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# HISTORICAL DEVELOPMENTS IN WOOD CHEMISTRY

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## ABSTRACT

Wood are one of the most important raw material source for forest products industry. Due to technological developments, researchers in the area of wood chemistry have been showing increased interest in the benefits of utilization wood based materials alone or together as an alternative lignocellulosic fiber sources for forest products industry.

However, utilization of woody matrials more efficiently and conservation natural resources have been paid special attention. For that reason, it should be carefully consider and beneficial to understanding chemical structure of those woody materials. Many new approaches and techniques have been developed for better understanding of wood chemical sturucture.

**Keywords:** Wood chemistry, cellulose, lignin, extractives, pulp and paper

# ODUN KİMYASI ALANINDA TARİHSEL GELİŞİMLER

## ÖZET

Orman ürünleri endüstrisi için odun en önemli bir hammadde kaynağıdır. Teknoljik gelişmeler sonucunda, odun kimyası üzerine çalışan araştırmacılar odundan, tek başına veya alternatif lignoselülozik lif kaynakları ile birlikte orman ürünleri endüstrisi için yeni ve ilginç faydalanma yaklaşımlarını ortaya koymaktadırlar.

Bununla birlikte, odundan daha etkili faydalanma ve doğal kaynakların korunması üzerine özel önem verilmektedir. Bu sebeple, odunsu maddelerin kimyasal yapılarının dikkatlice belirlenmesi ve amaca uygun kullanılması gerekir. Yeni teknik ve yaklaşımlar sayesinde odunun kimyasal yapısı daha iyi anlaşılmaya çalışılmaktadır.

**Anahtar kelimeler:** Odun kimyası, selüloz, lignin, ekstraktif maddeler, kağıt hamuru ve kağıt

## 1. INTRODUCTION

The major achievements in wood chemistry during the past seventy-five years are reviewed in this chapter. Emphasis is placed on the people who have been instrumental in the important developments in this field of wood science. These scientists are known throughout the world for their important contributions to wood chemistry.

Wood is mainly comprised of three polymeric constituents, namely, cellulose, hemicelluloses and lignin in the rough proportions of 2:1:1. Emphasis is placed on these components since they constitute about 95% of the dry matter of wood. Since cellulose and the hemicelluloses are polysaccharides, the carbohydrate fraction constitutes 70% of wood, while the polyphenolic polymer, lignin, accounts for 20-30% depending on the species. The "extractives" in wood, although not a structural component, comprise a small (1-10%) but economically important fraction of the woody biomass. These four classes of materials from wood are reviewed in this paper.

## 2. DEVELOPMENTS IN CELLULOSE CHEMISTRY

The foundations of polymer chemistry are tied closely with the elucidation of the structure of cellulose. The French chemist Anselme Payen was the first to note that most plant materials contain a resistant fraction with essentially the same composition of about 44% carbon, 6% hydrogen, and 49% oxygen, which was later determined to be cellulose. Subsequently, Haworth contributed a series of excellent papers which led to the elucidation of the glucopyranose chemical structure of the sugar units in the polysaccharide. Many early investigators felt that cellulose was an association or aggregation of small molecules; this, of course, was when the concept of high molecular weight polymers was still in the developmental stages. Karl Freudenberg at the University of Heildelberg then, provided strong evidence for the betaglycosidic linkages in cellulose. The final chain conformation polymeric structure of cellulose was firmly established through the exquisite work of Staudinger in 1953, for which he received the Nobel Prize (Figure 1) (Hon, 1994).

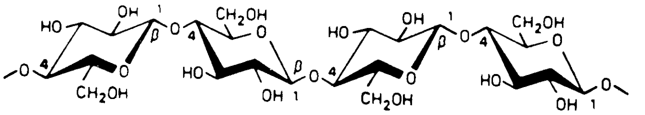


Figure 1. Structure of Cellulose

Still to be established was the nature of cellulose polymer chain associations. Early x-ray diffraction studies on cellulose showed definite diffraction rings indicating the crystalline nature of cellulose, and Nishikawa in Japan also found evidence of discontinuous sections in cellulose. These discontinuous sections were to be later referred to as amorphous fractions of cellulose, and thus, the crystalline-amorphous character of cellulose was established. A large variety of models for the cellulose structure have been published over the years with the model of Frey-Wyssling, showing distinct crystalline and amorphous sections, frequently cited.

Later work by Preston in England, however, demonstrated that native cellulose is a continuous crystalline polymer with occasional dislocations rather than having discrete domains (Figure 2) (Young ve Rowell 1986).

The greatest modern controversy in cellulose chemistry has been over the structure of the unit cell. The early models of Meyer and Misch were proposed before ideas of stereochemistry limited the possible conformations. These and all the other models proposed during this period depicted the unit cell as having the chains at the four corners of the unit cell running in one direction, with the central chain running in the opposite direction, or anti-parallel. It wasn't until the 1970's, when, computer technology was being increasingly applied to the complex problem of interpretation of x-ray diagrams, that a new model was proposed. Anatole Sarko and John Blackwell in the USA simultaneously published papers suggesting that all the chains in the unit cell run parallel, including the central chain. This model is now widely accepted as a more accurate interpretation of the unit cell structure of native cellulose (Figure 3). In addition Sarko and Blackwell's data indicated that the unit cell of the cellulose polymorph, cellulose II, from regenerated celluloses (i.e., rayon), is indeed an anti-parallel form of cellulose; and so, a controversy remains as to how the central chain is flipped from parallel to anti-parallel in the regeneration process (Young and Rowell 1986).

Cellulose derivatives were also prepared in the early years of polymer chemistry and eventually formed the basis of a large chemical and textile industry. It's hard to imagine today that the only materials available for fibers and fabrics 60 years ago were cellulose, silk and wool. Processing of cellulose to fibrous materials is still an important industry today and the modern developments include the creation of the high strength rayon fibers for such things as tire cord reinforcement (Rowell and Young). The high strength fibers were only realized after many years of experimentation on the chemical processing methods and changes were made in almost every step of the complicated process. It is still rather amazing that this "old" xanthate process is still the mainstay of the industry. The process is energy and capital intensive and carries heavy pollution loads. A promising alternate approach is the use of *N*-methylmorpholine-*N*-oxide for dissolution and spinning of regenerated cellulose fibers. Several companies have explored the method both in the USA and France.

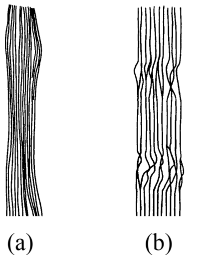

(a) (b)

Figure 2. Models of crystalline-amorphous cellulose most representative of (a) native cellulose and (b) regenerated cellulose.

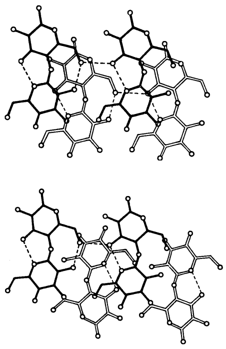


Figure 3. Parallel (a) and antiparallel (b) packing of sheets of cellulose as seen in cellulose I and II, respectively.

In the 1950's and 1960's considerable research effort was expended on the development of graft copolymers of cellulose with synthetic polymers. Major contributions in this area were made by Professor Vivian Stannett of North Carolina State University. He and his co-workers were able to graft a wide variety of vinyl polymers to cellulose substrates via gamma radiation and redox initiated free radical polymerization reactions (Phillips, et.al., 1972). There were great expectations for commercialization of this method since the surface of an inexpensive cellulose fiber could be easily modified with small amounts of an expensive polymer to give a surface copolymerized fiber with new, unique properties. However, these processes were never commercialized because it was not possible to limit the amount of homopolymer formed from the vinyl monomers. Thus large quantities of expensive synthetic polymers were formed which were not attached to the cellulose core fiber and represented lost revenue. Professor Raymond Young and Professor Ferencz Denes of the University of Wisconsin utilized plasma polymerization of gaseous monomers for attachment of thin polymeric layers at the surface of cellulosic materials, while limiting the homopolymer formation (Denes, et.al., 1994). Plasma polymerization has also be utilized by this group and Professor Turgut Sahin in Turkey to modify the properties of paper (Sahin, et. al., 2002; Sahin 2007).

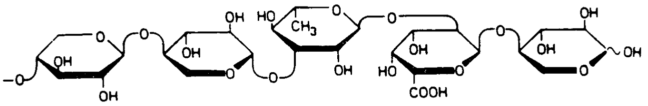
Probably the most significant discovery in recent years related to cellulose derivatives is the liquid crystalline behavior of these macromolecules. Liquid crystals of cellulose derivatives in highly concentrated solutions have been studied by Gray and coworkers in Canada and Zugenmaier in Germany. Gray determined the threshold volume fractions of the biphasic equilibria for the systems of hydroxylpropyl cellulose, cellulose acetate and ethyl cellulose in various solvents and Zngenmaier investigated the unusual optical properties (that are closely related to the pitch of the helicoidal structures) present in the systems of cellulose tricarbanilate in methyl ethyl ketone and ethyl cellulose in glacial acetic acid. There are a number of exciting applications for liquid crystalline polymers ranging from the production of superior strength fibers to use in twisted-nematic display devices and screens (Young and Rowell, 1986).

Celllulosic materials have also been utilized in medical applications. Films and tubes manufactured from cellulose have historically been used for the treatment of renal failure, but this use has declined in recent years displaced by synthetic blends. Although use of cellulose for dialysis is still practiced other new applications are emerging. The most promising new application of cellulose to medicine is the use of microbial cellulose synthesized by *Acetobacter xylinum* as a novel wound healing system and as a scaffold for tissue regeneration (Hoenich, 2006).

## 3. DEVELOPMENTS IN HEMICELLULOSE CHEMISTRY

The occurrence of sugars other than glucose in wood had been known for many years and these sugars were generally considered to be part of a group of carbohydrates known as hemicelluloses. This name can be traced back to E. Schulze who assumed that these materials were precursors to cellulose. It is now, well established that the sugars comprise a group of polysaccharides based on the pentoses, xylose and arabinose, and the hexoses, glucose, galactose, and mannose. The structure of the hemicelluloses was determined in the 1950's through the extensive studies of Professor Tore Timell at the College of Forestry in Syracuse, NY (Timell, 1965). Using traditional carbohydrate isolation and structural determination techniques, he and his coworkers convincingly established the structure of the two major groups of hemicelluloses in softwoods, the galactoglucomannans and the arabinoglucuronoxylans, and the two in the hardwoods, the glucomannans and the glucuronoxylans. Although the hemicelluloses in the two plant groups are similar, there are distinct structural differences (Table 1). With the advent of modern instrumental methods such as gas chromatography-mass spectroscopy it was possible to further refine the structure of the hemicelluloses. In 1977, Samuelson and coworkers reported that the reducing end of birch xylan had a very unusual sequence of five sugars, including rhamnose, as shown in Figure 4. This was an important discovery since it helped to explain the resistance of these polysaccharides to alkaline degradation reactions described below (Sjöström 1993).

The study of the alkaline degradation of hemicelluloses is very important because this represents the major yield losses in alkaline pulping systems and the saccharinic acid products create a large effluent load from these processes. Cellulose is not heavily degraded in the alkaline pulping liquors due to the crystalline structure. The curtailment of the alkaline endwise degradation of hemicelluloses has not yet been accomplished nor has there been suitable solutions found for the use of the degradation products. Considerable efforts were expended in the 1960's and 1970's to inhibit alkaline endwise degradation through reactions to block or modify the reducing ends of the polysaccharides by a variety of methods including derivatization, oxidation, and reduction. Although successful to varying degrees, all have proven too complicated or costly for implementation on a commercial scale (Isbell and Ann, 1943).



-ß-D-Xylp-(1-4)-ß-D–XyIp-(1–3)- -L-Rhap –(1-2)-alpha-D-Gal pA-(1-4)-D-Xyl p

Figure 4. Structure associated with reducing end group of birch xylan.

Table 1. Structural Components of Hemicelluloses.

| | **Amount** | | **Composition** | | |
|---|---|---|---|---|---|
| | Occurrence | (% of Wood) | Units* | Molar Ratios | Linkage |
| Galactoglucomannan | Softwood | 5-8 | ß-D-Manp | 3 | 1-4 |
| | | | ß -D-G1cp | 1 | 1-4 |
| | | | a-D-Galp | 1 | 1-6 |
| | | | Acetyl | 1 | |
| (Galacto)glucomannan | Softwood | 10-15 | ß -D-Manp | 4 | 1-4 |
| | | | ß -D-Glcp | 1 | 1-4 |
| | | | a-D-Galp | 0.1 | 1-6 |
| | | | Acetyl | 1 | |
| Arabinoglucuronoxylan | Softwood | 7-10 | ß -D-Xy1p | 10 | 1-4 |
| | | | 4-O-Me-a-D-G1cpA | 2 | 1-2 |
| | | | a-L-Araf | 1.3 | 1-3 |
| Arabinogalactan | Larchwood | 5-35 | ß -D-Galp | 6 | 1-6 |
| | | | ß -L-Araf | 2/3 | 1-6 |
| | | | ß -L-Arap | 1/3 | 1-3 |
| | | | 3-D-Glcp | A Little | 1-6 |
| Glucuronoxylan | Hardwood | 15-30 | ß -D-Xylp | 10 | 1-4 |
| | | | 4-O-Me-a-D-G1cpA | 1 | 1-2 |
| | | | Acetyl | 7 | |
| Glucomannan | Hardwood | 2-5 | ß -D-Manp | 1-2 | 1-4 |
| | | | ß -D-Glcp | 1 | 1-4 |

*a=alpha, p=pyranose, f=furanose, Me=methyl, Man=mannose, Glc=glucose, Gal=galactose, Ara=arabinose, Xyl=xylose, GlcpA=glucuronic acid

In the mid 1940's Isbell at the National Bureau of Standards in Washington D.C. published a series of papers elucidating the complicated mechanisms of alkaline endwise degradation of polysaccharides. He concluded that the predictable pattern of formation of the saccharinic acids is via a beta-elimination reaction subsequent to the now well known Lobry-DeBruyn Alberta Van Ekenstein sugar rearrangements (Isbell and Ann, 1943). Much later, Sjöstrom and coworkers in Finland carried out exhaustive analysis of the saccharinic acid products in the waste liquors from kraft pulping of wood. They developed excellent separation techniques based on carbon dioxide and accurately established the relative proportions of the various acids in the black liquors from kraft pulping of softwoods and hardwoods (Table 2). The tremendous quantities of salt formed in the separation process caused difficulties for use and disposal and thus commercialization (Sjostrom, 1993).

## 4. DEVELOPMENTS IN LIGNIN CHEMISTRY

The term lignin is derived from the Latin word for wood, lignum. Peter Klason in Sweden was the first to suggest that lignin is a polymer based on coniferyl alcohol. Karl Freudenburg from Heidelberg University then carried out a prolonged, exquisite study to elucidate details of the structure of this complicated polymer. As shown in Figure 5 for spruce lignin, the polyphenolic polymer is comprised of guaiacyl units connected by phenolic ether and carbon-carbon linkages. The predominant bond is the ß-O-4-linkage and this is the linkage that is mainly broken during the alkaline pulping of wood. Hardwood lignins differ from softwood in that they are comprised of about a 50/50 mixture of guaiacyl and syringyl moieties. Since the 5-position on the aromatic ring of the syringyl units contains a methoxyl substituent, there are less carbon-carbon linkages in hardwood lignins and more ß -O-4-links. This explains the greater ease for pulping of hardwoods versus softwoods (Sarkanen and Ludwig, 1971; Fengel and Wegener, 1984).

The structure and reactions of lignin have been further evaluated in recent years through the aid of C-13 NMR. This powerful analytical tool has been utilized by a number of investigators to verify many elements of Freudenberg's earlier proposed structure for lignin and to determine exact mechanisms of delignification in pulping. Notable in this area of research is Professor Josef Gierer of STFI in Sweden and, in the USA, Larry Landucci at the USDA Forest Products Laboratory, Professor Josef Gratzl at North Carolina State University and Professor John Ralph at the University of Wisconsin. All these investigators also contributed to the complete elucidation of the complex mechanisms of anthraquinone catalysis of delignification in alkaline pulping systems.

Table 2. Main hydroxcycarboxylic acid in kraft black liquors (kg/ton pulp*)*

| **Acid** | **Pine** | **Birch** |
|---|---|---|
| Glycolic | 30 | 25 |
| Lactic | 50 | 25 |
| 3,4-Dideoxypentonic | 30 | 10 |
| Glucoisosaccharinic | 110 | 35 |
| 2-Hydroxybutanoic | 15 | 60 |
| 3-Deoxypentonic | 15 | 10 |
| Xyloisosaccharinic | 15 | 25 |
| Others | 55 | 40 |
| Total | 320 | 230 |

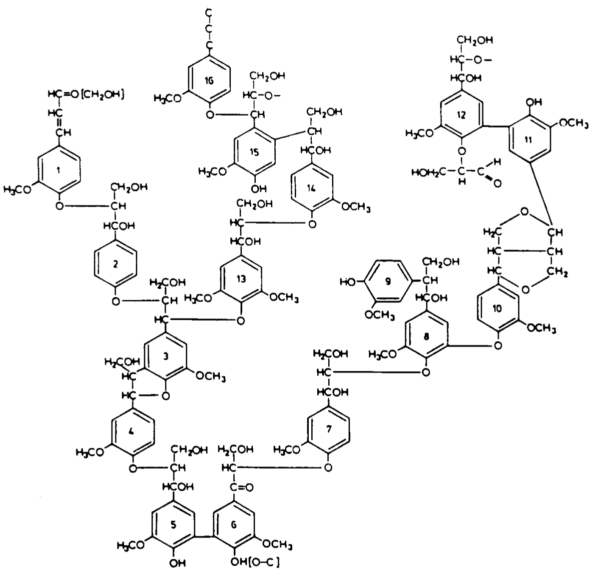


Figure 5. A structural segment of softwood lignin.

Lignification of plants is believed to proceed through a free radical coupling mechanism of monomeric coniferyl and sinapyl alcohol units. Freudenberg developed two theories of lignification and Professor Kyosti Sarkanen of the University of Washington later expounded on these theories in his classic book "Lignins: Occurrence, Formation, Structure and Reactions" published in 1971. "Zulaufverfahren" or bulk lignification occurs through the initial formation of dimers, i.e. dilignols, and trimers of the monomers, and then bulk conversion of these units to a random lignin polymer, while "Zutropfverfahren" or endwise lignification occurs by sequential addition of the monomers to a growing polymer chain. The two modes of lignification lead to different lignin polymers, with the endwise polymer containing a greater quantity of ß -O-4-linkages, consistent with the nature of lignin in wood (Fengel and Wegener, 1984).

Recent controversy over lignin biosynthesis has been debated between Professor Ralph’s group at the University of Wisconsin and Professor Norman Lewis of Washington State University. Professor Lewis contends that there is absolute proteinaceous control over the lignification process. However, as Professor Ralph states in his recent paper, the theory of “combinatorial” coupling of phenoxy radicals formed from monolignols under simple chemical control, based on the original work of Freudenburg, continues to accommodate all the currently know facts of lignin chemistry (Ralph et. al., 2007).

Crosslinking of lignin in plant material has been a subject of speculation since the early history of lignin chemistry. These bonds play a role in both the delignification and digestibility of plant materials for forage. In the 1990's Professor John Ralph of the University of Wisconsin carried out a series of C13-NMR studies to determine the occurrence and extent of these linkages. In a major effort to understand the role of hydroxycinnamates in crosslinking of the cell wall of forage lignins, Dr. Ralph and his coworkers synthesized a series of ether and ester linked model compounds which were then used to verify the existence of such structures in native lignin by C-13 NMR. Utilizing short- and long-range inverse C-13 /H-1 correlation techniques they were able to demonstrate the very specific single site esterification crosslinking with para-coumarates, thus proving a single biochemical pathway (Helm and Ralph, 1992).

The most recent models for both softwood and hardwood lignins are given in Figure 6 (Ralph et. al., 2007). The models incorporate all known linkages including ß-ether, phenylcoumaran, resinol, dibenzodioxocin, biphenyl ether, spirodienone, cinnamyl alcohol endgroups and glycerol endgroups (Ralph et. al., 2007; Helm and Ralph, 1992; Brunow, 2001; Boerjan et. al., 2003).

Lignin is not only removed from wood in the pulping reaction; small quantities which remain in the fibers after pulping must be removed in a series of bleaching reactions. Most of the bleaching reactions involve chlorine and chlorine dioxide reactions with the lignin. In the 1950's and 1960's, Professor Kyosti Sarkanen of the University of Washington elucidated the mechanisms of chlorine substitution and breakdown of the lignin macromolecule. The main reactions in acidic bleaching are electrophile substitution and side chain displacement, and oxidative cleavage of ether linkages and decomposition of aromatic rings (Fengel and Wegener, 1984).

Biotechnology of lignin has been under investigation for about 20 years and notable is the work of Karl-Erik Erickson in Sweden and Tent Kirk at the USDA Forest Products Laboratory in Madison. It has been suggested for years that peroxidase and laccase enzymes were important to lignification of plants and these types of enzymes have been shown by Freudenberg to produce lignin polymers in the laboratory by dehydrogenative polymerization. This is an intense area of current research and break-throughs are expected in the near future. The application of biotechnology to pulping is discussed in a following section.

Lignin utilization is a topic that has been intensely investigated since such large quantities are available from chemical pulping processes. The majority of lignin is currently burned for fuel value but higher grade uses are certainly a distinct possibility. A large number of investigators have evaluated the use of lignin as a substitute for phenol in phenol-formaldehyde adhesive applications. Crosslinking of the lignin for use in adhesives has been carried out by acid condensation, oxidative coupling and enzymatic treatment. Horst Nimz of the University of Hamburg produced particleboards with good strength properties by oxidative coupling with hydrogen peroxide; unfortunately, when applied on a pilot plant scale the method resulted in explosions and fires (Pizzi, 1982). The most promising approach in this area is the use of enzymes for wood and fiber bonding.

Scientists at the Novo Nordisk Company in Denmark have convincingly demonstrated that excellent fiberboards can be produced with a proprietary enzyme treatment and pressing at low temperatures. It is believed that the lignin is the reactive component in the bonding. This type of an approach would result in both considerable energy savings due to the low heat requirements and a drastic reduction in pollution problems.

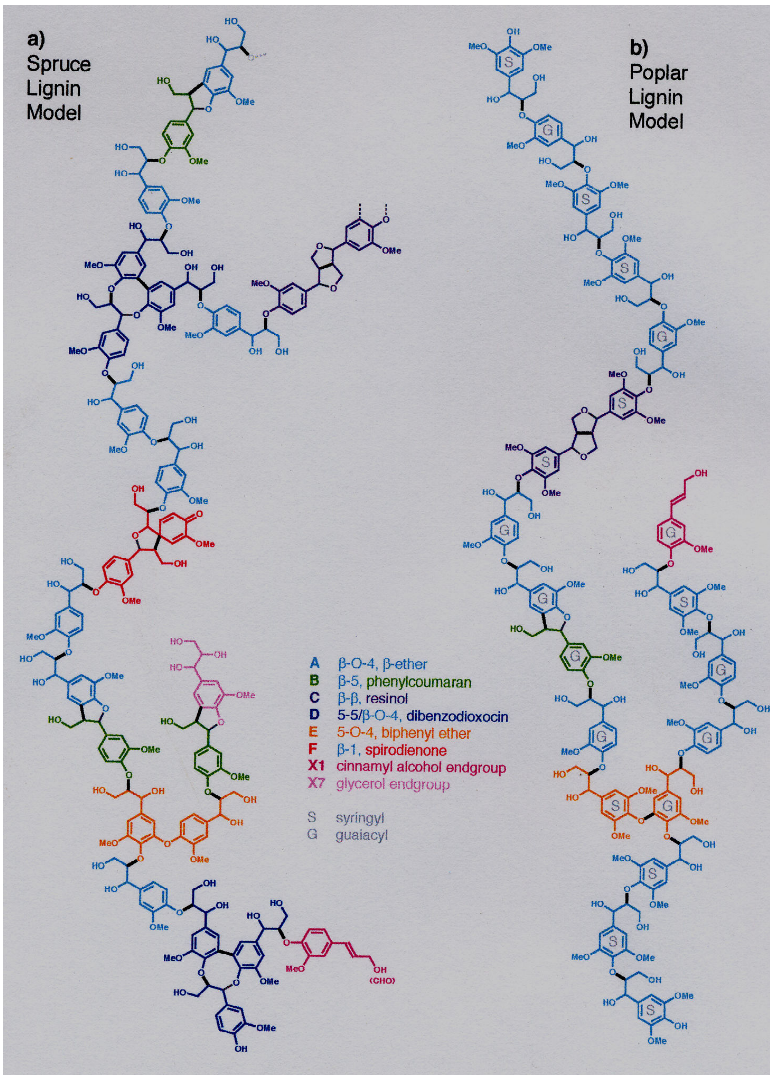


Figure 6. Lignin polymer model for softwoods (spruce) and hardwoods (poplar) (Ralph vd., 2007).

Another approach for improved utilization of lignin is through chemical modification. Of course, lignin derived from sulfite pulping is already sulfonated and these lignosulfonates and other technically sulfonated lignins have found uses as dispersants and emulsifiers. Professor Wolfgang Glasser at the Polytechnical Institute of Virginia employed classical chemical modification approaches to produce a variety of modified lignin products, such as the conversion to polyols by oxy-alkylation. These materials can then be further processed to form polyurethane foams, adhesives, and coatings (Glasser and Sarkanen, 1989).

## 5. DEVELOPMENTS IN EXTRACTIVE CHEMISTRY

"Extractives" is a general term for a wide variety of water and solvent soluble organic materials in wood which can be easily removed by simple extraction procedures. The extractives are nonstructural constituents and can be divided into three main categories. I. Terpenoids and Steroids; II. Fats and Waxes; and III. Phenolic Compounds. Although minor constituents in most wood species, the extractives can sometimes represent up to 40% of the dry weight of wood (Sjostrom, 1993; Fengel and Wegener, 1984). The extractives in the pine species have been economically very important for thousands of years, dating from the time of Theophrastus in Greece, who described the "Macedonian Method" for collection of extractives from wood.

The major developments in recent times have been on the determination of the exact structure of these complicated compounds, including the correct stereochemistry. Dwayne Zinkel of the USDA Forest Products Laboratory in Madison developed a number of sophisticated separation techniques for obtaining pure fractions of the extractives and performed extensive analysis of the materials for structural determination (Zinkel, 1975). In 1962, W. E. Hillis in Australia published the best summary of the state of knowledge of extractives at the time, entitled "Wood Extractives and Their Significance to the Pulp and Paper Industries" (Hills, 1962).

The development of methods for collection of terpenes and resin acids from kraft pulping of wood was indeed an important step, since previously these materials were collected as exudates by the labor intensive process of tapping live pine trees. Today terpenes are the basis of a large chemical industry, in uses ranging from scents and odorants, such as lemon and menthol, to medicinal uses such as the cough expectorant, terpin hydrate. The resin acids are used as chemical intermediates, paper sizes and in pressure sensitive tapes (Sjostrom, 1993; Fengel and Wegener, 1984).

Great strides have been made on utilization of extractives as wood adhesives. Both Richard Hemmingway of the USDA Southern Regional Laboratory in Pineville, Louisiana and A. Pizzi in Pretoria, South Africa have developed methods for conversion of wood tannins (Figure 7) to adhesives. Both have published excellent books which describe their work; "Wood Adhesives: Chemistry and Technology" in 1983 by Pizzi and "Plant Polyphenols" in 1992 and "Chemistry and Significance of Condensed Tannins" in 1989 by Hemmingway and others .

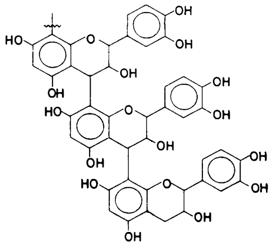


Figure 7. Structure of Pine Tannnin

## 6. DEVELOPMENTS IN PULPING CHEMISTRY

The conventional kraft and sulfite pulping processes are now over 100 years old, but are still viable in most parts of the world (Rydholm, 1965). Many modifications have been made to make these processes more economical and environmentally sound. However, these conventional systems are still plagued by extremely high capital costs and effluent problems. This has resulted in intensive research efforts on new pulping processes based on aqueous organic solvents and through the use of biotechnological approaches.

The original patents on aqueous alcohol pulping of wood were issued to Kleinert in Germany in the 1970's. Kendall Pye and Jairo Lora of Repap Technologies, Valley Forge, Pennsylvania, were instrumental in further developing the aqueous ethanol system for pulping of hardwood species. A pilot plant based on their process is in operation in Ontario, Canada, and a full scale plant is under construction. However, further important modifications to the process were necessary to realize a viable pulping method for softwoods. Lazlo Pazner at the University of British Columbia, Canada, developed a catalytic system based on magnesium chloride in aqueous ethanol which proved effective for delignifying softwoods (Young and Akhtar 1998). Professor Turgut Sahin of Suleyman Demirel University has recently demonstrated that advantages of base catalysis in ethanol pulping of jute (Sahin, 2003).

Solvent processes have also been developed by Professor Raymond Young at the University of Wisconsin and Gotlieb and Preuss of Veba Oil Company, Germany. The ester process developed by Dr. Young was based on three components, acetic acid, ethyl acetate and water which are miscible in roughly equal proportions. The unique feature of this approach is that after the pulping reaction the waste liquor can be split into two phases by addition of water which also precipitates the lignin. The upper organic phase is comprised of acetic acid and ethyl acetate and the lower aqueous phase is comprised of water and soluble sugars. The phases are easily separated by low energy decantation processes and recycled for reuse. The lignin is collected by filtration or centrifugation for use as a fuel or as a valuable chemical byproduct (Young and Akhtar 1998; Young, 1989).

Gotlieb and Preuss utilized high concentrations of aqueous acetic acid in their "Acetocell" pulping process. They obtained good strength pulps after a post-hydrolysis step (caustic solution) to remove acetate groups from the pulps and to condition the fibers for bonding. They also recovered about 2-3% furfural as a salable byproduct (Gottlieg et. al., 1992).

Another major development in pulping in recent years has been in the area of biopulping of wood and agricultural materials. This approach is based on the use of selected fungi to break down the lignin in lignocellulosic materials for subsequent mechanical disintegration. Dr. Masood Akhtar of the USDA Forest Products Laboratory in Madison has shown the viability of the technique for biomechanical pulping of aspen and Professor Raymond Young and Dr. H. Sabharwal of the University of Wisconsin in Madison have shown the applicability of the approach with agricultural materials such as kenaf and jute. The method utilizes low energy and minimizes pollution discharges. The plant material is simply treated with the fungus culture which is allowed to interact with the material for a period of 2-4 weeks, then the plant material is mechanically disintegrated in a disk refiner to yield a high strength pulp (Figure 8) (Young and Akhtar 1998; Young et. al., 1994). Professor Turgut Sahin of Suleyman Demirel University has recently demonstrated a synergistic effect of biochemical treatment in soda pulping of jute (Sahin, 2007). Pilot plant trials have been proposed to evaluate the process developed at the USDA Forest Products Laboratory in Madison .

## 7. CONCLUSION

The developments in wood chemistry over the past 75 years have indeed been monumental. During this period the structure of both crystalline cellulose and amorphous lignin were further elucidated and mechanisms of lignin reactions established. Cellulose derivatives are still a major chemical commodity and some of these derivatives have been demonstrated to show liquid crystalline behavior. Commercial utilization of lignin has not yet been greatly expanded but new developments in terms of modifications and derivatives bode a bright future. Although commercial methods to limit the loss of hemicelluloses in alkaline pulping also have not been realized, the structure and character of these polysaccharides have been established during this period. Utilization of extractives is well established and use of tannins for adhesives has already been commercialized. New wood pulping methods based on solvents and biotechnology now offer non-polluting alternatives to conventional approaches.

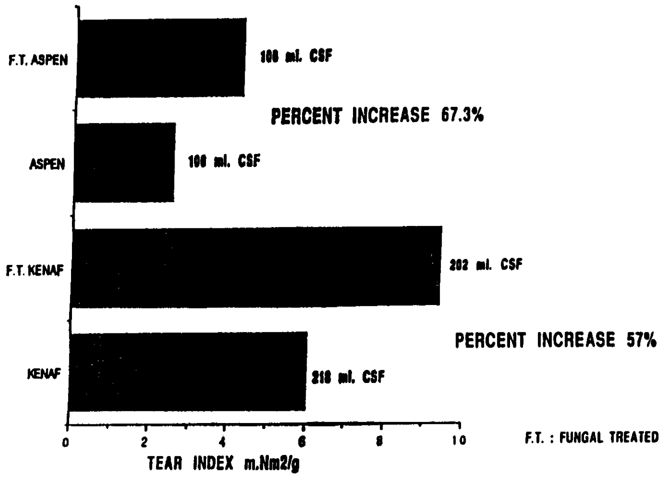


Figure 8. Comparative tear strength of untreated and fungal treated aspen and kenaf (biomechanical pulping).

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## Professor Emeritus Raymond A. Young

Raymond A. Young is an Emeritus Professor of Wood Chemistry at the University of Wisconsin-Madison. He served on the faculty for 30 years and carried out extensive research on organosolv (mainly organic acid) pulping of wood, biomechanical pulping of agro-based materials, fiber modification and characterization, plasma modification of lignocellulosics, chemical modification of cellulose and lignin, and surface activation and bonding of wood. He has received several million dollars in research grants during his tenure at the University of Wisconsin. Professor Young has over 180 publications including 20 book chapters, 8 books, 9 patents and numerous original research publications. He taught courses in Pulp & Paper, Carbohydrate Chemistry, Cellulose Chemistry and Ethnobotany at the University of Wisconsin. Professor Young holds a Ph.D. in Wood and Polymer Science from the University of Washington-Seattle and B.S. and M.S. degrees from State University of New York-Syracuse. He spent one year (1973) as a Fulbright Scholar at the Royal Institute of Technology, Stockholm, Sweden studying oxygen delignification and had a two-year Post-Doctoral Fellowship (1973-75) at the Textile Research Institute, associated with Princeton University, working on fiber surface characteristics and web bonding. He also was a Senior Fulbright Research Scholar for one year (1989) at the Aristotelian University, Thessaloniki, Greece evaluating surface activation and bonding of wood with natural polymers. He received several National Academy of Science scientific exchange awards to Poland (1979), the former Yugoslavia (1979), and to Romania (1990). In the year 2000, Professor Young received the Annual Award of the Japan Photopolymer Society for work on Plasma Modification of Materials. He has been an Emeritus Professor since 2004. Further information on the wood and polymer chemistry program at the University of Wisconsin is available at our website: http://forest.wisc.edu/facstaff/young/woodchem