The Kinetics and Mechanism Of

Wheat Straw Pulping

With Caustic Soda

by

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To my wife, my dad, and mum.

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ABSTRACT

In this work the first study of the kinetics of the pulping of Saudi Arabian wheat straw is presented. The rate constants and activation energies for the delignification and dissolution of carbohydrates (in the presence of sodium hydroxide) have been obtained, and the values suggest strongly that the mechanism for pulping involves physical diffusion-controlled processes.

Delignification was found to occur in two distinct stages. The initial rate is higher and the process has a low activation energy (14 ± 3 kJ mol^{-1}), consistent with a diffusion-controlled mechanism. The subsequent stage occurs after 90% delignification and is slower with an activation energy of 31.5 ± 6 kJ mol^{-1}. The value of the activation energy indicates that this process is also diffusion-controlled.

The dissolution of carbohydrate was also observed to occur in two stages. The initial process has an activation energy of 36 ± 3 kJ mol^{-1} and is followed by a slower process with an activation energy of 73.5 ± 39 kJ mol^{-1}. These values also indicate that the rate-determining step involves a high element of physical diffusion from the wheat straw.

Anthraquinone, widely used as a catalyst in the wood pulping industry, was found to have only a marginal effect on the rate of delignification of the wheat straw, but had a significant effect on the stability of the dissolved lignin at temperatures above 80 ^{o}C.

It has been observed that the molar mass of the dissolved lignin decreases as the severity of the process increases. This decrease in molar mass was catalysed by anthraquinone and resulted in complete degradation of lignin at 170 ^{o}C in 1.5h. These changes in lignin were monitored using FTIR, UV, and NMR spectroscopy.

The results from these studies were used to develop a qualitative mechanism for the pulping of wheat straw by sodium hydroxide.

This work is of current industrial relevance in some countries because of the renewed interest in finding uses for waste straw instead of burning it in fields, which causes detrimental environmental consequences due to CO_2 and smoke emission. Production of paper and other cellulosic materials are the potential outlets.

1 INTRODUCTION

1.1 General Introduction

The increasing demand of cellulose pulp for various end uses for paper and paper products necessitates continually searching and investigating all possible sources and means of production of fibrous raw material which could be capable of providing pulp (Mansour, 1985).

To supply future demand for pulp, the world's virgin forests will continue to be exploited, (Earl, 1975) and the fast growing, tropical single species plantations hold out the possibility of producing very large annual increments of timber over rotations of 6-8 years. In addition, it is expected that recycled paper products will increasingly be used to satisfy some of the world's demand for pulp. However, recycled pulp is normally suitable only for low grade paper and board and recycling has to meet the basic cost of collecting, sorting and de-inking. Cereal straw is considered to be another important possible source of pulp in the future (Staniforth, 1979).

The FAO (Food and Agricultural Organization) Annual Pulp and Paper Capacity Survey for 1988 provides estimates of pulp capacity for all non-wood fibrous materials, including agricultural residues. In 1988, the total world capacity to produce all types of paper pulp was 173.4 million tonnes, of which the non-wood pulp capacity as agricultural residues was 15.5 million tonnes (nearly 9%). Different types of non-wood raw materials are used of which only 35% is used from straw composing 15% bagasse, 11% from bamboo and just 8% from cereal straw fibres (FAO report 1988/1994).

Agricultural residues, particularly bagasse and rice straw, have become increasingly prominent sources of non-wood raw material for use in pulp and papermaking industries in recent times (Atchison, 1974; Aggrawala, 1971; Clark and Bagby, 1970 and Lintu, 1978).

Presently the most notable areas in which straw and bagasse are used in the production of pulp and paper are China and India, where the total pulping capacity for these materials is estimated to be as high as 8.9 million tonnes for China (about 52% of

the world capacity) and two million tonnes for India (about 13% of the world capacity) (FAO report 1988-1994).

Paper-making from wheat straw has long been carried out in China, India and other European countries. The manufacture of pulp and pulp products from wheat straw was carried out in most wheat-producing countries (Percival, 1974). However, the number of factories for processing cereal straw into pulp and pulp products has been decreasing in many parts of the world in recent years (Wiseman, 1996).

Pulp and paper can be made from many different non-wood fibrous plants, but whether or not a plant is well suited for this purpose depends largely on the shape of its cells. The suitability of pulp for making various types of paper is determined by the characteristics of a raw materials and the pulping processes used. One of the main characteristics of the raw material in determining its suitability for various papers is the fibre length. Most agricultural residues contain shorter fibres than those obtained from hardwood. Agricultural residues, particularly cereals and straws (particularly rice and wheat straws) have more in common with hardwood pulp than with the longer fibres in pulp from softwood conifers (Tabb, 1974).

Straw requires less power than wood in the pulp preparation stage and the lower lignin content of straw compared with wood enables it to be digested with smaller amounts of chemicals (Staniforth, 1979). Straw is rich in extraneous cells which have no value for papermaking. Shortness in fibre length and presence of cells other than fibrous cells both create problems in pulp processing. The chemical composition of straw also depends on the soil condition (Staniforth, 1979). The high silica content in straws creates difficulties both in papermaking and in chemical recovery. Evaporator additives (Misra, 1972), the desilication of black liquor (El-Ebiary, 1983), and sludge sedimentation and separation methods are needed to deal with the silica in strawpulping (Mansour, 1985). The high content of hemicellulose, which is readily dissolved in the caustic liquor used for pulping, is also a factor.

The hemicellulose content, particularly the pentosan fraction, is high in straw. The presence of high pentosan content causes distinct swelling of the fibre walls and makes the pulp respond easily to refining action and consequently the stock rapidly attains the

required degree of hydration and fibre bonding properties. This particular chemical characteristic of straw pulps leads to energy savings and is considered a major advantage over the use of conventional wood pulps.

The paper made from chemical straw pulp is characterized by more uniform formation, better surface smoothness and good ink receptivity (Kar et al., 1986 and Xiangju, 1986 and Lachenal et al., 1977).

1.2 Wheat and Its Classification

Among the world's crops, wheat is pre-eminent both in regard to its antiquity and its importance as a food of mankind. It is one of the most valuable cereals in many of the countries of the world. All wheats, whether wild or cultivated, belong to the genus *Triticum* of family *Gramineae*, the grass. *Triticum* is only one of some 600 genera belonging to this great family, which itself comprises well over 5000 species.

1.2.1 Growth

Wheat plants when fully headed-out are commonly from 2-5 ft. high but may be as short as 1 ft. or less when grown under very dry conditions or considerably over 5 ft. in height under conditions that are exceptionally favourable for vegetative growth (Pal, 1966 and Kipps, 1970).

1.2.2 Stems

The culms or straws are erect, elastic, cylindrical and more or less furrowed with smooth surfaces. When ripe, the colour of most wheats is a pale yellow. In normally-grown wheat plants, the majority of the culms possess six nodes, although straws with seven and also with five nodes are not uncommon. The nodes are solid and constricted, although outwardly they appear enlarged, see Figure 1.1A and 1.1B (Peterson, 1965 and Percival, 1974).

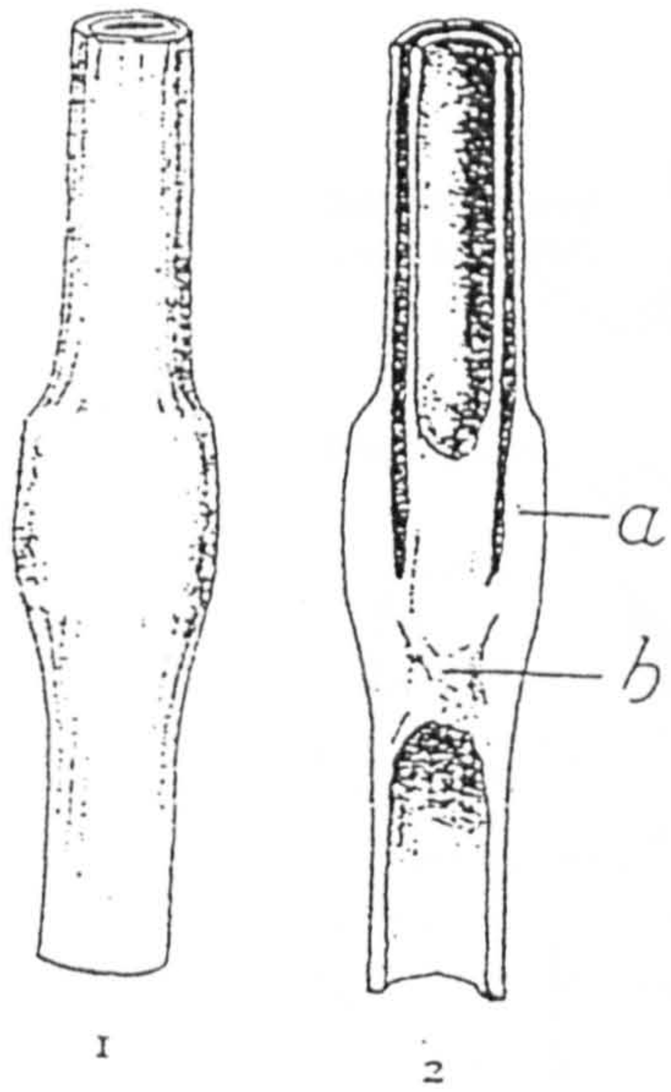


Figure 1.1A (1, Node; 2, longitudinal through the node (x2). *b*, Diaphragm; *a*, thickened leafbase) (Percival, 1974)

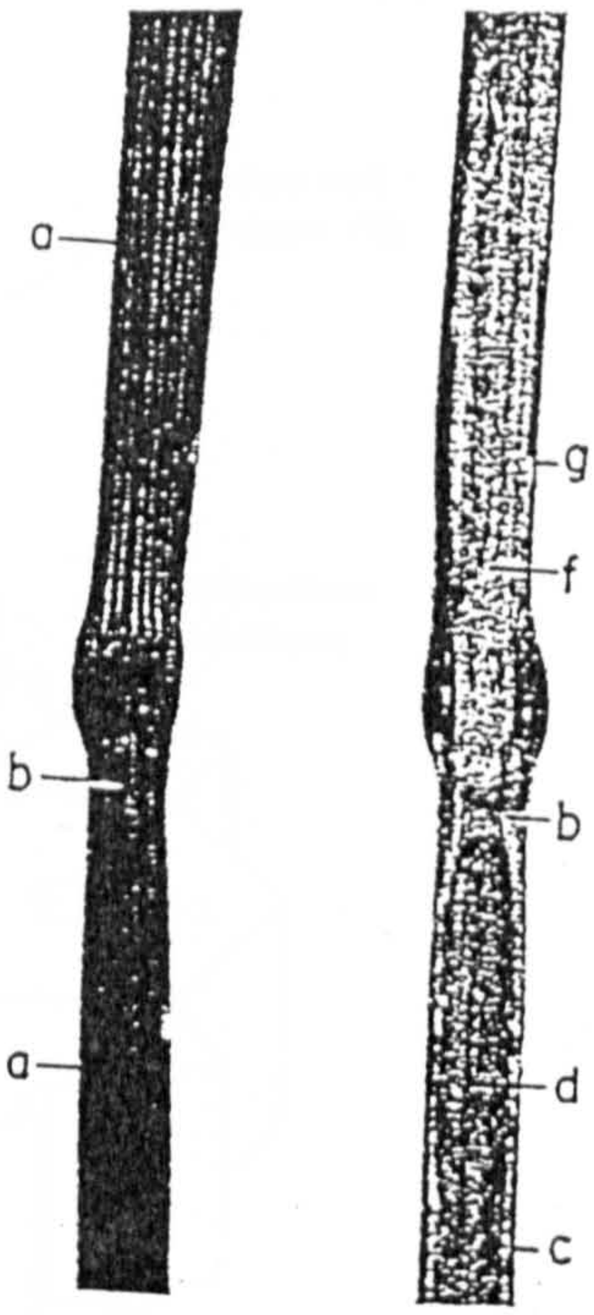


Figure 1.1B (Parts of wheat stem (stem:a, b, node; c, wall; d, hollow interior; f, pithy interior; g, stem wall enclosed by leaf sheath (Peterson, 1965).

This appearance is due to the swollen base of the leaf sheath covering the node. The internodes of mature wheat stems are hollow in most species and varieties (Peterson, 1965).

1.2.3 Fibres/Cell Wall

The plant cell is surrounded by a wall in nearly all stages of its development and the wall is an integral part of the plant cell. It is generally recognized that there are two kinds of wall, primary and secondary.

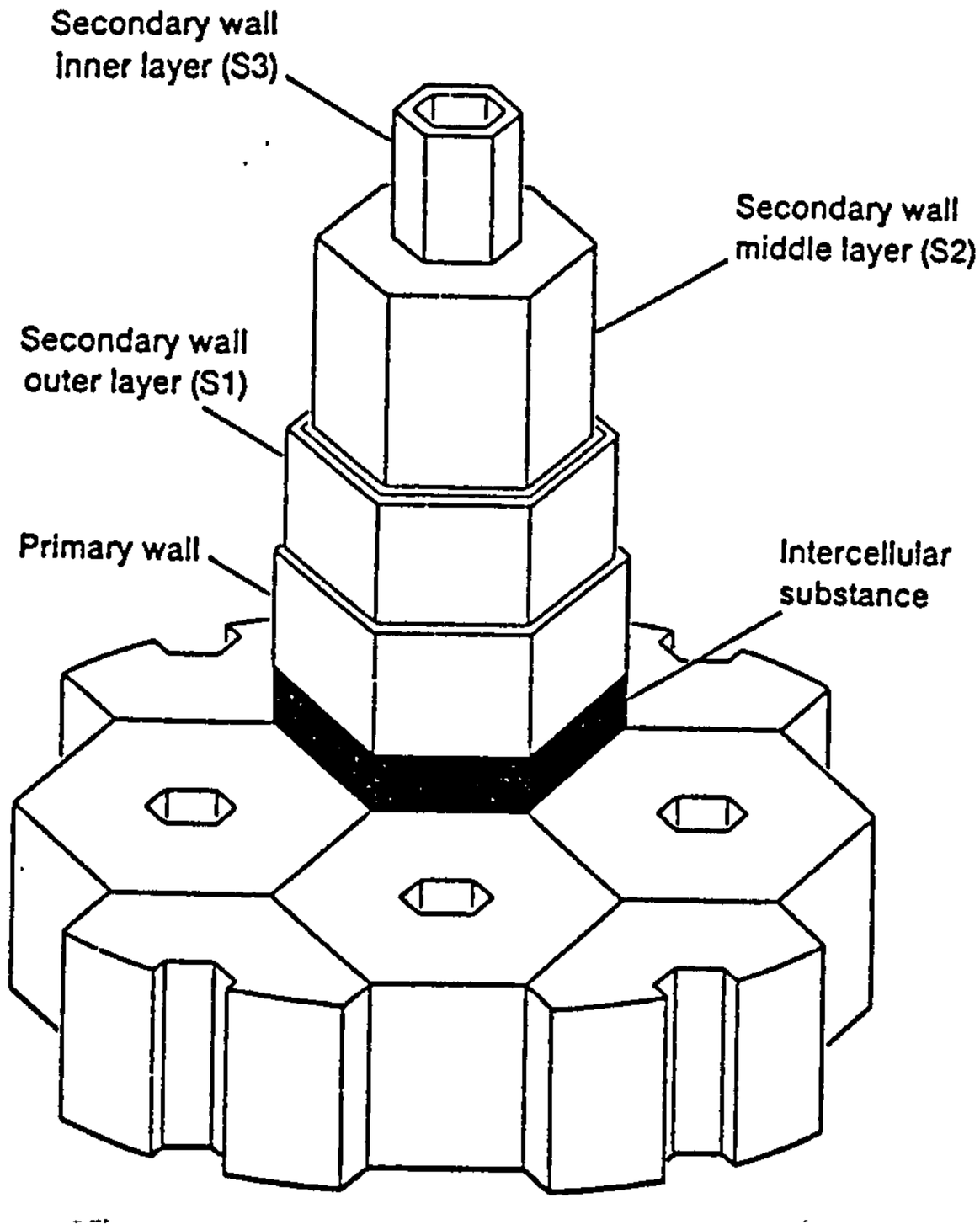


Figure 1.2 Secondary cell wall structure. A cross section of a fibre cell to illustrate the structure of its secondary wall. Typically the secondary wall consists of three layers, which differ from each other primarily in the orientation of their cellulose microfibrils. Cellulose microfibrils are highly ordered within any given layer of the secondary wall, but the orientation is different in each layer (Fosket, 1994).

The primary cell wall is laid down during cell growth, whereas the secondary wall is deposited after growth has ceased. Usually, the secondary wall (Figure 1.2) is very much thicker than the primary wall. Primary and secondary walls also differ in their chemical composition, thickness and physical properties. The following is the polymeric composition of primary and secondary walls:

* Polysaccharides
* Cellulose
* Hemicellulose
* Lignin
* Pectin
* Protein

In straw, the cell wall contents predominate with a low level of cell content most probably made up of dehydrated cytoplasmic materials. The cell consists mainly of

cellulose, hemicellulose and lignin, where the cellulose forms a skeleton which is surrounded by other substances functioning as matrix (hemicellulose) and encrusting (lignin) materials (Haygreen and Bowyer, 1971). However, the description by Van Soest (1982) states that the matrix is made up of cellulose, hemicellulose and lignin together with various low levels of gums, waxes and ash. It is clear that the biochemistry of the components and their interactions in the cell wall matrix is not yet completely understood.

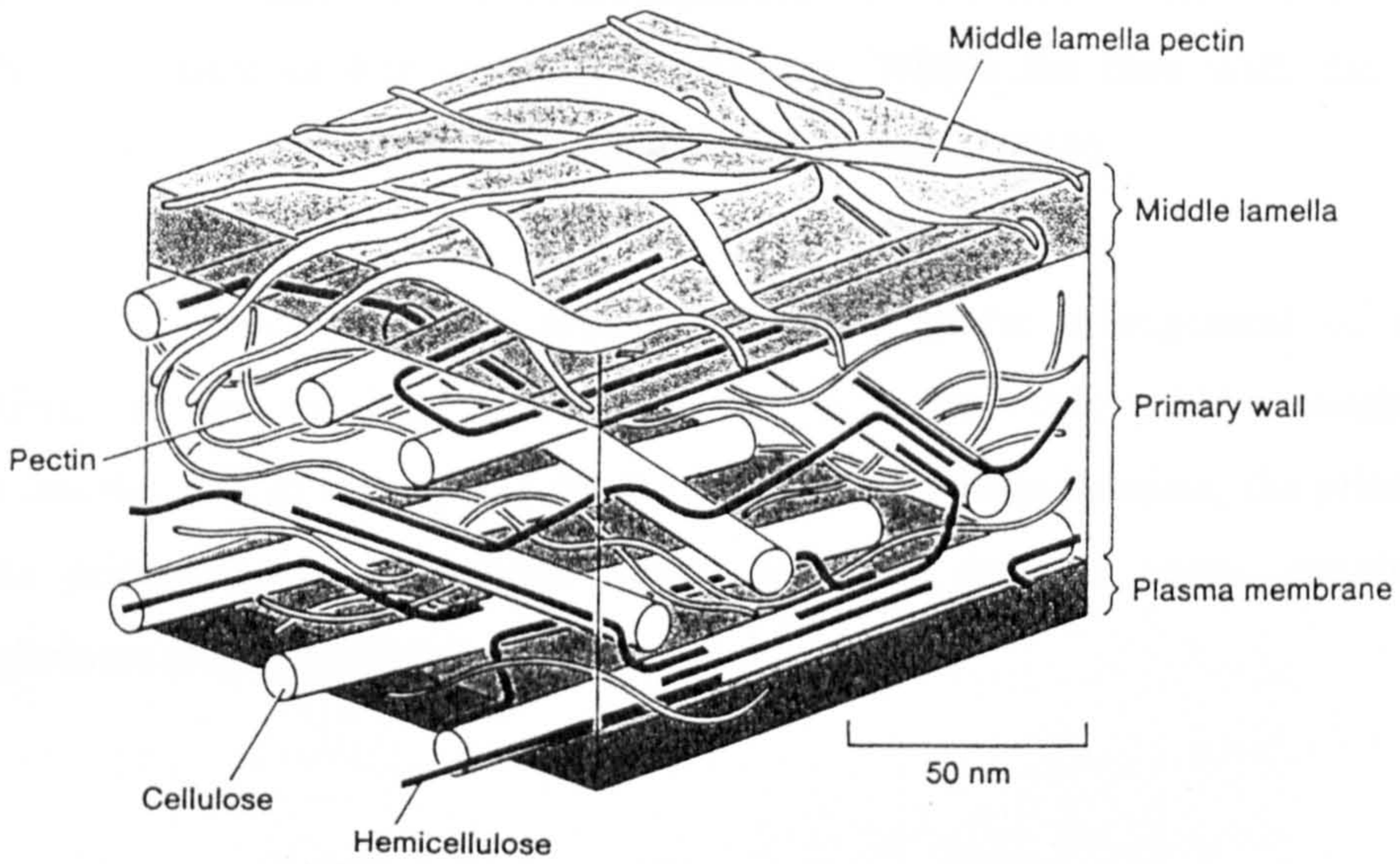


Figure 1.3. Hemicellulose xyloglucans adhere tightly to the surface of the cellulose microfibrils and cross link them. The cellulose microfibrils probably are completely coated with hemicellulose chains. The pectins are considered to form separate network of fibrous molecule that interdigitate with the cellulose-hemicellulose network, except in the regions of middle lamella, which is composed of primarily pectin (Fosket,1994).

The physical properties of cell walls arise from the interactions of the non-cellulosic polysaccharides with the cellulose microfibrils. Cellulose microfibrils individually are very strong, but they are not continuous around the circumference of the cells; however, the microfibrils are embedded within somewhat amorphous, gelatinous, pectins. Hemicelluloses, which are also fibrous, cover the cellulose microfibrils to which they are held by hydrogen bonds. The structure shown in Figure 1.3 represents a

simplified model for the structure of a cell wall showing the interactions of the three classes of polysaccharides (Panshin and de Zeeuw, 1964).

Short chains and low molecular weight hemicellulose are also part of the cell wall structure. The hemicellulose serves as the connecting agent that links or bonds microfibrils together (Stamn, 1964).

In regions of the fibre wall that are partially rich in cellulose, microfibrils tend to aggregate in ribbonlike masses, called lamellae, which become larger than the microfibrils such that their arrangements can be distinguished with the microscope after the lamellae have become more or less separated by beating. Within the fibre wall, the lignin is distributed between the lamellae (Macdonald and Franklin, 1969).

The fine structure of the primary wall is a sparse arrangement of cellulose microfibrils around the long axis of the cell in a very thin gel-like matrix which constitutes the bulk of this layer. Like the surrounding middle lamellae, the primary wall consists principally of amorphous lignin, but also contains pectic materials and hemicelluloses (Rollins and Tripp, 1961).

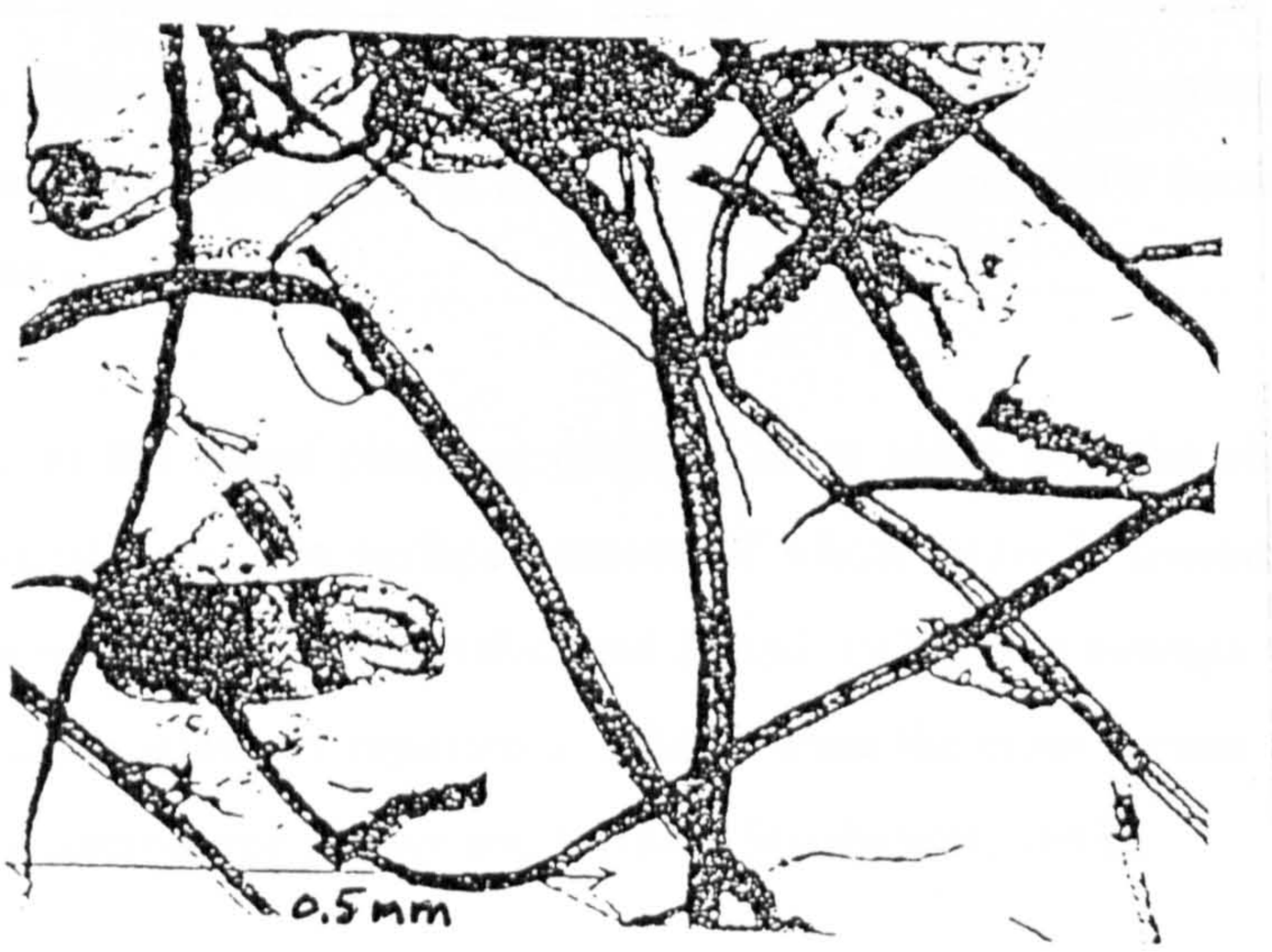


Figure 1.4. The Wheat Straw Fibre (Roelefsen, 1959 and Mansour, 1985).

The structure of fibres from wheat straw has been studied in detail (Roelefsen, 1959) (Figure 1.4), who reported that the structure in straw fibre is similar to that normally found in coniferous tracheids and wood fibres. Any differences in papermaking properties between all these kinds of fibres are not due to the differences in microscopic structure of the cell wall but to differences in the dimension of the fibres and their chemical constitution (Mansour, 1985).

1.2.4 Wheat Straw Composition And Uses

Wheat straw is a heterogeneous material. As noted earlier, the morphological components of straw consists of the stem separated at intervals by nodes. At the nodes a sheath that ends in a leaf blade is formed around the stem. Seed hulls (glumes) and foreign material are found in straw bales (Mansour, 1985; TAPPI, 1978 and Xiangju, 1986).

In general, the threshed grain of a wheat crop is of greater value than all the other parts of the wheat plant. However, the straw (including stems, leaves and chaff) also has value because of its agricultural and industrial uses. The main uses of wheat straw on the farm are as feed and bedding for livestock, as protection of the soil against wind or water erosion and for incorporation into the soil to improve its structure and fertility (Percival,1974). There are many wheat-growing regions where the quantity of straw produced is in excess of that which is needed for farm use and straw becomes available for industrial uses.

The stems of the wheat plant are of much more value than the chaff and dried leaves for industrial uses. The surface contour of wheat straw is smooth, making no place for foreign matter to adhere (Ibrahim and Fouad, 1973). The average percentage of cells content in wheat straw are reported as follows when the cross section of the stem is viewed under the microscope (Jayme and Harders-Steinhauser, 1941):

* Bast and Sclerenchyma fibres	50%
* Epidermis cells	15%
* Vessels	5%
* Parenchyma	30%

The epidermal, vessel and parenchyma cells are considered as extraneous cells other than fibrous cells and as such have no papermaking value. They adhere to each other forming aggregates even after beating (Mansour, 1985). Undoubtedly the presence of these extraneous cells present difficulties for bleaching processes. They form together with epithelial cells, the so called grit, and are removed by centricleaners. Removal of epithelial cells is observed to improve bleaching. Many parenchyma and epidermis cells are said to be lost during pulp washing (Mansour, 1985).

Wheat is a major agricultural crop in Saudi Arabia, which is among the leading countries of the world for the production of wheat crop producing about 4 million tonnes per year (Statistical Year Book, 1988). It yields a large amount of wheat straw as by-product which was estimated to be 3.6 million tonnes in 1987 (Fakeeha et al., 1990). A small portion of wheat straw is used for animal foddering but nearly 70% is burnt. In the late 1970's, about 5-6 million tonnes of cereal straw was produced each year in the U.K., which was largely disposed of by burning in the field (Staniforth, 1979); however, this practice is now banned because of widespread concern about the danger and nuisance posed (Larken, 1984). By the early 1990's, U.K. wheat straw production was 12-14 million tonnes a year. The unutilized straw could be used in the production of cellulosic material via pulping.

The overall composition of wheat straw varies according to its nature. For the denoded Saudi Arabian wheat straw used in this work, the dry weight composition was determined according to the TAPPI, standard method (Wood and Kellogg, 1988) to be:

* Moisture content	7.06%
* Ash	6.53%
* Lignin	22.94%
* Pentosans	33.33%
* α-Cellulose (by difference)	30.14%

1.2.5 Strawboards

Strawboards are manufactured from straw by pulping it in dissolved chemicals that soften the lignin and other cementing material and free the cellulose fibres (the straw may

or may not be cut into small pieces before cooking). The cooking is usually done with live steam, and may be carried out under pressure in closed digesters or at atmospheric pressure in open vats (Peterson,1965). The chemicals that are generally used are quicklime (CaO), sodium hydroxide (NaOH) and sodium sulfite (Na_2SO_3). Sodium sulfite is often used in combination with sodium carbonate (Na_2CO_3), and sodium hydroxide is sometimes used in combination with sodium sulfide (Na_2S) or with anthraquinone as catalyst. Various other chemicals are also used for pulping straw (Peterson, 1965).

The strawboard products are rough, yellowish-brown, stiff thick papers which are used for several different purposes. The thinner material is rolled on reels and is generally used to make the corrugated medium for paper boxes (cartons). The thicker strawboard is used for making tubular and cylindrical articles such as the open tubes used for mailing papers, etc., and there are a great variety of closed or covered cylindrical containers serving much the same purpose as do metal canisters or glass jars (Percival,1974).

1.2.6 Building Boards

Two kinds of pulps, a hydrated and an unhydrated pulp, are prepared for the manufacture of various types of building board from straw. Hydrated pulp is prepared in the same manner as for strawboard including the relatively long period of beating the pulp in the water. In the unhydrated pulp, the straw is cooked for a shorter time in less concentrated chemicals and, instead of being beaten in water, it is refined in machines using other methods for freeing the fibres. The hydrated and unhydrated pulps are pumped and stored separately in tanks and then chemicals such as rosin may be added for sizing and alum may be used for precipitating the sizing to make the board water-resistant (Percival, 1974).

The two kinds of straw pulps are blended with other pulps such as wood pulp in any desired proportions to produce various types of building boards. Adhesive may be used to cement together layers of pulp. The surface of the building board can also be treated and finished in various ways.

1.2.7 Paper

Wheat straw is one of the many non-wood sources of pulp for papermaking. To make good paper from straw, the pulp must be much freer from lignin and other non-fibrous materials than when used in making strawboard and building board and for many of the finer sorts of paper the pulp must be bleached. The straw is cooked with the same of chemicals as in the manufacture of strawboard, but the delignification process is carried further and additional chemicals are employed.

Paper made from bleached strawpulp is usually hard, smooth and brittle and these characteristics are useful to blend with wood pulp producing paper of better formation and smoother surface than most of the combinations of wood pulps alone. In some countries, especially in Europe and South America, nearly 75% of straw pulp is used in blends of pulp for making high-grade bond, writing, book, magazine, waxing, memo and other types of paper (Aronovsky, 1952).

Among the many methods of preparing fine pulp from straw, a popular method is the sulfate or Kraft process. The cut, cleaned straw is cooked under pressure in a mixed aqueous solution of sodium sulfide and caustic soda. The cooked straw is washed, screened and passed through other cleaning processes. The resulting pulp is bleached in a single stage with calcium hypochlorite and then washed, which gives a somewhat higher yield of bleached pulp than other methods.

However, the attention in pulp industry currently is focussed on developing methods for minimizing pollution and saving energy, because an inherent disadvantage of the Kraft process is the unpleasant odour emitted to the surroundings and the water pollution problems caused by bleached plant effluent. Therefore, an increasing interest is directed toward the development of sulfur-free pulping and chlorine-free bleaching processes (Sjostrom, 1981).

1.3 Chemistry Of Straw

The variations in chemical composition of straw greatly influence the condition and the amount and kind of chemicals used for the pulping of straw. The differences in yield of pulp, papermaking behaviour and variations in the physical properties of paper can often be traced to the variations in the chemical composition of straw.

1.3.1 Extraneous Substances

These are all non-cell wall components which can be extracted with such neutral solvents as hot water, alcohols, benzene, ethers, and acetone. Generally 3-10% of straw substances dissolve. This fraction is termed extraneous materials. The organic compounds present are low molecular weight carbohydrates, terpenes, aromatic and aliphatic acids, alcohols, tannins, colour substances, protein, lignin, alkaloids and soluble lignins. In addition, straw contains various other organic compounds, and small quantities of silica which has several undesirable effects: it blunts cutting machiney, reduces digestibility, interferes with pulping processes and renders combustion more difficult (Staniforth, 1979 and Smithson, 1958). The extraneous compounds of straw are of importance as they are the source of many straw by-products, lend straw its resistance to insects and decay, inhibit pulping and bleaching in some instances and give straw its odour, taste and colour (Macdonald and Franklin,1969 and Smithson, 1958).

1.3.2 Polysaccharides

The polysaccharides of straw are high molecular weight carbohydrates yielding simple sugars such as glucose, mannose and xylose upon hydrolysis with acid. The major polysaccharide component of straw is cellulose and the rest is mixture of short chain polysaccharides, hemicellulose. These components taken together make up the fraction termed holocellulose, which is, in effect, the total polysaccharides portion of extractive-free straw. Hemicellulose in straw is composed mainly of polymers of xylose. Hemicellulose dissolves in caustic soda whereas cellulose is largely insoluble. In this work the soluble material is referred to as 'carbohydrate', in accordance with current usage (Lawther et al., 1995).

1.3.3 Cellulose

Cellulose is the most abundant organic chemical in the world and is the major component of the cell walls of plant fibre. On complete hydrolysis it yields only the monosaccharide sugar D-glucose. Cellulose is isolated from the straw in an impure state, since it is associated with closely related polymers of mannose and xylose. Cellulose is a highly crystalline material.

The following factors make cellulose desirable for manufacture into paper:

* It is abundant, reproducible, easily harvested and is a low cost material.
* It always occurs in a fibrous form which possesses extremely high tensile strength.
* It has a great affinity for water, which facilitates the mechanical preparation of fibres.
* It is naturally white.
* It is insoluble in water and neutral organic solvents.
* It is resistant to many chemicals, which permits its isolation and purification from wood, agricultural residues etc., the most common sources of cellulose (Sjostrom, 1981).

Cellulose represents 40-43% of wheat straw (Pomeranz, 1978). It is unsuitable as a human food and is relatively inert in dough; cellulose has been viewed as an undesirable component in wheat products. Very little specific information is available concerning the occurrence, physical and biochemical properties and constitution of wheat cellulose because cellulose can be obtained more economically from wood or cotton and, as such, the industrial utilization of wheat cellulose has not been vigorously pursued (Jones, 1955 and Friedmann et al., 1967).

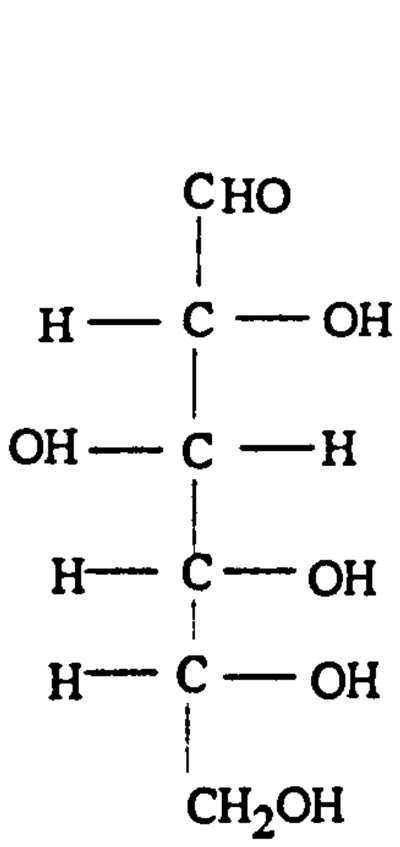
The observance of the occurrence of α-glucan in the water-soluble polysaccharides derived from the wheat flour has shown that there is a possible link between cellulose and pentosans. A possible hypothesis is that those hemicelluloses which cannot readily be extracted from plant material by aqueous alkali are merely entrapped in a cellulose matrix (Whistler and Hilbert, 1945). The exact mode by which cellulose and the pentosans are

synthesized by plants has not been thoroughly investigated; one hypothesis, that pentosans are formed directly from hexoses through the process of oxidative decarboxylation, is supported by the observation that free fructose and fructan in wheat stem decreases as lignification progresses and hemicellulose content increases (Kostrubin, 1955).

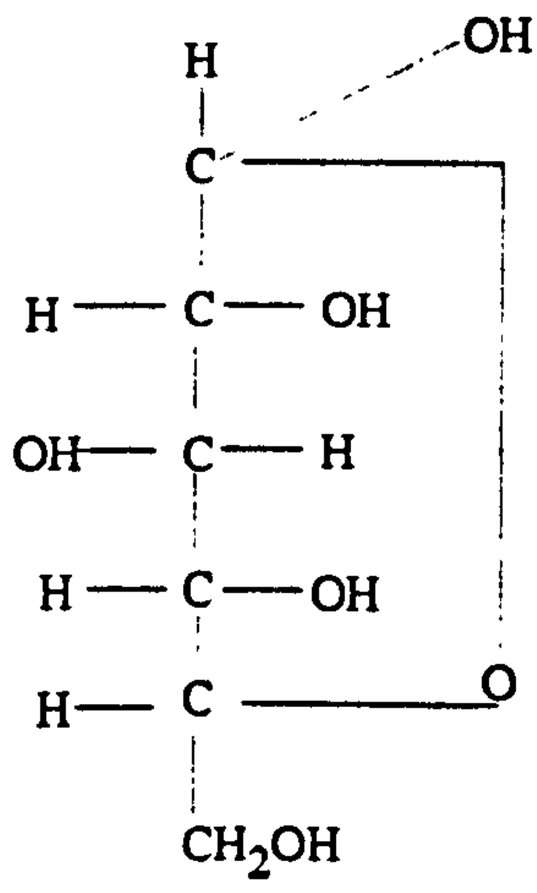
1.3.4 Chemical Structure Of Cellulose

The chemistry of cellulose started in 1838 with Payen, who showed by elemental analysis that plant tissues contain a major component having 44.4% carbon, 6.2% hydrogen and 49.3% oxygen, which is equivalent to an empirical formula of formula weight 162. Since its molecular weight in practice is much greater than 162, it was evident that cellulose is a polymer comprising a large number of repeating units (Macdonald and Franklin,1969). These units were derived from condensation of D-glucose.

D-glucose is depicted in simplest fashion as shown in Figure 1.5. The molecular form β, refers to the position of the OH group on carbonyl 1. When the group is on the opposite side of the chain from the hemiacetal ring (C1-O-C5), the sugar is called β; when on the same side as the ring it is α.



α-D-Glucose,aldehyde form



β-D-Glucose, hemiacetal for

Figure 1.5 α-D-Glucose, aldehyde form β-D-Glucose, hemiacetal form

(Macdonald and Franklin, 1969).

Cellulose can be hydrolyzed to D-glucose (Figure 1.6). The number of anydroglucose repeating units in a given cellulose molecule is commonly designated as degree of polymerization (DP). The molecular weight of cellulose is therefore equal for all practical purposes to 162 DP.

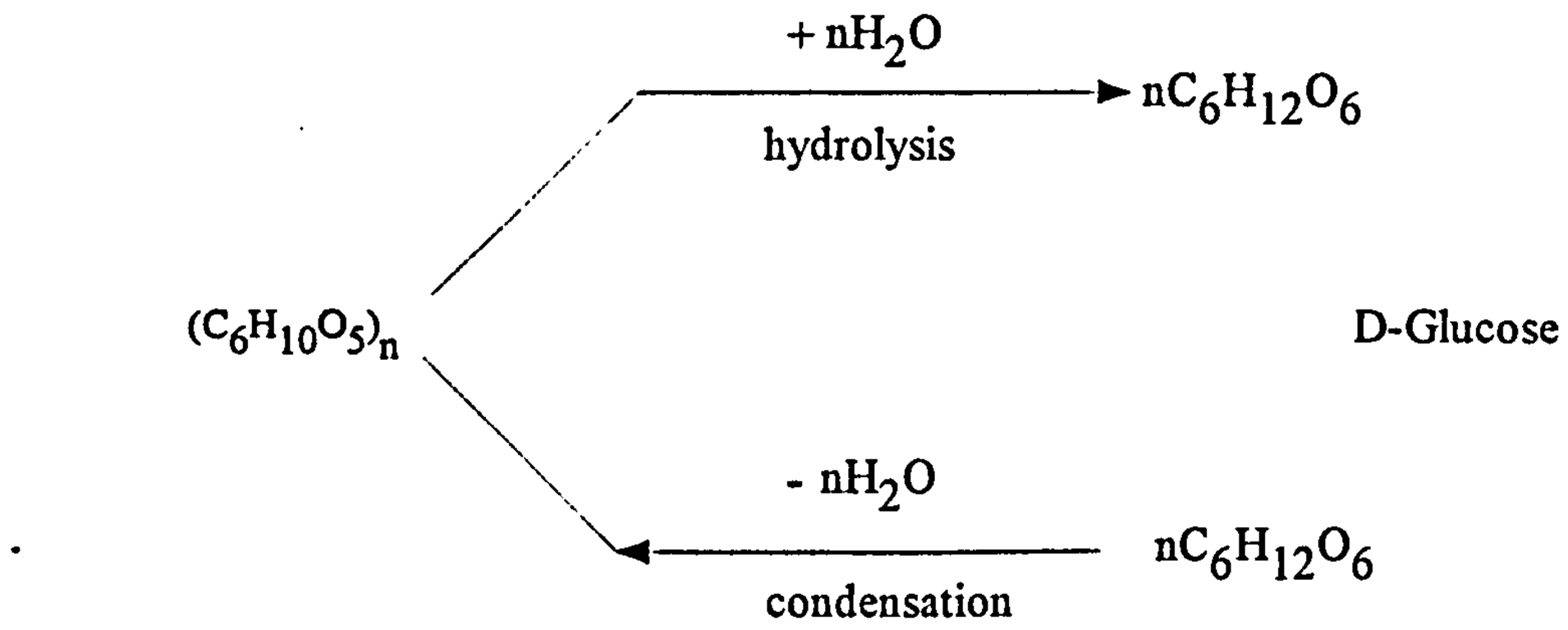


Figure 1.6 The hydrolysis of cellulose to D-Glucose

(Macdonald and Franklin, 1969).

The presently accepted values for DP of cellulose are 1000 to 15000 (molecular weight 162,000 to 2,430,000) depending on the source and extent of degradation of the specimen and also on the method used for determining DP (Macdonald and Franklin, 1969).

Cellulose consists of anhydroglucopyranose units which are joined to form a molecular chain. Therefore, cellulose is also called a linear-polymer glucan with a uniform chain structure. The units are bound by β-(1-4) glycosidic linkages. Two adjacent glucose units are linked by elimination of one molecule of water between their hydroxylic group at C-1 and C-4.

Cellulose possesses one reducing end and one non-reducing end (Figure 1.7). The reducing end is the C-1 position, where the ring structure may isomerize to the aldehyde form. There are OH groups at both ends of the cellulose chain; these OH groups show a different behaviour. The C-1-OH is an aldehyde hydrate group deriving from the ring formation by an intramolecular hemiacetal linkage. That is why the OH group at the C-1

end has reducing properties, while the OH group at the C-4 end of the cellulose chain is an alcoholic hydroxyl and therefore non-reducing (Conrad, 1971) (Figure 1.7).

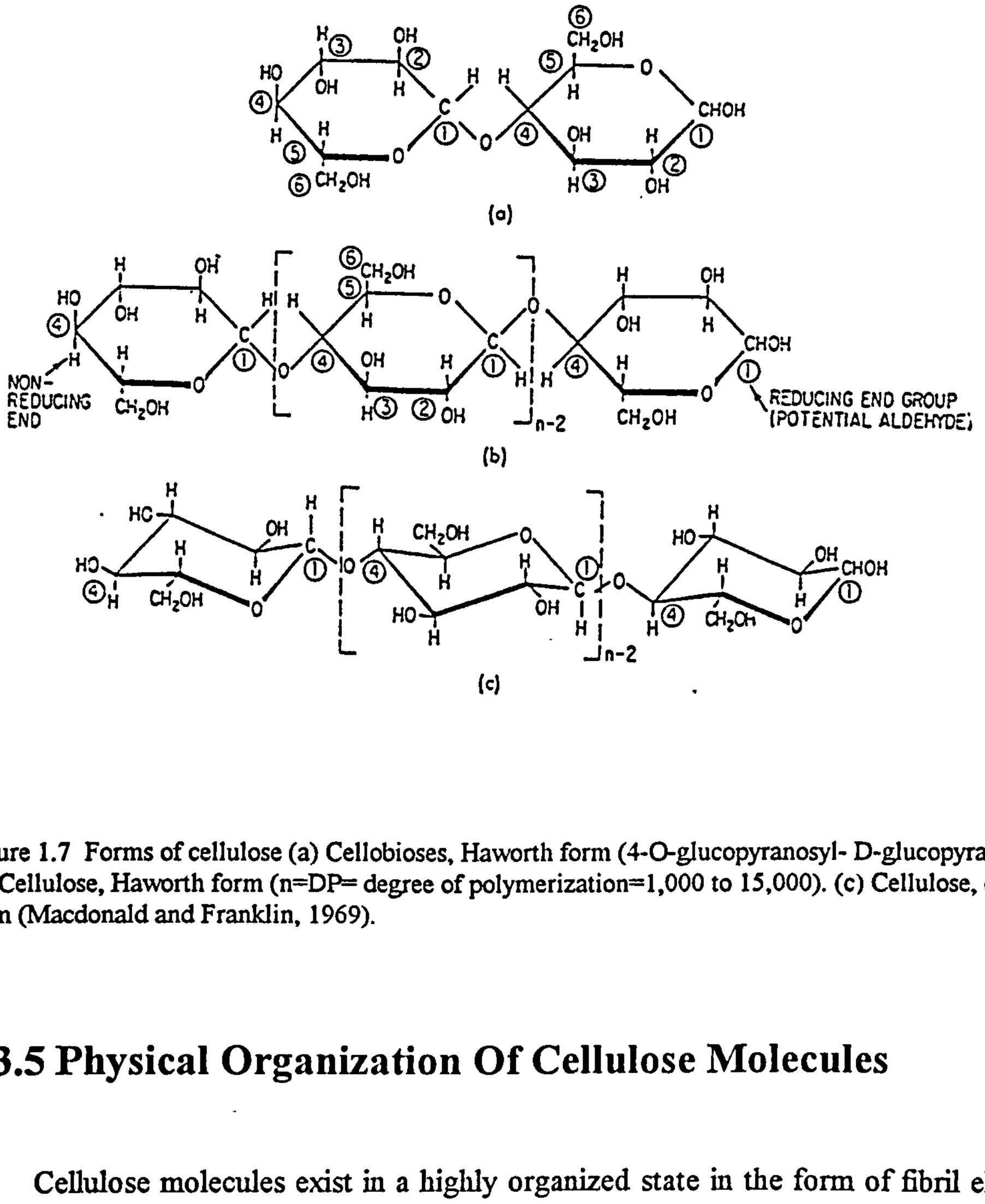


Figure 1.7 Forms of cellulose (a) Cellobioses, Haworth form (4-O-glucopyranosyl- D-glucopyranoside. (b) Cellulose, Haworth form (n=DP= degree of polymerization=1,000 to 15,000). (c) Cellulose, chair form (Macdonald and Franklin, 1969).

1.3.5 Physical Organization Of Cellulose Molecules

Cellulose molecules exist in a highly organized state in the form of fibril elements which, in turn, are organized to form the various cell walls of a fibre. The insolubility of cellulose in water and dilute aqueous alkali despite the presence of five oxygen atoms for each six carbons atoms is due to the extensive hydrogen bonding between (as well as within) the individual cellulose chains. This inter- and intramolecular bonding of cellulose is responsible for the physical, mechanical and chemical behaviour of cellulose, including its solubility.

Cellulose is highly crystalline as a result of the extensive hydrogen bonding but the degree of crystallinity varies greatly depending on the proposed methods for molecular

arrangement. An idealized representation of a cellulose crystal units cell is that of Mayer-Misch based on X-ray and electron diffraction measurements (Conrad, 1971) (Figure 1.8)

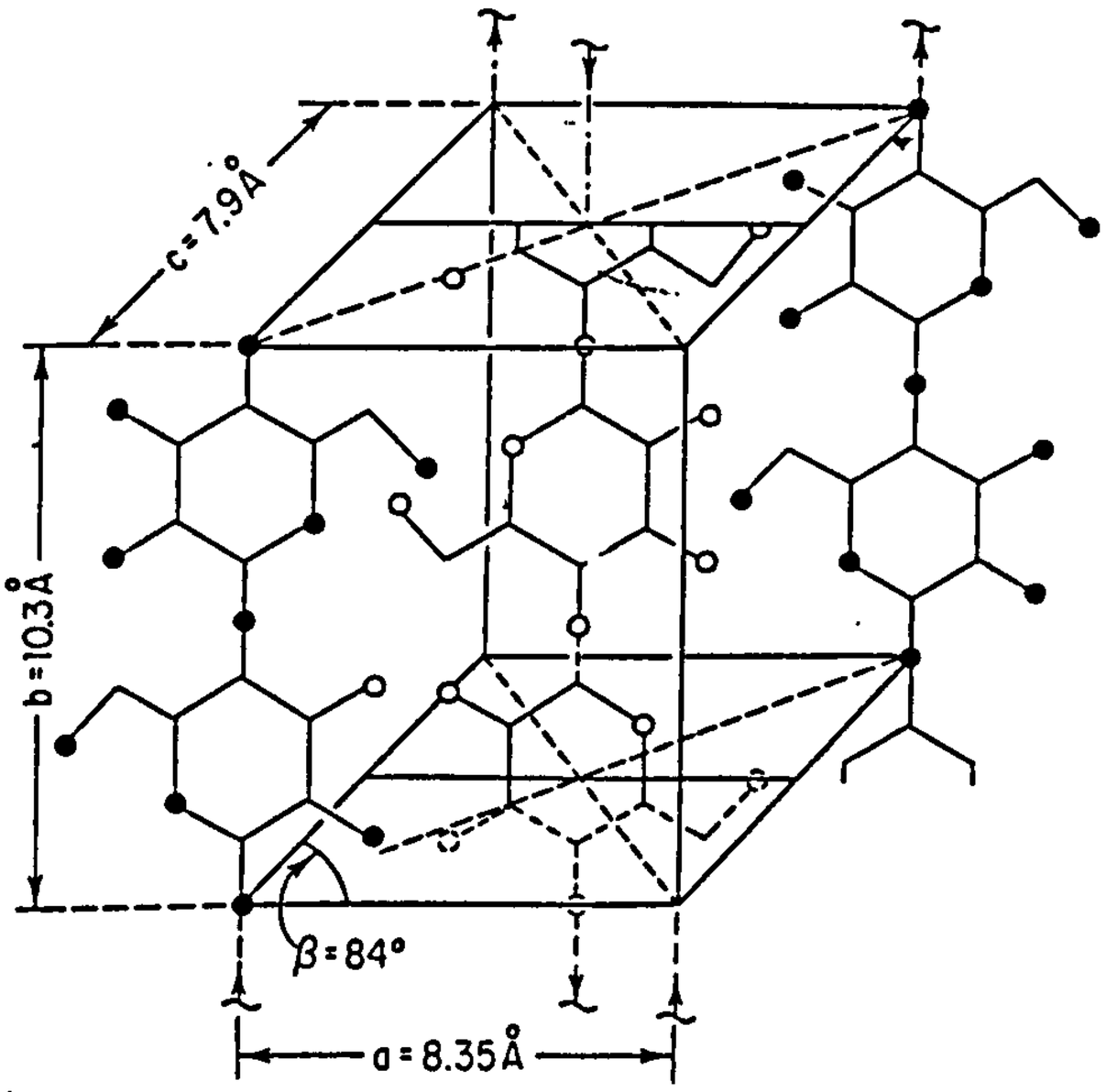


Figure 1.8 Unit cell of cellulose (Macdonald and Franklin, 1969)

1.3.6 Degradation Of Cellulose

The primary objective of most pulping and bleaching is to produce the highest possible yield of cellulose (and associated carbohydrates) with the least amount of degradation. However, considerable hydrolytic and oxidative degradation cannot be avoided.

The glycosidic bonds of cellulose are susceptible to both alkaline and acid hydrolysis. Hydrolytic scission is activated by the presence of certain oxygen groups and each scission of the acetal link produces two new hydroxyl groups, one of which is a potential reducing group. Carboxyl and carbonyl groups along a cellulose chain appear to increase the rate of acid hydrolysis (Macdonald and Franklin, 1969).

Alkaline hydrolysis tends to be effective in all celluloses because alkalis have good swelling power and hence are able to penetrate the well-ordered (crystallite) regions. However, in acid hydrolysis the swelling power is much reduced and the degree of crystallinity of the cellulose determines the effectiveness of hydrolysis.

1.3.7 Hemicellulose

Hemicellulose refers to mixtures of low molecular weight polysaccharides which are closely associated in plant tissues with cellulose. Hemicelluloses constitute about one-quarter of perennial plants and about one-third of annual plants (Conrad,1971). The name hemicellulose was proposed by Schulze in 1918 to designate those polysaccharides extractable from plants by alkaline solutions.

Hemicelluloses are usually extracted from plant tissue after removal of lipid and lignin. Lipids and lignin removal exposes the hemicellulose, permitting its easy dissolution in alkali and their separation in relatively pure condition (Conrad,1971).

They are found to be located in the middle lamellae and throughout the bulk of the plant fibre with some evidence for concentration towards the outer regions of the fibres. The parenchyma cells of the plant contain a greater percentage of hemicelluloses than do the fibre elements (Conrad,1971, Macdonald and Franklin, 1969). In their natural state, the hemicelluloses are generally considered to be non-crystalline.

The nomenclature for describing the hemicelluloses and pentosans is rather complex because of the number and complexity of the sugar moieties of which they comprise. Yet, for description purposes and because of the multiplicity of names used by various authors to describe certain pentose-containing polysaccharides, the term hemicellulose is generally used to refer to the water-insoluble polysaccharides (Aspinall, 1959).

The hemicelluloses are classed as non-cellulosic in nature to differentiate the system from that of cellulose, though D-glucose polymers are found in hemicelluloses as well as in cellulose. It is now known that hemicelluloses are not precursors of cellulose

and have no part in cellulose biosynthesis, but rather represent a distinctly separate group of polysaccharides which are independently produced in plants as structural components of the plant cell wall and make up a portion of the intercellular material called the middle lamella (Conrad,1971).

Hemicelluloses, composed largely of anhydro-D-xylose units, are widely distributed in the plant kingdom as cellular components and frequently they are referred to as plant cementing tissue (Smith and Montgomery, 1959). As far as the function of hemicelluloses in plants is concerned, evidence has indicated that once formed they are stable products of metabolism and their function appear to be purely structural (Whistler and Young, 1960). The common sugars which are structural units of hemicellulose polymers are shown in Figure 1.9.

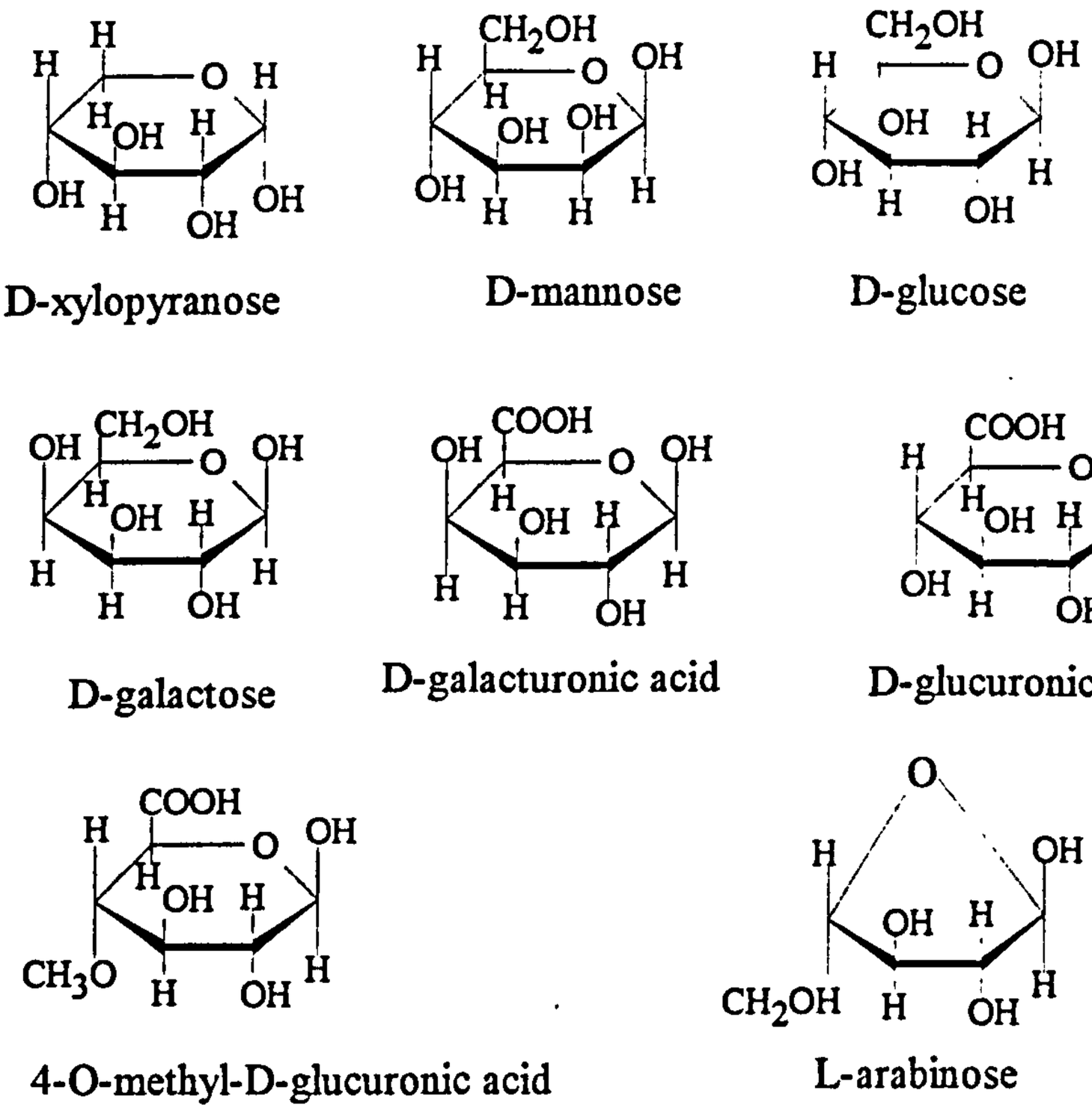


Figure 1.9 Monomeric units found in hemicellulose (Sjostrom, 1981).

Upon hydrolysis, hemicellulose and pentosans yield derivatives of pentoses and hexoses. The monomeric units frequently found in the wheat pentosans and

hemicelluloses are the pentose sugars D-xylose and L-arabinose (Figure 1.9). In addition, certain hexose sugars and their derivatives have been reported which include D-galactose, D-glucose, D-glucuronic acid and 4-O-methyl-D-glucuronic acid. In general, the hemicelluloses and pentosans which may be derived from cereals and grasses are characterized by the presence of L-arabinofuranose residues linked as single-unit side chains to a backbone of D-xylopyranose residues (Aspinall, 1959).

Recent work suggests that hemicellulose is mainly composed of polymers of pentosans made up of linked xylose units as a backbone with some arabinose single units as side chains (Macdonald and Franklin,1969 and Lawther et al., 1995).

Historically, the hemicelluloses were defined as that portion of the carbohydrates fraction of which could be more easily hydrolyzed by acids than cellulose. The use of alkali for the extraction of hemicelluloses has been most common. Lipids are usually removed by extraction with a hot azeotropic mixture of benzene and ethanol, and lignin is then often removed from the plant using sodium chlorite and acetic acid. Although some hemicelluloses are water soluble after isolation, they are not generally water extractable from plants prior to delignification. Annual plants are considered to be an excellent source of hemicellulose.

Alkaline extraction of the holocellulose is effective and the results of extraction depends on the type of alkali used, concentration and sequence. Ideally, total delignification of extractive-free wood or straw will result in a residue, holocellulose, comprising the total carbohydrate fraction (cellulose plus the hemicellulose).

1.3.8 Straw Hemicellulose

Many investigators have studied wheat straw hemicelluloses and generally agree that the structure contains a normal xylan backbone branched through position of xylose with side chains that end in L-arabinose. The presence of D-galactose, D-glucose and D-glucuronic acid have been reported in various concentrations by several investigators (Aspinall and Mahomed, 1954; Roudier, 1953 and Ehrenthal et al.,1954).

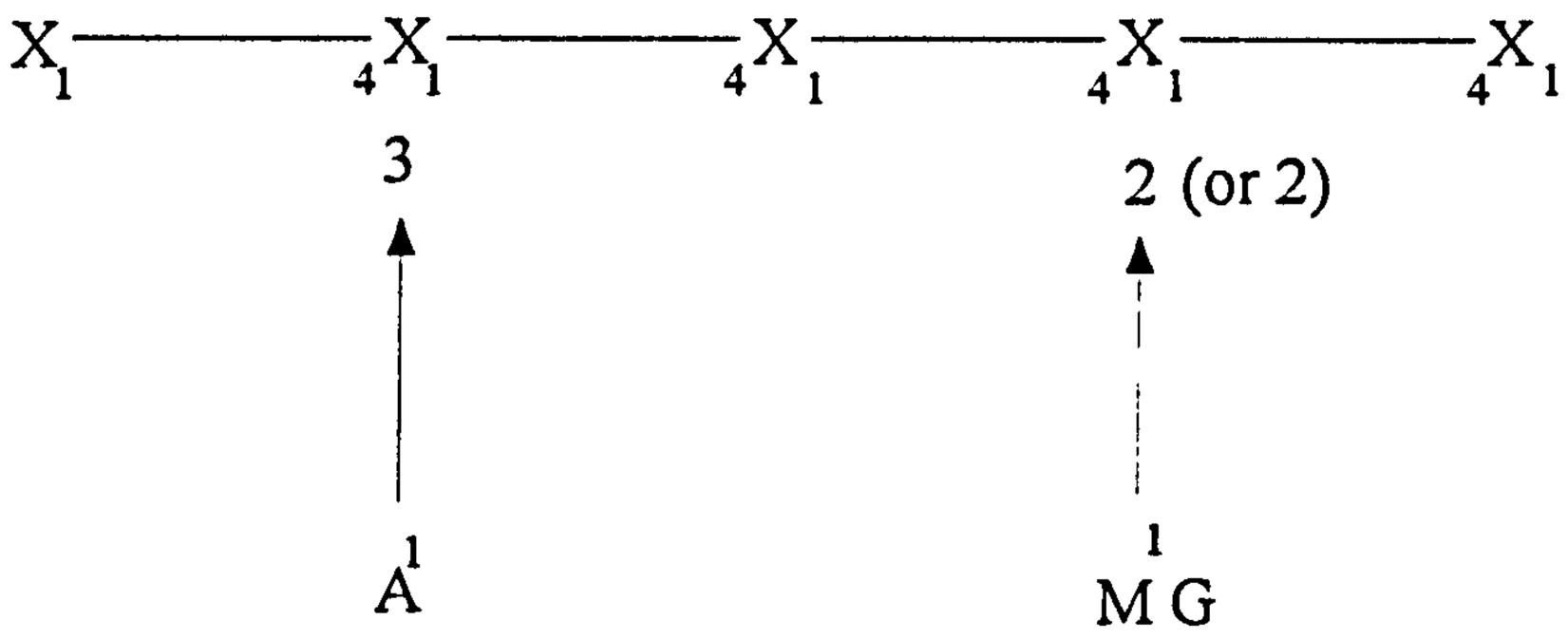


Figure 1.10 Diagrammatic structure of wheat straw hemicellulose. A represents L-arabinofuranose; X, D-xylopyranose; MG, 4-methyl-D-glucuronic acid. Subscripts refer to carbon atoms at which adjacent sugars are joined (Pomeranz, 1978).

The extraction of wheat straw with hot alkali gives a polymer composed primarily of xylose and arabinose (Roudier, 1953), whereas cold extraction gives rise to polysaccharides containing galactose and glucose as well (Pomeranz, 1978).

The structural studies using the classic organic chemical techniques of oxidation and methylation followed by hydrolysis, separation of cleavage products by chromatography, analysis by spectrophotometric methods and isolation of crystalline derivatives show that wheat straw hemicellulose is a highly branched polysaccharide (Dubois et al., 1956 and Pomeranz, 1978). Although, the structure for wheat straw hemicellulose has not yet been proved conclusively, the evidence indicates that the structure shown in the Figure 1.10 is plausible (Aspinall, 1959 and Pomeranz, 1978).

1.3.9 Significance Of Hemicellulose In Pulping

The effects of pulping reagents on hemicellulose are important not only from the standpoint of yield but also on the papermaking properties of the resultant pulps, as these properties depend on the amount, type, structure, degree of polymerization and location of the various hemicellulose component polymers (Macdonald and Franklin,1969). A very positive role is exerted by hemicellulose on fibre properties and bonding behaviour of papermaking fibres. It is considered that hemicellulose has an influence on water retention, swelling and plasticization of fibres by water. The presence of hemicellulose reduces the time and power required to soften and fibrillate fibres during mechanical

action in water, and the fibres are susceptible to absorption and swelling in water because of their general lack of crystallinity, and their irregular (and in some cases branched) molecular configuration.

The plasticization, partial water solubility and high surface area promoted by hemicellulose within fibres and on fibre surfaces lead to increased fibre-fibre contact during paper and paper formation and drying. Both the area of bonding and the bond strength per unit area appear to be increased by the presence of hemicellulose, though too high a hemicellulose content can be detrimental (Conrad,1971).

Hemicelluloses are also useful in that the pentosans fraction may be converted by distillation with strong mineral acids into furfural which is used to make valuable furan derivatives of industrial importance.

Although the presence of hemicellulose in papermaking is desirable, there are also certain drawbacks. The high degree of bonding produces papers of low opacity, that are hard and brittle in structure and low in absorbency. High hemicellulose content results in pulps of low drainage rate during washing and papermaking operations (Mansour, 1985).

Hemicellulose is closely related to cellulose in chemical structure and therefore exhibits a similar pattern of chemical reactions and degradations. In the solid phase, the rate of reaction of hemicellulose will be greater than that of cellulose because of greater accessibility of the hemicellulose as a result of its amorphous nature and location in the outer regions of the fibre (Macdonald and Franklin,1969 and Conrad,1971).

1.4 Lignin

Lignin is a complex, systematically-polymerized, highly aromatic substance which occurs in plants in close association with cellulose and hemicellulose polysaccharides. Lignin forms a cementing matrix that holds together the cellulose fibrils in the tracheid cells and between the tracheids cells and imparts considerable mechanical strength and permits the growth of plant structures. It provides a measure of hydrostability that is highly advantageous and may be associated with water-conducting tissues in bulk.

Lignin is basically an aromatic polymer comprising a heterogeneous, branched network system with no evident simple repeating unit and of high molecular weight. The system is amorphous and is possibly chemically bonded to the hemicellulose, although all work to prove chemical bonding has so far been inconclusive (Macdonald and Franklin,1969). It is emphasized that lignin is not designated as one individually defined compound, but rather it is a collective term for a group as similar very large molecules which are structurally closely related to one another, in a way analogous to certain other natural polymerization products such as cellulose and starch. Hence lignin occurs in many living plants and grasses, but its composition differs in all. Lignin is insoluble in water, in most organic solvents and in concentrated sulfuric acid. It exhibits a characteristic UV absorption spectrum and produces characteristic colour reactions when treated with a variety of phenols and aromatic amines.

The study of lignin is of considerable importance because greater understanding of the properties and reactions of lignin would be of significant assistance in improving the pulping and bleaching industries, in which huge quantities of lignin are obtained as a by-product in the form of so called black liquors, which are either burned or lost in pulp mill effluents. It is natural that attempts were made to exploit this potentially valuable raw material as a great potential source of organic chemical by-products. However, such utilization required some fundamental information on the chemical properties of the material. Thus in 1893, the Swedish scientist Peter Klason (the "father of lignin chemistry") initiated the first intensive and extensive investigation of lignin chemistry by studying one of the common commercial by-products, lignosulfonic acid.

The following are the valuable contributions of Klason to our knowledge of the chemistry of lignins:

* He developed the first method for the quantitative determination of lignin in plants.
* He was the first to isolate lignin by applying sulfuric acid.
* He discovered that if coniferyl alcohol was treated under the same conditions as those used in the sulfite process of pulping wood, this alcohol would be converted to a sulfonic acid possessing many properties similar to those of lignosulfonic acid.
* He was the first to suggest that the parent structure of lignin might be a phenylpropane derivative of the coniferyl type, a hypothesis which is still widely accepted.

1.4.1 Isolation Of Lignin

Lignin cannot be isolated from plants in substantial yield without degradation of its structure because it is susceptible to condensation reactions. Because of the variety of lignified plants in nature, of differences in their chemical compositions and even of differences between young and mature plants of the same species, many different methods of isolation have been recommended (Conrad, 1971; Brauns, 1952 and Sjostrom, 1981). The quantitative isolation of the lignin from the plant material has been achieved by the complete removal of the nonlignin components. For the removal of extraneous substances that might interfere in the lignin determination, pre-extraction is recommended. Typical treatments include washing with organic solvents (such as ether, alcohol, acetone or a mixture of acetone and benzene), cold or hot water, cold dilute alkali, or dilute acid. Some of these pretreatments are obviously not without effect on the lignin itself.

The direct method of quantitative isolation of lignin is by using either strong sulfuric acid or hydrochloric acid to dissolve the carbohydrates of plants leaving the lignin as a dark residue. This method is known as the Klason method, which is widely used to estimate the lignin content of straw and pulp. The various pulping and bleaching processes are generally used to dissolve lignin in order to liberate and clean cellulose fibres, rather than to isolate lignin for research purposes.

As far as lignin structural studies are concerned, there are other methods for isolation of lignin retaining its original structure such as "Cellulolytic Enzyme Lignin" (CEL) where the polysaccharides are removed by enzymes and another one is Bjorkman lignin, alternatively referred as "milled wood lignin" (MWL), which is considered as the best preparation and is widely used for lignin structural studies (Sjostrom, 1981).

1.4.2 Physical Properties Of Lignin

Lignin is a colourless material, which, when exposed to air, particularly in the presence of sunlight tends to become yellow. Thus, newsprint, which is made of

mechanically separated fibres from which lignin has not been removed, has short longevity (Haygreen and Bowyer, 1971).

Lignin is thermoplastic, i.e., it becomes soft and pliable at higher temperatures and hard again as cooling occurs. This characteristic of lignin is basic to the manufacture of the hardboard and other densified pulp products (Haygreen and Bowyer, 1971; Brauns,1952 and Goring, 1971).

Because of differences between lignins isolated from various plant sources and the alteration in the chemical constitution of lignin when it is treated with chemical reagents, it is important to note both the identity of the plant species and the method of isolation employed. For example, lignin preparations isolated by the usual chemical treatments are no longer thermoplastic. They have no melting point. When treated, they decompose and finally char, leaving a highly surface-active charcoal. They are insoluble in all common organic solvents and in cold dilute alkali. All the native and enzymatically-liberated lignins isolated have been found to be light tan to almost white amorphous powders which are soluble in MeOH, EtOH, dioxane, acetone, pyridine. dilute NaOH and glacial acetic acid, but insoluble in ether, benzene, petroleum ether and water.

In the isolation procedure the relative molar mass (molecular weight) of lignin can decrease because of degradation or increase because condensation may occur. Both effects may be present in the same sample. This, coupled with the difficulty of removing a large portion of the lignin without severe degradation, has made molecular weight determinations on isolated lignin very difficult to interpret. One view might be that a large sample of lignin exists as network polymer of virtually infinite molecular weight. Molecular weight determined on solutions of isolated lignins may not have any relationship to the molecular weight of protolignin. Swelling and solubility behaviours of lignin in plants is not inconsistent with the concept of an infinite-network polymer. Lignin fractions having low molecular weight are soluble in solvents with a wider range of solubility parameters and hydrogen-bonding capacities compared with the fractions with higher molecular weights.

Most molecular weight values for isolated lignins are in the range of 1000 to 12000, depending on the extent of chemical degradation and/or condensation during

isolation. Whether lignin is optically active is still debatable. All structures tentatively suggested for lignin contain asymmetric carbon atoms. However, the observed nonactivity of lignin does not preclude the presence of asymmetric centres in the structure (Conrad, 1971).

Based on X-ray diffraction evidence, lignin is non-crystalline; however, UV spectroscopy shows that lignin has some orientation in the middle lamellae. Lignin in plants acts like a capillary gel in that it can be swelled and has strong absorptivity properties for chemicals and gases. The observation that wood exhibits the same X-ray diffraction pattern as isolated wood cellulose would seem to indicate that the lignin in wood has no effect upon the diffraction. This would imply that lignin is ideally amorphous, i.e., it is not constructed of regularly arranged units, but that its structure forms a shapeless mass. Being amorphous, lignins do not have melting point, but they appear to soften and develop adhesive powers over a temperature range of about 70-110 °C.

Isolated lignins have the ability to act as dispersing agents for colloidal systems and are used in oil-well drilling muds and for the dispersion of pigments (Brauns,1952).

The technique of UV absorption spectroscopy has been applied extensively in lignin research furnishing characteristic feature for lignin which are utilized for structural and chemical reaction studies. Most native and enzymetically liberated lignin exhibit the characteristic absorption peak at 280 nm which has been used to measure the concentration of lignin in solution; although the peak at 200 to 210 nm is less affected by lignin condensation and carbohydrate byproducts (Figure 1.11) (Nord and Stevens, 1958 and Conrad, 1971).

The maximum at 280 nm persists in spite of any alteration to the material as caused by methylation, acetylation and treatment with sodium hydroxide.

Solvents for low molecular weight lignin include dioxane, pyridine, acetone and phenol. Generally, solubility of isolated lignin is related to the method of isolation. Some isolated lignins resist solution in any solvent (Macdonald and Franklin,1969).

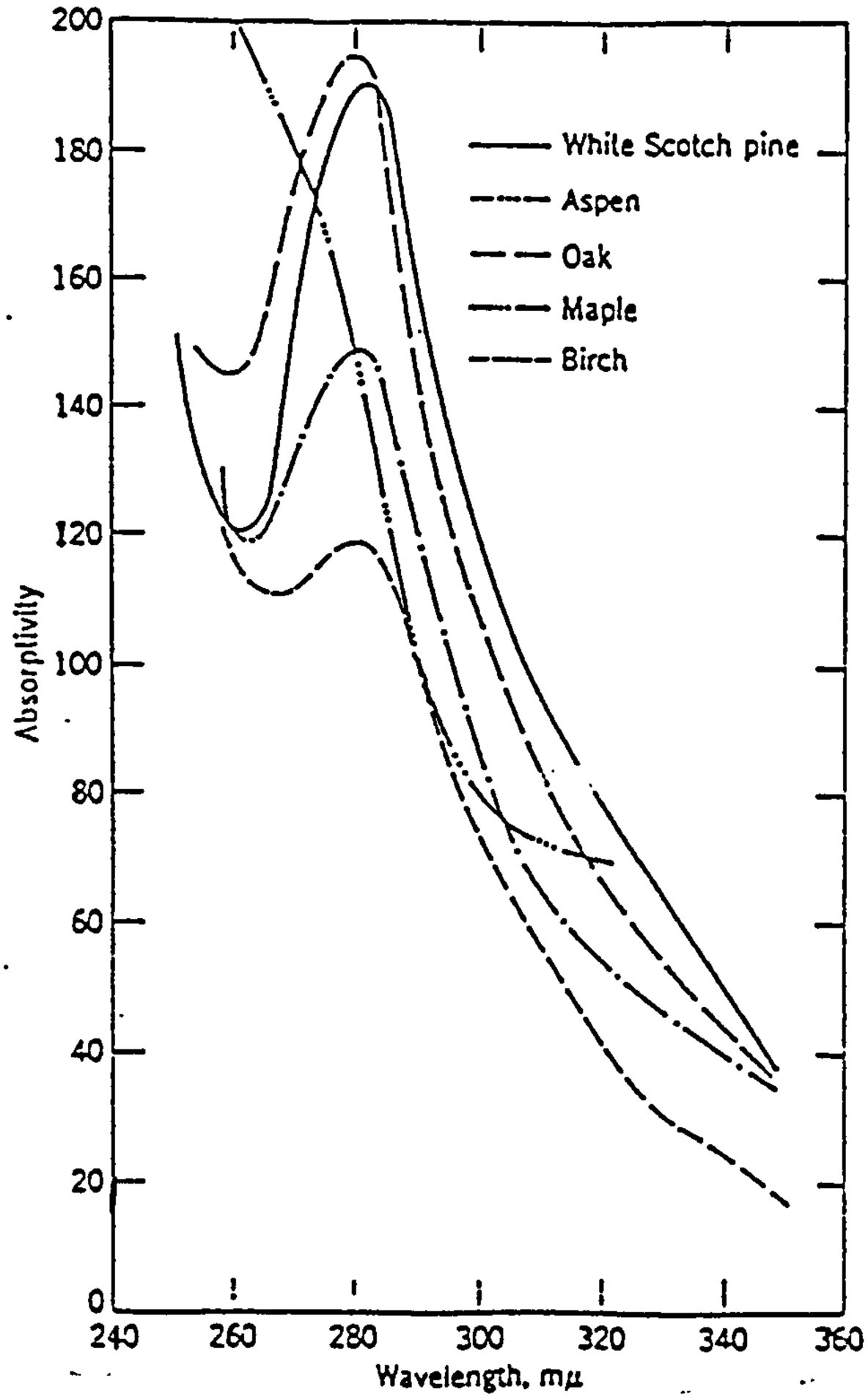
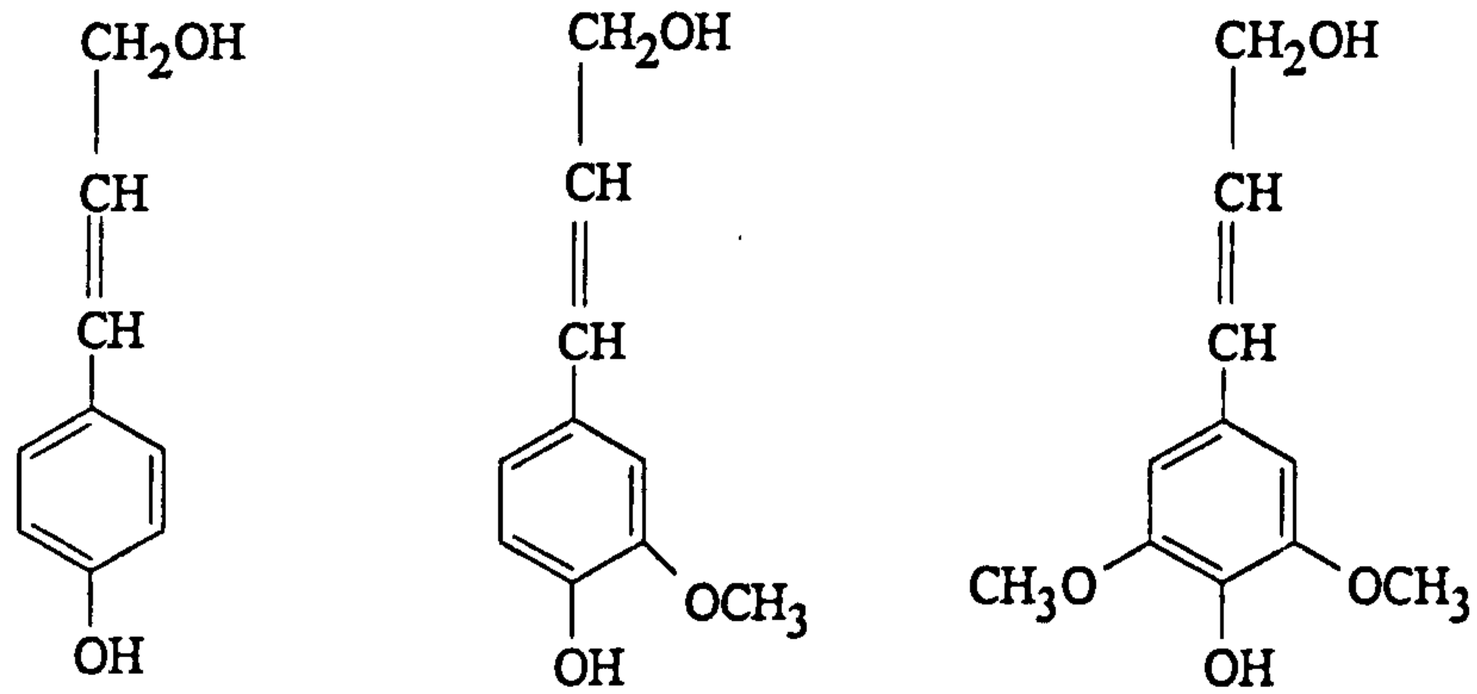


Figure 1.11 UV absorption spectra of native lignin. Absorptivity of 1% solution in a 1 cm thick cell (Conrad, 1971).

1.4.3 The Formation And Structure Of Lignin

Studies of lignin formation have been useful in explaining the possible structure of lignin. Although a large number of plant constituents have been postulated as lignin precursors, in most cases the evidence supporting hypotheses has been meagre. The most tenable theory would appear to be that lignin is a polymer of some compound or compounds with a phenylpropane skeleton (Conrad,1971 and Sjostrom, 1981).

For the formation and structure of lignin, investigations conducted by Erdtman (1930) were of great important. He studied the oxidative dimerization of various phenols in the biogenesis of natural products and reached the conclusion that lignin must be formed of the coniferyl alcohol type (Figure 1.12) via enzymatic dehydrogenation.



p-Coumaryl alcohol Sinapyl alcohol Coniferyl alcohol

Figure 1.12 (Sjostrom, 1981).

The lignin precursors p-coumaryl, coniferyl and sinapyl alcohols (Figure 1.12) are formed from glucose by a variety of enzymatic reactions involving oxidation, reduction, amination, deamination, decarboxylation, etc. The D-glucose generated in photosynthesis is transformed first to heptose phosphate derivatives which then cyclize to 5-dehydroquinic acid. The reaction sequence leads ultimately to phenylalanine with shikimic and phenylpyruvic acids as intermediates. This series of reactions is known as the shikimic acid route. It is reported that in the graminae, on the other hand, lignin is also formed through an alternative pathway proceeding via tyrosine (p-hydroxyphenylalanine). Phenylalanine is deaminated to cinnamic acid which then acquires aromatic hydroxyl and methoxyl groups. The final precursors are formed after reduction of the carboxyl group to a primary alcohol (Sjostrom, 1981). The precursors are probably present in the cambial tissues of gymnosperm as glucosides and become liberated by the action of a β-glucosidase (Figure 1.13).

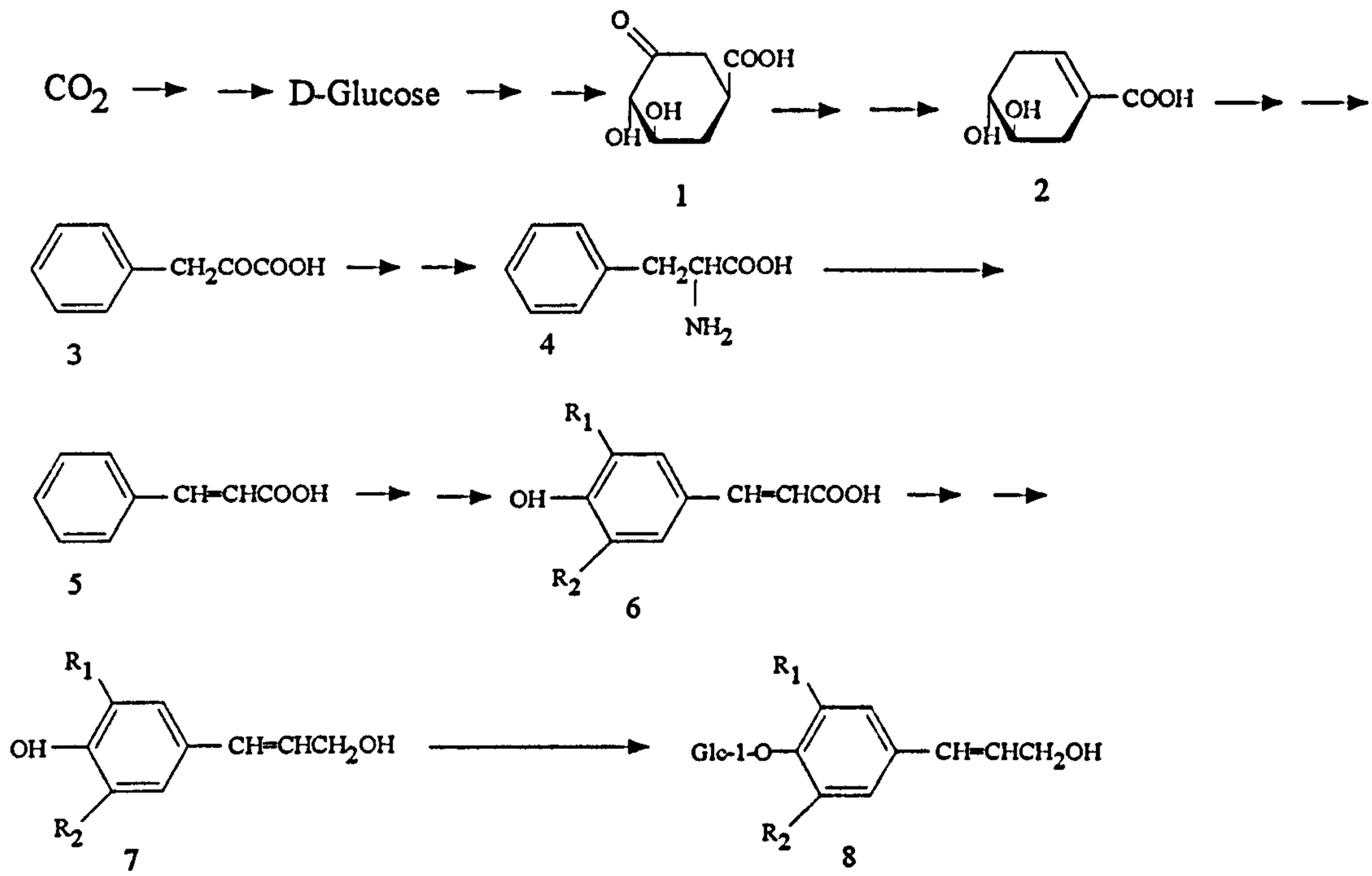


Figure 1.13 (Sjostrom, 1981)

Simplified reaction route illustrating the formation of lignin precursors.1,5-Dehydroquinic acid; 2, shikimic acid; 3 phenylpyruvic acid; 4, phenylalanine; 5, cinnamic acid; 6, ferulic acid (R_1 = H and R_2 = OCH_3); sinapic acid ($R_1 = R_2 = OCH_3$); and *p*-coumaric acid (R_1=R_2=H); 7, coniferyl alcohol (R_1=H and R_2=OCH_3), sinapyl alcohol (R_1=R_2=OCH_3) and p=coumaryl alcohol (R_1=R_2=H); 8, the corresponding glucosides of 7.

1.4.4 Chemical Structure Of Lignin

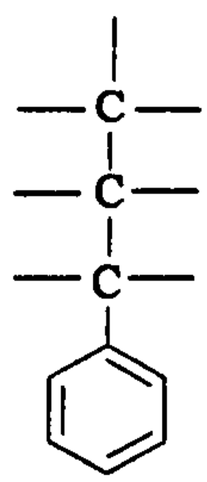
The structure of lignin (largely speculative) is that of a complex polymer whose complexity is due less to the multitude of its monomeric units, and more to the variety of ways in which these units may be joined (Sarkanen, 1963).

Nevertheless, the principal structural elements in lignin have been largely classified as the result of detailed studies on isolated lignin preparations from the CEL and Bjorkman methods using specific degradative techniques based on oxidation, reduction or hydrolysis under acidic and alkaline conditions. Much effort has been directed toward the clarification of the biosynthesis of lignin. Detailed identification of the reaction products has been possible by novel chromatographic techniques and spectroscopic methods developed during the last two decades (Casey, 1980).

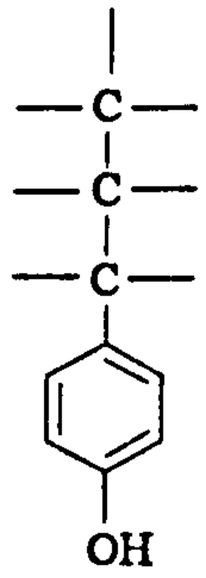
That lignin is a random polymer in which the phenylpropane building units are bonded to each other with ether and carbon-carbon linkages has been largely confirmed by chemical reactions, model compound reactions and the isolation of intermediates and lignin degradation products from both biochemical and chemical studies (Macdonald and Franklin,1969).

Although accurate data for elementary compositions of all lignins are still not available, it is generally agreed that isolated lignins, regardless of their source or the isolation procedure employed contain only the elements carbon, hydrogen and oxygen. Elementary and functional groups of analysis of lignin preparation give a range of values, the average formula being: $C_9H_{8.83}O_{2.37}(OCH_3)_{0.96.}$

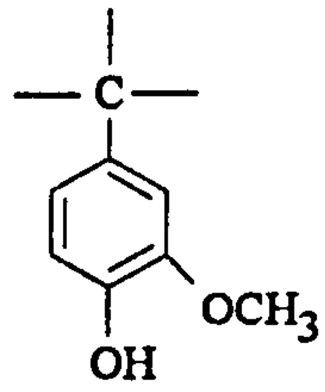
The functional groups of lignin are generally believed to include methoxyl, phenolic hydroxyl, primary and secondary alcoholic hydroxyl, benzyl alcohol groups, ether groups (aryl ethers and coumarin structures), carbonyl, carboxyl and conjugated carbonyls and other doubly bonded groups (Conrad,1971). The methoxyl group is considered to be the most characteristic structural feature of lignin. Based on biochemical synthesis and chemical studies of lignin, the speculative structures in the following Figure 1.14, shows the basic structural groups of which lignin is believed to be constructed (Freudenberg, 1964) (Figure 1.14)



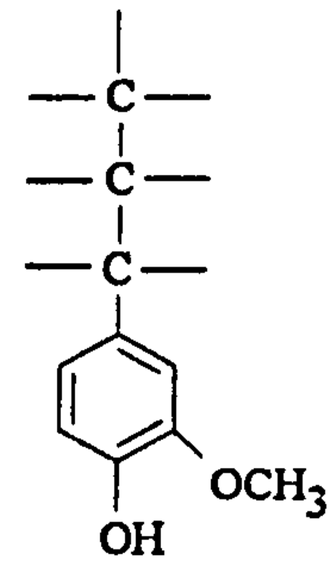
Phenylpropane



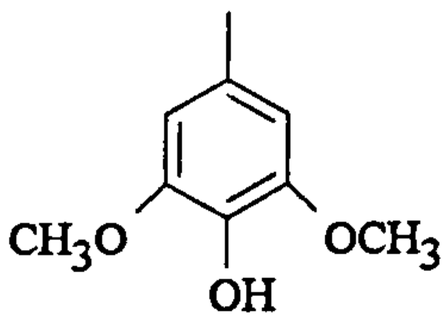
p-Hydroxyl phenylpropane



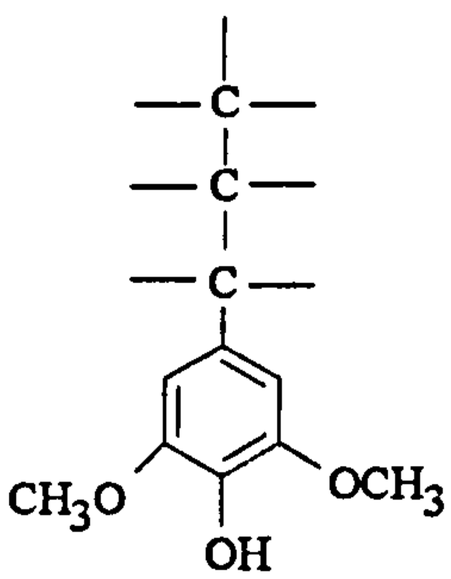
Guaiacyl



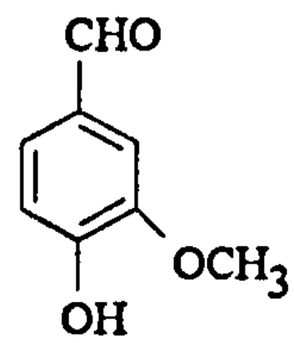
Guaiacyl propane



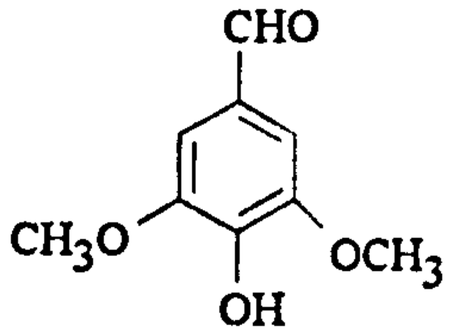
Syringyl



Syringyl propane



Vanillin



Syringaldehyde

Figure 1.14 Structural group related to lignin (Conrad, 1971; Macdonald and Franklin, 1969 and Freudenberg, 1964).

Freudenburg (1964), who did much of the biochemical work, has postulated the structural units of lignin and has shown how they may be joined together. The proposal received support based on NMR spectra of softwood lignin (Macdonald and Franklin,1969).

1.4.5 Phenylpropane - The Basic Structural Unit Of Lignin

There is considerable evidence that lignin consists mainly, if not entirely, of phenylpropane derived monomeric units as shown in Figure 1.15 The fact that *p*-hydroxybenzyl (a), vanillyl (b) and syringyl (c) derivatives have been obtained from the various types of lignin (Conrad,1971) clearly indicates that the benzene ring carries a hydroxyl group (or etherified hydroxyl) at the position para to the chain and either zero, one or two methoxyl groups at the position ortho to the phenolic oxygen function (Sarkanen and Ludwig, 1971).

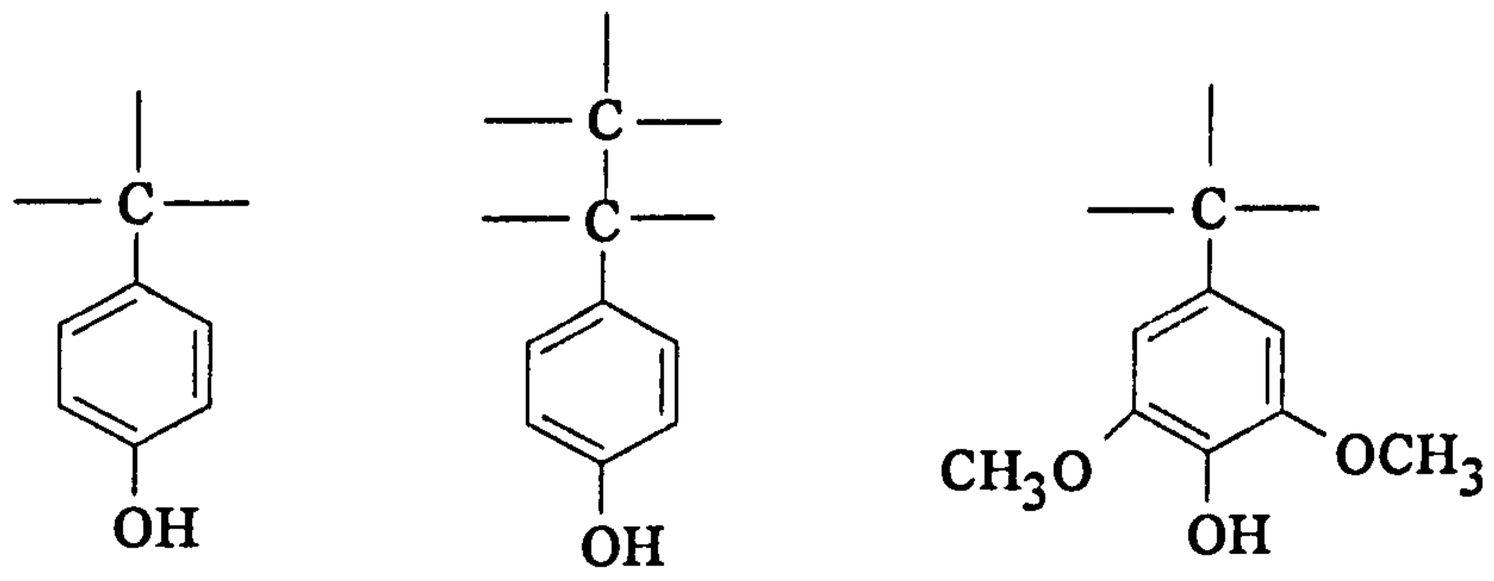


Figure 1.15 (Sarkanen and Ludwig, 1971).

1.4.6 Modes Of Combination Of Phenylpropane Units

It is generally accepted that in the lignin macromolecule, the monomeric phenylpropane units are joined together by both ether linkages and by C-C bonds. The C-C bonds are highly resistant to chemical degradation and constitute the main factor retarding the conversion the lignins to monomeric units during reactions of ethanolysis, hydrogenation etc. (Sjostrom, 1981). The following structures (Figure 1.16) shows where one head-to-head type is a biphenyl linkage in which two benzene rings are joined via a 5-5 bond (A); tail-to-tail linkage might involve an α-α-combination (B); a head-to-tail linkage would be exemplified by a β-5-combination (C).

Ethereal linkages may unite phenylpropane (D) units at just simple one-point combination which include a β-4-ether linkage (E) as is typified in the guaiacyl glycerol-β-arylether structure widely recognized as present in lignin (F) .

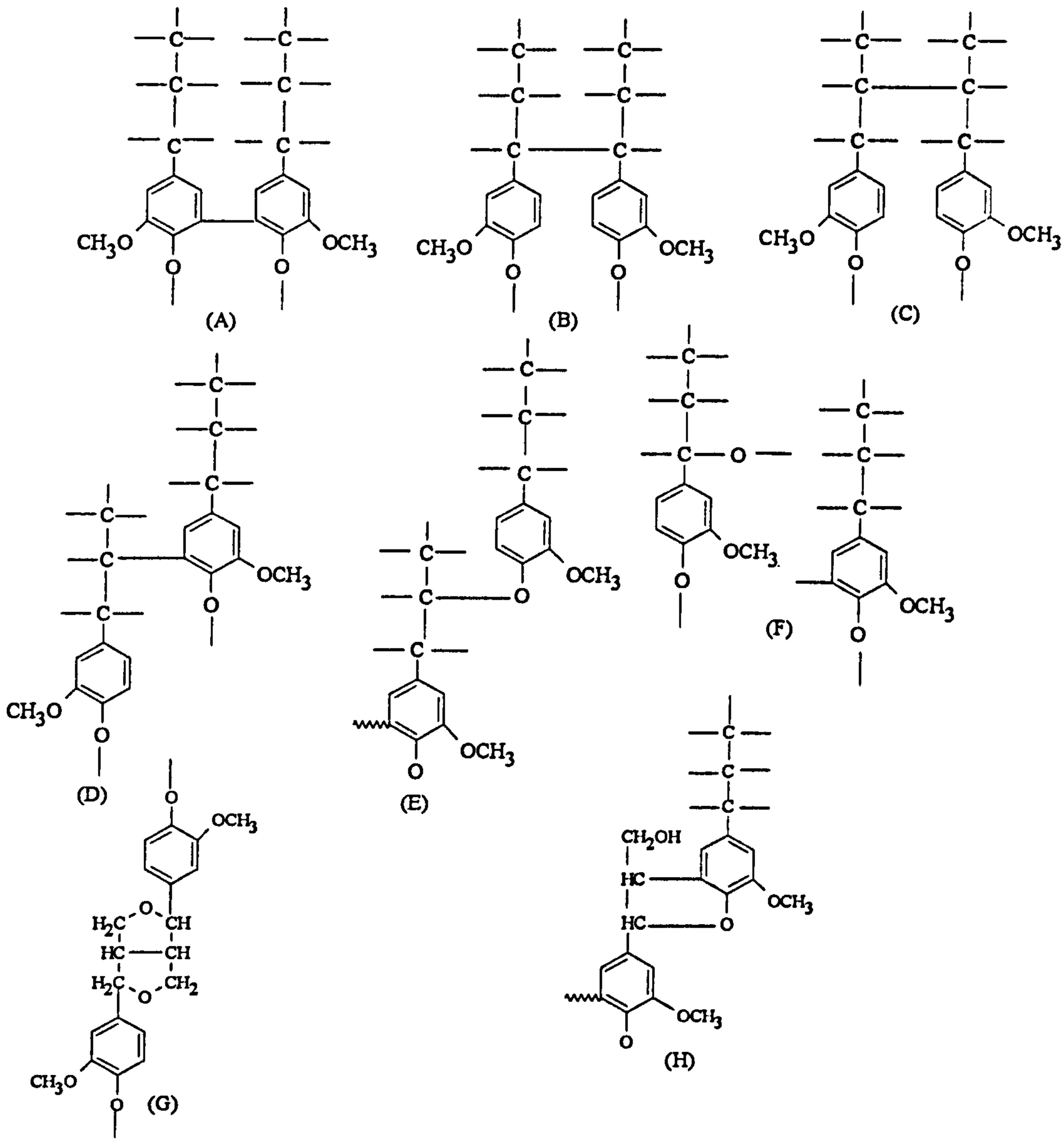


Figure 1.16 (Sjostrom, 1981).

Multiple points of attachment of phenylpropane units involving both ether and C-C linkages are those found in the benzofuran type (G) and in the pinoresinol-type (H) structures which are also believed to be present in the lignin.

However, it should be noted that proof of the existence of many of linkages in lignin is still lacking. They are speculative, suggested to explain certain aspects of the observed chemical behaviour of lignin (Sarkanen and Hergert, 1971).

1.4.7 Nature Of Polymer Chain

Most natural as well as synthetic polymers are constructed according to a head-to-tail principle, but the evidence seems to indicate that this is not entirely the case with lignin. The knowledge of lignin *in situ* is too meagre to justify any specific conclusion of lignin structure as a whole. However, the swelling and solubility characteristics of the lignin in wood conforms to the idea of an infinite network (Conrad,1971). All extant experimental results seem consistent with the concept that a substantial portion of the lignin *in situ* exists in the form of a three-dimensional cross-linked structure which becomes degraded to fragments of finite size by the cleavage of certain cross-linkages (Sarkanen and Hergert,1971).

1.4.8 Hypothetical Lignin Structure

A tentative structure illustrating the constitution of spruce lignin has been proposed by Freudenberg and Neish (1968) who concluded that in spruce milled wood lignin about one-half of the phenylpropane units are joined to each other by C-C bonds, whereas the others are joined by ether bridges in the following proposed lignin structure of spruce (Figure 1.17). The structure is not meant to be quantitative, but merely indicative of the possible nature of lignin.

It is evident from the following structure of lignin that the basic phenylpropane structures are methoxylated and are held together by dialkyl and alkyaryl ethers and C-C bonds. There is no evident pattern in the sequence of linkages which is consistent with the proposed random polymerization of coniferyl alcohol.

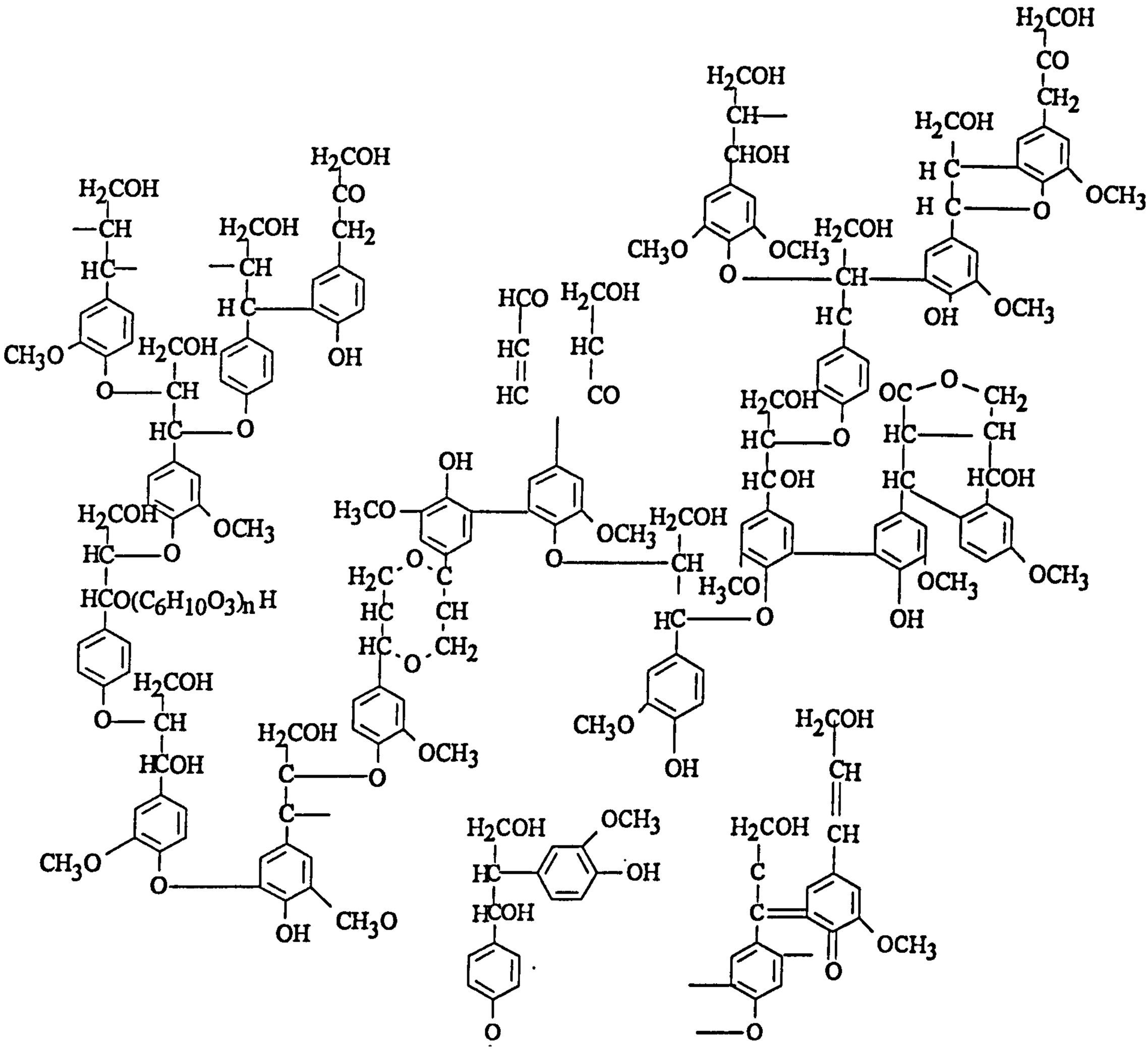


Figure 1.17 Partial structure of spruce lignin (Freudenberg and Neish, 1968).

1.4.9 Lignin-Carbohydrate Linkage

Lignin does not occur alone in nature but rather it coexists with the polysaccharide fraction of the cell-wall components. However, this does not necessarily imply that a chemical bond joins the lignin to the polysaccharides in the plant. Two theories are postulated in this regard. One is that, the carbohydrate of the plant is mechanically

enclosed by the encrusting material, lignin which is known as the mechanical encrustation theory. The other one is that a real chemical linkage exists between the carbohydrate and the lignin (Conrad, 1971 and Brauns, 1952). It was reported that almost all of the lignin and carbohydrate in different plants, softwood (angiosperm), hardwood (gymnosperm) and grass (graminaceous) plants exist in a state of chemical combination and contain structurally different molecular species of hemicellulose and lignin (Merewether, 1960 and Sarkanen and Hergert, 1971).

1.5 Kinetics

Delignification is a major chemical process in pulping and the kinetic studies on delignification have been developed for a long time based on measurement of the weight of removed lignin (Sabatier et al., 1993).

There are numerous studies on the kinetics of wood pulping (Kraft pulping) particularly by Russian workers and early work by Kleinert (Pen et al., 1989; Kleinert, 1966; Lemon and Teder, 1973; Kerr, 1970; Obst, 1985; Yan, 1980; Yan and Johnson, 1981 and Rekunen et al., 1980). A mathematical formulation was given as follows for the pulping kinetics of wood delignification which was shown to take place in three different stages or phases (Dolk et al., 1989).

$$w_g = \sum_{i=1}^{3} a_i e^{-k_i t} = a_1 e^{-k_1 t} + a_2 e^{-k_2 t} + a_3 e^{-k_3 t},$$

where w_g is the weight fraction of the insoluble residual lignin, a_i is the maximum fraction of lignin removal achievable in each phase ($\sum a_i = 1$ since $w_g = 1$ for $t = 0$) and k_i is the corresponding reaction rate constant (Sabatier et al., 1993). For example in the delignification of softwood by the Kraft pulping process, the three kinetically distinguishable phases are:

* A fast, initial delignification phase, where a portion of lignin is removed with a high consumption of alkali (Wilder and Daleski, 1964 and 1965 and Kleppe, 1970).

* A slower, bulk delignification phase which is observed to begin at higher temperature (140°C) and during this phase the main part of lignin is removed and the consumption of alkali is lower than in other phases (Kerr, 1970 and Rekunen et al., 1980).

* A very slow, the residual delignification phase, where the lignin removal slowed down (Shah et al., 1991 and Kondo and Sarkanen, 1984). It was thought that this phase involved inextricably bound lignin (Macdonald and Franklin, 1969) or modified lignin grafted on the cellulose crystallite (Wilson and Procter, 1970).

As far as straw is concerned, an extensive literature survey reveals that a number of kinetic studies have been done on alkaline straw pulping by other workers, particularly Chinese (Hongguang and Guangrui, 1986 and Fang et al., 1991) and some work by Russian workers on wood (Pen et al, 1989). However, none of the studies on straw have been sufficiently comprehensive to elucidate the overall reaction mechanism for soda pulping and none has been on Saudi wheat straw, which has a higher than average lignin content (~ 23%) compared with wheat straws from other countries (~ 20%). The lack of the knowledge of the kinetic behaviour during straw pulping restricts efficient control of the cook. An improperly operated cooking process may bring the cook to the residual phase and there is a danger of a serious loss in pulp yield. Therefore, an in-depth kinetic study has been undertaken here to investigate the effects of cooking time, temperature, alkali consumption and presence of anthraquinone (AQ) catalyst on the rate of delignification, carbohydrate dissolution and caustic consumption as they are important parameters in alkaline pulping (Shah et al., 1991).

1.6 Scope Of This Work

The work to be reported here is on the pulping of wheat straw from Saudi Arabia. Kinetic studies have been carried out to find the rate of the delignification and carbohydrate dissolution at various times (from 5min to 6h) using different levels of caustic soda over a range of temperatures (from 25 to 170 °C). The subsequent products were analyzed systematically by FTIR, UV, NMR (solid-state and in solution) spectroscopies and molar mass determination (GPC) to follow the physical and chemical changes occurring in the delignification.

2 THE KINETICS OF DELIGNIFICATION

2.1 Preliminary Studies

Before detailed studies of the kinetics of delignification of wheat straw were started, the kinetic runs and the analytical methods were tested and optimised.

2.1.1 Isolation and Determination Of Lignin

The methods for the quantitative isolation and determination of lignin have been widely described in the literature (Brauns, 1952 and Brauns and Brauns, 1960). The chemical so-called Klason method is the most popular, though UV analysis has also been used frequently (Wood and Kellogg, 1988). However, the chemical method is considered generally to be the best one if it is used with a full knowledge of its limitations and the correct procedure is followed (Brauns and Brauns, 1960 and Wood and Kellogg, 1988).

2.1.1.1 Klason Method

The Klason lignin analysis method is probably the simplest method which is widely used by most wood chemists for the determination of the lignin content of wood. The isolation of lignin is obtained upon treating wood or straw with sulfuric acid, which hydrolyzes the polysaccharides to water-soluble sugars, and the lignin is recovered as an insoluble residue (Brauns, 1952; Brauns and Brauns, 1960; Bethge et al., 1952; Theander and Westerlund, 1986 and TAPPI, 1983). The Klason method for lignin isolation has great utility as an analytical means of determining lignin content, but the highly condensed and altered Klason lignin which is isolated is considered unsuitable for characterization studies because it does not represent the lignin in the original lignocellulose, which is also known as protolignin (Wood and Kellogg, 1988). Also, the Klason method does not record the presence of acid-soluble lignin.

2.1.1.2 UV Method

UV spectroscopy is considered to be one of the useful photometric tools to quantify lignin (Jung and Himmelsbach, 1989). It is well known that lignin has a characteristic and very strong absorption in the UV spectrum with a peak in the

absorbance curve at 280 nm (Loras and Loschbrandt, 1956 and Hongguang and Guangrui, 1986). Many investigators have tried to use UV absorbance of lignin for quantitative determination in solution as well as residual lignin in pulp (Patterson and Hibbert, 1943; Loschbrandt, 1950; Bethge et al., 1952 and Bolker and Sommerville, 1962).

However, the absorption method for determination of lignin has been widely criticised due to the errors involved. Light scattering has been mentioned as one of the possibilities for error in the absorptiometric determination of lignin (Aulin-Erdtman and Erdtman, 1949, and Lange, 1945). The most obvious objection which has been raised against the use of absorptiometric determination of lignin is the variations arising due to differences in the treatment to which the lignin has been subjected (Loras and Loschbrandt, 1956 and 1961).

The UV method is very sensitive to changes in the molar extinction coefficient of the UV chromophore of lignin and it is not specific for lignin, because any non-lignin aromatic or other UV absorbing components in the sample will interfere (Wood and Kellogg, 1988).

2.1.1.3 Preferred Method For This Study

For this study, it was decided to use the Klason method as it is more reliable than the UV method. Separate analysis with UV showed the presence of 1.5% w/w acid-soluble lignin which would not have been recorded by Klason. It should be noted that as a result this small fraction has been omitted from the kinetic results.

However, the UV method is more sensitive than Klason at low levels of lignin. Therefore, despite the short comings, it was decided to do a limited amount of work using UV analysis of lignin to check that, when using low levels of caustic in experiments measuring the rate of caustic consumption, there was little delignification and that the lignin level could be recorded as constant for kinetic treatment purposes.

Table 2.1.1 Data for UV and Klason analysis of lignin.

No.	Time (h)	Method (non-ground straw)	Dissolved lignin/g		Dissolv.lignin % on straw	
			UV	Klason	UV	Klason
1	0.5	NS-BOMB-1	0.091	0.139	2.160	3.280
2	1	NS-BOMB-3	0.220	0.162	5.200	3.830
3	1.5	NS-BOMB-4	0.290	0.198	6.105	4.680

A few runs at intermediate caustic level were also done to compare Klason and UV results. They are shown in Table 2.1.1. It can be seen that on continued pulping the UV method recorded higher levels of delignification than Klason. This must have been due to the acid soluble lignin (which the Klason method does not detect) reaction being faster than reaction with standard Klason lignin at the intermediate stages of straw pulping.

2.1.1.4 Conclusions

* Despite the short comings of the Klason method for the determination of lignin, it can still be considered as the most reliable and standard method for analysis of lignin.

* Therefore it was decided to adopt Klason for the most of the kinetic studies, despite it being time consuming.

2.1.2 Determination of Lignin Content In Wheat Straw

The lignin content in untreated wheat straw obtained from the Al-Kharj region of Saudi Arabia was determined by the standard Klason method on a ground sample of clean, dry denoded straw taken in a 250 ml round-bottomed flask (Bethge et al., 1952 and Theander and Westerlund, 1986). The straw was hydrolyzed in 72% (12M) H_2SO_4, followed by dilute sulfuric acid kept in an autoclave at 125 °C for 1h further to hydrolyze and solubilize the polysaccharides; the insoluble residue was then dried and weighed as lignin. See Chapter 6 for further details. The Klason lignin content of the straw based on 5 replicate analyses was 22.9% w/w. This is in line with the previous finding of lignin from Riyadh straw (Fakeeha et al., 1990).

2.1.2.1 Pulping Runs In Metal Reactor

Ground Straw

A sample of straw which was previously washed and well dried to constant weight was ground in a coffee blender (Braun) to 40-60 mesh. To this 50 ml of deionized water containing 0.45g of caustic soda (NaOH) and 0.045g anthraquinone (AQ) as a catalyst were added. The whole material was transferred for pulping into a specifically designed stainless steel cylindrical reactor of total capacity 250 ml (see Chapter 6 for further details and picture). Throughout the runs the reactor was rotated about its horizontal axis inside an electric furnace to achieve good mixing of the reactants at controlled temperatures. After cooking the contents, the cylinder was cooled in a bucket of cold water and the pulp filtered as quickly as possible. In later experiments, the pulp was repeatedly washed with water to recover all the residual caustic which was found to be strongly absorbed to the pulp and unreacted straw. This caused variable results for titration of residual caustic in earlier experiments before the washing step was introduced.

The filtrate was reduced five-fold using a rotavapor (vacuum) and the concentrated extract was acidified with strong mineral acid (H_2SO_4) to get the lignin to precipitate. This was separated and dried in an oven to a constant weight, which was recorded. The

experiments were repeated with fresh straw samples with different run times and temperatures in the metal reactor. The results are shown in Table 2.1.2.

A run without the anthraquinone (AQ) catalyst was carried out in the metal reactor with a similar charge of straw and caustic soda at 125 °C for 2h to see any effect of the catalyst on the delignification process. Another experiment with the same charge of WS and soda-AQ was also carried at room temperature for 3h in a beaker with continuous stirring by using a magnetic stirrer. All the results are summarized in Table 2.1.2.

Table 2.1.2 Data for lignin analysis.

No.	Time (h)	Temp. (°C)	Method (ground straw)	Dissolved lignin/g	Dissolved lignin % on straw	a-x
1	2	140	I-BOMB-1	0.83	20.75	2.15
2	4	140	I-BOMB-2	1.01	25.25	-2.35
3	6	140	I-BOMB-3	0.98	24.50	-1.6
4	2	125	II-BOMB-1	0.86	21.50	1.4
5	4	125	II-BOMB-2	0.92	23.00	-0.1
6	6	125	II-BOMB-3	0.88	22.00	0.9
7	2	100	III-BOMB-1	0.78	19.50	3.4
8	4	100	III-BOMB-2	0.86	21.50	1.4
9	6	100	III-BOMB-3	0.81	20.25	2.65
10	2	125	IV-BOMB-0AQ	0.85	21.25	1.65
11	3	25	RL-ROOM	0.84	21.00	1.9

WS = 4g ; NaOH = 4g ; AQ = 0.045g ; H_2O 55 ml.

a-x = residual lignin % on straw.

2.1.2.2 Conclusions

* The extent of dissolution of lignin during pulping measured in the temperature range 100-140 °C with soda-AQ in the steel reactor for times of 2-6h with finely ground straw consistently gave near total delignification and in some runs (especially at 140 °C) it went somewhat beyond the total Klason lignin limit.

* Treatment without catalyst at 125 °C also gave total delignification.

* Treatment of finely ground straw with soda-AQ at room temperature gave the same results as running in the metal reactor at temperature of 100-140 °C.

The fact that the results were independent of the chemical method of pulping was strong evidence that grinding of the staw was leading to mechanical delignification. It was therefore decided that in order to avoid this effect in all subsequent experiments the straw was simply cut into 2-3 cm lengths prior to reaction.

2.1.3 Determination Of Silica (SiO_2) Content In Straw, Pulp And Lignin

2.1.3.1 Introduction

The chemical composition of black liquor, i.e., the chemical solute used for pulping, is strongly dependent on the nature of the raw material being pulped, the cooking chemicals used and conditions set in pulping. For any chemical recovery on a commercial scale it is essential to concentrate the weak black liquor and then burn it to recover the energy values. Initial low dilution of weak black liquor, very high viscosities of black liquor at medium/higher concentration, and high silica content are major obstacles in any recovery process. Generally, the presence of silica leads to problems related to scaling, clarification and precipitation in pulping (Rao, 1990). The silica content in black liquor is dependent not only on the raw material used, but equally on the pulping process followed and raw material preparation.

The overall high silica content of straw compared to wood causes a lot of difficulties both in papermaking and chemical recovery. It has been found generally that the concentration of silica is high in black liquor (4.5-6% or more) of straw, resulting in fouling of heat transfer surfaces and difficulties in pumping and concentration (Rao, 1990).

In black liquor, silica is present essentially as Na_2SiO_3 which undergoes hydrolysis to silicic acid as the pH is decreased. This happens with dilution by wash water leading to silicic acid scale deposition on filters, wires, screens and plates (Rao,1990). Consequently, black liquors become unstable and form precipitates on standing with pH falling from 10 to 8. The silica contained in precipitatated sediments settles down in the bottom of the black liquors tanks and becomes very hard scale (Rao, 1990).

The straw black liquors at lower pH and lower temperature propagate bacteria which drops the pH further leading to lignin precipitation below pH of 8. This was found to be one of the main causes of decay of straw black liquors (Juan and Ji, 1988 and Bildberg, 1987).

A study has also been reported that semichemical pulps and high yield pulps from straw have more silica in pulp and less silica in black liquors due to milder cooking conditions (Yue, 1987). Higher alkali concentration or pH in black liquor leads to greater dissolution of silica (SiO_2) in straw black liquor (Rao, 1990).

In view of that background it was decided to investigate the fate of silica in some pulping runs in the metal reactor.

2.1.3.2 Initial Experiments

Unlike wood, straw is a heterogeneous material with the stems separated at intervals by nodes. At the nodes a sheath that ends in leaf blades is formed around the stem. Seeds hulls (glumes) and foreign matter are found in straw bales. Obviously, before converting straw into pulp all undesirable materials are taken out. Apart from the removal of foreign matter and grains, nodes are eliminated since they have no papermaking values but which rather affect the value of bleached pulp (Mansour, 1985).

The determination of ash, which is closely equivalent to the SiO_2 content, of a wheat straw sample collected from Alkharj (south-west region of Saudi Arabia) was analyzed according to the Official Methods of Analyses (AOAC, 1984). In brief, 0.5g of dried straw sample previously ground to 40-60 mesh in a coffee blender (Braun) was weighed in a well dried, clean porcelein crucible. The crucible was placed in a Muffle furnace for ignition at 550 °C for 3h. After that the crucible was cooled to room temperature and was kept in a dessicator. Subsequently, the ash content was calculated gravimetrically. The ash content results from triplicate analyses of the wheat straw samples was found to be 6.53%.

Individually extracted lignin samples from different times of treatment with caustic and different temperatures were analyzed for ash by a similar procedure. Duplicate analysis were done for each sample. The arithmetic average of the duplicate runs for each sample are placed in the Table 2.1.3. Analysis was also carried in one experiment with lignin produced by water extraction (see Chapter 6) along with ash content results in the lignin.

Some samples of pulps were also selected randomly to check ash content in them as well. They, too, were treated similar to the procedure prescribed above and the subsequent silica content of the individual analysis are also placed in the Table 2.1.3 along with ash contents in the lignin.

Table 2.1.3 The ash content of different lignin and pulp samples.

Time (h)	Temp. °C	[AQ] (mol dm^{-3})	[NaOH] (mol dm^{-3})	Ash% (Lignin)	Ash% (Pulp)
1.5	25	0	2.02	2.80	
0.5	80	0	2.02	1.35	
1.0	80	0	2.02	3.20	
1.5*	80	0	2.02	7.0	
0.5	125	0	2.02	0.25	16.13
1.0	125	0	2.02	0.17	
1.5	125	0	2.02	0.85	16.24
0.5	150	0	2.02	0.18	12.08
1.0	150	0	2.02	1.63	
1.5	150	0	2.02	2.50	9.66
0.5	170	0	2.02	0.34	
1.5	170	0	2.02	24	
1.5*	170	0	2.02	0	
2.0	170	0	2.02	33.7	8.50
0.25	170	0.0013	2.02	0.29	
0.5	170	0.0013	2.02	5.97	
1.0	170	0.0013	2.02	43.77	
1.5	170	0.0013	2.02	40.30	

* Lignin extracted by water treatment (see Chapter Section 67)

2.1.3.3 Discussion

The results of the analysis of ash content of Saudi Arabian denoded and dried but otherwise untreated wheat straw from Al-Kharj, at 6.53% was less than that previously reported for Riyadh region straw, which was found to have 12.10% ash content (Fakeeha et al., 1990). This can be rationalized as being due to the higher mineral contents of straw from the Riyadh region compared with other regions. Also the lower content of ash in the straw used in this work was due to thorough removal of extraneous matter plus nodes from the straw before analysis and use.

The results in Table 2.1.3 show clearly that the selected samples of lignin were found to contain between 1-3% of ash for run times up to 1.5h in the temperature range 25-150 °C. However, when the temperature was increased to 170 °C with a similar charge of alkali and straw, initially the SiO_2 content was in line with the above results with a marginal increase; but as the cooking time went further up (0.5-1.5h), there was a significant increased of silica (>33%) coming out from the straw along with the lignin, while with added AQ catalyst the extracted lignin was found to contain 43% of ash content for cooking time of 1h at 170 °C.

It can be seen from the results that the semichemical pulps with milder cooking conditions are found to contain more silica than their corresponding lignins. However, as the temperature and cooking time were increased , the dissolution of silica increased and the ash content in lignin increased (33% in case of 2h cooking at 170 °C); while the corresponding pulp was detected to possess lower content of ash 8.50% (Table 2.1.3).

2.1.3.4 Conclusions

In view of the above results where the samples were found to contain from 1-3% ash it was decided not to correct them for ash content. However, with the samples from pulping runs at 170 °C at 1.5 h or more reaction time where upto 43% ash was found, correction was made by ashing all samples and substracting the ash content from the final lignin weights.

2.2 The Kinetic Studies

2.2.1 Delignification

In order to derive rate constants for the delignification of straw by cooking in aqueous caustic soda solutions, it was necessary to postulate a reaction scheme. The following basic scheme was adopted for the uncatalyzed reaction (Pen et al., 1989).

$$L^m + n^1NaOH^n \xrightarrow{k_L \text{ or } k_{Lb}} L_p \qquad \text{dissolution of lignin}$$

$$C^r + s^1\,NaOH^s \xrightarrow{k_C \text{ or } k_{Cb}} C_p \qquad \text{dissolution of carbohydrates}$$

where L = lignin and C = carbohydrate.

k_L is the rate constant for rate of disappearance of lignin, $-\frac{d[L]}{dt}$

k_{Lb} is the rate constant for rate of disappearance of caustic by reaction with lignin, $-\frac{d[NaOH]}{dt}$

k_C is the rate constant for rate of disappearance of carbohydrate, $-\frac{d[C]}{dt}$

k_{Cb} is the rate constant for disappearance of caustic by reaction with carbohydrate, $-\frac{d[NaOH]}{dt}$

n^1 and s^1 the number of moles of NaOH which react with 1 mole of lignin or carbohydrate, respectively.

For

$$-\frac{d[L]}{dt} = k_L[a-x]^m\,[b]^n = k'_L\,[a-x]^m,$$

where a = initial concentration of Klason lignin, x = amount of lignin reacted at time t and b = initial concentration of caustic soda, k'_L is the pseudo order rate constant, given by

$$k'_L = k_L[b]^n.$$

For first order in lignin (i.e., m = 1), the equation above can be integrated to yield

$$k_L = \frac{1}{t[b]^n} \ln\left(\frac{a}{a-x}\right).$$

Thus, a plot of ln (a–x) versus t should give a straight line with slope $-k_L [b]^n$.

Also, for the initial (i.e., $x \rightarrow 0$) reaction rate first order in lignin,

$$-\frac{d[L]_i}{dt} = k_L[a][b]^n.$$

If [a] is kept constant and [b] is varied in separate runs,

$$-\frac{d[L]_i}{dt} = \text{constant } [b]^n,$$

where constant $= k_L [a]$.

Taking logarithms, $\log\left(-\frac{d[L]_i}{dt}\right) = n \log[b] + \log(\text{constant})$.

Hence, a plot of log (initial rate) versus log (initial caustic concentration) has slope n and intercept $\log k_L [a]$.

2.2.2 Results

A series of runs were done in the metal reactor over the temperature range 25-170 °C with 4.23g straw (bone dry weight) in 55 ml water (deionized) and excess caustic concentrations in the range 1.01-4.04 mol dm^{-3}. The analyses for the dissolved lignin were done using the Klason method of analysis (for details see Chapter 6).

Conventional linear regression analyses were carried out with the basic data derived from the experiments. Figures 2.2.1-2.2.6 show first order plots of ln (unreacted lignin on straw) versus time using excess caustic concentration (2.02 mol dm^{-3}) at 25-170 °C. The data show a reasonable fit to first order kinetics, though there is scatter in some cases. Attempts to obtain second order and fractional power plots gave a much poorer fit than the first order ones. However, runs shown in Figures 2.2.4-2.2.6 with excess caustic at 125-170 °C differ from the runs at lower temperatures by displaying a change of slope which appears to show that the reaction

consists of two distinguishable phases: an initial phase and subsequent slower phase both conforming with first order kinetics. The values for the pseudo first order rate constants for the bulk and residual reaction rate constant were calculated from the slopes of the plots.

Figures 2.2.7-2.2.9 show plots of unreacted lignin on straw versus cooking time at 80 °C for six levels of caustic in the range 0.202-4.04 mol dm^{-3}. The log of the initial rates, $-d[L]_i/dt$ derived from these figures for the bulk and residual reaction are plotted in Figures 2.2.10 and 2.2.11 against log of the initial caustic concentration, (log $[NaOH]_i$).

The slope of the graph indicates that the order of the caustic for the bulk delignification reaction was 0.8 and approximately zero order for the residual reaction; the figures were used to derive the true delignification rate constants which are given in Table 2.2.1 using the relationship

$$k'_L = k_L[b]^n,$$

where n = 0.8 for the bulk reaction and 0 for the residual reaction.

Activation energies were derived from Arrhenius plots of ln k_L versus 1/T, shown in Figures 2.2.12 and 2.2.13 for the bulk and residual reactions, respectively. The values found for the activation energies from the slopes of the plots were:

E_a (bulk) = 14 ± 3 kJ mol^{-1},

E_a (residual) = 31.5 ± 6 kJ mol^{-1}

Table 2.2.1 Delignification Rate Constants 4.23g WS;
55 ml H_2O; NaOH 2.02 mol dm^{-3}.

Temp. °C	k_L' Bulk h^{-1}	k_L' Residual h^{-1}	k_L Bulk $(dm^3)^{0.8}\ mol^{-0.8}\ h^{-1}$	k_L Residual h^{-1}
25	0.53		0.34	
50	0.76		0.49	
80	1.08		0.69	
125	2.66	1.18	1.48	1.18
150	2.71	2.94	1.50	2.94
170	2.62	0.62	1.46	0.62

2.2.3 Discussion

The results show that the delignification of straw by cooking in aqueous caustic soda occurs in two reaction phases, a main bulk reaction followed by a residual phase. The change from one to the other occurs when residual lignin in straw is reduced to about 10%. The transition is more evident at temperature above 80 °C. The residual reaction is inherently slower than the bulk with the rate constants at (for example) 125 °C (Table 2.2.1) being:

Bulk reaction k_L = 1.48 $(dm^{-3})^{0.8}\ mol^{-0.8}\ h^{-1}$

Residual reaction k_L = 1.18 h^{-1}

The activation energy of the bulk reaction at 14 ± 3 kJ mol^{-1} and the residual reaction at 31.5 ± 6 kJ mol^{-1} are both low and indicative that rate controlling steps are mainly physical in nature. The most likely physical step to be rate controlling is

diffusion of caustic into the straw and or diffusion of lignin out of the straw into solution.

The delignification reaction is first order in lignin but fractional (bulk) or zero (residual) order in caustic indicating a complex mechanism for caustic consumption. One explanation for fractional order could be that diffusion outwards of the lignin product at high reaction concentration hinders increased diffusion inwards of caustic. This would have the the effect of reducing the slope of the log $(-d[L]_t/dt)$ versus log $[NaOH]_i$ plots in Figures 2.2.10 and 2.2.11 giving a fractional and zero order, respectively. Alternatively, but less likely, there could be two parallel reactions leading to lignin dissolution at lower caustic concentrations. At higher concentrations one of these reactions could be inhibited. Again this could reduce the slope of the plots and give a fractional order.

The first of these two explanations is favoured because it is consistent with a diffusion controlled mechanism as strongly indicated by the relatively low values for the activation energies for the delignification reactions.

The switch from the bulk delignification reaction to the slower residual one at about 10% residual lignin in straw could be due to the residual lignin being less accessible and/or being more chemically resistant. The fact that the activation energy for the residual reaction is higher than that for the bulk reaction could indicate a higher chemical element in the rate controlling step for the residual reaction. This would be the result of the chemical reaction for residual delignification being slower than for the bulk reaction and beginning to more closely approach the rate constant of the physical diffusion process in the residual stage.

The switch from the bulk reaction being fractional order with respect to caustic to zero order in the residual reaction is further confirmation of the complexity of the reaction and could again indicate a higher chemical rate controlling element in the residual phase.

These possible explanations are discussed further in Chapter 5, in conjunction with evidence obtained from the other studies carried out in this work.

The results for the rate constants shown in Table 2.2.1 at 170 °C need special consideration. It is clear that the bulk reaction rate constant and particularly the residual rate constants have fallen rather than risen as expected with increase in temperature to 170 °C. The reason for this is thought to be decomposition of lignin in solution evidence for which is discussed in Chapter 3.

2.2.4 Comparison With Results Reported In The Literature

As mentioned earlier, there are only a few papers in the literature on the kinetics of straw pulping. The presence of two reaction phases for delignification by caustic treatment has been reported for bagasse (Sabatier et al., 1993). The activation energy for the bulk phase was found to be 6.4 kJ mol^{-1} and 48 kJ mol^{-1} for the residual phase, compared with 14 ± 3 and 31.5 ± 6 kJ mol^{-1} found in this work. The values for the rate constants at 150 °C for the bulk reaction were 4.8 h^{-1} and 0.6 h^{-1} for the residual reaction, compared with 1.50 $(dm^3)^{0.8}$ $(mol^{-1})^{-0.8}$ h^{-1} and 2.94 h^{-1} found in this work. (Note the different orders in the bulk reactions.) Other work on sulfide/Kraft cooking of jute also found two delignification phases following a first phase of alkali consumption destroying acid groups as in the present (Wilson and Procter, 1970). Chinese workers (Hongguang and Guangrui, 1986) studied sulphite cooking of wheat straw in the temperature range 100-170 °C. Results at 170 °C showed a high level of delignification within 1h of cooking with two main phases followed by a very slow final phase for removal of the last 20% of the lignin. The activation energy of the first and second phases were 31 and 61 kJ mol^{-1}, respectively, and much higher for the third phase.

Other Chinese workers (Jianjuan et al., 1990) investigated caustic cooking of wheat straw and concluded that the rate controlling steps were physical rather than chemical, implying low activation energies for the rate controlling step.

Clearly the rate of sulfite delignification of straw is more chemically controlled than the rate using soda cooking, where the rate controlling step is mainly physical in nature.

The behaviour of straw in pulping with alkali is markedly different from work reported on wood, where invariably three or often more phases of reaction have been found (Kondo and Sarkanen, 1984; Kleinert, 1966 and Wilson and Procter, 1970). The activation energy found for phase one was 40 kJ mol^{-1}, 113-140 kJ mol^{-1} for the second phase and much higher for later phases. These activation energy values are in line with a chemically controlled reaction rate which Kondo and Sarkanen postulated was due to the cleavage of phenolic-ether or β-ether bonds in the lignin strucuture of wood.

2.2.5 Conclusions

* Delignification of wheat straw by caustic soda occurs in two reaction phases, a bulk phase followed by a slower residual phase at about 10% residual lignin on straw.

* The activation energies of both phases are low (14 ± 3 and 31.5 ± 6 kJ mol^{-1}), indicating that the rate controlling steps are more physical than chemical, i.e., the reactions are diffusion controlled.

* The delignification reaction is first order in lignin for both the bulk and the residual phase but fractional order in caustic for the bulk and zero order for the residual phase, indicating a complex reaction mechanism which could involve inhibition of the reaction by lignin diffusion out from the straw hindering inward diffusion of caustic, particularly at high caustic consumption in the bulk phase.

* The rate of reaction as measured by the amount of lignin in solution increases with increasing temperature until 170 °C when there is an apparent sudden drop particularly in the residual reaction rate, due it is thought to lignin decomposition in solution.

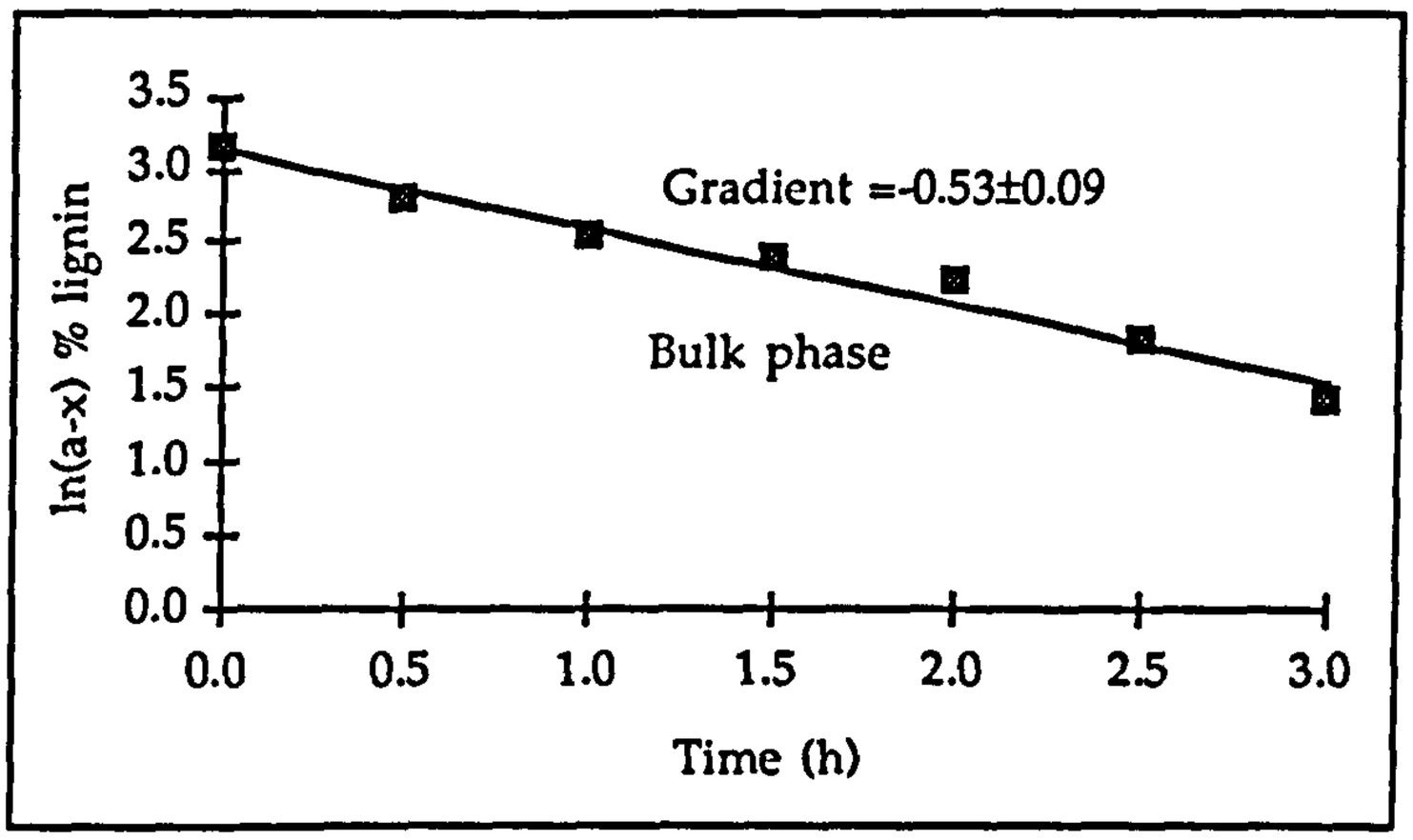


Figure 2.2.1

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 25 °C in 55 ml H_2O.

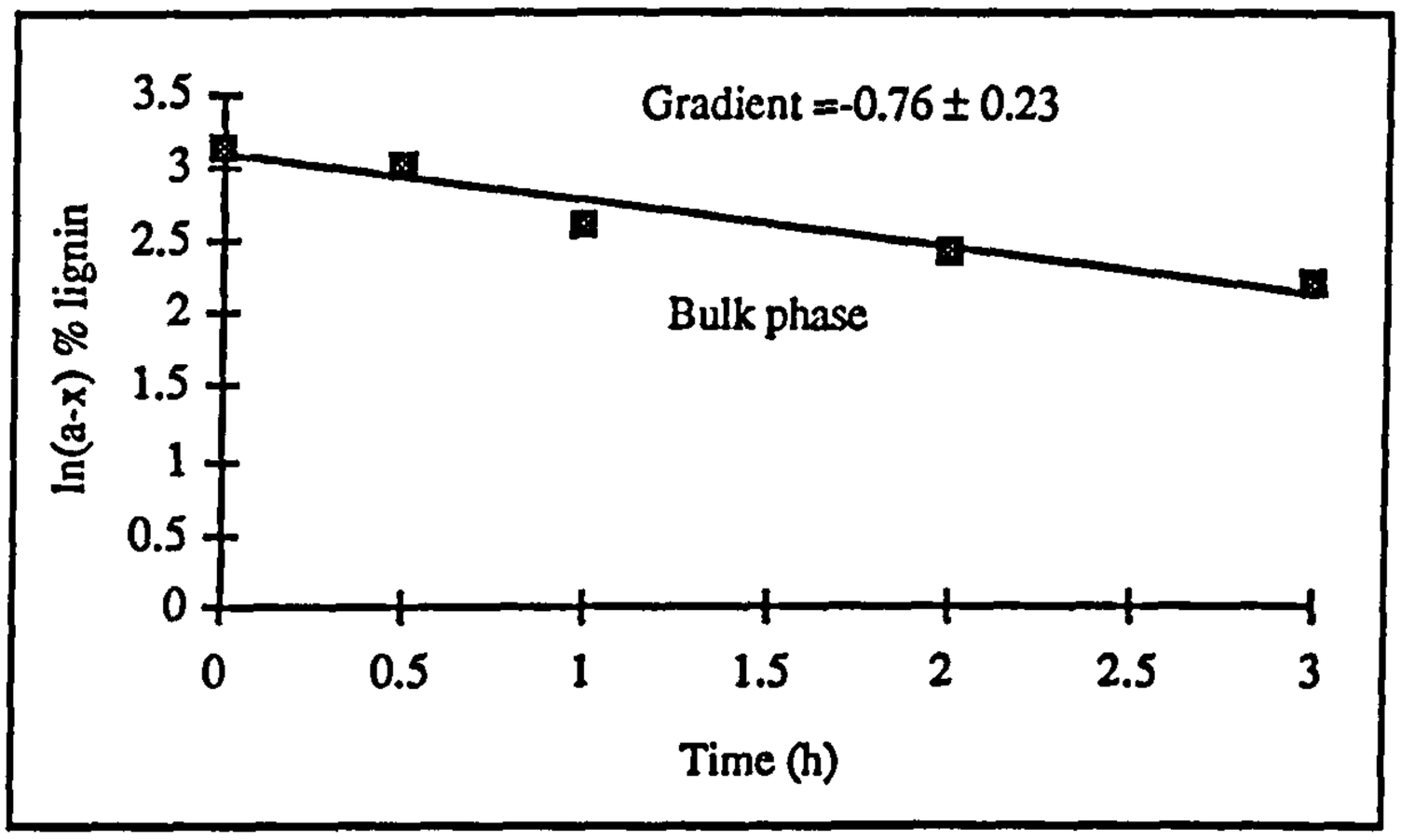


Figure 2.2.2

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 50 °C in 55 ml H_2O.

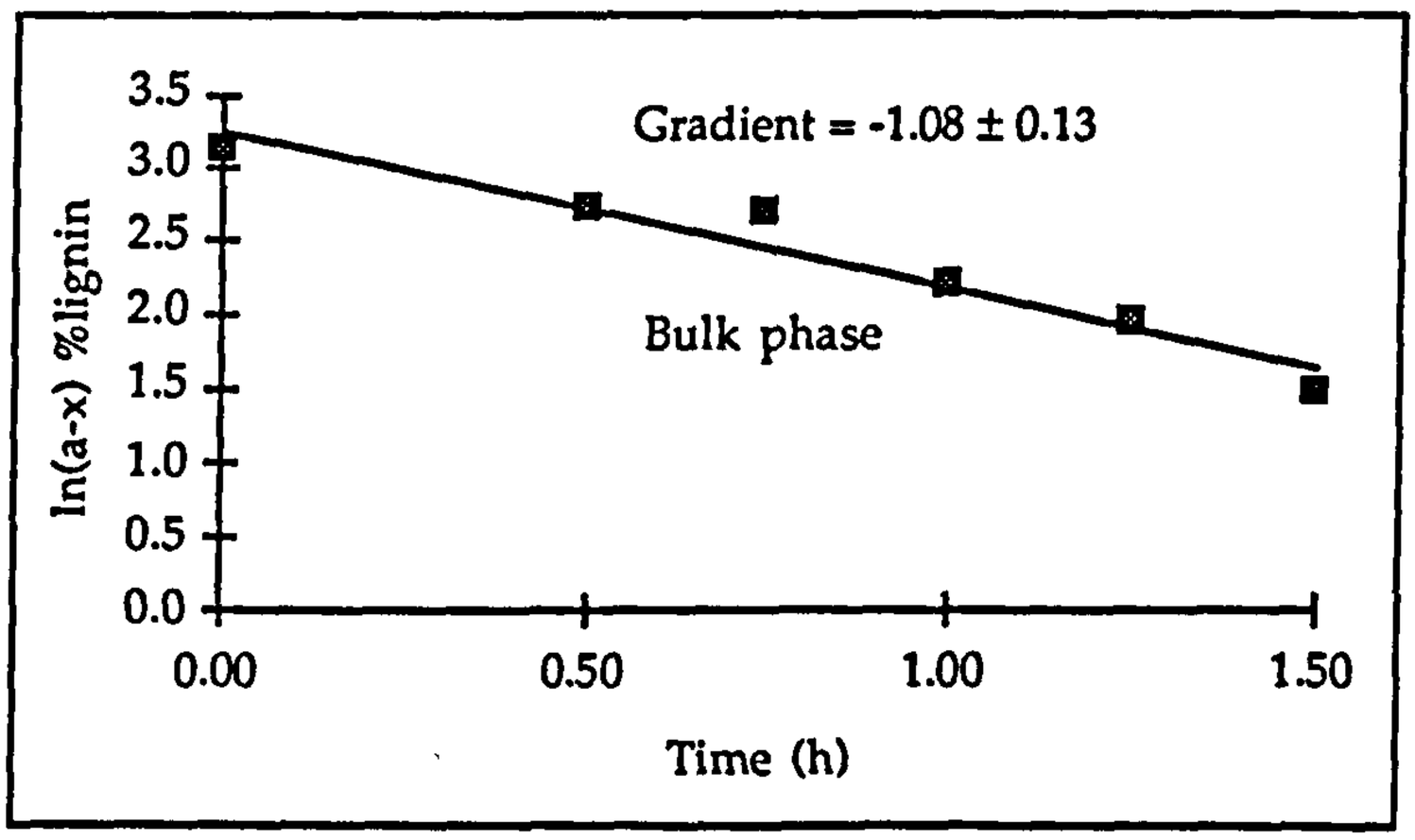


Figure 2.2.3

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 80 °C in 55 ml H_2O.

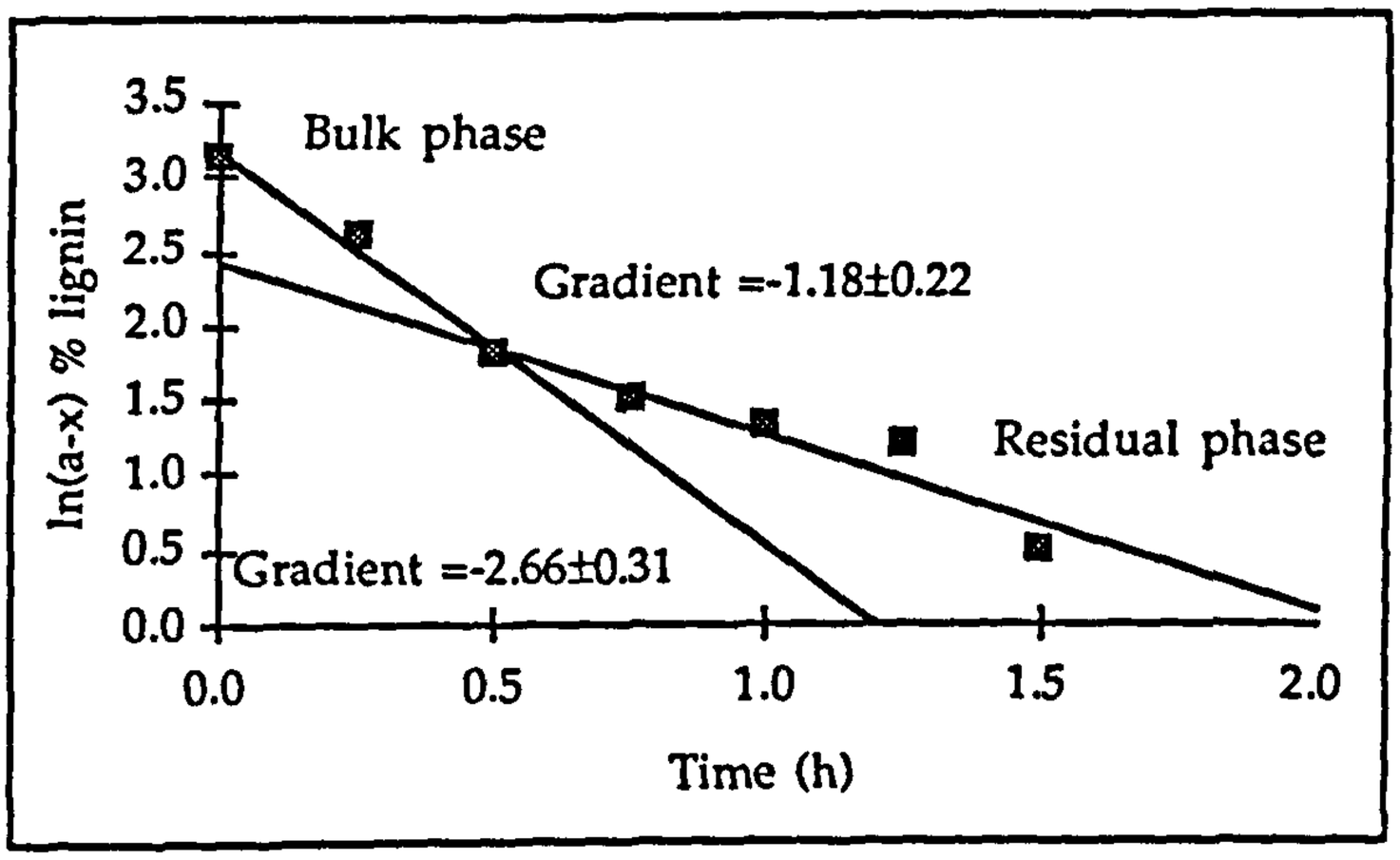


Figure 2.2.4

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 125 °C in 55 ml H_2O.

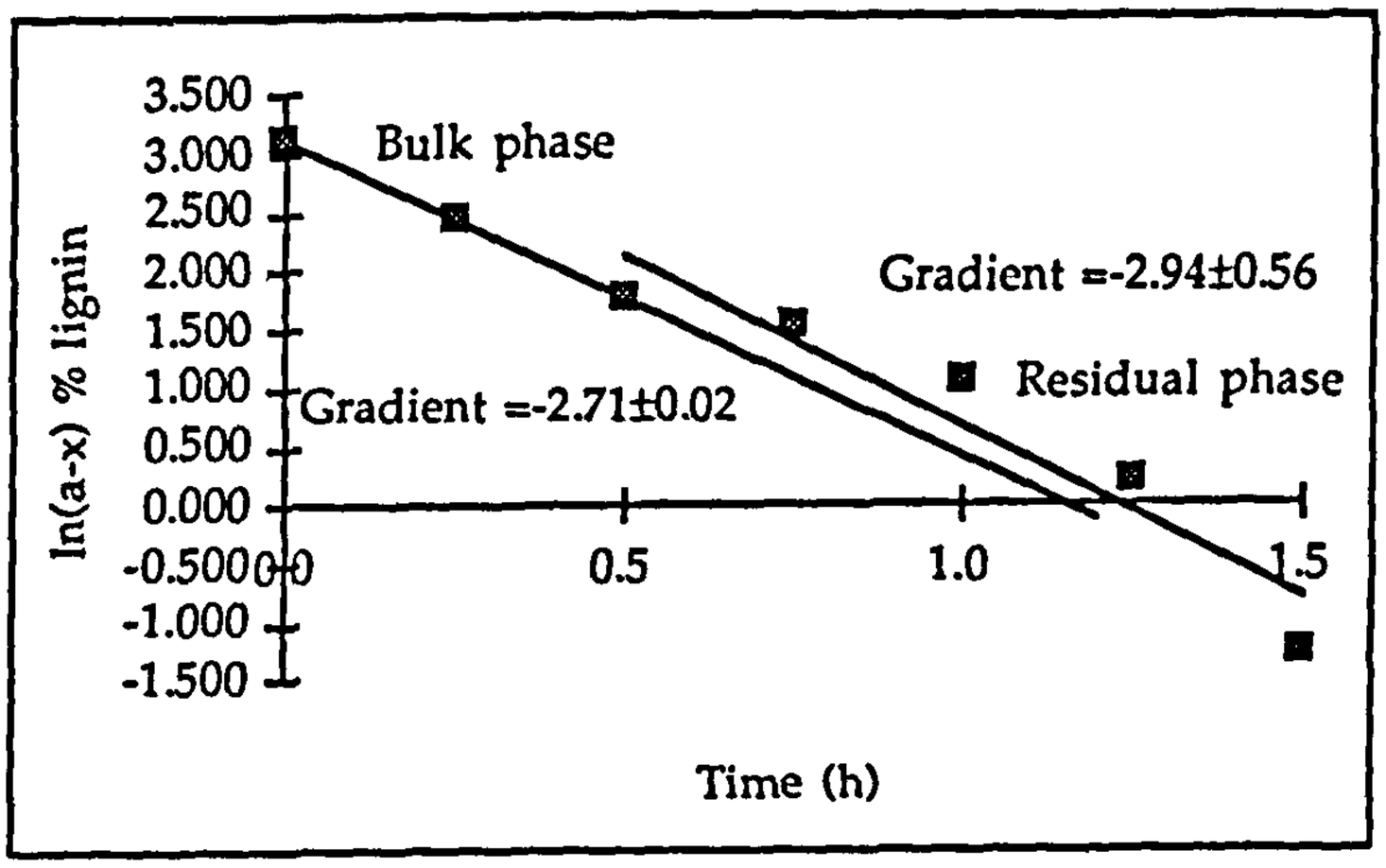


Figure 2.2.5

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 150 °C in 55 ml H_2O.

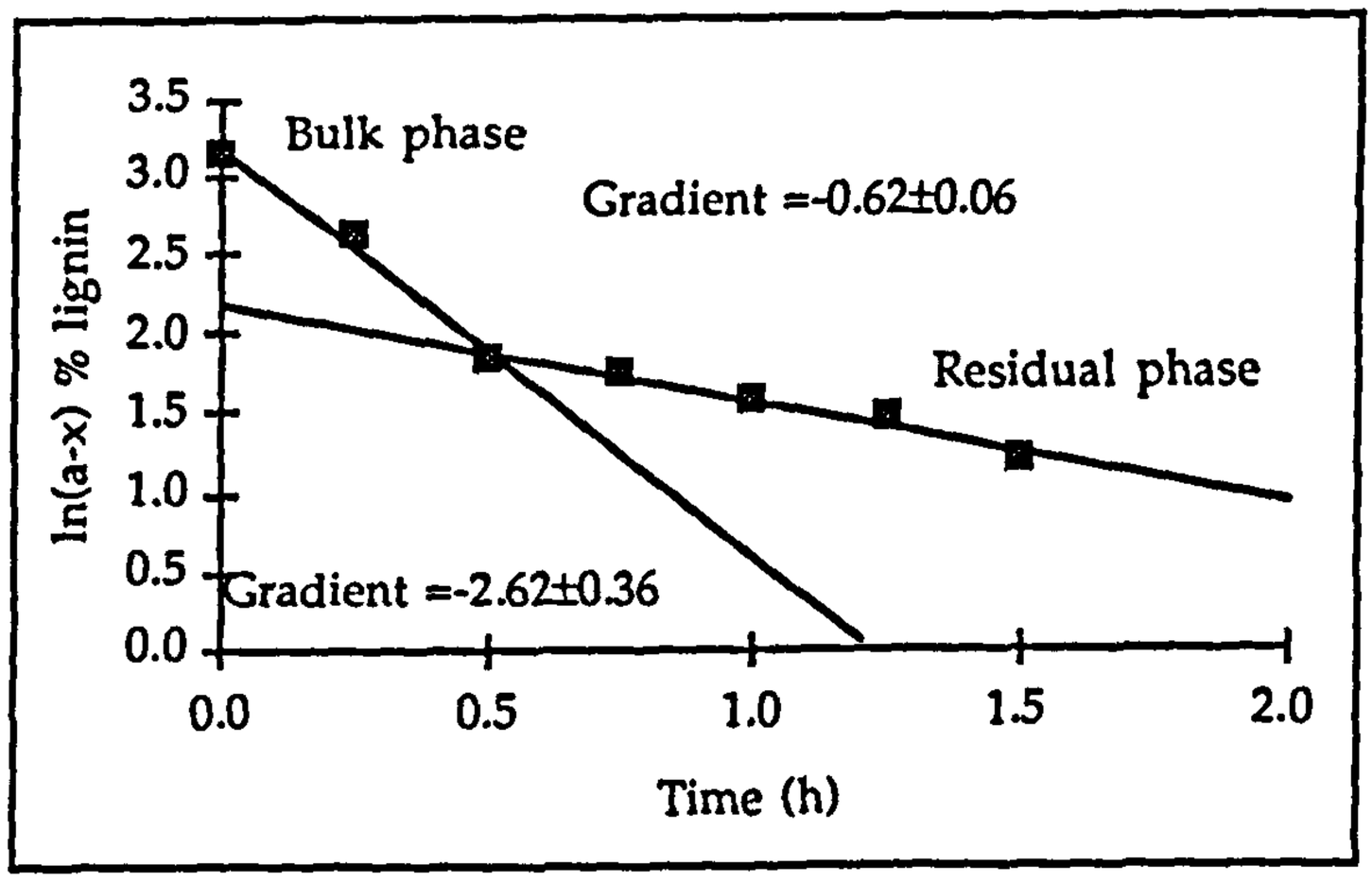


Figure 2.2.6

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (2.02 mol dm-3) at 170 °C in 55 ml H_2O.

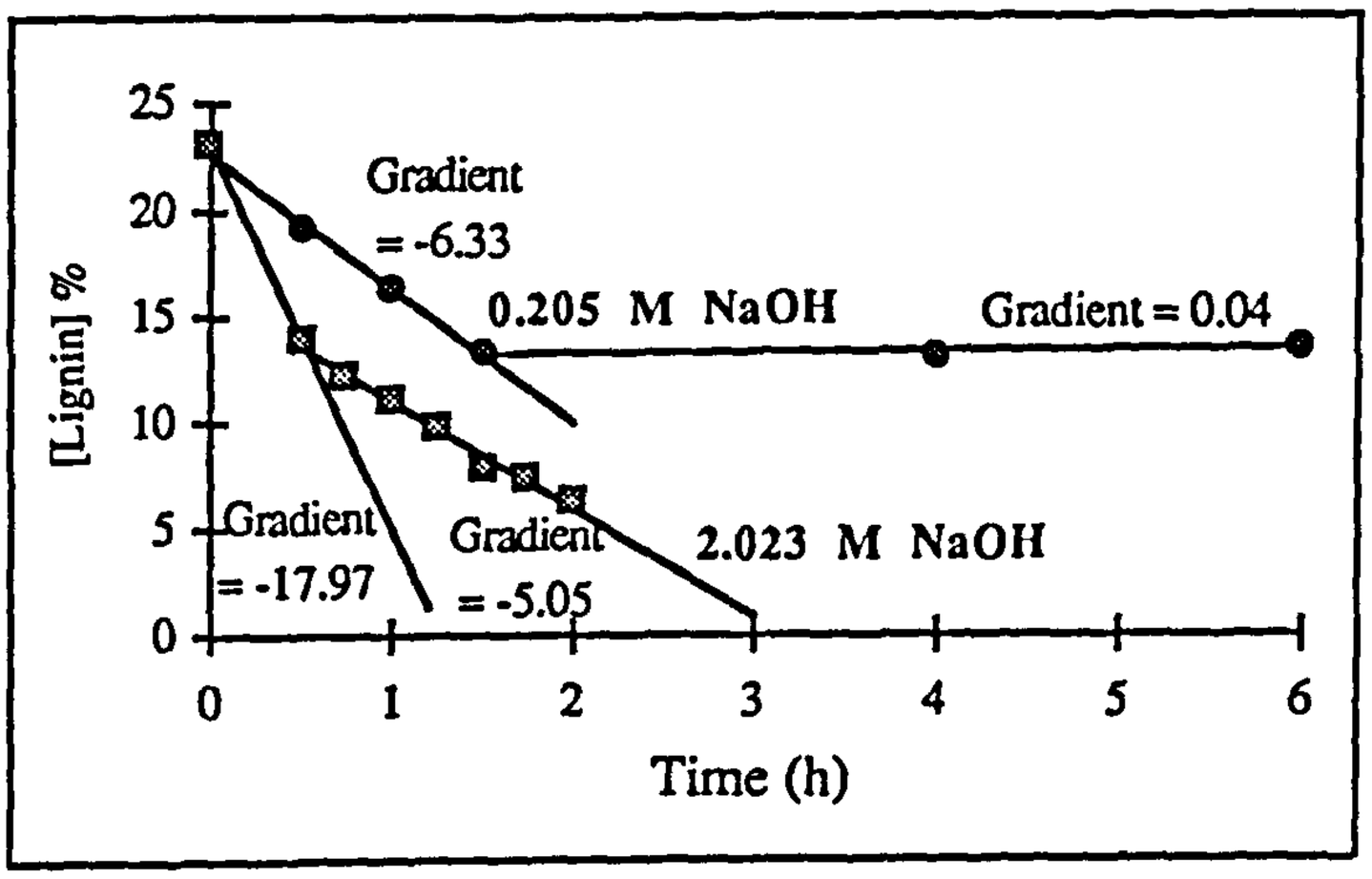


Figure 2.2.7

Plot of unreacted [lignin]% on straw (4.23g) versus cookiing time at 80 °C for bulk and residual reaction phases.

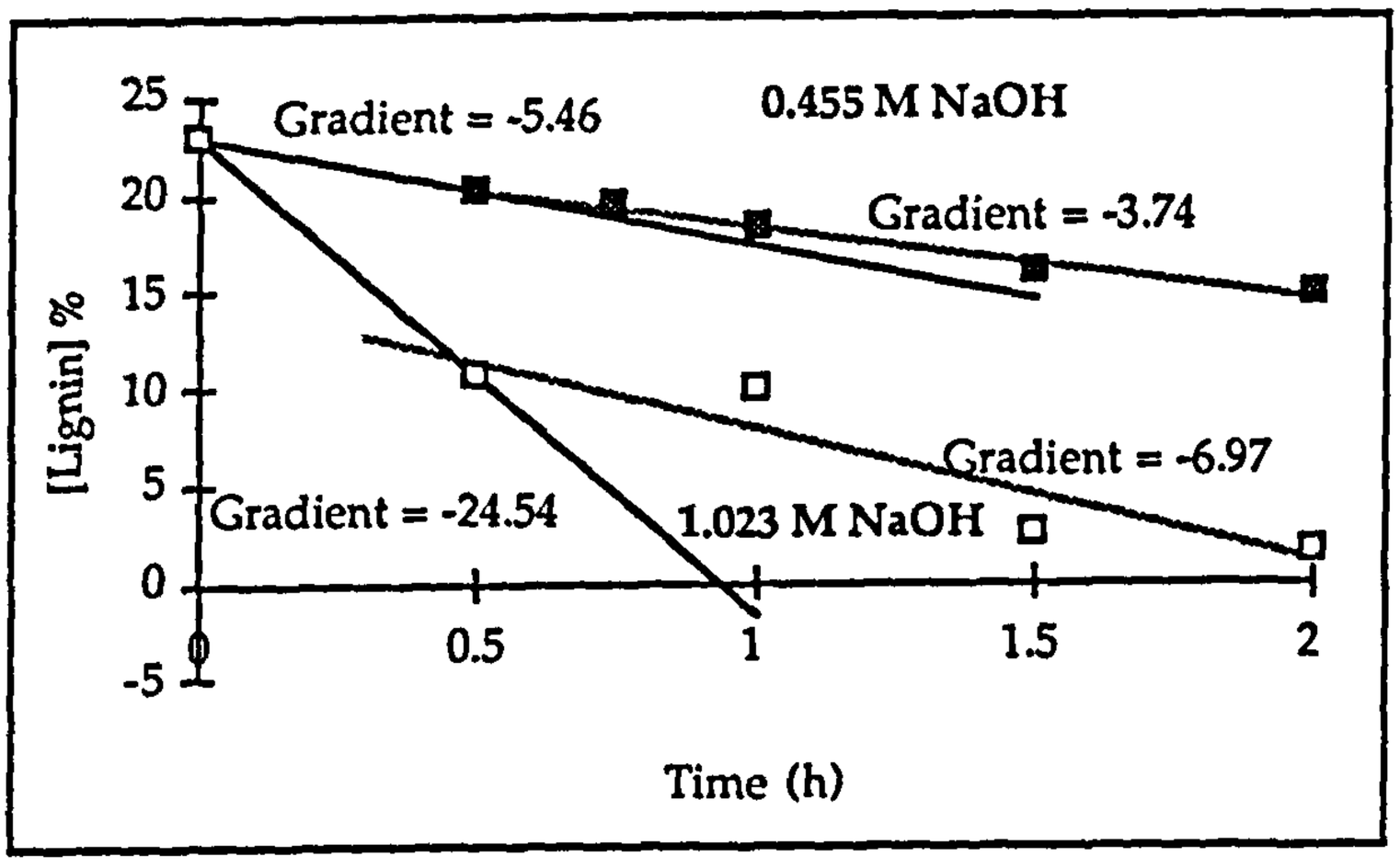


Figure 2.2.8

Plot of unreacted [lignin]% on straw (4.23g) versus cooking time at 80 °C for bulk and residual reaction phases.

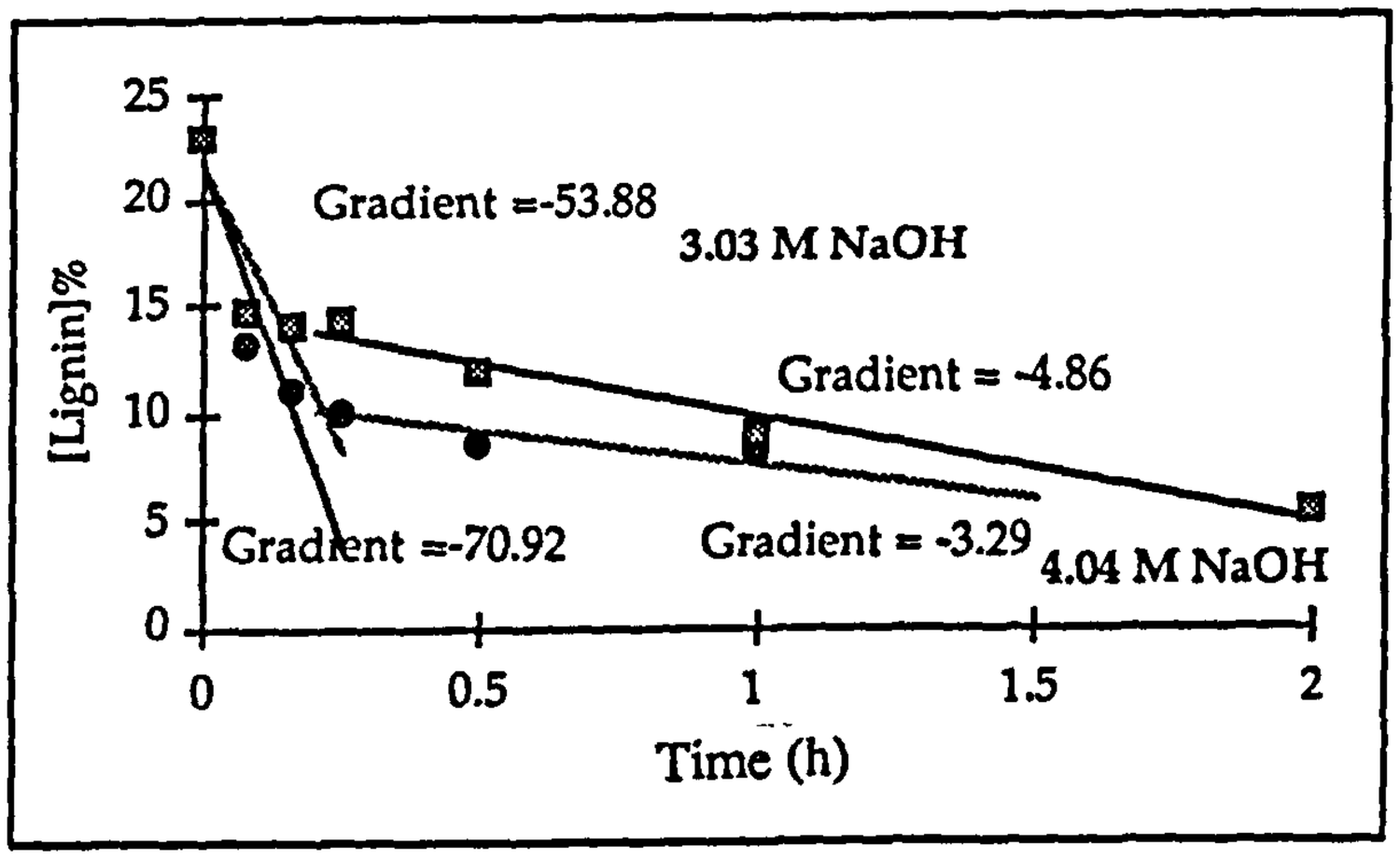


Figure 2.2.9

Plot of unreacted [lignin]% on straw (4.23g) versus cooking time at 80 °C for bulk and residual reaction phases.

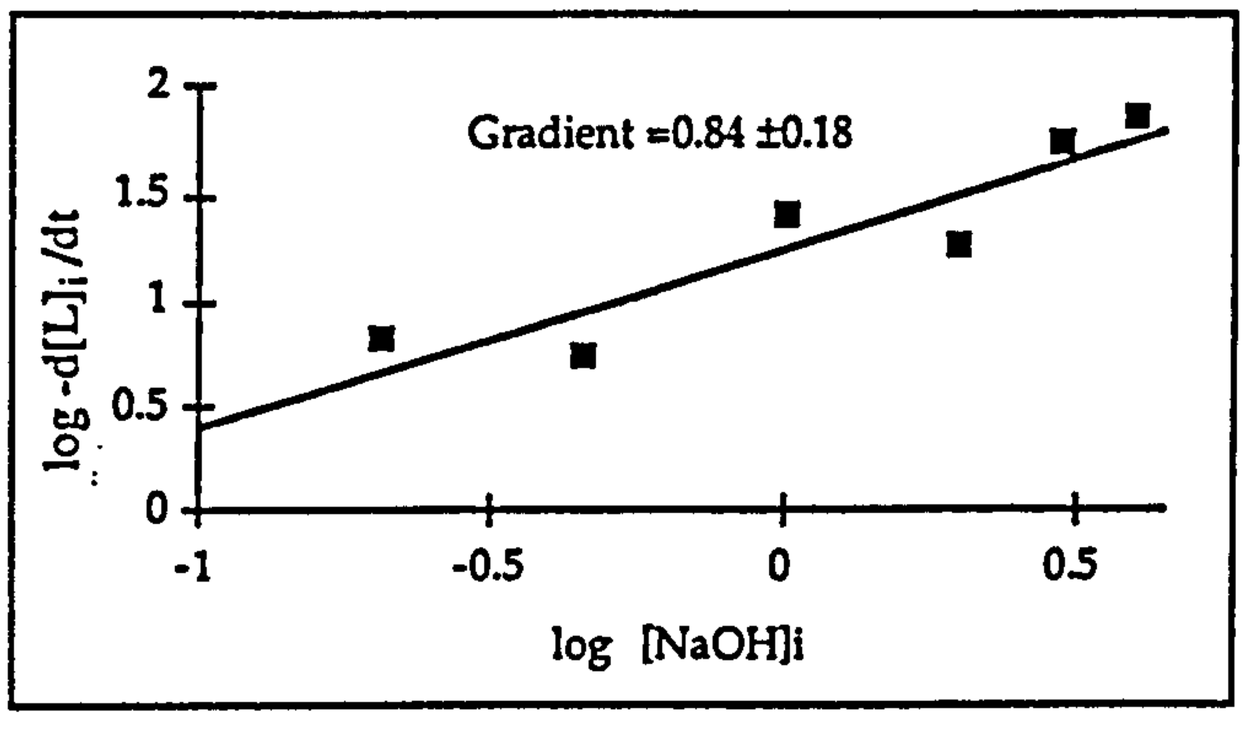


Figure 2.2.10

Plot of log initial rate $-d[L]_i/dt$ versus log $[NaOH]_i$ for bulk reaction phase and the gradient equals the order of reaction with respect to caustic

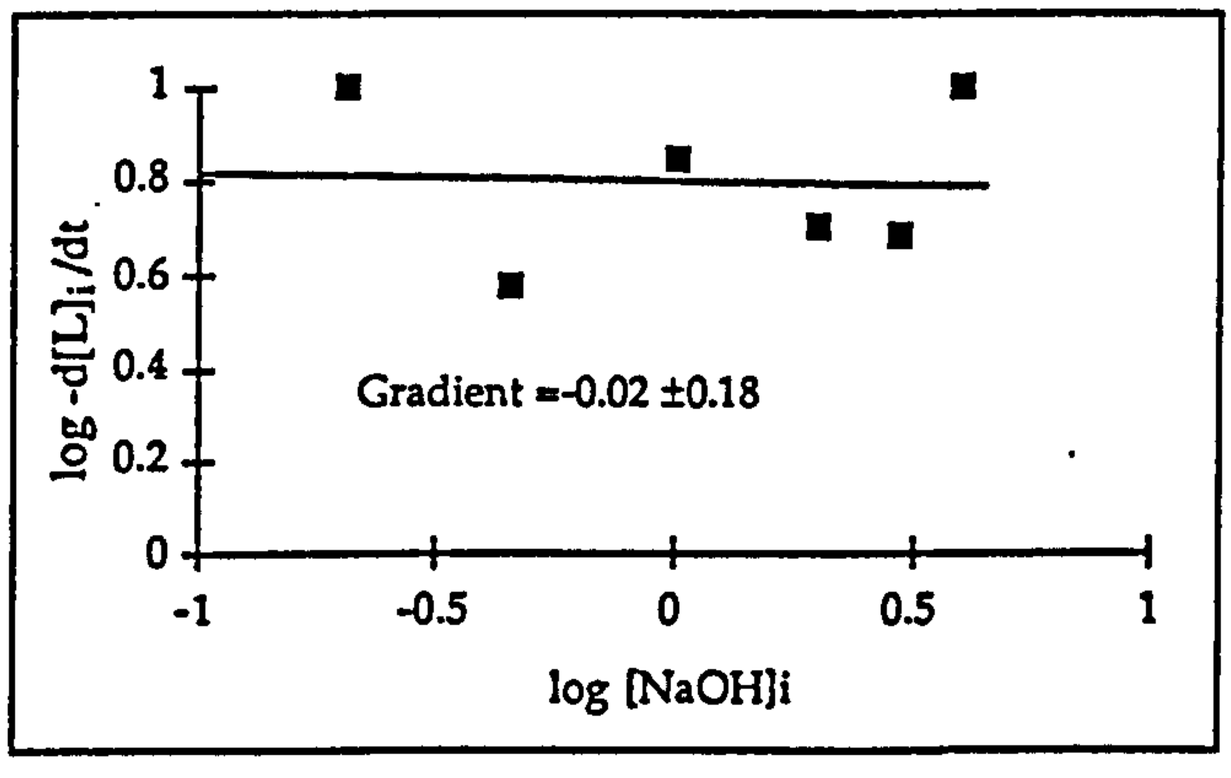


Figure 2.2.11

Plot of log initial rate $-d[L]_i/dt$ versus log $[NaOH]_i$ for residual reaction phase and the gradient equals the order of reaction with respect to caustic

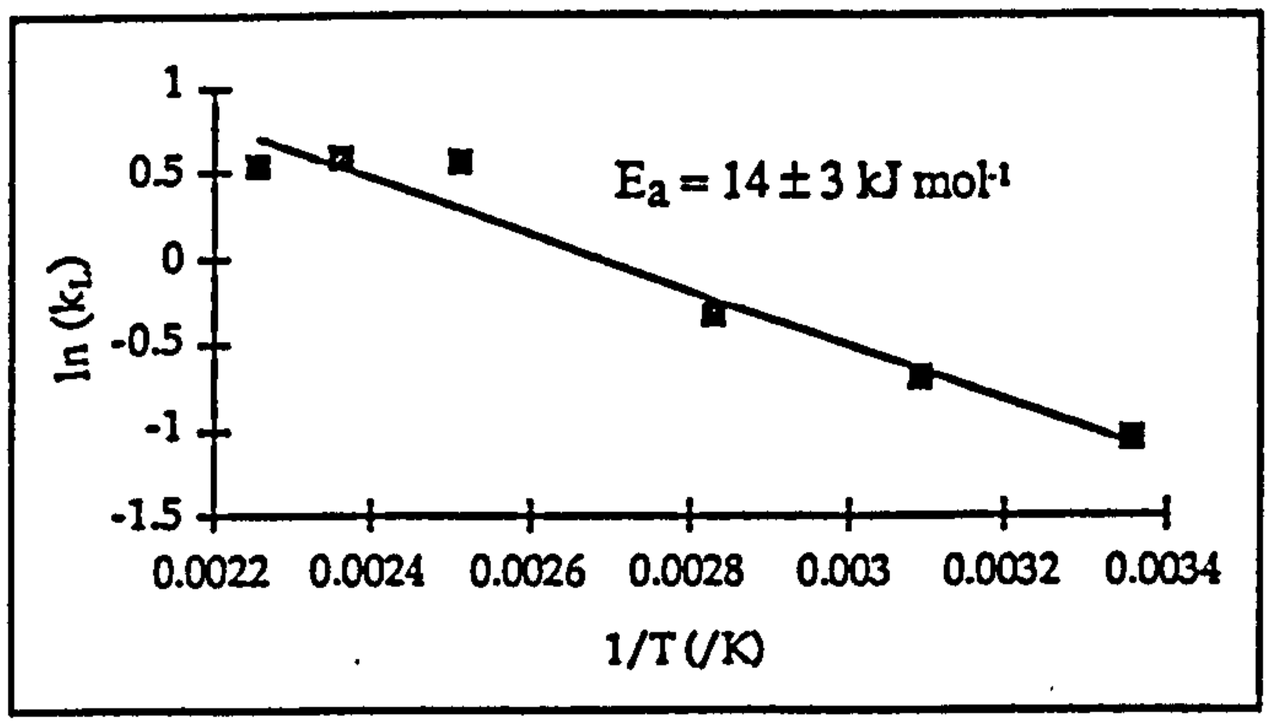


Figure 2.2.12

Arrhenius plot of ln k_L versus 1/T for bulk phase reaction of delignification

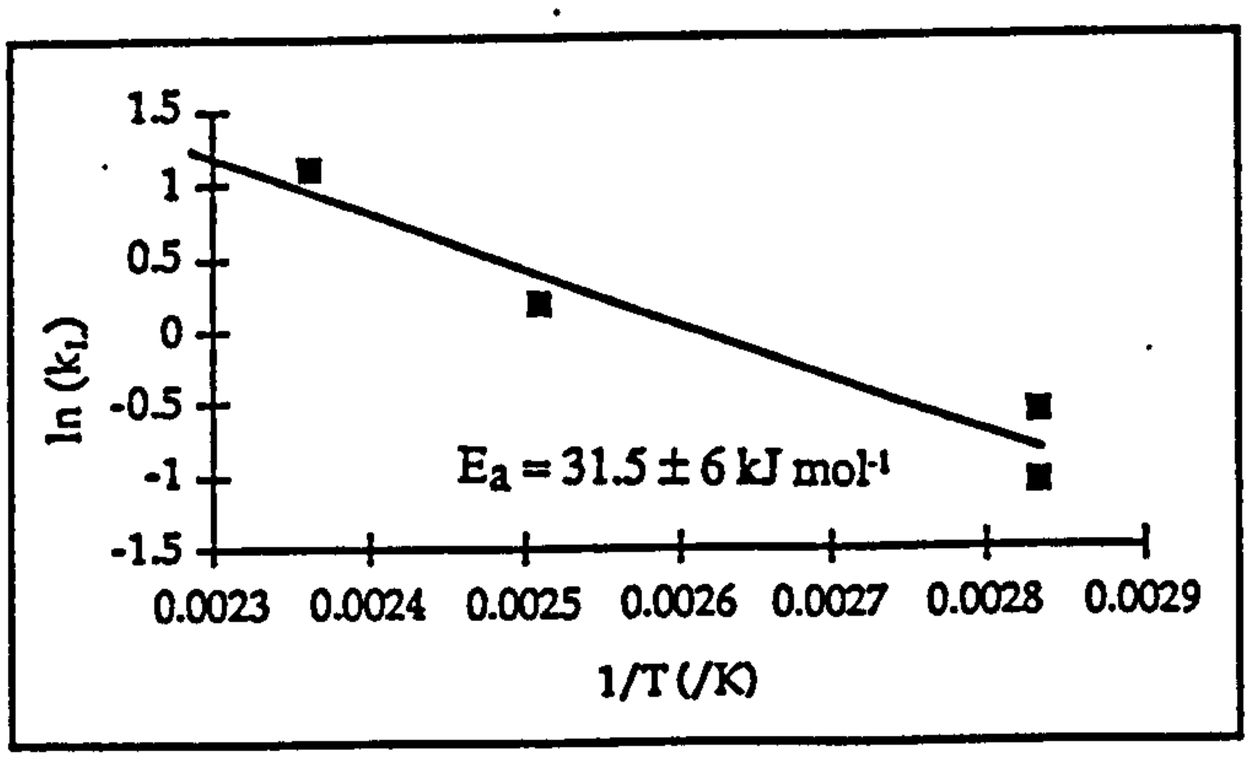


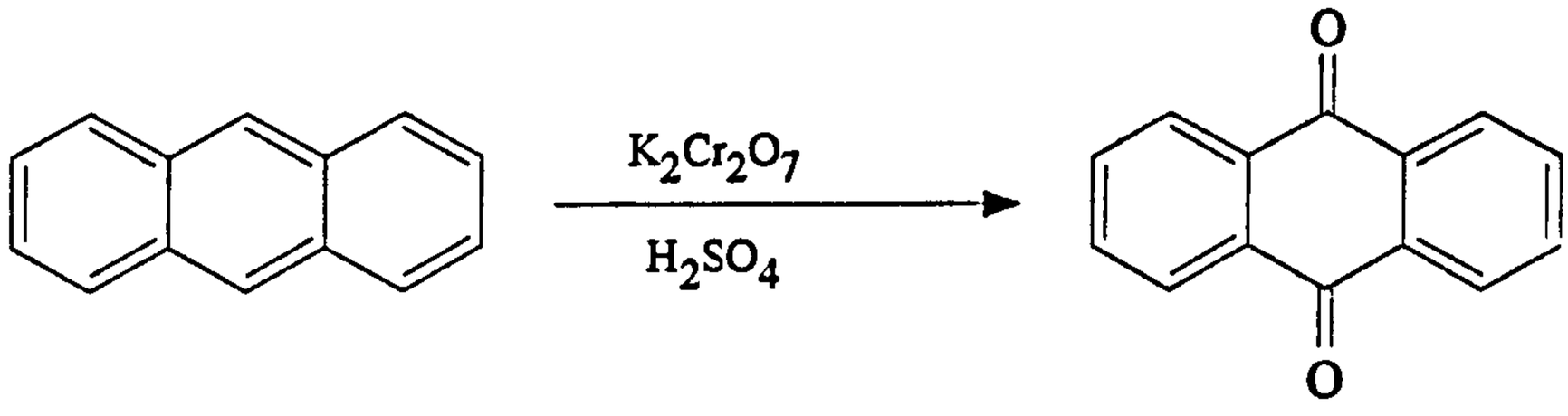
Figure 2.2.13

Arrhenius plot of ln k_L versus 1/T for residual phase reaction of delignification

2.3 Effect of Catalyst On The Rate Of Delignification

2.3.1 Introduction

9,10-anthraquinone (AQ) is a product of oxidation of anthracene. The chemical reaction is as follows:



Anthracene

9,10-Anthraquinone

Figure 2.3.1 Oxidation of anthracene in presence of acid to 9,10-anthraquinone (Morrison and Boyd, 1973)

In recent times, AQ has found application as a catalyst in pulp manufacture for papermaking. It is reported that AQ accelerates the rate of the delignification process in the wood pulping and paper industries especially in neutral sulphite cooking of pine (*Pinus radiata*) so that the kappa number (this is a widely used measure of the quality of the pulp) drops by a half under the same cooking conditions without AQ (Kettunen et al., 1979; Virkola et al., 1981). It is also reported that using AQ leads to the reduced consumption of the cooking liquor both in the bulk (main reaction stage) and residual phases (Ojanen et al., 1982) with a higher rate of delignification in the bulk phase. However, the mechanism of how AQ reduces cooking time and enhances delignification in pulping is still unknown (Shafi et al., 1993)

The development of pulp technology employing AQ has given an additional incentive for research on changes of lignin structure under alkaline cooking conditions (Evstigeneyev et al., 1992).

Extensive studies have been carried out on the effect of AQ on pulp and paper from pulpwood, where the presence of AQ during alkaline pulping of wood chips resulted in highly beneficial effects on the properties of pulp and paper obtained and led to better delignification, high yield, better pulp quality, lower alkali consumption and decreased chemical charge (Hassan et al., 1981; Fossum et al., 1980; Goel et al., 1980 and Cameron et al., 1982).

Work on the chemistry of soda-AQ pulping, the functional composition of lignin isolated from pulpwood liquors and its physio-chemical properties concluded that AQ accelerated the cleavage of β-O-4 alkyl aryl linkages as reflected by the soda-AQ lignin having a higher content of phenolic groups than soda lignin (Obst et al., 1979). Recently it has been shown that upon digestion of the lignin model compound guaiacyl-glycol-β-guaiacyl ether (I) in soda pulping liquor with a reduced form of AQ, the major products were the cleavage fragments guaiacol (III) and 2-methoxy-4-vinyl phenol (IV) via reaction pathway (A) as in the following Figure 2.3.2. It was also observed that in the absence of the oxidized form of AQ the pathway (B) was possible and the major product of the over all reaction is vinyl ether (V) (Obst et al., 1979 and Gierer et al., 1964).

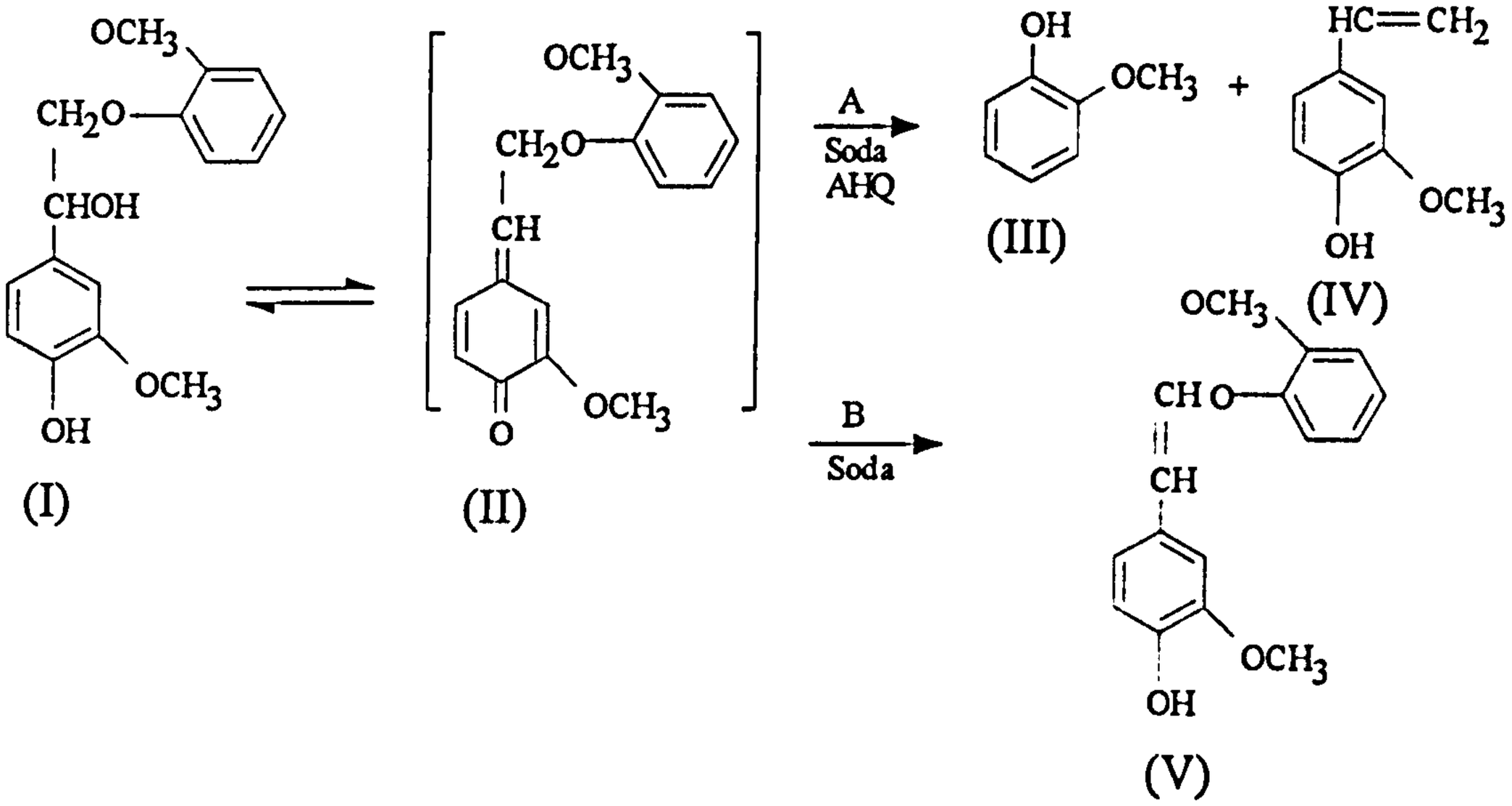


Figure 2.3.2 Reaction products upon alkaline digestion of guaiacyl-β-guaiacyl ether (Obst et al., 1979 and Landucci, 1980).

It was noted that the content of phenolic groups in lignin increased in the sequence: soda, soda-AQ and Kraft pulping (Funaoka and Abe, 1985). It is reported, on the basis of following product distribution from the model reactions, and upon analysis of the isolated lignin, that the accelerated delignification in soda-AQ cooks resulted from enhanced β-ether cleavages of free phenolic β-ether units; these units would include both the initial free phenolic β-ether in the original plant plus those formed during pulping as a result of the cleavage of β-ether bonding (Obst et al., 1979).

The phenolic hydroxyl groups have been identified as important from the standpoint of lignin dissolution during alkaline cooking as the compounds that accelerate alkaline delignification (sodium sulfide and anthraquinone) promote the formation of these phenolic hydroxyl groups (Lundquist et al., 1981 and Evstigeneyev et al., 1992).

In contrast to wood, very few studies have been reported in the literature for the production of pulp from non-wood plant fibres by pulping in the presence of AQ. Some

studies have reported that the presence of AQ as a catalyst during wheat straw pulping results in an improvment in the reactivity towards xanthation (Abou-state et al, 1986 and 1988).

2.3.2 Kinetic Treatment of Delignification With Anthraquinone

In order to derive rate constants for the catalyzed delignification reaction it was necessary to postulate a reaction scheme. The following basic scheme was used (Pen et al., 1989).

Reaction Scheme

1. $L + NaOH \xrightarrow{k_L} L_p$ non-catalytic delignification

   where L_p is lignin product

2. $C + NaOH \xrightarrow{k_C} C_p$ dissolution of hydrocarbons

   where C_p is hydrocarbon products

3. $C + AQ \rightarrow C_{ok} + AHQ$ catalyst reduction

   where C_{ok} is the product of the oxidation of hydrocarbons

4. $C_p + AQ \rightarrow C_{ok} + AHQ$ catalyst reduction

5. $L + AHQ + NaOH \xrightarrow{k_{Lk}} L_p + AQ$ catalytic delignification

6. $AHQ + L_p \xrightarrow{k_{AQ}} R$ poisoning reaction

$$-\frac{dL}{dt} = k_L [L]^m [NaOH]^n + k_{Lk} [L]^m [NaOH]^n [AHQ]^p$$

Following Pen et al., 1989,

$$[AHQ] = [AQ]_0 \times e^{-kAQxt}$$

$$\therefore \quad -\frac{dL}{dt} = k_L [L]^m [NaOH]^n + k_{Lk} [L]^m [NaOH]^n [AQ]_0^p \times e^{-kAQxt}.$$

At time ≈ 0, and taking m = 1 and n = 0.8 (see Section 2.2),

$$-\frac{d[L]_i}{dt} = k_L [L]_i [NaOH]_i^{0.8} + k_{Lk} [L]_i [NaOH]_i^{0.8} [AQ]_0^p,$$

where $[L]_i$ is the initial lignin concentration and $[NaOH]_i$ is the initial caustic concentration.

$$\therefore -\frac{d[L]_i}{dt} - k_L [L]_i [NaOH]_i^{0.8} = k_{Lk} [L]_i [NaOH]_i^{0.8} [AQ]_0^p$$

$$\therefore \log\left(-\frac{d[L]_i}{dt} - k_L [L]_i [NaOH]_i^{0.8}\right) = \log\left(k_{Lk} [L]_i [NaOH]_i^{0.8}\right) + p \log [AQ]_0.$$

Hence, a plot of $\log\left(-\frac{d[L]_i}{dt} - k_L[L]_i[NaOH]_i^{0.8}\right)$ versus $\log [AQ]_0$ is a straight line with slope p and intercept $\log\left(k_{Lk} [L]_i [NaOH]_i^{0.8}\right)$.

2.3.3 Results And Discussion

Plots for lignin % versus times are given in Figures 2.3.3-2.3.12 at 25 °C, 80 °C and 170 °C with anthraquinone 0.0013-0.013 mol dm^{-3} and caustic 0.202-2.02 mol dm^{-3}.

Table 2.3.1 Data for the effect of catalyst.

Figure No.	Temp °C	[AQ] mol dm^{-3}	[NaOH] mol dm^{-3}	$[L]_i$ % on straw	Extent of Reaction L dissolved %	
					0.5 h	1hr
2.3.3	25	0	2.02	22.9	27.7	44.8
2.3.4	25	0.0013	2.02	22.9	35.5	46.4
2.3.5	80	0	2.02	22.9	39.2	51.3
2.3.6	80	0.0013	2.02	22.9	34.8	60.5
2.3.7	80	0	0.20	22.9	17.0	27.9
2.3.8	80	0.0013	0.20	22.9	12.0	14.7
2.3.9	80	0.0065	0.20	22.9	4.60	10.3
2.3.10	80	0.013	0.20	22.9	16.7	28.7
2.3.11	170	0	2.02	22.9	70.1	76.0
2.3.12	170	0.0013	2.02	22.9	60.4	92.2
-	170	0.013	2.02	22.9	lignin decomposition	

The extent of delignification at 0.5h and 1h extracted from Figures 2.3.3-2.3.12 are summarized in Table 2.3.1. The results as shown in the Table are difficult to interpret, but it is clear that, under selected conditions, AQ has a catalytic effect on the rate of delignification. Runs with the high level of caustic after 1h reaction time in the presence of AQ show a greater extent of delignification than runs without AQ, particularly at higher

temperature (e.g., at 170 °C, 92% delignification was produced with AQ compared with 76% without AQ). However, with only 0.5h run time the reverse is true at both 80 °C and 170 °C. With the lower levels of caustic at 80 °C, there was no increase in the delignification rate even after 1h and in most cases a decrease was seen. At 170°C with the highest level of AQ (0.013 mol dm^{-3}) somewhat surprisingly all the lignin had decomposed and none was found in solution while for a concentration of AQ at a level of 0.0013 mol dm^{-3} 92% of the original lignin in the straw was found in the solution.

2.3.4 Conclusions

* Anthraquinone *does* have a catalytic effect on the rate of delignification, but in order to get the most benefit it is necessary to have excess caustic, increased temperature and >0.5h run time.

* High level of anthraquinone (10% on straw) at 170 °C results in complete decomposition of lignin.

* The general effect of anthraquinone even under the best conditions to suit the catalyst is relatively modest, as catalyst go.

In view of these rather variable results, the modest effect of anthraquinone catalyst and the relative complexity of interpreting the kinetic data as shown under the kinetic treatment, it was decided to conduct the main kinetic studies using caustic as pulping agent without anthraquinone.

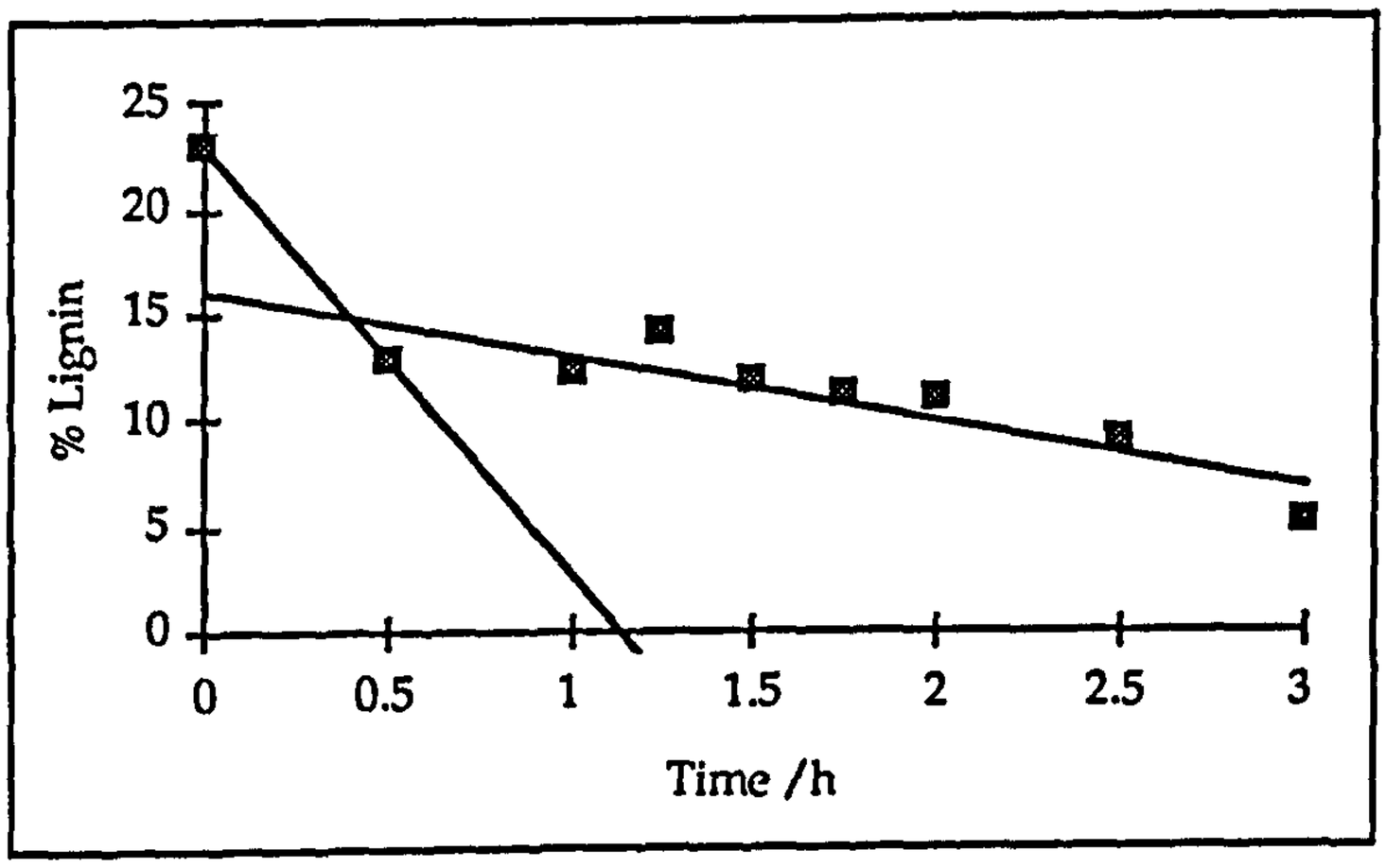


Figure 2.3.3

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 25 °C in 55 ml H_2O without anthraquinone.

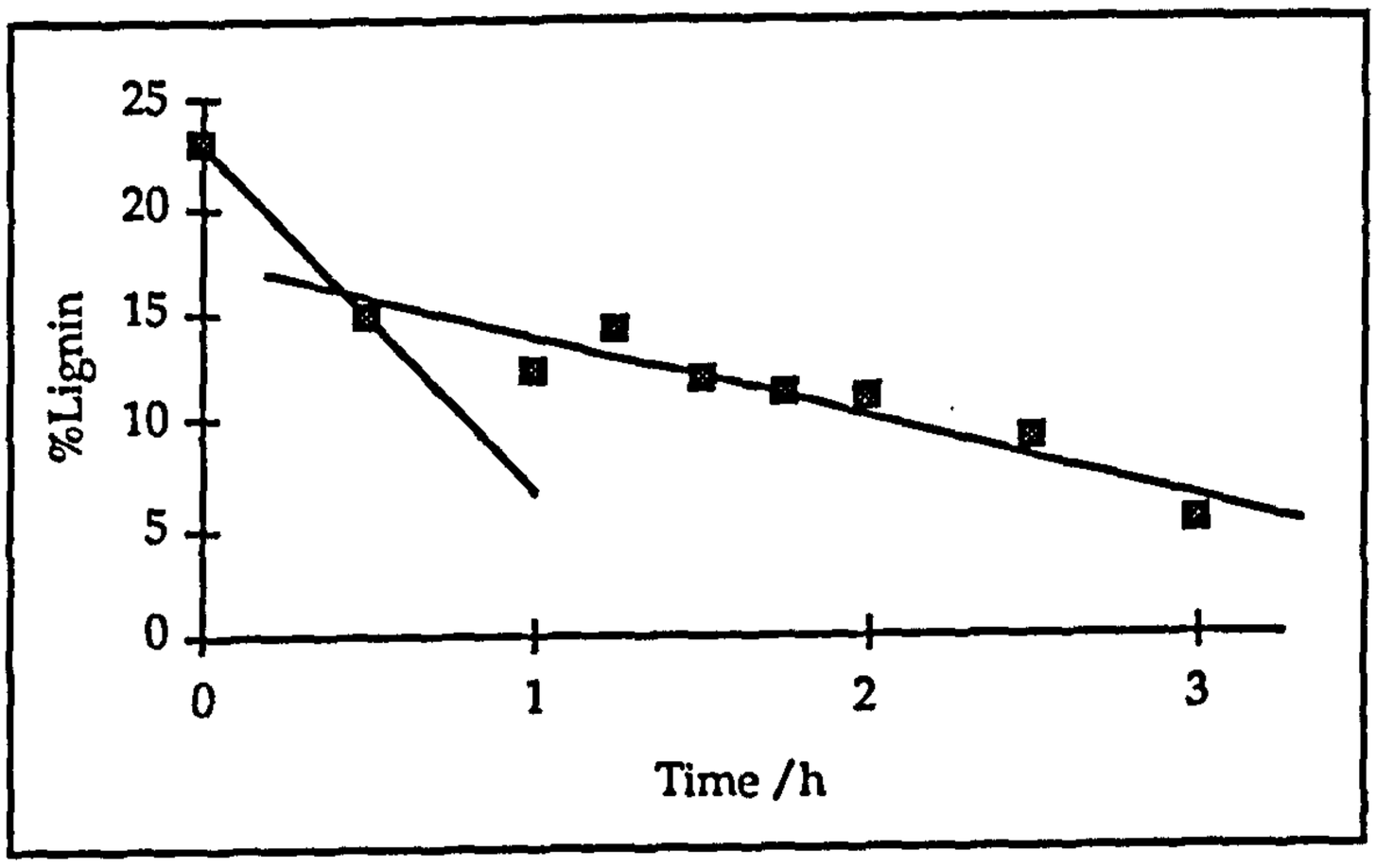


Figure 2.3.4
Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 25 °C in 55 ml H_2O with anthraquinone (0.0013 mol dm^{-3}).

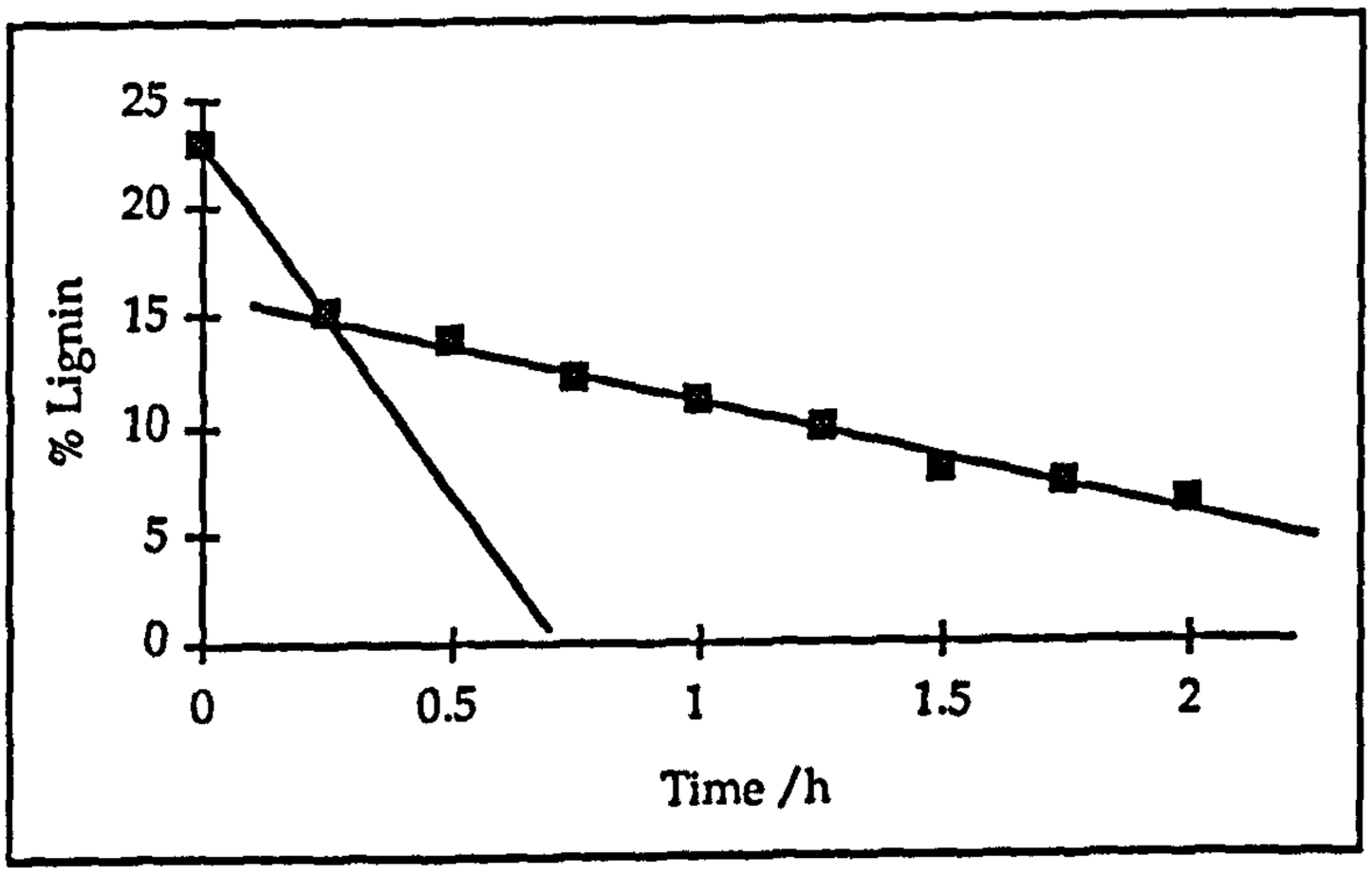


Figure 2.3.5

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 80 °C in 55 ml H_2O without anthraquinone

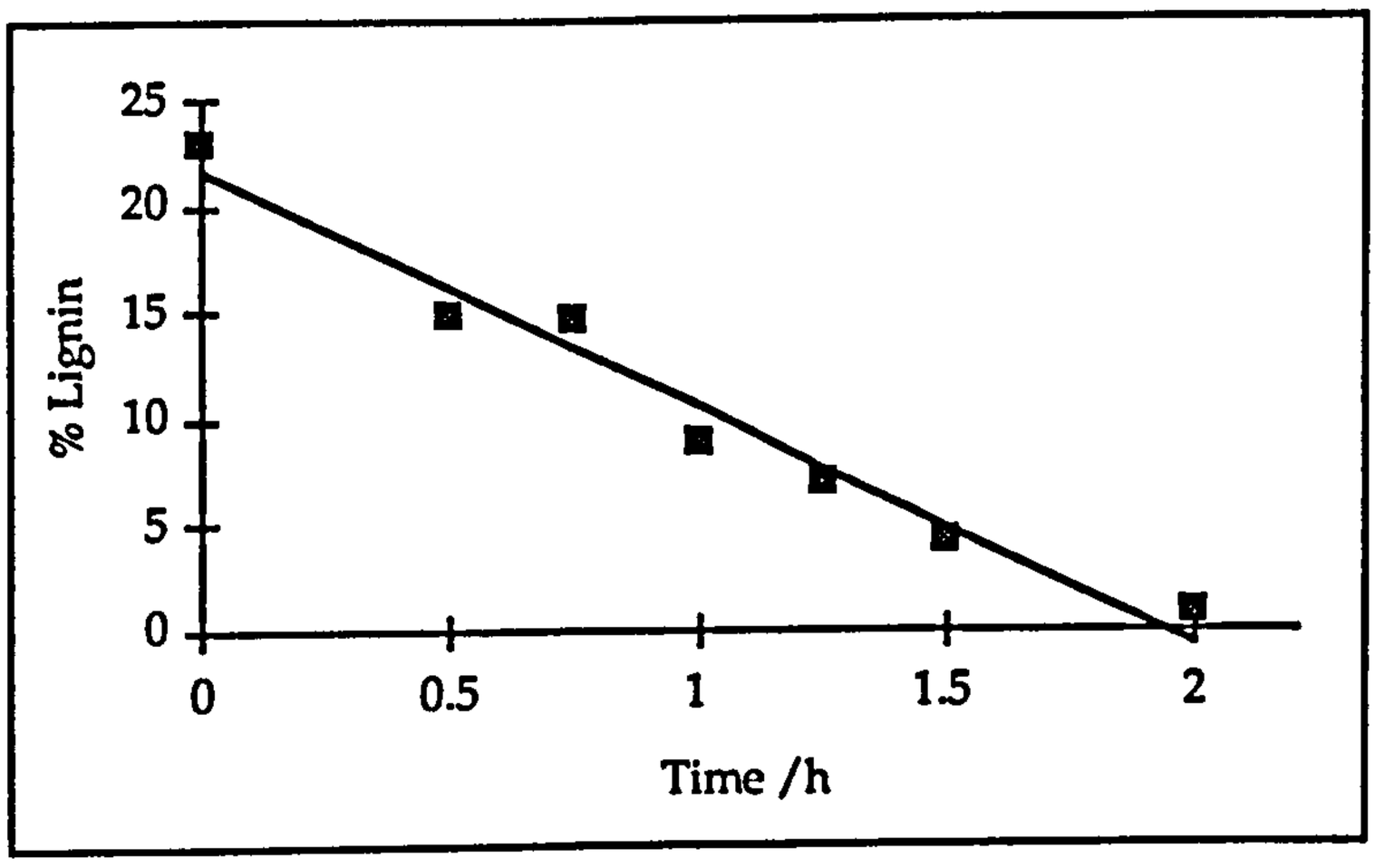


Figure 2.3.6

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 80 °C in 55 ml H_2O with anthraquinone (0.0013 mol dm^{-3}).

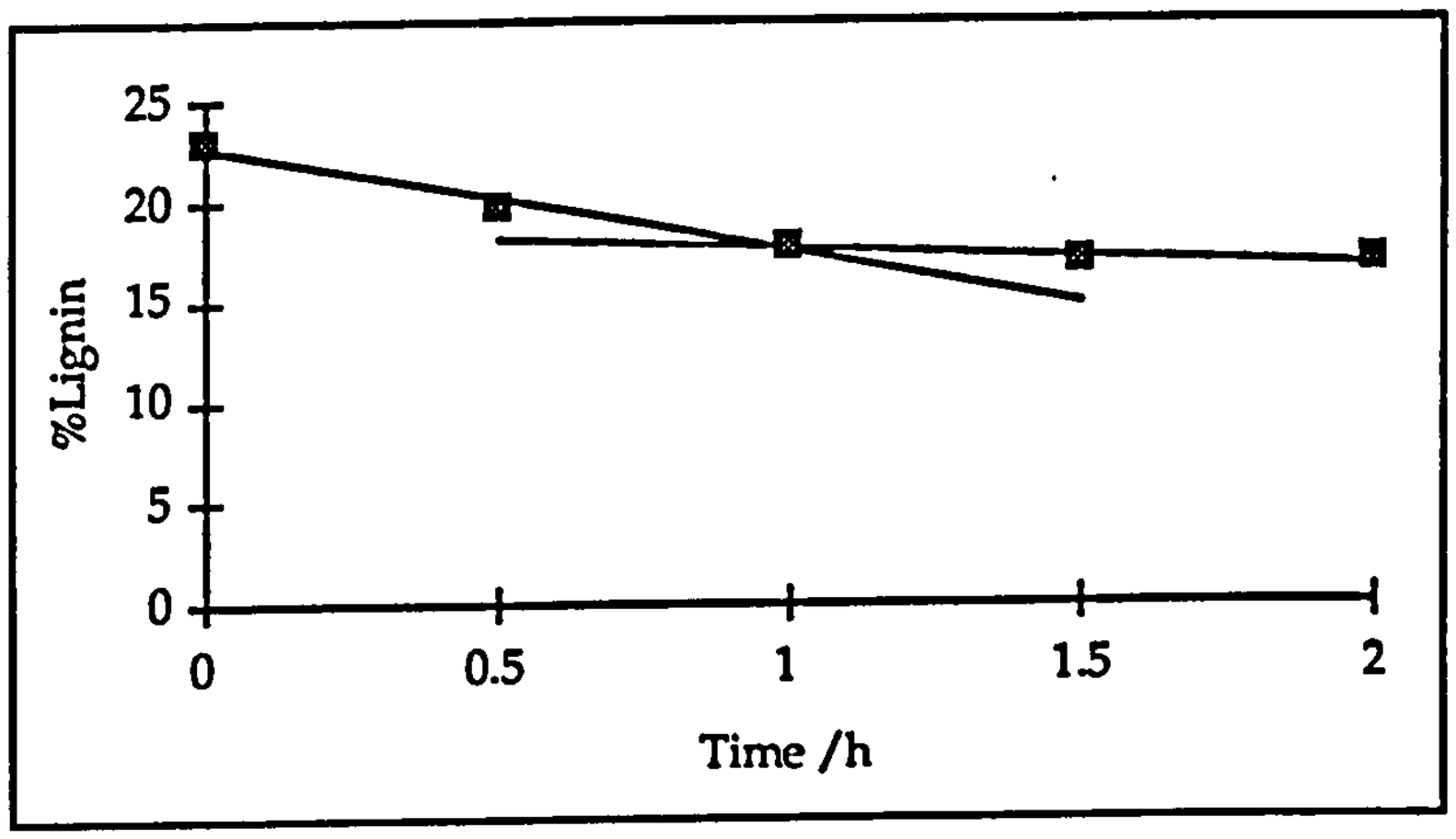


Figure 2.3.7

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (0.202 mol dm^{-3}) at 80 °C in 55 ml H_2O without anthraquinone.

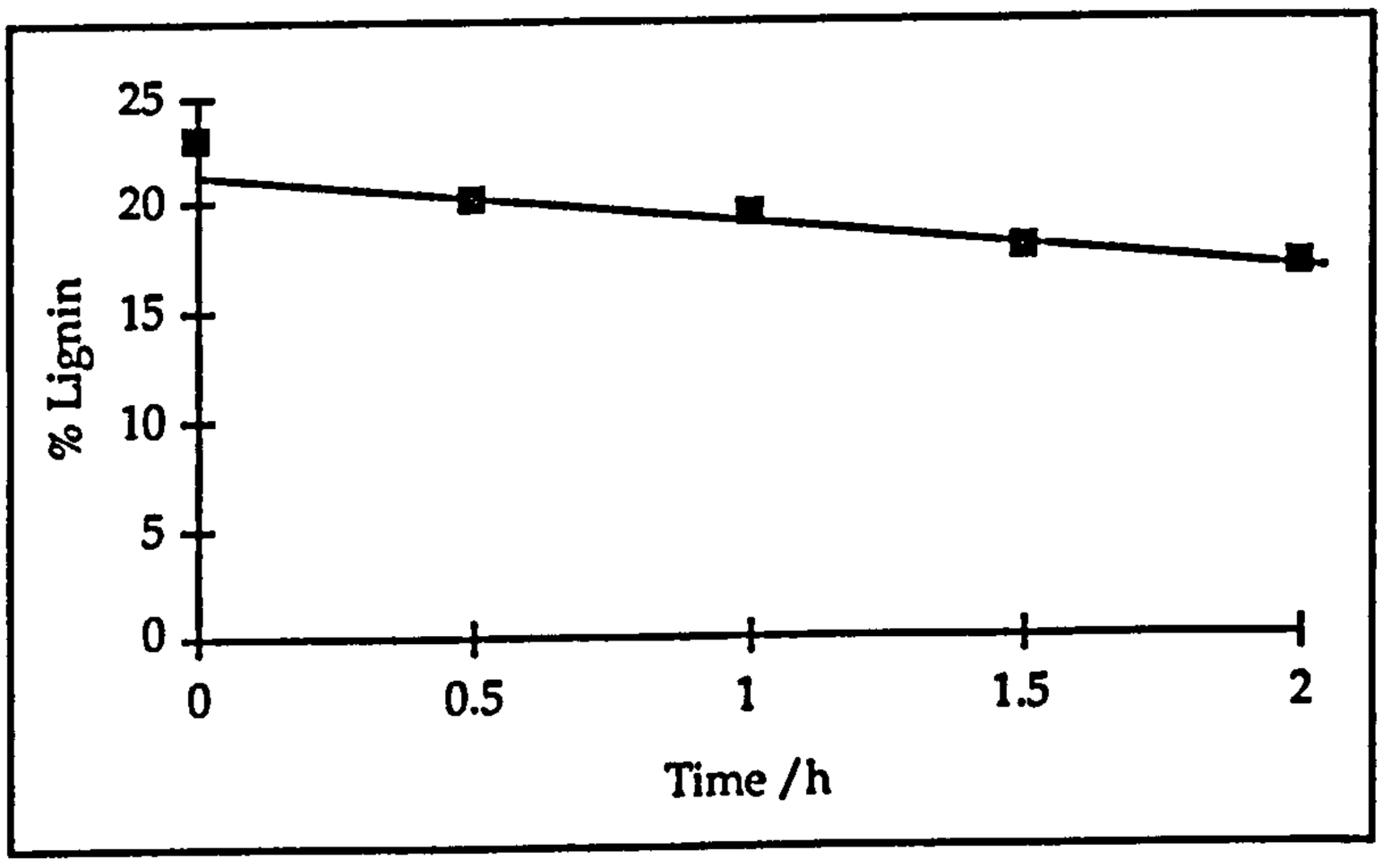


Figure 2.3.8
Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (0.202 mol dm^{-3}) at 80 °C in 55 ml H_2O with anthraquinone (0.0013 mol dm^{-3}).

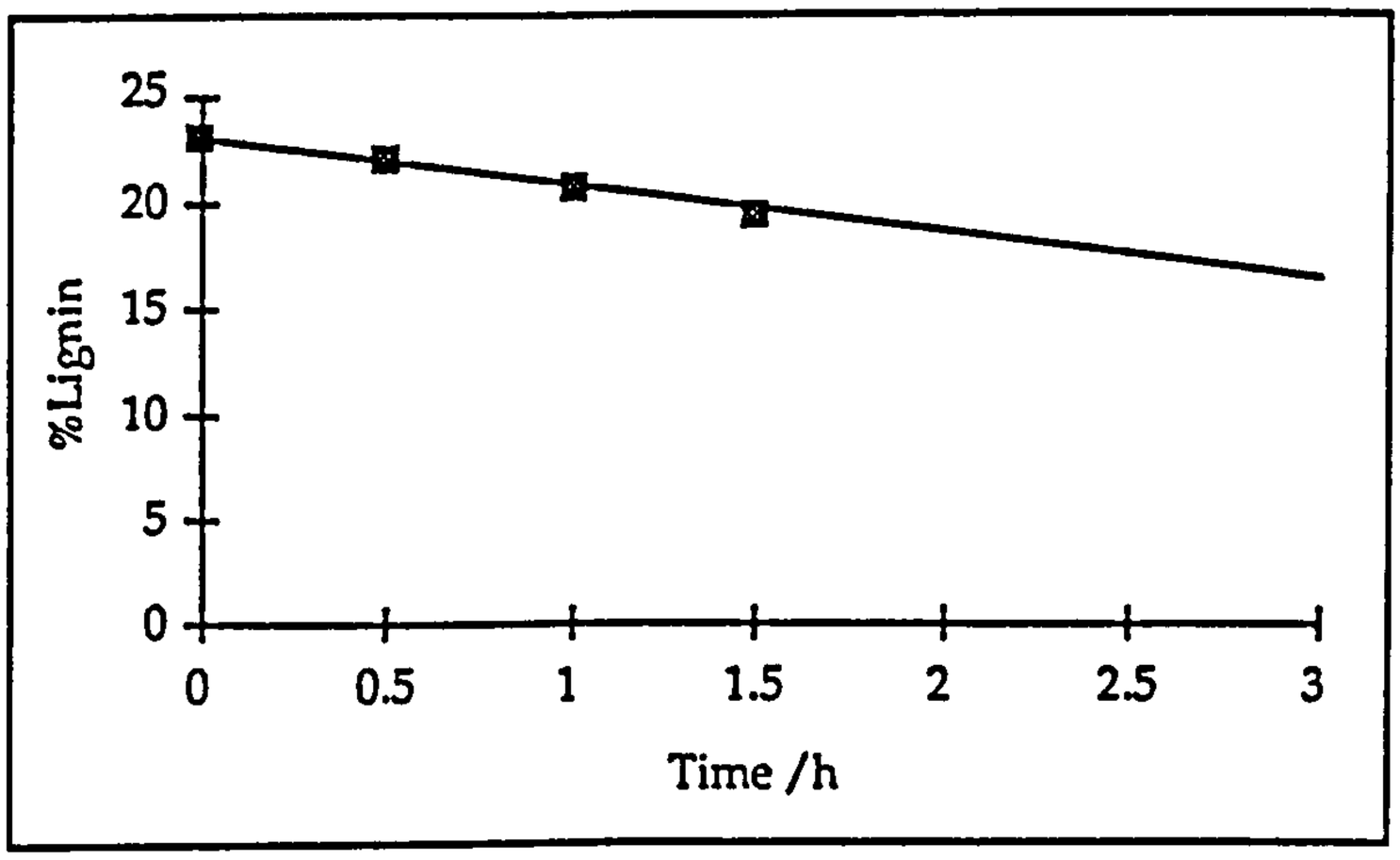


Figure 2.3.9

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (0.202 mol dm^{-3}) at 80 °C in 55 ml H_2O with anthraquinone (0.0065 mol dm^{-3}).

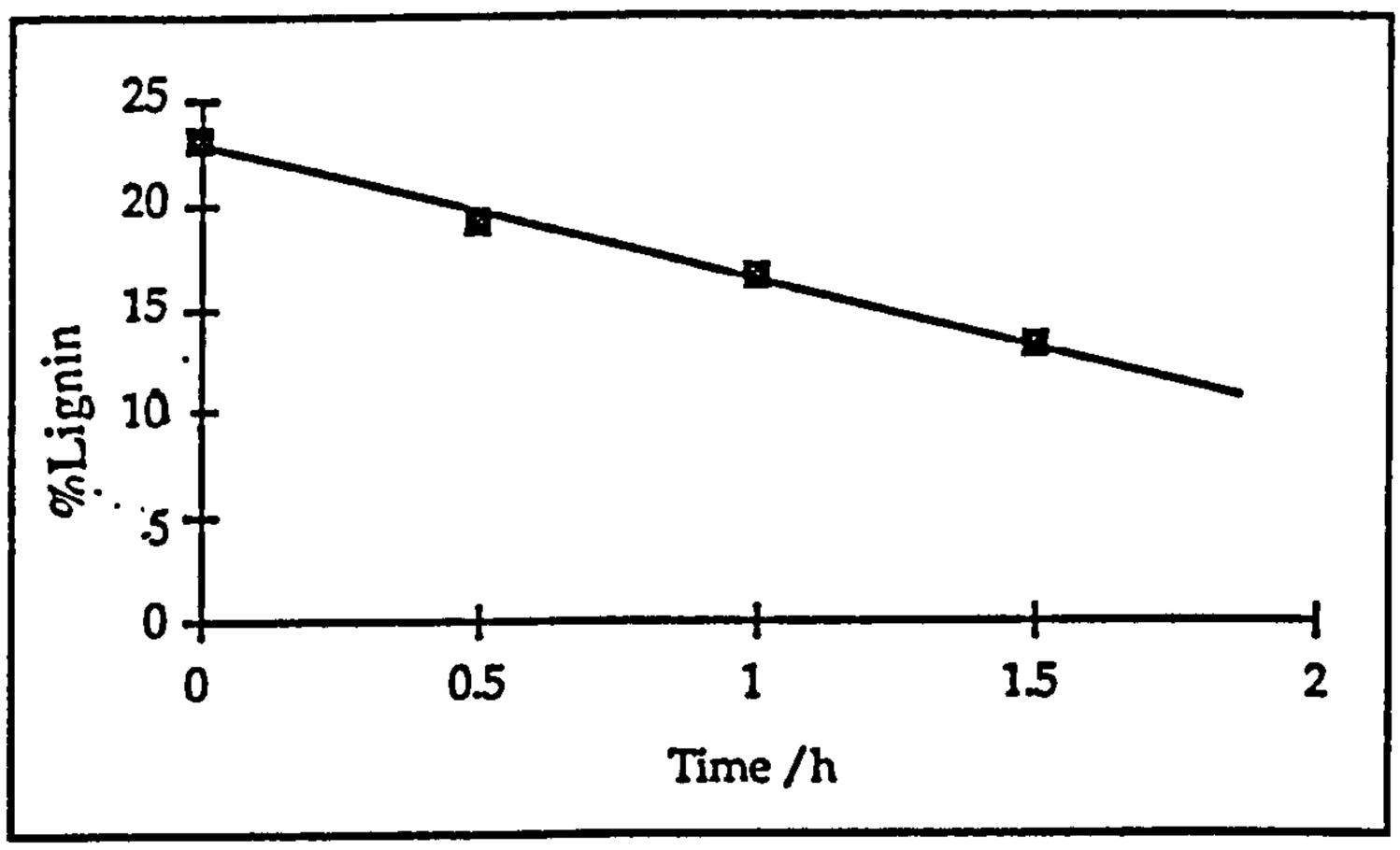


Figure 2.3.10

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (0.202 mol dm^{-3}) at 80 °C in 55 ml H_2O with anthraquinone 0.013 mol dm^{-3}).

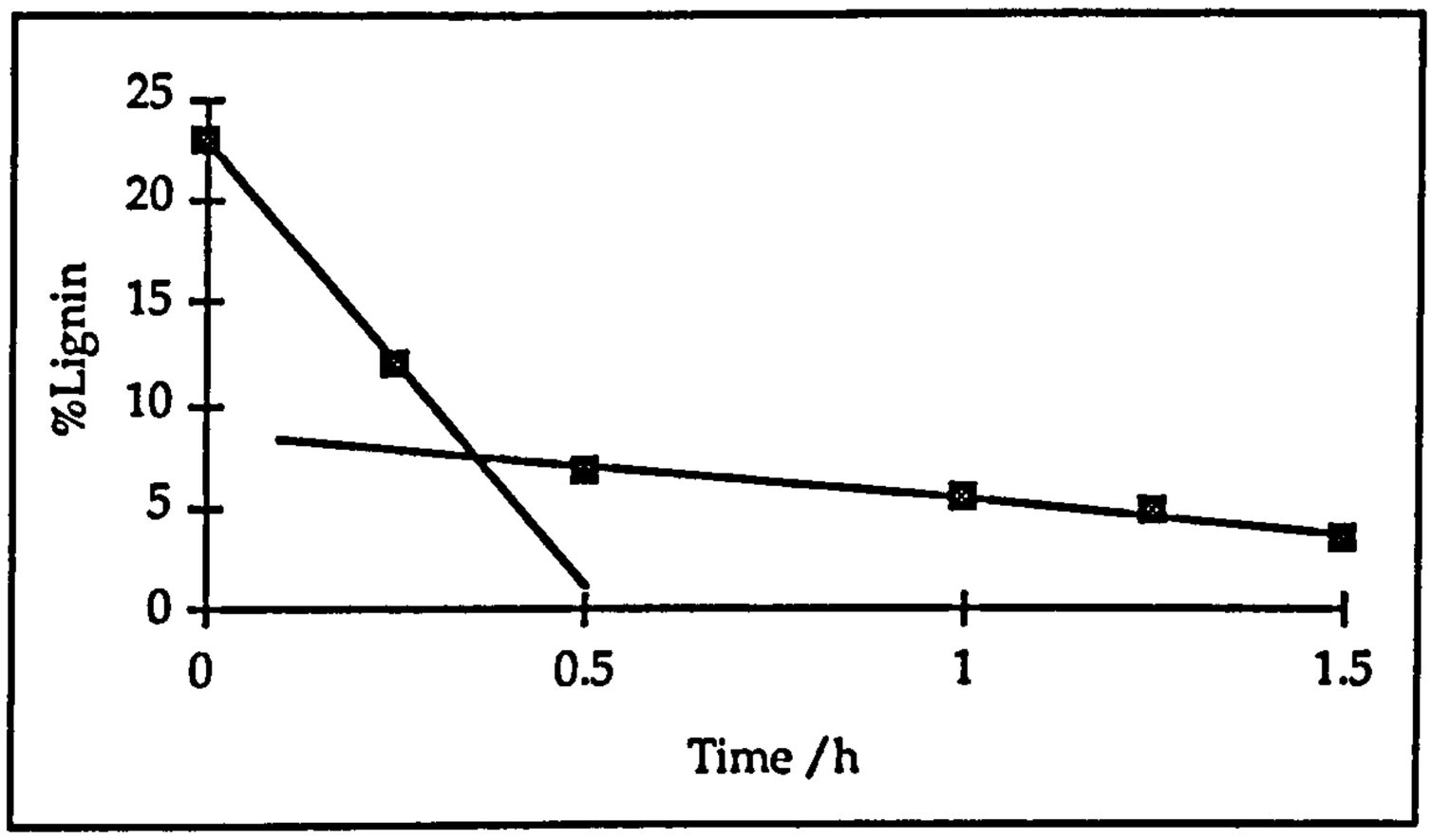


Figure 2.3.11

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 170 °C in 55 ml H_2O without anthraquinone.

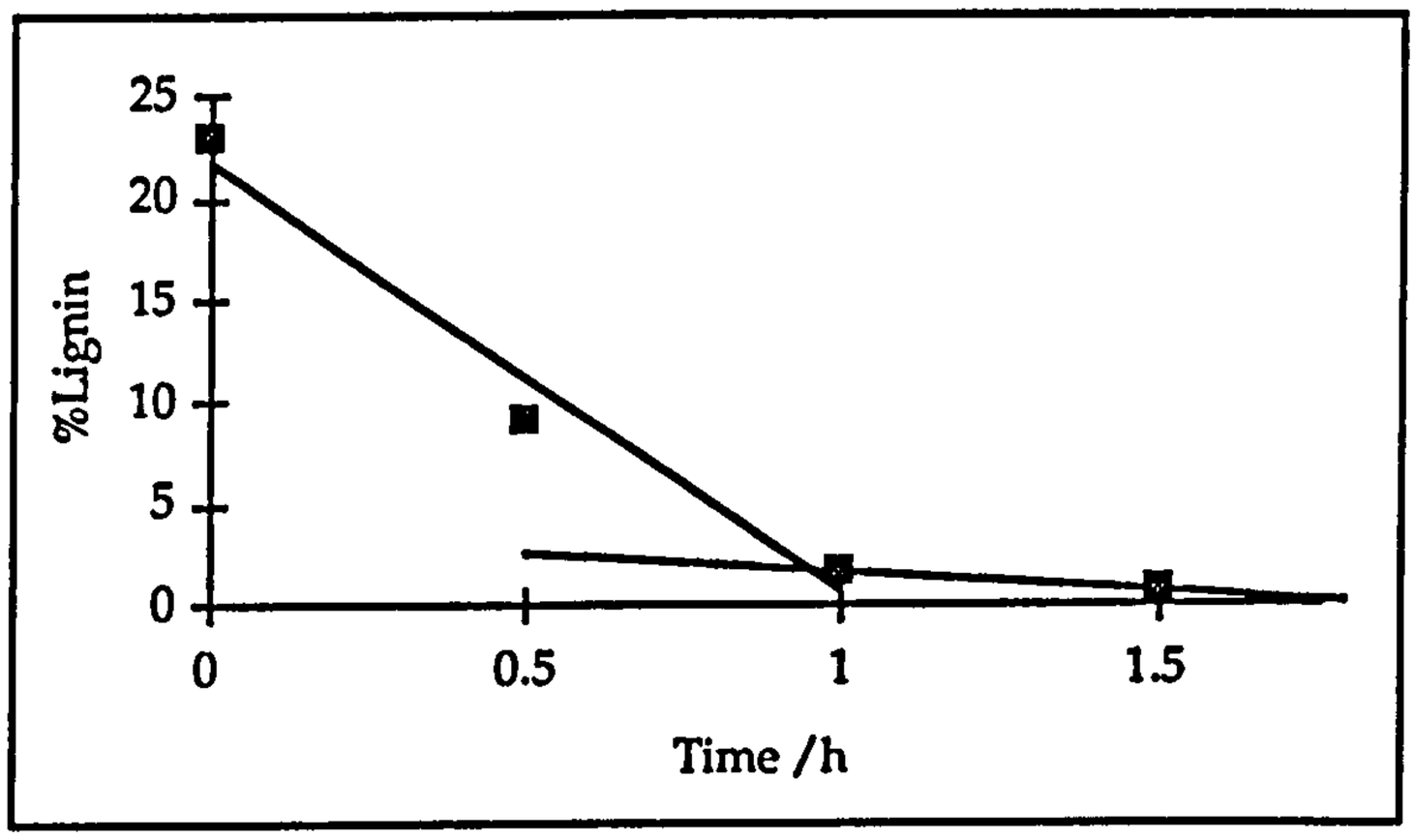


Figure 2.3.12

Plot of unreacted lignin% on straw (4.23g) versus cooking time in caustic (02.02 mol dm^{-3}) at 170 °C in 55 ml H_2O with anthraquinone 0.0013 mol dm^{-3}).

2.4 The Consumption Of Caustic During The Uncatalyzed Reaction

2.4.1 Introduction

In order to achieve a degree of delignification sufficient to allow wood or non-wood cooked materials to be reduced to fibres without vigorous mechanical treatment, a certain minimum charge of effective alkali is necessary. In the case of wood pulping, the amount of alkali required depends on the wood species and upon other factors, such as the size of the chips used (Clayton and Phelps, 1965).

A minimum concentration of alkali is required in order to keep dissolved components in solution. At alkali charges below the minimum even a large increase in the reaction times fails to produce satisfactory pulp. With too low an initial concentration the consumption of alkali during cook may result in the pH dropping too low to keep dissolved wood components in solution (Macdonald and Franklin, 1969). If the pH falls below a critical value, absorption or precipitation of lignin fragments upon the pulp can occur if the cook is prolonged, causing a decrease rather than a continuing increase in the quality of pulp, which, in turn, leads to a reduction in brightness, and increase in bleach requirements (Surewiez, 1962 and Petterson and Rydholm, 1961).

The knowledge of alkali consumption is very useful in explaining the consumptive roles of the various chemical functional groups present in lignocellulosic materials and gives information which helps explain the physico-chemical changes resulting in the treated lignocellulosic materials.

In wood, the consumption of alkali is generally rapid at the beginning of the cook. This is due to neutralization by the carboxylic acids formed as degradation products of the extracted wood hemicelluloses which occurs in the initial phases of cooking, after

which alkaline consumption is slowed down (Shah et al., 1991). The alkaline 'peeling' reaction sequence involving enolization and hydrolysis of β-alkoxycarbonyl bonds and degradation of the products of hydrolysis including isomerization as well as hydrolysis, to hydroxyl acids, are considered to be responsible for most of the alkali consumption.

As far as wheat straw is concerned the mechanism of delignification seems to be different from that of wood, and there is not a rapid initial phase of hemicellulose dissolution. Instead, initial alkali consumption is thought to be due to the saponification of uronic and acetyl esters and reaction with free carboxyl groups on the straw followed by acid neutralization of acidic products formed from alkaline degradation of cellulose, hemicellulose and lignin. Also, alkali dissolved in water is associated with the solids and left behind with them after solids separation (Pavlostathis and Gossett, 1985 and Browning, 1967).

2.4.2 Rate of Caustic Consumption With Excess Lignin

2.4.2.1 Introduction

In order to study caustic consumption in the pulping of wheat straw and obtain accurate analysis of caustic, runs were done in the metal reactor with excess straw (lignin present) and 0.0202 mol dm^{-3} caustic at different temperatures. This enabled the initial stages of delignification to be followed. The time of treatment was varied from 5min-6h at temperatures in the range 25-170 °C. Alkali consumption as a function of time was measured.

The remaining caustic after treatment of straw in the metal reactor was measured by titration with sulfuric acid. Initially, experiments for the titration of residual caustic gave variable results. This was shown to be due to strong absorption of some of the caustic by straw. Multiple washing of the pulp by water was necessarily to recover the caustic quantitatively. This was confirmed by a total sample titration (titration without solid separation) where the results corresponded to these obtained by the multiple washings method.

2.4.2.2 Kinetic Scheme

In accordance to the reaction scheme given in section 2.2,

$$-\frac{d[NaOH]_i}{dt} = k_{Lb}\left[NaOH_i - \dot{z}\right]^n[L]_i^m + k_{Cb}\left[NaOH_i - z\right]^s[C]_i^r$$

$$= k''_{Lb}\left[NaOH_i - z\right]^n + k''_{Cb}\left[NaOH_i - z\right]^s,$$

where k''_{Lb} and k''_{Cb} are the rate constants for the initial reaction of caustic with lignin and carbohydrate respectively, $k''_{Lb} = k_{Lb}[L]_i^m$ and $k''_{Cb} = k_{Cb}[C]_i^r$ and z is the amount of caustic reacted at any time.

Now n = 0.8 and s = 0.6 (see Chapters 2 and 4). For simplicity we assume that s = n.

Then,

$$-\frac{d[NaOH]_i}{dt} = k''_{Lb}\left[NaOH_i - z\right]^n + k''_{Cb}\left[NaOH_i - z\right]^s$$

$$= \left[NaOH_i - z\right]^n\left(k''_{Lb} + k''_{Cb}\right),$$

Therefore, $\log -\frac{d[NaOH]_i}{dt} = n \log\left[NaOH_i - z\right] + \log\left(k''_{Lb} + k''_{Cb}\right)$.

Hence, a plot of $\log -\frac{d[NaOH]_i}{dt}$ versus $\log [NaOH_i - z]$ will yield a straight line of slope n and intercept $\log\left(k''_{Lb} + k''_{Cb}\right)$. Clearly this will give the sum of two rate constants but not their individual values.

2.4.2.3 Results and Discussion

The above kinetic treatment results in the determination of the sum of two rate constants, not individual values. However, a semi-quantitative approach can give useful results. Figures 2.4.1-2.4.3 show plots of residual [NaOH]% on straw versus time with an initial charge of 0.045g NaOH, 4.23g straw and 55 ml water at 25 °C, 80 °C and 170 °C.

These graphs all show that there is a very rapid initial reaction of caustic in the first 10 minutes. The rates of the reaction are independent of temperature, as shown by the initial slopes of the plot which are more or less constant for 25 °C, 80 °C and 170 °C. Also, the quantities of caustic reacted in the initial stage are similar and approximately 80% of the initial caustic is consumed. Given the extent of the early depletion of the caustic with the relatively small initial caustic charge of 0.045g, the bulk rate of consumption in later stages of the reaction is very low corresponding to a very slow delignification stage.

The fast initial uptake of caustic is consistent with the results of Pavlostathis and Gossett (1985) who found the same pattern at 25 °C: with an initial charge of 2g NaOH per 100g of straw, 0.6g caustic was consumed within 10 minutes or less, followed by a much slower consumption. These authors concluded that the initial phase was mainly due to caustic neutralization of free acyl, carbonyl and other acidic groups on the straw. Subsequent consumption was associated with the liberation of acid groups resulting mainly from the hydrolysis of acyl-carbonyl esters as part of the solubilization of lignin and carbohydrates. In other words, the first few minutes consumption of caustic is mainly in neutralization readily available free acid groups.

As further evidence for this initial neutralization step, 4.23g straw in 55 ml water were titrated with 0.1M caustic solution using phenolphthalein as an indcator. The titre obtained before the system turned basic was equivalent to an uptake of 0.02g caustic equivalent to 0.005g NaOH per g straw. This figure of 0.02g compares with consumption of 0.03g shown in Figure 2.4.1 after 10 minutes reaction time. Thus, with

an initial charge of 0.045g of NaOH and 4.23g straw, two thirds of caustic is consumed within 10 minutes by the neutralization of free groups and one third in other ways, presumably more directly associated with the dissolution of lignin and carbohydrates.

It should be stressed that these results are highlighted by the low initial charge of caustic (0.045g for 4.23g straw). At higher level of caustic (0.45g or more), the effect of the initial acid groups neutralization step should be small as there are a finite number of groups which, once neutralized, will not affect any further caustic consumption. This is seen in Section 2.4.

2.4.2.4 Conclusions

* There is a rapid initial caustic consumption of 0.005g per g of straw within 10 minutes of reaction, thought to be due to neutralization of readily available free acid groups on the straw.

* Untreated caustic is strongly absorbed by straw and pulp but can be removed by repeated washing with water.

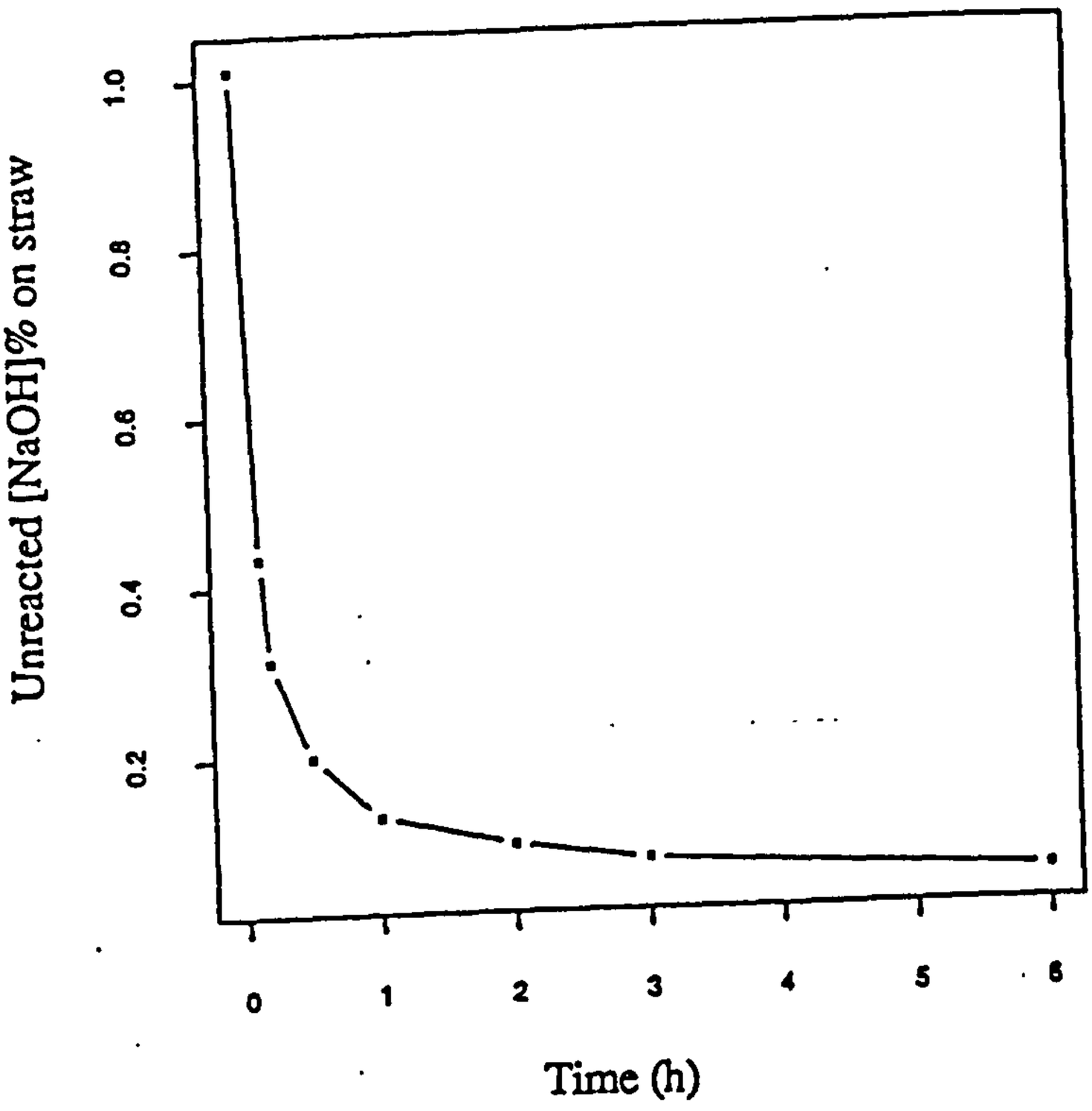


Figure 2.4.1

Plot of unreacted [NaOH]% on straw (4.23g) versus cooking time in caustic (0.0202 mol dm^{-3}, initial amount) at 25 °C in 55 ml H_2O.

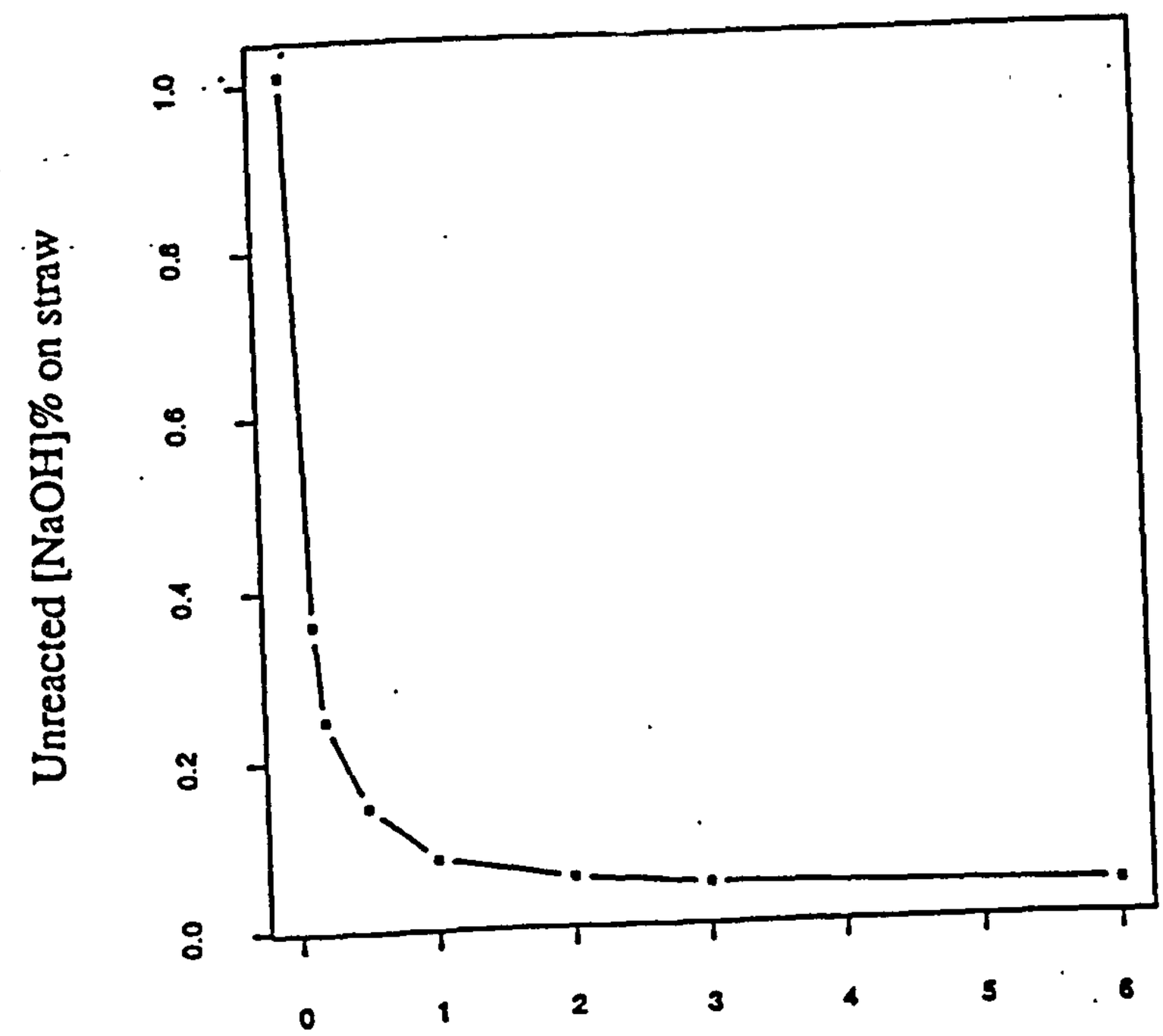


Figure 2.4.2

Plot of unreacted [NaOH]% on straw (4.23g) versus cooking time in caustic (0.0202 mol dm^{-3}, initial amount) at 80 °C in 55 ml H_2O.

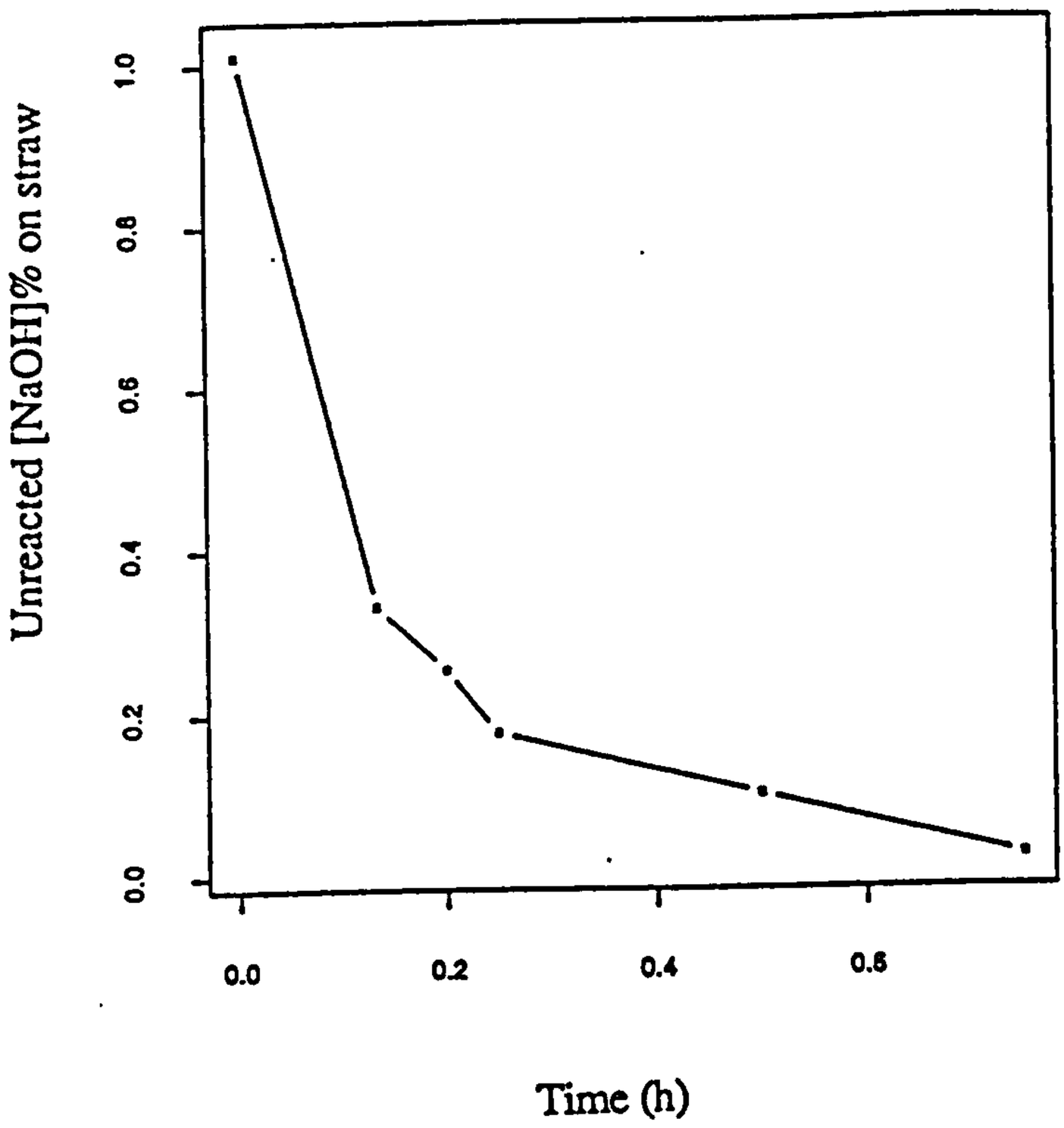


Figure 2.4.3

Plot of unreacted [NaOH]% on straw (4.23g) versus cooking time in caustic (0.0202 mol dm^{-3}, initial amount) at 170 °C in 55 ml H_2O.

2.4.3 Rate of Delignification Using Constant Initial Caustic And Variable Initial Straw

2.4.3.1 Introduction

In order to obtain some quantitative kinetic data from the study of caustic consumption, runs were done with a constant initial charge of 0.45g (0.202 mol dm^{-3}) caustic in 55 ml water and the initial charge of straw was varied. Only the early stages of the reaction were followed as this led to a kinetic treatment which could be readily intepreted as shown in the next section.

2.4.3.2 Kinetic Treatment

From the initial reaction rate,

$$-\frac{d[NaOH]_i}{dt} = k_{iLb}[NaOH]_i^n[L]_i^m + k_{iCb}[NaOH]_i^s[C]_i^r$$

and assuming constant initial caustic n = 0.8, m = 1 and r = 1 as (found previously)

$$-\frac{d[NaOH]_i}{dt} = k'_{Lb}[L]_i + k'_{Cb}[C]_i,$$

where $k'_{Lb} = k_{iLb}[NaOH]_i^{0.8}$ and $k'_{Cb} = k_{iCb}[NaOH]_i^s$.

Now, soluble carbohydrates content of straw is 33.3% w/w and lignin content is 22.94% (see Chapter 6), therefore,

$$[C]_i = \frac{33.33}{22.9}[L]_i \qquad \text{on weight basis,}$$

$$= \frac{33.33}{16,000} \times \frac{30,000}{22.9}[L]_i \qquad \text{on a molar basis}$$

Where the molar mass of lignin is taken as 30,000 and the molar mass of carbohydrate is taken as 16,000 (see Chapter 3 Section 6).

Hence,

$$-\frac{d[NaOH]_i}{dt} = k'_{Lb}[L]_i + k'_{Cb}\left(\frac{33.33}{16,000} \times \frac{30,000}{22.9}[L]_i\right)$$

$$= [L]_i \left(k'_{Lb} + 2.7\ k'_{Cb}\right),$$

and, therefore,

$$\log\left(-\frac{d[NaOH]_i}{dt}\right) = \log [L]_i + \left(k'_{Lb} + 2.7\ k'_{Cb}\right).$$

So, a plot of $\log\left(-\frac{d[NaOH]_i}{dt}\right)$ versus $\log [L]_i$ should give a straight line with slope 1 (if $m = n = 1$) and intercept $= \log\left(k'_{Lb} + 2.7\ k'_{Cb}\right)$.

2.4.3.3 Results and Discussion

Effect of Initial Acid Neutralization Reaction

In the previous section, neutralization of free acid groups on straw was found to consume 0.005g NaOH per g straw. Table 2.4.3.1 below shows the predicted consumption of caustic for the neutralising reaction compared with actual at 80 °C with 10 minutes reaction time in the steel reactor using an initial charge of 0.45g NaOH (0.202 mol dm^{-3}) with variable straw in 55 ml water.

Table 2.4.3.1 Consumption of caustic.

Straw Charge (g)	NaOH consumed for acid neutralization (g)	Total NaOH consumed in 10 minutes (g)
0.57	0.003	0.03
1.12	0.006	0.06
2.23	0.012	0.10

It can be seen from Table 2.4.3.1 that the initial neutralization step is predicted to consume 10% of the caustic at 10 minutes reaction, the other 90% being due (presumably) to the solubilization reaction of lignin and carbohydrate.

Effect of Lignin Concentration on Initial Results

Plots of unreacted caustic (g dm^{-3}) versus run time at 80 °C with 0.45g caustic and 0.57, 1.12 and 2.23g straw in 55 ml water are given in Figures 2.4.4-2.4.6 at 80 °C. In arriving at the caustic consumption shown in the figures, a correction has been made by subtracting the caustic consumed in acid neutralization from the total consumption. The values for log $\left(-\frac{d[NaOH]_i}{dt}\right)$ at 80 °C, derived from Figures 2.4.4-2.4.6, are plotted versus log $[L]_i$ in Figure 2.4.7.

The slope of the plot is close to unity, consistent with the assumption that m = n = 1, i.e., first order in lignin and carbohydrate.

The intercept of the line with the y axis in Figure 2.4.7 is 3.03.

Therefore, $\log\left(k'_{Lb} + 2.7\, k'_{Cb}\right) = 3.039,$

$$k'_{Lb} + 2.7\, k'_{Cb} = 1094,$$

or $k_{iLb}\,[NaOH]_i^{0.8} + 2.7\, k_{iCb}[NaOH]_i^{0.6} = 1094,$

and therefore, $0.39\, k_{iLb} + 1.05\, k_{iCb} = 1094.$

Given that the initial consumption of caustic associated with acid group neutralization has been removed from the initial reaction rate, it is not unreasonable to compare the values for the initial rate with those found in the experiments on the bulk delignification and carbohydrate dissolution for the bulk reactions.

It was found that for delignification and carbohydrate dissolution $k_L = 0.69\ (dm^3)^{0.8}\ mol^{-0.8}\ h^{-1}$ at 80 °C for the bulk delignification reaction and $k_C = 0.08\ (dm^3)^{0.6}\ mol^{-0.6}\ h^{-1}$ at 80 °C for the bulk carbohydrate dissolution reaction (see Chapters 2 and 4, respectively).

Comparison with the expression for $k_{iLb} + k_{iCb}$ inidicates that the molar rate of reaction of caustic is much higher than the rates of solubilization of lignin and carbohydrate. This can be quantified further as shown in the following Table 2.4.3.2.

Table 2.4.3.2 Molar ratio of caustic consumption with respect to total lignin and carbohydrate dissolution.

Time (h)	Lignin Dissolv. g	mol	Carbohydrate Dissol** g	mol	Caustic Consumed* g	mol	Ratio of caustic consumed to total L + C dissol. (mol)
0.5	0.12	$4x10^{-6}$	0.04	$2.6x10^{-6}$	0.16	$4x10^{-3}$	606
1	0.28	$9.3x10^{-6}$	0.10	$6.1x10^{-6}$	0.24	$6x10^{-3}$	390
1.5	0.41	$14x10^{-6}$	0.11	$7.03x10^{-6}$	0.26	$6.5x10^{-3}$	230

0.45g NaOH; 4.23g WS and 55 ml H_2O.

* Corrected for initial neutralization reaction

**estimated from runs at 2.23g NaOH.

all figures in the table are cumulative.

It can be seen that at 0.5h more than 600 moles NaOH reacted per mole of total lignin and carbohydrate dissolved. The number reduced with time of reaction but was still 230 at 1.5hr. This means that the effect of the caustic must be more than straight fission of lignin-carbohydrate units. Hydrolysis of esters with subsequent neutralization of carboxyl and acyl groups as postulated by Pavlostathis and Gossett (1985) may be among the main caustic consumption processes.

However, it is noteworthy that the cumulative amount of caustic consumption diminishes relative to lignin and carbohydrate dissolution with time of reaction. This might indicate a consecutive process whereby caustic reacts in some way with straw before lignin and carbohydrate dissolution occurs (other than neutralization of acid groups for which correction has already been made). Alternatively, there may be parallel reactions of caustic not immediately associated with lignin or carbohydarate dissolution. These could be reactions such as ester hydrolysis or functionalization of side groups which assist subsequent dissolution reactions.

While caustic consumption is high on a molar basis, the amount reacted weight for weight of lignin dissolved is of much smaller order, e.g., at 1.5h in Table 2.4.3.2, 0.26g NaOH is consumed for dissolution of 0.41g lignin and 0.11g carbohydrate for pulping down to 13% residual lignin on straw.

2.4.3.4 Conclusions

* The molar ratio of caustic to lignin reacted is very high, more than 600:1, at 0.5h cook. This is the amount reacted after correcting for initial neutralization of free acid groups present in the straw. This indicates that the reaction of caustic with straw is complex, e.g., hydrolysis followed by neutralization of acyl groups of lignin and carbohydrate units.

* As cooking proceeds the relative consumption of caustic diminishes, indicating some prereaction is required before dissolution of lignin and carbohydrate takes place.

* On a weight basis the amount of caustic required to dissolve lignin is approximately 0.5:1.

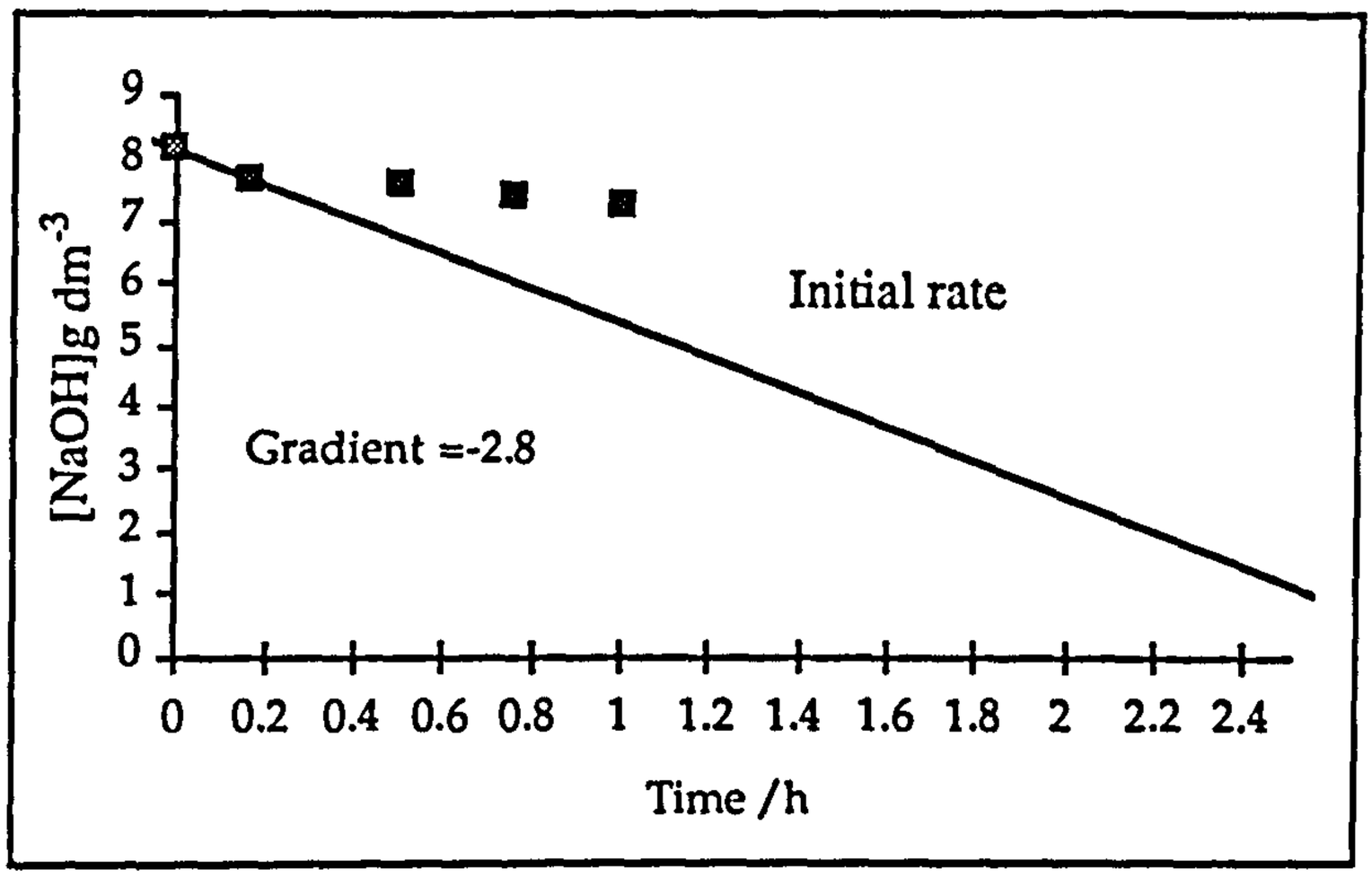


Figure 2.4.4

Plot of unreacted caustic versus cooking time in runs with initial weight of 0.45g NaOH in 55 ml water with 0.57 g straw at 80 °C.

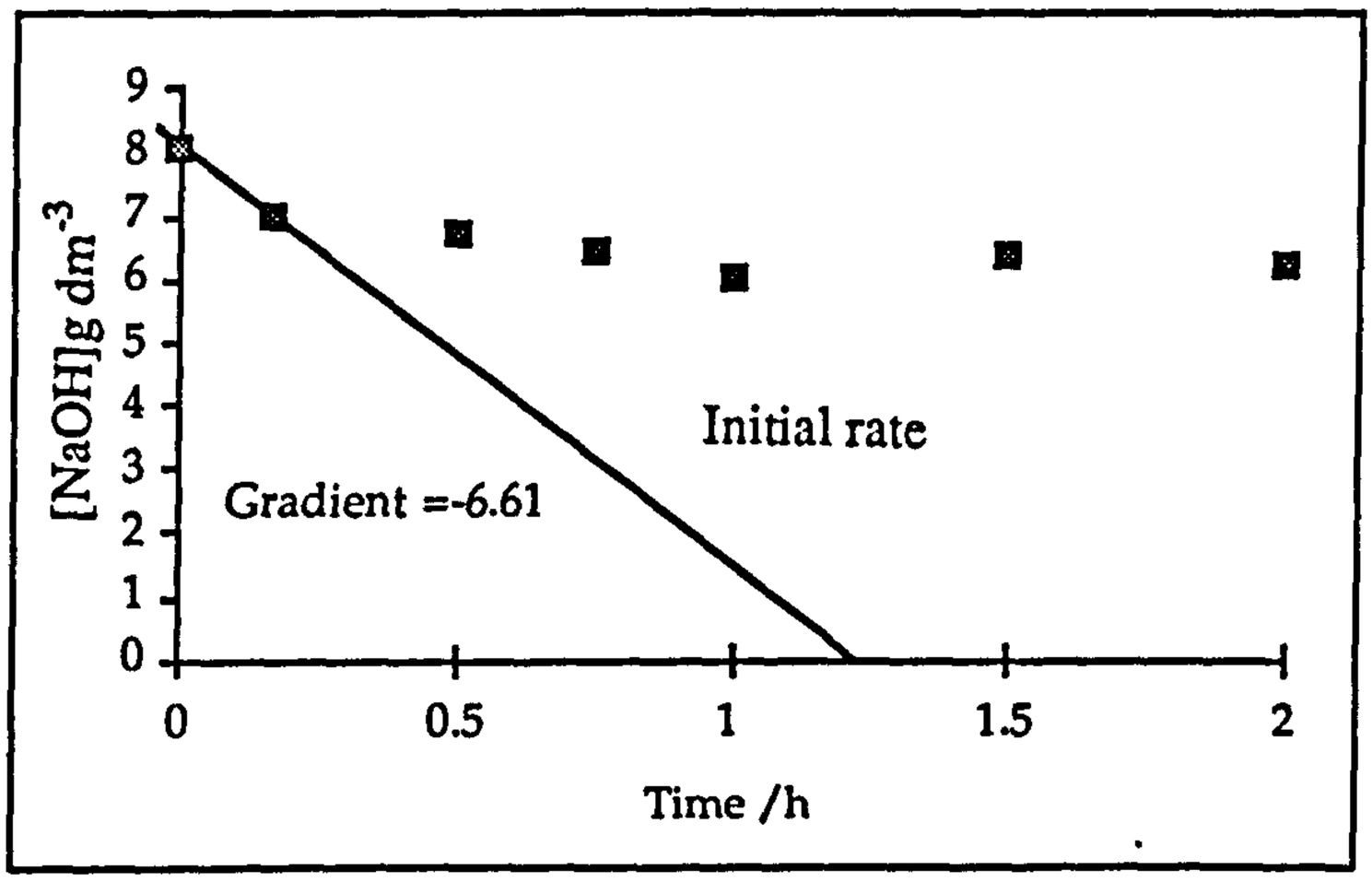


Figure 2.4.5

Plot of unreacted caustic versus cooking time in runs with initial weight of 0.45g NaOH in 55 ml water with 1.12 g straw at 80 °C.

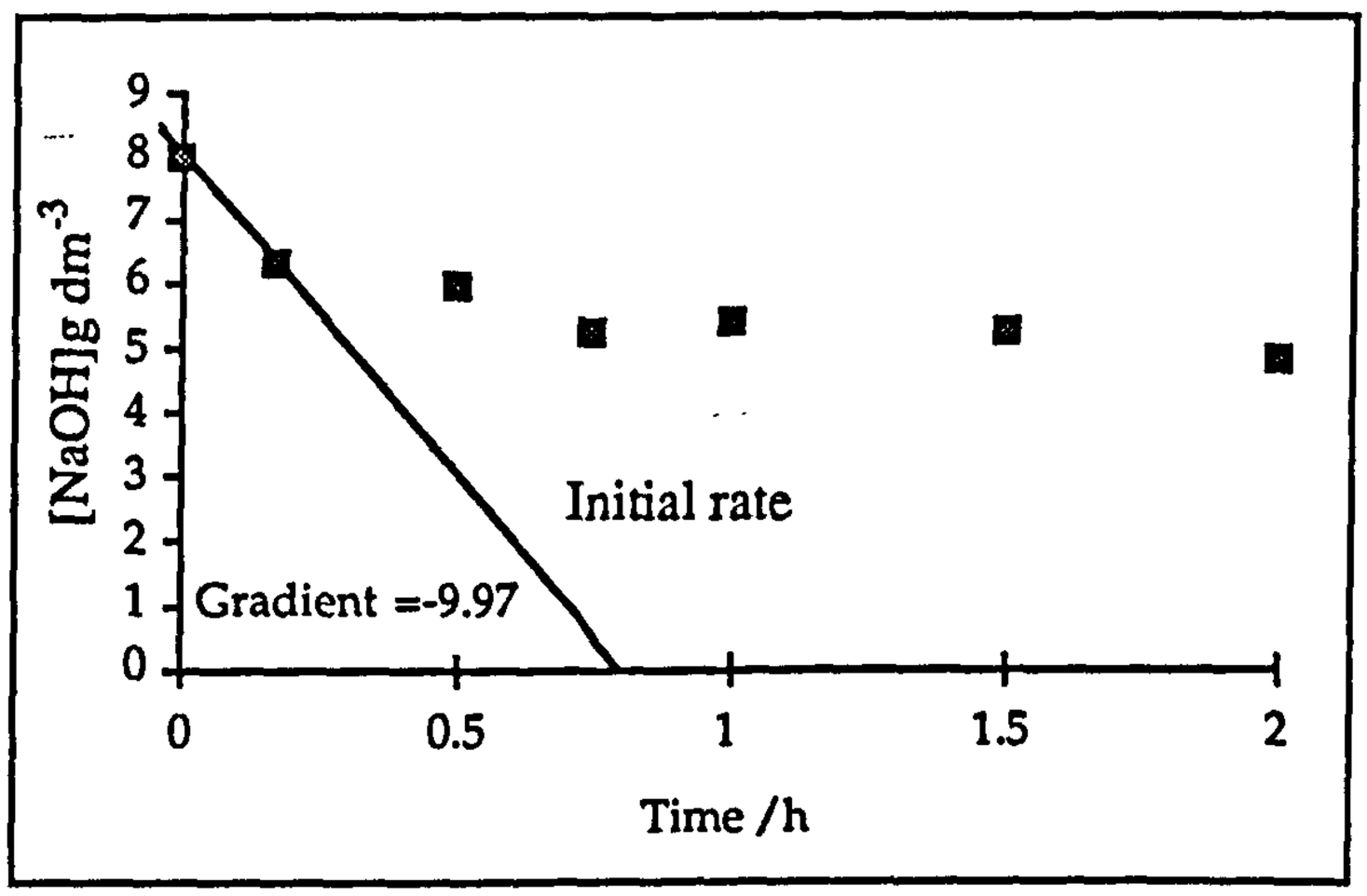


Figure 2.4.6

Plot of runreacted caustic versus cooking time in runs with initial weight of 0.45g NaOH in 55 ml water with 2.23 g straw at 80 °C.

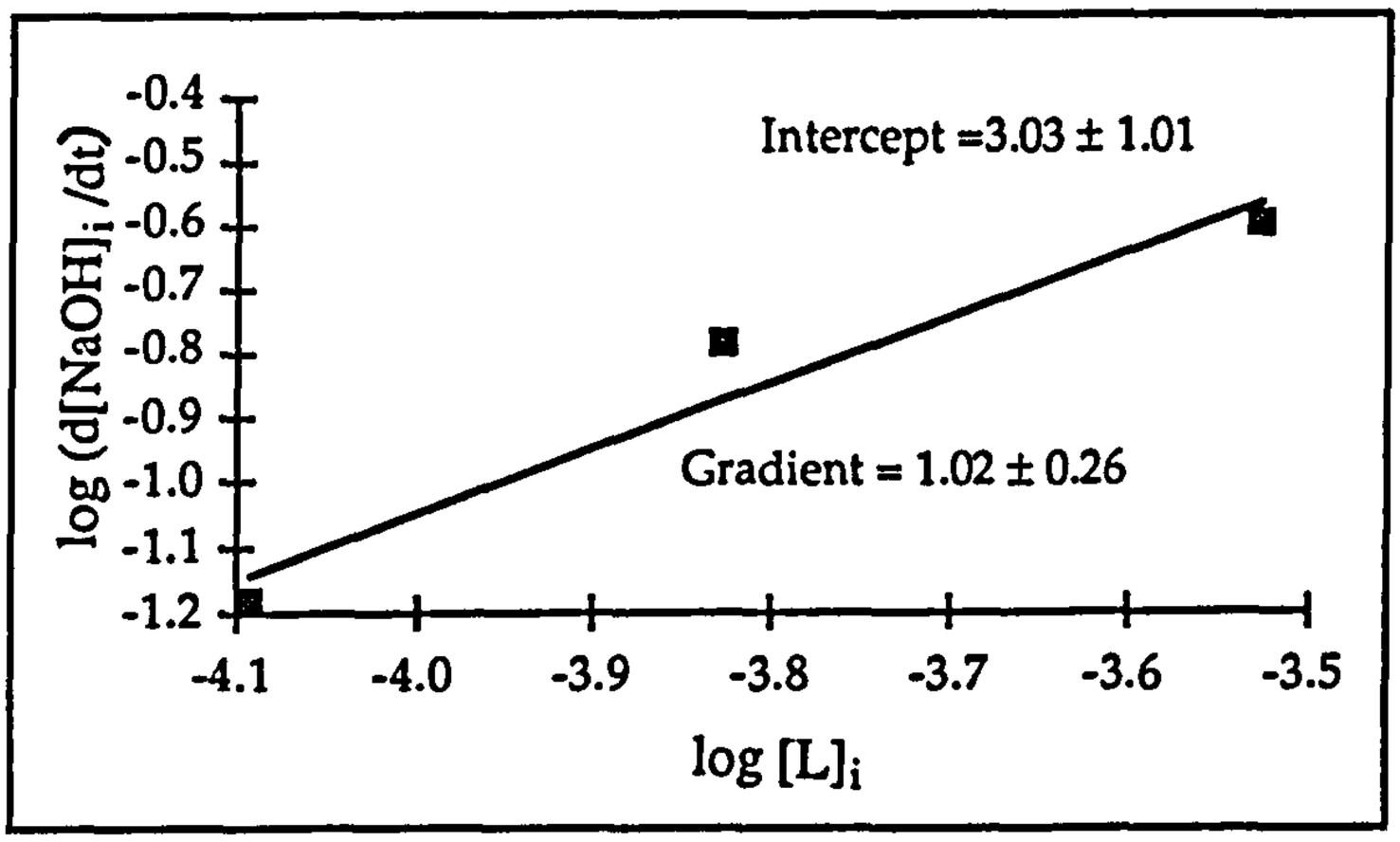


Figure 2.4.7

Plot of log $-d[NaOH]_i/dt$ versus log $[L]_i$ where the gradient equals the order of caustic consumption with respect to lignin at 80 °C.

3 THE CHARACTERIZATION OF STRAW, PULP AND LIGNIN PRODUCTS

A great mass of literature is devoted to the study of lignin and pulp from wood to gain the knowledge of the chemistry of lignin, particularly in formulating rational approaches to the development of new and improved bleaching processes (Bolker and Sommerville, 1963). In pursuit of that knowledge a variety of techniques have been utilized to get information on the actual chemical groups altered, removed from or added to lignin in the course of pulping and bleaching reactions.

As a result, the chemical structure of wood lignin is much better known presently than that of non-wood lignin, and a wealth of techniques are available for characterization of wood lignin and pulp (Sarkanen and Ludwig, 1971).

Grass-like materials differ greatly from wood in chemical composition and structure as well as in behaviour during the alkaline cooking process. There are some studies reported in the literature on the characterization of cellulose pulp, isolated lignin etc. from agricultural waste residues such as wheat straw, corn stalk, olive straw, sunflower etc. (Alacaide et al., 1991; Lawther et al, 1995 and Jung and Himmelsbach, 1989 and Smith and Hartley, 1983). These materials are potential sources of energy for ruminant animals and of raw materials for paper and board production (Morrison, 1980).

The objective here is to use the modern spectroscopic techniques of UV, FTIR, NMR (solid-state and solution for $^{1}H/^{13}C$) etc. for more extensive characterization of straw, pulp and lignin products similar to that which has been accomplished with wood studies (e.g., Chang et al., 1975) and to a lesser extent on straw (e.g., Jung and Himmelsbach, 1989).

3.1 Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy is considered to be one of the most useful tools because it has a high signal-to-noise ratio and can provide detailed information about lignin and lignin containing byproducts (Buta and Galletti, 1989 and Friese and Banarjee, 1992).

In order to get comparative information, IR spectra were carried out for three samples: ground wheat straw, delignified pulp and the extracted lignin.

The IR spectra for these samples are shown in the Figures 3.1.1 and 3.1.2, where their bands were identified by their wave numbers. The assignments of these bands are in accordance with those of Hergert (Sarkanen and Ludwig, 1971 and Jung and Himmelsbach, 1989). The relative intensity of each absorption band was calculated using the internal standard method after deducting the background absorption of the base line where the changes in the relative absorption intensity are assumed to reflect the changes in the structure and functional groups.

3.1.1 Straw

The bands at 910, 1040 and 1323 cm^{-1} represent the glycosidic linkages in cellulose and hemicelluloses (Fang et al., 1991 and Hongguang and Guangrui, 1986). The bands at 1040 and 1323 cm^{-1} also overlap with those for syringyl and guaiacyl groups and it is difficult to make a clear cut assignment in those regions. The band at 1156 cm^{-1} is C-O stretch while the band at 1650 cm^{-1} is for carbonyl (C=O) stretching due to p-substituted ketone or aryl aldehydes. The band at 1245-1265 cm^{-1} is for aromatic ring bending with C-O stretch. The 1245 cm^{-1} band may be attributed to syringyl and p-coumaryl and the 1265 cm^{-1} band to coniferyl groups. The absorbance band at 1367 cm^{-1} is due to vibration of carbonyl structures. The band at 1725 cm^{-1} has been assigned to carbonyl stretching in unconjugated ketone and carboxyl groups. The series of bands at 1657-1681cm^{-1} are assigned to carbonyl stretching of the various conjugated aromatic ketones. The bands at 1427, 1504-1515 and 1600 cm^{-1} are the bands arising from the aromatic

skeleton (Friese and Banarjee, 1992). The prominent broad absoption at 2910-3140 cm^{-1} was assigned for aliphatic C-H stretching (Bolker and Sommerville, 1963). The bands at 4330, 3440 and 3500 cm^{-1} are due to phenolic and alcoholic groups (Bolker and Sommerville, 1963 and Hergert, 1960).

3.1.2 Lignin

The IR spectra of straw and lignin are compared in Figure 3.1.1. The absorbance for the bands at 1044 and 1323 cm^{-1} representing hemicellulose, cellulose and probably syringyl and guaiacyl groups are markedly reduced in the lignin spectrum while the band at 1156 cm^{-1}, corresponding to C-O stretch, has broadened and the band at 1725 cm^{-1}, representing carbonyl stretch of unconjugated ketone and carbonyl groups, such as possibly p-coumaric ester, decreased as a result of cooking straw in alkali. The bands at 1504 and 1600 cm^{-1}, characteristic of aromatic compounds due to C=C vibrations of the benzene ring, remain the same as in straw (Bolker and Sommerville, 1963). The bands at 1245-1265 cm^{-1} for ring bending with C-O, stretch which could be due to aryl ethers, have disappeared in lignin. The bands at 945, 1160 and 1367 cm^{-1} have increased in lignin due to vibration of the carbonyl structures which are most probably created in lignin during cooking in presence of caustic. These carbonyl groups are generally said to be auxochrome in nature which make lignin become deep red in colour after cooking (Hongguang and Guangrui, 1986). The band at 2910 cm^{-1}, a C-H stretch, has become broader while the bands at 3430 and 3500 cm^{-1} remain the same as those seen in straw. In particular the band at 3500 cm^{-1} is said to be characteristic of lignin and is due to the various OH groups (Bolker and Sommerville, 1963).

3.1.3 Pulp

The assignment of the IR spectrum of pulp is compared with that of straw in Figure 3.1.2. This also shows significant changes in the absorption bands at 1245-1265 cm^{-1}, due to ring bending with C-O stretch, which has completely disappeared in the pulp spectrum along with the band at 1367 cm^{-1}, due to vibration of carbonyl structures. The characteristic absorption bands for lignin functional groups at 1504, 1600 and 1725 cm^{-1} have disappeared in the spectrum of pulp as a result of delignification. However, the

bands at 900, 1000, 1040 and 160 cm^{-1} are prominent which are due to bond bending vibrations which may be caused by CH_2CH as well as glycosidic linkages in cellulose and hemicellulose. A possible explanation for the changes could be that once lignin is removed the polysaccharides content is raised, causing strengthening of their absorption intensity in pulp (Hongguang and Guangrui, 1986).

3.1.4 Conclusions

The findings for the IR spectra are generally in line with results reported in the literature. In particular for lignin compared with straw the main effects of caustic treatment are:

* Significant loss of cellulose and hemicellulose (Hongguang and Guangrui, 1985).

* Possible reduction in syringyl and guaiacyl units (Fang et al., 1991).

* Loss of aryl ether structures (Adler, 1968).

* Reduction of ester structures (Scalbert et al., 1985).

* Significant increase in carbonyl groups and resultant colour (Bolker and Sommerville, 1962 and Xuanchu, 1981).

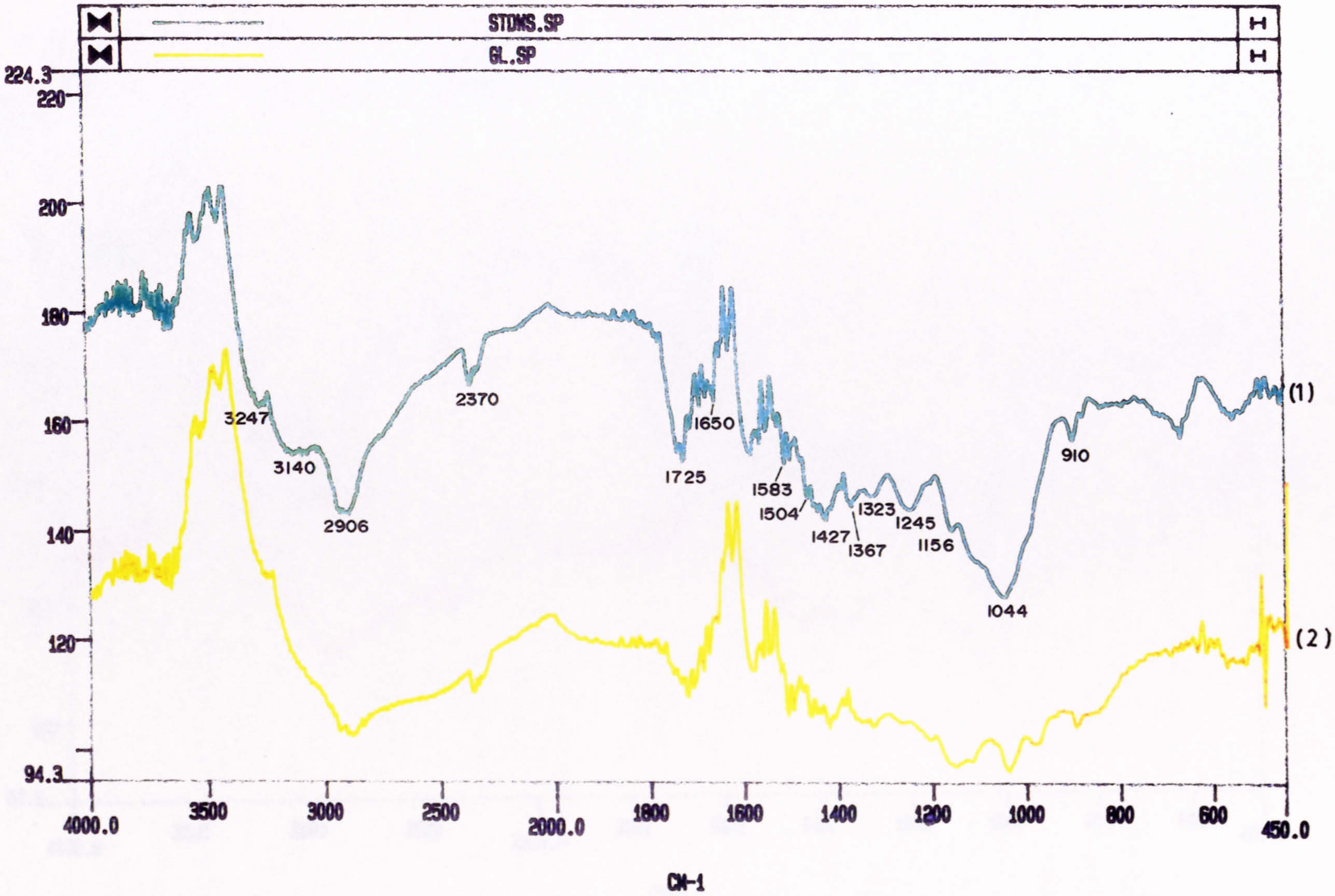


Figure 3.1.1 FT-IR spectra of (1) Wheat Straw; (2) Lignin.

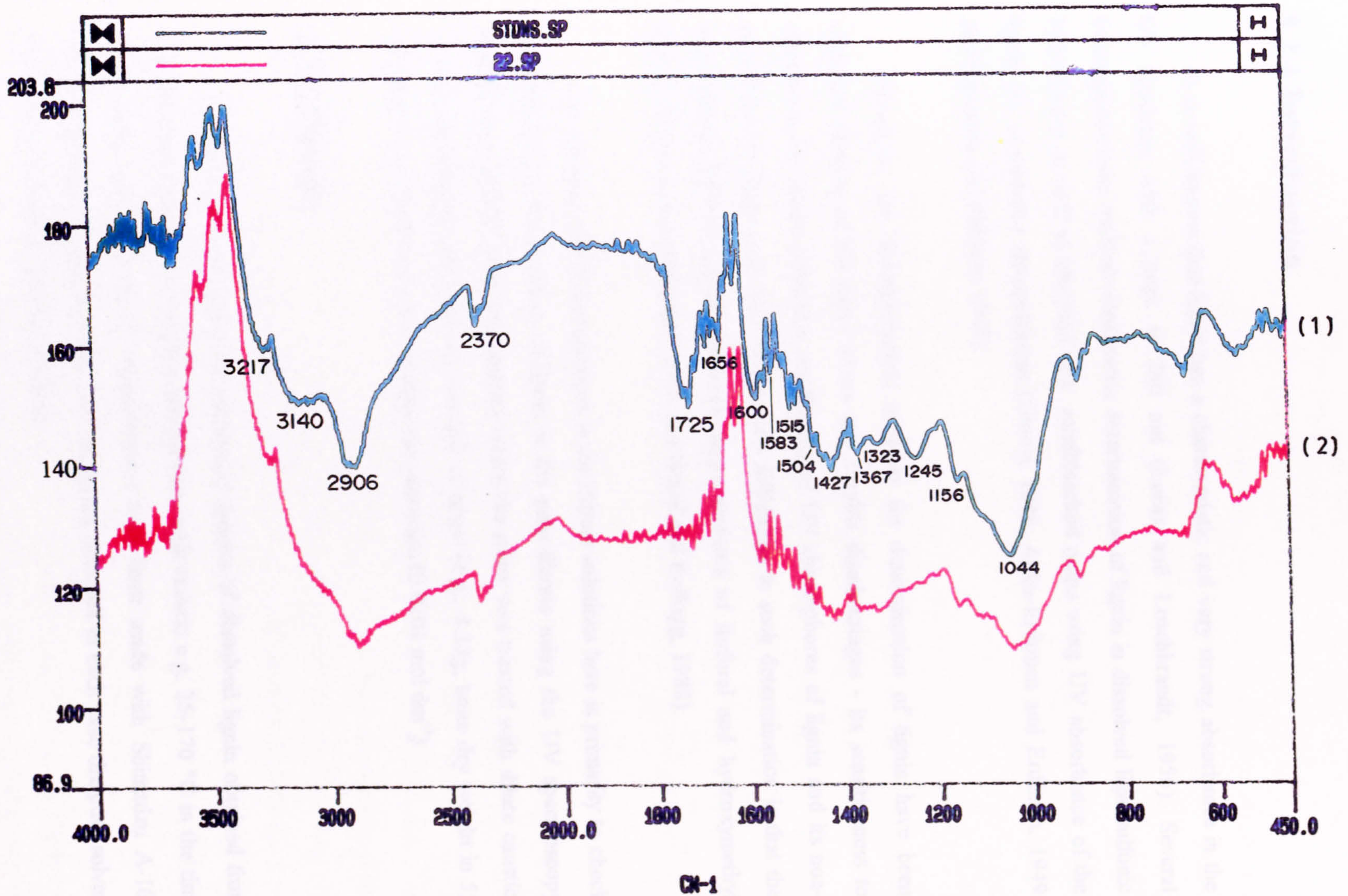


Figure 3.1.2 FT-IR spectra of (1) Wheat Straw; (2) Pulp.

3.2 UV Spectroscopy

3.2.1 Introduction

It is well known that lignin has a characteristic and very strong absorbance in the UV spectrum with a peak at 280 nm (Loras and Loschbrandt, 1956). Several investigators have studied colorimetric determination of lignin in dissolved lignosulfonic hydrolysates as well as bleached and semibleached pulps using UV absorbance of the lignin for quantitative determination (Giertz, 1945; Aulin-Erdtman and Erdtman, 1949 and Patterson and Hibbert, 1943).

However, the absorptiometric methods for determination of lignin have been criticized because of the many errors and notable disadvantages - its sensitiveness to changes in the molar extinction coefficients of UV chromphores of lignin and its non-specificity for lignin only. One of the main difficulties in such determination is that the lignosulfonic filtrates contain relatively large amounts of furfural and hydroxymethyl furfuryl (Loras and Loschbrandt, 1956 and Wood and Kellogg, 1988).

The purpose of UV investigation in the filtrate solutions here is primarily to check qualitatively for the presence of lignin in the pulp filtrate using the UV spectroscopy method especially in those experiments where the straw was treated with dilute caustic. In these experiments the standard strength of straw (e.g., 4.23g, bone dry weight in 55 ml water) was treated with mild caustic concentration (0.0202 mol dm^{-3}).

3.2.2 Results

Figure 3.2.1-3.2.3 show UV absorption spectra of dissolved lignin obtained from various straw treatment at various temperature with caustic e.g. 25-170 °C in the time range from 8min-6h. All the measurements have been made with Shimadzu A-160 spectrophotometer equipped with 1.00 cm quartz cells and in each case the pure solvent has been used as the reference solution.

Figure 3.2.1 shows the absorption spectra of dissolved lignin after treatment of 4.23g of straw (bone dry weight) in the metal reactor at 25 °C with 0.45g of caustic in 55 ml H_2O for times 0.5-3h.

Figure 3.2.2 shows the spectra obtained with similar standard charge of straw and caustic as above but at a temperature of 80 °C for the various range of times e.g. 8min-6h in the pressure vessel with 55 ml H_2O.

Figure 3.2.3 shows the absorption UV spectra of lignin after treatment with similar charge of straw and caustic as above at a temperature of 170 °C for 8min-0.75h in the metal reactor.

It can be seen that the intensity of the peak at 280 nm for lignin is not very prominent at shorter times of treatment (8-15 minutes) in the temperature range of 80 °C and 170 °C, which could be attributed to low dissolution of lignin. In other words, it would take more time in the case of lower initial alkali concentration (for a given solids concentration) to dissolve sufficient fraction of lignin groups. This is because of saponification and neutralization of acidic groups by caustic initially as was also observed by previous workers (Pavlostathis and Gossett, 1985).

Although 280 nm is usually employed when measuring the lignin content, 220 nm has also been used by some workers where the lignin has a high absorptivity, to detect lignin content quantitatively as "total lignin content". The absorbance of the lignin at 280 nm, as it is well known, may possibly be interfered with by other substances: contamination with furfural and hydroxymethyl furfural which have absorptivity in the same region formed during hydrolysis and may possibly affect the results (Loras and Loschbrandt, 1956). The effects of these compounds could be minimized by using the absorbance at 220 nm for the calculation of total lignin and the influence from possible contamination in the acid solution is taken care of by the calibration of the instrument against a blank.

The absorption intensity at 316 nm in UV spectra (Figures 3.2.1-3.2.3), which was reported to represent ester linkages in dissolved lignin (Fang et al., 1991) was not

prominent in the caustic solutions obtained at room-temperature (25 °C) (Figure 3.3.1) as well as at lower times of treatment at 80 °C and 170 °C e.g., 8min-2h and 8min-15minutes (Figures 3.2.2 and 3.2.3). However, it is significant at 3h and 6h of treatment at 80 °C (Figure 3.2.2) and 0.5-0.75h at 170 °C (Figure 3.2.3).

3.2.2 Conclusions

* The UV spectra of lignin produced by caustic treatment of straw show strong absorption peaks at 220, 280 and 310 nm which are typical of lignin as reported in the literature.

* The intensity of the peak at 280 nm, which is generally used to follow lignin content, is not very prominent at low time of cook but increases with higher cook times indicating that the lignin groups only begins to dissolve at higher temperatures.

* The peak at 220 and the one at 316 nm representing ester linkages also show the same pattern as found at 280 nm, and all increase with time of treatment up to 6h at 25 °C and 80 °C and 0.75h at 170 °C (the longer times were not studied at 170 °C).

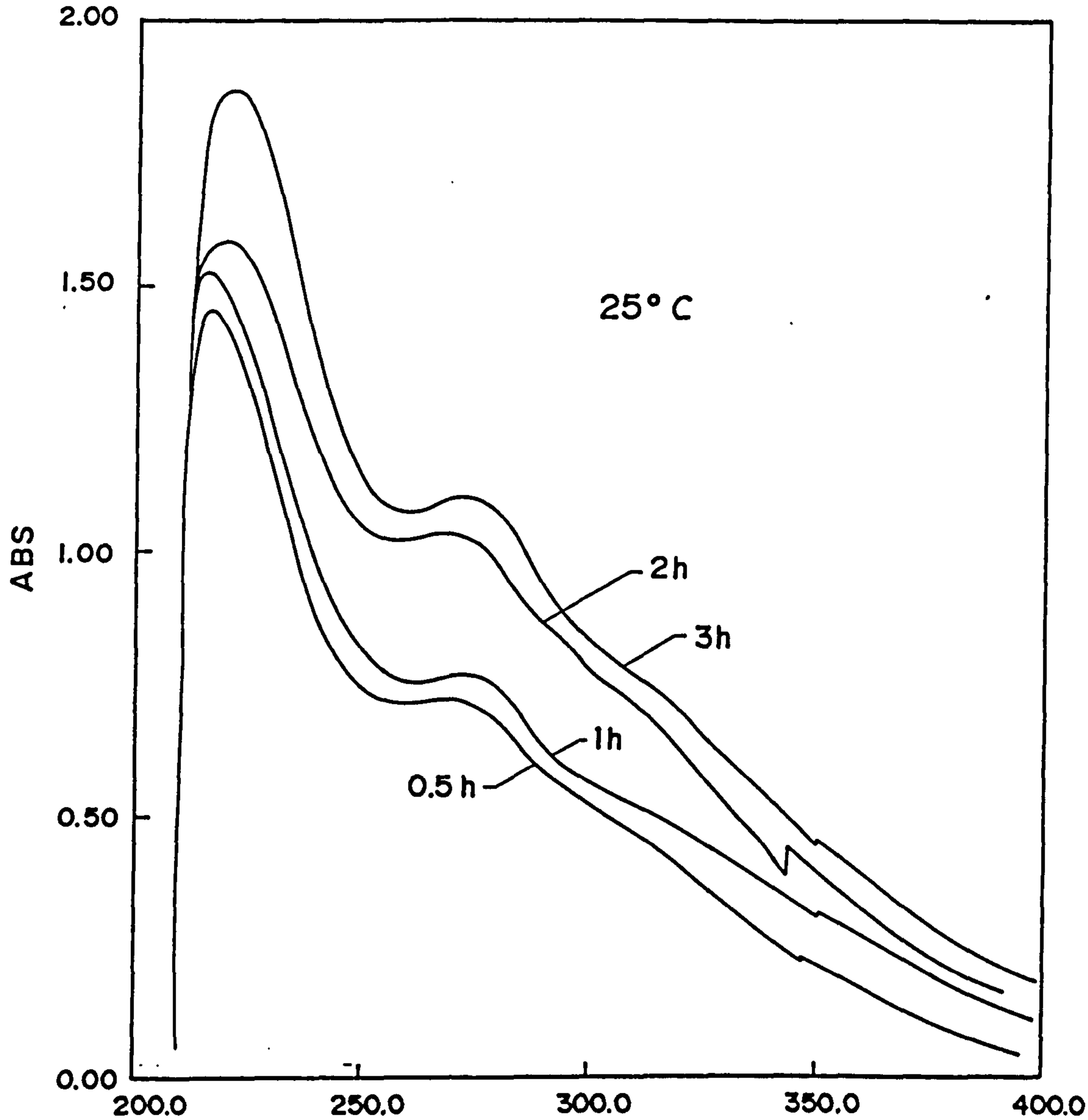


Figure 3.2.1 UV spectra of Wheat straw lignin obtained at 25°C.

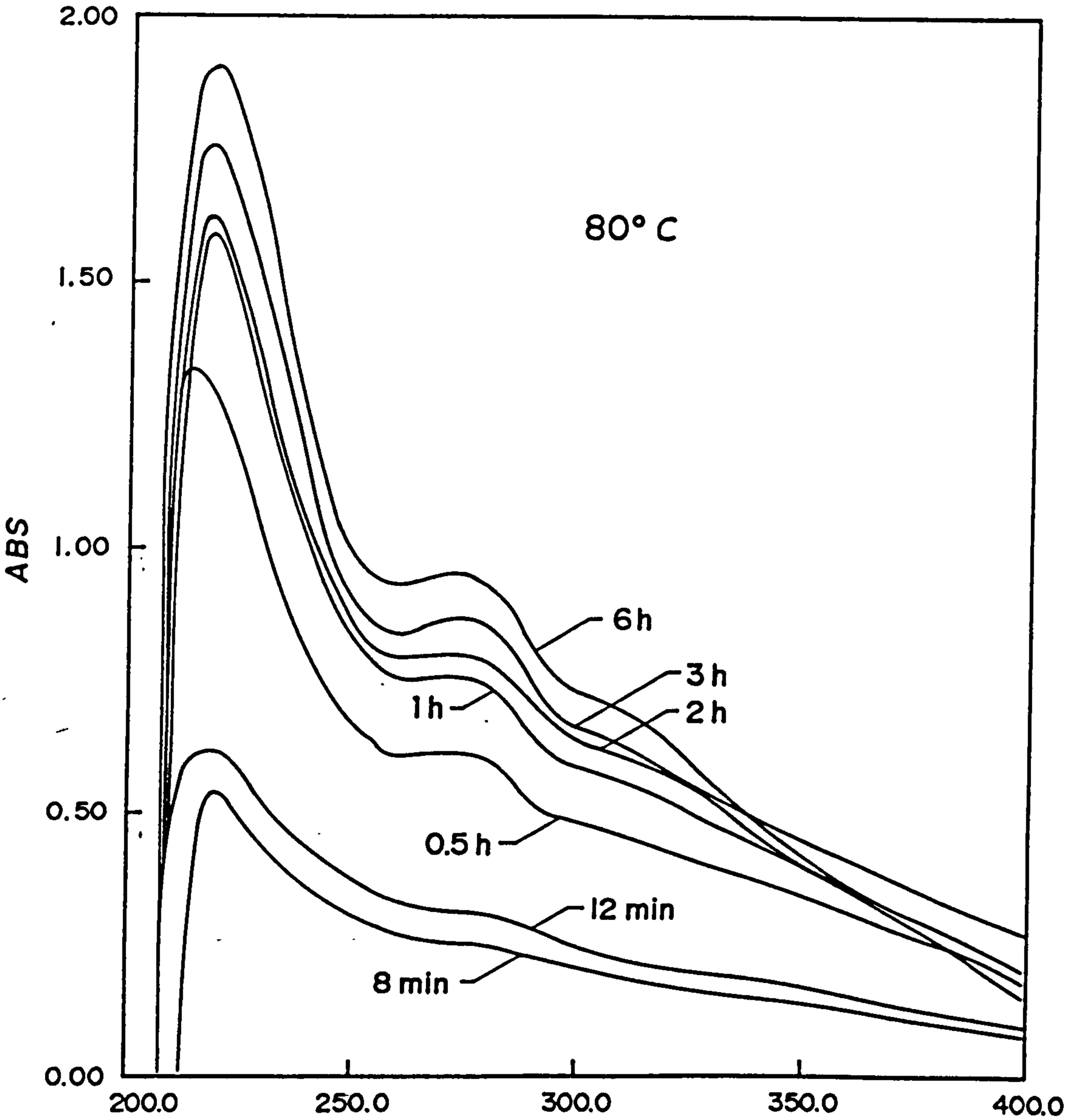


Figure 3.2.2 UV spectra of Wheat straw lignin obtained at 80°C.

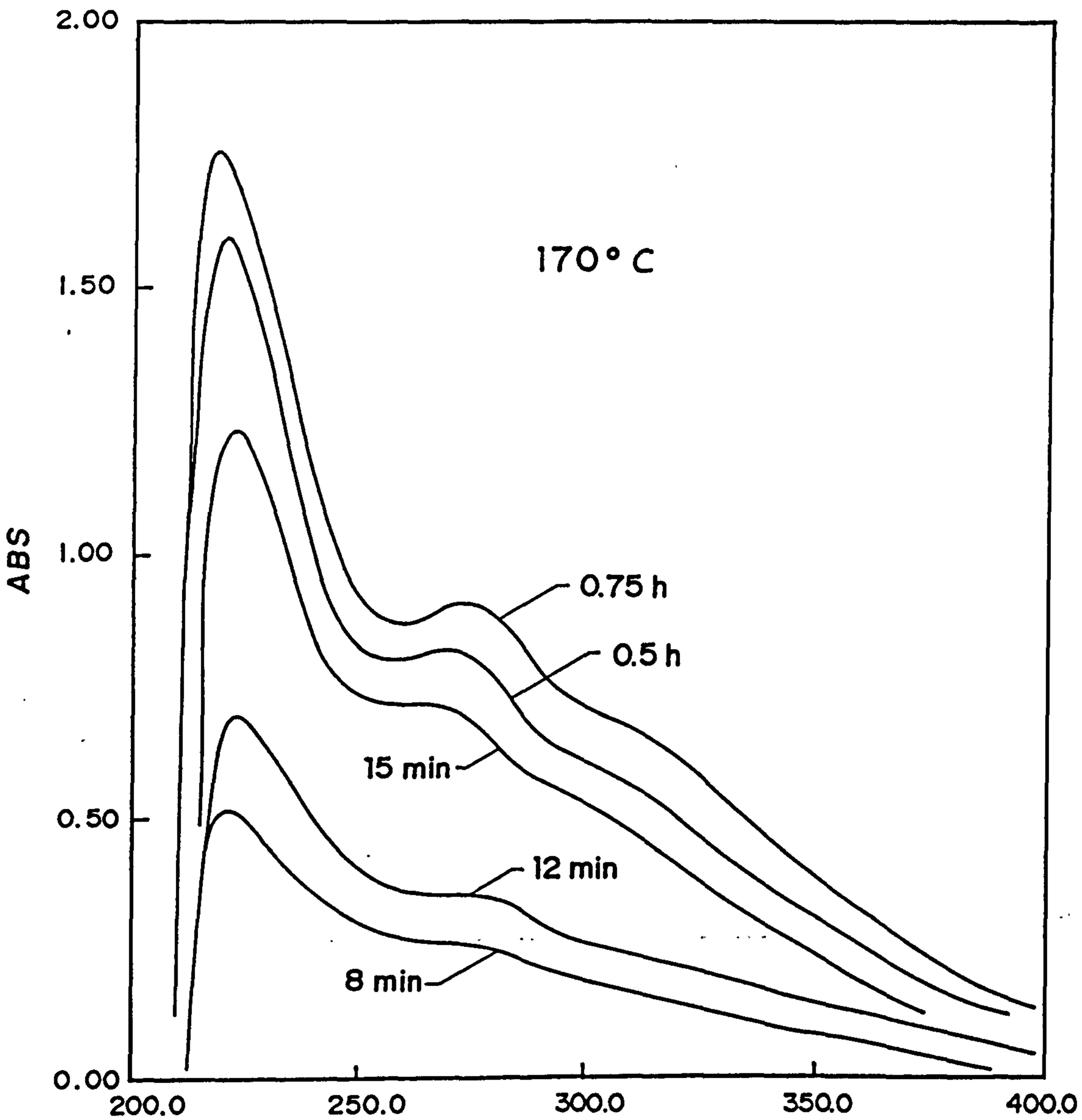


Figure 3.2.3 UV spectra of wheat straw lignin obtained at 170°C.

3.3 NMR Spectroscopy

The dissolved lignin from different runs in the metal reactor for various times of treatment in the temperature range 25-170 °C were analyzed systematically by ^{1}H solution NMR, solid state NMR and ^{13}C NMR to follow the changes occurring during and after delignification.

3.3.1 ^{1}H Solution NMR

3.3.1.1 Introduction

There has been rapid progress in both theoretical and experimental aspects of nuclear magnetic resonance (NMR), the interpretation of NMR spectra in most cases being straightforward in terms of signal areas (intensities), relaxation times, chemical shifts and coupling constants. These parameters provide the necessary information for solving a wide variety of problems in characterization of chemical compounds in the chemical and biological sciences (Emsely et al., 1967; Leyden and Cox, 1977 and Harris, 1983).

Most of the early work in NMR was focussed on ^{1}H NMR spectroscopy because the proton is the one most sensitive to NMR detection among the nuclei that give an NMR spectrum.

In spite of numerous investigations, the chemical structure of plant lignins have remained incompletely known (see Chapter 1). However, structural characterization of the complex lignin species remains a formidable challenge, despite the tremendous flexibility and power of modern NMR instruments.

Although the NMR technique efficiently distinguishes the different nuclei, extensive overlapping of signals remain the major obstacle to reliable chemical shift assignments and interpretation of lignin and its products (Scalbert et al, 1986).

3.3.1.2 Results And Discussion

The extracted fractions of lignin after treatment in the metal reactor with 4.45g of caustic and 55 ml H_2O for different times and different temperatures were subjected to ^1H NMR spectroscopy for analysis. In ^1H NMR studies reported in the literature, generally milled straw lignin, as the true representive of protolignin, was examined after acetylation (Lundquist, 1991). However, it is also possible to apply the same treatment for the structural elucidation of lignin and its products (Lundquist, 1979).

Most of the assignments were made according to the previously assigned data of ^1H NMR of lignin (Wood and Kellogg, 1988 and Feng et al., 1991 and Lundquist, 1991).

A series of ^1H NMR analyses were done on the extracted lignin from 0.5h-1.5h at different temperatures. The spectra obtained are placed in Figures 3.3.1, 3.3.2 and 3.3.3.

It can be seen from the Figures 3.3.1-3.3.3, that the ^1H NMR peaks are not well resolved, which could be attributed as due to the polymeric and complex nature of the chemical structure of the lignin. The proton in lignins give rise to intensive overlap of signals because of the many chemical environments. The signal broadening, which is obvious from the appearance of the lignin spectra, is due to a tendency of the lignin molecules towards rigidity caused by cross linking the presence of large rings in the macromolecular structure of the lignins and to spin-spin splitting effect (Ludwig et al.,1964). The presence of carbohydrates in lignin further complicate the picture and make spectra even more complex (Wood and Kellogg, 1988). The interpretation, therefore, has been made using spectral data obtained from ^1H NMR spectroscopic studies of lignin model compounds (Lundquist, 1980) and the shifts of proton nuclei in substructures of acetylated lignin and products (Wood and Kellogg, 1988).

Figure 3.3.1 shows lignin extracted after 0.5h treatment of straw with caustic of strength 2.02 mol dm^{-3} from 25-170 °C, for comparison and peak assignment, a milled straw lignin which was prepared according to a procedure prescribed in the literature (Wood and Kellogg, 1988) to get protolignin. Maximum care was taken not to destroy the true lignin structure in the straw (see Chapter 6 for details).

The peaks at 7.30-7.85 ppm in the milled straw lignin are assigned to aromatic hydrogen in 4-O-alkylated guiacylpropane moities. The regions at 7.08 ppm are aromatic hydrogens associated with carboxyl group in 4-O- alkylated syringylpropane moities. The corresponding peaks at 6.66 ppm and 6.85 ppm are aromatic hydrogens in 4-O-alkylated p-hydroxyphenylpropane moities. The 3.84 ppm peak is associated with methoxyl hydrogen in aromatic moities, hydrogen on C-β of β-5 phenylcoumarin (Figure 3.3.4) and axial hydrogen on Cγ of β-β biphenyl (Figure 3.3.5) substructures. The peaks at 0.95-1.56 are assigned of non-oxygenated aliphatics for hydrogen on CH_2-CH_2-CH_2 and $(CH_3)_2$-CH moities of acids.

Figure 3.3.1 shows that lignin produced from treatment of straw for 0.5h with caustic of 2.02 mol dm^{-3} concentration in 55 ml of water over the temperature range 25-170 °C does not show any significant affect on the guaiacyl and syringyl units of lignin. However, in the temperature range 80 °C to 170 °C, the β-aryl ether (Figure 3.3.6) and C-β of arylvanillyl group at 4.40 ppm start appearing indicating chemical changes are taking place in lignin produced upon treating straw with the caustic at higher temperatures. Peaks also appear with increased temperatures at 4.40 ppm and 5.08 ppm which are attributed to be due to coniferyl alcohol units and vanillyl alcohol units respectively (Lundquist, 1991, Figure 3.3.7). Also the p-hydroxyphenylpropane peak at 6.85 ppm decreases from 25-80 °C and then increased progressively in the range 80-170 °C.

However, if the time of treatment is increased from 0.5h to 1h and further to 1.5h then the corresponding intensities of the peaks which began to appear at 80-170 °C with 0.5h run time, start reducing substantially, presumably due to degradation of lignin at higher temperatures and times (Figures 3.3.1, 3.3.2 and 3.3.3).

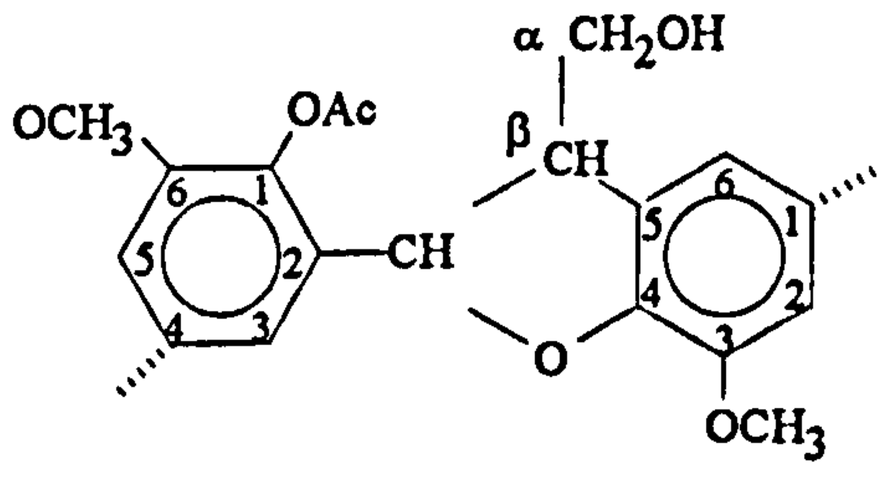


Figure 3.3.4. The phenyl courmarin type linkage (Ludwig et al., 1964).

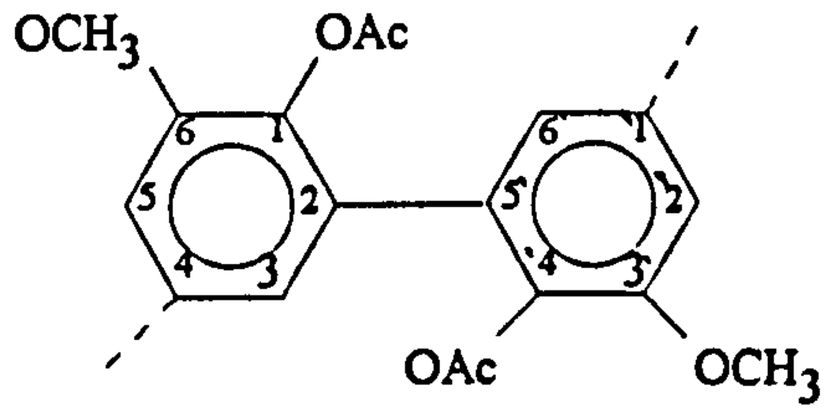


Figure 3.3.5. 5,5-biphenyl type linkage (Ludwig et al., 1964)

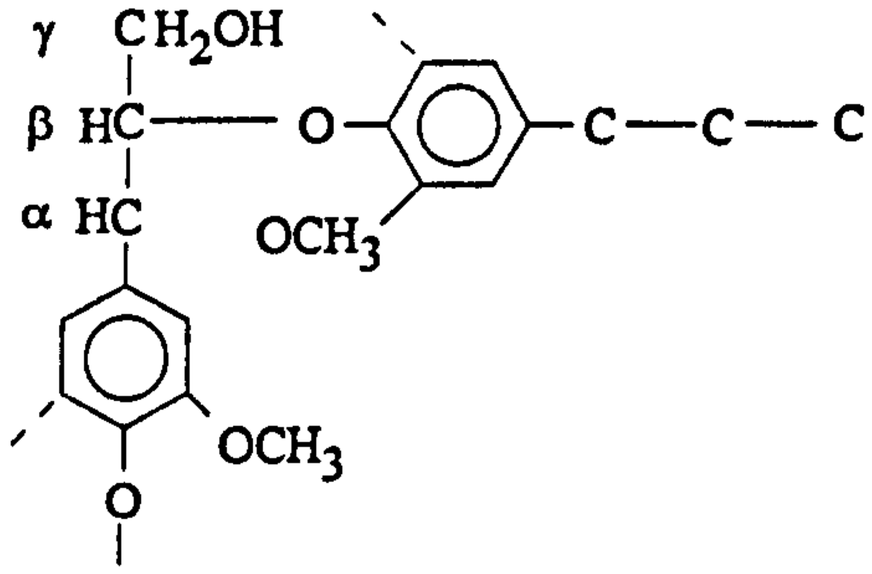


Figure 3.3.6. The β-arylether linkage (Lundquist, 1991).

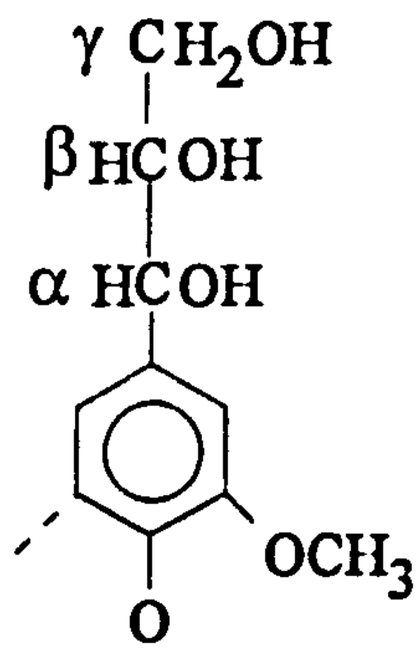


Figure 3.3.7 (Lundquist, 1991).

For example the obvious and significant effects of these changes can be seen clearly in Figure 3.3.2 which shows runs with straw samples treated with same charge of caustic as in Figure 3.3.1 but for a longer time of 1h. Here the prominent peaks at 7.08-7.30 ppm representing guaiacyl and syringyl units of lignin with p-hydroxyphenylpropane at 6.85 ppm start to decrease at 170 °C. As the time of treatment was further increased to 1.5h, these groups completely disappeared at 170 °C and a very prominent broad peak at 3.60 ppm representing the aliphatic hydrogen of carbonyl groups appeared (Figure 3.3.3). These results are in conformity with the results from the IR studies of lignin where the appearance of carbonyl groups could be attributed in lignin due to caustic treatment of straw at 170 °C.

3.3.1.3 Activation Energy

A preliminary study to help confirm the activation energy for the delignification process was carried out using relative values of ^{1}H NMR peak intensities of the prominent lignin groups at 7.08 ppm, 6.85 ppm, 5.08 ppm and 4.40 ppm from Figures 3.3.1-3.3.3 for 0.5h-1.5h straw and caustic treatment in the temperature range 25-170 °C.

The activation energy was computed from a plot of ln (rate of delignification) versus 1/T (shown in Figure 3.3.8). The rate of delignification (at temperature T) was found by plotting relative ^{1}H NMR peak intensities of the prominent lignin groups versus time. It was found that $E_a = 15.5 \pm 6.9$ kJ mol^{-1}. This is consistent with the value of $E_a = 14 \pm 3$ kJ mol^{-1} for the bulk reaction obtained from the rate constants (see Chapter 2).

3.3.1.4 Conclusions

* As cooking proceeds, typical lignin-like groups such as p-hydroxyphenylpropane, syringyl, guaiacyl and β-aryl ether appear in the dissolved product from alkali treatment of straw.

* As the severity of cooking is increased, particularly at 80 °C and above, these groups start reducing.

* At 170 °C with 1h or more cooking time many of the lignin groups disappeared and there is a marked growth in acid groups showing severe degradation of the lignin.

* The activation energy of 15.5 ± 6.9 kJ mol^{-1} for the rate of appearance of lignin-like groups up to 150 °C is similar to that for the delignification reaction as a whole, giving confirmation that it is the rate of lignin production that is being measured.

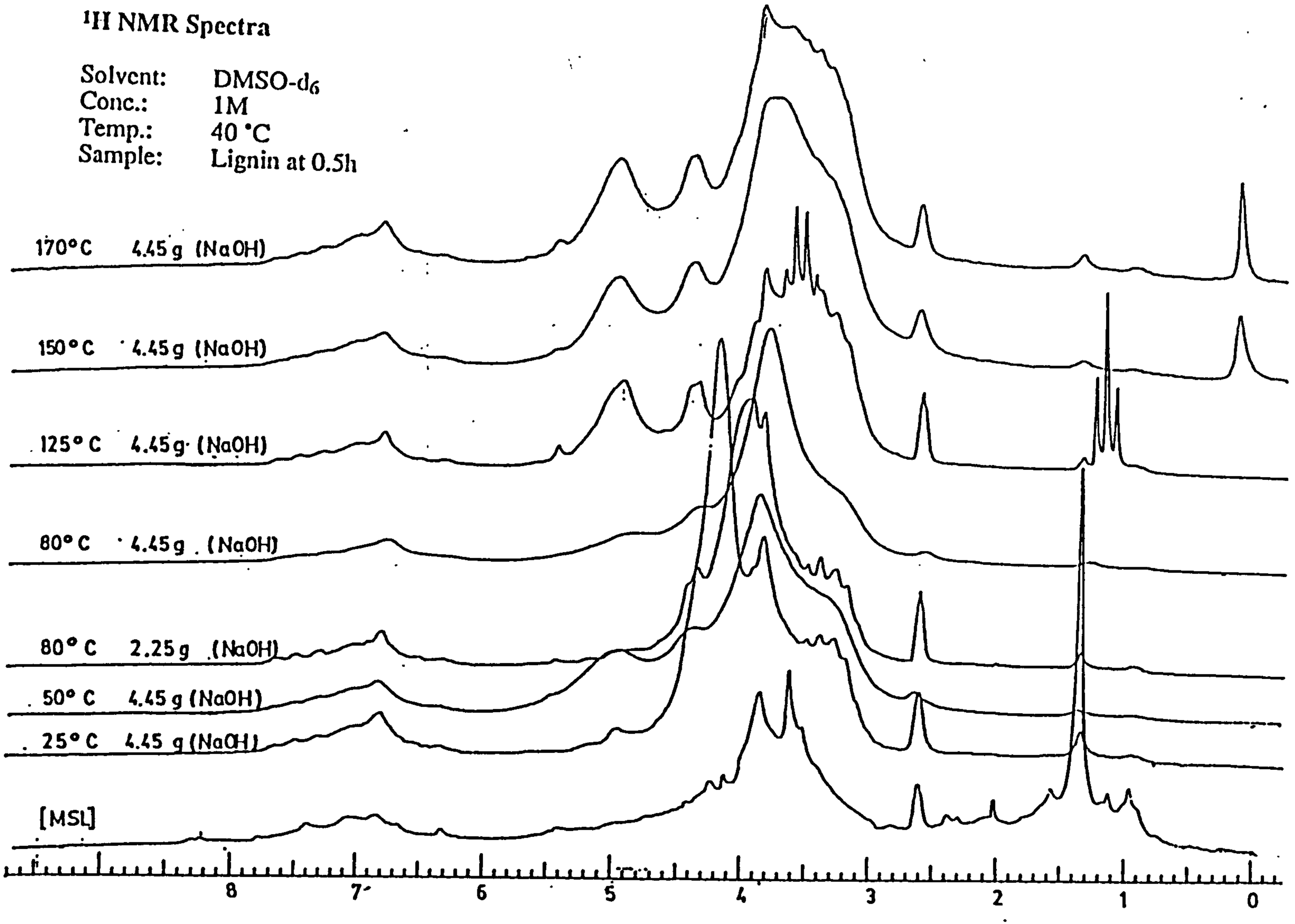


Figure 3.3.1 ^{1}H NMR spectra of dissolved lignin from wheat straw at different temperatures.

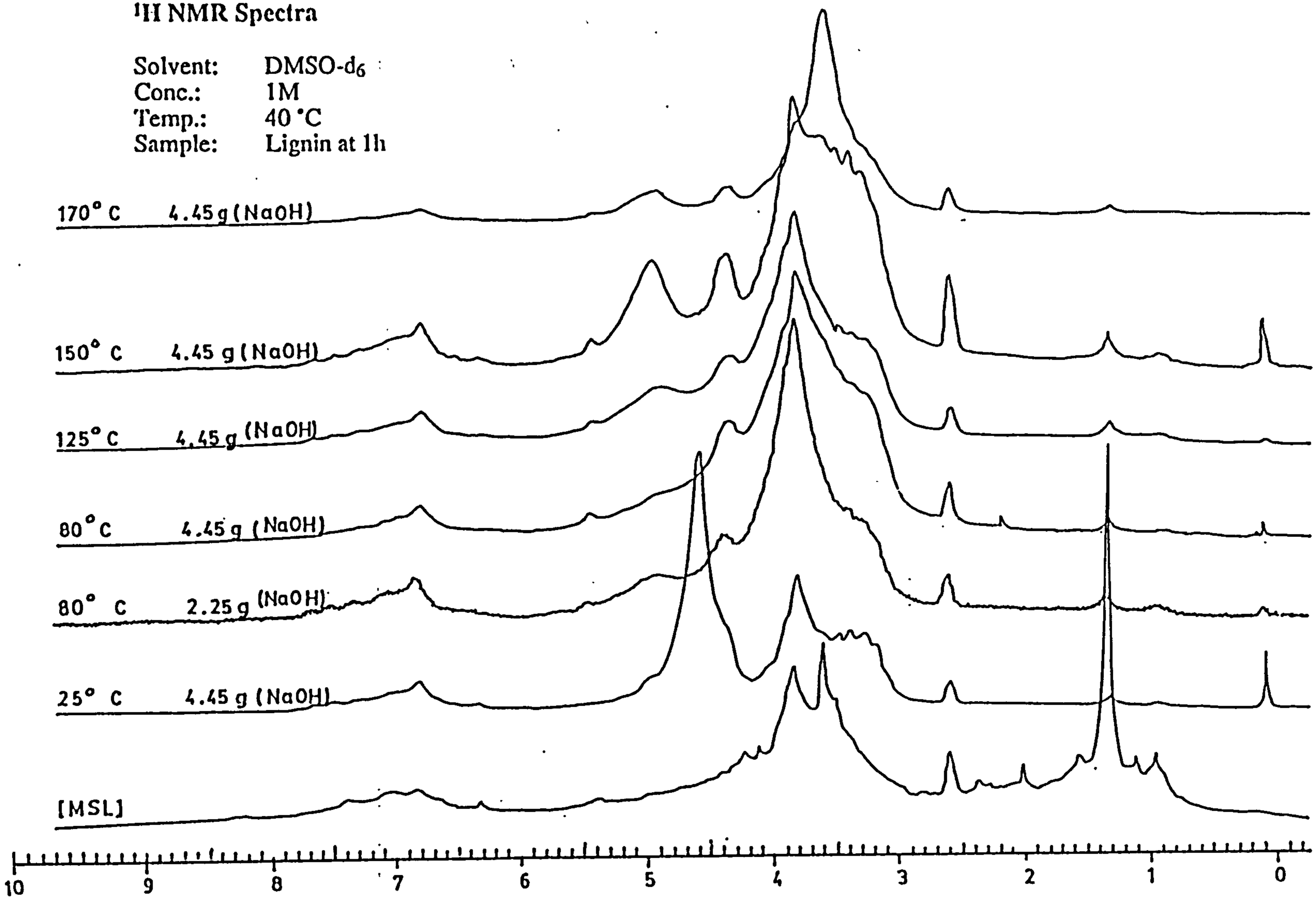


Figure 3.3.2 ^{1}H NMR spectra of dissolved lignin from wheat straw at different temperatures.

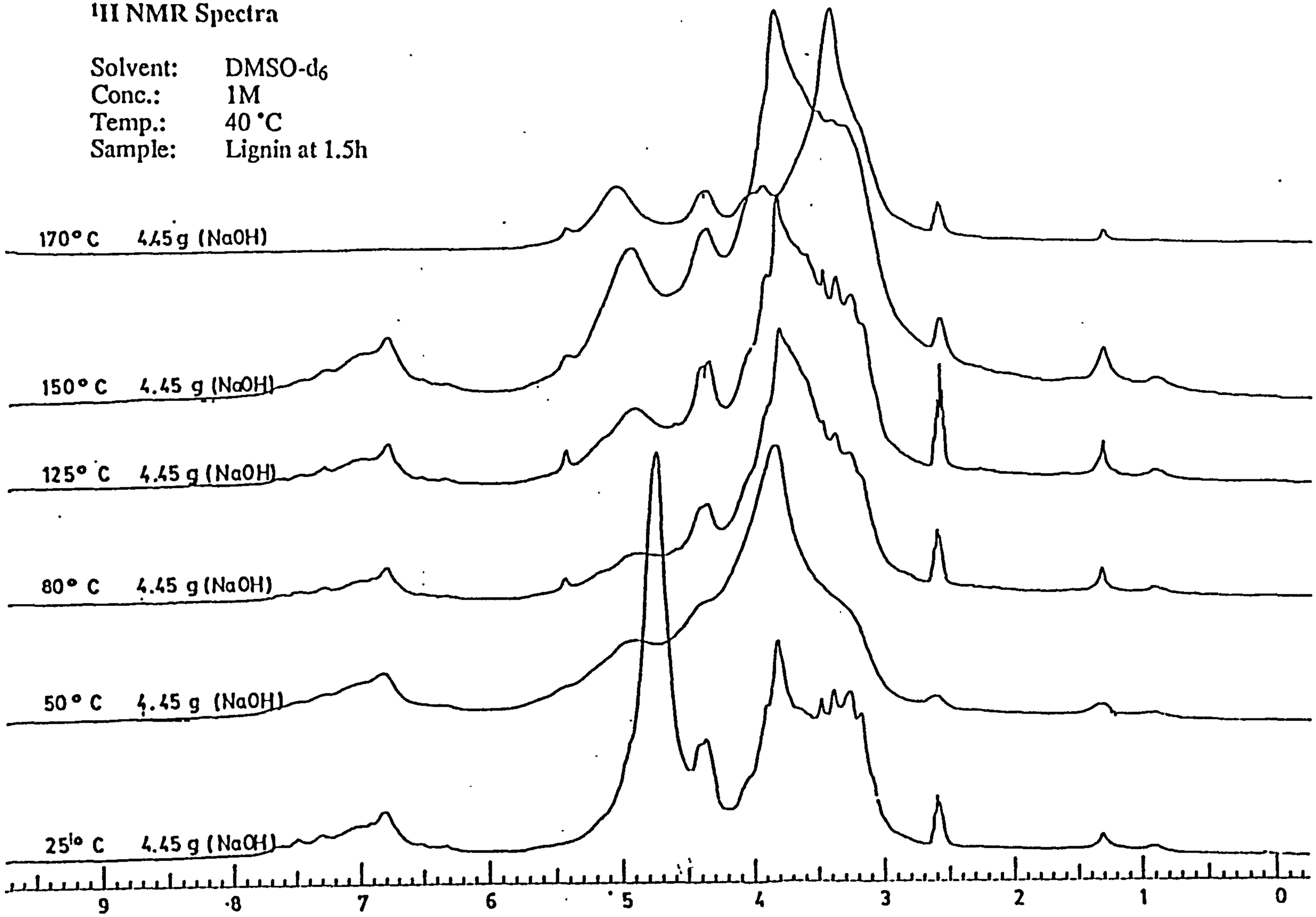


Figure 3.3.3 ^{1}H NMR spectra of dissolved lignin from wheat straw at different temperatures.

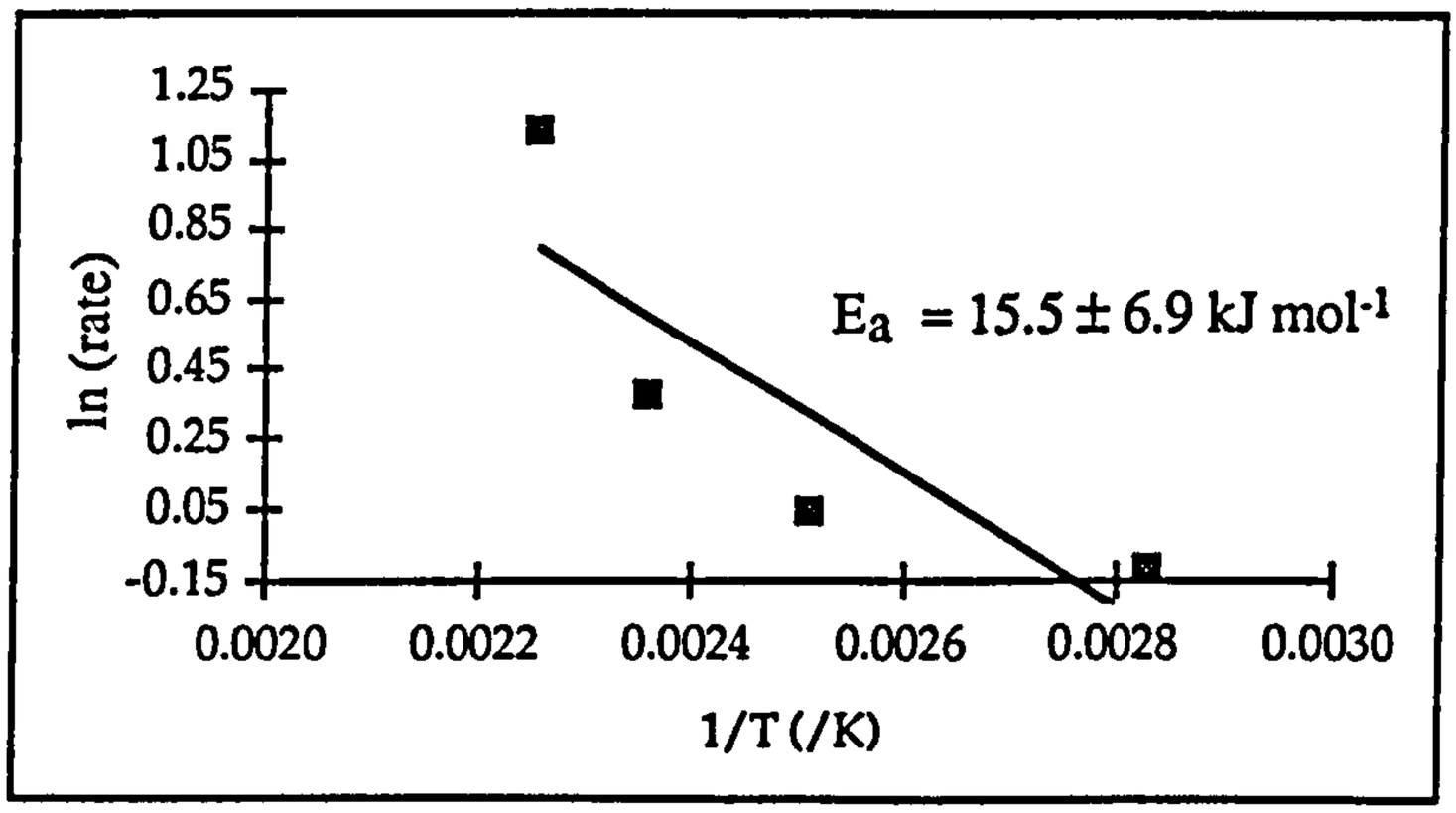


Figure 3.3.8

Activation energy for the rate of appearance of lignin like groups calculated from the ^{1}H NMR intensities of Syringyl and Guaiacyl groups of lignin.

3.3.2 Solid-State NMR

3.3.2.1 Introduction

The development of rapid and non-destructive techniques for fibre analysis has received considerable attention in recent years (Himmelsbach et al., 1983; Maciel et al., 1981 and Bartuska et al., 1980). The most popular current technique is solid-state NMR spectroscopy which is a non-destructive method of analysis (except that the sample must be ground). With the advent of solid-state NMR, ^{13}C NMR spectra of rigid materials can be obtained and the development made possible the use of NMR in the analysis of fibrous materials (Schaefer and Stesjskal, 1979). The technique of cross polarization with magic angle spinning (CP/MAS) in ^{13}C NMR has been applied by several workers recently with great success to a wide range of natural and synthetic macromolecules (Milkins et al., 1979), including the important constituents of plant fibres, i.e., carbohydrate, lignin, protein etc. (Himmelsbach et al., 1983 and Schaefer and Stesjskal, 1979). This technique uses is The CP/MAS ^{13}C NMR approach now provides a vital link of structural information between solid and solution states. As far as lignin is concerned, it should be possible to provide valuable details like the relationship between the solution-state and solid-state ^{13}C spectra of a soluble lignin and this relationship could be used to gain structural information about the lignin to know what are the structural differences between soluble and insoluble lignin. Also the ^{13}C NMR CP/MAS approach could help to obtain organic structural details on solid lignin samples including the lignin of intact plant materials (Maciel et al., 1981).

3.3.2.2 Results And Discussion

The structure and composition of three samples, ground wheat straw, pulp (after delignification) and the lignin extracted in the metal reactor, were investigated spectroscopically by solid-state NMR (Figure 3.3.10).

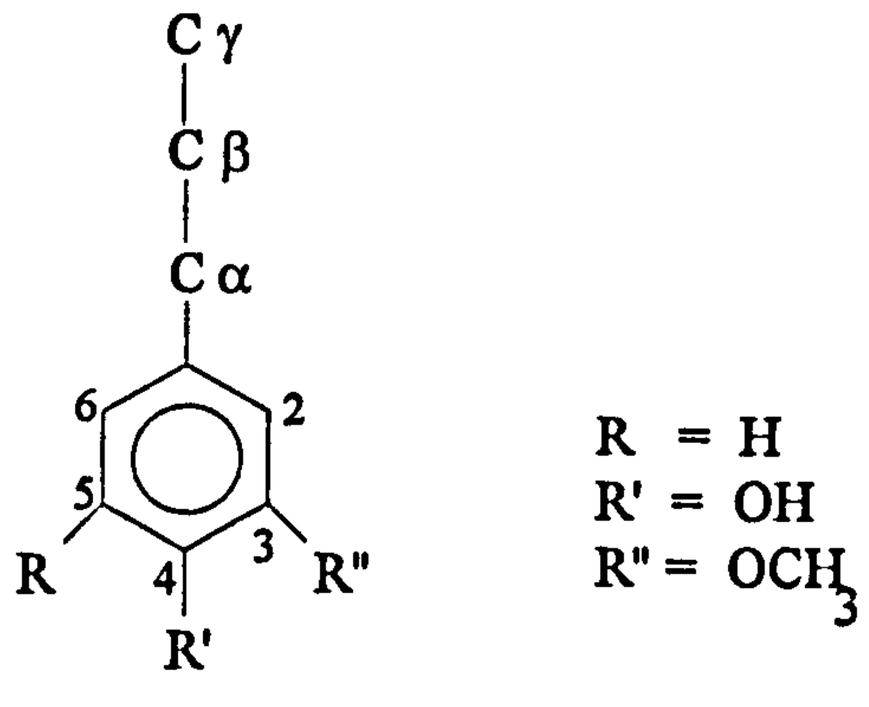
There is a general corresponding and similarity between the ^{13}C spectra of the solid state and solution samples of lignin. However, there are some obvious differences

in the characteristic-the high-field solution state ^{13}C spectra have a larger number of sharper and more distinct peaks, while each peak corresponding to the solid-state spectrum consist of a collection of peak envelopes of various ranges of linewidth. In addition to these, there are some apparent differences between the relative intensities of distinct regions of a corresponding solid/solution pair of spectra. These differences in spectral characteristic between solution and solid-state NMR approaches are well known and largely understood (Himmelsbach et al., 1983 and Maciel et al., 1981). Generally the differences in ^{13}C NMR signal intensities between the solid-state and liquid-state spectra arise because of the different polarization mechanisms involved in giving rise to ^{13}C magnetization measured in the two different types of experiments. In the solid-state CP/MAS experiment this magnetization arises from cross polarization with the proton spin reservoir, while in the typical liquid-state ^{13}C NMR experiment the ^{13}C magnetization is generated by ^{13}C spin-lattice relaxation, involving energy transfers with various energy modes in the system. While these two mechanisms for establishing and re-establishing ^{13}C magnetization have the ^{13}C-^{1}H dipolar interaction in common, they rely on motional characterisations in very different ways (Maciel et al., 1981).

The solid-state NMR spectrum in Figure 3.3.10 for the extracted fraction of wheat straw lignin after cooking in the metal reactor at room-temperature for 4h was analysed by the above instrument. The assignments of the peak in the solid-state ^{13}C NMR spectrum were made according to the acetal grass lignin assignments that had been previously isolated by Himmelsbach and Barton (1980). The lignin spectrum in Figure 3.4.1 (C) was found to contain primarily lignin which was indicated by signals in the regions 50-65, 70-90, 130-140 and 140-160 ppm. These are primarily due to aromatic methoxyl, protonated aliphatic, protonated aromatic, non-protonated non-oxygenated aromatic and phenolic non-etherified and etherified aromatic carbons, respectively. These signals are consistent with the signals previously obtained in the solid-state NMR spectra for lignin (Jung and Himmelsbach, 1989). The sharp signals observed at 56 ppm in the lignin spectrum (C, Figure 3.3.10) is attributed to methoxyl carbons (OCH_3). The aliphatic region of the spectrum (62-95 ppm) contain signals of carbohydrates which is also in consistent with the previous observations that there is a strong attachment of polysaccharides with lignin (Chang et al., 1975). The aromatic region of the lignin spectrum is relatively free from interfering carbohydrate signals. The signals at about 110 ppm is assigned for C-2/C-6 of syringyl (S) units of lignin and the signals at about 115

ppm is due to C-3/C-5 of p-coumaryl units or C-2/C-5 of coniferyl units of lignin (Himmelsbach and Barton, 1980).

Figure 3.3.11 displays the results of solid-state ^{13}C NMR analysis of the extracted lignins for 0.5h treatment of straw with caustic at different temperatures (25-170 °C). The comparison of the spectra between the three different temperature (25°C, 80 °C and 170 °C) in Figure 3.3.11 shows quite noticeable differences, especially in the aromatic region (105-170 ppm) where at 25 °C the spectrum of the lignin shows the most apparent presence of signals at 131-135 ppm, 120-124 ppm and about 115 ppm which could be attributed primarily to carbon atoms at the position 1,2 and 5 in the following lignin structure A (Maciel et al., 1981).



A

Figure 3.3.9

The strong NMR signal due to C-3/C-5 is observed around 155 ppm in the solid-state spectrum at all the above temperatures (Figure 3.3.11). This observation has also been noted in solution ^{13}C NMR spectra which is consistent with the previous studies where similar observation were noted for the solid-state ^{13}C NMR spectra of wood lignin (Ludemann and Nimz, 1974).

However, when the temperature was increased above 125 °C and 170 °C there are obvious changes, especially in the aromatic region where the relative peak intensities reduced and almost disappeared. The prominent peak at around 155 ppm is also markedly reduced, indicating that chemical changes take place on increasing the temperature on treatment of straw in presence of caustic (Figure 3.3.11). These results are in conformity with the previous observations for solution ^{1}H NMR/^{13}C NMR of

lignin where, too, the prominent lignin-like peaks markedly reduced and disappeared with longer time and higher temperature of treatment of straw with caustic (Figure 3.3.11) and Table 3.3.1).

However, the bands for lignin in the straw (A, Figure 3.3.10) are much less pronounced and the spectra are primarily characterized by carbohydrate signals. Generally, the carbohydrate moieties involved are glucose (in the form of cellulose) plus arabinose, xylose and glucose (in the form of hemicellulose) (Himmelsbach and Barton, 1980). The carbohydrate signals in the untreated straw spectrum (A, Figure 3.3.10) appear in the region 60-95 ppm. Similarly the spectra for pulps in Figure 3.3.12 and 3.3.13 for 1h and 1.5h time of treatment at different temperatures (80-150 °C) gave results showing the non-appearance of lignin-like groups after the delignification process. The pulp spectra show mostly carbohydrate signals in the aliphatic region (60-105 ppm). The signal around 62 ppm could be assigned to hydroxylmethylene (C-6 in hexopyranose and C-5 in pentofuranoses) (Himmelsbach and Barton, 1980 and Himmelsbach et al., 1983). The prominent signal centered at about 75 ppm is due to C2-C5 in hexopyranoses and C2-C4 in pentofuranoses while the sharp, well defined signal at about 105 ppm is attributed as a single carbon type signal for C-1 in both types of saccharides (Figures 3.3.12 and 3.3.13, Himmelsbach and Barton, 1980).

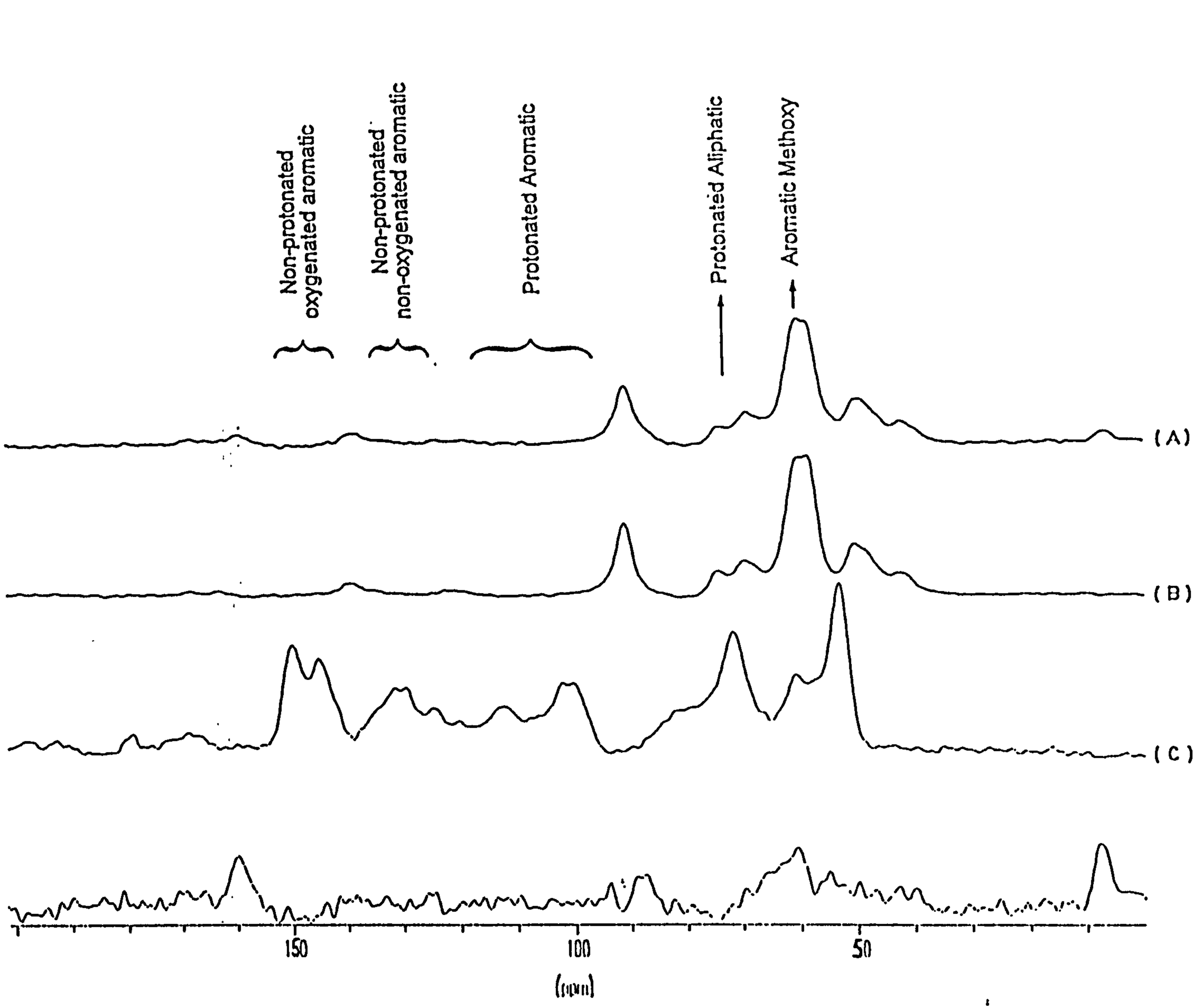


Figure 3.3.10 Solid-state ^{13}C NMR spectra of wheat straw (A); Pulp (B) and Lignin (C).

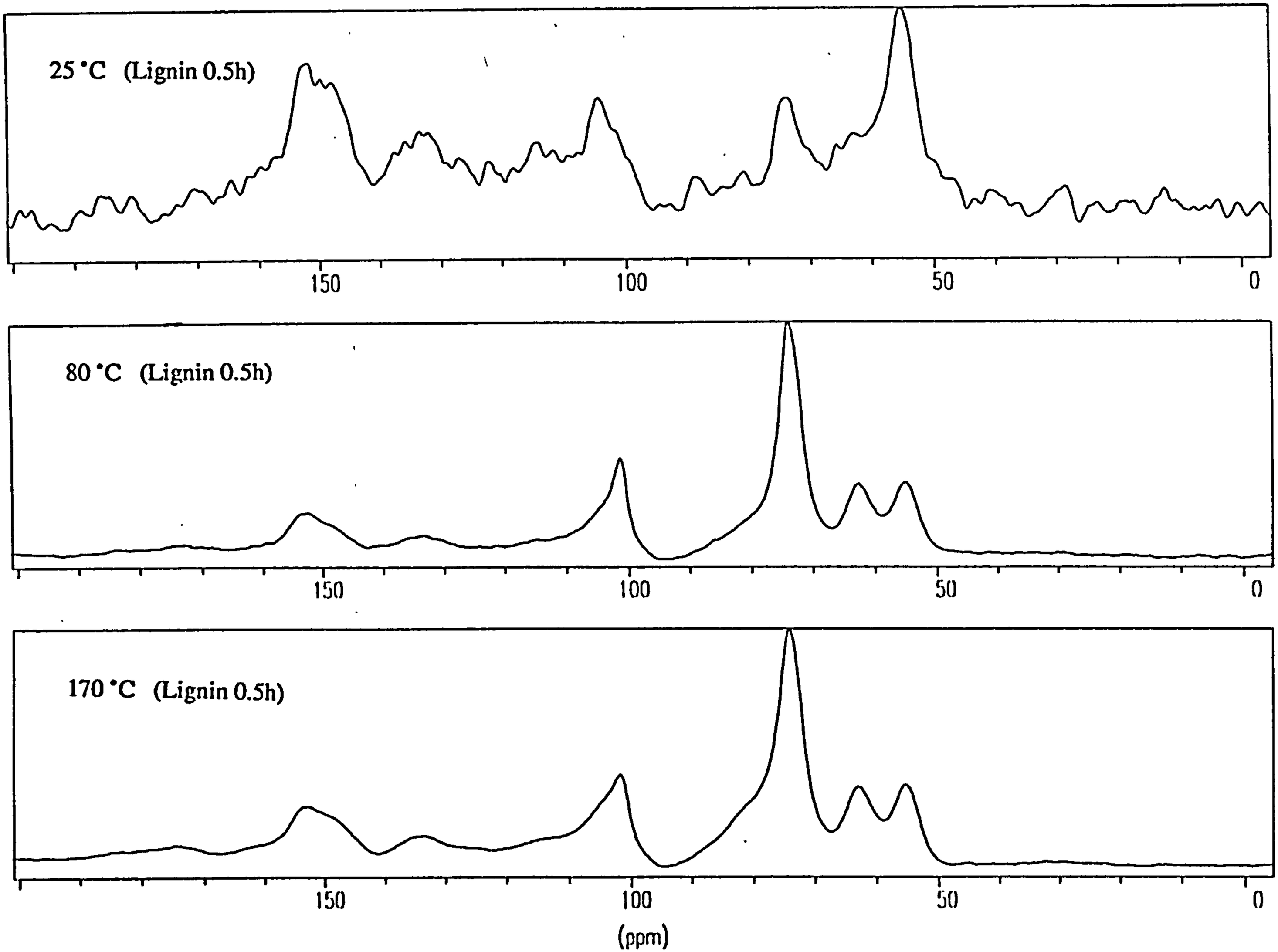


Figure 3.3.11 Solid-state ^{13}C NMR spectra of wheat straw.

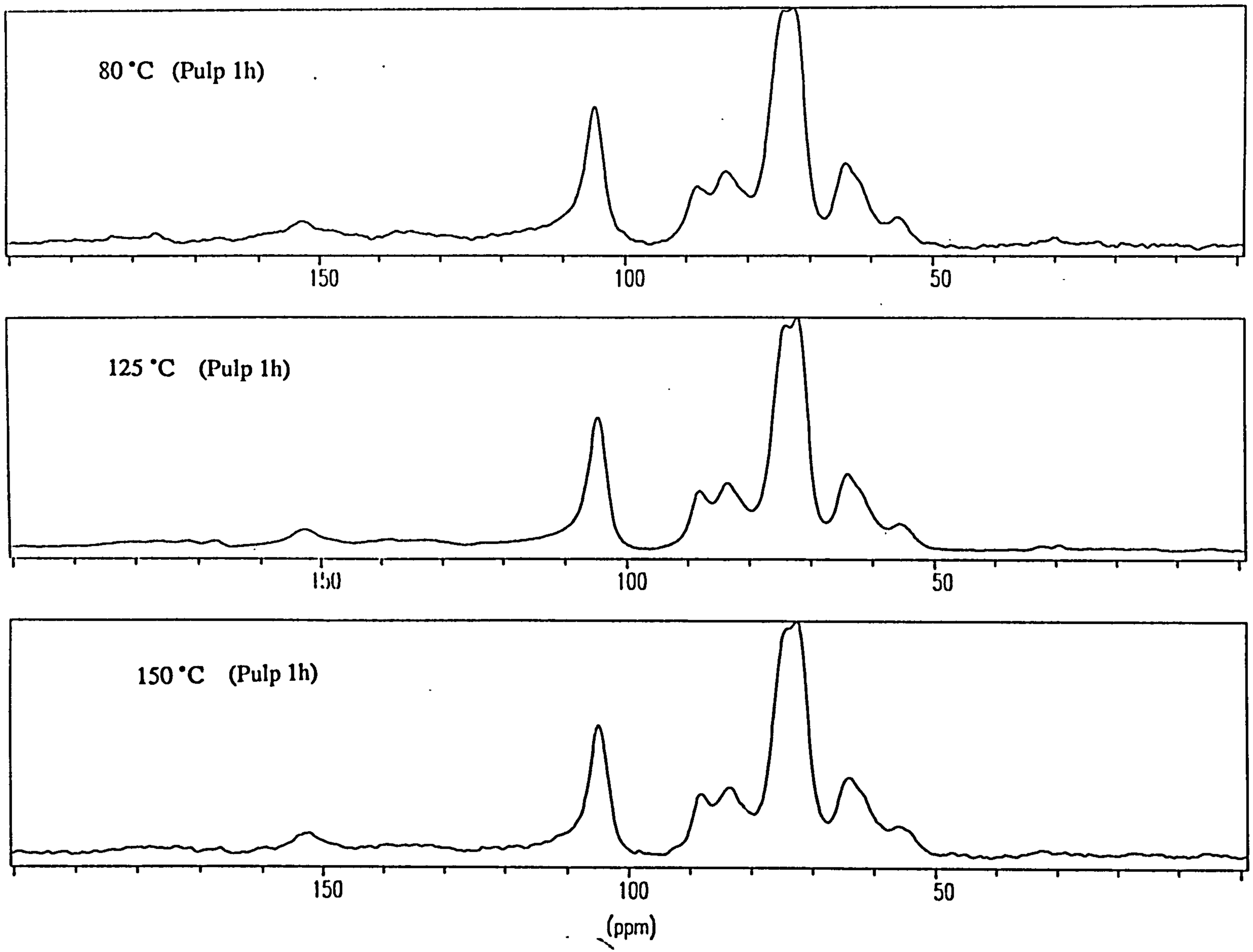


Figure 3.3.12 Solid-state ^{13}C NMR spectra of wheat straw.

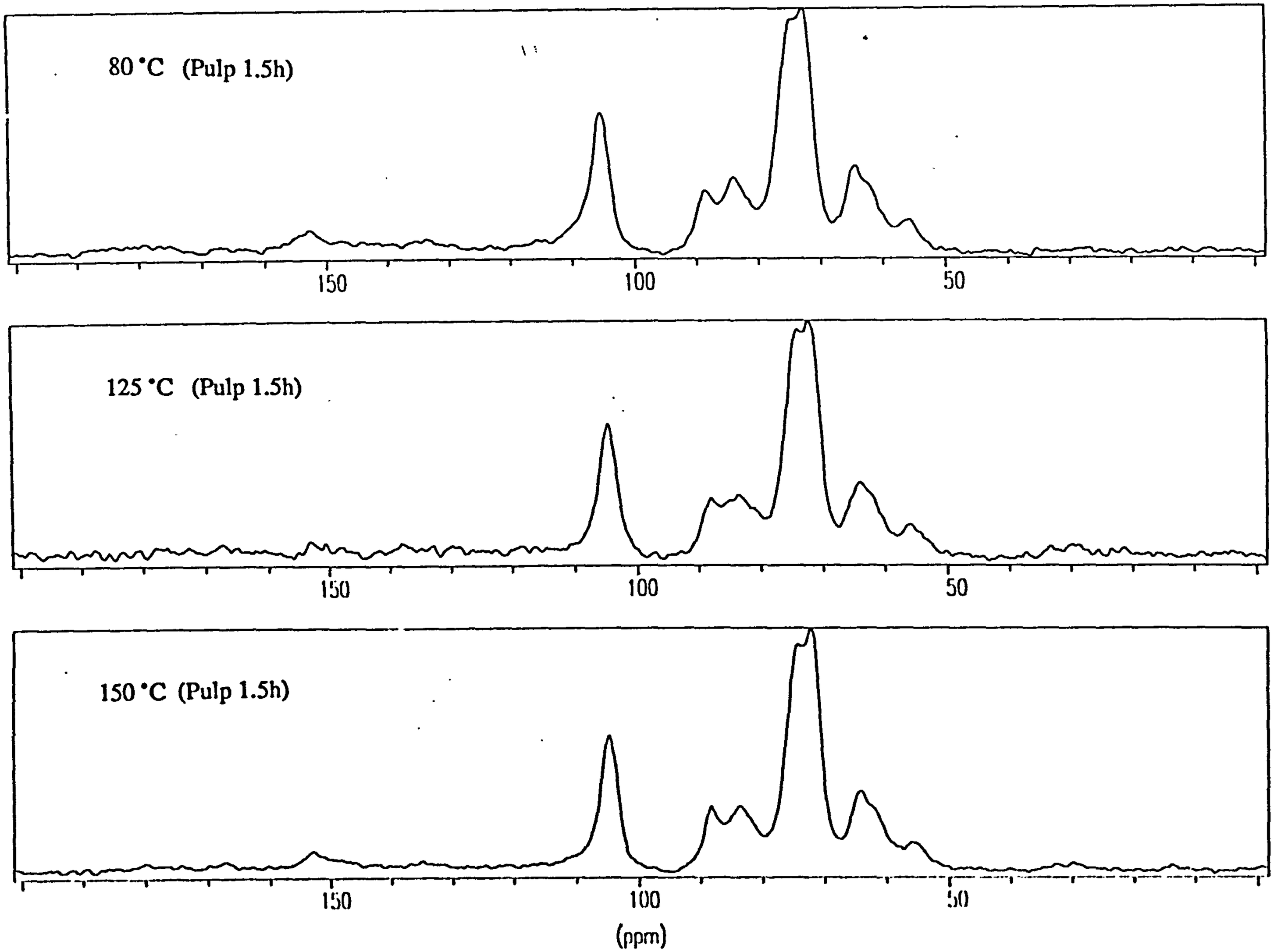


Figure 3.3.13 Solid-state ^{13}C NMR spectra of wheat straw.

3.3.3 ^{13}C NMR Spectroscopy

3.3.3.1 Introduction

The recent advances in Fourier transform NMR (FT-NMR) techniques have led to a rapid method for obtaining natural abundance ^{13}C NMR spectra. ^{13}C NMR spectroscopy has become comparable to ^{1}H NMR spectroscopy in terms of importance as a useful tool for the structural elucidation of organic substances inspite of the low natural abundance of ^{13}C (1.1%).

There are several advantages of ^{13}C NMR spectroscopy over ^{1}H NMR spectroscopy for structural determination of organic compounds (Wood and Kellogg, 1988). In ^{13}C NMR spectral data are obtained from the "backbone" of the molecule rather than from the exterior of the molecule as in ^{1}H NMR. So the ^{13}C NMR spectrum of a compound provides information about the nature of all carbons in the molecule. Another advantage is that ^{13}C NMR spectra are not complicated by spin-spin coupling, as the possibility of ^{13}C nuclei adjacent to each other in the same molecule is very low (1/10,000). Moreover, ^{13}C NMR spectra are usually obtained without the broadband noise of proton-coupling, so that only single signals are obtained for each ^{13}C resonance (Abraham and Loftus, 1979). In addition, the range of ^{13}C NMR chemical shifts in the majority of diamagnetic organic compounds is about 240 ppm (in δ scale) in comparison with about 12 ppm for ^{1}H NMR. The better resolution and less overlap of signals in ^{13}C NMR spectra of organic compounds, particularly of polymeric natural products such as lignin is very useful (Wood and Kellogg, 1988).

Thus, the characterization of lignin by ^{13}C NMR furnishes quite comprehensive data about the nature of carbons in lignin in terms of chemical structure (Ludemann and Nimz, 1974; Nimz et al., 1974 and Nimz et al., 1981).

However, several difficulties are still encountered in the interpretation of ^{13}C NMR spectra of lignin for assignments of signals because of the intensive overlap of signals due to the ^{13}C nuclei in lignin present in similar, but non-identical, environments (Wood and Kellogg, 1988).

In ^{13}C NMR spectroscopy, the three characteristic signals caused by carbon atoms α, β and γ particularly in β-O-4 structures are regarded as indicative for lignins. The three aromatic moieties occurring in lignin (guaiacyl, syringyl and p-hydroxyphenyl) also give quite distinguishable signals in the aromatic region of the spectrum (Nimz et al., 1981). Therefore, ^{13}C NMR spectroscopy is considered a valuable method for lignin classification and characterization.

3.3.3.2 Results And Discussion

The spectra for the extracted lignins after the treatment of straw with caustic in the metal reactor at different times (0.5h-1.5h) and different temperatures (25-170 °C) were obtained after 40,000 scans on a FX-Jeol NMR Spectrometer. They were all recorded below 40 °C. The sample was dissolved (50mg/0.5ml) in DMSO-d_6 with about 1% Me_4Si added as an internal reference at 0 ppm.

The simultaneous occurrence of lignin, polysaccharides and phenolic acids make the assignment more difficult especially in the aliphatic region at 10.30 to 59.90 ppm where the peak intensity is very high (Figure 3.3.14). The assignments of signals are established with literature data in deuterated dimethyl sulfoxide as a solvent and at the same temperature (Kovac et al., 1982; Lapierre et al., 1984 and Scalbert et al., 1986). Most of the signals were assigned according to the previously assigned data of wheat straw lignin (Nimz et al., 1981 and Scalbert et al., 1986). However, it is well established that chemical shifts values may vary with solvent used and the temperature; deviations of up to 2 ppm are commonly reported (Heyraud et al., 1979).

Figure 3.3.14 represents the lignin which was extracted by NaOH treatment of straw for 4h at 25 °C (4.23g bone dry weight straw with caustic 2.02 mol dm^{-3} in 55 ml H_2O, (see Chapter 6 for details). The well-dried fraction of the extracted lignin was subjected to the above spectrometer for ^{13}C NMR analysis. The spectrum shows strong signals for the guaiacyl-syringyl units of lignin in the aromatic part (104-160 ppm). The intensities of syringyl (S) at 104.50 ppm are for C-2/C-6 syringyl and the signals at 152.40 ppm for C-3/C-5 syringyl units of lignin whilst the guaiacyl residues (G) give signals at 119.70 ppm for C-6 unit and 147.90 ppm for C-3 unit indicating the presence

of these groups of lignin in the extracted lignin of wheat straw (Scalbert et al.,1986). The signals for p-hydroxyphenyl C-2/C6 H is assignable at 127.80 ppm (Scalbert et al.,1986). The signal intensity for the p-hydroxyphenyl unit is low which is probably due to overlapping by guaiacyl units (Nimz et al., 1981).

Although the monomeric composition of the extracted lignin shows significant level of guaiacyl and syringyl units, there are relatively low amounts of p-hydroxypehnyl units. The syringyl to guaiacyl units are in good agreement with previous results which was determined on wheat by alkaline nitrobenzene oxidation of cell wall or milled straw lignin (Higuchi and Kawamura, 1966) or by permanganate oxidation of Kraft lignin (Erickson et al., 1973). Wheat straw lignin seems to be richer in guaiacyl units than the average guaiacyl-syringyl of hardwood as formerly suggested (Glasser, 1983 and Nimz et al., 1981). However, the lower intensity of p-hydroxyphenyl unit in straw lignin is attributed to the existence of lignin heterogeneity in wheat straw (Lapierre et al., 1982). Actually, heterogeneity of monomeric composition has been suggested between not only different places but at different heights of a same internodes of wheat (Agosin et al., 1982). The lower amount of p-hydroxyphenyl unit in straw lignin has also been previously reported in the literature. Monocotyledons such as grasses have been found to contain considerably lower amounts of OH-containing lignin relative to hardwood lignin (Higuchi and Kawamura, 1966 and Erickson et al., 1973) This characteristic property is a useful tool to distinguish grasses and perhaps most of the monocotyledon lignins from dicotyledon lignins (Nimz et al., 1981). Reduced levels of p-hydroxyphenyl units could also be due to phenolic acid signals corresponding to esterified p-coumaric acid for C-2/C-6 and C-1 which are assigned at 130.34 ppm and at 125.70 ppm, respectively. The signal at 116.40 ppm is assigned to C-β ferulic ether which was reported to be formed due to acid hydrolysis in alkaline solution (Ludemann and Nimz, 1974). The presence of ferulic acid ethers has been well established in alkali treated lignin fractions in earlier reports (Nimz et al., 1981).

The ^{13}C NMR spectrum of the isolated fraction of lignin from the straw treated with caustic at 25 °C in Figure 3.3.14 reveals that the carbonyl content is higher which could be due to treatment of straw with excess caustic for a longer time (4 h).

The lignin fraction obtained from straw also contains significant amounts of non-lignin constituents particularly polysaccharides associated with lignin which are mainly composed of β-1→4 xylan backbone, e.g., signals at 101.30, 78.440, 76.11 and 73.42 ppm which are partially substituted with acetyl group at 30.7 and 27.9 ppm. The peak at 80.30 ppm might originate from β-1→4 glucan (Lundquist et al., 1977 and Scalbert et al., 1986). Terminal xylose units were identified at signals 76.11, 69.17 and 65.66 ppm which are assigned for non-reducing terminal xylose.

Relative to lignin signals in straw, the non-terminal xylose signals are higher in the extracted lignin (Figure 3.3.14). Association of lignin with hemicelluloses has been described in many species including softwood, hardwood and gramineae (Bjorkman, 1956; Erickson et al., 1973; Lundquist, 1980 and Morrison, 1974). Different methods for purification of lignin fractions could not give lignin with lower hemicellulose which indicate firmly that all the lignin fragments are linked to hemicellulose in the cell wall structure where the lignin is closely associated with hemicellulose (Scalbert et al., 1986).

Furthermore, the observation that grass lignins have fewer β-aryl ether linkages than hardwood or softwood is confirmed by the relatively low intensity observed for β-aryl ethers linkages in straw lignin at 59.90 ppm. This is in line with the previous studies which reported a similar observation and concluded that grass lignins contained fewer β-aryl ether linkages (Nimz et al.,1981). In grasses the most characteristic lignin structures (β-O-4) are much less pronounced and differ more from hardwood than softwood lignins. This is also said to be true for the signals indicated by Cγ-β-aryl ether and Cα-β-aryl ether. For this reason, grass lignins are said in their chemicals reaction (especially degradation like pulping) to behave more like softwood than hardwood (Lapierre et al., 1984 and Nimz et al., 1981). These characteristics are useful to distinguish grasses and perhaps all monocotyledons lignin from dicotyledon lignin according to their chemical compositions such as guaiacyl, syringyl, p-hydroxypehnyl units of lignin (Nimz et al., 1981).

Table 3.3.1 also shows the results of ^{13}C NMR analysis for the extracted lignin at different times (0.5-1.5 h) and different temperatures (25-170 °C) after the treatment of

straw by caustic (2.02 mol dm^{-3}) with 55 ml H_2O in the metal reactor (see Chapter 6 for details). The comparison of the results with the lignin results extracted at room temperature as in Figure 3.3.14 shows significant changes in the three characteristic aromatic nuclei regions of lignin, guaiacyl (G), syringyl (S) and p-hydroxyphenyl (H) which are distinguishable according to their corresponding signals in the aromatic region of the ^{13}C spectrum (about 104-160 ppm).

For short times, as the temperature was increased the syringyl and guaiacyl moieties first started increasing and then decreased upon continuing the treatment for a longer time (1.5h) at higher temperature (170 °C) in the dissolved lignin. For example, the C-6 guaiacyl unit at 119.70 ppm completely disappeared in dissolved lignin as the temperature went up along with cooking time to 1.5h at 170 °C indicating significant chemical changes take place in the lignin structure in the presence of caustic at longer times and higher temperature (Table 3.3.1). Also, the amounts of OH-residues such as p-hydroxyphenyl units are found to be absent in the dissolved lignin at higher temperature and longer time of treatment.

The data contained in Table 3.3.1 show that carbonyl resonances which could come from uronic acids and esters, in addition to cinnamic acids and esters, acetyl groups and other aliphatic ester which may all contribute to signals at 171.0-172.66 ppm. For example, C-6 in methyl uronates has been reported at 172.3 ppm (Himmelsbach and Barton, 1980). These results are in conformity with IR findings that the dissolved lignin have more carbonyl groups which might have been created or strengthened during caustic treatment of straw in the metal reactor.

These results are good in agreement with those results obtained by ^1H NMR where similar observations were found for the proton nuclei of these groups after appearing in the initial stages of cook. The lignin-like groups started decreasing with increased reaction times and temperatures and finally at 1.5 hours treatment of cooking time at 170°C, they disappeared in the corresponding dissolved lignin (Figure 3.3.3).

However, all the dissolved lignin at all times and all temperatures appear to contain significant amounts of non-lignin constituents particularly polysaccharides (Table 3.3.1). This is one of the indications that lignin fragments are very much linked to

hemicelluloses in the cell wall and so closely associated that even at higher temperatures and increased time of treatment these could not be separated out completely from lignin (Scalbert et al., 1986).

3.3.3.3 Activation Energy

Similar to the activation energy determined in ^{1}H NMR, in ^{13}C NMR too the prominent groups of lignin-like syringyl (S) and guaiacyl (G) were chosen to determine the activation energies for their appearance with temperature range from 25 °C at low cook times using their relative intensities in ^{13}C NMR spectra to compare the value with that of the values derived from overall kinetic delignification reactions. The ^{13}C NMR intensities of syringyl units in the extracted fractions of dissolved lignin at 104.50 ppm and 157.50 ppm were used along with guaiacyl units values at 119.70 ppm for the derivation of activation energies from Arrhenius plots of ln (rate of disappearance of lignin) versus 1/T which is shown in Figure 3.3.15. The values found for the activation energies from the slopes of the plots were 19.7-26.7 kJ mol^{-1} for these lignin groups which are more or less in line (allowing for errors) with the values obtained using Klason analysis method where the activation energies derived from Arrhenius plots for the overall delignification reactions were 14-31 kJ mol^{-1} for bulk and residual reactions (see Chapter 2).

3.3.3.4 Conclusions

* The ^{13}C NMR spectra for lignin extracted at 25 °C by caustic soda treatment of straw shows strong signals for the typical lignin-like guaiacyl and syringyl units with weaker signals for p-hydroxyphenyl units in line with published information on lignin extracted from straw and grasses in general.

* All three of the above units are reduced in amount with increasing temperature of cook: p-hydroxyphenyl units disappear at temperature above 25 °C whilst guaiacyl and syringyl reduce particularly above 125 °C with 1h or more cooking time.

* Phenolic esters such as those of coumaric acid tend to be present at low temperature and reduce at higher temperature.

* β-aryl ether signals are present at room temperature at relatively low intensities and disappear with increasing temperature until they are found completely absent at 170 °C.

* Significant amounts of polysaccharides materials are present in close association with lignin even at 170 °C indicating they are strongly linked together.

* The activation energies of 19.7-26.7 kJ mol^{-1} for the appearance of syringyl and guaiacyl lignin groups are of the same order as that found for the general delignification reaction.Table 3.5.1 ^{13}C Chemical shifts values (δ, ppm) for wheat straw lignin extracted at different times and temperatures.

* The relative intensities of the peaks for guaiacyl and syringyl indicate that the former is present in higher amounts.

* Qualitative comparison with the literature shows that the lignin dissolved from wheat straw is different from wood lignins e.g., in straw lignin contains fewer amonts of β-aryl ether linkages and more guaiacyl groups relative to syringyl.

Table 3.3.1 Carbon-13 chemical shifts values (δ, ppm) for wheat straw lignin extracted in metal reactor (bomb) at various temperatures and times.

Fig.3.3.14	25°	50°	80°	125°	150°	170°	Assignment*
ppm	ppm	ppm	ppm	ppm	ppm	ppm	
181.1	-	-	-	-	-	-	-CHO, cinnamaldehyde; -CO, aryl conjugated
171.30	(172.0)[172.0]	171.0 (172.0)[172.0]	-	(172.0)	(172.0)	172.66	-COOH aliphatic
166.0	-	-	-	-	-	-	Cχ , PC ester
156.50	156.7 (157.1)[156.1]	156.1 [156.2]	156.8 (156.8)[156.1]	156.71 (156.1)[156.0]	156.6 (156.1)[156.1]	156.7 (156.0)	
152.4	153.6 (152.3)	151.1 [151.0]	152.3	-	-	-	C-3/C5 S
147.9	148.2	[147.8]	-	-	-	-	C-3 G
133.4	-	[133.3]	-	-	-	(135.2)	C-1, S non-etherified; C-1 G non-etherfied.
130.3	-	- [130.1]	-	-	-	-	C-2 C-6 PC ester
125.7	[124.5]	- 125.0]	-	-	-	125.10 (125.9)	C-1, PC ester
127.8	-	-	-	-	-	-	C-2/C-6 H
119.7	119.6 (119.1)[119.0]	120.1[119.8]	119.7 [119.6]	119.5 (119.7)[119.5]	119.3 (119.9)[119.7]	(118.9)	C-6, G
116.4	116.5 (116.3)[116.0]	116.3 [115.3]	-	-	-	-	C-β FE ester
104.5	105.0 (105.7)[105.7]	105.8 [105.8]	105.3 (105.6)[105.6]	105.6 (105.6)[105.7]	105.6 (105.2)[105.7]	105.7 (105.7)[105.7]	C-2/C-6 S
101.3	102.1 (101.9)[101.5]	-	-	-	-	-	C-1 Xyl. internal unit
80..3	79.4(79.5)[79.5]	79.6[79.7]	79..9 (79.8)[79.4	79.4 (80.1)[79.4]	79.5 [79.3]	79.5	C-4, Glc. internal unit
78.44	78..6 (78.6)[78.7]	78..6(78.1)[77.9]	78.578.9)[77.9]	77.9 (79.0)[77.9]	78.1(78.3)[78.6]	78.0 [79.0]	Xyl. non-reducing end
76.9	77.2 (77.0)	77.8[76.0]	76.9(67.6)[76.7]	76.5(76.7)[76.7]	76.6 (76.8)[76.5]	76.678.0)[77.1]	Xyl non-reducing end
76.1	76.5 (76.6)[76.5]	-	-	-	-	(76.5)	C-4 Xyl. internal unit
73.4	74.1 (73.52)[73.5]	-	-	[73.5]	-	-	Cα-β- aryl ether
69.1	68.9 (68.9)[67.3]	68.9 [67.3]	68.9 (68.5)[67.2]	67.4 (68.9)[767.4]	68.9 (68.9)[67.4]	67.2 (67.22[67.9]	C-4 Xyl. non reducing end
65.6	-	64.5 [65.1]	(65.2)	-	-	(64.2)	C-5 Xyl. non reducing end
59.9	59.8 (59.8)[59.8]	59.9 [60.0]	59.9 (59.7)[59. 9]	59.9 (59.9)[59.9]	59.9 (59.8)[59.9]	59.9 (59.36)	C-χ, β- aryl ether
30.7	-	-	-	-	-	-	CH_3 acetyl in xylan
27.9	-	-	-	-	-	-	"

*Abbreviation: FE ferulic acid; G guaiacyl unit; Glc, glucose; H, p-hydroxyphenyl unit; PC, p-coumaric acid; S, Syringyl unit; Xyl, xylose; .

The values unbracketed represent the time 0.5h caustic treatment of straw; while the values in brackets (

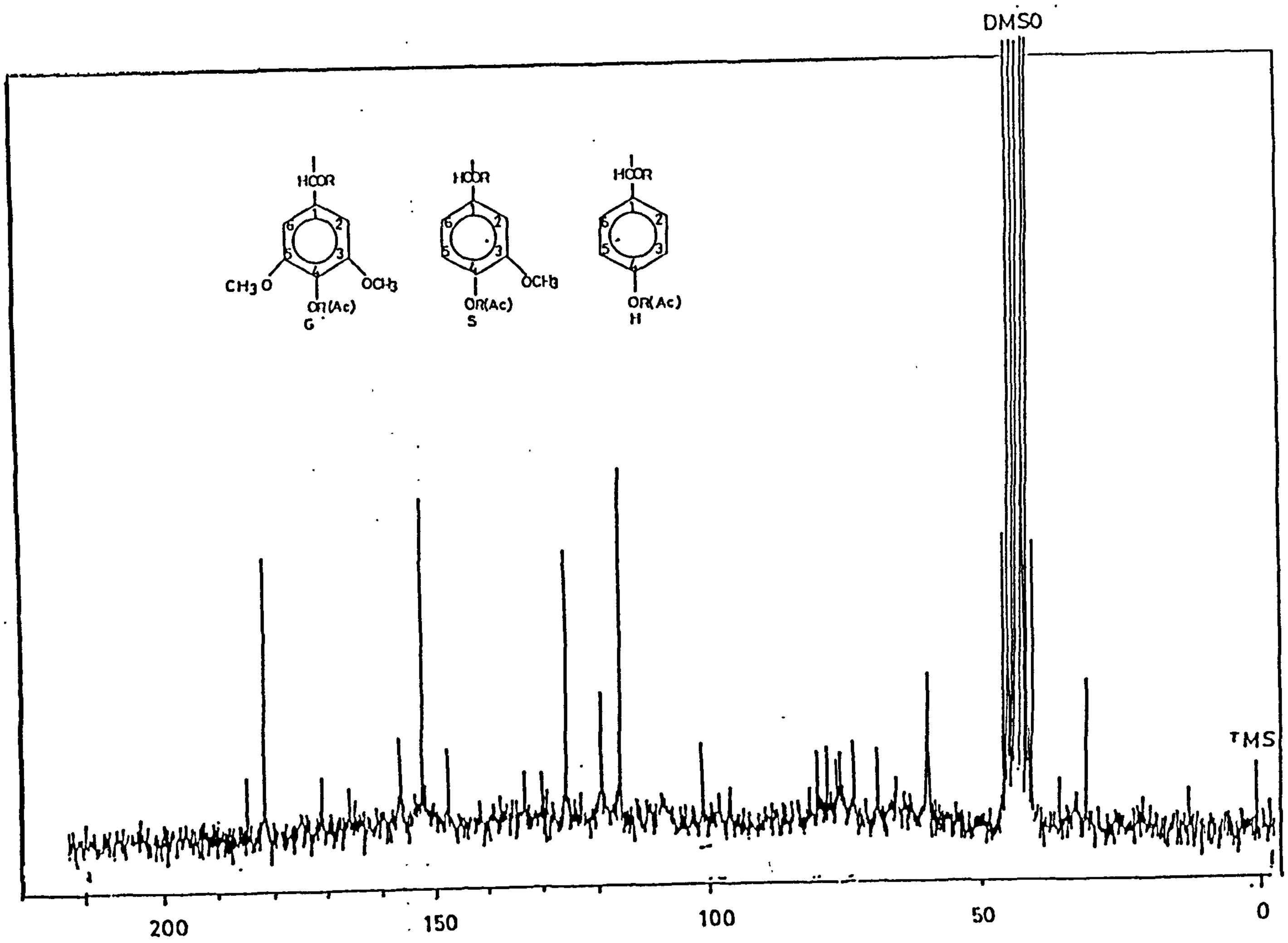


Figure 3.3.14 ^{13}C NMR spectra of the extracted wheat straw lignin after treatment in metal reactor with $NaOH+H_2O$ for 4h at 25 °C.

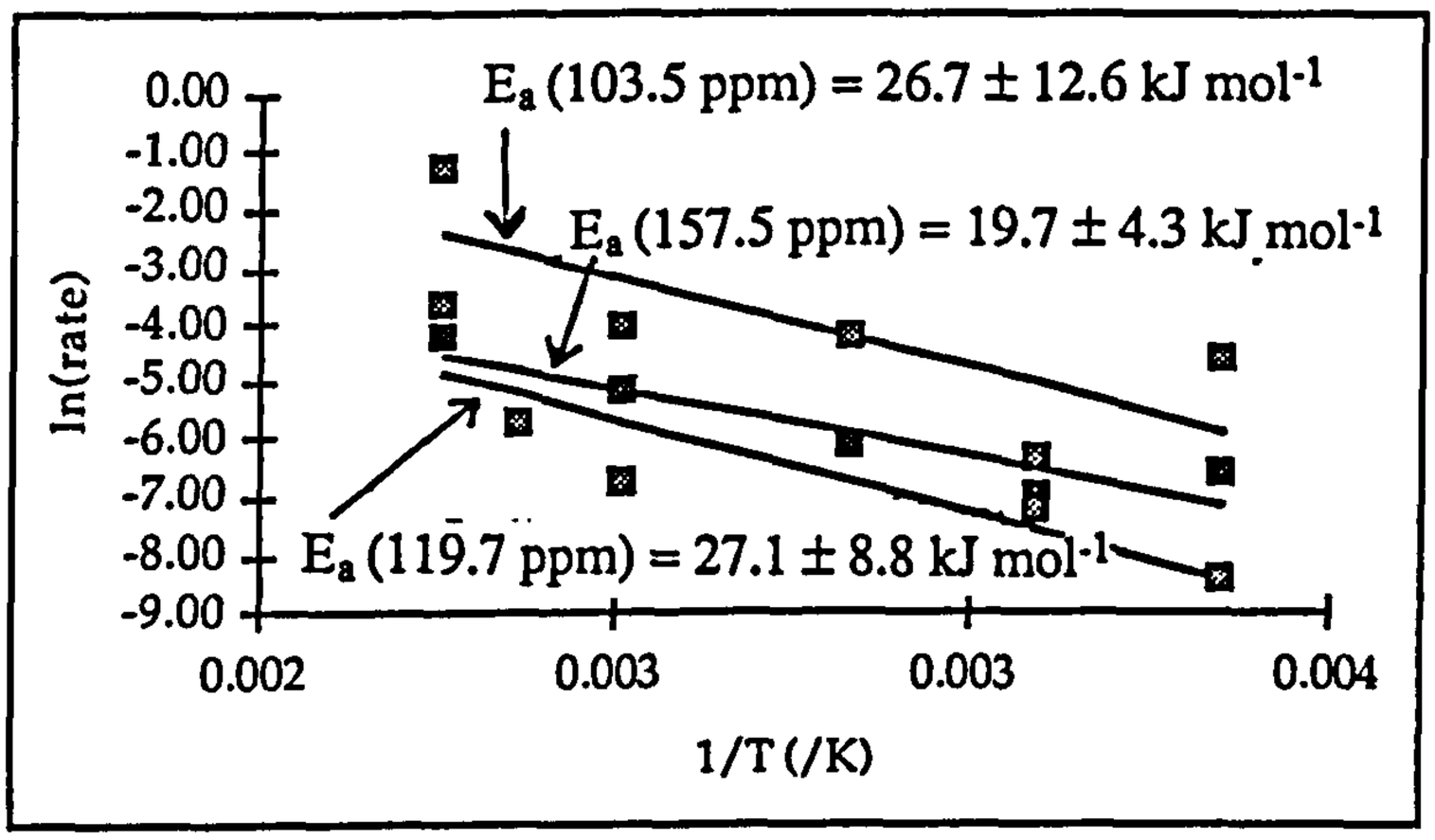


Figure 3.3.15

Activation energy for the rate of appearance of lignin like groups calculated from the ^{13}C NMR intensities for typically lignin groups.

3.4 Molecular Mass Determination Of Lignin

3.4.1 Introduction

The knowledge of the molecular mass distribution is of the utmost importance for elucidation of structure in polymeric materials. Many attempts have been made to determine the structure of lignin (Brauns, 1952). Lignin as such does not represent a definite, uniform compound, but is a collective term for a group of highly polarized compounds of very similar chemical properties but very different molecular masses. Due to the complex nature of lignin, so far no definite and entirely satisfactory molecular mass has been given, although every possible chemical and physical method has been used for the determination of molecular masses (Brauns, 1952 and Casey, 1980).

Since lignin is formed by enzymatic dehydrogenation followed by random oxidative coupling of monomeric and oligomeric phenols, and since it is never completely deprived of dehydrogenable phenolic hydroxyl groups or even of free hydroxyl radicals, the lignin structure may never cease to grow. In fact, plants are described as multicomponent cross-linked polymer systems in which carbohydrates and lignin are intimately associated through hydrogen and ether and ester covalent bonds (Erin'sh et al., 1976). It was observed that the actual molecular size of lignin may be irrelevant to pulping processes as lignin would in any event have to be degraded and modified to be dissolved (Casey, 1980). Whether by photo-irradiation or mechanical treatment, polymeric plant components would suffer alteration and these changes would affect physical appearance, mechanical properties and chemical reactivities alike.

3.4.2 Physical Means Of Molecular Mass Determination

Several physical methods for the determination of the molecular mass of wood lignin including the ebullioscopic, diffusion and ultracentrifuge techniques, have been used (Brauns, 1952). Different values of molecular mass ranging from 250-11000 M_n have been observed which were found due to the different types of lignin derivatives

but also with the same lignin preparations when different methods of measurements were used (Wedekind and Katz, 1929).

Molecular mass of isolated lignin or lignin sulfonate from wood have been determined and they ranged anywhere between 2,000 to more than 1,000,000 (Goring, 1971).

3.4.3 Chemical Means Of Molecular Mass Determination

By introducing or cleavage of known groups in reactions which take place quantitatively, the lowest possible "molecular mass" can often be determined with fairly good accuracy. However, this method becomes inaccurate when molecular mass has reached a certain value, at which point the analytical differences become too small to allow any conclusions to be drawn as to the exact number of atoms or groups introduced or removed. Lignin is such that the high molecular weight, determined by this method, cannot be considered to be the true molecular weight but is rather an equivalent mass of the lignin building unit.

The first attempt to determine the molecular mass of a wood lignin derivative by chemical means was made in 1900 (Seidal, 1900). The molecular mass was calculated to be about 500 for a sulfuric acid free lignin from the sodium content of a sodium lignosulfonate, assuming a monobasic acid. On the basis of elementary analysis it was shown that the formula was $C_{40}H_{44}O_{15}$, corresponding to a molecular mass of 764.6 for alkali winter rye straw lignin (Beckmann et al., 1921). From the methoxyl content of 15.8% they calculated a "minimum weight" of 296.6 for the benzoylated lignin building block and when the molecular mass of the benzoyl group was deducted from the latter, a minimum weight of 192.5 for the lignin building block was obtained. By dividing the molecular mass 764.6 (from the above formula) by the average minimum weight 194 they found that the number of hydroxyl groups capable of being benzoylated was four which is equal to the number of methoxyl groups. They also determined by titration the equivalent weight of an alkali winter rye straw lignin extracted with cold sodium hydroxide in MeOH and found a value of 382.2. Since the

lignin was bivalent, they calculated a molecular weight of 764.4. This value was confirmed by the results obtained by lowering of the freezing point of an aqueous sodium hydroxide solution saturated with lignin (Beckmann et al., 1921 and Brauns, 1952).

3.4.4 Molar Mass Determination In Wheat Straw

In the literature a wide range of molar mass values for wheat straw have been reported by different groups of workers. The soluble lignin complexes isolated from wheat straw (Triticum avense) and red clover (Trifolium pratense) were found to contain a lower mass fraction of >12000 and a higher molar mass fraction of >20,000. Molar mass values from <10,000 to >30,000 have been found by different groups of workers from their results (Lawther et al., 1995; Fang et al., 1991).

3.4.5 Gel Permeation Chromatography (GPC)

Since its introduction in 1960, gel permeation chromatography or simply (GPC), which is also known as size exclusion chromatography, has opened up the prospect of obtaining information on the whole molecular mass distribution of polymers in a fraction of the time required by other methods. For most applications, the practice of GPC is relatively simple and straightforward. The direct comparison of molecular mass distribution of a few related samples can provide a wealth of information. Problems are normally encountered when the results are reduced to molecular mass averages and numerical results for sample runs over a period of time are compared. The calibration in GPC is normally presented as log M (molecular mass) versus (elution volume). Small differences in the calibration with small differences in log M can be resolved with a quite arbitary molecular axis (Holding, 1993).

3.4.6 Preparation Of Lignin Samples

The lignin samples were prepared according to the standard Klason method after running in the rotating metal reactor at different temperatures and times with different concentrations of caustic and finally acidifying the subsequent solutions with H_2SO_4. The procedure was similar to that described in the section of delignification (see Chapter 6).

The well dried samples of lignin were submitted to the Polymer Supply & Characterization Centre (PSCC) at RAPRA Technology (England) to use its services in the study of lignin molecular mass determination for analysis using GPC.

3.4.7 GPC Results Of Lignin Analaysis

The results M_w & M_n lignin produced under various run conditions of straw pulping in cautic soda are shown in Table 3.4.1. The results have been interpreted in two ways. Those with the prefix D include a low molar mass component which appears distinctly separate in the GPC chromatography (see Figures 3.4.1-3.4.3B) and those prefixed R exclude it. Clearly, the different interpretations give markedly different results for the molar mass of lignins particularly for M_n which is 15 times lower when the low molar mass component is included. As far as the kinetics interpretation is concerned it is best to concentrate on values for M_n.

3.4.8 Discussion

The following can be observed from the results including the low molar mass peak denoted D in Table 3.4.1

1. There is generally some increase in M_n for lignin with increasing pulping time with caustic from 0.25-1.5 hours in the temperature range 80-170 °C. Typically increases are seen of 100 to 600 on M_n values which are mostly around 1500-2300.

2. Increasing temperature from 80 °C to 170 °C also results in increased values of M_n provided caustic is present. Comparison at constant run times over different temperatures shows an increase of 700 in M_n values, e.g., from 1600 at 80 °C to 2300 at 170 °C, for all 1h runs.

3. With only 10 minutes pretreatment with caustic followed by a run at 100 °C with water only, the result of M_n = 1900 was similar to runs with more prolonged caustic treatment. However when a run was done with the same pretreatment but with water at 170 °C the result was significantly reduced to M_n = 1000.

4. Addition of anthraquinone catalyst at 80 °C reduced molar mass by a very small amount from 1600 down to 1500.

5. The ratio of M_w to M_n (i.e., polydispersity) keeps within the range 13-19 over most conditions with caustic present. But with only a short pretreatment with caustic and subsequent heating in water the ratio falls markedly to 3 as a result of a disparate fall in M_w from 30,000 down to 3,000-4000 while M_n falls much less from 2,000 to 1000. Examination of the chromatogram in Figure 3.4.1 shows that the low molar mass peak is much more dominant with the very mild pulping conditions.

There are differences in the results excluding the low molar mass peak denoted R in the Table 3.4.1.

6. Values for M_n with two levels of caustic present are close to 30,000 in the temperature range 125-150 °C but at 170 °C there is a sudden drop to about 6,000. At 80°C molar mass is reduced somewhat to 24,000 with 0.5h treatment. With 1h treatment at 80 °C the normal level of around ~ 30,000 is found, but when anthraquinone catalyst is added there is a drastic reduction to 5600.

7. Increasing the run time from 0.5 to 1.5h at 125-170°C with caustic present produces a small increase in M_n of 5-25%.

8. M_w/M_n keeps within the range 1.1 to 12.

9. With only a 10 minutes pretreatment with caustic followed by a run at 100 °C in water only the result was a low value of 4500 and when the temperature of the run was increased to 170 °C with water only no high molar mass peaks were found at all.

3.4.9 Pulp Results

Only two measurements were done on pulps which, excluding the lower molar mass peak, gave M_n = 8900 for pulps from caustic runs for 15min at 170 °C and 10,600 for 1h at 170 °C. These results are 50% higher than the corresponding M_n values for lignin derived from the pulps. The results indicate that the lignin solubilized is degraded as pulping proceeds and/or lower molar mass material dissolves preferentially.

3.4.10 Straw

Attempts to measure the molar mass of untreated straw were unsuccessful because of the poor solubility in DMSO, THF, etc. under mild conditions.

3.4.11 Comparison With Literature Values

There is a wide variation of values for the molar mass of alkali-soluble straw lignin fragments in the literature. Typically values in the range 800-10,000 are quoted in texts (Kirk-Othmer, 1971). Some authors (Virkola et al., 1981) have found much lower values for M_n of 400 to 1,000 with M_w ranging from 1300 to 2,000 and a polydispersity of 2-4. Some increase in molar mass occurred with cooking time. By comparison the molar mass of wheat straw was found to be 1300 and 4700 for M_n and M_w respectively (Fang et al., 1991). Similarly low results of 1450 for the molar mass of lignin have been found in other work (Scalbert et al., 1986). These authors found two

distinct fractions for molar mass one with low molar mass and the other higher molar mass. Chinese authors (Jianjuin et al., 1990) found M_w 4,000-13,000 and M_n 2,000-6,000 for wheat straw lignin dissolved in alkali.

3.4.12 Conclusions

The wide range of results quoted in the literature and the findings in this work of both high and low molar mass fractions of lignin resulting from caustic treatment of straw, makes the data difficult to interpret clearly.

A set of hypotheses which fits all the evidence in this work and is consistent with the literature findings is as follows:

* Fragments of lignin are present in straw as low molar mass (M_n <2,000) species and probably predominantly as high molar mass (M_n >30,000) material some of which may be more susceptible to depolymerization by caustic than other fractions.

* Some of the low molar mass material is readily soluble under mild pulping conditions, e.g., only ten minutes treatment with caustic followed by boiling in water. Progressively high molar mass material is dissolved by increasing the severity of caustic treatment but when the temperature of pulping is increased to 170 °C with the higher run time of 1.5h or anthraquinone is added at lower temperature the high molar mass species is degraded to a lower molar mass material.

3.4.13 Choice of M_n Value For Kinetic Studies

The choice of M_n value relevant to use in the kinetic studies is open to question. It is the value or values present in the straw that are the most relevant. It was decided to use a figure of M_n = 30,000 as representing the bulk of the lignin as present in straw but it must be accepted that this choice is open to argument. The requirement to use

lignin molar mass in the kinetic treatment was limited to some of the runs on caustic consumption so the impact on the work of a wrong choice of M_n value is limited.

Table 3.4.1 GPC results for molar mass determination of lignin

Time (h)	Sample	Run No.	Mw	Mn	Polydispersity	Condition
0.5	1-125 bomb-1(EC) lignin (7180)	D035	29,700	2,100	14.4	
		D043	29,800	2,200	13.8	WS:4.23g NaOH:4.45g 55ml H_2O;125°C
		R035	48,400	32,900	1.5	
		R043	47,000	33,100	1.4	
1	2-125 bomb-3(EC) lignin (7183)	D066	27,900	2,100	13.3	
		D069	27,600	2,200	12.8	
		R066	46,400	32,900	1.4	
		R069	45,300	32,300	1.4	
1.5	3-125 bomb(EC) lignin (7185)	D067	27,800	2,200	12.6	
		D070	27,600	2,500	11.3	
		R076	43,100	30,900	1.4	
		R070	43,000	31,200	1.4	
0.5	1-OA bomb-1(HC) lignin (7186)	D039	15,800	1,300	12.5	WS:4.23g; NaOH: 2.225g 55 ml H_2O; 80°C
		D042	15,200	1,300	12.1	
		R039	33,700	23,900	1.4	
		R042	34,800	24,100	1.5	
0.5	2-OA bomb-2(HC) lignin (7189)	D038	22,900	1,500	15.1	
		D047	22,900	1500	13.5	
		R038	46,300	31,100	1.5	
		R047	45,200	31,800	1.4	
05	1-150 bomb-1(EC) lignin (7192)	D055	23,000	1,700	13.4	WS:4.23g NaOH: 4.45g 55 ml H_2O 150°C
		D060	24,200	1,900	12.8	
		R055	39,700	28,600	1.4	
		R060	39,900	28,600	1.4	
1	2-150 bomb-3(EC) lignin (7195	D054	27,200	2,100	12.9	
		D059	26,300	2,100	12.8	
		R054	42,100	30,800	1.4	
		R059	42,800	30,400	1.4	

Continued Table 3.4.1

1.5	3-150 bomb-5 (EC) lignin (7198)	D061	24,900	2000	12.8	
		D063	24,900	1,900	12.9	
		R061	43,900	31,800	1.4	
		R063	43,400	30,600	1.4	
0.25	HT- bomb-IA(OA) lignin (5483)	C725	33,300	1,700	19.0	WS: 4.23g
		C726	33,400	1,700	18.7	NaOH: 4.45g
		R	37,900	5,700	6.9	55 ml H_2O 170°C
		R	38,000	5,500	6.9	
0.5	1-WL-HTbomb-3(EC) lignin (7201)	D068	2,700	990	2.8	
		D071	3,000	1,100	2.8	
1.5	2-WL-HTbomb(EC) lignin	D074	3,800	1,100	3.4	
		D076	3,900	1,000	3.8	
1	HT bomb-3 (OA) lignin (5484)	D729	36,200	2,300	15.7	
		D730	36,200	2,300	15.7	
		R729	39,600	7,000	5.2	
		R730	38,600	7,000	5.2	
1	EC bomb-2 lignin(AQ) (5488)	D727	28,500	1,500	19.0	WS: 4.23g
		D728	28,100	1,500	18.7	NaOH: 4.45g
		R727	37,600	5,800	5.6	55 ml H_2O, 80°C
		R728	32,300	5,200	5.7	
3	WL-Room (OA) lignin (5487)	D731	47,100	1,900	24.8	WS:4.23g
		D732	49,200	1,900	25.9	NaOH,4.45g
		R731	52,600	4,500	11.6	55 ml H_2O,100°C
		R732	54,800	4,600	12.0	

Table 3.4.2 Summary of M_n Determination Results for Lignin

all with 4.23g Straw & 55 ml H_2O

Temp. °C	Time h	Caustic g	M_n Lignin D	R
80	0.5	2.225	1300	24,000
80	1.0	2.225	1600	31,000
80	1.0	4.45	1500	5,600
125	0.5	4.45	2150	33,000
125	1.0	4.45	2150	32,600
125	1.5	4.45	2350	31,550
150	0.5	4.45	1800	28,600
150	1.0	4.45	2100	30,000
150	1.5	4.45	1950	31,200
170	0.25	4.45	1700	5,600
170	1.0	4.45	2300	7,000
170	0.5*	4.45	1000	No high molar mass peak
170	1.5*	4.45	1,050	No high molar mass peak
25-100	2*	4.45	1900	4,550
25-100	3#	4.45	1900	4,550

* 4.45g NaOH at 25 °C + run with water only

+ washed & heated with H_2O only at 100°C

D include the low molar mass peak.

R exclude the low molar mass peak.

0.045g anthraquinone catalyst present.

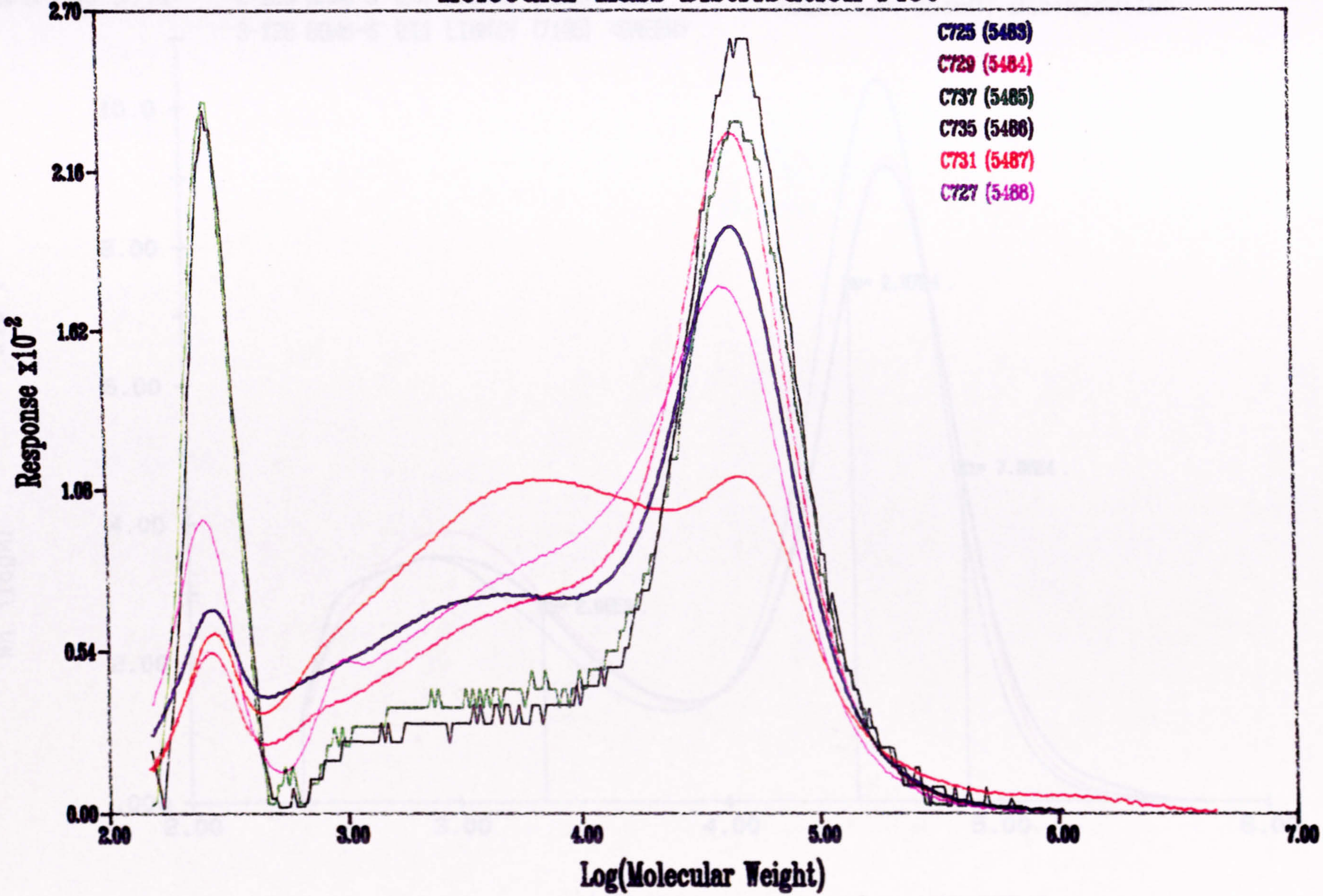


Figure 3.4.1. Molecular mass of lignin.

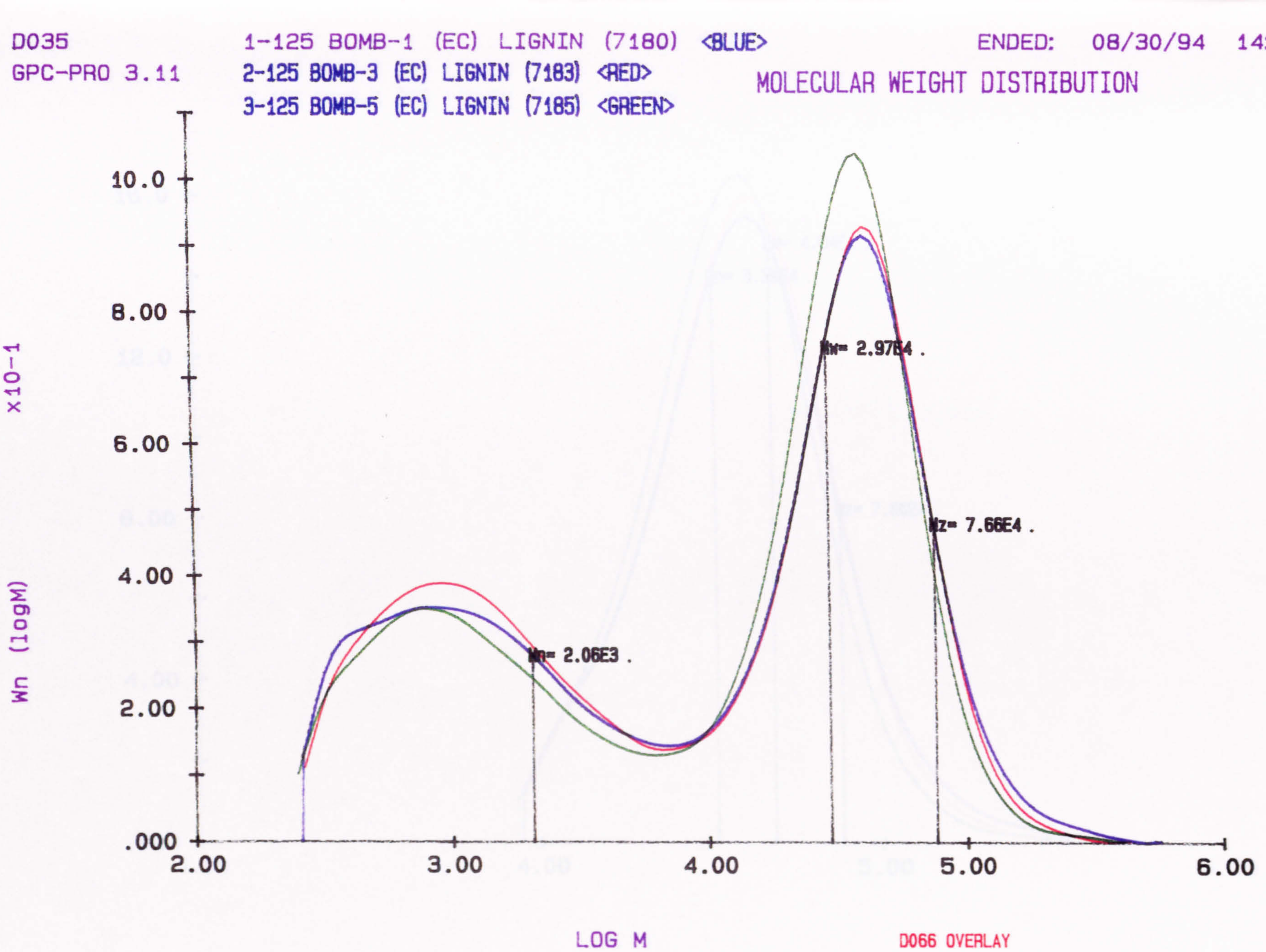


Figure 3.4.2A Molecular mass of lignin

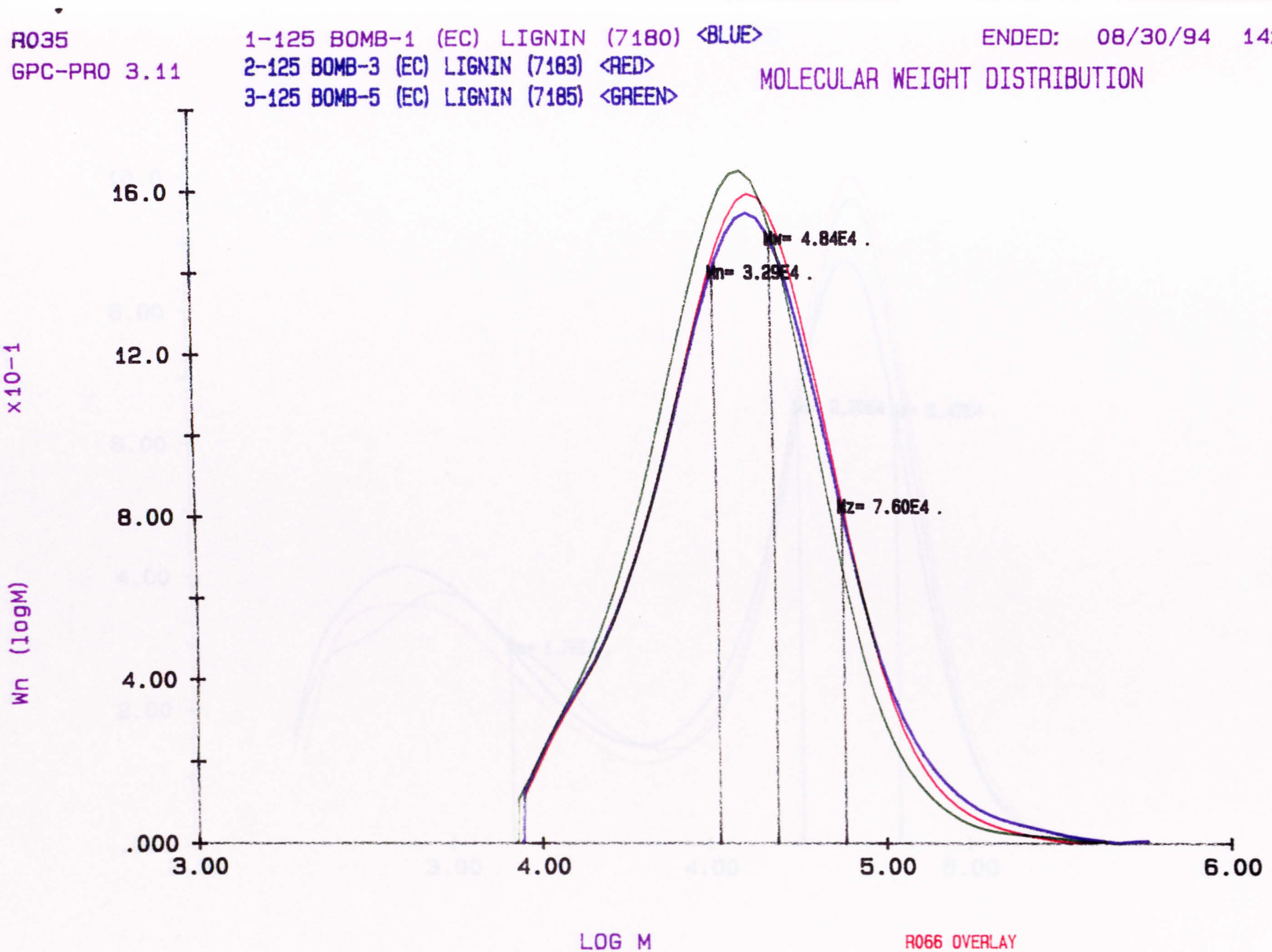


Figure 3.4.2B Molecular mass of lignin

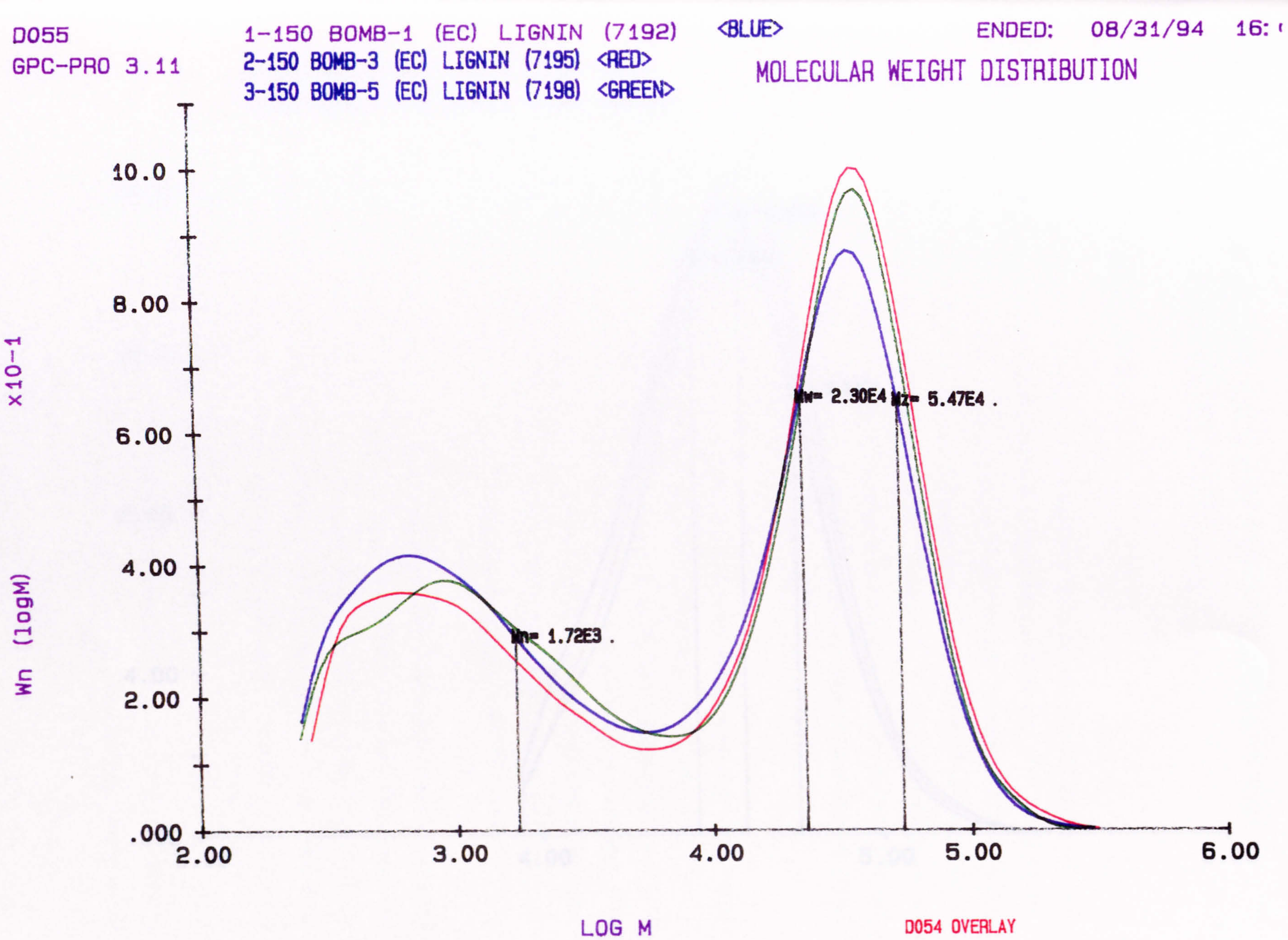


Figure 3.4.3A Molecular mass of lignin

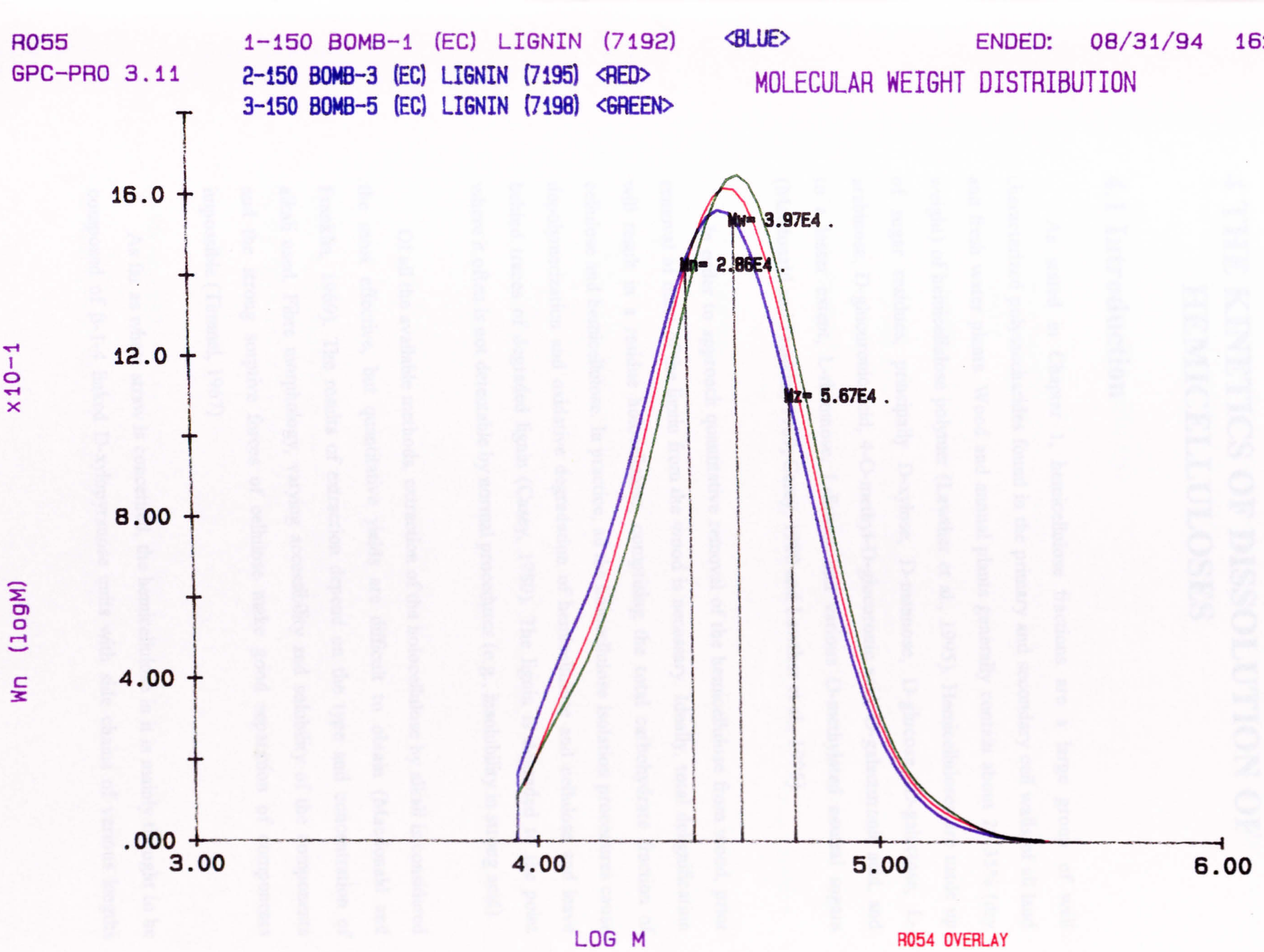


Figure 3.4.3B Molecular mass of lignin

4 THE KINETICS OF DISSOLUTION OF HEMICELLULOSES

4.1 Introduction

As stated in Chapter 1, hemicellulose fractions are a large group of well characterized polysaccharides found in the primary and secondary cell walls of all land and fresh water plants. Wood and annual plants generally contain about 20-35% (dry weight) of hemicellulose polymer (Lawther et al., 1995). Hemicelluloses are made up of sugar residues, principally D-xylose, D-mannose, D-glucose, D-galactose, L-arabinose, D-glucuronic acid, 4-O-methyl-D-glucuronic acid, D-galacturonic acid, and to a lesser extent, L-rhamnose, L-fucose and various O-methylated neutral sugars (Macdonald and Franklin, 1969; Casey, 1980 and Lawther et al., 1995).

In order to approach quantitative removal of the hemicellulose from wood, prior removal of most of the lignin from the wood is necessary. Ideally, total delignification will result in a residue holocellulose, comprising the total carbohydrate fraction of cellulose and hemicellulose. In practice, all the holocellulose isolation procedures cause depolymerization and oxidative degradation of hemicellulose and cellulose and leave behind traces of degraded lignin (Casey, 1980). The lignin is degraded to the point where it often is not detectable by normal procedures (e.g., insolubility in strong acid).

Of all the available methods, extraction of the holocellulose by alkali is considered the most effective, but quantitative yields are difficult to obtain (Macdonald and Franklin, 1969). The results of extraction depend on the type and concentration of alkali used. Fibre morphology, varying accessibility and solubility of the components and the strong sorptive forces of cellulose make good separation of components impossible (Timmel, 1967)

As far as wheat straw is concerned, the hemicellulose in it is mainly thought to be composed of β-1-4 linked D-xylopyranose units with side chains of various lengths

containing L-arabinose, D-glucuronic acid or its 4-O-methyl ether, D-galactose and possibly D-glucose (Lawther et al., 1995).

4.2 Kinetic Treatment

From the kinetic treatment given in Chapter 2, the dissolution of carbohydrates (hemicelluloses) is

$$C^r + s^l NaOH^s \xrightarrow{k_C \text{ or } k_{Cb}} C_p,$$

where k_C is the rate constant for the rate of disappearance of carbohydrate, $-\frac{d[C]}{dt}$, and k_{Cb} is the rate constant for the rate of disappearance of carbohydrate in the presence of base, $-\frac{d[NaOH]}{dt}$. s^l is the number of moles of NaOH which react with 1 mole of carbohydrate.

We have

$$-\frac{d[C]}{dt} = k_C [C]^r [NaOH]^s.$$

If [a] and [b] are the initial concentrations of carbohydrate and caustic, respectively, and x is the amount of carbohydrate reacted at time t then, when caustic is in excess:

$$-\frac{d[C]}{dt} = k_C [a-x]^r [b]^s.$$

$$= k'_C [a-x]^r,$$

where $k'_C = k_C [b]^s$ is the pseudo first order rate constant.

For first order in C, r = 1. Integrating,

$$k_C = \frac{1}{t[b]^s} \ln\left(\frac{a}{a-x}\right)$$

Therefore, a plot of ln (a-x) versus t, should give a straight line with slope $k_C [b]^s$

For initial reaction rate first order in carbohydrate,

$$-\frac{d[C]_i}{dt} = k_C\,[a]\,[b]^s.$$

If [a] is kept constant and [b] is varied in separate runs, we have

$$-\frac{d[C]_i}{dt} = \text{constant}\,[b]^s,$$

where constant = k_C [a]. Therefore,

$$\log\left(-\frac{d[C]_i}{dt}\right) = s \log [b] + \log \text{constant}.$$

A plot of log (initial rate) versus log (initial caustic concentration) has slope s and intercept log k_C [a].

4.3 Results

Figures 4.1-4.5 show first order plots of ln (unreacted carbohydrate on straw) versus time using excess caustic (2.02 mol dm^{-3}) at 50-170 °C. As in the case of delignification, the data show a reasonable fit to first order kinetics. In the runs at lower temperatures there is some indication of a fast initial rate followed by a slower one. This is most apparent at 125-170 °C where two distinct lines can be drawn in the rate plots showing a bulk reaction followed by a slower reaction phase.

The pseudo first order rate constants for the bulk and residual reactions when using excess caustic and the true reaction rate constants derived from Figures 4.1-4.5 are given in Table 4.1. The derivation of the true rate constants required the determination of the order s for caustic in the carbohydrate dissolution reaction. This was obtained for the bulk reaction using the data given in Figures 4.6 and 4.7 which show plots of unreacted carbohydrates on straw versus cooking time at 80 °C for four levels of caustic. The logs of initial rates $-d[C]_i/dt$ derived from Figures 4.6 and 4.7 are plotted in Figures 4.8 and 4.9 against log of initial caustic concentration (log $[NaOH]_i$). The order of caustic for carbohydrate dissolution calculated from the slope of the graphs was 0.6 for the bulk reaction which was used as the value of s to calculate the true bulk rate constants in

Table 4.1. Similarly the order of the reaction for the residual reaction was found to be 0.7 at 80 °C as derived from Figures 4.6 and 4.7.

Arrhenius plots for the bulk and residual reactions are shown in Fgures 4.10 and 4.11 respectively. The activation energies derived from the plots are 36 ± 3 kJ mol^{-1} for the bulk reaction and 73.5 ± 39 kJ mol^{-1} for the residual reaction. The latter figure is only approximate because of the small number of points in the plot.

4.4 Comparison With Results Reported In The Literature

Very few results are available in the literature on the dissolution of hemicellulose carbohydrate (pentosans) in straw pulping using caustic soda. Indian workers (Trivedi, 1975) confirmed that dissolution of pentosans by caustic treatment of straw was a much slower process than delignification, and pulps contained 24% of pentosans after an alkali treatment but when an acid treatment was given first this reduced pentosans in pulp to 1-2%. Other work on bagasse pulping with caustic soda found that dissolution of hemicellulose (pentosans) takes place towards the end of the residual phase of delignification, again confirming that delignification is faster (Sabatier et al., 1986).

4.5 Conclusions

* Like delignification, dissolution of carbohydrate occurs in bulk and residual phases, the change occurring at about 25% residual carbohydrate on straw; again, the transition is more evident at temperatures above 80 °C.

* Both the bulk and residual reaction rate is first order in carbohydrate and fractional order in caustic, i.e., indicative of the presence of a complex mechanism.

* The activation energy of the bulk reaction is 36 ± 3 kJ mol^{-1} and for the residual reaction 73.5 ± 39 kJ mol^{-1}. These values are appreciably higher than values for delignification though still quite low indicating that the rate determining steps are not wholly chemical particularly in the case of the bulk reaction.

* The rate constants for carbohydrate dissolution show that the residual reaction is inherently slower than the bulk reaction, and the residual rate constants are nearly 10 times lower.

* The slow residual reaction for carbohydrate starts much earlier in the cook than the delignification residual reaction, and hence the overall rate of carbohydrate dissolution is much slower than delignification.

* There is a regular increase with rising temperature in the values of both the bulk and residual rate constants until 170 °C, when a drop occurs in the residual rate indicating degradation of some of carbohydrate in solution such that it fails to be recorded by analysis.

Table 4.1 Carbohydrate Dissolution Rate Constants

WS: 4.23g; NaOH: 4.45g H_2O 55 ml

Figure No.	Temp °C	NaOH mol^{-3}	k_C' h^{-1}		k_C	
			Bulk	Residual	Bulk*	Residual**
4.1	50	2.02	0.08	-	0.06	-
4.2	80	2.02	0.26	-	0.17	-
4.3	125	2.02	1.72	0.02	1.12	0.012
4.4	150	2.02	1.89	0.25	1.23	0.15
4.5	170	2.02	3.16	0.21	2.06	0.12

* $(dm^3)^{0.6}\,(mol)^{-0.6}\,h^{-1}$

** $(dm^3)^{0.7}\,(mol)^{-0.7}\,h^{-1}$

4.6 Molar Mass Determination of Hemicellulose

4.6.1 Carbohydrate Results

As noted earlier, the carbohydrates which are reported in the literature to dissolve in caustic of the strength used in the experiments reported here are complex polysaccharides called pentosans which in wheat straw comprise mainly polymers of D-xylose monomeric units (Lawther et al., 1995). Such soluble carbohydrate material in plants is often referred to as hemicellulose.

Some preliminary experiments were done to isolate samples of hemicellulose after cooking straw in caustic soda and to measure the molecular mass of the samples by GPC analysis.

Table 4.2 shows a summary of the results for relative molar mass (M_n) determination on carbohydrate is extracted by caustic cooking of straw in the temperature range 80-170°C and run times 0.5-1.5h.

Table 4.2 Summary of M_n Determination Results for Carbohydrates

All with 4.23g straw & 55 ml H_2O

Temp °C	Time (h)	Caustic (g)	Carbohydrate M_n
80	0.5	2.25	230
80	1	2.25	295
125	0.5	4.45	240
150	0.5	4.45	235
150	1	4.45	225
150	1.5	4.45	250
170	1.5	4.45	280

It can be seen from the results in Table 4.2 that the values obtained for M_n for carbohydrate are relatively insensitive to changes in temperature, reaction time and caustic levels. The even more surprising thing about the results is the low value of about 250 for M_n.

The molar mass of D-xylose is 150. The value of 250 for M_n indicates that the pentosans have been reduced to 1-2 xylose units in the pulping process. By contrast molar mass of hemicellulose in, e.g., oat straw, is quoted much higher at 40-50 sugar units, i.e., molar mass 6000-7500 (Kirk-Othmer, 1971). Also literature values for wheat straw hemicellullose extracted under mild conditions average 16,000 from recent work (Lawther et al., 1995), 8,000 from earlier work (Aspinall and Mahomed, 1954) or 12,000 (Aspinall and Meek, 1956).

4.6.2 Choice of M_n Value For Kinetic studies

The low values of M_n = 250 was not considered relevant to the reaction rate measurements for carbohydrate dissolution, which must be controlled by the molar mass of the material in the straw. It was decided that the literature figure of 16,000 obtained under mild extraction conditions was the best choice for M_n. Again as in the case of lignin, the need to use a value for M_n in the interpretation of the kinetic data for carbohydrate dissolution was limited and therefore a wrong choice in the value of M_n was not critical.

4.6.3 Conclusions

* The effect of caustic pulping has been extensively to depolymerize the soluble carbohydrates in wheat straw.

* It was decided to use a figure of 16,000 for M_n of hemicellulose in the few runs where it was required in determining the kinetics of caustic consumption.

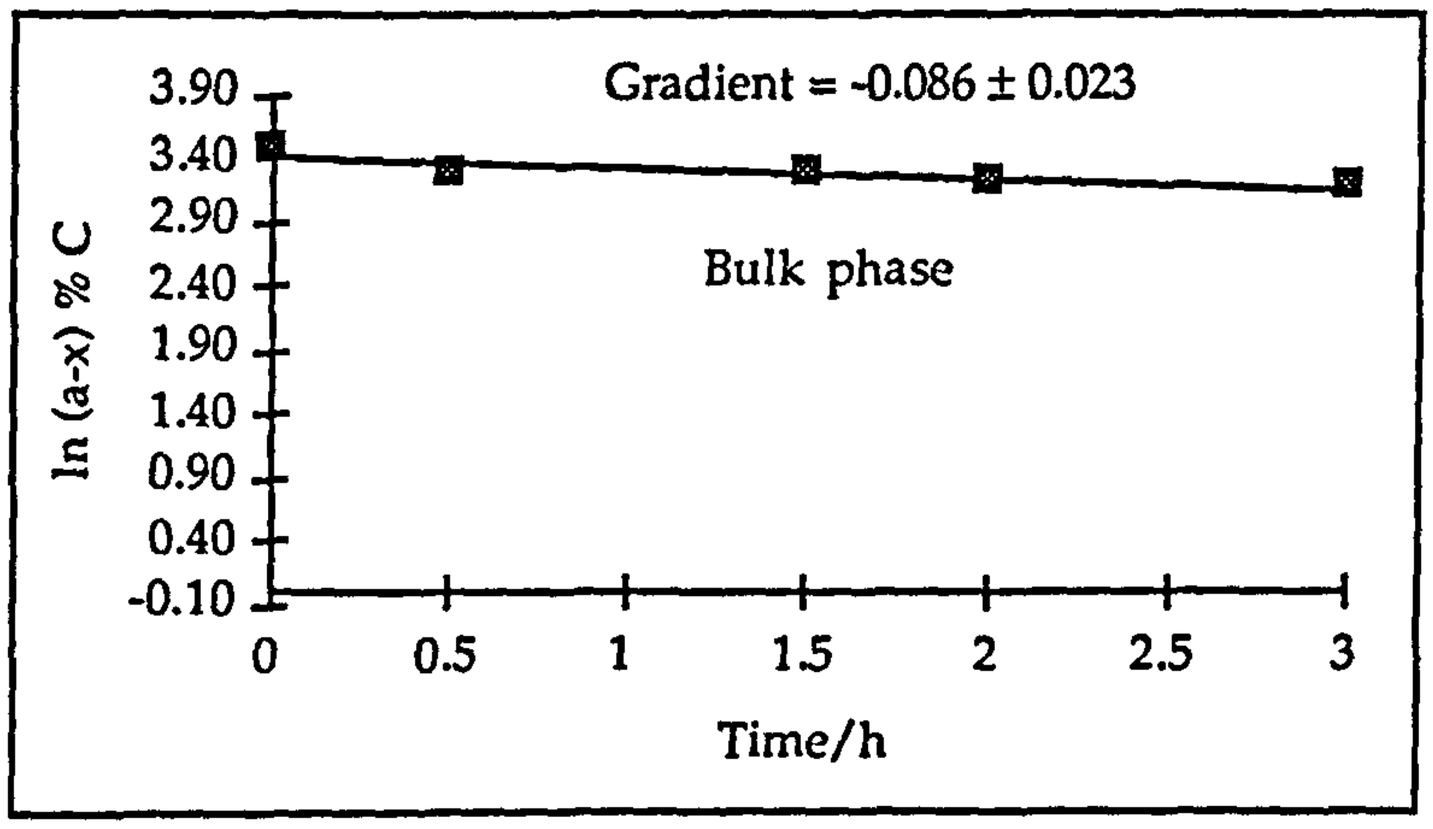


Figure 4.1

Plot of unreacted carbohydrate% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 50 °C in 55 ml H_2O

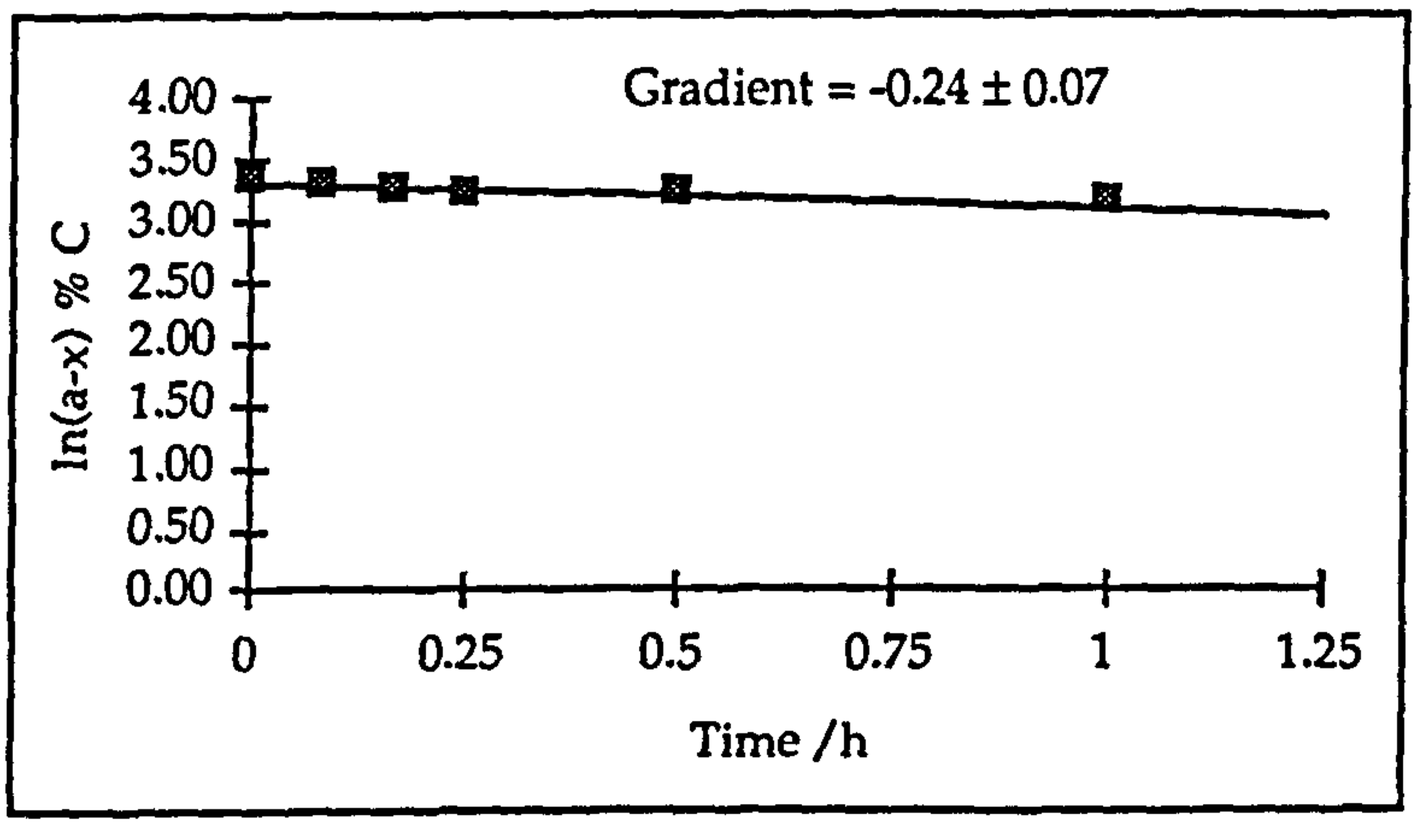


Figure 4.2

Plot of unreacted carbohydrate% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 80 °C in 55 ml H_2O

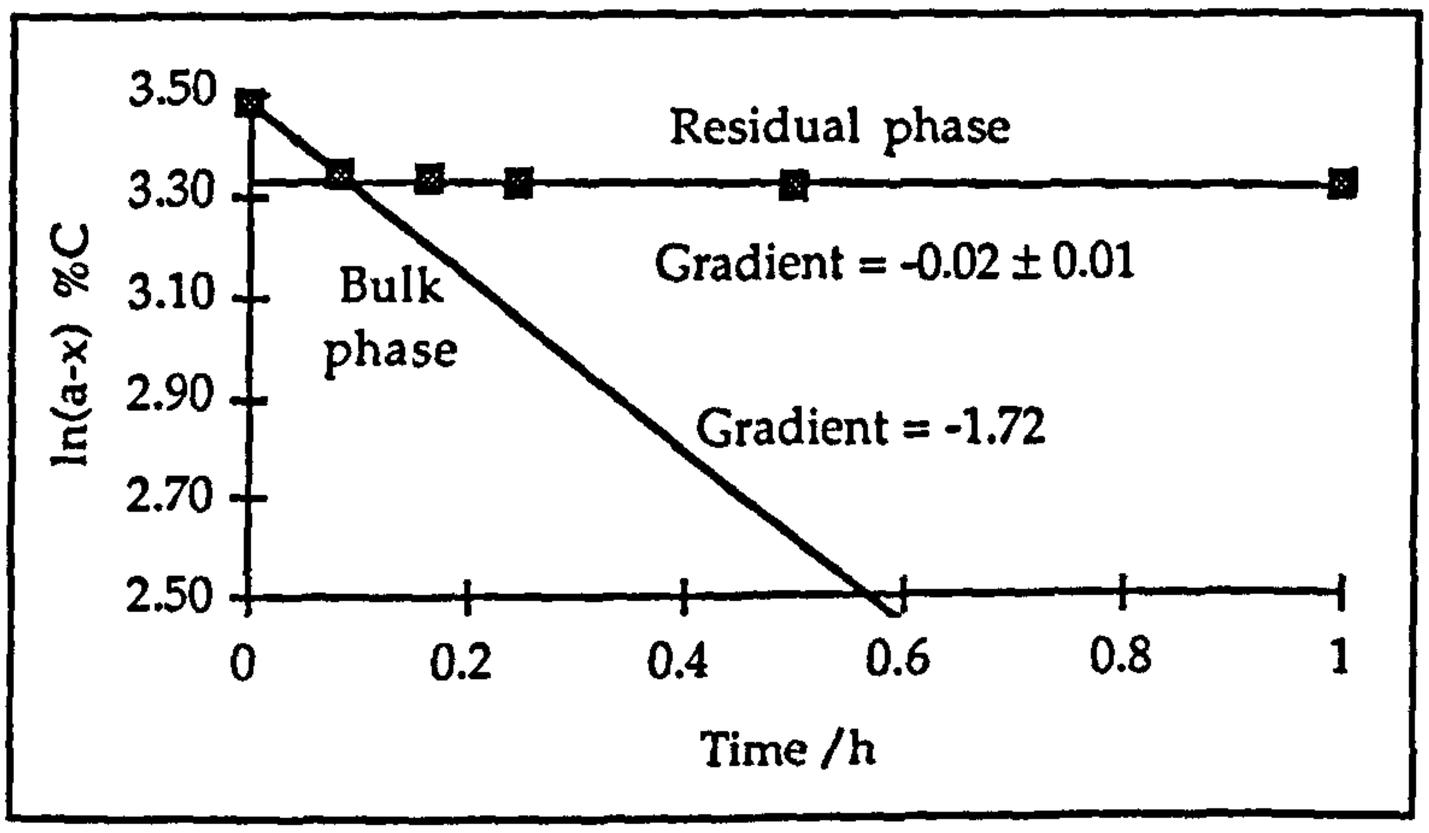


Figure 4.3

Plot of unreacted carbohydrate% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 125 °C in 55 ml H_2O

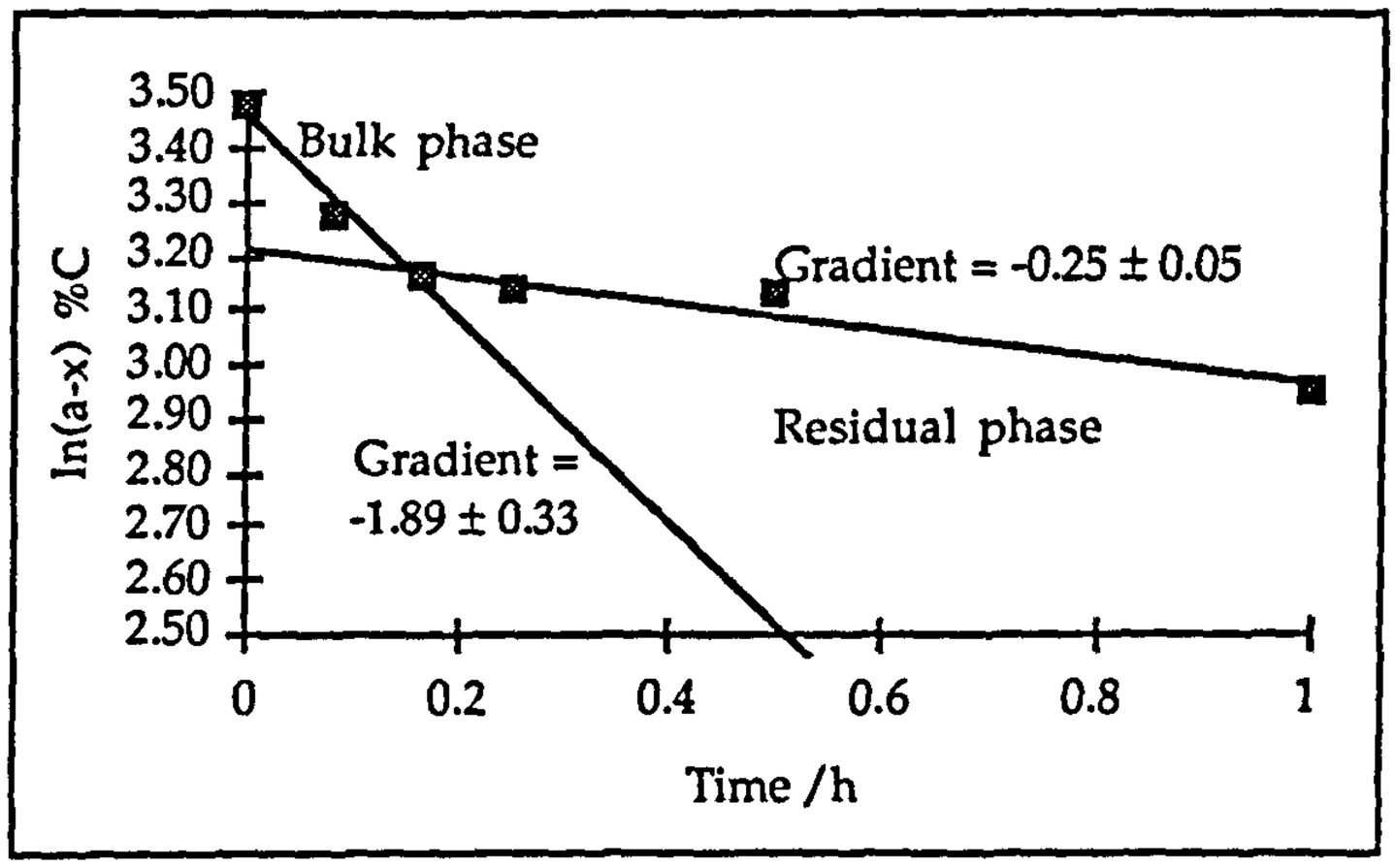


Figure 4.4

Plot of unreacted carbohydrate% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 150 °C in 55 ml H_2O.

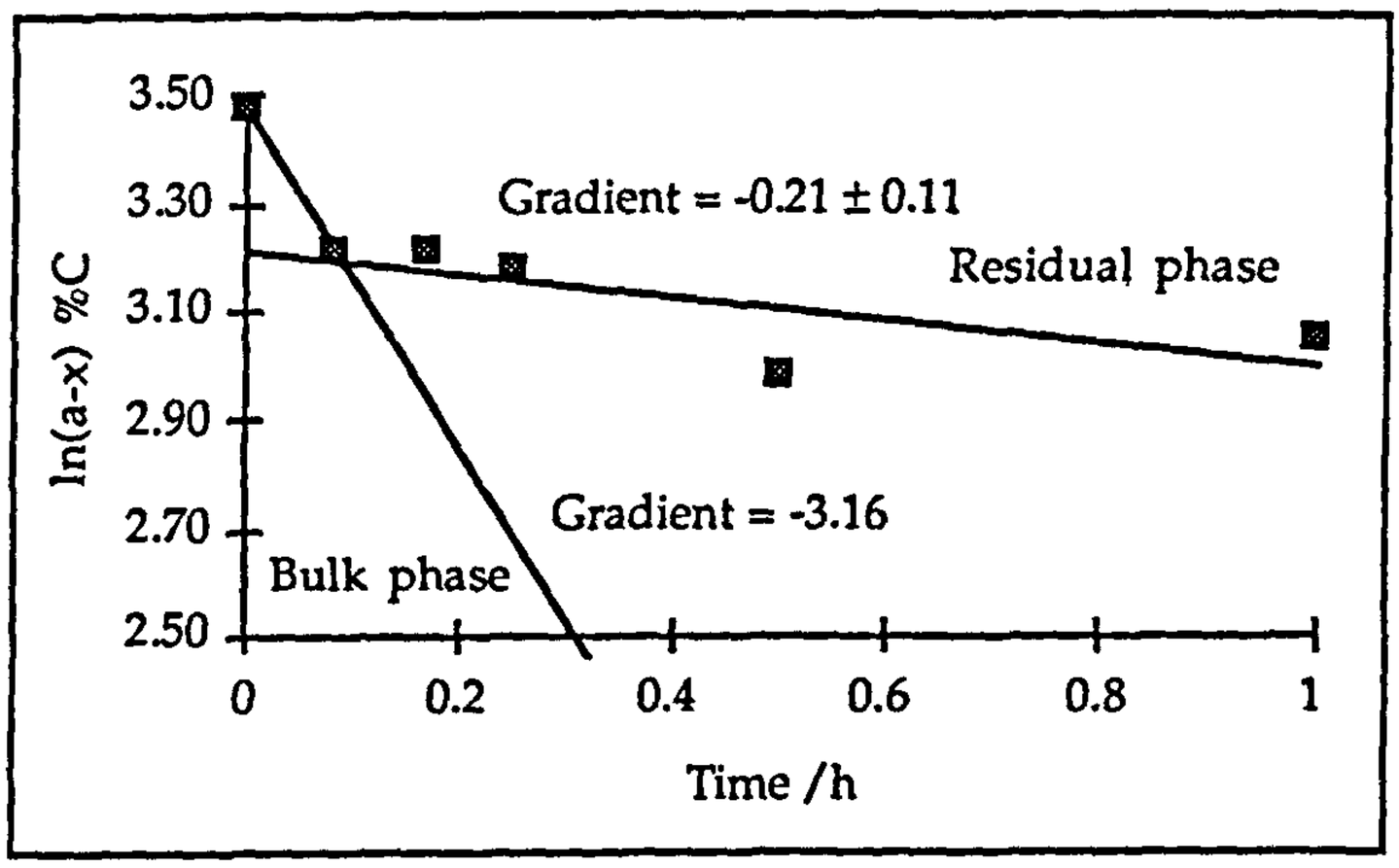


Figure 4.5

Plot of unreacted carbohydrate% on straw (4.23g) versus cooking time in caustic (2.02 mol dm^{-3}) at 170 °C in 55 ml H_2O.

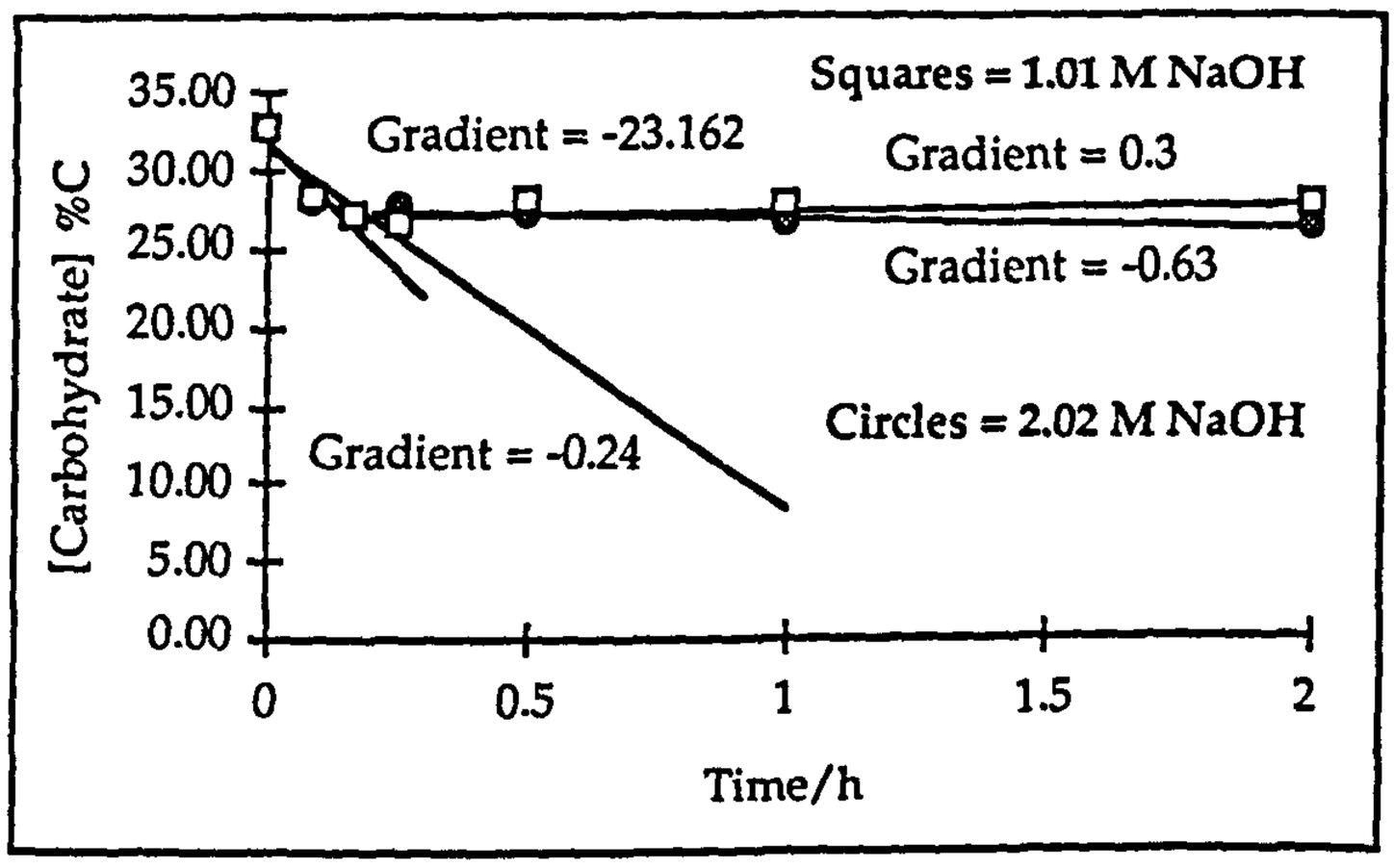


Figure 4.6

Plot of unreacted [carbohydrate]% on straw (4.23g) versus cooking time at 80 °C for bulk and residual reaction phases.

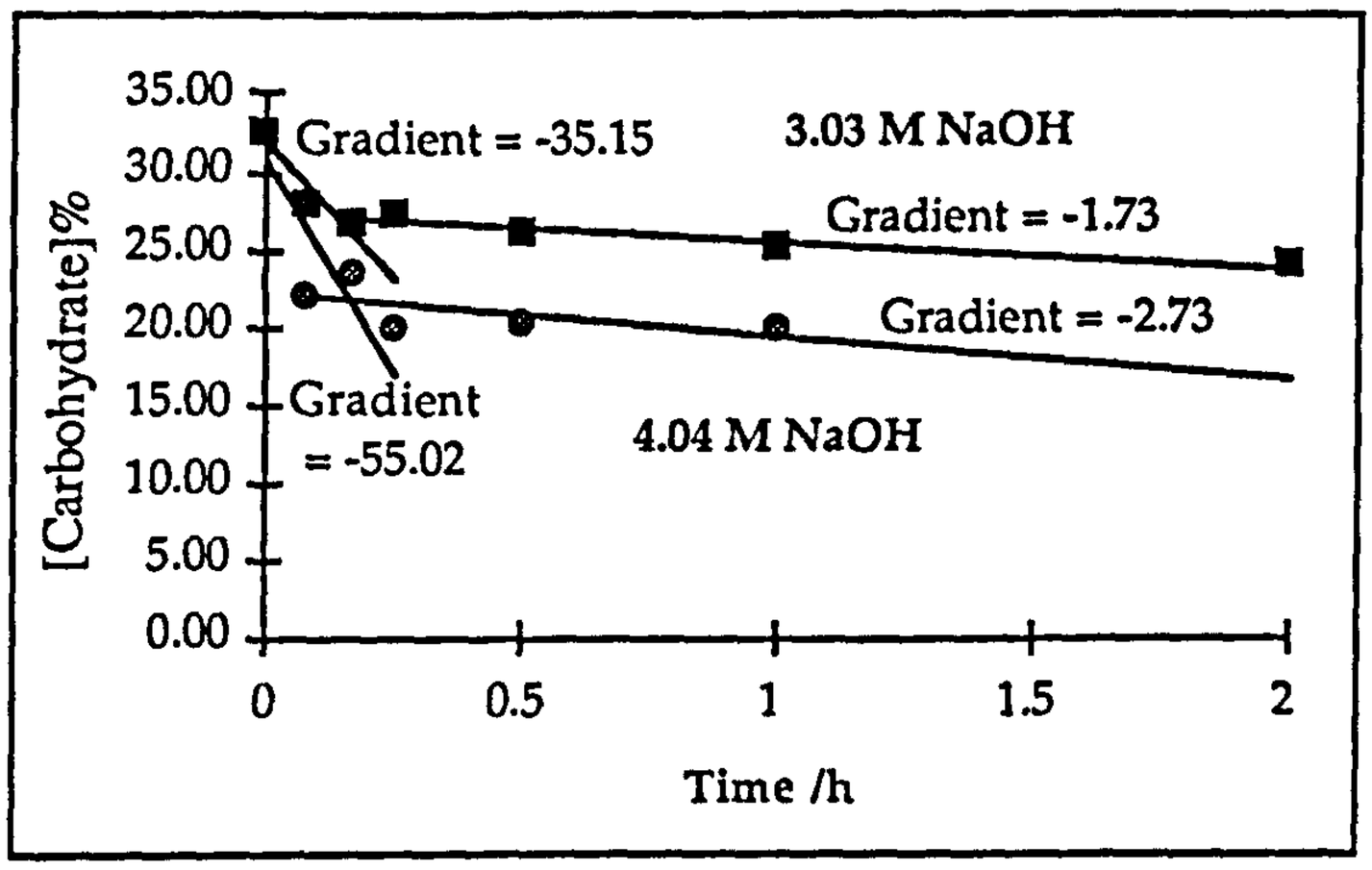


Figure 4.7

Plot of unreacted [carbohydrate]% on straw (4.23g) versus cooking time at 80 °C for bulk and residual reaction phases.

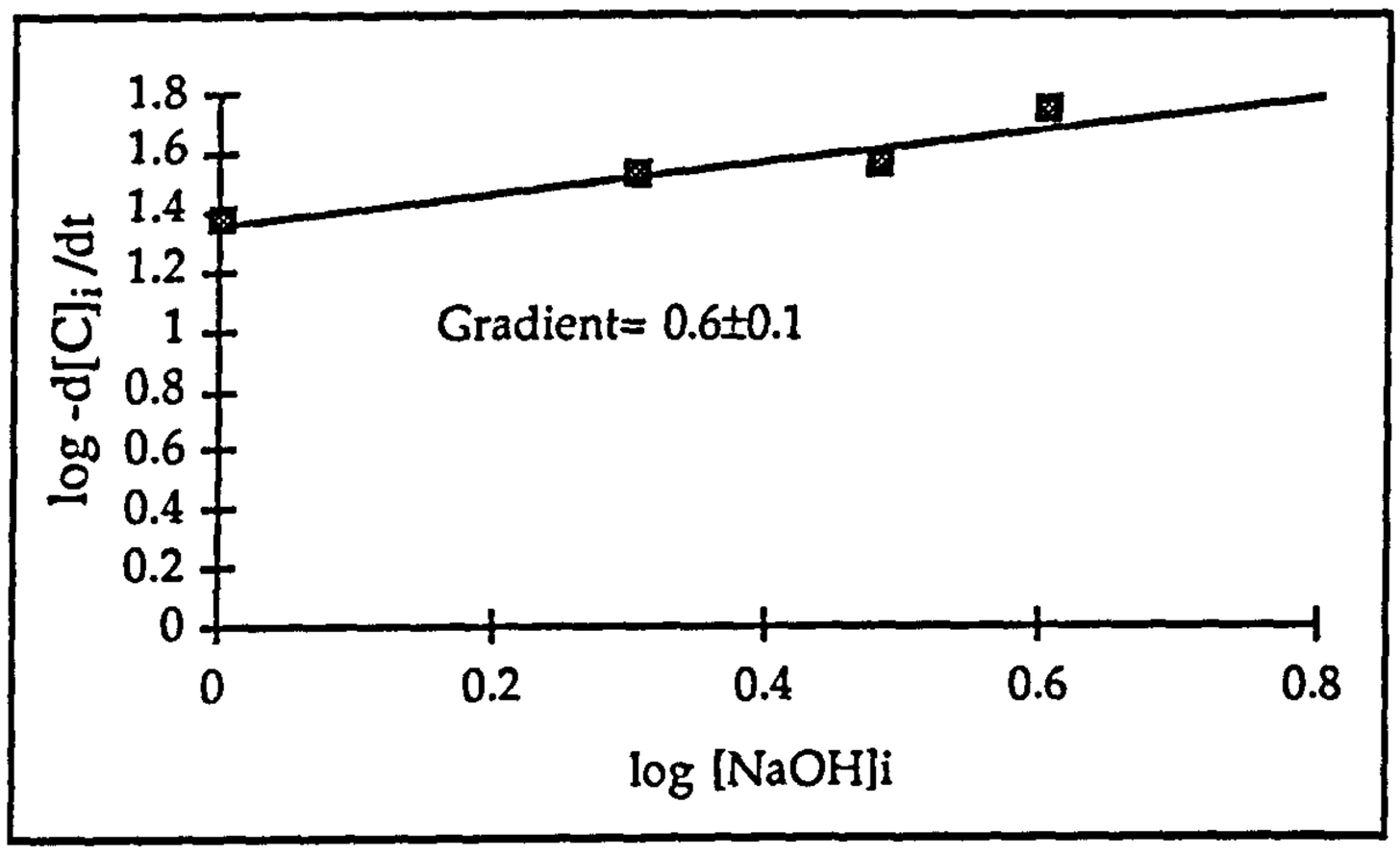


Figure 4.8

Plot of log initial rate -d[C]$_i$ /dt versus log [NaOH]$_i$ for bulk reaction phase and the gradient equals the order of reaction with respect to caustic.

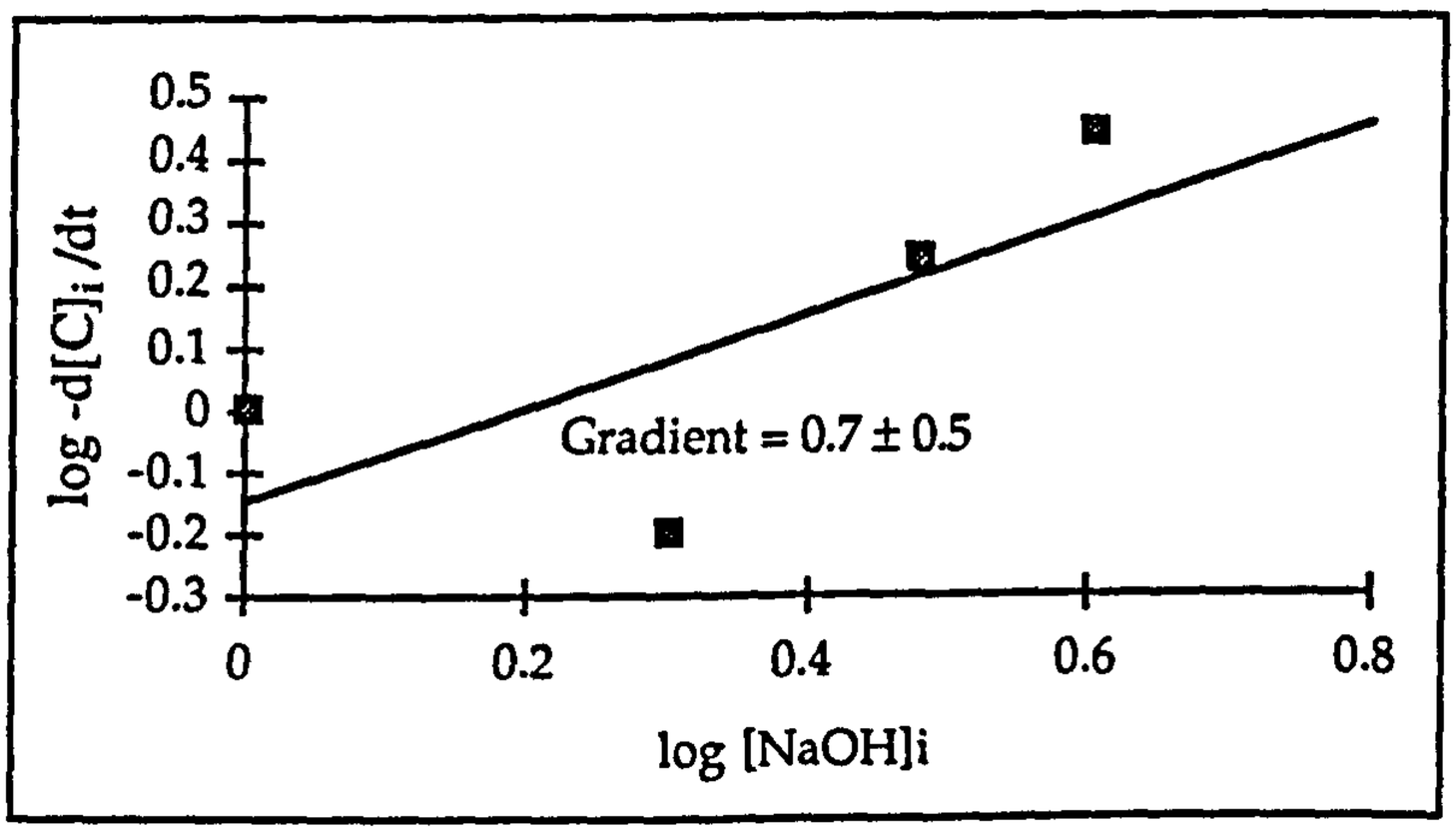


Figure 4.9

Plot of log initial rate -d[C]$_i$ /dt versus log [NaOH]$_i$ for residual phase and the gradient equals the order of reaction with respect to caustic.

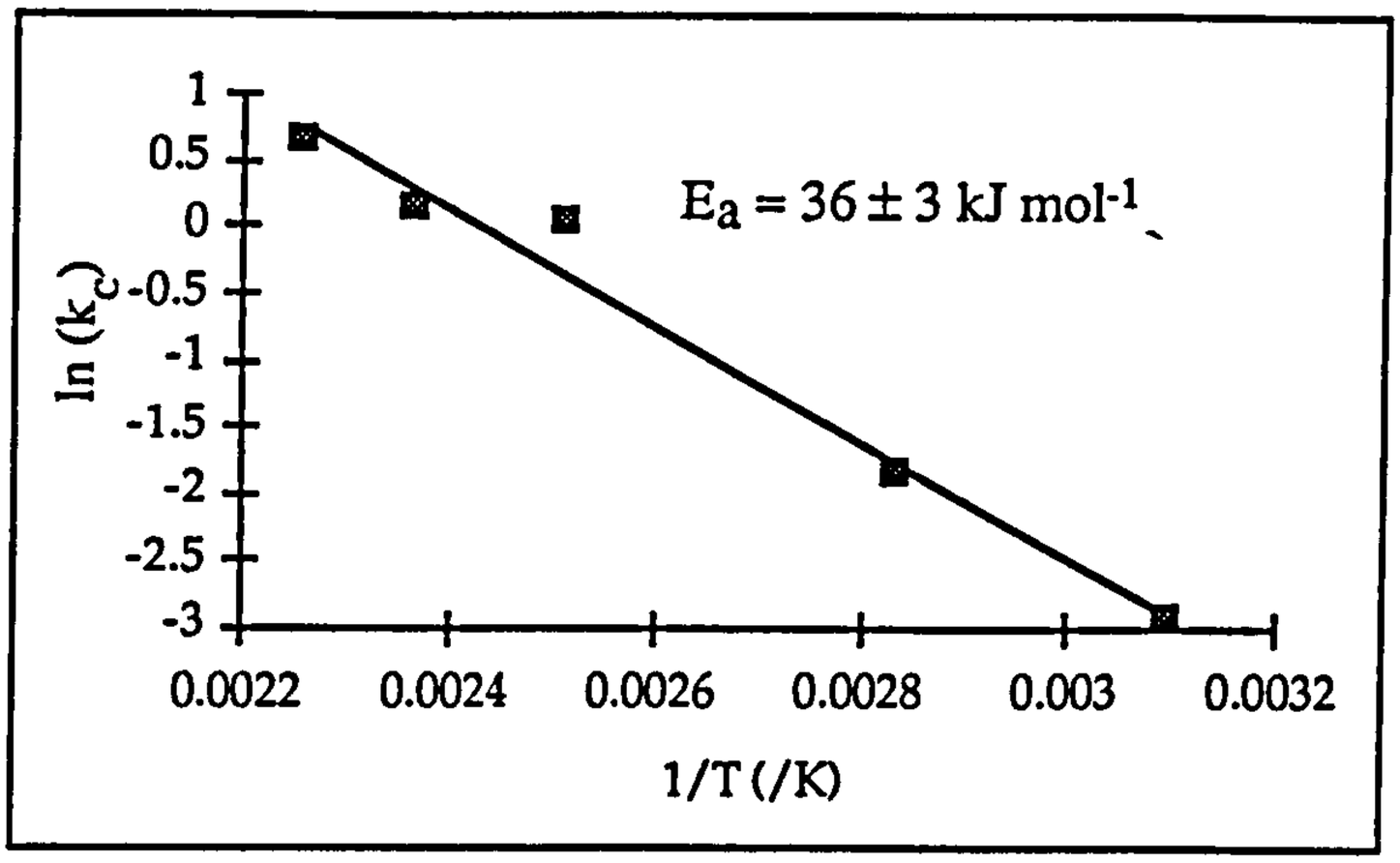


Figure 4.10

Arrhenius plot of ln k_C versus 1/T for bulk reaction phase of carbohydrate dissolution.

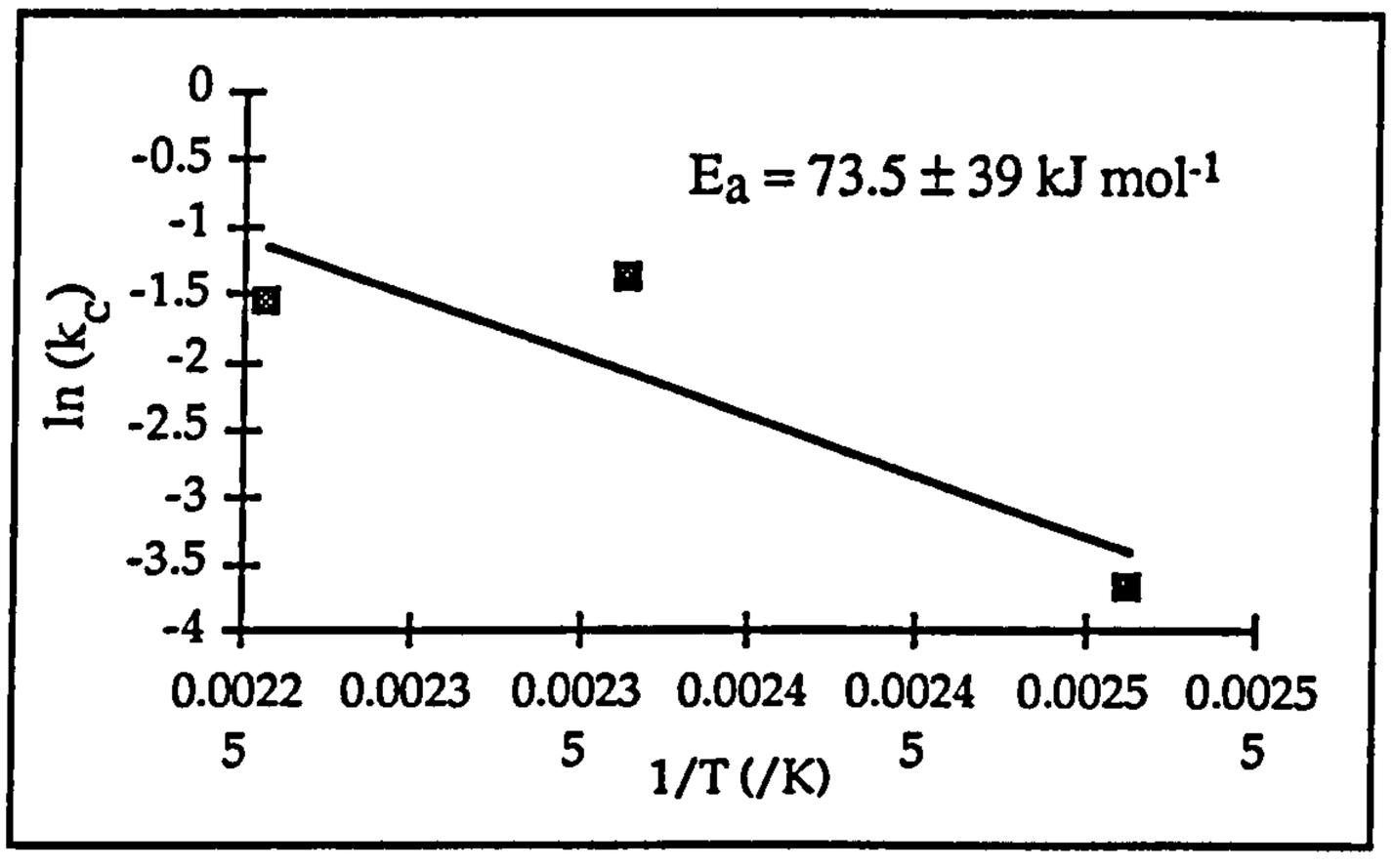


Figure 4.11

Arrhenius plot of ln k_C versus 1/T for residual reaction phase of carbohydrate dissolution.

5 DISCUSSION

The preceding chapters have discussed the results in the context of each section of work. The purpose of this chapter is to bring together the main information from experiments described in all the other chapters and to give overall conclusions. It is useful at this stage to bear in mind the analysis of the main components of denoded Saudi wheat straw used in all experiments contained by weight as follows:

Lignin	22.9%
Carbohhydrate	33.33%
Silica	6.53%
Cellulose (by difference)	30.14%

5.1 Delignification

5.1.1 Physical Nature Of The Reaction

1. The delignification of straw with caustic takes place in two main kinetic reaction phases, a bulk phase followed by a slower residual phase at about 10% residual lignin on straw.

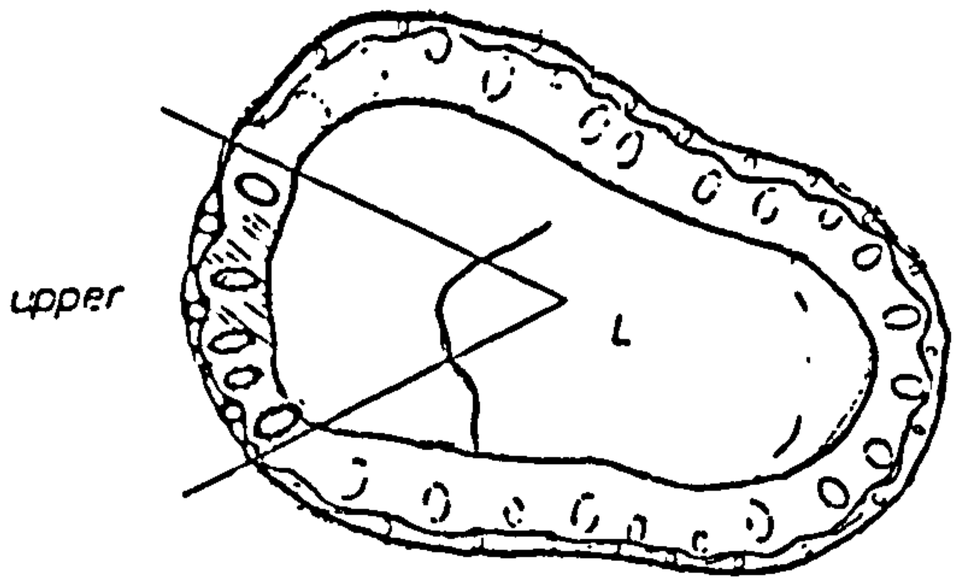
The presence of more than one phase is clearly shown at temperatures above 80 °C in the kinetic studies in Chapter 2. The reaction rate for the bulk phase is higher and activation energy lower than for residual phase, e.g., at 125 °C, k_L= 1.48 $(dm^3)^{0.8}$ $mol^{-0.8}$ h^{-1} and 1.18 h^{-1} and E_a = 14 ± 3 kJ mol^{-1} and 31.5 ± 6 kJ mol^{-1} respectively. This indicates that some of the lignin reacts more slowly either because it is less accessible and/or is somewhat chemically resistant because it is of a different chemical nature and more difficult to attack. The basic explanation must lie in the cellular nature of the straw and its heterogeneity

2. The rate of delignification reaction is diffusion controlled. The main evidence for this are the low activation energies for the bulk and the residual reactions which were found in the systematic kinetic studies over a range of temperature (25-170 °C) at different times (Chapter 2).

Further evidence for diffusion control comes from the complex nature of the reaction particularly as shown by the reaction rate being fractional order in lignin. This could indicate inhibition of the reaction by outwards diffusion of the lignin hindering the inwards diffusion of caustic. The relative modest effect of anthraquinone as catalyst as shown in Chapter 2 is also in line with diffusion control, because a catalyst would be expected to affect a chemically rate-controlled reaction but not a physically controlled one. Also, anthraquinone, being a large molecule, could be involved in diffusion controlled process in penetrating to the reactive surface of the straw.

3. Some further evidence of diffusion control can be drawn from the molar mass determination results in Chapter 3, where it is clear that lignin of large molar mass (M_n >30,000) is dissolved on treatment with caustic. Such large molecules could be slow to leave the structure of the straw and would also act as a barrier for the approach of caustic reactant, i.e., inward diffusion of caustic and outwards diffusion of the products of reaction could be important.

4. The rate of diffusion of reaction and products could be further affected by the structure of the straw which is of a cellular nature as shown in the Figure 5.1.



Densely lignified tissue; black
vascular tissue: dark shading
lignified paranchyma: light
unlignified tissue: white central
lumen: white marked L.

Figure 5.1 Outline drawing of transverse sections through upper and lower parts of an internode of the wheat (Triticum) (Juniper, 1990).

5. More definitive proof of the physical diffusion nature of reaction would have been obtained if it had been possible to grind the straw and to examine the effect of particle size on reaction rate; but as discussed in Chapter 2, there was a problem because of the mechanical delignification of straw on grinding. This is a well known phenomenon and is used in industrial paper making.

6. More evidence for a change in the nature of the delignification reaction as the cook proceeds comes from the molar mass determination in Chapter 2, which shows that progressively higher molar mass material is dissolved with increasing severity of caustic treatment with increase in temperature until 170 °C.

7. There is a drastic change in the nature of the delignification reaction at 170 °C compared with lower temperatures. This is evident from the molar mass measurements in Chapter 2, where the molar mass of lignin dissolved is suddenly reduced from 30,000 to <6,000 at 170 °C. When anthraquinone catalyst is present this depolymerization process begins to occur at 80 °C.

5.1.2 Chemical Nature Of The Reaction

1. The experiments on caustic consumption and characterization of the straw provide valuable information regarding the chemical nature of the reaction. The rapid initial uptake of caustic as found in Chapter 2 indicates that there are chemical groups probably of free acid types on the straw which are readily neutralized by caustic in the initial stage of reaction. Chapter 2 shows that the molar ratio of caustic to lignin reacted is very high, particularly at the initial stage of delignification reaction. This shows that the reaction is not a straight fission of lignin polymer units; probably extensive hydrolysis occurs with neutralization of carboxyl and acyl groups. As time proceeds, the cumulative amount of caustic consumption diminishes relative to lignin, indicating some sort of consecutive reaction in which caustic reacts with straw to prepare it for lignin dissolution or there are parallel reactions of caustic which occur at different rates.

2. The NMR, IR, UV characterization experiments shown in Chapter 3 shows extensive chemical changes occur as delignification proceeds.

3. The detailed NMR results in Chapter 3 show the presence of dissolved lignin containing typical lignin groups such as guaiacyl, syringyl, phenolic ester, β-aryl ether and p-hydroxyphenyl units up to 80 °C but as the temperature is increased, particularly with longer time of treatment, above 125 °C these groups start to diminish and at 170 °C there is a marked reduction in syringyl, *p*-hydroxyphenyl and guaiacyl units of lignin. These all indicate that at the middle stages of cook more typical lignin types molecules dissolve but

as the severity of cook increases with temperature particularly in combination with longer times of treatment, considerable degradation of the dissolved lignin occurs. As stated previously when 170 °C is reached as shown by molar mass determination, there is a degradation of the lignin material into much smaller units with many of the characteristic lignin groups absent and these no longer show in the NMR spectra.

4. The IR and UV results are broadly confirmatory if less definitive of the trends found above in NMR (Chaper 3).

5.2 Carbohydrate Dissolution

1. As shown by the kinetic studies in Chapter 2, carbohydrate dissolution takes place in a similar way to the delignification reaction and also occurs in two phases, a bulk followed by a residual phase with a complex mechanism. The residual reaction is 100 times slower than the bulk and both the reactions are appreciably slower than the rate of delignification, e.g,. at 125 °C, k_C = 1.12 $(dm^3)^{0.6}$ $(mol)^{-0.6}$ h^{-1} and 0.012 $(dm^3)^{0.7}$ $mol^{-0.7}$ h^{-1} for the bulk and the residual reactions, compared with 1.48 $(dm^3)^{0.8}$ $(mol)^{-0.8}$ h^{-1} and 1.18 h^{-1} for k_L.

2. The activation energies for bulk and residual phases of carbohydrate dissolution are 36 ± 3 kJ mol^{-1} and 73.5 ± 39 kJ mol^{-1} respectively, higher than the delignification reactions which are 14 ± 3 and 31.5 ± 6 kJ mol^{-1} respectively. The activation energies for carbohydrate dissolution are still relaltively low and indicate the rate determining steps are more physical than chemical in nature, particularly in the bulk reaction, just as in delignification.

3. Again at 170 °C, same degradation of the carbohydrate occurs compared with lower temperatures.

4. Throughout the pulping process some carbohydrate is dissolved in strong association with lignin and the remainder dissolves separately.

5.3 SiO_2 Dissolution

SiO_2 dissolves only very slowly at low and intermediate temperatures of cook but there is a rapid increase in dissolution rate with >33% of SiO_2 dissolved at 170 °C at 1.5h or more of cook. With anthraquinone catalyst present, SiO_2 dissolves somewhat faster at 170 °C, e.g., 43% dissolves in 1h of treatment.

5.4 Summary Of Kinetics Results

The kinetic studies resulted in the following values for rate constants for the delignification and carbohydrate dissolution reactions.

$$[L]^m + n^1\,[NaOH]^n \xrightarrow{k_L \text{ or } k_{Lb}} L_p \qquad \text{(lignin)}$$

$$[C]^r + s^1\,[NaOH]^s \xrightarrow{k_C \text{ or } k_{Cb}} C_p \qquad \text{(hemicellullose)}$$

m = 1 for both the bulk and residual reactions.

n = 0.8 for the bulk reaction.

n = 0 for the residual reaction.

s = 0.6 for the bulk reaction.

s = 0.7 for the residual reaction.

k_L bulk 80 °C	=	0.69 $(dm^3)^{0.8}\ mol^{-0.8}\ h^{-1}$
k_C bulk 80 °C	=	0.08 $(dm^3)^{0.6}\ mol^{-0.6}\ h^{-1}$
k_L bulk at 125° C	=	1.48 $(dm^3)^{0.8}\ mol^{-0.8}\ h^{-1}$
k_L residual 125° C	=	1.18 h^{-1}
k_C bulk at 125° C	=	1.05 $(dm^3)^{0.6}\ mol^{-0.6}\ h^{-1}$
k_C residual 125° C	=	0.012 $(dm^3)^{0.7}\ mol^{-0.7}\ h^{-1}$

Activation energy of delignification bulk reaction	=	14 ± 3 kJ mol^{-1}
Activation energy of delignification residual reaction	=	31.5 ± 6 kJ mol^{-1}
Activation energy of hemicellulose bulk dissolution	=	36 ± 3 kJ mol^{-1}
Activation energy of hemicellulose residual dissolution	=	73.5 ± 39 kJ mol^{-1}

5.5 Summary Of Delignification And Carbohydrate Dissolution Mechanisms

The overall mechanism of attack of caustic on straw may be summarized as follows:

1. There is initial rapid caustic consumption due to neutralization of free acidic type groups on the straw.

2. This is then followed by dissolution of lower molar mass lignin species M_n <2,000. A small amount of carbohydrate dissolves which is still linked to dissolved lignin. Parallel to this the majority of the carbohydrate dissolves separately at a slower rate than the delignification.

3. Progressively higher molar mass species of lignin (up to M_n = 30,000 or more) are dissolved by increasing the severity of caustic treatment, time and temperature. ^1H NMR studies indicate that up to 80 °C the dissolved lignin contains progressively more amounts of typically lignin groups but these diminish as temperature increases further, particularly at higher times of treatment. Carbohydrate continues to dissolve at a slower rate, partly along with lignin and partly separately (Figure 5.2)

4. When residual lignin is reduced to about 10% on straw the rate of delignification reduces either because the lignin remaining is inaccessible to caustic and/or is somewhat more chemically resistant.

5. At 170 °C with a longer time of caustic treatment (e.g., 1.5h) there is a rapid degradation of the lignin species. M_n of dissolved lignin reduces from 30,000 to <6000 and typically lignin groups rapidly diminish or disappear completely (Figure 5.3). There

is also a rapid increase in the rate of dissolution of silica with time of cook particularly at 1-1.5h.

6. The presence of anthraquinone (AQ) as catalyst only gives a small increase in the rate of lignin dissolution but it has a marked effect on the stability of the dissolved lingin and degradation of lignins to occur at temperatures lower than 170 °C

7. Although many chemical changes take place during caustic treatment of straw, the overall rates of delignification and carbohydrate dissolution are mainly controlled by physical diffusion processes.

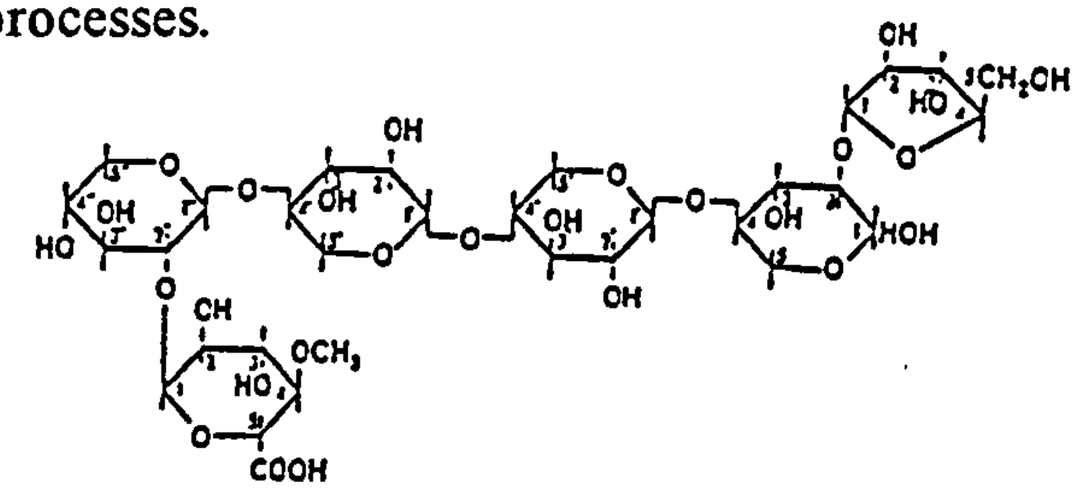
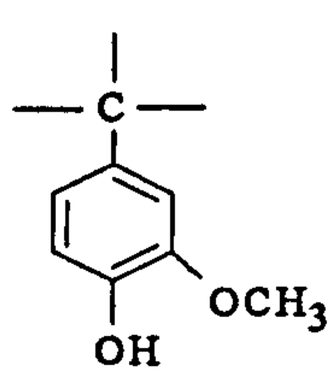
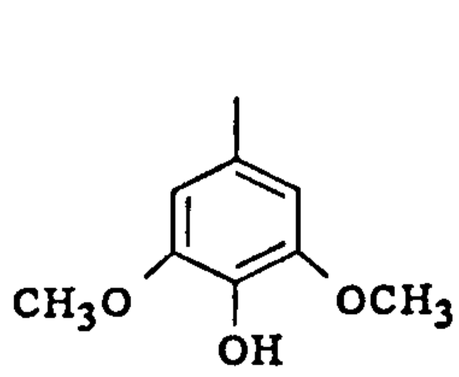


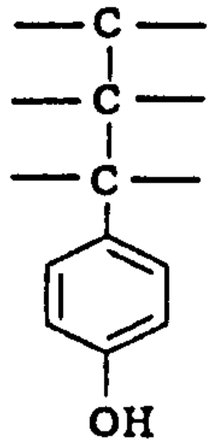
Figure 5.2 Carbohydrate adapted from Bailey (1973) and Heyraud (1979).



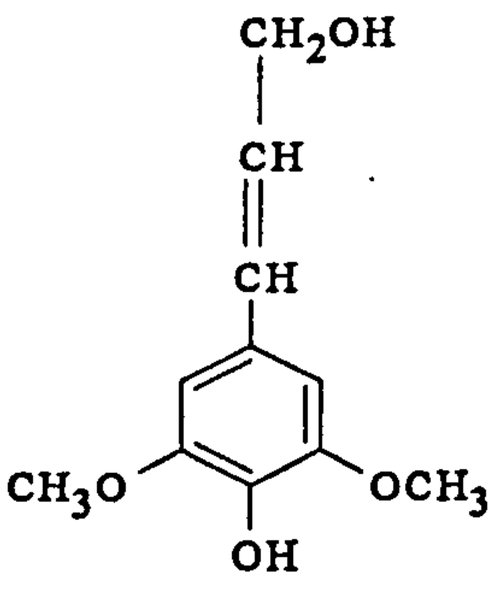
Guaiacyl



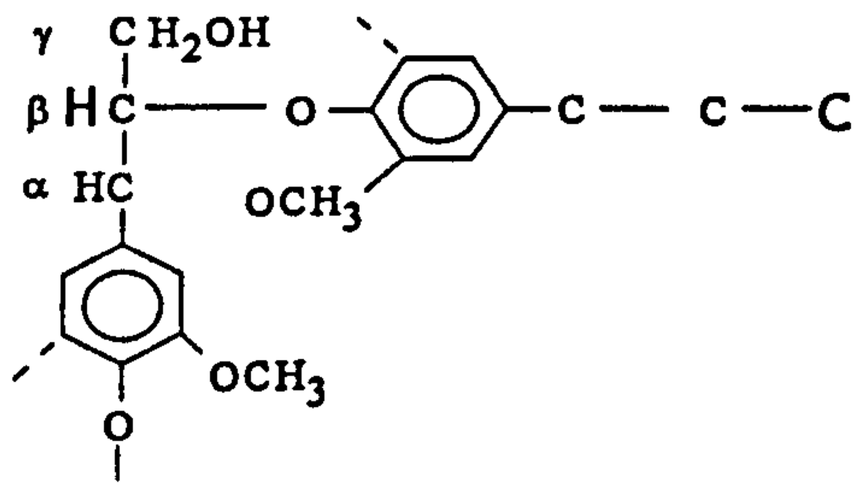
Syringyl



p-Hydroxyphenylpropane



Coniferyl alcohol



β-aryl ether linkage

Figure 5.3 Typical lignin units.

5.6 Comparison With Literature

There are numerous studies in the literature on the kinetics of wood pulping, particularly by Russians and the early work by Kleinert (1966). As mentioned earlier, there are only a few papers in the literature on the kinetic studies on alkaline straw pulping, which have been done mostly by Chinese workers. None of the studies on straw has been sufficiently comprehensive to elucidate the overall reaction mechanism for soda pulping and none has been on Saudi Arabian wheat straw, which was studied principally because the author is domiciled there, and because it has higher than average lignin content (~23%) compared with wheat straw from many other countries (~ 20% or less).

In this work, it has been found that the delignification of wheat straw by caustic soda occurs in two reaction phases, a bulk phase followed by a slower residual phase with activation energies of 14 ± 3 and 31.5 ± 6 kJ mol^{-1} respectively. This is in line with what has been reported in the literature.

For example, the presence of two reaction phases for delignification by caustic treatment has been reported for bagasse (Sabatier et al., 1993) who found low activation enérgies for the bulk phase of 6.4 kJ mol^{-1} and for the residual phase 48 kJ mol^{-1}. Other Chinese workers (Jianjuan et al., 1990) investigated caustic cooking of wheat straw and concluded that the rate controlling steps were physical rather than chemical, implying low activation energy for the rate controlling step.

The behaviour of straw in pulping with caustic is markedly different from the work reported on wood where invariably three or more phases of reaction have been found (Kondo and Sarkanen, 1984 and Wilson and Procter, 1970). The values for activation energies were found to be higher for the different phases which are said to be in line with a chemically controlled reaction rate due to the cleavage of phenolic-ether or β-aryl ether bonds in the lignin structure of wood.

Apart from the differences shown in the kinetic studies in wheat delignification reported here, the ^{13}C NMR results for lignin dissolved from wheat also show differences from the NMR results published in the literature for wood lignin. In particular, qualitative comparison with the literature on wood shows that wheat straw lignin contains higher guaiacyl to syringyl types units than is normally found in hardwood lignin.

There are very few studies in the literature on the dissolution of hemicellulose carbohydrate (pentosans) in straw pulping using caustic soda. Trivedi (1975) found that dissolution of pentosans by caustic treatment of straw was a slower process than delignification. Other work on bagasse pulping reported that dissolution of hemicellulose (pentosans) takes place towards the end of the residual phase (Sabatier et al., 1986) which all confirm the observations in this work that the deliginification is faster than carbohydrate dissolution.

SiO_2 dissolution is widely reported to cause problem in commercial pulping of straw. The reason why it did not interfere appreciably in the work was mainly because the straw was denoded before use and this reduced the SiO_2 content, since SiO_2 is mainly found around the nodes. Also, most commercial pulping is conducted over several hours at 170 °C, which favours SiO_2 dissolution.

5.7 Scope For Future Work

The following suggestions are made for future work.

* It would be useful to investigate in more detail the chemistry of delignification over each stage of the reaction and particularly at 170 °C.

* More detailed characterization studies of carbohydrate dissolved should be done by NMR.

* The role of anthraquinone could be investigated thoroughly, particularly at higher temperatures to understand the mechanism of lignin decomposition.

* A separate study needs to be carried on of pulp quality, particularly in the temperature range from 125-170 °C.

* Wheat straw from different sources could be examined to see the effect of different initial lignin contents on the pulping.

* Finally, the results could be used to select an optimum process for industrial scale use which would be environmentally friendly, energy efficient and minimise by-product formation.

6 EXPERIMENTAL

6.1 Chemicals

All the chemicals were of AR or GLR grade and were obtained from Sigma Chemical Company Ltd., Aldrich Chemical Company Ltd., and Fluka Chemie A.G. De-ionized water was used throughout for making the solutions.

All liquid volumes were measured in flasks calibrated in ml. All kinetic data are given in dm^3 units using the conversion 1,000 ml ≡ 1 dm^3 which was well within experimental error.

6.2 Wheat Straw

6.2.1 Sample Preparation

Wheat straw samples were collected from the Al-Kharj (south-west region) of Saudi Arabia in its crop season during January and Febuary. By way of preliminary treatment, the material was well dried after removing adhered sand, nodes, internodes and other foreign materials of no pulp value.

6.2.2 Determination Of Extract And Moisture Content

The air-dried wheat straw sample was weighed accurately (5g) and finely chopped to pass a 40-mesh screen, and then was placed in Soxhlet extractor with acetone-water (10:1,v/v). The chopped straw was then extracted for 48h continuously, after which the sample was air-dried and stored in a vacuum desiccator over P_2O_5 for 3 days. The dessicator dried sample of wheat straw was then weighed (as the extracted wheat straw). The moisture content was then calculated after taking accurately (1g) of the dried

extracted straw into a weighing bottle and drying of the specimen to a constant weight in an oven at 105 °C (about 4h). The moisture content of the straw was calculated as weight percentage from the weight loss (Wood and Kellogg, 1988).

The solvent from the acetone-water solution was dried and the residue was dried in a vacuum oven at 40 °C for 24h and weighed as the dried residue extract.

The extract content was then calculated using the following equation:

$$\frac{\text{Extract}}{\text{Oven} - \text{dry original wheat straw}} \% = \frac{100\,R}{W(1 - M/100) + R}$$

Where

R = is the weight of dried residue (g)

W = is the total weight of extracted straw (g)

M = is the moisture content (%)

RESULTS

The net results of Moisture content (M) of three replicates	=	7.06%
The net result of Extract content (E)	=	4.32%

6.3 Determination Of Klason Lignin

The standard Klason method was used being the most widely applied method and probably the simplest and overall the most reliable one despite its limitations for the determination of lignin on a number of repeated samples cleaned and dried wheat straw. To a ground sample of at least 20-mesh screen clean dried straw (4g) accurately weighed in a 250 ml round-bottomed flask was added 24 ml of 72% (12 M) sulfuric acid (H_2SO_4). The mixture was placed in a water-bath at 30 ± 0.5 °C and was stirred frequently to assure complete solution. After exactly 1 hour, it was diluted with 800 mL (3%) H_2SO_4 in a 1l

Erlenmeyer flask. The mouth of the flask was covered with aluminum foil tied with cotton and then was put in an autoclave for 1 hour at 120 °C.

While the resulting hydrolysis mixture was still warm, the acid insoluble materials was filtered off and thoroughly washed with water to remove the acid. The filtrate was dried to a constant weight at 75 °C for 15h and then weighed as Klason lignin (Theander and Westerlund, 1986 and Wood and Kellogg, 1988).

RESULT

The net result of triplicate analysis of the wheat straw sample was found to be = 22.94%

6.4 Determination Of Acid-Soluble Lignin

The filtrate obtained from the removal of the acid-insoluble lignin as above (Klason lignin content) was diluted with deionized water to a defined volume in the volumetric flask. The UV absorbance of this dilution was then measured at 280 and 220 nm (10 mm light path length) using 0.5 *N* H_2SO_4 as the reference solution with dilution of the filtrate whenever necessary to keep the absorbance in the range of 20-70% transmittance. The acid soluble lignin content in the straw was calculated as follows:

$$\frac{\text{Acid soluble lignin}}{\text{Oven dry original wheat straw}} \quad \% \quad \frac{100A_sV}{110\times1000W(1-M/100)(1+E/100)}$$

Where

A_S is the absorbance at λ 205 nm (A) (the average extinction coefficient for acid-soluble lignin is 110 litres/g-cm at λ 205 nm).

V is the total volume of filtrate (ml).

W is the weight of wheat straw (g).

M is the moisture content (%).

E is the extract content (%).

RESULT

The net result of acid-soluble lignin in the straw was found to be = 1.88%

6.5 Milled Straw Lignin (MSL)

6.5.1 Preparation Of MSL

In order to get lignin in its pure form as protolignin with minimum destruction of its original structure, the Bjorkman lignin method, which is also known as milled straw lignin, was used to isolate lignin from a wheat straw sample to analyse spectroscopically (Kellogg and Wood, 1988). The preparation was carried out as follows.

An air-dried straw sample (10g) was ground in a Braun blender to pass about 40-mesh and extracted first with acetone:water (9:1,v/v) by percolation at room temperature and then with ethanol:benzene (2:1, v/v). As lignin is heat-sensitive, the extractions were carried out below 40 °C. The extracted straw sample was then dried in a vacuum desiccator over phosphorous pentoxide (P_2O_5).

Accurately weighed extracted ground straw (5g) was placed in a 500 ml round-bottomed flask and was dispersed in 100 ml of fresh dioxane-water (96:4, v/v) which was stirred continuously using a mechanical stirrer at room temperature for 24h. The aqueous dioxane solution was then removed by centrifugation. This operation was repeated twice more with a stirring time of 6h instead of 24h. Finally, the aqueous dioxane solutions were combined and filtered. The insoluble materials were then freeze dried to get crude MSL.

6.5.2 Purification Of MSL

The above crude MSL was dissolved in glacial acetic acid-water (9:1, v/v) in the approximate ratio of 1g of MSL to 20 ml of solvent. The resulting solution was then added dropwise into 10 times the volume of deionized water in a centrifuge bottle under

mechanical stirring. The mixture was centrifuged, and the supernatant was removed. To the wet precipitate in the centrifuge bottle was added 25 ml of deionized water under mechanical stirring, then the water was removed by centrifugation. This operation was repeated two more times. Then the precipitate was stirred with 25 ml of deionized water and was freeze-dried to obtain MSL. The MSL was then dissolved in 25 ml of 1,2-dichloroethanol solvent, and the resulting solution was centrifuged to remove any insoluble material. The clear solution was then added dropwise into 10 times the volume of dried ether in a centrifuge bottle with occasional stirring and was centrifuged. The precipitate was washed twice with 25 ml of fresh ether, and finally with 25 ml of *n*-hexane by stirring and then extracted by subsequent centrifugation. After air-drying, the purified MSL was dried in a drying pistol at 50 °C in a vacuum over P_2O_5 for 48h. The weight of the MSL was calculated and was kept in a vacuum desiccator under P_2O_5 prior to use.

6.6 Reactions In Metal Reactor

6.6.1 Introduction

The pulping experiments were carried out in a specifically designed stainless steel cylindrical reaction vessel (bomb) (Figure 6.1) of total capacity 250 ml which was used only in the high pressure hazard laboratory. Throughout the runs the reactor was rotated about its horizontal axis inside an electric furnace to achieve good mixing of the reactants at controlled temperatures (Figure 6.2). The design of metal-bomb was as follows:

Pressure rating	=	6,122 bar
Internal radius	=	2 cm
Internal depth	=	16.5 cm
Volume	=	207 ml
Assume aqueous charge	=	55 ml
Ignoring solid content	=	55g H_2O
When vapourized 207 cc vapour weight	=	55g
Density	=	55/207g ml^{-1}

Specific vol. = 207/55g ml^{-1}

= 207/55 x $1/10^6$x 10^3 m^3kg^{-1}

= 0.004 m^3 kg^{-1}

From steam tables (Perry 6th edition pp. 3-24),

Spec. vol. m^3 kg^{-1}	Temp. K	Press. bar
0.007	1500	1000
0.0042	1000	900
0.0037	900	800
0.0035	800	600
0.002	600	150

Pressure will read-1000 bar at 1000 K with 50g loading in 207 cc volume.

Policy

* Loading not to exceed 55g of water

* Operating temperature maximum 450 K

* Safety cut off temperature 500 K

* Reactor to be used only in hazard laboratory

Calculation of rotation

$Nc = 76.65/\sqrt{D}$ where Nc = critical velocity/revolution min^{-1},

and D = internal diameter/ft.

$$= 76.65 / \sqrt{\frac{4}{2.5x12}}$$

$= 76.65/0.36$ = 213 rpm.

Optimum velocity N = ·70/100 Nc

= 70/100 x 213

= 149 rpm.

So, actual run velocities = 150 rpm.

· 6.6.2 Reagents And Apparatus

Sodium Hydroxide: AR grade conforming to ACS specification.

Water: deionized water.

Wheat Straw: Collected from Alkharj, Saudi Arabia, and extracted and dried well, cleaned and free from nodes and internodes.

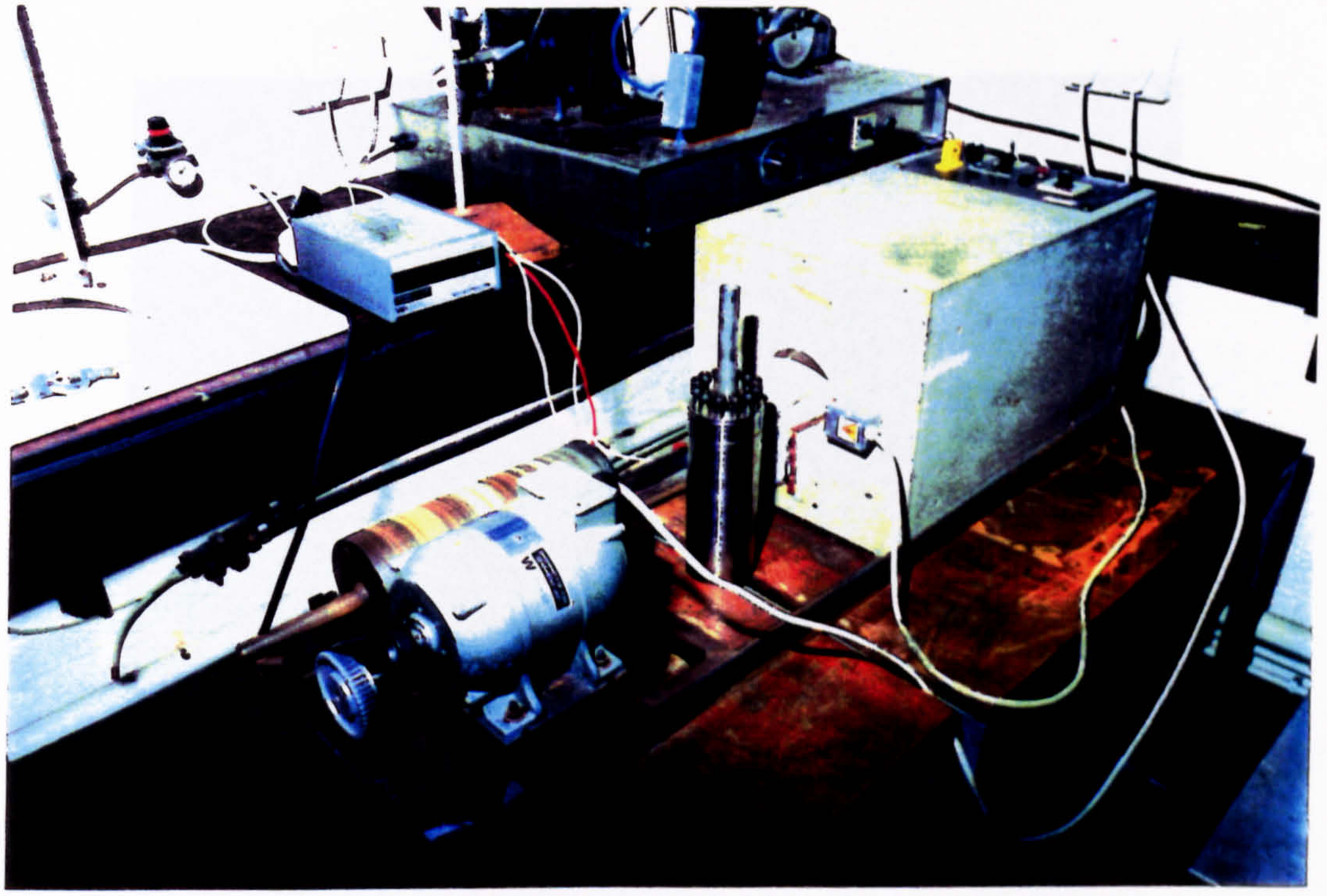


Figure 6.1 Metal reactor (bomb) and heating furnace

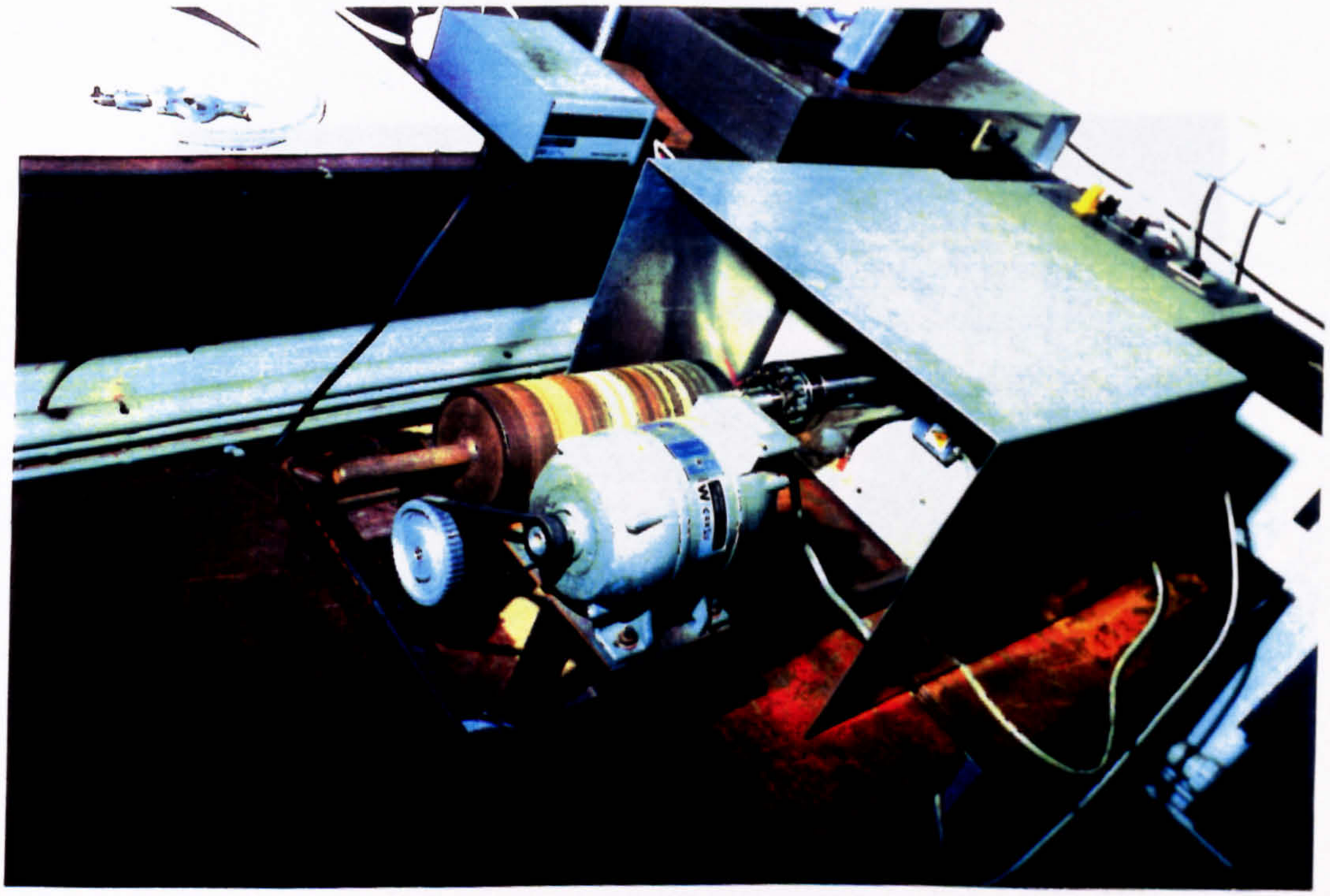


Figure 6.2 Metal reactor (bomb) in operation

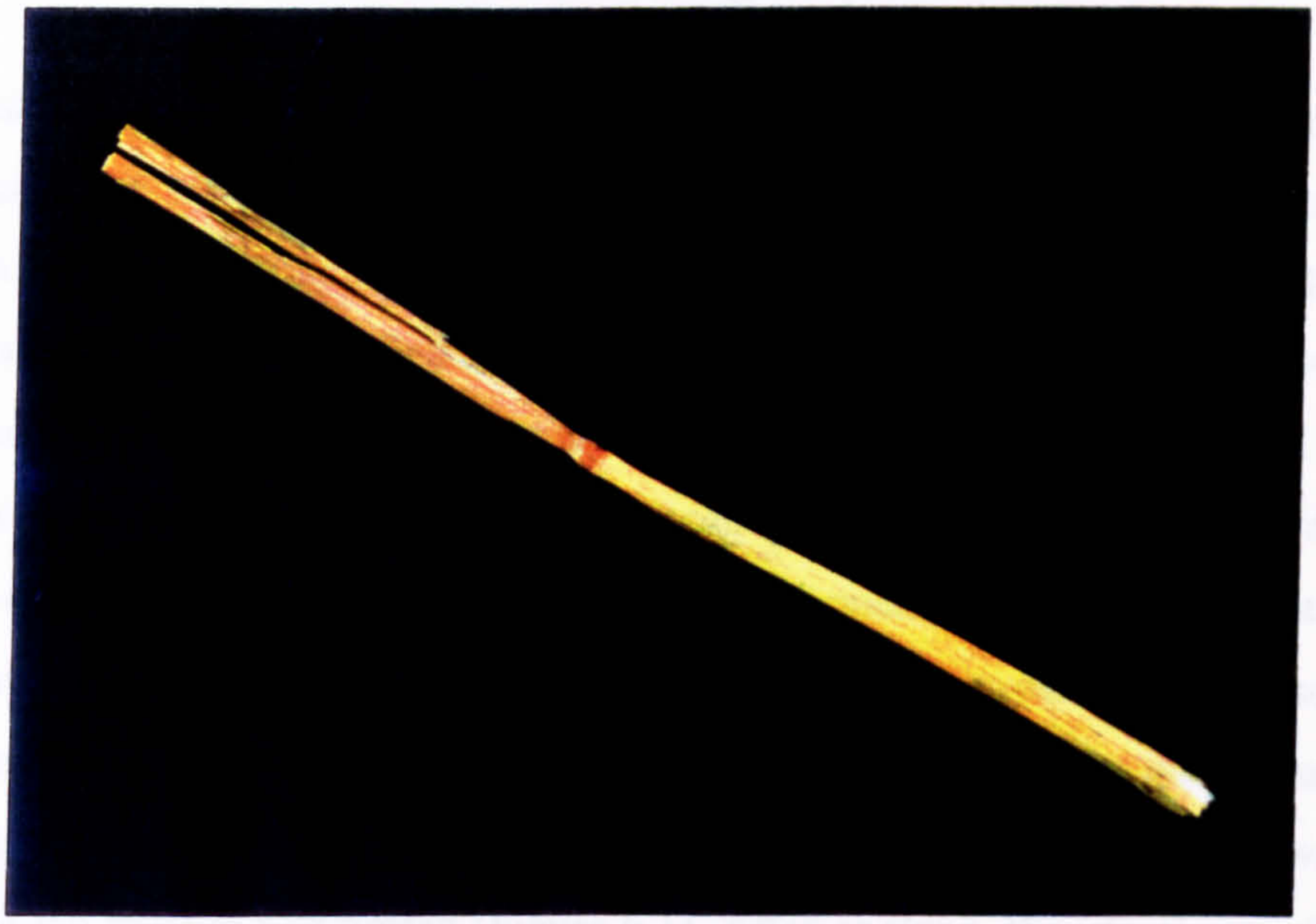


Figure 6.3 Wheat straw sample collected from Al-Kharj region (Saudi Arabia).

Figure 6.4 Wheat straw sample of 2-3 cm in length after denoding

6.6.3 General Procedure For Delignification

A wide range of pulping runs in the above metal reactor was successfully carried out on the sample of wheat straw previously denoded and was cut neatly into 2-3 cm lengths (Figure 6.3 and 6.4) (grinding the straw was avoided which caused mechanical pulping). The extracted straw was washed thoroughly with water, dried to a constant weight in a vacuum oven and a known weight was then mixed with caustic soda. A standard weight of 4.23g dry straw was used. Experiments were conducted over a range of temperature with different amounts of caustic soda over a range of temperatures (25-170 °C) at different times (5min-6h). A standard quantity of 55 ml deionized water was added in most of the experiments. After dissolution of the caustic in the water, the mixture was transferred to the above stainless-steel high pressure reaction vessel. The top of the vessel was bolted tightly and the mixture was heated (Figure 6.1). After cooking, the vessel was allowed to cool in a bucket containing cold water before it was opened. The brown mixture was filtered off under suction through a Buchner funnel. The pulp was washed repeatedly with water to recover all the residual caustic which was found to be strongly absorbed to the pulp and unreacted straw. 30% of the filtrate was used to determine the alkali content by titration.

The standard Klason method was used for the determination of lignin dissolved in the remaining 70% of the filtrate from pulping runs. The liquid volume was first reduced five-fold using a rotavapor (vacuum). The concentrated extract was then acidified with mineral acid (H_2SO_4) to give a precipitate of lignin which was separated by filtration. The precipitate was washed with warm water (two to three times) to remove traces of carbohydrate and the solute was dried to constant weight under vacuum. The weight of lignin was then calculated gravimetrically (Trivedi, 1975). The filtrate solution of sugar was collected separately in a defined volumetric flask and the contents made up to the mark with deionized water to use later for the analysis of carbohydrate.

6.6.4 Water Soluble Lignin

A preliminary examination of water soluble lignin was successfully carried out in a 500 ml beaker. A standard weight of straw (4.23g dry weight) was added in the beaker. To this 4g of caustic in 55 ml of deionzed water was added and throughly mixed and stirred for 3-5 min. After that the pulp was filtered off quickly and washed with multiple amounts of water. The pulp so obtained was returned to the beaker and a fresh 55 ml of water was added to this and the beaker was heated on magnetic stirrer for 3h at 80-90 °C. Then it was filtered and the pulp was washed with 2 to 3 washings of warm water. The filtrates were combined and the volume was reduced to 20% of its original amount under vacuum. The resulting volume was acidified with H_2SO_4 and the precipitate (so obtained) was filtered and washed with warm water. The subsequent precipitate was dried and weighed as lignin.

Similarly a few pulping runs were also done in the metal reactor instead of a beaker using standard strength of straw, caustic and water at different temperatures, 80 °C and 170 °C, in the range of times 0.5-1.5h. The subsequent process was carried out same as described in detail in the delignification section above.

6.6.5 Titration

The remaining alkali content after treatment of wheat straw samples was measured by the backtitration of 30% of the filtrate from pulping runs with dilute acid (0.1M H_2SO_4) using phenolphthalein as an indicator. The pH 8.3 with H_2SO_4 was chosen in order to stay above the pK_a's of most organic acids. In some cases as a check, titrations were carried out on the unfiltered reaction mixture to ensure that all the caustic was being removed from the straw in the filtration/washing procedure (Pavlostathis and Gossett, 1985). This is because of initial observation that the titration gave variable results due to strong absorption of caustic on straw before the total sample titration and subsequent thorough washing procedures were established. No instantaneous equilibrium after addition of

sulfuric acid was attained which, as reported earlier, could be due to the equilibrium between the interior of a fibrous material and the bulk of an electrolyte solution in which it is immersed (Browning, 1967 and Farrar and Neale, 1952). Therefore, a stable pH reading 8.3 ± 0.03 for at least a minute was taken as the end point.

6.6.6 UV Measurements Of Lignin

a) The well dried alkali soluble extracted lignin produced after treatment in the metal reactor for 4h at room-temperature was ground thoroughly and homogenized in 20% alkali solution. The impurities were filtered off and a clear solution was obtained and collected in a volumetric flask. The solutions of lignin were made up to known concentrations separately in 100 ml volumetric flasks and completed with deionized water.

The absorbance of these solutions were measured the characteristic strong lignin absorbance at 280 nm (Bethge et al., 1952) using a Shimadzu UV 160 UV-visible spectrometer.

The calibration graph for the lignin sample was a plot of absorbance versus concentration (Figure 6.5) and gave a linear correlation coefficient (r = 0.998) over the range of 1.1-3.7 μg/ml of lignin concentration in a final volume of 100 ml.

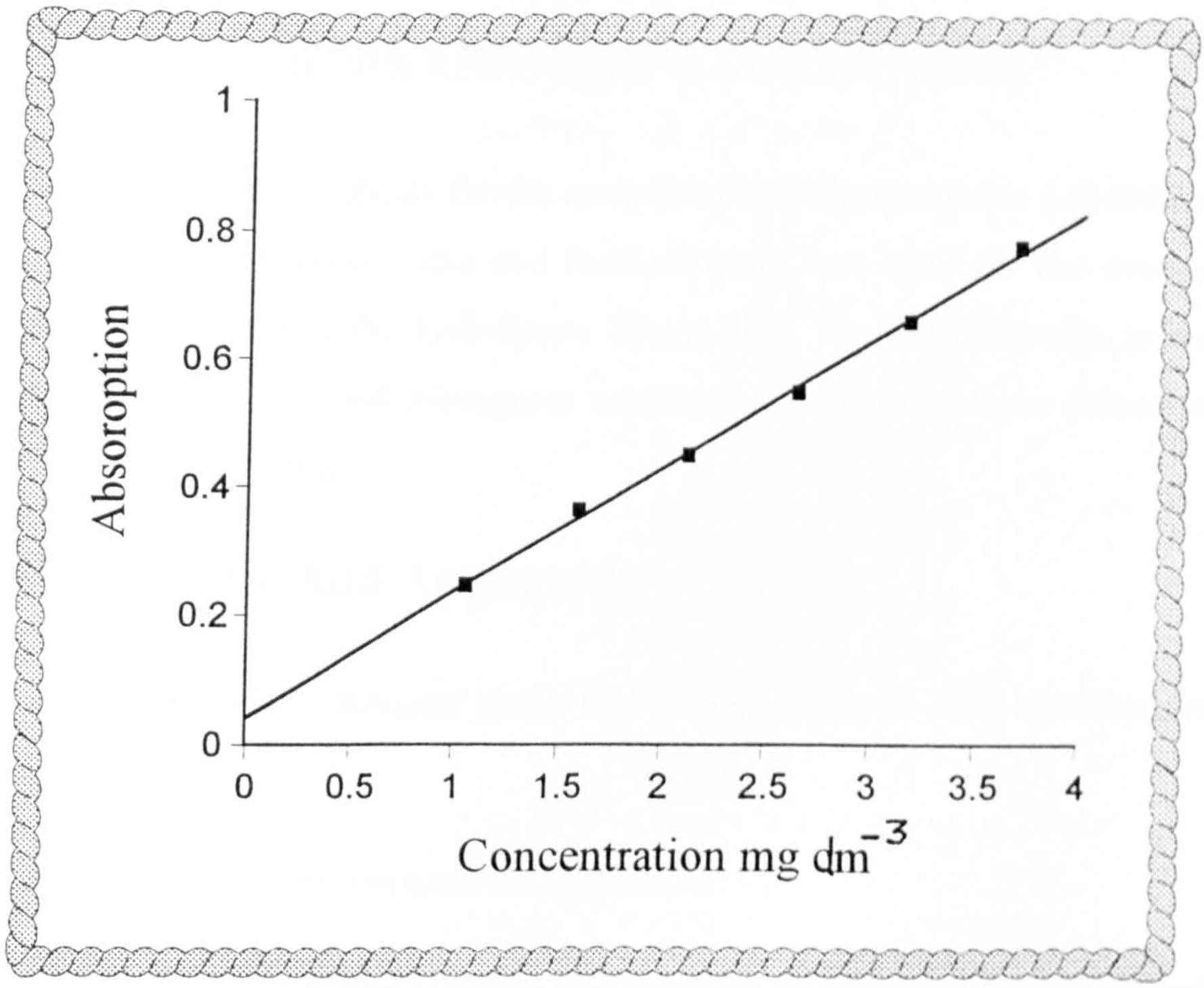


Figure 6.5 UV absorbance versus lignin concentration.

A qualitative lignin determination was made absorptiometrically in the caustic solution after pulping runs in metal reactor with constant caustic/variable initial straw and excess lignin experiments. The normal Klason method of lignin isolation in these experiments was rather difficult due to dilute caustic treatment with variable strength of straw. Three variable strength of straw runs, 0.57g, 1.12g, and 2.23g (bone dry weight), were done successively in the metal vessel with constant strength of caustic, 0.45g (0.02 mol dm^{-3}), and 55 ml deionized water at 80 °C for different times (10min-2h). The excess lignin runs with normal strength of straw, 4.23g (bone dry weight), with 0.045g of caustic in 55 ml deionized water were done in the metal reactor at variable times from 8min-6h. in the temperature range 25-170 °C (for Figures see Chapter 3).

6.7 Determination Of Sugar Concentration

One of the useful methods for the analysis of hydrolysates from polysaccharides such as starch, glycogen, plant gums and hemicelluloses was used for the determination of carbohydrate content in the hydrolysate filtrate after the delignification process carried out in the metal reactor and subsequent acidification process as above (Flood et al., 1949 and Dubois et al., 1956).

6.7.1 Reagents And Apparatus

Sulfuric Acid (H_2SO_4): Reagent grade 95.5% conforming to ACS specification, specific gravity 1.84.

Water: Deionized water was used throughout.

Phenol 80%: 80g of AR grade phenol was prepared by adding 20g of deionized water in 100 ml volumetric flask. The water-while liquid so formed is readily pipetted out. Schimadzu A-160 UV/Visible spectrometer; Quartz cells of 10 mm were used.

6.7.2 General Procedure

2 ml of carbohydrate solution obtained from the different runs of straw and caustic in the metal reactor for different times (5min-3h) and different temperatures (50-170 °C) were pipetted into a cleaned well dried colorimetric tube and 0.05 mL of 80% preprepared phenol solution was added to this accurately. Then 5 ml of concentrated sulfuric acid (H_2SO_4) was rapidly added such that the stream of acid was directed against the liquid surface rather than against the side of the tube in order to obtain good mixing. The tube was cooled with running tap water and allowed to stand about 10 minutes. The tube was then shaken and placed in a water-bath to warm at 25-30 °C for 20 minutes. After that the appearance of the characteristic pale-orange colour of (hexoses) D-xylose and L-arabinose at a wavelength of 480 nm was measured using a Schimadzu UV 160 UV-visible spectrometer similar to the procedure prescribed in the standard method of sugar analysis

(Dubois et al., 1953). The colour was stable for several hours; and the blank was prepared by substituting deionized water in place of sugar solution.

6.7.3 Standard Curve

A stock solution mixture containing 500 mg of equal quantities of D-xylose and L-arbinose was prepared in a 500 ml volumetric flask and filled with deionized water. Then sugar solutions of the concentration 2.5-22.5 mg were separately prepared in 100 ml volumetric flask made up to the mark with deionized water.

The absorbance of these solutions were measured by the characteristic UV absorption of sugar (xylose and arabinose) at a wavelength 480 nm using the same Schimadzu A-160 spectrometer after following the same procedure as described above. Figure 6.6 shows the resulting calibration plot of absorbance versus concentration.

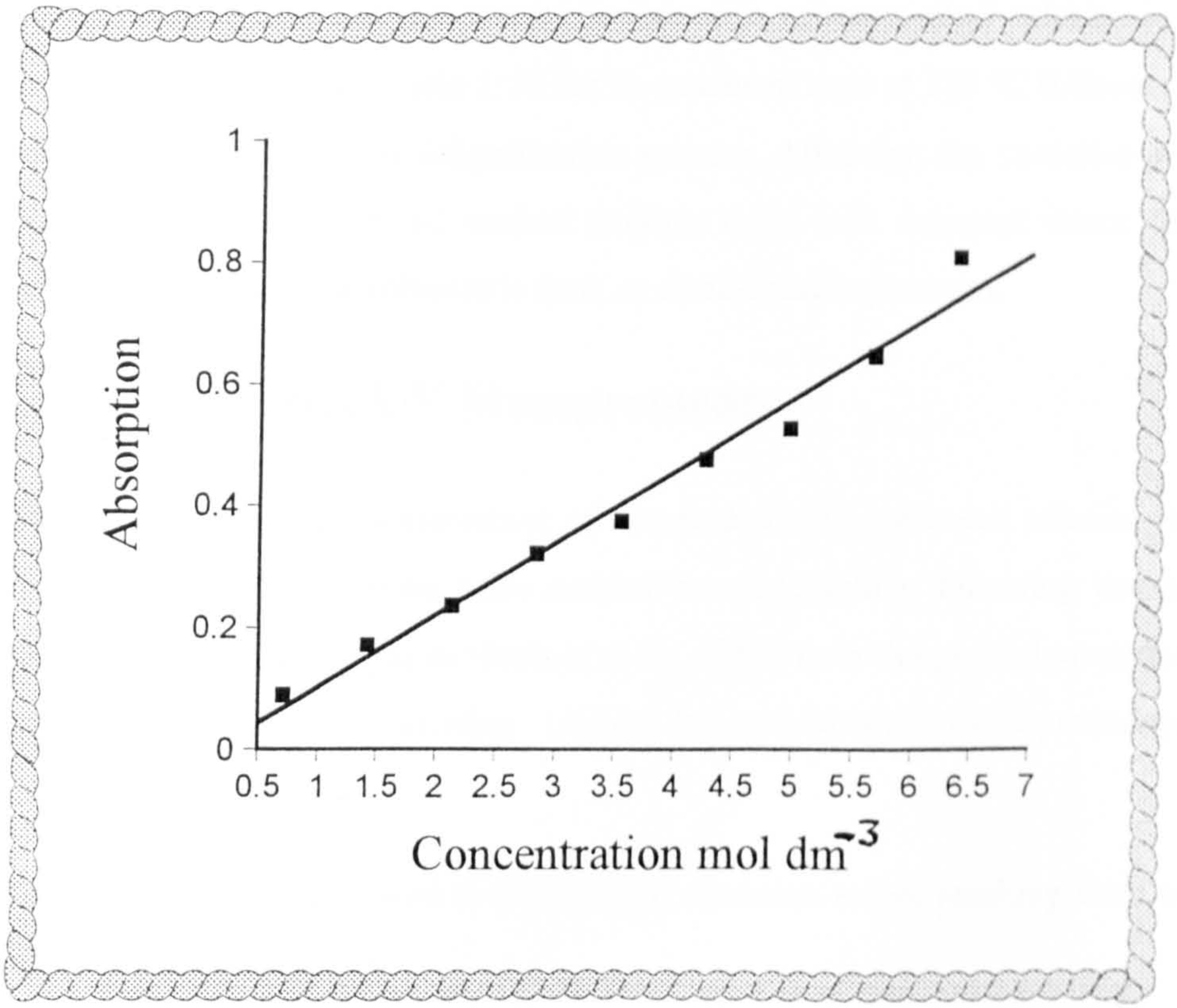


Figure 6.6 UV absorbance versus D-xylose-L-arabinose concentration.

6.7.4 Determination Of Pentosan Content In Straw

A simple method of an acid prehydrolysis was utilized to remove pentosans from wheat straw sample similar to the procedure described by an Indian worker (Trivedi, 1975).

In brief, 10g of the well-dried and cleaned wheat straw sample was accurately weighed having been cut into pieces of 2-3 cm in length. The sample was pretreated with commercial hydrochloric acid (strength 10.2N, specfic gravity 1.15) at ambient temperature for 1h with a solid to liquid ratio of 1:10. After the treatment, the residue was filtered out, washed thoroughly with deionized water and the filtrate was collected in a 500 ml volumetric flask as acid-soluble pentosan.

The residue so obtained was treated further with aqueous alkali solution in the metal reactor with a solid to liquor ratio 1:18 for 1h treatment time at 170 °C following the same procedure as described in the delignification process. After that the container was cooled and the contents filtered off and washed multiple times with deionzed water. The filtrate was combined in a marked volumetric flask as alkali-soluble pentosan

.6.7.5 Colorimetric UV Measurements

The colorimetric UV measurement of the acid-soluble pentosan solution as well as alkali-soluble pentosan solution were carried out successfully following the prescribed standard method of sugar analysis (Dubois et al., 1956) as in the general procedure for the determination of sugar concentration (xylose and arabinose) analysis procedure (Figure 6.7).

The solutions were prepared in triplicate to minimize errors resulting from accidental contamination with cellulose.

The calibration graph (Figure 6.6) for the standard sugar sample (xylose and arabinose) gave a linear correlation coefficient (r = 0.989) over the range of 0.7-6.4 ppm of sugar concentration in a final volume of 100 ml. The molar absorptivity calculated from the slope of the graph was 1.68×10^4 mol^{-1} cm^{-1}. The reproducibility of the method was determined by running four replicate sample each containing 6 ppm in the final solution. The relative standard deviation was 2.36%.

RESULTS

The net results of triplicate sample analysis found:

a) Acid-soluble pentosan content = 26.85%

b) Alkali-soluble pentosan content = 6.48

Total content = 33.33%

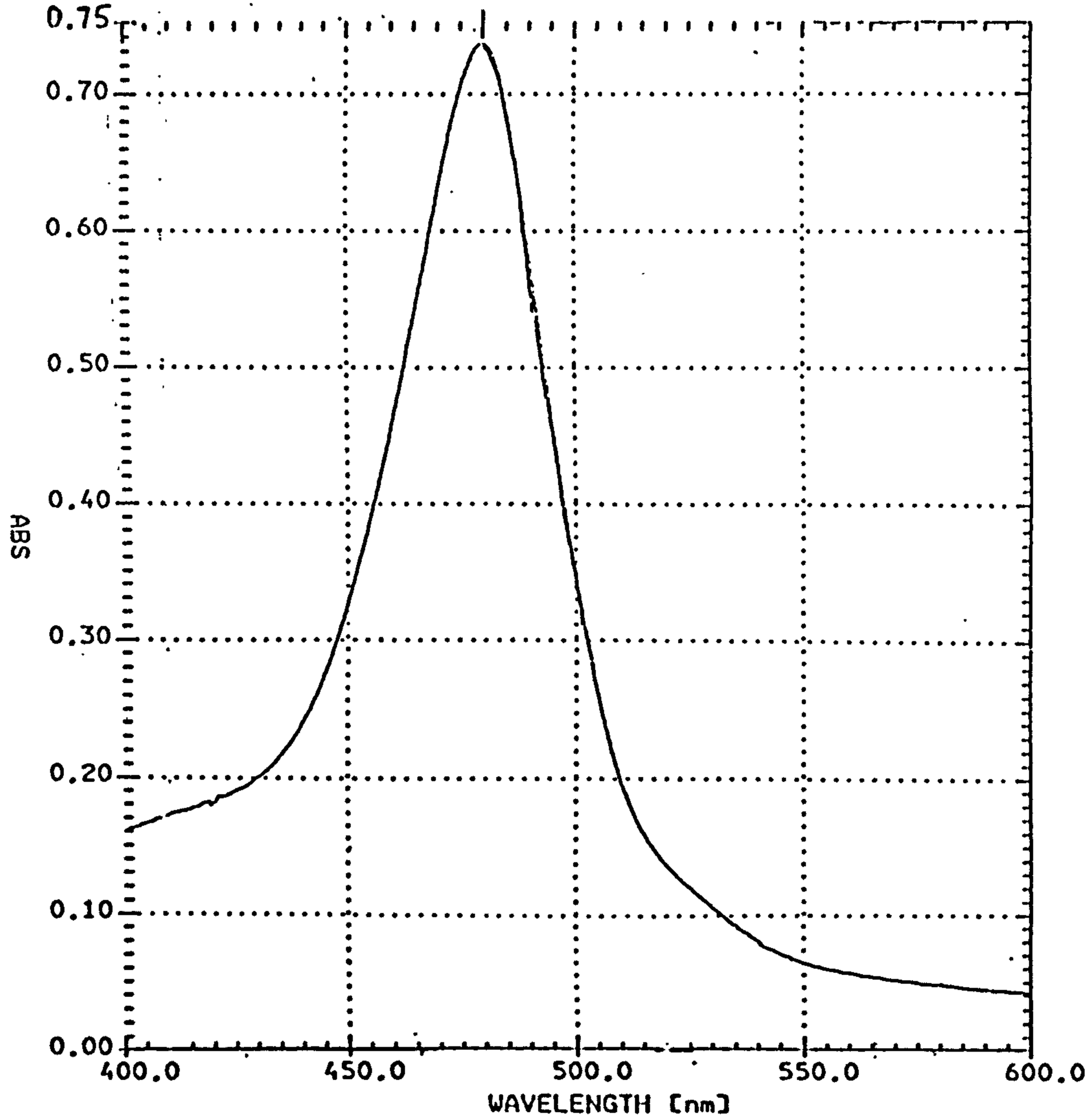


Figure 6.7 UV absorption curve of acid-soluble pentosans of wheat straw.

6.8 Lignin Product Analysis

6.8.1 Fourier-Transform Infrared Spectroscopy (FT-IR)

The FTIR spectra for lignin samples as well as raw material (wheat straw) and pulp were obtained on an Analect FX-6160 FT-IR spectrometer. Samples were run in the single-beam transmission mode as KBr disks (2mg of sample/58 mg of KBr). Each spectrum was the result of 128 scans of IR-grade KBr under ambient conditions. Spectral data were accumulated at 4 cm^{-1} resolution over the range 4000-450 cm^{-1}.

6.8.2 Solid-State NMR

Solid-state NMR spectra were obtained with the use of the CP/MAS technique. A Bruker 300 MSL NMR spectrophotometer operating at 76.8 Mhz for ^{13}C equipped with high power amplifier and a narrow-bore probe was employed for this purpose.

The samples were packed in a 5mm Kel-F rotor and spun at 5 KHz. Data were collected by taking 3556 scans using a 4.5 μs 90° pulse, a 5-ms contact time and a 6-s delay time. The data were processed with 30-Hz line broadening to improve the signal-noise ratio. The spectra were referenced to poly(dimethylsilane) (Patriarch System, Inc.,) at 1.84 ppm with respect to Me_4Si by placing 5 mg of the reference (wrapped in Teflon tape) at one end of the rotor.

The solid-state NMR spectra for the above samples were obtained with use of the CP/MAS technique. A Bruker 300 MSL NMR spectrometer operating at 67.8 Mhz for ^{13}C equipped with high power amplifier and a narrow bore was employed for this purpose.

The samples were packed in a 5 mm Kel-F rotor and spun at 5 KHz. Data were collected by taking 3556 scans using a 4.5 μs 90° pulse, a 5ms contact time and a 6s delay time. The spectra were processed with 30 Hz line broadening to improve the signal-noise

ratio. The spectra were referenced to poly(dimethylsilane) (Petrach System, Inc.) at 1.84 ppm with respect to Me_4Si by placing 5 mg of the reference (wrapped in Teflon tape) at one end of the rotor.

6.8.3 Solution NMR Spectroscopy

Solution NMR spectroscopy were obtained on a Jeol FX-90Q NMR spectrophotometer operating in the FT mode. All the spectra were recorded at ambient temperature of 26 °C and the sample concentration was generally 0.3 M in DMSO-d_6 as a solvent. Chemical shifts were determined relative to the internal standard tetramethylsilane (TMS) for ^1H and ^{13}C spectra.

6.8.4 ^1H NMR Spectra

The NMR spectra were obtained on a FX-90 Q Jeol Spectrometer. The ^1H observed frequency was 90 MHz, pulse width 20 μs (45^0); pulse delay auto set; acquisition time auto set, data point 8K, spectral width 1000 Hz, effective resolution 0.10 Hz, probe temperature 25 °C sample tubes 5 mm $^1H/^{13}C$ with dual probe and deuterium interlock. The sample was dissolved (50mg/0.5 ml) in Me_2SO-d_6 with about 1% Me_4Si added as an internal reference at 0 ppm.

6.8.5 ^{13}C NMR Spectroscopy

^{13}C observed was frequency 22.85 MHz; pulse width 10 μs (45°); pulse delay 155, acquisition time auto set; data points 8K; spectral width 5000 Hz; effective resolution 0.115 ppm; sample tube 10 mm; probe $^1H/^{13}C$ dual probe; ^1H noise decoupling and internal lock on deuterium signal of the solvent.

6.8.6 Gel Permeation Chromatography (GPC)

The lignin samples were prepared according to the standard Klason Method after running in the rotating metal reactor at different temperatures and times with different concentrations of caustic. The final solutions were acidified in sulfuric acid to precipitate the lignin and dried thoroughly, then submitted to the Polymer Supply & Characterization Centre (PSCC) at Rapra Technology (England) to use its services in the study of lignin molecular mass determination for analysis using GPC.

Sample solutions were prepared by adding 10 ml of dimethyl sulfoxide (DMSO) as a solvent to 20mg of lignin sample and warming (not more than 40°C) to dissolve; a small amount of 1,2-dichlorobenzene, in the solvent was added in solvent as an internal marker; after thorough mixing, the solutions were filtered to remove any impurities through a 0.2 micron PTFE membrane prior to the chromatography.

6.8.7 Sample Preparation For GPC Analysis

Sample solutions were prepared by adding 10 ml of dimethyl sulphoxide (DMSO) as solvent to 20 mg of lignin sample and warming (not more than 40°C) to dissolve; a small amount of 1,2-dichlorobenzene, in the solvent was added as an internal marker; after thorough mixing, the solutions were filtered to remove any impurities through a 0.2 micron PTFE membrane prior to the chromatography.

Chromatographic Conditions

Column:	PLgel 2 x mixed bed-B*, 30 cm, 10 microns
Solvent:	dimethylsulphoxide (DMSO) with lithium bromide
Flow rate:	1.0 mL/min (nominal)
Temperature:	80°C (nominal)

*Styrene-divinylbenzene column packing with reasonably broad molecular mass applicability.

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