of mixtures primarily composed of carbon dioxide, water vapour and acetic acid.

(ii) above $250^{\circ}C$, a wood specimen pyrolyses rapidly. If oxygen is present, the pyrolysis products may be oxidised in highly exothermic reactions and in an inert atmosphere exothermic peaks were absent;

(iii) above a temperature of about $400^{\circ}C$ (Ý $50^{\circ}C$) the samples appeared inactive.

3.4.2 Differential ScanningCalorimetry (DSC)

DTA and DSC are closely related because both monitor sample enthalpic changes relative to that of an inert reference material. As mentioned before, DTA shows the heat changes by measuring the temperature difference between a sample and a reference material as a function of temperature, while the sample and the reference material are subjected to a controlled temperature programme. DSC, on the other hand, instead of measurements being made of the temperature difference between two materials, the quantity measured is the heat needed to be supplied to or removed from the sample in order to keep its temperature equal to that of the reference material (see Fig.3.1b). Because the energy transferred is exactly equivalent in magnitude to the energy absorbed or evolved in the transition of the sample, the balancing energy yields a direct calorimetric measurement of the transition energy. Thus, in DSC the heat flux to the sample is measured of the transition energy. Thus in DSC the heat flux to the sample is measured (ASTM, 1983).

Heat flux, i.e. the transmitted thermal power, has the unit watt or milliwatt in the SI systems. Integration of the heat flux over time gives the heat consumption or the enthalpy change of a sample in mJ. DSC

measurements are usually performed with a dynamic temperature program to allow scanning of the temperature range of interest.

In so far as is ascertainable very little studies have been reported on the DSC techniques of wood previously. Woo and Schniewind (1987), have used dynamic DSC to evaluate the thermal degradation of three species - sugar pine, douglas fir and California black oak. They found that the DSC curves showed three more or less distinctive peaks indicating that thermal degradation reaction occur in 3 stages. Havens et al. (1976), have used DSC to estimate the energy capacity (which includes both sensible and decomposition heat effects) of dry pine and oak wood in an inert atmosphere (nitrogen). They found that the net internal heat effect due to decomposition is endothermic between 280°C and 500°C. Most investigators (Sandermann and Augustin, 1963; Sergeeva and Vaivads, 1954; Broido, 1966; Arseneau, 1961; Domansky and Rendois, 1962), using other techniques have estimated the internal primary heat effect due to decomposition of wood to be exothermic.

3.4.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is one of the thermal techniques used to determine general degradation characteristics and kinetic

parameters of materials under pyrolysis and combustion (Beall, 1969). It also gives information on the influence of additives and chemical modifications therein. The analysis includes a precise study of weight loss during programmed exposure to temperatures.

There are two common techniques:

(i) Isothermal thermogravimetry: In this case, the change in weight of the sample is recorded as a function of time at constant temperature at each of a series of temperatures.

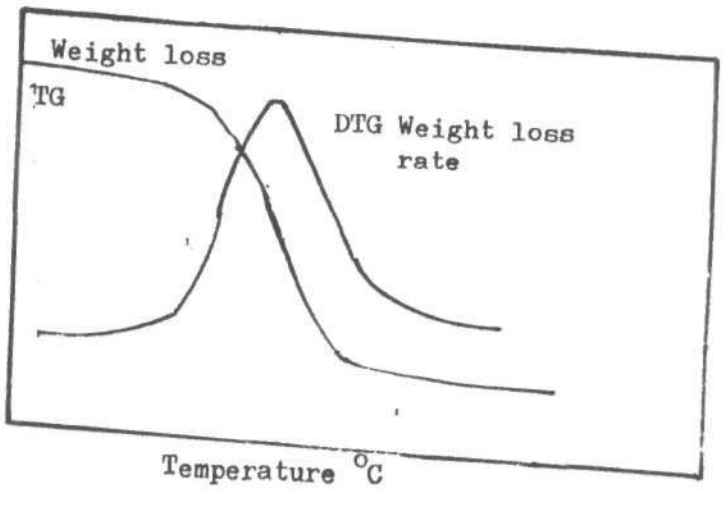
(ii) Dynamic thermogravimetry: The change in weight of the sample is recorded continuously and automatically as a function of both temperature and time as its temperature is raised at a given heating rate.

In the TG technique the sample (typically 1-10mg) is contained in a crucible, placed in a microbalance. The sample temperature and mass are monitored and recorded simultaneously. The first derivative of the mass change is also recorded as a DTG signal (derivative of the TG signal with respect to time, derivative thermogravimetry). Typical TG and DTG curves are as shown in Fig.3.2. The TG curve (Fig. 3.2a) follows a sigmoidal path depending for its shape upon reaction order, frequency factor, and the energy of activation. In some cases, the curve may involve two or more sigmoid

(Fig. 3.2b) with different inflection points, as a consequence of the differences in the reaction order or in the activation energy. The factors affecting the results of thermogravimetry have been widely analysed in the publications (Welker, 1976).

Research on the pyrolysis and combustion reactions of wood and its constituents have been made by thermogravimetric methods, both under conditions of stable temperature (isothermal TGA), (Sandermann and Augustin, 1963; Browne and Tang, 1962; Browne and Brenden, 1964; Eickner, 1962; McKnight, 1962; Tang, 1960), and also under dynamic conditions of steadily rising temperature (Browne and Tang, 1962; Tang and Neil, 1964; Tang, 1967; Eickner, 1962; Browne and Tang, 1963). The greater number of these experiments have been carried out in inert atmospheres (such as nitrogen or helium or in a vacuum). These authors found that TG curves show slow active degradation below 200°C and ascribed weight loss during this induction (initial) period mainly to loss of moisture content. Further loss in weight occurred 220-280°C and attributed to the loss of water, without definitely establishing whether this was desorption of sorbed water or removal of water of constitution. Practically, all of the weight loss (active pyrolysis-volatilisation of the wood) occurs between 250°C and 400°C, the total loss being 70 to 80% of the original

Figure 3.2



(a)

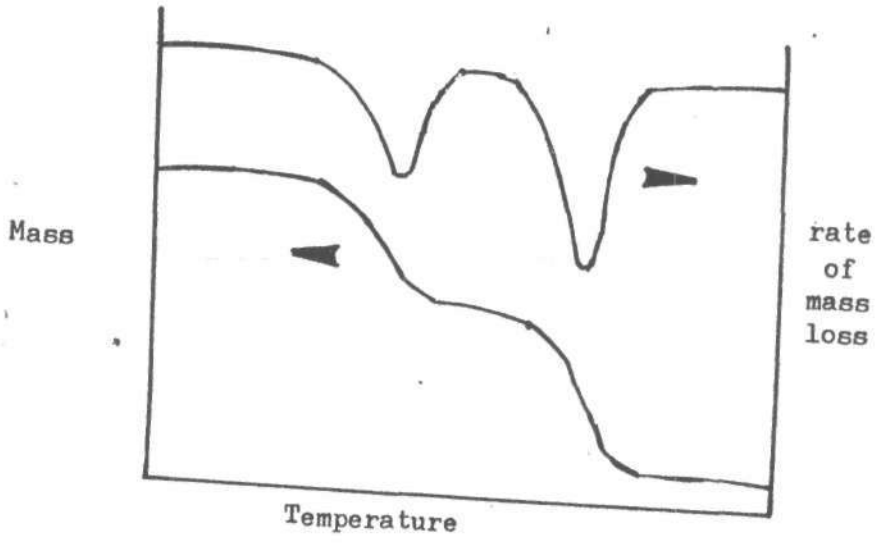


FIGURE 3.2: Typical TGA and DTG curves (a) one Sigmoidal (b) Two sigmoids

sample weight. In particular, the maximum rate of decomposition is equal to the rate of flammable volatile (glucosan) formation and seems to be an important criterion for the flammability of wood. Finally, they showed that glowing combustion of wood takes place in the temperature range 400-600°C. This was observed only in an oxidative atmosphere.

Studies of the behaviour of wood components individually and in combination approximating the composition of wood have shown that the thermal behaviour of wood is a composite of the behaviour of the individual components, and although their breakdown is not simultaneous there is little effect upon one another (Fang et al., 1966; Browne and Tang, 1962; Akita, 1959). For the major wood constituents, hemicellulose, cellulose and lignin, the breakdown temperatures are reported to be 200-260°C, 240 - 350°C and 280 - 500°C respectively.

Thermal analysis techniques have been applied to determine the effectiveness of various chemicals as fire retardants for wood (Fang et al., 1966; Browne and Tang, 1962, 1963; Tang and Neil, 1964; Hirata and Abe, 1973a, 1973b; Tang, 1967; Eickner, 1962). Thermogravimeric analysis curves from samples treated with various inorganic salts were basically similar in shape but revealed marked differences in the temperature of the onset of rapid pyrolysis and the amount of residue remaining at 400°C. The

threshold temperature and the apparent activation energy of the pyrolysis would be lowered, the residual char would be increase and the volatile products would be decreased in comparison with those of the untreated materials.

3.4.4 Kinetics Analysis of TGA Data

The kinetics of degradation can be analysed by means of TGA. Arrhenius kinetic parameters namely the frequency factor (or pre-exponential factor), activation energy and order of reaction may be calculated. Two approaches can be used (D'Souza, 1989): isothermal TGA, where mass loss with time is recorded at a constant temperature and dynamic TGA where mass loss curves are obtained by programmed heating. The dynamic technique is quicker in determining kinetic parameters, because kinetic analysis of the former data requires many experiments undertaken at a variety of temperatures. In addition isothermal experiments at low temperature may take considerable periods of time (days or weeks). Interpretation of dynamic TGA data, however, requires the use of theoretical approaches and mechanistic models in which simplifying assumptions have to be made. The values obtained depend upon the usual TGA parameters, and also on the particular mathematical model used.

Of the various techniques available (Freeman and Carrol, 1958; Anderson and Freeman, 1961; Freeman, 1964; Ozawa, 1965; Broido, 1969), the technique of Broido (1969), is of particular relevance to the pyrolysis study of wood as discussed later in section 4.3.6.

For any solid state decomposition reaction

$$aA_{(s)} \longrightarrow bB_{(s)} + cC_{(g)}, \qquad (3.1)$$

W_t, the weight at any time, t, is related to the fraction of the number of initial molecules not yet decomposed, y, by the equation

$$y = \frac{N}{N_O} = \frac{W_t - W_\infty}{W_O - W_\infty} \qquad (3.2)$$

and the reaction rate is given by

$$\frac{dy}{dt} = -ky^n \qquad (3.3)$$

at a constant temperature, where k is rate constant of decomposition and n is the reaction order.

The temperature dependence of equation (3.1) was assumed to follow the Arrhenius equation:

$$K = Ze^{-E/RT} \qquad (3.4)$$

where Z = pre-exponential factor, S^{-1}

E = apparent activation energy, J mol^{-1}

R = gas constant, J $molK^{-1}$

T - absolute temperature, K

Combining eqns. (3.3) and (3.4)

$$\frac{dy}{dt} = y^n e^{-E/RT} \qquad (3.5)$$

If $\beta = dT/dt$, the heating rate, then equation (3.5) may be

rearrange to give

$$dy/y^n = -(Z/\beta)e^{-E/RT}dT \qquad (3.6)$$

The TGA curve for such a reaction represents this last equation integrated from a temperature T at which y=1. Thus,

$$\int_y^1 dy/y^n = Z/\beta \int_{T_o}^{T} e^{-E/RT}dT \qquad (3.7)$$

Since most number of pyrolysis processes can be represented as first-order reactions, n=1, so that

$$\int_y^1 dy/y^n = \int_y^1 dy/y = -\ln y = \ln(1/y) \qquad (3.8)$$

Equation (3.7) becomes

$$\ln(1/y) = Z/\beta \int_{T_o}^{T} e^{-E/RT}dT \qquad (3.9)$$

Krenvelen et al. (1951), noting that almost the entire measurable reaction usually occurs within ±10% of T_m, the temperature of maximum reaction velocity, applied the following approximations to the right-hand part of eqn.(3.9):

$$e^{-E/RT} = (e^{-T_m/T})^{E/RT_M} \approx [(T/T_m)e^{-1}]^{E/RT_m} \qquad (3.10)$$

By integrating and taking logs of both sides of eq. (3.9), then one obtains

$$\ln\ln(1/y) = (E/RT_m + 1)\ln T + Const. \qquad (3.11)$$

Thus, a plot ln ln(1/y) vs ln T yields a straight line whose slope is related to the energy of activation.

Horowitz and Metzger (1963), introduced an alternate assumption that

$$e^{-E/RT} = (T_m/T)^2 e^{-E/RT} \qquad (3.12)$$

Therefore, eqn.(3.9) becomes

$$\ln(1/y) = Z/\beta(T_m/T)^2 \int_{T_o}^{T} e^{-E/RT} \qquad (3.13)$$

Integrating and taking logs, we have

$$\begin{aligned} \ln\ln(1/y) &= -(E/R)(1/T) + \text{constant} \\ &= -(E/R)(1/T) + \ln(ZR/\beta E.T_m^2) \end{aligned} \qquad (3.14)$$

For the pyrolysis of cellulose, this is the most accurate equation of the many integrated equations obtained by Broido (1969). The plot of ln ln(1/y) versus 1/T provides a straight line. The slope and intercept of the plot give the values of E, and Z, respectively.

Most of the thermal gravimetric studies of wood decomposition have been attempts to correlate thermal decomposition weight loss data by

determining the activation energy E, and frequency factor, Z, assuming the reaction order to be unity (i.e.n=1). Tang (1960), Stamm (1956), include data of Mclean (1951), and Akita (1959), reported activation energies and frequency factors obtained using isothermal gravimetric techniques. Hirata and Abe (1973b), and Tang (1976), reported activation energies and frequency factors for wood obtained using dynamic TGA. In summary, reported values of the activation energy for first order thermal decomposition of wood range from 23 to 54 Kcal/g .mol and frequency factors range from 3.3×10^5 to $6.53 \times 10^{16} sec^{-1}$. With salt-treated wood they obtained values from 24.7 to 34.8 kal/g mol.

CHAPTER FOUR

EXPERIMENTAL STRATEGY AND TECHNIQUES

4.1 MATERIALS

4.1.1 Wood Samples

According to Lauer (1958), in experiments with mixtures of tropical wood the most difficult task is the selection of species as well as their ratio, which should correspond approximately to actual conditions in a certain geographical area. The number of species, the differences owing to age, location, and unknown factors are excessive and provide great difficulty for systematic studies to be designed and undertaken. It was practically impossible therefore to have proper sampling and representative for the species so that the choice of species and the quantitative composition of mixtures used in this study are arbitrary, but made in collaboration with forestry experts at the spot. The hardwoods comprise heartwood and were chosen primarily because of their current and potential applicability to different end-uses. For the most part, little or nothing of the material is available, only the generic classifications and characteristics were known. Where greater detail of the materials is available, this is indicated in the results section. That the materials are all hardwoods is

for the simple fact that these are more commonly used for construction and for interior finishes than softwoods. The fourteen varieties of wood obtained from the African Timber and Plywood (AT & P) company in Sapele, Nigeria, are listed in Table 4.1. The characteristics and uses of the wood species have been fully described elsewhere (Bolza and Keating, 1972).

4.1.2 Flame Retardant Chemicals

The local flame retardants - potassium aluminium sulphate and calcium super-phosphate otherwise known as 'alum' and 'fertiliser' respectively were obtained from the National Superphosphate Fertiliser Company in Kaduna, Nigeria. They were used during flammability parameters measurement.

The flame-retardant chemicals selected from commercial products supplied by manufacturers were obtained from Bolton Institute, Bolton, England, and were used for LOI, DTA and TG/DTG runs. These include diammonium hydrogen phosphate (DAP), sodium borate (borax) and boric acid in a ratio of 1:1 by weight(B:B), diammonium hydrogen phosphate and borax combination in a ratio of 1:1 (DAP:B) and aluminium potassium sulphate (potassium alum) - (ALUM). Some of them have been recognised as good flame-retardants for wood. The mechanism of their effects are thought to be different from one another. The details of the flame retardants are shown in

Table 4.2.

TABLE 4.1. List of Timbers.

Botanical names	Trade/common names
Afzelia	Apa
Chlorophora excelsa	Iroko
Distemonanthus benthaminaus	Ayan
Entandrophragma cylindricum	Sapele
Guarea cedrata	Guarea
Isoberlina doka	Berlinia
Khaya ivorensis	Lagos
Lovoa trichiloides	African walnut
Mansonia altissima	Mansonia
Nauclea diderrichi	Opepe
Nesogordonia paparerifera	Danta
Piptadeniastrum africanum	Ekhimi
Terminalia superba	White afara
Triplochiton scleroxylon	Obeche

Table 4.2. The details of the flame retardants used

Flame retardants	Principal flame retardant elements
Local alum - assays - moisture 8.72%, insoluble matters 0.25%, Al_2O_3 16.56% and Ph 5% solution	K,Al,S
Single superphosphate fertiliser - assays moisture -3.28%, total phosphate ($T.P_2O_5$)- 23.40%, water soluble phosphate ($W.P_2O_5$)- 16.18% and free phosphoric acid ($F.P_2O_5$)- 0.41%.	Organic P
Diammonium hydrogen phosphate (DAP) $(NH_4)_2HPO_4$,(BDH GPR) reactive functionality - P - 0H, % active ingredient 100%, analysis of active components 23% P, 21% N, product name - generic.	P and N
Sodium tetraborate - $Na_2B_4O_7$ $10H_2O$ (BDH) reactive functionality B - OH, % active ingredient 100%, analysis of active component 37% B_2O_3, product name - borax.	B and Na
Boric acid - H_3BO_3 (BDH GPR)	B
Aluminium potassium sulphate (potassium alum - AIK $(SO_4)_2$.12 H_2O, minimum assay (ex AI) 99%.	K, S

4.2 SAMPLE PREPARATION

4.2.1 Samples Used for Measurement of Flammability Parameters

Specimens samples were first cut oversize and after air-dried for several weeks, they were cut and machined into splints of dimension 150 x 15 x 10mm. They were dried in the oven for 6-8 hrs. at 120±3°C until each sample reached equilibrium weight. After drying, the specimens were stored in conditioned room under controlled temperature and humidity conditions of 26°C and 70% (RH), to await testing. Ten specimens for each test per wood were used.

The treated samples were prepared by soaking five conditioned specimens of each wood in solutions of 10% alum and fertiliser respectively made in 500ml beakers for 48 hrs at room temperature (28°C) and air dried. Subsequently, they were dried in an oven at 60°C for 4hrs and then were kept in conditioned room at 26°C, 72% RH before the experiment.

To examine the effect of additive concentrations as well as their presence (amount) separate treatments were done with 7.5%, 15% and 20% alum and fertiliser concentrations.

4.2.2 Samples Used for LOI Tests

Test specimens were prepared from the air-dried samples as in section 4.2.1 above and were cut into strips of 100x6x3mm and conditioned at 20°C and 65% RH for 72hrs at Bolton Institute in Bolton, England.

For LOI experiments, the air-dried specimens were soaked in 5%, 10%, 15%, and 20% flame retardant solutions, heated for 1 hr at 80°C and remained soaked for two days at room temperature and then washed with tap water. The samples were air dried at room temperature and then oven dried at 40°C for 2 hrs and stored in the condition-room at 20°C and 65% RH for three days. The quantity of salt retained by the wood was calculated as the difference between the weights before and after treatment. Thereafter they were stored in nylon bags to minimise thermal exposure and attendant degradation. It is assumed that changes in physical and chemical composition would be negligible under these conditions of storage.

4.2.3 Samples Used for TG, DTA and DSC

The wood samples used for TGA, DTA and DSC analyses were sawdust from the wood. Samples were conditioned at 20°C and 65% RH. Those to be impregnated with a salt were soaked in solutions of concentrations 5%, 10% and 15% to provide the desired degree of treatment, boiled for 1hr and left

soaked at room temperature for approximately 48hrs. The sawdust is filtered, air dried, oven dried at 40°C and then conditioned at 20°C and 65% RH.

4.3 PROCEDURE

4.3.1 Measurement of Flammability Parameters

(i) Ignition and Burning Parameters:- A splint was clamped vertically on its upper end and ignited at the base with a cigarette lighter. As soon as the sample ignited the lighter was withdrawn. The ignition time was estimated by noting the time (seconds) between when the ignition flame was applied and removed after the specimen is lighted. The distance traversed by the char front was timed. Flame propagation rate was calculated using the equation

$$\text{Flame propagation rate} = \frac{\text{Distance moved by char front}}{\text{Time } (s)} \qquad (4.1)$$

Afterglow time was obtained by noting the time in second between the flame out and the last visually perceptible glow.

(ii) Orientation;- In the determination of flame propagation rate, two sets of experiments were performed on each wood type, viz., the vertical and horizontal orientations.

(iii) Density:- Density is identified as one of the factors that affect the burning of wood. The oven dry density was determined for each wood using the relation

$$\text{Density (gm/cm}^3\text{)} = \frac{\text{Oven – dry weight of sample (gm)}}{\text{Volume of sample at test (cm}^3\text{)}} \qquad (4.2)$$

(iv) Moisture content:- Moisture contents of each wood was determined as the percentage of mass of water per unit mass of oven-dry wood:

$$\text{Moisture content (\%)} = \frac{W_i - W_o}{W_o} \times 100 \qquad (4.3)$$

where W_i= conditioned weight of sample and W_o= oven-dry weight of the sample

4.3.2 Thermogravimetric Analysis (TGA)

Two different apparatus for the TGA/DTG tests were used. They are the Metler TA 3000/TG50 and Stanton Redcroft TG 760. The Metler TA3000/TG was used to analyse the thermal reaction of the original 'native' woods in Sokoto. Small shavings of each wood (6-10mg) were placed in the furnace of the metler under static air atmosphere and heated at the rate 10Kmin^{-1}. By means of a computer incorporated into the analyser, onset-, peak- and end- temperatures of pyrolysis/combustion were obtained. In addition, stepwise decomposition profiles, the kinetic data and the char yield of the timbers were obtained.

The Stanton Redcroft TG 760 interfaced to a 9900 computer thermal analyser and plotter was used to analyse the thermal reaction of the wood sawdust in the presence and absence of flame retardants. Approximately 5mg samples were analysed in static air under the linear programmed temperature condition (from ambient to 700°C) and the heating rate was $10kmin^{-1}$. For ease of cleaning a platinum crucible was used. Selected samples were tested for effect of heating rates.

4.3.3 Differential Thermal Analysis (DTA)

The DTA thermograms were obtained using the Stanton Redcroft 671B instrument. 5mg untreated and treated samples were analysed in static air at a heating rate of $10kmin.^{-1}$ The reference material was 5mg aluminium oxide.

4.3.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was carried out on untreated wood sawdust samples using a DuPont 910/DSC cell interfaced to a 9900 computer Thermal Analyser and plotter. The samples were prepared as with TG or DTA.

The instrument monitored the differential heat flow to the sample and reference and then the appropriate transition enthalpy ΔH was measured by integration on a time-base thermograph. The instrument was calibrated for

temperature and enthalpy response according to the melting point and heat of fusion of pure indium. The sample mass was 4mg packed into an aluminium crucible, and heated from ambient to 475°C at heating rate 10kmin^{-1} under static air. An empty aluminium pan was used as reference.

4.3.5 Limiting Oxygen Index (LOI)

The LOI values of all untreated and flame retardant samples, 100x6x3mm in size, were determined using the Stanton Redcroft FTA (flammability Tester apparatus) which has been produced in accordance with ASTM D2863-1977 (ASTM, 1977) and BS 2782: 1986 (BSI, 1982). Employing a butane burner flame the sample was ignited at the top and so-called candle-like burning was just sustained. The LOI value is obtained directly from the digital read out of the paramagnetic oxygen analyser which measures nitrogen-oxygen atmosphere concentration (volume %) flowing through the combustion chamber.

A simplified procedure for the determination of LOI at room temperature conditions can be summarised as follows:-

(i) After setting up the LOI equipment ready for use, a conditioned wood specimen is mounted in the sample holder, which is then positioned in the burning chamber, and the chimney placed over it, and the system is then purged with mixed gas for 30 seconds. The butane gas burner is lit and held at

the top of the specimen in order to ignite it. The height of the flame used during testing was within the limits of 12-25mm. The flame is held in contact until the specimen ignites (as yet there is no specified ignition time for wood) and the ignition time noted.

(ii) If the specimen burns for at least 3 mins. the concentration of oxygen is too high and must be reduced. The procedure is repeated until an oxygen concentration is reached at which the combustion is barely sustained. Conversely, if the flame, extinguishes before reaching the 3 mins. the concentration of oxygen is too low and must be increased until specimen is ignited and so called candle-like burning is just attained.

(iii) Either procedure is repeated until the LOI is determined (i.e., the concentration of oxygen which if reduced by 0.1% causes the burning to cease before 3 min). Once found the LOI should be repeated at least 3 times with successive determinations approaching the LOI from opposite levels of oxygen concentration, i.e. by alternatively increasing and decreasing the concentration of oxygen.

4.3.6 Calculation of Kinetic Parameters

Analyses of the kinetics of pyrolysis is done from TG results obtained from the Mettler TA3000/TG 50 under static air atmosphere.

Of the various techniques available as described in section 3.4.4, the Broido (1969), method is preferred because there is no need to make an assumption about the order of reaction and the equation

$$\ln(\ln[(1/y)]) = -\frac{E_a}{RT}\ln\frac{RZ}{E_a\beta}\cdot T_p^2 \qquad (4.4)$$

is used to calculate E_a. β is the heating rate ($10 kmin^{-1}$). T is the absolute temperature in Kelvin. T_P is the DTG peak temperature for a given decomposition stage. R is the gas constant, namely 8.3136 J/mol K and y is the mass fraction left up to temperature T, i.e. $y = (m - m_1)/m_2$ where m is the initial mass, m_1 is the mass loss up to temperature T and m_2 is the mass loss at the completion of the reaction.

After the activation energy has been calculated, the frequency factor, Z, can be calculated by using the method of Murray and White (Cabradilla and Zeronian, 1976) according to

$$Z = E_a e^{E_a/RT_p}/RT_p^2 \qquad (4.5)$$

Plots of ln (ln 1/y) against 1/T should result in a straight line yielding a slope of $-E_a/R$ and an intercept corresponding to

$$\ln\left(\frac{RZ}{E_a}\cdot T_p^2\right) \qquad (4.6)$$

Although the validity of the Broido method has been questioned (Cooney et al., 1983), the often preferred methods of Ozawa (1965), or ASTM E6 98 and similar methodologies (Freeman, 1964; Cooney et al., 1983; Kissinger, 1957), have not been used because of the anticipated decomposition mechanistic

dependence on heating rate. Furthermore, the Broido method enables more rapid analysis of a multistage decomposition to be undertaken.

4.3.7 Scanning Electron Microscopy (SEM)

SEM observations were made on untreated selected wood using PSEM - 500 Model, a Phillip-Holland scanning electron microscope operated at 20KV electron beam and 20A emission current. In order to develop surface detail and potential sites of degradation, samples were split across the grain with a knife edge. The samples surface to be examined were then mounted on metal stubs with adhesive tape and were coated with layer of gold to reduce the build up of electrostatic charge, prior to their examination. Electron micrographs of the samples were obtained from University of Aberdeen, Glasgow.

CHAPTER FIVE

RESULTS AND DISCUSSIONS (1): THERMAL AND BURNING BEHAVIOUR OF WOOD

5.1 INTRODUCTION

As mentioned before, the burning of a solid is essentially a three-stage process consisting of a heating phase, a thermal pyrolysis stage, and ignition/burning. The application of the heat source, such as a flame to a solid object, first raises the temperature adjacent to the source at some rate dependent upon the relative flux and temperature of the flame. Although thermoplastic polymers will melt and flow during this early heating stage, thermoset polymers and most natural products, such as wood, remain essentially unchanged (Hindersinn and Witschard, 1978).

At some later stage in the heating process, a pyrolytic decomposition occurs with the evlution of gaseous products whose flammability will depend upon the chemical composition of the original sample. The temperature and rate at which this stage occurs depend upon thermal stability of the material and the chemical decomposition reactions occurring under the existing conditions. With increasing higher temperatures, the rate of production of the gaseous degradation products increases until a mixture is

reached with the oxygen in the air that exceeds the flammability limits and ignition occurs. Continued burning at this stage is dependent upon the transfer of sufficient heat from the flame to the condensed phase to maintain an adequate supply of flammable gaseous decomposition products and upon a supply of oxygen from the surrounding atmosphere sufficient to support combustion (Hindersinn and Witschard, 1978; Essenhigh and Howard, 1966).

5.2 DETERMINATION OF THE BURNING PARAMETERS

The burning parameters such as ignition, burning rate, afterglow, etc, have been studied. Physical properties such as density, moisture content and sample orientation were examined in order to determined their effects on the burning characteristics. The values for these parameters vary between the selected hardwoods and the results show that they influence thermal properties to a degree.

5.2.1 Ignition and Burning Behaviour

The test data obtained for the fourteen woods listed in Table 4.1 are reported in Table 5.1. From the results, it is shown that the timbers may be ranked differently depending upon which of the parameters is considered and no simple correlation of the three parameters exists. Furthermore the fourteen timber species differ markedly in performance as far as their

TABLE 5.1. Ignition and Burning Properties.

Specimen	Ignition time (sec)	Flame spread rate (mm/s)	Afterglow (sec)
Apa	10	1.8	49
Iroko	9	2.0	652
Ayan	7	2.1	160
Sapele	9	1.4	133
Guarea	6	1.9	65
Berlinia	8	1.6	29
Lagos	6	2.4	274
Walnut	6	1.9	46
Mansonia	6	2.7	185
Opepe	9	2.1	0.6
Danta	10	1.9	148
Ekhimi	5	2.3	94
Afara	5	2.5	328
Obeche	3	2.4	408

flammability properties are concerned. The heartwood of some species e.g. Danta (Nesogordia paparifa) or Apa (Afzelia) will resist about 10 second flame application before ignition takes place, other species would need flame retardant treatment if resistance to immediate ignition is to be avoided, e.g. Obeche (Triplochiton scleroxylon). Even greater differences are seen with regard to afterglow tendencies from 0pepe (0.6s) to Iroko (652s). Using a simple match test method, workers in Switzerland and Israel (Israel Standard, 1969) noted similar variations among wood specimens and they were classified accordingly. Other flammability test methods (Lewin and Sello, 1975) have been used but it is difficult to compare results because for any given test method there is considerable variability because of the differences in apparatus, specimen size and position, time of exposure to flame or radiation and the general sample flammability characteristic tested.

In this study, under constant ignition and environmental conditions the principal factors affecting the flammability processes include the variation in the composition of the substrate ranging from different types of wood to different types of natural plant fibres/cells, and the effect of these on the phenomena of heat and mass transfer. In addition to these factors trace amounts of inorganic impurities or contamination could account for some of the observed differences (ASTM, 1993).

The appropriate expression for the combined effects of major parameters on flammability is given by the relationship (Saito, 1985):

$$t_{ig} = \frac{4}{\pi} k\rho c \left[\frac{T_{ig} - T_a}{q_{net}} \right]^2 \qquad (5.1)$$

where t_{ig} is the ignition time, T_{ig} is surface temperature at ignition, T_a is ambient temperature and q_{net} is net heat flux to the surface. The product *kpc* is the thermal inertia and so is directly proportional to t_{ig}. Considering the net flux q_{net} over a length l, then the spread rate is

$$v = \frac{4}{\pi} \left(\frac{q_{net}}{T_{ig} - T_a} \right)^2 \frac{1}{k\rho c} \qquad (5.2)$$

Therefore, if the flame spread rate, v is largely influenced by the thermal inertia of a given timber then it might be anticipated that an inverse relationship between t_{ig} and v might ensue. The plot in Fig 5.1. shows that for the materials tested there is a general linear relationship between v and $1/t_{ig}$ as expected from the relationship and assumption above.

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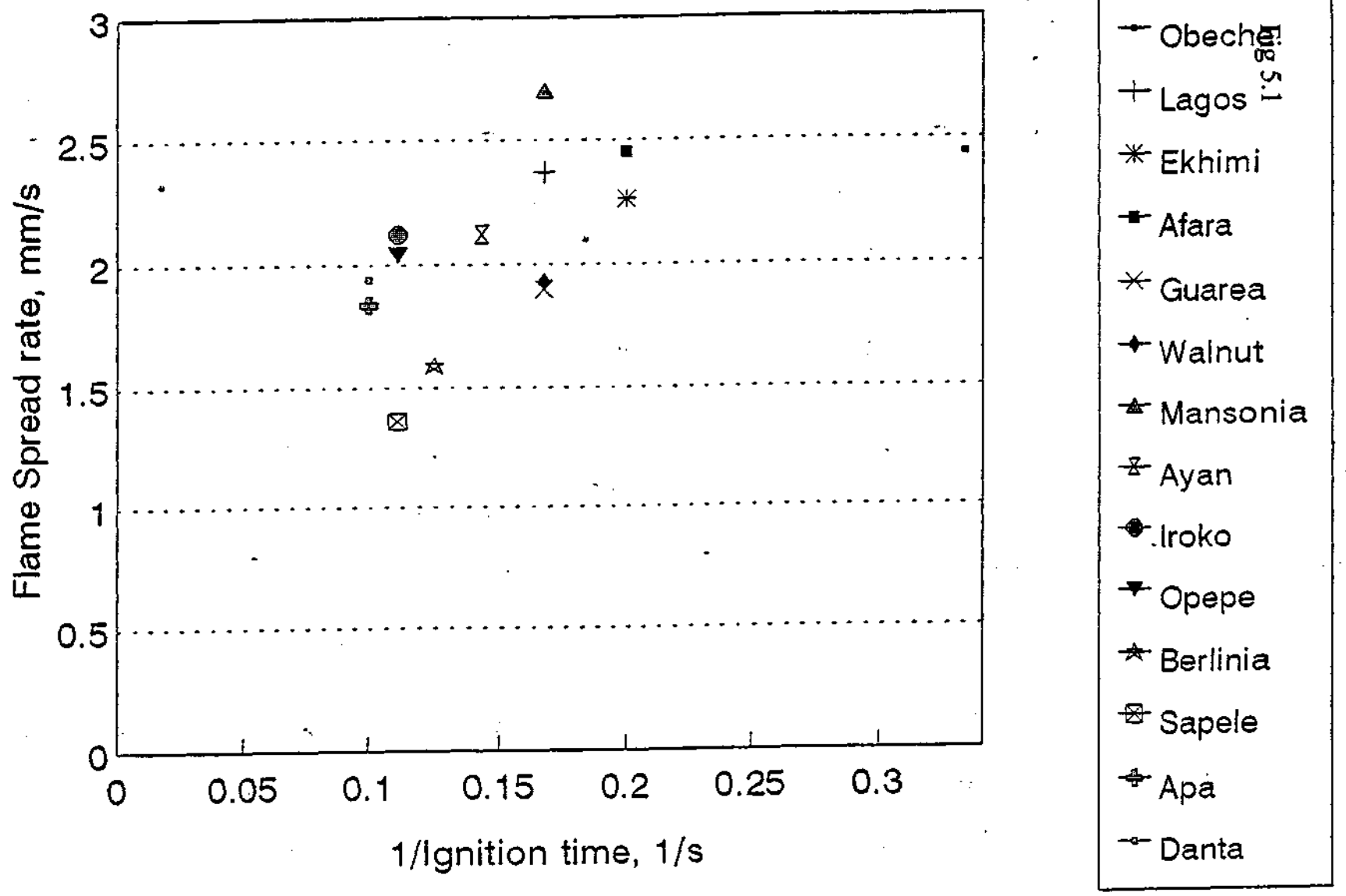


Fig 5.1

FIGURE 5.1: Mean flame spread rate versus reciprocal ignition time.

5.2.2 Effect of Orientation on Flame Spread

The average flame propagation rates in both horizontal and vertical orientations are shown in Fig 5.2. In all cases, flame propagation in the vertical orientation is higher than that of the horizontal orientation.

This can be explained from the fact that in the horizontal orientation, the flame forms a thin rod-like flame so that most of the heat is dissipated above the upper surface of the sample while in the vertical direction, the flame assumes a cylindrical shape around the vertical sample so that the flame volume is much greater resulting in more heat produced due to the effect of the flame flux, thereby increasing the rate of flame spread.

5.2.3 Effect of Density

The oven-dry densities determined for the 14 wood samples are shown in Table 5.2. and the effect of density on ignition time and burning rate is shown in Figs 5.3. and 5.4. In general, the results show an increase in ignition time and decrease in burning rate with increasing density. Some specimens, however, have different ignition time and/or flame rate values at similar densities. The reasons for this could be due to effects of morphological difference such as chemical composition, void volume within the cell walls, earlywood: latewood ratios and resin contents.

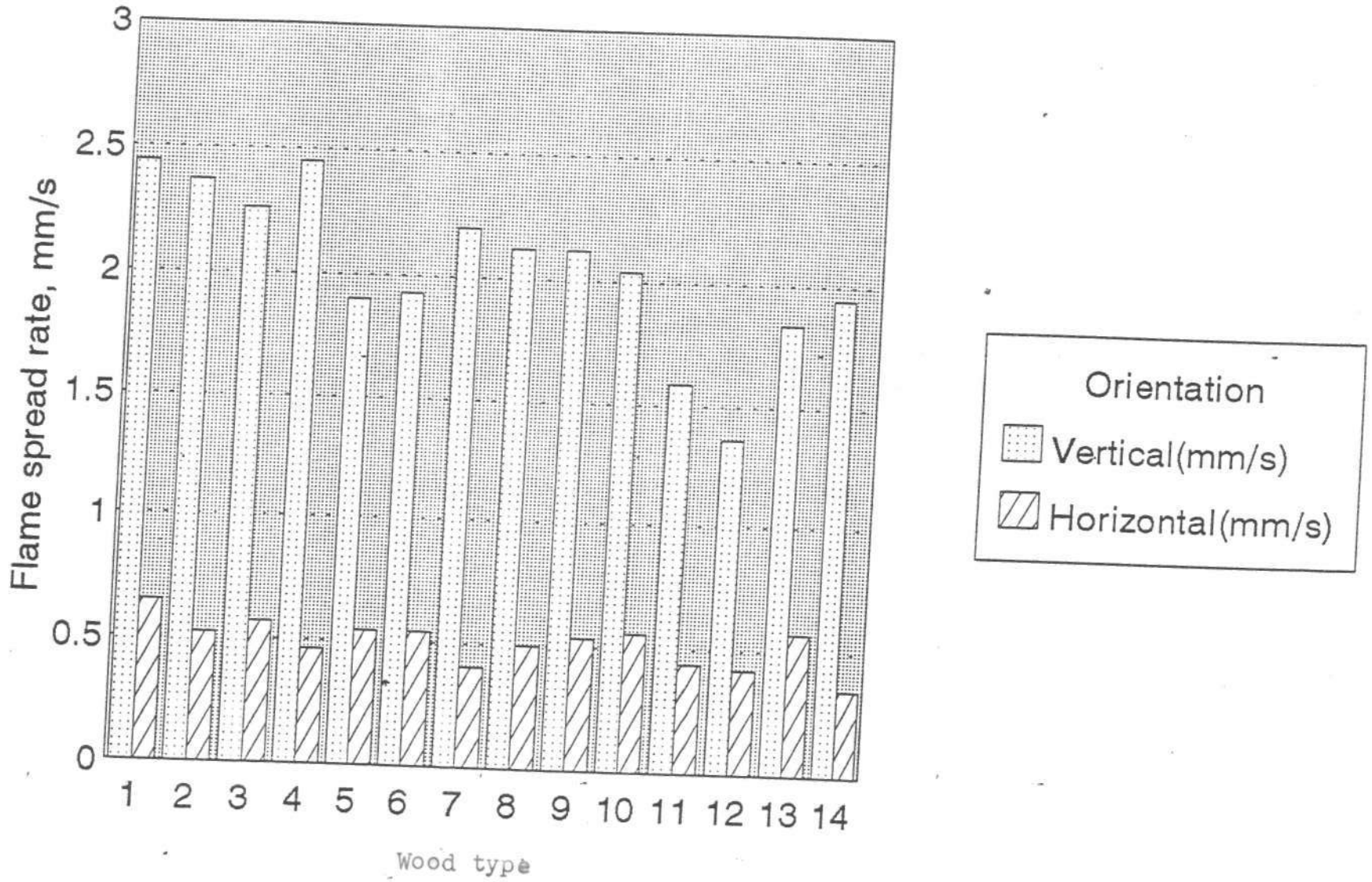


FIGURE: 5.2: Effect of sample orientation on burning behaviour, figure key 1 = Obeche 2 = Lagos, 3 = Ekhimi, 4 = Afara, 5 = Guarea, 6 = Walnut, 7 = Mansonia, 8 = Ayan, 9 = Opepe, 10 = Iroko, 11 = Berlinia, 12 = Sapele, 13 = Apa, 14 = Danta.

Table 5.2 Woods used and Respective Densities

Botanical names	Trade/common names	Density (gcm^{-1})
Afzelia	Apa	0.715
Chlorophora cxelsa	Iroko	0.675
Distemonathus benthaminaus	Ayan	0.636
Enthandrophragma cylindricum	Sapele	0.714
Guaera cedrata	Guaera	0.556
Isoberlinia doka	Berlinia	0.712
Khaya ivorensis	Lagos	0.445
Lovoa trichiliodes	African Walnut	0.583
Mansonia altissima	Mansonia	0.612
Nauclea diderrichi	Opepe	0.691
Nesogordonia Paparerifera	Danta	0.801
Piptadeniastrum africanum	Ekhimi	0.495
Terminalia superba	White afara	0.544
Triplochiton scelroxylon	Obeche	0.313

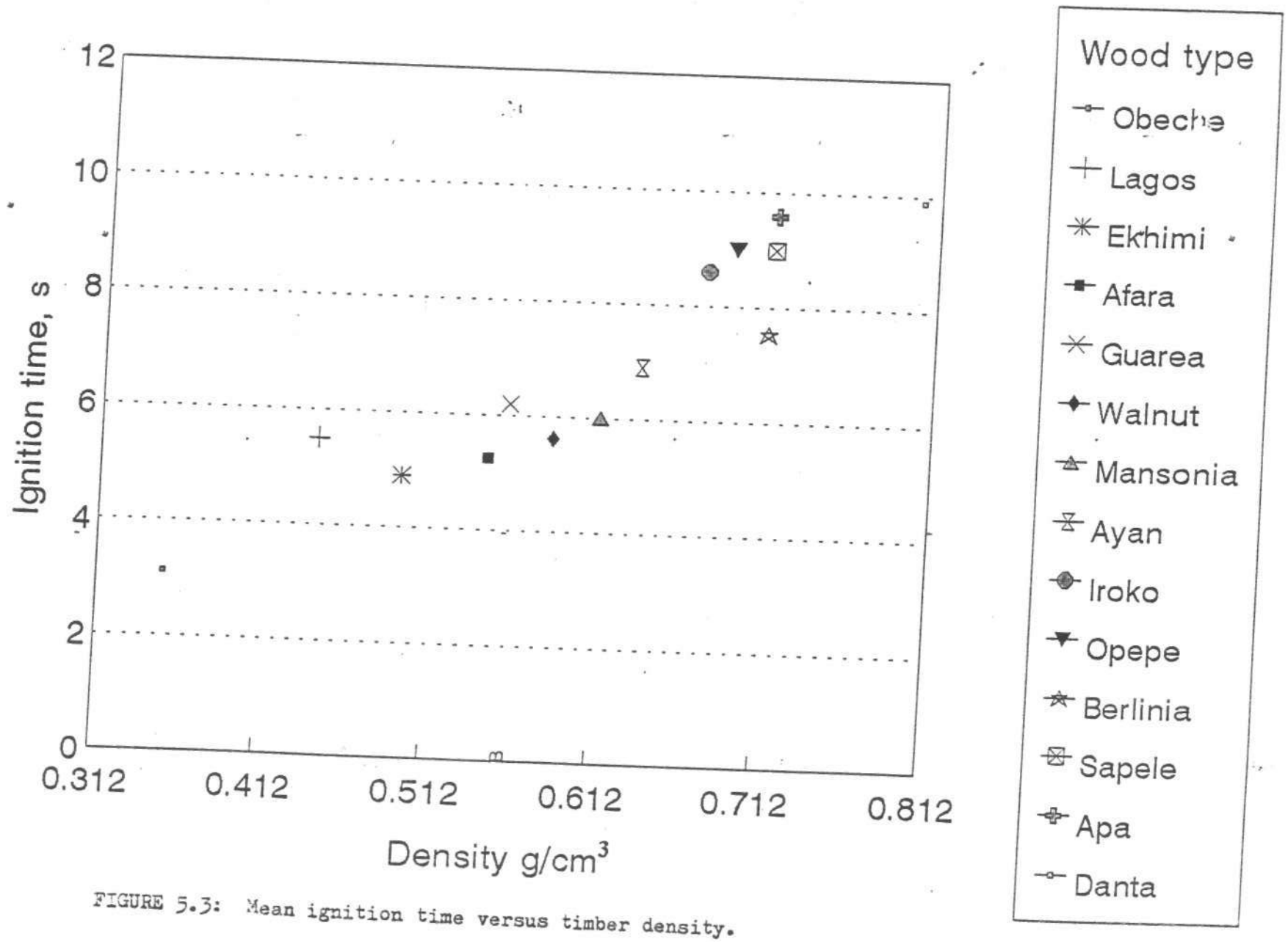


FIGURE 5.3: Mean ignition time versus timber density.

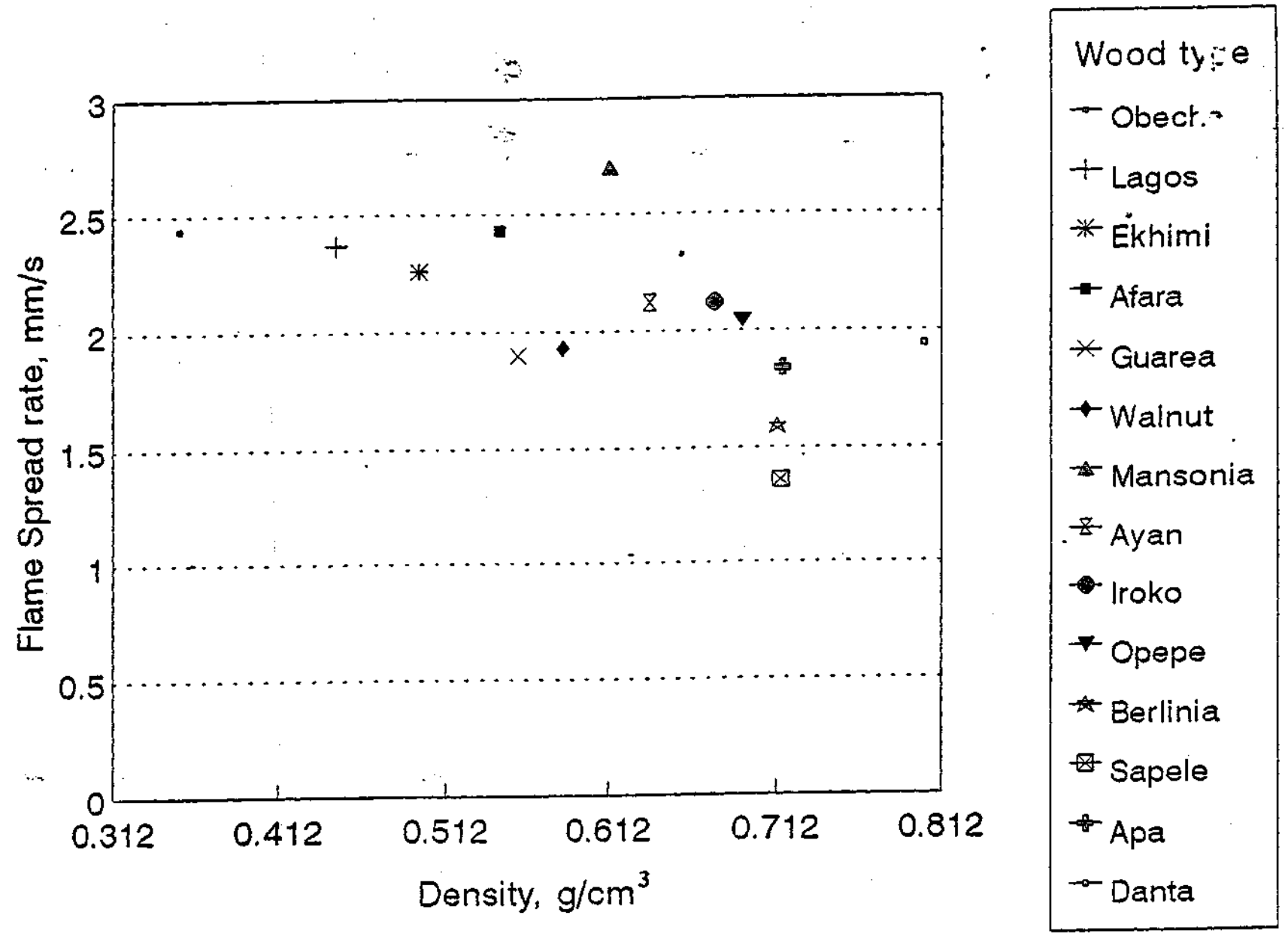


FIGURE 5.4: Mean flame spread rate versus timber density.

According to Panshin and de Zeeuw (1980), dense heavy hardwoods are more resistant to burning than highly resinous softwoods. In the present investigation, all the woods studied are hardwoods and in this respect, the results are in accord with this earlier observation. Low density woods theoretically burn more rapidly than denser woods because their high insulation value (as internal voids) reduces the heat loss from the burning zone, resulting in higher surface temperatures. This effect, often referred to as thermal inertia, is related to the product of thermal conductivity, specific gravity and thermal capacity, kpc (Thomas and Bullen, 1979).

Closer examination of Fig 5.4. suggests that once a certain oven-dry timber density is attained (above 0.6gcm^{-3}), then flame spread rate changes independently. This is difficult to explain, as it is expected that other factors such as the cellular nature of the wood, thermal conductivity, etc., are not likely to be exactly the same for all the timbers. Furthermore, the measurement technique for density cannot be said to be perfect; any procedure for wood density based on measuring weight and volume can be considered accurate only if the wood sample has been first extracted with suitable organic solvents to remove extraneous resins, oils, gums, fats, etc., (Parham and Gray, 1984; Taras and Saucier, 1967). These materials thicken cell walls, block potential sites for water adsorption and absorption, alter

potential wood swelling and shrinkage properties and thereby interfere with the accurate characterisation of wood tissue.

The plot of afterglow versus density is observed in Fig.5.5. where no obvious trend is seen. This is perhaps to be expected because afterglow depends largely on char structure whose density and composition we do not known; the presence of trace metal ions are important in this respect (see section 5.3.3), however.

5.2.4 Effect of Moisture Content

The effect of moisture on times-to-ignition and flame spread rates of conditioned and oven-dry woods are shown in Table 5.3. As expected, the data show that ignition times of conditioned woods are generally higher than those of corresponding oven-dry wood while the respective flame spread rates for conditioned woods are lower than those of oven-dry woods, except, in the case of Sapele (Entandrophragma cylindricum). Pyrolysis and ignition behaviours of materials are well known to be influenced by moisture and the result is typically associated with cellulosic materials (Fons, 1950; Martin et al., 1966; Schaeffer, 1967; Simms and Law, 1967; Williams, 1953). The difference arises from the fact that more time and heat will be required to vaporise the water content trapped in the conditioned woods. The case of Sapele cannot be explained and perhaps some further work is needed to understand its apparently

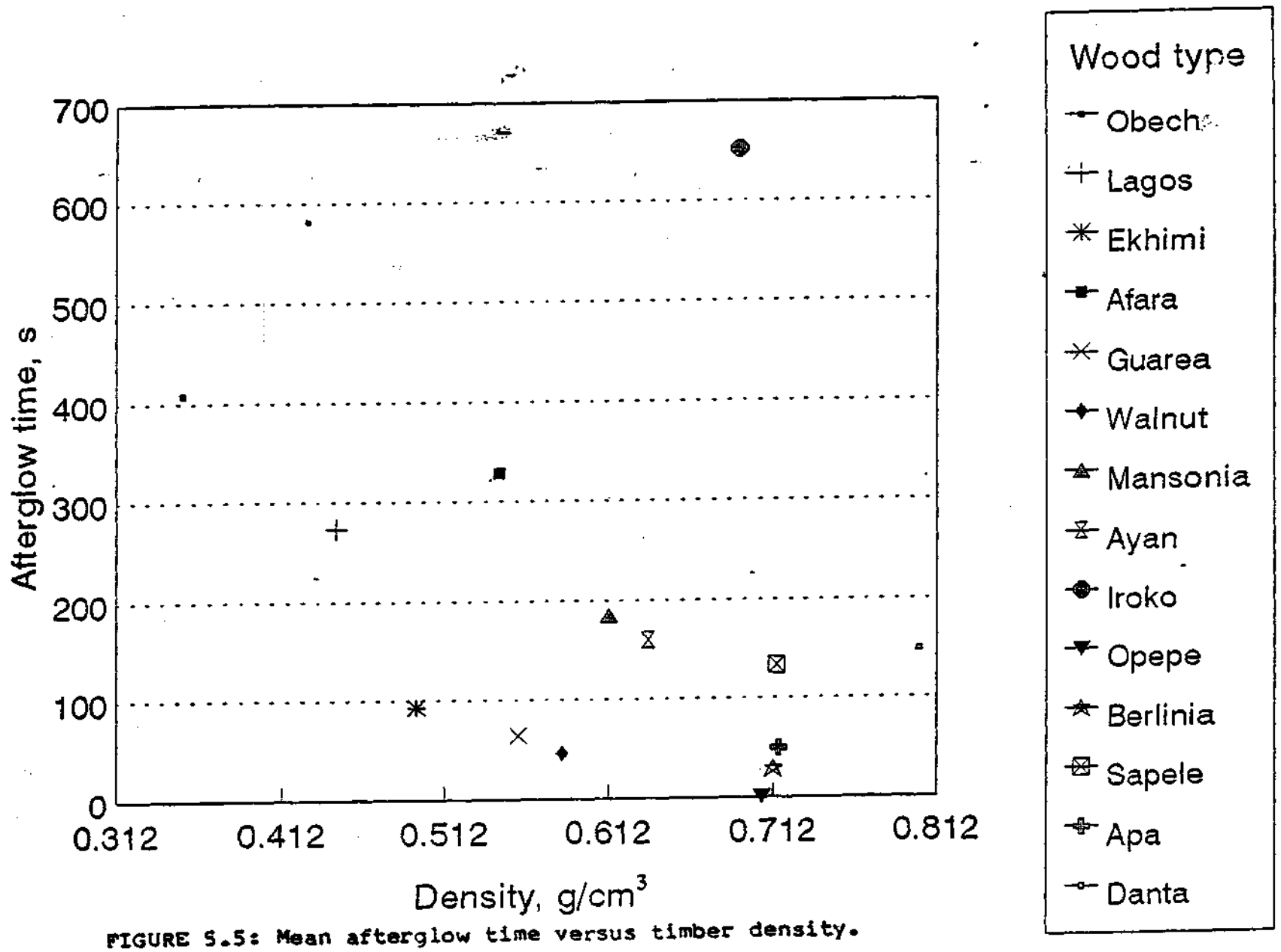


FIGURE 5.5: Mean afterglow time versus timber density.

Table 5.3. Average Ignition Times and Flame Spread Rates of Conditioned and Oven-dry Hardwoods.

Material	Ignition Time		Flame Spread Rate	
	Condition t_c (sec)	Oven-dry t_d (sec)	Condition v_c (mms^{-1})	Oven-dry v_d (mms^{-1})
Obeche	5.1	3.1	2.1	2.4
Lagos	7.4	5.5	2.3	2.4
Ekhimi	5.5	4.9	2.2	2.3
White Afara	6.2	5.2	2.4	2.6
Guarea	6.6	6.2	1.6	1.9
Walnut	6.2	5.6	1.7	1.9
Mansonia	8.2	6.0	2.0	2.7
Ayan	7.0	6.0	1.8	2.1
Opepe	8.2	1.2	1.9	2.1
Iroko	8.9	8.6	1.8	2.0
Berlinia	9.3	7.5	1.5	1.6
Sapele	10.0	9.0	1.6	1.4
Apa	9.6	9.6	1.7	1.8
Danta	10.6	9.9	1.8	1.9

anomalous thermal behaviour although error in determination may be a cause.

5.3 THERMAL BEHAVIOUR OF WOOD

It is generally accepted that during burning polymeric materials will first undergo some chemical reactions in the solid phase, then produce gaseous fuel which enters the flame zone, and leave residue in the solid phase. Therefore, the pyrolysis behaviour of the polymers will reflect those reactions taking place in the solid phase of polymers during combustion. Thus, characterising the pyrolysis process of wood will provide a knowledge of solid phase reactions for understanding the burning behaviour of the polymers.

5.3.1 TG Studies using Metler TA3000/TG50 - Pyrolysis Process of Wood

The thermogravimetric behaviour of all the timbers are typified by the TGA responses in Fig.5.6(a) - (c) for three timbers. From all ten TGA/DTG responses, identification of the start, peak and end decomposition temperatures and weight losses at maximum rates of mass loss for each decomposition step were identified as a function of timber density as shown in Figs 5.7-5.9. From these results the following observations are evident:

(i) All the timbers undergo pyrolysis and oxidation in two main discrete steps (steps 1 and 2) with the first step having at least two

stages. Qualitatively, all the ten woods yield thermogravimetric responses that are very similar.

(ii) The respective onset, peak and end temperature values for steps 1 and 2 respectively are strikingly similar for each timber type, i.e. they do not depend on the oven-dry density of each timber and thus reflect the underlying similar cellulose and lignin chemistries.

(iii) Of particular interest with regard to step 1 of the decomposition is that, while the shape and especially the relative intensity of the lower temperature DTG shoulder varies from sample to sample (see Figs 5.6(a) and 5.6(b)), the temperatures of the DTG peaks of all samples are almost identical (see Fig 5.7.). Each step 1 DTG maximum is close to 350°C which is typically associated with pure cellulose (Shafizadeh, 1968; Kilzer and Broido, 1965). The changes in the onset of the step 1 DTG response and the subsequent shoulder intensity is probably a consequence of the respective timber hemicellulose, lignin and inorganic contents (see below).

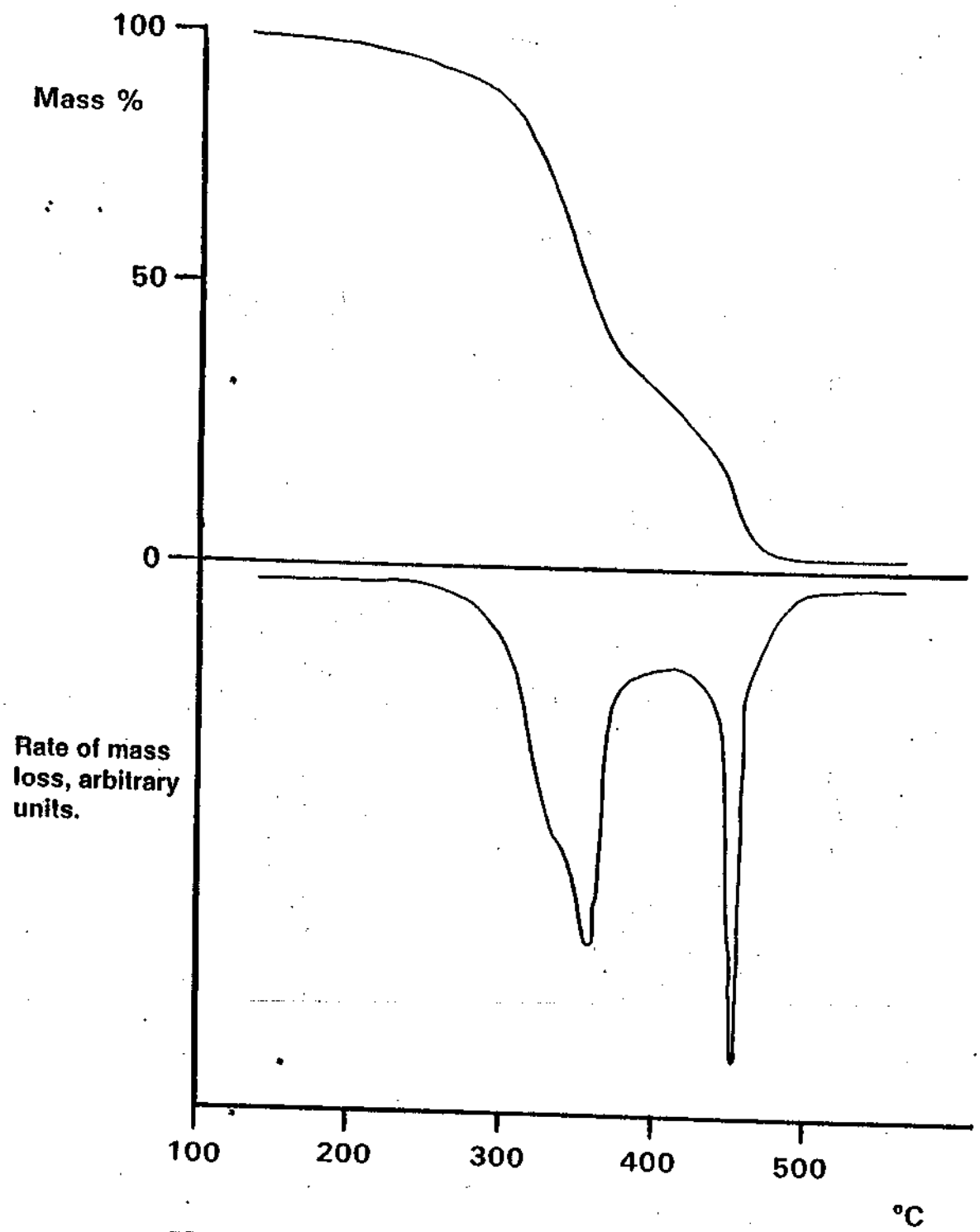


FIGURE 5.6(a): TG/DTG Curves of 6mg sample in air at $10Kmin^{-1}$ for Obeche.

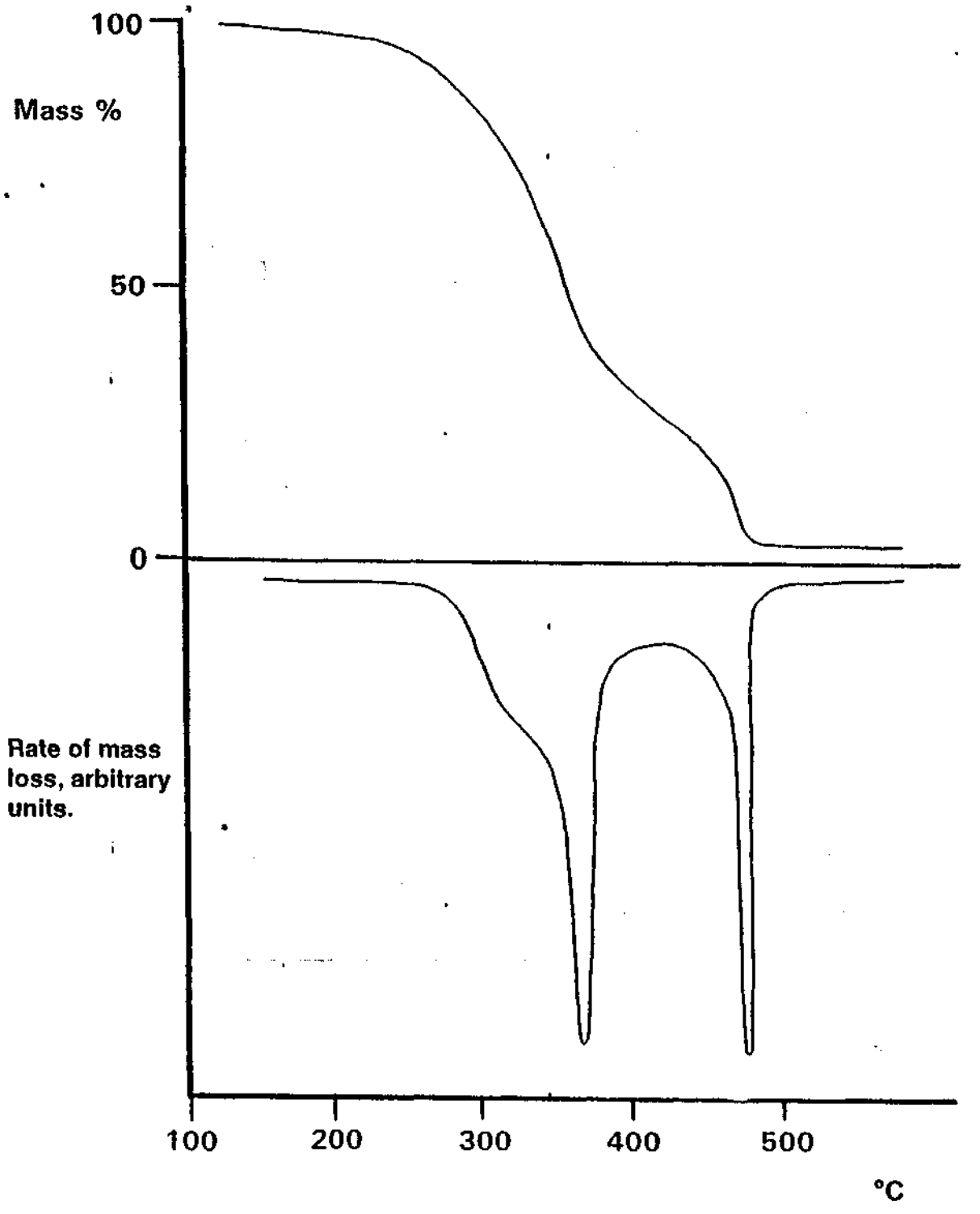
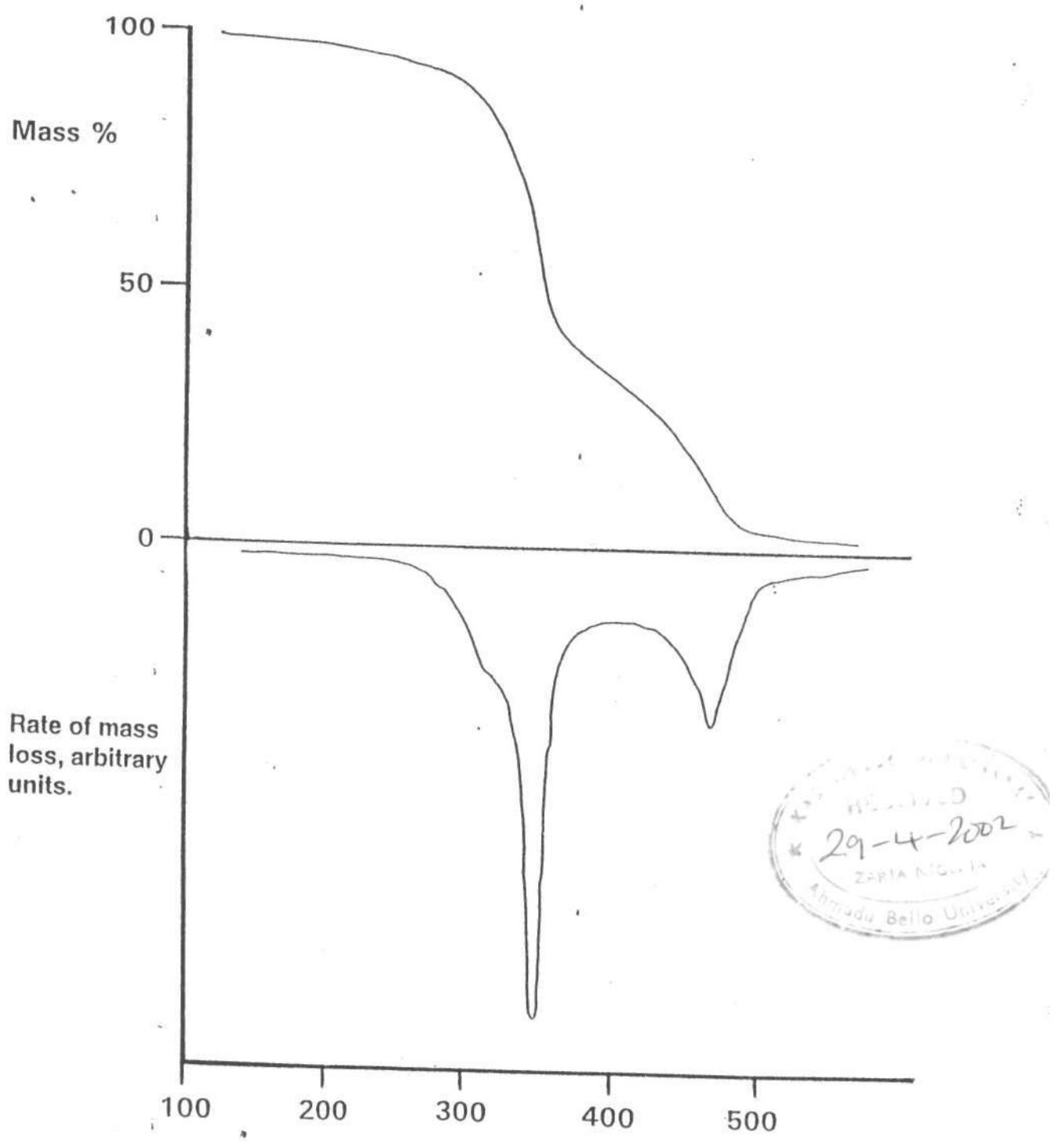


FIGURE 5.6 (b): TG/DTG Curves of 6mg sample in air at $10Kmin^{-1}$ for Ekhimi.



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FIGURE 5.6(c): TG/DTG Curves of 6mg sample in air at $10Kmin^{-1}$ for Walnut.

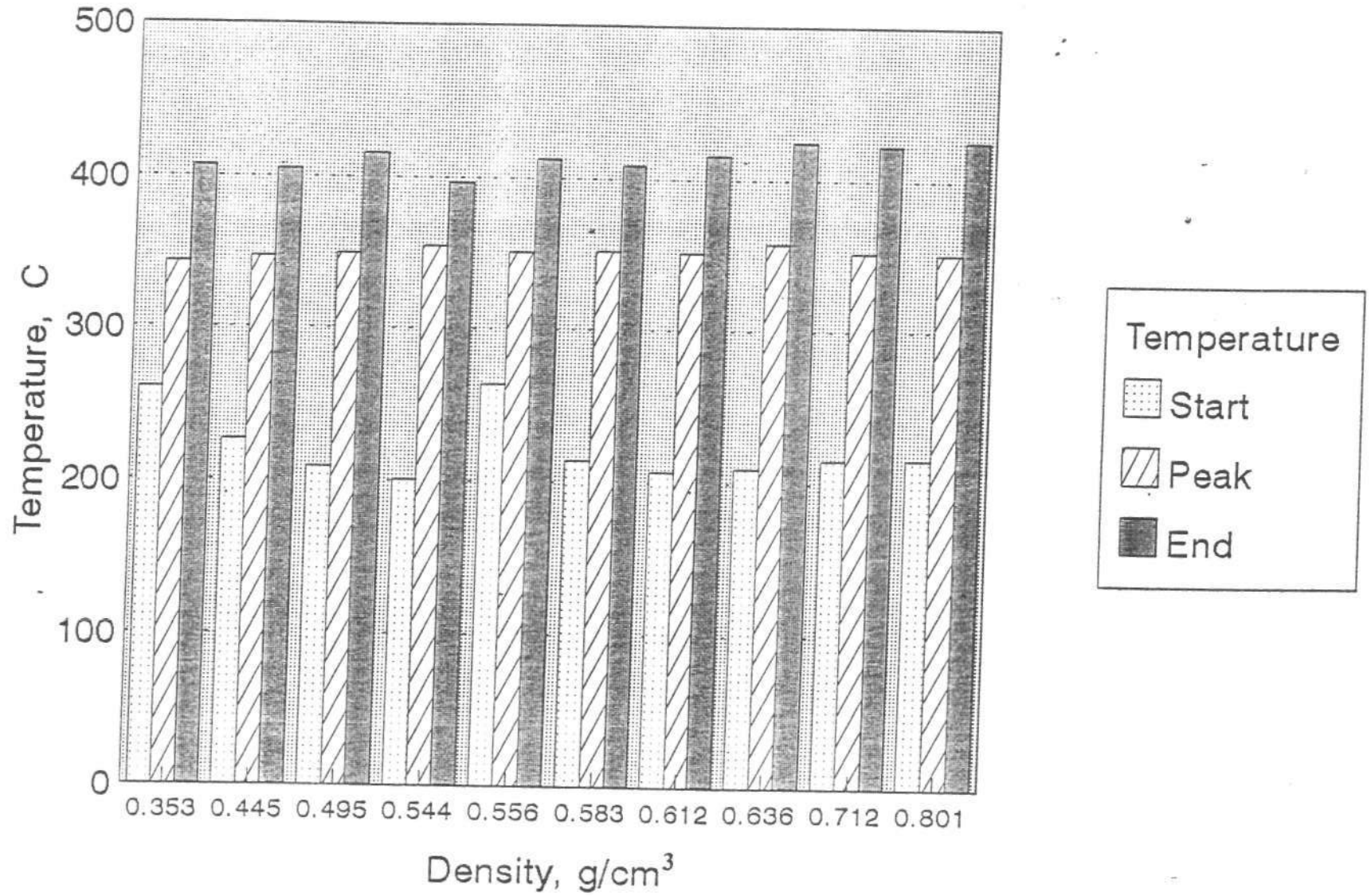


FIGURE 5.7: Step 1 TGA/DTG thermal degrdation/pyrolysis temperatures of selected timbers versus density.

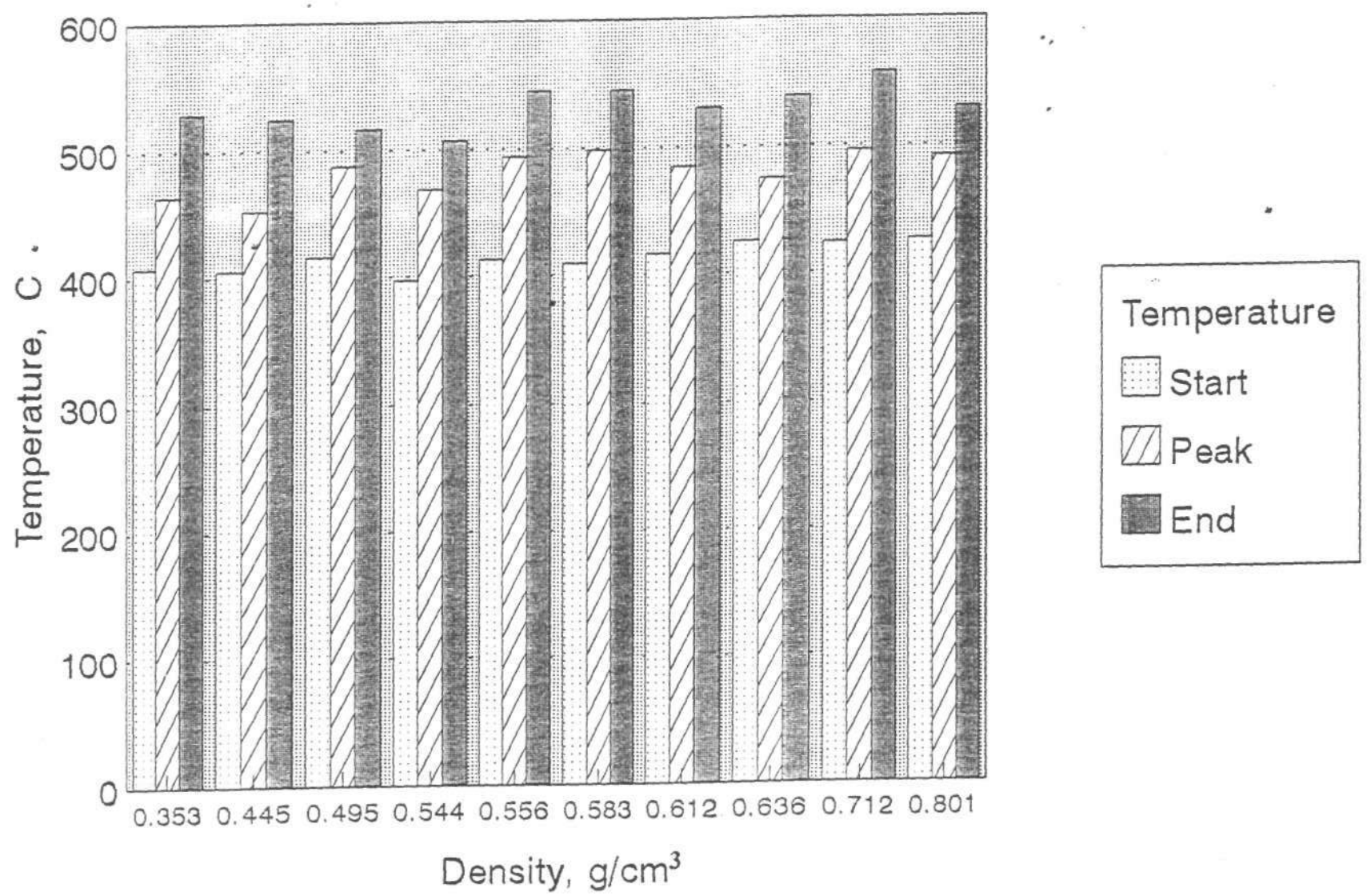


FIGURE 5.8: Step 2 TGA/DTG thermal degradation/pyrolysis temperatures of selected timbers versus density.

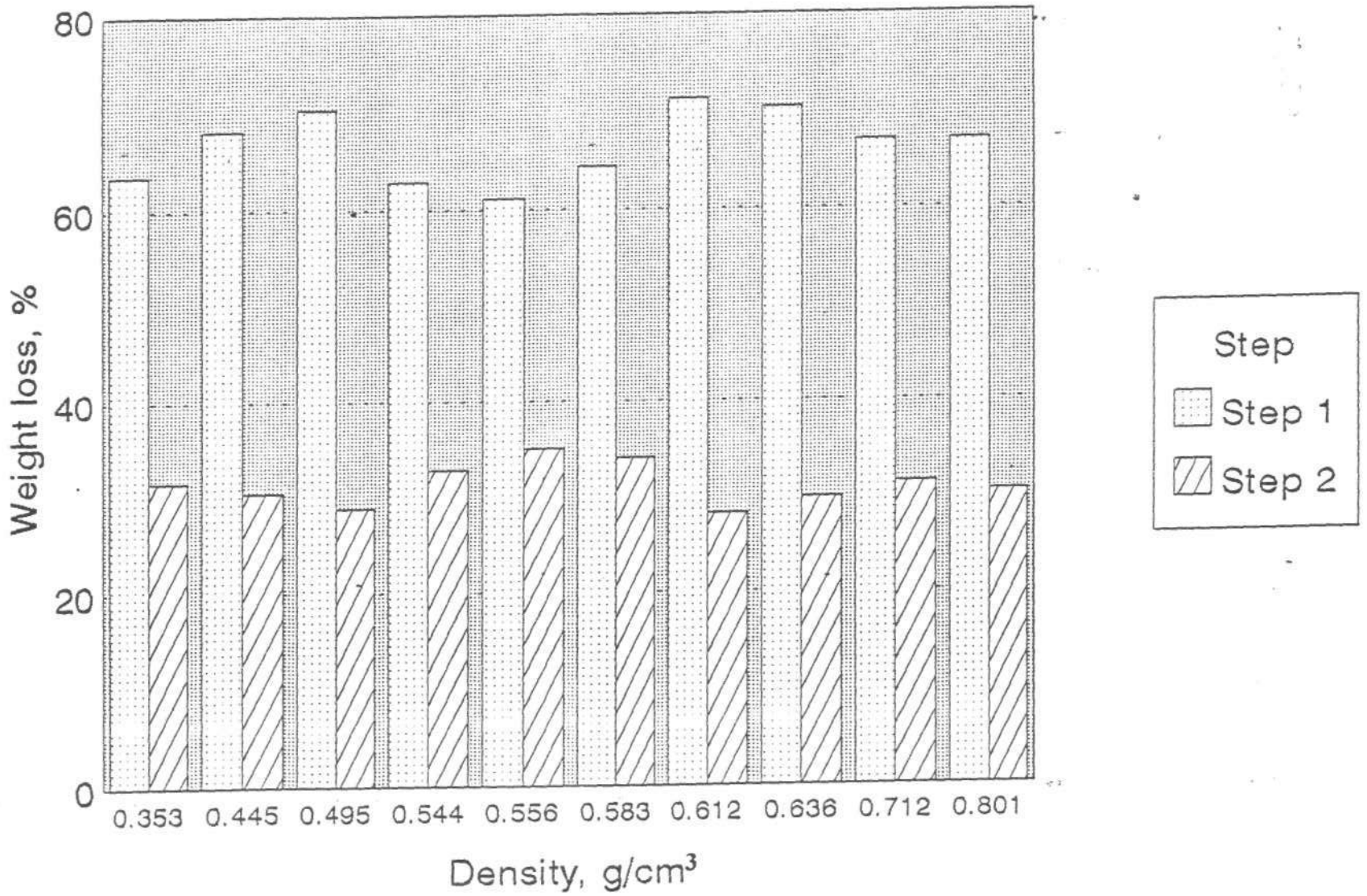


FIGURE 5.9: Step 1 and 2 TGA weight loss (%) of selected timbers versus density.

(iv) Similarly, it is observed that the respective weight losses at steps 1 and 2 maxima are similar for all wood types examined.

The first major weight loss transition (step 1) observed in this report may arise from gradual evolution of entrapped or occluded gases and volatiles such as air and water, followed by dehydration of the cellulose chain as well as non-destructive distillation of both liquid and cellulose components to volatile such as laevoglucosan. The second step entails catastrophic degradation of the products of the first step, i.e. laevoglucosan and, under air oxidative conditions, char oxidation. Cellulose, the major component of wood, is considered by many to undergo pyrolysis by two possible distinct routes as first described by Kilzer and Broido (1965): via cellulose chain depolymerisation to a laevoglucosan precursor and by chain dehydration wherein water and difficutly combustible carbonaceous char are formed. According to Shafizadeh (1968), when a cellulose material is heated, it undergoes two principal kinds of primary degradation reactions, namely dehydration and char forming, which are initiated at the lower temperature (approximately 200°C, see T_i values in Fig.5.7.) and continue at elevated temperatures; laevoglucosan or tar-forming reaction have significant rates at temperatures above 250°C and result in rapid volatilisation. Further, Shafizadeh noted that products of the primary reactions, if not removed from the heated environment, could further react

and decompose to provide a series of secondary compounds of lower molecular weight. When air is present, the combustible volatile products formed react with oxygen in the gas phase, and give rise to flaming ignition, whereas the oxidation of the charred residue in the solid phase leads to glowing combustion.

Woo and Schniewind (1987), investigated the thermal degradation of sugar pine, douglas fir and black oak by using DSC analysis. They found three peaks for all three species of wood but noted that the first peak cannot be identified without the application of increased pressure. Bradbury et al. (1979), proposed a three-step mechanism for the pyrolysis of cellulose in which an initial reaction (first step) leads to the formation of an 'active cellulose' which subsequently decomposes by two competitive first-order reactions, one yielding volatile and the other char and a gaseous fraction as discussed previously. More recent work, however, reviewed by Antal and Varhegyi (1995), casts doubt on these latter competing reactions and proposes that char is formed solely as a consequence of secondary volatile-solid interactions whose efficiency depends on the ability of the volatile to be retained by the decomposing cellulose mass. In the current experiment, use of a static air atmosphere will minimise the rate of volatile loss and so maximise char formation if this mechanism is valid.

The current TG/DTG results support a possible two-step series decomposition mechanism with a two-stage decomposition combined in step 1. The transitions or temperatures associated with these two stages, however, occur fairly close together for each wood. It is assumed that the initial stage in step 1 corresponds to the dehydration of hemicelluloses which have been found to be thermally least stable among wood components (Arseneau, 1971; Kass et al., 1970), and possibly lignin, while the second reaction may be associated with the thermal degradation of cellulose (Shafizadeh, 1968; Kilzer and Broido, 1965; Fairbridge et al., 1988), to form char with concurrent evolution of H_2O, CO and CO_2.

The second step observed at elevated temperatures (397-557°C) must be due to char oxidation (Dollimore and Hoath, 1981), again with evolution of CO and CO_2 (Price et al., 1968). Furthermore, the fact that the thermal parameters in Figs 5.7 - 5.9 are very close to each other means that the transitions highlighted here are closely related for all the timbers. In fact, it may be plausible to suggest that the products of pyrolysis are the same for all the timbers, although direct analysis would be required to confirm this hypothesis.

5.3.2 Kinetic Analysis of TGA Data and DTG

Figure 5.10(a) - (c) and 5.11 show the Broido plots for three different species of the timbers. Table 5.4. gives the kinetic parameters obtained for

each of the two steps of decomposition from the TG responses for all ten woods at the 10Kmin^{-1}. heating rates. These plots give rise to approximately straight lines and the results show almost identical slopes for each wood type at each decomposition step; thus there are no significant differences between species. The linear regressions have acceptable r^2 values, confirming that the plots are significant.

While step 1 comprises two mass loss stages, it is interesting to note that the Broido method fails to resolve these (see Figs 5.10 and 5.11) although the scatter of points in Fig.5.11 for $1/T > 1.5 \times 10^{-3}$ K^{-1}(i.e. temperature below 400°C) may be a consequence of these. Thus this step may be defined by only one average set of kinetic parameters. It is clear from Table 5.4. that the activation energies for the ten woods are in the range 100.6 - 135.9 KJmol^{-1}and 35.3 - 65.3 KJmol^{-1} for the first and second steps respectively. Thus the respective steps 1 and 2 kinetics for each of the woods are similar. Tang and Neil (1964), investigated the rate of decomposition of cellulose in atmosphere of helium and oxygen and found two different stages or types of reaction. The initial stage in the temperature range 240-310°C is controlled by pseudo-zero-order kinetics having an activation energy of 138.4 - 147 kJmol and the final stage in the temperature range 310 – 360°C, is pseudo-first-order having an activation energy of 221.9 - 232.8 kJmol . The rate of thermal decomposition of kraft and linen

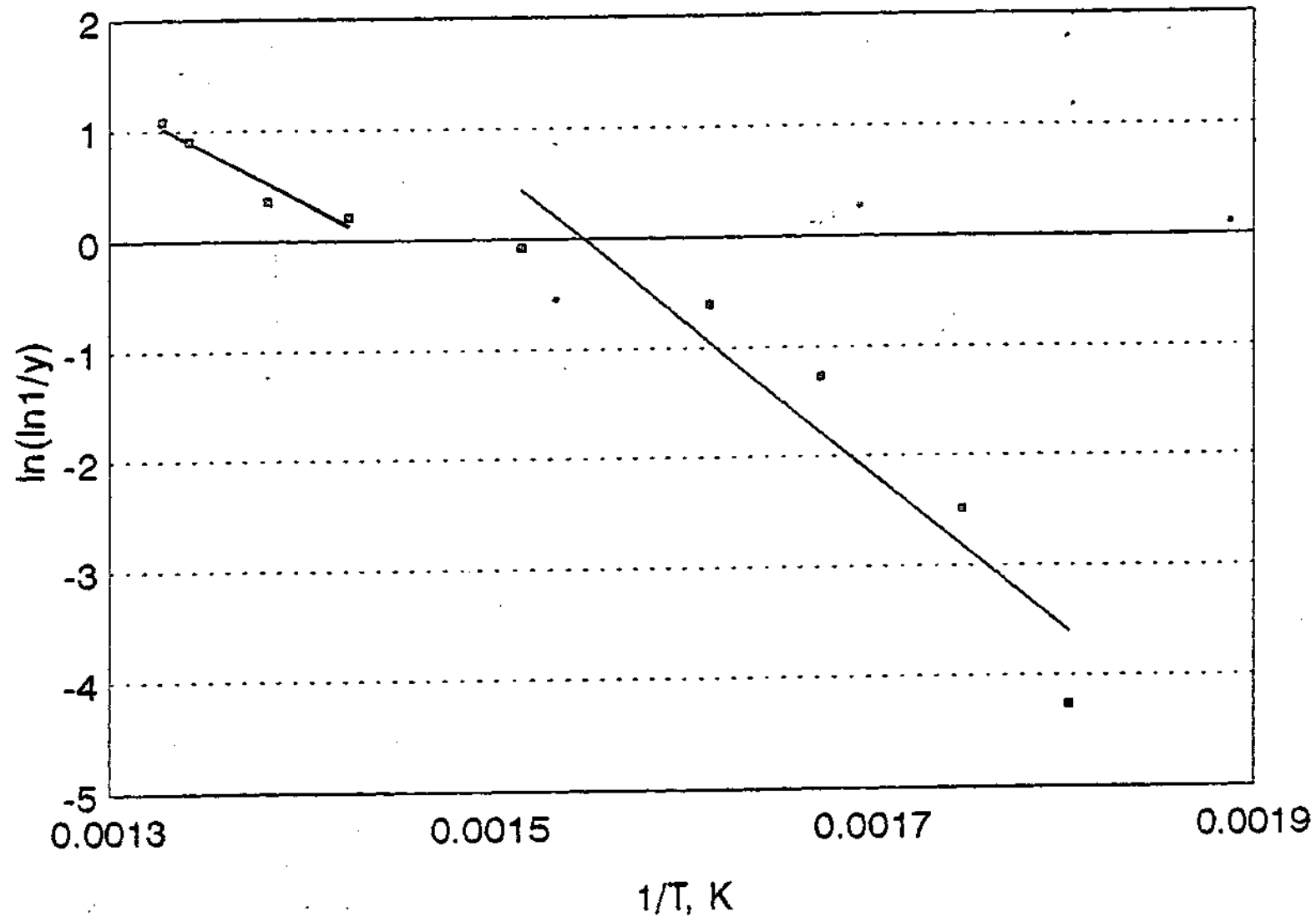


FIGURE 5.10(a): Arrhenius - type Broido plot for the TGA of Obeche.

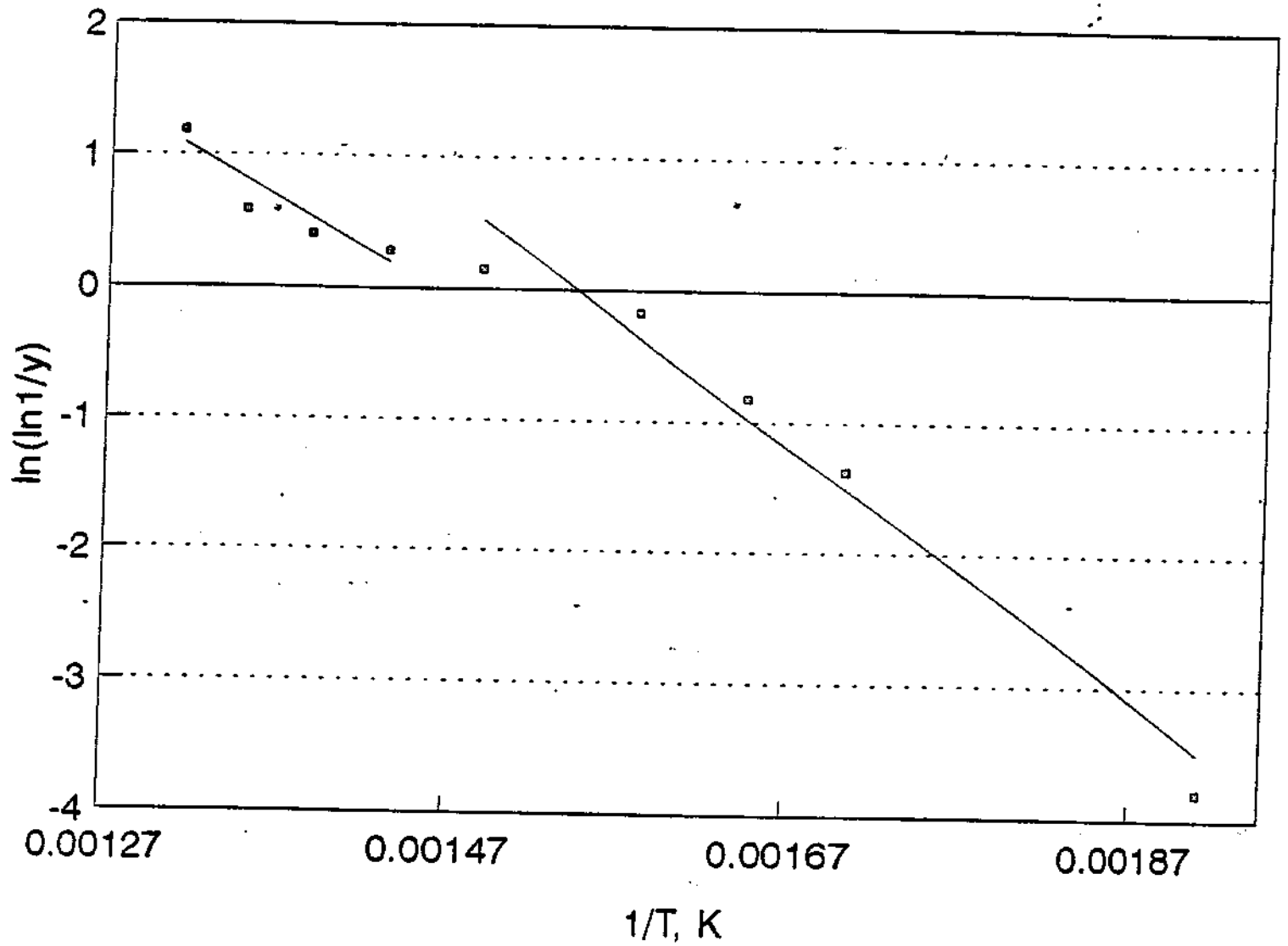


FIGURE 5.10(b): Arrhenius - type Broido plot for the TGA of Ekhimi.

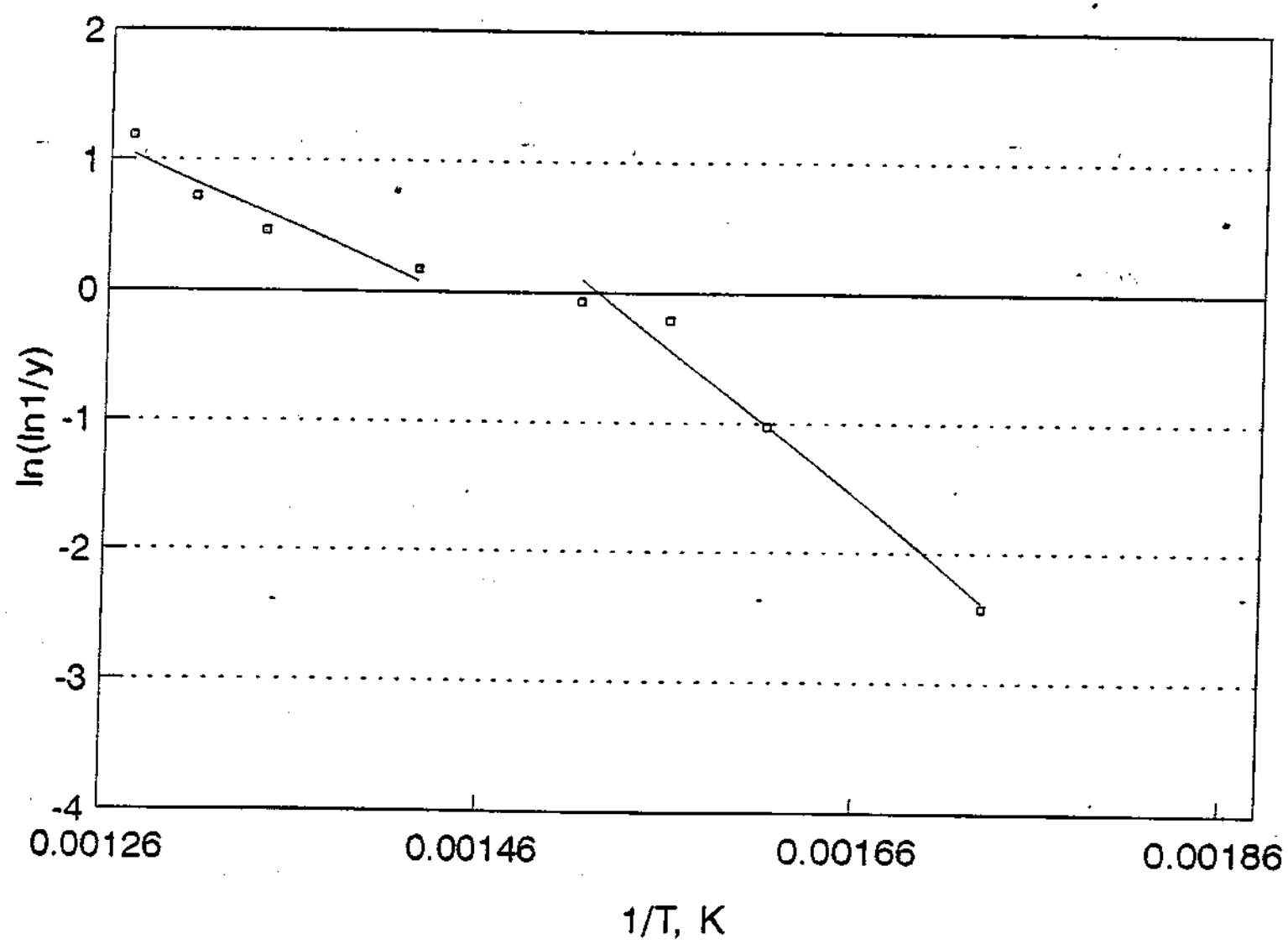


FIGURE 5.10(c): Arrhenius - type Broido plot for the TGA of Walnut.

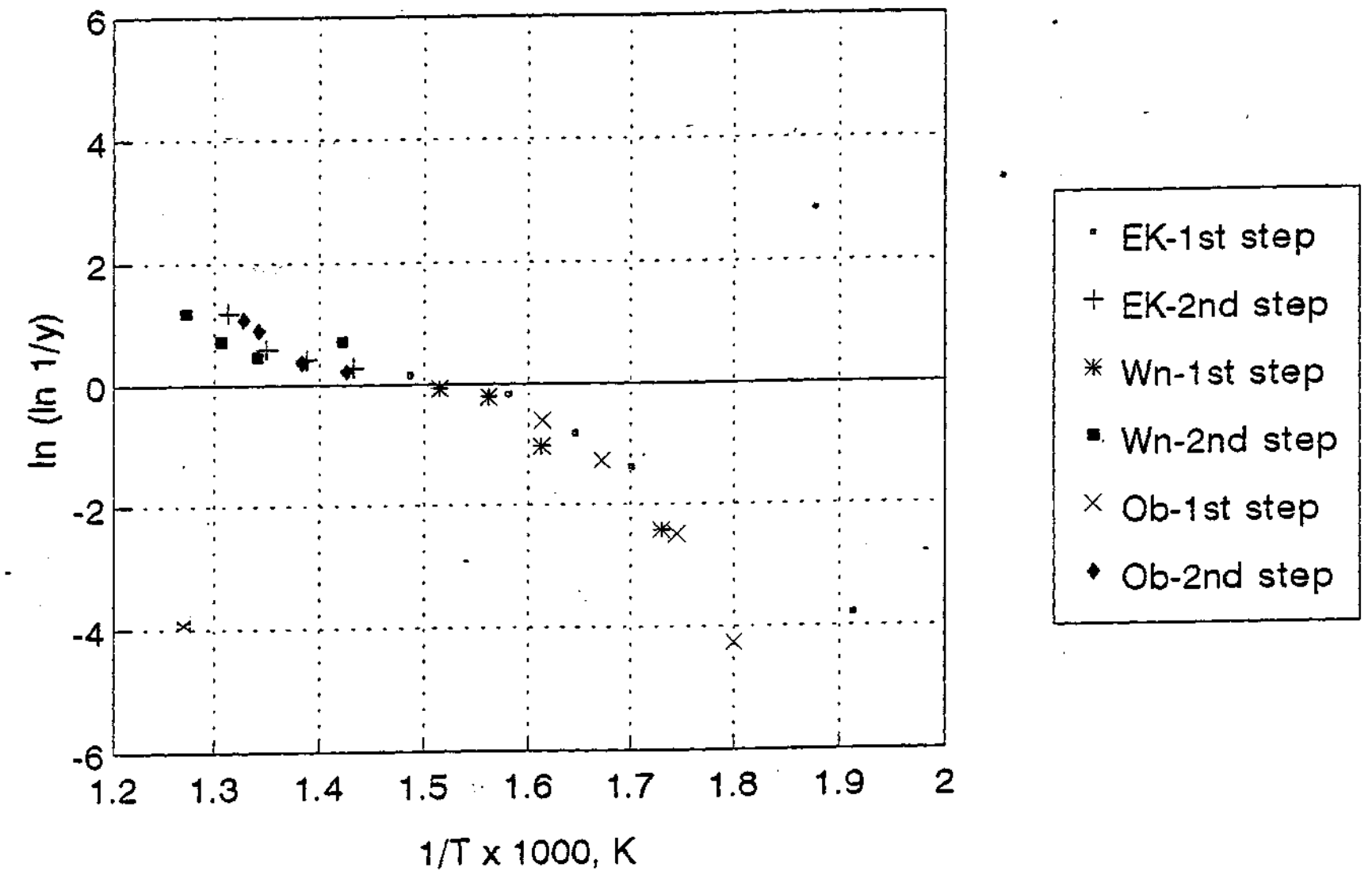


FIGURE 5.11: Combined Arrhenius ploits for the 3 timbers.

Table 5.4. Apparent Activation Energies and Pre-exponential factors for two stages of decomposition of the timbers at heating rates of 10K min^{-1}

Timber	Stage	Temp. Range (°C)	E_a ($KJmol^{-1}$)	$Z(s^{-1})$	r^2
Obeche	1st	260.3-407.3	112.350	$3.901x10^7$	0.894
	2nd	407.3-529.3	52.661	$1.094x10^3$	0.932
Lagos	1st	226.3-405.3	124.967	$4.978x10^9$	0.961
	2nd	405.3-524.3	65.34	$1.767x10^4$	0.888
Ekhimi	1st	209.0-416.0	582.282	$1.100x10^6$	0.970
	2nd	416.0-517.0	56.395	$2.378x10^3$	0.846
Afara	1st	201.0-397.0	116.386	$7.596x10^8$	0.959
	2nd	397.0-507.0	35.331	$4.532x10^1$	0.763
Guarea	1st	263.0-413.0	121.563	$1.774x10^9$	0.961
	2nd	413.0-545.0	49.063	$4x877x10^2$	0.942
Walnut	1st	214.3-409.3	100.576	$3.263x10^7$	0.976
	2nd	409.3-545.3	42.140	$1.400x10^2$	0.898
Mansonia	1st	207.0-416.0	104.791	$2.347x10^5$	0.995
	2nd	416.0-531.0	80.713	$1.903x10^2$	0.936
Ayan	1st	210.0-425.0	113.639	$3.384x10^8$	0.914
	2nd	425.0-537.0	38.322	$7.684x10^1$	0.813
Berlini	1st	215.3-423.3	135.975	$2.560x10^{11}$	0.917
	2nd	423.3-557.3	44.657	$2.099x10^2$	0.938
Danta	1st	216.0-426.0	120.406	$1.559x10^9$	0.982
	2nd	426.0-530.0	52.3	$9.539x10^2$	0.966

paper under vacuum was studied by Murphy (1962), in terms of the evolution of water, carbon monoxide, and carbon dioxide, in the low temperature range of 100-250°C. His data indicated two different stages: the initial reaction having an E_a value of 142 $KJmol^{-1}$. The former reactions were attributed to the decomposition of surface impurities, chain ends, and, in general, the secondary structures. The later reactions, were assigned to the decomposition of pure cellulose. In the Bradbury et al. (1979), model the two competitive reactions of volatile formation and char plus gas formation have respective activation energies of 198$KJmol^{-1}$ and 153 $KJmol^{-1}$. In a flowing oxygen-nitrogen atmosphere, however, Horrocks et al. (1985), have shown that the activation energy, E_a, of the rate-determining pyrolysis stages for cotton cellulose increases from 112 K $Jmol^{-1}$ at zero oxygen concentration to a value of 169$KJmol^{-1}$. at oxygen volume concentration of 30% or more for the temperature range from ambient to 500°C.

Table 5.5. lists the apparent activation energy values, E_a, at different stages/conditions derived by the respective authors above. While the cited kinetic parameters were determined for different cellulose materials using a variety of techniques and analytical assumptions, comparison of the published E_a values indicate that they probably describe lower temperature (i.e.< 400°C) and hence step 1 reactions. Thus our step 1 values agree with

Table 5.5. Derived Apparent Activation Energies of Pyrolysis, E_a from Different Authors.

Authors	Step, Condition or Temperature Range (°C)	E_a ($KJmol^{-1}$)
Tang & Neil(1964)	240-310	138.4-147.1
	310-360	221.9-232.8
Murphy(1962)	100-250	142.1
		164.7
Bradbury et al. (1979)	Volatile	198
	Gas + Char	153
	259-407	
Arseneau (1971)	Volatile	150
	Char formation	188
Horrocks et al. (1985)	Zero 0xygen conc. >30%	112
	25-500	169
Current work	Step1, 200-426 Step2,	
	397-557	100.6-135.9
		35.3-65.3

the lower temperature values range reported for degradation below 400°C by the six cited authors subject to the above caveat. In addition to these experimental variations, some differences may also be explained by the presence of lignin and hemicellulose in the wood samples in addition to inorganic impurities.

The series cellulose-to-volatile-to-char kinetic model of Antal and Varhegyi (1995), for pure cellulose suggests a single first step volatilisation which is first order and has an activation energy of 238 $KJmol^{-1}$. This idealised condition cannot occur in timber samples where, besides their lignin contents, metallic salt impurities promote dehydration reactions. The current results therefore represent apparent, averaged kinetic parameters which describe all reactions, whether in parallel or in series, present during step 1.

The E_a values calculated for step 2 char oxidation reactions (see Table 5.4.) are much lower than those for step 1 reactions and there are no literature values with which they may be compared. However, they do vary considerably with timber type possibly because oxidation reactions are again strongly influenced by impurities in the substrate as is evidence by their well-known afterglow-determining properties.

The values of pre-exponential factors in Table 5.4 show a very wide range, from 2.3 x 10^5. (Mansonia) to 2.6 x$10^{11}s^{-1}$ (Berlinia) for step 1 reactions and 4.5 x 10 s^{-1}(White Afara) to 1.8 x 10^4s^{-1}(Lagos) for step 2 reactions. These are 'apparent' values and are compounded by errors in E_a (see eqn (4.6)). Therefore, they cannot be used with confidence although two different ranges are observed for step 1 and 2 reactions. It is interesting to note, however, that in Table 5.4, the Z-values decrease as respective E_a value decrease, as is expected from equation (4.6) and is known as the so-called compensation effect (Budrugeac and Segal, 1995).

5.3.3 Char formation/Glowing combustion

Char yields (in weight %) and the respective ash values calculated from TG thermograms at around 35O°C and 5'50°C respectively are given in Table 5.6. The carbon content of each char is calculated as the difference between respective residues at 35O°C and 55O°C and probably is more indicative of the true char values. The results showed a substantial amount of char yield at 3OO°C in the range 20 - 45% depending on the wood sample. The high yields are due to the decomposition and dehydration at the relatively low heating rate of 10Kmin.$^{-1}$ while their differences are probably due to chemical factors, such as the minor components and inorganic

Table 5.6 Char yields from TG.

Specimen	Char at 350°C (%)	Ash at 550°C (%)	Carbon Content, (%)
Apa	32.6	1.0	31.6
Iroko	45.9	5.7	40.2
Ayan	29.6	1.1	28.5
Sapele	29.6	1.0	28.6
Guarea	38.9	0.9	38.0
Berlinia	33.0	1.9	31.1
Lagos	31.8	1.4	30.4
Walnut	36.0	1.1	34.9
Mansonia	28.8	0.8	28.0
Opepe	32.2	0.7	31.5
Danta	33.0	2.8	30.2
Ekhimi	29.6	0.9	28.7
Afara	37.8	4.4	33.4
Obeche	36.6	5.5	31.1

compounds present. According to Browne (1958), during pyrolysis at a low heating rate there is less disruption of the carbon-to-carbon residues which condense into char, whereas fast pyrolysis at higher temperatures tend to proceed much more violently with more disorderly disruption of chain

structures to form flammable volatiles and with less condensation of carbonaceous entities to form char.

Glowing or smouldering combustion arises from solid phase oxidation of chars remaining after evaporation of the volatile products. It will occur in an abundance of oxygen and depends on unburned material as well as on char. As observed before in Fig.5.5, there is no correlation between afterglow time and timber density. Even in the cases of woods having similar densities, the afterglow times are substantially different. A good example is the case of Iroko and Opepe where they have about equal densities; Iroko has average afterglow time of 652 sec., and Opepe has just 0.6 sec. average afterglow time. It is likely that such factors as the nature of the unburned materials remaining and the physical and chemical nature of the char may help to explain the results.

Figure 5.12, shows a general correlation between char formation at 350°C and afterglow time. Generally, the greater the char yield the higher the afterglow time as might be expected if the latter is related to carbon content. However, Figure 5.13 shows a similar ash (at 550°C) versus afterglow trend. This is an indication that afterglow also depends largely on the presence of inorganic salts.

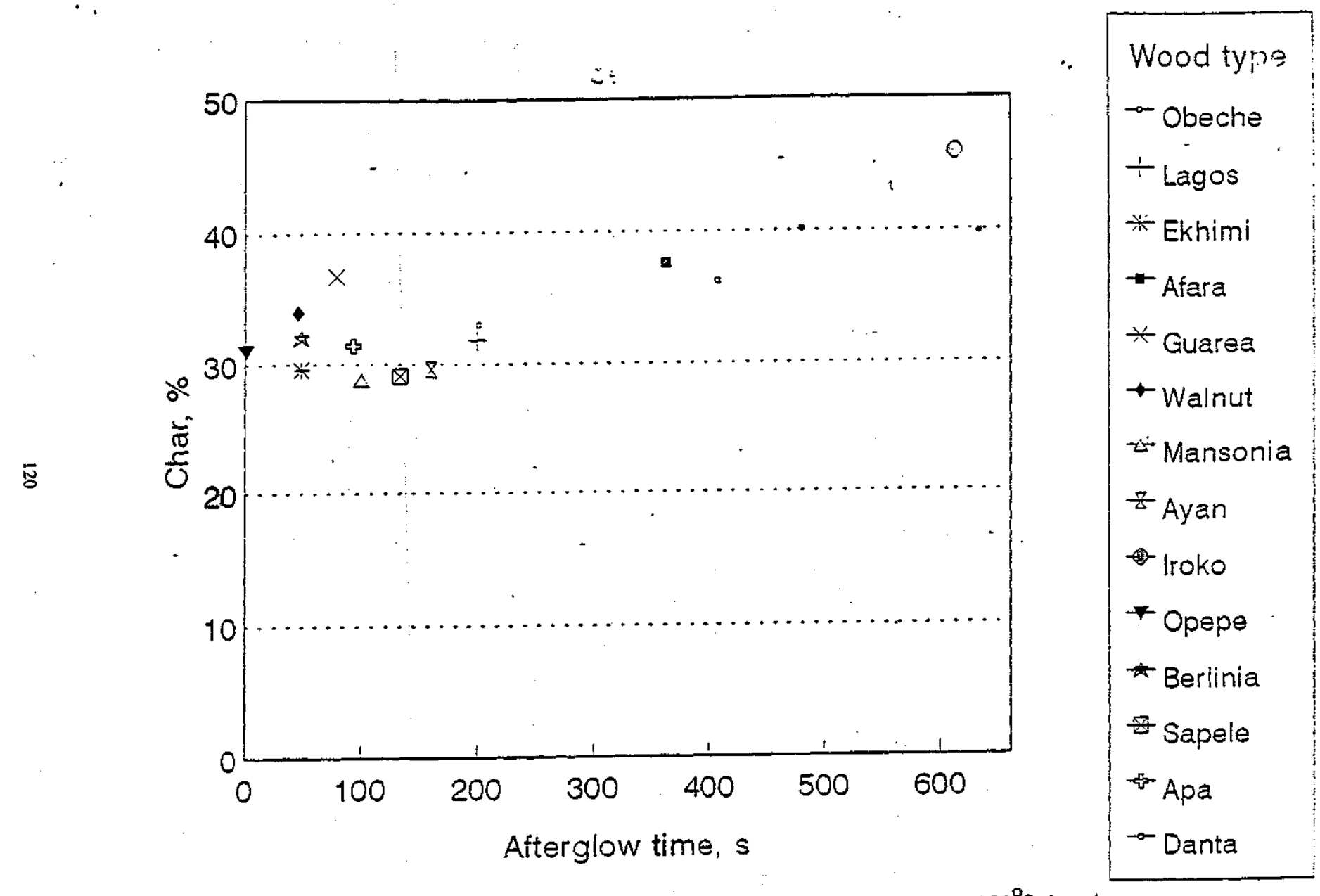


FIGURE 5.12: Afterglow time versus percentage residual char at 300°C in air.

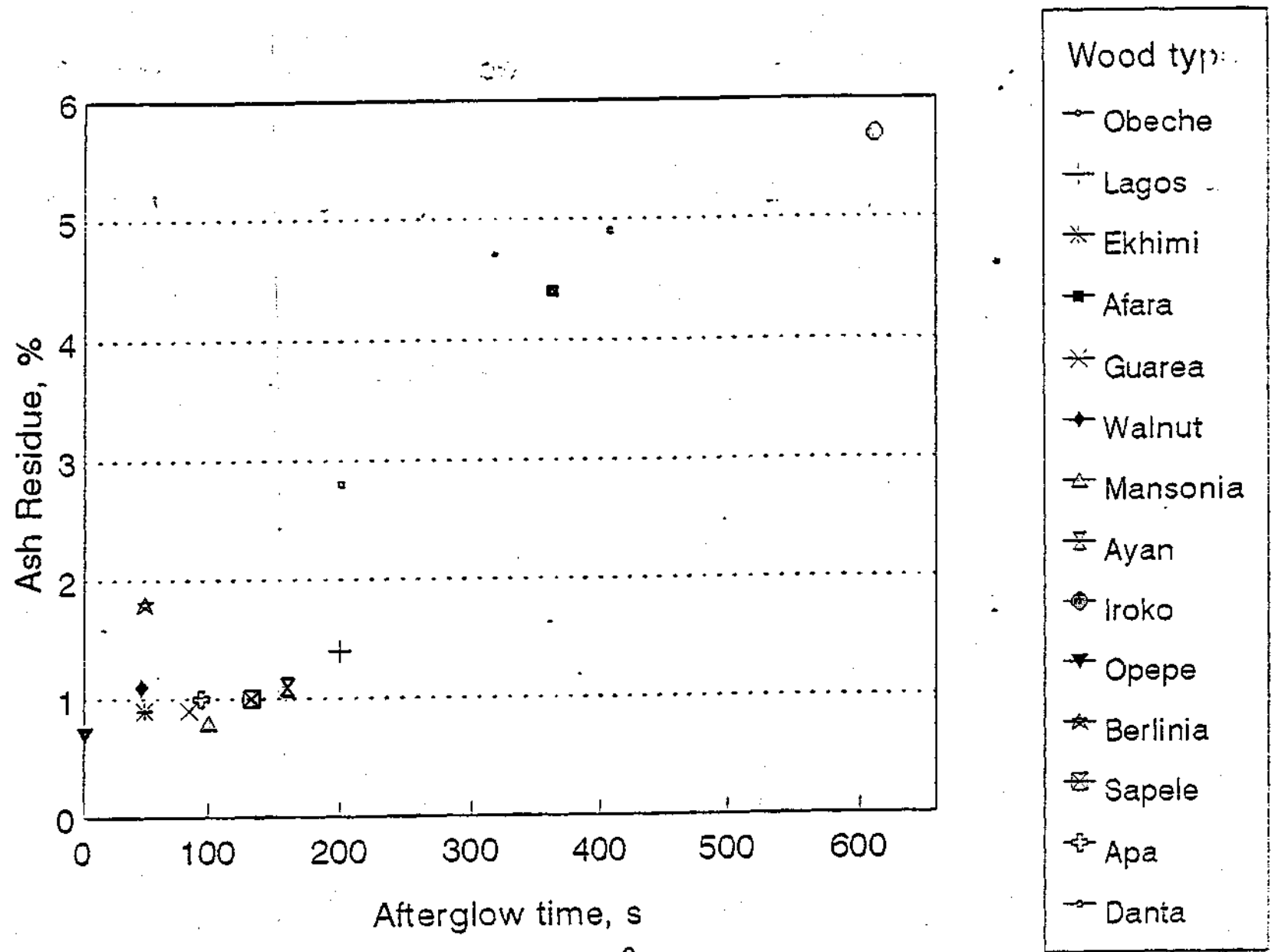


FIGURE 5.13: Percentage ash residue at 550°C versus afterglow time.

5.4 FURTHER THERMAL ANALYSIS

Thermal degradation of wood as discussed earlier in detail in chapter 1 and section 5.3, proceeds through two types of reactions. At the lower temperatures i.e. below 3OO°C, a gradual degradation takes place which probably involves dehydration, re-arrangement, formation of carboxyl and carbonyl groups, evolution of carbon dioxide, carbon monoxide and formation of carbonaceous char. At higher temperatures, a rapid volatilisation/depolymerisation of these units accompanied by the formation of intractable tars and carbonaceous residue occurs. The major product in the tar is levoglucosan, which may be present in yield of 40% or more (Shafizadeh, 1968) together with polymeric materials. These observations have been further studied in Bolton by DTA,TG/DTG and DSC analysis.

5.4.1 TG/DTG Using Stanton Redcroft TG 760

TG/DTG analysis of the 14 wood samples were carried out in air atmosphere from ambient temperature to 7OO°C and are shown in figures 5.14 (a)-(e) and the respective transitional data are shown in Table 5.7. The TG curves were basically similar in shape and show two significant areas of weight loss which may be considered as two stages of thermal degradation. However, in some of the wood the first stage consists of two steps.

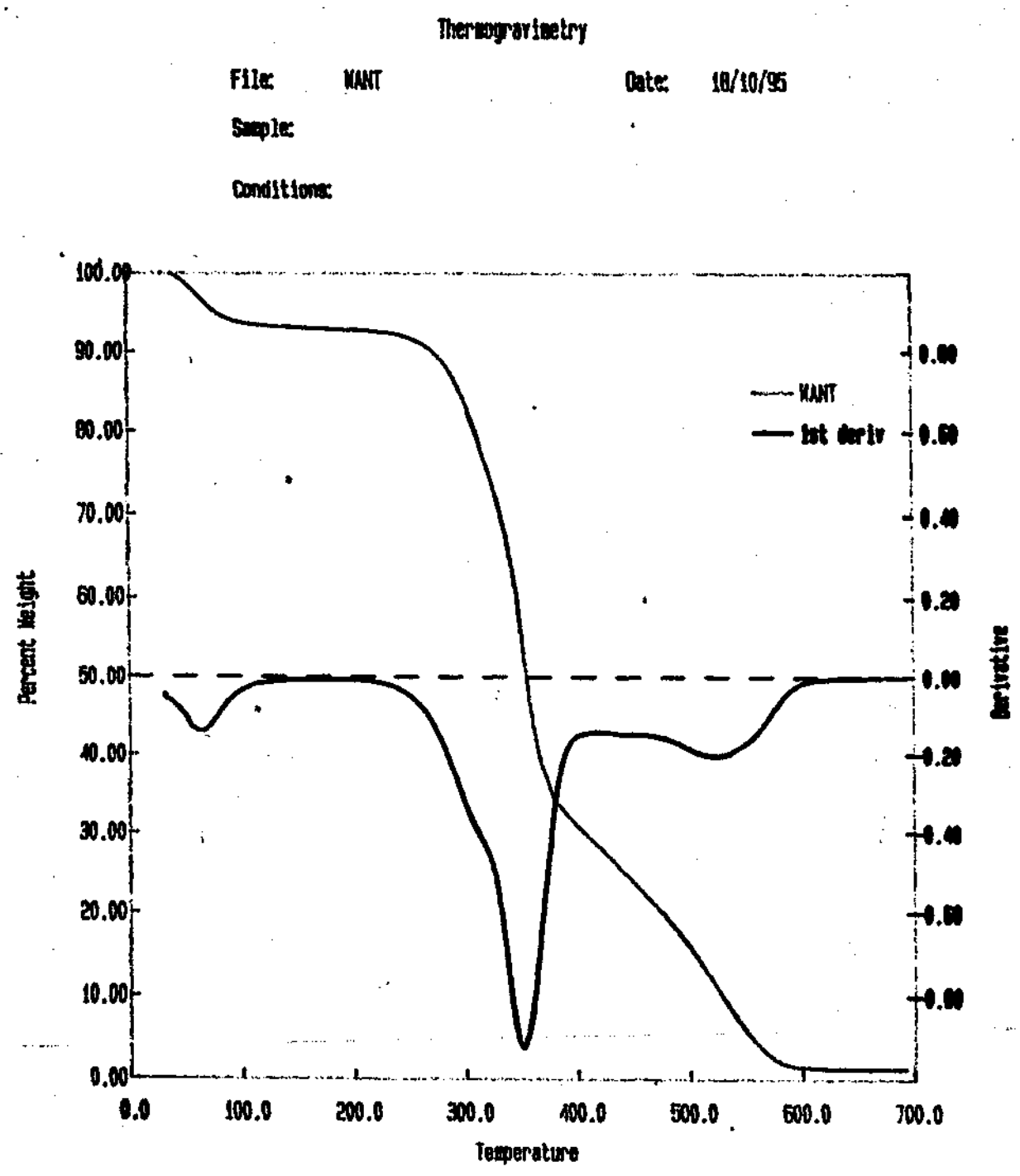


FIGURE 5.14(a): TGA and DTG responses of Walnut wood at 10K/min in static air.

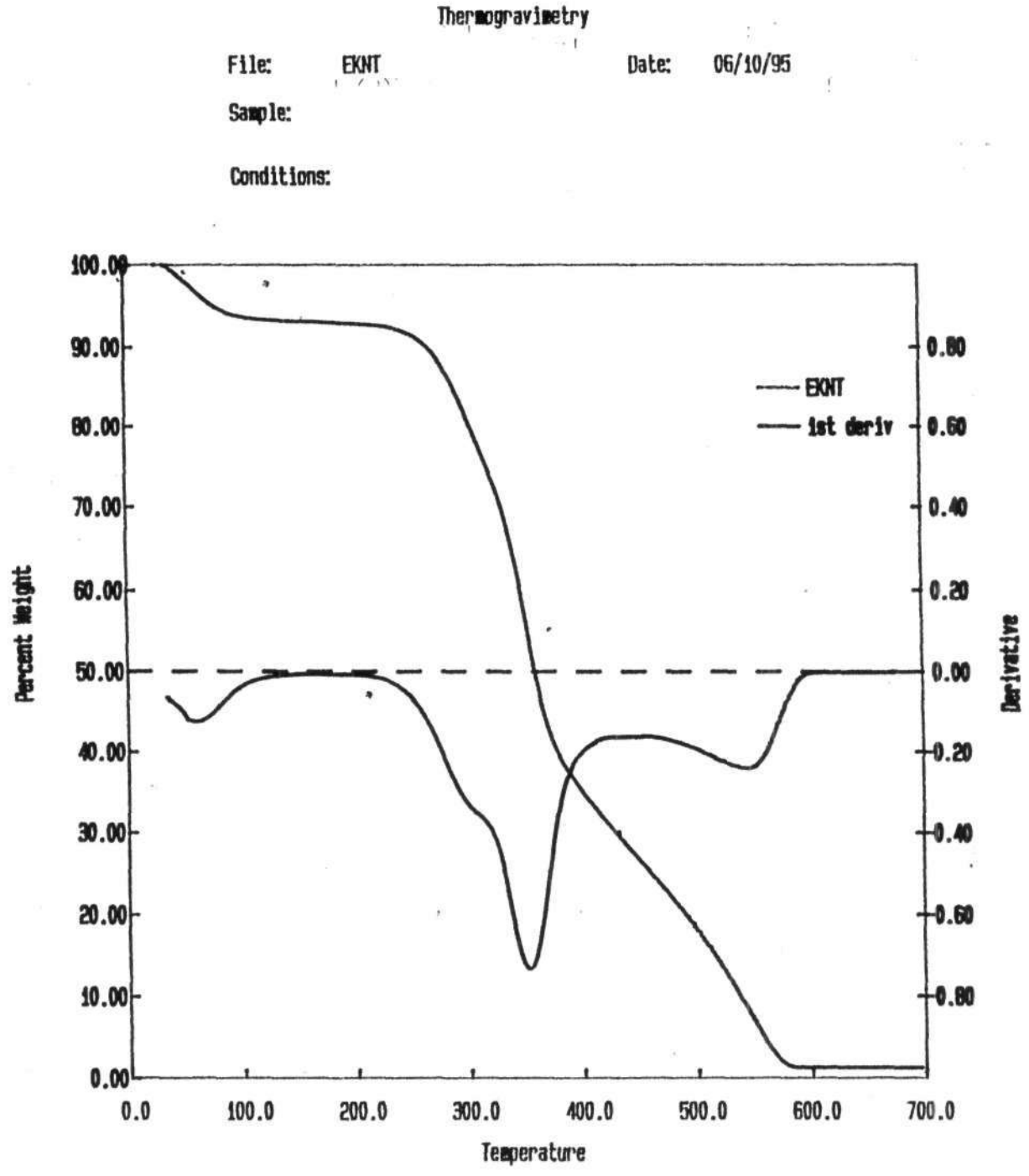


FIGURE 5.14(b): TGA and DTG responses of Ekhimi wood at 10K min^{-1} in static air.

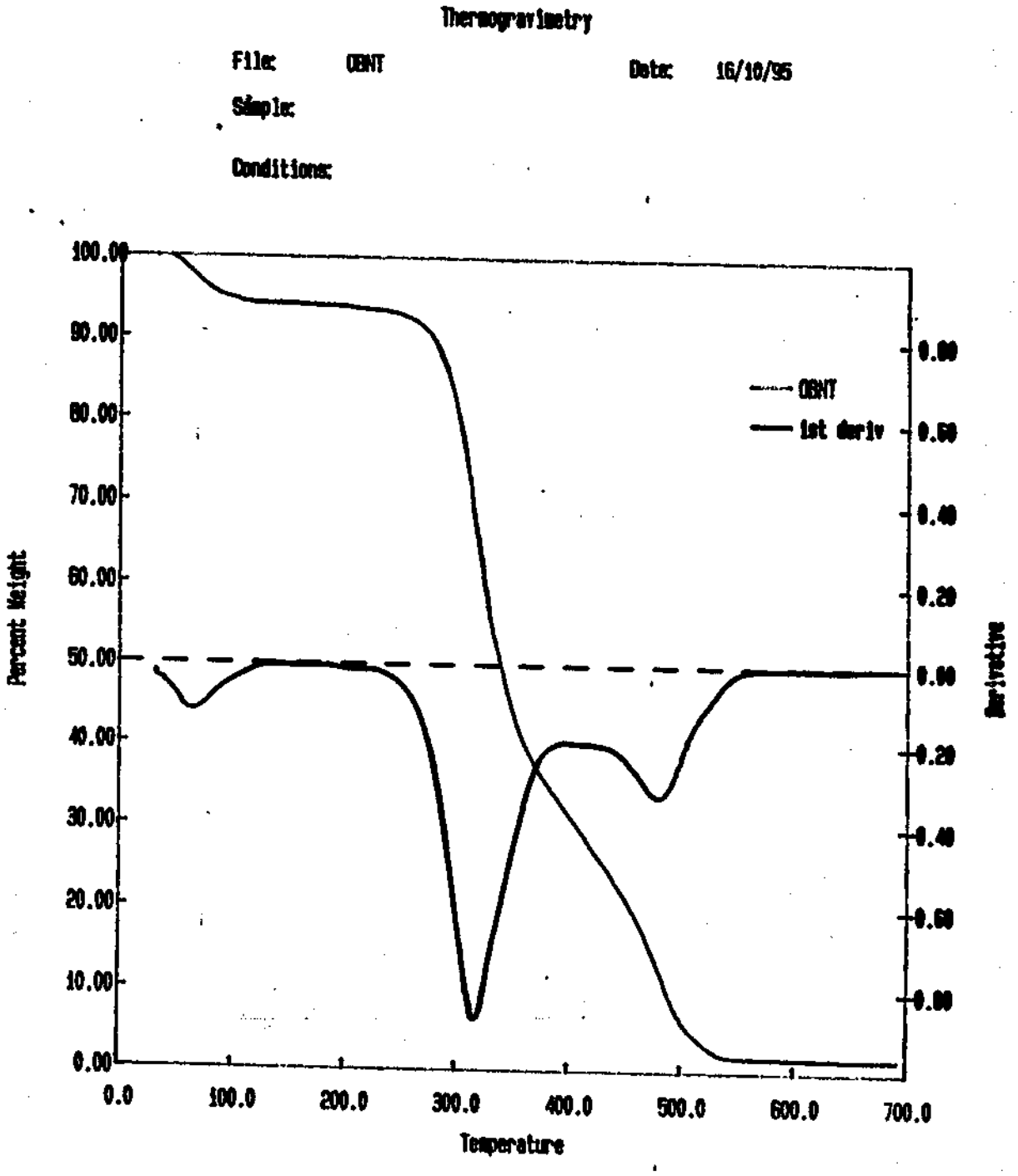


FIGURE 5.14(c) TGA and DTG responses of Obeche Wood at 10Kmin^{-1} in static air.

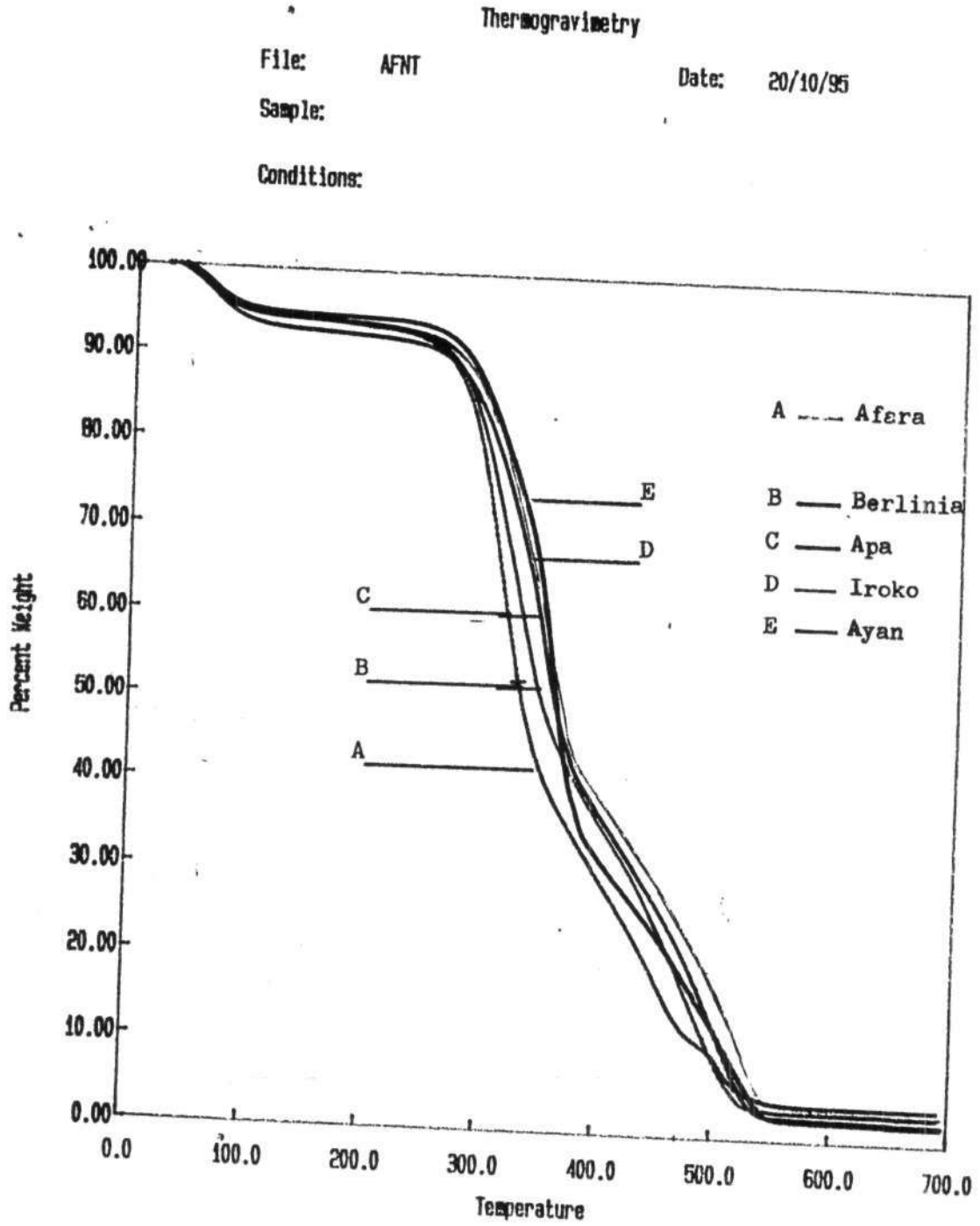


FIGURE 5.14(d): Combined TG curves in air at 10Kmin^{-1} for various wood samples.

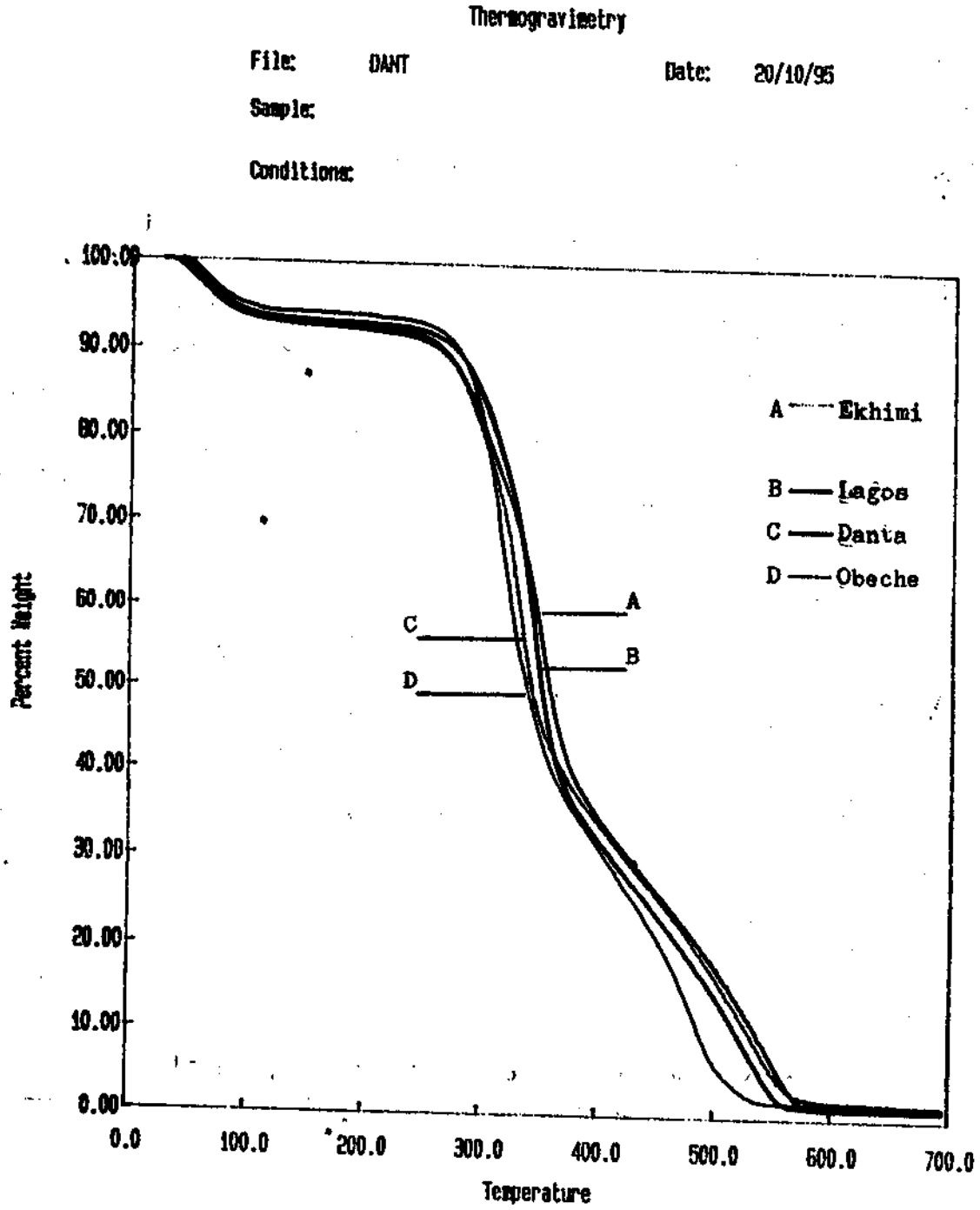


FIGURE 5.14(e) Combined TG curves in air at 10Kmin^{-1} for various wood samples.

Table 5.7: Main Pyrolysis temperature of various woods at $10Kmin^{-1}$ in air.

Sample	Stage	DTA CURVE		
		$T_{onset}(^oC)$	$T_{max}(^oC)$	$T_{end}(^oC)$
Apa	1st	216	347	420
	2nd	420	497	569
Iroko	1st	210	345	392
	2nd	392	521	569
Ayan	1st	209	357	417
	2nd	417	516	588
Sapele	1st	217	345	422
	2nd	422	525	590
Guarea	1st	220	340	410
	2nd	410	528	575
Berlinia	1st	216	326	405
	2nd	405	480	575
Lagos	1st	218	344	410
	2nd	410	529	577
Walnut	1st	210	351	426
	2nd	426	527	589
Mansonia	1st	209	353	426
	2nd	426	527	590
Opepe	1st	216	356	435
	2nd	435	-	620
Danta	1st	215	332	427
	2nd	429	535	569
Ekihimi	1st	210	351	418
	2nd	418	550	581
W/Afara	1st	201	314	390
	2nd	390	470	510
Obeche	1st	212	317	419
	2nd	419	482	549

The results are in general agreement with the foregoing results using Mettler TA3000/TG 50 considering the uncertainties of the determination and the variability within the species. In all the samples, the initial but small mass loss of about 5.0% below 100°C due to desorption of moisture and indicated by the DTG peak around 67°C was not considered as thermal degradation as usual. The first stage of thermal degradation is the high weight loss of 57-66% in the temperature range 200-400°C in the TG curves. It is presumably the degradation of soluble hemicelluloses, followed by dehydration/depolymerisation reactions of the cellulose,and accompanied by releases of volatile oxidation products such as laevoglucosan; this stage has been discussed in depth in section 5.3.

The second stage which occurred at high temperature (> 400°C) region with the weight losses in the range 25-33% is considered to be that in which the char residue left after the first pyrolysis stage decomposition reaction is further oxidised and volatilised. Probably, it involves C - O and C - C bond cleavage reactions. The char is converted to ash of 1.6 - 3.5% at 690°C during this process.

Comparison of these weight losses, transition temperatures, and char yields show that they are close for all the woods and suggested that the

thermal degradation proceeded through similar routes to approximately the same final mass, implying a similar final structure. It appeared plausible that the observed slight differences is because the structural components differ between woods and among species as mentioned earlier.

5.4.2 Effect of Heating Rate on the Pyrolysis

Intuitively, flammability of any organic material should be related in some way to the heating rate because during burning the temperature of a polymer surface in front of the advancing flame is rapidly raised from room temperature to the ignition temperature in a few seconds. At such high heating rates, it is possible that the pyrolysis process mechanism varies. Wood follow this general pattern and to quantify this assumption, wood samples were run at rates of 5, 10, 25 and 50°C min^{-1} under air condition.

Figures 5.15 - 5.17 give the respective pyrolysis results for Ekhimi, Iroko and Mansonia over the range of heating rates from 5°C min^{-1} to 50°C min^{-1}. The results show that the character of the pyrolysis process is changed for each wood with increasing heating rate. The most significant changes are that the TG curves were shifted to higher temperatures at higher heating rates, in particular the onset temperatures of the dehydration reaction is

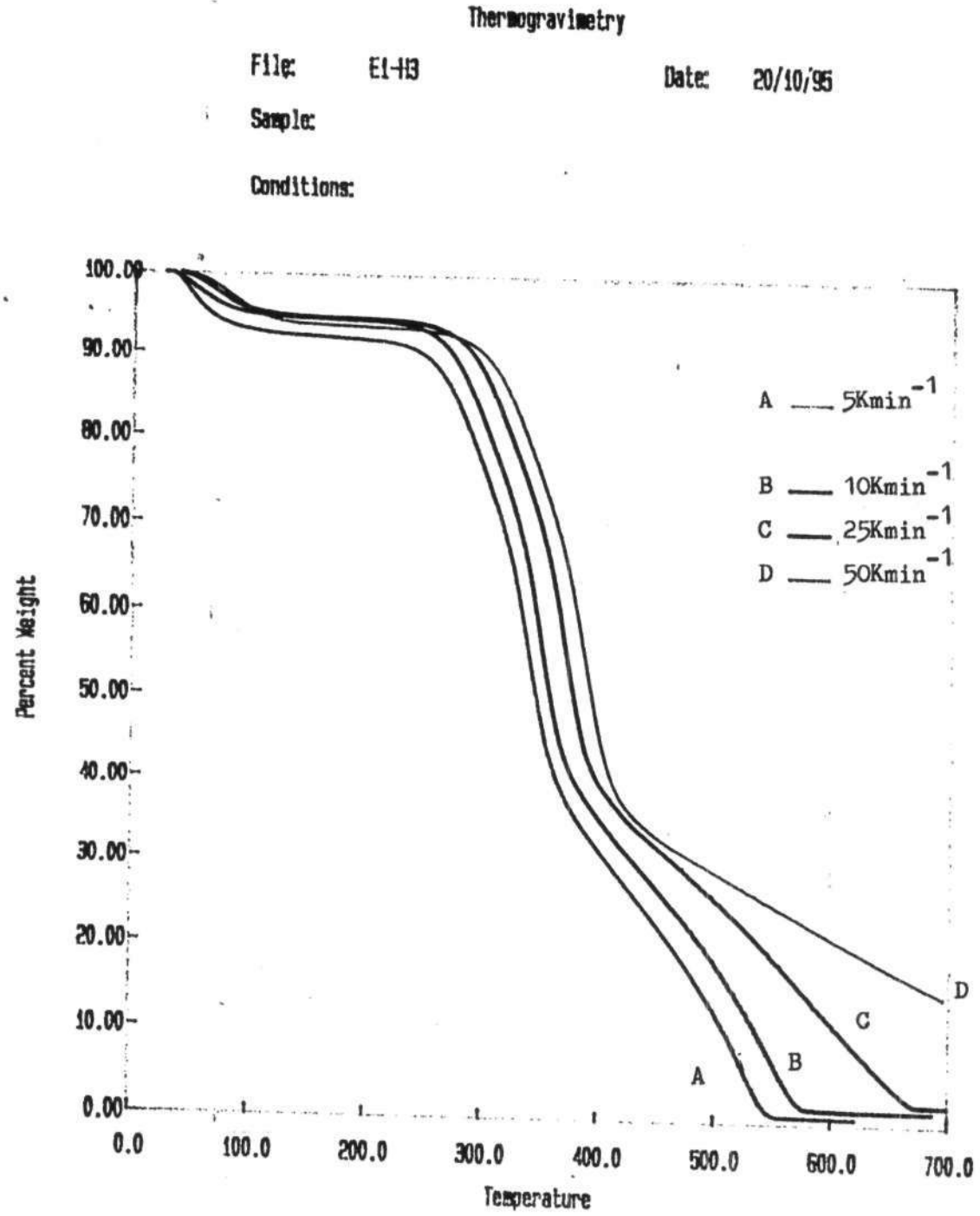


FIGURE 5.15: Effect of heating of rates on TG curve of Ekhimi wood in static air.

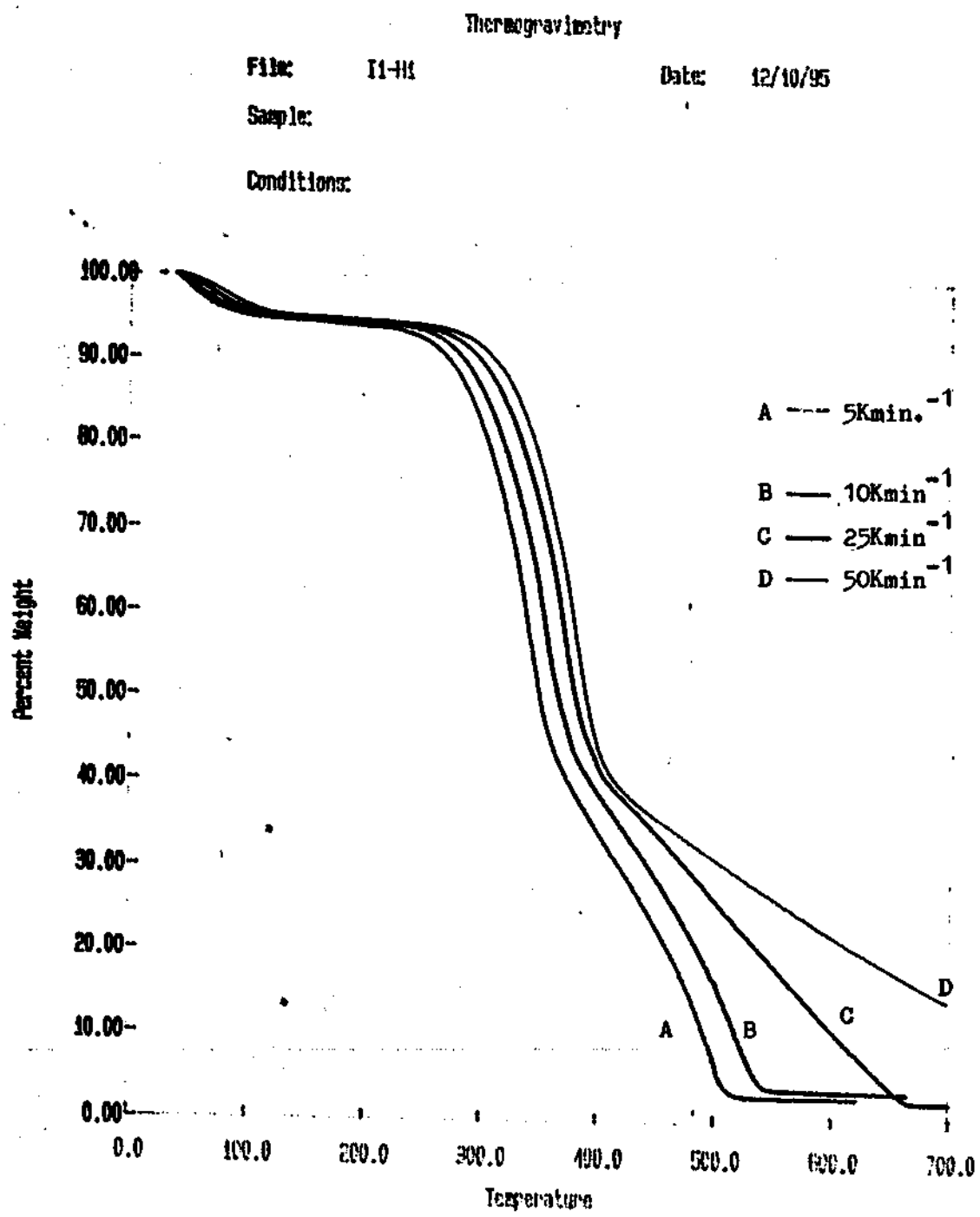


FIGURE 6.16: Effect of heating rates on TG curve of Iroko wood in static air.

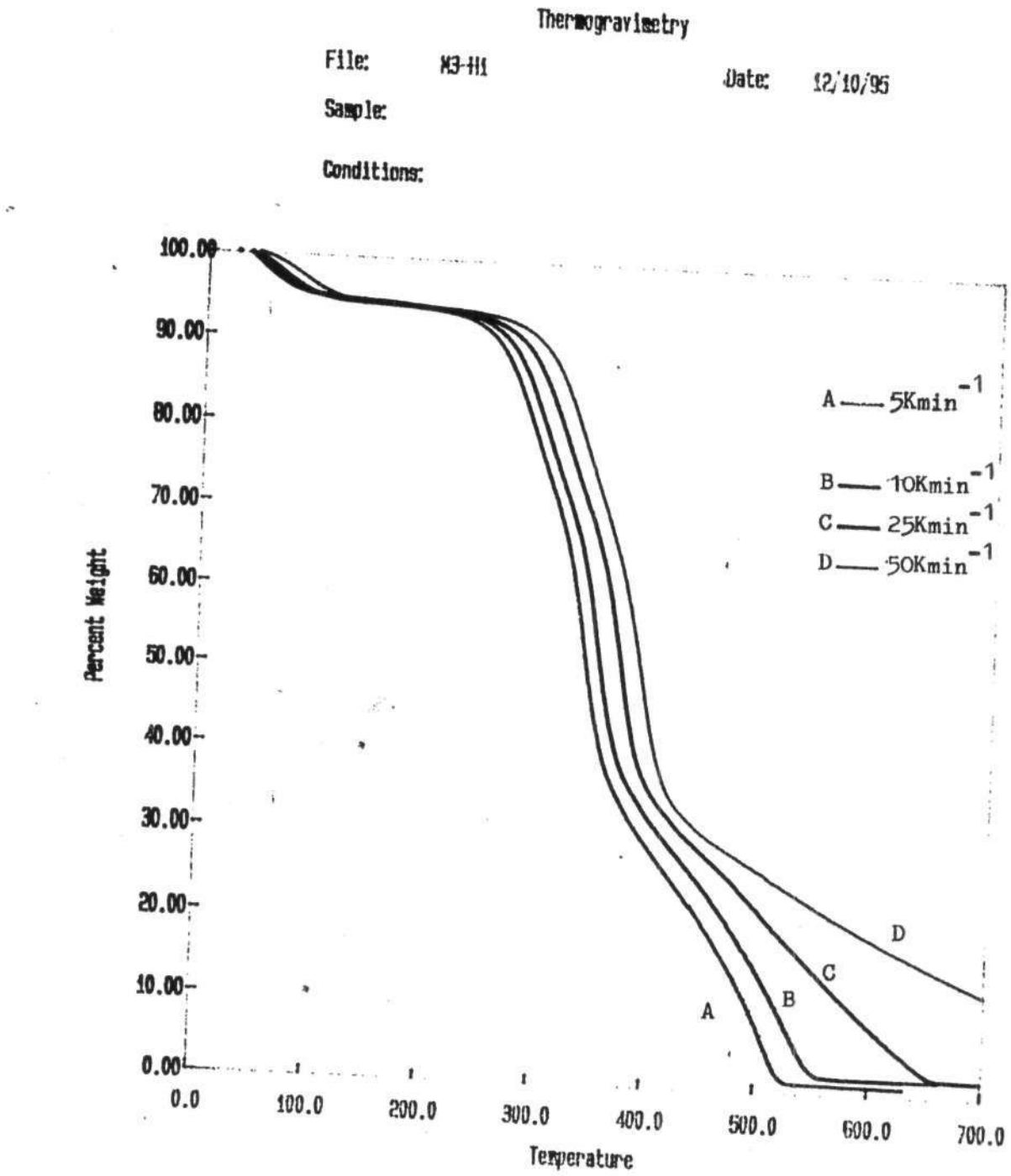


FIGURE 5.17: Effect of heating rates on TG Curve of Mansonia wood in static air.

raised and the mass loss during this stage is increased rapidly with increasing heating rate. The increased mass loss shows that at high heating rates a large quantity of volatile products will be rapidly produced during the first stage of thermal decomposition. Finally, for the tested woods, the final value of weight remaining (char/ash) increased slightly in all cases at higher heating rates. This is probably because at high heating rates there is insufficient reaction with oxygen and char residue, which reduces the oxidation of the residue.

5.4.3 DTA Studies

The DTA thermograms of wood samples shown in Figs 5.18(a)-(c) and 5.19 are typical of those obtained in this work. The peak temperatures (relating to the initiation, maximum and termination stages of pyrolysis) for various endotherms and exotherms were measured and are given in Table 5.8. The curves showed no significant differences. The DTA curve of each wood sample generally indicates one endothermic reaction and then two strong exothermic ones. The endothermic reactions, which peak around 70^0C for all the wood is caused by evaporation of sorbed moisture. The slight endothermic in the region below 260^0C can be attributed to

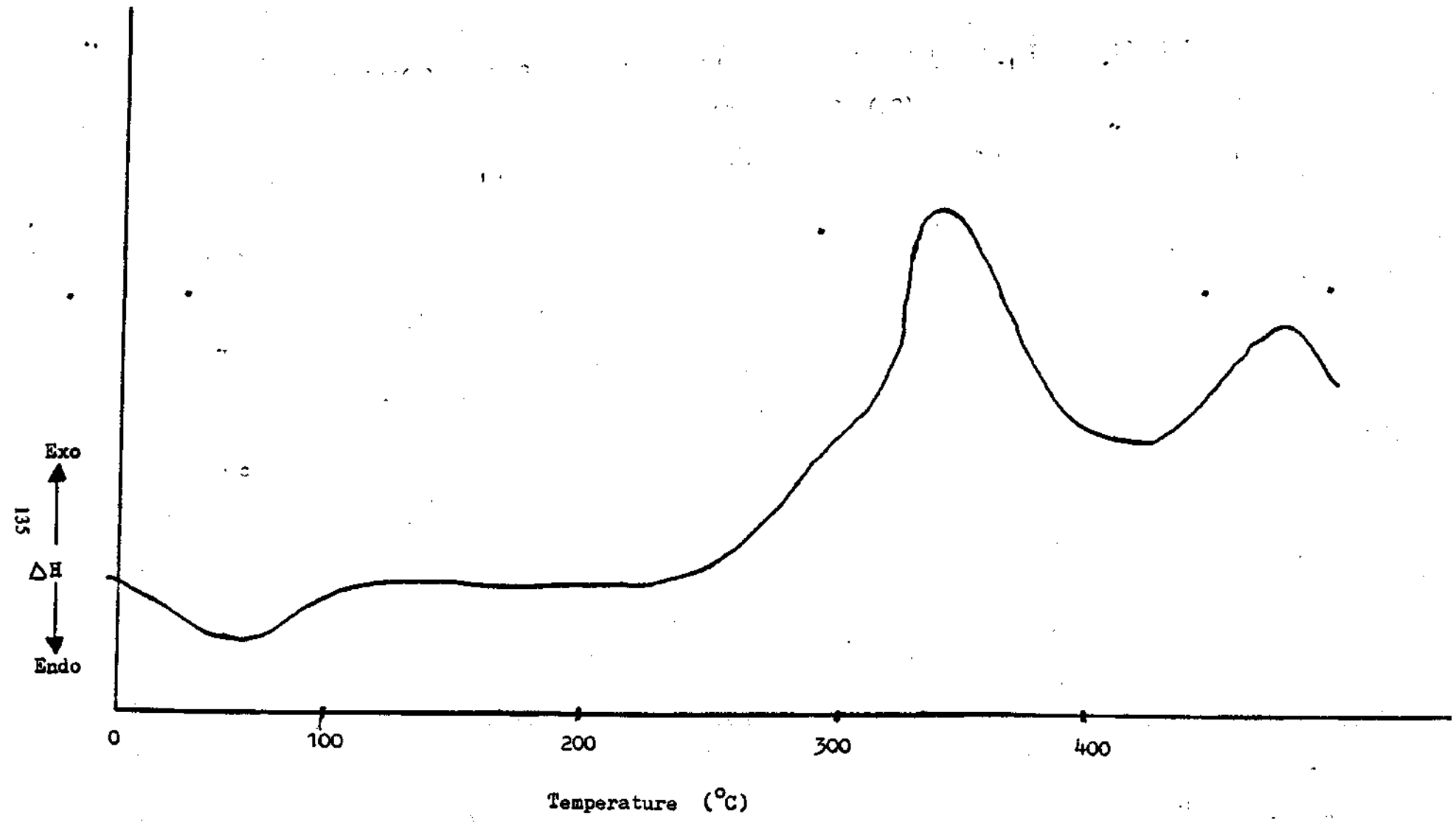


FIGURE 5.18(a): DTA curve of untreated Walnut wood at 10Kmin^{-1} in static air.

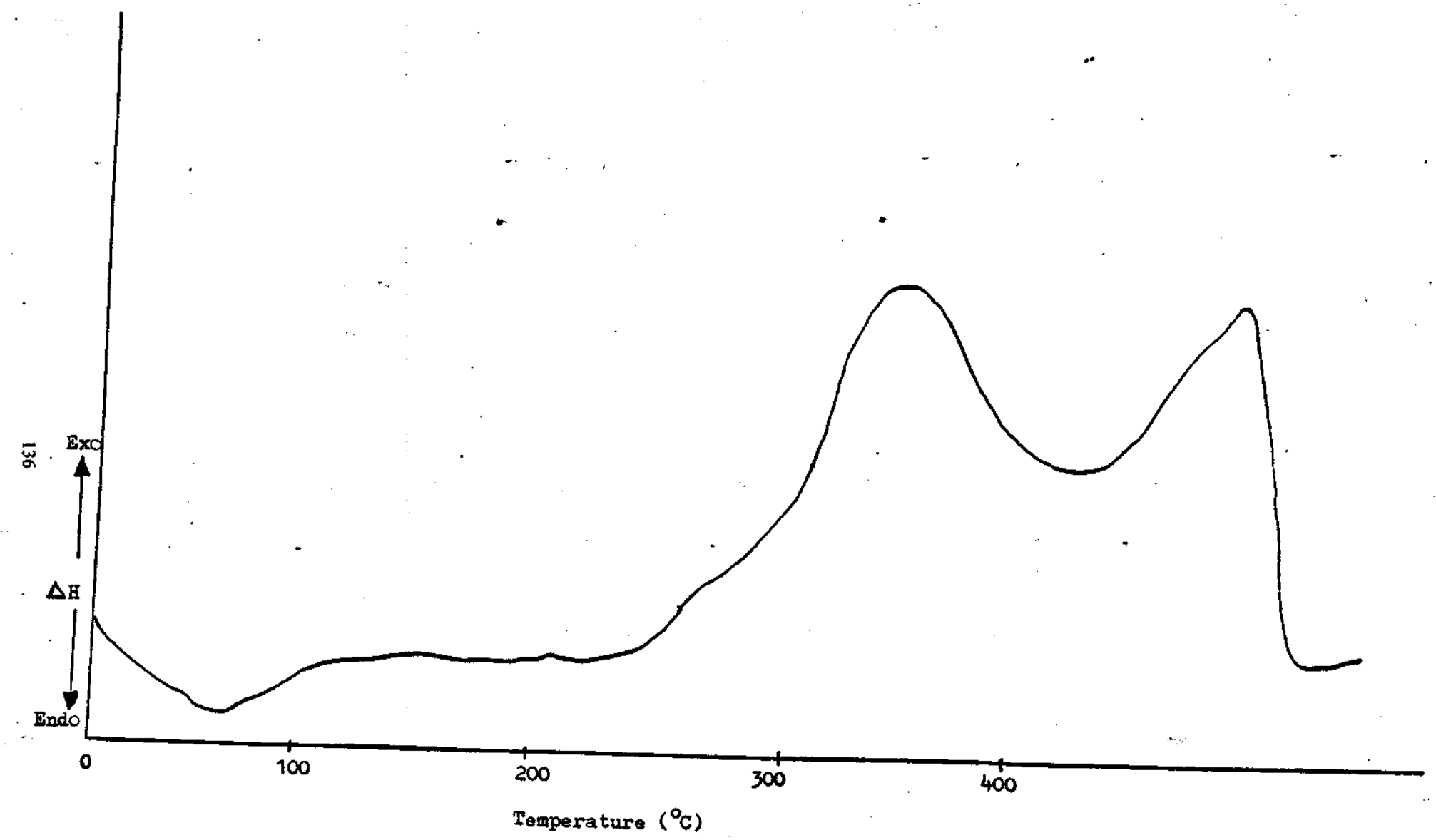


FIGURE 5.18(b) DTA curve of untreated Danta wood at 10Kmin^{-1} in static air.

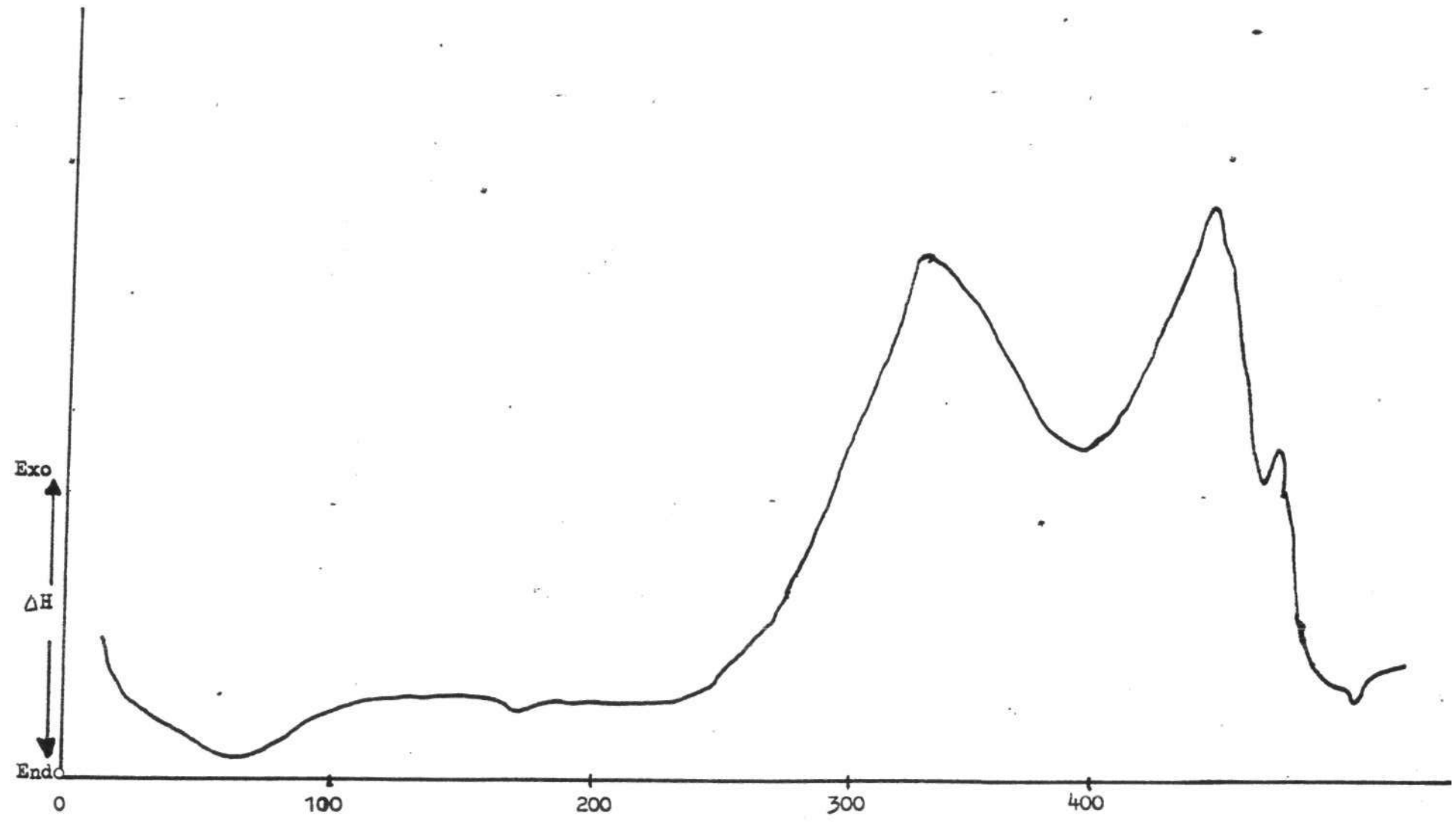


FIGURE 5.18 (c): DTA curve of untreated Obeche wood at 10Kmin^{-1} in static air.

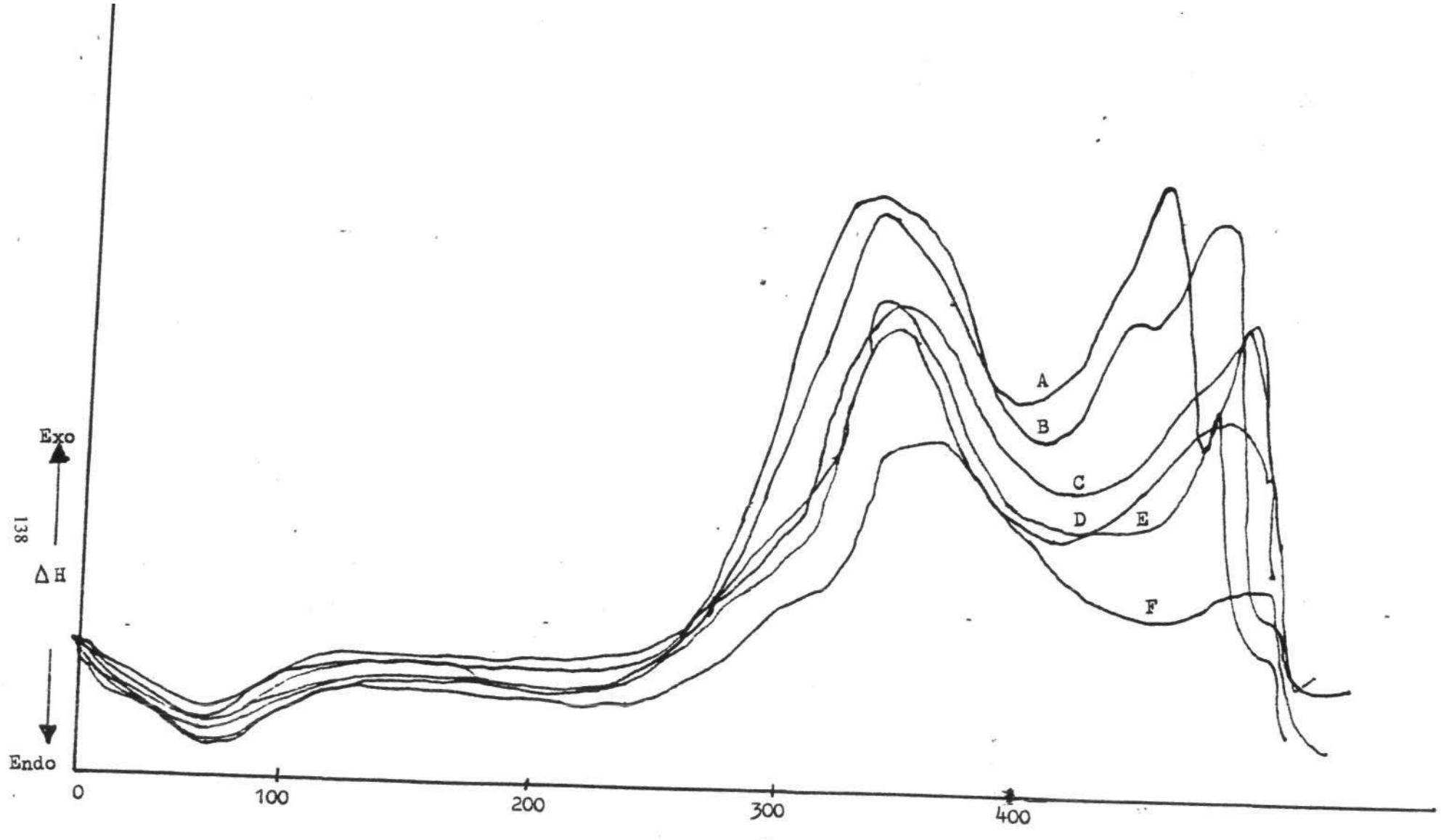


FIGURE 5.19 DTA analysis of various wood at 10Kmin^{-1} in static air, figure key; A = Obeche, B = Ayan, C = Danta, D = Walnut, E = Ekhimi, F = Opepe.

Table 5.8: Main Pyrolysis Temperatures at 10Kmin^{-1}

Sample	Stage	DTA CURVE			Nature of DTA peak
		T_{onset} ^{0}C)	T_{peak} (^{0}C)	T_{end}(^{0}C)	
Apa	1st	246	343	400	Exo-large
	2nd	400	450	-	"
Iroko	1st	249	348	394	"
	2nd	395	476	-	"
Ayan	1st	252	350	403	"
	2nd	403	471	500	"
Sapele	1st	251	345	395	"
	2nd	395	500	-	"
Guarea	1st	251	345	414	"
	2nd	414	500	-	"
Berlinia	1st	249	329	391	"
	2nd	391	436	454	"
Lagos	1st	251	345	412	"
	2nd	412	476	-	"
Walnut	1st	246	348	426	"
	2nd	426	500	-	"
Mansonia	1st	249	348	414	"
	2nd	414	436,500	-	"
Opepe	1st	251	355	452	"
	2nd	452	-	-	"
Danta	1st	249	345	421	"
	2nd	421	-	-	"
Ekhimi	1st	249	348	414	"
	2nd	414	-	-	"
W/Afara	1st	249	317	386	"
	2nd	386	452	478	"
Obeche	1st	246	338	400	"
	2nd	400	457	-	"

depolymerisation taken place, inparticular, the degradation of soluble hemicelluloses which is difficult to observe experimentally.

Probably, the first strong exothermicity in the temperature range 246-421^{0}C which peaks at about 329-350^{0}C for all wood corresponds to the decomposition/dehydration that results in the formation and evaporation of flammable volatile products. This may be followed with the flaming combustion of these volatiles. According to Kosik et al. (1982), flaming depends mainly on the concentration of volatile formed. The last large exotherm, peaking at around 470^{O}C, as usual indicates glowing combustion of the residual char, i.e., oxidation of the charred residue. As observed earlier, thermal decomposition of wood may have taken place through cleavage of the glucosidic group or by dehydration and breakdown of the anhydroglucose units. At low temperature some dehydration, elimination and breakdown of the sugar molecule results in gradual charring. This reaction takes place slowly until around 300^{O}C, when sufficient heat becomes available to induce a rapid cleavage of the glucosidic bond with evaporation of the products. This is possible because of the wood (cellulose) ability to undergo decomposition by at least two alternative pathways as discussed before and postulated by Kilzer and Broido (1965).

The differences in the previous studies reviewed by Beall (1971), and the current results or the small discrepancies between the wood curves in the investigations are not surprising since the composition of the wood of various species varies considerably. Moreover, different sample preparation techniques which sometimes cause disagreement in the results and create ambiguity when test results are compared. Also, any changes in sample mass can cause either a baseline drift or an instability (Beall, 1971). Furthermore, there is the necessity for maintaining a constant heating rate for the temperature interval of interest. A variation from linearity may produce an inflection in the differential output resembling that of a transition point. This is probably one of the troublesome effects observed from the equipment used.

5.4.4 DSC Studies

The reprsentative DSC - temperatures curves for the 14 wood types investigated are presented in Fig 5.20(a) - (c) and 5.21 and the various peak temperatures are provided in Table 5.9. Examination of the curves reveal that there are three major peaks for all the 14 species. The first peak, starts to appear at 30°C and reaches maximum at about 70°C as in DTA. It gave rise to a broad endothermic peak which could be traced to the removal of

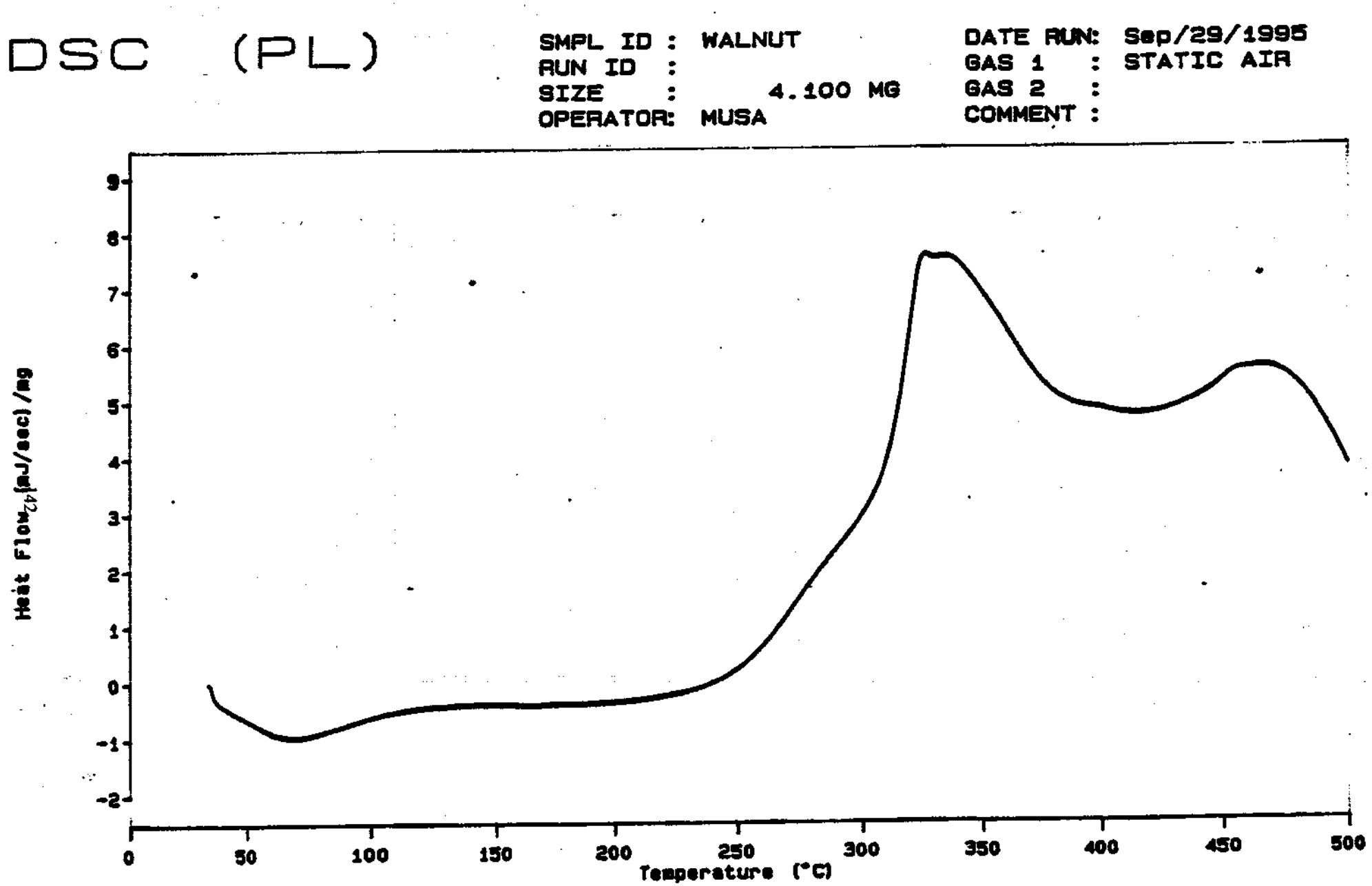


FIGURE 5.20(a): DSC curve of Walnut wood at 10K/min in air.

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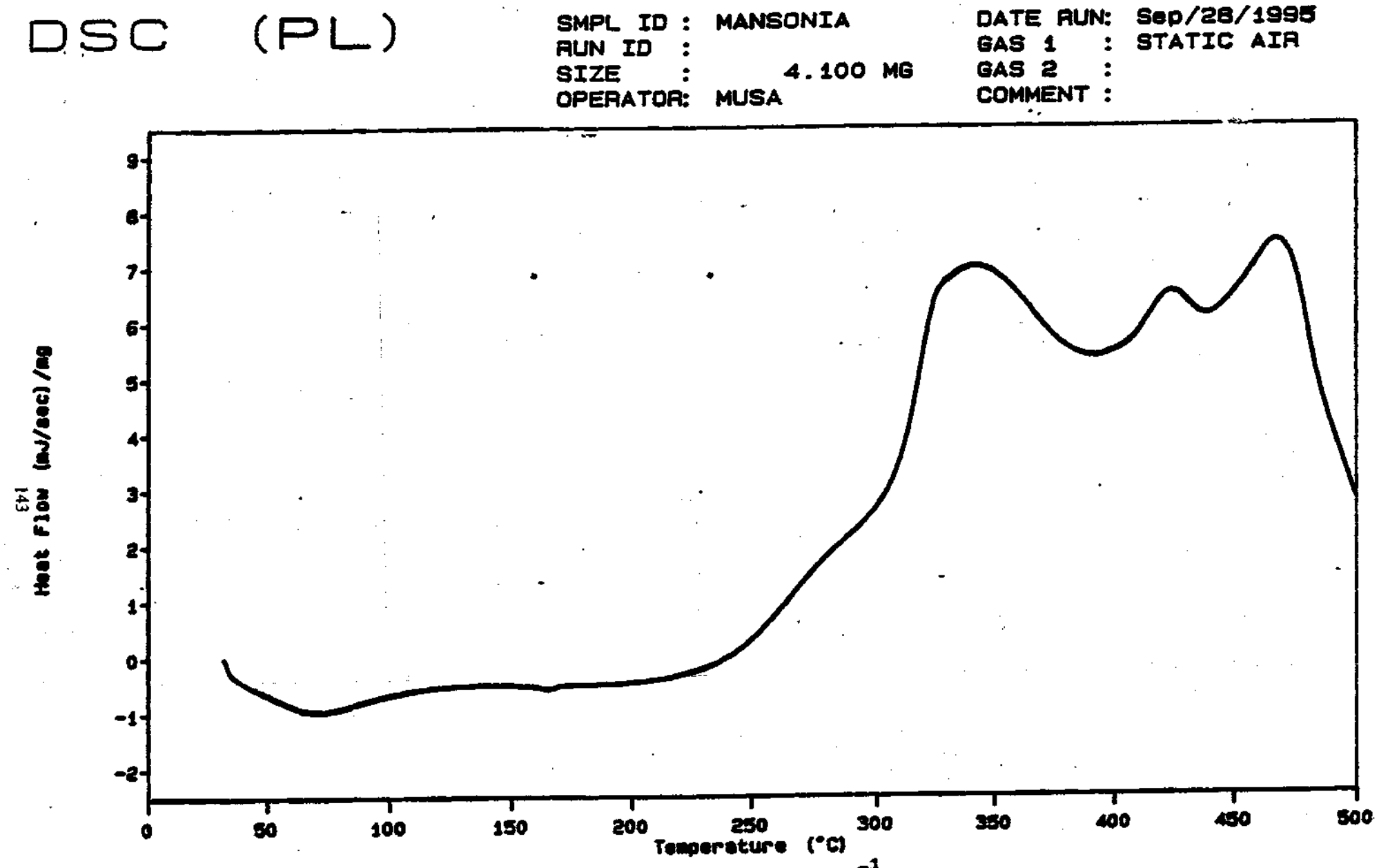


FIGURE 5.20(b) DSC curve of Mansonia wood at 10Kmin^{-1} in air.

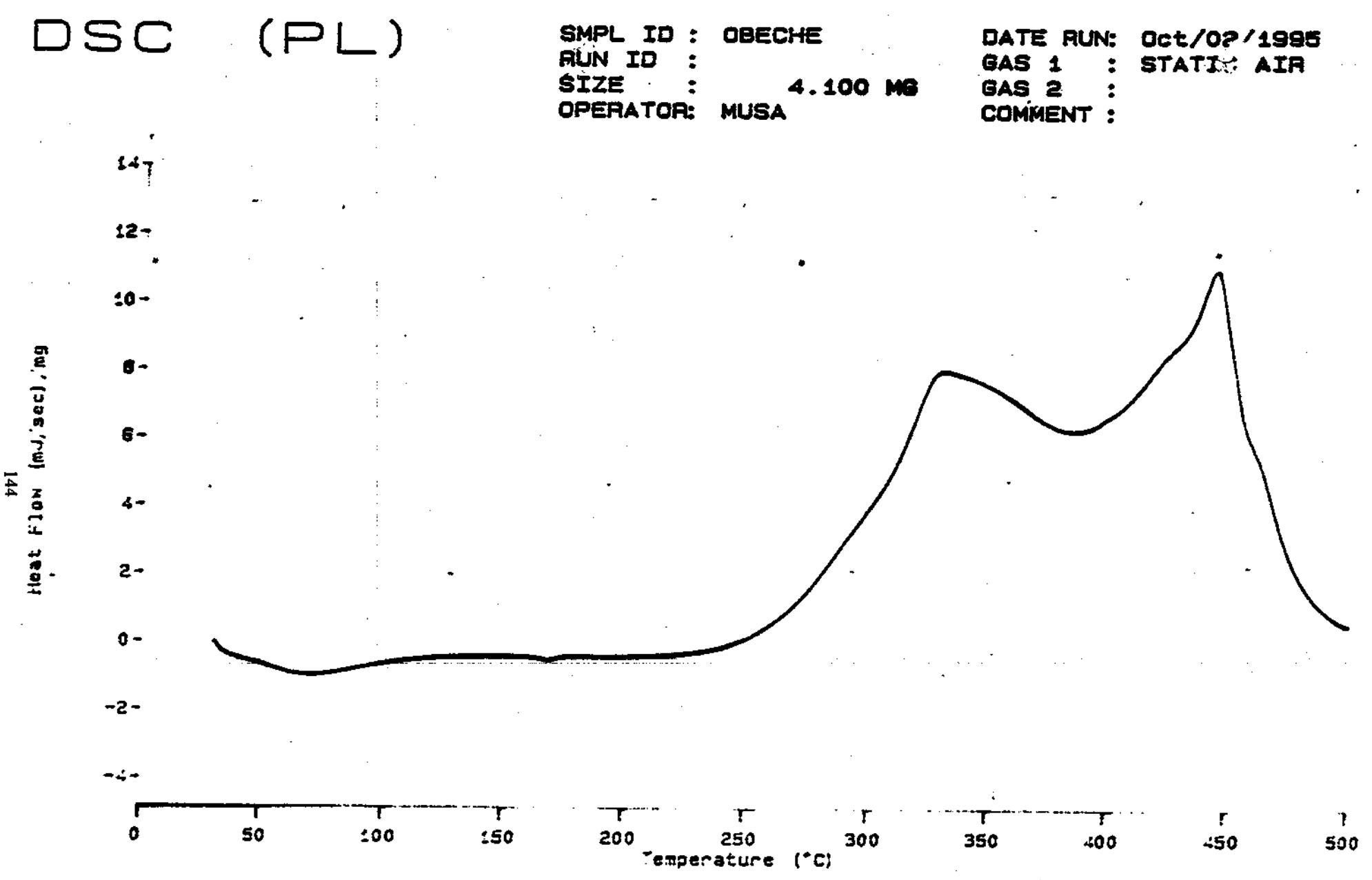


FIGURE 5.20(c): DSC curve of Obeche wood at 10Kmin^{-1} in air.

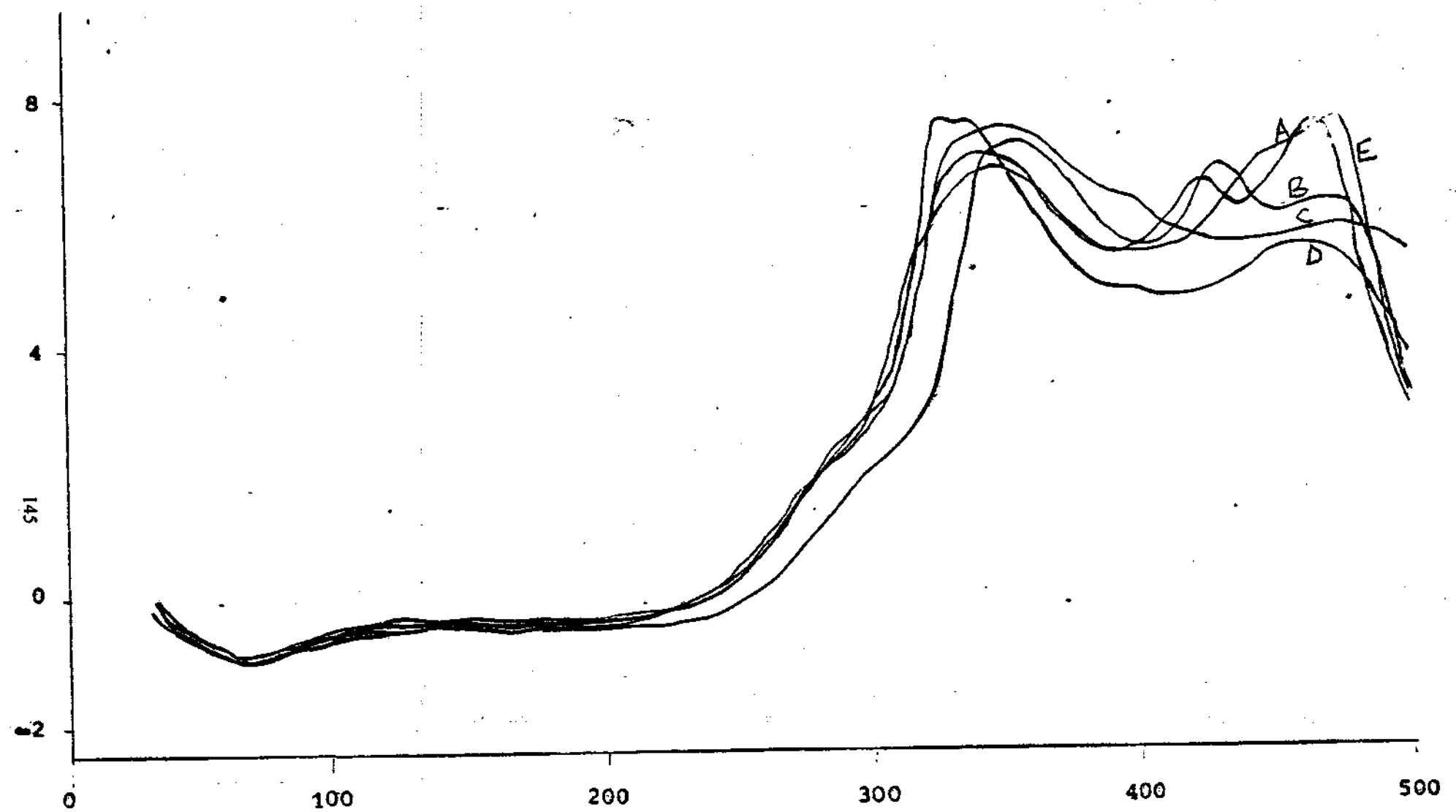


FIGURE 5.21: Combine DSC curves for some timbers; Figure key: A = Mansonia, B = Ayan, C = Opepe, D = Walnut, and E = Danta.

Table 5.9 Peak Temperatures in the DSC Curves for Wood Samples in Static air at $10^{O}C\ min^{-1}$

Sample	Initiation Temp (^{o}C)	Peak Temp (^{o}C)	Termina-tion Temp. (^{o}C)	Nature of the Peak.
Apa	283.6	322.0,351.44	378.5	Exo-Broad
	378.5	8.6	500.0	Exo large
Iroko	290.9	329.2,343.1	380.5	Exo-broad
	380.5	408.5	430.2	Exo-large
	430.2	461.0	500.0	Exo large
Ayan	313.7	353.7	400.0	Exo large
	400.0	430.0	450.5	Exo-large
	450.5	470.2	-	Exo large
Sapele	297.6	338.4	387.5	Exo large
	387.5	415.5	431.8	Exo-large
	431.8	465.1	500.0	Exo-large
Guarea	292.5	338.2	400.0	Exo large
	400.0	450.0,469.0	-	Exo broad
Berlinia	266.3	329.1,350.0	372.5	Exo broad
	372.5	431.7	450.7	Exo broad
	450.1	461.7	500.0	Exo Small
Lagos	295.9	335.9	382.4	Exo-large
	382.4	420.0	435.7	Exo-large
	435.7	460.0	500.0	Exo-large

Table 5.9: Continued

Sample	Initiation Temp (°C)	Peak Temp (°C)	Termina-tion Temp. (°C)	Nature of the Peak.
Walnut	302.8	325.9,340	400.0	Exo-large
	400.0	458.7	-	Exo-large
Mansonia	298.8	342.2	390.0	Exo-large
	390.0	425.4	440.0	Exo-large
	440.0	467.5	-	Exo-large
Opepe	303.6	347.3	430.0	Exo-broad
	430.0	477,4	-	Exo-large
Danta	287.1	343.9	400.1	Exo-large
	400.1	440.7,473.3	500.0	Exo-large
Ekhimi	295.1	339.4	408.5	Exo-large
	408.5	49.1	-	Exo-large
W,Afara	260.5	316.2	375.1	Exo-large
	375.1	413.7	435.5	Exo-large
	439.9	448.2	500.0	Exo-small
Obeche	283.5	329.9	380.6	Exo-large
	380.6	444.5	500.0	Exo-large
	400.1		-	

moisture from the wood. The second stage starts at about 260°C and peak occurred around 330.0 - 351.8°C and is exothermic for all the wood. The peaks do not indicate any discernible difference between species and is directly related to the degradation of hemicelluloses and cellulose

(Shafizadeh, 1968; Woo and Schniewind, 1987; Fairbridge et al., 1988). The thermal degradation of cellulose and lignin, however, may also contribute to this second peak reaction by depolymerisation of lignin and the amorphous regions of cellulose (Beall, 1971). In some of the species this second peak may possibly be enhanced by the presence of extractives which are degraded or polymerised at this temperature.

Kilzer and Broido (1965), and Bradbury et al. (1979), proposed that during this dehydration stage, cellulose decomposes by two competitive first-order reactions one yielding volatile (especially levoglucosan) and the other char and a gaseous fraction. Antal and Varhegyi (1995), however, casts doubt on these latter competing reactions and proposed that char is formed solely as a consequence of secondary volatile-solid interactions whose efficiency depends on the ability of the volatile to be retained by the decomposing cellulose mass. Over the region of present interest (260-400°C) the results appear inadequate to demonstrate any significant difference. All that can be said is that the present results are in agreement with the former view.

The third peaks reach their maximum at 408.5 - 459°C. This supports the possibility of oxidation of volatiles and the char. In some of the wood -

Iroko, Ayan, Sapele, Berlinia, Lagos and Mansonia there is a fourth peak at about 470°C. This may further indicate the above char oxidation.

5.5 BURNING BEHAVIOUR OF WOODS

5.5.1 LOI Values of Selected Woods

LOI values have been widely used for assessing the flammability of polymers. With wood, LOI values are generally between 22% and 35% (Alhaji, 1993). Thus, wood materials are difficultly flammable compared with most other polymeric materials.

In this work, the LOI values obtained for the different wood species as shown in Table 5.10 are between 22.4% to 31.7%, indicating that the selected tropical wood have inherent flame tolerance or resistance. Obeche has the lowest LOI value of 22.4%. Berlinia has the highest of about 31.7%. The rest lie within this range. The wide variability of LOI values among the wood is not unexpected. It is probably attributed to the different structural compositions and moisture content of the test specimens. However, attempts were made to ensure that the moisture content for the specimens were within the prescribed limits. It is also possible that the results could be affected by

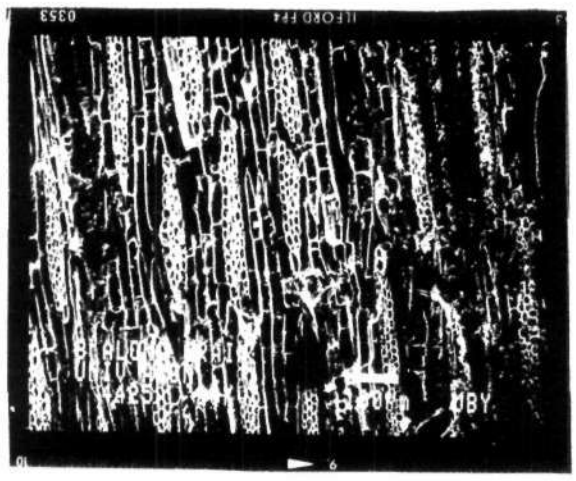
Table 5.10: LOI Values of Wood

Wood	LOI (O_2 %)
Apa	26,5
Iroko	27.4
Ayan	26.4
Sapele	24.7
Guarea	24.3
Berlinia	31.7
Lagos	25.9
Walnut	23.4
Mansonia	25.O
Opepe	27.8
Danta	23.6
Ekhimi	22.5
W.Afara	26.9
Obeche	22.4

numerous unexplained outside factors (environment/room conditions, experimental errors, etc) other than the materials inherent flammability. Moreover, in the course of test it was observed that the burning behaviour of most wood was erratic. In fact, the candle like-burning criterion was difficult to realise with some wood samples. In some cases, it was difficult to distinguish between weak slow flame and an afterglow so that erroneous results may be obtained in such cases. To avoid erratic results, several specimens (5-1O) were used per wood test.

5.6 SEM Studies

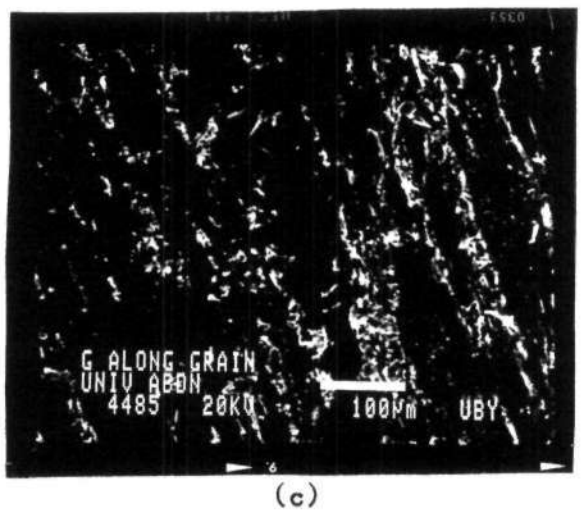
When viewed in SEM micrographs, untreated wood specimen is seen as having striations, voids and lacunae which in some samples coalesce to form network structure (Figs. 5.22 and 5.23). Thus, at X800 magnification, the micrograph reveal network wood structure although some fibrils are visible. However, at X1600 magnification the fibrils are clearly visible. These fibrils are potential reactive sites for a chemical reaction to take place with wood components.



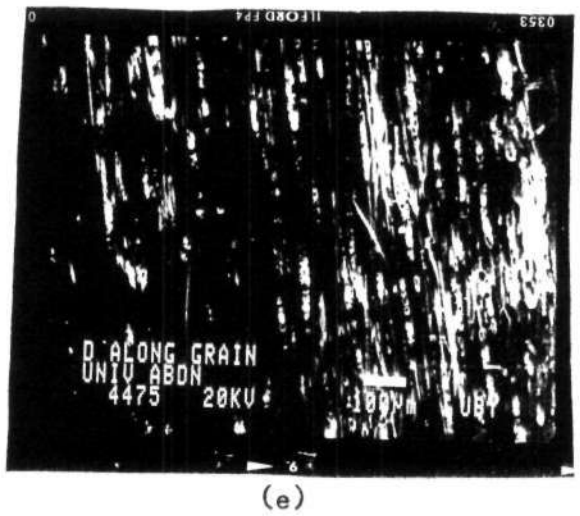
(a)



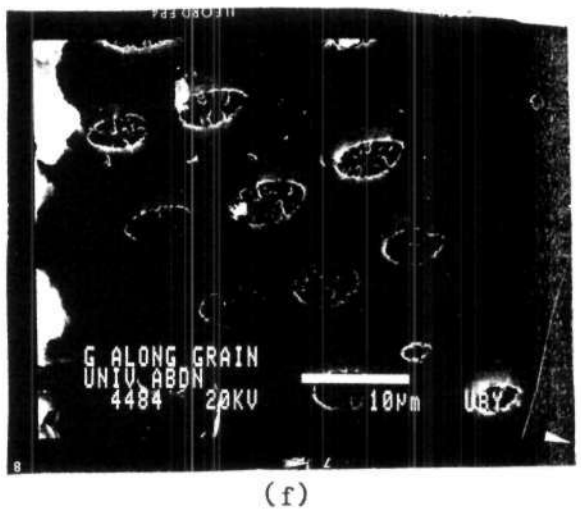
(b)



(c)



(e)



(f)

FIGURE 5.22: Scanning electron micrographs of wood (along grain) (a) Sapele at 800x, (b) at 1600x; (c) Berlinia at 800x, and (e) White afara at 800x and (f) at 1600x.

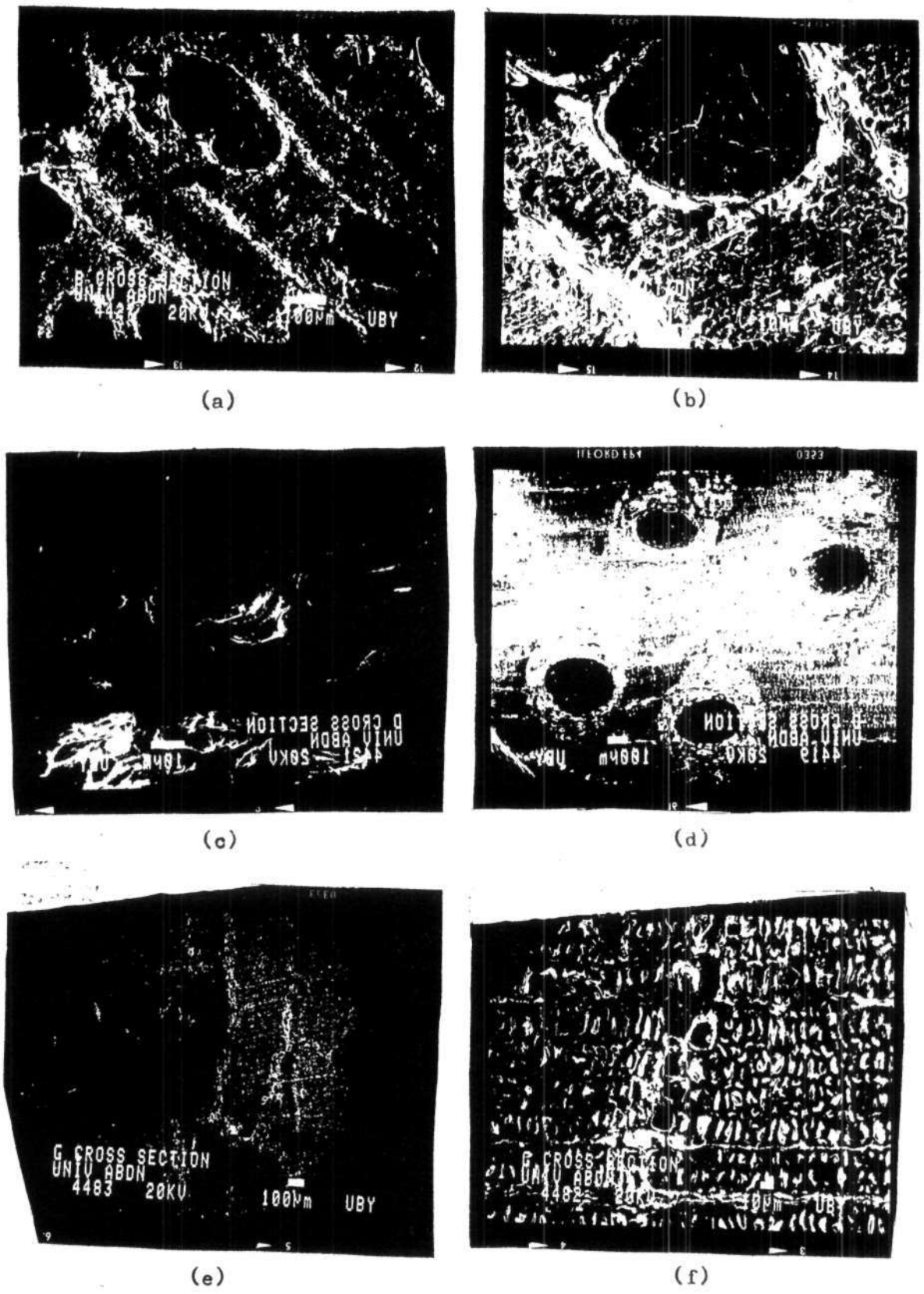


FIGURE 5.23: Scanning electron micrographs of wood (cross-section), (a) Sapele at 800x, (b) at 1600x; (c) Berlinia at 800x, (d) at 1600x and (e) White afara at 800x and (f) at 1600x.

CHAPTER SIX

RESULTS AND DISCUSSIONS (II): EFFECTS OF FLAME RETARDANTS ON THERMAL AND BURNING BEHAVIOUR OF WOODS

6.1 INTRODUCTION

Normal combustion of wood produces highly flammable gases which further support the combustion process (Shafizadeh, 1984, 1968, 1971; Browne, 1958; Peschek, 1930). Thus the wood is eventually converted to the major gaseous products of carbon monoxide, carbon dioxide, and water. In order to prevent this complete combustion, fire retardant chemicals are introduced into the wood structure such that when wood is exposed to flames or very high temperatures, the decomposition products are carbonaceous materials, i.e. char, and water, which do not support further combustion (Browne, 1958; LeVan, 1984; Shafizadeh and Chin, 1977). Thus, since flame retardant treated wood is gaining more acceptance every year it is necessary that the effects of flame-retardant on the physical, chemical, and mechanical properties of wood and how chemical treatment can prevent or retard flammability should be studied in order to provide sufficient information for safe use in wooden structures.

As already mentioned, the burning process of wood involves different stages which include (a) the heating of the flammable substrate (wood), (b) its subsequent degradation and decomposition, (c) the ignition of the flammable gases evolved, and (d), their continued self combustion/flame propagation. Normally, an efficient flame-retardant will operate by interfering with one or more of these steps either in a physical or a chemical way and the end result is the retardation and final elimination of the burning process mechanism. This can be accomplished in a variety of ways as has been outlined in chapter 2.

In chapter 5 it has been shown that under burning conditions tropical hardwood decomposes rapidly and produce a large amount of flammable volatiles, resulting in high flammability of these wood. This chapter covers the effectiveness of a number of possible flame-retardants to retard tropical wood flammability and discusses the probable mechanism involved in their flame-retarding action.

6.2 EFFECT OF ALUM AND FERTILIZER ON LAMMABILITY PROPERTIES

In section 5.2., it was reported on the flammability properties viz.- ignition time, flame rate, afterglow and char formation. The results showed that these burning parameters vary widely in accordance to the properties of

the wood itself, the conditions of temperature (thermal properties), sample geometry and the environment under which burning occurs. It is believed that these parameters may be altered greatly by the presence of retardants or combustion catalysts impregnated in the wood or on its surface.

In this section, the effect on burning parameters of impregnation with inorganic chemicals - potassium aluminum sulphate and supper phosphate, hereafter referred to as alum and fertiliser respectively, are reported.

6.2.1 Ignition Time and Burning Properties

Alum and fertiliser increased the ignition times of the wood (Table 6.1.) compared to the untreated control. Comparing their effectiveness, fertiliser treatment registered a higher ignition time for nine of the wood samples while alum treatment registered higher values for the other five samples.

Burning Rate:- Both the alum and fertiliser treated wood samples under went retarded burning compared to the respective untreated samples. As shown in Table 6.1., the alum treated samples generally have higher burning rates when compared to the fertiliser treated. Both were however, observed to burn at a marginally slower rate than the untreated control samples.

Table 6.1. Combustion Properties of Woods With Alum and Fertiliser Flame Retardants.

WOOD	FLAME RETARDANT (10% Conc.)	IGNITION TIME Sec.	BURNING RATE mms^{-1}	AFTERGLOW TIME, Sec.
Apa	-	10.0	1.8	49
Apa	Alum	10.5	1.6	-
Apa	Fertiliser	17.6	1.8	38
Iroko	-	9.0	2.0	612
Iroko	Alum	11.8	1.6	-
Iroko	Fertiliser	12.0	1.8	110
Ayan	-	7.0	2.1	160
Ayan	Alum	7.4	1.7	-
Ayan	Fertiliser	11.7	1.7	20
Sapele	-	9.0	1.4	133
Sapele	Alum	14.1	1.2	-
Sapele	Fertiliser	11.4	1.4	82
Guarea	-	6.0	1.9	65
Guarea	Alum	9.2	1.6	-
Guarea	Fertiliser	11.3	1.7	43
Berlinia	-	8.0	1.6	29
Berlinia	Alum	11.8	1.5	-
Berlinia	Fertiliser	14.9	1.4	20
Lagos	-	6.0	2.4	274
Lagos	Alum	12.5	2.0	-
Lagos	Fertiliser	6.9	2.1	85

Table 6.1. (CONTINUED)

WOOD	FLAME RETARDANT (10% Conc.)	IGNITION TIME Sec.	BURNING RATE mms^{-1}	AFTERGLOW TIME, Sec.
Walnut	-	6.0	1.9	46
Walnut	Alum	10.6	1.2	-
Walnut	Fertiliser	7.0	1.4	20
Mansonia	-	6.0	2.7	185
Mansonia	Alum	11.8	2.4	-
Mansonia	Fertiliser	12.6	2.3	11
Opepe	-	9.0	2.1	1
Opepe	Alum	12.0	1.6	-
Opepe	Fertiliser	12.1	1.6	-
Danta	-	10.0	1.9	148
Danta	Alum	11.8	1.6	-
Danta	Fertiliser	13.5	1.4	-
Afara	-	5.0	2.5	328
Afara	Alum	10.9	1.7	-
Afara	Fertiliser	8.4	1.8	115
Obeche	-	3.0	2.4	408
Obeche	Alum	9.0	1.7	-
Obeche	Fertiliser	2.7	2.2	23
Ekhimi	-	5.0	2.3	94
Ekhimi	Alum	8.6	1.9	-
Ekhimi	Fertiliser	11.4	1.8	20

Afterglow Time:- The alum treated samples did not show afterglow at all. Fertiliser decreased the afterglow time of the woods to 1 - 25sec. from 6-612 sec. (Table 6.1) for the untreated wood samples.

When combustion surface is exposed to fire, an efficient flame-retardant, among the various requirements, should prevent flaming and should preferably reduce the rate of degradation and charring; it should reduce ignitability and prevent afterglow. Hence, the above results clearly indicate that alum and fertiliser are acting as flame-retardants for these wood samples.

The differences observed in the flammability parameter values for the wood samples under similar burning and testing conditions (Table 6.1) are not unexpected as they can be attributed to the submicroscopic or chemical structure of wood as explained later.

6.2.2 Effect of Retardant Concentrations

The results shown in Figures 6.1 - 6.5 indicate that the flame inhibition properties is dependent upon the concentration of the alum and/or fertiliser solution while the results of the percentage add-on with additives concentration typified by Figure 6.6 , indicate that as the concentration of the dope increases, more of the salt is absorbed by the wood sample.

Generally, under atmospheric pressures the impregnation stage involves both the liquid penetration (capillary pressure action) into the wood cavities and the diffusion of dissolved chemicals. The capillary action takes place in the very small cell lumens and passage through unaspirated pit

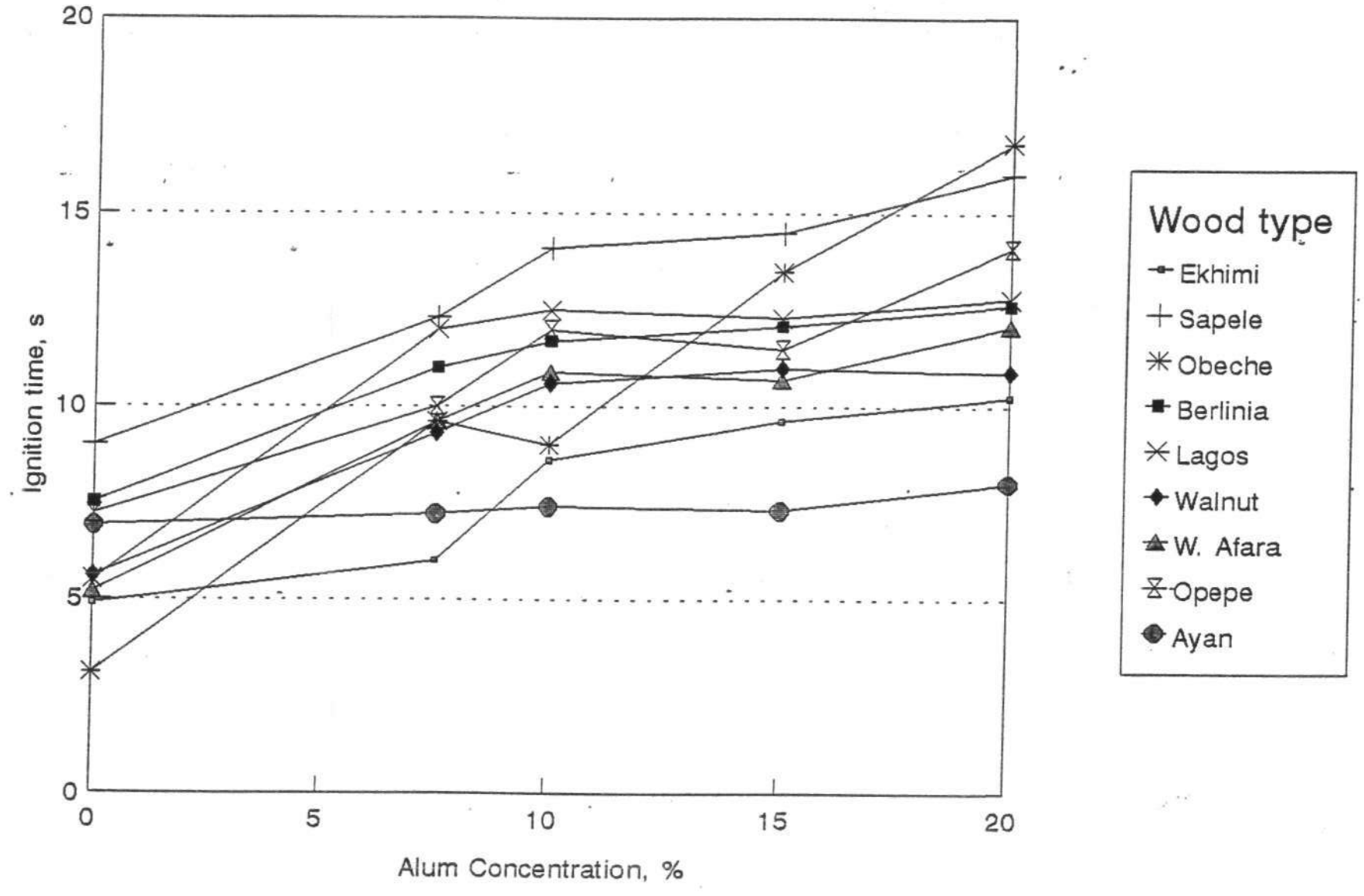


FIGURE 6.1: Effect of Alum concentration on ignition time for various wood.

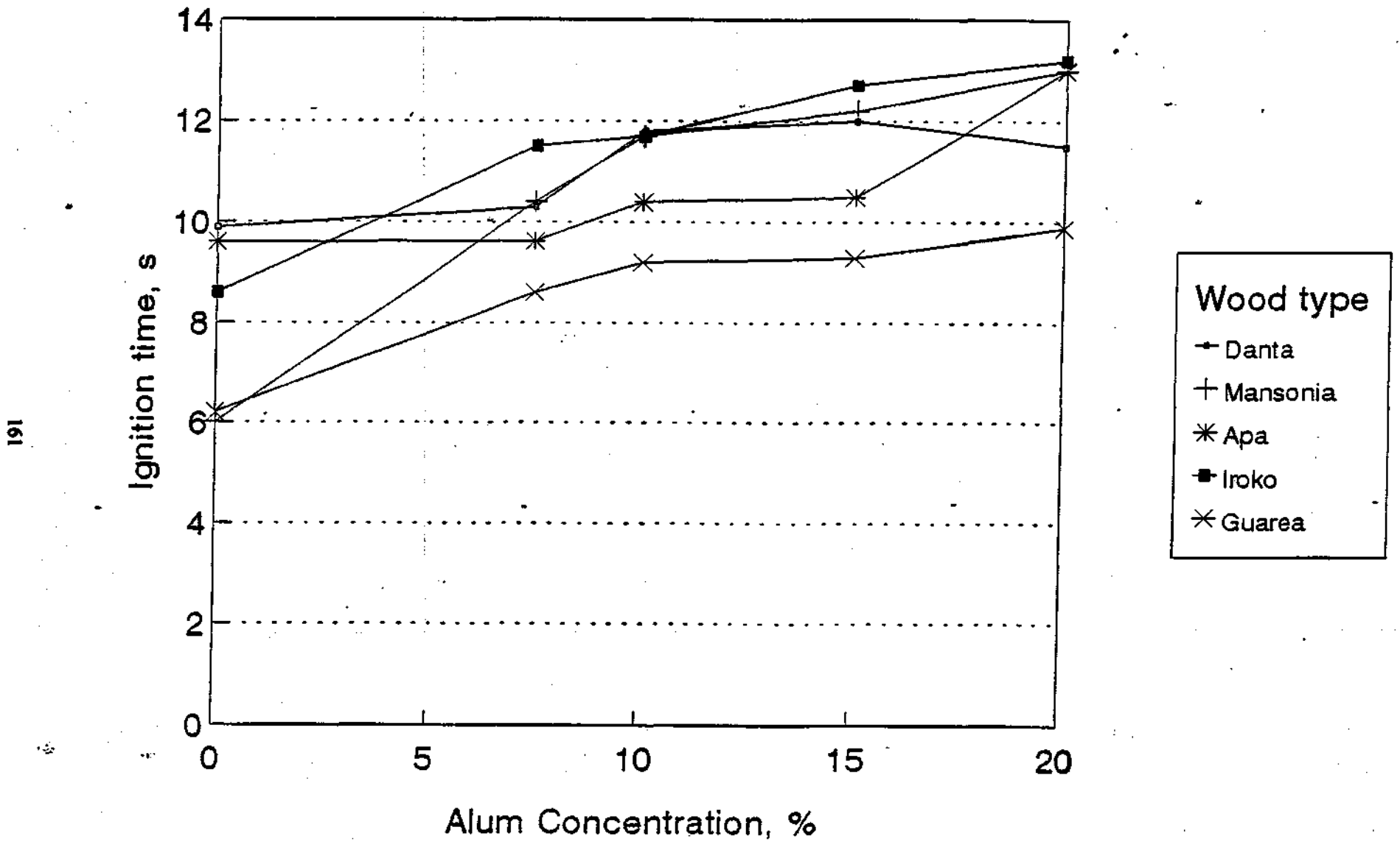


FIGURE 6.1: Effect of Alum concentration on ignition time for various wood.

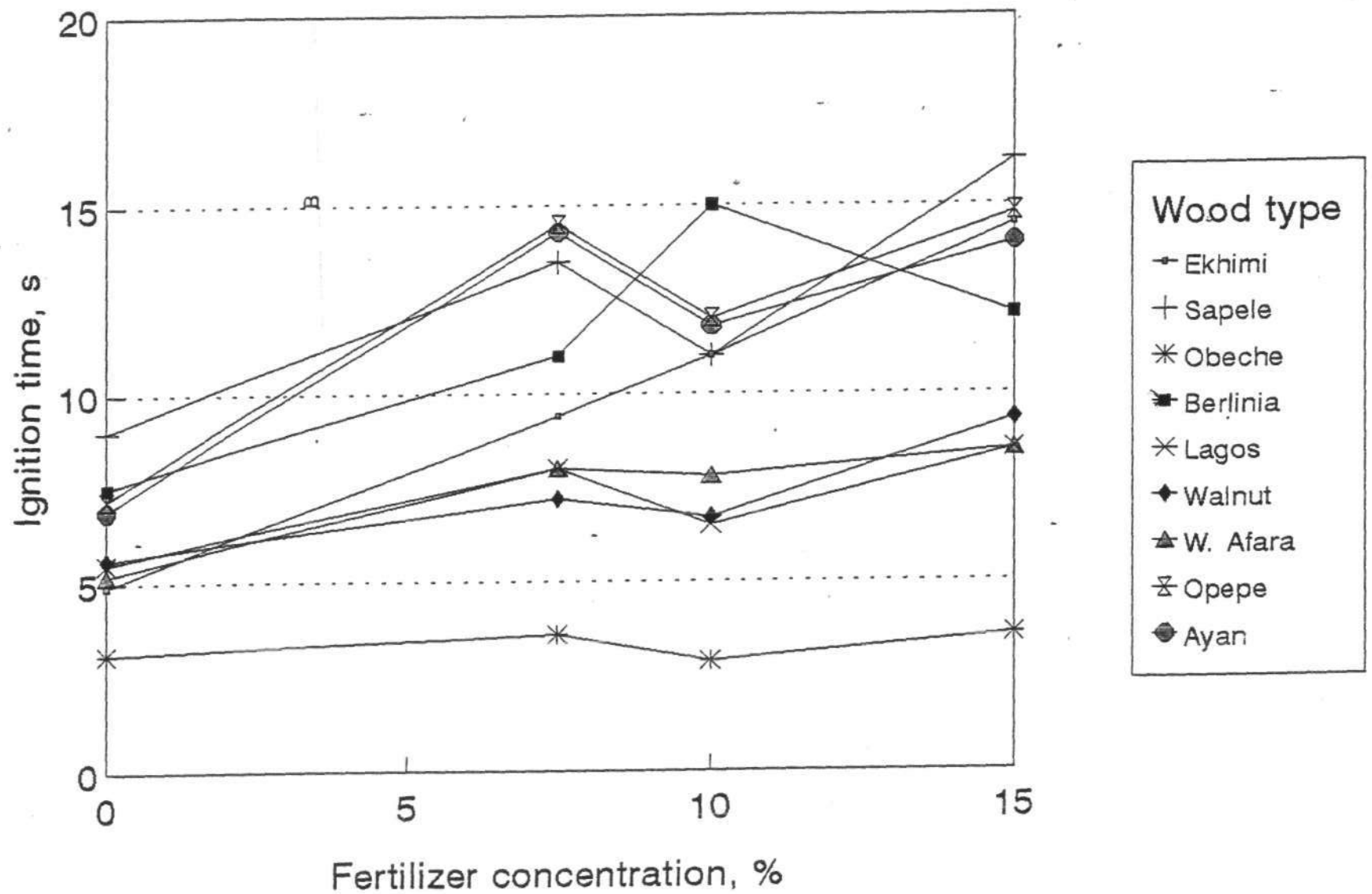


FIGURE 6.2: Effect of fertilizer concentration on ignition time for various wood.

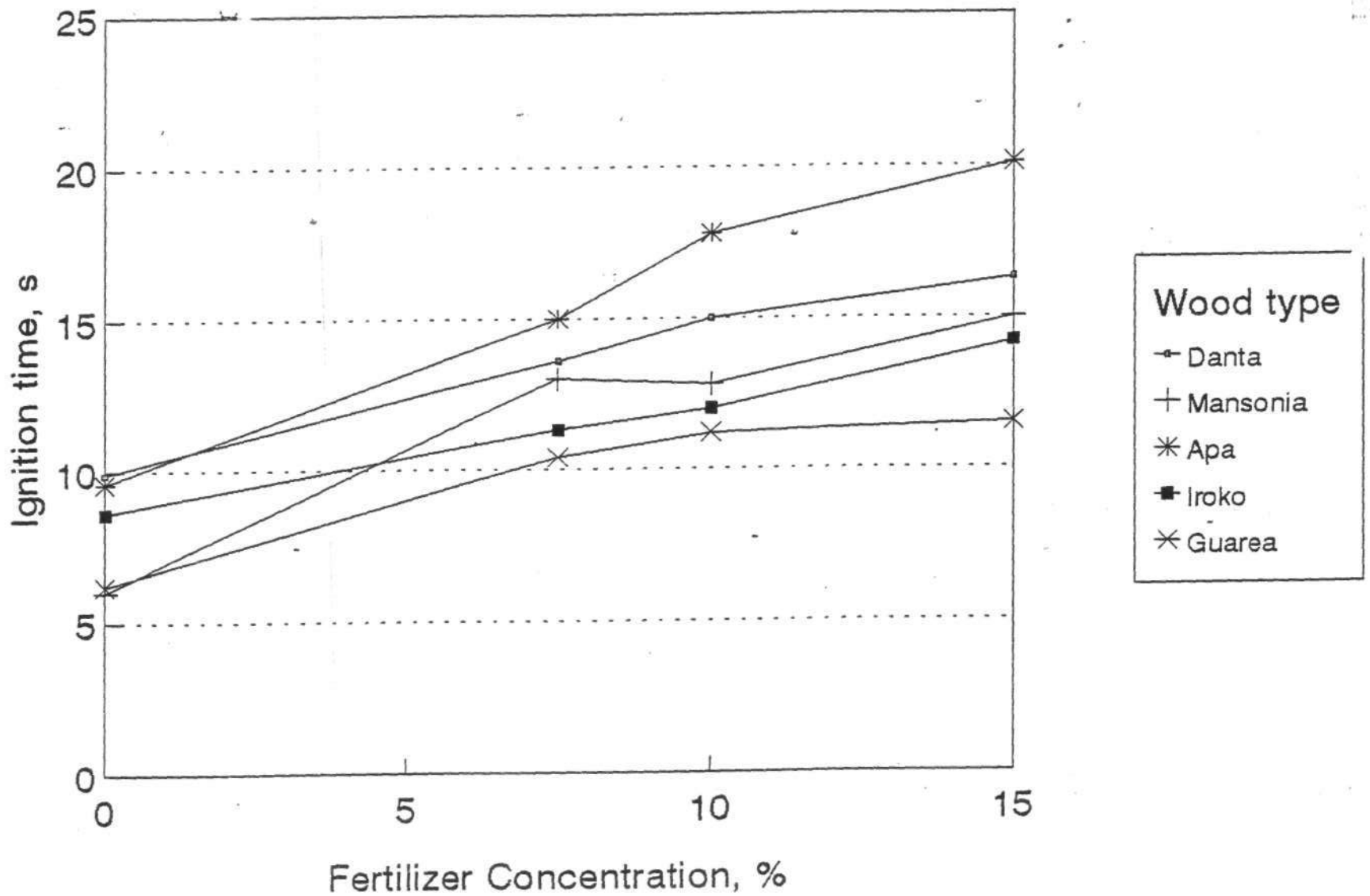


FIGURE 6.2: Continued.

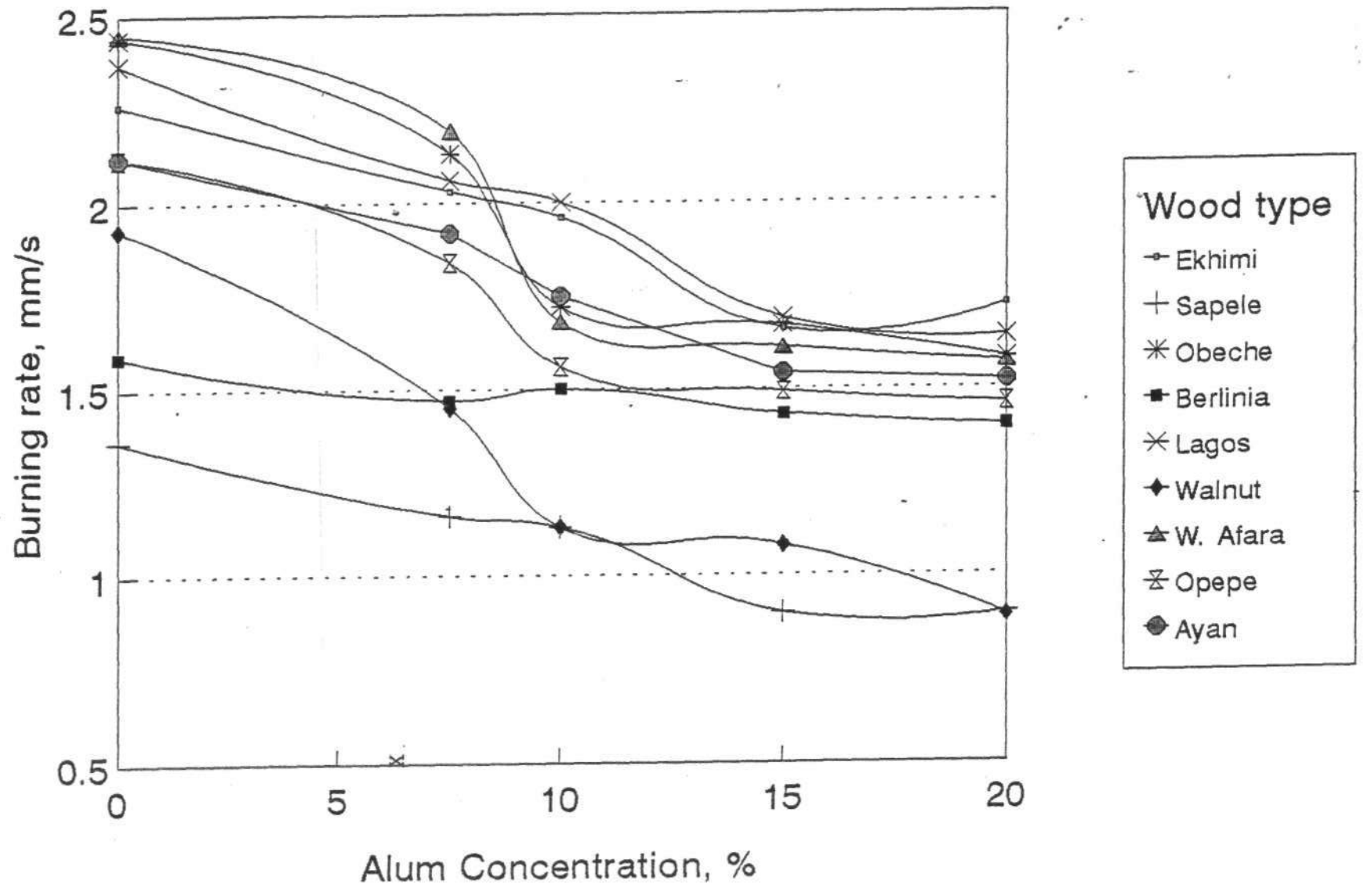


FIGURE 6.3: Effect of Alum concentration on Burning rate for various wood.

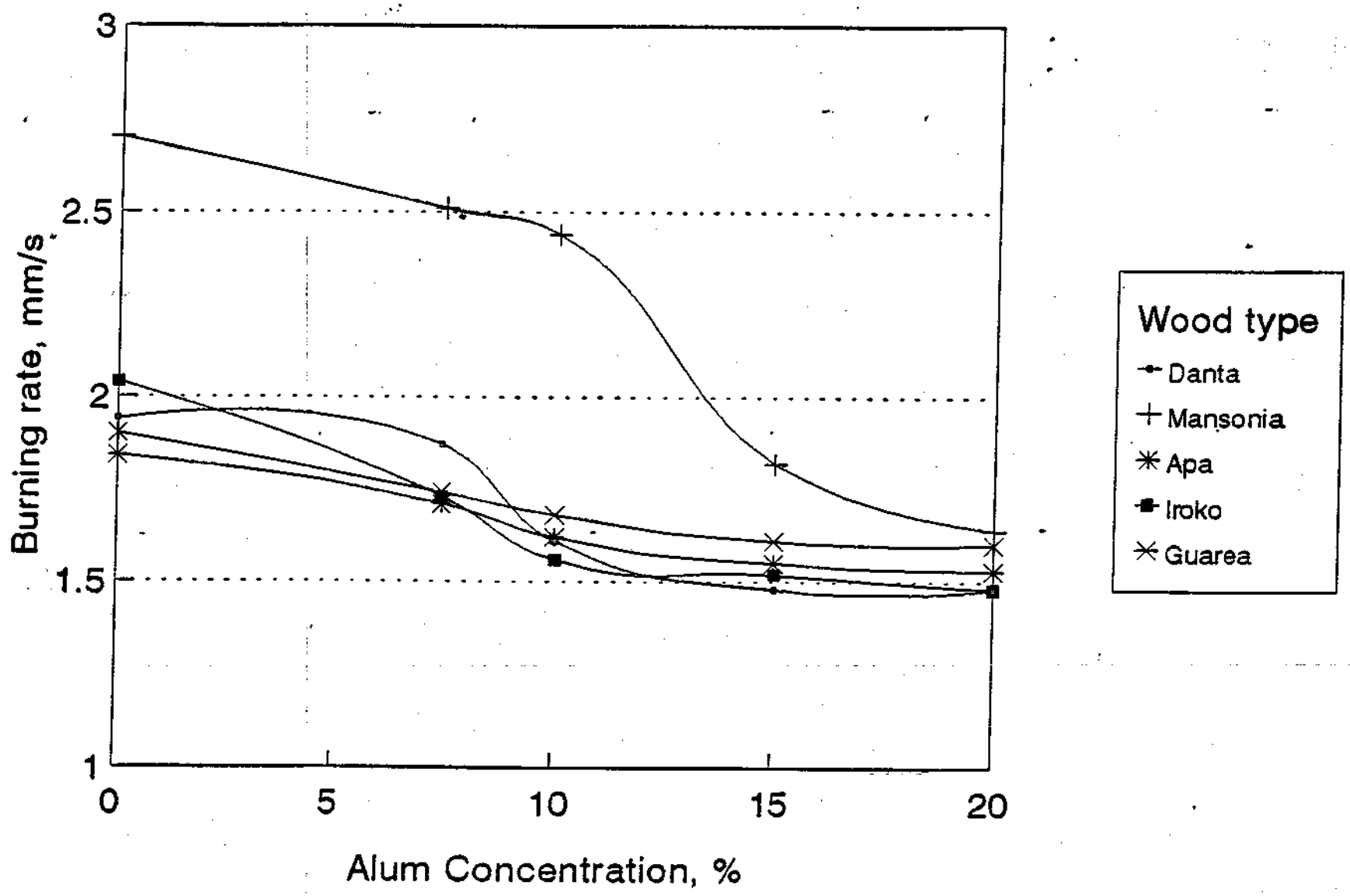


FIGURE 6.3: Continued.

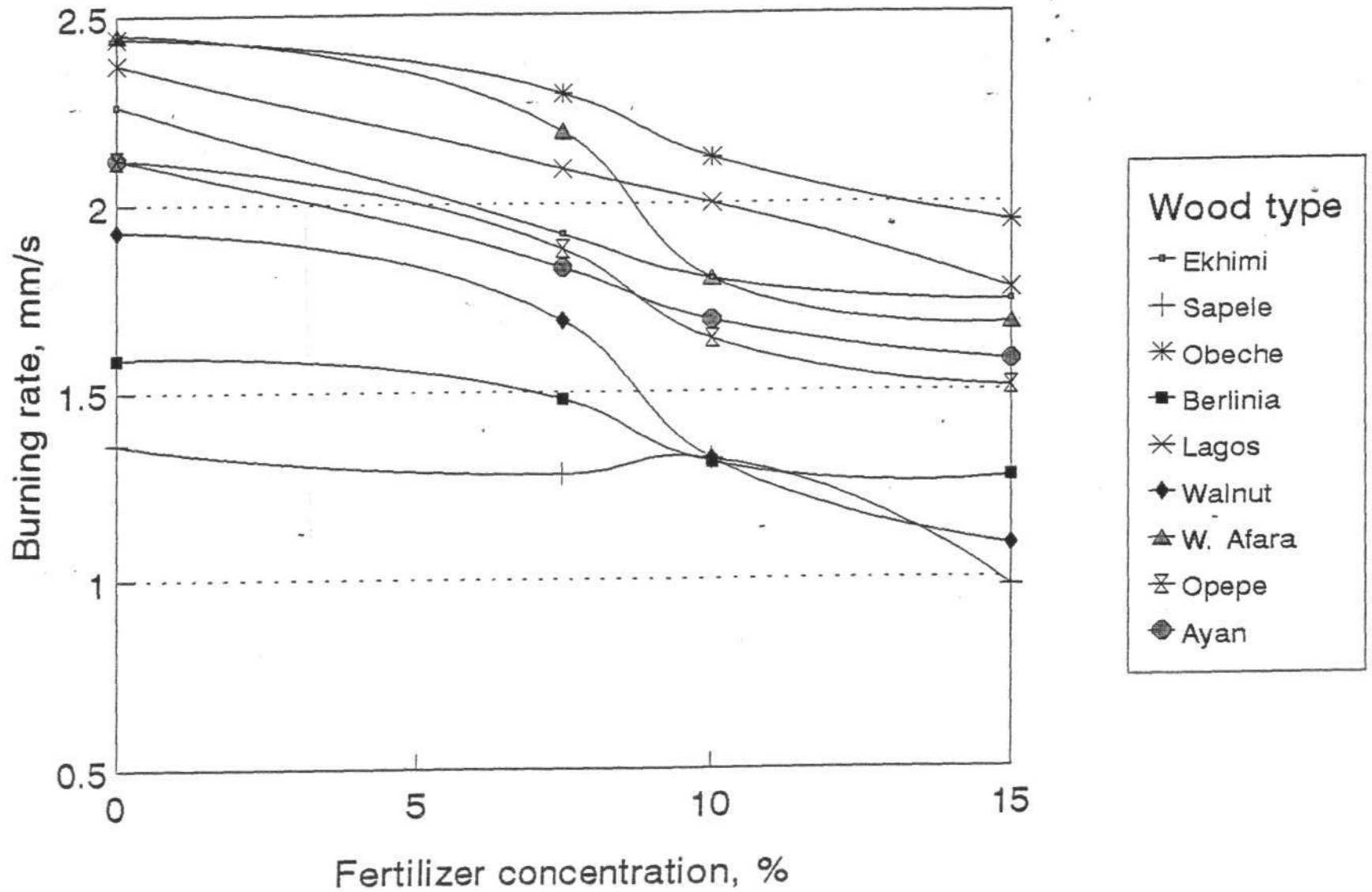


FIGURE 6.4 Effect of fertilizer concentration on Burning rate for various wood.

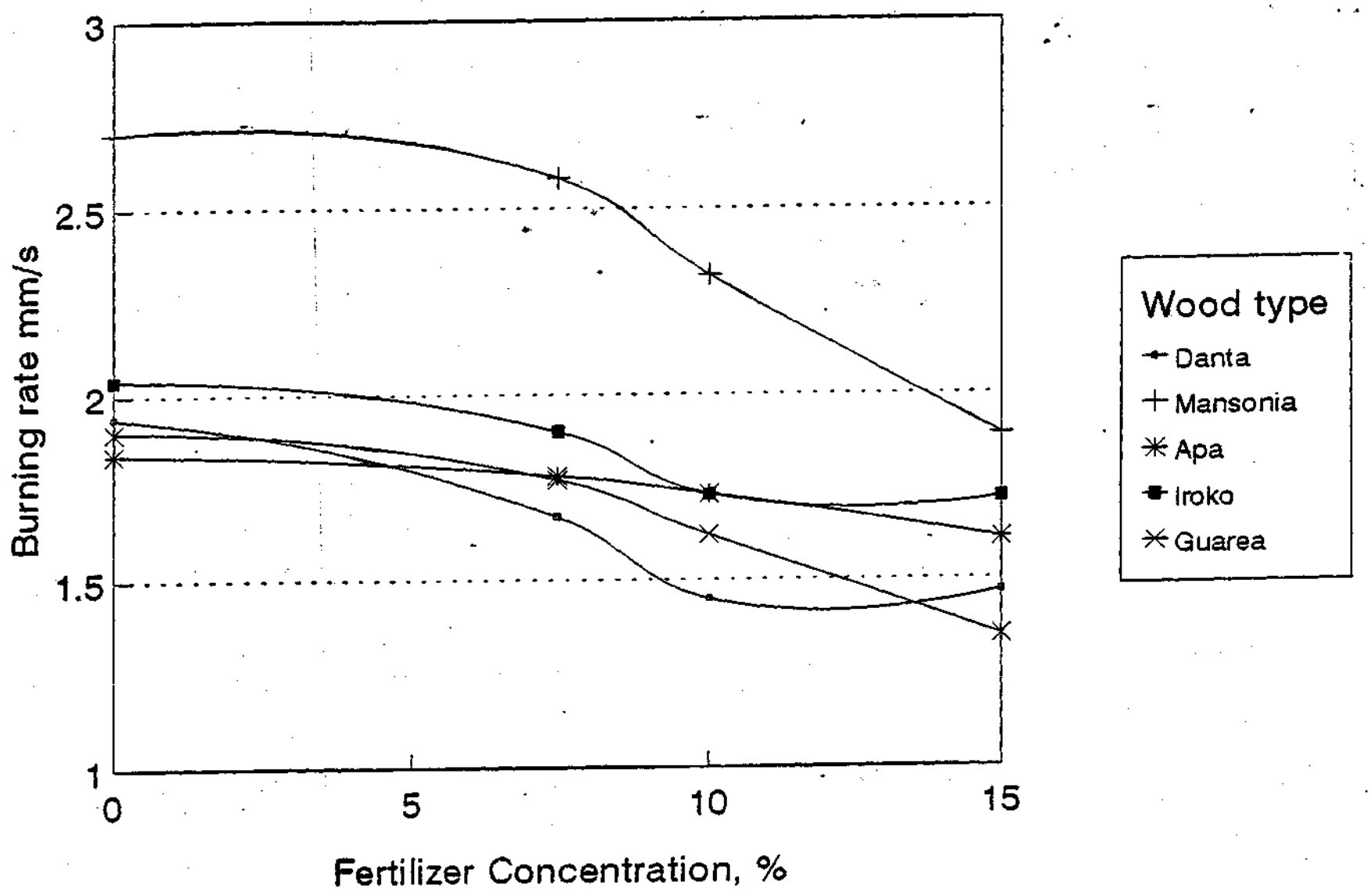


FIGURE 6.4: Continued.

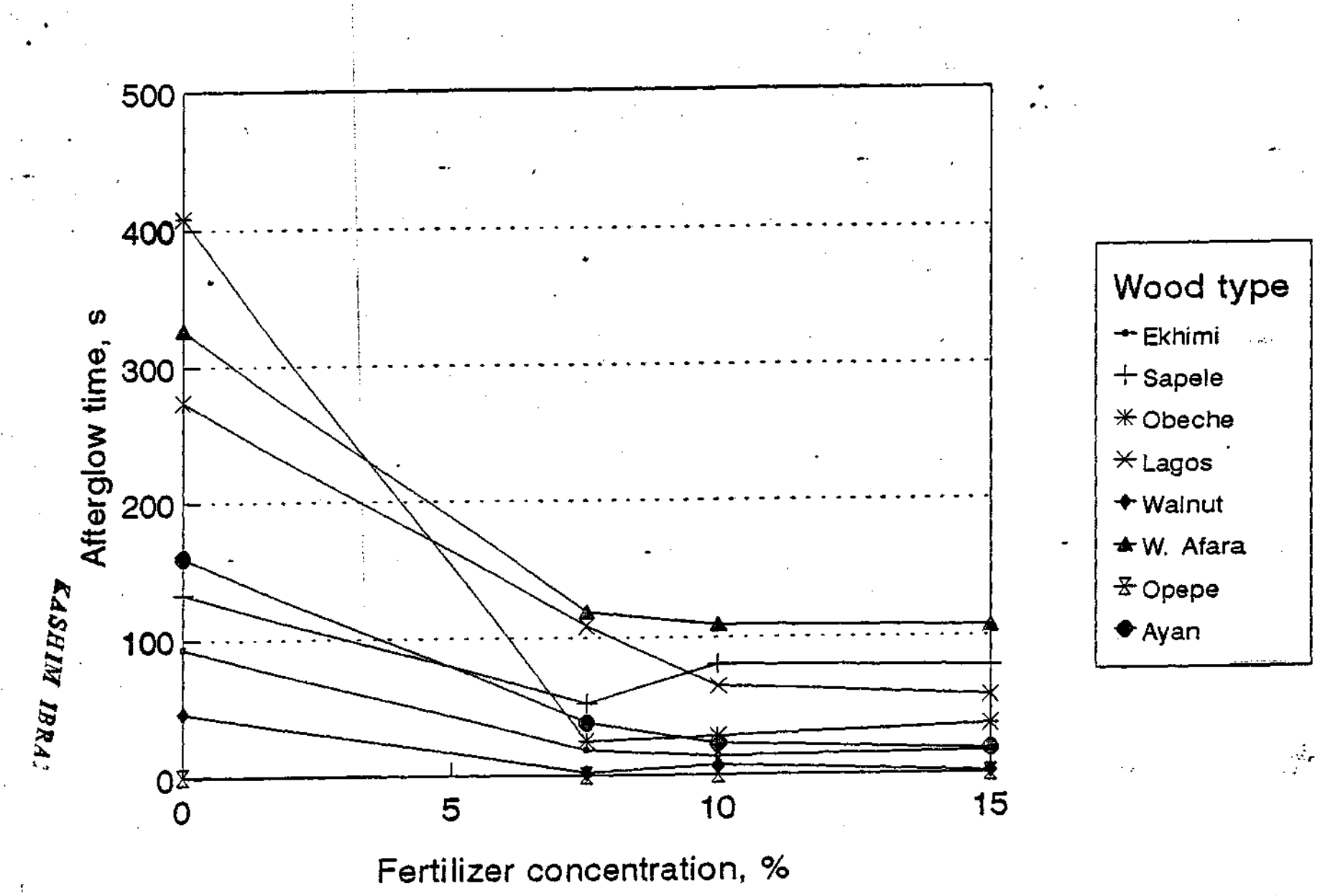


FIGURE 6.5: Effect fertilizer concentration on Afterglow time for various wood.

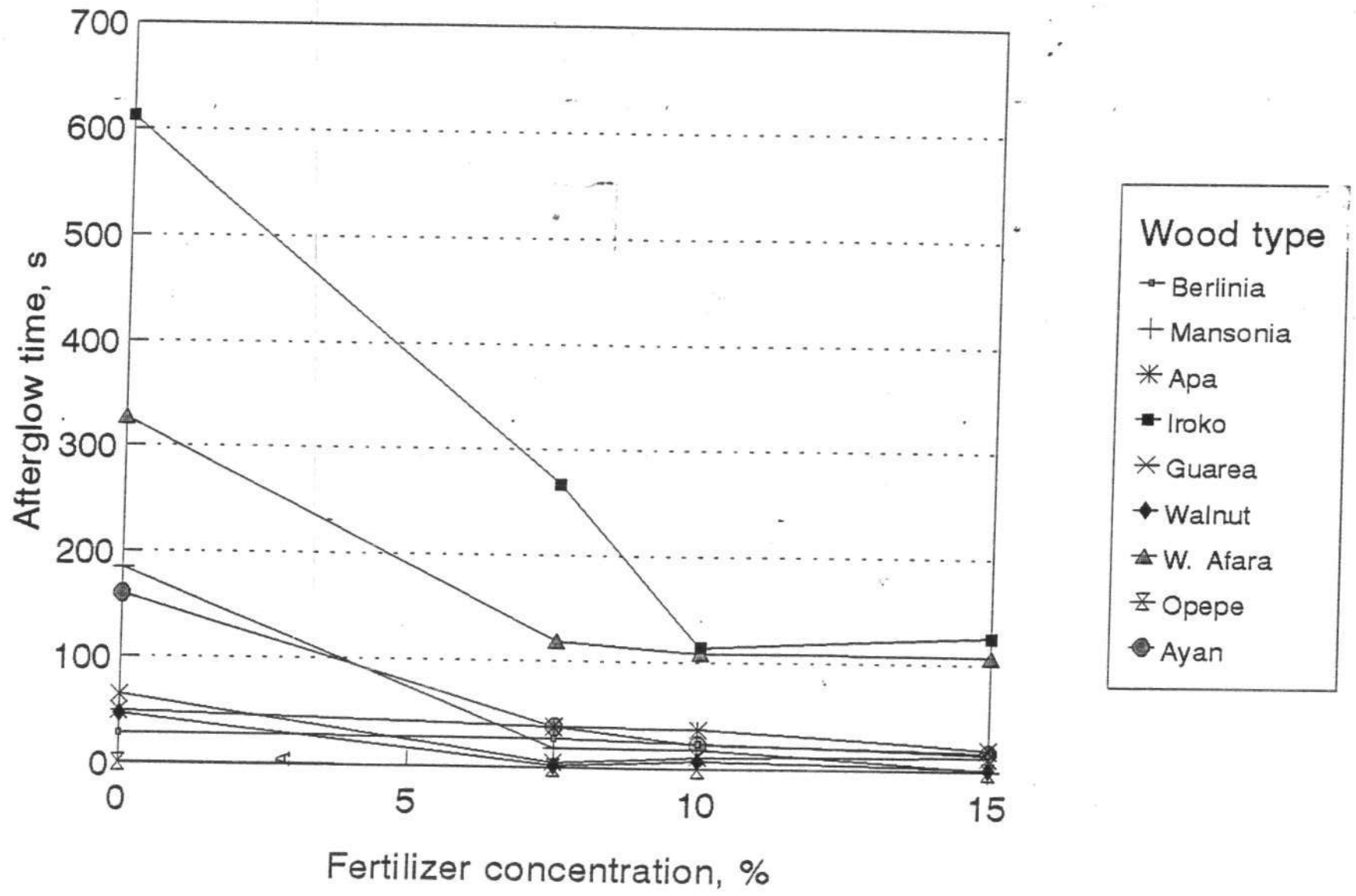


FIGURE 6.5: Continued.

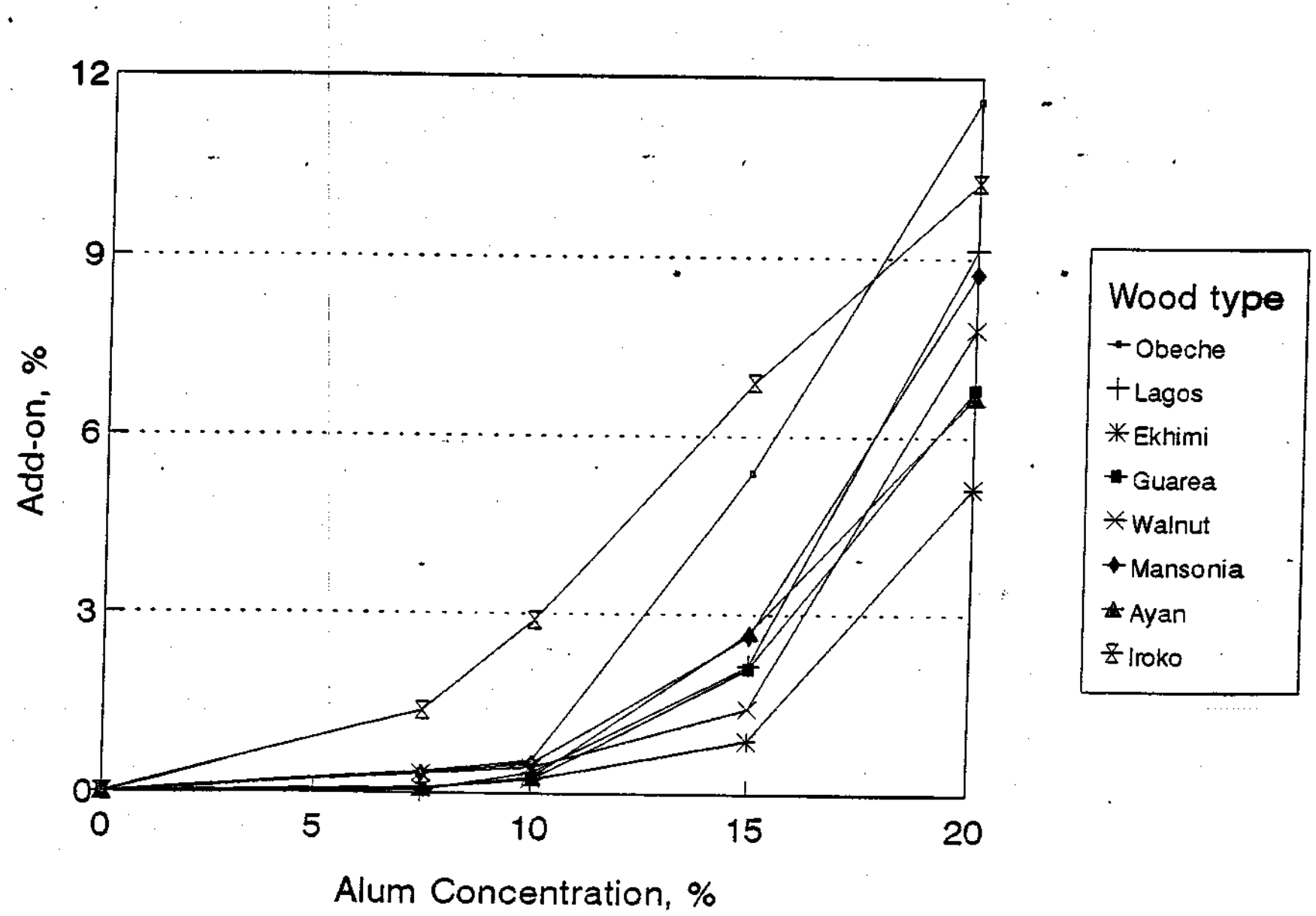


FIGURE 6.6: Percentage add-on versus alum concentration.

membranes and the rate of penetration depends on the pressure gradient, whereas diffusion takes place in the walls from positions of higher concentration to position of lower concentration and is controlled by the concentration of dissolved salts or flame-retardants. Thus, penetration is influenced both by the pore size distribution and capillary forces (phenomena of cohesion and adhesion and probably Figure 6.1 surface tension) while diffusion is regulated only by the total cross-sectional area of accessible pores.

These explanations can be expressed theoretically as follows: The Hagen - Poiseuille equation (Tsoumis, 1991):

$$Q = \frac{\pi r^4 \Delta p}{8 \eta l} \qquad (6.1)$$

describes the flow of a liquid in a straight capillary of circular section. Q = volume rate of flow, r = capillary radius, Δp = Pressure difference, ll= capillary length and η = liquid viscosity. It will be noticed that the flow rate is proportional to the fourth power of the capillary or pore radius so that flow is markedly affected by pore and capillary sizes as already mentioned. The equation also illustrates the difficulties imposed by any intrusion (tyloses) in the wood pores/channels. If we consider wood as a porous solid then Darcy's law applies

$$Q = \frac{BA\Delta P}{\eta l} \qquad (6.2)$$

where Q = volume rate of flow, A = cross-sectional area of the capillary, B - permeability constant, P = pressure drop across the specimen, η = liquid viscosity and l = specimen length.

According to Fick's first law of diffusion, the rate of diffusion is directly proportional to the concentration gradients. That is:

$$\frac{d\alpha}{dt} = -KA\frac{dC}{dx} \qquad (6.3)$$

where $d\alpha/dt$ = rate of transfer of the reagent (mole/hr) across an area A (cm^2) under a concentration gradient of dc/dx (mole cm^{-3} and K is the diffusion coefficient . This equation implies that the higher the concentration the higher the absorption. On the basis of these explanations, the test results agreed with the theoretical considerations.

6.2.3 Modelling the Results of the Experimental Data

An empirical evaluation of the relationship between the concentration and add-on (penetration), was obtained by design a move to fit the concentration versus add-on curves. Curve fitting using a natural log method was found to model the experimental data accurately. The results of the curve fitting exercise were plotted together with the original

concentration characteristic for the purpose of comparison. The equations are also shown. Some typical results are presented in Figures 6.6(a) – (e) for Ekhimi, Walnut, Obeche, Ayan and Iroko respectively. The figures show good approximation. It is also seen from the figures that as concentration increases there is higher degree of penetration/diffusion.

From the above graphs and equations therein, the concentration index denoted as Y can simply be defined as follows:

$$Y = a \ln x \qquad (6.4)$$

where x is add-on or penetration, and depend mainly on the wood complex itself. Therefore,

$$\frac{dY}{dx} = \frac{a}{x} \qquad (6.5)$$

This relation (equation 6.5), perfectly agreed with the Fick's law relation in (6.3). Both equations indicate that the concentration - add-on (penetration) relation is logarithmic.

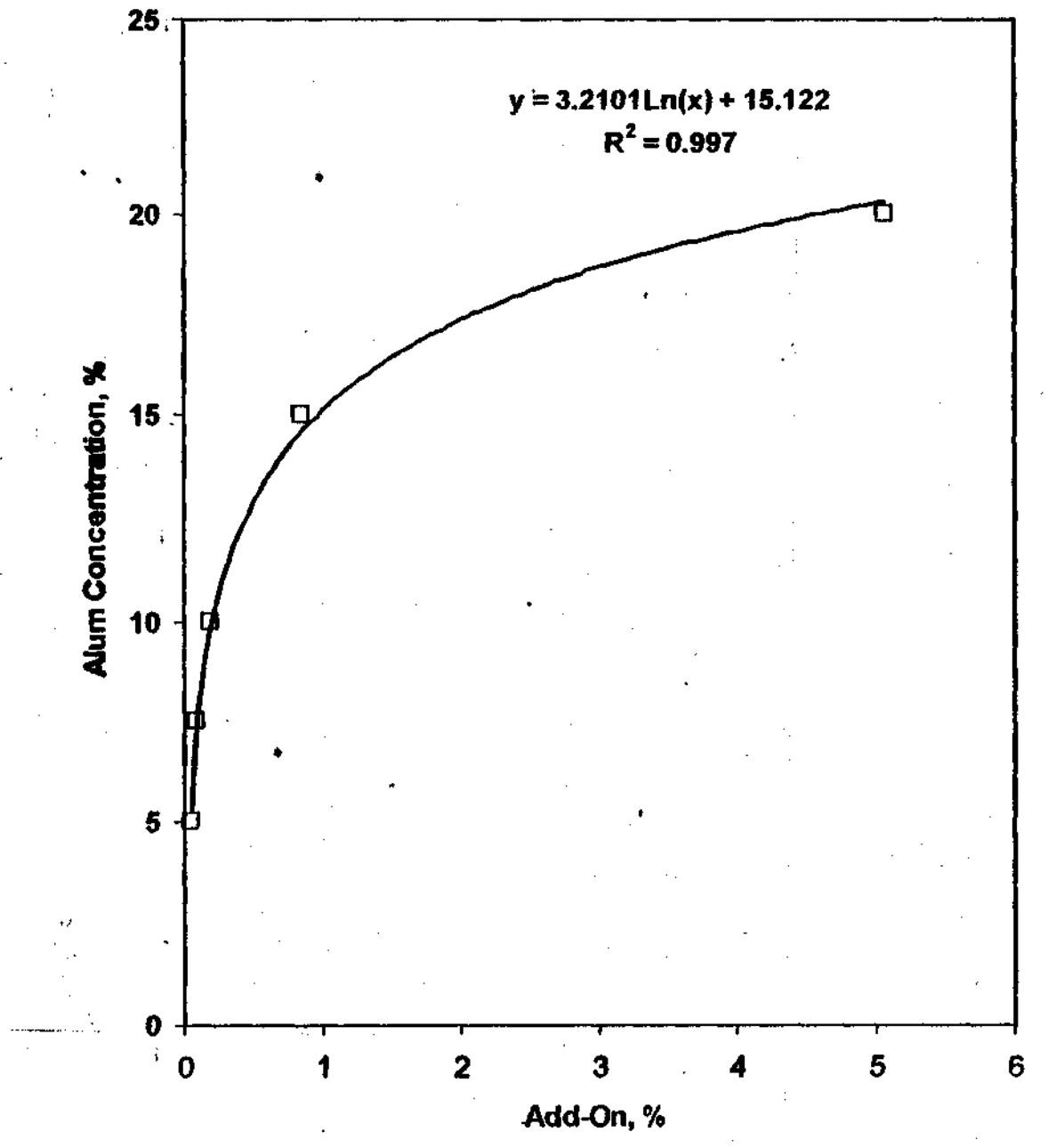


Fig. 6.6(a): Percentage Alum Concentration versus Add-on for Ekhimi

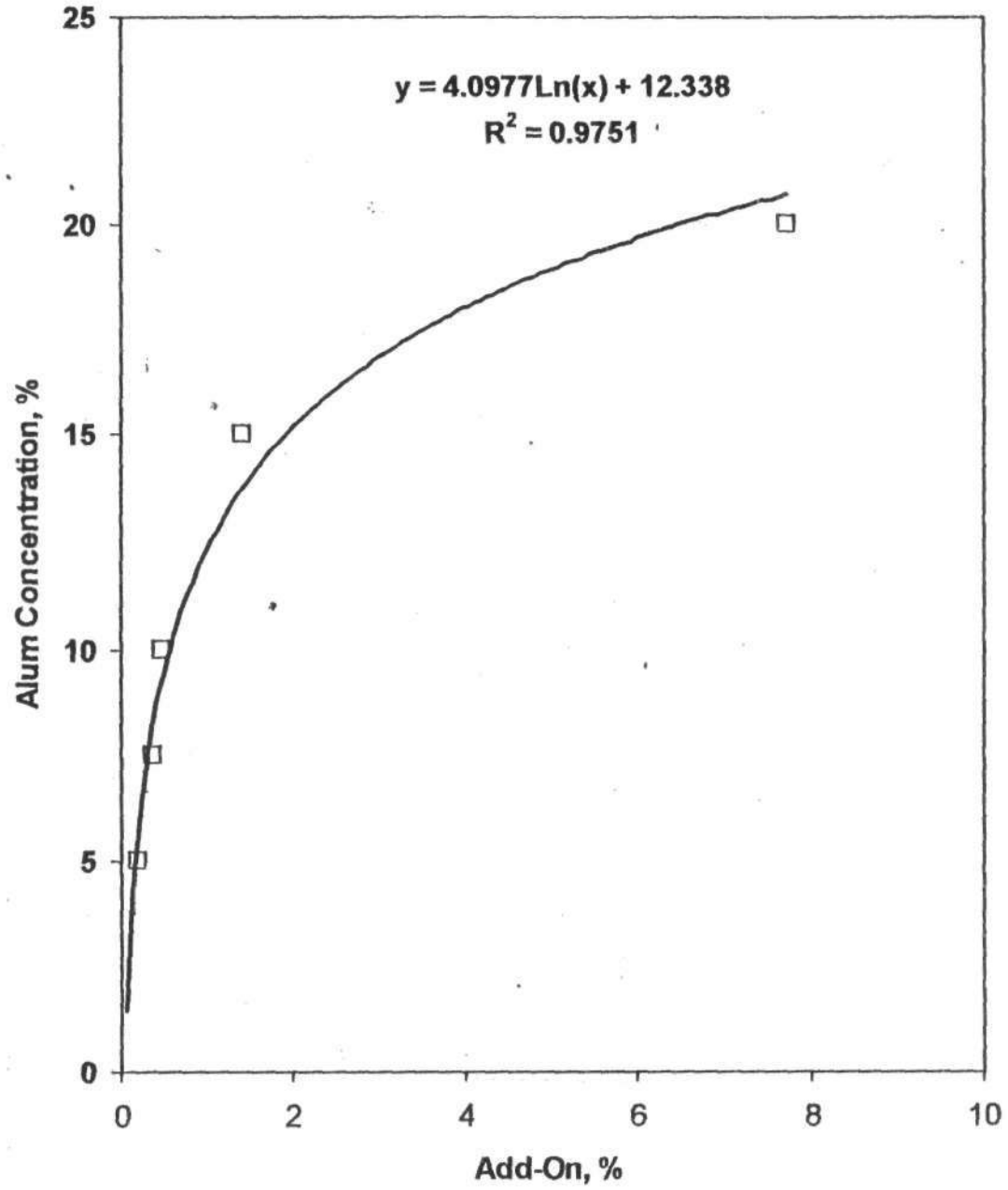


Fig. 6.6(b): Percentage Alum Concentration versus Add-on for Walnut

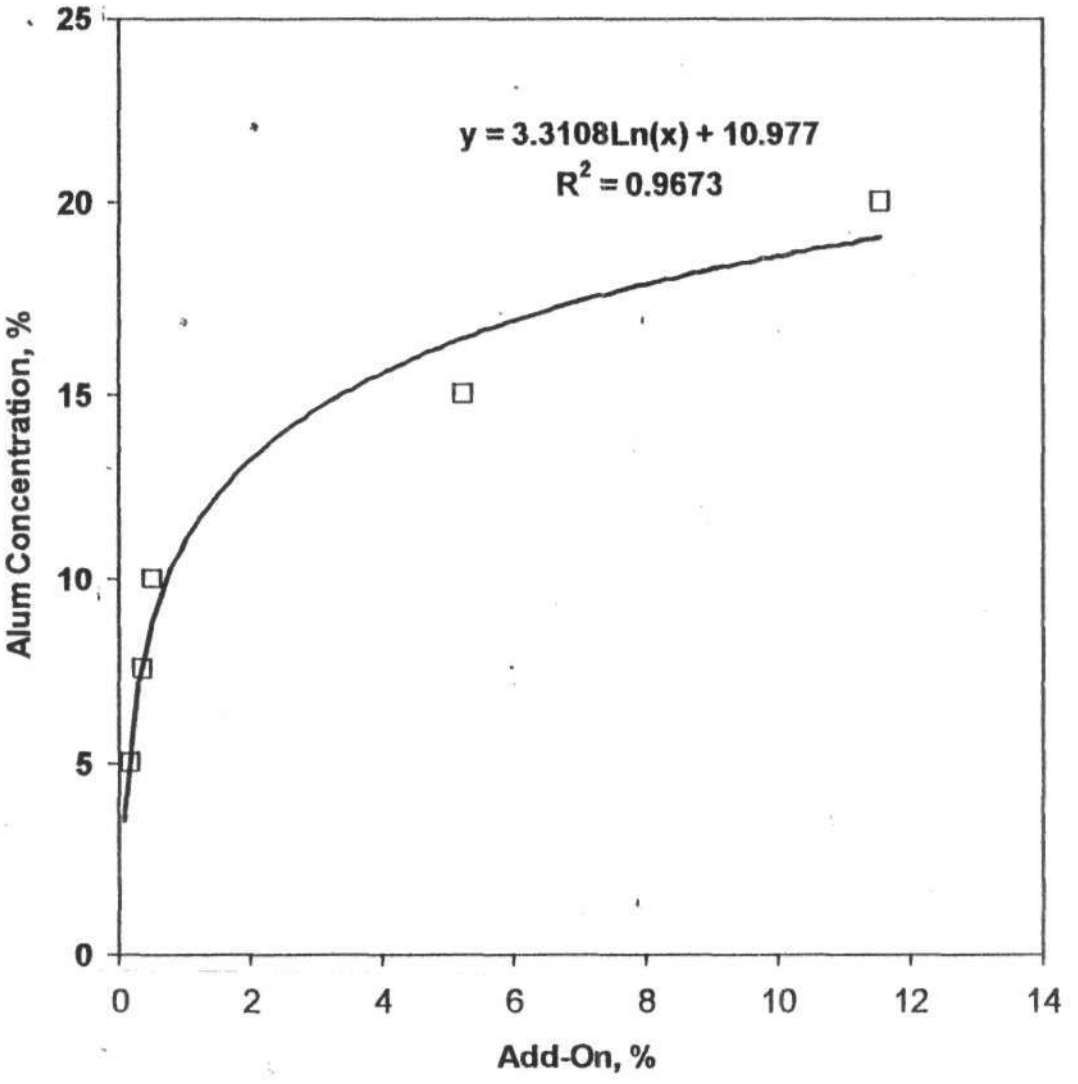


Fig. 6.6(c): Percentage Alum Concentration versus Add-on for Obeche

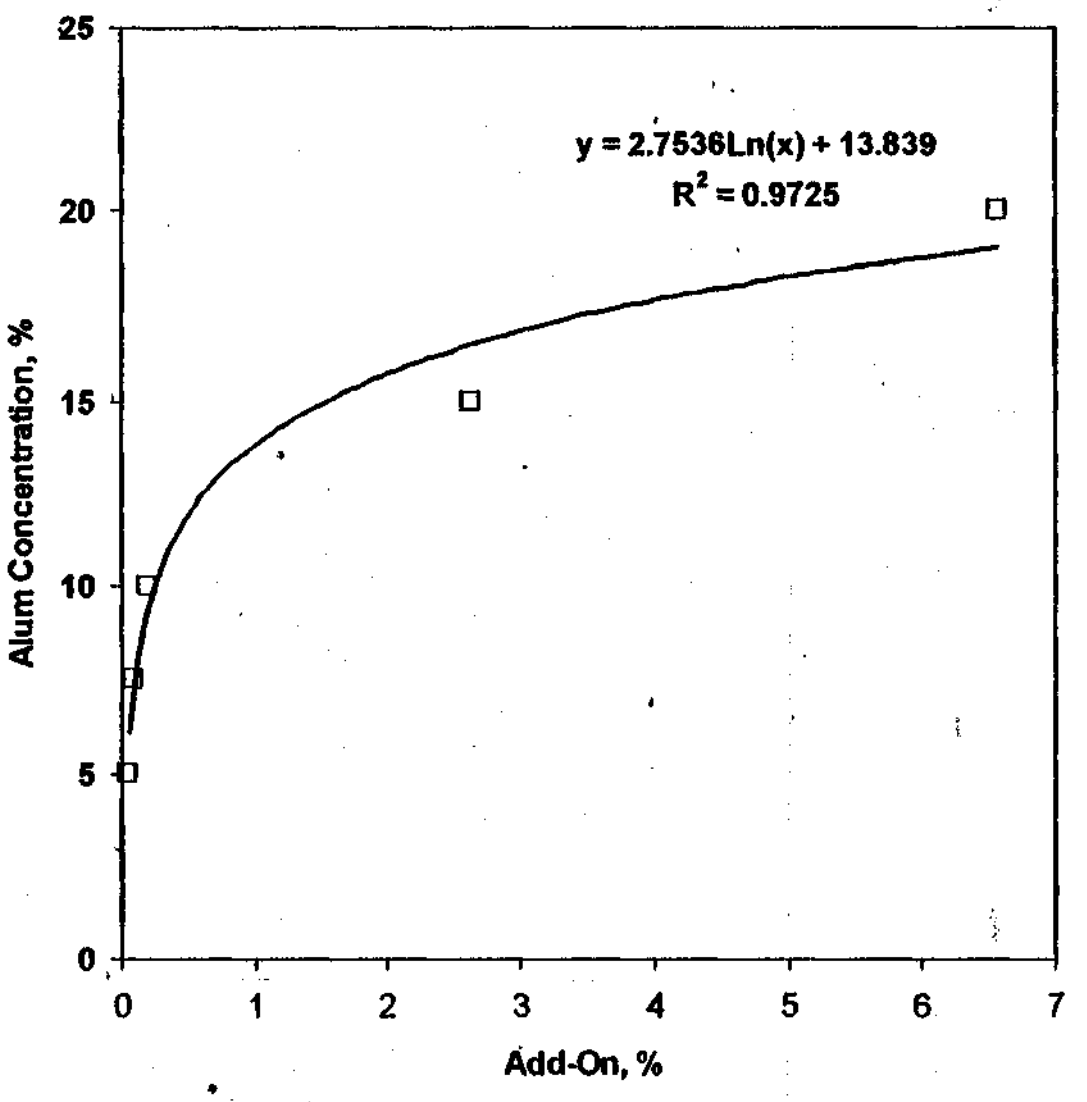


Fig. 6.6(d): Percentage Alum Concentration versus Add-on for Ayan

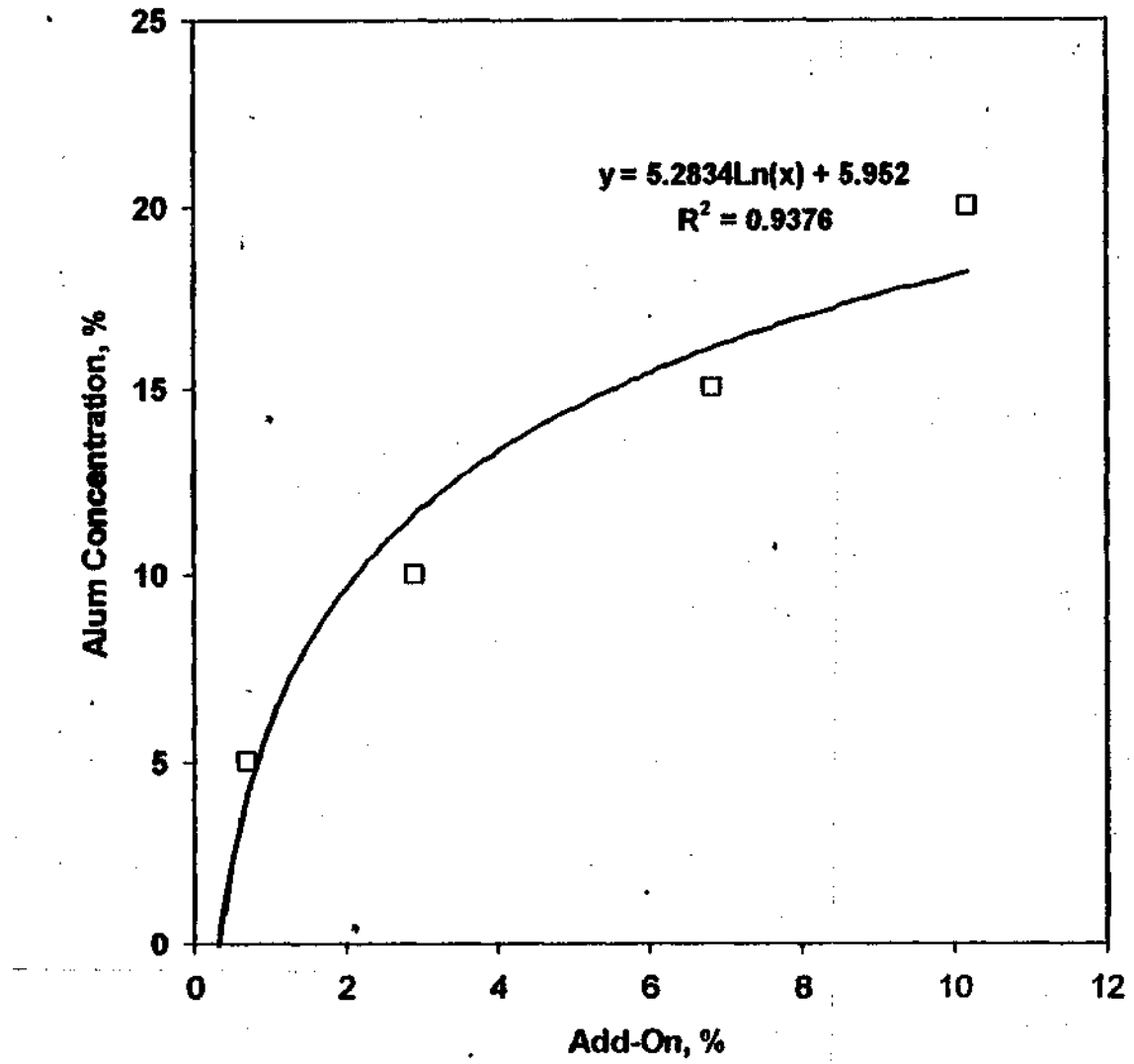


Fig. 6.6(e): Percentage Alum Concentration versus Add-on for Iroko

6.2.4 Mechanism of Action of Additives

The work of several investigators (Browne and Tang, 1962; Tang, 1967; Garba and Eboatu, 1990; Eboatu et al., 1992; Browne and Tang, 1963), have shown that flame retardant systems applied to wood function in the condensed phase in two ways:

(i) by reducing the temperature at which pyrolysis occurs and (ii) enhancing char formation at the expense of production of flammable volatile. Alum, at the flame temperatures, loses water of hydration and decomposes according to the equation:

$$K_2SO_4.Al_2(SO_4)_3.24H_2O = K_2SO_4 + Al_2O_3 + 3SO_3 + 24H_2O$$

This reaction is strongly endothermic, consumes thermal and radiant energy from the flame and slows the rate of pyrolysis of the wood. Also, the diluent and cooling effects of large amount of water vapour released into the fuel reduces the pyrolytic decomposition temperature. The alumina residue itself acts as a thermal shield on the surface of the wood substrate (Mackay, 1966), and it is also an excellent heat conductor that deflects heat away from the pyrolyzing surface. Furthermore, the gaseous products SO_3 and H_2O, evolved from the thermal decomposition are considered today as effective in the gas theory of flame retardancy. They dilute the combustible volatile

pyrolysates of cellulose, thereby reducing their concentration in the flame zone.

At the start of the twentieth century, numerous inorganic sulphates such as alum, gypsum, copperas, plaster of paris, etc were claimed to be flame proofing for cellulosic materials (Tang, 1967; Browne and Tang, 1963). Today only ammonium sulphate is being used in the cellulose area of wood and papers. This current result, however, has shown that alum can be effective for flame-retardancy of wood for indoor use. As the quantity of alum in the sample increases, the heat flux and rate of flammable gas generation decreases for the continued propagation of the flame and the sample self-extinguish and no afterglow.

The increasing ignition times as the alum concentration increases (Figure 6.1) may also be attributed to the endothermic heat of dehydration. The heat of hydration is effective in preventing ignition even in polymers with much higher heats of combustion because only a fraction of the heat of combustion is returned to the polymer substrate to continue the endothermic pyrolytic fuel-forming reactions and thus can reduce the rate of fuel production below that necessary to sustain flame.

The superphosphate fertiliser has been found to thermally decompose on heating around 160°C as observed by Eboatu et al. (1992) to yield

phosphorous - oxy acid. Further heating results in further degradation of the acid to phosphoric acid and water.

$$3C_a(H_2PO_4).H_2O + C_aSO_4 \longrightarrow 3C_aO + 3H_4P_4O_7 + H_2O + 7C_aSO_4$$

$$H_4P_2O_7 \longrightarrow 2H_2O + P_2O_5.$$

The phosphorous acids generated alter the pyrolytic decomposition of the cellulose into non-flammable gases and difficultly combustible carbonaceous char instead of the easily formed levoglucosan and other flammable tars. In addition, the char, calcium oxide and calcium sulphate may also form an insulating coating or layer on wood surfaces, thereby protecting the wood from any further pyrolysis.

6.2.5 Glowing Combustion/Afterglow

Afterglow is the flameless combustion of a cellulosic material after the igniting flame has been removed. It is the solid-phase oxidation of elemental carbon. Alum, perhaps functions as effective glow retardants through the physical mechanism; as stated earlier, during the flaming combustion, alum decomposes into an incombustible alumina residue. The alumina is thought to form a layer which coats the carbon surface thereby protecting it from any direct contact with oxygen of the air . Also, the large amount of water vapour released by the alum into the fuel serves as a diluent to reduce effective heat flux and oxygen concentration.

Fertiliser functions mainly by reducing the formation of CO_2: oxidation of carbon takes place through any or both of the following reactions:

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H = -94.4 \text{Kcal/mol}$$

$$2C + O_2 \longrightarrow 2CO \qquad \Delta H = -26.4 \text{Kcal/mol}$$

From these reactions, it is easier to form CO than CO_2 as seen from the amount of heat required. Hence, it is thought that fertiliser accelerates the formation of CO and inhibits the formation of CO_2 by following reaction

$$P_2O_5 + 5C \rightarrow 2P + 5CO$$

In addition, the polyphosphoric acids, being very viscous, are thought to be an excellent film-forming substance that can coat the surface as well. This would retard the diffusion of oxygen into the reaction layer of carbon.

6.2.6 Effectiveness of Retardants

Only very little comparison can be made on the effectiveness of alum and fertiliser at various retention to suppress flammability in woods as seen from these tests. This is because the chemical composition and structure of the contents in the woods differ in a characteristics way from one another. Even in a given timber or specie considerable differences also exist in the

wood content and composition between the stem, branches and roots. Moreover, dissolution of fertiliser was not possible after 15% concentration as can be seen from the figures.

The results based on the effects observed from flammability parameters indicate that alum is a better retardant. This was illustrated by a reduction its after glow combustion. The effect could be traced to its having a higher solubility in water than the fertiliser used in this study. The higher solubility ensures higher retention.

6.3 EFFECT OF FLAME RETARDANTS ON PYROLYSIS OF WOOD

6.3.1 Effect on Programmed TGA Pyrolysis

Dynamic TG and DTG curves for untreated wood and for wood treated with diammonium phosphate (DAP), aluminium potassium sulphate or potassium alum (ALUM), diammonium phosphate - borax (DAP:B) and borax - boric acid (B:B) were recorded in static air atmosphere and are shown in Figures 6.7 - 6.10. Table 6.2. lists the test samples and observed weight of sample remaining at different temperatures.

As discussed in the previous chapter, TG curves for the untreated woods indicate that after the initial loss of moisture, major loss in weight

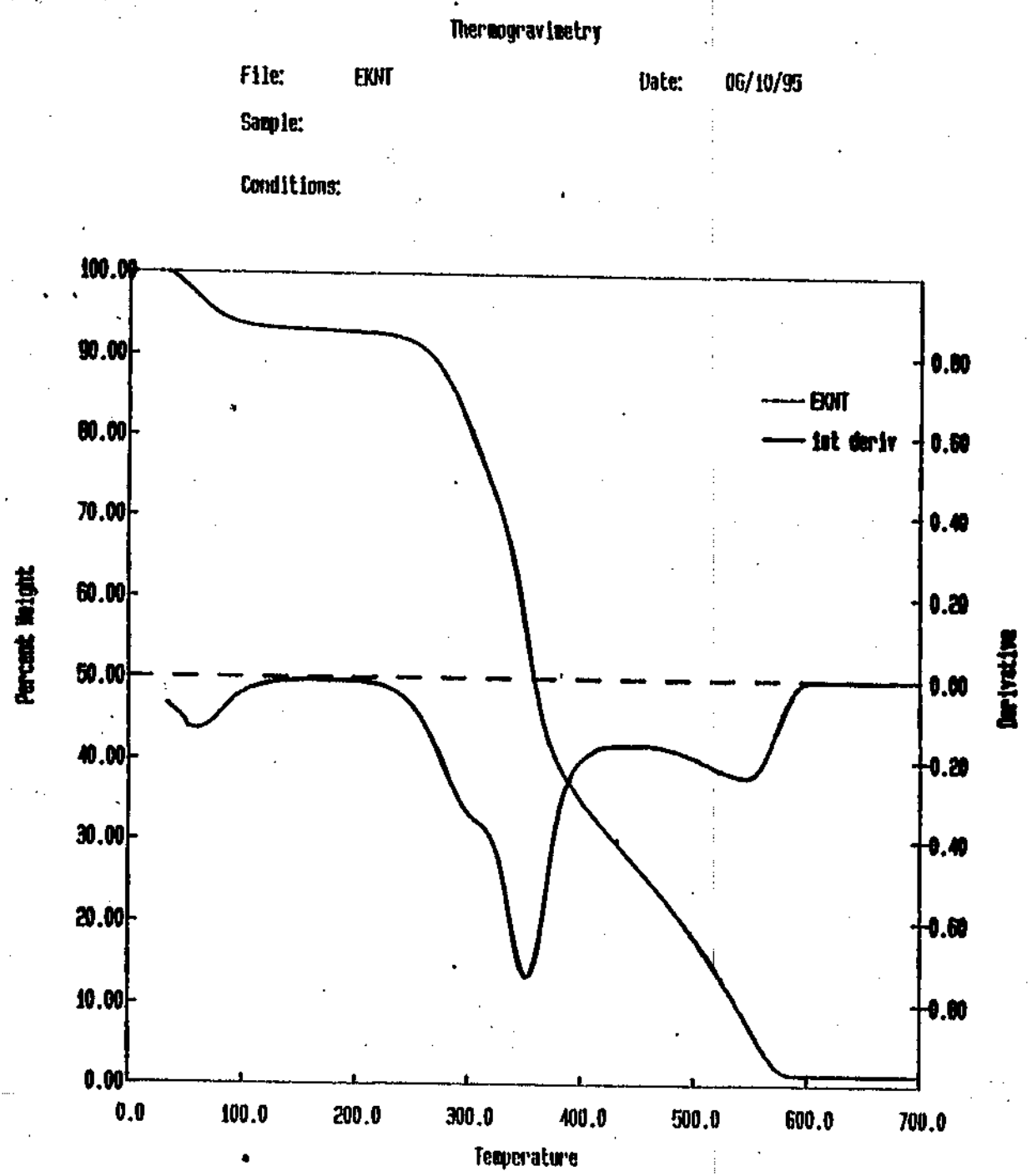


FIGURE 6.7(a): TGA and DTG responses of Ekhimi wood (untreated) at 10K min^{-1} in static air.

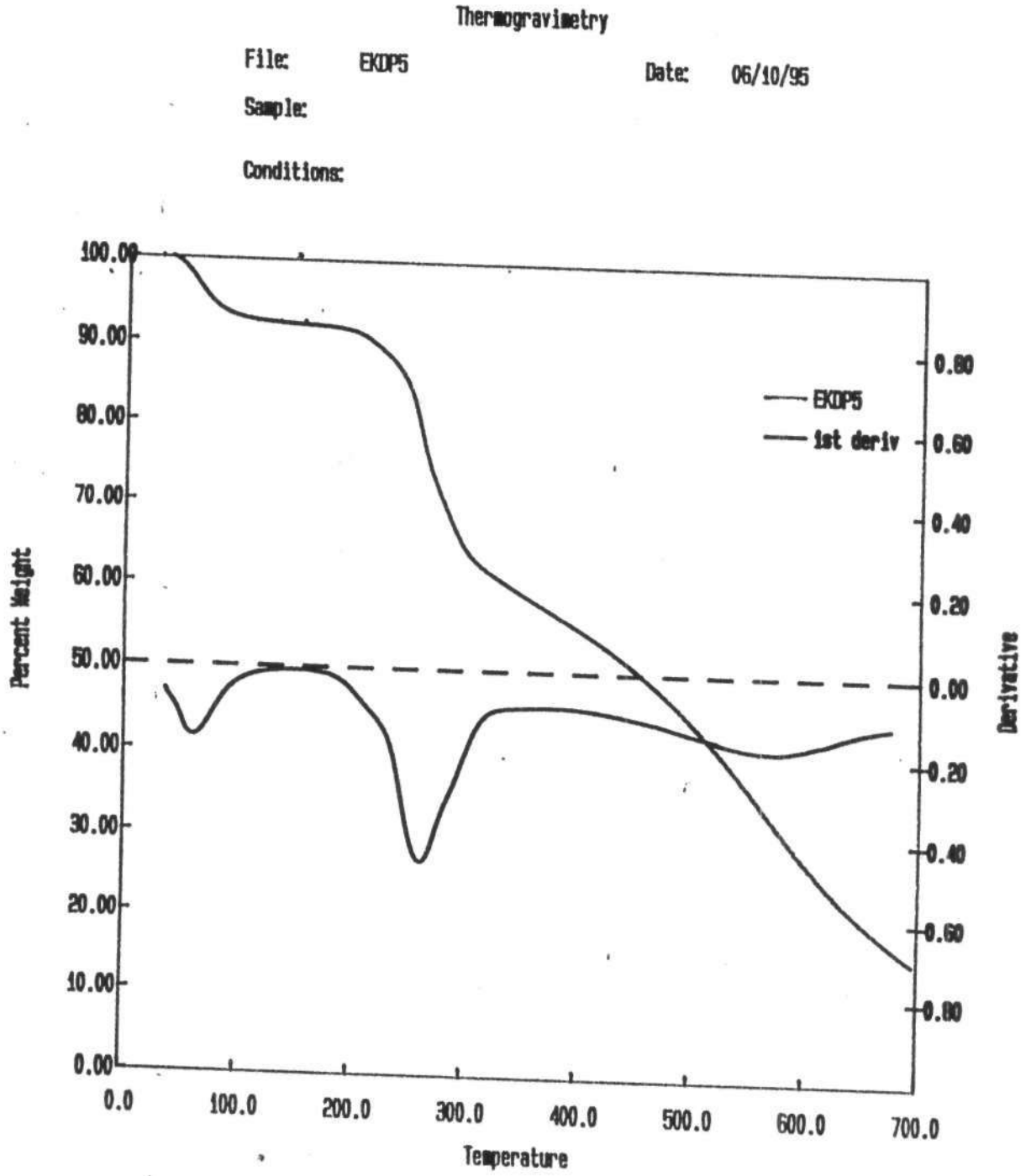


FIGURE 6.7(b) Effect of diammonium phosphate (DAP) on TGA and DTG responses of Ekhimi at 10Kmin^{-1} in static air, FR content 5% by weight.

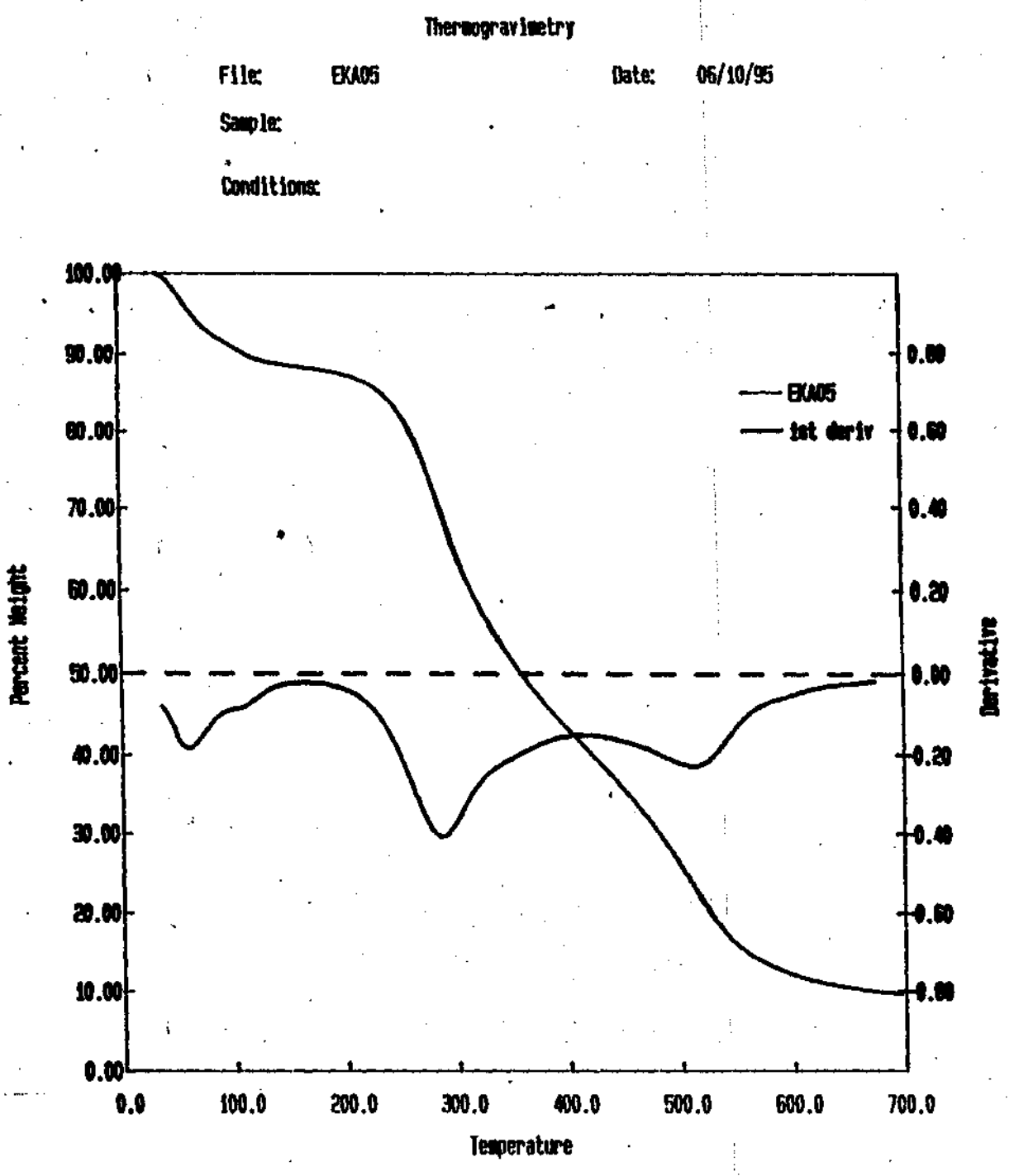


FIGURE 6.7(c) Effect of ALUM on TGA and DTG responses of Ekhimi wood at $10Kmin^{-1}$, in static air, FR content 5% by weight.

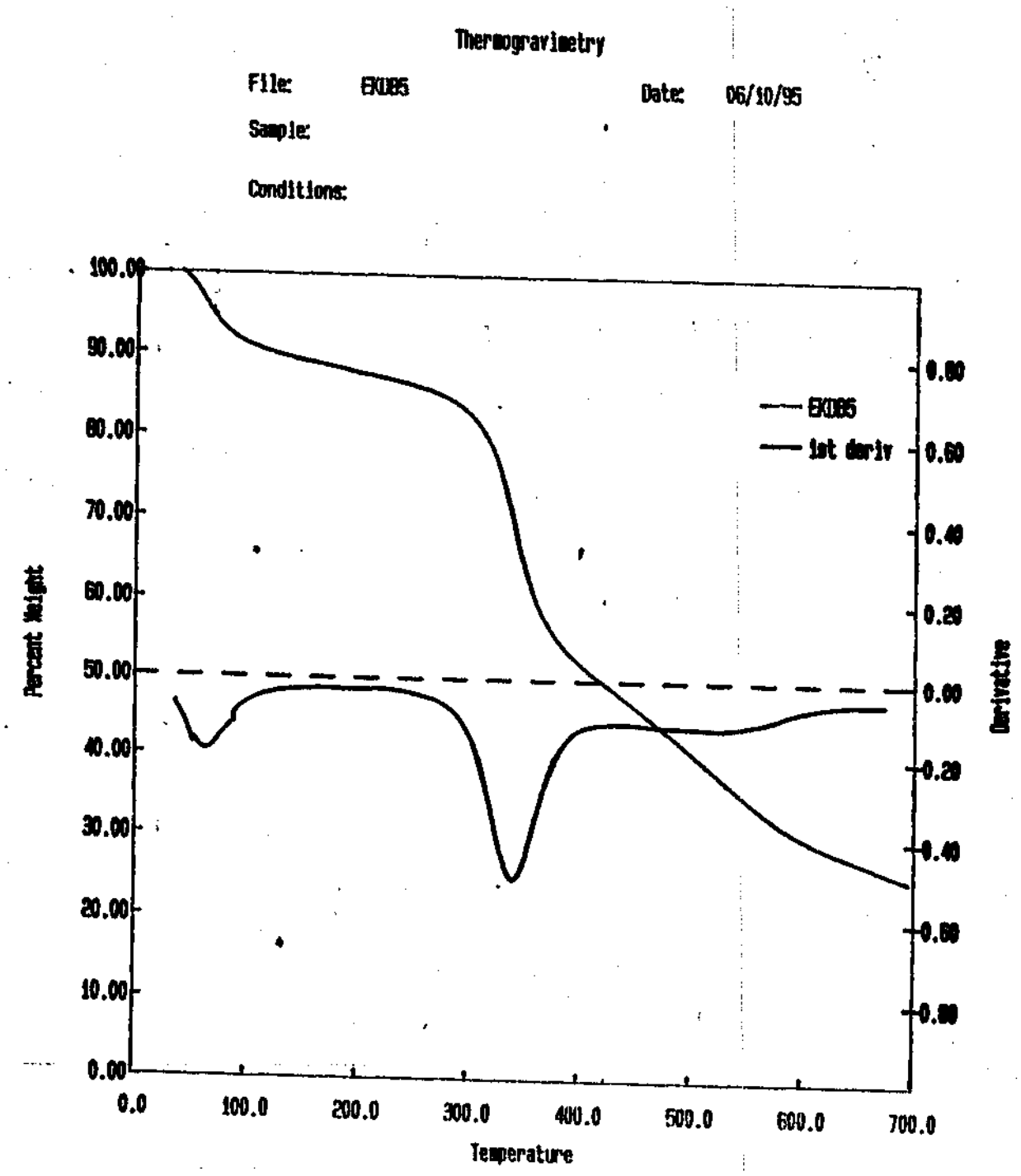


FIGURE 6.7(d) Effect of diammonium phosphate-borax combination (1:1 ratio) on TGA and DTG responses of Ekhimi wood at 10Kmin^{-1}, in static ait, FR content 5% by weight.

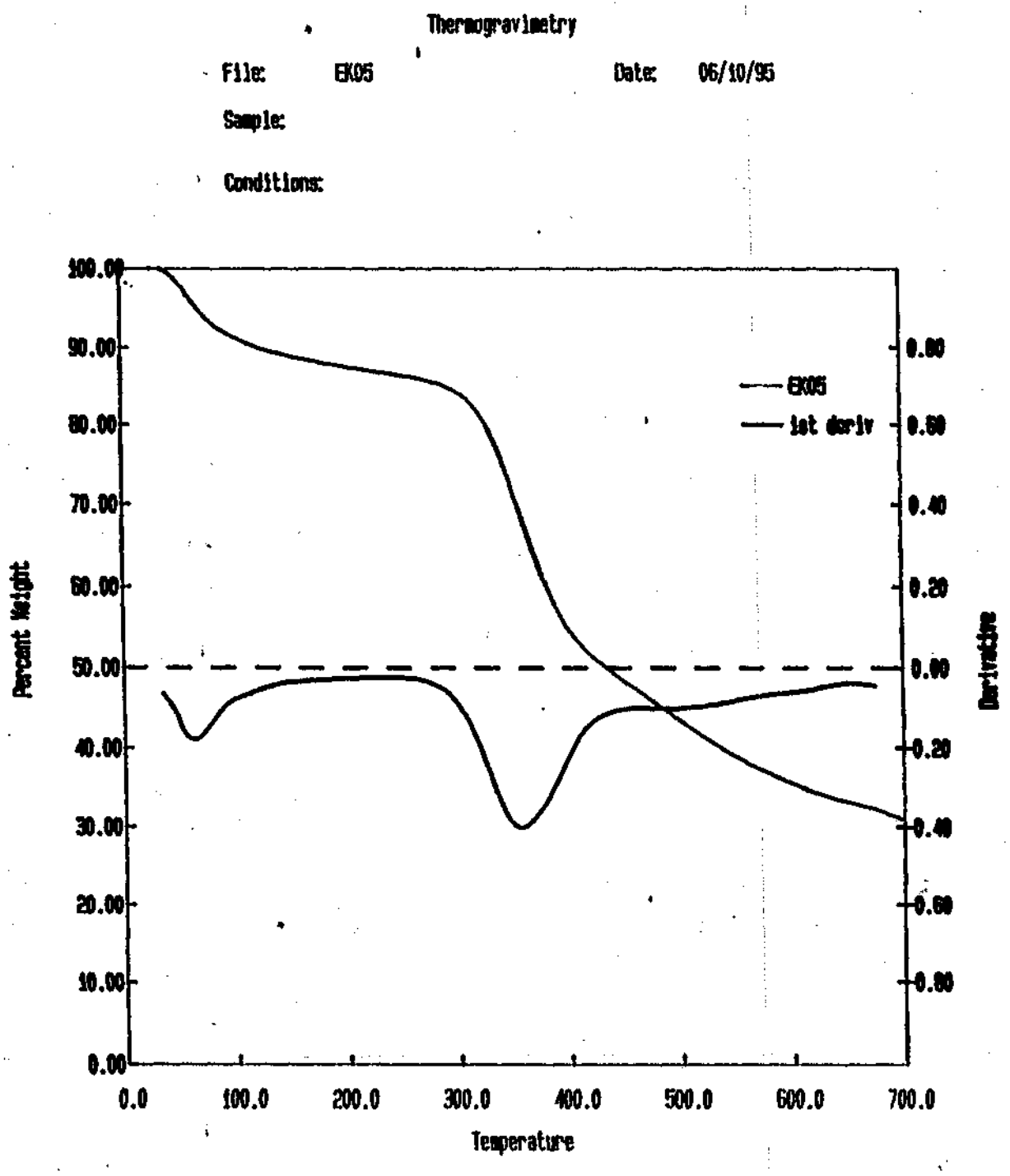


FIGURE 6.7(e): Effect of boric acid-borax combination (1:1 ratio) on TGA and DTG responses on Ekhimi wood at 10Kmin^{-1}, in static air, FR content 5% by weight.

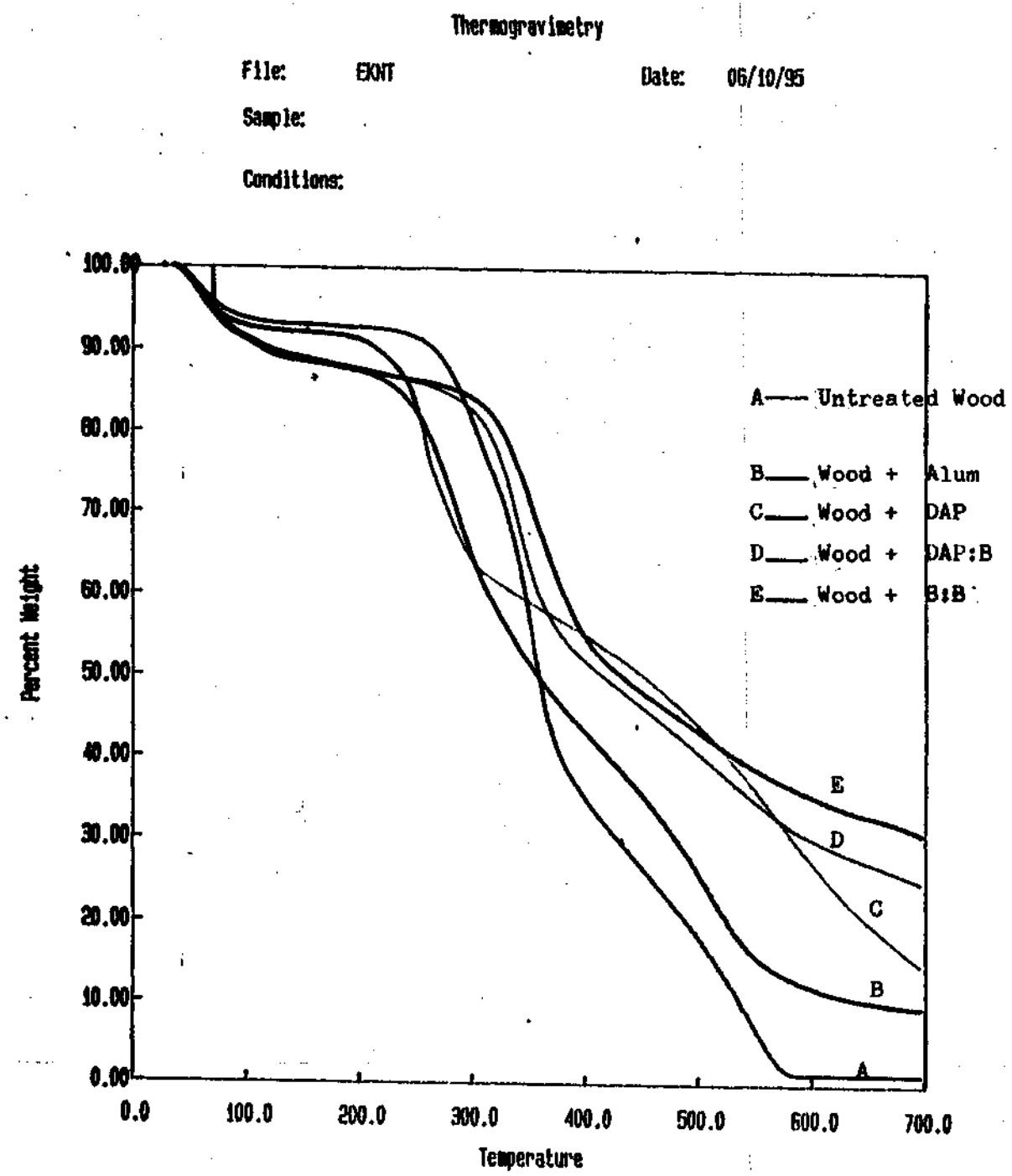


FIGURE 6.8: Effect of selected FR on TGA responses of Ekhimi wood at 10kmin,$^{-1}$ in static air, FR content 5% by weight.

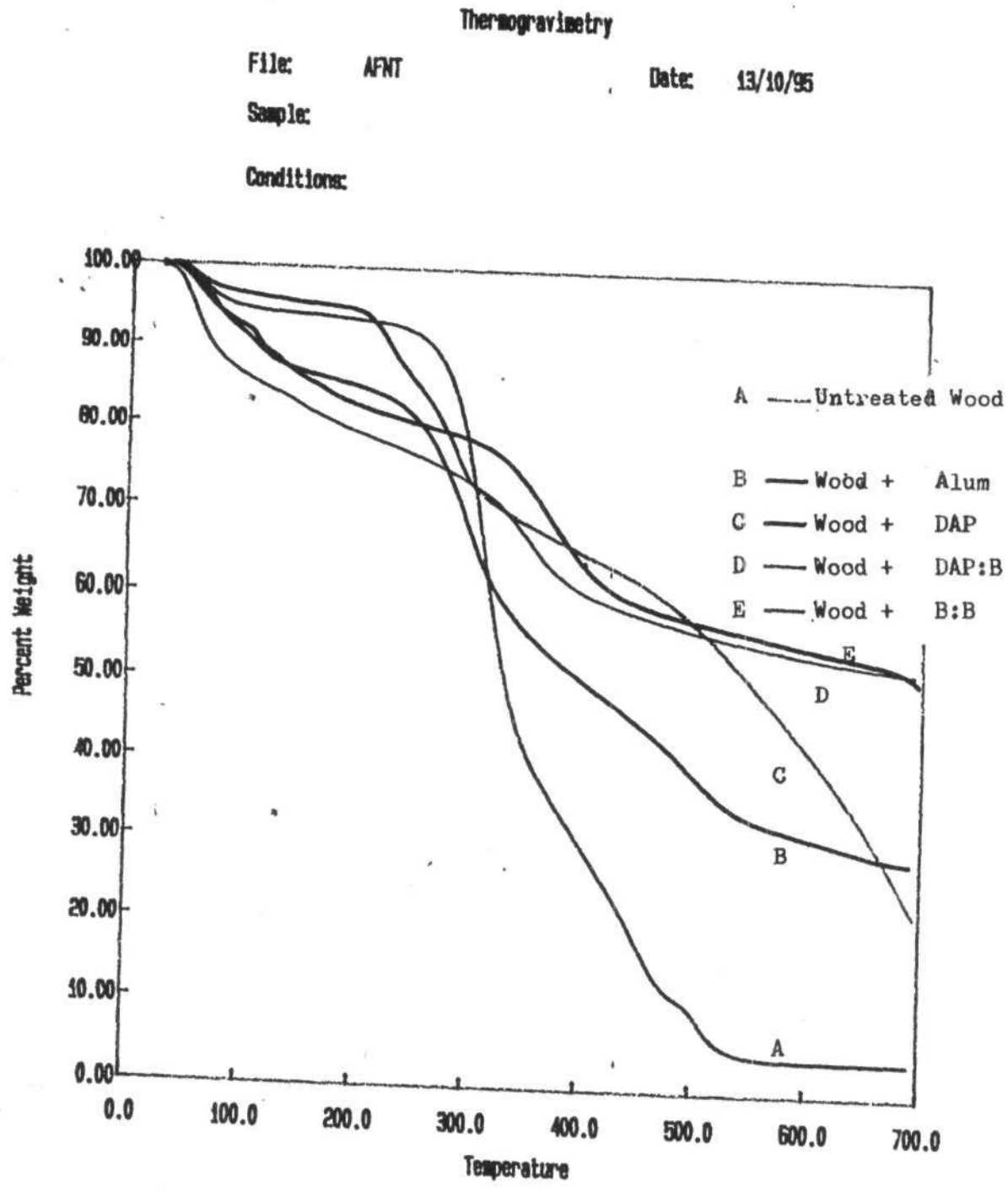


FIGURE 6.9: Effect of selected FR on TGA responses of white Afara wood at 10Kmin^{-1}, in static air.

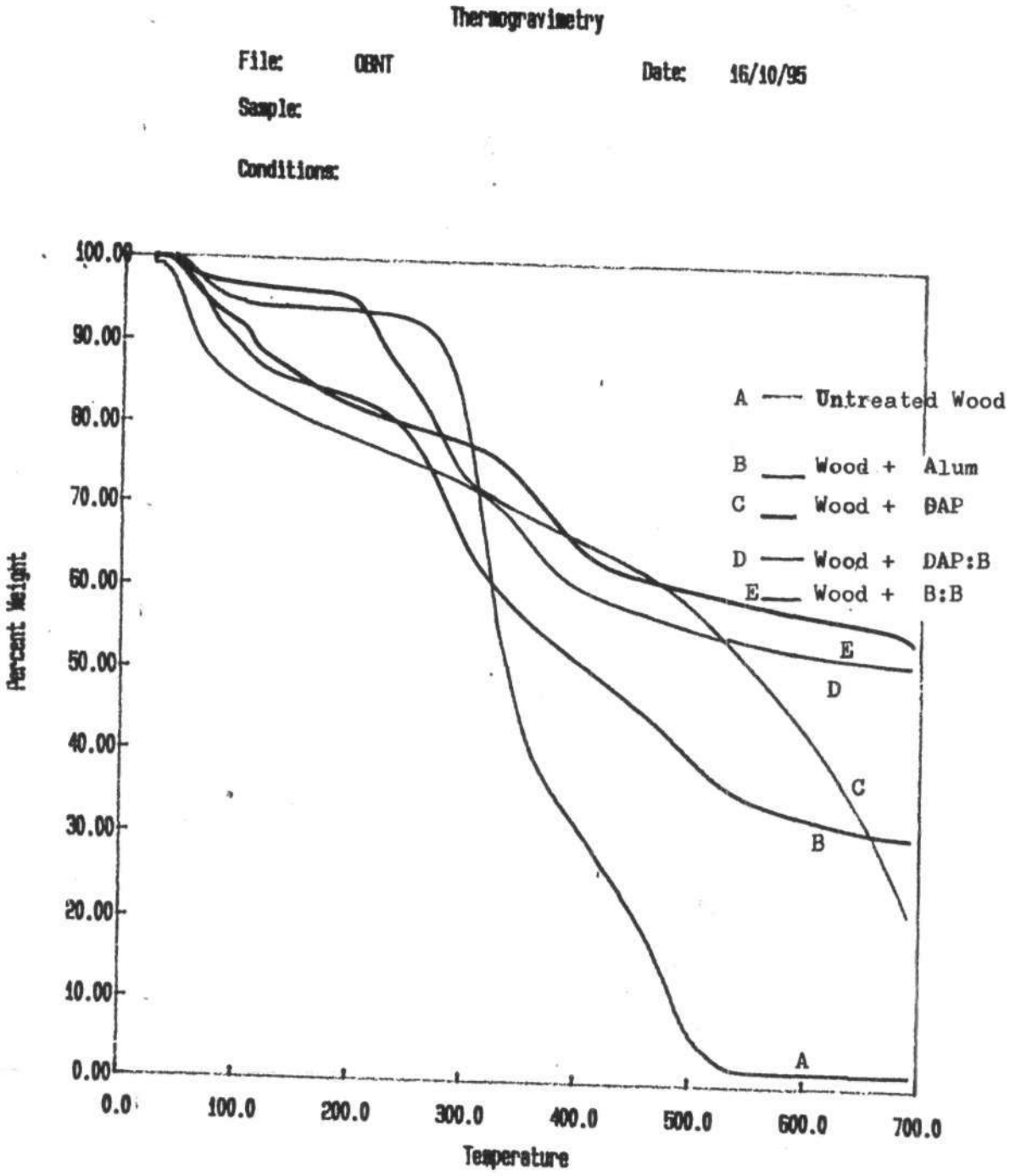


FIGURE 6.10: Effect of selected FR on TGA responses of Obeche wood at 10Kmin^{-1}, in static air, FR content 12.5% by weight.

Table 6.2. Effect of selected flame retardants on pyrolysis wood

WOOD	TREATMENT	TEMP OF ONSET OF ACTIVE PYROLYSIS °C	TEMP OF OXIDATION °C	WEIGHT OF SAMPLE (%) IN STATIC AIR AT TEMPERATURE							
		1st Stage	2nd Stage	200°C	250°C	300°C	350°C	400°C	450°C	500°C	550°C
Apa	-	216.3	420.0	92.03	91.17	83.00	57.72	37.18	26.68	12.17	2.55
	DAP	162.0		82.42	84.52	70.98	65.60	62.55	59.36	33.74	3.02
	ALUM	200.3		85.89	83.68	72.12	55.27	47.25	40.14	30.93	17.68
	DAB	258.8			81.23	78.13	68.43	60.87	57.08	53.22	46.40
	B-B	266.7				80.68	73.12	61.79	56.55	53.14	48.32
Iroko	-	210.2	392.4	93.28	92.44	85.04	60.09	38.80	29.29	17.32	3.60
	DAP	170.4		88.12	82.42	67.73	63.22	60.20	56.94	51.88	36.95
	ALUM	200.4		86.10	83.49	69.42	52.71	44.10	35.29	25.88	12.91
	DAB	259.7			83.95	80.40	67.01	56.25	51.02	45.35	35.41
	B-B	263.9			84.00	82.96	73.05	59.44	53.50	49.37	42.47
Ayan	-	209.3	416.9	94.23	93.56	85.90	56.23	31.89	23.21	12.65	2.17
	DAP	169.2		89.97	83.82	69.11	64.51	81.46	58.37	50.60	36.57
	ALUM	193.0		81.96	77.56	61.40	49.81	42.20	35.40	26.30	18.54
	DAB	263.9			81.31	78.17	71.42	62.97	60.00	57.60	53.95
	B-B	269.7				79.24	74.83	63.86	59.04	57.46	54.01
Sapele	-	212.7	421.7	92.83	92.13	83.20	50.83	31.23	23.13	13.93	1.84
	DAP	170.9		69.43	83.35	70.27	65.04	61.95	58.72	53.70	37.83
	ALUM	198.7		81.95	78.28	63.86	53.00	46.03	38.81	32.24	23.14
	DAB	254.5		81.58	79.27	76.34	70.09	62.65	59.86	57.63	54.79
	B-B	270.3		83.25	81.98	79.57	74.31	65.82	61.98	59.94	57.33
Guarea	-	220.3	388.1	93.06	91.69	81.51	45.48	29.14	2230	14.50	2.66
	DAP	176.6		90.55	84.06	70.79	66.30	63.20	59.91	54.85	38.38
	ALUM	208.7		82.56	79.51	65.27	52.19	46.05	41.06	35.04	27.09
	DAB	271.3				78.27	72.69	63.66	59.75		
	B-B										

Table 6.2. Continued

Berlina	-	215.6	405.0	93.33	92.19	80.34	44.65	36.08	24.18	88.95	3.01
	DAP	169.6		90.40	84.68	71.17	66.71	63.22	6025	55.27	39.55
	ALUM	190.7		86.28	83.50	7032	57.58	5032	43.68	34.77	21.96
	DAB	245.0		82.19	80.63	77.28	70.61	63.68	60.62	58.01	54.04
	B-B	273.0			81.65	79.51	73.82	63.92	59.47	56.92	53.58
Lagos	-	215.6	400.2	92.28	91.86	84.65	51.29	32.21	24.oo	14.27	1.36
	DAP	169.7		88.87	82.96	87.77	64.89	61.87	58.78	53.64	37.32
	ALUM	19o.7		61.86	78.94	64.60	51.16	44.05	37.7o	3o.03	21.30
	DAB	245.0		82.61	80.86	76.93	70.87	64.03	61.29	59.49	56.01
	B-B	273.0			81.44	79.09	73.55	64.31	6o.69	58.46	55.87
Walnut	-	210.9	**416.9**	92.56	91.84	84.01	57.10	30.90	23.70	15.89	1.54
	DAP	170.1		89.00	82.75	68.98	64.78	61.99	58.78	53.54	36.59
	ALUM	197.9		85.00	81.96	65.49	52.21	46.66	40.76	33.20	24.03
	DAB	266.1		77.58	75.97	72.43	66.39	59.43	56.86	54.95	52.30
	B-B	269.7		80.80	79.75	77.77	72.53	63.57	59.52	57.61	54.49
Mansonia	-	209.1	426	92.95	91.75	81.12	57.02	33.25	25.58	16.21	2.77
	DAP	171.0		89.55	84.46	68.93	63.39	59.88	56.73	54.27	36.80
	ALIM	196.5		84.83	81.68	67.03	50.55	42.58	36.20	28.27	17.20
	DAB	264.7				77.64	69,96	60.89	57.54	55.30	
	B-B	267.1				79.78	72.74	61.87	57.21	55.46	
Opepe	-	216.0	434.5	93.27	92.45	84.79	62.98	34.87	27.73	20.40	4.71
	DAP	169.5		89.87	84.64	67.92	63.89	60.80	57.94	53.37	38.81
	ALUM	199.7		87.22	85.59	71.85	50.88	41.66	34.82	26.3	15.55
	DAB	258.1		80.51	79.26	76.69	68.26	59.10	55.96	53.22	49.18
	B-B				83.58	81.54	72.83	60.91	56.20	52.86	47.69
Tiama	-	215..4	426.7	92.09	91.09	80.92	46.42	34.37	26.20	17.04	2.11
	DAP	169.9		91.17	85.87	71.53	65.70	62.15	58.62	53.07	37.72
	ALUM	189.9		85.00	81.53	65.99	52.01	44.52	36.77	27.49	17.60
	DAB	266.8			80.07	77.19	69.11	58.92	55.03	51.74	46.67
	B-B	269.9				80.72	74.47	63.66	58.83	54.82	52.80

Table 6.2. Continued

Ekhimi	-	210.0	417	92.18	91.63	81.03	52.31	34.955.12	26.74	18.07	1.37
	DAP	170.0		89.74	84.01	64.41	59.52	43.24	5047	44.23	27.49
	ALUM	197.4		86.41	82.71	64.91	51.83	52.06	35.58	26.10	12.02
	DAB	260.8		86.75	82.93	82.93	64.19	55.30	46.61	40.79	28.02
	B-B	270.4				84.38	71.95		48.38	43.59	-
Afara	-	200.7	389.7	93.12	91.26	77.05	41.78	29.84	18.10	9.68	4.05
	DAP	169.6		92.01	85.70	73.75	68.70	65.49	62.41	57.66	42.18
	ALUM	199.9		83.94	81.25	68.01	56.41	50.42	45.11	38.67	31.07
	DAB	268.8				73.30	67.43	60.96	58.49	56.69	53.90
	B-B	290.1				78.55	73.57	64.34	59.95	57.93	54.93
Obodhe	-	211.8	409.8	93.69	93.01	81.83	44.47	31.39	21.43	6.34	1.83
	DAP	170.1		91.71	85.45	73.99	69.37	66.26	62.96	58.29	43.46
	ALUM	199.8		82.15	79.04	65.79	57.01	51.57	46.23	39.83	32.79
	DAB	274.7			75.74	72.87	67.27	60.54	57.93	55.83	53.14
	B-B	289.7				78.06	73.32	65.57	62.03	60.44	57.75

(first stage) attributable to pyrolysis -dehydration/depolymerisation and decomposition reaction, began at about 215°C (onset temperature), and followed by gradual weight loss to slow oxidation of charred products from around 390°C (second stage). The wood completed their pyrolysis at about 500°C with a yield of 10-15% char/residue. The TG curves from samples treated with the various salts showed that the combustion process is affected differently by various additives. The results revealed marked difference in the temperature of the onset of rapid pyrolysis (1st stage) and the amount of residue remaining at any given temperature. The DAP samples indicated a low threshold temperature (about 170°C) with a high char yield of around 55% at 500°C. The alum samples showed threshold decomposition temperatures only slightly below that for the untreated corresponding wood but char yield is substantially higher than that for untreated wood.

Addition of DAP:B and B:B chemicals increases the onset decomposition temperatures as compared to corresponding untreated wood, but left a slightly higher amount of char. The onset of the thermal decomposition is found to occur at approximately the same temperature with both treatments and their weight losses about same too, indicating that the mode of degradation has been altered in essentially the same manner in both cases. For all of the salts used for treatment in this study, it may be assumed that weight loss for test samples up to 200°C came chiefly

from loss of moisture including loss of water by dehydration with salts that contain water of crystallisation (borax and alum), and some early-stage pyrolysis of hemicellulose in the wood. For the DAP samples, the weight losses in the temperature range 170 -320°C are probably the consequences of acid catalysed dehydration. For alum treated wood, the weight losses in the temperature range 190-350°C, not only came from loss of free moisture and water of crystallisation in the salt itself, but also from evolution of gaseous products from the thermal decomposition. This first stage temperature range of the DAP samples (170-320°C) is lower than that of the alum range (190-350°C) which in turn is lower than that of untreated woods (215-390°C).

During the second stage, in the temperature range 390°C-600°C for untreated wood, weight losses have been ascribed to the oxidation of volatile product precursor and char residue. Correspondingly, the temperature ranges for the oxidation of volatile product precursors and char residue of DAP samples (>320°C) and the alum samples (>350°C) are also lower, indicating that the oxidation processes become faster at a given temperature in the case of treated wood samples.

The TG curves of the DAP:B and B:B samples seems to exhibit only a single weight loss in the temperature range 270°C - 500°C. The weight losses came probably from loss of free moisture and water of crystallisation

which arose from dehydration of the salts. It could also have been from the hydrolytic attack of the hemicellulose portion of the wood by acid formed from decomposition of boric acid.

Final char yields (in weight %) for all the treated samples (Table 6.2) are much higher than for 'pure' corresponding wood, indicating a reduction in the amounts of low molecular weight gases formed during oxidative pyrolysis. The order of the effect of the flame retardant chemicals in increasing char formation is DAP:B > B:B > DAP > ALUM at the end of combustion. This type of ordering domonstrates the synergism effect of DAP:B and B:B on the thermal decomposition of selected wood.

It has been well established in section 6.2.2 that for a wood strip, as the concentration of the dope increases, more of the salt is absorbed by the wood samples. Using sawdust samples prepared under the same conditions reported before, the effects of the flame retardant at different concentrations of 5%, 10% and 15% by weight on selected wood were also assessed using the Stanton Redcroft TG 760. The results are given in Figs. 6.11 and 6.12 as representative for the 14 wood samples. It is observed that the TGA pyrolysis curves are additive concentration-dependent. The curves clearly show that flame retardants significantly reduce the weight loss (wood decomposition) and result in greater amount of char yield. For a given

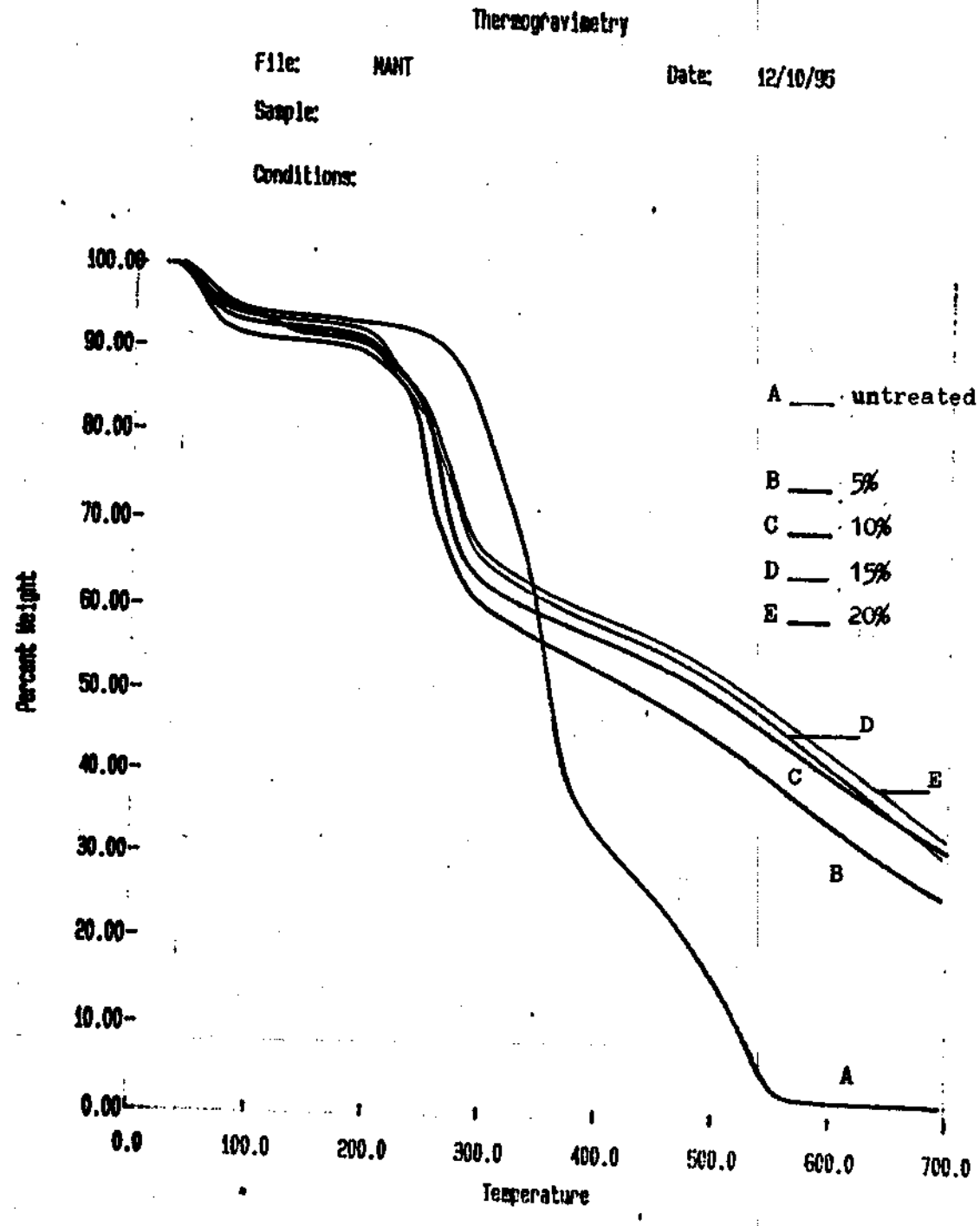


FIGURE 6.11(a) Effect of diammonium phosphate concentration on pyrolysis curve of mansonia wood at $10Kmin^{-1}$, in static air.

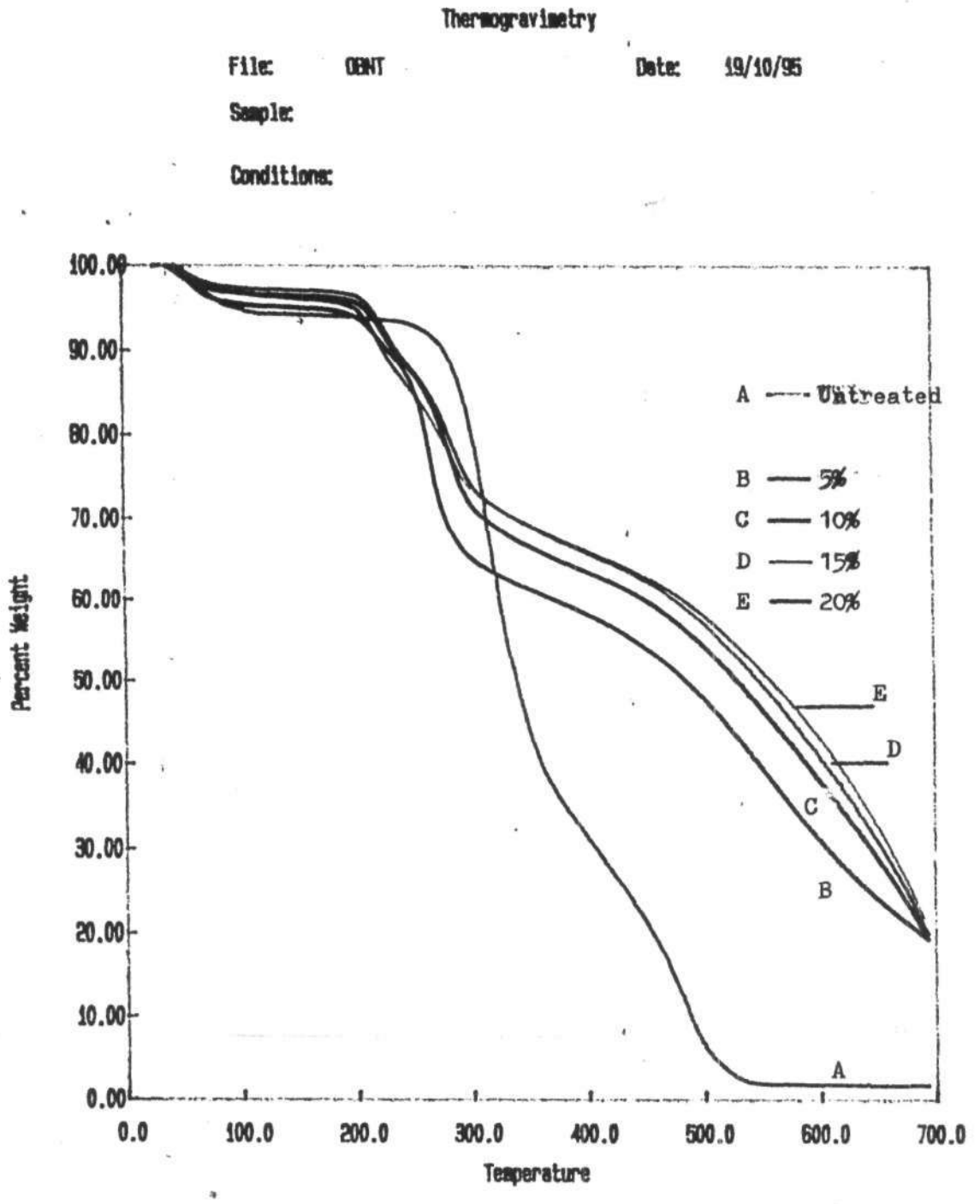


FIGURE 6.11(b) Effect of diammonium phosphate concentration on pyrolysis curves of Obeche wood at 10Kmin^{-1} in static air.

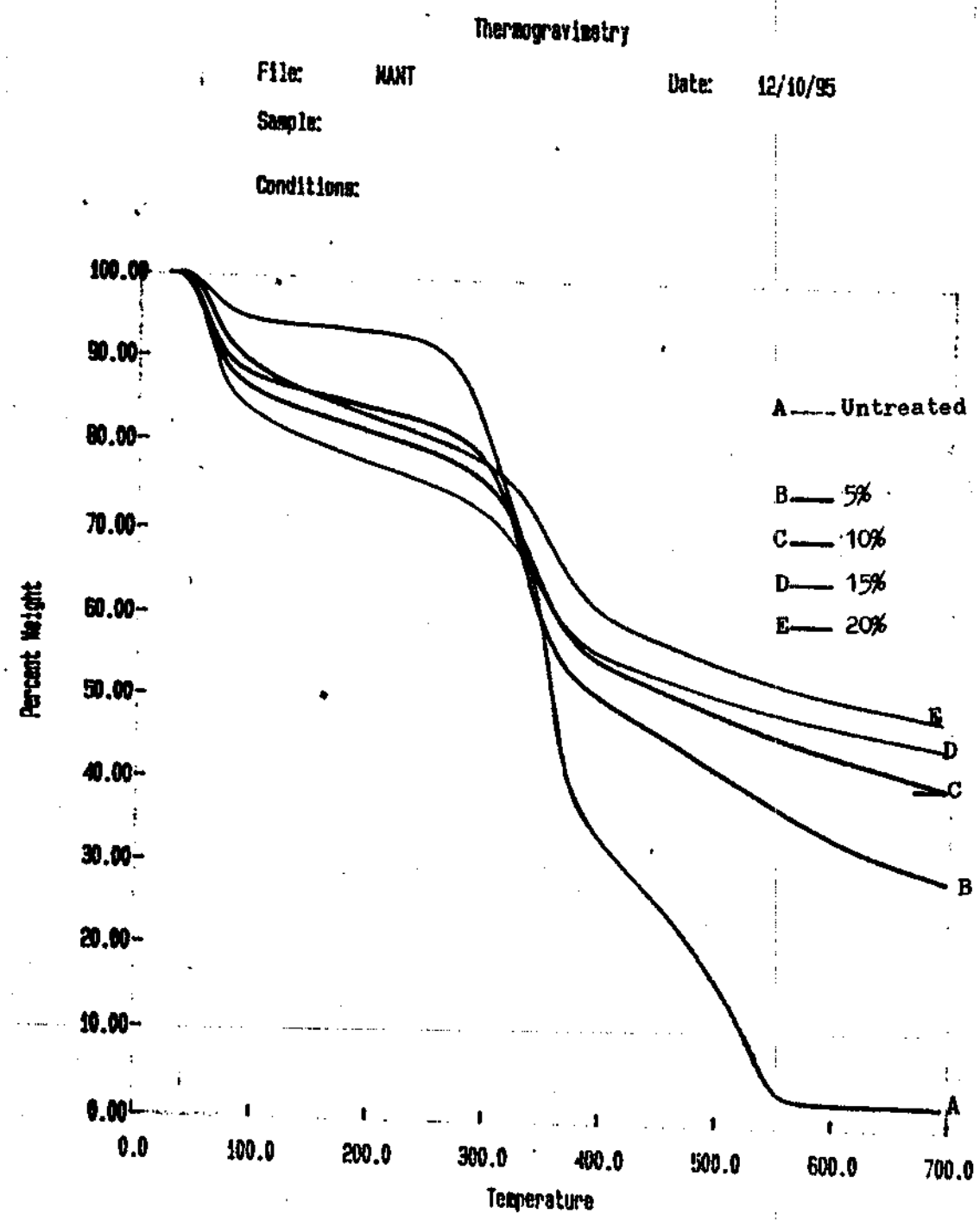


FIGURE 6.11(c): Effect of diammonium phosphate - borax combination (1:1 ratio) concentration on pyrolysis curves of mansonia wood at $10Kmin^{-1}$, in static air.

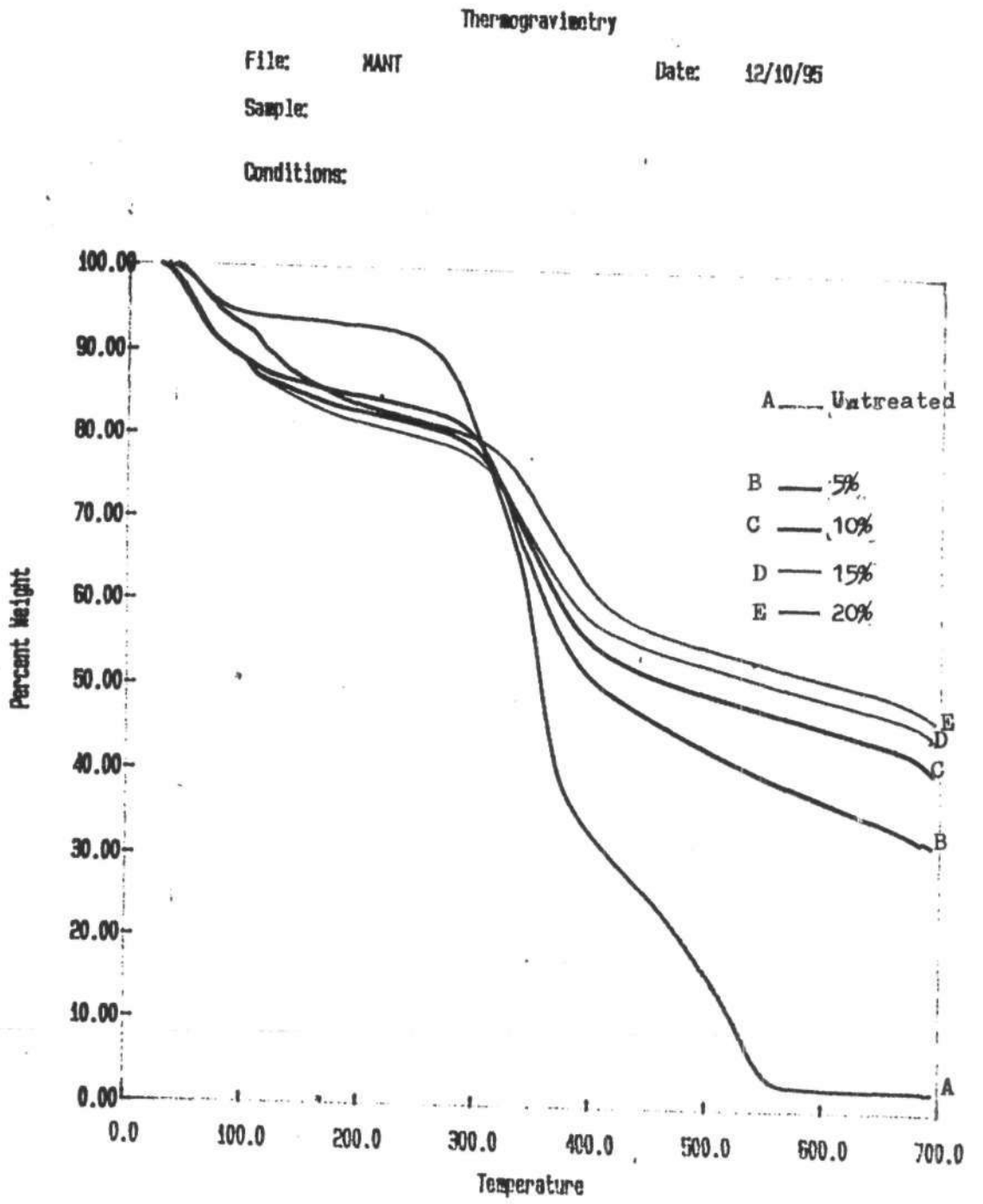


FIGURE 6.11(d): Effect of boric acid-borax combination (1:1 ratio) concentration on pyrolysis curves of mansonia wood at 10Kmin^{-1} in static air.

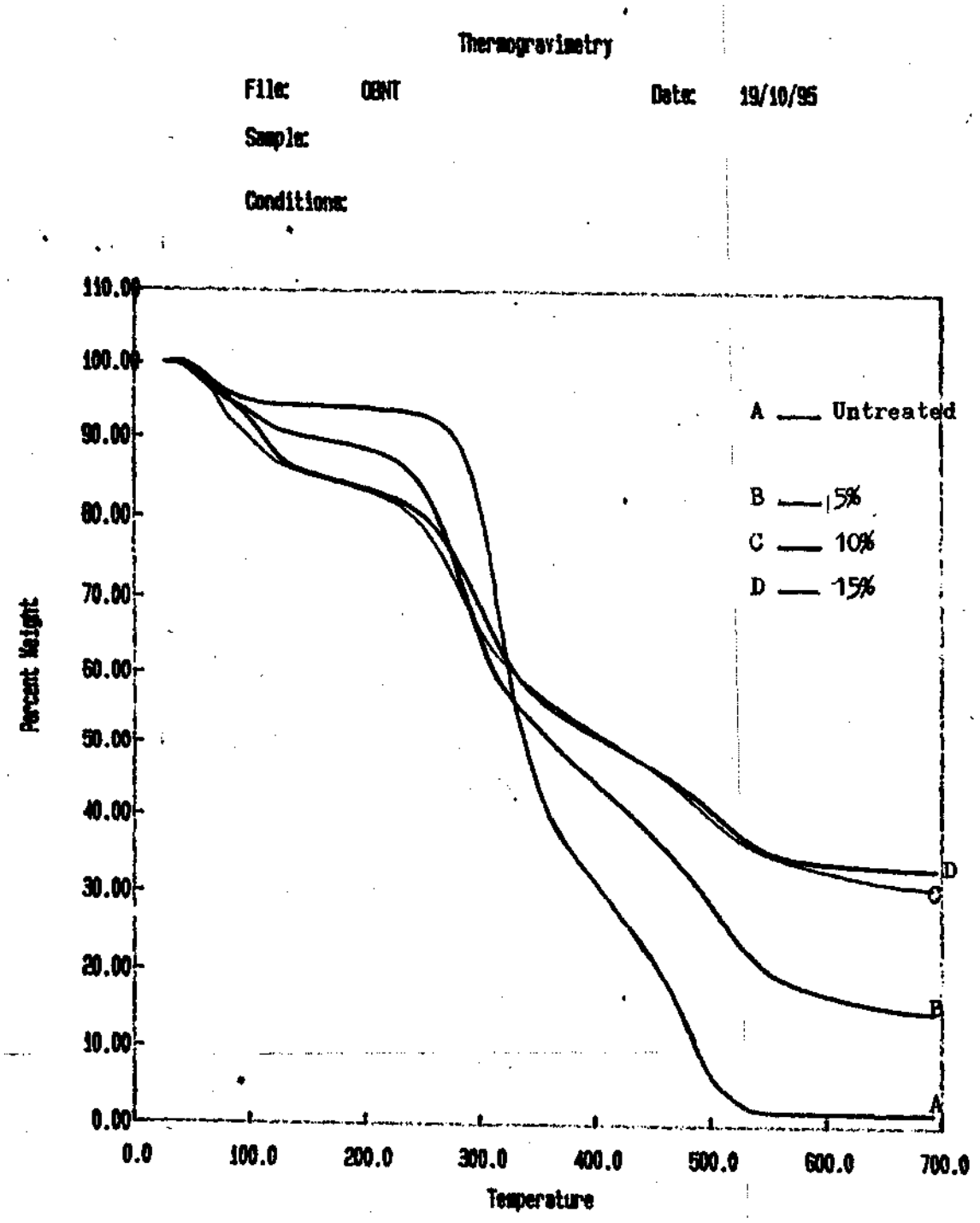


FIGURE 6.12(a) Effect of ALUM concentration on pyrolysis curves of Obeche wood at 10Kmin^{-1}, in static air.

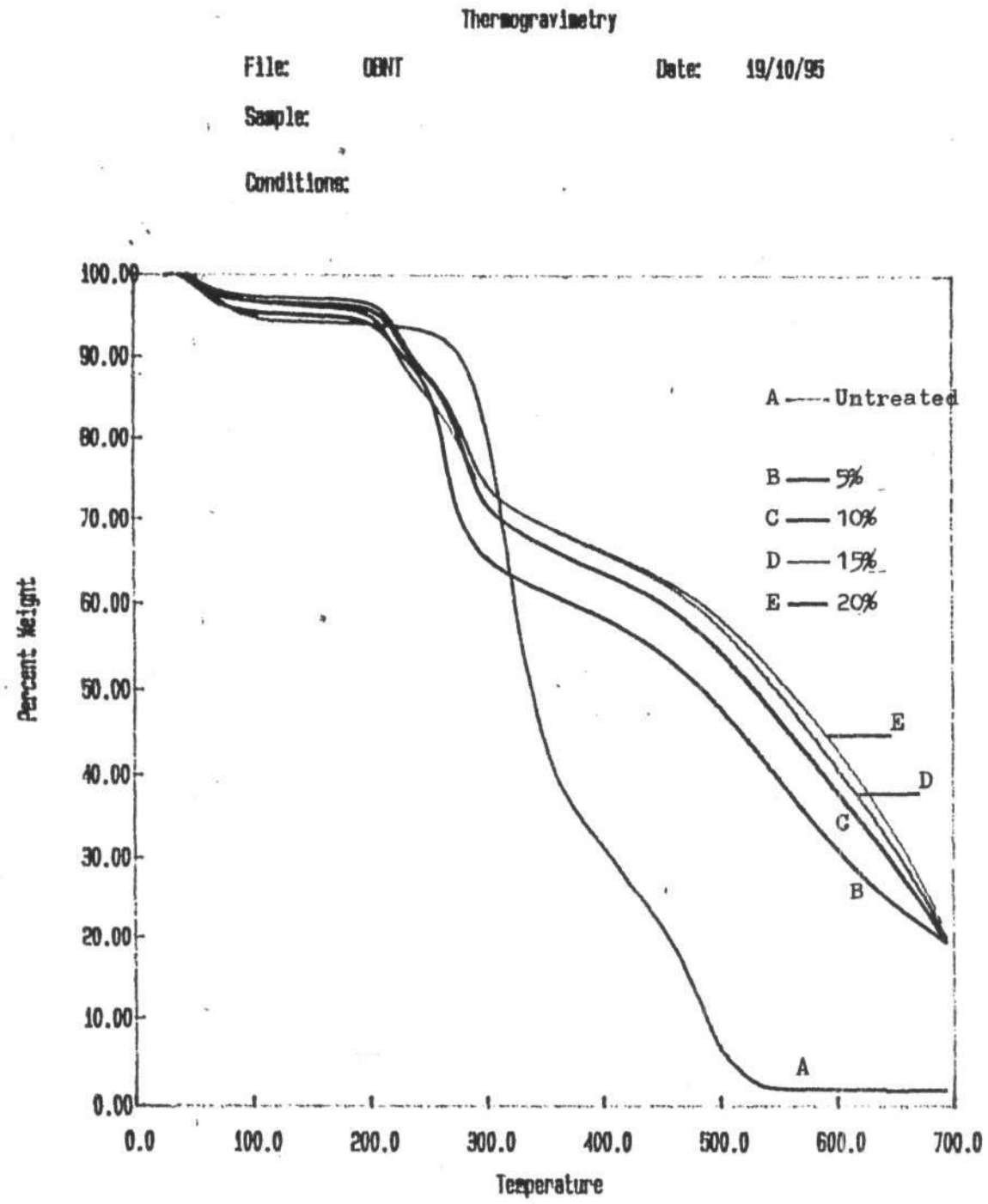


FIGURE 6.12(b): Effect of diammonium phosphate concentration on pyrolysis curves of Obeche wood at $10Kmin^{-1}$ in static air.

wood, char yield increases with flame retardant concentration. Of all candidate flame retardants studied, DAP:B, B:B and DAP (at the 15% level) promoted the highest char values indicating greater retardant activity. The remaining additive - alum is not as effective as the potential flame retardant listed above and may be classified as a second most effective. The results also show that for DAP and ALUM., high concentration flame retardant wood has much lower decomposition temperatures than low concentration flame retardant wood while the reverse is the case for DAP:B and B:B.

6.3.2 Effect on DTA Exotherm

The effect of selected flame retardants on typical DTA curves of wood are shown in Figs. 6.13 - 6.16. Previous results for untreated wood (section 5.4.3) indicate that the initial stage of pyrolysis is an endothermic reaction of loss of moisture near 120°C; at 200 - 250°C slight endothermic effect is still observed and the first major active pyrolysis (first stage) involved exotherm with flaming peak at about 335-400°C from the combustion of volatiles. Finally, the glowing combustion takes place during the second stage in the temperature range > 400°C (usually 400-600°C) until the entire sample had been consumed.

The results of the tests on treated samples show an endotherm below 120°C which is due to the evolution of sorbed water. Presence of possible

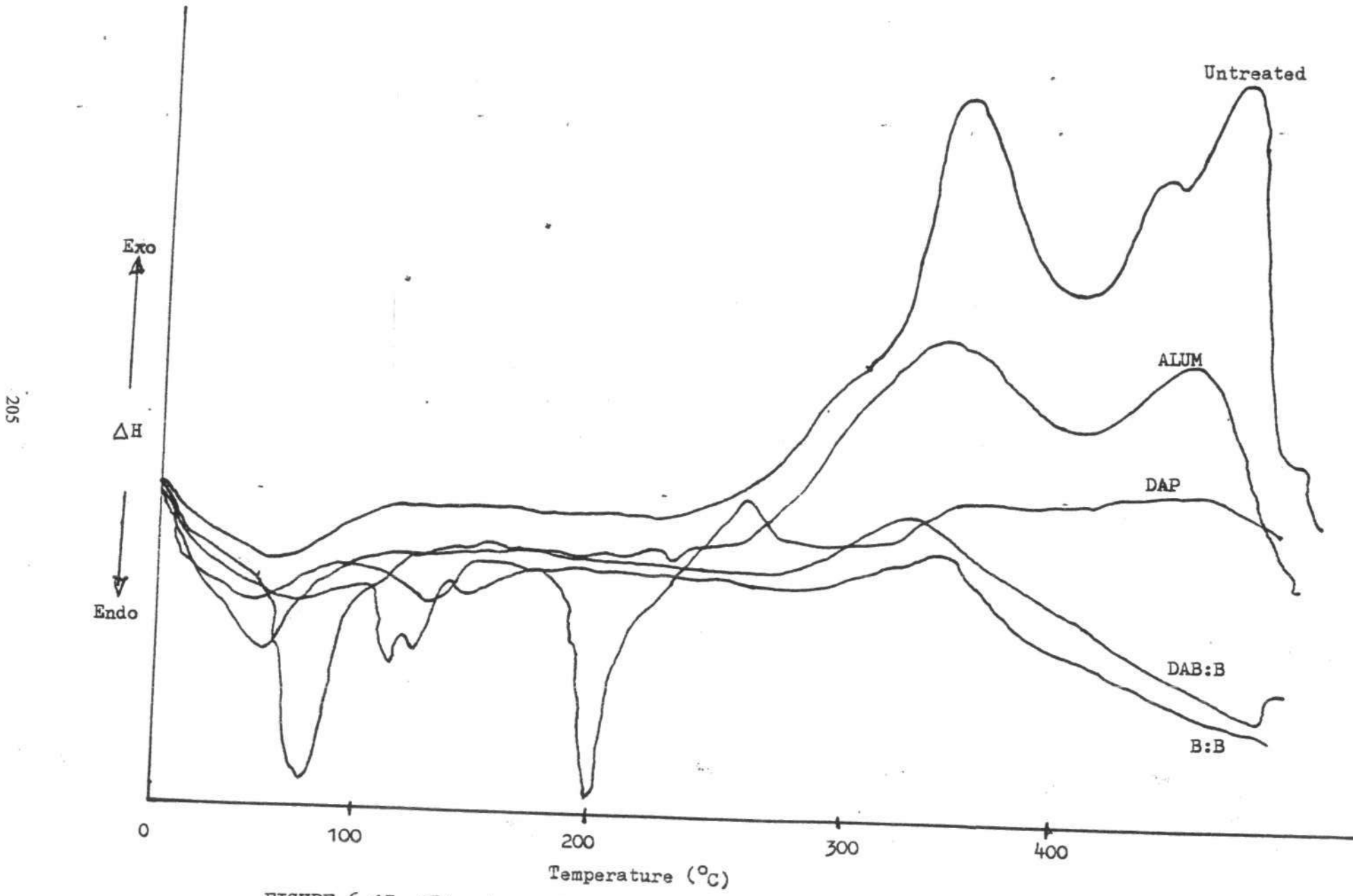


FIGURE 6.13 DTA - temperature curves for Ayan wood in air.

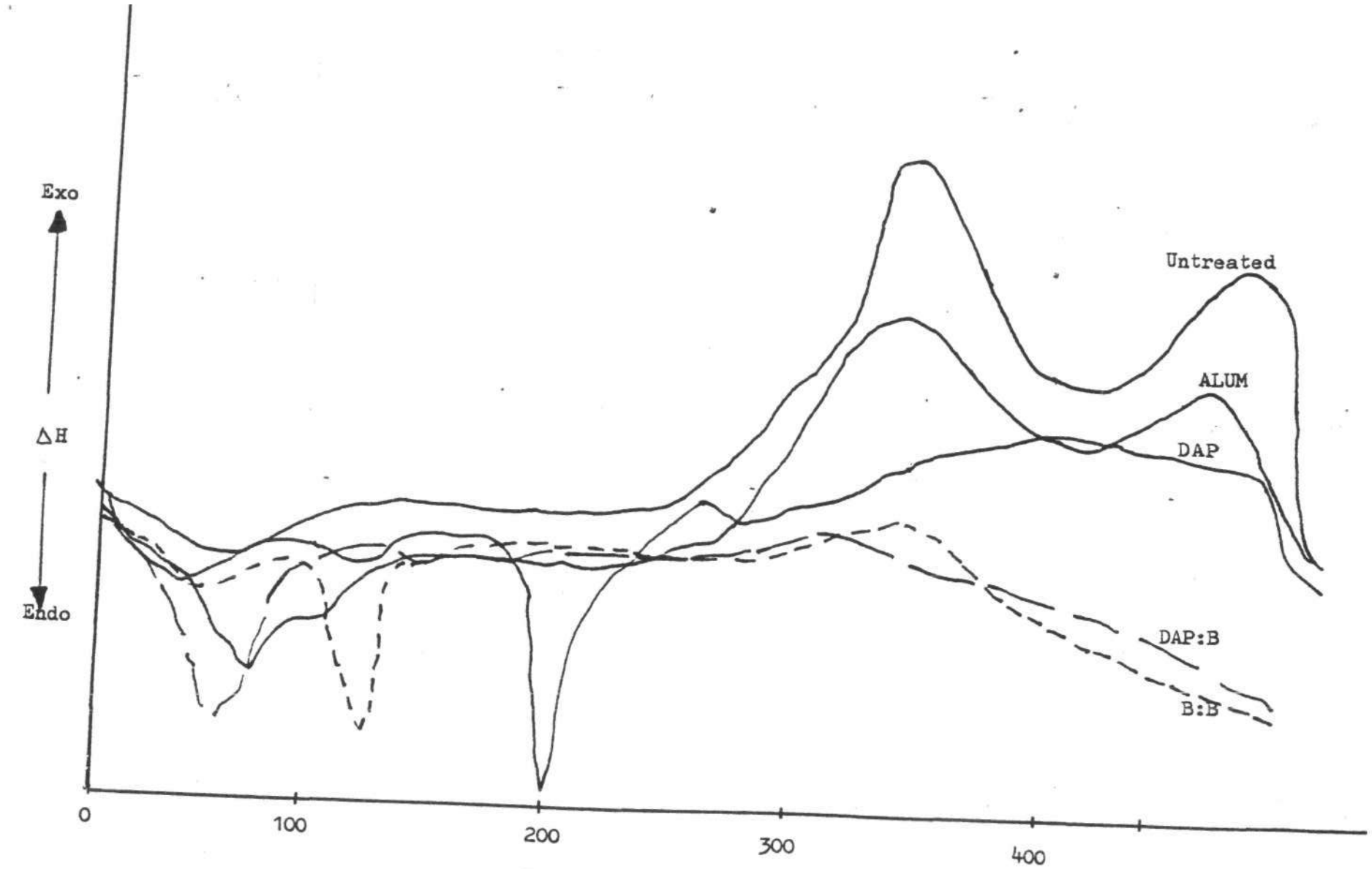


FIGURE 6.14: DTA - temperature curves for Walnut wood treated with selected flame-retardants in air.

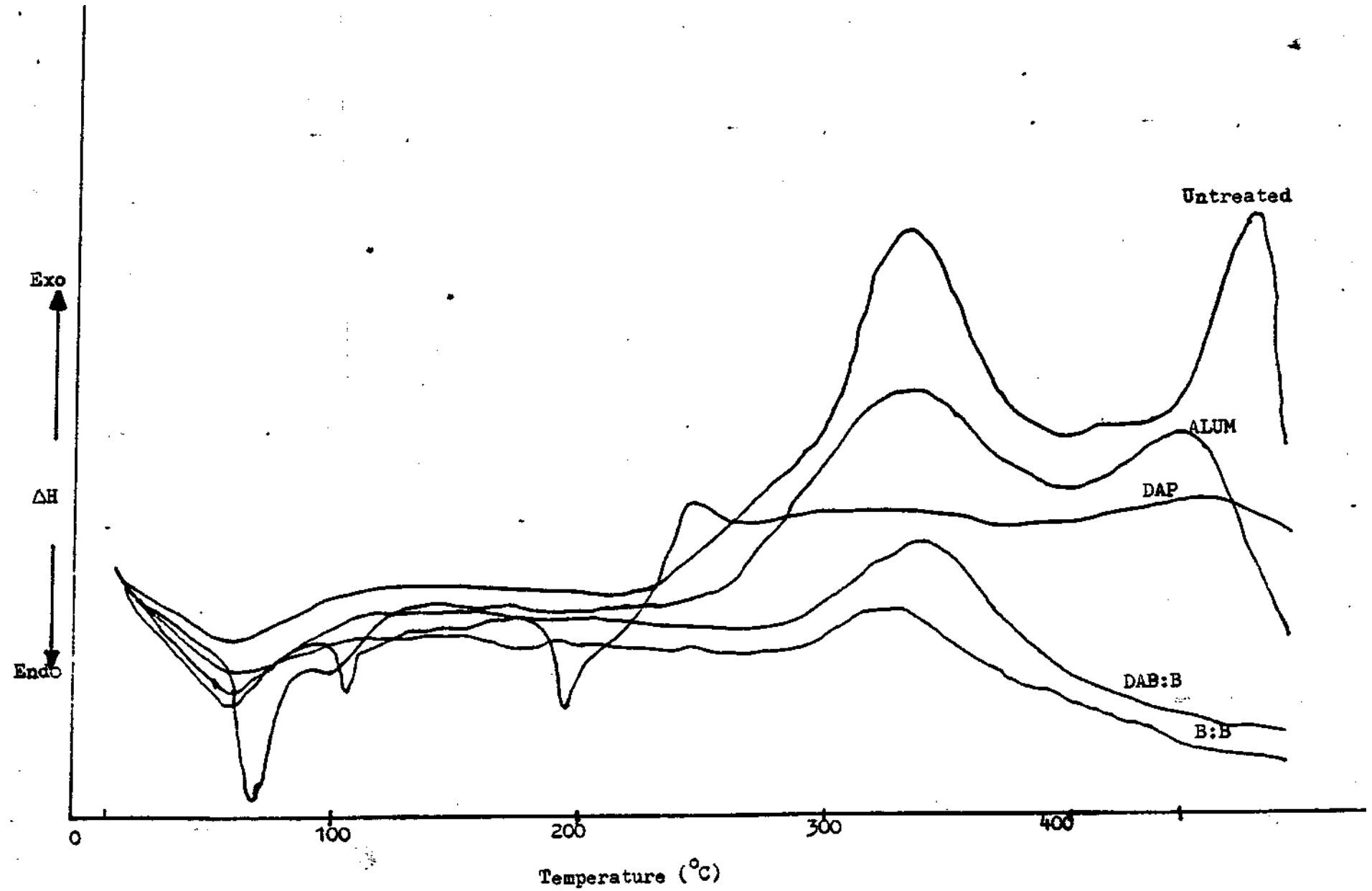


FIGURE 6.15: DTA-temperature curves for Ekhimi wood treated with selected flame retardants, in air.

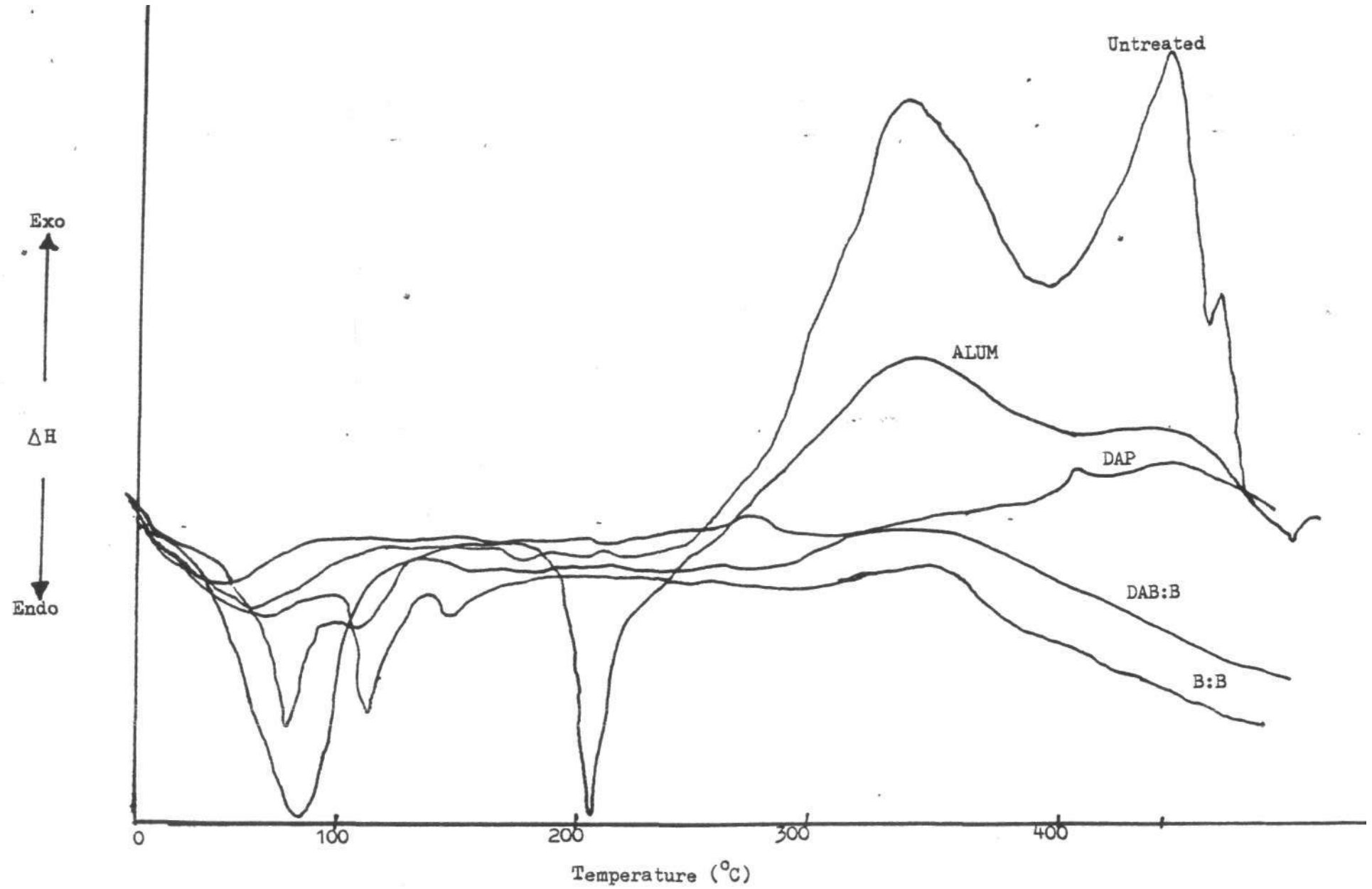


FIGURE 6.16: DTA -temperature curves for Obeche wood treated with selected flame-retardants, in air.

flame retardants - DAP:B, B:B and DAP, significantly reduced both the flaming and glowing exothermic intensities, with alum having a moderately marked effect. Compared to TGA, relative magnitudes of these flaming and glowing exothermic corresponded to the relative amount of char formed for the additives: DAP:B < B:B < DAP < ALUM.

The DTA curves of diammonium phosphate (DAP) treated samples indicate a sharp endotherm at about 200°C which can be attributed to DAP decomposition. This is followed by small exotherm peaking at about 270°C which may be attributed to the decomposition of samples leading to the formation and evaporation of volatile products. The samples are decomposed at lower temperatures compared to the corresponding 'pure' wood. The second stage exotherm which corresponds to oxidation of volatile and charred products started immediately. However, the rate of oxidation is slower when compared to untreated wood.

It seems also that exotherms due to oxidation of volatile products occurred at about 370°C while exotherm due to char oxidation occurred at temperature above 450°C. Similar results have been obtained by Akita and Kase (1982), and Hirata and Abe (1973a). According to Akita and Kase (1982), four peaks on the DTA curve of cellulose containing ammonium dihydrogen phosphate corresponded to the decomposition of the salt itself, to the pyrolysis of modified cellulose by the salt and of residual cellulose,

and to the secondary reaction of products generated from the pyrolysis of modified cellulose in the order of the occurrence, respectively.

A logical interpretation of this thermal degradation mechanism of DAP would seem to be that thermal degradation of DAP -treated wood commences with the generation of highly acidic reagents which alter the decomposition of the wood to such an extent that the primary decomposition route favours formation of carbonaceous char. At higher temperatures the acid reagent polymerises and the poly acid formed is more effective in catalysing the dehydration. Thus, during the first step of thermal degradation, released phosphoric acid will catalyse a series of heterolytic and homolytic cleavages of the substituents on the carbon chain of the condensation products which ultimately form carbonaceous char. In other words DAP breaks down in treated sample at around 200°C yielding primarily ammonia (NH_3) and phosphorous acid, P_2O_5.

$$(NH_4)_2HPO_4 \longrightarrow NH_3 + NH_4H_2PO_4$$

$$2NH_4H_2PO_4 \longrightarrow 2NH_3 + 3H_4O + P_2O_5$$

The NH_3 volatilizes while P_2O_5 is capable of catalysing the dehydration and decomposition of the wood constituents to produce more of the non-flammable gases and solid carbonaceous char. Probably, the P_2O_5 reacts with hydroxyl group of glucosan unit formed which could limit

laevoglucosan formation and thus account for the drastically reduced exothermic peak in flaming.

In the DTA curves of DAP:B and B:B samples endotherms which appear below 125°C may be due to the loss of sorbed moisture and the water of crystallisation. The increased endotherm is an indication of $Na_2B_4O_7.10H_2O$ loosing water and suggests that dehydration mechanism of the lewis base was initiated during decomposition of the borax. This is then followed by dehydration and depolymerisation up to around 290°C. The first and only reduced exotherms appear in the range 290-400°C and may be due to the simultaneous decomposition and oxidation of volatile products. The samples decomposed at slightly higher temperature when compared to 'original' wood and the rate of oxidation is faster but smaller than that of DAP. This is of some significance in view of this observation that DAP:B and B:B are capable of changing the nature of the DTA curves in the 270-450°C from strongly exothermic to mildly endothermic and needs further study. The second stage exotherm corresponding to oxidation of charred products did not appear at all in the two samples indicating very high degree of effective glow retardation.

Their flame retardancy may be postulated that the depolymerised fragments of wood were catalysed to form more char and less tar by depolymerisation and even aromatisation of the borax. As a result, the

flaming exotherm intensity is definitely reduced because less tar is made available. The almost complete prevention of glowing combustion could have come from the presence of boric acid which is a well-known excellent glow inhibitor (Browne, 1958) for cellulose. Compared with the DAP or borax or boric acid alone, whose ultimate efficiency is given by the effectiveness of the interaction between wood fragments and the phosphorous oxides or sodium oxides or acidic reagents, it is interesting that the only possibility for the efficiency to be enhanced would be for them to be converted into some degradation product other than oxides. This has been found to constitute the basis for the DAP:B or B:B synergistic effects observed in this work.

The DTA curves for ALUM treated samples show that the exotherm peaks (both for flaming and for glowing) are reduced in the case of treated samples. However, the degree of suppression indicates that ALUM is not as effective as the other flame retardants especially in reducing glowing. The initial large endotherm occurring below 160°C may be due to desorption of moisture and the large water of crystallisation and alum decomposition. The range 150-270°C corresponds to the dehydration and depolymerisation. The first exotherm (1st stage) occurring with a maximum at around 345°C is due to the decomposition of wood leading to the formation of volatile products. The second stage exotherm peaking at about 460°C may be

attributed to the oxidation of volatile and charred products. Alum breaks down to K_2SO_4, Al_2O_3, SO_3 and H_2O.

$$2KAl(SO_4)2.12H_2O \rightarrow k_2SO_4 + Al_2O_3 + 3SO_3 + 12H_2O$$

K_2SO_4 and Al_2O_3 are Lewis acids (Schuyten et al., 1954). The TGA and DTA result suggest that the dehydration mechanisms of a lewis acid is initiated during Alum decomposition. This catalytic process is sustained by Al_2O_3 . Pyrolysis temperature is lowered by the cooling effects of large amount of water vapour and the dilution of combustible volatile pyrolysates by SO_3.

6.4 EFFECT OF FLAME RETARDANTS ON LOI VALUES

The flammability of wood samples treated with the selected inorganic flame retardants as determined by the Stanton Redcroft FTA apparatus is presented in Table 6.3. Most of the chosen additives enhance flame retardancy in terms of LOI. The results clearly show that at 10% concentration level, the most effective treatment were diammonium phosphate (DAP) and boric acid - borax (B:B) followed by DAP - borax (DAP:B). ALUM gives very little rise to a high LOI values. It was observed that DAP, though most effective, gives rise to large smoke production and char yield compared to the rest additives. Clearly, this observation required further study.

Table 6.3. LOI (O_2%) Values of the Wood with Various Flame Retardants.

Flame Retardants at 7.5% Conc.	NT	DAP	ALUM	DAP:B	B:B
Apa	26.5	62.8	29.2	42.9	58.1
Iroko	27.4	75.0	29.5	43.1	55.2
Ayan	26.4	62.0	27.5	46.8	59.3
Sapele	24.7	68.7	26.5	57.8	65.2
Guarea	24.3	60.0	24.9	49.9	57.9
Berlinia	31.7	72.0	32.3	49.6	62.1
Lagos	25.9	77.2	27.5	68.3	67.5
Walnut	23.4	66.5	25.5	47.5	62.0
Mansonia	25.0	71.4	26.4	45.2	55.2
Opepe	27.8	58.2	28.6	36.7	52.0
Danta	23.6	60.4	24.7	43.2	47.1
Ekhimi	22.5	58.7	26.0	43.9	51.8
W.Afara	26.9	85.1	27.6	65.4	63.7
Obeche	22.4	95.1	23.6	45.2	54.6

6.5 POSSIBLE MECHANISMS OF THE RETARDANT ACTIVITY

The tar fraction mainly laevoglucosan, produced by the pyrolysis of cellulose has been regarded as highly flammable and largely responsible for the flammability of cellulosic materials (Shafizadeh, 1968, 1971; Shafizadeh and Foo, 1973). The tar burning in the gas phase fuels the flames and provides the heat needed for the pyrolysis reactions and propagation of the fire. According to the hypothesis of Parks et al. (1955), which was supported by Schewenker and Pacsu (1958), prevention of leavoglucosan formation by chemical means could decrease flammability of the resultant cellulose derivative.

As generally accepted, effective flame-retardants act either in the condensed phase or in the vapour phase above the decomposing polymer. Retardants which act in the gas phase exert their effect by functioning as either inert diluents or as free radical inhibitors which slow the oxidation processes and decrease the heat returned to the wood surface. Those retardants which act in the condensed phase may operate by several mechanisms. According to Barker (1964), they may inhibit the polymer pyrolysis so that it does not break down to produce the small volatile molecules necessary for flame propagation or more commonly, they may act to alter rather than inhibit this pyrolysis reaction. The alteration is such that the mode of pyrolysis is changed and leads to the production of less

flammable volatile (catalyses dehydration), or possibly dilution of the flammable mixtures during flaming combustion. Finally, they may also exert their effect in a physical rather than a chemical manner. In this case they act as a shield to prevent the transfer of heat from the flame back to the wood surface. This reduces the rate of polymer pyrolysis as well as its fuel production or flammability.

6.5.1 Diammonium Phosphate (DAP) - $(NH_4)_2HPO_4$

In this study the results have shown that the wood sample containing $(NH_4)_2HPO_4$, (DAP), is decomposed at lower temperature than the corresponding pure wood and enhance char formation by catalyzing the dehydration and decomposition reaction. This occurs because DAP is decomposed to NH_3, $(NH_4)H_2PO_4$ and H_3PO_4 on heating (Sekiguchi and Shafizadeh, 1984; George and Susott, 1971). The NH_3 facilitates decomposition by reacting with intermediate carbonyl compounds to form glycosylamines or schiff bases, that are readily dehydrated by a β - elimination process (Sekiguchi and Shadizadeh, 1984). Differential thermal analysis (DTA) by Tang and Eicher (1968) showed that the $(NH_4)H_2PO_4$) loses ammonia at 166°C to yield phosphoric acid, which undergoes further degradation:

$$(NH_4)_2HPO_4 \longrightarrow NH_3 + NH_4H_2PO_4$$
$$NH_4H_2PO_4 \longrightarrow NH_3 + H_3PO_4$$

$$2H_3PO_4 \longrightarrow H_2O + H_4P_2O_7$$
$$H_4P_2O_7 \longrightarrow 2H_2O + P_2O_5$$

The highly acidic reagents which result catalyse hydrolysis and decomposition (pyrolysis) of the wood to carbon and water by their reactivity with hydroxyl groups and by the avidity with which they absorb water. In this study, phosphoric acid, for example, may react first with the hydroxyl groups of glucosan units to form polyhydroxy aldehydes and ketones which could limit laeveoglucosan formation. Finally the H_3PO_4 groups may pyrolyze to regenerate the phosphoric acid and leave carbon and water. The overall reaction would then be:

$$nC_6H_7O_2(OH)_3 + 5nH_3PO_4 \longrightarrow 6nC + 5nH_2O + (5nH_3PO_4)$$

Saunders and Backus (1966), have suggested that liberated phosphoric acids change the course of the normal pyrolysis of the flammable substrate and accelerate elemental carbon formation by a carbonium-ion mechanism. Such a hypothesis is based on the fact that indeed with ammonium phosphates present the burning of cellulose yields a more carbonaceous char, with a corresponding reduction in the amount of flammable tars produced. The outstanding performance of the phosphoric acids liberated from the ammonium phosphates is attributed by Lyons (1970), to ester formation of the cellulose with the polymeric phosphoric acid. This would prevent the formation of laevoglucosan containing tars.

The decomposition of DAP apart from altering the course of the degradation of the flammable substrate certainly seem capable of additional reactivity in the gas phase by dilution of the flammable species and possibly inhibits the flame reactions. This may be due to the liberation of phosphoric acid and ammonia. Thus in the present investigation, the effect of DAP can be classified according to condensed and gas phases.

The generation of polyphosphoric acids also results in the effective elimination of afterglow in wood. The poly acid, being very viscous, is thought to be a film-forming substance that can coat the surface. This would retard the diffusion of oxygen into the reactive layer of carbon. Further Little (1947), suggested that the phosphoric acid generated from the thermal decomposition of the ammonium phosphates reacts via the following series of reactions (Pasek and McIntyre, 1976):

$$2H_3PO_4 + 5C \longrightarrow 2P + 5CO + 3H_2O$$

$$4P + 5O_2 \longrightarrow 2P_2O_5$$

$$P_2O_5 + 5C \longrightarrow 2P + 5CO.$$

The net heat liberated in these would be considerably less than that for the direct oxidation of carbon to CO_2. For CO_2 the heat of formation is 94.4K cal mol^{-1}, compared to only 26.4K cal mol^{-1} for CO.

6.5.2 DAP:Borax (DAP:B) - $(NH_4)_2HPO_4$:$Na_2B_4O_7.10H_2O$ and Boric:Borax (B:B) - H_3BO_3:$Na_2B_4O_7.10H_2O$

As earlier found from the test results (TG/DTG, DTA, and LOI results), it is reasonable to suggest that the condensed phase activity of the DAP:B is the same as that of the B:B. Both series seem to be capable of catalysing the wood decomposition at about the same temperature and rate and increasing the amount of residue remaining at the end of pyrolysis/flammability by about same amount. Both show complete termination of glowing combustion as can easily be seen from DTA thermogram and LOI observations.

Like the phosphates, the borates (borax) are very effective flame retardants for wood (Woods, 1967), and boric acid is considered excellent for afterglow suppression (Pitts, 1973). According to Gay-Lussac (Hird and Simms, 1953; Little, 1947), one of the mechanism of flame proofing cellulose was the coating of the fibre with non penetrable glass skin that excludes oxygen and prevents further propagation of combustion. Boric acid and the hydrated borate have low melting points and nicely fit this Gay Lussac, (Hird and Simms, 1953), theory of forming a glassy coating: when these compounds are exposed to a flame, H_3BO_3 (mp. 171°C) loses water and changes first to metaboric acid, HBO_2 and finally to boric oxide, (Pitts, 1973; Nies, 1964).

$$2H_3BO_3 \xrightarrow[-2H_2O]{130^oC-200^oC} 2HBO_2 \xrightarrow[-H_2O]{260-280^oC} B_2O_3$$

Above 325°C B_2O_3 softens to a glass and becomes pourable at about 450°C. In the case of borax, it dissolves in its own water of hydration, first swells to a frothy mass, then loses water, and finally fuses to a clear melt.

Another factor which may play a role in reducing the flammability of wood is the water vapour released into the gas phase by the dehydration of the borax. Ten water molecules act as a heat sink, reducing the amount of heat transferred to the polymer for its continued decomposition and as a diluent of the gaseous fuel, thus changing the composition and temperature of the gaseous mixtures formed within the flammability limits.

The flame retardant action of the B:B mixture can also be chemical in addition to the physical coating of the glassy matrix on wood. Hilado (1969), reported that the inorganic boron compounds do promote char formation in the burning process, as do the ammonium phosphates. According to Byrne et al. (1966), the mechanism involving the formation

of char is clearly related to the thermal reaction of boric acid with alcohol moieties. Moreover, prolonged exposure to flame causes the coating to dehydrate, generating water which cools the flame and cause it to extinguish. The boron residue may also react with the hydroxyl groups of the cellulose to generate additional quantities of water and form an inorganic char that is difficult to ignite and burn.

6.5.3 Alum

Alum is a form of alumina hydrate that has some utility as a flame retardant. It decomposes at about 240°C to yield both water and alumina functionalities to the flame retarding process. The evolution of water absorbs heat. The water cools the flame and dilutes the flammable gases. A detailed alum mechanism has been given in section 6.2.3.

CHAPTER SEVEN

CONCLUSIONS AND FURTHER WORK

7.1 CONCLUSION

A number of conclusions can be drawn from the investigations carried out in this project:-

(i) Fourteen species of tropical hardwoods have been studied under flaming and glowing conditions in static atmospheric air. For all the wood samples there is a high significant correlation between time of ignition and flame spread rate and timber density. The afterglow time was found to depend on char yield and ash residue. Moisture content, reduces ease of ignition and flame spread.

(ii) The rate of flame spread depends on the orientation of the sample; for each wood, vertical orientation gives a higher flame spread value than horizontal orientation.

(iii) The woods pyrolysed in air in two well defined stages. For most of the wood, the first stage occurred between 230-270^{O}C and comprise two adjacent mass loss transitions separated by about 30^{o}C. Each

stage involves competition between a char-forming reaction and a volatilisation.

(iv) The start-, peak- and end- temperatures of degradative transitions are similar for both stages for all wood samples and do not depend on timber density. All ourteen samples degraded to approximately the same final mass, implying a similar final structure.

(v) The activation energies for decomposition of all selected wood in air were similar in magnitude, which probably indicates that the decomposition weight loses took place through similar mechanisms. Fairly high activation energies are required for the first stage involving dehydration and chain scission reactions. Subsequent secondary product and char oxidation during stage 2 have significantly lower activation energies.

(vi) Two prominent exotherms were observed on the DTA curves of the "pure" wood samples. It is considered that the first peak at about 329-350°C and the second peak at around 450°C corresponded to the flaming combustion and char residual oxidation (glowing combustion) respectively. In fact, the DTA and DSC exotherms occurred concurrently with weight loss reaction of the TGA.

(vii) Differences in the LOI values (22%-32%) for the untreated wood were observed, and the highest value of 32% was obtained for the berlinia wood. This might suggest that the tropical wood studied have an inherent flame-retardant property.

(viii) Wood treated with the different inorganic salts is a material with well-reduced flammability according to the LOI values, ignition time, mass, burning rate, afterglow, etc.

(ix) Thermal curves for original and treated samples show considerable differences - the maximum rate of weight loss is much lower for treated sample than for original corresponding wood; the residue can amount to maximum of 51% for DAP:B and B:B, 44% for DAP and 30% for ALUM of the weight of the treated sample while for non-treated wood only a small amount of ash (less than 20%) is observed.

(x) The exothermic peak on DSC/DTA areas (both for flaming and for glowing) are reduced in the case of treated samples. The relative magnitude of these flaming and glowing exotherms corresponded to the relative amount of char formed for the additives. This conclusion confirms that the most effective treatments were DAP:B, B:B and DAP, followed by Alum and fertiliser.

(xi) There is no correlation between the effectiveness of the flame retardants as determined by LOI and the thermal analysis tests of the wood.

(xii) The flame retardants showed similar reactivity with each of the wood studied. Though it was not clearly determined whether the flame retardant acted directly with the undecomposed wood or with decomposition products, the thermal analysis data indicated that they can react readily with similar structures capable of undergoing phosphrylation and in general, the retardants function by complex processes that entail the vapour phase, the condensed phase, and the dehydration mechanisms.

(xiii) The results of the present investigation do not agree in one way with those of Shafizadeh (1968), Shafizadeh and Chin (1977), Shafizaseh et al. (1975) and others (Browne and Tang 1962, 1963; Brenden, 1972; Hirata and Abe, 1973; Tang, 1967; Woo and Schneiwind, 1987), who found that effective flame retardants alter the thermal decomposition of carbohydrates by lowering the onset temperature for decomposition. The present result show that DAP:B and B:B treated wood decomposes at temperatures approximately higher than those of corresponding "pure" wood.

7.2 FURTHER WORK

Substantial progress has been made in reaching an understanding of the fundamental mechanism of the pyrolysis and combustion of tropical wood and their alteration by added flame retardants. It was, however, not possible to undertake full detailed burning characterisation of wood within the time available for this work. Therefore for a further understanding of the burning behaviour of these woods to be developed, the following suggestions are recommended for further studies:

(i) Wood is a multicomponent, molecularly non-homogeneous materials in which part of the components exists in continuous separate intermingling structure . Since this work did not investigate the individual contribution and interaction between components, it will be interesting to study wood composition by spectrographic analysis such as GC - MS, C - NMR spectra prepared at different temperatures and then undertake thermal analysis to determine to some degree what contribution some of these components make to the thermal decomposition characteristics of the wood.

(ii) Most deaths in a fire are caused by the products of combustion, and aggravated in some cases by oxygen depletion rather than direct consumption in the fire. Hence, Gas chromatographic, infrared spectroscopic, mass spectrometric, and other methods could be used

to quantitatively and qualitatively analyse the main combustion products from these woods ("pure" and treated).

(iii) Heat evolved during burning is one measure of the flammability of the system. Further, it is often questioned whether flame-retardant treatments change the rate of heat release during a fire exposure. It is therefore necessary to determine the calorific values of these wood and investigate whether the volatile products released at the initial stages of olatilisation in the pyrolysis of wood treated with several individual flame retardant treatments have heats of combustion less than for untreated wood. This is required to complement the other thermal studies done.

(iv) A detailed, scanning electron microscopic study of untreated and treated wood should be conducted to reveal the internal structure of these wood. This type of study will help in elucidating the molecular arrangements of the main polymeric constituents.

(v) Smoke is produced in almost all fires and presents a major hazard to life too - inhalation of toxic gases and the reduction in visibility. It may be necessary therefore to study the smoke particle sizes as well as its composition.

(vi) It may be necessary to investigate thermal analysis (TGA/DTG and DSC) at various heating rates (10 - 100 $Kmin^{-1}$) and conditions - under air, nitrogen and vacuum, and then study the kinetics of degradation. This will perhaps put "paid" to the investigation of the effect of heating rates, atmospheric conditions, etc, on wood pyrolysis.

(vii) Consider the particular effectiveness of the flame retardant in conferring flame retardancy on wood and investigations some other forms of FR using inorganic and organic alike may have some interesting results. The chemistry of interaction between wood and the flame retardant could be studied in some greater detail.

(viii) The main disadvantages recorded for flame retardant wood as compared to untreated wood are strength loss and increased hygroscopicity, acidity and corrosivity, etc. Hence it is important to study the causes and magnitude of some of these side effects and then find a way to minimise them in order to utilise flame retardant wood more safely and efficiently.

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