PYROLYTIC DECOMPOSITION OF LIGNOCELLULOSIC MATERIALS

by

Ana Rita Fraga de Araújo

Department of Chemical Engineering and Chemical Technology
Imperial College of Science, Technology and Medicine
London

A thesis submitted for the degree of Doctor of Philosophy to the University of London and for the Diploma of Imperial College.

1990

To Ian for all the comprehension, love and help throughout this major task of my life.

ACKNOWLEDGEMENTS

This project was supervised by Dr.R.Kandiyoti, whom I wish to thank for giving me the opportunity to carry out this research programme, and for his advice and encouragement throughout the work.

I also wish to thank many colleagues within the Chemical Engineering Department for their assistance with this project; in particular Mr.R.J. Wood for all his valuable help and support with the electronics, and Mr.S.Ramsey for all his hard work in fabricating the many glass components. I also express my thanks to Dr.A.Gaines for his useful comments and assistance with some of the analytical experiments, and Dr.S.Gonenç for her humour and comradeship as we laboured many hours together in the laboratory.

Outside the Department I thank my government agency, The Brazilian Research Council (C.N.Pq.), for providing the financial support which enable me to undertake this research. Finally I extend my warmest thanks to Carminha and her "three little ones", Lourdes Vasconcelos, Thereza Maia, Abuendia Pinto, Ricardo Ferreira and Carlos Lopes for all their encouragement, good wishes and family support.

ABSTRACT

Improved experimental methods are described, using a wire–mesh reactor, for undertaking pyrolysis studies of lignocellulosic materials. This research programme commences with these experimental procedures being applied to two naturally occurring materials namely Sugar Cane Bagasse, an abundant industrial waste product in Brazil, and Silver Birch. The solid and liquid pyrolysis products, obtained for a wide range of pyrolysis parameters are collected, the pyrolysis yields determined, and the liquid products analysed. Particular emphasis is placed upon the measurement of the tar yield, and its product distribution, for Sugar Cane Bagasse. Based upon a detailed GC–MS analysis the product distribution of the pyrolysis tar of Sugar Cane Bagasse is shown to be broadly independent of the process parameters, and its major component is shown to be vinyl phenol. These researches are then subsequently complemented by a similar, in depth, study of the pyrolysis products of pure cellulose, lignin and their mixtures, and the measurement of the cellulose/lignin ratio of the above naturally occurring materials. A detailed examination of the total volatile yields as a function of the cellulose content of the synthetic materials and the yields of the pure components, coupled with a comparison of these results with those obtained from the naturally occurring materials is made; from this analysis an interaction between cellulose and lignin is shown to take place during the pyrolysis process in these lignocellulosic materials. For synthetic materials the total volatiles yield is seen to be lower than would be expected from the simple, arithmetic, addition of

the yields of the individual pure components, in contrast, to the naturally occurring materials where the yield of total volatiles is higher than would be expected, as calculated above. The influence of the morphology of lignocellulosic materials on the pyrolysis product yields, and their composition, is investigated in a further series of experiments, using the techniques of SEM and DSC, and discussed in relation to these new results.

CONTENTS

CHAPTER 1

CHAPTER 4

CHAPTER 5

CHAPTER 1

INTRODUCTION.

1.1 — Introduction: World Energy Supplies.

Energy flows constantly into and out of the earth's biosphere. The surface environment receives, by far, its major energy input via solar radiation, this is augmented by a small quantity of heat from the earth's interior, and the tidal energy from the earth–moon–sun gravitational system. The leaves of plants capture only a small fraction of this incident solar radiation and store it, chemically, by the mechanism of photosynthesis.

The solar energy contained in natural gas, petroleum, and coal is stored in a most useful form for mankind's needs, but unfortunately these energy resources build up or accumulate at an extremely slow rate; they also contain an infinitesimally small fraction of the solar energy that has been intercepted by the earth over millions of years. The entire energy content of the known fossil fuel reserves has been estimated to be equivalent to about 21 days of the total solar energy incident upon the Earth's surface[67]. In contrast trees, for example, are capable of storing solar energy in a relatively useful form at an absolute efficiency that may be low but which is, in relative terms, many times greater than that in the production of gas, petroleum, and coal.

1.2 – Problems Associated With Crude Oil.

1.2.1 – Chemical Feedstocks from Petroleum and Gas.

At present almost all our organic chemicals, and the synthetic organic polymeric materials derived from them, are obtained using either petroleum or natural gas as the primary feedstock. This dependence is now so great that the term petrochemicals has become synonymous with the chemical industry. However since 1973 petroleum and natural gas cannot, in general terms, any longer be considered to be inexpensive raw materials that are readily available from stable sources of supply. Furthermore, there is an increasing awareness of the finite nature of these fossil liquid and gaseous hydrocarbons, and their rate of depletion.

In the immediate future, oil will continue its undisputed leadership as the number one feedstock for the chemical industry; but then coal and hydrocarbons from oil shale and oil sands may, possibly, challenge its pre–eminence. Currently these fossil resources are substantially more expensive to process than oil; and since they are also finite, chemicals from biomass, the precursor of fossil fuels and the only renewable carbon source, will play an increasingly important role. When these stages will take place depends upon many factors only some of which may be foreseen, and, may depend in particular, on national and international policy decisions.

In 1973 the downward trend in prices of chemicals was abruptly halted; retrospectively the cheapness of these products may be seen as a temporary phenomenon, that occurred only because of the unrealistic oil price. Whilst it is true that the cost then of finding and producing oil was quite low, because a large proportion of total oil production was located in easily accessible regions, and thus in simple economic terms the low unit petroleum cost was justified, these simplistic market forces did not place a more realistic value upon oil reserves; no premium could, or would, be established that reflected the finite, and rapidly diminishing, stocks of crude oil. Hence there was then little or no economic incentive towards the development of alternative energy sources; this "cheap energy" policy has led to many of the industrial, chemical feedstock problems faced today by developing countries.

For the future, current indications are that, in general, greater demands will be made on renewable energy resources, particularly as feedstocks for carbon based chemicals.

1.2.2 – Fuels from Petroleum.

The increase in the relative cost of crude oil, over the last decade or so, has created obvious difficulties for all those developing countries which rely on oil products for the major proportion of their primary energy requirements. These problems will, most probably,

increase in the future; since the combination of ever diminishing reserves will probably continue to force up the true price of crude oil. Additionally for these countries, since increased per capita energy consumption is an unavoidable pre–requisite of economic development, the need to develop alternative energy sources, both renewable and non–renewable, is clear. Amongst the many possible energy sources the development of energy supplies from indigenous biomass is an area which has obvious interest and promise for the developing countries; and it is, therefore, receiving increasing attention. However only a few commercial production processes are available to date that utilize biomass for the production of either fuels or chemical feedstocks.

It may be argued that, for developing countries, the central issue is not their current dependence on petroleum itself but rather on petroleum technology, for power generation, fuels and chemicals production. As a direct consequence of the past massive consumption of petroleum the best understood, most efficient, and usually least expensive technologies for chemicals and energy production revolve around the use of oil; hence, in the limit, the existing technologies dictate the use of petroleum. Synthetic fuels themselves should be compatible with existing, high efficiency, energy installations; as yet little attention has been paid to this requirement. By the transformation of "low density BTU" materials, for example biomass, into higher ranking fuels with appropriate physical properties, so that they may be utilised in existing natural gas, oil, and coal burning equipment, with little or no additional investment in plant modifications or significant losses in

process efficiencies, the development of third world countries would be facilitated.

1.3 – Biomass: The Energy Reserve of the Future?

1.3.1 – Introduction.

Wood, the archetypal fuel from biomass, is one of the oldest energy sources known to man; it has been used for thousands of years to provide both heat and light. When liquid and gaseous fossil fuels were discovered the use of wood diminished for two reasons: firstly the many practical inconveniences associated with collecting, distributing and using it and, secondly, its low energy density. Biomass is gaining in importance as an energy source, due to the increasing real cost of hydrocarbon fossil fuels, with respect to third world primary products.

Globally, the amount of biomass produced each year through photosynthesis is vast. It has been estimated that net annual photosynthetic production of organic matter amounts to roughly 2×10^{11} tonnes[18,19,138,139]. However, if harvesting a particular biomass resource caused the degradation of the ecosystem that produced it then, obviously, its availability would be only temporary; serious and permanent environmental damage would probably result if the depletion continued. The first step, therefore, in assessing the potential for

biomass energy is to assess the quantity of biomass which is available on a continuous basis.

The important role that biomass plays now in the current world energy supply has only recently been recognised. Due to the non–commercial nature of most biomass fuels, energy supply estimates are still very approximate; however, biomass probably accounts for as much as one seventh of total world energy consumption[18,67]. Primarily this is due to the fact that two main biomass fuel forms, namely wood and charcoal, are the primary cooking and heating fuel for more that half of the world's population. The resulting deforestation that now afflicts many developing countries, and its potentially catastrophic consequences, for example, flooding and soil erosion are dramatic symptoms of an inappropriate use of biomass as an energy reserve.

1.3.2 – Fuels from Biomass.

An important feature of the present pattern of oil use in the developing countries, which is highly relevant to the planning of energy alternatives, is that of the centralisation of demand. The trend to urbanisation coupled with the tendency to locate industries in and around the major cities has led to a situation where, in many countries, the bulk of oil consumption is concentrated in just a few small areas. This has major implications in the analysis of petroleum replacement

options, primarily because of the cost of transporting bulky, low energy density biomass, from where it is produced to where it will be processed. This is true for all decentralised energy production systems and, in particular, the solar energy based biomass system; thus it provides a strong incentive for locating many energy conversion plants, for example biomass pyrolysis converters, as near as possible to the energy source they will use.

To utilise biomass resources for energy purposes, a wide variety of techniques is available. The most efficient way to use most forms of biomass, at least those with reasonably low moisture contents, is to burn them directly for heat as near as possible to where they are grown. The chemical energy of biomass can be converted directly into heat energy by combustion with relatively high efficiencies; therefore any thermal processing of biomass into a secondary fuel must be justified on a basis that offsets the expenditure of energy necessarily involved in such a step. However this direct approach has a limited application, because the demand for energy is often remote from biomass production areas, and also because heat is not the only form of energy required. To reduce transportation problems and to increase the versatility of biomass energy it is highly desirable to convert biomass into a variety of more convenient fuel forms. These intermediate fuels may then be used in a range of end–use devices to satisfy the full spectrum of energy needs.

There are, therefore, two major objectives when converting biomass into another fuel. First, to aim at improving the

"quality" of the fuel, by increasing its calorific value per unit volume or unit weight, in order to make storage and transport easier or more economical. Secondly, the fuel produced should be compatible with existing combustion equipment, burners, boilers, etc, or with existing patterns of energy use, these new fuels should also give rise to fewer problems associated with pollution than would direct combustion of the biomass.

1.3.3 — Chemical Feedstocks from Biomass.

Before the era of petrochemicals, various classes of chemicals were produced from biomass by such techniques as extraction, fermentation, and pyrolysis. The resinous exudates from pine trees provided the raw material for the naval stores industry. Extracts from the heart–wood of certain hardwoods, as well as the bark of various species, provided tannins, which as their name indicates, were important in tanning leather. The fermentation and the production of ethanol for beverages is still a major industry. The destructive distillation of wood to produce charcoal was once an important industry[3,51].

As an example of what may easily be achieved, Germany, shortly before the Second War when faced with a blockade on imported petroleum, devised a national programme designed to produce a variety of products based upon wood as a raw material. In addition to primary fuels and construction materials, it also proposed that the

basic materials for chemical industries would be synthesised. Whilst only some of these goals, during the difficult war years, were achieved, enough was accomplished to demonstrate the enormous potential of forest biomass. Sweden, admittedly on a somewhat limited scale, has supplemented its supplies of many critical chemical materials from wood[153]. As Petroleum and natural gas become scarcer, many products derived from wood would be expected to become economically more competitive with, if not cheaper, than the same products produced from fossil feedstocks.

Considerable quantities of chemicals produced from biomass are in use today. About 150 million kilogrammes of organic and amino acids are derived annually from a sugar or grain base by fermentation. Chemicals derived from wood, sometimes called silvichemicals, are for the most part by–products of the pulp and paper industry. Wood hydrolysis to glucose is still in use in the U.S.S.R.. Furfural is produced by strong acid treatment of pentose sugars from such agricultural residues as corn cobs or oat hulls. Phenolic acids extracted from the bark of various conifers are used as synthetic resin adhesives[120,122].

Bettinger and Kosstrin, gasified wood in a fluidised bed to produce urea, a chemical with world wide demand as a fertilizer. Ninety percent of the annual world urea production is used for fertilizer, while the rest is used in adhesive and plastics manufacture[11].

The future use of biomass can be divided into two

major categories. The first represents mainly an extension and expansion of the present use. The second category would involve conversion of cell wall polymers into low molecular weight chemical feedstocks. Chemicals such as methanol, ethanol, furfural, ethylene, butadiene, phenol, benzene could provide the basic building blocks for conversion to synthetic polymers[51].

1.4 – Sugar Cane: A Biomass Substitute For Oil.

In many equatorial zones the growth rate of native vegetation is very high, due to the super–abundance of sun and water; and in these regions the principal arable "energy" crop being grown today is sugar cane. Sugar cane plantations typically produce four tonnes of sugar and four tonnes of bagasse, the lignocellulosic residue of sugar cane, per acre per year; these high yields are largely due to the fact that sugar cane reaches maturity in six to eight months, hence it is frequently possible to obtain two harvests per year[18,19,21,110,114,154].

In several countries, most notably Brazil, the land area and ancillary resources being allocated to growing sugar cane are being dramatically increased. Very large quantities of sugar cane are now being grown, not simply for processing into raw sugar for sale on the world market, but, more importantly, as part of an intensive programme for the production of automotive fuels, specifically ethanol, from carbohydrates. By the application of modern fermentation

technology each acre of sugar cane also produces two tonnes of ethanol and, more recently, by the use of standard reforming processes, 1.4 tonnes of ethylene.

In 1983 approximately 8 x 10^9 litres of ethanol were produced from sugar cane in Brazil, equivalent to 1.4 x 10^5 barrels of petroleum per day. As a by–product more than 30 x 10^6 tonnes of Sugar Cane Bagasse were produced[16,21].

This programme is the prime example of biomass being used as a alternative energy source, not only to reduce drastically, and possibly supplant, the consumption of products derived from oil by the transportation sector in Brazil but also to provide chemical feedstocks for a small, but quickly growing chemical industry.

However, there is a growing realisation that even renewable resources have finite production limits; and that associated with these increasing volumes of sugar cane biomass there are similarly increasing volumes of bagasse residue, which has up until now, been of little or no commercial value. Indeed in general terms any form of biomass utilisation will always produce residues, whose transformation into commercial products will almost always substantially improve the economic viability of the total process.

Bagasse is the fibrous residue remaining after all the economically recoverable sugar has been extracted from the cane stalk of sugar cane, it is on average 25% of the weight of the stalk before

processing. The composition of bagasse is similar to that of other lignocellulosic materials[21,29,80,105,111,121,122,144,145,152]:

Cellulose	40–55%
Hemicellulose	20–30%
Lignin	20–25%
Ash	1.5–3.0%

The processing of sugar cane for manufacture of raw cane sugar and ethanol, generates large quantities of this lignocellulosic material solid wastes, namely bagasse. Every 1,000 tonnes of sugar cane produced, produces about 100 tonnes of raw sugar and approximately 100 tonnes of bagasse[21,29]. At present only a small quantity of this lignocellulosic residue is productively utilised, by being burnt on site at the sugar mills, to generate process power and heat. Although this burning of bagasse is "wasteful" in energy terms , since the heat of combustion of raw bagasse is very low, approximately 5.500 kJ/kg[56,114], it may be economically justified, since there is not, as yet, an alternative use or industrial outlet for this material. Additionally, large quantities of the bagasse still remain to be disposed of and are often piled up on adjoining land. Consequently proper and economic disposal of the bagasse wastes is a problem in the cane sugar industry.

The appropriate transformation of this biomass residue into a high density secondary source of energy would significantly increase the total energy yield of sugar cane plantations, as well as their profitability. More important however is the possibility of producing

either chemical feedstocks or high value products, for example light gases, methanol, syrups, and adhesives from processing this vast quantity of bagasse since ethanol, for use as a synthetic fuel, is now readily available by carbohydrate fermentation. However the commercial production of these chemical products is, at present, very problematic; since although simple thermal conversion processes appear to be attractive there is an insufficient understanding of the thermochemical conversion mechanisms in lignocellulosic materials.

1.5 – The Thermal Processing of Sugar Cane Bagasse.

Thermochemical processes are those that are based upon the high temperature degradation of an organic material. They are identified and labelled by those predominant chemical reactions taking place, namely:

Pyrolysis
Liquefaction – with solvent extraction
Hydrogenation
Hydrogasification
Combustion

Pyrolysis is the degradation of materials by the action of heat in the absence of oxygen; in general the complex organic molecules present in biomass begin to fragment at temperatures around

300^{0}C, and at about 500^{0}C pyrolysis rates are significant, see for example references 64,117,122,123. It is potentially the most interesting route for the production of chemical feedstocks from Sugar Cane Bagasse, since, in contrast to the other thermal processes, it requires less energy input, no additional reagents, relatively simple technology and produces very little residue[27].

Pyrolysis does have one important drawback however: it produces a complex mixture of products. To date the thermal decomposition of Sugar Cane Bagasse, which is a multistage exothermic and endothemic process, has received little systematic investigation. The production of "brown" tars have been observed, accompanied by a release of volatile components and changes of macromolecular structure, the gaseous products for the limited temperature range of 250^{0}C to 380^{0}C were found by Roque[111] and Varhegyi[145] to be:

20–110^{0}C	H_2O
110–170^{0}C	H_2O
170–250^{0}C	CO_2, CO, H_2O
250–310^{0}C	CO_2, CO, H_2
310–380^{0}C	CO, CH_4

Varhegyie and co–workers[144] have studied the decomposition of Sugar Cane Bagasse in a thermobalance system over the temperature range 200–450^{0}C; they reported that the decomposition of cellulose occurs about 350^{0}C. They could not investigate the decomposition of lignin since their experiments were undertaken at low

temperatures, up to about 450^0C. The thermal decomposition of lignin is reported to take place, in general, above 400^0C[17,42,65,105].

1.5.1 – Thermal Processing: Experimental Complexities.

The thermal decomposition of lignocellulosic materials takes place via a complex series of coupled chemical reactions, which are driven by mass and heat transfer processes[117]. It is, therefore, in principle rather difficult to unambiguously determine the path along which the pyrolysis of Sugar Cane Bagasse proceeds. The presence of competing secondary reactions may effectively mask many of the basic pyrolysis steps; hence, in the limit, unrepresentative results will be obtained on any biomass sample. Apparent contradictions between sets of published pyrolysis data, see for example references 22,30,84,117,121,122, indicates how, in past research, experimental techniques have not paid due regard to this potentially very serious problem. There are four main areas of experimental procedure that must be carefully controlled, or assessed, to ensure that the primary pyrolysis products are obtained; these are as follows:

a – The geometry of the experimental apparatus; which may, because of flawed design, promote secondary reactions such as, for example, cracking of primary tars on hot internal surfaces.

b – The experimental conditions; for example the careful control of heating rates and hold times, which is defined as the time for which the sample is maintained at the peak temperature and, most importantly, the residence time of primary volatile products within the hot zone of the reactor.

c – The physical properties of the specimen, in particular its particle size and morphology.

d – The chemical composition of the specimen, in particular the ratio of cellulose to lignin.

1.6 – Aim of this Research.

The primary aim of this research programme is to investigate the possibility of using a readily available "waste" product, namely Sugar Cane Bagasse, to produce, by the application of pyrolysis either a chemical feedstock or a range of fuels. The product distribution and yield of the pyrolysis tar is evaluated as a function of the process parameters, with particular emphasis being placed upon the peak pyrolysis temperature and the heating rate. Specimens of Silver Birch were also pyrolysed under similar conditions to those used for Sugar Cane Bagasse, and its product distribution and tar yield compared to that of Sugar Cane Bagasse in order to investigate the possible interaction of cellulose and lignin during pyrolysis. This

research programme was subsequently complemented by an investigation into the pyrolysis of pure cellulose and lignin, and of their mixtures, in order to better understand the complex interactions found in the pyrolysis of wood and Sugar Cane Bagasse. These experiments were undertaken with samples of the following compositions:

0%cellulose:100%lignin
25%cellulose:75%lignin
50%cellulose:50%lignin
75%cellulose:25%lignin
100%cellulose:0%lignin

These compositions were selected based upon the analysis of Sugar Cane Bagasse and Silver Birch, which showed that these two biomass substances have approximately the same structural chemical composition, namely 75%cellulose:25%lignin. The mixture 75%cellulose:25%lignin prepared in this part of this research programme may, therefore, be regarded as a sample of "synthetic" Sugar Cane Bagasse.

It should be noted that these experiments were performed in the same reactor and under identical experimental conditions, and that these samples were carefully prepared so as to have the same physical properties, in particular particle size and moisture content, as the specimens of Silver Birch and Sugar Cane Bagasse.

1.6.1 – Experimental and Analytical Procedures – An Overview.

The solid and liquid pyrolysis products obtained in a wire–mesh reactor, for a very wide range of process parameters, were collected and analysed. In contrast to previous research the fundamentally important pyrolysis processes parameters may be systematically investigated using this unique "constant geometry" wire–mesh reactor; for example slow and fast heating regimes are readily covered within its dynamic range of heating rates. Specifically heating rates in the range of 0.1^0C/second to 1000^0C/second were employed over a temperature range of 300^0C to 900^0C; with hold times, at the maximum temperature, of 0, 30 and 100 seconds. These experiments were undertaken in a stream of pure helium, which quickly swept the products from the hot reaction zone, in order to minimise the possibility of secondary processes occurring.

The cellulose and lignin content of the naturally occurring materials was determined using ^{13}C–NMR (Nuclear Magnetic Resonance) and confirmed by elemental analysis. The tars obtained were initially characterised by their product distribution, using two analytical techniques; Vapour Pressure Osmometry (VPO), to obtain an average molecular mass, and elemental analysis (CHN), to obtain an overall chemical composition. More importantly a detailed chemical analysis of selected tars was undertaken using gas chromatography–mass spectrometry (GC–MS); this technique was employed so that the major

volatile compounds in a tar sample could be identified. These pyrolytic tars were found to be complex mixtures of many light and heavy oil components, whose composition was broadly independent of the process parameters.

Char residues adhering to the wire–mesh were examined under the electron microscope, in a SEM system. An exploratory investigation of the pyrolysis process was undertaken using the technique of Differential Scanning Calorimetry. These experiments were performed in order to examine, from a different point of view, the gravimetric results obtained in the wire–mesh apparatus.

However, before reporting the new data obtained in this research, it is instructive to review now some past investigations of the, to date, most studied biomass system, namely wood, in order to provide essential background information and a framework within which this study may be placed. This review will provide an insight into the pyrolysis of lignocellulosic materials in general; and, therefore, the pyrolysis of Sugar Cane Bagasse. However the depth and complexity of the previous studies on the structure and pyrolysis of wood, dictates that even condensed reviews of either of these topics cannot be made very brief.

1.7 – The Structure and Composition of Wood.

Wood has an open, rigid, macromolecular structure, the cell walls have as their major components: cellulose, hemicellulose and lignin, and low molecular weight substances collectively called the extractive and mineral substances contained within the cells[3,31,40,51,122] as shown in Figure 1.7a.

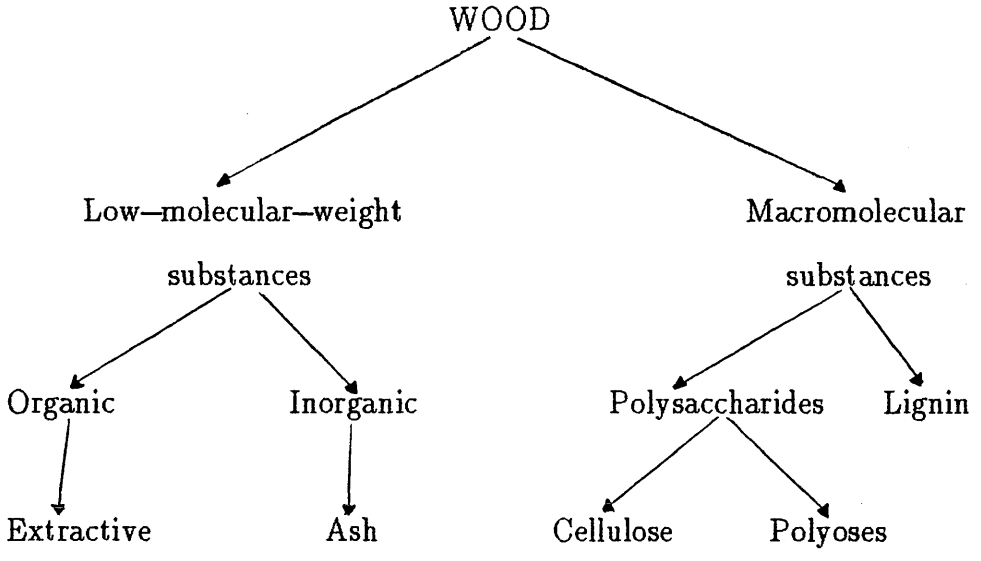


Figure 1.7a – General scheme of chemical wood components[40,51].

In wood, from temperate zones, the portions of macromolecular substances account for 97–99% by weight, while for tropical woods this value decreases to 90% by weight[40,51].

Cellulose is the major component of wood; it constitutes approximately one half, by weight, of both softwoods and hardwoods. Cellulose is a highly oriented, crystalline, linear polymer of glucose units which can be hydrolysed to glucose by the action of acids or enzymes. Hemicellulose is intimately mixed with cellulose in the cell wall; it also has a polymeric structure made of, for example, five carbon sugars such as xylose, or six carbon sugars, other than glucose. In contrast to these polysaccharide structures, molecules of lignin consist of an aromatic system composed of phenylpropane units; it has been shown that lignin is a tridimensional polymer[28,40,51,122,123,128,140].

Woods are complex agglomerations of individual cells whose elaborate walls, that together serve to define the morphology of the plant, provide its structural support and control the passage of water and nutrients. The formation, organisation, and properties of these cell walls are complex; however they all are formed predominantly of polysaccharide structures, of which cellulose is the most abundant and lignin an important component. There are other components of woods that are much more variable in structure and quantity, these collectively are called the "extractive"; these soluble compounds are often species or genus specific, for example bark, the outer material of woody plants, non–structural carbohydrates such as starch or sucrose, and proteins. In summary, cellulose, hemicellulose, and lignin are the main components of woody plant cell walls, whilst proteins are minority components[51,40,150,122,123,138].

Plant cell walls are built of cellulose microfibrils with

various relative orientations, and encrustated with a number of other compounds, see Figure 1.7b[150]. Cell walls are subdivided into primary and secondary structures according to their time of formation. The primary wall develops first and is often stretched during the differentiation of the cell, it is the only wall found in some cells. The secondary wall is laid down on the inside of the primary wall, usually after elongation of the cell has ceased, and is a characteristic feature of almost all wood cells[127,128].

The primary wall of a wood cell consists of a thin network of cellulose arranged and encrustated with hemicellulose, lignin, and other compounds. The secondary wall is laid down inside the primary wall and in most cells is considerably the thicker of the two. It can be subdivided into three layers according to the orientation of the microfibrils within it. The layer nearest the primary wall is termed the "S1" layer and the microfibrils in it are orientated nearly perpendicular to the long axis of the cell. The middle, or "S2" layer is by far the thickest and is built up of microfibrils running at a small angle to the long axis of the cell. The "S3" layer, lying nearest to the cell lumen, is a thin layer with the microfibrils again orientated in a nearly transverse direction. There may be a gradual transition in microfibril orientation from one layer to the next. The secondary wall is also incrustated with hemicellulose, and deposits of lignin and other substances. The "S3" layer may be overlaid inside the cell lumen by a covering termed the warty layer. This layer, so named on account of its small protrusions, when present, is laid down just prior to the death of the cell protoplasm and covers the entire layer, pit cavities and any

other wall sculpturing.

Individual cells are joined together by intercellular material between their primary walls. This middle lamella is an amorphous region, rich in lignin and low in cellulose and composed largely of pectin compounds. It is readily dissolved away by macerating solutions.

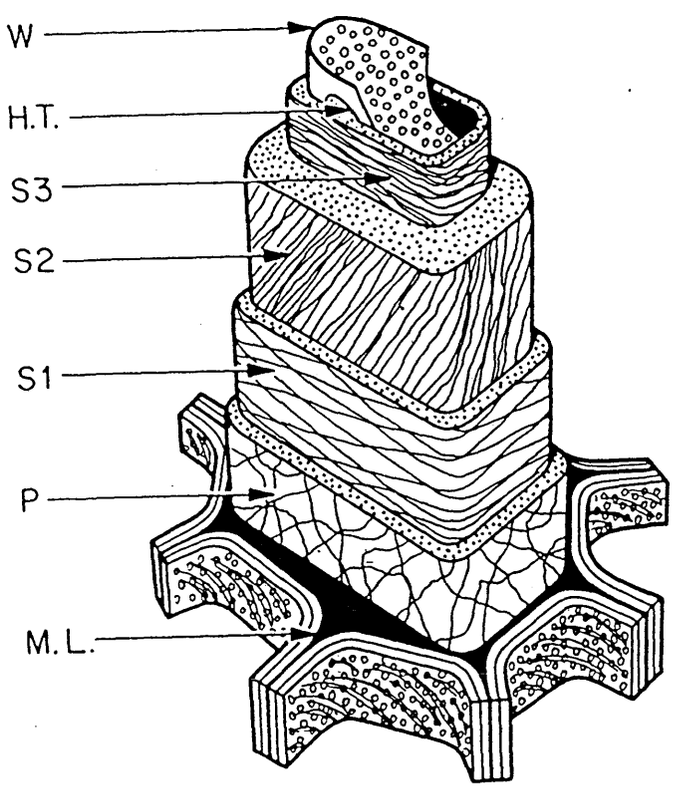


Figure 1.7b — A schematic diagram to illustrate the structure of the plant woody cell[150].

ML — middle lamella; P — primary wall; S1 — outer layer of the secondary wall; S2 — middle layer of the secondary wall;
S3 — innermost layer of the secondary wall; HT — helical thickening;
W — warty layer.

The three basic polymers that compose wood are as follows[31,40,51,84,122,123,138,150]:

Cellulose	$C_6H_{10}O_5$
Hemicellulose	$C_5H_8O_4$
Lignin	$C_9H_{10}O_3(OCH_3)_{0.9-1.7}$

In general, hardwoods contain about 43% cellulose, 35% hemicellulose and 22% lignin, whilst softwoods contain about 43% cellulose, 28% hemicellulose and 29% lignin, the remaining material being the "extractives", and trace quantities of inorganic substances[138].

The lignin content, by weight, corresponds approximately to 35–45% of the energy content in wood since, in general, lignin is the polymeric cell wall component with the highest energy content, consisting of more then 60% carbon and around 30% oxygen, This is contrasted by hemicellulose and α–cellulose with carbon contents of less than 50% and oxygen content of almost 50%[52,53,54,118].

1.7.1 – Cellulose.

Cellulose or, more precisely, α–cellulose is the most abundant organic material on earth, comprising approximately 50% of all biomass and an annual production of, about, 100 billion tonnes. It is a long chain polymer of β–D–glucose in the pyranose form, see Figure

1.7.1a, linked together by 1,4'–glycosidic bonds to form cellobiose residues, see Figure 1.7.1b, these are the repeating units in the cellulose chain[122,123,127,137].

There are important features of this unique structure; first a marked tendency for the individual cellulose chains to link together, by hydrogen bonding, to form regular extended structures, as shown in Figure 1.7.1c Secondly cellulose is completely insoluble in water, despite the presence of three hydroxyl groups on each anhydroglucose residue in the cellulose chain[14,96,137].

The chain length of cellulose, as determined by the measurements of samples of cellulose from different origins and treatment histories shows, not unexpectedly, considerable variation. Values for the degree of polymerisation (DP) range from 7000 to 10000 in woods, to as high as 15000 for cotton. Cellulose chemistry has been extensively examined and reported elsewhere[69]; the important structural features of cellulose with respect to its conversion into chemicals are that it is a linear polymer of glucose with a highly ordered crystalline structure that limits the accessibility of reagents and enzymes[69,127].

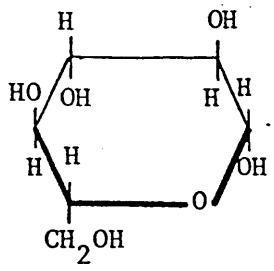


Figure 1.7.1a – β – D – Glucopyranose[122,123].

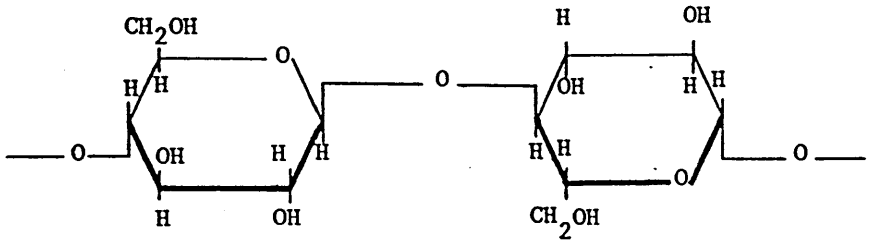


Figure 1.7.1b – Cellobiose residue[122,123].

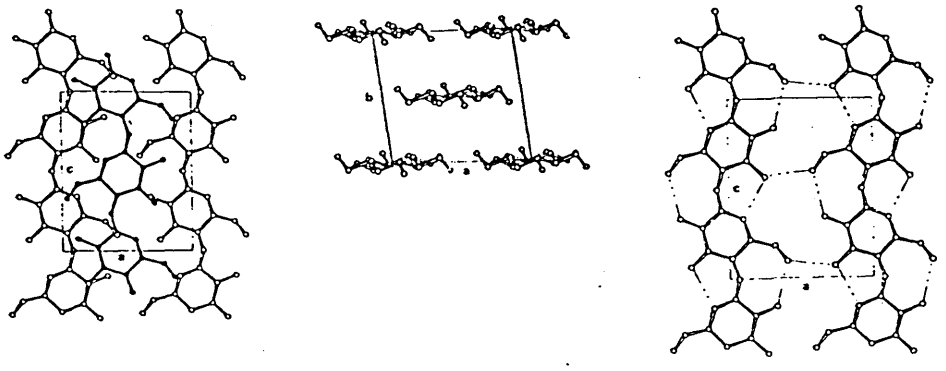


Figure 1.7.1c – Projections of the parallel chain model for cellulose[122,123].

1.7.2 – Hemicellulose.

Closely associated with the skeletal cellulose of the cell wall is another polysaccharide called hemicellulose. It differs from cellulose in that although water insoluble, it can be readily dissolved in strong alkali. This property has been used to separate hemicellulose from holocellulose, the total carbohydrate fraction containing α–cellulose and hemicellulose; thereby hemicellulose is extracted leaving behind pure α–cellulose[122,123,140,137].

Hemicellulose consists of, for the most part, sugars other than glucose, such as pentose and hexose; it is usually branched with a degree of polymerisation ranging from less than 100 to not more than 200 sugar units. Its greater solubility and susceptibility to hydrolysis with respect to cellulose results from its amorphous structure and low molecular weight[137].

Only a small range of hemicellulose structures are found in all plants; these frequently show small variations, for example, in molecular weight, and within the differing tissues of a given plant. In softwoods, which contain about 28% hemicellulose, the principal constituent sugars, in decreasing abundance, are mannose, galactose, xylose, glucose and arabinose. In hardwoods, which contain about 35% hemicellulose, the principal constituent sugars, again in decreasing abundance, are xylose, galactose, and mannose, with trace quantities of rhamanose and arabinose[115,140].

A general skeleton of hemicellulose is given by Theander[137], and is shown in Figure 1.7.2a. The basic difference between the hemicellulose of softwood and hardwood, is that in hardwood the hemicellulose does not contain the branches of arabinose as is presented in this figure.

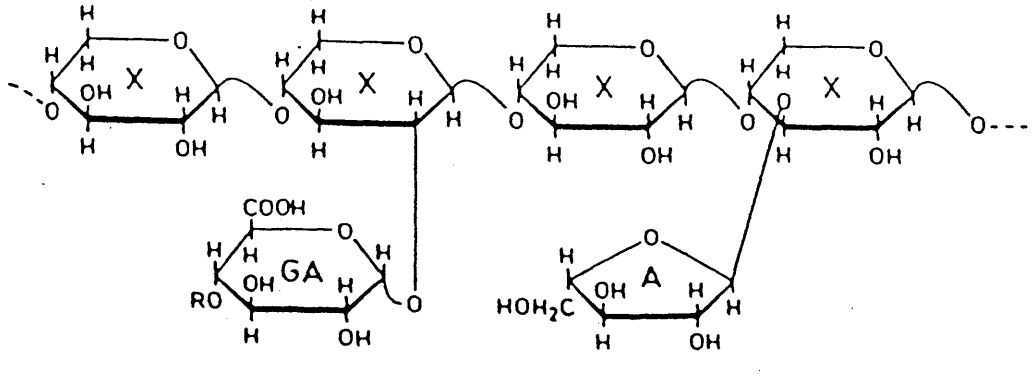


Figure 1.7.2a – Skeleton of Hemicellulose from Theander[137].

X = D–xylose; A = L–arabinose
GA = D–Glucuronic acid (R = H or CH_3)

1.7.3 – Lignin.

The third major cell wall component in woody plants is lignin, comprising approximately 25% of the cell wall material. The presence of lignin in a plant enables it to be classified as a wood. Lignin plays a vital role as the "cement" between the wood fibers, and as the stiffening agent within these fibers; it also serves as the barrier to enzymatic degradation of the cell wall[52,53,54,91,122,123,128].

For many years little progress was made in defining the chemical structure of the complex lignin polymer. It is only within the last two decades, based upon the work on the biosynthesis and formation of lignin in wood by Freudenberg[46], that a plausible chemical structure has been established. The lignin molecule in woody plants is now known to be a highly branched polymeric structure with polysaccharide cross linking, It is composed of phenylpropane–based monomeric units coupled by either ether linkages or various forms of carbon–carbon bonds. The molecular weight of lignin is very high and may be considered to be essentially infinite[46,52,53,54,95].

Lignins from grasses, softwoods, and hardwoods differ in chemical composition, mainly by methoxyl substitution and the degree of cross linking between phenyl groups. However their common structural features are dominant, see Figure 1.7.3a, which shows those features important for the conversion of lignin into low molecular weight products. The aromatic and phenolic character of lignin is clearly

apparent, as is the covalent carbon–carbon bonding that prevents decomposition to the elemental monomer by any mild processing steps[51].

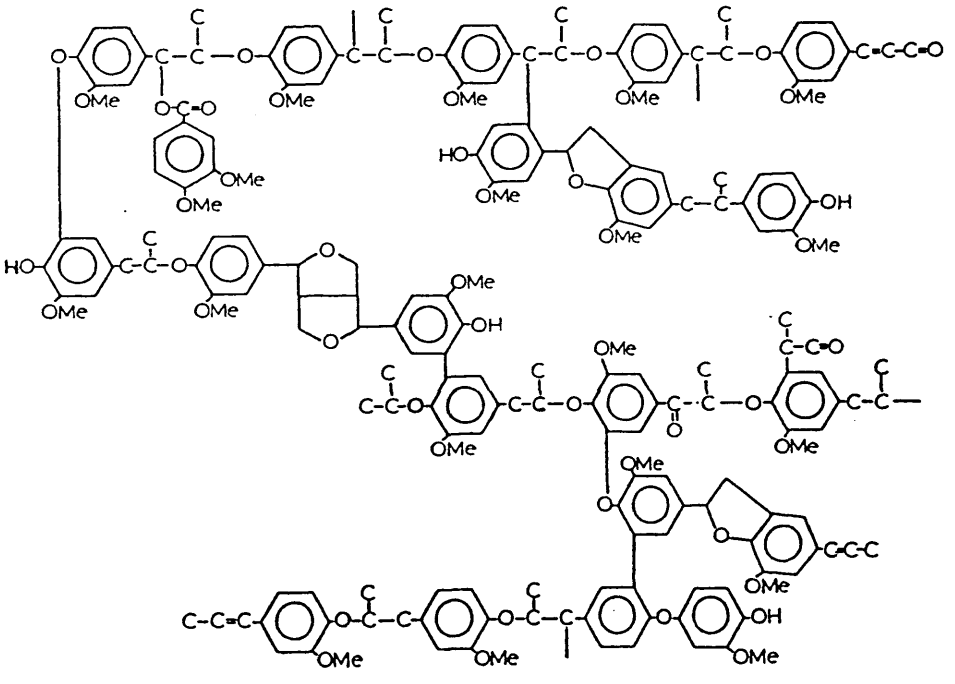


Figure 1.7.3a – Abbreviated skeletal schematic structure of lignin[51].

In general the molecular weight of any lignin sample depends upon its botanical origin. In its natural state, in a living cell wall, lignin probably exists as an infinite three–dimensional polymeric network, because it is produced in a random, free–radical, polymerisation

process. It has been shown that lignins obtained as by–products from the various stages in the pulping process are different from each other, and also differ in turn from the lignins found in wood hydrolysis residues, whether acidic or enzymatic, or from the lignins dissolved from wood by neutral solvents. The formation of carbon–carbon bonds internally in lignin, as a consequence of chemical treatment, has long been known responsible for the formation of unreactive lignin, inaccessible to further depolymerisation, even when drastic thermal conditions are applied[52,53,54]. In summary, therefore, the chemical structure and physical properties of lignins are highly dependent upon their origin and the method by which they have been isolated[52,53,54].

Lignin may be utilised as a feedstock for a number of chemicals now derived from petroleum and natural gas because of its unique combination of aromatic and aliphatic characteristics. However the large scale production of low–molecular–weight products from lignins, in direct competition with the petrochemical route, is restricted today by economic and technological constraints, see for example references[40,95].

1.8 – Pyrolysis of the Individual Major Components of Biomass.

Among the components of biomass, α–cellulose, hemicellulose and lignin, the thermal properties of cellulose have been most widely investigated and are best known because of its relative abundance and structural homogeneity.

1.8.1 – The Pyrolysis of Cellulose.

The thermal degradation of cellulose has been extensively studied by Shafizadeh, and it has been reported to occur in two steps[121,123,129]. The first takes place at temperatures below 300^{0}C. Degradation at this level is indicated by an increase in brittleness and a decrease in strength of the material. Chemical reactions that occur in this temperature range are oxidation, depolymerisation, dehydration, and decarboxylation. Products that may be evolved include carbon monoxide, water, and other low molecular weight compounds that contain carboxyl, carbonyl, and hydroxyl groups[20,27,117,126,129].

At temperature below 300^{0}C, cellulose decomposes by at least two competitive first order reactions[1]. As cellulose is heated, at about 220^{0}C the cellulose macromolecule undergoes a dehydration reaction to form anhydrocellulose. The anhydrocellulose later decomposes via two competitive first order reactions to the gaseous products and residual chars. At about 280^{0}C, a depolymerisation reaction starts to compete with the dehydration reaction and is responsible for the formation of tar, mainly levoglucosan[1].

Kilzer has made a study of possible mechanisms involved in the formation of carbon monoxide and water. Water is lost first through an inter–ring mechanism to produce dehydrocellulose, which decomposes to form carbon monoxide and additional water[76].

Heating of cellulose above 300^{0}C will result in char, tar, and gaseous products. Investigations into the tar fraction have revealed that the major component is levoglucosan[17,57,47,82,97,121,123,124,126,127,129,134,135]. Yields of 38% to 50% levoglucosan in the tar have been reported,[57,126,127,129] depending on the nature of the starting material and heating conditions. Heating under vacuum will increase yields to 78% levoglucosan, 18% light products and gases, and 6% to 9% char[126,127,129]. Levoglucosan is heat sensitive, but also volatile so that it will distill out of the reaction zone under vacuum conditions before it can undergo secondary reactions[89].

The mechanism by which levoglucosan is formed has been the object of considerable work. Researchers have proposed a mechanism in which levoglucosan formation is the major reaction in areas of high packing density, in these regions dehydration and hydrolysis reactions are said to be of secondary importance. In parts of the molecule with different physical characteristics, the predominance of reactions may be reversed, with dehydrations occurring to a large extent[55,126,127,129]. Levoglucosan can be formed through the migration of the hydrogen on the hydroxyl group of carbon number six, to the oxygen of carbon number four. The free radical centre thus formed, is then attached to carbon number one. The one–six linkage is preferred because the distance from one to six is less that that between any other neighboring carbon atoms[55,27].

Kilzer states that the formation of levoglucosan during

pyrolysis proceeds through a depolymerisation that involves the displacement of the C–1 oxygen with the C–4 oxygen. The C–6 hydroxyl could then attack carbon number one, displacing the one–four bridge and forming a one–six bridge, see Figure 1.8.1a[27,76].

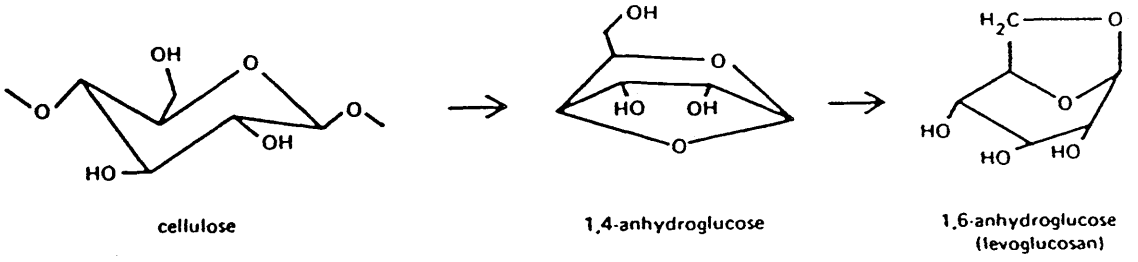


Figure 1.8.1a – Formation of levoglucosan according to Kilzer[76].

Shafizadeh states that the depolymerisation of cellulose occurs by intramolecular substitution of the one–four link in cellulose by one of the free hydroxyl groups to produce the first three anhydro sugars shown in Figure 1.8.1b[126,127,129].

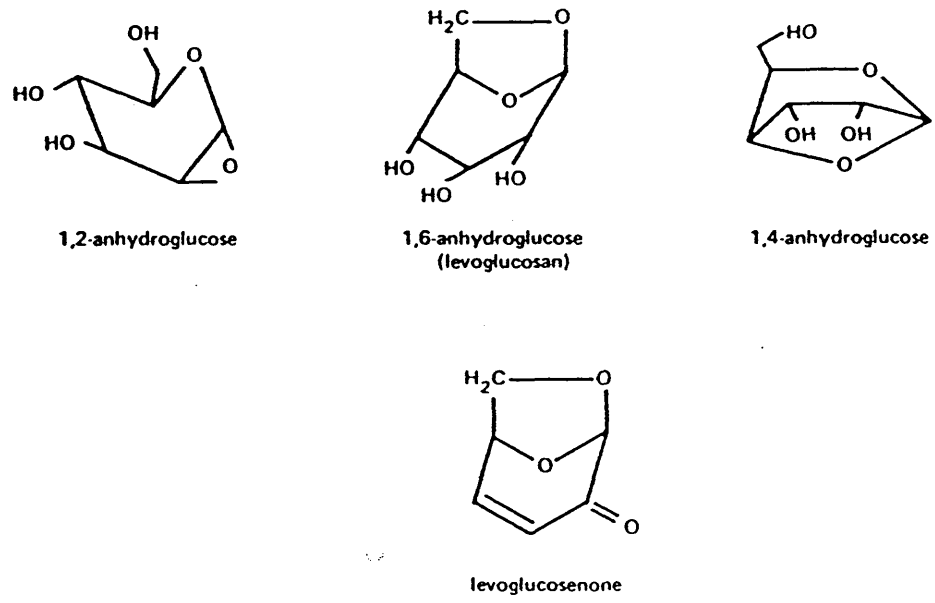


Figure 1.8.1b – Anhydroglucose and levoglucosenone structures[126,127,129].

Potential industrial applications of thermally degraded cellulose involve the hydrolysis of the tarry fraction. Hydrolysis gives a 50% yield of glucose based on cellulose. Sugars derived from pyrolysis of cellulose could then be used either as glucose or anhydro sugars[124]. Levoglucosenone that may be formed from levoglucosan, as can be seen in Figure 1.8.1b, is a polyfunctional substance that could possibly be used as an industrial intermediate[17].

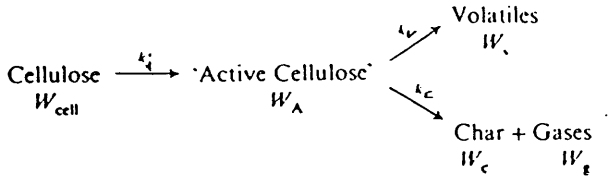
Some minor lighter products are always formed in cellulose pyrolysis. Formation of these products begins at temperatures lower than those required for levoglucosan formation, thus indicating that they do not arise from secondary reactions of levoglucosan[124,127,129]. The

volatile fraction is, however, qualitatively similar whether it comes from cellulose or levoglucosan[126].

In investigating the thermal decomposition of wood, cellulose has been the most frequently studied component. The principal reaction involved in pyrolysis of cellulose at high temperatures is depolymerisation to levoglucosan (1,6 anhydro→ β D–glucopyranose). The yields of levoglucosan or tar and other pyrolysis products depend on the feedstock and reaction conditions employed[124,127,129], as well as the reactor geometry of the pyrolysis apparatus.

Pure cellulose rapidly depolymerises within the temperature range of 325–375^{0}C[12]. The depolymerisation involves substitution of the 1 → 4 – glycosidic linkage in cellulose by 1 → 6 and other glycosidic linkages which provide a tarry mixture containing levoglucosan, other anhydrosugars, and some randomly linked low molecular weight sugar derivatives[82,117,121,124,127,129].

According to Shafizadeh[121,129] the chemical kinetics of cellulose pyrolysis could be represented by the three reaction model shown in Figure 1.8.1c. In this model it is assumed that the initiation reaction leads to the formation of an active cellulose, which subsequently decomposes by two competitive first order reactions: one yielding anhydro sugars, transglycosylation products, and the other char and gaseous fraction.



where

$$\frac{-d(W_{cell})}{dt} = k_i[W_{cell}]$$

$$\frac{d(W_A)}{dt} = k_i[W_{cell}] - (k_v + k_c)[W_A]$$

$$\frac{d(W_c)}{dt} = 0{\cdot}35k_c[W_A]$$

$$k_i = 1{\cdot}7 \times 10^{21} \exp[-(58\,000/RT)]\ \text{min}^{-1}$$

$$k_v = 1{\cdot}9 \times 10^{16} \exp[-(47\,300/RT)]\ \text{min}^{-1}$$

$$k_c = 7{\cdot}9 \times 10^{11} \exp[-(36\,000/RT)]\ \text{min}^{-1}$$

Figure 1.8.1c – Kinetic model for pyrolysis of pure cellulose under vacuum from Shafizadeh[121,129].

1.8.2 – The Pyrolysis of Hemicellulose.

Of the three major components of wood, the hemicelluloses are the most temperature sensitive, decomposing within the range of 200 to 260°C[17,51,140]. It is thought that hemicellulose degradation occurs in two steps: decomposition of the polymer into water soluble fragments, followed by conversion to very short or monomeric units that, in turn, decompose into volatiles[41]. In comparison with cellulose, hemicelluloses produce more gas, less tar, and about the same amount of aqueous distillate, but no levoglucosan.

It might be expected, based on the large number of five carbon sugars associated with the hemicelluloses, especially in hardwoods, that many furan derivatives would be obtained[146]. The five carbon sugars, when pyrolysed, have been shown to be a major source of acetic acid[57,75,97]. Browne has proposed that xylose units split to form two units of acetic acid and one formaldehyde, Figure 1.8.2a[17,140].

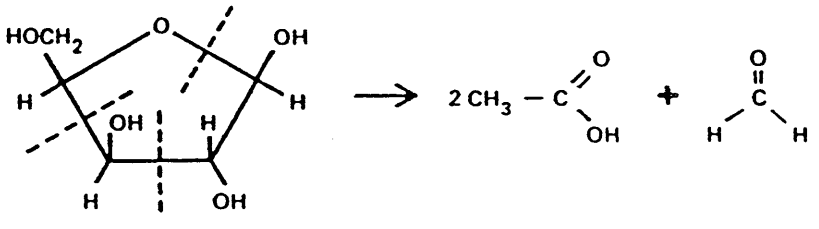


Figure 1.8.2a– Formation of acetic acid and formaldehyde from xylose[17].

1.8.3 – The Pyrolysis of Lignin.

The principal routes of breaking down lignin to monomeric compounds are:

Pyrolysis,
Hydrolysis,
Alkali fusion.

The chemicals obtained can be roughly classified as follows[40]:

Phenol and substituted phenols,
Benzenes and substituted benzenes,
Other saturated and unsaturated hydrocarbons,
Organic acids,
Gases such as CO, CO_2 and H_2.

Due to the higher carbon content, the amount of char and tar are generally higher than in wood pyrolysis. The tars from lignin pyrolysis contain numerous phenolic compounds[40].

When subjected to pyrolytic conditions, lignin produces aromatic compounds, and more char that cellulose[15,42,57,75]. Further, lignin produces no single predominating product analogous to levoglucosan from cellulose. The products of lignin pyrolysis reflect the complexity of

lignin molecules in which many repeating units are present with a variety of possible cross linkages[40].

The tarry residue from lignin pyrolysis has been investigated by various authors who found a mixture of phenolic compounds that are homologues of phenol and guaiacol[2]. Substituent groups are usually "para" to the phenolic hydroxyl, and usually possess three carbons or less. Substituents that have been reported are methyl, ethyl, propyl, isopropyl, vinyl, allyl, propenyl, carboxyl, carboxymethyl and carboxyaldehyde[2]. Fletcher has reported the finding of phenol, o–cresol, p–cresol, 2,4–xylenol, guaiacol, 4–ethyl guaiacol, and 4–propyl guaiacol[42], all of these are logical, based on the structure of lignin. Phenols found in the pyrolysis of wood are essentially similar to those reported for the pyrolysis of lignin.

The crude pyrolytic lignin tar is very complex mixture composed mainly of light and heavy oil components, some of which may be used as a chemical feedstock. Guaiacol is used for pharmaceutical purposes because of its antiseptic properties. The phenolic constituents of the pyrolytic tar may also be applied as adhesives[40]. The composition of the phenolic fraction has being shown to be dependent on the starting material. In the case of lignins from agricultural residues, for example sun–flower–shell and corn cobs, cresols were the dominant phenolic components, while using softwood lignin guaiacol amounted to about 50% of the phenolic mixtures[148].

The solid residue from the pyrolysis of lignin, in

differing reactors such as fluidised or fixed beds[101,135], may account for 55% of the total yield, but has been largely ignored by research workers. The gaseous products from lignin pyrolysis have been found to contain carbon monoxide, methane, and ethane[9,40,101].

1.9 – The Pyrolysis of Lignocellulosic Materials.

Biomass consists of many different types of dead and living plants cells, the structure and composition of which varies for the different parts and species of the plant. When biomass is subjected to heat, its components are fragmented and reformed into a range of gaseous, liquid and solid products. A mechanism of biomass pyrolysis has been suggested[9,117,122,123,125].

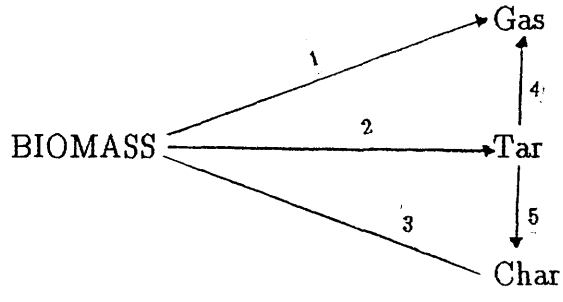


Figure 1.9a – Mechanism of biomass pyrolysis from Shafizadeh[122,123].

This mechanism is based on the transformation of biomass into three groups; The decomposition of biomass takes place by

three parallel reactions called primary reactions (1,2,3). The tar can then also be decomposed to gas or char, according to the two secondary parallel reactions (4,5)[64,122,123,125]. The specific products of the reaction are determined by:

Temperature of the reaction,
Heating rate,
Residence time of the sample at the peak temperature,
Reactor geometry,
Catalysis,
Particle size of the sample,
Pressure,
Solvent and others.

Pyrolysis of biomass involves different materials and methods, and provides a variety of products. In pyrolysis, biomass is decomposed by a series of 'n' primary reactions into primary products, each of which is acted upon by a series of secondary reactions. Char is assumed to be formed as the solid residue of the primary reactions and as solid material deposited in the course of secondary reactions[122,123].

The importance of these secondary reactions may be illustrated by a brief description of the stages of wood pyrolysis.

Past research[9,17,42,65,105] has shown that the thermal decomposition of wood does not progress at an even place, but rather in a step–wise manner, with the hemicelluloses breaking down first, at

temperatures of 200°C to 260°C. Cellulose follows in the temperature range 240°C to 350°C, with lignin being the last component to pyrolyse at temperature of 280°C to 500°C.

During the thermochemical process the complex structure of the wood is reduced to simpler gaseous components as follows[9,47,84]:

$$\text{WOOD} \longrightarrow \text{CO} + \text{CO}_2 + \text{H}_2\text{O} + \text{H}_2 + \text{CH}_4 + \text{Tar} + \text{Char} + \text{Ash}$$

The pyrolysis of wood has been studied as a zonal process; in general, a thermobalance was used as the reactor, the heating rate being at the order of 10°C/minute, and the carrier gas passed by the sample holder. The most comprehensive literature reviews providing data on the thermal decomposition of wood are as follows[17,92,104,116]:

Zone A – Below 200°C, in which only non combustible gases, primarily water vapour, with traces of carbon dioxide, formic and acetic acids, and glyoxal are produced. Dehydration is completed.

Zone B – From 200°C to 280°C, in which the same gases as in zone A are produced but with a greatly reduced quantity of water vapour, and some carbon monoxide. At this point the reactions are endothermic and the products are almost entirely non flammable.

Zone C – From 280^{0}C to 500^{0}C, in which active pyrolysis takes place under exothermic conditions leading to secondary reactions among the products. The products such as carbon monoxide, methane, etc, are largely combustible and include the highly flammable tars in the form of smoke particles. The charcoal residue catalyses secondary reactions.

Zone D – Above 500^{0}C, in which the residue consists primarily of charcoal which provides an extremely active site for further secondary reactions.

After all the free water has been removed from wood, at a temperature of 140°C, four classes of compounds are produced. These are non–condensible gases, (200^{0}C to 450^{0}C), carbon monoxide, carbon dioxide, hydrogen, and methane; condensable pyroligneous products (250^{0}C to 300^{0}C); condensable tar (300^{0}C to 400^{0}C); and charcoal[84,116,122].

In the present research programme, it will be seen that when wood is completely pyrolysed, the resulting products are significantly different to those that would be expected by the simple addition of the pyrolysis of the major components separately; this result demonstrates the importance of secondary reactions and of the interaction between cellulose and lignin.

From the above it has been shown that there are a

large number of competing reactions in pyrolysis; these reactions may be divided into two major categories[33,122]:

a – Molecule cracking – favoured by a separation of the molecules (eg. vapour phase which makes the bi–molecular reactions less probable),

b – Molecule building – favoured by the close proximity of the molecules found in condensed phases (eg. liquid or solid).

For example if the tar molecules formed initially do not vaporise quickly enough, they will have a tendency to form thermally stable larger tar molecules which in turn can eventually form char, hence type "b" behaviour predominates. It has been shown[27,109], that the conversion of char to gas or tar is the most difficult step in the pyrolysis of biomass. When wood is heated slowly it produces charcoal, tar and gases, but as the heating rate is increased less char is produced and at sufficiently high rates very little char is produced. In fact, at sufficiently high heating rates and temperatures, cellulose and probably all biomass can be nearly completely converted to volatiles, hence type "a" behaviour dominates. Broadly then, char yield decreases when heating rate increases[82,117,124]. Another general trend in pyrolysis, either in a fixed bed or in fluidised bed reactors[84,59,60,64,99,100,101,134,135,138], is for the yield of liquids to increase with increase in temperature up to about 500^{0}C and then decrease, and for the gas yield to increase, see Figure 1.9b. The decrease in tar yield with increase in

temperature is characteristic of secondary reactions.

The interactions between heating rate, residence time and maximum temperature are complex; that is to say they are not independent variables[9,27,61,82,97,117,122,123]. However, in general terms, these interactions may be summarised, according to Hatt and Bridgwater[64,122]:

Liquid products are favoured by rapid heating rate to a low temperature (about 500^0C);

Char products are favoured by slow heating to a low temperature;

Gaseous products are favoured by a high final temperature (above 500^0C), heating rate is less important.

It has been shown in the last decade that pyrolysis of high thermal severity, for example fast pyrolysis, can lead to much lower yields of char, and produce significant amounts of light unsaturated hydrocarbons, having a medium calorific value[47,48,59,60,84,99,118,135]. In contrast conventional pyrolysis, for example slow pyrolysis, yields about equal amounts of gases, char and tar[27,109,122,123].

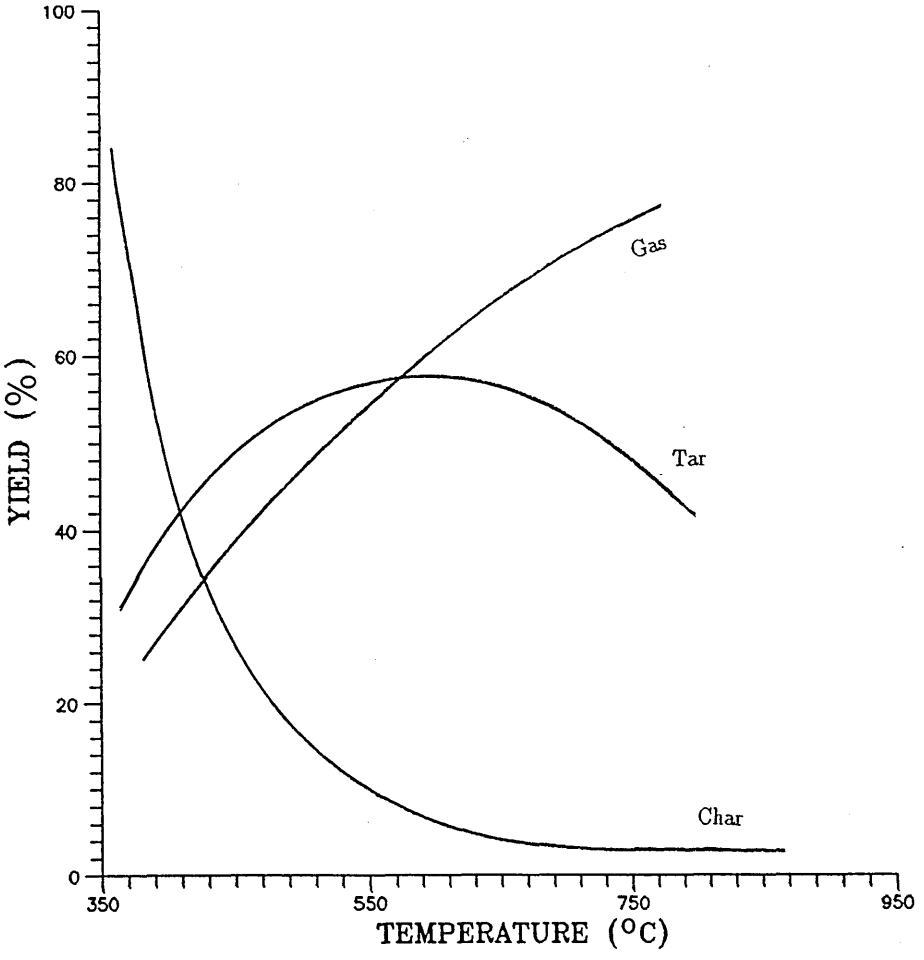


Figure 1.9b – A general view of the effect of pyrolysis temperature on the yield of the products[64].

1.9.1 – Pyrolysis Products from Lignocellulosic Materials.

Pyrolysis offers a rapid route to cracking all of the complex polymeric structures, for example lignin, found in lignocellulosic residue materials. As opposed to gasification, in which all structural identity is lost in the formation of simple molecules, pyrolysis offers high yields of liquid products that retain some of the integrity of the monomeric units present in the original polymers, cellulose and lignin.

Pyrolysis oils have been compared with number 6 fuel oil. The Table 1.9a gives typical properties of number 6 fuel oil and Garrett/Occidental's pyrolysis oil from municipal waste, and Tech–Air's pyrolysis oil from pine sawdust[78]. There is a striking similarity in the physical properties of the two pyrolysis oils produced from different sources, by different equipment. It should be noted that, although the Joules/gramme for pyrolysis oil was considerably lower than the Joules/gramme for number 6 fuel oil, the higher density of pyrolysis oil makes its Joules/litre value much closer to that of fuel oil. Both Garrett/Occidental's and Tech–Air's oils have been fired in oil burners.

Pyrolysis liquids offer promise as feedstocks for chemical opportunities[64,117,122,123]. The complexity of the starting material and the drastic nature of the pyrolysis process, however, yield many product components[117]; the pyrolysis of lignocellulosic materials results in a complex mixture of phenolics. There are in principal two

general routes for the development of this mixture: pyrolysis products must either be fractionated into simpler mixtures of components with similar chemical and/or physical properties, or pyrolysis products must be reformed into more useful chemicals and chemical intermediates. For example tars may be refined and used as diesel oil substitutes or in phenol–formaldehyde condensation resins.

	Number 6	Occidental	Tech–Air
C	85.7	57.0	59.5
H	10.5	7.7	7.0
S	3.5	0.2	0.01
N	N/A	1.1	0.9
O	2.0	33.2	34.8
Joules/gramme	42,300	24,600	24,600
Joules/litre	$34.5\ 10^6$	$26.7\ 10^6$	$27.6\ 10^6$
Density,g/ml	0.98	1.30	1.35

Table 1.9a — Typical properties of number 6 fuel oil and two pyrolytic oils[78].

1.10 – Summary.

It has been shown above that, for the developing countries, the pyrolysis of lignocellulosic materials has the potential to provide fuels with a high degree of energy concentration, that are also easy to store and use. Additionally, by this transformation, biomass may provide a renewable source of low molecule weight materials that are suitable for use as chemical feedstocks.

The morphology and composition of naturally occurring lignocellulosic materials is reviewed, and the influence of the pyrolysis parameters in determining the yields of the pyrolysis products of biomass, and its individual major components, is illustrated.

Sugar Cane Bagasse, a lignocellulosic waste product produced in very large quantities by the sugar cane industry of Brazil, appears to be a promising candidate for conversion into a more valuable commodity by the application of pyrolysis techniques.

CHAPTER 2

THE WIRE–MESH PYROLYSIS APPARATUS.

This Chapter commences with a brief introduction into the historical development of wire mesh pyrolysis reactors. There then follows a full and detail description of the experimental apparatus and procedures used in the present research programme.

2.1 – Introduction.

To date the most advanced laboratory technology for the investigation of flash pyrolysis has, so far, been developed and utilised for coal research; the methodology developed here for the pyrolysis of lignocellulosic materials reflects and draws upon, this past research effort.

The first wire–mesh reactor, used for coal pyrolysis, was designed by Loision and Chauvin[85]. In this reactor a paste made from coal and water was pressed into the holes of a single layer of stainless steel mesh. The mesh holding this paste was then dried under vacuum and the sample weight determined. Measurements were made with heating rates between 300^{0}C/second and 1500^{0}C/second with a maximum temperature of 1050^{0}C. Tar was recovered by washing down

the inside of the glass vessel with solvent. From the experimental details as described by these researchers, it can be seen that by loading the sample in a single layer mesh, heat transfer, between the mesh and the sample, was poor. A probable source of error, in their research, was their tar measurement procedure; tar, deposited on the inside of the glass vessel was, hopefully, fully recovered by solvent washing, the solvent evaporated, and the tar yield determined gravimetricaly. As their coal sample weight was approximately 40 milligrammes, which yielded, say, 7 milligrammes of tar, the possibility of incomplete recovery was high.

Juntgen and van Heek[71], constructed a wire–mesh reactor coupled to a mass spectrometer. They loaded a few milligrammes of coal by pressing the coal into the holes of the mesh, following the procedure described by Loisin and Chauvin[85]. These experiments were performed with a single fast heating rate, up to a peak temperature of 1000^0C. From their report, it can be seen that there was imperfect control of the time–temperature history of the sample, and no quantitative results of the primary products of pyrolysis were presented, even for compounds identified in their mass spectrometer. Only qualitative data could be obtained, describing the relative rate of the production of light hydrocarbon gases and hydrogen, resulting from the very small samples that were used.

From about 1974 onwards, Howard and co–workers, published a series of papers and review articles describing the development and application of a wire–mesh apparatus, with coal as the

sample[4,5,136]. The coal sample was sandwiched in between two layers of wire–mesh; in this way a significant improvement in heat transfer between the hot mesh and the sample was realised. Their reactor was able to operate from vacuum up to 20.3 MPa. Electrical power was supplied to the mesh from several 12V car batteries. With this constant voltage supply the power input will vary inversely with the sample holder resistance; thus an exponential approach to some final temperature, rather than a true linear increase, will result[50]. This power supply limited Anthony's experiments to a maximum temperature of 700^{0}C, at a heating rate of 180^{0}C/second, whilst final temperature of 1000^{0}C was only possible with heating rates of 650^{0}C/second or more[4,5].

As stated earlier the majority of wire–mesh reactors have been used in the field of coal science, see for example references 6,10,32,43,45,49,58,62,70,86,98,130,136; however in the past ten years a few of these systems have been modified and used in the field of biomass pyrolysis[59,60,77,99,100,101].

There are common defects on previous wire–mesh equipment which have imposed severe limitations in certain important parameters, for example the heating rate. In general these systems could only operate with a so called slow heating rate, viz 100^{0}C/second, if the maximum temperature was less than 700^{0}C; and with a fast heating rate, say 700–1000^{0}C/second, if the final temperature was about 1000^{0}C[10,62,130]. Therefore the time–temperature history to which the sample was subjected whilst under good control was severely limited.

The wire–mesh reactor used in this research programme into lignocellulosic pyrolysis represents a significant improvement upon previous wire–mesh reactors. This reactor was designed and constructed at Imperial College and concurrently employed in a coal pyrolysis study[50] as well as in this biomass research. In contrast to the work of previous researchers, all the fundamentally important pyrolysis process parameters may be systematically investigated using this unique "***constant geometry***" wire–mesh reactor.

2.2 – Description of the Apparatus.

The present wire mesh pyrolysis apparatus has two novel features; first an inert gas flows through the system and rapidly sweeps the products of pyrolysis away from the hot reaction zone into a liquid nitrogen cooled sinter trap; thus the secondary cracking or possible polymerisation of tar products is greatly reduced. The helium carrier gas flowing at 0.1 m/second gives an average volatile residence time, with the hot reaction zone centred on the sample holder, of approximately 5 milliseconds. Pyrolysis samples, of approximately 7 milligrammes in weight, are evenly distributed in a monolayer about the centre of the sample holder. Secondly the range of controlled heating rates that may be obtained with this reactor are large, slow and fast heating regimes are readily covered. For example heating rates from as low as almost 0^0C/second and up to 5000^0C/second may be used, for any peak temperature between ambient and 1200^0C. The time for

which the sample is maintained at the peak temperature, i.e. the hold time, may be readily set from zero to a very long time, for example 1000 seconds. With this "***constant geometry***" apparatus, which is described in detail below, important pyrolysis parameters, such as tar yield, may be systematically investigated.

The base of the apparatus was fabricated from 316 stainless steel, 16.8 cm in diameter and 3.4 cm thick, with six 2BA studs at its edge, as shown in Figure 2.2a. Upon this base two electrodes (6.6 x 1.0 x 0.6 cm) supported the wire–mesh; these electrodes have cooling water channels so as to avoid over heating, and hence possible damage to the apparatus, when running at high temperatures or for long hold times. A small, pyrex glass bell jar, with three ports, with the dimension shown in the Figure 2.2b, covered the wire–mesh. One side port was used for the inlet of the carrier gas and the other for evacuating the reactor when purging. The screw port on the top of this bell jar had a diameter of 4.2 cm, the trap for tar collection was attached there. Between the 0.4 cm flange on the bottom of this glass bell and the reactor base plate a 1/8 inch butyl rubber "O" ring was located to seal these two components together. The glass bell was pulled down by an aluminium clamping ring; 2BA studs from the base of the reactor passed through symmetrical clearance holes in the clamping ring and were capped by butterfly nuts. The cylindrical pyrex trap for tar collection was 3.2 cm in diameter and 14.0 cm long, with a sinter disc of porosity number 04 fused at 10.0 cm from one end. This trap was lowered through the top aperture of the glass bell until it rested upon the wire–mesh, as shown in Figure 2.2c;

an "O" ring was then placed over the tar trap and compressed by the screw cap. The Figure 2.2d shows the wire–mesh pyrolysis apparatus ready for an experimental run.

The 12 volts secondaries of two transformers were connected in series to supply 15 amperes to power the wire mesh. Their primary windings were connected to the mains supply, one via a "variac" variable transformer; this allowed the power demanded by the grid, for any given heating programme, to be roughly matched, or balanced, to the supply.

A microprocessor–controlled (Motorola 68008, 7.5 MHz) data logging system was used to sample the temperature at 20 millisecond intervals and generate a feedback control signal for the power modulation circuit, a thyristor a.c. regulator was used to control the length of time during each mains half–cycle for which power was applied to the grid. The combination of these two controls permitted any desired permutation of linear heating rate, holding period at maximum temperature and cooling rate to be specified. Heating rates may be varied in this new reactor from as low as almost $0^{o}C$/second to $5000^{o}C$/second. The maximum temperature can be varied between ambient and, about, $1200^{o}C$; however above, say, $900^{o}C$ hold times must be limited, for practical reasons, to approximately 300 seconds; this constraint is imposed to avoid possible damage to the experimental system.

A microcomputer (Sinclair QL) via a parallel interface

was used to control an analog–digital converter, in front of which there was a multiplexer, and before this a preamplifier. Each thermocouple was connected to the two stage signal conditioning/amplification circuit which had a gain of about 160:1, this was designed by the Electronics Workshop of the Chemical Engineering Department of Imperial College. This electronics module provided a 0–10 volts output signal into the A/D board from the thermocouple inputs of, approximately, 0–60 millivolts. Data and programme storage were provided by the two 120 Kbyte microdrives built into the QL microcomputer[50]. A dot–matrix printer was used as required to generate a hard copy of temperature and power data points.

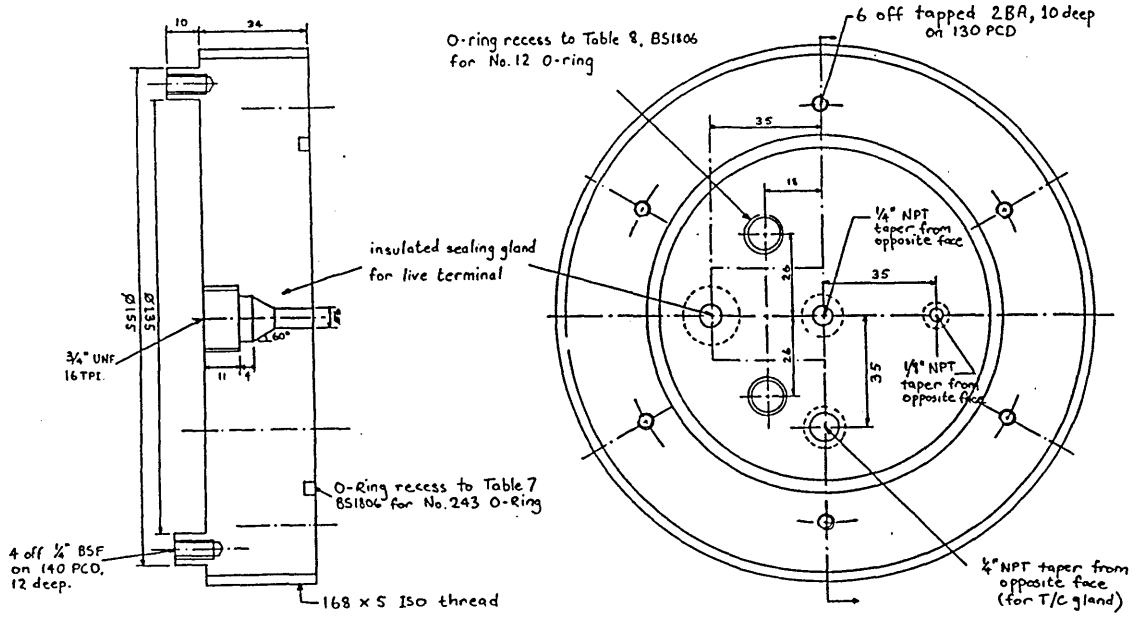


Figure 2.2a – The base for the wire–mesh pyrolysis reactor.

(from Gibbins[50])

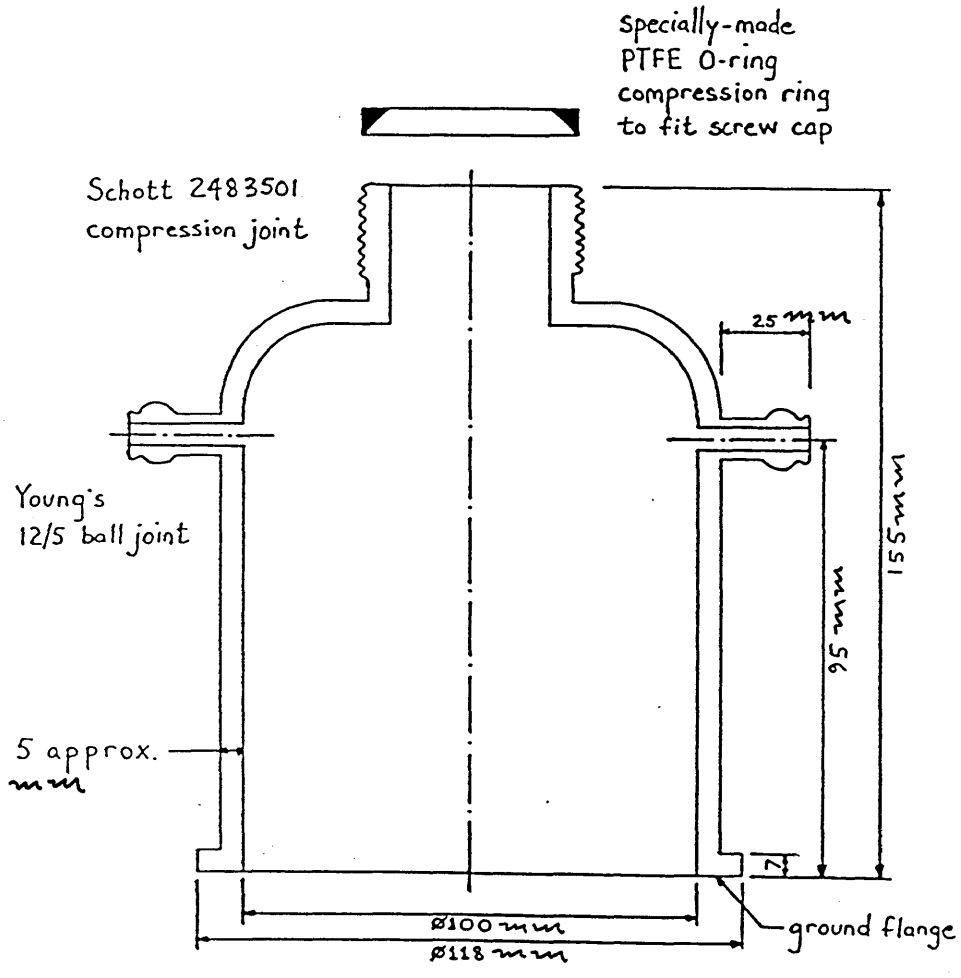


Figure 2.2b – The pyrex bell showing its dimensions.

(from Gibbins[50])

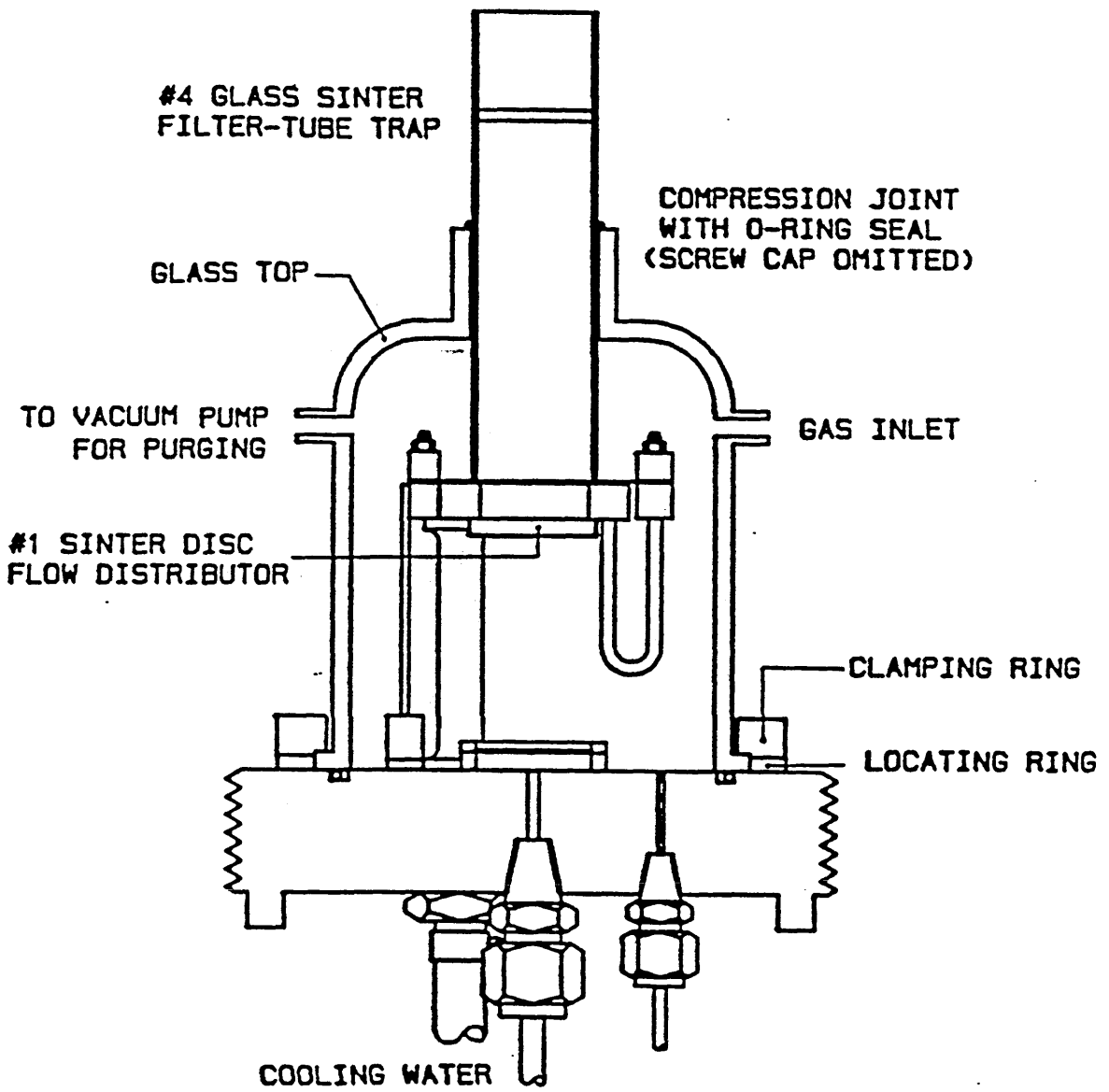


Figure 2.2c – The reactor with the pyrex bell and the trap for tar collection. (from Gibbins[50])

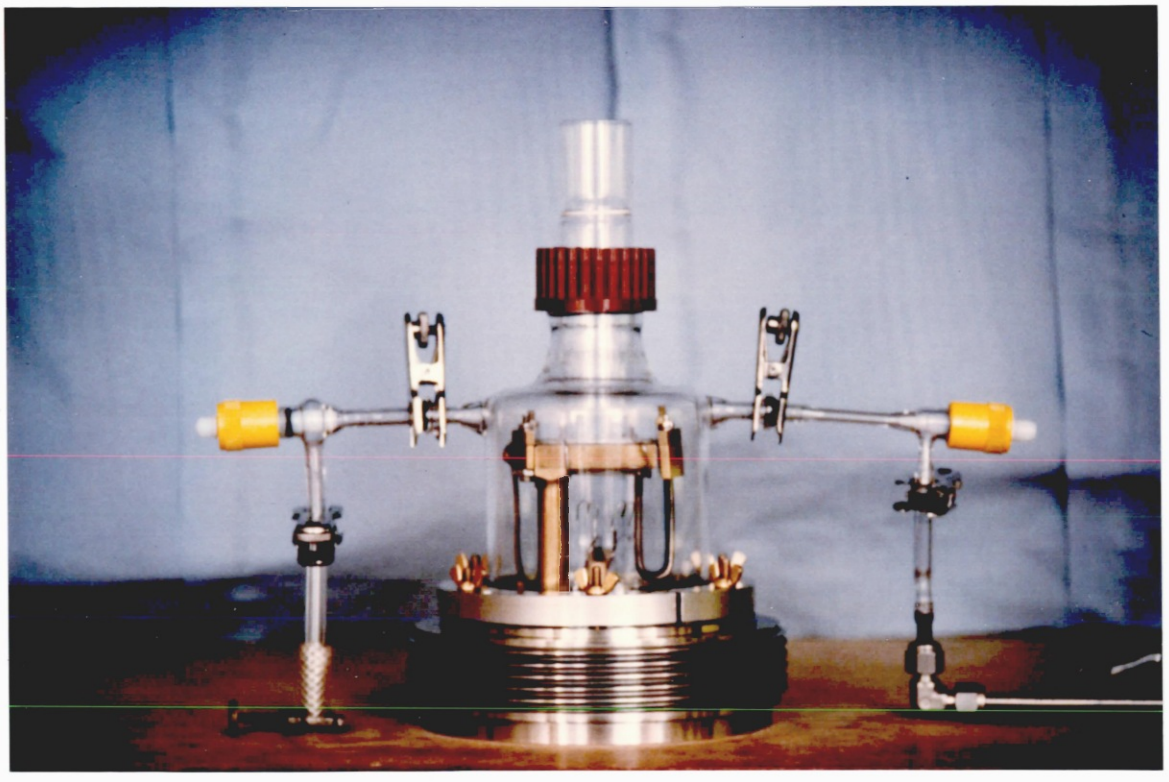


Figure 2.2d – The wire–mesh pyrolysis reactor ready for experimental run.

2.2.1 – Sample Holder.

The sample holder, Figure 2.2.1a, was made from woven 250 mesh (63 microns), AISI 304, cut to the dimensions 7.0 x 7.5 cm. After being cut to the above dimensions, the wire–mesh was folded over onto itself twice, so as to form an envelope; it was then washed with acetone, to remove any deposits of grease (e.g. from the hands). Clearly if the mesh had any grease, or foreign material, the final results would be inaccurate. This envelope prevented any sample being lost from the sides of the grid, and also ensured uniform temperature within the sample. The mesh was then located on the electrodes and the reactor assembled, evacuated and purged, as if for an experimental run; the screen was then prefired, so as to ensure absolute cleanliness, and thus avoid the possibility of any catalytic or secondary reactions during the sample thermal decomposition[60,62]. The prefiring of the screen was done manually; slowly the temperature was raised to about 1000^0C as judged by eye and held at this temperature for about 10 seconds, then the power was slowly reduced. After this treatment tests showed that the screen would never lose weight when subjected to the experimental conditions. The screen was then most carefully removed from the electrodes and kept in an enclosure until required for the experimental run.

It must be emphasised that after the acetone wash and until the last weighing following a run, the sample holder was always handled using tweezers and a spatula, so as to avoid any

contamination. As each run required a new wire–mesh, it was convenient to prepare a good number of screens before beginning a series of experimental runs.

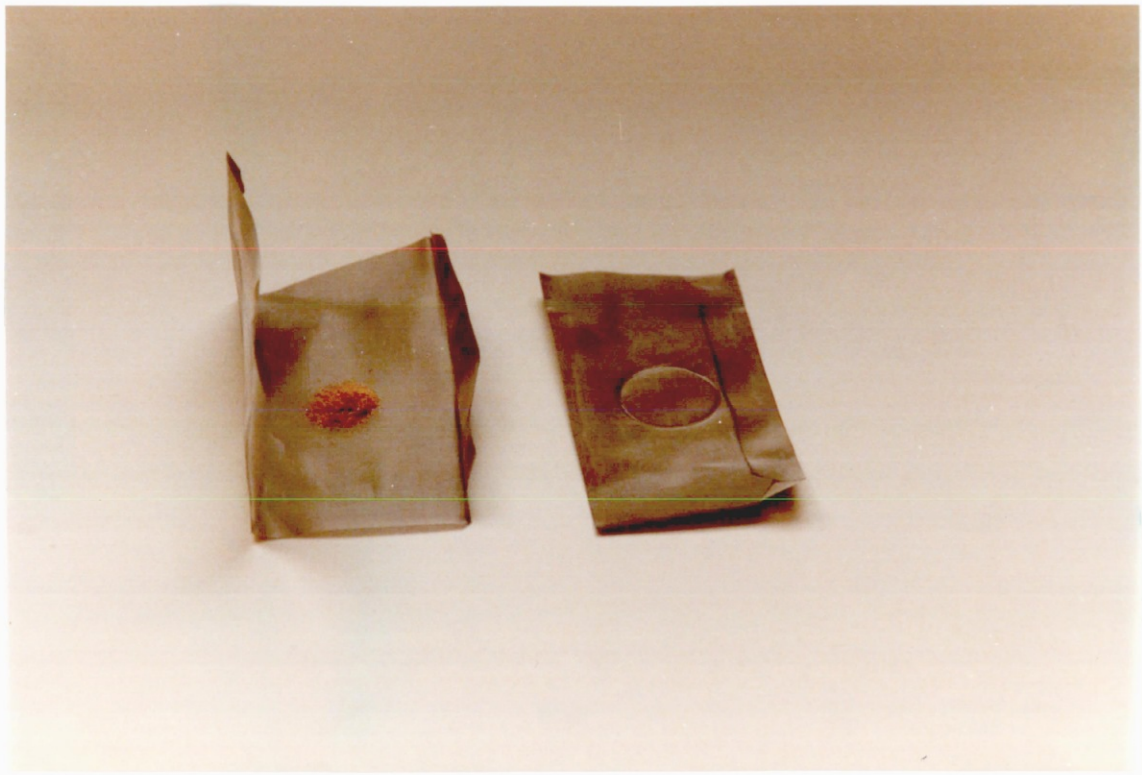


Figure 2.2.1a – The sample holder for the pyrolysis wire–mesh reactor.

2.3 – Sample Preparation.

2.3.1 – Sugar Cane Bagasse and Silver Birch.

The sample of Sugar Cane Bagasse originated from the " Usina Nossa Senhora das Maravilhas" – Pernambuco – Northeast of Brazil, and the sample of Silver Birch from the North of the United Kingdom.

Samples of Sugar Cane Bagasse and Silver Birch were cut into small pieces, of approximately 2cm in length, and pulverised in a coffee grinder; the grains were then sieved, to collect the 100–150 micron particles.

Both bulk materials were dried, in an oven flushed with nitrogen at 110^0C, overnight. After this, these specimens were placed in a small jar, and this jar was placed in a desiccator, at room temperature, which was flushed with nitrogen throughout the length of this research programme, to ensure dryness. Daily, before the experiments, a small sample, of about 60 milligrammes, of either Sugar Cane Bagasse or Silver Birch, was transferred from its jar, to a 10 millilitres bottle.

2.3.2 – Cellulose, Lignin and Their Mixtures.

The cellulose sample used in this research was fibrous Cellulose powder CF11 Whatman, and the lignin a proprietary Kraft lignin.

It was not possible to obtain either cellulose or lignin with dimensions as required for these experiments, specifically the mean particle size of the bulk material was smaller than that of the holes in the wire–mesh, that is 63 microns. Consequently the sample, in powder form, was prepared to the size 100–150 microns as follows:

20 grammes of the two constituents were placed into a 500 millilitres jar in the proportions as required; the jar containing this mixture was then covered and vigorously shaken until the sample was homogeneous.

Using a "KBr" hydraulic press and die, the mixture was pressed into several pastilles of about 1cm diameter and 0.3 cm thick.; then these pastilles were crushed into very small grains and sieved to obtain particles of the desired size, namely 100–150 microns.

After preparing these samples of cellulose, lignin and their mixtures, they were stored in the same manner as that used for the Sugar Cane Bagasse and the Silver Birch specimens, as described in Section 2.3.1, above.

2.4 – Run Procedure.

Approximately 10 milligrammes of dried, powdered (100 – 150 microns) sample were placed onto a small area in the centre of a preweighed and creased wire–mesh; which was then refolded and clamped between the brass electrodes. Carefully, the electrodes were tapped whilst gently sucking the surface of the grid with a 0.5 cm diameter glass tube attached to a vacuum cleaner; this procedure was to remove any and all particles of the sample smaller than the mesh size. A circle of 2.0 cm diameter was then impressed upon the centre of the mesh, as shown in Figure 2.2.1a; this circle marked the area which contained all the sample. Then, while gently tapping the electrodes, a 1.8 cm diameter glass tube attached to the vacuum cleaner, was used to evenly spread the sample, within this circular area, in a monolayer. The screen was then dismounted, weighed, and reinserted between the brass electrodes. Two pairs of 0.05 mm chromel–alumel thermocouples were placed through the screen, in such a way that they touched the sample; the two thermocouple readings were averaged to give the temperature–time history of the sample, a diagram of the apparatus with the thermocouples in position may be seen in Figure 2.4a. Due to the small sample size required in this reactor, and to ensure uniformity of temperature across the entire sample, particular care was taken in these experiments to obtain not only a uniform sample distribution but also to place the thermocouples at a representative location. Previous research[45,50] has shown that differences of the order of 50–100°C may

occur between a thermocouple placed in an area touching the sample, and another thermocouple located nearby in an empty area of the mesh.

The pyrex bell was pulled down onto the base of the reactor with the aluminium clamping ring, and then the weighed sinter tar trap was placed in the top port; the open top of the sinter trap was temporarily closed with a rubber bung, to allow the apparatus to be evacuated during purging. Through this rubber bung, passed a glass tube with a stopcock. The system was evacuated and simultaneously purged with a flow of helium gas, metered through a rotameter, into the reactor via a control valve. After the purging was complete, the stopcock was opened, establishing flow through the sinter; after which the bung could safely be removed without any risk of air entering the reactor. The linear velocity of the carrier gas, through the sinter disc, was set to 0.1 meter/second, which corresponded to a flow rate of approximately 8.0×10^{-5} m^3/second; the helium carrier gas was obtained from a cylinder through a low–pressure regulator set to give 0.5 atmosphere (gauge) outlet pressure, see Figure 2.4b.

The sample temperature was then raised at the desired rate to the desired peak temperature, held there and then cooled rapidly; under the programmed control of the microcomputer. The Figure 2.4c, shows a printout, of a typical experimental run, where the profile of the steps of the heating rate, temperature and hold time at the peak temperature are shown. Liquid nitrogen was carefully poured into the open top of the sinter trap throughout the entire experiment;

hence any volatile products, for example pyrolysis tars, would be condensed onto the lower surface of the sinter disc. After the run, the wire–mesh was removed from the electrodes and re–weighed to obtain the char yield; that is the weight of the mesh plus char minus the original weight of the mesh. The yield of volatile matter, was calculated by difference; this being the weight of the mesh plus sample minus the weight of mesh plus char. The sinter trap with tar was placed in an air oven for half an hour at 30°C to dry, and then weighed to determine the tar yield. This procedure was adopted based upon the results obtained from a simple auxiliary experiment. A thoroughly dried tar trap was moistened with distilled water and then heated at 30^0C for different periods of time; it was found that the initial weight was always obtained after not less than 30 minutes. This procedure ensured that any water contained in the tar, either from condensation due to the presence of liquid nitrogen or from pyrolysis reactions, was removed. The yield of gas plus water was calculated, being defined as the difference between the weight of total volatiles and the weight of tar. The weight of the sample, screen, sinter trap and char was determined to within $\pm$0.001 milligrammes; A five figure (Sartorius 2024 – i.e.reading to 0.00001 grammes) balance, enclosed in a glove box was used, this glove box was kept dry with silica gel. The balance output was monitored at 1 minute intervals by a microcomputer; when the same value was obtained for a minimum of 3 minutes then the weight was recorded, this could take up to 30 minutes.

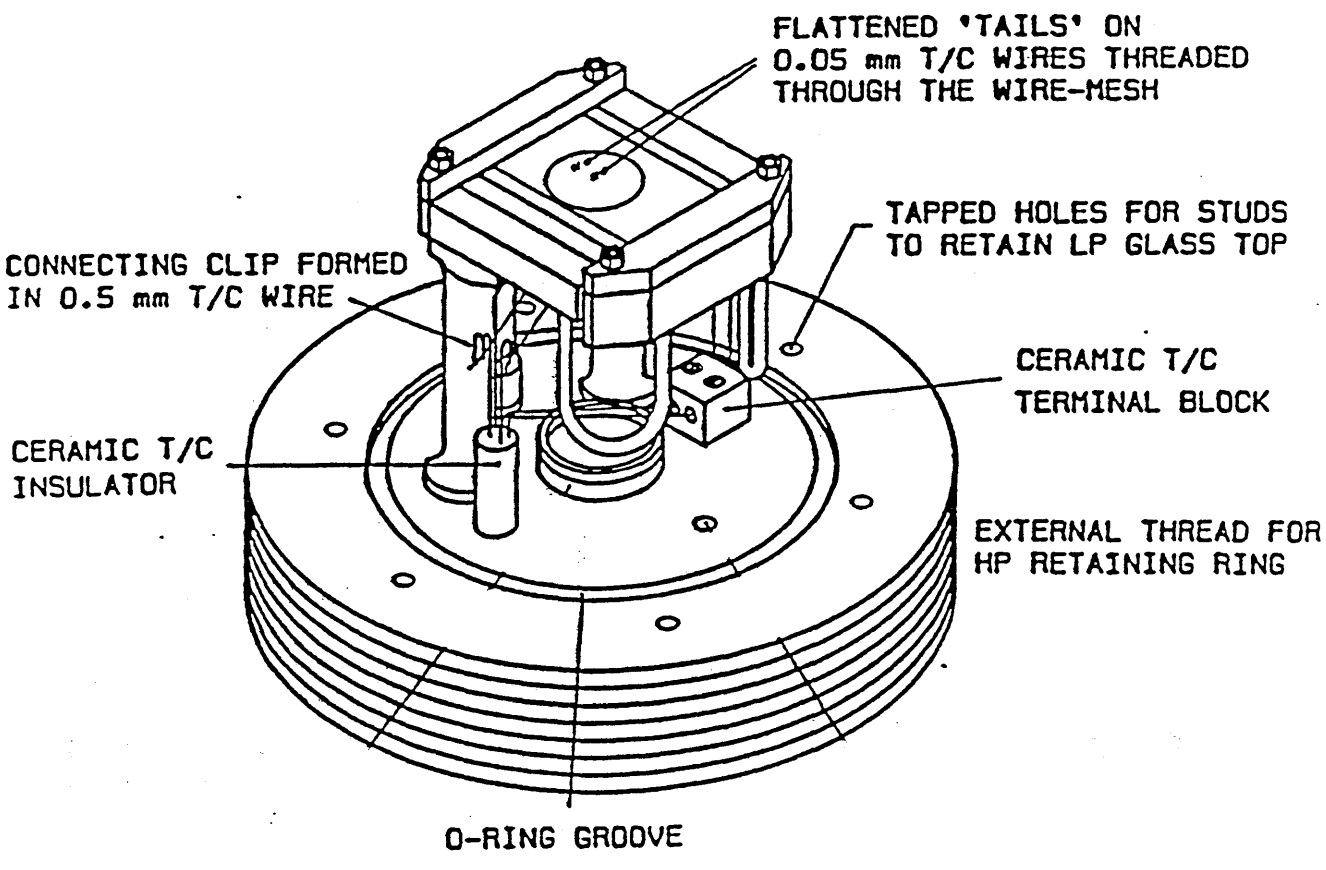


Figure 2.4a — The reactor with electrodes and the sample holder in position. (from Gibbins[50])

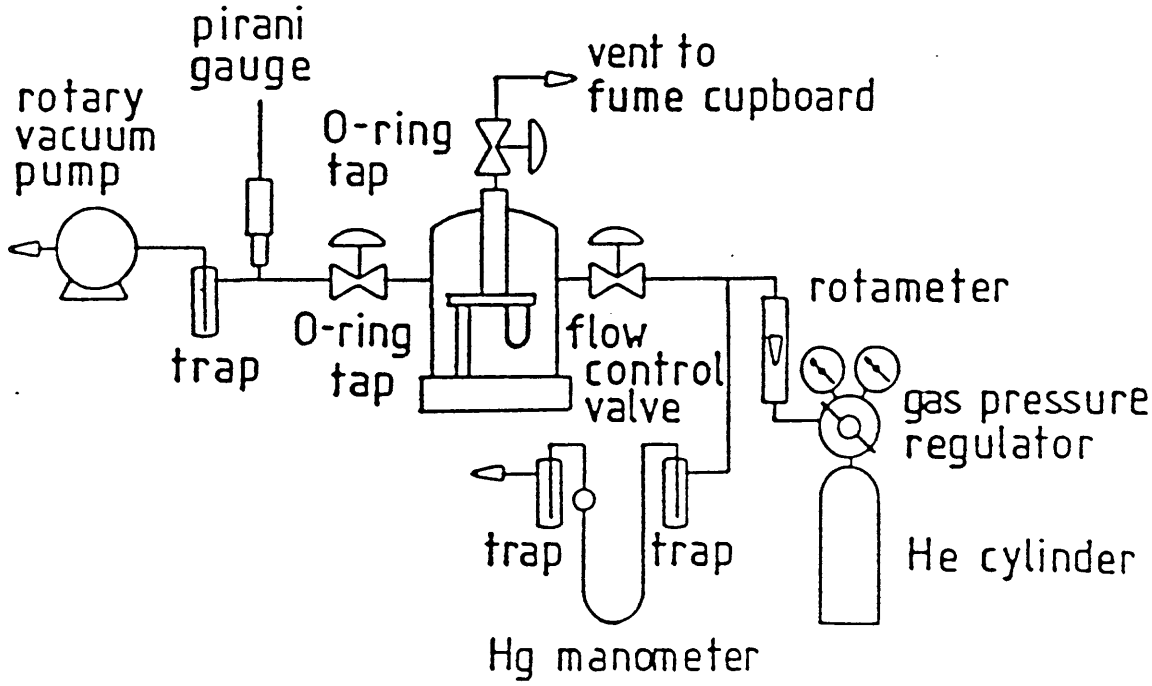


Figure 2.4b – Gas supply circuit.

(from Gibbins[50])

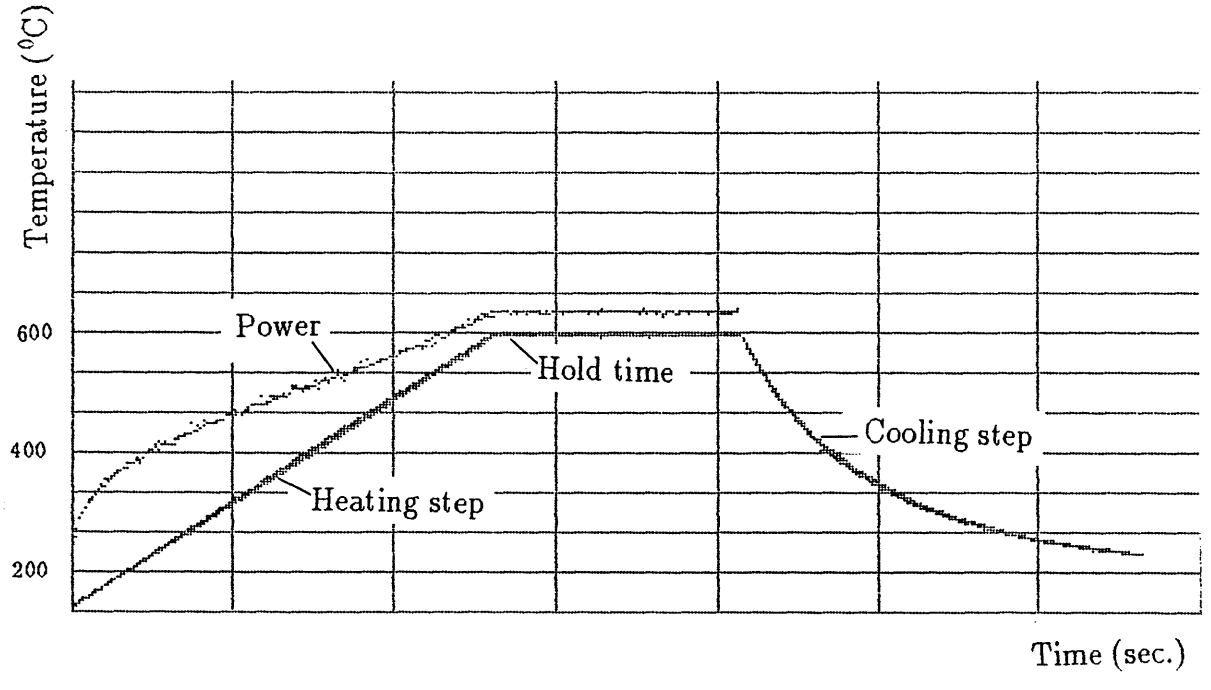


Figure 2.4c – Profile of heating rate, temperature and hold time for experimental run.

2.4.1 – Tar Extraction.

Following the determination of the tar yield, the tar was then extracted from the pores of the sinter for analysis. The sinter trap was held by an external rubber "O" ring and placed in the neck of a 125 millilitres conical vacuum flask such that the side of the trap, coated by the tar, was underneath, Figure 2.4.1a. 2 millilitres of methanol were poured into the top of the trap and a vacuum pump, connected to the flask, was switched on thereby sucking the solvent and the dissolved tar into the flask. Hence the tar, which had been found to be totally soluble in methanol, was washed out of and removed from the pores of the sinter. Following the initial solvent charge a further 8 millilitres of methanol (4 by 2 millilitres) was poured into the top of the trap, with the vacuum pump still running. When all 10 millilitres of solvent had passed through the trap in this manner the pump was switched off; it was observed that the sinter disc was now as white as before the pyrolysis run, see Figure 2.4.1b. The tar dissolved in the methanol was transferred, little by little, into a 10 millilitres specimen bottle, which was most carefully heated, under a nitrogen atmosphere, with the aid of a hair–drier, and finally placed in the air oven for 30 minutes at 30°C. The specimen bottle containing the pyrolysis tar was placed in a freezer until the tar was required for analysis.

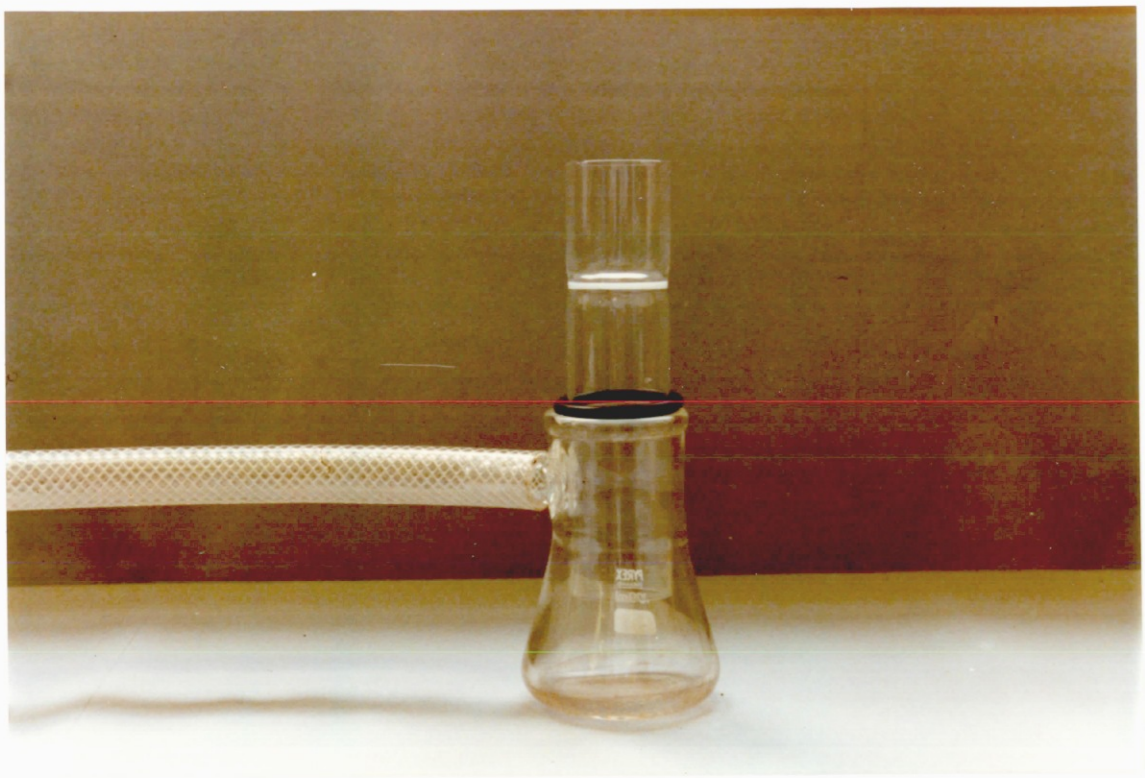


Figure 2.4.1a – The "Sinter trap" assembled for tar extraction.

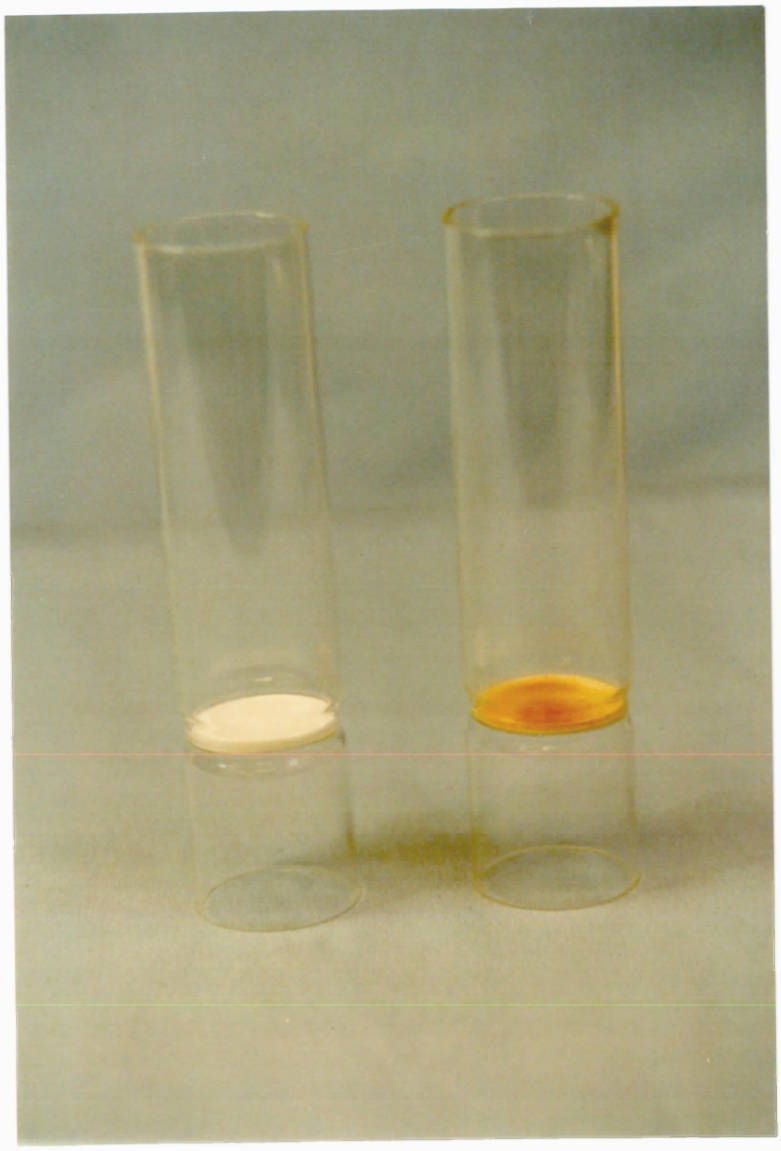


Figure 2.4.1b – The "sinter trap" before (left) and after (right) a pyrolysis run.

CHAPTER 3

THE PYROLYSIS OF LIGNOCELLULOSIC MATERIALS.

3.1 – Introduction.

Experimental results, obtained with the wire–mesh reactor described in Chapter 2 section 2, for the pyrolysis of Sugar Cane Bagasse and Silver Birch are presented in the first part of this chapter. These data are reported in two ways; in graphical form so that trends may be readily identified, in which either the raw results or the average yields of the products of pyrolysis, namely the total volatiles, tar, gas plus water and char are plotted, and also as tables, located at the end of this Chapter, where the results of all the products of pyrolysis are listed. The data for Sugar Cane Bagasse is presented first and then that of Silver Birch, and then these data are compared.

In the clearly distinct, but closely associated, second part of this Chapter the results obtained for the pyrolysis of cellulose, lignin, and their mixtures are presented and compared, in the same format as that of part one. A full discussion of these results, and their comparison with the data of other researchers, is presented in Chapter 5. However, as and when important features are revealed in these data they are identified, and briefly summarised in this Chapter. All the numerical values related to pyrolysis data presented in this chapter are calculated on a dry ash free basis (d.a.f.).

3.1.1 – Reproducibility of Experimental Data.

For all the average yields presented in these graphs, the maximum deviations, from the average value, are as follows:

Total volatiles	± 1%
Gas plus water	± 2%
Tar	± 2%
Char	± 1%

Most careful precautions were taken during weighing, for details see section 2.4; hence a five figure balance, placed in a glove box enclosure, was used and the mesh and the tar trap were always handled with tweezers and a spatula. However, since the tar collected was typically 4 milligrammes, in a trap weighing about 50 grammes, the experimental error may be attributed mainly to this.

After the final weighing, the mesh containing the char was most carefully opened and, with the help of a magnifying glass, the char was searched to determine if there were any biomass grains that were not pyrolysed. It will be seen that some of the results in the tables are marked "+", this symbol identifies those runs in which pyrolysis was judged not to be complete. Experimentally it was found that for peak temperature below 400^{0}C, with zero second hold time, reproducible results could not be obtained; two possible explanations for this observation are presented in this Chapter, see section 3.2.1.2. Therefore in order to present the large quantity of new data obtained in

this research programme, in the most easily understandable manner, the results obtained with a hold time of 30 seconds or more, i.e. those data that are reproducible, are presented first for each lignocellulosic material.

3.2 – The Effects of Heating Rate and Temperature, as a Function of the Hold Time, on the Pyrolysis Products of Sugar Cane Bagasse and Silver Birch.

3.2.1 – Sugar Cane Bagasse.

3.2.1.1 – Hold time = 30 seconds.

Figure 3.2.1a shows the effect of peak temperature on the yields of the products from the pyrolysis of Sugar Cane Bagasse, with a heating rate of 1°C/second and a hold time at the peak temperature, of 30 seconds. This figure shows that there is a smooth increase in the total volatiles for peak temperatures in the range above 400°C and until, about, 500°C; when conversion attains a constant maximum value. It can also be seen that increased conversion, in the peak temperature range of 400–500°C, is equally divided between tar and gas plus water.

A similar effect occurs at a fast heating rate, see Figure 3.2.1b for total volatiles, where the Sugar Cane Bagasse was heated, at 1000°C/second and, once again, kept at the peak temperature

for 30 seconds. This figure shows that total conversion increases in the temperature range 400–600°C, and that, in general, conversion to tar increases in the temperature range of 400–500°C and conversion to gas plus water in the range 500–600°C. After about 600°C the peak temperature does not affect the total yield of Sugar Cane Bagasse pyrolysis products.

Figures 3.2.1a and 3.2.1b are overlaid in Figures 3.2.1c, 3.2.1d and 3.2.1e in order to compare the total volatiles, tar and gas plus water yields, for heating rates of 1 and 1000°C/second. Figure 3.2.1c clearly shows that the total volatiles yield is always higher for heating rates of 1000°C/second than for 1°C/second. Figure 3.2.1d shows that at fast heating rates, that is 1000°C/second, about 12% more tar is produced than at slow heating rates, namely 1°C/second. In contrast heating rates do not, in general, appear to affect the production of gas plus water, see Figure 3.2.1e, except below, say, 600°C where the slow heating rate gives about 5% more gas plus water than the fast heating rate. In summary, the effects of slow and fast heating rates, at 30 seconds hold time, can be seen in Figure 3.2.1f, where the yield for both tar and gas plus water are plotted versus temperature.

These results differ from the data obtained by other researchers using either fixed bed or fluidised bed reactors[84,117,118,119,123,129,133,135], where, in general, tar yields decrease for temperatures above 500^{0}C. In these reactor systems secondary reactions, above 500^{0}C, will occur in either the vapour or solid phase. Given the high rates at which the initial thermal decomposition of biomass takes place, it does

seem unlikely that a particle could still be in its primary decomposition phase at a temperature above, about, 500^{0}C. Nevertheless the new results presented here, for the products of pyrolysis of Sugar Cane Bagasse, clearly attain a constant maximum value when the temperature reaches 500^{0}C; this behaviour is seen for both slow and fast heating rates. These observations in this wire–mesh reactor are, most probably, due to its reactor geometry, which freely permits the volatile products to be quickly expelled from the hot reaction zone before secondary reactions may substantially modify the primary product yield. Based upon these results an important experimental observation may be drawn, that when determining the primary reaction products, a carrier gas should flow through the sample; thus primary products are immediately quenched after leaving the hot zone of the reactor, and secondary reactions are drastically reduced.

In pyrolysis, in general, large amounts of tarry products are found sticking to the surfaces of the experimental apparatus, in, and around, the hot sample region, see for example[1,22,59, 60,84,99,100,101,118,119,135]. In such situations these residues are cracked again. However in <u>all</u> of the experiments contained within this research programme, <u>no</u> tar was found after a run, either on the mesh, or on the inside of the "bell jar"; see Chapter 2 section 2.4. This observation strongly supports the proposition that all the volatile products were swept from the pyrolysed sample, leaving only char in the mesh, and thus the possibility of secondary reactions taking place was greatly diminished.

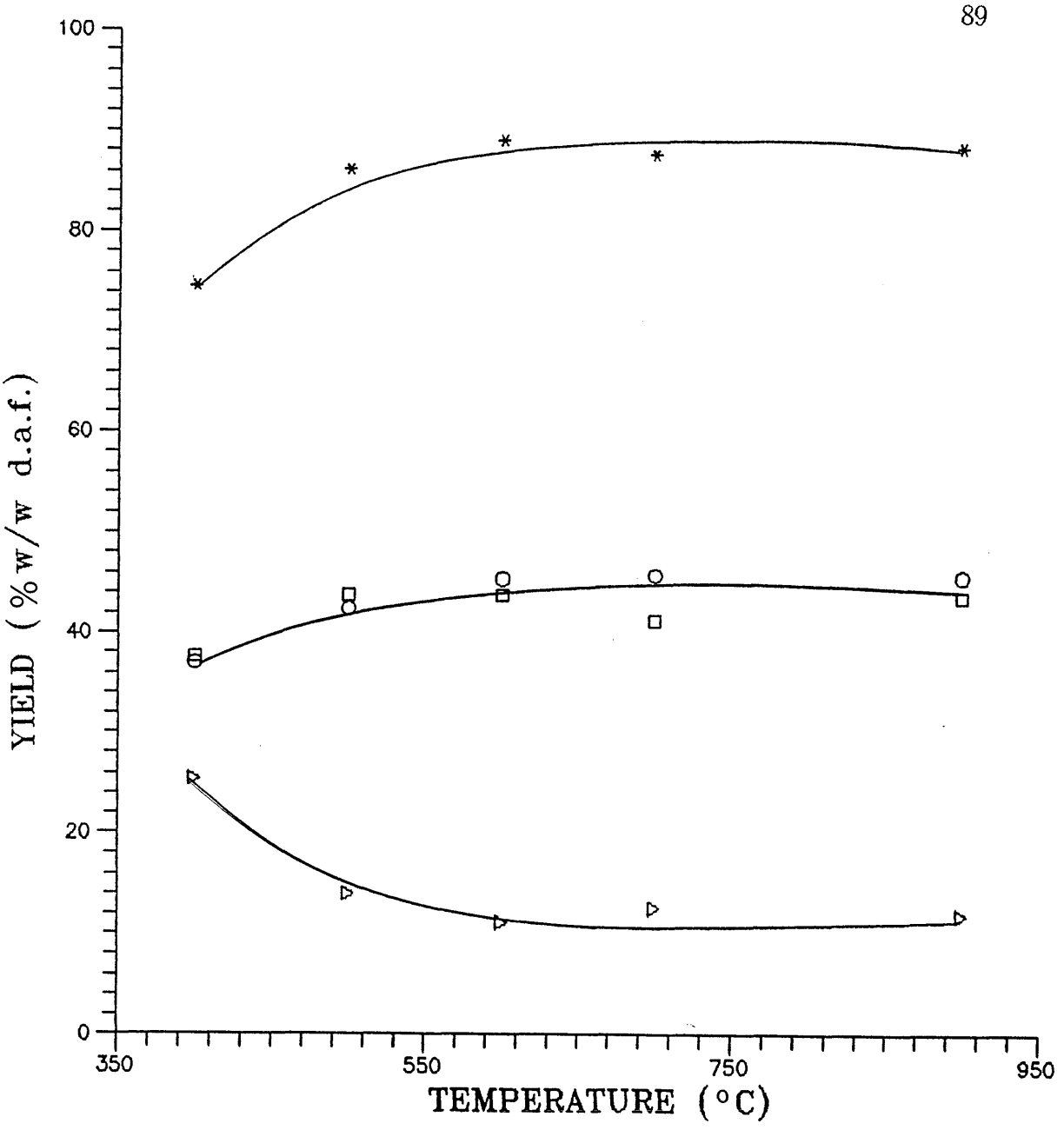


Figure 3.2.1a – The effect of the peak temperature on the yields of the products for the pyrolysis of Sugar Cane Bagasse, with a heating rate of 1^0C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

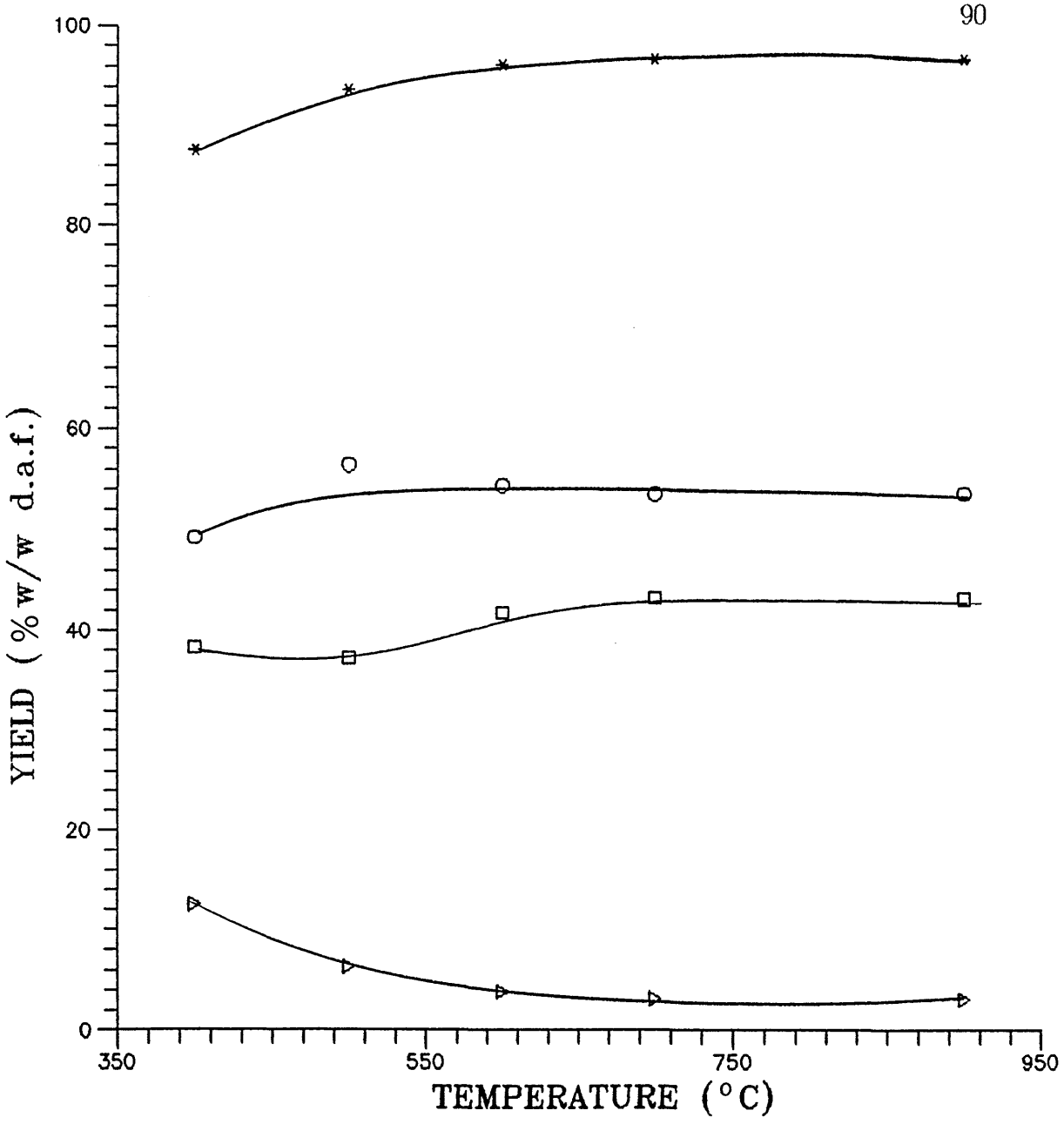


Figure 3.2.1b – The effect of the peak temperature on the yields of the products for the pyrolysis of Sugar Cane Bagasse, with a heating rate of 1000^{0}C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

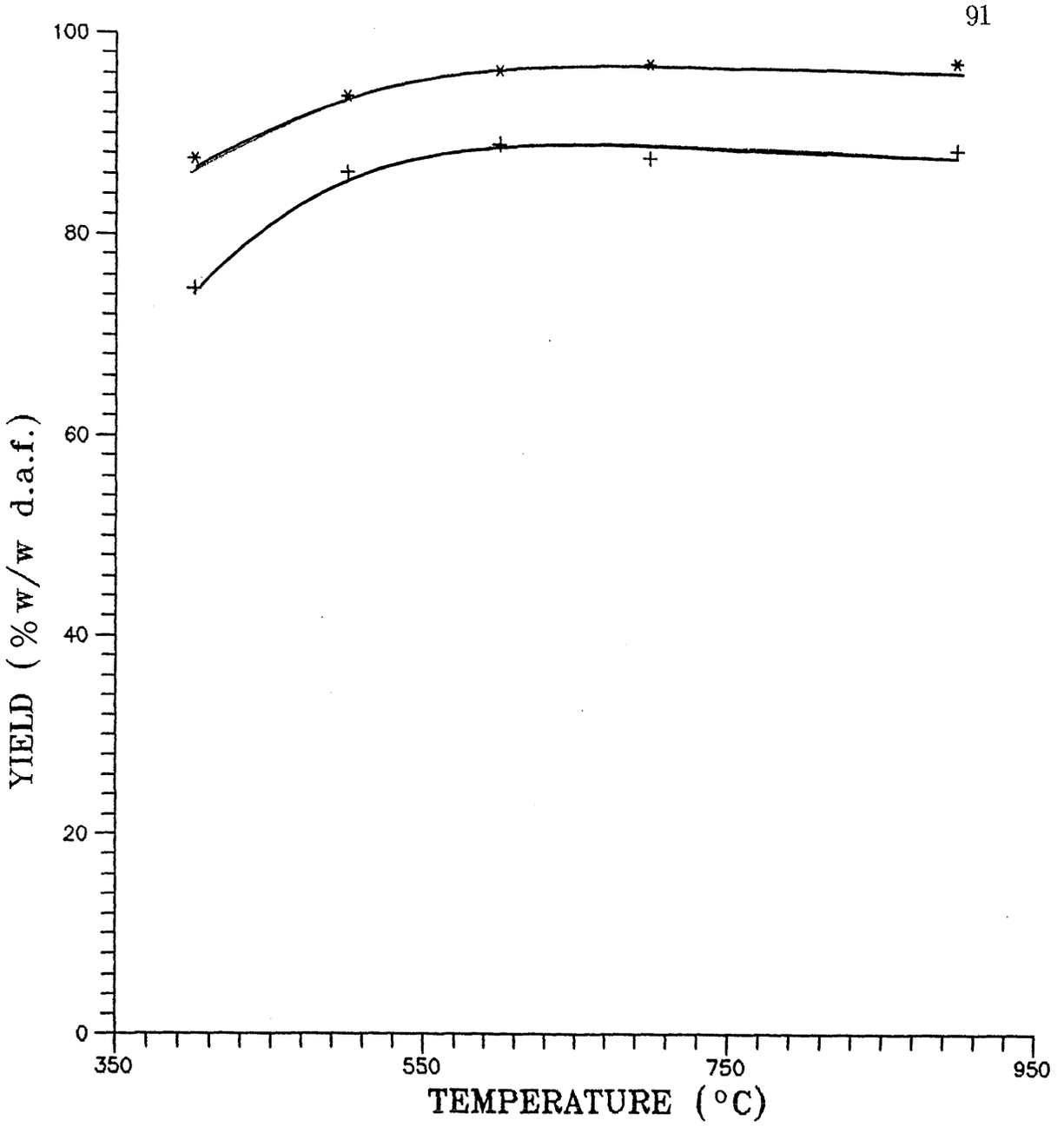


Figure 3.2.1c – The effect of the peak temperature on the yields of Total volatiles for the pyrolysis of Sugar Cane Bagasse, with 30 seconds hold time.

* = 1000^0C/second; + = 1^0C/second.

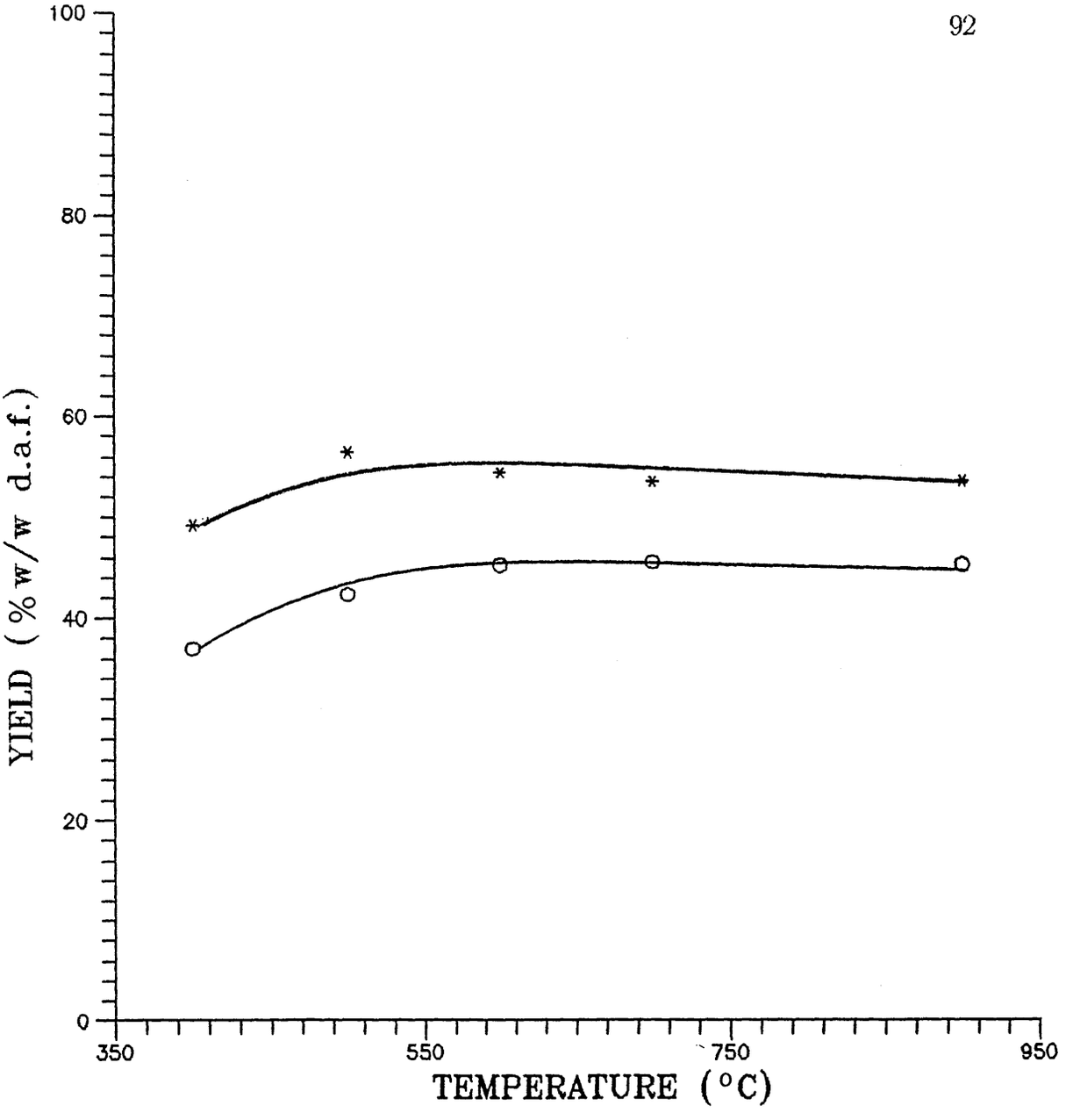


Figure 3.2.1d – The effect of the peak temperature on the yields of Tar for the pyrolysis of Sugar Cane Bagasse, with 30 seconds hold time.
* = 1000°C/second; 0 = 1°C/second.

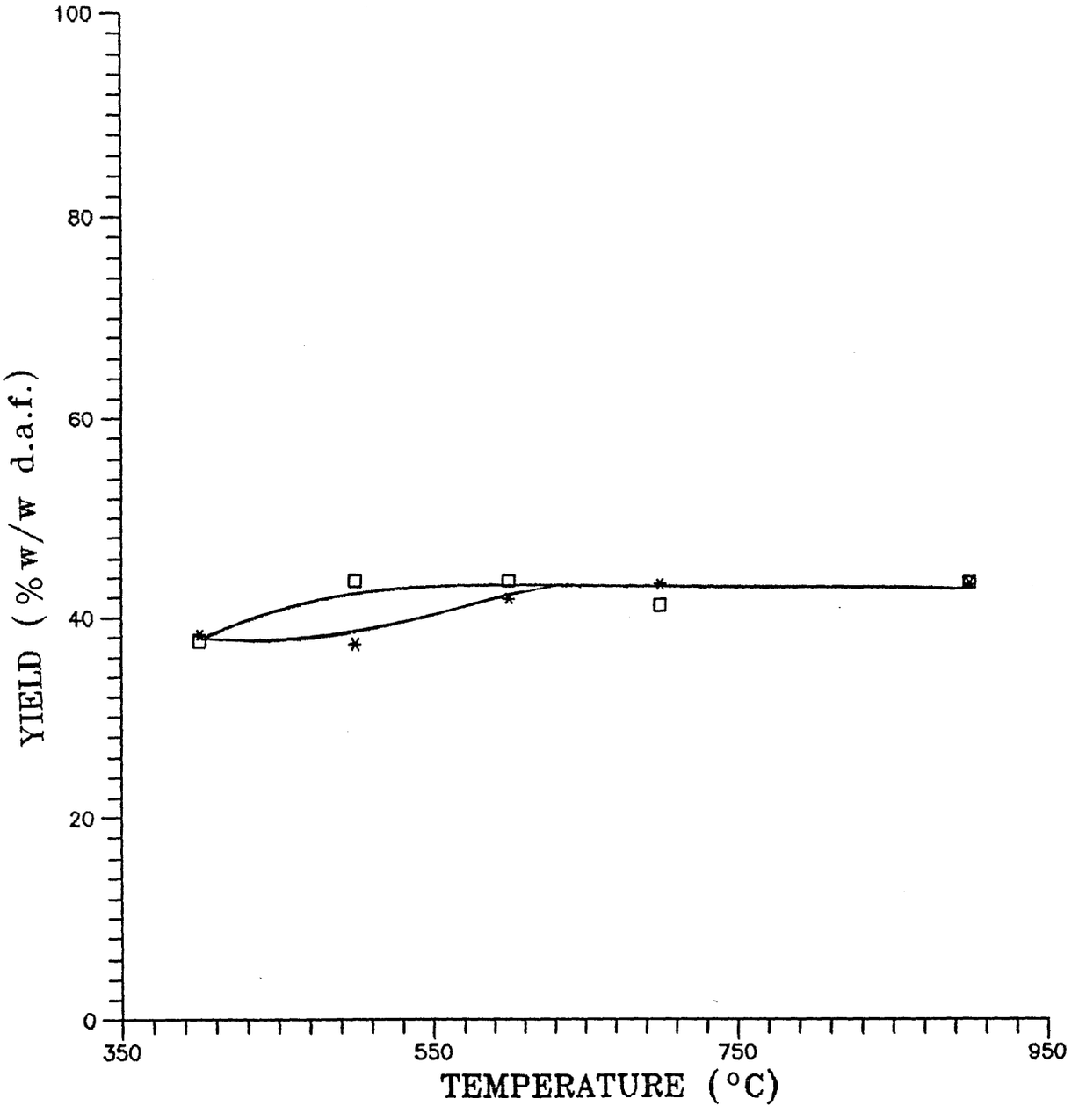


Figure 3.2.1e – The effect of the peak temperature on the yields of Gas plus water for the pyrolysis of Sugar Cane Bagasse, with 30 seconds hold time.

* = 1000^0C/second; □ = 1^0C/second.

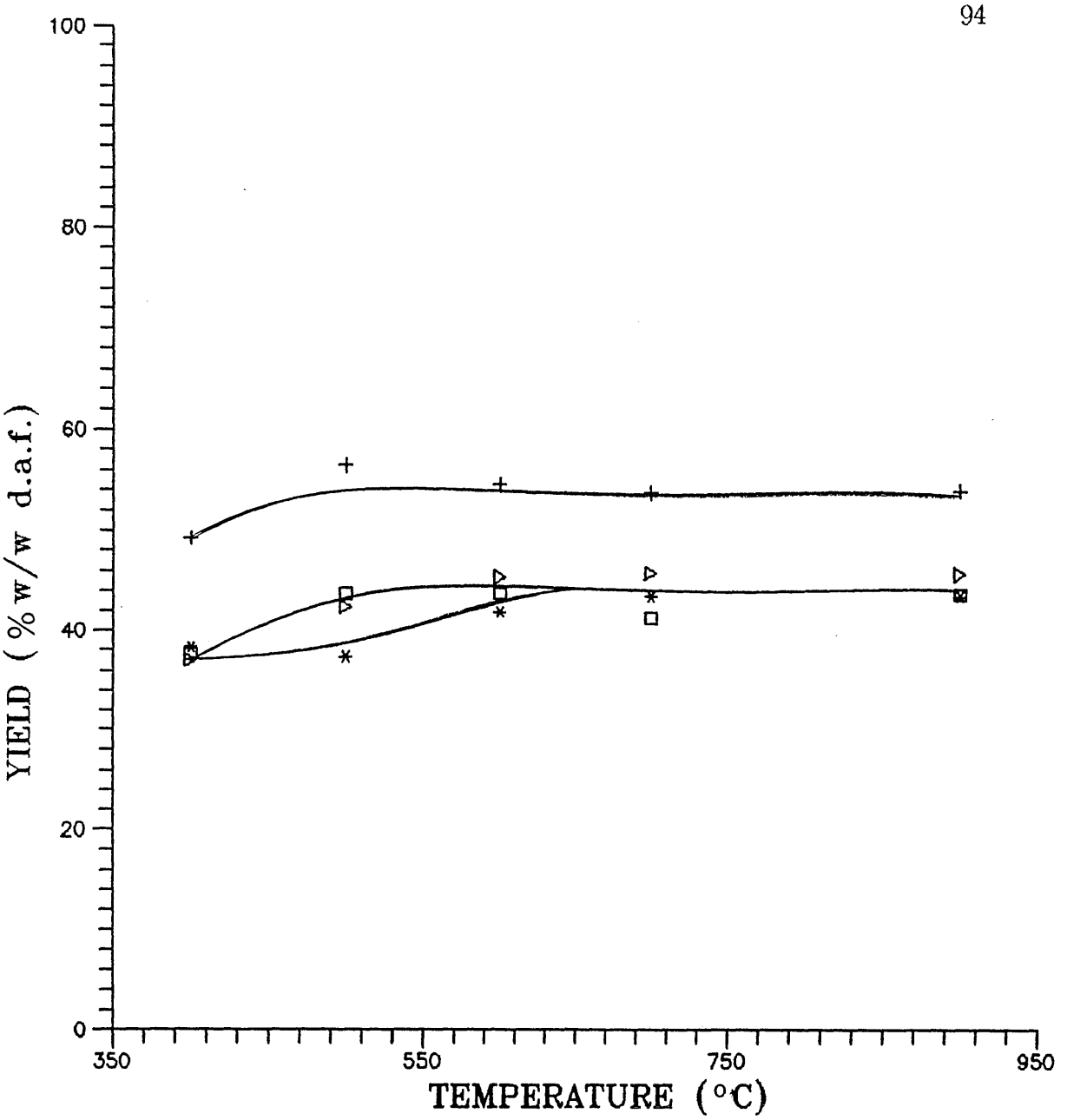


Figure 3.2.1f – The effect of the peak temperature on the yields of Tar and Gas plus water for the pyrolysis of Sugar Cane Bagasse, with 30 seconds hold time and different heating rates.

+ = 1000^{0}C/second and Δ = 1^{0}C/second (Tar).

* = 1000^{0}C/second and □ = 1^{0}C/second (Gas plus water).

3.2.1.2 — Hold time = 0 second.

The results from a similar set of experiments with a heating rate of 1^0C/second, but with zero hold time at the peak temperature, are shown in Figure 3.2.1g. In Figure 3.2.1g, as in Figure 3.2.1b where the hold time at the peak temperature was 30 seconds, there is an increase in the total volatile yield within the peak temperature range of 400–500°C; the increased yield is balanced between tar and gas plus water. Above 500^0C the yield of total volatiles was modified by increasing temperature. By the combination of Figures 3.2.1a and 3.2.1g, Figure 3.2.1h is derived; here the total volatiles, and also the yield of tar, gas plus water and char, is shown for the same heating rate, but with two different hold times at the peak temperature, namely zero and 30 seconds. From Figure 3.2.1h it is clear that at the slow heating rate, namely 1^0C/second, the hold time has no effect upon the ultimate yield of the pyrolysis products of Sugar Cane Bagasse and that the product yield increases with temperature in the range 400–500°C. Additionally, above 500°C the individual yield of each product remains constant. Furthermore, the hold time has no effect on the yield of the products when the sample is pyrolysed slowly; this is clearly seen in Figure 3.2.1i, where the Sugar Cane Bagasse was pyrolysed at 1^0C/second and kept at the peak temperature for zero, 30 and 100 seconds.

A further series of experiments, still with zero hold

time at the peak temperature but now at the fast heating rate of 1000^{0}C/second, are summarised in Figure 3.2.1j. For these conditions, and in particular for temperatures below 600°C, it was not possible to achieve reproducibility in the experimental results. To see better the effect of heating rate at temperatures below 600°C, the reader should examine Figure 3.2.1k. Here the yields of total volatiles are plotted for heating rates of 1, 100 and 1000°C/second, at peak temperatures of 480^{0}C, 500^{0}C and 600°C, with zero second hold time. This graph clearly shows a decrease of total volatiles with increasing heating rate. All the data obtained for 480^{0}C and 500°C, for either 1 or 100^{0}C/second, are plotted in Figures 3.2.1j and 3.2.1k as a representative average. In contrast, at 1000^{0}C/second there is significant scatter in the results, for the peak temperatures of 480^{0}C and 500°C, see Figure 3.2.1j, where all data points are shown since for this condition reproducibility was <u>not</u> achieved. It should be recalled here, as already noted at the beginning of this chapter, see page 85, that tabulated data marked with a "+" signify the occurrence of incomplete pyrolysis. Poor heat transfer from the grid to the sample has been observed previously with rapid pyrolysis at low temperatures, see[50,60]; when the grid was opened and examined by eye after these runs incomplete pyrolysis was readily detected.

The effect of temperature, heating rate, and hold time at the peak temperature on the total volatiles of Sugar Cane Bagasse pyrolysis are summarised in Figure 3.2.1L. Although the hold time has no effect on the total volatile yield for slow heating rates, it plays an important role if the Sugar Cane Bagasse sample is heated rapidly up

to a maximum peak temperatures of 600°C. There are two possible explanations for this observation; first, the elapsed time during the heating up period appears not to be long enough for thermal equilibrium to be established between the grid and the sample, even when the sample is distributed as a monolayer within the envelope–like mesh. Heat transfer processes are very important in pyrolysis. If, for example, the thermal conductivity of the specimen is relatively poor, then the temperature in the sample interior will be less than that at its surface. If heat transfer between the grid and the specimen surface is also poor then the combination of these two effects can produce a situation where the temperature of the grid is significantily greater than that of the sample interior. Generally if a specimen is heated rapidly, to a relatively low peak temperature, and then as soon as this peak temperature is reached the electrical circuit is broken and the sample rapidly cooled down, then the specimen may be, based upon previous research[50,59,60], as much as 30–50^{0}C below the temperature of the grid. Furthermore, since the pyrolysis of lignocellulosic materials, at low temperatures, is endothermic then the effects of temperature gradients within the specimen itself, and between the specimen and the apparatus will play an important role. Additionaly there is a short, but finite, period of time necessary for the coupled series of pyrolysis reactions to become complete; plausibly in those runs in which incomplete pyrolysis was observed this effect may be combined with that of heat transfer. Experimentally it has been found, in previous fast pyrolysis research[48,117,119], that if the hold time at the peak temperature is greater than or equal to 5 seconds, then reproducible results are obtained at 600^{0}C.

The trends observed in this research programme for Sugar Cane Bagasse are in broad agreement with the data of Lin and his coworkers, who have shown using a Curie point pyrolyzer JHP–2, in which the sample was pyrolysed rapidly, that for temperatures lower than 500^0C the quantity of char obtained, with zero hold time at the peak temperature, was significantly higher than when the hold time was longer. This difference diminished with reaction temperature, and disappeared if the temperature was above 500^0C[84].

In summary it has been found that Sugar Cane Bagasse readily pyrolyses, even at the low heating rate of 1^0C/second and with zero hold time. However at fast heating rates, and especially with maximum temperatures less than, say, 500^0C the hold time is an important parameter in determining the total char residue.

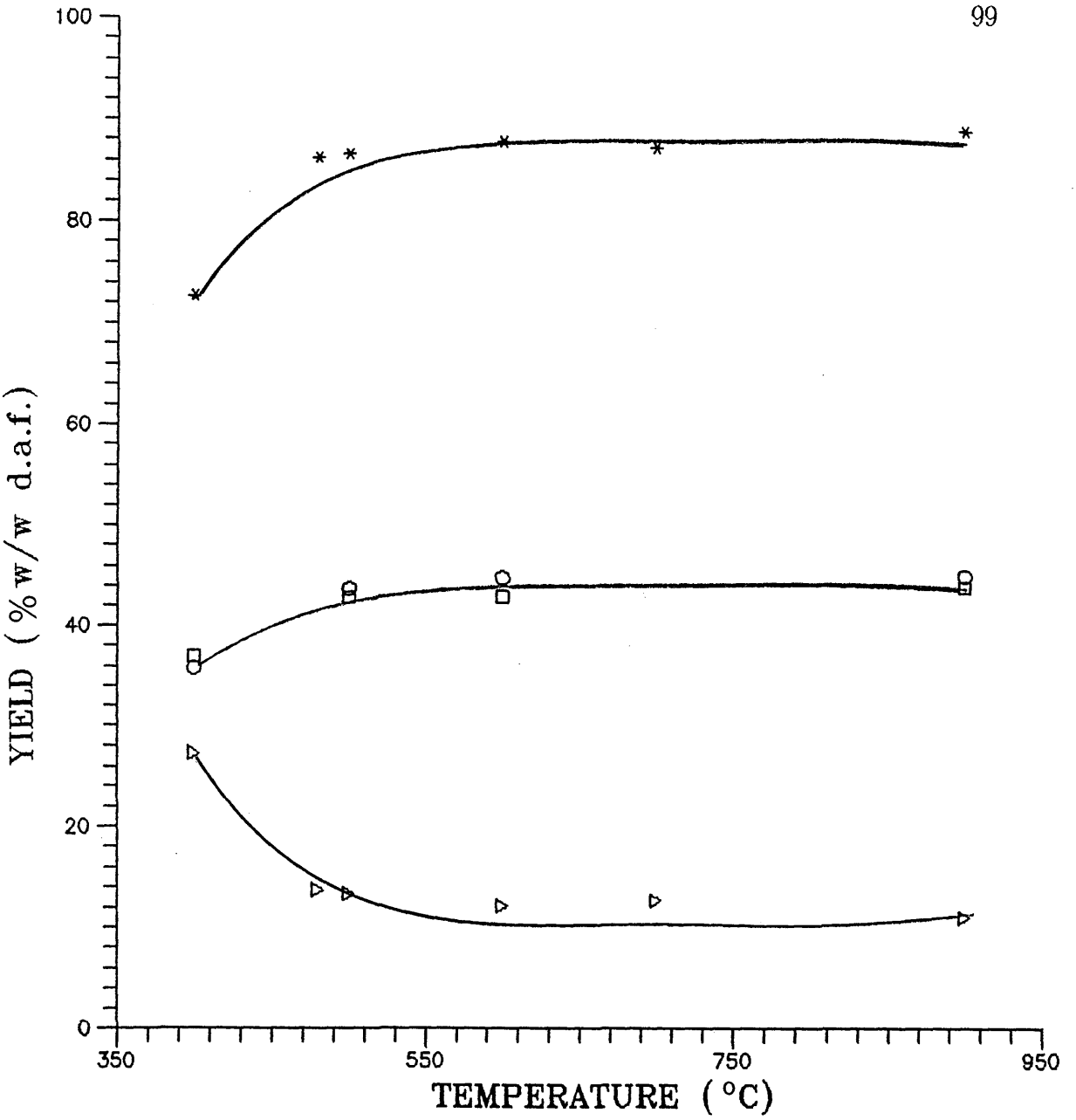


Figure 3.2.1g – The effect of the peak temperature on the yields of the products for the pyrolysis of Sugar Cane Bagasse, with a heating rate of 1^0C/second and zero second hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

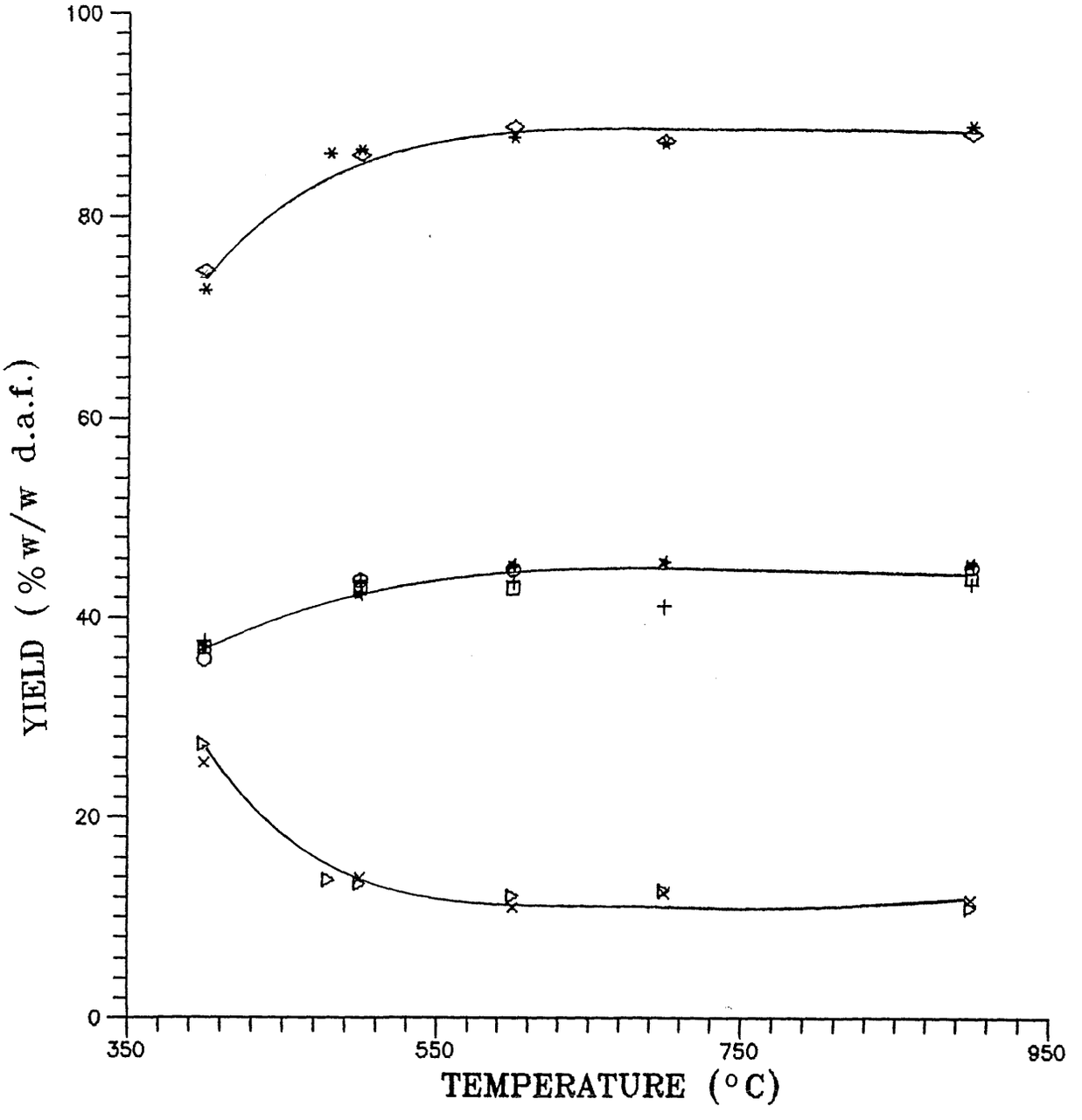


Figure 3.2.1h – The effect of the peak temperature on the yields of the products for the pyrolysis of Sugar Cane Bagasse, with a heating rate of 1^0C/second for different hold times.

* = Total volatiles; 0 = Tar; □ = Gas; Δ = Char (zero second).

◇ = Total volatiles; ✱ = Tar; + = Gas; X = Char (30 seconds).

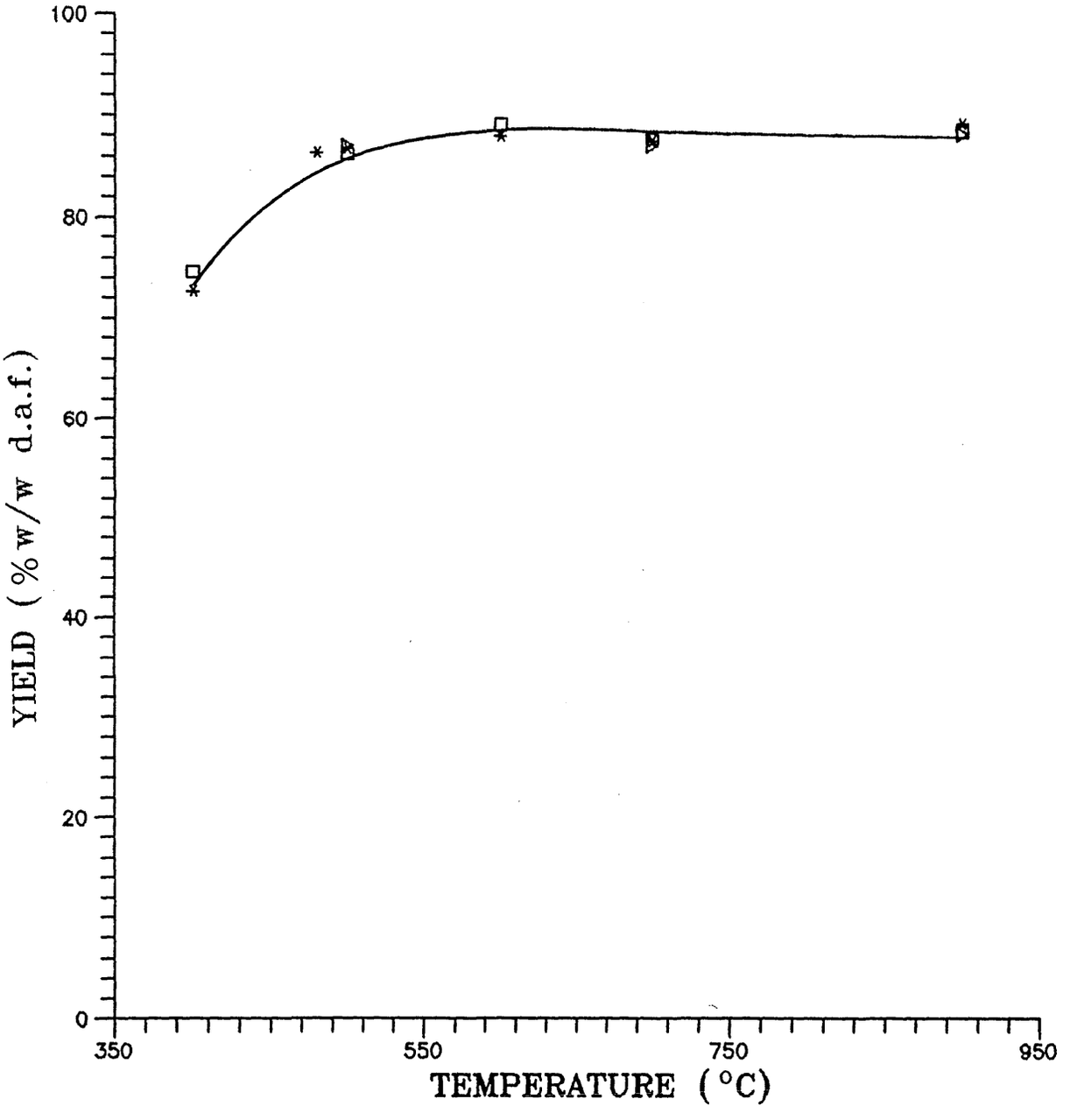


Figure 3.2.1i – The effect of hold time at the peak temperature on the yields of total volatiles for the pyrolysis of Sugar Cane Bagasse, with a heating rate of 1^0C/second.

* = zero second; □ = 30 seconds; Δ = 100 seconds.

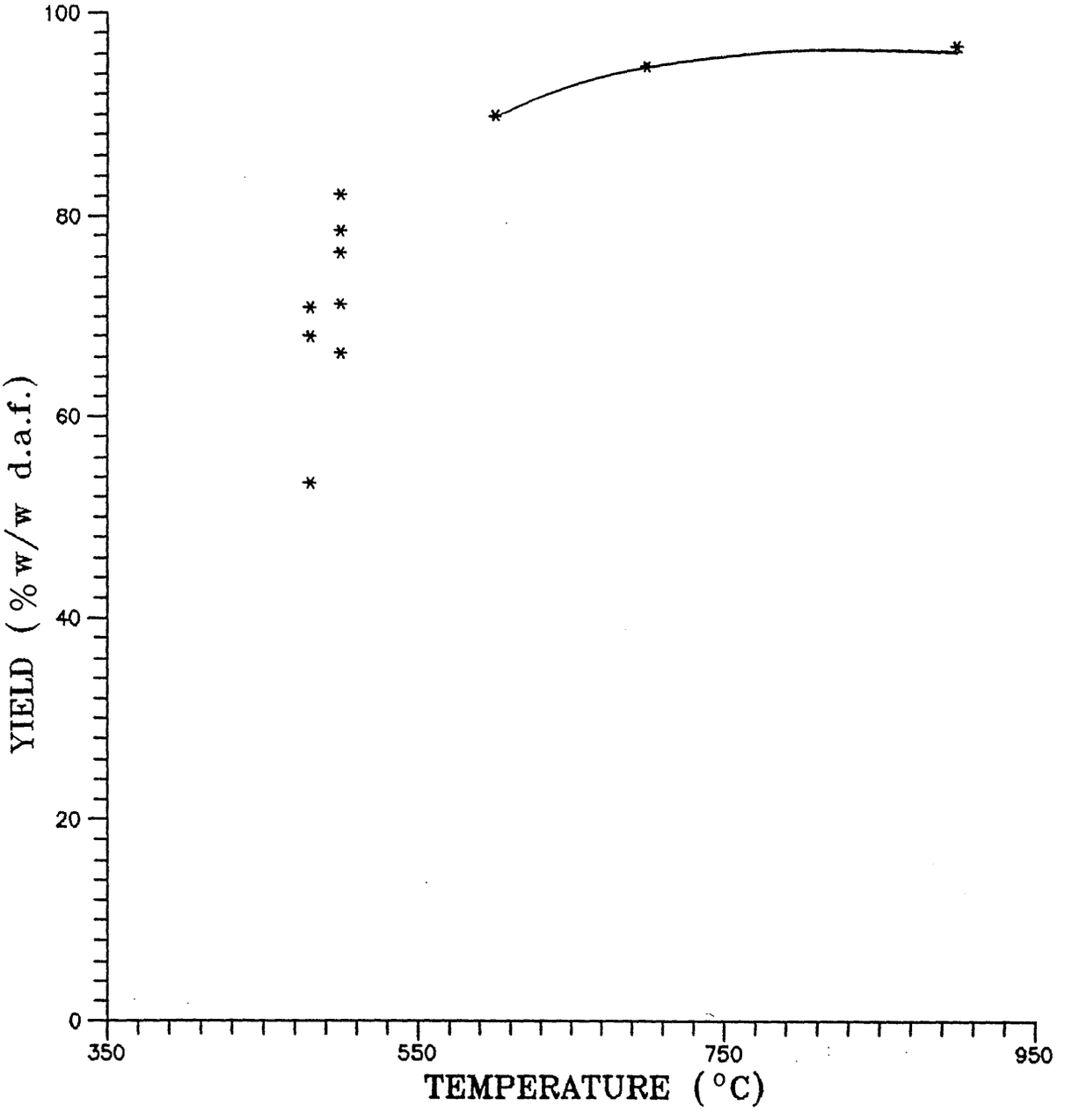


Figure 3.2.1j — The reproducibility of the yield of total volatiles for the pyrolysis of Sugar Cane Bagasse, with a heating rate of 1000^0C/second and zero second hold time.

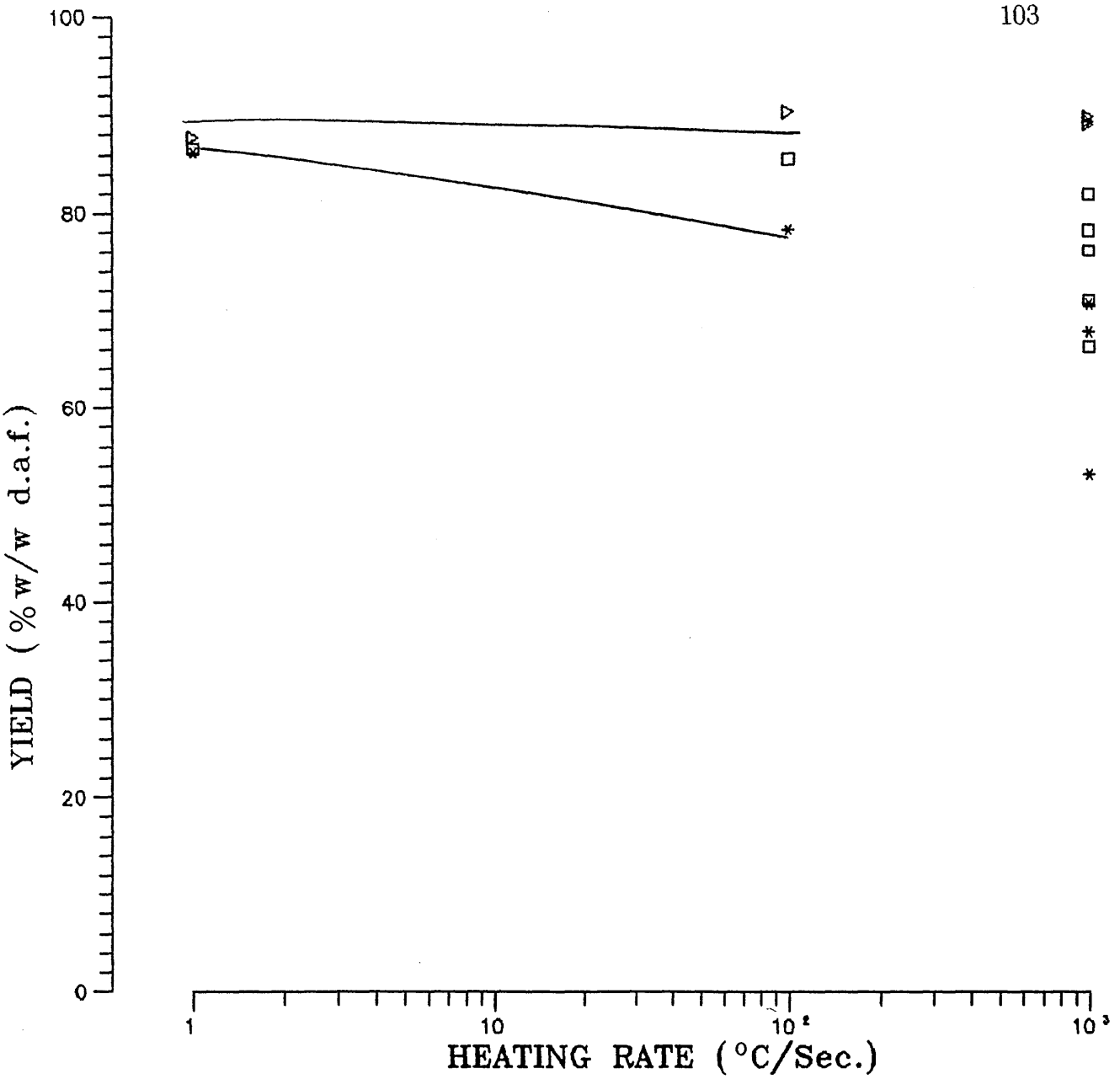


Figure 3.2.1k – The effect of heating rate on the yields of total volatiles for the pyrolysis of Sugar Cane Bagasse, for different peak temperatures and zero second hold time.

* = 480°C; □ = 500°C; Δ = 600°C.

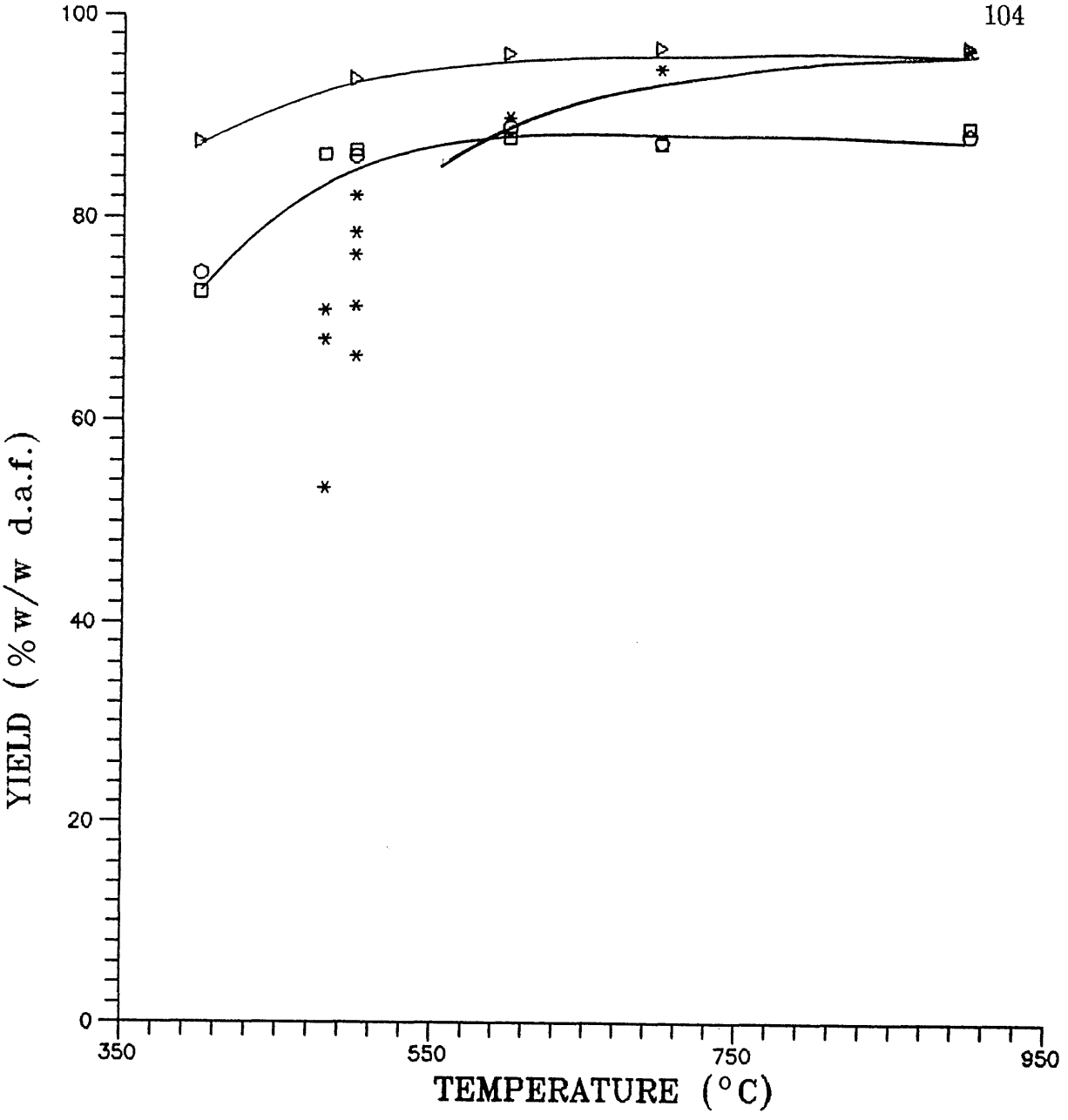


Figure 3.2.1L – The effect of the peak temperature on the yields of total volatiles for the pyrolysis of Sugar Cane Bagasse, at different heating rates and hold times.

* = 1000^{0}C/second; □ = 1^{0}C/second; (zero second).

Δ = 1000^{0}C/second; 0 = 1^{0}C/second; (30 seconds).

3.2.2 – Silver Birch.

3.2.2.1 – Hold time = 30 seconds.

Figure 3.2.2a shows the yield of the products of pyrolysis of Silver Birch, i.e. total volatiles, tar, gas plus water and char, versus peak temperature, at 1^0C/second heating rate and with a hold time of 30 seconds at the peak temperature. From this graph, it can be seen that there is an increase in the total volatiles with increasing the peak temperature, and that this enhancement is due to a slight increase in both tar and gas plus water yields. When the peak temperature reaches about 480^0C the conversion attains a constant maximum value.

A similar series of runs was then performed with Silver Birch for the same hold time but with the fast heating rate of 1000°C/second. These results are presented in Figure 3.2.2b. This graph shows that between 380^0C and 400°C there is a dramatic increase in the yield of total volatiles, from 71% to 89%, see also Table 3.5. Within the range 400^0C to 500°C the yield of total volatiles increases with the temperature and reaches a maximum, i.e. beyond 500°C the product yield is not increased.

Figures 3.2.2a and 3.2.2b are overlaid in Figures

3.2.2c, 3.2.2d and 3.2.2e where the total volatiles, tar and gas plus water are plotted for heating rates of 1^0C/second and 1000°C/second.

These results for the products of pyrolysis of Silver Birch are in agreement with those obtained for the products of Sugar Cane Bagasse as reported at the beginning of this Chapter. The similarity of these curves, in particular above 500^0C, demonstrates the absence of secondary reactions in Silver Birch pyrolysis, for the reasons previously discussed in section 3.2.1.1.

3.2.2.2 – Hold time = 0 second.

In Figure 3.2.2f, the total volatile yields are plotted versus peak temperature for both slow and fast heating rates. This Figure shows that for temperatures above 600^0C, the total volatile yield was enhanced at fast heating rates. In contrast, for temperatures below 600^0C the total volatile yield is higher for the slow heating rate. As with Sugar Cane Bagasse the existence of these two opposed regimes, which are demarcated by the peak temperature of 600^0C may, as described before in section 3.2.1.2, be due to two interrelated effects, namely the heating period being insufficiently long for heat to be transferred from the hot grid to the sample and pyrolysis reactions requiring a minimum length of time for completion.

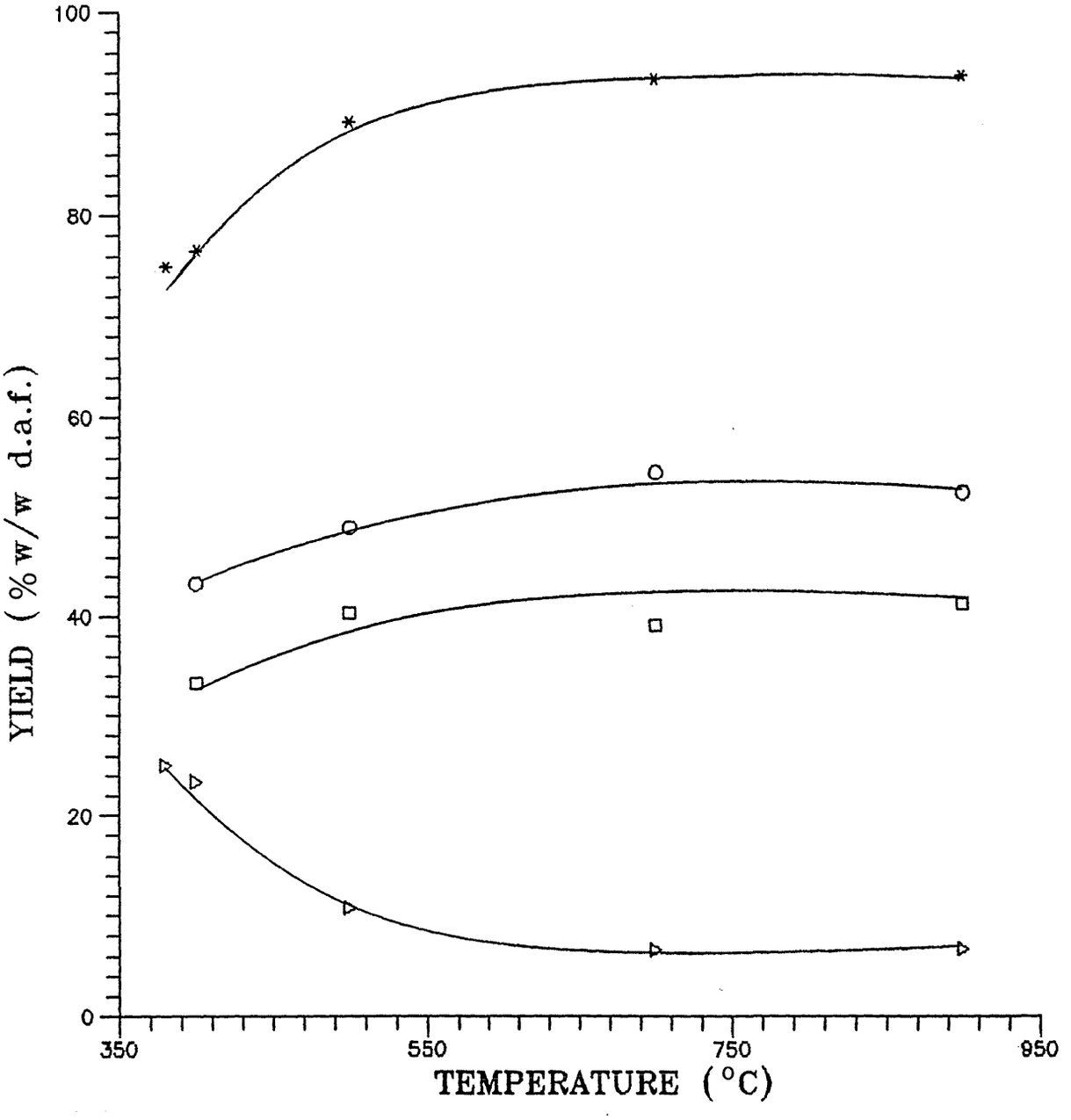


Figure 3.2.2a – The effect of the peak temperature on the yields of the products for the pyrolysis of Silver Birch, with a heating rate of 1^0C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

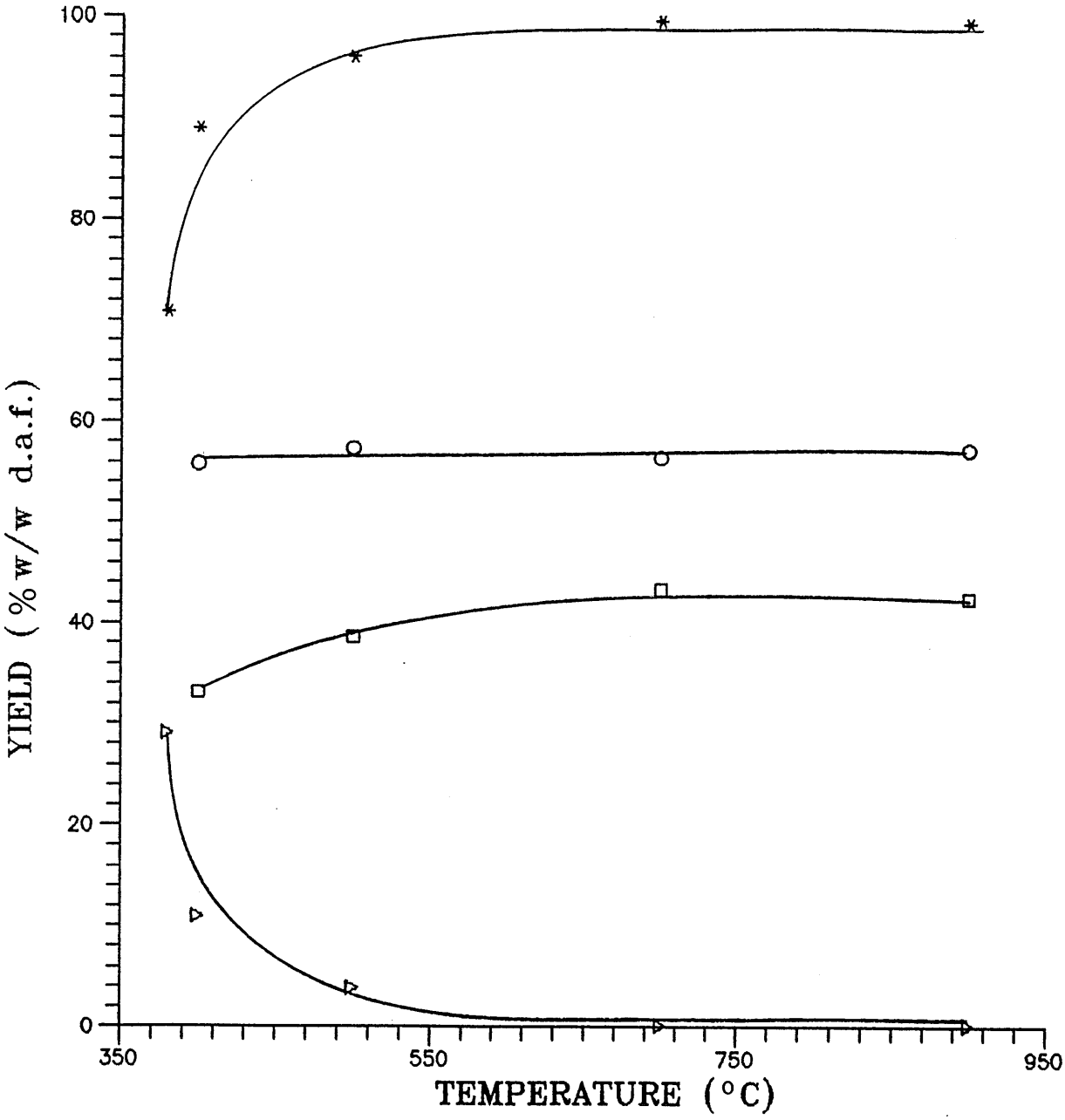


Figure 3.2.2b – The effect of the peak temperature on the yields of the products for the pyrolysis of Silver Birch, with a heating rate of 1000°C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

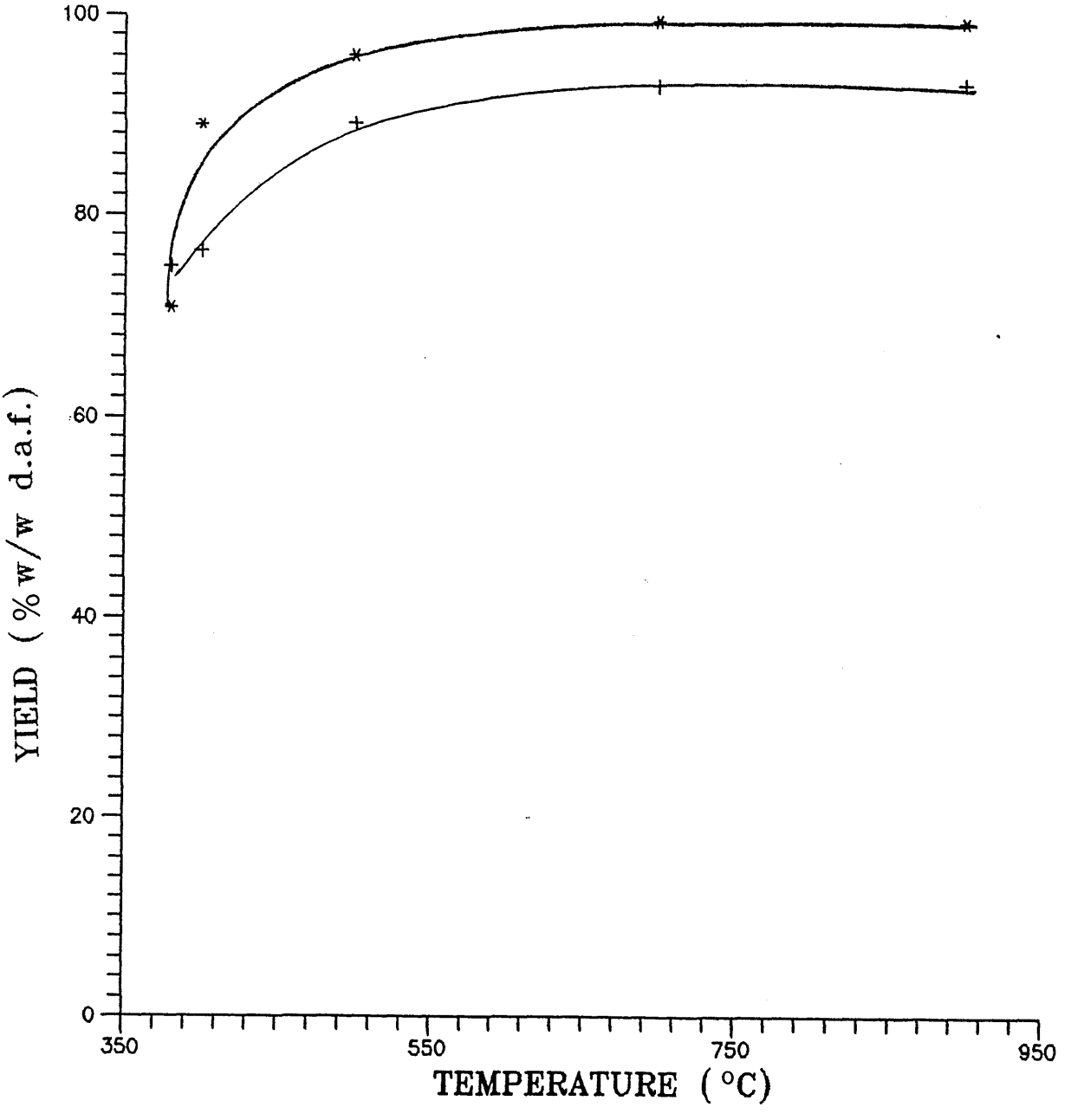


Figure 3.2.2c – The effect of the peak temperature on the yields of Total volatiles for the pyrolysis of Silver Birch, with 30 seconds hold time.

* = 1000^0C/second; + = 1^0C/second.

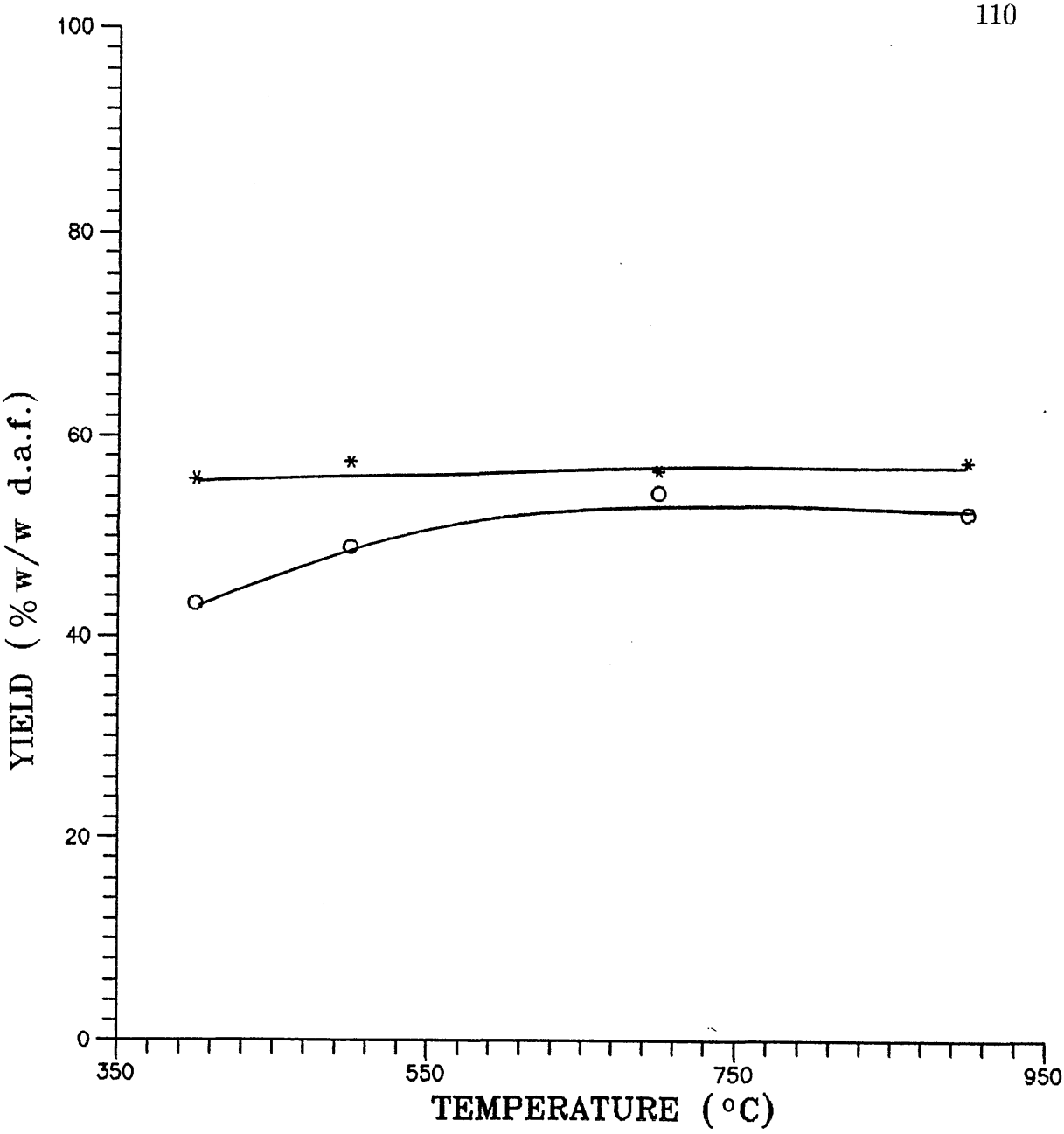


Figure 3.2.2d – The effect of peak temperature on the yields of Tar for the pyrolysis of Silver Birch, with 30 seconds hold time.

* = 1000^0C/second; 0 = 1^0C/second.

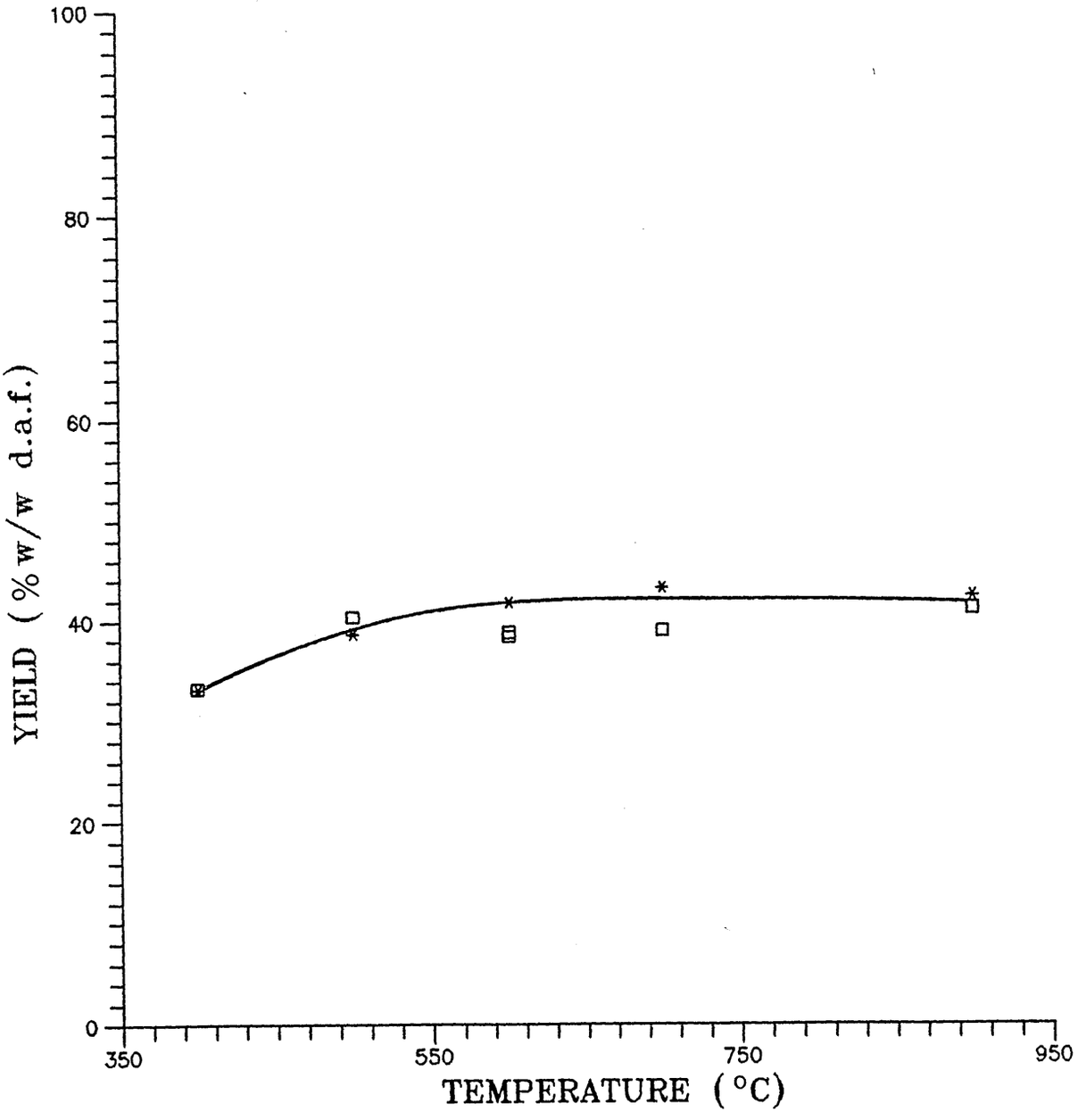


Figure 3.2.2e – The effect of the peak temperature on the yields of Gas plus water for the pyrolysis of Silver Birch, with 30 seconds hold time. * = 1000^0C/second; □ = 1^0C/second.

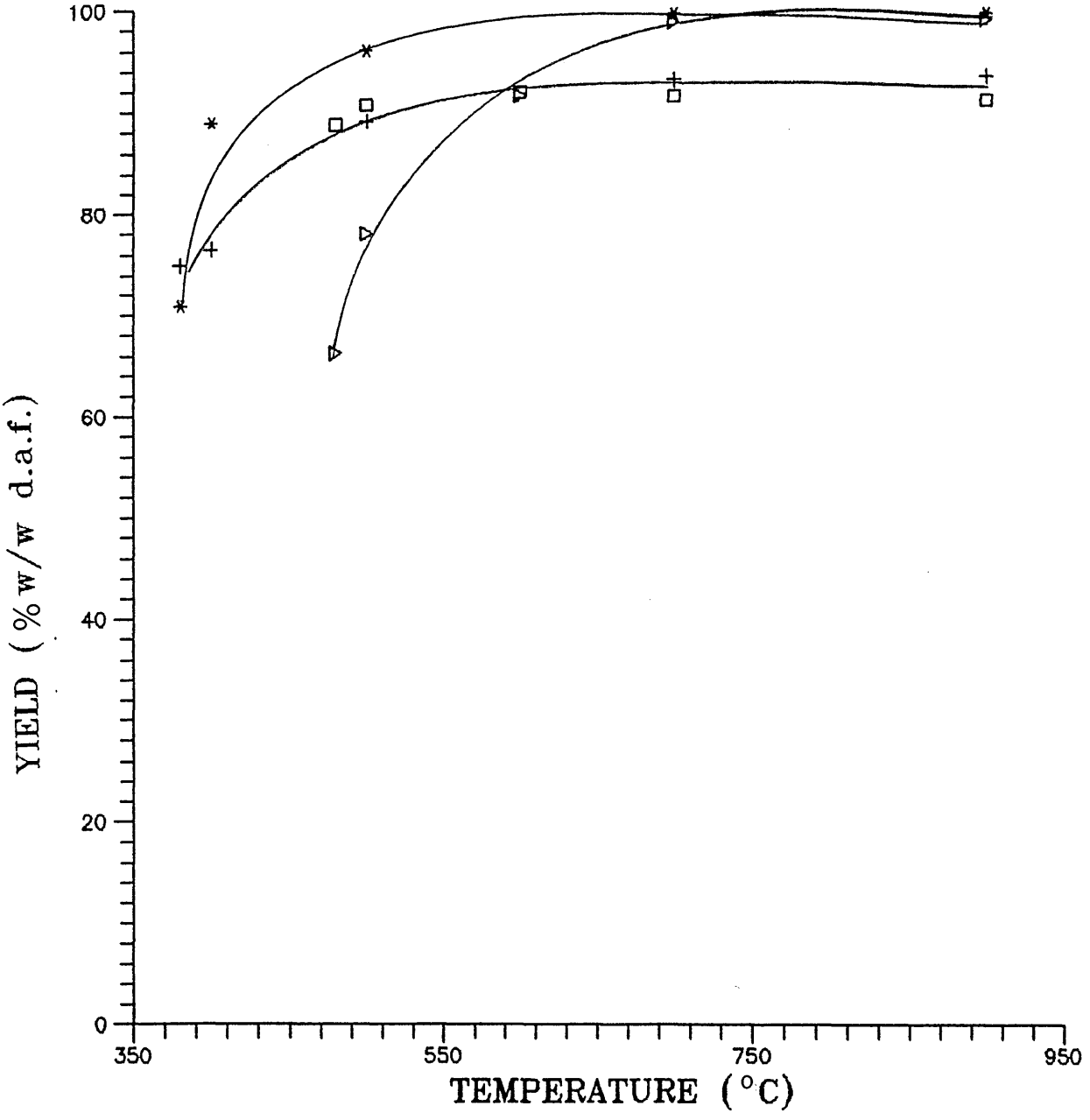


Figure 3.2.2f – The effect of the peak temperature on the yields of total volatiles for the pyrolysis of Silver Birch, at different heating rates and hold times.

Δ = 1000^{0}C/second; $\square$ = 1^{0}C/second; (zero second).

* = 1000^{0}C/second; + = 1^{0}C/second; (30 seconds).

3.3 – The Comparison Between the Pyrolysis of Sugar Cane Bagasse and Silver Birch.

Figures 3.3a and 3.3b respectively present the total volatiles and tar yields obtained by the pyrolysis of Sugar Cane Bagasse and Silver Birch, with 30 seconds hold time at the peak temperature, and for both slow and fast heating rates.

From these graphs it is clearly seen that the thermal decomposition of Silver Birch is slightly greater than that of Sugar Cane Bagasse; in particular Sugar Cane Bagasse pyrolysis produces lower yields of volatiles and thus higher char values, see Tables 3.2 and 3.5. This result is in agreement with the thermobalance pyrolysis studies of Ouensanga[105], who found higher yields for total volatiles from wood than from Sugar Cane Bagasse. It has been proposed that, in general, cellulose pyrolysis principally produces volatiles, whilst lignin pyrolysis primarily produces char[22,84,117,135,138]; this generalisation may indicate that Sugar Cane Bagasse has a somewhat higher lignin and lower cellulose content than that of Silver Birch. The validity of this general proposition, as applied to Sugar Cane Bagasse and Silver Birch, will be examined, in section 5.7, following the determination of the lignin content of these materials, see Chapter 4 section 2 and 3.

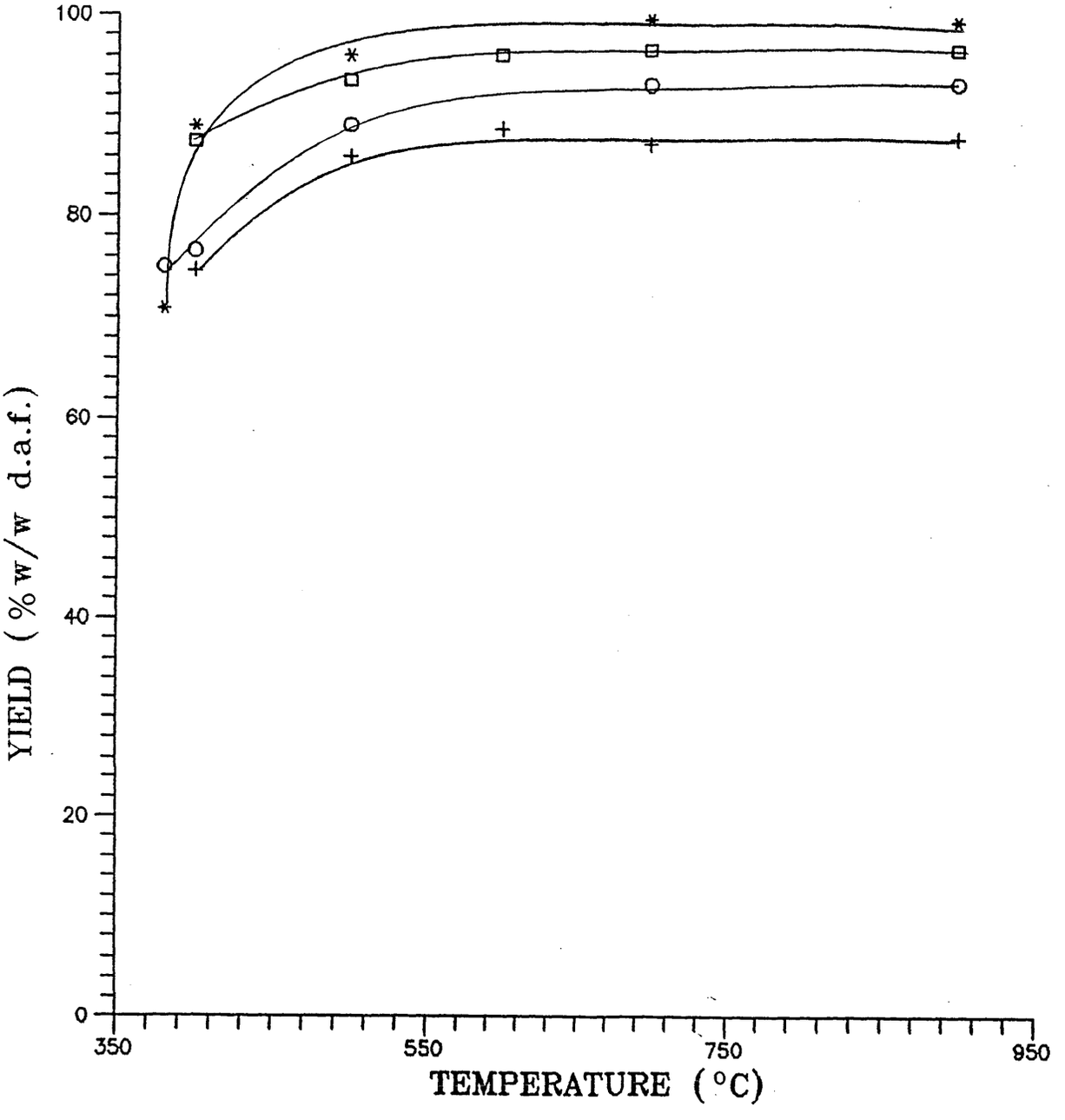


Figure 3.3a – The effect of the peak temperature on the yields of total volatiles for the pyrolysis of both Sugar Cane Bagasse and Silver Birch, with a hold time of 30 seconds.

+ = 1^0C/second; □ = 1000^0C/second; (Bagasse).

0 = 1^0C/second; * = 1000^0C/second; (Silver Birch).

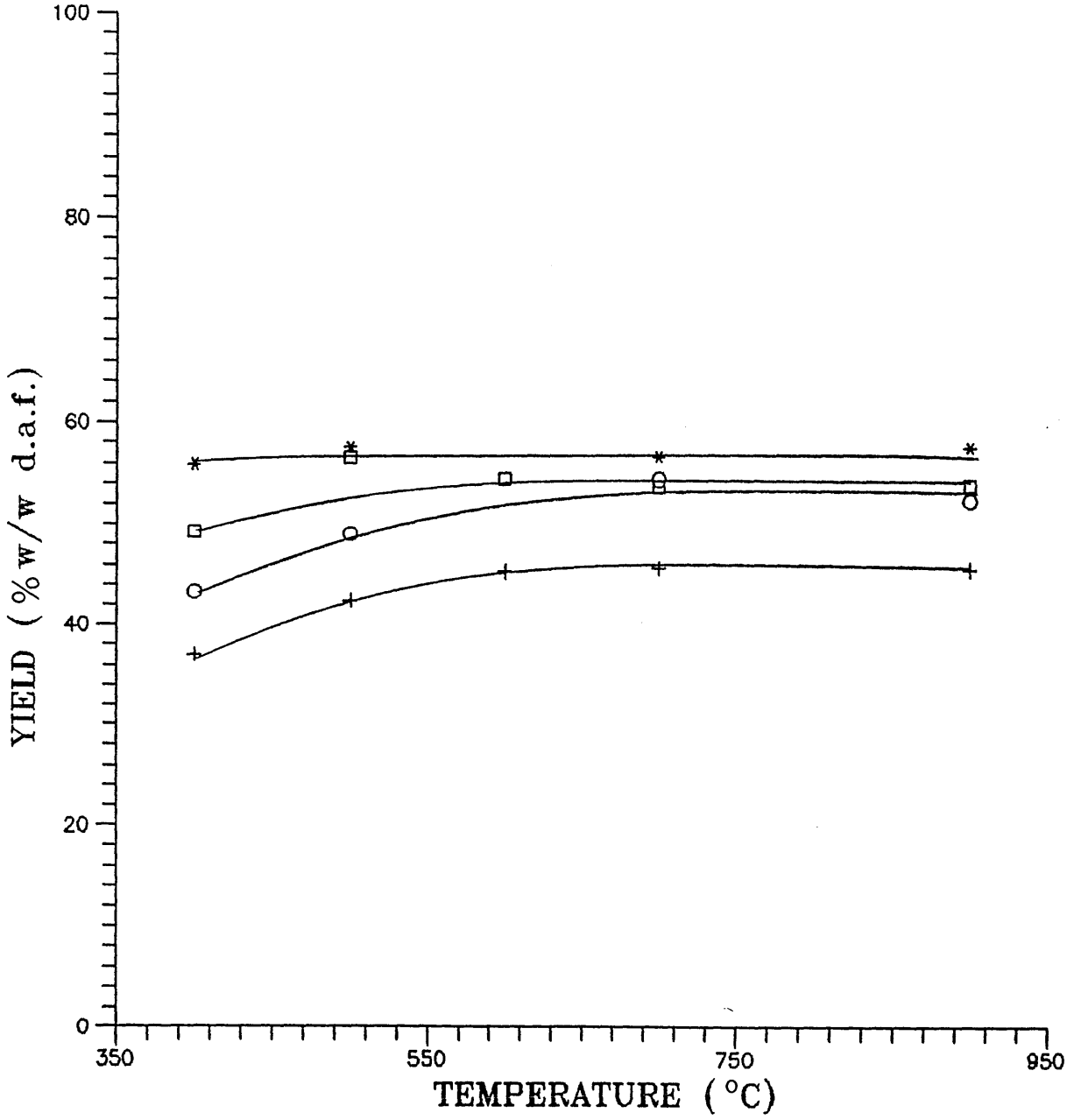


Figure 3.3b – The effect of the peak temperature on the yields of tar for the pyrolysis of both Sugar Cane Bagasse and Silver Birch, with a hold time of 30 seconds.

+ = 1^0C/second; □ = 1000^0C/second; (Bagasse).

0 = 1^0C/second; * = 1000^0C/second; (Silver Birch).

3.4 – Inequalities in the Yields of the Pyrolysis Products of Lignocellulosic Materials.

Woods, in general, contain approximately 25% lignin, see Chapter 1 section 1.7; which, in a wire–mesh reactor, at 600^{0}C and 1000^{0}C/second pyrolyses to give, say, 45% char[101], in contrast to cellulose which pyrolyses almost completely[59,60].

Since the components of biomass are known to be primarily cellulose and lignin, with only small quantities of ash and protein; it has been postulated that the total product yield derived by the pyrolysis of any biomass, for example Sugar Cane Bagasse, may be estimated by the linear combination of the yields of the pyrolysis products of cellulose and lignin taken in simple proportion[47,84]. It should be noted here that implicit in this statement is the assumption that lignin and cellulose pyrolyse independently.

In the light of the above postulate the yield of total volatiles obtained in this pyrolysis study for Sugar Cane Bagasse, namely 96%, and Silver Birch, namely 98%, are surprisingly high, for pyrolysis conditions see Tables 3.2 and 3.5. A further series of experiments was therefore undertaken with pure cellulose, pure lignin, and with their mixtures in the following proportions:

25%cellulose : 75%lignin

50%cellulose : 50%lignin

75%cellulose : 25%lignin

The aim of this pyrolysis study with these mixtures was to verify the reported char yield for cellulose and lignin, and to test the hypothesis of the independent pyrolysis of cellulose and lignin.

These sample mixtures, were prepared by pressing the compounds in an hydraulic press and KBr die; crushing the pellets formed and then sieving the powder to obtain particles of the required size, say 100–150 microns. This preparation procedure has been described in detail in Chapter 2 section 2.3.2.

3.5 – The Effects of Heating Rate and Temperature on the Pyrolysis Products of Cellulose, Lignin, and their Mixtures.

3.5.1 – Cellulose.

Figure 3.5.1a shows the effect of peak temperature on the yields of the products from the pyrolysis, of pure cellulose with a heating rate of 1^{0}C/second and a hold time at the peak temperature of 30 seconds. The results from a second set of experiments but with the

fast heating rate of 1000^{0}C/second are shown in Figure 3.5.1b. These two graphs are similar, in both there is a slight increase in the yield of total volatiles over the temperature range 400–600^{0}C, which is divided between tar and gas plus water products.

The result of overlaying Figures 3.5.1a and 3.5.1b is shown as Figure 3.5.1c; in which it can be clearly seen that the heating rate has no effect on the yields of either total volatiles or tar.

To verify the absence of any effect of the heating rate on the pyrolysis products of cellulose, further experiments where performed with a very low heating rate, namely 0.1^{0}C/second. These results are plotted in Figure 3.5.1d. In this figure, four curves representing the yields of all the pyrolysis products are observed; each being distinctly parallel to the heating rate axis. Furthermore, from Figure 3.5.1c, it is also seen that the char yield obtained from the pyrolysis of pure cellulose is almost zero, being not greater than 3%; and that this very low char yield is independent of the heating rate. In summary, the yields of the products of pyrolysis for cellulose are slightly dependent on temperature and not affected at all by the heating rate.

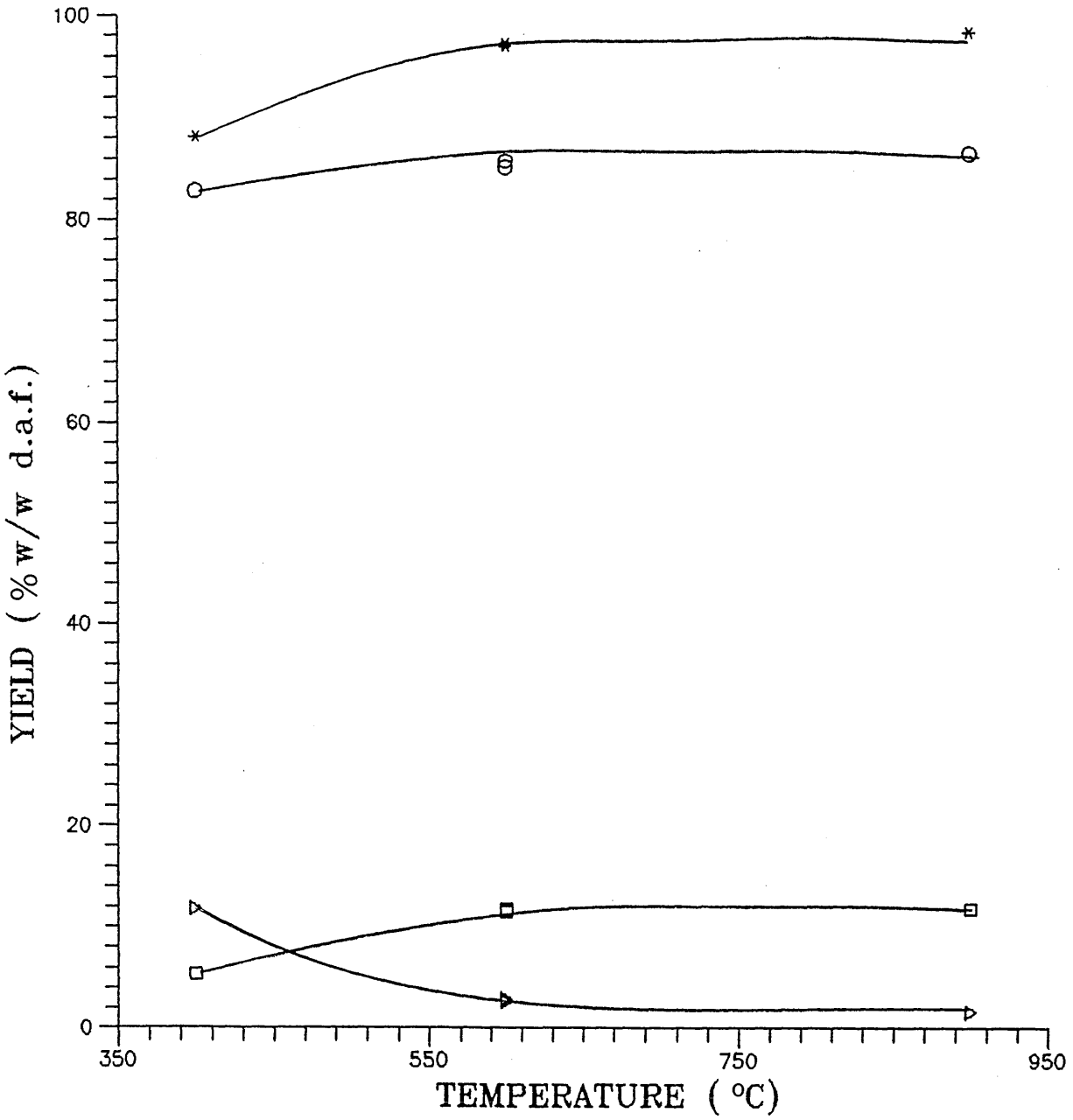


Figure 3.5.1a – The effect of the peak temperature on the yields of the products for the pyrolysis of Cellulose, with a heating rate of 1^0C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

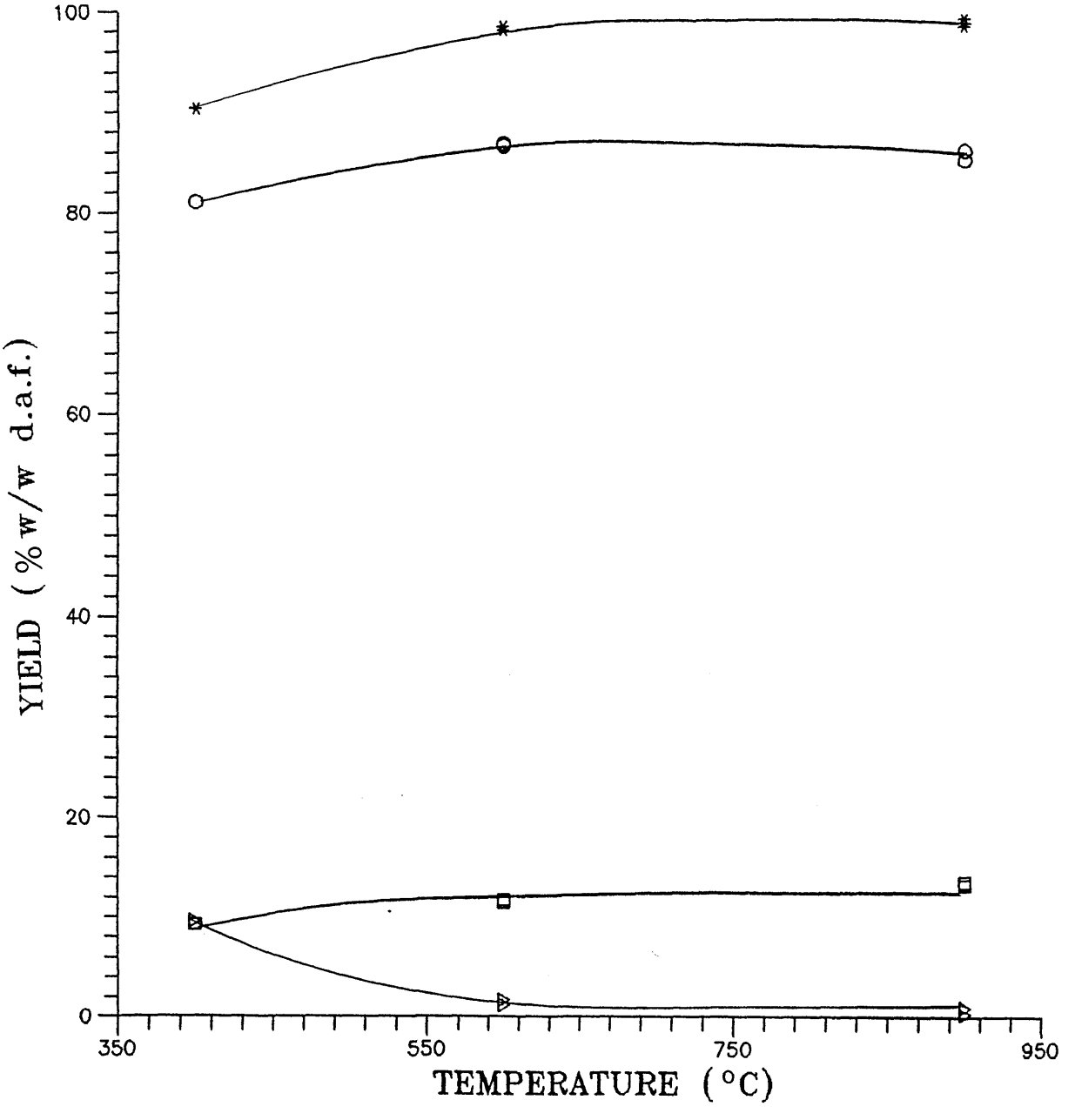


Figure 3.5.1b — The effect of the peak temperature on the yields of the products for the pyrolysis of Cellulose, with a heating rate of 1000^0C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

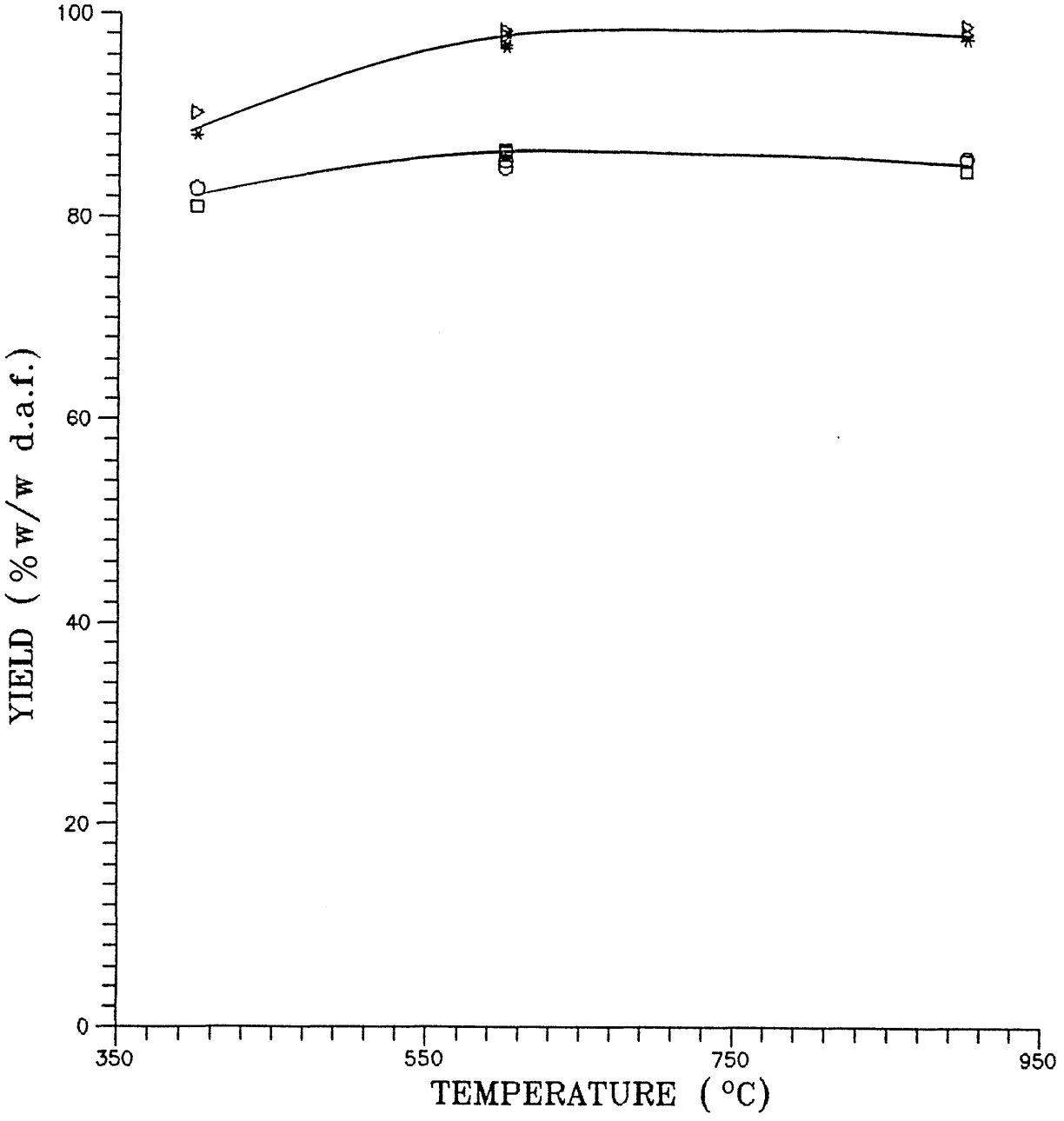


Figure 3.5.1c – The effect of the peak temperature on the yields of Total volatiles and Tar for the pyrolysis of Cellulose, with 30 seconds hold time and different heating rates.

Δ = 1000^{0}C/second; * = 1^{0}C/second; (Total volatiles).

$\square$ = 1000^{0}C/second; 0 = 1^{0}C/second; (Tar).

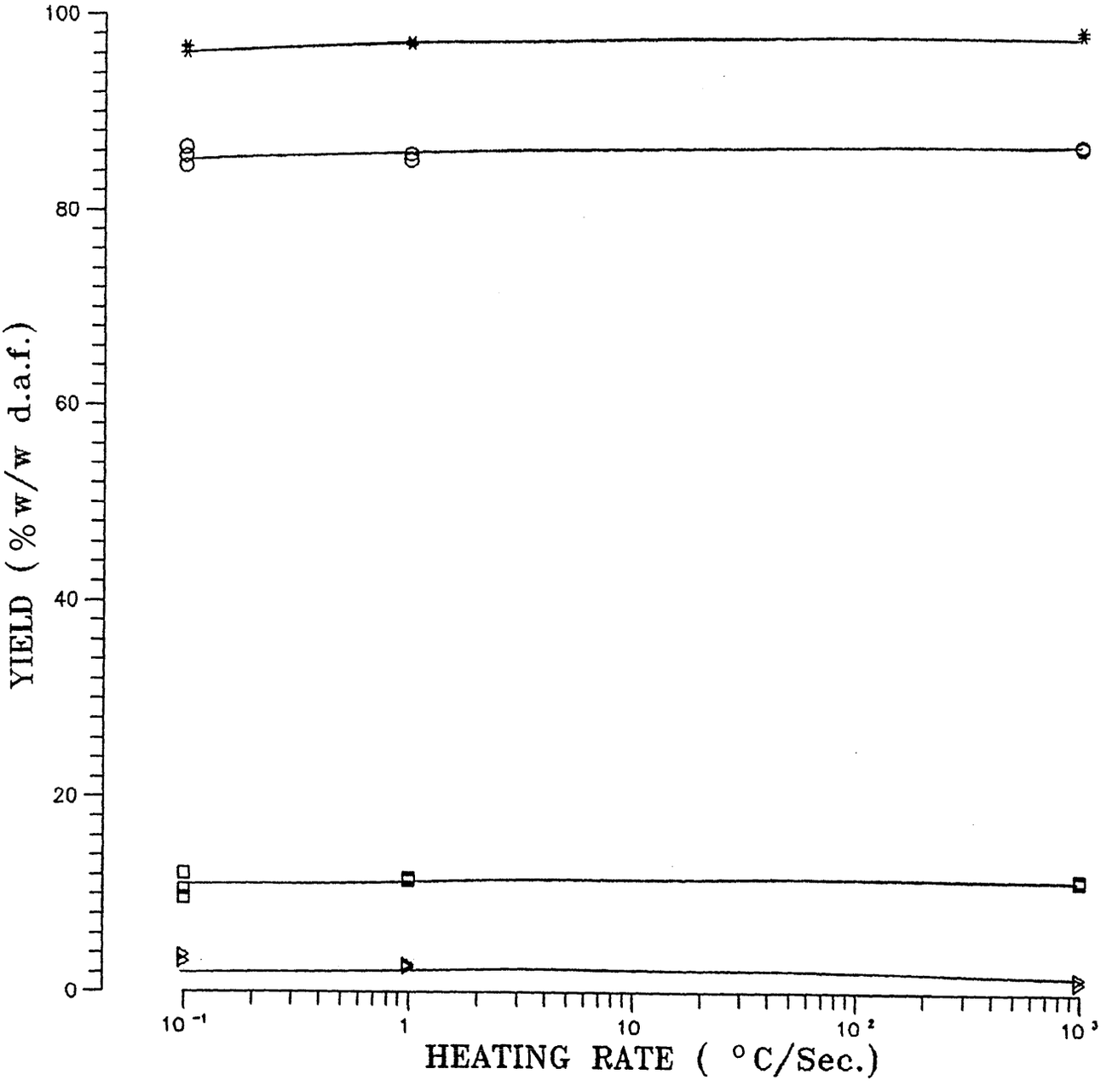


Figure 3.5.1d – The effect of heating rate on the yields of the products for the pyrolysis of Cellulose, with 30 seconds hold time at the peak temperature of 600^{0}C..

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

3.5.2 – Lignin.

Figures 3.5.2a and 3.5.2b show the effect of temperature on the pyrolysis products of pure lignin, at heating rates of 1^0C/second and 1000^0C/second respectively. These graphs have the same shape, both show an enhancement in the total volatile yield, in the temperature range 400–600^0C. When the heating rate was 1^0C/second then this enhancement was equally divided between tar and gas plus water products, however at 1000^0C/second, there was a 10% increase in the production of gas plus water, but only a 5% increase in tar production.

The effect of heating rate on the pyrolysis products is summarised in Figures 3.5.2c and 3.5.2d. From these two Figures it can be seen that the yield of total volatiles increases from 54% to 65%, with an increase in the heating rate from 0.1^0C/second to 1000^0C/second. and that the yields of both tar and gas plus water products were enhanced. This increase in total volatile yield with increasing heating rate is in marked contrast to the constant values obtained for the pyrolysis of pure cellulose.

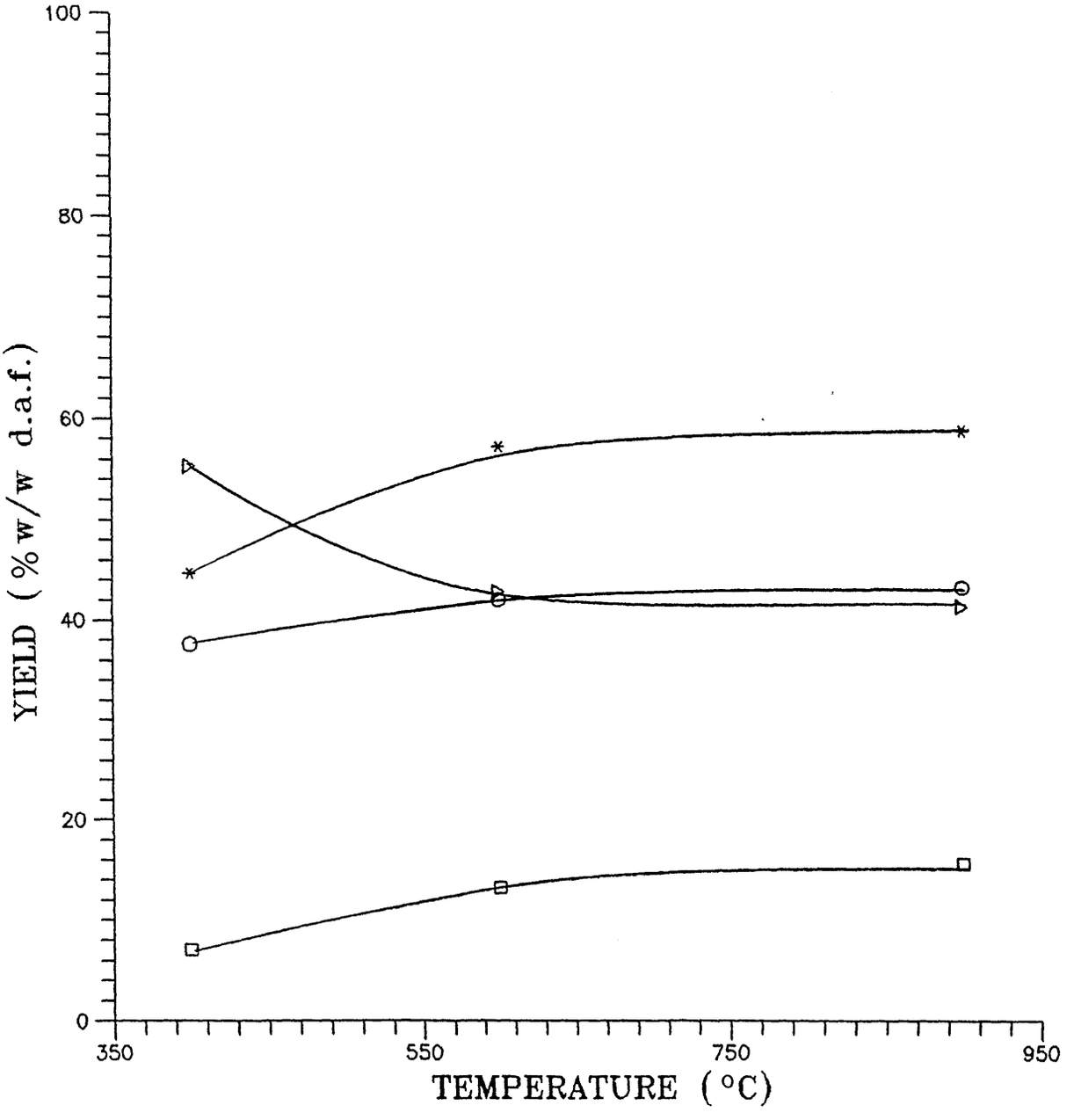


Figure 3.5.2a – The effect of the peak temperature on the yields of the products for the pyrolysis of Lignin, with a heating rate of 1^0C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

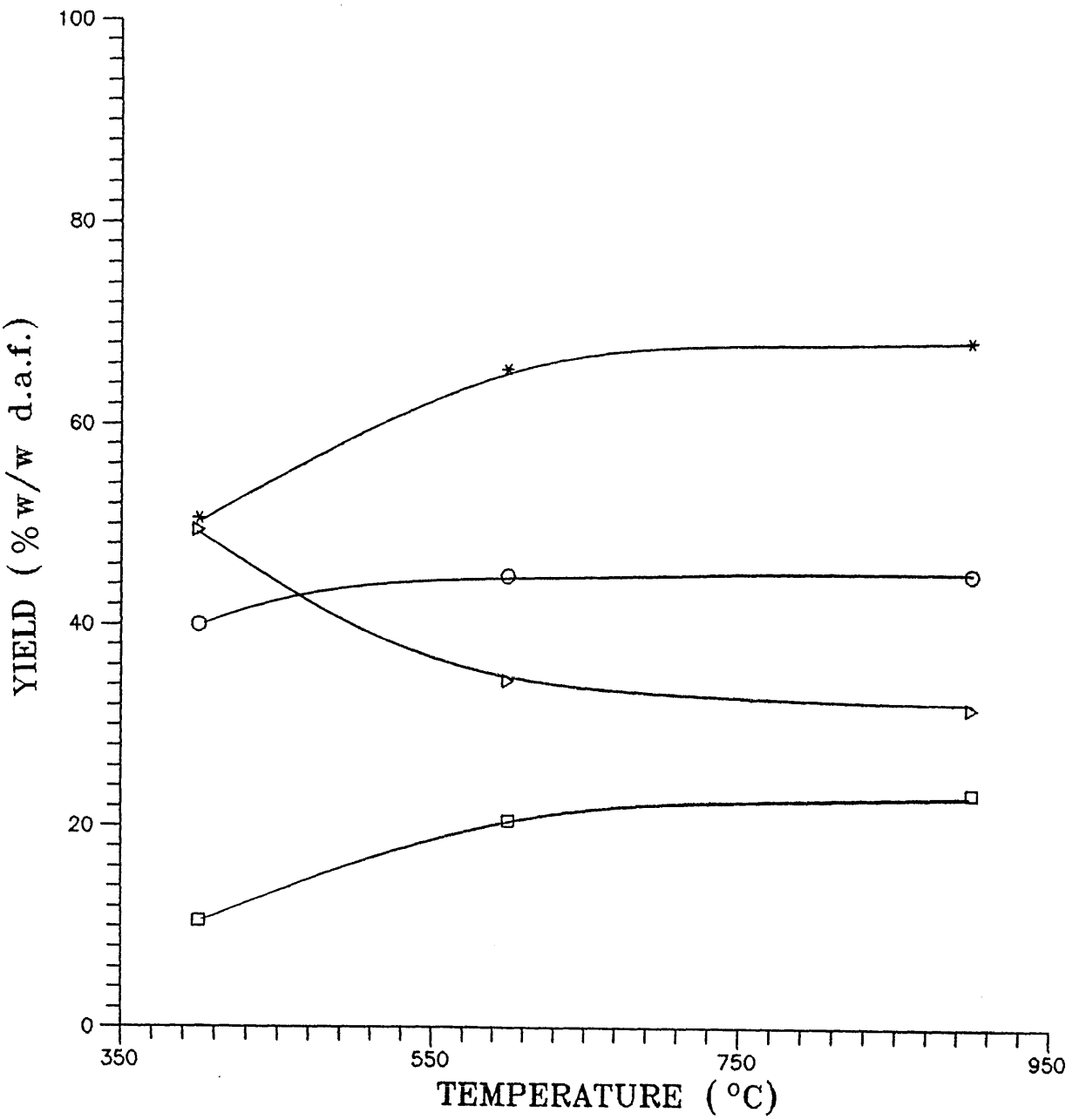


Figure 3.5.2b – The effect of the peak temperature on the yields of the products for the pyrolysis of Lignin, with a heating rate of 1000^0C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

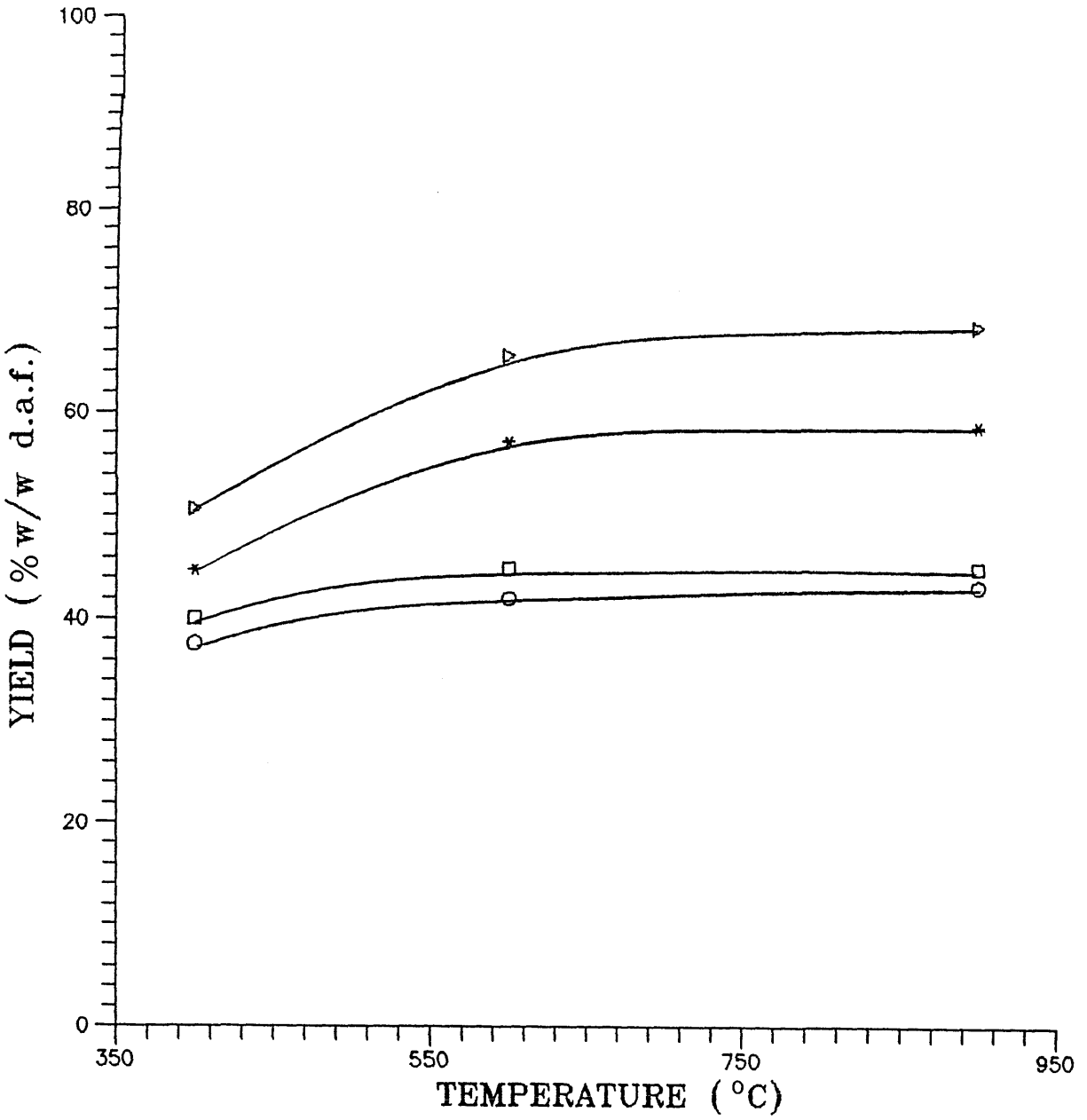


Figure 3.5.2c – The effect of the peak temperature on the yields of Total volatiles and Tar for the pyrolysis of Lignin, with 30 seconds hold time and different heating rates.

Δ = 1000^{0}C/second; * = 1^{0}C/second; (Total volatiles).

$\square$ = 1000^{0}C/second; 0 = 1^{0}C/second; (Tar).

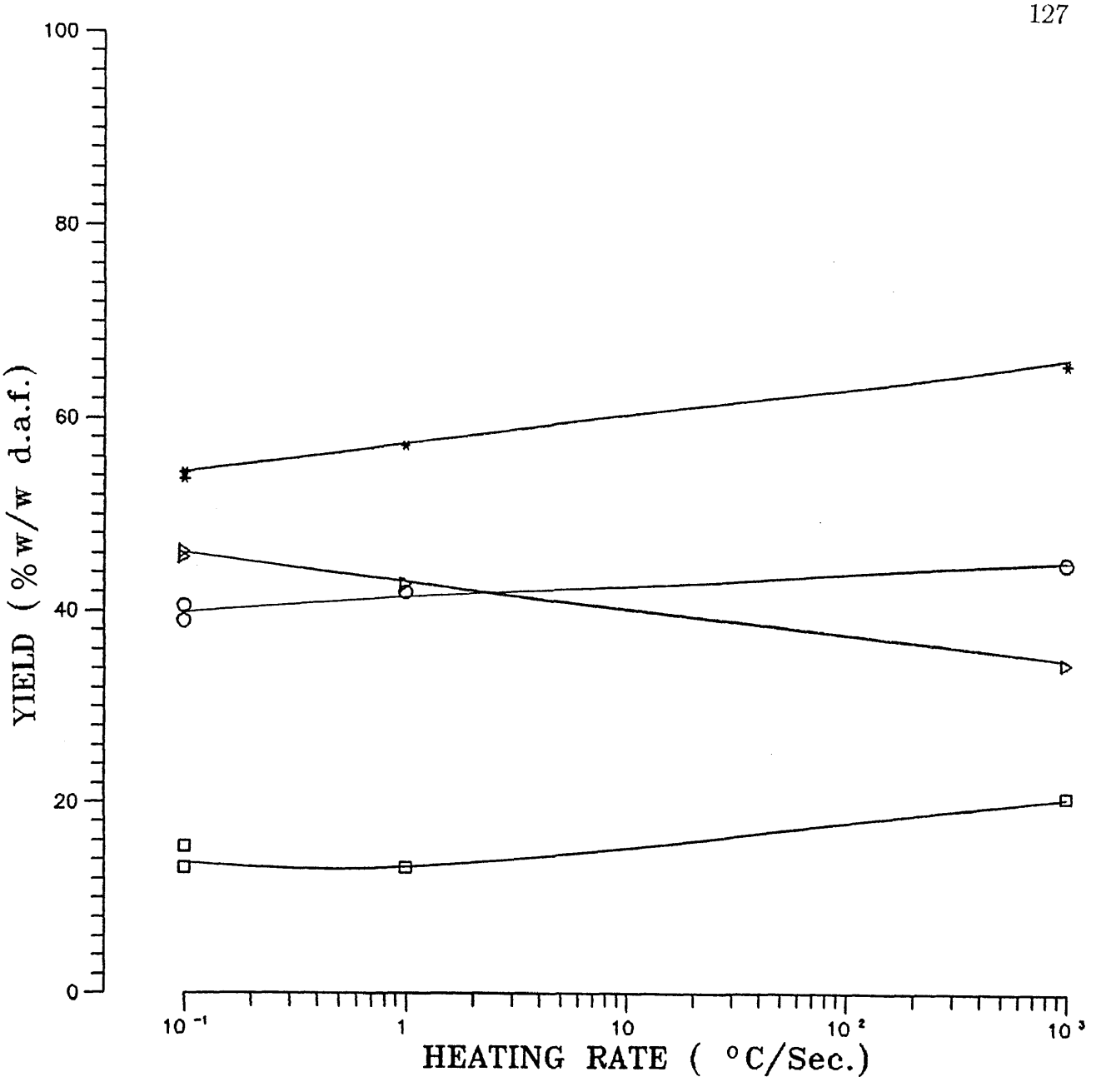


Figure 3.5.2d – The effect of heating rate on the yields of the products for the pyrolysis of Lignin, with 30 seconds hold time at the peak temperature of 600^{0}C..

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

3.5.3 – 25% Cellulose : 75% Lignin.

In Figure 3.5.3a the effect of temperature on the yields of all the pyrolysis products at the slow heating rate of 1^0C/second is shown. This figure shows that whilst the yield of total volatiles, tar, and gas plus water increases with increasing temperature for temperatures below 600^0C; for temperatures above 600^0C the yields of pyrolysis products are constant. Similar effects were observed with the fast heating rate, see Figure 3.5.3b, where the mixture was heated at 1000^0C/second; in both series of experiments the increased production of total volatiles was divided between tar and gas plus water.

Figure 3.5.3c, clearly shows the difference in yield obtained when the mixture was pyrolysed at either 1^0C/second or 1000^0C/second. From this graph it can be seen that the yield of total volatiles, tar and gas plus water was always greater with the high rather than the low heating rate, irrespective of the peak pyrolysis temperature. It is also seen from Figure 3.5.3c that this increase in the yield of total volatiles is mainly due to the production of tar rather than gas plus water.

Additional experiments were conducted, at a constant peak temperature of 600^0C, with the very low heating rate of 0.1^0C/second; these results are compared with those obtained at 1^0C/second and 1000^0C/second in Figure 3.5.3d. This figure shows that pyrolysis yields are unchanged by decreasing the heating rate below 1^0C/second.

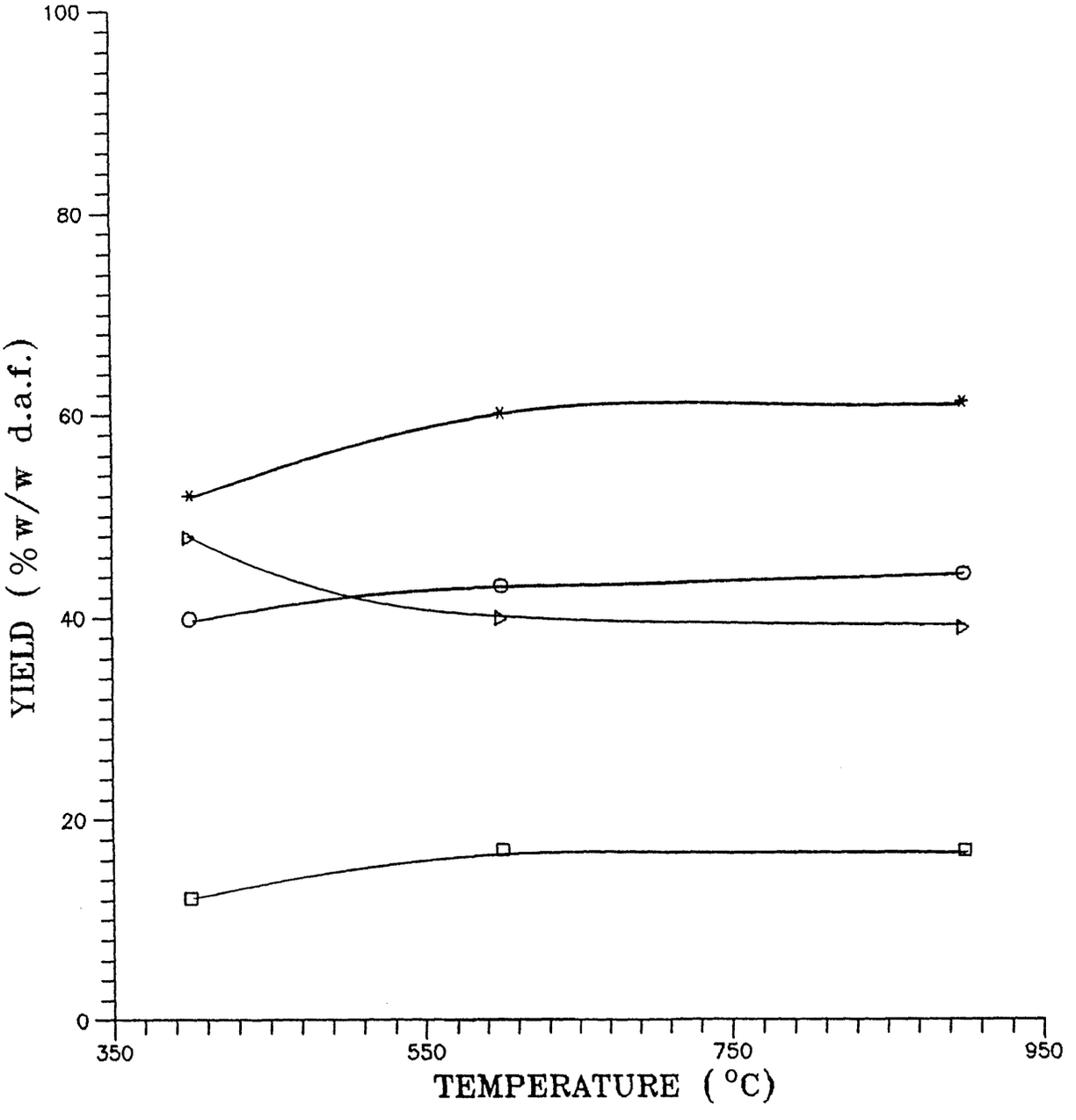


Figure 3.5.3a – The effect of the peak temperature on the yields of the products for the pyrolysis of the mixture 25%cellulose:75%lignin, with a heating rate of 1^0C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

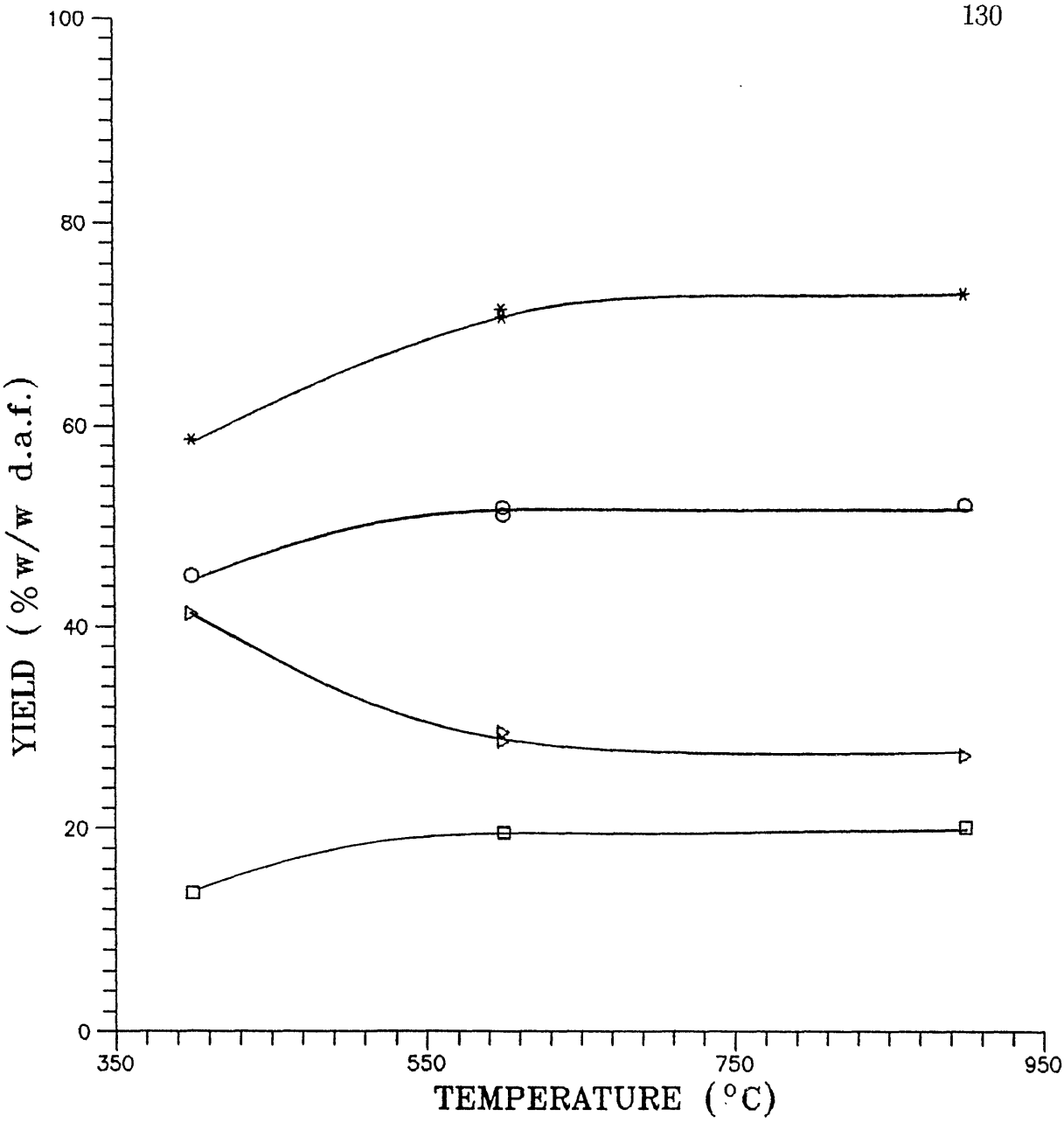


Figure 3.5.3b – The effect of the peak temperature on the yields of the products for the pyrolysis of the mixture 25%cellulose:75%lignin, with a heating rate of 1000^{0}C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

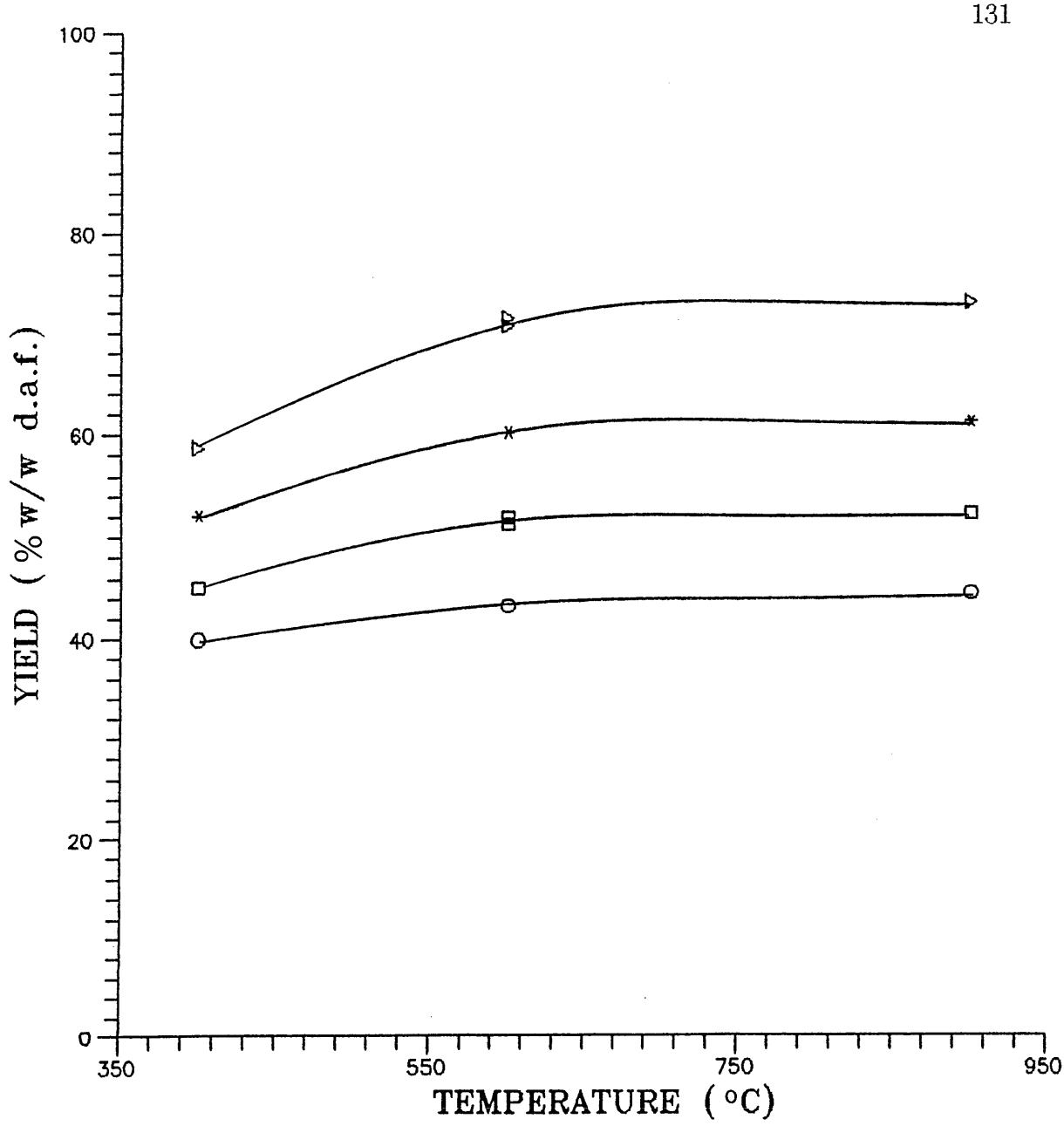


Figure 3.5.3c – The effect of the peak temperature on the yields of Total volatiles and Tar for the pyrolysis of the mixture 25%cellulose : 75%lignin, with 30 seconds hold time and different heating rates.

Δ = 1000^{0}C/second; * = 1^{0}C/second; (Total volatiles).

$\square$ = 1000^{0}C/second; 0 = 1^{0}C/second; (Tar).

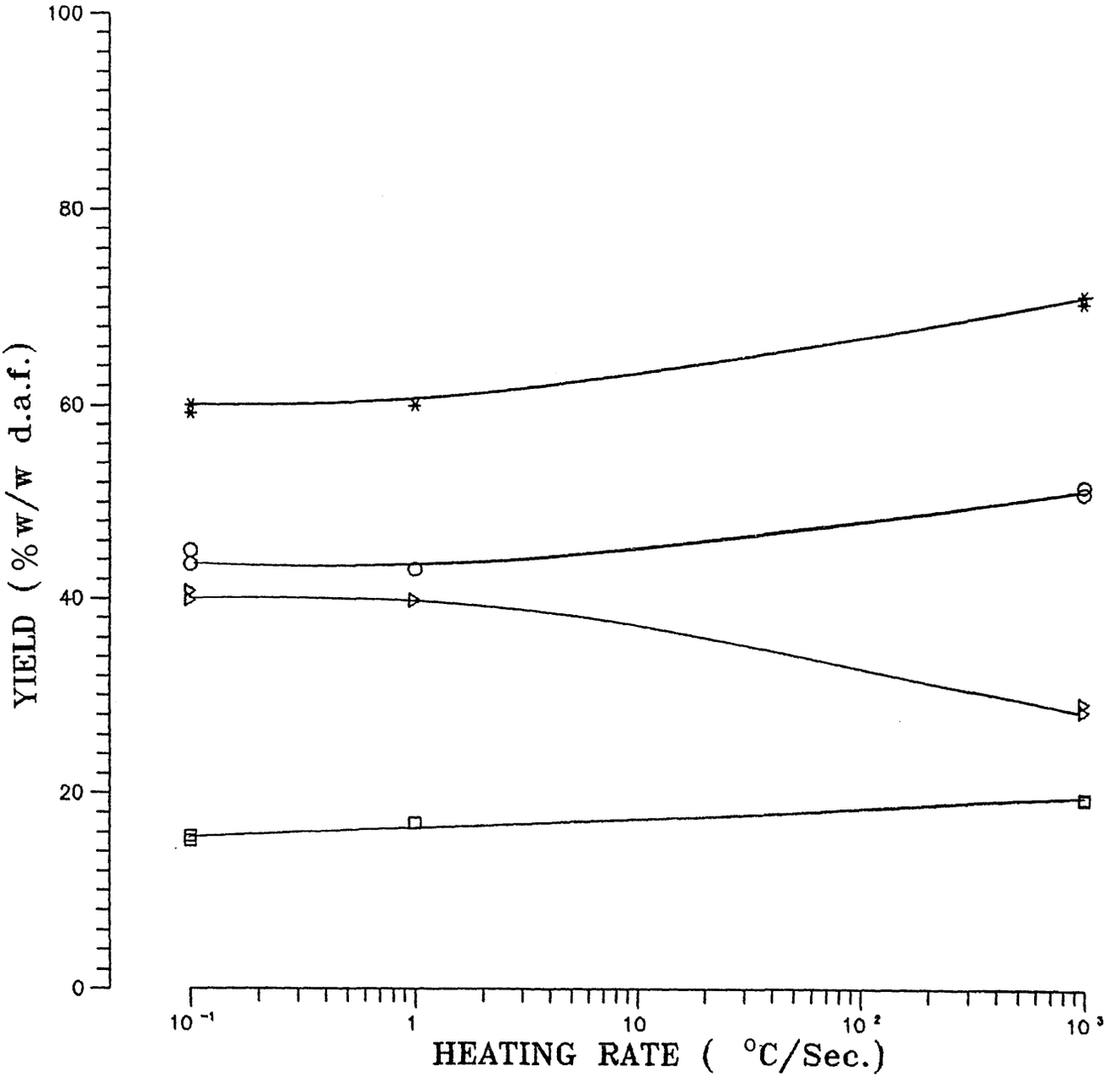


Figure 3.5.3d – The effect of heating rate on the yields of the products for the pyrolysis of the mixture 25%cellulose:75%lignin, with 30 seconds hold time at the peak temperature of 600^{0}C..

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

3.5.4 – 50% Cellulose : 50% Lignin.

Figures 3.5.4a and 3.5.4b display the pyrolysis yields for a specimen containing equal proportions of cellulose and lignin, at 1^0C/second and 1000^0C/second respectively, and with peak temperatures in the range 400–900^0C. Both heating rates demonstrate the same behaviour, namely an increase in the total volatile and tar yields and a corresponding decrease in the yield of gas plus water and char as the peak temperature increases from 400^0C to 600^0C; whilst above 600^0C the yield of all products remains constant.

Figures 3.5.4c and 3.5.4d show that heating rates less than 1^0C/second have no effect on the yields of pyrolysis products. In contrast, at heating rates greater that 1^0C/second the production of total volatiles, tar and gas plus water increases, and, obviously, there is a corresponding decrease in the yield of char.

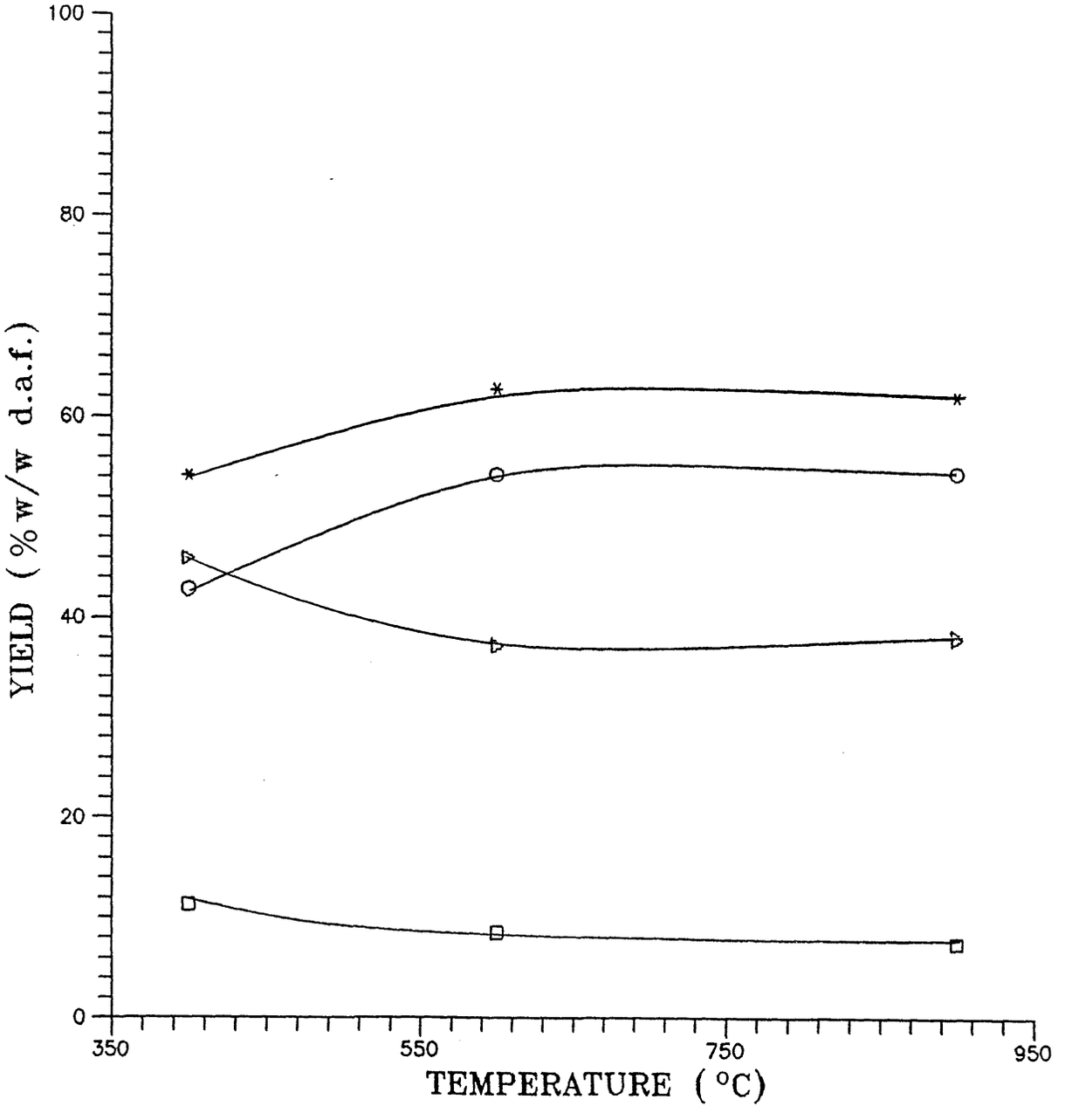


Figure 3.5.4a – The effect of the peak temperature on the yields of the products for the pyrolysis of the mixture 50%cellulose:50%lignin, with a heating rate of 1^0C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

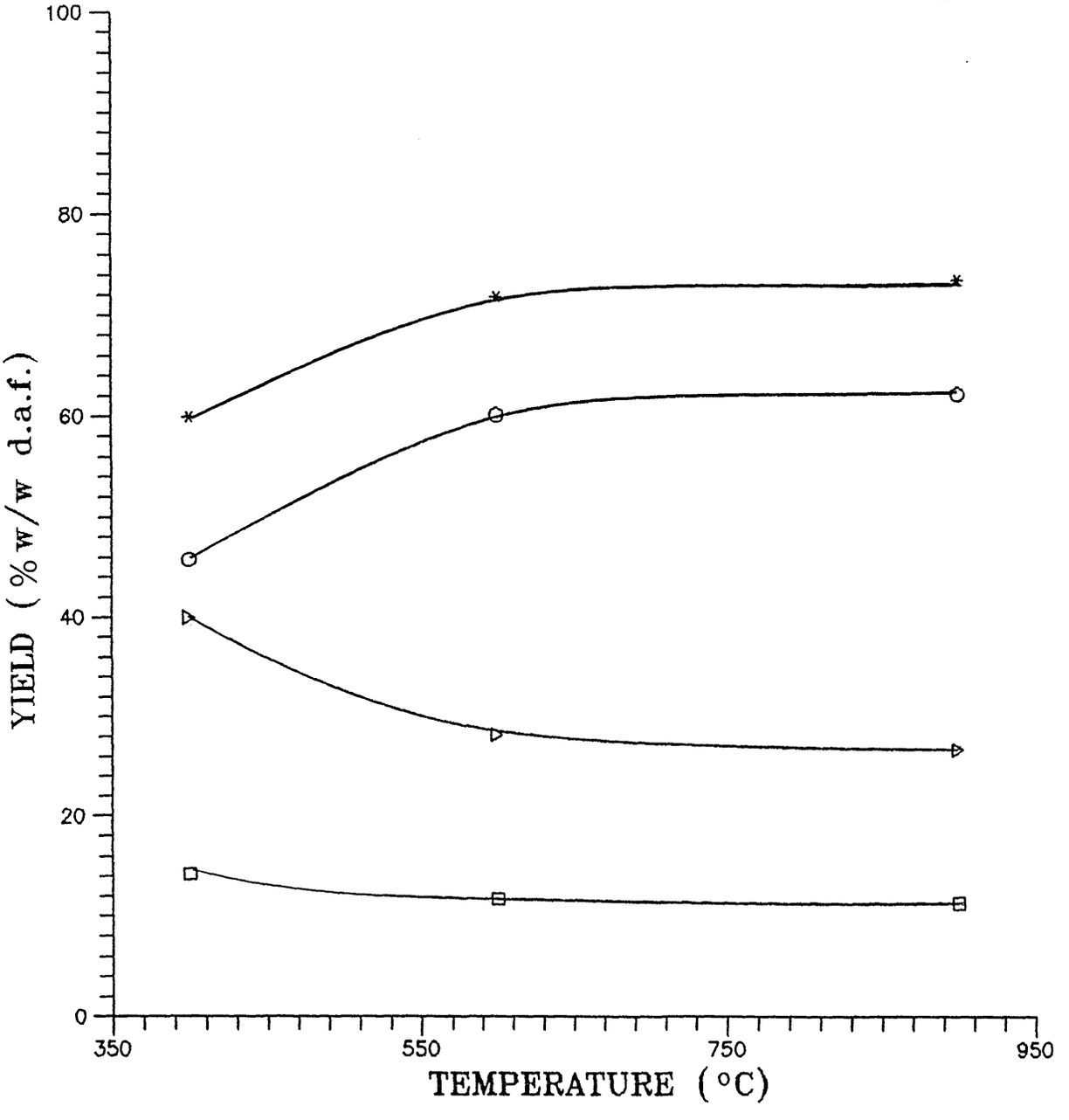


Figure 3.5.4b – The effect of the peak temperature on the yields of the products for the pyrolysis of the mixture 50%cellulose:50%lignin, with a heating rate of 1000°C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

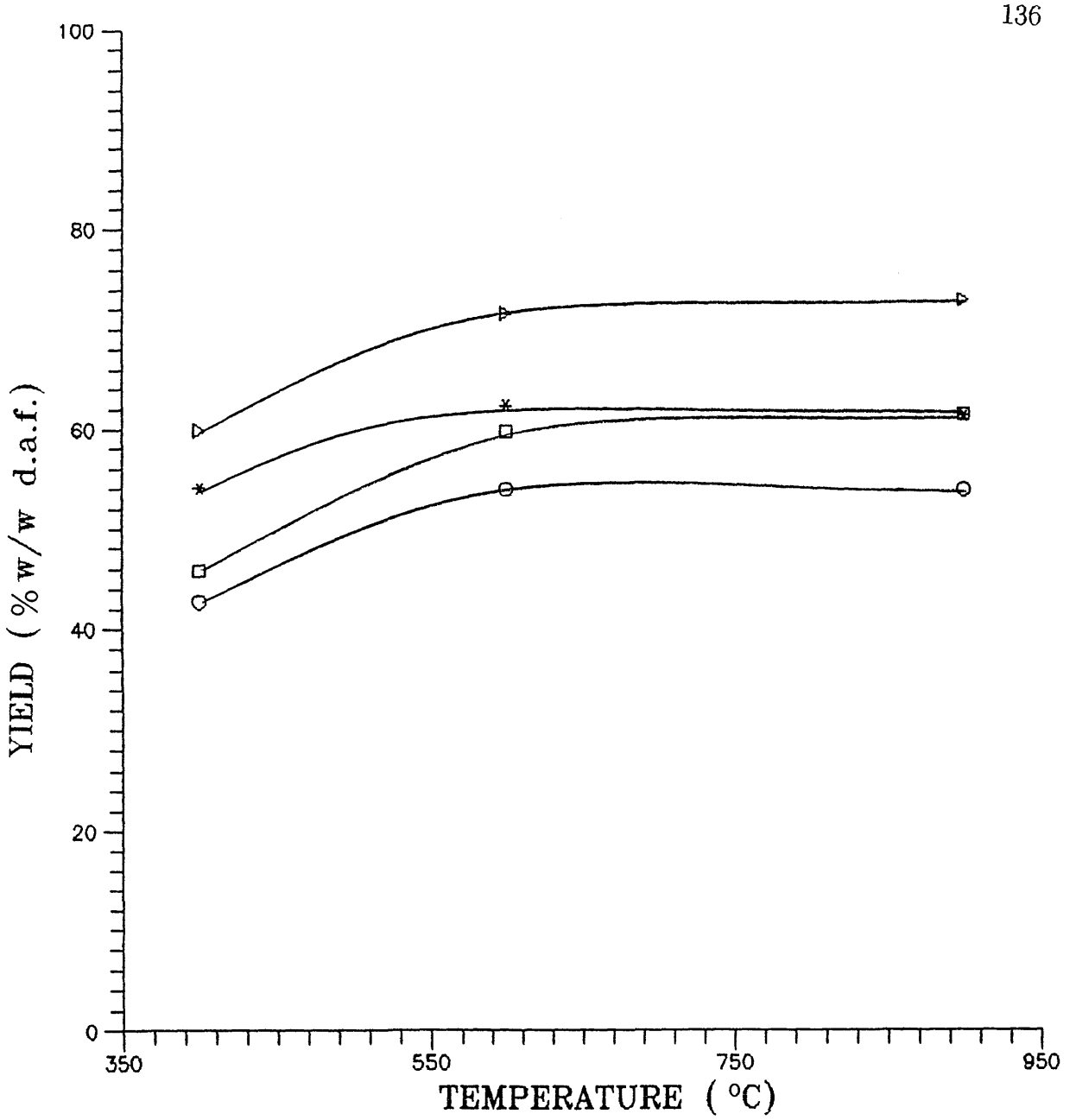


Figure 3.5.4c – The effect of the peak temperature on the yields of Total volatiles and Tar for the pyrolysis of the mixture 50%cellulose : 50%lignin, with 30 seconds hold time and different heating rates.

Δ = 1000^{0}C/second; * = 1^{0}C/second; (Total volatiles).

□ = 1000^{0}C/second; 0 = 1^{0}C/second; (Tar).

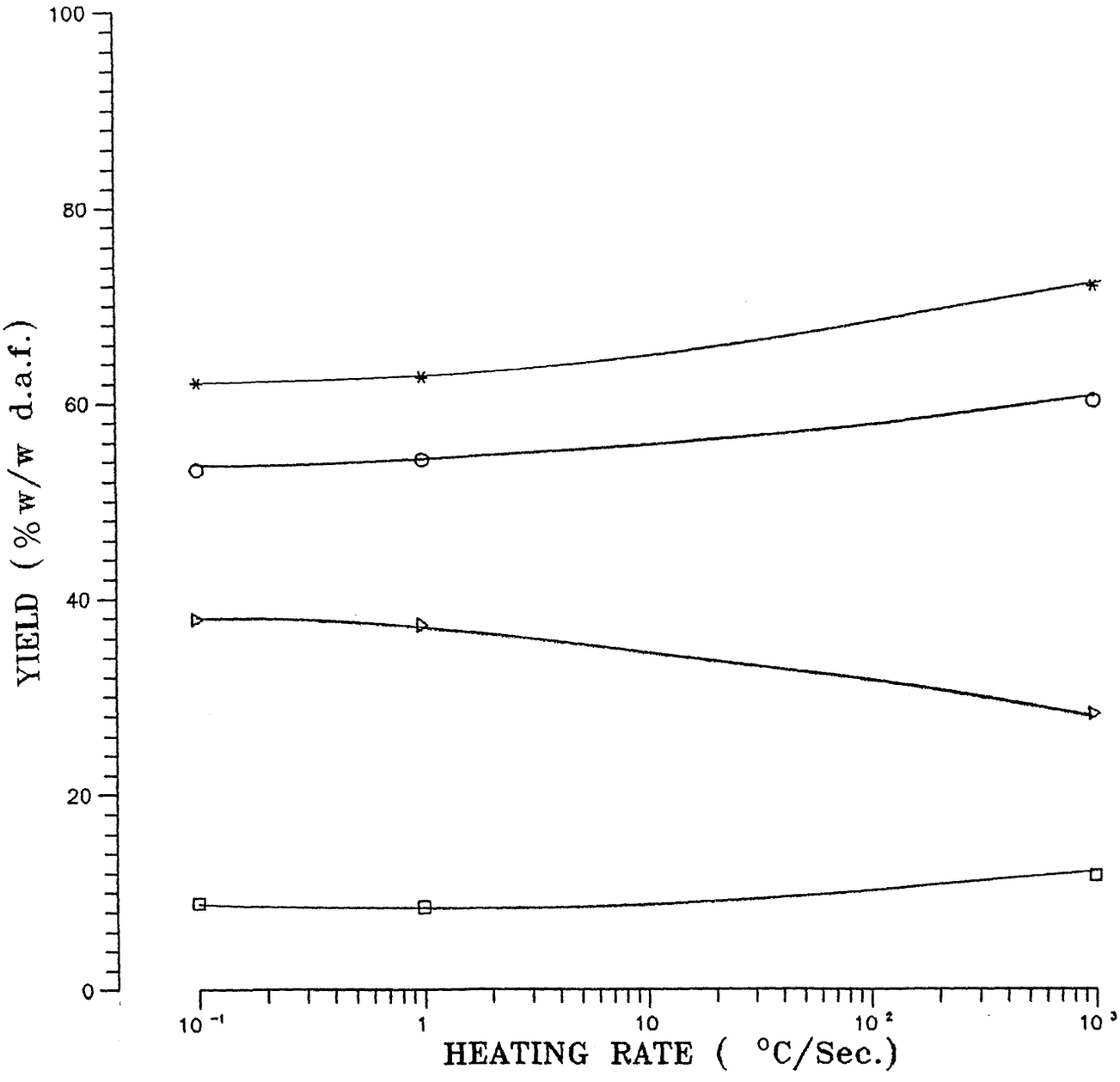


Figure 3.5.4d – The effect of heating rate on the yields of the products for the pyrolysis of the mixture 50%cellulose:50%lignin, with 30 seconds hold time at the peak temperature of 600°C..

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

3.5.5 – 75% Cellulose : 25% Lignin.

This mixture, namely 75%cellulose:25%lignin, may be termed "synthetic" Sugar Cane Bagasse, since the proportion of cellulose to lignin is very similar to that found in Sugar Cane Bagasse, say, 22%lignin or Silver Birch, say, 29%lignin see Chapter 4 section 4.2 and 4.3. The "synthetic" Sugar Cane Bagasse was prepared, as described in Chapter 2 section 2.3.2, and then pyrolysed at peak temperatures from 400^{0}C to 900^{0}C and at heating rates of 0.1^{0}C/second, 1^{0}C/second and 1000^{0}C/second.

Figures 3.5.5a and 3.5.5b, show the effect of peak temperature on the yield of pyrolysis products from this "synthetic" Sugar Cane Bagasse specimen. In Figure 3.5.5a the heating rate was 1^{0}C/second, whilst in Figure 3.5.5b it was 1000^{0}C/second, all the other parameters being the same in both cases. From these figures, it can be observed that the total volatile yield increases with increasing peak temperature until 600^{0}C; and that at peak temperatures beyond 600^{0}C the yield of total volatiles remained unaltered. The increase in the yield of total volatiles was solely due to the production of tar; i.e. the yield of gas plus water was completely independent of temperature.

To complete this study of the effect of heating rate on the pyrolysis of "synthetic" Sugar Cane Bagasse, a set of runs were

performed at the very slow heating rate of 0.1^{0}C/second. Figures 3.5.5c and 3.5.5d illustrate the effect of heating rate, where it may again be observed that below 1^{0}C/second the yields of the pyrolysis products were unaffected, but that increasing the heating rate above 1^{0}C/second increased the yield of total volatiles. This increase was due mainly to the increased production of tar, although some additional gas plus water was produced. Char, obviously, shows the opposite behaviour to that of total volatiles.

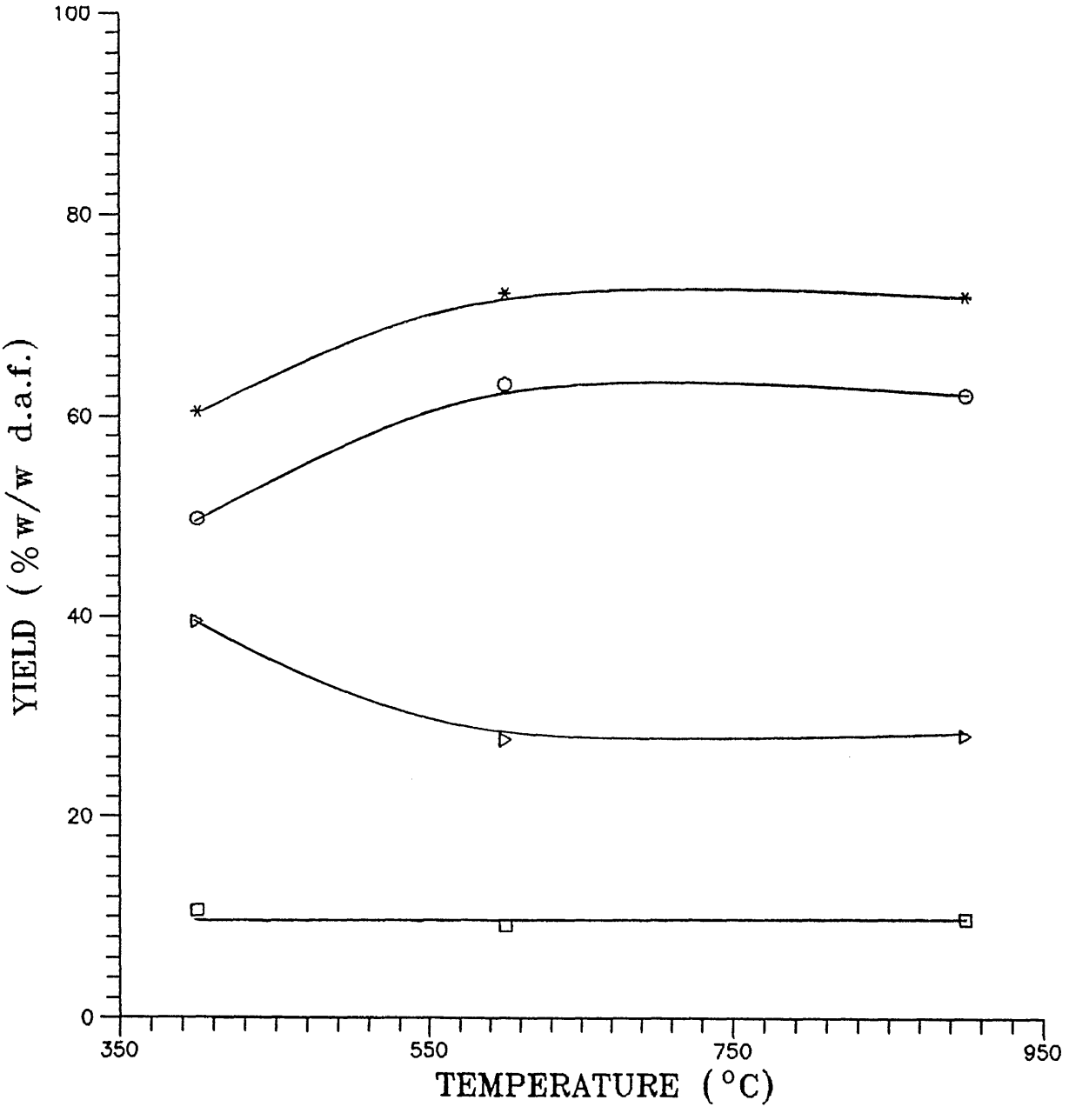


Figure 3.5.5a – The effect of the peak temperature on the yields of the products for the pyrolysis of the mixture 75%cellulose:25%lignin, with a heating rate of 1^0C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

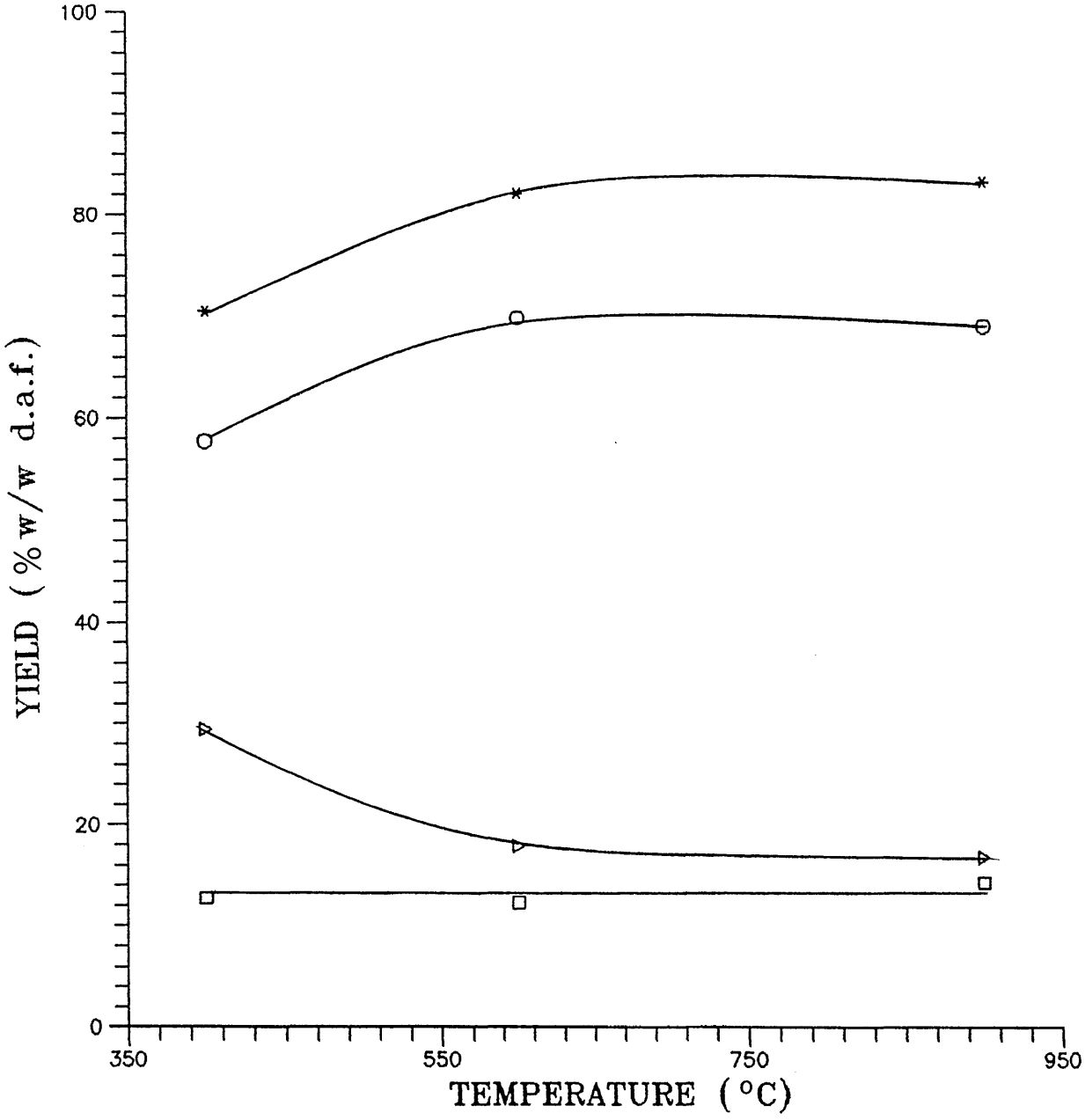


Figure 3.5.5b – The effect of the peak temperature on the yields of the products for the pyrolysis of the mixture 75%cellulose:25%lignin, with a heating rate of 1000^{0}C/second and 30 seconds hold time.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

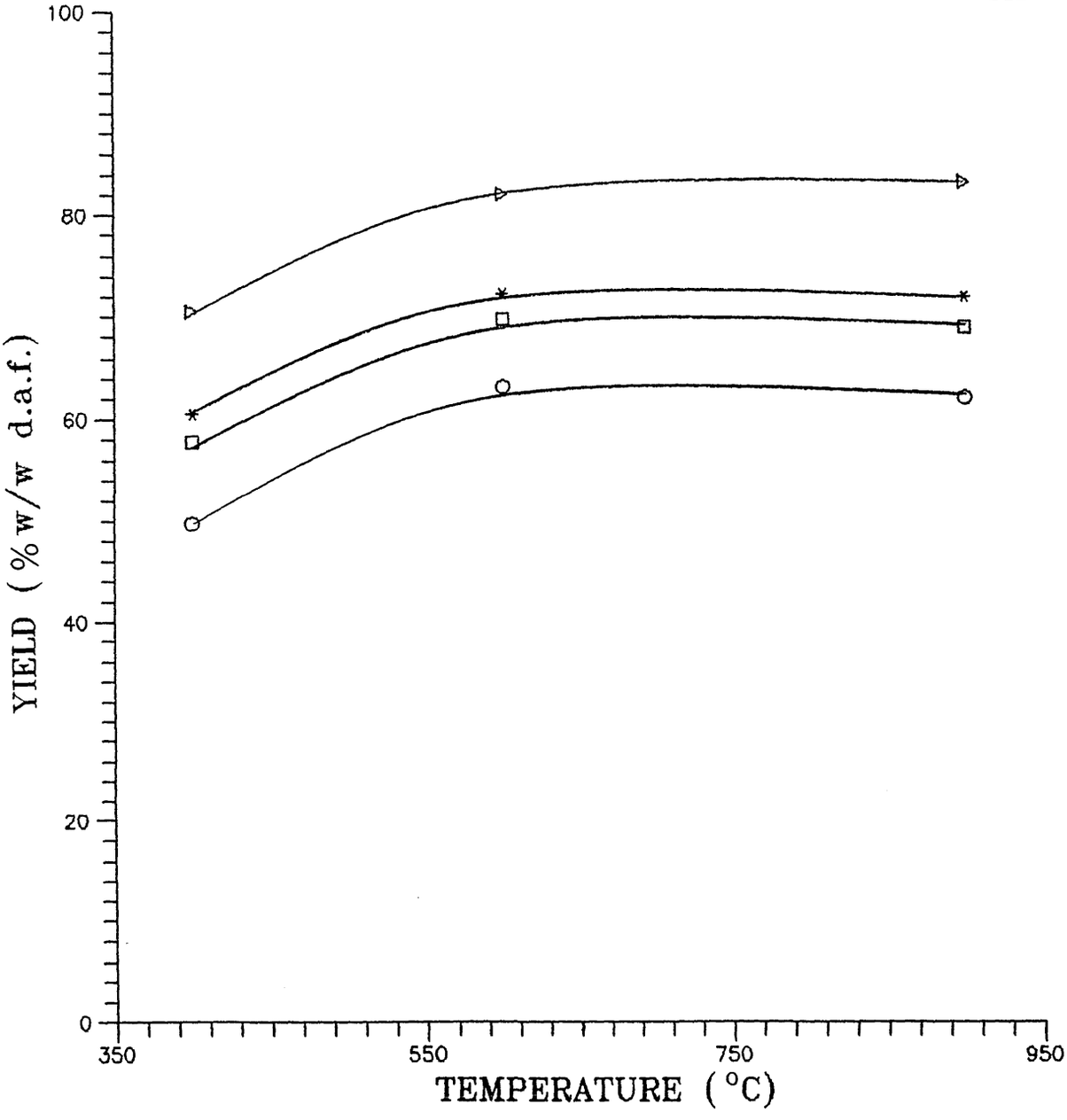


Figure 3.5.5c – The effect of the peak temperature on the yields of Total volatiles and Tar for the pyrolysis of the mixture 75%cellulose : 25%lignin, with 30 seconds hold time and different heating rates.

Δ = 1000^{0}C/second; * = 1^{0}C/second; (Total volatiles).

□ = 1000^{0}C/second; 0 = 1^{0}C/second; (Tar).

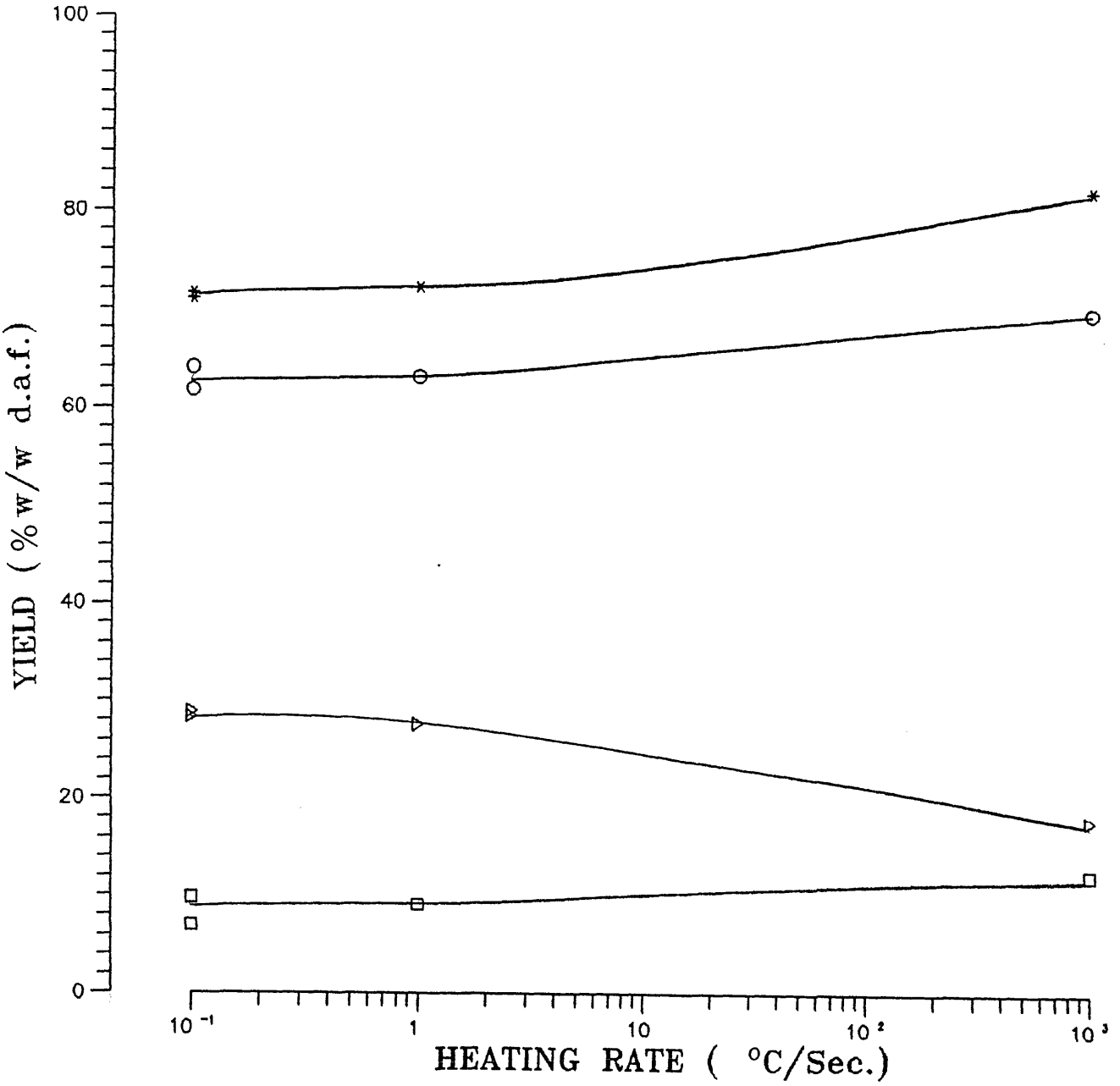


Figure 3.5.5d – The effect of heating rate on the yields of the products for the pyrolysis of the mixture 75%cellulose:25%lignin, with 30 seconds hold time at the peak temperature of 600°C.

* = Total volatiles; 0 = Tar; Δ = Char; □ = Gas plus water.

3.6 – Comparison Between the Pyrolysis Yields for Specimens with Differing Cellulose/Lignin Ratios.

A general summary showing how the yields of total volatiles and of tar products from the pyrolysis of cellulose, lignin and their mixtures were affected by the peak pyrolysis temperature and heating rate is presented in Figures 3.6a–3.6f; in all these experiments, the hold time at the peak temperature was 30 seconds.

The existence of two "key" values from these graphs is clear; the first being the peak temperature of 600^{0}C, and the second the heating rate of 1^{0}C/second. The production of total volatiles and tars increases with increasing temperature until 600^{0}C, however above 600^{0}C total volatiles and tar yields remain constant for both slow and fast heating rates; this behaviour is independent of the sample composition, see Figures 3.6a–3.6d. A similarly clearly defined area, may be observed in Figures 3.6e and 3.6f, where heating rates are plotted versus the yields of total volatiles and tar, for samples with differing cellulose/lignin ratios. It can be seen that 1^{0}C/second marks a boundary where the yield of either total volatiles or tar is unaffected by decreasing values of heating rates, and above which there is a slight increase in yield for virtually almost all sample compositions. The unique exception to this general trend is when the sample contains no lignin, that is to say specimens of 100% cellulose; for this case the yields of the products of pyrolysis are not affected by heating rate, see Figures 3.6e and 3.6f.

Figures 3.6g–3.6L illustrate the interactions between sample composition, temperature and heating rate on the yields of both total volatiles and tar. It may be clearly seen from all these graphs that there is a dramatic increase in these yields when the cellulose content of the sample is equal to, or greater than, 75% see, for example, Figures 3.6g and 3.6j; the numerical data are presented in Tables 3.11 and 3.12. The thermal fragmentation of these specimens is, therefore, significantily constrained when their lignin content is greater than, say, 25%; this important experimental observation is discussed in the following section. Furthermore increasing the heating rate to 1000^{0}C/second does enhance the total volatile and tar yields, however it does not modify the above behaviour.

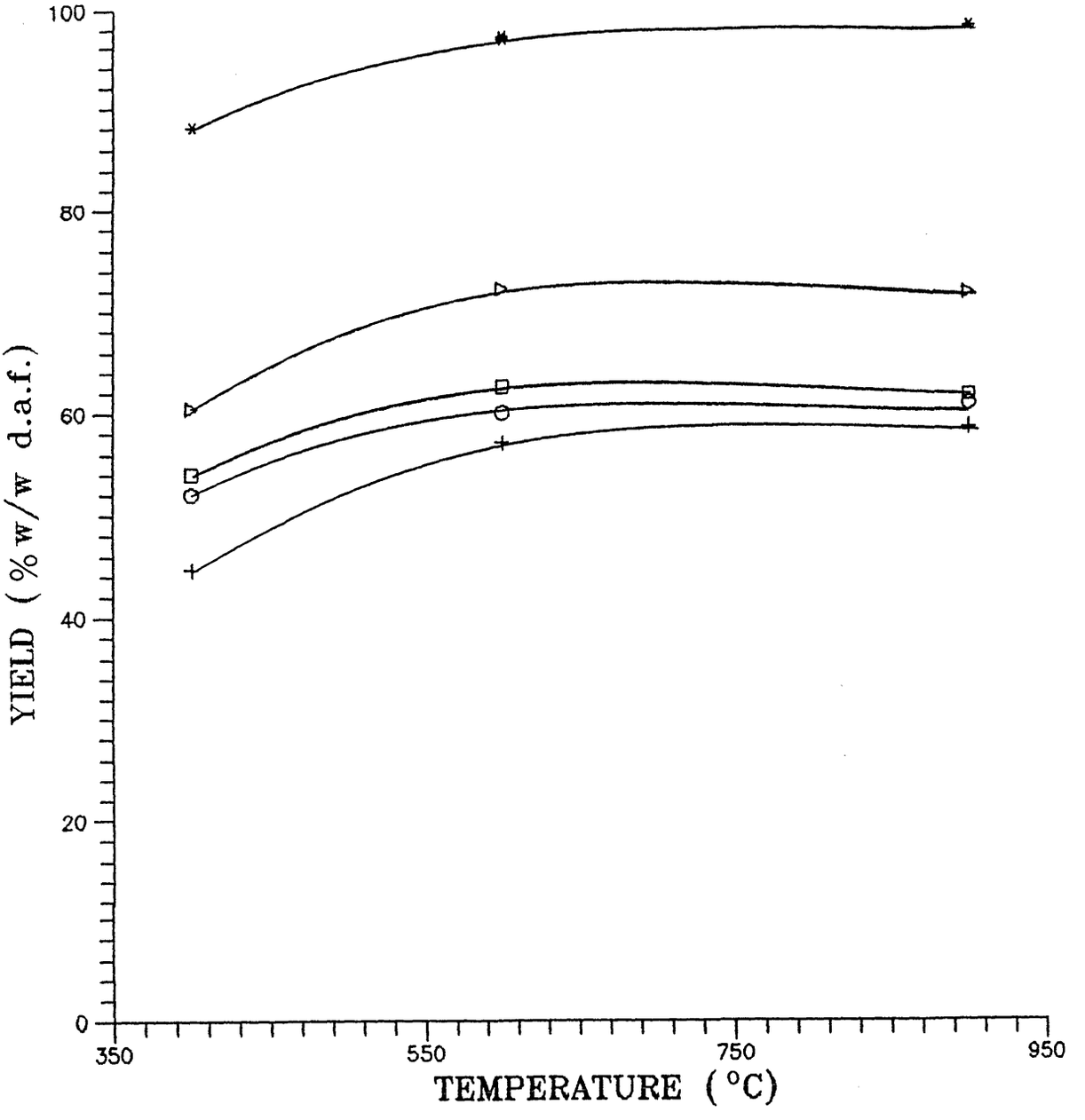


Figure 3.6a – The effect of the peak temperature on the yields of the Total volatiles for the pyrolysis of samples with differing composition, at the heating rate of 1^0C/second, and 30 seconds hold time.

* = Cellulose; + = Lignin; 0 = 25%cellulose:75%lignin;

□ = 50%cellulose:50%lignin; Δ = 75%cellulose:25%lignin.

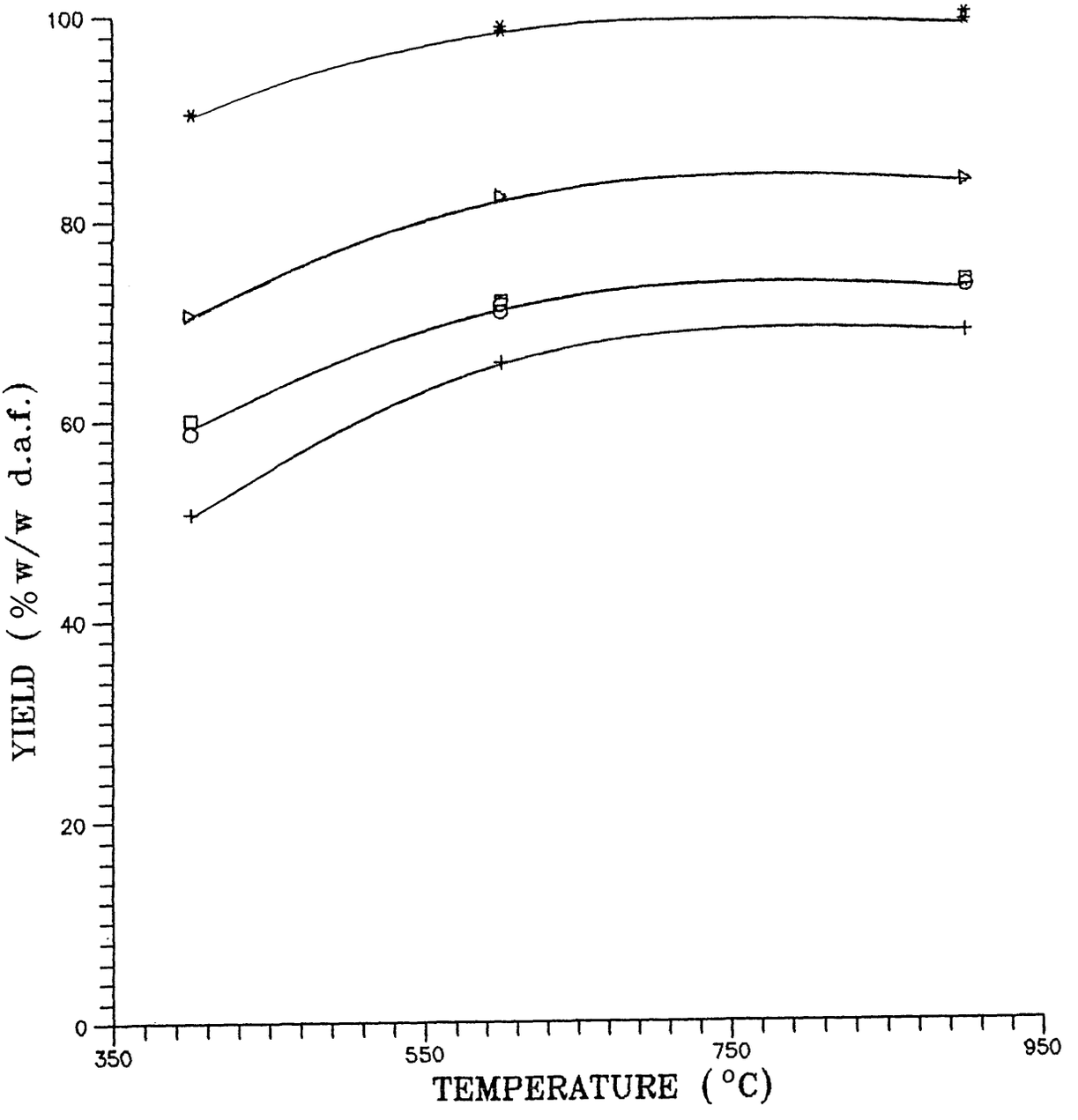


Figure 3.6b – The effect of the peak temperature on the yields of the Total volatiles for the pyrolysis of samples with differing composition, at the heating rate of 1000^0C/second, and 30 seconds hold time.

* = Cellulose; + = Lignin; 0 = 25%cellulose:75%lignin;

□ = 50%cellulose:50%lignin; Δ = 75%cellulose:25%lignin.

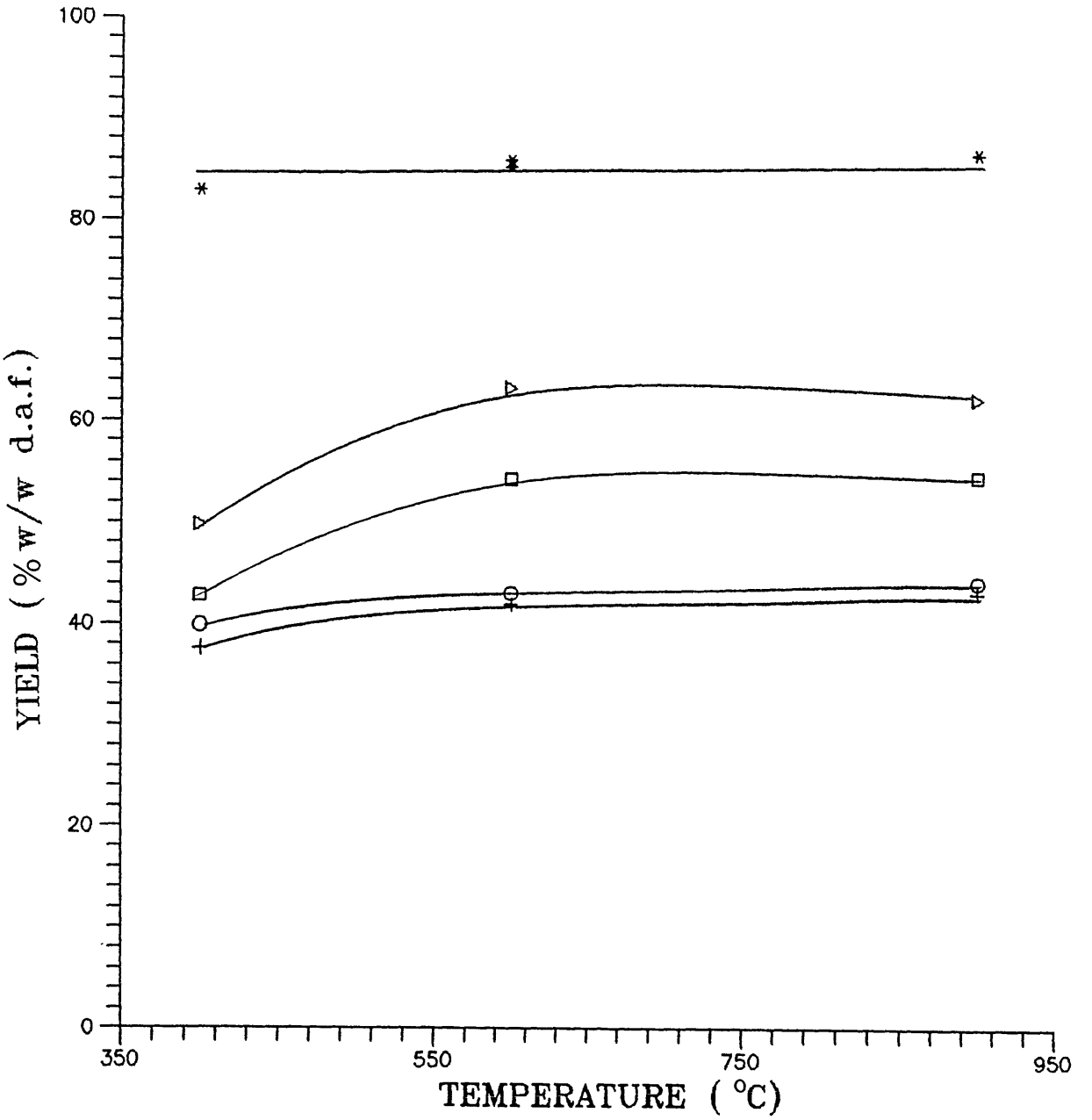


Figure 3.6c – The effect of the peak temperature on the yields of the Tar for the pyrolysis of samples with differing composition, at the heating rate of 1^0C/second, and 30 seconds hold time.

* = Cellulose; + = Lignin; 0 = 25%cellulose:75%lignin;

□ = 50%cellulose:50%lignin; Δ = 75%cellulose:25%lignin.

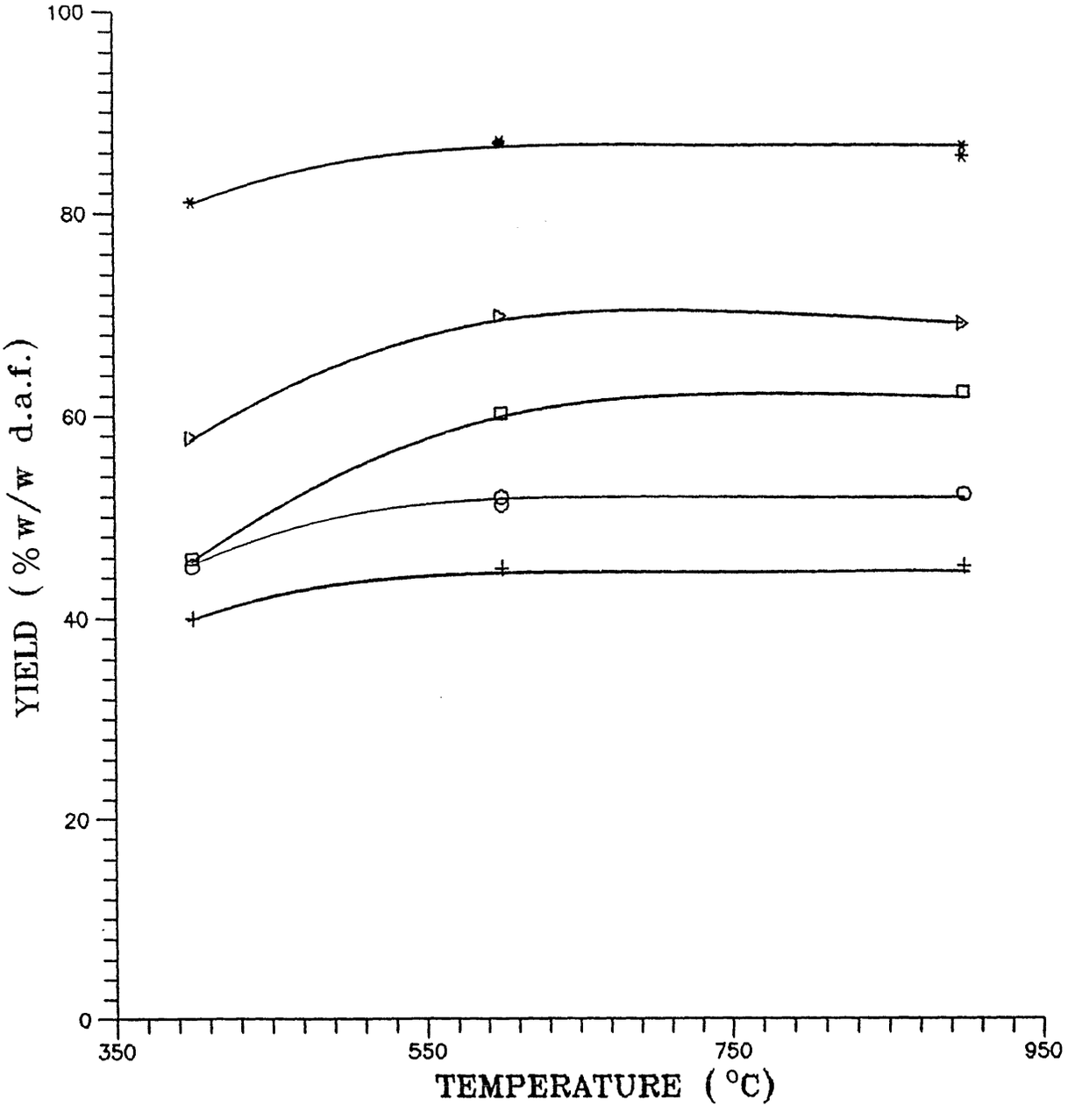


Figure 3.6d – The effect of the peak temperature on the yields of the Tar for the pyrolysis of samples with differing composition, at the heating rate of 1000°C/second, and 30 seconds hold time.

* = Cellulose; + = Lignin; 0 = 25%cellulose:75%lignin;

□ = 50%cellulose:50%lignin; Δ = 75%cellulose:25%lignin.

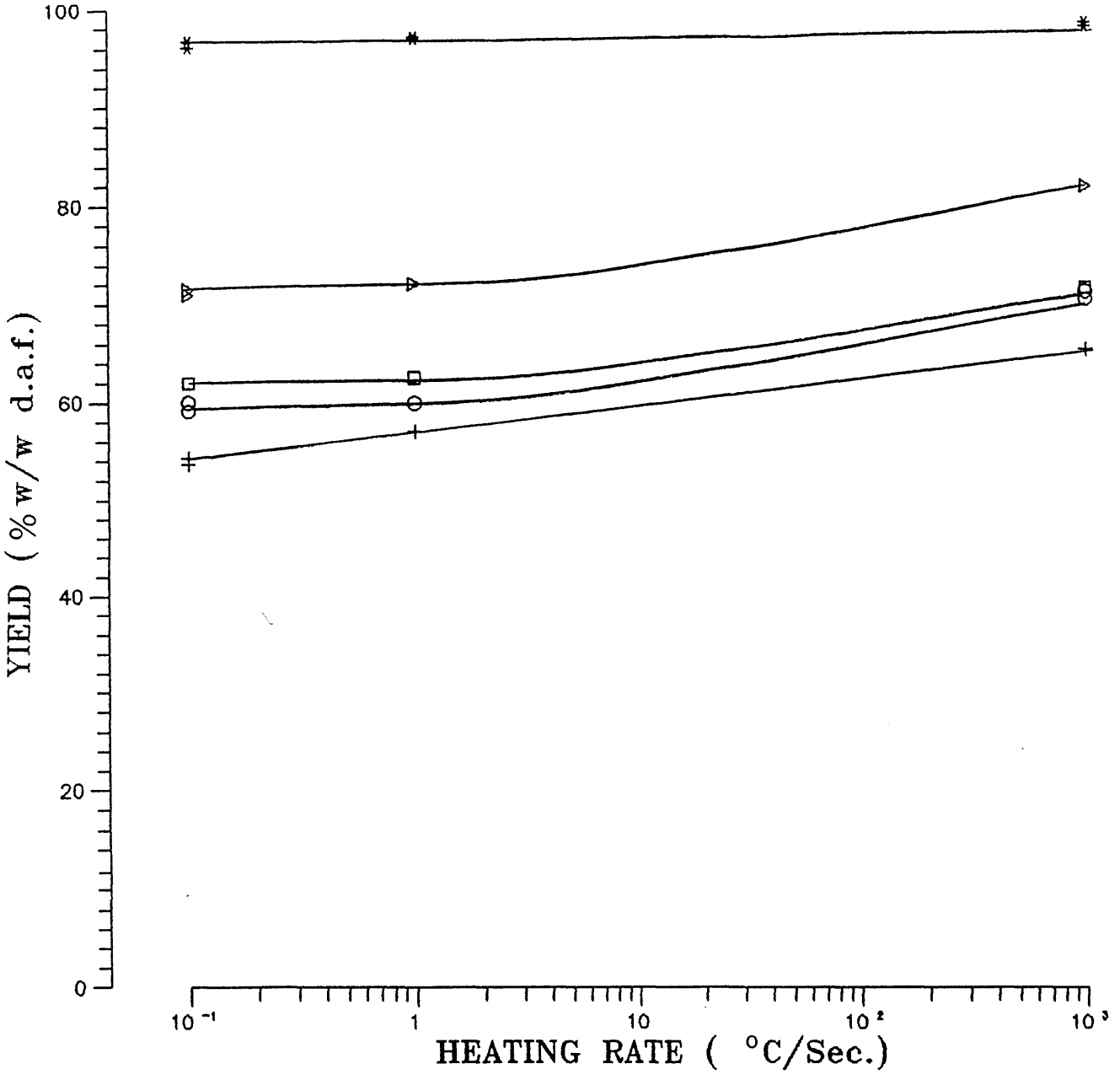


Figure 3.6e – The effect of heating rate on the yields of the Total volatiles for the pyrolysis of samples with differing composition, with 30 seconds hold time at the peak temperature of 600°C.

* = Cellulose; + = Lignin; 0 = 25%cellulose:75%lignin;

□ = 50%cellulose:50%lignin; Δ = 75%cellulose:25%lignin.

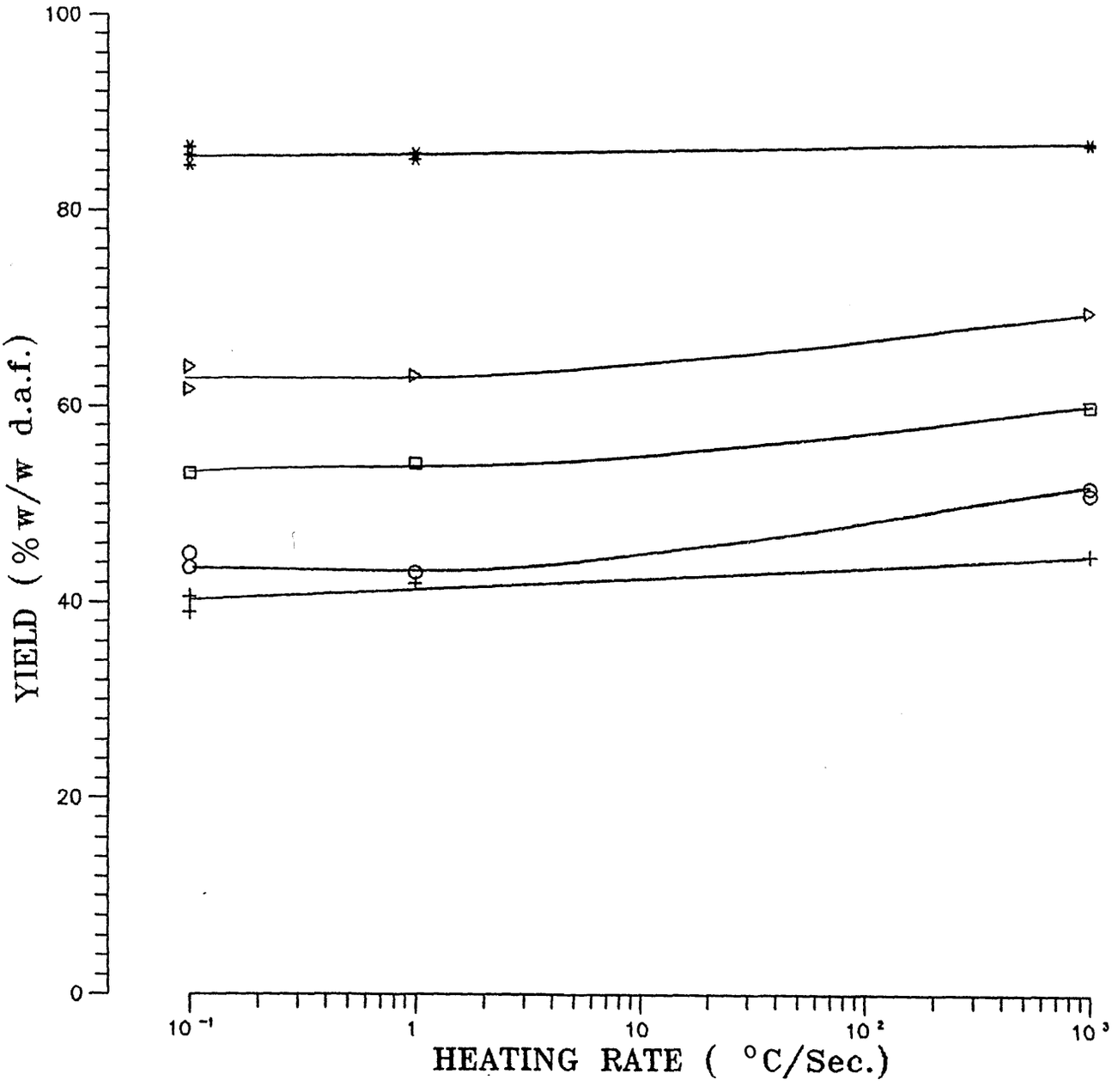


Figure 3.6f – The effect of heating rate on the yields of Tar for the pyrolysis of samples with differing composition, with 30 seconds hold time at the peak temperature of 600°C.

* = Cellulose; + = Lignin; 0 = 25%cellulose:75%lignin;

□ = 50%cellulose:50%lignin; Δ = 75%cellulose:25%lignin.

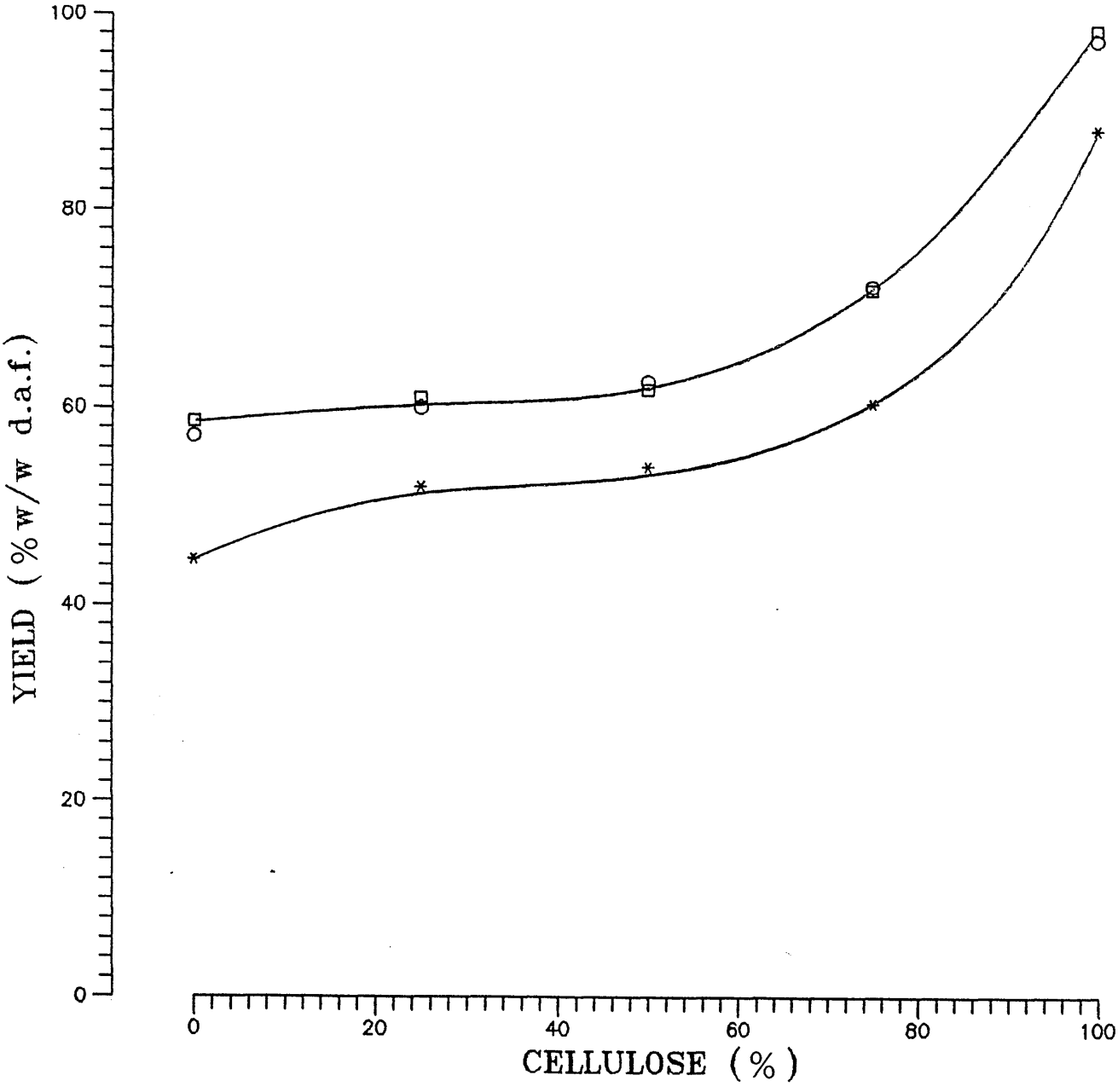


Figure 3.6g – The effect of the sample composition on the yields of the Total volatiles for the pyrolysis at different peak temperatures, with a heating rate of 1^0C/seconds and 30 seconds hold time.

* = 400^0C; 0 = 600^0C; □ = 900^0C.

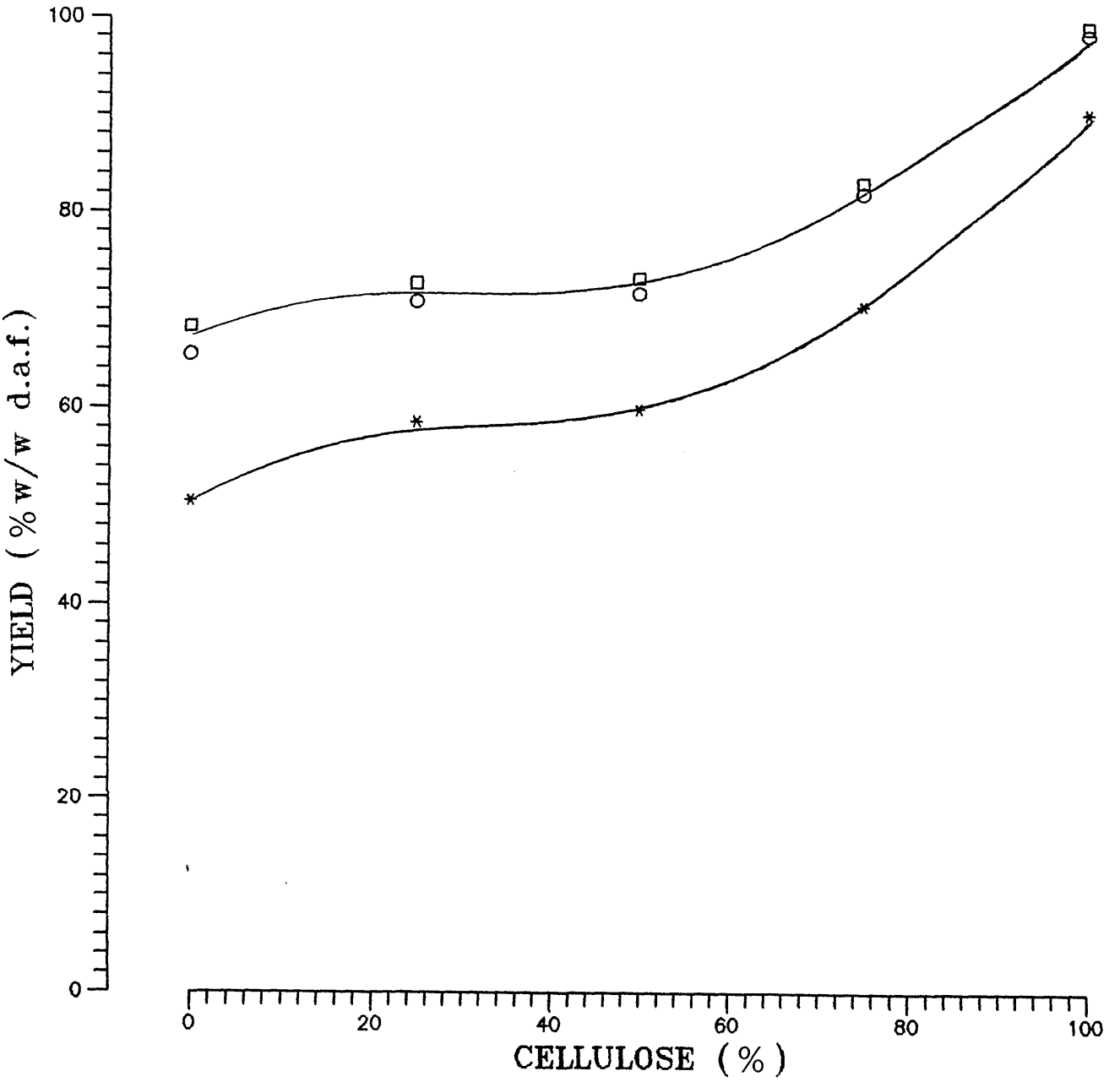


Figure 3.6h — The effect of the sample composition on the yields of the Total volatiles for the pyrolysis at different peak temperatures, with a heating rate of 1000^0C/seconds and 30 seconds hold time.

* = 400^0C; 0 = 600^0C; □ = 900^0C.

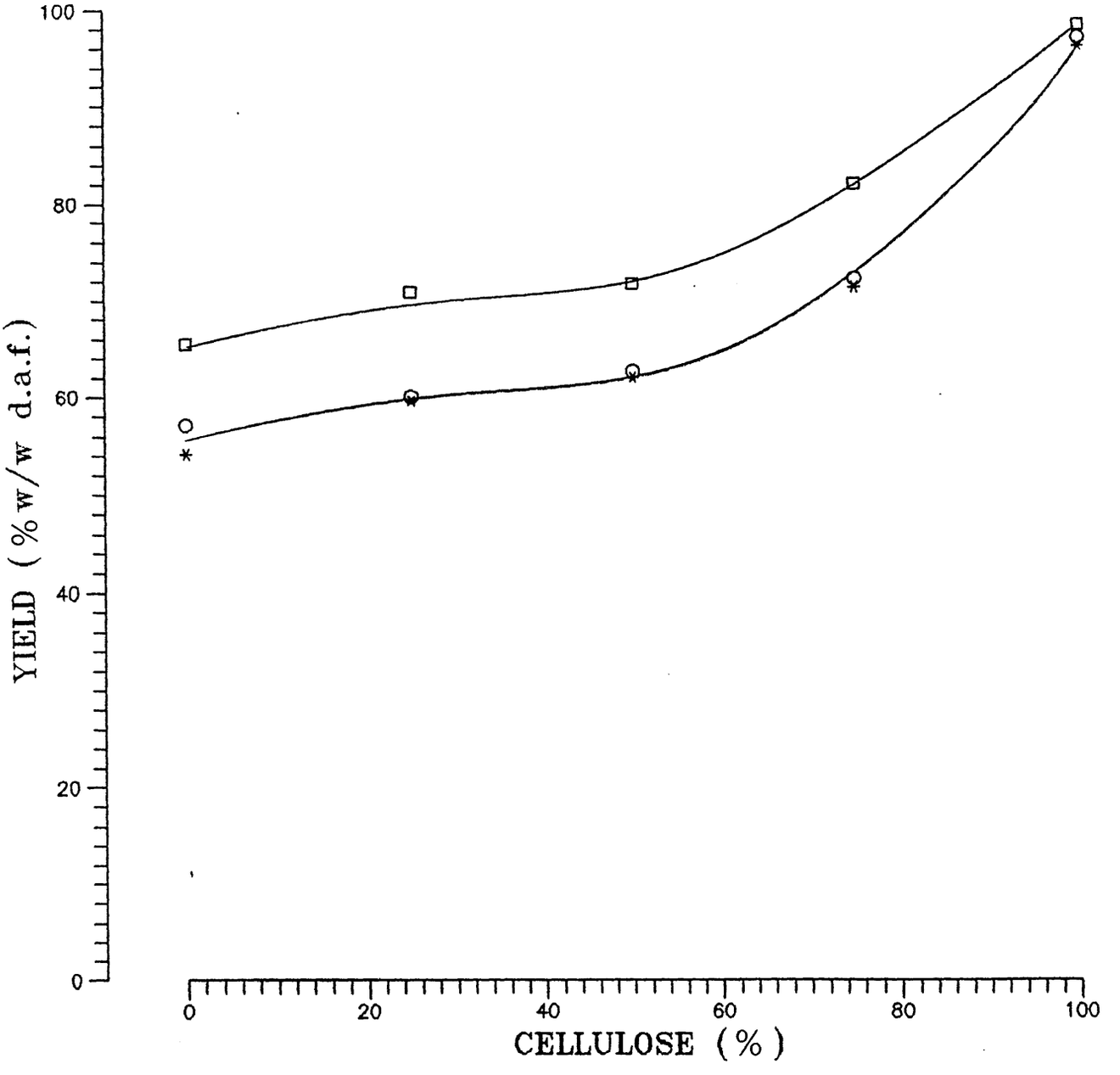


Figure 3.6i — The effect of the sample composition on the yields of the Total volatiles for the pyrolysis at different heating rates, with 30 seconds hold time at the peak temperature of 600^0C.

* = 0.1^0C/second; 0 = 1^0C/second; □ = 1000^0C/second.

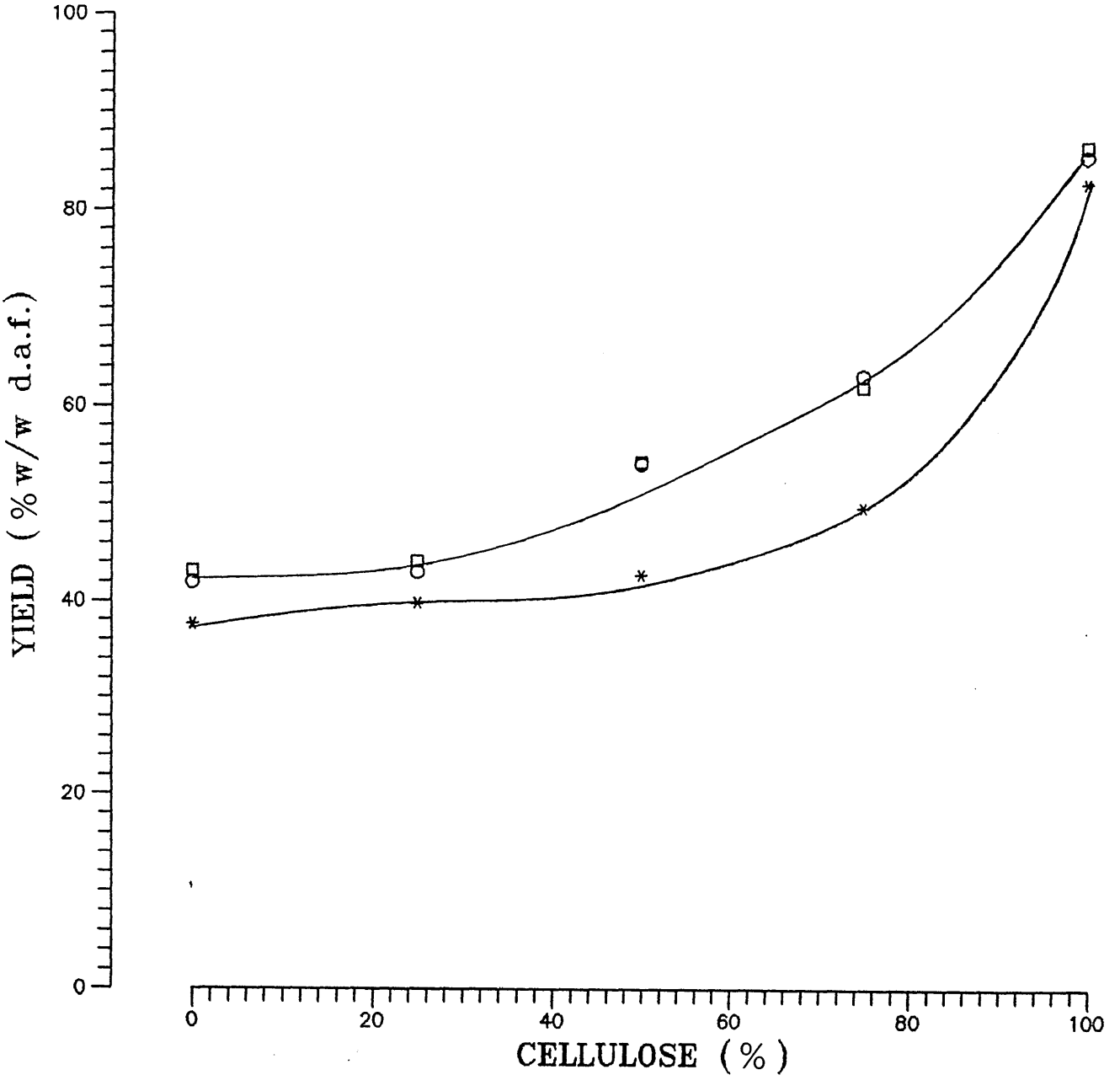


Figure 3.6j – The effect of the sample composition on the yields of Tar for the pyrolysis at different peak temperatures, with a heating rate of 1^0C/seconds and 30 seconds hold time.

* = 400^0C; 0 = 600^0C; □ = 900^0C.

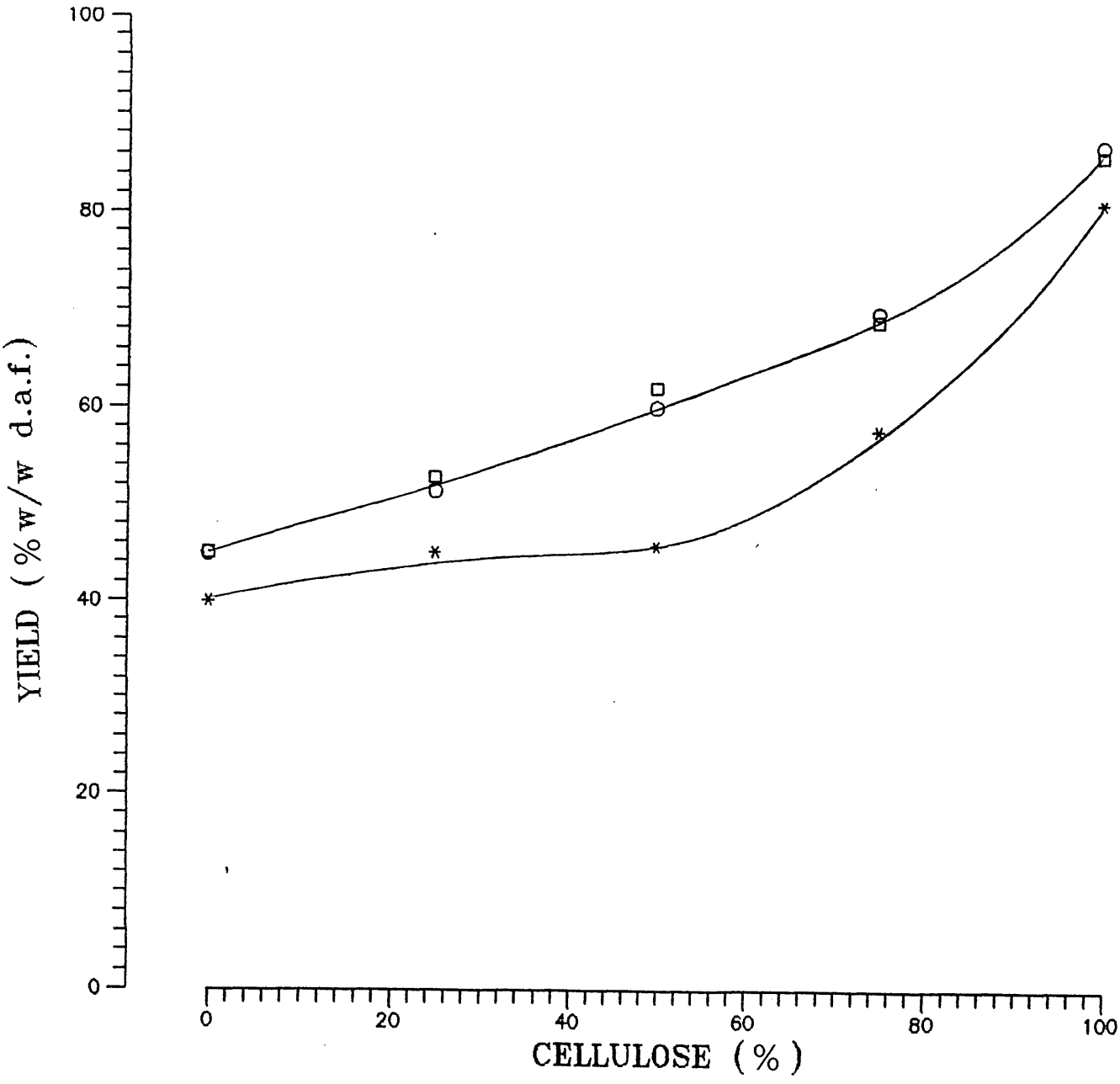


Figure 3.6k – The effect of the sample composition on the yields of Tar for the pyrolysis at different peak temperatures, with a heating rate of 1000^{0}C/seconds and 30 seconds hold time.

* = 400^{0}C; 0 = 600^{0}C; □ = 900^{0}C.

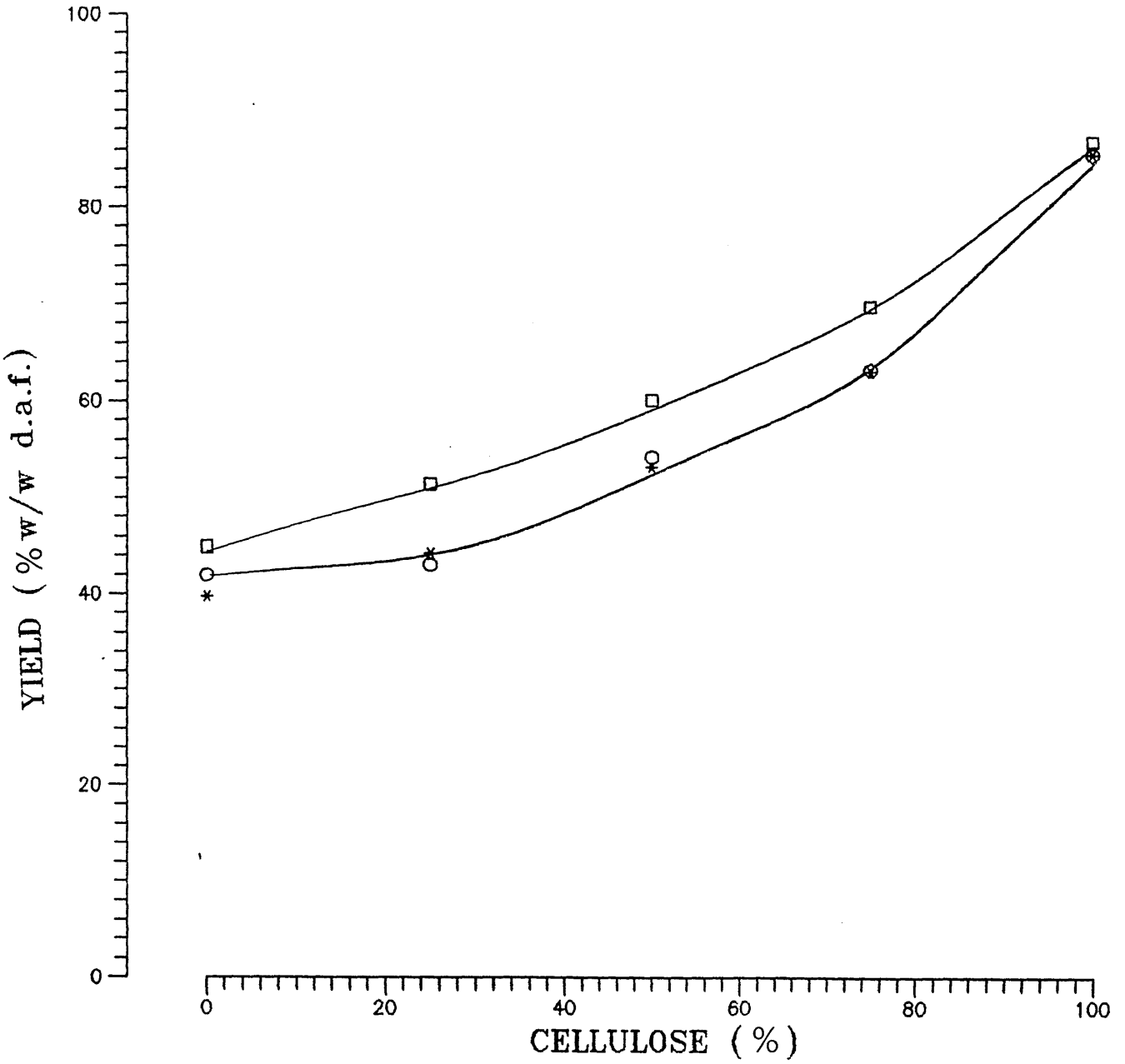


Figure 3.6L – The effect of the sample composition on the yields of Tar for the pyrolysis at different heating rates, with 30 seconds hold time at the peak temperature of 600^{0}C.

* = 0.1^{0}C/second; 0 = 1^{0}C/second; □ = 1000^{0}C/second.

3.7 – Summary.

These mixtures of cellulose, lignin, and also their pure components, were pyrolysed in order to investigate the very high yields of total volatiles obtained for Sugar Cane Bagasse and Silver Birch, as reported in this Chapter in section 3.4; the graphs 3.7a, 3.7b, and 3.7c are now presented to further this discussion.

There is very close agreement between the data obtained for pure cellulose, in this research programme and previously reported studies[117,126], specifically that at 600^{0}C pure cellulose is almost completely pyrolysed. Furthermore, from the data obtained in this research programme, the yield of total volatiles is independent of heating rate over the range 0.1^{0}C/second to 1000^{0}C/second.

If the lignin content of wood may be taken to be about 25%, see Chapter 1 section 1.7, then from Figure 3.7b the expected volatile yield, based upon this study of mixtures, is approximately 80%. However, as seen in the Figure 3.3a of section 3.3, a yield of total volatiles of 98% for Silver Birch and, slightly less, 96% for Sugar Cane Bagasse was obtained in this research programme; these data are broadly in agreement with past research conducted in a fluidised bed reactor[135], where the maximum total volatile yield for Silver Birch was about, say, 96%.

A possible, albeit unlikely, explanation for this

discrepancy is that the lignin content of the Silver Birch used in this research was much lower than the reported and currently accepted values. However, in order to obtain yields of 98% the lignin content would have to be, from Figure 3.7b, about 2%, i.e. reduced by approximately one order of magnitude. Therefore the cellulose/lignin ratio for this particular sample of Silver Birch, and also for the Sugar Cane Bagasse material, was determined using two independent techniques, namely ^{13}C – NMR (Nuclear Magnetic Resonance) and elemental analysis (CHN). These experiments and their results are described and discussed in the following Chapter, see sections 4.2 and 4.3; however it may be recorded here that the measured values for the lignin content of this Silver Birch, namely 29%, correlate well with those of past research[29,121,122]. Consequently this result coupled with the new values obtained for the lignin content of Sugar Cane Bagasse, namely 22%, see again sections 4.2 and 4.3, does <u>not</u> support the generalisation that, as the lignin content increases in a lignocellulosic material, then the total volatiles yield decreases, as presented in section 3.3.

The theoretical yields of total volatiles, see Tables 3.14, 3.17 and 3.20, were calculated based upon the hypothesis that lignin and cellulose pyrolyse independently, see again section 3.4; these values are also shown in Figures 3.7a, 3.7b and 3.7c. From these three graphs it is evident that this hypothesis is invalid, i.e. <u>cellulose and lignin do not pyrolyse independently</u>; see, for example, Figure 3.7b where the expected theoretical yield, at 1^0C/second and 75% cellulose, is 15% greater than the experimental value obtained in this study of mixtures.

Two further important observations may be drawn from these figures; first, the curves obtained at 600^{0}C may be readily overlaid upon those drawn for 900^{0}C, this re–enforces the observation already made that above 600^{0}C the yield of total volatiles for these lignocellulosic materials is independent of temperature. Secondly, the total volatile yield obtained in this research programme for the natural materials, namely Sugar Cane Bagasse and Silver Birch, are much greater, based upon a 25% lignin content, than that obtained with the mixture of similar composition.

In conclusion, the general proposition, that the total yield for the pyrolysis products of lignocellulosic materials may be obtained by the simple summation of the yield of the individual components, has been shown to be in error, and there exists a large, and until now unreported, difference between the total volatile yields obtained for natural and synthetic lignocellulosic materials. This important result will be fully discussed and reviewed in conjunction with other relevant information in Chapter 5, where further experimental work is reported, the aim of which was to investigate this new finding.

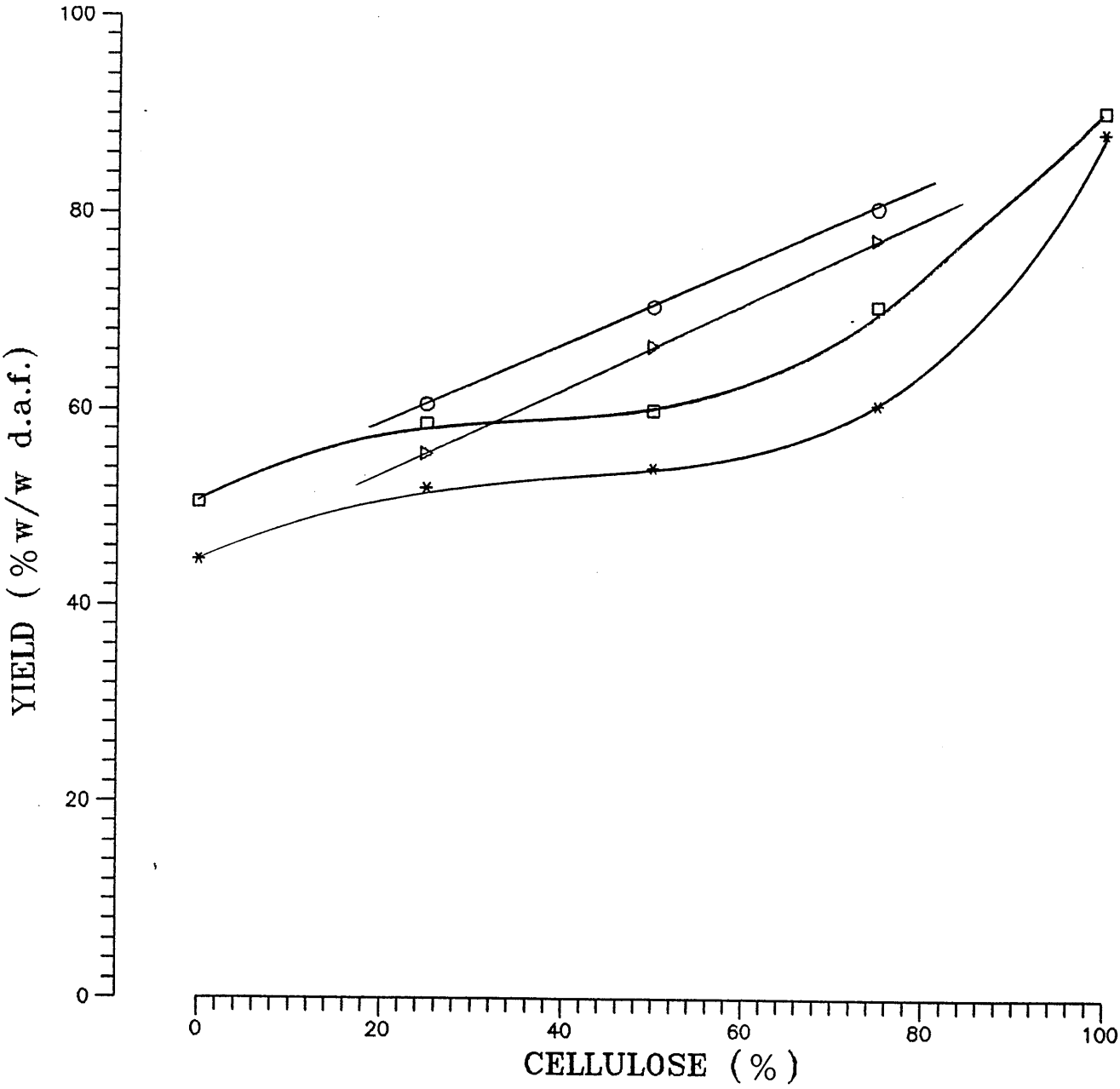


Figure 3.7a – The theoretical and experimental yields of total volatiles as a function of cellulose content and heating rate, at 400^{0}C and 30 seconds hold time.

* = 1^{0}C/second; □ = 1000^{0}C/second (experimental).

Δ = 1^{0}C/second; 0 = 1000^{0}C/second (theoretical).

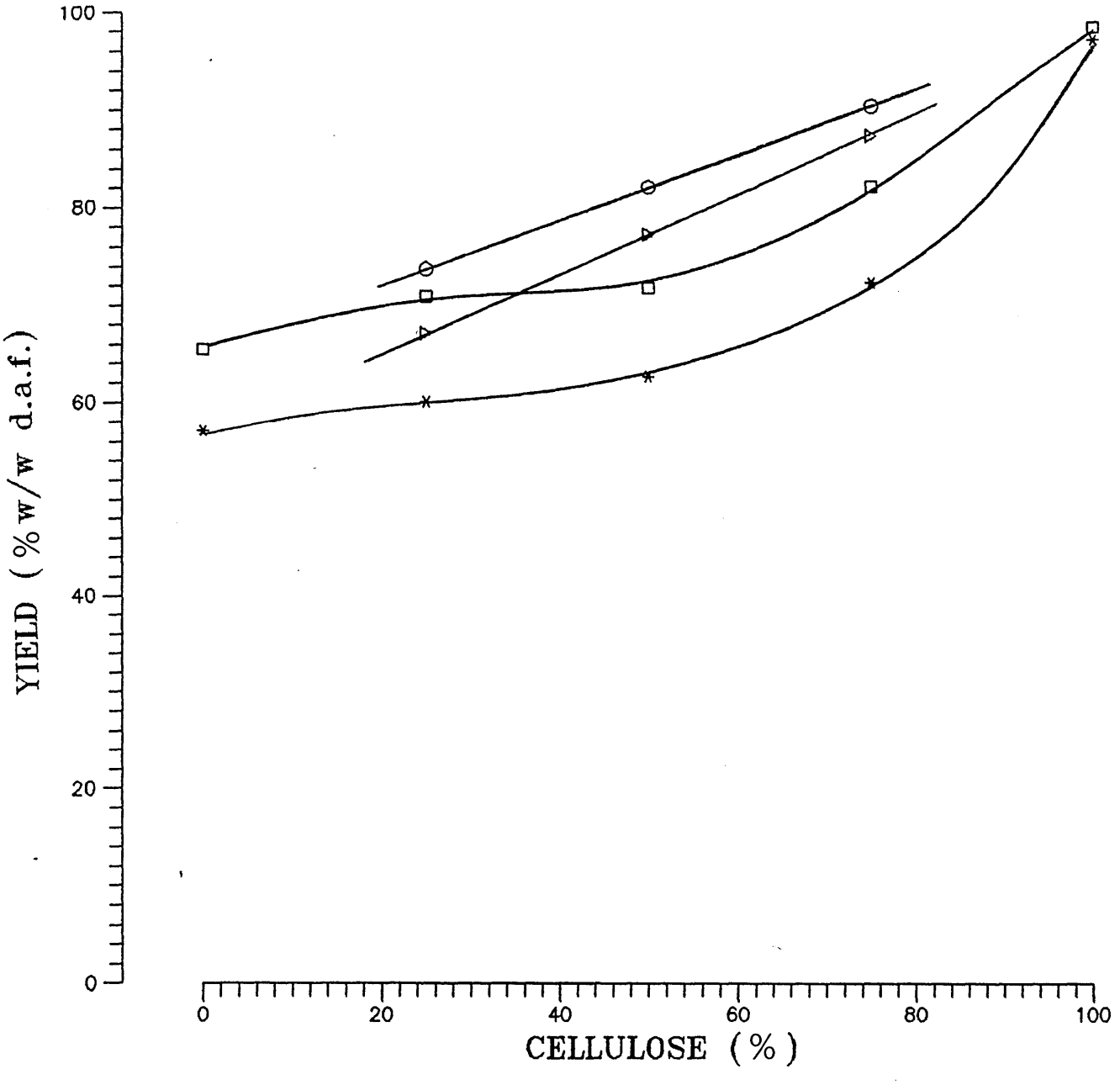


Figure 3.7b – The theoretical and experimental yields of total volatiles as a function of cellulose content and heating rate, at 600^{0}C and 30 seconds hold time.

* = 1^{0}C/second; □ = 1000^{0}C/second (experimental).

Δ = 1^{0}C/second; 0 = 1000^{0}C/second (theoretical).

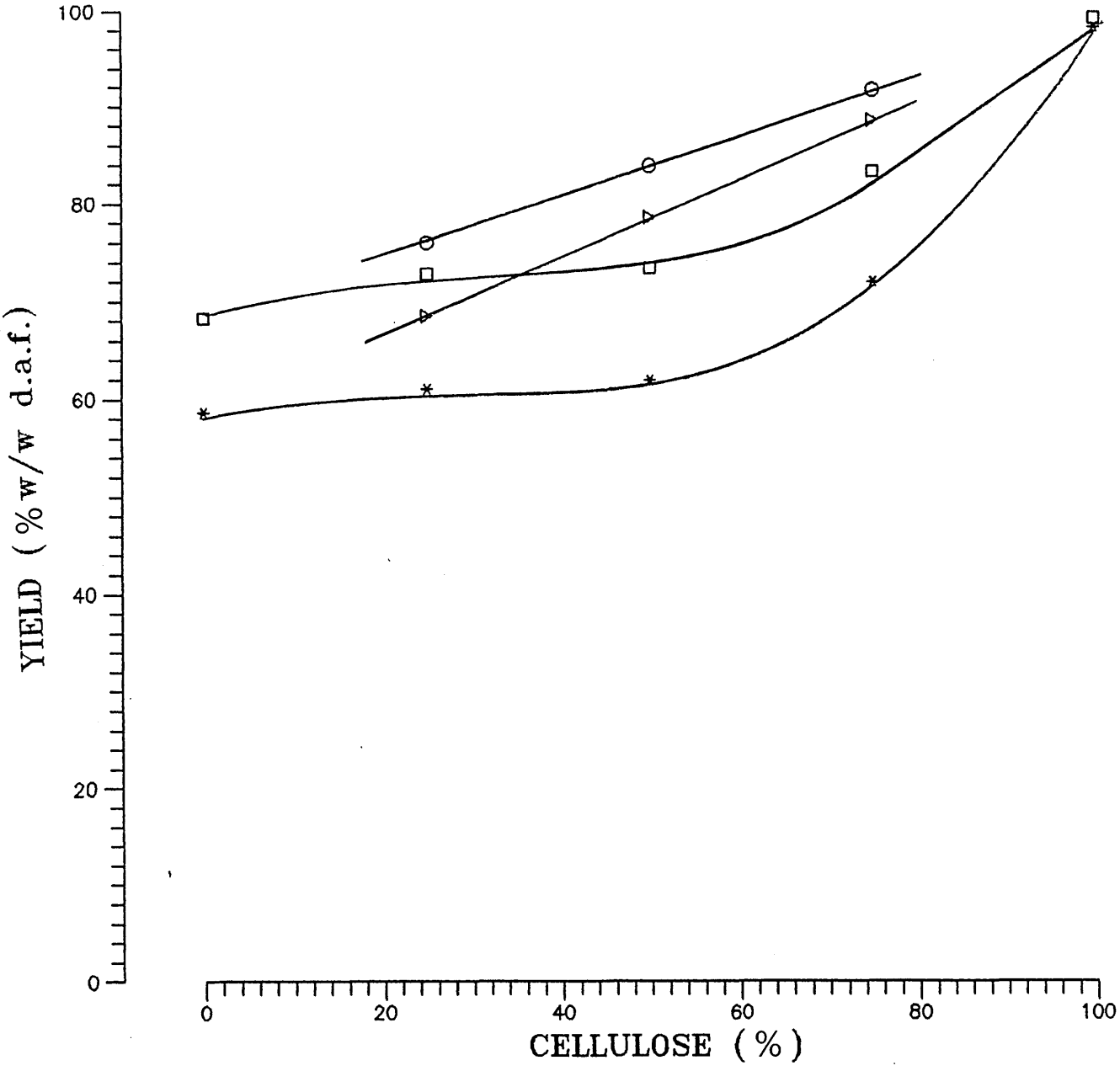


Figure 3.7c – The theoretical and experimental yields of total volatiles as a function of cellulose content and heating rate, at 900^{0}C and 30 seconds hold time.

* = 1^{0}C/second; □ = 1000^{0}C/second (experimental).

Δ = 1^{0}C/second; 0 = 1000^{0}C/second (theoretical).

Table 3.1 – The pyrolysis of **Sugar Cane Bagasse** in the wire–mesh reactor. Hold time at the peak temperature = 0 SECOND.
Sample size = 8–10 mg, 100–150 microns; carrier gas = helium with velocity 0.1 m/sec through mesh. Temp = temperature; Vol = total volatile; Gas = Gas plus water (by difference); H.Rate = heating rate; "+" = pyrolysis was not complete; n.d. = not determined.

	TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
+	200	1	01.2	98.8	n.d.	n.d.
+	200	100	00.2	99.8	n.d.	n.d.
+	200	100	00.4	99.6	n.d.	n.d.
+	200	1000	02.2	97.8	n.d.	n.d.
+	300	100	03.2	96.8	n.d.	n.d.
+	300	100	02.8	97.2	n.d.	n.d.
+	300	1000	04.3	95.7	n.d.	n.d.
	400	1	72.7	27.3	35.8	36.9
	400	1	73.1	26.9	n.d.	n.d.
+	400	100	29.5	70.5	n.d.	n.d.
+	400	100	15.0	85.0	n.d.	n.d.
+	400	100	27.7	72.3	n.d.	n.d.

see next page···

	TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
+	450	100	70.3	29.7	n.d.	n.d.
+	450	100	50.5	49.5	n.d.	n.d.
+	450	100	62.7	37.3	n.d.	n.d.
+	450	100	54.2	45.8	n.d.	n.d.
+	450	100	49.7	50.3	n.d.	n.d.
	480	1	86.9	13.1	n.d.	n.d.
	480	1	85.6	14.4	n.d.	n.d.
	480	100	79.5	20.5	n.d.	n.d.
	480	100	78.4	21.6	n.d.	n.d.
	480	100	77.9	22.1	n.d.	n.d.
	480	1000	70.9	29.1	n.d.	n.d.
	480	1000	68.0	32.0	n.d.	n.d.
+	480	1000	53.4	46.6	n.d.	n.d.
	500	1	86.2	13.8	n.d.	n.d.
	500	1	86.6	13.4	43.1	43.5
	500	1	86.7	13.3	44.4	42.3
	500	100	87.0	13.0	n.d.	n.d.
	500	100	85.1	14.9	n.d.	n.d.
	500	100	87.4	12.6	n.d.	n.d.
	500	100	86.4	13.6	n.d.	n.d.
	500	100	86.5	13.5	44.9	41.6

see next page···

	TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
	500	100	85.8	14.2	44.8	41.0
	500	1000	82.2	17.8	n.d.	n.d.
+	500	1000	66.3	33.7	34.1	32.2
	500	1000	78.6	21.4	43.3	35.3
	500	1000	76.4	23.6	42.2	34.2
	500	1000	71.3	28.7	40.1	31.2
	600	1	86.9	13.1	45.7	41.2
	600	1	89.2	10.8	44.8	44.4
	600	1	88.2	11.8	45.2	43.0
	600	1	87.2	12.8	43.8	43.4
	600	100	91.2	08.8	50.2	41.0
	600	100	90.4	09.6	48.4	42.0
	600	1000	89.5	10.5	48.3	41.2
	600	1000	90.3	09.7	50.0	40.3
	600	1000	89.9	10.1	50.3	39.6
	700	1	87.3	12.7	n.d.	n.d.
	700	100	93.8	06.2	n.d.	n.d.
	700	1000	95.2	04.8	n.d.	n.d.
	700	1000	94.2	05.8	49.5	44.7
	900	1	88.9	11.1	45.0	43.9

see next page···

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
900	100	93.6	06.4	53.4	40.2
900	100	94.0	06.0	53.2	40.8
900	1000	96.5	03.5	52.8	43.7
900	1000	96.8	03.2	53.2	43.6

Table 3.2 – The pyrolysis of **Sugar Cane Bagasse** in the wire–mesh reactor. Hold time at the peak temperature = 30 SECONDS.
Sample size = 8–10 mg, 100–150 microns; carrier gas = helium with velocity 0.1 m/sec through mesh. Temp = temperature; Vol = total volatile; Gas = Gas plus water (by difference); H.Rate = heating rate; "+" = pyrolysis was not complete; n.d. = not determined.

	TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
+	200	1	00.9	99.1	n.d.	n.d.
+	200	100	01.8	98.2	n.d.	n.d.
+	200	1000	02.8	97.2	n.d.	n.d.
+	300	1	20.6	79.4	n.d.	n.d.
+	300	100	20.2	79.8	n.d.	n.d.
+	300	1000	20.4	79.6	n.d.	n.d.
+	350	100	48.9	51.1	n.d.	n.d.
+	350	100	29.3	70.7	n.d.	n.d.
+	350	100	74.8	25.2	n.d.	n.d.
+	350	100	56.5	43.5	n.d.	n.d.
+	350	100	33.4	66.6	n.d.	n.d.
+	350	1000	55.5	44.5	n.d.	n.d.

see next page···

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
380	1	75.2	24.8	n.d.	n.d.
380	100	75.0	25.0	n.d.	n.d.
380	100	75.5	24.5	n.d.	n.d.
380	1000	85.3	14.7	n.d.	n.d.
400	1	75.0	25.0	n.d.	n.d.
400	1	73.6	26.4	n.d.	n.d.
400	1	74.6	25.4	37.1	37.5
400	1	74.1	25.9	36.8	37.3
400	100	81.8	18.2	43.0	38.8
400	100	83.0	17.0	45.1	37.9
400	100	81.2	18.8	42.4	38.8
400	1000	87.6	12.4	n.d.	n.d.
400	1000	87.5	12.5	n.d.	n.d.
400	1000	88.5	11.5	50.1	38.4
400	1000	88.5	11.5	48.6	39.9
400	1000	89.4	10.6	48.9	40.5
500	1	86.5	13.5	n.d.	n.d.
500	1	86.1	13.9	42.6	43.5
500	1	85.7	14.3	42.2	43.5
500	100	89.1	10.9	n.d.	n.d.
500	100	89.3	10.7	48.9	40.4

see next page···

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
500	100	89.9	10.1	45.7	44.2
500	1000	93.8	06.2	n.d.	n.d.
500	1000	92.7	07.3	n.d.	n.d.
500	1000	94.3	05.7	56.9	37.4
500	1000	93.6	06.4	56.4	37.2
500	1000	94.2	05.8	56.0	38.2
600	0.1	81.0	19.0	41.6	39.4
600	0.1	80.8	19.2	41.0	39.8
600	1	88.3	11.7	n.d.	n.d.
600	1	90.2	09.8	45.4	44.8
600	1	88.8	11.2	45.1	43.7
600	1	89.0	11.0	45.1	43.9
600	1	89.3	11.7	45.9	42.4
600	100	92.3	07.7	n.d.	n.d.
600	100	94.5	05.5	52.7	41.8
600	100	92.6	07.4	53.2	39.4
600	1000	96.5	03.5	n.d.	n.d.
600	1000	96.2	03.8	n.d.	n.d.
600	1000	95.5	04.5	54.9	40.6
600	1000	96.8	03.2	52.1	44.7
600	1000	95.7	04.3	54.6	43.1
600	1000	95.9	04.1	55.9	40.0

see next page···

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
700	1	86.7	13.3	45.6	41.1
700	1	88.3	11.7	n.d.	n.d.
700	100	93.1	06.9	53.1	40.0
700	1000	96.5	03.5	n.d.	n.d.
700	1000	97.1	02.9	n.d.	n.d.
700	1000	97.0	03.0	53.7	43.3
900	1	89.5	10.5	n.d.	n.d.
900	1	88.7	11.3	n.d.	n.d.
900	1	88.2	11.8	45.4	43.8
900	100	92.3	07.7	n.d.	n.d.
900	100	91.3	08.7	53.4	37.9
900	100	91.4	08.6	52.4	39.0
900	1000	96.3	03.7	n.d.	n.d.
900	1000	96.3	03.7	53.7	42.6
900	1000	98.1	02.9	53.6	44.5

Table 3.3 – The pyrolysis of Sugar Cane Bagasse in the wire–mesh reactor. Hold time at the peak temperature = 100 SECONDS. Sample size = 8–10 mg, 100–150 microns; carrier gas = helium with velocity 0.1 m/sec through mesh. Temp = temperature; Vol = total volatile; Gas = Gas plus water (by difference); H.Rate = heating rate; "+" = pyrolysis was not complete; n.d. = not determined.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
+ 200	1	1.1	98.9	n.d.	n.d.
+ 200	100	1.3	98.7	n.d.	n.d.
+ 200	1000	0.6	99.4	n.d.	n.d.
+ 300	1	19.4	80.6	n.d.	n.d.
+ 300	100	20.1	79.9	n.d.	n.d.
+ 300	1000	20.7	79.3	n.d.	n.d.
500	1	87.1	12.9	n.d.	n.d.
500	1	86.7	13.3	n.d.	n.d.
500	100	88.4	11.6	n.d.	n.d.
500	1000	92.7	07.3	n.d.	n.d.
700	1	86.9	13.1	n.d.	n.d.
700	100	93.1	06.9	n.d.	n.d.
700	1000	96.5	03.5	n.d.	n.d.

Table 3.4 – The pyrolysis of Silver Birch in the wire–mesh reactor. Hold time at the peak temperature = 0 SECOND. Sample size = 8–10 mg, 100–150 microns; carrier gas = helium with velocity 0.1 m/sec through mesh. Temp = temperature; Vol = total volatile; Gas = Gas plus water (by difference); H.Rate = heating rate; "+" = pyrolysis was not complete; n.d. = not determined.

	TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
	450	1	88.3	11.7	n.d.	n.d.
+	450	100	30.6	69.4	n.d.	n.d.
+	450	100	70.9	29.1	n.d.	n.d.
+	450	100	53.0	47.0	n.d.	n.d.
+	450	1000	43.8	56.2	n.d.	n.d.
+	450	1000	47.1	52.9	n.d.	n.d.
	480	1	88.9	11.1	n.d.	n.d.
	480	100	83.1	16.9	n.d.	n.d.
	480	1000	65.3	34.7	n.d.	n.d.
	480	1000	67.4	32.6	n.d.	n.d.
	500	1	90.8	09.2	n.d.	n.d.
	500	100	85.4	14.6	n.d.	n.d.

see next page···

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
500	1000	78.1	21.9	n.d.	n.d.
600	1	91.6	08.4	n.d.	n.d.
600	1	92.6	07.4	n.d.	n.d.
600	100	94.3	05.7	n.d.	n.d.
600	1000	91.7	08.3	n.d.	n.d.
700	1	91.7	08.3	n.d.	n.d.
700	100	94.8	05.2	n.d.	n.d.
700	1000	99.3	00.7	n.d.	n.d.
700	1000	98.7	01.3	n.d.	n.d.
900	1	91.3	08.7	n.d.	n.d.
900	100	95.9	04.1	n.d.	n.d.
900	1000	99.2	00.8	n.d.	n.d.

Table 3.5 – The pyrolysis of **Silver Birch** in the wire–mesh reactor.
Hold time at the peak temperature = 30 SECONDS.
Sample size = 8–10 mg, 100–150 microns; carrier gas = helium with velocity 0.1 m/sec through mesh. Temp = temperature; Vol = total volatile; Gas = Gas plus water (by difference); H.Rate = heating rate; "+" = pyrolysis was not complete; n.d. = not determined.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
380	1	75.0	25.0	n.d.	n.d.
380	100	71.5	28.5	n.d.	n.d.
380	1000	70.4	29.6	n.d.	n.d.
380	1000	71.3	28.7	n.d.	n.d.
400	1	76.6	23.4	43.3	33.3
400	100	81.7	18.3	49.0	32.7
400	1000	89.1	10.9	55.9	33.2
500	1	90.4	09.6	n.d.	n.d.
500	1	89.3	10.7	48.9	40.4
500	100	93.5	06.5	n.d.	n.d.
500	100	95.1	04.9	56.6	38.5
500	1000	95.8	04.2	n.d.	n.d.
500	1000	96.0	04.0	n.d.	n.d.

see next page···

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
500	1000	96.2	03.8	57.5	38.7
600	0.1	85.1	14.9	50.0	35.1
600	1	92.5	07.5	54.1	38.4
600	1	93.5	06.5	53.7	38.8
600	100	96.4	03.6	56.0	40.4
600	1000	98.6	01.4	56.8	41.8
700	1	91.9	08.1	n.d.	n.d.
700	1	91.4	08.6	n.d.	n.d.
700	1	93.4	06.6	54.3	39.0
700	100	96.0	04.0	n.d.	n.d.
700	100	97.1	02.9	57.0	40.1
700	1000	97.6	02.4	n.d.	n.d.
700	1000	99.8	00.2	56.5	43.3
900	1	93.3	06.7	52.2	41.1
900	100	96.3	03.7	55.1	41.2
900	1000	99.8	00.2	57.4	42.4

Table 3.6 – The pyrolysis of cellulose in the wire–mesh reactor.
Hold time at peak temperature = 30 SECONDS.
Sample size = 8–10 mg, 100–150 microns; carrier gas = helium with velocity 0.1 m/sec through mesh. Temp = temperature; Vol = total volatile; Gas = Gas plus water (by difference); H.Rate = heating rate.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
400	1	88.2	11.8	82.9	05.3
400	1000	90.4	09.6	81.1	09.3
600	0.1	96.8	03.2	84.6	12.2
600	0.1	96.2	03.8	85.6	10.6
600	0.1	96.2	03.8	86.5	09.7
600	1	97.1	02.9	85.3	11.8
600	1	97.4	02.6	85.9	11.5
600	1000	98.3	01.7	86.8	11.5
600	1000	98.8	01.2	87.0	11.8
900	1	98.4	01.6	86.6	11.8
900	1000	99.7	00.3	86.4	13.3
900	1000	99.0	01.0	85.4	13.6

Table 3.7 – The pyrolysis of **lignin** in the wire–mesh reactor.
Hold time at peak temperature = 30 SECONDS.
Sample size = 8–10 mg, 100–150 microns; carrier gas = helium with velocity 0.1 m/sec through mesh. Temp = temperature; Vol = total volatile; Gas = Gas plus water (by difference); H.Rate = heating rate.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
400	1	44.7	55.3	37.6	07.1
400	1000	50.6	49.4	40.0	10.6
600	0.1	53.8	46.2	40.6	13.2
600	0.1	54.4	45.6	39.0	15.4
600	1	57.2	42.8	42.0	13.2
600	1000	65.5	34.5	44.9	20.6
900	1	58.7	41.3	43.2	15.5
900	1000	68.3	31.7	45.0	23.3

Table 3.8 – The pyrolysis of **25%cellulose–75%lignin** in the wire–mesh reactor. Hold time at peak temperature = 30 SECONDS.
Sample size = 8–10 mg, 100–150 microns; carrier gas = helium with velocity 0.1 m/sec through mesh. Temp = temperature; Vol = total volatile; Gas = Gas plus water (by difference); H.Rate = heating rate.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
400	1	52.1	47.9	39.9	12.2
400	1000	58.7	41.3	45.1	13.6
600	0.1	59.2	40.8	43.6	15.6
600	0.1	60.1	39.9	45.0	15.1
600	1	60.1	39.9	43.1	17.0
600	1000	71.4	28.6	51.8	19.6
600	1000	70.6	29.4	51.1	19.5
900	1	61.1	38.9	44.2	16.9
900	1000	72.9	27.1	52.9	20.0

Table 3.9 – The pyrolysis of **50%cellulose–50%lignin** in the wire–mesh reactor. Hold time at peak temperature = 30 SECONDS.
Sample size = 8–10 mg, 100–150 microns; carrier gas = helium with velocity 0.1 m/sec through mesh. Temp = temperature; Vol = total volatile; Gas = Gas plus water (by difference); H.Rate = heating rate.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
400	1	54.1	45.9	42.8	11.3
400	1000	60.0	40.0	45.8	14.2
600	0.1	62.1	37.9	53.2	08.9
600	1	62.7	37.3	54.2	08.5
600	1000	71.8	28.2	60.1	11.7
900	1	61.9	38.1	54.4	07.5
900	1000	73.4	26.6	62.1	11.3

Table 3.10 – The pyrolysis of **75%cellulose–25%lignin** in the wire–mesh reactor. Hold time at peak temperature = 30 SECONDS.
Sample size = 8–10 mg, 100–150 microns; carrier gas = helium with velocity 0.1 m/sec through mesh. Temp = temperature; Vol = total volatile; Gas = Gas plus water (by difference); H.Rate = heating rate.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	VOL (%)	CHAR (%)	TAR (%)	GAS (%)
400	1	60.5	39.5	49.8	10.7
400	1000	70.5	29.5	57.8	12.7
600	0.1	71.6	28.4	61.8	09.8
600	0.1	71.1	28.9	64.1	07.0
600	1	72.3	27.7	63.2	09.1
600	1000	82.1	17.9	69.8	12.3
900	1	71.9	28.1	62.1	09.8
900	1000	83.2	16.8	68.9	14.3

Table 3.11 – The average of the yields of **total volatiles** for the pyrolysis of **cellulose**, **lignin**, **75%cellulose–25%lignin** (3C–1L), **50%cellulose–50%lignin** (C–L) and **25%cellulose–75%lignin** (1C–3L) in the wire–mesh reactor.

Hold time at peak temperature = 30 SECONDS.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	CEL (%)	LIG (%)	3C–1L (%)	C–L (%)	1C–3L (%)
400	1	88.2	44.7	60.5	54.1	52.1
400	1000	90.4	50.6	70.5	60.0	58.7
600	0.1	96.4	54.2	71.4	62.1	59.7
600	1	97.3	57.2	72.3	62.7	60.1
600	1000	98.6	65.5	82.1	71.8	71.0
900	1	98.4	58.7	71.9	61.9	61.1
900	1000	99.4	68.3	83.2	73.4	72.9

Table 3.12 – The average of the yields of tar for the pyrolysis of cellulose, lignin and 75%cellulose–25%lignin (3C–1L), 50%cellulose–50%lignin (C–L) and 25%cellulose–75%lignin (1C–3L) in the wire–mesh reactor.

Hold time at peak temperature = 30 SECONDS.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	CEL (%)	LIG (%)	3C–1L (%)	C–L (%)	1C–3L (%)
400	1	82.9	37.6	49.8	42.8	39.9
400	1000	81.1	40.0	57.8	45.8	45.1
600	0.1	85.6	39.8	63.0	53.2	44.3
600	1	85.6	42.0	63.2	54.2	43.1
600	1000	86.9	44.9	69.8	60.1	51.5
900	1	86.6	43.2	62.1	54.4	44.2
900	1000	85.9	45.0	68.9	62.1	52.9

Table 3.13 – The average of the yields of **char** for the pyrolysis of **cellulose**, **lignin** and **75%cellulose–25%lignin** (3C–1L), **50%cellulose–50%lignin** (C–L) and **25%cellulose–75%lignin** (1C–3L) in the wire–mesh reactor.

Hold time at peak temperature = 30 SECONDS.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	CEL (%)	LIG (%)	3C–1L (%)	C–L (%)	1C–3L (%)
400	1	11.8	55.3	39.5	45.9	47.9
400	1000	09.6	49.4	29.5	40.0	41.3
600	0.1	03.6	45.9	28.7	37.9	40.3
600	1	02.8	42.8	27.7	37.3	39.9
600	1000	01.5	34.5	17.9	28.2	29.0
900	1	01.6	41.3	28.1	38.1	38.9
900	1000	00.6	31.7	16.8	26.6	27.1

Table 3.14 – The experimental and theoretical results for the yields of **Total volatile** for the pyrolysis of the mixture **75%cellulose–25%lignin** in the wire–mesh reactor (experimental = 3C–1L^e, theoretical = 3C–1L^t). Hold time at peak temperature = 30 SECONDS.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	CEL (%)	LIG (%)	3C–1L^e (%)	3C–1L^t (%)
400	1	88.2	44.7	60.5	77.3
400	1000	90.4	50.6	70.5	80.5
600	0.1	96.4	54.2	71.4	85.9
600	1	97.3	57.2	72.3	87.3
600	1000	98.6	65.5	82.1	90.3
900	1	98.4	58.7	71.9	88.5
900	1000	99.4	68.3	83.2	91.6

Table 3.15 – The experimental and theoretical results for the yields of **tar** for the pyrolysis of the mixture **75%cellulose–25%lignin** in the wire–mesh reactor (experimental = 3C–1L^{e}, theoretical = 3C–1L^{t}).
Hold time at peak temperature = 30 SECONDS.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	CEL (%)	LIG (%)	3C–1L^{e} (%)	3C–1L^{t} (%)
400	1	82.9	37.6	49.8	71.6
400	1000	81.1	40.0	57.8	70.8
600	0.1	85.6	39.8	63.0	74.2
600	1	85.6	42.0	63.2	74.7
600	1000	86.9	44.9	69.8	76.4
900	1	86.6	43.2	62.1	75.8
900	1000	85.9	45.0	68.9	75.7

Table 3.16 – The experimental and theoretical results for the yields of **char** for the pyrolysis of the mixture **75%cellulose–25%lignin** in the wire–mesh reactor (experimental = 3C–1L^{e}, theoretical = 3C–1L^{t}).
Hold time at peak temperature = 30 SECONDS.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	CEL (%)	LIG (%)	3C–1L^{e} (%)	3C–1L^{t} (%)
400	1	11.8	55.3	39.5	22.7
400	1000	09.6	49.4	29.5	19.5
600	0.1	03.6	45.9	28.7	14.1
600	1	02.8	42.8	27.7	12.7
600	1000	01.5	34.5	17.9	09.7
900	1	01.6	41.3	28.1	11.5
900	1000	00.6	31.7	16.8	08.4

Table 3.17 – The experimental and theoretical results for the yields of **total volatile** for the pyrolysis of the mixture **50%cellulose–50%lignin** in the wire–mesh reactor (experimental = C–L^e, theoretical = C–L^t).
Hold time at peak temperature = 30 SECONDS.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	CEL (%)	LIG (%)	C–L^e (%)	C–L^t (%)
400	1	88.2	44.7	54.1	66.5
400	1000	90.4	50.6	60.0	70.5
600	0.1	96.4	54.2	62.1	75.3
600	1	97.3	57.2	62.7	77.3
600	1000	98.6	65.5	71.8	82.1
900	1	98.4	58.7	61.9	78.6
900	1000	99.4	68.3	73.4	83.9

Table 3.18 – The experimental and theoretical results for the yields of tar for the pyrolysis of the mixture **50%cellulose–50%lignin** in the wire–mesh reactor (experimental = C–L^e, theoretical = C–L^t).
Hold time at peak temperature = 30 SECONDS.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	CEL (%)	LIG (%)	C–L^e (%)	C–L^t (%)
400	1	82.9	37.6	42.8	60.3
400	1000	81.1	40.0	45.8	60.6
600	0.1	85.6	39.8	53.2	62.7
600	1	85.6	42.0	54.2	63.8
600	1000	86.9	44.9	60.1	65.9
900	1	86.6	43.2	54.4	64.9
900	1000	85.9	45.0	62.1	65.5

Table 3.19 – The experimental and theoretical results for the yields of **char** for the pyrolysis of the mixture **50%cellulose–50%lignin** in the wire–mesh reactor (experimental = C–L^e, theoretical = C–L^t).
Hold time at peak temperature = 30 SECONDS.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	CEL (%)	LIG (%)	C–L^e (%)	C–L^t (%)
400	1	11.8	55.3	45.9	33.5
400	1000	09.6	49.4	40.0	29.5
600	0.1	03.6	45.9	37.9	24.7
600	1	02.8	42.8	37.3	22.7
600	1000	01.5	34.5	28.2	17.9
900	1	01.6	41.3	38.1	21.4
900	1000	00.6	31.7	26.6	16.1

Table 3.20 – The experimental and theoretical results for the yields of **total volatile** for the pyrolysis of the mixture **25%cellulose–75%lignin** in the wire–mesh reactor (experimental = 1C–3L^{e}, theoretical = 1C–3L^{t}). Hold time at peak temperature = 30 SECONDS.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	CEL (%)	LIG (%)	1C–3L^{e} (%)	1C–3L^{t} (%)
400	1	88.2	44.7	52.1	55.6
400	1000	90.4	50.6	58.7	60.6
600	0.1	96.4	54.2	59.7	64.8
600	1	97.3	57.2	60.1	67.2
600	1000	98.6	65.5	71.0	73.8
900	1	98.4	58.7	61.1	68.6
900	1000	99.4	68.3	72.9	76.1

Table 3.21 – The experimental and theoretical results for the yields of **tar** for the pyrolysis of the mixture **25%cellulose–75%lignin** in the wire–mesh reactor (experimental = 1C–3L^{e}, theoretical = 1C–3L^{t}).
Hold time at peak temperature = 30 SECONDS.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	CEL (%)	LIG (%)	1C–3L^{e} (%)	1C–3L^{t} (%)
400	1	82.9	37.6	39.9	48.9
400	1000	81.1	40.0	45.1	50.3
600	0.1	85.6	39.8	44.3	51.3
600	1	85.6	42.0	43.1	52.9
600	1000	86.9	44.9	51.5	55.4
900	1	86.6	43.2	44.2	54.1
900	1000	85.9	45.0	52.9	55.2

Table 3.22 – The experimental and theoretical results for the yields of char for the pyrolysis of the mixture **25%cellulose–75%lignin** in the wire–mesh reactor (experimental = 1C–3L^{e}, theoretical = 1C–3L^{t}).
Hold time at peak temperature = 30 SECONDS.

TEMP (^{0}C)	H.RATE (^{0}C/SEC)	CEL (%)	LIG (%)	1C–3L^{e} (%)	1C–3L^{t} (%)
400	1	11.8	55.3	47.9	44.4
400	1000	09.6	49.4	41.3	39.4
600	0.1	03.6	45.9	40.3	35.2
600	1	02.8	42.8	39.9	32.8
600	1000	01.5	34.5	29.0	26.2
900	1	01.6	41.3	38.9	31.4
900	1000	00.6	31.7	27.1	23.9

CHAPTER 4

THE CHEMICAL ANALYSIS OF THE SPECIMENS AND THEIR CORRESPONDING LIQUID PYROLYSIS PRODUCTS.

4.1 – Introduction.

The analytical work reported in this Chapter was undertaken for three reasons. First, for the characterisation of the raw lignocellulosic materials used in this study, with particular emphasis being placed upon the accurate determination of the cellulose/lignin ratio for the natural occurring specimens; two independent methods were used, namely ^{13}C–Nuclear Magnetic Resonance, NMR, see section 4.2, and Elemental Analysis, CHN, see section 4.3. Secondly, for the broad characterisation of the pyrolysis tars, an exploratory search was made for any marked differences in the overall tar composition as a function of the pyrolysis conditions. The profile techniques of Vapour Pressure Osmometry, VPO, see section 4.4, and Elemental Analysis were used to conduct this survey; the objective of which was to select those pyrolysis tars, from the large number of tar specimens, that should be subjected to rigorous analysis. Finally, Gas Chromatography – Mass Spectrometry, GC–MS, spectra were obtained for the further characterisation of the tars produced by pyrolysing the natural and synthetic specimens, see section 4.5. In this final series of analytical experiments particular attention was paid to identifying the major compounds in the Sugar Cane Bagasse and Silver Birch pyrolysis tars.

4.2 – ^{13}C – Nuclear Magnetic Resonance.

Classical "wet chemistry" techniques normally enable the determination, on a weight basis, of the concentrations of individual compound classes, for example carbohydrates, in wood. However each of these groups of compounds has been shown to produce NMR signals in specific chemical–shift regions[35,79,87,143]. Thus, if the signal strength of an individual compound class, for example pure cellulose, is known, then it is possible to calculate from the NMR spectra the concentration of this compound class. This simple procedure may be used to obtain the cellulose/lignin ratio of a specimen by examination of the appropriate section of the NMR spectra. In general this NMR method is quicker and more accurate than the "wet chemistry" technique.

Solid–state ^{13}C–NMR spectra of selected specimens were acquired on a Bruker MSL–300 spectrometer using Bruker double resonance, double bearing, magic angle spinning, MAS, probe heads. The spectrometer was equipped with an 89 mm 7.05 tesla superconducting magnet, giving a proton resonance frequency of 300 MHz and a carbon–13 frequency of 75.468 MHz. Approximately 300 mg of sample was packed into 7 mm o.d. zirconium oxide rotors with Kel–F endcaps, and spun at 3500 to 4500 Hz. All spectra were acquired without any field locking, since the field drift is very small. Carbon–13 spectra were obtained using the standard cross polarisation, high power

dipolar decoupling, and magic angle sample spinning in conjunction with TOSS pulse sequences. An adamantane sample was used to give ^{13}C chemical shift referencing: the methylene resonance has a known chemical shift of 38.45 ppm relative to the normal standard of tetramethysilane. For further detailed explanation of this complex instrumental method see Dixon[34], Kalinowski[73] and Schaefer[113].

The ^{13}C CPMAS TOSS (Cross Polarisation with Magic Angle Spinning – Total Suppression of Side bands) spectra of the samples are shown in Figures 4.2a–4.2e. The signal assignments used for the samples of Sugar Cane Bagasse, Silver Birch and 50%cellulose:50%lignin, are based upon the results obtained from pure cellulose[35,79,94,106,143] and pure lignin[63,79,87,88,94,106].

From Figure 4.2a it can be seen that cellulose gave peaks at 65, 72, 89 and 105 ppm. The dominant resonances at 72 and 105 ppm are characteristic of the C–1, C–2, C–3 and C–5 carbons of cellulose; the shoulders at 64 and 89 ppm identify the cellulose carbons C–6 and C–4 respectively[35,79,94,106,143]. Each peak in this spectrum was given a symbol such as Ca, Cb, Cc, etc and the total area under these peaks was evaluated, and is reported in Table 4.2a.

Figure 4.2b shows the NMR spectrum of pure lignin. From this figure peaks are seen in the regions of 32, 55, 71, 105, 111, 131, 147 and 172 ppm. Signals at 32 ppm can be due to paraffinic carbons in fatty acids, and the methoxyl group in lignin gives rise to

the signal at 55 ppm[24,87,94]. The minor peak in the range 60 to 90 ppm lies within the region that is dominated by the presence of cellulose, see Figure 4.2a. The C–2 and C–6 carbons combine in the peak at 105 ppm, and the aromatic carbons in lignin are found at, approximately, 115, 130 and 150 ppm. The signal centred at 172 ppm may be assigned to the carbonyl carbon of lignin[24,87,94]. As in Figure 4.2a, each peak in Figure 4.2b was identified by a symbol La, Lb, Lc, etc, and the total area under these peaks was evaluated and is presented in Table 4.2a.

Figure 4.2c is the NMR spectrum of a "synthetic" material, whose composition was known to be, by weighing, 50%cellulose:50%lignin. From this spectrum the error in the determination of the cellulose and lignin content in the naturally occurring materials may be quantified. Signal assignments for this synthetic material were made based upon the results obtained for pure cellulose and pure lignin; the peaks characteristic of cellulose and lignin are identified in Figure 4.2c. The areas, representing the cellulose and lignin components were evaluated, and are reported in Table 4.2a; from these areas the percentage of cellulose and lignin was determined. These measurements gave 53.5% for the cellulose content and 49.8% for the lignin content of the synthetic material, which is in good agreement with its known composition. These results show that the ^{13}C NMR technique may be used to quantify the content of carbohydrates and lignin in these lignocellulosic materials.

Figures 4.2d and 4.2e are the ^{13}C–NMR spectra for Sugar Cane Bagasse and Silver Birch, respectively. The same procedure as above was used to determine the cellulose and lignin content in these specimens. As before the peaks of cellulose and lignin are indicated in the spectra, see again Figures 4.2d and 4.2e, and the total areas are presented in Table 4.2a. The cellulose and lignin content of these specimens of Sugar Cane Bagasse and Silver Birch, as determined by this ^{13}C–NMR technique is:

	Cellulose	Lignin
Bagasse	79.5%	22.3%
Silver Birch	73.2%	28.8%

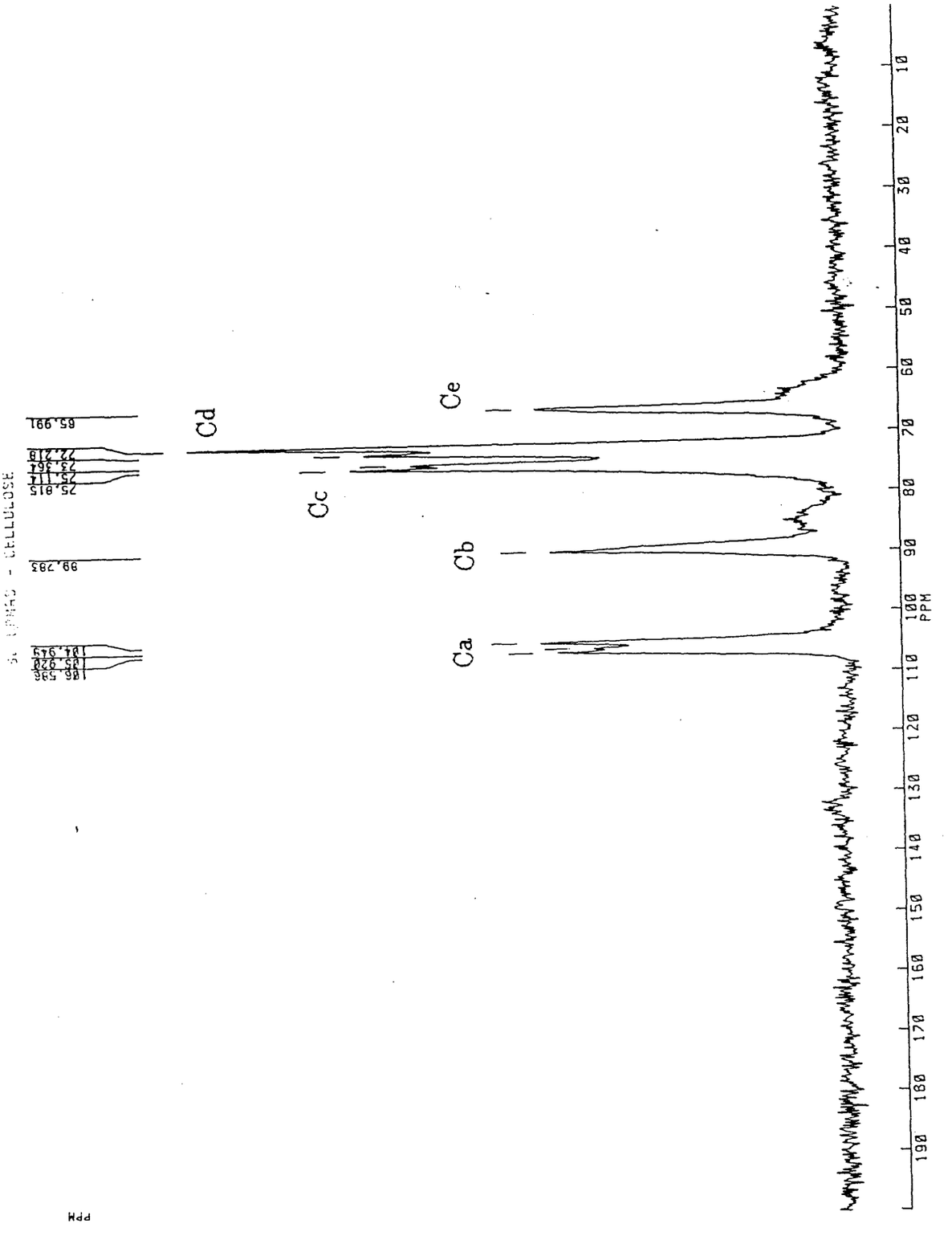


Figure 4.2a – ^{13}C – NMR – CPMAS TOSS – Cellulose.

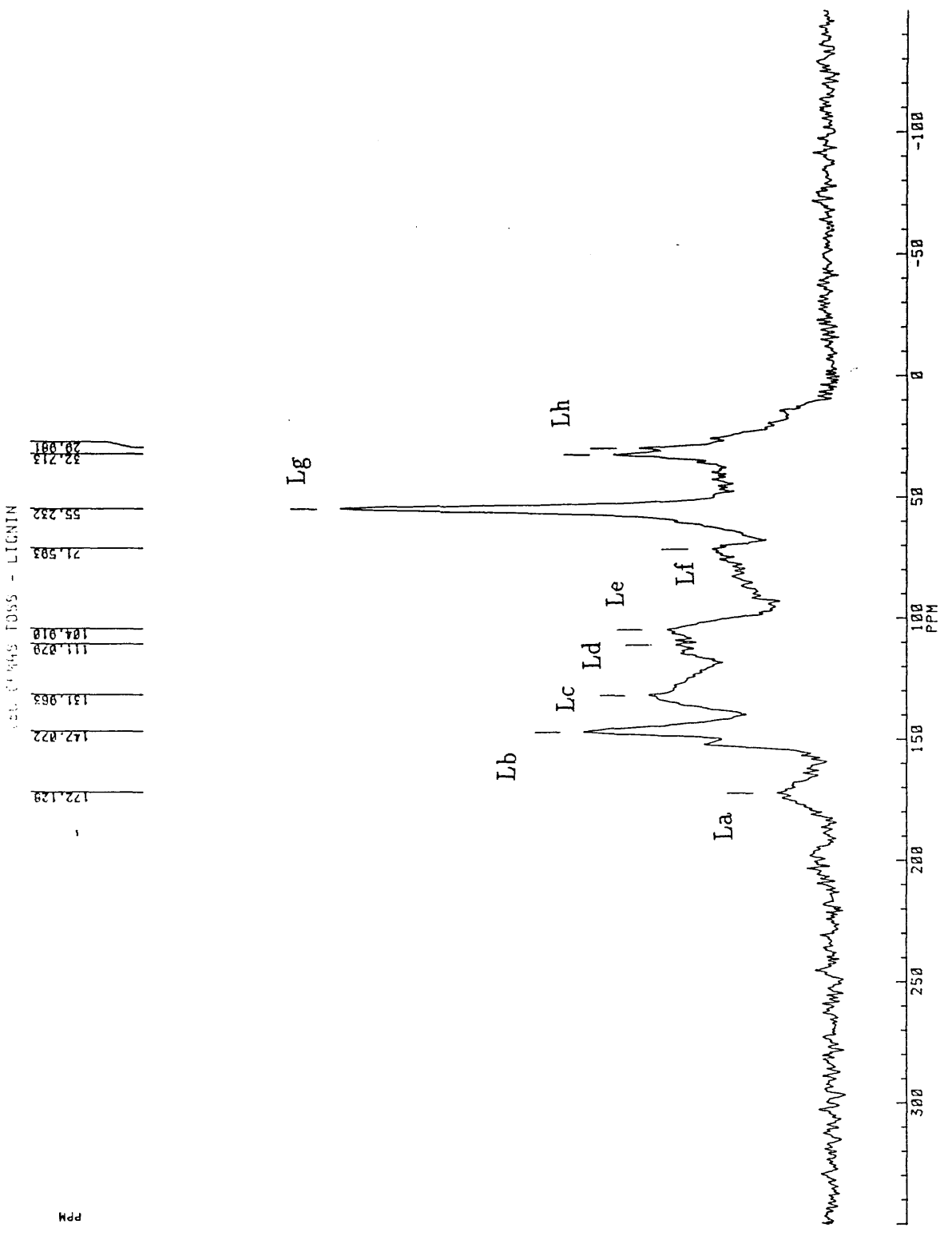


Figure 4.2b – ^{13}C – NMR – CPMAS TOSS – Lignin.

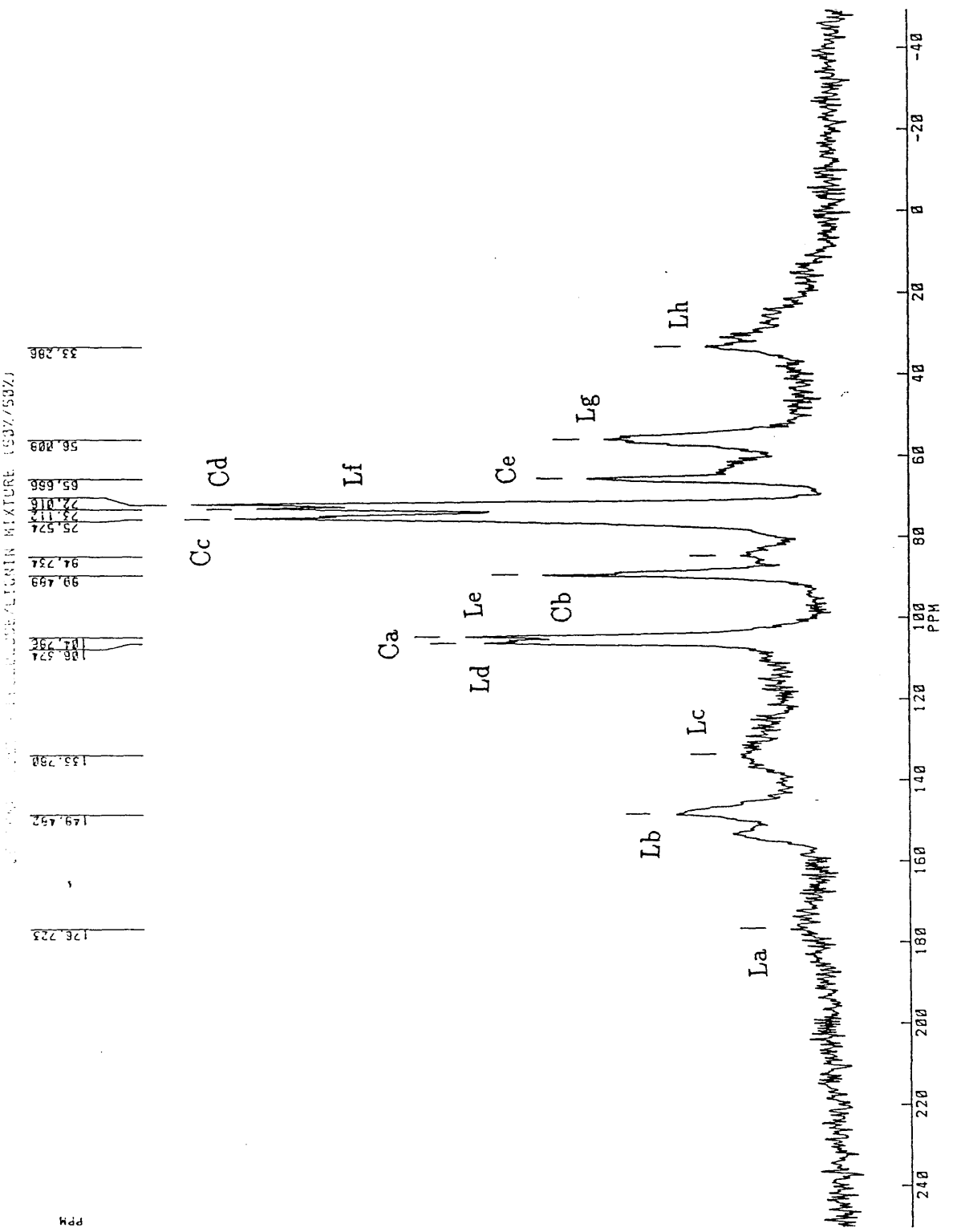


Figure 4.2c – ^{13}C – NMR – CPMAS TOSS – Mixture 50%Cel:50%Lig.

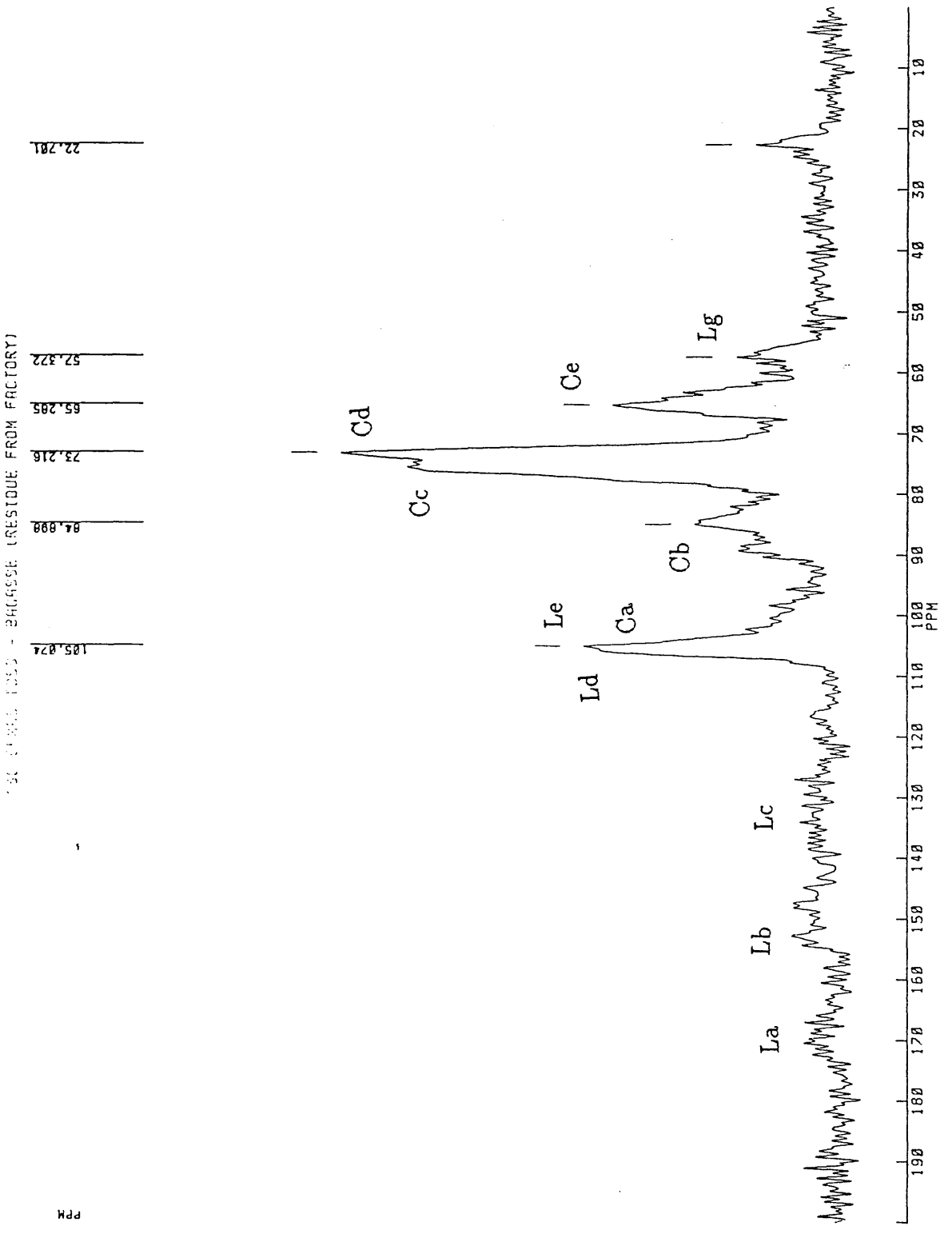


Figure 4.2d – ^{13}C – NMR – CPMAS TOSS – Sugar Cane Bagasse.

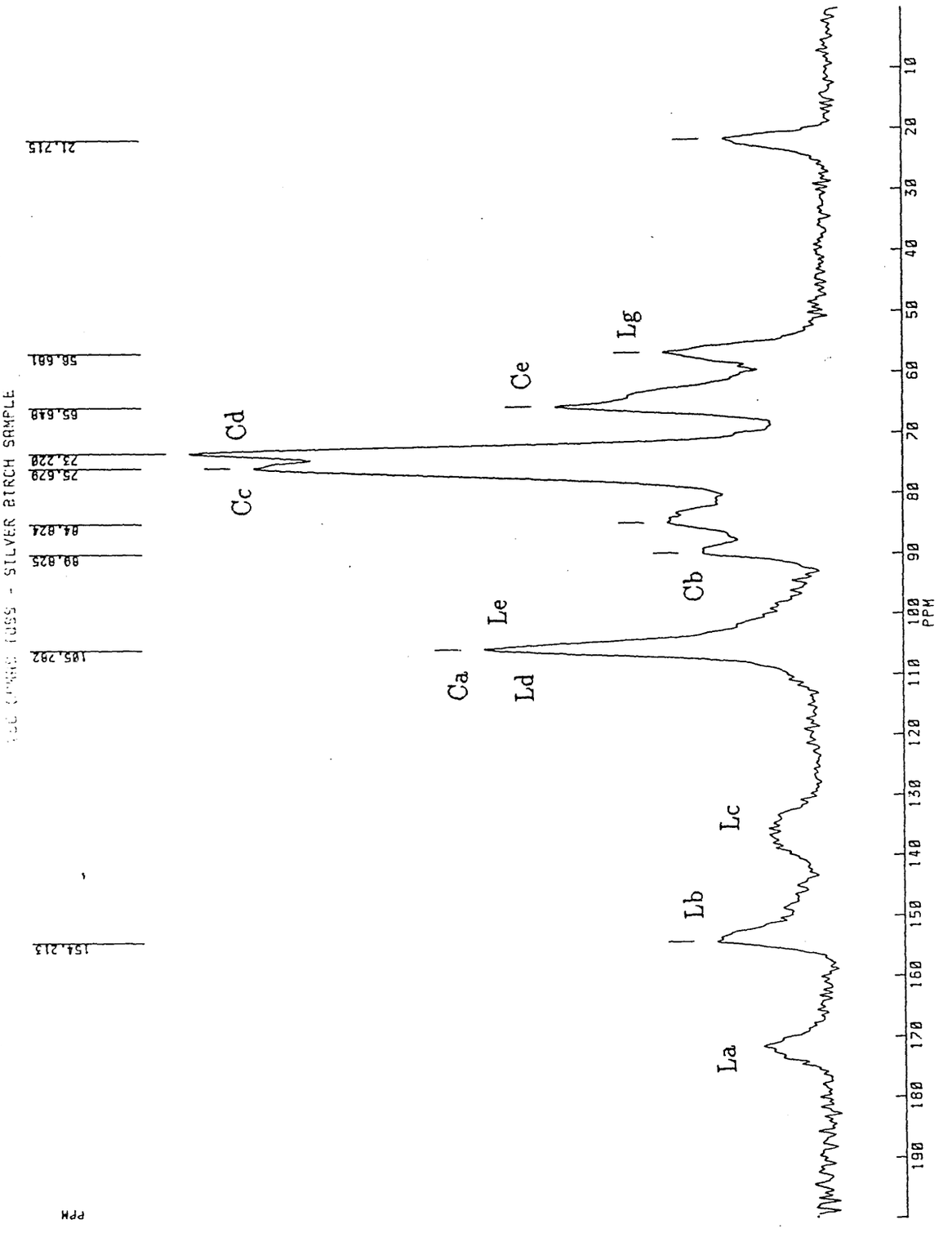


Figure 4.2e – ^{13}C – NMR – CPMAS TOSS – Silver Birch.

Sample	Cellulose	Lignin
Cellulose	894	0
Lignin	0	1125
50%Cel:50%Lig	478	560
Bagasse	711	251
Silver Birch	654	324

Table 4.2a – Areas corresponding to the content of cellulose and lignin in these lignocellulosic materials.

4.3 – Elemental Analysis.

The carbon/hydrogen ratio (by weight) was measured, using a Perkin Elmer 2400 CHN Elemental Analyser[26], for Sugar Cane Bagasse, Silver Birch, pure cellulose, pure lignin and the "synthetic" Sugar Cane Bagasse, namely 75%cellulose:25%lignin (3C–1L). The minimum error in these measurements of the carbon and hydrogen contents is governed by the accuracy of the elemental analyser, which has an absolute error of 1% for both elements. This value was used to calculate the total minimum error in these measurements, which is , therefore, not less than 15%, as shown in Figures 4.3a, 4.3b and 4.3c. These results are presented in Table 4.3a.

From Figure 4.3a it can be seen that there exists a linear relationship between the cellulose content and the carbon/hydrogen ratio. From the ^{13}C–NMR experiments, see section 4.2, the cellulose content of Sugar Cane Bagasse was found to be 79.5%, and that of Silver Birch 73.2%; these values, combined with the carbon/hydrogen ratio of these specimens, are also shown in Figure 4.3a. It can be seen that these natural lignocellulosic materials lie, within experimental error, on the straight line obtained for the synthetic materials. Therefore, by determining the carbon/hydrogen ratio of such naturally occurring materials their cellulose/lignin ratio may be estimated; it should be noted that due to the large error in the carbon/hydrogen values a more accurated measurement of the cellulose/lignin ratio is obtained from C^{13}–NMR data.

The carbon/hydrogen ratio of the pyrolysis tars obtained, with two different heating rates and a fixed peak temperature, from Sugar Cane Bagasse, Silver Birch and the "synthetic" mixtures was determined, see Table 4.3b. These results are shown graphically in Figure 4.3b, for the heating rate of 0.1^0C/second, and in Figure 4.3c for the fast heating rate of 1000^0C/second. From both figures it may be seen that when the lignin content is greater than, say, 25% the carbon/hydrogen ratio remains approximately constant. The low datum point in Figure 4.3c, for pure lignin, reflects a possibly large error in its measured hydrogen content, when compared to that of Nunn[101]. The carbon/hydrogen ratios of Sugar Cane Bagasse and Silver Birch tars lie on the smooth curves which were drawn from the "synthetic" materials data. Furthermore, see Figure 4.3b, the data points obtained for the Sugar Cane Bagasse and Silver Birch tars, produced at the moderated heating rate of 1^0C/second, lie upon the curve obtained for the "synthetic" mixtures which had been pyrolysed at 0.1^0C/second. Although the numerical values obtained for Sugar Cane Bagasse and Silver Birch tars are almost the same, irrespective of the heating rate, this may <u>not</u> be taken as an indication that their product distributions were identical, or even similar; this observation is confirmed by the GC–MS data for these tars, see section 4.5.

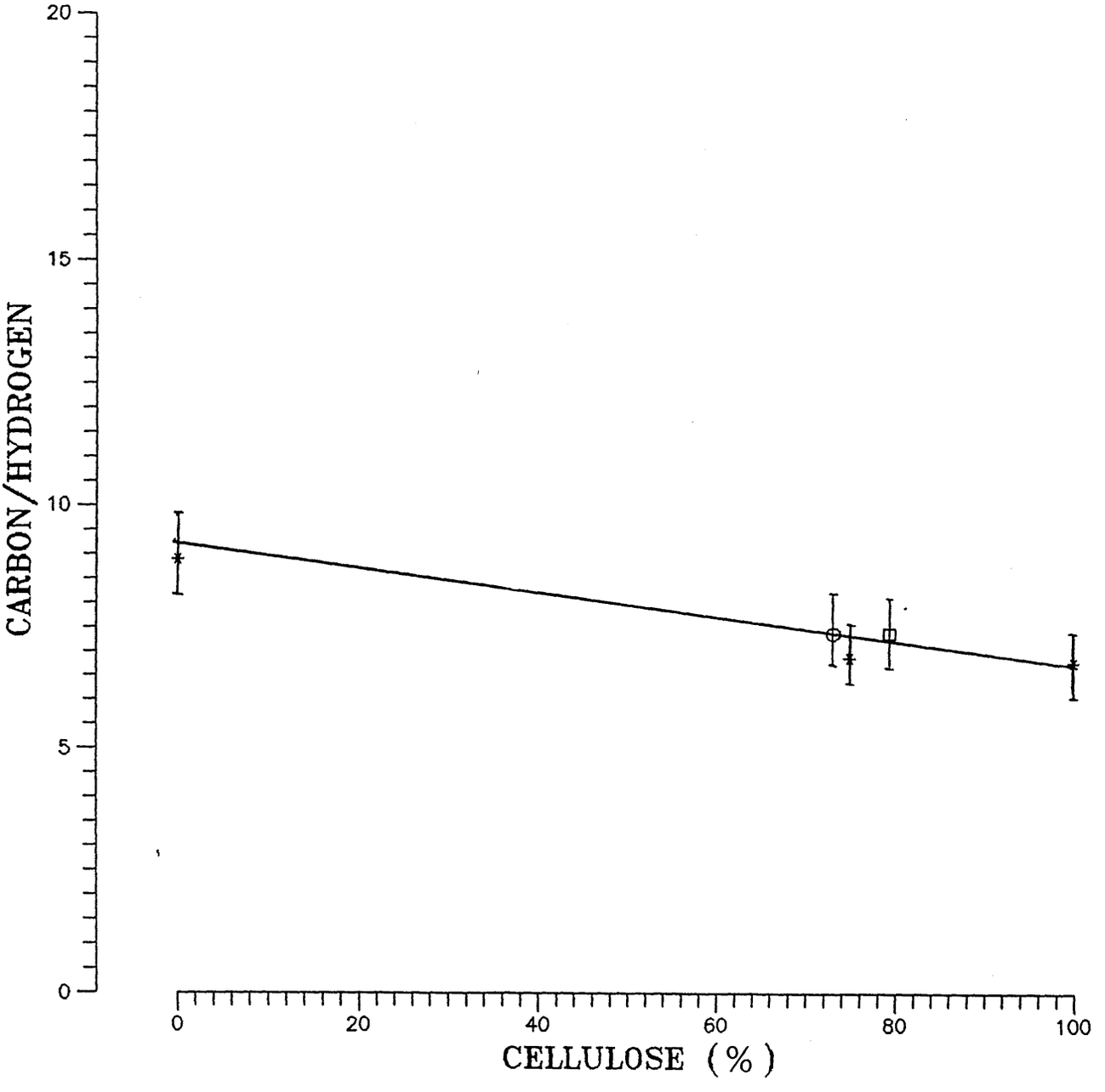


Figure 4.3a — Cellulose content in lignocellulosic materials as a function of the carbon/hydrogen ratio.

* = cellulose, lignin and "Synthetic" Bagasse

0 = Silver Birch; □ = Sugar Cane Bagasse.

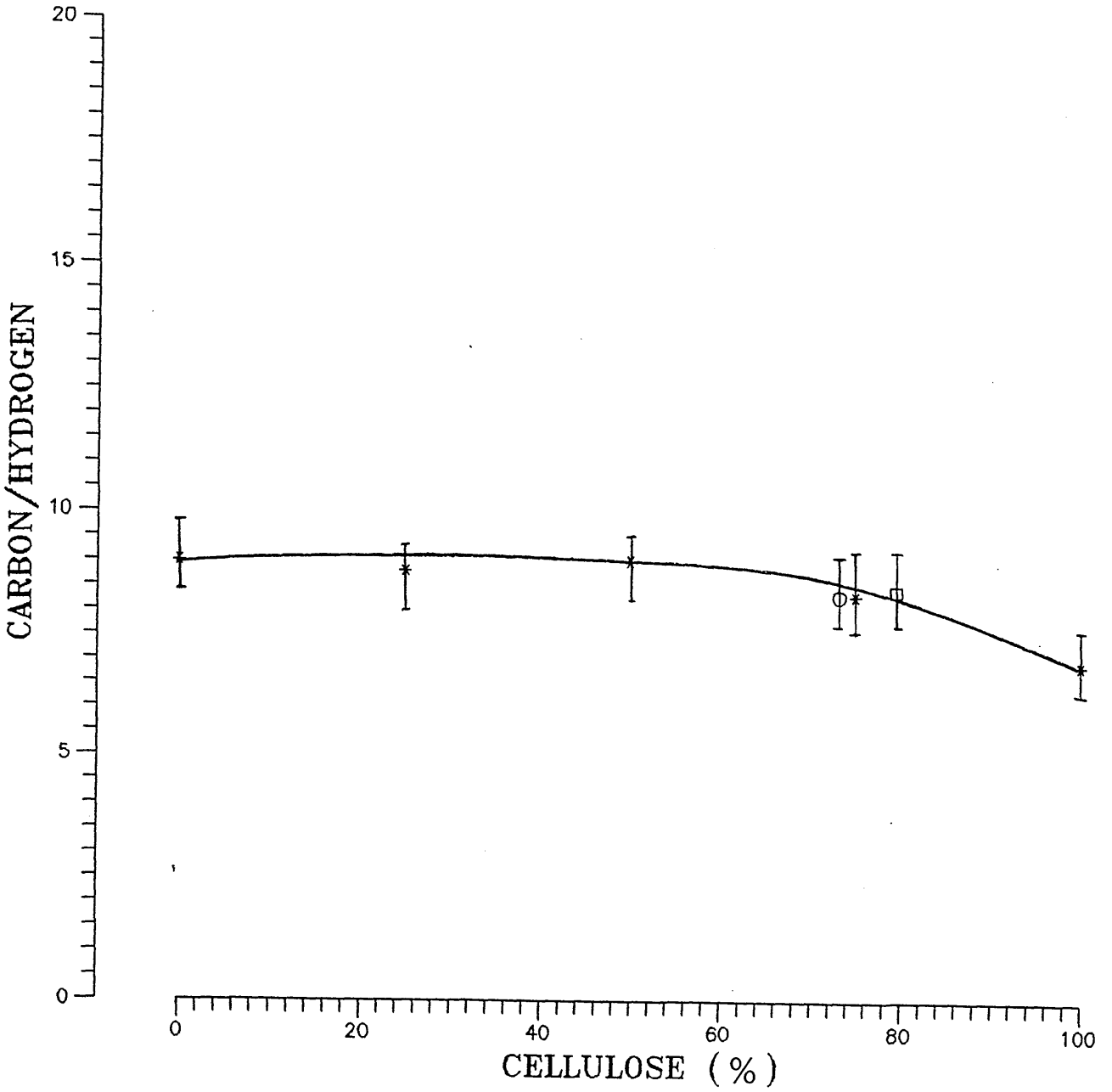


Figure 4.3b – Cellulose content as a function of the carbon/hydrogen ratio for the pyrolysis tars of lignocellulosic materials, obtained at 0.1^{0}C/second, 600^{0}C and 30 seconds hold time.

* = cellulose, lignin and "Synthetic" materials

0 = Silver Birch; □ = Sugar Cane Bagasse; (1^{0}C/second).

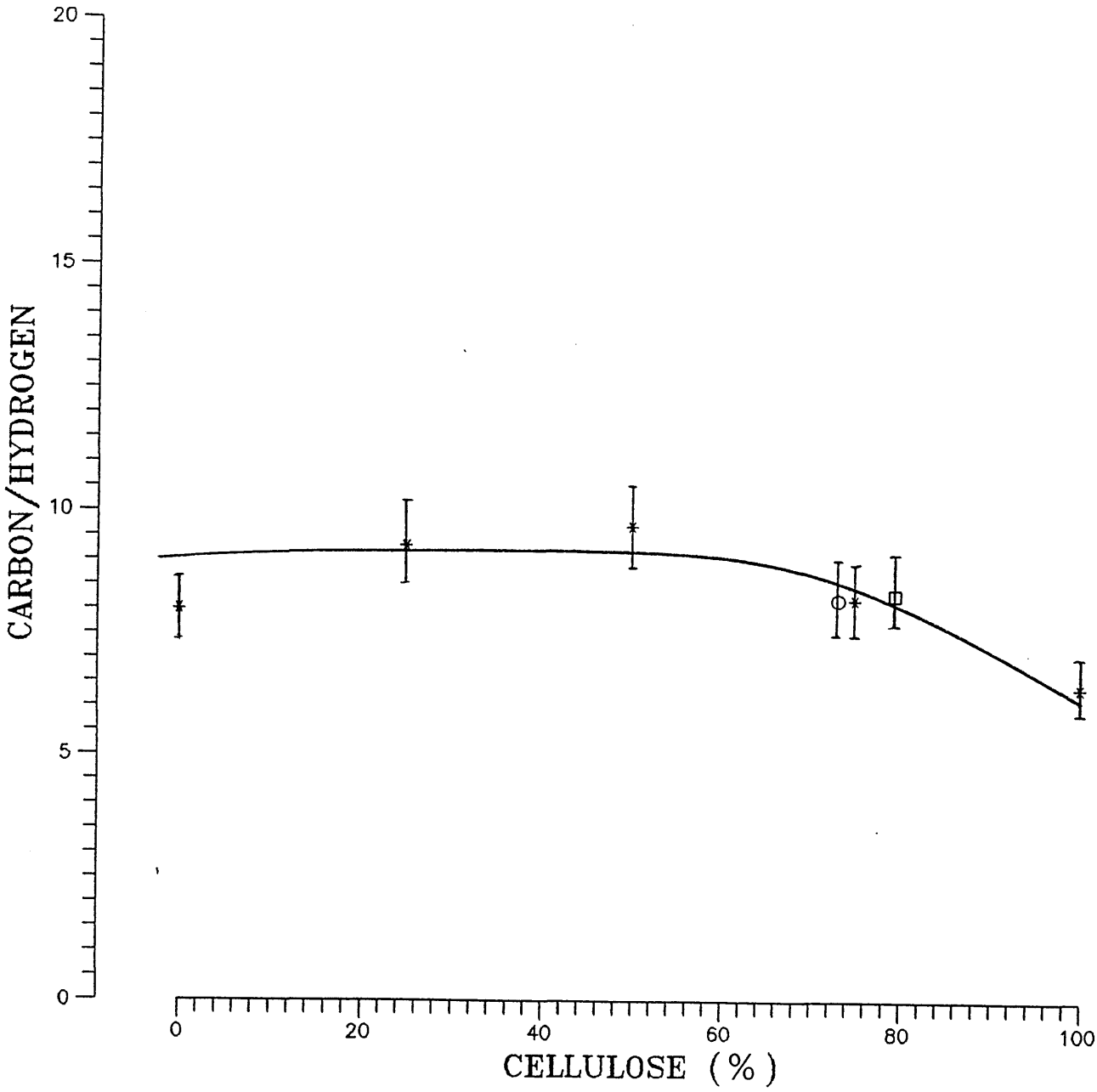


Figure 4.3c – Cellulose content as a function of the carbon/hydrogen ratio for the pyrolysis tars of lignocellulosic materials, obtained at 1000^{0}C/second, 600^{0}C and 30 seconds hold time.

* = cellulose, lignin and "Synthetic" materials

0 = Silver Birch; □ = Sugar Cane Bagasse.

Table 4.3a – Elemental Analysis of the Specimens used in pyrolysis.
3C–1L = 75%cellulose:25%lignin.

Specimen	Carbon (% by weight)	Hydrogen (% by weight)	C/H
Bagasse	46.3	6.3	7.4
Silver Birch	46.8	6.3	7.4
Cellulose	42.5	6.3	6.8
Lignin	53.5	6.0	8.9
3C–1L	44.2	6.4	6.9

Table 4.3b – Elemental Analysis of the Tar pyrolysis products.
Experimental conditions: peak temperature = 600^{0}C; hold time at the peak temperature = 30 seconds. H.Rate = heating rate.
3C–1L = 75%cellulose:25%lignin; C–L = 50%cellulose:50%lignin;
1C–3L = 25%cellulose:75%lignin.

Specimen	Carbon (% by weight)	Hydrogen (% by weight)	C/H	H.Rate (^{0}C/sec)
Bagasse	53.6	6.4	8.4	1
Bagasse	53.4	6.4	8.3	1000
Silver Birch	52.5	6.3	8.3	1
Silver Birch	52.4	6.4	8.2	1000
Cellulose	43.0	6.2	6.9	0.1
Cellulose	42.0	6.6	6.4	1000
Lignin	65.1	7.2	9.0	0.1
Lignin	61.2	7.7	8.0	1000
3C–1L	51.7	6.2	8.3	0.1
3C–1L	54.0	6.6	8.2	1000
C–L	64.9	7.2	9.0	0.1
C–L	63.8	6.6	9.7	1000
1C–3L	63.3	7.2	8.8	0.1
1C–3L	62.4	6.7	9.3	1000

4.4 — Vapour Pressure Osmometry.

The average molecular mass of these pyrolysis tars was obtained by Vapour Pressure Osmometry, VPO, using a Knauer Vapour Pressure Osmometer model 11.00. A brief discussion of the principle of this method is given below, followed by the experimental results.

Two matched thermistors are placed in a vapour saturated cell. The thermistors are connected to a Wheatstone Bridge and the cell temperature electronically thermostatted, to the very high stability of approximately $1/1000^{0}C$, this cell temperature was adjustable over a wide range. An equilibrium was attained between the two thermistors from which pure solvent drops hung, after 2 minutes the temperature difference between the two thermistors was zero. Then one of the solvent drops was replaced by a drop of sample solution, solvent vapour condensed on the thermistor surface as a result of the lower solvent vapour pressure. The heat resulting from condensation enthalpy raises the temperature of the solution drop, thereby raising its vapour pressure. Condensation of solvent vapour ends automatically when the vapour pressure of the solution drop reaches equilibrium with the vapour pressure of the pure solvent.

The resulting temperature difference between the two thermistors is proportional to the osmolal concentration. The measured

effect is slightly smaller than the theoretical value due to heat losses by conduction along the thermistor wire and convection within the measurement cell. Therefore the instrument must be calibrated with a series of osmolal calibration solutions made from standards of known molecular mass.

The Vapour Pressure Osmometer measures the total number of osmotically active particles. Using known sample concentrations the average molecular mass of the specimen in solution may be determined.

This technique was developed for the determination of the number average molecular mass of synthetic polymeric materials; from these studies, it has been shown that the upper limit of measurement is about 25000 and that the lower limit, which is governed by solute volatility, is around 100, see Billington[13]. There are several potentially severe experimental difficulties that must be carefully evaluated and controlled associated with vapour pressure osmometry measurements, for example variation of the instrumental calibration constant with molar mass, selection of an appropriate solvent, drop size etc; the combination of these parameters significantly increases not only the complexity but also the error in what appears to be, at first glance, a simple procedure, see again Billington[13].

Approximately 4 milligrammes of sugar cane bagasse or Silver Birch tars were placed into a 2 millilitres volumetric flask, and

the weight was determined on a five figure Sartorius balance. The 2 ml flask was filled with methanol, HPLC grade, from Sigma Chemicals Company. The concentration of the tar sample solution was calculated in grammes/litre and the average molecular mass determined by comparison to a similar concentration of phenanthrene, whose molecular mass is 178.2. The error associated with this analytical technique was estimated, from repetitive measurements of another known compound, namely dinonyl phthalate molecular mass 418.6, to be 20 units.

The number average molecular masses for the pyrolysis tars of Sugar Cane Bagasse and Silver Birch, obtained under differing pyrolysis conditions, are shown in Table 4.4a; these results are also presented graphically in Figures 4.4a and 4.4b. From these figures it can be seen that there appears to be a small overall decrease in the average molecular mass with increasing heating rate; for both Sugar Cane Bagasse and Silver Birch pyrolysis tars. Comparison between these figures shows that the tars produced from Silver Birch are, in general, of slightly greater average molecular mass than the corresponding Sugar Cane Bagasse tars; this observation is confirmed by the results obtained from the detailed gas chromatography–mass spectrometer analysis, see section 4.5.

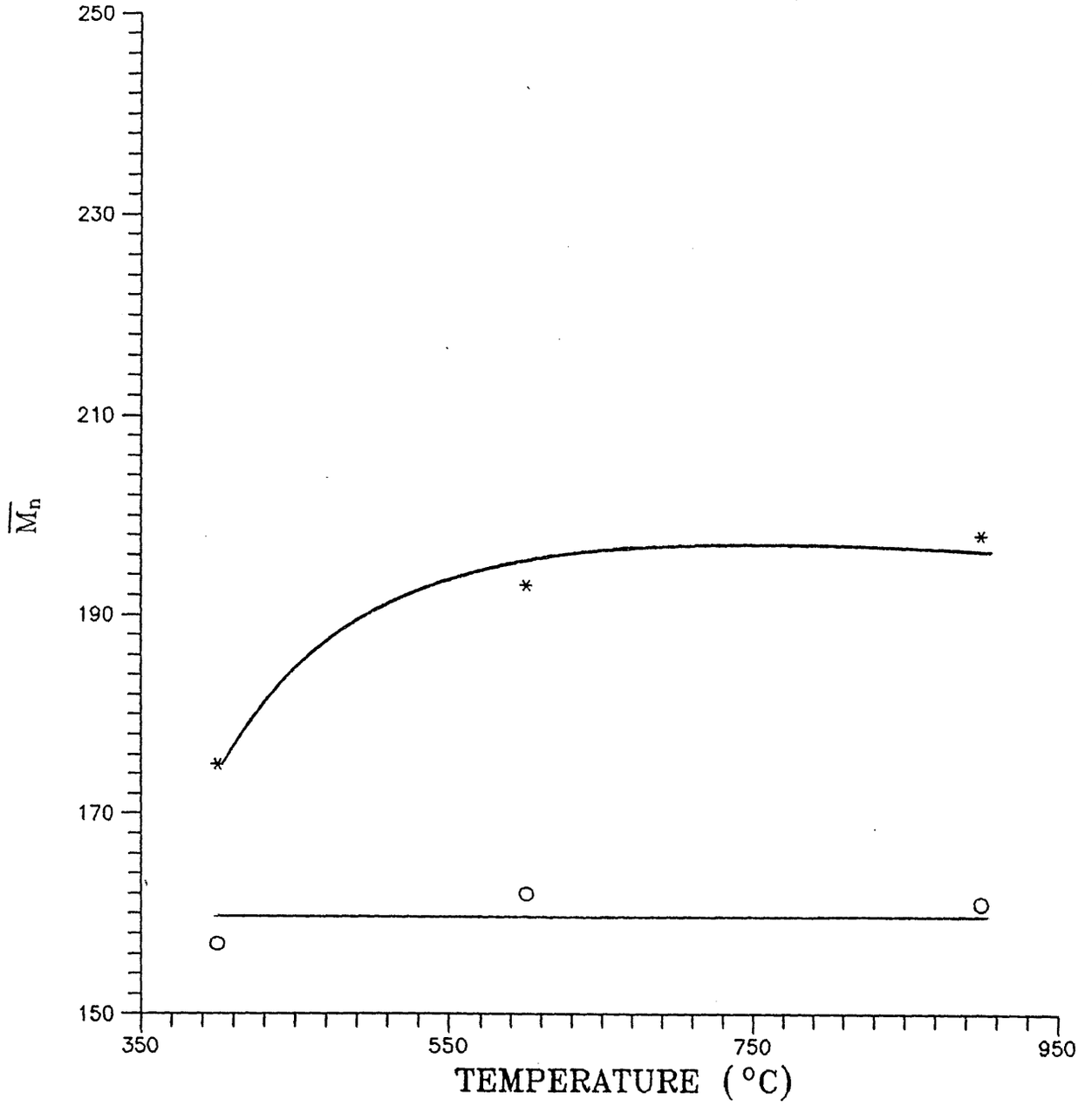


Figure 4.4a – Number average molecular mass as a function of peak temperature for the pyrolysis tar from Sugar Cane Bagasse at differing heating rates.

* = 1^0C/second ; 0 = 1000^0C/second.

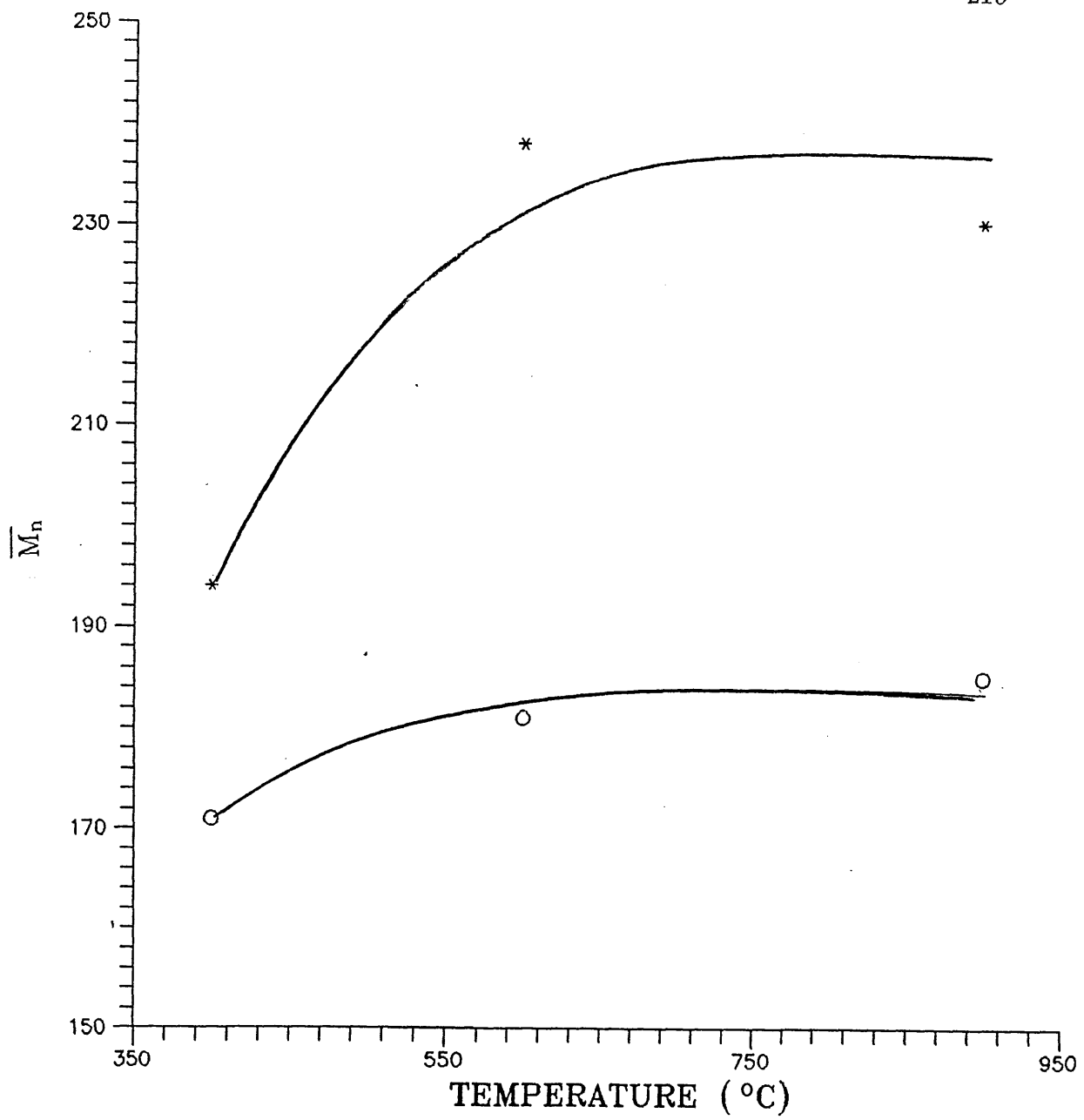


Figure 4.4b – Number average molecular mass as a function of peak temperature for the pyrolysis tar from Silver Birch at differing heating rates.

* = 1^0C/second ; 0 = 1000^0C/second.

Table 4.4a – The Average Molecular Mass ($\overline{M_n}$) of the pyrolysis tars.
Experimental conditions: hold time = 30 seconds.
Temp = temperature. H.Rate = heating rate.

Specimen	$\overline{M_n}$	Temp. (^{0}C)	H.Rate (^{0}C/sec)
Bagasse	175±10	400	1
Bagasse	157±10	400	1000
Bagasse	193±10	600	1
Bagasse	162±10	600	1000
Bagasse	198±10	900	1
Bagasse	161±10	900	1000
Silver Birch	194±10	400	1
Silver Birch	171±10	400	1000
Silver Birch	238±10	600	1
Silver Birch	181±10	600	1000
Silver Birch	230±10	900	1
Silver Birch	185±10	900	1000

4.5 – Gas Chromatography – Mass Spectrometry.

Gas Chromatography – Mass Spectrometry, GC–MS, was used to analyse the tars produced from the pyrolysis of the lignocellulosic materials. The objective of this analytical investigation was twofold; first the identification of the major primary compounds obtained by pyrolysing Sugar Cane Bagasse and Silver Birch. Secondly to establish, if possible, whether the Sugar Cane Bagasse tars originate primarily from the cellulose fraction of the bagasse, the lignin fraction of the bagasse or a combination of these two. Compound identifications were made by searching for correlations between these new data sets and the mass spectra of pure compounds as reported in previous published pyrolysis studies[8,36,37,38,66,72,91,112,121,122,129,134]. This procedure was adopted since the mass spectra library contained with the gas chromatography – mass spectrometry system employed in this research is tailored to the identification of pharmaceutical compounds; hence this data base is not relevant for the classes of compounds found in the pyrolysis tars of lignocellulosic materials. When making comparisons using reference spectra attention should be paid to important instrumental parameters, for example the ion source temperature and, in particular, the ionisation energy, since these can significantly modify the fragmentation pattern of samples that are thermally labile or readily fragmented[36].

The mass spectra of the major compounds in these

lignocellulosic materials tars, were obtained using a Kratos MS25 GC–MS system. A brief introduction to the principles of this technique is given below, followed by the experimental results.

The tars were separated in the gas chromatograph on a 25 meter by 0.22 mm internal diameter quartz capillary column coated with dimethyl siloxane, 0.25 microns film thickness, supplied by S.G.E LTD. Each tar sample was dissolved in a small quantity of methanol and 3 microlitres were injected into the gas chromatograph. The injection zone was set to 250^{0}C and the oven temperature held at 110^{0}C for 2 minutes, and then increased at 5^{0}C/minute up to 285^{0}C. Helium was used as the carrier gas, with a linear velocity of 30 cm/second. The electron impact mass spectra of these separated components were then obtained by their injection into the Kratos MS25.

The Kratos MS produced ions by the impact of 72 electrons volt. These ions were extracted from the ionisation chamber, accelerated and focused onto the source slit. The combined effect of the electrostatic and magnetic analysers was to focus ions with a given mass, but slightly varying energies and angular direction, onto the collector slit, which itself is at the position of double–focusing. When the ion beam passes through the collector slit it strikes the first dynode of the electron multiplier, this amplifies the ion current by up to 10^6 depending upon the multiplier voltage. This current is converted into a voltage which is then digitised and recorded, along with other important instrument parameters such as scan number and scan position, on a

minicomputer system. The minicomputer then processed the raw data and generated, if required, a cross scan report and also the individual fragmentation patterns. These GC–MS spectra are the characteristic "fingerprints" of the individual components of the complex liquids formed during the pyrolysis of the lignocellulosic materials.

A large number of tar samples were analysed by the GC–MS technique as the result obtained earlier, from the profile techniques of VPO and CHN, had not enabled a representative selection to be made. The differing pyrolysis conditions under which these tar samples were generated are presented in tabular form, see Table 4.5a. For every tar sample analysed its cross scan report is presented. The individual scan numbers are shown along the horizontal axis in these figures versus a representation of the ion current along the vertical axis, labelled intensity. If a large peak is observed at, for example, position "x" in the cross scan report, then the corresponding fragmentation pattern of this compound may be seen by consulting the report titled scan "x", where the m/z ratio is plotted versus the peak intensity, see Appendix 1.

Figure	Tar Sample	Pyrolysis Conditions
4.5a	Cellulose	0.1^0C/sec; 600^0C; 30sec.
4.5b	Cellulose	1^0C/sec; 600^0C; 30sec.
4.5c	Cellulose	1000^0C/sec; 600^0C; 30sec.
4.5d	Levoglucosan	N.A.
4.5e	Lignin	0.1^0C/sec; 600^0C; 30sec.
4.5f	Lignin	1000^0C/sec; 600^0C; 30sec.
4.5g	75%Cel:25%Lig	1000^0C/sec; 600^0C; 30sec.
4.5h	50%Cel:50%Lig	1000^0C/sec; 600^0C; 30sec.
4.5i	25%Cel:75%Lig	1000^0C/sec; 600^0C; 30sec.
4.5j	Bagasse	1^0C/sec; 400^0C; 30sec.
4.5k	Bagasse	1000^0C/sec; 400^0C; 30sec.
4.5l	Bagasse	1^0C/sec; 600^0C; 30sec.
4.5m	Bagasse	1000^0C/sec; 600^0C; 30sec.
4.5n	Bagasse	1^0C/sec; 900^0C; 30sec.
4.5o	Bagasse	1000^0C/sec; 900^0C; 30sec.
4.5p	Silver Birch	1^0C/sec; 400^0C; 30sec.
4.5q	Silver Birch	1000^0C/sec; 400^0C; 30sec.
4.5r	Silver Birch	1^0C/sec; 900^0C; 30sec.
4.5s	Silver Birch	1000^0C/sec; 900^0C; 30sec.

Table 4.5a – Samples analysed by GC–MS with their experimental pyrolysis conditions. N.A = not applicable

The cross scan reports for the cellulose pyrolysis tars (600^0C peak temperature and 30 seconds hold time, for the three heating rates of 0.1^0C/second, 1^0C/second and 1000^0C/second) are shown in Figures 4.5a, 4.5b and 4.5c, respectively. In Figure 4.5a the large peak at scan number 30 may be neglected since it can be assigned, based upon the detailed mass spectra data, to the methanol solvent; it is clearly seen, therefore, that the product distribution of these cellulose pyrolysis tars is independent of the heating rate. The relatively small number of compounds produced by pyrolysing cellulose reflects its simple linear structure, see Chapter 1, section 1.7; the broad peak, which may be used as a "semaphore" indicating the presence of cellulose, centred at scan number 418 has been identified in past research as levoglucosan[121,122,129]. The detailed output for scan 418 is presented in Figure 4.5c/scan418; analysis of this fragmentation pattern strongly suggests the assignment of levoglucosan. The characteristic m/z peaks for this compound have been reported to be, in descending order of ion intensity 60, 57, 73, 70, 98[36,72]. From Figure 4.5c it is also seen that this compound is, by far, the most abundant pyrolysis product of cellulose; in past research, conducted in a fluidised bed reactor, it has been reported that the yield of levoglucosan may be as high as 85%[134,135].

In order to verify the identification of this compound as levoglucosan, and also to check the experimental procedures, a pure sample of levoglucosan was obtained from the Sigma Chemical Company and subjected to the same GC–MS analysis procedure. The cross scan report for this specimen is shown in Figure 4.5d where a large peak

centred at scan number 436 is clearly seen. The fragmentation pattern is shown in Figure 4.5d/scan436. Two further injections of this pure levoglucosan were made and the fragmentation patterns obtained at 40eV and 15eV, see Figures 4.5d/scan102 and 4.5d/scan155. It is seen that the major peaks of levoglucosan namely 60, 57, 73, maintain a constant relationship; and that the parent ion, mass 162, is of secondary importance in this spectra of levoglucosan. The absence of the parent peak, $^{m/z}$ 162, in all these figures, shows that levoglucosan is very easily fragmented.

As a general rule unless the procedure outlined above is followed, (i.e. from a mass spectrum identify the most likely compound(s), obtain it in pure form, subject it to the same analytical procedure and show that it gives a wholly identical spectrum), no identification should be taken to be "correct", but must be regarded as tentative. Furthermore this procedure must be followed if quantitative results are desired in order to determine the sensitivity, or calibration constant, of the mass spectrometer and its associated gas chromatograph for the compound of interest. It can be seen therefore that for complex mixtures, such as pyrolysis tars, the quantification of product distributions is a difficult and laborious procedure.

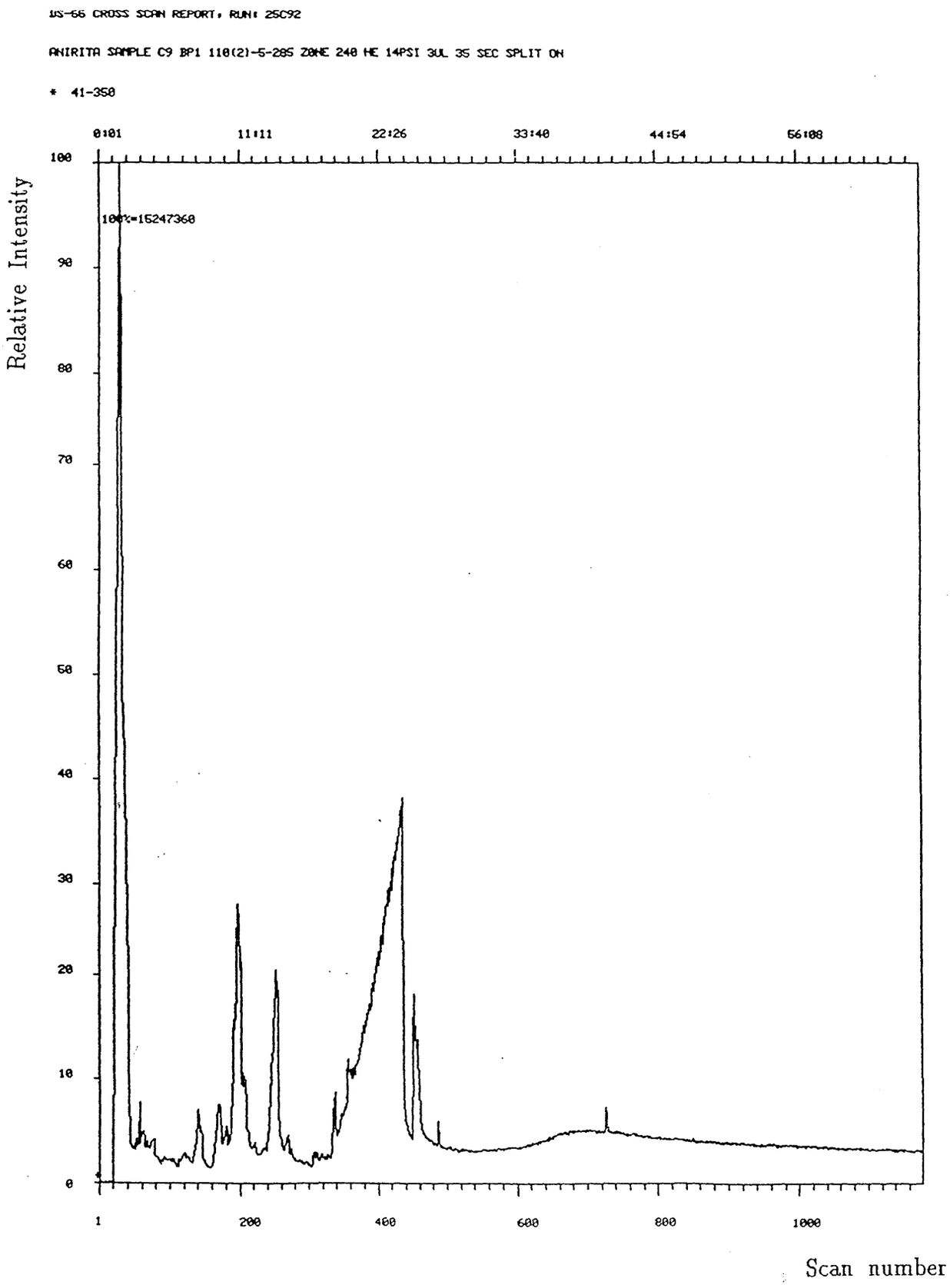


Figure 4.5a – Cellulose – Cross Scan Report.
(pyrolysis conditions 0.1^{0}C/sec; 600^{0}C; 30sec.)

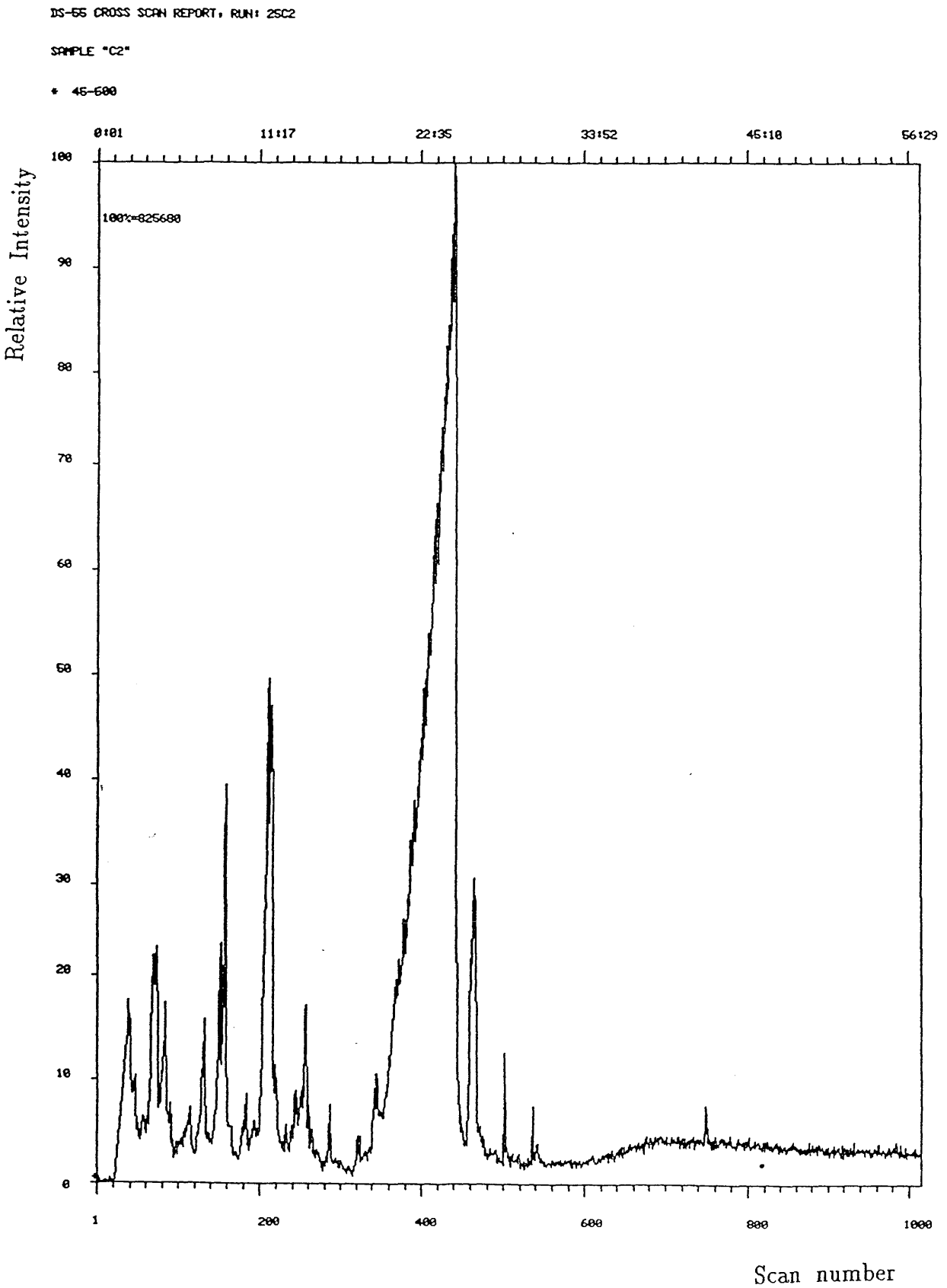


Figure 4.5b – Cellulose – Cross Scan Report.

(pyrolysis conditions 1^0C/sec; 600^0C; 30sec.)

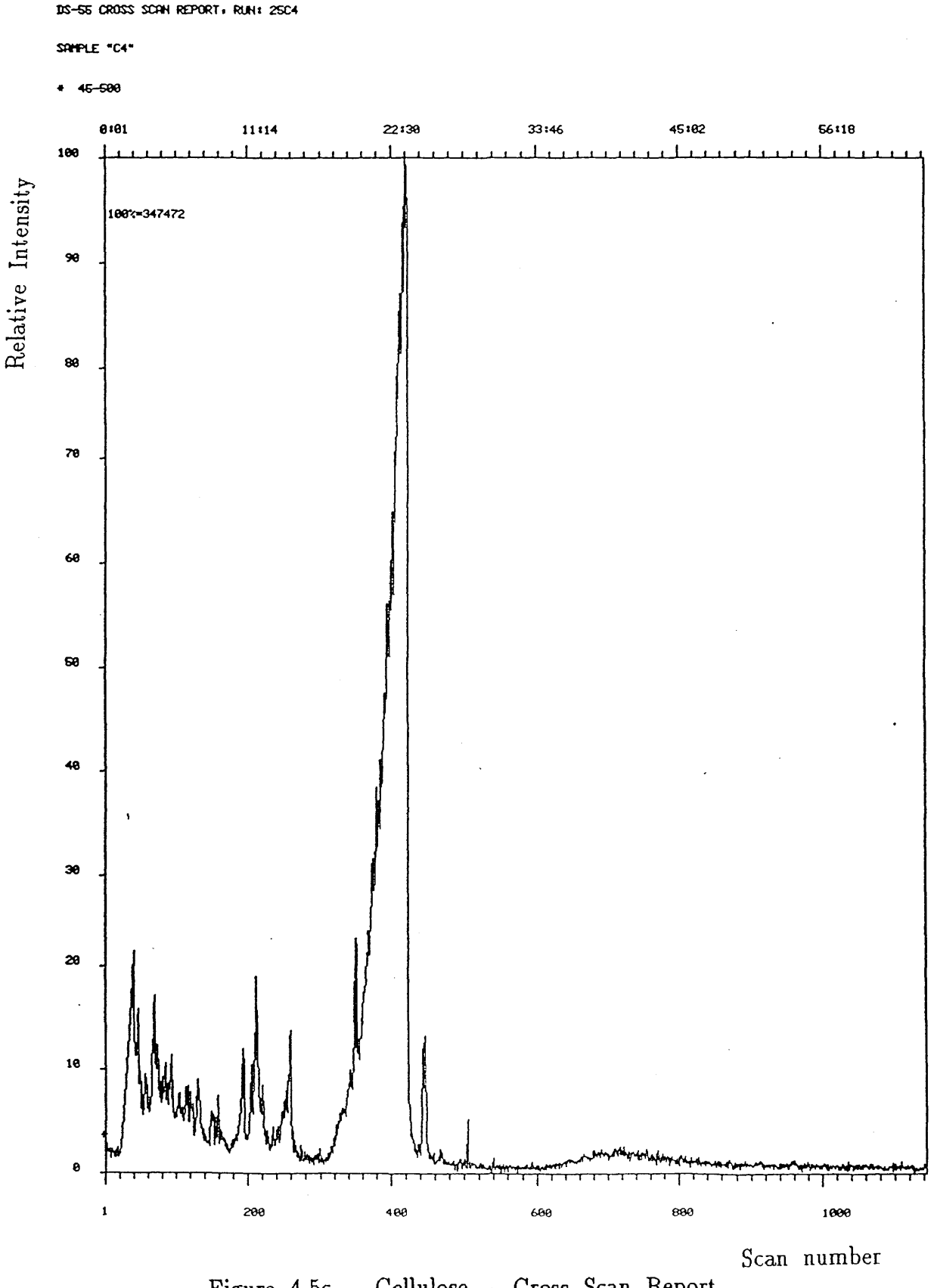


Figure 4.5c – Cellulose – Cross Scan Report.

(pyrolysis conditions 1000^{0}C/sec; 600^{0}C; 30sec.)

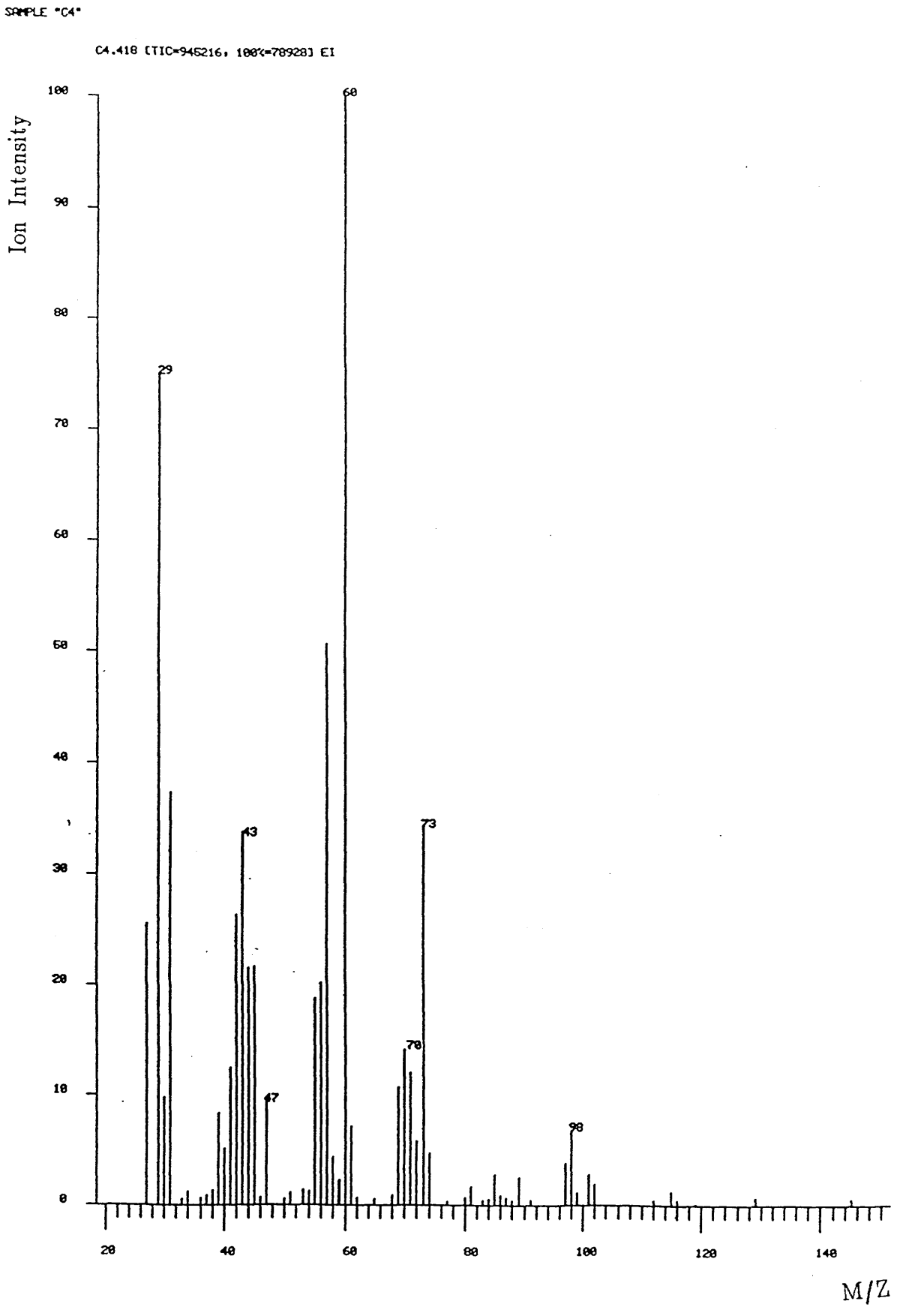


Figure 4.5c/scan418 — Fragmentation pattern of the major compound present in the cellulose pyrolysis tar at 72 eV.

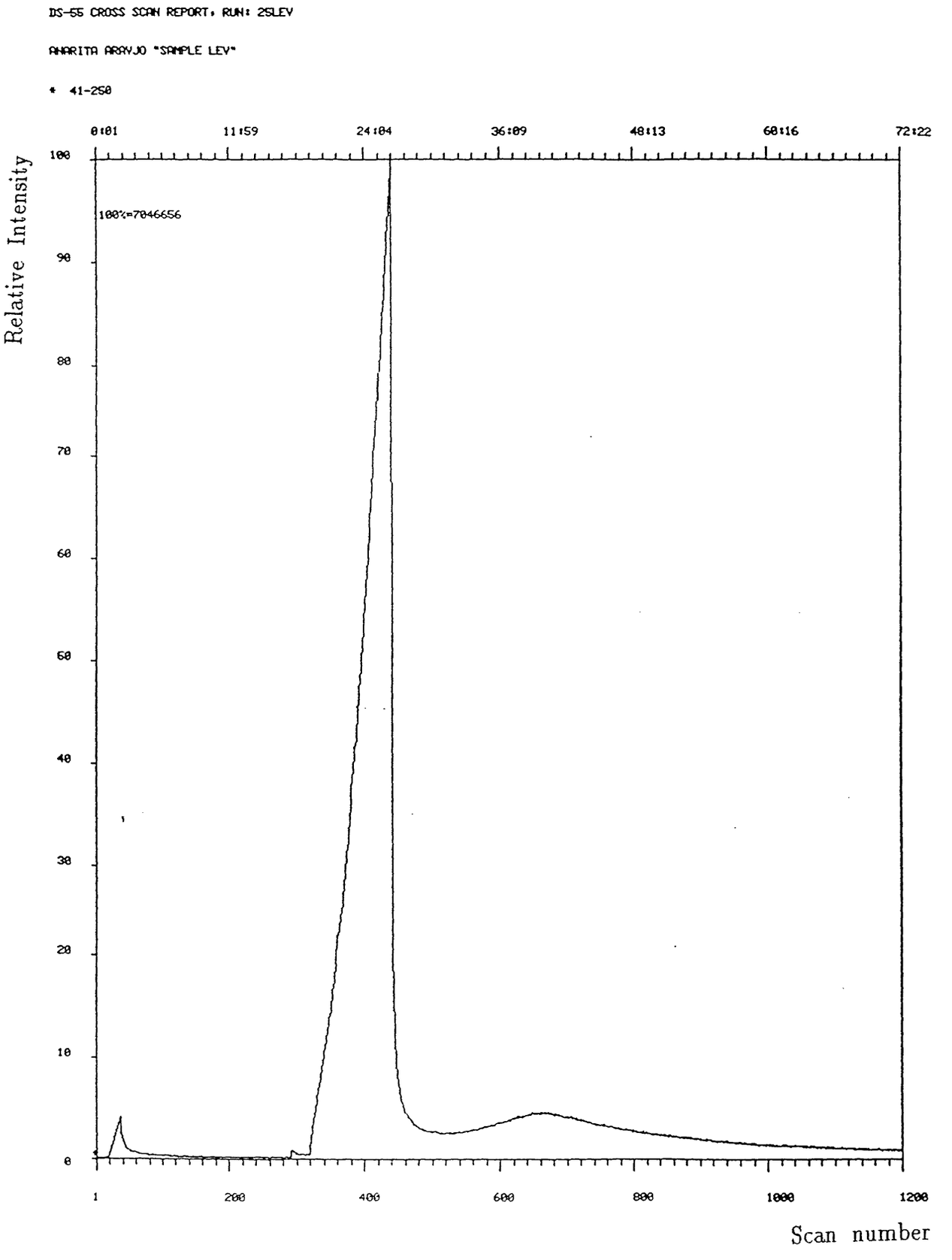


Figure 4.5d – Levoglucosan – Cross Scan Report.

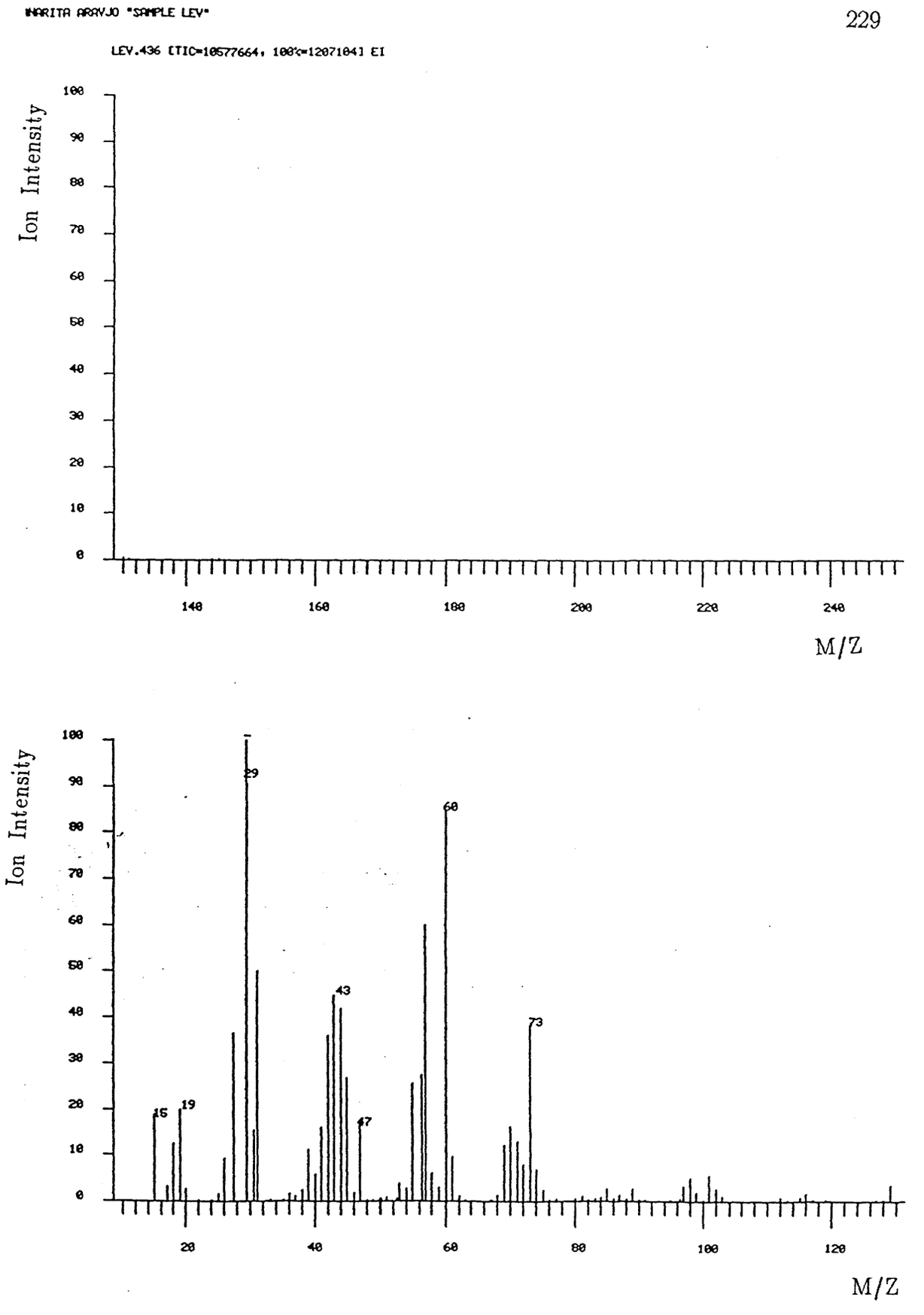


Figure 4.5d/scan436 – Fragmentation pattern of levoglucosan at 72 eV.

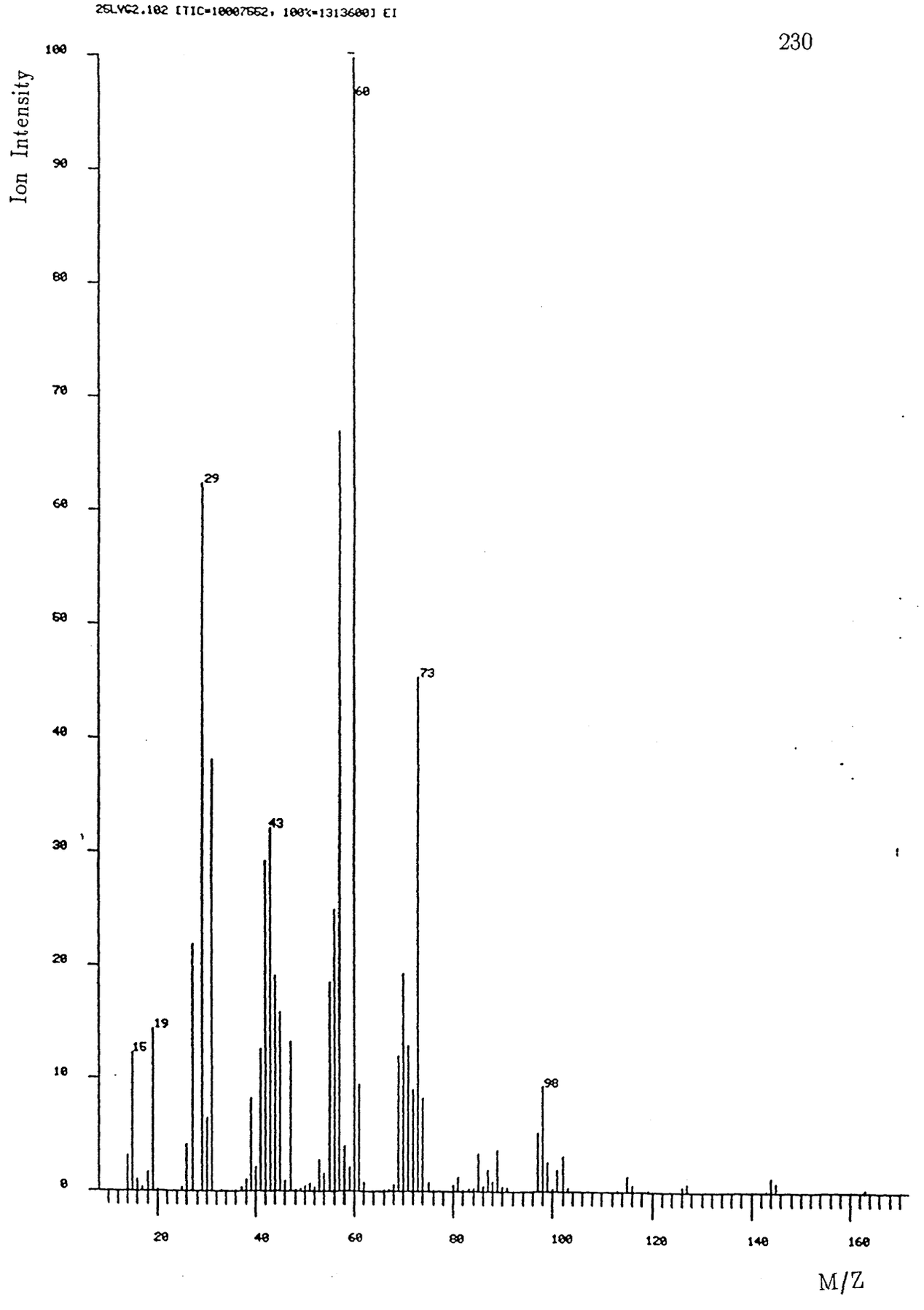


Figure 4.5d/scan102 – Fragmentation pattern of levoglucosan at 40 eV.

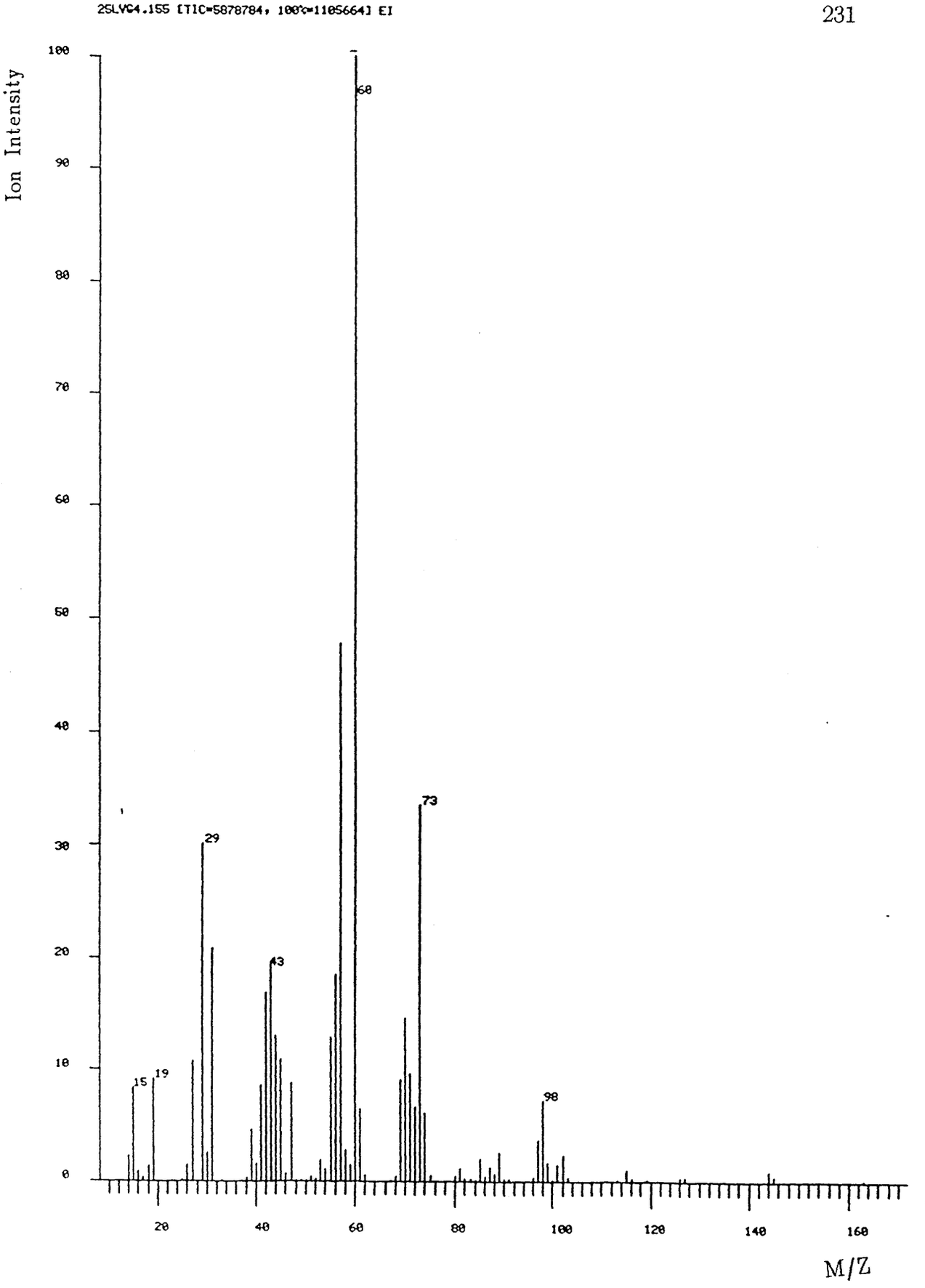


Figure 4.5d/scan155 – Fragmentation pattern of levoglucosan at 15 eV.

The cross scan reports for the lignin pyrolysis tars, obtained with the same experimental parameters as those used for cellulose and with heating rates of 0.1^{0}C/second and 1000^{0}C/second, are presented in Figures 4.5e and 4.5f. In contrast to the simple spectra obtained from the cellulose tars these lignin spectra are characterised by a large number of peaks over a very wide range of scan numbers from, say, scan 180 to, say, scan 700, indicating the presence of a large number of compounds. Past studies have examined in some detail the complex nature of lignin mass spectra; associations have been established between the source of the lignin, e.g. softwoods, hardwoods, grasses etc, and the product distribution of these pyrolysis tars, see for example references 36,37,91,112. There have been identified three major series, or groupings, of compounds in lignin tars; these are characterised by m/z peaks from 210 to 154 – the sinapyl series – from hardwoods, m/z peaks from 180 to 124 – the coniferyl series – from softwoods and the m/z peaks from 150 to 110 – the coumaryl series – from grassy materials[36,37]. From the detailed report of scan 233, see appendix 1, the major peaks at m/z 124 and 152 indicate that this lignin specimen was obtained from softwood.

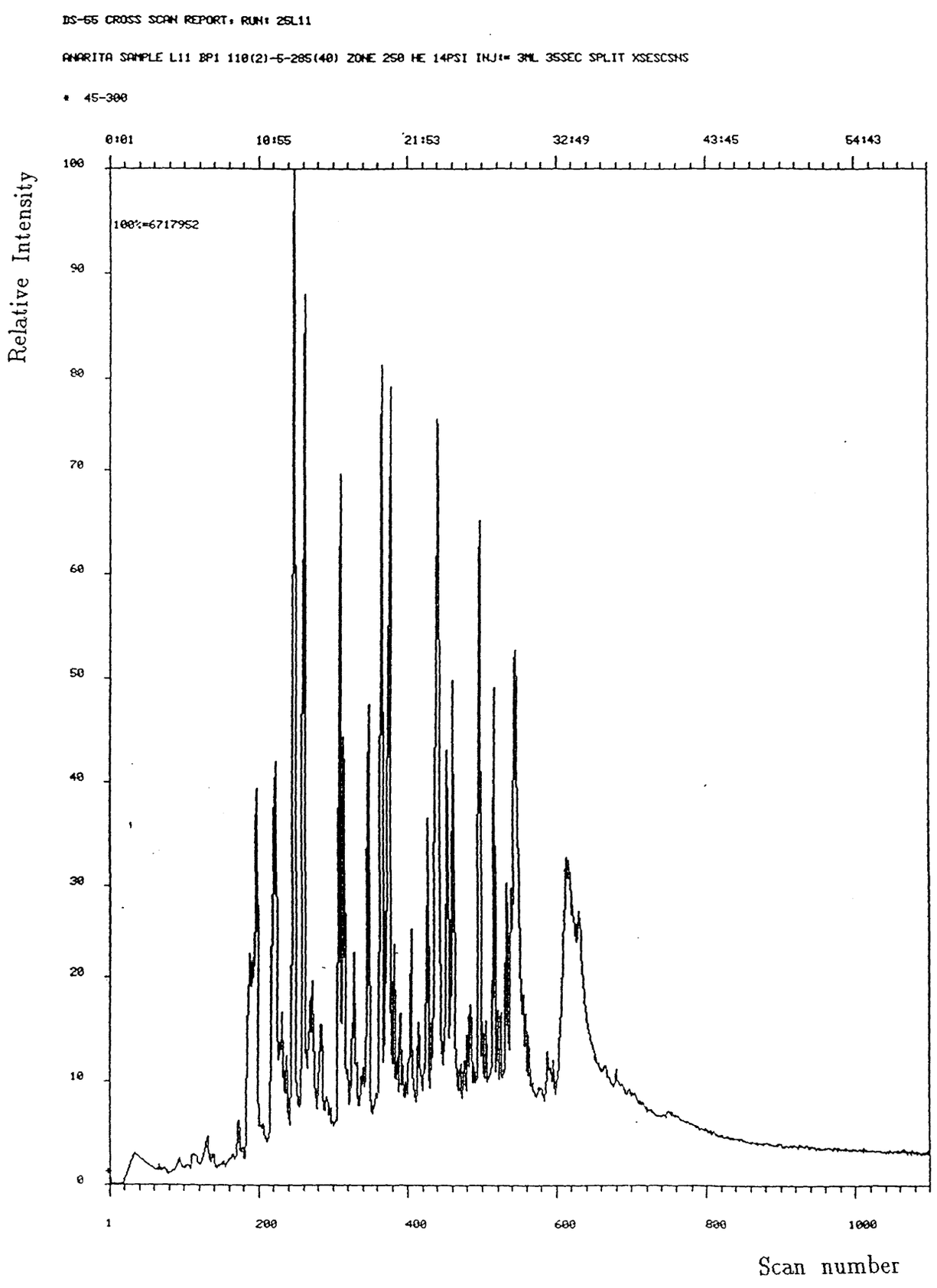


Figure 4.5e – Lignin – Cross Scan Report.

(pyrolysis conditions 0.1^0C/sec; 600^0C; 30sec.)

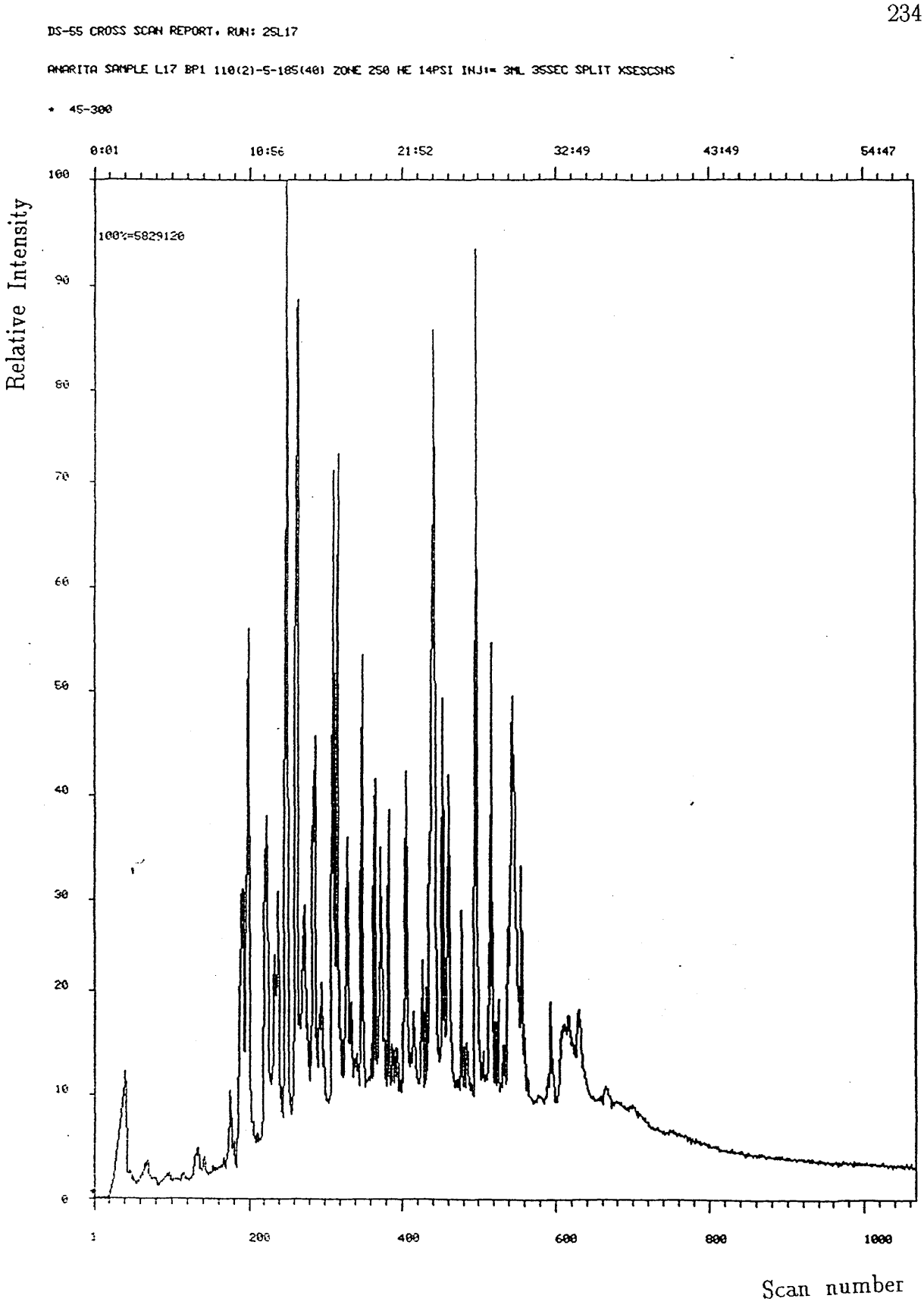


Figure 4.5f — Lignin — Cross Scan Report.

(pyrolysis conditions 1000^{0}C/sec; 600^{0}C; 30sec.)

The cross scan reports of the pyrolysis tars from the "synthetic" materials made in this study, that is the mixtures 75%cellulose:25%lignin, 50%cellulose:50%lignin and 25%cellulose:75%lignin, are presented in Figures 4.5g, 4.5h, and 4.5i; the pyrolysis conditions being identical to those used above. These three figures exhibit several important common features, in particular their product distribution is seen to be broadly constant. The characteristic lignin peak appearing at scan number 233, as identified above from the spectra of pure lignin is, in all three figures, the major component, even in Figure 4.5g where the specimen contained only 25%lignin. It should be noted that in all these specimens the levoglucosan peak, which is characteristic of cellulose, is seen, at a low intensity, at scan number 418; hence these spectra appear to be dominated by the presence of lignin pyrolysis products.

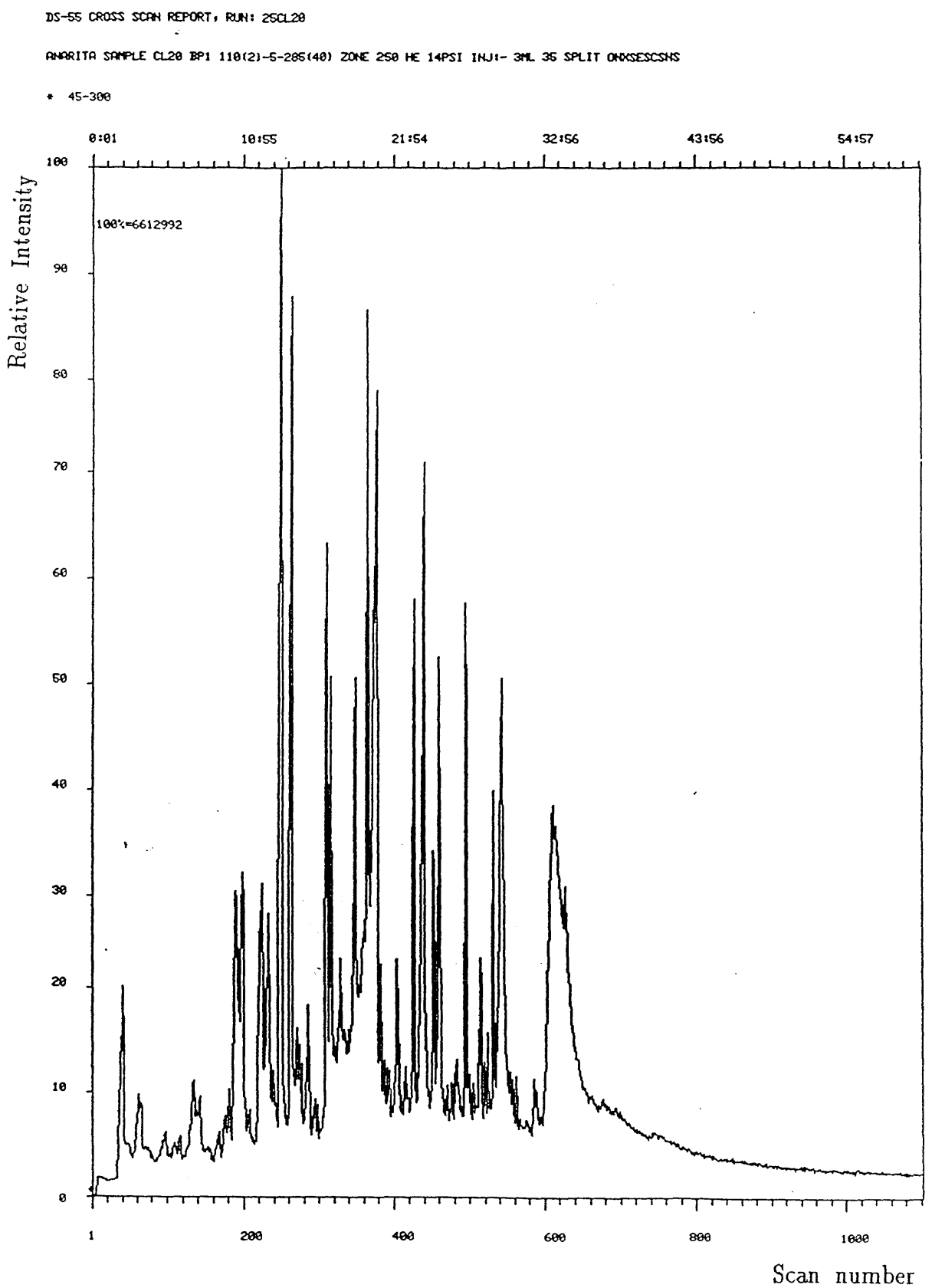


Figure 4.5g – Mixture 75%Cel:25%Lig – Cross Scan Report.
(pyrolysis conditions 1000^{0}C/sec; 600^{0}C; 30sec.)

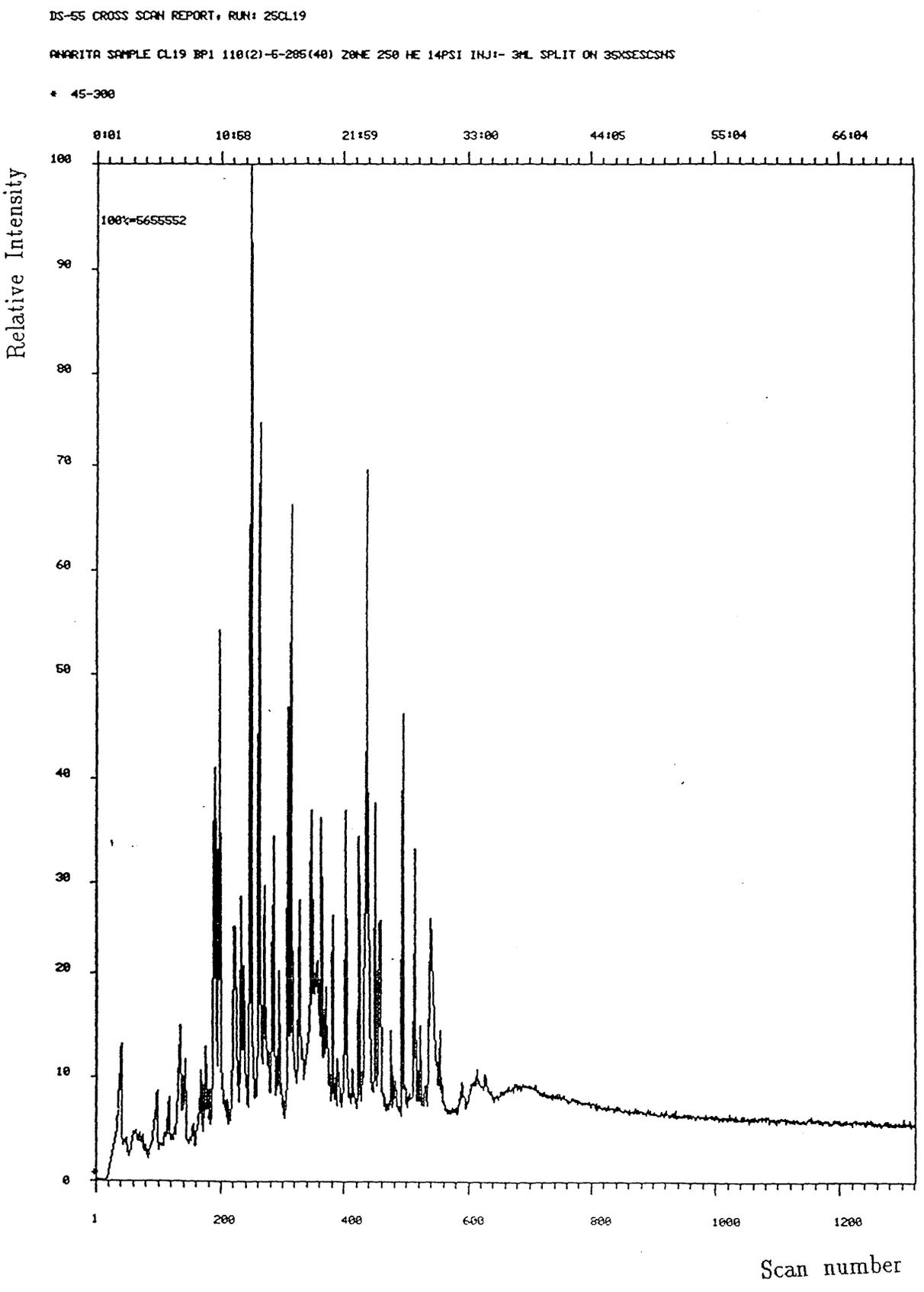


Figure 4.5h – Mixture 50%Cel:50%Lig – Cross Scan Report.
(pyrolysis conditions 1000^{0}C/sec; 600^{0}C; 30sec.)

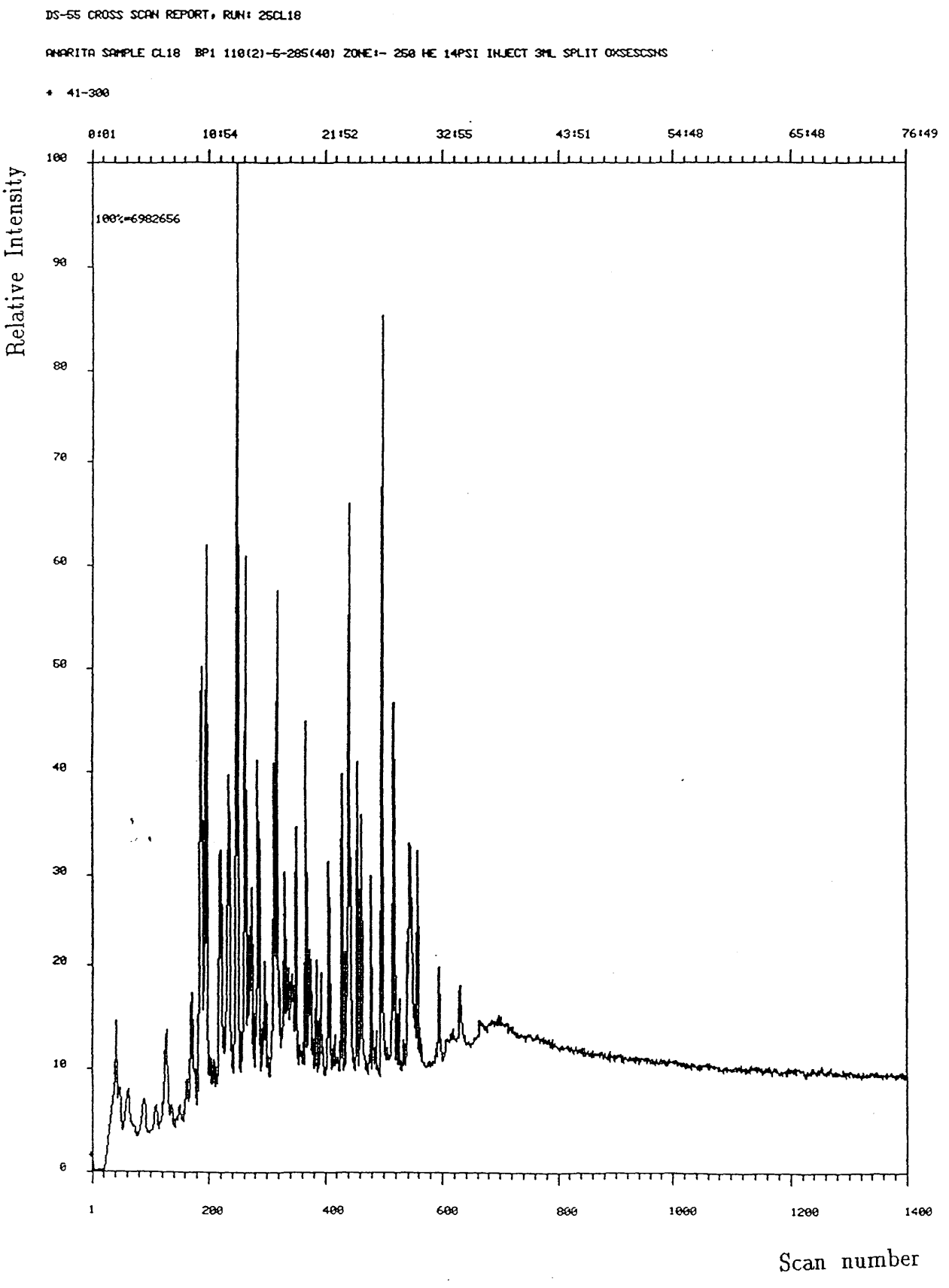


Figure 4.5i – Mixture 25%Cel:75%Lig – Cross Scan Report.
(pyrolysis conditions 1000^{0}C/sec; 600^{0}C; 30sec.)

Figures 4.5j–4.5n show the cross scan reports obtained for the pyrolysis tars of Sugar Cane Bagasse, over a wide range of peak temperatures, namely 400^{0}C to 900^{0}C, and heating rates, 1^{0}C/second and 1000^{0}C/second but with constant hold time, see Table 4.5a. These spectra are, from simple visual inspection, quite similar; and as bagasse contains approximately 25%lignin, see section 4.2 and 4.3, when Figure 4.5m is compared with 4.5g it is seen that the product distribution for this naturally occurring material is significantly less complex than that of the corresponding "synthetic" bagasse.

Indeed from Figure 4.5m it may be stated that, in general terms, there is only one major component in this pyrolysis tar, observed at scan number 195. The most intense fragmentation peak in scan number 195 is seen to have a m/z ratio of 120, see Figure 4.5m/scan195. This compound has been tentatively identified as vinyl–phenol based upon its reported fragmentation pattern, the characteristic m/z peaks for vinyl phenol are, in descending order of ion intensity, 120–91–26–119–39, see Hruza[66]. This assignment is further supported by previous pyrolysis research on grass–like materials, where this compound has been observed, see for example Evans[37].

The minor elements seen in Figure 4.5m, which <u>do not include levoglucosan</u>, have also been tentatively identified, based upon the work of past researchers[8,36,37,38,39,66,112], see Table 4.5b. The absence of levoglucosan indicates that, following its formation by

pyrolysis of the cellulose rich Sugar Cane Bagasse, levoglucosan has itself suffered thermal decomposition forming tars; or that the tar derives primarily from the lignin fraction of bagasse.

Further experimental work was undertaken the aim of which was to examine in greater detail the interaction between cellulose and lignin in these lignocellulosic materials, and the absence of levoglucosan in the pyrolysis tars; it is reported and discussed in Chapter 5 sections 5 to 8.

M/Z	Compound	Scan
58	2–propanone	44
96	2–cyclohexenone	56
96	2,5 dimethy furan	60
98	furfuryl alcohol	62
126	5(hydroxymethyl)furfural	74
114	hydroxy–2–penteno–1,5lactone	86
114	aliphatic	135
138	2–methoxy–4–methyphenol	171
120	**vinyl phenol**	195
152	4–ethyl guaiacol	225
150	2–methoxy–4–vinyl phenol	240
154	2,6 dimethoxy phenol	253
164	2–methoxy 4–propenyl phenol	260
152	aliphatic	275
168	2,6–dimethoxy–4–methyl phenol	297
182	ethyl syringol	332
180	vinyl syringol	347
194	dimethoxy–4–propenyl phenol	363
210	sinapyl alcohol	428

Table 4.5b – Compounds tentatively identified in Sugar Cane Bagasse tars.

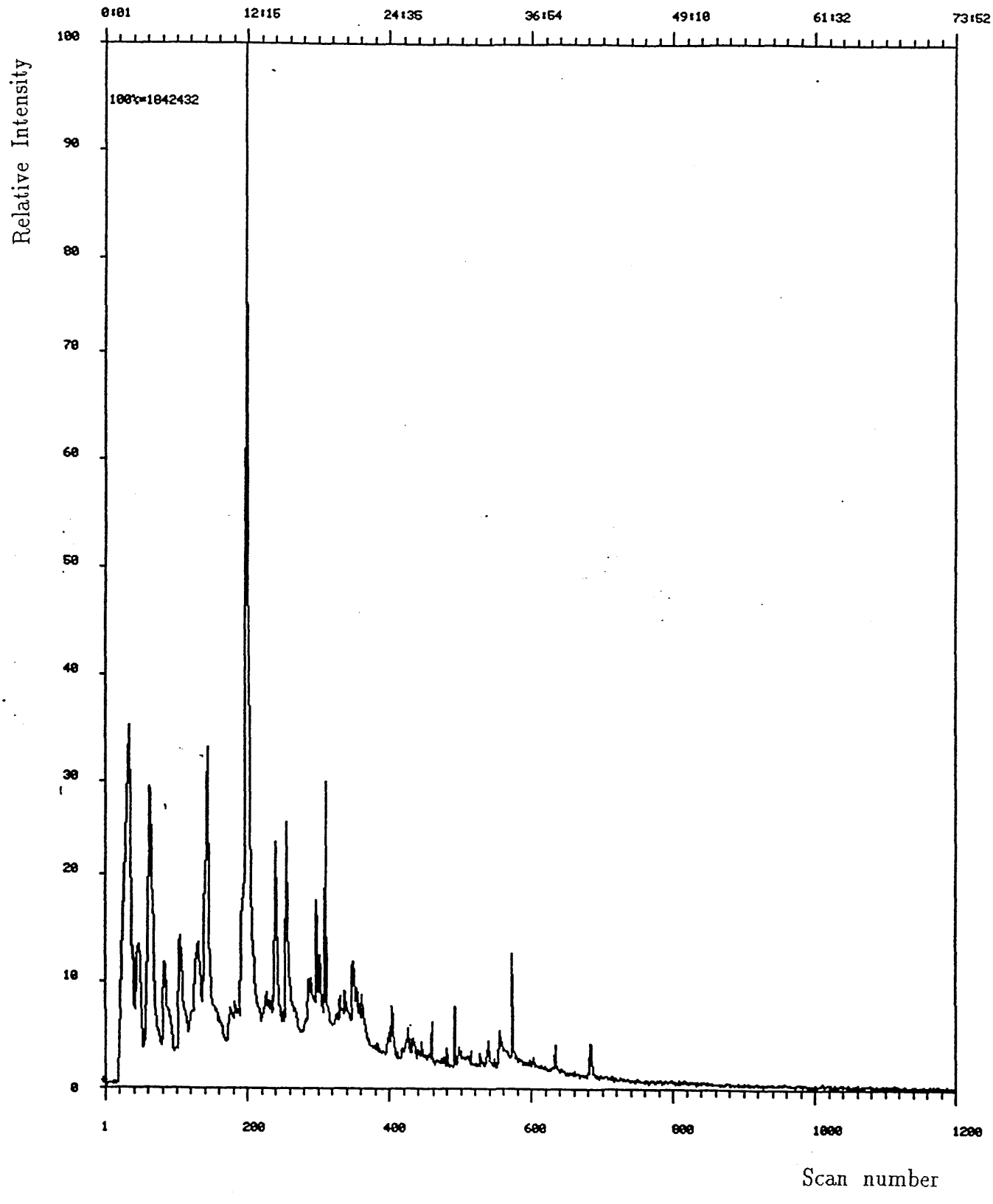


Figure 4.5j — Bagasse — Cross Scan Report.
(pyrolysis conditions 1^0C/sec; 400^0C; 30sec.)

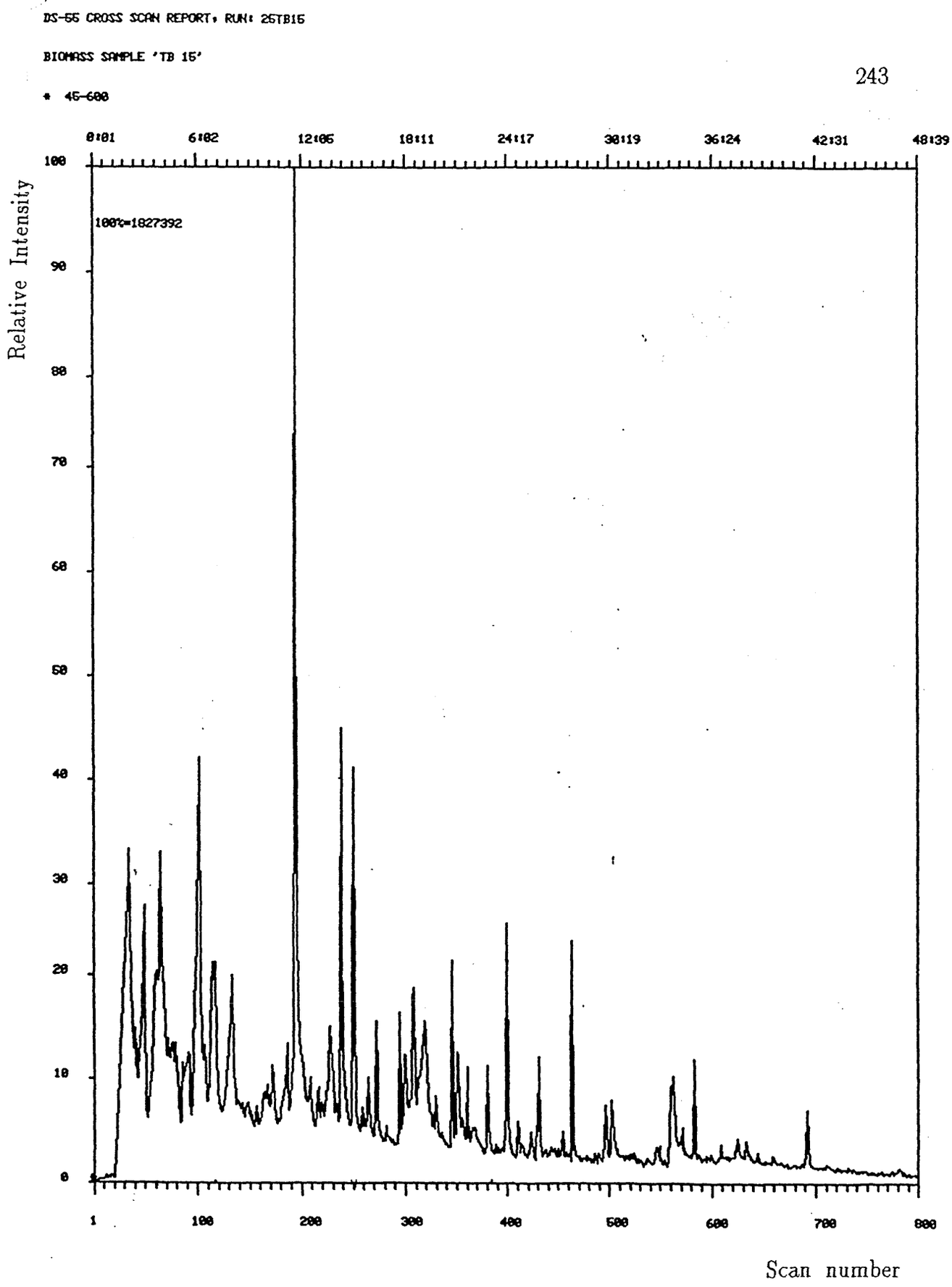


Figure 4.5k – Bagasse – Cross Scan Report.

(pyrolysis conditions 1000^0C/sec; 400^0C; 30sec.)

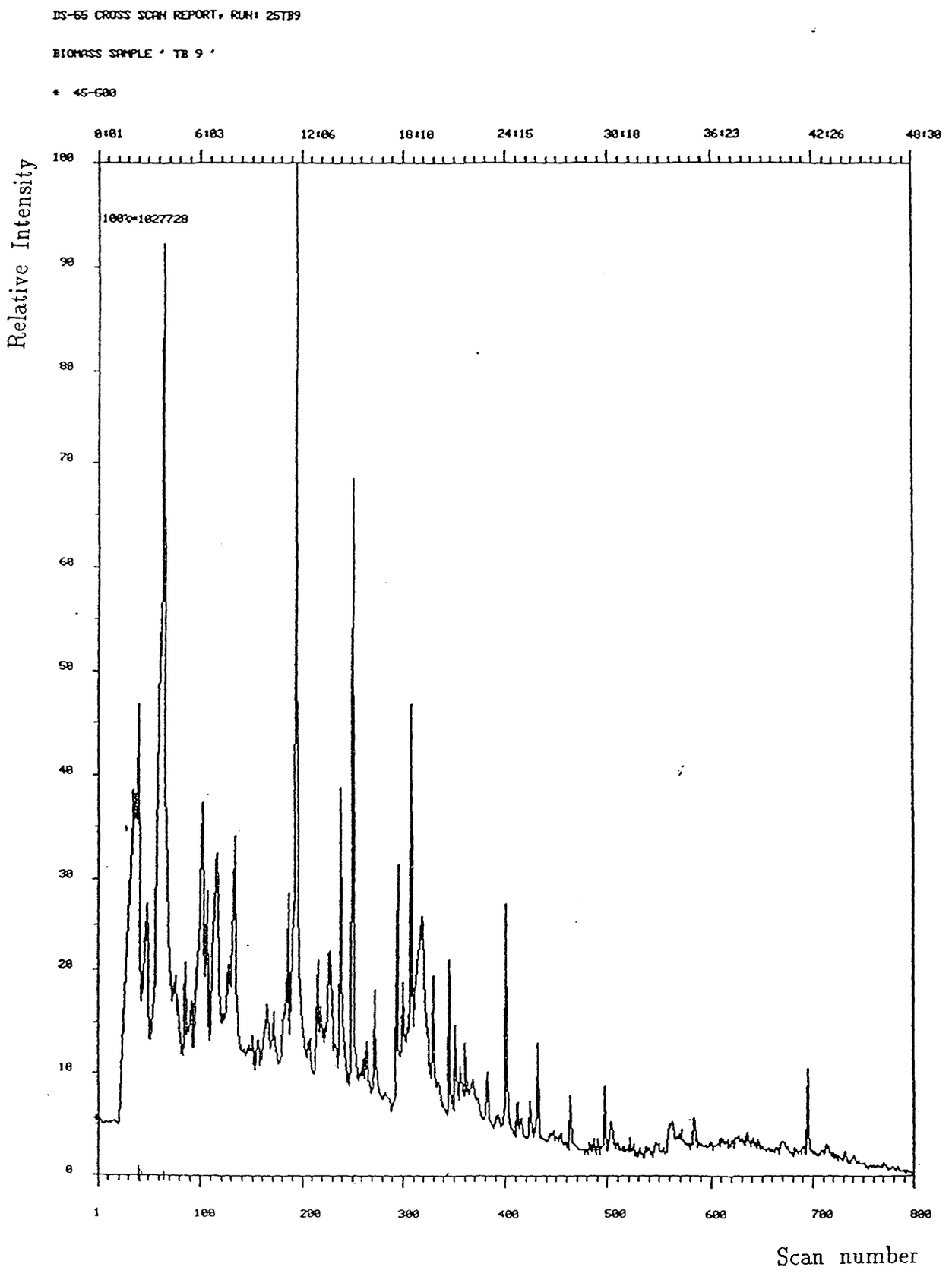


Figure 4.5l – Bagasse – Cross Scan Report.
(pyrolysis conditions 1^0C/sec; 600^0C; 30sec.)

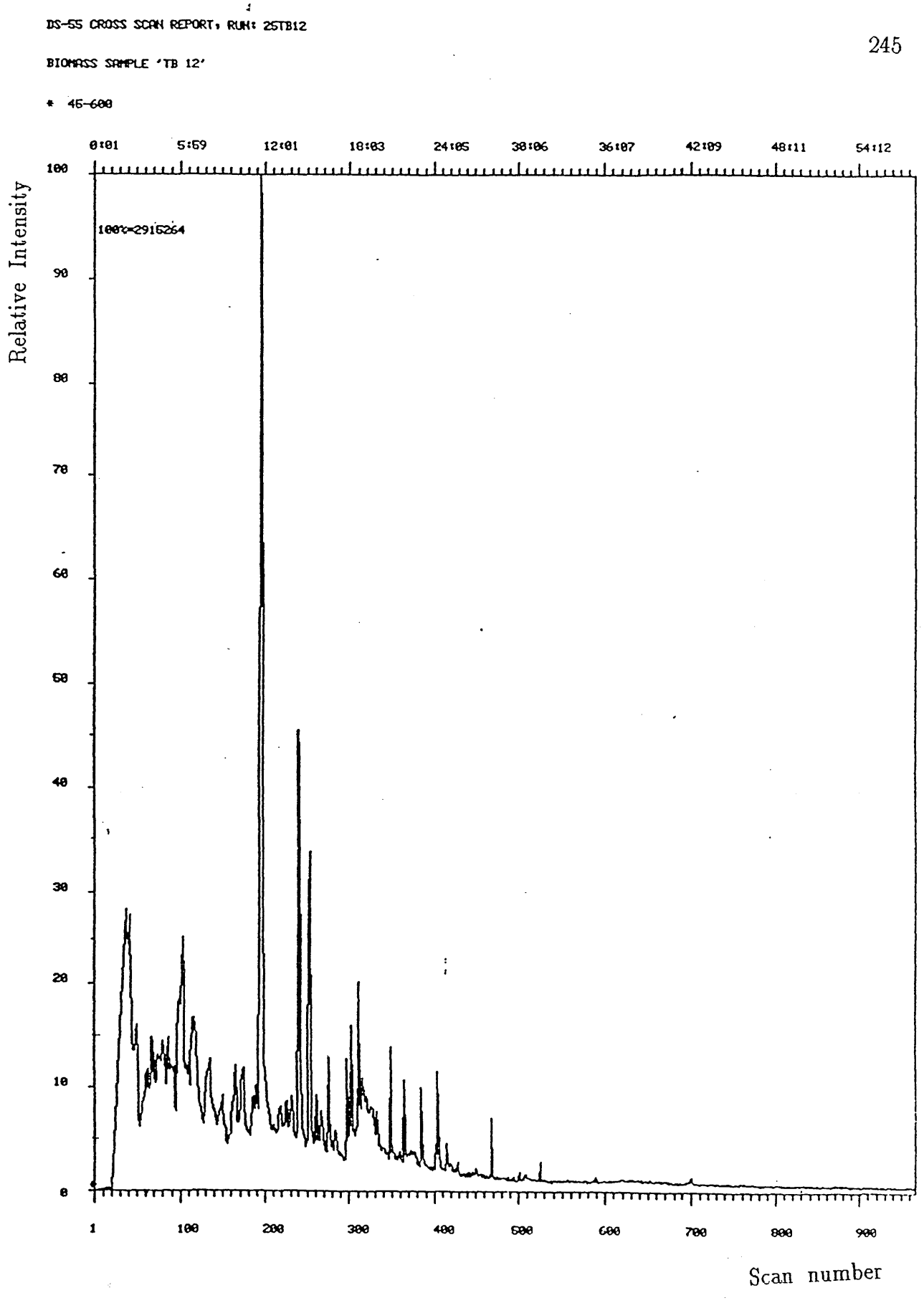


Figure 4.5m – Bagasse – Cross Scan Report.
(pyrolysis conditions 1000^{0}C/sec; 600^{0}C; 30sec.)

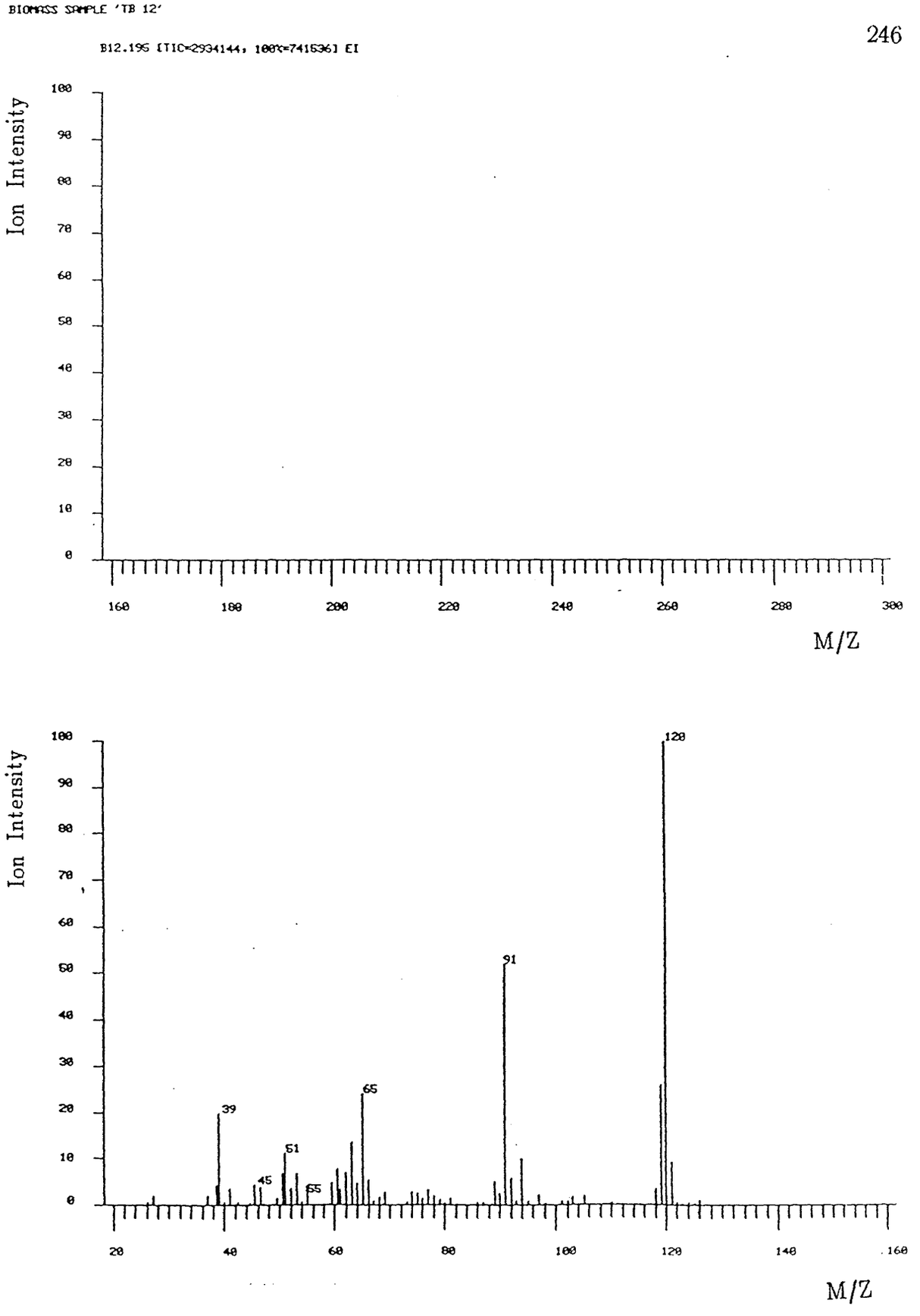


Figure 4.5m/scan195 — Fragmentation pattern of the major compound present in the Sugar Cane Bagasse pyrolysis tar at 72 eV.

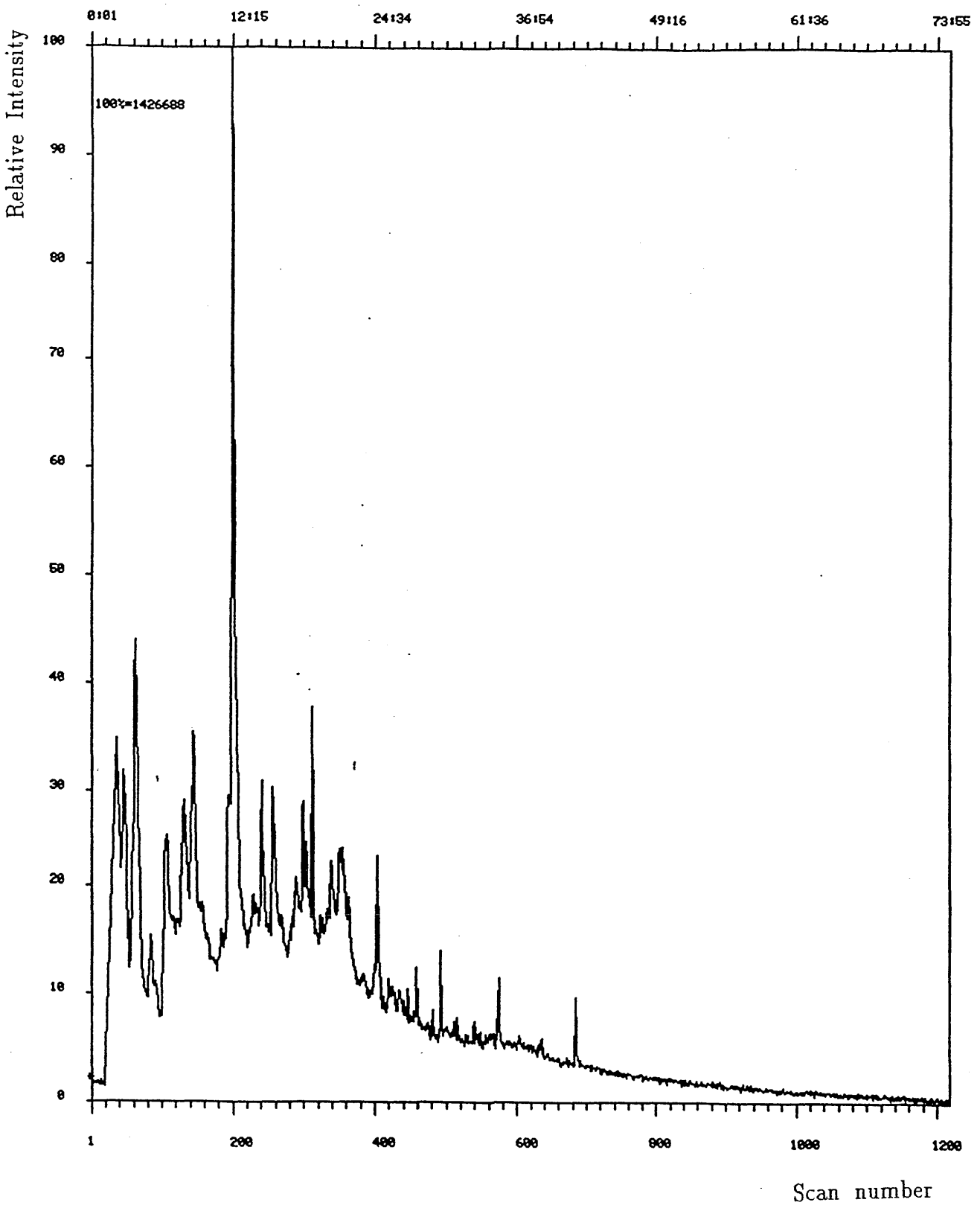


Figure 4.5n – Bagasse – Cross Scan Report.

(pyrolysis conditions 1^0C/sec; 900^0C; 30sec.)

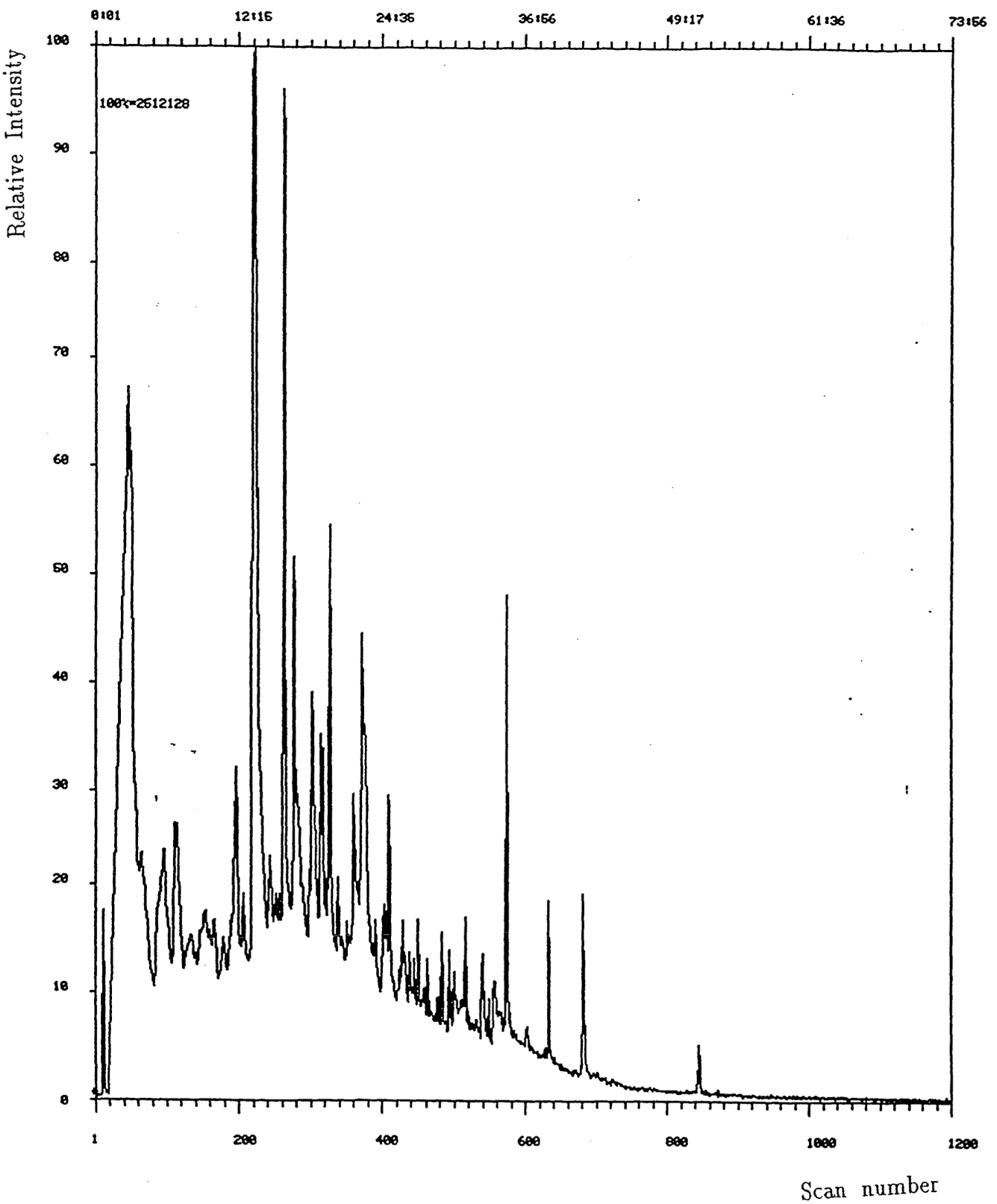


Figure 4.5o – Bagasse – Cross Scan Report.

(pyrolysis conditions 1000^{0}C/sec; 900^{0}C; 30sec.)

The cross scan reports for the Silver Birch pyrolysis tars are shown in Figure 4.5p–4.5s, for the pyrolysis conditions see again Table 4.5a. Again, by visual inspection, it can be seen that these spectra are substantially more complex than those obtained from the corresponding Sugar Cane Bagasse sample, see for example Figure 4.5s in comparison to 4.5o. Some of these compounds have been tentatively identified based upon past reported work[8,36,37,38,39,66,112], see Table 4.5c. The vinyl–phenol peak, which was tentatively assigned to the major compound of Sugar Cane Bagasse tar, scan number 195, is not seen in these reports; however levoglucosan, which is the major compound of cellulose tar, is present but only at a relatively low level.

M/Z	Compound	Scan
96	2–cyclohexenone	55
98	furfuryl alcohol	76
114	2–methyl–2–butenoic acid	99
126	5–hydromethoxyl furfural	151
166	2–methoxy–4 propylphenol	179
102	butyric acid	190
142	2–methylnaphthalene	196
166	aliphatic	233
150	2–methoxy–4–vinylphenol	235
154	2,6–dimethoxyphenol	250
180	vinyl syringol	265
152	dimethoxy–4–methylbenzene	152
168	dimethoxy–4–methyl phenol	292
164	methoxy–4–propenylphenol	297
166	4–methoxy–4–propylphenol	304
182	2,6–dimethoxy 4–ethylpenol	328
194	dimethoxy 4–propenylphenol	358
162	levoglucosan	411
210	sinapyl alcohol	418

Table 4.5c – Compounds tentatively identified in Silver Birch tars.

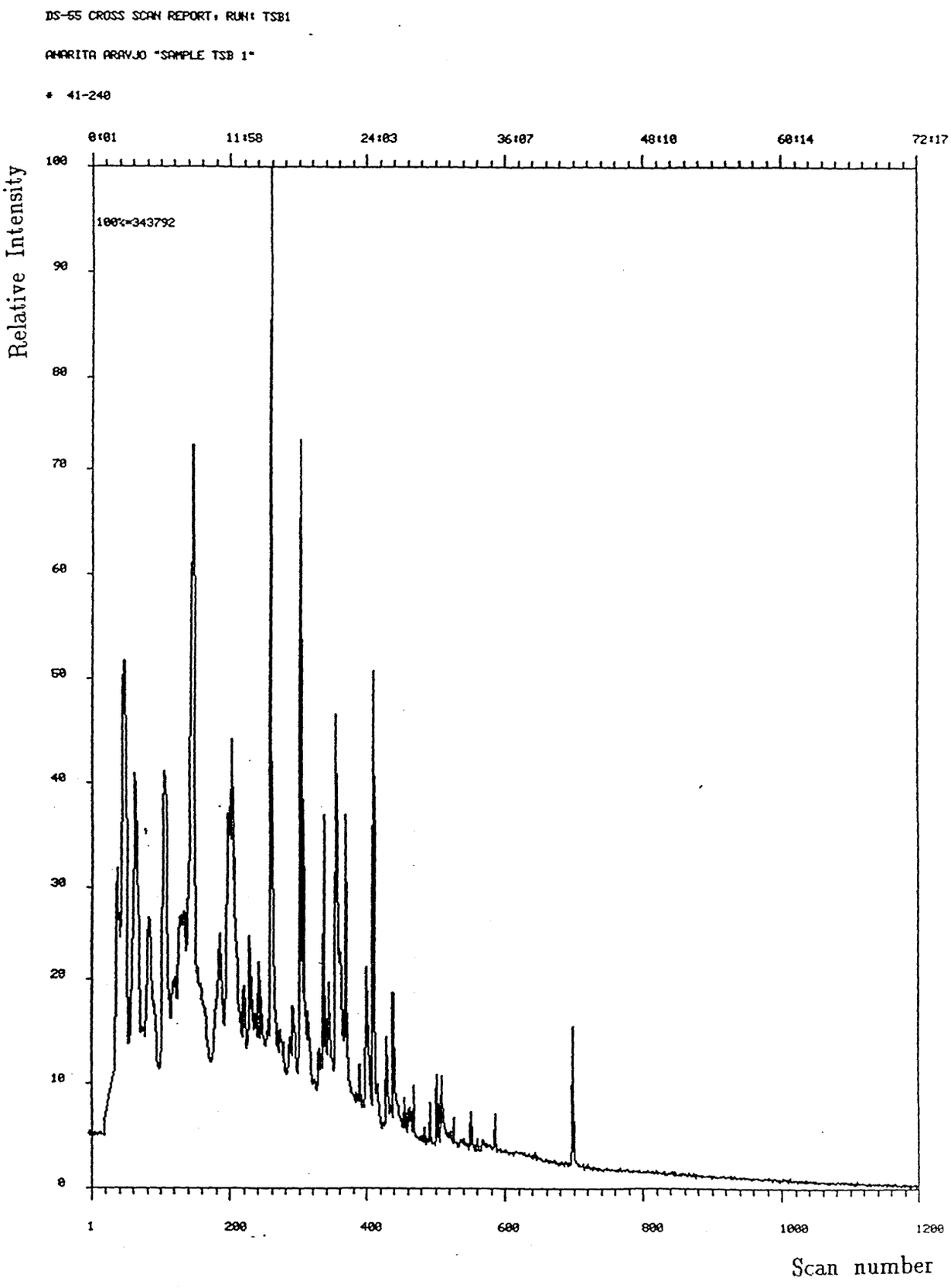


Figure 4.5p – Silver Birch – Cross Scan Report.
(pyrolysis conditions 1^0C/sec; 400^0C; 30sec.)

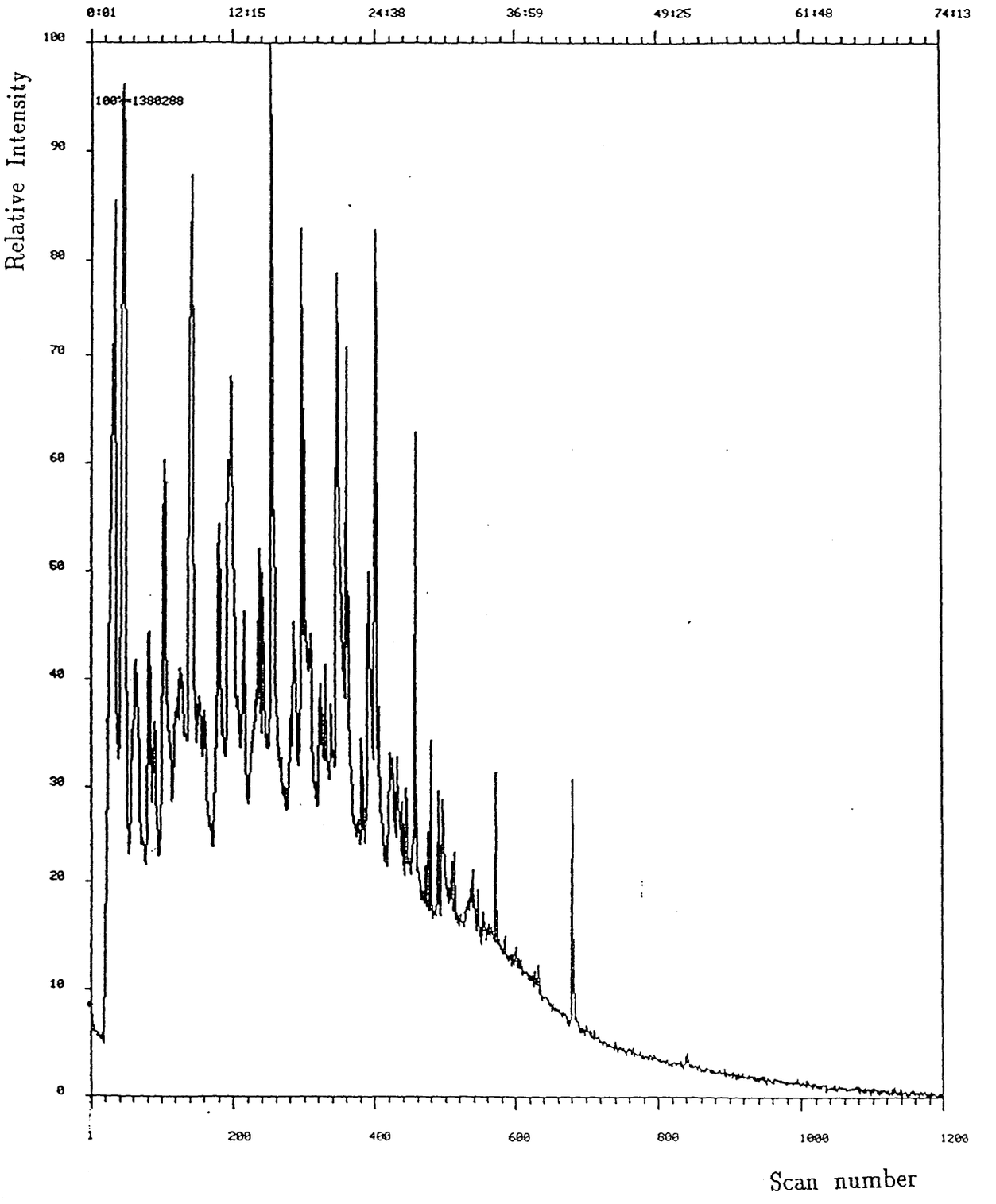


Figure 4.5q – Silver Birch – Cross Scan Report.

(pyrolysis conditions 1000^{0}C/sec; 400^{0}C; 30sec.)

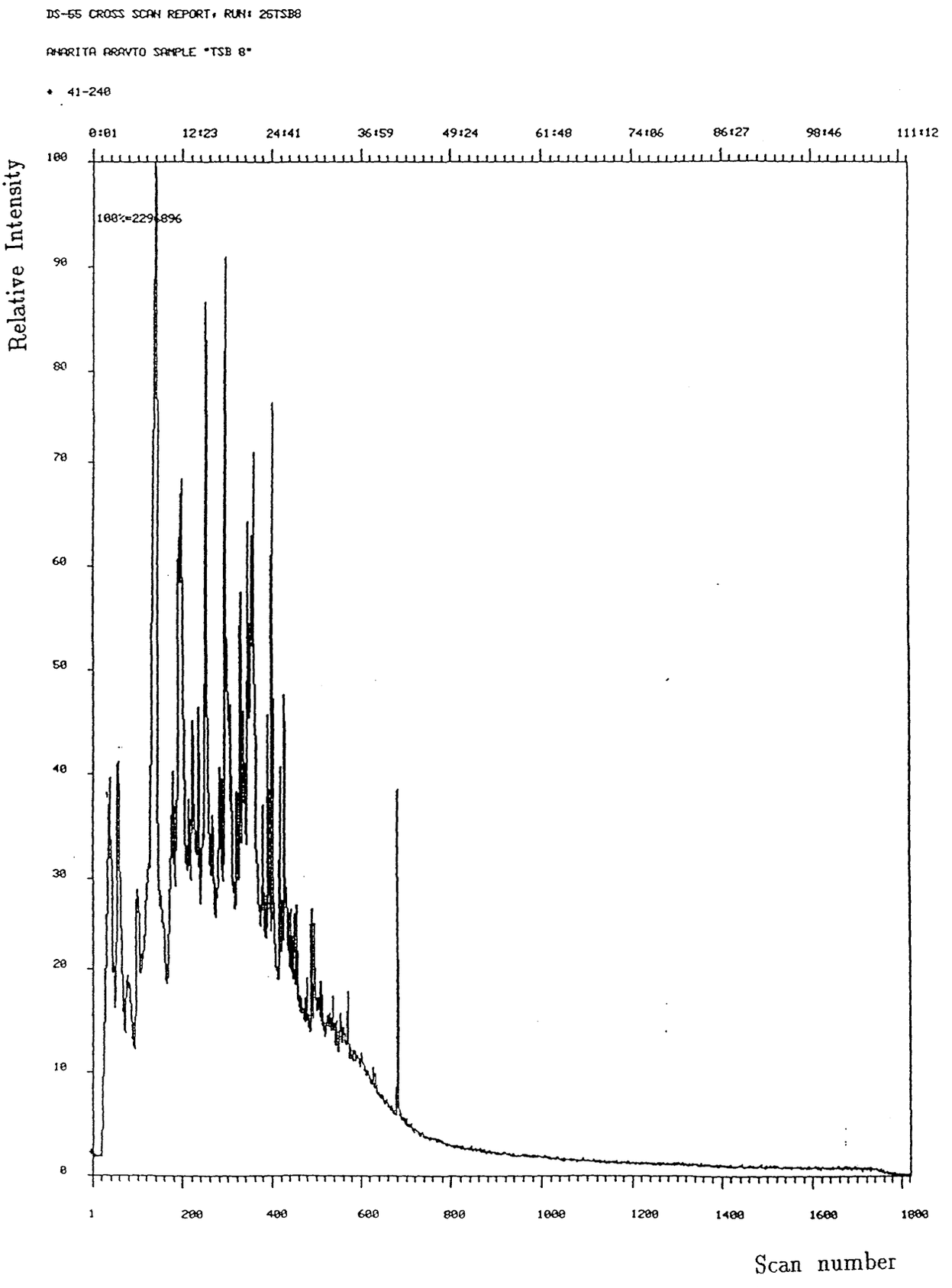


Figure 4.5r – Silver Birch – Cross Scan Report.

(pyrolysis conditions 1^0C/sec; 900^0C; 30sec.)

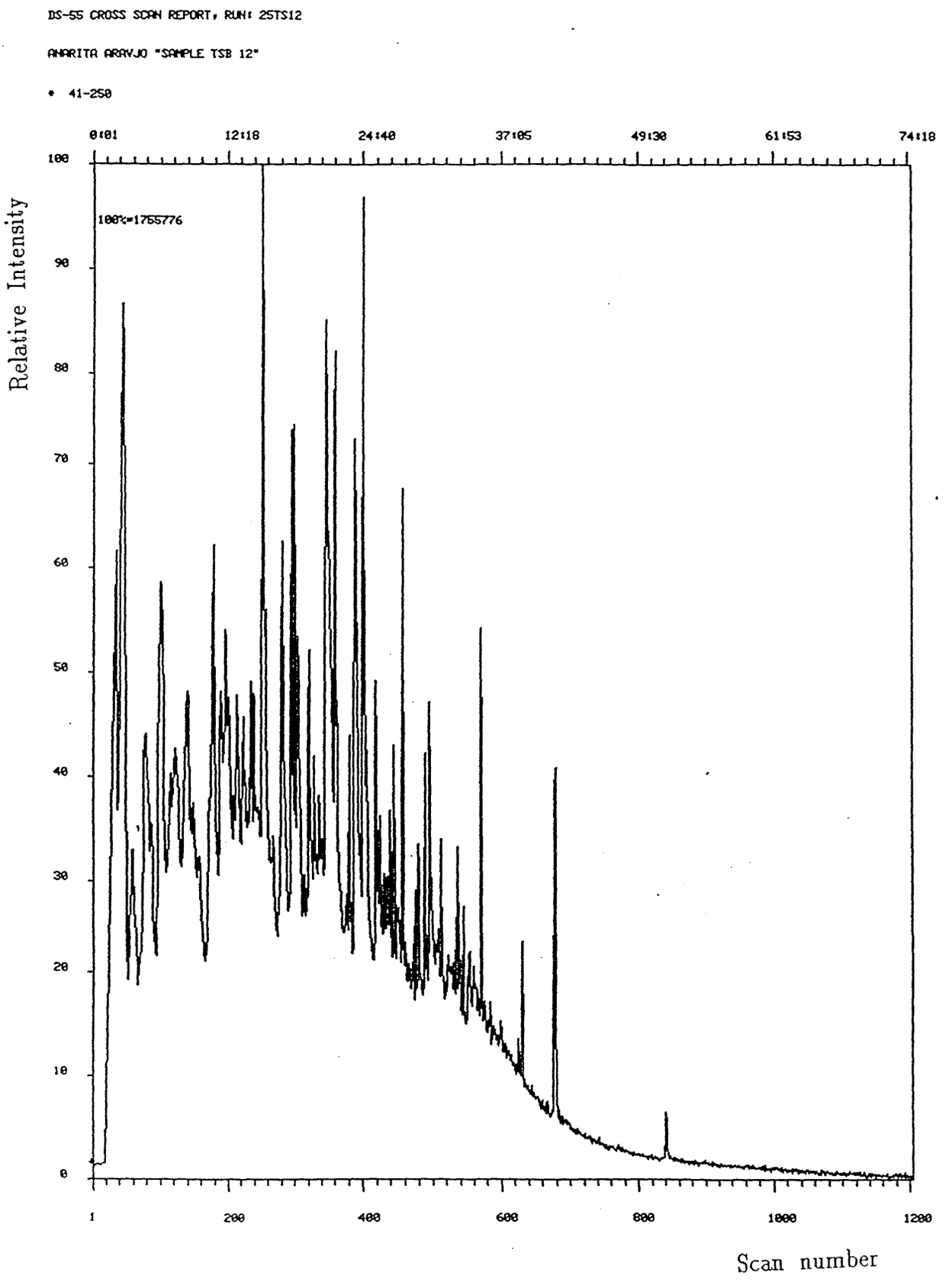


Figure 4.5s – Silver Birch – Cross Scan Report.

(pyrolysis conditions 1000^0C/sec; 900^0C; 30sec.)

4.6 – Summary.

It has been shown that ^{13}C–NMR may be used to determine the cellulose and lignin content of lignocellulosic materials. The profile techniques employed, namely VPO and CHN, did not reveal major changes in tar composition, as a function of the pyrolysis conditions, for either Sugar Cane Bagasse or Silver Birch. These results are confirmed by the detailed GC–MS analyses; which also showed that for Sugar Cane Bagasse:

1 – The pyrolysis tar had a simpler product distribution than the Silver Birch tar,

2 – The major compound in the pyrolysis tar was vinyl phenol,

3 – Levoglucosan, the major product of cellulose pyrolysis, was not present in the pyrolysis tar of Sugar Cane Bagasse and only in trace quantities in the pyrolysis tar of Silver Birch.

CHAPTER 5

DISCUSSION OF RESULTS AND CONCLUSIONS.

5.1 – Introduction.

In the first part of this chapter the yields of the pyrolysis products obtained in this study from pure cellulose, pure lignin, Sugar Cane Bagasse and Silver Birch are compared with the results past research. To facilitate these comparisons a simple framework, or matrix, is constructed by reviewing several different types of pyrolysis apparatus, for example fluidised bed, thermobalance, wire–mesh, in which experiments have been conducted using the above, or closely related, biomass materials. This approach is indicated since the number of direct comparisons that may be made, i.e. with the same biomass material in the same type of pyrolysis reactor, are severely limited. The important role of reactor geometry in determining the numerical value of pyrolysis yields is clearly seen in this review. For all experimental systems that are particularly prone to secondary reactions, for example fluidised beds, a decreasing tar yield with increasing peak temperature is seen to be a sensitive indicator of the existence of these reactions. It must be emphasised that if comparisons of the pyrolysis product yields in different systems, for a given material, are to be meaningful, then these comparisons must be undertaken with due care.

From this review it can be clearly seen that erroneous conclusions could readily be reached when comparing the yields from experimental apparatus of differing geometry or operational principles. All the numerical values related to pyrolysis data presented in this chapter have been calculated on a dry ash free basis (d.a.f.), unless otherwise indicated.

Following these discussions further experimental work is presented, the aim of which was to probe, in greater detail, the interaction taking place between cellulose and lignin during the pyrolysis process, as first shown in Chapter 3 section 3.7. In this part of this research programme two analytical procedures were employed, namely Scanning Electron Microscopy, SEM, and Differential Scanning Calorimetry, DSC. The combination of these new observations with the Gas 'Chromatography – Mass Spectrometry data already reported, see Chapter 4 section 4.5, enables a simple model to be proposed, based upon the individual morphology of these specimens, which provides insight into the pyrolysis of lignocellulosic materials in general, and Sugar Cane Bagasse in particular.

Finally the conclusions that may be drawn from this research programme are stated, and suggestions for further work, are presented.

5.2 – The Pyrolysis of Cellulose.

Stiles[134,135] used a fluidised bed for his investigations into the pyrolysis of lignocellulosic materials; his reactor was based upon the design of a quartz fluidised bed developed initially by Tyler[141,142]. Stiles's fluidised bed was made from AISI 316 stainless steel with an extended freeboard and variable height which enabled the volatile products to be contained within the hot zone for differing periods of time. The samples in powder form, cellulose <76microns, or Silver Birch, 76–152microns, were fed at the rate of 10–20g/h into the apparatus, the fluidised particles of the bed were acid washed sand. The volatiles were swept from the hot reaction zone and through a water cooled side arm, then into a liquid nitrogen cooled trap, a soxhlet extraction thimble and finally into a glass wool filled chamber. The tar yield was defined as the sum of the condensables in all these traps; tar was collected by washing these traps with an acetone/methanol mixture and subsequently concentrated by evaporation of the solvent. The char yield was evaluated by weighing the sand, ≃ 350 grammes, before and after each experiment, and the yield of gas plus water was obtained by difference.

Figure 5.2a presents graphically the effect of peak temperature on the tar yield obtained by the pyrolysis of pure cellulose as reported by Stiles[134,135]. These results were obtained with a residence time of 2.44 seconds for the volatiles in the freeboard. In this same figure, the new data obtained in this study for the pyrolysis

of pure cellulose with a heating rate of 1000^{0}C/second and a hold time at the peak temperature of 30 seconds, are also shown.

From Figure 5.2a, it can be seen clearly that for the fluidised bed reactor, there is a decrease in the tar yield with increasing temperature. At 400^{0}C the tar yield was about 80%, this decayed to, say, 46% when the peak temperature was raised to 600^{0}C, and drastically fell to approximately 3% at a peak temperature of 800^{0}C. In contrast to the data obtained in the fluidised bed, the tar yield in the wire–mesh reactor was about 81% at the peak temperature of 400^{0}C, and when this temperature reached 600^{0}C the yield of tar attained a constant, maximum, value of 87%.

From Stiles's results, it is obvious that secondary reactions played an important role in his pyrolysis experiments; indeed as he said "... At higher temperatures tar yields fall, while increasing vapour residence times result in greater loss of condensable product...and...These results suggest that increasing and significant amounts of cellulose tar coke or crack within this fluidised bed with increasing temperature..." (from Stiles and Kandiyoti, 1989).

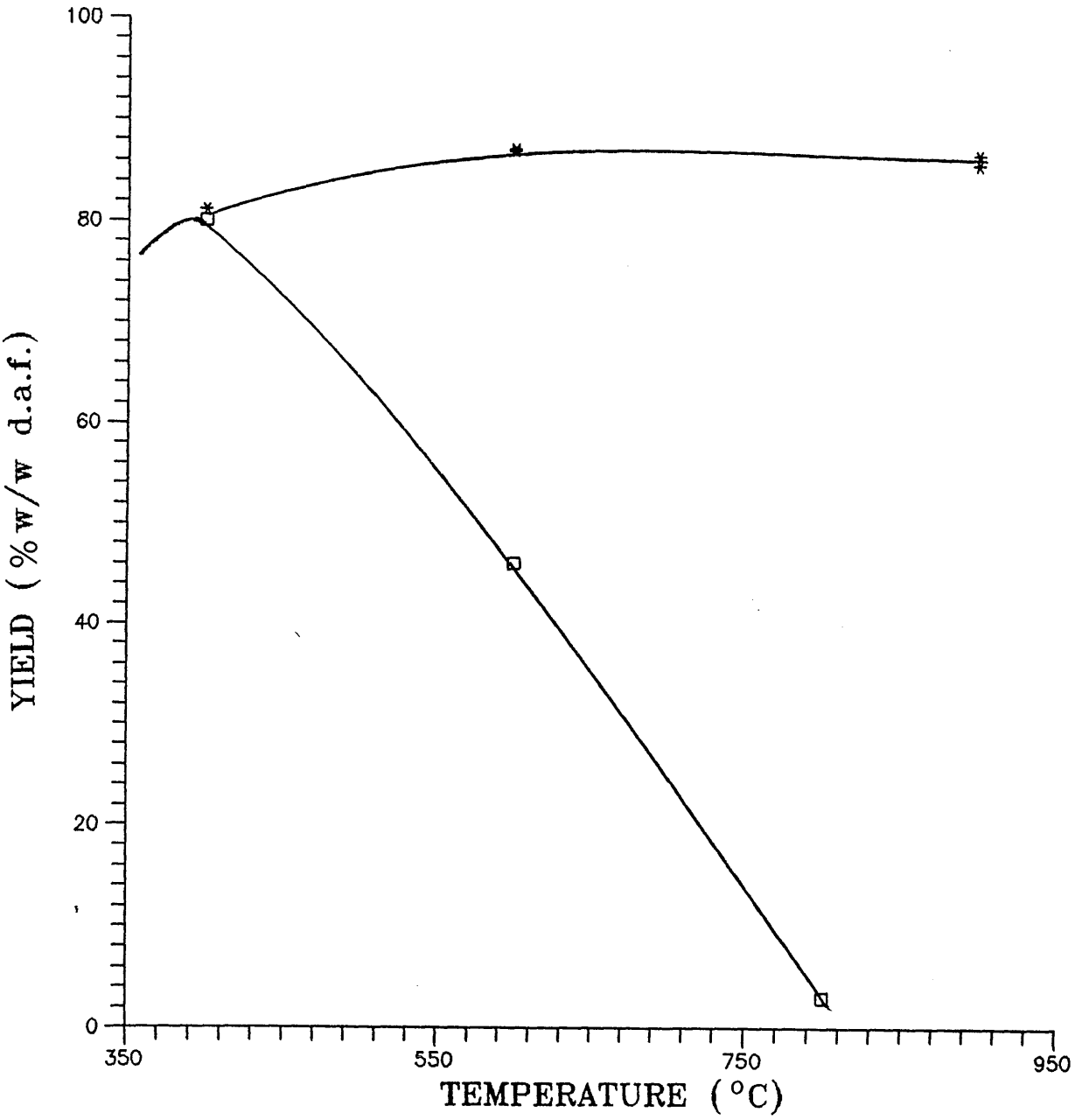


Figure 5.2a – The effect of peak temperature on the yield of cellulose tar in two different pyrolysis systems.

* = Present study; heating rate = 1000^0C/sec, hold time = 30 seconds.

□ = Fluidised bed; residence time = 2.44 sec. (Stiles[134,135])

A more exact and direct comparison may be made between the results obtained in this present study and those of Kim and coworkers[77], and Hajaligol and coworkers[59,60]; since these researchers pyrolysed cellulose in wire–mesh reactors. However there are two important and significant differences between their experimental procedure and that employed in this research programme; first their pyrolysis runs were performed in an environment of "stagnant" helium, that is to say there was no carrier gas to transport the primary tars away from the hot reaction zone. Secondly their cellulose was in "strip" form and not a finely divided powder, as used in this research. It may be noted here that, in Kim's and Hajaligol's results for the pyrolysis of cellulose, there was a marked decrease in tar yield above the peak temperature of, say, 500^0C.

The significance of these differences in experimental procedure is revealed in the following discussion.

In the wire–mesh apparatus of Hajaligol[59,60] the reaction conditions were as follows: heating rates of 100 to 100,000^{0}C/second; final temperature of 200 to 1100^{0}C; and hold times at the final temperatures from zero to more than 1000 seconds. The cellulose sample used weighed approximately 100 milligrammes and was cut from a thin strip of number 507 filter paper, having the dimensions of 2cm x 6cm x 0.0101cm. It should be recalled that these experiments were undertaken in a stagnant atmosphere of helium. Hence, after each run, volatiles in the vapour phase were flushed from the reaction vessel

by purging it with helium and condensing these products in traps. Tar was defined to be any material condensed on the wall of the reaction vessel at room temperature, and as any compounds contained within the traps with a boiling point of not less than 100^0C. Tar was recovered from the reaction vessel by washing the internal surfaces with a 2:1 (v/v) mixture of methanol and acetone; the total tar yield was then determined by evaporating this solvent and weighing the residue plus the increase in weight recorded for the external traps.

In Figures 5.2b and 5.2c, the effect of peak temperature on the yields of the pyrolysis products, namely total volatiles, tar, char and gas, at the heating rate of 1000^0C/second and with a hold time, at the peak temperature, of 30 seconds, is shown for this research and also that of Hajaligol.

It can be seen from Figure 5.2b, that the curves representing the yield of total volatiles in both of these reactors have, quite closely, the same profile. For both reactors there is a small increase in the yield of total volatiles over the temperature range 400–600^0C, after which the conversion attains a constant maximum value; furthermore at 900^0C Hajaligol measured a conversion (total volatiles) of about 97%, and, for the same experimental conditions, in this present study a conversion (total volatiles) of 99% was obtained; hence there appears to be good agreement between these two systems for the yield of total volatiles.

From Figure 5.2c, it can be seen that Hajaligol's constant total volatiles yield results from a decrease in the yield of tar and a corresponding increase in the yield of gas, with increasing temperature. Specifically Hajaligol's tar yield, at the peak temperature of 400^0C, was as high as 83%, and when the peak temperature was increased to 900^0C the tar yield diminished drastically, to, say, 50%. In contrast Hajaligol's yield of gas, at 400^0C, was about 10%, and at the peak temperature of 900^0C, increased to, about, 47%.

In contrast to the above results of Hajaligol, the tar yield determined in this research programme, showed only a small increase over the temperature range 400–600^0C. Furthermore, for a peak temperature of 600^0C or more, the yield of tar attained a maximum, constant value of, say, 85%, and the yield of gas plus water was also almost constant at, say, 12%; see Table 4.1 for detailed numerical values.

It is seen from the above that although the wire–mesh reactor used by Hajaligol[59,60] and that used in this present study have <u>almost</u> the same geometric features, the yields of tar and gas show marked differences. Arguably these differences demonstrate the influence of the two major dissimilarities between the experimental procedures, namely:

a – Carrier gas,

b – Sample size.

a – Carrier gas: In the wire–mesh apparatus used in this research programme, helium carrier gas was flowing constantly through the sinter disc trap with the linear velocity of 0.1 meter/second, as described in Chapter 2 section 2.4, throughout each experimental run. The action of this carrier gas is to sweep the products formed during pyrolysis rapidly, and continuously, from the hot zone of the reactor and into the cooled sinter trap; thereby greatly reducing the possibility of cracking the tar into gaseous products. This procedure, therefore, significantly diminished the number of secondary reactions taking place. Additionally, since in these experiments it was not necessary to recover the tar by washing the inside of the reactor vessel with solvent, the possibility of any tar loss, during the evaporation of the solvent, was removed. From the above results of Hajaligol and, in particular, the transposition of tar and gas yields, it is most likely that the absence of a carrier gas during an experimental run enhances the severity of secondary reactions. In Hajaligol's apparatus[59,60], during an experimental run, quasi–stable circulation patterns may be established by convection within the vicinity of the wire–mesh; hence the residence time of primary tars within the hot zone can be significantly increased, thus promoting either tar cracking or polimerisation reactions and , possibly, a combination of both processes. This is, most probably, the major cause for Hajaligol's tar yield being much lower than the tar yield obtained in this present research. This conclusion is supported, indirectly, by Hajaligol who stated that: "...The decreases in tar yield, above the peak temperature 700^{0}C, at zero hold time at this peak temperature, and above 400^{0}C, at 30 seconds hold time, in both cases

with a heating rate 1000^{0}C/second, undoubtedly is due to cracking reactions becoming more favoured at higher temperatures..." (from Hajaligol[59,60]).

b – Sample size: The cellulose sample used by Hajaligol and coworkers, was approximately 100 milligrammes of filter paper, in contrast to the granular specimens used in this research programme of about 7 milligrammes. The pyrolysis tar yields of Hajaligol, as presented in Figure 5.2c, strongly indicate that secondary reactions took place in his experiments. In addition to the source of secondary reactions identified above, i.e. the absence of a carrier gas, secondary reactions may also have occurred within the pores of these 100 milligrammes samples. It cannot be categorically stated that no secondary reactions occurred inside the samples used in the present study; however the possibility of such secondary reactions is greatly diminished by using granular specimens. These specimens have a much larger surface area per unit weight, as well as a higher porosity, than that of a strip sample; therefore volatile residence times within a granular cellulose bed will be substantially less than in a solid bed.

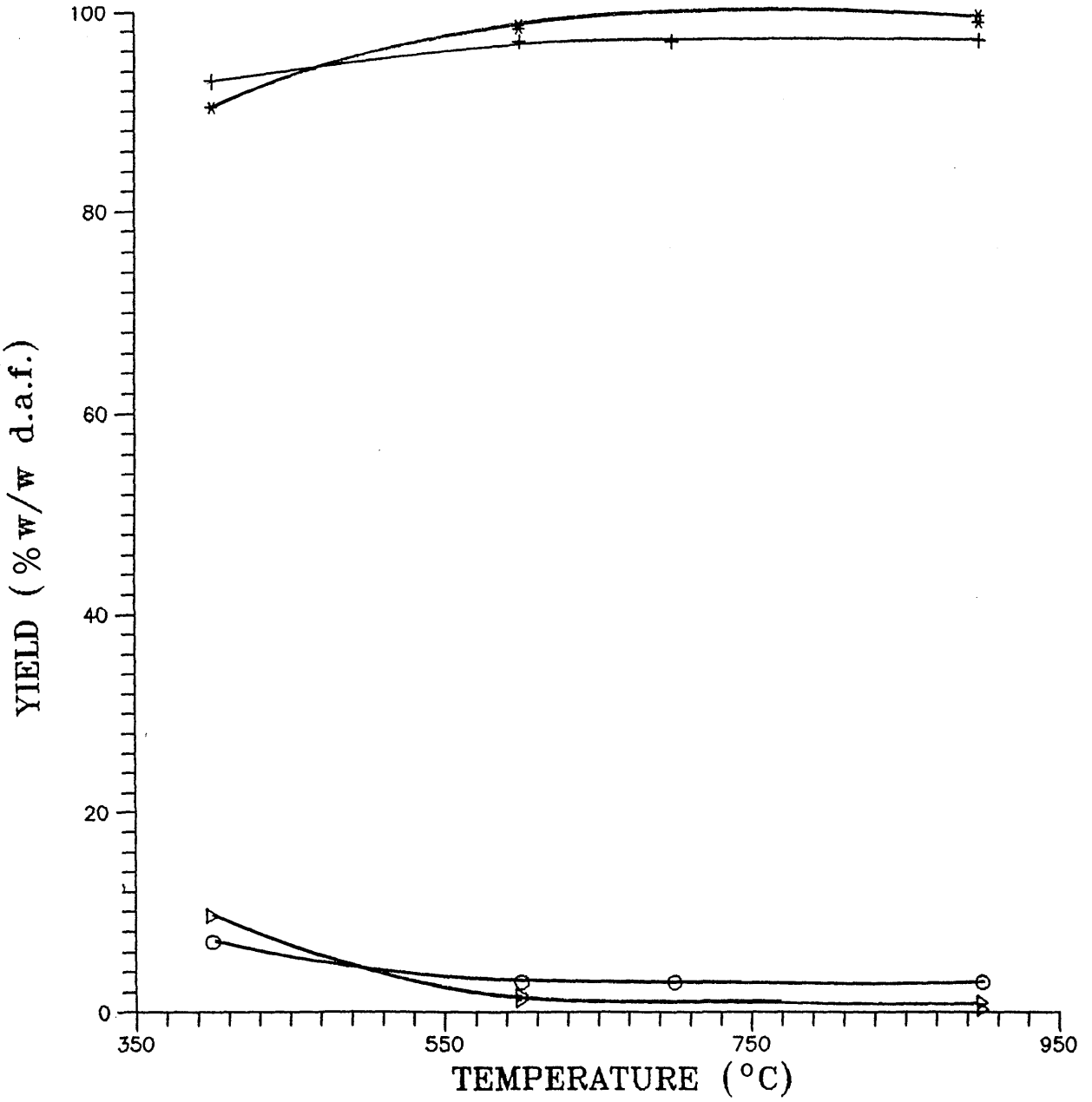


Figure 5.2b – The effect of peak temperature on the yield of total volatiles and char for the pyrolysis of cellulose in two different systems. Heating rate = 1000^0C/sec, hold time = 30 seconds (for both).

* = Total volatiles; Δ = Char → Present study

+ = Total volatiles; 0 = Char → Wire–mesh reactor (Hajaligol[59,60])

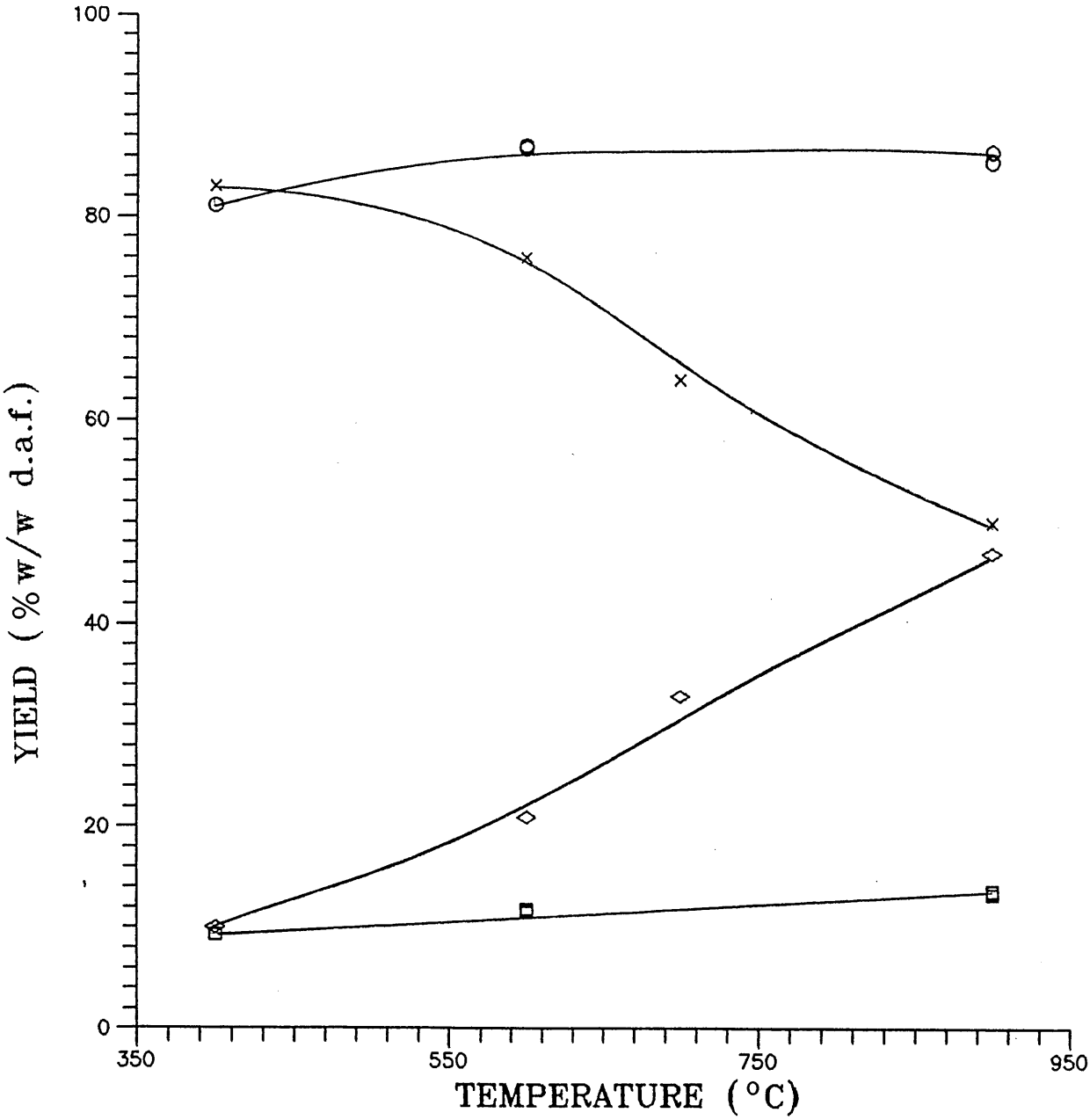


Figure 5.2c – The effect of peak temperature on the yield of tar and gas for the pyrolysis of cellulose in two different systems.

Heating rate = 1000^0C/sec, hold time = 30 seconds (for both).

0 = Tar; □ = Gas → Present study

X = Tar; ◇ = Gas → Wire–mesh reactor (Hajaligol[59,60])

Kim and coworkers[77] have also used a wire–mesh reactor, to study cellulose pyrolysis; it was very similar in design to that of Hajaligol, as were their experimental procedures[59,60]. Pyrolysis runs were, once again, conducted in a non–flowing atmosphere of helium, but now at pressures from 10 to 760 mm Hg. A fixed heating rate, of approximately 250^{0}C/second, was used to raise the sample temperature to either 650^{0}C, 800^{0}C or 900^{0}C. In nearly all of their experiments the sample was cooled as soon as it reached the peak temperature, i.e. zero hold time, whilst in the very few experiments for which the hold time was 15 seconds at the peak temperature, surprisingly, no experimental data were reported.

The cellulose material used in their study was number 4 Whatman filter paper, 0.25mm thick, cut to the dimensions of 0.8 by 1.2 cm, the sample weight was, therefore, about 14 milligrammes. In recovery mode, a helium sweep gas flushed volatiles down the vent line of their vessel and then sequentially through a dry ice trap, a liquid nitrogen trap filled with silica gel, and finally into a modified Carle Instruments Hydrogen transfer system, which enabled the pyrolysis gases to be collected[77]. The design of their apparatus should in principle, therefore, have enabled the collection of all the pyrolysis products; however, their reported material balance closure was not good, as can be seen below from Table 5.2a, where their results are presented. The reduced pressure and single heating rate used by Kim in his wire–mesh reactor do not permit detailed comparisons to be made between his results and those obtained in this present research; however some general conclusions may be drawn.

	Temperature (^{0}C)	Tar (%)	Gases (%)	Char (%)
a	650	53.6	23.4	2.2
a	800	39.5	35.9	3.4
b	800	40.8	38.5	4.1

Table 5.2a – Yields from cellulose pyrolysis in a wire–mesh reactor obtained by Kim[77].
a = 10 mm Hg; b = 760 mm Hg.

From Table 5.2a it is seen that the yield of tar, at 10 mm Hg, was significantly greater at 650^{0}C than that obtained at 800^{0}C. Decreasing tar yield with increasing peak temperature strongly suggests, once again, that significant secondary decomposition of the tar took place; hence secondary reactions most probably determined the numerical value of the tar yield in Kim's reactor.

From the above table it is seen that Kim, at atmospheric pressure and a peak temperature of 800^{0}C, obtained a char yield of 4.1% and a tar yield of 40.8%. However in this research programme the corresponding values for these yields were, 87% tar and 1% char; these values were constant over the range of peak temperatures 600–900^{0}C and with heating rates in the range 1^{0}C/second to 1000^{0}C/second. The large difference between the tar yield obtained by

Kim, at atmospheric pressure, and that of this present study is, most probably, due to the presence of secondary reactions in Kim's apparatus; the severity of which have been shown above, when examining his pyrolysis data at reduced pressure.

In conclusion the differences between the tar and the char yields obtained in this research programme and those reported in past research[59,60,77,134,135] have been shown to be due to the intensity of secondary reactions taking place in the experimental apparatus used by Hajaligol et al and Kim et al. The observation reported here that all of the pyrolysis products of cellulose attain a constant maximum value above 500^0C, which is itself independent of the heating rate in the range 0.1^0C/second to 1000^0C/second, was obtained because the experimental procedures employed in this research greatly reduce the effect of secondary reactions. The action of the helium carrier gas, which rapidly swept volatile products away from the hot reaction zone coupled with the granular nature of the specimens has been shown to be particularly important in minimising primary tar decomposition and re–polymerisation processes.

5.3 — The Pyrolysis of Lignin.

Nunn and co–workers[101] used for their studies of the pyrolysis of lignin the wire–mesh apparatus of Hajaligol[59,60]. The experimental procedures associated with their apparatus have already been reported in this Chapter, see section 5.2; in summary it may be recalled here that the minimum heating rate of their wire–mesh reactor was 100^0C/second; that the sample size was 100 milligrammes, and that the experimental runs were performed in a stagnant atmosphere of helium.

In Figures 5.3a and 5.3b, the results obtained during the present study of the pyrolysis of lignin and those of Nunn[101] are presented; these figures show graphically the effect of peak temperature on the yield of the lignin pyrolysis products. In both cases the heating rate was 1000^0C/second, however in the present study the sample was held at the peak temperature for 30 seconds, while in Nunn's the hold time was zero second.

From Figure 5.3a it can be seen that over the temperature range of 600–900^0C, the yields of total volatiles obtained by Nunn[101] are all higher than those obtained in this research programme; except for the datum at 400^0C, where the total volatiles yield of about 50% obtained in this study is much greater than that of Nunn who obtained only 5%. The higher total volatile yields obtained by Nunn may be partially explained by differences in the chemical composition of

Nunn's lignin, obtained from Sweet Gum Hardwood, and the softwood lignin used in this research programme. Furthermore it has previously been shown that when the same apparatus was used by Hajaligol to pyrolyse cellulose[59,60] secondary reactions played an important role in determining the yields of the pyrolysis products. There exists, therefore, a possibility that the lignin yields measured by Nunn have also been substantially affected by the action of tar cracking. From Figure 5.3b it may be seen that Nunn's tar yield increases with increasing peak temperature, over the range 400^{0}C to 600^{0}C, reaching a maximum of 52%; thereafter the yield of tar decreased to 45% at 900^{0}C. This decreasing tar yield, with increasing temperature may be taken to be strongly indicative of the existence of secondary reactions in Nunn's equipment. In contrast, the tar yield obtained in this present study at 400^{0}C was 40%, and at 600^{0}C and above, it attained a constant maximum value of 45%. Nunn's pyrolysis products, as those of Hajaligol, remained within the reaction vessel and in close proximity to the hot zone; there was, therefore, a high probability of tar cracking reactions on the surfaces of the hot mesh. The probability of secondary reactions taking place was, therefore, significantly higher in Nunn's study than in this research.

Furthermore the yields of the pyrolysis products, as determined by Nunn, may also have been distorted by a practical problem, described below, that he encountered during his experiments.

Lignin, following extraction from a wood cell, is in the form of a very fine powder[7], with a mean particle size of the order of

10 microns. The sample holder used in Nunn's experiments was a folded strip fabricated from 325 mesh (44 microns) stainless steel[59,60]. Nunn has reported encountering severe problems in retaining all of the lignin sample inside the 44 microns specimen holder. "...Attempts to prepare a 45–88 microns size fraction of lignin powder by dry sieving were unsuccessful because of excessive lignin losses and apparent clogging of the sieve openings. Small (≤100 microns thick) flakes were prepared by pressing 20 milligrammes lots of the powder between two 2.5 x 15 cm parallel plates mounted between the jaws of a hand–operated catalyst pelletizing press. The flakes adhered to the parallel plates and had to be chipped off with a microspatula. During this chipping process most of the 10 millimeters diameter flakes broke into fragments, which were too small for the heater grid. Several pressings were therefore needed to generate enough acceptable flakes for the pyrolysis experiments." (From Nunn et all 1985c).

In contrast the lignin specimens used in this research programme were prepared to the size of 100–150 microns, by pressing the powder sample in a " hydraulic press and die", crushing the pellet, and sieving the granules, as already described in Chapter 2 section 3. It is clear from the above that in Nunn's experiments there was a strong possibility of some of the pure lignin, or lignin char, being lost; and, obviously, any such loss will increase the apparent yield of total volatiles.

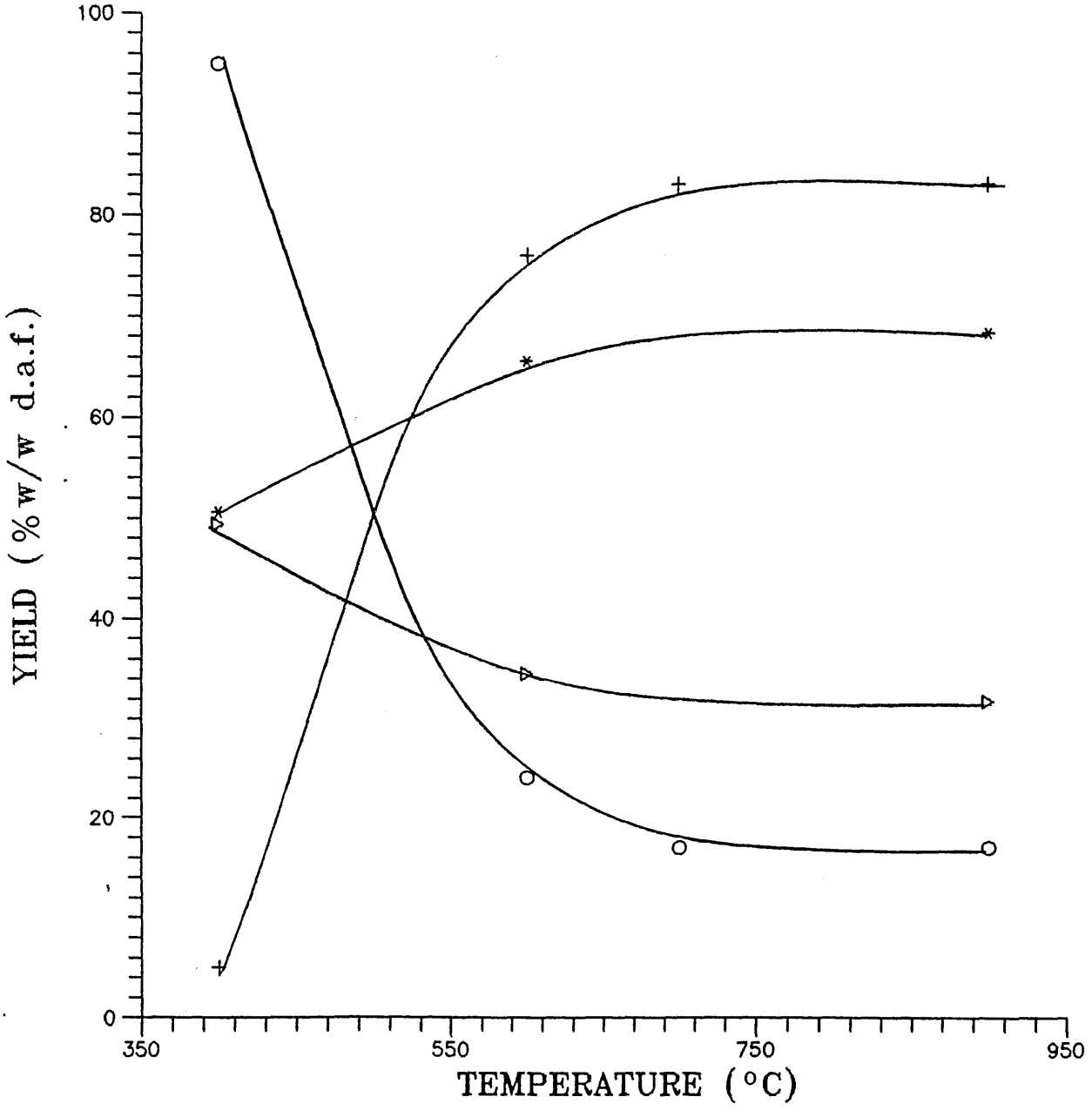


Figure 5.3a – The effect of peak temperature on the yield of total volatiles and char for the pyrolysis of lignin in two different systems. Heating rate = 1000^0C/second (for both).

* = Total volatiles; Δ = Char → (hold time = 30 seconds, sample = softwood lignin) – Present study.

+ = Total volatiles; 0 = Char → (hold time = 0 second, sample = hardwood lignin) – Wire–mesh reactor (Nunn[101])

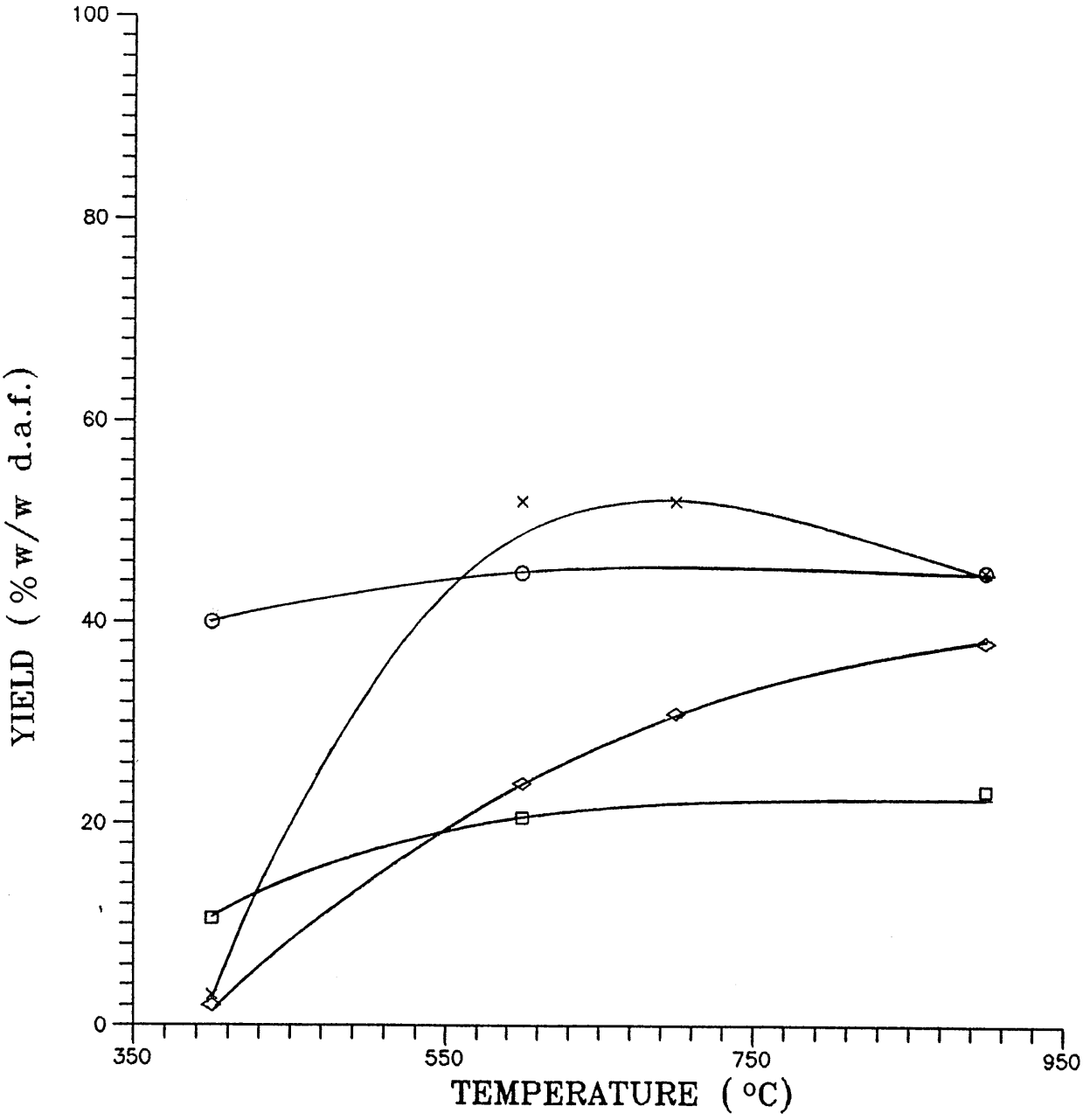


Figure 5.3b – The effect of peak temperature on the yield of tar and gas for the pyrolysis of lignin in two different systems.

Heating rate = 1000^0C/second (for both).

0 = Tar; □ = Gas → (hold time = 30 seconds, sample = softwood lignin) – Present study.

X = Tar; ◇ = Gas → (hold time = 0 second, sample = hardwood lignin) – Wire–mesh reactor (Nunn[101])

5.4 – The Pyrolysis of Lignocellulosic Materials.

5.4.1 – Biomass Pyrolysis in Wire–Mesh Systems.

In Figures 5.4a and 5.4b, the results obtained by Nunn[99,100] for the pyrolysis products of Sweet Gum Hardwood and those determined in this study for Sugar Cane Bagasse are presented. These Figures show the effect of peak temperature on product yields for these lignocellulosic materials; for both data sets the heating rate was 1000^{0}C/second and the hold time, at the peak temperature, was zero second.

From Figure 5.4a it can be seen that the yield of total volatiles for the Sweet Gum sample has a similar behaviour to that of Sugar Cane Bagasse. For Sugar Cane Bagasse, with a peak temperature of 600^{0}C, the total volatiles yield was, say, 90% and for peak temperatures of 700^{0}C or more there was no increase in this yield, which remained constant at about 96%. Nunn's total volatiles yield at 600^{0}C was, say, 78%, and for peak temperatures of 700^{0}C or more, it also attained a maximum value of about 93%.

However from Figure 5.4b it is seen that there exists a significant difference between the tar and gas yields for Sugar Cane Bagasse and Sweet Gum Hardwood. There are several possible explanations for these differences; for example specimen composition,

specimen morphology, specimen size, as well as the role of secondary reactions in cracking primary tars. Unfortunately Nunn does not report the cellulose/lignin ratio for his Sweet Gum Hardwood material, thus the contribution of this important parameter to the differing numerical values cannot be evaluated, even in a qualitative way. Specimen morphology presents a similar problem; Sweet Gum Hardwood is, obviously, a hardwood while Sugar Cane Bagasse is, broadly, a "grass like" material, hence its lignin fraction will almost certainly be arranged in a quite different, three dimensional, structure, reflecting a different range of "lignin type" compounds, to that found in Sweet Gum Hardwood.

The tar yield of, say, 50% obtained in this present study was independent of the peak temperature, within the range 600–900^{0}C. The tar yield of 53%, reported by Nunn was also constant for the restricted temperature range of 600–700^{0}C, after which it diminished to approximately 44%, as the peak temperature increased to 900^{0}C. This decrease in Nunn's tar yield may, once again, be taken as the indicator for the presence of secondary reactions; indeed as Nunn reported: "...The decrease in tar yield at temperature above 700^{0}C is believed to arise from its secondary cracking to light volatiles..." (from Nunn et all 1985b).

The reduction in Nunn's tar yield and, therefore, the corresponding enhancement in the yield of gaseous products above 700^{0}C, may be attributed, as before to two important experimental parameters, they are:

a — Carrier gas,

b — Sample size.

The importance of these parameters has already been discussed, in detail in this Chapter, see section 5.2; their effects may be summarised thus:

a — Increased residence time in the hot reaction zone enhances the cracking of tars.

b — Increased surface area per unit weight decreases the residence time of pyrolysis products in the specimen bed.

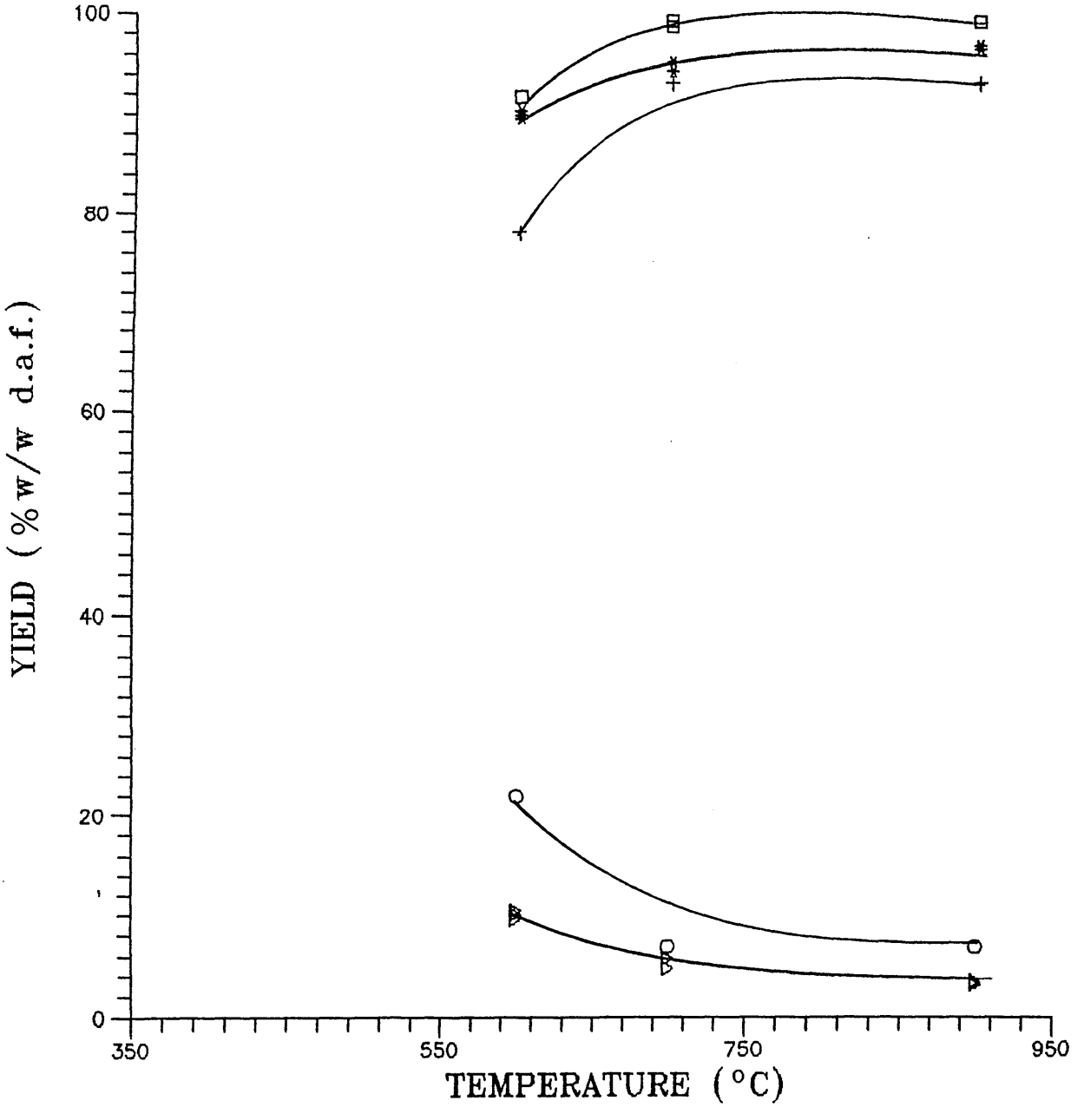


Figure 5.4a – The effect of peak temperature on the yield of total volatiles and char for the pyrolysis of lignocellulosic materials in two different systems.

Heating rate = 1000^{0}C/sec, hold time = 0 seconds (both)

* = Total volatiles; Δ = Char → Present study, Bagasse.

□ = Total volatiles → Present study, Silver Birch.

+ = Total volatiles; 0 = Char → Wire–mesh reactor (Nunn[99;100])

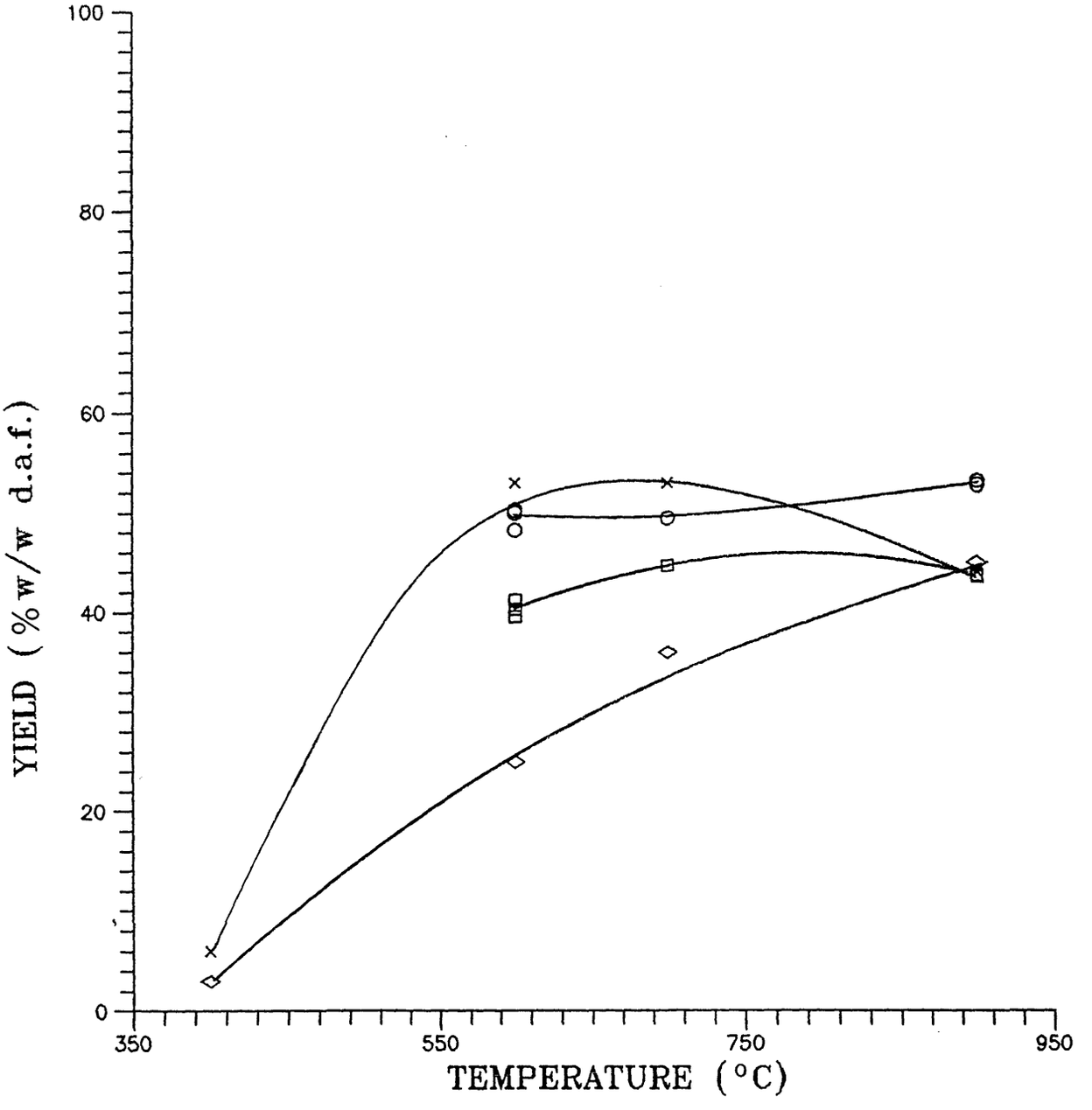


Figure 5.4b – The effect of peak temperature on the yield of tar and gas for the pyrolysis of lignocellulosic materials in two different systems. Heating rate = 1000^0C/sec, hold time = 0 seconds (both)

0 = Tar; □ = Gas → Present study, Bagasse.

X = Tar; ◇ = Gas → Wire–mesh reactor (Nunn[99,100])

5.4.2 – Biomass Pyrolysis in Fluidised Bed Systems.

Silver Birch has been pyrolysed by Stiles[134,135], in a fluidised bed reactor which has already been described in detail, see section 5.2. His results for the pyrolysis products yields, as a function of peak temperature, are presented in Figures 5.4c and 5.4d, in conjunction with the results obtained in this present study. It should be noted that the specimens for these two research programmes were made from the same process bulk material. The experimental parameters used in this present series of experiments were a heating rate of 1000^{0}C/second, and 30 seconds hold time at the peak temperature.

Figure 5.4c shows that in this present study about the same yield of total volatiles was obtained as that of Stiles, using these identical samples of Silver Birch. The yield of total volatiles reported by Stiles, at 400^{0}C, was about 83%; and at 600^{0}C this yield attained a maximum constant value of, say, 96%. In this research programme, using a wire–mesh reactor, the yield of total volatiles, at 400^{0}C, was about 89%, and at 600^{0}C this yield attained a maximum constant value of, say, 98%.

However from Figure 5.4d, it can be seen that Stiles's Silver Birch and cellulose tar yields exhibits the same behaviour, see section 5.2. At 400^{0}C Stiles's yield of Silver Birch pyrolysis tar was about 56%; this was drastically reduced to 8% when the peak

temperature was increased to 800^{0}C. As before decreasing tar yield with increasing temperature is the "semaphore" which strongly suggests the presence of many secondary reactions taking place within the apparatus. From Figure 5.4d., it appears that the primary tars obtained by Stiles were cracked to form gaseous products; his yield of gas plus water at 400^{0}C was, say, 27% and increased with increasing peak temperature to 88% at 800^{0}C. This behaviour is in marked contrast to that of the tar yield obtained in this research programme, where for specimens of identical composition and morphology the yield was constant at, say, 57% over the wide temperature range of 400–900^{0}C. This result once again strongly supports the premise that in the wire–mesh reactor used in this research programme secondary reactions, that is the cracking or polymerisation of primary tars, are greatly diminished.

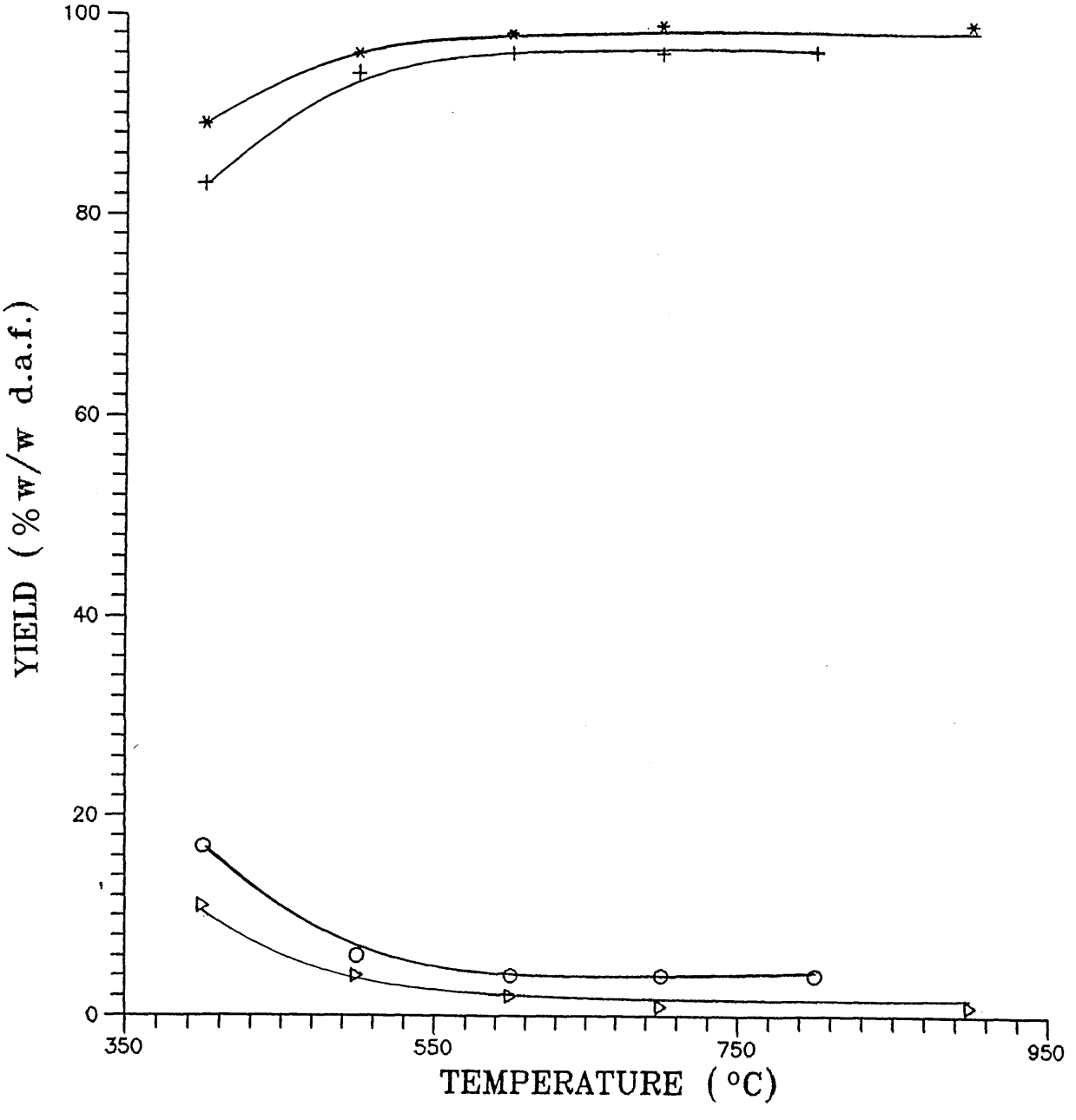


Figure 5.4c – The effect of peak temperature on the yield of total volatiles and char for the pyrolysis of lignocellulosic materials in two different systems. (sample = Silver Birch)

* = Total volatiles; Δ = Char → (heating rate = 1000°C/sec, hold time = 30 seconds) Present study.

+ = Total volatiles; 0 = Char → Fluidised bed reactor (Stiles[134,135]) – residence time = 2.44 seconds.

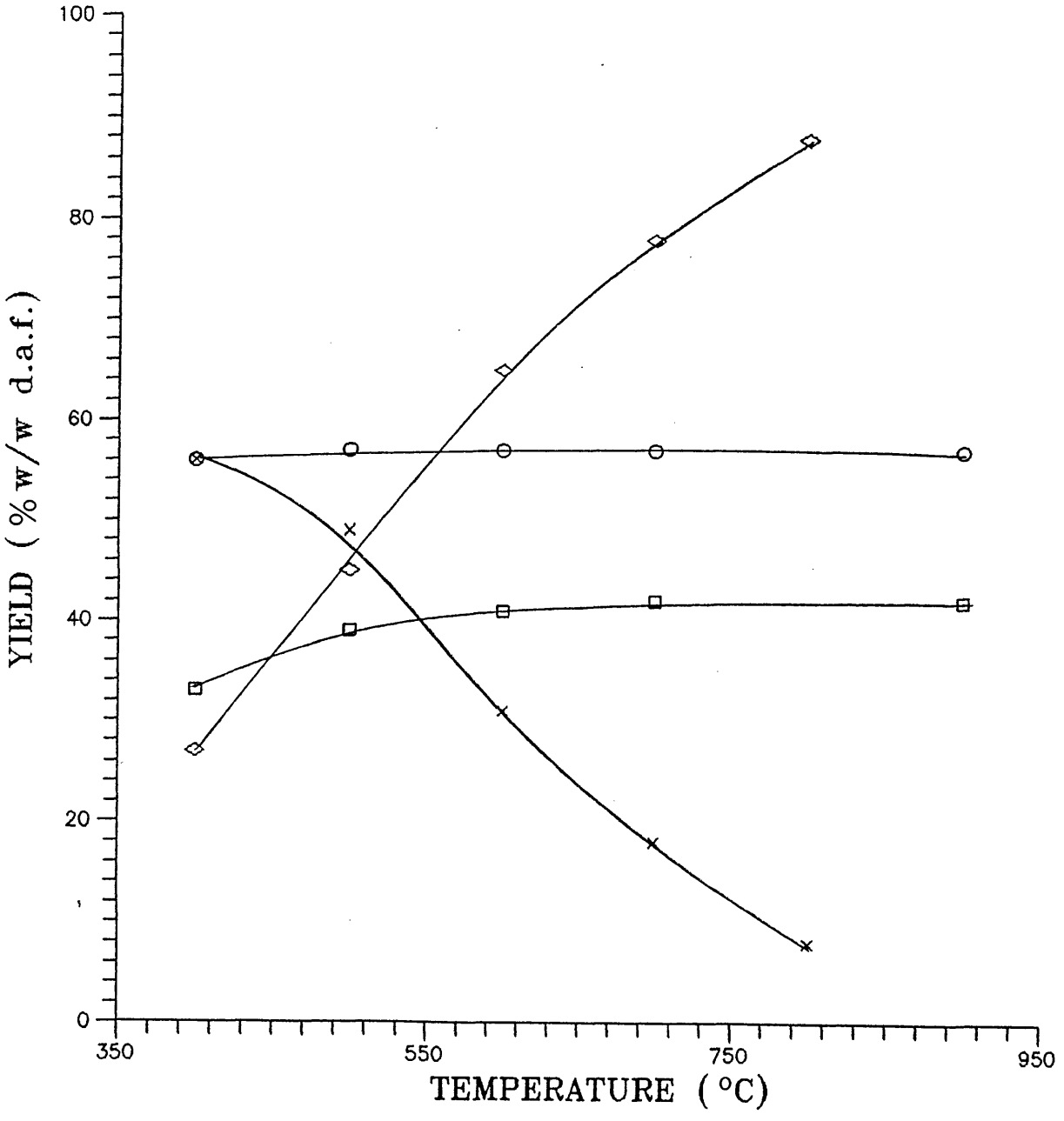


Figure 5.4d – The effect of peak temperature on the yield of tar and gas for the pyrolysis of lignocellulosic materials in two different systems.
0 = Tar; □ = Gas → (heating rate = 1000°C/sec, hold time = 30 seconds) Present study
X = Tar; ◇ = Gas → Fluidised bed reactor (Stiles[134,135]) – residence time = 2.44 seconds.

5.4.3 – Biomass Pyrolysis in Thermobalance Systems.

Deepchand[30] has performed pyrolysis studies in a themogravimetric balance, of some lignocellulosic materials, namely cellulose, Pinus Sylvestris wood and Sugar Cane Bagasse. The "reactor" which Deepchand employed was a Linseis L81 thermobalance; the weight loss of the sample was continuously monitored and recorded as the temperature was raised. A representative sample, weighing 2–3 milligrammes, was pyrolysed in this thermobalance at a heating rate of 10^0C/minute (0.16^0C/second) up to a maximum peak temperature of 500^0C. The nitrogen carrier gas flowed continuously over the sample throughout the entire experiment, at the flow rate of 100ml/minute. Only the yield of total volatiles and, obviously, of char were determined in these experiments. In Table 5.4a the yield of total volatiles and char, under the above pyrolysis conditions, for specimens of Sugar Cane Bagasse, cellulose and Pinus Sylvestris wood obtained by Deepchand are presented.

Sample	Volatiles (%)	Char (%)
Cellulose	89.8	10.2
Bagasse	72.7	27.3
Pinus	77.6	22.4

Table 5.4a – Pyrolysis yields of lignocellulosic materials obtained by Deepchand[30].

Deepchand's pyrolysis data agree moderately well with those obtained, for nominally the same materials, using the wire–mesh reactor. The data obtained in this present study have been reported in full in Chapters 3; here only selected results, i.e. those obtained with experimental conditions similar to those used by Deepchand, are shown in Table 5.4b. These data were obtained with a heating rate of 0.1^0C/second up to a peak temperature of 600^0C, and with a hold time, at the peak temperature, of 30 seconds.

Sample	Volatiles (%)	Char (%)
Cellulose	96.5	3.5
Bagasse	80.9	19.1
S.Birch	85.1	14.9

Table 5.4b – Pyrolysis yields of lignocellulosic materials obtained in the present study.

Comparison of Table 5.4a and 5.4b shows that the "ranking" of these materials is the same in both studies; that is to say that the yield of total volatiles decreases in the order cellulose, Silver Birch (Pinus) and Sugar Cane Bagasse. The larger char yields obtained by Deepchand for all of these materials is, if one may discount the possibility of a "constant" error in all of his results, which may be

inferred from the constant difference in yield of 6%, probably due to a subtle influence of reactor geometry.

In thermo–gravimetric analysis apparatus a small sample is suspended within, and in close proximity to, the walls of a micro furnace. A fine suspension wire passes down through a small hole in an upper radiation shield, which effectively "caps" the furnace and supports the specimen boat. Nitrogen gas flows downwards past the outer walls of the micro furnace and, since it cannot flow through its solid base, the residence time of primary volatiles, within the hot zone, may be substantially longer than would at first be estimated based upon the volumetric flow rate. Primary tars may polymerise near or on the specimen surface and thereby enhance the char yield.

5.5 – The Interaction between Cellulose and Lignin in Synthetic Materials.

In Chapter 3 section 3.7 a difference between the theoretical and experimental total volatile yields for natural and synthetic lignocellulosic materials was established; Figure 3.7b is reproduced here as an aide–mémoire, with the addition of the data points for Sugar Cane Bagasse and Silver Birch, as Figure 5.5a.

From Figure 5.5a it can be seen that for the synthetic materials the total volatile yields are lower than would be expected from the simple, arithmetic, addition of the yields of the individual pure components. This experimental observation is in contrast to the data obtained for the naturally occurring materials, where the yield of total volatiles is seen to be higher than would be expected, based upon the above calculation.

To probe the interaction between cellulose and lignin in these lignocellulosic materials further two additional analytical investigations were undertaken, namely Scanning Electron Microscopy and Differential Scanning Calorimetry, these results are presented in the following sections.

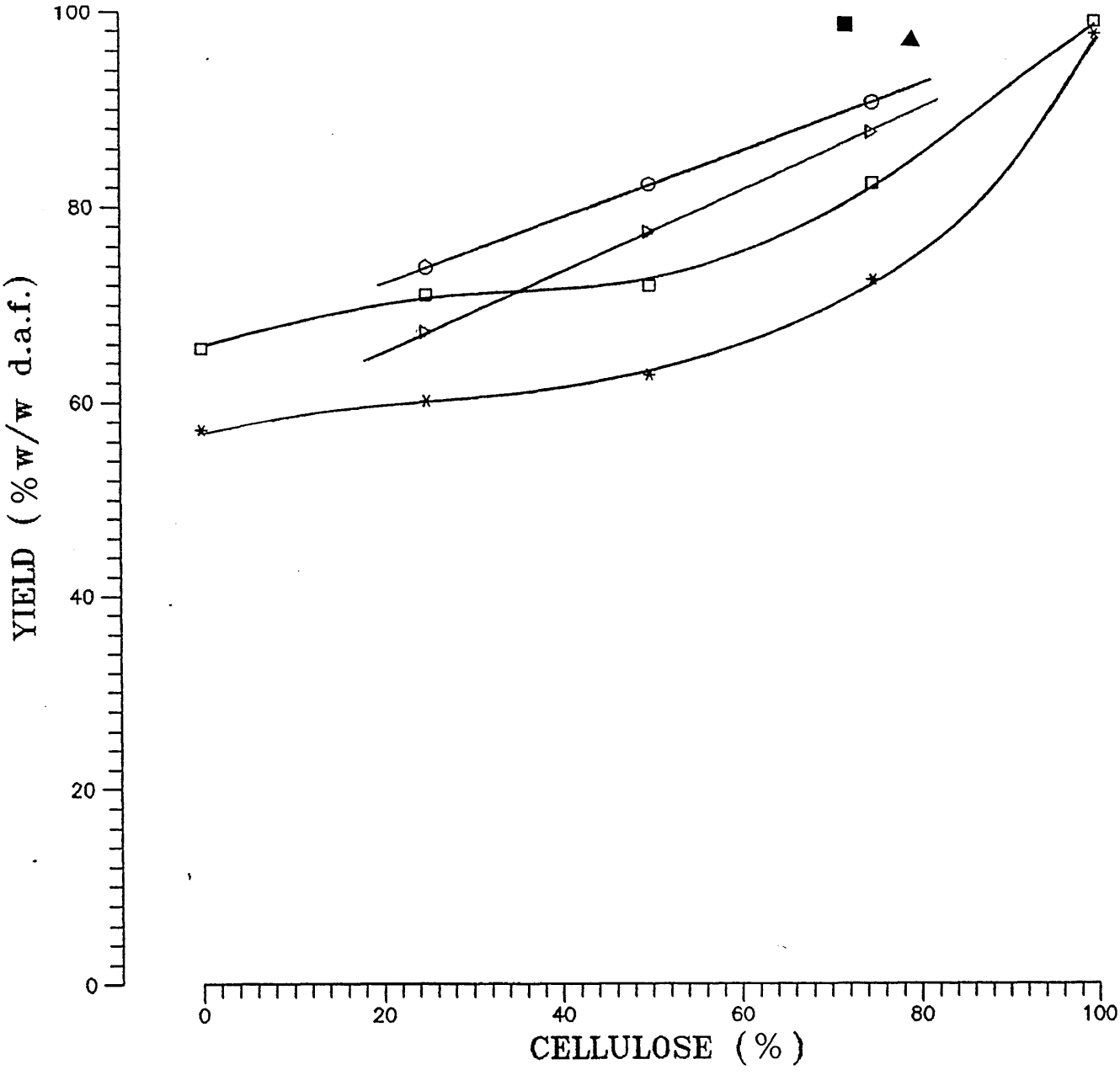


Figure 5.5a – The theoretical and experimental yields of total volatiles as a function of cellulose content and heating rate, at 600^{0}C and 30 seconds hold time.

* = 1^{0}C/second; □ = 1000^{0}C/second (experimental).

Δ = 1^{0}C/second; 0 = 1000^{0}C/second (theoretical).

▲ = Sugar Cane Bagasse; ■ = Silver Birch. (data at 1000^{0}C/second)

The photographs presented in Figures 5.5b to 5.5i were taken using a JEOL–220A Scanning Electron Microscope, "SEM", at a magnification of 200. These photographs are of the wire–mesh following pyrolysis of cellulose, lignin, and the synthetic materials at a peak temperature of 600^{0}C and a hold time, at this peak temperature, of 30 seconds; for the samples shown in photographs 5.5c–5.5g the heating rate was 1000^{0}C/second, while for the sample shown in photograph 5.5b it was 1^{0}C/second. Preparation of the mesh for microscopic examination, following a pyrolysis run, was a moderately difficult procedure. To begin with, the mesh envelope was gently opened and a small circle of approximately 7 mm diameter cut out using wire scissors, this specimen was then mounted onto a small metal holder, which would ultimately be inserted into the SEM, using electrically conducting paint. Before viewing, the sample was lightly coated with gold, using standard evaporation techniques, so as to minimise charge build up on the char residue. It should be noted that although all these manipulations were, of course, performed most carefully, it proved to be impossible to retain the loose particles of char through all these steps, only the char residue adhering to the mesh itself remained intact. Hence these photographs do <u>not</u> represent, in a quantitative way, the yield of char obtained for each pyrolysis experiment, however they do show, in a qualitative way, the important role that lignin plays in the pyrolysis of these specimens.

Figures 5.5b and 5.5c show the grid after the pyrolysis of pure cellulose, at 1^{0}C/second and 1000^{0}C/second respectively. In both of these photographs the wire–mesh is seen to be beautifully clean.

This pristine appearance diminishes with increasing lignin content of the sample, see Figures 5.5d–5.5g. It is readily seen that the fragments remaining from the pure lignin specimen, shown in Figure 5.5g, are very different to those of the pure cellulose sample, see again Figure 5.5c. It can be seen, from Figure 5.5g, that during pyrolysis at the fast heating rate of 1000^0C/second lignin swells and develops a plastic, mesomorphic, structure; hence during its plastic phase lignin may flow over the particles of cellulose and, to varying degrees, encapsulate them. Thus the volatile pyrolysis products of these entrapped cellulose particles will have to either diffuse slowly through this plastic layer or escape via bubble formation. The residence time within the hot zone, for volatiles from encapsulated cellulose granules will be substantially longer than those from uncoated particles, due to this physical process. A fraction of the cellulose tar has, therefore, an enhanced probability of undergoing further reactions within the pyrolysis mass and thereby increasing the char yield. This physical mechanism provides a possible explanation for the differences found between the theoretical and experimental yields of total volatiles for the "synthetic" woods, as shown in Figure 5.5a and reported in detail in section 3.7.

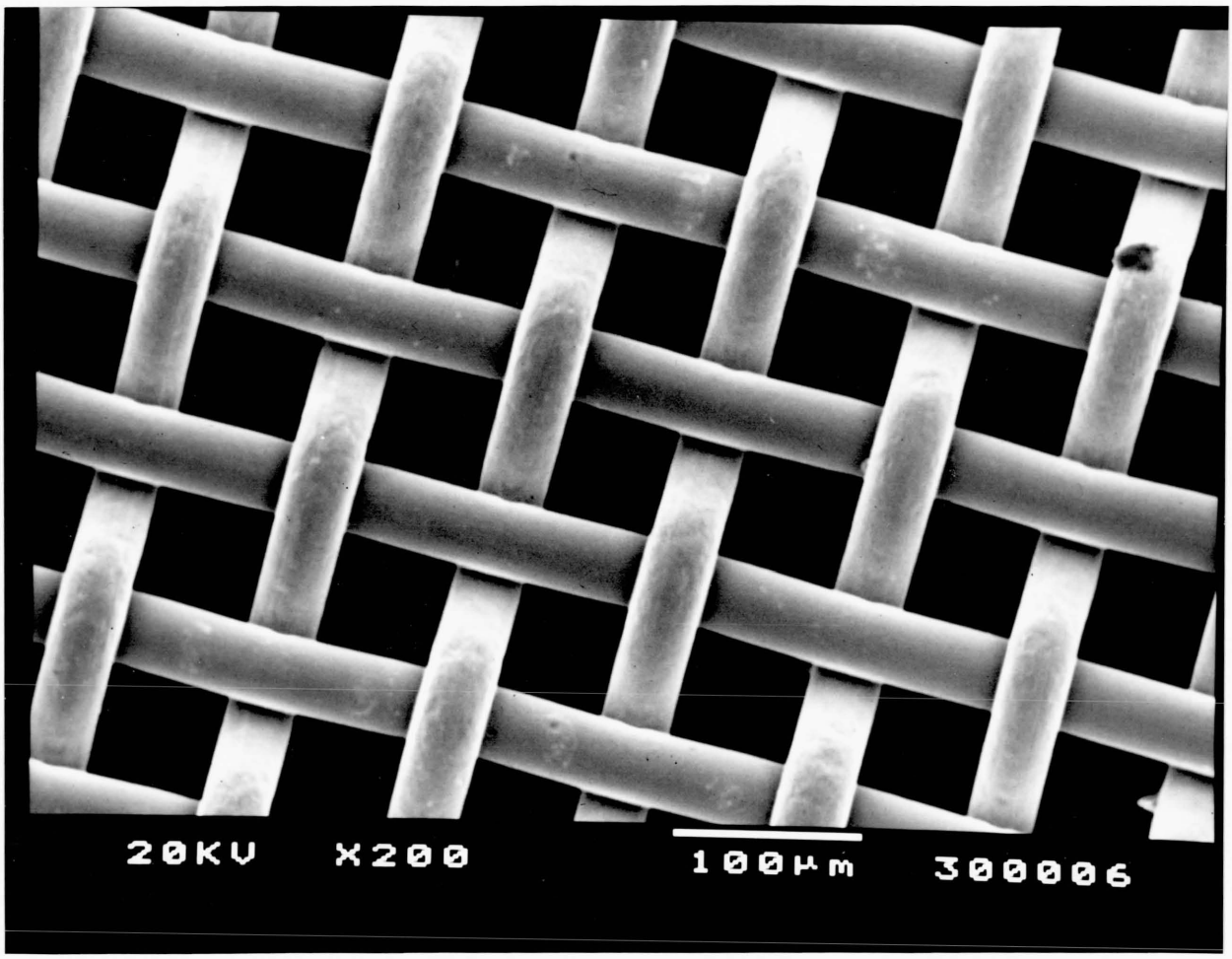


Figure 5.5b – The wire–mesh after the pyrolysis of pure cellulose.
Heating Rate = 1^0C/second; Temperature = 600^0C;
Hold Time = 30 seconds.

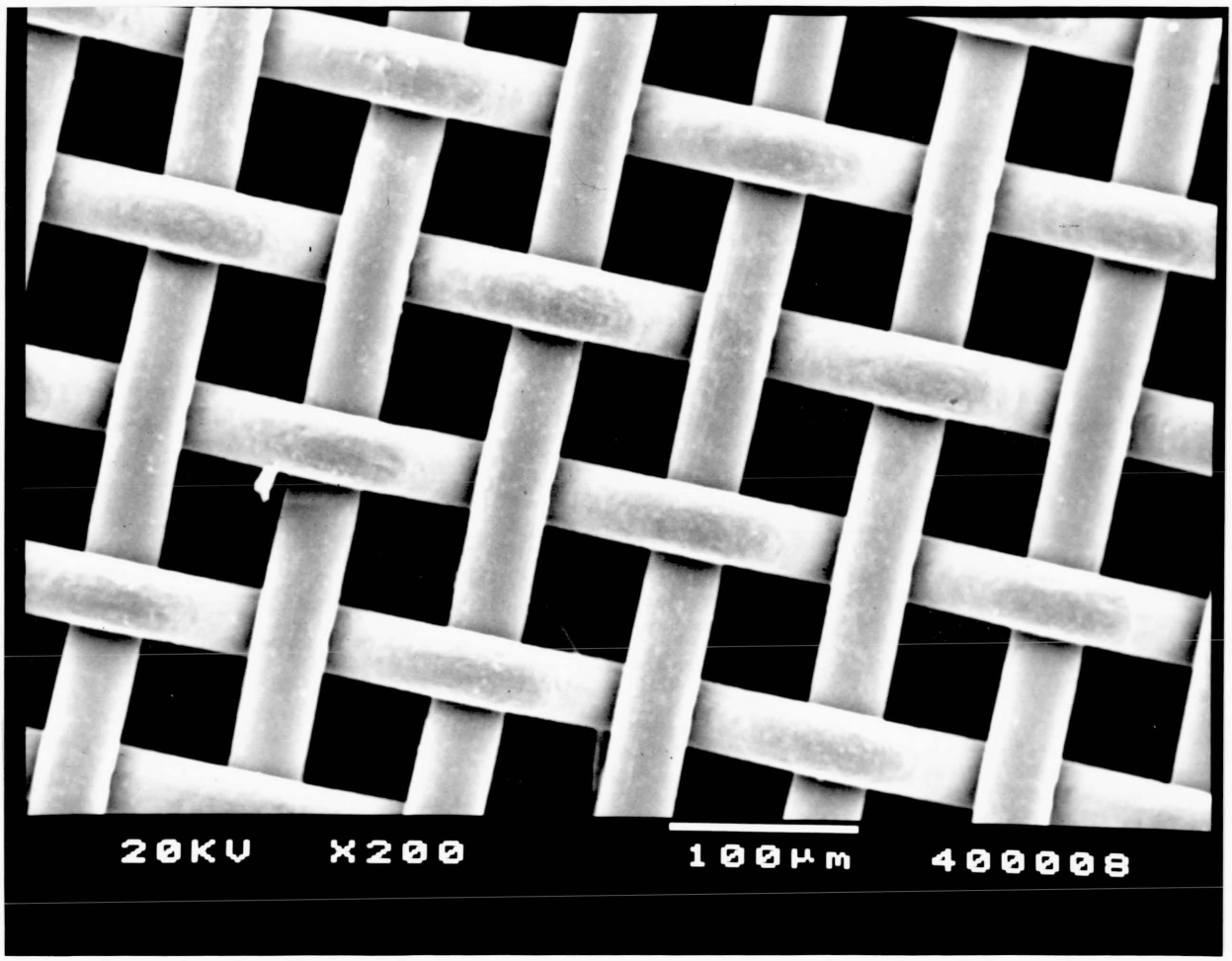


Figure 5.5c – The wire–mesh after the pyrolysis of pure cellulose.
Heating Rate = 1000^{0}C/second; Temperature = 600^{0}C;
Hold Time = 30 seconds.

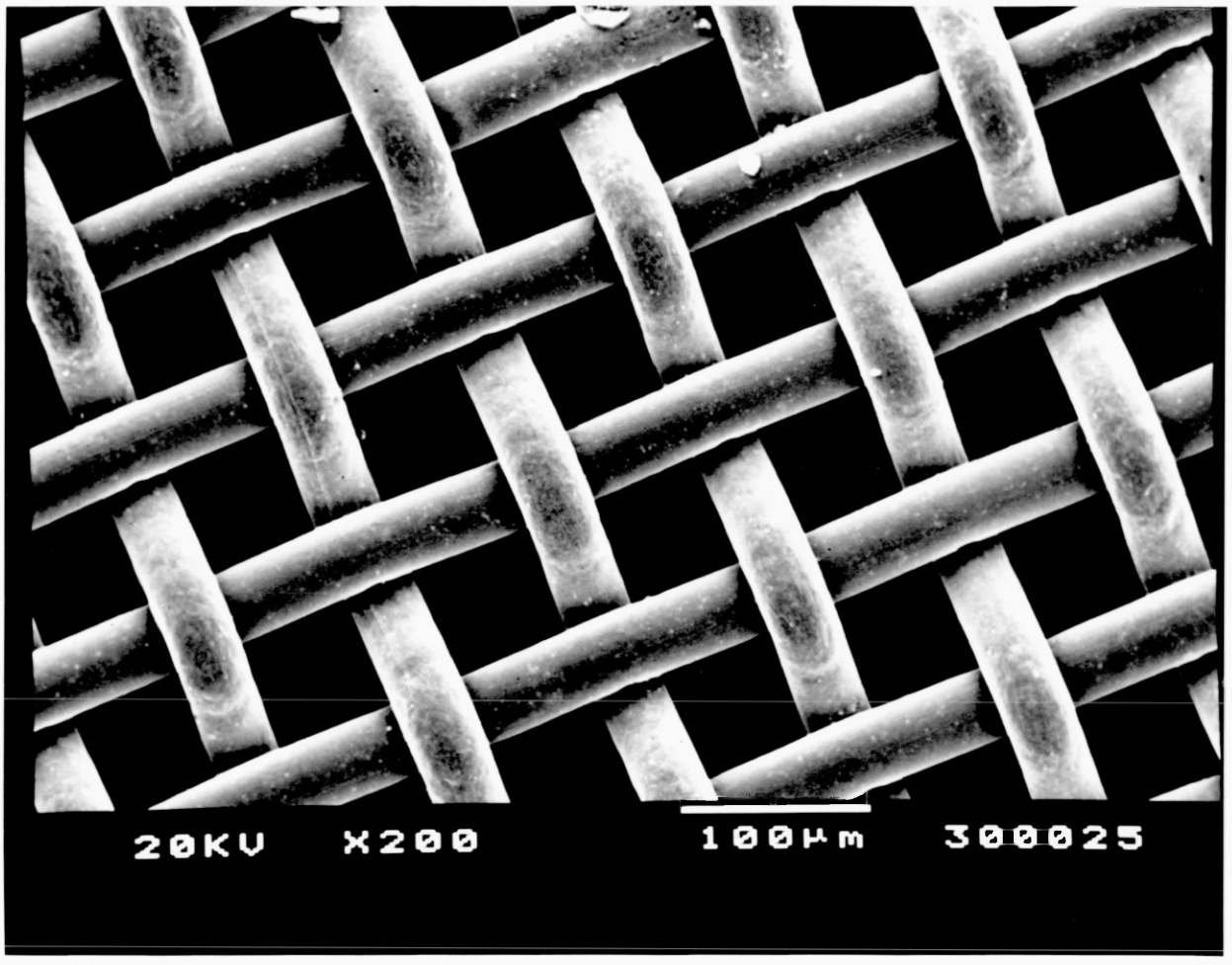


Figure 5.5d – The wire–mesh after the pyrolysis of the mixture 75%cellulose:25%lignin.

Heating Rate = 1000^{0}C/second; Temperature = 600^{0}C;

Hold Time = 30 seconds.

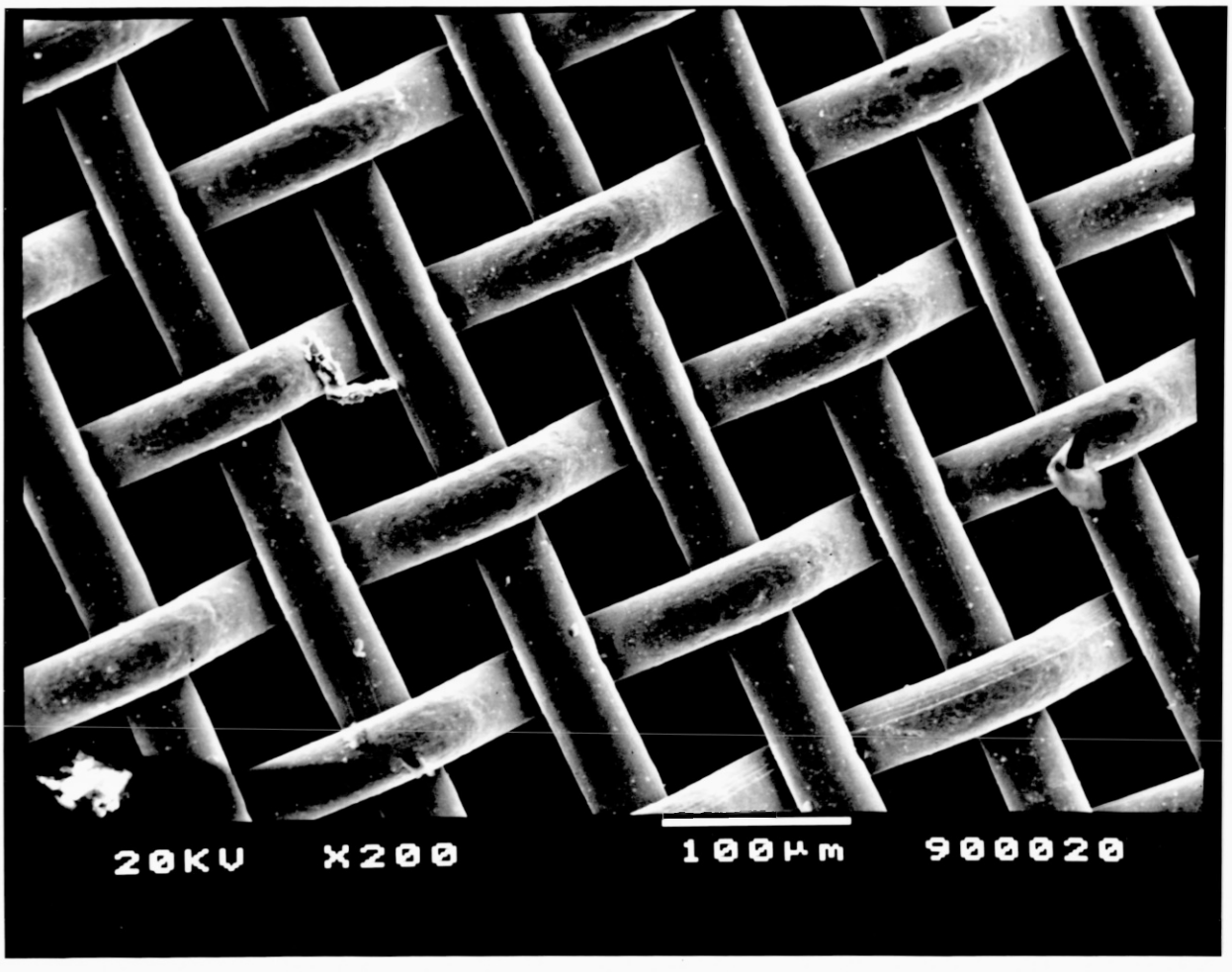


Figure 5.5e – The wire–mesh after the pyrolysis of the mixture 50%cellulose:50%lignin.

Heating Rate = 1000^{0}C/second; Temperature = 600^{0}C;

Hold Time = 30 seconds.

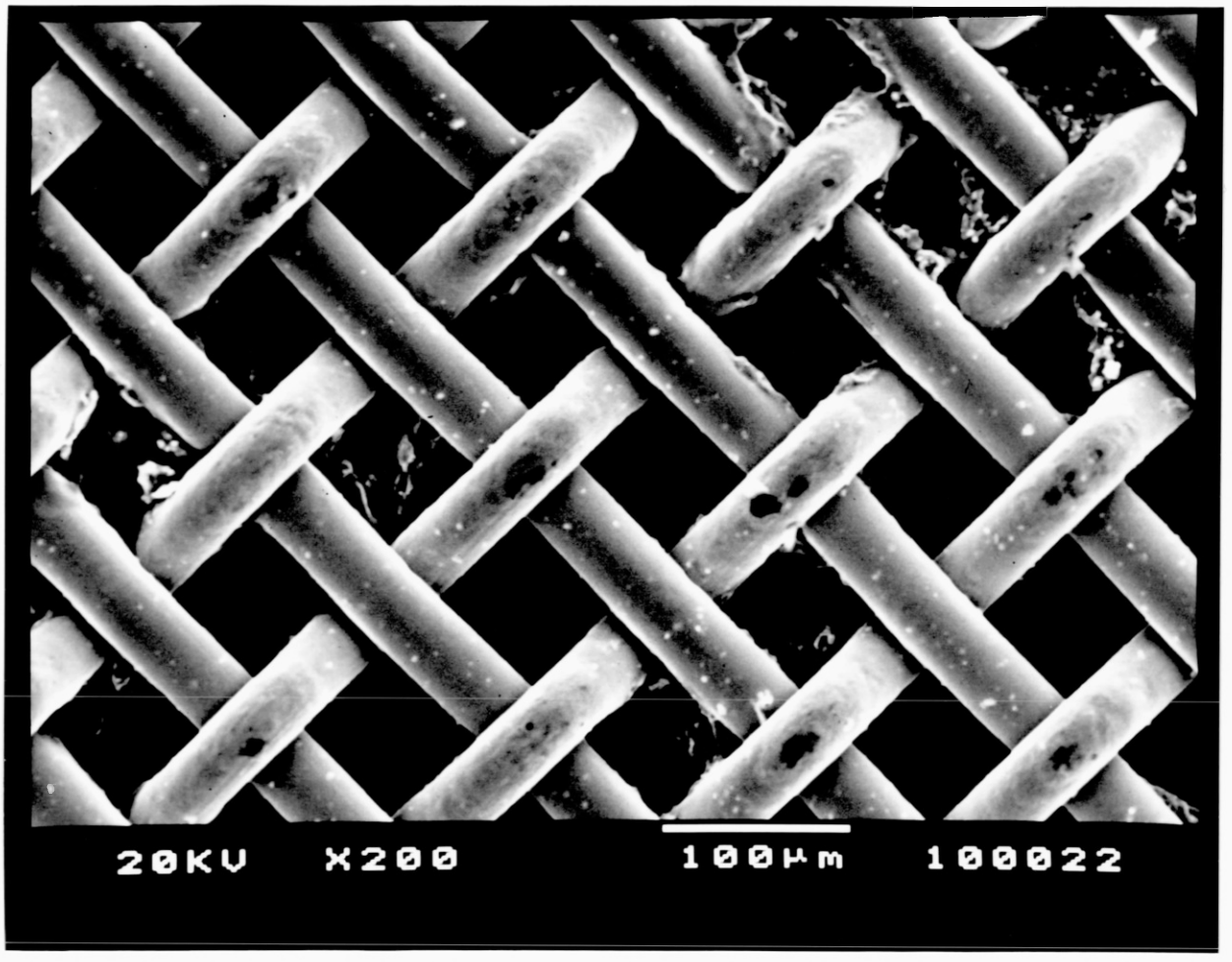


Figure 5.5f – The wire–mesh after the pyrolysis of the mixture 25%cellulose:75%lignin.

Heating Rate = 1000^0C/second; Temperature = 600^0C;

Hold Time = 30 seconds.

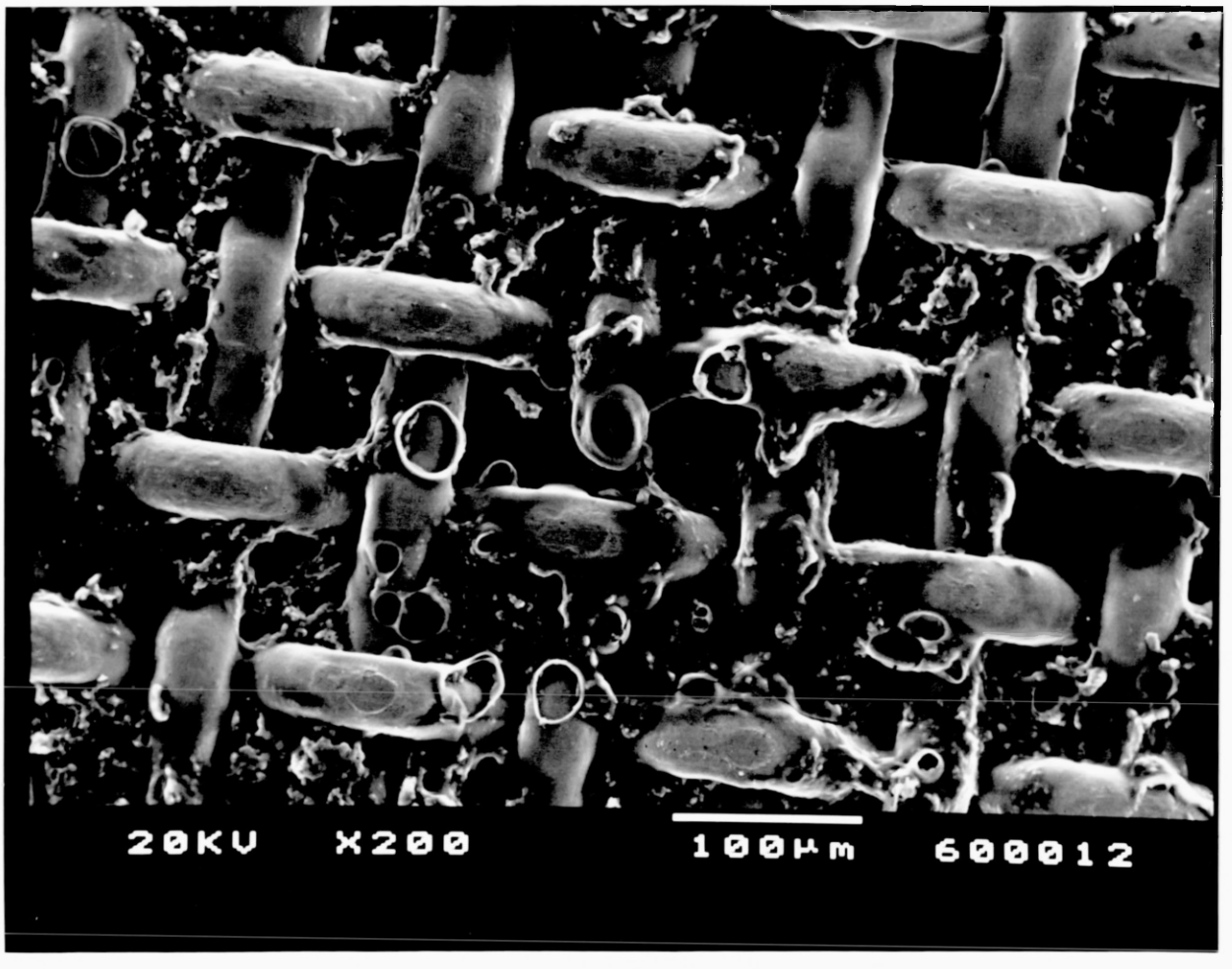


Figure 5.5g – The wire–mesh after the pyrolysis of pure lignin.
Heating Rate = 1000^0C/second; Temperature = 600^0C;
Hold Time = 30 seconds.

5.6 – The Interaction Between Cellulose and Lignin in Naturally Occurring Materials.

In the previous section a physical interaction between lignin and cellulose was identified that takes place during the pyrolysis of "synthetic" biomass. Investigation of the char fragments adhering to the wire–mesh, using the technique of SEM, established the plastic behaviour of pyrolysing lignin. Thus it appears that lignin can partially entomb the granular cellulose of these "synthetic" materials; this encapsulation process provides an explanation for the observed decrease in the yield of total volatiles below that which might be expected, based upon the simple summation of the individual yields of cellulose and lignin, as recorded in this research programme, see section 3.7.

However, the yields of total volatiles for both of the naturally occurring materials examined in this present study, namely Sugar Cane Bagasse and Silver Birch, are significantly greater than that obtained from a specimen of "synthetic" wood that has, approximately, the same cellulose/lignin ratio, see again Figure 5.5a. For the same pyrolysis conditions as that in Figure 5.5a it may be shown that, from the experimental values reported in Chapter 3 for the tar and gas yields of cellulose (tar 86%, gas 13%) and lignin (tar 45%, gas 20%), that by taking simple ratio's, using the measured lignin content of Sugar Cane Bagasse (22% lignin, 78% cellulose) and its tar yield of 56%, it appears that in Sugar Cane Bagasse levoglucosan, which has been shown to be the major pyrolysis product of cellulose, itself decomposes to tar and

gas. From the simple calculation, which contains the approximation that all of the cellulose content of Sugar Cane Bagasse is converted to levoglucosan, i.e. from the 22% lignin content of Sugar Cane Bagasse 9.9% of the total tar yield is produced hence the remaining 46% is obtained from the cellulose fraction; therefore the ratio of tar to gas yields for levoglucosan appears to be, about 5:4, and that for Sugar Cane Bagasse approximately 80% of the pyrolysis tar yield may derive from the products of the thermal decomposition of levoglucosan. The high total volatiles yields obtained for Sugar Cane Bagasse and Silver Birch are, in fact, slightly greater than even their summation values; a possible explanation for these observations is developed in what follows.

It should be noted that, in the above simple calculation, the assumption has been made that the tar yield from the lignin in Sugar Cane Bagasse and that of the pure lignin specimen are equivalent; this is, most probably, not totally correct since these lignins are different in nature. However, to a first approximation the tar yields from Sugar Cane Bagasse' lignin and pure lignin may be taken to be equal. Furthermore since the tar yield of Sugar Cane Bagasse is 56%, which greatly exceeds the total lignin content of the Sugar Cane Bagasse (22%), it is clear that the greater part of this tar must derive from the cellulose fraction.

The photograph presented in Figure 5.6a shows the wire–mesh after the pyrolysis of Sugar Cane Bagasse at 600^{0}C, with a heating rate of 1000^{0}C/second and a hold time of 30 seconds. This mesh was prepared and examined under the SEM using procedures

identical to those in section 5.5. Although the lignin content of Sugar Cane Bagasse, in bulk, is approximately 25%, the fragments remaining on the wire–mesh, in particular the small, black, "liquid–like" residue appear, from simple visual inspection, to be closer to those seen in Figure 5.5f, of a 75%lignin sample, than those seen in Figure 5.5d, corresponding to a 25%lignin "synthetic" wood.

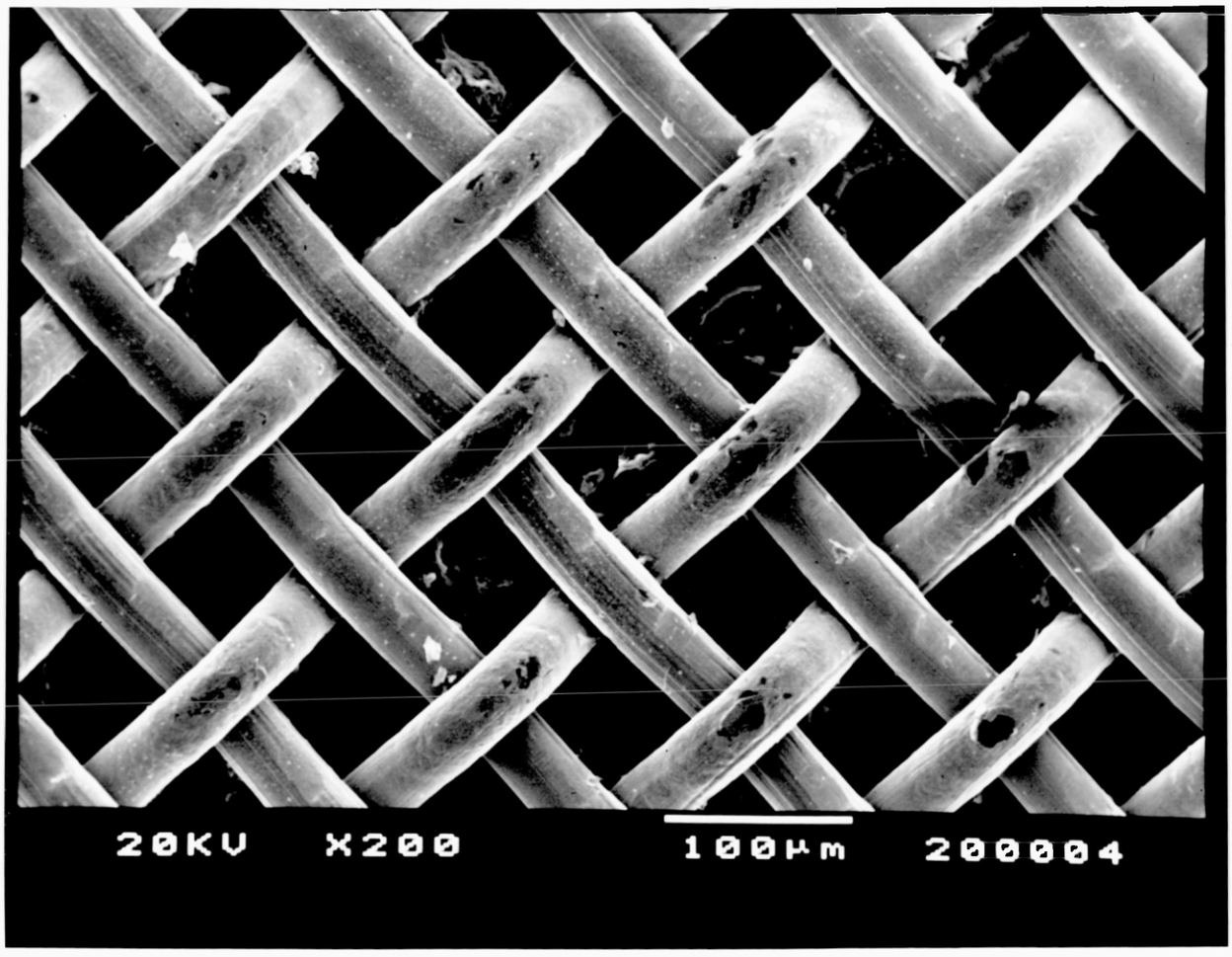


Figure 5.6a –The wire–mesh after the pyrolysis of Sugar Cane Bagasse.
Heating Rate = 1000^{0}C/second; Temperature = 600^{0}C;
Hold Time = 30 seconds.

5.7 – A Model for the Pyrolysis Process in Naturally Occurring Lignocellulosic Materials.

In order to further this discussion, attention will now be focused on the important morphological differences between the natural and synthetic materials used in the present study. For naturally occurring lignocellulosic materials it may be said that, in general terms, cellulose and lignin are in more intimate physical contact than in the synthetic materials and, more importantly, that these compounds are distributed in a highly non–uniform manner throughout the bulk of the specimen.

The intricate juxtapositions and interconnections of the individuals cells in a woody material generate a complex three–dimensional structure. The internal organisation of a typical cell wood has already been described in some detail (see section 1.7); in summary the cell wall has been seen to consist primarily of three overlapping layers, namely the middle lamella, the primary wall and a composite secondary wall. The connections between cells, which form the rigid framework of wood, are made solely between the middle lamella; these cross–linkages, and the middle lamella itself, have a high lignin and low cellulose content. In contrast the main body of a cell, that is all elements inwards of the primary layer, have a high cellulose and low lignin content. The interface between these two very different regions is the primary wall or layer, which consists of a thin network of cellulose encrusted with hemicellulose, lignin and other compounds.

At moderate peak pyrolysis temperatures, say 400^{0}C, cellulose decomposes rapidly; the primary product yields being, approximately, 9% char, 81% tar – which is mainly levoglucosan, and 9% gas, see Table 3.6. As the rigid, semi–permeable, outer layer of cells is composed primarily of lignin, the gaseous products formed within their cellulose rich centres, particularly during the initial stages of pyrolysis, cannot readily escape. Furthermore although lignin is thermally more stable than cellulose, primary lignin tars will form within, and flow over, the middle lamella, which itself will have developed a "plastic" type character; the combination of these two effects can greatly reduce the porosity of this layer. It has been reported that levoglucosan is also thermally unstable; with a low sublimation temperature, of the order of 100^{0}C, see Franklin[44]. Franklin's observation has been tested in this research programme, using the technique of differential scanning calorimetry, and verified; the complex thermogram of levoglucosan, together with those obtained for cellulose, lignin, and the natural and synthetic materials used in this study, are presented in the following section. Hence the volatilisation of levoglucosan at typical pyrolysis temperatures will be extremely rapid; it is, therefore, quite probable that relatively high internal pressures will be generated within a cell, leading to its explosive rupture. Severe fragmentation of the lignin rich outer cell wall and the destruction of the three–dimensional lignin network may occur with the rapid expulsion of the primary pyrolysis products.

Although the lignin content of two different materials

may be approximately the same, for example Sugar Cane Bagasse and Silver Birch, the chemical nature of their respective lignins is quite different. The strength of, and degree of cross–linking between, individual cells in these materials, is controlled by their unique lignin profiles, and reflected, therefore, in their basic physical properties, for example mechanical strength, density etc. In general terms it may be said that the internal structure of any very fast growing, light, fibrous species, for example Sugar Cane, is substantially weaker than that of a comparatively slow growing, high density wood, such as Silver Birch. The degree to which, and the elapsed time before, this process of cell rupture, as described above, takes place is, obviously, strongly related to the rigidity of the middle lamella in a particular material; in general the cells of a "high strength" material such as Silver Birch will maintain their integrity longer than those of the relatively "weak" Sugar Cane Bagasse. From this simple model it is seen that the primary pyrolysis products of these natural lignocellulosic materials, may be retained within the pyrolysing matrix for differing periods of time. Following cell rupture the partially pyrolysed lignin rich middle lamella will be, but to a degree dependent upon the morphology of the biomass, physically destroyed and its fragments then pyrolysed.

It has been reported in previous research, see for example references[121,122,129] and confirmed in this present study, that the major pyrolysis product of cellulose is levoglucosan, see section 4.5. However in this research programme the yield of levoglucosan obtained from a naturally occurring substance, namely Sugar Cane Bagasse, which contains approximately 75% cellulosic material was, based upon the

results of GC–MS analysis, almost nil, see again section 4.5. A closely similar, i.e. zero content, result was obtained for the pyrolysis tar obtained for Silver Birch, see again section 4.5; however for these tars the product distribution was somewhat more complex than that of Sugar Cane Bagasse tars. It has been shown, from the above model, that the residence time of the primary pyrolysis products within the hot zone, even with a fast flowing carrier gas, is enhanced; and that these products are localised until cell rupture occurs. Thus levoglucosan, produced by cellulose pyrolysis, is trapped under pressure within the pyrolysing cells and may itself rapidly undergo thermally induced decomposition; hence its absence in these pyrolysis tars. Based upon the GC–MS data reported in this present study the decomposition products of levoglucosan are, under these specific experimental pyrolysis conditions, predominantly phenols; past research has indicated the presence of significant quantities of phenolic compounds in Silver Birch pyrolysis tars[134]. In the case of Sugar Cane Bagasse the relatively simple product distribution, in contrast of that of Silver Birch, may be due to the shorter time interval required before the destruction of its lignin network.

This simple model, the broad details of which are supported in the following section where the data obtained in a short series of DSC experiments are reported, provides an insight into the pyrolysis process in these naturally occurring lignocellulosic materials.

5.8 – Differential Scanning Calorimetry of Lignocellulosic Materials.

A short series of pyrolysis experiments, of a qualitative nature, were performed in a Perkin–Elmer series 7 Differential Scanning Calorimeter, D.S.C. All the specimens under investigation, weighing between 1–3 milligrammes, were heated in platinum crucibles at a heating rate of 40^0C/minute from 50^0C to 710^0C, under a flowing nitrogen purge gas of 60cm^3/minute.

Figure 5.8a shows the thermogram obtained for a specimen of pure cellulose; a typical broad, smooth, endothermic decomposition peak is seen, with a peak temperature of 355^0C, and the onset of decomposition being 330^0C. The corresponding thermogram for pure 'lignin is shown in Figure 5.8b; the shape of this thermogram is, quite clearly, in marked contrast to that obtained for pure cellulose. For lignin the onset of decomposition is, once again, about 330^0C; however there is no clearly defined peak and, therefore, no peak temperature. The lignin thermogram shows a number of inflections, indicating the presence of overlapping, interrelated, events taking place during the pyrolysis process.

The thermogram obtained from a specimen of pure levoglucosan, the major product of cellulose pyrolysis, is shown in Figure 5.8c, superimposed upon the thermogram of pure cellulose, which is included for reference purposes. From Figure 5.8c it may be seen that

the thermal decomposition of levoglucosan is, when compared to that of pure cellulose, more complex. There are two major features in the levoglucosan thermogram; a smooth, narrow, peak centred at, say, 115^{0}C and a comparatively broad peak, centred at 300^{0}C, which is quite clearly the product of a number of individual overlapping peaks. The peak at 115^{0}C may be tentatively assigned to the sublimation of levoglucosan since, in the region of 115^{0}C whilst performing D.S.C runs, clear crystals, presumably of levoglucosan, were observed being swept from the instrument by the carrier gas. The broad, complex, endothermic peak centred at 300^{0}C may, therefore, be taken to be that of the thermal decomposition of levoglucosan. It may be noted here that these observations are in good agreement with those of Franklin[44]. The major thermal decomposition product of cellulose is levoglucosan which, from Figure 5.8c, is seen to be thermally unstable below its temperature of formation in pyrolysing cellulose. Therefore levoglucosan, as soon as it is evolved, may undergo flash decomposition within the cells of pyrolysing biomass.

The thermogram for Sugar Cane Bagasse is shown in Figure 5.8d, superimposed upon the curve for cellulose, which is included for reference purposes. From this figure it may be clearly seen that both the onset and peak temperatures for Sugar Cane Bagasse, which it should be recalled contains approximately 22% lignin, have increased, and that the area under the curve is much reduced; the numerical values are presented in Table 5.8a. Figure 5.8e shows the thermogram obtained for Silver Birch, where a similar effect to that of Sugar Cane Bagasse is

observed, namely that the onset and peak temperatures for this naturally occurring lignocellulosic material, containing approximately 29% lignin, have increased. In Figures 5.8f and 5.8g the thermograms for the "synthetic" bagasse 75%cellulose:25%lignin is presented; from the enlarged portion of the whole curve, presented in Figure 5.8g, it is seen that the onset temperature of decomposition of this mixture is now higher than that of pure cellulose by approximately 40^0C. Furthermore above the small peak seen in Figure 5.8f the curve steeply rises and has, quite closely, the same form as that of pure lignin, see again Figure 5.8b. Hence, above its decomposition peak, the thermogram of this "synthetic" bagasse is in complete contrast to those of either Sugar Cane Bagasse or Silver Birch where, after their respective decomposition peaks, their curves run approximately parallel to the horizontal axis.

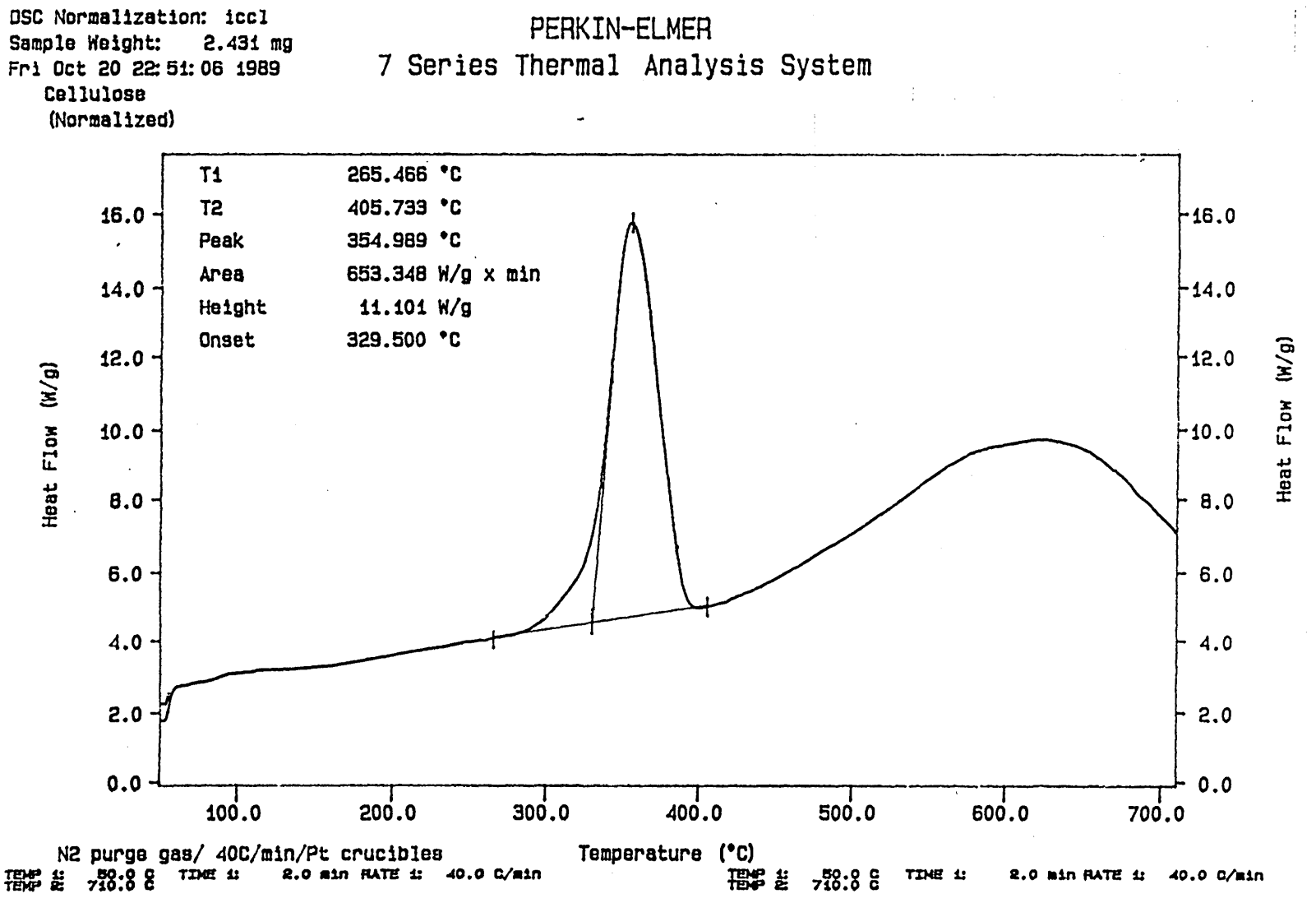


Figure 5.8a – DSC thermogram of Cellulose.

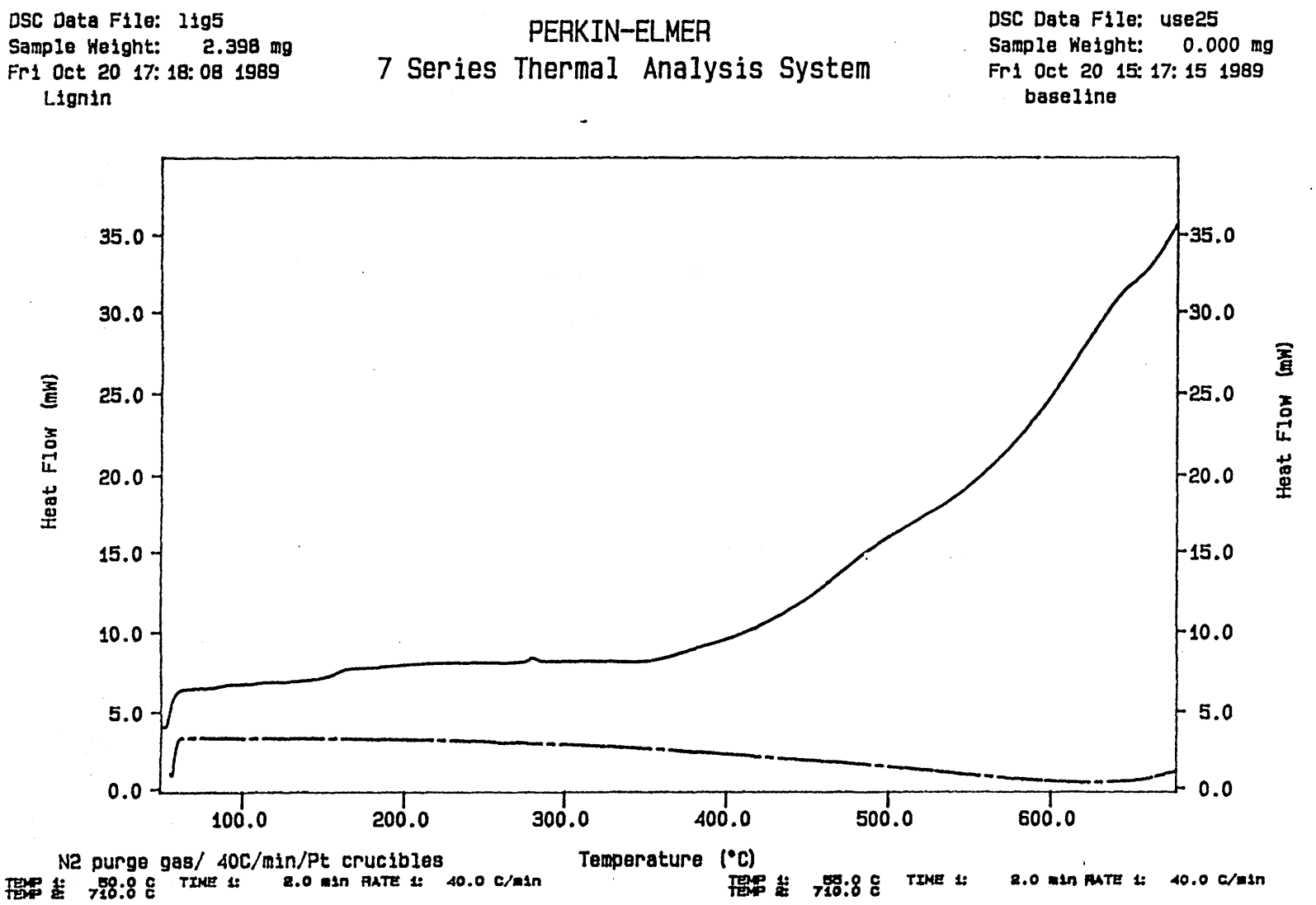


Figure 5.8b – DSC thermogram of Lignin.

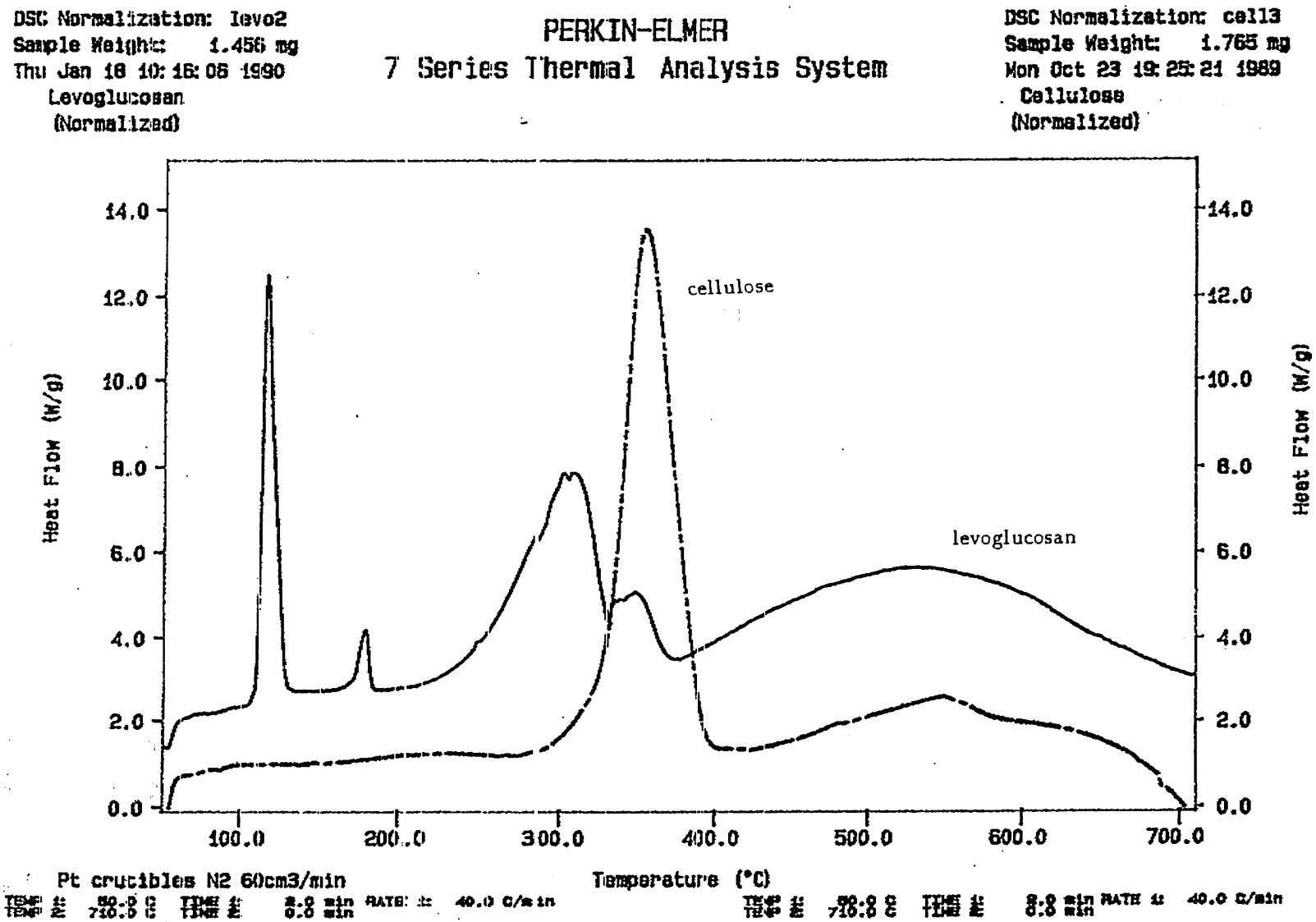


Figure 5.8c — DSC thermogram of levoglucosan.

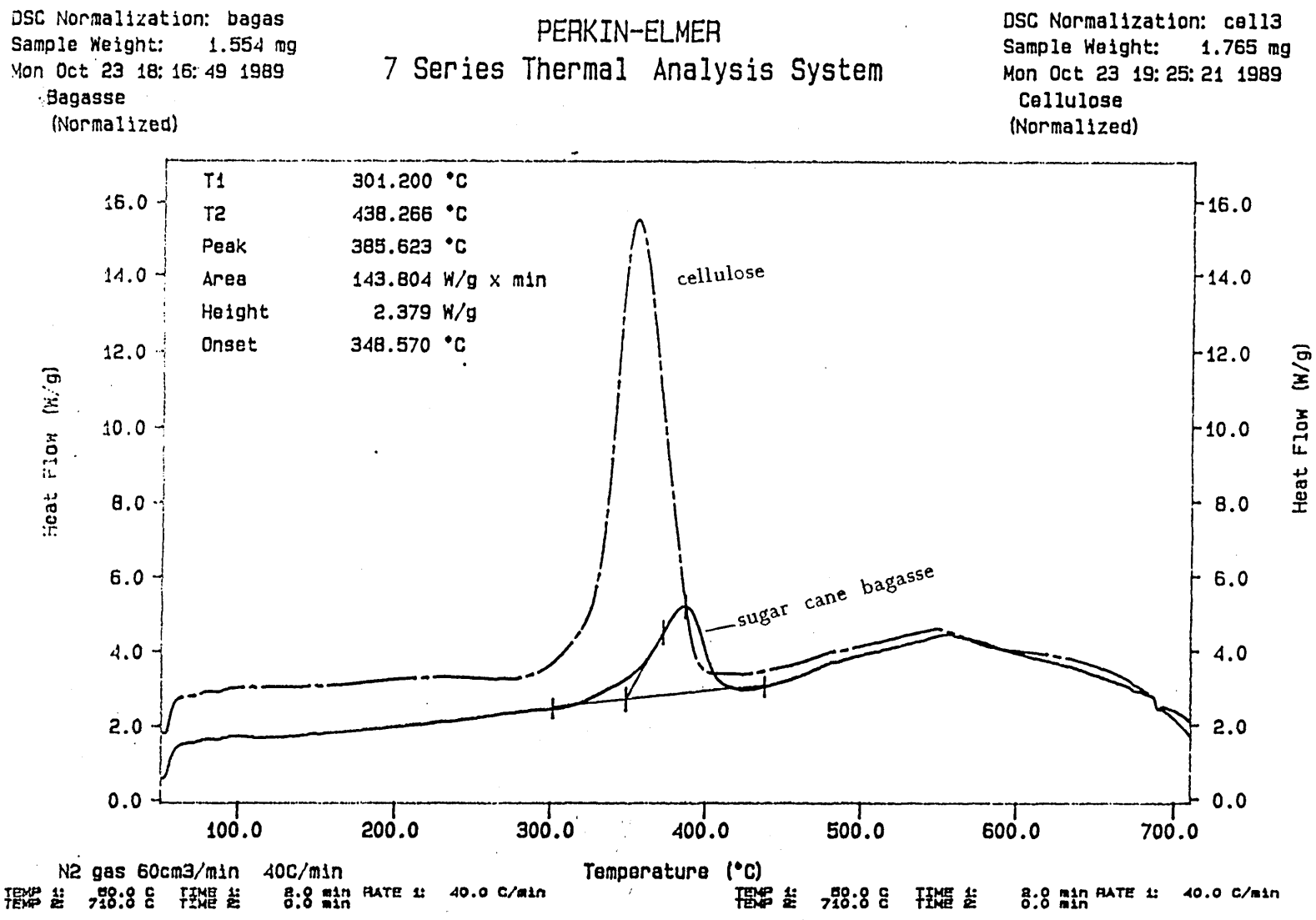


Figure 5.8d – DSC thermogram of Sugar Cane Bagasse.

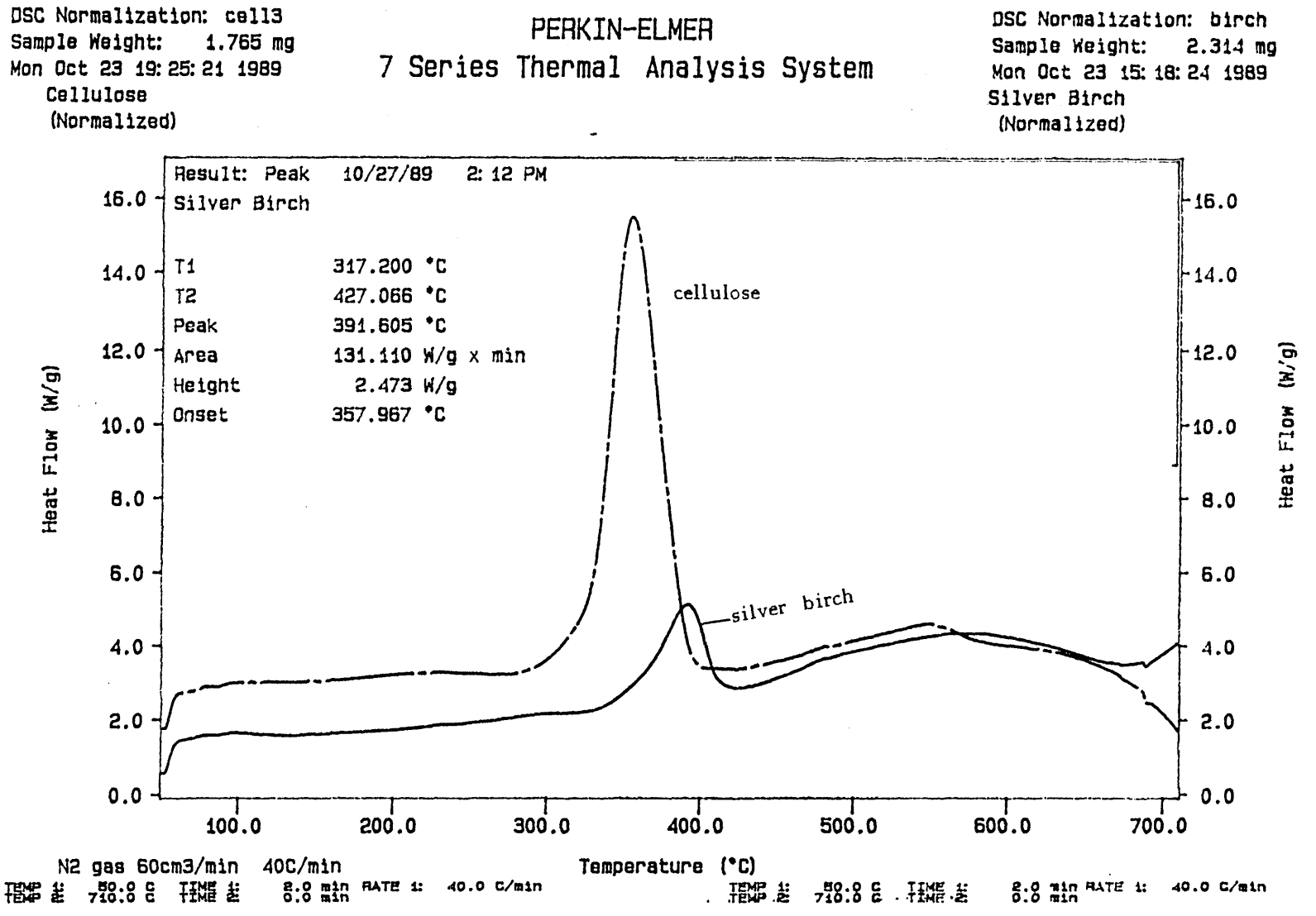


Figure 5.8e – DSC thermogram of Silver Birch.

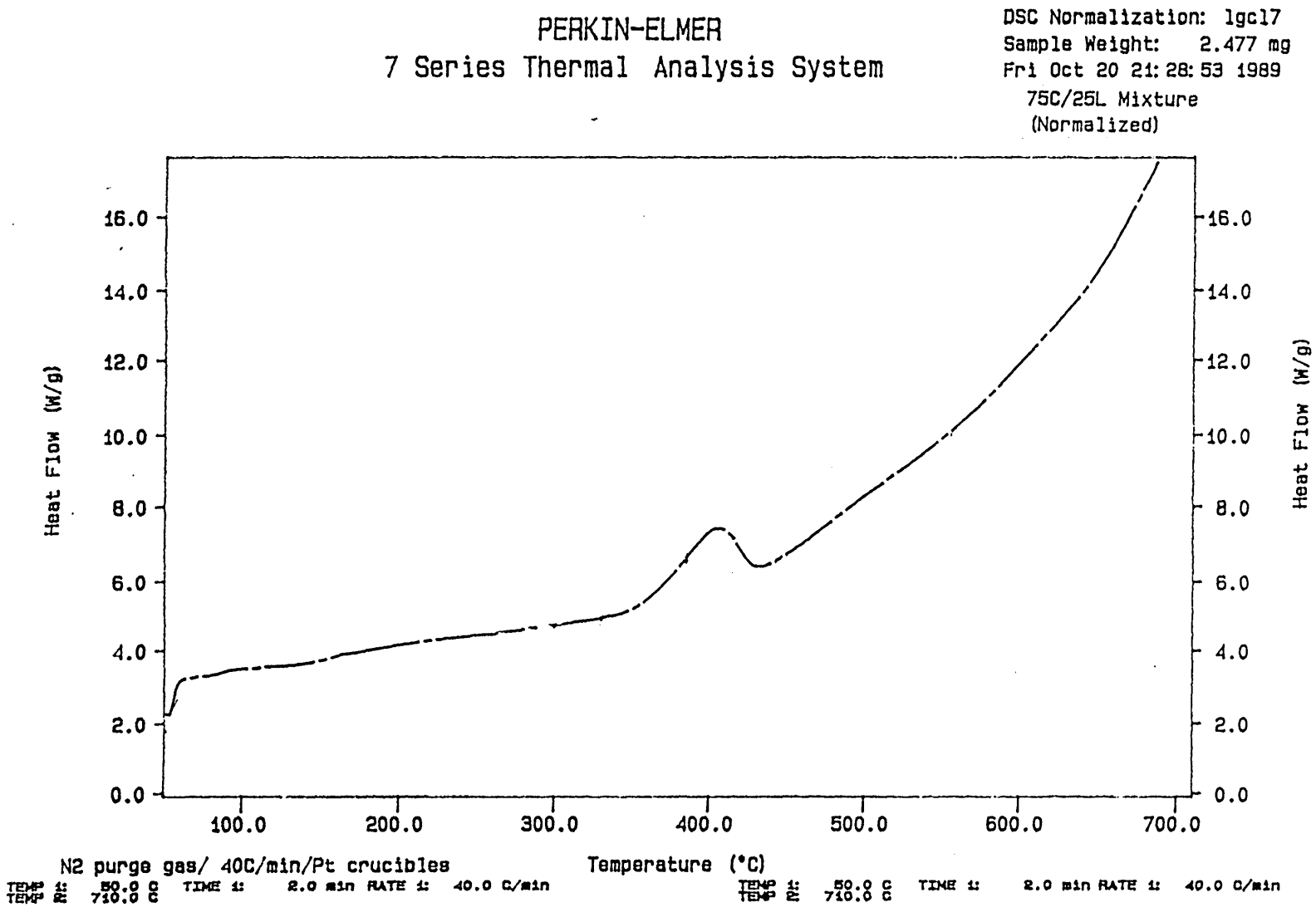


Figure 5.8f – DSC thermogram of the Mixture 75%cellulose:25%lignin.

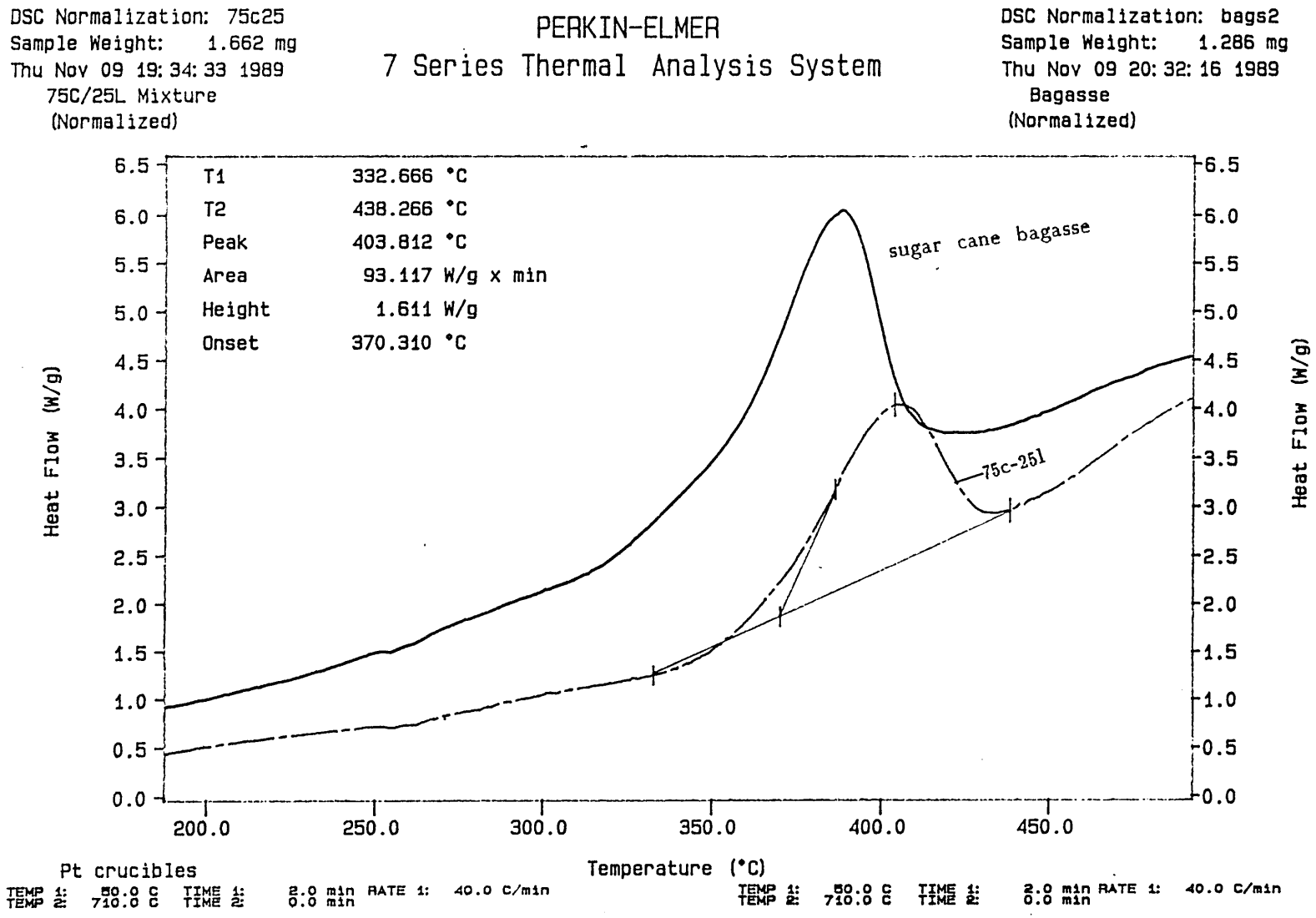


Figure 5.8g – DSC thermograms of the Mixture 75%cellulose:25%lignin and Sugar Cane Bagasse.

Sample	T_0	T_p	Area
Cellulose (Cel)	330	355	653
Lignin	330	n.d	n.d.
levoglucosan (Lev)	215	300	n.d.
Bagasse (SCB)	349	386	144
Silver Birch (SB)	358	392	131
75C–25L	370	404	93

Table 5.8a – Decomposition Temperatures of Lignocellulosic Materials. where T_0 = onset temperature (^{0}C) and T_p = peak temperature (^{0}C). n.d. = not determined; 75C–25L = 75%cellulose:25%lignin.

Examination of Table 5.8a reveals the following two relationships:

$$T_0(75C–25L) > T_0(SB) > T_0(SCB) > T_0(Cel) > T_0(lev).$$

$$T_p(75C–25L) > T_p(SB) > T_p(SCB) > T_p(Cel) > T_p(lev).$$

It can be seen, from Table 5.8a, that the "synthetic" bagasse, which has a lignin content intermediate to that of Sugar Cane Bagasse and Silver Birch, does not readily fit into this series; it exhibits the greatest shift in onset and peak temperatures. Furthermore the thermogram of this specimen, see again Figure 5.8f, above the small decomposition peak, retains the characteristic form and strong curvature

associated with the presence of lignin, seen again Figure 5.8b; whereas for both naturally occurring materials their thermograms above their decomposition peaks indicate the opposite, i.e. the absence of lignin. These exploratory investigations support the observations made earlier in this chapter; namely that cellulose and lignin do not pyrolyse independently in either the synthetic materials, for example 75%cellulose:25%lignin, where the "plastic" flow of lignin may encapsulate cellulose and thus decrease the total volatile yield, or in natural lignocellulosic materials, where the volatile yield is enhanced and controlled by the morphology of the biomass.

5.9 – Conclusions.

A number of conclusions may be drawn from this research programme into the pyrolysis of lignocellulosic materials, they are summarised and reported below.

From the large body of experimental data reported in Chapter 3 – The Pyrolysis of Lignocellulosic Materials – the following conclusions may be drawn. The pyrolysis of cellulose yields not more than 3% char at the very low heating rate of 0.1^0C/second, at the peak temperature of 600^0C and with 30 seconds hold time; higher char yields (12%) reported previously are shown to be due to the presence of secondary char forming reactions caused by different sample and reactor geometries. Furthermore at the fast heating rates of 1000^0C/second this char yield is effectively zero, being 1%, or less, for the same pyrolysis conditions as above (section 3.5). These findings appear to support the hypothesis that, at all heating rates, the primary products of cellulose pyrolysis are all volatiles. The maximum tar yield obtained for Sugar Cane Bagasse, at the relatively low peak temperature of 600^0C and with a heating rate of 1000^0C/second, is 56%, the corresponding total volatile yield is 96% (section 3.2.1.1). The tar yields for Sugar Cane Bagasse and Silver Birch are, in general, enhanced by approximately 10% when the heating rate is increased from 1^0C/second to 1000^0C/second, for the above pyrolysis conditions (section 3.3). The previously reported

decrease in tar yields, above 600^{0}C, for biomass materials as observed in other wire–mesh reactors may be attributed to the presence of secondary reactions; in this present study no reduction in yields were observed (sections 3.2.1.1 and 3.2.2.1). Finally, it was shown that in lignocellulosic materials the cellulose and lignin do not pyrolyse independently. For synthetic mixtures the total volatile yield is lower than would be expected from the simple, arithmetic, addition of the yields of the individual components. For the two naturally occurring lignocellulosic materials examined in this research programme, namely Sugar Cane Bagasse and Silver Birch, the total volatile yields are higher than would be expected, as calculated above (section 3.7).

From the analytical data reported in Chapter 4 – The Chemical Analysis of the Specimens and their Corresponding Liquid Pyrolysis Products – it has been shown that, in the absence of secondary reactions, the pyrolysis tar obtained from Sugar Cane Bagasse has a relatively simple product distribution, in contrast to that of Silver Birch. Furthermore the major component of Sugar Cane Bagasse tar is, as identified by GC–MS analysis, vinyl phenol. Therefore Sugar Cane Bagasse, an abundant "waste" product, appears to have a potentially valuable role to play as a chemical feedstock.

Finally, from Chapter 5 – Discussion of Results and Conclusions – two further conclusions may be drawn; first, the pyrolysis process in "synthetic" lignocellulosic materials appears to be controlled by the relatively slow thermal decomposition of lignin. In these materials pyrolysing lignin may, due to its "plastic" behaviour,

encapsulate cellulose particles. Secondly, in the naturally occurring materials studied in this research programme and, in particular, Sugar Cane Bagasse the rapid thermal decomposition of cellulose and the subsequent volatilisation and flash conversion of levoglucosan determines the pyrolysis products. The volatile products of levoglucosan may destroy the cellular structure and lignin framework of these materials during pyrolysis due to intracellular pressure.

5.10 – Recommendations for Future Work.

To further research in this field a number of developments are suggested below:

a – The destruction of the cellular framework of Sugar Cane Bagasse before pyrolysis, the subsequent measurement of the product distribution of the tar, and its comparison with the data reported here. The aim of this series of experiments would be to investigate the relationship between the residence time of levoglucosan in the pyrolysing biomass and its yield in the pyrolysis tar, and also the complexity of the tar product distribution.

b – The application of optical imaging and recording techniques to the wire–mesh apparatus. Observation of these lignocellulosic materials in situ, during a pyrolysis run, would enable the "plastic" behaviour of lignin to be further investigated. The mechanism by which volatiles escape from the pyrolysing mass, and in particular the rate of bubble formation, may be explored using such equipment; the increased residence time of encapsulated volatiles may be investigated as a function of the lignin content and specimen morphology.

c – Real time measurement of the product distribution and yield of the gaseous products, from both naturally occurring and synthetic materials, as a function of the elapsed time of the pyrolysis run, using on–line analytical instrumentation. This data would enable

rate information of the evolved gases to be obtained from specimens with the same cellulose/lignin ratio but differing morphology; differences observed when comparing these results may provide further insight into the physical nature of the pyrolysis process.

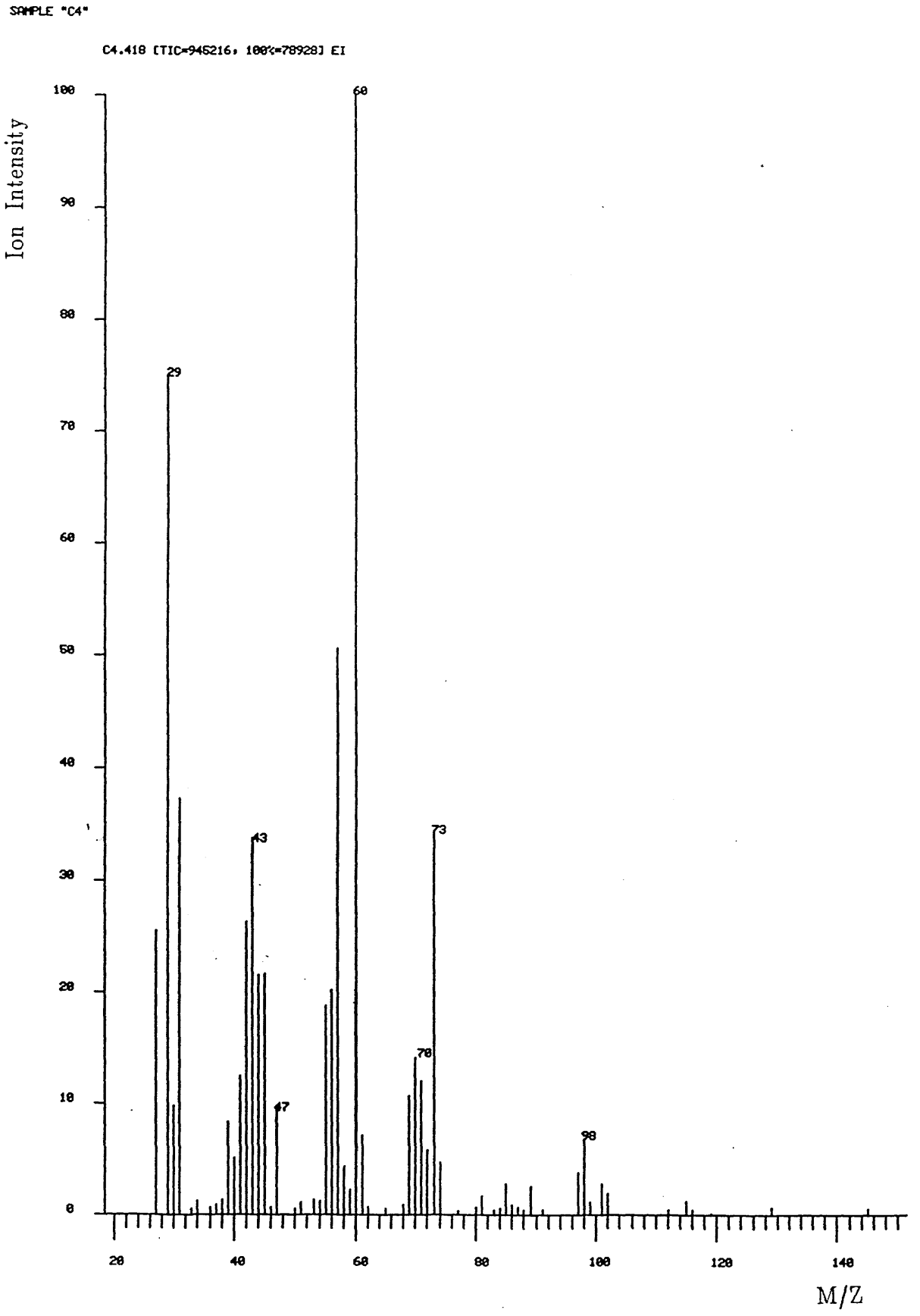
d – The pyrolysis of other biomass materials which have been selected for study based upon their simple morphology. In this research programme it has been shown that for Sugar Cane Bagasse, the product distribution is not, in general terms, complex. Possibly, therefore, pyrolysis tars from other "grass like" species will also exhibit this characteristic; which is a desirable feature if pyrolysis tars are to be used in the future as chemical feedstocks.

APPENDIX 1

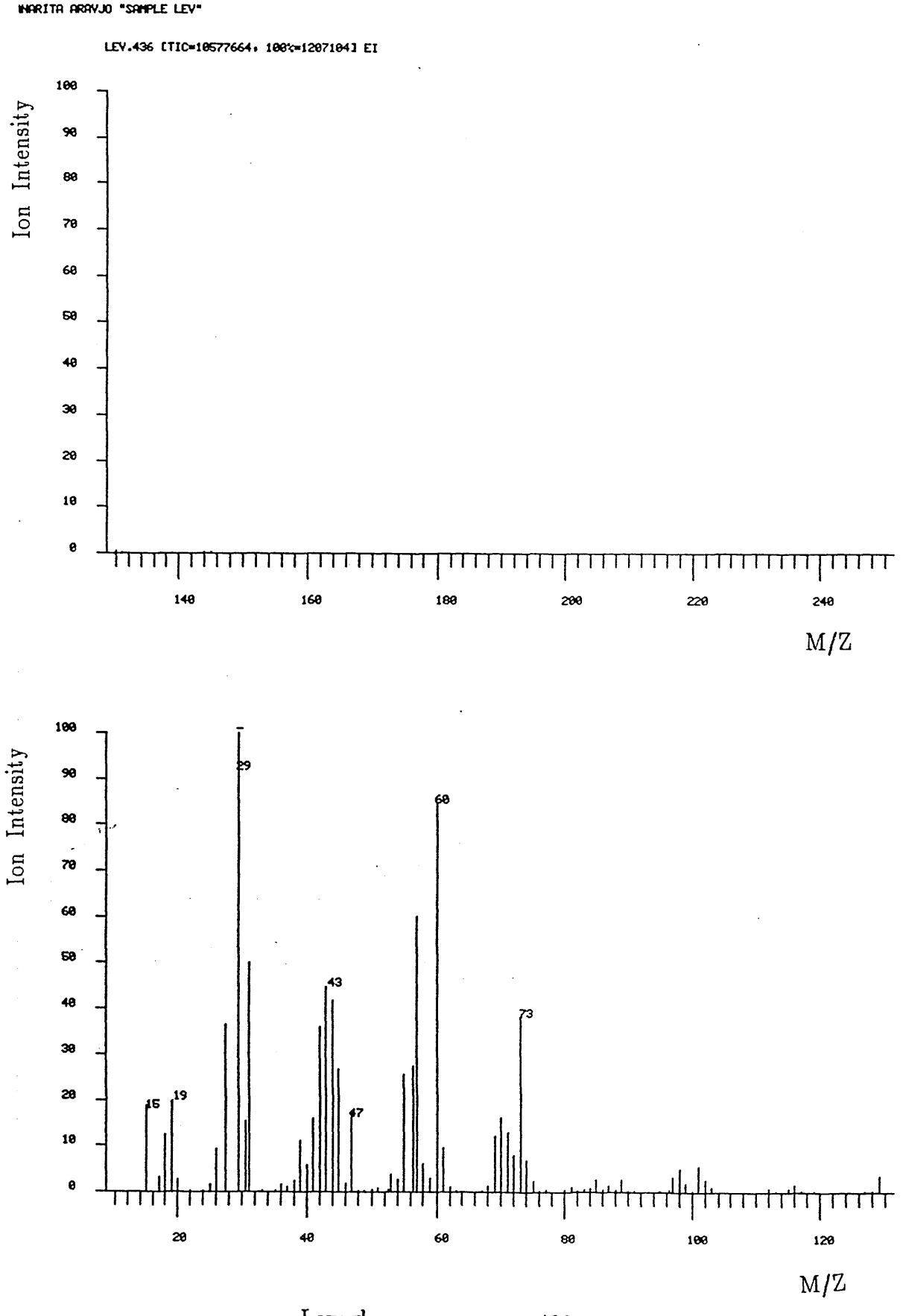
The fragmentation patterns of the compounds tentatively identified in the tars by the technique of Gas Chromatography – Mass Spectrometry, GC–MS, as described in Chapter 4, section 4.5, are presented in this Appendix.

	fragmentation pattern (M/Z in decreasing order of intensity)
Cellulose – scan 418	60,57,73,70,98.
Levoglucosan – scan 436	60,57,73,70,98.
Lignin – scan 233	152,124.
Synthetic mixture – scan 233	124.
Bagasse – scan 44	43,58,27,42.
Bagasse – scan 56	55,39,96,40,27,42.
Bagasse – scan 60	39,96,95,38.
Bagasse – scan 62	98,41,42,53,81.
Bagasse – scan 74	98,70,42,126.
Bagasse – scan 86	86,55,114,43.
Bagasse – scan 135	44,58,95,114.
Bagasse – scan 171	138,39,27,123.
Bagasse – scan 195	120,91,29,119,39.

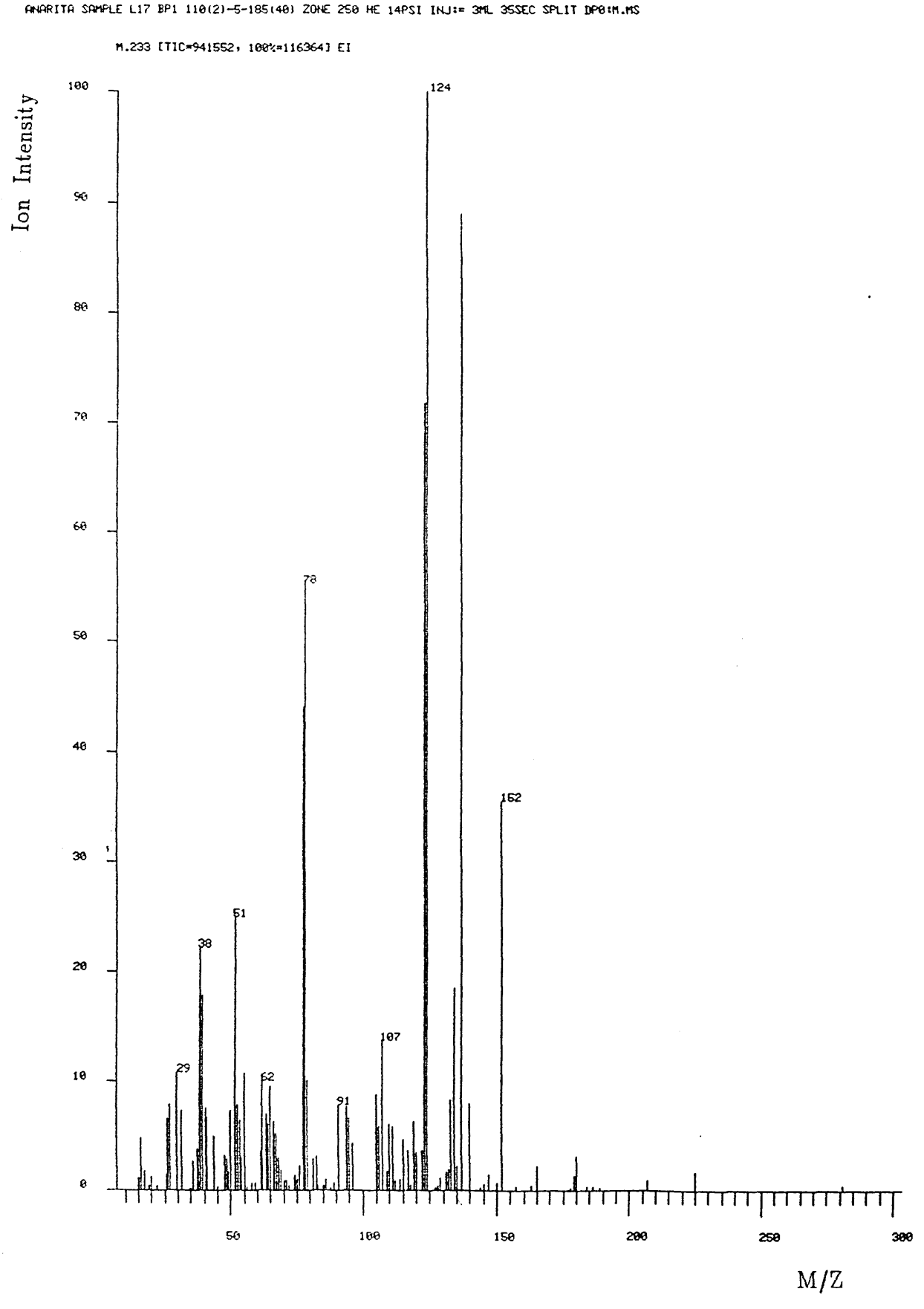
Bagasse – scan 225	137,152,39,91,122,94.
Bagasse – scan 240	135,150,107,91,39.
Bagasse – scan 253	154,139,111,96,107,93.
Bagasse – scan 260	164,149,77,103,91,55,39.
Bagasse – scan 275	152,151,109,77.
Bagasse – scan 297	168,153,125,53,65.
Bagasse – scan 332	167,182,77,107,79.
Bagasse – scan 347	180,165,137,66,39.
Bagasse – scan 363	194,91,77,119,79,39.
Bagasse – scan 428	210,122,167,84.



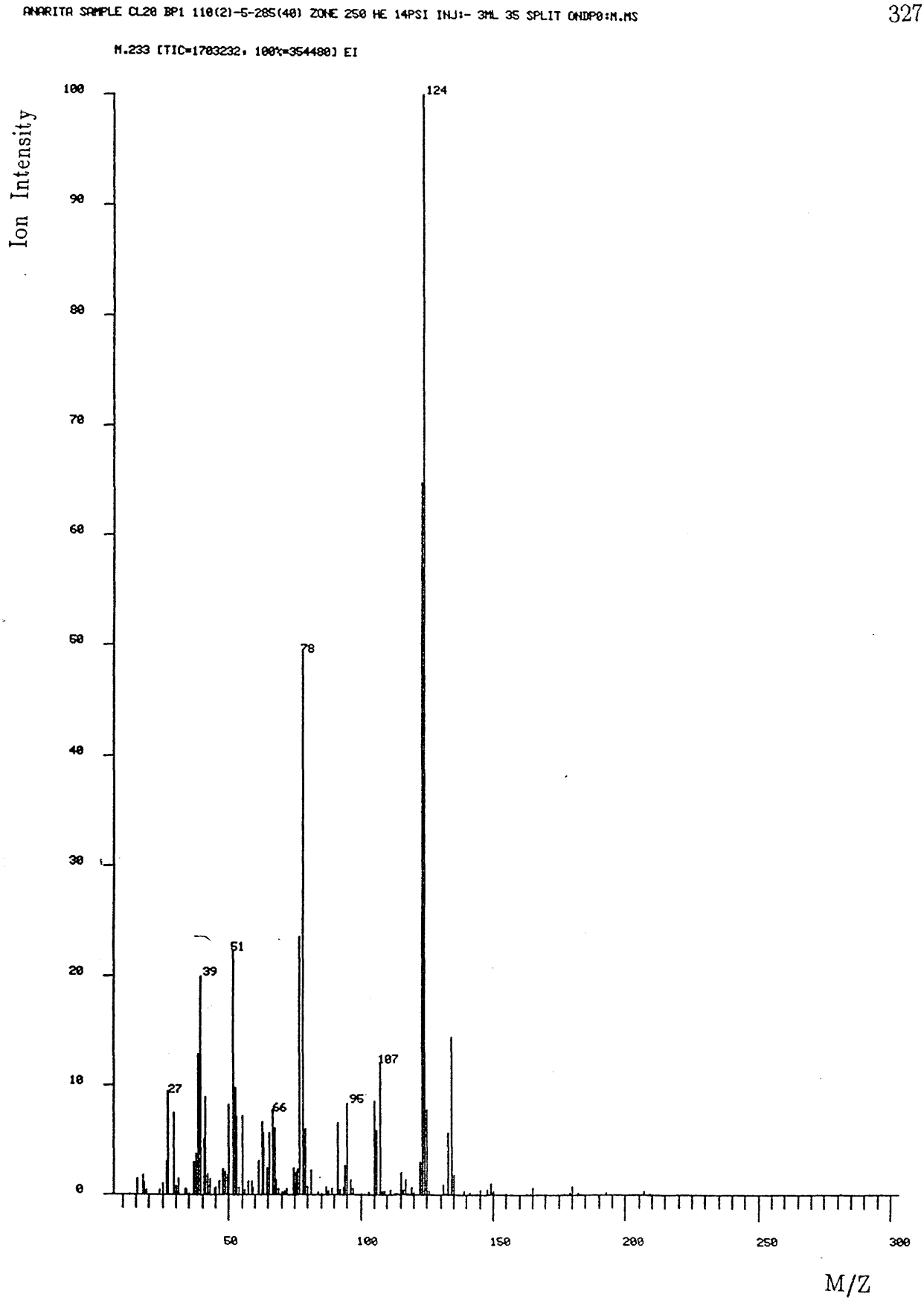
Cellulose — scan 418.



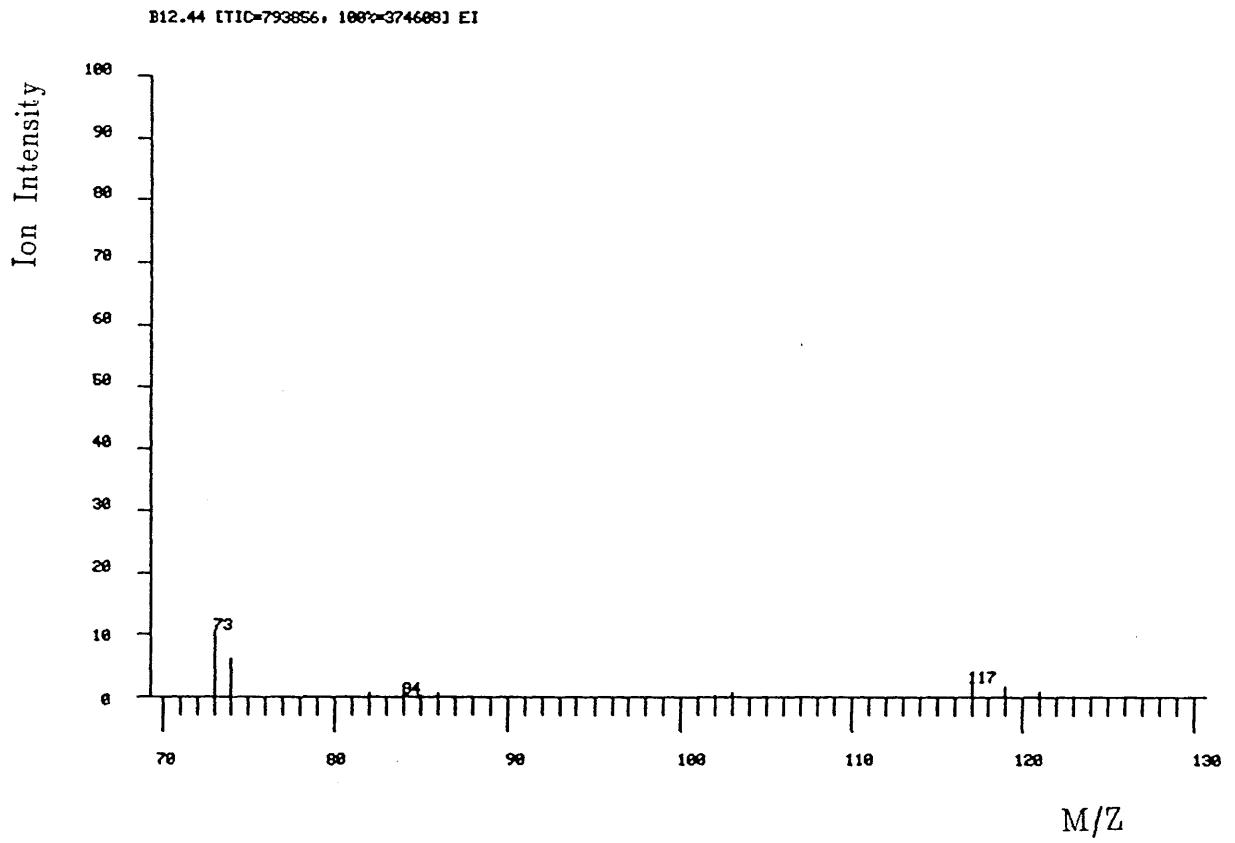
Levoglucosan — scan 436.

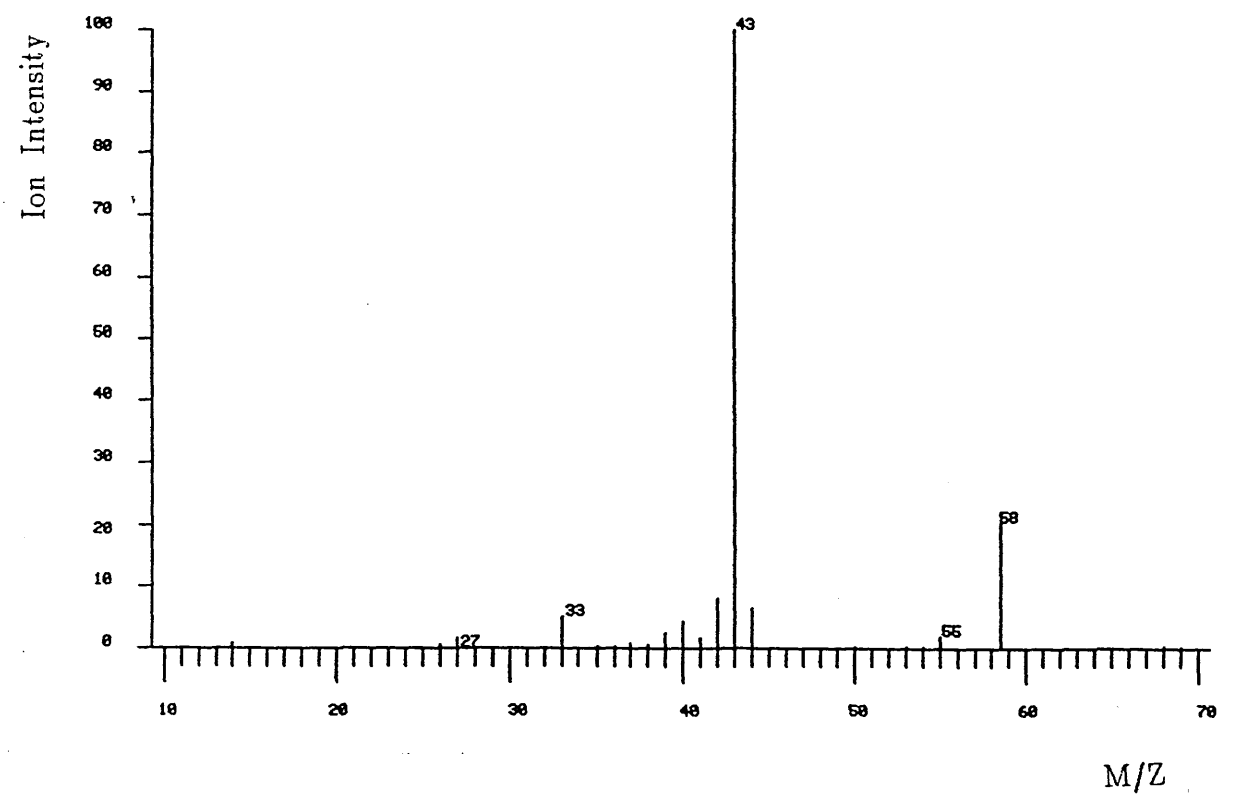


Lignin — scan 233.

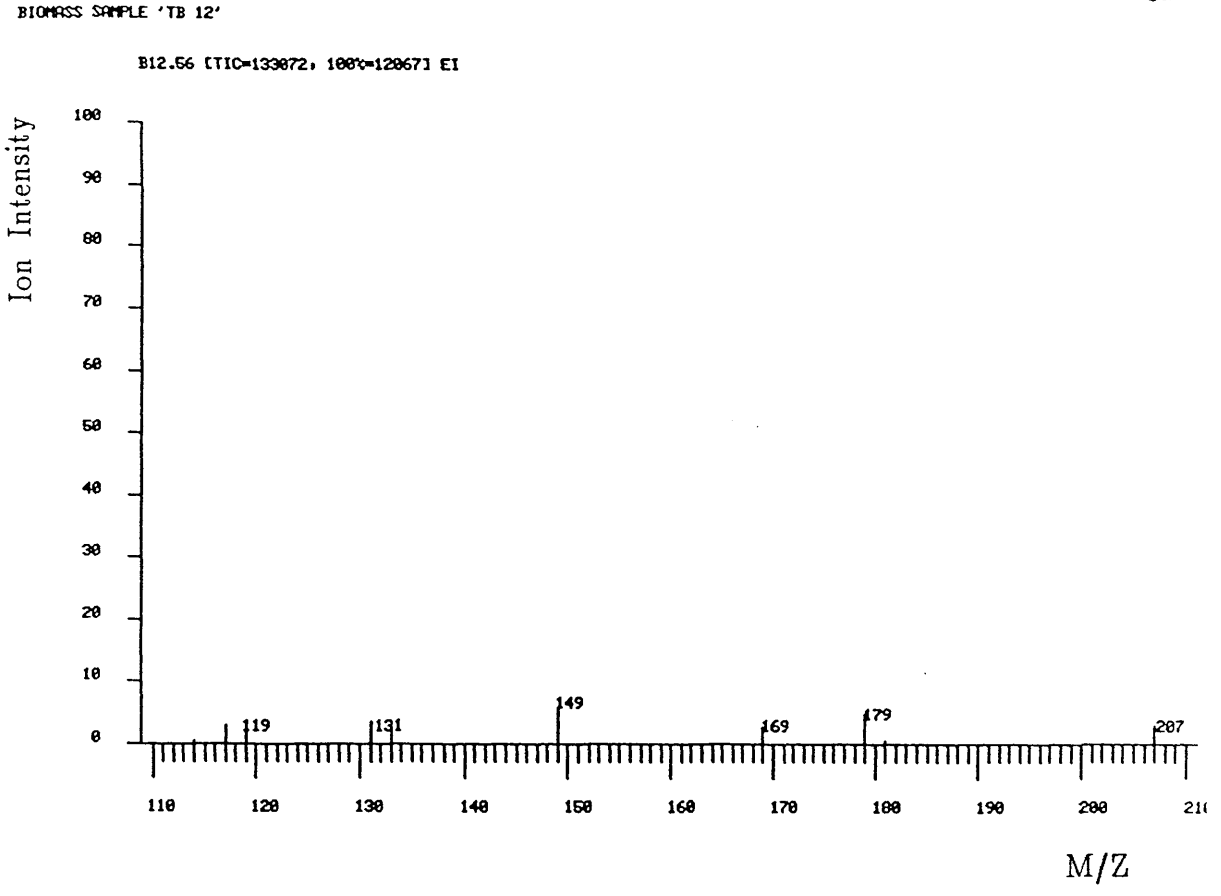


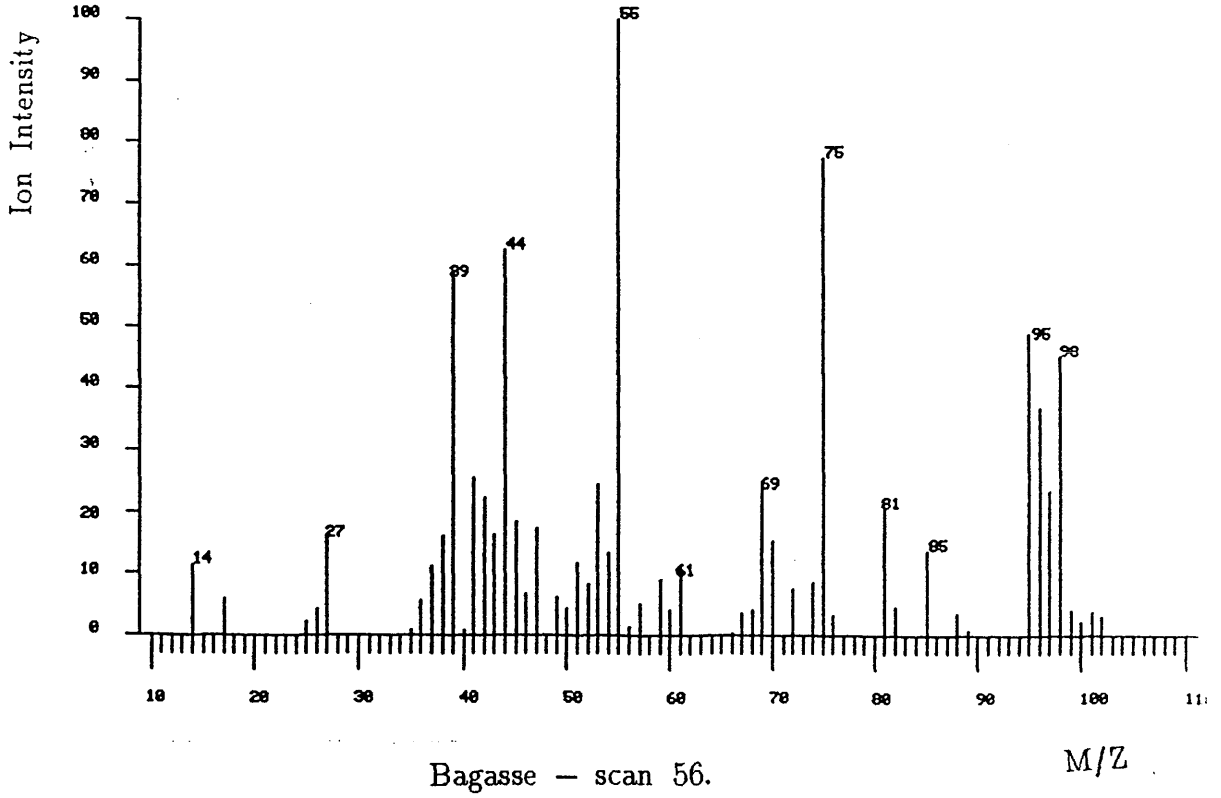
Synthetic mixture — scan 233.



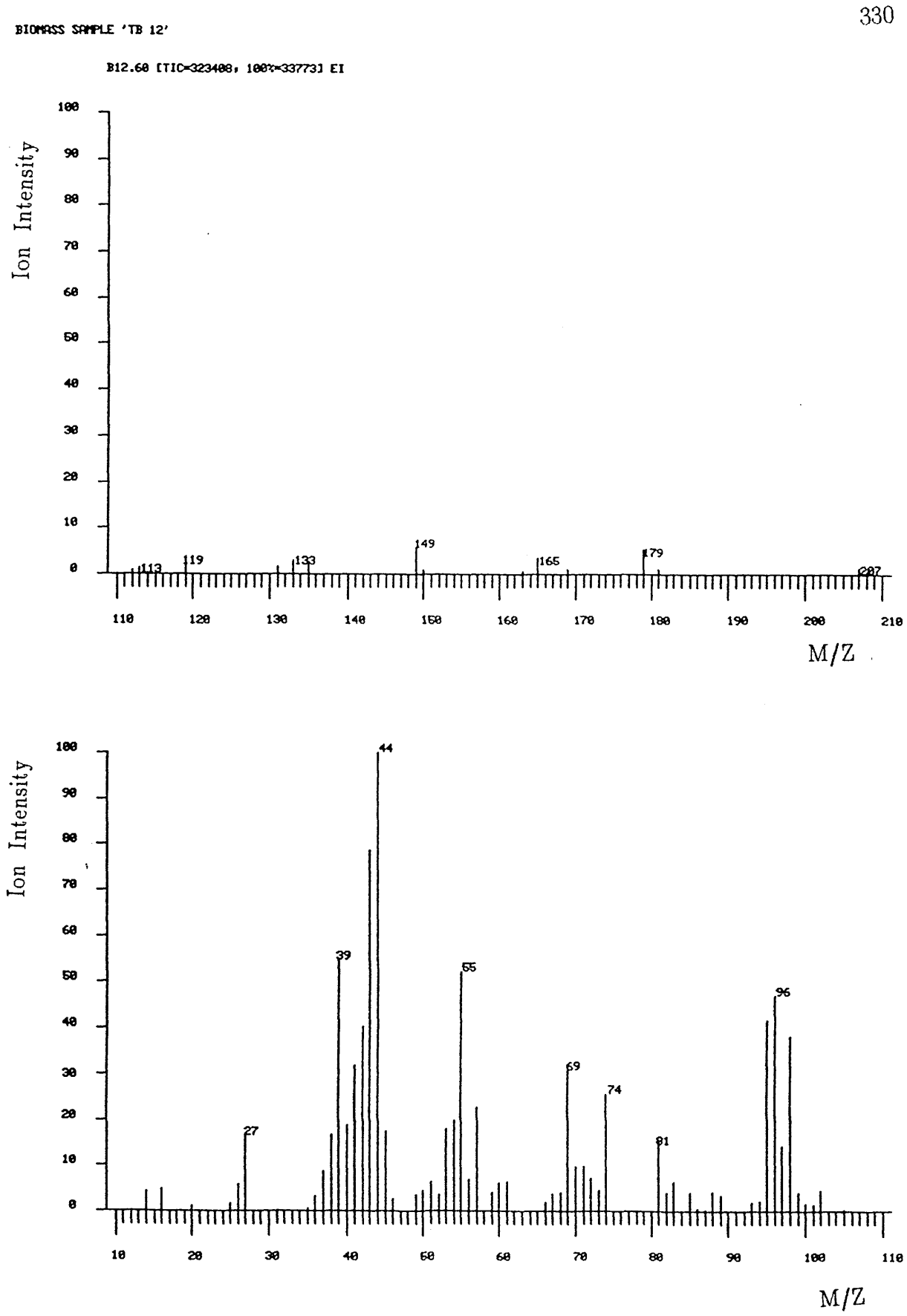


Bagasse — scan 44.

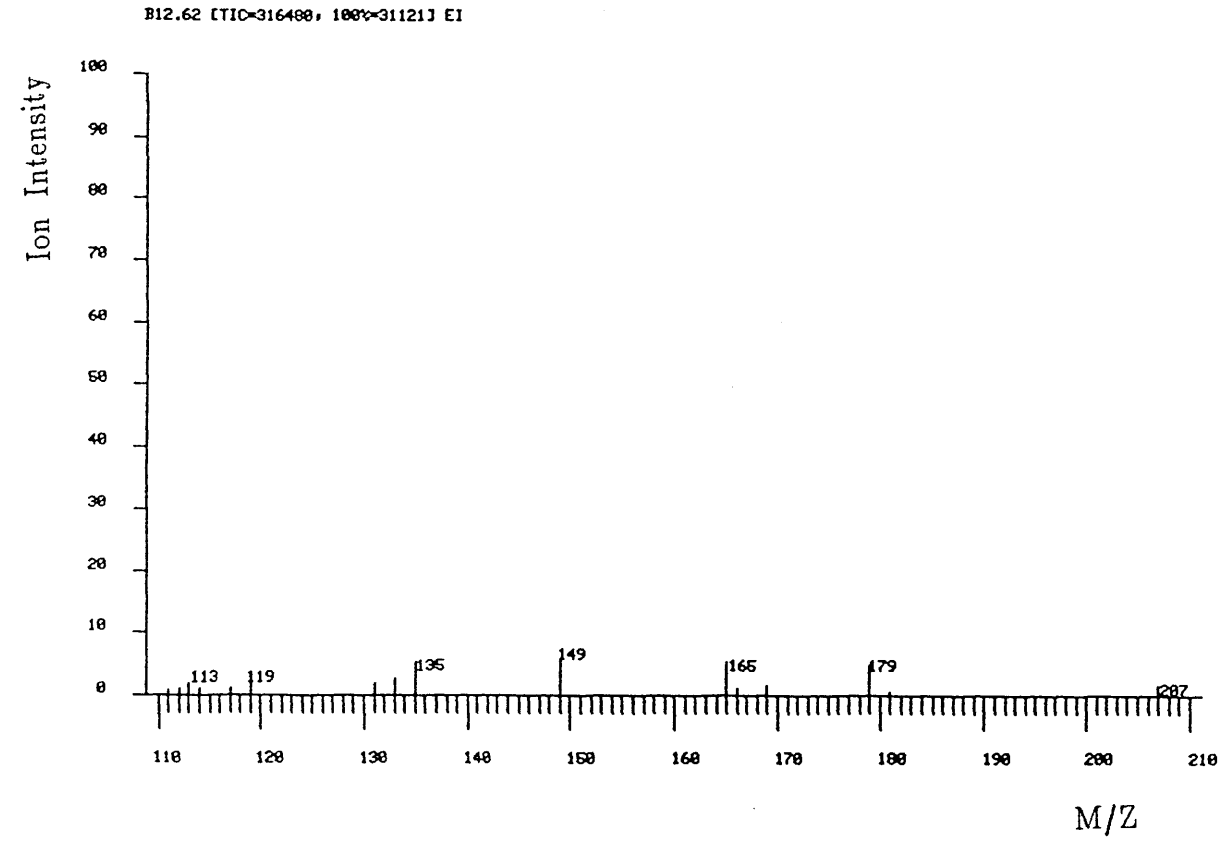


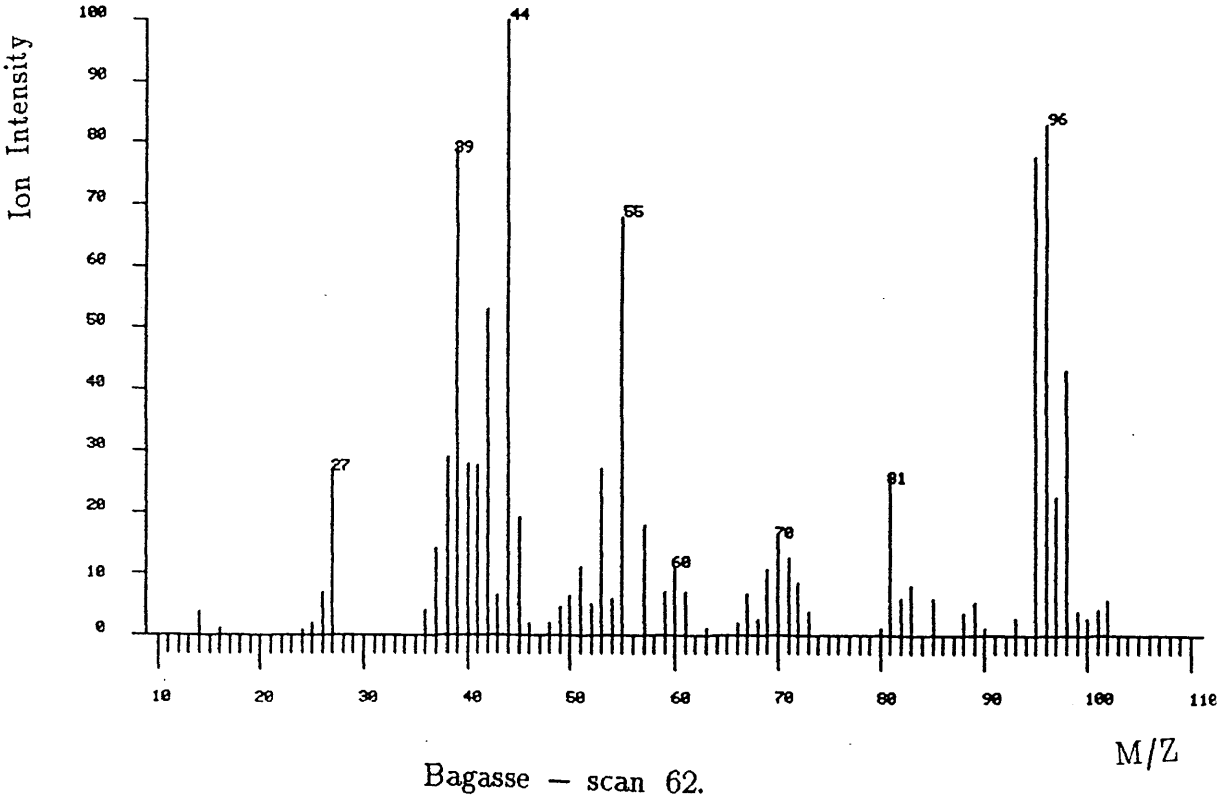


Bagasse — scan 56.

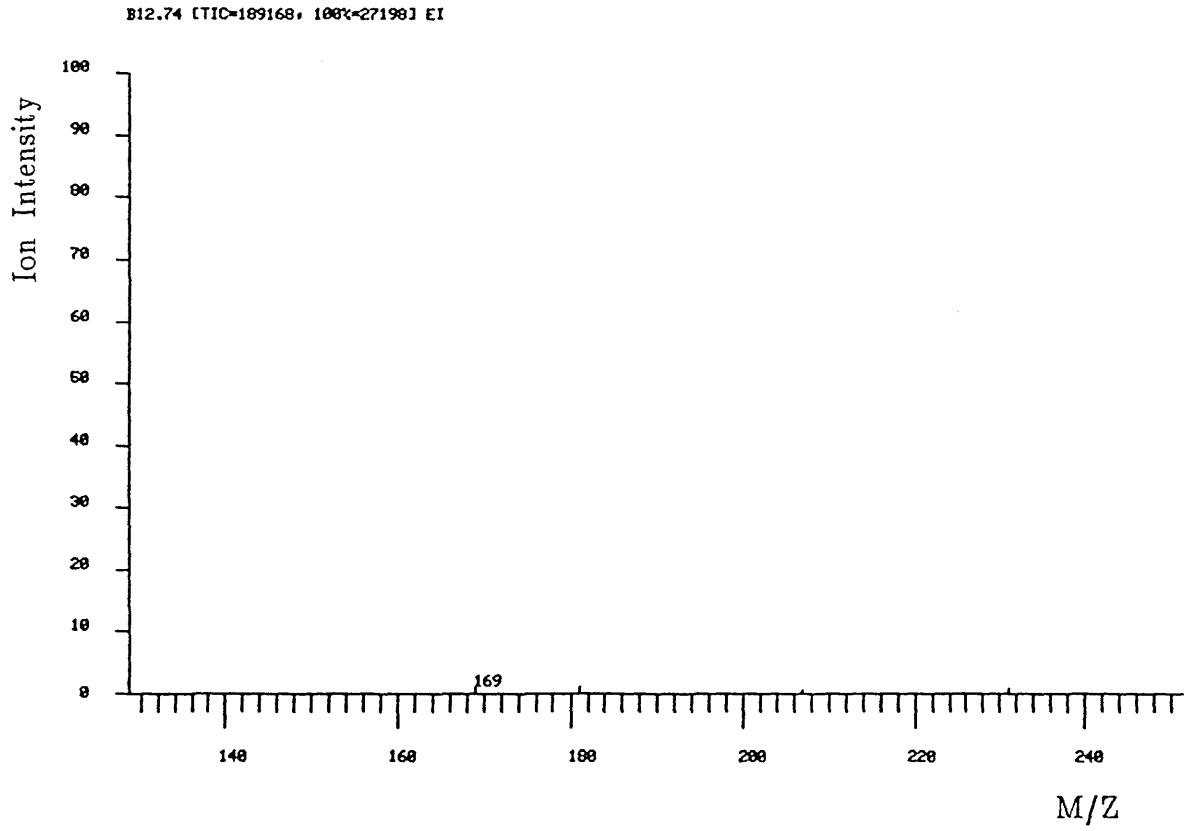


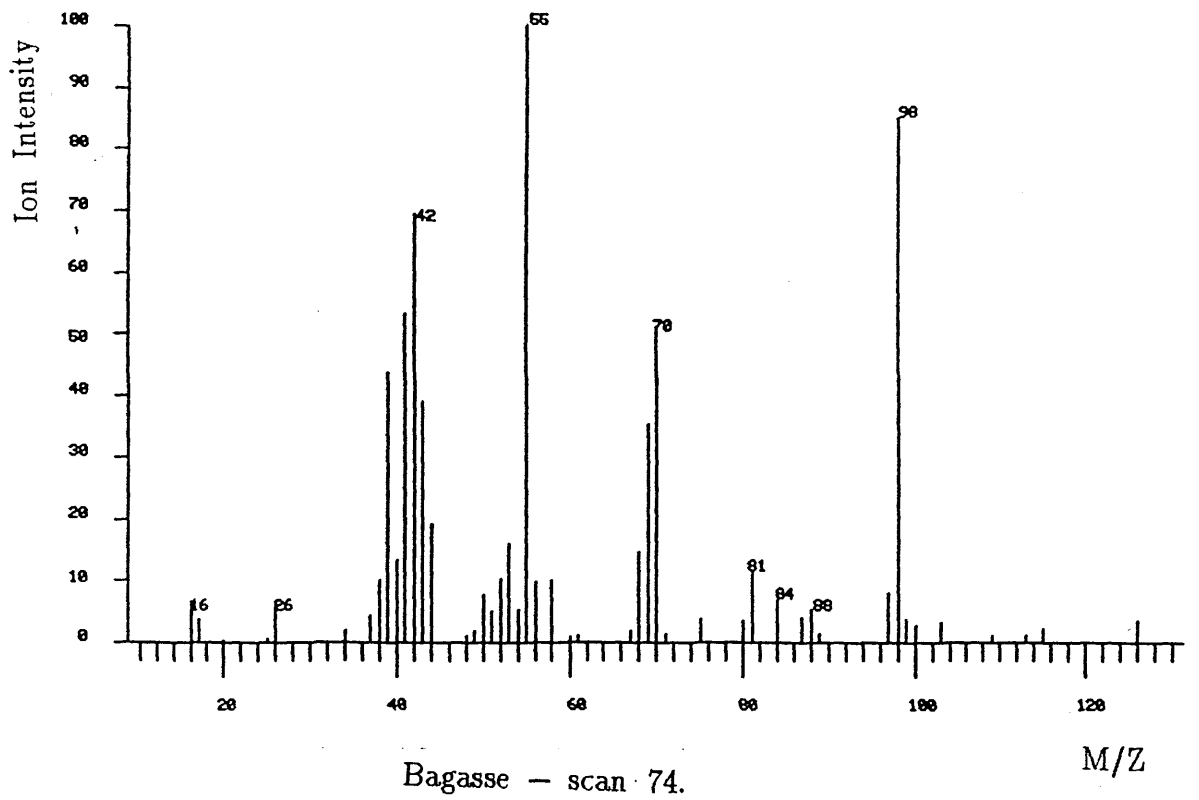
Bagasse — scan 60.



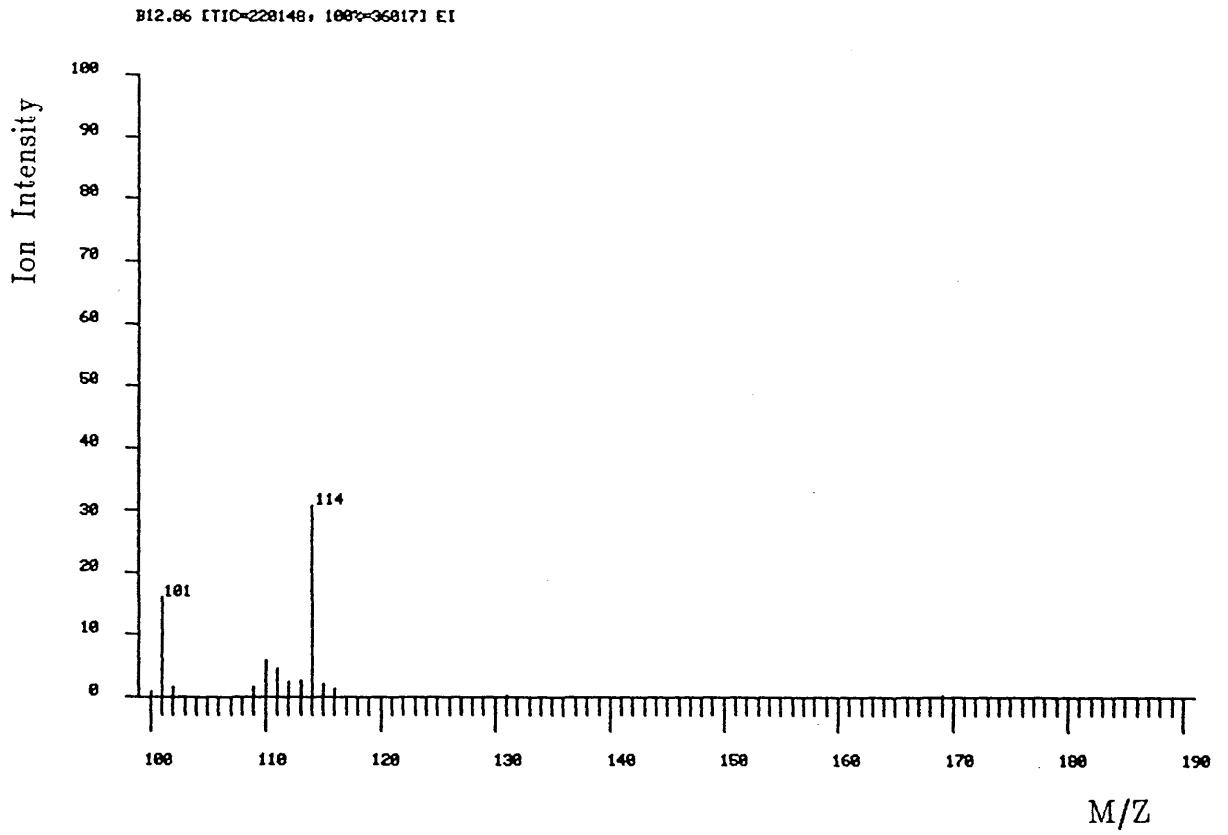


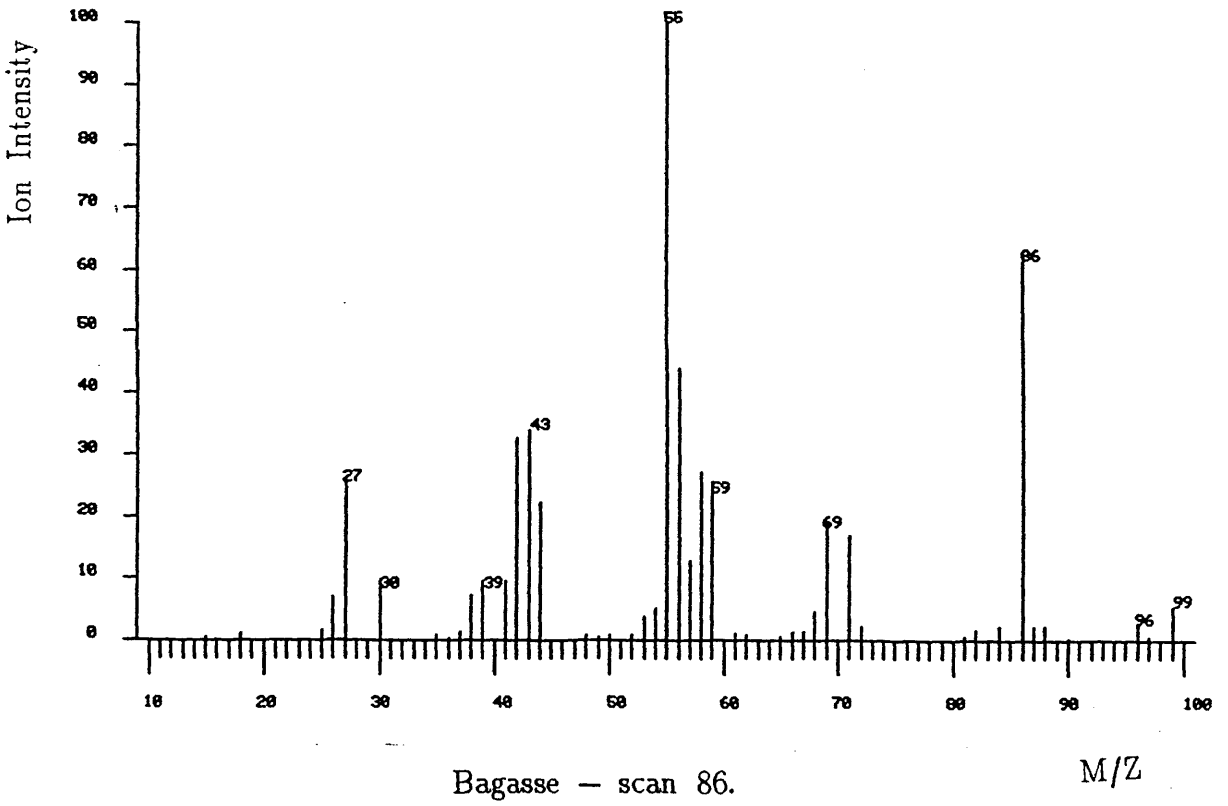
Bagasse — scan 62.



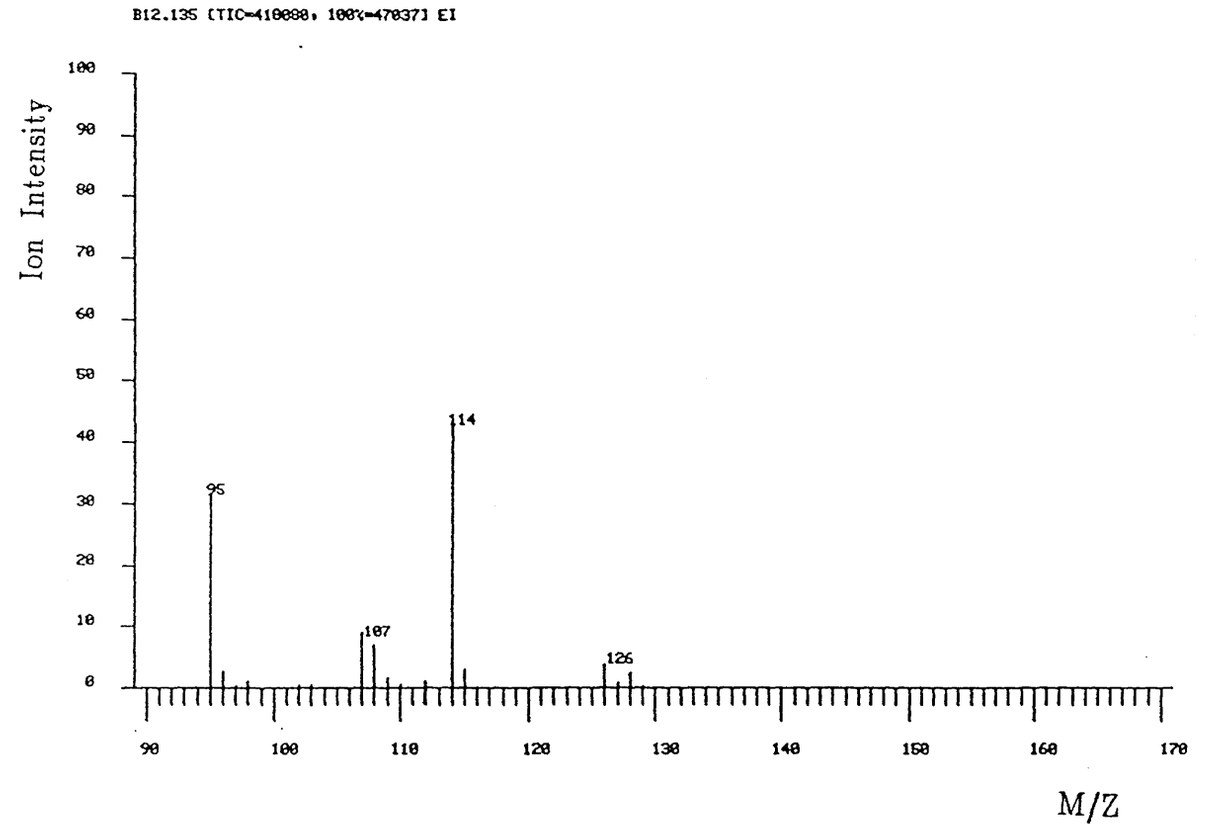


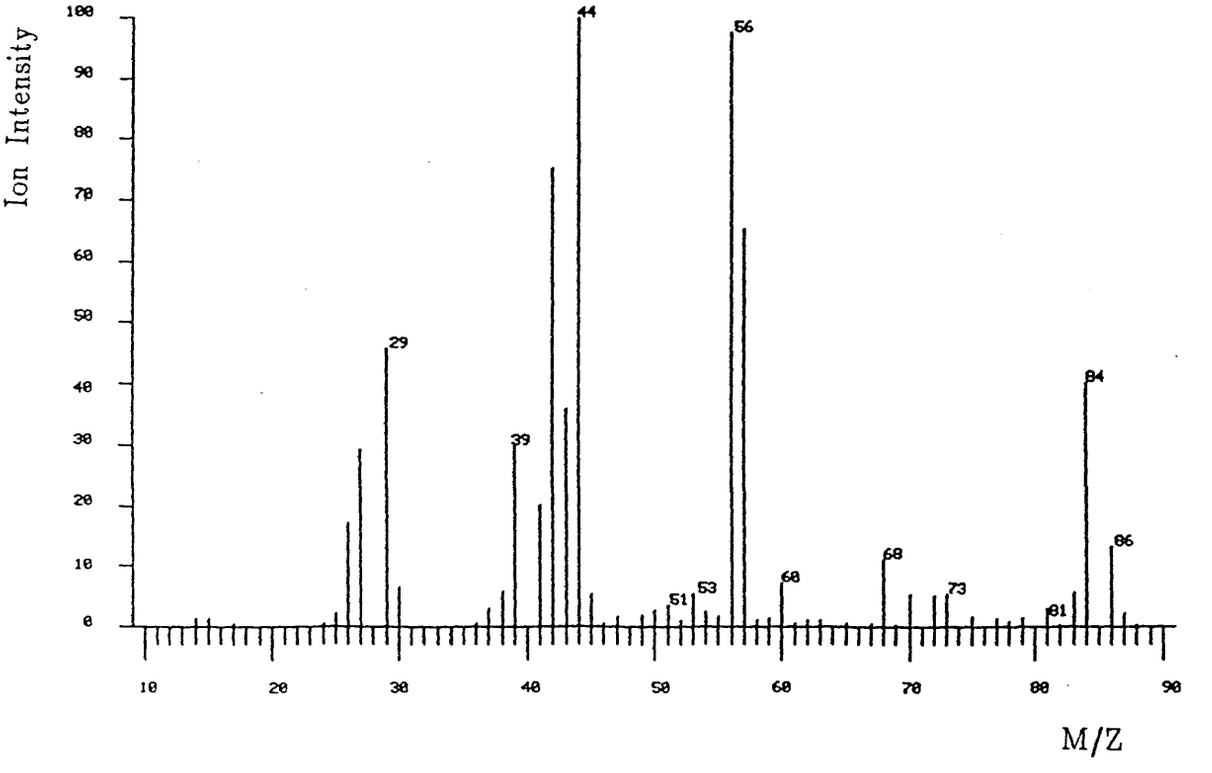
Bagasse — scan 74.



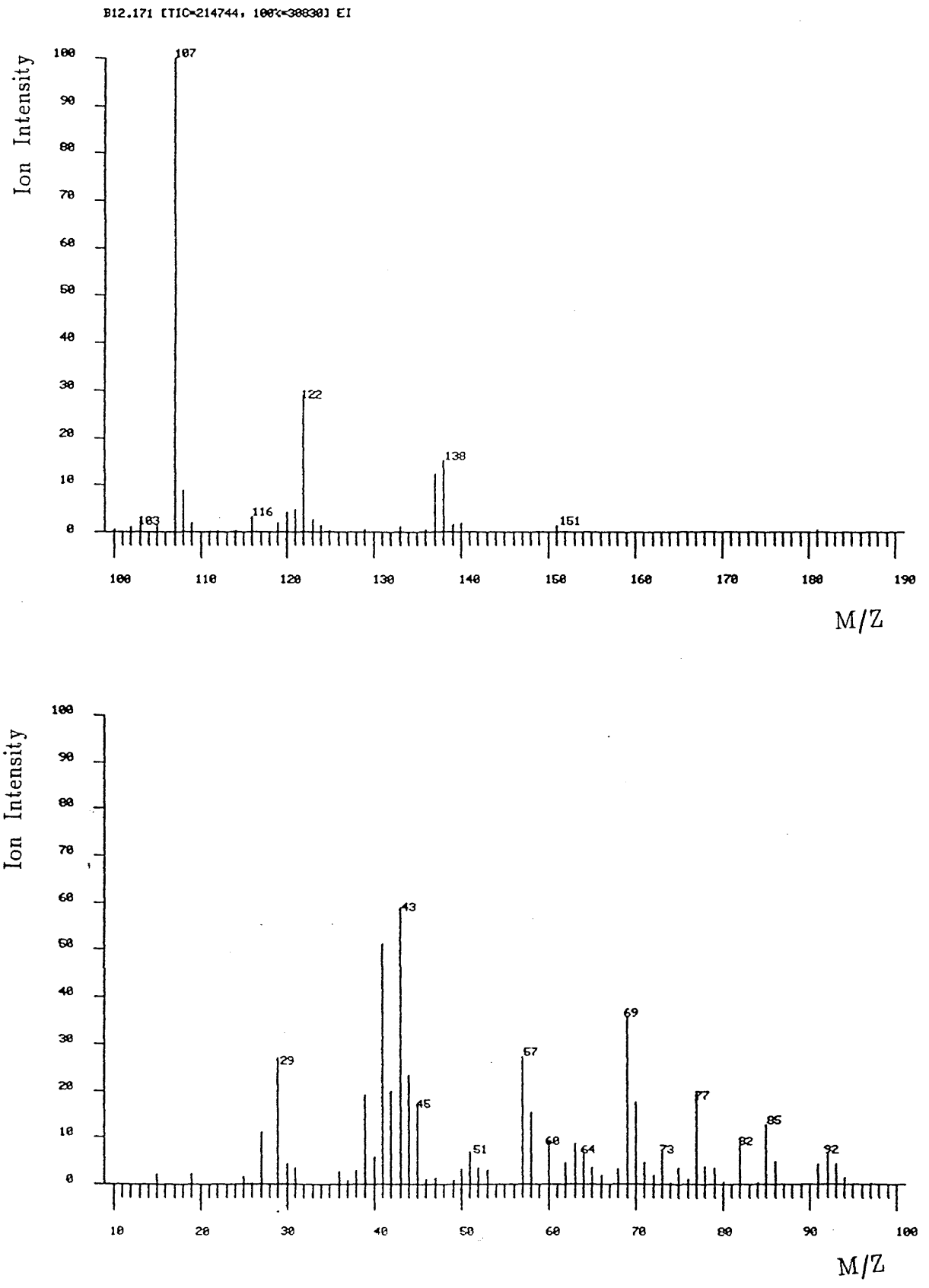


Bagasse — scan 86.

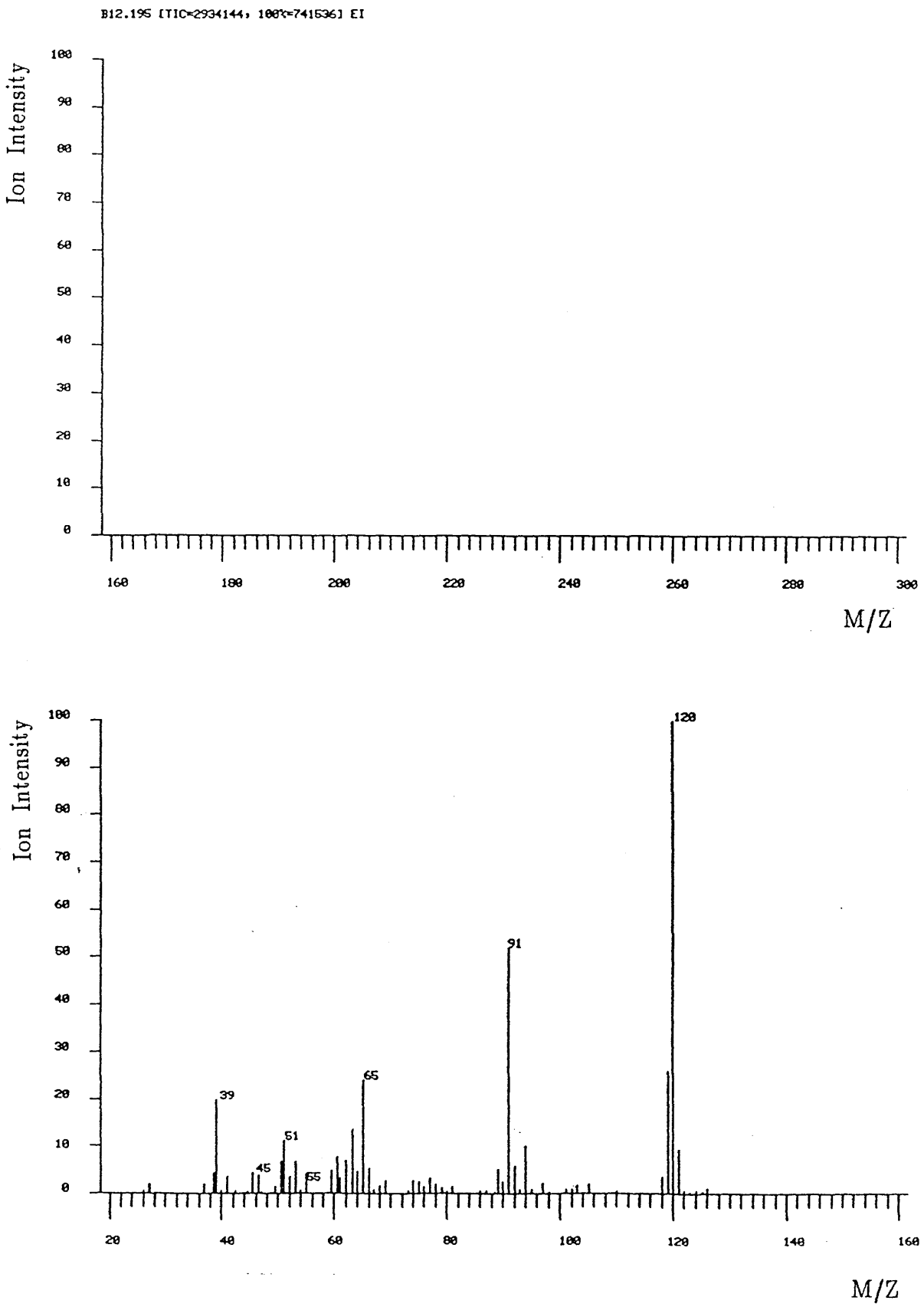




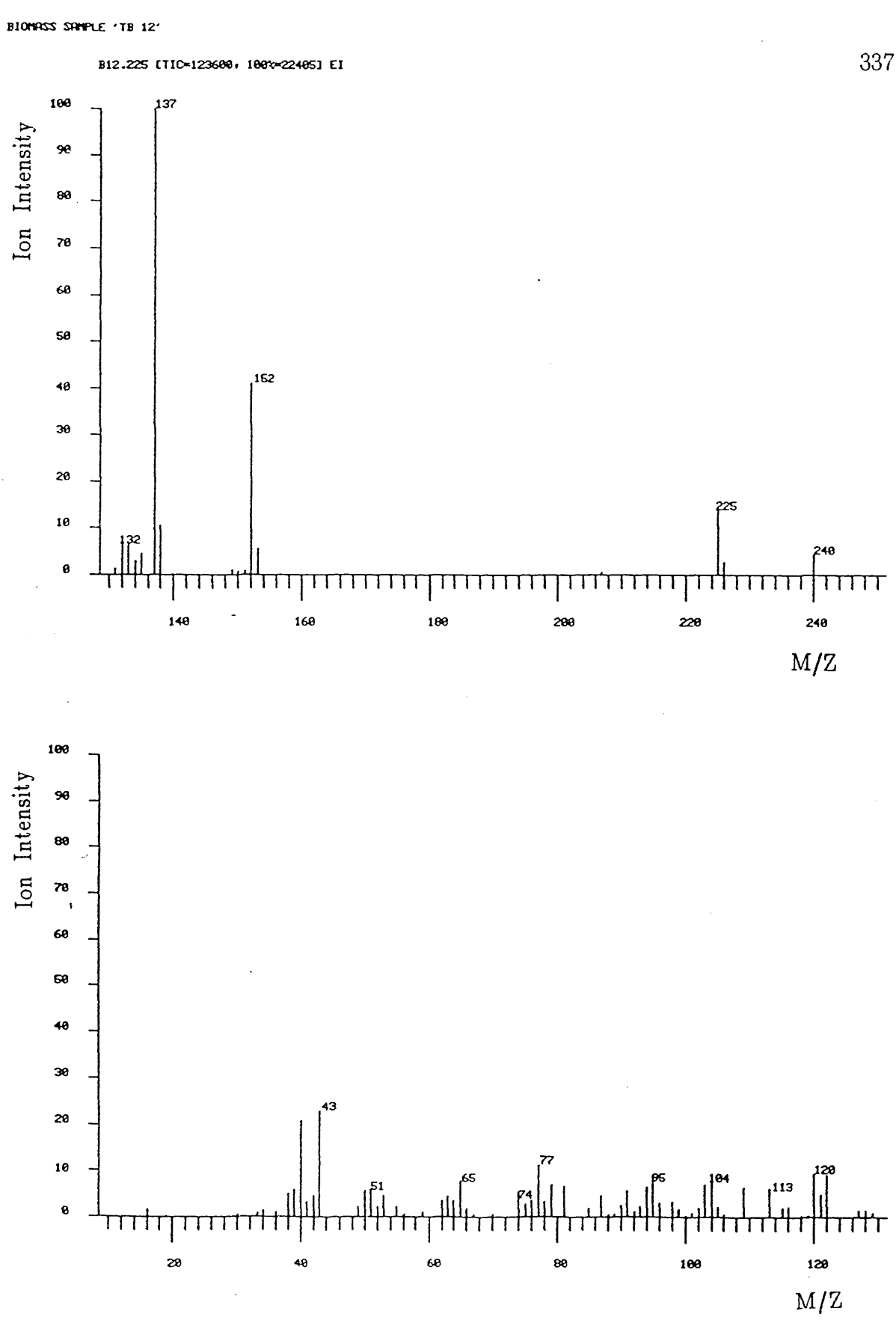
Bagasse — scan 135.



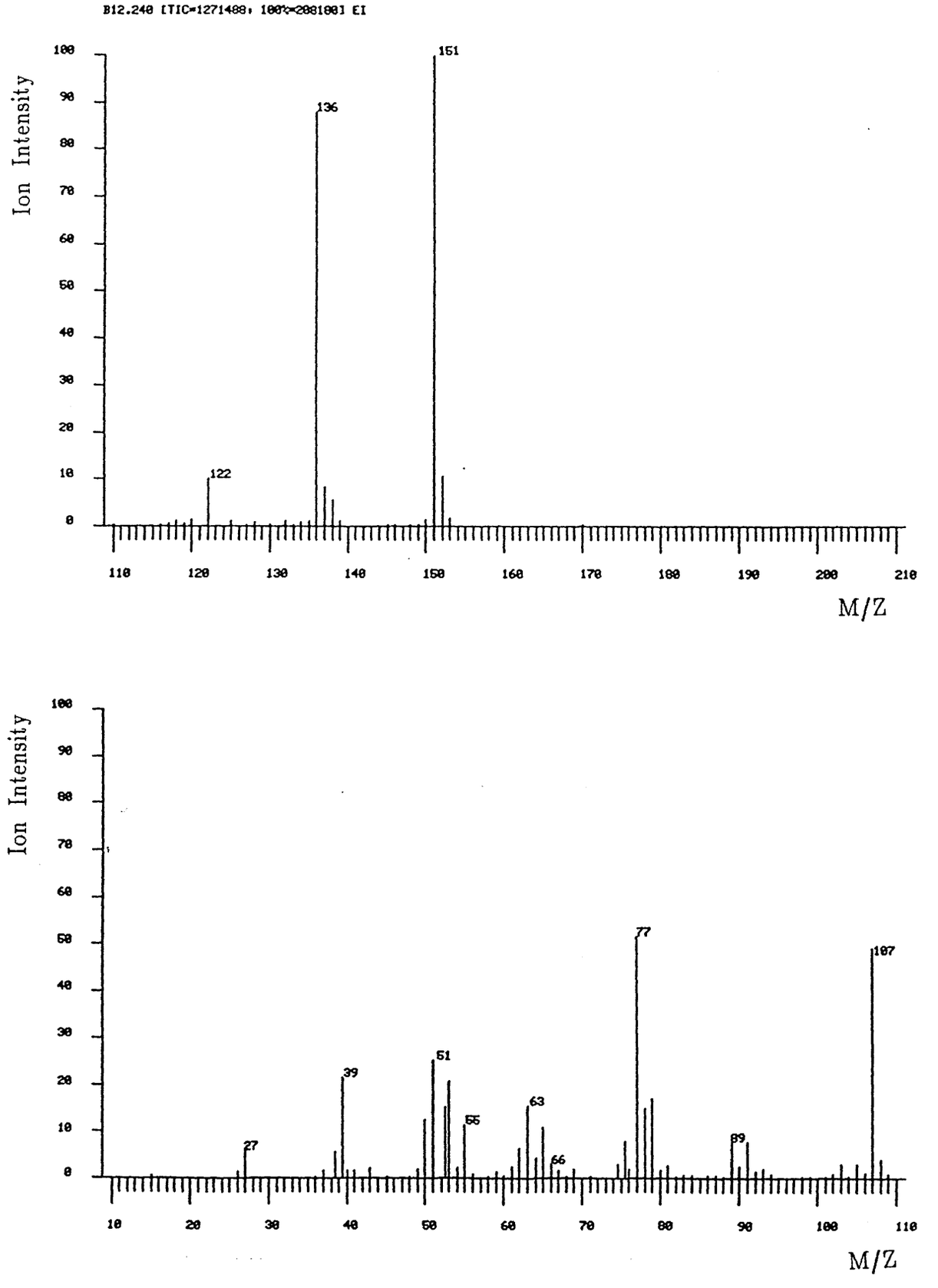
Bagasse – scan 171.



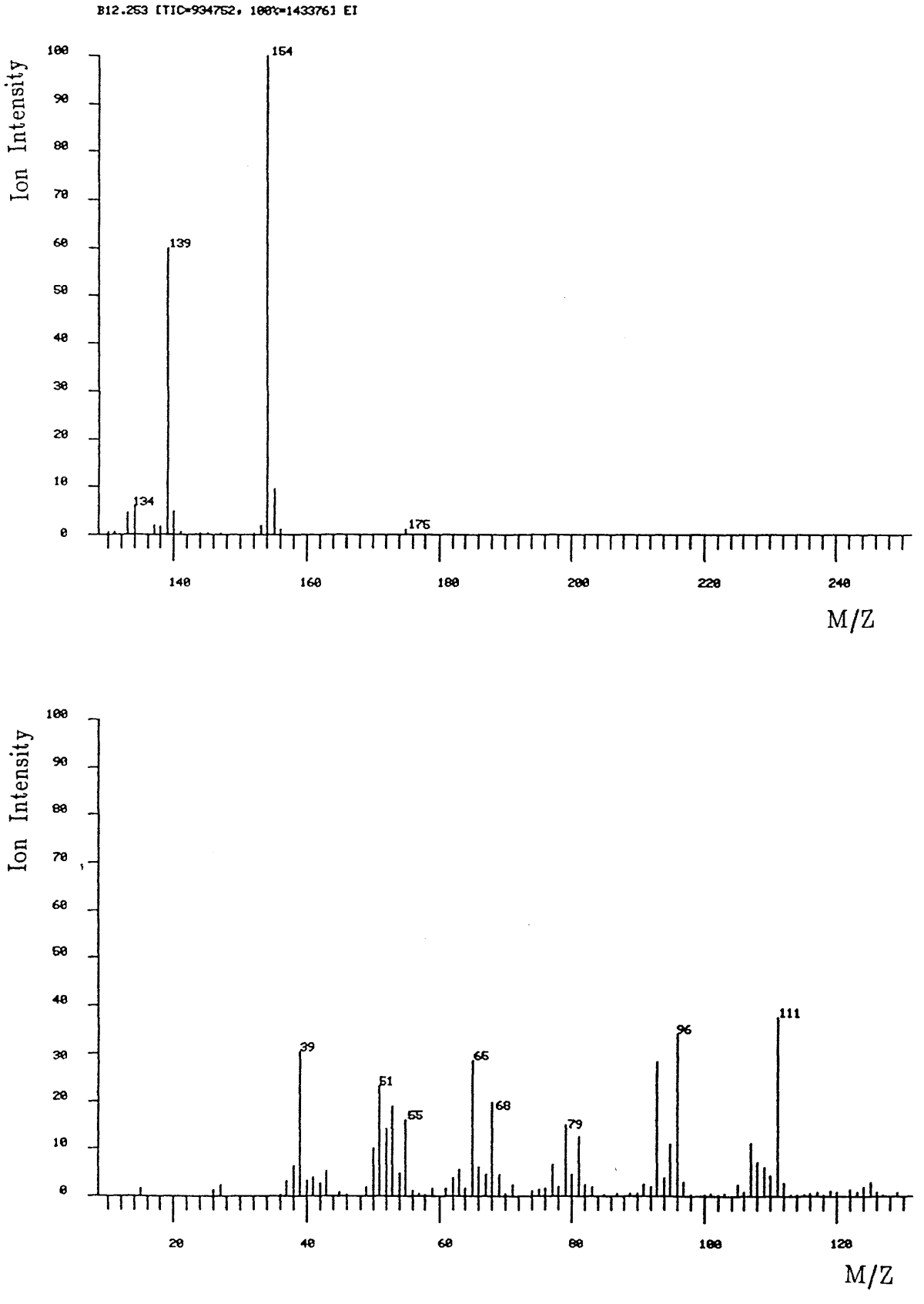
Bagasse – scan 195.



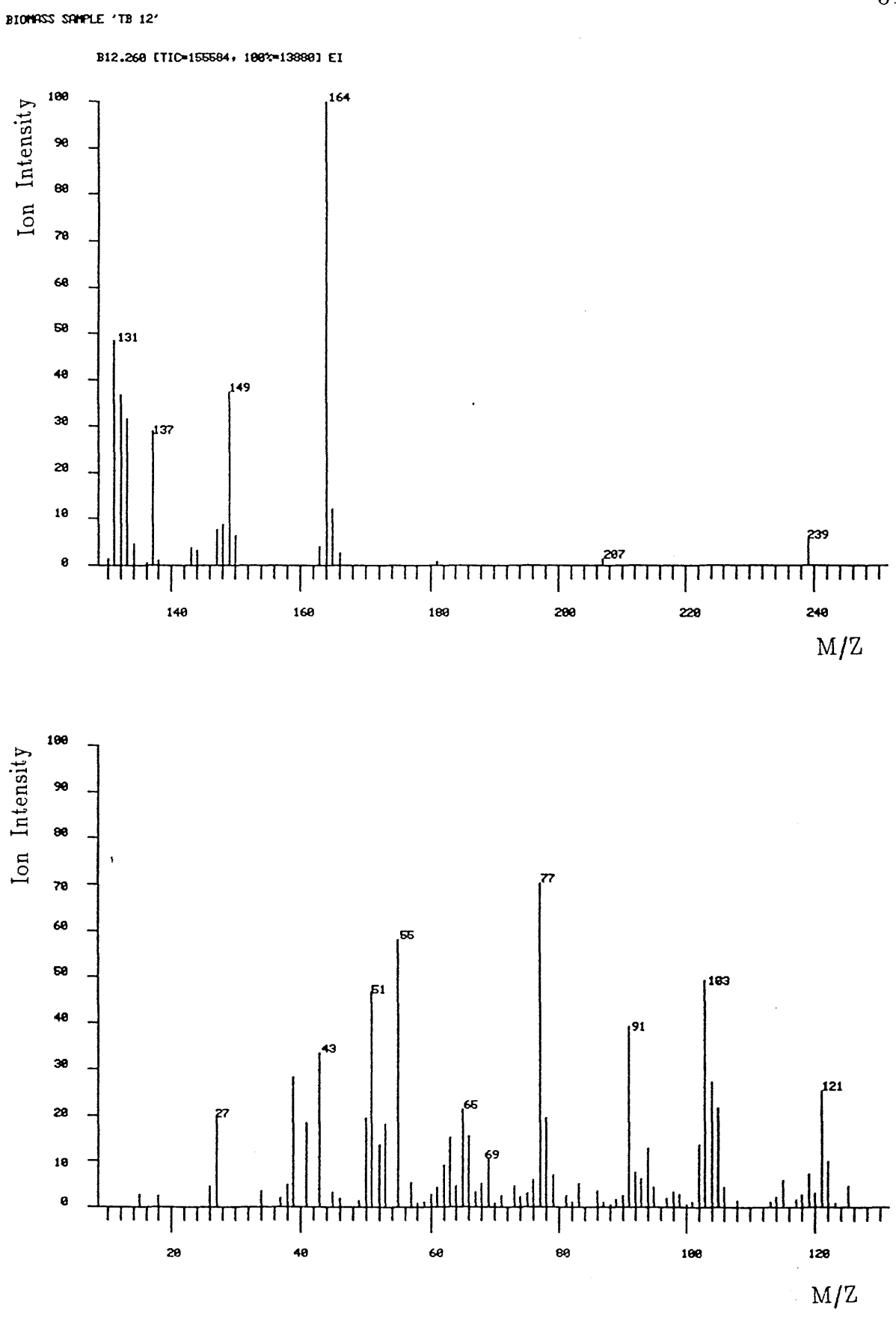
Bagasse — scan 225.



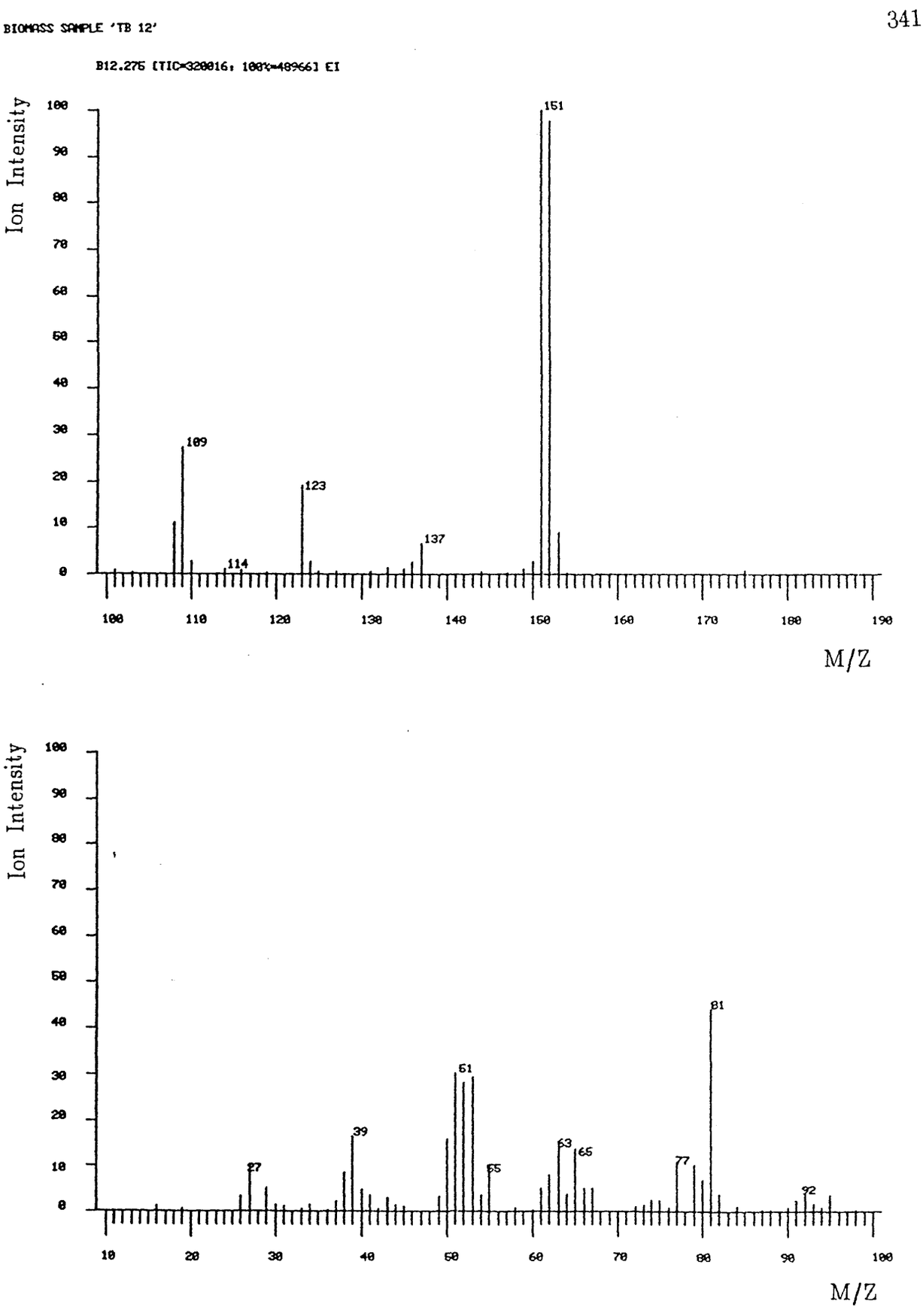
Bagasse — scan 240.



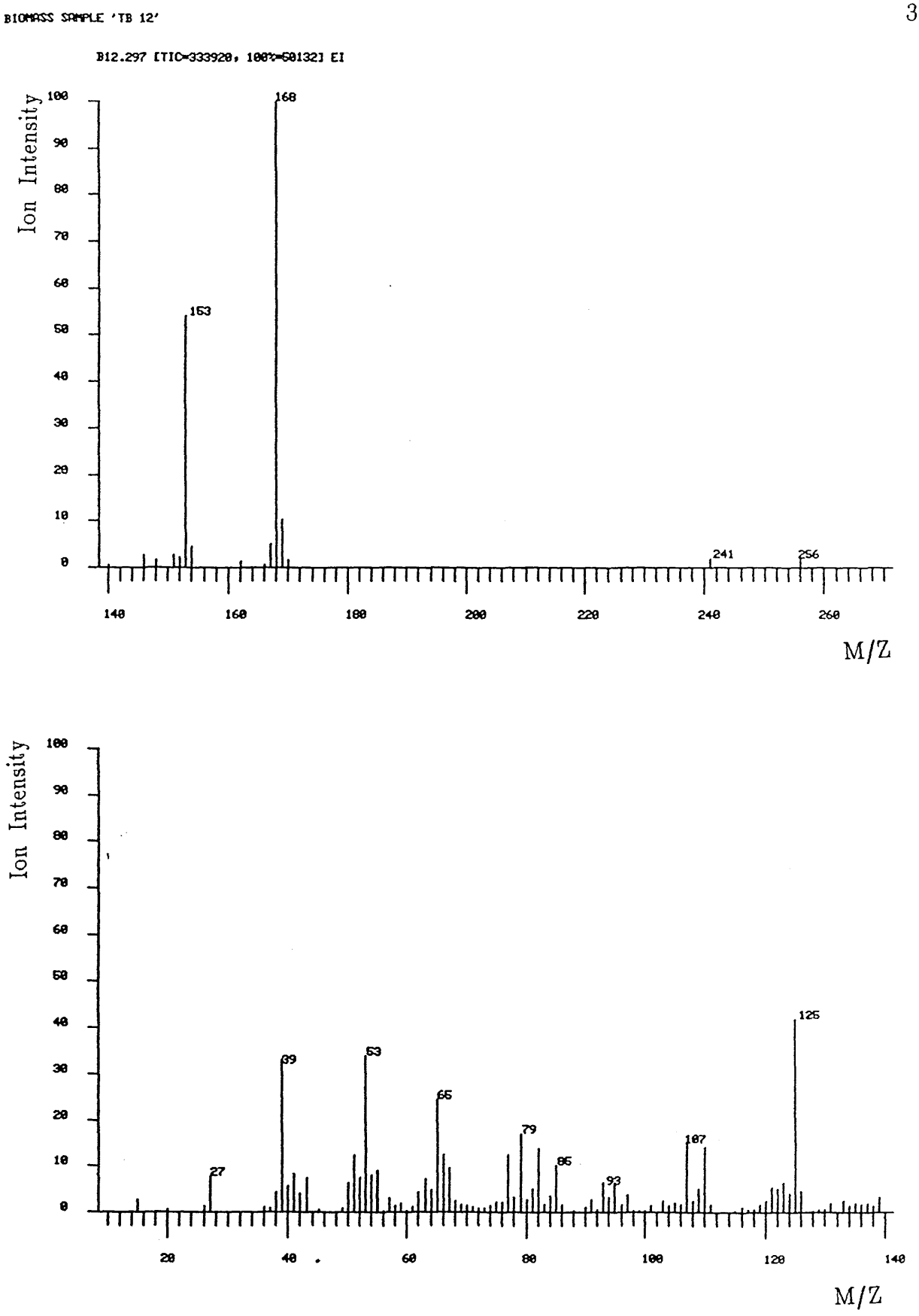
Bagasse — scan 253.



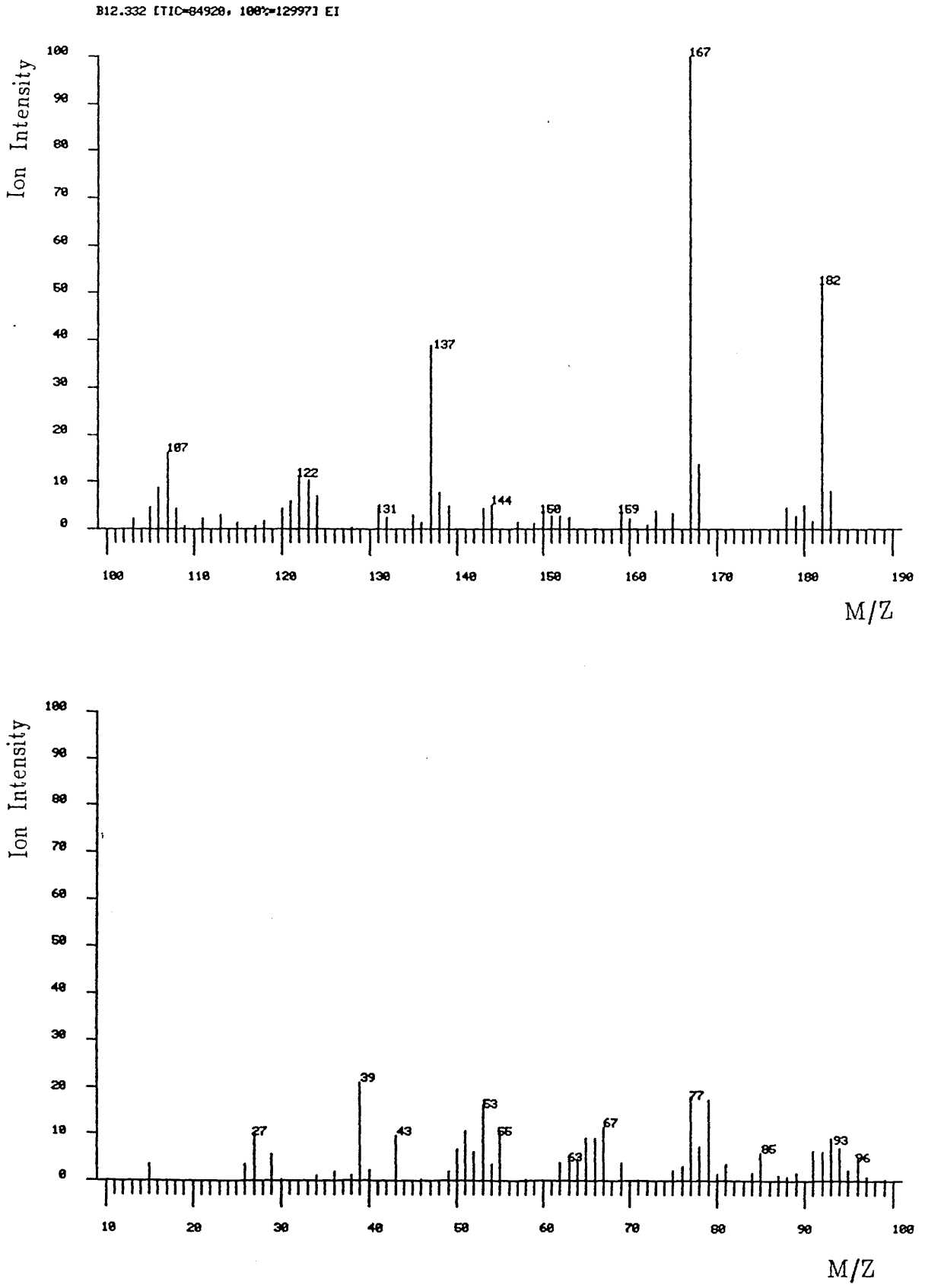
Bagasse — scan 260.



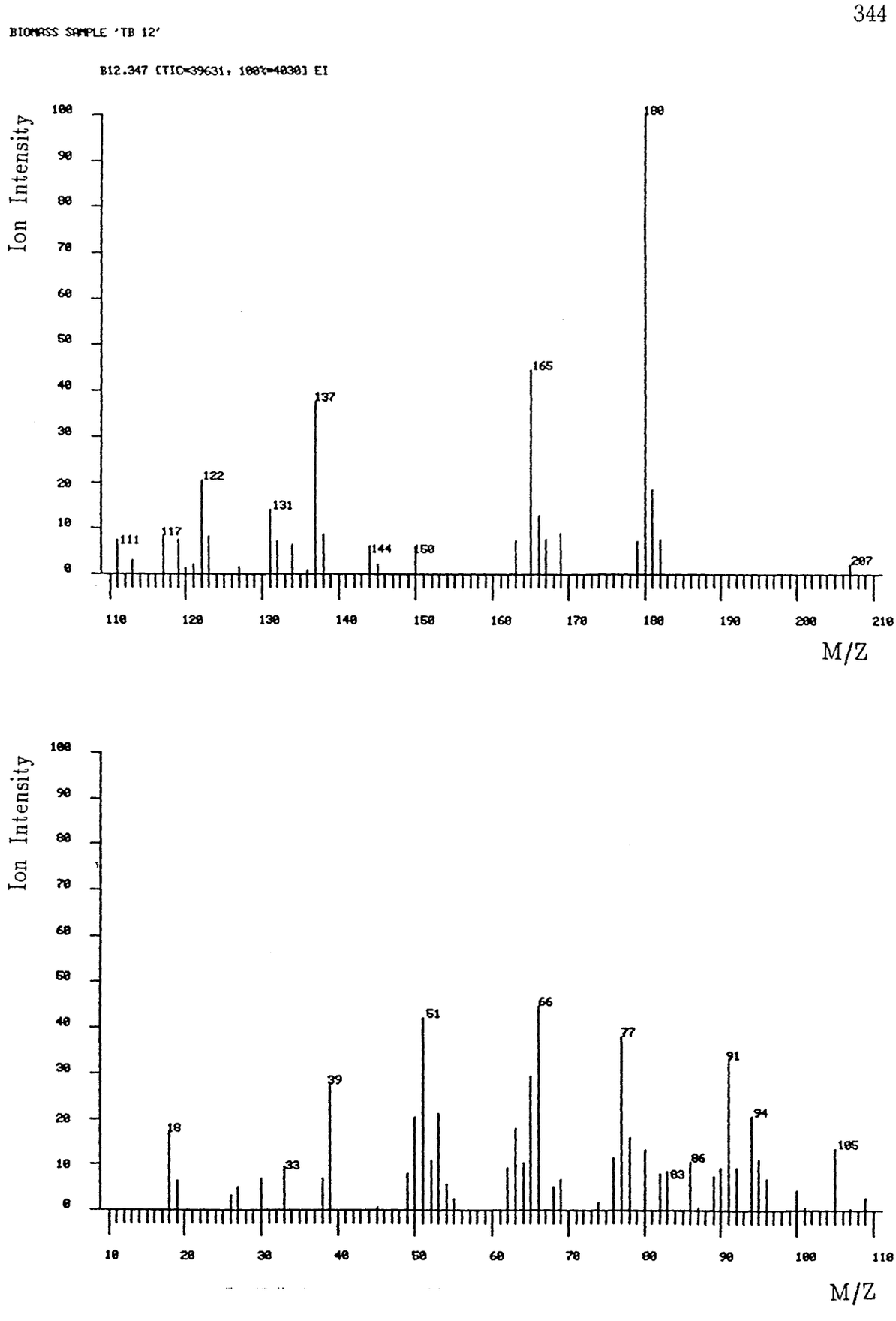
Bagasse — scan 275.



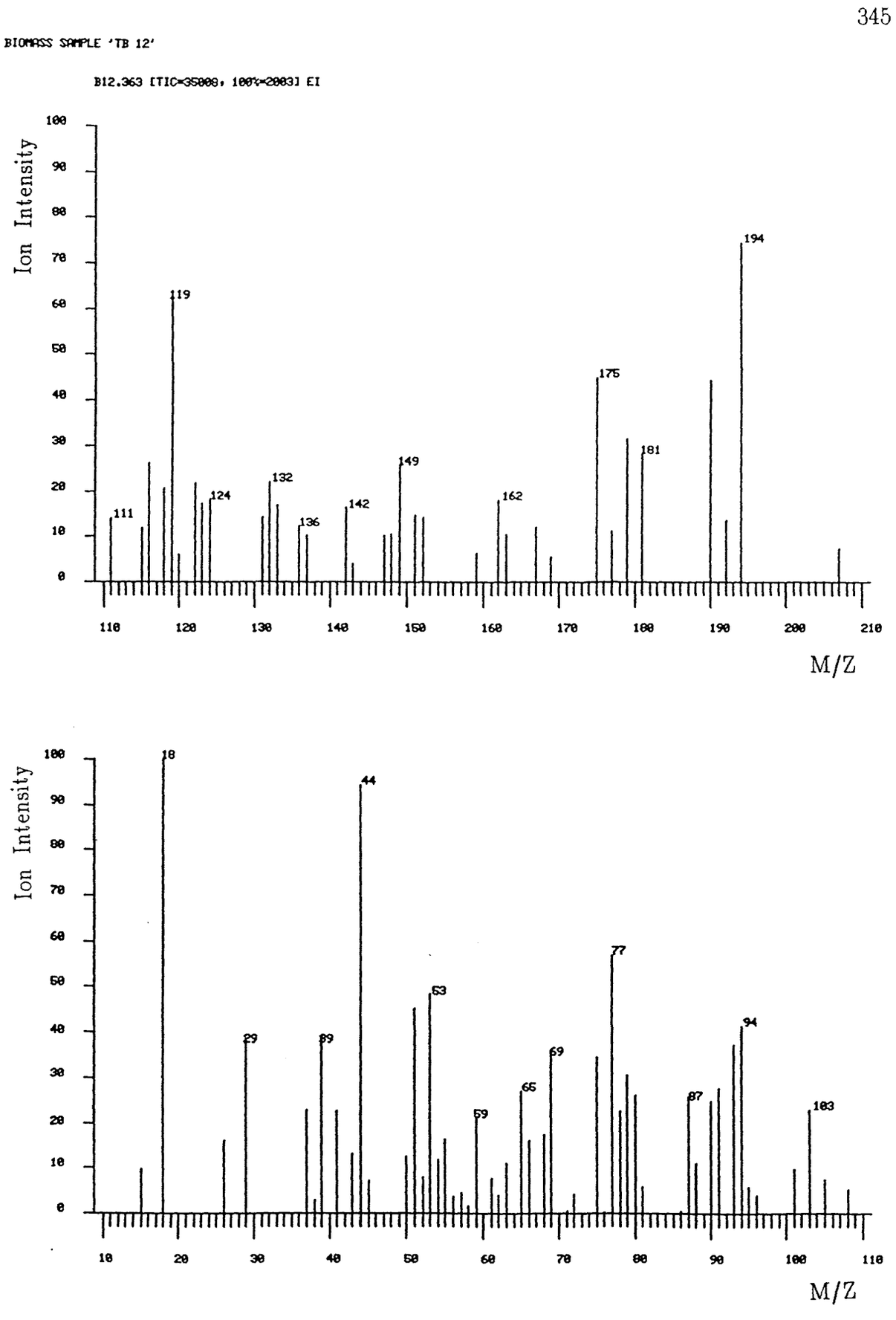
Bagasse – scan 297.



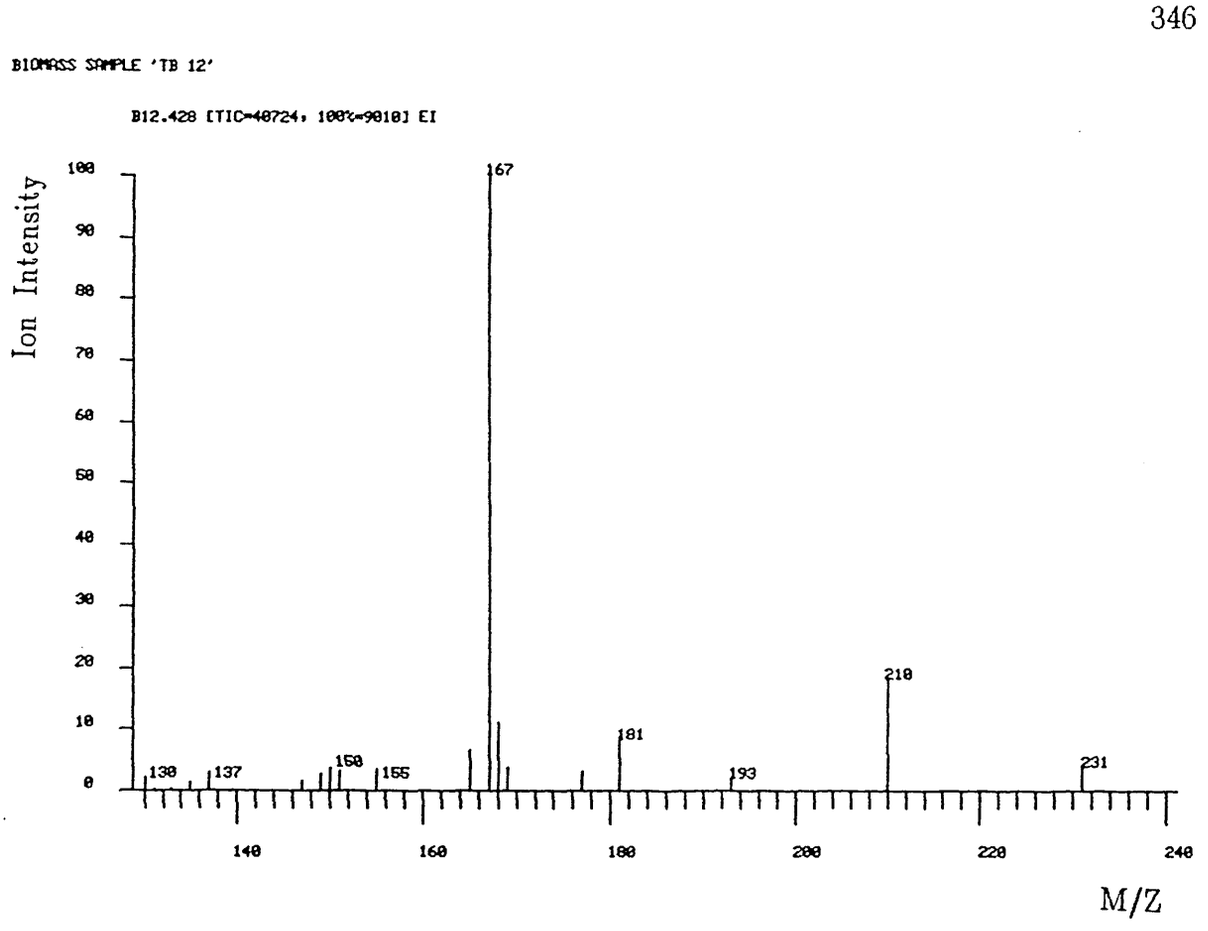
Bagasse — scan 332.

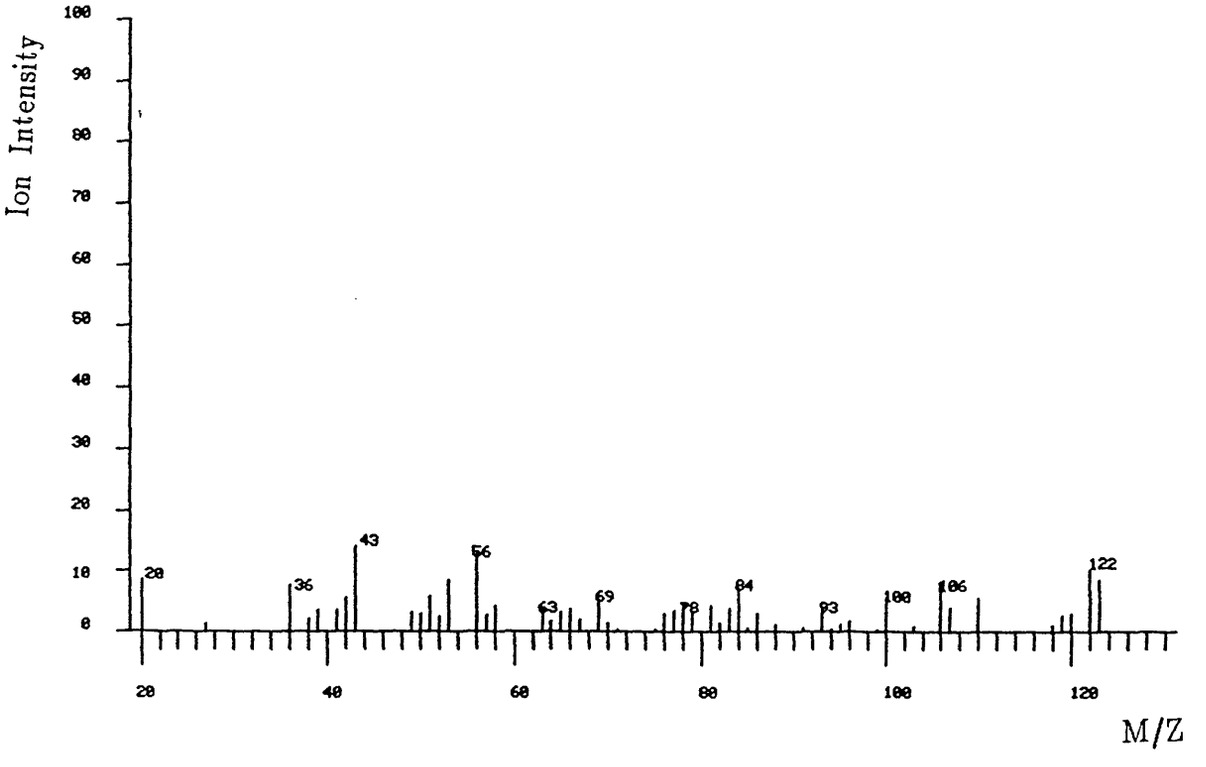


Bagasse — scan 347.



Bagasse — scan 363.





Bagasse — scan 428.

APPENDIX 2

Ash content of the Lignocellulosic materials used in this research programme.

	Ash content, dry basis.
Sugar Cane Bagasse	1.6%
Silver Birch	1.9%
Lignin	4.3%
Cellulose	< 0.0001%

REFERENCES

1 – Agrawal,R.. Kinetics of reactions involved in pyrolysis of cellulose. II – The modified Kilzer–Broito Model; The Canadian Journal of Chemical Engineering 66:413–8, 1988.

2 – Allan,G.G. and Mattila,T., High energy degradation in lignins – Their occurrence, Formation, Structure and Reactions, Sarkanen,K.V. and Ludwing,C.H., Eds., Wiley–Interscience, New York, Chap 14, 1971.

3 – Antal,M.J. Biomass pyrolysis: A review of the literature; Advances in Solar Energy; 1:61–111, 1983.

4 – Anthony,D.B.; Rapid devolatilization and hydrogasification of pulverised coal; D.Sc. Thesis, MIT, 1974.

5 – Anthony,D.B.; Howard,J.B.; Hottel,H.C. and Meissner,H.P.; Apparatus for determining high pressure coal–hydrogen reaction kinetics under rapid heating conditions; Rev. Sci Instrum. 45:992–5 1974.

6 – Arendt,P. Entgasung und Hydrierende Vargasung von Steinkohlen in Druckbereich von 0.1 bis 90 bar bei Aufheizgeschwindigkeiten von 100 bis 1000^{0}C/sec, Ph.D. thesis, Aachen 1980.

7 – ASTM. Standard Method of Test for Lignin in Wood, 848–50, 1956.

8 – Atlas of Mass Spectral Data. Stenhagen, E.et al; Interscience Pub. New York, 1969.

9 – Beall,F.C. and Eickner,H.W.; Thermal decomposition of wood components: a review of the literature, U.S.D.A. Forest Service Research Paper. FPL 130; May 1970.

10 – Bautista,J.R.; Russel,W.B. and Saville,D.A.; Time–resolved pyrolysis product distributions of softening coals, Ind. Eng. Chem. Fundam.; 25:536–44, 1986.

11 – Bettinger,J.A. and Kosstrin,H.M. Gasification of wood to produce Urea. Energy Progress 2(4):109–14, 1984.

12 – Bilbao,R.; Arauzo,D. and Millera,A.; Kinetics of thermal decomposition of cellulose. Part I: Influence of experimental conditions. Thermochimica Acta, 120:121–31, 1987.

13 – Billington,N.C.; Molar Mass Measurements in Polymer Science. The Anchor Press, London 1977.

14 – Blackwell,J; Kolpak,F.J. and Gardner,.H.; Structures of native regenerated cellulose; In: Cellulose Chemistry and Technology, by Arthur,J.C.Jr; Ed American Chemical Society, Washington, D.C. 1977.

15 – Bobrov,P.A., Thermal decomposition of wood with superheated steam, Lesokhim.Promst., 4:9, 1935. Chem. Abstr 29:8310[8].

16 – Brazilian Ministry of Industry and Commerce – Proalcool; 1984.

17 – Browne,F.L. Theories on the combustion of wood and its control U.S.Forest prod. lab., Rep. 2136, Madison, Wis. 1958 p.59.

18 – Calvin,M. and Calvin,G. As plantas como fonte de energia. Atualidade – Conselho Nacional do Petroleo 69:100–1, 1979.

19 – Calvin,M Hydrocarbons from plants: Analytical methods and observations. Die Naturwissenschaften 67:525–23, 1980.

20 – Clark,I.T.; Hydrolysis of sorbitol, Ind. Eng. Chem., 50:1125, 1958.

21 – Cane Sugar Refining in the United States: Its Economic Importance; U.S. Sugar Refiner's Association, Washington, 1971.

22 – Caubet,S. et all Thermochemical conversion of biomass: Gasification by flash pyrolysis study. Solar Energy 6(29):565–72, 1982.

23 – Chou,T and Chang,K. Gasification of Bagasse in the presence of a pilot flame in a modified fludized bed. Ind. Eng. Chem. Process Des. Dev. 20:161–5, 1981.

24 – Colson,P.; Jennings,H.J. and Smith,I.C.P. Composition, sequence, and conformation of polymers and oligomers of glucose as revealed by Carbon–13 Nuclear Magnetic Resonance. J. of the Amer. Chem. Soc; 96:8081–7, 1974.

25 – Coughlin,R.W. and Davoudzadeh,F. Coliquefaction of lignin and bituminous coal. Fuel; 65:95–106, 1986.

26 – Culmo,R.F. and Swanson,K.J.; The Pittsburg Conference, Atlantic City, N.J. paper 1083.

27 – Curtis,L.J. and Miller,D.J.; Transport Model with radiative heat transfer for rapid cellulose pyrolysis, Ind. Eng. Chem. Res.; 27:1775–83, 1988.

28 – Dadswell,H.E. and Hillis,M.E. Wood In: Hillis,M.E. Wood Extractives: and Their Significance to the Pulp and Paper Industries. N.Y., Academic Press, 1963 p.3.

29 – Dasgupta,A.; Weston,R.F. and Nemerow,N.L.; Anaerobic digestion of lignocellulosic residues from sugar cane processing in Energy From Biomass Wastes XI, Ed by Klass,D.L.; Chicago USA, p.613–36, 1988.

30 – Deepchand,K. A note on the pyrolysis behaviour of sugar cane fibrous products. Biological Wastes 20:203–8, 1987.

31 – DeGroot,.F.et all; First chemical events in pyrolysis of wood; Journal of Analytical and Applied Pyrolysis; 13:221–31, 1988.

32 – Desypris,J.; Murdoch,P. and Williams,A.; Investigation of the flash pyrolysis of some coals; Fuel, 61:807–16, 1982.

33 – Diebold,J. Workshop summary. In: Specialist's Workshop on Fast Pyrolysis of Biomass. Proceedings. Copper Mountain, Solar Energy Research Inst. 1980 p.3.

34 – Dixon, W.T.; Journal Chem. Phys. 77:1800, 1982.

35 – Dorman,D and Roberts,J.D.; Nuclear Magnetic Resonance Spectroscopy. C–13 Spectra of some pentose and hexose aldopyranoses. Jounal of the American Chem. Soc. 92:1355–61, 1970.

36 – Evans,R.J.; Milne,T.A. and Soltys,M.N.; "a" Mass spectrometric behaviour of levoglucosan under different ionisation conditions and implications for studies of cellulose pyrolysis. J. Anal. Applied Pyrolysis; 6:273–83, 1984.

37 – Evans,R.J.; Milne,T.A. and Soltys,M.N.; "b" Molecular–beam sampling/mass spectrometric studies of the primary pyrolysis mechanisms of biomass fossil organic matter, and Synthetic polymers; Amer. Chem Soc Div of Fuel Chemistry 29:20–31, 1984.

38 – Faix,O.; Meier,D. and Fortmann,I.; Pyrolysis– GC–MS of two trimeric lignin model compounds with alkyl–aryl ether structure. J. Anal. Applied Pyrolysis. 14:135–48, 1988.

39 – Faix,O.; Meier,D. and Grobe,I.; Studies on isolated lignins and lignins in woody materials by pyrolysis–GC–MS and off–line pyrolysis–GC with flame ionization detection. J. Anal. Applied Pyrolysis; 11:403–16, 1987.

40 – Fengel,D. and Wegner,G. Wood–chemistry, ultra structure, reactions, Walter de ruyter. Berlin – N.Y. 26–65, 1984.

41 – Fengel,D.; On the changes of the wood and its components within the temperature range up to 200^{0}C. I – Hot and cold water extracts of thermally treated spruce wood, Holz Roh Werkst., 24:9, 1966.

42 – Fletcher,T.L. and Harris,E.E., Products from the destructive distillation of Douglas–fir lignin, Tappi, 35:536, 1952.

43 – Fong,W.S.; Peters,W.A. and Howard,J.B.; Apparatus for determining high–temperature, high–pressure coal plastic behaviour under rapid heating conditions; Rev. Sci. Instrum.; 56:586–91, 1985.

44 – Franklin,W.E.; Direct pyrolysis of cellulose and cellulose derivatives in a mass spectrometer with a data system. Analytical Chemistry; 51:992–6, 1979.

45 – Freihaut,J.D.; Zabielski,M.F. and Seery,D.J.; Reaction induced temperature deviations during coal devolatilisation in a heated grid; ACS DFC prepr.; 27(2):89–98, 1982.

46 – Freudenberg,K.; Lignin: its constitution and formation from p–hydroxycinnamyl alcohols; Science; 148:595; 1965.

47 – Funazukuri,T.; Hudgins,R.R. and Silveston,P.L.; Product yield correlations for cellulose flash pyrolysis; Journal of Analytical and Applied Pyrolysis. 13:103–22, 1988.

48 – Funazukuri,T.; Hudgins,R.R. and Silveston,P.L.; Product distribution for flash pyrolysis of cellulose in a coil pyrolyzer. J. Anal. and Applied Pyrolyisis. 10:225–49, 1987.

49 – Gavalas,G.R. and Wilks,K.A.; Intraparticle mass transfer in coal pyrolysis; AIChE 26:201–12, 1980

50 – Gibbins,J.R.; Investigation of primary coal pyrolysis processes using a variable heating rate wire–mesh apparatus; Ph.D. Thesis, University of London 1988.

51 – Goldstein,I.S. Wood as a source of chemical feedstocks. AICHE Symposium series. 74:111–4, 1982.

52 – Glasser,W.G.; Lignin; In: Fundamental Thermochemical Biomass Conversion; by Overend,R.P.; Milne,T.A. and Mudge,L.K.; Elsevier App. Science Pub.; London 1985, Chapter3, p 61–76

53 – Glasser,W.G.. Chemicals from lignocellulose, Biotechnology. Bioengineering Symposium, 6:298, 1976.

54 – Glasser,W.G.. Biomass availability and Utility for chemicals. In: Organic Chemicals from Biomass. by Goldstein,I.S.; CRC Press, Inc: Florida – U.S.A. 1981.

55 – Golova,O.P. and Krylova,R.G., Thermal decomposition of cellulose and its structure, Dokl. Akad. Nauk SSSR, 115:419, 1957; Chem. Abstr. 52:4979e.

56 – Gomes da Silva,J et al; J.Science 201:903, 1978

57 – Goos,A.W., The thermal decomposition of wood, in Wood Chemistry, Wise,L.E. and Jahn,E.C., Eds.,Reinhold, New York, Chap 20, 1952.

58 – Hajaligol,M.; Peters,W.A. ans Howard,J,B.; Intraparticle nonisothermalities in coal pyrolysis; Energy and Fuels, 2:430–7, 1988.

59 – Hajaligol,M. et al Product composition and kinetics for rapid pyrolysis of cellulose. Ind. Eng. Chem. Proc. Des. Dev. 21:457–65, 1982.

60 – Hajaligol,M. et al Product composition and kinetics for rapid pyrolysis of cellulose. In: Specialist's Workshop on Fast Pyrolysis of Biomass. Proceeding Copper Mountain, Solar energy Res.Inst. 215–236; 1980.

61 – Hall,D.O.; Barnard G.W. and Moss,P.A. in: Biomass for Energy in the Developing Countries. Pergamon Press Ltd, Oxford – UK. 1982.

62 – Hamilton,L.H.; Ayling,A.B. and Shiboaka,M.; A new experimental device for pyrolysing coal particles under controlled conditions over a wide range of heating rates, Fuel, 58:873–6, 1979.

63 – Hatcher,P.G. et all; Solid–state ^{13}C NMR of sedimentary humic substances: New revelations on their chemical composition; In Aquatic and terrestrial Humic Materials; by: Christman,R.F. and Gjessing,E.T.; Ed. Ann Arbor Science, p37–82, 1983.

64 – Hatt,B. W. and Bridgwater,A.V. Conversion of biomass to fuels by thermal process. The Watt Committee on Energy, London, 62–8; 1979.

65 – Hawley,L.F. and Wiertelak,J. Effect of mild heat teatment on the chemical composition of wood, Ind. Eng. Chem., 23:184, 1931.

66 – Hruza,D.; Praag,M and Heinsohn,jr. Isolation and identification of the components of the tar of hickory wood smoke. J. Agr. Food Chem. 22:123–6, 1974.

67 – Hubbert,M.K. The energy resources of the earth; Scientific American Sept:61–70, 1971

68 – Iatridis,B. and Gavalas,G.R.; Pyrolysis of a precipitated kraft lignin; Ind. Eng. Chem. Prod. Res. Dev., 18:127–30, 1979.

69 – Immergut,E.H.; Cellulose; In: The Chemistry of Wood; by: Browning,B.L.; Ed. Interscience, New York, Chapter 4, 1963.

70 – Jain,R.; Mathematical modeling and experimental studies of thermal reactions of coal; Ph.D. Thesis, CIT, Pasadena, California. 1980

71 – Juntgen,H. and van Heek,K.L.; Gas release from coal as a function of the rate of heating, Fuel, 47:103–17, 1968.

72 – Kaaden,A. et al; Analytical pyrolysis of carbohydrates. Journal of Analytical and Applied Pyrolysis; 5:199–220, 1983.

73– Kalinowski,H.O.; Berger,S. and Braun,S.; ^{13}C NMR spektroskopie; Thieme, Stuttgart 1984.

74 – Kato,K. and Takahashi,N.; Agr. Biol. Chemi. ; 31:519, 1967.

75 – Katzen,R., Muller,R.E. and Othmer,D.F. Destructive distillation of lignocellulose, Ind. Eng. Chem., 35:302, 1943.

76 – Kilzer,F.J. and Broido,A., Speculation on the nature of cellulose pyrolysis, Pyrodynamics, 2:151–63, 1963.

77 – Kim,N; Trautz,A. and Miller,D.J.; Flash pyrolysis of cellulose in the presence of K_2CO_3; in: Energy From Biomass and Wastes XI, Ed by Klass,D.L., Chicago USA, p.839–52, 1988.

78 – Knight,J.A.; Utilization and/or stabilization of pyrolytic oil from pyrolysis of agricultural, municipal and other wastes, Georgia Institute of Technology, Atlanta, 1977.

79 – Kogel,I et al; Chemical composition of the organic matter in forest soils – Forest litter; Soil Science; 2:124–36; 1988.

80 – Lançcas,F. H.P.L.C. Analysis of sugar cane bagasse hydrogenation products. 1 – group–type separation. Journal of Liquid Chromatrography 9(1):217–28, 1986.

81 – Levelton,B.H. and O'Connor,D.V.; An evaluation of wood waste energy conversion systems, a study commissioned by the British Columbia Wood Waste Energy Coordinating Committee, Environment Canada; Vancouver, 1978.

82 – Lewellen,P.C. et al. Cellulose pyrolysis kinetics and char formation mechanism. Sixteenth Symp. International on Combustion, The Combustion Inst. 1471–80; 1977.

83 – Liquid Fuels from coal. Published by National Coal Board, United Kingdom, p.19–August 1978.

84 – Lin,F.S.; Chang,T.S. and Rei,M.H.; Rapid pyrolysis of rice hull in a Curie–point pyrolyzer; Agricultural Wastes; 18:103–21, 1986.

85 – Loisin,R. and Chauvin,R.; Rapid pyrolysis of coal; Chim. Ind. Paris, 91:269–75, 1964.

86 – Lowenthal,G.; Wanzl,W. and van Heek,K.H.; Kinetics of swelling of coal particles during pyrolysis and hydropyrolysis; Proc. Int. Conf. on Coal Sci; Sydney 1985.

87 – Ludemann,H.D. and Nimz,H.; Carbon–13 Nuclear Magnetic Resonance spectra of lignins. Biochem. and Biophys. Research Comm. 52:1162–9, 1973.

88 – Maciel,G.E. et all; A ^{13}C NMR study of four lignins in the solid and solution states; Makromol. Chem.; 182:2297–304, 1981.

89 – Madorsky,S.L., Hart,V.E. and Straus,S., Thermal degradation of cellulosic materials, J.Res.Natl.Bur.Stand, 60:343, 1958.

90 – Martin,D. Environ. Prot. Survey 1978 p.14.

91 – Meuzelaar,H.L.C.; Haverkamp,J. and Hileman,F.D.; in: Pyrolysis Mass Spectrometry of Recent and Fossil Biomaterials – Compedium and Atlas, Vol 3, Elsevier Scientific Pub. Comp. 1982.

92 – Merritt,R.W. and White,A.H., Partial hydrolysis of wood, Ind. Eng. Chem., 35:297, 1943.

93 – McDonald,E.C., Howard,J. and Bennett,B. Chemicals from forest products by supercritical fluid extraction. In: Fluid Phase Equilibria. Amsterdam; 10:337–44, 1983.

94 – Mishra,S.P.; Neilson,G.W. and Symons,M.C.R. Determination of the composition and sequence of glucan containing mixed linkages by carbon–13 NMR. J. Amer. Chem. Society 95:606–9, 1973.

95 – Nelson,D.A.; Samuels,W.D. and Hallen,R.T.; Alkaline cleavage of model lignin compounds; Energy and Fuel; 1:239–42, 1987.

96 – Nevell,T.P., A qualitative X–ray study of the oxidation of cotton cellulose by nitrogen dioxide, J.Text.Inst., 42:139, 1951.

97 – Nikitin,N.I., Thermal decomposition of wood, in The Chemistry of Cellulose and Wood, Israel Program for Scientific Translations, Jerusalem, chap 25, 1966.

98 – Niksa,S.J.; Time–resolved kinetics of rapid coal devolatilization, Ph.D. Thesis, Princeton, NJ. 1982.

99 – Nunn,T.R. et al; "a" Studies of the rapid pyrolysis of sweet gum hardwood; In: Fundamental Thermochemical Biomass Conversion. by: Overend,R.P.; Milne,T.A. and Mudge,L.K.; Elsevier App. Science Pub. London 1985, Chapter16 pp293–314.

100 – Nunn,T.R. et al; "b" Product compositions and kinetics in a rapid pyrolysis of sweet gum hardwood. Ind. Eng. Chem. Proc. Des. Dev. ; 24:836–44, 1985.

101 – Nunn,T.R. et al; "c" Product compositions and kinetics in rapid pyrolysis of milled wood lignin. Ind. Eng. Chem. Proc. Des. Dev.; 24:844–52, 1985.

102 – Olcay, A. et al. The supercritical gas extraction of lignites and wood. In: Chemical Engineering at Supercritical Fluid Conditions, Paulaitis,M.. et al. Ann Arbor Science 1983 p.409–17.

103 – Oshima,M.; Wood Chemistry, Novyes Data, N.J. 1965.

104 – Othmer,D.F. and Schuring,W.F., Destructive distillation of maple wood, Ind.Eng.Chem., 33:88, 1941.

105 – Ouensanga,A. and Picard,C.; Thermal degradation of sugar cane bagasse; Thermochimica Acta, 125:89–97, 1988.

106 – Radlein,D.; Piskorz,J. and Scott; Lignin derived oils from the fast pyrolysis of poplar wood. J. Anal. Applied Pyrolysis 12:51–9, 1987.

107 – Rahman,M. and Vahrman,M. The smaller molecules obtainable from coal and their significance, part 2: High pressure extraction at 200–300°C. Fuel; 50:318–28, 1971.

108 – Ramiah,M.V.; Thermogravimetric and differential thermal analysis of cellulose, hemicellulose and lignin. J. Appl. Polym. Science, 14:1323–37, 1970.

109 – Reed,T.B. et al. Perspectives in heat transfer requirements and mechanism for fast pyrolysis. In Specialist's Workshop on Fast Pyrolysis of Biomass. Proceeding. Copper Mountain, Solar Energy Research Institute, 7–20; 1980.

110 – Rodriguez,R; Magne,P. and Deglise. Sugar cane bagasse as a feedstock for an industrial fast pyrolysis process under development. Journal of Analytical and Applied Pyrolysis. 12:301–18, 1987.

111 – Roque–Diaz, P. Studies on thermal decomposition and combustion mechanism of bagasse under non–isothermal conditions. Thermochimica Acta, 93:349–52, 1985.

112 – Saiz–Jimenez, et al; Chemical characterization of recent and buried wood by analytical pyrolysis – comparison of pyrolysis data with ^{13}C NMR and wet chemical data. J. Anal. and Applied Pyrorlysis, 11:437–50, 1987.

113 – Schaefer,J. and Stejskal,E.O.; Journal Amer. Chem. Soc. 98:1031, 1976.

114 – Schuchardt,U and Matos,F.A.P.; Liquefaction of sugar cane bagasse with formate and water. Fuel 61:106–10, 1982.

115 – Schuerch,C.; The hemicellulose; In: The Chemistry of Wood; by: Browning,L.; Ed. Interscience, New York, Chap 5 1963.

116 – Schwenker,R.F.r., and Pascu,E., Pyrolytic degradation products of cellulose, Ind. Eng. Chem., 2:83, 1957.

117 – Scott,D.S. et al; The role of temperature in the fast pyrolysis of cellulose and wood; Ind. Eng. Chem. Res.; 27:8–15, 1988.

118 – Scott,D.S. and Piskorz,J.; "a" The flash pyrolysis of aspen–poplar wood. The Canadian Journal of Chemical Engineering 60:666–74 1982.

119 – Scott,D.S. and Piskorz,J.; "b" Fast pyrolysis of biomass in: Klass,D.L. and Emert,G.M.; Fuels From Biomass And Wastes. Michigan; Ann Arbor Science; 421–34, 1982.

120 – Seeley,D.B.; Cellulose saccharification for fermentation industry applications, Biotechnology, Bioengineering Symposium, 6:285–92, 1976.

121 – Shafizadeh,F.; Pyrolytic reactions and products of biomass; In: Fundamental Thermochemical Biomass Conversion; by: Overend,R.P.; Milne,T.A. and Mudge,L.K.; Elsevier App Science Pub. London, Chapter 11, 183–218; 1985.

122 – Shafizadeh,F.; Introduction to pyrolysis of biomass – Review; Journal of Analytical and Applied Pyrolysis; 3:283–305, 1982.

123 – Shafizadeh,F.; Introduction to Pyrolysis of biomass In: Specialist's Workshop on Fast Pyrolysis of Biomass. Proceeding. Copper Mountain, Solar Energy Research Inst. 79–103; 1980.

124 – Shafizadeh,F. et al. Thermal degradation of 6–chlorocellulose and cellulose – zinc chloride mixture. Journal of Applied Polymer Science 22:1183–93, 1978.

125 – Shafizadeh,F. and Chin,P.P.S. ACs Symposium series 43:57, 1977.

126 – Shafizadeh,F.; Industrial pyrolysis of cellulose materials, Appl. Polym. Symp., 28:153, 1975.

127 – Shafizadeh,F. and Fu,Y.L. Pyrolysis of cellulose. Adv. Carbohydr. Chem., 29:113–22, 1973.

128 – Shafizadeh,F. and McGinnins,G.D. Morphology and biogenesis of cellulose and plant cell walls. Adv. Carbohydr. Chem.; 26:297–347, 1971.

129 – Shafizadeh,F.; Pyrolysis and combustion of cellulosic materials. Advance Carbohydr.Chem. 23:419–74, 1968.

130 – Solomon,P.R. and Colket,M.B.; Coal devolatilization; Proc. 17^{th} (int.) on Combustion; 131–43; 1979.

131 – Soltes,E.J.; Chemicals and energy from wood – a pratical approach, Paper presented at University of Maine, Pulp and Paper Summer Institute, Orono, 1977.

132 – Stangeby,P.C. and Sears,P.L.; Rapid pyrolysis and hydropyrolysis of Canadian coals, Final report to Can. Dept. of Energy, Mines and Resources, 1978.

133 – Steinberg,M and Bhatt,B.; Flash pyrolysis and hydropyrolysis of coal. In Specialist's Workshop on Fast Pyrolysis of Biomass. Proceedings. Copper Mountain, Solar Energy Research Institute. 1980 pp 58–78

134 – Stiles,H.N. and Kandiyoti,R.; Secondary reactions of flash pyrolysis tars measured in a fluidized bed pyrolysis reactor with some novel design features. Fuel, 68:275–82, 1989.

135 – Stiles,H.N.; Secondary reactions of pyrolytic tars. Ph.D. Thesis. Imperial College – University of London, 1986.

136 – Suuberg,E.M. Rapid pyrolysis and hydropyrolysis of coal. Ph.D. Thesis, University of Cambridge 1977.

137 – Theander,O.; Cellulose, hemicellulose and extractives. In: Fundamental Thermochemical Biomass Conversion; by: Overend,R.P.; Milne,T.A. and Mudge,L.K.; Elsevier App. Science Pub. – London, chapter 2, p35–60, 1985.

138 – Tillman,D.A. Wood as an Energy Resource. Academic Press, N.Y. 1978.

139 – Tillman,D.A. et al. Fuels and energy from reneawable resources, Academic Press. N.Y. 249; 1977.

140 – Timell,T.E. Wood hemicelluloses: part I. Advances Carbohydrate Chemistry. 19:247–303, 1964.

141 – Tyler,R.J.; Flash pyrolysis of coal 1. Devolatilization of a Victorian brown coal in a small fluidized bed reactor. Fuel, 58:680–6, 1979.

142 – Tyler,R.J.; Flash pyrolysis of colas. Devolatilization of bituminous colas in a small fluidized–bed reactor. Fuel, 59:218–26, 1980.

143 – Usui,T. et al; ^{13}C Nucelar Magnetic Resonance spectra of glucobioses, glucotrioses and glucans. J.C.S. Perkin I; 2425–32, 1973.

144 – Varhegyi,G. and Antal,M.J.; Kinetics of the thermal decomposition of cellulose and sugar cane bagasse; Energy and Fuels, 3:329–35, 1989.

145 – Varhegyi,G. and Antal,M.J.; Simultaneous thermogravimetric mass spectrometric studies of the thermal decomposision of biopolymers. 2– sugar cane bagasse in the presence and absence of catalysts. Energy and Fuel, 2:273–7, 1988.

146 – Wenzl,H.F.J. Further destructive processing of wood, in The Chemical Technology of Wood, Academic Press, New York, chap 5, 1970.

147 – Whitehurst,D.D. et.al. New characterization techniques for coal–derived liquids. Fuel; 61:994–1006, 1982.

148 – Wienhaus,O et al; ellst.Pap. 29:125–128, 1980.

149 – Wilson,M.A.; Pugmire,R.. and Grant,D.M.; Nuclear magnetic resonance spectroscopy of soils and related materials. Org. Geochem. 5:121–9, 1983.

150 – Wilson,K. and White,D.J.B.; The anatomy of Wood: its Diversity and Variability, Stobart and Son LTD, London 1986.

151 – Wiser,W. Preprint Fuel Division ACs Meeting 20:122 1975

152 – Yokoyama,S; Ogi,T; Koguchi,K.; Direct liquefaction of wood by catalysts (Part 2)– Effects of variety of wood on yields and properties of heavy oils. Sekiyu Gakkaishi, 3(29):262–5, 1986.

153 – Young,H.E.; Forest Biomass Inventory – The basis for complete tree utilization, paper presented at TAPPI Conference, 1977.

154 – Zafforoni,E. Possibilidades de Euphorbia tirucalli e Euphorbia lathyris como alternativas energeticas. Energia – Fontes Alternativas. 14:12–5, 1981.

LIST OF FIGURES.

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 5

LIST OF TABLES.

CHAPTER 5